

Spectrum of He atom: Triplet and singlet state

Pauli exclusion principle:

No two electrons in an atom can occupy the same quantum state.

The quantum state is specified by the four quantum numbers; no two electrons can have the same set.



Wolfgang Pauli

The Nobel Prize in Physics 1945
"for the discovery of the Exclusion Principle,
also called the Pauli Principle"

Triplet and singlet state

1) He must have an anti-symmetric wave function (under interchange of the 2 electrons)

$$\Psi(2,1) = \frac{1}{\sqrt{2}} [\psi_{\alpha}(2)\psi_{\beta}(1) - \psi_{\beta}(2)\psi_{\alpha}(1)] = -\Psi(1,2)$$

$$\text{If } \alpha = \beta \text{ then } \Psi = 0$$

2) The 2 electrons must have different quantum numbers: α and β :
Pauli exclusion principle

Two possibilities for having an anti-symmetric wave function:

$$\Psi^A(1,2) = \psi^S(r_1, r_2)\chi^A(1,2)$$

spatial ψ and spin χ

$$\Psi^A(1,2) = \psi^A(r_1, r_2)\chi^S(1,2)$$

Triplet and singlet state

Addition of spins in a 2-electron system

$$\vec{S} = \vec{s}_1 + \vec{s}_2 \quad M_S = m_{s1} + m_{s2} \quad ; \quad S = 0, 1 \quad M_S = -1, 0, 1$$

$$|S = 1, M_S = 1\rangle = |\uparrow, \uparrow\rangle$$

$$|S = 1, M_S = 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)$$

$$|S = 1, M_S = -1\rangle = |\downarrow, \downarrow\rangle$$

$$|S = 0, M_S = 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)$$

A triplet of symmetric spin wave functions

A singlet of an anti-symmetric spin wave function

Two distinct families of quantum states in Helium:

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Ortho-helium: triplet states

$$\psi^A \chi^S$$

Para-helium: singlet states

$$\psi^S \chi^A$$

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Singlet and Triplet

Ordering of singlet and triplet states

Symmetric and Anti-symmetric spatial wave functions

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_{n_1 l_1 m_1}(\vec{r}_1) \psi_{n_2 l_2 m_2}(\vec{r}_2) \pm \psi_{n_2 l_2 m_2}(\vec{r}_1) \psi_{n_1 l_1 m_1}(\vec{r}_2)]$$

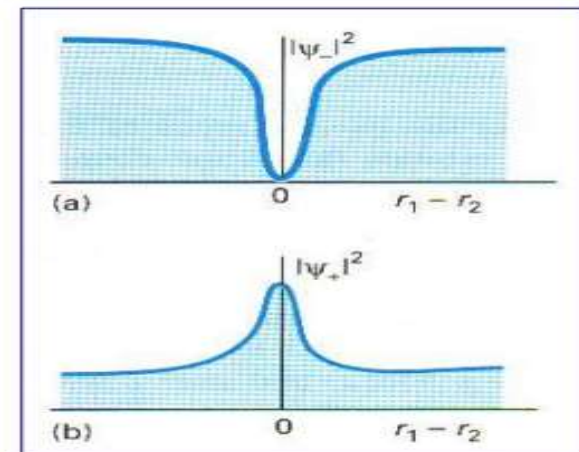
If: $\vec{r}_1 \approx \vec{r}_2$ density becomes small for $|\Psi_{-}(\vec{r}_1, \vec{r}_2)|^2$

→ Fermi-hole

While density of $|\Psi_{+}(\vec{r}_1, \vec{r}_2)|^2$ increases

Effect of "exchange"; a "force" related to the Pauli principle

→ quantum interference



Singlet and Triplet

Fermi-hole in case of an anti-symmetric spatial wave function

$$|\Psi_-(\vec{r}_1, \vec{r}_2)|^2$$

In this state the electrons tend to be distanced from each other

- less repulsion
- more binding

For the triplet states (or symmetric spin states)

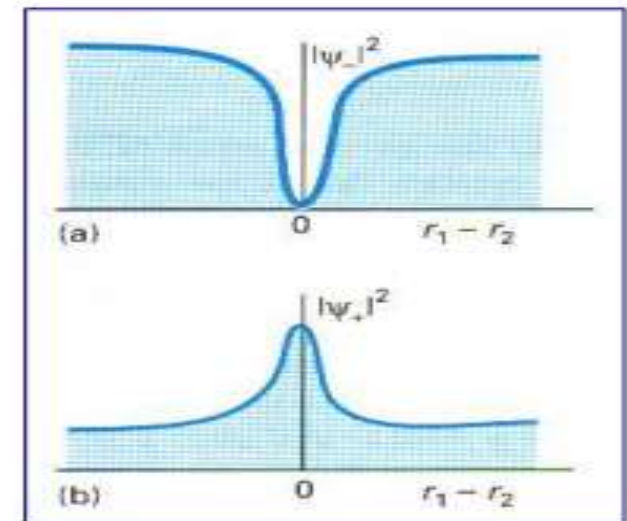
Conversely, in case of symmetric spatial function

$$|\Psi_+(\vec{r}_1, \vec{r}_2)|^2$$

Electrons tend to be close to each other

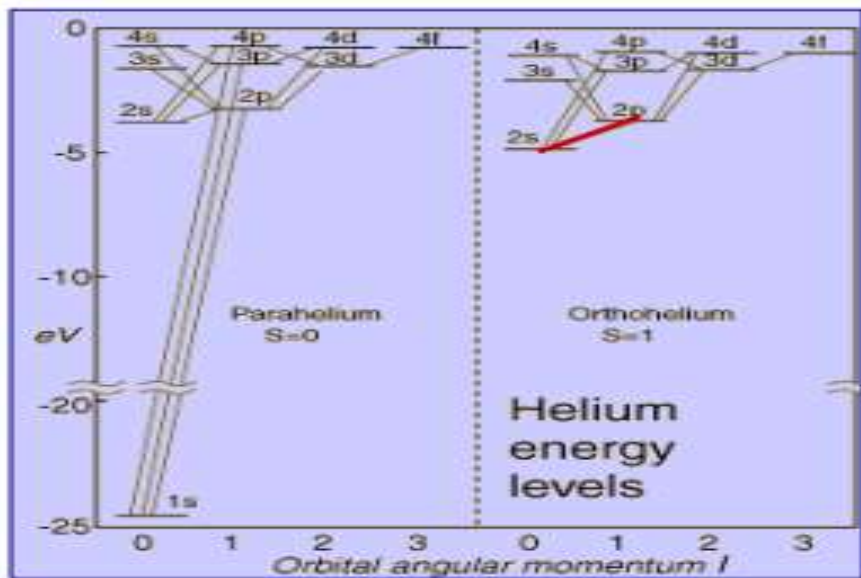
- more repulsion
- less binding energy

→ Triplet states are lower in energy than corresponding singlets



He atom Spectra

"Singly-excited" states in Helium, with one electron in (1s)



Selection rules: similar as in H

$$\Delta n = \text{free}$$

$$\Delta l = \pm 1$$

$$\Delta m = -1, 0, +1$$

$$\Delta S = 0$$

(1s)(2s) levels are metastable

Ortho and Para Helium

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Helium Atom and its Spectrum

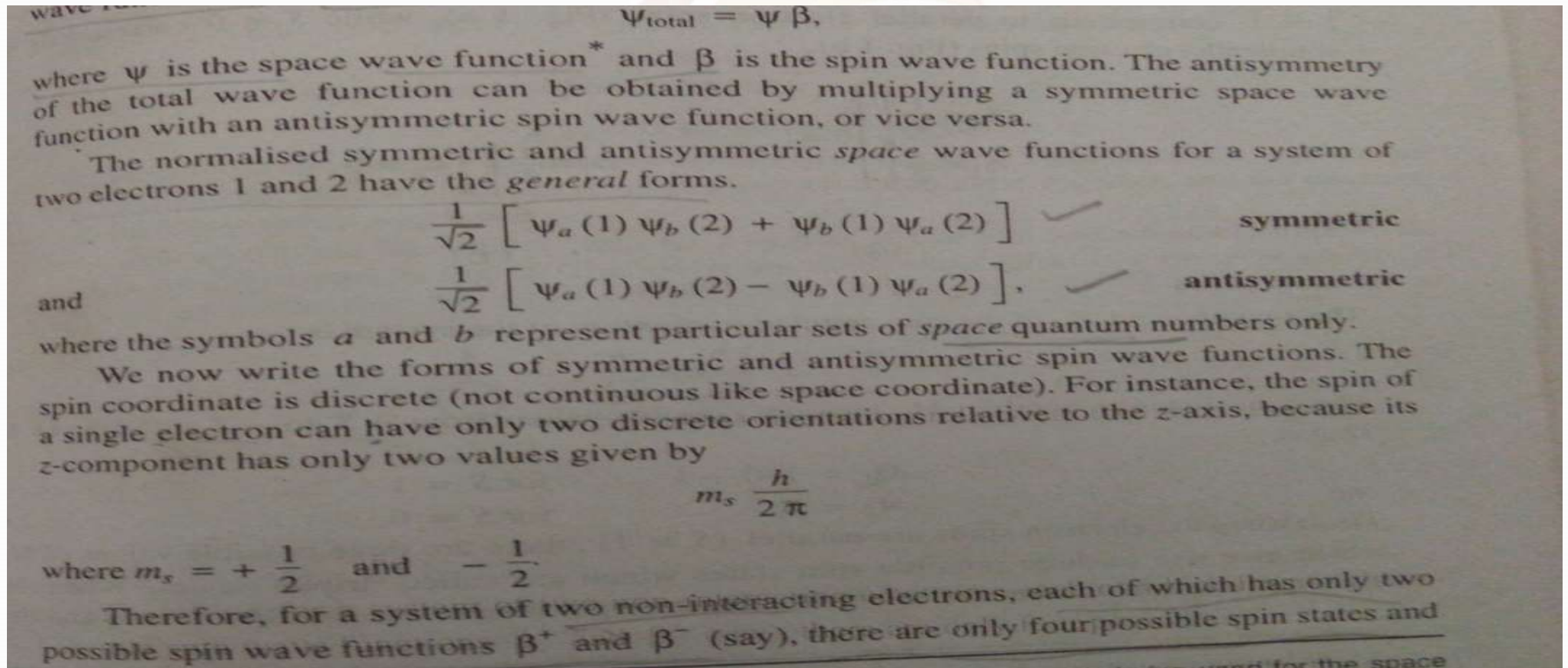
1. Exchange Force

The quantum mechanical treatment of identical particles leads to a rather strange property of such particles which has no classical analogy. *Two identical particles, such as two electrons in the same atom or two neutrons (or protons) in the same nucleus, act as if they move under the influence of a force whose sign (attractive or repulsive) depends on the relative orientation of their spin.* This is called an 'exchange force'. For example, if in an atom the spins of two electrons are "parallel", the electrons act as if they repel each other. (This has nothing to do with the coulombian repulsion between the electrons). If, on the other hand, the spins are "antiparallel", the electrons act as if they attract each other.

Let us consider a system containing two electrons ; for example, He atom or Li^+ ion. We ignore any interactions (like the coulomb interaction) between the electrons. According to Pauli's principle, the *total* wave function of the system must be *antisymmetric with respect to the exchange of space and spin coordinates of the two electrons.* The total wave function for the system can be written as a product of a space wave function and a spin wave function. That is

$$\Psi_{\text{total}} = \Psi \beta,$$

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so only four possible spin wave functions. We may write these wave functions in their normalised *specific* forms :

$$\left. \begin{array}{l} \beta_1^+ \beta_2^+ \\ \frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- + \beta_1^- \beta_2^+] \\ \beta_1^- \beta_2^- \end{array} \right\} \text{symmetric (triplet states)}$$

$$\frac{1}{\sqrt{2}} [\beta_1^+ \beta_2^- - \beta_1^- \beta_2^+] \text{ antisymmetric (singlet state)}$$

The first three are symmetric (interchanging the sub-scripts 1 and 2 makes no change in the wave function) and describe the so-called 'triplet' states of the system. The last one is antisymmetric (interchanging the sub-scripts 1 and 2 changes the sign) and describes the so-called singlet state.

Let us have a physical interpretation of the triplet and the singlet states. The spin quantum number for each of the two electrons 1 and 2 is $\frac{1}{2}$ ($s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$). The magnitude of the spin angular momentum \vec{S} of the system is

$$|\vec{S}| = \sqrt{S(S+1)} \frac{h}{2\pi},$$

where S takes all possible values from $(s_1 + s_2)$ to $(s_1 - s_2)$ differing by 1. Thus

$$S = 1, 0.$$

$S = 1$ corresponds to parallel electron spins (Fig. 1 a), while $S = 0$ corresponds to antiparallel electron spins (Fig. 1 b).

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$$\begin{array}{c} \uparrow \\ \Delta_2 = \frac{1}{2} \\ \uparrow \\ \Delta_1 = \frac{1}{2} \\ \hline S = 1 \end{array}$$

(a)

$$\begin{array}{c} \uparrow \quad \downarrow \\ \Delta_1 = \frac{1}{2} \quad \Delta_2 = \frac{1}{2} \\ \hline S = 0 \end{array}$$

(b)

(Fig. 1)

The z -component S_z of the spin angular momentum of the system is

$$S_z = M_S \frac{h}{2\pi}$$

where the quantum number M_S takes all possible values from $+S$ to $-S$ differing by 1. That is,

$$M_S = 1, 0, -1 \quad \text{for } S = 1$$

and

$$M_S = 0 \quad \text{for } S = 0.$$

Thus, when the electron spins are parallel ($S = 1$), there are three possible values of M_S which give rise to three possible spin states which are called 'triplet' states. When the electron spins are antiparallel ($S = 0$), the only possible value for M_S is zero and the

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spin state is called 'singlet' state. In other words, *triplet states correspond to parallel spins, while the singlet state corresponds to antiparallel spins.*

We can now explain the exchange force existing between two electrons of a system. If the spins of the two electrons are parallel, there are three possible spin wave functions which are all symmetric, In order to have the total wave function antisymmetric; the space wave function must therefore be antisymmetric, which is

$$\frac{1}{\sqrt{2}} \left[\psi_a(1) \psi_b(2) - \psi_b(1) \psi_a(2) \right],$$

where 1 and 2 represent the space coordinates of the electrons 1 and 2. Let us consider the situation when the electrons are close together, that is, their space coordinates have almost the same values. In this case, $\psi_a(1) \approx \psi_a(2)$ and $\psi_b(1) \approx \psi_b(2)$. As a consequence

$$\psi_a(1) \psi_b(2) \approx \psi_b(1) \psi_a(2),$$

so that the antisymmetric space wave function has a value practically zero. The result is that the probability density will be very small. This means that there is little chance of finding two parallel-spin (triplet state) electrons close together, and the electrons act as if they repel each other.

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On the other hand, if the spins of the two electrons are antiparallel, there is only one spin wave function which is antisymmetric. The corresponding space wave function must therefore be symmetric, which is

$$\frac{1}{\sqrt{2}} \left[\psi_a(1) \psi_b(2) + \psi_b(1) \psi_a(2) \right].$$

If the electrons happen to have almost the same space coordinates, that is, $\psi_a(1) = \psi_a(2)$ and $\psi_b(1) = \psi_b(2)$, then the wave function becomes

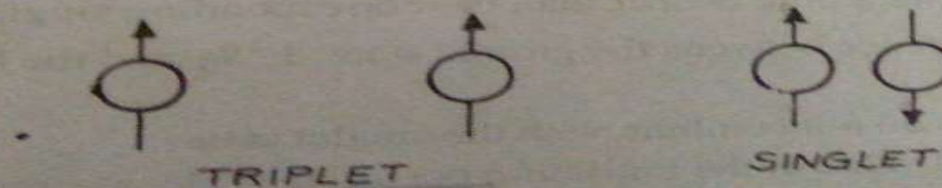
$$\sqrt{2} \psi_b(1) \psi_a(2).$$

Thus, the probability density will have the value

$$2 \psi_b^*(1) \psi_a^*(2) \psi_b(1) \psi_a(2),$$

which is twice the average probability density over all space. Thus, there is a large chance of finding two antiparallel-spin (singlet state) electrons close together, and the electrons act as if they attract each other.

The triplet and the singlet cases for a system of two non-interacting electrons as He atom, are illustrated in Fig. 2. This quantum-mechanical effect is a consequence of the Pauli's principle that the total wave function of a system of two electrons must be antisymmetric.



He- Atom

2. Spectrum of Helium

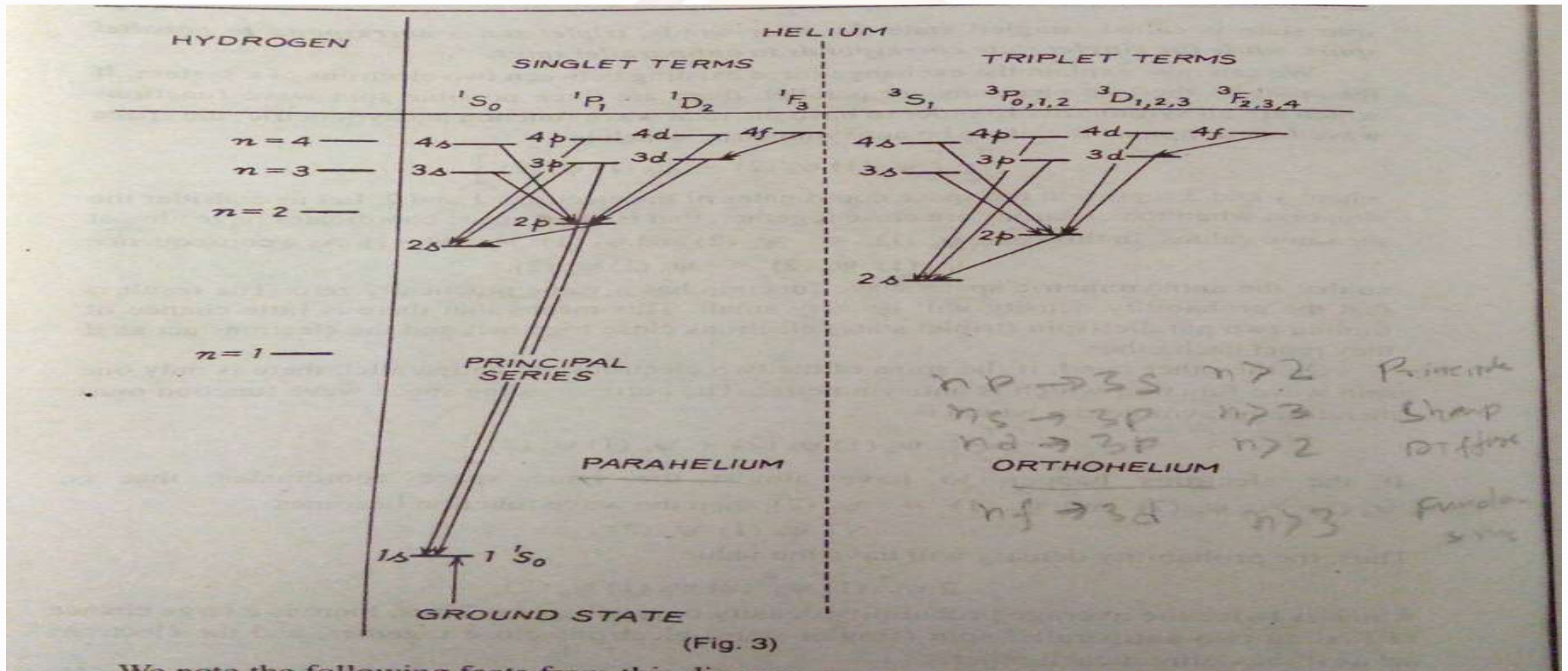
The emission spectrum of helium resembles the spectrum of a mixture of two alkali atoms. There are two each of the principal, sharp, diffuse and fundamental series, all having different limits. These can be analysed into two sets of terms, with no apparent relation between them. These are singlet and triplet terms, as shown in the energy-level diagram in Fig. 3.

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He Spectra



We note the following facts from this diagram

He Spectra

We note the following facts from this diagram :

(i) For each singlet energy state there is a corresponding triplet energy state, but there is no triplet state corresponding to the ground singlet state (1^1S_0) of the He atom.

(ii) The triplet states lie a little deeper than the corresponding singlet states.

(iii) The energy difference between the ground state 1^1S_0 and the lowest excited state is relatively large.

(iv) The triplet states do not combine with the singlet states.

(v) The experimental value of the ionisation potential of He, as obtained from the limit of the principal series ($1^1S_0 - m^1P_1$) is 24.58 eV, and the total binding energy of the ground state of He is 78.98 eV.

The division into non-combining singlet and triplet states gave rise to the idea that the helium occurs in two forms, parahelium and orthohelium. Atoms of the parahelium have antiparallel electron spins giving singlet states, while the atoms of the orthohelium have parallel electron spins giving triplet states. An orthohelium atom can lose excitation energy in a collision and become an atom of parahelium, while a parahelium atom can gain

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excitation energy^{viii} in a collision and become an atom of orthohelium. Ordinary helium is therefore a mixture of both. This explanation is partially correct. We now know that the splitting of the He terms into two practically non-combining systems follows from quantum mechanics.

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