Bosons: particles with symmetric wave function

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

can be at the same single-particle quantum state

$\psi_+ = \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)$ → obviously symmetric!

Fermions: particles with anti-symmetric wave function

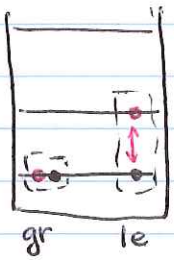
$$\psi_- = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$$

if $a = b$ $\psi_- \equiv 0$ (i.e. such situation is impossible)

(Pauli exclusion principle)

Example: two non-interacting particles in an infinite square well
(as two neutral atoms in an optical trap)

Distinguishable particles:



Ground state: $\psi_{gr}(x_1,x_2) = \frac{2}{L}\sin\frac{\pi x_1}{L}\sin\frac{\pi x_2}{L}$

$E_{gr} = 2\cdot\frac{\pi^2\hbar^2}{2mL^2} = 2E_0$

First excited state

$\psi_{1e}(x_1,x_2) = \frac{2}{L}\sin\frac{\pi x_1}{L}\sin\frac{\pi x_2}{2L}$

or

$\frac{2}{L}\sin\frac{\pi x_2}{L}\sin\frac{\pi x_1}{2L}$

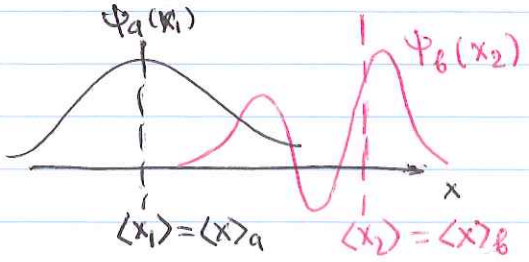
$E_{1e} = E_0 + 4E_0 = 5E_0$

Bosons: $\psi_{gr}^{(bosons)} = \psi_{gr} = \frac{2}{L}\sin\frac{\pi x_1}{L}\sin\frac{\pi x_2}{L}$ $\quad E_{gr}^{(boson)} = 2E_0$

$$\psi_{1e}^{(boson)} = \frac{2}{L}\left(\sin\frac{\pi x_1}{L}\sin\frac{\pi x_2}{2L} + \sin\frac{\pi x_2}{L}\sin\frac{\pi x_1}{2L}\right) \quad E_{1e}^{(boson)} = 5E_0$$

Fermions: $\psi_{gr}^{(ferm)} = \frac{2}{L}\left(\sin\frac{\pi x_1}{L}\sin\frac{\pi x_2}{2L} - \sin\frac{\pi x_2}{L}\sin\frac{\pi x_1}{2L}\right)$ $\quad E_{gr}^{(ferm} = 5E_0$

Exchange interaction



Let is calculate the average distance (squared) b/w the two particles

$\hat{d}^2 = (\hat{x}_1 - \hat{x}_2)^2$

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

$= \langle x_1\rangle^2 + \langle x_2\rangle^2 + 2\langle x_1 x_2\rangle$

Distinguishable particles: $\psi_d = \psi_a(x_1)\psi_b(x_2)$

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

$\langle x_2^2\rangle = \langle x^2\rangle_b$

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

Thus $\langle d^2\rangle_d = \langle x^2\rangle_a + \langle x^2\rangle_b + 2\langle x\rangle_a \langle x\rangle_b$

Identical particles: $\psi_\pm = \frac{1}{\sqrt{2}} (\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1))$

$$|\psi_\pm|^2 = \frac{1}{2}\Big\{ |\psi_a(x_1)|^2 |\psi_b(x_2)|^2 + |\psi_a(x_2)|^2 |\psi_b(x_1)|^2 \pm \big\{ \psi_a^*(x_1)\psi_b(x_1)\psi_b^*(x_2)\psi_b(x_1) + \psi_a(x_1)\psi_b^*(x_1)\psi_b(x_2)\psi_a^*(x_1) \big\} \Big\}$$

$$\langle x_1^2\rangle = \frac{1}{2}\Big\{ \langle x^2\rangle_a + \langle x^2\rangle_b \pm \Big[\int x_1^2 \psi_a^*(x_1)\psi_b(x_1) dx_1 \underbrace{\int \psi_b^*(x_2)\psi_a(x_2) dx_2}_{=0 \text{ if } a\neq b} + \text{c.c} \Big] = \frac{1}{2}\langle x^2\rangle_a + \frac{1}{2}\langle x^2\rangle_b = \langle x_2^2\rangle$$

($\langle x_1^2\rangle = \langle x_2^2\rangle$ since the particles are identical)

$$\langle x_1 x_2\rangle = \frac{1}{2}2\langle x\rangle_a\langle x_b\rangle \pm \frac{1}{2}\Big[\underbrace{\underbrace{\int x_1 \psi_a^*(x_1)\psi_b(x_1) dx_1}_{\langle x\rangle_{ab}} \underbrace{\int x_2 \psi_a(x_2)\psi_b^*(x_2) dx_2}_{(\langle x\rangle_{ab})^*}}_{|\langle x\rangle_{ab}|^2} + \text{c.c} \Big]$$

$$\langle x_1 x_2\rangle = \langle x\rangle_a\langle x\rangle_b \pm |\langle x\rangle_{ab}|^2$$

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2 = \langle d^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2$$

Bosons: $\langle d^2 \rangle_{ind} = \langle d^2 \rangle_d - 2|\langle x \rangle_{ab}|^2 \leq \langle d^2 \rangle_d$

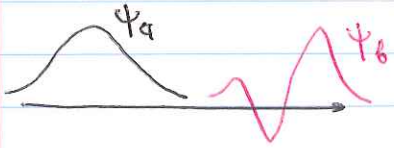
The particles are closer than in the distinguishable case

Fermions: $\langle d^2 \rangle_{ind} = \langle d^2 \rangle_d + 2|\langle x_{ab} \rangle|^2 \geq \langle d^2 \rangle_d$

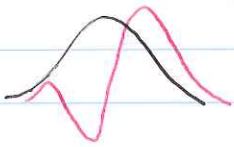
The particles are <u>farther</u> away

$$\langle x \rangle_{ab} = \int x \underbrace{\psi_a^*(x)\psi_b(x)\,dx}_{\text{overlap of the two states}}$$

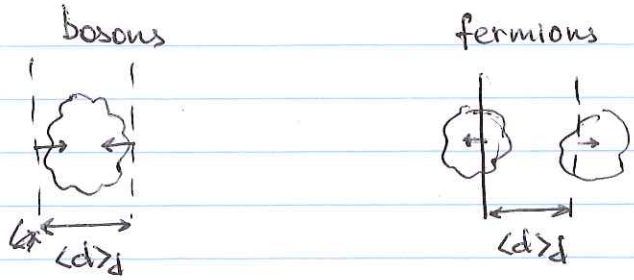
Although we cannot claim that a large overlap means large $\langle x \rangle_{ab}$, but obviously it ~~is~~ gets smaller as the overlap decreases



$\Rightarrow \langle x \rangle_{ab} \to 0$



$\Rightarrow \langle x_{ab} \rangle$ can be large



It looks like there is a "force" that pulls posons together, but pushes fermions away

So it looks like electrons would always push each other apart? But how then molecular bonds are formed?

So far, we considered only the <u>spatial</u> wave function (i.e. particle's state was described only using a $\psi(\vec{r})$ wave function). In reality all particles have spins, and usually their spatial and spin states are independent, and their total wave function consists of a spatial part and spin part

$$|1\rangle = |\psi(\vec{r}_1)\rangle\,|\chi(\vec{s})\rangle$$

For an electron (spin 1/2 particle)

$|\chi(\vec{s})\rangle = |\uparrow\rangle$ $(S_z = +\frac{1}{2}\hbar)$ or $|\downarrow\rangle$ $(S_z = -\frac{1}{2}\hbar)$ or their combinations.

Total wavefunction of a two-electron system then

$$|1,2\rangle = |\psi(\vec{r}_1,\vec{r}_2)\rangle\,|\chi(\vec{s}_1,\vec{s}_2)\rangle$$

Since electrons are fermions, the total wave function must be anti-symmetric

$$|1,2\rangle = -|2,1\rangle \longrightarrow \begin{cases}\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1)\\ \chi(\vec{s}_1,\vec{s}_2) = \chi(\vec{s}_2,\vec{s}_1)\end{cases}$$

or

$$\begin{cases}\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_2,\vec{r}_1)\\ \chi(\vec{s}_1,\vec{s}_2) = -\chi(\vec{s}_2,\vec{s}_1)\end{cases}$$

Thus, two electrons may have both symmetric or anti-symmetric wave functions $\psi(\vec{r}_1,\vec{r}_2)$, depending on the symmetry of their spin function.

Two - electron spin addition

$$\vec{S}_1 + \vec{S}_2 = \vec{S}$$

$\vec{S}_1 \uparrow\downarrow \vec{S}_2$ $\quad S = 0$ (singlet)

$$\chi_{S=0} = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right)$$

$$\chi_{S=0}(\vec{S}_1, \vec{S}_2) = - \chi_{S=0}(\vec{S}_2, \vec{S}_1)$$

thus

$$\psi_{S=0}(\vec{r}_1, \vec{r}_2) = \psi_{S=0}(\vec{r}_2, \vec{r}_1)$$

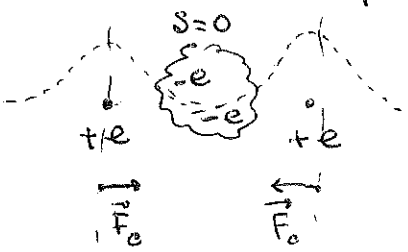
$\uparrow \vec{S}_2$ $\quad S = 1$, $m_S = 0, \pm 1$

$\uparrow \vec{S}_1$ $\quad$ (triplet)

$$\chi_{S=1} = \begin{cases} |\uparrow_1\rangle |\uparrow_2\rangle \\ \frac{1}{\sqrt{2}} \left(|\uparrow_1\rangle |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2 \right) \\ |\downarrow\rangle_1 |\downarrow\rangle_2 \end{cases}$$

$$\psi_{S=1}(\vec{r}_1, \vec{r}_2) = \infty - \psi_{S=1}(\vec{r}_2, \vec{r}_1)$$

So in a H_2 molecule two electrons can be drawn together, forming a covalent bond if their spins are anty parallel



Two protons are attracted by means of higher electron density (Coulumb attraction)

However, if we flip a spin of one of the electrons, we'll change the symmetry of their joint spin state, and thus their spatial distribution will change to become anti-symmetric. Electrons would move farther apart, breaking the bond between the protons.