Helium atom

☆ $E(He^+, 1\,^2S_{\frac{1}{2}}) = -\frac{Z^2}{2} = -2$ (in the atom units)

$(n\,^{2S+1}L_J)$

Experimentally, neutral He ground state energy $E_{gs} = -2.903$

excited state of neutral He

2 classes $\left[\begin{array}{lll} \text{singlet} & E_s & 1s2s\,^1S_0 \\ & \text{IV} & \\ \text{triplet} & E_t & 1s2s\,^3S_1 \end{array} \right.$ $\updownarrow$ $0.5eV \sim 10^3$ larger than the spin-spin interaction !!

$(^{2S+1}L_J)$

☆ We want to understand the large energy differences betwen triplet and singlet.

☆ For E_{gs}, doesnot involve the pauli principle, but the excited states does.

$$H = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}}_{H_0} + \underbrace{\frac{1}{|r_1 - r_2|}}_{H'}$$

The zero-order unsymmetrized WF for the ground state

$$\psi_0(1s1s\,^1S_0) = \phi_{1s}(r_1)\,\phi_{1s}(r_2)\,\chi_1\chi_2, \quad \phi_{1s}(r) = \sqrt{\frac{Z^3}{\pi}}\,e^{-Zr}$$

Since the spatial WFs are the same, the spinors must be diffent,

Also, we have to make it anti-sym

$$\Rightarrow \psi_0 = \phi_{1s}(r_1)\,\phi_{1s}(r_2)\,\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$$

$$\Rightarrow E_0 = -\frac{Z^2}{2} - \frac{Z^2}{2} = -4$$

1st order energy shift

$$\Delta E^{(1)} = \langle \phi_{1s}(r_1)\phi_{1s}(r_2) \,|\, \frac{1}{|r_1 - r_2|} \,|\, \phi_{1s}(r_1)\phi_{1s}(r_2) \rangle = \frac{5}{8} Z$$

by using $\frac{1}{|r_1 - r_2|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>}\right)^{\ell} P_\ell(\cos\theta)$ and some algebra.

$\Rightarrow E_0 + \Delta E^{(1)} = -2.75$.

Variation $W\!F$ $\quad Z \to \underset{\text{eff } Z}{\lambda}$ in $\psi_0 \to \frac{\lambda^3}{\pi} e^{-\lambda(r_1 + r_2)}$

$\langle H \rangle = \lambda^2 - 2\lambda Z + \frac{5}{8}\lambda$, $\quad \frac{\partial \langle H \rangle}{\partial \lambda} = 0$, $\Rightarrow \lambda = Z - \frac{5}{16}$

$\langle H \rangle_{He} = -\left(2 - \frac{5}{16}\right)^2 = -2.8477$ (very close to $E_{exp} = -2.903$)

$\boxed{\text{Excited states of He}}$

W.F. for $2e^-$: (spatial W.F.) $\times$ (spin W.F.)

$\frac{1}{2} \otimes \frac{1}{2} = \begin{cases} 1 & \text{triplet} : \uparrow\uparrow,\ \downarrow\downarrow\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \quad \text{symmetric} \\ 0 & \text{singlet} : \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \quad \text{anti-symmetric} \end{cases}$

Must make the whole W.F. anti-sym.

- spin singlet $\Rightarrow$ spatial W.F. sym $= \frac{1}{\sqrt{2}}(\phi_{1s}(r_1)\phi_{2s}(r_2) + \phi_{1s}(r_2)\phi_{2s}(r_1)$ $\quad (\psi_4)$
- spin triplet $\Rightarrow$ anti-sym spatial W.F

$$= \frac{1}{\sqrt{2}}\left(\phi_{1s}(r_1)\phi_{2s}(r_2) - \phi_{1s}(r_2)\phi_{2s}(r_1) \right]$$

(ψ_1, ψ_2, ψ_3)

Now consider the $e^- e^-$ coulomb int.

$\psi_{1,2,3,4}$ are already the eigenbasis since Coulomb int has nothing to do with spin.

$$\left\langle \psi_{1,2,3} \left| \frac{1}{|r_1-r_2|} \right| \psi_{1,2,3} \right\rangle = \frac{1}{2}\int dr_1^3 \int dr_2^3 \, \frac{\left(\phi_{1s}(r_1)\phi_{2s}(r_2) - \phi_{1s}(r_2)\phi_{2s}(r_1)\right)^2}{|r_1-r_2|}$$

$$\equiv \quad J - K$$

$$\left\langle \psi_4 \left| \frac{1}{|r_1-r_2|} \right| \psi_4 \right\rangle = \frac{1}{2}\int dr_1^3 \int dr_2^3 \, \frac{\left(\phi_{1s}(r_1)\phi_{2s}(r_2) + \phi_{1s}(r_2)\phi_{2s}(r_1)\right)^2}{|r_1-r_2|}$$

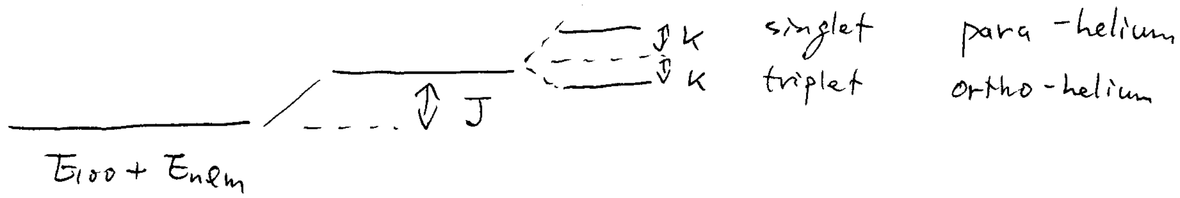
$$\equiv \quad J + K$$

where

$$J = \int dr_1^3 \, dr_2^3 \, \frac{\phi_{1s}^2(r_1)\,\phi_{2s}^2(r_2)}{|r_1-r_2|} \geq 0$$

$$K = \int dr_1^3 \, dr_2^3 \, \frac{\phi_{1s}(r_1)\phi_{2s}(r_1) \;\; \phi_{1s}(r_2)\phi_{2s}(r_2)}{|r_1-r_2|} \geq 0$$

And the energy splitting is $\boxed{2K}$



To evaluate K, math trick : $\rho(r_1) \equiv \phi_{1s}(r_1)\phi_{2s}(r_1)$

then $$K = \int dr_2^3 \, \rho(r_2) \int \frac{dr_1^3 \, \rho(r_1)}{|r_1-r_2|}$$

This just looks like the static potential in EM.

distribution $\rho(r_1)$ generates a potential $\Phi(r_2) = \int \frac{dr_1^3 \, \rho(r_1)}{|r_1-r_2|}$

and $\nabla^2 \Phi(r_2) = -4\pi \rho(r_2)$

$$\Rightarrow \quad K = \int dr_2^3 \, \rho(r_2)\,\Phi(r_2) = -\frac{1}{4\pi}\int dr_2^3 \left[\underbrace{\overset{0}{\nabla\cdot\left(\vec{\nabla}\Phi(r_2)\,\Phi(r_2)\right)}}_{\text{surface term}} - \left(\vec{\nabla}\Phi(r_2)\right)^2 \right]$$

$$\Rightarrow \quad K = \frac{1}{4\pi} \int d r_2^3 \underbrace{(\vec{\nabla}\phi)^2}_{} \geq 0$$

It can be worked out ! $(E\text{-field})^2$

$$K = \left(\frac{4}{27}\right)^2 = 0.0219 \quad (0.597\,eV)$$

$\Rightarrow \quad {}^1S_0 - {}^3S_1$ splitting $\sim 1.19\,eV$ $(\sim 2\,\Delta E_{exp})$

The physics is clear

spin singlet, spatial WF is sym, e^-e^- get closer $\Delta E \uparrow$

triplet, " anti-sym, " kept faraway $\Delta E \downarrow$

☆ Although the original Hamiltonian is spin-independent the statistics makes the spin effect matter.