Covalent Binding — Exchange Interaction

Electrons are spin-$\frac{1}{2}$ $\left(\frac{\hbar}{2}\right)$ fermions

$\Rightarrow$ total wavefunction must be antisymmetric under interchange of any 2 electrons.

Spin-Statistics Theorem.

$$\psi_{total}(\vec{r}) = \psi_{space}(\vec{r})\, \psi_{spin}$$

← no $\vec{r}$ dependence.

ψ_{spin}

$$|s=0,\ m_s=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle\right)$$

Spin-0 singlet antisymmetric $1 \leftrightarrow 2$

$$|s=1,\ m_s=+1\rangle = |\uparrow_1\uparrow_2\rangle$$

$$|s=1,\ m_s=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle\right)$$

$$|s=1,\ m_s=-1\rangle = |\downarrow_1\downarrow_2\rangle$$

spin-1 triplet

symmetric $1 \leftrightarrow 2$

ψ_{total} is antisymmetric

If ψ_{spin} is anti $\Rightarrow$ ψ_{space} is sym.

If ψ_{spin} is sym. $\rightarrow$ ψ_{space} is antisym.

1-dimensional

$$\psi(x_1,x_2) = \begin{cases} \psi_c(x_1,x_2) = \psi_a(x_1)\,\psi_b(x_2) \\ \psi_{sym}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right] \\ \psi_{ANTI}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)\right] \end{cases}$$

Expectation value of the square of the separation.

$$\langle \Delta x^2 \rangle_\psi = \langle \psi | (x_2 - x_1)^2 | \psi \rangle$$

$$= \langle x_1^2 \rangle_\psi + \langle x_2^2 \rangle_\psi - 2\langle x_1 x_2 \rangle_\psi$$

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① Distinguishable Particles (classical) ψ_c

$$\langle x_1^2 \rangle_c \equiv \langle \psi_c | x_1^2 | \psi_c \rangle \equiv \int_{x_1=-\infty}^{+\infty} \int_{x_2} x_1^2\, \psi_c^*(x_1,x_2)\, \psi_c(x_1,x_2)\, dx_1\, dx_2$$

$$= \int_{x_1} x_1^2\, \psi_a^*(x_1)\psi_a(x_1)\, dx_1 \underbrace{\int_{x_2} \psi_b^*(x_2)\psi_b(x_2)\, dx_2}_{1} = \langle x_1^2 \rangle_a$$

$$\langle x_2^2 \rangle_c = \langle x_2^2 \rangle_b$$

$$\langle x_1 x_2\rangle_c = \langle \psi_c | x_1 x_2 | \psi_c\rangle = \langle \psi_a | x_1 | \psi_a\rangle \langle \psi_b | x_2 | \psi_b\rangle$$

$$= \int_{x_1} x_1 |\psi_a(x_1)|^2 dx_1 \int_{x_2} x_2 |\psi_b(x_2)|^2 dx_2 = \langle x\rangle_a \langle x\rangle_b$$

$$\langle \Delta x^2\rangle_c = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a \langle x\rangle_b$$

Indistinguishable particles – Symmetric

$$\psi_s(x_1,x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right]$$

$$\langle x_1^2\rangle_s = \langle \psi_s | x_1^2 | \psi_s\rangle$$

$$= \frac{1}{2}\Big[\int_{x_1} x_1^2 |\psi_a(x_1)|^2 dx_1 \underbrace{\int_{x_2} |\psi_b(x_2)|^2 dx_2}_{1}$$

$$+ \underbrace{\int_{x_2} |\psi_a(x_2)|^2 dx_2}_{1} \int_{x_1} x_1^2 |\psi_b(x_1)|^2 dx_1$$

$$+ \int_{x_1} x_1^2 \psi_a^*(x_1)\psi_b(x_1)dx_1 \cancelto{0}{\int_{x_2} \psi_b^*(x_2)\psi_a(x_2)dx_2}$$

$$+ \int_{x_1} x_1^2 \psi_b^*(x_1)\psi_a(x_1)dx_1 \cancelto{0}{\int_{x_2} \psi_a^*(x_2)\psi_b(x_2)dx_2}\Big]$$

$$\langle x_1^2\rangle_s = \frac{1}{2}\left[\langle x^2\rangle_a + \langle x^2\rangle_b\right]$$

$$\langle x_2^2\rangle_s = \frac{1}{2}\left[\langle x^2\rangle_a + \langle x^2\rangle_b\right]$$

$$\langle x_1 x_2\rangle_s = \frac{1}{2}\Big[\int_{x_1} x_1 |\psi_a(x_1)|^2 dx_1 \int_{x_2} x_2 |\psi_b(x_2)|^2 dx_2$$

$$+ \int_{x_1} x_1 |\psi_b(x_1)|^2 dx_1 \int_{x_2} x_2 |\psi_a(x_2)|^2 dx_2$$

$$+ \int_{x_1} x_1 \psi_a^*(x_1)\psi_b(x_1) dx_1 \int_{x_2} x_2 \psi_b^*(x_2)\psi_a(x_2) dx_2$$

$$+ \int_{x_1} x_1 \psi_b^*(x_1)\psi_a(x_1) dx_1 \int_{x_2} x_2 \psi_a^*(x_2)\psi_b(x_2) dx_2\Big]$$

$$= \frac{1}{2}\left[\langle x\rangle_a \langle x\rangle_b + \langle x\rangle_b \langle x\rangle_a + 2\langle x\rangle_{ab}\langle x\rangle_{ba}\right]$$

$$= \langle x\rangle_a \langle x\rangle_b + |\langle x\rangle_{ab}|^2$$

$$\langle \Delta x^2\rangle_s = \underbrace{\langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b}_{\langle \Delta x^2\rangle_c} - 2|\langle x\rangle_{ab}|^2$$

$$\langle \Delta x^2\rangle_c - 2|\langle x\rangle_{ab}|^2$$