How should we define two particles as being antisymmetric or symmetric to each other?

→ ψ_{symm}

$$\psi_{symm} = \frac{\psi(1,2)+\psi(2,1)}{\sqrt{2}}$$

→ ψ_{anti}

$$\psi_{anti} = \frac{\psi(1,2)-\psi(2,1)}{\sqrt{2}}$$

where $\frac{1}{\sqrt{2}}$ is the normalization constant in both cases.

However, we are still neglecting to consider something. Let us use He as an example:

He = $1s^2$, where A = 1s and B = 1s. In this case, the total wave function is described as:

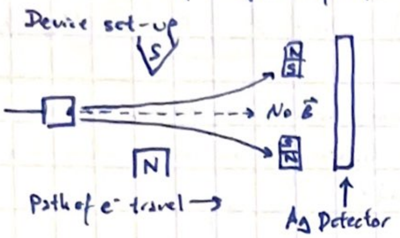
$$\psi_{He} = \frac{\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(2)\psi_{1s}(1)}{\sqrt{2}} = 0$$

→ The wave function describing $2e^-$ in Helium cannot ~~be~~ $= 0$. We are missing the spin, which distinguishes one particle from another.

Stern-Gerlach Experiment:

→ Consideration of magnetic field

Device set-up



If the electron is in state $l=1$, we would expect to see:

on the Ag detector. Corresponding to $m_l = +l, 0, -l$.

However, the experimental results obtained appeared like:

- Confirmed that angular momentum is quantized in space, and $s = \pm 1/2$.

The spin of an e^- ~~is~~ corresponds to a new type of angular momentum, and is the "fourth quantum number":

→ Since $l_z = m_l\hbar$, $m_s = \pm \frac{1}{2}\hbar$.

The spin operator, $\hat{s}$, when applied to a ~~wave function~~ measured spin, α or β, will return $m_s = \pm\frac{1}{2}\hbar$. These two states are defined as α and β, which correspond to up and down spin respectively:

$$\psi_{m_s} = \tfrac{1}{2}\hbar = \alpha\ (\uparrow) \qquad \psi_{m_s} = -\tfrac{1}{2}\hbar = \beta\ (\downarrow)$$

$$E_{e^-} = E_{orb} + E_{spin}, \quad \psi_e = \psi_{n,l,m_l}(\vec{r}) \cdot \begin{Bmatrix}\alpha \\ \beta\end{Bmatrix}$$

Modifying the expression for ψ_{He}, we get:

$$\psi_{He} = \frac{\psi_{1s}(1)\alpha(1)\psi_{1s}(2)\beta(2) - \psi_{1s}(2)\alpha(2)\psi_{1s}(1)\beta(1)}{\sqrt{2}} = \psi_{1s}(1)\psi_{1s}(2)\,\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}$$

"Spin cone" Similar to how

$\hat{s}$:

$$\hat{S}_z\alpha = \tfrac{\hbar}{2}\alpha \qquad \hat{S}^2\alpha = \tfrac{3}{4}\hbar^2\alpha = \hbar^2 s(s+1)\alpha$$

$$\hat{S}_z\beta = -\tfrac{\hbar}{2}\beta \qquad \hat{S}^2\beta = \tfrac{3}{4}\hbar^2\beta = \hbar^2 s(s+1)\beta$$

$\hat{S}_x\alpha = \frac{\hbar}{2}\beta$ → Not an eigenfunction

$\hat{S}_x\beta = \frac{\hbar}{2}\alpha$ → Not an eigenfunction

$\hat{S}_x(\alpha+\beta) = \frac{\hbar}{2}\beta + \frac{\hbar}{2}\alpha$ → eigenfunction.

$\hat{S}_x(\alpha-\beta)$ also an eigenfunction.

- α and β are not eigenfunctions of S_x and S_y, as shown:

$$\left.\begin{aligned} \hat{S}_x\alpha &= \tfrac{\hbar}{2}\beta \\ \hat{S}_x\beta &= \tfrac{\hbar}{2}\alpha \\ \hat{S}_y\alpha &= \tfrac{i\hbar}{2}\beta \\ \hat{S}_y\beta &= -\tfrac{i\hbar}{2}\alpha \end{aligned}\right\}$$

α and β are orthogonal to e/o and normalized

$$\int \alpha^*\alpha\, d\sigma = \int \beta^*\beta\, d\sigma = 1$$

$$\int \alpha^*\beta\, d\sigma = \int \beta^*\alpha\, d\sigma = 0$$

$\psi = \alpha + \beta$: Is this wave function an eigenfunction of the z operator?

$$\hat{S}_z\psi = \hat{S}_z\alpha + \hat{S}_z\beta = \tfrac{\hbar}{2}\alpha - \tfrac{\hbar}{2}\beta = \tfrac{\hbar}{2}(\alpha - \beta)$$

μ_o has equal probability of measuring α and β in z.

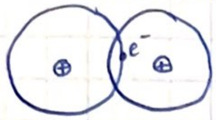
Is $\psi = \alpha + \beta$ and eigenfunction of the spin operator, $\hat{S}$?

$\hat{S}\psi = \tfrac{3}{4}\hbar^2(\alpha + \beta)$ Yes

Is $\psi = \alpha + \beta$ an eigenfunction of the x operator, $\hat{S}_x$?

$$\hat{S}_x\psi = \tfrac{\hbar}{2}\beta + \tfrac{\hbar}{2}\alpha = \tfrac{\hbar}{2}(\alpha + \beta)$$

Chemical Bonds - Consider H_2^+:



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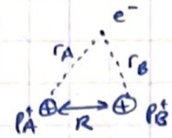


"MOLCAO" or "LCAO" - Linear combination of orbitals

- Note that $|\Delta E|$ from $e^- + p^+$ (H) is 1317 kJ/mol
- Similarly, $|\Delta E|$ from $H \to H_2$ is 436 kJ/mol

→ Forming diatomic hydrogen is very favorable in comparison to the formation of H from p^+ and e^-

$$K = K_e + K_A + K_B$$

$$U = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_A} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_B} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}$$

The Probability Statement may be expanded to

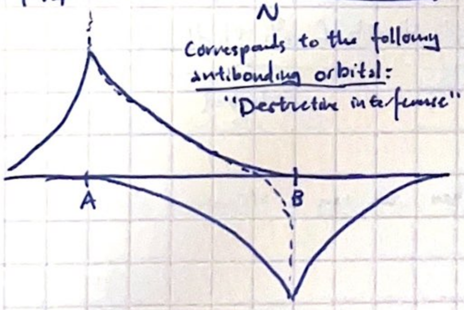
$$P = |\psi|^2 = \frac{|\psi_A|^2 + |\psi_B|^2 + \psi_A^*\psi_B + \psi_A\psi_B^*}{N}$$:

The most e^- density is at the midpoint b/w A and B.

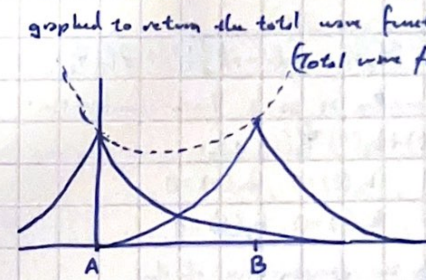
$$P = |\psi|^2 = \frac{|\psi_A|^2 + |\psi_B|^2 - \psi_A^*\psi_B + \psi_A\psi_B^*}{N}$$

Corresponds to the following antibonding orbital:

"Destructive interference"



In this case, the wave function, ψ, may be represented as $\psi = b_A\psi_A + b_B\psi_B$. Since $\psi_{1s} \sim e^{-r/a_0}$, this can be graphed to return the total wave function:



There are also two possible outcomes with 2 probabilities:

Outcomes:

$b_A = b_B$, or

$b_A = -b_B$.

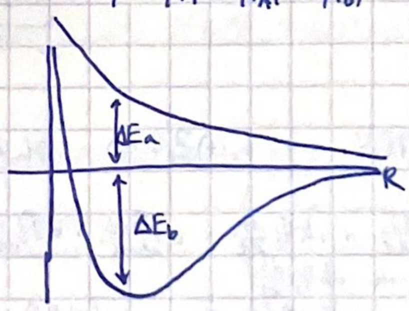
Probabilities:

$|b_A|^2 = |b_B|^2$

And 2 options for the wave function:

$$\psi = \frac{\psi_A + \psi_B}{\sqrt{2}} \text{ or } \psi = \frac{\psi_A - \psi_B}{\sqrt{2}}.$$

$$P = |\psi|^2 = |\psi_A|^2 + |\psi_B|^2$$



↳ NOT TO SCALE

→ Where

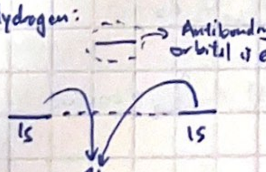
a = antibonding

b = bonding

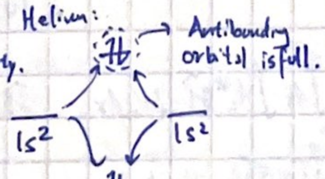
Note that $|\Delta E_a|$ is actually greater than $|\Delta E_b|$.

This is the reason why H_2 exists but He_2 does not.

Hydrogen:



Helium:



The values of the probabilities, b_A, and b_B are both dependent on time, therefore, we can apply this information for spectroscopy applications:

The wave function changes from $\psi_{n=1}$ to $\psi_{n=2}$, and as such the probabilities are also changed: these changes

$\Delta E = E_{final} - E_{initial}$ may be measured to determine the wavelengths.