Review: $\psi_{tot} = \psi_1 \psi_2 \in H_{tot} = H_1 \otimes H_2$

$$\hat{O}_1 : \langle \psi_1 | \hat{O}_1 \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle$$

$$\hat{O}_1 \hat{O}_2 : \langle \psi_1 | \hat{O}_1 \psi_1 \rangle \langle \psi_2 | \hat{O}_2 \psi_2 \rangle$$

$$\hat{O}_1 + \hat{O}_2 : \langle \psi_1 | \hat{O}_1 \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle + \langle \psi_1 | \psi_1 \rangle \langle \psi_2 | \hat{O}_2 \psi_2 \rangle$$

For: $\vec{S} = \vec{S}_1 + \vec{S}_2$: $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$

$$\hat{S}^2 = (\vec{S}_1 + \vec{S}_2) \cdot (\vec{S}_1 + \vec{S}_2)$$

$$= \hat{S}_1^2 + \hat{S}_2^2 + 2 \underbrace{\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2}_{\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}}$$

Naively: $\overbrace{\uparrow\uparrow, \downarrow\downarrow}, \uparrow\downarrow, \downarrow\uparrow$

Demanding eigenspinors of $\hat{S}^2$ and $\hat{S}_z$:

$$\left.\begin{array}{ll} & \underline{\hat{S}_z} \\ \chi_+ = \uparrow\uparrow & m_s = +1 \\ \chi_0 = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) & m_s = 0 \\ \chi_- = \downarrow\downarrow & m_s = -1 \end{array}\right\} \begin{array}{l} s = 1 \\ \hat{S}^2 \chi_{\substack{+ \\ 0 \\ -}} = 2\hbar^2 \chi_{\substack{+ \\ 0 \\ -}} \end{array}$$

$\hbar^2 s(s+1)$

"triplet"

$$\chi_s = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \qquad m_s = 0, \quad s = 0 \qquad \text{"singlet"}$$

Note: Not necessary for ψ_{tot} to factorize completely.

$$\psi_{tot} = \frac{1}{\sqrt{2}}(\psi_{321}\chi_+ + \psi_{320}\chi_-) \neq \psi_{nlm}\chi$$

$$\langle \psi_{tot} | \psi_{tot} \rangle = 1$$

$$= \frac{1}{2}\Big(\cancelto{1}{\int \psi_{321}^* \psi_{321} dV} \cancelto{1}{\langle \chi_+ | \chi_+ \rangle}$$

$$+ \cancelto{1}{\int \psi_{320}^* \psi_{320} dV} \cancelto{1}{\langle \chi_- | \chi_- \rangle}$$

$$+ \cancelto{0}{\int \psi_{321}^* \psi_{320} dV} \cancelto{0}{\langle \chi_+ | \chi_- \rangle}$$

$$+ \cancelto{0}{\int \psi_{320}^* \psi_{321} dV} \cancelto{0}{\langle \chi_- | \chi_+ \rangle} \Big)$$

$$= \frac{2}{2} = 1$$

$$\hat{O}_{space} + \hat{O}_{spin} : \frac{1}{2}\Big(\int \psi_{321}^* \hat{O}_{space} \psi_{321} dV \langle \chi_+ | \chi_+ \rangle$$

$$+ \int \psi_{321}^* \psi_{321} dV \langle \chi_+ | \hat{O}_{spin} \chi_+ \rangle$$

$$+ \cdots \Big) \quad 8 \text{ terms total}$$

$$\hat{O}_{space} \hat{O}_{spin} : \frac{1}{2}\Big(\int \psi_{321}^* \hat{O}_{space} \psi_{321} dV \langle \chi_+ | \hat{O}_{spin} \chi_+ \rangle$$

$$+ \cdots \Big) \quad 4 \text{ terms total}$$

Two-particle Systems

$x_1 y_1 z_1$
$x_2 y_2 z_2$

$\Psi(\vec{r},t) \longrightarrow \Psi(\vec{r}_1, \vec{r}_2, t)$ not necessarily $\Psi(\vec{r}_1,t)\Psi(\vec{r}_2,t)$

$$\hat{H}_{tot} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

$$\int \Psi^*(\vec{r}_1,\vec{r}_2,t)\,\Psi(\vec{r}_1,\vec{r}_2,t)\,d^3r_1\,d^3r_2 = 1$$

TDSE: $i\hbar \frac{\partial \Psi_{tot}}{\partial t} = \hat{H}_{tot}\Psi_{tot}$ not $i\hbar\frac{\partial \Psi_1}{\partial t} = \hat{H}_1\Psi_1$

$i\hbar\frac{\partial \Psi_2}{\partial t} = \hat{H}_2\Psi_2$

Assume general solution expands in a basis of separable solutions (stationary states): $\Psi(\vec{r}_1,\vec{r}_2,t) = \sum_n \psi_n(\vec{r}_1,\vec{r}_2)\,e^{-i\frac{E_n}{\hbar}t}$

$\sum$ assumes discrete (use k for cont.)

Where $\psi_n(\vec{r}_1,\vec{r}_2)$ satisfy TISE: $\hat{H}_{tot}\psi_n(\vec{r}_1,\vec{r}_2)$

$$= E_n \underbrace{\psi_n(\vec{r}_1,\vec{r}_2)}$$

form an orthonormal basis of $H_{tot} = H_1 \otimes H_2$

Is that all ??? No !!!

2 particles : 1, 2

Each of these must be in some state: ψ_a or ψ_b

We might write: $\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$

If 2 particles are the same, what is the effect of swapping them?

$$P_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$$

$$P_{12}^2\psi(\vec{r}_1, \vec{r}_2) = P_{12}\psi(\vec{r}_2, \vec{r}_1) = \psi(\vec{r}_1, \vec{r}_2)$$

eigenvalue eqn.

P_{12} has eigenvalues ± 1

How is $\psi(\vec{r}_1, \vec{r}_2)$ related to $\psi(\vec{r}_2, \vec{r}_1)$?

$+1$: $P_{12}\psi(\vec{r}_1, \vec{r}_2) = +1\,\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$

-1 : $P_{12}\psi(\vec{r}_1, \vec{r}_2) = -1\,\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$

$\psi_+ = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$ bosons

$\psi_- = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$ fermions

ψ_a

$\psi_- = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)\right) = 0$