Atoms with multiple electrons

$$E_p = \sum_{\forall \text{ Electron}} - \frac{Z e^2}{4\pi \varepsilon_0 r_i} + \sum_{\substack{\forall \text{ pair of} \\ \text{electrons}}} \frac{e^2}{4\pi \varepsilon_0 r_{ij}}$$

The electrons are not independent → interact

Approximate solutions only

The Helium atom   He,   H⁻,   Li⁺
                         $z=2$ $z=1$ $z=3$

$$E_p = -\frac{Z e^2}{4\pi \varepsilon_0 r_1} - \frac{Z e^2}{4\pi \varepsilon_0 r_2} + \frac{e^2}{4\pi \varepsilon_0 r}$$

1. approximation: 3. term (electron-
electron interaction)
independent particle
model
H-like wavefct. Ψ_{n,ℓ,m_ℓ} for both electrons

Energy of the groundstate: $E_{He} = -2 \frac{R h c Z^2}{1^2} = -109 eV$

Experimentally $E_{He} = -79 eV$

Because e-e interaction was neglected
(repulsion : + energy)

2. approximation: interaction considered as
perturbation

the electron moves in the field of the
nucleus and the average (central) field
of the 2. electron
⤳ 2. electron shields the charge of nucleus

$$E_{He} = -2 \frac{R h c (Z-S)^2}{1^2}$$

↓
$-79 eV$ → $S = 0,32$ shielding factor
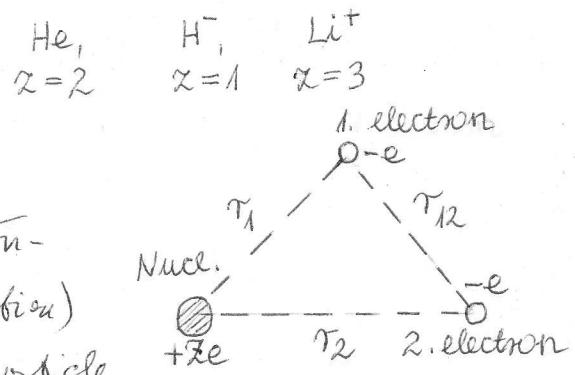
— The possible electron states

1. Independent particle model

$\{n, l, m_l\} \to a$ $\{n', l', m_l'\} \to b$

1. electron in state a }
2. electron in state b } $\to \Psi_{atom} = \Psi_a(1)\,\Psi_b(2)$

$|\Psi_{atom}|^2 = |\Psi_a(1)|^2 \cdot |\Psi_b(2)|^2$

2. Shielding potential perturbation

Assumed to be central $\mapsto \frac{1}{r}$ changes some $\to$

$\to R_{n\ell}(r)$ changes   but Y_{ℓ, m_ℓ} is the same

But the electrons are indistinguishable !

States $\Psi_a(1)\Psi_b(2)$ and $\Psi_a(2)\Psi_b(1)$ must have the
same energy

$\to \Psi_{atom}$ must reflect this symmetry, i.e.

$(\Psi_{atom})^2$ must not change when exchanging electron $1 \leftrightarrow 2$

b state $\underline{\quad\overset{2}{\circ}\quad}$ $\underline{\quad\overset{1}{\circ}\quad}$ $\underline{\quad\overset{\circ}{\circ}\quad}$ } Any
a state $\underline{\quad\overset{1}{\circ}\quad}$ $\underline{\quad\overset{2}{\circ}\quad}$ $\underline{\quad\overset{\circ}{\circ}\quad}$

$\Psi = \Psi_a(1)\Psi_b(2) \quad \Psi_a(2)\Psi_b(1) \quad \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) \pm \Psi_a(2)\Psi_b(1)]$

The symmetry requirement is fulfilled by the states

$\Psi_{atom} = \frac{1}{\sqrt{2}}[\Psi_a(1)\Psi_b(2) \pm \Psi_a(2)\Psi_b(1)]$

Symmetric $\Psi_S = [\; + \;]$ $\Psi_S(1,2) = \Psi_S(2,1)$

Antisymmetric $\Psi_A = [\; - \;]$ $\Psi_A(1,2) = -\Psi_A(2,1)$

The energies of the symmetric and antisymmetric states are different.

Reason: ψ_A assume the two electrons close in space their wavefunction would be very similar
→ $\psi_A = 0$ ⇒ Therefore in ψ_A the electrons are further away → less interaction between them. Unlike for ψ_S where there is no such effect.

⤳ Sets of 2 stationary states and energy level systems
(except when $a = b$ ⤳ $\psi_A = 0$, only $\psi_S \exists$.)

<u>Spin</u> : was not included in "a" and "b"

There may be two $s = \frac{1}{2}$ spin electrons parallel $\vec{s}' = 1$ $(\frac{1}{2}, \frac{1}{2})$ on antiparallel $\vec{s} = 0$ $(\frac{1}{2}, -\frac{1}{2})$

triplet $M_S = +1, 0, -1$ singlet $M_S = 0$
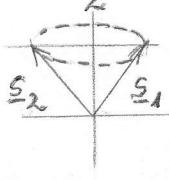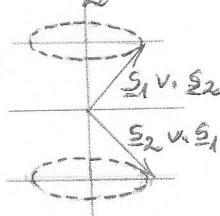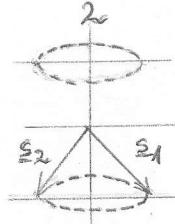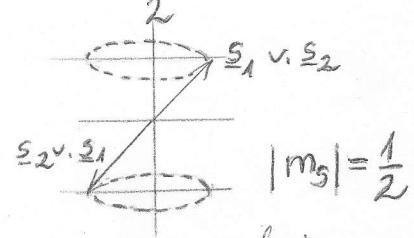
$M_S = +1$ $|m_S| = \frac{1}{2}$

The two electron spin wavefunctions as combinations of the on electron spin wavefunctions. χ_+ and χ_-

Singlet
antisymmetric $\chi_A = \frac{1}{\sqrt{2}}\left[\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)\right]$ $M_S = 0$

Triplet
symmetric $\chi_S = \begin{cases} \chi_+(1)\chi_+(2) & +1 \\ \frac{1}{\sqrt{2}}\left[\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)\right] & 0 \\ \chi_-(1)\chi_-(2) & -1 \end{cases}$

The total electron wavefunction of the atom =

(orbital wavefunction) x (spin wavefunction)

By spectral measurements   (ψ_S and ψ_A have different energies)

ψ_S (orbit) always singlet $\longrightarrow$ χ_A is attached

ψ_A (orbit) always triplet $\longrightarrow$ χ_S — " —

Therefore!

The total wavefunction of the system of electrons
is always antisymmetric

He: $S=0$ parahelium /with singlet states/

$S=1$ ortohelium /with triplet states/

Probability of transitions between triplet
and singlet states is small $\rightarrow$ would require
spin rearrangement/

He : mixture of two gases with ratio 1:3

The energies

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2}$$

$$\hat{H}_{12} = -\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$i = 1,2$

$$\hat{H}_i \psi_a(i) = E_a \psi_a(i)$$

$$\hat{H}_i \psi_b(i) = E_b \psi_b(i)$$

$$(\hat{H}_1 + \hat{H}_2)\psi = (E_a + E_b)\psi$$

where $\psi = \psi_A$ or ψ_S

Using the above:

The energy

$$E = \int \psi^* \hat{H} \psi \, d\tau = E_a + E_b + \underbrace{\int \psi^* \hat{H}_{12} \psi \, d\tau}_{\text{this must be calculated}}$$

$$\int \psi^* H_{12} \psi \, d\tau = C' \pm K \quad \begin{array}{l} + \text{ symmetric} \\ - \text{ antisymmetric} \end{array} \quad \begin{array}{l} \text{orbital} \\ \text{wavefct.} \end{array}$$

$$C' = \iint_{1\,2} \frac{e^2}{4\pi \varepsilon_0 r_{12}} |\psi_a(1)|^2 d\tau_1 |\psi_b(2)|^2 d\tau_2 \quad \text{Coulomb integral}$$

$$K = \iint_{1\,2} \frac{e^2}{4\pi \varepsilon_0 r_{12}} \psi_a^*(1) \psi_b(1) d\tau_1 \, \psi_b^*(2)\psi_a(2) d\tau_2 \quad \text{Interaction integral}$$

$C \rightarrow$ interaction between $\varrho_1 = -e|\psi_a(1)|^2$ and $\varrho_2 = -e|\psi_b(2)|^2$

$K > 0$

$K \rightarrow$ ——— " ——— $\varrho_1' = -e\psi_a^*(1)\psi_b(1)$ and $\varrho_2' = -e\psi_b^*(2)\psi_a(2)$

$$E = E_a + E_b + C' \pm K \qquad \text{charge distributions}$$

For ψ_S (singlet) $\quad + K$ higher $\Big\}$
ψ_A (triplet) $\quad - K$ lower $\Big\}$

$2K$ energy difference between the energy levels of pare- and orto-helium.

	S = 0					S = 1		
	ns	np	nd	nf		ns	np	nd	nf

(1 of the electron in the 1s state)

$n=1$ for $s=0$ only, because $1s-1s$ is symmetric $\rightarrow \psi$ must be ψ_A
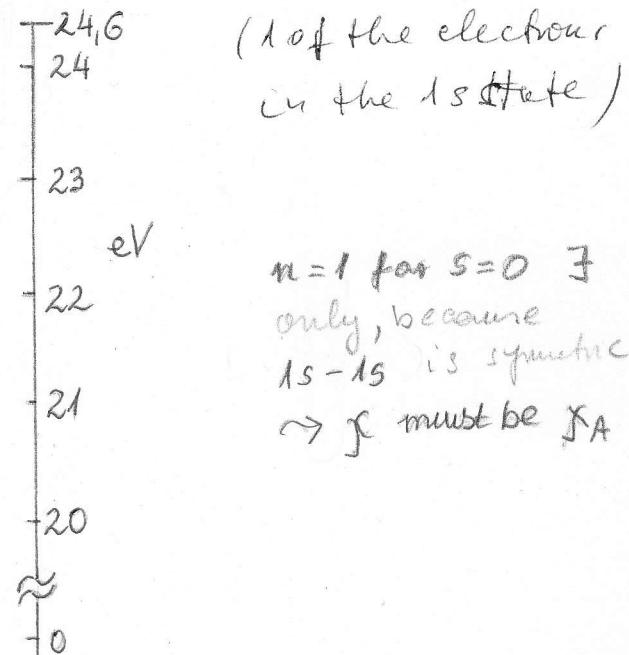
The exclusion principle

Atom with multiple electrons

Each electron characterized by quantum numbers n, l, m_e, m_s

Energy: depends on n, l (ignoring spin-orbit interaction)

With given n, l: a certain number of "equivalent" electrons: these differ only in m_e and m_s

Pauli principle : In an atom all the quantum numbers of 2 electrons can not be identical

This is equivalent with the complete wavefunction of the system being antisymmetric

$$\begin{vmatrix} \Psi_a(1) & \Psi_a(2) \\ \Psi_b(1) & \Psi_b(2) \end{vmatrix} = \Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1) \quad \begin{array}{l} \text{determinant} \\ \text{for 2 electrons} \end{array}$$

An atom with N electrons

$a = \{n, l, m_e, m_s\} \qquad b = \{n_e' l', m_e' m_s'\} \qquad c = \cdots$

The wavefunction of the N electron system is

$$\Psi_{abc\ldots} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_a(1) & \Psi_a(2) & \Psi_a(3)\ldots \\ \Psi_b(1) & \Psi_b(2) & \Psi_b(3)\ldots \\ \Psi_c(1) & \Psi_c(2) & \Psi_c(3)\ldots \\ \vdots & \vdots & \ddots \end{vmatrix}$$

$\Psi_{abc\ldots}$ is antisymmetric since exchange of 2 electrons $\equiv$ exchange of 2 columns in the determinant $\rightarrow$ it changes sign

2 electrons with identical sets of quantum numbers

e.g. $a = b \rightarrow$ 2 rows identical $\rightarrow$ determinant $= 0$

Conclusion: properties of multielectron systems: atoms molecules, solids

Principle of antisymmetricity: electrons, protons, neutrons etc.
$\Rightarrow$ fermions