Identical Particles:

Suppose we have, where x_1 and x_2 are two identical particles.

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + V_{pair}(|x_1 - x_2|) + V_{ext}(x_1) + V_{ext}(x_2)$$

with permutation symmetry:

let particle 1 to be represented by $|k'\rangle$
particle 2 to be represented by $|k''\rangle$

then under permutation: $V \otimes V \Longleftrightarrow V \otimes V$

$$|k'\rangle \otimes |k''\rangle \Longleftrightarrow |k''\rangle \otimes |k'\rangle$$

We define permutation operator P_{12} to exchange particle 1 and particle 2.

$$P_{12} |k'\rangle \otimes |k''\rangle = |k''\rangle \otimes |k'\rangle$$

clearly we observe $P_{12} = P_{21}$ and $P_{12}^2 = 1$

hence $P_{12} = \pm 1$ $\Leftarrow$ eigenvalue.

Now suppose we have observable operators that act on specific particle.

i.e. $$A_1 |a'\rangle \otimes |a''\rangle = a' |a'\rangle \otimes |a''\rangle \quad (1)$$
and
$$A_2 |a'\rangle \otimes |a''\rangle = a'' |a'\rangle \otimes |a''\rangle \quad (2)$$

Now apply P_{12} on (1) and insert $1 = P_{12}^{-1} P_{12}$

$$\hookrightarrow \quad P_{12} A_1 P_{12}^{-1} P_{12} |a'\rangle_{(1)} \otimes |a''\rangle_{(2)} = a' P_{12} |a'\rangle_{(1)} \otimes |a''\rangle_{(2)}$$

or $$P_{12} A_1 P_{12}^{-1} |a''\rangle_{(1)} \otimes |a'\rangle_{(2)} = a' |a''\rangle_{(1)} \otimes |a'\rangle_{(2)}$$

second particle with state a'

So above equality is true when $\boxed{P_{12} A_1 P_{12}^{-1} = A_2}$

Now if we consider a permutation invariant Hamiltonian:

$$\boxed{P_{12} H P_{12}^{-1} = H}$$

suggests $[P_{12}, H] = 0 \Rightarrow P_{12}$ is constant of motion.

Now we introduce the eigenkets of P_{12}: $|k' k''\rangle$

$$P_{12} |k' k''\rangle_{\pm} = \frac{1}{\sqrt{2}} \left(|k'\rangle \otimes |k''\rangle \pm |k''\rangle \otimes |k'\rangle \right.$$

$$P_{12} |k' k''\rangle \overset{!}{=} \pm |k' k''\rangle_{\pm}$$

Now we can introduce P_{ij}, which exchanges particle i and j

such: $$P_{ij} |k'\rangle |k''\rangle \cdots |k^{i}\rangle |k^{i+1}\rangle \cdots |k^{j}\rangle \cdots .$$
$$= |k'\rangle |k''\rangle \cdots |k^{j}\rangle |k^{j+1}\rangle \cdots |k^{i}\rangle \cdots .$$

Clearly $P_{ij}^2 = I$ with eigen value ± 1

Note generally $[P_{ij}, P_{kl}] \neq 0$

but $[P_{ij}, P_{kl}] = 0$ if $(i,j) \cap (k,l) = \emptyset$

Symmetrization Postulate:

Bosons
- ⇒ $P_{ij}\,|N \text{ identical bosons}\rangle = +\,|N \text{ identical bosons}\rangle$
- ⇒ Bosons have integer spins.

Fermion
- ⇒ $P_{ij}\,|N \text{ identical Fermions}\rangle = -\,|N \text{ identical Fermions}\rangle$
- ⇒ Fermions have half-integer spins

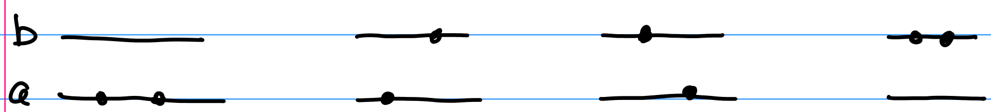
Composite Systems: (Many bosons or fermions make up one particle)

Boson + Boson = Boson

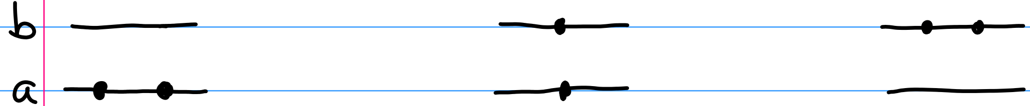
Boson + Fermion = Fermion

Fermion + Fermion = Boson.

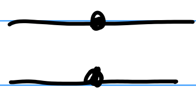
Two particle / Two level systems



$|a\rangle|a\rangle$ $\quad |a\rangle|b\rangle$ $\quad |b\rangle|a\rangle$ $\quad |b\rangle|b\rangle$ } Distinguishable Particles (Maxwell-Boltzmann)



$|a\rangle|a\rangle$ $\quad \frac{1}{\sqrt{2}}\left(|a\rangle|b\rangle + |b\rangle|a\rangle\right)$ $\quad |b\rangle|b\rangle$ } Indistinguishable Boson



$\frac{1}{\sqrt{2}}\left(|a\rangle|b\rangle - |b\rangle|a\rangle\right)$ } Indistinguishable Fermion

Two electron system

$\Rightarrow$ Since electrons are Fermions, the total wave function has eigenvalue -1 under P_{12} permutation.

$$P_{12}\, \psi(\underset{\substack{\uparrow \\ \text{position} \\ \text{(orbital)}}}{x_1}, \underset{\substack{\uparrow \\ \text{spin} \\ (\pm 1)}}{\sigma_1}; x_2, \sigma_2) = -\psi(x_2, \sigma_2; x_1, \sigma_1)$$

Two electron total wave-function:

$$\psi(x_1, \sigma_1; x_2, \sigma_2) = \psi_{\uparrow\uparrow}(x_1, x_2)|\uparrow\uparrow\rangle + \psi_{\downarrow\downarrow}(x_1, x_2)|\downarrow\downarrow\rangle$$
$$+ \psi_{\downarrow\uparrow}(x_1, x_2)|\downarrow\uparrow\rangle + \psi_{\uparrow\downarrow}(x_1, x_2)|\uparrow\downarrow\rangle$$

know $\quad S_{1+2} = \vec{S}_1 + \vec{S}_2 = \vec{S}_1 \otimes 1 + 1 \otimes \vec{S}_2$

$$S^2 = \begin{cases} s = 0 \to 0 & \text{singlet (anti-symmetric)} \longrightarrow \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ s = 1 \to 2\hbar^2 & \text{triplet (symmetric)} \longrightarrow |\uparrow\uparrow\rangle,\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),\ |\downarrow\downarrow\rangle \end{cases}$$

We can write $P_{12} = P_{12}^{(orbit)} P_{12}^{(spin)}$

then $P_{12}\psi_{orb}(x_1, x_2)\,\chi(s_1, s_2) = \psi_{orb}(x_2, x_1)\,\chi(s_2, s_1)$

$$= -\psi_{orb}(x_1, x_2)\,\chi(s_1, s_2)$$

$\hookrightarrow$ $P_{12}^{orb} P_{12}^{spin} \psi_{orb}(x_1, x_2)\chi(s_1, s_2) = -\psi_{orb}(x_1, x_2)\chi(s_1, s_2)$

Hence: Case 1: $\chi(s_1, s_2) = (\text{triplet})$

then $P_{12}^{spin}\chi(\text{triplet}) = +\chi(\text{triplet})$

so $P_{12}^{orb}\psi_{orb}(x_1, x_2) = -\psi_{orb}(x_1, x_2)$

Case 2: $\chi(s_1, s_2) = (\text{singlet})$

then $P_{12}^{spin}\chi(\text{singlet}) = -\chi(\text{singlet})$

so $P_{12}^{orb}\psi_{orb}(x_1, x_2) = +\psi_{orb}(x_1, x_2)$

We can express $P_{12}^{(spin)} = \frac{1}{2}\left(1 + \frac{\vec{\sigma}_1 \cdot \vec{\sigma}_2}{2}\right)$

$$\vec{S}_1 \cdot \vec{S}_2 = \begin{cases} \text{triplet} & \hbar^2/4 \qquad \sigma_1 \cdot \sigma_2 = 1 \qquad P_{12}^{spin} = +1 \\ \text{singlet} & -\frac{3}{4}\hbar^2 \qquad \sigma_1 \cdot \sigma_2 = -3 \qquad P_{12}^{spin} = -1 \end{cases}$$

$\psi_{orb}(x_1, x_2)$: $|\psi_{orb}(x_1,x_2)|^2$ provides the probability of finding electron 1 in a volume element d^3x_1 and electron 2 in a volume element d^3x_2.

<u>Consider 2 orbital states A, B:</u>

For 1 electron: $w_A(x)\left|\begin{smallmatrix}\uparrow\\ \downarrow\end{smallmatrix}\right\rangle$ or $w_B(x)\left|\begin{smallmatrix}\uparrow\\ \downarrow\end{smallmatrix}\right\rangle$

For 2 electrons

$$\psi_{orb}(x_1,x_2) = \frac{1}{\sqrt{2}}\left[w_A(x_1)w_B(x_2) \pm w_A(x_2)w_B(x_1)\right]$$

symmetric and anti-symmetric combination.

then

$$|\psi_{orb}(x_1,x_2)|^2 = \frac{1}{2}\int d^3x_1\, d^3x_2 \left\{|w_A(x_1)|^2|w_B(x_2)|^2 + |w_A(x_2)|^2|w_B(x_1)|^2 \pm 2\underbrace{\left[w_A(x_1)w_B(x_2)w_A^*(x_2)w_B^*(x_1)\right]}_{\text{exchange density}}\right\}$$

What about finding the electron at the same position, i.e. $x_1 = x_2 = x$?

$$|\psi_{orb}(x_1=x, x_2=x)|^2 = \int d^3x_1\, d^3x_2 \left\{|w_A(x)|^2|w_B(x)|^2 \pm |w_A(x)|^2|w_B(x)|^2\right\}$$

so

$$|\psi_{orb}(x,x)|^2 = \begin{cases} 0 & \text{if } \psi_{orb}: \text{antisymmetric} \rightarrow \chi_{spin}: \text{symmetric (triplet)} \\ \text{Doubled} & \text{if } \psi_{orb}: \text{symmetric} \rightarrow \chi_{spin}: \text{anti-symmetric (singlet)} \end{cases}$$