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Electron spin statistics

α, β

$\hat{S}_1^2 \alpha(1) = s(s+1)\hbar^2 \alpha(1) = \frac{3}{4}\hbar^2 \alpha(1)$ for $s = \frac{1}{2}$

$\left.\begin{array}{l} \hat{S}_{z1}\alpha(1) = \frac{\hbar}{2}\alpha(1) \\ \hat{S}_{z2}\beta(1) = -\frac{\hbar}{2}\beta(1) \end{array}\right]$ single electron

for He, 2-electron $\underbrace{\overset{\phi_1}{\alpha(1)\alpha(2)} \quad \overset{\phi_2}{\beta(1)\beta(2)}}$ $\alpha(1)\beta(2)$ $\beta(1)\alpha(2)$

$\hat{S} = \hat{S}_1 + \hat{S}_2$

$\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$

$\phi_3 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ $\quad \phi_4 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

up exchange of 1 and 2
$\phi_1 \longrightarrow \phi_1$ $\quad m_s = +1$
$\phi_2 \longrightarrow \phi_2$ $\quad m_s = -1$ symmetric, triplet $\hat{S}^2$ $\quad S=1$ $\quad \hat{S}_1\phi = 2\hbar^2\phi$
$\phi_3 \longrightarrow \phi_3$ $\quad m_s = 0$
$\phi_4 \longrightarrow \phi_4$] anti-symmetric, singlet $S=0$
$m_s = 0$

Helium full wavefunction $\Psi = \underbrace{\psi(1,2)}_{\text{spatial}} \underbrace{f(1,2)}_{\text{spin}} = 1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

$= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$

Slater determinant

$\Psi(1,2,\cdots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1) & \cdots \\ \phi_1(2) & \phi_2(2) & \phi_3(2) & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}$ electron

spin orbital

(1) interchange of two rows flips the sign

(2) two column are the same, then zero : exclusion principle

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Example

$\phi_2(2s)$ $\uparrow\downarrow$

$\phi_1(1s)$ $\uparrow\downarrow$

$\phi_1\alpha \ \phi_1\beta \ \phi_2\alpha \ \phi_2\beta$

$$\Psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) \\ \phi_1(3)\alpha(3) & \phi_1(3)\beta(3) & \phi_2(3)\alpha(3) & \phi_2(3)\beta(3) \\ \phi_1(4)\alpha(4) & \phi_1(4)\beta(4) & \phi_2(4)\alpha(4) & \phi_2(4)\beta(4) \end{vmatrix}$$

Li : $1s^2 2s^1$

$$\text{if } \Psi(1s1s1s) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\alpha(3) \end{vmatrix} = 0$$

$$\Psi(1s^2 2s^1) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \equiv$$

$\uparrow$ / $\uparrow\downarrow$ and $\downarrow$ / $\uparrow\uparrow$) same energy

ground state of Li is doublet

$$\Rightarrow \Psi_g = C_1 \left| \begin{smallmatrix}\uparrow \\ \uparrow\downarrow\end{smallmatrix} \right\rangle + C_2 \left| \begin{smallmatrix}\downarrow \\ \uparrow\downarrow\end{smallmatrix} \right\rangle$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z_1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Z_1}{a_0}r}$$

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z_2}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Z_2 r}{a}\right) e^{-\frac{Z_2 r}{2a_0}}$$

apply variation theorem minimize $\langle \Psi | \hat{H} | \Psi \rangle$ with respect to Z_1, Z_2

$\Rightarrow$ $Z_1 = 2.69$ $\quad E_{min} = -201.2$ eV ($\approx 1\%$)

$Z_2 = 1.78$ $\quad E_{exp} = -203.48$ eV

SEASON

$$\hat{H} = h_{pq}\hat{a}_p\hat{a}_q^{\dagger} + h_{pqrs}\frac{1}{2}\hat{a}_p\hat{a}_q\hat{a}_r^{\dagger}\hat{a}_s^{\dagger}$$

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quantum state

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Hartree Fock SCF

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze^2}{r_i}\frac{1}{4\pi\epsilon_0} + \sum_{i=1}^{N-1}\sum_{j=1}^{N}\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{ij}}$$

$$\iint -\frac{\hbar^2}{2m}\nabla^2 - V(1)$$

Perturbation treatment of the Li ground state

$$\hat{H}^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_1} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_2} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_3}$$

$$\hat{H}' = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{12}} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{23}} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{13}}$$

$$\psi^{(0)} = \frac{1}{\sqrt{6}}\left[1s(1)1s(2)2s(3)\alpha(1)\beta(2)\alpha(3) - 1s(1)2s(2)1s(3)\alpha(1)\alpha(2)\beta(3) - 1s(1)1s(2)2s(3)\beta(1)\alpha(2)\alpha(3) + 1s(1)2s(2)1s(3)\beta(1)\alpha(2)\alpha(3) + 2s(1)1s(2)1s(3)\alpha(1)\alpha(2)\beta(3) - 2s(1)1s(2)1s(3)\alpha(1)\beta(2)\alpha(3)\right]$$

$$E^{(0)} = -\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2}\right)\frac{1}{4\pi\epsilon_0}\frac{Z^2e^2}{2a_0} = -275.5\ \text{eV}$$

$$E^{(1)} = \langle\psi^{(0)}|\hat{H}'|\psi^{(0)}\rangle = 2\iint 1s^2(1)2s^2(2)\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{12}}dv_1dv_2 + \iint 1s^2(1)1s^2(2)\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{12}}dv_1dv_2 - \iint 1s(1)2s(2)1s(2)2s(1)\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{12}}dv_1dv_2$$

$$= 2\underbrace{J_{1s2s}}_{\frac{1}{4\pi\epsilon_0}\frac{17}{81}\frac{Ze^2}{a_0}} + \underbrace{J_{1s1s}}_{\frac{5}{8}\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{a_0}} - K_{1s2s} \rightarrow \frac{16}{729}\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{a_0}$$

$$= 83.5\ \text{eV}$$

$$E = E^{(0)} + E^{(1)} = -192.0\ \text{eV} \quad (\text{exp: } -203.5\ \text{eV})$$

Spin magnetic moment

fine structure $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$

$\vec{m}_L = -\frac{e}{2m_e}\vec{L} \Rightarrow$ we guess $\vec{m}_s = -g_e\frac{e}{2m_e}\vec{S}$ $g_e = 2(1+\frac{\alpha}{2\pi}+\cdots) = 2.00231930436$

electron g factor

$$|\vec{m}_s| = g_e\frac{e}{2m_e}|\vec{S}| = g_e\sqrt{\frac{3}{4}}\frac{e\hbar}{2m_e}$$

$$\vec{m}_I = g_N\frac{e}{2m_p}\vec{I} \equiv \gamma\vec{I}$$

$$E = -\vec{m}_I\cdot\vec{B} = -\gamma(I_x\vec{i} + I_y\vec{j} + I_z\vec{k})(B\vec{k}) = -\gamma BI_z = -\gamma\hbar BM_I \quad M_I = -I, -I+1, \cdots I$$

$$\hat{H}|M_I\rangle = -\gamma B\hat{I}_z|M_I\rangle = -\gamma BM_I\hbar|M_I\rangle$$

$$h\nu = |\Delta E| = |\gamma|\hbar B|\Delta M_I\rangle = |\gamma|\hbar B, \quad \nu = \frac{|\gamma|}{2\pi}B = |g_N|\frac{e}{4\pi m_p}B$$