H. 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)

$$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\,\phi_{2s}(\vec{r}_2)+\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\right]\cdot\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right] \quad (46)$$

(symmetric) (anti-symmetric) [singlet]

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

$$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\,\phi_{2s}(\vec{r}_2)-\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\right]\cdot\begin{cases}\alpha(1)\alpha(2)\\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]\\ \beta(1)\beta(2)\end{cases} \quad (47)$$

(anti-symmetric) (symmetric) [triplet]

Aside (Optional)

Using Eqs. (46) and (47) to set up self-consistency equations to solve for ϕ_{1s} $(\mathcal{E}_{1s})$ and ϕ_{2s} $(\mathcal{E}_{2s})$, one gets the Hartree-Fock approximation. The approximation takes proper account of the anti-symmetric requirement of many-electron wavefunctions.

Q: Will S=0 state and S=1 states have different energies?

$$\hat{H}_{He} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \qquad (8)$$

[Note: $\hat{H}_{He}$ has no terms depending on spins. But value of S turns out to be important!]

S=0 state (singlet)

$$E_{singlet} = \iint \frac{1}{2}\left[\phi^*_{1S}(\vec{r}_1)\phi^*_{2S}(\vec{r}_2) + \phi^*_{1S}(\vec{r}_2)\phi^*_{2S}(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1S}(\vec{r}_1)\phi_{2S}(\vec{r}_2) + \phi_{1S}(\vec{r}_2)\phi_{2S}(\vec{r}_1)\right] d^3r_1\, d^3r_2 \qquad (48)^{+}$$

S=1 state (triplet)

$$E_{triplet} = \iint \frac{1}{2}\left[\phi^*_{1S}(\vec{r}_1)\phi^*_{2S}(\vec{r}_2) - \phi^*_{1S}(\vec{r}_2)\phi^*_{2S}(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1S}(\vec{r}_1)\phi_{2S}(\vec{r}_2) - \phi_{1S}(\vec{r}_2)\phi_{2S}(\vec{r}_1)\right] d^3r_1\, d^3r_2 \qquad (49)^{+}$$

[They are not the same, by inspection]

[+] Where does the spin part go?

Roughly,

$$E_{\text{singlet}} = \underbrace{[\text{some terms}]}_{I\ \&\ J_{1s,2s}} + \text{terms like} \iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{2s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\,d^3r_1\,d^3r_2 \qquad (50)$$

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

- $K_{1s,2s}$ 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, $E_{\text{triplet}} < E_{\text{singlet}}$

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

$$K_{a,b} \equiv \int \phi_a^*(\vec{r}_1)\, \phi_b^*(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\, \phi_a(\vec{r}_2)\, \phi_b(\vec{r}_1)\, d^3r_1\, d^3r_2 \qquad (51)$$

- entirely quantum effect
- Exchange Coulomb Integral[+]

compared with

$$J_{a,b} \equiv \int \phi_a^*(\vec{r}_1)\, \phi_b^*(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\, \phi_a(\vec{r}_1)\, \phi_b(\vec{r}_2)\, d^3r_1\, d^3r_2 \qquad (52)$$

- has classical interpretation
- Direct Coulomb Integral

[+] $K_{a,b}$ arises because of the anti-symmetric requirement of many-electron wavefunctions, and it is due to $\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ term.

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

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

antisymmetric

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

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 electrons to be close, higher energy!]
(likes)

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

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

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

<u>Why?</u>

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

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

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

Hund's Rules (See Optional Aside)

- Rules on how to fill a few electrons into

p ⇅ — — OR ↑ ↑ — ?

d ↑ ↑ ↑ ↑ — OR ↑ ↑ ↑ ↑ — ?

Formally, do different QM calculations and find lowest energy filling

Practically, summarize the results of many QM calculations into emprical rules — $\underbrace{\text{Hund}}_{\text{student of Born}}$'s rule

Recall: Term Symbol

Helium atom

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

electrons in $\overbrace{L=0}^{\text{"S" in middle}}$ ↓ (to 1s)

$2S+1=1$ (upper LH corner) ↑ (to S)

$$^1S_0$$

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

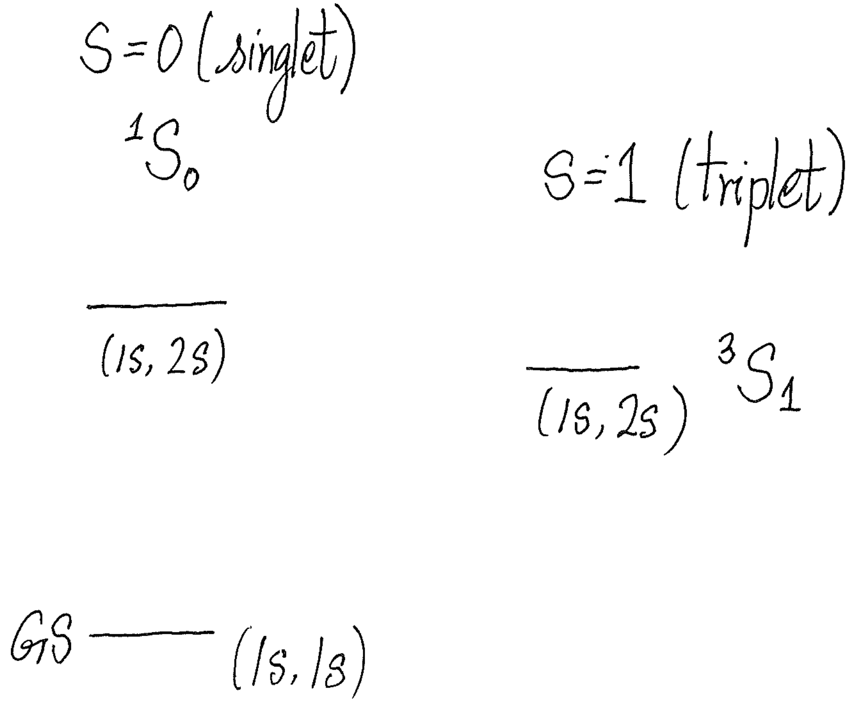
$$1s \Rightarrow l=0 \quad , \quad 2s \Rightarrow l=0 \qquad \therefore \underbrace{L=0}_{\text{the "S" in the center}}$$

$$^3S_1$$

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

↖ the "1" in lower corner

He-atom



Higher excited states can be grouped into singlet and triplet states

- 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

$\Rightarrow \boxed{\text{magnetism has a quantum origin!}}$

(∵ $\underbrace{\text{exchange integral}}_{K_{A,B}}$ 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)
    ∴ due to electron-electron $\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ interaction

- Following interaction of two angular momentum

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

spin-half

(e.g. $S_i = 1/2$; $S_j = 1/2$)

$\frac{3\tilde{K}}{4}$ $S=0$

$\uparrow \tilde{K} \downarrow$

$-\frac{\tilde{K}}{4}$ $S=1$

$$H = -K \underbrace{\sum_{(ij)}}_{\text{nearest neighbors (nn)}} \vec{S}_i\cdot\vec{S}_j \quad (53)$$

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

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)