# Singlet and triplet states in helium
# The Pauli principle and the “exchange force”
# Para- and ortho Helium

**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"**

# Phrasing of the Pauli principle

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

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

If $\alpha = \beta$ then $\Psi = 0$

2) The 2 electrons must have different quantum numbers: $\alpha$ and $\beta$:
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 $\psi$ and spin $\chi$

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

# Addition of spins in a 2-electron system

$\vec{S} = \vec{s}_1 + \vec{s}_2 \qquad M_S = m_{s_1} + m_{s_2}$ ; S= 0, 1 $M_S$ = -1, 0, 1

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

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

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

A triplet of symmetric spin wave functions

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

A singlet of an anti-symmetric spin wave function

Two distinct families of quantum states in Helium:

Ortho-helium: triplet states $\psi^A \chi^S$

Para-helium: singlet states $\psi^S \chi^A$

# Ordering of singlet and triplet states

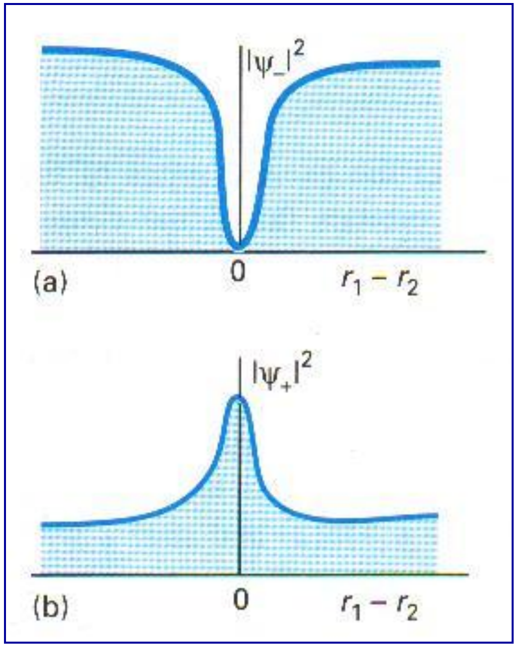
Symmetric and Anti-symmetric spatial wave functions

$$\Psi_{\pm}(\vec{r}_1,\vec{r}_2)=\frac{1}{\sqrt{2}}\left[\psi_{n_1l_1m_1}(\vec{r}_1)\psi_{n_2l_2m_2}(\vec{r}_2)-\psi_{n_2l_2m_2}(\vec{r}_1)\psi_{n_1l_1m_1}(\vec{r}_2)\right]$$

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

→ Fermi-hole

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




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

→ quantum interference

# Ordering of singlet and triplet states

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

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

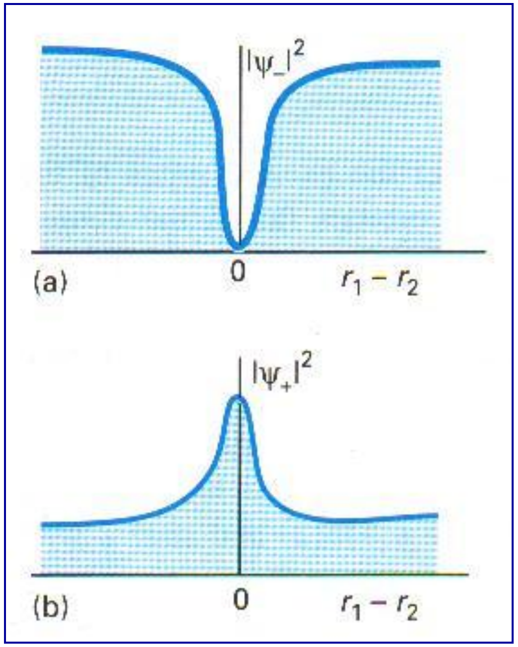
In this state the electrons tend to be distanced from each other
→ less repulsion
→ more binding
For the triplet states (or symmetric spin states)

Conversely, in case of symmetric spatial function

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

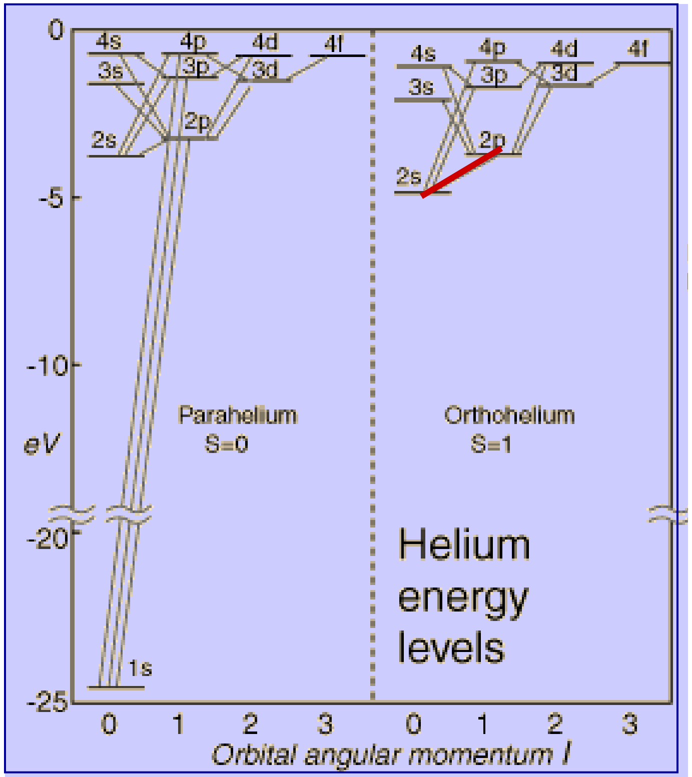
Electrons tend to be close to each other
→ more repulsion
→ less binding energy

→Triplet states are lower in energy than corresponding singlets



# Energy levels and Spectral lines in Helium

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




Selection rules: similar as in H

$\Delta n = free$

$\Delta \ell = \pm 1$

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

$\Delta S = 0$

(1s)(2s) levels are metastable

Ortho and Para Helium