

P423 - Lecture 11 : Exchange forces, atoms.

Indistinguishable particles : Only states with $\hat{P}_{12} \Psi(\vec{r}_1, \vec{r}_2) = \pm \Psi(\vec{r}_1, \vec{r}_2)$

are allowed. Here $\hat{P}_{12} \Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_2, \vec{r}_1)$ is the particle permutation operator.

BOSONS : integer spin, $\hat{P}_{12} \Psi(\vec{r}_1, \vec{r}_2) = +\Psi(\vec{r}_1, \vec{r}_2)$

FERMIONS : half-integer spin, $\hat{P}_{12} \Psi(\vec{r}_1, \vec{r}_2) = -\Psi(\vec{r}_1, \vec{r}_2)$

DISTINGUISHABLE PARTICLES : (e.g. one electron + 1 proton)

\Rightarrow wave func does not need to be eigenstate of \hat{P}_{12} .

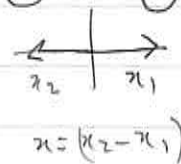
Careful : wave func need not be product states. For example, consider two 1d particles in the state:

$$\Psi(x_1, x_2) = A (x_1 - x_2) e^{-\frac{(x_1 - x_2)^2}{2\sigma^2}}$$

Is that a Boson or Fermion state?

(This would be one of the eigenstates of two identical particles connected by a spring $\textcircled{m} \text{---} \text{---} \text{---} \text{---} \textcircled{m}$)

\rightarrow See the reduced mass problem in the homework



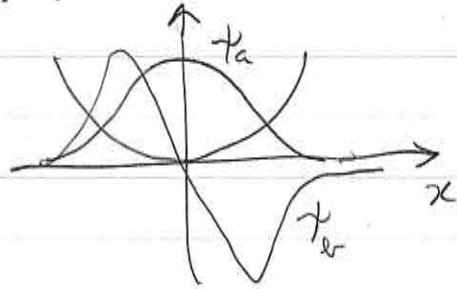
2)

Exchange forces

Consider two states $\psi_a(x)$ and $\psi_b(x)$ that are orthonormal.

Let's calculate $\langle (x_1 - x_2)^2 \rangle$, the expectation value of the distance between them.

For example $\psi_a(x)$ can be $n=0$ Harmonic oscillator, $\psi_b(x)$ $n=1$:



Let's consider the three cases:

a) Distinguishable: $\psi_D = \psi_a(x_1) \psi_b(x_2)$

b) Indistinguishable Bosons: $\psi_+ = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) + \psi_b(x_1) \psi_a(x_2)]$

c) Indistinguishable Fermions: $\psi_- = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) - \psi_b(x_1) \psi_a(x_2)]$

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$$

a) Distinguishable: $\langle x_1^2 \rangle = \int dx_1 x_1^2 |\psi_a(x_1)|^2 \underbrace{\int dx_2 |\psi_b(x_2)|^2}_{=1} = \langle x^2 \rangle_a$

$\langle x_2^2 \rangle = \underbrace{\int dx_1 |\psi_a(x_1)|^2}_{=1} \int dx_2 x_2^2 |\psi_b(x_2)|^2 = \langle x^2 \rangle_b$

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

Hence $\langle (x_1 - x_2)^2 \rangle_D = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x_a \rangle \langle x_b \rangle$

b, c: Identical particles:

$$\begin{aligned} \langle x_1^2 \rangle_{\pm} &= \frac{1}{2} \left[\int dx_1 x_1^2 |\psi_a(x_1)|^2 \int dx_2 |\psi_b(x_2)|^2 \right. \\ &\quad \left. + \int dx_1 x_1^2 |\psi_b(x_1)|^2 \int dx_2 |\psi_a(x_2)|^2 \right. \\ &\quad \left. \pm \int dx_1 x_1^2 \psi_a^*(x_1) \psi_b(x_1) \int dx_2 \psi_b^*(x_2) \psi_a(x_2) \right. \\ &\quad \left. \pm \int dx_1 x_1^2 \psi_b^*(x_1) \psi_a(x_1) \int dx_2 \psi_a^*(x_2) \psi_b(x_2) \right] \\ &= \frac{1}{2} \left[\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0 \right] \end{aligned}$$

Similarly, $\langle x_2^2 \rangle_{\pm} = \frac{1}{2} \left[\langle x^2 \rangle_b + \langle x^2 \rangle_a \right]$

f)

Now,

$$\begin{aligned}
 \langle x_1, x_2 \rangle &= \frac{1}{2} \left[\int dx_1 x_1 |\psi_a(x_1)|^2 \int dx_2 x_2 |\psi_b(x_2)|^2 \right. \\
 &\quad + \int dx_1 x_1 |\psi_b(x_1)|^2 \int dx_2 x_2 |\psi_a(x_2)|^2 \\
 &\quad \pm \int dx_1 x_1 \psi_a^*(x_1) \psi_b(x_1) \int dx_2 x_2 \psi_b^*(x_2) \psi_a(x_2) \\
 &\quad \left. \pm \int dx_1 x_1 \psi_b^*(x_1) \psi_a(x_1) \int dx_2 x_2 \psi_a^*(x_2) \psi_b(x_2) \right] \\
 &= \frac{1}{2} \left[\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab} \right] \\
 &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2
 \end{aligned}$$

where $\langle x \rangle_{ab} \equiv \int dx x \psi_a^*(x) \psi_b(x)$ is a new "classical" term called exchange integral.

So

$$\begin{aligned}
 \langle x_1, -x_2 \rangle_{\pm} &= \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2 \\
 &= \langle x^2 \rangle_D \mp 2 |\langle x \rangle_{ab}|^2
 \end{aligned}$$

Effect of indistinguishability

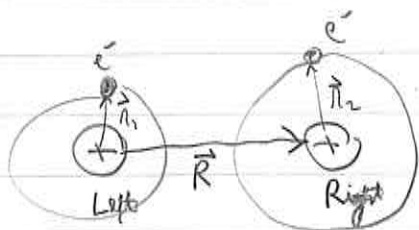
\Rightarrow Bosons are "closer together". }
 Fermions are "further apart". } than distinguishable particles.

This difference explains the chemical bond in a molecule as we shall see in a moment.

But note an interesting thing: If the states do not overlap, $\langle x \rangle_{ab} = 0$, there is no observable difference between distinguishable and indistinguishable particles. In other words, we can assume that two electrons very far apart (one in Victoria, the other in Paris) are distinguishable particles with no consequence for our calculations. But in reality, they are always in an antisymmetric state.

So far our discussion assumed spinless particles. In reality, particles always have spin. Let's now consider orbital states together with spin.

Two particle state with spin: The H₂ molecule



$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{1}{4\pi\epsilon_0} \left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \right) + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - (\vec{R} + \vec{r}_2)|}$$

Can not solve exactly. But we can consider variational wave functions and calculate $\langle H \rangle$.

to get estimate of their energies. Heitler-London approx:

$$|S\rangle = \frac{1}{\sqrt{2}} \left[\psi_{1,0,0}^L(\vec{r}_1) \psi_{1,0,0}^R(\vec{r}_2) + \psi_{1,0,0}^R(\vec{r}_1) \psi_{1,0,0}^L(\vec{r}_2) \right] \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad \text{"Spin Singlet"}$$

$$|1^{st} \text{ excited state} \rangle = \frac{1}{\sqrt{2}} \left[\psi_{1,0,0}^L(1) \psi_{1,0,0}^R(2) - \psi_{1,0,0}^R(1) \psi_{1,0,0}^L(2) \right] \left\{ \frac{1}{\sqrt{2}} (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) \right\} \quad \text{"Spin triplet"}$$

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Note how $|G\rangle$ is space-symmetric and spin-antisymmetric, while

$|1^{\text{st}} \text{ excited state}\rangle$ is space-antisymmetric and spin-symmetric.

The energy difference between these two states is called J , the exchange interaction.

So we can write down an effective Hamiltonian for the H_2 molecule that only depends on spin:

$$H_{\text{eff}} = \frac{J}{\hbar^2} \vec{S}_1 \cdot \vec{S}_2$$

Note: $H_{\text{eff}} = \frac{J}{2\hbar^2} [(\vec{S}_1 + \vec{S}_2)^2 - (S_1^2 + S_2^2)] = \frac{J}{2} \frac{\hbar^2}{\hbar^2} [j(j+1) - \frac{3}{2}] = \begin{cases} \frac{J}{4} & \text{for triplet } (j=1) \\ -\frac{3}{4}J & \text{for singlet } (j=0) \end{cases}$

$$\text{So } \Delta E = J.$$

This is called exchange interaction.

⇒ Fundamental origin of magnetism.