L58-Pauli Exclusion Principle

Wednesday, February 10, 2016 14:07

* Quantum mechanical multi-particle states:

- for indistinguishable particles, $P(\vec{r}_1, \vec{r}_2) = P(\vec{r}_2, \vec{r}_1)$

define P_{12} "exchange parity" operator: $P_{12}\,\Psi(\vec{r}_1, \vec{r}_2) \equiv \Psi(\vec{r}_2, \vec{r}_1)$

if $\boxed{P_{12}\Psi_\pm = \pm\Psi_\pm}$ then $P_\pm(\vec{r}_2, \vec{r}_1) = (P_{12}\Psi_\pm)^*(P_{12}\Psi_\pm) = \pm\Psi_\pm^* \cdot \pm\Psi_\pm = P_\pm(\vec{r}_1, \vec{r}_2)$

so the probability is invariant under particle exchange.

solution: let $\Psi_\pm = A(\Psi \pm P_{12}\Psi)$ [anti] symmetrized wave function

then $P_{12}\Psi_\pm = A(P_{12}\Psi \pm P_{12}P_{12}\Psi) = \pm A(\Psi \pm P_{12}\Psi) = \pm\Psi_\pm$

$$\Psi_\pm(\vec{r}_1, \vec{r}_2) = A\left(\Psi_a(\vec{r}_1)\Psi_b(\vec{r}_2) \pm \Psi_b(\vec{r}_1)\Psi_a(\vec{r}_2)\right)$$

normalization: $\langle\Psi_\pm|\Psi_\pm\rangle = |A|^2\left(\langle\Psi_a|\Psi_a\rangle_1\langle\Psi_b|\Psi_b\rangle_2 \pm \langle\Psi_a|\Psi_b\rangle_1\langle\Psi_b|\Psi_a\rangle_2 \pm \langle\Psi_b|\Psi_a\rangle_1\langle\Psi_a|\Psi_b\rangle_2 + \langle\Psi_b|\Psi_b\rangle_1\langle\Psi_a|\Psi_a\rangle\right) = 2.$

$\langle\Psi_a|\Psi_a\rangle = 1 \quad \langle\Psi_a|\Psi_b\rangle = 0$

- spin-statistics theorem: P_{12} (particle exchange) has the same properties as rotating the relative co-ordinate space by 360° for half-integer spin, this incurs a (-) sign

+ : Bosons particles with integer spin $S = 0, 1, 2, \ldots$

− : Fermions " " half-integer spin $S = 1/2, 3/2, \ldots$

for a hand-waving argument involving a "perfect murder" with "twists in the plot", see http://math.ucr.edu/home/baez/spin_stat.html

* Pauli Exclusion principle: no two identical fermions can occupy the same single-particle state: ie $\Psi_a = \Psi_b$

$$\Psi_-^{aa}(\vec{r}_1, \vec{r}_1) = A\left(\Psi_a(\vec{r}_1)\Psi_a(\vec{r}_2) - \Psi_a(\vec{r}_1)\Psi_a(\vec{r}_2)\right) = 0$$

* note that $[\mathcal{H}, P_{12}] = 0$ since $\mathcal{H}_{12} = \mathcal{H}_{21}$ and $\mathcal{H}_{12} P_{12} = P_{12} \mathcal{H}_{21}$
thus particle exchange parity is a constant of the motion

[anti]symmetric states are always [anti]symmetric.

* Slater determinant – used to antisymmetrize an n-particle wavefunction built from single-particle states:
– given the 3 (or n) single-particle wave-functions $\psi_a(x), \psi_b(x), \psi_c(x)$

let $\psi_{abc}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(x_1) & \psi_a(x_2) & \psi_a(x_3) \\ \psi_b(x_1) & \psi_b(x_2) & \psi_b(x_3) \\ \psi_c(x_1) & \psi_c(x_2) & \psi_c(x_3) \end{vmatrix}$ [determinant has 6 terms]

$$= \frac{1}{\sqrt{3}} \left(\psi_a(x_1)\psi_b(x_2)\psi_c(x_3) + a\to b\to c\to a + a\to c\to b\to a - \psi_a(x_1)\psi_b(x_3)\psi_c(x_2) - \dots - \dots \right)$$

then $P_{23}\,\psi_{abc} =$ [switch bottom and top rows] $= -\psi_{abc}$

likewise, $P_{12}\psi_{abc} = P_{23}\psi_{abc} = P_{31}\psi_{abc} = -\psi_{abc}$

ie. ψ_{abc} is completely antisymmetric, as required by the Pauli Exclusion Principle.

* Exchange "Force": calculate $\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

for $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \Rightarrow \psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi(x_1, x_2) \pm \psi(x_2, x_1)\right)$

A) distinguishable particles:

$$\langle x_1^2 \rangle = \int dx_1 dx_2\ \psi_a^*(x_1)\psi_b^*(x_2)\, x_1^2\, \psi_a(x_1)\psi_b(x_2) = \int dx_1\, \psi_a^* x_1^2 \psi_a \cdot \int dx_2\, \psi_b^* \psi_b = \langle x^2 \rangle_a$$

$$\langle x_2^2 \rangle = \dots\ x_2^2\ \dots = \int dx_1\, \psi_a^* \psi_a \cdot \int dx_2\, \psi_b^* x_2^2 \psi_b = \langle x^2 \rangle_b$$

$$\langle x_1 x_2 \rangle = \dots\ x_1 x_2\ \dots = \int dx_1\, \psi_a^* x_1 \psi_a \cdot \int dx_2\, \psi_b^* x_2 \psi_b = \langle x \rangle_a \langle x \rangle_b$$

$$\boxed{\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a - 2\langle x \rangle_a \langle x \rangle_b + \langle x^2 \rangle_b}$$

B) identical particles:

$$\langle x_1^2\rangle = \int dx_1 dx_2 \; \frac{1}{\sqrt{2}}\left(\psi_{ab}^*(x_1,x_2) \pm \psi_{ab}^*(x_2,x_1)\right) x_1^2 \; \frac{1}{\sqrt{2}}\left(\psi_{ab}(x_1,x_2) \pm \psi_{ab}(x_2,x_1)\right)$$

$$= \frac{1}{2}\left[\int dx_1 \psi_a^* x_1^2 \psi_a \cdot \int dx_2 \psi_b^* \psi_b + \int dx_1 \psi_b^* x_1^2 \psi_b \cdot \int dx_2 \psi_a^* \psi_a\right]$$

$$\pm \frac{1}{2}\left[\int dx_1 \psi_a^* x_1^2 \psi_b \cdot \int dx_2 \psi_b^* \psi_a + \text{complex conjugate}\right]$$

$\int dx_2 \psi_b^* \psi_a = 0$

$$= \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right) \qquad \text{likewise} \quad \langle x_2^2\rangle = \frac{1}{2}\left[\langle x^2\rangle_a + \langle x^2\rangle_b\right] = \langle x_1^2\rangle$$

$$\langle x_1 x_2\rangle = \frac{1}{2}\left[\int dx_1 \psi_a^* x_1 \psi_a \cdot \int dx_2 \psi_b^* x \psi_b + \int dx_1 \psi_b^* x_1 \psi_b \cdot \int dx_2 \psi_a^* x_2 \psi_a\right]$$

$$\pm \frac{1}{2}\left[\underbrace{\int dx_1 \psi_a^* x_1 \psi_b}_{\langle x\rangle_{ab}} \cdot \underbrace{\int dx_2 \psi_b^* x \psi_a}_{\langle x\rangle_{ab}^*} + \int dx_1 \psi_b^* x_1 \psi_a \cdot \int dx_2 \psi_a^* x_2 \psi_b\right]$$

$$= \langle x\rangle_a \langle x_a\rangle \pm |\langle x\rangle_{ab}|^2$$

thus $\langle (x_1 - x_2)^2\rangle = \underbrace{\langle x^2\rangle_a - 2\langle x\rangle_a\langle x\rangle_b + \langle x^2\rangle_b}_{\langle (x_1-x_2)^2\rangle \text{ distinguishable particles.}} \mp \underbrace{2|\langle x\rangle_{ab}|^2}_{\text{bosons/fermions.}}$

* example: H_2 covalent bond

$$\Psi(\vec{r}_1,\vec{r}_2) = \underbrace{\Psi(\vec{R})}_{\text{CM, free}} \cdot \underbrace{\psi(\vec{r})}_{\text{relative}} \cdot \underbrace{\chi(s)}_{\substack{\text{total spin} \\ \text{singlet, antisym.}}}$$

Thus $\psi(\vec{r})$ should be symmetric so that $\Psi(\vec{r}_1,\vec{r}_2)$ is antisym.

- thus the electrons spend more time between the two nucleus and help to bond the molecule covalently.