

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 $P_{12} \psi_{\pm} = \pm \psi_{\pm}$ 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 $P_{12} \psi_{\pm} = A(P_{12} \psi \pm P_{12} P_{12} \psi) = \pm A(\psi \pm P_{12} \psi) = \pm \psi_{\pm}$

$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = A(\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1) \psi_a(\vec{r}_2))$

normalization: $\langle \psi_{\pm} | \psi_{\pm} \rangle = |A|^2 (\langle \psi_a | \psi_a \rangle \langle \psi_b | \psi_b \rangle \pm \langle \psi_a | \psi_b \rangle \langle \psi_b | \psi_a \rangle \pm \langle \psi_b | \psi_a \rangle \langle \psi_a | \psi_b \rangle + \langle \psi_b | \psi_b \rangle \langle \psi_a | \psi_a \rangle) = 2$
 $\langle \psi_a | \psi_a \rangle = 1$ $\langle \psi_a | \psi_b \rangle = 0$

- 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 $S=0, 1, 2, \dots$

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

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 $\psi_a = \psi_b$

$\psi_{-}^{aa}(\vec{r}_1, \vec{r}_1) = A(\psi_a(\vec{r}_1) \psi_a(\vec{r}_1) - \psi_a(\vec{r}_1) \psi_a(\vec{r}_1)) = 0$

- * note that $[H, P_{12}] = 0$ since $H_{12} = H_{21}$ and $H_{12} P_{12} = P_{12} H_{21}$
 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 $\psi_a(x), \psi_b(x), \psi_c(x)$

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

$$= \frac{1}{\sqrt{3}} \left(\begin{vmatrix} \psi_a(x_1) & \psi_b(x_2) & \psi_c(x_3) \\ -\psi_a(x_1) & \psi_b(x_3) & \psi_c(x_2) \end{vmatrix} + \dots \right)$$

then $P_{23} \psi_{abc} = [\text{switch 2nd and 3rd bottom rows}] = -\psi_{abc}$

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

A) distinguishable particles:

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

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

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

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

B) identical particles:

$$\begin{aligned}
 \langle x_1^2 \rangle &= \int dx_1 dx_2 \frac{1}{\sqrt{2}} (\psi_{ab}^*(x_1, x_2) \pm \psi_{ab}^*(x_2, x_1)) x_1^2 \frac{1}{\sqrt{2}} (\psi_{ab}(x_1, x_2) \pm \psi_{ab}(x_2, x_1)) \\
 &= \frac{1}{2} \left[\int dx_1 \psi_a^* x_1^2 \psi_a \cdot \int dx_2 \psi_b^* \psi_b + \int dx_1 \psi_b^* x_1^2 \psi_b \cdot \int dx_2 \psi_a^* \psi_a \right] \\
 &\quad \pm \frac{1}{2} \left[\int dx_1 \psi_a^* x_1^2 \psi_b \cdot \int dx_2 \psi_b^* \psi_a + \text{complex conjugate} \right] \\
 &= \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) \quad \text{like wise} \quad \langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) = \langle x_1^2 \rangle
 \end{aligned}$$

$$\begin{aligned}
 \langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int dx_1 \psi_a^* x_1 \psi_a \cdot \int dx_2 \psi_b^* x_2 \psi_b + \int dx_1 \psi_b^* x_1 \psi_b \cdot \int dx_2 \psi_a^* x_2 \psi_a \right] \\
 &\quad \pm \frac{1}{2} \left[\underbrace{\int dx_1 \psi_a^* x_1 \psi_b}_{\langle x \rangle_{ab}} \cdot \underbrace{\int dx_2 \psi_b^* x_2 \psi_a}_{\langle x \rangle_{ab}^*} + \int dx_1 \psi_b^* x_1 \psi_a \cdot \int dx_2 \psi_a^* x_2 \psi_b \right] \\
 &= \langle x \rangle_a \langle x_a \rangle \pm |\langle x \rangle_{ab}|^2
 \end{aligned}$$

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

2017-02-03

* 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.