# Wave function for identical particles

Since particles ($e^-$) are identical we can write,

$$\underbrace{P(\vec{r}_1, \vec{r}_2)}_{\text{prob. of finding electron 1 at } \vec{r}_1 \text{ and electron 2 at } \vec{r}_2} = \underbrace{P(\vec{r}_2, \vec{r}_1)}_{\text{prob. of finding electron 1 at } \vec{r}_2 \text{ and electron 2 at } \vec{r}_1}$$

$$\left|\psi(\underbrace{\vec{r}_1}_{\text{electron 1 at } \vec{r}_1}, \underbrace{\vec{r}_2}_{\text{electron 2 at } \vec{r}_2})\right|^2 = \left|\psi(\underbrace{\vec{r}_2}_{\text{electron 1 at } \vec{r}_2}, \underbrace{\vec{r}_1}_{\text{electron 2 at } \vec{r}_1})\right|^2$$

There are only 2 ways this can occur.

① $\psi_S(\vec{r}_1, \vec{r}_2) = \psi_S(\vec{r}_2, \vec{r}_1)$

OR

② $\psi_A(\vec{r}_1, \vec{r}_2) = -\psi_A(\vec{r}_2, \vec{r}_1)$

## Two-particle wavefunction

Symmetric Wave Fn $\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)\right]$

Antisymmetric Wave Fn $\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\,\psi_a(\vec{r}_2)\right]$

## Correct Way

SYMMETRIC $\psi_S(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)\right]$

ANTISYMMETRIC $\psi_A(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)\right]$

## Spin-statistics theorem (Pauli)

Particles of *half-odd-integral* spin ($s = 1/2, 3/2, 5/2$ etc) have *antisymmetric wavefunctions*. They are called *Fermions*. Ex($e^-$, p, n)

Particle with *integer spin* ($s = 0, 1, 2, 3 \ldots$) have wavefunctions which are *symmetric* under the interchange of any 2 particles. They are called *bosons*. (ex. photon spin 1, $He^4$)

Electron has spin 1/2 so it is a fermion. So wavefunction for electrons in an atom must be *antisymmetric*.

For antisymmetric wavefunctions (fermions) Pauli exclusion principle holds.

Pauli exclusion principle - no 2 electrons can be in same state.

EX. $2e^-$ wavefunction

$$\psi_A(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)\right]$$

$$\psi_A(1,2) = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)\right]$$

If $\psi_a = \psi_b$ then $\boxed{\psi_A = 0!}$ NOT POSSIBLE

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Actually, $\psi_A(1,2) = \underbrace{\psi(\vec{r}_1,\vec{r}_2)}_{\text{space part}}\,\underbrace{\chi(1,2)}_{\text{spin part}}$

$$\psi_A(1,2,\dots N) = \underbrace{\psi(\vec{r}_1,\vec{r}_2,\dots\vec{r}_N)}_{\text{space part}}\;\underbrace{\chi(1,2,\dots N)}_{\text{spin part}}$$

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

$\tilde{r}$ ↓ spin part ↙

where $\psi_\alpha(1) = \phi_\alpha(\vec{r}_1)\chi_\alpha$ and $\psi_\beta = \phi_\beta(\vec{r})\chi_\beta$

A~~ctually~~, If $\alpha = \beta$, then $\psi_A = 0$ !

For 3 electrons,

$$\psi_A(1,2,3) = \frac{1}{\sqrt{3!}}\Big[\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3) - \psi_\alpha(1)\psi_\beta(3)\psi_\alpha(1)$$

$$- ~~\psi~~\, \psi_\beta(1)\psi_\alpha(2)\psi_\gamma(3) + \psi_\beta(1)\psi_\alpha(3)\psi_\gamma(2)$$

$$+ \psi_\gamma(1)\psi_\beta(3)\psi_\alpha(2) - \psi_\gamma(1)\psi_\beta(2)\psi_\alpha(3)\Big]$$

| | $\alpha$ | $\beta$ | $\alpha$ |
|---|---|---|---|
| + | 1 | 2 | 3 |
| − | 1 | 3 | 2 |
| + | 2 | 3 | 1 |
| − | 2 | 1 | 3 |
| + | 3 | 1 | 2 |
| − | 3 | 2 | 1 |

For $N$ fermions, we can write antisymmetric wavefunction as a "Slater determinant".

3 particles

EX -
$$\psi_{(1,2,3)} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_\alpha(1) & \psi_\alpha(2) & \psi_\alpha(3) \\ \psi_\beta(1) & \psi_\beta(2) & \psi_\beta(3) \\ \psi_\gamma(1) & \psi_\gamma(2) & \psi_\gamma(3) \end{vmatrix}$$

Note: here $\psi_\alpha(1) \equiv \phi_\alpha(\vec{r}_1)\,\chi_\alpha(1)$ e.g. $|\underset{\text{space part}}{s_1}\ \underset{\text{spin part}}{\uparrow_1}$

2 particles
$$\psi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_\alpha(1) & \psi_\alpha(2) \\ \psi_\beta(1) & \psi_\beta(2) \end{vmatrix}$$

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

In general,

$$\psi(1,2,\ldots N) = \frac{1}{\sqrt{N!}} \sum_P \underset{\text{sign of permutation}}{\epsilon_P}\ \underset{\text{orbitals}}{\psi_{\alpha_1}(P1)}\,\psi_{\alpha_2}(P2)\cdots\psi_{\alpha_N}(PN)$$

For 2 particles we can factor the space part & spin part.

So either,

$$\Psi_A(1,2,\ldots N) = \overbrace{\psi_A(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)}^{\text{space part}}\,\overbrace{\chi_S(1,2,\ldots N)}^{\text{spin part}}$$

OR

$$\Psi_A(1,2,\ldots N) = \underbrace{\psi_S(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)}_{\text{space part}}\,\underbrace{\chi_A(1,2,\ldots N)}_{\text{spin part}}$$

For <u>spatially antisymmetric</u> wavefunction, electrons tend to be far apart from each other.

$$\psi_A(\vec{r}_1=r,\vec{r}_2=r) = 0 \Rightarrow$$

Spatially antisymmetric wavefn has lower energy than spatially symmetric wavefunction

Ex. $\psi_A = \frac{1}{\sqrt{2}}\left[\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_a(\vec{r}_2)\phi_b(\vec{r}_1)\right]$

# Case of 2 electrons (He atom)

$$\psi_T(1,2) = \psi_S(\vec{r}_1, \vec{r}_2)\, X_A(1,2)$$

spatial part spin part

OR

$$\psi_T(1,2) = \psi_A(\vec{r}_1, \vec{r}_2)\, X_S(1,2)$$

spatial part spin part

For 2 electrons, $\vec{S} = \vec{S}_1 + \vec{S}_2 \rightarrow \boxed{S = 0, 1}$

**SINGLET** $S = 0$ $\quad (\alpha_1\beta_2 - \alpha_2\beta_1)\frac{1}{\sqrt{2}}$ OR $(\uparrow_1\downarrow_2 - \uparrow_2\downarrow_1)\frac{1}{\sqrt{2}}$

$M_S = 0 \; (S_z = S_{1z} + S_{2z} = 0)$

ANTISYMMETRIC

**TRIPLET** $S = 1$

$m_s = 1 \quad \alpha_1\alpha_2$ or $\uparrow_1\uparrow_2$

4 states → $m_s = 0 \quad (\alpha_1\beta_2 + \alpha_2\beta_1)\frac{1}{\sqrt{2}}$

$m_s = -1 \quad \beta_1\beta_2$ or $\downarrow_1\downarrow_2$

all symmetric

$\chi_{\text{singlet}}\ (S=0)$

Either,

$$\psi_T(1,2) = \psi_S(\vec{r}_1,\vec{r}_2)\left[\alpha_1\beta_2 - \alpha_2\beta_1\right]\frac{1}{\sqrt{2}} \qquad \left[\uparrow\downarrow - \downarrow\uparrow\right]$$

OR

$(S=1)$

$$\psi_T(1,2) = \psi_A(\vec{r}_1,\vec{r}_2)\,\chi_{\text{triplet}} \qquad \begin{bmatrix}\uparrow\uparrow \\ \uparrow\downarrow + \downarrow\uparrow \\ \downarrow\downarrow\end{bmatrix}$$

EX. <u>He</u>

<u>Ground state</u> $1s^2 \rightarrow S=0, L=0$ $\;{}^1S$ state

$$\psi_{{}^1S} = \underbrace{\phi(\vec{r}_1)\,\phi(\vec{r}_2)}_{1s\ \text{orbital}}\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)\right]$$

ONLY 1 possible state

<u>1st excited state</u> $1s^1 2s^1 \rightarrow \boxed{S=0,1}\ \boxed{L=0}$

possible 4 states

SINGLET $S=0 \rightarrow {}^1S$

$$\psi_{1S}(1,2) = \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) + \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right]\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)$$

TRIPLET $S=1 \rightarrow {}^3S$

$$\psi_{3S}(1,2) = \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) - \phi_{1s}(\vec{r})\phi_{2s}(\vec{r}_2)\right]\frac{1}{\sqrt{2}} \cdot \chi_{\text{triplet}} \leftarrow (M_S = \pm 1, 0)$$

Ex. He <u>1st excited state</u> $(1s^1 2s^1)$

$$\boxed{E_{^3S} < E_{^1S}}$$

Reason: Triplet state has antisymmetric space part

$(\psi_S(\vec{r}_1 = r, \vec{r}_2 = r) \neq 0) \leftarrow$ singlet

$\psi_A(\vec{r}_1 = r, \vec{r}_2 = r) = 0\,! \leftarrow$ triplet

Electrons are unlikely to be close → less repulsive energy

$$E(S=1) < E(S=0)$$

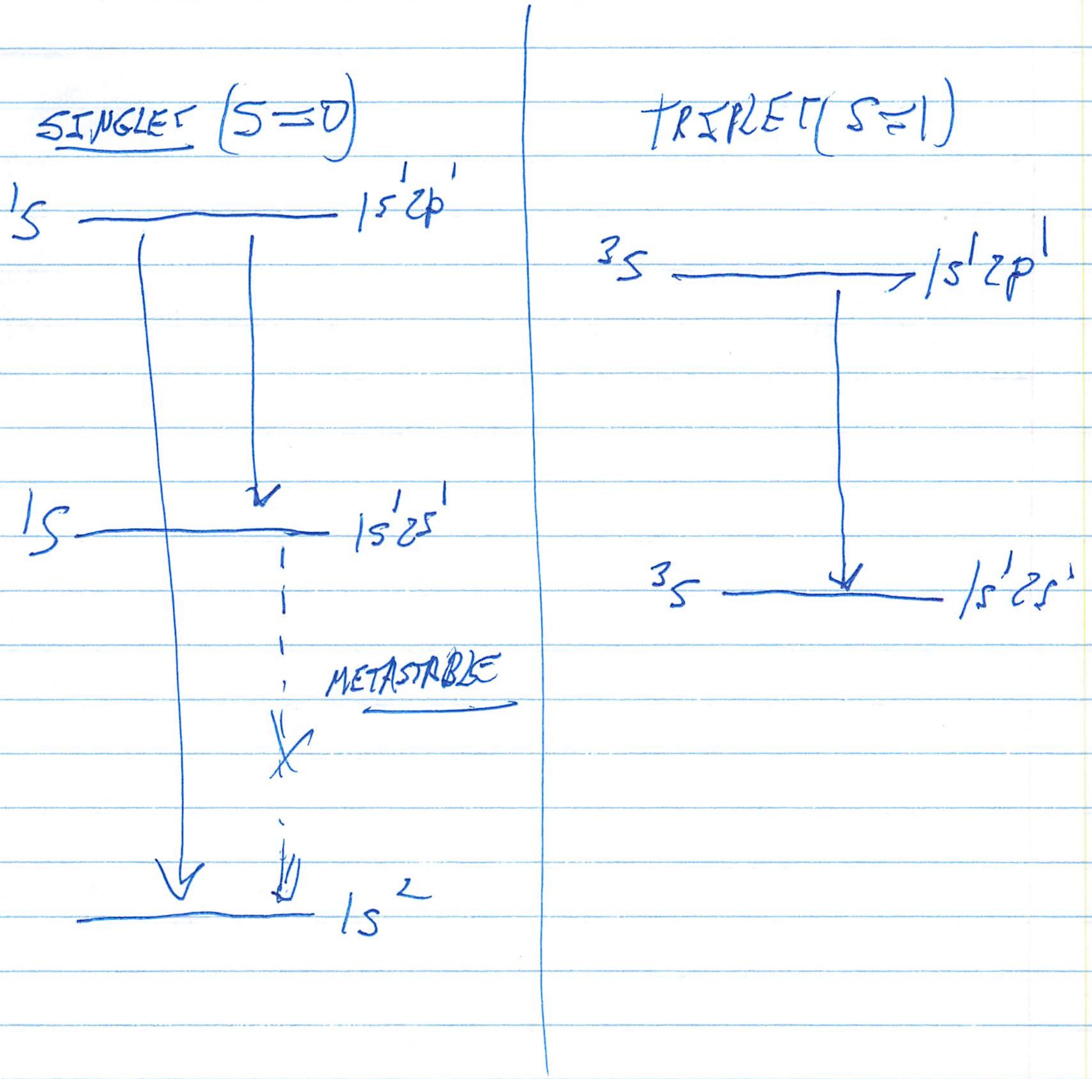
$$\begin{tikzcd} E(S=1) & E(S=0) \\ \psi_A \chi_S \arrow[u] & \psi_S \chi_A \arrow[u] \end{tikzcd}$$

triplet $\uparrow_1 \uparrow_2 \rightarrow \psi_A \chi_S$ $\qquad \psi_S \chi_A \leftarrow$ singlet

$\uparrow_1 \downarrow_2 + \uparrow_2 \downarrow_1$

$\downarrow_1 \downarrow_2$

# Energy levels of helium



## Ground state of the atom

$$\psi_0(\vec{r}_1, \vec{r}_2) \cong \psi_{1s}(\vec{r}_1)\, \psi_{1s}(\vec{r}_2) \;\&\; \text{spin part}\; \tfrac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta)$$

## Ignore spin part

$$\psi_{1s}(\vec{r}) \cong \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} = \text{hydrogen wavefunction with } Z = 2$$

$$E_0 = -(13.6\,\text{eV})\,(Z^2/1^2) \times \underset{\uparrow\ \text{2 electrons}}{2} = \boxed{-108.8\,\text{eV}}$$

## Correction ΔE due to Coulomb repulsion of electrons

$$\Delta E_{Coul} \cong \int d^3r_1 \int d^3r_2\, \psi_0^*(\vec{r}_1, \vec{r}_2) \left[\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}\right] \psi_0(\vec{r}_1, \vec{r}_2)$$

$$\Delta E_C = \frac{1}{\pi^2} \int d^3r_1 \int d^3r_2 \left(\frac{Z}{a_0}\right)^6 e^{-4r_1/a_0}\, e^{-4r_2/a_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \frac{e^2}{4\pi\epsilon_0}$$

Let $u_1 = 4r_1/a_0$, $u_2 = 4r_2/a_0$ $\quad d^3r_1 = (a_0/4)^3 d^3u_1 \quad d^3r_2 = (a_0/4)^3 d^3u_2$

$$\Delta E_C = \frac{64 e^2}{\pi^2 \cancel{a_0^6}\, 4\pi\epsilon_0} \left(\frac{\cancel{a_0}}{4}\right)^6 \left(\frac{4}{a_0}\right) \underbrace{\left[\int d^3u_1 \int d^3u_2\, e^{-u_1} e^{-u_2} \frac{1}{|\vec{u}_1 - \vec{u}_2|}\right]}_{= I}$$

$$\Delta E_c = \left[\frac{e^2}{4\pi\epsilon_0 a_0}\right] \frac{\overset{1}{\cancel{256}}}{16\pi^2} \cdot I$$

where $$I \cong \int d^3r_1 \int d^3r_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \cong 20\pi^2$$

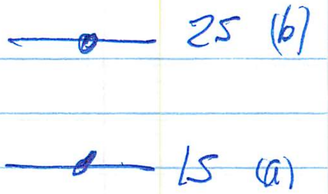
$$\Delta E_c = \underset{\overset{\uparrow}{27.2\text{eV}}}{\left[\frac{e^2}{4\pi\epsilon_0 a_0}\right]} \underset{\overset{\uparrow}{5/4}}{\left[\frac{20}{16}\right]} \cong \boxed{34\text{eV}}$$

$$E_{tot} \cong -108.8\text{eV} + 34\text{eV} \cong \boxed{-74.8\text{eV}}$$

Expt value is $\boxed{-78.9\text{eV}}$ !

Reason: Still have $\psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\phi(\vec{r}_2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]/\sqrt{2}$

but $\phi$ is altered due to Coulomb repulsion



What about excited states of Helium?

singlet

$$\psi_A(1,2) = \psi_S(\vec{r}_1,\vec{r}_2)\,\chi_A(1,2)$$

OR

triplet

$$\psi_A(1,2) = \psi_A(\vec{r}_1,\vec{r}_2)\,\chi_S(1,2)$$

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$$\psi_\pm(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_a(\vec{r}_1)\,\phi_b(\vec{r}_2) \pm \phi_a(\vec{r}_2)\,\phi_b(\vec{r}_1)\right] \chi_\mp$$

↑ ignore ($\chi_+ = \chi_S$, $\chi_- = \chi_A$)

$$E \cong \underbrace{E_{1s}^{Z=2} + E_{2s}^{Z=2}}_{E_0\ (\text{ignoring Coulomb repulsion between electrons})} + \Delta E$$

$$\Delta E = \frac{1}{2}\int d^3r_1 \int d^3r_2 \left[\phi_a^*(1)\,\phi_b^*(2) \pm \phi_a^*(2)\,\phi_b^*(1)\right] \frac{e^2}{4\pi\epsilon_0 r_{12}} \left[\phi_a(1)\,\phi_b(2) \pm \phi_a(2)\,\phi_b(1)\right]$$

$$\Delta E = \iint \frac{d^3r_1\, d^3r_2\, e^2}{4\pi\epsilon_0 r_{12}} \left[ |\phi_a(1)|^2 |\phi_b(2)|^2 \right]$$

direct integral

J

$$\left.\begin{aligned} &\pm \frac{1}{2} \int d^3r_1 \int d^3r_2\ \phi_a^*(1)\, \phi_b(1)\ \phi_b^*(2)\, \phi_a(2)\ \frac{e^2}{4\pi\epsilon_0 r_{12}} \\ &\qquad\qquad = \\ &\pm \frac{1}{2} \int d^3r_1 \int d^3r_2\ \phi_a^*(2)\, \phi_b(2)\ \phi_b^*(1)\, \phi_a(1)\ \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned}\right\} \pm K$$

$$\boxed{\Delta E = J \pm K}$$

exchange integral

where $K = \int d^3r_1 \int d^3r_2\ \phi_a^*(1)\, \phi_b(1)\ \frac{e^2}{4\pi\epsilon_0 r_{12}}\ \phi_b^*(2)\, \phi_b(2) \geq 0$

SINGLET symmetric spatial wave f'n $E = E_0 + J + K$

TRIPLET antisymmetric spatial wavef'n $E = E_0 + J - K$

Again, this agrees with Hund's rule!

$$\boxed{\Delta E_{S/A} = 2K}$$