e-e Coulomb interaction in He as perturbation for $(1s)(2s)$ or $(1s)(2p)$

$$\text{Energy} = E^{(0)} + J_\ell \pm K_\ell$$

+ means $S=0$ — means $S=1$

S - total spin for 2 electrons
$\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$

Main effect

$$\frac{1}{2}\left(1 + \sigma^{(1)} \cdot \sigma^{(2)}\right)$$

$$\vec{S} = \vec{S}^{(1)} + \vec{S}^{(2)}$$

$$= \frac{1}{2}\left(1 + \frac{4}{\hbar^2} \vec{S}^{(1)} \cdot \vec{S}^{(2)}\right)$$

$$= \frac{1}{2}\left(1 + \frac{2}{\hbar^2}\left(\vec{S}^2 - \vec{S}^{(1)2} - \vec{S}^{(2)2}\right)\right)$$

$$= \frac{1}{2}\left(1 + \frac{2}{\hbar^2}\left(S(S+1) - \tfrac{3}{4} - \tfrac{3}{4}\right)\hbar^2\right) \qquad S = 0, 1$$

$$= -1 + S(S+1) \quad \begin{cases} -1 & S=0 \\ +1 & S=1 \end{cases}$$

$$E \longrightarrow \quad \pm 1 = -\frac{1}{2}\left(1 + \vec{\sigma}^{(1)} \vec{\sigma}^{(2)}\right)$$

$$= E^{(0)} + J_\ell - \frac{1}{2}\left(1 + \vec{\sigma}^{(1)} \vec{\sigma}^{(2)}\right) K_\ell$$

$$= E^{(0)} + J_\ell - K_\ell - \frac{1}{2} \vec{\sigma}^{(1)} \vec{\sigma}^{(2)} K_\ell$$

$$\underbrace{J_\ell - \tfrac{1}{2} K_\ell}_{\text{indp. spin}} \quad \underbrace{-\tfrac{1}{2} \vec{\sigma}^{(1)} \cdot \vec{\sigma}^{(2)} K_\ell}_{\text{depends on spin}}$$

$$\updownarrow \vec{\sigma}^{(1)} \qquad \updownarrow \vec{\sigma}^{(2)}$$

N spins $\quad \mathcal{H} = \underbrace{(\mathbb{C}^2) \otimes (\mathbb{C}^2) \otimes \dots \otimes (\mathbb{C}^2)}_{N \text{ times}}$

$$\longrightarrow H = -K \sum_{i=1}^{N-1} \vec{\sigma}^{(i)} \vec{\sigma}^{(i+1)}$$

1-D heisenberg model $\quad \uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \uparrow\uparrow$

H-atom: $H^{(0)} = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r}$

$E_n = -\frac{13.6}{n^2}$ eV

degeneracy of electron states: $2n^2$

spinstate $\uparrow$ $\quad$ $\uparrow$ $l = 0, 1, \dots, n-1$

① Fine structure
② Hyperfine structure
③ Lamb shift

① $E = \sqrt{m^2c^4 + p^2c^2}$

take $p \ll mc \rightarrow$ $\quad E = mc^2\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2}$

$$E = mc^2\left(1 + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\left(\frac{p^2}{m^2c^2}\right)^2 + \dots\right)$$

$$E = \underbrace{mc^2}_{\text{constant absorb into zero point}} + \underbrace{\frac{p^2}{2m}}_{\text{CM} \to \text{QM}} - \underbrace{\frac{1}{8}\frac{p^4}{m^3c^2}}_{\text{ooo, new}}$$

$$H = \underbrace{H_0}_{\frac{\vec{p}^2}{2\mu} - \frac{e^2}{r} \leftarrow H_0} - \underbrace{\frac{1}{8}\frac{p^4}{\mu^3c^2}}_{\lambda H_1}$$

$$\lambda H_1^{rel} = -\frac{1}{2\mu c^2}\left(\frac{p^2}{2\mu}\right)^2 = -\frac{1}{2\mu c^2}\left(H_0 + \frac{e^2}{r}\right)^2$$

$\langle n, l', m' | \lambda H_1^{rel} | n, l, m\rangle$ $\quad$ H_1^{rel} doesn't depend on spin

$\hookrightarrow$ diagonal

$$\lambda E_{nlm}^{(1),rel} = \langle nlm | \frac{1}{2\mu c^2}\left(H_0 + \frac{e^2}{r}\right)^2 | n, l, m\rangle$$

$$= -\frac{1}{2\mu c^2}\langle nlm | H_0^2 + H_0\frac{e^2}{r} + \frac{e^2}{r}H_0 + \frac{e^4}{r^2} | n, l, m\rangle$$

$$= -\frac{1}{2\mu c^2}\left(\left(E_n^{(0)}\right)^2 + 2E_n^{(0)}e^2\langle nlm | \frac{1}{r} | nlm\rangle + e^4\langle nlm | \frac{1}{r^2} | nlm\rangle\right)$$

$$\langle nlm | \frac{1}{r} | nlm\rangle = \frac{1}{a_0 n^2}$$

$$\langle nlm | \frac{1}{r^2} | nlm\rangle = \frac{1}{a_0^2 n^3 (l+1/2)}$$

$$\langle nlm | \frac{1}{r^3} | nlm\rangle = \frac{1}{a_0^3 n^3 l(l+1/2)(l+1)}$$

$$\rightarrow \lambda E_{nlm}^{(1),rel} = -\frac{1}{2}\mu c^2 \alpha^2\left(\frac{\alpha^2}{n^3(l+1/2)} - \frac{3\alpha^2}{4n^4}\right)$$

α^2

$$\lambda H_1^{s-o} = \frac{1}{2m_e^2c^2}\,\frac{e^2}{r^3}\,\vec{S}\cdot\vec{L}$$

$$\vec{J} = \vec{L} + \vec{S}$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

usual states: $|n, l, m_l, s, m_s\rangle$ $\quad$ $s = 1/2$, $m_s = \pm 1/2$

add angular momentum $\longrightarrow$ $|n, j, m_j, l, s\rangle$

$$l \otimes 1/2 = \underset{j}{(l+1/2)} \oplus \underset{j}{(l-1/2)}$$