IDENTICAL PARTICLES

Say you have 2 electrons: electron is a fundamental particle, can't modify its intrinsic properties

... 2 e^- are <u>TRULY</u>! <u>INDISTINGUISHABLE</u>

$\Rightarrow \nexists$ any experiment that can tell the difference

Consider 2-particle ψ where pcle 1 & 2 are indistinguishable

$\Rightarrow$ require that all measurable info. encoded in $\psi(\vec{r}_1, \vec{r}_2)$ must be INVARIANT under particle exchange $\vec{r}_1 \longleftrightarrow \vec{r}_2$

Physical Info:

- $\text{Prob}(q) = |\langle e_q | \psi \rangle|^2$
- $\rho(x) = \psi^*(x)\psi(x) = |\psi|^2$
- $\vec{j}(x) = \text{Re}\left[\psi^*(x)\frac{\hat{p}}{m}\psi(x)\right]$

none are affected by change $\psi(x) \to \underline{e^{i\alpha}}\,\psi(x)$

constant phase factor

$\psi^*\psi = |\psi|^2$ unaffected ... <u>constant</u> phase α so that $\hat{p}$ in $\vec{j}$ doesn't change it

Introduce exchange operator $\hat{P}_{12}$ that swaps $\vec{r}_1 \longleftrightarrow \vec{r}_2$

Start with $\Psi(\vec{r}_1, \vec{r}_2)$ for 2 identical particles

... suppose that $\hat{P}_{12}\Psi(\vec{r}_1, \vec{r}_2) = e^{i\alpha}\Psi(\vec{r}_2, \vec{r}_1)$

FINE! nothing physical changes

... now apply it again!

$$\underbrace{\hat{P}_{12} \cdot \hat{P}_{12}}_{\text{by definition, 2 swaps must do NOTHING AT ALL}} \Psi(\vec{r}_1, \vec{r}_2) = e^{2i\alpha}\Psi(\vec{r}_1, \vec{r}_2)$$

$\therefore \; e^{2i\alpha} = 1 = e^{i2\pi n}$

$\therefore \; e^{i\alpha} = e^{i\pi n} = \pm 1$

$\hat{P}_{12}\Psi(\vec{r}_1, \vec{r}_2) =$

$$\boxed{\Psi(\vec{r}_2, \vec{r}_1) = \pm \Psi(\vec{r}_1, \vec{r}_2) \quad \text{for 2 identical pcles}}$$

SIXTH AXIOM of QM

⊕ no analogue in CM

⊕ + sign: Ψ is "SYMMETRIC" under exchange $\equiv$ "Ψ_S"

− sign: Ψ is "ANTI-SYMM" under exchange $\equiv$ "Ψ_A"

Part II of the axiom:

Two identical FERMIONS / BOSONS have wavef^{n}s that are ANTI-SYMM / SYMMETRIC under exchange

where

FERMIONS ≡ pcles with HALF-INTEGER spin s
BOSONS ≡ " " INTEGER " s

[ANTI]-SYMMETRIZING an existing $\psi(\vec{r}_1, \vec{r}_2)$

e.g. given $\psi(x_1, x_2) = A\,(x_1 - x_2)\, e^{-x_1^2/2}\, e^{-x_2^2}$

can Symmetrize / Anti-symmetrize it as follows:

$$\psi_{\substack{S\\A}}(x_1, x_2) = \underset{\substack{\text{norm}^{\underline{n}}\\\text{constant}}}{C_n} \left[\psi(x_1, x_2) \pm \psi(x_2, x_1) \right]$$

more common example: (know the single-particle states of each particle ... but not which one is which if they are identical!)

e.g. chemistry! helium: $|n\,l\,m_l\,m_s\rangle = |1\,0\,0\,\pm\tfrac{1}{2}\rangle$
$= 1s\uparrow$ and $1s\downarrow$

then 2-pcle $\psi(\vec{r}_1, \vec{r}_2)$ factorizes into $\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2)$

From DISC 1, if ψ_a & ψ_b are orthogonal, (single-pcle states)

then normalization C is just $1/\sqrt{2}$:

$$\psi_{\substack{S \\ A}}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right]$$

For more than 2 identical fermions, SLATER DET.

$$\psi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\vec{r}_1) & \psi_b(\vec{r}_1) & \psi_c(\vec{r}_1) & \cdots \\ \psi_a(\vec{r}_2) & \psi_b(\vec{r}_2) & \psi_c(\vec{r}_2) & \cdots \\ \psi_a(\vec{r}_3) & \cdots & & \\ \cdots & & & \end{vmatrix}$$

Swapping ANY TWO identical $\left\{ \begin{matrix} \text{bosons} \\ \text{fermions} \end{matrix} \right\}$ must

leave $\psi(\vec{r}_1, \vec{r}_2, \cdots)$ $\left\{ \begin{matrix} \text{unchanged} \\ \text{sign-change only} \end{matrix} \right\}$

PAULI EXCLUSION PRINCIPLE for fermions

Consequence of axiom: Two identical fermions cannot be in the same |single-particle state⟩

PROOF: Try it! $\psi(\vec{r}_1,\vec{r}_2) = \psi_a(\vec{r}_1)\cdot\psi_a(\vec{r}_2)$

anti-symm: $\psi_A(\vec{r}_1,\vec{r}_2) = C\left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)\right]$

$$= C\left[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

$$= \emptyset = \text{non-existent wavefunction}$$

FYI: "parallel" consequence for bosons → Bose-Einstein condensate

TWO-PARTICLE OPERATORS, NOTATION

e.g. Hamiltonian for two helium electrons: e-e repulsion; spin-spin interac^n

$$\mathcal{H}(\vec{r}_1,\vec{r}_2) = \left(\frac{\hat{p}_1^2}{2m} - \frac{kZe^2}{r_1}\right) + \left(\frac{\hat{p}_2^2}{2m} - \frac{kZe^2}{r_2}\right) + \frac{ke^2}{|\vec{r}_1-\vec{r}_2|} - A\hat{\vec{s}}_1\cdot\hat{\vec{s}}_2 + \dots$$

$$= \frac{1}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - kZe\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \dots$$

∇_1^2: $\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2$

FULL Two-particle wavefunction involves both space & spin parts

$$\underset{\text{of 1 pcle}}{|\text{FULL STATE}\rangle} = \underset{\text{for an electron in a central potential}}{\overset{\text{e.g.}}{|n\,l\,m_l\,m_s\rangle}} \cong \underbrace{\psi_{nlm_l}(r,\theta,\phi)}_{\text{space part, usually } R_{nl}(r)\,Y_{lm_l}(\theta,\phi)} \times \underbrace{\chi_{m_s}}_{\text{spin part, usually with basis}}$$

$$\begin{pmatrix}1\\0\end{pmatrix} \equiv |+\tfrac{1}{2}\rangle_{m_s}$$

$$\begin{pmatrix}0\\1\end{pmatrix} \equiv |-\tfrac{1}{2}\rangle_{m_s}$$

e.g. two electrons of helium ground state:

one in $|1s\uparrow\rangle \equiv |1\,0\,0\,+\tfrac{1}{2}\rangle_{nlm_lm_s}$

other in $|1s\downarrow\rangle = |1\,0\,0\,-\tfrac{1}{2}\rangle_{nlm_lm_s}$

Anti-symmetrized 2-electron wavefunc^n =

$$\frac{1}{\sqrt{2}}\Big[\psi_{100}(r_1,\theta_1,\phi_1)\,\psi_{100}(r_2,\theta_2,\phi_2)\cdot\begin{pmatrix}1\\0\end{pmatrix}_1\begin{pmatrix}0\\1\end{pmatrix}_2$$

swapped

particle index

$$-\psi_{100}(\vec{r}_2)\,\psi_{100}(\vec{r}_1)\cdot\begin{pmatrix}1\\0\end{pmatrix}_2\begin{pmatrix}0\\1\end{pmatrix}_1\Big]$$

also swapped

$$= \frac{1}{\sqrt{2}}\, \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\left[\begin{pmatrix}1\\0\end{pmatrix}_1\begin{pmatrix}0\\1\end{pmatrix}_2 - \begin{pmatrix}0\\1\end{pmatrix}_1\begin{pmatrix}1\\0\end{pmatrix}_2\right]$$

Apply $\hat{S}_{1z} = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}_1$ ← particle index on operator, just like on states

↑ Pauli spin matrix for spin $1/2$

means "operates on pcle #1 ONLY"

only operates on this part

e.g. apply $\hat{S}_{1z}\,\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\begin{pmatrix}1\\0\end{pmatrix}_1\begin{pmatrix}0\\1\end{pmatrix}_2$

$$= \underbrace{\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)}\begin{pmatrix}0\\1\end{pmatrix}_2 \cdot \left[\hat{S}_{1z}\cdot\begin{pmatrix}1\\0\end{pmatrix}_1\right]$$

$$= \text{space part}\ \begin{pmatrix}0\\1\end{pmatrix}_2 \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}_1\begin{pmatrix}1\\0\end{pmatrix}_1$$

Two spin-1/2 particles : singlet & triplet

Recall two bases for $s_1 = \frac{1}{2} \oplus s_2 = \frac{1}{2}$:

$2 \times 2 = 4$ states

① $|\underbrace{s_1}_{\frac{1}{2}} \underbrace{s_2}_{\frac{1}{2}} ; m_{s_1} m_{s_2}\rangle = |m_1 m_2\rangle = |\pm\frac{1}{2}, \pm\frac{1}{2}\rangle_{m_1 m_2}$

shorthand $= \{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}_{m_1 m_2}$

② $|\underbrace{s_1}_{\frac{1}{2}} \underbrace{s_2}_{\frac{1}{2}} ; S M\rangle = |S\, M\rangle = \{|0,0\rangle, |1,\pm 1\rangle, |1,0\rangle\}_{SM}$

shorthand

$= 1 + 3 = 4$ states

Correspondence :

⊕ stretched state for identical spins is always symmetric under exchange

$$|1\ +1\rangle_{SM} = |\uparrow\uparrow\rangle_{m_1 m_2}$$
$$|1\ 0\rangle_{SM} = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right]_{m_1 m_2}$$
$$|1\ -1\rangle_{SM} = |\downarrow\downarrow\rangle_{m_1 m_2}$$

$S=1$ TRIPLET symmetric

$$|0\ 0\rangle_{SM} = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]_{m_1 m_2}$$

$S=0$ SINGLET anti-symm.

recall: building CG tables...

B. then apply step-down operator $\hat{S}_- = \hat{s}_{1-} + \hat{s}_{2-}$

$|1\ \ {+1}\rangle_{SM}$ ← A. START with stretched state ≡ max m_1, m_2, M, S

$|1\ \ 0\rangle_{SM}$

steps down: M $\quad m_1 \quad m_2$

PRESERVES exchange symm. within a "MULTIPLET" of a given total S

C. build $|0\ \ 0\rangle_{SM}$ by making it ORTHOGONAL to the other $M=0$ state(s)

$= \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$

$\updownarrow$ same M

$|1\ \ 0\rangle_{SM} = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right]$

symmetric

$\therefore$

EXCHANGE FORCE DISC 1

calc: $\langle (x_1 - x_2)^2 \rangle$ distance^2 betw two identical particles in state

$$\psi_{S/A} \equiv \psi_{\pm} = \frac{1}{\sqrt{2}} \left[\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2) \right]$$

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2 \left| \langle x \rangle_{ab} \right|^2$$

OVERLAP TERM

$$\langle x \rangle_{ab} \equiv \int x \, \psi_a^*(x) \psi_b(x) \, dx$$

FINDING: $\langle (x_1 - x_2)^2 \rangle = \langle \Delta x_{12}^2 \rangle$ = average particle spacing is $\left\{ \begin{matrix} \text{SMALLER} \\ \text{BIGGER} \end{matrix} \right\}$ for 2 identical $\left\{ \begin{matrix} \text{BOSONS} \\ \text{FERMIONS} \end{matrix} \right\}$

- Quick motivation: 2 IDENTICAL FERMIONS can never occupy the same position:

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

- Effect only significant if ψ_a & ψ_b OVERLAP SIGNIFICANTLY

SPACE x SPIN = TOTAL W.F. is what you have to symm./anti-symm.

e.g. two electrons:

$$|STATE\rangle = \underset{\text{anti-symm.}}{\chi_{S=0}} \cdot \underset{\text{symm.}}{\psi(\vec{r}_1, \vec{r}_2)}$$

OR

$$|STATE\rangle = \underset{\text{symmetric}}{\chi_{S=1}} \cdot \underset{\text{anti-symm.}}{\psi(\vec{r}_1, \vec{r}_2)}$$

total is antisymmetric $\because$ two electrons

SPIN parts · SPACE parts

$n=1$
$l=0$
$m_l=0$

e.g. He ground state: both electrons in 1s shell

$$\therefore \text{spatial } \psi(\vec{r}_1, \vec{r}_2) = \underset{\substack{100 \\ n l m_l}}{\psi(\vec{r}_1)} \cdot \underset{\substack{100 \\ n l m_l}}{\psi(\vec{r}_2)} = \text{symmetric}$$

$$\therefore \text{spin } \chi = \text{anti-symmetric} = \text{total spin } \emptyset \equiv (S=0)$$

$$= \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle_{12} - |\downarrow\uparrow\rangle_{12} \right]$$