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

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

could be

2s	↑	↓	↓	↑
1s	↑	↓	↑	↓

but $\psi(1,2)$ must be anti-symmetric

Spatial Part | Spin Part

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

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

(symmetric) | (anti-symmetric) [singlet]

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

[∵ $m_s=+1,0,-1$]

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

(anti-symmetric) | (symmetric) [triplet]

Aside (Optional)

Using Eqs. (47a) and (47b) to set 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.

[+] In equation for ϕ_{1s}, the electron in ϕ_{2s} contributes to the effective Hamiltonian
In equation for ϕ_{2s}, the electron in ϕ_{1s} contributes to the effective Hamiltonian
> coupled equations for ϕ_{1s} and ϕ_{2s}

Spatial forms in Eqs. (47a) (47b) imply more complicated terms in effective Hamiltonian

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

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

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

S=0 state (singlet)

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

S=1 state (triplet)

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

[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 no classical analogy [inspect states and coordinates] (entirely quantum)
- called exchange Coulomb integral (or indirect Coulomb integral)

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

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

Recall

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

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

$\psi_{\text{spatial}}^{(\text{anti-sym})}(\vec{r}_1, \vec{r}_2)$ <u>forbids</u> electrons to be <u>at the same place</u>

Important idea!

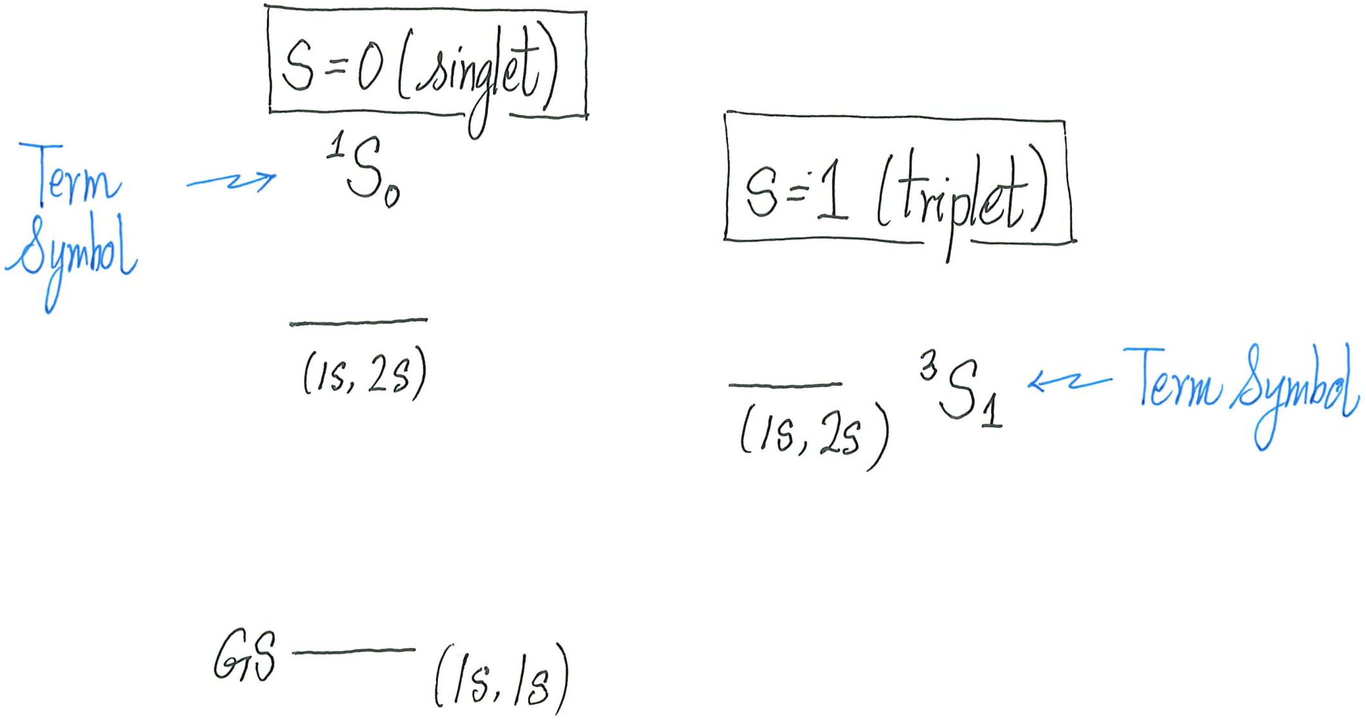
Good!

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

He - atom



Higher excited states can be grouped into $\underbrace{\text{singlet and triplet states}}_{\because \text{ involving 2 electrons}}$

- This is also the physics behind the Hund's rules[+]

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

[also works for electrons in d and f states]

Why?

- 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 "Thinking like a physicist"!

[+] 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 — $\underbrace{\text{Hund's}}_{\text{student of Born}}$ rules

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[+] Different fillings correspond to different wavefunctions [Slater Determinants]

Recall: Term Symbol

Helium atom

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

electrons in $\overbrace{L=0}^{\text{"S" in middle}}$

2S+1=1 (upper LH corner)

$$^1S_0$$

L=0, S=0 ⇒ J=0 (lower corner)

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

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

$$^3S_1$$

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

the "1" in lower corner

- Big Physics that emerges... Origin of Magnetism

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

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

in Helium 1st excited state

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

(∵ $\underbrace{\text{exchange integral}}_{K_{A,B}\ (\text{sign})}$ determines $\underbrace{\text{alignment}}_{\text{"ferromagnetic"}}$ or $\underbrace{\text{anti-alignment}}_{\text{"anti-ferromagnetic"}}$)

due to $\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$, electromagnetic interaction + quantum requirement on $\psi(1,2)$

Let there be Magnets

- Atoms (some, not all) are like a small magnetic

  [Fe, Co, Ni have aligned electrons' spins in 3d]
- It is the 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 $\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ interaction

Models: Following interaction of two angular momentum

$$\mathcal{H} \sim \underbrace{-\tilde{K}}_{\text{energy}} \frac{\vec{S}_i}{\hbar}\cdot\frac{\vec{S}_j}{\hbar}$$

energy set by exchange integral

(assume $\tilde{K} > 0$)

spin-half

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

$$\begin{array}{lll} \text{——} \ \frac{3\tilde{K}}{4} & S = 0 & \uparrow \\ & & \tilde{K} \\ \text{——} \ -\frac{\tilde{K}}{4} & S = 1 & \downarrow \end{array}$$

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

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

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

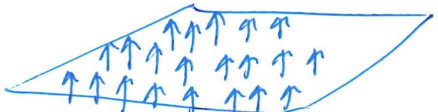
Curie temperature T_c : $kT_c \sim \tilde{K}$ ($T > T_c$ destroys ferromagnets)

Think like a Physicist

T = 0 K (zero temperature) Want to get lowest energy configuration?

All $\vec{\mu}$'s aligned ⇒ make use of $\underbrace{(-\tilde{K})\ \text{(aligned neighbors)}}_{\text{many pairs of neighbors}}$

∴ T = 0K



ordered (ferromagnetic)

T ≠ 0K Thermal Physics ⇒ Want to minimize $F = U \underset{\text{"minus"}}{-} \overset{\text{temperature}}{T} \underset{\text{entropy}}{\underbrace{S}}$

∴ Temperature tends to randomize the system

(e.g. flip one spin out of N spins ⇒ N ways ⇒ $\underbrace{N \text{ microstates}}_{k\ln N = \text{entropy}}$)

$\underbrace{kT\ \text{(thermal energy)}}_{\text{wants to randomize alignment}}$ competes with $\underbrace{\tilde{K}\ \text{(exchange energy)}}_{\text{prefers alignment}}$

High Temp ⇒ destroys ferromagnetic order   Low Temp ⇒ ferromagnetic order