(c) Back to Helium atom Ground State (2-electron system)

$$\text{"a"} = \underbrace{1s\uparrow}_{\phi_{1s}\alpha} \quad (n=1, l=0, s=\tfrac{1}{2}, m_s=+\tfrac{1}{2}) \qquad \text{"b"} = \underbrace{1s\downarrow}_{\phi_{1s}\beta} \quad (n=1, l=0, s=\tfrac{1}{2}, m_s=-\tfrac{1}{2})$$

$$\psi_{GS}^{(He)} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\uparrow}(1) & \phi_{1s\uparrow}(2) \\ \phi_{1s\downarrow}(1) & \phi_{1s\downarrow}(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[\phi_{1s\uparrow}(1)\,\phi_{1s\downarrow}(2) - \phi_{1s\uparrow}(2)\,\phi_{1s\downarrow}(1)\right]$$

$$= \frac{1}{\sqrt{2}}\left[\phi_{1s}(1)\alpha(1)\,\phi_{1s}(2)\beta(2) - \phi_{1s}(2)\alpha(2)\,\phi_{1s}(1)\beta(1)\right] \quad (38)$$

[Either term won't work (as shown), but this combination works]

$$= \phi_{1s}(1)\,\phi_{1s}(2)\,\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \qquad \text{(factorizing)}$$

$$= \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}_{\psi_{spatial}} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\psi_{spin}} \qquad (39)$$

(both e^- in 1s) (must be this form to be right!)

Physics to learn:

Not true for general $(N\neq 2)$-electron wavefn's

- 2-electron wavefunction can be factorized into

$$\underbrace{\psi_{total}(1,2)}_{\text{emphasize it is the full 2-electron wavefunction}} = \underbrace{\text{"spatial part } \psi_{spatial}\text{"}}_{\text{related to atomic orbitals } (n\,\ell\, m_\ell)} \cdot \underbrace{\text{"spin part } \psi_{spin}\text{"}}_{\text{adding two } s=\frac{1}{2} \text{ spins (AM's)}} \quad (40)$$

[emphasize it is the full 2-electron wavefunction]

adding two $s=\frac{1}{2}$ spins (AM's): did this! Singlet $(S=0)$, Triplet $(S=1)$

- For $\psi_{total}(1,2)$ to be anti-symmetric, could have

ψ_{total}	$=\ \psi_{spatial}$	$\cdot\ \psi_{spin}$
Antisymmetric	symmetric	antisymmetric
	antisymmetric	symmetric

(41)

Back to $\psi_{GS}^{(He)} = \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}$ (39)

ground state

$= \underbrace{\psi_{spatial}(\vec{r}_1, \vec{r}_2)}_{\text{Symmetric}} \cdot \underbrace{\psi_{spin}(1,2)}_{\text{Antisymmetric}}$

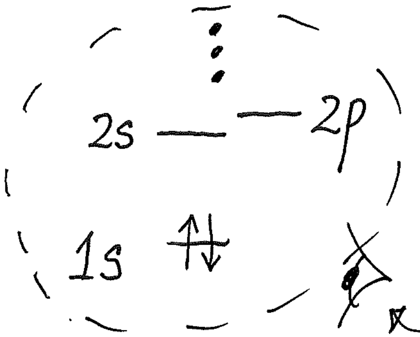
(only one option!)

For He ground state, because $\varepsilon_{1s} < \varepsilon_{2s} < \varepsilon_{2p} < \cdots$,
put two electrons in ϕ_{1s}.

$\psi_{spatial}(\vec{r}_1, \vec{r}_2) = \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}$ is the only choice

[symmetric w.r.t. interchanging $\vec{r}_1$ & $\vec{r}_2$]

$\therefore$ Must go with Antisymmetric $\psi_{spin}(1,2)$



Eq. (39) is what such a figure really means!

↑↓ $\boxed{\text{Which electron has up-spin \& which has down-spin?}}$

A big question that hits at the heart of QM!

Inspect:

$$\psi_{spin}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)\right] \qquad \text{(from Eq. (39))}$$

$$= \frac{1}{\sqrt{2}}\underbrace{\left[|\uparrow\rangle_1\,|\downarrow\rangle_2 - |\downarrow\rangle_1\,|\uparrow\rangle_2\right]}_{} \qquad (40)^{+} \text{ (anti-symmetric)}$$

a superposition (minus sign guarantees anti-symmetry) of ↑↓ and ↓↑

[makes sense! if we specify either one, it will give $\psi^{(wrong)}$!]

+ Here, we see quantum entanglement.

- Eq. (40) is the only anti-symmetric superposition that reflects "one is up & the other is down"

- $\begin{cases} \phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) \text{ is the only choice} \\ \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right] \text{ is also the only choice} \end{cases}$

$\Rightarrow \psi_{GS}^{(He)}$ is the $\underbrace{\text{unique (only one)}}$ ground state of He atom

Q: What is the spin (quantum number) of $\psi_{GS}^{(He)}$?

- Only one state $\Rightarrow$ can't be $\underbrace{S=1}_{\text{we are adding } s_1=\frac{1}{2},\ s_2=\frac{1}{2}}$ (there would be $2S+1=3$ states)

($m_s=0$)

$\Rightarrow$ $\boxed{\text{He ground state has } S=0}$ (spin singlet state)

Gaining something from nothing!

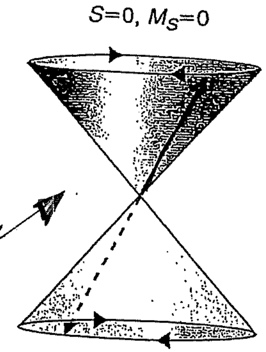
- When we add two spin-½ angular momenta

  each could be up ($\uparrow$ OR α) OR down ($\downarrow$ OR β)

  the total Spin (quantum number) could be $S=0$ OR $S=1$

- The $S=0$ (so $m_s=0$ only) singlet state is

$$\psi_{spin}^{(S=0)} = \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right]$$
$$= \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad (41)$$



Vector Model

Singlet state

Two spin angular momenta tend to be anti-parallel

Mathematical form of $S=0, m_s=0$ state and the corresponding vector model

He ground state: final words – How about ground state energy?

GOOD Think like a physicist!

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

[p. AP-VII-13]

[THE Helium problem] (Difficult!)

- Went through various approximations to rescuse single-electron states (atomic orbitals)

At the end,

$$\psi^{He}_{GS}(1,2) = \phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) \cdot \psi^{(S=0)}_{spin} \quad (39)$$

[at best a reasonable approximation]

{ Atomic orbital (Hartree, self-consistency) + Filling in electrons (Pauli Principle)

Q: Want to get an energy from (39) for $\hat{H}_{He}$?

[expectation value!]

- $\hat{H}_{He}$ does <u>not</u> depend on spin $\Rightarrow$ Inner product of spin parts gives 1

$$\therefore\ E_{GS} = \iint \phi_{1s}^*(\vec{r}_1)\,\phi_{1s}^*(\vec{r}_2)\Big[\overbrace{\hat{h}_1(\vec{r}_1) + \hat{h}_2(\vec{r}_2) + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}}^{\hat{H}_{He}}\Big]\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2 \quad (42)$$

(Done!)

[it is <u>NOT</u> quite $\varepsilon_{1s} + \varepsilon_{1s}$, as guessed naively]

$$= \int \phi_{1s}^*(\vec{r}_1)\hat{h}_1(\vec{r}_1)\phi_{1s}(\vec{r}_1)\,d^3r_1 + \int \phi_{1s}^*(\vec{r}_2)\,\hat{h}_2(\vec{r}_2)\,\phi_{1s}(\vec{r}_2)\,d^3r_2$$

same actually

$$+ \iint \phi_{1s}^*(\vec{r}_1)\,\phi_{1s}^*(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2$$

$$\equiv I_1 + I_2 + \underbrace{J_{1s,1s}}_{\text{as defined previously [direct Coulomb integral]}} \quad (43)$$

Remark (Optional):

- Take Eq. (43) for "E_{GS}" as expectation value of $\hat{H}_{He}$ w.r.t. trial wavefunction $\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\cdot\psi_{spin}^{(S=0)}$ in Eq. (39.)
- Do variational method by varying the function $\phi_{1s}(\vec{r})$, i.e. look for optimal function $\phi_{1s}(\vec{r})$
- Result is the self-consistent equation for finding $\phi_{1s}(\vec{r})$ in Hartree approximation (as in Appendix B)
- This is the formal approach to develop Hartree and Hartree-Fock approximations (see Blinder, "Basic Concepts of Self-consistent-field Theory", Am. J. Phys. 33, 431-443 (1965)).

(d) Adding two spin-½ angular momenta: Revisited

$$s_1 = 1/2\,,\ \underbrace{m_{s_1} = \pm 1/2}_{|\uparrow\rangle_1,\ |\downarrow\rangle_1} \quad ; \quad s_2 = 1/2\,,\ \underbrace{m_{s_2} = \pm 1/2}_{|\uparrow\rangle_2,\ |\downarrow\rangle_2}$$

• 4 possibilities: $|1/2, \underline{m_{s_1} = \pm 1/2}\,; 1/2, \underline{m_{s_2} = \pm 1/2}\rangle$ OR $|m_{s_1}; m_{s_2}\rangle$

	$\alpha(1)\alpha(2)$	$\beta(1)\beta(2)$	$\alpha(1)\beta(2)$	$\alpha(2)\beta(1)$
OR	$\lvert +1/2; +1/2\rangle$	$\lvert -1/2; -1/2\rangle$	$\lvert +1/2; -1/2\rangle$	$\lvert -1/2; +1/2\rangle$
OR	$\lvert\uparrow\rangle_1 \lvert\uparrow\rangle_2$	$\lvert\downarrow\rangle_1 \lvert\downarrow\rangle_2$	$\lvert\uparrow\rangle_1 \lvert\downarrow\rangle_2$	$\lvert\downarrow\rangle_1 \lvert\uparrow\rangle_2$
	symmetric	symmetric	Neither symmetric NOR anti-symmetric	

[OK! Can go with Anti-sym $\psi_{spatial}$]

[no good for constructing 2-electron wavefns]

- Invoke total spin AM $\Rightarrow$ $S=0$ and $S=1$

  $|S, m_s\rangle$ also labels 4 states

- Already know that: Singlet state $|S=0, m_s=0\rangle$ is

$$\psi_{spin}^{(S=0)} \text{ or } |S=0, m_s=0\rangle = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right] \quad (41)$$

(anti-symmetric)

[vector model: two spins tend to anti-align]

$\boxed{\text{Anti-symmetric } \psi_{spin} \text{ goes with symmetric } \psi_{spatial}}$

- Triplet states: $\underbrace{|S=1, m_s=1\rangle}_{}$, $\underbrace{|S=1, m_s=-1\rangle}_{}$, $\underbrace{|S=1, m_s=0\rangle}_{}$
- Easy to see that: $\alpha(1)\alpha(2)$ or $|\uparrow\rangle_1 |\uparrow\rangle_2$ ($\because$ z-components add up to give $m_s=1$)

$\beta(1)\beta(2)$ or $|\downarrow\rangle_1 |\downarrow\rangle_2$ ($\because$ z-components add up to give $m_s=-1$)

$\boxed{\text{What is this?}}$

What is $|S=1, m_s=0\rangle$?

The only combination left is a superposition of $|\uparrow\rangle_1|\downarrow\rangle_2$ and $|\downarrow\rangle_1|\uparrow\rangle_2$

$$\psi_{spin}^{(S=1, m_s=0)} \text{ or } |S=1, m_s=0\rangle = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right] \quad \text{(Symmetric)}$$

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2\right] \quad (44)$$

∴ The $\underline{S=1}$ (triplet) states are $\underline{\text{symmetric}}$!

$\alpha(1)\,\alpha(2)\quad [\,|\uparrow\rangle_1 |\uparrow\rangle_2\,]$

$(S=1,\ \underline{m_s=1})$

$\beta(1)\,\beta(2)\quad [\,|\downarrow\rangle_1 |\downarrow\rangle_2\,]$

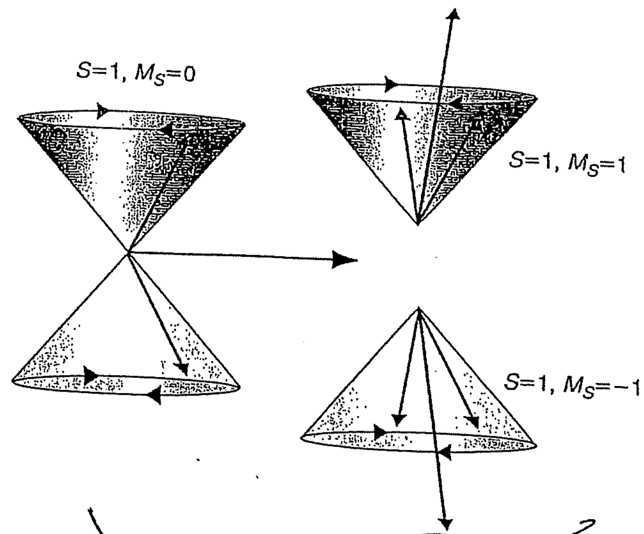
$(S=1,\ \underline{m_s=-1})$

$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

OR $\frac{1}{\sqrt{2}}[\,|\uparrow\rangle_1|\downarrow\rangle_2+|\downarrow\rangle_1|\uparrow\rangle_2\,]$

$(S=1,\ \underline{m_s=0})$

Symmetric ψ_{spin} goes with anti-symmetric $\psi_{spatial}$ (45)



triplet states

Vector Model
S=1 states
[tend to align]

Take-Home Message

$$S=0,\ m_s=0^{+}: \quad \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right] \quad \text{Antisymmetric spin part "spin singlet"}$$

$$S=1, \left.\begin{array}{ll} m_s=1 & \alpha(1)\alpha(2) \\ m_s=0^{+} & \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right] \\ m_s=-1 & \beta(1)\beta(2) \end{array}\right\} \text{Symmetric spin parts "spin triplet"} \qquad (46)$$

for adding two spin-half AM's

$^{+}$These states are interesting superposition of $|\uparrow\rangle_1|\downarrow\rangle_2$ & $|\downarrow\rangle_1|\uparrow\rangle_2$. They are quantum entangled states.

Summary of Sec. G

- N-electron wavefunction can be written as a Slater Determinant that gaurantees anti-symmetry (single-particle states are invoked)
- Pauli Exclusion Principle is a consequence [must be anti-symmetric]
- 2-electron wavefunction can be factorized $\psi_{2\text{-electron}} = \psi_{spatial} \cdot \psi_{spin}$
- 2-electron ψ_{spin} is related to adding to spin-½ AM's
- $S=0$ $(m_s=0)$ (singlet) has antisymmetric ψ_{spin}
- $S=1$ $(m_s=1,0,-1)$ (triplet) has symmetric ψ_{spin}