Multielectron Atom.

Helium:

$$\hat{H} = \underbrace{\hat{H}_H(1) + \hat{H}_H(2)}_{\text{1-e Hamiltonians}} + \underbrace{\hat{H}_{12}}_{\substack{e\text{-}e \text{ repulsion} \\ (2e \text{ Hamiltonian})}}$$

1. Atomic Units ⇝
2. New quantum number → electron spin (m_s)
3. Antisymmetry of the wavefunction - Postulate 6
4. Hartree-Fock method

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \qquad E_H = \frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2}$$

	SI	Atomic Units.
Mass:	$m_e = 9.11 \cdot 10^{-31}$ kg	⟼
Charge:	$e = 1.602 \cdot 10^{-19}$ C	⟼
Angular momentum:	$\hbar = \frac{h}{2\pi} = 1.054 \cdot 10^{-34}$ Js	⟼
Distance (Bohr)	$a_0 = 5.29 \cdot 10^{-11}$ m	⟼
Energy (Hartree)	$E_H = 4.359 \cdot 10^{-18}$ J	⟼

Hamiltonian for a Lithium atom.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2 + \nabla_3^2\right) \quad \} \text{ Kinetic Energy}$$

$$-\frac{3e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3}\right) \quad \} \text{ Coulomb Attraction } e-N$$

$$+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}\right) \quad \} \text{ Coulomb Repulsion } e-e$$

$\hat{H} =$

} Calculations for helium atom: • We can Slove Energy of an atom with great accuracy

• $\Delta E = E_{He^+} - E_{He}$

Electron Spin ←

He: $\Psi(r_1, r_2) = 1s(r_1)\,1s(r_2)$

Li: $\Psi(r_1, r_2, r_3) = 1s(r_1)\,1s(r_2)\,2s(r_3)$

Why?

$\uparrow$ 2s

Li

$\uparrow\downarrow$ 1s

$\uparrow$ ⋮ $\uparrow\downarrow$ 1s

He^+ He

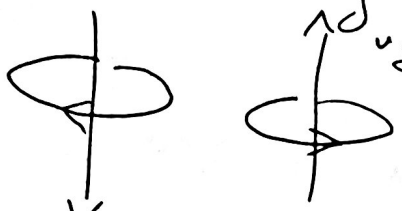
Na D-line

0.4 nm - splitting $\lambda \sim 590$ nm

(electron has two states)

What is the Electron Spin?

"Classically"



{ rotating charge

Spin Angular momentum.

"Imagine a ball that is rotating except it's not a ball and it is not rotating"

Q.M.

→ follows from Relativistic Q.M. (Dirac's)

Define it by analogy to $\hat{L}_z, \hat{L}^2$

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi)$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

$\hat{S}_z$

$\hat{S}^2$

↓

old spin angular momentum operator

"Eigenfunctions $\alpha(\sigma)$ and $\beta(\sigma)$ are orthonormal

$$\int \alpha^*(\sigma)\alpha(\sigma)\,d\sigma = 1 \qquad \int \alpha^*(\sigma)\beta(\sigma)\,d\sigma = 0$$

$$\int \beta^*(\sigma)\beta(\sigma)\,d\sigma = 1 \qquad \int \beta^*(\sigma)\alpha(\sigma)\,d\sigma = 0$$

Wavefunction Becomes: $\Psi(r,\theta,\varphi,\sigma) = \underbrace{\Psi(r,\theta,\varphi)}_{\text{spatial}}\underbrace{\alpha(\sigma)}_{\text{spin-orbital}}$

Pauli Exclusion Principle

No electron can have same values of $\underbrace{n, l, m_l, m_s}_{\text{quantum Numbers}}$

Recall: $\overline{\Psi}_{100\frac{1}{2}} = \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}} \alpha(\sigma)$

$\overline{\Psi}_{100-\frac{1}{2}} = \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}} \beta(\sigma)$

$\int \overline{\Psi}^*_{100\frac{1}{2}} \overline{\Psi}_{100-\frac{1}{2}} r^2 \sin\theta \, dr \, d\theta \, d\phi \, d\sigma =$ ($\int d\phi = 4\pi$)

$= \int \Psi^*_{100} \Psi_{100} r^2 dr \, 4\pi \int \alpha^*(\sigma)\beta(\sigma) d\sigma =$

Postulate 6

All electronic wavefunctions must be antisymmetric under the interchange of any two electrons.

Helium: $\overline{\Psi}(\vec{r}_1, \vec{r}_2) \rightarrow \overline{\Psi}(1,2) = 1s\alpha(1)\, 1s\beta(2)$ ↘ e's are indistinguish

$\overline{\Psi}(1,2) = 1s\alpha(2)\, 1s\beta(1)$ ↗

Therefore the wavefunction must be a linear comb. of all poss

(+) $\overline{\Psi}(1,2) = 1s\alpha(1)\, 1s\beta(2) + 1s\alpha(2)\, 1s\beta(1)$

Interchange: (−) $\overline{\Psi}(1,2) = 1s\alpha(1)\, 1s\beta(2) - 1s\alpha(2)\, 1s\beta(1)$

$\overline{\Psi}(2,1) =$

Normalization No =

Helium Atom correctly:

$$\underline{\Psi}(1,2) = 1s(1)\,1s(2)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

$$E = \frac{N}{D} = \frac{\int \underline{\Psi}^*(1,2)\,\hat{H}\,\underline{\Psi}(1,2)\,d\vec{\nu}_1\,d\vec{\nu}_2}{\int \underline{\Psi}^*(1,2)\,\underline{\Psi}(1,2)\,d\vec{\nu}_1 d\vec{\nu}_2}$$

$$N = \iint 1s^*(1)1s^*(2)\left(\alpha^*(1)\beta^*(2) - \alpha^*(2)\beta^*(1)\right)\cdot$$

$\cdot \hat{H}$ (No S-O coupling in $\hat{H}$) $1s(1)1s(2)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) d\vec{\nu}_1\,d\vec{\nu}_2\,d\vec{\sigma}_1\,d\vec{\sigma}_2 =$

$$= \int 1s^*(1)\,1s^*(2)\,\hat{H}\,1s(1)1s(2)\,d\vec{\nu}_1 d\vec{\nu}_2 \cdot$$

$$\cdot \int \left(\alpha^*(1)\beta^*(2)\alpha(1)\beta(2) - \alpha^*(2)\beta^*(1)\alpha(1)\beta(2)\right.$$

$$\left. - \alpha^*(1)\beta^*(2)\alpha(2)\beta(1) + \alpha^*(2)\beta^*(1)\alpha(2)\beta(1)\right) d\vec{\sigma}_1\,d\vec{\sigma}_2 =$$

$$= 2\int 1s^*(1)1s(2)\,\hat{H}\,1s(1)1s(2)\,d\vec{\nu}_1 d\vec{\nu}_2$$

Single Slate Determinant:

$$\underline{\Psi}(\nu_1,\nu_2) = \frac{1}{\sqrt{2}} \cdot \begin{vmatrix} \text{orb 1} & \text{orb 2} \\ \downarrow & \downarrow \\ 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} \begin{matrix} \leftarrow e1 \\ \leftarrow e2 \end{matrix}$$

Properties of Determinants:

→ they change the sign upon exchange of 2 colums or rows

→ they equal 0 if two rows or colums are identical.

P.E.P. is satisfied / Postulate 6 is satisfied.

$$\Phi_{(1\ldots N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & & \phi_N(2) \\ \vdots & & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

Single state Determinant leads to Hartree-Fock theory.

Not a true function

(Modern Quantum Chemistry Szebo, Dover Pub!)

HF: Electrons are moving in an average (effective) field of the electrons,

Helium atom $Z_{eff} = \frac{27}{16}$

But where is the 2nd electron exactly? Electron Correlation!

$EC = E_{true} - E_{HF}$