Upgrading your knowledge on the Pauli Exclusion Principle

- It is related to the symmetry of many-electron wavefunctions with respect to interchanging the coordinates of indistinguishable particles
- Pay attention — Big idea here!

E. General Requirement on Many-(Indistinguishable)-electron Wavefunction

- **Many-electron wavefunctions must be anti-symmetric (change sign) with respect to interchanging the coordinates of two electrons**

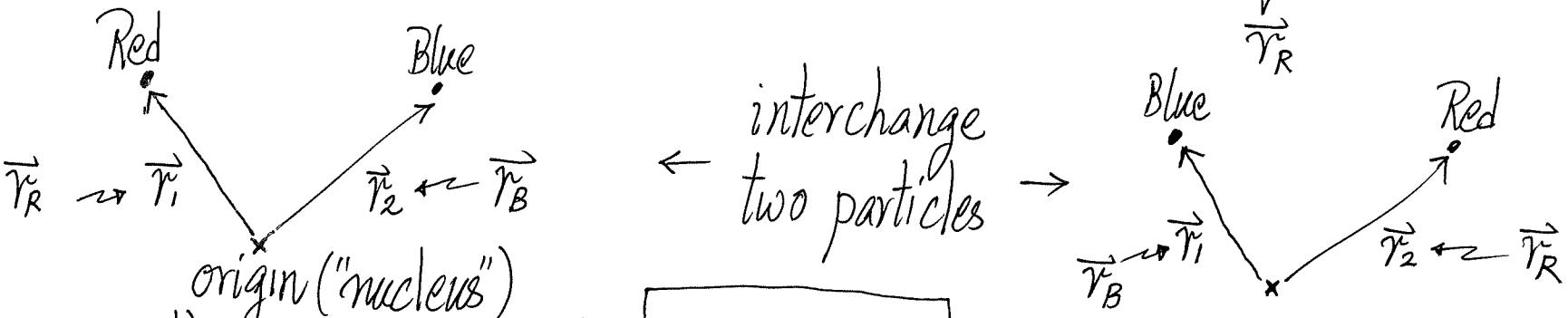
Contexts

- Electrons in an atom, a molecule, a solid ($\sim 10^{23}$ electrons in cm^3 of solid)
- Many-electron systems
- The electrons are identical particles (全同粒子) [contrast to red, green, blue, ... balls]
- When electrons "live" in a system, they are indistinguishable (不可分辨的)
  (e.g. the two electrons in a helium atom)
  the $\sim 10^{23}$ electrons in a piece of metal

How does indistinguishability affect the form of many-electron wavefunction?

- Two distinguishable particles (red ball, blue ball)

General 2-particle wavefunction $\psi^{(dist.)}(\underbrace{\text{red ball coordinates}}_{\vec{r}_R}, \underbrace{\text{blue ball coordinates}}_{\vec{r}_B})$



$\psi^{(dist.)}(\vec{r}_R = \vec{r}_1, \vec{r}_B = \vec{r}_2)$ OR $\psi^{(dist.)}(\vec{r}_1, \vec{r}_2)$

Two different situations

$\psi^{(dist.)}(\vec{r}_R = \vec{r}_2, \vec{r}_B = \vec{r}_1)$ OR $\psi^{(dist.)}(\vec{r}_2, \vec{r}_1)$

⇓

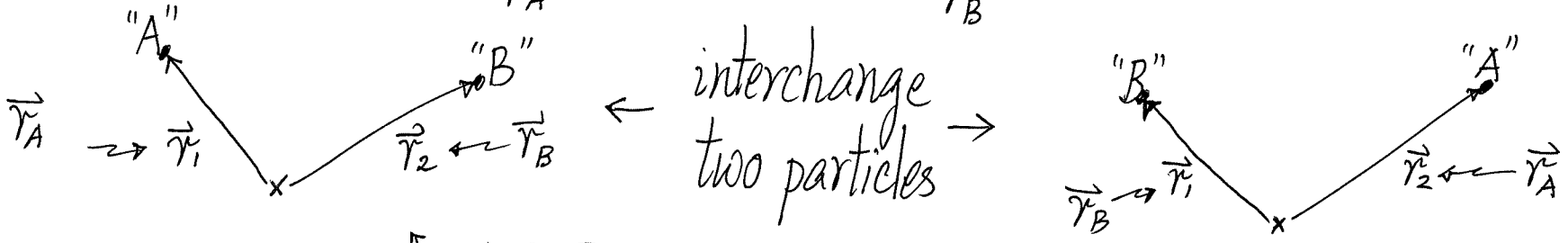
Impose NO requirement on form of $\psi^{(dist.)}(\vec{r}_R, \vec{r}_B)$

identical otherwise

- Very different for two indistinguishable particles (call them A & B)

ψ (particle A coordinates , particle B coordinates)

$\vec{r}_A$ $\vec{r}_B$



$\psi(\vec{r}_A = \vec{r}_1 , \vec{r}_B = \vec{r}_2)$

OR

$\psi(\vec{r}_1 , \vec{r}_2)$

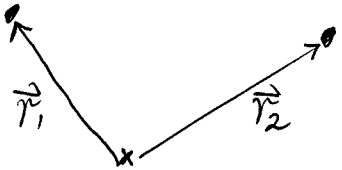
For indistinguishable particles, same physical situation

$\psi(\vec{r}_A = \vec{r}_2 , \vec{r}_B = \vec{r}_1)$

OR

$\psi(\vec{r}_2 , \vec{r}_1)$

Same situation



impose relation between $\psi(\vec{r}_1, \vec{r}_2)$ & $\psi(\vec{r}_2, \vec{r}_1)$

Key idea

The situation is:

"One particle takes on $\vec{r}_1$, and the other takes on $\vec{r}_2$"

↖ [but can't tell which particle is which] ↗

- Following notations in standard textbooks:

$$\psi(1,2) \quad \text{versus} \quad \psi(2,1)$$

1 ↖ refers to one particle

2 ↖ refers to the other particle

Question becomes: Restriction on $\psi(1,2)$ due to indistinguishability of two particles?

- Born's interpretation of wavefunction in QM
  related to $|\psi|^2$ (not ψ itself)

(25) $$\boxed{|\psi(1,2)|^2 = |\psi(2,1)|^2}$$

- For 2 indistinguishable particles, both sides refer to the probability density of finding one particle at "1" and the other particle at "2"

- Eq. (25) is the restriction imposed due to indistinguish particles
- Eq. (25) is about $|\psi|^2$
- Eq. (25) is the Key Result (must understand)
- Argument works for general many-particle wavefunctions
  [don't need to invoke single-particle states up to now]

Possible Consequences of $|\psi(1,2)|^2 = |\psi(2,1)|^2$

(i) $\psi(1,2) = \psi(2,1)$ (26) ← Work for Bosons†

Wavefunction is symmetric w.r.t. interchanging two particles

• A general statement for many-boson wavefunctions

(ii) $\psi(1,2) = -\psi(2,1)$ (27) ← Work for Fermions†

Wavefunction is Anti-symmetric (change sign) w.r.t. interchanging two particles

• A general statement for many-fermion wavefunctions

Nature made only these two choices†

† All particles have either integer spins or half-integer spin. All (spin 1/2, 3/2, 5/2, ...) particles are fermions. All spin 0, 1, 2, ... particles are bosons.

Electron has $s = 1/2$ (spin-half)

$\Rightarrow$ Electrons are fermions

Key concept

$\therefore$ **Many-electron Wavefunction must be anti-symmetric w.r.t. interchanging two particles** (28)

- Applicable to all cases: electrons in atom (He, C, Na, U, ...)
  electrons in molecule (H_2, CO_2, H_2O, C_6H_6, ...)
  electrons in solid (metals, insulators, semiconductors, ...)
- Eq. (28) must be satisfied
  - true for general $\Psi(1,2)$ or $\Psi(1,2,\cdots,N)$ (N-electron)
  - even if general Ψ is approximated by product of single-particle states (e.g. Hartree or Hartree-Fock)

Next Question: How to enforce (28) in terms of electrons occupying single-particle states?

[Ans: Pauli Exclusion Principle]

Extension/Further Reading (Optional)

- See chapter on "Identical Particles" in standard textbooks
- Relation between spin and "statistics" (fermions or bosons) has a deeper root in quantum field theory

F. Enforcing (28) in terms of electrons occupying single-particle states

- Background: Independent Particle Approximation (IPA) recused the notions of single-electron states

e.g. ψ_{1s}, ψ_{2s}, ψ_{2p_x}, ψ_{2p_y}, ψ_{2p_z}, ψ_{3s}, ...

even if we include the (s), m_s label (spin), we have

$\underbrace{\psi_{1s,\uparrow}}$, $\underbrace{\psi_{1s,\downarrow}}$, $\underbrace{\psi_{2s,\uparrow}}$, $\underbrace{\psi_{2s,\downarrow}}$, ...

OR

$\psi_{1s}\cdot\alpha$, $\psi_{1s}\cdot\beta$, $\psi_{2s}\cdot\alpha$, $\psi_{2s}\cdot\beta$, ...

Picture: Fill electrons into single-electron states to get at ground state and excited states of an atom

Question: How to satisfy (28) as we fill in electrons?

- Recall: Helium Ground State

Picture: "Put both electrons into 1s atomic orbital, with one being spin-up and another spin-down"

(ϕ_{1s} (by Hartree approx., say))

This simple statement carries BIG PHYSICS! (Un-noticed at elementary level)

- Let's try something that won't work

$$\psi^{(wrong)}(1,2) = \underbrace{\phi_{1s}(1)\alpha(1)}_{\text{one particle in 1s with up-spin}} \cdot \underbrace{\phi_{1s}(2)\beta(2)}_{\text{the other particle in 1s with down-spin}}$$

["multiply"]

← nice try, but illegal!

But $\psi^{(wrong)}(2,1) = \phi_{1s}(2)\alpha(2) \cdot \phi_{1s}(1)\beta(1)$ $\boxed{\neq -\psi^{(wrong)}(1,2)}$ ← Not satisfying (28).

(a) Let's step back and consider the two-electron case carefully

- One electron in a single-electron state "a"$^+$ of wavefunction ϕ_a
- The other electron in a single-electron state "b"$^+$ of wavefunction ϕ_b

Try: $\psi(1,2) \stackrel{?}{=} \phi_a(1)\,\phi_b(2)$ Does it work?

→ No! It is neither symmetric nor antisymmetric w.r.t. interchanging 1 & 2

Try: $\psi(1,2) \stackrel{?}{=} \phi_a(2)\,\phi_b(1)$ Does it work?

How to construct a legal $\psi(1,2)$ that satisfies (28)?

+ The label "a" (and "b") can include spin label, e.g. "a" could be "1s↑", "b" could be "1s↓" (He ground state) or "2s↑" ("2s↓") (He excited states)

A proper two-electron anti-symmetric wavefunction is:

Key Concept! →

$$\Psi_{2\text{-fermion}}(1,2) = \frac{1}{\sqrt{2}}\left[\phi_a(1)\,\phi_b(2) - \phi_a(2)\,\phi_b(1)\right] \quad (29)$$

(when ϕ_a, ϕ_b are normalized) → normalization ↑ ; "minus sign" ↖ (Big Physics† enters)

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_a(1) & \phi_a(2) \\ \phi_b(1) & \phi_b(2) \end{vmatrix} \quad (30)$$

← Determinant (Slater determinant) (Big Physics† enters)

Check:

$$\Psi_{2\text{-fermion}}(2,1) = \frac{1}{\sqrt{2}}\left[\phi_a(2)\,\phi_b(1) - \phi_a(1)\,\phi_b(2)\right] = -\Psi_{2\text{-fermion}}(1,2)$$

∴ (28) is satisfied! It works!

†Big Physics:

- Pauli Exclusion Principle, Quantum Entanglement, Quantum Computing, Magnetism, Quantum teleportation, ..., differences between Fermi gas and Bose gas all started from here!

- What if 3 electrons in ϕ_a, ϕ_b, ϕ_c?

$$\Psi_{3\text{-electron}}(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \phi_a(3) \\ \phi_b(1) & \phi_b(2) & \phi_b(3) \\ \phi_c(1) & \phi_c(2) & \phi_c(3) \end{vmatrix} \quad (31)^{\dagger}$$

(generalizing Eq. (30))

- Interchanging 1 & 2

⇒ <u>interchanging two columns</u> of a determinant

⇒ gives a minus sign[‡], thus anti-symmetric (as required)

---

† This form is called <u>Slater Determinant</u>, after J.C. Slater who contributed much to the Quantum Theory of Matter.

‡ This follows from determinant mathematics.

Aside: How about two-particle symmetric wavefunction[+] (bosons)?

- 2 bosons in two different states ϕ_a and ϕ_b

$$\psi_{2\text{-boson}}(1,2) = \frac{1}{\sqrt{2}}\left[\phi_a(1)\,\phi_b(2) + \phi_a(2)\,\phi_b(1)\right] \qquad (32)$$

[symmetric w.r.t. interchanging 1 & 2]

- 2 bosons in same state ϕ_a

$$\psi_{2\text{-boson}}(1,2) = \phi_a(1)\,\phi_a(2) \text{ is symmetric}$$

[+] Remark: These ways of constructing symmetric wavefunctions are also useful in understanding atoms (see later)

(b) Pauli Exclusion Principle

- Eq.(29) OR (30): If state "a" = state "b",

  then $\Psi_{2\text{-fermion}}(1,2) = 0$ for all coordinates 1 & 2

  $\Rightarrow$ unphysical! (not allowed to happen!)

$\therefore$ For $\Psi_{2\text{-fermion}}$, which is anti-symmetric, to hold, "a" and "b" must be different states, OR simply put "the two electrons cannot occupy the same state" (Pauli Exclusion Principle)

Pauli Exclusion Principle is a consequence of the anti-symmetric Ψ requirement

- invoke single-electron states (approximation, thus less general)
- general

Pauli Exclusion Principle works for many-electron systems (not only two)

- 3 electrons in states ϕ_a, ϕ_b, ϕ_c

$$\psi_{3\text{-fermion}}(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \phi_a(3) \\ \phi_b(1) & \phi_b(2) & \phi_b(3) \\ \phi_c(1) & \phi_c(2) & \phi_c(3) \end{vmatrix}$$

"Slater Determinant"

(31)+

If any two of "a", "b", "c" are equal, then two identical rows

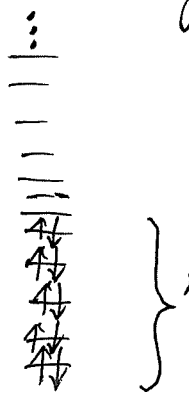
$\Rightarrow$ Determinant = 0 $\Rightarrow$ Pauli Exclusion Principle!

- Ex: How about 6 electrons in 6 states?

+ The "3!" is the number of terms if we write the determinant into a form analogous to Eq. (29). Each ϕ is assumed to be normalized.

Aside: Comparing Ground States of Non-interacting Fermions and Bosons

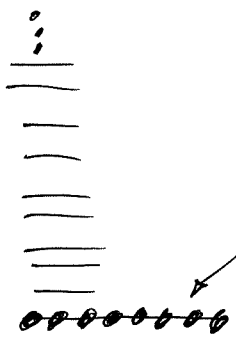
Non-interacting Fermions



Must stack up due to Pauli Exclusion Principle

[attain a high energy even at T = 0K]

Non-interacting Bosons



All in single-particle lowest energy state

∴ Ideal Fermi Gas and Ideal Bose Gas behave differently!

↯ Fermi-Dirac statistics

↯ Bose-Einstein statistics

↖ ↗ See statistical physics/mechanics course

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

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

$$= \frac{1}{\sqrt{2}}\left[\phi_{1s}(1)\alpha(1)\,\phi_{1s}(2)\beta(2) - \phi_{1s}(2)\alpha(2)\,\phi_{1s}(1)\beta(1)\right] \quad (33)$$

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

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

$$= \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}_{\psi_{spatial}} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\psi_{spin}} \quad (34)$$

Physics to learn:

- 2-electron wavefunction can be factorized into

  Not true for general (N≠2)-electron wavefns

$$\Psi_{total}(1,2) = \text{"spatial part } \Psi_{spatial}\text{"} \cdot \text{"spin part } \Psi_{spin}\text{"} \qquad (35)$$

[emphasize it is the full 2-electron wavefunction]

related to atomic orbitals $(n\ell m_\ell)$

adding two $s=1/2$ spins (AM's) did this! Singlet $(S=0)$, Triplet $(S=1)$

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

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

(36)

Back to $\psi_{GS}^{(He)} = \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)} \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}$ (34)

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

Symmetric Antisymmetric

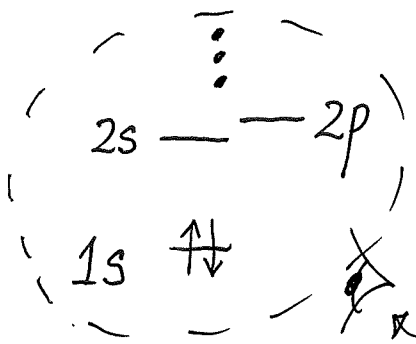
For He ground state, because $\mathcal{E}_{1s} < \mathcal{E}_{2s} < \mathcal{E}_{2p} < \cdots$,

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. (34) 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:

$$\psi_{spin}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \quad \text{(from Eq. (34))}$$

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right] \quad (37)^+ \text{ (anti-symmetric)}$$

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

- $\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)$ is the only choice

- $\frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2\right]$ is also the only choice

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

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

- Only one state ($m_S = 0$) ⇒ can't be $S=1$ (there would be $2S+1 = 3$ states)

we are adding $s_1 = 1/2$, $s_2 = 1/2$

⇒ **He ground state has $S=0$** (spin singlet state)

Gaining something from nothing!

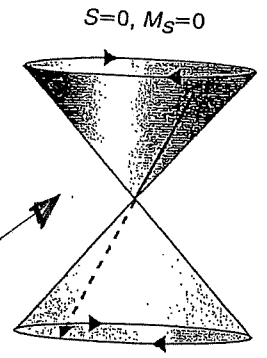
- When we add <u>two</u> spin-½ angular momenta
  - each could be up ($\uparrow$ or α) or down ($\downarrow$ or β)

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

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

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

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



Singlet state

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

Two spin angular momenta tend to be anti-parallel

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

Think like a physicist!

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

[p. AP-VII-15]

[THE Helium problem] (Difficult!)

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

At the end,

$$\Psi^{He}_{GS}(1,2) = \phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2) \cdot \Psi^{(S=0)}_{spin} \quad (34)$$

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

Q: Want to get an energy from (34) for $\hat{H}_{He}$?

[expectation value!]

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

$$E_{GS} = \iint \phi_{1S}^*(\vec{r}_1)\,\phi_{1S}^*(\vec{r}_2)\Big[\overbrace{\hat{h}_1(\vec{r}_1) + \hat{h}_2(\vec{r}_2) + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}}^{\hat{H}_{He}}\Big]\phi_{1S}(\vec{r}_1)\,\phi_{1S}(\vec{r}_2)\,d^3r_1\,d^3r_2 \qquad (39)$$

(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 ↗

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

$$\equiv I_1 + I_2 + \underbrace{J_{1S,1S}} \qquad (40)$$

as defined previously [direct Coulomb integral]

Remark (Optional):

- Take Eq. (39) 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. (34)
- 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

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

- 4 possibilities: $|\frac{1}{2}, m_{s_1} = \pm\frac{1}{2};\ \frac{1}{2}, m_{s_2} = \pm\frac{1}{2}\rangle$ 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	$\lvert+\frac{1}{2};+\frac{1}{2}\rangle$	$\lvert-\frac{1}{2};-\frac{1}{2}\rangle$	$\lvert+\frac{1}{2};-\frac{1}{2}\rangle$	$\lvert-\frac{1}{2};+\frac{1}{2}\rangle$
OR	$\underbrace{\lvert\uparrow\rangle_1 \lvert\uparrow\rangle_2}_{\text{symmetric}}$	$\underbrace{\lvert\downarrow\rangle_1 \lvert\downarrow\rangle_2}_{\text{symmetric}}$	$\underbrace{\lvert\uparrow\rangle_1 \lvert\downarrow\rangle_2}_{\text{Neither symmetric nor anti-symmetric}}$	$\underbrace{\lvert\downarrow\rangle_1 \lvert\uparrow\rangle_2}_{\text{Neither symmetric nor anti-symmetric}}$

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

↑ [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

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

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right] \quad (38)$$

(anti-symmetric)

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

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

- Triplet states: $|S=1, m_s=1\rangle$, $|S=1, m_s=-1\rangle$, $|S=1, m_s=0\rangle$

- 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 $m_s=-1$)

  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 $|\downarrow\rangle_1|\uparrow\rangle_2$

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

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

∴ The $S=1$ (triplet) states are symmetric!

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

$(S=1,\ m_S=1)$

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

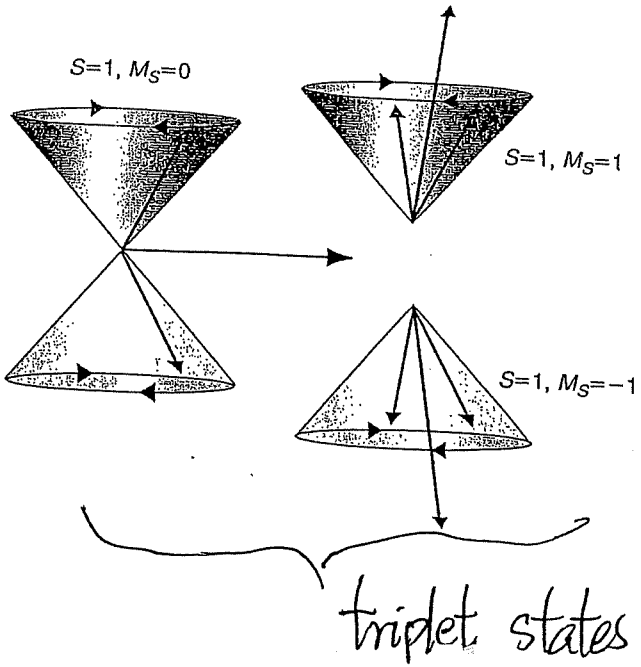
$(S=1,\ m_S=-1)$

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

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

$(S=1,\ m_S=0)$

Symmetric ψ_{spin} goes with anti-symmetric $\psi_{spatial}$ (42)



Vector Model
$S=1$ states
[tend to align]

Take-Home Message

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

$S=1$,

$m_s=1$ $\quad \alpha(1)\alpha(2)$

$m_s=0^+$ $\quad \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]$

$m_s=-1$ $\quad \beta(1)\beta(2)$

} Symmetric spin parts "spin triplet" (43)

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. F

- N-electron wavefunction can be written as a Slater Determinant that gaurantees anti-symmetry
- 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-$\frac{1}{2}$ AM's
- $S=0$ ($m_s=0$) (singlet) has antisymmetric Ψ_{spin}
- $S=1$ ($m_s=1, 0, -1$) (triplet) has symmetric Ψ_{spin}