Review: Distinct - no symmetrization of ψ_{tot} under x-change of particles

Bosons - symmetrization " "

Fermions - antisymmetrization " " ⇒ Pauli Exclusion

Spin-Statistics Theorem:

Bosons - integer spin

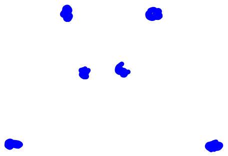
Fermions - $\frac{1}{2}$-integer spin (most of "particles" we see)

X-change force ($\langle (x_1 - x_2)^2 \rangle$)

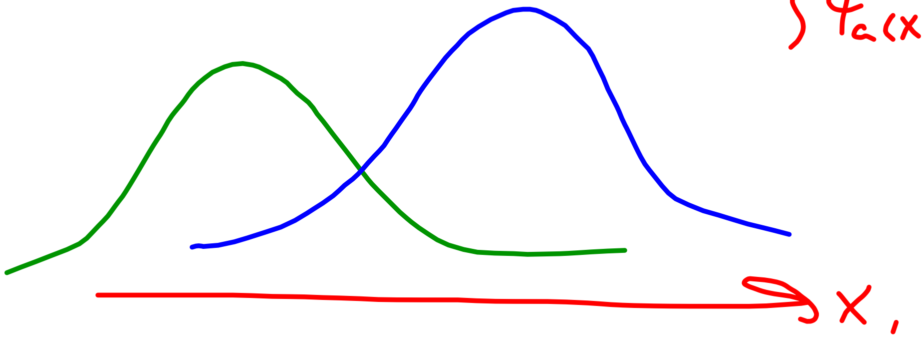
Distinct

Symm. Spatial ψ "attraction"

Antisymm. spatial ψ "repulsion"



$$\int \psi_a^*(x_1)\,\psi_b(x_1)\,dx_1$$



If we have 2 states: $A\ \frac{1}{\sqrt{2}}\left(\psi_a(x_1)\psi_b(x_2)-\psi_b(x_1)\psi_a(x_2)\right)$

If we have 3 states: $A\ \frac{1}{\sqrt{6}}\Big(\psi_a(x_1)\psi_b(x_2)\psi_c(x_3)-\psi_a(x_2)\psi_b(x_1)\psi_c(x_3)$

$-\psi_a(x_1)\psi_b(x_3)\psi_c(x_2)-\psi_a(x_3)\psi_b(x_2)\psi_c(x_1)$

$+\psi_a(x_2)\psi_b(x_3)\psi_c(x_1)+\psi_a(x_3)\psi_b(x_1)\psi_c(x_2)\Big)$

In what systems do we need to worry about symmetrization? Electrons in atoms!!

Electrons in Atoms "Chemistry"

$$\hat{H} = \sum_{j=1}^{Z} \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right) \frac{Ze^2}{r_j} \right)$$
$$+ \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right) \sum_{j\neq k}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

Solving this would suck!!

So..., a) Ignore e-e interactions and solve TISE.

b) We account for e-e interactions through symmetrization considerations.

Ignoring e-e:

$$\hat{H}\psi_{tot} = \sum_{j=1}^{Z} H_j^{\text{hyd w/ } Ze} \psi_{tot} = E_{tot}\psi_{tot}$$

Assume: $\psi_{tot} = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)\psi_c(\vec{r}_3)\ldots$

Changes: $E_n \propto -\frac{(e^2)^2}{n^2} \Rightarrow E_n^Z \propto -\frac{(Ze^2)^2}{n^2} = Z^2 E_n$

Helium (Example)

$\psi_a(\vec{r}_1), \psi_b(\vec{r}_2), \chi^1_\pm, \chi^2_\pm$

For electrons ψ_{tot} has to be antisymmetric under $1 \leftrightarrow 2$.

$\psi_{tot} = \psi_{space}\,\psi_{spin}$

~~A A = S~~
A S = A
S A = A
~~S S = S~~

If the states are the <u>same</u> then that part has to be symmetric!!

$\psi^1_a \psi^2_a \chi^1_+ \chi^2_-$ A: $\frac{1}{\sqrt{2}}(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_1)\psi_a(\vec{r}_2))$

$\times$ Spin

Could we: $\psi_{tot} = \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- - \chi^1_-\chi^2_+)$

Enumerating energy levels for He in increasing energy:

Ignoring e-e interactions, $E_{tot} = \underset{\substack{\shortparallel \\ -\frac{(Ze^2)^2}{n^2}}}{E_n} + E_{n'}$

$$\psi_{tot} = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- - \chi^1_-\chi^1_+)$$

$$\psi_{tot} = \psi_{100}(\vec{r}_1), \psi_{200}(\vec{r}_2), \chi^1_\pm, \chi^2_\pm$$

$$\overbrace{\frac{1}{\sqrt{2}}(\psi^1_{100}\psi^2_{200} + \psi^2_{100}\psi^1_{200})}^{\text{symm spatial}}\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- - \chi^1_-\chi^2_+)$$

$$\underbrace{\frac{1}{\sqrt{2}}(\psi^1_{100}\psi^2_{200} - \psi^2_{100}\psi^1_{200})}_{\text{antisym. spatial}}\left\{\begin{array}{l}\frac{1}{\sqrt{2}}(\chi^1_+\chi^2_- + \chi^1_-\chi^2_+) \\ \chi^1_+\chi^2_+\end{array}\right.$$

e-e int.

symm. case ⇒ closer together ⇒ E is higher (parahelium)
antisymm. case ⇒ further apart ⇒ E is lower (orthohelium)