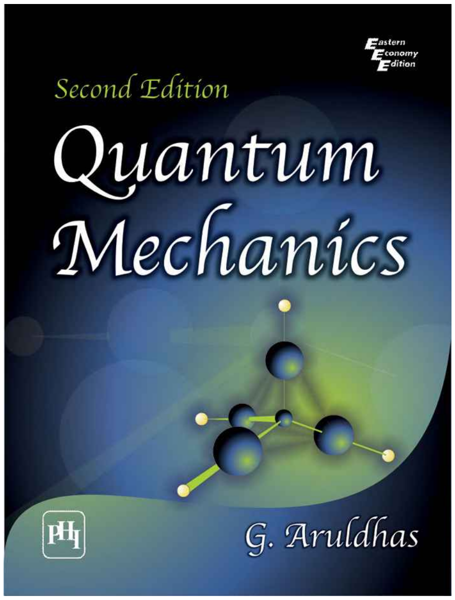

Eastern Economy Edition

Second Edition

Quantum Mechanics

G. Aruldhas

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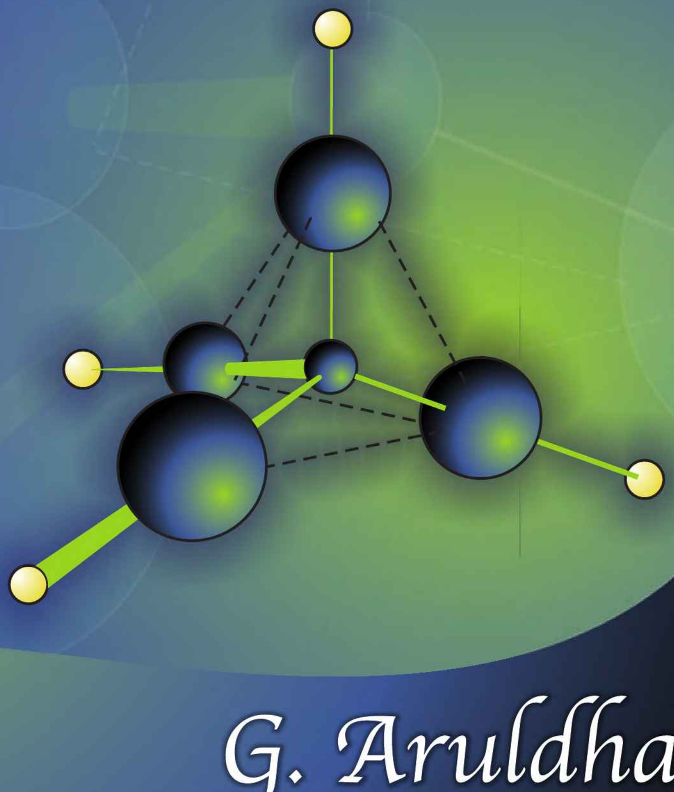

G. Aruldhas

QUANTUM MECHANICS

SECOND EDITION

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G. Aruldhas

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To

My Parents

Gnanasigamoni & Rajammal

who taught me the merits of discipline
and the rewards of education

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Preface

The aim of this revised second edition is to bring in new materials, worked examples and problems that makes the book more broad based and useful. These have been done keeping in mind the dual goals of the first edition, i.e., to help students to build a thorough conceptual understanding of Quantum Mechanics and to develop a more positive and realistic impression of the subject.

A new chapter on field quantization is added as most of the Universities have this as a part of the course. Classical field equation both in the Lagrangian and Hamilton's form, quantization of non-relativistic Schrödinger equation and relativistic scalar, spinor and vector fields have been discussed. The mechanism that holds the atoms together in a molecule are discussed in the chapter on Chemical Bonding. It includes the molecular orbital, valence bond and Hückel methods alongwith hybridization and Hückel's treatment of benzene molecule. New sections on Rayleigh scattering and Raman scattering have been added to the chapter on time dependent perturbation theory.

Learning how to approach and solve problems is a basic part of any physics course, since it helps the understanding of the subject. Additional worked examples and problems, ninety four in all, illustrating the various concepts involved have also been included in most of the chapters. A solutions manual is available from the publisher for the use of teachers.

The author is grateful to Prof. V.K. Vaidyan, Prof. V.U. Nayar, Prof. C.S. Menon and Prof. V.S. Jayakumar for their constant encouragement and support. The help received from Asitha L.R. and Divya P.S. during the preparation of the manuscript is acknowledged. I also express my gratitude to those who have

given meaning to my life—my wife Myrtle and members of my family—Vinod and Anitha, Manoj and Bini, Ann and Suresh and grand children. Finally, I express my sincere thanks to the publisher, PHI Learning for their unfailing co-operation and for the meticulous processing of the manuscript.

Above all, I thank Lord Jesus Christ who has given me the wisdom, might and guidance all through my life.

G. ARULDHAS

Preface to the First Edition

The concepts and formulation of quantum mechanics are not elementary in the sense that they are easily understood. They are based on the outcome of considerable theoretical research supported by experimental evidence. The quantum mechanical approach to physical problems cannot be explained or expressed comprehensively in simple non-mathematical terms. Often it is the gap between the high-theoretical treatments and the descriptive accounts found in many of the texts that makes the subject a difficult one for students. The present book, *Quantum Mechanics,* is expected to bridge this gap. Simple and elegant mathematical techniques have been used to elucidate the physical concepts.

The book has originated from a series of lectures on quantum mechanics which the author had given for a number of years at the postgraduate level in different universities in Kerala and as such the material is thoroughly class-tested. It is designed as a textbook not only for postgraduate students of physics and chemistry but also for students offering an advance course in quantum mechanics. Emphasis is given for giving the students a thorough understanding of the basic principles and their applications to various physical and chemical problems. Details of mathematical steps are provided wherever found necessary. Physical ideas contained in the results have been discussed. Every effort has been taken to make the book explanatory, exhaustive and user friendly.

In Chapters 1–14, the non-relativistic areas of quantum mechanics have been dealt with whereas the relativistic aspect is discussed in Chapter 15. Chapter 1 serves as an introduction to quantum theory bringing out the historical events that led to the development of quantum ideas and its subsequent progressive advances. It also discusses the inadequacies of quantum theory. In Chapter 2, wave nature of matter, the uncertainty principle, the time-dependent and time-independent Schrödinger equations are introduced along with a discussion on the physical significance of the wavefunction. Chapter 3, the core of the book, deals with the general formalism of quantum mechanics. It presents the basic ideas of vector space, Hermitian operators, postulates of quantum mechanics, momentum representation and equations of motion. Chapters 4 and 5 discuss the energy eigenvalues and eigenfunctions of certain simple potentials on the basis of Schrödinger method. The Heisenberg's formulation of quantum mechanics based on matrices is presented in Chapter 6. The different types of symmetries and the related conservation laws are the subject of discussion in Chapter 7. A detailed chapter on angular momentum (both orbital and spin), a topic of fundamental importance in physics, is also included.

Chapters 9–12 treat the important approximation methods, the variation, WKB, time-independent and time-dependent perturbation methods. The application of these techniques to study the ground state of two electron atoms, Stark effect in hydrogen, the deuteron ground state, alpha emission, spin-orbit interaction, transition probability, emission and absorption of radiation and selection rules is treated in the related chapters. The information provided by many electron atoms is of considerable importance for the understanding of the structure of molecules and their properties. The scattering phenomenon is very important as it represents one of the best methods of studying the properties of atoms, nuclei and interaction of elementary particles among themselves. Even the concept of an atom is the outcome of a scattering experiment.

The book concludes with a chapter on relativistic wave equation which accounts for electron spin, electron magnetic moment, the concept of hole and many other interesting phenomena.

Considerable attention is devoted to worked examples in the text. More than hundred examples ranging from simple plug-in type to fairly complicated ones have been fully worked out. About 150 problems, given at the end of respective chapters, are useful for the understanding of the basic concepts and applications. Answers to these problems are also provided at the end of the text. The review questions may serve as the basis for self-study, class discussion, assignments, etc.

It is with deep sense of gratitude and pleasure that I acknowledge my indebtedness to my students for all the discussions and questions they have raised. I am likewise indebted to Dr. A.D. Damodaran, Dr. V.K. Vaidyan, Dr. C.S. Menon, Dr. V. Ramakrishnan and Professor Jose Davidson for their support and cooperation. Last, but not least, I acknowledge my gratitude to my wife Myrtle Grace and children for the encouragement, cooperation and academic environment they have provided throughout my career.

Finally, I express my sincere thanks to the publishers, PHI Learning for the meticulous processing of the manuscript both during editorial and production stages.

G. ARULDHAS

Chapter 1

Origin of the Quantum Theory

1.1 LIMITATIONS OF CLASSICAL PHYSICS

The first scientific attempt to study the nature of light radiation was that of Sir Isaac Newton who proposed the corpuscular theory of light. According to this theory, light consists of tiny perfectly elastic particles, called *corpuscles* which travel in all directions in straight lines with the velocity of light. It could not explain phenomena such as interference, diffraction and polarization. It predicted that the velocity of light is more in a denser medium than that in a rarer medium.

The theory that light is propagated as a wave through a hypothetical elastic medium called *ether* was developed by Huygens, Young and Fresnel. They considered light as propagation of mechanical energy. It got established as it could explain most of the experimentally observed phenomena including the velocity of light in different media. A completely different concept regarding the nature of light was proposed by Maxwell in the second half of the nineteenth century. According to him, light consists of electromagnetic waves with their electric and magnetic fields in planes perpendicular to the direction of propagation. The electric and magnetic fields associated with the wave are governed by Maxwell's equations. Predictions of Maxwell were confirmed experimentally by Hertz. The electromagnetic theory of light was received well though it had failed to explain phenomena such as photoelectric effect and emission of light.

Thus, towards the end of the nineteenth century there was a sense of completion among the physicists as they thought that classical physics was capable of explaining all observable phenomena. Then came a series of important experimental discoveries starting with X-rays in 1895, radioactivity in 1896 and electron in 1897, which could not be explained, on the basis of classical physics. In addition, lot of experimental observations starting with black-body radiation and optical spectra accumulated could not be explained by the classical theory.

Black-body Radiation Curves

The spectral energy density u_ν of black-body radiation from a black-body cavity depends only on frequency n and temperature T of the cavity. Based on thermodynamic arguments, Wien attempted to explain the observed spectral energy density verses frequency ν curves. The agreement with experimental results was good only in the high-frequency region (Figure 1.1). Treating radiation inside a black body as standing electromagnetic waves, Rayleigh and Jeans estimated the number of modes of vibration per unit volume in the frequency range ν and $\nu + d\nu$ and evaluated the spectral energy density u_ν by taking its product with the average energy of an oscillator of frequency ν. Their expression agreed with experiment only at low frequencies. The methods based on classical theories thus failed to give a single formula that could agree with the experimental black-body radiation curve for the entire frequency range. There is no wonder that this disagreement led to a complete revision of our ideas of physics.

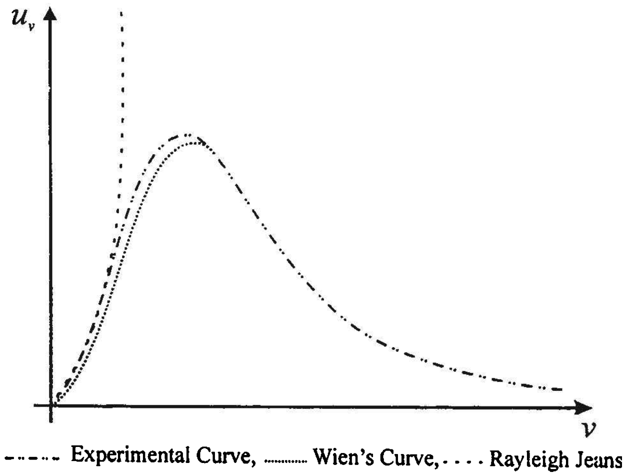


Figure 1.1 Black-body radiation curve.

Optical Spectra

Each chemical element showed characteristic emission spectrum consisting of discrete lines. Comparatively, simple spectrum was observed for hydrogen atom. In 1885, J.J. Balmer arranged them in the form of a series and had suggested the following empirical formula for the wavelength:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, 5, \cdots \tag{1.1}$$

where, R is the Rydberg constant for hydrogen. Later, other spectral series were also discovered (Table 1.1) and they were found to obey the formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \tag{1.2a}$$

where

$$m = 1, 2, 3, \cdots \qquad n = (m + 1), (m + 2), (m + 3), \cdots \tag{1.2b}$$

The regularities found in the spectral lines indicate that there must be some general mechanism in the emission of light. The classical theories failed to give the correct mechanism responsible for the spectral series in hydrogen.

Table 1.1 The Hydrogen Spectral Series

	Quantum number		
Name of series	*Lower state* (m)	*Upper state* (n)	*Region*
Lyman series	$m = 1$	$n = 2, 3, 4, \cdots$	Ultraviolet
Balmer series	$m = 2$	$n = 3, 4, 5, \cdots$	Visible
Paschen series	$m = 3$	$n = 4, 5, 6, \cdots$	Infrared
Brackett series	$m = 4$	$n = 5, 6, 7, \cdots$	Infrared
Pfund series	$m = 5$	$n = 6, 7, 8, \cdots$	Infrared

Photoelectric Effect

When light is incident on certain metallic surfaces, electrons are released. These are called *photoelectrons* and the phenomenon is called *photoelectric effect*. Some of the important conclusions arrived from a detailed investigation of the phenomenon are listed below.

1. The energy distribution of the photoelectrons is independent of the intensity of the incident light.
2. The maximum kinetic energy of the photoelectrons from a given metal is found to be proportional to the frequency of the incident radiation.
3. For a given metal, photoelectrons are not emitted if the frequency of the incident light is below a certain threshold value, whatever be the intensity of incident light.
4. For a given frequency, the number of photoelectrons emitted is directly proportional to the intensity of incident light.
5. There seems to be no time lag between the onset of irradiation and the resulting photocurrent.

Though attempts were made to explain these aspects on the basis of classical ideas, the different conclusions stood unexplained.

Specific Heat of Solids

In solids, the atoms vibrate about their equilibrium positions in their lattice sites. Based on the law of equipartition of energy, the average energy of a simple harmonic oscillator is kT, where k is the Boltzmann constant and T is the absolute temperature. An atom can vibrate about three mutually perpendicular directions, the average energy of an atom is $3kT$. Then the energy per gram atom is $3NkT = 3RT$, N being the Avogadro's number and R, the gas constant. This leads to a value of $C_v = 3R$, which is known as the Dulong and Petit's law. At ordinary temperatures, solids generally obey this relation, which is based on classical theory. However, when the temperature is lowered the specific heat decreases and goes to zero when $T \to 0$ K. Thus, the classical ideas failed to explain the variation of specific heat of solids with temperatures.

Thus, by 1900 scientists were convinced that a number of experimentally observed phenomena could not be explained on the basis of classical physics and certain new revolutionary ideas are needed to understand things better.

1.2 PLANCK'S QUANTUM HYPOTHESIS

The problem that confronted Max Planck was a theoretical explanation for the black-body radiation curves. As already mentioned, the Wien's formula agreed well with experimental results at high frequencies whereas the one due to Rayleigh and Jeans agreed at low frequencies. In 1900, Planck modified Wien's formula in such a way that it fitted with the experimental curves precisely and then he looked for a sound theoretical basis for the formula. He assumed that the atoms of the walls of the black body behave like tiny electromagnetic oscillators each with a characteristic frequency of oscillation. The oscillators emit electromagnetic energy into the cavity and absorb electromagnetic energy from it. Planck then boldly put forth the following suggestions regarding the atomic oscillators:

1. An oscillator can have energies given by

$$E_n = nh\nu, \qquad n = 0, 1, 2, 3, \ldots \tag{1.3}$$

   where ν is the oscillator frequency and h is a constant known as *Planck's constant*. Its value is 6.626×10^{-34} Js. In other words, the oscillator energy is *quantized*.

2. Oscillators can absorb or emit energy only in discrete units called *quanta*. That is

$$\Delta E_n = \Delta nh\nu = h\nu \tag{1.4}$$

An oscillator, in a quantized state, neither emits nor absorbs energy.

The average energy ε of an oscillator can be evaluated on the basis of canonical distribution formula:

$$\varepsilon = \frac{\sum_{n=0}^{\infty} \varepsilon_n \exp\,[-\varepsilon_n/(kT)]}{\sum_{n=0}^{\infty} \exp\,[-\varepsilon_n/(kT)]}$$

$$= \frac{\sum_{n=0}^{\infty} nh\nu \exp\,[-nh\nu/(kT)]}{\sum_{n=0}^{\infty} \exp\,[-nh\nu/(kT)]}$$

$$= \frac{h\nu}{\exp\,[h\nu/(kT)] - 1} \tag{1.5}$$

The quantization condition, Eq. (1.3), thus invalidates the theorem of equipartition of energy which is based on classical physics. It is known that the number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$ is $(8\pi\nu^2/c^3)\ d\nu$. With the above expression for average energy ε, the spectral energy density u_ν is given by:

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{\exp\,[h\nu/(kT)] - 1} \tag{1.6}$$

Equation (1.6) is the Planck's radiation formula which reduces to the Wien's or Rayleigh–Jeans law according as

$$\frac{h\nu}{kT} >> 1 \quad \text{or} \quad \frac{h\nu}{kT} << 1$$

Planck's explanation of the black-body radiation curves in 1900 provided the crucial step in the development of quantum ideas in physics which was put on a firm basis by the pioneering work of Einstein, Bohr and others in later years. The concept that energy is quantized was so radical that Planck himself was reluctant to accept it. This can be seen from his own words "my futile attempts to fit the elementary quantum of action (that is the quantity h) somehow into the classical theory continued for a number of years and they cost me a great deal of effort".

1.3 EINSTEIN'S THEORY OF PHOTOELECTRIC EFFECT

Einstein succeeded in explaining photoelectric effect on the basis of quantum ideas. He assumed that electromagnetic radiation travels through space in discrete quanta called *photons* as during the emission and absorption processes. The energy of a photon of frequency ν is $h\nu$. When light photon of energy $h\nu$ is incident on a metallic surface, part of energy $h\nu_0$ is used to free the electron from the metallic surface and the other part appears as kinetic energy $\frac{1}{2}mv^2$ of the photoelectrons. The conservation of energy requires

$$h\nu = h\nu_0 + \frac{1}{2}mv^2 \tag{1.7}$$

where $h\nu_0$, referred to as the *work function*, depends on the nature of the emitter. The frequency ν_0 is called the *threshold frequency*. This relation accounted for the experimental observations regarding photoelectric effect.

Though Planck quantized the energy of an oscillator, he believed that light travels through space as an electromagnetic wave. However, Einstein's photon hypothesis suggests that it travels through space not like a wave but like a particle. The photon hypothesis is thus in direct conflict with the wave theory of light. Millikan who verified Einstein's hypothesis calls it a 'bold, not to say reckless, hypothesis'.

In the photon picture, each photon transports a linear momentum $p = E/c = h\nu/c$, where E is the photon energy. This conclusion can also be deduced from the theory of relativity. The relativistic expression for energy E is given by:

$$E^2 = c^2p^2 + m_0^2c^4$$

where c is the velocity of light and m_0 is the rest mass of the particle. Since the rest mass of the photon is zero,

$$E = cp \quad \text{or} \quad p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{1.8}$$

This equation contains in it both particle concept (E and p) and wave concept (ν and λ). Confirmation of particle nature of radiation was provided by Compton effect. Compton effect is discussed in the next section.

1.4 COMPTON EFFECT

The spectrum of X-rays scattered from a graphite block contains intensity peaks at two wavelengths, one at the same wavelength λ as the incident radiation and the other at a longer wavelength λ'. Assuming the incoming X-ray beam as an assembly of photons of energy hc/λ, Compton was able to show that

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0c}(1 - \cos\phi) \tag{1.9}$$

where m_0 is the rest mass of electron, c is the velocity of light and ϕ is the scattering angle. The factor $h/(m_0c)$ is called the *Compton wavelength*. The Compton shift $\Delta\lambda$ varies between zero (for $\phi = 0$, corresponding to a grazing collision) and $2h/(m_0c)$ (for $\phi = 180°$, corresponding to head-on collision).

Agreement of Eq. (1.9) with the experimental results confirms the particle nature of radiation.

1.5 QUANTUM THEORY OF SPECIFIC HEAT

Einstein explained the anomaly in the specific heat of solids using quantum ideas. He replaced the $3N$ degrees of freedom of N atoms of the solid by $3N$ oscillators, all having the same frequency ν_E. Quantization of the energy of the oscillators leads to the following expression for the vibrational specific heat

$$
\begin{aligned}
C_v &= 3Nk\left(\frac{h\nu_E}{kT}\right)^2 \frac{\exp\,[h\nu_E/(kT)]}{\{\exp\,[h\nu_E/(kT)] - 1\}^2} \\
&= 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} \qquad (1.10)
\end{aligned}
$$

where $\theta_E = h\nu_E/k$ defines the Einstein temperature. At ordinary temperatures $T >> \theta_E$, the expression for C_v approaches the Dulong and Petit law. At low temperatures, $T << \theta_E$.

$$C_v = 3Nk\left(\frac{\theta_E}{T}\right)^2 \exp\left(-\frac{\theta_E}{T}\right) \qquad (1.11)$$

which is not in agreement with the experimental T^3 dependence.

Debye improved the Einstein's model by assuming different frequencies of vibration for the $3N$ oscillators and distributing them as in black-body radiation. A cut-off frequency ν_D was also assumed. Debye derived the following T^3 law for C_v when $h\nu_D/(kT) >> 1$.

$$C_v = \frac{12\pi^4}{5} Nk\left(\frac{kT}{h\nu_D}\right)^3 \qquad (1.12)$$

The agreement between the Debye model and the experimental observations is good.

1.6 BOHR MODEL OF HYDROGEN ATOM

Rutherford, based on the results of α-scattering experiment, was the first to propose the nuclear model of the atom. In this model, the positive charge is confined to a very small sphere called the *nucleus* and the electrons move around it. This model of the atom is highly unstable as a moving electric charge radiates energy. Consequently, the electron in the Rutherford model of the atom spirals into the nucleus. Moreover, it failed to explain the observed sharp spectral lines of atoms. The concept of the nuclear model of the atom was thus available for Bohr in 1913.

The emission spectral lines of hydrogen were grouped into several series which fit the empirical formula, Eq. (1.2). A theoretical explanation of the hydrogen spectrum, based on quantum ideas, was first formulated by N. Bohr in 1913. He based his arguments on two assumptions, now known as Bohr's postulates:

Postulate 1 An electron moves only in certain allowed circular orbits, which are stationary states in the sense that no radiation is emitted. The condition for such states is that the orbital angular momentum of the electron equals an integral multiple of $\hbar\,(= h/2\pi)$, called *modified Planck's constant.* Therefore,

$$mvr = n\hbar, \qquad n = 1, 2, 3, \ldots \tag{1.13}$$

Postulate 2 Emission or absorption of radiation occurs only when the electron makes a transition from one stationary state to another. The radiation has a definite frequency ν_{mn} given by the condition:

$$h\nu_{mn} = E_m - E_n \tag{1.14}$$

Consider a hydrogen atom in which the electron of mass m moves with velocity v in a circular orbit of radius r centred in its nucleus. For simplicity, the nucleus is assumed to be at rest. The Coulombic attraction between the electron and the proton provides the necessary centripetal force. That is

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{ke^2}{r^2} \tag{1.15}$$

In this expression e is the electronic charge measured in coulombs and ε_0 is a constant called the *permittivity of vacuum.* The experimental value of ε_0 is 8.854×10^{-12} $C^2N^{-1}m^{-2}$. For convenience, we have written

$$k = \frac{1}{4\pi\varepsilon_0} = 8.984 \times 10^9 \text{ Nm}^2\text{C}^{-2} \tag{1.16}$$

The kinetic energy (T) of the electron is then given by

$$T = \frac{1}{2}mv^2 = \frac{ke^2}{2r} \tag{1.17}$$

From Eq. (1.13), the velocity of the electron in its nth orbit is

$$v_n = \frac{n\hbar}{mr} \tag{1.18}$$

Substituting this value of v_n in Eq. (1.15), we get

$$r_n = \frac{n^2\hbar^2}{kme^2} \tag{1.19}$$

The state for which $n = 1$ is called the *ground state* while states for which $n > 1$ are called the *excited states*. The radius of the orbit in the ground state is called the *Bohr radius* and is usually denoted by a_0.

In SI units, we get

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.53\ \text{Å} \tag{1.20}$$

The potential energy $V(r)$ of the electron proton system is

$$V(r) = -\frac{ke^2}{r} \tag{1.21}$$

The total energy of the hydrogen atom in the nth state is

$$E_n = T + V = \frac{ke^2}{2r_n} - \frac{ke^2}{r_n} = -\frac{ke^2}{2r_n}$$

Therefore,

$$E_n = -\frac{k^2me^4}{2\hbar^2}\frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.22}$$

Substituting the values of constants, we have

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -\frac{13.6}{n^2}\ \text{eV}, \qquad n = 1, 2, 3, \ldots \tag{1.23}$$

Substitution of Eq. (1.22) in Eq. (1.14) gives the frequency of the spectral line when the electron drops from the mth to nth state

$$\nu_{mn} = \frac{k^2 2\pi^2 me^4}{h^3}\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \qquad m > n \geq 1 \tag{1.24}$$

For hydrogen like systems (He^+, Li^{+2}, Be^{+3}), the energy is given by

$$E_n = -\frac{Z^2k^2me^4}{2\hbar^2n^2} = -\frac{Z^2me^4}{(4\pi\varepsilon_0)^2 2\hbar^2n^2}, \qquad n = 1, 2, 3, \cdots \tag{1.25}$$

where Z is the atomic number of the system. Bohr model was highly successful in explaining the spectrum of hydrogen and hydrogen like atoms.

Three electronic length scales used in numerical calculations are the Bohr radius a_0, Eq. (1.20); the Compton wavelength $\lambda_c = h/m_0c$ and the **fine structure constant** α defined by

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137} \tag{1.25a}$$

Often the Bohr formula, Eq. (1.23) is expressed in terms of Rydberg constant R_H defined by

$$R_H = \frac{\mu e^4}{8\varepsilon_0^2 ch^3} \tag{1.25b}$$

For solving numerical problems, often we require the following relations connecting these parameters:

$$a_0 = \frac{\hbar}{\alpha mc} \quad \text{and} \quad R_H = \frac{\mu c\alpha^2}{2h} \tag{1.25c}$$

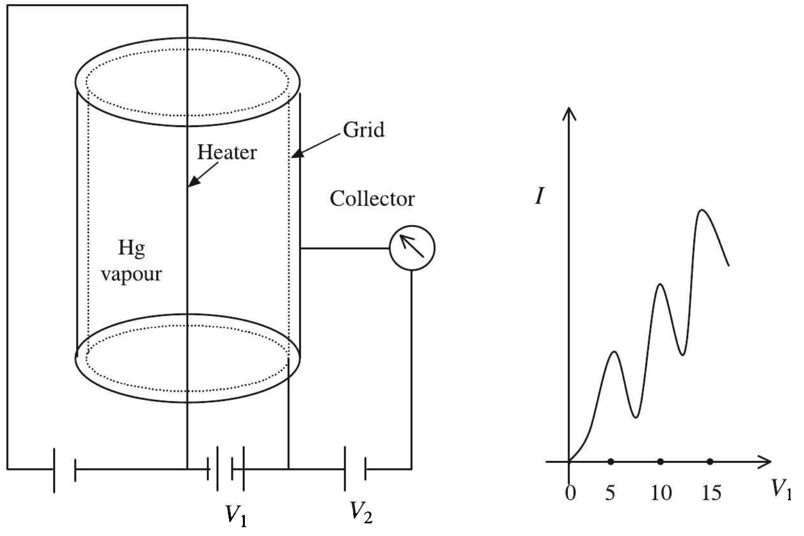
The Rydberg constant for an atom with a nucleus of infinite mass is denoted by R_∞. Then in the expression for R_H, μ has to be replaced by m, the mass of electron.

1.7 EXISTENCE OF STATIONARY STATES

Einstein's photoelectric equation proved unambiguously that electromagnetic radiation interacts with matter like an assembly of discrete quanta of energy. In 1914, Franck and Hertz reported an ingenious experiment to prove that mechanical energy is also absorbed by atoms in discrete quanta.

The experimental set-up consists of an electrically heated filament (cathode) along the axis of a cylindrical grid which is surrounded by a collector (anode). The whole set-up is placed in a quartz chamber filled with mercury vapour; refer to Figure 1.2(a). Electrons from the filament are accelerated to the grid by a positive potential V_1. A small retarding potential V_2 ($V_2 << V_1$) between the grid and anode retards the accelerated electrons. The electrons collected by the anode give rise to a current which is measured by a micrometer. The plot of collector current verses the accelerating potential V_1 is shown as in Figure 1.2(b). When V_1 is increased from zero to a critical potential V_c, the accelerated electrons make only elastic collisions with the atoms of mercury. However, when $V_1 = V_c$, the electrons make inelastic collisions near the grid and give the entire kinetic energy to mercury atoms. After losing their energy, the electrons are unable to overcome the retarding potential V_2 leading to a sharp fall in current. Electrons which have not made inelastic collisions reach the anode giving a small current. The first drop occurs at 4.9 V and a spectral line appears simultaneously in the emission spectrum of the mercury vapour at 253.6 nm, the value corresponding to a photon energy of 4.9 eV.

When the potential is increased further, the region where the electrons reach the critical energy of 4.9 eV moves closer to the filament. After losing the energy to mercury vapour by inelastic collision, the electron picks up energy on their way to the grid resulting in an increase of current. A second inelastic collision occurs near the grid, when $V_1 \cong 2V_c$ and a second current



(a) (b)

Figure 1.2 (a) Experimental arrangement of Franck and Hertz, (b) Plot of collector current verses accelerating voltage.

minimum occurs as shown in Figure 1.2(b). A similar behaviour is found at integral multiples of V_c. That is, the mercury atoms absorb mechanical energy in quanta of 4.9 eV. Thus, the occurrence or minima in the I verses V_1 curve can be explained only by the existence of stationary states in the atom.

1.8 WILSON–SOMMERFELD QUANTIZATION RULE

In 1915, Wilson and Sommerfeld proposed independently a more general quantization rule in which the Hamilton's equations of motion are first solved in the independent variables $q_1, q_2, \ldots, q_n$ and $p_1, p_2, \ldots, p_n$. The stationary states are those for which the action integral of any periodic motion equals an integer times h.

$$\oint p_i \, dq_i = n_i h, \qquad n_i = 0, 1, 2, \ldots, n \tag{1.26}$$

where the integration $\oint$ is over one cycle of motion. In circular orbits, the orbital angular momentum $L = mvr$ is a constant of motion. Hence for circular orbits Eq. (1.26) reduces to

$$\oint mvr \, d\phi = nh \quad \text{or} \quad mvr = \frac{nh}{2\pi} \tag{1.27}$$

which is Bohr's quantization rule, Eq. (1.13). In the following sections, we shall apply the general quantization rule to some cases of interest.

1.9 ELLIPTIC ORBITS OF HYDROGEN ATOM

The simplest force that is associated with point particles is the mutual central force acting along the line joining the two. Consider the two particles of the hydrogen atom with the nucleus of charge Ze fixed at the origin and the electron of mass m moving relative to the nucleus (refer to Figure 1.3). As per classical mechanics, the first integrals of the equations of motion of the system are

$$mr^2\dot{\theta} = L \quad \text{(a constant)} \tag{1.28}$$

and

$$\frac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2} + V(r) = E \qquad \text{(a constant)} \tag{1.29}$$

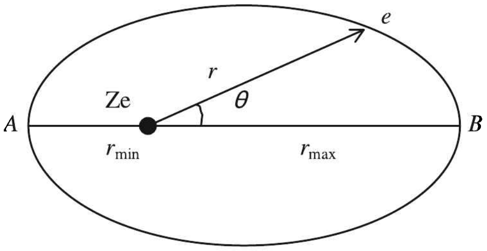


Figure 1.3 Parameters of the ellipse.

where

$$V(r) = -\frac{ke^2}{r} \tag{1.30}$$

L and E are the angular momentum and total energy of the system respectively. The radial momentum $p_r = m\dot{r}$ and the angular momentum $L = p_\theta$ obey the quantization rules:

$$\oint p_\theta \, d\theta = kh \quad \text{and} \quad \oint p_r \, dr = n_r h \tag{1.31}$$

where k and n_r are integers. Since p_θ is constant,

$$p_\theta \oint d\theta = kh \quad \text{or} \quad p_\theta 2\pi = 2\pi L = kh \tag{1.32}$$

From Eq. (1.29), we have

$$p_r = m\dot{r} = \pm\sqrt{2m\left(E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{L^2}{2mr^2}\right)} \tag{1.33}$$

The positive value of p_r corresponds to the increase of r from $r_{\min}$ to $r_{\max}$ and the negative value to the other half of the elliptical path. Therefore,

$$\oint p_r\,dr = 2\int_{r_{\min}}^{r_{\max}} \sqrt{2m\left(E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{L^2}{2mr^2}\right)}\,dr = 2\pi\left(e^2\sqrt{\frac{m}{-2E}} - L\right)$$

Combining this result with Eqs. (1.31) and (1.32), we get

$$\frac{2\pi e^2}{4\pi\varepsilon_0}\sqrt{\frac{m}{-2E}} = \left(k + n_r\right)h = nh \tag{1.34}$$

where the principal quantum number, $n = n_r + k$. Solving for E, we have

$$E = -\frac{k^2 me^4}{2\hbar^2 n^2} = -\frac{me^4}{\left(4\pi\varepsilon_0\right)^2 2\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots \tag{1.35}$$

which is same as Eq. (1.22). It may be mentioned here that no restriction is made to circular orbits while deriving Eq. (1.35).

At points A and B, $\frac{dr}{dt} = 0$ and this happens for $r = r_{\min}$ and $r = r_{\max}$. When $\frac{dr}{dt} = 0$, from Eq. (1.33), we get

$$r^2 + \frac{e^2 r}{4\pi\varepsilon_0 E} - \frac{L^2}{2mE} = 0 \tag{1.36}$$

and the sum of the roots of this equation is given by

$$r_{\min} + r_{\max} = -\frac{e^2}{4\pi\varepsilon_0 E}$$

As $r_{\min} + r_{\max} = 2a$, the semi-major axis of the ellipse is

$$a = -\frac{e^2}{(4\pi\varepsilon_0)2E} \tag{1.37}$$

Substitution of the value of E gives a_n, the length of the semi-major axis of the nth orbit

$$a_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} = n^2 a_0 \tag{1.38}$$

where a_0 is the Bohr radius.

Elliptic orbits of hydrogen atom was first solved by Sommerfeld as an example of the general quantization rule. The energy is dependent on the principal quantum number n which is the sum of k and n_r. Therefore, all orbits for which $k + n_r = n$ has the same value, will have the same energy. States of motion corresponding to the same energy are said to be *degenerate*. Among all orbits having the same value of n, one will be a circular one for which $n_r = 0$, $k = n$. This explains why the energy expression is the same as the one by Bohr's theory for circular orbits. The case $k = 0$ was ruled out by Sommerfeld as it corresponds to motion of the electron along a straight line through the nucleus. Electron orbits for $n = 1, 2, 3$ are shown in Figure 1.4.

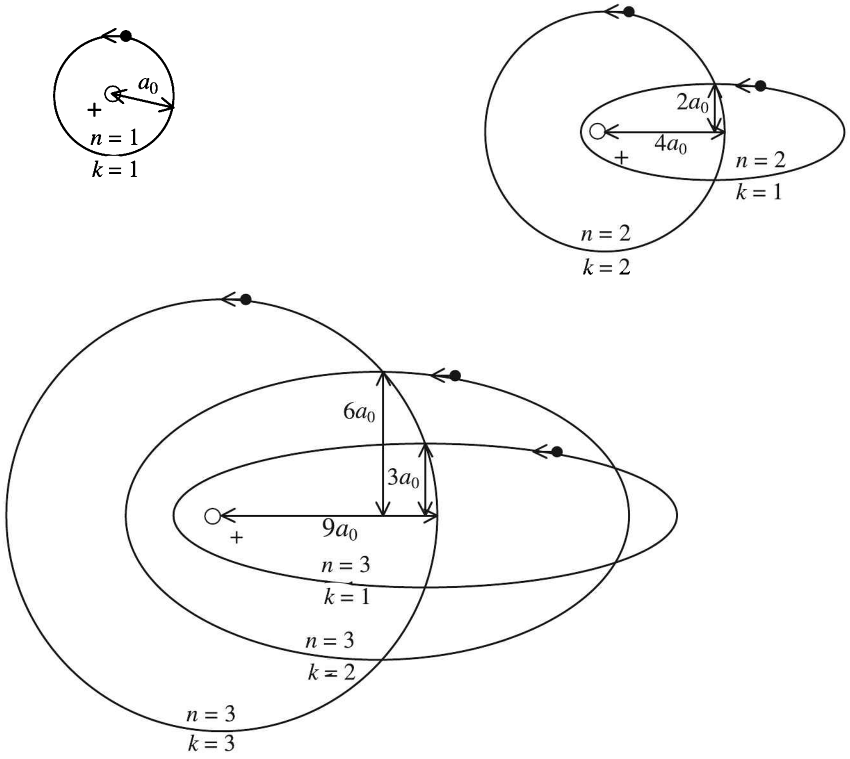


Figure 1.4 Sommerfeld electron orbits for $n = 1, 2, 3$.

1.10 THE HARMONIC OSCILLATOR

The displacement x with time t of a harmonic oscillator of frequency ν_0 is given by

$$x = x_0 \sin (2\pi\nu_0 t) \tag{1.39}$$

The force constant k and frequency n_0 are related by the expression:

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad \text{or} \quad k = 4\pi^2 m\nu_0^2 \tag{1.40}$$

Therefore, the potential energy is

$$V = \frac{1}{2}kx^2 = 2\pi^2 m\nu_0^2 x_0^2 \sin^2(2\pi\nu_0 t)$$

The kinetic energy is

$$T = \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = 2\pi^2 m \nu_0^2 x_0^2 \cos^2(2\pi \nu_0 t)$$

And the total energy is

$$E = T + V = 2\pi^2 m \nu_0^2 x_0^2 \tag{1.41}$$

According to the quantization rule

$$\oint p_x \, dx = nh \quad \text{or} \quad m \oint \frac{dx}{dt} \, dx = nh \tag{1.42}$$

When x completes one cycle, t changes by period $T = 1/\nu_0$. Hence, substituting the values of dx/dt and dx, we get

$$4\pi^2 m \nu_0^2 x_0^2 \int_0^{1/\nu_0} \cos^2(2\pi \nu_0 t) \, dt = nh, \qquad n = 0, 1, 2, \ldots$$

On solving, we get

$$2\pi^2 m \nu_0 x_0^2 = nh \quad \text{or} \quad x_0 = \left(\frac{nh}{2\pi^2 m \nu_0} \right)^{1/2} \tag{1.43}$$

Substituting the value of x_0 in Eq. (1.41), we have

$$E_n = nh\nu_0 = n\hbar\omega, \qquad n = 0, 1, 2, \ldots \tag{1.44}$$

That is, according to old quantum theory, the energies of a linear harmonic oscillator are integral multiples of $h\nu_0 = \hbar\omega$.

1.11 THE RIGID ROTATOR

A *rigid rotator* consists of two mass points connected by a massless rod. As the rotator is rigid, potential energy is zero. A rigid rotator restricted to move in a plane is described by an angle coordinate θ. The momentum conjugate to the angle coordinate $p_\theta = I\dot{\theta} = I\omega$, where I is the moment of inertia, is a constant of motion. The quantization rule reduces to

$$\int_0^{2\pi} p_\theta \, d\theta = Jh \quad \text{or} \quad p_\theta = \frac{Jh}{2\pi}, \qquad J = 0, 1, 2, \ldots \tag{1.45}$$

That is, the angular momentum p_θ is an integral multiple of $h/2\pi$. With this value of $p_\theta = I\omega$ the energy of a classical rotator $E = I\omega^2/2$ reduces to

$$E_J = \frac{J^2 h^2}{8\pi^2 I}, \qquad J = 0, 1, 2, \ldots \tag{1.46}$$

To describe a rigid rotator in space, one requires the two coordinates θ and ϕ of the polar coordinates. Application of the quantization rule gives the same expression as the one in Eq. (1.45) for the total angular momentum and

$$p_\phi = \frac{mh}{2\pi}, \qquad m = -J, -J+1, \ldots, J-1, J \tag{1.47}$$

for the component of angular momentum along the z-axis. The energy is independent of the quantum number m and is given by Eq. (1.46). Each energy level is $(2J + 1)$ fold degenerate.

1.12 PARTICLE IN A BOX

Consider a particle of mass m moving inside a rectangular box of sides a, b and c without the influence of any force. Let us assume that the collision with the walls of the box is perfectly elastic. The cartesian axes are taken along the edges of the box. The linear momentum p_x, p_y and p_z are constants of motion and change sign during collision with the walls. Applying the rule of quantization:

$$\oint p_x\, dx = 2ap_x = n_x h$$

We get

$$p_x = \frac{n_x h}{2a}, \qquad n_x = 0, 1, 2, \ldots$$

Similarly,

$$p_y = \frac{n_y h}{2b}, \qquad n_y = 0, 1, 2, \ldots$$

and

$$p_z = \frac{n_z h}{2c}, \qquad n_z = 0, 1, 2, \ldots$$

The total energy

$$E_{n_x, n_y, n_z} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{1.48}$$

In the case of a cubical box of side a

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{1.49}$$

The energy of the system is thus quantized.

1.13 THE CORRESPONDENCE PRINCIPLE

The *correspondence principle* of Bohr states that the quantum physics reduces to classical physics at large quantum numbers. To explain the principle, Bohr used a simple illustration based on the line spectra of one electron atom.

Classically, during the periodic motion in a stationary orbit, the frequency of the light emitted by the atom is equal to its frequency of revolution ν_r. From Eqs. (1.17) and (1.18), we get

$$\nu_r = \frac{v_n}{2\pi r_n} = \frac{me^4}{(4\pi\varepsilon_0)^2 2\pi n^3 \hbar^3} \tag{1.50}$$

For the transition $(n + 1) \to n$, the frequency of the emitted radiation (ν) is given by Eq. (1.24) as

$$\nu = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right] = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^3}\left[\frac{2n+1}{n^2(n+1)^2}\right] \tag{1.51}$$

It is clear that $\nu \to \nu_r$, when $n \to \infty$, as required by the correspondence principle.

1.14 THE STERN-GERLACH EXPERIMENT

The concept of vector atom model was introduced to explain certain experimental observations in the atomic spectra of complex atoms. This atom model has the two special features: *spatial quantization* and the *electron spin*. Direct experimental confirmation of these features was provided by the Stern-Gerlach experiment.

The magnetic moment $\boldsymbol{\mu}$ of an atom arises due to orbital and spin motions of the electrons. In a uniform magnetic field, the magnetic moment vector experiences a torque which tends to turn the direction of $\boldsymbol{\mu}$ and hence that of angular momentum with the magnetic field. This makes the vector $\boldsymbol{\mu}$ to precess around the field keeping a fixed angle θ with the field. If the magnetic field is nonuniform, the atom with the magnetic moment experiences an additional translatory motion. Hence, if an atom with a magnetic moment is shot in the x-direction through a magnetic field which increases along the z-axis, it will be deflected in the positive or negative z-direction. The shift will depend on the value of μ_z. If μ_z takes continuous values the beam would spread out into a continuous band in the xz-plane. Instead, if there is space quantization each atom will enter the magnetic field in a particular quantum state defined with the magnetic field direction as the axis. Consequently, the beam will split into separate beams and produce a series of distinct spots or sharp lines, one for each possible value of μ_z.

In their experiment, Stern and Gerlach passed a collimated beam of silver atoms through an inhomogeneous magnetic field produced by a specially designed electromagnet (Figure 1.5). While passing through the magnetic field, the beam splits into two parts, one travelling upwards and the other downwards, producing two spots on the screen.

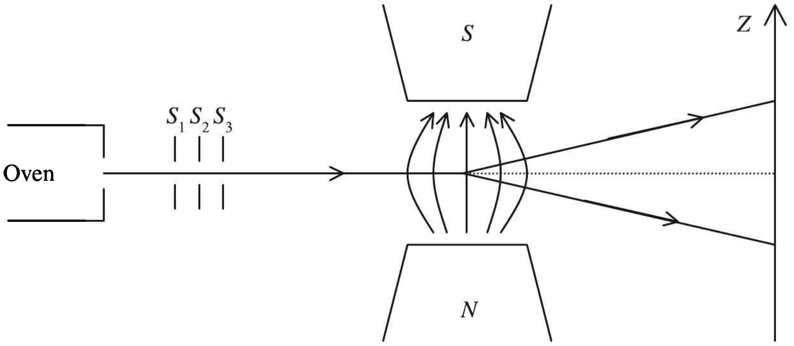


Figure 1.5 The Stern–Gerlach experiment.

In the ground state, the outer electron of silver atom is in an *s*-state (5*s*). Therefore, it has no orbital angular momentum and consequently no orbital magnetic moment. The observation of 2 spots suggests that all electrons have an intrinsic magnetic moment of the same magnitude with two possible orientations—parallel or antiparallel to the magnetic field. The origin of this magnetic moment can be understood if it is assumed that the electron of the silver atom has an intrinsic spin angular momentum. If the spin of the electron is s, the z-component of spin can have $2s + 1$ orientations. As two spots have been observed experimentally $2s + 1 = 2$ or $s = 1/2$. That is, the spin of electron is 1/2. Thus, spin, first detected in the Stern-Gerlach experiment, has become an 'observable'.

1.15 INADEQUACY OF QUANTUM THEORY

The quantum theory developed by Max Planck, Einstein and Bohr was found to be adequate in explaining certain phenomena such as black-body radiation, photoelectric effect, harmonic oscillator, rigid rotator, spectral lines of hydrogen atom, etc. However, it was inadequate to explain number of cases. Some of them are:

1. The general quantization rule is valid only for periodic systems. Hence the quantum theory is not applicable to non-periodic cases.
2. Even in the case of hydrogen spectrum, the theory could explain only the broad features.
3. Application of the quantum theory to helium atom, hydrogen molecule, etc., led to results contrary to experiments.
4. Failed to account the concept of half odd integer quantum numbers which are necessary for explaining Zeeman effect and fine structure of

spectral lines. In other words, it failed to account for the concept of spin.

5. It failed to give a method for evaluating transition probabilities and intensities of spectral lines.
6. The theory was unsuccessful in explaining the dispersion of light.

These shortcomings suggest that the quantum theory is not a very general one and the defects cannot be removed by extensions and modifications. Therefore, one has to look for a more basic theory to account for all phenomena.

WORKED EXAMPLES

EXAMPLE 1.1 The work function of barium and tungsten are 2.5 eV and 4.2 eV, respectively. Check whether these materials are useful in a photocell, which is to be used to detect visible light.

Wavelength (λ) of visible light is in the range 4000–7000Å.

$$\text{Energy of 4000-Å light} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{4000 \times 10^{-10} \times 1.6 \times 10^{-19}}$$
$$= 3.106 \text{ eV}$$

and

$$\text{Energy of 7000-Å light} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{7000 \times 10^{-10} \times 1.6 \times 10^{-19}} = 1.77 \text{ eV}$$

The work function of tungsten is 4.2 eV which is more than the energy range of visible light. Hence barium is the only material useful for the purpose.

EXAMPLE 1.2 Verify Eq.(1.23) for the energy of the hydrogen atom in the *n*th state.

From Eq. (1.23), we have

$$E_n = -\frac{me^4}{8\varepsilon_0{}^2h^2}\frac{1}{n^2} = -\frac{(9.11 \times 10^{-31}\text{ kg})(1.6 \times 10^{-19}\text{C})^4}{8(8.85 \times 10^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2})^2(6.626 \times 10^{-34}\text{Js})^2n^2}$$

$$= -\frac{21.703 \times 10^{-19}}{n^2}\text{ J}$$

$$= -\frac{21.703 \times 10^{-19}\text{ J}}{(1.6 \times 10^{-19}\text{ J/eV})\,n^2}$$

$$= -\frac{13.56}{n^2}\text{ eV}$$

EXAMPLE 1.3 Calculate the maximum wavelength that hydrogen in its ground state can absorb. What would be the next maximum wavelength?

Maximum wavelength corresponds to minimum energy. Hence the jump from ground state to first excited state gives the maximum λ.

Energy of the ground state = –13.6 eV

$$\text{Energy of the first excited state} = -\frac{13.6}{4} = -3.4 \text{ eV}$$

$$\text{Energy of the } n = 3 \text{ state} = -\frac{13.6}{9} = -1.5 \text{ eV}$$

Maximum wavelength corresponds to the energy = 13.6 – 3.4 = 10.2 eV

Maximum wavelength

$$= \frac{c}{\nu} = \frac{hc}{E_2 - E_1} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ m/s})}{10.2 \times 1.6 \times 10^{-19} \text{ J}} = 122 \text{ nm}$$

The next maximum wavelength corresponds to jump from ground state to the second excited state. This requires an energy = 13.6 – 1.5 = 12.1 eV. This corresponds to the wavelength:

$$\lambda = \frac{hc}{E_3 - E_1} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^8 \text{ m/s})}{12.1 \times 1.6 \times 10^{-19} \text{ J}} = 103 \text{ nm}$$

EXAMPLE 1.4 A hydrogen atom in a state having a binding energy of 0.85 eV makes a transition to a state with an excitation energy of 10.2 eV. Calculate the energy of the emitted photon.

Excitation energy of a state is the energy difference between that state and the ground state.

Excitation energy of the given state = 10.2 eV

Energy of the state having excitation energy

$$10.2 \text{ eV} = -13.6 + 10.2 = -3.4 \text{ eV}$$

Energy of the emitted photon during transition from –0.85 eV to –3.4 eV

$$= -0.85 - (-3.4) = 2.55 \text{ eV}$$

Let the quantum number of – 0.85 eV state be n and that of –3.4 eV state be m. Then

$$\frac{13.6}{n^2} = 0.85 \quad \text{or} \quad n = 4$$

$$\frac{13.6}{m^2} = 3.4 \quad \text{or} \quad m = 2$$

The transition is from $n = 4$ to $m = 2$ state

EXAMPLE 1.5 Determine the ionization energy of the He$^+$ ion. Also calculate the minimum frequency a photon must have to cause ionization.

Energy of a hydrogen like atom in the ground state = $-Z^2 \times 13.6$ eV

The ground state energy of He$^+$ ion = -4×13.6 eV = -54.4 eV

Ionization energy of He$^+$ ion = 54.4 eV

The minimum frequency of a photon that can cause ionization

$$\nu = \frac{E}{h} = \frac{54.4 \times 1.6 \times 10^{-19}\,\text{J}}{6.626 \times 10^{-34}\ \text{Js}} = 13.136 \times 10^{15}\ \text{Hz}$$

EXAMPLE 1.6 Calculate the velocity and frequency of revolution of the electron of the Bohr hydrogen atom in its ground state.

From Eqs. (1.17) and (1.18), the velocity of the electron of a hydrogen atom in its ground state

$$v_1 = \frac{e^2}{2\varepsilon_0 h} = \frac{(1.6 \times 10^{-19})^2}{2\,(8.85 \times 10^{-12})\,6.626 \times 10^{-34}}\ \text{ms}^{-1} = 2.18 \times 10^6\ \text{ms}^{-1}$$

From Eq. (1.50), the frequency of revolution of the electron in the ground state

$$\nu_1 = \frac{me^4}{4\varepsilon_0{}^2 h^3} = \frac{(9.11 \times 10^{-31})\,(1.6 \times 10^{-19})^4}{4\,(8.85 \times 10^{-12})^2 (6.626 \times 10^{-34})^3} = 6.55 \times 10^{15}\ \text{Hz}$$

EXAMPLE 1.7 What potential difference must be applied to stop the fastest photoelectrons emitted by a surface when electromagnetic radiation of frequency 1.5×10^{15} Hz is allowed to fall on it. The work function of the surface is 5 eV.

Energy of the photon = $h\nu = (6.626 \times 10^{-34})\ (1.5 \times 10^{15})$ J

$$= \frac{(6.626 \times 10^{-34})(1.5 \times 10^{15})}{1.6 \times 10^{-19}}$$

$$= 6.212\ \text{eV}$$

Energy of the fastest electron = 6.212 − 5.0 = 1.212 eV

Hence, the potential difference required to stop the fastest electron is 1.212 V.

EXAMPLE 1.8 X-rays with $\lambda = 1.0$ Å are scattered from a metal block. The scattered radiation are viewed at 90° to the incident direction. Evaluate the Compton shift.

$$\text{Compton shift } \Delta\lambda = \frac{h}{m_0 c}(1 - \cos\phi)$$

$$= \frac{6.626 \times 10^{-34}(1 - \cos 90)}{(9.11 \times 10^{-31})\,(3 \times 10^8)}$$

$$= 2.42 \times 10^{-12} \text{ m}$$

$$= 0.024 \text{ Å}$$

EXAMPLE 1.9 From a sodium surface, light of wavelength 3125Å and 3650 Å causes emission of electrons whose maximum kinetic energy is 2.128 eV and 1.595 eV, respectively. Estimate Planck's constant and work function of sodium.

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \text{kinetic energy}$$

$$\frac{hc}{3125 \times 10^{-10}} = \frac{hc}{\lambda_0} + 2.128 \times 1.6 \times 10^{-19}$$

$$\frac{hc}{3650 \times 10^{-10}} = \frac{hc}{\lambda_0} + 1.595 \times 1.6 \times 10^{-19}$$

$$\frac{hc}{10^{-10}}\left(\frac{1}{3125} - \frac{1}{3650}\right) = 0.533 \times 1.6 \times 10^{-19}$$

Therefore,

$$h = \frac{0.533 \times 1.6 \times 10^{-19} \times 10^{-10} \times 3125 \times 3650}{525 \times 3 \times 10^{8}} = 6.176 \times 10^{-34} \text{ Js}$$

From the first equation, the work function

$$\frac{hc}{\lambda_0} = \frac{6.176 \times 10^{-34} \times 3 \times 10^{8}}{3125 \times 10^{-10}} - 2.128 \times 1.6 \times 10^{-19}$$

$$= 2.524 \times 1.6 \times 10^{-19} \text{ J}$$

$$= 2.524 \text{ eV}$$

REVIEW QUESTIONS

1. How classical physics failed to account for the spectral distribution of energy density in a black body?
2. Explain photoelectric effect. Define the terms: work function, threshold frequency and cut-off wavelength.
3. Briefly outline the mechanism by which photoelectrons are emitted.
4. List out the basic experimental results of the photoelectric phenomena.
5. Write the expression for the velocity of photoelectrons emitted when radiation of wavelength λ is incident on a photosensitive surface, the threshold wavelength being λ_0.
6. What is Compton effect? Explain its significance.

7. Explain the assumptions of Planck with regard to cavity radiation and of Einstein with regard to photoelectric effect.
8. How particle nature of radiation was confirmed by the photoelectric effect and Compton effect?
9. Explain the postulates of Bohr with regard to hydrogen atom.
10. Apply Bohr's theory to singly-ionized helium atom. What relationship exists between this spectrum and the hydrogen spectrum?
11. Can a hydrogen atom absorb a photon whose energy exceeds its binding energy?
12. What are the different possibilities of spectral line emission for the hydrogen atom when the electron is excited to the $n = 5$ state?
13. State and explain the general quantization rule. Explain how it leads to Bohr's postulate regarding stationary states.
14. Sketch Sommerfeld electron orbits for $n = 4$.
15. Explain the significance of Stern–Gerlach experiment.

PROBLEMS

1. Light of wavelength 2000 Å falls on a metallic surface. If the work function of the surface is 4.2 eV, what is the kinetic energy of the fastest photoelectrons emitted? Also, calculate the stopping potential and threshold wavelength for the metal.
2. What is the work function of a metal, if the threshold wavelength for it is 580 nm? If light of 475 nm wavelength falls on the metal, what is its stopping potential?
3. How much energy is required to remove an electron from the $n = 8$ state of a hydrogen atom?
4. Calculate the frequency of the radiation that just ionizes a normal hydrogen atom.
5. A photon of wavelength 4 Å strikes an electron at rest and scattered at an angle of 150° to its original direction. Find the wavelength of the photon after collision.
6. When radiation of wavelength 1500 Å is incident on a photocell, electrons are emitted. If the stopping potential is 4.4 volts, calculate the work function, threshold frequency and threshold wavelength.
7. If a photon has wavelength equal to the Compton wavelength of the particle, show that the photon's energy is equal to the rest energy of the particle.
8. X-rays of wavelength 1.4 Å are scattered from a block of carbon. What will be the wavelength of scattered X-rays at (i) 180°, (ii) 90°, (iii) 0°?

9. Determine the maximum wavelength that hydrogen in its ground state can absorb. What would be the next wavelength that would work?

10. Construct the energy level diagram for doubly-ionized lithium.

11. What is the potential energy and kinetic energy of an electron in the ground state of the hydrogen atom?

12. Show that the magnitude of the potential energy of an electron in any Bohr orbit of the hydrogen atom is twice the magnitude of its kinetic energy in that orbit. What is the kinetic energy of the electron in the $n = 3$ orbit. What is its potential energy in the $n = 4$ orbit?

Chapter 2

Wave Mechanical Concepts

2.1 WAVE NATURE OF PARTICLES

The theory that radiation travels in space in the form of waves got established as it successfully explained the optical phenomena like reflection, refraction, interference, diffraction and polarization. However, to explain photoelectric effect and Compton effect one needs the particle or corpuscular nature of radiation. Thus, radiation possesses wave-particle duality. Sometimes it behaves like a wave and at times like a particle.

Matter Waves

The dual nature of radiation prompted Louis de Broglie to extend it to material particles also. He reasoned that (i) nature is strikingly symmetric in many ways, (ii) our observable universe is composed entirely of radiation and matter, (iii) if light has a dual nature, perhaps matter has also. Since matter is composed of particles, his reasoning suggested that one should look for a wave-like behaviour for matter. In other words, de Broglie assumed that a wave is associated with a particle in motion, called *matter wave*, which may be regarded as localized with the particle. Again he suggested that the wavelength of matter wave be given by the same relationship, namely

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{2.1}$$

where m is the mass and v is the velocity of the particle. This relation is often referred to as the *de Broglie relation.*

Electron Diffraction Experiment

The concept of wave nature of material particles was independently tested by Davisson and Germer and by G.P. Thomson. Thomson's experimental arrangement is analogous to Laue's X-ray diffraction method. The arrangement as shown in Figure 2.1(a) consists of a discharge tube in which a beam of electrons from a cathode *C* is accelerated by a potential difference ranging from 10,000 to 50,000 volts. The electrons collimated by the tube *A* fall on a thin gold film of thickness of the order of 10^{-6} cm. The apparatus is evacuated to avoid collision of electrons with the molecules of the gas. The diffracted beam is allowed to fall on a fluorescent screen *S* or on a photographic plate *P*. The photograph of the diffracted beam has a system of concentric rings, as shown in Figure 2.1(b). Measuring the radii of the rings and the distance between the film and photographic plate, the angle of diffraction θ can be obtained. Knowing the distance between atomic planes *d*, the wavelength of the diffracted beam can be calculated. The experiment clearly demonstrates the wave nature of electron as diffraction pattern can only be produced by waves.

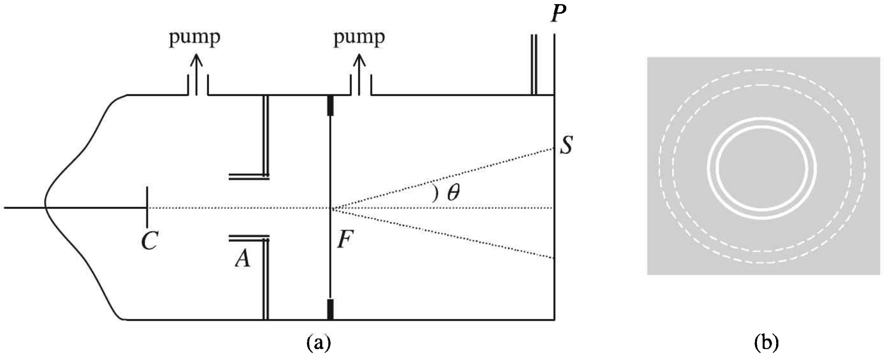


Figure 2.1 (a) Thomson's apparatus for electron diffraction, (b) diffraction pattern of a beam of electrons by thin gold foil.

In the acceleration process the electron behaves like a particle, in the diffraction process it behaves like a wave and in the detector it behaves like a particle. The electron which showed wave aspect in one part of the experiment showed particle aspect in two other parts of the same experiment. That is, for a complete description of physical phenomena, both particle and wave aspects of material particles are required. Hence, the new theory which we are looking for must account for the dual nature of radiation and matter.

Standing Wave of an Electron in the Orbit

An electron orbiting around a nucleus at a distance *r* is a bounded one and therefore the motion is represented by a standing wave. Only certain definite number of wavelengths can now exist in an orbit, otherwise the wave after travelling once round the orbit will be out of phase with the previous one. Mathematically,

$$\oint \frac{ds}{\lambda} = n, \qquad n = 1, 2, \ldots \tag{2.2}$$

where the integration is over one complete revolution. Substituting $\lambda = h/(mv)$, Eq. (2.2) reduces to

$$\oint mv\, ds = nh, \qquad n = 1, 2, \ldots \tag{2.3}$$

which is a form of the *general quantization rule*. For circular orbits, $ds = r\, d\theta$

$$mvr \oint d\theta = nh \quad \text{or} \quad mvr = \frac{nh}{2\pi}, \qquad n = 1, 2, \ldots \tag{2.4}$$

which is *Bohr's quantization rule*. Thus, the de Broglie relation gives the quantization rule in a refined way which was earlier introduced as an ad hoc hypothesis. The standing wave patterns of the electron in an orbit are illustrated in Figure 2.2.

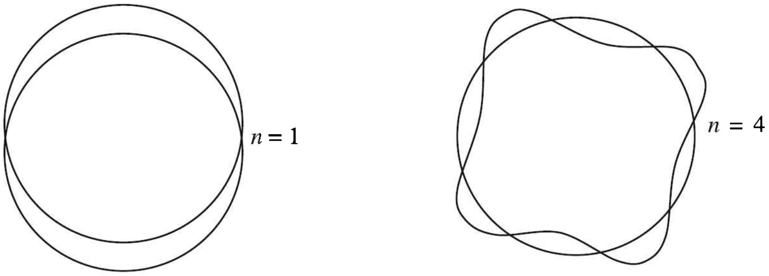


Figure 2.2 Standing wave patterns of an electron in an orbit for $n = 1$ and $n = 4$.

2.2 THE UNCERTAINTY PRINCIPLE

As per classical ideas, it is possible to determine all dynamical variables of a system to any desired degree of accuracy. This principle of determinism is the backbone of classical physics.

Position-momentum Uncertainty

The position of a plane wave is completely indeterminate as it is of infinite extent. Therefore, when waves are assigned to particles in motion an indeterminacy arises automatically in the formalism because an electron wave of definite frequency is not localized. Heisenberg analysed this indeterminacy and proposed that no two canonically conjugate quantities can be measured simultaneously. For the canonically conjugate variables x and p_x, mathematically, the principle is stated as

$$\Delta x\,\Delta p_x \cong h \tag{2.5}$$

The uncertainty relation can be illustrated by the *single-slit experiment* discussed below.

Single-slit experiment. Consider a beam of monoenergetic electrons of speed v_0 moving along the y-axis. Let us try to measure the position x of an electron and its velocity component v_x in the vertical direction (x-axis). To measure x, we insert a screen S_1 which has a slit of width Δx (Figure 2.3). If an electron passes through this slit, its vertical position is known to this accuracy. This can be improved by making the slit narrower.

As the electron has a wave nature, it will undergo diffraction at the slit giving the pattern as in Figure 2.3. Just at the time of reaching the slit, the velocity v_x of the electron is zero. The formation of the diffraction pattern shows that the electron has developed velocity component v_x after crossing the slit. For the first minimum, the theory of diffraction gives

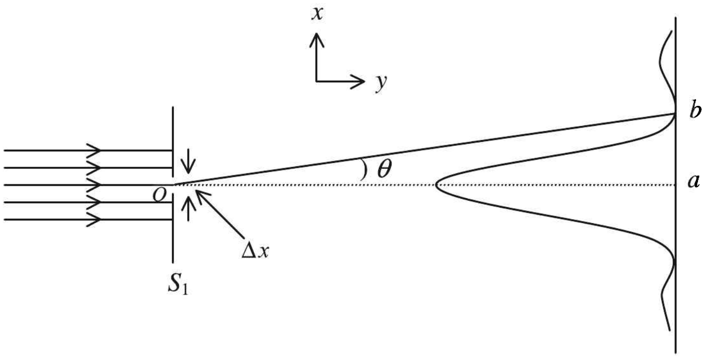


Figure 2.3 Illustration of Heisenberg uncertainty principle—single-slit experiment.

$$\sin\theta \cong \theta = \frac{\lambda}{\Delta x} \tag{2.6}$$

where λ is the wavelength of the electron beam. Let t be the time of transit from o to a and v_{xb} be the value of v_x at b. Then

$$v_0 t = oa \qquad \text{and} \qquad v_{xb} = \frac{ab}{t}$$

$$\tan\theta \cong \theta = \frac{ab}{oa} = \frac{tv_{xb}}{v_0 t} = \frac{v_{xb}}{v_0} \tag{2.7}$$

From Eqs. (2.6) and (2.7), we get

$$\frac{\lambda}{\Delta x} = \frac{v_{xb}}{v_0}$$

Replacing λ by h/mv_0 and taking v_{xb} as a rough measure of uncertainty Δv_x in v_x

$$\frac{h}{mv_0\Delta x} \cong \frac{\Delta v_x}{v_0} \quad \text{or} \quad \Delta x \Delta p_x \cong h \tag{2.8}$$

which is the desired relation. In the same way, we have

$$\Delta y \Delta p_y \cong h \quad \text{and} \quad \Delta z \Delta p_z \cong h \tag{2.9}$$

As the product of uncertainties is a universal constant, the more precisely we determine one variable, the less accurate is our determination of the other variable.

Before the introduction of the slit, the electrons travelling along the y-axis had the definite value of zero for p_x. By introducing the slit we measured the x-coordinate of the particles to an accuracy Δx, but this measurement introduced an uncertainty into the p_x values of the particles. Thus, the act of measurement introduced an uncontrollable disturbance in the system being measured which is a consequence of the wave particle duality.

Though the result is based on a particular experimental set-up, it is a very general one since it is independent of the particle mass and constants of the apparatus used. Heisenberg assumed it to be a fundamental law of nature. Therefore, the new mechanics we are looking for must abandon the deterministic model and allow only for probable values for dynamical variables.

The new mechanics was formulated independently by Werner Heisenberg (1925) and Erwin Schrödinger (1926). Heisenberg based his mechanics on matrix methods whereas Schrödinger used the idea of wave nature of electron. Introducing relativistic ideas, P.A.M. Dirac generalized quantum mechanics.

Uncertainty Relations for other Variables

Uncertainty relations can also be obtained for other pairs of canonically conjugate variables. For a free particle moving along x-axis, energy E is given by

$$E = \frac{p_x^2}{2m} \quad \text{or} \quad \Delta E = \frac{p_x}{m}\Delta p_x = v_x\,\Delta p_x$$

Therefore,

$$\Delta E = \frac{\Delta x}{\Delta t}\Delta p_x \quad \text{or} \quad \Delta E\,\Delta t = \Delta x\,\Delta p_x$$

Hence

$$\Delta E\,\Delta t \cong h \tag{2.10}$$

This equation indicates that if a system maintains a particular state for time Δt, its energy is uncertain at least by $\Delta E = h/\Delta t$.

The uncertainty for the pair of variables, component of angular momentum along the direction perpendicular to the plane of the orbit (L_z) of a particle and the angular position (ϕ) can be obtained as follows:

$$L_z^2 = 2IE$$

On differentiating, we get

$$L_z\,\Delta L_z = I\Delta E$$

where

$$L_z = I\omega = I\frac{\Delta\phi}{\Delta t}$$

Therefore,

$$I\,\frac{\Delta\phi}{\Delta t}\Delta L_z = I\,\Delta\,E$$

Using Eq. (2.10), we have

$$\Delta\phi\,\Delta L_z = \Delta E\ \Delta t = h \tag{2.11}$$

These uncertainty relations are very useful in explaining number of observed phenomena which the classical physics failed. We shall now consider some of them.

Applications of Uncertainty Relations

Ground state energy of hydrogen atom. The classical expression for the total energy of the electron in the ground state is given by

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 a} \tag{2.12}$$

where a is the radius of the first orbit. Let the uncertainty in the position of the electron Δx be of the order of a. More correctly, the product of uncertainties is given by $\hbar$. Therefore,

$$a\Delta p \cong \hbar \quad \text{or} \quad \Delta p \cong \frac{\hbar}{a} \tag{2.13}$$

Taking the momentum to be of the order of $\hbar/a$, we get

$$E = \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a} \tag{2.14}$$

For the ground state, the energy E has to be minimum. For this, dE/da must be zero. Denoting the minimum radius by a_0, we have

$$\frac{dE}{da} = 0 = \frac{-\hbar^2}{ma_0^3} + \frac{e^2}{4\pi\varepsilon_0 a_0^2}$$

or

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \tag{2.15}$$

With this value of a, Eq. (2.14) becomes

$$E = -\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = -\frac{me^4}{8\varepsilon_0^2 h^2} \tag{2.16}$$

which is the ground state energy of the hydrogen atom.

Width of spectral lines. Spectral lines have finite width due to various factors. One such factor is the natural broadening which is a direct consequence of uncertainty principle. Atoms remain in the excited state for a finite time τ, called the *life time*; before making a transition. Hence there will be an uncertainty in time of the order of τ. Then

$$\tau \Delta E \cong \hbar \quad \text{or} \quad \Delta \nu \cong \frac{1}{2\pi\tau} \tag{2.17}$$

For most of the states, the life time $\tau = 10^{-8}$ s. Hence, $\Delta \nu \cong 10^8$ Hz. This spreading is experimentally observed when the pressure is very low.

Mass of meson. Yukawa proposed that nuclear forces are due to an exchange of mesons. Uncertainty principle may be used to derive a relation between mass of meson (m) and the range (r_0) of nuclear force. When one nucleon exerts force on the other, a meson is created. During transit, its position is uncertain by an amount r_0. Use of the uncertainty relation gives

$$r_0 \Delta p \cong \hbar \quad \text{or} \quad \Delta p \cong \frac{\hbar}{r_0} \tag{2.18}$$

For a relativistic particle $p = mc$. Taking the uncertainty in momentum to be of this order, we obtain

$$mc \cong \frac{\hbar}{r_0} \quad \text{or} \quad m = \frac{\hbar}{r_0 c} \tag{2.19}$$

For $r_0 = 1.5 \times 10^{-13}$ cm, $m \cong 200\, m_e$, where m_e is the electron mass.

Nonexistence of electron in the nucleus. For an electron to exist inside a nucleus, the uncertainty in its position must be at least of the order of $2r_0$, r_0 being the radius of the nucleus. The uncertainty in the electron momentum is then

$$\Delta p \cong \frac{\hbar}{2r_0} \tag{2.20}$$

For a typical nucleus $r_0 \cong 10^{-14}$ m. Hence

$$\Delta p \cong \frac{1.055 \times 10^{-34}}{2 \times 10^{-14}} \cong 5.28 \times 10^{-21} \text{ kgms}^{-1}$$

The momentum of the electron must at least be of this order. The kinetic energy of the electron

$$T = \frac{p^2}{2m} = \frac{(5.28 \times 10^{-21})^2}{2(9.1 \times 10^{-31})} \text{J} \cong 95.7 \text{ MeV} \tag{2.21}$$

In β-decay, the energy of the emitted electron is usually of the order of few MeV. Therefore one does not expect the electron to be a constituent of the nucleus.

2.3 THE PRINCIPLE OF SUPERPOSITION

Two or more waves can traverse the same space independently of one another. Hence the total displacement at any point due to number of waves is simply the vector sum of the displacements produced by the individual waves. This is known as the *principle of superposition*. This principle is very important in the different branches of physics, namely optics, acoustics, electrical engineering, etc. Superposition principle allows us to analyse a complicated wave motion as a combination of number of simple harmonic motions. Though the linear superposition of waves is important in optics, sound, etc., it is unknown in the classical theory of particles. Since wave motion is assigned to particles in motion, we tentatively extend it to matter waves also. The concept of superposition of states would allow us the construction of wave packets.

2.4 WAVE PACKET

We have already seen that matter exhibits wave-like behaviour under suitable conditions. When the momentum of a particle is well defined, the wave can be of infinite extent. Therefore, a free particle moving along x-axis with a well defined momentum is described by an infinite plane wave $\Psi(x, t)$ given by

$$\Psi(x, t) = A_0 \exp [i(kx - \omega t)] \tag{2.22}$$

where the wave vector $k = 2\pi/\lambda$ and ω is the angular frequency. In the case of electromagnetic waves, the electromagnetic field varies in space and time. Sound waves can be described by the pressure variation in space and time. In other words, to describe wave motion, one requires a quantity which varies in space and time. In analogy with these, to describe matter waves associated with particles in motion, one requires a quantity which varies in space and time. This variable quantity, called the *wave function*, $\Psi(x, t)$, must be large in regions where the particle is likely to be found and small in the region where it is less likely to be found. That is, the wave function of a particle in conformity with the uncertainty principle must be localized in a small region around it. The wave function of the matter wave which is confined to a small region of space as in Figure 2.4 is termed as a *wave packet* or *wave group*.

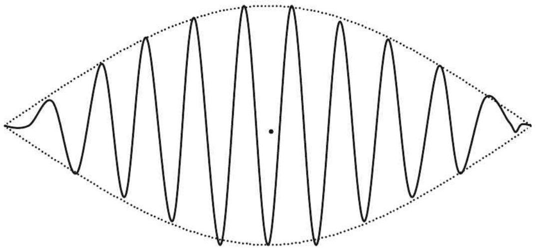


Figure 2.4 Representation of a wave packet.

Mathematically, a wave packet can be constructed by the superposition of an infinite number of plane waves with slightly differing k values.

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) \exp\left[ikx - i\omega(k)t\right] dk \tag{2.23}$$

As the particle is localized, we are interested in the superposition which leads to a wave group which travels without change of shape. This is possible when $A(k)$ is zero everywhere except for the small range of k values

$$\left(k_0 - \frac{\Delta k}{2}\right) < k < \left(k_0 + \frac{\Delta k}{2}\right), \quad \text{where } \Delta k << k_0 \tag{2.24}$$

As k lies in a very small interval, expanding $\omega(k)$ as a power series in $(k - k_0)$ about k_0, we have

$$\omega(k) = \omega(k_0) + (k - k_0)\left(\frac{d\omega}{dk}\right)_{k=k_0} + \cdots \tag{2.25}$$

Neglecting higher order terms and writing

$$\omega(k_0) = \omega_0 \quad \text{and} \quad \left(\frac{d\omega}{dk}\right)_{k=k_0} = \frac{d\omega}{dk}$$

we have

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) \exp\left[ikx - i\omega_0 t + i(k - k_0)\left(\frac{d\omega}{dk}\right)t\right] dk \tag{2.26}$$

Adding and subtracting $ik_0 x$ to the exponential, we get

$$\Psi(x,t) = F(x,t) \exp\left[i(k_0 x - \omega_0 t)\right] \tag{2.27}$$

where

$$F(x,t) = \int_{k_0-(\Delta k/2)}^{k_0+(\Delta k/2)} A(k) \exp\left[i(k - k_0)\left(x - \frac{d\omega}{dk}t\right)\right] dk \tag{2.28}$$

Equation (2.27) represents a plane wave with propagation constant k_0 and angular frequency ω_0 modulated by $F(x, t)$ which depends on x and t through $[x - (d\omega/dk)t]$. It follows that the wave packet moves with the group velocity

$$v_g = \frac{d\omega}{dk} \tag{2.29}$$

While the envelope of the wave packet (dotted line in Figure 2.4) moves with the group velocity v_g, the individual waves of the packet travels with velocity v_p called *phase velocity* or *wave velocity*. It is the wave group that carries the energy and what we measure experimentally is the group velocity.

It can easily be proved that the group velocity of the wave packet v_g is the same as the velocity of the material particle. Consider the relations

$$E = \hbar\omega \quad \text{and} \quad p = \hbar k$$

The group velocity

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} \tag{2.30}$$

For a free nonrelativistic particle

$$E = \frac{p^2}{2m} \quad \text{or} \quad \frac{dE}{dp} = \frac{p}{m} = v \tag{2.31}$$

For a relativistic particle, we have

$$E^2 = c^2p^2 + m_0{}^2c^4$$

Therefore,

$$\frac{dE}{dp} = \frac{c^2p}{E} = \frac{c^2m_0v/\sqrt{1 - (v^2/c^2)}}{m_0c^2/\sqrt{1 - (v^2/c^2)}} = v \tag{2.32}$$

Thus, the velocity of a particle and the group velocity of the corresponding wave packet are the same. The phase velocity

$$v_p = \frac{\omega}{k} = \frac{E}{p} = \frac{mc^2}{mv} = \frac{c^2}{v} \tag{2.33}$$

It has no physical significance and is not a measurable quantity.

2.5 TIME-DEPENDENT SCHRÖDINGER EQUATION

The nature of the wave function $\Psi(x, t)$ for localized and nonlocalized free particles have been discussed in the previous section. However, for detailed study of systems, we require the equation of motion for $\Psi(x, t)$ which was formulated by Erwin Schrödinger in 1926. Schrödinger equation is a fundamental one in quantum mechanics as Newton's equation in classical physics.

One-dimensional Equation for a Free Particle

The wave function of a localized free particle is the one given in Eq. (2.23). For a free particle, the classical expression for energy is

$$E = \frac{p_x^2}{2m} \tag{2.34}$$

Replacing p_x by $k\hbar$ and E by $\hbar\omega$, we get

$$\omega = \frac{\hbar k^2}{2m} \tag{2.35}$$

Substituting this value of ω in Eq. (2.23)

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) \exp\left[i\left(kx - \frac{\hbar k^2}{2m}t\right)\right] dk \tag{2.36}$$

Differentiating $\Psi(x, t)$ with respect to t, we get

$$\frac{\partial \Psi}{\partial t} = \frac{-i\hbar}{2m} \int_{-\infty}^{\infty} k^2 A(k) \exp\left[i\left(kx - \frac{\hbar k^2}{2m}t\right)\right] dk \tag{2.37}$$

Differentiating $\Psi(x, t)$ twice with respect to x, we get

$$\frac{\partial^2 \Psi}{\partial x^2} = -\int_{-\infty}^{\infty} k^2 A(k) \exp\left[i\left(kx - \frac{\hbar k^2}{2m}t\right)\right] dk \tag{2.38}$$

Combining Eqs. (2.37) and (2.38), we have

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \tag{2.39}$$

which is the *one-dimensional Schrödinger equation* for a free particle.

Operators for Momentum and Energy

To obtain the operators for momentum and energy, Eq. (2.39) may be written as

$$\left(i\hbar \frac{\partial}{\partial t}\right)\Psi(x,t) = \frac{1}{2m}\left(-i\hbar \frac{\partial}{\partial x}\right)\left(-i\hbar \frac{\partial}{\partial x}\right)\Psi(x,t) \tag{2.40}$$

From a comparison of Eqs. (2.34) and (2.40), it may be concluded that the energy E and momentum $\mathbf{p}$ can be considered as the differential operators

$$E \to i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad p_x \to -i\hbar \frac{\partial}{\partial x} \tag{2.41}$$

operating on the wave function $\Psi(x, t)$. Equation (2.39) is obtained even if the operator for p is taken as $i\hbar\partial/\partial x$ in place of $-i\hbar\partial/\partial x$. The choice of the negative sign is very significant which is explained in Section 2.7.

Extension to Three Dimensions

The one-dimensional treatment given above can easily be extended to three dimensions. The three-dimensional wave packet can be written as

$$\Psi(\mathbf{r}, t) = \int_{-\infty}^{\infty} A(\mathbf{k}) \exp\left[i\left(\mathbf{k}\cdot\mathbf{r} - \omega t\right)\right] dk_x \, dk_y \, dk_z \tag{2.42}$$

Proceeding on similar lines as in the one-dimensional case we get the three-dimensional Schrödinger equation for a free particle as

$$i\hbar \frac{\partial \Psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) \tag{2.43}$$

An analysis similar to the one made for one-dimensional system leads to the following operators for energy and momentum

$$E \to i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \mathbf{p} \to -i\hbar\nabla \tag{2.44}$$

Inclusion of Forces

Modification of the free particle equation to a system moving in a potential $V(\mathbf{r}, t)$ can easily be done. The classical energy expression for such a system is given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \tag{2.45}$$

Schrödinger then made the right guess regarding the operators for $\mathbf{r}$ and t as

$$\mathbf{r} \to \mathbf{r} \quad \text{and} \quad t \to t \tag{2.46}$$

Replacing E, $\mathbf{p}$, $\mathbf{r}$ and t in Eq. (2.45) by their operators and allowing the operator equation to operate on the wave function $\Psi(\mathbf{r}, t)$, we get

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \left[\frac{-h^2}{2m}\nabla^2 + V(\mathbf{r}, t)\right]\Psi(\mathbf{r}, t) \tag{2.47}$$

which is the *time-dependent Schrödinger equation* for a particle of mass m moving in a potential $V(\mathbf{r}, t)$. The quantity in the square bracket in Eq. (2.47) is the *operator for the Hamiltonian of the system.* In general, its solution will be complex because of the presence of i in the equation. The equation cannot be relativistically invariant as it contains first derivative in time and second derivate in space coordinates.

2.6 INTERPRETATION OF THE WAVE FUNCTION

Probability Interpretation

The wave function $\Psi(\mathbf{r}, t)$ has no physical existence since it can be complex. Also, it cannot be taken as a direct measure of the probability at $(\mathbf{r}, t)$ since the probability is real and nonnegative. However, $\Psi(\mathbf{r}, t)$ must in some way be an index of the presence of the particle at $(\mathbf{r}, t)$. A universally accepted statistical interpretation was suggested by Born in 1926. He interpreted the product of $\Psi(\mathbf{r}, t)$ and its complex congugate Ψ^* as the position probability density $P(\mathbf{r}, t)$

$$P(\mathbf{r}, t) = \Psi^* (\mathbf{r}, t)\ \Psi(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 \tag{2.48}$$

The quantity $|\Psi(\mathbf{r}, t)|^2 d\tau$ is then the probability of finding the system at time t in the small volume element $d\tau$ surrounding the point $\mathbf{r}$. When $|\Psi(\mathbf{r}, t)|^2\, d\tau$ is integrated over the entire space one should get the total probability, which is unity. Therefore,

$$\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\tau = 1 \tag{2.49}$$

For Eq. (2.49) to be finite, $\Psi(\mathbf{r}, t)$ must tend to zero sufficiently rapidly as $r \rightarrow \pm \infty$. Hence, one can multiply $\Psi(\mathbf{r}, t)$ by a constant, say N, so that $N\Psi$ satisfies the condition in Eq. (2.49). Then

$$|N|^2 \int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\tau = 1 \tag{2.50}$$

The constant N is called the *normalization constant* and Eq. (2.50) the *normalization condition.* Since the Schrödinger equation is a linear differential equation, $N\Psi$ is a solution of it. The wave functions for which the integral in Eq. (2.49) does not converge will be treated depending on the nature of the functions.

Probability Current Density

The probability of finding a system, described by a wave function $\Psi(\mathbf{r}, t)$ in a finite volume V in space is given by $\int_v \Psi^*\Psi\, d\tau$ and this changes as the wave function evolves in time. To study this, consider the Schrödinger equation and its complex conjugate form, as under:

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}=\left[\frac{-h^2}{2m}\nabla^2+V(\mathbf{r})\right]\Psi \tag{2.51}$$

and

$$-i\hbar\frac{\partial\Psi^*}{\partial t}=\left[\frac{-h^2}{2m}\nabla^2+V(\mathbf{r})\right]\Psi^* \tag{2.52}$$

Here, the potential V is assumed to be real. Multiplying Eq. (2.51) by Ψ^* and Eq. (2.52) by Ψ from left and subtracting one from the other

$$i\hbar\left(\Psi^*\frac{\partial\Psi}{\partial t}+\Psi\frac{\partial\Psi^*}{\partial t}\right)=\frac{-\hbar^2}{2m}\left[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right]$$

or

$$\frac{\partial}{\partial t}(\Psi^*\Psi)=\frac{i\hbar}{2m}\left[\nabla\cdot(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)\right] \tag{2.53}$$

Integrating, we get

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\Psi^*\Psi\,d\tau=\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\nabla\cdot\left(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*\right)d\tau$$

$$=\frac{i\hbar}{2m}\left[\left(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*\right)\right]_{-\infty}^{\infty} \tag{2.54}$$

If we have a localized wave packet, which is the situation in almost all cases, Ψ and $\Psi^* \to 0$ as $r \to \pm\infty$ and the right-hand side of Eq. (2.54) vanishes. Then

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\Psi^*\Psi\,d\tau=0 \quad \text{or} \quad \int_{-\infty}^{\infty}\Psi^*\Psi\,d\tau=\text{constant in time} \tag{2.55}$$

That is, the normalization integral is constant in time.

By defining a vector $\mathbf{j}(\mathbf{r}, t)$, called the *probability current density.*

$$\mathbf{j}(\mathbf{r},t)=\frac{i\hbar}{2m}\left(\Psi\nabla\Psi^*-\Psi^*\nabla\Psi\right) \tag{2.56}$$

and substituting in Eq. (2.53), we get

$$\frac{\partial P(\mathbf{r},t)}{\partial t}+\nabla\cdot\mathbf{j}(\mathbf{r},t)=0 \tag{2.57}$$

Equation (2.57) is the *equation of continuity* for probability, which is analogous to the equation of continuity in hydrodynamics and electrodynamics. With this definition of probability current density, Eq. (2.57) becomes a quantum mechanical probability conservation equation. It may be noted that if Ψ is real, the vector $\mathbf{j}(\mathbf{r}, t)$ vanishes. Writing the integral form of Eq. (2.57) over a finite volume V and using Gauss theorem, we get

$$\frac{\partial}{\partial t}\int_V P(\mathbf{r},t)\,d\tau = -\int_V \nabla\cdot\mathbf{j}\,d\tau = -\oint_s \mathbf{j}\cdot ds \tag{2.58}$$

where s is the area of the enclosed volume V. This result suggests that any decrease in probability in a region is accompanied by an outflow of probability across its surface. In other words, if the probability of finding a system in some region increases with time, the probability of finding the system outside decreases by the same amount.

Expectation Value

The definition of probability density immediately allows the calculation of the *expectation value* of the position vector of a particle. Consider a large number of measurements of the position vector $\mathbf{r}$ of a particle made when it is in a particular state. Ensure that the particle has the same wave function $\Psi(\mathbf{r}, t)$ before each measurement. The average of all the different values is the 'expectation value' $\langle\mathbf{r}\rangle$ of the position coordinate. As $|\Psi(\mathbf{r}, t)|^2$ represents the probability with which the value $\mathbf{r}$ occurs in the measurement, $\langle\mathbf{r}\rangle$ can be written as

$$\langle\mathbf{r}\rangle = \int \mathbf{r}\Psi^*\Psi\,d\tau = \int \Psi^*\mathbf{r}\,\Psi\,d\tau \tag{2.59}$$

In this definition, the wave function Ψ is a normalized one. The necessity for sandwiching $\mathbf{r}$ between Ψ^* and Ψ would be made clear in the latter part of this section. Based on similar arguments the expectation value of a function of $\mathbf{r}$ may be written as

$$\langle f(\mathbf{r})\rangle = \int \Psi^*(\mathbf{r}, t) f(\mathbf{r})\Psi(\mathbf{r}, t)\,d\tau \tag{2.60}$$

Left multiplying the time dependent-Schrödinger equation, Eq. (2.47), by Ψ^* and integrating from $-\infty$ to ∞, we get

$$\int_{-\infty}^{\infty} \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi\,d\tau = \int_{-\infty}^{\infty} \Psi^*\left(-\frac{\hbar^2}{2m}\nabla^2\right)\Psi\,d\tau + \int_{-\infty}^{\infty} \Psi^* V\,\Psi\,d\tau$$

or

$$\left\langle i\hbar\frac{\partial}{\partial t}\right\rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2\right\rangle + \langle V\rangle \tag{2.61}$$

Therefore,

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle \tag{2.62}$$

which is the quantum analogue of the classical energy expression. That is sandwiching of the operator between Ψ^* and Ψ is consistent with the Schrödinger equation. Here, we have assumed that the average motion of the wave packet to be the same as the classical motion of the particle. This requirement is further justified by the Ehrenfest's theorem (refer to Section 2.7).

From the above discussion, we can reasonably take the expectation value of any dynamical variable A whose operator is A_{0p} as

$$\langle A \rangle = \int \Psi^* A_{0p} \Psi \, d\tau \tag{2.63}$$

If the wave function is not normalized,

$$\langle A \rangle = \frac{\int \Psi^* A_{0p} \Psi d\tau}{\int \Psi^* \Psi d\tau} \tag{2.64}$$

Since the space coordinates have been integrated out, the expectation value is a function of time only.

2.7 EHRENFEST'S THEOREM

Correspondence between the motion of a classical particle and the motion of a wave packet was worked out by Ehrenfest in 1927. In the limit when the wave packet associated with a particle reduces to a point, one expects the particle to behave like a classical one. Consider the one-dimensional motion of a particle of mass m. The time derivative of $\langle x \rangle$ is given by

$$\frac{d\langle x \rangle}{dt} = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \Psi^* x \Psi dx = \int_{-\infty}^{\infty} \left(\frac{\partial \Psi^*}{\partial t} x \Psi + \Psi^* x \frac{\partial \Psi}{\partial t} \right) dx \tag{2.65}$$

Substituting the values of $\partial \Psi / \partial t$ and $\partial \Psi^* / \partial t$ from Eqs. (2.51) and (2.52), we get

$$\frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \left(x\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - x\Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right) dx \tag{2.66}$$

Integrating the second term by parts twice and using the condition that Ψ and its derivative tends to zero as $x \to \pm\infty$ (for a localized packet), we have

$$\int_{-\infty}^{\infty} x\Psi \frac{\partial^2 \Psi^*}{\partial x^2} dx = \int_{-\infty}^{\infty} \Psi^* \frac{\partial^2 (x\Psi)}{\partial x^2} dx = \int_{-\infty}^{\infty} \Psi^* \left(2\frac{\partial \Psi}{\partial x} + x \frac{\partial^2 \Psi}{\partial x^2} \right) dx$$

Hence

$$\frac{d\langle x\rangle}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(x\Psi^*\frac{\partial^2\Psi}{\partial x^2} - 2\Psi^*\frac{\partial\Psi}{\partial x} - \Psi^* x\frac{\partial^2\Psi}{\partial x^2}\right)dx$$

$$= \frac{1}{m}\int_{-\infty}^{\infty}\Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\, dx$$

Therefore,

$$m\frac{d\langle x\rangle}{dt} = \langle p_x\rangle \tag{2.67}$$

In the limit the wave packet reduces to a point, $\langle x\rangle = x$ and = $\langle p_x\rangle = p_x$, and Eq. (2.67) reduces to the classical equivalent

$$m\frac{dx}{dt} = p_x \tag{2.68}$$

The time rate of change of $\langle p_x\rangle$ is given by

$$\frac{d}{dt}\langle p_x\rangle = \frac{d}{dt}\int_{-\infty}^{\infty}\Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\, dx$$

$$= -i\hbar\int_{-\infty}^{\infty}\left[\frac{\partial\Psi^*}{\partial t}\frac{\partial\Psi}{\partial x} + \Psi^*\frac{\partial}{\partial x}\left(\frac{\partial\Psi}{\partial t}\right)\right]dx \tag{2.69}$$

Again substituting $\partial\Psi/\partial t$ and $\partial\Psi^*/\partial t$, we get

$$\frac{d\langle p_x\rangle}{dt} = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left[\Psi^*\frac{\partial}{\partial x}\left(\frac{\partial^2\Psi}{\partial x^2}\right) - \frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x}\right]dx$$

$$+\int_{-\infty}^{\infty}\left(V\Psi^*\frac{\partial\Psi}{\partial x} - \Psi^*\frac{\partial V\Psi}{\partial x}\right)dx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left[\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2}\right) - \frac{\partial\Psi^*}{\partial x}\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}\frac{\partial\Psi}{\partial x}\right]dx$$

$$+\int_{-\infty}^{\infty}\Psi^*\left(-\frac{\partial V}{\partial x}\right)\Psi\, dx$$

$$= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left[\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial^2\Psi}{\partial x^2}\right) - \frac{\partial}{\partial x}\left(\frac{\partial\Psi^*}{\partial x}\cdot\frac{\partial\Psi}{\partial x}\right)\right]dx + \left\langle-\frac{\partial V}{\partial x}\right\rangle$$

The first term on the right side can easily be integrated out and is equal to zero since Ψ^* and $\partial\Psi/\partial x$ are zero as $x \to \pm\infty$. Hence

$$\frac{d\langle p_x\rangle}{dt} = \left\langle\frac{-\partial V}{\partial x}\right\rangle = \langle F_x\rangle \tag{2.70}$$

When the wave packet reduces to a point, Eq. (2.70) becomes Newton's second law of motion. Generalizing Eqs. (2.67) and (2.70), we obtain

$$\langle \mathbf{p}\rangle = m\frac{d\langle \mathbf{r}\rangle}{dt} \quad \text{and} \quad \langle \mathbf{F}\rangle = \frac{d\langle \mathbf{p}\rangle}{dt} \tag{2.71}$$

Equation (2.71), called the *Ehrenfest's theorems*, are the quantum equivalent of the equations of motion of a classical particle. Reduction of the wave packet to a point means the violation of uncertainty principle. Hence, uncertainty principle limits the equivalence of quantum and classical mechanics.

If $i\hbar\nabla$, instead of $-i\hbar\nabla$, is selected as the operator for $\mathbf{p}$, we would have obtained

$$\frac{d\langle \mathbf{p}\rangle}{dt} = -\langle \mathbf{F}\rangle$$

which is not the quantum analogue of Newton's second law of motion. The selection of the operator $-i\hbar\nabla$ for the dynamical variable $\mathbf{p}$ is thus justified.

2.8 TIME-INDEPENDENT SCHRÖDINGER EQUATION

The time-dependent Schrödinger equation, Eq. (2.47), describes the evolution of quantum systems using time-dependent wave function $\Psi(\mathbf{r}, t)$. It completely neglects the time dependence of the operators. More about these aspects will be discussed in Section 3.9. If the Hamiltonian operator does not depend on time, the variables $\mathbf{r}$ and t of the wave function $\Psi(\mathbf{r}, t)$ can be separated into two functions $\psi(\mathbf{r})$ and $\phi(t)$.

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\,\phi(t) \tag{2.72}$$

Substituting this value of $\Psi(\mathbf{r}, t)$ in Eq. (2.47) and dividing throughout by $\psi(\mathbf{r})\phi(t)$ we get

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\psi(\mathbf{r})}\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi(\mathbf{r}) \tag{2.73}$$

The left side of this equation is a function of time and right side a function of space coordinates. Since t and $\mathbf{r}$ are independent variables, each side must be equal to a constant, say E. This gives rise to the equations

$$\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = -\frac{iE}{\hbar} \tag{2.74}$$

and

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{2.75}$$

Solution of Eq. (2.74) is straightforward and is given by

$$\phi(t) = C \exp\left(-\frac{iEt}{\hbar}\right) \tag{2.76}$$

where C is a constant. The equation for $\psi(r)$, Eq. (2.75), is the *time-independent Schrödinger equation* or simply *Schrödinger equation.* Since $\psi(\mathbf{r})$ determines the amplitude of the wave function $\Psi(\mathbf{r}, t)$, it is called the *amplitude equation.* Equation (2.72) now takes the form

$$\Psi(\mathbf{r}, \mathrm{t}) = \psi(\mathbf{r}) \exp\left(-\frac{iEt}{\hbar}\right) \tag{2.77}$$

The constant C is included in the normalization constant for $\psi(\mathbf{r})$.

Significance of the separation constant, E, can be understood by differentiating $\Psi(\mathbf{r}, t)$ in Eq. (2.72) with respect to time and multiplying by $i\hbar$. Then

$$i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} = E\Psi(\mathbf{r}, t) \tag{2.78}$$

Multiplying both sides of Eq. (2.78) by Ψ^* from left and integrating over the space coordinates from $-\infty$ to ∞, we get

$$\int_{-\infty}^{\infty} \Psi^*\left(i\hbar\frac{\partial}{\partial t}\right)\Psi(\mathbf{r}, t)\, dt = E \tag{2.79}$$

As the left side of Eq. (2.79) is the expectation value of the energy operator, the constant E is the energy of the system. The same can be understood from Eq. (2.75) as

$$-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

is the operator associated with the Hamiltonian of the system.

2.9 STATIONARY STATES

The solution of the time-independent Schrödinger equation, Eq. (2.75), can be obtained if the explicit form of $V(\mathbf{r})$ is known. It is found that in general a system has a set of well-defined energy values E_n, for $n = 1, 2, 3, \ldots$ with corresponding wave functions $\psi_n(\mathbf{r})$. Including the time dependent part, the wave function of the system is

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp\left(-\frac{iE_n t}{\hbar}\right) \tag{2.80}$$

$$= \Psi_n(\mathbf{r}, 0) \exp\left(-\frac{iE_n t}{\hbar}\right) \tag{2.81}$$

The probability density $P(\mathbf{r}, t)$ is then given by

$$P(\mathbf{r}, t) = |\Psi_n(\mathbf{r}, t)|^2 = |\Psi_n(\mathbf{r}, 0)|^2 = \text{constant in time} \tag{2.82}$$

where $n = 1, 2, 3, \ldots$. The states for which the probability density is constant in time are called *stationary states*. The time-dependent factor exp $(-iE_n t/\hbar)$ of such states are governed by the energy E_n of the particle.

It can be seen that in stationary states, the expectation value of an observable whose operator does not depend on time explicitly is a constant in time. Then

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi_n^*(\mathbf{r}, 0) \exp\left(\frac{iE_n t}{\hbar}\right) A \Psi_n(\mathbf{r}, 0) \exp\left(-\frac{iE_n t}{\hbar}\right) d\tau$$

$$= \int_{-\infty}^{\infty} \Psi_n^*(\mathbf{r}, 0)\, A\, \Psi_n(\mathbf{r}, 0)\, d\tau$$

$$= \text{constant in time} \tag{2.83}$$

It is obvious from Eq. (2.56) that for stationary states the probability current density $\mathbf{j}(\mathbf{r}, t)$ is also constant in time. As $\partial P/\partial t = 0$ for such states, from the equation of continuity for probability, Eq. (2.57), we have

$$\nabla \cdot \mathbf{j} = 0 \tag{2.84}$$

A stationary state is a *bound one* if the corresponding wave function $\psi(\mathbf{r})$ or probability density $|\psi(\mathbf{r})|^2$ vanishes at infinity. That is, for bound states

$$\lim_{r \to \infty} \psi(\mathbf{r}) = 0 \tag{2.85}$$

N. Bohr was the first to postulate the existence of stationary states. These are the states on which physical measurements are performed. Spectral transitions are induced between such states. Owing to these reasons, solution of the time-independent Schrödinger equation for different systems is of fundamental importance in quantum mechanics.

In stationary states, the probability density is constant in time. If a particle is in a superposition state (of stationary states) like

$$\Psi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r}) \exp\left(-\frac{iE_n t}{\hbar}\right) \tag{2.86}$$

the probability density

$$P(\mathbf{r}, t) = |\Psi(\mathbf{r}, t)|^2 = \sum_n |c_n|^2 \, |\psi_n(\mathbf{r})|^2$$

$$+ \sum_m \sum_n c_m^* c_n \psi_m^* \psi_n \exp\left[\frac{i(E_m - E_n)t}{\hbar}\right] \tag{2.87}$$

Hence, if a particle is in a superposition state, in general, the probability density depends on time.

2.10 ADMISSIBILITY CONDITIONS ON THE WAVE FUNCTION

In the preceding sections, we have discussed the Schrödinger equation and interpretation of the wave function. However, we have not formulated the conditions to be satisfied by a wave function. A physical system is described by the probability density $|\Psi(\mathbf{r}, t)|^2$ and the normalization integral, Eq. (2.49). For the probability density to be unique and the total probability to be unity, the wave function must be finite and single valued at every point in space. The probability current density $\mathbf{j}$, Eq. (2.56), another important parameter of the probability interpretation, contains Ψ and $\nabla\Psi$. Hence Ψ has to be continuous and $\nabla\Psi$ must be finite. The Schrödinger equation has the term $\nabla^2\Psi$. For $\nabla^2\Psi$ to exist $\nabla\Psi$ must be continuous. For a wave function $\Psi(\mathbf{r}, t)$ to be acceptable, $\Psi(\mathbf{r}, t)$ and $\nabla\Psi$ must be finite, single valued and continuous at all points in space.

WORKED EXAMPLES

EXAMPLE 2.1 Calculate the de Broglie wavelength of an electron having a kinetic energy of 1000 eV. Compare the result with the wavelength of X-rays having the same energy.

$$\text{Kinetic energy } T = \frac{p^2}{2m} = 1000 \text{ eV} = 1.6 \times 10^{-16} \text{ J}$$

and

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{Js}}{[2(9.11 \times 10^{-31} \text{kg})(1.6 \times 10^{-16} \text{J})]^{1/2}}$$

$$= 0.39 \times 10^{-10} \text{ m} = 0.39 \text{ Å}$$

For X-rays,

$$\text{Energy} = \frac{hc}{\lambda}$$

Therefore,

$$\lambda = \frac{(6.626 \times 10^{-34}\,\text{J s})(3 \times 10^{8}\,\text{m/s})}{1.6 \times 10^{-16}\,\text{J}} = 12.42\ \text{Å}$$

Hence

$$\frac{\text{Wavelength of X-rays}}{\text{de Broglie wavelength of electron}} = \frac{12.42\,\text{Å}}{0.39\,\text{Å}} = 31.85$$

EXAMPLE 2.2 Determine the de Broglie wavelength of an electron that has been accelerated through a potential difference of 100 V.

The energy gained by the electron = 100 eV

Therefore,
$$\frac{p^2}{2m} = 100\ \text{eV}$$

or

$$p = \left[2\left(9.11 \times 10^{-31}\,\text{kg}\right)\left(100 \times 1.6 \times 10^{-19}\,\text{J}\right)\right]^{1/2}$$

$$= 5.399 \times 10^{-24}\ \text{kg ms}^{-1}$$

Hence

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34}\,\text{J s}}{5.399 \times 10^{-24}\,\text{kg ms}^{-1}} = 1.23 \times 10^{-10}\ \text{m} = 1.23\ \text{Å}$$

EXAMPLE 2.3 Electron scattering experiment gives a value of 2×10^{-15} m for the radius of a nucleus. Estimate the order of energies of electrons used for the experiment. Use relativistic expressions.

For electron scattering experiment, the de Broglie wavelength of electrons used must be of the order of 4×10^{-15} m, the diameter of the atom. If T is the kinetic energy, the relativistic expression for momentum is given by

$$p = m_0 c\left[\left(1 + \frac{T}{m_0 c^2}\right)^2 - 1\right]^{1/2}$$

or

$$\frac{h^2}{\lambda^2} = m_0^2 c^2\left[\left(1 + \frac{T}{m_0 c^2}\right)^2 - 1\right]$$

or

$$\left(1 + \frac{T}{m_0 c^2}\right)^2 = \frac{h^2}{\lambda^2 m_0^2 c^2} + 1$$

$$= \frac{(6.626 \times 10^{-34})^2}{(16 \times 10^{-30})(9.11 \times 10^{-31})^2(3 \times 10^8)^2} + 1$$

$$= 3.6737 \times 10^5$$

On solving, we get

$$T = 605.1m_0c^2 = 605.1(9.11 \times 10^{-31})(3 \times 10^8)^2 \text{ J}$$
$$= 310 \times 10^6 \text{ eV} = 310 \text{ MeV}$$

EXAMPLE 2.4 An electron has a speed of 500 m/s with an accuracy of 0.004%. Calculate the certainty with which we can locate the position of the electron.

$$\text{Momentum, } p = mv = (9.11 \times 10^{-31} \text{ kg})(500 \text{ m/s})$$

and

$$\text{Percentage accuracy} = \frac{\Delta p}{p} \times 100 = 0.004$$

or

$$\Delta p = \frac{0.004 \times 9.11 \times 10^{-31} \times 500}{100} = 182.2 \times 10^{-34} \text{ kg ms}^{-1}$$

Hence

$$\Delta x \cong \frac{h}{\Delta p} = \frac{6.626 \times 10^{-34} \text{Js}}{182.2 \times 10^{-34} \text{ kg ms}^{-1}} = 0.0364 \text{ m}$$

The position of the electron cannot be measured to accuracy less than 0.036 m.

EXAMPLE 2.5 The average lifetime of an excited atomic state is 10^{-9} s. If the spectral line associated with the decay of this state is 6000 Å, estimate the width of the line.

We have

$$\Delta t = 10^{-9} \text{ s}, \quad \lambda = 6000 \times 10^{-10} \text{ m} = 6 \times 10^{-7} \text{ m}$$

and

$$E = \frac{hc}{\lambda} \quad \text{or} \quad \Delta E = \frac{hc}{\lambda^2}\Delta\lambda$$

Multiplying both sides by Δt, we get

$$\Delta E \cdot \Delta t = \frac{hc}{\lambda^2}\Delta\lambda \cdot \Delta t \cong h$$

Therefore,

$$\Delta\lambda = \frac{\lambda^2}{c\Delta t} = \frac{36 \times 10^{-14} \text{m}^2}{(3 \times 10^8 \text{m/s})(10^{-9} \text{ s})} = 12 \times 10^{-13} \text{ m}$$

EXAMPLE 2.6 An electron in the $n = 2$ state of hydrogen remains there on the average of about 10^{-8}s, before making a transition to $n = 1$ state. Estimate the uncertainty in the energy of the $n = 2$ state. What fraction of the transition energy is this? What is the wavelength and width of this line in the spectrum of hydrogen atom?

$$\Delta E \geq \frac{h}{\Delta t} = \frac{6.626 \times 10^{-34}\,\text{Js}}{10^{-8}\,\text{s}} = 6.626 \times 10^{-26}\,\text{J} = 4.14 \times 10^{-7}\,\text{eV}$$

Energy of the $n = 2 \rightarrow n = 1$ transition $= -13.6\ \text{eV}\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 10.2$ eV

and

$$\text{Fraction, } \frac{\Delta E}{E} = \frac{4.14 \times 10^{-7}}{10.2} = 4.06 \times 10^{-8}$$

Wavelength,

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\,\text{J s})(3 \times 10^{8}\,\text{m/s})}{10.2 \times 1.6 \times 10^{-19}\,\text{J}} = 1.218 \times 10^{-7}\ \text{m} = 122\ \text{nm}$$

Width of the line in the spectrum is obtained as

$$\Delta\lambda = \frac{\Delta E}{E}\lambda$$

or

$$\Delta\lambda = 4.06 \times 10^{-8} \times 1.218 \times 10^{-7} = 4.95 \times 10^{-15}\ \text{m} = 4.95 \times 10^{-6}\,\text{nm}$$

EXAMPLE 2.7 Normalize the wave function $\psi(x) = A \exp(-ax^2)$, A and a are constants over the domain $-\infty \leq x \leq \infty$.

Taking A as the normalization constant, we have

$$A^2 \int_{-\infty}^{\infty} \psi^* \psi\ dx = A^2 \int_{-\infty}^{\infty} \exp(-2ax^2)\ dx = 1$$

Using the result

$$\int_{-\infty}^{\infty} \exp(-2ax^2)\ dx = \sqrt{\frac{\pi}{2a}}$$

we get

$$A = \left(\frac{2a}{\pi}\right)^{1/4} \text{ and } \psi(x) = \left(\frac{2a}{\pi}\right)^{1/4} \exp(-ax^2)$$

EXAMPLE 2.8 A particle constrained to move along x-axis in the domain $0 \le x \le L$ has a wave function $\psi(x) = \sin(n\pi x/L)$, where n is an integer. Normalize the wave function and evaluate the expectation value of its momentum.

The normalization condition gives

$$N^2 \int_0^L \sin^2 \frac{n\pi x}{L}\, dx = 1 \quad \text{or} \quad N^2 \int_0^L \frac{1}{2}\left(1 - \cos\frac{2n\pi x}{L}\right) dx = 1$$

Then

$$N^2 \frac{L}{2} = 1 \quad \text{or} \quad N = \sqrt{\frac{2}{L}}$$

The normalized wave function is

$$\sqrt{\frac{2}{L}}\, \sin\frac{n\pi x}{L}$$

The expectation value of the momentum is obtained as

$$\begin{aligned} \langle p_x \rangle &= \int_0^L \psi^* \left(-i\hbar \frac{d}{dx}\right) \psi\, dx \\ &= -i\hbar \frac{2}{L} \frac{n\pi}{L} \int_0^L \sin\frac{n\pi x}{L} \cos\frac{n\pi x}{L}\, dx \\ &= -i\hbar \frac{n\pi}{L^2} \int_0^L \sin\frac{2n\pi x}{L}\, dx \\ &= 0 \end{aligned}$$

EXAMPLE 2.9 Give the mathematical representation of a spherical wave travelling outward from a point, and evaluate its probability current density.

The mathematical representation of a spherical wave travelling outwards from a point is given by

$$\psi(r) = \frac{A}{r} e^{ikr}$$

where A is a constant and k is the wave vector. The probability current density is

$$\begin{aligned} j &= \frac{i\hbar}{2m}(\psi \nabla \psi^* - \psi^* \nabla \psi) \\ &= \frac{i\hbar}{2m} |A|^2 \left[\frac{e^{ikr}}{r} \nabla\left(\frac{e^{-ikr}}{r}\right) - \frac{e^{-ikr}}{r} \nabla\left(\frac{e^{ikr}}{r}\right)\right] \end{aligned}$$

$$= \frac{i\hbar}{2m}|A|^2\left[\frac{e^{ikr}}{r}\left(-\frac{ik}{r}e^{-ikr} - \frac{e^{-ikr}}{r^2}\right) - \frac{e^{-ikr}}{r}\left(\frac{ik}{r}e^{ikr} - \frac{e^{ikr}}{r^2}\right)\right]$$

$$= \frac{i\hbar}{2m}|A|^2\left(\frac{-2ik}{r^2}\right)$$

$$= \frac{\hbar k}{mr^2}|A|^2$$

EXAMPLE 2.10 The time-independent wave function of a particle of mass m moving in a potential $V(x) = \alpha^2 x^2$ is

$$\psi(x) = \exp\left(-\sqrt{\frac{m\alpha^2}{2\hbar^2}}x^2\right)$$

α being a constant. Find the energy of the system.

We have,

$$\psi(x) = \exp\left(-\sqrt{\frac{m\alpha^2}{2\hbar^2}}x^2\right)$$

On differentiating with respect to x, we get

$$\frac{d\psi}{dx} = -\sqrt{\frac{2m\alpha^2}{\hbar^2}}x\exp\left(-\sqrt{\frac{m\alpha^2}{2\hbar^2}}x^2\right)$$

Differentiating again with respect to x, we have

$$\frac{d^2\psi}{dx^2} = -\sqrt{\frac{2m\alpha^2}{\hbar^2}}\left[1 - \sqrt{\frac{2m\alpha^2}{\hbar^2}}x^2\right]\exp\left(-\sqrt{\frac{m\alpha^2}{2\hbar^2}}x^2\right)$$

Substituting these in the time-independent Schrödinger equation, we obtain

$$-\frac{\hbar^2}{2m}\left(-\sqrt{\frac{2m\alpha^2}{\hbar^2}} + \frac{2m\alpha^2}{\hbar^2}x^2\right) + \alpha^2 x^2 = E$$

On solving, we get

$$\hbar\sqrt{\frac{\alpha^2}{2m}} - \alpha^2 x^2 + \alpha^2 x^2 = E \quad \text{or} \quad E = \frac{\hbar\alpha}{\sqrt{2m}}$$

EXAMPLE 2.11 For a particle of mass m, Schrödinger initially arrived at the wave equation

$$\frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = \frac{\partial^2\Psi}{\partial x^2} - \frac{m^2c^2}{\hbar^2}\Psi$$

Show that a plane wave solution of this equation is consistent with the relativistic energy momentum relationship.

For plane waves, we have

$$\Psi(x,t) = A \exp\left[i\left(kx - \omega t\right)\right]$$

Substituting this solution in the given wave equation, we obtain

$$\frac{(-i\omega)^2}{c^2}\Psi = (ik)^2\Psi - \frac{m^2c^2}{\hbar^2}\Psi$$

or

$$\frac{-\omega^2}{c^2} = -k^2 - \frac{m^2c^2}{\hbar^2}$$

Multiplying by $c^2\hbar^2$ and writing $\hbar\omega = E$ and $k\hbar = p$, we get

$$E^2 = c^2p^2 + m^2c^4$$

which is the *relativistic energy–momentum relationship.*

EXAMPLE 2.12 An electron of rest mass m_0 is accelerated by an extremely high potential of V volts. Show that its wavelength is:

$$\lambda = \frac{hc}{[eV(eV + 2m_0c^2)]^{1/2}}$$

Energy gained by the electron in the potential = Ve

The relativistic expression for kinetic energy $= \dfrac{m_0c^2}{(1 - v^2/c^2)^{1/2}} - m_0c^2$

Equating the two and rearranging,

$$\frac{m_0c^2}{(1 - v^2/c^2)^{1/2}} - m_0c^2 = Ve$$

$$\left(1 - \frac{v^2}{c^2}\right)^{1/2} = \frac{m_0c^2}{Ve + m_0c^2}$$

or

$$1 - \frac{v^2}{c^2} = \frac{m_0^2c^4}{(Ve + m_0c^2)^2}$$

$$\frac{v^2}{c^2} = \frac{(Ve + m_0c^2)^2 - m_0^2c^4}{(Ve + m_0c^2)^2} = \frac{Ve\,(Ve + 2\,m_0c^2)}{(Ve + m_0c^2)^2}$$

$$v = \frac{c\,[Ve\,(Ve + 2\,m_0c^2)]^{1/2}}{Ve + m_0c^2}$$

de Broglie wavelength $\lambda = \dfrac{h}{mv} = \dfrac{h\,(1 - v^2/c^2)^{1/2}}{m_0 v}$

$$\lambda = \frac{h}{m_0}\,\frac{m_0c^2}{Ve + m_0c^2}\,\frac{Ve + m_0c^2}{c\,[Ve\,(Ve + 2m_0c^2)]^{1/2}}$$

$$= \frac{hc}{[Ve\,(Ve + 2m_0c^2)]^{1/2}}$$

EXAMPLE 2.13 Show that the phase velocity of a relativistic electron is $v_p = c\left[1 + \dfrac{m_0^2c^2\lambda^2}{h^2}\right]^{1/2}$ where λ is its de Broglie wavelength.

For relativistic electron

$$E^2 = c^2p^2 + m_0^2c^4 = c^2p^2\left(1 + \frac{m_0^2c^4}{c^2p^2}\right)$$

Phase velocity $\quad v_p = \dfrac{E}{p} = c\left(1 + \dfrac{m_0^2c^4}{c^2p^2}\right)^{1/2}$

Since de Broglie wavelength $\lambda = \dfrac{h}{p}$

$$v_p = c\left(1 + \frac{m_0^2c^2\lambda^2}{h^2}\right)^{1/2}$$

EXAMPLE 2.14 Find the probability current density $\mathbf{j}(\mathbf{r}, t)$ associated with the charged particle of charge e and mass m in a magnetic field of vector potential **A** which is real.

The Hamiltonian of the system is:

$$H = \frac{1}{2m}(\mathbf{p} - \frac{e}{c}\mathbf{A})^2 = -\frac{\hbar^2}{2m}\nabla^2 + \frac{ie\hbar}{2mc}(\nabla.\mathrm{A}) + \frac{ie\hbar}{mc}(\mathrm{A}.\nabla) + \frac{e^2A^2}{2mc^2}$$

The time dependent Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \frac{ie\hbar}{2mc}[(\nabla.\mathbf{A})\Psi + (\nabla\Psi)\mathbf{A}] + \frac{ie\hbar}{mc}\,\mathbf{A}.\nabla\Psi + \frac{e^2A^2}{2mc^2}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Its complex conjugate equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi^* - \frac{ie\hbar}{2mc}[(\nabla.\mathbf{A})\Psi^* + (\nabla\Psi^*)\mathbf{A}] - \frac{ie\hbar}{mc}\,\mathbf{A}.\nabla\Psi^* + \frac{e^2A^2}{2mc^2}\Psi^* = -\,i\hbar\frac{\partial\Psi^*}{\partial t}$$

Multiplying the first equation by Ψ^* from left and the complex conjugate equation by Ψ and subtracting, we have

$$-\frac{\hbar^2}{2m}[\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*] + \frac{ie\hbar}{2mc}[\Psi^* (\nabla \mathrm{A})\Psi + \Psi(\nabla \mathrm{A})\Psi^*]$$

$$+\frac{ie\hbar}{2mc}[\Psi^*(\nabla\Psi)\,.\,\mathrm{A} + \Psi(\nabla\Psi^*)\,.\,\mathrm{A}] + \frac{ie\hbar}{2mc}[\Psi^*\mathrm{A}\,.\,(\nabla\Psi) + \Psi\mathrm{A}\,.\,(\nabla\Psi^*)]$$

$$= i\hbar\left(\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right)$$

$$\frac{\partial}{\partial t}(\Psi^*\Psi) = \frac{i\hbar}{2m}[\nabla.(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)] + \frac{e}{mc}\Psi^*\Psi(\nabla\mathbf{A})$$

$$+\frac{e}{mc}[\Psi^*(\nabla\Psi) + \Psi(\nabla\Psi^*)].\mathbf{A}$$

$$\frac{\partial}{\partial t}(\Psi^*\Psi) = \nabla.\left[\frac{i\hbar}{2m}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) + \frac{e}{mc}(\Psi^*\Psi\mathbf{A})\right]$$

Defining the probability current density vector $\mathbf{j}(\mathbf{r}, t)$ by

$$\mathbf{j}(\mathbf{r}, t) = \frac{i\hbar}{2m}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi) - \frac{e}{mc}(\Psi^*\Psi\mathbf{A})$$

The equation reduces to

$$\frac{\partial}{\partial t}P(\mathbf{r}, t) + \nabla.\,\mathbf{j}(\mathbf{r}, t) = 0$$

which is the familiar equation of continuity for probability.

EXAMPLE 2.15 Using time independent Schrödinger equation, find the potential $V(x)$ and energy E for which the wave function

$$\psi(x) = \left(\frac{x}{x_0}\right)^n e^{-x/x_0}, \qquad n, x_0 \text{ – constants}$$

is an eigenfunction. Assume that $V(x) \to 0$ as $x \to \infty$.

Differentiating the wave function with respect to x,

$$\frac{d\psi}{dx} = \frac{n}{x_0}\left(\frac{x}{x_0}\right)^{n-1} e^{-x/x_0} - \frac{1}{x_0}\left(\frac{x}{x_0}\right)^n e^{-x/x_0}$$

$$\frac{d^2\psi}{dx^2} = \frac{n(n-1)}{x_0^2}\left(\frac{x}{x_0}\right)^{n-2} e^{-x/x_0} - \frac{2n}{x_0^2}\left(\frac{x}{x_0}\right)^{n-1} e^{-x/x_0} + \frac{1}{x_0^2}\left(\frac{x}{x_0}\right)^n e^{-x/x_0}$$

$$= \left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]\left(\frac{x}{x_0}\right)^n e^{-x/x_0}$$

$$= \left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]\psi(x)$$

Substituting in the Schrödinger's equation,

$$-\frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]\psi + V\psi = E\psi$$

which gives the operator equation

$$E - V(x) = -\frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x} + \frac{1}{x_0^2}\right]$$

When $x \to \infty$, $V(x) \to 0$. Hence

$$E = -\frac{\hbar^2}{2mx_0^2}$$

$$V(x) = \frac{\hbar^2}{2m}\left[\frac{n(n-1)}{x^2} - \frac{2n}{x_0 x}\right]$$

REVIEW QUESTIONS

1. Explain de Broglie's hypothesis. Why the wave nature of matter is not apparent in our daily observations?
2. For a complete description of physical phenomena, both particle and wave aspects of material particles are required. Comment.
3. Illustrate the uncertainty principle on the basis of single-slit experiment.
4. Explain the uncertainty principle. How does it account for the natural line width of spectral lines?
5. Does the concept of Bohr orbits violate the uncertainty principle?
6. Prove the nonexistence of electron in the nucleus on the basis of uncertainty principle.
7. Consider the standing wave of an electron in an orbit and obtain Bohr's quantization rule.
8. What is a wave packet? How is it represented analytically and diagrammatically?
9. Prove that the velocity of a particle and the velocity of the corresponding wave packet are the same.

10. Outline the probability interpretation of the wave function.
11. Show that any decrease in probability in a region is accompanied by an outflow of probability across its surface.
12. State the quantum analogue of the classical energy expression $E = (p^2/2m) + V(r)$ and explain its significance.
13. Is the time-dependent Schrödinger equation relativistically invariant? Explain.
14. Schrödinger equation of a free particle results when E is replaced by $i\hbar(\partial/\partial t)$, p_x by $-i\hbar(\partial/\partial x)$ or $i\hbar(\partial/\partial x)$ in $E = p_x^2/(2m)$ and the resulting operator equation operates on the wave function. Why is $i\hbar(\partial/\partial x)$ not acceptable?
15. Explain the significance of Ehrenfest's theorem.
16. In the definition for the expectation value of an observable the operator associated with the observable is sandwiched between ψ^* and ψ. Why?
17. What are stationary states? In stationary states, show that the probability current density is constant in time.
18. Define probability current density. What is its value when the wave function is real?
19. Outline the various admissibility conditions on the wave function of a system.
20. Explain the principle of superposition of states. Prove that the probability density of a particle in a superposition state depends on time.
21. Directly demonstrate the superposition property of the Schrödinger equation.
22. Distinguish between group velocity and phase velocity.
23. Uncertainty principle limits the equivalence of quantum and classical mechanics: comment.

PROBLEMS

1. What is the de Broglie wavelength of an electron accelerated from rest by a potential of 200 V?
2. Evaluate the ratio of the de Broglie wavelength of electron to that of proton when (a) both have the same kinetic energy (b) the electron kinetic energy is 1000 eV and that of proton is 100 eV.
3. Proton beam is used to obtain information about the size and shape of atomic nuclei. If the diameter of nuclei is of the order of 10^{-15} m, what is the approximate kinetic energy to which protons are to be accelerated? Use relativistic expressions.

4. Estimate the velocity of neutrons needed for the study of neutron diffraction of crystal structures, if the interatomic spacing in the crystal is of the order of 2 Å. Also, estimate the kinetic energy of neutrons corresponding to this velocity.
5. Estimate the energy of electrons needed for the study of electron diffraction of crystal structures, if the interatomic spacing in the crystal is of the order of 2 Å.
6. A bullet of mass 0.03 kg is moving with a velocity of 500 ms^{-1}. The speed is measured accurate to 0.02%. Calculate the uncertainty in x. Also, comment on the result.
7. Wavelength can be determined with an accuracy of one in 10^8. What is the uncertainty in the position of a 10-Å photon when its wavelength is simultaneously measured?
8. If the position of a 5-keV electron is located within 2 Å, what is the percentage uncertainty in its momentum?
9. The uncertainty in the velocity of a particle is equal to its velocity. Show that the uncertainty in its location is its de Broglie wavelength.
10. The wave function of a particle of mass m moving in a potential $V(x)$ is

$$\Psi(x,t) = A \exp\left(-ikt - \frac{km}{\hbar}x^2\right)$$

where A and k are constants. Find the explicit form of the potential $V(x)$.

11. The time-independent wave function of a system is $\psi(x) = A \exp(ikx)$, k is a constant. Check whether it is normalizable in the domain $-\infty < x < \infty$. Calculate the probability current density for this function.
12. Show that the phase velocity v_{p} for a particle with rest mass m_0 is always greater than the velocity of light and that v_{p} is a function of wavelength.
13. Show that the wavelength of a particle of rest mass m_0 with kinetic energy T is given by the relativistic formula

$$\lambda = \frac{hc}{\sqrt{T^2 + 2m_0c^2T}}$$

14. An electron moves with a constant velocity 1.1×10^6 m/s. If the velocity is measured to a precision of 0.1 per cent, what is the maximum precision with which its position could be simultaneously measured.
15. What is the ratio of the kinetic energy of an electron to that of a proton if their wavelengths are equal?
16. Calculate the probability current density $j(x)$ for the wave function:

$$\psi(x) = u(x) \exp\,[i\phi\,(x)], \qquad u,\phi \text{ real}$$

17. Find the form of the potential for which $\psi(r)$, a constant, is a solution of the Schrödinger equation.

18. Obtain the form of the equation of continuity for probability, if the potential in the Schrödinger equation is of the form $V(r) = V_1(r) + iV_2(\mathbf{r})$, where V_1 and V_2 are real.

19. For a one dimensional wave function of the form,

$$\Psi(x, t) = A \exp[i\phi(x, t)]$$

show that the probability current density can be written as: $j = \frac{\hbar}{m} | A |^2 \frac{\partial \phi}{\partial x}$

20. $\psi_0(x)$ and $\psi_1(x)$ be the normalized ground and first excited state energy eigenfunctions of a linear harmonic oscillator. At some instant of time $\mathrm{A}\psi_0 + \mathrm{B}\psi_1$, A and B are constants, is the wave function of the oscillator. Show that $\langle x \rangle$ is in general different from zero.

21. Waves on the surface of water travel with a phase velocity $v_p = \sqrt{g\lambda / 2\pi}$, where g is the acceleration due to gravity and λ is the wavelength of the wave. Show that the group velocity of a wave packet comprised these waves is $v_p/2$.

Chapter 3

General Formalism of Quantum Mechanics

Based on the wave nature of matter we have developed the Schrödinger equation (which is the basic equation of quantum mechanics), the physical significance of the wave function and the uncertainty principle in Chapter 2. A more systematic presentation of the mathematical formalism of quantum mechanics along with a set of basic postulates will be discussed in this chapter.

3.1 LINEAR VECTOR SPACE

Vector in a Three-dimensional Space

A vector in three dimensions is a physical quantity having both magnitude and direction. A vector of magnitude 1 is called a *unit vector*. To represent an arbitrary vector, we introduce unit vectors, say $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$, along the positive direction of a right-handed system *OXYZ* of three mutually perpendicular axes. Then any vector $\mathbf{a}$ can be expressed as

$$\mathbf{a} = a_1\mathbf{e}_1 + a_2\mathbf{e}_2 + a_3\mathbf{e}_3 \tag{3.1}$$

where a_1, a_2, a_3, are scalars. Given a vector $\mathbf{a}$ the scalars a_1, a_2, a_3 in Eq. (3.1) are uniquely determined. The unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ are said to form a *basis* for the set of all vectors in three dimensions. Further, since these are unit vectors along mutually perpendicular directions, we say that $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ form an *orthonormal basis*. The scalars a_1, a_2, a_3 in Eq. (3.1) are the components of $\mathbf{a}$ in the basis ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$). We may represent $\mathbf{a}$ as a column vector:

$$\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \tag{3.2}$$

The components of $\mathbf{e}_1$ are 1, 0, 0; those of $\mathbf{e}_2$ are 0, 1, 0 and those of $\mathbf{e}_3$ are 0, 0, 1. Hence, on expressing them as column vectors, we have

$$\mathbf{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{e}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{3.3}$$

The totality of vectors in three dimensions is called a *three-dimensional space.* Given two vectors

$$\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \quad \text{and} \quad \mathbf{b} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} \tag{3.4}$$

in this space, the *scalar product* or *inner product* of **a** and **b**, denoted by $\mathbf{a} \cdot \mathbf{b}$ or $(\mathbf{a}, \mathbf{b})$, is defined as

$$(\mathbf{a}, \mathbf{b}) = \sum_{i=1}^{3} a_i b_i \tag{3.5}$$

Vectors in an *n*-dimensional Space

We now generalize these concepts to an n-dimensional real space, with the vectors $\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n$ forming an orthonormal basis. A vector **a** can be expressed in this orthonormal basis as

$$\mathbf{a} = \sum_{i=1}^{n} a_i \mathbf{e}_i \tag{3.6}$$

The totality of all n-dimensional vectors is called an *n-dimensional space*, or simply an *n-vector space.* In this space, the inner product is defined as

$$(\mathbf{a}, \mathbf{b}) = \sum_{i=1}^{n} a_i b_i \tag{3.7}$$

If the vectors are complex, that is, if the components of the vectors are complex numbers, the *inner product* is defined as

$$(\mathbf{a}, \mathbf{b}) = \sum_{i=1}^{n} a_i^* b_i \tag{3.8}$$

where, for any complex number z, z^* denotes the conjugate. Thus, we observe that for any vector **a**,

$$(\mathbf{a}, \mathbf{a}) = \sum_{i=1}^{n} a_i^* a_i = \sum_{i=1}^{n} |a_i|^2 \tag{3.9}$$

is real. We then define the norm (N) of a vector **a** by

$$N = (\mathbf{a}, \mathbf{a})^{1/2} \tag{3.10}$$

A vector whose norm is unity is said to be normalized. Thus, for a normalized vector **a**, we have

$$(\mathbf{a}, \mathbf{a}) = \sum_{i=1}^{n} a_i^* a_i = \sum_{i=1}^{n} |a_i|^2 = 1 \tag{3.11}$$

Two vectors **a** and **b** are said to be orthogonal if

$$(\mathbf{a}, \mathbf{b}) = 0 \tag{3.12}$$

Using the concept of inner product, we say that the vectors $\mathbf{a}_1$, $\mathbf{a}_2$, ... form an *orthonormal set* if and only if

$$(\mathbf{a}_i, \mathbf{a}_j) = \delta_{ij}, \qquad i, j = 1, 2, \ldots \tag{3.13}$$

where δ_{ij} is the *Kronecker delta* defined by

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{3.14}$$

In an n-dimensional space, a set of n vectors $\mathbf{a}_1$, $\mathbf{a}_2$, ..., $\mathbf{a}_n$ are said to be linearly dependent if there exist scalars c_1, c_2, ..., c_n not all zero such that

$$\sum_{i=1}^{n} c_i \mathbf{a}_i = 0 \tag{3.15}$$

The vectors are linearly independent if no relation of the form Eq. (3.15) exists unless $c_1 = c_2 = \cdots = c_n = 0$

A set of n linearly independent vectors $\mathbf{a}_1$, $\mathbf{a}_2$, ..., $\mathbf{a}_n$ spans an n-dimensional space and any vector $\boldsymbol{\phi}$ which lies in this space can be expressed in the form

$$\boldsymbol{\phi} = \sum_{i=1}^{n} c_i \mathbf{a}_i \tag{3.16}$$

This set of vectors is complete if there is no other vector which falls in this set of linearly independent vectors.

The generalization of these concepts to an infinite-dimensional space, called *vector space* is straightforward.

Hilbert Space

In the vector space we considered, the unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, ... form the orthonormal basis. Alternately, a space can be defined in which a set of functions $\phi_1(x)$, $\phi_2(x)$, $\phi_3(x)$, ... form the orthonormal unit vectors of the coordinate system. The corresponding infinite-dimensional linear space is called a *function space*. In quantum mechanics, very often we deal with complex functions and the corresponding function space is called the *Hilbert space*.

Orthogonal Functions

We shall now consider some of the important definitions regarding orthogonal functions.

(i) The *inner product* or *scalar product* of two functions $F(x)$ and $G(x)$ defined in the interval $a \le x \le b$, denoted as (F, G) or $(F|G)$, is

$$(F, G) = \int_a^b F^*(x)\, G(x)\, dx \tag{3.17}$$

The notation (F,G) for the scalar product of functions $F(x)$ and $G(x)$ is sometimes referred to as *bracket notation*.

(ii) Two functions $F(x)$ and $G(x)$ are *orthogonal* if their inner product is zero.

$$(F, G) = \int_a^b F^*(x)\, G(x)\, dx = 0 \tag{3.18}$$

(iii) The *norm* of a function is defined by square root of inner product of the function with itself

$$N = (F, F)^{1/2} = \left[\int_a^b |F(x)|^2\, dx\right]^{1/2} \tag{3.19}$$

(iv) A function is *normalized* if its norm is unity.

$$(F, F)^{1/2} = \left[\int_a^b |F(x)|^2\, dx\right]^{1/2} = 1 \tag{3.20}$$

or

$$(F, F) = \int_a^b F^*(x) F(x)\, dx = 1 \tag{3.20a}$$

where the integral on the right-hand side is called the *normalization integral*.

(v) Functions that are orthogonal and normalized are called *orthonormal functions*. From Eqs. (3.18) and (3.20a), we get

$$(F_i, F_j) = \delta_{ij}; \qquad i, j = 1, 2, \ldots \tag{3.21}$$

(vi) A set of functions $F_1(x)$, $F_2(x)$, $F_3(x)$, ... is *linearly dependent* if a relation of the type

$$\sum_i c_i F_i(x) = 0 \tag{3.22}$$

exists, where the c_i's are not all zero. Otherwise they are *linearly independent.*

(vii) A set of linearly-independent functions $F_1(x)$, $F_2(x)$, ... is *complete*, if there is no other function which falls in the set of linearly-independent functions.

The *expansion theorem* states that any function $\phi(x)$ defined in the same interval can be expanded in terms of the set of linearly-independent functions as

$$\phi(x) = \sum_i c_i F_i(x) \tag{3.23}$$

The complete set need not be orthonormal. However, it is convenient to use orthonormal sets. In such a case, the coefficients in Eq. (3.23) are given by

$$c_i = (F_i, \phi) \tag{3.24}$$

The expansion of a function in terms of a complete orthonormal set of functions is of fundamental importance in quantum mechanics.

3.2 LINEAR OPERATOR

An *operator* can be defined as the rule by which a different function is obtained from any given function. Therefore, in

$$g(x) = \hat{A}\, f(x)$$

the operator $\hat{A}$ operating on $f(x)$ gives the function $g(x)$. So, in

$$g(x) = \hat{A}\, f(x) = [f(x)]^2$$

the operator squares the function $f(x)$. The operator $\hat{A}$ differentiates the function $f(x)$ with respect to x if

$$g(x) = \hat{A}\, f(x) = \frac{d}{dx} f(x)$$

An operator is said to be *linear* if it satisfies the relation

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x) \tag{3.25}$$

where c_1 and c_2 are constants. In

$$g(x) = \frac{d}{dx}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1 \frac{d}{dx} f_1(x) + c_2 \frac{d}{dx} f_2(x)$$

the operator (d/dx) is linear. The operator which squares a function is not linear since

$$\begin{aligned} \hat{A}\,[c_1 f_1(x) + c_2 f_2(x)] &= [c_1 f_1(x) + c_2 f_2(x)]^2 \\ &= c_1^2 f_1^2 + c_2^2 f_2^2 + 2c_1 c_2 f_1 f_2 \\ &\neq c_1 f_1^2 + c_2 f_2^2 \end{aligned}$$

Linear operators are the most important ones in quantum mechanics and therefore we shall consider only such operators.

The sum and difference of operators $\hat{A}$ and $\hat{B}$ are defined by:

$$(\hat{A} \pm \hat{B})f(x) = \hat{A}f(x) \pm \hat{B}f(x) \tag{3.26}$$

Addition is commutative:

$$\hat{A} + \hat{B} = \hat{B} + \hat{A}$$

Addition is associative:

$$(\hat{A} + \hat{B}) + \hat{C} = \hat{A} + (\hat{B} + \hat{C})$$

The product of two operators $\hat{A}$ and $\hat{B}$ is defined by:

$$\hat{A}\hat{B}\, f(x) = \hat{A}[\hat{B}f(x)]$$

Multiplication is associative:

$$\hat{A}(\hat{B} + \hat{C})f(x) = (\hat{A}\hat{B} + \hat{A}\hat{C})f(x)$$

Commutator of operators $\hat{A}$ and $\hat{B}$, denoted by $[\hat{A},\hat{B}]$, is defined as:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{3.27a}$$

It follows that

$$[\hat{A}, \hat{B}] = -\,[\hat{B}, \hat{A}] \tag{3.27b}$$

If $\hat{A}\hat{B}\, f(x) = \hat{B}\hat{A}\, f(x)$, that is $[\hat{A},\hat{B}] = 0$, $\hat{A}$ and $\hat{B}$ are said to *commute.* If $\hat{A}\hat{B} + \hat{B}\hat{A} = 0$, $\hat{A}$ and $\hat{B}$ are said to *anticommute*. The anticommutator of $\hat{A}$ with $\hat{B}$ is usually denoted as $[\hat{A}, \hat{B}]_+$. An operator can be applied in succession on the same function. This is written as follows

$$\hat{\alpha}\,\hat{\alpha}\,\hat{\alpha}\cdots\hat{\alpha} f = \hat{\alpha}^n f \tag{3.28a}$$

and

$$[\hat{\alpha}^m, \hat{\alpha}^n] = \hat{\alpha}^m\hat{\alpha}^n - \hat{\alpha}^n\hat{\alpha}^m = \hat{\alpha}^{m+n} - \hat{\alpha}^{m+n} = 0 \tag{3.28b}$$

That is, the powers of the same operator commute. The *inverse operator* $\hat{A}^{-1}$ is defined by the relation

$$\hat{A}\,\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = 1 \qquad (3.29)$$

An operator commutes with its inverse since

$$[\hat{A}, \hat{A}^{-1}] = \hat{A}^{-1}\hat{A} - \hat{A}^{-1}\hat{A} = 0$$

As an example of commutator, consider the operators $\hat{x}$ and (d/dx)

$$\left[\frac{d}{dx}, \hat{x}\right] f(\hat{x}) = \frac{d(\hat{x}, f)}{dx} - \hat{x}\frac{df}{dx} = f$$

Hence

$$\left[\frac{d}{dx}, \hat{x}\right] = 1 \quad \text{or} \quad \left[\hat{x}, \frac{d}{dx}\right] = -1 \qquad (3.30)$$

For convenience, we shall denote an operator associated with a dynamical variable by the same letter without cap in the rest of the book.

3.3 EIGENFUNCTIONS AND EIGENVALUES

Often an operator A operating on a function multiplies the function by a constant.

$$A\psi(x) = a\psi(x) \qquad (3.31)$$

where a is a constant with respect to x. The function $\psi(x)$ is called the *eigenfunction* of the operator A corresponding to the *eigenvalue* a. In

$$\frac{de^{kx}}{dx} = k\,e^{kx} \qquad (3.32)$$

e^{kx} is an eigenfunction of the operator d/dx corresponding to the eigenvalue k. It may be pointed out here that formulation of quantum mechanics is dominated by ideas connected with the solution of such eigenvalue equations.

In general, we have a set of values a for which eigenfunctions exist. Denoting the set by a running index m, we can write the eigenvalue equation as

$$A\psi_m(x) = a_m\psi_m(x), \qquad m = 1, 2, \ldots \qquad (3.33)$$

As $A\psi_m(x)$ is unique, we cannot have different a_m associated with a single ψ. However, we may have a given a_m associated with a large number of ψ_m. Now the eigenvalue is said to be *degenerate*. If all the eigenvalues of an operator are discrete, it is said to have a *discrete spectrum*. The continuous eigenvalues allowed for certain operators form a *continuous spectrum*. In certain cases the eigenvalues may be discrete over a certain range and continuous over the rest.

3.4 HERMITIAN OPERATOR

Let us consider two arbitrary functions $\psi_m(x)$ and $\psi_n(x)$. The operator A is said to be *Hermitian* if

$$\int_{-\infty}^{\infty} \psi_m{}^* A\psi_n \, dx = \int_{-\infty}^{\infty} (A\psi_m)^* \psi_n \, dx = \left(\int_{-\infty}^{\infty} \psi_n{}^* A\psi_m \, dx \right)^* \tag{3.34}$$

In bracket notation

$$(\psi_m, A\psi_n) = (A\psi_m, \psi_n) = (\psi_n, A\psi_m)^* \tag{3.34a}$$

An operator is said to be **anti-Hermitian** if

$$(\psi_m, A\psi_n) = -(A\psi_m, \psi_n) = -(\psi_n, A\psi_m)^* \tag{3.34b}$$

Two important theorems regarding Hermitian operators which we use throughout quantum mechanics are the following.

Theorem 3.1 The eigenvalues of Hermitian operators are real.

Proof Consider a Hermitian operator A. Its eigenvalue equation be

$$A\psi_n = a_n\psi_n$$

Taking inner product with ψ_n, we get

$$(\psi_n, A\psi_n) = a_n(\psi_n, \psi_n) = a_n \tag{3.35}$$

Since A is Hermitian, we have

$$(\psi_n, A\psi_n) = (A\psi_n, \psi_n) = a_n^* (\psi_n, \psi_n) = a_n^* \tag{3.36}$$

It follows from Eqs. (3.35) and (3.36) that $a_n = a_n^*$ which is possible only when a_n is real. Real eigenvalues of Hermitian operators play a very important role in quantum mechanics.

Theorem 3.2 Any two eigenfunctions of a Hermitian operator that belong to different eigenvalues are orthogonal.

Proof Let ψ_m and ψ_n be the eigenfunctions of the operator A corresponding to the eigenvalues a_m and a_n respectively. Then

$$A\psi_m = a_m\psi_m, \qquad A\psi_n = a_n\psi_n \tag{3.37}$$

From Eq. (3.37), we obtain

$$(\psi_n, A\psi_m) = a_m(\psi_n, \psi_m)$$

Since operator A is Hermitian,

$$(A\psi_n, \psi_m) = a_m(\psi_n, \psi_m) \quad \text{or} \quad a_n(\psi_n, \psi_m) = a_m(\psi_n, \psi_m)$$

or

$$(a_n - a_m)(\psi_n, \psi_m) = 0$$

As $a_n \neq a_m$, we have

$$(\psi_n, \psi_m) = 0 \tag{3.38}$$

Hence, the eigenfunctions ψ_n and ψ_m are orthogonal.

Schmidt Orthogonalization Procedure

When eigenvalues are degenerate, the above arguments fail. However, one can form orthogonal linear combinations from the functions belonging to different eigenvalues. Let ψ_i and ψ_j be two normalized eigenfunctions of the Hermitian operator A having the same eigenvalue a. Then

$$A\psi_i = a\psi_i, \qquad A\psi_j = a\psi_j \tag{3.39}$$

The linear combination of ψ_i and ψ_j is given by

$$\psi_k = c_1\psi_i + c_2\psi_j \tag{3.40}$$

where c_1 and c_2 are constants. Also,

$$A\psi_k = A(c_1\psi_i + c_2\psi_j) = a(c_1\psi_i + c_2\psi_j) \tag{3.41}$$

that is, ψ_k is also an eigenfunction of the operator A with the same eigenvalue a.

We assume that

$$(\psi_i, \psi_k) = 0 \quad \text{and} \quad (\psi_k, \psi_k) = 1 \tag{3.42}$$

Then

$$(\psi_i, \psi_k) = 0 \quad \text{gives} \quad c_1 = -c_2(\psi_i, \psi_j) \tag{3.43}$$

and

$$(\psi_k, \psi_k) = 1 \quad \text{gives} \quad c_1^2 + c_2^2 + c_1c_2[(\psi_i, \psi_j) + (\psi_j, \psi_i)] = 1 \tag{3.44}$$

The constants are assumed to be real. From Eqs. (3.43) and (3.44), we have

$$c_2 = \frac{1}{\sqrt{1 - |(\psi_i, \psi_j)|^2}} \quad \text{and} \quad c_1 = -\frac{(\psi_i, \psi_j)}{\sqrt{1 - |(\psi_i, \psi_j)|^2}}$$

Hence

$$\psi_k = \frac{\psi_j - (\psi_i, \psi_j)\psi_i}{\sqrt{1 - \left|(\psi_i, \psi_j)\right|^2}} \tag{3.45}$$

This ψ_k is a normalized eigenfunction of the operator A corresponding to the eigenvalue a. It is orthogonal to ψ_i. This procedure is a case of *Schmidt orthogonalization* procedure for systems having two-fold degeneracy. Similar procedure can be followed for higher order degenerate cases.

3.5 POSTULATES OF QUANTUM MECHANICS

Postulates are not unknown in physics. They often serve as the basis of physical theories. Though they cannot be proved, one can prove the conclusions derived on the basis of the postulates. The success or failure of the postulates depends on the strength of the experimental results. There are different ways of stating the basic postulates of quantum mechanics, but the following formulation seems to be satisfactory.

Postulate 1: Wave function

The state of a system having n degrees of freedom can be completely specified by a function Ψ of coordinates $q_1, q_2, \ldots, q_n$ and time t which is called the *wave function* or *state function* or *state vector* of the system. Ψ and its derivatives must be continuous, finite and single valued over the domain of the variables of Ψ. All possible information about the system can be derived from this wave function.

The wave function Ψ as such is not an observable, but in some way it is related to the presence of the particle. Its physical interpretation has already been discussed in Section 2.5. The representation in which the wave function is a function of coordinates and time is called the *coordinate representation*. In the *momentum representation*, the wave functions are functions of the momentum components and time. The details worked out in this book are in the coordinate representation.

Postulate 2: Operators

To every observable physical quantity there corresponds a Hermitian operator or matrix. The operators in quantum mechanics are derived from the Poisson bracket of the corresponding pair of classical variables according to the rule

$$[Q, R] = i\hbar\{q, r\} \tag{3.46}$$

where Q and R are the operators selected for the dynamical variables q and r and $\{q, r\}$ is the Poisson bracket of q and r.

Some of the important operators associated with observables in the coordinate representation are given in Table 3.1.

Table 3.1 Classical observables and their quantum mechanical operators

Observable	*Classical form*	*Operator in coordinate representation*
Coordinates	x, y, z	x, y, z
Function of coordinate	$f(x, y, z)$	$f(x, y, z)$
Momentum components	p_x, p_y, p_z	$-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}$
Momentum	$\mathbf{p}$	$-i\hbar\nabla$
Energy	E	$i\hbar\frac{\partial}{\partial t}$

Operators representing some of the other dynamical variables take the following form:

Kinetic energy operator. For a particle of mass m and momentum $\mathbf{p}$, the kinetic energy

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$T = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\nabla^2 \tag{3.47}$$

Hamiltonian operator. For a particle of mass m moving in a potential $V(x, y, z)$, the Hamiltonian

$$H = \frac{p^2}{2m} + V(x, y, z)$$

or

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z) \tag{3.48}$$

Angular momentum components. The angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3 \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \tag{3.49}$$

where the operators representing the components of $\mathbf{L}$ are:

$$L_x = yp_z - zp_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = zp_x - xp_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{3.50}$$

$$L_z = xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

We shall next see some of the important commutation relations of position and momentum operators. It is obvious from Eq. (3.30) that

$$\left[x, -i\hbar\frac{d}{dx}\right] = i\hbar \quad \text{or} \quad [x, p_x] = i\hbar \tag{3.51}$$

Similarly,

$$[y, p_y] = i\hbar, \qquad [z, p_z] = i\hbar \tag{3.52}$$

and

$$[x, p_y] = [x, p_z] = [y, p_x] = [y, p_z] = [z, p_x] = [z, p_y] = 0 \tag{3.53}$$

The above commutation relations can be combined into a single one as

$$[q_j, p_k] = i\hbar\delta_{jk} \tag{3.54}$$

The following two commutation relations can also be proved

$$[q_j, q_k] = 0, \qquad [p_j, p_k] = 0 \tag{3.55}$$

When observables are represented by matrices, the condition for a matrix A to be Hermitian is

$$A = A^\dagger \tag{3.55a}$$

where $A^\dagger$ is formed by transposing the matrix A^*.

Postulate 3: Expectation Value

When a system is in a state described by a wave function Ψ, the expectation value of any observable A is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* A \Psi \, d\tau \tag{3.56}$$

where A in the integral is the operator associated with the observable A. In Eq. (3.56), the wave function Ψ is assumed to be normalized. If the wave function is not normalized

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* A \Psi \, d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi \, d\tau} \tag{3.57}$$

As already discussed in Section 2.6, the sandwiching of the operator between Ψ^* and Ψ is a necessity.

Postulate 4: Eigenvalues

The possible values which a measurement of an observable, whose operator is A, can give are the eigenvalues a_i of the equation

$$A\psi_i = a_i \psi_i, \qquad i = 1, 2, \ldots, n \tag{3.58}$$

The eigenfunctions (ψ_i) form a complete set of n independent functions.

The normalized eigenfunctions of an operator A be ψ_i, $i = 1, 2, \ldots$ belonging to the eigenvalues a_i, $i = 1, 2, \ldots$. The expectation value of the observable A when it is in a state ψ_n is given by

$$\langle A \rangle = \int \psi_n^* A \psi_n \, d\tau = \int \psi_n^* a_n \psi_n \, d\tau = a_n \tag{3.59}$$

That is, when an experiment is performed to determine the value of an observable A in a particular state, the value we expect in the measurement is its eigenvalue. In other words, the eigenvalues of an operator are the only experimentally measurable quantities. Hence the eigenvalues always give a real number. We have already seen that the eigenvalues of Hermitian operators are real. Therefore operators associated with physical quantities must be Hermitian.

When the wave function ϕ of a system is not an eigenfunction, it can be expressed as a linear combination of ψ_i's as they form a complete set. Expanding ϕ in terms of ψ_i's, we get

$$\phi = \sum_i c_i \psi_i \tag{3.60}$$

where the coefficients c_i's are given by

$$c_i = \int_{-\infty}^{\infty} \psi_i^* \phi \, d\tau, \qquad i = 1, 2, \ldots \tag{3.61}$$

In such a situation

$$\begin{aligned}\langle A \rangle = \int \phi^* A \phi \, d\tau &= \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \psi_i^* A \psi_j \, d\tau \\ &= \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \psi_i^* a_j \psi_j d\tau \\ &= \sum_i |c_i|^2 a_i \end{aligned} \tag{3.62}$$

If ω_i is the probability for occurrence of the eigenvalue a_i in a measurement of the observable A,

$$\langle A \rangle = \sum_i \omega_i a_i \tag{3.63}$$

Since a_i's are constants, from Eqs. (3.62) and (3.63), we have

$$\omega_i = |c_i|^2 \tag{3.64}$$

Hence the coefficients c_1, c_2, ... are called the *probability amplitudes*. If the system is in one of the eigenstates, say ψ_k, Eq. (3.61) gives

$$c_i = \int \psi_i^* \psi_k \, d\tau = \delta_{ik}$$

Consequently,

$$\omega_i = |c_i|^2 = |\delta_{ik}|^2$$

Hence, Eq. (3.63) can be written as

$$\langle A \rangle = \sum_i \omega_i a_i = \sum_i |\delta_{ik}|^2 a_i = a_k \tag{3.65}$$

That is, when the system is in an eigenstate ψ_k, the probability for the occurrence of the value a_k in a measurement of A is unity. In other words, we will certainly be getting the value a_k in the measurement.

An important eigenvalue equation is that of the Hamiltonian operator given by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}) \tag{3.66}$$

$\psi_i(\mathbf{r})$ is the eigenfunction of the Hamiltonian operator corresponding to the eigenvalue E_i. This equation is the time-independent Schrödinger equation which we have already derived in Section 2.7.

Postulate 5: Time Development of a Quantum System

The first-four postulates describe the concept of a quantum system at a given instant of time whereas the fifth one deals with the time development of a system. The time development can be studied systematically with the help of equations of motion which could be differential equations of the physical variables describing the system. The state vector or wave function Ψ ($\mathbf{r}$, t) which describes the state of system as fully as possible may be brought into the picture.

Postulate: The time development of a quantum system can be described by the evolution of state function in time by the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\Psi(\mathbf{r}, t) \tag{3.67}$$

where H is the Hamiltonian operator of the system which is independent of time.

This procedure of considering the state function depends on coordinates and time and the operator to be independent of time is called the *Schrödinger picture* or *Schrödinger representation.* As time development of a quantum system is an important topic, it is considered in detail latter (in Section 3.9). However, it is mentioned here to complete the discussion regarding the postulates.

3.6 SIMULTANEOUS MEASURABILITY OF OBSERVABLES

We have been discussing the measurement of one observable at a time. If two observables are simultaneously measurable in a particular state of a given system, then the state function is an eigenfunction of both the operators. Two observables are said to be *compatible*, if their operators have a common set of eigenfunctions. The following two theorems indicate the connection between compatible observables and commuting operators.

Theorem 3.3 Operators having common set of eigenfunctions commute.

Proof Consider operators A and B with the common set of eigenfunctions ψ_i, $i = 1, 2, \ldots$ as

$$A\psi_i = a_i\,\psi_i, \quad \text{and} \quad B\psi_i = b_i\psi_i \tag{3.68}$$

Then

$$AB\psi_i = A(b_i\psi_i) = b_iA\psi_i = a_ib_i\psi_i \tag{3.69}$$

and

$$BA\psi_i = B(a_i\psi_i) = a_iB\psi_i = a_ib_i\psi_i \tag{3.70}$$

Since $AB\psi_i = BA\psi_i$, A commutes with B. Hence the result.

Theorem 3.4 Commuting operators have common set of eigenfunctions.

Proof Consider two commuting operators A and B. The eigenvalue equation for A be

$$A\psi_i = a_i\psi_i, \qquad i = 1, 2, \ldots \tag{3.71}$$

Operating both sides from left by B

$$BA\psi_i = a_iB\psi_i$$

Since B commutes with A

$$A(B\psi_i) = a_i(B\psi_i) \tag{3.72}$$

That is, $B\psi_i$ is an eigenfunction of A with the same eigenvalue a_i. If A has only nondegenerate eigenvalues, $B\psi_i$ can differ from ψ_i only by a multiplicative constant, say b_i

$$B\psi_i = b_i\psi_i \tag{3.73}$$

In other words ψ_i is a simultaneous eigenfunction of both A and B.

3.7 GENERAL UNCERTAINTY RELATION

The general uncertainty relation follows from what we have discussed so far in this chapter. The *uncertainty* (ΔA) in a dynamical variable A is defined as the root mean square deviation from the mean. Here mean implies expectation value. Therefore,

$$(\Delta A)^2 = \langle (A - \langle A\rangle)^2\rangle \tag{3.74a}$$

$$= \langle A^2 - 2A\langle A\rangle + \langle A\rangle^2\rangle$$

$$= \langle A^2\rangle - \langle A\rangle^2 \tag{3.74b}$$

Consider two Hermitian operators, A and B. Let their commutator is given by

$$[A, B] = iC \tag{3.75}$$

It is convenient to define a new operator R by

$$R = A + imB \tag{3.76}$$

where m is an arbitrary real number. The inner product of $R\psi$ with itself must be greater than or equal to zero. That is,

$$(R\psi, R\psi) = \int (A^* - imB^*)\ \psi^*\ (A + imB)\psi\, d\tau \geq 0$$

or

$$\int A^*\psi^*(A + imB)\psi d\tau - im \int B^*\psi^*(A + imB)\psi\, d\tau \geq 0 \tag{3.77}$$

Since A and B are Hermitian Eq. (3.77) becomes

$$\int \psi^*(A - imB)\ (A + imB)\psi\, d\tau \geq 0 \tag{3.77a}$$

or

$$\int \psi^*(A^2 - mC + m^2B^2)\psi\, d\tau \geq 0$$

Then

$$\langle A^2\rangle - m\langle C\rangle + m^2\langle B^2\rangle \geq 0 \tag{3.78}$$

The inequality in Eq. (3.78) must hold regardless of the size of m. To find the value of m for which the left-hand side of Eq. (3.78) is minimum, we have to differentiate it with respect to m and set it to zero

$$-\langle C\rangle + 2m\langle B^2\rangle = 0 \quad \text{or} \quad m = \frac{\langle C\rangle}{2\langle B^2\rangle} \tag{3.79}$$

Eliminating m between Eqs. (3.78) and (3.79), we get

$$\langle A^2\rangle\ \langle B^2\rangle \geq \frac{\langle C\rangle^2}{4} \tag{3.80}$$

This equation is very general and is valid for any two operators A and B obeying Eq. (3.75).

Let us now evaluate the commutator of $(A - \langle A\rangle)$ with $(B - \langle B\rangle)$.

$$\begin{aligned}[A - \langle A\rangle, B - \langle B\rangle] &= (A - \langle A\rangle)\ (B - \langle B\rangle) - (B - \langle B\rangle)\ (A - \langle A\rangle) \\ &= AB - BA \\ &= iC \end{aligned} \tag{3.81}$$

Hence in Eq. (3.80), A can be replaced by $A - \langle A\rangle$ and B by $B - \langle B\rangle$.

$$\langle (A - \langle A\rangle)^2\rangle\ \langle (B - \langle B\rangle)^2\rangle \geq \frac{\langle C\rangle^2}{4}$$

Using Eq. (3.74a), we have

$$(\Delta A)^2\ (\Delta B)^2 \geq \frac{\langle C\rangle^2}{4}$$

or

$$(\Delta A)\,(\Delta B) \geq \frac{\langle C \rangle}{2} \tag{3.82}$$

This is the *general uncertainty relation* which expresses the limitation to the accuracy with which one can hope to measure the values of two incompatible observables. If the operators A and B commute, $C = 0$ and then

$$(\Delta A)\,(\Delta B) = 0 \tag{3.83}$$

In the case where $A = x$ and $B = p_x$, the commutator of operators representing x and p_x gives $[x, p_x] = i\hbar$ and the inequality in Eq. (3.82) takes the familiar form

$$(\Delta x)\,(\Delta p_x) = \frac{\hbar}{2} \tag{3.84}$$

which was introduced as Heisenberg's uncertainty relation (Section 2.2)

3.8 DIRAC'S NOTATION

The state of a system can be represented by a vector called *state vector* in the vector space. Dirac introduced the symbol $|\ \rangle$, called the *ket vector* or simply *ket* to denote a state vector which will take different forms in different representations. To distinguish the ket vectors corresponding to different states, a label is introduced in the ket. Thus, the state vector corresponding to $\psi_a(\mathbf{r})$ is denoted by the ket $|a\rangle$. Corresponding to every vector, $|a\rangle$ is defined a conjugate vector $|a\rangle^*$ for which Dirac used the notation $\langle a|$ which is called a *bra vector* or simply *bra*. The conjugate of a ket vector is a bra vector and vice versa. A scalar in the ket space becomes its complex conjugate in the bra space. The bra–ket notation is a distorted form of the *bracket* notation. Thus, the bracket symbol $(\ |\ )$ is distorted to $\langle\ |$ and $|\ \rangle$ in the Dirac notation. The words 'bra' and 'ket' were derived from the word bracket by dropping the letter '*c*'.

Operation by an operator A on a ket vector produces another ket vector.

$$A|a\rangle = |a'\rangle \tag{3.85}$$

Operation on a bra vector from the right by A gives another bra vector

$$\langle b|A = \langle b'| \tag{3.86}$$

In terms of bra and ket vectors, the definition of the inner product of the state vectors ψ_a and ψ_b takes the form

$$(\psi_a, \psi_b) = \int \psi_a^* \, \psi_b \, d\tau = \langle a|b\rangle \tag{3.87}$$

The *norm* of a ket $|a\rangle$, denoted by $\langle a|a\rangle$ is a real nonnegative number. That is

$$\langle a|a\rangle \geq 0 \tag{3.88}$$

The equality sign holds only if $|a\rangle = 0$. The ket $|a\rangle$ is said to be *normalized* if

$$\langle a|a\rangle = 1 \tag{3.89}$$

Kets $|a\rangle$ and $|b\rangle$ are *orthogonal* if

$$\langle a|b\rangle = 0 \tag{3.90}$$

The *orthonormality relation* is expressed as

$$\langle a_i|a_j\rangle = \delta_{ij} \tag{3.91}$$

In this notation, the condition for an operator to be Hermitian is

$$\langle a|A|b\rangle = \langle b|A|a\rangle^* \tag{3.92}$$

Compared to conventional notation, Dirac's notation is compact.

3.9 EQUATIONS OF MOTION

The motion of a physical system can be systematically studied only with the help of equations of motion. If the state is known at a particular time, they allow the determination of the state at a previous or future time. As the state of a physical system is described as fully as possible by a state vector in the vector space, the equation of motion could be an equation for the state vector. State vector as such is not an observable. But the expectation value of a dynamical variable $\langle A\rangle$ is an observable quantity. Therefore, the variation with time of $\langle A\rangle$ can be considered as an equation of motion. The definition of $\langle A\rangle$, Eq. (3.56), suggests that the variation with time of $\langle A\rangle$ may be due to one of the following situations:

1. The state vector changes with time but the operator remains constant (*Schrödinger representation* or *Schrödinger picture*),
2. The operator changes with time while the state vector remains constant (*Heisenberg representation* or *Heisenberg picture*).
3. Both state vector and operator change with time (*interaction representation* or *interaction picture*).

Schrödinger Representation

We are very familiar with the wave mechanical approach to quantum mechanics and therefore it is appropriate to start with the Schrödinger representation. As already stated (Section 3.5), in this picture the state vectors are time-dependent kets $|\psi_s(t)\rangle$ and the operators are constants in time. The equation of motion is then an equation for $|\psi_s(t)\rangle$, the subscript 's' is to indicate Schrödinger picture. The ket $|\psi_s(t)\rangle$ varies in accordance with the time-dependent Schrödinger equation

$$i\hbar\frac{d}{dt}|\psi_s(t)\rangle = H|\psi_s(t)\rangle \tag{3.93}$$

As the Hamiltonian H is independent of time, Eq. (3.93) can be integrated to give

$$|\psi_s(t)\rangle = \exp\left(-\frac{iHt}{\hbar}\right)|\psi_s(0)\rangle \tag{3.94}$$

Here, the operator exp $(-iHt/\hbar)$ is defined as

$$\exp\left(-\frac{iHt}{\hbar}\right) = \sum_{n=0}^{\infty}\frac{(-iHt/\hbar)^n}{n!} \tag{3.95}$$

Equation (3.94) reveals that the operator exp $(-iHt/\hbar)$ changes the ket $|\psi_s(0)\rangle$ into ket $|\psi_s(t)\rangle$. Since H is Hermitian and t is real, this operator is unitary and the norm of the ket remains unchanged. The Hermitian adjoint of Eq. (3.93) is

$$-i\hbar\frac{d}{dt}\langle\psi_s(t)| = \langle\psi_s(t)|H^\dagger = \langle\psi_s(t)|H \tag{3.96}$$

whose solution is

$$\langle\psi_s(t)| = \langle\psi_s(0)|\exp\left(\frac{iHt}{\hbar}\right) \tag{3.97}$$

Next we consider the time derivative of expectation value of the operator A_s. The time derivative of $\langle A_s\rangle$ is given by

$$\frac{d}{dt}\langle A_s\rangle = \frac{d}{dt}\langle\psi_s(t)|A_s|\psi_s(t)\rangle \tag{3.98}$$

where A_s is the operator representing the observable A. Replacement of the factors

$$\frac{d}{dt}|\psi_s(t)\rangle \quad \text{and} \quad \frac{d}{dt}\langle\psi_s(t)|$$

using Eqs. (3.93) and (3.96) gives

$$\frac{d}{dt}\langle A_s\rangle = \frac{1}{i\hbar}\langle\psi_s(t)|A_sH - HA_s|\psi_s(t)\rangle + \langle\psi_s(t)|\frac{\partial A_s}{\partial t}|\psi_s(t)\rangle$$

or

$$\frac{d}{dt}\langle A_s\rangle = \frac{1}{i\hbar}\left[A_s, H\right] + \left\langle\frac{\partial A_s}{\partial t}\right\rangle \tag{3.99}$$

If A_s has no explicit dependence on time, we get

$$i\hbar\frac{d}{dt}\langle A_s\rangle = \left[A_s, H\right] \tag{3.100}$$

If the operator A_s commutes with the Hamiltonian, it is a constant in time.

Heisenberg Representation

In this representation, the time dependence is completely taken up by the operators. This leaves the state vectors fixed in time. Let us use the unitary operator exp $(iHt/\hbar)$ to change the state vectors and operators of the Schrödinger picture. The state vector $|\psi_H\rangle$ and the operator A_H are defined as under:

$$|\psi_H\rangle = \exp\left(\frac{iHt}{\hbar}\right)|\psi_s(t)\rangle \tag{3.101}$$

and

$$A_H(t) = \exp\left(\frac{iHt}{\hbar}\right) A_s \exp\left(-\frac{iHt}{\hbar}\right) \tag{3.102}$$

Substituting the value of $|\psi_s(t)\rangle$ from Eq. (3.94) in Eq. (3.101), we get

$$|\psi_H\rangle = \exp\left(\frac{iHt}{\hbar}\right) \exp\left(-\frac{iHt}{\hbar}\right) |\psi_s(0)\rangle = |\psi_s(0)\rangle \tag{3.103}$$

Thus, even if A_s does not depend on time explicitly, A_H generally depends on time. From Eqs. (3.103), (3.101) and (3.102), it is obvious that at $t = 0$ the state vectors and operators are the same in the two representations. Since H commutes with exp $(\pm iHt/\hbar)$, it follows from Eq. (3.102)

$$H_H = \exp\left(\frac{iHt}{\hbar}\right) H \exp\left(-\frac{iHt}{\hbar}\right) = H \tag{3.104}$$

That is, the Hamiltonian is the same in both Heisenberg and Schrödinger representations.

Differentiation of A_H with respect to time gives

$$\frac{dA_H}{dt} = \frac{iH}{\hbar}\exp\left(\frac{iHt}{\hbar}\right)A_s\exp\left(-\frac{iHt}{\hbar}\right) - \frac{i}{\hbar}\exp\left(\frac{iHt}{\hbar}\right)A_sH\exp\left(-\frac{iHt}{\hbar}\right)$$

$$+ \exp\left(\frac{iHt}{\hbar}\right)\frac{\partial A_s}{\partial t}\exp\left(-\frac{iHt}{\hbar}\right) \tag{3.105}$$

By virtue of Eq. (3.102) the third term on the right side is $\partial A_H/\partial t$. Remembering that H commutes with exp $(\pm iHt/\hbar)$ we have from Eq. (3.105)

$$\frac{dA_H}{dt} = \frac{1}{i\hbar}[A_H, H] + \frac{\partial A_H}{\partial t} \tag{3.106}$$

If A_H has no explicit dependence on t,

$$i\hbar\frac{dA_H}{dt} = [A_H, H] \tag{3.106a}$$

which is the *Heisenberg equation of motion* that replaces the Schrödinger equation of motion.

Interaction Representation

Another representation introduced by Dirac, called interaction representation, is very useful in problems involving perturbations. Let the Hamiltonian of the system consists of two parts

$$H = H^0 + H' \tag{3.107}$$

where H^0 does not depend explicitly on time and H may depend on time. There is no strict rule for the division of H into H^0 and H'. H^0 may represent the Hamiltonian for a relatively simple system and H' some additional interaction, which is dependent on time. The interaction picture is defined by the equations

$$|\psi_{\mathrm{I}}(t)\rangle = \exp\left(\frac{iH^0t}{\hbar}\right)|\psi_{\mathrm{s}}(t)\rangle \tag{3.108}$$

and

$$A_{\mathrm{I}}(t) = \exp\left(\frac{iH^0t}{\hbar}\right) A_{\mathrm{s}} \exp\left(-\frac{iH^0t}{\hbar}\right) \tag{3.109}$$

Differentiating Eq. (3.108) with respect to time and multiplying by $i\hbar$, we get

$$i\hbar\frac{d|\psi_{\mathrm{I}}(t)\rangle}{dt} = -H^0|\psi_{\mathrm{I}}(t)\rangle + \exp\left(\frac{iH^0t}{\hbar}\right) i\hbar\frac{d|\psi_{\mathrm{s}}(t)\rangle}{dt} \tag{3.110}$$

We have

$$i\hbar\frac{d}{dt}|\Psi_{\mathrm{s}}(t)\rangle = (H^0 + H')|\psi_{\mathrm{s}}(t)\rangle$$

$$= (H^0 + H')\exp\left(-\frac{iH^0t}{\hbar}\right)|\psi_{\mathrm{I}}(t)\rangle$$

Since H^0 commutes with $\exp(-iH^0t/\hbar)$, using the above result Eq. (3.110) can be written as

$$i\hbar\frac{d}{dt}|\psi_{\mathrm{I}}(t)\rangle = H_{\mathrm{I}}'|\psi_{\mathrm{I}}(t)\rangle \tag{3.111}$$

where

$$H_{\mathrm{I}}' = \exp\left(\frac{iH^0t}{\hbar}\right) H' \exp\left(-\frac{iH^0t}{\hbar}\right) \tag{3.112}$$

Equation (3.111) is the equation of motion for $\psi_{\mathrm{I}}(t)$ which is similar to the time-dependent Schrödinger equation with H_{I}' replacing H. If $H_{\mathrm{I}}' = 0$, $\psi_{\mathrm{I}}(t)$ is constant in time. That is, if the interaction term H' is absent, the interaction picture is the same as the Heisenberg picture. Differentiation of (3.109) with respect to time gives

$$\frac{dA_I}{dt} = \frac{1}{i\hbar}\left[A_I, H^0\right] + \frac{\partial A_I}{\partial t} \tag{3.113}$$

From Eqs. (3.111) and (3.113), it is evident that the state vector changes in accordance with H' whereas the dynamical variables change in accordance with H^0. In the interaction picture part of the time dependence is assigned to the state vector and part to the dynamical variable.

3.10 MOMENTUM REPRESENTATION

As we have discussed in earlier sections, the wave function is a function of the coordinates and time. In such a case, we have the coordinate or position representation. In certain cases, it is convenient to work in the momentum representation in which the state function of a system $\phi(p, t)$ is taken as a function of the momentum and time. In the coordinate representation, the operator for the coordinate r is simply r and the operator for $\mathbf{p}$ is $-i\hbar\nabla$. However, in the momentum representation, the momentum $\mathbf{p}$ is represented by the operator $\mathbf{p}$ itself and the coordinate is represented by a differential operator. Since $p = k\hbar$, the momentum space is equivalent to a k-space in which the operator for k is k itself. Relations in the momentum representation equivalent to the ones in the coordinate representation can easily be derived.

Probability Density

For a one-dimensional system, the Fourier representation of $\Psi(x, t)$ is given by

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Phi(k, t) \exp(ikx)\, dk \tag{3.114}$$

$$\Phi(k, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) \exp(-ikx)\, dx \tag{3.115}$$

Changing the variable from k to p, we get

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) \exp\left(\frac{ipx}{\hbar}\right) dp \tag{3.116}$$

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) \exp\left(-\frac{ipx}{\hbar}\right) dx \tag{3.117}$$

Then

$$\int \Psi^*(x, t)\, \Psi(x, t)\, dx = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \Phi^*(p, t) \exp\left(-\frac{ipx}{\hbar}\right) dp \int_{-\infty}^{\infty} \Phi(p', t) \exp\left(\frac{ip'x}{\hbar}\right) dp'$$

Changing the order of integration, we have

$$\int_{-\infty}^{\infty} \Psi^*\Psi\, dx = \frac{1}{\hbar}\int_{-\infty}^{\infty} \Phi^*(p, t)dp \int_{-\infty}^{\infty} \Phi(p', t)dp' \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\left[\frac{i}{\hbar}(p'-p)x\right] dx$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty} \Phi^*(p, t)dp \int_{-\infty}^{\infty} \Phi(p', t)\, dp'\hbar\delta(p'-p)$$

where $\delta(p'-p)$ is the Dirac delta function (Appendix III)

$$\int_{-\infty}^{\infty} \Psi^*(x, t)\ \Psi(x, t)\ dx = \int_{-\infty}^{\infty} \Phi^*(p, t)\ \Phi(p, t)\ dp \qquad (3.118)$$

It follows that the probability density in the momentum representation is $|\Phi(p, t)|^2$.

Operator for Position Coordinate

The expectation value of the position coordinate x is

$$\langle x\rangle = \int_{-\infty}^{\infty} \Psi^*(x, t)\ x\ \Psi(x, t)\ dx$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \Phi^*(p, t)\ \exp\left(-\frac{ipx}{\hbar}\right)\ dp \int_{-\infty}^{\infty} \Phi(p', t)\ x\ \exp\left(\frac{ip'x}{\hbar}\right) dp'$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \Phi^*(p, t)\ \exp\left(-\frac{ipx}{\hbar}\right) dp \int_{-\infty}^{\infty} \Phi(p', t)\left(\frac{\hbar}{i}\frac{\partial}{\partial p'}\right) \exp\left(\frac{ip'x}{\hbar}\right) dp' \qquad (3.119)$$

Integration by parts gives,

$$\int_{-\infty}^{\infty} \Phi(p', t)\frac{\partial}{\partial p'}\exp\left(\frac{ip'x}{\hbar}\right) dp' = \left[\Phi(p',t)\exp\left(\frac{ip'x}{\hbar}\right)\right]_{-\infty}^{\infty}$$

$$- \int_{-\infty}^{\infty} \exp\left(\frac{ip'x}{\hbar}\right)\frac{\partial}{\partial p'}\Phi(p', t)\ dp'$$

The integrated term vanishes since $\Phi(p', t) = 0$ at $p' = \pm\infty$. Hence

$$\langle x\rangle = i\hbar\int_{-\infty}^{\infty} \Phi^*(p, t)\ dp \int_{-\infty}^{\infty} \frac{\partial}{\partial p'}\Phi(p', t)\ dp'\ \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \exp\left[\frac{i}{\hbar}(p' - p)x\right] dx$$

$$= i\hbar\int_{-\infty}^{\infty} \Phi^*(p, t)\ dp \int_{-\infty}^{\infty} \frac{\partial}{\partial p'}\Phi(p', t)\ \delta(p' - p)\, dp'$$

$$= \int_{-\infty}^{\infty} \Phi^*(p, t)\left(i\hbar\frac{\partial}{\partial p}\right)\Phi(p, t)\, dp \tag{3.120}$$

The operator associated with the coordinate x in the momentum representation is then $i\hbar\frac{\partial}{\partial p}$. Generalizing, the operator associated with the vector $\mathbf{r}$ in the momentum representation is $i\hbar\nabla p$, where ∇p is the gradient in the p-space.

Operator for Momentum

We shall next investigate the operator for momentum in the momentum representation. In the coordinate representation

$$\langle p\rangle = \int_{-\infty}^{\infty} \Psi^*(x, t)\left(-i\hbar\frac{d}{dx}\right)\Psi(x, t)\, dx$$

$$= \frac{-i\hbar}{2\pi\hbar}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} \Phi^*(p, t)\exp\left(-\frac{ipx}{\hbar}\right)dp \int_{-\infty}^{\infty}\frac{\partial}{\partial x}\Phi(p', t)\exp\left(\frac{ip'x}{\hbar}\right)dp'$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty}\Phi^*(p, t)\, dp \int_{-\infty}^{\infty}\Phi(p', t)\, p'dp'\ \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left[\frac{i}{\hbar}(p'-p)x\right]dx$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty}\Phi^*(p, t)\, dp \int_{-\infty}^{\infty}\Phi(p', t)\, p'\hbar\delta(p'-p)dp'$$

$$= \int_{-\infty}^{\infty}|\Phi(p, t)|^2 p\, dp \tag{3.121}$$

Thus the operator for momentum in the momentum space is p itself.

Equation of Motion

The equation of motion in the momentum space can easily be obtained by differentiating Eq. (3.117) with respect to time and multiplying by $i\hbar$

$$i\hbar\frac{\partial}{\partial t}\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} i\hbar\frac{\partial}{\partial t}\Psi(x, t)\exp\left(-\frac{ipx}{\hbar}\right)dx$$

Replacing $i\hbar\frac{\partial}{\partial t}$ inside the integral by

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

we get

$$i\hbar\frac{\partial}{\partial t}\Phi\,(p,\,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)\,dx \tag{3.122}$$

Integration by parts gives

$$\int_{-\infty}^{\infty}\frac{\partial^2}{\partial x^2}\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)dx=\left[\exp\left(-\frac{ipx}{\hbar}\right)\frac{\partial\Psi}{\partial x}\right]_{-\infty}^{\infty}$$

$$+\frac{ip}{\hbar}\int_{-\infty}^{\infty}\frac{\partial\Psi}{\partial x}\exp\left(-\frac{ipx}{\hbar}\right)dx$$

The integrated term vanishes as $\partial\Psi/\partial x$ vanishes at $x = \pm\,\infty$. Integrating again, we get

$$\int_{-\infty}^{\infty}\frac{\partial^2}{\partial x^2}\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)dx=\left(\frac{ip}{\hbar}\right)^2\int_{-\infty}^{\infty}\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)dx$$

Equation (3.122) now reduces to

$$i\hbar\frac{\partial}{\partial t}\Phi\,(p,\,t)=\frac{1}{\sqrt{2\pi\hbar}}\frac{p^2}{2m}\int_{-\infty}^{\infty}\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)dx$$

$$+\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}V\Psi(x,t)\ \exp\left(-\frac{ipx}{\hbar}\right)dx$$

Using Eqs. (3.116) and (3.117), we get

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}\Phi\,(p,\,t) &= \frac{p^2}{2m}\Phi(p,t)\\ &\quad+\int_{-\infty}^{\infty}V\Phi(p',t)\,dp'\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\exp\left[\frac{i}{\hbar}(p'-p)x\right]dx\\ &=\frac{p^2}{2m}\Phi(p,t)+\int_{-\infty}^{\infty}V\Phi(p',t)\,dp'\,\delta(p'-p)\\ &=\frac{p^2}{2m}\Phi(p,t)+V(x)\,\Phi(p,t)\end{aligned}$$

or

$$i\hbar\frac{\partial}{\partial t}\Phi\,(p,\,t)=\left[\frac{p^2}{2m}+V(x)\right]\Phi(p,t) \tag{3.123}$$

which is the *equation of motion in the momentum representation.*

WORKED EXAMPLES

EXAMPLE 3.1 A and B are two operators defined by

$$A\psi(x) = \psi(x) + x \quad \text{and} \quad B\psi(x) = \frac{d\psi}{dx} + 2\psi(x)$$

Check for their linearity.

An operator O is said to be linear if

$$O\,[c_1 f_1(x) + c_2 f_2(x)] = c_1 O\, f_1(x) + c_2 O\, f_2(x)$$

For the operator A, $A\,[c_1 f_1(x) + c_2 f_2(x)] = c_1 f_1(x) + c_2 f_2(x) + x$

$$c_1 A\, f_1(x) + c_2 A\, f_2(x) = c_1 f_1(x) + c_2 f_2(x) + c_1\, x + c_2\, x$$

The above two right-hand sides are not equal. Hence operator A is not linear. Again for the operator B,

$$\begin{aligned} B\,[c_1 f_1(x) + c_2 f_2(x)] &= \frac{d}{dx}\,[c_1 f_1(x) + c_2 f_2(x)] + 2[c_1 f_1(x) + c_2 f_2(x)] \\ &= c_1 \frac{d}{dx}\, f_1(x) + c_2 \frac{d}{dx}\, f_2(x) + 2c_1 f_1(x) + 2c_2 f_2(x) \\ &= \frac{d}{dx} c_1 f_1(x) + 2c_1 f_1(x) + \frac{d}{dx} c_2 f_2(x) + 2c_2 f_2(x) \\ &= c_1 B\, f_1(x) + c_2 B\, f_2(x) \end{aligned}$$

Hence operator B is linear.

EXAMPLE 3.2 Prove that the operators $i\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ are Hermitian.

Consider the integral

$$\int_{-\infty}^{\infty} \psi_m^* \left(i\frac{d}{dx}\right) \psi_n\, dx$$

Integrating it by parts and noting that ψ_m and ψ_n are zero at the end points.

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m^* \left(i\frac{d}{dx}\right) \psi_n\, dx &= i\left[\psi_m^* \psi_n\right]_{-\infty}^{\infty} - i\int_{-\infty}^{\infty} \psi_n \frac{d}{dx} \psi_m^*\, dx \\ &= \int_{-\infty}^{\infty} \left(i\frac{d}{dx}\psi_m\right)^* \psi_n\, dx \end{aligned}$$

which is the condition for $i\frac{d}{dx}$ to be Hermitian. Hence $i\frac{d}{dx}$ is Hermitian. Now

$$\int_{-\infty}^{\infty} \psi_m^* \frac{d^2\psi_n}{dx^2}\, dx = \left[\psi_m^* \frac{d\psi_n}{dx}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{d\psi_n}{dx}\frac{d\psi_m^*}{dx}\, dx$$

$$= -\left[\frac{d\psi_m^*}{dx}\psi_n\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\psi_n\frac{d^2\psi_m^*}{dx^2}dx = \int_{-\infty}^{\infty}\frac{d^2\psi_m^*}{dx^2}\psi_n\, dx$$

Hence, $\frac{d^2}{dx^2}$ is Hermitian. The integrated terms in the above equations are zero since ψ_m and ψ_n are zero at the end points.

EXAMPLE 3.3 Show that the cartesian coordinates (r_1, r_2, r_3) and the cartesian components of angular momentum (L_1, L_2, L_3) obey the commutation relations

(i) $[L_k, r_l] = i\hbar r_m$ (ii) $[L_k, r_k] = 0$,

where k, l, m are a cyclic permutation of 1, 2, 3.

(i) $[L_k, r_l]\psi = (L_k r_l - r_l L_k)\psi$

$$= -i\hbar\left[\left(r_l\frac{\partial}{\partial r_m} - r_m\frac{\partial}{\partial r_l}\right)r_l\psi - r_l\left(r_l\frac{\partial}{\partial r_m} - r_m\frac{\partial}{\partial r_l}\right)\psi\right]$$

$$= -i\hbar\left(r_l\frac{\partial r_l}{\partial r_m}\psi + r_l^2\frac{\partial\psi}{\partial r_m} - r_m\frac{\partial r_l\psi}{\partial r_l} - r_m r_l\frac{\partial\psi}{\partial r_l} - r_l^2\frac{\partial\psi}{\partial r_m} + r_l r_m\frac{\partial\psi}{\partial r_l}\right)$$

$$= -i\hbar(r_l\,\delta_{lm} - r_m)\psi$$

$$= i\hbar r_m\,\psi$$

Hence $[L_k, r_l] = i\hbar r_m$.

(ii) $[L_k, r_k]\psi = -i\hbar\left[\left(r_l\frac{\partial}{\partial r_m} - r_m\frac{\partial}{\partial r_l}\right)r_k\psi - r_k\left(r_l\frac{\partial}{\partial r_m} - r_m\frac{\partial}{\partial r_l}\right)\psi\right] = 0$

Therefore,

$$[L_k, r_k] = 0$$

EXAMPLE 3.4 If A and B are Hermitian operators, show that $(AB + BA)$ is Hermitian and $(AB - BA)$ is not Hermitian.

Since A and B are Hermitian, we have

$$(\psi_m, A\psi_n) = (A\psi_m, \psi_n),\ (\psi_m, B\psi_n) = (B\psi_m, \psi_n)$$

$$\int\psi_m^*\,(AB + BA)\,\psi_n dx = \int\psi_m^*\,AB\psi_n\,dx + \int\psi_m^*BA\psi_n\,dx$$

$$= \int B^*A^*\psi_m^*\psi_n\,dx + \int A^*B^*\,\psi_m^*\psi_n\,dx$$

$$= \int(AB + BA)^*\psi_m^*\,\psi_n\,dx$$

Hence $(AB + BA)$ is Hermitian. Now

$$\int\psi_m^*\,(AB - BA)\,\psi_n\,dx = \int(B^*A^* - A^*B^*)\,\psi_m^*\psi_n\,dx = -\int(AB - BA)^*\psi_m^*\psi_n\,dx$$

Hence $(AB - BA)$ is not Hermitian.

EXAMPLE 3.5 If x and p_x are the coordinate and momentum operators, prove that

$$[x, p_x^n] = ni\hbar p_x^n$$

$$\begin{aligned}[x, p_x^n] &= [x, p_x^{n-1}\, p_x] = [x, p_x]\, p_x^{n-1} + p_x\, [x, p_x^{n-1}]\\ &= i\hbar p_x^{n-1} + p_x\, ([x, p_x]\, p_x^{n-2} + p_x\, [x, p_x^{n-2}])\\ &= 2i\hbar p_x^{n-1} + p_x^2([x, p_x]\, p_x^{n-3} + p_x\, [x, p_x^{n-3}])\\ &= 3i\hbar p_x^{n-1} + p_x^3\, [x, p_x^{n-3}]\end{aligned}$$

Continuing, we get

$$[x, p_x^n] = ni\hbar p_x^{n-1}$$

EXAMPLE 3.6 The wavefunction of a particle in a state is

$$\psi = N \exp\left(-\frac{x^2}{2\alpha}\right), \qquad \text{where } N = \left(\frac{1}{\pi\alpha}\right)^{1/4}$$

Evaluate (Δx) (Δp).

For evaluating (Δx) (Δp), we require the values of $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$ and $\langle p^2\rangle$. Since ψ is symmetrical about $x = 0$, $\langle x\rangle = 0$.

$$\langle x^2\rangle = N^2 \int_{-\infty}^{\infty} x^2 \exp\left(\frac{-x^2}{\alpha}\right) dx = \frac{\alpha}{2}$$

$$\begin{aligned}\langle p\rangle &= -i\hbar N^2 \int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{2\alpha}\right) \frac{d}{dx} \exp\left(\frac{-x^2}{2\alpha}\right) dx\\ &= \text{Constant} \int_{-\infty}^{\infty} x \exp\left(\frac{-x^2}{\alpha}\right) dx\\ &= 0 \qquad \text{(since integrand is odd)}\end{aligned}$$

$$\begin{aligned}\langle p^2\rangle &= (-i\hbar)^2\, N^2 \int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{2\alpha}\right) \frac{d^2}{dx^2} \exp\left(\frac{-x^2}{2\alpha}\right) dx\\ &= \frac{\hbar^2 N^2}{\alpha} \int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{\alpha}\right) dx - \frac{\hbar^2 N^2}{\alpha^2} \int_{-\infty}^{\infty} x^2 \exp\left(\frac{-x^2}{\alpha}\right) dx\\ &= \frac{\hbar^2}{\alpha} - \frac{\hbar^2}{2\alpha} \qquad \text{(refer to Appendix A)}\\ &= \frac{\hbar^2}{2\alpha}\end{aligned}$$

Hence

$$(\Delta x)^2\, (\Delta p)^2 = \langle x^2\rangle\, \langle p^2\rangle = \frac{\alpha}{2}\frac{\hbar^2}{2\alpha} = \frac{\hbar^2}{4}$$

or

$$(\Delta x)\,(\Delta p) = \frac{\hbar}{2}$$

EXAMPLE 3.7 Show that the linear momentum is not quantized.

The operator for x-component of linear momentum is $-i\hbar\frac{d}{dx}$. Let $\psi_k(x)$ be its eigenfunction corresponding to the eigenvalue a_k. The eigenvalue equation is

$$-i\hbar\frac{d}{dx}\psi_k(x) = a_k\psi_k(x) \quad \text{or} \quad \frac{d\psi_k(x)}{\psi_k(x)} = \frac{i}{\hbar}a_k\,dx$$

Integrating, we get

$$\psi_k(x) = C\exp\left(\frac{i}{\hbar}a_k x\right)$$

where C is a constant. Function $\psi_k(x)$ will be finite for all real values of a_k. Hence all real values of a_k are proper eigenvalues and they form a continuous spectrum. In other words, linear momentum is not quantized.

EXAMPLE 3.8 Can we measure the kinetic and potential energies of a particle simultaneously with arbitrary precision?

$$\text{Operator for kinetic energy, } T = -\frac{\hbar^2}{2m}\nabla^2$$

$$\text{Operator for potential energy, } V = V(r)$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2, V\right]\psi = -\frac{\hbar^2}{2m}\nabla^2(V\psi) - V\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi$$

$$= -\frac{\hbar^2}{2m}(\nabla^2 V)\,\psi$$

$$\neq 0$$

Since the operators of the two observables do not commute, simultaneous measurement of both is not possible. Simultaneous measurement is possible if V is a constant.

EXAMPLE 3.9 If the wave function for a system is an eigenfunction of the operator associated with the observable A, show that $\langle A^n\rangle = \langle A\rangle^n$.

Eigenfunctions and eigenvalues of operator associated with the observable A be ψ and α respectively.

$$\langle A^n\rangle = \int \psi^* A^n \psi\, d\tau$$

$$= \int \psi^* A^{n-1} A\psi\, d\tau$$

$$= \alpha\int \psi^* A^{n-1}\psi\, d\tau$$

$$= \alpha^2 \int \psi^* A^{n-2} \psi \, d\tau$$

$$= \alpha^n \int \psi^* \psi \, d\tau$$

$$= \alpha^n$$

and

$$\langle A \rangle^n = \left(\int \psi^* A \psi \, d\tau \right)^n$$

$$= \left(\alpha \int \psi^* \psi \, d\tau \right)^n$$

$$= \alpha^n$$

Hence $\langle A^n \rangle = \langle A \rangle^n$.

EXAMPLE 3.10 The wave function ψ of a system is expressed as a linear combination of normalized eigenfunctions ϕ_i, $i = 1, 2, \ldots$ of the operator α of the observable A as $\psi = \Sigma_i c_i \phi_i$. Show that $\langle A^n \rangle = \Sigma_i |c_i|^2 a_i^n$, where $\alpha\phi_i = a_i\phi_i$, $i = 1, 2, \ldots$

Given that

$$\psi = \sum_i c_i \, \phi_i, \qquad \text{where } c_i = \int_{-\infty}^{\infty} \phi_i^* \psi \, d\tau, \quad i = 1, 2, \ldots$$

Then

$$\langle A^n \rangle = \int_{-\infty}^{\infty} \psi^* \alpha^n \psi \, d\tau$$

$$= \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \phi_i^* \alpha^n \phi_j \, d\tau$$

$$= \sum_i \sum_j c_i^* c_j a_j^n \int_{-\infty}^{\infty} \phi_i^* \phi_j \, d\tau$$

$$= \sum_i |c_i|^2 a_i^n$$

since the ϕ's are orthonormal.

EXAMPLE 3.11 The Hamiltonian operator of a system is

$$H = -\frac{d^2}{dx^2} + x^2$$

Show that $Nx \exp(-x^2/2)$ is an eigenfunction of H and determine the eigenvalue. Also, evaluate N by normalization of the function.

$$\psi = N\, x \exp\left(\frac{-x^2}{2} \right), \quad N \text{ is a constant}$$

$$H\psi = \left(\frac{-d^2}{dx^2} + x^2 \right) Nx \exp\left(\frac{-x^2}{2} \right)$$

$$= Nx^3 \exp\left(\frac{-x^2}{2}\right) - N\frac{d}{dx}\left[\exp\left(\frac{-x^2}{2}\right) - x^2 \exp\left(\frac{-x^2}{2}\right)\right]$$

$$= 3N\, x \exp\left(\frac{-x^2}{2}\right)$$

$$= 3\psi$$

Hence eigenvalue of H is 3. The normalization condition gives

$$N^2 \int_{-\infty}^{\infty} x^2 \exp(-x^2)\, dx = 1$$

$$N^2 \frac{\sqrt{\pi}}{2} = 1 \quad \text{or} \quad N = \left(\frac{2}{\sqrt{\pi}}\right)^{1/2}$$

The normalized function is

$$\psi = \left(\frac{2}{\sqrt{\pi}}\right)^{1/2} x \exp\left(\frac{-x^2}{2}\right)$$

EXAMPLE 3.12 Obtain the form of the wave function for which the uncertainty product $(\Delta x)\,(\Delta p) = \hbar/2$.

We have seen that the left-hand side of Eq. (3.78) is minimum when

$$m = \frac{\langle C \rangle}{2\langle B^2 \rangle}$$

This implies that

$$(A + \mathrm{i}mB)\psi = 0$$

The uncertainties (ΔA) and (ΔB) are defined by

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle, \qquad (\Delta B)^2 = \langle (B - \langle B \rangle)^2 \rangle$$

We have also proved that

$$[A, B] = [A - \langle A \rangle, B - \langle B \rangle] = iC$$

Hence, the product $(\Delta A)^2\,(\Delta B)^2$ will be minimum when

$$[(A - \langle A \rangle) + \mathrm{i}m(B - \langle B \rangle)]\psi = 0$$

Identifying x with A and p with B

$$[(x - \langle x \rangle) + \mathrm{i}m\,(p - \langle p \rangle)]\,\psi = 0 \quad \text{and} \quad m = \frac{\hbar}{2(\Delta p)^2}$$

Then

$$\frac{d\psi}{dx} + \left[\frac{2(\Delta p)^2}{\hbar^2}\left(x - \langle x \rangle\right) - \frac{i\langle p \rangle}{\hbar}\right]\psi = 0$$

or

$$\frac{d\psi}{\psi} = -\left[\frac{2(\Delta p)^2}{\hbar^2}(x - \langle x\rangle) - \frac{i\langle p\rangle}{\hbar}\right]dx$$

Integrating and replacing Δp with $\hbar/(2\Delta x)$, we get

$$\psi = N \exp\left[-\frac{(x - \langle x\rangle)^2}{4(\Delta x)^2} + \frac{i\langle p\rangle x}{\hbar}\right]$$

Normalization of the wave function is straightforward which gives

$$\psi = \left(\frac{1}{2\pi(\Delta x)^2}\right)^{1/4} \exp\left[-\frac{(x - \langle x\rangle)^2}{4(\Delta x)^2} + \frac{i\langle p\rangle x}{\hbar}\right]$$

EXAMPLE 3.13 Find the eigenfunctions and nature of eigenvalues of the operator

$$\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}$$

Let ψ be the eigenfunction corresponding to the eigenvalue λ. Then the eigenvalue equation is given by

$$\left(\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}\right)\psi = \lambda\psi$$

Consider the function $u = x\psi$. Differentiating with respect to x, we get

$$\frac{du}{dx} = \psi + x\frac{d\psi}{dx}$$

$$\frac{d^2u}{dx^2} = \frac{d\psi}{dx} + \frac{d\psi}{dx} + x\frac{d^2\psi}{dx^2} = 2\frac{d\psi}{dx} + x\frac{d^2\psi}{dx^2}$$

Dividing throughout by x,

$$\frac{1}{x}\frac{d^2u}{dx^2} = \left(\frac{2}{x}\frac{d}{dx} + \frac{d^2}{dx^2}\right)\psi$$

Combining this equation with the first one,

$$\frac{1}{x}\frac{d^2u}{dx^2} = \lambda\psi \quad \text{or} \quad \frac{d^2u}{dx^2} = \lambda u$$

Its solution is:

$$u = c_1 e^{\sqrt{\lambda}x} + c_2 e^{-\sqrt{\lambda}x} \quad \text{where } c_1 \text{ and } c_2 \text{ are constants.}$$

For u to be a physically acceptable function, $\sqrt{\lambda}$ must be imaginary, say $i\beta$. Also, at $x = 0$, $u = 0$. Hence $c_1 + c_2 = 0$, $c_1 = -c_2$. Consequently,

$$u = c_1(e^{i\beta x} - e^{-i\beta x}), \quad \psi = \frac{1}{x}c_1(e^{i\beta x} - e^{-i\beta x})$$

$$\psi = c\,\frac{\sin \beta x}{x}$$

EXAMPLE 3.14. A particle is constrained in a potential $V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise. In the x-representation, the wave function of the particle is given by

$$\psi(x) = \sqrt{\frac{2}{a}}\,\sin\frac{2\pi x}{a}$$

Determine the momentum function $\Phi(p)$.

From Eq. (3.117),

$$\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} \psi(x)\, e^{-\frac{ipx}{\hbar}}\, dx$$

In the present case, it reduces to

$$\Phi(p) = \frac{1}{\sqrt{\pi\hbar a}}\, I$$

where

$$I = \int_0^a \sin\frac{2\pi x}{a} e^{-\frac{ipx}{\hbar}}\, dx$$

Integrating by parts,

$$I = \left[-\frac{\hbar}{ip}\sin\frac{2\pi x}{a} e^{-\frac{ipx}{\hbar}}\right]_0^a - \int_0^a \left(-\frac{\hbar}{ip}\right) e^{-\frac{ipx}{\hbar}}\, \frac{2\pi}{a}\cos\frac{2\pi x}{a}\, dx$$

Since the integrated term is zero,

$$I = \frac{2\pi\hbar}{ipa}\left[\cos\frac{2\pi x}{a}\left(-\frac{\hbar}{ip}\right) e^{-\frac{ipx}{\hbar}}\right]_0^a - \frac{2\pi\hbar}{ipa}\int_0^a \left(-\frac{\hbar}{ip}\right) e^{-\frac{ipx}{\hbar}} \left(-\frac{2\pi}{a}\right)\sin\frac{2\pi x}{a}\, dx$$

$$= \frac{2\pi\hbar}{ipa}\left(-\frac{\hbar}{ip}\right)\left(e^{-ipa/\hbar} - 1\right) + \frac{4\pi^2\hbar^2}{a^2p^2}\, I$$

$$I\left(1 - \frac{4\pi^2\hbar^2}{a^2p^2}\right) = \frac{2\pi\hbar^2}{ap^2}\left(e^{-ipa/\hbar} - 1\right)$$

$$I = \frac{2\pi a\hbar^2}{a^2p^2 - 4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}} - 1\right)$$

With this value of I,

$$\Phi(p) = \frac{1}{\sqrt{\pi\hbar a}}\,\frac{2\pi a\hbar^2}{a^2p^2 - 4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}} - 1\right)$$

$$= \frac{2\pi^{1/2}a^{1/2}\hbar^{3/2}}{a^2p^2 - 4\pi^2\hbar^2}\left(e^{-\frac{ipa}{\hbar}} - 1\right)$$

EXAMPLE 3.15 A particle is in a state $|\psi\rangle = \left(\frac{1}{\pi}\right)^{1/4}\exp(-x^2/2)$. Find Δx and Δp_x. Hence evaluate the uncertainty product $(\Delta x)(\Delta p_x)$.

For the wave function, we have

$$\langle x\rangle = \left(\frac{1}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\,e^{-x^2}\,dx = 0$$

since the integrand is an odd function of x.

$$\langle x^2\rangle = \left(\frac{1}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^2\,e^{-x^2}\,dx = 2\left(\frac{1}{\pi}\right)^{1/2}\frac{\sqrt{\pi}}{4} = \frac{1}{2} \qquad \text{(Appendix A)}$$

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{1}{2}$$

$$\langle p_x\rangle = \left(\frac{1}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-x^2/2}\left(-i\hbar\frac{d}{dx}\right)e^{-x^2/2}dx$$

$$= i\hbar\left(\frac{1}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x\,e^{-x^2}dx = 0$$

$$\langle p_x^2\rangle = \left(\frac{1}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-x^2/2}\,(-i\hbar)^2\frac{d^2}{dx^2}\,e^{-x^2/2}dx$$

$$= \left(\frac{1}{\pi}\right)^{1/2}\hbar^2\int_{-\infty}^{\infty} e^{-x^2}dx - \left(\frac{1}{\pi}\right)^{1/2}\hbar^2\int_{-\infty}^{\infty} x^2\,e^{-x^2}dx$$

$$= \left(\frac{1}{\pi}\right)^{1/2} \hbar^2 \pi^{1/2} - \left(\frac{1}{\pi}\right)^{1/2} \hbar^2 \frac{\pi^{1/2}}{2} = \frac{\hbar^2}{2} \qquad \text{(Appendix A)}$$

$$(\Delta p_x)^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = \frac{\hbar^2}{2}$$

The uncertainty product

$$(\Delta x).(\Delta p_x) = \frac{\hbar}{2}$$

EXAMPLE 3.16 For a one dimensional bound particle, show that

(i) $\frac{d}{dt} \int\limits_{-\infty}^{\infty} \Psi^*(x, t)\, \Psi(x, t)\, dx = 0$, Ψ need not be a stationary state.

(ii) If the particle is in a stationary state at a given time, that it will always remain in a stationary state.

(i) Consider the Schrödinger equation and its complex conjugate form:

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi(x, t)$$

$$-i\hbar \frac{\partial\, \Psi^*(x, t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi^*(x, t)$$

Multiplying the first equation by Ψ^* and the second by Ψ from left and subtracting the second from the first one, we have

$$i\hbar \left[\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right] = -\frac{\hbar^2}{2m} \left[\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right]$$

$$\frac{\partial}{\partial t}(\Psi^* \Psi) = \frac{i\hbar}{2m} \left[\frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \right]$$

Integrating over x,

$$\int\limits_{-\infty}^{\infty} \frac{\partial}{\partial t}(\Psi^* \Psi) dx = \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right]_{-\infty}^{\infty}$$

$$\frac{\partial}{\partial t} \int\limits_{-\infty}^{\infty} (\Psi^* \Psi) dx = \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right]_{-\infty}^{\infty}$$

Since the state is a bound one $\Psi = 0$ as $x \to \pm\infty$. Hence the right hand side of the above equation is zero. The integrated quantity will be a function of time only. Hence

$$\frac{d}{dt}\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx = 0$$

(ii) Let the particle is in a stationary state at $t = 0$. H be its Hamiltonian which is time independent and E its energy eigenvalues. Then

$$H\,\Psi(x,0) = E\,\Psi(x,0)$$

Using Eq. (3.94), we have

$$\Psi(x,t) = \exp\left(-\frac{iHt}{\hbar}\right)\Psi(x,0)$$

Operating from left by H and using the commutability of H with $\exp\left(-\frac{iHt}{\hbar}\right)$, we have

$$H\Psi(x,t) = \exp\left(-\frac{iHt}{\hbar}\right)H\Psi(x,0)$$

$$= E\exp\left(-\frac{iHt}{\hbar}\right)\Psi(x,0) = E\,\Psi(x,t)$$

Hence $\Psi(x,t)$ represents a stationary state at all times.

EXAMPLE 3.17 The solution of the Schrödinger equation for a free particle of mass m in one dimension is $\Psi(x,t)$. At $t = 0$,

$$\Psi(x,0) = A\exp\left(-\frac{x^2}{a^2}\right)$$

Find the probability amplitude in momentum space at $t = 0$ and at time t.

From Eq. (3.117)

$$\Phi(p,0) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\Psi(x,0)\exp\left(-\frac{ipx}{\hbar}\right)dx$$

$$= \frac{A}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp\left(-\frac{x^2}{a^2}-\frac{ipx}{\hbar}\right)dx$$

$$= \frac{A}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp\left(\frac{-x^2}{a^2}\right)\cos\left(\frac{px}{\hbar}\right)dx$$

Here, the other term having $\sin(px/\hbar)$ reduces to zero. Using standard integral,

$$\Phi(p,0) = \frac{Aa}{\sqrt{2\hbar}}\exp\left(-\frac{p^2a^2}{4\hbar^2}\right)$$

The Schrödinger equation in the momentum space, Eq. (3.123), is:

$$i\hbar\frac{\partial}{\partial t}\Phi(p,t)=\frac{p^2}{2m}\Phi(p,t)$$

$$\frac{\partial}{\partial t}\Phi(p,t)=\frac{-ip^2}{2m\hbar}\Phi(p,t)$$

It can easily be written as:

$$\Phi(p,t)=B\exp\left(\frac{-ip^2t}{2m\hbar}\right)$$

At $t = 0$, $\Phi(p,0)=B$. Hence

$$\Phi(p,t)=\frac{Aa}{\sqrt{2\hbar}}\exp\left(\frac{-p^2a^2}{4\hbar^2}-\frac{ip^2t}{2m\hbar}\right)$$

EXAMPLE 3.18 Write the time dependent Schrödinger equation for a free particle in the momentum space and obtain the form of the wave function.

The Schrödinger equation in the momentum space is:

$$i\hbar\,\frac{\partial\Phi(\boldsymbol{p},t)}{\partial t}=\frac{p^2}{2m}\Phi(\boldsymbol{p},t)$$

$$\frac{\partial\Phi}{\partial t}=\frac{-ip^2}{2\hbar m}\Phi(\boldsymbol{p},t)$$

$$\frac{d\Phi}{\Phi}=\frac{-ip^2}{2\hbar m}dt$$

Integrating,

$$\ln\Phi=\frac{-ip^2t}{2\hbar m}+\text{ Constant}$$

$$\Phi(\boldsymbol{p},t)=A\exp\left(\frac{-ip^2t}{2\hbar m}\right)\quad\text{where A is constant.}$$

When $t = 0$, $\Phi(\boldsymbol{p}, 0) = A$. Hence

$$\Phi(\boldsymbol{p},t)=\Phi(\boldsymbol{p},0)\exp\left(\frac{-ip^2t}{2\hbar m}\right)$$

which is the form of wave function in momentum space.

REVIEW QUESTIONS

1. What is Hilbert space?
2. When do you say two functions are orthonormal?
3. State and explain the expansion theorem.
4. With examples explain linear operator.
5. Define the commutator of two operators. Evaluate the commutators of $\left[x, \frac{d}{dx}\right]$ and $\left[\frac{d}{dx}, F(x)\right]$.
6. What are eigenfunctions and eigenvalues of an operator?
7. Define a Hermitian operator. Show that the eigenvalues of a Hermitian operator are real.
8. Show that eigenfunctions of a Hermitian operator belonging to different eigenvalues are orthogonal.
9. Outline Schmidt orthogonalization procedure for a doubly degenerate system.
10. Distinguish between coordinate and momentum representations. What are the operators for coordinate and momentum in the two representations?
11. Explain the connection between operators in quantum mechanics and Poisson bracket of the corresponding classical variables.
12. Outline the different postulates of quantum mechanics.
13. The eigenvalues of an operator are the only experimentally measurable quantities. Comment.
14. Only Hermitian operators are associated with physical quantities. Why?
15. The wave function of a system is expressed as a linear combination of eigenfunctions of the operator associated with an observable A. Why the coefficients of the linear combination are called the probability amplitudes?
16. Define the uncertainty (ΔA) in the measurement of a dynamical variable. State and explain the general uncertainty relation.
17. Outline Dirac's bra and ket notation.
18. Explain Schrödinger picture. Obtain the time derivative of the expectation value of an observable in it.
19. Explain Heisenberg picture. Obtain the equation of motion for an operator in it.
20. If the Hamiltonian $H(t) = H^0 + H'(t)$, show that the state vector changes in accordance with $H'(t)$ whereas the dynamical variables change in accordance with H^0 in the interaction picture.
21. Distinguish between Heisenberg and Schrödinger pictures. Show that the state vectors and operators are the same in both the pictures at $t = 0$.

22. Deduce the equation of motion in the momentum representation.
23. Is simultaneous measurement of energy and momentum with arbitrary precision possible?
24. Can we measure the kinetic and potential energies of a particle simultaneously with arbitrary precision?

PROBLEMS

1. Prove the following commutator relation:

$$\big[[A, B], C\big] + \big[[B, C], A\big] + \big[[C, A], B\big] = 0$$

2. Evaluate the commutators:

$$\text{(i)} \left[\frac{\partial}{\partial x}, \frac{\partial^2}{\partial x^2}\right], \qquad \text{(ii)} \left[\frac{\partial}{\partial x}, F(x)\right]$$

3. Show that the cartesian linear momentum components (p_1, p_2, p_3) and the cartesian components of angular momentum (L_1, L_2, L_3) obey the commutation relations: (i) $[L_k, p_l] = i\hbar p_m$, (ii) $[L_k, p_k] = 0$, where k, l, m are cyclic permutation of 1, 2, 3.
4. Prove the following commutation relations: (i) $[L_k, r^2] = 0$, (ii) $[L_k, p^2] = 0$, where r is the radius vector and p is the linear momentum.
5. If operators A and B are Hermitian, show that $i[A, B]$ is Hermitian.
6. What relation must exist between Hermitian operators A and B in order that AB is Hermitian?
7. For the angular momentum components L_x and L_y, check whether $L_xL_y + L_yL_x$ is Hermitian.
8. Show that the commutator

$$\big[x, [x, H]\big] = -\frac{\hbar^2}{m}$$

where H is the Hamiltonian operator.

9. Prove that the function

$$\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

is an eigenfunction of the Laplacian operator and determine the eigenvalue.

10. Check whether the operator $-i\hbar x\frac{d}{dx}$ is Hermitian.
11. If A is a Hermitian operator and ψ is its eigenfunction, show that (i) $\langle A^2\rangle = \int |A\psi|^2\, d\tau$ and (ii) $\langle A^2\rangle \geq 0$.
12. Prove the following commutation relations in the momentum representation:

(i) $[x, p_x] = [y, p_y] = [z, p_z] = i\hbar$,

(ii) $[x, y] = [y, z] = [z, x] = 0$

13. Show that the function exp $(i\mathbf{k} \cdot \mathbf{r})$ is simultaneously an eigenfunction of the operators $-i\hbar\nabla$ and $-\hbar^2\nabla^2$ and find the eigenvalues.

14. The normalized wave function of a particle is $\psi(x) = A \exp(iax - ibt)$, where A, a and b are constants. Evaluate the expectation value of its momentum.

15. Two normalized degenerate eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ of an observable satisfies the condition

$$\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, dx = a,$$

where a is real. Find a normalized linear combination of ψ_1 and ψ_2 that is orthogonal to $\psi_1 - \psi_2$.

16. The ground state wave function of a particle of mass m is given by $\psi(x) = \exp(-\alpha^2 x^4/4)$ with energy eigenvalue $\hbar^2\alpha^2/m$. What is the potential in which the particle moves?

17. If an operator A is Hermitian, show that the operator $B = iA$ is anti-Hermitian.

18. Find the eigenvalues and eigenfunctions of the operator $\dfrac{d}{dx}$.

19. An operator A contains time as a parameter. Using time dependent Schrödinger equation for the Hamiltonian H and the Hermitian property of H, show that

$$\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle [H, A]\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle$$

20. Find the value of the operator products

(i) $\left(\dfrac{d}{dx} + x\right)\left(\dfrac{d}{dx} + x\right)$ (ii) $\left(\dfrac{d}{dx} + x\right)\left(\dfrac{d}{dx} - x\right)$

21. Evaluate the commutator (i) $[x, p_x^2]$ (ii) $[xyz, p_x^2]$.

22. By what term the operators $(x^2 p_x^2 + p_x^2 x^2)$ and $\dfrac{1}{2}(xp_x + p_x x)^2$ differ?

23. The Laplace transform operator L is defined by $Lf(x) = \displaystyle\int_0^{\infty} e^{-sx} f(x)\, dx$

(i) Is the operator L linear? (ii) Evaluate Le^{ax} if $s > a$.

24. The operator e^A is defined by the equation:

$$e^A = 1 + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \cdots$$

Show that $e^D = T_1$, where $D = \frac{d}{dx}$ and T_1 is defined by $T_1 f(x) = f(x + 1)$

25. Find the Hamiltonian operator of a charged particle in an electromagnetic field described by the vector potential A and scalar potential ϕ.

Chapter 4

One-Dimensional Energy Eigenvalue Problems

The problem of finding the energy eigenvalues and eigenfunctions of the Hamiltonian (energy operator) is very important since they play a very crucial role in the understanding of atomic, molecular and crystal structures, chemical bonding, optical, electrical and other properties of substances. In this chapter we shall apply the ideas developed so far to the solution of some simple one-dimensional energy eigenvalue problems. In each case, we solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{4.1}$$

to obtain energy eigenvalues E and the energy eigenfunctions. The solution of these simple models may also emphasize the difference between classical and quantum descriptions of systems.

4.1 SQUARE-WELL POTENTIAL WITH RIGID WALLS

Consider a particle of mass m moving in a one-dimensional potential specified in Figure 4.1.

$$V(x) = \begin{cases} 0, & -a < x < a \\ \infty, & |x| > a \end{cases} \tag{4.2}$$

The time-independent Schrödinger equation for the region $|x| < a$ is

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{or} \quad k^2 = \frac{2mE}{\hbar^2} \tag{4.3}$$

whose solution is

$$\psi(x) = A \sin(kx) + B \cos(kx) \tag{4.4}$$

As $V(x) = \infty$ at $x = \pm a$, $\psi(\pm a) = 0$. Application of this boundary condition gives

$$A \sin(ka) + B \cos(ka) = 0 \tag{4.5}$$

and

$$-A \sin(ka) + B \cos(ka) = 0 \tag{4.6}$$

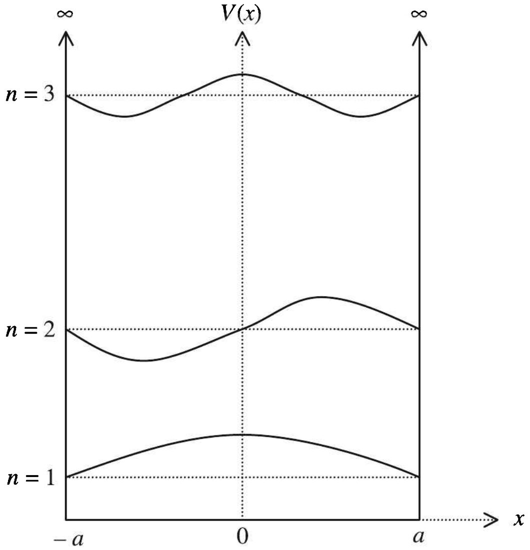


Figure 4.1 The infinite potential well and the eigenfunctions of $n = 1, 2, 3$ states.

From Eqs. (4.5) and (4.6), we get

$$B \cos(ka) = 0, \qquad A \sin(ka) = 0 \tag{4.7}$$

The solution $A = 0$, $B = 0$ leads to the physically unacceptable solution $\psi = 0$. The other possible cases are $A = 0$, $B \neq 0$ and $A \neq 0$, $B = 0$. The first condition gives

$$\cos(ka) = 0; \qquad ka = \frac{n\pi}{2}, \qquad n = 1, 3, 5, \ldots$$

or

$$k^2 = \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{4a^2}$$

or

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \qquad n = 1, 3, 5, \ldots \tag{4.8}$$

The eigenfunction corresponding to this energy eigenvalue is

$$\psi_n(x) = B\ \cos\frac{n\pi x}{2a}, \qquad n = 1, 3, 5, \ldots \tag{4.9}$$

The second condition leads to

$$E_n = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \qquad n = 2, 4, 6, \ldots \tag{4.10}$$

with the eigenfunction

$$\psi_n(x) = A\ \sin\frac{n\pi x}{2a}, \qquad n = 2, 4, 6, \ldots \tag{4.11}$$

The quantum number $n = 0$ is not included as it corresponds to the trivial solution $\psi(x) = 0$. The normalization of the wave function gives $A = B = 1/\sqrt{a}$. Thus, confinement of the particle in the box led to the quantization of the energy which is given by

$$E_n = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \qquad n = 1, 2, 3, 4, \ldots \tag{4.12}$$

The complete set of eigenfunctions are

$$\psi_n(x) = \begin{cases} \dfrac{1}{\sqrt{a}}\sin\dfrac{n\pi x}{2a}, & n = 2, 4, 6, \ldots \\ \dfrac{1}{\sqrt{a}}\cos\dfrac{n\pi x}{2a}, & n = 1, 3, 5, \ldots \end{cases} \tag{4.13}$$

These eigenfunctions for the first-three states are also illustrated in Figure 4.1. From Eq. (4.13) it is evident that the wave functions corresponding to odd quantum numbers are symmetric with respect to the operation $x \to -x$ whereas those for even quantum numbers are antisymmetric.

The energy and the wave function of the ground state are

$$E_1 = \frac{\pi^2\hbar^2}{8ma^2} \quad \text{and} \quad \psi_1(x) = \frac{1}{\sqrt{a}}\cos\frac{\pi x}{2a} \tag{4.14}$$

That is, any particle confined in a box must have a certain minimum energy called the *zero-point energy*, which is a manifestation of the uncertainty principle. This is understandable since an uncertainty of order a in position implies an uncertainty of order $\hbar/(2a)$ in momentum which in turn gives a minimum kinetic energy of $\hbar^2/(8ma^2)$.

For a particle trapped in the potential well $V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise, the energy eigenvalues and eigenfunctions are

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad \text{and} \quad \psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}, \quad n = 1, 2, 3, \cdots \tag{4.14a}$$

4.2 SQUARE-WELL POTENTIAL WITH FINITE WALLS

Consider a particle of mass m moving inside a potential well with finite barriers of height V_0 (Figure 4.2)

$$V(x) = \begin{cases} V_0 & x < -a \\ 0 & -a < x < a \\ V_0 & x > a \end{cases} \tag{4.15}$$

The wave equation in region 2 is the same as Eq. (4.3) with solution given by Eq. (4.4) which leads to symmetric ($n = 1, 3, 5, \ldots$) and antisymmetric ($n = 2, 4, 6, \ldots$) wave functions. In regions 1 and 3

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi \tag{4.16}$$

It is convenient to consider the two different cases: (i) $E < V_0$ and (ii) $E > V_0$

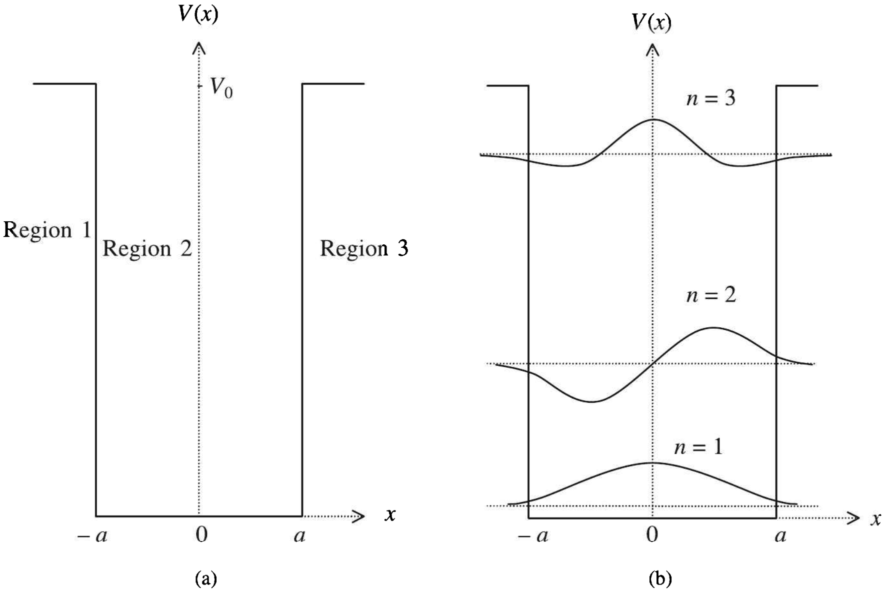


Figure 4.2 (a) The square-well potential with finite walls (b) the wave functions.

Case (i): $E < V_0$

Equation (4.16) can now be written as

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi, \qquad \alpha^2 = \frac{2m}{\hbar^2}(V_0 - E) \tag{4.16a}$$

whose solution is

$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x} \tag{4.17}$$

where α is positive, C and D are constants. If D is not zero, $\psi(x) \rightarrow \infty$ as $x \rightarrow \infty$ (region 3), which is physically unacceptable. Similar arguments leads to $C = 0$ in region 1. Thus, the wave function for the different regions are

$$\psi(x) = \begin{cases} De^{\alpha x} & x < -a \\ A\sin(kx) + B\cos(kx) & -a < x < a \\ Ce^{-\alpha x} & x > a \end{cases} \tag{4.18}$$

where

$$k^2 = \frac{2mE}{\hbar^2} \tag{4.19}$$

The wave function in region 2 can either be symmetric or antisymmetric about the origin (Section 4.1). Hence, we can match either the symmetric or the antisymmetric wave function of region 2 to the wave function of regions 1 and 3 at a time. Accordingly, the solutions in region 2 may be divided into two types: symmetric function and antisymmetric function.

Symmetric function in region 2, $A = 0$: The continuity conditions on ψ and its derivative at $x = \pm a$ gives

$$De^{-\alpha a} = B\cos(ka) \quad \text{and} \quad D\alpha e^{-\alpha a} = Bk\sin(ka) \tag{4.20a}$$

$$Ce^{-\alpha a} = B\cos(ka) \quad \text{and} \quad C\alpha e^{-\alpha a} = Bk\sin(ka) \tag{4.20b}$$

From Eq. (4.20), it is obvious that $C = D$ and

$$ka\tan(ka) = \alpha a \tag{4.21}$$

Antisymmetric function in region 2, $B = 0$: Use of continuity conditions at $x = \pm a$ gives

$$De^{-\alpha a} = -A\sin(ka) \quad \text{and} \quad D\alpha e^{-\alpha a} = Ak\cos(ka) \tag{4.22a}$$

$$Ce^{-\alpha a} = A\sin(ka) \quad \text{and} \quad -C\alpha e^{-\alpha a} = Ak\cos(ka) \tag{4.22b}$$

From Eq. (4.22), we obtain $C = -D$ and

$$ka\cot(ka) = -\alpha a \tag{4.23}$$

The energy eigenvalues are obtained by solving Eqs. (4.21) and (4.23) graphically or numerically. Defining

$$ka = \beta \quad \text{and} \quad \alpha a = \gamma$$

equations (4.21) and (4.23) take the form

$$\beta \tan \beta = \gamma \tag{4.21a}$$

$$\beta \cot \beta = -\gamma \tag{4.23a}$$

The constants β and γ are related by the equation

$$\beta^2 + \gamma^2 = \frac{2mV_0a^2}{\hbar^2} \tag{4.24}$$

which is the equation of a circle in $\beta\gamma$-plane with radius $(2mV_0a^2/\hbar^2)^{1/2}$. A graphical procedure is followed to solve Eq. (4.21a). To get the solution, the curve representing the variation of $\beta \tan \beta$ against β is plotted (continuous curve) along with circles of radii $(2mV_0a^2/\hbar^2)^{1/2}$ for different values of V_0a^2 (Fig. 4.3). As β and γ can have only positive values, the intersection of the two curves in the first quadrant gives the energy levels for $n = 1, 3, 5, \ldots$ The intersection of the circle with the curves of Eq. (4.21a) be $\beta_1, \beta_2, \beta_3, \ldots$ Then

$$\beta^2 = k^2a^2 = \frac{2mEa^2}{\hbar^2} \quad \text{or} \quad E_n = \frac{\hbar^2\beta_n^{\ 2}}{2ma^2} \tag{4.25}$$

A similar construction for the solution of Eq. (4.23a) (dashed curves) gives the energy levels for $n = 2, 4, 6, \ldots$

For a given particle, the number of bound states depend on the height and width of the potential through the factor V_0a^2. From Figure 4.3, it follows that there will be

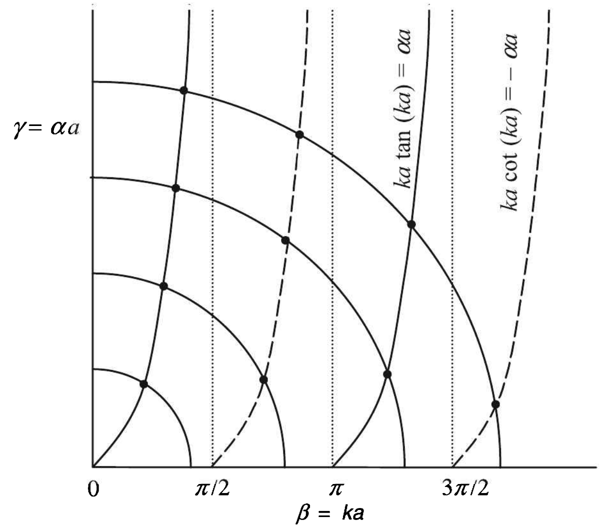


Figure 4.3 Graphical solution of Eqs. (4.21) and (4.23) for 4 values of V_0a^2. Continuous curve is $ka \tan (ka) = \alpha a$. Dashed curve is $ka \cot (ka) = -\alpha a$. The dots show the intersections.

$$\text{One intersection,} \qquad \text{if } 0 < \text{radius} < \frac{\pi}{2}$$

$$\text{Two intersections,} \qquad \text{if } \frac{\pi}{2} < \text{radius} < \pi$$

$$\text{Three intersections,} \qquad \text{if } \pi < \text{radius} < 3\frac{\pi}{2}$$

and so on. That is, there will be

One energy level of the first type (symmetric) for $0 < V_0 a^2 < \dfrac{\pi^2\hbar^2}{8m}$

Two (one symmetric and one antisymmetric) for $\dfrac{\pi^2\hbar^2}{8m} < V_0 a^2 < \dfrac{4\pi^2\hbar^2}{8m}$

Three (2 symmetric and one antisymmetric) for $\dfrac{4\pi^2\hbar^2}{8m} < V_0 a^2 < \dfrac{9\pi^2\hbar^2}{8m}$

and so on.

The first-three bound state eigenfunctions are represented in Figure 4.2(b). In region 2, the wave functions are similar to those in a potential well with infinite walls. However, they have tails in regions 1 and 3. The points $x = \pm a$ are the classical turning points for the well. Wave functions have tails beyond the classical turning points mean a finite probability for the particle to be outside the well. In other words, the quantum mechanical particle has *tunnelled* or *leaked* into the classically forbidden regions.

Case (ii): $E > V_0$

In the region $E > V_0$, the quantity $V_0 - E$ is negative which makes α imaginary. Consequently, the solution of Eq. (4.16) for $\psi(x)$ is sinusoidal in regions 1 and 3, too. Hence the probability density is distributed over all space and the particle is not bound.

4.3 SQUARE POTENTIAL BARRIER

The potential function of the type in Figure 4.4 allows exact solution for the equation of motion. The potential $V(x)$ is defined by

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 < x < a \\ 0 & x > 0 \end{cases} \tag{4.26}$$

Consider a stream of particles of mass m approaching the square barrier from left. Classically, if the energy of the particle $E < V_0$ it is always reflected whereas it is transmitted if $E > V_0$. However, quantum mechanically it can be

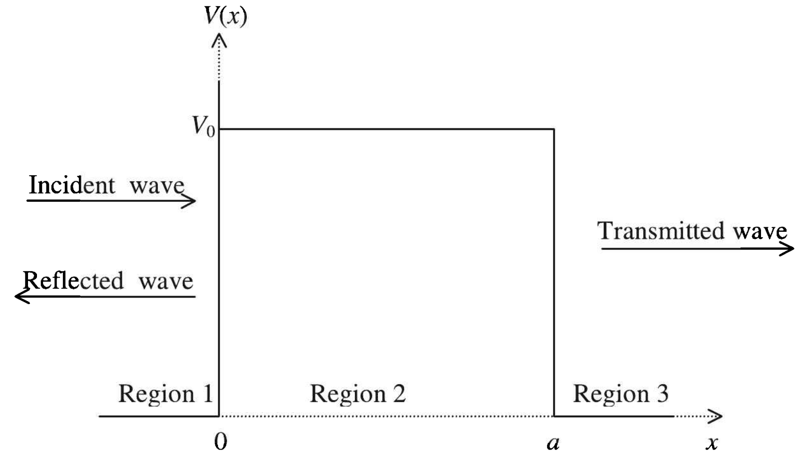


Figure 4.4 Representation of one-dimensional square barrier.

seen that there is always a finite probability for a particle to penetrate or leak through the barrier and continue its forward motion even if $E < V_0$. This phenomenon, called *quantum mechanical tunnelling,* is possible because of the wave nature of matter.

Case (i): $E < V_0$

The Schrödinger equation for the three regions of the potential are:

$$\frac{d^2\psi_1}{dx^2} = -k^2\psi_1, \quad k^2 = \frac{2mE}{\hbar^2}, \quad x \le 0 \tag{4.27}$$

$$\frac{d^2\psi_2}{dx^2} = \alpha^2\psi_2, \quad \alpha^2 = \frac{2m(V_0 - E)}{\hbar^2}, \quad 0 \le x \le a \tag{4.28}$$

$$\frac{d^2\psi_3}{dx^2} = -k^2\psi_3, \quad x \ge a \tag{4.29}$$

whose solutions are respectively

$$\psi_1 = e^{ikx} + Ae^{-ikx} \tag{4.30}$$

$$\psi_2 = Be^{\alpha x} + Ce^{-\alpha x} \tag{4.31}$$

$$\psi_3 = De^{ikx} \tag{4.32}$$

The plane wave e^{ikx} represents the incident particles travelling from left to right and Ae^{-ikx} represents the stream of reflected particles travelling from right to left. For simplicity the amplitude of the incident wave is taken as one. In region 3, we expect only waves travelling from left to right. In region 2, the exponentially increasing function $Be^{\alpha x}$ is also an acceptable wave function like the exponentially decreasing $Ce^{-\alpha x}$, since the barrier is of finite extent.

The probability density of the incident, reflected and transmitted waves are 1, $|A|^2$ and $|D|^2$, respectively. Consequently, the transmission coefficient $T = |D|^2$ and the reflection coefficient $R = |A|^2$. The two are connected by the relation $R + T = 1$. As we are mainly interested in the transmission and reflection coefficients, the determination of all the constants are not necessary. The continuity conditions on the wave functions and their first derivatives at $x = 0$ and at $x = a$ give

$$1 + A = B + C \tag{4.33a}$$

$$ik - ikA = \alpha B - \alpha C \tag{4.33b}$$

and

$$Be^{\alpha a} + Ce^{-\alpha a} = De^{ika} \tag{4.34a}$$

$$\alpha Be^{\alpha a} - \alpha Ce^{-\alpha a} = ikDe^{ika} \tag{4.34b}$$

On solving Eq. (4.34), we get

$$B = \frac{D}{2\alpha}(\alpha + ik)\, e^{ika-\alpha a} \tag{4.35a}$$

$$C = \frac{D}{2\alpha}(\alpha - ik)e^{ika+\alpha a} \tag{4.35b}$$

From Eqs. (4.33) and (4.35), we have

$$A = \frac{D(\alpha + ik)}{\alpha - ik}e^{ika-\alpha a} - \frac{\alpha + ik}{\alpha - ik} \tag{4.36}$$

Substitution of the values of A, B and C in Eq. (4.33a) gives

$$D = -\frac{2ik\alpha e^{-ika}}{(\alpha^2 - k^2)\sinh(\alpha a) - 2i\alpha k\cosh(\alpha a)} \tag{4.37}$$

Now

$$T = |D|^2 = DD^* = \frac{4k^2\alpha^2}{(\alpha^2 - k^2)^2\sinh^2(\alpha a) + 4\alpha^2k^2\cosh^2(\alpha a)} \tag{4.38}$$

Therefore,

$$R = 1 - T = \frac{(\alpha^2 + k^2)^2\sinh^2(\alpha a)}{(\alpha^2 - k^2)^2\sinh^2(\alpha a) + 4\alpha^2k^2\cosh^2(\alpha a)} \tag{4.39}$$

For broad high barrier,

$$\alpha a \gg 1 \text{ and } \sinh(\alpha a) = \cosh(\alpha a) \to \frac{1}{2}e^{\alpha a}$$

So,

$$T = \frac{16k^2\alpha^2e^{-2\alpha a}}{(\alpha^2 - k^2)^2 + 4\alpha^2k^2} = \frac{16\,k^2\alpha^2e^{-2\alpha a}}{(\alpha^2 + k^2)^2} \tag{4.40}$$

Substitution of the values of α^2 and k^2 in Eq. (4.40) gives

$$T = \frac{16E(V_0 - E)e^{-2\alpha a}}{V_0^2} \tag{4.41}$$

An illustration of the wave function in the three regions is given in Figure 4.5.

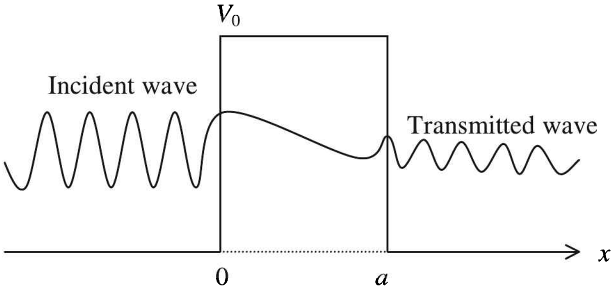


Figure 4.5 Illustration of the wave function in the three regions corresponding to $E < V_0$. The reflected wave in region 1 and the exponentially increasing wave in region 2 are not shown.

The phenomenon of barrier penetration has numerous applications in physics. The most important one is the explanation of alpha emission by nuclei.

Case (ii): $E > V_0$

When the energy of the particle is greater than the height of the barrier, the wave function in the region $0 < x < a$ also becomes trigonometric and is given by

$$\psi(x) = Ee^{i\beta x} + Fe^{-i\beta x}, \qquad \beta^2 = \frac{2m}{\hbar^2}(E - V_0)$$

The constants A (in Eq. 4.30) and F are finite as reflection can occur at $x = 0$ and $x = a$. Figure 4.6 illustrates the waves (without reflected ones) in the different regions.

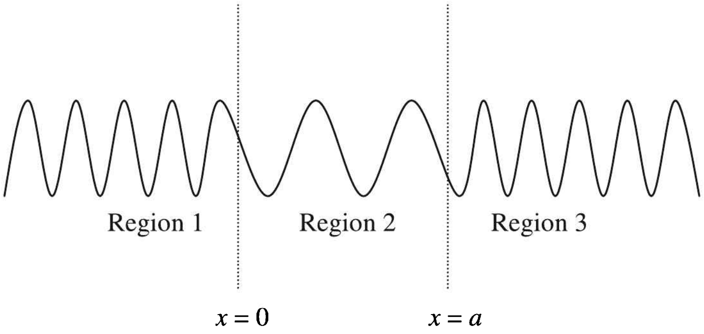


Figure 4.6 Illustration of the wave function in the three regions corresponding to $E > V_0$.

4.4 ALPHA EMISSION

Alpha particles are held inside a nucleus by strong attractive short-range nuclear forces. However, when they are outside the nucleus there exists strong Coulomb repulsive force between the residual nucleus and the alpha particle because both are positively charged. Figure 4.7 shows the variation of the potential with the alpha particle distance from the centre of the nucleus. If the residual nuclear charge is Ze, the repulsive Coulomb potential beyond the attractive nuclear potential is $2Ze^2/r$. The radius (r_1) of the nuclear-alpha particle attraction is approximately equal to nuclear radius. If r_2 is the point at which the alpha particle energy E exceeds the Coulomb potential,

$$E = \frac{2Ze^2}{r_2} \quad \text{or} \quad r_2 = \frac{2Ze^2}{E} \tag{4.42}$$

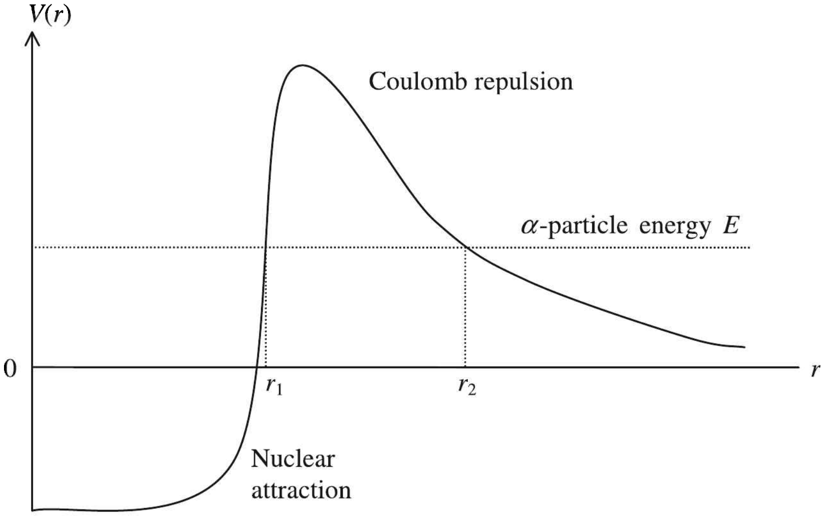


Figure 4.7 The variation of potential with the α-particle distance from the centre of the nucleus.

Treating the potential in the $r_1 < r < r_2$ as a one-dimensional square barrier, we get

$$T = \frac{16E(V_0 - E)}{V_0^2} \exp\left[-\sqrt{\frac{8m}{\hbar^2}(V_0 - E)}\; a\right] \tag{4.43}$$

or

$$T \cong \exp\left[-\sqrt{\frac{8m}{\hbar^2}(V_0 - E)}\; a\right] \tag{4.44}$$

As the real barrier is not a square, more rigorously

$$T \cong \exp\left[-\int_{r_1}^{r_2}\sqrt{\frac{8m}{\hbar^2}\left(\frac{2Ze^2}{r} - E\right)}\,dr\right] \tag{4.45}$$

It is estimated that an α-particle within a nucleus moves with a velocity of about 10^7 ms^{-1}. The radius of a heavy nucleus like uranium has a value of about 10^{-14} m. Hence, the alpha particle strikes the wall of the barrier at the rate of about 10^{21} times per second. The probability that the particle penetrates at each time it hits the wall is given by the transmission coefficient T. Therefore, the probability that it comes out in one second is $P \cong 10^{21}T$. The mean life time

$$\tau = \frac{1}{P} = \frac{1}{10^{21}T} \tag{4.46}$$

If λ is the decay constant

$$\lambda = \frac{1}{\tau} \cong 10^{21} \exp\left\{-\left[\frac{8m}{\hbar^2}(V_0 - E)a^2\right]^{1/2}\right\} \tag{4.47}$$

or

$$\ln \lambda = A + BE \tag{4.48}$$

where A and B are constants. Equation (4.48) is *Geiger–Nuttal law*. Thus, the barrier penetration could explain the phenomenon of α-decay.

4.5 BLOCH WAVES IN A PERIODIC POTENTIAL

As the next example we shall consider the motion of an electron in a one-dimensional periodic potential. A one-dimensional metal crystal consisting of a number of stationary positive ions provides a periodic potential of period d (Figure 4.8). That is

$$V(x + nd) = V(x), \qquad n = 0, 1, \ldots \tag{4.49}$$

For discussion, consider a crystal lattice with N ions in the form of a closed loop. The Schrödinger equation at points x and $(x + d)$ is then

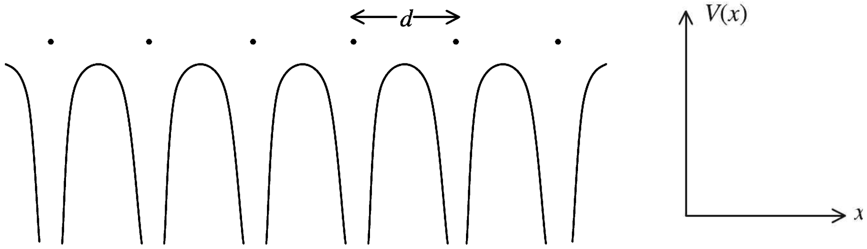


Figure 4.8 One-dimensional crystal lattice along with the periodic potential.

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x) = 0 \tag{4.50}$$

and

$$\frac{d^2\psi(x+d)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi(x+d) = 0 \tag{4.51}$$

respectively. Here we have used Eq. (4.49). Since $\psi(x)$ and $\psi(x + d)$ satisfy the same equation, the two can differ only by a multiplicative constant, say α.

$$\psi(x + d) = \alpha\psi(x) \quad \text{and} \quad \psi(x + Nd) = \alpha^N\,\psi(x) \tag{4.51a}$$

Since the lattice is in the form of a ring

$$\psi(x + Nd) = \alpha^N\psi(x) = \psi(x) \tag{4.52}$$

Hence,

$$\alpha^N = 1 \quad \text{or} \quad \alpha^N = e^{2\pi i n} \text{ for } n = 0, 1, \ldots (N-1)$$

Therefore,

$$\alpha = e^{2\pi i n/N}, \qquad n = 0, 1, \ldots, (N-1) \tag{4.53}$$

It means that

$$\psi(x) = e^{ikx}u(x) \tag{4.54}$$

where

$$u(x + d) = u(x) \quad \text{and} \quad k = \frac{2\pi n}{Nd}, \quad n = 0, \pm 1, \pm 2, \ldots \tag{4.55}$$

The justification for Eq. (4.54) can easily be done by replacing x by $(x + d)$

$$\begin{aligned}\psi(x + d) &= e^{ik(x+d)}\,u(x + d)\\ &= e^{ikd}\,e^{ikx}\,u(x)\\ &= e^{ikd}\,\psi(x)\\ &= e^{2\pi ni/N}\psi(x)\\ &= \alpha\psi(x)\end{aligned}$$

which is Eq. (4.51a). Equation (4.54) with the condition in Eq. (4.55) is called the *Bloch theorem.* That is, the solution of Schrödinger equation of a periodic potential will have the form of a plane wave modulated by a function having the periodicity of the lattice. Functions of the type as in Eq. (4.54) are sometimes referred to as *Bloch functions.*

4.6 KRONIG-PENNEY SQUARE-WELL PERIODIC POTENTIAL

In the preceding section, we have considered a one-dimensional metal crystal consisting of a number of positive ions providing a periodic potential. The approximation of the periodic potential in Figure 4.8 is known as the *Kronig–Penney potential* which is illustrated in Figure 4.9. The width of each well be a and that of each barrier be b. The period of the potential $d = a + b$. Then

$$V[x + n(a + b)] = V(x + nd) = V(x) \tag{4.56}$$

We have already seen that in a periodic potential of the form in Eq. (4.56), the one-electron wave functions are the Bloch functions in Eq. (4.54), where $u(x)$ has the periodicity of the lattice. In the region $0 < x < a$, $V(x) = 0$ and the Schrödinger equation takes the form

$$\frac{d^2\psi_1}{dx^2} + k_1^2\psi_1 = 0, \qquad k_1^2 = \frac{2mE}{\hbar^2} \tag{4.57}$$

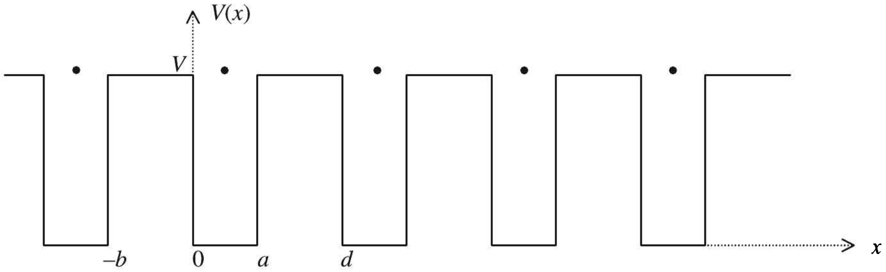


Figure 4.9 The Kronig–Penney periodic potential.

In the region $-b < x < 0$, $V(x) = V$. Then

$$\frac{d^2\psi_2}{dx^2} - k_2^2\psi_2 = 0, \qquad k_2^2 = \frac{2m(V - E)}{\hbar^2}, \quad V > E \tag{4.58}$$

According to Bloch theorem, the solution of Eqs. (4.57) and (4.58) must be of the type

$$\psi_1 = e^{ikx}u_1(x) \qquad 0 < x < a \tag{4.59}$$

$$\psi_2 = e^{ikx}u_2(x) \qquad -b < x < 0 \tag{4.60}$$

Substitution of Eq. (4.59) in Eq. (4.57) and Eq. (4.60) in Eq. (4.58) gives

$$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (k_1^2 - k^2)u_1(x) = 0 \tag{4.61}$$

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (k_2^2 + k^2)u_2(x) = 0 \tag{4.62}$$

For Eq. (4.61), let us assume a solution of the form

$$u_1(x) = e^{mx} \tag{4.63}$$

With this value of $u_1(x)$, Eq. (4.61) reduces to

$$m^2 + 2ikm + (k_1^2 - k^2) = 0, \qquad 0 < x < a \tag{4.64}$$

or

$$m = i(k_1 - k), \quad -i(k_1 + k)$$

Hence the solution of Eq. (4.61) is

$$u_1(x) = A \exp [i(k_1 - k)x] + B \exp [-i(k_1 + k)x], \quad 0 < x < a \quad (4.65)$$

In the same way

$$u_2(x) = C \exp [(k_2 - ik)x] + D \exp [- (k_2 + ik)x], \quad -b < x < 0 \quad (4.66)$$

The wave functions and their derivatives must be continuous at $x = 0$. That is

$$u_1(x)\big|_{x=0} = u_2(x)\big|_{x=0} \quad \text{and} \quad \left.\frac{du_1}{dx}\right|_{x=0} = \left.\frac{du_2}{dx}\right|_{x=0} \quad (4.67)$$

These conditions give

$$A + B = C + D \quad (4.68a)$$

and

$$i(k_1 - k)A - i(k_1 + k)B = (k_2 - ik)C - (k_2 + ik)D \quad (4.68b)$$

As the potential is periodic, the value of the wave function at $x = a$ must be equal to that at $x = -b$. Hence

$$u_1(x)\big|_{x=a} = u_2(x)\big|_{x=-b} \quad \text{and} \quad \left.\frac{du_1}{dx}\right|_{x=a} = \left.\frac{du_2}{dx}\right|_{x=-b} \quad (4.69)$$

With these conditions in Eq. (4.65) and Eq. (4.66), we have

$$\begin{aligned} &A \exp [i(k_1 - k)a] + B \exp [-i(k_1 + k)a] \\ &\quad = C \exp [-(k_2 - ik)b] + D \exp [(k_2 + ik)b] \end{aligned} \quad (4.70a)$$

and

$$\begin{aligned} &i(k_1 - k) A \exp [i(k_1 - k)a] - i(k_1 + k)B \exp[-i(k_1 + k)a] \\ &\quad = (k_2 - ik)C \exp [- (k_2 - ik)b] - (k_2 + ik)D \exp [(k_2 + ik)b] \end{aligned} \quad (4.70b)$$

For a nontrivial solution of Eqs. (4.68) and (4.70), the determinants of the coefficients of A, B, C and D should vanish. This gives the relation

$$\frac{k_2^2 - k_1^2}{2k_1k_2} \sinh (k_2b) \sin (k_1a) + \cosh (k_2b) \cos (k_1a) = \cos (kd) \quad (4.71)$$

As k_2 and k_1 are functions of energy the left side is a function of energy.

The right side of Eq. (4.71) can have values only between +1 and −1 whereas the left side can have values outside this range. Therefore, Eq. (4.71) can be satisfied only for values of E for which the left-hand side remains between +1 and −1. That is, in a crystal, only certain energy bands are allowed for the electron and there are regions of energy which are forbidden. In other words, in a one-dimensional crystal, the periodicity of the potential together with the condition $u(x + Nd) = u(x)$ led to the concept of energy bands.

The transcendental Eq. (4.71) can be solved graphically. For that, the left side of Eq. (4.71) is plotted as a function of *E/V* (continuous curve) and the limiting lines of cos (*kd*) = ±1 (broken lines) are also drawn (Figure 4.10). The energy ranges for which cos (*kd*) is between −1 and +1 are the allowed ones. In the figure, these are *AB*, *CD*, *EF*, etc.

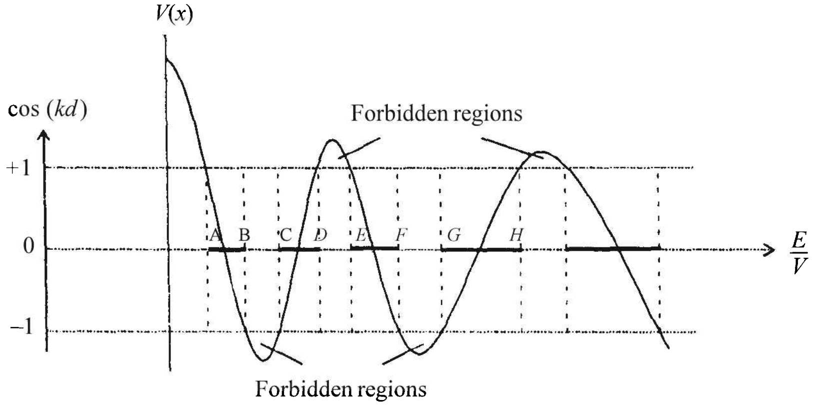


Figure 4.10 Graphical evaluation of energy values in the Kronig–Penney model.

4.7 LINEAR HARMONIC OSCILLATOR: SCHRÖDINGER METHOD

The problem of linear harmonic oscillator is of importance since many systems of interest can be approximated to it. Its potential energy $V = \frac{1}{2}kx^2$, k is the force constant, is a continuous function of the coordinate x and therefore is completely different from systems we considered so far where the potential is constant over a region.

Wave Equation

With the force constant expression in Eq. (1.40), the potential V is given by

$$V = \frac{1}{2} 4\pi m \nu_0^2 x^2 = \frac{1}{2} m\omega^2 x^2 \tag{4.72}$$

The time-independent Schrödinger equation of the linear harmonic oscillator is then

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2 x^2\right)\psi = 0 \tag{4.73}$$

It is convenient to work with a new variable y and a new parameter λ defined by

$$y = \left(\frac{m\omega}{\hbar}\right)^{1/2} x \quad \text{and} \quad \lambda = \frac{2E}{\hbar\omega} \tag{4.74}$$

In terms of these quantities, Eq. (4.73) reduces to

$$\frac{d^2\psi}{dy^2} + (\lambda - y^2)\,\psi = 0 \tag{4.75}$$

Asymptotic Solution

We shall investigate first the solution of Eq. (4.75), when $y \to \infty$. When y is very large, $\lambda - y^2 \cong y^2$ and Eq. (4.75) becomes

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0 \tag{4.76}$$

Its asymptotic solutions are

$$\psi(x) = e^{\pm y^2/2} \tag{4.77}$$

since substitution of Eq. (4.77) in Eq. (4.76) gives

$$\frac{d^2\psi}{dy^2} = (y^2 + 1)e^{\pm y^2/2} \cong y^2\psi$$

Out of the two asymptotic solutions, $e^{y^2/2}$ is not acceptable as it diverges when $|y| \to \infty$. The exact solution of Eq. (4.75) may be written as

$$\psi = e^{-y^2/2}\,H(y) \tag{4.78}$$

where $H(y)$ is a function of y and the product $e^{-y^2/2}H(y)$ tends to zero as $|y| \to \infty$.

Series Solution

Substitution of Eq. (4.78) in Eq. (4.76) gives

$$\frac{d^2H(y)}{dy^2} - 2y\frac{dH}{dy} + (\lambda - 1)H = 0 \tag{4.79}$$

which is known as the *Hermite equation*. We shall look for $H(y)$, a series solution of the type

$$H(y) = \sum_{n=0}^{\infty} a_n y^n \tag{4.80}$$

Equation (4.80) when substituted in Eq. (4.79), we have

$$\sum_{k=0}^{\infty}\left[(k + 1)(k + 2)a_{k+2} - (2k + 1 - \lambda)a_k\right]y^k = 0 \tag{4.81}$$

For the validity of this equation, coefficient of each power of y must vanish separately. Coefficient of y^k when equated to zero gives the recurrence relation

$$a_{k+2} = \frac{2k + 1 - \lambda}{(k + 1)(k + 2)} a_k \tag{4.82}$$

This formula allows the calculation of all even coefficients in terms of a_0 and the odd coefficients in terms of a_1. Equation (4.80) will have only odd coefficients if $a_0 = 0$ and even coefficients if $a_1 = 0$. Thus we have two independent solutions for Eq. (4.80) and a linear combination of the two will be the most general solution. The two solutions are:

$$H_e(y) = a_0 + a_2y^2 + a_4y^4 + \cdots \tag{4.83}$$

and

$$H_o(y) = y(a_1 + a_3y^2 + a_5y^4 + \cdots) \tag{4.84}$$

Energy Eigenvalues

When $k \to \infty$ in Eq. (4.82), we get

$$\frac{a_{k+2}}{a_k} = \frac{2}{k} \tag{4.85}$$

Consider the Taylor series expansion of exp (y^2)

$$\exp\left(y^2\right) = \sum_{0,2,4} \frac{1}{(k/2)!} y^k \tag{4.86}$$

The ratio of the coefficients of the successive terms in Eq. (4.86) is

$$\frac{a_{k+2}}{a_k} = \frac{(k/2)!}{\left[(k/2) + 1\right]!} = \frac{1}{(k/2) + 1} \cong \frac{2}{k} \tag{4.87}$$

where k is large. Therefore, for large values of k, $\psi = \exp(-y^2/2)H(y)$ tends to behave like exp $(y^2/2)$, if the series is even, and y exp $(y^2/2)$ if the series is odd; which is not acceptable. This unrealistic solution can be avoided if the series in Eq. (4.80) terminates after a finite number of terms. In such a situation, $\psi(y)$ will tend to zero as $y \to \infty$ because of the factor exp $(-y^2/2)$. The series can be terminated by selecting λ in such a way that $(2k + 1 - \lambda)$ vanishes for $k = n$. Thus one of the series becomes a polynomial and the other can be eliminated by setting the first coefficient to zero. Substitution of the value of λ gives

$$2n + 1 - \frac{2E}{\hbar\omega} = 0$$

or

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots \tag{4.88}$$

The energy value of an oscillator based on quantum theory is

$$E_n = n\hbar\omega, \qquad n = 0, 1, 2, \ldots$$

From the two expressions, it is evident that the quantum mechanical energy value is higher than the quantum theory value by $\frac{1}{2}\hbar\omega$, which is the energy possessed by the lowest state $n = 0$. The oscillator will have this energy even at absolute zero. This energy of $\frac{1}{2}\hbar\omega$ is called the *zero-point energy* which is a manifestation of uncertainty principle. $E = 0$ means that both position and momentum are well defined which is a violation of uncertainty principle. It can be shown that the minimum energy of an oscillator without violating uncertainty principle is $\frac{1}{2}\hbar\omega$. Figure 4.11(a) illustrates the energy values as given by Eq. (4.88).

Energy Eigenfunctions

When $\lambda = 2n + 1$, Eq. (4.79) reduces to

$$\frac{d^2H_n(y)}{dx^2} - 2y\frac{dH_n(y)}{dy} + 2nH_n(y) = 0 \tag{4.89}$$

The solutions of Eq. (4.89) are the Hermite polynomials $H_n(y)$ of degree n. The energy eigenfunctions can now be expressed as

$$\psi_n(y) = N_nH_n(y)\exp\left(-\frac{y^2}{2}\right), \qquad y^2 = \frac{m\omega}{\hbar}x^2 \tag{4.90}$$

The first-four Hermite polynomials are

$$H_0(y) = 1 \tag{4.91a}$$

$$H_1(y) = 2y \tag{4.91b}$$

$$H_2(y) = 4y^2 - 2 \tag{4.91c}$$

$$H_3(y) = 8y^3 - 12y \tag{4.91d}$$

The normalization condition leads to

$$|N_n|^2\left(\frac{\hbar}{m\omega}\right)^{1/2}\int_{-\infty}^{\infty} H_n^2(y)\exp\left(-y^2\right)dy = 1$$

or

$$|N_n|^2\left(\frac{\hbar}{m\omega}\right)^{1/2}\pi^{1/2}2^n(n!) = 1$$

or

$$N_n = \left[\left(\frac{m\omega}{\hbar\pi}\right)^{1/2}\frac{1}{2^n(n!)}\right]^{1/2} \tag{4.92}$$

The normalized eigenfunctions and the ground state eigenfunction are given by

$$\psi_n(y) = \left[\left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \frac{1}{2^n (n!)}\right]^{1/2} H_n(y) \exp\left(\frac{-y^2}{2}\right) \tag{4.93}$$

$$\psi_0(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \tag{4.94}$$

The wave functions $\psi_n(x)$ and the probability density $|\psi_n(x)|^2$ of the lowest four states are also illustrated in Figure 4.11.

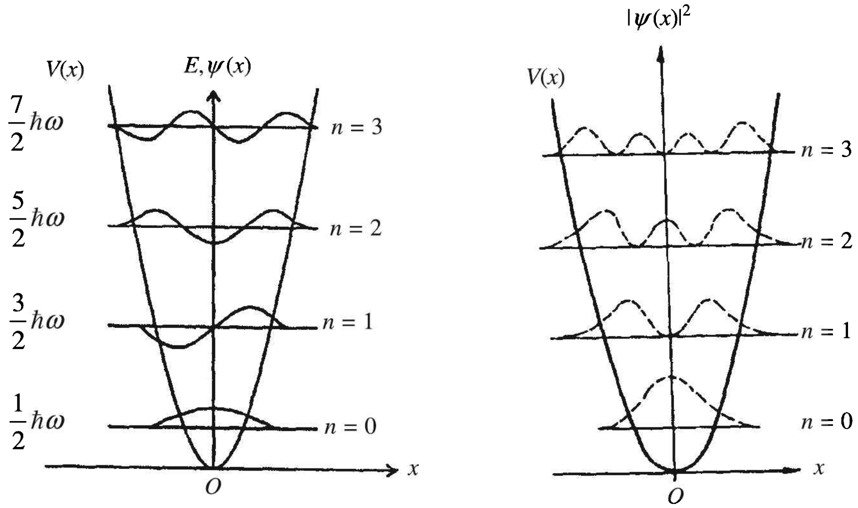


Figure 4.11 (a) Energy levels (E_n) and wave functions $\psi_n(x)$ of the lowest four states of the linear harmonic oscillator (b) probability density $|\psi_n(x)|^2$ of the lowest four states.

It may also be noted from the figure that oscillator eigenfunctions are even for even values of n and odd for odd values of n. This is understandable as exp $(-y^2/2)$ is always even and $H_n(y)$ is even or odd according as n is even or odd. It may also be noted that the quantum oscillator can be found outside the parabolic potential barrier since ψ does not vanish at the classical turning points. In other words, the particles can penetrate the barrier to some extent. This barrier penetration is an important feature of quantum mechanics.

Another interesting point to be noted in connection with the results is the nature of probability distribution of classical and quantum oscillators. Classically, the probability of finding the oscillator at a given point is inversely proportional to its velocity at that point. The total energy

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 \quad \text{or} \quad v = \sqrt{\frac{2E - kx^2}{m}}$$

Therefore the classical probability

$$P_c \propto \sqrt{\frac{m}{2E - kx^2}} \tag{4.95}$$

This probability is minimum at $x = 0$ (mean position) and maximum at the extreme positions. In the quantum case, for $n = 0$, the probability is maximum at $x = 0$ and as the quantum number increases the maximum probability moves towards the extreme positions. Figure 4.12 shows the probability density $|\psi_{10}|^2$ and the classical probability distribution (dotted line) for the same energy. Though the two distributions become more and more similar for high quantum numbers, the rapid oscillations of $|\psi_n|^2$ is still a discrepancy.

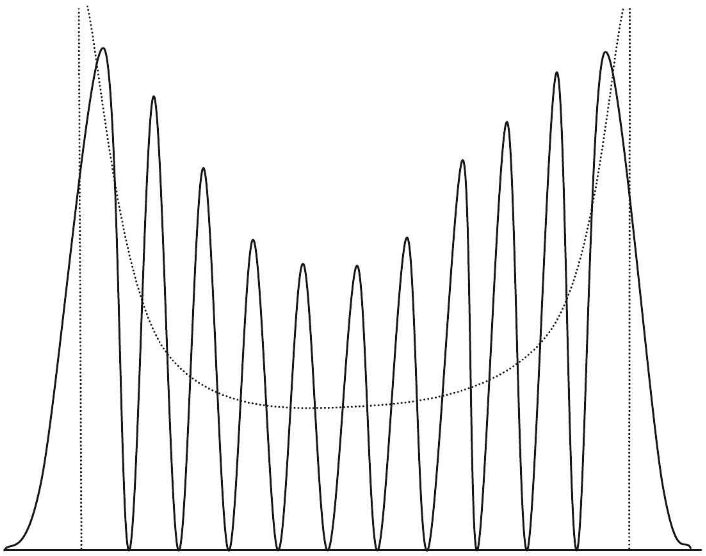


Figure 4.12 The probability density $|\psi|^2$ for the state $n = 10$ (solid curve) and for a classical oscillator of the same total energy (broken curve).

4.8 LINEAR HARMONIC OSCILLATOR: OPERATOR METHOD

The operator method of solving for the energy eigenvalues of the linear harmonic oscillator is based on the basic commutation relation

$$[x, p] = i\hbar \tag{4.96}$$

where x and p are the coordinate and momentum operators. The Hamiltonian of a linear harmonic oscillator is

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2x^2 \tag{4.97}$$

It is convenient to introduce two new operators a and $a^\dagger$ defined by

$$a = \left(\frac{m\omega}{2\hbar}\right)^{1/2} x + i\left(\frac{1}{2m\hbar\omega}\right)^{1/2} p \tag{4.98}$$

and

$$a^{\dagger} = \left(\frac{m\omega}{2\hbar}\right)^{1/2} x - i\left(\frac{1}{2m\hbar\omega}\right)^{1/2} p \tag{4.99}$$

where $a^{\dagger}$ is the Hermitian adjoint of a. From Eqs. (4.98) and (4.99), we get

$$\begin{aligned} aa^{\dagger} &= \frac{m\omega}{2\hbar}x^2 + \frac{1}{2m\hbar\omega}p^2 + \frac{i}{2\hbar}(px - xp) \\ &= \frac{H}{\hbar\omega} + \frac{1}{2} \end{aligned} \tag{4.100}$$

In the same way

$$a^{\dagger}a = \frac{H}{\hbar\omega} - \frac{1}{2} \tag{4.101}$$

From Eqs. (4.100) and (4.101), one can write the following expressions

$$H = \frac{\hbar\omega}{2}\left(aa^{\dagger} + a^{\dagger}a\right) \tag{4.102}$$

and

$$[a, a^{\dagger}] = 1 \tag{4.103}$$

Therefore,

$$\begin{aligned} [a, H] &= \frac{a\hbar\omega}{2}\left(aa^{\dagger} + a^{\dagger}a\right) - \frac{\hbar\omega}{2}\left(aa^{\dagger} + a^{\dagger}a\right)a \\ &= \frac{\hbar\omega}{2}\left[a^2, a^{\dagger}\right] \\ &= \frac{\hbar\omega}{2}\left\{a\left[a, a^{\dagger}\right] + \left[a, a^{\dagger}\right]a\right\} \\ &= \hbar\omega a \end{aligned} \tag{4.104}$$

In the same way

$$[a^{\dagger}, H] = -\,\hbar\omega a^{\dagger} \tag{4.105}$$

To obtain the energy levels of the oscillator, we have to calculate the matrix of the Hamiltonian and diagonalize it. However, if we work in the energy representation in which the eigenvectors of H form the basis of the space, the matrix of H would be diagonal

$$\langle m|H|n\rangle = E_n\langle m|n\rangle = E_n\delta_{mn} \tag{4.106}$$

where E_n is the energy eigenvalue of the nth state. Next, we shall evaluate the matrix of the product $a^{\dagger}a$.

$$\langle n|a^\dagger a|n\rangle = \left\langle n\left|\frac{H}{\hbar\omega} - \frac{1}{2}\right|n\right\rangle = \frac{E_n}{\hbar\omega} - \frac{1}{2} \tag{4.107}$$

The matrix of $a^\dagger a$ can also be written as

$$\begin{aligned}\langle n|a^\dagger a|n\rangle &= \langle n|a^\dagger|m\rangle\,\langle m|a|n\rangle\\ &= \langle m|a|n\rangle^\dagger\langle m|a|n\rangle\\ &= |\langle m|a|n\rangle|^2 \geq 0\end{aligned} \tag{4.108}$$

From Eqs. (4.107) and (4.108), we have

$$\frac{E_n}{\hbar\omega} - \frac{1}{2} \geq 0 \quad \text{or} \quad E_n \geq \frac{1}{2}\hbar\omega \tag{4.109}$$

Now consider the eigenvalue equation $H|n\rangle = E_n|n\rangle$. Operating from left by a, we get, $aH|n\rangle = E_n a|n\rangle$. But from Eq. (4.104), $aH = Ha + \hbar\omega a$, and therefore, we have

$$(Ha + \hbar\omega a)|n\rangle = E_n a|n\rangle$$

or

$$Ha|n\rangle = (E_n - \hbar\omega)a|n\rangle \tag{4.110}$$

That is, if $|n\rangle$ is an eigenvector of H with an eigenvalue E_n, $a|n\rangle$ is also an eigenvector of H corresponding to an eigenvalue lowered by $\hbar\omega$. In a similar way, we can show that

$$Ha^\dagger|n\rangle = (E_n + \hbar\omega)a^\dagger|n\rangle \tag{4.111}$$

The operators $a^\dagger$ and a are respectively known as *raising* and *lowering operators.* It follows that the kets $a^\dagger|n\rangle$ and $a|n\rangle$ are also eigenkets of H corresponding to the eigenvalues $(E_n + \hbar\omega)$ and $(E_n - \hbar\omega)$, respectively.

Denoting the ground-state eigenket corresponding to the minimum eigenvalue E_0 by $|0\rangle$, we have

$$Ha|0\rangle = (E_0 - \hbar\omega)a|0\rangle \tag{4.112}$$

As $E_n \geq \hbar\omega$, this equation is possible only if

$$a|0\rangle = 0 \quad \text{or} \quad a^\dagger a\,|0\rangle = 0 \tag{4.113}$$

In other words,

$$\left(\frac{H}{\hbar\omega} - \frac{1}{2}\right)\left|0\right\rangle = 0 \quad \text{or} \quad \left(\frac{E_0}{\hbar\omega} - \frac{1}{2}\right)\left|0\right\rangle = 0 \tag{4.114}$$

As $|0\rangle \neq 0$,

$$E_0 - \frac{1}{2}\hbar\omega = 0 \quad \text{or} \quad E_0 = \frac{1}{2}\hbar\omega \tag{4.115}$$

When the eigenvalue equation $H\,|0\rangle = E_0\,|0\rangle$ is operated from left by $a^\dagger$, we are led to

$$Ha^\dagger|0\rangle = (E_0 + \hbar\omega)a^\dagger|0\rangle \tag{4.116}$$

That is, $a^\dagger\ |0\rangle$ is an eigenket of H with eigenvalue $E_0 + \hbar\omega = (3/2)\ \hbar\omega$. Repeated operation by $a^\dagger$ raises the eigenvalue every time by $\hbar\omega$. Consequently,

$$E_n = E_0 + n\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots \tag{4.117}$$

with the eigenket $(a^\dagger)^n\ |0\rangle$. Thus,

$$|0\rangle, \quad a^\dagger|0\rangle, \quad (a^\dagger)^2|0\rangle, \quad \ldots, \quad (a^\dagger)^n|0\rangle, \ldots \qquad n = 0, 1, 2, \ldots \tag{4.118}$$

form a series of eigenkets corresponding to the eigenvalues E_n, $n = 0, 1, 2, \ldots$ given by Eq. (4.117).

The form of these eigenkets can easily be obtained from Eq. (4.113). From Eqs. (4.98) and (4.99), we get

$$a = \frac{1}{(2m\hbar\omega)^{1/2}}\left(m\omega x + \hbar\frac{d}{dx}\right), \quad a^\dagger = \frac{1}{(2m\hbar\omega)^{1/2}}\left(m\omega x - \hbar\frac{d}{dx}\right)$$

Substituting the value of a in Eq. (4.113), we have

$$\left(m\omega x + \hbar\frac{d}{dx}\right)\psi_0 = 0 \quad \text{or} \quad \frac{d\psi_0}{\psi_0} = -\frac{m\omega x}{\hbar}\,dx$$

Integrating, we get

$$\psi_0 = N_0 \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \tag{4.119}$$

We have already seen that $\psi_1 = a^\dagger\psi_0$. Hence

$$\psi_1 = N_1\left(m\omega x - \hbar\frac{d}{dx}\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right) \tag{4.120}$$

Repeated operation by $a^\dagger$ from left gives

$$\psi_n = N_n\left(m\omega x - \hbar\frac{d}{dx}\right)^n \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \tag{4.121}$$

This result is identical to the one we derived by the Schrödinger method.

According to Eq. (4.110), the operator a annihilates a quantum of energy $\hbar\omega$ and therefore it is sometimes referred to as *annihilation* or *destruction* operator. Similarly, the operator $a^\dagger$ creates a quantum of energy $\hbar\omega$, Eq. (4.111), and therefore it is called a *creation operator*. The creation and annihilation operators $a^\dagger$ and a play important roles in the quantum theory of the electromagnetic field.

4.9 THE FREE PARTICLE

In this section we shall look into the free particle Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -k^2\psi \tag{4.122}$$

where $k^2 = 2mE/\hbar^2$. For a given value of E, we have two solutions

$$\psi(x) = Ae^{ikx} \quad \text{and} \quad \psi(x) = Ae^{-ikx} \tag{4.123}$$

The free particle solutions are thus degenerate. The energy has to be real and positive to make the eigenfunction finite at $x = \infty$ and $x = -\infty$. The solution e^{ikx} corresponds to the particle moving in the positive x direction with $+\hbar k$ momentum and e^{-ikx} corresponds to the particle moving in the negative x direction with $-\hbar k$ momentum. However, the energy is same in both the cases. Thus, all real positive values are allowed eigenvalues.

Box Normalization

In the usual sense it is not possible to normalize a free-particle wave function as the normalization integral diverges. One way to overcome the situation is to restrict the domain of the particle under investigation to an arbitrarily large length L and to impose periodic boundary conditions at the end-points. Because of the periodic condition k is allowed to take only the discrete values:

$$k = \frac{2\pi n}{L}, \qquad n = 0, \pm 1, \pm 2, \ldots \tag{4.124}$$

The normalization can now be carried out by integrating between the limits $-L/2$ and $L/2$, which leads to

$$\psi(x) = \frac{1}{\sqrt{L}}e^{ikx} \tag{4.125}$$

The wave function is said to be *box normalized.* In three dimensions, the normalization is done in an arbitrarily large but finite cubical box of length L.

Delta Function Normalization

Normalization of wave functions of the type in Eq. (4.123) can also be carried out using delta function. One of the representations of delta function (also refer to Appendix C) is

$$\delta(x - x_0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\left[ik(x - x_0)\right]dk \tag{4.126}$$

Let $\psi_k(x)$ and $\psi_{k'}(x)$ be two wave functions belonging to wave numbers k and k'. The normalization integral in the infinite space is

$$\int_{-\infty}^{\infty} \psi_{k'}^* \psi_k \, dx = \delta_{kk'} \tag{4.127}$$

where $\delta_{kk'}$ is the Kronecker delta. As the energy eigenvalues are continuous, the Kronecker delta δ_{mn} is replaced by delta function in the delta function normalization. Equation (4.127) with delta function normalization is written as

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \psi_{k'}^* \psi_k \, dx = \delta(k - k') \tag{4.128}$$

The delta function normalized free particle wave function is then

$$\psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \tag{4.129}$$

The delta function normalization is thus a useful technique for the normalization of eigenfunction with continuous eigenvalues.

WORKED EXAMPLES

EXAMPLE 4.1 For an electron in a one-dimensional infinite potential well of width 1 Å, calculate (i) the separation between the two lowest energy levels (ii) the frequency and wavelength of the photon corresponding to a transition between these two levels (iii) in what region of the electromagnetic spectrum is this frequency/wavelength?

(i) We have $2a$ = 1Å = 10^{-10} m. We also know

$$E_n = \frac{\pi^2 \hbar^2 n^2}{8ma^2}$$

Therefore,

$$\begin{aligned} E_2 - E_1 = \frac{3\pi^2\hbar^2}{8ma^2} &= \frac{3\pi^2 \times \left(1.055 \times 10^{-34}\right)^2 \times 4}{8 \times 9.1 \times 10^{-31} \times 10^{-20}} \\ &= 1.812 \times 10^{-17} \text{ J} \\ &= 113.27 \text{ eV} \end{aligned}$$

(ii) We have

$$h\nu = 1.812 \times 10^{-17} \text{ J}$$

or

$$\nu = 2.7 \times 10^{16} \text{ Hz}$$

Therefore,

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{2.7 \times 10^{16}} = 1.1 \times 10^{-8} \text{ m}$$

(iii) This frequency falls in the vacuum ultraviolet region.

EXAMPLE 4.2 Show that the energy and wave function of a particle in a square well of finite depth V_0 reduces to the energy and wave function of a square well with rigid walls in the limit $V_0 \to \infty$.

For a well of finite depth, Eq. (4.21) gives

$$ka \tan(ka) = \alpha a \quad \text{or} \quad \tan(ka) = \frac{\alpha}{k}$$

Also, from Eqs. (4.19), and (4.16), we have

$$k^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \alpha^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

Hence

$$\tan(ka) = \sqrt{\frac{V_0 - E}{E}}$$

When $V_0 \to \infty$, $\tan(ka) \to ka$. Then

$$ka = \frac{n\pi}{2} \quad \text{or} \quad k^2a^2 = \frac{n^2\pi^2}{4}$$

Hence

$$E_n = \frac{\pi^2\hbar^2n^2}{8ma^2}$$

which is Eq. (4.12).

Equation (4.18) gives the wave function for a particle in a square well with finite depth. When $V_0 \to \infty$, $\alpha \to \infty$, the wave function reduces to

$$\psi(x) = \begin{cases} 0 & x < -a \\ A\sin(kx) + B\cos(kx) & -a < x < a \\ 0 & x > a \end{cases}$$

which is the wave function of a particle in a square well with rigid walls.

EXAMPLE 4.3 A harmonic oscillator is in the ground state. (i) Where is the probability density maximum? (ii) What is the value of maximum probability density?

(i) The ground state wave function is

$$\psi_0(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

Probability density is

$$P(x) = \psi_0{}^*\psi_0 = \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \exp\left(-\frac{m\omega x^2}{\hbar}\right)$$

$P(x)$ will be maximum at the point where

$$\frac{dP}{dx} = 0$$

or

$$\left(\frac{m\omega}{\hbar\pi}\right)^{1/2}\left(-\frac{m\omega}{\hbar}\right)2x\exp\left(-\frac{m\omega x^2}{\hbar}\right)=0$$

or

$$x = 0$$

Therefore, the probability density is maximum at $x = 0$.

(ii) $P(0) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/2}$

EXAMPLE 4.4 A 1-eV electron got trapped inside the surface of a metal. If the potential barrier is 4.0 eV and the width of the barrier is 2 Å, calculate the probability of its transmission.

If L is the width of the barrier, the transmission coefficient

$$T = 16\frac{E}{V}\left(1-\frac{E}{V}\right)\exp\left[-\frac{2L}{\hbar}\sqrt{2m(V-E)}\right]$$

$$= 16 \times \frac{1}{4} \times \frac{3}{4} \times \exp\left(-\frac{2 \times 2 \times 10^{-10}}{1.05 \times 10^{-34}}\sqrt{2 \times 9.1 \times 10^{-31} \times 3 \times 1.6 \times 10^{-19}}\right)$$

$$= 0.085$$

EXAMPLE 4.5 Complete the steps involved in deriving Eq. (4.66) from Eq. (4.62).

Assuming the solution, $u_2 = \exp(m_1 x)$ and differentiating both sides with respect to x, we get,

$$\frac{du_2}{dx} = m_1 \exp(m_1 x) \quad \text{and} \quad \frac{d^2u_2}{dx^2} = m_1^2 \exp(m_1 x)$$

Substitution of these values in Eq. (4.62) gives

$$m_1^2 + 2ikm_1 - (k_2^2 + k^2) = 0, \qquad -b < x < 0$$

or

$$m_1 = \frac{-2ik \pm \sqrt{-4k^2 + 4\left(k_2^2 + k^2\right)}}{2}$$

On solving, we get two values of m_1:

$$m_1 = -ik + k_2 \quad \text{and} \quad -ik - k_2$$

Therefore, the final solution is

$$u_2 = C\exp[(k_2 - ik)x] + D\exp[-(k_2 + ik)x], \quad -b < x < 0$$

which is Eq. (4.66).

EXAMPLE 4.6 Show that the probability density of the linear harmonic oscillator in an arbitrary superposition state is periodic with the period equal to the period of the oscillator.

The time-dependent wave function of the linear harmonic oscillator in a superposition state is

$$\Psi(x,t) = \sum_n C_n \psi_n(x) \exp\left(-\frac{iE_n t}{\hbar}\right)$$

where $\psi_n(x)$ is the time-independent wave function of the harmonic oscillator in the nth state. Now, the probability density

$$P(x,t) = |\Psi(x,t)|^2 = \sum_m \sum_n C_m^* C_n \psi_m^* \psi_n \exp\left[\frac{i(E_m - E_n)t}{\hbar}\right]$$

It is obvious that $P(x, t)$ is dependent on time. Let us investigate what happens to $P(x, t)$ if t is replaced by $t + (2\pi/\omega)$. It follows that

$$\exp\left[\frac{i(E_m - E_n)}{\hbar}\left(t + \frac{2\pi}{\omega}\right)\right] = \exp\left[\frac{i(E_m - E_n)t}{\hbar}\right]\exp\left[\frac{i(E_m - E_n)}{\hbar}\frac{2\pi}{\omega}\right]$$

$$= \exp\left[\frac{i(E_m - E_n)t}{\hbar}\right]$$

as $(E_m - E_n)$ is an integral multiple of $\hbar\omega$. That is, $P(r, t)$ is periodic with period $2\pi/\omega$, the period of the linear harmonic oscillator.

EXAMPLE 4.7 For harmonic oscillator wave functions, find the value of $(\psi_k, x\psi_n)$.

For Hermite polynomials

$$H_{n+1}(y) - 2yH_n(y) + 2nH_{n-1}(y) = 0$$

Substituting the values of H_{n+1}, H_n and H_{n-1} in terms of the oscillator wave functions (Eq. 4.93) and dropping

$$\left(\frac{\hbar\pi}{m\omega}\right)^{1/4} \exp\left(\frac{y^2}{2}\right)$$

from all terms, we get

$$\left[2^{n+1}(n+1)!\right]^{1/2} \psi_{n+1} - 2y(2^n n!)^{1/2} \psi_n + 2n\left[2^{n-1}(n-1)!\right]^{1/2} \psi_{n-1} = 0$$

or

$$(n+1)^{1/2} \psi_{n+1} - \sqrt{2}\, y\, \psi_n + n^{1/2} \psi_{n-1} = 0$$

Since $y = (m\omega/\hbar)^{1/2} x$, inner product of this equation with ψ_k gives

$$(n+1)^{1/2}\left(\psi_k,\psi_{n+1}\right)-\left(\frac{2m\omega}{\hbar}\right)^{1/2}\left(\psi_k,x\,\psi_n\right)+n^{1/2}\left(\psi_k,\psi_{n-1}\right)=0$$

or

$$\left(\psi_k,x\,\psi_n\right)=\left(\frac{(n+1)\,\hbar}{2m\omega}\right)^{1/2}\left(\psi_k,\psi_{n+1}\right)+\left(\frac{n\,\hbar}{2m\omega}\right)^{1/2}\left(\psi_k,\psi_{n-1}\right)$$

or

$$(\psi_k, x\psi_n)=\begin{cases}\sqrt{\dfrac{\hbar(n+1)}{2m\omega}} & \text{if } k=n+1\\[2ex] \sqrt{\dfrac{\hbar n}{2m\omega}} & \text{if } k=n-1\\[2ex] 0 & \text{if } k\neq n\pm 1\end{cases}$$

EXAMPLE 4.8 Evaluate $\langle x^2\rangle$, $\langle p^2\rangle$, $\langle V\rangle$ and $\langle T\rangle$ for the states of a harmonic oscillator.

From Example 4.7, we have

$$(n+1)^{1/2}\psi_{n+1}-\left(\frac{2m\omega}{\hbar}\right)^{1/2}x\,\psi_n+n^{1/2}\psi_{n-1}=0$$

Multiplying from left by x and then taking inner product of the resulting equation with ψ_n, we get

$$(n+1)^{1/2}\left(\psi_n,x\psi_{n+1}\right)-\left(\frac{2m\omega}{\hbar}\right)^{1/2}\left(\psi_n,x^2\psi_n\right)+n^{1/2}\left(\psi_n,x\psi_{n-1}\right)=0$$

Then

$$\langle x^2\rangle=\left(\psi_n,x^2\psi_n\right)=\frac{\hbar}{2m\omega}(2n+1)$$

and

$$\langle p^2\rangle=-\hbar^2\left(\psi_n,\frac{d^2\psi_n}{dx^2}\right)$$

Schrödinger equation for harmonic oscillator is

$$\frac{d^2\psi_n}{dx^2}=-\frac{2mE_n}{\hbar^2}\psi_n+\frac{m^2\omega^2x^2}{\hbar^2}\psi_n$$

Substituting this value of $\frac{d^2\psi_n}{dx^2}$ and using the result for $\langle x^2\rangle$, we get

$$\begin{aligned}\langle p^2\rangle&=2mE_n-m^2\omega^2\frac{\hbar}{2m\omega}(2n+1)\\&=(2n+1)\,m\hbar\omega-\frac{2n+1}{2}\,m\hbar\omega\end{aligned}$$

$$= \left(n + \frac{1}{2}\right) m\hbar\omega$$

Expectation value of potential energy

$$\langle V\rangle = \frac{1}{2}k\langle x^2\rangle$$

Substituting the values of k and $\langle x^2\rangle$, we get

$$\langle V\rangle = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega = \frac{E_n}{2}$$

Expectation value of kinetic energy

$$\langle T\rangle = \frac{1}{2m}\left\langle p^2\right\rangle = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega = \frac{E_n}{2}$$

EXAMPLE 4.9 Show that the zero point energy of $\frac{1}{2}\hbar\omega$ of a linear harmonic oscillator is a manifestation of the uncertainty principle.

The average position and momentum of a classical harmonic oscillator bound to the origin is zero. As per the Ehrenfest's theorem this rule must be true for the quantum mechanical case also. Hence

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \langle x^2\rangle$$

and

$$(\Delta p)^2 = \langle p^2\rangle - \langle p\rangle^2 = \langle p^2\rangle$$

For the total energy E,

$$\langle E\rangle = \frac{1}{2m}\langle p^2\rangle + \frac{1}{2}k\langle x^2\rangle, \qquad (\text{where } k = m\omega^2)$$

$$= \frac{1}{2m}(\Delta p)^2 + \frac{1}{2}k\,(\Delta x)^2$$

Replacing $(\Delta p)^2$ with the help of the relation

$$(\Delta p)^2(\Delta x)^2 \geq \frac{\hbar^2}{4}$$

we get

$$\langle E\rangle \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2$$

For the right-hand side to be minimum, the differential of $\langle E\rangle$ with respect to $(\Delta x)^2$ must be zero

$$\frac{-\hbar^2}{8m(\Delta x)^4_{\min}} + \frac{1}{2}k = 0 \quad \text{or} \quad (\Delta x)^2_{\min} = \frac{\hbar}{2m\omega}$$

and

$$\langle E\rangle_{\min} = \frac{\hbar^2}{8m}\frac{2m\omega}{\hbar} + \frac{1}{2}m\omega^2\frac{\hbar}{2m\omega} = \frac{1}{2}\hbar\omega$$

EXAMPLE 4.10 A stream of particles of mass m and energy E moves towards the potential step $V(x) = 0$ for $x < 0$ and $V(x) = V_0$ for $x > 0$. If the energy of the particles $E > V_0$, show that the sum of fluxes of the transmitted and reflected particles is equal to the flux of incident particles.

The Schrödinger equations for regions 1 and 2 (Figure 4.13) are

$$\frac{d^2\psi_1}{dx^2} + k_0{}^2\psi = 0, \qquad k_0^2 = \frac{2mE}{\hbar^2}, \text{ (for } x < 0)$$

$$\frac{d^2\psi_2}{dx^2} + k^2\psi = 0, \qquad k^2 = \frac{2m(E - V_0)}{\hbar^2}, \text{ (for } x > 0)$$

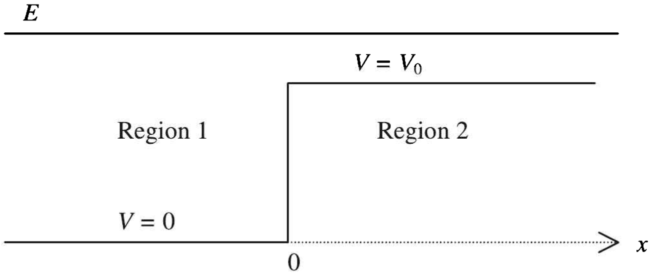


Figure 4.13 Potential step.

The solutions of the two equations are

$$\psi_1 = \exp(ik_0x) + A\exp(-ik_0x) \qquad (\text{for } x < 0)$$

$$\psi_2 = B\exp(ikx) \qquad (\text{for } x > 0)$$

For convenience, the amplitude of the incident wave is taken as 1. The second term in ψ_1, a wave travelling from right to left, is the reflected wave whereas ψ_2 is the transmitted wave. It may be noted that in region 2 we will not have a wave travelling from right to left. The continuity conditions on ψ and its derivative at $x = 0$ gives

$$1 + A = B \quad \text{and} \quad k_0(1 - A) = kB$$

Simplifying, we get

$$A = \frac{k_0 - k}{k_0 + k} \quad \text{and} \quad B = \frac{2k_0}{k_0 + k}$$

The flux of particles for the incident wave (Problem 2.11) = $\dfrac{k_0\hbar}{m}$

The magnitude of flux of particles for the reflected wave = $\dfrac{k_0\hbar}{m}|A|^2$

The flux of particles for the transmitted wave = $\dfrac{k\hbar}{m}|B|^2$

$$\text{Sum of reflected and transmitted flux} = \frac{\hbar}{m}\left[k_0|A|^2 + k|B|^2\right]$$

$$= \frac{\hbar k_0}{m}\left[\frac{(k_0-k)^2}{(k_0+k)^2} + \frac{4kk_0}{(k_0+k)^2}\right]$$

$$= \frac{\hbar k_0}{m}$$

which is the incident flux.

EXAMPLE 4.11 A particle of mass m confined to move in a potential $V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise. The wave function of the particle at time $t = 0$ is given by

$$\psi(x, 0) = A \sin\frac{5\pi x}{a}\cos\frac{2\pi x}{a}$$

(i) Normalize $\psi(x, 0)$ (ii) Find $\psi(x, t)$ (iii) Is $\psi(x, t)$ a stationary state? It is given that

$$\psi(x, 0) = A \sin\frac{5\pi x}{a}\cos\frac{2\pi x}{a} = \frac{A}{2}\left(\sin\frac{7\pi x}{a} + \sin\frac{3\pi x}{a}\right)$$

(i) The normalization condition gives

$$\frac{A^2}{4}\int_0^a\left(\sin\frac{7\pi x}{a} + \sin\frac{3\pi x}{a}\right)^2 dx = 1$$

$$\frac{A^2}{4}\int_0^a\left(\sin^2\frac{7\pi x}{a} + \sin^2\frac{3\pi x}{a} + 2\sin\frac{7\pi x}{a}\sin\frac{3\pi x}{a}\right)dx = 1$$

$$\frac{A^2}{4}\left(\frac{a}{2} + \frac{a}{2}\right) = 1 \quad \text{or} \quad A = \frac{2}{\sqrt{a}}$$

Normalized $\psi(x, 0)$ is:

$$\psi(x, 0) = \frac{1}{\sqrt{a}}\left(\sin\frac{7\pi x}{a} + \sin\frac{3\pi x}{a}\right)$$

For a particle in an infinite square well the eigenvalues and eigenfunctions are:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad \text{and} \quad \phi_n(x) = \left(\frac{2}{a}\right)^{1/2}\sin\frac{n\pi x}{a}, \quad n = 1, 2, 3, \ldots$$

Hence

$$\psi(x, 0) = \frac{1}{\sqrt{2}}(\phi_7 + \phi_3)$$

(ii) The time dependence of a state is given by

$$\psi(x,t) = \psi(x,0)\, e^{-iEt/\hbar}$$

Hence $\psi(x, t)$ in this case is:

$$\psi(x,t) = \frac{1}{\sqrt{2}}(\phi_7\, e^{-iE_7t/\hbar} + \phi_3\, e^{-iE_3t/\hbar})$$

(iii) It is not a stationary state since $\psi(x, t)$ is a superposition state.

EXAMPLE 4.12 A particle of mass m and charge e moving in a one dimensional harmonic potential is subjected to an electric field ε in the x-direction. Find the energy levels and eigenfunctions.

Additional potential energy due to the electric field $\varepsilon = -e\varepsilon x$. The Schrödinger equation of the oscillator is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \left(\frac{1}{2}kx^2 - e\varepsilon x\right)\psi = E\psi\ ; \quad k = m\omega^2$$

Introducing a new variable x_1 defined by

$$x_1 = x - \frac{e\varepsilon}{k}$$

$$\frac{1}{2}kx_1^2 = \frac{1}{2}k\left(x - \frac{e\varepsilon}{k}\right)^2 = \frac{1}{2}kx^2 - e\varepsilon x + \frac{e^2\varepsilon^2}{2k}$$

$$\frac{1}{2}kx^2 - e\varepsilon x = \frac{1}{2}kx_1^2 - \frac{e^2\varepsilon^2}{2k}$$

Since $dx = dx_1$, with this expression for the modified potential energy

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx_1^2} + \frac{1}{2}kx_1^2\,\psi = \left(E + \frac{e^2\varepsilon^2}{2k}\right)\psi$$

Writing $$E' = E + \frac{e^2\varepsilon^2}{2k}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx_1^2} + \frac{1}{2}kx_1^2\psi = E'\psi$$

which is the Schrödinger equation of a single harmonic oscillator. The energy eigenvalues are:

$$E_n' = \left(n + \frac{1}{2}\right)\hbar\omega; \quad n = 0, 1, 2, \ldots$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{e^2\varepsilon^2}{2k} = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{e^2\varepsilon^2}{2m\omega^2}$$

The eigenfunctions are given by

$$\psi_n = \left[\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{1}{2^n\, n!}\right]^{1/2} H_n\,(\sqrt{m\omega/\hbar}\, x_1)\exp\left(-\frac{m\omega x_1^2}{2\hbar}\right)$$

EXAMPLE 4.13 Consider a particle of mass m in the one dimensional short range potential

$$V(x) = -V_0\delta(x), \quad V_0 > 0$$

where $\delta(x)$ is Dirac delta function. Find the energy of the system.

The Schrödinger equation for such a potential is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} - V_0\,\delta(x)\,\psi(x) = E\,\psi(x)$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE\,\psi}{\hbar^2} = -\frac{2mV_0}{\hbar^2}\delta(x)\,\psi$$

Since the potential is attractive the equation to be solved, when $E < 0$, is:

$$\frac{d^2\psi}{dx^2} - k^2\psi = -\frac{2mV_0}{\hbar^2}\delta(x)\,\psi; \quad k^2 = -\frac{2mE}{\hbar^2}$$

The solution everywhere except at $x = 0$ must satisfy the equation:

$$\frac{d^2\psi}{dx^2} - k^2\psi = 0$$

and for the solution to vanish at $x \to \pm\infty$, we must have

$$\psi(x) = \begin{cases} e^{-kx}, & x > 0 \\ e^{kx}, & x < 0 \end{cases} \tag{i}$$

The normalization factor is assumed to be unity. Integrating the original equation from $-\lambda$ to $+\lambda$, λ being an arbitrarily small positive number.

$$\left[\frac{d\psi}{dx}\right]_{-\lambda}^{\lambda} - k^2\int_{-\lambda}^{\lambda}\psi\,dx = -\frac{2mV_0}{\hbar^2}\int_{-\lambda}^{\lambda}\delta(x)\,\psi(x)\,dx$$

The integral on the right side becomes $-\dfrac{2mV_0}{\hbar^2}\,\psi(0)$ (Appendix C). Hence, in the limit $\lambda \to 0$, the above equation becomes

$$\left(\frac{d\psi}{dx}\right)_{x=0+} - \left(\frac{d\psi}{dx}\right)_{x=0-} = -\frac{2mV_0}{\hbar^2}\psi(0)$$

Substituting the values of the left hand side from Eq. (i)

$$-k\,\psi(0) - k\,\psi(0) = -\frac{2mV_0}{\hbar^2}\psi(0)$$

$$k = \frac{mV_0}{\hbar^2} \quad \text{or} \quad -\frac{2mE}{\hbar^2} = \frac{m^2V_0^{\,2}}{\hbar^4}$$

$$E = -\frac{mV_0^{\,2}}{2\hbar^2}$$

EXAMPLE 4.14 Consider the one dimensional problem of a particle of mass m in a potential $V = \infty$ for $x < 0$; $V = 0$ for $0 \le x \le a$ and $V = V_0$ for $x > a$. Obtain the wave functions and show that the bound state energies ($E < V_0$) are given by

$$\tan\frac{\sqrt{2mE}}{\hbar}a = -\sqrt{\frac{E}{V_0 - E}}$$

The Schrödinger equation for the different regions are:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \qquad k^2 = \frac{2mE}{\hbar^2}, \qquad 0 \le x \le a$$

$$\frac{d^2\psi}{dx^2} - k_1^2\psi = 0, \qquad k_1^2 = \frac{2m}{\hbar^2}(V_0 - E), \qquad x > a$$

The solution of these equations are:

$$y = A\sin kx + B\cos kx \qquad 0 \le x \le a$$

$$\psi = Ce^{-k_1x} + De^{k_1x} \qquad x > a$$

where A, B, C and D are constants. Applying the boundary conditions $\psi = 0$ at $x = 0$ and $\psi \to 0$ as $x \to \infty$

$$y = A\sin kx \qquad 0 \le x \le a$$

$$\psi = Ce^{-k_1x} \qquad x > a$$

The requirement that ψ and $\frac{d\psi}{dx}$ are continuous at $x = a$ gives

$$A\sin ka = Ce^{-k_1a}$$

$$Ak\cos ka = -Ck_1e^{-k_1a}$$

Dividing one by the other,

$$\tan ka = -\frac{k}{k_1}$$

$$\tan\left(\frac{\sqrt{2mE}\,a}{\hbar}\right) = -\left(\frac{E}{V_0 - E}\right)^{1/2}$$

EXAMPLE 4.15 Consider a stream of particles of mass m each moving in the positive x-direction with kinetic energy E towards the potential barrier

$$V(x) = 0 \quad \text{for} \quad x \le 0 \quad \text{and} \quad V(x) = \frac{3E}{4} \quad \text{for } x > 0$$

Find the fraction of the particles reflected at $x = 0$.

The Schrödinger equations for the different regions are:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \quad k^2 = \frac{2mE}{\hbar^2} \qquad x \le 0$$

$$\frac{d^2\psi}{dx^2} - \frac{2m}{\hbar^2}\left(\frac{3E}{4} - E\right)\psi = 0 \qquad x > 0$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{k}{2}\right)^2 \psi = 0, \qquad x > 0$$

The solution of the first equation is:

$$\psi = e^{ikx} + re^{-ikx}, \quad x \le 0$$

where r is the amplitude reflection coefficient since e^{-ikx} represents a wave travelling in the negative x-direction. The solution of the second equation is:

$$\psi = te^{ikx/2}, \quad x > 0$$

where t is the amplitude transmission coefficient. It is also oscillatory, since the height of the barrier is less than the kinetic energy of the particle. As the wave function is continuous at $x = 0$,

$$1 + r = t$$

As the derivative $d\psi/dx$ is continuous at $x = 0$,

$$k\,(1 - r) = \frac{kt}{2}$$

Solving the two equations, $r = 1/3$ and hence one-ninth of the particles are reflected at $x = 0$.

EXAMPLE 4.16 An electron of mass m is contained in a cube of side a which is fairly large. If it is in an electromagnetic field characterised by the vector potential $A = B_0 x\,\hat{y}$, $\hat{y}$ is the unit vector along y-axis determine the energy levels and eigenfunctions.

The Hamiltonian operator of the electron having charge $-e$ is:

$$H = \frac{1}{2m}\left[p_x^2 + \left(p_y + \frac{B_0 e x}{c}\right)^2 + p_z^2\right]$$

where p_x, p_y, p_z are operators.

We can easily prove the following commutation relations:

$$[H, p_y] = [H, p_z] = 0 \quad \text{and} \quad [H, p_x] \neq 0$$

Hence, by virtue of Eq. (3.106a) p_y and p_z are constants. The Schrödinger equation is:

$$\frac{1}{2m}\left[-\hbar^2\frac{d^2}{dx^2} + \frac{B_0^2 e^2 x^2}{c^2} + \frac{2\,B_0 e\;p_y x}{c} + p_y^2 + p_z^2\right]\psi = E\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \left(\frac{B_0^2 e^2 x^2}{2mc^2} + \frac{B_0 e\;p_y x}{mc} + \frac{p_y^2}{2m}\right)\psi = \left(E - \frac{1}{2m}p_z^2\right)\psi$$

Introducing a new variable x_1 defined by

$$x_1 = x + \frac{cp_y}{B_0 e}$$

$$x_1^2 = x^2 + \frac{2cp_y x}{B_0 e} + \frac{c^2 p_y^2}{B_0^2 e^2}$$

Multiplying by $B_0^2 e^2/2mc^2$,

$$\frac{B_0^2 e^2 x_1^2}{2mc^2} = \frac{B_0^2 e^2 x^2}{2mc^2} + \frac{B_0 e\;p_y x}{mc} + \frac{p_y^2}{2m}$$

In terms of the new variable, the Schrödinger equation takes the form:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx_1^2} + \frac{1}{2}\frac{B_0^2 e^2 x_1^2 \psi}{mc^2} = \left(E - \frac{1}{2m}p_z^2\right)\psi$$

The form of this equation is similar to that of the Schrödinger equation for a simple harmonic oscillator. Hence, the energy eigenvalues are:

$$E - \frac{1}{2m}p_z^2 = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0,\ 1,\ 2,\ \ldots$$

$$E=\left(n+\frac{1}{2}\right)\hbar\omega+\frac{1}{2m}p_z^2, \quad n = 0, 1, 2, \ldots$$

where

$$m\omega^2=\frac{B_0^2\, e^2}{mc^2} \quad \text{or} \quad \omega=\frac{B_0 e}{mc}$$

The eigenfunctions are given by

$$\psi_n(x_1)=\left[\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^n n!}\right]^{1/2} H_n(\sqrt{\alpha}\, x_1)\, e^{-\alpha x_1^2/2}$$

Here

$$\alpha=\frac{m\omega}{\hbar}=\frac{B_0 e}{c\hbar}$$

EXAMPLE 4.17 A harmonic oscillator moves in a potential

$$V(x)=\frac{1}{2}kx^2+cx$$

where c is a constant. Find the energy eigenvalues.

The Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\left(\frac{1}{2}kx^2+cx\right)\psi=E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}k\left(x^2+\frac{2}{k}cx\right)\psi=E\psi$$

Changing the variable to x_1 by defining $x_1 = x + c/k$,

$$x_1^2=x^2+\frac{2c}{k}x+\frac{c^2}{k^2}$$

$$x^2+\frac{2c}{k}x=x_1^2-\frac{c^2}{k^2}$$

Since $dx_1 = dx$, the Schrödinger equation reduces to

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx_1^2}+\frac{1}{2}k\left(x_1^2-\frac{c^2}{k^2}\right)\psi=E\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx_1^2}+\frac{1}{2}kx_1^2=\left(E+\frac{c^2}{2k}\right)\psi=E'\psi$$

$$E'=E+\frac{c^2}{2k}$$

Hence the energy eigenvalues are:

$$E_n'=\left(n+\frac{1}{2}\right)h\nu \quad \text{or} \quad E_n=\left(n+\frac{1}{2}\right)\hbar\omega-\frac{c^2}{2k}$$

REVIEW QUESTIONS

1. A particle confined in a box must have a certain minimum energy called zero point energy. Comment.
2. Sketch graphs of wave function ψ and of $|\psi|^2$ for the n = 3 and 4 states of a particle trapped in a potential well of infinite depth.
3. Write the Schrödinger equation and the form of the wave function in the different regions of a square well with finite depth.
4. Explain symmetric and antisymmetric wave functions with examples.
5. Explain quantum mechanical tunnelling.
6. In barrier penetration problem, why the exponentially increasing function $e^{\alpha x}$, where α is given by

   $$\alpha^2=\frac{2m(V_0-E)}{\hbar^2}$$

   is also an acceptable solution inside the barrier.
7. A particle having energy E is incident on a finite barrier of height $V_0 (E < V_0)$. Illustrate the wave function in the different regions.
8. Explain how barrier tunnelling accounts for α-decay by certain nuclei.
9. What are Bloch functions? State and explain Bloch theorem.
10. In a one-dimensional crystal, the periodicity of the potential led to the concept of energy bands. Explain.
11. Explain why the quantum oscillator is found outside the parabolic potential barrier.
12. Sketch graphs of ψ and $|\psi|^2$ for the first 4 states of the one-dimensional harmonic oscillator.
13. What is zero-point energy of harmonic oscillator? How is it explained?

PROBLEMS

1. Obtain the energy eigenvalues and eigenfunctions of a particle trapped in the potential $V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise.
2. Show that the wave functions for the different energy levels of the particle trapped in the square well in Problem 1 are orthogonal.
3. Calculate the expectation values of position $\langle x \rangle$ and of the momentum $\langle p_x \rangle$ of the particle trapped in the one-dimensional box of Problem 1.
4. An electron in a one-dimensional infinite potential well (Section 4.1) goes from the $n = 4$ to the $n = 2$ level. The frequency of the emitted photon is 3.43×10^{14} Hz. Find the width of the box.
5. Evaluate the probability of finding the trapped particle of Problem 1 between $x = 0$ and $x = a/n$, when it is in the nth state.
6. An alpha particle is trapped in a nucleus of radius 1.4×10^{-15} m. What is the probability that it will escape from the nucleus, if its energy is 2 MeV? The potential barrier at the surface of the nucleus is 4 MeV.
7. The wave function of a particle confined in a box of length a is

$$\psi(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{\pi x}{a}\right), \qquad 0 < x < a$$

   Calculate the probability of finding the particle in the region $0 < x < a/2$.
8. Find $\langle x \rangle$ and $\langle p \rangle$ for the nth state of the linear harmonic oscillator.
9. For the nth state of the linear harmonic oscillator, evaluate the uncertainty product $(\Delta x)\,(\Delta p)$.
10. A stream of particles of mass m and energy E moves towards the potential step of Worked Example 4.10. If the energy of particles $E < V_0$, show that there is a finite probability of finding the particles in the region $x > 0$. Also, determine the flux of (i) incident particles (ii) reflected particles (iii) the particles in region 2. Comment on the result.
11. A beam of 12 eV electrons is incident on a potential barrier of height 30 eV and width 0.05 nm. Calculate the transmission coefficient.
12. For the linear harmonic oscillator in its ground state, show that the probability of finding the particle outside the classical limits is about 16 per cent.
13. An electron moves in a one-dimensional potential of width 8 Å and depth 12 eV. Find the number of bound states present.
14. A linear harmonic oscillator is in the first excited state (i) where is its probability density maximum? (ii) what is the value of maximum probability density?

15. Sketch the probability density $|\psi|^2$ of the linear harmonic oscillator as a function of x for $n = 13$. Compare the result with that of the classical oscillator of the same total energy and discuss the limit $n \to \infty$.

16. Calculate the energy levels and wave functions of a particle of mass m moving in the one-dimensional potential well defined by

$$V(x) = \begin{cases} \infty & \text{for } x < 0 \\ \frac{1}{2}m\omega^2 x^2 & \text{for } x > 0 \end{cases}$$

17. The strongest IR absorption band of $^{12}C^{16}O$ molecule occurs at 6.43×10^{13} Hz. If the reduced mass of $^{12}C^{16}O$ is 1.185×10^{-26} kg, calculate (i) the approximate zero-point energy (ii) the force constant of the CO bond.

18. For the nth state of the linear harmonic oscillator, what range of x values is allowed classically.

19. An electron is confined in the ground state of a one-dimensional harmonic oscillator such that $\Delta x = 10^{-10}$ m. Assuming that $\langle T \rangle = \langle V \rangle$, find the energy in eV required to excite it to its first excited state.

20. An electron having energy E = 1 eV is incident upon a rectangular barrier of potential energy $V_0 = 2$ eV. How wide must the barrier, so that the transition probability is 10^{-3}?

21. A particle of mass m confined to move in a potential $V(x) = 0$ for $0 \le x \le a$ and $V(x) = \infty$ otherwise. The wave function of the particle at time $t = 0$ is:

$$\psi(x, 0) = A\left(2\sin\frac{\pi x}{a} + \sin\frac{3\pi x}{a}\right)$$

(i) Normalize $\psi(x, 0)$ (ii) Find $\psi(x, t)$, (iii) Is $\psi(x, t)$ a stationary state?

22. The force constant of HCl molecule is 480 Nm^{-1} and its reduced mass is 1.63×10^{-27} kg. At 300K, what is the probability that the molecule is in its first excited vibrational state?

23. For a one dimensional harmonic oscillator, using creation and annihilation operators, show that

$$(\Delta x)(\Delta p) = \left(n + \frac{1}{2}\right)\hbar$$

Chapter 5

Three-Dimensional Energy Eigenvalue Problems

In the previous chapter we applied the basic ideas developed to certain important one-dimensional potential problems. In this chapter, we demonstrate how effectively quantum mechanics explains most of the important features of some of the three-dimensional problems.

5.1 PARTICLE MOVING IN A SPHERICALLY SYMMETRIC POTENTIAL

In a spherically symmetric problem, the potential depends only on the distance of the particle from a fixed point. The time independent Schrödinger equation for such a system is

$$\nabla^2 \psi(r) + \frac{2m}{\hbar^2}(E - V)\psi(r) = 0 \tag{5.1}$$

Since the potential is spherically symmetric, it is convenient to work in spherical polar coordinates r, θ, ϕ, $(0 \le r \le \infty,\ 0 \le \theta \le \pi,\ 0 \le \phi \le 2\pi)$. Expressing Eq. (5.1) in polar coordinates, we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2}(E - V)\,\psi = 0 \tag{5.2}$$

Separation of the Equation

Equation (5.2) can be separated into three equations by writing

$$\psi(r,\ \theta,\ \phi) = R(r)\ \Theta\ (\theta)\ \Phi(\phi) \tag{5.3}$$

Substituting this form of ψ in Eq. (5.2) and multiplying by

$$\frac{r^2 \sin^2\theta}{R\Theta\Phi}$$

we obtain

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\ \frac{d\Theta}{d\theta}\right) + \frac{2m}{\hbar^2}[E-V(r)]r^2\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \tag{5.4}$$

The left-hand side of Eq. (5.4) is a function of r and θ and the right side is a function of ϕ alone. This is possible when each side is a constant, say m^2. Then

$$\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi) \tag{5.5}$$

and

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\ \frac{d\Theta}{d\theta}\right) + \frac{2m}{\hbar^2}[E-V(r)]\,r^2\sin^2\theta = m^2 \tag{5.6}$$

Dividing both sides of Eq. (5.6) by $\sin^2\theta$ and rearranging, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left(E - V\right)r^2 = -\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\ \frac{d\Theta}{d\theta}\right) + \frac{m^2}{\sin^2\theta}$$

This is possible when both sides are equal to a constant, say λ. Consequently, we get the θ-equation and the radial equation:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\ \frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \tag{5.7}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left[E - V(r)\right]R - \frac{\lambda}{r^2}R = 0 \tag{5.8}$$

Thus, the three-dimensional wave equation (5.2) is separated into three one-dimensional equations (5.5), (5.7) and (5.8).

Solution of the ϕ-equation

The solution of Eq. (5.5) is straightforward and is given by

$$\Phi(\phi) = Ae^{\pm im\phi}$$

For Φ to be single valued, $\Phi(\phi) = \Phi(\phi + 2\pi)$. Therefore

$$Ae^{\pm im\phi} = Ae^{\pm im(\phi+2\pi)} \quad \text{or} \quad 1 = e^{\pm im2\pi}$$

This is possible only if $m = 0, 1, 2, \ldots$ The quantum number m is called the *magnetic quantum number*. The normalization condition gives

$$1 = \int_0^{2\pi} \Phi^* \Phi \, d\phi = |A|^2 \int_0^{2\pi} d\phi$$

Then

$$|A|^2 2\pi = 1 \quad \text{or} \quad A = \frac{1}{\sqrt{2\pi}}$$

except for an arbitrary phase factor which can be taken as zero. The normalized solution is then

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \qquad m = 0, \pm 1, \pm 2, \ldots \tag{5.9}$$

Some of the normalized $\Phi(\phi)$ are given in Table 5.1. As $\sin(|m|\phi)$ and $\cos(|m|\phi)$ are also solutions of Eq. (5.5), the real form of the solutions are also listed in the table.

Table 5.1 The First-few Normalized $\Phi(\phi)$ functions

$\lvert m \rvert$	*Complex form*	*Real form*
0	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$	$\Phi_0 = \frac{1}{\sqrt{2\pi}}$
1	$\Phi_1 = \frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\Phi_{1\cos} = \frac{1}{\sqrt{\pi}} \cos\phi$
	$\Phi = \frac{1}{\sqrt{2\pi}} e^{-i\phi}$	$\Phi_{1\sin} = \frac{1}{\sqrt{\pi}} \sin\phi$
2	$\Phi_2 = \frac{1}{\sqrt{2\pi}} e^{i2\phi}$	$\Phi_{2\cos} = \frac{1}{\sqrt{\pi}} \cos(2\phi)$
	$\Phi_{-2} = \frac{1}{\sqrt{2\pi}} e^{-i2\phi}$	$\Phi_{2\sin} = \frac{1}{\sqrt{\pi}} \sin(2\phi)$

Solution of the θ-equation

To solve the θ-equation, a new variable $z = \cos\theta$ is introduced. On differentiating, we get

$$dz = -\sin\theta \, d\theta$$

We may also write

$$\frac{d}{d\theta} = -\sin\theta \frac{d}{dz} = -\left(1 - z^2\right)^{1/2} \frac{d}{dz}$$

In terms of z, Eq. (5.7) is

$$\frac{d}{dz}\left[\left(1 - z^2\right)\frac{d\Theta(z)}{dz}\right] + \left(\lambda - \frac{m^2}{1 - z^2}\right)\Theta(z) = 0 \tag{5.10}$$

which is associated Legendre equation. Equation (5.10) has poles at $z = \pm 1$. For physically acceptable solution,

$$\lambda = l(l + 1), \qquad l = 0, 1, 2, \ldots \qquad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

The solution of Eq. (5.10) is the Legendre polynomial $P_l(z)$ for $m = 0$ and the associated Legendre polynomials $P_l^{|m|}(z)$ for $m \neq 0$. The normalized solution is then

$$\Theta(\theta) = N_{lm} P_l^{|m|}(z) \tag{5.11}$$

where N_{lm} is the normalization constant. The normalization condition is

$$\left|N_{lm}\right|^2 \int_{-1}^{+1} P_k^{|m|}(z)\, P_l^{|m|}(z)\, dz = 1$$

The orthogonality relation for associated Legendre polynomials

$$\int_{-1}^{+1} P_k^{|m|}(z)\, P_l^{|m|}(z) dz = \frac{2}{(2l + 1)} \frac{\left(l + |m|\right)!}{\left(l - |m|\right)!} \delta_{lk} \tag{5.12}$$

leads to

$$\Theta_l^m(\theta) = \varepsilon \sqrt{\frac{2l + 1}{2} \frac{\left(l - |m|\right)!}{\left(l + |m|\right)!}}\, P_l^m\left(\cos\theta\right) \tag{5.13}$$

where $\varepsilon = (-1)^m$ for $m > 0$ and $\varepsilon = 1$ for $m \leq 0$ as per the established phase convention.

Spherical Harmonics

The solution of the angular part of the equation, called the *spherical harmonics*, is independent of E and $V(r)$. Combining Eqs. (5.9) and (5.13), the normalized angular part of the wave function is

$$Y_{l,m}(\theta, \phi) = \varepsilon \sqrt{\frac{2l + 1}{4\pi} \frac{\left(l - |m|\right)!}{\left(l + |m|\right)!}}\, P_l^m\left(\cos\theta\right) e^{im\phi} \tag{5.14}$$

where

$$l = 0, 1, 2, \ldots \qquad m = 0, \pm 1, \pm 2, \ldots, \pm l \tag{5.15}$$

The spherical harmonics are mutually orthogonal and the first-few of them are given in Table 5.2.

Table 5.2 The First-few Spherical Harmonics

Complex form	*Real form*
$Y_{0,0} = \dfrac{1}{(4\pi)^{1/2}}$	$Y_{0,0} = \dfrac{1}{(4\pi)^{1/2}}$
$Y_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta = \left(\dfrac{3}{4\pi}\right)^{1/2} \dfrac{z}{r}$
$Y_{1,1} = -\left(\dfrac{3}{8\pi}\right)^{1/2} (\sin\theta) e^{i\phi}$	$Y_{1,1\cos} = \left(\dfrac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi = \left(\dfrac{3}{4\pi}\right)^{1/2} \dfrac{x}{r}$
$Y_{1,-1} = \left(\dfrac{3}{8\pi}\right)^{1/2} (\sin\theta) e^{-i\phi}$	$Y_{1,1\sin} = \left(\dfrac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi = \left(\dfrac{3}{4\pi}\right)^{1/2} \dfrac{y}{r}$
$Y_{2,0} = \left(\dfrac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_{2,0} = \left(\dfrac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) = \left(\dfrac{5}{16\pi}\right)^{1/2} \left(\dfrac{3z^2}{r^2} - 1\right)$
$Y_{2,1} = -\left(\dfrac{15}{8\pi}\right)^{1/2} (\sin\theta\cos\theta) e^{i\phi}$	$Y_{2,1\cos} = \left(\dfrac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi = \left(\dfrac{15}{4\pi}\right)^{1/2} \dfrac{xz}{r^2}$
$Y_{2,-1} = \left(\dfrac{15}{8\pi}\right)^{1/2} (\sin\theta\cos\theta) e^{-i\phi}$	$Y_{2,1\sin} = \left(\dfrac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi = \left(\dfrac{15}{4\pi}\right)^{1/2} \dfrac{yz}{r^2}$
$Y_{2,2} = \left(\dfrac{15}{32\pi}\right)^{1/2} (\sin^2\theta) e^{2i\phi}$	$Y_{2,2\cos} = \left(\dfrac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos(2\phi) = \left(\dfrac{15}{16\pi}\right)^{1/2} \dfrac{x^2 - y^2}{r^2}$
$Y_{2,-2} = \left(\dfrac{15}{32\pi}\right)^{1/2} (\sin^2\theta) e^{-2i\phi}$	$Y_{2,2\sin} = \left(\dfrac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin(2\phi) = \left(\dfrac{15}{16\pi}\right)^{1/2} \dfrac{xy}{r^2}$

The presence of the factor $e^{im\phi}$ makes the spherical harmonics complex in general. Often it is advantageous to work with real form. We have already seen that a linear combination of degenerate eigenfunctions of a degenerate level is also an eigenfunction with the same eigenvalue. Thus, one can express Y_{11} and $Y_{1,-1}$ in the real form by taking a suitable linear combination of them. Similar linear combinations are taken for other spherical harmonics also. The real forms of the first-few of them are also listed in Table 5.2.

Radial Equation

To solve the radial equation, Eq. (5.8), the explicit form of the potential $V(r)$ is needed. However, this can be expressed in the form of a one-dimensional equation by writing

$$R(r) = \frac{\chi(r)}{r} \tag{5.16}$$

The radial equation now reduces to

$$\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{l\,(l+1)\hbar^2}{2mr^2}\right)\chi = 0 \tag{5.17}$$

This has the form of a one-dimensional Schrödinger equation of a particle of mass m moving in the direction of r in a field of effective potential

$$V_{\text{eff}} = V(r) + \frac{l\,(l+1)\hbar^2}{2mr^2} \tag{5.18}$$

The additional potential $l(l + 1)\ \hbar^2/(2mr^2)$ is a repulsive one and corresponds to a force $l(l + 1)\ \hbar^2/(mr^3)$. The centrifugal force $mr\omega^2$ can be written in terms of the orbital angular momentum L as

$$mr\omega^2 = \frac{\left(mr^2\omega\right)^2}{mr^3} = \frac{L^2}{mr^3} \tag{5.19}$$

This form of the centrifugal force and the force corresponding to the additional potential suggest that L^2 can be taken as

$$L^2 = l(l+1)\hbar^2 \tag{5.20}$$

This shrewed guess regarding the value of L^2 is put on firm theoretical basis in Chapter 8. As the quantum number l is associated with the orbital angular momentum, it is called the *orbital angular momentum quantum number.* Often we say that the orbital angular momentum is $l\hbar$, though the exact value is $[l(l+1)]^{1/2}\hbar$. If $V(r)$ is Coulombic $(-ZZ'e^2/r)$, the additional potential is negligible at large distances. However, this becomes the dominant term at close distances. Figure 5.1 gives a plot of V_{eff} as a function of r for a Coulomb potential.

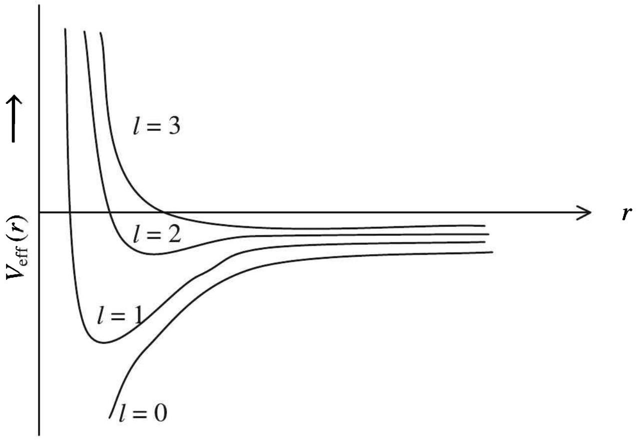


Figure 5.1 The effective potential V_{eff} verses r for a Coulomb potential.

5.2 SYSTEM OF TWO INTERACTING PARTICLES

So far we have considered the motion of a particle in a potential field. However, there are situations wherein we have two interacting particles moving in a three-dimensional space. The wave equation of such a system can be reduced into two one-particle equations, one representing the translational motion of the centre of mass and the other the relative motion of the two particles.

Hamiltonian Operator

The position vectors and masses of the two particles are shown in Figure 5.2. The radius vector of the centre of mass

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{5.21}$$

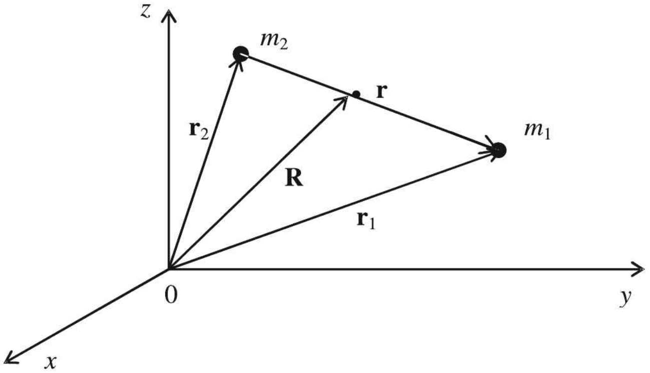


Figure 5.2 System of two interacting particles.

The relative position vector is given by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{5.22}$$

From Eqs. (5.21) and (5.22), we have

$$\mathbf{r}_1 = \mathbf{R} + \frac{m_2\mathbf{r}}{m_1 + m_2}, \qquad \mathbf{r}_2 = \mathbf{R} - \frac{m_1\mathbf{r}}{m_1 + m_2} \tag{5.23}$$

The momenta of the two particles can be written as

$$\mathbf{p}_1 = m_1\dot{\mathbf{r}}_1 = m_1\dot{\mathbf{R}} + \mu\dot{\mathbf{r}}, \quad \mathbf{p}_2 = m_2\dot{\mathbf{r}}_2 = m_2\dot{\mathbf{R}} - \mu\dot{\mathbf{r}} \tag{5.24}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{5.25}$$

is called the *reduced mass of the particles.* Assuming the potential to be dependent only on the distance between the two particles, the Hamiltonian of the system is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(r) \tag{5.26}$$

Substituting the values of p_1 and p_2

$$H = \frac{1}{2}(m_1 + m_2)\dot{\mathbf{R}}^2 + \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\mu^2\dot{\mathbf{r}}^2 + V(r)$$

$$= \frac{1}{2M}p_R^2 + \frac{1}{2\mu}p_r^2 + V(r) \tag{5.27}$$

where $M = m_1 + m_2, p_R = M\dot{\mathbf{R}}$ and $p_r = \mu\dot{\mathbf{r}}$. Replacing the dynamical variables by the corresponding operators and writing

$$\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \quad \text{and} \quad \nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{5.28}$$

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r) \tag{5.29}$$

The time-independent Schrödinger equation is then

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\psi_T(\mathbf{R}, \mathbf{r}) = E_T\psi_T(\mathbf{R}, \mathbf{r}) \tag{5.30}$$

Wave Equation for Relative Motion

Equation (5.30) can be separated into two equations by writing

$$\psi_T(\mathbf{R}, \mathbf{r}) = \chi(\mathbf{R})\ \psi(\mathbf{r}) \tag{5.31}$$

With this form of $\psi_T(\mathbf{R}, \mathbf{r})$, Eq. (5.30) reduces to

$$-\frac{\hbar^2}{2M}\frac{1}{\chi}\nabla_R^2\chi(\mathbf{R}) = \frac{\hbar^2}{2\mu}\frac{1}{\psi(\mathbf{r})}\nabla_r^2\psi(\mathbf{r}) + E_T - V \tag{5.32}$$

For the validity of Eq. (5.32), each side must be equal to a constant, say E_t. That is

$$-\frac{\hbar^2}{2M}\nabla_R^2\chi(\mathbf{R}) = E_t\chi(\mathbf{R}) \tag{5.33}$$

and

$$-\frac{\hbar^2}{2\mu}\nabla_r^2\psi(\mathbf{r}) + V(\mathbf{r})\ \psi(\mathbf{r}) = (E_T - E_t)\ \psi(\mathbf{r}) \tag{5.34}$$

As Eq. (5.33) is the same as a free-particle equation of mass M, it describes the translational motion of the system in space. Equation (5.34) is the same as the Schrödinger equation of a particle of mass μ moving in a field of potential

$V(\mathbf{r})$ and represents the relative motion of the two particles. The energy for the relative motion is $E_T - E_t = E$. In the coordinate system in which the centre of mass is at rest, $E_t = 0$ and then E is the total energy of the system. Thus, the Schrödinger equation for relative motion is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\,\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.35}$$

In the following sections we shall consider two important systems of two particles, the rigid rotator and hydrogen atom.

5.3 RIGID ROTATOR

A *rigid rotator* consists of two masses m_1 and m_2 separated by a fixed distance r. Consider the rotation of the system about an axis passing through the centre of mass and perpendicular to the plane containing the two masses. For free rotation, the potential $V(r) = 0$. As r is fixed, the wave function will depend only on the angles θ and ϕ. In spherical polar coordinates, the Schrödinger equation for relative motion reduces to

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta,\phi) = E\psi(\theta,\phi) \tag{5.36}$$

or

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu r^2 E}{\hbar^2}\psi(\theta,\phi) = 0 \tag{5.37}$$

Writing

$$\frac{2\mu r^2 E}{\hbar^2} = \frac{2IE}{\hbar^2} = \lambda \tag{5.38}$$

and

$$\psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi) \tag{5.39}$$

Equation (5.37) reduces to the following two equations:

$$\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi) \tag{5.40}$$

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta(\theta) = 0 \tag{5.41}$$

where $I = \mu r^2$ is the moment of inertia of the rotator and m^2 is a constant. These equations are the same as Eqs. (5.5) and (5.7). Hence, the rigid rotator wave functions are the spherical harmonics $Y_{lm}(\theta, \phi)$. From the solution, it follows that $\lambda = l(l + 1)$. From Eq. (5.38) the energy eigenvalues are

$$E_l = \frac{l(l+1)\hbar^2}{2I}, \qquad l = 0, 1, 2, \ldots \tag{5.42}$$

This constitutes a set of quantized energy levels with $(l+1)\hbar^2/I$ separation between any two consecutive levels, (l is the quantum number of the lower state). Since $(2l+1)$ values of m are possible for a given value of l, each state is $(2l+1)$-fold degenerate.

5.4 HYDROGEN ATOM

Theory of hydrogen atom is of fundamental importance as it provides the basis for the theory of many electron systems. Also, this is the only atom for which exact solution of the Schrödinger equation is possible. For discussion we shall consider hydrogen like atom which consists of a nucleus of charge Ze and an electron of charge $-e$ separated by a distance r. The potential is Coulombic and is given by

$$V(r) = -\frac{kZe^2}{r} \tag{5.43}$$

The time-independent Schrödinger equation for relative motion is given by

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{kZe^2}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.44}$$

Radial Equation

Expressing Eq. (5.44) in spherical polar coordinates (r, θ, ϕ) and separating the variables as in Section (5.1) by writing

$$\psi(r, \theta, \phi) = R(\mathbf{r})\,\Theta(\theta)\,\Phi(\phi) \tag{5.45}$$

we get the radial equation as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - \frac{l(l+1)\hbar^2}{2\mu r^2} + \frac{kZe^2}{r}\right]R = 0 \tag{5.46}$$

The solution of the angular part is the spherical harmonics $Y_{lm}(\theta, \phi)$.

To solve Eq. (5.46), let us introduce a variable ρ and a constant λ defined by

$$\rho = \sqrt{\frac{-8\mu E}{\hbar^2}}\,r, \qquad \lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{\mu}{-2E}} \tag{5.47}$$

As E is negative for bound states, ρ and λ are real quantities. In terms of the new variable, Eq. (5.46) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\frac{1}{4} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right]R = 0 \tag{5.48}$$

Solution of the radial equation. Its asymptotic solution can be investigated first. When $\rho \to \infty$, Eq. (5.48) reduces to

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0$$

Its solutions are $R = e^{-\rho/2}$ and $e^{\rho/2}$. Out of these two solutions, only $e^{-\rho/2}$ is acceptable since $e^{\rho/2} \to \infty$ as $\rho \to \infty$. The exact solution of Eq. (5.48) be

$$R(\rho) = e^{-\rho/2}\, F(\rho) \tag{5.49}$$

Substitution of Eq. (5.49) in Eq. (5.48) gives the differential equation satisfied by $F(\rho)$ as

$$\rho^2 \frac{d^2F}{d\rho^2} + \rho(2-\rho)\frac{dF}{d\rho} + \left[\rho\lambda - l(l+1) - \rho\right]F(\rho) = 0 \tag{5.50}$$

When $\rho = 0$, we get

$$l(l+1)F(0) = 0 \quad \text{or} \quad F(0) = 0, \quad l \neq 0 \tag{5.51}$$

Therefore if we try a power series solution for $F(\rho)$ it must not contain a constant term. Hence

$$F(\rho) = \sum_{k=0}^{\infty} a_k \rho^{c+k} \tag{5.52}$$

With this value of $F(\rho)$, Eq. (5.50) reduces to

$$\sum_k a_k(\lambda - 1 - c - k)\rho^{c+k+1} + \sum_k a_k(c^2 + 2ck + k^2 + c + k - l^2 - l)\rho^{c+k} = 0 \tag{5.53}$$

Equation (5.53) is valid for all values of ρ only if the coefficient of each power of ρ vanishes separately. Equating the coefficient of ρ^c to zero, we have

$$a_0(c^2 + c - l^2 - l) = 0$$

or

$$c^2 + c - l^2 - l = 0 \qquad (\text{as } a_0 \neq 0)$$

or

$$(c - l)(c + l + 1) = 0$$

Therefore,

$$c = l \quad \text{or} \quad c = -(l+1) \tag{5.54}$$

If $c = -(l + 1)$, the first term in $F(\rho)$ would be a_0/ρ^{l+1} which tends to infinity as $\rho \to 0$. Hence $c = l$ is the only acceptable value. Setting the coefficient of ρ^{l+k+1} in Eq. (5.53) to zero, we obtain

$$a_{k+1} = \frac{l + k + 1 - \lambda}{(k+1)(k+2l+2)}a_k \tag{5.55}$$

This recursion relation allows us to determine the coefficients a_1, a_2, a_3, ... in terms of a_0 which is quite arbitrary. For large values of k, we get from Eq. (5.55)

$$\frac{a_{k+1}}{a_k} = \frac{1}{k}$$

In the expansion

$$e^{\rho} = \sum_{k=0}^{\infty} \frac{1}{k!}\rho^k = \sum_{k=0}^{\infty} A_k \rho^k$$

$$\frac{A_{k+1}}{A_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1} \underset{k\to\infty}{\longrightarrow} \frac{1}{k}$$

Hence as $k \to \infty$, the series for $F(\rho)$ behaves like $\rho^l e^{\rho}$ and

$$R(\rho) = e^{-\rho/2}\rho^l e^{\rho} = \rho^l e^{\rho/2}$$

This value of $R(\rho)$ is not acceptable and therefore the series must break off after a certain value of k, say n'. For this to happen $a_{n'+1}$ must be zero. Then, from Eq. (5.55)

$$l + n' + 1 - \lambda = 0, \qquad n' = 0, 1, 2, \ldots \tag{5.56}$$

Energy Eigenvalues

Defining a new quantum number n by

$$n = l + n' + 1 = \lambda = \frac{kZe^2}{\hbar}\sqrt{\frac{\mu}{-2E}}$$

Squaring and simplifying

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = -\frac{\mu Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots \tag{5.57}$$

Since n' and l are integers including zero

$$n = 1, 2, \ldots \tag{5.58}$$

As $n \geq l + 1$, the highest possible value of l is $n - 1$. Thus

$$l = 0, 1, 2, \ldots, (n - 1) \tag{5.59}$$

The new quantum number n is called the *principal quantum number* which determines the energy. For hydrogen $Z = 1$ and the reduced mass $\mu \approx m$, the mass of electron.

The energy E_n is the same as the one obtained by Bohr on the basis of quantum ideas. The major difference is the occurrence of the concept of stationary states and the quantization of energy as a consequence of the solution of the Schrödinger equation.

Radial Wave Functions

The above restriction in energy makes the series for $F(\rho)$ into a polynomial. Writing

$$F(\rho) = \rho^l L(\rho) \tag{5.60}$$

Equation (5.50) reduces to

$$\rho \frac{d^2L(\rho)}{d\rho^2} + (2l+2-\rho)\frac{dL(\rho)}{d\rho} + (n-l-1)\,L(\rho) = 0 \tag{5.61}$$

The associated Laguerre polynomial of order p and degree $(q-p)$, denoted as $L_q^p\,(\rho)$, satisfies the equation

$$\rho \frac{d^2L_q^p}{d\rho^2} + (p+1-\rho)\frac{dL_q^p}{d\rho} + (q-p)\,L_q^p(\rho) = 0 \tag{5.62}$$

Equations (5.61) and (5.62) are identical if $L(\rho)$ is taken as $L_{n+l}^{2l+1}(\rho)$. Hence

$$R_{nl}(r) = N\, e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) \tag{5.63}$$

The normalization integral

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1$$

allows the determination of the constant N. Hence

$$\frac{n^3\hbar^6}{8\mu^3Z^3k^3e^6}|N|^2 \int_0^\infty e^{-\rho}\rho^{2l}\left(L_{n+l}^{2l+1}\right)^2 \rho^2 d\rho = 1$$

Using the orthogonal properties of associated Laguerre polynomials

$$\frac{n^3\hbar^6}{8\mu^3Z^3k^3e^6}|N|^2 \frac{2n[(n+l)!]^3}{(n-l-1)!} = 1$$

or

$$|N| = \pm\left\{\left(\frac{2Z\mu ke^2}{n\hbar^2}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} \tag{5.64}$$

Thus, the normalized radial wave functions are

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_H}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho) \tag{5.65}$$

where

$$a_H = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \tag{5.66}$$

The negative sign is selected to make R_{10} positive. As μ is approximately equal to the electron mass, $a_H \approx a_0$, the Bohr radius. Some of the radial wave functions are given in Table 5.3. It may be noted that at the origin the wave functions R_{10}, R_{20}, R_{30} are finite whereas R_{21}, R_{31}, R_{32} are zero.

Table 5.3 The First-six Radial Wave Functions of a Hydrogen-like Atom

n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/(a_0)}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/(2a_0)}$
	1	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/(2a_0)}$
3	0	$\frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+\frac{2Z^2r^2}{a_0^2}\right)e^{-Zr/(3a_0)}$
	1	$\frac{4\sqrt{2}}{54}\left(\frac{Z}{3a_0}\right)^{3/2}\frac{Zr}{a_0}\left(6-\frac{Zr}{a_0}\right)e^{-Zr/(3a_0)}$
	2	$\frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/(3a_0)}$

Wave Functions of Hydrogen-like Atom

The complete wave function for hydrogen-like atom is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{5.67}$$

where

$$n = 1, 2, 3, \ldots, \quad l = 0, 1, 2, 3, \ldots, (n-1), \quad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

The explicit form of the wave function for some of the states are

$$\psi_{100} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \tag{5.68a}$$

$$\psi_{200} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right)e^{-Zr/(2a_0)} \tag{5.68b}$$

$$\psi_{210} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a_0}\right)^{5/2} r\, e^{-Zr/(2a_0)}\cos\theta \tag{5.68c}$$

$$\psi_{21,\pm1} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} re^{-Zr/(2a_0)}(\sin\theta)e^{\pm i\phi} \tag{5.68d}$$

It may be noted that the expressions for the $l = 1$ state contain the factor r^1. The $l = 2$ states will have the factor r^2 and so on. The presence of the factor r^l makes the wave function zero at $r = 0$ except for the *s*-states.

Radial Probability Density

For the state specified by the wave function ψ_{nlm}, the probability of finding the electron in a volume element $d\tau$ is

$$|\psi_{nlm}|^2 d\tau = |R_{nl}|^2\,|Y_{lm}|^2\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

The probability of finding the electron in a thin spherical shell bounded by radii r and $(r + dr)$ is then

$$P(r)\,dr = |R_{nl}|^2\, r^2\, dr \int_0^{\pi}\int_0^{2\pi} |Y_{lm}|^2 \sin\theta\, d\theta\, d\phi$$

Since the spherical harmonics are normalized to unity

$$P_{nl}(r)\,dr = |R_{nl}|^2\, r^2\, dr \tag{5.69}$$

The *radial probability density* $P_{nl}(r)$ is defined as the probability of finding the electron of the hydrogen atom at a distance r from the nucleus. Then

$$P_{nl}(r) = r^2|R_{nl}|^2 \tag{5.70}$$

Plots of radial probability density for some of the states are illustrated in Figure 5.3.

For the ground state, a maximum probability density P_{10} exists at a radial position given by

$$\frac{dP_{10}}{dr} = 0 \quad \text{or} \quad \left(2r - \frac{2r^2}{a_0}\right)e^{-2r/a_0} = 0 \quad \text{or} \quad r = a_0$$

The maximum occurs at a distance equal to the Bohr radius from the origin. Though the radial probability density is maximum at the Bohr radius, a spherical distribution of the ground state probability cannot be overlooked.

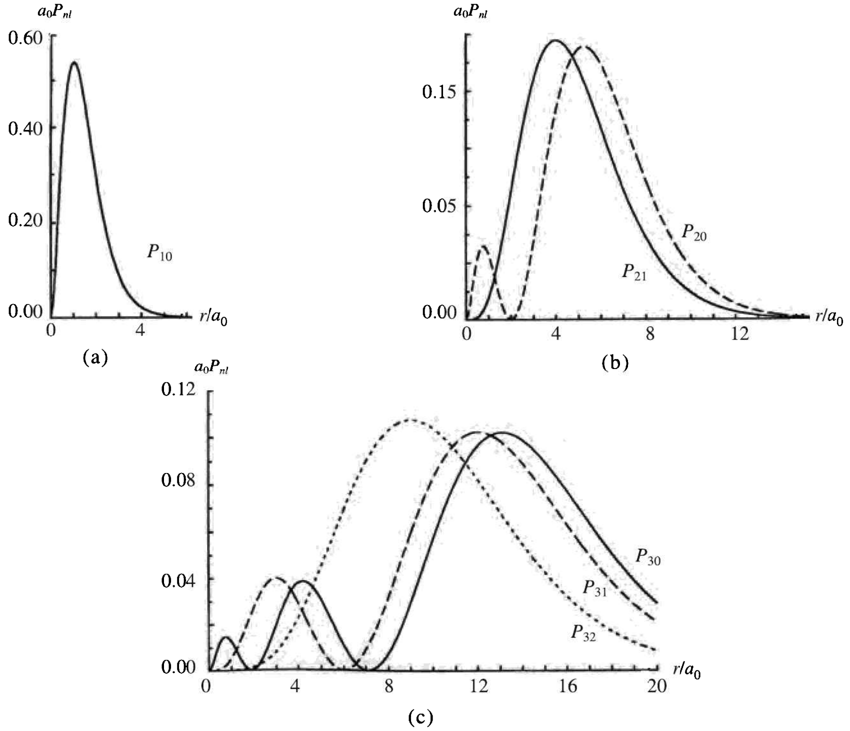


Figure 5.3 The radial probability density $P_{nl}(r)$ for the hydrogen like atom.

5.5 HYDROGENIC ORBITALS

The three quantum numbers n, l, m specify the hydrogen atom wave functions and describe the motion of the electron. The wave function ψ_{nlm} of the electron in the hydrogen atom is referred to as the *hydrogenic orbital.* When $l = 0, 1, 2, 3, \ldots$, the electron is defined as an s, p, d, f, g, etc., electron. This notation is derived from an old description of spectral series: sharp series, principal series, diffuse series and fundamental series. An electron with $l = 0$ is an s-electron and the corresponding wave function is called an s-orbital. The wave functions corresponding to $l = 1$ are the p-orbitals and those for $l = 2$ are d-orbitals and so on. Thus the symbol 3d is a shortened notation for the electronic wave function having $n = 3$, $l = 2$ and $m = 2, 1, 0, -1, -2$.

The wave function $\psi_{nlm}(r, \theta, \phi)$ can be written as the product of the two functions $R_{nl}(r)$ and $Y_{lm}(\theta, \phi)$. For a given value of l, m can have the values $l, (l - 1), (l - 2), \ldots, 1, 0, -1, \ldots, -l$ and the radial part $R_{nl}(r)$ is the same for all the $(2l + 1)$ wave functions. Hence, the wave functions are represented often by the angular part $Y_{lm}(\theta, \phi)$ only. Thus, the state having $n = 2$, $l = 1$ have $m = 1, 0, -1$ and the states are sometimes denoted as $2p_1$, $2p_0$ and $2p_{-1}$. We have already discussed in Section 5.1 how real forms of spherical harmonics are formed. The linear combination of $2p_1$ and $2p_{-1}$ gives one combination with the factor cos ϕ and the other with the factor sin ϕ (Table 5.2). The one with the cos ϕ factor is denoted as $2p_x$ and the other as $2p_y$. The $2p_0$ is denoted as $2p_z$. Similar notations are used for higher states also.

Representation of orbitals are usually done in two ways: in the first method, graphs of $Y_{lm}(\theta, \phi)$ and in the second method contour surfaces of constant probability density are drawn. Polar representations of the angular part of s, p and d orbitals are illustrated in Figure 5.4. These plots represent surfaces in three dimensions, the distance from the origin to a point on the graph will be proportional to the square of the angular part, $|Y_{lm}(\theta, \phi)|^2$ of the orbital.

The s-orbital wave functions depend only on r and therefore they are spherically symmetric. Each p-orbital has two lobes. For p_x, p_y and p_z, the lobes are along x, y and z axes with yz, xz and xy as nodal planes. Four of the five d-orbitals have four lobes and two nodal planes each. The fifth one (d_{z^2}-orbital) has two lobes along the z-axis and a ring (charge distribution) in the xy plane.

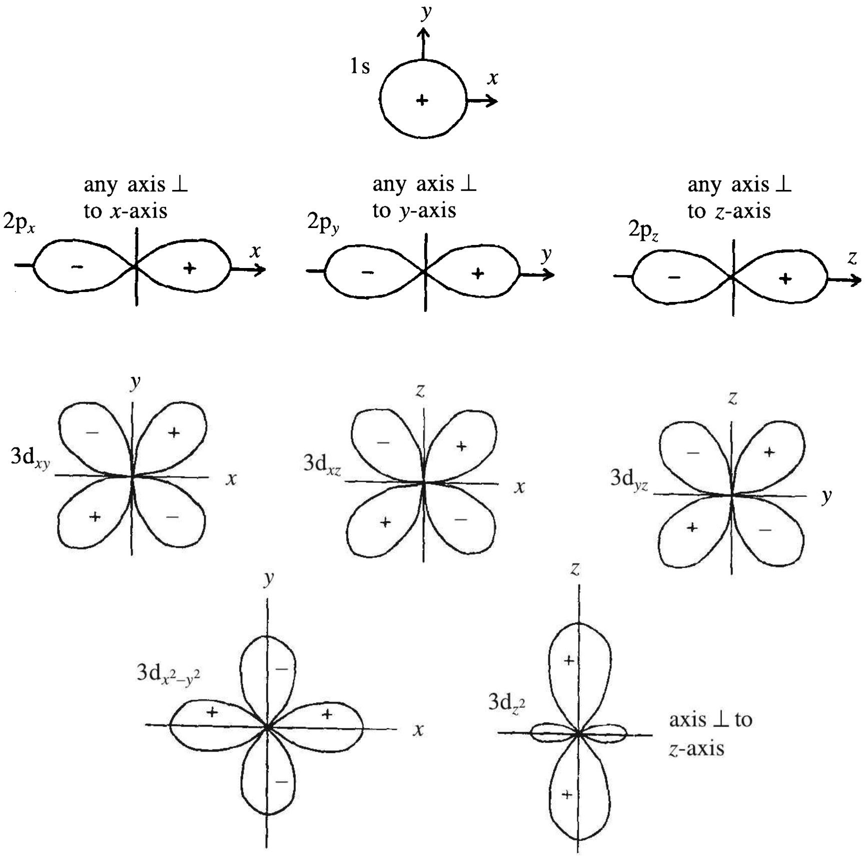


Figure 5.4 Polar representations of $|Y_{lm}(\theta,\phi)|^2$of hydrogen s, p and d orbitals. The distance of the curve from the origin is proportional to the square of the angular part of the atomic orbital.

5.6 THE FREE PARTICLE

A free particle has three degrees of freedom and its time-independent Schrödinger equation is

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5.71}$$

Plane Wave Solution

In cartesian coordinates, writing

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z) \tag{5.72}$$

Equation (5.71) can be separated into the three equations:

$$\frac{d^2X(x)}{dx^2} + k_x^2 X(x) = 0, \quad k_x^2 = \frac{2mE_x}{\hbar^2} \tag{5.73a}$$

$$\frac{d^2Y(y)}{dy^2} + k_y^2 Y(y) = 0, \quad k_y^2 = \frac{2mE_y}{\hbar^2} \tag{5.73b}$$

$$\frac{d^2Z(z)}{dz^2} + k_z^2 Z(z) = 0, \quad k_z^2 = \frac{2mE_z}{\hbar^2} \tag{5.73c}$$

where

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m} \tag{5.74}$$

The solution of Eq. (5.73a) is

$$X(x) = C \exp(ik_x x) \tag{5.75}$$

$X(x)$ will be finite for all real values of k_x. Similar solutions for y and z coordinates are possible. Combining the three solutions, we get

$$\psi(\mathbf{r}) = A \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{5.76}$$

where A is the normalization constant. In the usual sense, the eigenfunctions are not normalizable. In such situations, one can resort to what is known as *box normalization* by restricting the domain of $\psi(\mathbf{r})$ to an arbitrarily large but finite cube of side L centred at the origin. The box normalized plane wave solution is given by

$$\psi(\mathbf{r}) = \frac{1}{L^{3/2}} \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{5.77}$$

Spherical Wave Solution

Laplacian $\nabla^2\psi(\mathbf{r})$ in Eq. (5.71) is expressed in (r, θ, ϕ) coordinates and the variables are separated by writing $\psi(\mathbf{r})$, as in Eq. (5.45). The radial equation, Eq. (5.8), with $V = 0$ takes the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right)+\left[\frac{2mE}{\hbar^2}-\frac{l\left(l+1\right)}{r^2}\right]R_l(r)=0 \tag{5.78}$$

Defining

$$k^2 = \frac{2mE}{\hbar^2}, \quad \text{and} \quad \rho = kr \tag{5.79}$$

Equation (5.78) reduces to

$$\frac{d^2R_l(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR_l}{d\rho}+\left[1-\frac{l\left(l+1\right)}{\rho^2}\right]R_l(\rho)=0 \tag{5.80}$$

By writing

$$R(\rho) = Z(\rho)\rho^{-1/2} \tag{5.81}$$

Equation (5.80) can be written as

$$\frac{d^2Z(\rho)}{d\rho^2}+\frac{1}{\rho}\frac{dZ(\rho)}{d\rho}+\left\{1-\left[\frac{l+(1/2)}{\rho}\right]^2\right\}Z(\rho)=0 \tag{5.82}$$

which is Bessel's equation. Its general solution is

$$Z(\rho) = A'J_{l+(1/2)}(\rho) + B'J_{-[l+(1/2)]}(\rho)$$

Then

$$\begin{aligned} R(\rho) &= \frac{A'}{\rho^{1/2}}J_{l+(1/2)}(\rho) + \frac{B'}{\rho^{1/2}}J_{-[l+(1/2)]}(\rho) \\ &= Aj_l(\rho) + Bn_l(\rho) \end{aligned} \tag{5.83}$$

where A and B are constants, $j_l(\rho)$ and $n_l(\rho)$ are the spherical Bessel functions and spherical Neumann functions respectively, and are defined by

$$j_l(\rho) = \left(\frac{\pi}{2\rho}\right)^{1/2} J_{l+(1/2)}(\rho) \tag{5.84}$$

and

$$n_l(\rho) = \left(-1\right)^{l+1}\left(\frac{\pi}{2\rho}\right)^{1/2} J_{-[l+(1/2)]}(\rho) \tag{5.85}$$

Explicit expressions for the first-few j's and n's are

$$j_0(\rho)=\frac{\sin\rho}{\rho} \tag{5.86a}$$

$$j_1(\rho)=\frac{\sin\rho}{\rho^2}-\frac{\cos\rho}{\rho} \tag{5.86b}$$

$$j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3}{\rho^2}\cos\rho \tag{5.86c}$$

$$n_0(\rho) = -\frac{\cos\rho}{\rho} \tag{5.86d}$$

$$n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho} \tag{5.86e}$$

$$n_2(\rho) = -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos\rho - \frac{3}{\rho^2}\sin\rho \tag{5.86f}$$

For small and large values of ρ, the behaviour of $j_l(kr)$ and $n_l(kr)$ are given by

$$j_l(\rho) \underset{\rho\to 0}{\to} \frac{\rho^l}{1.3.5...(2l+1)}, \quad j_l(\rho) \underset{\rho\to\infty}{\to} \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \tag{5.87a}$$

$$n_l(\rho) \underset{\rho\to 0}{\to} -\frac{1.3.5...(2l-1)}{\rho^{l+1}}, \quad n_l(\rho) \underset{\rho\to\infty}{\to} -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right) \tag{5.87b}$$

The solution of the free particle equation corresponding to a definite energy $E = \hbar^2k^2/(2m)$ and a definite orbital angular momentum $[l(l + 1)]^{1/2}\,\hbar$ can be written as

$$\psi_{k,l}(r, \theta, \phi) = [A_l j_l(kr) + B_l n_l(kr)]Y_{lm}(\theta, \phi) \tag{5.88}$$

The most general solution corresponding to a definite energy is

$$\psi_k(r, \theta, \phi) = \sum_{l=0}^{\infty} [A_l j_l(kr) + B_l n_l(kr)]Y_{lm}(\theta, \phi) \tag{5.89}$$

The requirement that ψ must be finite everywhere makes the constant $B_l = 0$, since $n_l(kr)$ is not finite at the origin. The well-behaved wave function of free particle is then

$$\psi_k(r, \theta, \phi) = \sum_{l=0}^{\infty} A_l Y_{lm}(\theta, \phi)\, j_l(k, r) \tag{5.90}$$

If the particle moves only in the region $kr > 0$, the solution which is not regular at the origin is also as important as the regular one and we have to use Eq. (5.89). In the theory of scattering we will have occasion to use this important result.

5.7 THREE-DIMENSIONAL SQUARE-WELL POTENTIAL

The three-dimensional square well of finite depth is illustrated in Figure 5.5 and is defined by

$$V(r) = \begin{cases} -V_0 & 0 < r < a \\ 0 & r > a \end{cases} \tag{5.91}$$

where a is the radius of the sphere having spherical symmetry.

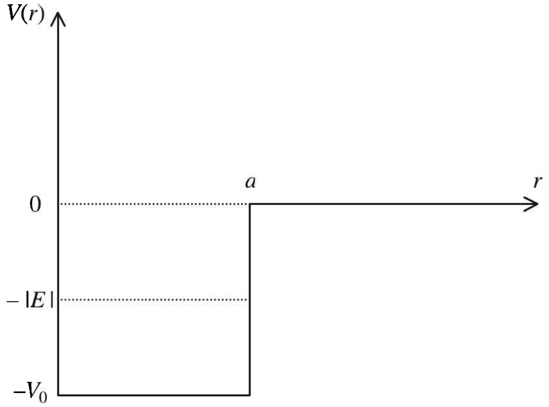


Figure 5.5 Three-dimensional square-well potential.

From Eq. (5.8), the radial equation for a state with definite angular momentum is given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right) + \left[\frac{2\mu}{\hbar^2}(V_0 - |E|) - \frac{l(l+1)}{r^2}\right]R_l = 0, \qquad 0 < r < a \tag{5.92}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_l}{dr}\right) + \left[\frac{-2\mu|E|}{\hbar^2} - \frac{l(l+1)}{r^2}\right]R_l = 0, \qquad r > a \tag{5.93}$$

The solutions of these equations for cases with finite angular momentum ($l \neq 0$) is too much involved since one has to deal with spherical Bessel and Hankel functions. Let us consider here the simpler case of s-state ($l = 0$) which is sufficient for understanding the ground state of most of the systems of interest. To solve Eqs. (5.92) and (5.93) let us write

$$R_l = \frac{u}{r}, \quad k_1^2 = \frac{2\mu|E|}{\hbar^2}, \quad k_2^2 = \frac{2\mu}{\hbar^2}(V_0 - |E|) \tag{5.94}$$

In terms of these quantities, for s-states

$$\frac{d^2u}{dr^2} + k_2^2 u = 0, \qquad 0 < r < a \tag{5.95}$$

and

$$\frac{d^2u}{dr^2} - k_1^2 u = 0, \qquad r > a \tag{5.96}$$

The respective solutions of these equations are

$$u(r) = A \sin (k_2 r) + B \cos (k_2 r) \tag{5.97}$$

and

$$u(r) = C \exp (-k_1 r) + D \exp (k_1 r) \tag{5.98}$$

where A, B, C and D are constants. As $u(r)$ must tend to zero as $r \to 0$, the constant B has to be zero. The solution $\exp (k_1 r)$ is not finite as $r \to \infty$. This makes $D = 0$. Hence the acceptable solutions are

$$u(r) = A \sin (k_2 r) \qquad 0 < r < a \tag{5.99}$$

and

$$u(r) = C \exp (-k_1 r) \qquad r > a \tag{5.100}$$

Applying the continuity conditions on $u(r)$ and du/dr at $r = a$, we have

$$A \sin (k_2 a) = C \exp (-k_1 a) \tag{5.101}$$

and

$$Ak_2 \cos (k_2 a) = -k_1 C \exp (-k_1 a) \tag{5.101a}$$

Dividing one by the other, we have

$$k_2 \cot (k_2 a) = -k_1 \tag{5.102}$$

Equation (5.102) is similar to Eq. (4.23) of the one-dimensional square well. Therefore, the graphical solution of Section 4.2 is applicable. It follows that no solution exists unless $V_0 a^2 > \pi^2 \hbar^2 / (8\mu)$ and there will be a bound state if

$$\frac{\pi^2 \hbar^2}{8\mu} < V_0 a^2 \leq \frac{9\pi^2 \hbar^2}{8\mu} \tag{5.103}$$

5.8 THE DEUTERON

An interesting application of the three-dimensional square-well potential is to the ground state of deuteron nucleus. *Deuteron* is the smallest nucleus in which a proton and a neutron are held together by the nuclear potential. Study of this two particle system helps to understand the nature of nuclear force, nuclear size, etc. The binding energy of deuteron $|E| = 2.226$ MeV and therefore k_1 can be calculated from Eq. (5.94). Equation (5.103) can then be used to determine the parameters of the square-well potential. It follows from Eq. (5.102) that

$$\cot (k_2 a) = -\frac{k_1}{k_2} = \left(\frac{|E|}{V_0 - |E|} \right)^{1/2} \tag{5.104}$$

Since the binding energy $|E|$ is small compared to the depth of the potential V_0, to get an approximate range–depth relation, we can set

$$\frac{|E|}{V_0 - |E|} \approx 0 \tag{5.105}$$

and therefore

$$\cot(k_2 a) = 0 \quad \text{or} \quad k_2 a = \frac{\pi}{2}$$

and

$$\frac{2\mu V_0}{\hbar^2} a^2 \cong \frac{\pi^2}{4} \quad \text{or} \quad V_0 a^2 = \frac{\pi^2 \hbar^2}{8\mu} = \frac{\pi^2 \hbar^2}{4m} \tag{5.106}$$

where $m = m_p = m_n$, the mass of the nucleon.

The range of the nuclear potential is approximately 1.4×10^{-15} m. Hence

$$V_0 = \frac{\pi^2 \hbar^2}{4ma^2} \cong 52 \text{ MeV} \tag{5.107}$$

which justifies our assumption $V_0 >> |E|$. Further insight can be obtained from the wave function in the region $r > a$. The form of the function $\exp(-k_1 r)$ suggests that $1/k_1$ may be taken as a measure of the spatial extent of the deuteron. That is, the probability of finding the particle is maximum in the region $0 < r < 1/k_1$

$$\frac{1}{k_1} = \left(\frac{\hbar^2}{m|E|}\right)^{1/2} \tag{5.108}$$

From Eqs. (5.106) and (5.108), we have

$$\frac{1/k_1}{a} = \frac{2}{\pi}\sqrt{\frac{V_0}{|E|}} \cong 3 \tag{5.109}$$

It means that the range of the wave function of the deuteron ($1/k_1$) is considerably greater than the range of the potential (a). That is, the deuteron is a loosely bound structure with the nucleons spending considerable time outside the range of the potential.

WORKED EXAMPLES

EXAMPLE 5.1 A particle of mass m moves in a three-dimensional box of sides a, b, c. If the potential is zero inside and infinity outside the box, find the energy eigenvalues and eigenfunctions.

As the potential is infinity, the wave function ψ outside the box must be zero. Inside the box, the Schrödinger equation is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2mE}{\hbar^2}\psi(x, y, z) = 0$$

The equation can be separated into three equations by writing

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

Substituting this value of ψ and simplifying

$$\frac{d^2X(x)}{dx^2}+\frac{2m}{\hbar^2}E_xX(x)=0$$

$$\frac{d^2Y(y)}{dy^2}+\frac{2m}{\hbar^2}E_yY(y)=0$$

$$\frac{d^2Z(z)}{dz^2}+\frac{2m}{\hbar^2}E_zZ(z)=0$$

where $E = E_x + E_y + E_z$. Use of the boundary condition $X(x) = 0$ at $x = 0$ and at $x = a$ and the normalization condition gives

$$E_x = \frac{n_x^2\pi^2\hbar^2}{2ma^2}, \qquad n_x = 1, 2, 3, \ldots$$

and

$$X(x) = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi x}{a}$$

$n_x = 0$ is left out which makes $X(x)$ zero everywhere. Similar relations result for the other two equations. Combining the three, we get

$$E=\frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right); \qquad n_x, n_y, n_z = 1, 2, 3, \ldots$$

Then

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c}$$

EXAMPLE 5.2 In Example 5.1, if the box is a cubical one of side a, derive expression for energy eigenvalues and eigenfunctions. What is the zero-point energy of the system? What is the degeneracy of the first and second excited states?

The energy eigenvalues and eigenfunctions are

$$E_{n_xn_yn_z}=\frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2+n_y^2+n_z^2\right)$$

and

$$\psi_{n_xn_yn_z}(x, y, z) = \sqrt{\frac{8}{a^3}}\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{a}\sin\frac{n_z\pi z}{a}$$

Then

$$\text{Zero-point energy } E_{111} = \frac{3\pi^2\hbar^2}{2ma^2}$$

The three-independent states having quantum numbers (1, 1, 2), (1, 2, 1), (2, 1, 1) for (n_x, n_y, n_z) have the energy

$$E_{112} = E_{121} = E_{211} = \frac{6\pi^2\hbar^2}{2ma^2}$$

which is the first excited state and is three-fold degenerate. The energy of the second excited state is

$$E_{122} = E_{212} = E_{221} = \frac{9\pi^2\hbar^2}{2ma^2}$$

It is also a three-fold degenerate.

EXAMPLE 5.3 A rigid rotator is constrained to rotate about a fixed axis. Find out its normalized eigenfunctions and eigenvalues.

As the axis of rotation is always along a fixed direction, the rotator moves in a particular plane. If this plane is taken as the *xy* plane, θ is always 90° and the wave function ψ is a function of ϕ only. The Schrödinger equation now reduces to

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{d^2\psi(\phi)}{d\phi^2}\right) = E\psi(\phi)$$

or

$$\frac{d^2\psi(\phi)}{d\phi^2} = -\frac{2\mu r^2 E\psi}{\hbar^2} = -\frac{2IE\psi}{\hbar^2}$$

or

$$\frac{d^2\psi(\phi)}{d\phi^2} = -m^2\psi(\phi), \quad \text{where} \quad m^2 = \frac{2IE}{\hbar^2}$$

The solution of this equation is

$$\psi(\phi) = A \exp\,(im\phi), \qquad m = 0, \pm 1, \pm 2, \ldots$$

The energy eigenvalues are given by

$$E_m = \frac{\hbar^2 m^2}{2I}, \quad m = 0, \pm 1, \pm 2, \ldots$$

Normalized eigenfunctions are

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}}\exp\,(im\phi), \qquad m = 0, \pm 1, \pm 2, \ldots$$

EXAMPLE 5.4 Calculate the energy difference between the stationary states $l = 1$ and $l = 2$ of the rigid molecule H_2. Use Bohr frequency rule to estimate the frequency of radiation involved during transition between these two states. Suggest a method for determining the bond length of hydrogen molecule.

The energy of a rigid rotator is given by

$$E_l = \frac{l(l+1)\hbar^2}{2I}, \qquad l = 0, 1, 2, \ldots$$

Then

$$E_1 = \frac{\hbar^2}{I} \quad \text{and} \quad E_2 = \frac{3\hbar^2}{I}$$

According to Bohr's frequency rule

$$\nu = \frac{E_2 - E_1}{h} = \frac{2\hbar^2}{Ih} = \frac{h}{2\pi^2 I}$$

where

$$\text{Moment of inertia } I = \mu r^2 = \frac{mm}{m+m} r^2 = \frac{m}{2} r^2$$

Here m is the mass of hydrogen atom and r is the bond length of hydrogen molecule. Substituting this value of I

$$\nu = \frac{h}{\pi^2 m r^2} \quad \text{or} \quad r = \left(\frac{h}{\pi^2 m \nu}\right)^{1/2}$$

EXAMPLE 5.5 Solve the time-independent Schrödinger equation for a three-dimensional harmonic oscillator whose potential energy is

$$V = \frac{1}{2}(k_1 x^2 + k_2 y^2 + k_3 z^2)$$

The theory we developed for a linear harmonic oscillator can easily be extended to the case of three-dimensional oscillator. The Schrödinger equation for the system is

$$\frac{-\hbar^2}{2m}\nabla^2 \psi(x,y,z) + V\psi(x,y,z) = E\psi(x,y,z)$$

This equation can be separated into three equations by writing the wave function

$$\psi(x,y,z) = X(x)\, Y(y)\, Z(z)$$

The Schrödinger equation now separates into three equations of the form

$$\frac{d^2X(x)}{dx^2} + \frac{2m}{\hbar^2}\left(E_x - \frac{1}{2}m\omega_x^2 x^2\right)X(x) = 0$$

$$\frac{d^2Y(y)}{dy^2} + \frac{2m}{\hbar^2}\left(E_y - \frac{1}{2}m\omega_y^2 y^2\right)Y(y) = 0$$

$$\frac{d^2Z(z)}{dz^2} + \frac{2m}{\hbar^2}\left(E_z - \frac{1}{2}m\omega_z^2 z^2\right)Z(z) = 0$$

where $E_x + E_y + E_z = E$, the total energy of the system, and

$$\omega_x = \sqrt{\frac{k_1}{m}}, \qquad \omega_y = \sqrt{\frac{k_2}{m}}, \qquad \omega_z = \sqrt{\frac{k_3}{m}}$$

Using the results of linear harmonic oscillator (Section 4.7)

$$E_x = \left(n_x + \frac{1}{2}\right)\hbar\omega_x, \qquad n_x = 0, 1, 2, \ldots$$

$$E_y = \left(n_y + \frac{1}{2}\right)\hbar\omega_y, \qquad n_y = 0, 1, 2, \ldots$$

$$E_z = \left(n_z + \frac{1}{2}\right)\hbar\omega_z, \qquad n_z = 0, 1, 2, \ldots$$

The eigenfunctions are given by

$$\psi_{n_x n_y n_z} = N H_{n_x}(\xi x) H_{n_y}(\eta y) H_{n_z}(\zeta z) \exp\left[-\frac{1}{2}\left(\xi^2 x^2 + \eta^2 y^2 + \zeta^2 z^2\right)\right]$$

where N is the normalization constant and

$$\xi = \left(\frac{m\omega_x}{\hbar}\right)^{1/2}, \qquad \eta = \left(\frac{m\omega_y}{\hbar}\right)^{1/2}, \qquad \zeta = \left(\frac{m\omega_z}{\hbar}\right)^{1/2}$$

Use of Eq. (4.92) gives

$$N = \frac{\xi^{1/2}\eta^{1/2}\zeta^{1/2}}{\pi^{3/4}\left(2^{n_x+n_y+n_z}\, n_x!\, n_y!\, n_z!\right)^{1/2}}$$

EXAMPLE 5.6 For the ground state of the hydrogen atom, evaluate the expectation value of the radius vector r of the electron.

Wave function of the ground state

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\langle r\rangle = \int \psi_{100}^* r \psi_{100}\, d\tau = \frac{1}{\pi a_0^3}\int_0^\infty r^3 e^{-2r/a_0}\, dr \int_0^\pi \int_0^{2\pi} \sin\theta\, d\theta\, d\phi$$

The integration over the angular coordinates gives 4π. Using the relation in Appendix A-9, the r-integral can be evaluated

$$\langle r\rangle = \frac{4}{a_0^3}\frac{3!}{(2/a_0)^4} = \frac{3}{2}a_0$$

The expectation value of r in the ground state of hydrogen atom is $3a_0/2$.

EXAMPLE 5.7 Show that the three 2p-eigenfunctions of hydrogen atom are orthogonal to each other.

We have the three 2p-eigenfunctions (Eq. 5.68c and 5.68d)

$$\psi_{210} = c_1 r e^{-r/2a_0} \cos\theta$$

and

$$\psi_{21,\pm 1} = c_2 r e^{-r/2a_0} (\sin\theta)\, e^{\pm i\phi}$$

where c_1 and c_2 are constants. The ϕ-dependent part of $\psi^*_{21,1}\,\psi_{21,-1}$ gives $e^{-2i\phi}$. The corresponding ϕ integral becomes

$$\int_0^{2\pi} e^{-2i\phi}\, d\phi = \frac{1}{-2i}\left[e^{-2i\phi}\right]_0^{2\pi} = 0$$

$$\text{The } \phi\text{-integral of } \int \psi^*_{210}\,\psi_{211}\, d\tau = \int_0^{2\pi} e^{i\phi}\, d\phi = 0$$

$$\text{The } \phi\text{-integral of } \int \psi^*_{210}\psi_{21,-1}\, d\tau = \int_0^{2\pi} e^{-i\phi}\, d\phi = 0$$

Hence the three $2p$-eigenfunctions of hydrogen atom are orthogonal to each other.

EXAMPLE 5.8 Prove that the 1s, 2p and 3d orbitals of a hydrogen-like atom show a single maximum in the radial probability curves. Obtain the values at which these maxima occur.

The radial probability density $P_{nl} = r^2|R_{nl}|^2$, where

$$R_{10} = (\text{constant}) \exp\left(-\frac{Zr}{a_0}\right)$$

$$R_{21} = (\text{constant})\; r \exp\left(-\frac{Zr}{2a_0}\right)$$

$$R_{32} = (\text{constant})\; r^2 \exp\left(-\frac{Zr}{3a_0}\right)$$

P_{nl} will be maximum when $dP_{nl}/dr = 0$. Therefore

$$\frac{dP_{10}}{dr} = 0 = (\text{constant})\left(2r - \frac{2Zr^2}{a_0}\right)\exp\left(-\frac{2Zr}{a_0}\right), \quad \text{or} \quad r = \frac{a_0}{Z}$$

$$\frac{dP_{21}}{dr} = 0 = (\text{constant})\left(4r^3 - \frac{Zr^4}{a_0}\right)\exp\left(-\frac{Zr}{a_0}\right), \quad \text{or} \quad r = \frac{4a_0}{Z}$$

In the same way

$$\frac{dP_{32}}{dr} = 0 \text{ gives } r = \frac{9a_0}{Z}$$

In general, $r_{\max} = \dfrac{n^2 a_0}{Z}$.

Note: The result $r_{\max} = a_0/Z$ suggests that the 1s – orbital of other atoms shrink in proportion to the increase in atomic number.

EXAMPLE 5.9 If the interelectronic repulsion in helium is ignored, what would be its ground-state energy and wave function?

Helium atom has two electrons and $Z = 2$. The ground-state energy and wave function of hydrogen-like atom are

$$E_1 = -\frac{k^2 Z^2 m e^4}{2\hbar^2} = -13.6Z^2 \text{ eV}$$

and

$$\psi_{100} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$$

When the interelectronic repulsion is neglected, the energy of the system is the sum of the energies of the two electrons and the wave function is the product of the two functions. Then

$$\text{Energy } E = -13.6Z^2 - 13.6Z^2 = -108.8 \text{ eV}$$

and

$$\text{Wave function } \psi = \psi_1(r_1)\psi_2(r_2) = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \exp\left[-\frac{Z(r_1 + r_2)}{a_0}\right]$$

where r_1 and r_2 are the radius vector of electrons 1 and 2 respectively.

EXAMPLE 5.10 Evaluate the most probable distance of the electron of the hydrogen atom in its 2p state. What is the radial probability at that distance?

The radial probability density $P_{nl}(r) = r^2|R_{nl}|^2$, where

$$R_{21} = \left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{a_0\sqrt{3}} r \exp\left(-\frac{r}{2a_0}\right)$$

Therefore,

$$P_{21}(r) = r^2 R_{21}^2 = \frac{1}{24a_0^5} r^4 \exp\left(-\frac{r}{a_0}\right)$$

For P_{21} to be maximum

$$\frac{dP_{21}}{dr} = \frac{1}{24a_0^5}\left(4r^3 - \frac{r^4}{a_0}\right)\exp\left(-\frac{r}{a_0}\right) = 0$$

or $r = 4a_0$. The most probable distance is four times the Bohr radius.

$$P_{21}(4a_0) = \frac{32}{3a_0} \exp(-4)$$

EXAMPLE 5.11 A positron and an electron form a short-lived atom called *positronium* before the two annihilate to produce gamma rays. Calculate in electron volts, the ground-state energy of positronium.

The positron has a charge +e and mass equal to the electron mass. The mass μ in the energy expression of hydrogen atom (Eq. 5.57) is the reduced mass which for positronium atom is

$$\frac{m_e m_e}{2m_e} = \frac{m_e}{2}$$

where, m_e is the electron mass. Hence the energy of the positronium atom is half the energy of hydrogen atom:

$$E_n = -\frac{k^2 m_e e^4}{4\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots$$

The ground-state energy is then

$$\frac{-13.6}{2} \text{ eV} = -6.8 \text{ eV}$$

EXAMPLE 5.12 A mesic atom is formed by a muon of mass 207 times the electron mass, charge - e and the hydrogen nucleus. Calculate (i) the energy levels of the mesic atom (ii) radius of the mesic atom and (iii) wavelength of the $2p \rightarrow 1s$ transition.

(i) The system is similar to that of hydrogen atom. Hence the energy levels are given by

$$E_n = -\frac{\mu e^4}{(4\pi\varepsilon_0)^2\, 2\hbar^2}\frac{1}{n^2} \qquad n = 1, 2, 3, \ldots$$

where μ is the proton-muon reduced mass which is 186 m_e.

(ii) Radius of the mesic atom will also be similar to that of Bohr radius, Eq. (1.19)

$$r_1 = \frac{\hbar^2}{k\mu e^2}, \quad k = 8.984 \times 10^9 \text{ N m}^2\text{C}^{-2} \text{ (Eq. 1.16)}$$

$$= \frac{(1.05 \times 10^{-34} \text{ J.s})^2}{(8.984 \times 10^9 \text{ N m}^2\text{C}^{-2})} \times \frac{1}{(186 \times 9.1 \times 10^{-31} \text{ kg})} \times \frac{1}{(1.6 \times 10^{-19} \text{ C})^2}$$

$$= 2.832 \times 10^{-13} \text{ m} = 283.2 \times 10^{-15} \text{ m} = 283.2 \text{ fm}$$

(iii) $$E_2 - E_1 = \frac{k^2 \mu e^4}{2\hbar^2}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= \frac{(8.984 \times 10^9 \text{ Nm}^2\text{C}^{-2})^2 (186 \times 9.1 \times 10^{-31} \text{ kg}) (1.6 \times 10^{-19}\text{C})^4}{2\,(1.05 \times 10^{-34} \text{ J.s})^2} \times \frac{3}{4}$$

$$= 304527.4 \times 10^{-21} \text{ J} = 1903.3 \text{ eV}$$

$$\lambda = \frac{hc}{E_2 - E_1} = \frac{(6.626 \times 10^{-34}\ \text{J.s})\ (3 \times 10^8\ \text{m/s})}{304527.4 \times 10^{-21}\ \text{J}}$$

$$= 0.65275 \times 10^{-9}\ \text{m} = 0.653\ \text{nm}$$

EXAMPLE 5.13 A particle of mass m is in a spherically symmetric attractive potential of radius a. Find the minimum depth of the potential needed to have two bound states of zero angular momentum.

The spherically symmetric attractive potential is defined by

$$V(r) = \begin{cases} -V_0 & 0<r<a \\ 0 & r>a \end{cases}$$

When the particle is having zero angular momentum, the radial equation is given by Eqs. (5.95) and (5.96).

$$\frac{d^2u}{dr^2} + k_2^2 u = 0 \qquad 0 < r < a$$

$$\frac{d^2u}{dr^2} - k_1^2 u = 0 \qquad r > a$$

where

$$k_1^2 = \frac{2m\,|\,E\,|}{\hbar^2}; \quad k_2^2 = \frac{2m}{\hbar^2}(V_0 - |E|) \text{ and } R(r) = \frac{u}{r}$$

For solution refer section 5.7. For one bound state the depth V_0 is given by Eq. (5.103):

$$\frac{\pi^2\hbar^2}{8m} < V_0 a^2 < \frac{9\pi^2\hbar^2}{8m}$$

Hence for two bound states,

$$V_0 > \frac{9\pi^2\hbar^2}{8ma^2}$$

EXAMPLE 5.14 A rigid rotator having moments of inertia I, rotates freely in the xy plane. If ϕ is the angle between the x-axis and the rotator axis, find (i) the energy eigenvalues and eigenfunctions (ii) the angular speed (iii) $\psi(t)$ for $t > 0$ if $\psi(0) = A \cos^2 \phi$.

(i) The energy eigenvalues and eigenfunctions (refer Example 5.3) are:

$$E_m = \frac{m^2\hbar^2}{2I} \text{ and } \psi = \frac{1}{\sqrt{2\pi}}\exp(im\phi), \quad m = 0, \pm 1, \pm 2, \ldots.$$

At $t = 0$,

$$\psi(0) = A\cos^2\phi = \frac{A}{2}(1 + \cos 2\phi)$$

$$\psi(0) = \frac{A}{2} + \frac{A}{4}(e^{i2\phi} + e^{-i2\phi})$$

The first term corresponds to $m = 0$. In the second term, one term corresponds to $m = 2$ and the other one to $m = -2$.

(ii) The angular speed $\dot{\phi}$ is given by

$$E_m = \frac{1}{2}I\dot{\phi}^2 \quad \text{or} \quad \frac{m^2\hbar^2}{2I} = \frac{1}{2}I\dot{\phi}^2$$

$$\dot{\phi} = \frac{m\hbar}{I}$$

(iii) $$\psi(t) = \frac{A}{2} + \frac{A}{4}e^{2i\phi}e^{-iE_2t/\hbar} + \frac{A}{4}e^{-2i\phi}e^{-iE_{-2}t/\hbar}$$

$$= \frac{A}{2} + \frac{A}{4}\exp\left[2i\left(\phi - \frac{\hbar t}{I}\right)\right] + \frac{A}{4}\exp\left[-2i\left(\phi + \frac{\hbar t}{I}\right)\right]$$

EXAMPLE 5.15 A particle of mass m is confined to the interior of a hollow spherical cavity of radius R_1 with impenetrable walls. Find the pressure exerted on the walls of the cavity by the particle in its ground state.

The radial wave equation with $V(r) = 0$ is:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2mE}{\hbar^2} - \frac{l(l+1)}{r^2}\right]R = 0$$

For the ground state, $l = 0$. Writing

$$R(r) = \frac{\chi(r)}{r}$$

the radial equation reduces to [refer Eq. (5.17)]

$$\frac{d^2\chi}{dr^2} + k^2\chi = 0, \quad k^2 = \frac{2mE}{\hbar^2}, \quad r < R$$

The solution of this equation is:

$$\chi = A \sin kr + B \cos kr \text{ , } A \text{ and } B \text{ are constants.}$$

R is finite at $r = 0$. That is at $r = 0$, $\chi = Rr = 0$. This leads to $B = 0$. Hence

$$\chi = A \sin kr$$

The condition that $R = 0$ at $r = R_1$ gives

$$0 = A \sin kR_1$$

As A cannot be zero,

$$kR_1 = n\pi \quad \text{or} \quad k = \frac{n\pi}{R_1}, \quad n = 1, 2, 3, \ldots$$

Hence the solution is:

$$\chi = A \sin \frac{n\pi r}{R_1}, \quad n = 1, 2, 3, \ldots$$

Normalization gives

$$\chi_n = \sqrt{\frac{2}{R_1}} \sin \frac{n\pi r}{R_1}, \quad n = 1, 2, 3, \ldots$$

with the condition that

$$k = \frac{n\pi}{R_1} \quad \text{or} \quad E_n = \frac{\pi^2\hbar^2 n^2}{2mR_1^2}$$

The average force F exerted radially on the walls by the particle is given by

$$F = \left\langle -\frac{\partial V}{\partial R} \right\rangle = -\left\langle \frac{\partial H}{\partial R} \right\rangle = -\frac{\partial \langle H \rangle}{\partial R} = -\frac{\partial E}{\partial R}$$

The particle is in its ground state. Hence $n = 1$ and

$$F = -\frac{\partial E_1}{\partial R} = \frac{\pi^2\hbar^2}{mR_1^3}$$

The pressure exerted on the walls is:

$$p = \frac{F}{4\pi R_1^2} = \frac{\pi\hbar^2}{4mR_1^5}$$

EXAMPLE 5.16 At time $t = 0$, the wave function for hydrogen atom is:

$$\Psi(\mathbf{r}, 0) = \frac{1}{\sqrt{10}} \left(2\Psi_{100} + \Psi_{210} + \sqrt{2}\, \Psi_{211} + \sqrt{3}\, \Psi_{21,-1} \right)$$

where the subscripts are values of the quantum numbers n, l, m.

(i) What is the expectation value for the energy of the system?

(ii) What is the probability of finding the system with $l = 1$, $m = 1$?

(i) The expectation value of the energy of the system

$$\langle E \rangle = \langle \Psi | H | \Psi \rangle$$

$$= \frac{1}{10} \langle (2\Psi_{100} + \Psi_{210} + \sqrt{2}\Psi_{211} + \sqrt{3}\Psi_{21,-1}) \\ |H| (2\Psi_{100} + \Psi_{210} + \sqrt{2}\Psi_{211} + \sqrt{3}\Psi_{21,-1}) \rangle$$

$$= \frac{1}{10} \langle (2\Psi_{100} + \Psi_{210} + \sqrt{2}\Psi_{211} + \sqrt{3}\Psi_{21,-1})$$
$$| (2E_1\Psi_{100} + E_2\Psi_{210} + \sqrt{2}E_2\Psi_{211} + \sqrt{3}E_2\Psi_{21,-1}) \rangle$$

$$= \frac{1}{10}\left(4E_1 + E_2 + 2E_2 + 3E_2\right) = \frac{1}{10}(4E_1 + 6E_2)$$

Since $E_1 = -13.8$ eV and $E_2 = -3.4$ eV

$$\langle E \rangle = \frac{1}{10}(-54.4 \text{ eV} - 20.4 \text{ eV}) = -7.48 \text{ eV}$$

(ii) The required probability is given by

$$P = \frac{2}{10}\langle 211 | 211 \rangle = \frac{2}{10} = \frac{1}{5}$$

REVIEW QUESTIONS

1. What are spherical harmonics? Are they mutually orthogonal?
2. Are the rigid rotator energy levels degenerate? Explain.
3. Assuming the oxygen molecule to be rigid, give a method of determining its bond length.
4. List the quantum numbers required to specify the state of the electron in the hydrogen atom. What are their allowed values?
5. What is angular momentum quantum number? Why is it called so?
6. What is magnetic quantum number? Explain its significance.
7. What are atomic orbitals? Explain some of the uses of atomic orbitals.
8. What are p and d-orbitals? Give polar representations of their angular part.
9. For what states of the hydrogen atom, the electron's probability density distribution spherically symmetric.
10. Name the quantum system for which the spacing between adjacent energy levels (i) increases as energy increases, (ii) increases as energy decreases and (iii) remains constant as energy increases.
11. What is positronium? Why is its energy eigenvalues are half of the energy eigenvalues of the hydrogen atom?
12. A negative muon can take the place of electron around a nucleus. Muonic atoms have hydrogen-like spectra with energy eigenvalues higher by a factor of about $200Z^2$. Explain.
13. Unlike the finite square-well potential, the Coulomb potential gives an infinite number of bound states. Why?

14. The eigenfunctions of hydrogen atom which we determined do not form a complete set. Why?

PROBLEMS

1. Neglecting electron spin degeneracy, prove that the hydrogen atom energy levels are n^2 fold degenerate.
2. Calculate the expectation value of the potential energy V of the electron in the 1s state of hydrogen atom. Using this result, evaluate the expectation value of kinetic energy, T.
3. Evaluate the most probable distance of the electron of the hydrogen atom in its 3d-state.
4. In a stationary state of the rigid rotator, show that the probability density is independent of the angle ϕ.
5. Calculate the energy difference between the first-two rotational energy levels of CO molecule, if the intermolecular separation is 1.131 Å. Mass of carbon atom is 19.9217×10^{-27} kg, mass of oxygen atom is 26.5614×10^{-27} kg. Assume the molecule to be rigid.
6. What is the probability of finding the 1s-electron of the hydrogen atom at distances (i) $a_0/2$ and (ii) a_0 from the nucleus.
7. What is the probability of finding the 2s-electron of hydrogen atom at a distance of (i) a_0 from the nucleus (ii) $2a_0$ from the nucleus?
8. For hydrogen atom in a stationary state defined by quantum numbers n, l and m, prove that

$$\langle r\rangle = \int_0^\infty r^3 |R_{nl}|^2 \, dr$$

9. Calculate the size, i.e. $\langle r^2\rangle^{1/2}$ for the hydrogen atom in its ground state.
10. Estimate the value of $(\Delta r)^2$ for the ground state of hydrogen atom.
11. Calculate the number of revolutions per second which a rigid diatomic molecule makes when it is in the (i) $l = 2$ state (ii) $l = 5$ state; given that the moment of inertia of the molecule is I.
12. In Worked Example 5.5, if the oscillator is isotropic (i) what would be the energy eigenvalues? (ii) what is the degeneracy of the state n?
13. Find the number of energy states and energy levels in the range $E < \dfrac{15h^2}{8ma^2}$ for a particle in a cubical box of side a.

14. Evaluate the radius for which the radial probability distribution $P(r)$ is maximum for the $1s$, $2p$ and $3d$ orbitals of hydrogen atom. Compare your result with that of Bohr theory. Prove that, in general, when $l = n - 1$, $P(r)$ peaks at the Bohr atom value for circular orbits

15. Evaluate the difference in wavelength $\Delta\lambda = \lambda_H - \lambda_D$ between the first line of Balmer series (λ_H) for a hydrogen atom and the corresponding line for a deuterium atom.

16. A quark having mass one third the mass of a proton is confined in a cubical box of side 1.8×10^{-15} m. Find the excitation energy in MeV from first excited state to the second excited state.

17. A system consisting of HCl molecules is at a temperature of 300 K. In the vibrational ground state, what is the ratio of number of molecules in the ground rotational state to the number in the first excited state? The moment of inertia of the HCl molecule is 2.3×10^{-47} kg m^2.

Chapter 6

Heisenberg Method

The Schrödinger form of quantum mechanics, which we have been discussing so far is based on the wave nature of matter and the assignment of differential operators to observables. In this form, differential equations have to be solved to determine the eigenvalues and eigenfunctions of operators which give all details regarding the system. An alternate form of quantum mechanics formulated by Heisenberg is equally powerful in explaining physical phenomena. In this chapter, we shall discuss some of the salient features of this form of quantum mechanics.

6.1 THE HEISENBERG METHOD

Heisenberg's form of quantum mechanics was formulated in 1925. In this approach, observables are represented by matrices in a suitable function space defined by a complete set of orthonormal functions. The resulting laws and equations of motion have a resemblance to those in classical mechanics. It may be mentioned here that matrices can also be introduced even in Schrödinger formulation.

While discussing the evolution of a physical system with time (Section 3.9), we considered three representations: Schrödinger, Heisenberg and interaction representations. In Schrödinger representation, the time dependence is assigned to the wave function or state vector, leaving the operator time independent. In the Heisenberg representation, the time dependence is shifted to operators, leaving the state vector fixed in time. Probably he attempted to base his quantum mechanics on physical quantities. He concentrated on his equation of motion for an operator given by Eq. (3.100)

$$i\hbar \frac{dA}{dt} = [A, H] \tag{6.1}$$

Another fundamental equation of Heisenberg method is his commutation relation

$$[x, p_x] = i\hbar \tag{6.2}$$

and similar relations for other pairs of variables. He used these two fundamental equations to obtain matrices for operators.

6.2 MATRIX REPRESENTATION OF WAVE FUNCTION

Consider the complete orthonormal set of functions $u_1, u_2, \ldots, u_n$ which form the basis of a coordinate system in the Hilbert space. The expansion theorem states that any function $\psi(x)$ can be expanded in terms of these basis functions as

$$|\psi(x)\rangle = \sum_i c_i |u_i\rangle \tag{6.3}$$

The coefficient c_i can be determined with the help of the equation

$$c_i = \langle u_i | \psi \rangle$$

The coefficients $c_1, c_2, \ldots, c_n$ represent the components of the vector ψ in the Hilbert space. As the u_i's are known ψ can be specified if the c_i's are known. Hence the set of the coefficients $c_1, c_2, \ldots, c_n$ is said to form a representation of the wave function with respect to the basis $u_1, u_2, \ldots, u_n$. In matrix notation, we specify the vector ψ by its components $c_1, c_2, \ldots, c_n$ and write it as a column vector

$$\psi = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \tag{6.3a}$$

This is often abbreviated as $[c_i]$ and we call it the *matrix representation of the function* ψ.

6.3 MATRIX REPRESENTATION OF OPERATOR

Consider a dynamical variable whose operator A transforms function ϕ into another function ψ. Then

$$|\psi\rangle = A|\phi\rangle \tag{6.4}$$

In terms of the basis functions

$$|\psi\rangle = \sum_{j=1}^{n} c_j|u_j\rangle, \qquad c_j = \langle u_j|\psi\rangle \tag{6.5}$$

and

$$|\phi\rangle = \sum_{j=1}^{n} a_j|u_j\rangle, \qquad a_j = \langle u_j|\phi\rangle \tag{6.6}$$

Substituting these expressions for ψ and ϕ in Eq. (6.4), we get

$$\sum_{j=1}^{n} c_j|u_j\rangle = A \sum_{j=1}^{n} a_j|u_j\rangle = \sum_{j=1}^{n} A|u_j\rangle\, a_j$$

Multiplying from left by $\langle u_i|$

$$c_i = \sum_{j=1}^{n} \langle u_i|A|u_j\rangle\, a_j = \sum_{j=1}^{n} A_{ij}\, a_j, \qquad i = 1, 2, \ldots, n \tag{6.7}$$

where

$$A_{ij} = \langle u_i|A|u_j\rangle \tag{6.8}$$

The square array of numbers

$$\begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix}$$

form the elements of a matrix. This matrix is equivalent to the complete specification of the operator A. It is the *matrix representation of the operator* A with respect to the basis $u_1, u_2, \ldots, u_n$. The matrix elements are defined by Eq. (6.8). In terms of the matrix elements of the operator A, Eq. (6.7) takes the form:

$$\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \tag{6.9}$$

Though we considered an n-dimensional function space, the formulation is applicable to an infinite-dimensional space also.

6.4 PROPERTIES OF MATRIX ELEMENTS

It is straightforward to prove that the matrix elements obey the rules of matrix algebra for addition, subtraction, multiplication, associativity and distributivity. Two important properties of operators that are needed in quantum mechanics follow from the above definition of matrix elements.

Consider a Hermitian operator A. Using Eqs. (6.8) and (3.34), the matrix element is

$$A_{ij} = \langle u_i | A | u_j \rangle = \langle A u_i | u_j \rangle = \langle u_j | A | u_i \rangle^* = A^*_{ji} \tag{6.10}$$

That is, the diagonal elements ($i = j$) are real and off-diagonal elements (i, j) and (j, i) on either side of the diagonal are complex conjugates. In other words, if the u_i's form a complete set of functions and A is a Hermitian operator, then the matrix representing the operator is Hermitian. If the functions u_i are eigenfunctions of the Hermitian operator A itself

$$A_{ij} = \langle u_i | A | u_j \rangle = a_j \langle u_i | u_j \rangle = a_j \delta_{ij} \tag{6.11}$$

That is, the resulting matrix is diagonal. This leads to the important result that the matrix representation of an operator with respect to its own eigenfuncions is diagonal and the matrix elements are the eigenvalues of the operator.

6.5 SCHRÖDINGER EQUATION IN MATRIX FORM

The time-dependent Schrödinger equation in the differential operator form is

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = H \Psi(r, t) \tag{6.12}$$

In terms of the basis vectors $|u_i\rangle$

$$\Psi(r, t) = \sum_{j=1} c_j(t)\, u_j(r) \tag{6.13}$$

With this value of Ψ, Eq. (6.12) becomes

$$i\hbar \frac{d}{dt} \sum_j c_j(t) u_j(r) = H \sum_j c_j(t) u_j(r)$$

Operating from left by $\langle u_i|$, we get

$$i\hbar \frac{d}{dt} \sum_j c_j(t) \left\langle u_i | u_j \right\rangle = \sum_j \left\langle u_i | H | u_j \right\rangle c_j(t)$$

or

$$i\hbar \frac{dc_i(t)}{dt} = \sum_j H_{ij} c_j(t), \qquad i = 1, 2, \ldots \tag{6.14}$$

where H_{ij} are the matrix elements of the Hamiltonian. Thus, the Schrödinger equation in matrix form constitutes a system of simultaneous differential equations for the time-dependent expansion coefficients $c_i(t)$.

6.6 EIGENVALUE PROBLEMS

A quantum mechanical problem can be formulated either in differential equation form or in matrix form. We have already seen the differential equation formulation in earlier chapters. In both the forms, the solution consists of finding the eigenvalues and eigenfunctions of the operator associated with the observable. If the problem is solved in the differential equation form for the eigenvalues and eigenfunctions, one can use these orthonormal eigenfunctions as the basis for the matrix representation of the operator. We then get the matrix of the operator in the diagonal form with the eigenvalues as diagonal elements.

For matrix representation with arbitrary basis functions, consider the eigenvalue equation of the operator A with eigenvalue a

$$A\psi = a\psi \tag{6.15}$$

Expanding the arbitrary eigenfunction ψ in terms of the complete set of orthonormal kets, $|u_i\rangle$, $i = 1, 2, \ldots, n$, we get

$$\sum_{j=1}^{n} c_j A|u_j\rangle = a \sum_{j=1}^{n} c_j|u_j\rangle$$

Operating from left by $\langle u_i|$, we have

$$\sum_{j=1}^{n} c_j\langle u_i|A|u_j\rangle = a \sum_{j=1}^{n} c_j\langle u_i|u_j\rangle$$

Therefore,

$$\sum_{j=1}^{n} A_{ij}\, c_j = ac_i, \qquad i = 1, 2, \ldots, n \tag{6.16}$$

The matrix form of Eq. (6.16) is

$$\begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = a \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \tag{6.17}$$

Equation (6.17), called the *matrix eigenvalue equation* of the operator A, represents the n linear homogeneous equations:

$$\begin{aligned} (A_{11}-a)c_1 + {} & A_{12}c_2 + \cdots + A_{1n}c_n = 0 \\ A_{21}c_1 + {} & (A_{22}-a)c_2 + \cdots + A_{2n}c_n = 0 \\ \vdots \qquad & \qquad \vdots \qquad\qquad \vdots \qquad \vdots \\ A_{n1}c_1 + {} & A_{n2}c_2 + \cdots + (A_{nn}-a)c_n = 0 \end{aligned} \tag{6.18}$$

For a nontrivial solution of these simultaneous equations, the secular determinant must vanish

$$\begin{vmatrix} A_{11}-a & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22}-a & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn}-a \end{vmatrix} = 0 \tag{6.19}$$

Expansion of the determinant gives a polynomial of nth degree in a. It has n possible solutions, the n eigenvalues of the operator A. For each eigenvalue, Eq. (6.18) can be solved for the c_i's which gives the eigenfunction in the form of a column matrix.

The eigenvalues of the matrix eigenvalue problem will be independent of the representation used to solve it. As mentioned, if one uses a representation based on the normalized eigenfunctions of the operator itself, the resulting matrix will be diagonal. If one uses the eigenfunctions of the Hamiltonian

$$\Psi_n = \psi \exp\left(-\frac{iE_n t}{\hbar}\right) \tag{6.20}$$

for a representation

$$A_{mn}(t) = \langle \Psi_m | A | \Psi_n \rangle = \exp\left[\frac{i(E_m - E_n)t}{\hbar}\right] \langle \psi_m | A | \psi_n \rangle$$

$$= A_{mn}(0) \exp\left(\frac{i\omega_{mn} t}{\hbar}\right) \tag{6.21}$$

where

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \tag{6.22}$$

is often referred to as the *transition frequency* between states m and n.

To simplify notation, one often derives all relations for matrix elements which are independent of time and then generalize, since exactly similar relations hold for matrices which depend on time.

6.7 UNITARY TRANSFORMATIONS

Transformation of a wave function or state vector Ψ describing a system into another wavefunction or state vector Ψ' is often required. Let a wave vector $|\Psi\rangle$ describing the state of a system is transformed into another state vector $|\Psi'\rangle$ by allowing a unitary operator U to operate on Ψ. The new state vector also gives a complete description of the state. Transformations defined by unitary operators are called *unitary transformations*.

Consider two wave functions Ψ and Φ of a system. When a unitary transformation is applied on both Ψ and Φ, we get

$$\Psi' = U\Psi \quad \text{and} \quad \Phi' = U\Phi \tag{6.23}$$

Let A be a linear Hermitian operator such that

$$A\Psi = \Phi \tag{6.24}$$

Writing $A'\Psi' = \Phi'$, we get

$$A'\,U\Psi = U\Phi = UA\Psi \quad \text{or} \quad A'U = UA \tag{6.25}$$

Multiplying from right by $U^\dagger$

$$A' = UAU^\dagger \quad \text{or} \quad A = U^\dagger A'U \tag{6.26}$$

One can easily prove the following results regarding unitary transformations:

1. If A is Hermitian, A' is also Hermitian.
2. Operator equations remain unchanged in form.
3. The eigenvalues of A and A' are the same.
4. Expectation value remains unchanged in a unitary transformation.
5. The normalization is preserved in such transformation.

Change of Basis

Choice of a basis for matrix representation is purely arbitrary. As different representations are possible, transformation from one complete orthonormal set of basis functions to another has to be considered.

Let the two set of basis functions be $\{u_i\}$ and $\{v_i\}$, $i = 1, 2, \ldots, n$. It is obvious that one can expand the u_i's in terms of the other

$$u_n = \sum_m U_{mn} v_m \tag{6.27}$$

where the expansion coefficient

$$U_{mn} = \langle v_m | u_n \rangle \tag{6.28}$$

It can now be proved that the set of coefficients U_{mn} are the elements of a unitary matrix.

$$\begin{aligned}(UU^\dagger)_{mn} &= \sum_k U_{mk}\,(U^\dagger)_{kn} = \sum_k U_{mk}\,U^*_{nk} \\ &= \sum_k \langle v_m|u_k\rangle \langle v_n|u_k\rangle^* \\ &= \sum_k \langle v_m|u_k\rangle\,\langle u_k|v_n\rangle \\ &= \langle v_m|v_n\rangle \\ &= \delta_{mn}\end{aligned} \tag{6.29}$$

Hence, U is a unitary matrix. In matrix notation

$$UU^{\dagger} = I \tag{6.30}$$

Let a wave function ψ is represented in the basis $\{u_n\}$ by the coefficients c_n forming a column vector c and in the basis $\{v_m\}$ by the coefficients b_m forming a column vector b. That is,

$$|\psi\rangle = \sum_n c_n|u_n\rangle, \qquad c_n = \langle u_n|\psi\rangle \tag{6.31}$$

and

$$|\psi\rangle = \sum_m b_m|v_m\rangle, \qquad b_m = \langle v_m|\psi\rangle \tag{6.32}$$

Substituting the value of $|\psi\rangle$ from Eq. (6.31) in Eq. (6.32), we get

$$b_m = \sum_n \langle v_m|u_n\rangle\, c_n = \sum_n U_{mn}\, c_n \tag{6.33}$$

In matrix notation

$$b = Uc \tag{6.34}$$

Next, we shall investigate how a matrix changes during a change of basis. Let A and A' be matrices representing an operator A in the basis $\{u_n\}$ and $\{v_n\}$, respectively. Then

$$A_{kl} = \langle u_k|A\,|u_l\rangle \text{ and } A'_{mn} = \langle v_m|A\,|v_n\rangle \tag{6.35}$$

Expanding $|v_m\rangle$ and $|\,v_n\rangle$ in terms of $|\,u\rangle$ and replacing the expansion coefficients, we have

$$|v_m\rangle = \sum_k d_k|\,u_k\rangle = \sum_k \langle u_k|\,v_m\rangle|\,u_k\rangle$$

and

$$|\,v_n\rangle = \sum_l f_l|\,u_l\rangle = \sum_l \langle u_l|\,v_n\rangle|\,u_l\rangle$$

Substituting these values of $|v_m\rangle$ and $|v_n\rangle$ in Eq. (6.35)

$$\begin{aligned} A'_{mn} &= \sum_k \sum_l \langle u_k|v_m\rangle^* \langle u_k|A\,|u_l\rangle\ \langle u_l|v_n\rangle \\ &= \sum_k \sum_l \langle v_m|u_k\rangle \langle u_k|A\,|u_l\rangle\ \langle u_l|v_n\rangle \\ &= \sum_k \sum_l U_{mk}\, A_{kl}\, (U^{\dagger})_{ln} \end{aligned} \tag{6.36}$$

In matrix form, we get

$$A' = UAU^{\dagger} \quad \text{or} \quad A = U^{\dagger} A'U \tag{6.37}$$

That is, the same unitary transformation that transforms one complete set of vectors into another transforms the matrix representation of an operator from one set into the other through Eq. (6.37).

6.8 LINEAR HARMONIC OSCILLATOR: MATRIX METHOD

As an example of matrix method, let us consider a linear harmonic oscillator which we have already solved by differential equation and operator methods. Its Hamiltonian is

$$H = \frac{p^2}{2m_0} + \frac{1}{2} m_0\omega^2 x^2 \tag{6.38}$$

where ω is the frequency of the oscillator. The operators p and x are infinite Hermitian matrices satisfying the fundamental commutation relation in Eq. (6.2). The equation of motion, Eq. (6.1), for the operator x in the Heisenberg picture is

$$\begin{aligned} i\hbar \frac{dx}{dt} &= [x, H] \\ &= \frac{1}{2m_0}\left[x, p^2\right] + \frac{1}{2} m_0\omega^2 \left[x, x^2\right] \\ &= \frac{1}{2m_0}\left(p\,[x, p] + [x, p]\,p\right) \end{aligned}$$

Therefore,

$$i\hbar \frac{dx}{dt} = \frac{i\hbar p}{m_0}$$

or

$$\dot{x} = \frac{p}{m_0} \tag{6.39}$$

In the same way

$$\dot{p} = -m_0\omega^2 x \tag{6.40}$$

Differentiating Eq. (6.39) with respect to t and combining it with Eq. (6.40), we have

$$\ddot{x} + \omega^2 x = 0 \tag{6.41}$$

In matrix form, this equation can be written as

$$(\ddot{x})_{mn} + \omega^2 x_{mn} = 0 \tag{6.42}$$

It follows from Eq. (6.21)

$$x_{mn}(t) = x_{mn}(0) \exp\,(i\omega_{mn}\,t) \tag{6.43}$$

where $\omega_{mn} = (E_m - E_n)/\hbar$. From Eq. (6.43), we have

$$(\ddot{x})_{mn} = -\omega^2_{mn}\, x_{mn}(0) \exp\,(i\omega_{mn}t) = -\omega^2_{mn}\, x_{mn} \tag{6.44}$$

Combining Eqs. (6.42) and (6.44)

$$(\omega_{mn}^2 - \omega^2)\, x_{mn}(t) = 0 \quad \text{or} \quad (\omega_{mn}^2 - \omega^2)\, x_{mn}(0) = 0 \tag{6.45}$$

It is convenient to derive relations for matrix elements which are independent of time. Generalization is not difficult as similar relations hold for matrices which depend on time. As $\omega_{mm} = 0$, $x_{mm} = 0$. In view of Eq. (6.45), all matrix elements $x_{mn}(0)$ vanish except those for which the transition frequency $\omega_{mn} = \pm\omega$. Therefore

$$x_{mn}(0) = 0 \quad \text{if} \quad \omega_{mn} \neq \pm\omega; \quad x_{mn}(0) \neq 0 \quad \text{if} \quad \omega_{mn} = \pm\,\omega \tag{6.46}$$

That is, for a given value of m only two x_{mn} elements are nonvanishing: $n = m + 1$ and $n = m - 1$.

$$x_{m,m-1} \text{ corresponds to } \omega_{m,m-1} = \frac{E_m - E_{m-1}}{\hbar} = +\omega \tag{6.47a}$$

and

$$x_{m,m+1} \text{ corresponds to } \omega_{m,m+1} = \frac{E_m - E_{m+1}}{\hbar} = -\omega \tag{6.47b}$$

The structure of x matrix would then be

$$(x) = \begin{pmatrix} 0 & x_{01} & 0 & 0 & 0 & \cdots \\ x_{10} & 0 & x_{12} & 0 & 0 & \cdots \\ 0 & x_{21} & 0 & x_{23} & 0 & \cdots \\ 0 & 0 & x_{32} & 0 & x_{34} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{6.48}$$

The elements of the p matrix can be obtained with the help of Eqs. (6.39) and (6.43)

$$p_{mn}(0) = im_0\omega_{mn}\, x_{mn}(0) \tag{6.49}$$

In view of Eq. (6.47), the nonvanishing elements of the p matrix are

$$p_{m,m-1} = im_0\omega x_{m,m-1} \quad \text{and} \quad p_{m,m+1} = -im_0\omega x_{m,m+1} \tag{6.50}$$

The structure of the p matrix is

$$(p) = im_0\omega \begin{pmatrix} 0 & -x_{01} & 0 & 0 & 0 & \cdots \\ x_{10} & 0 & -x_{12} & 0 & 0 & \cdots \\ 0 & x_{21} & 0 & -x_{23} & 0 & \cdots \\ 0 & 0 & x_{32} & 0 & -x_{34} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{6.51}$$

The Heisenberg's equation of motion of an operator thus allows us to get the structure of the x and p matrices.

To get the elements of the x and p matrices, we have to use the other fundamental equation of Heisenberg's method. The diagonal (m, m) elements of the fundamental commutation relation, Eq. (6.2), is

$$(xp)_{mm} - (px)_{mm} = i\hbar \tag{6.52}$$

Substituting the matrices for x and p and using matrix multiplication procedures, we get

$$2im_0\omega \begin{pmatrix} x_{01}x_{10} & 0 & 0 & 0 & \cdots \\ 0 & -x_{01}x_{10}+x_{12}x_{21} & 0 & 0 & \cdots \\ 0 & 0 & -x_{12}x_{21}+x_{23}x_{32} & 0 & \cdots \\ 0 & 0 & 0 & -x_{23}x_{32}+x_{34}x_{43} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} = i\hbar\delta_{mn} \tag{6.53}$$

where δ_{mn} is the unit matrix. Equating the elements on both sides, we have

$$\left.\begin{aligned} x_{01}x_{10} &= \frac{\hbar}{2m_0\omega} \\ -x_{01}x_{10} + x_{12}x_{21} &= \frac{\hbar}{2m_0\omega} \\ -x_{12}x_{21} + x_{23}x_{32} &= \frac{\hbar}{2m_0\omega} \\ \vdots \qquad & \qquad \vdots \end{aligned}\right\} \tag{6.54}$$

Solving this system of equations, we get

$$\left.\begin{aligned} x_{01}x_{10} &= \frac{\hbar}{2m_0\omega} \\ x_{12}x_{21} &= \frac{2\hbar}{2m_0\omega} \\ x_{23}x_{32} &= \frac{3\hbar}{2m_0\omega} \\ \vdots \qquad & \qquad \vdots \\ x_{m,m+1}\, x_{m+1,m} &= \frac{(m+1)\hbar}{2m_0\omega} \\ \vdots \qquad & \qquad \vdots \end{aligned}\right\} \tag{6.55}$$

Since x is a Hermitian

$$|x_{m,m+1}|^2 = \frac{(m+1)\hbar}{2m_0\omega} \quad \text{or} \quad x_{m,m+1} = \left[\frac{(m+1)\hbar}{2m_0\omega}\right]^{1/2} \tag{6.56}$$

Then

$$x_{m,m-1} = \left(\frac{m\hbar}{2m_0\omega}\right)^{1/2} \tag{6.57}$$

From Eqs. (6.50), (6.56) and (6.57), we have

$$p_{m,\,m+1}\, p_{m+1,m} = (-im_0\omega\, x_{m,m+1})\,(im_0\omega\, x_{m+1,m}) = \frac{m_0\omega(m+1)\hbar}{2}$$

or

$$p_{m,m+1} = \left[\frac{m_0\omega(m+1)\hbar}{2}\right]^{1/2} \tag{6.58}$$

Similarly

$$p_{m,m-1} = \left(\frac{m_0\omega m\hbar}{2}\right)^{1/2} \tag{6.59}$$

Now

$$\begin{aligned}(x^2)_{nn} = (xx)_{nn} &= \sum_k x_{nk}x_{kn} = x_{n,n+1}\, x_{n+1,n} + x_{n,n-1}\, x_{n-1,n}\\ &= \frac{(n+1)\hbar}{2m_0\omega} + \frac{n\hbar}{2m_0\omega}\\ &= \frac{(2n+1)\hbar}{2m_0\omega}\end{aligned} \tag{6.60}$$

and

$$(p^2)_{nn} = \frac{m_0\omega(n+1)\hbar}{2} + \frac{m_0\omega n\hbar}{2} = \frac{m_0\omega(2n+1)\hbar}{2} \tag{6.61}$$

The Hamiltonian matrix is then

$$\begin{aligned}H_{nn} &= \frac{1}{2m_0}\frac{m_0\omega}{2}(2n+1)\hbar + \frac{m_0\omega^2}{2}\frac{(2n+1)\hbar}{2m_0\omega}\\ &= \frac{(2n+1)\hbar\omega}{2}\end{aligned} \tag{6.62}$$

The eigenvalues E_n of the Hamiltonian are given by

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots \tag{6.63}$$

which is the same as the one we obtained in Sections (4.7) and (4.8). Using Eqs. (6.56) to (6.59), one can write the explicit form of the matrices $x(0)$ and $p(0)$.

$$x(0) = \left(\frac{\hbar}{2m_0\omega}\right)^{1/2} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{6.64}$$

and

$$p(0) = \left(\frac{m_0\omega\hbar}{2}\right)^{1/2} \begin{pmatrix} 0 & -\sqrt{1} & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & -\sqrt{2} & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & -\sqrt{3} & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{4} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{6.65}$$

Thus, the energy quantization of the harmonic oscillator results from the application of the equation of motion of an operator, Eq. (6.1), along with the fundamental commutation relation in Eq. (6.2).

WORKED EXAMPLES

EXAMPLE 6.1 The base vectors of a representation are

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Construct a transformation matrix U for transformation to another representation having base vectors

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}.$$

The transformation matrix U must be such that

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Solving, we get

$$U_{11} = \frac{1}{\sqrt{2}}, \qquad U_{21} = \frac{1}{\sqrt{2}}, \qquad U_{12} = -\frac{1}{\sqrt{2}}, \qquad U_{22} = \frac{1}{\sqrt{2}}$$

Then

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}, \qquad U^\dagger = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

It follows that $UU^\dagger = 1$. Hence U is unitary.

EXAMPLE 6.2 Prove that the fundamental commutation relation $[x, p_x] = i\hbar$ remains unchanged under unitary transformation.

Let U be the unitary operator that effects the transformation. Then

$$x' = UxU^\dagger \text{ and } p_x' = Up_xU^\dagger$$

$$\begin{aligned} [x', p_x'] &= x'p_x' - p_x'x' \\ &= (UxU^\dagger)(Up_xU^\dagger) - (Up_xU^\dagger)(UxU^\dagger) \\ &= Uxp_xU^\dagger - Up_xxU^\dagger \\ &= U(xp_x - p_xx)U^\dagger \\ &= Ui\hbar U^\dagger \\ &= i\hbar UU^\dagger \\ &= i\hbar \end{aligned}$$

Hence the result.

EXAMPLE 6.3 The raising ($a^\dagger$) and lowering (a) operators of harmonic oscillator satisfy the relations

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle; \quad n = 0, 1, 2, \ldots$$

Obtain the matrices for a and $a^\dagger$.

Multiplying the first equation from left by $\langle n'|$, we get

$$\langle n'|a|n\rangle = \sqrt{n}\,\langle n'|n-1\rangle = \sqrt{n}\delta_{n',n-1}$$

This equation gives the matrix elements of a

$$\langle 0|a|1\rangle = 1; \qquad \langle 1|a|2\rangle = \sqrt{2}; \qquad \langle 2|a|3\rangle = \sqrt{3}; \ldots$$

Multiplying the second equation from left by $\langle n'|$, we have

$$\langle n'|a^\dagger|n\rangle = \sqrt{n+1}\,\langle n'|n+1\rangle = \sqrt{n+1}\ \delta_{n',n+1}$$

The matrix elements are

$$\langle 1|a^\dagger|0\rangle = 1; \qquad \langle 2|a^\dagger|1\rangle = \sqrt{2}; \qquad \langle 3|a^\dagger|2\rangle = \sqrt{3}; \ldots$$

The complete matrices are

$$a = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}, \quad a^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}$$

REVIEW QUESTIONS

1. State and explain the fundamental equations of the Heisenberg method.
2. Explain the matrix representation of wave functions.
3. Prove that the matrix representation of an operator with respect to its own eigenfunctions is diagonal and the matrix elements are the eigenvalues of the operator.
4. Show that the eigenvalues of the matrix eigenvalue problem will be independent of the representation used.
5. What is a unitary transformation? In a unitary transformation, show that (i) the operator equations remain unchanged in form (ii) the Hermitian nature of an operator is preserved (iii) normalization is preserved.
6. Explain how a matrix representation changes during a change of basis.

PROBLEMS

1. Show that the expectation and eigenvalues of operators do not change with unitary transformation.
2. A representation is given by the base vectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Construct the transformation matrix U for transformation to another representation consisting of basic vectors

$$\begin{pmatrix} \dfrac{1}{\sqrt{2}} \\ \dfrac{i}{\sqrt{2}} \end{pmatrix} \text{ and } \begin{pmatrix} \dfrac{1}{\sqrt{2}} \\ -\dfrac{i}{\sqrt{2}} \end{pmatrix}$$

Also show that the matrix is unitary.

3. For 2×2 matrices A and B, show that the eigenvalues of AB are the same as those of BA.
4. Prove the following: (i) the scalar product is invariant under a unitary transformation (ii) the trace of a matrix is invariant under unitary transformation and (iii) if $[A, B]$ vanishes in one representation, it vanishes in any other representation.
5. Show that a linear transformation which preserves length of vectors is represented by an orthogonal matrix.

Chapter 7

Symmetry and Conservation Laws

Symmetry plays an important role in understanding numerous phenomena in physics. By considering the symmetries of a physical system one can obtain certain constants of motion. These constants of motion reveal lot of information regarding the system under consideration. In this chapter, we exploit the connection between some of the important symmetry operations and the associated conservation laws.

7.1 SYMMETRY TRANSFORMATIONS

A unitary transformation (Section 6.7) is said to be infinitesimal if the associated unitary operator is very close to a unit operator. We can then write

$$U = I + i\varepsilon G \tag{7.1}$$

where I is the unit operator, ε a real arbitrary small parameter and G a Hermitian operator.

$$U^{\dagger}U = (I - i\varepsilon G^{\dagger})\,(I + i\varepsilon G) \cong I + i\varepsilon\,(G - G^{\dagger}) \tag{7.2}$$

Since ε is small, the term in ε^2 is neglected. For U to be unitary

$$G - G^{\dagger} = 0 \quad \text{or} \quad G = G^{\dagger} \tag{7.3}$$

The operator G is called the *generator* of the infinitesimal unitary transformation.

If an infinitesimal unitary transformation is performed, the transformed wave function is given by

$$\psi' = \psi + \delta\psi = (I + i\varepsilon G)\psi \tag{7.4}$$

In the case of a dynamical variable, the transformed operator

$$\begin{aligned} A' &= UAU^{\dagger} = (I + i\varepsilon G)\, A\, (I - i\varepsilon G) \\ &\cong A + i\varepsilon\, (GA - AG) \\ &= A + i\varepsilon\, [G, A] \end{aligned} \tag{7.5}$$

A dynamical variable A is said to be invariant under a unitary transformation if

$$A' = UAU^{\dagger} = A \tag{7.6}$$

It follows from Eq. (7.5) that this condition is satisfied if

$$[G, A] = 0 \tag{7.7}$$

That is, dynamical variables that commute with the generator G of the infinitesimal unitary transformation are said to be *invariant* under the transformation concerned.

A particular case of interest is when $A = H$, the Hamiltonian of the system. The condition then reduces to

$$[G, H] = 0 \tag{7.8}$$

Since G commutes with the Hamiltonian, it is a constant of motion. Consequently, observables proportional to G will also be constants of motion. A transformation that leaves the Hamiltonian invariant is called a *symmetry transformation*. Thus, the existence of a symmetry transformation implies the conservation of a dynamical variable for the system. A symmetry transformation conserves probabilities and preserves the Hermitian nature of the operator also.

The symmetries associated with geometrical operations like displacement, rotation and inversion in space and time, called *geometrical symmetries*, are the important space–time symmetries one considers normally. Out of these, the displacement in space and time and rotations in space come under *continuous symmetry* and those associated with space inversion and time reversal come under *discrete symmetry*. In the next few sections we shall discuss the nature and properties of the operators and conservation laws associated with these space–time symmetries.

7.2 TRANSLATION IN SPACE: CONSERVATION OF LINEAR MOMENTUM

Translation in Space

Consider a particle in one dimension. We shall find out the effect of translation on its wave function in the Schrödinger picture. Let S and S' be two reference frames with S' shifted from S by ρ, and x and x' be the coordinates of a point P with respect to S and S' respectively (Figure 7.1).

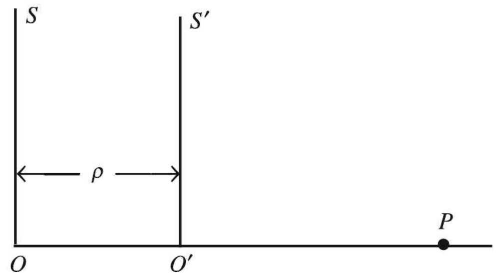


Figure 7.1 Two reference frames S and S' shifted by ρ.

ψ and ψ' be the form of a typical wave function in S and S'. We shall assume that the physical properties of an isolated system will not change by a translation of the system by an arbitrary amount ρ. Hence, for the physical point P

$$\psi(x) = \psi'(x') \quad \text{and} \quad x' = x - \rho \tag{7.9}$$

Therefore

$$\psi'(x - \rho) = \psi(x)$$

or

$$\psi'(x) = \psi(x + \rho) \tag{7.10}$$

where ρ is infinitesimal. Expanding Eq. (7.10), we get

$$\psi'(x) = \psi(x) + \rho\frac{\partial\psi(x)}{\partial x} = (1 + i\rho G_x)\psi(x) \tag{7.11}$$

where

$$G_x = -i\frac{\partial}{\partial x} = -\frac{i\hbar}{\hbar}\frac{\partial}{\partial x} = \frac{p_x}{\hbar} \tag{7.12}$$

As $\psi(x)$ and $\psi'(x)$ are the wave function of the same physical state referred to S and S', they can be taken as expressing the same physical state in terms of two different bases in the Hilbert space. The wave function $\psi(x)$ is transformed to $\psi'(x)$ by the action of the operator $i\rho G_x$ on $\psi(x)$. Therefore G_x is often referred to as the *generator of infinitesimal translation* in the x-direction. In view of Eq. (7.12), the momentum operator becomes the generator of the infinitesimal translation in space. Denoting the position eigenstate for a particle at the coordinate x measured from O and O' respectively by $|x\rangle$ and $|x\rangle'$

$$\psi(x) = \langle x|\psi\rangle \quad \text{and} \quad \psi'(x) = {}'\langle x|\psi\rangle \tag{7.13}$$

where

$$
\begin{aligned}
{}'\langle x\,|\psi\rangle &= \left(1 + \frac{i\rho p_x}{\hbar}\right)\psi(x) \\
&= \left(1 + \frac{i\rho p_x}{\hbar}\right)\langle x|\psi\rangle
\end{aligned}
$$

$$= \left\langle x \middle| \left(1 + \frac{i\rho p_x}{\hbar}\right) \middle| \psi \right\rangle \tag{7.14}$$

Therefore,

$$'\langle x| = \left\langle x \middle| \left(1 + \frac{i\rho p_x}{\hbar}\right)\right. \tag{7.15}$$

Taking conjugates,

$$|x\rangle' = \left(1 - \frac{i\rho p_x}{\hbar}\right) \left| x \right\rangle \tag{7.16}$$

which is the relation connecting the basis states $|x\rangle$ and $|x\rangle'$ defined with respect to S and the translated frame S' respectively.

Translation through some finite distance ρ could be regarded as a succession of N infinitesimal translations. Equation (7.16) then gives

$$\begin{aligned} |x\rangle' &= \lim_{N\to\infty} \left(1 - \frac{i\rho p_x}{\hbar}\right)^N \left| x \right\rangle \\ &= \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} \left(\frac{i\rho p_x}{\hbar}\right)^N \left| x \right\rangle \\ &= \exp\left(-\frac{i\rho p_x}{\hbar}\right)^N \left| x \right\rangle \end{aligned} \tag{7.17}$$

and

$$'\langle x| = \left\langle x \middle| \exp\left(-\frac{i\rho p_x}{\hbar}\right)\right. \tag{7.18}$$

The corresponding relation between the wave functions of a physical state $|\psi\rangle$ is given by

$$\psi'(x) = {}'\langle x|\psi\rangle = \left\langle x \middle| \exp\left(\frac{i\rho p_x}{\hbar}\right) \middle| \psi \right\rangle = \exp\left(\frac{i\rho p_x}{\hbar}\right)\psi(x)$$

Generalization to three dimensions is straightforward

$$\psi'(\mathbf{r}) = \exp\left(\frac{i\boldsymbol{\rho}}{\hbar}\cdot\mathbf{p}\right)\psi(\mathbf{r}) \tag{7.19}$$

where $\mathbf{p}$ is the momentum of the particle. For an n-particle system, the form of the equation will be the same as Eq. (7.19) but $\mathbf{p}$ stands for $\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 + \cdots + \mathbf{p}_n$.

Conservation of Linear Momentum

From a generalization of Eq. (7.16), the unitary infinitesimal translation operator is given by

$$U_{\mathrm{T}} = I - \frac{i\rho \cdot \mathbf{p}}{\hbar}$$

It follows immediately

$$\begin{aligned} H' &= U_{\mathrm{T}} H U_{\mathrm{T}}^{\dagger} \\ &= \left(I - \frac{i\rho \cdot \mathbf{p}}{\hbar}\right) H \left(I + \frac{i\rho \cdot \mathbf{p}}{\hbar}\right) \\ &\cong H - \frac{i\rho}{\hbar}[\mathbf{p}, H] \qquad (7.20) \end{aligned}$$

Hence, invariance of the Hamiltonian under translation in space requires that the linear momentum operator **p** must commute with *H*. This implies that the linear momentum of the system is conserved. Thus, the conservation of linear momentum of a physical system is a consequence of the translational invariance of the Hamiltonian of the system. Equation (7.20) holds good only for isolated systems wherein *H* does not contain a potential energy term which is usually a function of **r**.

7.3 TRANSLATION IN TIME: CONSERVATION OF ENERGY

For an infinitesimal time translation τ, in a similar way

$$\begin{aligned} \Psi'(x, t) &= \Psi(x, t + \tau) = \Psi(x, t) + \tau \frac{\partial \Psi}{\partial t} \\ &= \Psi(x, t) + \frac{i}{\hbar} \tau \left(-i\hbar \frac{\partial}{\partial t}\right) \Psi(x, t) \\ &= \left[1 + i\tau \left(-\frac{H}{\hbar}\right)\right] \Psi(x, t) \qquad (7.21) \end{aligned}$$

Consequently, $(-H/\hbar)$ may be defined as the generator of time translations on quantum mechanical wavefunctions.

The unitary operator corresponding to infinitesimal displacement τ in time of the system is given by

$$U = I - \frac{i\tau}{\hbar} H \qquad (7.22)$$

where *H* is the Hamiltonian which is independent of time. The invariance of the Hamiltonian under translation in time requires that

$$H' = UHU^{\dagger} = H \quad \text{or} \quad UH = HU \qquad (7.23)$$

It is obvious from the form of U that it commutes with H as it is independent of time. The time independence of H means that the total energy of the system is conserved. Thus, the total energy of the system is conserved if the system is invariant under translation in time. If H depends on time, it will not be invariant under translation in time.

7.4 ROTATION IN SPACE: CONSERVATION OF ANGULAR MOMENTUM

Rotation in Space

Let $Oxyz$ (S-frame) and $Ox'y'z'$ (S'-frame) be two coordinate systems. The system $Ox'y'z'$ is rotated anticlockwise through an angle θ about the z-axis. A point P whose coordinates with respect to the two systems (Figure 7.2), are connected by the relations:

$$x' = x\cos\theta + y\sin\theta, \quad y' = -x\sin\theta + y\cos\theta, \quad z' = z \tag{7.24}$$

When θ is infinitesimal, $\cos\theta \to 1$ and $\sin\theta \to \theta$. Then

$$x' = x + y\theta, \quad y' = -x\theta + y, \quad z' = z \tag{7.25}$$

The wavefunction at a physical point P has a definite value independent of the system of coordinate. Therefore, the form of the wave function in S and S' are related by

$$\psi'(\mathbf{r}') = \psi(\mathbf{r}) \tag{7.26}$$

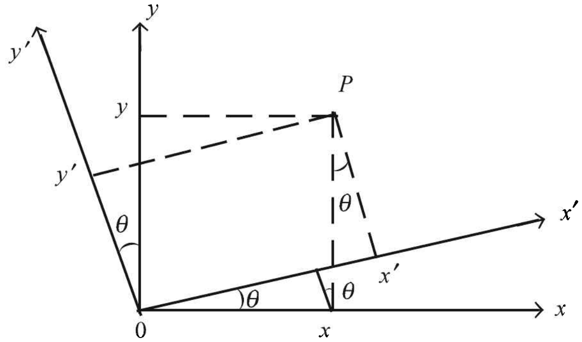


Figure 7.2 Rotation of the $Ox'y'z'$ coordinate system through an angle θ about z-axis.

Substituting for x', y', z' from Eq. (7.25), we have

$$\psi'(x + y\theta, -x\theta + y, z) = \psi(x, y, z) \tag{7.27}$$

For convenience replacing x by $x - y\theta$, and y by $y + x\theta$ on both sides

$$\psi'(x, y, z) = \psi(x - y\theta, y + x\theta, z) \tag{7.28}$$

$$= \psi(x, y, z) + \theta\left(-y\frac{\partial\psi}{\partial x} + x\frac{\partial\psi}{\partial y}\right)$$

$$= \psi(x, y, z) + \frac{i\theta}{\hbar}\left[x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)\right]\psi(x, y, z)$$

Since the operator associated with L_z is

$$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

we have

$$\psi'(\mathbf{r}) = \left(1 + \frac{i\theta}{\hbar}L_z\right)\psi(\mathbf{r}) \tag{7.29}$$

Thus, $L_z/\hbar$ is the generator of infinitesimal rotation about the z-axis. For rotation about any arbitrary axis,

$$\psi'(\mathbf{r}) = \left(1 + \frac{i\theta}{\hbar}\mathbf{n}\cdot\mathbf{L}\right)\psi(\mathbf{r}) \tag{7.30}$$

where **n** is the unit vector along the arbitrary axis.

Rotation through a finite angle θ can be considered as a succession of N infinitesimal rotations each one through an angle θ/N. Proceeding as in the case of translation in space, we get the rule for the transformation of the wave function between the basis states $|\mathbf{r}\rangle$ of position referred to S and $|\mathbf{r}\rangle'$ referred to the rotated frame S'.

$$\psi'(\mathbf{r}) = \exp\left(i\theta\frac{\mathbf{n}\cdot\mathbf{L}}{\hbar}\right)\psi(\mathbf{r}) \tag{7.31}$$

Equation (7.31) can be written in terms of $|\mathbf{r}\rangle$ and $|\mathbf{r}\rangle'$ as below

$${}'\langle\mathbf{r}|\psi\rangle = \left\langle\mathbf{r}\left|\exp\left(i\theta\frac{\mathbf{n}\cdot\mathbf{L}}{\hbar}\right)\right|\psi\right\rangle$$

or

$$|\mathbf{r}\rangle' = \exp\left(-i\theta\frac{\mathbf{n}\cdot\mathbf{L}}{\hbar}\right)\left|\mathbf{r}\right\rangle \tag{7.32}$$

For an n-particle system, the angular momentum operator **L** is the sum of angular momentum operators of the individual particles.

Conservation of Angular Momentum

The unitary operator corresponding to an infinitesimal rotation θ about an arbitrary axis **n** (Eq. 7.30) is given by

$$U_R(\mathbf{n}, \theta) = I + \frac{i\theta}{\hbar}\,\mathbf{n} \cdot \mathbf{J} \tag{7.33}$$

where **J** is the total angular momentum. For H to be invariant under the transformation, H' must equal H.

$$\begin{aligned} H' &= U_R H U_R^\dagger \\ &= \left(I + \frac{i\theta}{\hbar}\mathbf{n}\cdot\mathbf{J}\right) H \left(I - \frac{i\theta}{\hbar}\mathbf{n}\cdot\mathbf{J}\right) \\ &= H + \frac{i\theta}{\hbar}\mathbf{n}\cdot [\mathbf{J}, H] \end{aligned} \tag{7.34}$$

That is the condition for invariance of H requires that $[\mathbf{J}, H] = 0$. Thus, conservation of total angular momentum is a consequence of the rotational invariance of the system.

7.5 SPACE INVERSION: PARITY CONSERVATION

So far we have been discussing continuous symmetry operations. We now consider a discrete symmetry transformation, the reflection through the origin. This operation is called *space inversion* or *parity operation*. Associated with such an operation, there is a unitary operator, called the *parity operator* which is usually denoted by the letter P. For a single-particle wave function $\psi(\mathbf{r})$, parity operator P is defined by

$$P\psi(\mathbf{r}) = \psi(-\mathbf{r}) \tag{7.35}$$

For a system of several particles

$$P\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_n) = \psi(-\mathbf{r}_1, -\mathbf{r}_2, -\mathbf{r}_3, \ldots, -\mathbf{r}_n) \tag{7.36}$$

It follows from Eq. (7.35) that

$$P^2\psi(\mathbf{r}) = P\psi(-\mathbf{r}) = \psi(\mathbf{r}) \tag{7.37}$$

It is evident from Eq. (7.37) that $\psi(\mathbf{r})$ is an eigenfunction of P^2 with eigenvalue 1 and therefore the eigenvalues of P are -1 or $+1$. That is, the eigenfunctions either change sign (odd parity) or do not change sign (even parity) under inversion. Denoting, the eigenfunctions corresponding to even and odd eigenstates by $\psi_+(\mathbf{r})$ and $\psi_-(\mathbf{r})$, we have

$$P\psi_+(\mathbf{r}) = \psi_+(-\mathbf{r}) = \psi_+(\mathbf{r}) \tag{7.38a}$$

and

$$P\psi_-(\mathbf{r}) = \psi_-(-\mathbf{r}) = -\psi_-(\mathbf{r}) \tag{7.38b}$$

The eigenstates $\psi_+(\mathbf{r})$ and $\psi_-(\mathbf{r})$ are orthogonal, therefore

$$\langle \psi_+(\mathbf{r}) \mid \psi_-(\mathbf{r})\rangle = 0 \tag{7.39}$$

It can easily be proved that the parity operator P is Hermitian and unitary. That is

$$P = P^\dagger \quad \text{and} \quad PP^\dagger = PP = 1 \tag{7.40}$$

The effect of the parity operator P on observables $\mathbf{r}$, $\mathbf{p}$ and $\mathbf{L}$ can easily be obtained with the help of Eq. (7.35)

$$P\mathbf{r}\psi(\mathbf{r}) = -\mathbf{r}\psi(-\mathbf{r}) = -\mathbf{r}P\psi(\mathbf{r})$$

$$P\mathbf{r} = -\mathbf{r}P \quad \text{or} \quad P\mathbf{r}P^\dagger = -\mathbf{r}PP^\dagger = -\mathbf{r} \tag{7.41}$$

Similar considerations give

$$P\mathbf{p}P^\dagger = -\mathbf{p} \quad \text{and} \quad P\mathbf{L}P^\dagger = \mathbf{L} \tag{7.42}$$

If the parity operator P leaves the Hamiltonian H invariant, i.e. $PHP^\dagger = H$, then we say that the system has *space inversion symmetry* and the parity operator commutes with the Hamiltonian. In other words, the parity is conserved. If the weak nuclear interaction is neglected, the parity operator commutes with the Hamiltonian of atomic and nuclear systems. It is now well established that in strong interactions, parity is conserved. However, it is not conserved in beta decay, decay of π^+ or π^- meson, etc., as they are caused by weak interactions.

The parity of atomic wavefunctions is determined by the angular factor and is given by $(-1)^l$ (Example 7.1). For many electron atoms, the parity of an atomic state is found by adding the l values of the electrons in the electron configuration that gives rise to the state. The concept of parity is very useful for the classification of electronic states in molecules. The electronic wavefunctions are classified as even or odd on the basis of parity. For even functions we use the subscript g from the German word gerade meaning even and for odd wave functions the subscript u from the word ungerade.

7.6 TIME REVERSAL

Another important discrete transformation is one in which the time is reversed, $t' = -t$. Denoting the wave function after time reversal by $\Psi'(\mathbf{r}, t')$, we have

$$\Psi'(\mathbf{r}, t') = T\Psi(\mathbf{r}, t), \quad t' = -t \tag{7.43}$$

where T is the operator that effects the transformation. Let A be a time-independent operator associated with an observable and A' be its transform. Consider the equation

$$A\psi = \phi \tag{7.44}$$

Then

$$\phi' = TA\psi = TAT^{-1}T\psi = (TAT^{-1})T\psi = (TAT^{-1})\Psi'$$

or

$$\phi' = A'\psi' \qquad \text{where } A' = TAT^{-1} \tag{7.45}$$

We shall now investigate the effect of the operator T on observables. To be in conformity with the time-reversal invariance in classical mechanics, we require that the position operator **r** be left unchanged and the momentum operator shall change sign under time reversal. Mathematically,

$$\mathbf{r}' = T\mathbf{r}T^{-1} = \mathbf{r}, \quad \mathbf{p}' = T\mathbf{p}T^{-1} = -\mathbf{p}, \quad \mathbf{L}' = T\mathbf{L}T^{-1} = -\mathbf{L} \tag{7.46}$$

We now evaluate the fundamental commutation relation $[x', p_x']$

$$[x', p_x'] = [TxT^{-1}, Tp_xT^{-1}]$$

By virtue of Eq. (7.46)

$$TxT^{-1} = x \quad \text{and} \quad Tp_xT^{-1} = -p_x$$

Therefore

$$[x', p_x'] = [x, -p_x] = -i\hbar \tag{7.47}$$

The value of $[x', p_x']$ commutator can also be written as

$$[x', p_x'] = T[x, p_x]T^{-1} = T(i\hbar)T^{-1} \tag{7.48}$$

From Eqs. (7.47) and (7.48), we have

$$T(i\hbar)T^{-1} = -i\hbar \tag{7.49}$$

which is possible only if T operating on any number changes it into its complex conjugate. Hence, T is not a linear operator. An operator A is said to be *antilinear* if

$$A[c_1\psi_1(x) + c_2\psi_2(x)] = c_1^*A\psi_1 + c_2^*A\psi_2 \tag{7.50}$$

Let us now investigate, the effect of time reversal ($t \to t' = -t$) in the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = H\,\Psi(\mathbf{r}, t) \tag{7.51}$$

of a particle moving in a time-independent potential $V(\mathbf{r})$. Since $\mathbf{r}' = \mathbf{r}$ and $\mathbf{p}' = -\mathbf{p}$, the Hamiltonian operator for a spinless particle under time reversal is invariant. Hence

$$[T, H] = 0 \tag{7.52}$$

Operating Eq. (7.51) from left by T and noting $[T, H] = 0$

$$T\left[i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)\right] = HT\Psi(\mathbf{r}, t) \tag{7.53}$$

In view of the result $T(i\hbar) = -i\hbar T$, Eq. (7.53) reduces to

$$-i\hbar\frac{\partial}{\partial t'}\Psi'(\mathbf{r}, t') = H\Psi'(\mathbf{r}, t') \quad \text{or} \quad i\hbar\frac{\partial}{\partial t}\Psi'(\mathbf{r}, t') = H\Psi'(\mathbf{r}, t') \tag{7.54}$$

Thus, the Schrödinger equation satisfied by the time-reversed function $\Psi'(\mathbf{r}, t')$ has also the same form as the original one.

As the nonlinear operator T performs the time reversal and complex conjugation, it is possible to consider it as the product of a linear operator U and a complex conjugation operator K:

$$T = UK \tag{7.55}$$

To ensure the norm of Ψ' and Ψ equal, the linear operator U has to be unitary

$$\begin{aligned}\langle \Psi' | \Psi' \rangle &= \langle UK\Psi | UK\Psi \rangle \\ &= \langle K\Psi | U^\dagger U | K\Psi \rangle \\ &= \langle K\Psi | K\Psi \rangle \\ &= \langle \Psi | \Psi \rangle^* \\ &= \langle \Psi | \Psi \rangle \end{aligned} \tag{7.56}$$

The above simplification is possible only if $U^\dagger U = 1$. $\langle \Psi|\Psi\rangle^* = \langle \Psi|\Psi\rangle$, since the norm is real. Since U is unitary and K is antiunitary, the time-reversal operator T is antiunitary. Under time reversal, for the position operator $\mathbf{r}$ to remain unchanged and the momentum operator to change sign, the operator U should be reduced to the unit operator. This is the case in the coordinate representation. The explicit form depends on the system and type of representation.

It may be noted here that the time-reversal invariance of the Schrödinger equation results only if the commutator $[T, H] = 0$. At one time it was thought that all Hamiltonians satisfied the time reversal invariance condition. However, now it is established that Hamiltonian corresponding to weak nuclear interaction is not time-reversal invariant.

WORKED EXAMPLES

EXAMPLE 7.1 Prove that the parity of spherical harmonics $Y_{1,m}(\theta, \phi)$ is $(-1)^l$.

When a vector $\mathbf{r}$ is reflected through the origin, we get the vector $-\mathbf{r}$. In spherical polar coordinates, this operation corresponds to the following changes in the angles θ and ϕ, leaving r unchanged:

$$\theta \to (\pi - \theta) \quad \text{and} \quad \phi \to (\phi + \pi)$$

We have

$$Y_{1,m}(\theta, \phi) = C P_l^m(\cos\theta) \exp(im\phi), \ (C \text{ is constant})$$

Therefore,

$$\begin{aligned} Y_{l,m}(\pi - \theta, \phi + \pi) &= C P_l^m[\cos(\pi - \theta)] \exp[im(\phi + \pi)] \\ &= C P_l^m(-\cos\theta) \exp(im\phi) \exp(im\pi) \\ &= C P_l^m(\cos\theta)(-1)^{l+m} \exp(im\phi)(-1)^m \\ &= (-1)^l Y_{l,m}(\theta, \phi) \end{aligned}$$

During simplification we have used the result $P_n^m(-x) = (-1)^{n+m} P_n^m(x)$. That is the parity of spherical harmonics is given by $(-1)^l$.

EXAMPLE 7.2 If $\psi_+(\mathbf{r})$ and $\psi_-(\mathbf{r})$ are the eigenfunctions of the parity operator belonging to even and odd eigenstates, show that they are orthogonal.

From definition, we have

$$P\psi_+(\mathbf{r}) = \psi_+(\mathbf{r}) \quad \text{and} \quad P\psi_-(\mathbf{r}) = -\psi_-(\mathbf{r})$$

Then

$$\langle \psi_+(\mathbf{r}) | \psi_-(\mathbf{r}) \rangle = \langle \psi_+(\mathbf{r}) | PP | \psi_-(\mathbf{r}) \rangle$$

Here, we have used the result $P^2 = 1$. Since P is Hermitian

$$\langle \psi_+(\mathbf{r}) | \psi_-(\mathbf{r}) \rangle = \langle P\psi_+(\mathbf{r}) | P | \psi_-(\mathbf{r}) \rangle = -\langle \psi_+(\mathbf{r}) | \psi_-(\mathbf{r}) \rangle$$

Therefore,

$$\langle \psi_+(\mathbf{r}) | \psi_-(\mathbf{r}) \rangle = 0. \text{ Hence } \psi_+(\mathbf{r}) \text{ and } \psi_-(\mathbf{r}) \text{ are orthogonal.}$$

EXAMPLE 7.3 Use the concept of parity to find which of the following integrals are nonzero: (i) $\langle 2s | x | 2p_y \rangle$ (ii) $\langle 2p_x | x | 2p_y \rangle$. The functions in the integrals are hydrogen-like wave functions.

We have the result that the integral $\int_{-\infty}^{\infty} f(x)\, dx$ is zero if $f(x)$ is an odd function and finite if it is an even function. In $\langle 2s | x | 2p_y \rangle$ the parity of the function $\langle 2s|$ is $(-1)^0 = 1$. Hence the parity is even. The parity of the function $|2p_y\rangle$ is $(-1)^1 = -1$, which is odd. Hence the parity of the given integral is even × odd × odd which is even. The value of the integral is therefore finite. The parity of the integrand in $\langle 2p_x | x | 2p_y \rangle$ is odd × odd × odd which is odd. Hence the integral vanishes.

EXAMPLE 7.4 Obtain the generators G_z, G_x and G_y for infinitesimal rotation of a vector about z, x and y axes respectively.

The generator for infinitesimal rotation about the z-axis is the coefficient of $i\theta$ in $(1 + i\theta\, G_z)$, where θ is the infinitesimal rotation angle. Let A be a vector with components A_x, A_y, A_z. If the vector rotates about the z-axis through θ,

$$A'_x = A_x \cos\theta + A_y \sin\theta, \quad A'_y = -A_x \sin\theta + A_y \cos\theta, \quad A'_z = A_z$$

Since rotation is infinitesimal $\cos\theta \cong 1$ and $\sin\theta \cong \theta$ and the above equation in matrix form is

$$\begin{pmatrix} A'_x \\ A'_y \\ A'_z \end{pmatrix} = \begin{pmatrix} 1 & \theta & 0 \\ -\theta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} 0 & \theta & 0 \\ -\theta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right] \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$$

Comparing the coefficient of right-hand side with $1 + i\theta G_z$, we get

$$G_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Proceeding on similar lines the generators G_x and G_y for rotation about x and y-axis are given by

$$G_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \qquad G_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$$

REVIEW QUESTIONS

1. What is symmetry transformation? Prove that a symmetry transformation conserves probabilities.
2. A conservation law implies the existence of a symmetry transformation for the system. Comment.
3. Explain how the momentum operator becomes the generator of infinitesimal translation in space.
4. Prove that $L/\hbar$, where L is the angular momentum operator, is the generator of infinitesimal rotation about an arbitrary axis.
5. Wave functions possess even or odd parity. Explain.
6. Conservation of angular momentum is a consequence of the rotational invariance of the system. Substantiate.
7. Explain the effect of parity operator on the observables **r**, **p** and **L**.
8. Why time-reversal operator is not linear?
9. Discuss the effect of time reversal in the time-dependent Schrödinger equation.

PROBLEMS

1. Prove that the parity operator is Hermitian and unitary.
2. Use the concept of parity to find which of the following integrals are nonzero: (i) $\langle 2s|x^2|2p_x\rangle$ (ii) $\langle 2p_x|x^2|2p_x\rangle$ (iii) $\langle 2p|x|3d\rangle$. The functions in the integrals are hydrogen-like wave functions.
3. For a spinless particle moving in a potential $V(r)$, show that the time reversal operator T commutes with the Hamiltonian.
4. Show that the time reversal operator operating on any number changes it into its complex conjugate.
5. Show that the parity operator commute with the orbital angular momentum operator.

Chapter 8

Angular Momentum

Angular momentum is an important and interesting property of physical systems both in classical and quantum mechanics. In this chapter, we shall consider the operators representing angular momentum components and their eigenvalues, eigenvectors and matrix representation. While developing the eigenvalue theory, the necessity for half-integral quantum numbers and the concept of an intrinsic angular momentum called spin will be felt. In the end, the addition of angular momenta will also be considered.

8.1 THE ANGULAR MOMENTUM OPERATORS

In classical mechanics, the angular momentum **L** of a particle is defined as the vector product of its position vector **r** and the linear momentum **p**:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_x)\hat{k} \tag{8.1}$$

Replacing the momentum components p_q by $-i\hbar\frac{\partial}{\partial q}$, where q is the coordinate, expression for the operators of L_x, L_y and L_z can be obtained as

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{8.2a}$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{8.2b}$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{8.2c}$$

In spherical polar coordinates, the operator for the components of angular momentum and L^2 are given by

$$\begin{aligned} L_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\,\cos\phi\frac{\partial}{\partial\phi}\right) \\ L_y &= i\hbar\left(-\cos\phi\,\frac{\partial}{\partial\theta} + \cot\theta\,\sin\phi\,\frac{\partial}{\partial\phi}\right) \\ L_z &= -i\hbar\frac{\partial}{\partial\phi} \end{aligned} \tag{8.3}$$

and

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{8.4}$$

For detailed study on angular momentum one should have the commutation relations obeyed by these operators.

8.2 ANGULAR MOMENTUM COMMUTATION RELATIONS

The commutation relations of the components of **L** can easily be obtained in cartesian coordinates

$$\begin{aligned} [L_x, L_y] &= [(yp_z - zp_y), (zp_x - xp_z)] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \end{aligned} \tag{8.5}$$

In these commutators, p_q stands for $-i\hbar\frac{\partial}{\partial q}$. In the second and third terms on the right side of the Eq. (8.5), all the variables involved commute with each other. Hence both of them vanish. Since y and p_x commute with z and p_z,

$$[yp_z, zp_x] = yp_x[p_z, z] = -i\hbar yp_x \tag{8.6}$$

Based on similar arguments, we get

$$[zp_y, xp_z] = p_y x[z, p_z] = i\hbar xp_y \tag{8.7}$$

Hence

$$[L_x, L_y] = i\hbar(xp_y - yp_x) = i\hbar L_z$$

The commutators $[L_y, L_z]$ and $[L_z, L_x]$ can be obtained in the same way and we have

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y \tag{8.8}$$

That is, the components of angular momentum do not commute with one another and therefore they are not measurable simultaneously. In other words, if the system is in an eigenstate of one angular momentum component, it will not be simultaneously in an eigenstate of either of the others. These commutation relations hold for the components of total angular momentum $\mathbf{L} = \Sigma L_i$ of a system of particles also. The commutation relations in Eq. (8.8) can be written in a compact form as

$$\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L} \tag{8.9}$$

In the usual sense the vector product of a vector with itself is zero. Hence, we have to consider $\mathbf{L}$ as a vector operator and not as a usual vector. The left-hand side has to be considered as a determinant and has to be expanded before the term-by-term comparison with the right-hand side.

Next, we shall consider the commutator of L^2 with the components of $\mathbf{L}$.

$$\begin{aligned}[L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= 0 + L_y\,[L_y, L_x] + [L_y, L_x]\,L_y + L_z\,[L_z, L_x] + [L_z, L_x]\,L_z \\ &= L_y\,(-i\hbar L_z) + (-i\hbar L_z)\,L_y + i\hbar L_z L_y + i\hbar L_y L_z \\ &= 0\end{aligned}$$

Hence we conclude that,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \tag{8.10}$$

The square of the angular momentum commutes with its components. That is, the total angular momentum can be measured simultaneously with any one component. As the components among themselves are noncommuting, one cannot measure L^2, L_x, L_y, L_z simultaneously. Therefore, we cannot have a representation in which all the four are diagonal. The eigenvalue problem is therefore approached in such a way that L^2 and one of the components, say L_z, have simultaneous eigenvectors. The selection of L_z is completely arbitrary. The commutation relations in Eqs. (8.8) and (8.10) form the foundation for the theory of angular momentum.

We shall next consider the operators L_x and L_y. Instead of working with L_x and L_y, it is found more convenient to work with the operators L_+ and L_- defined by

$$L_+ = L_x + iL_y,\ L_- = L_x - iL_y \tag{8.11}$$

The operator L_+ is called the *raising operator* and L_-, the *lowering operator*; the reason for the names would be clear in Section 8.5. From the definition of L_+ and L_- it is evident that they commute with L^2. Therefore,

$$[L^2, L_+] = 0,\quad [L^2, L_-] = 0 \tag{8.12}$$

and

$$\begin{aligned}[L_z, L_+] &= [L_z, L_x] + i[L_z, L_y] \\ &= i\hbar L_y + \hbar L_x \\ &= \hbar L_+\end{aligned}$$

The other commutators can also be evaluated in the same way and we have the relations

$$\left.\begin{aligned}[L_z, L_-] &= -\hbar L_- \\ [L_x, L_+] &= -\hbar L_z \\ [L_x, L_-] &= \hbar L_z \\ [L_y, L_+] &= -i\hbar L_z \\ [L_y, L_-] &= i\hbar L_z\end{aligned}\right\} \tag{8.13}$$

We also have

$$[L_+, L_-] = 2\hbar L_z \tag{8.14}$$

and

$$L_+ L_- = L^2 - L_z^2 + \hbar L_z, \quad L_- L_+ = L^2 - L_z^2 - \hbar L_z \tag{8.15}$$

8.3 EIGENVALUES AND EIGENFUNCTIONS OF L^2 AND L_Z

The eigenvalue equation for L^2 in spherical polar coordinates can be written as

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y = \lambda\hbar^2 Y \tag{8.16}$$

where $\lambda\hbar^2$ is the eigenvalue of L^2 and Y is the corresponding eigenfunction. Rearranging, we get

$$\left[\frac{1}{\sin\theta} \left(\frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y + \lambda Y = 0 \tag{8.17}$$

which is the same as the angular part of the Schrödinger equation of a system moving in a potential $V(r)$ (Section 5.1). The solution gives $\lambda = l(l + 1)$ with eigenfunctions

$$Y = Y_{lm}(\theta, \phi) = \varepsilon \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} p_l^{|m|} (\cos\theta) e^{im\phi} \tag{8.18}$$

where

$$l = 0, 1, 2, 3, \ldots \quad \text{and} \quad m = 0, \pm 1, \pm 2, \ldots, \pm l$$

and $\varepsilon = (-1)^m$ for $m > 0$ and $\varepsilon = 1$ for $m \leq 0$. The form of L_z, in Eq. (8.3) immediately gives

$$L_z Y_{lm} = -i\hbar \frac{\partial}{\partial\phi} Y_{lm}(\theta, \phi) = m\hbar\, Y_{lm}(\theta, \phi) \tag{8.19}$$

Thus, the spherical harmonics $Y_{lm}(\theta, \phi)$ are eigenfunctions of L^2 and L_z with eigenvalues $l(l + 1)\hbar^2$ and $m\hbar$ respectively.

8.4 GENERAL ANGULAR MOMENTUM

Number of experimental results such as spectra of alkali metals, anomalous Zeeman effect, Stern–Gerlach experiment, etc., could be explained only by invoking the concept that the electron in an atom possesses an additional intrinsic angular momentum involving half integral quantum numbers. However, the definition of angular momentum based on classical physics led to the $2l + 1$ integral values $m\hbar$, $m = 0, \pm 1, \pm 2, \ldots, \pm l$ for the z-component of angular momentum. In other words, the definition of angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is not general enough to include half integral quantum numbers and therefore one may take the definition of general angular momentum as the commutation relations given by

$$\left[J_x, J_y\right] = i\hbar J_z, \quad \left[J_y, J_z\right] = i\hbar J_x, \quad \left[J_z, J_x\right] = i\hbar J_y \tag{8.20}$$

where symbol $\mathbf{J}$ is used for the general angular momentum. The components of $\mathbf{J}$ and the operators J^2, $J_+ = J_x + iJ_y$ and $J_- = J_x - iJ_y$ obey all the commutation relations derived for the operators $\mathbf{L}$, L_+ and L_-.

8.5 EIGENVALUES OF J^2 AND J_z

The square of the general angular momentum $\mathbf{J}$ commutes with its components J_x, J_y and J_z. However, the components, among themselves are noncommuting. Therefore J^2 and one component, say J_z can have simultaneous eigenkets at a time. Denoting the simultaneous eigenkets by $|\lambda m\rangle$, the eigenvalue equation for J^2 and J_z is given by

$$J^2|\lambda m\rangle = \lambda|\lambda m\rangle \tag{8.21}$$

and

$$J_z|\lambda m\rangle = m|\lambda m\rangle \tag{8.22}$$

Equation (8.21) can be written as

$$\left(J_x^2 + J_y^2\right)|\lambda m\rangle + m^2|\lambda m\rangle = \lambda|\lambda m\rangle$$

Multiplying from left by bra $\langle\lambda m|$ and rearranging

$$\langle\lambda m|J_x^2|\lambda m\rangle + \langle\lambda m|J_y^2|\lambda m\rangle = \left(\lambda - m^2\right) \tag{8.23}$$

Since J_x and J_y are Hermitian, their eigenvalues must be real and therefore the left side of Eq. (8.23) must be positive. Hence

$$\lambda - m^2 \geq 0 \quad \text{or} \quad \lambda \geq m^2 \tag{8.24}$$

Operating Eq. (8.21) from left by J_+, we get

$$J_+J^2|\lambda m\rangle = \lambda J_+|\lambda m\rangle$$

Since J^2 commutes with J_+

$$J^2J_+|\lambda m\rangle = \lambda J_+|\lambda m\rangle \tag{8.25}$$

That is, $|\lambda m\rangle$ and $J_+|\lambda m\rangle$ are eigenkets of J^2 with the same eigenvalue λ. Premultiplying Eq. (8.22) by J_+, we have

$$J_+J_z|\lambda m\rangle = mJ_+|\lambda m\rangle$$

But $[J_z, J_+] = \hbar J_+$ or $J_+J_z = J_zJ_+ - \hbar J_+$. Replacing J_+J_z in the above equation, we get

$$\left(J_zJ_+ - \hbar J_+\right)|\lambda m\rangle = mJ_+|\lambda m\rangle$$

or

$$J_zJ_+|\lambda m\rangle = (m + \hbar)J_+|\lambda m\rangle \tag{8.26}$$

Thus, $J_+|\lambda m\rangle$ is an eigenket of J_z with the eigenvalue $(m + \hbar)$ and of J^2 with the same eigenvalue λ. Since operation by J_+ generates a state with the same magnitude of angular momentum but with a z-component higher by $\hbar$, it is called a *raising operator.*

Repeated operation by J_+ increases the eigenvalue of J_z in steps. This has to be stopped at some point, otherwise the condition in Eq. (8.24) will be violated. The maximum allowed value of m for a given value of λ without violating Eq. (8.24) be μ. Then

$$J_z|\lambda\mu\rangle = \mu|\lambda\mu\rangle \tag{8.27}$$

Operation by J_+ from left gives

$$J_z J_+|\lambda\mu\rangle = (\mu + \hbar)J_+|\lambda\mu\rangle$$

Eigenvalue of $(\mu + \hbar)$ is not possible since μ is the highest eigenvalue. Hence,

$$J_+|\lambda\mu\rangle = 0$$

Premultiplying by J_- and using the result

$$J_-J_+ = J^2 - J_z^2 - \hbar J_z$$

we get

$$J_-J_+|\lambda\mu\rangle = 0 \quad \text{or} \quad \left(J^2 - J_z^2 - \hbar J_z\right)|\lambda\mu\rangle = 0$$

Therefore,

$$\left(\lambda - \mu^2 - \hbar\mu\right)|\lambda\mu\rangle = 0$$

As $|\lambda\mu\rangle \neq 0, \quad \lambda - \mu^2 - \hbar\mu = 0$. So

$$\lambda = \mu(\mu + \hbar) \tag{8.28}$$

Operating Eq. (8.27) from left by J_-, we get

$$J_-J_z|\lambda\mu\rangle = \mu J_-|\lambda\mu\rangle$$

or

$$J_zJ_-|\lambda\mu\rangle = (\mu - \hbar)J_-|\lambda\mu\rangle \tag{8.29}$$

For the maximum eigenvalue μ, we have

$$J^2|\lambda\mu\rangle = \lambda|\lambda\mu\rangle \quad \text{or} \quad J^2J_-|\lambda\mu\rangle = \lambda J_-|\lambda\mu\rangle$$

That is, $J_-|\lambda\mu\rangle$ is an eigenket of J^2 and J_z with the eigenvalues λ and $\mu - \hbar$ respectively. Hence J_- is called a *lowering operator*. J_+ and J_- together is often referred to as *ladder operators*. Repeating the lowering operation by J_-, n times, we get

$$J_z J_-^n|\lambda\mu\rangle = (\mu - n\hbar)J_-^n|\lambda\mu\rangle$$

Again there must be a cut-off value for n, otherwise the condition in Eq. (8.24) will be violated. The minimum value of m without violating the condition $\lambda \geq m^2$ be $\mu - n\hbar$. Then

$$J_z J_-^{n+1}|\lambda\mu\rangle = \left[\mu - (n+1)\hbar\right]J_-^{n+1}|\lambda\mu\rangle = 0$$

Since $[\mu - (n + 1)\hbar] \neq 0$

$$J_-^{n+1}|\lambda\mu\rangle = 0$$

or

$$J_- J_-^n|\lambda\mu\rangle = 0$$

or

$$J_+ J_- J_-^n|\lambda\mu\rangle = 0$$

Replacing J_+J_-, we have

$$\left(J^2 - J_z^2 + \hbar J_z\right)J_-^n|\lambda\mu\rangle = 0$$

or

$$\left[\lambda - (\mu - n\hbar)^2 + \hbar(\mu - n\hbar)\right]J_-^n|\lambda\mu\rangle = 0$$

As $J_-^n|\lambda\mu\rangle \neq 0$, $\lambda - (\mu - n\hbar)^2 + \hbar(\mu - n\hbar) = 0$. Substituting the value of λ from Eq. (8.28), we find

$$(n+1)(2\mu - n\hbar) = 0$$

Since $(n+1) \neq 0$,

$$2\mu - n\hbar = 0 \quad \text{or} \quad \mu = \frac{n\hbar}{2} \tag{8.30}$$

where n is the number of steps from the maximum eigenvalue μ to the minimum eigenvalue $\mu - n\hbar$. The number of steps n is always an integer including zero. Writing j for $n/2$, the maximum and minimum eigenvalues of J_z are $j\hbar$ and $-j\hbar$ respectively. In other words, for a given value of j, the eigenvalues of J_z are $m\hbar$ where $m = j, j - 1, \ldots, -j$. Since n is always an integer, the possible values of j are 0, 1/2, 1, 3/2, ... Thus, half-integral quantum numbers have emerged automatically from the general treatment of angular momentum, a result we have been looking for. Denoting the simultaneous eigenvector of the operators J^2 and J_z with eigenvalues $j(j + 1)\hbar^2$ and $m\hbar$ by $|jm\rangle$, we get

$$J^2|jm\rangle = j(j+1)\hbar^2|jm\rangle \tag{8.31}$$

and

$$J_z\,|jm\rangle = m\hbar\,|jm\rangle \tag{8.32}$$

where j = 0, 1/2, 1, 3/2, ..., and $m = -j, -j+1, ..., j$.

8.6 ANGULAR MOMENTUM MATRICES

The states $|jm\rangle$ form a complete orthonormal set and they can be used as a basis for the matrix representation of an angular momentum. In this representation a function F of the angular momentum components can be represented by a matrix with elements $\langle j'm'|F|jm\rangle$. The rows of the matrix will be labelled by the j' and m' values and the column by the j, m values.

Matrices for J^2 and J_z

As J^2 commutes with J_z, the matrices for J^2 and J_z will be diagonal. In that representation, J_x and J_y will not be diagonal since J_z does not commute with J_x and J_y. Multiplication of Eqs. (8.31) and (8.32) from left by $\langle j'm'|$ gives

$$\langle j'm'|J^2|jm\rangle = j(j+1)\hbar^2\delta_{jj'}\delta_{mm'} \tag{8.33}$$

and

$$\langle j'm'|J_z|jm\rangle = m\hbar\delta_{jj'}\delta_{mm'} \tag{8.34}$$

The presence of the factors $\delta_{jj'}$ and $\delta_{mm'}$ indicates that the matrices are diagonal as expected. The explicit form of the J^2 and J_z matrices are given in Tables 8.1 and 8.2. They are of infinite dimensions.

Table 8.1 Matrix for J^2:$\langle j'm'|\,J^2|jm\rangle = j(j+1)\hbar^2\,\delta_{jj'}\delta_{mm'}$

	j	0	1/2	1	...
	m	0	1/2 −1/2	1 0 −1	...
j'	m'				
0	0	0	(0)	(0)	...
1/2	1/2 −1/2	(0)	$\begin{bmatrix}3\hbar^2/4 & 0\\ 0 & 3\hbar^2/4\end{bmatrix}$	(0)	...
1	1 0 −1	(0)	(0)	$\begin{bmatrix}2\hbar^2 & 0 & 0\\ 0 & 2\hbar^2 & 0\\ 0 & 0 & 2\hbar^2\end{bmatrix}$	...
⋮	⋮	⋮	⋮	⋮	

Table 8.2 Matrix for $J_z : \langle j'm' \mid J_z \mid jm \rangle = m\hbar\, \delta jj' \delta mm'$

	j	0	1/2	1	...
	m	0	1/2 −1/2	1 0 −1	...
j'	m'				
0	0	0	(0)	(0)	...
1/2	1/2 −1/2	(0)	$\begin{bmatrix} \hbar/2 & 0 \\ 0 & -\hbar/2 \end{bmatrix}$	(0)	...
1	1 0 −1	(0)	(0)	$\begin{bmatrix} 1\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1\hbar \end{bmatrix}$	...
⋮	⋮	⋮	⋮	⋮	

Matrices for J_+, J_-, J_x and J_y

From Eq. (8.26)

$$J_z J_+ \lvert jm \rangle = (m+1)\hbar J_+ \lvert jm \rangle \tag{8.35}$$

This implies that $J_+ \lvert jm \rangle$ is an eigenket of J_z with eigenvalue $(m + 1)\hbar$. The eigenvalue equation for J_z with eigenvalue $(m + 1)\hbar$ can also be written as

$$J_z \lvert j, m+1 \rangle = (m+1)\hbar \lvert j, m+1 \rangle \tag{8.36}$$

Since the eigenvalues of J_z, Eqs. (8.35) and (8.36), are equal, the eigenvectors can differ at the most by a multiplicative constant, say a_m.

$$J_+ \lvert jm \rangle = a_m \lvert j, m+1 \rangle \tag{8.37}$$

Similarly, we get

$$J_- \lvert jm \rangle = b_m \lvert j, m-1 \rangle \tag{8.38}$$

where

$$a_m = \langle j, m+1 \lvert J_+ \rvert jm \rangle \quad \text{or} \quad a_m^* = \langle jm \lvert J_- \rvert j, m+1 \rangle \tag{8.39}$$

$$b_m = \langle j, m-1 \lvert J_- \rvert jm \rangle \quad \text{or} \quad b_{m+1} = \langle jm \lvert J_- \rvert j, m+1 \rangle \tag{8.40}$$

Comparison of Eqs. (8.39) and (8.40) gives

$$a_m^* = b_{m+1} \tag{8.41}$$

Operating Eq. (8.37) from left by J_-, we have

$$J_- J_+ \lvert jm \rangle = a_m J_- \lvert j, m+1 \rangle$$

Replacing $J_- J_+$ (Eq. 8.15) and using Eq. (8.38), we get

$$\left(J^2 - J_z^2 - \hbar J_z\right) | jm\rangle = a_m b_{m+1} | jm\rangle$$

or

$$\left[j(j+1) - m^2 - m\right]\hbar^2 | jm\rangle = | a_m |^2 | jm\rangle$$

or

$$a_m = \left[j(j+1) - m(m+1)\right]^{1/2} \hbar \tag{8.42}$$

With this value of a_m

$$J_+ | jm\rangle = \left[j(j+1) - m(m+1)\right]^{1/2} \hbar | j, m+1\rangle \tag{8.43}$$

or

$$\langle j'm' | J_+ | jm\rangle = \left[j(j+1) - m(m+1)\right]^{1/2} \hbar \delta_{jj'} \delta_{m',m+1} \tag{8.44}$$

Similarly,

$$\left\langle j'm' \middle| J_- \middle| jm\right\rangle = \left[j(j+1) - m(m-1)\right]^{1/2} \hbar \delta_{jj'} \delta_{m',m-1} \tag{8.45}$$

Equations (8.44) and (8.45) give the matrix elements for J_+ and J_-. They are infinite-dimensional matrices like the J^2 and J_z matrices. The nature of the Kronecker deltas in Eqs. (8.44) and (8.45) indicates that all nonvanishing elements occur in blocks along the diagonal corresponding to $j' = j$. The block matrices corresponding to $j = 0$, 1/2 and 1 are given below. The rows are labelled by the value of m' and the columns by the value of m. The nonvanishing matrices for J_x and J_y are evaluated using the relation

$$J_x = \frac{1}{2}(J_+ + J_-) \quad \text{and} \quad J_y = \frac{1}{2i}(J_+ - J_-) \tag{8.46}$$

For $j = 0$

$$J_+ = 0, \quad J_- = 0, \quad J_x = 0, \quad J_y = 0 \tag{8.47}$$

For $j = 1/2$

$$\left.\begin{aligned} J_+ &= \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad J_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \\ J_x &= \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad J_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \end{aligned}\right\} \tag{8.48}$$

For $j = 1$

$$\left.\begin{aligned} J_+ &= \hbar\begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \quad J_- = \hbar\begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \\ J_x &= \frac{1}{\sqrt{2}}\hbar\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad J_y = \frac{1}{\sqrt{2}}\hbar\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \end{aligned}\right\} \tag{8.49}$$

Without a word about the eigenvector, the discussion would not be complete. The eigenvector with respect to the $|jm\rangle$ basis will be a column vector of infinite extent. The appropriate part of this infinite column vector would be used for the particular cases: $j = 0, j = 1/2, j = 1, \ldots$

8.7 SPIN ANGULAR MOMENTUM

To account for the multiplicity of atomic states, *Uhlenbeck* and *Goudsmit* proposed in 1925 that an electron in an atom possesses an intrinsic angular momentum in addition to orbital angular momentum. This intrinsic angular momentum **S** is called the *spin angular momentum* whose projection on the z-axis can have the values $S_z = m_s\hbar$, $m_s = \pm 1/2$. The maximum measurable component of spin angular momentum in units of $\hbar$ is called the *spin of the particle* and is usually denoted by s. They also suggested that the spin angular momentum gives rise to an intrinsic magnetic moment μ_s given by

$$\mu_s = -\frac{e}{m}\mathbf{S} \tag{8.50}$$

Assuming that all the stable and unstable particles to have spin angular momentum **S**, we expect its components S_x, S_y and S_z to obey the general commutation relations of Eq. (8.20) and S^2 and S_z to have the eigenvalues $s(s+1)\hbar^2$ and $m_s\hbar$, $m_s = -s, -s+1, \ldots, s$ respectively.

Spin-(1/2) systems

Most of the stable elementary particles, electrons, protons, neutrons, etc., come under this category. The matrices, representing, S_x, S_y and S_z are obtained directly from the J_x, J_y and J_z matrices by taking the part corresponding to $j = 1/2$. Hence

$$S_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad S_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad S_z = \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{8.51}$$

Often it is convenient to work with a matrix $\boldsymbol{\sigma}$ defined by

$$\mathbf{S} = \frac{1}{2}\hbar\,\boldsymbol{\sigma} \tag{8.52}$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{8.53}$$

The σ_x, σ_y and σ_z matrices are called the *Pauli's spin matrices*. From the definition, it is obvious that their eigenvalues are ± 1. These matrices satisfy the relations

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \tag{8.54}$$

$$\sigma_x\sigma_y = i\sigma_z, \qquad \sigma_y\sigma_z = i\sigma_x, \qquad \sigma_z\sigma_x = i\sigma_y \tag{8.55}$$

$$\sigma_x\sigma_y + \sigma_y\sigma_x = \sigma_y\sigma_z + \sigma_z\sigma_y = \sigma_z\sigma_x + \sigma_x\sigma_z = 0 \tag{8.56}$$

Pauli was the first to recognize the necessity of two-component state vectors to explain certain observed features of atomic spectra.

8.8 SPIN VECTORS FOR SPIN-(1/2) SYSTEM

Including spin, the spin-(1/2) system (electron) has now four degrees of freedom, the three position coordinates (x, y, z) and another observable pertaining to spin. Taking the z-component S_z as the fourth observable, the electron wave function can be written as $\psi(\mathbf{r}, S_z)$ or $\psi(\mathbf{r}, m_s)$, the coordinate m_s takes the values +1/2 or −1/2. When the interaction between the spin and space parts is negligible, the wave function

$$\psi(\mathbf{r}, m_s) = \phi(\mathbf{r})\ \chi(m_s) \tag{8.57}$$

where $\phi(\mathbf{r})$ represents the part that depends on the space coordinates and $\chi(m_s)$, the part that depends on the spin coordinates.

The eigenvectors of the spin matrices S_x, S_y and S_z can easily be obtained by writing the eigenvalue equation. Since the matrices are 2 × 2, the eigenvectors must be column vectors with two components. The eigenvalue equation for S_z with eigenvalue $\hbar/2$ is

$$\frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}a_1\\ a_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}a_1\\ a_2\end{pmatrix} \quad \text{or} \quad \begin{pmatrix}a_1\\ -a_2\end{pmatrix} = \begin{pmatrix}a_1\\ a_2\end{pmatrix}$$

It is evident that $a_2 = 0$. The normalization condition gives

$$|a_1|^2 = 1 \quad \text{or} \quad a_1 = 1$$

The eigenvector of the matrix S_z corresponding to the eigenvalue $\hbar/2$ is then

$$\begin{pmatrix}1\\ 0\end{pmatrix}$$

Proceeding on similar lines, the eigenvector for the eigenvalue $-\hbar/2$ is

$$\begin{pmatrix}0\\ 1\end{pmatrix}$$

These eigenvectors are denoted by α and β and are usually called the *spin-up* and *spin-down* states respectively:

$$\alpha = \begin{pmatrix}1\\ 0\end{pmatrix}, \qquad \beta = \begin{pmatrix}0\\ 1\end{pmatrix} \tag{8.58}$$

The two-component eigenvectors of spin-(1/2) particles are sometimes called *spinors*. Eigenvectors of S_x and S_y can also be found in the same way. The spin matrices of a spin–(1/2) system along with eigenvalues and eigenvectors are tabulated in Table 8.3.

Table 8.3 Spin Matrices S_x, S_y and S_z of a Spin-(1/2) System with Their Eigenvalues and Eigenvectors

Spin component	*Spin matrix*	*Eigenvalue*	*Eigenvectors*
S_x	$\frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$	$\begin{cases}\frac{\hbar}{2}\\ -\frac{\hbar}{2}\end{cases}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ 1\end{pmatrix}$ $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -1\end{pmatrix}$
S_y	$\frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$	$\begin{cases}\frac{\hbar}{2}\\ -\frac{\hbar}{2}\end{cases}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\end{pmatrix}$ $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -i\end{pmatrix}$
S_z	$\frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$	$\begin{cases}\frac{\hbar}{2}\\ -\frac{\hbar}{2}\end{cases}$	$\begin{pmatrix}1\\ 0\end{pmatrix}$ $\begin{pmatrix}0\\ 1\end{pmatrix}$

8.9 ADDITION OF ANGULAR MOMENTA

Addition of angular momenta is very important in the study of atomic spectra, structure of nuclei, etc. In this section, we shall consider the general problem of the addition of two angular momenta. Consider two noninteracting systems having angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ and eigenkets $|j_1m_1\rangle$ and $|j_2m_2\rangle$ respectively. That is,

$$J_1^2\,|\,j_1m_1\rangle = j_1(j_1+1)\hbar^2\,|\,j_1m_1\rangle \tag{8.59a}$$

$$J_{1z}|\,j_1m_1\rangle = m_1\hbar\,|\,j_1m_1\rangle \tag{8.59b}$$

and

$$J_2^2\,|\,j_2m_2\rangle = j_2(j_2+1)\hbar^2\,|\,j_2m_2\rangle \tag{8.60a}$$

$$J_{2z}|\,j_2m_2\rangle = m_2\hbar\,|\,j_2m_2\rangle \tag{8.60b}$$

where

$$m_1 = j_1, j_1-1, \ldots, -j_1; \qquad m_2 = j_2, j_2-1, \ldots, -j_2$$

Since the two systems are noninteracting

$$[J_1, J_2] = 0 \quad \text{and} \quad \left[J_1^2, J_2^2\right] = 0 \tag{8.61}$$

and therefore the operators J_1^2, J_{1z}, J_2^2, J_{2z} form a complete set with simultaneous eigenkets $|j_1m_1, j_2m_2\rangle$, which is a product of $|j_1m_1\rangle$ and $|j_2m_2\rangle$. For given values of j_1 and j_2

$$|j_1m_1, j_2m_2\rangle = |j_1m_1\rangle\, |j_2m_2\rangle = |m_1m_2\rangle \tag{8.62}$$

Since m_1 and m_2 can respectively have $(2j_1 + 1)$ and $(2j_2 + 1)$ orientations, the subspace with definite values of j_1 and j_2 will have $(2j_1 + 1)\,(2j_2 + 1)$ dimensions.

Clebsh–Gordan Coefficients

For the total angular momentum vector $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$,

$$\mathbf{J} \times \mathbf{J} = i\hbar\mathbf{J} \tag{8.63}$$

Also, it follows that

$$\left[J^2, J_z\right] = 0, \qquad \left[J^2, J_1^2\right] = \left[J^2, J_2^2\right] = 0 \tag{8.64}$$

The orthonormal eigenkets of J^2 and J_z be $|jm\rangle$. Since J^2 commutes with J_z,J_1^2 and J_2^2, they form another complete set and their simultaneous eigenkets will be $|j_1j_2\; jm\rangle$. For given values of j_1 and j_2, $|j_1j_2\; jm\rangle = |jm\rangle$. The completeness of the known kets $|m_1m_2\rangle$ allows us to express the unknown kets $|jm\rangle$ as a linear combination of $|m_1m_2\rangle$.

$$|jm\rangle = \sum_{m_1, m_2} C_{jmm_1m_2} |m_1m_2\rangle \tag{8.65}$$

The coefficients of this linear combination are called *Clebsh–Gordan coefficients* or *Wigner coefficients* or *vector coupling coefficients*. Multiplying Eq. (8.65) with the bra $\langle m_1m_2|$, we get

$$\langle m_1m_2 \mid jm\rangle = C_{jmm_1m_2} \tag{8.66}$$

Substituting this value of the coefficient in Eq. (8.65), we have

$$|jm\rangle = \sum_{m_1, m_2} |m_1m_2\rangle\langle m_1m_2 | jm\rangle \tag{8.67}$$

As the coefficients $\langle m_1m_2|jm\rangle$ relates two orthonormal bases, they form a unitary matrix. In the matrix formed by these elements, m_1, m_2 label the rows and j, m label the columns. The parameters j_1 and j_2 are not appearing explicitly in the coefficients as we are working for definite values of j_1 and j_2. In the strict sense the coefficients would be $\langle j_1m_1,\, j_2m_2 | j_1j_2\; jm\rangle$. The inverse of Eq. (8.67) is given by

$$|m_1m_2\rangle = \sum_{j, m} \langle jm|m_1m_2\rangle |jm\rangle \tag{8.68}$$

where the summation over m is from $-j$ to j and j is from $|j_1 - j_2|$ to $j_1 + j_2$. The unitary character of Clebsh–Gordan coefficients is expressed by the equations

$$\sum_{j,m} \langle m_1 m_2 | jm \rangle \langle jm | m_1' m_2' \rangle = \langle m_1 m_2 | m_1' m_2' \rangle = \delta m_1 m_1' \delta m_2 m_2' \tag{8.69a}$$

and

$$\sum_{m_1, m_2} \langle jm | m_1 m_2 \rangle \langle m_1 m_2 | j'm' \rangle = \langle jm | j'm' \rangle = \delta jj' \, \delta mm' \tag{8.69b}$$

where

$$\langle jm | m_1 m_2 \rangle = \langle m_1 m_2 | jm \rangle^* \tag{8.69c}$$

Selection Rules

Operating Eq. (8.67) from left by J_z, we have

$$J_z | jm \rangle = \sum_{m_1, m_2} (J_{1z} + J_{2z}) | m_1 m_2 \rangle \langle m_1 m_2 | jm \rangle$$

or

$$m\hbar | jm \rangle = \sum_{m_1, m_2} (m_1 + m_2)\hbar | m_1 m_2 \rangle \langle m_1 m_2 | jm \rangle$$

Replacing $|jm\rangle$ using Eq. (8.67) and rearranging, we get

$$\sum_{m_1, m_2} (m - m_1 - m_2) | m_1 m_2 \rangle \langle m_1 m_2 | jm \rangle = 0 \tag{8.70}$$

which is valid only if the coefficient of each term vanishes separately. This leads to one of the rules of vector atom model, that is

$$m = m_1 + m_2 \tag{8.71}$$

We shall next find out how the various m and j values arise from the values of m_1 and m_2. For given values of j_1 and j_2, m_1 can have values from j_1 to $-j_1$ and m_2 from j_2 to $-j_2$ in integral steps. Since $m = m_1 + m_2$, the possible values of m are $j_1 + j_2$, $j_1 + j_2 - 1$, $j_1 + j_2 - 2$, ..., $-(j_1 + j_2)$. The largest value $(j_1 + j_2)$ can occur only once when $m_1 = j_1$ and $m_2 = j_2$. The value of j corresponding to this m value is also $(j_1 + j_2)$. The next largest value of m is $j_1 + j_2 - 1$ which can occur in two ways: $m_1 = j_1$, $m_2 = j_2 - 1$ or $m_1 = j_1 - 1$, $m_2 = j_2$. This gives rise to the two known $|m_1 m_2\rangle$ kets $|j_1, j_2 - 1\rangle$ and $|j_1 - 1, j_2\rangle$ leading to two linearly independent $|jm\rangle$ combinations. We can have $m = j_1 + j_2 - 1$ when $j = (j_1 + j_2)$ or $(j_1 + j_2 - 1)$ as can be seen from the following. When $j = j_1 + j_2$, m can have the values $j_1 + j_2$, $j_1 + j_2 - 1$, ..., $-(j_1 + j_2)$. When $j = j_1 + j_2 - 1$, m can have the values $j_1 + j_2 - 1$, $j_1 + j_2 - 2$, ..., $-(j_1 + j_2 - 1)$. Thus, $m = j_1 + j_2 - 1$ can result from $j = (j_1 + j_2)$ or $(j_1 + j_2 - 1)$. This process is continued and the results are summarised in Table 8.4.

Table 8.4 Values of j and m for Different Values of m_1 and m_2

m_1	m_2	m	j
j_1	j_2	j_1+j_2	j_1+j_2
j_1	j_2-1	j_1+j_2-1	j_1+j_2
j_1-1	j_2		j_1+j_2-1
j_1	j_2-2	j_1+j_2-2	j_1+j_2
j_1-1	j_2-1		j_1+j_2-1
j_1-2	j_2		j_1+j_2-2
⋮	⋮	⋮	⋮
j_1	j_2-k	j_1+j_2-k	j_1+j_2
j_1-1	j_2-k+1		j_1+j_2-1
j_1-2	j_2-k+2		j_1+j_2-2
⋮	⋮		⋮
j_1-k	j_2		j_1+j_2-k
⋮	⋮	⋮	⋮

The smallest value of j occurs for

$$j_1 - k = -j_1 \quad \text{or} \quad j_2 - k = -j_2$$

That is when $k = 2j_1$ or $2j_2$. The smallest value of j is then

$$j_1 + j_2 - 2j_1 = j_2 - j_1 \quad \text{or} \quad j_1 + j_2 - 2j_2 = j_1 - j_2$$

In other words, the permitted values of j are

$$(j_1+j_2), (j_1+j_2-1), (j_1+j_2-2), \ldots, |j_1-j_2| \tag{8.72}$$

which is the *triangle rule of the vector atom model.*

Recursion Relations

Recursion relations connecting Clebsh–Gordan coefficients would be very useful in evaluating explicit expressions for them. Operating Eq. (8.67) from left by J_- and replacing J_- by $J_{1-} + J_{2-}$ on the right-hand side, we get

$$J_-|jm\rangle = \sum_{m'_1, m'_2} (J_{1-} + J_{2-})|m'_1 m'_2\rangle\langle m'_1 m'_2|jm\rangle$$

Using Eq. (8.45)

$$\begin{aligned}
&[j(j+1)-m(m-1)]^{1/2}\hbar|j, m-1\rangle \\
&= \sum_{m'_1, m'_2} [j_1(j_1+1) - m'_1(m'_1-1)]^{1/2}\hbar|m'_1-1, m'_2\rangle\langle m'_1 m'_2|jm\rangle \\
&+ \sum_{m'_1, m'_2} [j_2(j_2+1) - m'_2(m'_2-1)]^{1/2}\hbar|m'_1, m'_2-1\rangle\langle m'_1 m'_2|jm\rangle
\end{aligned} \tag{8.73}$$

Multiplying both sides by $\langle m_1 m_2 |$, we get

$$\begin{aligned}[j(j+1)-m(m-1)]^{1/2}\langle m_1 m_2 | j, m-1\rangle \\ = [j_1(j_1+1)-m_1(m_1+1)]^{1/2}\langle m_1+1, m_2 | jm\rangle \\ +[j_2(j_2+1)-m_2(m_2+1)]^{1/2}\langle m_1, m_2+1 | jm\rangle \end{aligned} \tag{8.74}$$

Repeating the procedure with J_+ in the place of J_-

$$\begin{aligned}[j(j+1)-m(m+1)]^{1/2}\langle m_1 m_2 | j, m+1\rangle \\ = [j_1(j_1+1)-m_1(m_1-1)]^{1/2}\langle m_1-1, m_2 | jm\rangle \\ +[j_2(j_2+1)-m_2(m_2-1)]^{1/2}\langle m_1, m_2-1 | jm\rangle \end{aligned} \tag{8.75}$$

Equations (8.74) and (8.75) are the recursion relations required for the computation of the Clebsh–Gordan coefficients.

Computation of Clebsh–Gordan Coefficients

The Clebsh–Gordan coefficient matrix $\langle m_1 m_2 | jm\rangle$ has $(2j_1 + 1)(2j_2 + 1)$ rows and columns. However, it breaks up into smaller matrices depending on the value of m. It can be seen from Table 8.4 that there will be a 1 × 1 submatrix for which $m = j_1 + j_2$ and $j = j_1 + j_2$. Then there will be a 2 × 2 submatrix for which $m = j_1 + j_2 - 1$ and $j = j_1 + j_2$ or $j = j_1 + j_2 - 1$. The rank of these matrices increases by unity until a maximum is reached and remains in that level for 1 or more submatrices, thereafter it decreases by unity until the last 1 × 1 submatrix is reached. For convenience, the first 1 × 1 submatrix is selected as +1. That is

$$\langle j_1, j_2 | j_1 + j_2, j_1 + j_2\rangle = +1 \tag{8.76}$$

To compute the next 2 × 2 submatrix set $m_1 = j_1$, $m_2 = j_2 - 1$, $j = j_1 + j_2$ and $m = j_1 + j_2$ in Eq. (8.74). On simplification, we get

$$(j_1 + j_2)^{1/2}\langle j_1, j_2 - 1 | (j_1 + j_2), j_1 + j_2 - 1\rangle = j_2^{1/2}\langle j_1 j_2 | j_1 + j_2, j_1 + j_2\rangle$$

Using the result in Eq. (8.76)

$$\langle j_1, j_2 - 1 | j_1 + j_2, j_1 + j_2 - 1\rangle = \left(\frac{j_2}{j_1 + j_2}\right)^{1/2} \tag{8.77}$$

Proceeding on similar lines with $m_1 = j_1 - 1$, $m_2 = j_2$, $j = j_1 + j_2$ and $m = j_1 + j_2$ in Eq. (8.74), we have

$$\langle j_1 - 1, j_2 | j_1 + j_2, j_1 + j_2 - 1\rangle = \left(\frac{j_1}{j_1 + j_2}\right)^{1/2} \tag{8.78}$$

Equations (8.77) and (8.78) give two of the elements for which $j = j_1 + j_2$ and $m = j_1 + j_2 - 1$. The other two elements:

$$\langle j_1, j_2-1 | j_1+j_2-1, j_1+j_2-1\rangle \text{ and } \langle j_1-1, j_2 | j_1+j_2-1, j_1+j_2-1\rangle$$

are evaluated using the unitary nature of the transformation matrix, Eq. (8.69). While evaluating these elements, it is the practice to take the element having the form $\langle j_1, j - j_1 | jj\rangle$ which involves the highest value of m_1 as real and positive.

Using Eq. (8.69b), we get

$$\langle j_1+j_2, j_1+j_2-1 | j_1, j_2-1\rangle\langle j_1, j_2-1 | j_1+j_2-1, j_1+j_2-1\rangle$$
$$+ \langle j_1+j_2, j_1+j_2-1 | j_1-1, j_2\rangle\langle j_1-1, j_2 | j_1+j_2-1, j_1+j_2-1\rangle = 0$$

Since $\langle jm | m_1m_2\rangle = \langle m_1m_2 | jm\rangle^*$, the above equation reduces to

$$\left(\frac{j_2}{j_1+j_2}\right)^{1/2} \langle j_1, j_2-1 | j_1+j_2-1, j_1+j_2-1\rangle$$
$$+ \left(\frac{j_1}{j_1+j_2}\right)^{1/2} \langle j_1-1, j_2 | j_1+j_2-1, j_1+j_2-1\rangle = 0$$

Use of the convention that the first element is real and positive gives

$$\langle j_1, j_2-1 | j_1+j_2-1, j_1+j_2-1\rangle = \left(\frac{j_1}{j_1+j_2}\right)^{1/2} \tag{8.79}$$

and

$$\langle j_1-1, j_2 | j_1+j_2-1, j_1+j_2-1\rangle = -\left(\frac{j_2}{j_1+j_2}\right)^{1/2} \tag{8.80}$$

The next submatrix which is 3 × 3 may be obtained in the same way. Using Eqs. (8.74), (8.77) and (8.78) we can get three elements for which $j = j_1 + j_2$ and $m = j_1 + j_2 - 2$. Another three elements corresponding to $j = j_1 + j_2 - 1$ and $m = j_1 + j_2 - 1$ are obtained using Eqs. (8.79), (8.80) and (8.74). Equation (8.69b) is used to obtain a normalized set of coefficients that are orthogonal to the other six. As in the 2 × 2 case, the element $\langle j_1, j_2 - 2 | j_1 + j_2 - 2, j_1 + j_2 - 2\rangle$ is selected to be positive. The results of 2 × 2 and 3 × 3 submatrices are listed in Tables 8.5 and 8.6. The recursion relation, Eq. (8.75), can also be used for computing Clebsh–Gordan coefficients, if we start from the other end corresponding to $j = j_1 + j_2$ and $m = -(j_1 + j_2)$.

Table 8.5 Clebsh–Gordan Coefficients for $|m_1m_2\rangle = |j_1, j_2 - 1\rangle$ and $|j_1 - 1, j_2\rangle$

		$\|jm\rangle$	
m_1	m_2	$\left\|j_1+j_2,\ j_1+j_2-1\right\rangle$	$\left\|j_1+j_2-1,\ j_1+j_2-1\right\rangle$
j_1	$j_2 - 1$	$\left(\dfrac{j_2}{j_1+j_2}\right)^{1/2}$	$\left(\dfrac{j_1}{j_1+j_2}\right)^{1/2}$
$j_1 - 1$	j_2	$\left(\dfrac{j_1}{j_1+j_2}\right)^{1/2}$	$-\left(\dfrac{j_2}{j_1+j_2}\right)^{1/2}$

Table 8.6 Clebsh–Gordan Coefficients for $|m_1m_2\rangle = |j_1, j_2 - 2\rangle$, $|j_1 - 1, j_2 - 1\rangle$ and $|j_1 - 2, j_2\rangle$

		$\|jm\rangle$		
m_1	m_2	$\left\|j_1+j_2, j_1+j_2-2\right\rangle$	$\left\|j_1+j_2-1,\ j_1+j_2-2\right\rangle$	$\left\|j_1+j_2-2, j_1+j_2-2\right\rangle$
j_1	$j_2 - 2$	$\left[\dfrac{j_2(2j_2-1)}{(j_1+j_2)A}\right]^{1/2}$	$\left[\dfrac{j_1(2j_2-1)}{(j_1+j_2)B}\right]^{1/2}$	$\left[\dfrac{j_1(2j_1-1)}{AB}\right]^{1/2}$
$j_1 - 1$	$j_2 - 1$	$\left[\dfrac{4j_1j_2}{(j_1+j_2)A}\right]^{1/2}$	$\dfrac{j_1-j_2}{\left[(j_1+j_2)B\right]^{1/2}}$	$-\left[\dfrac{(2j_1-1)(2j_2-1)}{AB}\right]^{1/2}$
$j_1 - 2$	j_2	$\left[\dfrac{j_1(2j_1-1)}{(j_1+j_2)A}\right]^{1/2}$	$-\left[\dfrac{j_2(2j_1-1)}{(j_1+j_2)B}\right]^{1/2}$	$\left[\dfrac{j_2(2j_2-1)}{AB}\right]^{1/2}$

where $A = 2j_1 + 2j_2 - 1$ and $B = j_1 + j_2 - 1$.

WORKED EXAMPLES

EXAMPLE 8.1 What is the value of the uncertainty product (ΔL_x) (ΔL_y) in a representation in which L^2 and L_z have simultaneous eigenfunctions. Comment on the value of this product when $l = 0$.

If the commutator of operators A and B obey the relation $[A, B] = iC$, then

$$(\Delta A)\,(\Delta B) \geq \frac{|\langle C\rangle|}{2}$$

In the representation in which L^2 and L_z have simultaneous eigenfunctions,

$$[L_x, L_y] = i\hbar L_z$$

Therefore, it follows that

$$(\Delta L_x)(\Delta L_y) \geq \frac{\hbar}{2}|\langle L_z\rangle| \geq \frac{\hbar}{2} m\hbar \geq \frac{m\hbar^2}{2}$$

This is understandable as $Y_{lm}(\theta, \phi)$ is not an eigenfunction of L_x and L_y, when $l \neq 0$. When $l = 0$, $m = 0$, $Y_{00} = 1/\sqrt{(4\pi)}$. Therefore,

$$(\Delta L_x)(\Delta L_y) \geq 0$$

EXAMPLE 8.2 Express the operators for angular momentum components L_x, L_y and L_z in spherical polar coordinates

The gradient in spherical coordinates is given by

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

where $\hat{r}, \hat{\theta}$ and $\hat{\phi}$ are unit vectors along r, θ and ϕ directions. The angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = -i\hbar(\mathbf{r} \times \nabla)$$

$$= -i\hbar\left(\mathbf{r} \times \hat{r}\frac{\partial}{\partial r} + \mathbf{r} \times \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \mathbf{r} \times \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}\right)$$

Since $\mathbf{r} = r\hat{r}, \hat{r} \times \hat{r} = 0$, $\hat{r} \times \hat{\theta} = \hat{\phi}$ and $\hat{r} \times \hat{\phi} = -\hat{\theta}$,

$$L = -i\hbar\left(\hat{\phi}\frac{\partial}{\partial \theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right)$$

Resolving the unit vectors $\hat{\theta}$ and $\hat{\phi}$ in cartesian components (Appendix B), we have

$$\hat{\theta} = \cos\theta\cos\phi\hat{i} + \cos\theta\sin\phi\hat{j} - \sin\theta\hat{k}$$

and

$$\hat{\phi} = -\sin\phi\hat{i} + \cos\phi\hat{j}$$

Substituting the values of $\hat{\theta}$ and $\hat{\phi}$, we get

$$L = -i\hbar\left[(-\sin\phi\hat{i} + \cos\phi\hat{j})\frac{\partial}{\partial \theta} - (\cos\theta\cos\phi\hat{i} + \cos\theta\sin\theta\hat{j} - \sin\phi\hat{k})\frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\right]$$

Collecting the coefficients of $\hat{i}, \hat{j}$ and $\hat{k}$, we get

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial \theta} + \cos\phi\cot\theta\frac{\partial}{\partial \phi}\right)$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial \theta} - \sin\phi\cot\theta\frac{\partial}{\partial \phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial \phi}$$

EXAMPLE 8.3 A particle is in an eigenstate of J_z. Prove that $\langle J_x \rangle = \langle J_y \rangle = 0$. Also, find the value of $\langle J_x^2 \rangle$ and $\langle J_y^2 \rangle$.

Let the eigenstate of J_z be $|jm\rangle$. We have

$$J_x = \frac{J_+ + J_-}{2} \quad \text{and} \quad J_y = \frac{J_+ - J_-}{2i}$$

Also,

$$\langle J_x\rangle = \frac{1}{2}\langle jm|\,J_+\,|\,jm\,\rangle + \frac{1}{2}\langle jm|\,J_-|\,jm\rangle$$

$$= \frac{1}{2}\sqrt{j(j+1) - m(m+1)}\hbar\langle\, jm\,|\,j,\, m+1\rangle$$

$$+ \frac{1}{2}\sqrt{j(j+1) - m(m-1)}\hbar\,\langle jm|\,j,\; m-1\rangle$$

$$= 0$$

since $\langle jm|\,j, m+1\rangle = \langle jm|\,j, m-1\rangle = 0$. Similarly, we get $\langle J_y\rangle = 0$. We have the relation,

$$J_x^2 + J_y^2 = J^2 - J_z^2$$

In the eigenstate $|jm\rangle$, this relation can be written as

$$\left\langle jm\left|\left(J_x^2 + J_y^2\right)\right|jm\right\rangle = \left\langle jm\left|\left(J^2 - J_z^2\right)\right|jm\right\rangle$$

$$\left\langle jm\left|\,J_x^2\right|jm\right\rangle + \left\langle\, jm\left|\,J_y^2\right|jm\right\rangle = j(j+1)\,\hbar^2 - m^2\hbar^2$$

It is expected that $\left\langle J_x^2\right\rangle = \left\langle J_y^2\right\rangle$ and therefore

$$\left\langle J_x^2\right\rangle = \left\langle J_y^2\right\rangle = \frac{1}{2}\left[j(j+1)\hbar^2 - m^2\hbar^2\right]$$

EXAMPLE 8.4 Derive matrices for the operators J^2, J_z, J_x and J_y for $j = 3/2$.

For $j = 3/2$, the allowed values of m are 3/2, 1/2, –1/2 and –3/2. With these values for j and m, matrices for J^2 and J_z are written with the help of Eqs. (8.33) and (8.34).

$$J^2 = \frac{15}{4}\hbar^2\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix}, \qquad J_z = \frac{1}{2}\hbar\begin{pmatrix}3 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & -3\end{pmatrix}$$

Equations (8.44) and (8.45) give the matrices for J_+ and J_-.

$$J_+ = \hbar\begin{pmatrix}0 & \sqrt{3} & 0 & 0\\ 0 & 0 & 2 & 0\\ 0 & 0 & 0 & \sqrt{3}\\ 0 & 0 & 0 & 0\end{pmatrix}, \qquad J_- = \hbar\begin{pmatrix}0 & 0 & 0 & 0\\ \sqrt{3} & 0 & 0 & 0\\ 0 & 2 & 0 & 0\\ 0 & 0 & \sqrt{3} & 0\end{pmatrix}$$

We also have the expressions:

$$J_x = \frac{1}{2}(J_+ + J_-) \quad \text{and} \quad J_y = \frac{1}{2i}(J_+ - J_-)$$

Matrices for J_x and J_y follow from the expressions:

$$J_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \qquad J_y = \frac{\hbar}{2i} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

EXAMPLE 8.5 Components of arbitrary vectors **A** and **B** commute with those of $\boldsymbol{\sigma}$. Show that $(\boldsymbol{\sigma}\cdot\mathbf{A})\,(\boldsymbol{\sigma}\cdot\mathbf{B}) = \mathbf{A}\cdot\mathbf{B} + i\boldsymbol{\sigma}\,.\,(\mathbf{A}\times\mathbf{B})$.

We have

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\mathbf{A})\,(\boldsymbol{\sigma}\cdot\mathbf{B}) &= (\sigma_x A_x + \sigma_y A_y + \sigma_z A_z)\,(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z) \\ &= \sigma_x^2 A_x B_x + \sigma_y^2 A_y B_y + \sigma_z^2 A_z B_z + \sigma_x\sigma_y A_x B_y + \sigma_y\sigma_x A_y B_x \\ &\quad + \sigma_x\sigma_z A_x B_z + \sigma_y\sigma_z A_y B_z + \sigma_z\sigma_y A_z B_y + \sigma_z\sigma_x A_z B_x\end{aligned}$$

Using Eqs. (8.54), (8.55) and (8.56)

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\mathbf{A})\,(\boldsymbol{\sigma}\cdot\mathbf{B}) &= (\mathbf{A}\cdot\mathbf{B}) + i\sigma_z\,(A_x B_y - A_y B_x) \\ &\quad + i\sigma_y\,(A_z B_x - A_x B_z) + i\sigma_x\,(A_y B_z - A_z B_y) \\ &= (\mathbf{A}\cdot\mathbf{B}) + i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B})\end{aligned}$$

EXAMPLE 8.6 The vector **J** gives the sum of angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$. Prove that

$$[J_x, J_y] = i\hbar J_z, \quad [J_y, J_z] = i\hbar J_x, \quad [J_z, J_x] = i\hbar J_y$$

Is $\mathbf{J}_1 - \mathbf{J}_2$ an angular momentum?

It is given that $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. Therefore,

$$\begin{aligned}[J_x, J_y] &= [J_{1x} + J_{2x}, J_{1y} + J_{2y}] \\ &= [J_{1x}, J_{1y}] + [J_{1x}, J_{2y}] + [J_{2x}, J_{1y}] + [J_{2x}, J_{2y}] \\ &= i\hbar J_{1z} + 0 + 0 + i\hbar J_{2z} \\ &= i\hbar(J_{1z} + J_{2z}) \\ &= i\hbar J_z\end{aligned}$$

By cyclic permutation of the coordinates we can write the other two commutation relations. Writing, $\mathbf{J}_1 - \mathbf{J}_2 = \mathbf{J}'$

$$\begin{aligned}[J'_x, J'_y] &= [J_{1x} - J_{2x}, J_{1y} - J_{2y}] \\ &= [J_{1x}, J_{1y}] - [J_{1x}, J_{2y}] - [J_{2x}, J_{1y}] + [J_{2x}, J_{2y}] \\ &= i\hbar J_{1z} - 0 - 0 + i\hbar J_{2z} \\ &= i\hbar(J_{1z} + J_{2z})\end{aligned}$$

which is not the operator for J'_z. Hence $\mathbf{J}_1 - \mathbf{J}_2$ is not an angular momentum.

EXAMPLE 8.7 If the angular momentum operators obey the rule $[J_x, J_y] = -i\hbar J_z$ and similar commutation relations for the other components, evaluate the commutators $[J^2, J_x]$ and $[J^2, J_+]$. What would be the roles of J_+ and J_- in the new situation?

We know that

$$\begin{aligned}[J^2, J_x] &= [J_x^2, J_x] + [J_y^2, J_x] + [J_z^2, J_x]\\ &= J_y\,[J_y, J_x] + [J_y, J_x]\,J_y + J_z\,[J_z, J_x] + [J_z, J_x]\,J_z\\ &= i\hbar J_yJ_z + i\hbar J_zJ_y - i\hbar J_zJ_y - i\hbar J_yJ_z\\ &= 0\end{aligned}$$

Similarly, $[J^2, J_y] = 0$. Therefore

$$[J^2, J_+] = [J^2, J_x] + i\,[J^2, J_y] = 0$$

Let us evaluate $[J_z, J_+]$ and $[J_z, J_-]$.

$$[J_z, J_+] = [J_z, J_x] + i[J_z, J_y] = -i\hbar J_y - \hbar J_x = -\hbar J_+$$

Similarly, $[J_z, J_-] = \hbar J_-$.

Hence with the new definition, J_+ would be a lowering operator and J_- would be a raising operator.

EXAMPLE 8.8 For Pauli's matrices, prove that: (i) $[\sigma_x, \sigma_y] = 2i\sigma_z$ (ii) $\sigma_x\sigma_y\sigma_z = i$.

(i) We have

$$\mathbf{S} = \frac{1}{2}\hbar\sigma \quad \text{and} \quad [S_x, S_y] = i\hbar S_z$$

Substituting the values of S_x, S_y and S_z, we get

$$\left[\frac{1}{2}\hbar\sigma_x, \frac{1}{2}\hbar\sigma_y\right] = i\hbar\frac{1}{2}\hbar\sigma_z \quad \text{or} \quad [\sigma_x, \sigma_y] = 2i\sigma_z$$

(ii) We also have

$$\begin{aligned}\sigma_x\sigma_y\sigma_z &= \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\\ &= \begin{pmatrix}i & 0\\ 0 & -i\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\\ &= \begin{pmatrix}i & 0\\ 0 & i\end{pmatrix}\\ &= i\end{aligned}$$

EXAMPLE 8.9 Obtain the Clebsh–Gordan coefficients for a system having $j_1 = 1$ and $j_2 = 1/2$.

The system has two angular momenta with $j_1 = 1$ and $j_2 = 1/2$. The allowed values of j are 3/2 and 1/2. For $j = 3/2$, $m = 3/2, 1/2, -1/2, -3/2$ and for $j = 1/2$, $m = 1/2$ and $-1/2$. The number of $|jm\rangle$ eigenstates is thus six and the 6×6 matrix reduces to two 1×1 and two 2×2 matrices details of which are given in Table 8.7. The elements

$$\langle 1, 1/2 \mid 3/2, 3/2\rangle, \quad \langle 1, -1/2 \mid 3/2, 1/2\rangle, \quad \langle 0, 1/2 \mid 3/2, 1/2\rangle,$$
$$\langle 1, -1/2 \mid 1/2, 1/2\rangle \quad \text{and} \quad \langle 0, 1/2 \mid 1/2, 1/2\rangle$$

are easily evaluated with the help of Eqs. (8.76) through Eq. (8.80) and are listed in the table. Evaluation of the remaining elements are done as detailed below.

$\langle 0, -1/2 \mid 3/2, -1/2\rangle$: Setting $j = 3/2$, $m = 1/2$, $m_1 = 0$ and $m_2 = -1/2$ in Eq. (8.74), we get

$$2\langle 0, -1/2 \mid 3/2, -1/2\rangle = 2^{1/2} \langle 1, -1/2 \mid 3/2, 1/2\rangle + \langle 0, 1/2 \mid 3/2, 1/2\rangle$$

Substituting the two coefficients on the right side from Table 8.7. We have

$$\langle 0, -1/2|3/2, -1/2\rangle = \sqrt{2/3}$$

$\langle -1, 1/2 \mid 3/2, -1/2\rangle$: Setting $j = 3/2$, $m = 1/2$, $m_1 = -1$ and $m_2 = 1/2$ in Eq. (8.74) and proceeding as in the previous case, we have

$$2\langle -1, 1/2 \mid 3/2, -1/2\rangle = 2^{1/2} \langle 0, 1/2 \mid 3/2, 1/2\rangle$$

or

$$\langle -1, 1/2 \mid 3/2, -1/2\rangle = 1/\sqrt{3}$$

$\langle 0, -1/2 \mid 1/2, -1/2\rangle$: Setting $j = 1/2$, $m = 1/2$, $m_1 = 0$, $m_2 = -1/2$ in Eq. (8.74) gives the value as $1/\sqrt{3}$.

$\langle -1, 1/2| 1/2, -1/2\rangle$: Again, setting $j = 1/2$, $m = 1/2$, $m_1 = -1$, $m_2 = 1/2$ in Eq. (8.74) gives the value as $-\sqrt{(2/3)}$.

The last two coefficients could have been evaluated by following the procedure used for the derivation of Eqs. (8.79) and (8.80). Obviously, the last element

$$\langle -1, -1/2|3/2, -3/2\rangle = 1$$

Table 8.7 Clebsh–Gordan Coefficients for $j_1 = 1$ and $j_2 = 1/2$

		$\lvert j,m\rangle$					
m_1	m_2	$\lvert 3/2, 3/2\rangle$	$\lvert 3/2, 1/2\rangle$	$\lvert 1/2, 1/2\rangle$	$\lvert 3/2, -1/2\rangle$	$\lvert 1/2, -1/2\rangle$	$\lvert 3/2, -3/2\rangle$
1	1/2	1					
1	−1/2		$1/\sqrt{3}$	$\sqrt{2/3}$			
0	1/2		$\sqrt{2/3}$	$-1/\sqrt{3}$			
0	−1/2				$\sqrt{2/3}$	$\sqrt{1/3}$	
−1	1/2				$\sqrt{1/3}$	$-\sqrt{2/3}$	
−1	−1/2						1

EXAMPLE 8.10 An electron is in a state described by the wave function

$$\psi = \frac{1}{\sqrt{4\pi}}\left(\cos\theta + e^{-i\phi}\sin\theta\right) R(r), \quad \int_0^\infty |R(r)|^2\, r^2 dr = 1$$

where θ and ϕ are respectively the polar and azimuth angles

(i) What are the possible values of L_z?

(ii) What is the probability of obtaining each of the possible values of L_z?

(i) From Table 5.2, we have

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \quad \text{and} \quad Y_{1,-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{-i\phi}$$

Hence the given wave function can be written as:

$$\psi = \frac{1}{\sqrt{3}}\left(\mathrm{Y}_{10} + \sqrt{2}\, Y_{1,-1}\right) R(r)$$

The possible values of L_z are 0 and $-\hbar$.

(ii) $\int |\psi|^2 d\tau = \frac{1}{3}\int |R(r)|^2 \, |(Y_{10} + \sqrt{2}\, Y_{1,-1})|^2 \, r^2 \sin\theta \, d\theta \, d\phi \, dr$

$$\left|\left(Y_{10} + \sqrt{2}\, Y_{1,-1}\right)\right|^2 = \left(Y_{10} + \sqrt{2}\, Y_{1,-1}\right)^* \left(Y_{10} + \sqrt{2}\, Y_{1,-1}\right)$$

$$= Y_{10}^* Y_{10} + 2Y_{1,-1}^* Y_{1,-1} + \sqrt{2}\left(Y_{10}^* Y_{1,-1} + Y_{1,-1}^* Y_{10}\right)$$

$$= \frac{3}{4\pi}(\cos^2\theta + \sin^2\theta) + \frac{3}{4\pi}(e^{-i\phi}\cos\theta\sin\theta + e^{i\phi}\sin\theta\cos\theta)$$

$$= \frac{3}{4\pi} + \frac{3}{4\pi}\sin\theta\cos\theta\,(e^{i\phi} + e^{-i\phi})$$

$$= \frac{3}{4\pi}\left(1 + \sin 2\theta \cos\phi\right)$$

$$\int |\psi|^2 d\tau = \frac{1}{4\pi}\int_0^\infty |R(r)|^2\, r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \left(1 + \sin 2\theta \cos\phi\right) d\phi$$

$$= \frac{1}{2}\int_0^\pi \sin\theta \, d\theta = 1$$

That is the given wave function is normalized. The probability density is then $P = |\psi|^2$. Hence, the probability of obtaining $L_z = 0$ is $(1/\sqrt{3})^2 = 1/3$. The probability of obtaining $L_z = -1\hbar$ is $(\sqrt{2/3})^2 = 2/3$.

EXAMPLE 8.11 An operator P describing the interaction of two spin 1/2 particles is $P = a + b\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2$, where a and b are constants, and $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are Pauli matrices of the two spins. The total spin angular momentum $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 = \frac{1}{2}\hbar(\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2)$. Show that P, S^2 and S_z can be measured simultaneously.

P, S^2 and S_z can be measured simultaneously if

$$[P, S^2] = [P, S_z] = [S^2, S_z] = 0$$

We know that $[S^2, S_z] = 0$. From the definition,

$$S^2 = \frac{\hbar^2}{4}\left(\sigma_1^2 + \sigma_2^2 + 2\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2\right)$$

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \frac{2S^2}{\hbar^2} - \tfrac{1}{2}\left(\sigma_1^2 + \sigma_2^2\right)$$

Since for each particle,

$$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3I$$

where I is unit matrix.

$$\tfrac{1}{2}\left(\sigma_1^2 + \sigma_2^2\right) = \tfrac{1}{2}(3I + 3I) = 3I$$

Hence

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \frac{2S^2}{\hbar^2} - 3I$$

$$\left[S^2, P\right] = \left[S^2, a\right] + b\left[S^2, \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2\right] = b\left[S^2, \frac{2S^2}{\hbar^2} - 3I\right]$$

$$= b\left[S^2, \frac{2S^2}{\hbar^2}\right] - b\left[S^2, 3I\right] = 0$$

$$\left[S_z, P\right] = \left[S_z, a\right] + b\left[S_z, \frac{2S^2}{\hbar^2} - 3I\right] = 0$$

Since S^2 and S_z commutes with P, all the three can be measured simultaneously.

EXAMPLE 8.12 Obtain the Hamiltonian operator for a free electron having magnetic moment $\boldsymbol{\mu}$ in an external magnetic field B_z in the z-direction in the electron's reference frame. If another constant magnetic field B_y is applied in the y-direction, obtain the time rate of change of $\boldsymbol{\mu}$ in the Heisenberg picture.

The magnetic moment of the electron

$$\boldsymbol{\mu} = -\frac{e}{m}\mathbf{S} = -\frac{e\hbar}{2m}\boldsymbol{\sigma} = -\mu_B\boldsymbol{\sigma}$$

where we have used Eq. (8.52) and μ_B is the Bohr magneton. The Hamiltonian

$$H' = -\boldsymbol{\mu}\cdot\mathbf{B} = -\mu_z B_z = \mu_B\,\sigma_z B_z$$

With the total magnetic field applied $B = B_y\hat{y} + B_z\hat{z}$, the total Hamiltonian

$$H = \mu_B(\sigma_z B_z + \sigma_y B_y)$$

From Eq. (3.106a),

$$\frac{d\boldsymbol{\mu}}{dt} = \frac{1}{i\hbar}[\mu, H] = \frac{1}{i\hbar}[-\mu_B\boldsymbol{\sigma}, \mu_B(\sigma_z B_z + \sigma_y B_y)]$$

$$= -\frac{\mu_B^2}{i\hbar}[\sigma_x\hat{x} + \sigma_y\hat{y} + \sigma_z\hat{z}, \sigma_z B_z + \sigma_y B_y]$$

$$= -\frac{\mu_B^2}{i\hbar}[\sigma_x, \sigma_z]B_z\hat{x} + [\sigma_x, \sigma_y]B_y\hat{x} + [\sigma_y, \sigma_z]B_z\hat{y}$$

$$+ [\sigma_y, \sigma_y]B_y\hat{y} + [\sigma_z, \sigma_z]B_z\hat{z} + [\sigma_z, \sigma_y]B_y\hat{z}$$

Using the commutation relations among σ_x, σ_y, σ_z (Refer Example 8.8)

$$\frac{d\boldsymbol{\mu}}{dt} = \frac{i}{\hbar}\mu_B^2[-2i\sigma_y B_z\hat{x} + 2i\sigma_z B_y\hat{x} + 2i\sigma_x B_z\hat{y} - 2i\sigma_x B_y\hat{z}]$$

$$= \frac{2}{\hbar}\mu_B^2\,[(\sigma_y B_z - \sigma_z B_y)\,\hat{x} - \sigma_x B_z\,\hat{y} + \sigma_x B_y\,\hat{z}]$$

$$= \frac{2}{\hbar}\mu_B^2\,[\boldsymbol{\sigma}\times\mathbf{B}] = -\frac{2}{\hbar}\mu_B^2\,[\mathbf{B}\times\boldsymbol{\sigma}]$$

$$= \frac{e}{m}[\mathbf{B}\times\boldsymbol{\mu}]$$

which is the time rate of change of magnetic moment.

EXAMPLE 8.13 Obtain the energy levels of a symmetric top molecule with principal moments of inertia $I_1 = I_2 = I \neq I_3$.

Let (x, y, z) be the co-ordinates of a body fixed co-ordinate system. The Hamiltonian

$$H = \frac{1}{2}\left(\frac{L_x^2}{I_1} + \frac{L_y^2}{I_2} + \frac{L_z^2}{I_3}\right) = \frac{1}{2I}(L_x^2 + L_y^2) + \frac{1}{2I_3}L_z^2$$

$$= \frac{1}{2I}L^2 + \frac{1}{2}\left(\frac{1}{I_3} - \frac{1}{I}\right)L_z^2$$

$|\,lm\rangle$ are the simultaneous eigenkets of L^2 and L_z. The Schrödinger equation is:

$$\left[\frac{1}{2I}L^2 + \frac{1}{2}\left(\frac{1}{I_3} - \frac{1}{I}\right)L_z^2\right] \mid lm\rangle = E \mid lm\rangle$$

$$E_{lm} = \frac{\hbar^2}{2I}l(l+1) + \frac{\hbar^2}{2}\left(\frac{1}{I_3} - \frac{1}{I}\right)m^2$$

which is the energy expression for symmetric top. This energy expression can be expressed in the familiar form by writing

$$\frac{\hbar^2}{2I} = B, \quad \frac{\hbar^2}{2I_3} = C$$

$$E_{lm} = B\, l(l+1) + (C - B)\, m^2$$

The constants B and C are rotational constants.

$$l = 0, 1, 2, \cdots ; \; m = 0, \pm 1, \pm 2, \cdots, \pm l$$

EXAMPLE 8.14 Kets $\mid j, m\rangle$ are the simultaneous eigenkets of J^2 and J_z. Show that $\mid j, m\rangle$ are also eigenkets of $[J_x, J_+]$ and of $[J_y, J_+]$. Find the eigenvalues of each of these commutators.

Operating $[J_x, J_+]$ on the eigenkets $|j\, m\rangle$,

$$\begin{aligned}[J_x, J_+]\mid j\, m\rangle &= J_x J_+ \,|j\, m\rangle - J_+ J_x \,|j\, m\rangle \\ &= \frac{1}{2}(J_+ + J_-)\, J_+ |j\, m\rangle - J_+ \frac{1}{2}(J_+ + J_-)\, |j\, m\rangle \\ &= \frac{1}{2}J_+J_+|j\, m\rangle + \frac{1}{2}J_-J_+|j\, m\rangle - \frac{1}{2}J_+J_+|j\, m\rangle - \frac{1}{2}J_+J_-|j\, m\rangle \\ &= \frac{1}{2}J_-J_+|j\, m\rangle - \frac{1}{2}J_+J_-|j\, m\rangle\end{aligned}$$

From Eq. (8.15),

$$J_-J_+ = J^2 - J_z^2 - \hbar J_z \text{ and } J_+J_- = J^2 - J_z^2 + \hbar J_z$$

Hence

$$\begin{aligned}[J_x, J_+] \mid j\, m\rangle &= \frac{1}{2}(J^2 - J_z^2 - \hbar J_z) \mid j\, m\rangle - \frac{1}{2}(J^2 - J_z^2 + \hbar J_z) \mid j\, m\rangle \\ &= -\hbar J_z \mid j\, m\rangle = -m\hbar^2 \mid j\, m\rangle\end{aligned}$$

That is, $\mid j, m\rangle$ are eigenkets of $[J_x, J_+]$ with eigenvalues $-m\hbar^2$

$$
\begin{aligned}
[J_y, J_+] \,|\, j\, m\rangle &= (J_y J_+ - J_+ J_y) \,|\, j\, m\rangle \\
&= \frac{1}{2i}(J_+ - J_-)\, J_+ \,|\, j\, m\rangle - \frac{1}{2i} J_+ (J_+ - J_-) \,|\, j\, m\rangle \\
&= -\frac{1}{2i} J_- J_+ \,|\, j\, m\rangle + \frac{1}{2i} J_+ J_- \,|\, j\, m\rangle \\
&= -\frac{1}{2i}(J^2 - J_z^2 - \hbar J_z) \,|\, j\, m\rangle + \frac{1}{2i}(J^2 - J_z^2 + \hbar J_z) \,|\, j\, m\rangle \\
&= \frac{1}{i}\hbar J_z \,|\, j\, m\rangle = \frac{1}{i} m\hbar^2 \,|\, j\, m\rangle \\
&= -\, i\, m\hbar^2 \,|\, j\, m\rangle
\end{aligned}
$$

That is $|\, j, m\, \rangle$ are eigenkets of the commutator $[J_y, J_+]$ with eigenvalues $-\, i\, m\hbar^2$.

REVIEW QUESTIONS

1. State the commutation relations obeyed by the components of angular momentum and express them in vector notation.
2. Though the angular momentum components J_x, J_y and J_z commute with J^2, we cannot have a representation in which J^2, J_x, J_y and J_z are diagonal. Why?
3. What are ladder operators? Why are they called so?
4. In a representation in which L^2 and L_z have simultaneous eigenfunctions, what is the value of the uncertainty product (ΔL_x) (ΔL_y). Comment on the value of this product when $l = 0$
5. The definition of angular momentum given by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is not a general one. Why? Define a general angular momentum operator.
6. State the eigenvalue–eigenvector relations for the operators J^2 and J_z. Hence obtain the matrices for J^2 and J_z.
7. What do you understand by 'spin-up' and 'spin-down' states? What are spinors? Write the bra spinor corresponding to the

   $$\text{ket} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
8. For a spin-1/2-system, state the matrices for S_x, S_y and S_z. List their eigenvalues with the corresponding eigenvectors.
9. What are Clebsh–Gordan coefficients? Explain their significance.
10. How many angular momentum states arise for a system with two angular momenta $j_1 = 1$ and $j_2 = 1/2$? Specify the states.

11. If $\mathbf{J}_1$ and $\mathbf{J}_2$ represent angular momentum operators, are $\mathbf{J}_1 + \mathbf{J}_2$ and $\mathbf{J}_1 - \mathbf{J}_2$ angular momenta? Explain.

12. What do you understand by 'spin of an electron'?

PROBLEMS

1. Obtain expressions for L_+, L_- and L^2 in spherical polar coordinates.

2. Show that the raising and lowering operators J_+ and J_- are Hermitian conjugates.

3. Prove that the spin matrices S_x and S_y have $\pm\hbar/2$ eigenvalues.

4. Evaluate the commutator $[L_x, L_y]$ in the momentum representation.

5. Evaluate the following commutators

(i) $[L_x, [L_y, L_z]]$ (ii) $[L_y^2, L_x]$ (iii) $[L_x^2, L_y^2]$

6. Prove by direct matrix multiplication that the Pauli matrices anticommute and they follow the commutation relations $[\sigma_x, \sigma_y] = 2i\sigma_z$, xyz cyclic.

7. Obtain the normalized eigenvectors of σ_x and σ_y matrices.

8. Using Pauli's spin matrix representation reduce each of the operators:

(i) $S_x^2 S_y S_z^2$ (ii) $S_x^2 S_y^2 S_z^2$ (iii) $S_x S_y S_z^3$

9. Determine the total angular momentum that may arise when the following angular momenta are added:

(i) $j_1 = 1, j_2 = 1$ (ii) $j_1 = 3, j_2 = 4$ (iii) $j_1 = 2, j_2 = 1/2$

10. Determine the orbital momenta of two electrons in units of $\hbar$

(i) both in d-orbitals (ii) both in p-orbitals (iii) in the configuration p^1d^1

11. For any vector **A**, show that $[\boldsymbol{\sigma}, \mathbf{A}\cdot\boldsymbol{\sigma}] = 2i\mathbf{A}\times\boldsymbol{\sigma}$

12. Evaluate the Clebsh–Gordan coefficients for a system having

$$j_1 = 1/2 \quad \text{and} \quad j_2 = 1/2$$

13. Obtain the matrix of Clebsh–Gordan coefficients for $j_1 = 1$ and $j_2 = 1$.

14. The sum of the two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ are given by $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. If the eigenkets of J_1^2 and J_2^2 are $|j_1m_1\rangle$ and $|j_2m_2\rangle$ respectively, find the number of eigenstates of J^2.

15. If the eigenvalues of J^2 and J_z are given by $J^2|\lambda m\rangle = \lambda|\lambda m\rangle$ and $J_z|\lambda m\rangle = m|\lambda m\rangle$ show that $\lambda \geq m^2$.

16. The eigenfunctions of the Pauli spin operator σ_z are α and β. Show that $(\alpha+\beta)/\sqrt{2}$ and $(\alpha-\beta)/\sqrt{2}$ are the eigenfunctions of σ_x and $(\alpha+i\beta)/\sqrt{2}$ and $(\alpha-i\beta)/\sqrt{2}$ are eigenfunctions of σ_y.

17. An electron in a state is described by the wave function:

$$\psi = \frac{1}{\sqrt{4\pi}}(e^{i\phi}\sin\theta + \cos\theta)R(r), \qquad \int_0^\infty | R(r) |^2 r^2 dr = 1$$

where θ and ϕ are the polar and azimuth angles respectively. (i) Is the given wave function normalized? (ii) What are the possible values expected in a measurement of the z-component L_z of the angular momentum of the electron in this state? (iii) What is the probability of obtaining each of the possible values in (ii)?

18. The rotational part of a Hamiltonian of a diatomic molecule is $\frac{1}{2I}(L_x^2 + L_y^2) + \frac{1}{I}L_z^2$, I is moment of inertia. Find the energy eigenvalues and eigenfunctions.

19. The spin functions for a free electron in a basis in which S^2 and S_z are diagonal are $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$ with S_z eigenvalues $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ respectively. Using this basis find the eigenvalues and normalized eigenkets of S_x and S_y.

20. The $Y_{lm}(\theta, \phi)$ form a complete set of orthonormal functions of (θ, ϕ). Prove that

$$\sum_{l} \sum_{m=-l}^{l} | Y_{lm}\rangle\langle Y_{lm} | = 1$$

where 1 is the unit operator.

21. Operators J_+ and J_- are defined by $J_+ = J_x + iJ_y$ and $J_- = J_x + iJ_y$, where J_x and J_y are the x and y components of the general angular momentum J. Prove that

(i) $J_+ | j,m \rangle = [j(j+1) - m(m+1)]^{1/2}\, \hbar\, | j, m+1 \rangle$

(ii) $J_- | j,m \rangle = [j(j+1) - m(m-1)]^{1/2}\, \hbar\, | j, m-1 \rangle$

Chapter 9

Time-Independent Perturbation Theory

We considered, in the earlier chapters, some of the systems for which the Schrödinger equation is exactly solvable. However, the potential energy of most of the real systems are different from those considered and an exact solution is not possible. Different approximate methods such as time-independent perturbation method, variation method, WKB approximation, self-consistent procedure, etc., have therefore been developed to obtain approximate solution of systems.

9.1 BASIC CONCEPTS

In the time-independent perturbation approach, a known solution of a system whose Hamiltonian is only slightly different from that of the system under consideration is used as the starting point. The Hamiltonian operator H representing the total energy of the system can be written as

$$H = H^0 + H' \tag{9.1}$$

where H^0 is called the *unperturbed Hamiltonian*, whose nondegenerate eigenvalues E_n^0, $n = 1, 2, \ldots$ and eigenfunctions ψ_n^0 are assumed to be known and the time-independent operator H', called the *perturbation*, is small. These functions ψ_n^0, $n = 1, 2, \ldots$ form a complete orthonormal basis. These correspond to the eigenvalue equation

$$H^0\psi_n^0 = E_n^0\psi_n^0, \qquad n = 1, 2, \ldots \tag{9.2}$$

Our aim here is to solve the Schrödinger equation

$$H\psi_n = E_n\psi_n \tag{9.3}$$

If we write the Hamiltonian H of the perturbed system as

$$H = H^0 + \lambda H' \tag{9.4}$$

as the parameter λ changes from 0 to 1, the Hamiltonian changes from H^0 to H and the eigenfunction from ψ_n^0 to ψ_n. We can, therefore, expand E_n and ψ_n in terms of the parameter λ as

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{9.5}$$

$$\psi_n = \psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots \tag{9.6}$$

where the terms independent of λ are known as *zeroth order terms* (unperturbed ones), those in λ are first order, those in λ^2 second order, and so on. Thus, $E_n^{(1)}$ and $\psi_n^{(1)}$ are respectively the *first-order correction* to the energy and wave function, $E_n^{(2)}$ and $\psi_n^{(2)}$ the respective *second-order correction* and so on. Substituting these in Eq. (9.3), we get

$$\begin{aligned}&(H^0 + \lambda H')\,(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)\\ &\quad= (E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)\,(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \cdots)\end{aligned}$$

or

$$\begin{aligned}&(H^0 - E_n^0)\psi_n^0 + \lambda(H'\psi_n^0 + H^0\psi_n^{(1)} - E_n^{(1)}\psi_n^0 - E_n^0\psi_n^{(1)})\\ &\quad+ \lambda^2(H'\psi_n^{(1)} + H^0\psi_n^{(2)} - E_n^{(2)}\psi_n^0 - E_n^{(1)}\psi_n^{(1)} - E_n^0\psi_n^{(2)}) = 0\end{aligned} \tag{9.7}$$

Since λ is arbitrary, the coefficient of each power of λ must vanish separately and therefore we have

$$H^0\psi_n^0 = E_n^0\psi_n^0 \tag{9.8}$$

$$H'\psi_n^0 + H^0\psi_n^{(1)} = E_n^{(1)}\psi_n^0 + E_n^0\psi_n^{(1)} \tag{9.9}$$

$$H'\psi_n^{(1)} + H^0\psi_n^{(2)} = E_n^{(2)}\psi_n^0 + E_n^{(1)}\psi_n^{(1)} + E_n^0\psi_n^{(2)} \tag{9.10}$$

As we are interested only up to second order, we neglect equations beyond Eq. (9.10). Equation (9.8) is identical to Eq. (9.2) as expected since it refers to perturbation of zero order.

9.2 NONDEGENERATE ENERGY LEVELS

We have not so far specified whether the unperturbed energy level is nondegenerate or degenerate. First, we shall consider perturbations on energy levels that are nondegenerate. For convenience, we shall use the wave function itself to label the states.

First-order Correction to the Energy

Multiplying Eq. (9.9) from the left by $\langle \psi_n^0 |$, we get

$$\langle \psi_n^0 | H' | \psi_n^0 \rangle + \langle \psi_n^0 | H^0 | \psi_n^{(1)} \rangle = E_n^{(1)} \langle \psi_n^0 | \psi_n^0 \rangle + E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle \quad (9.11)$$

Since H^0 is Hermitian, the second term on the left reduces to $E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle$, and Eq. (9.11) gives

$$E_n^{(1)} = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (9.12)$$

In simplified form, Eq. (9.12) can be written as

$$E_n^{(1)} = \langle n | H' | n \rangle \quad (9.13)$$

which is often referred to as *matrix elements*. The first order correction to the energy is thus the average value of the perturbation over the corresponding unperturbed states of the system.

First-order Correction to Wave Function

The first-order correction to the wave function is written as a linear combination of the unperturbed wave functions of the system.

$$\psi_n^{(1)} = \sum_{l=1}^{\infty} a_l \psi_l^0 \quad (9.14)$$

Substitution of Eq. (9.14) in Eq. (9.9) and multiplication from the left by $\langle \psi_m^0 |$ gives

$$\langle \psi_m^0 | H' | \psi_n^0 \rangle + \sum_{l=1}^{\infty} a_l E_l^0 \langle \psi_m^0 | \psi_l^0 \rangle = E_n^{(1)} \langle \psi_m^0 | \psi_n^0 \rangle + \sum_{l=1}^{\infty} a_l E_n^0 \langle \psi_m^0 | \psi_l^0 \rangle$$

or

$$\langle \psi_m^0 | H' | \psi_n^0 \rangle + a_m E_m^0 = a_m E_n^0$$

or

$$a_m = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} = \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0} \quad (9.15)$$

All the a's except a_n in Eq. (9.14) can be calculated using Eq. (9.15). The coefficient a_n is found to be zero from the normalization condition $\langle \psi_n | \psi_n \rangle = 1$. It follows that

$$\psi_n^{(1)} = \sum_m{}' \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0} | \psi_m^0 \rangle \quad (9.16)$$

Consequently, the energy and wave function corrected to first order are

$$E_n = E_n^0 + \langle n | H' | n \rangle \quad (9.17)$$

and

$$\psi_n = \psi_n^0 + \sum_m{}' \frac{\langle m|H'|n\rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle \tag{9.18}$$

where the prime on the sum means that the state $m = n$ should be excluded.

Second-order Correction to the Energy

The same procedure is used to obtain the second-order correction to the energy from Eq. (9.10). Multiplying Eq. (9.10) from left by $\langle \psi_n^0 |$ and using the Hermitian nature of H^0, we get

$$\langle \psi_n^0 | H' | \psi_n^{(1)} \rangle = E_n^{(2)} \langle \psi_n^0 | \psi_n^0 \rangle + E_n^{(1)} \langle \psi_n^0 | \psi_n^{(1)} \rangle \tag{9.19}$$

The form of $\psi_n^{(1)}$, Eq. (9.16), suggests that the second term on the right vanishes. Therefore,

$$E_n^{(2)} = \langle \psi_n^0 | H' | \psi_n^{(1)} \rangle \tag{9.20}$$

Substituting the value of $\psi_n^{(1)}$ in Eq. (9.20), we have

$$E_n^{(2)} = \sum_m{}' \frac{\langle \psi_m^0 |H'| \psi_n^0 \rangle \langle \psi_n^0 |H'| \psi_m^0 \rangle}{E_n^0 - E_m^0} = \sum_m{}' \frac{\langle m|H'|n\rangle \langle n|H'|m\rangle}{E_n^0 - E_m^0} \tag{9.21}$$

If H' is Hermitian $\langle n | H' | m \rangle = \langle m | H' | n \rangle^*$. Then

$$E_n^{(2)} = \sum_m{}' \frac{|\langle m|H'|n\rangle|^2}{E_n^0 - E_m^0} \tag{9.22}$$

Since $|\langle m | H' | n \rangle|^2$ is always positive, the sign of the correction is determined by the denominator. The second-order correction in energy to level n due to levels for which $E_n^0 > E_m^0$ is positive whereas that due to levels for which $E_n^0 < E_m^0$ is negative.

Second-order Correction to Wave Function

The second-order correction to the wave function $\psi_n^{(2)}$ is written as a linear combination of the unperturbed wave function of the system:

$$\psi_n^{(2)} = \sum_k b_k \psi_k^0 \tag{9.23}$$

Substitution of Eq. (9.23) in Eq. (9.10) and multiplication from left by $\langle \psi_l^0 |$ gives

$$\sum_m{}' a_m \langle l | H' | m \rangle + \sum_k b_k \langle l | H^0 | k \rangle = E_n^{(2)} \langle l | n \rangle + \sum_m{}' a_m E_n^{(1)} \langle l | m \rangle + \sum_k b_k E_n^0 \langle l | k \rangle$$

The first term on the right is zero. Rearranging, we get

$$b_l(E_l^0 - E_n^0) = E_n^{(1)}a_l - \sum_m{}' a_m\langle l\,|\,H'\,|\,m\rangle$$

Substituting the values of the a's and $E_n^{(1)}$, we have

$$b_l = \frac{\langle n|H'|n\rangle\langle l|H'|n\rangle}{\left(E_l^0 - E_n^0\right)\left(E_n^0 - E_l^0\right)} - \sum_m{}' \frac{\langle m|H'|n\rangle\langle l|H'|m\rangle}{\left(E_n^0 - E_m^0\right)\left(E_l^0 - E_n^0\right)}$$

$$= \sum_m{}' \frac{\langle m|H'|n\rangle\langle l|H'|m\rangle}{\left(E_n^0 - E_m^0\right)\left(E_n^0 - E_l^0\right)} - \frac{\langle n|H'|n\rangle\langle l|H'|n\rangle}{\left(E_n^0 - E_l^0\right)^2} \tag{9.24}$$

The normalization condition of the wave function shows that the coefficient b_n is zero. It follows that the energy and wave function of the system corrected to second order in the perturbation is

$$E_n = E_n^0 + \langle n\,|\,H'\,|\,n\rangle + \sum_m{}' \frac{\left|\langle n|H'|m\rangle\right|^2}{E_n^0 - E_m^0} \tag{9.25}$$

and

$$\psi_n = \psi_n^0 + \sum_m{}' a_m\psi_m^0 + \sum_l{}' b_l\psi_l^0 \tag{9.26}$$

where the coefficients a_m and b_l are given by Eq. (9.15) and (9.24), respectively. The prime on the sum again signifies the omission of the states $m = n$ or $l = n$ as the case may be.

9.3 ANHARMONIC OSCILLATOR: FIRST-ORDER CORRECTION

Consider a particle of mass m subjected to a one-dimensional potential

$$V(x) = \frac{1}{2}m\omega^2x^2 + bx^4 \tag{9.27}$$

where ω is the angular frequency and b is a small parameter independent of x. If b were zero, the potential would correspond to that of a harmonic oscillator. The inclusion of the term bx^4 in the potential changes the system from a harmonic oscillator to an anharmonic oscillator. We shall calculate the first-order correction to the ground state energy, which is given by

$$E^{(1)} = \langle 0\,|\,bx^4\,|\,0\rangle \tag{9.28}$$

In terms of creation ($a^\dagger$) and annihilation (a) operators,

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a + a^\dagger) \tag{9.29}$$

and

$$E^{(1)} = b\left(\frac{\hbar}{2m\omega}\right)^2 \langle 0|(a + a^\dagger)(a + a^\dagger)(a + a^\dagger)(a + a^\dagger)|0\rangle \quad (9.30)$$

When expanded, the expression on the right will have 16 terms with four factors of a or $a^\dagger$ or both. A product operator like $a^\dagger a a^\dagger a$ gives zero for the matrix element since $a|0\rangle = 0$. Also, in a product operator like $a\, a^\dagger a^\dagger a^\dagger$, the number of a's and $a^\dagger$'s are not equal. In such a case, $a a^\dagger a^\dagger a^\dagger|0\rangle$ will be different from $|0\rangle$ leading to zero value for $\langle 0|a a^\dagger a^\dagger a^\dagger|0\rangle$. Hence, the two nonvanishing terms in the present case will be $\langle 0|a a a^\dagger a^\dagger|0\rangle$ and $\langle 0|a a^\dagger a a^\dagger|0\rangle$. The relations:

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \quad \text{and} \quad a|n\rangle = \sqrt{n}\,|n-1\rangle \quad (9.31)$$

give

$$\langle 0|a a a^\dagger a^\dagger|0\rangle = 2 \quad \text{and} \quad \langle 0|a a^\dagger a a^\dagger|0\rangle = 1 \quad (9.32)$$

Hence, from Eq. (9.30)

$$E^{(1)} = 3b\left(\frac{\hbar}{2m\omega}\right)^2 \quad (9.33)$$

Then, the corrected ground state energy is

$$E_0 = \frac{1}{2}\hbar\omega + 3b\left(\frac{\hbar}{2m\omega}\right)^2 \quad (9.34)$$

9.4 THE GROUND STATE OF HELIUM

Helium atom consists of a nucleus of charge Ze at the origin and two electrons with radius vectors r_1 and r_2 (Figure 9.1).

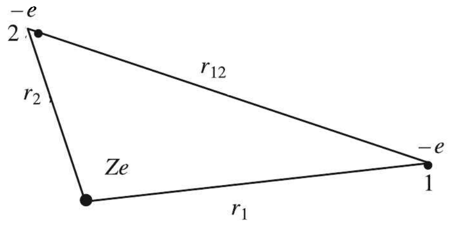


Figure 9.1 The helium atom.

Neglecting the motion of the nucleus, the Hamiltonian of the system is

$$H = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \quad (9.35)$$

where ∇_1 and ∇_2 refer to the coordinates of electrons 1 and 2 respectively. The term $e^2/4\pi\varepsilon_0 r_{12}$ represents the electrostatic repulsion between the two electrons. Writing,

$$H(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} \quad \text{and} \quad H(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \tag{9.36}$$

Equation (9.35) can be rewritten as

$$H = H(1) + H(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{9.36a}$$

The Schrödinger equation corresponding to $H(1)$ and $H(2)$ are exactly solvable and the solutions are simply hydrogenic wavefunctions. That is,

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\right)\psi_1^0 = E_1^0\psi_1^0 \tag{9.37}$$

where

$$E_1^0 = \frac{-Z^2me^4}{(4\pi\varepsilon_0)^2 2\hbar^2}; \quad \psi_1^0 = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} \exp\left(-\frac{Zr_1}{a_0}\right) \tag{9.38}$$

and

$$\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}\right)\psi_2^0 = E_2^0\psi_2^0 \tag{9.39}$$

where

$$E_2^0 = \frac{-Z^2me^4}{(4\pi\varepsilon_0)^2 2\hbar^2}; \quad \psi_2^0 = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} \exp\left(-\frac{Zr_2}{a_0}\right) \tag{9.40}$$

Here $a_0 = 4\pi\varepsilon_0\hbar^2/me^2$, the Bohr radius. The wave function and energy eigenvalue corresponding to $H(1) + H(2)$ are:

$$\psi^0 = \psi_1^0\psi_2^0, \; E^0 = E_1^0 + E_2^0 = -2Z^2W_H \tag{9.41}$$

where

$$W_H = \frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = 13.6 \text{ eV} \tag{9.42}$$

Hence $H(1) + H(2)$ can be regarded as the unperturbed Hamiltonian and $e^2/4\pi\varepsilon_0 r_{12}$ as the perturbing Hamiltonian. First-order correction to the ground state energy is then

$$E^{(1)} = \iint \psi_1^{0*}\psi_2^{0*} \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_1^0\psi_2^0 \, d\tau_1 d\tau_2$$

Substituting the values of ψ_1^0 and ψ_2^0, we get

$$E^{(1)} = \frac{Z^6 e^2}{4\pi\varepsilon_0 \pi^2 a_0^6} \iint \frac{1}{r_{12}} \exp\left[-\frac{2Z}{a_0}(r_1 + r_2)\right] d\tau_1 d\tau_2 \tag{9.43}$$

where

$$d\tau_1 = r_1^2 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1; \qquad d\tau_2 = r_2^2 \sin\theta_2 \, dr_2 \, d\theta_2 \, d\phi_2$$

Evaluation of the integral in Eq. (9.43) may be done by expanding $1/r_{12}$ in terms of Legendre polynomials. The integration in Eq. (9.43) (also refer to Example 9.7) leads to a value of $5ZW_H/4$ for the first-order correction to the ground state. The energy corrected to the first-order is then given by

$$E = -2Z^2 W_H + \frac{5}{4} Z W_H = -\left(2Z^2 - \frac{5}{4} Z\right) W_H \tag{9.44}$$

It may be noted that $E^{(1)}$ is about 31% of E^0, since

$$\frac{E^{(1)}}{E^0} = \frac{5ZW_H/4}{2Z^2 W_H} = \frac{5}{8Z} \tag{9.45}$$

The correction is subtractive which is understandable since the effect of the electron–electron interaction is to reduce the electron nucleus attraction. The result holds good for two electron atoms like Li^+, Be^{++}, B^{3+}, etc., with $Z = 3, 4, 5, \ldots$

9.5 EFFECT OF ELECTRIC FIELD ON THE GROUND STATE OF HYDROGEN

When an atom is placed in a uniform electric field, the energy levels are shifted. The shifting of energy levels produce a splitting of spectral lines, called *Stark effect*, which was first observed by Stark in hydrogen atom in 1913.

Consider an atom situated at the origin. Let an electric field **E** is applied along the positive z-axis. If **r** is the position vector of the electron, the electric dipole moment $\mu = -e\mathbf{r}$ interacts with the electric field **E** giving an additional potential energy to the electron

$$H' = -\mu \cdot \mathbf{E} = erE \cos\theta = eEz; \quad e\text{-positive} \tag{9.46}$$

where θ is the angle the position vector makes with the z-axis. Since this extra energy term is very small, it can be treated as a perturbation on

$$H^0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{ke^2}{r}; \quad k = \frac{1}{4\pi\varepsilon_0} \tag{9.47}$$

The ground state of the hydrogen atom is nondegenerate and the first-order correction to the energy

$$E^{(1)} = \langle \psi_{100} | eEr \cos\theta | \psi_{100} \rangle \tag{9.48}$$

where ψ_{100} is the hydrogen ground state wave function:

$$\psi_{100} = \frac{1}{\left(\pi a_0^3\right)^{1/2}} \exp\left(-\frac{r}{a_0}\right) \tag{9.49}$$

The θ part of the integral in Eq. (9.48) vanishes as

$$\int_0^\pi \cos\theta \sin\theta \, d\theta = -\int_0^\pi \cos\theta \, d(\cos\theta) = 0$$

Hence, the ground state of hydrogen atom will not show a first-order Stark effect and we have to calculate the second-order energy shift.

The second-order energy shift is estimated using Eq. (9.22). The calculation is easily done by a method due to Dalgarno and Lewis which avoids the sum over the infinite number of states in Eq. (9.22). Instead of working with Eq. (9.22) they went back to Eq. (9.20) and found an operator F (scalar function) such that

$$F\psi_1^0 = \psi_1^{(1)} \tag{9.50}$$

Equations (9.20) and (9.9) now reduce to

$$E_1^{(2)} = \langle \psi_1^0 | H'F | \psi_1^0 \rangle \tag{9.51}$$

and

$$H'\psi_1^0 + H^0F\psi_1^0 = E_1^{(1)}\psi_1^0 + FE_1^0\psi_1^0 \tag{9.52}$$

Since $E_1^{(1)}$ is zero and $E_1^0\psi_1^0 = H^0\psi_1^0$,

$$(FH^0 - H^0F)\psi_1^0 = H'\psi_1^0 \tag{9.53}$$

Since the scalar function F commutes with $-ke^2/r$ in H^0, the relation

$$\nabla^2(F\psi_1^0) = F\nabla^2\psi_1^0 + \psi_1^0\nabla^2F + 2\nabla\psi_1^0 \cdot \nabla F \tag{9.54}$$

reduces Eq. (9.53) to

$$\frac{\hbar^2}{2\mu}(\psi_1^0\,\nabla^2F + 2\nabla\psi_1^0 \cdot \nabla F) = H'\psi_1^0 \tag{9.55}$$

This gives the differential equation that determines the operator F. Substituting the value of ψ_1^0 in Eq. (9.55)

$$\nabla^2F - \frac{2}{a_0}\frac{\partial F}{\partial r} = \frac{2\mu}{\hbar^2} eEr\cos\theta \tag{9.56}$$

The angular part of the right-hand side of Eq. (9.56) comes from $\cos\theta$ which is the Legendre polynomial P_1. Therefore, F may be assumed to be of the following form

$$F = f(r)P_1 \tag{9.57}$$

This value of F when substituted in Eq. (9.56) gives the equation satisfied by $f(r)$ which leads to

$$F = -\frac{\mu}{\hbar^2} eEa_0\left(\frac{r}{2} + a_0\right) r\cos\theta \tag{9.58}$$

The second-order correction is then

$$E_1^{(2)} = \langle \psi_1^0 | H'F | \psi_1^0 \rangle$$

$$= -\frac{\mu}{\hbar^2} e^2E^2a_0 \frac{1}{\pi a_0^3} \int_0^{\pi}\int_0^{2\pi} \cos^2\theta \sin\theta\, d\theta\, d\phi \int_0^{\infty} \left(\frac{r^5}{2} + a_0 r^4\right) \exp\left(-\frac{2r}{a_0}\right) dr$$

$$= -\frac{4\mu}{3\hbar^2}\frac{e^2E^2}{a_0^2}\int_0^{\infty}\left(\frac{r^5}{2} + a_0 r^4\right) \exp\left(-\frac{2r}{a_0}\right) dr$$

On solving, we get

$$E_1^{(2)} = -\frac{9\mu}{4\hbar^2} e^2E^2a_0^4 = -\frac{9}{4k}a_0^3 E^2 \tag{9.59}$$

since $a_0 = \hbar^2/k\mu e^2$. Standard integral (refer to Appendix A-9) has been used in deriving Eq. (9.59). The ground state energy corrected to second order is found to be

$$E_1 = E_1^0 - \frac{9}{4k} a_0^3 E^2 \tag{9.60}$$

As the correction is proportional to the square of E, it is often referred to as the *quadratic Stark effect.*

Physically, the correction term $(-9/4k)a_0^3E^2$ is due to the distortion of the charge distribution of the 1s-electron by the electric field $\mathbf{E}$ and therefore we may say that the atom has been polarized by the field. The extent of this polarization is measured by the polarizability α, which is defined as the ratio of the induced electric dipole moment $\boldsymbol{\mu}$ to the external field $\mathbf{E}$

$$\boldsymbol{\mu} = \alpha\mathbf{E} \tag{9.61}$$

The energy of an induced dipole in an applied field is given by $-(1/2)\alpha E^2$. Equating this energy change with the energy due to perturbation calculation, we have

$$-\frac{1}{2}\alpha E^2 = -\frac{9}{4k}a_0^3E^2 \quad \text{or} \quad \alpha = \frac{9}{2k}a_0^3 \tag{9.62}$$

The polarizability α for hydrogen atom in the ground state is thus $(9/2k)a_0^3$.

9.6 DEGENERATE ENERGY LEVELS

The unperturbed wave function ψ_n^0 is a unique one in the nondegenerate case. When a degeneracy exists, a linear combination of the degenerate wave functions can be taken as the unperturbed wave function. For simplicity, consider a case in which E_n^0 is two-fold degenerate. Let ψ_n^0 and ψ_l^0 be eigenfunctions corresponding to eigenvalues $E_n^0 = E_l^0$ and a linear combination of the two be

$$\phi = c_n \psi_n^0 + c_l \psi_l^0 \tag{9.63}$$

where c_n and c_l are constants.

First-order Correction

Replacing ψ_n^0 in Eq. (9.9) by ϕ, we get

$$H' \,|\, (c_n \psi_n^0 + c_l \psi_l^0)\rangle + H^0 \,|\, \psi_n^{(1)}\rangle = E_n^{(1)} \,|\, (c_n \psi_n^0 + c_l \psi_l^0)\rangle + E_n^0 \,|\, \psi_n^{(1)}\rangle \tag{9.64}$$

Multiplying Eq. (9.64) from left by $\langle \psi_n^0 |$, we have

$$\begin{aligned} c_n \langle \psi_n^0 | H' | \psi_n^0 \rangle + c_l \langle \psi_n^0 | H' | \psi_l^0 \rangle + \langle \psi_n^0 | H^0 | \psi_n^{(1)} \rangle \\ = c_n E_n^{(1)} + E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle \end{aligned} \tag{9.65}$$

Since H^0 is Hermitian,

$$\langle \psi_n^0 | H^0 | \psi_n^{(1)} \rangle = E_n^0 \langle \psi_n^0 | \psi_n^{(1)} \rangle$$

and Eq. (9.65) reduces to

$$(H'_{nn} - E_n^{(1)})\, c_n + H'_{nl} c_l = 0 \tag{9.66}$$

Operating Eq. (9.64) from left by $\langle \psi_l^0 |$, we have

$$H'_{lm} c_n + (H'_{ll} - E_n^{(1)}) c_l = 0 \tag{9.67}$$

Equations (9.66) and (9.67) together form a set of simultaneous equations for the coefficients c_n and c_l. A nontrivial solution of these equations exists only if the determinant of the coefficients vanish

$$\begin{vmatrix} H'_{nn} - E_n^{(1)} & H'_{nl} \\ H'_{ln} & H'_{ll} - E_n^{(1)} \end{vmatrix} = 0 \tag{9.68}$$

This is called the *secular equation* and its two solutions are:

$$E_{n\pm}^{(1)} = \frac{1}{2}\left(H'_{nn} + H'_{ll}\right) \pm \frac{1}{2}\left[\left(H'_{nn} - H'_{ll}\right)^2 + 4\,|\,H'_{nl}\,|^2\right]^{(1/2)} \tag{9.69}$$

Now, the corrected energies are:

$$E_n = E_n^0 + E_{n+}^{(1)} \quad \text{and} \quad E_l = E_n^0 + E_{n-}^{(1)} \tag{9.70}$$

Both the energies will be real as the diagonal matrix elements H'_{nn} and H'_{ll} of the Hermitian operator H' are real. If $H'_{nn} = H'_{ll}$ and $H'_{nl} = 0$, $E_{n+} = E_{n-}$ and the degeneracy is not removed in the first order.

When the two roots of Eq. (9.68) are distinct, each (say E_{n+}) can be used to calculate the ratio c_n/c_l either from Eq. (9.66) or from Eq. (9.67). The normalization condition $c_n^2 + c_l^2 = 1$ allows us to calculate the values of c_n and c_l. The values of c_n and c_l thus determined gives the desired linear combination associated with the level $E_n^0 + E_{n+}$. In a similar way, the combination associated with the level $E_n^0 + E_{n-}$ can also be evaluated.

9.7 EFFECT OF ELECTRIC FIELD ON THE n = 2 STATE OF HYDROGEN

The first excited state ($n = 2$) of hydrogen atom is four-fold degenerate since it has the (l, m) values (0, 0), (1, 0), (1, 1) and (1, –1). As before, let the electric field **E** is applied along the positive z-axis which interacts with the electric dipole moment giving the perturbing Hamiltonian (Eq. 9.46), $H' = eEz = erE \cos\theta$. The four degenerate states may conveniently be specified by the quantum numbers (nlm) as

$$|nlm\rangle: \ |200\rangle, \ |210\rangle, \ |211\rangle, \ |21, -1\rangle$$

As the state is four-fold degenerate, the application of the perturbation theory for degenerate states requires the evaluation of sixteen matrix elements of H'. Of these, the four diagonal matrix elements are zero since they correspond to the same parity (H' is of odd parity). The off-diagonal matrix elements between states of different m values (10 in numbers) are zero since

$$\int_0^{2\pi} \exp\,[i(m' - m)\phi]\; d\phi = 0 \quad \text{if} \quad m' \neq m$$

The remaining two matrix elements $\langle 200|H'|210\rangle$ and $\langle 210|H'|200\rangle$ are the only nonvanishing ones. These can be evaluated using the values of

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^{3/2}}\left(2 - \frac{r}{a_0}\right)\exp\left(-\frac{r}{2a_0}\right) \tag{9.71}$$

and

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^{3/2}}\frac{r}{a_0}\exp\left(-\frac{r}{2a_0}\right)\cos\theta \tag{9.72}$$

Therefore

$$\langle 200|H'|210\rangle = \frac{eE}{32\pi a_0^4}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(2-\frac{r}{a_0}\right)r^2 \exp\left(-\frac{r}{a_0}\right)\cos^2\theta\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{eE}{16a_0^4}\int_0^{\pi}\cos^2\theta \sin\theta\, d\theta \int_0^{\infty}\left(2r^4-\frac{r^5}{a_0}\right)\exp\left(-\frac{r}{a_0}\right)dr$$

Using standard integrals (Appendix A-9), we have

$$\langle 200|H'|210\rangle = -3eEa_0 \tag{9.73}$$

Similarly

$$\langle 210|H'|200\rangle = -3eEa_0 \tag{9.74}$$

The perturbation matrix is therefore

$$H' = \begin{array}{c} (nlm)\rightarrow \\ \downarrow \\ (200) \\ (210) \\ (211) \\ (21,-1) \end{array} \begin{array}{cccc} (200) & (210) & (211) & (21,-1) \\ & & & \\ \end{array}$$

$$H' = \begin{array}{c|cccc} (nlm)\rightarrow\downarrow & (200) & (210) & (211) & (21,-1) \\ \hline (200) & 0 & -3eEa_0 & 0 & 0 \\ (210) & -3eEa_0 & 0 & 0 & 0 \\ (211) & 0 & 0 & 0 & 0 \\ (21,-1) & 0 & 0 & 0 & 0 \end{array} \tag{9.75}$$

The secular determinant is then

$$\begin{vmatrix} -E_2^{(1)} & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \tag{9.76}$$

The four roots of this determinantal equation are $3eEa_0$, $-3eEa_0$, 0 and 0. The states $|200\rangle$ and $|210\rangle$ are affected by the electric field whereas the states $|211\rangle$ and $|21,-1\rangle$ are not. The four-fold degeneracy is thus lifted partially. Eigenstates corresponding to these eigenvalues can be evaluated using Eq. (9.66) or (9.67) and the normalization condition for the coefficients. For the eigenvalue $3eEa_0$, from Eq. (9.66), $c_n/c_l = -1$ and the condition $c_n^2 + c_l^2 = 1$ gives $c_n = 1/\sqrt{2}$ and $c_l = -1/\sqrt{2}$. The eigenstate corresponding to the eigenvalue $3eEa_0$ is then $(|200\rangle - |210\rangle)/\sqrt{2}$. In a similar way the eigenstate for the eigenvalue $-3eEa_0$ is $(|200\rangle + |210\rangle)/\sqrt{2}$. The energies along with the eigenstates of the $n = 2$ state of hydrogen atom in an electric field E along the z-direction is illustrated in Figure 9.2.

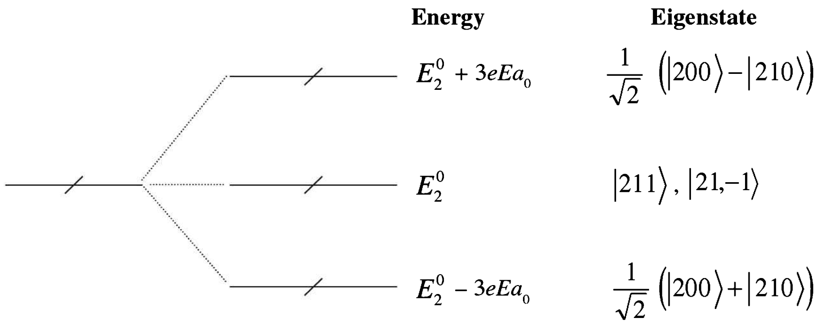


Figure 9.2 Energies and wave functions of the first excited state of hydrogen atom in an electric field E.

The hydrogen atom in the first excited state thus possesses a permanent electric dipole moment of magnitude $3ea_0$ with three different orientations—one state parallel to the external electric field, one state antiparallel to the field and two states with zero component along the field. The states $|211\rangle$ and $|21, -1\rangle$ do not possess dipole moments and therefore do not have a first-order interaction with the field.

9.8 SPIN-ORBIT INTERACTION

Electron in an atom moves in a central potential $V(r)$ (assumed to be spherically symmetric) that is produced by the nucleus and other electrons. The interaction between its orbital and spin magnetic moments introduces an additional term in the energy of the system. The phenomenon is referred to as **spin-orbit interaction**. The spin-orbit Hamiltonian H_{so} is given by

$$H_{so} = \xi(r)\ \mathbf{L} \cdot \mathbf{S}; \qquad \xi(r) = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr} \tag{9.77}$$

H_{so} is zero for s-states since $S = 0$ for such states. For an electron in a hydrogen atom, the potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{or} \quad \frac{dV}{dr} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \tag{9.78}$$

Substituting the value of dV/dr,

$$H_{so} = \frac{Ze^2}{8\pi\varepsilon_0 m^2c^2}\frac{\mathbf{L}\cdot\mathbf{S}}{r^3} \tag{9.79}$$

Having discussed the basis of spin-orbit interaction, the next step is to evaluate its effect on the energy levels. Since H_{so} is very weak compared to the energy level separations of the atom, it can be treated as a perturbation on the unperturbed Hamiltonian H^0. The total Hamiltonian H for the hydrogen like atom including spin-orbit interaction

$$H = H^0 + H_{so} = H^0 + \frac{Ze^2}{8\pi\varepsilon_0 m^2 c^2} \frac{\mathbf{L.S}}{r^3} \tag{9.80}$$

Since $\mathbf{J} = \mathbf{L} + \mathbf{S}$,

$$J^2 = L^2 + S^2 - 2\mathbf{L{\cdot}S} \quad \text{or} \quad \mathbf{L{\cdot}S} = \frac{J^2 - L^2 - S^2}{2}$$

$$H = H^0 + \frac{Ze^2}{8\pi\varepsilon_0 m^2 c^2} \frac{J^2 - L^2 - S^2}{2r^3} \tag{9.81}$$

The unperturbed Hamiltonian H^0 has degenerate eigenvalues for a given n and l except for $l = 0$ states. However one can avoid working with degenerate perturbation theory by using the basis $|\, lsjm \rangle$ since L^2, S^2, J^2 and J_z commute. The expectation value of $J^2 - L^2 - S^2$ is given by

$$\left\langle \left(J^2 - L^2 - S^2\right) \right\rangle = \left[j(j+1) - l(l+1) - s(s+1)\right] \hbar^2 \tag{9.82}$$

The expectation value of $1/r^3$ for hydrogenic wave function is:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2Z^3}{n^3 a_0^3\, l(l+1)\,(2l+1)} \tag{9.83}$$

where a_0 is the Bohr radius. Consequently

$$E_{so} = \frac{Z^4 e^2 \hbar^2}{8\pi\varepsilon_0 m^2 c^2 a_0^3} \frac{j\,(j+1) - l(l+1) - s(s+1)}{n^3 l\,(l+1)\,(2l+1)} \tag{9.84}$$

The spin-orbit energy is independent of m_j and, therefore, each level is $(2j + 1)$ fold degenerate. As anticipated, for s-electron, the spin-orbit interaction is zero since $l = 0$ and $j = s$. In terms of fine structure constant α, Eq. (9.84) can be written as:

$$E_{so} = \frac{Z^4 \alpha^4 mc^2}{2n^3} \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)\,(2l+1)} \tag{9.85}$$

This form of the formula gives the energy shift in terms of mc^2, the rest energy of the electron. Use of Eq. (1.15c) gives

$$E_{so} = \frac{Z^4 \alpha^2 R}{n^3} \frac{j\,(j+1) - l\,(l+1) - s\,(s+1)}{l\,(l+1)\,(2l+1)} \tag{9.86}$$

This version of the formula gives the shift in terms of Rydberg constant R which is the ground state energy of hydrogen atom.

For a given value of n and l, j is equal to either $l + 1/2$ or $l - 1/2$. The effect of spin-orbit interaction is to make the states $j = l - 1/2$ to have a lower energy than that with $j = l + 1/2$. These doublet levels constitute the **fine structure** of the hydrogen atom spectrum. The doublet separation ΔE is given by the energy difference between the $j = l + 1/2$ and $j = l - 1/2$ states. Substitution and simplification leads to

$$\Delta E = \frac{Z^4\alpha^2 R}{n^3}\,\frac{2l+1}{l(l+1)(2l+1)} = \frac{Z^4\alpha^2 R}{n^3\, l(l+1)} \tag{9.87}$$

The doublet separation depends on the principal quantum number n and the orbital quantum number l.

WORKED EXAMPLES

EXAMPLE 9.1 Calculate the first-order correction to the ground state energy of an anharmonic oscillator of mass m and angular frequency ω subjected to a potential:

$$V(x) = \frac{1}{2}m\omega^2x^2 + bx^4$$

where b is a parameter independent of x. The ground state wave function is

$$\psi_0^0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

The first-order correction to the ground state energy

$$E_0^{(1)} = \langle\psi_0^0|H'|\psi_0^0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} b \int_{-\infty}^{\infty} x^4 \exp\left(-\frac{m\omega x^2}{\hbar}\right)dx$$

Using the result in Appendix A-3, we get

$$E_0^{(1)} = b\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{3\sqrt{\pi}}{4}\left(\frac{\hbar}{m\omega}\right)^{5/2} = \frac{3b\hbar^2}{4m^2\omega^2}$$

EXAMPLE 9.2 A simple harmonic oscillator of mass m_0 and angular frequency ω is perturbed by an additional potential bx^3. Evaluate the second-order correction to the ground state energy of the oscillator.

The second-order correction to the ground state energy is given by

$$E_0^{(2)} = \sum_m{}' \frac{|\langle 0|H'|m\rangle|^2}{E_0^0 - E_m^0}, \qquad \text{where } H' = bx^3$$

In terms of $a^\dagger$ and a,

$$x = \left(\frac{\hbar}{2m_0\omega}\right)^{1/2}(a + a^\dagger)$$

Then

$$\langle 0|x^3|m\rangle = \left(\frac{\hbar}{2m_0\omega}\right)^{3/2} \langle 0|(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)|m\rangle; \quad m = 1, 2, \ldots$$

$$= \left(\frac{\hbar}{2m_0\omega}\right)^{3/2} \left[\langle 0|aaa|3\rangle + \langle 0|aaa^\dagger + aa^\dagger a|1\rangle\right]$$

The other contributions vanish. For the nonvanishing ones, we have

$$\langle 0|aaa|3\rangle = \sqrt{6} \quad \text{and} \quad \langle 0|aaa^\dagger + aa^\dagger a|1\rangle = 2 + 1 = 3$$

Therefore,

$$E_0^{(2)} = b^2\left(\frac{\hbar}{2m_0\omega}\right)^3 \left(\frac{6}{-3\hbar\omega} + \frac{9}{-\hbar\omega}\right) = -\frac{11b^2\hbar^2}{8m_0^3\omega^4}$$

EXAMPLE 9.3 Work out the splitting of the ^{1}P → ^{1}S transition of an atom placed in a magnetic field B along z-axis.

For ^{1}P level, S = 0 and therefore the magnetic moment of the atom is purely orbital. The interaction energy between magnetic moment and the field is

$$H' = -\mu_z B = \frac{e}{2m_0} L_z B$$

m_0 is the mass of electron and L_z is the z-component of orbital angular momentum. The first-order correction to energy of the ^{1}P state is

$$E^{(1)} = \left\langle lm \left| \frac{e}{2m_0} L_z B \right| lm \right\rangle = \frac{e\hbar}{2m_0} Bm_l, \qquad m_l = 1, 0, -1$$

The ^{1}P level thus splits into three levels (Figure 9.3). The ^{1}S level has neither orbital nor spin-magnetic moment. Hence it is not affected by the field and the ^{1}P → ^{1}S transition splits into three lines.

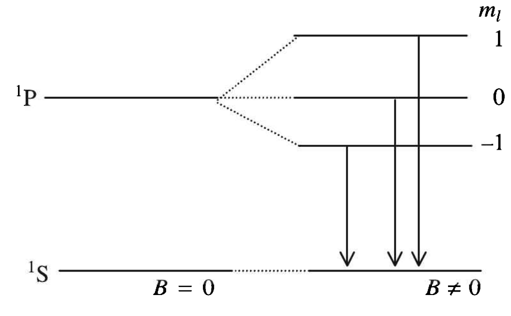


Figure 9.3 Splitting of ^{1}P → ^{1}S transition of an atom in a magnetic field.

Note:

1. If the system has more than one electron $l_z = l_{1z} + l_{2z} + \ldots$
2. Splitting of a spectral line into three components in presence of a magnetic field is an example of normal Zeeman effect. This dependence of energy on m is the reason why m is called the magnetic quantum number.

EXAMPLE 9.4 The unperturbed wave functions of a particle trapped in an infinite square well of bottom a are

$$\psi_n^0 = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}$$

If the system is perturbed by raising the floor of the well by a constant amount V_0, evaluate the first- and second-order corrections to the energy of the n^{th} state.

The first-order correction to the energy of the n^{th} state is

$$E_n^{(1)} = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^0 \right\rangle = \left\langle \psi_n^0 \middle| V_0 \middle| \psi_n^0 \right\rangle = V_0 \left\langle \psi_n^0 \middle| \psi_n^0 \right\rangle = V_0$$

Hence, the corrected energy levels are lifted by the amount V_0. The second-order correction to the energy is

$$E_n^{(2)} = \sum_m{}' \frac{\left|\left\langle \psi_m^0 \middle| H' \middle| \psi_n^0 \right\rangle\right|^2}{E_n^0 - E_m^0} = \sum_m{}' \frac{V_0^2 \left|\left\langle \psi_m^0 \middle| \psi_n^0 \right\rangle\right|^2}{E_n^0 - E_m^0} = 0$$

Hence, the second-order correction to the energy is zero.

EXAMPLE 9.5 A particle of mass m_0 and charge e oscillates along x-axis in a one-dimensional harmonic potential with an angular frequency ω. If an electric field ε is applied along the x-axis, evaluate the first- and second-order corrections to the energy of the nth state.

The potential energy due to the field ε is $-e\varepsilon x$. Therefore, the perturbation $H' = -e\varepsilon x$ and the first-order correction $E_n^{(1)} = -e\varepsilon\langle n | x | n\rangle$. Hence, in terms of a and $a^\dagger$,

$$x = \left(\frac{\hbar}{2m_0\omega}\right)^{1/2} (a + a^\dagger)$$

Then

$$E_n^{(1)} = -e\varepsilon \left(\frac{\hbar}{2m_0\omega}\right)^{1/2} \langle n|(a + a^\dagger)|n\rangle = 0$$

and

$$E_n^{(2)} = \sum_m{}' \frac{|\langle n|H'|m\rangle|^2}{E_n^0 - E_m^0}$$

where

$$\langle n|H'|m\rangle = -e\varepsilon\left(\frac{\hbar}{2m_0\omega}\right)^{1/2} \langle n|(a + a^\dagger|m\rangle$$

Here m can take all integral values except n. The non-vanishing elements correspond to $m = (n + 1)$ and $(n - 1)$ is

$$E_n^{(2)} = e^2\varepsilon^2 \frac{\hbar}{2m_0\omega}\left[\frac{\left(\sqrt{n+1}\right)^2}{-\hbar\omega} + \frac{\left(\sqrt{n}\right)^2}{\hbar\omega}\right] = -\frac{e^2\varepsilon^2}{2m_0\omega^2}$$

EXAMPLE 9.6 A rotator having a moment of inertia I and an electric dipole moment μ executes rotational motion in a plane. Estimate the first- and second-order corrections to the energy levels when the rotator is acted on by an electric field ε in the plane of rotation.

The energy eigenvalues and eigenfunctions of a plane rotator (Example 5.3) are:

$$E_m = \frac{\hbar^2 m^2}{2I} \quad \text{and} \quad \psi(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

and

$$\text{The perturbation } H' = -\mu\varepsilon \cos\phi = -\frac{\mu\varepsilon}{2}(e^{i\phi} + e^{-i\phi})$$

We also have

$$E_n^{(1)} = \langle n|H'|n\rangle = -\frac{\mu\varepsilon}{2\pi}\int_0^{2\pi} \cos\phi \, d\phi = 0$$

and

$$E_n^{(2)} = \sum_m{}' \frac{|\langle n|H'|m\rangle|^2}{E_n^0 - E_m^0}$$

where

$$\langle n\,|\,H'\,|\,m\rangle = -\frac{\mu\varepsilon}{4\pi}\int_0^{2\pi} e^{-in\phi}(e^{i\phi} + e^{-i\phi})e^{im\phi}\, d\phi$$

$$= -\frac{\mu\varepsilon}{4\pi}\left[\int_0^{2\pi} e^{i(m+1-n)\phi}\, d\phi + \int_0^{2\pi} e^{i(m-1-n)\phi}\, d\phi\right]$$

The integrals are finite when $m = n - 1$ (first one) and $m = n + 1$ (second one). Therefore,

$$E_n^{(2)} = \left(-\frac{\mu\varepsilon}{4\pi}\right)^2\left(\frac{4\pi^2}{E_n^0 - E_{n-1}} + \frac{4\pi^2}{E_n^0 - E_{n+1}}\right)$$

$$= \left(-\frac{\mu\varepsilon}{4\pi}\right)^2 \frac{4\pi^2 2I}{\hbar^2}\left(\frac{1}{2n-1}-\frac{1}{2n+1}\right)$$

$$= \frac{\mu^2\varepsilon^2 I}{\hbar^2\left(4n^2-1\right)}$$

EXAMPLE 9.7 Evaluate the first-order perturbation correction integral in Eq. (9.43).

As already mentioned the integration of Eq. (9.43) may be done by expanding $1/r_{12}$ in terms of Legendre polynomials. This expansion is given by

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}\; Y_{lm}^*(\theta_1\phi_1)\; Y_{lm}(\theta_2\phi_2)$$

where $r_<$ means the smaller of r_1 and r_2 and $r_>$ is the larger of r_1 and r_2. Substituting this value of $1/r_{12}$ in Eq. (9.43) and multiplying by $4\pi\, Y_{00}\, Y_{00}^*$ which equals unity, we get

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\int_0^{\infty}\!\!\int_0^{\infty} \exp\left(-\frac{2Zr_1}{a_0}\right)\exp\left(-\frac{2Zr_2}{a_0}\right)\frac{r_<^l}{r_>^{l+1}}\, r_1^2r_2^2\, dr_1\, dr_2$$

$$\times \int_0^{2\pi}\!\!\int_0^{\pi} Y_{lm}^*(\theta_1\phi_1)\; Y_{00}(\theta_1\phi_1)\; \sin\theta_1\, d\phi_1\, d\theta_1$$

$$\int_0^{2\pi}\!\!\int_0^{\pi} Y_{00}^*(\theta_2\phi_2)\; Y_{lm}(\theta_2\phi_2)\; \sin\,\theta_2\, d\phi_2\, d\theta_2$$

As the spherical harmonics are normalized, the angular part gives $\delta_{l0}\delta_{m0}\delta_{l0}\delta_{m0}$. The presence of Kronecker deltas makes all the terms in the series vanish except $l = m = 0$. Then

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^{\infty}\!\!\int_0^{\infty} \exp\left(-\frac{2Zr_1}{a_0}\right)\exp\left(-\frac{2Zr_2}{a_0}\right)\frac{1}{r_>}\; r_1^2r_2^2\, dr_1\, dr_2$$

First, we shall integrate over r_1 and then over r_2. In the range $0 \le r_1 \le r_2$, we have $r_> = r_2$ and in the range $r_2 \le r_1 \le \infty$, we have $r_> = r_1$. Then

$$E^{(1)} = \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^{\infty} \exp\left(-\frac{2Zr_2}{a_0}\right) r_2 \left(\int_0^{r_2} \exp\left(-\frac{2Zr_1}{a_0}\right) r_1^2\, dr_1\right) dr_2$$

$$+\ \frac{16Z^6e^2}{4\pi\varepsilon_0 a_0^6}\int_0^{\infty} \exp\left(-\frac{2Zr_2}{a_0}\right) r_2^2 \left(\int_{r_2}^{\infty} \exp\left(-\frac{2Zr_1}{a_0}\right) r_1\, dr_1\right) dr_2$$

From the table of integrals (Appendix A-9, 15, 16), integration over the variable r_1 and then over r_2 is carried out. This gives the correction to the energy

$$E^{(1)} = \frac{5}{4} Z W_H$$

EXAMPLE 9.8 A rigid rotator in a plane is acted on by a perturbation represented by

$$H' = \frac{V_0}{2}\,(3\cos^2\phi - 1) \quad \text{where } V_0 \text{ is a constant.}$$

Calculate the ground state energy up to the second order in the perturbation.

The energy eigenvalues and eigenfunctions of a plane rotator (Example 5.3) are given by

$$E_m = \frac{m^2\hbar^2}{2I}, \quad m = 0, \pm 1, \pm 2, \ldots$$

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp\,(im\phi)$$

Except the ground state all levels are doubly degenerate. The first order correction to the ground state energy is:

$$E_0^{(1)} = \langle \psi \mid H' \mid \psi \rangle = \left\langle \psi \mid \frac{V_0}{2}\left(3\cos^2\phi - 1\right) \mid \psi \right\rangle$$

$$= \left\langle \psi \mid \frac{3V_0}{2}\cos^2\phi \mid \psi \right\rangle - \left\langle \psi \mid \frac{V_0}{2} \mid \psi \right\rangle$$

$$= \frac{3}{4}V_0 - \frac{V_0}{2} = \frac{V_0}{4}$$

The second order energy correction

$$E_0^{(2)} = \sum_m{}' \frac{|\langle 0|H'|m\rangle|^2}{E_0^0 - E_m^0}$$

$$\langle 0 \,|\, H' \,|m\rangle = \frac{V_0}{2}\int_0^{2\pi} \frac{1}{\sqrt{2\pi}}\,(3\cos^2\phi - 1)\,\frac{1}{\sqrt{2\pi}}\,e^{im\phi}d\phi$$

$$= \frac{3V_0}{4\pi}\int_0^{2\pi} \cos^2\phi\; e^{im\phi}\; d\phi - \frac{V_0}{4\pi}\int_0^{2\pi} e^{im\phi}\; d\phi$$

We can write $\cos^2\phi = (1 + \cos 2\phi)/2$. Also, the second integral vanishes. Hence

$$\langle 0 \, |H' \mid m\rangle = \frac{3V_0}{8\pi}\int_0^{2\pi}(1+\cos 2\phi)\ e^{im\phi}d\phi = \frac{3V_0}{8\pi}\int_0^{2\pi}\cos 2\phi\ e^{im\phi}d\phi$$

since the other integral vanishes. Expressing cos 2ϕ in exponential,

$$\langle 0 \, |H' \mid m\rangle = \frac{3V_0}{16\pi}\int_0^{2\pi}(e^{i2\phi}+e^{-i2\phi})e^{im\phi}d\phi$$

$$= \frac{3V_0}{16\pi}\int_0^{2\pi} e^{i(m+2)\phi}d\phi + \frac{3V_0}{16\pi}\int_0^{2\pi} e^{i(m-2)\phi}d\phi$$

The first integral is finite when $m = -2$, the second one is finite when $m = +2$ and their values are equal to $3V_0/8$. $E_{\pm 2} = 2\hbar^2/I, E_0 = 0$. Hence

$$E_0^0 - E_2^0 = E_0^0 - E_{-2}^0 = -\frac{2\hbar^2}{I}$$

Consequently,

$$E_0^{(2)} = \frac{(3V_0 |8)^2}{-2\hbar^2/I} + \frac{(3V_0 |8)^2}{-2\hbar^2/I} = -\frac{9}{64}\frac{V_0^2 I}{\hbar^2}$$

EXAMPLE 9.9 A plane rigid rotator in the first excited state is subjected to the interaction

$$H' = \frac{V_0}{2}(3\cos^2\phi - 1), \text{ where } V_0 \text{ is constant.}$$

Calculate the energies to first order in H'.

For a plane rotator,

$$E_m = \frac{\hbar^2 m^2}{2I}; \quad \psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

Except the $m = 0$ state, all states are doubly degenerate. The energy and wave function of the first excited state are:

$$E_{\pm 1} = \frac{\hbar^2}{2I}, \quad \psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$$

The first order energy corrections are given by the roots of Eq. (9.68):

$$\begin{vmatrix} H'_{11} - E_1^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_1^{(1)} \end{vmatrix} = 0$$

$$H'_{11} = H'_{22} = \frac{1}{2\pi}\int_0^{2\pi}\frac{V_0}{2}(3\cos^2\phi - 1)\, d\phi$$

$$= \frac{V_0}{4\pi}\left[3\int_0^{2\pi} \cos^2\phi\, d\phi - \int_0^{2\pi} d\phi\right] = \frac{V_0}{4\pi}\left(3\pi - 2\pi\right) = \frac{V_0}{4}$$

$$H'_{12} = H'_{21} = \frac{1}{2\pi}\int_0^{2\pi} e^{-i\phi}\,\frac{V_0}{2}(3\cos^2\phi - 1)\, e^{-i\phi} d\phi = \frac{3V_0}{8}$$

The secular determinant takes the form

$$\begin{vmatrix} \dfrac{V_0}{4} - E_1^{(1)} & \dfrac{3V_0}{8} \\ \dfrac{3V_0}{8} & \dfrac{V_0}{4} - E_1^{(1)} \end{vmatrix} = 0$$

$$(E_1^{(1)})^2 - \frac{V_0}{2}E_1^{(1)} - \frac{5V_0^2}{64} = 0$$

The roots of this equation are $-\dfrac{V_0}{8}$ and $\dfrac{5V_0}{8}$. The corrected energies are:

$$E = \frac{\hbar^2}{2I} + \frac{5V_0}{8} \quad \text{and} \quad \frac{\hbar^2}{2I} - \frac{V_0}{8}$$

EXAMPLE 9.10 A one dimensional box of length a contains two particles each of mass m. The interaction between the particles is described by a potential of the type $V(x_1, x_2) = \lambda\delta(x_1 - x_2)$ where δ is Dirac delta function. Calculate the ground state energy to first order in λ.

The interaction between the particles can be treated as the perturbation. The Hamiltonian without that will be the unperturbed part. Without the δ potential,

$$V(x_1, x_2) = \begin{cases} 0 & 0 \le x_1, x_2 \le a \\ \infty & \text{Otherwise} \end{cases}$$

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m}\frac{d^2}{dx_2^2} + V(x_1, x_2)$$

From the results of an infinitely deep potential well, the energy and wave functions are:

$$E_{nk} = \frac{\pi^2\hbar^2}{2ma^2}(n^2 + k^2), \qquad n, k = 1, 2, 3, \ldots$$

$$\psi_{nk}(x_1, x_2) = \psi_n(x_1)\,\psi_k(x_2) = \frac{2}{a}\sin\left(\frac{n\pi x_1}{a}\right)\sin\left(\frac{k\pi x_2}{a}\right)$$

For the ground state, $n = k = 1$

$$E_{11}^0 = \frac{\pi^2\hbar^2}{ma^2} \quad \text{and} \quad \psi_{11}^0(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$$

$$H' = \lambda\delta(x_1 - x_2)$$

The first order correction to the ground state energy

$$\Delta E = \langle 11 \mid H' \mid 11 \rangle$$

$$= \left(\frac{2}{a}\right)^2 \int_0^a\int_0^a \lambda\delta(x_1 - x_2)\sin^2\left(\frac{\pi x_1}{a}\right)\sin^2\left(\frac{\pi x_2}{a}\right) dx_1\, dx_2$$

$$= \left(\frac{2}{a}\right)^2 \lambda \int_0^a \sin^4\left(\frac{\pi x_1}{a}\right) dx_1 = \frac{4\lambda}{a^2}.\frac{3}{8}a = \frac{3\lambda}{2a}$$

Corrected energy

$$E' = E_{11}^0 + \Delta E = \frac{\pi^2\hbar^2}{ma^2} + \frac{3\lambda}{2a}$$

EXAMPLE 9.11 Consider the infinite square well defined by

$$V(x) = 0 \quad \text{for} \quad 0 \le x < a \quad \text{and} \quad V(x) = \infty \text{ otherwise}$$

Using first order perturbation theory, calculate the energy of the first two states of the potential well if a portion defined by $V(x) = \frac{V_0 x}{a}$, V_0 is a small constant, $0 \le x \le a$ is sliced off.

From Example 4.1, the energy eigenvalues and eigenfunctions of the unperturbed Hamiltonian are:

$$E_n^0 = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad \psi_n^0 = \sqrt{\tfrac{2}{a}}\sin\frac{n\pi x}{a}, \quad n = 1, 2, 3, \ldots$$

The perturbation $H' = \frac{V_0 x}{a}$ which is represented in Figure 9.4.

The first order correction to the energy for the $n = 1$ state is:

$$\left\langle \psi_1^0 \left| \frac{V_0 x}{a} \right| \psi_1^0 \right\rangle = \frac{V_0}{a}\frac{2}{a}\int_0^a x\sin^2\frac{\pi x}{a}\, dx$$

$$= \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\left(1 - \cos\frac{2\pi x}{a}\right) dx$$

$$= \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\,dx - \frac{2V_0}{a^2}\int_0^a \frac{x}{2}\cos\frac{2\pi x}{a}\,dx$$

$$= \frac{V_0}{2} + 0 = \frac{V_0}{2}$$

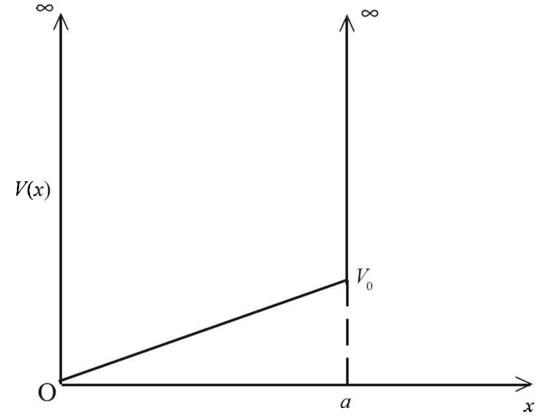


Figure 9.4 Sliced infinite potential well.

The first order correction to the $n = 2$ state is:

$$\left\langle \psi_2^0 \left| \frac{V_0 x}{a} \right| \psi_2^0 \right\rangle = \frac{V_0}{a}\frac{2}{a}\int_0^a x\sin^2\frac{2\pi x}{a}\,dx$$

$$= \frac{V_0}{2}$$

The corrected energies are:

$$\frac{\pi^2\hbar^2}{2ma^2} + \frac{V_0}{2} \quad \text{and} \quad \frac{2\pi^2\hbar^2}{ma^2} + \frac{V_0}{2}$$

REVIEW QUESTIONS

1. Explain briefly the principle of time-independent perturbation theory.
2. Write the unperturbed and total Hamiltonians for a two-electron atom along with the unperturbed wave functions.
3. Why the hydrogen atom in the ground state does not show a first-order Stark effect?
4. Explain quadratic Stark effect.

5. Why do we say that the hydrogen atom in the first excited state possesses a permanent dipole moment?
6. What is spin-orbit interaction? Define spin-orbit coupling constant. Why is it very large in heavy elements?
7. For s-electron, the spin-orbit interaction is zero. Why?
8. For hydrogen, the spin-orbit interaction is maximum for the 2p-electrons. Why?
9. The second-order correction to the energy of the ground state is always negative. Why?

PROBLEMS

1. Evaluate the first- and second-order corrections to the energy of the $n = 1$ state of an oscillator of mass m and angular frequency ω subjected to a potential

$$V(x) = \frac{1}{2}m\omega^2 x^2 + bx$$

where b is independent of x and $bx << \frac{1}{2}m\omega^2 x^2$.

2. Calculate the ground state energy up to first order; of the anharmonic oscillator having a potential energy

$$V = \frac{1}{2}m\omega^2 x^2 + ax^3; \qquad ax^3 \ll \frac{1}{2}m\omega^2 x^2$$

a is independent of x.

3. Evaluate the first order correction to the energy of the nth state of the anharmonic oscillator having the potential energy

$$V = \frac{1}{2}m\omega^2 x^2 + bx^4; \qquad bx^4 \ll \frac{1}{2}m\omega^2 x^2$$

4. A simple harmonic oscillator of mass m and angular frequency ω is perturbed by an additional potential $(1/2)bx^2$. Obtain the first- and second-order corrections to the ground state energy.
5. Show that each energy level with $l > 0$ of a one-electron system splits into two levels when spin-orbit interaction is included. Derive an expression for the separation between the two levels.
6. The matrices for the unperturbed (H^0) and perturbation (H') Hamiltonians in the orthonormal basis $|\phi_1\rangle$ and $|\phi_2\rangle$ are:

$$H^0 = \begin{pmatrix} E_0+\varepsilon & 0 \\ 0 & E_0-\varepsilon \end{pmatrix}, \quad H' = \begin{pmatrix} 0 & A \\ A & 0 \end{pmatrix}$$

Determine (i) the first-order correction to energy (ii) second-order correction to energy (iii) wave function corrected to first-order.

7. Given the matrix for H^0 and H' as

$$H^0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}, \quad H' = \begin{pmatrix} 0 & -A \\ -A & 0 \end{pmatrix}$$

In the orthonormal basis $|1\rangle$ and $|2\rangle$, determine (i) the energy eigenvalues and (ii) energy eigenfunctions.

8. Prove the Lande interval rule which states that in a given *L-S* term, the energy difference between two adjacent *J*-levels is proportional to the larger of the two values of *J*.

9. An interaction of the nuclear angular momentum of an atom (I) with electronic angular momentum (J) causes a coupling of the **I** and **J** vectors: $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The interaction Hamiltonian is of the type H_{int} = constant $\mathbf{I}.\mathbf{J}$. Treating this as a perturbation, evaluate the first order correction to the energy.

10. A particle in a central potential has an orbital angular momentum quantum number $l = 3$. If its spin $s = 1$, find the energy levels and degeneracies associated with the spin-orbit interaction.

11. Consider the infinite square well $V(x) = 0$ for $-a \le x \le a$ and $V(x) = \infty$ for $|x| > a$ with the bottom defined by $V(x) = V_0 x/a$, V_0 constant, is sliced off. Treating the sliced off part as a perturbation to the regular infinite square well, evaluate the first order correction to the energy of the ground and first excited states.

12. Draw the energy levels including the spin-orbit interaction for $n = 3$ and $n = 2$ states of hydrogen atom, and calculate the spin-orbit doublet separation of the $2p$, $3p$ and $3d$ states. Rydberg constant for hydrogen is 1.097×10^7 m^{-1}.

Chapter 10

The Variation Method

To apply perturbation method, there must be a closely related problem with exact solution. Often systems of interest may not satisfy this condition. In the variation method, one has to make some guess of the wavefunction, then apply the variational principle to improve the guessed wavefunction and obtain an upper bound for the ground state energy. The results of the method depend considerably on our ability to make a good guess of the form of the wavefunction. Though this method is usually applied to obtain the ground state energy and wavefunction, extension to excited states is also possible.

10.1 THE VARIATIONAL PRINCIPLE

The essential idea of the method is to evaluate the expectation value $\langle H \rangle$ of the Hamiltonian operator H of the system with respect to a trial wavefunction ϕ. The variational principle states that the ground state energy

$$E_1 \leq \langle H \rangle = \langle \phi | H | \phi \rangle \tag{10.1}$$

The equality holds if the trial wavefunction is the same as the ground state wavefunction of the system and the value $\langle H \rangle$ is an upper limit to the ground state energy. If the trial wavefunction is not normalized

$$\langle H \rangle = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \tag{10.2}$$

This ratio is often referred to as *Rayleigh ratio.*

For a proof of the theorem, express the trial wavefunction ϕ as a linear combination of the true (but unknown) wavefunctions ψ_1, ψ_2, ψ_3, ... of the Hamiltonian of the system corresponding to eigenvalues E_1, E_2, E_3, ...

$$\phi = \sum_i a_i \,|\psi_i\rangle \tag{10.3}$$

and

$$\langle H\rangle = \sum_i \sum_j a_i^* a_j \langle \psi_i | H | \psi_j \rangle$$

$$= \sum_i \sum_j a_i^* a_j E_j \left\langle \psi_i | \psi_j \right\rangle = \sum_i |a_i|^2 E_i \tag{10.4}$$

Writing $E_i = E_1 + \Delta E_i$, where E_1 is the ground state energy, we get

$$\langle H\rangle = E_1 \sum_i |a_i|^2 + \sum_i |a_i|^2 \,\Delta E_i \tag{10.5}$$

Since $\Sigma_i |a_i|^2 = 1$ and ΔE_i is positive,

$$\langle H\rangle \geq E_1 \tag{10.6}$$

The variational procedure described above is due to Lord Rayleigh. In practice, the trial wavefunction ϕ is selected in terms of one or more variable parameters and the value of $\langle H\rangle$ evaluated. The value of $\langle H\rangle$ when minimized with respect to each of the parameter, one gets the closest estimate possible with the selected trial function. A good trial function is a slight modification of a known wavefunction whose Hamiltonian is only slightly different from the Hamiltonian of the system under consideration.

10.2 RAYLEIGH–RITZ METHOD

Often, it is found convenient to use a linear combination of fixed basis functions ψ_i, $i = 1, 2, ..., n$ as the trial wavefunction and to treat the expansion coefficients as variable parameters. We shall assume that the basis functions ψ_i's form a complete orthonormal set.

$$\phi = \sum_{i=1}^{n} c_i \left|\psi_i\right\rangle \tag{10.7}$$

where c_i's are complex or real coefficients. This procedure is referred to *Rayleigh–Ritz method*. With the above trial function in Eq. (10.2)

$$E = \langle H\rangle = \frac{\sum_i \sum_j c_i^* c_j \left\langle \psi_i | H | \psi_j \right\rangle}{\sum_i \sum_j c_i^* c_j \left\langle \psi_i | \psi_j \right\rangle} = \frac{\sum_i \sum_j c_i^* c_j H_{ij}}{\sum_i \sum_j c_i^* c_j S_{ij}} \tag{10.8}$$

where

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle \quad \text{and} \quad S_{ij} = \langle \psi_i | \psi_j \rangle \tag{10.9}$$

To find the minimum value of $\langle H \rangle$, we differentiate Eq. (10.8) with respect to c_k^* and set

$$\frac{\partial E}{\partial c_k^*} = 0, \qquad k = 1, 2, \ldots, n \tag{10.10}$$

Then

$$\frac{\partial E}{\partial c_k^*} \sum_i \sum_j c_i^* c_j S_{ij} + E \sum_j c_j S_{kj} = \sum_j c_j H_{kj}$$

or

$$\sum_{j=1}^{n} c_j \left(H_{kj} - E S_{kj} \right) = 0, \qquad k = 1, 2, \ldots, n \tag{10.11}$$

We can derive an equation similar to Eq. (10.11) with coefficients c_i^*, $i = 1, 2, \ldots, n$ instead of c_i, if Eq. (10.8) is differentiated with respect to c_k and $\partial E / \partial C_k$ is set to zero, we get

$$\sum_{i=1}^{n} c_i^* \left(H_{ik} - E S_{ik} \right) = 0, \qquad k = 1, 2, \ldots, n \tag{10.12}$$

which is the Hermitian adjoint of Eq. (10.11).

Equation (10.11) is a set of n simultaneous homogeneous linear equations in variables $c_1, c_2, \ldots, c_n$. For a nontrivial solution,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \tag{10.13}$$

This nth degree polynomial of E leads to a set of n values for E, the lowest is the one closest to the ground state energy with the selected trial wave function.

10.3 VARIATION METHOD FOR EXCITED STATES

To extend the variation method to excited states, one has to select trial wavefunctions which are orthogonal to the true eigenfunctions of the lower states. The trial wavefunction of the $(n + 1)$th state be ϕ_{n+1}. The normalized eigenfunctions of the lower states which are orthogonal to ϕ_{n+1} be ψ_i, $i = 1, 2, \ldots, n$. Since ϕ_{n+1} is orthogonal to the ψ_i's, the coefficients $a_1, a_2, \ldots, a_n$ in Eq. (10.3) are zero. Consequently, Eq. (10.4) reduces to

$$\langle H \rangle = |a_{n+1}|^2 E_{n+1} + |a_{n+2}|^2 E_{n+2} + \ldots \tag{10.14}$$

or

$$\langle H \rangle \geq E_{n+1} \tag{10.15}$$

Trial wavefunctions orthogonal to eigenfunctions of the lower states can be obtained as outlined below. The ground state variational function ϕ_1 is first obtained. The coefficient a_1 of Eq. (10.3) is then $\langle \psi_1 | \phi_1 \rangle$. The function

$$\phi_2 = \phi_1 - \langle \psi_1 | \phi_1 \rangle \psi_1 \tag{10.16}$$

is orthogonal to the ground state wavefunction ψ_1 since

$$\langle \psi_1 | \phi_2 \rangle = \langle \psi_1 | \phi_1 \rangle - \langle \psi_1 | \phi_1 \rangle \langle \psi_1 | \psi_1 \rangle = 0 \tag{10.17}$$

With ϕ_2 as the trial wavefunction, we obtain $\langle H \rangle \geq E_2$. In a similar way, the trial function

$$\phi_3 = \phi_1 - \langle \psi_1 | \phi_1 \rangle \psi_1 - \langle \psi_2 | \phi_1 \rangle \psi_2 \tag{10.18}$$

which is orthogonal to ψ_1 and ψ_2, allows us to get the energy of excited state E_3. The generalization of Eq. (10.18) gives

$$\phi_{n+1} = \phi_1 - \sum_{i=1}^{n} \langle \psi_i | \phi_1 \rangle \psi_i \tag{10.19}$$

where ϕ_1 is the ground state variational function which is orthogonal to the exact ground state function.

10.4 THE HELLMANN–FEYNMAN THEOREM

The variation method assumes a fixed Hamiltonian and investigates how the energy changes as the trial wavefunction is changed. However, the Hellmann–Feynman approach investigates how the energy changes as the Hamiltonian varies. If a system is characterised by a Hamiltonian H that depends on a parameter R, the *Hellmann–Feynman theorem* states that

$$\frac{dE}{dR} = \left\langle \frac{\partial H}{\partial R} \right\rangle \tag{10.20}$$

where E is the energy of the system. When the Hamiltonian depends on R, its energy E also depends on R.

The proof of the theorem is straightforward. Let $\psi(R)$ is an exact normalized eigenfunction.

$$E(R) = \langle \psi(R) | H(R) | \psi(R) \rangle$$

On differentiation with respect to R, we get

$$\frac{dE}{dR} = \left\langle \frac{\partial \psi}{\partial R} \middle| H \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{\partial H}{\partial R} \middle| \psi \right\rangle + \left\langle \psi \middle| H \middle| \frac{\partial \psi}{\partial R} \right\rangle$$

Using the Hermitian property of H, we have

$$\frac{dE}{dR} = E\left\langle \frac{\partial \psi}{\partial R}\middle|\psi\right\rangle + \left\langle \frac{\partial H}{\partial R}\right\rangle + E\left\langle \psi\middle|\frac{\partial \psi}{\partial R}\right\rangle$$

$$= E\frac{d}{dR}\langle\psi|\psi\rangle + \left\langle \frac{\partial H}{\partial R}\right\rangle \tag{10.21}$$

The first term is zero since $\langle\psi|\psi\rangle = 1$. Hence the result.

The advantage of the Hellmann–Feynman theorem is that the operator $\partial H/\partial R$ might be very simple. For example, if the total Hamiltonian $H = H^0 + Rx$, then $\partial H/\partial R = x$ which does not contain the part H^0. In actual calculations, one can use the wave function obtained from perturbation theory as the true wave function to evaluate $\partial H/\partial R$.

10.5 THE GROUND STATE OF HELIUM

The helium atom consists of two electrons and a nucleus with two protons and two neutrons. We have already investigated its ground state by time-independent perturbation method (Section 9.4). The Hamiltonian of the system, Eq. (9.35), contains two independent hydrogenic Hamiltonians and the electron–electron repulsion term e^2/r_{12}. The exact solution of the two hydrogenic Hamiltonians is just the product of two normalized hydrogenic ground state wavefunctions:

$$\phi = \phi_1(r_1)\phi_2(r_2) = \frac{Z^3}{\pi a_0^3}\exp\left[-\frac{Z}{a_0}(r_1 + r_2)\right] \tag{10.22}$$

where $\phi_1(r_1)$ and $\phi_2(r_2)$ are normalized hydrogenic wave functions.

Owing to the screening of the attraction of any one electron to the nucleus by the other electron, the nuclear charge is not exactly $2e$ but expected to be lesser. This suggests that the effective atomic number Z' may be regarded as the variable parameter and the function in Eq. (10.22) corresponding to nuclear charge $Z'e$ may be taken as the trial wavefunction. It is convenient to rewrite the Hamiltonian as

$$H = \left(-\frac{\hbar^2\nabla_1^2}{2m} - \frac{Z'ke^2}{r_1}\right) + \left(-\frac{\hbar^2\nabla_2^2}{2m} - \frac{Z'ke^2}{r_2}\right) + (Z' - Z)ke^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{ke^2}{r_{12}} \tag{10.23}$$

The expectation value of H with the trial wavefunction in Eq. (10.22) (Z replaced by Z') is

$$\langle H\rangle = \left\langle \phi_1\middle|-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Z'ke^2}{r_1}\middle|\phi_1\right\rangle + \left\langle \phi_2\middle|-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Z'ke^2}{r_2}\middle|\phi_2\right\rangle$$

$$+ (Z' - Z)\left\langle \phi_1\middle|\frac{ke^2}{r_1}\middle|\phi_1\right\rangle + (Z' - Z)\left\langle \phi_2\middle|\frac{ke^2}{r_2}\middle|\phi_2\right\rangle + \left\langle \phi_1\phi_2\middle|\frac{ke^2}{r_{12}}\middle|\phi_1\phi_2\right\rangle \tag{10.24}$$

The value of first and second terms on the right are equal and each is $-Z'^2W_H$, where $W_H = k^2me^4/(2\hbar^2)$. Then

$$\left\langle \phi_1 \left| \frac{ke^2}{r_1} \right| \phi_1 \right\rangle = \frac{Z'^3ke^2}{\pi a_0^3} \int_\theta^{2\pi} d\phi \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\infty r_1 \exp\left(-\frac{2Z'r_1}{a_0}\right) dr_1$$

$$= \frac{Z'^3ke^2}{\pi a_0^3} 4\pi \frac{1}{(2Z'/a_0)^2}$$

$$= \frac{Z'ke^2}{a_0}$$

$$= 2Z'W_H \tag{10.25}$$

Similarly

$$\left\langle \phi_2 \left| \frac{ke^2}{r_2} \right| \phi_2 \right\rangle = 2Z'W_H \tag{10.26}$$

From Example (9.7), we have

$$\left\langle \phi_1\phi_2 \left| \frac{ke^2}{r_{12}} \right| \phi_1\phi_2 \right\rangle = \frac{5}{4} Z'W_H \tag{10.27}$$

Putting all the terms together in Eq. (10.24), we get

$$\langle H \rangle = -2Z'^2W_H + 4(Z' - Z)Z'W_H + \frac{5}{4}Z'W_H \tag{10.28}$$

Minimizing $\langle H \rangle$ with respect to Z'

$$0 = -4Z'W_H + 8Z'W_H - 4ZW_H + \frac{5}{4}W_H \tag{10.29}$$

or

$$Z' = Z - \frac{5}{16} \tag{10.30}$$

With this value of Z', Eq. (10.28) gives

$$E = \langle H \rangle = -2\left(Z - \frac{5}{16}\right)^2 W_H \tag{10.31}$$

Substitution of W_H = 13.6 eV leads to a ground state energy of –77.46 eV for helium atom. The experimental value is –78.975 eV.

A trial wave function without the concept that the attraction of an electron to the nucleus is partially screened by the other electron would have led to a ground state energy of only –75 eV. Hylleraas with a trial function

$$\phi = A(1 + cr_{12})\exp\left[-\frac{Z'}{a_0}(r_1 + r_2)\right] \tag{10.32}$$

where Z' and r_{12} are variable parameters, and (A is constant) obtained a value of –78.7 eV for the ground state energy of helium.

10.6 THE GROUND STATE OF THE DEUTERON

The deuteron is a system of two particles, a proton and a neutron, of almost equal mass m held together by an attractive short-range force. This short-range force between the nuclear particles can be described by the *Yukawa potential*

$$V(r) = -V_0\frac{e^{-r/\beta}}{r/\beta}; \quad V_0 \text{ and } \beta \text{ are constants.} \tag{10.33}$$

The binding energy of the deuteron is the ground state energy of this two-particle system. In the centre of mass system, the Hamiltonian for the s-state is

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \tag{10.34}$$

where μ is the proton–neutron reduced mass which is equal to $m/2$ and r is the proton–neutron separation. The ground state energy may be estimated using the trial function.

$$\phi = \exp\left(-\frac{\alpha r}{\beta}\right) \tag{10.35}$$

in which α is the variable parameter. As the trial function depends only on r, ∇^2 in spherical polar coordinates contains only the radial derivative:

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \tag{10.36}$$

Therefore,

$$\langle H\rangle = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\dfrac{-\hbar^2}{2\mu}\left\langle\phi\left|\dfrac{d^2}{dr^2}\right|\phi\right\rangle - \dfrac{\hbar^2}{2\mu}\left\langle\phi\left|\dfrac{2}{r}\dfrac{d}{dr}\right|\phi\right\rangle + \langle\phi|V(r)|\phi\rangle}{\langle\phi|\phi\rangle} \tag{10.37}$$

while evaluating integrals in Eq. (10.37), the factor $d\tau$ contributes the angular integrations

$$\int_0^{2\pi} d\phi = 2\pi \quad \text{and} \quad \int_0^{\pi} \sin\theta\, d\theta = 2 \tag{10.38}$$

Hence the angular part contributes a factor of 4π in all the integrations. We shall perform the integrations one-by-one (Appendix A).

$$\langle\phi|\phi\rangle = 4\pi\int_0^{\infty} r^2 \exp\left(-\frac{2\alpha r}{\beta}\right)dr = 4\pi\frac{2!}{(2\alpha/\beta)^3} = \frac{\pi\beta^3}{\alpha^3} \tag{10.39}$$

$$\left\langle \phi \left| \frac{d^2}{dr^2} \right| \phi \right\rangle = 4\pi \frac{\alpha^2}{\beta^2} \int_0^\infty r^2 \exp\left(-\frac{2\alpha r}{\beta}\right) dr = \frac{\pi\beta}{\alpha} \tag{10.40}$$

$$\left\langle \phi \left| \frac{2}{r} \frac{d}{dr} \right| \phi \right\rangle = -8\pi \frac{\alpha}{\beta} \int_0^\infty r \exp\left(-\frac{2\alpha r}{\beta}\right) dr = -\frac{2\pi\beta}{\alpha} \tag{10.41}$$

$$\langle \phi | V(r) | \phi \rangle = -4\pi V_0 \beta \int_0^\infty r \exp\left(-\frac{2\alpha + 1}{\beta} r\right) dr = -\frac{4\pi V_0 \beta^3}{(2\alpha + 1)^2} \tag{10.42}$$

Substituting the values of these integrals in Eq. (10.37), we get

$$E = \langle H \rangle = \frac{\hbar^2 \alpha^2}{2\mu\beta^2} - \frac{4V_0 \alpha^3}{(2\alpha + 1)^2} \tag{10.43}$$

Minimizing the energy with respect to α, we have

$$0 = \frac{\hbar^2 \alpha}{\mu\beta^2} - \frac{4V_0 \alpha^2 (2\alpha + 3)}{(2\alpha + 1)^3} \tag{10.44}$$

Writing

$$\gamma^2 = \frac{2\mu V_0 \beta^2}{\hbar^2} \tag{10.45}$$

Equation (10.44) reduces to

$$\gamma^2 = \frac{2\mu V_0 \beta^2}{\hbar^2} = \frac{(2\alpha + 1)^3}{2\alpha(2\alpha + 3)} \tag{10.46}$$

which is the value of α corresponding to the minimum energy. From Eq. (10.43)

$$E = \frac{\hbar^2}{2\mu\beta^2} \left[\alpha^2 - \frac{8\mu V_0 \beta^2 \alpha^3}{(2\alpha + 1)^2} \right] \tag{10.47}$$

Use of Eq. (10.46) reduces Eq. (10.47) to

$$E_{\text{min}} = -\frac{\hbar^2}{2\mu\beta^2} \frac{\alpha^2 (2\alpha - 1)}{2\alpha + 3} \tag{10.48}$$

where α is given by Eq. (10.46). A relation between β and V_0, called *range depth relation*, is obtained by substituting the experimental binding energy (E_{min}) of 2.226 MeV in Eq. (10.48). The relation checked for a range $\beta \cong 1.4 \times 10^{-13}$ cm, which corresponds to a meson mass of 270 m_e (m_e, mass of electron). The agreement is satisfactory.

WORKED EXAMPLES

EXAMPLE 10.1 Optimize the trial function $e^{-\alpha r}$ and evaluate the ground state energy of the hydrogen atom

The trial function $\phi = e^{-\alpha r}$. The Hamiltonian of the atom

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{ke^2}{r}, \quad k = \frac{1}{4\pi\varepsilon_0}$$

As in Section 10.6, the trial function depends only on r. Hence, ∇^2 in spherical polar coordinates contains only the radial derivatives. Therefore

$$\langle H\rangle\langle\phi|\phi\rangle = -\frac{\hbar^2}{2\mu}\left[\left\langle\phi\left|\frac{d^2}{dr^2}\right|\phi\right\rangle + \left\langle\phi\left|\frac{2}{r}\frac{d}{dr}\right|\phi\right\rangle\right] - \left\langle\phi\left|\frac{ke^2}{r}\right|\phi\right\rangle$$

The angular part of $d\tau$ contributes a factor 4π to the integrals in the above equation. Hence

$$\left\langle\phi\left|\frac{d^2}{dr^2}\right|\phi\right\rangle = 4\pi\alpha^2\int_0^\infty r^2\, e^{-2\alpha r}dr = \frac{\pi}{\alpha}$$

$$\left\langle\phi\left|\frac{2}{r}\frac{d}{dr}\right|\phi\right\rangle = -8\pi\alpha\int_0^\infty re^{-2\alpha r}dr = -\frac{2\pi}{\alpha}$$

$$\left\langle\phi\left|\frac{ke^2}{r}\right|\phi\right\rangle = 4\pi ke^2\int_0^\infty re^{-2\alpha r}dr = \frac{\pi ke^2}{\alpha^2}$$

$$\langle\phi|\phi\rangle = 4\pi\int_0^\infty r^2e^{-2\alpha r}dr = \frac{\pi}{\alpha^3}$$

Therefore, we get

$$\langle H\rangle\frac{\pi}{\alpha^3} = -\frac{\hbar^2}{2\mu}\left(\frac{\pi}{\alpha} - \frac{2\pi}{\alpha}\right) - \frac{\pi ke^2}{\alpha^2}$$

or

$$\langle H\rangle = \frac{\hbar^2\alpha^2}{2\mu} - \alpha ke^2$$

Minimizing with respect to α, we have

$$0 = \frac{\hbar^2\alpha}{\mu} - ke^2 \quad \text{or} \quad \alpha = \frac{\mu ke^2}{\hbar^2}$$

With this value of α

$$E_{\min} = \langle H\rangle_{\min} = -\frac{\mu k^2e^4}{2\hbar^2}$$

and the optimum wave function is

$$\phi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp\left(\frac{-r}{a_0}\right)$$

where a_0 is the Bohr radius.

These results are the same as those obtained in Chapter 5. It is so, because the trial function happens to be of the same form as the exact wave function.

EXAMPLE 10.2 Estimate the ground state energy of a one-dimensional harmonic oscillator of mass m and angular frequency ω using a Gaussian trial function.

We have, Hamiltonian of the system

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

and the Gaussian trial function

$$\phi(x) = A \exp(-\alpha x^2)$$

where A and α are constants. The normalization condition gives

$$1 = |A|^2 \int_{-\infty}^{\infty} \exp\left(-2\alpha x^2\right) dx = |A|^2 \left(\frac{\pi}{2\alpha}\right)^{1/2}$$

Normalized trial function

$$\phi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp\left(-\alpha x^2\right)$$

Therefore,

$$\langle H\rangle = -\frac{\hbar^2}{2m}\left\langle \phi \left| \frac{d^2}{dx^2} \right| \phi \right\rangle + \frac{1}{2}m\omega^2 \langle \phi | x^2 | \phi \rangle$$

where

$$\left\langle \phi \left| \frac{d^2}{dx^2} \right| \phi \right\rangle = -\left(\frac{2\alpha}{\pi}\right)^{1/2} 2\alpha \int_{-\infty}^{\infty} \exp\left(-2\alpha x^2\right) dx + \left(\frac{2\alpha}{\pi}\right)^{1/2} 4\alpha^2 \int_{-\infty}^{\infty} x^2 \exp\left(-2\alpha x^2\right) dx$$

$$= -\left(\frac{2\alpha}{\pi}\right)^{1/2} 2\alpha \left(\frac{\pi}{2\alpha}\right)^{1/2} + \left(\frac{2\alpha}{\pi}\right)^{1/2} 4\alpha^2 \frac{1}{4\alpha}\left(\frac{\pi}{2\alpha}\right)^{1/2}$$

$$= -\alpha$$

and

$$\langle \phi | x^2 | \phi \rangle = \left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 \exp\left(-2\alpha x^2\right) dx = \frac{1}{4\alpha}$$

Then, we have

$$\langle H\rangle = \frac{\hbar^2\alpha}{2m} + \frac{1}{2}m\omega^2\frac{1}{4\alpha} = \frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}$$

Minimizing with respect to α

$$0 = \frac{d\langle H\rangle}{d\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} \quad \text{or} \quad \alpha = \frac{m\omega}{2\hbar}$$

With this value of α

$$\langle H\rangle_{\min} = \frac{1}{2}\hbar\omega$$

same as the value we obtained in Chapter 4. Hence the trial wave function is the exact eigenfunction.

EXAMPLE 10.3 The Schrödinger equation of a particle confined to the positive x-axis is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + mgx\psi = E\psi$$

with $\psi(0) = 0$, $\psi(x) \to 0$ as $x \to \infty$ and E is the energy eigenvalue. Use the trial function $x\,e^{-ax}$ and obtain the best value of the parameter a.

We have the Hamiltonian

$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + mgx$$

and the trial function

$$\phi(x) = xe^{-ax}$$

Then, we get

$$\langle\phi|\phi\rangle = \int_0^\infty x^2 e^{-2ax}dx = \frac{1}{4a^3}$$

$$\left\langle\phi\left|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right|\phi\right\rangle = \frac{\hbar^2}{m}a\int_0^\infty x\,e^{-2ax}dx - \frac{\hbar^2a^2}{2m}\int_0^\infty x^2e^{-2ax}dx$$

$$= \frac{\hbar^2}{4ma} - \frac{\hbar^2}{8ma}$$

$$= \frac{\hbar^2}{8ma}$$

$$\langle\phi|mgx|\phi\rangle = mg\int_0^\infty x^3e^{-2ax}\,dx = \frac{3mg}{8a^4}$$

$$\langle H\rangle = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{[\hbar^2/(8ma)] + [3mg/(8a^4)]}{1/(4a^3)} = \frac{\hbar^2 a^2}{2m} + \frac{3}{2}\frac{mg}{a}$$

Minimizing $\langle H\rangle$ with respect to a, we have

$$0 = \frac{\hbar^2}{2m}2a - \frac{3}{2}\frac{mg}{a^2} \quad \text{or} \quad a = \left(\frac{3}{2}\frac{m^2 g}{\hbar^2}\right)^{1/3}$$

which is the best value of the parameter a so that $\langle H\rangle$ is minimum.

EXAMPLE 10.4 A particle of mass m moves in the attractive central potential $V(r) = -g^2/r^{3/2}$, g is a constant. Using the normalized function $(k^3/8\pi)^{1/2}\, e^{-kr/2}$ as trial function, estimate an upper bound to the energy of the lowest state. Given that

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}, \text{ if } n \text{ is positive and } a > 0; \quad \int_0^\infty \sqrt{x}\, e^{-ax}\,dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}.$$

The expectation value of the Hamiltonian

$$\langle H\rangle = \langle\phi\,|\,H\,|\,\phi\rangle$$

$$= \frac{k^3}{8\pi}4\pi\int_0^\infty r^2 e^{-kr/2}\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{g^2}{r^{3/2}}\right]e^{-kr/2}dr$$

The factor 4π outside the integral comes from the integration of the angular part and r^2 inside the integral comes from the volume element $d\tau$.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)e^{-kr/2} = \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)e^{-kr/2} = \left(\frac{k^2}{4} - \frac{k}{r}\right)e^{-kr/2}$$

Hence

$$\langle H\rangle = \frac{k^3}{2}\left(-\frac{\hbar^2}{2m}\right)\int_0^\infty r^2 e^{-kr/2}\left(\frac{k^2}{4} - \frac{k}{r}\right)e^{-kr/2}dr - \frac{k^3}{2}g^2\int_0^\infty r^{1/2}e^{-kr}dr$$

$$= -\frac{\hbar^2 k^5}{16m}\int_0^\infty r^2 e^{-kr}dr + \frac{\hbar^2 k^4}{4m}\int_0^\infty r e^{-kr}dr - \frac{k^3 g^2}{2}\int_0^\infty r^{1/2}e^{-kr}dr$$

$$= -\frac{\hbar^2 k^5}{16m}\frac{2}{k^3} + \frac{\hbar^2 k^4}{4m}\frac{1}{k^2} - \frac{k^3 g^2}{2}\frac{1}{2k}\sqrt{\frac{\pi}{k}}$$

$$= \frac{\hbar^2 k^2}{8m} - \frac{\sqrt{\pi}\, g^2 k^{3/2}}{4}$$

For $\langle H \rangle$ to be minimum $\frac{\partial \langle H \rangle}{\partial k} = 0$. That is

$$\frac{\hbar^2 k}{4m} - \frac{3\sqrt{\pi}}{8} g^2 \, k^{1/2} = 0$$

This leads to two values for k,

$$k = 0 \quad \text{and} \quad k^{1/2} = \frac{3\sqrt{\pi}\, g^2 m}{2\hbar^2}$$

The first one can be discarded as it leads to $\psi = 0$. Hence the upper bound to the energy of the lowest state is:

$$\langle H \rangle_{\min} = \frac{81\pi^2 g^8 m^3}{128\hbar^6} - \frac{27\pi^2 g^8 m^3}{32\hbar^6} = -\frac{27\pi^2 g^8 m^3}{128\hbar^2}$$

EXAMPLE 10.5 The Hamiltonian of a particle of mass m is:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + bx^4$$

where b is constant. Use the trial function $\phi(x) = Ae^{-\alpha^2 x^2}$, where α is the variable parameter, to evaluate the energy of the ground state. Given that

$$\int_0^\infty \exp(-\alpha x^2)\, dx = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} \qquad \int_0^\infty x^2 \exp(-\alpha x^2)\, dx = \frac{\sqrt{\pi}}{4}\frac{1}{\alpha^{3/2}}$$

$$\int_0^\infty x^4 \exp(-\alpha x^2)\, dx = \frac{3\sqrt{\pi}}{8}\frac{1}{\alpha^{5/2}}$$

The Hamiltonian H and the trial function $\phi(x)$ are $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + bx^4$ and $\phi(x) = Ae^{-\alpha^2 x^2}$.

The normalization condition gives

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2\alpha^2 x^2} dx$$

$$1 = |A|^2 \left(\frac{\pi}{2\alpha^2}\right)^{1/2} \quad \text{or} \quad |A|^2 = \left(\frac{2\alpha^2}{\pi}\right)^{1/2}$$

$$\langle H \rangle = \langle\phi|\, H\, |\phi\rangle = \langle\, \phi\, |\, -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + bx^4\, |\, \phi\, \rangle$$

$$= \frac{\hbar^2}{2m}|\, A\, |^2\, 2\alpha^2 \int_{-\infty}^{\infty} e^{-2\alpha^2 x^2} dx - \frac{\hbar^2}{2m}|\, A\, |^2\, 4\alpha^4 \int_{-\infty}^{\infty} x^2 e^{-2\alpha^2 x^2} dx$$

$$+\, b\, |\, A\, |^2 \int_{-\infty}^{\infty} x^4\, e^{-2\alpha^2 x^2} dx$$

$$= \frac{\hbar^2\alpha^2}{m} - \frac{\hbar^2\alpha^2}{2m} + \frac{3b}{16}\frac{1}{\alpha^4}$$

$$= \frac{\hbar^2\alpha^2}{2m} + \frac{3}{16}\frac{b}{\alpha^4}$$

Minimizing $\langle H\rangle$ with respect to α, we have

$$\frac{\partial\langle H\rangle}{\partial\alpha} = 0 = \frac{\hbar^2\alpha}{m} - \frac{3}{4}\frac{b}{\alpha^5}$$

$$\alpha^2 = \left(\frac{3}{4}\frac{bm}{\hbar^2}\right)^{1/3}$$

Substituting this value of α, we get

$$\langle H\rangle_{\min} = \frac{3}{4}\left(\frac{3}{4}\right)^{1/3}\left(\frac{b\hbar^4}{m^2}\right)^{1/3} = \left(\frac{3}{4}\right)^{4/3}\left(\frac{b\hbar^4}{m^2}\right)^{1/3}$$

EXAMPLE 10.6 An harmonic oscillator is described by the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + Ax^4$$

Determine its ground state energy by selecting

$$\psi = \frac{\lambda^{1/2}}{\pi^{1/4}}\exp\left(\frac{-\lambda^2 x^2}{2}\right)$$

where λ is variable parameter, as the variational trial wave function.

With the trial function ψ the expectation value of H is:

$$\langle H\rangle = \lambda\pi^{-1/2}\int_{-\infty}^{\infty} e^{-\lambda^2 x^2/2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + Ax^4\right)e^{-\lambda^2 x^2/2} dx$$

Using the values of the first three integrals in Appendix A,

$$\langle H\rangle = \frac{\hbar^2\lambda^2}{4m} + \frac{3A}{4\lambda^4}$$

Minimizing $\langle H \rangle$ with respect to the variable parameter λ,

$$0 = \frac{\partial \langle H \rangle}{\partial \lambda} = \frac{\hbar^2 \lambda}{2m} - \frac{3A}{\lambda^5}$$

$$\lambda = \left(\frac{6mA}{\hbar^2} \right)^{1/6}$$

Substituting this value of λ,

$$\langle H \rangle = \frac{\hbar^2}{4m} \left(\frac{6mA}{\hbar^2} \right)^{1/3} + \frac{3A}{4} \left(\frac{\hbar^2}{6mA} \right)^{2/3}$$

$$= \frac{3^{1/3}}{2} \left(\frac{\hbar^2}{2m} \right)^{2/3} A^{1/3} + \frac{3^{1/3}}{4} \left(\frac{\hbar^2}{2m} \right)^{2/3} A^{1/3}$$

$$= \frac{3^{4/3}}{4} \left(\frac{\hbar^2}{2m} \right)^{2/3} A^{1/3}$$

$$= 1.082 \left(\frac{\hbar}{2m} \right)^{2/3} A^{1/3}$$

It may be noted that numerical integration gives a co-efficient of 1.08 illustrating the usefulness of variation method. It may also be noted that perturbation technique is not possible as there is no way to split H into an unperturbed part and a perturbation.

REVIEW QUESTIONS

1. Explain the variational principle.
2. The result of the variation method always gives an upper limit for the ground state energy of the system. Why?
3. Outline the variation method used for obtaining approximate value of ground state energy of a system
4. If the first-($n - 1$) exact eigenfunctions of a particular system are known, write a formal expression for a variational trial function for the nth excited state.
5. Explain briefly the variation method for excited states.
6. State and prove Hellmann–Feynman theorem.

PROBLEMS

1. A trial function ϕ differs from an eigenfunction ψ_E so that $\phi = \psi_E + \alpha\phi_1$, where ψ_E and ϕ_1 are orthonormal and $\alpha \ll 1$. Show that $\langle H \rangle$ differs from E only by a term of order α^2; find this term.
2. Evaluate the ground state energy of a harmonic oscillator of mass m and angular frequency ω using the trial function:
$$\phi(x) = \begin{cases} \cos\dfrac{\pi x}{2a} & -a \le x \le a \\ 0 & |x| > a \end{cases}$$
3. A particle of mass m moving in the potential
$$V(x) = \begin{cases} kx & x > 0 \\ \infty & x < 0 \end{cases}$$
where k is a constant. Optimize the trial wavefunction $\phi = xe^{-ax}$, where a is the variable parameter and estimate the groundstate energy of the system.
4. The Hamiltonian of a system is given by
$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} - a\delta(x)$$
where a is a constant and $\delta(x)$ is Dirac's delta function. Estimate the ground state energy of the system using a Gaussian trial function.
5. Evaluate the ground state energy of hyrdogen atom using a Gaussian trial function. Given
$$\int_0^\infty x^{2n} \exp(-\lambda x^2)dx = \frac{\pi^{1/2}(2n)!}{2^{2n+1}n!\,\lambda^{(2n+1)/2}}$$
and
$$\int_0^\infty x^{2n+1} \exp(-\lambda x^2)dx = \frac{n!}{2\lambda^{n+1}}$$
6. A particle of mass m is moving in an one dimensional box defined by the potential $V = 0$, $0 \le x \le a$ and $V = \infty$ otherwise. Estimate ground state energy using the trial function:
$$\psi(x) = Ax(a - x),\ 0 \le x < a$$
7. Evaluate by variation method, the energy of the first excited state of a linear harmonic oscillator using the trial function:
$$\phi = Nx \exp(-\lambda x^2)$$
where λ is a variable parameter.

Chapter 11

WKB Approximation

The *Wentzel, Kramers, Brillouin* (WKB) *approximation* is a technique for obtaining approximate solution of one-dimensional Schrödinger equation or a wave equation which can be separated into equations each of which contains only single independent variable. It demonstrates the connection between the classical, quantum theory and quantum mechanics. It is based on the expansion of the wave function in powers of $\hbar$. The zero, first and second, powers of $\hbar$ respectively give the classical, quantum theory and higher-order results. It is also called the *classical approximation* since it gives the classical result when $\hbar$ is set zero. This method is applicable especially when the potential is slowly varying.

11.1 THE WKB METHOD

The one-dimensional Schrödinger equation of a particle moving in a region of constant potential V_0 is

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \qquad \text{where } k^2 = 2m\frac{E - V_0}{\hbar^2} \tag{11.1}$$

Its solution is

$$\psi = e^{\pm ikx} \tag{11.2}$$

If the potential is not constant, k in Eq. (11.1) is a function of x given by

$$k^2 = 2m\frac{E - V(x)}{\hbar^2} \tag{11.3}$$

For convenience, we shall assume that $E > V(x)$. Writing the solution of Schrödinger equation in the following form and substituting it in Eq. (11.1), we get

$$\psi = \exp\left[\frac{i}{\hbar}S(x)\right] \tag{11.4}$$

$$\left(\frac{dS}{dx}\right)^2 - i\hbar\frac{d^2S}{dx^2} - k^2\hbar^2 = 0 \tag{11.5}$$

The solution of this equation gives the form of the function $S(x)$. Expanding $S(x)$ in powers of $\hbar$, we get

$$S(x) = S_0(x) + S_1(x)\hbar + S_2(x)\frac{\hbar^2}{2} + \cdots \tag{11.6}$$

Substituting Eq. (11.6) in Eq. (11.5) and retaining terms up to $\hbar$, we have

$$\left(\frac{dS_0}{dx}\right)^2 - k^2\hbar^2 + \left(2\frac{dS_0}{dx}\frac{dS_1}{dx} - i\frac{d^2S_0}{dx^2}\right)\hbar = 0 \tag{11.7}$$

The term $-k^2\hbar^2$ is included with the term independent of $\hbar$, since

$$k^2\hbar^2 = \frac{2m[E - V(x)]\hbar^2}{\hbar^2} = 2m[E - V(x)]$$

For Eq. (11.7) to be valid, the coefficient of each power of $\hbar$ must vanish separately. Then

$$\left(\frac{dS_0}{dx}\right)^2 - k^2\hbar^2 = 0 \quad \text{or} \quad \frac{dS_0}{dx} = \pm k\hbar \tag{11.8}$$

and

$$2\frac{dS_0}{dx}\frac{dS_1}{dx} - i\frac{d^2S_0}{dx^2} = 0 \tag{11.9}$$

For better results, one has to include terms in $\hbar^2$ also. Integration of Eqs. (11.8) and (11.9) gives $S_0(x)$ and $S_1(x)$. It follows from Eq. (11.8)

$$S_0(x) = \pm\int k\hbar\, dx = \pm\int [2m(E - V(x)]^{1/2}\, dx \tag{11.10}$$

With this value of $S_0(x)$, Eq. (11.9) becomes

$$\frac{dS_1}{dx} = \frac{i}{2k}\frac{dk}{dx} \tag{11.11}$$

Integrating, we get

$$S_1 = \frac{i}{2} \ln k \quad \text{or} \quad iS_1 = \ln k^{-1/2} \quad \text{or} \quad \exp(iS_1) = k^{-1/2} \tag{11.12}$$

Restricting to two terms in Eq. (11.6), it follows from Eqs. (11.4), (11.6) and (11.12) that

$$\psi = A \exp\left(\frac{i}{\hbar} S_0\right) \exp(iS_1) = \frac{A}{k^{1/2}} \exp\left(\pm i \int k\, dx\right) \tag{11.13}$$

where A is a constant and k is given by Eq. (11.3). The general solution will be a linear combination of the two terms, one with each sign. The wavevector k is real and therefore the solution is oscillatory. The probability density

$$\psi\psi^* = \frac{|A|^2}{k} \exp\left(\pm i \int k\, dx\right) \exp\left(\mp i \int k\, dx\right) = \frac{|A|^2}{k} \tag{11.14}$$

As $p = k\hbar$, the probability density is inversely proportional to the velocity. This is understandable because classically the time spent by a particle in a region is inversely proportional to the velocity.

In quantum mechanics, particles can even penetrate classically disallowed regions and therefore we have to consider the case $E < V(x)$. For $E < V(x)$, the basic equation is

$$\frac{d^2\psi}{dx^2} - \gamma^2\psi = 0, \quad \gamma^2 = \frac{2m[V(x) - E]}{\hbar^2} \tag{11.15}$$

Proceeding in the same fashion, the solution of Eq. (11.15) can be written as

$$\psi = \frac{B}{\gamma^{1/2}} \exp\left(\pm \int \gamma\, dx\right) \tag{11.16}$$

where B is a constant. The most general solution is a linear combination of the two terms, one with each sign. One term is an exponentially increasing one whereas the other is an exponentially decreasing one. At this stage, we cannot leave the exponentially increasing solution since the region in which $E < V(x)$ is usually of finite extent. When $E \cong V(x)$, both the quantities k and γ tend to zero. Consequently ψ goes to infinity and the approximation fails. The point at which $E = V(x)$ is called the *classical turning point*, since at this point a classical particle would stop and begin to move in the opposite direction.

11.2 THE CONNECTION FORMULAS

On one side of a turning point we have an exponential solution and on the other side an oscillatory one. Near the turning point, $E \approx V(x)$ and the WKB solution breaks down. To get the complete solution, the wave function near the turning points must be connected with the WKB solutions for the regions $E > V(x)$ and $E < V(x)$. In most of the cases one requires only the connection formulas and not the exact solution near the turning points.

We now consider a turning point at $x = x_1$, as in Figure 11.1. Assuming a smoothly varying potential, $V(x)$ can be expanded in a Taylor series (neglecting higher order terms in the expansion)

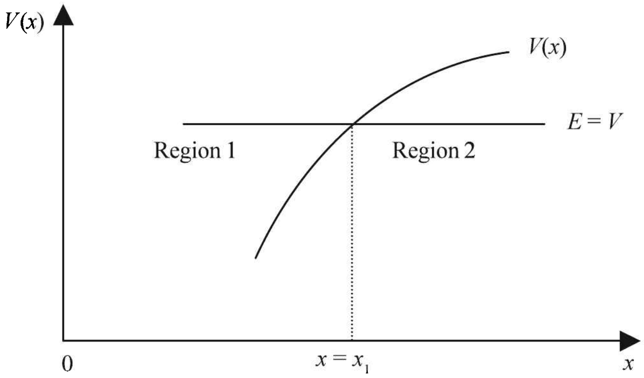


Figure 11.1 A turning point at $x = x_1$.

$$V(x) = V(x_1) + \left(\frac{\partial V}{\partial x}\right)_{x=x_1}(x - x_1) \tag{11.17}$$

This assumption amounts to approximating the potential by a straight line. Since $V(x_1) = E$, the Schrödinger equation near $x = x_1$ is

$$\frac{d^2\psi}{dx^2} - \frac{2m}{\hbar^2}\left(\frac{\partial V}{\partial x}\right)_{x=x_1}(x - x_1)\psi = 0 \tag{11.18}$$

As the first step, one has to work out independent solutions of Eq. (11.18) for the regions $x < x_1$ (two solutions) and $x > x_1$ (two solutions). The next step is to carry these solutions to regions where WKB solutions are applicable and then to obtain connection formulas. Suitable connection formulas were obtained by Kramers which are summarised below. For each turning point we will have two connection formulas. We will have two cases, in one the barrier is to the right of the turning point x_1 and in the other the barrier is to the left of the turning point x_2.

Barrier to the right of the turning point:

$$\begin{aligned} &\frac{2}{k^{1/2}}\cos\left(\int_x^{x_1} k\,dx - \frac{\pi}{4}\right) \leftarrow \frac{1}{\gamma^{1/2}}\exp\left(-\int_{x_1}^{x} \gamma\,dx\right) \\ &\frac{1}{k^{1/2}}\sin\left(\int_x^{x_1} k\,dx - \frac{\pi}{4}\right) \rightarrow -\frac{1}{\gamma^{1/2}}\exp\left(\int_{x_1}^{x} \gamma\,dx\right) \end{aligned} \tag{11.19}$$

Barrier to the left of the turning point:

$$\begin{aligned}
\frac{1}{\gamma^{1/2}} \exp\left(-\int_x^{x_2} \gamma\, dx\right) &\rightarrow \frac{2}{k^{1/2}} \cos\left(\int_{x_2}^{x} k\, dx - \frac{\pi}{4}\right) \\
-\frac{1}{\gamma^{1/2}} \exp\left(\int_x^{x_2} \gamma\, dx\right) &\leftarrow \frac{1}{k^{1/2}} \sin\left(\int_{x_2}^{x} k\, dx - \frac{\pi}{4}\right)
\end{aligned} \tag{11.20}$$

In both the cases the cosine term is connected to the decreasing exponential and the sine term to the increasing exponential. Because of the negative sign, the increasing exponential term approaches minus infinity. For accurate results it is advisable to use Eqs. (11.19) and (11.20) in the directions indicated by the arrow. In most of the cases the error involved in not following the arrow is fairly small. The WKB approximation breaks down if the turning points are close to the top of the barrier.

11.3 VALIDITY OF WKB METHOD

While deriving the solution in Eq. (11.13) we neglected terms beyond S_1 in the expansion in Eq. (11.6). This is possible only if

$$\frac{\hbar S_1}{S_0} \ll 1 \quad \text{or} \quad \hbar \frac{dS_1/dx}{dS_0/dx} \ll 1 \tag{11.21}$$

The values of S_1 and S_0 when substituted, this condition reduces to

$$\left|\frac{dk/dx}{k^2}\right| \ll 1, \qquad \text{where } k^2 = \frac{2m}{\hbar^2}\,[E - V(x)] \tag{11.22}$$

Hence the approximation is valid for systems having large mass, high energy and the potential slowly varying. Since the de Broglie wavelength $\lambda = h/p = 2\pi/k$, the above condition can also be stated as

$$\frac{\lambda}{2\pi}\frac{1}{k}\left|\frac{dk}{dx}\right| \ll 1 \tag{11.23}$$

In this form, the condition means that the fractional change in k in the distance $\lambda/(2\pi)$ must be small compared to unity.

11.4 BARRIER PENETRATION

An important application of the WKB method is the problem of barrier penetration by particles. Figure 11.2 represents a barrier on which particles of energy $E < V(x)$ are incident from left.

Classically all the particles will be reflected back at $x = x_1$. However, because of the wave nature of the particles, some of them may leak through the barrier resulting in a transmitted wave.

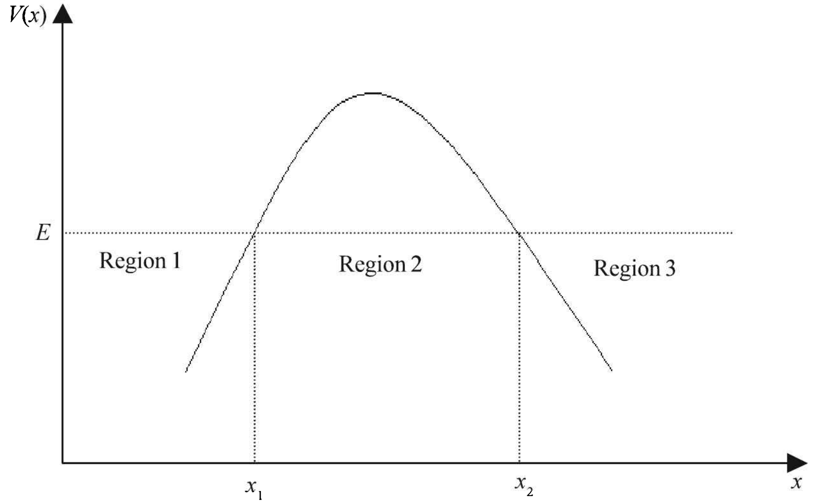


Figure 11.2 A particle of energy E penetrating a barrier.

In region 3, only a transmitted wave exists which can be represented by

$$\psi_3 = \frac{A}{k^{1/2}} \exp\left[i\left(\int_{x_2}^{x} k\,dx - \frac{\pi}{4}\right)\right] \tag{11.24}$$

To facilitate the application of the connection formulas, Eq. (11.24) can be written as

$$\psi_3 = \frac{A}{k^{1/2}}\left[\cos\left(\int_{x_2}^{x} k\,dx - \frac{\pi}{4}\right) + i\sin\left(\int_{x_2}^{x} k\,dx - \frac{\pi}{4}\right)\right] \tag{11.25}$$

Using Eq. (11.20), the wave function for the region $x_1 < x < x_2$ is

$$\psi_2 = \frac{A}{2\gamma^{1/2}} \exp\left(-\int_{x}^{x_2} \gamma\,dx\right) - \frac{Ai}{\gamma^{1/2}} \exp\left(\int_{x}^{x_2} \gamma\,dx\right) \tag{11.26}$$

To get the wave function in the region $x < x_1$, the connection formulas in Eq. (11.19) have to be applied. For that, we have to modify Eq. (11.26) as

$$\psi_2 = \frac{A}{2\gamma^{1/2}} \exp\left(-\int_{x_1}^{x_2} \gamma\,dx + \int_{x_1}^{x} \gamma\,dx\right) - \frac{Ai}{\gamma^{1/2}} \exp\left(\int_{x_1}^{x_2} \gamma\,dx - \int_{x_1}^{x} \gamma\,dx\right) \tag{11.27}$$

The wave function in region 1 can be written in the following form

$$\psi_1 = -\frac{A}{2k^{1/2}}\frac{1}{\alpha} \sin\left(\int_{x}^{x_1} k\,dx - \frac{\pi}{4}\right) - \frac{2Ai}{k^{1/2}}\,\alpha\cos\left(\int_{x}^{x_1} k\,dx - \frac{\pi}{4}\right) \tag{11.28}$$

where

$$\exp\left(\int_{x_1}^{x_2} \gamma\, dx\right) = \alpha \tag{11.29}$$

Replacing sine and cosine terms by exponentials

$$\psi_1 = -\frac{Ai}{k^{1/2}}\left(\alpha - \frac{1}{4\alpha}\right) \exp\left[i\left(\int_{x}^{x_1} k\, dx - \frac{\pi}{4}\right)\right]$$

$$-\frac{Ai}{k^{1/2}}\left(\alpha + \frac{1}{4\alpha}\right)\exp\left[-i\left(\int_{x}^{x_1} k\, dx - \frac{\pi}{4}\right)\right] \tag{11.30}$$

Equation (11.30) can be put in a different form using the rule

$$\exp\left[i\left(\int_{x}^{x_1} k\, dx - \frac{\pi}{4}\right)\right] = \exp\left[-i\left(\int_{x_1}^{x} k\, dx + \frac{\pi}{4}\right)\right] \tag{11.31}$$

$$\psi_1 = -\frac{Ai}{k^{1/2}}\left(\alpha - \frac{1}{4\alpha}\right)\exp\left[-i\left(\int_{x_1}^{x} k\, dx + \frac{\pi}{4}\right)\right]$$

$$-\frac{Ai}{k^{1/2}}\left(\alpha + \frac{1}{4\alpha}\right)\exp\left[i\left(\int_{x_1}^{x} k\, dx + \frac{\pi}{4}\right)\right] \tag{11.32}$$

The first term on the right side of Eq. (11.32) represents a wave travelling in the negative x-direction and the second represents a wave travelling in the positive x-direction. The one travelling in the positive direction is the incident wave and the other is the reflected wave. The evaluation of transmission coefficient T and reflection coefficient R is straightforward. Therefore,

$$\text{Amplitude of the incident wave} = -\frac{Ai\left(\alpha + \dfrac{1}{4\alpha}\right)}{k^{1/2}} \tag{11.33}$$

$$\text{Amplitude of the reflected wave} = -\frac{Ai\left(\alpha - \dfrac{1}{4\alpha}\right)}{k^{1/2}} \tag{11.34}$$

$$\text{Amplitude of the transmitted wave} = \frac{A}{k^{1/2}} \tag{11.35}$$

Then

$$T = \frac{1}{\left(\alpha + \dfrac{1}{4\alpha}\right)^2} \quad \text{and} \quad R = \frac{\left(\alpha - \dfrac{1}{4\alpha}\right)^2}{\left(\alpha + \dfrac{1}{4\alpha}\right)^2} \tag{11.36}$$

It follows from Eq. (11.36) that $R + T = 1$, as expected. For a broad, high barrier $\alpha \gg 1$ and

$$T \cong \frac{1}{\alpha^2} = \exp\left(-2\int_{x_1}^{x_2} \gamma\, dx\right) \tag{11.37}$$

If the barrier is square, Eq. (11.37) becomes

$$T \cong \exp\left[-2\gamma\,(x_2 - x_1)\right] \tag{11.38}$$

which is Eq. (4.44) in Section 4.4. Barrier tunnelling is very important as it provides theoretical explanation of α-decay.

11.5 ALPHA EMISSION

As an example of barrier tunnelling, we shall now discuss the emission of α-particles by nuclei. The variation of the potential against the distance from the centre of the nucleus is illustrated in Figure 4.7. The radius of the nucleus –alpha particle attraction r_1 is approximately equal to the nuclear radius r_0. Denoting the distance at which the α-particle energy E is equal to the Coulomb potential by r_2, we have for an α-particle with zero angular momentum.

$$r_2 = \frac{2Ze^2}{E} \tag{11.39}$$

where Z is the nuclear charge of the residual nucleus. For the evaluation of the transmission coefficient, Eq. (11.37), we require the value of the integral $\int \gamma dr$, where $\gamma^2 = 2m(V - E)/\hbar^2$ between the limits r_0 and r_2.

$$\int_{r_0}^{r_2} \gamma\, dr = \left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{r_0}^{r_2} \left(\frac{2Ze^2}{r} - E\right)^{1/2} dr \tag{11.40}$$

The introduction of a new variable ρ defined by

$$\cos\rho = \left(\frac{rE}{2Ze^2}\right)^{1/2} \tag{11.41}$$

makes the evaluation of the integral easier. On simplification, we get

$$\int_{r_0}^{r_2} \gamma\, dr = \left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{2Ze^2}{E^{1/2}} \left[\cos^{-1}\left(\frac{r_0E}{2Ze^2}\right)^{1/2} - \left(\frac{r_0E}{2Ze^2}\right)^{1/2}\left(1 - \frac{r_0E}{2Ze^2}\right)^{1/2}\right] \tag{11.42}$$

The transmission coefficient and decay constant λ (Section 4.4) are then given by

$$T = \exp\left(-2\int_{r_0}^{r_2} \gamma\, dr\right) \tag{11.43}$$

and

$$\lambda = 10^{21} T = 10^{21} \exp\left(-2\int_{r_0}^{r_2} \gamma\, dr\right) \tag{11.44}$$

These formulas fit fairly well with the experimental data on alpha decay.

11.6 BOUND STATES IN A POTENTIAL WELL

We now consider the application of WKB method to find the bound states of a particle moving in the one-dimensional potential well shown in Figure 11.3. Classically, for $E < 0$, the particle will oscillate back and forth between the turning points x_1 and x_2 where the kinetic energy vanishes. However, quantum mechanically things are different. The requirement that ψ must be finite allows only exponentially decreasing wave function in the regions $x < x_1$ (region 1) and $x > x_2$ (region 3). When we move from region 1 to region 2, the turning point is to the left of the classical region (barrier to the left of the turning point) and when we move from region 2 to region 3, the turning point is to the right of the classical region (barrier to the right of the turning point).

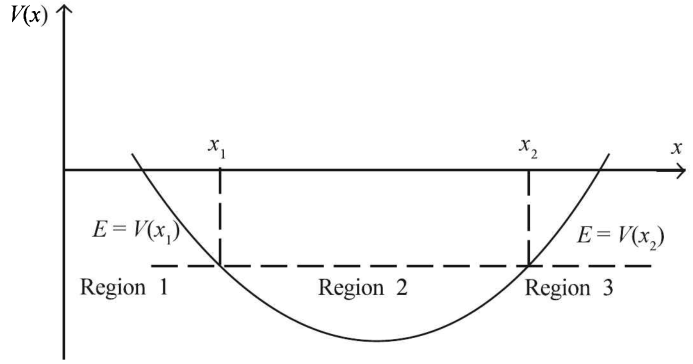


Figure 11.3 A potential well with linear turning points at x_1 and x_2.

The unnormalized exponentially decreasing wave function in region 1 can be written as (Eq. 11.16).

$$\psi_1 = \frac{1}{\gamma^{1/2}} \exp\left(-\int_{x}^{x_1} \gamma\, dx\right), \qquad x < x_1 \tag{11.45}$$

where

$$\gamma^2 = \frac{2m[V(x) - E]}{\hbar^2} \tag{11.45a}$$

We now apply the connection formula, Eq. (11.20), to get the wave function in region 2.

$$\psi_2 = \frac{2}{k^{1/2}} \cos\left(\int_{x_1}^{x} k\,dx - \frac{\pi}{4}\right), \qquad x_1 < x < x_2 \tag{11.46}$$

where

$$k^2 = \frac{2m[E - V(x)]}{\hbar^2} \tag{11.46a}$$

The wave function in region 3 is also an exponentially decaying one. According to Eq. (11.19), the wave function which connects region 2 with the decreasing exponential in region 3 is

$$\cos\left(\int_{x_1}^{x_2} k\,dx - \frac{\pi}{4}\right)$$

Equation (11.46) has therefore to be modified as

$$\psi_2 = \frac{2}{k^{1/2}} \cos\left(\int_{x_1}^{x_2} k\,dx + \int_{x_2}^{x} k\,dx - \frac{\pi}{4}\right) \tag{11.47}$$

Since, cos $(-\theta)$ = cos θ and sin $(-\theta)$ = – sin θ, Eq. (11.47) can be written as:

$$\psi_2 = \frac{2}{k^{1/2}} \cos\left(\int_{x_1}^{x_2} k\,dx\right) \cos\left(\int_{x}^{x_2} k\,dx + \frac{\pi}{4}\right)$$

$$+ \frac{2}{k^{1/2}} \sin\left(\int_{x_1}^{x_2} k\,dx\right) \sin\left(\int_{x}^{x_2} k\,dx + \frac{\pi}{4}\right)$$

or

$$\psi_2 = -\frac{2}{k^{1/2}} \cos\left(\int_{x_1}^{x_2} k\,dx\right) \sin\left(\int_{x}^{x_2} k\,dx - \frac{\pi}{4}\right)$$

$$+ \frac{2}{k^{1/2}} \sin\left(\int_{x_1}^{x_2} k\,dx\right) \cos\left(\int_{x}^{x_2} k\,dx - \frac{\pi}{4}\right) \tag{11.48}$$

From a comparison of Eq. (11.48) with Eq. (11.19), it follows that the second term in Eq. (11.48) is the one that connects with the decreasing exponential in region 3, while the first term connects with the increasing exponential. Since an increasing exponential in region 3 is not acceptable, the first term of Eq. (11.48) must vanish. This is possible only if

$$\cos \int_{x_1}^{x_2} k\,dx = 0 \quad \text{or} \quad \int_{x_1}^{x_2} k\,dx = \left(n + \frac{1}{2}\right)\pi, \qquad n = 0, 1, 2, \ldots \tag{11.49}$$

Substituting the value of k from Eq. (11.46a) in Eq. (11.49), we get

$$\left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{x_1}^{x_2} [E - V(x)]^{1/2}\,dx = \left(n + \frac{1}{2}\right)\pi, \qquad n = 0, 1, 2, \ldots \tag{11.50}$$

which gives the allowed energy values. It is evident from Eq. (11.50) that it is possible to connect the wave functions in regions 2 and 3 only for certain discrete values of energy.

The classical linear momentum $p = [2m\,(E - V)]^{1/2}$ and therefore Eq. (11.50) can be written as

$$2\int_{x_1}^{x_2} p\,dx = \left(n + \frac{1}{2}\right)h, \qquad n = 0, 1, 2, \ldots \tag{11.51}$$

The left side of this equation is the integral of linear momentum over a complete cycle of motion (from x_1 to x_2 and back to x_1). Hence Eq. (11.51) can also be written as

$$\oint p\,dx = \left(n + \frac{1}{2}\right)h, \qquad n = 0, 1, 2, \ldots \tag{11.52}$$

which is simply the Sommerfeld quantum condition with half integer rather than integer quantum numbers. While deriving the above quantum condition asymptotic solutions which are valid only several wavelengths away from the turning points have been smoothly connected. This is possible only when n is large.

WORKED EXAMPLES

EXAMPLE 11.1 Obtain the energy values of harmonic oscillator by the WKB method.

The classical turning points of the oscillator are those points at which the potential $V(x) = E$. That is

$$\frac{1}{2}m\omega^2 x^2 = E \quad \text{or} \quad x_1 = -\left(\frac{2E}{m\omega^2}\right)^{1/2} \quad \text{and} \quad x_2 = \left(\frac{2E}{m\omega^2}\right)^{1/2}$$

For a particle, constrained to move between classical turning points x_1 and x_2 in a potential well, the energies can be obtained from the condition in Eq. (11.51). We have

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad \text{or} \quad p = \left[2m\left(E - \frac{1}{2}m\omega^2 x^2\right)\right]^{1/2}$$

Substituting this value of p in Eq. (11.51), we get

$$\int_{x_1}^{x_2} \left[2m\left(E - \frac{1}{2}m\omega^2 x^2\right)\right]^{1/2} dx = \left(n + \frac{1}{2}\right)\pi\hbar, \quad n = 0, 1, 2, \ldots$$

Writing

$$\sin\theta = \left(\frac{m\omega^2}{2E}\right)^{1/2} x$$

the above integral reduces to

$$\int_{-\pi/2}^{\pi/2} (2mE)^{1/2} \cos^2\theta \left(\frac{2E}{m\omega^2}\right)^{1/2} d\theta = \left(n + \frac{1}{2}\right)\pi\hbar$$

or

$$\frac{2E}{\omega}\int_{-\pi/2}^{\pi/2} \cos^2\theta\, d\theta = \left(n + \frac{1}{2}\right)\pi\hbar$$

or

$$\frac{2E}{\omega}\frac{\pi}{2} = \left(n + \frac{1}{2}\right)\pi\hbar \quad \text{or} \quad E = \left(n + \frac{1}{2}\right)\hbar\omega$$

EXAMPLE 11.2 Show that the integer n in the expression $\oint p\, dx = (n + \frac{1}{2})h$ is the number of nodes of the WKB wave function between the classical turning points x_1 and x_2.

The given expression $\oint p\, dx = (n + \frac{1}{2})h$ is equivalent to

$$2\int_{x_1}^{x_2} p\, dx = (n + \tfrac{1}{2})h \quad \text{or} \quad \int_{x_1}^{x_2} k\, dx = (n + \tfrac{1}{2})\pi$$

When this value of $\int_{x_1}^{x_2} k\, dx$ is substituted in the wave function ψ_2 in Eq. (11.48), it follows that n is the number of nodes of the wave function between the classical turning points x_1 and x_2.

EXAMPLE 11.3 Deduce Eq. (11.42) from Eq. (11.40).

$$\int_{r_0}^{r_2} \gamma\, dr = \left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{r_0}^{r_2} \left(\frac{2Ze^2}{r} - E\right)^{1/2} dr \qquad (11.40)$$

Writing

$$\left(\frac{rE}{2Ze^2}\right)^{1/2} = \cos\rho$$

Equation (11.40) reduces to

$$\int_{r_0}^{r_2} \gamma\, dr = -\frac{4Ze^2}{E^{1/2}}\left(\frac{2m}{\hbar^2}\right)^{1/2} \int \sin^2\rho\, d\rho$$

Since $r_2 = 2Ze^2/E$, at the upper limit $\cos{}^2\rho = 1$ or $\rho = 0$. The lower limit is

$$\cos^{-1}\left(\frac{r_0E}{2Ze^2}\right)^{1/2} = \cos^{-1}\sqrt{a}$$

where $a = r_0E/(2Ze^2)$. With these limits

$$\int_{r_0}^{r_2} \gamma\, dr = \frac{4Ze^2}{E^{1/2}}\sqrt{\frac{2m}{\hbar^2}} \int_0^{\cos^{-1}\sqrt{a}} \sin^2\rho\, d\rho$$

where

$$\int_0^{\cos^{-1}\sqrt{a}} \sin^2\rho\, d\rho = \int \frac{1-\cos(2\rho)}{2}\, d\rho = \frac{1}{2}[\rho]_0^{\cos^{-1}\sqrt{a}} - \frac{1}{2}\left[\frac{\sin(2\rho)}{2}\right]_0^{\cos^{-1}\sqrt{a}}$$

$$= \frac{1}{2}\cos^{-1}\sqrt{a} - \frac{1}{2}[\sin\rho\cos\rho]_0^{\cos^{-1}\sqrt{a}}$$

$$= \frac{1}{2}\cos^{-1}\sqrt{a} - \frac{1}{2}\left[\sqrt{1-\cos^2\rho}\,\cos\rho\right]_0^{\cos^{-1}\sqrt{a}}$$

$$= \frac{1}{2}\cos^{-1}\sqrt{a} - \frac{1}{2}\sqrt{a}\sqrt{1-a}$$

Then

$$\int_{r_0}^{r_2} \gamma\, dr = \frac{2Ze^2}{E^{1/2}}\left(\frac{2m}{\hbar^2}\right)^{1/2}\left[\cos^{-1}\sqrt{\frac{r_0E}{2Ze^2}} - \sqrt{\frac{r_0E}{2Ze^2}}\sqrt{\left(1-\frac{r_0E}{2Ze^2}\right)}\right]$$

which is Eq. (11.42).

REVIEW QUESTIONS

1. Explain WKB approximation.
2. What do you understand by a classical turning point? How could one get the turning points if the potential is known?
3. List the connection formulas and explain them.
4. Discuss briefly the validity conditions of WKB approximation.

5. The WKB method is valid for systems in which the potential is slowly varying. Why?
6. For a particle constrained to move between classical turning points in a potential well, how the energies are obtained by the WKB method.
7. Compare the quantum condition of Wilson–Sommerfeld with the one in WKB method.
8. The quantum condition

$$\int_{x_1}^{x_2} k\, dx = \left(n + \frac{1}{2}\right)\pi$$

is expected to be good only when n is large. Why?

PROBLEMS

1. Solve the one-dimensional infinite potential well problem (Section 4.1) using the WKB method and compare with the exact solution.
2. Estimate the energy levels of a particle moving in the potential:

$$V(x) = \begin{cases} \infty & x < 0 \\ Ax & x > 0 \end{cases}$$

where A is a constant.

3. Find the energy levels of a particle moving in the potential $V(x) = V_0 \mid x \mid$, V_0 being a positive constant.

Chapter 12

Time-Dependent Perturbation Theory

The time-dependent Schrödinger equation of systems whose Hamiltonian is independent of time is separable in spatial and time coordinates. Their eigenfunctions are of the form

$$\Psi\,(\mathbf{r},t) = \psi\,(\mathbf{r})\,\exp\left(-\frac{iEt}{\hbar}\right)$$

where $\psi(r)$ satisfies the time-independent Schrödinger equation

$$H\psi\,(\mathbf{r}) = E\psi(\mathbf{r})$$

The time-dependent part of the eigenfunction disappears when we consider the physically relevant quantity $|\Psi|^2$, the position probability density. Expectation values of observables are also constant in time. In one sense, what we have done so far may rightly be called *quantum statics.*

12.1 INTRODUCTION

In large number of systems the Hamiltonian may depend on time (*quantum dynamics*) resulting in the absence of stationary states. Again perturbation methods can be applied for those problems in which the Hamiltonian H may be written as the sum of two terms

$$H(\mathbf{r},\, t) = H^0(\mathbf{r}) + H'(\mathbf{r},\, t) \tag{12.1}$$

where $H^0(\mathbf{r})$ is the time-independent and $H'(\mathbf{r}, t)$ is the time-dependant part. Our main interest is in problems for which $H' << H^0$. The time-dependant Schrödinger equation to be solved is

$$i\hbar\frac{\partial\Psi}{\partial t} = H(\mathbf{r}, t)\,\Psi(\mathbf{r}, t) \tag{12.2}$$

where $H(\mathbf{r}, t)$ is of the form given in Eq. (12.1). Let Ψ_n^0, $n = 1, 2, ...$ be the stationary state eigenfunctions of the unperturbed Hamiltonian H^0 forming a complete orthonormal set. The Ψ_n^0's are of the form

$$\Psi_n^0 = \psi_n^0 \exp\left(-\frac{iE_nt}{\hbar}\right), \qquad n = 1, 2, ... \tag{12.3}$$

and obey the equations

$$i\hbar\frac{\partial\Psi_n^0}{\partial t} = H^0\Psi_n^0, \qquad n = 1, 2, ... \tag{12.4}$$

In the presence of the perturbation $H'(t)$, the states of the system may be expressed as a linear combination of Ψ_n^0's as

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t)\,\Psi_n^0 = \sum_n c_n(t)\psi_n^0(\mathbf{r}) \exp\left(-\frac{iE_nt}{\hbar}\right) \tag{12.5}$$

where $c_n(t)$'s are expansion coefficients. Substituting Eqs. (12.1) and (12.5) in Eq. (12.2), we get

$$i\hbar\frac{\partial}{\partial t}\sum_n c_n(t)\,\psi_n^0(\mathbf{r}) \exp\left(-\frac{iE_nt}{\hbar}\right) = (H^0 + H')\sum_n c_n(t)\,\psi_n^0(\mathbf{r}) \exp\left(-\frac{iE_nt}{\hbar}\right) \tag{12.6}$$

Using Eqs. (12.4) and (12.3), Eq. (12.6) reduces to

$$i\hbar\sum_n \frac{dc_n(t)}{dt}\psi_n^0 \exp\left(-\frac{iE_nt}{\hbar}\right) = \sum_n c_n(t)\,H'\psi_n^0 \exp\left(-\frac{iE_nt}{\hbar}\right) \tag{12.7}$$

For convenience, we shall use the Dirac's notation for states. Multiplying Eq. (12.7) from left by $\langle k|$ and using the orthonormality of states

$$\begin{aligned} i\hbar\frac{dc_k(t)}{dt} &= \sum_n c_n(t)\langle k|H'|n\rangle \exp\frac{i(E_k - E_n)t}{\hbar} \\ &= \sum_n c_n(t)\,H'_{kn} \exp(i\omega_{kn}t) \end{aligned} \tag{12.8}$$

where

$$H'_{kn} = \langle\psi_k^0|H'|\psi_n^0\rangle = \langle k|H'|n\rangle \quad \text{and} \quad \omega_{kn} = \frac{E_k - E_n}{\hbar} \tag{12.9}$$

The summation symbol in Eq. (12.8) stands for summation over the discrete states and integration over the continuum states. Equation (12.8) is exact since we have not made any assumption so far.

12.2 FIRST-ORDER PERTURBATION

Replacing H' by $\lambda H'$ as in time-independent perturbation theory and expressing the coefficient $c_n(t)$ as a power series in λ, we get

$$c_n(t) = c_n^{(0)}(t) + \lambda^1 c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots \tag{12.10}$$

Substituting this value of $c_n(t)$ in Eq. (12.8) and replacing H'_{kn} by $\lambda H'_{kn}$, we have

$$i\hbar\left(\frac{dc_k^{(0)}}{dt} + \lambda^1 \frac{dc_k^{(1)}}{dt} + \lambda^2 \frac{dc_k^{(2)}}{dt} + \cdots\right)$$

$$= \sum_n \lambda H'_{kn}(\mathbf{r}, t)\left(c_n^{(0)}(t) + \lambda^1 c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots\right) \exp(i\omega_{kn}t) \tag{12.11}$$

Equating the coefficients of λ^0 (zeroth order), λ^1 (first order), λ^2 (second order)

$$\frac{d}{dt}c_k^{(0)} = 0 \tag{12.12}$$

$$i\hbar\frac{d}{dt}c_k^{(1)} = \sum_n c_n^{(0)} H'_{kn} \exp(i\omega_{kn}t) \tag{12.13}$$

$$i\hbar\frac{d}{dt}c_k^{(2)} = \sum_n c_n^{(1)} H'_{kn} \exp(i\omega_{kn}t) \tag{12.14}$$

Equation (12.12) implies that the coefficient $c_k^{(0)}$ is constant in time which is understandable as the zero-order Hamiltonian is time-independent. From Eq. (12.13), the first-order contribution to c_n is

$$c_n^{(1)}(t) = \frac{1}{i\hbar}\int \sum_n c_n^{(0)} H'_{kn}(\mathbf{r}, t) \exp(i\omega_{kn}t)\, dt \tag{12.15}$$

We are interested in the case where the system is initially ($t = 0$) in the unperturbed state n, so that all $c_k^{(0)}$'s are zero except $c_n^{(0)}$ which is unity. Now the perturbation H' is switched on for a time t and its effect on the states is studied. For times after t, $H' = 0$ and therefore $c_k = c_k(t)$ for time greater than t. Equation (12.15) now reduces to

$$c_k^{(1)}(t) = \frac{1}{i\hbar}\int_0^t H'_{kn}(\mathbf{r}, t') \exp(i\omega_{kn}t')\, dt' \tag{12.16}$$

The perturbation H' has induced transition to other states and after a time t the probability that a transition to state k has occurred is given by $|c_k^{(1)}(t)|^2$. Instead, if the system is in a more complicated initial state, one can study its behaviour by a superposition process.

12.3 HARMONIC PERTURBATION

As an example of these general results we consider a system such as an atom or molecule exposed to harmonic perturbation (electromagnetic radiation). For convenience, we shall assume that the involved states are discrete. A harmonic perturbation with an angular frequency ω has the form

$$H'(\mathbf{r},t) = 2\,H'(\mathbf{r})\cos(\omega t) = H'(\mathbf{r})\,[\exp(i\omega t) + \exp(-i\omega t)] \quad (12.17)$$

With this perturbation in Eq. (12.9) and remembering that the involved integral is over the space coordinates

$$H'_{kn} = \langle k|H'|n\rangle\,[\exp(i\omega t) + \exp(-i\omega t)] \quad (12.18)$$

If this value of H'_{kn} is inserted in Eq. (12.16), we have

$$c_k^{(1)}(t) = \frac{H'_{kn}}{i\hbar}\int_0^t \{\exp[i(\omega_{kn}+\omega)t'] + \exp[i(\omega_{kn}-\omega)t']\}\,dt'$$

$$= -\frac{H'_{kn}}{\hbar}\left\{\frac{\exp[i(\omega_{kn}+\omega)t]-1}{\omega_{kn}+\omega} + \frac{\exp[i(\omega_{kn}-\omega)t]-1}{\omega_{kn}-\omega}\right\} \quad (12.19)$$

The first term on the right side of Eq. (12.19) has a maximum value when $\omega_{kn} + \omega \simeq 0$ or $E_k \simeq E_n - \hbar\omega$, whereas the second term is maximum when $E_k \simeq E_n + \hbar\omega$. In other words, the effect of harmonic perturbation with angular frequency ω is to receive from the system or transfer to the system the quantum of energy $\hbar\omega$. The first one corresponds to *induced or stimulated emission* whereas the second to *induced absorption* or simply absorption. Since the emission takes place in the presence of the electromagnetic radiation, it is referred to as stimulated emission. Since only one term is important at a given time, for discussion we shall consider the second term. Retaining the second term, we get

$$c_k^{(1)}(t) = -\frac{H'_{kn}}{\hbar}\,\frac{\exp[i(\omega_{kn}-\omega)t]-1}{\omega_{kn}-\omega}$$

or

$$c_k^{(1)}(t) = -\frac{H'_{kn}}{\hbar}\,\frac{\exp[i(\omega_{kn}-\omega)t/2]}{\omega_{kn}-\omega}\left\{\exp\left[\frac{i(\omega_{kn}-\omega)t}{2}\right] - \exp\left[-\frac{i(\omega_{kn}-\omega)t}{2}\right]\right\}$$

$$= -\frac{2iH'_{kn}}{\hbar}\,\frac{\exp[i(\omega_{kn}-\omega)t/2]}{\omega_{kn}-\omega}\,\sin\frac{(\omega_{kn}-\omega)t}{2} \quad (12.20)$$

If the system is initially in the state $|n\rangle$ (at $t = 0$), the probability $P_{n\to k}$ of finding the system in the discrete state $|k\rangle$ after a time t is $\left|c_k^{(1)}\right|^2$

$$P_{n\to k}(t) = \left|c_k^{(1)}\right|^2 = \frac{4\left|H'_{kn}\right|^2}{\hbar^2}\frac{\sin^2(\omega_{kn}-\omega)t/2}{(\omega_{kn}-\omega)^2} \tag{12.21}$$

An interesting feature of the result is that the transition probability oscillates sinusoidally as a function of time. Probability $P_{n\to k}$ versus $(\omega_{kn} - \omega)$ plot is as shown in Figure 12.1. The central peak has a height of $\left|H'_{kn}\right|^2 t^2/\hbar^2$ and a width of about $2\pi/t$ and therefore the area under the main peak is proportional to t. That is, the probability of finding the system in state k is proportioned to t. It may be noted that the probability of finding the system in a state whose energy differs considerably from the initial state E_n is smaller than the probability of finding it in a neighbouring energy state.

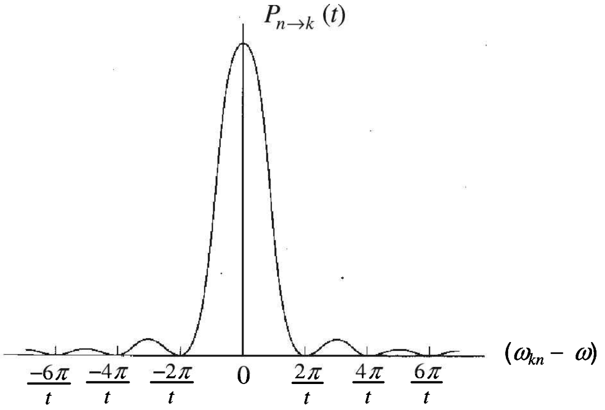


Figure 12.1 Plot of probability $P_{n\to k}$ versus $(\omega_{kn} - \omega)$.

12.4 TRANSITIONS TO CONTINUUM STATES

So far we considered transition between discrete states n and k. We shall now consider transitions from a discrete state n to a continuum of states around E_k, where the density of state is $\rho(E_k)$. The number of states in the energy range E_k to $(E_k + dE_k)$ is $\rho(E_k)\, dE_k$ and the total probability for transition into range dE_k is

$$P(t) = \frac{4}{\hbar^2}\int_{dE_k} \left|H'_{kn}\right|^2 \frac{\sin^2(\omega_{kn}-\omega)t/2}{(\omega_{kn}-\omega)^2}\rho(E_k)\, dE_k \tag{12.22}$$

When t is large, the width of the main peak becomes small and only limited number of final states contribute to the above integral. Consequently, we can regard H'_{kn} and $\rho(E_k)$ as constants over this range.

To evaluate the integral, the variable of integration may be changed from E_k to x by defining

$$x = \frac{(\omega_{kn} - \omega)t}{2} = \left(\frac{E_k - E_n}{\hbar} - \omega\right)\frac{t}{2}; \quad dx = \frac{t}{2\hbar}dE_k \tag{12.23}$$

Now, Eq. (12.22) gives

$$P(t) = \frac{2t}{\hbar}|H'_{kn}|^2 \ \rho(E_k) \int \frac{\sin^2 x}{x^2}\ dx \tag{12.24}$$

The transition from the state E_n into a state E_k can be on either side of E_n. Though the integral is over a small range of $\omega_{kn}-\omega$, the limits on x can be extended to $\pm\infty$ as the integrand is very small outside the actual range. The integral is a standard one and is given by

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\ dx = \pi \tag{12.25}$$

Equation (12.24) then takes the very simple form

$$P(t) = \frac{2\pi}{\hbar} t |H'_{kn}|^2 \rho(E_k) \tag{12.26}$$

The number of transitions per unit time called the *transition probability*, is usually denoted by the letter ω

$$\omega = \frac{2\pi}{\hbar}|H'_{kn}|^2 \rho(E_k) \tag{12.27}$$

Equation (12.27) is called *Fermi's Golden Rule*. The transition probability is proportional to the square of the matrix element of the amplitude of the harmonic perturbing term between states n and k and to the density of final states. The intensities of spectral lines are proportional to these transition probabilities as they depend on the rate of transfer of energy between the electromagnetic field and the system.

12.5 ABSORPTION AND EMISSION OF RADIATION

An exact treatment of the absorption and emission of electromagnetic radiation by atoms and molecules requires the quantization of the electromagnetic radiation field. However, we shall discuss here a semi-classical treatment which gives considerable insight into the phenomenon of absorption and emission.

The Electromagnetic Field

The electromagnetic field is completely specified by the vector potential **A** and scalar potential ϕ. The electric field $\boldsymbol{\varepsilon}$ associated with the vector potential is given by

$$\boldsymbol{\varepsilon} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi \tag{12.28}$$

For plane electromagnetic wave

$$\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \tag{12.29}$$

with solution

$$\mathbf{A}\ (\mathbf{r},\ t) = \mathbf{A}_0\ (\omega)\ \exp\ [\pm i(\mathbf{k}\cdot\mathbf{r} - \omega t] \tag{12.30}$$

where $\mathbf{A}_0(\omega)$ is a constant, $\mathbf{k}$ is the propagation vector and ω is the angular frequency.

$$\mathbf{A}_0\ (\omega)\cdot\mathbf{k} = 0 \quad\text{and}\quad \omega = ck \tag{12.31}$$

A more general solution of $\mathbf{A}(\mathbf{r}, t)$ is

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0(\omega)\ [\exp\ (i\ \mathbf{k}\cdot\mathbf{r} - i\omega t) + \exp\ (-i\mathbf{k}\cdot\mathbf{r} + i\omega t)] \tag{12.32}$$

For plane electromagnetic waves it is possible to select $\mathbf{A}$ and ϕ in such a way that

$$\nabla\cdot\mathbf{A} = 0 \quad\text{and}\quad \phi = 0 \tag{12.33}$$

The electric field associated with such a plane wave is

$$\boldsymbol{\varepsilon} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} = \mathbf{A}_0\ \frac{\omega}{c} i\ [\exp\ (i\mathbf{k}\cdot\mathbf{r} - i\omega t) - \exp\ (-i\mathbf{k}\cdot\mathbf{r} + i\omega t)] \tag{12.34}$$

The average value of the electric field is

$$\bar{\varepsilon}^2 = 2\frac{\omega^2}{c^2}|\mathbf{A}_0|^2 \tag{12.35}$$

The energy density $\rho(\omega)$ in an electromagnetic wave

$$\rho(\omega) = \frac{\bar{\varepsilon}^2}{2} = \frac{\omega^2}{c^2}|\mathbf{A}_0|^2 \tag{12.36}$$

In general the electromagnetic radiation is not strictly monochromatic but has a small spread of frequencies. Since any radiation can be taken as the superposition of harmonic plane waves

$$\mathbf{A}(\mathbf{r}, t) = \int \mathbf{A}_0(\omega)\ [\exp\ (i\mathbf{k}\cdot\mathbf{r} - i\omega t) + \exp\ (-i\mathbf{k}\cdot\mathbf{r} + i\omega t)]\ d\omega \tag{12.37}$$

The Hamiltonian Operator

The Hamiltonian H of a charged particle in an electromagnetic field is

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + e\phi \tag{12.38}$$

Since ϕ and $\nabla\cdot\mathbf{A}$ are zero, the corresponding operator is

$$H = -\frac{\hbar^2}{2m}\ \nabla^2 + \frac{ie\hbar}{mc}\ \mathbf{A}\cdot\nabla + \frac{e^2}{2mc^2}|\mathbf{A}|^2 \tag{12.39}$$

An electron in an atom has an additional potential energy $V(r)$. As the third term in Eq. (12.39) is very small in comparison with the other two, the Hamiltonian of the atom in the presence of electromagnetic radiation is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) + \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla \tag{12.40}$$

$$= H^0 + H' \tag{12.41}$$

where the unperturbed Hamiltonian H^0 and the perturbation H' are given by

$$H^0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad \text{and} \quad H' = \frac{ie\hbar}{mc}\mathbf{A}\cdot\nabla \tag{12.42}$$

Electric Dipole Approximation

The wavelength of radiation in the visible to radiofrequency regions of the electromagnetic spectrum is much larger than the size of the systems (atoms, ions, etc.) with which it interacts. For visible light (the worst case) wavelength $\cong 5 \times 10^{-5}$ cm or $k = 2\pi/\lambda \cong 10^5$ cm^{-1}. Since the size of an atom $r \cong 10^{-8}$ cm, $kr \cong 10^{-3}$ and

$$\exp(\pm i\mathbf{k}\cdot\mathbf{r}) \cong 1 \tag{12.43}$$

It follows from Eq. (12.37) that

$$A(\mathbf{r}, t) = \int \mathbf{A}_0(\omega)\,[\exp(i\omega t) + \exp(-i\omega t)]\,d\omega \tag{12.44}$$

Substituting this value of $A(\mathbf{r}, t)$ in Eq. (12.42)

$$H' = \frac{ie\hbar}{mc}\int [\exp(i\omega t) + \exp(-i\omega t)]\mathbf{A}_0(\omega)\cdot\nabla\,d\omega$$

$$= \frac{ie\hbar}{mc}\int [\exp(i\omega t) + \exp(-i\omega t)]\,|\mathbf{A}_0(\omega)|\,\nabla_A\,d\omega \tag{12.45}$$

where ∇_A is the component of ∇ along the polarization vector $\mathbf{A}_0$.

We now evaluate the matrix element $H'_{kn}(t)$ of the perturbation H' between the states k and n. While evaluating, integration over ω may be separated from integration over space coordinates.

$$H'_{kn}(t) = \frac{ie\hbar}{mc}\langle k|\nabla_A|n\rangle \int [\exp(i\omega t) + \exp(-i\omega t)]\,A_0(\omega)\,d\omega \tag{12.46}$$

The matrix element $\langle k|\nabla_A|n\rangle$ can easily be converted into the more familiar dipole moment matrix element as detailed below. The commutator of r with H^0 is

$$[r, H^0] = \left[r, \frac{p^2}{2m} + V\right]$$

$$= \frac{\left[r, p^2\right]}{2m}$$

$$= \frac{\mathbf{p}[r, \mathbf{p}]}{m}$$

$$= \frac{i\hbar \mathbf{p}}{m}$$

$$= \frac{\hbar^2 \nabla}{m} \tag{12.47}$$

since

$$[A, B^n] = nB^{n-1}\,[A, B] \tag{12.48}$$

We have

$$\left\langle k \middle| \left[r, H^0\right] \middle| n \right\rangle = \left\langle k \middle| rH^0 \middle| n \right\rangle - \left\langle k \middle| H^0 r \middle| n \right\rangle$$

Since H^0 is Hermitian, using Eq. (12.48) we get

$$\frac{\hbar^2}{m}\langle k|\nabla|n\rangle = E_n^0 \langle k|r|n\rangle - E_k^0 \langle k|r|n\rangle$$

or

$$\langle k|\nabla|n\rangle = \frac{m}{\hbar^2}\left(E_n^0 - E_k^0\right)\langle k|r|n\rangle = -\frac{m}{\hbar}\omega_{kn}\langle k|\mathbf{r}|n\rangle$$

or

$$\left\langle k \middle| e\nabla_A \middle| n \right\rangle = -\frac{m}{\hbar}\omega_{kn}\left\langle k \middle| er_A \middle| n \right\rangle \tag{12.49}$$

where r_A is the component of **r** in the polarization direction.

In deriving Eq. (12.49) we have assumed that $kr << 1$ and $\exp(ikr) \cong 1$. Since $e\mathbf{r}$ is an electric dipole moment, this approximation means the replacement of the atom by an electric dipole. Hence, the approximation is called a *dipole approximation* and $\langle k\,|\,er_A\,|\,n\rangle = \mu_{kn}$ is called the *transition dipole moment.* When the wavelength λ of the electromagnetic radiation is large, the wave 'sees' the atom or molecule as a dipole. But when λ is small compared to the dimensions of the atom, the radiation 'sees' the individual charges of the dipole and not the dipole as a whole. In such a case, the electric field at the individual charges will be different. If the higher-order terms in the expansion of $\exp(ikr)$ are retained, we will have terms corresponding to *multipole radiations.* They are very important only in the emission and absorption of X-rays. Higher-order terms are important in the other regions of the electromagnetic spectrum, if the dipole matrix element is zero. Substituting the value of $\langle k\,|\,e\nabla_A\,|\,n\rangle$ in Eq. (12.46), we get

$$H'_{kn}(t) = -\frac{i}{c}\,\omega_{kn}\,\langle k\,|\,er_A\,|\,n\rangle \int [\exp(i\omega t) + \exp(-i\omega t)]\,\mathbf{A}_0(\omega)\,d\omega \tag{12.50}$$

Transition Probability

As the factor $\langle k|er_A|n\rangle$ is the component of $\langle k|e\mathbf{r}|n\rangle$ in the polarization direction,

$$|\langle k|er_A|n\rangle|^2 = |\langle k|e\mathbf{r}|n\rangle|^2\cos^2\theta \tag{12.51}$$

where θ is the angle between the direction of polarization and $\langle k|e\mathbf{r}|n\rangle$. Since radiation is isotropic, $\langle k|e\mathbf{r}|n\rangle$ is not restricted to a single plane as assumed. Taking all directions into consideration,

$$|\langle k|er_A|n\rangle|^2 = \frac{1}{3}|\langle k|e\mathbf{r}|n\rangle|^2 = \frac{1}{3}|\langle k|\mu|n\rangle|^2 = \frac{1}{3}|\mu_{kn}|^2 \tag{12.52}$$

where

$$\mu_{kn} = \langle k|e\mathbf{r}|n\rangle \tag{12.52a}$$

The probability that H' has induced a transition from state n to state k is given by $\left|c_k^{(1)}\right|^2$. Substituting the value of $H'_{kn}(t)$ in Eq. (12.16) and retaining the term that corresponds to absorption only

$$c_k^{(1)}(t) = -\frac{\omega_{kn}}{c\hbar}\langle k|er_A|n\rangle\int A_0(\omega)\,d\omega\int_0^t \exp\,[i(\omega_{kn}-\omega)t']\,dt'$$

$$= -\frac{\omega_{kn}}{ic\hbar}\langle k|er_A|n\rangle\int A_0(\omega)\frac{\exp\,[i(\omega_{kn}-\omega)t]-1}{\omega_{kn}-\omega}\,d\omega \tag{12.53}$$

or

$$\left|c_k^{(1)}(t)\right|^2 = \frac{4\omega_{kn}^2}{3c^2\hbar^2}|\mu_{kn}|^2\int|A_0(\omega)|^2\frac{\sin^2[(\omega_{kn}-\omega)t/2]}{(\omega_{kn}-\omega)^2}\,d\omega \tag{12.54}$$

where Eq. (12.52) is used to replace $|\langle k|er_A|n\rangle|^2$. The factor $|A_0(\omega)|^2$ is fairly broad and the remaining factor in the integral is sharply peaked about $\omega = \omega_{kn}$. Therefore, we may replace $|A_0(\omega)|^2$ by $|A_0(\omega_{kn})|^2$ and take it outside the integral. To evaluate the integral the variable of integration may be changed from ω to x defined by $x = (\omega - \omega_{kn})t/2$

$$\left|c_k^{(1)}(t)\right|^2 = \frac{2t}{3\hbar^2}|\mu_{kn}|^2\rho(\omega_{kn})\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\,dx \tag{12.55}$$

Equation (12.36) has been used to replace $|A_0(\omega_{kn})|^2$ in Eq. (12.54). The value of the integral in Eq. (12.55) is π and the probability per unit time for absorption:

$$\omega = \frac{2\pi}{3\hbar^2}|\mu_{kn}|^2\rho(\omega_{kn}) \tag{12.56}$$

The term representing emission has a large value when $\omega_{kn} + \omega = 0$ or $E_k = E_n - \hbar\omega$. Evaluation of the transition probability leads to the same result as that for absorption. In the emission process, the electromagnetic field gains energy $\hbar\omega$ from the atom or molecule and therefore in the output we have two photons, one that caused the transition and the other from the transition. In other words, an amplification of photons has taken place which forms the basis for light amplification by stimulated emission of radiation (laser).

12.6 EINSTEIN'S *A* AND *B* COEFFICIENTS

The semi-classical treatment of radiation discussed in Section 12.5 accounts for absorption and stimulated emission. In addition to these two, an atom or molecule in an excited state can make a transition to a lower state by emitting a photon without the influence of an applied electromagnetic field. Only with the addition of this 'spontaneous emission', it was possible to account all the contributions to the emission of radiation from an excited state. Quantization of the electromagnetic field is necessary to explain the mechanism involved in the process. However, an elegant approach of Einstein, formulated in 1917, interrelates the three processes and allows us to calculate the transition probability for spontaneous emission.

Einstein considered a system (an atom) with two states in equilibrium with radiation of density $\rho(\omega)$. The number of molecules in the lower state n be N_n and those in the upper state m be N_m. The probability per unit time or transition rate for an atom in state n to absorb a photon and to undergo a transition to state m is directly proportional to $\rho(\omega)$. That is,

$$\text{The transition rate for absorption} = B_{n\to m}\, \rho(\omega) \tag{12.57}$$

where the constant $B_{n\to m}$ is called the *Einstein's B coefficient for induced absorption*. Therefore,

$$\text{The number of transitions from state } n \text{ to state } m = N_n B_{n\to m} \rho(\omega) \tag{12.58}$$

Denoting *Einstein's coefficient for stimulated emission* from state m to state n by $B_{m\to n}$,

$$\text{The number of transitions from state } m \text{ to state } n = N_m B_{m\to n} \rho(\omega) \tag{12.59}$$

Einstein inferred that $B_{n\to m} = B_{m\to n}$. At thermal equilibrium, when there is no net transfer of energy between the system and the field

$$N_n B_{n\to m} \rho(\omega) = N_m\, B_{m\to n} \rho(\omega) \tag{12.60}$$

Since $B_{n\to m} = B_{m\to n}$, this implies that $N_n = N_m$ which is not in accordance with Boltzmann distribution

$$\frac{N_n}{N_m} = \exp\left(\frac{\hbar\omega_{mn}}{kT}\right), \quad \omega_{mn} = \frac{E_m - E_n}{\hbar} \tag{12.61}$$

where k is the Boltzmann constant and T is the absolute temperature. Einstein, therefore, proposed that there must be an additional contribution to the emission process which does not depend on the radiation. He simply wrote the additional contribution as $N_m A_{m\to n}$, where $A_{m\to n}$ is the *Einstein's coefficient for spontaneous emission*. Now at thermal equilibrium,

$$N_m A_{m\to n} + N_m B_{m\to n}\, \rho(\omega_{mn}) = N_n B_{n\to m}\, \rho(\omega_{mn}) \tag{12.62}$$

Substituting the value of N_n from Eq. (12.61) in Eq. (12.62), we get

$$A_{m\to n} = B_{n\to m} \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right] \rho(\omega_{mn}) \tag{12.63}$$

It follows from Planck's radiation law that

$$\rho(\omega_{mn}) = \frac{2\hbar\omega_{mn}^3}{\pi c^3} \frac{1}{\exp\left[\hbar\omega_{mn}/(kT)\right]-1} \tag{12.64}$$

Use of this result in Eq. (12.63) gives

$$\frac{A_{m\to n}}{B_{m\to n}} = \frac{2\hbar\omega_{mn}^3}{\pi c^3} = \frac{8\pi h\nu_{mn}^3}{c^3} \tag{12.65}$$

Since the transition rate for absorption is the same as the probability per unit time, from Eqs. (12.56) and (12.57), we get

$$B_{m\to n} = \frac{2\pi}{3\hbar^2}|\mu_{mn}|^2 = \frac{2\pi e^2}{3\hbar^2}\,|\langle m|\mathbf{r}|n\rangle|^2 \tag{12.66}$$

$$= \frac{8\pi^2\varepsilon_0\alpha c}{3\hbar}|\langle m|r|n\rangle|^2 \tag{12.66a}$$

and

$$A_{m\to n} = \frac{4\omega_{mn}^3}{3\hbar c^3}\,|\mu_{mn}|^2$$

$$= \frac{4\omega_{mn}^3}{3\hbar c^3} e^2|\langle m|\mathbf{r}|n\rangle|^2$$

$$= \frac{16\pi\varepsilon_0\alpha\omega_{mn}^3}{3c^2}\,|\langle m|\mathbf{r}|n\rangle|^2 \tag{12.67}$$

where

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} = \frac{1}{137}$$

is the fine structure constant. It is evident from Eq. (12.67) that the coefficient for spontaneous emission increases as the cube of transition frequency. It follows from Eqs. (12.66), (12.67) and (12.64) that

$$\frac{\text{Spontaneous emission}}{\text{Stimulated emission}} = \frac{N_m}{N_m}\frac{A_{m\to n}}{B_{m\to n}\rho(\omega_{mn})} = \exp\left(\frac{\hbar\omega}{kT}\right) - 1 \tag{12.68}$$

Hence at thermal equilibrium, if $\omega << kT/\hbar$ the number of stimulated emissions far exceeds the number of spontaneous emissions whereas reverse is the situation if $\omega >> kT/\hbar$.

12.7 SELECTION RULES

Calculation of transition probability for absorption, stimulated emission and spontaneous emission has been reduced to the evaluation of the transitions dipole moment

$$\mu_{kn} = \langle \psi_k | \boldsymbol{\mu} | \psi_n \rangle \tag{12.69}$$

where $\boldsymbol{\mu} = -e\mathbf{r}$. Transition between all states are not allowed. The 'selection rules' specify the transitions that may occur on the basis of dipole approximation. Transitions for which the transition dipole moment is nonzero are *allowed transitions* and those for which it is zero are *forbidden transitions*. The transition dipole moment can be considered as a measure of the imbalance created in the electromagnetic field when the electron makes a transition between states.

We have already seen that the parity of an atomic orbital with quantum number l is $(-1)^l$. The s and *d*-orbitals have even parity whereas p and f-orbitals have odd parity. The parity of the integrand of the transition dipole moment μ_{kn} is

$$(-1)^{l_k} (-1) (-1)^{l_n} = (-1)^{l_k + l_n + 1}$$

which is even, if the two orbitals have opposite parity and odd if they have the same parity. Group theoretical considerations suggest that a transition dipole moment will be finite only when the integrand is totally symmetric under symmetry operation of the system. Therefore, the only allowed electric dipole transitions are those involving a change in parity. This is called the *Laporte selection rule*.

For hydrogenic atoms, we may specify the states by the usual quantum numbers n, l, m. For a transition to be allowed, the dipole moment matrix element $\langle n'l'm' | \mathbf{r} | nlm \rangle$ must be finite. On the basis of Laporte selection rule, this matrix element will be finite only when

$$l' - l = \Delta l = \pm 1 \tag{12.70}$$

To obtain the selection rule on the quantum number m, we may write the matrix element as

$$\langle n'l'm' | \mathbf{r} | nlm \rangle = \hat{i} \langle n'l'm' | x | nlm \rangle + \hat{j} \langle n'l'm' | y | nlm \rangle + \hat{k} \langle n'l'm' | z | nlm \rangle \tag{12.71}$$

If the radiation is plane polarized with the electric field in the z-direction, the z-component of the dipole moment is the only relevant quantity which is given by $\langle n'l'm' | r \cos \theta | nlm \rangle$. The ϕ-part of this integral

$$\int_0^{2\pi} \exp [i(m - m')\phi] \, d\phi = \text{finite}$$

only when

$$m' = m \quad \text{or} \quad \Delta m = 0 \tag{12.72}$$

If the radiation is polarized in the xy-plane, we have to calculate the matrix elements of x and y. However, it is found convenient to evaluate the matrix element of $x \pm iy$ since it is always possible to get the values corresponding to x and y by the relations

$$x = \frac{1}{2}\,[(x + iy) + (x - iy)] \tag{12.73}$$

and

$$y = \frac{1}{2i}\,[(x + iy) - (x - iy)] \tag{12.74}$$

In polar coordinates

$$x \pm iy = r \sin\theta \cos\phi \pm ir \sin\theta \sin\phi = r \sin\theta \exp(\pm i\phi) \tag{12.75}$$

Now the matrix element of $x \pm iy$ is

$$\langle n'l'm' \,|\, r \sin\theta \exp(\pm i\phi) \,|\, nlm\rangle = f(r, \theta) \int_0^{2\pi} \exp[i(m - m' \pm 1)\phi]\, d\phi \tag{12.76}$$

The ϕ-part is nonvanishing only when

$$m' - m = \Delta m = \pm 1 \tag{12.77}$$

Therefore, for arbitrary polarization, the general selection rule is

$$\Delta m = 0, \pm 1 \tag{12.78}$$

The radial part of the integral $\langle n'l'm' \,|\, \mathbf{r} \,|\, nlm\rangle$ is nonvanishing whatever be the values of n', l', n and l. Any value of Δn is therefore allowed when transitions are in conformity with the other selection rules. Thus, the selection rules for hydrogenic atoms are

$$\Delta l = \pm 1, \qquad \Delta m = 0, \pm 1 \tag{12.79}$$

The origin of the selection rule $\Delta l = \pm 1$ may be linked to the spin angular momentum of photon which is equal to 1. When a photon is emitted or absorbed, to conserve the total angular momentum, the orbital angular momentum of the electron in the atom changes by ±1. An absorption or emission of a photon may increase the orbital angular momentum of the electron ($\Delta l = +1$) depending on the orientation of the electron's angular momentum with the angular momentum of the photon. The selection rules we have discussed are valid only for dipole transitions. The magnetic component of the electromagnetic field can interact with the magnetic moment of the electron in the atom and induce *magnetic dipole transitions*. Such transitions are 10^5-times weaker than those allowed under electric dipole transitions. As the selection rules for these transitions are different, transitions which are forbidden under one category may be active in the other. Another type of transitions is the *electric quadrupole transitions* wherein the spatial variation of the electric field interacts with the electric quadrupole moment. The selection rule for such transitions are $\Delta l = 0, \pm 2$. These transitions are 10^8-times weaker than electric dipole transitions.

12.8 RAYLEIGH SCATTERING

In this section we shall consider the polarization produced by an external electromagnetic field in a medium. Consider a system in a state n represented by the wave function Ψ_n^0. If the system is subjected to an alternating electric field of strength $\varepsilon = \varepsilon_0 \cos \omega t$, the perturbed wave function Ψ_n of the system in the presence of the perturbing radiation is given by

$$\Psi_n = \Psi_n^0 + \sum_k C_k^{(1)} \Psi_k^0 \tag{12.80}$$

The dipole moment associated with the state n is then

$$\langle \mu \rangle = \langle \Psi_n | er_A | \Psi_n \rangle \tag{12.81}$$

where er_A is the dipole moment in the direction of polarization. Substituting the value of Ψ_n,

$$\begin{aligned}\langle \mu \rangle &= \left\langle \left(\Psi_n^0 + \sum_k C_k^{(1)} \Psi_k^0 \right) \middle| er_A \middle| \left(\Psi_n^0 + \sum_k C_k^{(1)} \Psi_k^0 \right) \right\rangle \\ &= \langle \Psi_n^0 | er_A | \Psi_n^0 \rangle + \sum_k C_k^{(1)*} \langle \Psi_k^0 | er_A | \Psi_n^0 \rangle \\ &\quad + \sum_k c_k^{(1)\delta} \langle \Psi_n^0 | er_A | \Psi_k^0 \rangle + \sum_k \sum_m C_k^{(1)*} C_m^{(1)} \langle \Psi_k^0 | er_A | \Psi_m^0 \rangle \end{aligned} \tag{12.82}$$

The first term on the right side of Eq. (12.82) is zero since the perturbation er_A is odd which reduces the integrand to an odd function. The last term can be neglected since it corresponds to second order perturbation. Using Eqs. (12.3) and (12.9),

$$\langle \mu \rangle = \sum_k C_k^{(1)*} e^{i\omega_{kn}t} \langle k | er_A | n \rangle + \sum_k C_k^{(1)} e^{-i\omega_{kn}t} \langle n | er_A | k \rangle \tag{12.83}$$

where

$$\omega_{kn} = \frac{(E_k - E_n)}{\hbar}$$

For the electromagnetic radiation, the vector potential $\mathbf{A}(\mathbf{r}, t)$ is given by Eq. (12.32). In the dipole approximation, as $\exp(i\,\mathbf{k.r}) \cong 1$, Eq. (12.32) reduces to

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_0(\omega)\,(e^{i\omega t} + e^{-i\omega t}) \tag{12.84}$$

If the radiation is monochromatic $\mathbf{A}_0(\omega) = \mathbf{A}_0$. Substituting this value of $\mathbf{A}(\mathbf{r}, t)$ in Eq. (12.42),

$$H' = \frac{ie\hbar}{mc}|\mathbf{A}_0|\,\nabla_A\,(e^{i\omega t} + e^{-i\omega t}) \tag{12.85}$$

where ∇_A is the component of ∇ along the direction of $\mathbf{A}_0$ which is the direction of polarization. The matrix element $H'_{kn}(t)$ of the perturbation between the states k and n can be written with the help of Eq. (12.50):

$$H'_{Rn}(t) = -\frac{i\omega_{kn}\mathbf{A}_0}{c}\,\langle k / er_A / n\rangle\,(e^{i\omega t} + e^{-i\omega t}) \tag{12.86}$$

The evaluation of the coefficient $C_k^{(1)}(t)$ is now straightforward. This value of $H'_{kn}(t)$ in Eq. (12.16) gives

$$C_k^{(1)}(t) = -\frac{\omega_{kn}\,\mathbf{A}_0}{c\hbar}\langle k / er_A / n\rangle \int_0^t \left(e^{i(\omega_{kn}+\omega)t'} + e^{i(\omega_{kn}-\omega)t'}\right)dt'$$

$$= \frac{i\omega_{kn}\,\mathbf{A}_0\,\langle k \mid er_A \mid n\rangle}{c\hbar}\left[\frac{e^{i(\omega_{kn}+\omega)t}}{\omega_{kn}+\omega} + \frac{e^{i(\omega_{kn}-\omega)t}}{\omega_{kn}-\omega}\right] + \text{Constant} \tag{12.87}$$

For convenience, the constant in Eq. (12.87) is set to zero since it will contain only $\mathbf{A}_0$, the maximum value of the vector potential. This is not going to add to the polarization. The matrix element $\langle k \mid er_A \mid n \rangle$ can be written in the shortened form μ_{kn}.

We now proceed to evaluate the dipole moment associated with the state n. Since radiation is isotropic, from Eq. (12.52), we have

$$\left|\langle k \mid er_A \mid n \rangle\right|^2 = \frac{1}{3}\left|\mu_{kn}\right|^2 \tag{12.88}$$

Substituting the value of $C_k^{(1)}$ from Eq. (12.87) in Eq. (12.83),

$$\langle\mu\rangle = -\sum_k \frac{i\omega_{kn}\mathbf{A}_0}{3c\hbar}\left|\mu_{kn}\right|^2 e^{i\omega_{kn}t}\left[\frac{e^{-i(\omega_{kn}+\omega)t}}{\omega_{kn}+\omega} + \frac{e^{-i(\omega_{kn}-\omega)t}}{\omega_{kn}-\omega}\right]$$

$$+\sum_k \frac{i\omega_{kn}\mathbf{A}_0}{3c\hbar}\left|\mu_{kn}\right|^2 e^{-i\omega_{kn}t}\left[\frac{e^{i(\omega_{kn}+\omega)t}}{\omega_{kn}+\omega} + \frac{e^{i(\omega_{kn}-\omega)t}}{\omega_{kn}-\omega}\right]$$

$$= \sum_k \frac{i\omega_{kn}\mathbf{A}_0}{3c\hbar}\left|\mu_{kn}\right|^2\left[-\frac{e^{-i\omega t}}{\omega_{kn}+\omega} - \frac{e^{i\omega t}}{\omega_{kn}-\omega} + \frac{e^{i\omega t}}{\omega_{kn}+\omega} + \frac{e^{-i\omega t}}{\omega_{kn}-\omega}\right]$$

$$= \sum_k \frac{i\omega_{kn}\mathbf{A}_0}{3c\hbar} |\mu_{kn}|^2 \left[\frac{e^{i\omega t} - e^{-i\omega t}}{\omega_{kn} + \omega} - \frac{e^{i\omega t} - e^{-i\omega t}}{\omega_{kn} - \omega} \right]$$

$$= -\sum_k \frac{2\omega_{kn}\mathbf{A}_0}{3c\hbar} |\mu_{kn}|^2 \left[\frac{1}{\omega_{kn} + \omega} - \frac{1}{\omega_{kn} - \omega} \right] \sin \omega t \tag{12.89}$$

$$= \sum_k \frac{4\omega_{kn}\mathbf{A}_0\omega}{3c\hbar} |\mu_{kn}|^2 \frac{\sin \omega t}{\omega_{kn}^2 - \omega^2} \tag{12.90}$$

We have selected **A** and ϕ such that $\phi = 0$. Hence, from Eq. (12.28), the electric field ε associated with the electromagnetic wave is given by

$$\varepsilon = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = -\frac{A_0}{c} i\omega (e^{i\omega t} - e^{-i\omega t})$$

$$= \frac{2A_0\omega}{c} \sin \omega t \tag{12.91}$$

Consequently,

$$\langle \mu \rangle = \sum_k \frac{2}{3\hbar} \frac{\omega_{kn} |\mu_{kn}|^2}{\omega_{kn}^2 - \omega^2} \varepsilon \tag{12.92}$$

The dipole moment $\langle \mu \rangle$ varies sinusoidally with the angular frequency ω of the incident electromagnetic radiation. The system will, therefore, radiate light of angular frequency ω which will be in phase with the incident radiation. Hence, it will be coherent and this type of coherent scattering by atomic system is referred to as **Rayleigh scattering**. The polarization of the medium $P = N\langle \mu \rangle$ where N is the number of atoms in unit volume. Since

$$P = \alpha\varepsilon \tag{12.93}$$

where α is the polarizability of the medium,

$$\alpha = \frac{2N}{3\hbar} \sum_k \frac{\omega_{kn} |\mu_{kn}|^2}{\omega_{kn}^2 - \omega^2} \tag{12.94}$$

12.9 RAMAN SCATTERING

The phenomenon of light scattering with a different frequency, called **incoherent scattering**, was first observed by Sir. C.V. Raman in 1928. This phenomenon can also be treated by time dependent perturbation methods. To understand its origin, one has to calculate the dipole moment for the transition from state m to state n when the system is subjected to an electromagnetic radiation of frequency ν. The wave function of the states m and n are

$$\Psi_m = \Psi_m^0 + \sum_l C_l \, \Psi_l^0 \tag{12.95}$$

$$\Psi_n = \Psi_n^0 + \sum_k C_k \Psi_k^0 \tag{12.96}$$

The dipole moment matrix element for the transition is then

$$\left\langle \Psi_m \mid er_A \mid \Psi_n \right\rangle = \left\langle (\Psi_m^0 + \sum_l C_l \Psi_l^0) \right\rangle \Bigg| \, er_A \, \Bigg| \left\langle (\Psi_n^0 + \sum_k C_k \Psi_k^o) \right\rangle$$

$$= \left\langle \Psi_m^0 \mid er_A \mid \Psi_n^0 \right\rangle + \sum_l \left\langle C_l^* \, \Psi_l^0 \mid er_A \mid \Psi_n^0 \right\rangle$$

$$+ \sum_k C_k \left\langle \Psi_m^0 \mid er_A \mid \Psi_k^0 \right\rangle + \sum_l \sum_k C_l^* C_k \left\langle \Psi_l^0 \mid er_A \mid \Psi_k^0 \right\rangle \tag{12.97}$$

where er_A is the dipole moment in the direction of polarization. The last term in Eq. (12.97) is left out since it corresponds to second order perturbation. Using Eqs. (12.3) and (12.9),

$$\left\langle \Psi_m \middle| er_A \middle| \Psi_n \right\rangle = \left\langle m \middle| er_A \middle| n \right\rangle e^{i\omega_{mn}t} + \sum_l C_l^* \left\langle l \middle| er_A \middle| n \right\rangle e^{i\omega_{ln}t}$$

$$+ \sum_k C_k \left\langle m \middle| er_A \middle| k \right\rangle e^{i\omega_{mk}t} \tag{12.98}$$

Substituting the coefficients C_l^* and C_k from Eq. (12.87),

$$\left\langle \Psi_m \middle| er_A \middle| \Psi_n \right\rangle = \mu_{mn} e^{i\omega_{mn}t} - \sum_l \frac{i\omega_{lm} \mathrm{A}_0}{c\hbar} \mu_{lm}^* \mu_{ln} \left[\frac{e^{i(\omega_{ln} - \omega_{lm} - \omega)t}}{\omega_{lm} + \omega} + \frac{e^{i(\omega_{ln} - \omega_{lm} + \omega)t}}{\omega_{lm} - \omega} \right]$$

$$+ \sum_k i\omega_{kn} \mathrm{A}_0 \mu_{kn}^* \mu_{mk} \left[\frac{e^{i(\omega_{kn} + \omega_{mk} + \omega)t}}{\omega_{kn} + \omega} + \frac{e^{i(\omega_{kn} + \omega_{mk} - \omega)t}}{\omega_{kn} - \omega} \right] \tag{12.99}$$

It may be noted that

$$\omega_{ln} - \omega_{lm} = \frac{E_l - E_n}{\hbar} - \frac{E_l - E_m}{\hbar} = \frac{E_m - E_n}{\hbar} = \omega_{mn}$$

$$\omega_{kn} + \omega_{mk} = \frac{E_k - E_n}{\hbar} + \frac{E_m - E_k}{\hbar} = \frac{E_m - E_n}{\hbar} = \omega_{mn}$$

Since the summations over l and k are completely equivalent, we may replace them by a summation over j. Consequently

$$e^{i(\omega_{ln} - \omega_{lm} \mp \omega)t} = e^{i(\omega_{mn} \mp \omega)t}$$

and

$$e^{i(\omega_{kn}+\omega_{mk}\pm\omega)t} = e^{i(\omega_{mn}\pm\omega)t}$$

Equation (12.99) now reduces to

$$\left\langle\Psi_m\left|er_A\right|\Psi_n\right\rangle = \mu_{mn}e^{i\omega_{mn}t} - \sum_j \frac{i\omega_{jm}\mathbf{A}_0}{c\hbar}\mu_{mj}\mu_{jn}\left[\frac{e^{i(\omega_{mn}-\omega)t}}{\omega_{jm}+\omega} + \frac{e^{i(\omega_{mn}+\omega)t}}{\omega_{jm}-\omega}\right]$$

$$+ \sum_j \frac{i\omega_{jn}\mathbf{A}_0}{c\hbar}\mu_{jn}\mu_{mj}\left[\frac{e^{i(\omega_{mn}+\omega)t}}{\omega_{jn}+\omega} + \frac{e^{i(\omega_{mn}-\omega)t}}{\omega_{jn}-\omega}\right] \tag{12.100}$$

Rearranging

$$\left\langle\Psi_m\left|er_A\right|\Psi_n\right\rangle = \mu_{mn}e^{i\omega_{mn}t} + \sum_j \frac{iA_0\mu_{mj}\mu_{jn}}{c\hbar}\left[\frac{\omega_{jn}}{\omega_{jn}-\omega} - \frac{\omega_{jm}}{\omega_{jm}+\omega}\right]e^{i(\omega_{mn}-\omega)t}$$

$$+ \sum_j \frac{i}{c\hbar}A_0\mu_{mj}\mu_{jn}\left[\frac{\omega_{jn}}{\omega_{jn}+\omega} - \frac{\omega_{jm}}{\omega_{jm}-\omega}\right]e^{i(\omega_{mn}+\omega)t} \tag{12.101}$$

The real part of Eq. (12.101) is

$$\left\langle\Psi_m\left|er_A\right|\Psi_n\right\rangle = \mu_{mn}\cos\omega_{mn}t + \sum_j \frac{\mathbf{A}_0}{c\hbar}\mu_{mj}\mu_{jn}\left[\frac{\omega_{jn}}{\omega_{jn}-\omega} - \frac{\omega_{jm}}{\omega_{jm}+\omega}\right]\sin(\omega-\omega_{mn})\,t$$

$$+ \sum_j \frac{A_0}{c\hbar}\mu_{mj}\mu_{jn}\left[\frac{\omega_{jm}}{\omega_{jm}-\omega} - \frac{\omega_{jn}}{\omega_{jn}+\omega}\right]\sin\left(\omega+\omega_{mn}\right)t \tag{12.102}$$

Thus, there are three terms in the expression for dipole moment associated with the transition from state m to state n. The first term corresponds to the usual spontaneous emission. This line will be absent if the matrix element μ_{mn} is zero. One of the additional terms corresponds to a line of angular frequency $(\omega - \omega_{mn})$ and the other to $(\omega + \omega_{mn})$. They are respectively called the **Stokes Raman** and **anti-Stokes Raman** lines. Since the scattered frequencies depend on ω_{mn}, a characteristic frequency of the molecule, a study of such incoherent scattering gives very valuable information about the molecular structure.

For the additional terms to be finite , the matrix elements $\langle m \mid er_A \mid j\rangle$ and $\langle j \mid er_A \mid n\rangle$ must simultaneously be finite. For this to happen, therefore, both m and n should combine with an intermediate state j such that transitions m to j and j to n can take place directly. The selection rule for a transition between two states is $\Delta l = \pm 1$. Hence, for the simultaneous finiteness of both the matrix elements we should have $\Delta l = 0, \pm 2$. The selection rule $\Delta l = 0$ corresponds to scattering of light of incident frequency and $\Delta l = \pm 2$ corresponds to scattering at frequencies $\omega \pm \omega_{mn}$.

WORKED EXAMPLES

EXAMPLE 12.1 A system in an unperturbed state n is suddenly subjected to a constant perturbation $H'(r)$ which exists during time $0 \rightarrow t$. Find the probability for transition from state n to state k and show that it varies simple harmonically with,

$$\text{Angular frequency} = \frac{E_k - E_n}{2\hbar} \quad \text{and} \quad \text{Amplitude} = 4\frac{|H'_{kn}|^2}{(E_k - E_n)^2}$$

Equation (12.16) gives the value of $c_k^{(1)}(t)$. When the perturbation is constant in time, $H'_{kn}(r)$ can be taken outside the integral. Therefore,

$$c_k^{(1)}(t) = \frac{H'_{kn}(r)}{i\hbar}\int_0^t \exp\,(i\omega_{kn}t')dt' = -\frac{H'_{kn}}{\hbar\omega_{kn}}[\exp(i\omega_{kn}t) - 1]$$

$$= -\frac{H'_{kn}}{\hbar\omega_{kn}}\exp\left(i\omega_{kn}\frac{t}{2}\right)\left[\exp\left(i\omega_{kn}\frac{t}{2}\right) - \exp\left(-i\omega_{kn}\frac{t}{2}\right)\right]$$

$$= -\frac{2iH'_{kn}}{\hbar\omega_{kn}}\exp\left(i\omega_{kn}\frac{t}{2}\right)\sin\left(\omega_{kn}\frac{t}{2}\right)$$

or

$$\left|c_k^{(1)}(t)\right|^2 = \frac{4}{\hbar^2}\frac{|H'_{kn}|^2}{\omega_{kn}^2}\sin^2\left(\omega_{kn}\frac{t}{2}\right)$$

which is the probability for transition from state n to state k. From the expression it is obvious that the probability varies simple harmonically with

$$\text{Angular frequency } \frac{\omega_{kn}}{2} = \frac{E_k - E_n}{2\hbar}$$

Then

$$\text{The amplitude of vibration } \frac{4|H'_{kn}|^2}{\hbar^2\omega_{kn}^2} = \frac{4|H'_{kn}|^2}{(E_k - E_n)^2}$$

EXAMPLE 12.2 Evaluate Einstein's A coefficient for the transition from state $|310\rangle$ to state $|200\rangle$ in the hydrogen atom.

From Eq. (12.67),

$$A_{m\rightarrow n} = \frac{16\pi\varepsilon_0\alpha\omega_{mn}^3}{3c^2}\,|\langle m|\,\mathbf{r}\,|n\rangle|^2$$

We have

$$\psi_{200} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2 - \frac{r}{a_0}\right)\exp\,(-r/2a_0)$$

$$\psi_{310} = \frac{4}{27(2\pi)^{1/2} a_0^{5/2}}\, r\left(1 - \frac{r}{6a_0}\right) \exp\,(-r/3a_0)\, \cos\,\theta$$

Substituting ψ_{200} and ψ_{310},

$$\langle 310 \mid z \mid 200 \rangle = \langle 310 \mid r\cos\theta \mid 200 \rangle$$

$$= \frac{1}{54\pi a_0^4} \int_0^{\infty} \left(2r^4 - \frac{8r^5}{6a_0} + \frac{r^6}{6a_0^2}\right) e^{-5r/6a_0}\, dr \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

Using standard integrals (Appendix A),

$$\langle 310 \mid z \mid 200 \rangle = \frac{1}{54\pi a_0^4} \times \frac{144}{5}\left(\frac{6a_0}{5}\right)^5 \times \frac{4\pi}{3} = 1.7695 a_0$$

$$|\langle 310 \mid z \mid 200 \rangle|^2 = 3.13 a_0^2$$

The ϕ part of the integral in $\langle 310 \mid x \mid 200 \rangle$ and $\langle 310 \mid y \mid 200 \rangle$ vanishes (Example 12.3). Hence

$$|\langle 310 \mid r \mid 200 \rangle|^2 = 3.13 a_0^2$$

$$\omega_{32} = 2\pi\nu_{32} = \frac{2\pi(E_3 - E_2)}{h}$$

$$= \frac{2\pi}{h}(3.024 \times 10^{-19}\,\text{J}) = \frac{2\pi \times 3.024 \times 10^{-19}\,\text{J}}{6.626 \times 10^{-34}\ \text{J.s}}$$

$$= 2.87 \times 10^{15}\ \text{s}^{-1}$$

$$A_{3\to 2} = \frac{16\pi\,(8.854 \times 10^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2})\,(2.87 \times 10^{15}\text{s}^{-1})^3\ 3.13\,(0.53 \times 10^{-10}\text{m})^2}{3\,(3 \times 10^8\ \text{m.s}^{-1})^2\ 137}$$

$$= 2.5 \times 10^{-3}\ \text{s}^{-1}$$

EXAMPLE 12.3 Calculate Einstein B coefficient for the $n = 2$, $l = 1$, $m = 0$, $\to$ $n = 1$, $l = 0$, $m = 0$ transition in the hydrogen atom.

Einstein's B coefficient is given by

$$B_{m\to n} = \frac{8\pi^2 \varepsilon_0 \alpha c}{3\hbar} |\langle m \mid \mathbf{r} \mid n \rangle|^2$$

To get the value of $\langle 210 \mid \mathbf{r} \mid 100 \rangle$, we require the values of $\langle 210 \mid x \mid 100 \rangle$, $\langle 210 \mid y \mid 100 \rangle$, $\langle 210 \mid z \mid 100 \rangle$. In spherical polar coordinates $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $z = r\cos\theta$.

$$\psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$$

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

$$\langle 210 \mid x \mid 100\rangle = \text{Constant} \times r\text{-part} \times \theta\text{-part} \times \int_0^{2\pi} \cos\phi \, d\phi = 0$$

$$\langle 210 \mid y \mid 100\rangle = \text{Constant} \times r\text{-part} \times \theta\text{-part} \times \int_0^{2\pi} \sin\phi \, d\phi = 0$$

$$\langle 210 \mid z \mid 100\rangle = \langle 210 \mid r \cos\theta \mid 100\rangle$$

$$= \frac{1}{4\sqrt{2}\pi a_0^4} \int_0^\infty r^4 e^{-3r/2a_0} \, dr \int_0^\pi \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{4\sqrt{2}\pi a_0^4} \frac{4!}{(3/2a_0)^5} \frac{2}{3} 2\pi = 4\sqrt{2} \left(\frac{2}{3}\right)^5 a_0$$

$$|\langle 210 \mid \mathbf{r} \mid 100\rangle|^2 = 32 \left(\frac{2}{3}\right)^{10} a_0^2 = 0.1558 \times 10^{-20} \text{ m}^2$$

$$B = \frac{8\pi^2 (8.854\times10^{-12} \text{C}^2\text{N}^{-1}\text{m}^{-2}) (3 \times 10^8 \text{ms}^{-1}) (0.1558 \times 10^{-20} \text{m}^2)}{3 \times 137 (1.055\times10^{-34} \text{J.s})}$$

$$= 7.56 \times 10^9 \text{ N}^{-1} \text{ m}^2 \text{ s}^{-2}$$

EXAMPLE 12.4 Obtain the selection rule for electric dipole transitions of a linear harmonic oscillator.

Consider a charged particle having a charge e executing simple harmonic motion along the x-axis about a point where an opposite charge is situated. At a given instant, the dipole moment is ex, where x is the displacement from the mean position. Harmonic oscillator wave function is

$$\psi_n(y) = N_n H_n(y) \exp\left(-\frac{y^2}{2}\right), \quad \text{where } y = \left(\frac{m\omega}{\hbar}\right)^{1/2} x$$

and

The dipole matrix element $\langle k|y|n\rangle$ = (Constant) $\int H_k(y)\, y\, H_n(y) \exp(-y^2) dy$
For Hermite polynomials

$$yH_n(y) = nH_{n-1}(y) + \frac{1}{2} H_{n+1}(y)$$

Substituting this value of $yH_n(y)$, we get

$$\langle k|y|n\rangle = (\text{Constant}) \int H_k(y)\ [nH_{n-1}(y) + \frac{1}{2}H_{n+1}(y)]\ \exp\ (-y^2)\,dy$$

In view of the orthogonality relation

$$\int H_k(y)\ H_n(y)\ \exp\ (-y^2)dy = (\text{constant})\ \delta_{kn}$$

$\langle k|y|n\rangle$ is finite only when $k = n - 1$ or $k = n + 1$. That is, the harmonic oscillator selection rule is

$$k - n = \pm 1 \quad \text{or} \quad \Delta n = \pm 1$$

EXAMPLE 12.5 Which of the following transitions are electric dipole allowed?

(i) 1*s* → 2*s* (ii) 1*s* → 2*p* (iii) 2*p* → 3*d* (iv) 3*s* to 5*d*.

(i) 1*s* → 2*s*: The allowed electric dipole transitions are those involving a change in parity. The quantum number $l = 0$ for both 1*s* and 2*s*. Hence both the states have the same parity and the transition is not allowed.

(ii) 1*s* → 2*p*: The quantum number l for 1*s* is zero and for 2*p* is 1. Hence the transition is allowed.

(iii) 2*p* → 3*d*: The l value for 2*p* is 1 and for 3*d* is 2. The transition is allowed.

(iv) 3*s* → 5*d*: The l value for 3*s* is zero and for 5*d* is 2. As both states have same parity, the transition is not allowed.

EXAMPLE 12.6 A hydrogen atom in the 2*p* state is placed in a cavity. Find the temperature of the cavity at which the transition probabilities for stimulated and spontaneous emissions are equal.

The probability for stimulated emission = $B\rho(\nu)$

The probability for spontaneous emission = A

When the two are equal

$$A = B\rho(\nu)$$

$$\rho(\nu) = \frac{A}{B} = \frac{8\pi h\nu_{21}^3}{c^3}$$

The radiation density $\rho(\nu)$ is given by Eq. (12.64). Hence

$$\frac{8\pi h\nu_{21}^3}{c^3}\ \frac{1}{e^{h\nu_{21}/kT} - 1} = \frac{8\pi h\nu_{21}^3}{c^3}$$

$$\frac{1}{e^{h\nu_{21}/kT} - 1} = 1 \quad \text{or} \quad e^{h\nu_{21}/kT} = 2$$

$$T = \frac{h\nu_{21}}{k \ln 2}$$

$$h\nu_{21} = (10.2 \text{ eV})\ (1.6\times10^{-19} \text{ J/eV}) = 16.32 \times 10^{-19} \text{ J}$$

$$T = \frac{16.32 \times 10^{-19}\text{ J}}{(1.38 \times 10^{-23} \text{ J/K})\ 0.693} = 17.1 \times 10^{4}\text{ K}$$

EXAMPLE 12.7 A particle of mass m having charge e, confined to a three dimensional cubical box of side $2a$, is acted on by an electric field:

$$E = E_0 e^{-\alpha t}, \quad t > 0 \quad (\alpha\text{-Constant})$$

in the x direction. Calculate the probability that the charged particle in the ground state at $t = 0$ is excited to the first excited state by the time $t = \infty$.

The energy eigenfunctions and eigenvalues of a particle in a cubical box of side $2a$ is given by (refer Example 5.2)

$$E_{jkl} = \frac{\pi^2 \hbar^2}{8ma^2}(j^2 + k^2 + l^2); \quad j,\ k,\ l = 1,\ 2,\ 3,\ \ldots$$

$$\Psi_{jkl} = \frac{1}{\sqrt{a^3}} \sin\frac{j\pi x}{2a} \sin\frac{k\pi y}{2a} \sin\frac{l\pi z}{2a} = |j\ k\ l\rangle$$

Then the ground state is $|111\rangle$ and the first excited states are $|211\rangle, |121\rangle, |112\rangle$. Since the electric field is along the x-axis, the dipole moment $\mu = ex$ and the perturbation

$$H' = -\mu\cdot E = -eE_0 x\, e^{-\alpha t}$$

The transition probability for a transition from state n to state m is given by

$$P = \left| c_m^{(1)} \right|^2 = \frac{1}{\hbar^2} \left| \int_0^{\infty} H'_{mn} \exp\,(i\omega_{mn} t)\, dt \right|^2$$

where $\omega_{mn} = (E_m - E_n)/\hbar$, $c_m^{(1)}$ is given in Eq. (12.16) and H'_{mn} is the transition moment.

$$H'_{mn} = \langle 111\, | H' |\, 211\rangle = \langle 111\, | -eE_0 x e^{-\alpha t} |\, 211\rangle$$

$$= -eE_0 e^{-\alpha t} \langle 111\, | x |\, 211\rangle$$

$$= \frac{-eE_0 e^{-\alpha t}}{a^3} \int_0^{2a} x \sin\frac{\pi x}{2a} \sin\frac{\pi x}{a}\, dx \int_0^{2a} \sin^2\frac{\pi y}{2a}\, dy \int_0^{2a} \sin^2\frac{\pi z}{2a} dz$$

$$= \frac{-e\ E_0\ e^{-\alpha t}}{a^3}\left(-\frac{32a^2}{9\pi^2} \right).\, a.a = \frac{32aeE_0 e^{-\alpha t}}{9\pi^2}$$

$$\langle 111 \mid H' \mid 121 \rangle = -\frac{eE_0 e^{-\alpha t}}{a^3} \int_0^{2a} x \sin^2 \frac{\pi x}{2a}\, dx \int_0^{2a} \sin \frac{\pi y}{2a} \sin \frac{\pi y}{a}\, dy \int_0^{2a} \sin^2 \frac{\pi z}{2a}\, dz = 0$$

In the same way,

$$\langle 111 \mid H' \mid 112 \rangle = 0$$

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{\pi^2 \hbar^2}{8ma^2} (2^2 + 1^2 + 1^2 - 1^2 - 1^2 - 1^2) = \frac{3\pi^2 \hbar^2}{8ma^2}$$

Consequently,

$$P = \left(\frac{32aeE_0}{9\pi^2 \hbar} \right)^2 \left| \int_0^{\alpha} \exp(-\alpha t + i\omega_{21} t)\, dt \right|^2$$

$$= \left(\frac{32aeE_0}{9\pi^2 \hbar} \right)^2 \frac{1}{\alpha^2 + \omega_{21}^2}$$

REVIEW QUESTIONS

1. Distinguish between stimulated emission and spontaneous emission.
2. Explain Fermi's golden rule.
3. A perturbation $H'(t)$ is on in a system for a time t. State and explain the expression for calculating the probability that a transition has occurred to state k from state n during this time.
4. Obtain the Hamiltonian operator for a charged particle in an electromagnetic field.
5. Explain what is dipole approximation.
6. What is electric dipole transition moment? Explain its importance.
7. Explain the principle of lasers.
8. What are Einstein's A and B coefficients? State the relation between the two.
9. Spontaneous emission far exceeds stimulated emission in the visible region whereas the reverse is the situation in the microwave region. Why?
10. What do you understand by a selection rule? Explain Laporte selection rule.
11. It is easier to obtain laser action at the infrared wavelengths as compared to visible region. Why?

PROBLEMS

1. Calculate the electric dipole transition moment $\langle 2p_z | \mu_z | 2s \rangle$ for the $2s \rightarrow 2p_z$ transition in a hydrogen atom.
2. Calculate Einstein's A coefficient for the $n = 2$, $l = 1$, $m = 0 \longrightarrow n = 1$, $l = 0$, $m = 0$ transition in the hydrogen atom.
3. Prove the following: (i) If the source temperature is 1000 K in the optical region (λ = 5000 Å), the emission is predominantly due to spontaneous transitions. (ii) If the source temperature is 300 K in the microwave region (λ = 1 cm) the emission is predominantly due to stimulated emission. Boltzmann constant is 1.38×10^{-23} J K^{-1}.
4. Obtain Einstein's A coefficient for a one-dimensional harmonic oscillator of angular frequency ω in its nth state.
5. Calculate the rates of stimulated and spontaneous emission for the transition 3p $\rightarrow$ 2s (H_α line) of hydrogen atom, taking the atoms are at a temperature of 1000 K.
6. A harmonic oscillator in the ground state is subjected to a perturbation

$$H' = -x \exp\left(-\frac{t^2}{t_0^2}\right) \quad \text{from } t = 0 \text{ to } t = \infty$$

Calculate the probability for transition from the ground state, given that

$$\int_0^\infty \exp(-\alpha t^2 + i\omega t)\, dt = -i\sqrt{\frac{\pi}{\alpha}} \exp\left(-\frac{\omega^2}{4\alpha}\right)$$

7. The time varying Hamiltonian $H'(t)$ induces transitions between states $|j\rangle$ and $|k\rangle$. Using time dependent perturbation theory, show that the probability for a transition from state $|j\rangle$ to state $|k\rangle$ is the same as the probability for a transition from state $|k\rangle$ to state $|j\rangle$.
8. Find the B coefficient for emission from the $2p \rightarrow 1s$ state of the hydrogen atom. Hence evaluate the probability per unit time for spontaneous emission from $2p$ state to $1s$ state of the hydrogen atom.
9. A quantum mechanical system is initially in the ground state $|0\rangle$. At $t = 0$, a perturbation of the form $H'(t) = H_0 e^{-\alpha t}$, α-constant, is applied. Show that the probability that the system is in state $|1\rangle$ after long time is:

$$P_{10} = \frac{|\langle 0 | H_0 | 1 \rangle|^2}{\hbar^2(\alpha^2 + \omega_{10})^2}, \quad \omega_{10} = \frac{(E_1 - E_0)}{\hbar}$$

Chapter 13

Many Electron Atoms

The information provided by atoms are of considerable importance for the understanding of structures of molecules and their properties. In this chapter we intend to discuss certain basics which are required for understanding structures of many electron atoms. As electrons are indistinguishable, symmetry considerations have to be imposed on the wave function. We shall apply the basic ideas to the energy levels of helium and then to systems containing more than two electrons.

13.1 INDISTINGUISHABLE PARTICLES

Particles that can be substituted for each other with no change in the physical situation are said to be *indistinguishable* (or *identical*). For example, n electrons are indistinguishable. We may be able to specify their positions, but it is not possible to say which electron is at a particular position. Therefore, interchanging the coordinates of any two electrons does not change the Hamiltonian. In other words, the Hamiltonian of the system is symmetric in the coordinates of the particles. For convenience, mathematically this is written as

$$H(1, 2, 3, \ldots, n) = H(2, 1, 3, \ldots, n) \tag{13.1}$$

where each number represents all the coordinates, both position and spin, of one of the particles.

Particle Exchange Operator

Consider a two-particle system. Its energy eigenvalue equation be

$$H(1, 2)\ \psi(1, 2) = E\psi(1, 2)$$

Since labelling does not matter, interchanging 1 and 2, we get

$$H(2, 1)\psi(2, 1) = E\psi(2, 1)$$

In view of Eq. (13.1), this can be written as

$$H(1, 2)\psi(2, 1) = E\psi(2, 1) \tag{13.2}$$

We define a *particle exchange operator* P_{12} such that when it operates on a state, interchanges all the coordinates of particles 1 and 2. Thus,

$$P_{12}\psi(1, 2) = \psi(2, 1) \tag{13.3}$$

Equation (13.2) can now be written as

$$H(1, 2)\ P_{12}\psi\ (1, 2) = EP_{12}\ \psi(1, 2) = P_{12}E\psi(1,2) = P_{12}\,H(1, 2)\psi(1, 2)$$

It follows that

$$H(1, 2)\ P_{12} = P_{12}\ H(1, 2) \quad \text{or} \quad [P_{12}, H(1, 2)] = 0 \tag{13.4}$$

That is, the particle exchange operator is a constant of motion. Since particles are indistinguishable, any operator representing a physical property of the system must be symmetric with respect to particle interchange. Therefore, it follows from Eq. (13.4) that any operator representing physical property must commute with the particle exchange operator and eigenfunctions of physical variables will also be eigenfunctions of the particle exchange operator.

Consider the function $\psi(1, 2)$ which is an eigenfunction of P_{12} with eigenvalue p.

$$P_{12}\psi(1, 2) = p\psi(1, 2)$$

or

$$\psi(2, 1) = p\psi(1, 2) \tag{13.5}$$

Operating both sides by P_{12}, we get

$$\psi(1, 2) = pP_{12}\ \psi(1, 2) = p^2\ \psi(1, 2)$$

Hence

$$p^2 = 1 \quad \text{or} \quad p = \pm 1 \tag{13.6}$$

That is, the eigenvalues of the particle exchange operator is either +1 or –1. It follows from Eq. (13.5) that

$$P_{12}\psi(2, 1) = \pm\psi(1, 2) \tag{13.7}$$

Symmetric and Antisymmetric Wave Functions

A wave function is *symmetric* if the interchange of any pair of particles among its arguments leaves it unchanged. If the interchange of any pair of particles changes the sign of ψ, it is said to be *antisymmetric*. Equation (13.7) then means that any physically acceptable wave function representing two identical particles must be either symmetric or antisymmetric with respect to an interchange of the particles. Generalizing, the principle of indistinguishability requires that the wave function must be either symmetric or antisymmetric with respect to the interchange of any pair of particles.

We shall next prove that the symmetry character of a wave function does not change with time. Let the wave function $\Psi(1, 2, ..., n, t)$ is symmetric at a particular time t. $H\Psi$ is then symmetric since H is symmetric in its arguments. The Schrödinger equation states that

$$i\hbar\frac{\partial}{\partial t}\Psi(1, 2, ..., n, t) = H(1, 2, ..., n)\,\Psi(1, 2, ..., n, t) \tag{13.8}$$

Since $H\Psi$ is symmetric, $\partial\Psi/\partial t$ is also symmetric. Then the wave function at an infinitesimally latter time $t + dt$ given by $\Psi + (\partial\Psi/\partial t)dt$ is also symmetric. This procedure can be continued to cover large time intervals. In similar fashion, if Ψ is antisymmetric at any time, it is always antisymmetric. Thus, a wave function which is symmetric continues to be symmetric and a wave function which is antisymmetric continues to be antisymmetric. In other words, the symmetry character of a wave function does not change with time.

Symmetric and Antisymmetric Functions from Unsymmetrized Functions

We shall discuss now how symmetric and antisymmetric wave functions can be constructed from the unsymmetrized solution of the Schrödinger equation, Eq. (13.8). As the Hamiltonian does not depend on time, the stationary solutions

$$\Psi(1, 2, ..., n, t) = \psi(1, 2, ..., n)\exp\left(-\frac{iEt}{\hbar}\right) \tag{13.9}$$

are possible, where E is the energy eigenvalue. If two particles are interchanged in Eq. (13.8), it remains the same as it simply corresponds to a relabelling of the particles. In this way $n!$ solutions are possible from one solution, each corresponds to one of the $n!$ permutations of the n arguments. All these $n!$ solutions correspond to the same energy. The degeneracy arising due to this interchange of indistinguishable particles is called *exchange degeneracy*. Any linear combination of these solutions is also a solution of the wave equation. The sum of all these functions is a symmetrical unnormalized wave function ψ_s. This is obvious since the interchange of any pair of particles changes any one of the terms in ψ_s into another and the latter into the former. For example, in a two-particle system the $n!$ solutions are $\psi(1, 2)$ and $\psi(2, 1)$. A sum of the two is

$$\psi_s = \psi(1, 2) + \psi(2, 1)$$

An interchange of 1 and 2 changes $\psi(1,2)$ to $\psi(2,1)$ and $\psi(2,1)$ to $\psi(1,2)$. In a three-particle system

$$\psi_s = \psi(1,2,3) + \psi(1,3,2) + \psi(3,2,1) + \psi(2,1,3) + \psi(2,3,1) + \psi(3,1,2)$$

An antisymmetric unnormalized wave function ψ_{as} can be constructed by adding together all the permuted functions obtained from the original solution by an even number of interchanges of pairs of particles and subtracting the sum of all the permuted functions obtained by odd number of interchanges of pairs of particles. Thus, in the two-particle system

$$\psi_{as} = \psi(1, 2) - \psi(2, 1)$$

where, in $\psi(1, 2)$ we have a zero interchange and in $\psi(2, 1)$ a single interchange. In the three-particle system

$$\psi_{as} = [\psi(1, 2, 3) + \psi(2, 3, 1) + \psi(3, 1, 2)] - [\psi(2, 1, 3) + \psi(1, 3, 2) + \psi(3, 2, 1)]$$

13.2 PAULI PRINCIPLE

Consider a system of noninteracting indistinguishable particles. The Hamiltonian of such a system can be written as

$$H(1, 2, ..., n) = H(1) + H(2) + \cdots + H(n) \tag{13.10}$$

The approximate energy eigenfunction will be a simple product of one particle eigenfunctions. If $u_a(1)$, $u_b(2)$, ..., $u_n(n)$ are the n one-particle eigenfunctions, then

$$\psi(1, 2, ..., n) = u_a(1)\, u_b(2), ..., u_n(n) \tag{13.11}$$

and

$$E = E_a + E_b + E_c + \cdots + E_n \tag{13.12}$$

where $u_a(1)$, $u_b(2)$ ... and E_a, E_b, ... satisfy the relations:

$$H(1)\, u_a(1) = E_a u_a(1); \quad H(2)\, u_b(2) = E_b u_b(2), \ ... \tag{13.13}$$

Our assumption that state u_a is occupied by particle 1, u_b by particle 2 and so on is not correct since the particles are indistinguishable. All that we can say is that one particle is in state u_a, a second is in u_b and so on. Thus, for a system consisting of two particles, the possible eigenfunctions are $u_a(1)u_b(2)$ and $u_a(2)u_b(1)$. The symmetric and antisymmetric combinations are:

$$\psi_s = u_a(1)u_b(2) + u_a(2)u_b(1) \tag{13.14}$$

and

$$\psi_{as} = u_a(1)u_b(2) - u_a(2)u_b(1) = \begin{vmatrix} u_a(1) & u_a(2) \\ u_b(1) & u_b(2) \end{vmatrix} \tag{13.15}$$

If both the particles are put in the same state, say u_a, then

$$\psi_s = u_a(1)u_a(2) + u_a(2)u_a(1) = 2\, u_a(1)u_a(2) \tag{13.16}$$

and

$$\psi_{as} = u_a(1)u_a(2) - u_a(2)u_a(1) = 0 \tag{13.17}$$

As discussed, the symmetry or antisymmetry of a state function is an important law of nature and experiments have shown that the particular state of symmetry of a system is related to the spin of the identical particles. Pauli demonstrated that:

(i) Systems of identical particles with half-odd-integer spins (spin $\frac{1}{2}$, $\frac{3}{2}$, ...) are described by antisymmetric wave functions. Such particles obey Fermi–Dirac statistics and are called *fermions*.

(ii) Systems of identical particles with integer spins (spin 0, 1, 2, ...) are described by symmetric wave functions. Such particles obey Bose–Einstein statistics and are called *bosons*.

Equation (13.17) shows that the antisymmetric wave function vanishes when two identical particles have the same set of coordinates. In other words, two identical fermions cannot occupy the same state. This is one form of *Pauli's exclusion principle*. As the spin of electron is 1/2, the Pauli principle is commonly defined as "No two electrons can have the same set of quantum numbers".

Generalising for an n-particle system, the normalized antisymmetric combination can be written as

$$\psi_{\text{as}}(1, 2, \ldots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_a(1) & u_a(2) & \cdots & u_a(n) \\ u_b(1) & u_b(2) & \cdots & u_b(n) \\ \vdots & \vdots & & \vdots \\ u_n(1) & u_n(2) & \cdots & u_n(n) \end{vmatrix} \tag{13.18}$$

The factor $1/\sqrt{n!}$ is the normalization constant and the determinant is called the *Slater determinant*. The function is fully antisymmetric, since the interchange of two electrons is equivalent to interchanging two columns of the determinant, which amounts to multiplying it by –1. To get a zeroth order product function that is an eigenfunction of spin and orbital angular momentum operators, sometimes we may have to take a linear combination of the Slater determinants of a configuration (Example 13.4). Instead of writing the determinant, often the following form is used:

$$\psi_{\text{as}}(1, 2, \ldots, n) = \frac{1}{\sqrt{n!}} \sum_{1}^{n!} (-1)^p \, P u_a(1) \, u_b(2) \ldots u_n(n) \tag{13.19}$$

where P represents the permutation operator and p is the number of interchanges (even or odd) involved in the particular permutation.

13.3 INCLUSION OF SPIN

We have been ignoring so far the spin of the identical particles though the number in $H(1, 2, \ldots)$ includes both position and spin coordinates. It can be included in the formalism by taking the single particle eigenfunction to include both position wave function and spin function. If the Hamiltonian of the system does not contain space-spin interaction terms, the eigenfunctions of a particle including spin can be written as the product of space and spin parts (Eq. 8.57).

$$\psi(\mathbf{r}, m_s) = \phi(\mathbf{r})\chi(m_s) \tag{13.20}$$

The spin function describes only the orientation of the particle's spin. Each space coordinate can take infinite number of values whereas a particle having spin s can have only $2s + 1$ orientations. A convenient set of spin eigenfunctions are column vectors of $(2s + 1)$ rows with zeros in all positions except one. We have already seen (in Section 8.8) the two-spin eigenfunctions of S_Z for a spin-(1/2) system:

$$\chi\left(\frac{1}{2}\right) = \alpha = \begin{pmatrix}1\\0\end{pmatrix}, \quad \chi\left(-\frac{1}{2}\right) = \beta = \begin{pmatrix}0\\1\end{pmatrix} \tag{13.21}$$

The three-spin eigenfunctions of S_z for $s = 1$ are

$$\chi(1) = \begin{pmatrix}1\\0\\0\end{pmatrix}, \quad \chi(0) = \begin{pmatrix}0\\1\\0\end{pmatrix}, \quad \chi(-1) = \begin{pmatrix}0\\0\\1\end{pmatrix} \tag{13.22}$$

For $s = 3/2$, we have

$$\chi\left(\frac{3}{2}\right) = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \quad \chi\left(\frac{1}{2}\right) = \begin{pmatrix}0\\1\\0\\0\end{pmatrix}, \quad \chi\left(-\frac{1}{2}\right) = \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \quad \chi\left(-\frac{3}{2}\right) = \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \tag{13.23}$$

The procedure outlined in Section 13.1 can be followed for the construction of symmetric and antisymmetric many-particle wavefunctions from unsymmetrized functions that include the spin. However, often it is convenient to select the eigenfunctions of S^2 and S_Z, where, $S = S_1 + S_2 + \cdots + S_n$, the total spin of the identical particles, as the unsymmetrized spin functions from which symmetrized functions can be constructed.

Including spin functions, the two types of states can be expressed as follows:

Boson states:

$$\psi_s = \begin{cases} \psi_s(\text{spatial}) & \chi_s(\text{spin}) \\ \psi_{\text{as}}(\text{spatial}) & \chi_{\text{as}}(\text{spin}) \end{cases} \tag{13.24}$$

Fermion states:

$$\psi_{\text{as}} = \begin{cases} \psi_s(\text{spatial}) & \chi_{\text{as}}(\text{spin}) \\ \psi_{\text{as}}(\text{spatial}) & \chi_s(\text{spin}) \end{cases} \tag{13.25}$$

13.4 SPIN FUNCTIONS FOR TWO-ELECTRONS

The discussion on the spin functions presented in the preceding section can be used to construct spin product functions for two-electrons. The spin matrices for an electron are the (2 × 2) matrices (Section 8.7).

$$S_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z = \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (13.26)$$

The normalized eigenfunctions of S_z Eq. (13.21) are eigenfunctions of S^2 too with the eigenvalue $s(s + 1)\hbar^2 = (3/4)\hbar^2$. If we have number of electrons, then the spin product functions can conveniently be written as

$$\alpha(1)\alpha(2)\beta(3)\alpha(4)\beta(5)\ \ldots \quad \text{or simply} \quad \alpha\alpha\beta\alpha\beta\ \ldots$$

It means that electrons 1, 2, 4 are in spin-up states and 3, 5 are in spin-down states.

In a system with two identical electrons, the possible spin product functions are $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$. These are orthonormal since one electron spin functions are orthonormal. Of these, $\alpha\alpha$ and $\beta\beta$ are symmetric and the other two are neither symmetric nor antisymmetric. Symmetric and antisymmetric combinations of $\alpha\beta$ and $\beta\alpha$ can be formed. These are listed in Table 13.1 along with the other functions and the eigenvalues. The first-three are symmetric and together behave like a single particle of spin $s = 1$. The fourth one is antisymmetric and behaves like a particle of spin $s = 0$. These are sometimes called the *triplet* and *singlet states* respectively.

Table 13.1 Two-electron Spin Product Functions with the S^2 and S_z Eigenvalues

*Spin product functions**	*Symmetry character*	*Eigenvalue of* $S_z = S_{1z} + S_{2z}$	*Eigenvalue of* $S^2 = (S_1 + S_2)^2$
$\alpha\alpha$	Symmetric	$\hbar$	$2\hbar^2$
$(\alpha\beta + \beta\alpha)/\sqrt{2}$	Symmetric	0	$2\hbar^2$
$\beta\beta$	Symmetric	$-\hbar$	$2\hbar^2$
$(\alpha\beta - \beta\alpha)/\sqrt{2}$	Antisymmetric	0	0

*$(1/\sqrt{2})$ is the normalization factor.

13.5 SPIN FUNCTIONS FOR THREE-ELECTRONS

A system with three identical electrons can be considered as 1 + 2 electrons. We can then combine the α and β of the single electron ($s = 1/2$) with the triplet two electron functions ($s = 1$) and with the singlet function ($s = 0$). The first one gives two groups of three-electron spin functions corresponding to $s = 3/2$ and $s = 1/2$, resulting in a quartet ($s = 3/2$) and a doublet ($s = 1/2$) group of spin states. The other one gives a group corresponding to $s = 1/2$. These functions are eigenfunctions of S^2 and S_Z, where S is the total spin of three, electrons. The results are listed in Table 13.2.

Table 13.2 Three-electron Spin Product Functions with the S^2 and S_z Eigenvalues

Spin product functions	*Eigenvalue of* $S_z = S_{1z} + S_{2z} + S_{3z}$	*Eigenvalue of* $S^2 = (S_1 + S_2 + S_3)^2$
$\alpha\alpha\alpha$	$(3/2)\hbar$	$(15/4)\hbar^2$
$(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)/\sqrt{3}$	$(1/2)\hbar$	$(15/4)\hbar^2$
$(\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha)/\sqrt{3}$	$(-1/2)\hbar$	$(15/4)\hbar^2$
$\beta\beta\beta$	$(-3/2)\hbar$	$(15/4)\hbar^2$
$(2\beta\alpha\alpha - \alpha\alpha\beta - \alpha\beta\alpha)/\sqrt{6}$	$(1/2)\hbar$	$(3/4)\hbar^2$
$(\beta\alpha\beta + \beta\beta\alpha - 2\alpha\beta\beta)/\sqrt{6}$	$(-1/2)\hbar$	$(3/4)\hbar^2$
$(\alpha\alpha\beta - \alpha\beta\alpha)/\sqrt{2}$	$(1/2)\hbar$	$(3/4)\hbar^2$
$(\beta\alpha\beta - \beta\beta\alpha)/\sqrt{2}$	$(-1/2)\hbar$	$(3/4)\hbar^2$

The first-four states in Table 13.2 are symmetric in the interchange of any pair of particles. The first pair of doublet states is symmetric in the interchange of electrons 2 and 3 and the second is antisymmetric in 2 and 3.

13.6 THE HELIUM ATOM

An example of a system having more than one electron is the helium atom. Its ground state energy was discussed by 'perturbation' (Section 9.4) and 'variation' (Section 10.5) methods without considering the symmetry effects of the spin of the electrons. We shall now illustrate the evaluation of the energy of the ground and first excited states by considering the fact that electrons are identical fermions and therefore the total wave function must be antisymmetric. It is convenient to use the perturbation technique for the evaluation.

All the terms except the last one in the Hamiltonian, Eq. (9.35), can be used as the unperturbed part with the product of hydrogenic wave function ($Z = 2$) as unperturbed eigenfunctions:

$$\psi^0 = \psi_1^0\psi_2^0 = \frac{Z^3}{\pi a_0^3} \exp\left[-\frac{Z(r_1 + r_2)}{a_0}\right] \tag{13.27}$$

The unperturbed energy

$$E^0 = -2Z^2W_H = -8 \times 13.6 \text{ eV} = -108.8 \text{ eV} \tag{13.28}$$

Ground State

The ground state of helium is the $1s^2$ state. As both the electrons are in the ψ_{100} state, $\psi^0 = \psi_{100}(r_1)\psi_{100}(r_2)$. Since this space state is symmetric, the spin state that multiplies it must be antisymmetric so that the total wave function is antisymmetric. Using the antisymmetric spin product function from Table (13.1), the zeroth-order helium wave function for the ground state is

$$\psi^0 = \psi_{100}(r_1)\psi_{100}(r_2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{13.29}$$

As the Hamiltonian does not contain spin-dependent terms, the energy is not affected by the inclusion of spin functions. Therefore, the energy of the ground state will be the same as the one given by Eq. (9.44).

First Excited State

The excited states of helium consist of one electron in the hydrogenic ground state and the other in an excited state. The wave function $\psi(\mathbf{r})$ is then

$$\psi(\mathbf{r}) = \psi_{100}\psi_{nlm} \tag{13.29a}$$

The excitation of both the electrons needs more energy than the ionization energy of the atom. Considering the first excited state, the possible electronic configurations are 1s2s and 1s2p. Except for electron exchange, the first one is nondegenerate and the second one three-fold degenerate since the electron in the p-state has the possibilities $m = 0, \pm 1$. The exchange degeneracy doubles this number. We shall consider here only the 1s2s state.

For applying perturbation method, the electrostatic repulsion between the electrons, e^2/r_{12} except for the factor $4\pi\varepsilon_0$ in the denominator can be treated as perturbation on the rest of the Hamiltonian. Taking exchange degeneracy into account, the two unperturbed states are

$$\psi_{100}(r_1)\psi_{200}(r_2) \quad \text{and} \quad \psi_{100}(r_2)\psi_{200}(r_1)$$

As the spin part of the wavefunction does not contribute to the energy, the perturbation for these two-degenerate states can easily be evaluated as outlined in Section (9.6). The perturbation matrix has the form

$$\begin{pmatrix} J & K \\ K & J \end{pmatrix} \tag{13.30}$$

where J and K are the *Coulomb energy* or *direct energy* and *exchange energy,* respectively. These are given by

$$J = \iint \psi^*_{100}(r_1)\,\psi^*_{200}(r_2)\frac{e^2}{r_{12}}\,\psi_{100}(r_1)\psi_{200}(r_2)\,d\tau_1\,d\tau_2 \tag{13.31}$$

and

$$K = \iint \psi^*_{100}(r_1)\,\psi^*_{200}(r_2)\frac{e^2}{r_{12}}\,\psi_{100}(r_2)\,\psi_{200}(r_1)\,d\tau_1\,d\tau_2 \tag{13.32}$$

Both J and K are always positive. The eigenvalues of the perturbation matrix can be obtained from the solution of the determinant

$$\begin{vmatrix} J - E^{(1)} & K \\ K & J - E^{(1)} \end{vmatrix} = 0 \tag{13.33}$$

where $E^{(1)}$ is the first-order correction to the energy. From Eq. (13.33), we get

$$E^{(1)} = J + K \quad \text{and} \quad E^{(1)} = J - K \tag{13.34}$$

These energies correspond to the normalized eigenfunctions:

$$\psi_+ = \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\,\psi_{200}(r_2) + \psi_{100}(r_2)\,\psi_{200}(r_1)] \tag{13.35}$$

and

$$\psi_- = \frac{1}{\sqrt{2}}[\psi_{100}(r_1)\,\psi_{200}(r_2) - \psi_{100}(r_2)\,\psi_{200}(r_1)] \tag{13.36}$$

respectively. The first of these is symmetric in the interchange of r_1 and r_2 whereas the second is antisymmetric. Combining these wavefunctions with the spin functions for a two-electron system (Section 13.4) and retaining only antisymmetric total wave functions, we get

$$\psi(s) = \frac{\psi_+(\alpha\beta - \beta\alpha)}{\sqrt{2}} \tag{13.37}$$

$$\psi(t) = \psi_-\begin{cases}\alpha\alpha \\ (\alpha\beta+\beta\alpha)/\sqrt{2} \\ \beta\beta\end{cases} \tag{13.38}$$

where $\psi(s)$ and $\psi(t)$ refer to the singlet and triplet states, respectively. The energy of the singlet (E_s) and triplet (E_t) states corrected to first order are

$$E_s = -2Z^2W_H + J + K \tag{13.39}$$

and

$$E_t = -2Z^2W_H + J - K \tag{13.40}$$

A simple interpretation of the Coulomb energy follows, if Eq. (13.31) is written as

$$J = \iint |\psi_{100}(r_1)|^2\,|\psi_{200}(r_2)|^2\,\frac{e^2}{r_{12}}\,d\tau_1\,d\tau_2 \tag{13.41}$$

The quantities $(-e)|\psi_{100}(r_1)|^2\,d\tau_1$ and $(-e)|\psi_{200}(r_2)|^2\,d\tau_2$ represent the charge associated with the volume elements $d\tau_1$ and $d\tau_2$, respectively. Therefore, J is equivalent to the classical electrostatic interaction between two charge distributions. The exchange energy K has no such classical counterpart. It should be considered as a quantum mechanical correction to the Coulomb integral. Figure 13.1 represents the variation of $|\psi_-|^2$ and $|\psi_+|^2$ against $r_1 - r_2$. It follows from the figure that the probability of finding the two electrons in the same infinitesimal region around $r_1 = r_2$ is zero if they are described by ψ_-. However, there is a small increase in the probability, if they are described by ψ_+. That is, the electrons that occupy ψ_- tend to avoid one another whereas they tend to be near one another, if they occupy ψ_+. Therefore, the electron-electron repulsion energy can be expected to be lower for ψ_- than for ψ_+. Consequently, the effect on the Coulomb potential energy will be a reduction from J to $J - K$ for electrons in ψ_- and an increase from J to $J + K$ for electrons in ψ_+.

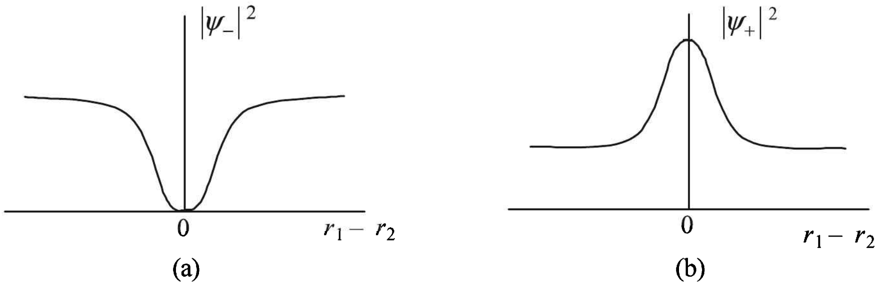


Figure 13.1 The variation of $|\psi_-|^2$ and $|\psi_+|^2$ against $r_1 - r_2$.

The dip in the probability density $|\psi_-|^2$ curve around $r_1 \simeq r_2$ is called a *Fermi hole* and the increase in $|\psi_+|^2$ in the same region is called a *Fermi heap*.

The state described by the singlet is often referred to as *parahelium* and the triplet state as *orthohelium*. The orthohelium has somewhat lower energy than that of parahelium, which has been verified experimentally. The ground state is obviously parahelium whereas the excited states come in both forms.

13.7 CENTRAL FIELD APPROXIMATION

A crude description of the ground state of helium atom assumes both the electrons in 1s hydrogenic orbitals with $Z = 2$. An improved discussion (variation method) assumes the concept that the attraction of an electron to the nucleus is partially screened by the other electron. This approach of a screened nucleus with an effective nuclear charge can be extended to other many electron atoms.

The starting point for the calculation of energy of many electron atoms except the light ones is the *central field approximation*. In this procedure, each electron is assumed to move in a spherically symmetric potential $V(r)$ produced by the nucleus and all the remaining electrons. Two methods are commonly used for obtaining the central potential $V(r)$. They are the Thomas–Fermi method and the self consistent field method of Hartree. The Thomas–Fermi method is simple but less accurate whereas Hartree's method is more cumbersome.

13.8 THOMAS–FERMI MODEL OF THE ATOM

The Thomas–Fermi model of the atom is a statistical one in which the electrons are treated as a gas obeying Fermi–Dirac statistics. In this model, the central potential $V(r)$ is assumed to be slowly varying, slow enough to have number of electrons in an electron wavelength. In other words, many electrons are localized within a volume over which the potential is almost a constant. As electrons are treated as a gas of fermions, one can apply the concept of cells in phase space to the states of individual electrons.

The volume of phase space occupied by electrons which have momenta less than p and are in the volume dV is $(4/3)\pi p^3\, dV$. The number of cells (states) corresponding to this volume is $2(4/3)\pi p^3\, dV/h^3$. The factor of 2 is included to account for the two possible spin states. Assuming that all these states are occupied, the number of electrons per unit volume $n(r)$ whose kinetic energy does not exceed $p^2/(2m)$ is given by

$$n(r) = \frac{8\pi p^3}{3h^3} = \frac{p^3}{3\pi^2\hbar^3} \tag{13.42}$$

For the electrons not to escape from the nucleus, the maximum allowed kinetic energy at any distance r from the nucleus is $-V(r)$. That is,

$$\frac{p^2}{2m} = -V(r) \tag{13.43}$$

From Eqs. (13.42) and (13.43)

$$n(r) = \frac{[-2mV(r)]^{3/2}}{3\pi^2\hbar^3} \tag{13.44}$$

The electrostatic potential $-V(r)/e$ and the charge density $-en(r)$ obey the Poisson equation

$$\frac{1}{e}\nabla^2 V(r) = -4\pi e n(r) \tag{13.45}$$

The potential is spherically symmetric since the nucleus is at the origin and therefore

$$\nabla^2 V = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right) \tag{13.46}$$

With this value of $\nabla^2 V$, Eq. (13.45) reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right) = -4\pi e^2 n(r) \tag{13.47}$$

Substituting the value of $n(r)$ from Eq. (13.44) in Eq. (13.47)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right) = -\frac{4e^2}{3\pi\hbar^3}[-2mV(r)]^{3/2} \tag{13.48}$$

When $r \to 0$ the leading term in the potential is due to the nucleus, so that $V(r) \to -Ze^2/r$. Therefore, it is convenient to introduce the function $\chi(r)$ defined by

$$V(r) = -\frac{Ze^2\chi(r)}{r} \tag{13.49}$$

Substituting this value of $V(r)$ in Eq. (13.48), we have

$$\frac{d^2\chi}{dr^2} = \frac{4e^3(2m)^{3/2}Z^{1/2}}{3\pi\hbar^3}\,\frac{\chi^{3/2}}{r^{1/2}} \tag{13.50}$$

Equation (13.50) can be expressed in a dimensionless form by writing

$$r = bx \tag{13.51}$$

The parameter b is to be defined later. In terms of the new variable, Eq. (13.50) reduces to

$$\frac{d^2\chi}{dx^2} = b^{3/2}\,\frac{4e^3(2m)^{3/2}Z^{1/2}}{3\pi\hbar^3}\,\frac{\chi^{3/2}}{x^{1/2}} \tag{13.52}$$

We select the value of b in such a way that the coefficient of $\chi^{3/2}/x^{1/2}$ is unity. This gives

$$b = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3}\frac{\hbar^2}{me^2}\,\frac{1}{Z^{1/3}} = \frac{0.8853a_0}{Z^{1/3}} \tag{13.53}$$

With this substitution Eq. (13.52) becomes

$$\frac{d^2\chi}{dx^2} = \frac{\chi^{3/2}}{x^{1/2}} \tag{13.54}$$

which is called the *dimensionless Thomas–Fermi equation.* As $V(r) \to -Ze^2/r$ when $r \to 0$, by virtue of Eq. (13.49), $\chi(0) = 1$. As $r \to \infty$ there will not be any net charge inside the sphere of radius r, so that V falls off more rapidly than $1/r$ and $rV(r) \to 0$. Hence $\chi(\infty) = 0$.

Solution of Eq. (13.54) subject to these boundary conditions was first computed by Bush and Caldwell (1931). Knowledge of $\chi(x)$ allows the determination of charge distribution in the atom and the r-dependence of the potential $V(r)$ (Eq. 13.49). As it is a statistical model, one can expect better results as Z increases.

13.9 HARTREE EQUATION

Consider an atom with Z electrons. Its Hamiltonian is

$$H = \sum_{i=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\right] + \frac{1}{2}\sum_{i,j\neq i}\frac{e^2}{r_{ij}} \tag{13.55}$$

where $r_{ij} = |\,r_j - r_i\,|$. The second term on the right represents the interaction between the electrons. Writing

$$H_i = -\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i) \quad \text{and} \quad V_{ij} = \frac{e^2}{r_{ij}} \tag{13.56}$$

We get

$$H = \sum_i H_i + \frac{1}{2} \sum_{i,j \neq i} V_{ij} \tag{13.57}$$

The Schrödinger equation to be solved is

$$H\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) = E\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) \tag{13.58}$$

which is a partial differential equation in 3Z-dimensions.

In the variation method, the procedure followed is to assume a trial wave function with variable parameters, calculate $\langle H \rangle$ and then minimize $\langle H \rangle$ with respect to the parameters. However, Hartree followed a different procedure in which the variational method itself is used to select the trial wave function. To apply the variational procedure, we shall assume that the trial function is of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) = u_1(\mathbf{r}_1)\, u_2(\mathbf{r}_2), ..., u_Z(\mathbf{r}_Z) \tag{13.59}$$

where $u_1(\mathbf{r}_1)$, $u_2(\mathbf{r}_2)$, ... are normalized single-particle functions. That is

$$\int u_i^* u_i \, d\tau_i = 1, \qquad i = 1, 2, ..., Z \tag{13.60}$$

The single particle functions can be obtained so that the trial function minimizes $\langle H \rangle$. With the trial function in Eq. (13.59), $\langle H \rangle$ can be written as

$$\langle H \rangle = \int u_1^* u_2^* ... u_Z^* \left(\sum_i H_i + \frac{1}{2} \sum_{i,j \neq i} V_{ij} \right) u_1 u_2, ..., u_Z \, d\tau \tag{13.61}$$

where $d\tau = d\tau_1 d\tau_2 ... d\tau_Z$. As H_i operates only on the coordinates of ith electron and V_{ij} operates on the coordinates of electrons i and j, Eq. (13.61) reduces to

$$\langle H \rangle = \sum_i \int u_i^* \left(H_i + \frac{1}{2} \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right) u_i d\tau_i \tag{13.62}$$

The next step is the minimization of $\langle H \rangle$ with respect to u_1^*, u_2^*, ... one at a time. Minimization with respect to u_i^* gives

$$\delta \langle H \rangle = \sum_i \int \delta u_i^* \left(H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right) u_i \, d\tau_i = 0 \tag{13.63}$$

where the variation δu_i^* satisfies the equation

$$\int \delta u_i^* u_i \, d\tau_i = 0, \qquad i = 1, 2, 3, ..., Z \tag{13.64}$$

Neglecting the factor $\frac{1}{2}$ in Eq. (13.63) amounts to double counting of the repulsive electronic term. This will be taken care of in the end. Solution of

Eq. (13.63) is subject to these Z-equations of constraints. To use the method of Lagrangian multipliers, multiply each of the equations (13.64) by a multiplier ε_i and subtract the sum from Eq. (13.63). We have

$$\sum_i \int \delta u_i^* \left(H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j \, d\tau_j - \varepsilon_i \right) u_i \, d\tau_i = 0 \tag{13.65}$$

As the variations δu_i^* are independent, the coefficient of each δu_i^* in Eq. (13.65) vanishes. This gives

$$\left(H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j \, d\tau_j \right) u_i = \varepsilon_i u_i \tag{13.66}$$

Substituting the values of H_i and V_{ij} in Eq. (13.66), we get

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i} \int \frac{1}{r_{ij}} |u_j(\mathbf{r}_j)|^2 \, d\tau_j \right] u_i(\mathbf{r}_i) = \varepsilon_i u_i(\mathbf{r}_i) \tag{13.67}$$

This integro-differential equation is called the *Hartree equation*. It is an eigenvalue equation for electron i located at $\mathbf{r}_i$, moving in a potential

$$V_i(\mathbf{r}_i) = -\frac{Ze^2}{r_i} + e^2 \sum_{j \neq i} \int \frac{1}{r_{ij}} |u_j(\mathbf{r}_j)|^2 \, d\tau_j \tag{13.68}$$

The first term is the attractive Coulomb potential due to the nuclear charge Ze and the second term is a repulsive contribution due to the charge density of all the other electrons. The charge density associated with the jth electron $e|u_j(\mathbf{r}_j)|^2$ will be known only when we solve Eq. (13.67). Therefore, one has to go in for an iterative procedure assuming an approximate form for the u_i's. The insertion of the refined wave function back into the equation leads to a better one. This process is continued until the wave functions are *self consistent* to a high degree of accuracy. The potential thus obtained is called the *self-consistent potential.*

The total energy E is then obtained by substituting the wave function from the solution of the Hartree equations into Eq. (13.58). This energy is not equal to the sum of all single-particle energies obtained by the solution of the Hartree equation which amounts to double counting the repulsive interelectronic interaction. The expression for the energy E is then

$$E = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i,j \neq i} \int u_i^* \frac{1}{r_{ij}} |u_j(\mathbf{r}_j)|^2 u_i \, d\tau_i \, d\tau_j \tag{13.69}$$

The trial wave function in Eq. (13.59) does not take Pauli's exclusion principle into account. For better results one has to use an antisymmetrized wave function in place of the simple product function in Eq. (13.59).

13.10 HARTREE–FOCK EQUATION

In the Hartree method, the many electron wave function is simply a product of one-electron wave functions. This is not acceptable when the particles are indistinguishable. The Hartree–Fock method incorporates the effect of exchange symmetry into the formalism. In his theory, Fock used an antisymmetrized trial wave function for the variational calculations. The wave function including the spin is assumed to take the form of a Slater determinant of one-electron wave functions:

$$\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_Z) = \frac{1}{\sqrt{Z!}}\begin{vmatrix} u_1(\mathbf{x}_1) & u_1(\mathbf{x}_2) & \cdots & u_1(\mathbf{x}_Z) \\ u_2(\mathbf{x}_1) & u_2(\mathbf{x}_2) & \cdots & u_2(\mathbf{x}_Z) \\ \vdots & \vdots & & \vdots \\ u_Z(\mathbf{x}_1) & u_Z(\mathbf{x}_2) & \cdots & u_Z(\mathbf{x}_Z) \end{vmatrix} \qquad (13.70)$$

where $\mathbf{x}_1$, $\mathbf{x}_2$, $\cdots$ represent the coordinates, both space and spin.

The Hamiltonian of a system having Z interacting electrons is given by Eq. (13.55). It can be written in the form

$$H = \sum_i H_i(\mathbf{r}_i) + \frac{1}{2}\sum_{i,j\neq i} v(\mathbf{r}_i, \mathbf{r}_j) \qquad (13.71)$$

The Schrödinger equation to be solved is

$$H\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_Z) = E\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_Z) \qquad (13.72)$$

As this equation is not separable, we can express the eigenfunctions of H as a linear combination of determinantal eigenfunctions of $\sum_i H_i(\mathbf{r}_i)$. As it is convenient to work with a single determinant as the ground state wave function of the interacting system one has to rewrite the Hamiltonian as

$$H = \sum_i [H_i(\mathbf{r}_i) + F(\mathbf{r}_i)] + \left[\frac{1}{2}\sum_{i,j\neq i} v(\mathbf{r}_i, \mathbf{r}_j) - \sum_i F(\mathbf{r}_i)\right] \qquad (13.73)$$

The second term on the right is the modified interaction term.

We can now take the modified single Zth order determinant of one-electron functions whose orbital factors are eigenfunctions of the equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + F(\mathbf{r})\right]\phi(\mathbf{r}) = \varepsilon\phi(\mathbf{r}) \qquad (13.74)$$

and the operator F has to be selected so as to minimize the total energy. Use of a single determinant with these functions as the ground state wavefunction is known as the *Hartree–Fock method*. The choice of F in accordance with the variational principle is given by

$$\langle n|F|m\rangle = \sum_i \left[\langle in|v|im\rangle - \langle ni|v|im\rangle\right] \qquad (13.75)$$

It may be noted here that the Hamiltonian is not affected by this choice of F, however, the one-electron functions u_i change.

Next, let us proceed to get the explicit form of the Hartree–Fock equation (13.74). Writing Eq. (13.75) in the integral form, we have

$$\begin{aligned}\int u_n^*(\mathbf{x})F(\mathbf{r})u_m(\mathbf{x})d\mathbf{x} &= \sum_i \iint u_i^*(\mathbf{x}_1)u_n^*(\mathbf{x}_2)\, v(\mathbf{r}_1,\mathbf{r}_2)u_i(\mathbf{x}_1)u_m(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \\ &\quad - \sum_i \iint u_n^*(\mathbf{x}_1)u_i^*(\mathbf{x}_2)v(\mathbf{r}_1,\mathbf{r}_2)u_i(\mathbf{x}_1)u_m(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \\ &= \sum_i \int u_n^*(\mathbf{x}_2)\left[\int |u_i(\mathbf{x}_1)|^2\, v\,(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{x}_1\right]u_m(\mathbf{x}_2)d\mathbf{x}_2 \\ &\quad - \sum_i \int u_n^*(\mathbf{x}_2)\left[\int u_i^*(\mathbf{x}_1)u_m(\mathbf{x}_1)v(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{x}_1\right]u_i(\mathbf{x}_2)d\mathbf{x}_2\end{aligned} \tag{13.76}$$

we have interchanged $\mathbf{x}_1$ and $\mathbf{x}_2$ in the second integral which is possible as the value of the definite integral does not depend on the variable of integration. Under the same rule, replacing the variable $\mathbf{x}_2$ by $\mathbf{x}$, we get

$$\begin{aligned}\int u_n^*(\mathbf{x})\; F(\mathbf{r})\; u_m(\mathbf{x})\; d\mathbf{x} &= \int u_n^*(\mathbf{x}) \sum_i \left[\int |u_i(\mathbf{x}_1)|^2\, v(\mathbf{r}_1,\mathbf{r}_2)u_m(\mathbf{x})d\mathbf{x}_1\right. \\ &\quad \left. - \int u_i^*(\mathbf{x}_1)u_m(\mathbf{x}_1)v(\mathbf{r}_1,\mathbf{r}_2)u_i(\mathbf{x})d\mathbf{x}_1\right]d\mathbf{x}\end{aligned} \tag{13.77}$$

From a comparison of the two sides, it follows that

$$\begin{aligned}F(\mathbf{r})\; u_m(\mathbf{r}) &= \sum_i \int |u_i(\mathbf{x}_1)|^2\, v\,(\mathbf{r}_1,\, \mathbf{r})u_m(\mathbf{x})d\mathbf{x}_1 \\ &\quad - \sum_i \int u_i^*(\mathbf{x}_1)\; u_m(\mathbf{x}_1)\; v\,(\mathbf{r}_1,\, \mathbf{r})u_i(\mathbf{x})\; d\mathbf{x}_1\end{aligned} \tag{13.78}$$

As $u(\mathbf{x})$ is the product of orbital part $\phi\,(r)$ and a spin function, the integral implies a sum over the two values of the spin variable. Carrying out the sum over the spin variable, we have

$$\begin{aligned}F(\mathbf{r})\phi_m(\mathbf{r}) &= \sum_i \int |\phi_i(\mathbf{r}_1)|^2\; v\,(\mathbf{r}_1,\mathbf{r})\phi_m(\mathbf{r})\; d\mathbf{r}_1 \\ &\quad - \sum_{\substack{i \\ \text{spin}\, i\, =\, \text{spin}\, m}} \int \phi_i^*(\mathbf{r}_1)\psi_m(\mathbf{r}_1)v(\mathbf{r}_1,\mathbf{r})\phi_i(\mathbf{r})\; d\mathbf{r}_1\end{aligned} \tag{13.79}$$

The second term on the right vanishes if u_i and u_m have different spin factors. In nonferromagnetic systems, the numbers of electrons with opposite spin are equal and therefore Eq. (13.79) reduces to

$$F(\mathbf{r})\ \phi_m(\mathbf{r}) = 2 \sum_{i=1}^{Z/2} \int |\phi_i(\mathbf{r}_1)|^2\, v\, (\mathbf{r}_1, \mathbf{r})\ \phi_m(\mathbf{r})\ d\mathbf{r}_1$$

$$- \sum_{i=1}^{Z/2} \int \phi_i^*(\mathbf{r}_1)\ \psi_m(\mathbf{r}_1)\ v\ (\mathbf{r}_1, \mathbf{r})\ \phi_i(\mathbf{r})\ d\mathbf{r}_1 \qquad (13.80)$$

The Hartree–Fock equation (Eq. 13.74) for the function $\phi_m(\mathbf{r})$ now becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right] \phi_m(\mathbf{r}) + 2\sum_{i=1}^{Z/2} \int |\phi_i(\mathbf{r}_1)|^2\, v\ (\mathbf{r}_1, \mathbf{r})\ d\mathbf{r}_1 \phi_m(\mathbf{r})$$

$$- \sum_{i=1}^{Z/2} \phi_i(\mathbf{r}) \int \phi_i^*(\mathbf{r}_1)\ \phi_m(\mathbf{r}_1)\ v(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 = \varepsilon_m\ \phi_m(\mathbf{r}) \qquad (13.81)$$

There will be one such equation for each of the $Z/2$ different functions $\phi_m(\mathbf{r})$ appearing in the ground state determinant. The operator $F(\mathbf{r})$ depends on all these functions. Hence the set of $Z/2$ simultaneous equations have to be solved by an interactive procedure until a sufficient degree of self consistency is reached. The third term on the left side of Eq. (13.81) is called the *exchange term*. Without this term the equation would reduce to Hartree equation in which the ground state wave function consists of a simple product of one-electron functions.

WORKED EXAMPLES

EXAMPLE 13.1 N noninteracting bosons are in an infinite potential well defined by $V(x) = 0$ for $0 < x < a$; $V(x) = \infty$ for $x < 0$ and for $x > a$. Find the ground state energy of the system. What would be the ground state energy if the particles are fermions?

The energy eigenvalues of a particle in the infinite square well (Problem 4.1) is given by

$$E_n = \frac{\pi^2\hbar^2 n^2}{2ma^2}; \qquad n = 1, 2, \ldots$$

As the particles are bosons, all the N particles will be in the $n = 1$ state. Hence the total energy

$$E = \frac{N\pi^2\hbar^2}{2ma^2}$$

If the particles are fermions, a state can have only two of them, one spin-up and the other spin-down. Therefore, the lowest $N/2$ states will be filled. The total ground state energy will be

$$E = 2\frac{\pi^2\hbar^2}{2ma^2}\left[1^2 + 2^2 + \cdots + \left(\frac{N}{2}\right)^2\right]$$

$$= \frac{\pi^2\hbar^2}{ma^2}\frac{1}{6}\left[\frac{N}{2}\left(\frac{N}{2}+1\right)\left(2\frac{N}{2}+1\right)\right]$$

$$= \frac{\pi^2\hbar^2}{24ma^2}N(N + 1)(N + 2)$$

If N is very large $\sum_{n=1}^{N/2} n^2 \simeq \int_1^{N/2} n^2\, dn = \frac{1}{3}\left(\frac{N}{2}\right)^3$

Then the total energy

$$E = \frac{\pi^2\hbar^2}{ma^2}\frac{1}{3}\left(\frac{N}{2}\right)^3 = \frac{\pi^2\hbar^2 N^3}{24ma^2}$$

EXAMPLE 13.2 Consider two noninteracting electrons described by the Hamiltonian

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(x_1) + V(x_2)$$

where $V(x) = 0$ for $0 < x < a$; $V(x) = \infty$ for $x < 0$ and for $x > a$. If both the electrons are in the same spin state, what is the lowest energy and eigenfunction of the two electron system?

As the electrons are noninteracting, the wavefunction of the system $\psi(1, 2)$ can be written as

$$\psi(1, 2) = \psi(1)\psi(2)$$

With this wave function, the Schrödinger equation for the system breaks into two one-particle equations:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(1)}{dx_1^2} + V(x_1)\psi(1) = E^{(1)}\psi(1)$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(2)}{dx_2^2} + V(x_2)\psi(2) = E^{(2)}\psi(2)$$

where $E^{(1)} + E^{(2)} = E$, the total energy of the system. The energy eigenvalues and eigenfunctions for a single particle in such a potential (Problem 4.1) are

$$E_{n_1}^{(1)} = \frac{\pi^2\hbar^2 n_1^2}{2ma^2}, \qquad \psi_{n_1}(1) = \sqrt{\frac{2}{a}}\sin\frac{n_1\pi x_1}{a}, \qquad n_1 = 1, 2, \ldots$$

and

$$E_{n_2}^{(2)} = \frac{\pi^2\hbar^2 n_2^2}{2ma^2}, \quad \psi_{n_2}(2) = \sqrt{\frac{2}{a}} \sin \frac{n_2\pi x_2}{a}, \quad n_2 = 1, 2, \ldots$$

As both the electrons are in the same spin state, the possible combination of spin functions are $\alpha\alpha$ or $\beta\beta$, both symmetric. Hence the space function must be antisymmetric. As the electrons are either spin-up ($\alpha\alpha$) or spin-down ($\beta\beta$), $n_1 = n_2 = 1$ is not possible. Both $\alpha\alpha$ and $\beta\beta$ are symmetric. The next possibility is $n_1 = 1$, $n_2 = 2$. Now,

$$\text{The energy of the state } (n_1 = 1,\ n_2 = 2) = \frac{\pi^2\hbar^2}{2ma^2} + \frac{4\pi^2\hbar^2}{2ma^2} = \frac{5\pi^2\hbar^2}{2ma^2}$$

and

$$\text{The energy eigenfunction } \psi(1, 2) = \frac{2}{a} \sin\frac{\pi x_1}{a} \sin \frac{2\pi x_2}{a}$$

When the two electrons are interchanged, the eigenfunction

$$\psi(2, 1) = \frac{2}{a} \sin\frac{\pi x_2}{a} \sin \frac{2\pi x_1}{a}$$

Since both the states have the same energy, the space wave function of the system is a linear combination of the two functions. The antisymmetric combination is $\psi(1, 2) - \psi(2, 1)$. To get the complete energy eigenfunction, this space part has to be multiplied by $\alpha\alpha$ or $\beta\beta$.

Hence,

$$\text{The energy eigenvalue } E = \frac{5\pi^2\hbar^2}{2ma^2}$$

EXAMPLE 13.3 Show that for a system of two identical particles, of spin I, the ratio of the number of states which are symmetric under spin interchange to the number of states which are antisymmetric under spin interchange is $(I + 1)/I$.

We shall denote the m_I values of the two spins by m_I and m'_I. The spin states of the combined system are given by $|m_I(1)\rangle\,|m'_I(2)\rangle$. The products $|m_I(1)\rangle\,|m_I(2)\rangle$ corresponding to $m_I = m'_I$ will be symmetric and we will have $(2I + 1)$ such product functions. The number of product functions corresponding to $m_I \neq m'_I$ will be $2I(2I + 1)$. With these, we have to form combinations of the type:

$$|m_I(1)\rangle\,|m'_I(2)\rangle \pm |m'_I(1)\rangle\,|m_I(2)\rangle$$

where plus sign gives symmetric and minus sign gives antisymmetric functions. As we take two product functions to form such a combination, we will have $\left(\frac{1}{2}\right)2I(2I + 1)$ symmetric and $\left(\frac{1}{2}\right)2I(2I + 1)$ antisymmetric combinations.

$$\begin{aligned}\text{The total number of symmetric combinations} &= (2I + 1) + \frac{1}{2}2I(2I + 1)\\ &= (I + 1)\,(2I + 1)\end{aligned}$$

Hence

$$\frac{\text{Number of symmetric combinations}}{\text{Number of antisymmetric combinations}} = \frac{(I + 1)(2I + 1)}{I(2I + 1)} = \frac{I + 1}{I}$$

EXAMPLE 13.4 Give the zeroth-order wave functions for helium atom (i) in the ground state ($1s^2$) (ii) in the excited state 1s2s. Also, express them in the form of Slater determinants.

(i) From Eq. (13.29), the zeroth-order wave function for helium atom in the $1s^2$ state is

$$1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

In terms of Slater determinant, this takes the form

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\,\alpha(1) & 1s(2)\alpha(2) \\ 1s(1)\,\beta(1) & 1s(2)\beta(2) \end{vmatrix}$$

(ii) From Eqs. (13.37) and (13.38), the zeroth-order wave functions in the 1s2s state are

$$\psi_1 = \frac{1}{\sqrt{2}}\,[1s(1)2s(2) + 1s(2)2s(1)]\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\frac{1}{\sqrt{2}}$$

$$\psi_2 = \frac{1}{\sqrt{2}}\,[1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2)$$

$$\psi_3 = \frac{1}{\sqrt{2}}\,[1s(1)2s(2) - 1s(2)2s(1)]\,[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\frac{1}{\sqrt{2}}$$

$$\psi_4 = \frac{1}{\sqrt{2}}\,[1s(1)2s(2) - 1s(2)2s(1)]\,\beta(1)\beta(2)$$

For 1s2s configuration, we have the following spin-orbital combinations: $1s\alpha$, $1s\beta$, $2s\alpha$ and $2s\beta$ leading to four Slater determinants (the normalization factor $1/\sqrt{2}$ not included.

$$D_1 = \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) \end{vmatrix}$$

$$D_2 = \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 2s(1)\beta(1) & 2s(2)\beta(2) \end{vmatrix}$$

$$D_3 = \begin{vmatrix} 1s(1)\beta(1) & 1s(2)\beta(2) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) \end{vmatrix}$$

$$D_4 = \begin{vmatrix} 1s(1)\beta(1) & 1s(2)\beta(2) \\ 2s(1)\beta(1) & 2s(2)\beta(2) \end{vmatrix}$$

A comparison of the above wave functions with these determinants shows that ψ_1, ψ_2, ψ_3, ψ_4 are equal to the determinants $(D_2 - D_3)/2$, $D_1/\sqrt{2}$, $(D_2 + D_3)/2$ and $D_4/\sqrt{2}$, respectively.

EXAMPLE 13.5 Prove that it is impossible to construct a completely antisymmetric spin function for three electrons.

Let a, b, c, stand for three functions and 1, 2, 3 for three identical particles. In the function $a(1)\, b(2)\, c(3)$, particle 1 is in a, particle 2 is in b and particle 3 in c. Let us proceed without specifying that these functions correspond to space or spin functions. The third-order Slater determinant for the case is

$$\frac{1}{\sqrt{6}}\begin{vmatrix} a(1) & a(2) & a(3) \\ b(1) & b(2) & b(3) \\ c(1) & c(2) & c(3) \end{vmatrix}$$

This is completely antisymmetrized as interchange of two spins amounts to interchanging two columns of the determinant, which multiplies it by –1. Let us now specify the functions a, b, c as that due to electron spins. Let $a = \alpha$, $b = \beta$ and $c = \beta$ in the above determinant. The determinant reduces to

$$\frac{1}{\sqrt{6}}\begin{vmatrix} \alpha(1) & \alpha(2) & \alpha(3) \\ \beta(1) & \beta(2) & \beta(3) \\ \beta(1) & \beta(2) & \beta(3) \end{vmatrix}$$

As the second and third rows of the determinant are identical, its value is zero. In whatever way we select a, b, c two rows of the determinant will be equal. Therefore, we cannot construct a completely antisymmetric three-electron spin functions.

EXAMPLE 13.6 Find an expression for the electron density $n(r)$ in the Thomas–Fermi model in terms of the Thomas–Fermi function $\chi(x)$.

From Eq. (13.44),

$$\text{The electron density } n(r) = \frac{[-2mV(r)]^{3/2}}{3\pi^2\hbar^3}$$

Substituting the value of $V(r)$ from Eq. (13.49), we get

$$n(r) = \frac{\left(2mZe^2\chi/r\right)^{3/2}}{3\pi^2\hbar^3}$$

Replacement of r with the help of Eqs. (13.51) gives

$$n(r) = \frac{\left(2mZe^2\right)^{3/2}}{3\pi^2\hbar^3}\left(\frac{\chi}{bx}\right)^{3/2}$$

Substitution of the value of b from Eq. (13.53) gives

$$n(r) = \frac{32Z^2}{9\pi^3 a_0^3}\left(\frac{\chi}{x}\right)^{3/2}$$

where a_0 is the Bohr radius. This is the required result.

EXAMPLE 13.7 Two particles of mass m are in a three dimensional box of sides a, b, c ($a > b > c$). The potential representing the interaction between the particles is $V = A\delta(\mathbf{r}_1 - \mathbf{r}_2)$, where δ is the Dirac delta function. Using first order perturbation theory, calculate the lowest possible energy of the system if they are: (i) spin zero identical particles (ii) spin 1/2 identical particles with spins parallel. Given that

$$\int_0^a \sin^4 \frac{\pi x}{a} dx = \frac{3}{8} a$$

The energy eigenvalues and eigenfunctions of a particle in a rectangular box of side a, b, c are given by (Example 5.1)

$$E = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right); \quad n_x,\ n_y,\ n_z = 1, 2, 3, \ldots$$

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

(i) For a system of spin zero particles, the total wave function must be symmetric for interchange of any pair of particles. Hence, for the two particle system, the unperturbed wave function can be taken as the product of two single particle wave function which is symmetric. That is:

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\, \psi(\mathbf{r}_2)$$

$$= \frac{8}{abc} \sin\frac{\pi x_1}{a} \sin\frac{\pi y_1}{b} \sin\frac{\pi z_1}{c} \sin\frac{\pi x_2}{a} \sin\frac{\pi y_2}{b} \sin\frac{\pi z_2}{c}$$

The unperturbed energy

$$E_0 = \frac{\pi^2 \hbar^2}{m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)$$

The Hamiltonian representing the interaction between the two particles

$$H' = A\delta(\mathbf{r}_1 - \mathbf{r}_2) \qquad (A\text{-Constant})$$

can be taken as the perturbation. The first order correction to the energy

$$E_s^{(1)} = \int \psi_s^*(\mathbf{r}_1, \mathbf{r}_2)\, A\delta\, (\mathbf{r}_1 - \mathbf{r}_2) \psi_s(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2$$

$$= A \int |\, \psi_s(\mathbf{r}_1, \mathbf{r}_1)\, |^2 d\tau_1$$

$$= A\left(\frac{8}{abc}\right)^2 \int_0^a \int_0^b \int_0^c \left(\sin\frac{\pi x_1}{a} \sin\frac{\pi y_1}{b} \sin\frac{\pi z_1}{c}\right)^4 dx_1 dy_1 dz_1$$

$$= A\left(\frac{8}{abc}\right)^2 \int_0^a \sin^4\frac{\pi x_1}{a}\,dx_1 \int_0^b \sin^4\frac{\pi y_1}{b}\,dy_1 \int_0^c \sin^4\frac{\pi z_1}{c}\,dz_1$$

$$= A\left(\frac{8}{abc}\right)^2 \frac{3a}{8}\cdot\frac{3b}{8}\cdot\frac{3c}{8} = \frac{27A}{8abc}$$

Consequently, the energy corrected to first order

$$E_s = \frac{\pi^2\hbar^2}{m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)+\frac{27A}{8abc}$$

(ii) For a system of spin 1/2 particles, the total wave function must be antisymmetric for interchange of any pair of particles. As the spins are parallel, the spin wave function is symmetric and, therefore, the space part must be antisymmetric. One of the particles will be in the ground state ψ_{111} and the other will be in the first excited state ψ_{211} since $1/a^2 < 1/b^2 < 1/c^2$. The antisymmetric combination is then given by

$$\psi_a(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{111}(\mathbf{r}_1)\psi_{211}(\mathbf{r}_2) - \psi_{111}(\mathbf{r}_2)\psi_{211}(\mathbf{r}_1)\right]$$

The unperturbed energy

$$E_a = \frac{\pi^2\hbar^2}{2m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}+\frac{4}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)$$

$$= \frac{\pi^2\hbar^2}{2m}\left(\frac{5}{a^2}+\frac{2}{b^2}+\frac{2}{c^2}\right) = \frac{\pi^2\hbar^2}{m}\left(\frac{5}{2a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)$$

The first order correction to the energy is:

$$E_a^{(1)} = \int \psi_a^*(\mathbf{r}_1,\mathbf{r}_2)A\delta(\mathbf{r}_1-\mathbf{r}_2)\psi_a(\mathbf{r}_1,\mathbf{r}_2)\; d\tau_1 d\tau_2$$

which reduces to zero when ψ_a^* and ψ_a are substituted. Hence

$$E_a = \frac{\pi^2\hbar^2}{m}\left(\frac{5}{2a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)$$

EXAMPLE 13.8 A one dimensional infinite potential well of width a contains two spinless particles each of mass m. The potential representing the interaction between the particles $V = A\delta(x_1 - x_2)$. Calculate the ground state energy of the system corrected to first order in A.

The energy eigenvalues and eigenfunctions of a particle in an infinite square well of width a is given by

$$E_n = \frac{\pi^2\hbar^2 n^2}{2ma^2}, \quad n=1, 2, 3, \ldots\ldots$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\frac{n\pi x}{a}$$

For the two particle system the unperturbed wave function

$$\psi_{nk}(x_1, x_2) = \psi_n(x_1)\,\psi_k(x_2) = \frac{2}{a}\sin\frac{n\pi x_1}{a}\sin\frac{k\pi x_2}{a}$$

$$E_{nk} = \frac{\pi^2\hbar^2}{2ma^2}(n^2+k^2), \quad n, k = 1, 2, 3, \ldots$$

For the ground state, $n = k = 1$. The unperturbed ground state energy is then

$$E_{11} = \frac{\pi^2\hbar^2}{ma^2}$$

Next we consider the perturbation $H' = A\delta(x_1 - x_2)$. The first order correction to the ground state energy

$$E^{(1)} = A\left(\frac{2}{a}\right)^2 \int_0^a\int_0^a \sin^2\frac{\pi x_1}{a}\sin^2\frac{\pi x_2}{a}\,\delta(x_1 - x_2)\,dx_1 dx_2$$

$$= A\frac{4}{a^2}\int_o^a \sin^4\frac{\pi x_1}{a}\,dx_1 = \frac{3A}{2a}$$

Hence, the first order corrected ground state energy

$$E_{11} = \frac{\pi^2\hbar^2}{ma^2} + \frac{3A}{2a}$$

EXAMPLE 13.9 Two identical bosons, each of mass m move in the one dimensional harmonic potential $V = \frac{1}{2}m\omega^2x^2$. They also interact with each other via the potential $V_{int} = \alpha e^{-\beta(x_1 - x_2)^2}$ where α and β are positive parameters. Compute the ground state energy of the system to first order in the parameter α.

Since the particles are bosons, both of them can remain in the ground state. The V_{int} term can be treated as a perturbation. The ground state wavefunction of a harmonic oscillator, Eq. (4.94) is:

$$\left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

Hence the unperturbed wavefunction of the ground state for this two particle system is:

$$\psi_0(x_1, x_2) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega x_1^2}{2\hbar}\right)\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega x_2^2}{2\hbar}\right)$$

$$= \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} \exp\left[-\frac{m\omega}{2\hbar}(x_1^2 + x_2^2)\right]$$

First order correction to the energy

$$E^{(1)} = \frac{m\omega\alpha}{\hbar\pi}\int\int_{-\infty}^{\infty} \exp\left[-\frac{m\omega}{\hbar}(x_1^2 + x_2^2) - \beta(x_1 - x_2)^2\right] dx_1 dx_2$$

$$= \frac{m\omega\alpha}{\hbar\pi}\frac{1}{\sqrt{\dfrac{m\omega}{\hbar} + 2\beta}}$$

The ground state energy of the system is therefore,

$$E = \hbar\omega + \frac{m\omega\alpha}{\hbar\pi}\frac{1}{\sqrt{\dfrac{m\omega}{\hbar} + 2\beta}}$$

EXAMPLE 13.10 Consider the rotation of the hydrogen molecule H_2. How does the identity of the two nuclei affect the rotational spectrum? Discuss the type of transition that occurs between the rotational levels.

The rotational energy levels of hydrogen molecule are given by

$$E = \frac{\hbar^2 l(l+1)}{2I}, \quad l = 0, 1, 2, \ldots$$

The total wave function of the molecule ψ is the product of electronic (ψ_e), vibrational (ψ_v), rotational (ψ_r) and nuclear (ψ_n) wave functions.

$$\psi = \psi_e \psi_v \psi_r \psi_n$$

The spin of proton is half. Hence the total wave function ψ must be antisymmetric to nuclear exchange. Since ψ_e and ψ_v are symmetric to nuclear exchange, the product $\psi_r\psi_n$ must be antisymmetric. For l = 0, 2, 4, ..., the rotational wave function ψ_r is symmetric with respect to nuclear exchange and for l = 1, 3, 5, ..., it is antisymmetric. Hence, the antisymmetric ψ_n combines with ψ_r of even l states and the symmetric ψ_n combines with ψ_r of odd l states. As there is no interconversion between symmetric and antisymmetric nuclear spin states, transitions can take place between odd l values and between even l values. Since 3 symmetric nuclear spin functions and one anitsymmetric functions are possible (Table 13.1), the transitions between odd l values are observed to be strong. In other words, there will be an alternation in intensity of the rotational spectrum of H_2 molecule.

Note: The hydrogen molecules corresponding to antisymmetric nuclear spin states are called **para-hydrogen** and those corresponding to symmetric spin states are called **ortho-hydrogen**.

REVIEW QUESTIONS

1. Show that the symmetry character of a wave function does not change with time.
2. What is particle exchange operator? what are its eigenvalues? Show that it is a constant of motion.
3. Illustrate exchange degeneracy with example?
4. Explain how symmetric and antisymmetric wave functions are constructed from unsymmetrized solution of the Schrödinger equation of a system of indistinguishable particles.
5. What is Slater determinant? How does it incorporate Pauli principle?
6. List the various spin product functions with S^2 and S_z eigenvalues for a three-electron system.
7. What is central field approximation? How did Hartree obtain the central field in his theory of many electron atom?
8. What do you understand by self-consistent potential?
9. What are singlet and triplet states?
10. What are orthohelium and parahelium? Why orthohelium has somewhat lower energy than that of parahelium in the excited states?
11. Explain why the ground state of helium exists in the para form whereas the excited states come in both forms.
12. Explain Fermi hole and Fermi heap.
13. In helium atom if the interaction Hamiltonian is treated as perturbation, what is the degeneracy of the zeroth-order wave function if the configuration is (i) $1s^2$ (ii) 1s2s (iii) 1s2p.
14. The energy of a state does not depend on the spin wave function. Why?
15. Write the zeroth-order wave function for the 1s2s excited state of helium atom.

PROBLEMS

1. Show that if a wave function $\psi(1, 2, ..., n)$ is an energy eigenfunction of a symmetric Hamiltonian that correspond to a nondegenerate eigenvalue, it is either symmetric or antisymmetric.

2. Sixteen noninteracting electrons are confined in a potential $V(x) = \infty$ for $x < 0$ and $x > 0$; $V(x) = 0$, $0 < x < a$. (i) What is the energy of the least energetic electron in the ground state? (ii) What is the energy of the most energetic electron in the ground state? (iii) What is the Fermi energy E_f of the system?

3. What is the ground state energy and wave function for two identical particles in the potential defined, in Problem 2, if the two particles are (i) bosons (ii) fermions.

4. Consider two identical particles described by the Hamiltonian

$$H = \frac{p_1^2(x_1)}{2m} + \frac{p_2^2(x_2)}{2m} + \frac{1}{2}m\omega^2 x_1^2 + \frac{1}{2}m\omega^2 x_2^2$$

   Obtain the energy spectrum of this system. Discuss its degeneracy.

5. In the Thomas–Fermi model, show that the radius of a sphere which encloses a fixed fraction of all the electrons is proportional to $Z^{-1/3}$.

6. Prove that the three column vectors given in Eq. (13.22) are the spin eigenfunctions of S_z of a spin $s = 1$ system. Also prove that they are mutually orthogonal.

7. Show that α and β are eigenfunctions of S_x^2 but not of S_x.

8. Obtain the zeroth-order wave function for helium atom in the excited state 1s2p.

9. Obtain the zeroth-order wave function for the state 1s^{2}2s of lithium atom.

10. Consider a system of two identical particles occupying any of three energy levels A, B and C having energies E, $2E$ and $3E$ respectively. The level A is doubly degenerate (A_1 and A_2) and the system is in thermal equilibrium. Find the possible configurations and the corresponding energy in the following cases:
    (i) The particles obey Fermi statistics
    (ii) The particles obey Bose statistics
    (iii) The particles are distinguishable and obey Boltzmann statistics.

11. Consider the helium atom with no interaction between the two electrons
    (i) Write the wave function of the excited state 1s2s and indicate the total spin of each.
    (ii) Show that the functions are antisymmetric with respect to electron exchange.

12. Consider the rotational spectrum of the homonuclear diatomic molecule $^{14}N_2$. Show that the ratio of intensities of adjacent rotational lines is approximately 2 : 1.

Chapter 14

Scattering

In *scattering*, a beam of particles is allowed to pass close to a scattering material, called target and their energies and angular distributions are measured. In the process, the target may remain in its original state (elastic scattering) or brought to a different state (inelastic scattering).

In bound states, the energy eigenvalues are negative and discrete. In such cases the main interest is in the energy eigenvalues since they are related to the frequencies of the observed spectral line. The wave functions are important, if we are interested in the intensities of observed frequencies. In the case of scattering, we are mainly interested in the angular distribution of the scattered particles which in turn is related to the wave function. The study of scattering is important as it represents one of the best methods of studying the properties of atoms, nuclei and interaction of elementary particles between themselves and with atomic and nuclear systems. Even the concept of the atom is an outcome of a scattering experiment, Rutherford's analysis of α-scattering.

Two different approaches are possible for the study of scattering. In the first approach, the differential equation for the scattering of waves by obstacles is set up and its asymptotic solution obtained. In this method a detailed examination of the processes in the scattering region is not done. In the other approach, scattering is considered as a transition from an initial state of given momentum to a final state of different momentum of the same energy. The evaluation of rate of transition is done with the help of time-dependent perturbation theory. In this chapter, elastic scattering by the first approach is considered.

14.1 SCATTERING CROSS-SECTION

Consider a beam of particles of mass m travelling along the z-axis with velocity v and scattered by a scattering potential V (target) centred at the origin. The incident particles experience a force only when they are inside a sphere of radius r_0, the range of the scattering potential. Due to interaction with the scattering potential, the incident particles in general get scattered in all directions. After leaving the sphere they once again travel in straight lines. The angle between the initial and final straight line paths is called the *scattering angle* (θ). The experimental arrangement is illustrated in Figure 14.1.

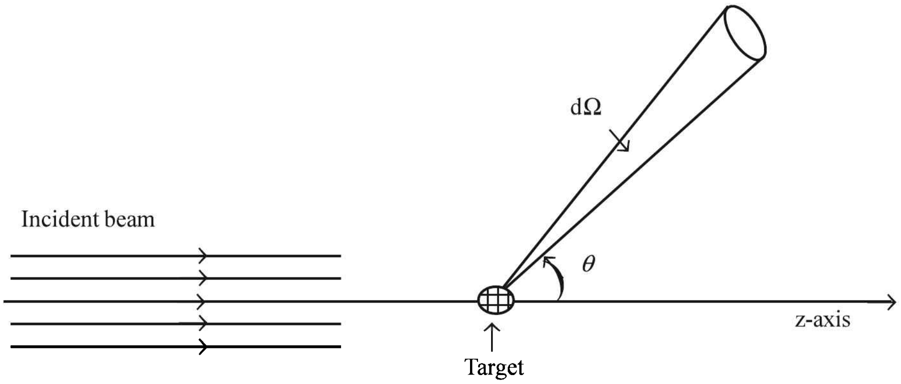


Figure 14.1 Schematic diagram of a scattering experiment. $d\Omega$—solid angle in the direction (θ,ϕ), θ—scattering angle.

Results of experiments on scattering are usually expressed in terms of differential scattering cross-section or total scattering cross-section. Let N be the number of incident particles crossing unit area normal to the beam in unit time and n be the number of particles scattered into solid angle $d\Omega$ in the direction (θ, ϕ) in unit time. The *differential scattering cross-section* σ (θ, ϕ) is defined by

$$\sigma(\theta, \phi) = \frac{n/d\Omega}{N} \tag{14.1}$$

where $n/d\Omega$ is the number of particles scattered per unit solid angle.

The solid angle $d\Omega$ in the direction $(\theta, \phi) = \dfrac{r \sin\theta \, d\varphi \, r d\theta}{r^2} = \sin\theta \, d\varphi d\theta$

The *total cross-section* σ is the integral of σ (θ, ϕ) over the entire solid angle. That is,

$$\sigma = \int \sigma(\theta, \phi)\, d\Omega = \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} \sigma(\theta, \phi)\, d\phi \tag{14.2}$$

Both $\sigma(\theta, \phi)$ and σ have the dimension of area and hence the name cross-section. For a spherically symmetric potential, $\sigma(\theta, \phi)$ is independent of ϕ and σ becomes

$$\sigma = 2\pi \int_0^\pi \sigma(\theta) \sin\theta \, d\theta \tag{14.3}$$

Note: Cross-sections are usually measured in barns, 1 barn = 10^{-24} cm^2.

14.2 SCATTERING AMPLITUDE

The Schrödinger equation we have to consider for the scattering of a two-particle system is the same as the one we developed in Section 5.2. If the potential V depends only on the relative distance r between the two particles, in the centre of mass system, the Schrödinger equation for relative motion is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\psi = E\psi, \quad \mu = \frac{mM}{m+M} \tag{14.4}$$

where m is the mass of the incident particle and M the mass of the target.

At large distances from the scatterer, the effect of the potential is negligible and the parallel beam of the incident particles can be represented by the plane wave

$$\psi_i \to A \exp(i\mathbf{k}\cdot\mathbf{r}) \quad \text{as} \quad V(r) \to 0 \tag{14.5}$$

where the wave vector

$$\mathbf{k} = \frac{\mathbf{p}}{\hbar} = \mu\frac{\mathbf{v}}{\hbar} \tag{14.6}$$

As the incident beam is along the z-axis

$$\psi_i \to A e^{ikz} \tag{14.7}$$

The detector is far away from the scatterer and we are interested only in the asymptotic form of the scattered wave. As the scattered intensity depends on θ and ϕ, the spherically diverging scattered wave can be represented as

$$\psi_s \xrightarrow[r\to\infty]{} A f(\theta, \phi)\frac{e^{ikr}}{r} \tag{14.8}$$

where $f(\theta, \phi)$ is called the *scattering amplitude*. For spherically symmetric potentials, the scattering amplitude $f(\theta, \phi)$ depends only on θ. Thus,

$$e^{ikz} \quad \text{and} \quad \frac{f(\theta)e^{ikr}}{r}$$

are two eigenstates of the particle and the most general asymptotic solution can be written as

$$\psi \xrightarrow[r\to\infty]{} A\left[e^{ikz} + \frac{f(\theta)\, e^{ikr}}{r}\right] \tag{14.9}$$

We shall next deduce the relation between the scattering amplitude $f(\theta)$ and the differential scattering cross-section $\sigma(\theta)$. The probability current density vector **j** (**r**, t) is given by

$$\mathbf{j}\,(\mathbf{r}, t) = \frac{\hbar}{2i\mu}[\psi^* \nabla\psi - (\nabla\psi^*)\psi] \tag{14.10}$$

If **j** (**r**, t) is calculated with the wave function in Eq. (14.9), we get interference terms between the incident and scattered waves. These do not appear in the usual experimental arrangements and therefore we can calculate the incident and scattered probability current densities by substituting the two parts of ψ separately in Eq. (14.10).

$$j_i = \frac{\hbar k\,|A|^2}{\mu} = \frac{p\,|A|^2}{\mu} = v|A|^2 \tag{14.11}$$

and

$$j_s = \frac{\hbar|A|^2}{2i\mu}\,|\,f(\theta)\,|^2\,\frac{2ik}{r^2} = v\,|\,f(\theta)\,|^2\,|A|^2\,\frac{1}{r^2} \tag{14.12}$$

where $1/r^2$ is the solid angle subtended by unit area of the detector at the scattering centre. Also,

$$\begin{aligned}\sigma(\theta) &= \frac{\text{Probability current density of the scattered wave per unit solid angle}}{\text{Probability current density of the incident wave}}\\ &= \frac{v|f(\theta)|^2|A|^2}{v|A|^2}\\ &= |f(\theta)|^2\end{aligned} \tag{14.13}$$

The scattering amplitude is thus related to the experimentally observable differential scattering cross-section. Since $\sigma(\theta)$ has the dimension of (length)^2, $f(\theta)$ has the dimension of length.

Two techniques commonly employed to evaluate the scattering amplitude—the *partial wave analysis* and the *Born approximation*—are explained in the Sections 14.4 and 14.11.

14.3 PARTIAL WAVES

A plane wave e^{ikz} can be expanded as a linear combination of spherical waves (Example 14.2) as

$$e^{ikz} = \sum_{l=0}^{\infty} i^l(2l+1)\, j_l\,(kr)P_l\,(\cos\,\theta) \tag{14.14}$$

$j_l(kr)$ is the *spherical Bessel function* of order l and P_l are the *Legendre polynomials*. Each term on the right-hand side represents a spherical wave. The plane wave is thus equivalent to the superposition of an infinite number of spherical waves and the individual waves are called *partial waves*. The waves with $l = 0, 1, 2, \ldots$ are respectively called the s-wave, the p-wave, d-wave and so on. The notation is borrowed from atomic spectroscopy. Asymptotically,

$$j_l(kr) \to \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right) \tag{14.15}$$

Writing $\sin\left(kr - \frac{l\pi}{2}\right)$ in terms of exponentials and substituting it in Eq. (14.14), we get

$$e^{ikz} = \sum_{l=0}^{\infty} \frac{i^l(2l+1)}{2ik} P_l(\cos\theta) \frac{1}{r}\left[\exp\left(ikr - i\frac{l\pi}{2}\right) - \exp\left(-ikr + i\frac{l\pi}{2}\right)\right] \tag{14.16}$$

This form shows that each partial wave can be represented as the sum of an incoming and an outgoing spherical wave.

In scattering problems, the first few spherical waves are the most important ones. The s-partial wave will be independent of the angle θ and hence spherically symmetric about the origin. Results of extremely low energy scattering can be explained satisfactorily with s-wave alone. If the energy is slightly higher, one needs p-wave also to explain the observed value.

14.4 SCATTERING BY A CENTRAL POTENTIAL: PARTIAL WAVE ANALYSIS

The method of partial wave is an elegant procedure for the analysis of elastic scattering. It is done in two steps. First, a wave function ψ which represents the sum of the incident and scattered waves is obtained in terms of the partial waves. Secondly, the asymptotic value of this ψ is equated to the ψ given in Eq. (14.9).

The Asymptotic Solution

The Schrödinger equation that describes the scattering is given by Eq. (14.4). The wave function ψ has to be independent of ϕ, as the incident particles are along the z-axis. Separating the variables as in Section 5.1, we get the solution of Eq. (14.4) as

$$\psi(r, \theta) = R_l(r)\, P_l(\cos\theta), \qquad l = 0, 1, 2, \ldots \tag{14.17}$$

where $R_l(r)$ satisfies the radial equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR_l}{dr}\right) + \left[\frac{2\mu E}{\hbar^2} - \frac{2\mu V}{\hbar^2} - \frac{l(l+1)}{r^2}\right] R_l = 0 \tag{14.18}$$

Outside the range of the potential ($r > r_0$), this equation reduces to the free-particle equation:

$$\frac{d^2R_l}{dr^2}+\frac{2}{r}\frac{dR_l}{dr}+\left[k^2-\frac{l(l+1)}{r^2}\right]R_l = 0 \tag{14.19}$$

where

$$k^2 = \frac{2\mu E}{\hbar^2} \tag{14.20}$$

Differential equation (14.19) has two independent solutions $j_l(kr)$ and $n_l(kr)$, where $j_l(kr)$ is the spherical Bessel function (Eq. 5.84) and $n_l(kr)$ is the spherical Neumann function Eq. (5.85). The general solution of Eq. (14.19) is then

$$R_l(kr) = A'j_l(kr) - B'n_l(kr)$$

where A' and B' are constants. Though the function $n_l(kr)$ is not finite at $r = 0$, it is retained as we are interested only in the asymptotic solution. Asymptotically, using Eq. (5.87), we have

$$R_l(kr) \underset{r\to\infty}{=} \frac{A'}{kr}\sin\left(kr-\frac{l\pi}{2}\right)+\frac{B'}{kr}\cos\left(kr-\frac{l\pi}{2}\right) \tag{14.21}$$

We shall now investigate what happens when there is a potential. When $V(r) \neq 0$, the value of the constant B_l'/A_l' has to be determined by solving Eq. (14.18) inside the scattering region and then matching it with the asymptotic solution, Eq. (14.21). Writing the new constants A_l and δ_l in terms of A' and B' by the relations $A' = A_l \cos\delta_l$ and $B' = A_l \sin\delta_l$, we have the asymptotic solution of Eq. (14.18) as

$$R_l(kr) = \frac{A_l}{kr}\sin\left(kr-\frac{l\pi}{2}+\delta_l\right), \quad l = 0, 1, 2, \ldots \tag{14.22}$$

where δ_l's are called the *phase shifts*. The phase shift δ_l measures the amount by which the phase of the radial function for angular momentum quantum number l differs from the corresponding one for the $V = 0$ case. The most general asymptotic solution is then

$$\psi(r, \theta) = \sum_{l=0}^{\infty} \frac{A_l}{kr}\sin\left(kr-\frac{l\pi}{2}+\delta_l\right) P_l(\cos\theta) \tag{14.23}$$

where A_l is the asymptotic amplitude.

The Scattering Amplitude

Equating this asymptotic form of the wave function with the ψ given by Eq. (14.9)

$$e^{ikz} + f(\theta)\frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} \frac{A_l}{kr}\sin\left(kr-\frac{l\pi}{2}+\delta_l\right)P_l(\cos\theta) \tag{14.24}$$

Replacing e^{ikz} using Eqs. (14.14) and (14.15), we have

$$\sum_{l=0}^{\infty} \frac{(2l+1)i^l}{kr} \sin\left(kr - \frac{l\pi}{2}\right) P_l(\cos\,\theta) + f(\theta)\frac{e^{ikr}}{r}$$

$$= \sum_{l=0}^{\infty} \frac{A_l}{kr} \sin\left(kr - \frac{l\pi}{2} + \delta_l\right) P_l\,(\cos\,\theta) \tag{14.25}$$

Writing the sine function in exponential form and equating the coefficients of e^{-ikr} on both sides, we get

$$\sum_{l=0}^{\infty} (2l+1)i^l\, e^{il\pi/2} P_l\,(\cos\,\theta) = \sum_{l=0}^{\infty} A_l\, e^{il\pi/2} \exp\,(-i\delta_l)\, P_l\,(\cos\,\theta) \tag{14.26}$$

Since Eq. (14.26) is valid for all values of θ, using the orthogonal property of Legendre polynomials

$$A_l = i^l\,(2l+1)\,\exp\,(i\delta_l) \tag{14.27}$$

Comparison of the coefficient of e^{ikr} on both sides of Eq. (14.25) gives

$$\sum_{l=0}^{\infty} \frac{(2l+1)i^l e^{-il\pi/2}}{2ikr} P_l\,(\cos\,\theta) + \frac{f(\theta)}{r} = \sum_{l=0}^{\infty} \frac{i^l\,(2l+1)e^{2i\delta l}}{2ikr} e^{-il\pi/2}\, P_l(\cos\,\theta)$$

or

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)\, i^l e^{-il\pi/2}\, [\exp\,(2i\delta_l) - 1]\, P_l(\cos\,\theta) \tag{14.28}$$

we have

$$i^l = e^{i\pi l/2}$$

and

$$\exp\,(2i\delta_l) - 1 = \exp\,(i\delta_l)\,[\exp\,(i\delta_l) - \exp\,(-i\delta_l)] = 2i\,\exp\,(i\delta_l)\,\sin\delta_l \tag{14.29}$$

Hence Eq. (14.28) is rewritten as:

$$f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1)\,\exp\,(i\delta_l)\, P_l\,(\cos\,\theta)\,\sin\,\delta_l \tag{14.30}$$

Equation (14.30) represents the basic result of the partial wave analysis which gives $f(\theta)$ as a sum of contributions from all partial waves. Equation (14.23) written in the exponential form allows a simple physical interpretation. Substituting the value of A_l (from Eq. (14.27) in Eq. (14.23), we get

$$\psi(r,\,\theta) = \sum_{l=0}^{\infty} \frac{i^l\,(2l+1)}{2ikr} \left\{\exp\left[i\left(kr - \frac{1}{2}l\pi + 2\delta_l\right)\right] - \exp\left[-i\left(kr - \frac{1}{2}l\pi\right)\right]\right\} P_l(\cos\,\theta) \tag{14.31}$$

From Eqs. (14.16) and (14.31), it follows that the effect of the scattering potential is to shift the phase of the outgoing waves relative to that of the incoming waves. This is reasonable, since at large distances the incoming waves are not aware of the potential that exists near the origin.

The Scattering Cross-section

The differential scattering cross-section

$$\sigma(\theta) = |f(\theta)|^2 = \frac{1}{k^2}\left|\sum_{l=0}^{\infty}(2l+1)\exp(i\delta_l)\,P_l(\cos\theta)\sin\delta_l\right|^2 \tag{14.32}$$

Equation (14.32) was first derived by Faxen and Holtzmark. Lord Rayleigh derived a similar expression for wave diffraction. The total cross-section

$$\sigma = \int_0^{\pi}\sigma(\theta)\,d\Omega = \int_0^{\pi}\sigma(\theta)(2\pi\sin\theta)\,d\theta = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l \tag{14.33}$$

In deriving Eq. (14.33) the orthogonal property of Legendre polynomial is used. The differential and total cross-sections are thus given in terms of the phase shifts δ_l of the partial waves. For understanding the scattering problem, one should therefore know the phase shifts δ_l, $l = 0, 1, 2, \ldots$

For s-wave scattering, the differential scattering cross-section $\sigma_0(\theta)$ and the total cross-section σ_0 are given by:

$$\sigma_0(\theta) = \frac{\sin^2\delta_0}{k^2} \quad \text{and} \quad \sigma_0 = \frac{4\pi}{k^2}\sin^2\delta_0 \tag{14.34}$$

It may be noted that both the cross-sections do not depend on the angle θ. Often s-wave contribution is the most dominant part in most of the experiments. It may also be noted from Eq. (14.32) that $\sigma(\theta)$ contains terms representing interference between different partial waves whereas the total cross section σ in Eq. (14.33) does not contain such terms. If all phase shifts except δ_0 and δ_1 are negligible

$$\sigma(\theta) = \frac{1}{k^2}[\sin^2\delta_0 + 9\sin^2\delta_1\cos^2\theta + 6\sin\delta_0\sin\delta_1\cos(\delta_0 - \delta_1)\cos\theta] \tag{14.35}$$

and

$$\sigma = \frac{4\pi}{k^2}(\sin^2\delta_0 + 3\sin^2\delta_1) \tag{14.36}$$

As already mentioned, the first term on the right of Eq. (14.35) is spherically symmetric. The second term has the factor $\cos^2\theta$ which has the same value at θ and $\pi - \theta$ and therefore symmetric between forward and backward directions. The presence of $\cos\theta$ in the third term produces a forward–backward asymmetry and may become large even if $\sin\delta_0 \gg \sin\delta_1$. Though, the p-wave contribution to the total cross-section is negligible, it is felt in the differential cross-section through cross-terms with the lower partial waves.

Optical Theorem

For the case $\theta = 0$, we get from Eq. (14.30)

$$f(0) = \frac{1}{k}\sum_{l=0}^{\infty} (2l+1)\exp(i\delta_l)\sin\delta_l \tag{14.37}$$

The imaginary part of this scattering amplitude is given by

$$\operatorname{Im} f(0) = \frac{1}{k}\sum_{l=0}^{\infty} (2l+1)\sin^2\delta_l \tag{14.38}$$

Comparing Eq. (14.38) and Eq. (14.33), we get

$$\sigma = \frac{4\pi}{k}\operatorname{Im} f(0) \tag{14.39}$$

This relation is known as the *optical theorem* in analogy with the relation in optics between the absorption coefficient and the imaginary part of the complex index of refraction.

Ramsaur–Townsend Effect

If the bombarding energy is very small, $kr_0 \ll 1$ and all phase shifts for $l > 0$ are almost zero. If in addition, the potential is such that $\delta_0 = \pi$, $\sin\delta_0 = 0$ and the scattering cross-section vanishes. This phenomenon of no scattering is called the *Ramsaur–Townsend effect.* They observed extremely small scattering cross-section for electrons of rare gas atoms at a bombarding energy of 0.7 eV.

14.5 SIGNIFICANT NUMBER OF PARTIAL WAVES

In the partial wave analysis of scattering, at sufficiently low energies, s-wave ($l = 0$) scattering will be the dominant one. As energy increases, contributions from higher l values become important. The question that arises immediately is that up to what partial wave one has to consider for a given energy. For spherically symmetric potentials, its influence is felt only in the region of a sphere of radius r_0 around the scattering centre. Classically, for a particle with impact parameter b, linear momentum $p = k\hbar$ and angular momentum $l\hbar$, we have

$$l\hbar = k\hbar b \quad \text{or} \quad l = kb \tag{14.40}$$

When the impact parameter $b > r_0$, the particle will not 'see' the potential region and therefore a classical particle do not get scattered if $l > kr_0$. Hence we need consider partial waves up to $l = kr_0$.

The same result can be derived quantum mechanically, but a rigorous proof is very much involved. We shall only give a qualitative argument. The function $j_l\,(kr)$ steeply increases for small values of kr and is proportional to $(kr)^l$. It has its first and the largest maximum near $kr \cong l$ and decreases with kr rapidly. If $kr << l$, the value of $j_l(kr)$ will be extremely small. As this is the region where the scattering potential is large, the lth partial wave will not be affected much by the potential and its contribution to scattering will be very small. When $kr_0 \cong l$, the first maximum of this partial wave lies around kr_0 beyond which the potential is negligible. Hence we need consider only up to the partial wave for which $l \cong kr_0$. At sufficiently low energies ($k \cong 0$), as already mentioned the scattering is mainly due to s-wave only. If $kr_0 \cong 1$ contribution due to p-wave has also to be considered. At very high energies, contributions from $l = 0$ to $l = kr_0$ are significant and the partial wave analysis becomes quite complicated. In such a case it is much easier to use the Born approximation (Section 14.11) which is more accurate at higher energies.

14.6 SCATTERING BY AN ATTRACTIVE SQUARE-WELL POTENTIAL

Number of important aspects of scattering can be illustrated by studying the scattering by an attractive square-well potential defined by

$$V(r) = \begin{cases} -V_0 & 0 < r < a \\ 0 & r > a \end{cases} \tag{14.41}$$

The radial part of the Schrödinger equation that describes the scattering is given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}(E + V_0)\,R - \frac{l(l+1)}{r^2}R = 0 \tag{14.42}$$

Writing

$$R = \frac{u}{r} \tag{14.43}$$

we get

$$\frac{d^2u}{dr^2} + \left[\frac{2\mu E}{\hbar^2} + \frac{2\mu V_0}{\hbar^2} - \frac{l(l+1)}{r^2}\right]u = 0 \tag{14.44}$$

For the s-state

$$\frac{d^2u}{dr^2} + k_1^2u = 0, \qquad \text{where } k_1^2 = \frac{2\mu}{\hbar^2}(E + V_0) \qquad r < a \tag{14.45}$$

and

$$\frac{d^2u}{dr^2} + k^2u = 0, \qquad \text{where } k^2 = \frac{2\mu E}{\hbar^2}; \qquad r > a \tag{14.46}$$

The solutions of these equations are:

$$u = A \sin (k_1 r), \qquad r < a \tag{14.47}$$

and

$$u = C \sin (kr) + D \cos (kr), \qquad r > a \tag{14.48}$$

In the region $r < a$, the solutions $R = u/r = (1/r) \cos (k_1 r)$ is not considered as it is not finite at $r = 0$. In the region $r > a$, the solution which is not regular at the origin is also included. The solution in the region $r > a$ can be written as

$$u = B \sin (kr + \delta_0), \qquad r > a \tag{14.49}$$

As the wave function and its derivative are continuous at $r = a$

$$A \sin (k_1 a) = B \sin (ka + \delta_0)$$

and

$$Ak_1 \cos (k_1 a) = Bk \cos (ka + \delta_0)$$

Dividing one by the other, we get

$$\tan (ka + \delta_0) = \frac{k}{k_1} \tan (k_1 a) \tag{14.50}$$

or

$$\delta_0 = \tan^{-1}\left[\frac{k}{k_1} \tan \left(k_1 a\right)\right] - ka \tag{14.51}$$

Substitution of δ_0 in Eq. (14.34) enables us to estimate the cross-section for *s*-wave scattering. We shall investigate some of the important features of this low energy scattering in the next section.

14.7 BREIT-WIGNER FORMULA

The solution of the radial part of the Schrödinger equation that describes *s*-wave scattering by an attractive square-well potential has been discussed in the previous section. We shall now consider the case of very low energy scattering by such a potential. Expanding $\tan (ka + \delta_0)$ in Eq. (14.50) and rearranging, we get

$$\left[1 + \frac{k}{k_1} \tan (ka) \tan (k_1 a)\right] \tan \delta_0 = \frac{k}{k_1} \tan (k_1 a) - \tan (ka) \tag{14.52}$$

If the potential is shallow, for very low energy scattering ($ka << 1$ and $\tan (ka) \cong ka$), k/k_1 is very small and the factor in square-bracket on the left side of Eq. (14.52) is $\cong 1$. It follows from Eq. (14.52) that

$$\tan \delta_0 = ka \left[\frac{\tan (k_1 a)}{k_1 a} - 1\right] \tag{14.53}$$

If the depth of the potential is gradually increased, at certain stage k_1a will go through $\pi/2$. This is the condition for the appearance of a bound state in an attractive square-well potential, Eq. (5.103). When k_1a goes through $\pi/2$, $\tan\delta_0 \to \infty$. This means that the phase shift also goes through $\pi/2$. When $\delta_0 = \pi/2$, it follows from Eq. (14.33) the total cross-section

$$\sigma = \frac{4\pi}{k^2} \tag{14.54}$$

which is the maximum value. In other words, if there is a bound state as energy tends to zero and the phase shift δ_0 goes through $\pi/2$, the cross-section reaches the maximum value. This is called *resonance*.

We shall now investigate the behaviour of the cross-section near resonance. Let the resonant energy be E_r. The phase shift δ_0 will be a function of E_r. As the phase shift at resonance is $\pi/2$,

$$\sin\delta_0(E_r) = 1 \text{ and } \cos\delta_0(E_r) = 0 \tag{14.55}$$

Expanding $\sin\delta_0$ and $\cos\delta_0$ near $E = E_r$ by Taylor series, we have

$$\begin{aligned}\sin\delta_0(E) &= \sin\delta_0(E_r) + \left[\frac{\partial\sin\delta_0}{\partial E}\right]_{E=E_r}(E - E_r)\\ &= \sin\delta_0(E_r) + \left[\cos\delta_0\frac{d\delta_0}{dE}\right]_{E=E_r}(E - E_r)\\ &\cong 1\end{aligned} \tag{14.56}$$

and

$$\begin{aligned}\cos\delta_0(E) &= \cos\delta_0(E_r) - \left[\sin\delta_0(E)\frac{d\delta_0}{dE}\right]_{E=E_r}(E - E_r)\\ &= -\frac{d\,\delta_0(E_r)}{dE}(E - E_r)\\ &= -\frac{2}{\Gamma}(E - E_r)\end{aligned} \tag{14.57}$$

where

$$\frac{2}{\Gamma} = \frac{d\delta_0(E_r)}{dE} \tag{14.58}$$

The significance of Γ will be known soon. The scattering amplitude $f_0(\theta)$, Eq. (14.30), now takes the form

$$f_0(\theta, E) = \frac{1}{k}\exp\,[i\delta_0(E)]\sin\delta_0(E) \tag{14.59}$$

The $1/k$ variation of the scattering amplitude with energy is very slow. The rapidly varying part comes from the phase shift δ_0. Denoting the contribution due to the phase shift part by $f_0(\delta)$, we have

$$f_0(\delta) = \exp\,[i\delta_0(E)] \sin\,\delta_0(E) = \frac{\sin \delta_0(E)}{\exp(-i\delta_0)} = \frac{\sin \delta_0}{\cos \delta_0 - i \sin \delta_0}$$

Substituting the values of sin δ_0 and cos δ_0 from Eqs. (14.56) and (14.57), we get

$$f_0(\delta) = \frac{1}{[-2(E - E_r)/\Gamma] - i} = - \frac{\Gamma/2}{(E - E_r) + (i\Gamma/2)} \tag{14.60}$$

The total cross-section is given by

$$\sigma = \frac{4\pi}{k^2} \left| f_0(\delta) \right|^2 = \frac{4\pi}{k^2} \frac{\Gamma^2/4}{(E - E_r)^2 + \Gamma^2/4} \tag{14.61}$$

which is the *Breit–Wigner formula* for resonant cross-sections. The parameter Γ represents the *width of the resonant curve.*

14.8 SCATTERING LENGTH

Evaluation of scattering cross-section needs knowledge of phase shifts δ_l, $l = 0, 1, 2, \cdots$. In most of the cases the s-wave ($l = 0$) contribution is the predominant one. A simple case occurs if the energy E or kr_0, where r_0 is the range of the potential, is very low so that only s-state is involved in the scattering. In such a case, we have from Eq. (14.30)

$$f_0(\theta) = \frac{1}{k} \exp\,(i\delta_0) \sin\,\delta_0 \tag{14.62}$$

The limiting value of energy for which Eq. (14.34) is valid is called the *zero energy* and that of $- f(\theta)$ as $E \to 0$ is called the *scattering length* which is usually denoted by a. That is

$$a = \lim_{E \to 0}\, [-f(\theta)] = -\frac{1}{k} \exp\,(i\delta_0) \sin\,\delta_0 \tag{14.63}$$

It follows from Eqs. (14.34) and (14.63) that the zero-energy cross-section

$$\sigma_0 = 4\pi a^2 \tag{14.64}$$

If $V(r)$ is weak, δ_0 will be very small which makes $\exp\,(i\delta_0) \cong 1$ and $\sin\,\delta_0 \cong \delta_0$. Consequently, we have from Eq. (14.63)

$$a = \lim_{E \to 0} \left(-\frac{\delta_0}{k} \right) \tag{14.65}$$

In other words in the zero energy limit, $\delta_0 = -ka$.

The concept of scattering length is extensively used in the investigations relating to the scattering of thermal neutrons.

14.9 EXPRESSION FOR PHASE SHIFTS

To derive an expression for phase shift, let us consider the radial part of the Schrödinger equation that describes the scattering, Eq. (14.44).

$$\frac{d^2u_l(r)}{dr^2}+\left[\frac{2\mu E}{\hbar^2}-\frac{2\mu V}{\hbar^2}-\frac{l(l+1)}{r^2}\right]u_l(r)=0$$

where $u_l = rR_l(r)$. In the incident wave region $V = 0$ and therefore

$$\frac{d^2u_l}{dr^2}+\left[k^2-\frac{l(l+1)}{r^2}\right]u_l(r) = 0, \qquad \text{where } k^2 = \frac{2mE}{\hbar^2} \tag{14.66}$$

whose solution is

$$u_l(kr) = kr\, j_l\,(kr) \tag{14.67}$$

Asymptotically,

$$u_l(kr) \xrightarrow[r\to\infty]{} \sin\left(kr-\frac{l\pi}{2}\right) \tag{14.68}$$

Similarly the asymptotic solution of

$$\frac{d^2v_l}{dr^2}+\left[k^2-\frac{2\mu V(r)}{\hbar^2}-\frac{l(l+1)}{r^2}\right]v_l=0 \tag{14.69}$$

is

$$v_l\,(kr) \xrightarrow[r\to\infty]{} \sin\left(kr-\frac{l\pi}{2}+\delta_l\right) \tag{14.70}$$

Multiplying Eq. (14.66) by v_l, Eq. (14.69) by u_l and subtracting, we get

$$v_l\frac{d^2u_l}{dr^2} - u_l\frac{d^2v_l}{dr^2} = -\frac{2\mu V}{\hbar^2}u_lv_l \tag{14.71}$$

Integrating from $r = 0$ to r and remembering that $u_l\,(0) = v_l\,(0) = 0$

$$v_l\frac{du_l}{dr} - u_l\frac{dv_l}{dr} = -\frac{2\mu}{\hbar^2}\int_0^r V(r')\,u_l(r')\,v_l\,(r')\,dr'$$

Allowing $r \to \infty$ and substituting the values of $u_l(r)$ and $v_l(r)$ from Eqs. (14.68) and (14.70), we have

$$k\sin\left(kr-\frac{l\pi}{2}+\delta_l\right)\cos\left(kr-\frac{l\pi}{2}\right)-k\sin\left(kr-\frac{l\pi}{2}\right)\cos\left(kr-\frac{l\pi}{2}+\delta_l\right)$$

$$= -\frac{2\mu}{\hbar^2}\int_0^\infty V(r)u_l(kr)v_l\,(kr)\,dr$$

or

$$k \sin \delta_l = -\frac{2\mu}{\hbar^2}\int_0^\infty V(r)u_l(kr)v_l(kr)\,dr \tag{14.72}$$

This expression for sin δ_l is exact. At high energies for weak potential, the phase shifts are small and

$$u_l(kr) \cong v_l(kr) \cong krj_l(kr) \tag{14.73}$$

As spherical Bessel function is related to the ordinary Bessel function by the relation

$$j_l(kr) = \left(\frac{\pi}{2kr}\right)^{1/2} J_{l+(1/2)}(kr) \tag{14.74}$$

Then

$$\sin\delta_l = \delta_l = -\frac{2\mu k}{\hbar^2}\int_0^\infty V(r)j_l^2(kr)r^2\,dr \tag{14.75}$$

$$= -\frac{\pi\mu}{\hbar^2}\int_0^\infty V(r)\,[J_{l+(1/2)}(kr)]^2\,r\,dr \tag{14.76}$$

This expression is known as the *Born approximation for phase shifts* which is valid only for weak potentials. It follows from Eq. (14.76) that an attractive potential ($V \le 0$) leads to positive phase shifts whereas a repulsive potential ($V \ge 0$) to negative phase shifts.

14.10 INTEGRAL EQUATION

The partial wave analysis of scattering which is based on the expansion of a plane wave in terms of spherical waves is more suitable for spherically symmetric potentials. Moreover, it is useful at relatively low energies. A more general analysis requires the expressing of the wave function in the form of an integral equation.

The Schrödinger equation for the scattering of a two-particle system, Eq. (14.4), can be written in the convenient form as

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = U(r)\psi(\mathbf{r}) \tag{14.77}$$

where

$$k^2 = \frac{2\mu E}{\hbar^2}, \qquad U(r) = \frac{2\mu V(r)}{\hbar^2} \tag{14.78}$$

We have to obtain a solution of Eq. (14.77) whose asymptotic value has the form of Eq. (14.9). Writing Eq. (14.9) as

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \psi_s \tag{14.79}$$

and substituting it in Eq. (14.77), we get

$$(\nabla^2 + k^2)(e^{i\mathbf{k}\cdot\mathbf{r}} + \psi_s) = U(r)\psi(\mathbf{r}) \tag{14.80}$$

Since $(\nabla^2 + k^2)\, e^{i\mathbf{k}\cdot\mathbf{r}} = 0$, Eq. (14.80) reduces to

$$(\nabla^2 + k^2)\psi_s = U(r)\psi(\mathbf{r}) = -\rho(\mathbf{r}) \tag{14.81}$$

Equation (14.81) is an inhomogeneous equation wherein the inhomogeneous term itself depends on $\psi(\mathbf{r})$. Its solution is obtained by Green's function method. Let G $(\mathbf{r}, \mathbf{r}')$ called the *Greens's function*, be the solution of the inhomogeneous equation with a delta function source. That is

$$(\nabla^2 + k^2)\mathrm{G}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{14.82}$$

The solution of the scattering equation for the density function $\rho(\mathbf{r})$ can then be written as

$$\psi_s = \int \mathrm{G}\,(\mathbf{r}, \mathbf{r}')\, \rho(\mathbf{r}')\, d\tau' \tag{14.83}$$

Using Green's-function techniques and contour integration

$$\mathrm{G}\,(\mathbf{r}, \mathbf{r}') = \frac{-\exp\,(ik\,|\mathbf{r} - \mathbf{r}'|)}{4\pi\,|\mathbf{r} - \mathbf{r}'|} \tag{14.84}$$

It follows immediately that

$$\psi_s(\mathbf{r}) = -\frac{1}{4\pi}\int \frac{\exp\,(ik\,|r - r'|)}{|r - r'|}\, U(\mathbf{r}')\psi(\mathbf{r}')\, d\tau' \tag{14.85}$$

where $\mathbf{r}$ is the position of the scattered particle after being scattered in the region $\mathbf{r}' \cong 0$. The scattered wave ψ_s at the point $\mathbf{r}$ has the form of the superposition of spherical waves originating from all points $\mathbf{r}'$ with amplitudes $U(r')\psi(\mathbf{r}')$. Figure 14.2 illustrates the vectors $\mathbf{r}$ and $\mathbf{r}'$. Let $\hat{n}$ be the unit vector in the direction of the vector $\mathbf{r}$. Since $\mathbf{r}$ is very large, it follows from Figure 14.2 that

$$|\mathbf{r} - \mathbf{r}'| \cong r - \hat{n}\,\cdot\,\mathbf{r}' \tag{14.86}$$

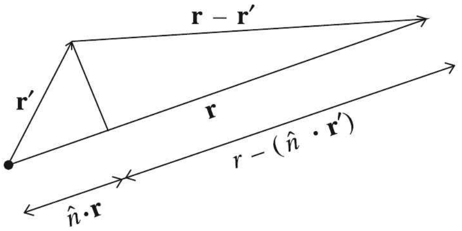


Figure 14.2 The vectors **r** and **r′** in a scattering problem.

In the centre of mass system, the momentum $\mathbf{k}'$ of the elastically scattered particle is equal in magnitude to the momentum of the incident particle (k). That is $\mathbf{k}' = k\hat{n}$. Hence

$$k\,|\mathbf{r} - \mathbf{r}'| = k(r - \hat{n} \cdot \mathbf{r}') = kr - \mathbf{k}' \cdot \mathbf{r}' \tag{14.87}$$

Replacing $|\mathbf{r} - \mathbf{r}'|$ in the denominator of Eq. (14.85) by r, the wave function for the scattering problem can be written as

$$\psi(\mathbf{r}) \xrightarrow[r\to\infty]{} \exp\,(i\mathbf{k} \cdot \mathbf{r}) - \frac{1}{4\pi} \int \frac{\exp\,[i(kr - \mathbf{k}' \cdot \mathbf{r}')]}{r} U(r')\psi(\mathbf{r}')\, d\tau' \tag{14.88}$$

Equation (14.88) is the *integral equation* for the wave function since ψ appears under the integral sign on the right-hand side. Comparing Eq. (14.88) with Eq. (14.9), we get

$$f(\theta) = -\frac{1}{4\pi} \int \exp\,(-i\mathbf{k}' \cdot \mathbf{r}')\, U(r')\psi(r')\, d\tau' \tag{14.89}$$

from which the differential scattering cross-section $\sigma(\theta)$ can be calculated.

14.11 THE BORN APPROXIMATION

The wave function $\psi(r')$ is required to evaluate Eq. (14.89). Born used an iteractive procedure for its evaluation. In the first Born approximation, $\psi(r')$ in the integral, Eq. (14.89) is replaced by the incoming plane wave, $\exp\,(i\mathbf{k} \cdot \mathbf{r}')$. This leads to an improved value for the wave function $\psi(r)$ which is used in the integral in the second Born approximation. This iterative procedure is continued till both the input and output ψ's are almost equal. As higher-order approximations are complicated, we shall restrict our discussion only to first Born approximation.

Replacing $\psi(r')$ in the integral in Eq. (14.89) by $\exp\,(i\mathbf{k} \cdot \mathbf{r}')$, we get

$$f(\theta) = -\frac{1}{4\pi} \int \exp\,[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}']\, U(r')\, d\tau' \tag{14.90}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are the wave vectors in the incident and scattered directions, respectively. The quantity $(\mathbf{k} - \mathbf{k}')\hbar = \mathbf{q}\hbar$ is then the momentum transfer from the incident particle to the scattering potential (refer to Figure 14.3). In other words, the change in momentum $\mathbf{q}\hbar$ due to collision is given by

$$q\hbar = (\mathbf{k} - \mathbf{k}')\hbar \quad \text{or} \quad |q| = 2|k|\sin\frac{\theta}{2} \tag{14.91}$$

Replacing $(\mathbf{k} - \mathbf{k}')$ by $\mathbf{q}$ in Eq. (14.90), we get

$$f(\theta) = -\frac{1}{4\pi} \int \exp\,(i\mathbf{q} \cdot \mathbf{r}')U(r')\, d\tau' \tag{14.92}$$

The angular integration in Eq. (14.92) can easily be carried out by taking the direction of $\mathbf{q}$ as the polar axis. Denoting the angle between $\mathbf{q}$ and $\mathbf{r}'$ by θ'.

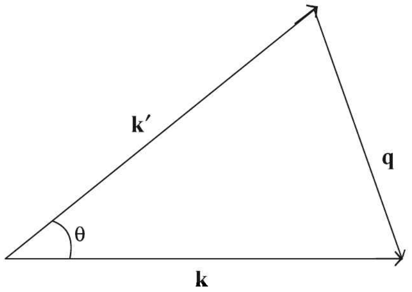


Figure 14.3 Representation of the wave vectors **k**, **k′** and **q**. The vector **k** points in the incident direction, **k′** in the scattered direction.

$$f(\theta) = -\frac{1}{4\pi}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \exp\,(iq\,r'\cos\theta')\,U(r')\,r'^2\sin\theta'\,d\phi'\,d\theta'\,dr' \quad (14.93)$$

Integration over ϕ gives 2π. The θ-integral can easily be evaluated by writing

$$\cos\theta' = x \quad \text{or} \quad -\sin\theta'\,d\theta' = dx$$

we get

$$\int_0^{\pi} \exp\,(iqr'\cos\theta')\sin\theta'\,d\theta' = \int_{-1}^{1} \exp\,(iqr'x)\,dx$$

$$= \frac{\exp\,(iqr') - \exp\,(-iqr')}{iqr'}$$

$$= \frac{2\sin\,(qr')}{qr'} \quad (14.94)$$

Substituting the value of the angular part in Eq. (14.93)

$$f(\theta) = -\frac{2\mu}{\hbar^2}\int_0^{\infty} \frac{\sin\,(qr')}{qr'}\,V(r')r'^2\,dr' \quad (14.95)$$

from which $\sigma(\theta)$ can be calculated. It may be noted from Eq. (14.95) that the only variable parameter in $f(\theta)$ is the magnitude of the momentum transfer $q\hbar$, where q is given by Eq. (14.91). Thus, the scattering cross-section depends on the momentum of the incident particle $k\hbar$ and the scattering angle θ through the combination $q = 2k\sin\,(\theta/2)$.

14.12 SCATTERING BY SCREENED COULOMB POTENTIAL

As an example of Born approximation, we shall consider the scattering of a particle having charge $Z'e$ by an atomic nucleus of charge Ze. The interaction between the two is usually screened by the atomic electrons surrounding the nucleus. The potential representing the interaction can be written as

$$V(r) = -\frac{ZZ'e^2}{r} e^{-\alpha r} \tag{14.96}$$

where α is the parameter which determines the screening by atomic electrons. With this value of $V(r)$, the scattering amplitude $f(\theta)$ (in Eq. 14.95) becomes

$$\begin{aligned} f(\theta) &= \frac{2\mu ZZ'e^2}{\hbar^2 q} \int_0^\infty \sin(qr') \exp(-\alpha r')\, dr' \\ &= \frac{2\mu ZZ'e^2}{\hbar^2 q} \frac{q}{q^2 + \alpha^2} \\ &= \frac{2\mu ZZ'e^2}{\hbar^2 (q^2 + \alpha^2)} \end{aligned} \tag{14.97}$$

Therefore,

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{2\mu ZZ'e^2}{\hbar^2}\right)^2 \frac{1}{\left(q^2 + \alpha^2\right)^2} \tag{14.98}$$

If the momentum transfer $q \gg \alpha$,

$$q^2 + \alpha^2 \cong q^2 = 4k^2 \sin^2 \frac{\theta}{2}$$

and

$$\sigma(\theta) = \frac{\mu^2 Z^2 Z'^2 e^4}{4\hbar^4 k^4 \sin^4(\theta/2)} \tag{14.99}$$

which is *Rutherford's scattering formula* for scattering by a pure Coulomb potential $-ZZ'e^2/r$.

14.13 VALIDITY OF BORN APPROXIMATION

In the Born approximation, $\psi(r')$ in Eq. (14.89) was replaced by $\exp(i\mathbf{k}\cdot\mathbf{r}')$, which is valid only if the scattered wave ψ_s in Eq. (14.85) is small compared to the plane wave. The scattered wave ψ_s is likely to be maximum in the interaction region, where $r \cong 0$. With $r \cong 0$ in Eq. (14.85), the condition reduces to

$$\left| \frac{1}{4\pi} \int \frac{\exp(-ikr')}{r'} U(r') \exp(i\mathbf{k}\cdot\mathbf{r}')\, d\tau' \right| \ll 1 \tag{14.100}$$

where $\mathbf{k}\cdot\mathbf{r}' = kr' \cos\theta'$ and $d\tau' = r'^2 \sin\theta'\, d\theta'\, d\phi'\, dr'$. Integration over ϕ gives 2π. Integration over θ' can be done using the substitution $\cos\theta' = x'$. Carrying out the angular integration, Eq. (14.100) reduces to

$$\left| \int_0^\infty \frac{\exp(ikr')}{r'} U(r') \frac{\sin(kr')}{kr'} r'^2 dr' \right| \ll 1$$

or

$$\frac{2\mu}{k\hbar^2}\left|\int_0^\infty \exp(ikr')\sin(kr')\,V(r')\,dr'\right| \ll 1 \qquad (14.101)$$

If the energy is sufficiently high, sin (kr') will be a rapidly varying function and the value of the integral in Eq. (14.101) will be very small. A weak potential also makes the integral small. When energy is high the factor $2\mu/(k\hbar^2)$ will also be very small. Hence Born approximation is valid for weak potentials at high energies.

14.14 LABORATORY AND CENTRE OF MASS COORDINATE SYSTEMS

To describe scattering experiments, two coordinate systems are in use: the *laboratory coordinate system* (L) and the *centre of mass coordinate system* (C.M.). In the laboratory system, the scattering centre is initially at rest whereas in the other system the centre of mass of the two interacting particles is always at rest. This means that the coordinate systems move relative to one another with a velocity equal to the velocity of the centre of mass in the laboratory system ($v_{\text{C.M.}}$). Since the centre of mass is always at rest, its total momentum is always zero.

Experimental observations are usually done in the laboratory system. The centre of mass system is more convenient for calculations because in this system, the two body problem with six degrees of freedom reduces to two one-body problems each with three degrees of freedom. One of these motions corresponds to the free motion of the centre of mass and the other corresponds to the motion of the two particles relative to each other or to their centre of mass.

To get the relationships between the two systems, consider a particle of mass m moving in the positive z-direction with velocity v_L and colliding with another particle of mass M at rest at the origin O. After collision, it gets scattered in the direction (θ_L, ϕ_L). The motion in the laboratory system is illustrated in Figure 14.4.

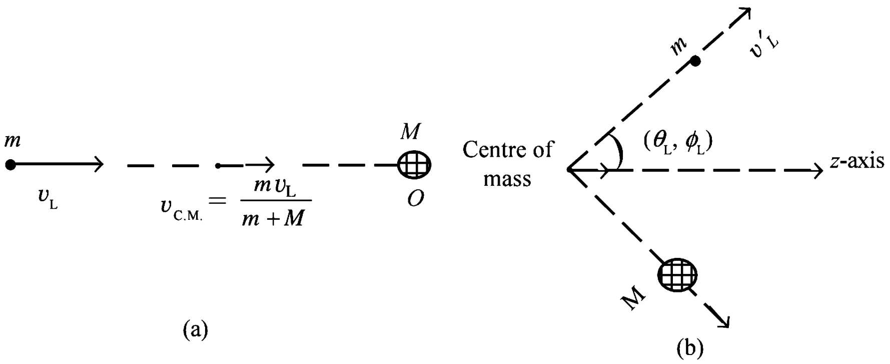


Figure 14.4 Motion of a particle in the laboratory system (a) before collision (b) after collision.

The velocity of the centre of mass

$$v_{\text{C.M.}} = \frac{mv_{\text{L}}}{m + M} \tag{14.102}$$

Next, let us examine the experiment with respect to an observer located at the centre of mass. The observer sees the particle M approaching him from right with velocity $-mv_{\text{L}}/(m + M)$ and the particle m approaching him from left with velocity

$$v_{\text{c}} = v_{\text{L}} - v_{\text{C.M.}} = v_{\text{L}} - \frac{mv_{\text{L}}}{m + M} = \frac{Mv_{\text{L}}}{m + M} \tag{14.103}$$

After collision, to keep the centre of mass at rest, the two particles must be scattered in the opposite directions (elastic scattering assumed) with speeds unchanged. The collision process in the centre of mass system is illustrated in Figure 14.5.

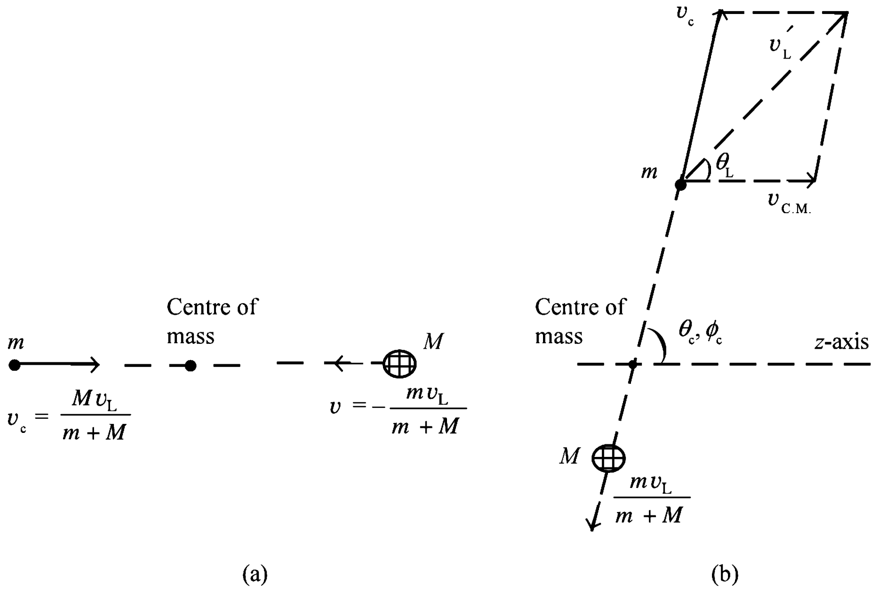


Figure 14.5 Motion of a particle in the centre of mass system (a) before collision (b) after collision.

Since the two systems move relative to one another with velocity $v_{\text{C.M.}}$, from Figure 14.5(b), we have

$$\begin{aligned} v'_{\text{L}} \cos \theta_{\text{L}} &= v_{\text{c}} \cos \theta_{\text{c}} + v_{\text{C.M.}} \\ v'_{\text{L}} \sin \theta_{\text{L}} &= v_{\text{c}} \sin \theta_{\text{c}} \\ \phi_{\text{L}} &= \phi_{\text{c}} \end{aligned} \tag{14.104}$$

It follows that

$$\tan \theta_L = \frac{\sin\theta_c}{\cos\theta_c + (v_{C.M.}/v_c)} = \frac{\sin\theta_c}{\cos\theta_c + \alpha} \tag{14.105}$$

where $\alpha = m/M$. When M is infinitely large in comparison with m, $\theta_L \cong \theta_c$ and the recoil is negligible. In such a case, the scatterer behaves like a fixed one.

The relation between $\sigma_c(\theta_c, \phi_c)$, and $\sigma_L(\theta_L, \phi_L)$, the differential scattering cross-section in centre of mass and laboratory systems, can be obtained using the condition that the number of particles scattered into a given solid angle must be the same in both the systems. Then

$$N\sigma_c\,(\theta_c, \phi_c)\, d\Omega_c = N\sigma_L(\theta_L, \phi_L)\, d\Omega_L \tag{14.106a}$$

and

$$\sigma_c(\theta_c, \phi_c) \sin\theta_c\, d\theta_c\, d\phi_c = \sigma_L(\theta_L, \phi_L) \sin\theta_L\, d\theta_L\, d\phi_L \tag{14.106b}$$

From Eq. (14.104), $d\phi_c = d\phi_L$ and from Eq. (14.105)

$$\frac{\sin^2\theta_L}{\cos^2\theta_L} = \frac{\sin^2\theta_c}{(\cos\theta_c + \alpha)^2}$$

or

$$\frac{1}{\cos^2\theta_L} = \frac{\sin^2\theta_c + (\cos\theta_c + \alpha)^2}{(\cos\theta_c + \alpha)^2} = \frac{1 + \alpha^2 + 2\alpha\cos\theta_c}{(\cos\theta_c + \alpha)^2}$$

or

$$\cos\theta_L = \frac{|\alpha + \cos\theta_c|}{(1 + \alpha^2 + 2\alpha\cos\theta_c)^{1/2}}, \quad \text{where } \alpha = \frac{m}{M} \tag{14.107}$$

On differentiation, we get

$$\sin\theta_L\, d\theta_L = \frac{|1 + \alpha\cos\theta_c|}{(1 + \alpha^2 + 2\alpha\cos\theta_c)^{3/2}} \sin\theta_c\, d\theta_c$$

Consequently,

$$\sigma_L(\theta_L, \phi_L) = \frac{(1 + \alpha^2 + 2\alpha\cos\theta_c)^{3/2}}{|1 + \alpha\cos\theta_c|}\, \sigma_c(\theta_c, \phi_c) \tag{14.108}$$

If $M >> m$, $\alpha = m/M \cong 0$ and $\sigma_L(\theta_L, \phi_L) = \sigma_c\,(\theta_c, \phi_c)$. When the two masses are equal, $\alpha = 1$ and from Eq. (14.105), $\theta_L = \theta_c/2$ which leads to

$$\sigma_L(\theta_L, \phi_L) = 4\sigma(2\theta_L, \phi_L)\cos\theta_L$$

As θ_c increases from 0 to π, θ_L increases from 0 to $\pi/2$ which amounts to no scattering in the backward direction. In other words, in the laboratory system the entire scattering is in the forward hemisphere.

WORKED EXAMPLES

EXAMPLE 14.1 A beam of particles is incident normally on a thin metal foil of thickness t. If N_0 is the number of nuclei per unit volume of the foil, show that the fraction of incident particles scattered in the direction (θ, ϕ) is $\sigma(\theta, \phi)\, N_0 t\, d\Omega$, where $d\Omega$ is the small solid angle in the direction (θ, ϕ).

From Eq. (14.1), the differential scattering cross-section

$$\sigma(\theta, \phi) = \frac{n/d\Omega}{N}$$

where n is the number scattered into solid angle $d\Omega$ in the direction (θ, ϕ) in unit time and N is the incident flux. Therefore,

$$n = \sigma(\theta, \phi) N\, d\Omega$$

This is the number scattered by a single nucleus.

The number of nuclei in a volume, $At = N_0 At$

The number scattered by $N_0 At$ nuclei $= \sigma(\theta, \phi) N\, d\Omega\, N_0 At$

Number of particles striking an area $A = NA$

Fraction scattered in the direction $(\theta, \phi) = \dfrac{\sigma(\theta, \phi) N\, d\Omega\, N_0 At}{NA} = \sigma(\theta, \phi)\, N_0 t\, d\Omega$

EXAMPLE 14.2 Establish the expansion of a plane wave in terms of an infinite number of spherical waves.

Free particles moving parallel to z-axis can be described by the plane wave

$$\psi_k = e^{ikz} = e^{ikr\cos\theta}$$

The wave function of a free particle in space is also given by Eq. (5.90). When the free particles are along the z-axis, the wave function must be independent of the angle ϕ which allows only $m = 0$. This reduces the associated Legendre polynomials in $Y_{lm}(\theta, \phi)$ to Legendre polynomials $P_l(\cos\theta)$. Equating the two expressions for wave function, we get

$$\sum_{l=0}^{\infty} A_l\, j_l(kr) P_l\, (\cos\theta) = e^{ikr\cos\theta}$$

Multiplying both sides by $P_l\, (\cos\theta)$ and integrating over $\cos\theta$, we have

$$A_l\, j_l(kr) \frac{2}{2l+1} = \int_{-1}^{+1} e^{ikr\cos\theta} P_l\, (\cos\theta)\, d\, (\cos\theta)$$

$$= \left[\frac{P_l(\cos\theta) e^{ikr\cos\theta}}{ikr} \right]_{-1}^{+1} - \int_{-1}^{+1} \frac{e^{ikr\cos\theta}}{ikr} P_l'\, (\cos\theta)\; d(\cos\theta)$$

The second term on the right leads to term $1/r^2$ and therefore it vanishes as $r \to \infty$. Since

$$P_l(1) = 1, \quad P_l(-1) = (-1)^l P_l(1) = e^{il\pi}, \qquad \text{as } r \to \infty$$

we get

$$A_l \frac{2}{2l+1} j_l(kr) = \frac{1}{ikr}\left(e^{ikr} - e^{-ikr} e^{il\pi}\right)$$

or

$$A_l \frac{2}{2l+1} \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right) = \frac{e^{il\pi/2}}{ikr}\left\{\exp\left[i\left(kr - \frac{l\pi}{2}\right)\right] - \exp\left[-i\left(kr - \frac{l\pi}{2}\right)\right]\right\}$$

or

$$A_l = (2l + 1)e^{il\pi/2} = (2l + 1)i^l$$

Consequently,

$$e^{ikz} = \sum_{l=0}^{\infty} (2l + 1)\ i^l j_l\,(kr) P_l\ (\cos\theta)$$

This is *Bauer's formula.*

EXAMPLE 14.3 In a scattering experiment, the potential is spherically symmetric and the particles are scattered at such energy that only s and p waves need be considered. (i) Show that the differential cross-section $\sigma(\theta)$ can be written in the form $\sigma(\theta) = a + b \cos\theta + c \cos^2\theta$. (ii) What are the values of a, b, c in terms of phase shifts? (iii) What is the value of total cross-section in terms of a, b, c?

(i) The scattering amplitude

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty} (2l + 1) \exp\,(i\delta_l)\ P_l\ (\cos\theta)\ \sin\ \delta_l$$

$$= \frac{1}{k}\ [\exp\,(i\delta_0) \sin\,\delta_0 + 3 \exp\,(i\delta_1) \cos\theta \sin\,\delta_1]$$

since

$$P_0(\cos\theta) = 1 \quad \text{and} \quad P_1(\cos\theta) = \cos\theta$$

It follows

$$\sigma(\theta) = |f(\theta)|^2 = \frac{1}{k^2}[\sin^2\delta_0 + 6\sin\delta_0 \sin\delta_1 \cos(\delta_0 - \delta_1) \cos\theta + 9\sin^2\delta_1 \cos^2\theta]$$

This can be written as

$$\sigma(\theta) = a + b\cos\theta + c\cos^2\theta$$

(ii) Comparing the above two equations, we get

$$a = \frac{\sin^2\delta_0}{k^2}, \quad b = \frac{6}{k^2} \sin\delta_0 \sin\delta_1 \cos(\delta_0 - \delta_1), \quad c = \frac{9}{k^2} \sin^2\delta_1$$

(iii) Total cross-section

$$\sigma = \frac{4\pi}{k^2}\,(\sin^2\delta_0 + 3\sin^2\delta_1) = 4\pi a + \frac{4\pi c}{3} = 4\pi\left(a + \frac{c}{3}\right)$$

EXAMPLE 14.4 Consider scattering by a central potential by the methods of partial wave analysis and Born approximation. When δ_l is small, prove that the expressions for scattering amplitude in the two methods are equivalent. Given that

$$\sum_l (2l+1)\,P_l\,(\cos\,\theta)\;\;j_l^2\,(kr) = \frac{\sin qr}{qr}, \quad \text{where } q = 2k\,\sin\,\frac{\theta}{2}$$

Since $i^l = e^{il\pi/2}$, the scattering amplitude given by Eq. (14.28) reduces to

$$f(\theta) = \frac{1}{2ik}\sum_l (2l+1)\left[\exp\,(2i\delta_l) - 1\right]P_l\,(\cos\,\theta)$$

Since δ_l is very small, $\exp\,(2i\delta_l) - 1 \cong 2i\delta_l$. Therefore,

$$f(\theta) \cong \frac{1}{k}\sum_l (2l+1)\,P_l\,(\cos\,\theta)\delta_l$$

Substituting the value of δ_l from Eq. (14.75), we get

$$f(\theta) = -\frac{2\mu}{\hbar^2}\sum_l (2l+1)\,P_l\,(\cos\,\theta)\int_0^\infty V(r)\,j_l^2(kr)r^2\,dr$$

$$= -\frac{2\mu}{\hbar^2}\int_0^\infty \frac{\sin\,(qr)}{qr}\,V(r)r^2\,dr$$

which is the expression for scattering amplitude under Born approximation (Eq. 14.95).

EXAMPLE 14.5 Evaluate the scattering amplitude in the Born approximation, for scattering by the Yukawa potential

$$V(r) = \frac{V_0 e^{-\alpha r}}{r}$$

where V_0 and α are constants. Also show that $\sigma(\theta)$ peaks in the forward direction ($\theta = 0$) except at zero energy and decreases monotonically as θ varies from 0 to π.

Substituting the given potential in the expression for $f(\theta)$

$$f(\theta) = -\frac{2\mu}{q\hbar^2}\int_0^\infty V(r)\;r\,\sin\,(qr)\;dr, \quad \text{where } q = 2k\,\sin\,\frac{\theta}{2}$$

we get

$$f(\theta) = -\frac{2\mu V_0}{q\hbar^2}\int_0^\infty e^{-\alpha r}\sin(qr)\,dr$$

Writing $I = \int_0^\infty e^{-\alpha r}\sin(qr)\,dr$ and integrating by parts, we have

$$I = -\left[e^{-\alpha r}\frac{\cos(qr)}{q}\right]_0^\infty - \frac{\alpha}{q}\int_0^\infty \cos(qr)\,e^{-\alpha r}\,dr$$

$$= \frac{1}{q} - \frac{\alpha}{q}\left[e^{-\alpha r}\frac{\sin(qr)}{q}\right]_0^\infty - \frac{\alpha^2}{q^2}\int_0^\infty \sin(qr)\,e^{-\alpha r}\,dr$$

$$= \frac{1}{q} - \frac{\alpha^2}{q^2}I$$

Therefore, $I = q/(q^2+\alpha^2)$. Hence

$$f(\theta) = -\frac{2\mu V_0}{\hbar^2(q^2+\alpha^2)} = -\frac{2\mu V_0}{\hbar^2\left[\alpha^2+4k^2\sin^2(\theta/2)\right]}$$

and

$$\sigma(\theta) = |f(\theta)|^2 = \frac{4\mu^2V_0^2}{\hbar^4\left[\alpha^2+4k^2\sin^2(\theta/2)\right]^2}$$

$\sigma(\theta)$ is maximum when $4k^2\sin^2(\theta/2) = 0$, that is when $\theta = 0$. $\sigma(\theta)$ decreases from this maximum value as $\theta \to \pi$.

EXAMPLE 14.6 Obtain an expression for the phase shift δ_0 for s-wave scattering by the potential

$$V(r) = \begin{cases}\infty & \text{for } 0 \le r \le a\\ 0 & \text{for } r > a\end{cases}$$

Assuming that the scattering is dominated by the $l = 0$ term, show that the total cross-section $\sigma_0 \cong 4\pi a^2$.

For the s-state, as $V = \infty$, the wave function = 0 for $r \le a$. For $r > a$, from Eq. (14.46)

$$\frac{d^2u}{dr^2} + \frac{2mEu}{\hbar^2} = 0, \quad \text{where } R = \frac{u}{r}$$

The solution is

$$u = B\sin(kr+\delta_0), \qquad \text{where } k^2 = \frac{2mE}{\hbar^2}, \qquad r > a$$

As $u = 0$ at $r = a$, $B \sin (ka + \delta_0) = 0$ or $\sin (ka + \delta_0) = 0$, we have

$$ka + \delta_0 = n\pi, \qquad (n \text{ is an integer})$$

or

$$\delta_0 = n\pi - ka$$

When scattering is dominated by $l = 0$, E/k is very small and therefore $\sin ka \cong ka$.

$$\begin{aligned}\text{Total cross-section } \sigma_0 &= \frac{4\pi}{k^2} \sin^2\delta_0 \\ &= \frac{4\pi}{k^2} \sin^2(n\pi - ka) \\ &= \frac{4\pi}{k^2} \sin^2(ka) \\ &\cong 4\pi a^2\end{aligned}$$

EXAMPLE 14.7 Outline the steps involved in deriving Eq. (14.33):

From Eq. (14.32):

$$\sigma(\theta) = \frac{1}{k^2}\left|\sum_{l=0}^{\infty} (2l + 1) \exp (i\delta_l)\, P_l(\cos\theta)\sin\delta_l\right|^2$$

The total cross-section $\sigma = \int \sigma(\theta)\, d\Omega$, where $d\Omega$ is the solid angle in the direction θ.

$$d\Omega = 2\pi \sin \theta\, d\theta$$

$$\sigma = \frac{2\pi}{k^2}\int_0^{\pi} \left[\sum_{l=0}^{\infty}(2l + 1) \exp (i\delta_l)\, P_l(\cos\theta) \sin\delta_l\right]$$

$$\times \left[\sum_{l'=0}^{\infty}(2l' + 1) \exp (-i\delta_{l'})\, P_{l'} (\cos\theta) \sin\delta_{l'}\right]\sin\theta\, d\theta$$

For Legendre polynomials we have the orthogonality relation

$$\int_{-1}^{+1} P_l (x)\, P_m(x)dx = \frac{2}{2l+1}\, \delta_{lm}$$

Changing the variable of integration from θ to x by defining $\cos \theta = x$ and using the orthogonal property of Legendre polynomials

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty} (2l + 1) \sin^2\delta_l$$

EXAMPLE 14.8 Using Born approximation, calculate the differential and total cross sections for scattering of a particle of mass m off the δ-function potential $V(\mathbf{r}) = g\delta(\mathbf{r})$, where g is constant.

From Eq. (14.92), the scattering amplitude

$$f(\theta) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int \exp(i\mathbf{q}.\mathbf{r}')\ V(\mathbf{r}')d\tau'$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and $|\ q\ | = 2k \sin \theta/2$. Here $\mathbf{k}$ and $\mathbf{k}'$ are respectively the wavevectors of the incident and scattered waves. Substituting the value of $V(r)$

$$f(\theta) = -\frac{mg}{2\pi\hbar^2}\int \exp\ (i\mathbf{q}.\mathbf{r}')\ \delta(\mathbf{r}')d\tau'$$

Using the definition of δ-function, Eq. (C.5) of Appendix C,

$$f(\theta) = -\frac{mg}{2\pi\hbar^2}$$

Differential scattering cross section

$$\sigma(\theta) = |f(\theta)|^2 = \frac{m^2g^2}{4\pi^2\hbar^4}$$

Since the distribution is isotropic, the total cross section

$$\sigma = 4\pi\sigma(\theta) = \frac{m^2g^2}{\pi\hbar^4}$$

EXAMPLE 14.9 For an attractive square well potential,

$$V(r) = -V_0 \text{ for } 0<r<r_0 \text{ and } V(r) = 0 \text{ for } r>r_0$$

Find the energy dependence of the phase shift δ_0 by Born approximation. Hence show that at high energies,

$$\delta_0(k) \to \frac{mr_0V_0}{\hbar^2k} \quad \text{where } k^2 = \frac{2mE}{\hbar^2}$$

In the Born approximation, the phase shift δ_l is given by Eq.(14.75). Then the phase shift

$$\delta_0 = \frac{2mk}{\hbar^2}V_0\int_0^{r_0} j_0^2(kr)\ r^2dr; \quad k^2 = \frac{2mE}{\hbar^2}$$

Since $j_0(kr) = \dfrac{\sin\ (kr)}{kr}$

$$\delta_0 = \frac{2mkV_0}{\hbar^2k^2}\int_0^{r_0} \sin^2(kr)\ dr = \frac{2mkV_0}{\hbar^2k^2}\int_0^{r_0} \frac{1-\cos 2kr}{2}\ dr$$

$$= \frac{2mkV_0}{\hbar^2 k^2}\left[\frac{r_0}{2} - \frac{\sin 2kr_0}{4k}\right]$$

$$= \frac{mV_0}{\hbar^2 k^2}\left[kr_0 - \tfrac{1}{2}\sin(2kr_0)\right]$$

which is the energy dependence of the phase shift δ_0. At high energies $k \to \infty$. When $k \to \infty$, the second term

$$\frac{mV_0}{2\hbar^2 k^2}\sin(2kr_0) \to 0$$

Hence, at high energies

$$\delta_o(k) \to \frac{mr_0V_0}{\hbar^2 k}$$

REVIEW QUESTIONS

1. Define differential scattering cross-section and total cross-section. What is the unit in which they are measured?
2. What is scattering amplitude? How is it related to scattering cross-section?
3. Distinguish between laboratory coordinate system and centre of mass coordinate system. State the relation connecting the differential cross-section in these two systems.
4. In the laboratory system prove that the entire scattering is in the forward hemisphere when the mass of the projectile is equal to the mass of the scattering centre.
5. What are partial waves?
6. In a scattering experiment, one need consider partial waves up to $l = kr_0$, where r_0 is the range of the potential. Substantiate.
7. Define scattering length. How is it related to zero energy cross-section?
8. Explain (i) optical theorem (ii) Ramsauer–Townsend effect.
9. What is phase shift? Explain the nature of phase shift in the case of repulsive and attractive potentials.
10. Discuss the validity conditions for Born approximation.

PROBLEMS

1. In the Born approximation, calculate the scattering amplitude for scattering from the square-well potential $V(r) = -V_0$ for $0 < r < r_0$ and $V(r) = 0$ for $r > r_0$.

2. In Problem 1, if the geometrical radius of the scatterer is much less than the wavelength associated with the incident particles, show that the scattering will be isotropic.

3. Consider scattering by the attractive square-well potential of Problem 1. Obtain an expression for the scattering length. Hence, show that, though the bombarding energy tends to zero, the s-wave scattering cross-section σ_0 tends to a finite value.

4. Use the Born approximation to calculate the differential cross-section for scattering by the central potential $V(r) = \alpha/r^2$, where α is a constant. Given that

$$\int_0^\infty \frac{\sin x}{x}\,dx = \frac{\pi}{2}$$

5. Consider scattering by the Yukawa potential

$$V(r) = \frac{V_0 \exp(-\alpha r)}{r}$$

where V_0 and α are constants. In the limit $E \longrightarrow 0$, show that the differential scattering cross-section is independent of θ and ϕ.

6. Show that an attractive potential leads to positive phase shifts whereas a repulsive potential to negative phase shifts.

7. Use Born approximation to obtain differential scattering cross-section when a particle moves in the potential

$$V(r) = -V_0 \exp\left(-\frac{r}{r_0}\right)$$

V_0 and r_0 are positive constants. Given that

$$\int_0^\infty x e^{-ax} \sin(bx)\,dx = \frac{2ab}{(a^2+b^2)^2}$$

8. Calculate the scattering amplitude for a particle moving in the potential

$$V(r) = V_0 \frac{(c-r)}{r} \exp\left(-\frac{r}{r_0}\right)$$

where V_0 and r_0 are constants. Given that

$$\int_0^\infty e^{-ax} \sin(bx)\,dx = \frac{b}{a^2+b^2}$$

9. In scattering from a potential $V(r)$; the wave function $\psi(r)$ is written as an incident plane wave plus an outgoing scattered wave: $\psi = e^{ikz} + f(r)$. Derive a differential equation for $f(r)$ in the first Born approximation.

10. Use Born approximation to calculate the differential scattering cross section for a particle of mass m moving in the potential $V(r) = A \exp(-r^2/a^2)$, A and a are constants. Given that

$$\int_0^\infty e^{-a^2x^2} \cos bx \, dx = \frac{\sqrt{\pi}}{2a} \exp\left(\frac{-b^2}{4a^2}\right)$$

11. A particle of mass m and energy E is scattered by a spherically symmetric potential $A\delta(r - a)$, where A and a are constants. Calculate the differential scattering cross section when the energy is very high.

12. For the attractive square well potential

$$V = -V_0 \quad \text{for} \quad 0 \le r < a; \quad V = 0 \quad \text{for} \quad r > a$$

Calculate the scattering cross section for a low energy particle by the method of partial wave analysis. Compare the result with the Born approximation result.

Chapter 15

Relativistic Wave Equations

The quantum mechanics developed so far does not satisfy the requirements of special theory of relativity as it is based on a nonrelativistic Hamiltonian. The wave equation we used to discuss physical problems is of first order in time and of second order in space coordinates. This contradicts the space–time symmetry requirement of relativity. These difficulties suggest two ways of obtaining relativistic wave equations: (i) to use a relativistic Hamiltonian for a free particle in place of nonrelativistic one (ii) to try for a first-order equation in both space and time coordinates. Though Schrödinger himself suggested the first possibility (1926), its implications were studied in detail by Klein and Gordon (1926). Hence, it is popularly known as Klein–Gordon equation. It does not say anything about the spin of the particle. It is now used to describe spin zero particles such as π-meson, K-meson, etc. Based on the second idea, Dirac developed his relativistic wave equation. The concept of spin has evolved automatically from Dirac's theory which is applicable to spin-(1/2) systems.

15.1 KLEIN–GORDON EQUATION

The nonrelativistic Schrödinger equation was obtained by replacing $\mathbf{p}$ by $-i\hbar\nabla$ and E by $i\hbar\frac{\partial}{\partial t}$ in the classical energy expression of a free particle $E = p^2/(2m)$ and allowing the resulting operator equation to operate on the wave function. The corresponding relativistic energy relation is

$$E^2 = c^2p^2 + m^2c^4 \tag{15.1}$$

where m is the rest mass of the particle. For convenience, rest mass will be denoted by m in this chapter. Replacing E and $\mathbf{p}$ by the respective operators, we get the operator equation

$$-\hbar^2\frac{\partial^2}{\partial t^2} = -c^2\hbar^2\nabla^2 + m^2c^4 \tag{15.2}$$

Allowing this operator equation to operate on the wave function $\Psi(\mathbf{r}, t)$

$$-\hbar^2\frac{\partial^2\Psi(\mathbf{r},t)}{\partial t^2} = -\hbar^2c^2\nabla^2\,\Psi(\mathbf{r}, t) + m^2c^4\,\Psi(\mathbf{r}, t) \tag{15.3}$$

which is *Klein–Gordon equation* or *Schrödinger's relativistic equation*. Rearranging, we get

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Psi\,(\mathbf{r}, t) = \frac{m^2c^2}{\hbar^2}\,\Psi(\mathbf{r}, t) \tag{15.4}$$

or

$$\Box\,\Psi(\mathbf{r}, t) = \frac{m^2c^2}{\hbar^2}\,\Psi(\mathbf{r}, t);\ \Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} \tag{15.5}$$

where $\Box$ is the *de Alembertian operator* which is relativistically invariant. Therefore, Eq. (15.5) is relativistically invariant if Ψ transforms like a scalar.

Plane-wave Solution

The plane wave represented by

$$\Psi(\mathbf{r}, t) = \exp\,[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \tag{15.6}$$

is an eigenfunction of both energy and momentum operators with eigenvalues $\hbar\omega$ and $k\hbar$ respectively. Substitution of Eq. (15.6) in Eq. (15.4) gives

$$(\hbar\omega)^2 = c^2\hbar^2k^2 + m^2c^4$$

or

$$\hbar\omega = \pm\,(c^2\hbar^2k^2 + m^2c^4)^{1/2} \tag{15.7}$$

This means that the energy eigenvalue can have both positive and negative values. Klein and Gordon were not able to give a consistent explanation for the negative energy.

15.2 INTERPRETATION OF THE KLEIN–GORDON EQUATION

In the nonrelativistic case, the position probability density $P(\mathbf{r}, t)$ is defined as $|\Psi\,(\mathbf{r}, t)|^2$ and the probability current density $j(\mathbf{r}, t)$ is given by Eq. (2.56). $P(\mathbf{r}, t)$ and $j(\mathbf{r}, t)$ satisfy the equation of continuity, Eq. (2.57), which is invariant under Lorentz transformation. Therefore, it is reasonable to expect the same continuity relation to be valid in the relativistic case, too.

Multiplying Eq. (15.3) on the left by Ψ^*, and the complex conjugate equation on the left by Ψ and then subtracting one from the other, we get

$$\Psi^* \frac{\partial^2 \Psi}{\partial t^2} - \Psi \frac{\partial^2 \Psi^*}{\partial t^2} = c^2(\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*)$$

or

$$\frac{\partial}{\partial t}\left(\Psi^* \frac{\partial \Psi}{\partial t} - \Psi \frac{\partial \Psi^*}{\partial t}\right) = c^2 \nabla \cdot (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)$$

or

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) + \nabla \cdot j(\mathbf{r}, t) = 0 \tag{15.8}$$

which is the equation of continuity. Here,

$$P(\mathbf{r}, t) = \frac{i\hbar}{2mc^2}\left(\Psi^* \frac{\partial \Psi}{\partial t} - \Psi \frac{\partial \Psi^*}{\partial t}\right) \tag{15.9}$$

and

$$j(\mathbf{r}, t) = \frac{i\hbar}{2m}(\Psi \nabla \Psi^* - \Psi^* \nabla \Psi) \tag{15.10}$$

That is, to get the equation of continuity in the relativistic theory, we have to define the position probability density by Eq. (15.9) and the probability current density by Eq. (15.10). This expression for $j(\mathbf{r}, t)$ is identical with the one in the nonrelativistic case. However, the expression for $P(\mathbf{r}, t)$ is completely different from the one in the nonrelativistic case.

We now investigate Eq. (15.9) in detail. If Ψ is real $P(\mathbf{r}, t)$ vanishes. When Ψ is complex, to get a better picture, Eq. (15.9) can be written as

$$\begin{aligned} P(\mathbf{r}, t) &= \left[\Psi^* i\hbar \frac{\partial \Psi}{\partial t} + \Psi\left(-i\hbar \frac{\partial}{\partial t}\right)\Psi^*\right]\frac{1}{2mc^2} \\ &= \frac{1}{2mc^2}[\Psi^* E \Psi + \Psi E \Psi^*] \\ &= \frac{E}{mc^2}|\Psi|^2 \end{aligned} \tag{15.11}$$

It follows from Eq. (15.11) that $P(\mathbf{r}, t)$ is positive when E is positive and negative when E is negative. In other words, the probability density takes both positive and negative values. Hence $P(\mathbf{r}, t)$ given by Eq. (15.9) cannot be regarded as position probability density.

Due to these reasons the Klein–Gordon equation was at first discarded. This dilemma was resolved by Pauli and Weisskopf in 1934. They interpreted eP as the electrical charge density and ej as the corresponding electric current density. This is reasonable as charges can take positive or negative values. If the system has a single particle of given charge, P cannot have different signs at different points. That means the theory is useful only to a system of particles having both signs of charges. With this reinterpretation, it is considered as a relativistic equation for a system of arbitrary number of particles and their antiparticles.

15.3 PARTICLE IN A COULOMB FIELD

A *Coulomb field* is described by a potential of the type $V(r) = -Ze^2/r$. The wave equation for a charged particle in the Coulomb field $V(r)$ can be obtained by writing $E - V(r)$ in place of E in Eq. (15.1), replacing $\mathbf{p}$ and E by their operators and allowing the resulting operator equation to operate on $\Psi(\mathbf{r}, t)$:

$$(E - V)^2 = c^2p^2 + m^2c^4 \tag{15.12}$$

or

$$\left(i\hbar\frac{\partial}{\partial t} + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\Psi(\mathbf{r}, t) = (-c^2\hbar^2\nabla^2 + m^2c^4)\,\Psi(\mathbf{r}, t) \tag{15.13}$$

Since the potential is independent of time, Eq. (15.13) can be separated with respect to the variables $\mathbf{r}$ and t by writing

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\left(-\frac{iEt}{\hbar}\right) \tag{15.14}$$

Substituting this value of $\Psi(\mathbf{r}, t)$ in Eq. (15.13) and rearranging, we get

$$\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2 \psi(\mathbf{r}) = (-c^2\hbar^2\nabla^2 + m^2c^4)\psi(\mathbf{r}) \tag{15.15}$$

Equation (15.15) can be separated in spherical coordinates by writing

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) \tag{15.16}$$

and expressing ∇^2 in (r, θ, ϕ) coordinates. On simplification, we get the radial equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{l(l+1)}{r^2}R = \frac{1}{c^2\hbar^2}\left[m^2c^4 - \left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2\right]R \tag{15.17}$$

Equation (15.17) reduces to the nonrelativistic radial equation for hydrogen atom if we put $E = E' + mc^2$ and assume that E' and $Ze^2/4\pi\varepsilon_0 r$ are very small in comparison with mc^2. If we define

$$\rho = \alpha r, \qquad \text{where } \alpha^2 = \frac{4(m^2c^4 - E^2)}{c^2\hbar^2} \tag{15.18}$$

and

$$\gamma = \frac{Ze^2}{4\pi\varepsilon_0 c\hbar}, \qquad \lambda = \frac{2E\gamma}{c\hbar\alpha} \tag{15.18a}$$

Equation (15.17) reduces to

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)-\gamma^2}{\rho^2}\right]R=0 \tag{15.19}$$

The form of Eq. (15.19) is the same as that of Eq. (5.48) except for the factor $l(l+1)-\gamma^2$ in place of $l\ (l + 1)$. If we write

$$s(s + 1) = l(l+1)-\gamma^2 \tag{15.20}$$

Equation (15.19) takes a convenient form

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right)+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{s(s+1)}{\rho^2}\right]R=0 \tag{15.21}$$

It follows from Section 5.4 that a well-behaved solution of Eq. (15.21) exists only if

$$\lambda = n' + s + 1, \qquad n' = 0, 1, 2, \ldots \tag{15.22}$$

and s has to be nonnegative to make $R(r)$ finite at the origin. The value of s can be obtained from Eq. (15.20) as

$$s = \frac{-1\pm(1+4l^2+4l-4\gamma^2)^{1/2}}{2} = -\frac{1}{2}\pm\left[\left(l+\frac{1}{2}\right)^2-\gamma^2\right]^{1/2} \tag{15.23}$$

For $l > 0$, the plus sign leads to a positive value for s and minus sign to a negative value. For $l = 0$, both the s values given by Eq. (15.20) are negative and the function $R(r)$ diverges at the origin. Since γ is very small in most of the cases of interest (Z-small) the plus sign leads to s very close to zero and the minus sign gives s close to -1. In the case of heavy nuclei, the interaction at short distances between nuclei and π-mesons is no longer Coulombic and the divergence of $R(r)$ at the origin is not of interest. Substituting the values of s(+ sign) and λ in Eq. (15.22), we get

$$\frac{E\gamma}{(m^2c^4-E^2)^{1/2}} = n'+\frac{1}{2}+\left[\left(l+\frac{1}{2}\right)^2-\gamma^2\right]^{1/2} \tag{15.24}$$

$$= n'+\frac{1}{2}+\left(l+\frac{1}{2}\right)\left[1-\frac{\gamma^2}{2\left(l+\frac{1}{2}\right)^2}\right] \tag{15.24a}$$

Writing

$$n' + l + 1 = n, \qquad \left[n-\frac{\gamma^2}{2\left(l+\frac{1}{2}\right)}\right]^2 = A$$

and rearranging, we have

$$\frac{E^2\gamma^2}{A} = m^2c^4 - E^2$$

or

$$E = mc^2\left(1+\frac{\gamma^2}{A}\right)^{-1/2}$$

or

$$E = mc^2\left(1-\frac{\gamma^2}{2A} + \frac{3\gamma^4}{8A^2}\right) = mc^2\left(1-\frac{\gamma^2A^{-1}}{2}+\frac{3\gamma^4A^{-2}}{8}\right)$$

Expanding A^{-1} and A^{-2} by binomial series and retaining terms up to γ^4

$$E = mc^2\left\{1-\frac{\gamma^2}{2n^2}\left[1+\frac{2\gamma^2}{2n\left(l+\frac{1}{2}\right)}\right] + \frac{3\gamma^4}{8n^4}\right\}$$

$$= mc^2\left[1 - \frac{\gamma^2}{2n^2} - \frac{\gamma^4}{2n^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right)\right] \tag{15.25}$$

The first term in Eq. (15.25) is the 'rest energy' and the second term $-mc^2\gamma^2/(2n^2)$ $= -Z^2me^4/(2\hbar^2n^2)$ is simply the 'nonrelativistic energy expression' of the hydrogen atom. The third term is the 'relativistic correction' which removes the l-degeneracy. This term is often referred to the *fine structure energy*. From Eq. (15.25), the total spread of the fine structure levels for a given n is

$$-\frac{mc^2\gamma^4}{2n^4}\left[\left(\frac{n}{n-1+\frac{1}{2}}-\frac{3}{4}\right)-\left(\frac{n}{\frac{1}{2}}-\frac{3}{4}\right)\right]=\frac{2mc^2\gamma^4}{n^3}\frac{n-1}{2n-1}$$

The spread observed experimentally in the hydrogen spectrum is only about half of this. Agreement is better for π-mesonic atoms.

15.4 DIRAC'S EQUATION FOR A FREE PARTICLE

The occurrence of negative probability density (in Section 15.2) is due to the presence of time derivatives in the expression for $P(\mathbf{r}, t)$. This can be avoided by not allowing any time derivative other than the first order to appear in the wave equation. When the wave equation is of first order in time, it must be first order in space coordinates too. Dirac was probably influenced by the Maxwell's equations as they are first order equations in both space and time coordinates.

As in Klein–Gordon equation, we can start from the basic energy equation, Eq. (15.1).

$$E = \pm (c^2p^2 + m^2c^4)^{1/2}$$

Replacing E by $i\hbar\,\partial/\partial t$ and p by $-i\hbar\nabla$ and allowing the resulting operator equation to operate on the wavefunction $\Psi(\mathbf{r}, t)$, we get

$$i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} = \pm(-c^2\hbar^2\nabla^2 + m^2c^4)^{1/2}\,\Psi(\mathbf{r}, t) \tag{15.26}$$

To proceed further, we have to define the square root of an operator which is not yet defined. However, Dirac boldly wrote

$$c^2p^2 + m^2c^4 = [c(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta mc)]^2 \tag{15.27}$$

and then searched for conditions to be placed on the α's and β so that the equation is valid. For Eq. (15.27) to hold true, we must have

$$\left.\begin{aligned} \alpha_x^2 = \alpha_y^2 = \alpha_z^2 = \beta^2 = 1 \\ \alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \\ \alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0 \end{aligned}\right\} \tag{15.28}$$

That is, the α's and β anticommute in pairs and their squares are unity. These properties immediately suggest that they cannot be numbers. Already, we have a set of anticommuting matrices, the Pauli's spin matrices. Hence, it is convenient to express them in terms of matrics. The energy can now be written as

$$E = \pm c(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z + \beta mc) \tag{15.29}$$

The positive or negative sign can be taken since replacement of α by $-\alpha$ and β by $-\beta$ does not change the relationships between α's and β. Hence the relativistic Hamiltonian of a particle can be taken as

$$E = H = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 \tag{15.29a}$$

Replacing E and $\mathbf{p}$ by their operators and allowing the resulting operator equation to operate on $\Psi(\mathbf{r}, t)$, we have

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -ic\hbar\left(\alpha_x\frac{\partial}{\partial x} + \alpha_y\frac{\partial}{\partial y} + \alpha_z\frac{\partial}{\partial z}\right)\Psi(\mathbf{r}, t) + \beta mc^2\,\Psi(\mathbf{r}, t) \tag{15.30}$$

which is *Dirac's relativistic equation* for a free particle.

15.5 DIRAC MATRICES

The Hamiltonian in Eq. (15.29a) has to be Hermitian and therefore the matrices α_x, α_y, α_z and β must be Hermitian and hence square. The eigenvalues of all the four matrices are ± 1, since their squares are unity. We have

$$\alpha_x = \alpha_x\beta^2 = \alpha_x\beta\beta = -\beta\alpha_x\beta$$

and

$$\text{tr}\ \alpha_x = \text{tr}\ (-\beta\alpha_x\beta) = -\text{tr}\ (\alpha_x\beta^2) = -\text{tr}\ \alpha_x \tag{15.31}$$

In the third step the cyclic property of trace of matrices, i.e. tr (ABCD) = tr (BCDA), is used. It is evident from (15.31) that tr $\alpha_x = 0$ which is possible only when the number of +1 eigenvalues is equal in number to the −1 eigenvalues. This restricts the dimension n of α_x to an even number. These results are applicable to α_y, α_z and β matrices also.

We have already three anticommuting 2 × 2 matrices, the Pauli's spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The squares of each of these matrices is unity. It can be shown that a fourth matrix that anticommutes with these three cannot be found. The next possibility is $n = 4$. Arbitrarily, β matrix is taken to be diagonal with two +1 eigenvalues and two −1 eigenvalues. Then one can easily find the 3 other 4 × 4 matrices anticommuting with β and satisfying the other conditions specified by Eq. (15.28). They are:

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \tag{15.32a}$$

$$a_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \tag{15.32b}$$

$$\alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \tag{15.32c}$$

$$\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{15.32d}$$

Obviously these matrices are Hermitian since σ_x, σ_y and σ_z are Hermitian. The matrices given in Eqs. (15.32a) – (15.32d) are the Dirac matrices in the standard representation. Other representations are also possible. Since α's and β are 4 × 4 matrices, the Dirac wavefunction $\Psi(\mathbf{r}, t)$ must be a four-column vector:

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}, \qquad \Psi^\dagger = (\Psi_1^*, \Psi_2^*, \Psi_3^*, \Psi_4^*) \tag{15.33}$$

These wavefunctions do not transform as four vectors. They are sometimes referred to as *Dirac spinors.*

The counterpart of a Schrödinger operator in Dirac's theory is a 4 × 4 diagonal matrix. Thus, the Schrödinger operators x and p_x are represented as:

$$x \Rightarrow \begin{pmatrix} x & 0 & 0 & 0 \\ 0 & x & 0 & 0 \\ 0 & 0 & x & 0 \\ 0 & 0 & 0 & x \end{pmatrix}, \qquad p_x \Rightarrow \begin{pmatrix} p_x & 0 & 0 & 0 \\ 0 & p_x & 0 & 0 \\ 0 & 0 & p_x & 0 \\ 0 & 0 & 0 & p_x \end{pmatrix} \tag{15.34}$$

15.6 COVARIANT FORM OF DIRAC EQUATION

To make sure relativistic invariance, Dirac required that the equation must be of first order in time and space coordinates (Section 15.4). Though this requirement is achieved (Eq. 15.30), it is not in the covariant form. We shall now express it in the covariant form. Multiplying Eq. (15.30) by $\beta/(c\hbar)$ and using the result $\beta^2 = 1$, we get

$$i\beta\alpha \cdot \nabla\Psi + \frac{i\beta}{c}\frac{\partial\Psi}{\partial t} - \frac{mc}{\hbar}\Psi = 0$$

or

$$i\beta \sum_{k=1}^{3} \alpha_k \frac{\partial\Psi}{\partial x_k} + \frac{i\beta}{c}\frac{\partial\Psi}{\partial t} - \frac{mc}{\hbar}\Psi = 0 \tag{15.35}$$

Introducing a new matrix γ defined by

$$\gamma_k = -i\beta\alpha_k, \qquad k = 1, 2, 3 \quad \text{and} \quad \gamma_4 = \beta \tag{15.35a}$$

Equation (15.35) takes the form

$$-\sum_{k=1}^{3} \gamma_k \frac{\partial\Psi}{\partial x_k} - \frac{\gamma_4}{ic}\frac{\partial\Psi}{\partial t} - \frac{mc}{\hbar}\Psi = 0$$

Defining the four vector x_μ to have components

$$x_1, x_2, x_3, x_4 = ix_0 = ict \tag{15.36}$$

the above equation can be written as

$$\left(\sum_{\mu=1}^{4} \gamma_\mu \frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar} \right)\Psi = 0 \tag{15.36a}$$

In the covariant formulation, it is the practice to write

$$\sum_{\mu=1}^{4} x_\mu y_\mu \text{ as } x_\mu y_\mu \quad \text{and} \quad \frac{\partial}{\partial x_\mu} \text{ as } \partial_\mu$$

Equation (15.36a) now takes the form

$$\left(\gamma_\mu \frac{\partial}{\partial x_\mu} + \frac{mc}{\hbar}\right)\Psi = 0 \tag{15.37}$$

which is also written as

$$\left(\gamma_\mu \partial_\mu + \frac{mc}{\hbar}\right)\Psi = 0 \tag{15.37a}$$

Equation (15.37a) is the covariant form of Dirac equation. That is, if the state vector transforms under Lorentz transformation in the prescribed form, Dirac's equation is relativistically invariant. If it does not transform in the required way, it is possible to construct Lorentz covariant from Ψ.

15.7 PROBABILITY DENSITY

Dirac's wave equation and its Hermitian conjugate equation are given by:

$$i\hbar \frac{\partial \Psi}{\partial t} = -ic\hbar\boldsymbol{\alpha} \cdot \nabla\Psi + \beta mc^2\Psi \tag{15.38}$$

and

$$-i\hbar \frac{\partial \Psi^\dagger}{\partial t} = ic\hbar\nabla\Psi^\dagger \cdot \boldsymbol{\alpha} + \Psi^\dagger\beta mc^2 \tag{15.39}$$

The Hermitian property of α and β and the rule that the order of factors in any matrix product is reversed on Hermitian conjugation are used while writing Eq. (15.39). Multiplying Eq. (15.38) by $\Psi^\dagger$ on left, Eq. (15.39) by Ψ on right and subtracting one from the other, we get

$$i\hbar\left(\Psi^\dagger \frac{\partial \Psi}{\partial t} - \frac{\partial \Psi^\dagger}{\partial t}\Psi\right) = -ic\hbar\,(\Psi^\dagger\boldsymbol{\alpha} \cdot \nabla\Psi + \nabla\Psi^\dagger \cdot \boldsymbol{\alpha}\Psi)$$

or

$$\frac{\partial}{\partial t}(\Psi^\dagger\Psi) + \nabla \cdot (c\Psi^\dagger\boldsymbol{\alpha}\,\Psi) = 0$$

or

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} + \nabla \cdot j(\mathbf{r}, t) = 0 \tag{15.40}$$

where

$$P(\mathbf{r}, t) = \Psi^\dagger\Psi \quad \text{and} \quad j(\mathbf{r}, t) = c\Psi^\dagger\boldsymbol{\alpha}\Psi \tag{15.41}$$

Equation (15.40) is the continuity equation and the quantities $P(\mathbf{r}, t)$ and $j(\mathbf{r}, t)$ can be interpreted as probability density and probability current density. The expression for P has the same form as the nonrelativistic one. In the nonrelativistic limit, $j(\mathbf{r}, t)$ in Eq. (15.41) reduces to the one in Eq. (2.56). The normalization integral in Dirac's formalism takes the form

$$\int \Psi^{\dagger}(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d\tau = 1 \tag{15.42}$$

The expectation value of any operator A is defined by

$$\langle A \rangle = \int \Psi^{\dagger}(\mathbf{r}, t)\, A\Psi(\mathbf{r}, t)\, d\tau \tag{15.43}$$

where the wave function Ψ is a normalized one.

15.8 PLANE WAVE SOLUTION

With 4×4 matrices for α and β and a column vector with four rows for Ψ, Dirac's equation is equivalent to four simultaneous first-order differential equations that are linear and homogeneous in the four components Ψ_1, Ψ_2, Ψ_3 and Ψ_4. We now try plane wave solutions of the form

$$\Psi_j(\mathbf{r}, t) = u_j\, e^{i(kr - \omega t)}, \quad j = 1, 2, 3, 4 \tag{15.44}$$

These Ψ_j's are eigenfunctions of energy and momentum with eigenvalues $E = \hbar\omega$ and $\mathbf{p} = \mathbf{k}\hbar$ respectively. Substitution of Eqs. (15.44) and (15.33) in Eq. (15.30) gives

$$Eu = (c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2)u \tag{15.45}$$

where u is a four column vector partitioned into two components as given below.

$$u = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = \begin{pmatrix} v \\ w \end{pmatrix}, \quad v = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}, \quad w = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix} \tag{15.46}$$

Substituting Eq. (15.46) in Eq. (15.45), we get

$$E\begin{pmatrix} v \\ w \end{pmatrix} = c\begin{pmatrix} 0 & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & 0 \end{pmatrix}\begin{pmatrix} v \\ w \end{pmatrix} + mc^2\begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}\begin{pmatrix} v \\ w \end{pmatrix} \tag{15.47}$$

Carrying out the multiplication and rearranging, we have

$$(E - mc^2)v = c(\boldsymbol{\sigma} \cdot \mathbf{p})w \tag{15.48}$$

$$(E + mc^2)w = c(\boldsymbol{\sigma} \cdot \mathbf{p})v \tag{15.49}$$

Remember that each one of these represents two equations as σ is a 2×2 matrix and v and w are two-component column vectors.

Multiplying Eq. (15.48) by $(E + mc^2)$ and replacing $(E + mc^2)w$ on the right side by Eq. (15.49), we have

$$(E^2 - m^2c^4)v = c(\boldsymbol{\sigma}\cdot\mathbf{p})\, c(\boldsymbol{\sigma}\cdot\mathbf{p})v = c^2(\boldsymbol{\sigma}\cdot\mathbf{p})^2 v \tag{15.50}$$

Since

$$(\boldsymbol{\sigma}\cdot\mathbf{p})^2 = p^2,$$

$$(E^2 - m^2c^4)v = c^2p^2v \quad \text{or} \quad (E^2 - c^2p^2 - m^2c^4)v = 0 \tag{15.51}$$

For a nontrivial solution, $v \neq 0$. Hence

$$E^2 - c^2p^2 - m^2c^4 = 0 \quad \text{or} \quad E = \pm(c^2p^2 + m^2c^4)^{1/2} \tag{15.52}$$

Thus, Dirac equation gives positive and negative energy solutions as in the Klein-Gordon equation.

We shall now determine the energy eigenfunctions. There will be four independent solutions: two for E_+ and two for E_-. In principle, one can use either Eq. (15.48) or Eq. (15.49). From Eq. (15.48), $v = c(\boldsymbol{\sigma}\cdot\mathbf{p})w/(E - mc^2)$. When $p = 0$, $E_+ = mc^2$, v becomes indeterminate. Hence, Eq. (15.49) is used with E_+ and Eq. (15.48) with E_-. For convenience, we may take v or w to be arbitrary and then determine the other.

E_+ eigenvalue: Taking the simplest possibilities

$$v = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and using the relation

$$(\boldsymbol{\sigma}\cdot\mathbf{p}) = \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix} \tag{15.53}$$

we get two independent solutions for E_+. From Eq. (15.49), with

$$v = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

We have

$$\begin{aligned} w &= \frac{c(\boldsymbol{\sigma}\cdot\mathbf{p})v}{E_+ + mc^2} \\ &= \frac{c}{E_+ + mc^2}\begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} cp_z/(E_+ + mc^2) \\ cp_+/(E_+ + mc^2) \end{pmatrix}, \quad \text{where } p_+ = p_x + ip_y \end{aligned} \tag{15.54}$$

For the other solution

$$v = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

We have

$$w = \frac{c}{E_+ + mc^2}\begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \begin{pmatrix} cp_-/(E_+ + mc^2) \\ -cp_z/(E_+ + mc^2) \end{pmatrix}, \quad \text{where } p_- = p_x - ip_y \tag{15.55}$$

Thus, for the eigenvalue E_+, the two independent solutions are:

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ cp_z/(E_+ + mc^2) \\ cp_+/(E_+ + mc^2) \end{pmatrix} \quad \text{and} \quad u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ cp_-/(E_+ + mc^2) \\ -cp_z/(E_+ + mc^2) \end{pmatrix} \tag{15.56}$$

In the same way, for E_-, the two solutions are:

$$u^{(3)} = \begin{pmatrix} cp_z/(E_- - mc^2) \\ cp_+/(E_- - mc^2) \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad u^{(4)} = \begin{pmatrix} cp_-/(E_- - mc^2) \\ -cp_z/(E_- - mc^2) \\ 0 \\ 1 \end{pmatrix} \tag{15.57}$$

In the nonrelativistic limit, $|p| << mc$, $|p_x| << mc$, $|p_y| << mc$ and $|p_z| << mc$. Therefore, $E_+ \cong mc^2$ and $E_- \cong -mc^2$. Consequently,

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad u^{(3)} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad u^{(4)} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{15.58}$$

As we decrease **p**, the third and the fourth components of $u^{(1)}$ and $u^{(2)}$ decrease and finally become zero whereas the first and second components remain the same. Hence, the first and second together are often referred to as *large components* and the third and fourth as *small components*. For $u^{(3)}$ and $u^{(4)}$, the first and the second are small components.

15.9 NEGATIVE ENERGY STATES

Each of Eqs. (15.48) and (15.49) consists of two equations, since σ is a 2×2 matrix. Hence E_+ and E_- occur twice. When $p = 0$, $E_+ = mc^2$ and $E_- = -mc^2$. The energy spectrum of a free particle has two branches corresponding to E_+ and E_-: one starting at mc^2 and extending to $+\infty$ as $|p| \longrightarrow \infty$ and the other starting at $-mc^2$ and extending to $-\infty$ as $|p| \longrightarrow \infty$ (Figure 15.1). The two branches are separated by a *forbidden gap* of width $2mc^2$. No energy level exists in the forbidden gap.

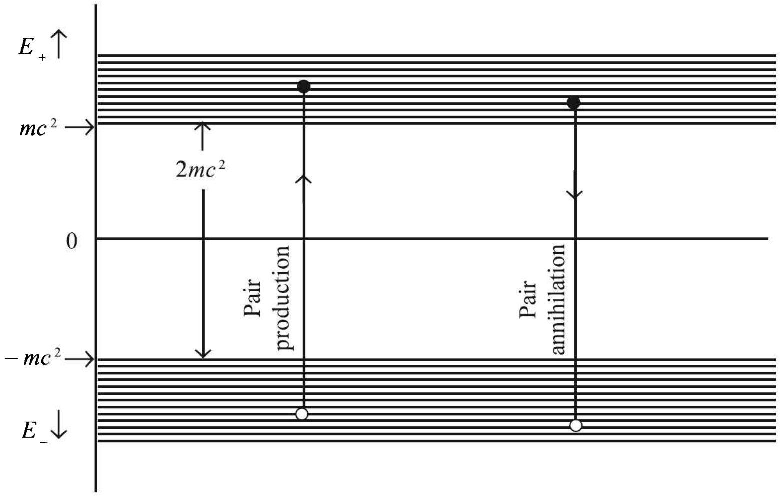


Figure 15.1 The energy levels of a free Dirac particle.

It is very difficult to imagine such negative energy states because even a small perturbation could cause a transition in an electron in a positive energy state to a state of negative energy, thereby releasing an enormous amount of energy. No such thing takes place in reality. To solve this difficulty, Dirac assumed that all negative energy states are ordinarily occupied by electrons and this sea of *negative energy electrons* have no physically observable effects. It is further assumed that when electron occupying the negative energy state picks up energy and goes to the positive energy state, it takes its place as an ordinary observable electron. The empty space in the midst of the negative energy states behaves as if it is a particle of positive charge. It responds to electric and magnetic fields. The empty space is called a *hole*. This explanation was accepted in 1932 when positron was discovered.

15.10 SPIN OF THE DIRAC PARTICLE

The spin of an electron carries no energy and therefore it can be observed only through its coupling with the orbital motion of the electron. This can be demonstrated through the conservation of total angular momentum and through the spin–orbit coupling energy.

We have already seen that a dynamical variable that is conserved should commute with the Hamiltonian. Consider the orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. The time rate of change of L_x for a particle, whose Hamiltonian is given by Eq. (15.29a), in the Heisenberg picture is

$$\begin{aligned} i\hbar\frac{dL_x}{dt} &= [L_x, H] \\ &= [yp_z - zp_y, c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2] \\ &= [yp_z, c\alpha_y p_y] - [zp_y, c\alpha_z p_z] \end{aligned} \tag{15.59}$$

since α and β commute with $\mathbf{r}$ and $\mathbf{p}$, all the other commutators vanish. Equation (15.59) now takes the form

$$\begin{aligned} i\hbar\frac{dL_x}{dt} &= c[y,\, p_y]p_z\alpha_y - c[z,\, p_z]\, p_y\alpha_z \\ &= ic\hbar[\alpha_y p_z - \alpha_z p_y] \end{aligned} \tag{15.60}$$

Equation (15.60) shows that L_x is not a constant of motion. Similar relations hold good for L_y and L_z. Hence, the orbital angular momentum $\mathbf{L}$ is not a constant of motion. However, on physical grounds we expect the system to have a total angular momentum which is a constant of motion. Therefore, there must be another contribution to angular momentum, such that the commutator of its x-component with H is the negative of the right side of Eq. (15.60).

We now show that the desired additional contribution comes from the operator $|\hbar\boldsymbol{\sigma}'$, where

$$\boldsymbol{\sigma}' = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \tag{15.61}$$

The equation of motion of its x-component is

$$\begin{aligned} i\hbar\frac{d\sigma'_x}{dt} &= [\sigma'_x,\, c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2] \\ &= [\sigma'_x,\, c\alpha_x p_x] + [\sigma'_x,\, c\alpha_y p_y] + [\sigma'_x,\, c\alpha_z p_z] \end{aligned} \tag{15.62}$$

since σ'_x commutes with β. It is not very difficult to prove that

$$[\sigma'_x,\, \alpha_x] = 0, \quad [\sigma'_x,\, \alpha_y] = 2i\alpha_z, \quad [\sigma'_x,\, \alpha_z] = -2i\alpha_y \tag{15.63}$$

Substituting these commutators in Eq. (15.62), we have

$$i\hbar\frac{d\sigma'_x}{dt} = -2ic(\alpha_y p_z - \alpha_z p_y)$$

or

$$i\hbar\frac{d}{dt}\left(\frac{1}{2}\hbar\sigma'_x\right) = -ic\hbar(\alpha_y p_z - \alpha_z p_y) \tag{15.64}$$

which is the negative of the right side of Eq. (15.60). Similar expressions hold good for the other components of $\boldsymbol{\sigma}'$ also. Combining Eqs. (15.60) and (15.64), we have

$$\frac{d}{dt}\left(L_x + \frac{1}{2}\hbar\sigma'_x\right) = 0 \quad \text{or} \quad L_x + \frac{1}{2}\hbar\sigma'_x = \text{constant} \tag{15.65}$$

It is now obvious that $\mathbf{L} + \frac{1}{2}\hbar\boldsymbol{\sigma}'$ commutes with the Hamiltonian and can therefore be taken as the total angular momentum. From the structure of the $\boldsymbol{\sigma}'$ matrix we can write

$$\sigma_x'^2 = \sigma_y'^2 = \sigma_z'^2 = 1$$

This gives the eigenvalues of $\frac{1}{2}\hbar\sigma'$ as $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. Hence, the additional part

$$\mathbf{S} = \frac{1}{2}\hbar\sigma' = \frac{1}{2}\hbar\begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix} \tag{15.66}$$

can be interpreted as the spin angular momentum of the electron. Thus, the concept of spin has evolved automatically from Dirac's Hamiltonian.

15.11 MAGNETIC MOMENT OF THE ELECTRON

We now discuss the intrinsic magnetic moment associated with the spin of the electron. For that, we consider an electron in an electromagnetic field having a vector potential **A** and scalar potential ϕ. Replacing E by $E - e\phi$ and **p** by $\mathbf{p} - (e\mathbf{A}/c)$, we get the Dirac equation:

$$[E - e\phi - \alpha \cdot (c\mathbf{p} - e\mathbf{A}) - \beta mc^2]\, \Psi(\mathbf{r}, t) = 0 \tag{15.67}$$

Operating Eq. (15.67) on the left by

$$(E - e\phi) + \alpha \cdot (c\mathbf{p} - e\mathbf{A}) + \beta mc^2$$

we get

$$[E - e\phi + \alpha\cdot (c\mathbf{p} - e\mathbf{A}) + \beta mc^2]\, [E - e\phi - \alpha\cdot (c\mathbf{p} - e\mathbf{A}) - \beta mc^2]\Psi = 0 \tag{15.68}$$

Since β commutes with E,

$$\beta mc^2(E - e\phi) - (E - e\phi)\beta mc^2 = 0 \tag{15.69}$$

The anticommuting property of β with α gives

$$-\alpha \cdot (c\mathbf{p} - e\mathbf{A})\beta mc^2 - \beta mc^2\, \alpha \cdot (c\mathbf{p} - e\mathbf{A}) = 0 \tag{15.70}$$

Equation (15.68) now takes the form

$$\begin{aligned}\{(E - e\phi)^2 &- [\alpha \cdot (c\mathbf{p} - e\mathbf{A})]^2 - m^2c^4 - (E - e\phi)\, \alpha \cdot (c\mathbf{p} - e\mathbf{A}) \\ &+ \alpha \cdot (c\mathbf{p} - e\mathbf{A})\, (E - e\phi)\}\Psi = 0 \end{aligned}\tag{15.71}$$

The second term in Eq. (15.71) can be simplified using the relation

$$(\alpha \cdot \mathbf{P})\, (\alpha \cdot \mathbf{Q}) = (\mathbf{P} \cdot \mathbf{Q}) + i\sigma' \cdot (\mathbf{P} \times \mathbf{Q}) \tag{15.72}$$

where **P** and **Q** are operators commuting with α. Simplification also requires

$$\begin{aligned}(c\mathbf{p} - e\mathbf{A}) \times (c\mathbf{p} - e\mathbf{A})\Psi &= (-ce\, \mathbf{P} \times \mathbf{A} - ce\, \mathbf{A} \times \mathbf{P})\Psi \\ &= ice\hbar(\nabla \times \mathbf{A} + \mathbf{A} \times \nabla)\Psi \\ &= ice\hbar[(\nabla \times \mathbf{A})\Psi + \nabla\Psi \times \mathbf{A} + \mathbf{A} \times \nabla\Psi]\end{aligned}$$

Since the second and third terms together is zero and the magnetic induction of the electromagnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, the above equation reduces to

$$(c\mathbf{p} - e\mathbf{A}) \times (c\mathbf{p} - e\mathbf{A})\, \Psi = ice\hbar\mathbf{B}\, \Psi \tag{15.73}$$

Identifying both **P** and **Q** with (c**p** – e**A**)

$$[\boldsymbol{\alpha} \cdot (c\mathbf{p} - e\mathbf{A})]^2\Psi = (c\mathbf{p} - e\mathbf{A})^2\, \Psi - ce\hbar\, \boldsymbol{\sigma}' \cdot \mathbf{B}\Psi \tag{15.74}$$

Next we consider the last two terms of Eq. (15.71)

$$\begin{aligned}
&[-(E - e\phi)\, \boldsymbol{\alpha} \cdot (c\mathbf{p} - e\mathbf{A}) + \boldsymbol{\alpha} \cdot (c\mathbf{p} - e\mathbf{A})\, (E - e\phi)]\Psi \\
&\quad = [e\boldsymbol{\alpha} \cdot (E\mathbf{A} - \mathbf{A}E) - c\boldsymbol{\alpha} \cdot (E\mathbf{p} - \mathbf{p}E) + ce\boldsymbol{\alpha} \cdot (\phi\mathbf{p} - \mathbf{p}\phi) \\
&\quad\quad - e^2\boldsymbol{\alpha} \cdot (\phi A - A\phi)]\Psi
\end{aligned} \tag{15.75}$$

where the result that E commutes with $\boldsymbol{\alpha}$ is used. In this equation (E**p** – **p**E) = 0 since E commutes with **p**. As ϕ is a scalar, $\phi\mathbf{A} - \mathbf{A}\phi = 0$

$$(\phi\mathbf{p} - \mathbf{p}\phi)\Psi = -i\hbar\phi\, \nabla\Psi + i\hbar\nabla(\phi\Psi) = i\hbar(\nabla\phi)\Psi \tag{15.76}$$

$$(E\mathbf{A} - \mathbf{A}E)\Psi = i\hbar\frac{\partial(\mathbf{A}\Psi)}{\partial t} - i\hbar\mathbf{A}\frac{\partial\Psi}{\partial t} = i\hbar\frac{\partial A}{\partial t}\Psi \tag{15.77}$$

Hence, the last two terms of Eq. (15.71) together gives

$$\begin{aligned}
[ie\hbar\boldsymbol{\alpha} \cdot \frac{\partial\mathbf{A}}{\partial t} + ice\hbar\boldsymbol{\alpha} \cdot \nabla\phi]\Psi &= ice\hbar\boldsymbol{\alpha} \cdot \left(\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} + \nabla\phi\right)\Psi \\
&= -ice\hbar\boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon}\Psi
\end{aligned} \tag{15.78}$$

where $\boldsymbol{\varepsilon}$ is the electric field associated with the electromagnetic field. Combining all the contributions, Eq. (15.71) can now be written as

$$[(E - e\phi)^2 - (c\mathbf{p} - e\mathbf{A})^2 - m^2c^4 + ce\hbar\boldsymbol{\sigma}' \cdot \mathbf{B} - ice\hbar\boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon}]\Psi = 0 \tag{15.79}$$

The first-three terms are precisely what one gets in relativity for a charged particle in an electromagnetic field.

To get the physical significance of the last two terms in Eq. (15.79), one has to consider the nonrelativistic limit of the equation. The total energy E includes the rest energy mc^2 and $e\phi << mc^2$. Writing E as

$$E = E' + mc^2 \tag{15.80}$$

and assuming that $E' << mc^2$ in the nonrelativistic limit, we get

$$\begin{aligned}
(E - e\phi)^2 - m^2c^4 &= (E - e\phi + mc^2)\, (E - e\phi - mc^2) \\
&= (E' + 2mc^2 - e\phi)\, (E' - e\phi) \\
&\cong 2mc^2(E' - e\phi)
\end{aligned} \tag{15.81}$$

Substituting this result in Eq. (15.79) and dividing throughout by $2mc^2$, we have

$$E'\Psi = \left[\frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + e\phi - \frac{e\hbar}{2mc}\boldsymbol{\sigma}' \cdot \mathbf{B} + \frac{ie\hbar}{2mc}\boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon}\right]\Psi \tag{15.82}$$

The third term on the right side of Eq. (15.82) has the form of a magnetic moment $e\hbar\sigma'/(2mc)$ interacting with a magnetic field **B**. We have seen in Section 15.7 for a free particle with positive energy, the first and the second components of the four-component Ψ are the large components in the nonrelativistic limit. It can be proved that the same result is applicable even if the particle is not free. Therefore, the operator σ' Eq. (15.61) operating on the four-component Ψ is equivalent to σ'-operating on the large components alone. The corresponding magnetic moment of the electron is then given by

$$\boldsymbol{\mu} = \frac{e\hbar\sigma}{2mc} = \frac{e\mathbf{S}}{mc}, \qquad \text{since } \mathbf{S} = \frac{1}{2}\hbar\sigma \tag{15.83}$$

which is the value postulated by Uhlenbeck and Goudsmit. In the nonrelativistic limit, the last term of Eq. (15.82) tends to zero.

15.12 SPIN–ORBIT INTERACTION

We shall now proceed to show that the spin–orbit interaction also comes out automatically from the Dirac equation. The Dirac's Hamiltonian for an electron in a central field $V(r)$

$$H = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(r) \tag{15.84}$$

satisfies the wave equation

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = H\,\Psi(\mathbf{r},t) \tag{15.85}$$

As the Hamiltonian does not depend on time, Ψ can be written as

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})\exp\left(-\frac{iEt}{\hbar}\right) \tag{15.86}$$

This means that Ψ is an eigenfunction of $i\hbar(\partial/\partial t)$ with eigenvalue E. Again we write E as in Eq. (15.80) and the time independent $\psi(\mathbf{r})$, by two components as

$$\psi(\mathbf{r}) = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \tag{15.87}$$

where ψ_1 represents the first-two components and ψ_2 the other two. Writing the Dirac matrices also in the form

$$\boldsymbol{\alpha} = \begin{pmatrix}0 & \sigma\\ \sigma & 0\end{pmatrix}, \quad \beta = \begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix} \tag{15.88}$$

the equation satisfied by $\psi(\mathbf{r})$ can be written as

$$\begin{pmatrix}0 & c\sigma\cdot\mathbf{p}\\ c\sigma\cdot\mathbf{p} & 0\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} + \begin{pmatrix}mc^2 & 0\\ 0 & -mc^2\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} + V\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \left(E' + mc^2\right)\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \tag{15.89}$$

This equation can be separated into the following two coupled equations

$$(E' - V)\psi_1 - c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_2 = 0 \tag{15.90}$$

and

$$(E' + 2mc^2 - V)\psi_2 - c\,(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_1 = 0 \tag{15.91}$$

From Eq. (15.91), we get

$$\psi_2 = \frac{c(\boldsymbol{\sigma}\cdot\mathbf{p})\psi_1}{2mc^2\left(1+\dfrac{E'-V}{2mc^2}\right)}$$

$$= \left(1+\frac{E'-V}{2mc^2}\right)^{-1} \frac{c(\boldsymbol{\sigma}\cdot\mathbf{p})\psi_1}{2mc^2}$$

$$\cong \left(1-\frac{E'-V}{2mc^2}\right) \frac{c(\boldsymbol{\sigma}\cdot\mathbf{p})\psi_1}{2mc^2} \tag{15.92}$$

since $(E' - V) << 2mc^2$. Substituting this value of ψ_2 in Eq. (15.90)

$$E'\psi_1 = V\psi_1 + \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_1 - \frac{1}{4m^2c^2}\,(\boldsymbol{\sigma} \cdot \mathbf{p})\,(E' - V)(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_1 \tag{15.93}$$

The second and third term on the right side of Eq.(15.93) can be simplified using the properties of σ matrices and the results

$$[\mathbf{p}, V] = \mathbf{p}V - V\mathbf{p} = -i\hbar\nabla V \tag{15.94}$$

and

$$(\boldsymbol{\sigma} \cdot \mathbf{B})\,(\boldsymbol{\sigma} \cdot \mathbf{C}) = \mathbf{B} \cdot \mathbf{C} + i\boldsymbol{\sigma} \cdot (\mathbf{B} \times \mathbf{C}) \tag{15.95}$$

where **B** and **C** are operators. It follows that

$$(\boldsymbol{\sigma} \cdot \mathbf{p})\,(\boldsymbol{\sigma} \cdot \mathbf{p}) = (\sigma_x p_x + \sigma_y p_y + \sigma_z p_z)\,(\sigma_x p_x + \sigma_y p_y + \sigma_z p_z)$$

$$= (\sigma_x^2 p_x^2 + \sigma_y^2 p_y^2 + \sigma_z^2 p_z^2)$$

$$= p_x^2 + p_y^2 + p_z^2 = p^2 \tag{15.96}$$

Since E' commutes with σ and $\mathbf{p}$, use of the results $\mathbf{p}V = V\mathbf{p} - i\hbar\nabla V$ and Eq. (15.95) gives

$$(\boldsymbol{\sigma} \cdot \mathbf{p})\,(E' - V)\,(\boldsymbol{\sigma} \cdot \mathbf{p}) = E'(\boldsymbol{\sigma} \cdot \mathbf{p})\,(\boldsymbol{\sigma} \cdot \mathbf{p}) - (\boldsymbol{\sigma} \cdot \mathbf{p}V)\,(\boldsymbol{\sigma} \cdot \mathbf{p})$$

$$= E'p^2 - (\boldsymbol{\sigma} \cdot V\mathbf{p})\,(\boldsymbol{\sigma} \cdot \mathbf{p}) + i\hbar(\boldsymbol{\sigma} \cdot \nabla V)\,(\boldsymbol{\sigma} \cdot \mathbf{p}) \tag{15.97}$$

$$= E'p^2 - [(V\mathbf{p} \cdot \mathbf{p}\,) + i\boldsymbol{\sigma} \cdot (V\mathbf{p} \times \mathbf{p})]$$

$$+\, i\hbar[(\nabla V \cdot \mathbf{p}) + i\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p})]$$

$$= E'p^2 - Vp^2 + i\hbar(\nabla V \cdot \mathbf{p}) - \hbar\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}) \tag{15.98}$$

With these simplifications, Eq. (15.93) can now be written as

$$E'\psi_1 = \left[V + \frac{p^2}{2m} - \frac{E'p^2}{4m^2c^2} + \frac{Vp^2}{4m^2c^2} - \frac{i\hbar}{4m^2c^2}(\nabla V \cdot \mathbf{p}) + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}) \right] \psi_1 \tag{15.99}$$

Since the potential is spherically symmetric

$$\nabla V \cdot \mathbf{p} = -i\hbar \nabla V \cdot \nabla = -i\hbar \frac{dV}{dr}\frac{\partial}{\partial r} \tag{15.100}$$

and

$$\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}) = \frac{1}{2m^2c^2}\,\frac{\hbar}{2}\boldsymbol{\sigma} \cdot \frac{1}{r}\frac{dV}{dr}\,(\mathbf{r} \times \mathbf{p})$$

$$= \frac{1}{2m^2c^2}\,\frac{1}{r}\frac{dV}{dr}\mathbf{S} \cdot \mathbf{L} \tag{15.101}$$

where use has been made of Eq. (15.66). With these simplifications, it follows from Eq. (15.99) that

$$E'\psi_1 = \left(V + \frac{p^2}{2m} - \frac{E'-V}{4m^2c^2}p^2 - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S} \right)\psi_1 \tag{15.102}$$

The first and second terms on the right side together give the nonrelativistic Schrödinger equation. In the third term, we may replace $(E' - V)$ by $p^2/(2m)$ which is understandable as it is only a second-order term. When this is done, the term will be $p^4/(8m^3c^2)$. It has the form of the classical relativistic mass correction as can be seen from the following:

$$\begin{aligned} E' &= E - mc^2 \\ &= (c^2p^2 + m^2c^4)^{1/2} - mc^2 \\ &= mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8c^4m^4}\right) - mc^2 \\ &= \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{c^2m^3} \end{aligned} \tag{15.103}$$

The last term in Eq. (15.102) has no classical analogue. It is the spin–orbit interaction energy which is seen to appear here as an automatic consequence of the Dirac equation.

15.13 RADIAL EQUATION FOR AN ELECTRON IN A CENTRAL POTENTIAL

The relativistic Hamiltonian for an electron in a central potential $V(r)$ given by Eq. (15.84) can be written in an alternate form by taking $\mathbf{P} = \mathbf{r}$ and $\mathbf{Q} = \mathbf{p}$ in Eq. (15.72) as

$$(\boldsymbol{\alpha}\cdot\mathbf{r})\,(\boldsymbol{\alpha}\cdot\mathbf{p}) = \mathbf{r}\cdot\mathbf{p} + i\boldsymbol{\sigma}'\cdot\mathbf{L} \tag{15.104}$$

Let us define a new operator k by the relation

$$k\hbar = \beta(\boldsymbol{\sigma}'\cdot\mathbf{L} + \hbar)$$

$$(k-\beta)\hbar = \beta\boldsymbol{\sigma}'\cdot\mathbf{L} \tag{15.105}$$

or

$$\boldsymbol{\sigma}'\cdot\mathbf{L} = \frac{(k-\beta)\hbar}{\beta} \tag{15.106}$$

Substituting this value of $\boldsymbol{\sigma}'\cdot\mathbf{L}$ and multiplying both sides by $(\boldsymbol{\alpha}\cdot\mathbf{r})$, Eq. (15.104) takes the form

$$(\boldsymbol{\alpha}\cdot\mathbf{r})^2\,(\boldsymbol{\alpha}\cdot\mathbf{p}\,) = (\boldsymbol{\alpha}\cdot\mathbf{r})\left[\mathbf{r}.\mathbf{p}+\frac{i(k-\beta)\hbar}{\beta}\right] \tag{15.107}$$

or

$$\boldsymbol{\alpha}\,.\,\mathbf{p} = \frac{\boldsymbol{\alpha}\cdot\mathbf{r}}{r^2}\left(\mathbf{r}\cdot\mathbf{p}-i\hbar+\frac{ik\hbar}{\beta}\right) \tag{15.108}$$

since $(\boldsymbol{\alpha}\cdot\mathbf{r})^2 = r^2$. This expression for $(\boldsymbol{\alpha}\cdot\mathbf{p})$ can conveniently be expressed in terms of radial momentum operator p_r and radial velocity operator α_r defined by

$$p_r = \frac{\mathbf{r}\cdot\mathbf{p}-i\hbar}{r} \quad\text{and}\quad \alpha_r = \frac{\boldsymbol{\alpha}\cdot\mathbf{r}}{r} \tag{15.109}$$

In terms of p_r and α_r, Eq. (15.108) reduces to

$$\boldsymbol{\alpha}\cdot\mathbf{p} = \alpha_r\left(p_r+\frac{ik\beta\hbar}{r}\right) \tag{15.110}$$

since $ik\hbar/\beta = ik\hbar\beta/\beta^2 = ik\hbar\beta$. Substituting this value of $\boldsymbol{\alpha}\cdot\mathbf{p}$ in Eq. (15.84)

$$H = c\alpha_r p_r + \frac{ic\hbar\alpha_r k\beta}{r} + \beta mc^2 + V(r) \tag{15.111}$$

It can easily be verified that the operator k commutes with the Hamiltonian in Eq. (15.111).

Next we shall proceed to evaluate the eigenvalues of the operator k. Squaring Eq. (15.105), we get

$$k^2\hbar^2 = (\boldsymbol{\sigma}'\cdot\mathbf{L})^2 + 2\hbar\,(\boldsymbol{\sigma}'\cdot\mathbf{L}) + \hbar^2 \tag{15.112}$$

It follows from Eq. (15.72) that

$$\begin{aligned}(\boldsymbol{\sigma}'\cdot\mathbf{L})\,(\boldsymbol{\sigma}'\cdot\mathbf{L}) &= L^2 + i\boldsymbol{\sigma}'\cdot(\mathbf{L}\times\mathbf{L})\\ &= L^2 + i\boldsymbol{\sigma}'\cdot i\hbar\mathbf{L}\\ &= L^2 - \hbar(\boldsymbol{\sigma}'\cdot\mathbf{L})\end{aligned} \tag{15.113}$$

Consequently,

$$k^2\hbar^2 = L^2 + \hbar(\boldsymbol{\sigma}' \cdot \mathbf{L}) + \hbar^2 \tag{15.114}$$

Since

$$\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}' \quad \text{and} \quad S^2 = s(s+1)\,\hbar^2 = \frac{3\hbar^2}{4}$$

we have

$$\begin{aligned} k^2\hbar^2 &= L^2 + 2\mathbf{S}\cdot\mathbf{L} + \frac{3\hbar^2}{4} + \frac{\hbar^2}{4} \\ &= (\mathbf{L}+\mathbf{S})^2 + \frac{\hbar^2}{4} \\ &= J^2 + \frac{\hbar^2}{4} \end{aligned} \tag{15.115}$$

where $\mathbf{J} = \mathbf{L} + \mathbf{S}$, is the total angular momentum. Since J^2 has the eigenvalues $j(j+1)\hbar^2$, the above equation reduces to

$$k^2 = j(j+1) + \frac{1}{4} = \left(j + \frac{1}{2}\right)^2 \tag{15.116}$$

As $j = 1/2, 3/2, 5/2, \ldots$, the possible values of k are $\pm 1, \pm 2, \pm 3, \ldots$

The operators H and k commute and hence we can have a representation in which they are diagonal. It follows from the definition (Eq. 15.109) that $\alpha_r^2 = 1$ and $\alpha_r\beta + \beta\alpha_r = 0$. Also we have $\beta^2 = 1$. Hermitian matrices satisfying these relations can be 2×2 matrices and we select them as

$$\alpha_r = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{15.117}$$

As α_r and β are 2×2 matrices, the radial part of the wave function has the two components

$$\begin{pmatrix} \dfrac{F(r)}{r} \\ \dfrac{G(r)}{r} \end{pmatrix} \tag{15.118}$$

To obtain the radial equation for an electron moving in a central potential, as the first step one has to replace α_r, β and p_r in Eq. (15.111) using Eq. (15.117) and relation

$$p_r = -i\hbar\frac{\partial}{\partial r} - \frac{i\hbar}{r} \tag{15.119}$$

The resulting operator equation is then allowed to operate on the radial function in Eq. (15.118). This leads to the two-component equation:

$$\begin{aligned}&-ic\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\left(\frac{\partial}{\partial r}+\frac{1}{r^2}\right)\begin{pmatrix}\frac{F}{r}\\[4pt] \frac{G}{r}\end{pmatrix}+\frac{ic\hbar k}{r}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\frac{F}{r}\\[4pt] \frac{G}{r}\end{pmatrix}\\ &+mc^2\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\frac{F}{r}\\[4pt] \frac{G}{r}\end{pmatrix}+(V-E)\begin{pmatrix}\frac{F}{r}\\[4pt] \frac{G}{r}\end{pmatrix}=0\end{aligned} \tag{15.120}$$

Writing it into two equations:

$$\frac{dF}{dr}-\frac{kF}{r}-\frac{1}{c\hbar}(E+mc^2-V)G=0 \tag{15.121}$$

and

$$\frac{dG}{dr}+\frac{kG}{r}+\frac{1}{c\hbar}(E-mc^2-V)F=0 \tag{15.122}$$

One can solve these equations for the energy eigenvalues if the explicit form of $V(r)$ is known.

15.14 THE HYDROGEN ATOM

We now use Eqs. (15.121) and (15.122) to find the energy eigenvalues of hydrogen atom. For hydrogen atom, $V(r) = -Ze^2/4\pi\varepsilon_0 r$. It is convenient to introduce numerical substitutions defined by

$$\alpha=\frac{\left(m^2c^4-E^2\right)^{1/2}}{c\hbar}=\left(\frac{mc^2+E}{c\hbar}\right)^{1/2}\left(\frac{mc^2-E}{c\hbar}\right)^{1/2}=\alpha_1^{1/2}\alpha_2^{1/2} \tag{15.123}$$

where

$$\alpha_1=\frac{mc^2+E}{c\hbar},\qquad \alpha_2=\frac{mc^2-E}{c\hbar} \tag{15.124}$$

Introducing a new variable ρ defined by

$$\rho=\alpha r \tag{15.125}$$

Equations (15.121) and (15.122) can be reduced to

$$\frac{dF}{d\rho}-\frac{kF}{\rho}-\left(\frac{\alpha_1}{\alpha}+\frac{\gamma}{\rho}\right)G=0,\qquad \gamma=\frac{Ze^2}{4\pi\varepsilon_0 c\hbar} \tag{15.126}$$

and

$$\frac{dG}{d\rho}+\frac{kG}{\rho}-\left(\frac{\alpha_2}{\alpha}-\frac{\gamma}{\rho}\right)F=0 \tag{15.127}$$

As in the nonrelativistic case let us look for solution of the form

$$F(\rho) = \sum_{n=0}^{\infty} a_n \rho^{s+n} e^{-\rho}, \qquad a_0 \neq 0 \tag{15.128}$$

and

$$G(\rho) = \sum_{n=0}^{\infty} b_n \rho^{s+n} e^{-\rho}, \qquad b_0 \neq 0 \tag{15.129}$$

Substituting these equations in Eqs. (15.126) and (15.127) and equating the coefficients of ρ^{s+n-1} to zero, we get

$$(s + n - k)a_n - a_{n-1} - \gamma b_n - \frac{\alpha_1}{\alpha} b_{n-1} = 0 \tag{15.130}$$

and

$$(s + n + k)b_n - b_{n-1} + \gamma a_n - \frac{\alpha_2}{\alpha} a_{n-1} = 0 \tag{15.131}$$

When $n = 0$

$$(s - k)a_0 - \gamma b_0 = 0 \quad \text{and} \quad (s + k)b_0 + \gamma a_0 = 0 \tag{15.132}$$

For Eq. (15.132) to have nonvanishing solution, the determinant

$$\begin{vmatrix} s-k & -\gamma \\ \gamma & s+k \end{vmatrix} = 0 \quad \text{or} \quad s = \pm(k^2 - \gamma^2)^{1/2} \tag{15.133}$$

The negative solution is not acceptable as it would make F and G diverge at the origin. Hence the positive sign is the only acceptable solution. When $n > 0$, a relation between a_n and b_n can be obtained by multiplying Eq. (15.131) by α and (15.130) by α_2 and subtracting

$$b_n\,[(s + n + k)\alpha + \alpha_2\gamma] = a_n\,[\alpha_2\,(s + n - k) - \alpha\gamma] \tag{15.134}$$

where we have used the relation $\alpha^2 = \alpha_1\,\alpha_2$. As in the nonrelativistic case, regular solutions are possible only if both the series (15.128) and (15.129) terminate. Let this occurs at $n = n'$ so that $a_{n'+1} = b_{n'+1} = 0$. Replacing n by $(n' + 1)$ in Eq. (15.130), we have

$$(s + n' + 1 - k)\,a_{n'+1} - a_{n'} - \gamma b_{n'+1} - \frac{\alpha_1}{\alpha}\,b_{n'} = 0 \tag{15.135}$$

In view of the condition $a_{n'+1} = b_{n'+1} = 0$, Eq. (15.135) reduces to

$$b_{n'} = -\frac{\alpha}{\alpha_1} a_{n'}, \qquad n' = 0, 1, 2, \ldots \tag{15.136}$$

Equation (15.131) also gives the same condition between $b_{n'}$ and $a_{n'}$. The energy levels can be obtained by setting $n = n'$ in Eq. (15.134) and using Eq. (15.136)

$$-\frac{\alpha}{\alpha_1} a_{n'} \left[(s + n' + k)\,\alpha + \alpha_2 \gamma\right] = a_{n'} \left[\alpha_2 (s + n' - k) - \alpha\gamma\right]$$

or

$$2\alpha\,(s + n') = \gamma(\alpha_1 - \alpha_2)$$

Substituting the values of α_1, α_2, α and squaring, we get

$$(m^2c^4 - E^2)\,(s + n')^2 = E^2\gamma^2 \tag{15.137}$$

or

$$E = mc^2 \left[1 + \frac{\gamma^2}{(s+n')^2}\right]^{-1/2} \tag{15.138}$$

Expanding in powers of γ^2 and retaining terms of order γ^4

$$E = mc^2 \left[1 - \frac{\gamma^2}{2n^2} - \frac{\gamma^4}{2n^4}\left(\frac{n}{|k|} - \frac{3}{4}\right)\right] \tag{15.139}$$

where $n = n' + |k| = n' + j + \frac{1}{2}$ is the total quantum number of hydrogen atom (Section 5.4) and $|k|$ takes the values 1, 2, ..., n. To label the energy levels by l, the orbital angular momentum quantum number, we have to extend the discussion to nonrelativistic limit. When this is done, the values of l in terms of k are

$$l = |k| = j + \frac{1}{2} \qquad \text{for } k < 0$$

$$l = k - 1 = j - \frac{1}{2} \qquad \text{for } k > 0$$

The complete degeneracy of the energy level for a given n in the nonrelativistic case is partly lifted by relativistic effects. The coarse structure of the energy levels is determined by the quantum number n and the fine structure by $|k|$ or j. The total spread in the energy of the fine structure levels for a given value of n can easily be found by taking the difference in energy for the states $|k| = 1$ and $|k| = n$ which comes out as $mc^2\gamma^4(n - 1)/(2n^4)$. This is in agreement with experiment. The energy level scheme of the hydrogen atom for $n = 1$, 2, and 3 are illustrated in Figure 15.2.

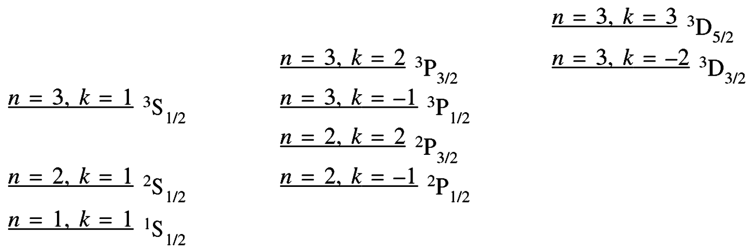


Figure 15.2 Energy-level scheme of hydrogen atom for n = 1, 2, and 3.

15.15 LAMB SHIFT

The energy level scheme for hydrogen atom (Figure 15.2) shows that degeneracy exists between the $^2S_{1/2}$ and $^2P_{1/2}$, the $^3S_{1/2}$ and $^3P_{1/2}$, the $^3P_{3/2}$ and $^3D_{3/2}$ etc. levels. The two states of a degenerate pair are eigenstates of k with opposite eigenvalues. As per Eq. (15.139) the levels $^2S_{1/2}$ and $^2P_{1/2}$ of the $n = 2$ state (in the spectroscopic notation this is $^2S_{1/2}$ and $^2P_{1/2}$) are degenerate. However, in 1947 Lamb and Rutherford observed a splitting of 1057 MHz between these two states which is called the *Lamb shift.*

Theoretical considerations on Lamb shift is beyond the scope of present discussion. The shift was accounted for on the basis of quantum electrodynamics. An interaction of the electron with its own field leads to a shifting of the $^2S_{1/2}$ energy level to a higher energy, producing energy difference between $^2S_{1/2}$ and $^2P_{1/2}$ levels.

WORKED EXAMPLES

EXAMPLE 15.1 Show that the following matrices form a representation of Dirac's matrices:

$$\alpha_x = \begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} \sigma_z & 0 \\ 0 & -\sigma_z \end{pmatrix}, \quad \beta = \begin{pmatrix} 0 & iI \\ -iI & 0 \end{pmatrix}$$

If these matrices obey the relations in Eq. (15.28), then they form a representation of Dirac's matrices.

$$\alpha_x^2 = \begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix}\begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix} = \begin{pmatrix} \sigma_x^2 & 0 \\ 0 & \sigma_x^2 \end{pmatrix} = 1$$

$$\alpha_y^2 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}\begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} = 1$$

$$\alpha_z^2 = \begin{pmatrix} \sigma_z & 0 \\ 0 & -\sigma_z \end{pmatrix}\begin{pmatrix} \sigma_z & 0 \\ 0 & -\sigma_z \end{pmatrix} = \begin{pmatrix} \sigma_z^2 & 0 \\ 0 & \sigma_z^2 \end{pmatrix} = 1$$

$$\beta^2 = \begin{pmatrix} 0 & iI \\ -iI & 0 \end{pmatrix}\begin{pmatrix} 0 & iI \\ -iI & 0 \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} = 1$$

and

$$\alpha_x\alpha_y + \alpha_y\alpha_x = \begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix}\begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} + \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}\begin{pmatrix} \sigma_x & 0 \\ 0 & -\sigma_x \end{pmatrix} = 0$$

The remaining relations can also be proved. Hence, the above four matrices form a representation of Dirac's matrices.

EXAMPLE 15.2 The probability current density is defined by the relation $\mathbf{j}(\mathbf{r}, t) = c\Psi^\dagger\alpha\Psi$, where Ψ is the four-component wave vector. Write expressions for j_x, j_y and j_z in terms of the components of Ψ.

We have

$$\mathbf{j}\,(\mathbf{r},\,t) = c\Psi^{\dagger}\boldsymbol{\alpha}\Psi,$$

Then

$$j_x = c\Psi^{\dagger}\alpha_x\Psi$$

$$j_x = c\begin{pmatrix}\Psi_1^* & \Psi_2^* & \Psi_3^* & \Psi_4^*\end{pmatrix}\begin{pmatrix}0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\end{pmatrix}$$

$$= c\begin{pmatrix}\Psi_1^* & \Psi_2^* & \Psi_3^* & \Psi_4^*\end{pmatrix}\begin{pmatrix}\Psi_4\\ \Psi_3\\ \Psi_2\\ \Psi_1\end{pmatrix} = c\left(\Psi_1^*\Psi_4 + \Psi_2^*\Psi_3 + \Psi_3^*\Psi_2 + \Psi_4^*\Psi_1\right)$$

Proceeding on similar line

$$j_y = ic\left(-\Psi_1^*\Psi_4 + \Psi_2^*\Psi_3 - \Psi_3^*\Psi_2 + \Psi_4^*\Psi_1\right)$$

and

$$j_z = c\left(\Psi_1^*\Psi_3 - \Psi_2^*\Psi_4 + \Psi_3^*\Psi_1 - \Psi_4^*\Psi_2\right)$$

EXAMPLE 15.3 Prove that the operator $c\boldsymbol{\alpha}$, where $\boldsymbol{\alpha}$ stands for Dirac matrix, can be interpreted as the velocity operator.

In the Heisenberg picture, the equation of motion of position vector **r** which has no explicit time dependence is given by

$$\frac{d\mathbf{r}}{dt} = \frac{1}{i\hbar}\,[\mathbf{r},\,H]; \qquad H = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2$$

Since $\boldsymbol{\alpha}$ commutes with x, the x-component of the above equation reduces to

$$\begin{aligned}\frac{dx}{dt} &= \frac{1}{i\hbar}[x,\,H]\\ &= \frac{1}{i\hbar}(xH - Hx)\\ &= \frac{c}{i\hbar}(x\alpha_x p_x - \alpha_x p_x x)\\ &= \frac{c}{i\hbar}\alpha_x\,(xp_x - p_x x)\\ &= c\,\alpha_x\end{aligned}$$

In the same way,

$$\frac{dy}{dt} = c\alpha_y \quad \text{and} \quad \frac{dz}{dt} = c\alpha_z$$

Hence $c\boldsymbol{\alpha}$ is the velocity vector.

EXAMPLE 15.4 Show that $(\boldsymbol{\alpha} \cdot \mathbf{A})\,(\boldsymbol{\alpha} \cdot \mathbf{B}) = (\mathbf{A} \cdot \mathbf{B}) + i\boldsymbol{\sigma}' \cdot (\mathbf{A} \times \mathbf{B})$, where **A** and **B** commute with $\boldsymbol{\alpha}$ and

$$\boldsymbol{\sigma}' = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}$$

We have

$$\begin{aligned}(\boldsymbol{\alpha} \cdot \mathbf{A})\,(\boldsymbol{\alpha} \cdot \mathbf{B}) &= (\alpha_x A_x + \alpha_y A_y + \alpha_z A_z)\,(\alpha_x B_x + \alpha_y B_y + \alpha_z B_z) \\ &= \alpha_x^2 A_x B_x + \alpha_y^2 A_y B_y + \alpha_z^2 A_z B_z + \alpha_x \alpha_y A_x B_y + \alpha_x \alpha_z A_x B_z \\ &\quad + \alpha_y \alpha_x A_y B_x + \alpha_y \alpha_z A_y B_z + \alpha_z \alpha_x A_z B_x + \alpha_z \alpha_y A_z B_y\end{aligned}$$

Since $\alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1$, $\alpha_x \alpha_y = -\alpha_y \alpha_x$ and the cyclic relations

$$\begin{aligned}(\boldsymbol{\alpha} \cdot \mathbf{A})\,(\boldsymbol{\alpha} \cdot \mathbf{B}) &= (\mathbf{A} \cdot \mathbf{B}) + \alpha_x \alpha_y (A_x B_y - A_y B_x) \\ &\quad + \alpha_y \alpha_z (A_y B_z - A_z B_y) + \alpha_z \alpha_x (A_z B_x - A_x B_z)\end{aligned}$$

where

$$\alpha_x \alpha_y = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}\begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} = \begin{pmatrix} \sigma_x \sigma_y & 0 \\ 0 & \sigma_x \sigma_y \end{pmatrix} = i\begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix} = i\sigma_z'$$

Using this results and the cyclic relations, we get

$$(\boldsymbol{\alpha} \cdot \mathbf{A})\,(\boldsymbol{\alpha} \cdot \mathbf{B}) = (\mathbf{A} \cdot \mathbf{B}) + i\boldsymbol{\sigma}' \cdot (\mathbf{A} \times \mathbf{B})$$

EXAMPLE 15.5 Consider the one dimensional Dirac equation:

$$i\hbar \frac{\partial \psi}{\partial t} = [c\alpha p_z + \beta mc^2 + V(z)]\psi; \quad p_z = -i\hbar \frac{\partial}{\partial z}$$

$$\alpha = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

Show that (i) $\sigma = \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}$ commutes with H (ii) The one dimensional Dirac equation can be written as two coupled first order differential equations.

The Hamiltonian

$$H = c\alpha\left(-i\hbar \frac{\partial}{\partial z}\right) + \beta mc^2 + V(z)$$

The commutator

$$[\sigma, \alpha] = \left[\begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}, \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}\right] = \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}\begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} - \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix}\begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}$$

$$= \begin{pmatrix} 0 & \sigma_z^2 \\ \sigma_z^2 & 0 \end{pmatrix} - \begin{pmatrix} 0 & \sigma_z^2 \\ \sigma_z^2 & 0 \end{pmatrix} = 0$$

In the same way,

$$[\sigma, \beta] = \left[\begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}, \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}\right] = 0$$

Hence

$$[\sigma, H] = c\,[\sigma, \alpha]\, p_z + [\sigma, \beta]\, mc^2 = 0$$

As $[\sigma, H] = 0$, the two operators σ and H have common eigenfunctions. σ is a diagonal matrix. Let its eigenfunction be

$$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$$

$$\sigma \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ -\psi_2 \\ \psi_3 \\ -\psi_4 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix} - \begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \psi_4 \end{pmatrix}$$

From the form of σ, it is obvious that $\begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \psi_4 \end{pmatrix}$ are eigenfunctions of σ with eigenvalues +1 and –1 respectively. Substituting these functions in the Dirac equation, we have

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix} = \left(-i\hbar c\, \alpha \frac{\partial}{\partial z} + \beta mc^2 + V \right) \begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix}$$

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \psi_4 \end{pmatrix} = \left(-i\hbar c\, \alpha \frac{\partial}{\partial z} + \beta mc^2 + V \right) \begin{pmatrix} 0 \\ \psi_2 \\ 0 \\ \psi_4 \end{pmatrix}$$

$$\alpha \begin{pmatrix} \partial\psi_1/\partial z \\ 0 \\ \partial\psi_3/\partial z \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \partial\psi_1/\partial z \\ 0 \\ \partial\psi_3/dz \\ 0 \end{pmatrix} = \frac{\partial}{\partial z} \begin{pmatrix} \psi_3 \\ 0 \\ \psi_1 \\ 0 \end{pmatrix}$$

$$\beta \begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ 0 \\ \psi_3 \\ 0 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ 0 \\ -\psi_3 \\ 0 \end{pmatrix}$$

In the same way,

$$\alpha\begin{pmatrix}0\\ \partial\psi_2/\partial z\\ 0\\ \partial\psi_4/\partial z\end{pmatrix}=\begin{pmatrix}0&0&1&0\\0&0&0&-1\\1&0&0&0\\0&-1&0&0\end{pmatrix}\begin{pmatrix}0\\ \partial\psi_2/\partial z\\ 0\\ \partial\psi_4/\partial z\end{pmatrix}=\frac{\partial}{\partial z}\begin{pmatrix}0\\-\psi_4\\0\\-\psi_2\end{pmatrix}$$

Substituting this in the Dirac equations, we have

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_1\\0\\\psi_3\\0\end{pmatrix}=-i\hbar c\frac{\partial}{\partial z}\begin{pmatrix}\psi_3\\0\\\psi_1\\0\end{pmatrix}+mc^2\begin{pmatrix}\psi_1\\0\\-\psi_3\\0\end{pmatrix}+V(z)\begin{pmatrix}\psi_1\\0\\\psi_3\\0\end{pmatrix}$$

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}0\\\psi_2\\0\\\psi_4\end{pmatrix}=-i\hbar c\frac{\partial}{\partial z}\begin{pmatrix}0\\-\psi_4\\0\\-\psi_2\end{pmatrix}+mc^2\begin{pmatrix}0\\\psi_2\\0\\-\psi_4\end{pmatrix}+V(z)\begin{pmatrix}0\\\psi_2\\0\\\psi_4\end{pmatrix}$$

Each of these represents two coupled differential equations.

REVIEW QUESTIONS

1. Explain how Klein–Gordon equation leads to positive and negative probability density values.
2. Klein–Gordon equation is considered as a relativistic equation for a system of arbitrary number of particles and their antiparticles. Why?
3. State the expression for energy of a charged particle obeying Klein–Gordon equation in a Coulomb potential. Explain the significance of the different terms.
4. Dirac preferred a first-order equation both in time and space coordinates. Why?
5. The dimension of Dirac's matrices has to be even. Why?
6. Express Dirac's equation in the covariant form.
7. Obtain expression for probability density and probability current density in the Dirac formalism.
8. Give the energy spectrum of a free Dirac particle and explain pair production and pair annihilation.
9. What are negative energy states? What is a hole?
10. What is Lamb shift?
11. The prediction of magnetic moment, spin–orbit interaction and concept of hole are the remarkable successes of Dirac's theory. Comment.
12. Give the physical interpretation of Dirac's α matrix.

PROBLEMS

1. Starting from the Klein–Gordon equation, obtain the equation of continuity.
2. Derive expressions for the probability density and probability current density in the Dirac theory.
3. For a Dirac particle moving in a central potential, show that the orbital angular momentum is not a constant of motion.
4. If radial momentum p_r and radial velocity α_r for an electron in a central potential are defined by

   $$p_\mathrm{r} = \frac{\mathbf{r}\cdot\mathbf{p} - i\hbar}{r} \qquad \alpha_\mathrm{r} = \frac{\boldsymbol{\alpha}\cdot\mathbf{r}}{r},$$

   show that

   $$\boldsymbol{\alpha}\cdot\mathbf{p} = \alpha_\mathrm{r} p_\mathrm{r} + \frac{i\hbar k\beta\alpha_\mathrm{r}}{r}$$

   where

   $$k = \frac{\beta(\boldsymbol{\sigma}'\cdot\mathbf{L} + \hbar)}{\hbar}$$

5. Obtain the eigenvalues of the operator

   $$k = \frac{\beta(\boldsymbol{\sigma}'\cdot\mathbf{L} + \hbar)}{\hbar}$$

6. If one wants to write the relativistic energy E of a free particle as

   $$\frac{E^2}{c^2} = (\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc)^2$$

   show that the α's and β have to be matrices and establish that they are nonsingular and Hermitian.
7. If $\boldsymbol{\sigma}' = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}$

   show that

   (i) $\sigma_x'^2 = \sigma_y'^2 = \sigma_z'^2 = 1$

   (ii) $[\sigma_x', \alpha_x] = 0$, $[\sigma_x', \alpha_y] = 2i\alpha_z$, $[\sigma_x', \alpha_z] = -2i\alpha_y$

   where $\boldsymbol{\sigma}$ is the Pauli matrix and α_x, α_y, α_z are the Dirac matrices.
8. Show that Matrix $\boldsymbol{\sigma}'$ as defined in Problem 7 is not a constant of motion.
9. Show that Dirac's Hamiltonian for a free particle commutes with the operator $\boldsymbol{\sigma}\cdot\mathbf{p}$ where $\mathbf{p}$ is the momentum operator and σ is the Pauli spin operators in the space of four component spinors.

Chapter 16

Elements of Field Quantization

The quantum mechanics we discussed so far dealt with a single particle or with systems having a fixed number of particles. Consequently, we were able to consider only processes in which the number of particles remain constant. Processes such as the beta decay, positron-electron pair creation and many of the processes occurring at high energies are beyond the scope of this formalism. Dirac's hole theory permits the creation of electron-positron pairs. The total lack of interaction between the electrons filling the infinite sea of negative energy states is yet another point without explanation. From these, it is obvious that a new theory should be developed to account for such phenomena. The result is the **quantum field theory**. The quantization of the electromagnetic field was the first to be achieved followed by the application of the techniques to other fields. At the early stages this was regarded as a ***second quantization***, the fields to be quantized were the wave functions used in one particle and many particle quantum mechanics. The quantization of energy and angular momentum is referred to as the ***first quantization***.

16.1 CONCEPTS OF CLASSICAL MECHANICS

The Lagrangian field theory is based on the classical mechanics formulated by Lagrange and Hamilton. In this section we summarize some of the basic ideas of classical mechanics which we need for the development of field theory.

(i) At any time the configuration of a mechanical system having n degrees of freedom is defined by the n generalized co-ordinates $q_1, q_2, q_3, \ldots, q_n$. The time derivatives $\dot{q}_1, \dot{q}_2, \dot{q}_3, \ldots, \dot{q}_n$ are the generalized velocities.

(ii) The Lagrangian L of a system is:

$$L(q, \dot{q}, t) = T(q, \dot{q}, t) - V(q) \tag{16.1}$$

where q stands for $q_1, q_2, q_3, \ldots, q_n$ and $\dot{q}$ stands for $\dot{q}_1, \dot{q}_2, \dot{q}_3, \ldots, \dot{q}_n$. The Lagrange's equations of motion are given by

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0, \quad i = 1, 2, 3, \ldots, n \tag{16.2}$$

(iii) The generalized momentum p_i conjugate to the generalized coordinate q_i is defined as:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \tag{16.3}$$

In terms of p_i, the Lagrange's equations of motion are:

$$\dot{p}_i = \frac{\partial L}{\partial q_i}; \quad i = 1, 2, 3, \ldots \tag{16.4}$$

(iv) The Hamiltonian H of a system is:

$$H(q, p, t) = \sum_i p_i \dot{q}_i - L(q, \dot{q}, t) \tag{16.5}$$

and the Hamilton's canonical equations of motion are:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}; \quad i = 1, 2, 3, \ldots, n \tag{16.6}$$

(v) The motion of a conservative holonomic system from its position at time t_1 to its position at time t_2 follows a path for which the line integral, called the **action integral**,

$$I = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt \tag{16.7}$$

has a stationary value, where $q_i(t)$ and $\dot{q}_i(t)$ are to be varied such that

$$\delta q_i(t_1) = \delta q_i(t_2) = 0$$

That is, the actual paths are the ones satisfying the variational principle

$$\delta I = \delta \int L\, dt = 0 \tag{16.8}$$

(vi) The Poisson bracket of two functions $F(q, p, t)$ and $G(q, p, t)$, written as $[F,G]$, is defined as:

$$[F,G]=\sum_i\left[\frac{\partial F}{\partial q_i}\frac{\partial G}{\partial p_i}-\frac{\partial F}{\partial p_i}\frac{\partial G}{\partial q_i}\right] \tag{16.9}$$

The equation of motion of function F in terms of Poisson bracket is:

$$\frac{dF}{dt}=[F,H]+\frac{\partial F}{\partial t} \tag{16.10}$$

16.2 CLASSICAL FIELD EQUATION—LAGRANGIAN FORM

For a mechanical system of particles, the number of independent degrees of freedom is finite. The quantization of such a system is done by the following procedures:

(i) Replacing the dynamical variables by corresponding operators as per postulate 2, Section 3.5. This makes the co-ordinates and momenta to follow the basic commutation relations:

$$[q_i, q_k]=[p_i, p_k]=0 \quad \text{and} \quad [q_i, p_k]=i\hbar\delta_{ik} \tag{16.11}$$

(ii) The classical equation of motion is then converted into quantum equation by replacing the Poisson bracket by the corresponding commutator bracket of the operators.

Co-ordinates of a Field

A physical system having infinite number of degrees of freedom is called a **field**. Hence it may be regarded as a system having infinite number of particles. A system of particles is specified by the position coordinates q_i, $i = 1, 2, 3, ...$ and their dependence on time t. In analogy with this concept, a field is specified by its amplitude $\Psi(\mathbf{r}, t)$ at all points of space and the dependence of these amplitudes on the time. In other words, the amplitudes $\Psi(\mathbf{r}, t)$ at all points $\mathbf{r}$ can be regarded as co-ordinates describing the field.

The amplitude function $\Psi(\mathbf{r}, t)$ can be expanded in terms of some complete orthonormal set of functions $u_k(\mathbf{r})$ as:

$$\Psi(\mathbf{r}, t) = \sum_k C_k(t)\ u_k(\mathbf{r}) \tag{16.12}$$

Here the expansion coefficients $C_k(t)$ can be considered as the field co-ordinates and the field equations are expressed either in terms of ψ or C_k depending on the situation.

Lagrangian Density

The basic ideas of classical mechanics mentioned in Section 16.1 with suitable modifications can be adopted for obtaining the classical field equations and their quantization. We expect the field Lagrangian to be a function of the field amplitude $\Psi(\mathbf{r}, t)$. One modification is the introduction of a **Lagrangian density** L which is a function of Ψ, $\nabla\Psi, \dot{\Psi}$ and t:

$$L = L(\Psi, \nabla\Psi, \dot{\Psi}, t) \tag{16.13}$$

The dependence on $\nabla\Psi$ is due to the continuous dependence of Ψ on $\mathbf{r}$.The Lagrangian L of the field would be an integral of L over the space

$$L = \int_V L\,(\Psi, \nabla\Psi, \dot{\Psi}, t)\, d^3\mathbf{r} \tag{16.14}$$

The variational principle that corresponds to Eq. (16.8) is:

$$\delta \int_{t_1}^{t_2} L\, dt = \delta \int_{t_1}^{t_2}\int_V L\,(\Psi, \nabla\Psi, \dot{\Psi}, t)\, d^3\mathbf{r}\, dt = 0$$

$$\int_{t_1}^{t_2}\int_V (\delta L)\, d^3\mathbf{r}\, dt = 0 \tag{16.15}$$

where the variation $\delta\Psi$ of Ψ is subjected to the condition:

$$\delta\Psi(\mathbf{r}, t_1) = \delta\Psi(\mathbf{r}, t_2) = 0 \tag{16.16}$$

Field Equation

The variation in L can easily be written from its form, Eq. (16.13):

$$\delta L = \frac{\partial L}{\partial \Psi}\delta\Psi + \frac{\partial L}{\partial(\nabla\Psi)}\delta(\nabla\Psi) + \frac{\partial L}{\partial\dot{\Psi}}\delta\dot{\Psi}$$

$$= \frac{\partial L}{\partial \Psi}\delta\Psi + \sum_{x,y,z} \frac{\partial L}{\partial(\partial\Psi/\partial x)}\delta\left(\frac{\partial\Psi}{\partial x}\right) + \frac{\partial L}{\partial\dot{\Psi}}\delta\dot{\Psi} \tag{16.17}$$

Here, the summation over x, y, z means the sum of the three terms with y and z substituted for x. Since

$$\delta\left(\frac{\partial\Psi}{\partial x}\right) = \frac{\partial}{\partial x}(\delta\Psi) \quad \text{and} \quad \delta\dot{\Psi} = \delta\left(\frac{\partial\Psi}{\partial t}\right) = \frac{\partial}{\partial t}(\delta\Psi)$$

Eq. (16.17) reduces to

$$\delta L = \frac{\partial L}{\partial \Psi}\delta\Psi + \sum_{x,y,z} \frac{\partial L}{\partial(\partial\Psi/\partial x)}\frac{\partial}{\partial x}(\delta\Psi) + \frac{\partial L}{\partial\dot{\Psi}}\frac{\partial}{\partial t}(\delta\Psi) \tag{16.18}$$

Substituting this value of δL in Eq. (16.15), we have

$$\int_{t_1}^{t_2}\int \left[\frac{\partial L}{\partial \Psi}\delta\Psi + \sum_{x,y,z} \frac{\partial L}{\partial(\partial\Psi/\partial x)}\frac{\partial}{\partial x}(\delta\Psi) + \frac{\partial L}{\partial\dot{\Psi}}\frac{\partial}{\partial t}(\delta\Psi)\right] d^3\mathbf{r}\, dt = 0 \tag{16.19}$$

Integrating the last term of Eq. (16.19) by parts,

$$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{\Psi}} \frac{\partial}{\partial t}(\delta \Psi)\, dt = \left[\frac{\partial L}{\partial \dot{\Psi}} \delta \Psi\right]_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\Psi}}\right) \delta \Psi\, dt$$

$$= -\int_{t_1}^{t_2} \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\Psi}}\right) \delta \Psi\, dt \tag{16.20}$$

since the integrated term vanishes by virtue of Eq. (16.16).

The second term in Eq. (16.19) can also be integrated by parts with respect to the space coordinates:

$$\int \sum_{x,y,z} \frac{\partial L}{\partial(\partial\Psi/\partial x)} \frac{\partial(\delta \Psi)}{\partial x} d^3\mathbf{r}$$

$$= \sum_{x,y,z} \iint \left[\int \frac{\partial L}{\partial(\partial\Psi/\partial x)} \frac{\partial(\delta \Psi)}{\partial x} dx\right] dydz$$

$$= \sum_{x,y,z} \left[\iint \left(\frac{\partial L}{\partial(\partial\Psi/\partial x)} \delta \Psi\right) dydz - \int_V \frac{\partial}{\partial x} \frac{\delta L}{\partial(\partial\Psi/\partial x)} \delta\ \Psi\, d^3\mathbf{r}\right]$$

$$= -\sum_{x,y,z} \int \frac{\partial}{\partial x} \frac{\partial L}{\partial(\partial\Psi/\partial x)} \delta \Psi\, d^3\mathbf{r} \tag{16.21}$$

since the first term vanishes either because Ψ falls off rapidly at infinity or it obeys periodic boundary conditions at the walls of a large but finite box. Equation (16.19) can now be written as:

$$\int_{t_1}^{t_2} dt \int d^3\mathbf{r} \left[\frac{\partial L}{\partial \Psi} - \sum_{x,y,z} \frac{\partial}{\partial x}\left(\frac{\partial L}{\partial(\partial\Psi/\partial x)}\right) - \frac{\partial}{\partial t}\frac{\partial L}{\partial \dot{\Psi}}\right] \delta \Psi = 0 \tag{16.22}$$

Equation (16.15) or Eq. (16.22) is valid for any arbitrary variation $\delta \Psi$ at each point in space and, therefore, the integrand in the square bracket of Eq. (16.22) must vanish. Hence

$$\frac{\partial L}{\partial \Psi} - \sum_{x,y,z} \frac{\partial}{\partial x}\left(\frac{\partial L}{\partial(\partial\Psi/\partial x)}\right) - \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\Psi}}\right) = 0 \tag{16.23}$$

Equation (16.23) is the **classical field equation** in terms of the Lagrangian density $L(\Psi, \nabla\Psi, \dot{\Psi}, t)$. It is the analogue of the Euler-Lagrange's equations.

Functional Derivative

To understand the similarity with classical mechanics, Eq. (16.23) has to be expressed in terms of Lagrangian of the field L. For this, derivatives of L with respect to Ψ and $\dot{\Psi}$ at particular points, called **functional derivatives** and denoted by $\partial L/\partial\Psi$ and $\partial L/\partial\dot{\Psi}$, are required. The value of a function at a point r depends on the value of its arguments, whereas the value of a functional depends on the values of its arguments over a whole region or range. Expressions for functional derivatives can be obtained by dividing the volume V into small cells and replacing volume integrals by summations over these cells. The volume of the i^{th} cell is denoted by $\delta\tau_i$ and the average values of Ψ, $\nabla\Psi$ and $\dot{\Psi}$ in the i^{th} cell are distinguished by adding a subscript i. In the limit all the $\delta\tau_i$ approach zero

$$\sum_i L\,[\Psi_i, (\nabla\Psi)_i, \dot{\Psi}_i, t]\,\delta\tau_i \rightarrow L(\Psi, \dot{\Psi}) \tag{16.24}$$

The t integrand in Eq. (16.22) can now be written as:

$$\sum_i \left\{\frac{\partial L}{\partial\Psi} - \sum_{x,y,z}\frac{\partial}{\partial x}\left[\frac{\partial L}{\partial(\partial\Psi/\partial x)}\right]\right\}_i \delta\Psi_i\delta\tau_i + \sum_i \left(\frac{\partial L}{\partial\dot{\Psi}}\right)_i \delta\dot{\Psi}_i\,\delta\tau_i \tag{16.25}$$

Assuming all the $\delta\Psi_i$'s and $\delta\dot{\Psi}_i$'s are zero except for a particular $\delta\Psi_j$, the functional derivative of L with respect to Ψ for a point in the j^{th} cell can be defined as:

$$\frac{\partial L}{\partial\Psi} = \lim_{\delta\tau_j\to 0}\frac{\delta L}{\delta\Psi_j\,\delta\tau_j} \tag{16.26}$$

In the same way,

$$\frac{\partial L}{\partial\dot{\Psi}} = \lim_{\delta\tau_j\to 0}\frac{\delta L}{\delta\dot{\Psi}_j\,\delta\tau_j} \tag{16.27}$$

Using Eq. (16.24), we can write these equations as:

$$\frac{\partial L}{\partial\Psi} = \lim_{\delta\tau_j\to 0}\frac{\delta L}{\delta\Psi_j\,\delta\tau_j} = \frac{\partial L}{\partial\Psi} - \sum_{xyz}\frac{\partial}{\partial x}\left[\frac{\partial L}{\partial(\partial\Psi/\partial x)}\right] \tag{16.28}$$

and

$$\frac{\partial L}{\partial\dot{\Psi}} = \lim_{\delta\tau_j\to 0}\frac{\delta L}{\delta\dot{\Psi}_j\,\delta\tau_j} = \frac{\partial L}{\partial\dot{\Psi}} \tag{16.28a}$$

The additional term in Eq. (16.28a) vanished since $\mathcal{L}$ is not a function of $\nabla\dot{\Psi}$. Substitution of Eqs. (16.28) and (16.28a) in Eq. (16.23), the classical field equation takes the form:

$$\frac{\partial}{\partial t}\frac{\partial L}{\partial\dot{\Psi}} - \frac{\partial L}{\partial\Psi} = 0 \tag{16.29}$$

which resembles the Lagrange's equation for a system of particles.

16.3 CLASSICAL FIELD EQUATION—HAMILTONIAN FORM

In particle mechanics, to pass on from the Lagrangian form to Hamiltonian form, we define a momentum p_i conjugate to each co-ordinate q_i. In analogy with Eq. (16.3), the momentum P_i conjugate to the canonical co-ordinate Ψ_i is defined by

$$P_i = \frac{\partial L}{\partial \dot{\Psi}_i} \tag{16.30}$$

In terms of functional derivatives,

$$P_i = \left(\frac{\partial L}{\partial \dot{\Psi}_i}\right)\delta\tau_i \tag{16.31}$$

where $\delta\tau_i$ is the volume of the i^{th} cell. In view of Eqs. (16.29) and (16.31),

$$\dot{P}_i = \left(\frac{\partial L}{\partial \Psi_i}\right)\delta\tau_i \tag{16.32}$$

The analogy with particle mechanics gives for the Hamiltonian

$$H = \sum_i P_i \dot{\Psi}_i - L \tag{16.33}$$

Going over to the continuum limit, where Ψ_i is regarded as the value of $\Psi(r, t)$ in the i^{th} cell

$$\begin{aligned} H &= \lim_{\delta\tau_i \to 0} \left[\sum_i \pi_i \dot{\Psi}_i \delta\tau_i - \sum_i L_i \delta\tau_i\right] \\ &= \int [\pi(\mathbf{r}, t)\, \dot{\Psi}(\mathbf{r}, t) - L]\, d^3\mathbf{r} \\ &= \int H\, d^3(\mathbf{r}) \end{aligned} \tag{16.34}$$

where

$$H = \pi(\mathbf{r}, t)\, \dot{\Psi}(\mathbf{r}, t) - L \tag{16.35}$$

is called the **Hamiltonian density** and $\pi(\mathbf{r}, t)$, called the **conjugate field**, is:

$$\pi(\mathbf{r}, t) = \frac{\partial L}{\partial \dot{\Psi}} = \frac{\partial L}{\partial \dot{\Psi}} \tag{16.36}$$

Substituting this value of π in Eq. (16.29),

$$\frac{\partial \pi}{\partial t} - \frac{\partial L}{\partial \Psi} = 0 \quad \text{or} \quad \dot{\pi} = \frac{\partial L}{\partial \Psi} \tag{16.37}$$

The variation of L produced by variations of ψ and $\dot{\psi}$ can be written as:

$$\begin{aligned} \delta L &= \int \left(\frac{\partial L}{\partial \Psi}\delta\Psi + \frac{\partial L}{\partial \dot{\Psi}}\delta\dot{\Psi}\right) d^3\mathbf{r} \\ &= \int \left(\dot{\pi}\,\delta\Psi + \pi\,\delta\dot{\Psi}\right) d^3\mathbf{r} \end{aligned}$$

$$= \int [\dot{\pi}\,\delta\Psi + \delta(\pi\dot{\Psi}) - \dot{\Psi}\delta\pi]\, d^3\mathbf{r} \tag{16.38}$$

We have

$$H = \int H\, d^3\mathbf{r} = \int (\pi\dot{\Psi} - L)\, d^3\mathbf{r}$$

$$\delta H = \int \delta(\pi\dot{\Psi})\; d^3\mathbf{r} - \delta\int L\; d^3\mathbf{r}$$

Using Eq. (16.14),

$$\delta H + \delta L = \int \delta(\pi\dot{\Psi})\; d^3\mathbf{r} \tag{16.39}$$

Combining Eqs. (16.38) and (16.39),

$$\delta H = \int (\dot{\Psi}\delta\pi - \dot{\pi}\,\delta\Psi)\; d^3\mathbf{r} \tag{16.40}$$

The variation of H produced by variations of Ψ and π is:

$$\delta H = \int \left(\frac{\partial H}{\partial\Psi}\delta\Psi + \frac{\partial H}{\partial\pi}\delta\pi \right) d^3\mathbf{r} \tag{16.41}$$

Comparison of Eqs. (16.40) and (16.41) for arbitrary variations $\delta\Psi$ and $\delta\pi$ gives

$$\dot{\Psi} = \frac{\partial H}{\partial\pi} \quad \text{and} \quad \dot{\pi} = -\frac{\partial H}{\partial\Psi} \tag{16.42}$$

These are referred to as **classical field equations in Hamiltonian form.**

Consider a functional F of Ψ and π. Expressing F as the volume integral of the corresponding **functional density** $\mathfrak{I}(\Psi, \pi, t)$, the time rate of change of the function F is:

$$\frac{dF}{dt} = \int \left(\frac{\partial\mathfrak{I}}{\partial t} + \frac{\partial\mathfrak{I}}{\partial\Psi}\dot{\Psi} + \frac{\partial\mathfrak{I}}{\partial\pi}\dot{\pi} \right) d^3\mathbf{r} = \frac{\partial F}{\partial t} + \int \left(\frac{\partial\mathfrak{I}}{\partial\Psi}\dot{\Psi} + \frac{\partial\mathfrak{I}}{\partial\pi}\dot{\pi} \right) d^3\mathbf{r}$$

Replacing $\dot{\Psi}$ and $\dot{\pi}$ using Eq. (16.42),

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \int \left(\frac{\partial F}{\partial\Psi}\frac{\partial H}{\partial\pi} - \frac{\partial F}{\partial\pi}\frac{\partial H}{\partial\Psi} \right) d^3\mathbf{r} \tag{16.43}$$

The second term on the right is defined as the Poisson bracket for two field variables. Hence

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\}_{P.B} \tag{16.44}$$

$$\{F, H\}_{P.B} = \int \left(\frac{\partial F}{\partial\Psi}\frac{\partial H}{\partial\pi} - \frac{\partial F}{\partial\pi}\frac{\partial H}{\partial\Psi} \right) d^3\mathbf{r} \tag{16.45}$$

16.4 QUANTIZATION OF THE FIELD

To quantize the field, we regard the field variables Ψ and π as operator functions. Just as the quantum conditions,

$$[q_i, q_j] = [p_i, p_j] = 0; \quad [q_i, q_j] = i\hbar\, \delta_{ij} \tag{16.46}$$

were used for the transition from classical to quantum particle mechanics, we achieve the transition from classical to quantum field theory by requiring that

$$[\Psi_i, \Psi_j] = [P_i, P_j] = 0 \quad \text{and} \quad [\Psi_i, P_j] = i\hbar\, \delta_{ij} \tag{16.47}$$

Assuming the cell volumes are very small, Eq. (16.47) can be rewritten in terms of Ψ and π in the following forms:

$$[\Psi(\mathbf{r}, t), \Psi(\mathbf{r}', t)] = [\pi(\mathbf{r}, t), \pi(\mathbf{r}', t)] = 0 \tag{16.48a}$$

$$[\Psi(\mathbf{r}, t), \pi(\mathbf{r}', t)] = i\hbar\delta\,(\mathbf{r}, \mathbf{r}') \tag{16.48b}$$

where $\delta(\mathbf{r}, \mathbf{r}') = 1/\delta\tau_i$ if $\mathbf{r}$ and $\mathbf{r}'$ are in the same cell and zero otherwise. In the limit, the cell volume approach zero, $\delta(\mathbf{r}, \mathbf{r}')$ can be replaced by the three dimensional Dirac δ-function $\delta(\mathbf{r} - \mathbf{r}')$. The quantum conditions for the canonical field variables Ψ and π then become

$$[\Psi(\mathbf{r}, t), \Psi(\mathbf{r}', t)] = [\pi(\mathbf{r}, t), \pi(\mathbf{r}', t)] = 0 \tag{16.49a}$$

$$[\Psi(\mathbf{r}, t), \pi(\mathbf{r}', t)] = i\hbar\, \delta(\mathbf{r} - \mathbf{r}') \tag{16.49b}$$

By making Ψ and π non-commuting operators, we convert H, L etc., also into operators; which have eigenvalues, eigenstates, etc.

The equation of motion for any quantum dynamical variable F is obtained from Eq. (16.44) by replacing the Poisson bracket by the commutater bracket divided by $i\hbar$ or from Eq. (3.106).

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \frac{1}{i\hbar}[F, H] \tag{16.50}$$

Equations (16.49) and (16.50) completely describe the behaviour of the quantized field specified by the Hamiltonian.

16.5 QUANTIZATION OF THE SCHRÖDINGER EQUATION

As an example of the field quantization technique, we shall consider the quantization of the non-relativistic Schrödinger equation in this section. The name Schrödinger field is used for a field $\Psi(\mathbf{r}, t)$ satisfying the Schrödinger equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \tag{16.51}$$

Equation (16.51) is the quantized equation of motion of a particle of mass m moving in a potential V. Here $\Psi(\mathbf{r}, t)$ is thought of as a classical field, which can be quantized by converting it into an operator using the procedure described earlier. Since it is the second time the equation is being quantized, it is referred to as the **second quantization**.

To start with, we note that the Lagrangian density L taken in the form:

$$L = i\hbar\Psi^*\dot{\Psi} - \frac{\hbar^2}{2m}\nabla\Psi^*.\nabla\Psi - V(\mathbf{r}, t)\Psi^*\Psi \tag{16.52}$$

reduces the classical field equation, Eq. (16.23), to the familiar Schrödinger equation, Eq. (16.51). Ψ and Ψ^* in Eq. (16.52) can be considered as independent fields giving the Lagrange's equations of motion. The variation with respect to Ψ^* in Eq. (16.23) directly gives Eq. (16.51) while variation with respect to Ψ gives the complex conjugate of Eq. (16.51):

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* \tag{16.53}$$

The momentum canonically conjugate to Ψ is:

$$\pi = \frac{\partial L}{\partial\dot{\Psi}} = i\hbar\,\Psi^* \tag{16.54}$$

where we have used the expression for L given in Eq. (16.52). Using Eqs. (16.52) and (16.54), the Hamiltonian density H now becomes

$$H = \pi\dot{\Psi} - L = \frac{\hbar^2}{2m}\nabla\Psi^*.\nabla\Psi + V(\mathbf{r}, t)\Psi^*\Psi \tag{16.55a}$$

$$= -\frac{i\hbar}{2m}\nabla\,(i\hbar\Psi^*)\,.\,\nabla\Psi - \frac{i}{\hbar}V\,(i\hbar\Psi^*)\,\Psi$$

$$= -\frac{i\hbar}{2m}\nabla\pi.\nabla\Psi - \frac{i}{\hbar}V\pi\Psi \tag{16.55b}$$

Using Eq. (16.55a), the Hamiltonian H is given by

$$H = \int_V H\,d^3\mathbf{r} = \int_V \left(\frac{\hbar^2}{2m}\nabla\Psi^*.\nabla\Psi + V\Psi^*\Psi\right)d^3\mathbf{r} \tag{16.56}$$

The classical field equations in the Hamiltonian form are given by Eq. (16.42). It follows from the discussion on functional derivatives, Eq. (16.28),

$$\dot{\Psi} = \frac{\partial \mathrm{H}}{\partial\pi} = \frac{\partial H}{\partial\pi} - \nabla\cdot\frac{\partial H}{\partial(\nabla\pi)} \tag{16.57}$$

$$\dot{\pi} = -\frac{\partial \mathrm{H}}{\partial\Psi} = -\left(\frac{\partial H}{\partial\Psi} - \nabla\cdot\frac{\partial H}{\partial\nabla\Psi}\right) \tag{16.58}$$

These equations can be expressed in the familiar form by substituting the value of H from Eq. (16.55b). Now,

$$\dot{\Psi} = -\frac{i}{\hbar} V\Psi + \frac{i\hbar}{2m} \nabla^2 \Psi$$

Multiplying by $i\hbar$,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \tag{16.59}$$

Replacement of H in Eq. (16.58) gives

$$\dot{\pi} = \frac{i}{\hbar} V\pi - \frac{i\hbar}{2m} \nabla^2 \pi$$

Since $\pi = i\hbar\Psi^*$ (Eq. 16.54), this equation becomes

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \tag{16.60}$$

Equations (16.59) and (16.60) are the familiar classical equation and its complex conjugate for the Schrödinger field. This validates the expressions for Lagrangian density, Eq.(16.52) and the Hamiltonian density derived from it, Eq. (16.55).

Since Ψ is now an operator, Ψ^* is to be interpreted as the Hermitian adjoint of Ψ rather than its complex conjugate and it is usually denoted by $\Psi^\dagger$. Now, H is Hermitian and the quantized Hamiltonian is the operator that represents the total energy of the field. The quantum condition in Eq. (16.49b) reduces to

$$[\Psi(\mathbf{r}, t), \Psi^\dagger(\mathbf{r}', t)] = \delta(\mathbf{r} - \mathbf{r}') \tag{16.61}$$

The N-representation

We have not yet given any explicit representation for the new operators Ψ and H. One could easily expand Ψ in terms of some complete orthonormal set of functions $\{u_k\}$ which carry all the space dependence of Ψ, leaving the operator properties of Ψ to be expressed through the expansion coefficients which depend on the time:

$$\Psi(\mathbf{r}, t) = \sum_k a_k(t)\, u_k(\mathbf{r}) \tag{16.62}$$

Equation (16.54) now takes the form:

$$\Psi^\dagger(\mathbf{r}, t) = \frac{1}{i\hbar} \pi(\mathbf{r}, t) = \sum_k a^\dagger{}_k(t)\, u_k^*(\mathbf{r}) \tag{16.63}$$

The most convenient choice for the u_k is the set of single particle energy eigenfunctions which satisfy

$$-\frac{\hbar^2}{2m}\nabla^2 u_k + V u_k = E_k u_k \qquad (16.64)$$

The coefficients $a_k(t)$ and $a^\dagger{}_k(t)$ are operators and suitable commutation relations for them have to be obtained.

System of Bosons

Multiplying Eq. (16.62) by $u_l^*(\mathbf{r})$ and integrating over the whole range of the variable

$$\int u_l^*(\mathbf{r})\, \Psi(\mathbf{r}, t) d^3\mathbf{r} = \sum_k a_k(t) \int u_l^*(\mathbf{r}) u_k(\mathbf{r})\, d^3\mathbf{r}$$

Using the orthonormality of the u_ks,

$$a_k(t) = \int u_k^*(\mathbf{r})\, \Psi(\mathbf{r}, t) d^3\mathbf{r} \qquad (16.65)$$

Similarly one can show that

$$a_k^\dagger(t) = \int u_k(\mathbf{r})\, \Psi^\dagger(\mathbf{r}, t) d^3\mathbf{r} \qquad (16.66)$$

The commutator of a_k with $a_k^\dagger$ is:

$$[a_k, a_l^\dagger] = \int\int u_k^*(\mathbf{r})\, u_l(\mathbf{r}')[\Psi(\mathbf{r}, t), \Psi^\dagger(\mathbf{r}', t)] d^3\mathbf{r}\, d^3\mathbf{r}' \qquad (16.67)$$

Use of the commutator in Eq. (16.61) reduces Eq. (16.67) to

$$\begin{aligned}[a_k, a_l^\dagger] &= \int\int u_k^*(\mathbf{r})\, u_l(\mathbf{r}') d^3\mathbf{r}\, d^3\mathbf{r}'\, \delta(\mathbf{r} - \mathbf{r}') \\ &= \int u_k^*(\mathbf{r})\, u_l(\mathbf{r})\, d^3\mathbf{r} \\ &= \delta_{kl} \qquad (16.68)\end{aligned}$$

In a similar way,

$$[a_k, a_l] = [a_k^\dagger, a_l^\dagger] = 0 \qquad (16.69)$$

It is obvious from the commutation relations that the amplitudes a_k and $a_k^\dagger$, infinite in numbers, are behaving as operators. These operators are similar to those introduced in Section 4.8, except that here we have an infinite number of them.

Another useful operator, called **number operator**, representing the total number of particles is defined by

$$N = \int \Psi^\dagger\, \Psi\, d^3\mathbf{r} \qquad (16.70)$$

Substitution of Eqs. (16.62) and (16.63) gives

$$\begin{aligned}
N &= \sum_k \sum_l a_k^\dagger a_l \int u_k^*(\mathbf{r})\, u_l(\mathbf{r})\, d^3\mathbf{r} \\
&= \sum_k \sum_l a_k^\dagger\, a_l\, \delta_{kl} = \sum_k a_k^\dagger\, a_k \\
&= \sum_k N_k \qquad (16.71)
\end{aligned}$$

where $$N_k = a_k^\dagger\, a_k \qquad (16.72)$$

We shall now show that each N_k commutes with all others.

$$\begin{aligned}
[N_k\,,\, N_l] &= [a_k^\dagger\, a_k\,,\; a_l^\dagger\, a_l] \\
&= [a_k^\dagger\, a_k\,,\; a_l^\dagger\,]a_l + a_l^\dagger[a_k^\dagger\, a_k\,,\; a_l\,] \\
&= a_k^\dagger\,[a_k\,,\, a_l^\dagger\,]\, a_l + [a_k^\dagger,\, a_l^\dagger\,]\, a_k a_l + a_l^\dagger\, a_k^\dagger[\, a_k\,, a_l] + a_l^\dagger\,[a_k^\dagger\,, a_l]a_k \\
&= a_k^\dagger\, \delta_{kl}\, a_l + 0 + 0 + a_l^\dagger\, (-\delta_{kl})\, a_k \\
&= 0 \qquad (16.73)
\end{aligned}$$

Since each N_k commutes with all others, they can have simultaneous eigenkets and can be diagonalized simultaneously. Labelling the eigenkets by the eigenvalues n_1, n_2, n_3, ..., n_k, ..., ∞, the states of the quantized field in the representation in which each N_k is diagonal are the kets

$$\left|\, n_1, n_2, n_3, \ldots, n_k, \ldots \right\rangle$$

Next let us find the eigenvalues of the operator N_k. Its eigenvalue equation is:

$$N_k \Psi(n_k) = n_k \Psi(n_k) \qquad (16.74)$$

where n_k is the eigenvalue. Multiplying the equation from left by $\Psi^\dagger(n_k)$ and integrating over the entire space.

$$\begin{aligned}
n_k &= \int \Psi^\dagger(n_k)\, N_k \Psi(n_k) d^3\mathbf{r} = \int \Psi^\dagger(n_k)\, a_k^\dagger\, a_k \Psi(n_k) d^3\mathbf{r} \\
&= \int \left|\, a_k \Psi(n_k) \right|^2 d^3\mathbf{r} \geq 0 \qquad (16.75)
\end{aligned}$$

That is, the eigenvalues of N_k are all positive integers including zero:

$$n_k = 0, 1, 2, \ldots, \infty \qquad (16.76)$$

Since the lowest eigenvalue of N_k is zero, there must exist an eigenket $|0\rangle$ such that $N_k|0\rangle = 0$ for all k. The lowest normalized eigenket with no particle in the state $|0\rangle$ is called the **vacuum state**.

To understand the significance of the operator N_k, substitute the value of $\Psi(\mathbf{r}, t)$, Eq. (11.62), in the field Hamiltonian H, Eq. (16.56):

$$H = \sum_k \sum_l a_k^\dagger a_l \int \left(\frac{\hbar^2}{2m} .\nabla u_k^* . \nabla u_l + V u_k^* u_l \right) d^3\mathbf{r} \tag{16.77}$$

Integrating the first term by parts, we have

$$\int \nabla u_k^* . \nabla u_l d^3\mathbf{r} = \int u_k^* \; \nabla u_l ds - \int u_k^* \; \nabla^2 u_l \; d^3\mathbf{r} \tag{16.78}$$

Since $u_k \to 0$ at the infinite bounding surface, the first term on the right side vanishes, Consequently,

$$H = \sum_k \sum_l a_k^\dagger a_l \int u_k^* \left(-\frac{\hbar^2}{2m} \nabla^2 u_l + V u_l \right) d^3\mathbf{r} \tag{16.79}$$

Using the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 u_l + V u_l = E_l u_l$$

$$H = \sum_k \sum_l a_k^\dagger a_l \int u_k^* E_l \; u_l \; d^3\mathbf{r} = \sum_k \sum_l a_k^\dagger a_l E_l \int u_k^* \; u_l \; d^3\mathbf{r}$$

$$= \sum_k a_k^\dagger \; a_k E_k = \sum_k N_k E_k \tag{16.80}$$

The eigenvalue of the Hamiltonian H of the field in the state $|n_1, n_2, n_3, ..., n_k, ...\rangle$ is:

$$E = \langle H \rangle = \sum_k n_k E_k \tag{16.81}$$

It is evident from Eq.(16.81) that n_k is the number of particles in the state u_k with energy E_k and hence N_k can be regarded as the particle number operator in the k^{th} state. This justifies the name number operator for N. Since a given state u_k can be occupied by any number of particles of the same energy, the field represents an **assembly of bosons**.

Creation and Annihilation Operators

We have already introduced the creation and annihilation operators in Section 4.8. The commutater of a_k with N_k is:

$$[a_k, N_k] = [a_k, a_k^\dagger a_k] = [a_k, a_k^\dagger] a_k + a_k^\dagger \, [a_k, a_k]$$

$$= a_k \tag{16.82}$$

In a similar way,

$$[a_k^\dagger \, , N_k] = -a_k^\dagger \tag{16.83}$$

From Eq. (16.82), we have

$$N_k a_k = a_k N_k - a_k$$

Allowing the operator equation to operate on $\Psi(n_k)$,

$$\begin{aligned} N_k a_k \Psi(n_k) &= (a_k N_k - a_k)\,\Psi(n_k) \\ &= a_k n_k \Psi(n_k) - a_k \Psi(n_k) \\ &= (n_k - 1)\, a_k \Psi(n_k) \end{aligned} \tag{16.84}$$

This means that, if $\psi(n_k)$ is an eigenket of N_k with eigenvalue n_k, $a\psi(n_k)$ is also an eigenket of N_k with the eigenvalue lowered by 1. That is, the number of particles in the k^{th} state is decreased by 1. Hence, we can consider a_k as an **annihilation or destruction operator** for the state k of the field. In a similar way, we can show that

$$N_k\, a_k^{\dagger}\, \psi(n_k) = (n_k + 1)\, a_k^{\dagger}\, \psi(n_k) \tag{16.85}$$

This equation implies that $a_k^{\dagger}\psi(n_k)$ is also an eignket of N_k with an eigenvalue increased by 1 or the number of particles in the k^{th} state is increased by 1. Hence, we can consider $a_k^{\dagger}$ as a **creation operator** for the state k of the field. Mathematically, we can then write

$$a_k \,|\, n_1, n_2, \ldots, n_k, \ldots\rangle = \sqrt{n_k}\;|\, n_1, n_2, \ldots, n_k - 1, \ldots\rangle \tag{16.86}$$

$$a_k^{\dagger} \,|\, n_1, n_2, \ldots, n_k, \ldots\rangle = \sqrt{n_k + 1}\;|\, n_1, n_2, \ldots, n_k + 1, \ldots\rangle \tag{16.87}$$

A general state vector of the field is given by

$$|\, n_1, n_2, \ldots, n_k, \ldots\rangle = \frac{1}{(n_1!\, n_2! \ldots n_k! \ldots)^{1/2}} (a_1^{\dagger})^{n_1} (a_2^{\dagger})^{n_2} \ldots (a_k^{\dagger})^{n_k} \ldots |\, 0\rangle \tag{16.88}$$

System of Fermions

The commutation relations in Eq.(16.68) and (16.69) led to a system of bosons. For a system of fermions, the number of particles n_k in any state should be restricted to 0 and 1, to be in accordance with Pauli's exclusion principle. Jordan and Wigner has shown that this condition could be realized by replacing the above commutation relations by the following anticommutation relations:

$$[a_k\,,\, a_l^{\dagger}]_+ = \delta_{kl}; \quad [a_k\,,\, a_l]_+ = [a_k^{\dagger}\,,\, a_l^{\dagger}]_+ = 0 \tag{16.89}$$

From Eq. (16.89), we have

$$a_k a_k^{\dagger} + a_k^{\dagger} a_k = 1 \quad \text{and} \quad a_k a_k = a_k^{\dagger} a_k^{\dagger} = 0 \tag{16.90}$$

Again, we define the particle number operator in the k^{th} state N_k by

$$N_k = a_k^{\dagger} a_k \tag{16.91}$$

Each N_k commutes with all the others and, therefore, they can be diagonalized simultaneously. The eigenvalues of N_k can be obtained by evaluating the square of N_k^2;

$$N_k^2 = a_k^\dagger a_k a_k^\dagger a_k = a_k^\dagger (a_k a_k^\dagger) a_k = a_k^\dagger (1 - a_k^\dagger a_k) a_k$$

$$= a_k^\dagger a_k = N_k \tag{16.92}$$

since the second term is zero by virtue of Eq. (16.90). N_k is diagonal with eigenvalue n_k and, therefore, N_k^2 would also be diagonal with eigenvalue n_k^2. Hence Eq. (16.92) is equivalent to

$$n_k^2 = n_k \quad \text{or} \quad n_k^2 - n_k = 0$$

$$n_k(n_k - 1) = 0 \tag{16.93}$$

which gives

$$n_k = 0,\ 1 \tag{16.94}$$

Thus, the eigenvalues of N_k are 0 and 1. As in the case of bosons, we can define a number operator N representing the total number of particles by

$$N = \sum_k N_k \tag{16.95}$$

The eigenvalues of N are the positive integers including zero as before.

The expression, Eq. (16.79) which was valid for bosons is also valid for fermions. Again, the energy eigenvalues are given by Eq. (16.81). The following relations also result from the anticommutation rules in Eq. (16.89):

$$a_k \,|\, n_1, n_2, ..., n_k, ...\rangle = (-1)^{S_k} n_k \,|\, n_1, n_2, ..., (n_k - 1), ...\rangle \tag{16.96}$$

$$a_k^\dagger |\, n_1, n_2, ..., n_k, ...\rangle = (-1)^{S_k} (1 - n_k) \,|\, n_1, n_2, ..., (n_k + 1), ...\rangle \tag{16.97}$$

$$|\, n_1, n_2, ..., n_k, ...\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} ... (a_k^\dagger)^{n_k} ... |0\rangle \tag{16.98}$$

where

$$S_k = \sum_{r=1}^{k-1} n_r \tag{16.99}$$

A representation for the operators a and $a^\dagger$ can be obtained if the system has only one state. The number operator N_k has the eigenvalues 0 and 1. Hence N_k can be represented by the diagonal matrix:

$$N_k = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{16.100}$$

Matrices for a and $a^\dagger$ satisfying the condition $a_k a_k = a_k^\dagger a_k^\dagger = 0$ are:

$$a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad a^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{16.101}$$

The kets representing the eigenvalues zero and one for the operator N_k can be expressed as:

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{16.102}$$

In real situations, the number of states of the system is infinite and not single as assumed. Hence, explicit simple matrices like the preceding ones is not possible.

16.6 RELATIVISTIC FIELDS

In Section 16.5, we considered the quantization of the non-relativistic Schrödinger equation which represents either a system of bosons or fermions. Because of the close relationship between the wave equation and spin of particles and that between spin and statistics, the relativistic field can consistently be quantized by using only one of the statistics. Therefore, the field equation representing a system of bosons will be different from the one that represents a system of fermions. As examples of relativistic fields we will be considering the Klein-Gordon field (spin 0 - scalar field), the Dirac field (spin 1/2–spinor field) and the electromagnetic field (spin 1–vector field).

In relativistic fields, invariably the equations are written in the covariant form with Einstein summation convention. A position four-vector x having components x_1, x_2, x_3, x_4 is written as:

$$x_\mu = (x_1, x_2, x_3, x_4) = (\mathbf{x}, x_4)$$

where **x** stands for the usual three dimensional position vector with components x, y, z. In covariant form, it is the practice to write

$$\frac{\partial}{\partial t} \text{ as } \partial_t \text{ and } \frac{\partial}{\partial x_\mu} \text{ as } \partial \mu$$

In writing

$$\sum_{\mu=1}^{4} x_\mu y_\mu = x_\mu y_\mu$$

the Einstein convention is used according to which a repeated Greek index indicate that we have to sum over all possible values of the index.

Natural Units

In relativistic quantum field theory, it is customary to use the system of units called **natural system of units**. In this system, there is only one fundamental unit which is the unit of mass. Both $\hbar$ and c are dimensionless and of magnitude unity:

$$\hbar = c = 1$$

Energy E has the dimension of mc^2 and momentum p that of mc. In natural units, both E and p should have the dimension of mass $[M]$. In the relation $E = \hbar\omega$, with $\hbar = 1$, we see that the energy has the dimension of $[T]^{-1}$. Hence T^{-1} must equal $[M]$. That is, the dimension of time in natural units is $[M]^{-1}$. In the same way, in $p = \hbar k$, p has the dimension of $[L]^{-1}$. As the dimension of p is $[M]$, in natural units, length has the dimension of $[M]^{-1}$. A quantity which has the dimension $[A] = M^\alpha L^\beta T^\gamma$ in S.I. has the dimension $[A]_{nu}$ given by

$$[A]_{nu} = [M]^\alpha \, [M]^{-\beta} \, [M]^{-\gamma} = [M]^{\alpha-\beta-\gamma}$$

Thus, force which is defined as the rate of change of mometum has the dimension of MLT^{-2}. In natural units its dimension is $[M]\,[M]^{-1}\,[M]^2 = [M]^2$. The dimension of some of the quantities in natural units are given in Table 16.1.

Table 16.1 Dimension of Some Quantities in Natural Units

Quantity	*Dimension*	*Quantity*	*Dimension*
Mass	$[M]$	Momentum	$[M]$
Length	$[M]^{-1}$	Force	$[M]^2$
Time	$[M]^{-1}$	Electric charge	$[M]^0$
Energy	$[M]$	Action	$[M]^0$

16.7 THE KLEIN-GORDON FIELD

The simplest relativistic equation is the Klein-Gordon equation, Eq. (15.5) which in natural units, takes the form:

$$(\partial_\mu \partial_\mu - m^2)\, \phi\,(\mathbf{x}, t) = 0 \quad or \quad (\partial_\mu \partial_\mu - m^2)\, \phi(x) = 0 \tag{16.103}$$

where $\mathbf{x}$ stands for the usual three dimensional position vector and x stands for the space-time co-ordinate four-vector ($\mathbf{x}$, ict). The interpretation of this equation as a single particle equation led to the occurrence of negative probability density. This difficulty can be removed if the Klein-Gordon field $\phi(x)$ is quantized. In general, the field $\phi(x)$ is complex.

A suitable Lagrangian density that could reproduce the Klein-Gordon equation is:

$$L_{KG} = -(\partial_\mu \phi \, \partial_\mu \phi^* + m^2 \phi\phi^*) \tag{16.104}$$

where ϕ and ϕ^* are independent fields. Instead, we may write ϕ and ϕ^* in terms of real fields ϕ_1 and ϕ_2 as:

$$\phi(x) = \frac{1}{\sqrt{2}}[\phi_1\,(x) - i\phi_2\,(x)] \tag{16.105a}$$

$$\phi^*(x) = \frac{1}{\sqrt{2}}[\phi_1\,(x) + i\phi_2(x)] \tag{16.105b}$$

Fields $\phi_1(x)$ and $\phi_2(x)$ satisfy Eq. (16.103). In terms of $\phi_1(x)$ and $\phi_2(x)$,

$$\begin{aligned} L_{KG}(x) &= -\tfrac{1}{2}\,\partial_\mu(\phi_1 - i\phi_2)\,\partial_\mu(\phi_1 + i\phi_2) - \tfrac{1}{2}m^2(\phi_1 - i\phi_2)(\phi_1 + i\phi_2) \\ &= -\tfrac{1}{2}(\partial_\mu\phi_1\partial_\mu\phi_2 + \partial_\mu\phi_2\partial_\mu\phi_1) - \tfrac{1}{2}m^2(\phi_1^2 + \phi_2^2) \\ &= -\tfrac{1}{2}\sum_{r=1}^{2}(\partial_\mu\phi_r\partial_\mu\phi_r + m^2\phi_r^2) \end{aligned} \tag{16.106}$$

The conjugate momentum field follows from Eq. (16.106) as:

$$\pi_r(x) = \frac{\partial L}{\partial\dot{\phi}_r} = i\partial_4\phi_r = \dot{\phi}_r \tag{16.107}$$

The Hamiltonian density is defined by

$$H = \sum_{r=1}^{2}\pi_r(x)\,\dot{\phi}_r(x) - L \tag{16.108}$$

The Hamiltonian can be expressed in terms of the Hamiltonian density:

$$\begin{aligned} H &= \int H(x)\, d^3\mathbf{x} \\ &= -\sum_{r=1}^{2}\int \partial_4\phi_r\partial_4\phi_r\, d^3\mathbf{x} + \tfrac{1}{2}\sum_{r=1}^{2}\int(\partial_\mu\phi_r\partial_\mu\phi_r + m^2\phi_r^2)\,d^3\mathbf{x} \end{aligned} \tag{16.109}$$

where the integral extends over the entire space. The Hamilton's equations of motion in the Heisenberg picture become

$$\dot{\phi}(\mathbf{x}, t) = i\left[H(t),\ \phi\ (\mathbf{x}, t)\right] \tag{16.110}$$

$$\dot{\pi}\ (\mathbf{x}, t) = i\left[H(t),\ \pi(\mathbf{x}, t)\right] \tag{16.111}$$

The next step is to quantize the field. The canonical quantization rule gives the following commutation relations for the fields ϕ_r and the momentum fields π_r:

$$[\phi_r(\mathbf{x}, t), \pi_s(\mathbf{x}', t)] = i\delta_{rs}\ \delta(\mathbf{x} - \mathbf{x}') \tag{16.112}$$

$$[\phi_r(\mathbf{x}, t), \phi_s(\mathbf{x}', t)] = [\pi_r(\mathbf{x}, t), \pi_s(\mathbf{x}', t)] = 0 \tag{16.113}$$

Since $\phi(x)$ transforms as a scalar under Lorentz transformation and possesses no intrinsic degrees of freedom, the spin of the Klein-Gordon field is zero. Also, as the Lagrangian density L is not gauge invariant, the particles described by ϕ carry no charge.

The expansion of $\phi(x)$ in terms of a complete set of orthonormal solutions of the Klein-Gordon equation is necessary to quantize ϕ_1 and ϕ_2. A plane wave solution of Klein-Gordon equation is of the form:

$$u(\mathbf{k}) = \frac{1}{\sqrt{2V\omega_k}} \exp(\pm ikx) \tag{16.114}$$

where
$$kx = k_\mu x_\mu = k.\mathbf{x} - \omega t \tag{16.115}$$

and
$$\omega_k^2 = k^2 + m^2 \tag{16.116}$$

Expanding $\phi(x)$ in terms of the complete set of plane wave solutions, we have

$$\phi_r(x) = \sum_k \frac{1}{\sqrt{2V\omega_k}} [a_r(\mathbf{k})e^{ikx} + a_r^\dagger(\mathbf{k})e^{-ikx}] \tag{16.117}$$

where the operators $a_r(\mathbf{k})$ and $a_r^\dagger(\mathbf{k})$ are taken to be the Hermitian adjoints of each other, to ensure the hermicity of $\phi(\mathbf{x}, t)$. Summation is taken over the wave vector **k** allowed by the boundary conditions. From the canonical commutation relations, Eqs. (16.112) and (16.113), one obtains the commutation relations for the $a_r(\mathbf{k})$ and $a_r^\dagger(\mathbf{k})$:

$$[a_r(\mathbf{k}), a_s^\dagger(\mathbf{k}')] = \delta_{rs}\delta(\mathbf{k} - \mathbf{k}') \tag{16.118}$$

$$[a_r(\mathbf{k}), a_s(\mathbf{k}')] = [a_r^\dagger(\mathbf{k}), a_s(\mathbf{k}')] = 0 \tag{16.119}$$

These are the typical commutation relations for bosons. Substitution of $\phi_1(x)$ and $\phi_2(x)$ using Eq. (16.117) in Eq. (16.105),

$$\phi(x) = \frac{1}{\sqrt{2}} \sum_k \frac{1}{\sqrt{2V\omega_k}} [a_1(\mathbf{k})e^{ikx} + a_1^\dagger(\mathbf{k})e^{-ikx}]$$

$$- \frac{i}{\sqrt{2}} \sum_k \frac{1}{\sqrt{2V\omega_k}} [a_2(\mathbf{k})e^{ikx} + a_2^\dagger(\mathbf{k})e^{-ikx}]$$

$$= \sum_k \frac{1}{\sqrt{2V\omega_k}} \left[\frac{1}{\sqrt{2}}\left(a_1(\mathbf{k}) - ia_2(\mathbf{k})\right)\right] e^{ikx} + \sum_k \frac{1}{\sqrt{2V\omega_k}} \left[\frac{1}{\sqrt{2}}(a_1^\dagger(\mathbf{k}) - a_2^\dagger(\mathbf{k})\right] e^{-ikx}$$

$$= \sum_k \frac{1}{\sqrt{2V\omega_k}} [a(\mathbf{k})e^{ikx} + b^\dagger(\mathbf{k})e^{-ikx}] \tag{16.120}$$

$$\phi^\dagger(x) = \sum_k \frac{1}{\sqrt{2V\omega_k}} [a^\dagger(\mathbf{k})e^{-ikx} + b(\mathbf{k})e^{ikx}] \tag{16.121}$$

where

$$a(\mathbf{k}) = \frac{1}{\sqrt{2}} [a_1(\mathbf{k}) - ia_2(\mathbf{k})] \tag{16.122}$$

$$b^\dagger(\mathbf{k}) = \frac{1}{\sqrt{2}}[a_1{}^\dagger(\mathbf{k}) - ia_2{}^\dagger(\mathbf{k})] \tag{16.123}$$

$$b(\mathbf{k}) = \frac{1}{\sqrt{2}}[a_1(\mathbf{k}) + ia_2(\mathbf{k})] \tag{16.124}$$

$$a^\dagger(\mathbf{k}) = \frac{1}{\sqrt{2}}[a_1{}^\dagger(\mathbf{k}) + ia_2{}^\dagger(\mathbf{k})] \tag{16.124a}$$

The operators $a(\mathbf{k})$, $b(\mathbf{k})$ and their Hermitian adjoints $a^\dagger(\mathbf{k})$, $b^\dagger(\mathbf{k})$ satisfy the commutation relations

$$[a(\mathbf{k}), a^\dagger(\mathbf{k}')] = [b(\mathbf{k}), b^\dagger(\mathbf{k}')] = \delta(\mathbf{k} - \mathbf{k}') \tag{16.125}$$

with all other commutators vanishing. Calculations give the diagonal form of charge Q and Hamiltonian H in terms of these operators:

$$Q = e\sum_k [a^\dagger(\mathbf{k})\ a(\mathbf{k}) - b^\dagger(\mathbf{k})\ b(\mathbf{k})] \tag{16.126}$$

$$H = \sum_k [a^\dagger(\mathbf{k})\ a(\mathbf{k}) + b^\dagger(\mathbf{k})\ b(\mathbf{k})] \tag{16.127}$$

The operators $a^\dagger(\mathbf{k})$ and $a(\mathbf{k})$ can now respectively be interpreted as the creation and destruction operators for a positively charged particle, and $b^\dagger(\mathbf{k})$ and $b(\mathbf{k})$ are similar operators for a negatively charged particle, in each case the wave vector being **k**. We can have two **particle number operators** $N^+(\mathbf{k})$ and $N^-(\mathbf{k})$ defined by

$$\mathrm{N}^+(\mathbf{k}) = a^\dagger(\mathbf{k})\ a(\mathbf{k})\ ;\ N^-(\mathbf{k}) = b^\dagger(\mathbf{k})\ b(\mathbf{k}) \tag{16.128}$$

The eigenvalues of both these operators are:

$$n_\pm(\mathbf{k}) = 0, 1, 2, ..., \infty \tag{16.129}$$

The positively and negatively charged particles have identical properties except for the sign of their charge. In relativistic quantum field theory, every charged particle is accompanied by an antiparticle having opposite charge. This is a very general result in field theory. Examples of particle-antiparticle pair are the charged π^+ and π^- particles, K^+ and K^- particles and so on. The charge in question may be either electric charge or some other conserved quantum number like strangeness or hypercharge. The electrically neutral K^0 meson has an antiparticle $\bar{K}^0$ which is also electrically neutral. These two particles carry opposite hypercharge.

16.8 THE DIRAC FIELD

The covariant form of the Dirac equation, Eq. (15.37a), in natural units, takes the form:

$$(\gamma_\mu \partial_\mu + m)\, \Psi(x) = 0 \tag{16.130}$$

A possible Lagrangian density from which we can get the Dirac equation is:

$$L = -\bar{\Psi}(x)\, (\gamma_\mu \partial_\mu + m)\, \Psi(x) \tag{16.131}$$

where

$$\bar{\Psi}(x) = \Psi^\dagger(x) \gamma^4 \tag{16.132}$$

which is referred to as the **Dirac adjoint of** Ψ. The conjugate fields of Ψ and $\bar{\Psi}$ are:

$$\pi(x) = \frac{\partial L}{\partial \dot{\Psi}} = -\frac{\partial}{\partial \dot{\Psi}} \left(\bar{\Psi} \sum_{k=1}^{3} \gamma_k \partial_k \Psi + \bar{\Psi} \frac{\gamma_4}{i} \dot{\Psi} + \bar{\Psi} m \Psi \right)$$

$$= -\frac{1}{i} \bar{\Psi}\, \gamma_4 = i\Psi^\dagger \gamma_4 \gamma_4 = i\Psi^\dagger \tag{16.133}$$

$$\bar{\pi}(x) = \frac{\partial L}{\partial \dot{\bar{\Psi}}} = 0 \tag{16.134}$$

The previously applied canonical quantization will not work for the Dirac equation since

$$[\, \bar{\Psi}(x), \bar{\pi}(x') \,] = [\, \bar{\Psi}, 0 \,] = 0 \neq \delta(\mathbf{x} - \mathbf{x}') \tag{16.135}$$

Moreover, particles with $s = 1/2$ are fermions and in the non-relativistic limit these were quantized by means of anticommutation relations (Section 16.5). The Hamiltonian density arising out of Eq. (16.131) is:

$$\begin{aligned} H &= \pi \dot{\Psi} - L \\ &= i\Psi^\dagger \dot{\Psi} + \bar{\Psi}\, (\gamma_\mu \partial_\mu + m)\, \Psi \\ &= i\Psi^\dagger\, \dot{\Psi} + \bar{\Psi} \sum_{k=1}^{3} \gamma_k \partial_k \Psi + \bar{\Psi} \frac{\gamma_4}{i} \dot{\Psi} + m\bar{\Psi}\Psi \\ &= i\Psi^\dagger \dot{\Psi} + \bar{\Psi} \sum_{k=1}^{3} \gamma_k \partial_k \Psi - i\Psi^\dagger \dot{\Psi} + m\bar{\Psi}\Psi \\ &= \bar{\Psi}(x) \sum_{k=1}^{3} \gamma_k \partial_k \Psi(x) + m\, \bar{\Psi}(x)\, \Psi(x) \end{aligned} \tag{16.136}$$

Consequently, the field Hamiltonian

$$H = \sum_{k=1}^{3} \int_V \bar{\Psi}(x)\, \gamma_k \partial_k \Psi(x)\, d^3\mathbf{x} + m \int_V \bar{\Psi}(x) \Psi(x)\, d^3\mathbf{x} \tag{16.137}$$

The plane wave solution of the Dirac equation (Section 15.8) is of the form given in Eq. (15.44), where the u's are given by Eq. (15.46). Calculations give two independent solutions for the positive energy and another two independent solutions for the negative energy. Here, it is found useful to modify the definition of these plane wave spinors. For a free particle in a volume V, the plane wave solutions with normalization compatible with Section 15.8 are:

$$\phi_r(\mathbf{p}) = \sqrt{\frac{m}{VE_p}}\, u_r(\mathbf{p})\, e^{ipx},\ r = 1, 2 \tag{16.138}$$

$$\phi_{r+2}(\mathbf{p}) = \sqrt{\frac{m}{VE_p}}\, v_r(\mathbf{p})\, e^{-ipx},\ r = 1, 2 \tag{16.139}$$

where

$$u_r(\mathbf{p}) = \left(\frac{E_p+m}{2m}\right)^{1/2} \begin{pmatrix} \chi_r \\ \dfrac{(\sigma.\mathbf{p})\,\chi_r}{E_p+m} \end{pmatrix},\ r = 1, 2 \tag{16.140a}$$

$$v_r(\mathbf{p}) = \left(\frac{E_p+m}{2m}\right)^{1/2} \begin{pmatrix} \dfrac{(\sigma.\mathbf{p})\,\chi_r}{E_p+m} \\ \chi_r \end{pmatrix},\ r = 1, 2 \tag{16.140b}$$

with

$$\chi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix},\ \chi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{16.141}$$

$$E_p = \sqrt{p^2+m^2},\ px = \mathbf{p}\cdot\mathbf{x} - Et \tag{16.142}$$

The functions $\phi_1(x)$ and $\phi_2(x)$ are the solutions of the free particle Dirac equation corresponding to positive energy and momentum (E_p, $\mathbf{p}$) while $\phi_3(x)$ and $\phi_4(x)$ correspond to negative energy and momentum ($-E_p$, $-p$).

We may now expand the Dirac field operator $\Psi(x)$ and $\bar{\Psi}(x)$ as a superposition of free particle solutions:

$$\Psi(x) = \sum_p \sum_{r=1}^{2} \sqrt{\frac{m}{VE_p}}\,[c_r(\mathbf{p})\, u_r(\mathbf{p})\, e^{ipx} + d_r^\dagger(\mathbf{p})\, v_r(\mathbf{p})\, e^{-ipx}] \tag{16.143}$$

$$= \Psi^+(x) + \Psi^-(x) \tag{16.144}$$

The last line indicates the decomposition into positive and negative frequency contributions. In the classical field theory the amplitude $c_r(\mathbf{p})$ and $d_r(\mathbf{p})$ are complex numbers. However, here they are operators. For $\bar{\psi}(x)$, we have the expression:

$$\bar{\psi}(x) = \sum_p \sum_{r=1}^{2} \sqrt{\frac{m}{VE_p}} \, [c_r^\dagger(\mathbf{p}) \, u_r(\mathbf{p}) e^{-ipx} + d_r(\mathbf{p}) \, v_r(\mathbf{p}) e^{ipx}] \quad (16.145)$$

Substituting Eqs. (16.143) and Eq. (16.145) in Eq. (16.137) and carrying out the volume integration, we get

$$H = \sum_p \sum_{r=1}^{2} E_p \, [c_r^\dagger(\mathbf{p}) \, c_r(\mathbf{p}) - d_r(\mathbf{p}) \, d_r^\dagger(\mathbf{p})] \quad (16.146)$$

The momentum **P** is found to be

$$\mathbf{P} = \sum_p \sum_{r=1}^{2} \mathbf{p} \, [c_r^\dagger(\mathbf{p}) \, c_r(\mathbf{p}) - d_r(\mathbf{p}) \, d_r^\dagger(\mathbf{p})] \quad (16.147)$$

As in the Klein-Gordon theory, if commutation relations for the field operators are followed then the field Hamiltonian would not be positive definite. In addition, the concept of filled sea of negative energy levels requires an exclusion principle limiting the number of particles in a given state. As already indicated, the way out of this difficulty is to demand anticommutation relations for the field operators:

$$[c_r(\mathbf{p}), c_s^\dagger(\mathbf{p}')]_+ = [d_r(\mathbf{p}), d_s^\dagger(\mathbf{p}')]_+ = \delta_{rs} \delta(\mathbf{p} - \mathbf{p}') \quad (16.148a)$$

$$[c_r, c_s]_+ = [c_r^\dagger, c_s^\dagger]_+ = [d_r, d_s]_+ = [d_r^\dagger, d_s^\dagger]_+ = 0 \quad (16.148b)$$

The Hamiltonian, Eq. (16.146) can now be rewritten using the anticommutation relations in Eq. (16.148). The second term in Eq. (16.146),

$$-d_r(\mathbf{p}) \, d_r^\dagger(\mathbf{p}) = d_r^\dagger(\mathbf{p}) \, d_r(\mathbf{p}) - 1$$

Consequently,

$$H = \sum_p \sum_{r=1}^{2} E_p \, [c_r^\dagger(\mathbf{p}) \, c_r(\mathbf{p}) + d_r^\dagger(\mathbf{p}) \, d_r(\mathbf{p})] + E_0 \quad (16.149)$$

$$\mathbf{P} = \sum_p \sum_{r=1}^{2} \mathbf{p} \, [c_r^\dagger(\mathbf{p}) \, c_r(\mathbf{p}) + d_r^\dagger(\mathbf{p}) \, d_r(\mathbf{p})] + P_0 \quad (16.150)$$

where E_0 and P_0 are zero point energy and momentum respectively and are given by

$$E_0 = -\sum_p \sum_{r=1}^{2} E_p \quad (16.151a)$$

$$\mathbf{P}_0 = -\sum_p \sum_{r=1}^{2} \mathbf{p} \quad (16.151b)$$

Subtracting out the zero point energy, momentum

$$H = \sum_{p} \sum_{r=1}^{2} E_p [c_r^\dagger(\mathbf{p})\, c_r(\mathbf{p}) + d_r^\dagger(\mathbf{p})\, d_r(\mathbf{p})] \tag{16.152}$$

$$\mathbf{P} = \sum_{p} \sum_{r=1}^{2} \mathbf{p}\, [c_r^\dagger(\mathbf{p})\, c_r(\mathbf{p}) + d_r^\dagger(\mathbf{p})\, d_r(\mathbf{p})] \tag{16.153}$$

The zero point momentum is actually zero, by cancellation of **p** and –**p**. The energy is now positive definite. In the form given in Eqs. (16.152) and (16.153), we have the normal products for the Dirac field, which avoids the zero point term. In this form all annihilation operators are written to the right of creation operators.

From the expression for Hamiltonian, Eq.(16.146), it follows that $c_r^\dagger(\mathbf{p})\, c_r(\mathbf{p})$ and $d_r(\mathbf{p})\, d_r^\dagger(\mathbf{p})$ are the number operators for the positive and negative energy particles respectively. By Eq. (16.147) also $d_r(\mathbf{p})$ $d_r^\dagger(\mathbf{p})$ is the number operator for negative energy particles of momentum –**p**. Thus, from the form of H and **P**, it follows that $d_r(\mathbf{p})$ creates a negative electron with $(-E, -p)$ and $d_r^\dagger(\mathbf{p})$ is the corresponding annihilation operator. According to Dirac's hole theory, the vacuum state is the one with all positive energy states empty and all negative energy states filled. When a negative energy electron is annihilated, a hole is created which behaves as if it is a particle of positive charge, called **positron**. In other words, the annihilation of a negative energy electron can be interpreted in the hole theory as the creation operator of a positron. Thus, a positive energy electron is created by $c_r^\dagger(\mathbf{p})$ and annihilated by $c_r(\mathbf{p})$. The operator

$$N_r^+(\mathbf{p}) = c_r^\dagger(\mathbf{p})\, c_r(\mathbf{p}) \tag{16.154}$$

is interpreted as the occupation number operator for positive energy electrons. The operator $d_r^\dagger(\mathbf{p})$ creates a positron, whereas $d_r(\mathbf{p})$ annihilates a positron. The operator

$$N_r^-(\mathbf{p}) = d_r^\dagger(\mathbf{p})\, d_r(\mathbf{p}) \tag{16.155}$$

is the number operator for positrons of positive energy. The anticommutation relations, Eqs. (16.148a) and (16.148b), imply that each state can at most be singly occupied. Hence, the eigenvalues (occupation numbers) of the number operators $N_r^+(\mathbf{p})$ and $N_r^-(\mathbf{p})$ is either 0 or 1. The operator $c_r^\dagger(\mathbf{p})$ with $r = 1$, $\mathbf{p} = 0$ creates an election at rest with $s_z = 1/2$ with $r = 2$, $\mathbf{p} = 0$ creates an electron at rest with $s_z = -1/2$. In terms of number operators, the Hamiltonian and momentum are :

$$H = \sum_{p} \sum_{r=1}^{2} E_P \left[N_r^+(\mathbf{p}) + N_r^-(\mathbf{p}) \right] \tag{16.156}$$

$$\mathbf{P} = \sum_{p} \sum_{r=1}^{2} \mathbf{p}\left[N_r^+(\mathbf{p}) + N_r^-(\mathbf{p})\right] \tag{16.157}$$

Dirac field is thus quantized by means of anticommutation rules.

16.9 CLASSICAL THEORY OF ELECTROMAGNETIC FIELDS

The classical electrodynamics is based on Maxwell's equations for the electric and magnetic fields **E** and **B**. In rationalised units, also called **Hearyside-Lorentz units**, these equations can be written as:

$$\nabla \cdot \mathbf{E} = \rho \tag{16.158}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{16.159}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{16.160}$$

$$\nabla \times \mathbf{B} = \frac{\partial \mathbf{E}}{\partial t} + j \tag{16.161}$$

Here $\rho(\mathbf{x}, t)$ is the charge density and $j(\mathbf{x}, t)$ is the current density. Instead of **E** and **B**, the field equations can also be expressed in terms of a vector potential **A** and a scalar potential ϕ. Equation (16.160) implies

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{16.162}$$

With this definition of **B**, Eq. (16.159) takes the form:

$$\nabla \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t}\right) = 0 \tag{16.163}$$

Since the curl of the gradient of a scalar function is zero, from Eq. (16.163), we have

$$\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\nabla\phi \quad (\phi \text{ is scalar potential})$$

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi \tag{16.164}$$

which gives the electric field in terms of the potentials **A** and ϕ.

The other two equations, Eqs. (16.158) and (16.161) can also be expressed in terms of **A** and ϕ. Substituting the value of **E** in Eq. (16.158),

$$\nabla^2\phi + \frac{\partial}{\partial t}(\nabla \cdot \mathbf{A}) = -\rho \tag{16.165}$$

Substituting Eqs. (16.162) and (16.164) in Eq. (16.161), we have

$$\nabla \times (\nabla \times \mathbf{A}) + \frac{\partial}{\partial t}\left(\frac{\partial \mathbf{A}}{\partial t} + \nabla \phi\right) = j$$

$$\nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} + \frac{\partial^2 \mathbf{A}}{\partial t^2} + \nabla . \frac{\partial \phi}{\partial t} = j$$

$$\nabla^2 \mathbf{A} - \frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla\left(\nabla \cdot \mathbf{A} + \frac{\partial \phi}{\partial t}\right) = - j \tag{16.166}$$

The solutions of Maxwell's equations is thus reduced to solving the coupled equations (16.165) and (16.166) for **A** and ϕ.

The potentials as defined earlier are not unique. We can decouple these two equations using Gauge invariance. The transformation

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \nabla \wedge \tag{16.167}$$

$$\phi \to \phi' = \phi - \frac{\partial \wedge}{\partial t} \tag{16.168}$$

where $\wedge$ an arbitrary scalar function leaves **B** and **E** unchanged. The fact that $\nabla \times \nabla \wedge = 0$ leaves **B** unchanged by the transformation. The electric field **E**, Eq. (16.164), becomes

$$\mathbf{E} = -\frac{\partial}{\partial t}(\mathbf{A} + \nabla \wedge) - \nabla\left(\phi - \frac{\partial \wedge}{\partial t}\right)$$

$$= - \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi$$

which is the same as Eq. (16.164). That is, the gauge transformations to (A', ϕ') lead to the same **E** and **B** as before and hence the transformations leave Maxwell's equations invariant. One can use this invariance to select the family of potentials (**A**, ϕ) such that the coupling term in Eq. (16.166)

$$\nabla \cdot \mathbf{A} + \frac{\partial \phi}{\partial t} = 0 \tag{16.169}$$

The freedom available in the definitions of Eqs. (16.167) and (16.168) together is called **gauge transformations** and the condition in Eq. (16.169) is known as **Lorentz gauge condition**. Equation (16.169) can be written as:

$$\frac{\partial A_1}{\partial x_1} + \frac{\partial A_2}{\partial x_2} + \frac{\partial A_3}{\partial x_3} + \frac{\partial (i\phi)}{\partial (it)} = 0$$

$$\frac{\partial A_1}{\partial x_1} + \frac{\partial A_2}{\partial x_2} + \frac{\partial A_3}{\partial x_3} + \frac{\partial A_4}{\partial x_4} = 0$$

$$\frac{\partial A_\mu}{\partial x_\mu} = 0 \quad \text{or} \quad \partial_\mu A_\mu = 0 \tag{16.170}$$

It can easily be shown that the three components of the vector **j** and charge density ρ form the four-vector

$$j = (\mathbf{j},\ ic\rho) \tag{16.171}$$

The components of the vector potential **A** and the scalar potential ϕ form the four-vector potential:

$$A = (\mathbf{A},\ i\phi) \tag{16.172}$$

From Eq. (16.162), we have

$$B_1 = \frac{\partial A_3}{\partial x_2} - \frac{\partial A_2}{\partial x_3} \tag{16.173a}$$

$$B_2 = \frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1} \tag{16.173b}$$

$$B_3 = \frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2} \tag{16.173c}$$

From Eq. (16.164),

$$E_1 = -\frac{\partial A_1}{\partial t} - \frac{\partial \phi}{\partial x_1} \quad \text{or} \quad iE_1 = \frac{\partial A_1}{\partial (it)} - \frac{\partial (i\phi)}{\partial x_1}$$

$$iE_1 = \frac{\partial A_1}{\partial x_4} - \frac{\partial A_4}{\partial x_1} = F_{41} \text{ (say)} \tag{16.174a}$$

$$iE_2 = \frac{\partial A_2}{\partial x_4} - \frac{\partial A_4}{\partial x_2} = F_{42} \tag{16.174b}$$

$$iE_3 = \frac{\partial A_3}{\partial x_4} - \frac{\partial A_4}{\partial x_3} = F_{43} \tag{16.174c}$$

In general,

$$F_{\mu\nu} = \frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_\nu}, \quad F_{\mu\nu} = -F_{\nu\mu} \tag{16.175a}$$

$$F_{k4} = -iE_k, \quad F_{ij} = \epsilon_{ijk} B_k \tag{16.175b}$$

where

$\epsilon_{ijk} = 0$ if two indices are equal
$\epsilon_{ijk} = 1$ if i, j, k are distinct and in cyclic order
$\epsilon_{ijk} = -1$ if i, j, k are distinct and not in cyclic order.

These are the components of the antisymmetric tensor $F_{\mu\nu}$ defined by

$$F_{\mu\nu} = \begin{pmatrix} 0 & B_z & -B_y & -iE_x/c \\ -B_z & 0 & B_x & -iE_y/c \\ B_y & -B_x & 0 & -iE_z/c \\ iE_x/c & iE_y/c & iE_z/c & 0 \end{pmatrix} \tag{16.176}$$

which is the **electromagnetic field four-tensor.**

16.10 QUANTIZATION OF ELECTROMAGNETIC FIELD

The electromagnetic field, an example of a vector field, is described classically in terms of $A(\mathbf{A}, i\phi)$, where $\mathbf{A}$ is the vector potential and ϕ is the scalar potential. The field strengths are given by the antisymmetric tensor $F_{\mu\nu}$, Eq. (16.176). To incorporate the principles of quantum theory into this classical field theory, the field quantization is developed.

The electromagnetic quanta has zero rest mass and as such the classical field equation can be written by setting $m = 0$ in the Klein-Gordon equation, Eq. (16.103):

$$\partial_\mu \partial_\mu A_\nu(x) = 0, \quad \nu = 1, 2, 3, 4 \tag{16.177}$$

Compared to Eq. (16.103), quantization of Eq. (16.177) is difficult due to the following reasons:

(i) Equation (16.177) is equivalent to Maxwell's equations only if it is combined with the Lorentz gauge condition, Eq. (16.170), which implies that all the four components of A are not independent. However, canonical quantization procedure is valid only if they are independent.

(ii) The components A_1, A_2, A_3 are real, whereas $A_4 = i\phi$ is imaginary. Hence, it is not possible to treat all the four components on the same footing.

(iii) Invariance of the field under gauge transformation makes different quantization procedures for different gauges unavoidable.

To overcome the above difficulties, one can use different gauges. Two particularly important gauges are the Lorentz gauge and Coulomb gauge. The problems associated with (i) and (ii) have, however, been successfully solved by a procedure due to Gupta and Bleuler. We use the Lorentz gauge defined by Eq. (16.170) and at first ignore the imaginary character of A_4. In other words we treat all the four A_μ's as independent and Hermitian. This procedure too allows us to obtain certain important results about the quantization of electromagnetic field. In analogy with Eq. (16.106), the Lagrangian density

$$L(x) = -\tfrac{1}{2}\partial_\mu A_\nu \partial_\mu A_\nu \tag{16.178}$$

Expanding the field operator $A_\mu(x)$ in terms of the complete set of plane wave solutions of Eq. (16.177), we have

$$A_\mu(x) = \frac{1}{\sqrt{V}}\sum_k \frac{1}{\sqrt{2\omega_k}} \sum_{r=1}^{4} [a_r(\mathbf{k}) \in_\mu^{(r)}(\mathbf{k}) e^{ikx} + a_r^\dagger(\mathbf{k}) \in_\mu^{(r)*}(\mathbf{k}) e^{-ikx}] \tag{16.179}$$

where $\omega_k = |\,\mathbf{k}\,| > 0$. For each $\mathbf{k}$, $\in^{(r)}(\mathbf{k})$, $r = 1, 2, 3, 4$ form a set of four linearly independent orthonormal vectors in the k-space. $\in_\mu^{(r)}$ is completely arbitrary and is the projection of $\in^{(r)}$ in the x_μ-axis. Therefore,

$$\in_{\mu}^{(r)*}(\mathbf{k})\in_{\mu}^{(s)}(\mathbf{k}') = \delta_{rs}\delta_{kk'} \qquad (16.180)$$

$$\sum_{r=1}^{4}\in_{\mu}^{(r)}(\mathbf{k})\in_{\mu}^{(r)*}(\mathbf{k}) = \delta_{\mu\mu'} \qquad (16.181)$$

To understand more about Eq. (16.179) we shall make a definite choice of the polarization vectors $\in^{(r)}(\mathbf{k})$. Since $\in^{(r)}$ is arbitrary, $\in^{(3)}(\mathbf{k})$ can be taken as the component along **k** and $\in^{(1)}(\mathbf{k})$ and $\in^{(2)}(\mathbf{k})$ perpendicular to it. With these conventions, we call $\in^{(1)}(\mathbf{k})$ and $\in^{(2)}(\mathbf{k})$ as the transverse polarizations and $E^{(3)}(\mathbf{k})$ as the longitudinal polarization. Then it follows:

$$\in_{\mu}^{(r)}(\mathbf{k}) = \delta_{\mu r}\in^{(r)}(\mathbf{k}) \qquad (16.182)$$

With this choice, Eq. (16.179) reduces to

$$A_{\mu}(x) = \frac{1}{\sqrt{V}}\frac{1}{\sqrt{2\omega_k}}[a_{\mu}(\mathbf{k})\in^{(\mu)}(\mathbf{k})\,e^{ikx} + a_{\mu}^{\dagger}(\mathbf{k})\in^{(\mu)*}(\mathbf{k})e^{-ikx}] \qquad (16.183)$$

As quantization postulates, in analogy with Eqs. (16.116) and (16.117), we have

$$[a_{\mu}(\mathbf{k}), a_{\nu}^{\dagger}(\mathbf{k}')] = \delta_{\mu\nu}\,\delta(\mathbf{k} - \mathbf{k}') \qquad (16.184)$$

$$[a_{\mu}(\mathbf{k}), a_{\nu}(\mathbf{k}')] = [a_{\mu}^{\dagger}(\mathbf{k}), a_{\nu}^{\dagger}(\mathbf{k}')] = 0 \qquad (16.185)$$

The operators $a_{\mu}^{\dagger}(\mathbf{k}), a_{\mu}(\mathbf{k})$ and $a_{\mu}^{\dagger}(\mathbf{k})\,a_{\mu}(\mathbf{k}) = N(\mathbf{k})$ could be interpreted as the creation, annihilation and the number operators respectively, of the particle called photon of momenum **k**, energy ω_k and polarization vector $\in^{(\mu)}$. The three polarization states in space indicate that the photons have spin 1 with z-component of spin 1, 0, –1. A physical interpretation of $\in^{(4)}$ is much more involved. A photon with polarization along $\in^{(4)}$ is called a **time like photon**.

The momenta conjugate to the field $A_{\mu}(x)$ is:

$$\pi_{\mu} = \frac{\partial L}{\partial \dot{A}_{\mu}} \qquad (16.186)$$

The Lagrangian density, Eq.(16.178), reduces to

$$L = -\frac{1}{2}\partial_{\mu}\,A_{\nu}\,\partial_{\mu}A_{\nu} = -\frac{1}{2}\left[\frac{\partial A_{\nu}}{\partial x_k}\cdot\frac{\partial A_{\nu}}{\partial x_k} + \frac{\partial A_{\nu}}{\partial x_4}\cdot\frac{\partial A_{\nu}}{\partial x_4}\right]$$

$$= -\frac{1}{2}\left[\frac{\partial A_{\nu}}{\partial x_k}\cdot\frac{\partial A_{\nu}}{\partial x_k} + \frac{\partial A_{\nu}}{i\partial t}\cdot\frac{\partial A_{\nu}}{i\partial t}\right]$$

$$= -\frac{1}{2}\left[\frac{\partial A_{\nu}}{\partial x_k}\cdot\frac{\partial A_{\nu}}{\partial x_k} - \dot{A}_{\nu}^{2}\right] \qquad (16.187)$$

Consequently,

$$\pi_\mu = \dot{A}_\mu \tag{16.188}$$

The Hamiltonian density H is given by

$$\begin{aligned} H(x) &= \pi_\mu \dot{A}_\mu - L = \pi_\mu \pi_\mu + \frac{1}{2}\left[\frac{\partial A_\mu}{\partial x_k} \cdot \frac{\partial A_\mu}{\partial x_k} - \dot{A}_\mu^2\right] \\ &= \pi_\mu \pi_\mu + \frac{1}{2}(\nabla \cdot A_\mu) \cdot (\nabla \cdot A_\mu) - \frac{1}{2}\pi_\mu \pi_\mu \\ &= \frac{1}{2}\pi_\mu \pi_\mu + \frac{1}{2}(\nabla \cdot A_\mu) \cdot (\nabla \cdot A_\mu) \end{aligned} \tag{16.189}$$

where Eq. (16.186) is used. The field Hamiltonian

$$H = \int_V H(x)\, d^3\mathbf{x} \tag{16.190}$$

Substituting $H(x)$ and using Eqs. (16.179),

$$\begin{aligned} H &= \sum_k \frac{1}{2}[a_\mu(\mathbf{k})\, a_\mu^\dagger(\mathbf{k}) + a_\mu^\dagger(\mathbf{k})\, a_\mu(\mathbf{k})]\, \omega_k \\ &= \sum_k \frac{1}{2}[a_\mu(\mathbf{k}), a_\mu^\dagger(\mathbf{k})]_+ \,\omega_k = \sum_k \sum_\mu \left[N_\mu(\mathbf{k}) + \frac{1}{2}\right]\omega_k \end{aligned} \tag{16.191}$$

The total energy of the field is:

$$E = \sum_k \sum_{\mu=1}^{4} \left[n_\mu(\mathbf{k}) + \frac{1}{2}\right]\omega_k \tag{16.192}$$

where $n_\mu(\mathbf{k}) = 0, 1, 2, \ldots, \infty$ (16.193)

In the Gupta-Bleuler formalism, the above referred difficulties are solved by modifying the definition of scalar product and requiring only the expectation values of operators, rather than the operators themselves to obey the classical equations.

REVIEW QUESTIONS

1. Why a field is specified by its amplitude $\Psi(\mathbf{r}, t)$ and the dependence of these amplitudes on time?
2. State the classical field equation and explain the quantities involved therein.
3. State and explain the classical field equation in Hamiltonian form.
4. Define the conjugate field $\pi(\mathbf{r}, t)$. State the commutation relations obeyed by the field amplitude $\Psi(\mathbf{r}, t)$ and the conjugate field.

5. What are creation, annihilation and number operators? Why are they called so?
6. If $\psi(n_k)$ is an eigenket of $N_k = a_k^\dagger a_k$ with eigenvalue n_k, show that $a\psi(n_k)$ is also an eigenket of N_k with the eigenvalue lowered by 1. Also, show that $a^\dagger\psi(n_k)$ is an eigenket of N_k with an eigenvalue increased by 1.
7. State the anticommutation relations obeyed by the creation and annihilation operators for a system of fermions. Hence show that the number of particles in any state is either zero or 1.
8. In relativistic quantum field theory, every charged particle is accompanied by an antiparticle having opposite charge. Substantiate.

PROBLEMS

1. Define the number operator N_k. For a system of bosons, show that (i) the commutator $[N_k, N_l] = 0$, (ii) all positive integers including zero are the eigenvalues of N_k.
2. What are creation ($a^\dagger$) and annihilation (a) operators? In the state $|n_1, n_2, n_3, ..., n_k, ...\rangle$ for a system of bosons, show that

$$a_k |n_1, n_2, n_3, ..., n_k, ...\rangle = \sqrt{n_k}\, |n_1, n_2, ..., (n_k - 1), ...\rangle$$

$$a_k^\dagger |n_1, n_2, n_3, ..., n_k, ...\rangle = \sqrt{n_k + 1}\, |n_1, n_2, ..., (n_k + 1), ...\rangle$$

3. For a system of fermions, define the number operator N_k and show that its eigenvalues are zero and one.
4. The classical Schrödinger field $\Psi(\mathbf{r}, t)$ can be quantized by converting it into an operator by taking the Lagrangian density of the system as

$$L = i\hbar\Psi^*\dot{\Psi} - \frac{\hbar^2}{2m}\nabla\Psi^* \cdot \nabla\Psi - V(r, t)\,\Psi^*\Psi$$

Derive the Hamiltonian density for the system. Hence show that this value of L leads to the familiar classical equation for $\Psi(\mathbf{r}, t)$ and $\Psi^*(\mathbf{r}, t)$.

5. State Maxwell's electromagnetic equations in terms of the electric field E and magnetic field B associated with it. Express them in the form of two coupled equations in terms of the vector potential A and scalar potential ϕ.

Chapter 17

Chemical Bonding

The mechanism that holds the atoms together in molecules was a basic question confronting the chemists for a long time. With the advent of quantum mechanics elegant methods were developed. An exact solution of the Schrödinger equation for a molecule is not possible because even the simplest one consists of two nuclei and one electron. To simplify the solution, Born-Oppenheimer approximation is therefore adopted, in which it is assumed that the nuclei may be treated as stationary while the electrons move around them. This approximation is fairly valid as the nuclei are much heavier than an electron. Two such approaches are there for the calculation of molecular structure, the *Molecular Orbital (MO) and the Valence Bond (VB) methods.* Most of the modern computational works make use of the MO theory.

17.1 BORN-OPPENHEIMER APPROXIMATION

In molecules, one has to deal with not only the moving electrons but also the moving nuclei. The Hamiltonian representing the motion of a molecule is:

$$H = -\frac{\hbar^2}{2\,m_e}\sum_i \nabla_i^2 - \sum_\alpha \frac{\hbar^2}{2\,m_\alpha}\nabla_\alpha^2 - \sum_\alpha\sum_i \frac{kZ_\alpha e^2}{r_{i\alpha}} + \sum_\alpha\sum_{\beta>\alpha}\frac{k\,Z_\alpha\,Z_\beta\,e^2}{r_{\alpha\beta}} + \sum_i\sum_{j>i}\frac{ke^2}{r_{ij}} \tag{17.1}$$

where i, j refer to electrons, α, β to nuclei and $k = 1/4\pi\varepsilon_0$, ε_0 being the permitivity of vacuum. The first and second terms of Eq. (17.1) are the operators for the kinetic energy of the electrons and nuclei respectively. The third term is the potential energy of attraction between the electrons and nuclei and the fourth term is the potential energy of repulsion between the nuclei. The quantities $r_{i\alpha}$ is the distance between electron i and nucleus α and $r_{\alpha\beta}$ is the distance between nuclei α and β. The last term is the potential energy of the repulsion between the electrons, r_{ij} being the distance between the electrons i and j.

An exact solution corresponding to this Hamiltonian is not possible because even the simplest molecule consists of two nuclei and one electron. To simplify the solution, Born and Oppenheimer utilized the fact that the nuclei are much heavier than electrons. Therefore, to a good approximation, we can treat the nuclei as stationary. Consequently, the Hamiltonian representing the electronic motion is:

$$H = -\frac{\hbar^2}{2\,m_e}\sum_i \nabla_i^2 - \sum_\alpha\sum_i \frac{kZ_\alpha e^2}{r_{i\alpha}} + \sum_i\sum_{j>i}\frac{ke^2}{r_{ij}} + \sum_\alpha\sum_{\beta>\alpha}\frac{kZ_\alpha Z_\beta e^2}{r_{\alpha\beta}} \tag{17.2}$$

The internuclear distances $r_{\alpha\beta}$ are not variables, but are constants. The contribution from the last term of Eq. (17.2) is independent of the electronic coordinates and hence is a constant for a given nuclear configuration. The approximation of separating the electronic and nuclear motions is called the **Born-Oppenheimer approximation**. This approximation causes practically no error in the ground electronic energy levels of diatomic molecules.

17.2 MOLECULAR ORBITAL METHOD

In the molecular orbital method developed by Mulliken, acceptable molecular wavefunctions called **molecular orbitals** that describe molecular energy states are derived first. These molecular orbitals extend and embrace all the nuclei in it and will be polycentric, every electron contributes to the strength of every bond. They have the same significance as do atomic orbitals. Molecular quantum numbers are associated with these orbitals. Once the molecular orbitals are obtained, the system of electrons are built up by filling the orbitals with electrons in accordance with Pauli's exclusion principle. The problem in MO theory is therefore to construct reasonable molecular orbitals. This can be done in number of ways. As molecules consist of atoms, molecular orbitals may be taken as a function of atomic orbitals centered on the individual atoms. The most commonly used approach for obtaining the MO is the Linear Combination of Atomic Orbitals, abbreviated as *LCAO approximation*. In this approach, the molecular orbital ψ is written as a linear combination of the atomic orbitals as:

$$\psi = c_1\psi_1 + c_2\psi_2 + \cdots \tag{17.3}$$

where ψ_1, ψ_2, ... are the individual atomic orbitals. The constants c_1, c_2, ... are to be selected in such a way that the energy given by ψ is minimum. To generate an effective MO by LCAO method, the combining atomic orbitals must have (i) energies of comparable magnitude (ii) considerable overlapping and (iii) the same symmetry. If the orbitals have different energies, the electron will tend to remain most of the time in the atomic orbital which has the lowest energy. As the first example, we shall consider the molecular orbitals of the H_2^+ ion.

17.3 MO TREATMENT OF HYDROGEN MOLECULE ION

The simplest of the diatomic molecule is H_2^+, the hydrogen molecule ion, consisting of an electron of charge $-e$ associated with two protons a and b each with positive charge $+e$ separated by a distance R (Figure 17.1). The electron when in the neighbourhood of a can be described by the atomic orbital ψ_a centred on a and when it is in the neighbourhood of b is described by the atomic orbital ψ_b centred on b, ψ_a and ψ_b are 1s atomic orbitals given by

$$\psi_a = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_a/a_0}, \quad \psi_b = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_b/a_0} \tag{17.4}$$

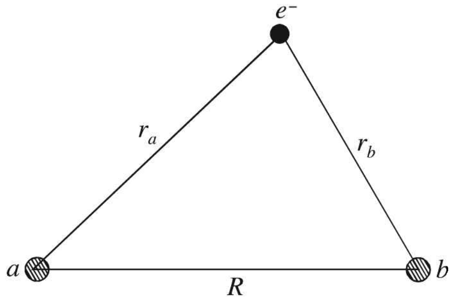


Figure 17.1 The H_2^+ molecule.

The first step is to find a set of molecular orbitals for the molecule such that it resembles ψ_a when the electron is in the neighbourhood of a and resembles ψ_b when the electron is in the neighbourhood of b. Hence, a reasonable MO will be a linear combination of ψ_a and ψ_b.

$$\psi = c_1\psi_a + c_2\psi_b \tag{17.5}$$

where c_1 and c_2 are constants to be selected so that the energy is a minimum. The energy E of the system is given by the Schrödinger equation:

$$H\psi = E\psi, \quad E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{17.6}$$

From Eq. (17.2), the Hamiltonian of the system is:

$$H = \frac{-\hbar^2}{2m}\nabla^2 - \frac{ke^2}{r_a} - \frac{ke^2}{r_b} + \frac{ke^2}{R} \tag{17.7}$$

The last term represents the electrostatic repulsion between the nuclei and m is the mass of the electron. Substituting the value of ψ in Eq. (17.6), we get

$$E = \frac{\langle (c_1\psi_a + c_2\psi_b) | H | (c_1\psi_a + c_2\psi_b) \rangle}{\langle (c_1\psi_a + c_2\psi_b) | (c_1\psi_a + c_2\psi_b) \rangle}$$

As the atomic orbitals ψ_a and ψ_b are normalized,

$$E = \frac{|c_1|^2 \langle \psi_a | H | \psi_a \rangle + c_1^* c_2 \langle \psi_a | H | \psi_b \rangle + c_2^* c_1 \langle \psi_b | H | \psi_a \rangle + |c_2|^2 \langle \psi_b | H | \psi_b \rangle}{|c_1|^2 + |c_2|^2 + c_1^* c_2 \langle \psi_a | \psi_b \rangle + c_2^* c_1 \langle \psi_b | \psi_a \rangle} \tag{17.8}$$

The integrals, $\langle \psi_a | H | \psi_a \rangle = H_{aa}, \ \langle \psi_b | H | \psi_b \rangle = H_{bb}$ (17.9a)

are known as **Coulomb integrals**,

$$\langle \psi_a | H | \psi_b \rangle = H_{ab}, \ \langle \psi_b | H | \psi_a \rangle = H_{ba} \tag{17.9b}$$

as **resonance or exchange integrals** and

$$\langle \psi_a | \psi_b \rangle = \langle \psi_b | \psi_a \rangle = S \tag{17.9c}$$

as **overlap integral**. H_{aa} and H_{bb} are the energies of the atomic orbitals ψ_a and ψ_b in the molecular skeleton. $H_{ab} = H^*_{ba}$ since H is hermitian.

Since the selection of the wavefunction ψ is arbitrary, according to the variational theorem (Section 10.1),

$$E \geq E_0 \tag{17.10}$$

where E_0 is the exact ground state energy of the system. To get the value of c_1 and c_2, the energy E has to be minimised with respect to these constants taking H_{aa}, H_{bb}, H_{ab}, H_{ba} as constants. E will then be a function of c_1 and c_2. As the atomic orbitals ψ_a and ψ_b are real, from Eq. (17.8),

$$E(c_1^2 + c_2^2 + 2c_1c_2S) = c_1^2H_{aa} + c_2^2H_{bb} + 2c_1c_2H_{ab}$$

For the energy to be minimum, $\partial E/\partial c_1 = 0$. Then

$$E(2c_1 + 2c_2S) = 2c_1H_{aa} + 2c_2H_{ab}$$

$$(H_{aa} - E)c_1 + (H_{ab} - ES)c_2 = 0 \tag{17.11}$$

The condition $\partial E/\partial c_2 = 0$ gives

$$(H_{ab} - ES)\, c_1 + (H_{bb} - E)\, c_2 = 0 \tag{17.12}$$

These simultaneous homogeneous equations in c_1 and c_2 have non-trivial solutions only if

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{vmatrix} = 0 \tag{17.13}$$

This determinant, called the **secular determinant**, gives

$$(H_{aa} - E)\,(H_{bb} - E) - (H_{ab} - ES)^2 = 0 \tag{17.14}$$

and the two roots for E are the allowed energy values of the system.

For the homonuclear diatomic molecule H_2^+, as the nuclei a and b are identical, $H_{aa} = H_{bb}$ and Eq. (17.14) reduces to

$$(H_{aa} - E + H_{ab} - ES)(H_{aa} - E - H_{ab} + ES) = 0 \tag{17.15}$$

The two values of energy are:

$$E_1 = \frac{(H_{aa} + H_{ab})}{1+S}, \quad E_2 = \frac{(H_{aa} - H_{ab})}{1-S} \tag{17.16}$$

Since $H_{aa} - E = ES - H_{ab}$ when energy is E_1, from Eq. (17.11), we have

$$(ES - H_{ab})c_1 + (H_{ab} - ES)c_2 = 0 \quad \text{or} \quad c_1 = c_2 \tag{17.17}$$

Similarly with the second value for energy, we have $H_{aa} - E = H_{ab} - ES$ and, therefore, from Eq. (17.12), we have $c_1 = -c_2$. Consequently, the wave functions corresponding to energies E_1 and E_2 are respectively,

$$\psi_1 = c_1(\psi_a + \psi_b) \quad \text{and} \quad \psi_2 = c_2(\psi_a - \psi_b) \tag{17.18}$$

Normalization gives

$$\psi_1 = \frac{\psi_a + \psi_b}{\sqrt{2+2S}}, \quad \psi_2 = \frac{\psi_a - \psi_b}{\sqrt{2-2S}} \tag{17.19}$$

The Coulomb integral

$$H_{aa} = \langle \psi_a | \frac{\hbar^2}{2m}\nabla^2 - \frac{ke^2}{r_a} | \psi_a \rangle - \langle \psi_a | \frac{ke^2}{r_b} | \psi_a \rangle + \langle \psi_a | \frac{ke^2}{R} | \psi_a \rangle \tag{17.20}$$

The first term on the right is simply the ground state energy of the hydrogen atom E_H since the operator in it is the hydrogen atom Hamiltonian and ψ_a is the one electron wavefunction. The nuclear repulsion term, ke^2/R is independent of the electronic coordinates. Writing

$$V_{aa} = \langle \psi_a | \frac{ke^2}{r_b} | \psi_a \rangle \quad \text{and} \quad V_{ab} = \langle \psi_a | \frac{ke^2}{r_a} | \psi_b \rangle \tag{17.21}$$

$$H_{aa} = E_H - V_{aa} + \frac{ke^2}{R} \tag{17.22}$$

$$H_{ab} = E_H S - V_{ab} + \frac{ke^2}{R} S \tag{17.23}$$

The value of the quantities V_{aa}, V_{ab}, S and the nuclear repulsion energy ke^2/R depend on the internuclear distance R and are always positive. The overlap $S = 0$, if the two nuclei are infinitely separated and $S = 1$ if they are together. Substitution of Eqs. (17.22) and (17.23) in Eq. (17.16) gives

$$E_1 = E_H - \frac{(V_{aa} + V_{ab})}{1 + S} + \frac{ke^2}{R} \tag{17.24}$$

and

$$E_2 = E_H - \frac{(V_{aa} - V_{ab})}{1 - S} + \frac{ke^2}{R} \tag{17.25}$$

The MO ψ_1 has an energy E_1 lower than that of the atomic orbitals from which it is formed (Figure 17.2). However, in the case of ψ_2 the energy E_2 is higher than that of the atomic orbitals.

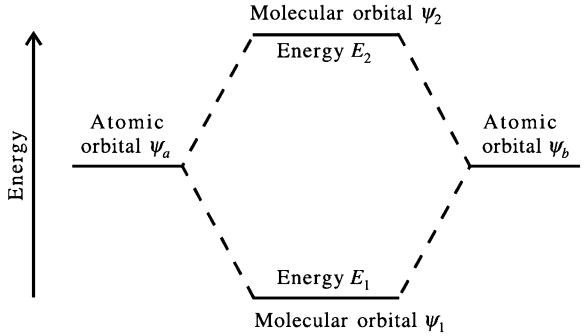


Figure 17.2 Energies of molecular orbitals and their constituent atomic orbitals.

The wavefunction ψ_1 corresponds to the situation in which there is a build up of electron density between the two nuclei and a more effective screening of one nucleus from the other. In other words, a bond has been formed which is described by a *bonding molecular orbital.* The other possibility ψ_2 corresponds to the situation in which there is a depletion of charge between the two nuclei and a larger nuclear repulsion resulting in an *antibonding orbital.* Figure 17.3 illustrates the formation of bonding and antibonding orbitals from two 1s atomic orbitals. Both these orbitals are symmetrical about the internuclear axis. Molecular orbitals which are symmetrical about the internuclear axis are designated by σ (sigma) and those which are not symmetrical about the internuclear axis are designated by π (pi). The bonding orbital discussed is represented by the symbol $1s\sigma$ since it is produced from two 1s atomic orbitals. The antibonding state is represented by the symbol

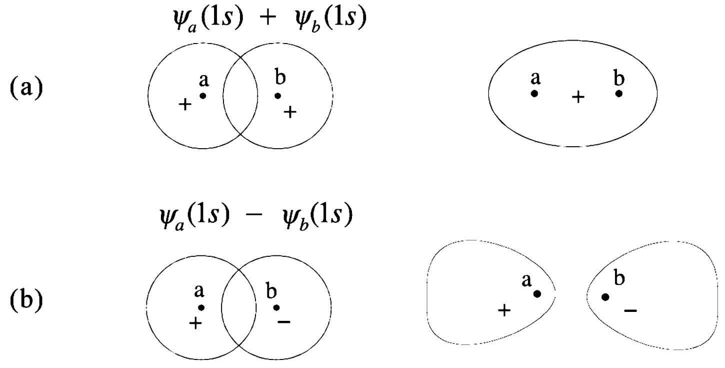


Figure 17.3 Combination of 1s orbitals to form (a) bonding orbital $1s\sigma$ (b) antibonding orbitals $1s\sigma^*$.

$1s\sigma^*$, star representing higher energy. Probability density for the bonding and antibonding states are shown in Figure 17.4.

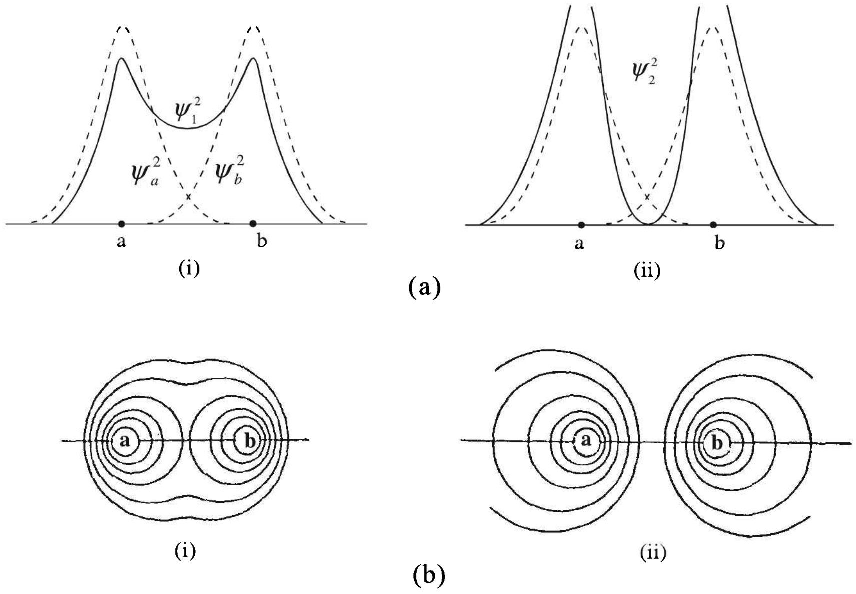


Figure 17.4 The hydrogen molecule ion (a) probability density functions. Full lines represent ψ_1^2 or ψ_2^2; broken lines represent ψ_a^2 or ψ_b^2. (b) contours of equal electron density for ψ_1^2 and ψ_2^2.

17.4 MO TREATMENT OF HYDROGEN MOLECULE

The treatment of hydrogen molecule in MO theory is essentially the same as that of H_2^+ molecule. The Hamiltonian operator for H_2 molecule is:

$$H = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a1}} - \frac{ke^2}{r_{b1}}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{b2}} - \frac{ke^2}{r_{a2}}\right) + \frac{ke^2}{r_{12}} + \frac{ke^2}{R} \tag{17.26}$$

where 1 and 2 represent electrons and *a* and *b* protons (Figure 17.5).

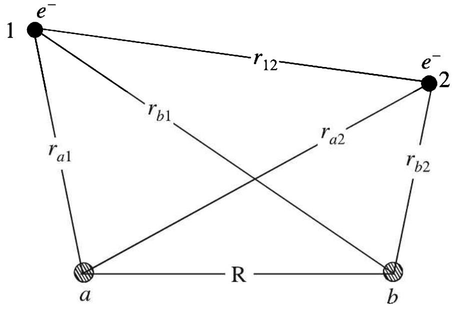


Figure 17.5 Inter particle distances in hydrogen molecule.

Writing,
$$H(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a1}} - \frac{ke^2}{r_{b1}} \tag{17.27a}$$

$$H(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{a2}} - \frac{ke^2}{r_{b2}} \tag{17.27b}$$

$$H = \left(H(1) + \frac{ke^2}{R}\right) + \left(H(2) + \frac{ke^2}{R}\right) + \frac{ke^2}{r_{12}} - \frac{ke^2}{R} \tag{17.28}$$

We shall compute the expectation value of H with a trial wavefunction. As the term $-ke^2/R$ is independent of electronic coordinates, it makes no difference to electronic wavefunction whether it is retained in the Hamiltonian or incorporated later in the energy expression as an additional term $-ke^2/R$.

The Hamiltonian inside the brackets in Eq. (17.28) is the same as the one solved for H_2^+ molecule. Therefore, one can reasonably take that in the ground state of hydrogen molecule both the electrons occupy the bonding orbital ψ_1 of H_2^+ which is symmetric with respect to the interchange of nuclei *a* and *b*. The trial wavefunction for the hydrogen molecule can then be written as:

$$\psi_{mo} = \psi_1(1)\psi_1(2) = \frac{\psi_a(1) + \psi_b(1)}{\sqrt{2+2S}} \cdot \frac{\psi_a(2) + \psi_b(2)}{\sqrt{2+2S}}$$

$$= \frac{1}{2(1+S)}[\psi_a(1) + \psi_b(1)][\psi_a(2) + \psi_b(2)] \tag{17.29}$$

We now include the electron spin and Pauli's principle into the formalism. Spin functions for the two electron system are given in (Table 13.1):

$$\text{Symmetric:}\quad \begin{cases} \alpha(1)\,\alpha(2) \\ \dfrac{1}{\sqrt{2}}[\alpha(1)\,\beta(2)+\beta(1)\,\alpha(2)] \\ \beta(1)\,\beta(2) \end{cases} \tag{17.30a}$$

$$\text{Antisymmetric:}\quad \frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2)-\beta(1)\,\alpha(2)] \tag{17.30b}$$

$\alpha(1)$ means the first electron is in a 'spin up' state, $\beta(1)$ means the first electron is in a 'spin down' state and so on. According to Pauli's principle, the total wavefunction must be antisymmetric with respect to the interchange of the two electrons. Therefore, the symmetric ψ_{mo} (Eq. 17.29) has to combine with the antisymmetric spin part leading to the wavefunction:

$$\frac{1}{2\,(1+S)}[\psi_a(1)+\psi_b(1)]\,[\psi_a(2)+\psi_b(2)]\,\frac{1}{\sqrt{2}}[\alpha\ (1)\,\beta\ (2)-\beta(1)\,\alpha(2)]$$

This is a singlet state as its spin $S = 0$. The energy is not affected by the inclusion of spin part as the Hamiltonian does not contain spin terms. The space part, Eq. (17.29), can then be taken as the MO for the evaluation of energy. With Eq. (17.29) as trial wavefunction,

$$\langle\psi_{mo}|H|\psi_{mo}\rangle = \left\langle\psi_{mo}\left|H(1)+\frac{ke^2}{R}\right|\psi_{mo}\right\rangle + \left\langle\psi_{mo}\left|H(2)+\frac{ke^2}{R}\right|\psi_{mo}\right\rangle$$

$$+\left\langle\psi_{mo}\left|\frac{ke^2}{r_{12}}\right|\psi_{mo}\right\rangle - \left\langle\psi_{mo}\left|\frac{ke^2}{R}\right|\psi_{mo}\right\rangle$$

$$E = 2E_1(R) + \left\langle\psi_{mo}\left|\frac{ke^2}{r_{12}}\right|\psi_{mo}\right\rangle - \frac{ke^2}{R} \tag{17.31}$$

where E_1 is the energy of the H_2^+ molecule (Section 17.3). Substituting the value of E_1 from Eq. (17.24), we get

$$E = 2E_H - \frac{2\,(V_{aa}+V_{ab})}{1+S} + \frac{ke^2}{R} + \left\langle\psi_{mo}\left|\frac{ke^2}{r_{12}}\right|\psi_{mo}\right\rangle \tag{17.32}$$

After computing the contribution due to the electron-electron repulsion, the total energy is minimized with respect to the internuclear separation R. Coulson from a refined variational calculation obtained $r_0 = 0.732$ Å for the equilibrium internuclear distance and a dissociation energy $D_e = 3.49$ eV. The experimental values are 0.74 Å and 4.75 eV respectively.

The MO given in Eq. (17.29) may be written in the form:

$$\psi_{mo} = \frac{1}{2(1+S)} [\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2) + \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)] \tag{17.33}$$

The first two terms correspond to the situation in which both the electrons are associated with the same proton. These represent the ionic structures $H_a^- H_b^+$ and $H_a^+ H_b^-$ respectively. However, the third and fourth terms represent the situation in which the electrons are shared equally by both the protons and hence they correspond to covalent structures of the hydrogen molecule. The MO selected gives equal importance to ionic and covalent structures which is probably causing the disagreement with the experimental values.

17.5 DIATOMIC MOLECULAR ORBITALS

The general ideas that have been developed regarding bonding in H_2^+ and H_2 molecules can be extended to other homonuclear diatomic molecules. It is often advantageous to classify molecular orbitals in terms of their symmetry about internuclear axis. As the atoms *a* and *b* are identical, the mid-point of the *a–b* bond is a centre of symmetry for the molecule. If an inversion of a molecular orbital about the centre of symmetry does not change the sign of ψ, it is said to be even and is denoted by the symbol *g* as a subscript. If the sign changes, the orbital is said to be odd and a subscript *u* is assigned to the symbol. Here, *g* and *u* stand for the German words gerade (means even) and ungerade (means odd) respectively.

Combination of Two *s*-orbitals

As already discussed (Section 17.3), the combination of two 1s orbitals gives rise to the formation of a bonding (1sσ) and an antibonding (1sσ^*) orbitals. There is a build up of electron charge between the nuclei leading to the formation of a bond in the case of bonding orbital and a depletion of charge between the nuclei in the case of antibonding orbital. In the above notation, the bonding and antibonding orbitals are respectively denoted by $1s\sigma_g$ and $1s\sigma_u^*$. Two 2*s* atomic orbitals combine to form again a bonding ($2s\sigma_g$) and an antibonding ($2s\sigma_u^*$) molecular orbitals of the same shapes as $1s\sigma_g$ and $1s\sigma_u^*$ orbitals.

Combination of *s* and p_x Orbitals

A *s*-orbital may combine with a *p*-orbital if the lobes of the *p*-orbital point along the internuclear axis. A bonding MO results when the adjacent lobes have the same sign and an antibonding MO when the adjacent lobes are of opposite sign (Figure 17.6).

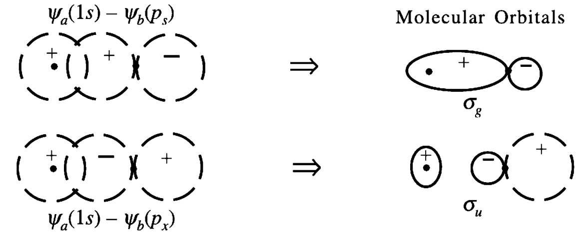


Figure 17.6 Combination of s and p_x atomic orbitals.

Combination of Two *p*-orbitals

The two lobes of each of the three p-orbitals have opposite sign. If the internuclear axis is taken as the x direction, two p_x-atomic orbitals combine to give the MO's $2p_x\sigma_g$ and $2p_x\sigma_u{}^*$ as represented in Figure 17.7. Both have symmetry about the bond axis. However, the combination of two p_y-orbitals give the molecular orbitals $2p_y\pi_u$ and $2p_y\pi_g{}^*$ (Figure 17.8). The $p_y\pi_u$ MO consists of two streamers, one above and one below the nuclei. In this case, the bonding orbital is odd and the antibonding orbital is even unlike the earlier ones. Formation of π molecular orbitals from atomic p_z orbitals is similar to the one from atomic p_y orbitals.

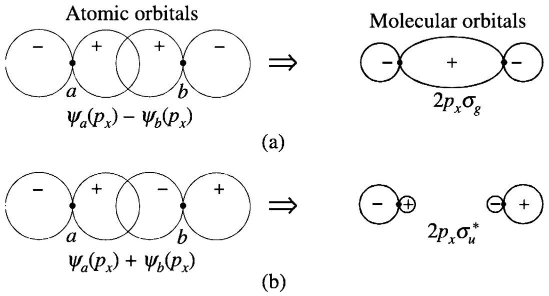


Figure 17.7 Formation of (a) bonding orbital $2p_x\sigma_g$ and (b) antibonding $2p_x\sigma_u{}^*$ molecular orbitals from two p_x orbitals,

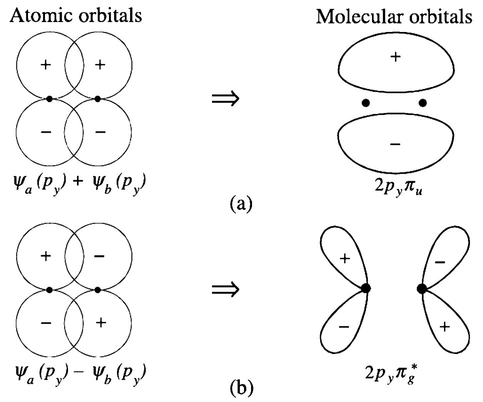
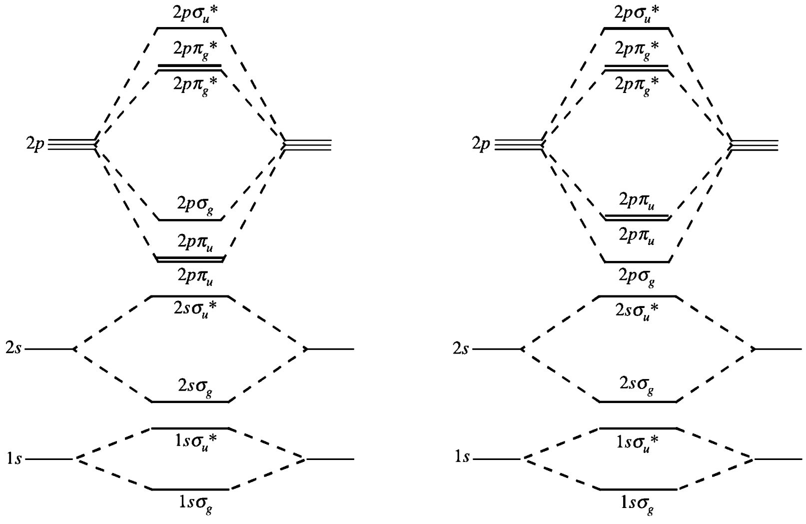


Figure 17.8 Formation of (a) bonding orbital $2p_y\pi_u$ and (b) antibonding orbital $2p_y\pi_g{}^*$ from two p_y-orbitals (combination is the same for p_z-orbitals).

A point to be noted in the combination of atomic orbitals is that the possibility for the combination of 1s and 2s atomic orbitals or *s* and *p* orbitals of two identical atoms is not possible as their energies are completely different.

Molecular Orbital Energy Level Diagram

For discussing the electronic configuration of molecules, it would be convenient if the MO's are arranged in the increasing order of energy. It may be noted here that the energy levels of molecular orbitals of diatomic molecules resulting from 2*p* orbitals are somewhat uncertain as the atomic number of the atom increases. For molecules lighter than O_2, the $2p\pi_u$ orbitals lie higher than the $2p\sigma_g$ orbitals. However, for molecules heavier than O_2, the $2p\pi_u$ orbitals are of lower energy than $2p\sigma_g$ orbitals. Exceptions occur for this general rule. Figure 17.9 gives the molecular orbital energy level diagram for homonuclear diatomic molecules.



(a) (b)

Figure 17.9 Molecular orbital energy level diagram for homonuclear diatomic molecules (a) heavier than O_2 (b) lighter than O_2.

An alternate terminology suggested by R.S. Mulliken for the orbitals $2s\sigma$ to $2p\sigma^*$ is also in use. Its sequence is:

$$\begin{aligned} z\sigma\ (2s\sigma) < y\sigma\ (2s\sigma^*) < x\sigma\ (2p_x\sigma) < w\pi\ (2p_y\pi = 2p_z\pi) \\ < v\pi\ (2p_y\pi^* = 2p_z\pi^*) < u\sigma\ (2p_x\sigma^*) \end{aligned}$$

The earlier notation is given inside the brackets. This notation can also be used for one-quantum and 3-quantum molecular orbitals by writing (*K*) and (*M*) before the Mulliken symbol. Thus (*K*)$z\sigma$ stands for $1s\sigma$, (*M*)$y\sigma$ for $3s\sigma^*$ and so on.

17.6 ELECTRONIC CONFIGURATION OF DIATOMIC MOLECULES

Once the molecular orbitals are obtained, electrons can be assigned to the orbitals consistent with Pauli's exclusion principle. Each MO holds two electrons of opposite spins. When the orbitals are degenerate, Hund's rule which states that the arrangement with the highest total spin generally lies lowest applies.

Homonuclear Diatomic Molecules

H_2: The number of electrons in hydrogen molecule is two. The MO $1s\sigma$ is formed from two H($1s$) atomic orbitals. As both the electrons are in the lowest bonding molecular orbital, the two electron bond of hydrogen molecule is stronger than the one electron bond of H_2^+.

$$2\text{H}(1s) \Rightarrow \text{H}_2[(1s\sigma_g)^2]$$

He_2: The overlap of two helium $1s$ orbitals gives the bonding $1s\sigma_g$ and antibonding $1s\sigma_u^*$ molecular orbitals with two electrons in each. The superposition of two electrons in the bonding orbitals and two in the antibonding orbitals leads to no bonding. Hence He_2 molecule does not exist under normal condition.

$$2\text{He}(1s^2) \Rightarrow \text{He}_2[(1s\sigma_g)^2(1s\sigma_u{}^*)^2]$$

Li_2: Lithium atom has an electronic configuration $1s^22s$. Molecular orbitals have to be constructed from $1s$ as well as the $2s$ atomic orbital. The presence of two electrons in the bonding $1s\sigma_g$ orbital and two in the antibonding orbital $1s\sigma_u^*$ leads to cancellation of the bonding between the two Li atoms. Hence the bonding between the Li atoms results from the pairing of the $2s$ electrons in the bonding orbital $2s\sigma_g$. Writing KK for $(1s\sigma_g)^2$ $(1s\sigma_u^*)^2$, the ground electronic configuration of Li_2 is written as:

$$\text{Li}_2\ [KK\ (2s\sigma_g)^2]$$

The other alkali metals have an analogous configuration. In the subsequent discussion, we shall treat such inner shell electrons as non-bonding.

C_2: Carbon molecule has 12 electrons. The electrons are distributed as:

$$C_2\ [KK\ (2s\sigma_g)^2\ (2s\sigma_u{}^*)^2\ (2p\sigma_g)^2\ (2p\pi_u)^2]$$

The orbital $2p\pi_u$ is doubly degenerate. According to Hund's rule, the term with the highest total spin will have a lower energy. If both the electrons occupy one of the degenerate MO's, their spins must be antiparallel giving a total spin of zero. However, if one electron is in one of the degenerate MO's and the other electron in the other MO, their spins will be parallel giving a total spin of one. This term will be the lowest. As $2p\pi_u$ and $2p\sigma_g$ MO's have nearly the same energy, an alternate ground state configuration is also possible.

$$[KK\,(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^1\,(2p\pi_u)^3]$$

In this configuration also, two of the electrons will have their spins parallel giving a net spin of one, leading to a triplet term.

N_2: The fourteen electrons in the nitrogen molecule are distributed as:

$$N_2\ [KK\,(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^2\,(2p\pi_u)^4]$$

The bonding orbitals $(2p\sigma_g)^2$ $(2p\pi_u)^4$ are not cancelled by the corresponding antibonding orbitals. These six bonding electrons give triple bond N ≡ N, one bond being σ and the other two are π bonds. In this configuration, a strong binding is expected as it has 8 bonding and 2 antibonding electrons, apart from the K electrons. As N_2 has 2 more bonding electrons than C_2, its dissociation energy is expected to be larger which is confirmed by experiments.

O_2: The O_2 molecule has two more electrons than the N_2 molecule. Since the next MO $2p\pi_g^*$ is degenerate, the two additional electrons will go in these antibonding orbitals one each with parallel spins (Hund's rule). This gives the electronic configuration,

$$O_2\ [KK\,(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^2\,(2p\pi_u)^4\,(2p\pi_g^*)^2]$$

Since the electrons in the last degenerate orbital have parallel spins, the O_2 molecule becomes paramagnetic which is confirmed experimentally.

The strength of a bond in a molecule is the net effect of the bonding and antibonding electrons of the occupied orbitals. The **bond order** b is defined as one-half the difference between the number of bonding electrons (n) between the atoms of interest and the antibonding electrons (n^*):

$$b = \frac{1}{2}(n - n^*)$$

Bonding MO's produce charge building between the nuclei and antibonding MO's produce charge depletion between the nuclei. Therefore, removal of an electron from an antibonding MO increases the dissociation energy (D_e) or decreases the bond length of the bond, whereas removal of an electron from a bonding MO decreases D_e or increases the bond length. For example, the highest filled MO in O_2 is antibonding. The removal of an electron from the antibonding orbital of O_2 increases the D_e from 5.08 to 6.48 eV. In N_2, removal of an electron from the highest filled bonding MO decreases the dissociation energy from 9.91 to 8.85 eV. As energy is always required to ionize a stable molecule, the removal of bonding or antibonding electrons decreases the total molecular energy.

Heteronuclear Diatomic Molecules

Effective combination of atomic orbitals from two different atoms is possible only if they have (i) similar energies (ii) sufficiently overlapping charge clouds and (iii) the same symmetry properties with respect to the internuclear axis.

Hence, depending on the energy, 1*s* of one atom may combine with 2*p* of another and so on. We shall consider some examples.

When two different atoms form a diatomic molecule, the electron distribution in a covalent bond between the two atoms may not be symmetrical and the electron pair may be closer to one atom. This imbalance may result in a ***polar bond*** which is a covalent bond in which the electron pair is shared unequally by the two atoms. The atom that draws the bonding electron pair to it more strongly is called the more electronegative atom which has a net positive charge. Thus, a ***polar covalent bond*** consists of two electrons in an orbital of the form:

$$y = c_a\psi_a + c_b\psi_b$$

The proportion of the orbital ψ_a in the bond is c_a^2 and that of ψ_b is c_b^2. In a non-polar bond, $c_a^2 = c_b^2$. In a pure ionic bond such as A^+B^-, $c_a^2 = 0$ and $c_b^2 = 1$. As an example, we shall consider the HF molecule.

HF: In this case the energy levels of the AO's of the two atoms are not equal. Some MO's will contain a larger contribution from one constituent AO than the other. The electronic configuration of hydrogen and fluorine atoms are:

$$\text{H} : 1s^1 \qquad \text{F}: 1s^2\, 2s^2\, 2p^5$$

From spectroscopic studies it is found that the 1*s* orbital of hydrogen and 2*p* orbitals of fluorine have comparable energies and, therefore, the $1s^2$ and $2s^2$ electrons of fluorine remain in atomic orbitals only. As the internuclear axis is taken as the *x*-axis, the hydrogen 1*s* orbital allows a greater overlap with the $2p_x$ fluorine orbital than that with $2p_y$ or $2p_z$ orbital. In Figure 17.10(a), the overlapping orbitals have the same sign and hence give a bonding MO. However, in Figure 17.10(b), the hydrogen 1*s* is overlapped by both the lobes of the $2p_y$ orbital of fluorine so that the bonding and antibonding effects are cancelled. Thus, the overlap between H (1*s*) and F ($2p_x$) orbitals is mainly responsible for the bonding orbital $2p_x\sigma$. The rest of the electrons in fluorine remain in the $2p_y$ and $2p_z$ atomic orbitals. The electronic configuration of HF can then be written as:

$$\text{HF } [K\ 2s^2\ (2p_x\sigma)^2\ (2p_y)^2\ (2p_z)^2]$$

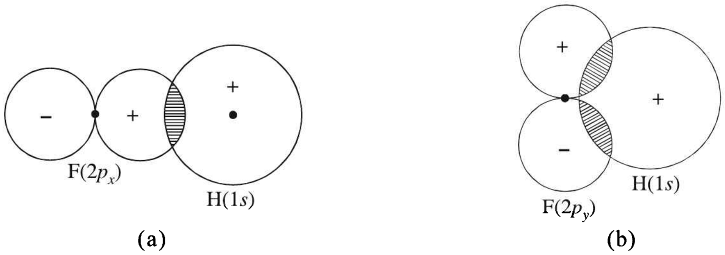


Figure 17.10 Overlap of (a) H(1*s*) and F($2p_x$) (b) H(1*s*) and F($2p_y$) in HF molecule.

The general form of the molecular orbital of HF is thus

$$\psi = c_H\psi_H + c_F\psi_F$$

where ψ_H is H(1*s*) orbital and ψ_F is $F(2p_x)$ orbital. The energy of the H(1*s*) orbital is –13.6 eV and that of $F(2p_x)$ = –18.6 eV, 5 eV lower than the H(1*s*) orbital (Figure 17.11). It follows that the bonding σ-orbital in HF is mainly $F(2p_x)$ and the antibonding σ-orbital is mainly *H*(1*s*) orbital in character.

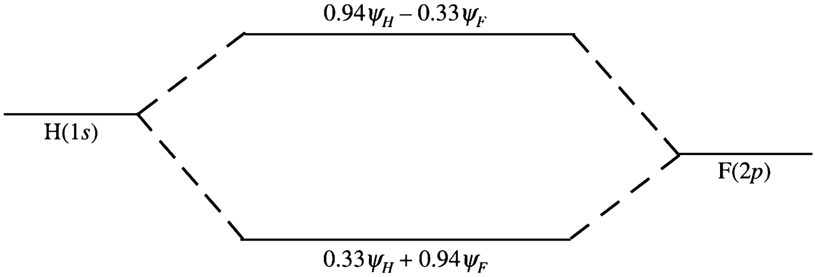


Figure 17.11 The atomic orbital energy of H(1*s*) and F(2*p*) and the molecular orbital they form.

17.7 VALENCE BOND METHOD

Heitler and London were the first to apply quantum mechanics to valency problems in 1927 by giving a quantum mechanical treatment of the hydrogen molecule. Their ideas were later extended by Slater and Pauling to give a general theory of chemical bonding and the theory is now known as the **Valence Bond (VB) method** or the **Heitler, London, Slater and Pauling (HLSP) method**. In this method, atoms are assumed to maintain their individual identity in a molecule and the bond arises due to the interaction of the valence electrons when the atoms come closer. That is, a bond is formed when a valence electron in one atomic orbital pairs its spin with that of another valence electron in the other atomic orbital. It amounts to considering molecules as composed of atomic cores and bonding valence electrons. In other words, VB method considers bringing the atoms with their associated electrons together and allowed to interact to form the bond and thereby the molecule.

17.8 THE VALENCE BOND TREATMENT OF H_2

The Heitler-London treatment of the ground state of H_2 molecule considers the molecule as two ground state hydrogen atoms. Consider the two hydrogen atoms far apart so that there is no interaction between them. Labelling the electrons as 1 and 2, the nuclei as *a* and *b* and the electron-nucleus distances by r_{a1} and r_{b2} (Figure 17.5), the Schrödinger equations are:

$$H_a(1)\ \psi_a(1) = E_a\psi_a(1), \qquad H_b(2)\ \psi_b(2) = E_b\psi_b(2) \tag{17.34}$$

where $E_a = E_b = E_H$, the ground state energy of the hydrogen atom and $\psi_a(1)$ and $\psi_b(2)$ are the 1*s* hydrogenic wavefunction.

$$H_a(1) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{ke^2}{r_{a1}}, \qquad H_b(2) = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{ke^2}{r_{b2}} \tag{17.35}$$

When the two atoms are brought closer and if there is no interaction between the two, the total Hamiltonian of the system

$$H = H_a(1) + H_b(2) \tag{17.36}$$

It amounts to assuming that electron 1 is moving about proton *a* and electron 2 is moving about proton *b*. This system of two hydrogen atoms can be described by the wavefunction:

$$\psi_1(1, 2) = \psi_a(1)\ \psi_b(2) \tag{17.37}$$

with energy eigenvalue $E_a + E_b$ since

$$\begin{aligned}[H_a(1) + H_b(2)]\ \psi_a(1)\ \psi_b(2) &= H_a(1)\ \psi_a(1)\ \psi_b(2) + H_b(2)\ \psi_a(1)\ \psi_b(2)\\ &= E_a\psi_a(1)\ \psi_b(2) + E_b\psi_a(1)\ \psi_b(2)\\ &= (E_a + E_b)\ \psi_a(1)\ \psi_b(2) \qquad (17.38)\end{aligned}$$

The electrons are indistinguishable and, therefore, an equally good description of the molecule with the same energy is given by the structure in which electron 1 is associated with atom *b* and electron 2 is associated with atom *a* giving the wavefunction,

$$\psi_2(2,1) = \psi_a(2)\ \psi_b(1) \tag{17.39}$$

In other words, $\psi_1(1,2)$ and $\psi_2(2,1)$ are eigenfunctions of the Hamiltonian $H_a + H_b$ with eigenvalue $(E_a + E_b)$. The two functions differ only in the interchange of the two electrons between the orbitals. Hence, this degeneracy is referred to as the ***exchange degeneracy*** and the wavefunctions of the two electron system, must be a linear combination of $\psi_1(1,2)$ and $\psi_2(2,1)$.

The Hamiltonian of the hydrogen molecule given by Eq. (17.26) can be written as:

$$H = H_a(1) + H_b(2) + H' + \frac{ke^2}{R} \tag{17.40}$$

where
$$H' = -\frac{ke^2}{r_{b1}} - \frac{ke^2}{r_{a2}} + \frac{ke^2}{r_{12}} \tag{17.41}$$

As the term ke^2/R is independent of electronic co-ordinates, its contribution may be incorporated at the final stage as an additional term ke^2/R.

One can solve the problem using either the perturbation method or the variation method. We shall follow the perturbation method as done by Heitler and London. Since an exchange of the two electrons leave the Hamiltonian H unchanged, the wavefunctions must either be symmetric or antisymmetric with respect to such an exchange. The symmetric ψ_s and antisymmetric ψ_{as} combinations are:

$$\psi_s = N_s\,[\psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1)] \tag{17.42a}$$

$$\psi_{as} = N_a\,[\psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1)] \tag{17.42b}$$

where N_s and N_a are normalization constants. Normalization condition gives

$$N_s^2 = \frac{1}{2(1+S^2)},\quad N_a^2 = \frac{1}{2(1-S^2)} \tag{17.43}$$

where S is given by Eq. (17.9c). The inclusion of electron spin and Pauli's principle leads to the Heitler-London wavefunctions:

$$N_s\,[\psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1)]\frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)] \tag{17.44}$$

$$N_a\,[\psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1)]\begin{cases}\alpha(1)\,\alpha(2)\\ \frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2)+\alpha(2)\,\beta(1)]\\ \beta(1)\,\beta(2)\end{cases} \tag{17.45}$$

The first one, Eq. (17.44), corresponds to a singlet (**S** = 0) and the second one to a triplet (**S** = 1). As the Hamiltonian does not contain spin terms, the energy is not affected by the inclusion of spin part. The space parts alone can then be taken as the unperturbed wavefunctions for the evaluation of energy.

A perturbation calculation is then carried out with H' (Eq. 17.41) as perturbation. The first order correction to the energy E' is the diagonal matrix element of the perturbing Hamiltonian corresponding to the unperturbed wavefunctions. Then

$$\begin{aligned} E_1' &= N_s^2\big\langle\big(\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)\big)\;|H'|\;\big(\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)\big)\big\rangle \\ &= \frac{(2J+2K)}{2(1+S^2)} = \frac{J+K}{1+S^2} \end{aligned} \tag{17.46}$$

where $$J = \langle\psi_a(1)\psi_b(2)|\,H'\,|\psi_a(1)\psi_b(2)\rangle \tag{17.47}$$

$$K = \langle\psi_a(1)\psi_b(2)|\,H'\,|\psi_a(2)\psi_b(1)\rangle \tag{17.48}$$

J and K are called **Coulomb and exchange integrals** respectively. In these expressions, the ψ's are hydrogen 1*s* wavefunction. The energy of the singlet state corrected to first order

$$E_s = 2E_H + \frac{J+K}{1+S^2} + \frac{ke^2}{R} \tag{17.49}$$

The first order correction to the triplet state

$$E_2' = \frac{J-K}{1-S^2} \tag{17.50}$$

The energy of the triplet state

$$E_a = 2E_H + \frac{J-K}{1-S^2} + \frac{ke^2}{R} \tag{17.51}$$

The Coulomb integral represents the interaction of the classical electron charge cloud about one nucleus with the charge in the other nucleus and the interaction of the two charge clouds with one another. Exchange integral represents a non-classical interaction. It is a consequence of the inclusion of both ψ_1 (1,2), Eq. (17.37), and ψ_2 (2,1), Eq. (17.39), in the unperturbed wavefunction. The two functions differ only in the interchange of the electrons between the orbitals ψ_a and ψ_b.

The overlap integral S is zero, when the two protons are far apart and is equal to 1 when they are in contact. For large R, both K and J tend to zero. For intermediate values both are negative and the magnitude of K is several times larger than that of J. Hence E_s can have a value less than $2E_H$, while E_a is always above $2E_H$. Figure 17.12 shows the plots of E_1' and E_2' against the internuclear distance R which shows a minimum for the ψ_s combination corresponding to the formation of the stable molecule. Hence the normalized

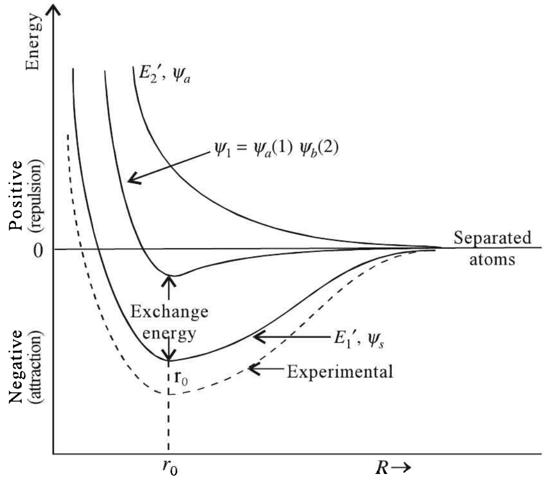


Figure 17.12 Plot of energies E_1' and E_2' against internuclear distance R.

bonding valence bond molecular orbital is the one given by Eq. (17.42a). The state characterised by the ψ_{as} combination corresponds to repulsion for all values of R. The equilibrium internuclear distance r_0 is the one corresponding to the minimum of the ψ_s curve. The Heitler-London treatment gives $D_e = 3.15$ eV and $r_0 = 0.85$ Å. The agreement with the experimental value of $D_e = 4.75$ eV and $R = 0.74$ Å is only reasonable. The major contribution to the binding of the molecule comes from exchange degeneracy.

17.9 REFINEMENTS OF SIMPLE MO AND VB APPROXIMATIONS

For the hydrogen ground state, excluding the spin part, the unnormalized LCAO-MO wavefunction (Eq. 17.29) is:

$$\psi_{mo} = \psi_a(1)\ \psi_a(2) + \psi_b(1)\ \psi_b(2) + \psi_a(1)\ \psi_b(2) + \psi_a(2)\ \psi_b(1) \qquad (17.52)$$

and the VB wavefunction, Eq. (17.42a), is:

$$\psi_{VB} = \psi_a(1)\ \psi_b(2) + \psi_a(2)\ \psi_b(1) \qquad (17.53)$$

The first refinement of the Heitler-London function was done by Wang in 1928 by introducing an orbital exponent α in the 1s function, Eq. 17.4. Wang replaced $1/a_0$ by the adjustable parameter α and wrote

$$\psi_a(1) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{a1}} \qquad (17.54)$$

$$\psi_b(1) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} e^{-\alpha r_{b1}} \qquad (17.55)$$

For each value of R, α was varied to minimize the energy by variation method. At the equilibrium value of R (0.74 Å), the optimum value of $\alpha = 1.166$. This yielded a D_e value of 3.78 eV.

Another improvement, *the generalized VB method*, is obtained by introducing ionic character into the Heitler-London function. This is understandable as there is a finite probability of finding both electrons near the same nucleus. Hence, a more complete valence bond wavefunction may be written as:

$$\psi_{VB,\mathrm{ref}} = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) + \lambda[\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2)] \qquad (17.56)$$

where $\lambda(R)$ is the variational parameter which indicates the extent of ionic character in the VB function. The subscript in $\psi_{VB,\mathrm{ref}}$ indicates the refined VB function. This trial function represents *ionic-covalent resonance*. The additional term in Eq. (17.56) must possess the same symmetry as the initial wavefunction. As H_2 dissociates to neutral hydrogen atoms, $\lambda(\infty) = 0$ and we get the VB function, Eq. (17.42a). When $\lambda(R) = 1$, we get the LCAO-MO function, Eq. (17.33). We have now two variable parameters α and λ in the VB function. The correct function is obtained by varying them so as to minimize the total electronic energy. A variational calculation of Weinbaum using 1s-AO's with the orbital exponent gave $\lambda = 0.26$, $\alpha = 1.19$ at equilibrium internuclear distance. This resulted in a D_e value of 4.03 eV, an improvement over the Heitler-London-Wang value of 3.78 eV.

Refinement of the LCAO-MO is done by including contributions from the lowest lying excited states with the same symmetry as the ground state. This is often referred to as the *configuration interaction (CI)*. The first excited configuration of H_2 is $(1s\sigma_g)(1s\sigma_u^*)$, one is even and the other is odd. Hence the state is not having the same symmetry as the ground state. However, the next excited configuration $(1s\sigma_u^*)^2$ has the same symmetry. Therefore, for a more complete MO wavefunction, we must add a term arising from the antibonding orbital which leads to the refined MO wavefunction:

$$\psi_{mo,\text{ref}} = [1s(1)\ \sigma_g][1s(2)\ \sigma_g] + k[1s(1)\ \sigma_u^*][1s(2)\ \sigma_u^*] \tag{17.57}$$

Since $1s\sigma_g$ and $1s\sigma_u^*$ are given by Eq. (17.19),

$$\psi_{mo,\text{ref}} = [\psi_a(1) + \psi_b(1)][\psi_a(2) + \psi_b(2)] + k[\psi_a(1) - \psi_b(1)][\psi_a(2) - \psi_b(2)] \tag{17.58}$$

where the variable parameter k indicates the extent of mixing of the antibonding orbital into the bonding orbital. Here ψ_a and ψ_b are 1s wavefunctions with a variable orbital exponent.

Weinbaum's (1933) calculations yielded a bond length of 0.757 Å and a dissociation energy $D_e = 4.03$ eV. One can improve the calculations either by using better forms for the MO's of each configuration or by including more configuration function or both. Using 33 configuration functions and expanding the MO's in elliptic co-ordinates, Hagstrom (1963) obtained $D_e = 4.71$ eV quite close to the experimental value of 4.75 eV.

From Eqs. (17.56) and (17.58), it can easily be seen that the two wavefunctions $\psi_{VB,\text{ref}}$ and $\psi_{mo,\text{ref}}$ are equivalent if $\lambda = (1 + k)/(1 - k)$. With this value of λ, Eq. (17.56) gives

$$\psi_{VB,\text{ref}} = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) + \frac{(1+k)}{(1-k)}\,[\psi_a(1)\psi_a(2) + \psi_b(1)\psi_b(2)]$$

$$\begin{aligned}(1 - k)\psi_{VB,\text{ref}} = {} & [\psi_a(1) + \psi_b(1)] + [\psi_a(2) + \psi_b(2)] \\ & + k[\psi_a(1) - \psi_b(1)]\,[\psi_a(2) - \psi_b(2)]\end{aligned} \tag{17.59}$$

From Eqs. (17.58) and (17.59), we have

$$\psi_{VB,\text{ref}} = \frac{1}{(1-k)}\,\psi_{mo,\text{ref}} \tag{17.60}$$

As the functions are not yet normalized, the factor $1/(1 - k)$ can be included in that.

17.10 DIRECTED BONDS

The central theme in the MO treatment was that the electron pairs forming the bond were delocalized and not concentrated between the nuclei. However, in the VB picture the electrons in a molecule occupy atomic orbitals and the overlap of atomic orbitals results in the formation of a bond, larger the overlap stronger is the bond. It may therefore be considered that the VB theory represents a localized picture of the chemical bond. In this localized picture, the direction in which maximum overlap occurs will be the direction of the bond. The concepts of directed valence and hybridization are a direct consequence of the VB theory.

Consider the structure of water molecule. The electron configuration of the oxygen atom is:

$$1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$$

The two unpaired electrons in the $2p_y$ and $2p_z$ orbitals which are at right angles are available for bonding with the $1s$ orbital of hydrogen atoms. The *s*-orbital can overlap to the same extent in all directions as it is spherically symmetric, whereas the *p*-orbitals have certain preferred directions. Therefore, if the concept of directed valence is valid, we should get a water molecule with HOH angle 90° (Figure 17.13).

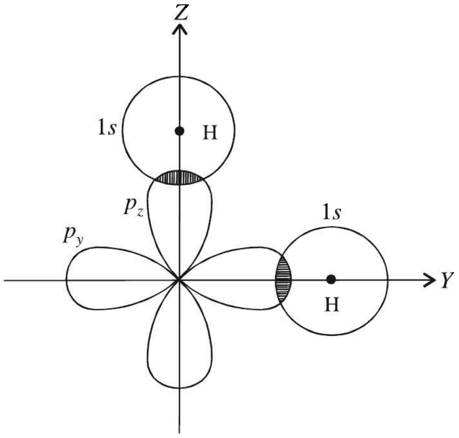


Figure 17.13 The formation of water molecule. $2p_x$ orbital is not shown.

However, the actual value is 104.5°. When the water molecule is formed, the electrons in the OH bond are drawn towards the oxygen atom making the hydrogen atom slightly positive. The mutual repulsion between the hydrogens is partly responsible for the increase in the angle. In the case of H_2Se and H_2S the angles are 91° and 93° respectively, which is very close to the predicted value.

17.11 HYBRIDIZATION

The concept of directed valence could explain bond angles only in certain molecules. It failed in large number of cases especially with carbon compounds. The electronic configuration of the normal state of carbon is:

$$1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 0}$$

As the lobes of the two valence electrons are perpendicular, one may expect the carbon atom to form two bonds at right angles to each other. However, in a molecule like CH_4 it is found to form four equivalent bonds directed towards the corners of a tetrahedron. This is possible only if one of the 2*s* electrons is promoted to the vacant $2p_z$ orbital giving the excited electronic configuration

$$1s^2\ 2s^1\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$$

The four orbitals available now for bonding will not be equivalent. However, if there is mixing of the 2*s* and 2*p* orbitals, four orbitals of the same shape and energy are possible. The process of mixing of pure orbitals is called **hybridization** and the resulting mixed orbitals are called **hybrid orbitals**. Mathematically, a linear combination of the pure orbitals in proper proportion have to be found. The resulting hybrid orbitals do not retain the characteristics of the original orbitals. Three types of hybridizations are possible between *s* and *p*-orbitals. They are (i) *sp* hybridization (ii) sp^2 hybridization and (iii) sp^3 hybridization.

sp Hybridization

A linear combination of *s* and *p*-orbitals in proper proportion gives hybrid *sp* orbitals. The angle between the directions of the maxima of the two resulting orbitals is 180°. Mathematically, the two *sp* hybrid wavefunctions are:

$$\begin{aligned}\psi_{sp}(\mathrm{i}) &= \frac{1}{\sqrt{2}}[\psi(s) + \psi(p_x)]\\ \psi_{sp}(\mathrm{ii}) &= \frac{1}{\sqrt{2}}[\psi(s) - \psi(p_x)]\end{aligned} \tag{17.61}$$

Figure 17.14 shows how these hybrids which point in opposite directions arise from the two combinations. The combination $\psi_{sp}(\mathrm{i})$ has a large lobe with positive sign since the positive signs of both $\psi(s)$ and $\psi(p_x)$ orbitals coincide. In $\psi_{sp}(\mathrm{ii})$ the large lobe with positive sign is on the other side since $-\psi(p_x)$ appears in the expression. As the orbitals $\psi_{sp}(\mathrm{i})$ and $\psi_{sp}(\mathrm{ii})$ protrude more than the *s* and *p*-orbitals, considerable overlapping is possible resulting in stronger bonds. Formation of $BeCl_2$ molecule using *sp* hybrid orbitals of Be is illustrated in Figure 17.15.

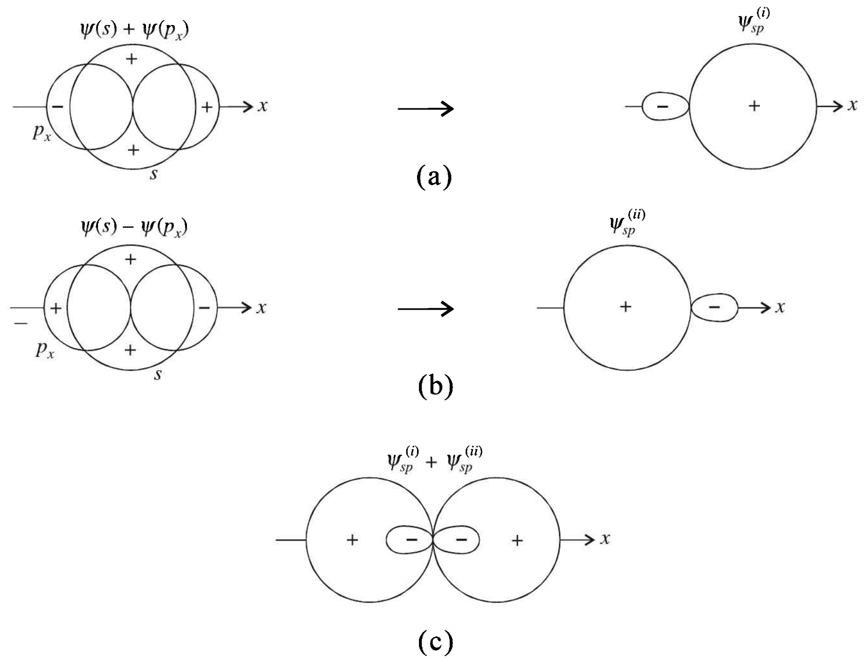


Figure 17.14 Polar representation of *sp* hybrid orbitals (a) ψ_{sp}(i) (b) ψ_{sp}(ii) (*c*) ψ_{sp}(i) + ψ_{sp}(ii).

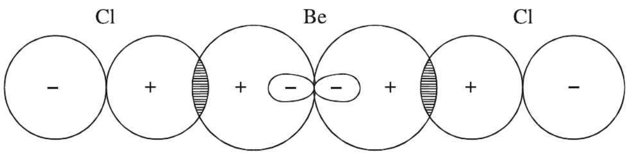


Figure 17.15 Formation of $BeCl_2$ molecule using ψ_{sp}(i), ψ_{sp}(ii) and $3p_x$ orbitals of chlorine.

*sp*² Hybridization

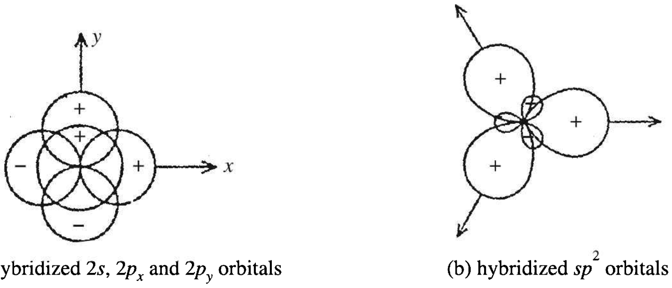
The functions involved in sp^2 hybridization are one s, p_x and p_y. Their linear combination results in three equivalent orbitals which are coplanar and oriented at 120° to each other. The lobes of p_z-orbital which is not used for hybridization lies above and below this plane. The electrons in the sp^2-orbitals are contained in this plane and do not possess any angular momentum. Equations for the three sp^2 orbitals are:

$$\psi_{sp^2}(\text{i}) = \frac{1}{\sqrt{3}}\psi(s) + \sqrt{\frac{2}{3}}\psi(p_x)$$

$$\psi_{sp^2}(\text{ii}) = \frac{1}{\sqrt{3}}\psi(s) - \frac{1}{\sqrt{6}}\psi(p_x) + \frac{1}{\sqrt{2}}\psi(p_y) \qquad (17.62)$$

$$\psi_{sp^2}(\text{iii}) = \frac{1}{\sqrt{3}}\psi(s) - \frac{1}{\sqrt{6}}\psi(p_x) - \frac{1}{\sqrt{2}}\psi(p_y)$$

Figure 17.16 illustrates the formation of the sp^2 hybrid orbitals from the component orbitals. Boron atom has an electronic configuration $1s^2\ 2s^2\ 2p_x^1$. The promotion of one $2s$ electron gives the excited state $1s^2\ 2s^1\ 2p^1_x\ 2p_y^1$ resulting in the formation of three sp^2 hybrid orbitals. In boron trichloride molecule, the sp^2 hybrid orbitals of boron overlap with the $3p_x$ atomic orbitals of the chlorine atoms and gives the coplanar structure with bond angle 120°.



(a) unhybridized $2s$, $2p_x$ and $2p_y$ orbitals (b) hybridized sp^2 orbitals

Figure 17.16 sp^2 hybrid orbitals from component orbitals.

sp^3 Hybridization

The hybridization of one $2s$ and three $2p$ orbitals results in four equivalent hybrid orbitals concentrated along the tetrahedral axes. This process is sp^3 hybridization (Figure 17.17) and the angle between the direction of the maxima of any two orbitals being 109°28′. The four orbitals do not retain their individual s and p characteristics.

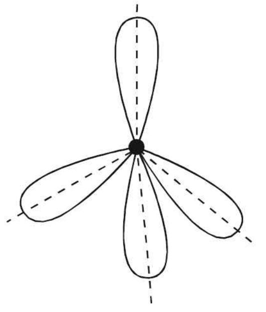


Figure 17.17 sp^3 hybrid orbitals.

The four combinations which are mutually orthogonal and normalized are:

$$\psi_{sp^3}(\text{i}) = \frac{1}{2}\psi(s) + \frac{\sqrt{3}}{2}\psi(p_z)$$

$$\psi_{sp^3}(\mathrm{ii}) = \frac{1}{2}\psi(s) + \sqrt{\frac{2}{3}}\psi(p_x) - \frac{1}{2\sqrt{3}}\psi(p_z)$$

$$\psi_{sp^3}(\mathrm{iii}) = \frac{1}{2}\psi(s) - \frac{1}{\sqrt{6}}\psi(p_x) + \frac{1}{\sqrt{2}}\psi(p_y) - \frac{1}{2\sqrt{3}}\psi(p_z) \qquad (17.63)$$

$$\psi_{sp^3}(\mathrm{iv}) = \frac{1}{2}\psi(s) - \frac{1}{\sqrt{6}}\psi(p_x) - \frac{1}{\sqrt{2}}\psi(p_y) - \frac{1}{2\sqrt{3}}\psi(p_z)$$

The carbon in CH_4 is sp^3 hybridized and each one of the tetrahedrally directed lobes overlaps with the *s*-orbital of hydrogen giving rise to four equivalent carbon hydrogen σ bonds. The overlap is very effective and the charge distribution is symmetrical along the CH internuclear axis.

Other Hybridizations

In addition to the three types discussed earlier, there are number of different types of hybridizations giving rise to different spatial arrangements of orbitals. Table 17.1 lists some of the hybridizations alongwith molecular examples. The directional and overlapping properties of hybrid orbits are different from those of the constituent atomic orbitals. In short the concept of hybridization helps us to understand shape and structure of molecules in a better way.

Table 17.1 Certain Hybrid Orbitals with Examples

No. of orbitals	*Atomic-orbital combinations*	*Spatial arrangement*	*Example*
2	sp	Linear	C_2H_2, CO_2, CN^-
3	sp^2	Trigonal	BCl_3, C_2H_4, NO^-_3
4	sp^3 or d^3s	Tetrahedral	CH_4, C_2H_6, MoO_4^{2-}
	dsp^2	Square planar	$PtCl_4^{2-}$, $Ni(CN)_4^{2-}$
5	dsp^3	Trigonal bipyramid	PCl_5, $Fe(Co)_5$
6	d^2sp^3	Octahedron	PF_6^-, SF_6, $Fe(CN)_6^{3-}$

Hybridization and Shape of Molecules

The concept of hybridization could account for the shape of molecules better than that based on the idea of directed valence. As examples consider the case of ammonia and water molecules. The five outer electrons of the central nitrogen ($2s^2\ 2p^3$) of ammonia uses the four tetrahedral orbitals formed by sp^3 hybridization in the following way. Three electrons occupy three orbitals singly and two electrons with opposite spins occupy the fourth orbital. The two electrons occupying the fourth orbital is often referred to as *lone pair electrons*. The sharing of the singly occupied orbitals with 1*s* electron of hydrogen leads to 3 bonding orbitals and one lone pair of electrons in ammonia. In the same way the six outer electrons of the oxygen atom ($2s^2\ 2p^4$) in water can occupy the four tetrahedral orbitals, two occupied by single electrons and the other two by lone pair of electrons. The singly occupied orbitals can then accomodate the electrons of hydrogen atoms forming the water molecule.

The bonding pair of electrons are under the influence of two nuclei, whereas the lone pair electrons are under the influence of only one nucleus. Therefore, the order of repulsion between electron pairs is likely to be as

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair

In CH_4 there is no lone pair, whereas there is one in NH_3 and two in water. This accounts for the decrease in the bond angle as one goes from CH_4 (109.5°) to NH_3(107.3°) to H_2O (104.5°).

17.12 SEMI-EMPIRICAL π-ELECTRON MO METHODS

We have been discussing so far MO and VB theories in the broadest sense. As the calculations are difficult, many semi-empirical methods have been developed. We shall now introduce a semi-empirical MO theory which is used successfully to handle the π-electrons of planar conjugated molecules.

π-electron Approximation

In planar conjugated organic molecules, the planar framework is formed by the σ-electrons and the π-MOs have a node in the molecular plane. Consequently, the π-electron density is fairly separated from the σ-electron density. Hence, the molecular orbitals for π-electrons in conjugated systems may be treated independently of σ-electrons. In the ***π-electron approximation***, they are treated separately by incorporating the effects of the σ-electrons and the nuclei into an effective π-electron Hamiltonian H_π:

$$H_\pi = \sum_{k=1}^{n} H_\pi^{\text{core}}(k) + \sum_{k=1}^{n} \sum_{l>k} \frac{ke^2}{r_{kl}} \tag{17.64}$$

$$H_\pi^{\text{core}}(k) = -\frac{\hbar^2}{2m} \nabla_k^2 + V_k \tag{17.65}$$

where n is the number of π-electrons and V_k is the potential energy of the k^{th} π-electron in the field produced by the σ-electrons and nuclei. The variational procedure is then applied to get the π-electron energy E_π. The Hückel MO method, the free electron MO method and the Pariser-Parr-Pople method are the three major π-electron methods. Out of these, the most important one is the Hückel MO method.

17.13 THE HÜCKEL MO METHOD

The Hückel MO method is the one that is extensively used in the case of planar conjugated molecules. In such cases, the molecule of N carbon atoms form a rigid σ framework which is the plane of the molecule. The σ and π electrons are contained in the planes perpendicular to each other. The interaction between the σ and π electrons is negligible. Therefore, in conjugated molecules, the molecular orbital for the π system is selected as a linear combination of $2p_\pi$ AO's of carbon atom that are perpendicular to the molecular plane. Designating the p_π atomic orbitals as ϕ_i, i refers to the carbon atom, the molecular orbital can be written as:

$$\psi = \sum_{i=1}^{N} c_i \, \phi_i \tag{17.66}$$

where the c_i's are constants. If H is the π electron Hamiltonian operator, from Section 10.2, the energy eigenvalues E are found by solving the determinant, Eq. (10.13):

$$| H_{ij} - ES_{ij} | = 0 \tag{17.67}$$

The coefficients c_i's can be determined by solving the set of N simultaneous homogeneous equations, Eq. (10.11):

$$\sum_{i=1}^{N} c_i (H_{ij} - S_{ij}E) = 0 \tag{17.68}$$

where

$$H_{ij} = \langle \phi_i \mid H \mid \phi_j \rangle \quad \text{and} \quad S_{ij} = \langle \phi_i \mid \phi_j \rangle \tag{17.69}$$

To solve Eqs. (17.67) and (17.68), Hückel introduced the four approximations:

(i) All the C-C bond lengths are the same.

(ii) The matrix elements $H_{ii} = \langle \phi_i \mid H \mid \phi_i \rangle$, called **Coulomb integral**, represent the energy of the electron in a $2p$-orbital on the i^{th} carbon atom. All such integrals will be equal to α since we are dealing with only carbon atoms.

(iii) The exchange or resonance integrals H_{ij} are defined as:

$$H_{ij} = \langle \phi_i \mid H \mid \phi_j \rangle = \beta \tag{17.70}$$

if the i^{th} carbon atom is adjacent to the j^{th} carbon atom. Otherwise $H_{ij} = 0$.

(iv) We ignore overlap and hence $S_{ii} = 1$ and $S_{ij} = 0$.

17.14 HÜCKEL TREATMENT OF BENZENE

To illustrate the Hückel molecular orbital method, we consider the benzene molecule which is planar. The sp^2 hybridized six carbon atoms are at the vertices of a regular hexagon. Three σ bonds are formed one with each hydrogen atom and two with neighbouring carbon atoms. The σ framework, with the numbering of the carbon atoms is shown in Figure 17.18. The 4th electron in

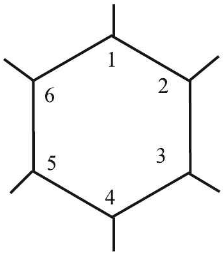


Figure 17.18 The σ-framework for the benzene molecule.

each carbon is in a $|2p_z\rangle$ state forming π-bonds with two neighbouring carbon atoms. As the lobes of the π-orbital are on both the sides of the plane of the molecule, the π-electron density is completely separated from the σ-electron density. These π-bonds contribute to the reactivity of the molecule and, therefore, it is sufficient to study these bonds. By the second and third approximations, the non-vanishing matrix elements are:

$$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha \tag{17.71}$$

and

$$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = \beta \tag{17.72}$$

It may also be noted that $H_{ij} = H_{ji}$. For benzene, the determinant, Eq. (17.67) becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{17.73}$$

Dividing by β^6 and writing $\in = (\alpha - E)/\beta$, we have

$$\begin{vmatrix} \in & 1 & 0 & 0 & 0 & 1 \\ 1 & \in & 1 & 0 & 0 & 0 \\ 0 & 1 & \in & 1 & 0 & 0 \\ 0 & 0 & 1 & \in & 1 & 0 \\ 0 & 0 & 0 & 1 & \in & 1 \\ 1 & 0 & 0 & 0 & 1 & \in \end{vmatrix} = 0 \tag{17.74}$$

$$(\in + 1)^2 (\in - 1)^2 (\in + 2)(\in - 2) = 0 \tag{17.75}$$

which gives the six real roots.

$$E = \alpha + 2\beta,\ \alpha + \beta,\ \alpha + \beta,\ \alpha - \beta,\ \alpha - \beta,\ \alpha - 2\beta \tag{17.76}$$

Since β is negative, the six π-electrons are distributed in the energy levels as illustrated in Figure 17.19. As the level $\alpha + \beta$ is doubly degenerate, it accomodates 4 electrons.

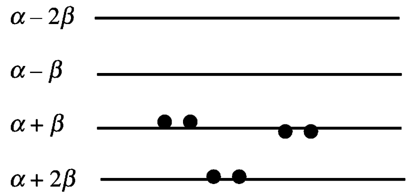


Figure 17.19 π-electron distribution in the ground state of benzene.

Substituting these values of E in Eq. (17.68), we can get the c's. This leads to the following combination of ϕ's for the HMO's:

$$\begin{aligned}
\psi_1 &= \frac{1}{\sqrt{6}}\,(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)\\
\psi_2 &= \frac{1}{\sqrt{12}}\,(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)\\
\psi_3 &= \frac{1}{2}\,(\phi_2 - \phi_3 + \phi_5 - \phi_6)\\
\psi_4 &= \frac{1}{2}\,(\phi_2 + \phi_3 - \phi_5 - \phi_6) \qquad (17.77)\\
\psi_5 &= \frac{1}{\sqrt{12}}\,(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)\\
\psi_6 &= \frac{1}{\sqrt{6}}\,(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)
\end{aligned}$$

In complex systems, a computer may be required to compute the energies and the HMO's. As the functions must possess the symmetry properties of the molecule, often group theory helps to determine some of the functions.

WORKED EXAMPLES

EXAMPLE 17.1 Write the electronic configuration of N_2 molecule in the MO concept and explain the formation of the triple bond $N \equiv N$.

The 14 electrons in the nitrogen molecule are distributed as:

$$KK(2s\sigma_g)^2\,(2s\sigma_u{}^*)^2\,(2p_x\sigma_g)^2\,(2p_y\pi = 2p_z\pi)^4$$

The presence of two electrons in the bonding orbital $2s\sigma_g$ and two electrons in the antibonding $2s\sigma_u{}^*$ leads to no bonding. The remaining bonding orbitals

$(2p_x\sigma_g)^2$ $(2p_y\pi = 2p_z\pi)^4$ are not cancelled by the corresponding antibonding orbitals. These six bonding electrons give the triple bond $N \equiv N$, one bond being σ and the other two are π bonds.

EXAMPLE 17.2 Write the electronic configuration of O_2 and S_2 and account for their paramagnetism.

The sixteen electrons in the O_2 molecule are distributed as:

$$KK(2s\sigma_g)^2\ (2s\sigma_u{}^*)^2\ (2p\sigma_g)^2\ (2p\pi_u)^4\ (2p\pi_g{}^*)^2$$

where KK stands for $(1s\sigma_g)^2\ (1s\sigma_u{}^*)^2$. The orbital $2p\pi_g{}^*$ is degenerate. Hence the two electrons in that antibonding orbital will go one each with parallel spins (Hund's rule). Since the last two electrons are with parallel spins, the net spin is one and the molecule is paramagnetic.

The electronic configuration of S = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ and, therefore, the electronic configuration of S_2 is:

$$KKLL(3s\sigma)^2\ (3s\sigma^*)^2\ (3p_x\sigma)^2\ (3p_y\pi = 3p_z\pi)^4\ (3p_y\pi^* = 3p_z\pi^*)^2$$

where LL stands for the $n = 2$ electrons. The orbitals $3p_y\pi^* = 3p_z\pi^*$ can accommodate 4 electrons. By Hund's rule the two available electrons will enter each of these with their spins parallel, giving a paramagnetic molecule.

EXAMPLE 17.3 The removal of an electron from the O_2 molecule increases the dissociation energy from 5.08 to 6.48 eV, whereas in N_2 the removal of the electron decreases the energy from 9.91 to 8.85 eV. Substantiate.

Bonding MO's produce charge building between the nuclei and antibondig MO's charge depletion between the nuclei. Hence, removal of an electron from an antibonding MO increases the dissociation energy D_e or decreases the bond length of the bond, whereas removal of an electron from a bonding MO decreases D_e or increases the bond length. The electronic configuration of O_2 is:

$$KK(2s\sigma_g)^2\ (2s\sigma_u{}^*)^2\ (2p_x\sigma_g)^2\ (2p_y\pi_u = 2p_z\pi_u)^4\ (2p\pi_g{}^*)^2$$

The highest filled MO is antibonding. Hence removal of an electron increases the D_e from 5.08 to 6.48 eV. The electronic configuration of N_2 is:

$$KK(2s\sigma_g)^2\ (2s\sigma_u{}^*)^2\ (2p_x\sigma_g)^2\ (2p_y\pi_u = 2p_z\pi_u)^4$$

Removal of an electron from the highest filled bonding orbital decreases the dissociation energy from 9.91 to 8.85 eV.

EXAMPLE 17.4 Discuss the type of bonding in the heteronuclear diatomic molecule NO. Why the bond in NO^+ is expected to be shorter and stronger than that of NO?

Nitrogen and oxygen are close to each other in the periodic table and, therefore, their AO's are of similar energy. The nitrogen atom has seven electrons and the oxygen atom 8. The energy levels of the various MO's are the same as for homonuclear diatomic molecules. Consequently the electronic configuration of NO molecule is:

$$KK(2s\sigma_g)^2\ (2s\sigma_u{}^*)^2\ (2p_x\sigma_g)^2\ (2p_y\pi_u = 2p_z\pi_u)^4\ (2p\pi_g{}^*)^1$$

The inner shell is non-bonding, the bonding and antibonding $(2s\sigma_g)$ and $(2s\sigma_u{}^*)$ orbitals cancel. Though the four electrons in $(2p_y\pi_u = 2p_z\pi_u)^4$ orbital can give two π bonds, a half bond is cancelled by the presence of one electron in the antibonding $2p\pi_g{}^*$ orbital. This leads to a σ-bond $(2p_x\sigma_g)^2$, a full π bond and a half π bond from the $2p$ electrons. The molecule is paramagnetic since it has an unpaired electron. Removal of an electron from the system means the removal of an electron from the antibonding orbital. Hence, the bond in NO^+ is expected to be shorter and stronger.

EXAMPLE 17.5 Give the steps involved in deriving Eq. (17.19) from Eq. (17.18). What will be the normalization factor if the two nuclei are at infinite distance?

Equation (17.18) states that

$$\psi_1 = c_1(\psi_a + \psi_b), \quad \psi_2 = c_2(\psi_a - \psi_b)$$

Normalization of ψ_1 gives

$$|c_1|^2 \langle(\psi_a + \psi_b)\,|\,(\psi_a + \psi_b)\rangle = 1$$

$$|c_1|^2\,[\langle\psi_a|\psi_a\rangle + \langle\psi_b|\psi_b\rangle + \langle\psi_a|\psi_b\rangle + \langle\psi_b|\psi_a\rangle] = 1$$

$$c_1^2\,[1 + 1 + S + S] = 1$$

$$c_1 = \frac{1}{\sqrt{2+2S}}, \quad \psi_1 = \frac{\psi_a + \psi_b}{\sqrt{2+2S}}$$

Normalization of ψ_2 gives

$$|c_2|^2\,[\langle\psi_a|\psi_a\rangle + \langle\psi_b|\psi_b\rangle - \langle\psi_a|\psi_b\rangle - \langle\psi_b|\psi_a\rangle] = 1$$

$$c_2 = \frac{1}{\sqrt{2-2S}}, \quad \psi_2 = \frac{\psi_a - \psi_b}{\sqrt{2-2S}}$$

When the two nuclei are at infinite distance, the overlap integral $\langle\psi_a|\psi_b\rangle = \langle\psi_b|\psi_a\rangle = 0$. Hence the normalization factor for both ψ_1 and ψ_2 is $1/\sqrt{2}$.

EXAMPLE 17.6 The Heitler-London wave functions for hydrogen molecule are:

$$\psi_s = N_s\,[\psi_a(1)\ \psi_b(2) + \psi_a(2)\ \psi_b(1)]$$

$$\psi_{as} = N_a\,[\psi_a(1)\ \psi_b(2) - \psi_a(2)\ \psi_b(1)]$$

Evaluate the normalization constants N_s and N_a. What will be the normalization factor, if the nuclear separation is infinite?

The normalization condition of the symmetric Heitler-London trial function gives

$$|N_s|^2 \left\langle [\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)] \middle| [\psi_a(1)\psi_b(2)+\psi_a(2)\psi_b(1)] \right\rangle = 1$$

$$|N_s|^2 [\langle \psi_a(1)\psi_b(2) | \psi_a(1)\psi_b(2)\rangle + \langle \psi_a(1)\psi_b(2) | \psi_a(2)\psi_b(1)\rangle$$

$$+ \langle \psi_a(2)\psi_b(1) | \psi_a(1)\psi_b(2)\rangle + \langle \psi_a(2)\psi_b(1) | \psi_a(2)\psi_b(1)] = 1$$

$$|N_s|^2 [1 + S^2 + S^2 + 1] = 1, \; N_s = \frac{1}{\sqrt{2+2S^2}}$$

since

$$\langle \psi_a(1)|\psi_a(1)\rangle = \langle \psi_b(2)|\psi_b(2)\rangle = \langle \psi_a(2)|\psi_a(2)\rangle = \langle \psi_b(1)|\psi_b(1)\rangle = 1$$

and

$$\langle \psi_a(1)\psi_b(2)|\psi_a(2)\psi_b(1)\rangle = \langle \psi_a(1)|\psi_b(1)\rangle\langle \psi_b(2)|\psi_a(2)\rangle = S.S = S^2$$

In the same way,

$$N_a = \frac{1}{\sqrt{2 - 2S^2}}$$

For infinite nuclear separation, $S = 0$, $N_s = N_a = \frac{1}{\sqrt{2}}$

EXAMPLE 17.7 Compare the MO wavefunction of hydrogen molecule with that of the valence bond theory.

Equation (17.52) gives the MO wavefunction, whereas Eq. (17.53) gives the Heitler-London function for hydrogen molecule

$$\psi_{mo} = \text{Constant } [\psi_a(1)\, \psi_a(2) + \psi_b(1)\, \psi_b(2) + \psi_a(1)\, \psi_b(2) + \psi_b(1)\, \psi_a(2)]$$

$$\psi_{HL} = \text{Constant } [\psi_a(1)\, \psi_b(2) + \psi_a(2)\, \psi_b(1)]$$

The first two terms in ψ_{mo} represent the possibility of both the electrons being on the same proton at the same time.These represent the ionic structures $H_a^- H_b^+$ and $H_a^+ H_b^-$. The third and the fourth terms represent the possibility in which the electrons are shared equally by both the protons and hence they correspond to covalent structures. Both the terms in the valance bond wavefunction correspond to covalent structures as one electron is associated with one nucleus and the second electron is associated with the other nucleus.

EXAMPLE 17.8 Write the electronic configuration of Na_2 and S_2 molecules in the MO concept.

The electronic configuration of Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$
The electronic configuration of Na_2 molecule is:

$$Na_2\ [KK(2s\sigma)^2\ (2s\sigma^*)^2\ (2p_y\pi = 2p_z\pi)^4\ (2p_x\sigma)^2\ (2p_y\pi^* = 2p_z\pi^*)^4\ (2p_x\sigma^*)^2\ (3s\sigma)^2]$$
$$= Na_2\ [KKLL(3s\sigma)^2]$$

This result may be compared with the electronic configuration of Li_2, another alkali metal.

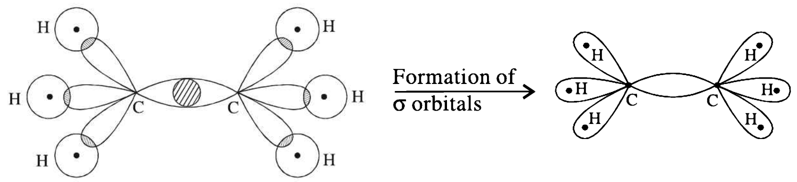
The electronic configuration of S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
The electronic configuration of S_2 molecule is:

$$S_2\ [KKLL\ (3s\sigma)^2\ (3s\sigma^*)^2\ (3p_x\sigma)^2\ (3p_y\pi = 3p_z\pi)^4\ (3p_y\pi^* = 3p_z\pi^*)^2]$$

Though the orbitals $3p_y\pi^* = 3p_z\pi^*$ can accomodate 4 electrons, there are only two. Hence by Hund's rule one electron will enter each of these with their spins parallel giving a paramagnetic molecule.

EXAMPLE 17.9 Sketch the molecular orbital formation in ethane and ethylene.

Ethane (C_2H_6): In ethane each carbon atom is sp^3 hybridized. Three of these hybrid orbitals in each carbon atom overlap with the *s*-orbitals of three hydrogen atoms and the 4th one with the corresponding one of the other carbon atom. All the bonds are of σ type. The molecular orbital formation is illustrated in Figure 17.20.



sp^3 hybrids of C and 1s atomic orbitals of H

Molecular Orbitals

Figure 17.20 Molecular orbital formation in ethane.

Ethylene (C_2H_4): Each carbon atom is sp^2 hybridized. Two of these form localized σ type MO by overlapping with 1*s* orbital of hydrogen atom and the third overlaps with the second carbon forming another localized σ MO (Figure 17.21a). These three σ bonds lie in a plane, the molecular plane. Each carbon atom is left with a singly occupied *p*-orbital with its axis perpendicular to the plane of the molecule. The lateral overlap of these two *p*-orbitals give a π bond (Figure 17.21b), the second bond between the two carbon atoms. The plane of the molecule is the nodal plane of the π orbital.

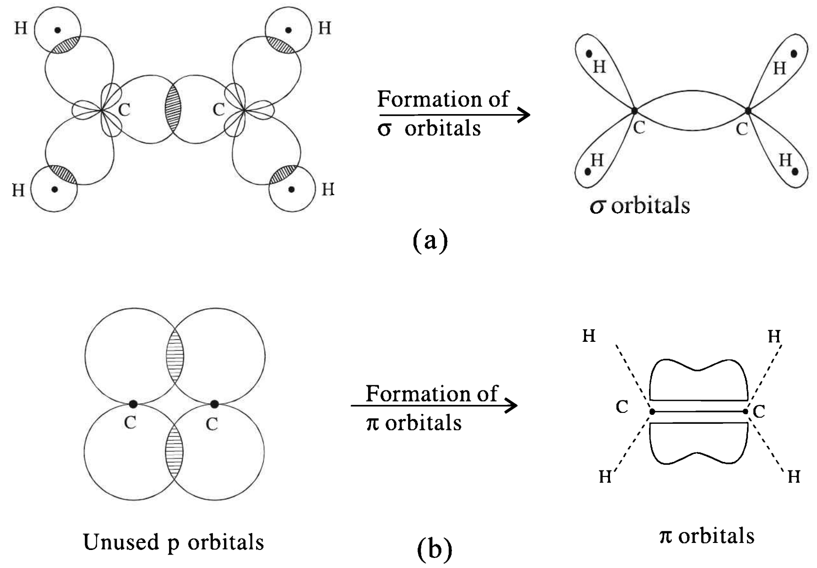


Figure 17.21 Formation of (a) σ orbitals (b) π orbital in ethylene.

EXAMPLE 17.10 Prove that the angle between any two of the sp^3 hybrids is 109°28′.

It can be proved that the linear combination of three p-orbitals $\phi = ap_x + bp_y + cp_z$ can give rise to another p-orbital oriented in a direction depending on the values of the constants a, b, and c. Consider an appropriate combination p_1 of the three p-orbitals in the direction of the first bond. Then the wavefunction of the hybrid of the first bond can be written as:

$$\psi_1 = c_1 s + c_2 p_1$$

where c_1 and c_2 are constants.

As all the four hybrids are equivalent, each one must have the same amount of s-character and the same amount of p-character. Hence each bond will have ¼ s-character and ¾ p-character. That is ψ_1^2 must contain ¼ s^2 and ¾ p^2. Therefore, $c_1^2 = 1/4$ and $c_2^2 = 3/4$.

The hybrid orbital of the first bond: $\psi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_1$

The hybrid orbital of the second bond: $\psi_2 = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_2$

Since ψ_1 and ψ_2 are orthogonal,

$$\langle \psi_1 | \psi_2 \rangle = \left\langle \left(\frac{1}{2}s + \frac{\sqrt{3}}{2}p_1 \right) \middle| \frac{1}{2}s + \frac{\sqrt{3}}{2}p_2 \right\rangle = 0$$

$$\frac{1}{4}\langle s | s \rangle + \frac{3}{4}\langle p_1 | p_2 \rangle + \frac{\sqrt{3}}{4}\langle s | p_2 \rangle + \frac{\sqrt{3}}{4}\langle p_1 | s \rangle = 0$$

The net overlap between a s- and a p-orbital centered on the same nucleus is zero which makes the third and the 4th term zero. Writing $p_2 = p_1 \cos\theta_{12}$,

$$\frac{1}{4} + \frac{3}{4}\langle p_1 \mid p_1 \rangle \cos\theta_{12} = 0$$

$$\cos\theta_{12} = -\frac{1}{3} \quad \text{or} \quad \theta_{12} = 109°28'$$

REVIEW QUESTIONS

1. What is LCAO approximation? List the conditions to be satisfied by the contributing atomic orbitals to generate an effective MO.
2. Outline the molecular orbital method.
3. Explain the significance of (i) Coulomb integral (ii) exchange integral and (iii) overlap integral.
4. What are bonding and antibonding orbitals? Illustrate with a diagram, the combination of two 1s orbitals forming bonding and antibonding orbitals.
5. Illustrate with the help of diagrams the probability density functions of the participating atomic orbitals and the molecular orbitals of a H_2^+ ion.
6. Represent in a diagram contours of equal electron density for bonding and antibonding orbitals of H_2^+ ion.
7. Write the product of atomic orbitals corresponding to ionic and covalent structures of the hydrogen molecule.
8. Explain with diagrams the combination of (i) s- and p_x-orbitals (ii) two p-orbitals.
9. Illustrate with a diagram the molecular orbital energy level diagram of homonuclear diatomic molecules.
10. Give the electronic configuration of Be_2, C_2 and HF molecules.
11. Explain the valence bond method of Heitler and London.
12. Explain the concept of exchange degeneracy.
13. Outline the Heitler-London wavefunctions for hydrogen molecule. What are singlet and triplet states of hydrogen?
14. With example, explain directed bonds.
15. What is hybridization? Explain with figure the formation of sp^2 and sp hybrid orbitals from component orbitals.
16. What are lone pair electrons? Give examples.
17. Explain the type of hybridization in water molecule. Account for the difference in HOH angle from the theoretical value.

18. Illustrate with examples how the concept of hybridization helps one to understand the shapes and the structures of molecules.
19. On the basis of MO concept, account for the paramagnetism shown by O_2 molecule.
20. Explain why the ground state of the hydrogen molecule is a binding state and the first excited state is an unstable one.
21. For most molecules the simple MO theory overestimates the ionic terms, whereas the simple VB theory underestimates these terms. Comment on this statement.
22. Distinguish between π molecular orbitals and σ orbitals.

PROBLEMS

1. (i) Write the electronic configuration of N_2 molecule and N_2^+ ion.
   (ii) Explain the type of bonding in them.
   (iii) Which one has the longer equilibrium bond length?
   (iv) Which one has larger dissociation energy?
2. Using MO concept of electronic configuration of molecules, show that (i) oxygen is paramagnetic (ii) the removal of an electron from O_2 decreases the bond length (iii) evaluate the bond order of the O_2 molecule.
3. Write the electronic configuration of the F_2 molecule and explain how the configurations of Cl_2 and Br_2 are analogous to that of F_2.
4. On the basis of directed valence, illustrate how the *p*-valence shell orbitals of nitrogen atom combine with the *s*-orbitals of the attached hydrogen atoms to give molecular orbitals for the NH_3 molecule.
5. A gas consisting of B_2 molecules is found to be paramagnetic. What pattern of molecular orbitals must apply in this case?
6. Find the relative bond strengths of (i) F_2 molecule and F_2^+ ion (ii) F_2 and O_2 molecules.
7. In *sp* hybridization, show that the angle between the two hybrid bonds is 180°.
8. Show that the three hybrid bonds in sp^2 hybridization are inclined to each other by 120°.
9. Explain with a diagram the nature of bonding in benzene molecule.

Appendix A

Some Useful Integrals

1. $\int_0^\infty \exp(-ax^2)\, dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

2. $\int_0^\infty x^2 \exp(-ax^2)\, dx = \frac{\sqrt{\pi}}{4}\frac{1}{a^{3/2}}$

3. $\int_0^\infty x^4 \exp(-ax^2)\, dx = \frac{3\sqrt{\pi}}{8}\frac{1}{a^{5/2}}$

4. $\int_0^\infty x^6 \exp(-ax^2)\, dx = \frac{15\sqrt{\pi}}{16}\frac{1}{a^{7/2}}$

5. $\int_0^\infty x \exp(-ax^2)\, dx = \frac{1}{2a}$

6. $\int_0^\infty x^3 \exp(-ax^2)\, dx = \frac{1}{2a^2}$

7. $\int_0^\infty x^5 \exp(-ax^2)\, dx = \frac{1}{a^3}$

8. $\int_{-\infty}^{\infty} x^n \exp(-ax^2)\, dx = 0, \qquad \text{if } n \text{ is odd}$

9. $\int_{0}^{\infty} x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}, \qquad n \geq 0, \quad a > 0$

10. $\int_{0}^{\infty} \frac{x\, dx}{e^x - 1} = \frac{\pi^2}{6}$

11. $\int_{0}^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$

12. $\int_{0}^{\infty} e^{-ax} \cos bx\, dx = \frac{a}{a^2 + b^2}, \qquad a > 0$

13. $\int_{0}^{\infty} e^{-ax} \sin bx\, dx = \frac{b}{a^2 + b^2}, \qquad a > 0$

14. $\int_{0}^{\infty} \cos bx \exp(-a^2x^2)\, dx = \frac{\sqrt{\pi}}{2a} \exp\left(-\frac{b^2}{4a^2}\right), \qquad a > 0$

15. $\int x\, e^{ax}\, dx = \frac{ax - 1}{a^2} e^{ax}$

16. $\int x^2 e^{ax}\, dx = \left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right) e^{ax}$

Appendix B

Coordinate Transformation

1. The relations between rectangular and spherical coordinates:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\,\sin\phi, \qquad z = r\cos\theta$$

2. Elementary lengths and volume element in spherical polar coordinates:
   Elementary lengths: dr, $r\,d\theta$, $r\sin\theta\,d\phi$
   Volume element: $dr \times r\,d\theta \times r\sin\theta\,d\phi = r^2\sin\theta\,d\theta\,d\phi\,dr$

3. The orthonormal unit vectors $\hat{\mathbf{r}}$, $\hat{\boldsymbol{\theta}}$ and $\hat{\boldsymbol{\phi}}$ of the spherical coordinates satisfy the relations:

$$\hat{r}\cdot\hat{\theta} = \hat{r}\cdot\hat{\phi} = \hat{\phi}\cdot\hat{\theta} = 0$$

$$\hat{r}\cdot\hat{r} = \hat{\theta}\cdot\hat{\theta} = \hat{\phi}\cdot\hat{\phi} = 1$$

$$\hat{r}\times\hat{\theta} = \hat{\phi}; \quad \hat{r}\times\hat{\phi} = -\hat{\theta}; \qquad \hat{\theta}\times\hat{\phi} = \hat{r}$$

4. Unit vectors $\hat{r}$, $\hat{\theta}$ and $\hat{\phi}$ in terms of the rectangular unit vectors $\hat{\imath}$, $\hat{\jmath}$, $\hat{k}$:

$$\hat{r} = \hat{\imath}\,\sin\theta\cos\phi + \hat{\jmath}\sin\theta\sin\phi + \hat{k}\,\cos\theta$$

$$\hat{\theta} = \hat{\imath}\,\cos\theta\cos\phi + \hat{\jmath}\,\cos\theta\sin\phi - \hat{k}\sin\theta$$

$$\hat{\phi} = -\hat{\imath}\,\sin\phi + \hat{\jmath}\,\cos\phi$$

5. Unit vectors $\hat{i}$, $\hat{j}$, $\hat{k}$ in terms of $\hat{r}$, $\hat{\theta}$, $\hat{\phi}$:

$$\hat{i} = \hat{r}\sin\theta\cos\phi + \hat{\theta}\cos\theta\cos\phi - \hat{\phi}\sin\phi$$

$$\hat{j} = \hat{r}\sin\theta\sin\phi + \hat{\theta}\cos\theta\sin\phi + \hat{\phi}\cos\phi$$

$$\hat{k} = \hat{r}\cos\theta - \hat{\theta}\sin\theta$$

6. Gradient operator ∇ in spherical polar coordinates:

$$\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$$

7. Laplacian operator ∇^2 in spherical polar coordinates:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Appendix C

Dirac Delta Function

The Dirac delta function $\delta(x)$ is not a function in the usual mathematical sense. In the normal sense a function will have a definite value for each point in its domain. The delta function $\delta(x)$ acquires a meaning only when it appears in an integral. *The Dirac delta function* $\delta(x)$ is defined by the conditions:

$$\delta(x) = \begin{cases} 0, & x \neq 0 \\ \infty, & x = 0 \end{cases} \tag{C.1}$$

such that

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1 \tag{C.2}$$

By making a change of origin, we can write Eq. (C.1) as

$$\delta(x - x_0) = \begin{cases} 0, & x \neq x_0 \\ \infty, & x = 0 \end{cases} \tag{C.3}$$

such that

$$\int_{-\infty}^{\infty} \delta(x - x_0)\, dx = 1 \tag{C.4}$$

If $f(x)$ is an arbitrary function, well defined at $x = 0$, then the integration of $f(x)$ with the delta function selects the value of $f(x)$ at the origin

$$\int f(x)\delta(x)\ dx = f(0) \tag{C.5}$$

Here, the integration is over the domain in which $f(x)$ is defined, provided the range includes the origin. It follows from Eq. (C.2) that

$$\int f(x)\delta(x-x_0)\ dx = f(x_0) \tag{C.6}$$

where the range of integration must include the point $x = x_0$.

Generalization of Dirac delta function to three-dimensional space is straightforward. If **r** is the position vector with components x, y, z, then the three-dimensional delta function:

$$\delta(\mathbf{r}-\mathbf{r}_0) = \delta(x-x_0)\ \delta(y-y_0)\ \delta(z-z_0) \tag{C.7}$$

such that

$$\int f(\mathbf{r})\delta\ (\mathbf{r}-\mathbf{r}_0)\ d\mathbf{r} = f(\mathbf{r}_0) \tag{C.8}$$

where the range of integration includes the point (x_0, y_0, z_0).

Properties of the Delta Function

(i) The delta function is an even function: $\delta(-x) = \delta(x)$

(ii) $x\delta(x) = 0$

(iii) $x\delta(x-x_0) = x_0\ \delta(x-x_0)$

(iv) $f(x)\ \delta(x-x_0) = f(x_0)\ \delta(x-x_0)$

(v) $\delta(ax) = \frac{1}{a}\delta(x), \qquad a > 0$ (C.9)

(vi) $\delta(x^2-a^2) = \frac{1}{2|a|}[\delta(x-a) + \delta(x+a)]$

(vii) $\int \delta(x-b)\ \delta(a-x)\ dx = \delta(a-b)$

Representation of Delta Function

Mathematically, delta function can be considered as the limit of a function which becomes more peaked at the origin when a parameter approaches zero. Many such representations are available. Some of them are

$$\delta(x) = \lim_{g\to\infty} \frac{\sin(gx)}{\pi x} \tag{C.10}$$

which tends to infinity (peaked) when $x = 0$. An equally good representation is

$$\delta(x - x_0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\,[ik(x-x_0)]\ dk \tag{C.11}$$

Some of the other expressions which can be used to define $\delta(x)$ are

$$\delta(x) = \lim_{a \to 0} \frac{1}{\pi} \frac{a}{x^2 + a^2} \tag{C.12}$$

$$\delta(x) = \lim_{a \to 0} \frac{1}{\sqrt{\pi} a} \exp\left(-\frac{x^2}{a^2}\right) \tag{C.13}$$

The integral representation of the three-dimensional delta function can be written as

$$\delta(\mathbf{r} - \mathbf{r}_0) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \exp\,[ik(\mathbf{r} - \mathbf{r}_0)]\, d\mathbf{k} \tag{C.14}$$

where **k** is a vector with components k_x, k_y and k_z and $d\mathbf{k} = dk_x dk_y\, dk_z$.

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Answers to Problems

Chapter 1

1. 2.012 eV; 2.012 V; 2958 Å

2. 2.14 eV; 0.48 V

3. 0.21 eV

4. 3.28×10^{15} Hz

5. 4.045 Å

6. 3.88 eV; 9.4×10^{14} Hz; 3191Å

8. 1.45 Å; 1.42 Å; 1.4 Å

9. 122 nm; 103 nm

11. –27.2 eV; 13.6 eV

12. 1.51 eV; –1.7 eV

Chapter 2

1. $\lambda = 0.868$ Å

2. (i) 42.85 (ii) 13.55

3. 618.2 MeV

4. 1.98×10^3 ms^{-1}; 20.5×10^{-3} eV

5. 37.65 eV

6. $\Delta x = 2.2 \times 10^{-31}$ m

7. $\Delta x = 10^{-10}$ m

8. 8.7 %

10. $V(x) = 2mk^2x^2$

11. Not normalizable; $j = \hbar k|A|^2/m$

13. $\lambda = \dfrac{hc}{\sqrt{T^2 + 2m_0c^2T}}$

14. $\Delta x = 6.6 \times 10^{-7}$ m

15. 1836

16. $j(x) = \dfrac{\hbar u^2}{m}\dfrac{\partial \phi}{\partial x}$

17. V = constant

18. $\dfrac{\partial P(\mathbf{r},t)}{\partial t} + \nabla \cdot j\,(\mathbf{r}, t) = \dfrac{2V_2}{\hbar} P\,(\mathbf{r}, t)$

Chapter 3

2. (i) Zero (ii) $\dfrac{\partial F}{\partial x}$

6. $[A, B] = 0$

7. Hermitian

9. $-(k_1^2 + k_2^2 + k_3^2)$

10. Not Hermitian

13. $\hbar k$; $\hbar^2 k^2$

14. $a\hbar$

15. $\psi = \dfrac{\psi_1 + \psi_2}{\sqrt{2+2a}}$

16. $V = \dfrac{\hbar^2}{2m}\alpha^4 x^6 - \dfrac{3\hbar^2\alpha^2 x^2}{2m} + \dfrac{\hbar^2\alpha^2}{m}$

18. ia, a is real; $\psi = c\exp(iax)$, c-constant

20. (i) $\dfrac{d^2}{dx^2} + 2x\dfrac{d}{dx} + x^2 + 1$ (ii) $\dfrac{d^2}{dx^2} - x^2 - 1$

21. (i) $2\hbar^2 \dfrac{\partial}{\partial x}$ (ii) $2yz\hbar^2 \dfrac{\partial}{\partial x}$

22. $\dfrac{-3}{2}\hbar^2$

23. (i) Yes (ii) $\dfrac{1}{s-a}$

25. $H = -\dfrac{\hbar^2}{2m}\nabla^2 + \dfrac{ie\hbar}{2mc}\nabla\cdot\mathbf{A} + \dfrac{ie\hbar}{mc}\mathbf{A}\cdot\nabla + \dfrac{e^2}{2mc^2}A^2 + e\phi$

Chapter 4

1. $E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$, $n = 1, 2, \ldots$, $\psi_n(x) = \left(\dfrac{2}{a}\right)^{1/2} \sin\dfrac{n\pi x}{a}$

3. $\langle x \rangle = \dfrac{a}{2}$; $\langle p_x \rangle = 0$

4. 17.8×10^{-10} m

5. $\dfrac{1}{n}$

6. 0.122

7. 0.5

8. $\langle x \rangle = \langle p \rangle = 0$

9. $(\Delta x)\,(\Delta p) = \left(n + \dfrac{1}{2}\right)\hbar$

10. (i) $\dfrac{\hbar k_0}{m}$ (ii) $-\dfrac{\hbar k_0}{m}$ (iii) Zero; $k_0^2 = \dfrac{2mE}{\hbar^2}$

11. 0.44

13. 5

14. (i) $\pm\dfrac{1}{\alpha}$ (ii) 0.415α, $\alpha = \pm\sqrt{\dfrac{m\omega}{\hbar}}$

16. $E_n = (n + \frac{1}{2})\hbar\omega$, $n = 1, 3, 5, \ldots$, Harmonic oscillator wave functions with the appropriate n

17. (i) 0.133 eV (ii) 1860 N m^{-1}

18. $-\left[\dfrac{(2n+1)\hbar}{m\omega}\right]^{1/2} < x < \left[\dfrac{(2n+1)\hbar}{m\omega}\right]^{1/2}$

19. 3.79 eV

20. 8.1×10^{-8} cm

21. (i) $\sqrt{\dfrac{2}{5a}}\left(2\sin\dfrac{\pi x}{a} + \sin\dfrac{3\pi x}{a}\right)$

(ii) $\psi(x,t) = \dfrac{2}{\sqrt{5}}\sqrt{\dfrac{2}{a}}\sin\dfrac{\pi x}{a}e^{-iE_1t/\hbar} + \dfrac{1}{\sqrt{5}}\sqrt{\dfrac{2}{a}}\sin\dfrac{3\pi x}{a}e^{-iE_3t/\hbar}$

$E_1 = \dfrac{\pi^2\hbar^2}{2ma^2}$ $E_3 = \dfrac{9\pi^2\hbar^2}{2ma^2}$ (iii) No

22. 1.02×10^{-6}

Chapter 5

2. $\langle V\rangle = -\dfrac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}$; $\langle T\rangle = \dfrac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$

3. $9a_0$

5. 7.64×10^{-23} J

6. (i) $\dfrac{0.37}{a_0}$ (ii) $\dfrac{0.54}{a_0}$

7. (i) $\dfrac{0.37}{8a_0}$ (ii) Zero

9. $\sqrt{3}\,a_0$

10. $\dfrac{3a_0^2}{4}$

11. (i) $\dfrac{\sqrt{6}\hbar}{2\pi I}$ (ii) $\dfrac{\sqrt{30}\hbar}{2\pi I}$

12. (i) $E_n = \left(n + \dfrac{3}{2}\right)\hbar\omega$, $n = 0, 1, 2, \ldots$, (ii) $\dfrac{(n+1)(n+2)}{2}$

13. 14, 6

14. a_0, $4a_0$, $9a_0$

15. 0.18 nm

16. 565.2 MeV

17. 0.375

Chapter 6

2. $U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \end{pmatrix}$

Chapter 7

2. (i) Zero (ii) Nonzero (iii) Nonzero

Chapter 8

1. $L_+ = \hbar\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)e^{i\phi}$; $L_- = \hbar\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)e^{-i\phi}$

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

4. $i\hbar L_z$

5. (i) Zero (ii) $-i\hbar(L_y L_z + L_z L_y)$

   (iii) $i\hbar(L_x L_z L_y + L_x L_y L_z + L_z L_y L_x + L_y L_z L_x)$

7. Eigenvector of σ_x: $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

   Eigenvector of σ_y: $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}$

8. (i) $\left(\frac{\hbar}{2}\right)^5 \sigma_y$ (ii) $\left(\frac{\hbar}{2}\right)^6$ (iii) $\left(\frac{\hbar}{2}\right)^5 i$

9. (i) 2, 1, 0 (ii) 7, 6, 5, 4, 3, 2, 1 (iii) $\frac{5}{2}, \frac{3}{2}$

10. (i) $\sqrt{20}, \sqrt{12}, \sqrt{6}, \sqrt{2}, 0$ (ii) $\sqrt{6}, \sqrt{2}, 0$

    (iii) $\sqrt{12}, \sqrt{6}, \sqrt{2}$

12. Nonzero $\langle m_1 m_2 \mid jm\rangle$ are

$$\left\langle \frac{1}{2}, \frac{1}{2}\middle| 1\ 1\right\rangle = \left\langle -\frac{1}{2}, -\frac{1}{2}\middle| 1, -1\right\rangle = 1; \left\langle -\frac{1}{2}, \frac{1}{2}\middle| 0\ 0\right\rangle = \frac{-1}{\sqrt{2}}$$

$$\left\langle \frac{1}{2}, -\frac{1}{2}\middle| 1\ 0\right\rangle = \left\langle -\frac{1}{2}, \frac{1}{2}\middle| 1, 0\right\rangle = \left\langle \frac{1}{2}, -\frac{1}{2}\middle| 0,\ 0\right\rangle = \frac{1}{\sqrt{2}}$$

13. Nonzero $\langle m_1 m_2 \mid jm\rangle$ are

$$\langle 1\;1 \mid 2\;2\rangle = \langle -1, -1 \mid 2, -2\rangle = 1$$

$$\langle 1\;0 \mid 2\;1\rangle = \langle 1, 0 \mid 1\;1\rangle = \langle 0\;1 \mid 2\;1\rangle = \langle 0, -1 \mid 2, -1\rangle = \langle -1, 0 \mid 2, -1\rangle$$

$$= \langle 1, -1 \mid 1\;0\rangle = \langle 0, -1 \mid 1, -1\rangle = \frac{1}{\sqrt{2}}$$

$$\langle 0, 1 \mid 1\;1\rangle = \langle -1, 1 \mid 1, 0\rangle = \langle -1,\; 0 \mid 1, -1\rangle = -\frac{1}{\sqrt{2}}$$

$$\langle 1, -1 \mid 2, 0\rangle = \langle -1, 1 \mid 2, 0\rangle = \frac{1}{\sqrt{6}};\quad \langle 1, -1 \mid 0\;0\rangle = \langle -1, 1 \mid 0\;0\rangle = \frac{1}{\sqrt{3}}$$

$$\langle 0\;0 \mid 0\;0\rangle = -\frac{1}{\sqrt{3}};\quad \langle 0\;0 \mid 2, 0\rangle = \sqrt{\frac{2}{3}}$$

14. $(2j_1 + 1)\,(2j_2 + 1)$

17. (i) Yes (ii) 0 and $\hbar$ (iii) $\frac{1}{3}, \frac{2}{3}$

18. $\frac{\hbar^2}{2I}[l(l+1) + m^2];\quad Y_{lm}(\theta, \phi)$

19. $\pm\frac{\hbar}{2};\quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix};\quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}$ and $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}$

Chapter 9

1. $0, \frac{-b^2}{2m\omega^2}$

2. Zero

3. $\frac{3b\hbar^2(2n^2 + 2n + 1)}{4m^2\omega^2}$

4. $\frac{b\hbar}{4m\omega};\; -\frac{\hbar b^2}{16m^2\omega^3}$

5. $\frac{Z^4\alpha^2 hcR}{n^3 l(l+1)}$

6. (i) Zero (ii) $E_0 + \varepsilon + \frac{A^2}{2\varepsilon};\quad E_0 - \varepsilon - \frac{A^2}{2\varepsilon}$

(iii) $|\phi_1\rangle + \frac{A}{2\varepsilon}|\phi_2\rangle;\quad |\phi_2\rangle - \frac{A}{2\varepsilon}|\phi_1\rangle$

7. $E_0 + A;\; E_0 - A$ (ii) $\frac{1}{\sqrt{2}}(|1\rangle - |2\rangle);\; \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

9. $a[F(F+1) - I(I+1) - J(J+1)]$, a-constant

10. $E_{so} = \begin{cases} 3\xi\hbar^2, & j = 4 \\ -\xi\hbar^2, & j = 3 \\ -4\xi\hbar^2, & j = 2 \end{cases}$ ξ-constant

$$d = \begin{cases} 9, & j = 4 \\ 7, & j = 3 \\ 5, & j = 2 \end{cases}$$

11. Zero, Zero

12. 36.53 m^{-1}, 10.82 m^{-1}, 3.61 m^{-1}

Chapter 10

1. $\alpha^2 \langle \phi_1 | H | \phi_1 \rangle$

2. $\left(\dfrac{\pi^2 - 6}{3} \right)^{1/2} \dfrac{\hbar\omega}{2}$

3. $a = \left(\dfrac{3km}{2\hbar^2} \right)^{1/3}$; $\quad E = \dfrac{9}{4} \left(\dfrac{2k^2\hbar^2}{3m} \right)^{1/3}$

4. $E = \dfrac{-ma^2}{\pi\hbar^2}$

5. $E = -\dfrac{8}{3\pi} \dfrac{\mu e^4}{2\hbar^2}$

6. $\dfrac{10\hbar^2}{2ma^2}$

7. $\dfrac{3\hbar\omega}{2}$

Chapter 11

1. $E_n = \left(n + \dfrac{1}{2} \right)^2 \dfrac{\pi^2\hbar^2}{8ma^2}, \quad n = 0, 1, 2, \ldots$

2. $E_n = \left(\dfrac{\hbar^2}{2m} \right)^{1/3} \left[\dfrac{3}{4} \pi A (2n + 1) \right]^{2/3}, \quad n = 0, 1, 2, \ldots$

3. $E_n = \left(\dfrac{\hbar^2}{2m} \right)^{1/3} \left[\dfrac{3}{8} (2n + 1) V_0 \pi \right]^{2/3}, \quad n = 0, 1, 2, \ldots$

Chapter 12

1. $3ea_0$

2. $A = 7 \times 10^{-2}\ \text{s}^{-1}$

4. $A_{n \to k} = \dfrac{2e^2\omega^2 n}{3mc^3}$

5. $7.6 \times 10^{-13}\ \text{s}^{-1}$; $2.24 \times 10^{7}\ \text{s}^{-1}$

6. $\dfrac{\pi t_0^2}{2m\hbar\omega} \exp\left(-\dfrac{\omega^2 t_0^2}{2} \right)$

8. $B = 7.56 \times 10^{9}\ \text{N}^{-1}\ \text{m}^2\ \text{s}^{-2}$, $A = 6.97 \times 10^{-2}\ \text{s}^{-1}$

Chapter 13

2. (i) $\dfrac{\pi^2\hbar^2}{2ma^2}$ (ii) $\dfrac{32\pi^2\hbar^2}{ma^2}$ (iii) $\dfrac{32\pi^2\hbar^2}{ma^2}$

3. (i) $\dfrac{\pi^2\hbar^2}{ma^2}$, $\psi(x, m_s) = \dfrac{2}{a}\left(\sin\dfrac{\pi x_1}{a}\right)\left(\sin\dfrac{\pi x_2}{a}\right)\chi(m_s)$

$$\chi(m_s) = \alpha\alpha,\ \beta\beta,\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}}$$

(ii) $\dfrac{\pi^2\hbar^2}{ma^2}$, $\psi(x, m_s) = \dfrac{\sqrt{2}}{a}\left(\sin\dfrac{\pi x_1}{a}\right)\left(\sin\dfrac{\pi x_2}{a}\right)(\alpha\beta - \beta\alpha)$

4. $E_n = (n + 1)\,\hbar\omega$, $n = 0, 1, 2, \ldots$; $(n + 1)$-fold degenerate

8. $\dfrac{1}{2}[1s(1)\ 2p_0(2) + 1s(2)\ 2p_0(1)]\ [\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$

$\dfrac{1}{\sqrt{2}}\ [1s(1)\ 2p_0(2) - 1s(2)\ 2p_0(1)]\,\chi(m_s)$

$$\chi(m_s) = \alpha\alpha,\ \beta\beta,\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}}$$

and eight similar functions for $1s$ with $2p_1$ and $1s$ with $2p_{-1}$.

9. $$\psi^\circ = \frac{1}{\sqrt{6}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) & 1s(3)\alpha(3) \\ 1s(1)\beta(1) & 1s(2)\beta(2) & 1s(3)\beta(3) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) & 2s(3)\alpha(3) \end{vmatrix}$$

10. (i) $\begin{array}{cccccc} (A_1, A_2) & (A_1, B) & (A_2, B) & (A_1, C) & (A_2, C) & (B, C) \\ 2E & 3E & 3E & 4E & 4E & 4E \end{array}$

(ii) Those in (i) plus $\begin{array}{cccc} (A_1, A_1) & (A_2, A_2) & (B, B) & (C, C) \\ 2E & 2E & 4E & 6E \end{array}$

(iii) Those in (i), (ii) plus $\begin{array}{cccccc} (A_2, A_1) & (B, A_1) & (B, A_2) & (C, A_1) & (C, A_2) & (C, B) \\ 2E & 3E & 3E & 4E & 4E & 5E \end{array}$

11. $\psi_{\text{sing}} = \dfrac{1}{2}[\psi_{100}(r_1)\,\psi_{200}(r_2) + \psi_{100}(r_2)\,\psi_{200}(r_1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

$\psi_{\text{trip}} = \dfrac{1}{\sqrt{2}}[\psi_{100}(r_1)\,\psi_{200}(r_2) - \psi_{100}(r_2)\,\psi_{200}(r_1)]\,\chi(m_s)$

$\chi(m_s) = \alpha(1)\,\alpha(2),\ \ \beta(1)\beta(2),\ \ \dfrac{[\alpha(1)\beta(2) + \beta(1)\alpha(2)]}{\sqrt{2}}$

Chapter 14

1. $f(\theta) = \dfrac{2\mu V_0}{\hbar^2 q^3}\ [\sin(qr_0) - r_0 q\ \cos(qr_0)]$, $q = 2k\ \sin\dfrac{\theta}{2}, k^2 = \dfrac{2mE}{\hbar^2}$

3. $a = r_0 \left[1 - \frac{\tan(k_0 r_0)}{k_0 r_0} \right], \quad \sigma_0 = 4\pi r_0^2 \left(1 - \frac{\tan k_0 r_0}{k_0 r_0} \right)^2$

4. $\sigma(\theta) = \dfrac{\pi^2 \mu^2 \alpha^2}{4k^2 \hbar^4 \sin^2 \frac{\theta}{2}}$

7. $\sigma(\theta) = \dfrac{16\mu^2 V_0^2 r_0^6}{\hbar^4 \left(1 + q^2 r_0^2\right)^4}$

8. $f(\theta) = \dfrac{-2\mu V_0}{\hbar^2} \left[\dfrac{c r_0^2}{1 + q^2 r_0^2} - \dfrac{2 r_0^3}{\left(1 + q^2 r_0^2\right)^2} \right]$

9. $(\nabla^2 + k^2) f(r) = U(r) e^{ikz}, \quad k^2 = \dfrac{2\mu E}{\hbar^2}, \quad U(r) = \dfrac{2\mu V}{\hbar^2}$

10. $\dfrac{\pi\mu^2 A^2 a^6}{4\hbar^4} e^{-q^2 a^2/2}$

11. $\dfrac{4m^2 a^2 A^2}{q^2 \hbar^2} \sin^2 qa$

12. $\dfrac{16\pi a^2 \mu^2 V_o^2}{9\hbar^2}$; Both give same result at low energies.

Chapter 15

2. $P(\mathbf{r}, t) = \Psi^\dagger \Psi; \qquad \mathbf{j}(\mathbf{r}, t) = c\, \Psi^\dagger \alpha \Psi$

5. ±1, ±2, ±3, ...

Chapter 16

4. $\mathcal{H} = -\dfrac{i\hbar}{2m} \nabla\pi \cdot \nabla\Psi - \dfrac{i}{\hbar} V\pi\Psi$

5. $\nabla \cdot \mathbf{E} = \rho, \quad \nabla \times \mathbf{E} = -\dfrac{\partial B}{\partial t}, \quad \rho(\mathbf{x}, t)$-charge density

$\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{B} = \dfrac{\partial \mathbf{E}}{\partial t} + \mathbf{j}, \quad \mathbf{j}(\mathbf{x}, t)$-current density

$$\nabla^2 \phi + \frac{\partial}{\partial t}(\nabla \cdot \mathbf{A}) = -\rho, \quad \nabla^2 A - \frac{\partial^2 A}{\partial t^2} - \nabla\left(\nabla \cdot \mathbf{A} + \frac{\partial \phi}{\partial t} \right) = -\mathbf{j}$$

Chapter 17

1. (i) $N_2[KK(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^2\,(2p\pi_u)^4]$

   $N_2^+[KK(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^2\,(2p\pi_u)^3]$

   (iii) N_2^+ (iv) N_2

2. (iii) $b = 2$

3. $F_2\,[KK\,(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\pi_u)^4\,(2p\sigma_g)^2\,(2p\pi_g^*)^4]$

$Cl_2\,[KKLL\,(3s\sigma_g)^2\,(3s\sigma_u^*)^2\,(3p\pi_u)^4\,(3p\sigma_g)^2\,(3p\pi_g^*)^4]$

$Br_2\,[KKLLMM\,(4s\sigma_g)^2\,(4s\sigma_u^*)^2\,(4p\pi_u)^4\,(4p\sigma_g)^2\,(4p\pi_g^*)^4]$

5. $B_2[KK\,(2s\sigma_g)^2\,(2s\sigma_u^*)^2\,(2p\sigma_g)^1\,(2p\pi_u)^1]$

6. (i) F_2^+ bond is stronger (ii) O_2 bond is stronger.

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