G. Helium Excited State and Origin of Magnetism: Brief Overview

- **Picture**: one electron in ϕ_{1s}, another in ϕ_{2s}

could be

2s	↑	↓	↓	↑
1s	↑	↓	↑	↓

Spatial Part — **Spin Part**

$\boxed{\text{one state}}$ (S=0)

$$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\,\phi_{2s}(\vec{r}_2)+\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\right]\cdot\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right] \tag{44}$$

(symmetric) (anti-symmetric) [singlet]

$\boxed{\text{three states}}$ (S=1)

$$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\,\phi_{2s}(\vec{r}_2)-\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\right]\cdot\begin{cases}\alpha(1)\,\alpha(2)\\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]\\ \beta(1)\,\beta(2)\end{cases} \tag{45}$$

(anti-symmetric) (symmetric) [triplet]

Aside:

Using Eqs. (44) and (45) to see up self-consistency equations to solve for ϕ_{1s} (ε_{1s}) and ϕ_{2s} (ε_{2s}), one gets the Hartree-Fock approximation. The approximation takes proper account of the anti-symmetric requirement of many-electron wavefunctions.

- Will $S=0$ state and $S=1$ states have different energies?

$$\hat{H}_{He} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|} \qquad (10)$$

$S=0$ state

$$E_{singlet} = \iint \frac{1}{2}\left[\phi^*_{1s}(\vec{r}_1)\phi^*_{2s}(\vec{r}_2) + \phi^*_{1s}(\vec{r}_2)\phi^*_{2s}(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) + \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right] d^3r_1\, d^3r_2 \qquad (46)^+$$

$S=1$ state

$$E_{triplet} = \iint \frac{1}{2}\left[\phi^*_{1s}(\vec{r}_1)\phi^*_{2s}(\vec{r}_2) - \phi^*_{1s}(\vec{r}_2)\phi^*_{2s}(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) - \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right] d^3r_1\, d^3r_2 \qquad (47)^+$$

[They are not the same, by inspection]

[+] Where does the spin part go?

Roughly,

$$E_{\text{singlet}} = \underbrace{[\text{some terms}]}_{I\ \&\ J_{1s,2s}} + \text{terms like} \iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{2s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\,d^3r_1\,d^3r_2 \tag{48}$$

$$E_{\text{triplet}} = \overbrace{[\text{some terms}]}^{I\ \&\ J_{1s,2s}} - \text{terms like} \overbrace{\iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{2s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\,d^3r_1\,d^3r_2}^{\text{called } K_{1s,2s}}$$

- $K_{1s,2s}$ has <u>no</u> classical analogy [inspect states and coordinates] (entirely quantum)
- called <u>exchange Coulomb integral</u> (or indirect Coulomb integral)

For helium atom, $E_{\text{triplet}} < E_{\text{singlet}}$

$$\Rightarrow \boxed{S=1 \text{ is a lower energy excited state than } S=0}$$

$$K_{a,b} \equiv \int \phi_a^*(\vec{r}_1)\, \phi_b^*(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_a(\vec{r}_2)\, \phi_b(\vec{r}_1)\, d^3r_1\, d^3r_2 \qquad (49)$$

- entirely quantum effect
- Exchange Coulomb Integral[†]

compared with

$$J_{a,b} \equiv \int \phi_a^*(\vec{r}_1)\, \phi_b^*(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_a(\vec{r}_1)\, \phi_b(\vec{r}_2)\, d^3r_1\, d^3r_2 \qquad (50)$$

- has classical interpretation
- Direct Coulomb Integral

[†] $K_{a,b}$ arises because of the anti-symmetric requirement of many-electron wavefunctions

- 1st excited state is <u>S=1</u> state

<u>Physical Reason</u>: S=1 has

$$\underset{\text{antisymmetric}}{\psi^{(\text{anti-sym})}_{\text{spatial}}} = \frac{1}{\sqrt{2}}\Big[\overbrace{\underbrace{\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) - \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)}_{\text{can't find electrons at the same place!}}}^{\text{this is zero for } \vec{r}_1 = \vec{r}_2}\Big]$$

$$\boxed{\psi^{(\text{anti-sym})}_{\text{spatial}}(\vec{r}_1, \vec{r}_2)\ \underline{\text{forbids}}\ \text{electrons to be}\ \underline{\text{at the same place}}}$$

Important idea!

Good!

lowers Coulomb Repulsion $\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ between them because electrons can't get too close!

[In contrast, $\psi^{(\text{sym})}_{\text{spatial}}$ (S=0 state) allows (likes) electrons to be close, higher energy!]

- This is the physics behind the <u>Hund's rule</u>[+]

2 electrons in p states: $\underbrace{\uparrow \quad \uparrow \quad -\!-}_{\text{Hund's rule prefers this}}$ OR $\uparrow\!\downarrow \quad -\!- \quad -\!-$

Hund's rule prefers this [also works for electrons in d and f states]

<u>Why?</u>

- ψ_{spin} is symmetric $\Rightarrow$ $\psi_{spatial}$ is anti-symmetric
  $\Rightarrow$ avoid electrons to be at same place
  $\Rightarrow$ suppress Coulomb repulsion
  $\Rightarrow$ lower energy, thus preferred!

This is really <u>"Thinking like a physicist"</u>!

[+] Extending to many-electron cases is more involved. But conclusion remains. Or else, do QM calculation with Slater Determinant.

Recall: Term Symbol

Helium atom

- Ground State [two electrons in 1s, spin (S=0) singlet

$$^1S_0$$

- 1st excited state [one electron in 1s, another in 2s, spin (S=1) triplet

$$1s \Rightarrow l=0 \;,\quad 2s \Rightarrow l=0 \qquad \therefore \underbrace{L=0}_{\text{the "S" in the center}}$$

$$^3S_1$$

$$\underset{(2S+1=\underline{\underline{3}})}{S=1} \;,\; L=0 \Rightarrow J=\underline{\underline{1}}$$

↖ the "1" in lower corner

- Big Physics that emerges...

$S=1$ {two spins tend to align}

is preferred over $S=0$ {two anti-aligned spins}

in Helium 1st excited state

$\Rightarrow$ magnetism has a quantum origin!

($\because$ exchange integral determines $\underbrace{\text{alignment}}_{\text{"ferromagnetic"}}$ OR $\underbrace{\text{anti-alignment}}_{\text{"anti-ferromagnetic"}}$)

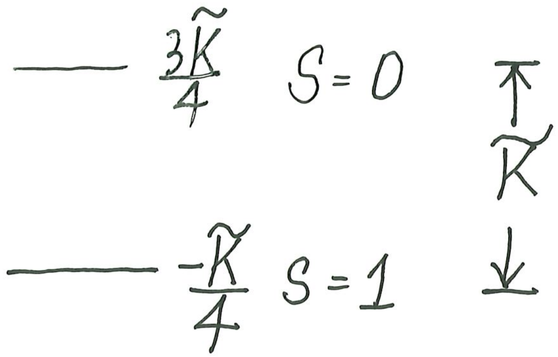
Let there be Magnets

- Atoms (some, not all) are like a small magnetic
  [Fe, Co, Ni have aligned electrons' spins in 3d]
- It is spins, thus $\vec{\mu}_s$, that matter
  [spin is very quantum]
- Ferromagnetic materials: $\vec{\mu}$'s of neighboring atoms aligned
  - Mechanism is NOT due to classical EM dipole-dipole interaction
    [can't explain why Fe, Co, Ni, Gd are ferromagnetic at room temp.]
  - Mechanism is quantum (due to exchange Coulomb integral)
    $\therefore$ due to electron-electron $\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ interaction

- Following interaction of two angular momentum

$$\mathcal{H} \sim \underbrace{-\tilde{K}}_{\substack{\text{energy}\\ \text{set by exchange integral}\\ (\text{assume } \tilde{K}>0)}} \frac{\vec{S}_i}{\hbar}\cdot\frac{\vec{S}_j}{\hbar}$$

$$\left(\text{e.g. } \overset{\text{spin-half}}{S_i = 1/2 \; ; \; S_j = 1/2}\right)$$



$$H = -\tilde{K}\sum_{\underbrace{(ij)}_{\text{nearest neighbors (nn)}}} \vec{S}_i\cdot\vec{S}_j$$

$\left(\underbrace{\underline{\text{Heisenberg}}}_{1928}\ \underline{\text{model}}\text{ of ferromagnetism}\right)$

an array of $\vec{\mu}$ (thus $\vec{S}$) ($\tilde{K}$ is called the exchange interaction energy)

Big Physics : Short-range (n.n.) interaction could lead to long-range order

Curie temperature T_c : $kT_c \sim \tilde{K}$ ($T>T_c$ destroys ferromagnets)