Helium: $H = \frac{\vec{p}_1^{\,2}}{2m} - \frac{ze^2}{r_1} + \frac{\vec{p}_2^{\,2}}{2m} - \frac{ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$

Ground state energy

$\psi_{grnd} = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) \otimes |s=0, m_s=0\rangle$

$z=2$ $\quad z=2$

b/c nucleus has 2 protons

1^{st} order correction is $\langle n|\lambda H_1|n\rangle$

$\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$ has no spin component

coulomb repulsion

charge density of electron 1 $\quad$ charge density of electron 2

$\lambda E^{(1)} = \int d^3r_1 \int d^3r_2 \; e|\psi_{100}(\vec{r}_1)|^2 \frac{1}{|\vec{r}_1-\vec{r}_2|^2} \cdot e|\psi_{100}(\vec{r}_2)|^2$

$\Leftrightarrow$ can combine ψ_{100} & ψ_{100}^* b/c we know $\psi_{100} = \psi_{100}^*$

so it's okay to rearrange

$E_{grnd} = -108.8\,eV + \frac{5}{8}\frac{ze^2}{a_0} = -74.8\,eV$

$z=2$

$34\,eV$

$E_{grnd}^{experiment} = -78.98$

1st excited states are $(1s)(2s)$, $(1s)(2p)$ $\quad$ ($n=2$, $n=2$) $\quad$ degenerate w/ just H_0

$\lambda H_1 = \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$ doesn't act on spin $[\lambda H_1, \vec{S}_z] = 0 = [\lambda H_1, L_z]$

perturbation won't effect m_l or m_s

$(1s)(2s)$ $\quad l=0$ $\quad$ total spin $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$

since $l=0$, $\vec{J} = \vec{L} + \vec{S}$, $j=0$ or 1

$S = 0, 1$

$\mathcal{L} = S, P, D, \ldots$

$l = 0, 1, 2, \ldots$

${}^{2s+1}\mathcal{L}_j$

$s=0$ & $l=0$

$j = 0+0 = 0$

${}^1S_0$ $\quad s=0, j=0$

${}^3S_1$ $\quad s=1, j=1$

$V_a \otimes V_b = V_{a+b} \oplus V_{a+b-1} \oplus \ldots \oplus V_{|a-b|}$

$s=0$ & $l=1$

$j = 1+0 = 1$

$V_1 \otimes V_0 = V_{1+0} = V_1$

$1+0 = |1-0|$

$a+b \quad a+b-1 \quad |a-b|$

$(1s)(2p)$ $\quad l=1$ $\quad$ total spin $= 0$ or $1 = \vec{S}$

$l=0 \quad l=1$ $\quad n=2$

$S=1,\ l=1 = 2+1+0$

Total ang. momentum: $1 \otimes 1 = 2 \oplus 1 \oplus 0$ $\quad {}^3P_2 \quad {}^3P_1 \quad {}^3P_0$

$l=1 \otimes S=1$ $\quad$ j values

$1 \otimes 0 = 1$ $\quad {}^1P_1 \quad s=0,\ l=1$

$l=1 \otimes S=0$ $\quad$ j values

2 dof for each electron

$(1s)(2s)$ $\quad {}^1S_0 \quad {}^3S_1$ $\quad 2\times 2 = 1+3 = 4$ states

#states $\quad 1 \quad 3 \quad m_s = 1, 0, -1$

$(1s)(2p)$ $\quad {}^3P_2 \quad {}^3P_1 \quad {}^3P_0 \quad {}^1P_1$ $\quad 12 = 4 \times 3$

#states $\quad 5 \quad 3 \quad 1 \quad 3$ $\quad m_s = -\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}$ $\quad m_l = -1, 0, 1$

$j=2$: $m_j = 2, 1, 0, -1, -2$ $\quad j=1$: $m_j = 1, 0, -1$

16 1^{st} excited states

Define $\psi^{\pm}_{lm}(\vec r_1, \vec r_2) = \frac{1}{\sqrt 2}\left(\psi_{100}(\vec r_1)\psi_{2lm}(\vec r_2) \pm \psi_{2lm}(\vec r_1)\psi_{100}(\vec r_2)\right)$

$l=0$ or $l=1$ $\quad$ (2s) $\quad$ (2p)

$m=0$

${}^1S_0$

$s=0 \to$ sym $\otimes$ anti

$l=0$ $\quad \psi_{0,0}$?

$\psi^{S,+}_{tot} = \psi^{+}_{0,0}(\vec r_1, \vec r_2) \otimes |s=0, m_s=0\rangle$

${}^3S_1$

$s=1 \to$ anti $\otimes$ sym ?

$l=0 \to \psi_{0,0}$?

$\psi^{S,-}_{tot} = \psi^{-}_{0,0}(\vec r_1, \vec r_2) \otimes |s=1, m_s\rangle$

${}^1P_1$

$s=0 \to$ sym $\otimes$ anti ?

$l=1 \to \psi_{1,m_l}$?

$\psi^{P,+}_{tot} = \psi^{+}_{1,m}(\vec r_1, \vec r_2) \otimes |s=0, m_s=0\rangle$

${}^3P_{2,1,0}$

$s=1 \to$ anti $\otimes$ sym ?

$l=1 \to \psi_{1,m}$?

$\psi^{P,-}_{tot} = \psi^{-}_{1,m}(\vec r_1, \vec r_2) \otimes |s=1, m_s\rangle$ $\quad m_l = 1, 0, -1 \quad m_s = 1, 0, -1$

$\frac{e^2}{|r_1 - r_2|}$ diagonal in space of states

doesn't change m_s, m_l

symmetric under $\vec r_1 \leftrightarrow \vec r_2$ $\quad$ b/c $|\vec r_1 - \vec r_2| = |\vec r_2 - \vec r_1|$

only depends on if sym or anti

$$\lambda E^{\pm}_l = \int d^3 r_1 \int d^3 r_2\ \psi^{\pm}_{l,0}(r_1, r_2)^* \frac{e^2}{|r_1 - r_2|} \psi^{\pm}_{l,0}(r_1, r_2)$$

$$\lambda E^{\pm}_l = J_l \pm K_l$$

$$J_l = e^2 \int d^3 r_1 \int d^3 r_2\ |\psi_{100}(\vec r_1)|^2 \frac{1}{|r_1 - r_2|} |\psi_{200}(\vec r_2)|^2 > 0$$

$$K_l = e^2 \int d^3 r_1 \int d^3 r_2\ \psi^*_{100}(r_1)\psi^*_{210}(r_2) \frac{1}{|r_1 - r_2|} \psi_{210}(r_1)\psi_{100}(r_2) > 0$$

trust me

$J_\ell > 0 \qquad K_\ell > 0$

$+$ spatial symmetric spin antisymmetric $\rightarrow s=0$

$-$ spatial antisymmetric spin symmetric $\rightarrow s=1$

spin 1 states have lower energy than spin 0 states

16 states $\quad {}^1S_0 \quad {}^3S_1 \quad {}^3P_2 \quad {}^3P_1 \quad {}^3P_0 \quad {}^1P_1$

$^1P_1$

$^3P_{0,1,2}$

$^1S_0$

$^3S_1$

J_ℓ K_ℓ depends on ℓ

lowest energy for given ℓ given orbital has $s=1$

1st Hunds rule