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

"a" = $\underbrace{1s\uparrow}_{\phi_{1s}\alpha}$ $(n=1, \ell=0, s=\frac{1}{2}, m_s=+\frac{1}{2})$ "b" = $\underbrace{1s\downarrow}_{\phi_{1s}\beta}$ $(n=1, \ell=0, s=\frac{1}{2}, m_s=-\frac{1}{2})$

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

$$= \frac{1}{\sqrt{2}}\left[\phi_{1s}(1)\alpha(1)\,\phi_{1s}(2)\beta(2) - \phi_{1s}(2)\alpha(2)\,\phi_{1s}(1)\beta(1)\right] \quad (37)$$

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

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

$$= \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}_{\psi_{spatial}} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\psi_{spin}} \quad (38)$$

Physics to learn:

- 2-electron wavefunction can be factorized into

$$\Psi_{total}(1,2) = \text{"spatial part } \Psi_{spatial}\text{"} \cdot \text{"spin part } \Psi_{spin}\text{"} \qquad (39)$$

[emphasize it is the full 2-electron wavefunction]

"spatial part $\Psi_{spatial}$": related to atomic orbitals $(n\ell m_\ell)$

"spin part Ψ_{spin}": adding two $s=1/2$ spins (AM's)

did this! Singlet $(S=0)$, Triplet $(S=1)$

Not true for general $(N\neq 2)$-electron wavefns

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

Ψ_{total}	$=$	$\Psi_{spatial}$	$\cdot$	Ψ_{spin}
Antisymmetric		symmetric	$\cdot$	antisymmetric
		antisymmetric	$\cdot$	symmetric

(40)

Back to $\psi_{GS}^{(He)} = \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}\cdot\underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]}$ (38)

$= \underbrace{\psi_{spatial}(\vec{r}_1,\vec{r}_2)}\cdot\underbrace{\psi_{spin}(1,2)}$ (only one option!)

Symmetric Antisymmetric

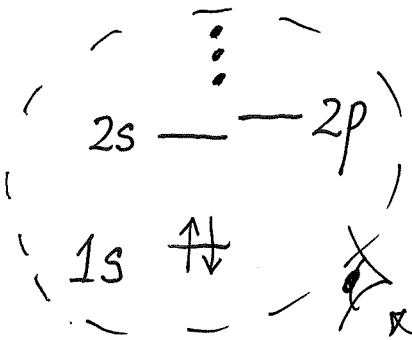
For He ground state, because $\mathcal{E}_{1s} < \mathcal{E}_{2s} < \mathcal{E}_{2p} < \cdots$,

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 $\vec{r}_1$ & $\vec{r}_2$]

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



← Eq. (38) is what such a figure really means!

↑↓ → Which electron has up-spin & which has down-spin?

A big question that hits at the heart of QM!

Inspect:

$$\psi_{spin}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad \text{(from Eq. (38))}$$

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right] \quad (39)^+ \text{ (anti-symmetric)}$$

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. (39) is the <u>only</u> <u>anti-symmetric</u> superposition that reflects "one is up & the other is down"

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

→ $\psi_{GS}^{(He)}$ is the <u>unique (only one)</u> ground state of He atom

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

- Only <u>one</u> state ⇒ <u>can't be $S=1$</u> (there would be $2S+1=3$ states)
  ($m_S=0$)
  we are adding $s_1=1/2$, $s_2=1/2$
  ⇒ <u>He ground state has $S=0$</u> (spin singlet state)

Gaining something from nothing!

- When we add <u>two</u> spin-½ angular momenta
  - each could be up ($\uparrow$ or α) or down ($\downarrow$ or β)

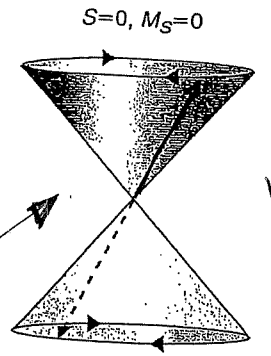
  the total Spin (quantum number) could be $S=0$ or $S=1$

- The $S=0$ (so $m_s=0$ only) <u>singlet</u> state is

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

$$= \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad (40)$$

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



Vector Model

Singlet state

Two spin angular momenta tend to be anti-parallel

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

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,

$$\Psi_{GS}^{He}(1,2) = \phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) \cdot \Psi_{spin}^{(S=0)} \quad (38)$$

[at best a reasonable approximation] { Atomic orbital (Hartree) + Filling in electrons (Pauli Principle)

Q: Want to get an energy from (38) for $\hat{H}_{He}$?

[expectation value!]

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

$\therefore$ $E_{GS} = \iint \phi_{1S}^*(\vec{r}_1)\, \phi_{1S}^*(\vec{r}_2) \overbrace{\left[\hat{h}_1(\vec{r}_1) + \hat{h}_2(\vec{r}_2) + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \right]}^{\hat{H}_{He}} \phi_{1S}(\vec{r}_1)\, \phi_{1S}(\vec{r}_2)\, d^3r_1\, d^3r_2$ (41)

(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 ↗

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

$\equiv I_1 + I_2 + \underbrace{J_{1S,1S}}$ (42)

as defined previously [<u>direct Coulomb integral</u>]

Remark (Optional):

- Take Eq. (42) for "E_{GS}" as expectation value of $\hat{H}_{He}$ w.r.t. trial wavefunction $\phi_{1S}(\vec{r}_1)\,\phi_{1S}(\vec{r}_2)\cdot\chi_{spin}^{(S=0)}$ in Eq. (38)
- 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)).