Identical particles

Any two objects with the same intrinic properties.

Examples:

Two electron

Two protons

Two Hydrogen atoms

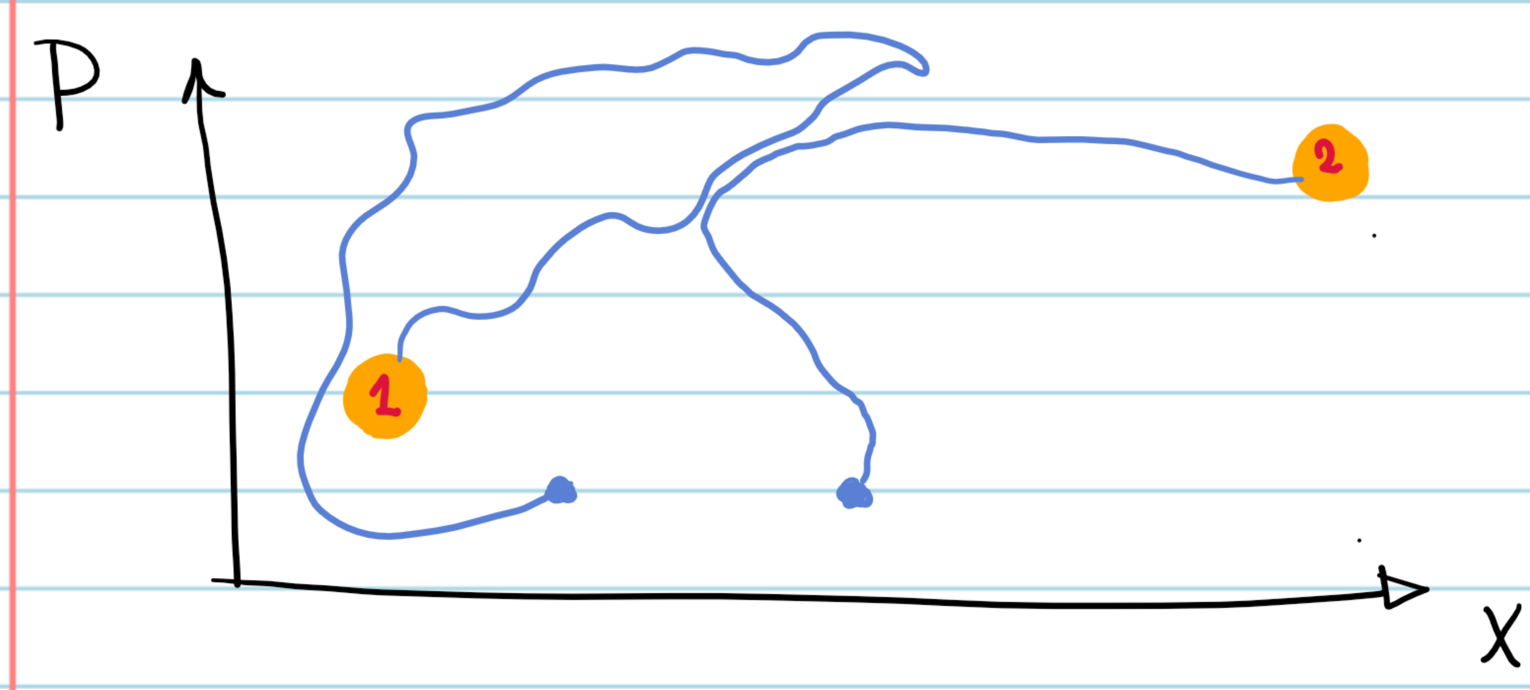
Two identical balls

Two " cups

Distinguishability of identical particles

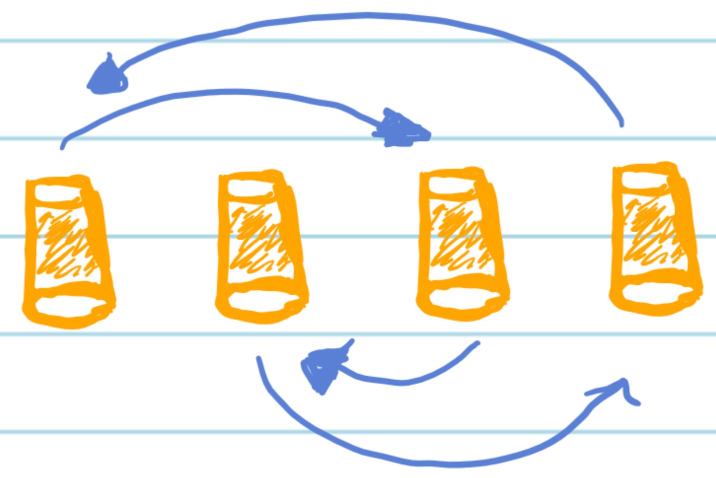
Classically identical particles are distinguishable.

This is b/c we can track them



We can track them

So we can distinguish them.



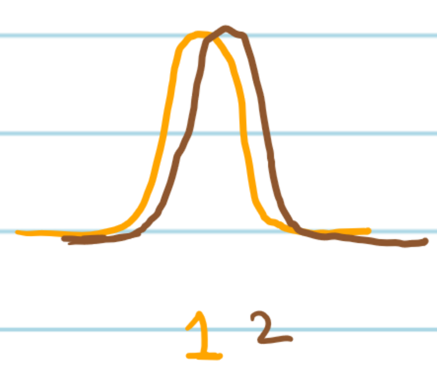
The cups can be tracked and we can at all times know their exact position & momentum.

Indistinguishibility in QM

Due to the uncertainity relation in QM, we cannot assign a trajectory to identical particles in QM.

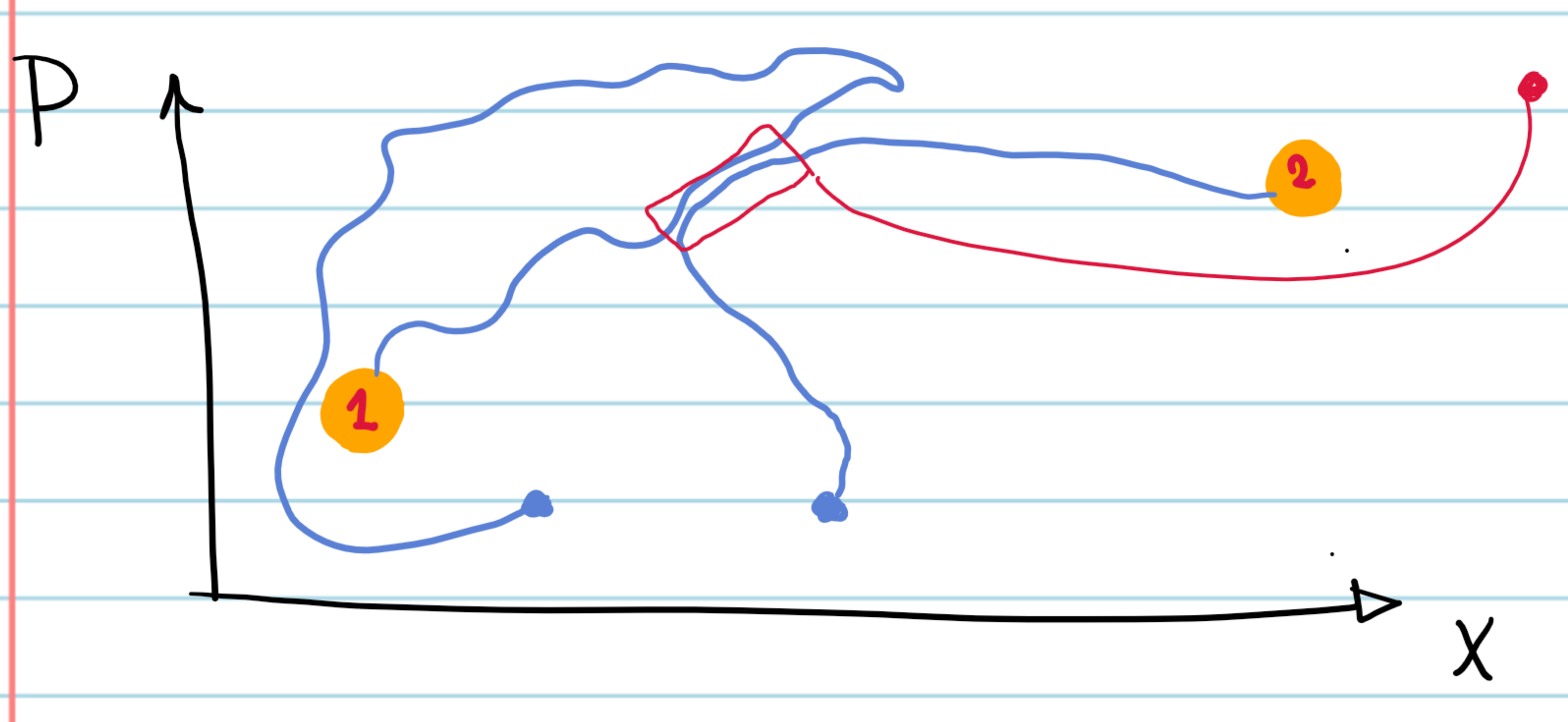
So **indistinguishibility** is a fundamental property of identical particles in QM.

Two electrons



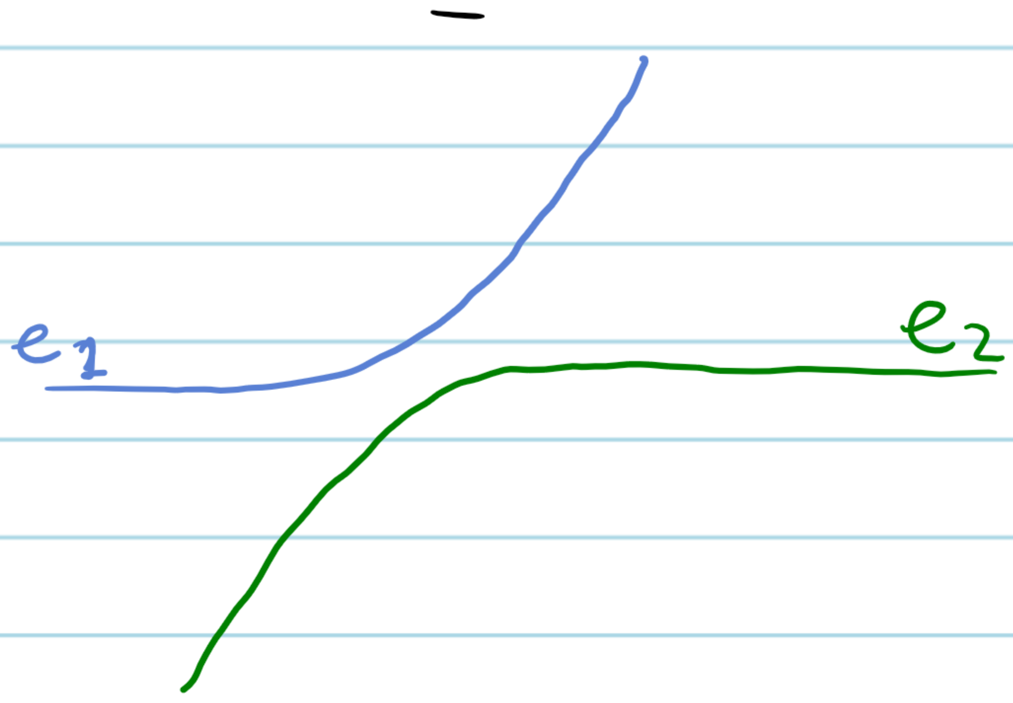
The two are not distinguishable.

Classically, the extent (var) of the wave function can be set to zero, so, they can be distinguished.

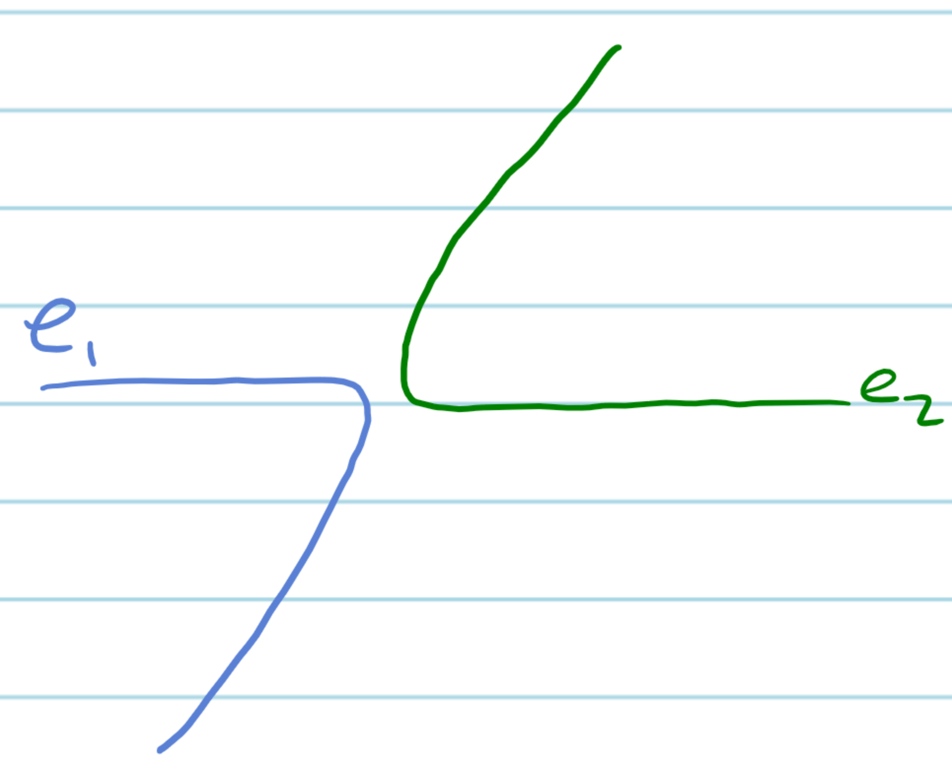


The quantum wave function of the two particles overlap and we cannot know which is which.

Case 1



Case 2



Now, is our current mathematical model ready for this & consistent with indistinguishability of particles?

Example $|\psi\rangle_1$ & $|\psi\rangle_2 \in \mathcal{H}$

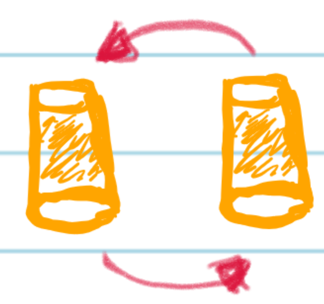
Let's use the following notation for the composite system:

$$|\psi\rangle_{AB} = |\psi_1\rangle_A \otimes |\psi\rangle_B = |\psi_1\rangle|\psi_2\rangle$$

Can this describe an indistinguishable state between particles A & B?

How can we test? SWAP them!

If $|\psi\rangle_{AB}$ is to describe an indistinguishable state of A & B, then swapping the labels, should not change the state.



The state should be invariant under permutation (up to a phase).

But is it?

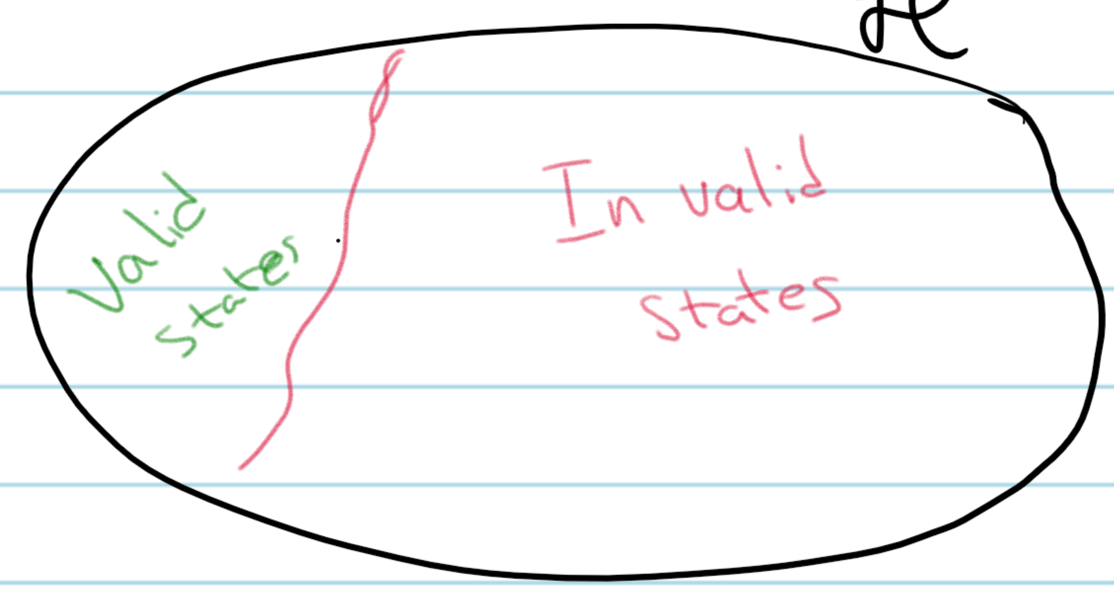
$$|\psi\rangle_{AB} = |\psi_1\rangle_A|\psi_2\rangle_B \longrightarrow |\psi_2\rangle_A|\psi_1\rangle_B$$ which is not the same.

We need to add sth to our model

* The states of composite particles does not automatically account for indistinguishability and we need/will add a new ingredient for this.

More specifically

$\mathcal{H}^{\otimes n}$ → Hilbert space of n identical particles.



Some of the states cannot give a valid decription for identical particles.

→ Our task in this chapter is to find the subspace of Valid states.

But, what is a valid state ?

$$|\psi_{AB}\rangle = |\psi_1\rangle_A |\psi_2\rangle_B \xrightarrow{\text{SWAP}} |\psi_2\rangle_A |\psi_1\rangle_B \equiv \boxed{e^{i\varphi}} |\psi_1\rangle_A |\psi_2\rangle_B$$

Could this be any phase ?

Let's apply the SWAP twice : $(\text{SWAP})^2 = \mathbb{1}$

$$|\psi_{AB}\rangle = |\psi_1\rangle_A |\psi_2\rangle_B \to e^{i\varphi} |\psi_2\rangle_A |\psi_1\rangle_B \to e^{2i\varphi} |\psi_1\rangle_A |\psi_2\rangle_B = |\psi_1\rangle_A |\psi_2\rangle_B$$

$$e^{2i\varphi} = 1 \implies \underbrace{\varphi = (2l+1)\pi}_{} \quad \text{or} \quad \underbrace{2l\pi}_{}$$

$$e^{i\varphi} \longrightarrow -1 \quad \text{or} \quad 1$$

Valid states →

States that are either symmetric or anti-symmetric under SWAP → permutation.

* Note: This was for two identical particles, but for the rest, we will generalize to n particles.

Permutation group

To identify the set of valid states, we need to first understand permutations and the permutation group S_n

$$P \in D(S_n(V)) \subset \mathcal{L}(V^{\otimes n})$$

$$P: \underbrace{V \otimes V \otimes \cdots V}_{n} \longrightarrow \underbrace{V \otimes V \otimes \cdots V}_{n}$$

For simplicity $V = \mathcal{H}$.

Consider $|\psi_1\rangle, |\psi_2\rangle, \cdots |\psi_n\rangle \in \mathcal{H}$

$$P\left(|\psi_1\rangle|\psi_2\rangle \cdots |\psi_n\rangle\right) = |\psi_{\sigma(1)}\rangle |\psi_{\sigma(2)}\rangle \cdots |\psi_{\sigma(n)}\rangle$$

$\sigma \in S_n$: $\sigma(i) = j$ → Permutation $\quad \begin{matrix} 1 & 2 & \cdots & n \\ \sigma(1) & \sigma(2) & \cdots & \sigma(n) \end{matrix} \Big) \sigma$

e.g. SWAP $\quad \begin{pmatrix} 1 & 2 \end{pmatrix} \Big) \sigma \quad \begin{pmatrix} 2 & 1 \end{pmatrix}$: $\begin{cases} \sigma(1) = 2 \\ \sigma(2) = 1 \end{cases}$

Permutation group

Example: $S_2 = \{(1,2), (2,1)\}$ $\xrightarrow{\text{Rep.}}$ $D(S_2) = \{\mathbb{1}, P_{12}\}$

$S_3 = \{(1,2,3), (2,1,3), (3,2,1), (1,3,2), (2\ 3\ 1), (3\ 1\ 2)\}$

$$\Rightarrow D(S_3) = \{\mathbb{1}, P_{12}, P_{13}, P_{23}, P_{231}, P_{312}\}$$

Note: We use P_{ij} for the permutations that swap i with j.

For instance, for $\sigma = (2,1,3) \rightarrow P_{213} \equiv P_{12}$.

This kind of permutations is called a "Transposition".

Symmetrization Postulates

For N identical particles, the state should be either symmetric or anti-symmetric under permutation, i.e.

$$\forall P \in D(S_n): \quad P\left(|\psi_1\rangle|\psi_2\rangle \cdots |\psi_n\rangle\right) = \pm\left(|\psi_1\rangle|\psi_2\rangle \cdots |\psi_n\rangle\right)$$

↓ When is it (-1)?

Example:

$*$ $n=2$

$|\psi\rangle = |\psi_1\rangle|\psi_2\rangle \longrightarrow \psi_1 \neq \psi_2 \Rightarrow$ Not a valid state.

Symmetric state: $\dfrac{|\psi_1\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_1\rangle}{\sqrt{2}} = |\psi_s\rangle$

Anti- " " : $\dfrac{|\psi_1\rangle|\psi_2\rangle - |\psi_2\rangle|\psi_1\rangle}{\sqrt{2}} = |\psi_A\rangle$

$D(S_2) = \{\mathbb{1}, P_{12}\}$

$$\mathbb{1}|\psi_s\rangle = |\psi_s\rangle, \quad \mathbb{1}|\psi_A\rangle = |\psi_A\rangle$$

$$P_{12}|\psi_s\rangle = |\psi_s\rangle, \quad P_{12}|\psi_A\rangle = -|\psi_A\rangle$$

Example $n=3$

$$|\psi_s\rangle = \frac{1}{6}\Big[|\psi_1\rangle|\psi_2\rangle|\psi_3\rangle + |\psi_2\rangle|\psi_1\rangle|\psi_3\rangle + |\psi_3\rangle|\psi_2\rangle|\psi_1\rangle + |\psi_1\rangle|\psi_3\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_3\rangle|\psi_1\rangle + |\psi_3\rangle|\psi_1\rangle|\psi_2\rangle\Big]$$

* Check that $\forall P \in D(S_n)$: $P|\psi_s\rangle = |\psi_s\rangle$.

How about $|\psi_A\rangle$? $\mathbb{1}|\psi_A\rangle = |\psi_A\rangle$, $P_{ij}|\psi_A\rangle = -|\psi_A\rangle$

$P_{ij} P_{i'j'} |\psi_A\rangle = |\psi_A\rangle$: e.g. $P_{231} = P_{12}P_{13}$

$$|\psi_A\rangle = \frac{1}{6}\Big[|\psi_1\rangle|\psi_2\rangle|\psi_3\rangle - |\psi_2\rangle|\psi_1\rangle|\psi_3\rangle - |\psi_3\rangle|\psi_2\rangle|\psi_1\rangle - |\psi_1\rangle|\psi_3\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_3\rangle|\psi_1\rangle + |\psi_3\rangle|\psi_1\rangle|\psi_2\rangle\Big]$$

But how?

Decomposition of permutations

There's a theorem that indicates any permutation can be decomposed in terms of transpositions σ_{ij}.

$$\sigma_{ij}: \begin{cases} \sigma_{ij}(i) = j \\ \sigma_{ij}(j) = i \\ \sigma_{ij}(\ell \neq i \text{ or } j) = \ell \end{cases}$$

Only swaps i with j and leave everyone else unchanged.

Any $\sigma = \sigma_{i_1 j_1} \sigma_{i_2 j_2} \cdots$

It is also possible to show that while the decomposition is not unique, the number of transpositions in the decomposition mod 2 is unique i.e. there are odd or even # of transpositions.

Similarly, for $\sigma_{ij} \to P_{ij} = P(\sigma_{ij})$.

And, $\forall P \in D(S_n)$: if $\sigma = \prod_{\ell}^{m} \sigma_{i_\ell j_\ell}$ then

$$P = \prod_{\ell}^{m} P_{i_\ell j_\ell}.$$

Remarks

* P_{ij} is Hermitian. $\to \langle \psi_1 \psi_2 \ldots \psi_n | P_{ij} | \psi_1 \psi_2 \ldots \psi_n \rangle = \langle P_{ij}^\dagger \rangle = |\langle \psi_i | \psi_j \rangle|^2$
* $P_{ij}^2 = \mathbb{1}$
* P_{ij} is unitary.
* $\lambda(P_{ij}) = \pm 1$. $\to$ For sym states $+1$
  For Asym " -1.

* From the symmetrization postulate:

We are looking for states that are eigenstates of all $P \in D(S_n)$ & with the right phase.

For $|\psi_S\rangle$: $\forall P \in D(S_n)$: $P|\psi_S\rangle = |\psi_S\rangle$

For $|\psi_A\rangle$: $P|\psi_A\rangle = \begin{cases} -|\psi_A\rangle & \text{if } P \text{ is odd.} \\ |\psi_A\rangle & \text{if } P \text{ is even.} \end{cases}$

This is b/c $P = \prod_{\ell=1}^{m} P_{i_\ell j_\ell}$ and $P|\psi_A\rangle = (-1)^m |\psi_A\rangle$ if m is odd, $(-1)^m = -1$
" " is even, $(-1)^m = 1$.

$\forall \sigma \in S_n$, We define the $\text{sign}(\sigma) = \begin{cases} -1 & P \text{ is odd.} \\ +1 & P \text{ is even.} \end{cases}$

Example: S_3: $\text{Sign}[(1,2,3)] = \text{Sign}[(2,3,1)] = \text{Sign}[(3,1,2)] = 1$

$\text{Sign}[(2,1,3)] = \text{Sign}[(3,2,1)] = \text{Sign}[(1,3,2)] = -1$.

Now, how do we make the symmetric & anti-symmetric?

Let's go back to the permutation group. We construct two operators A & S:

$$S = \frac{1}{n!} \sum_{P \in D(S_n)} P \qquad A = \frac{1}{n!} \sum_{P \in D(S_n)} \text{Sign}(P)\, P$$

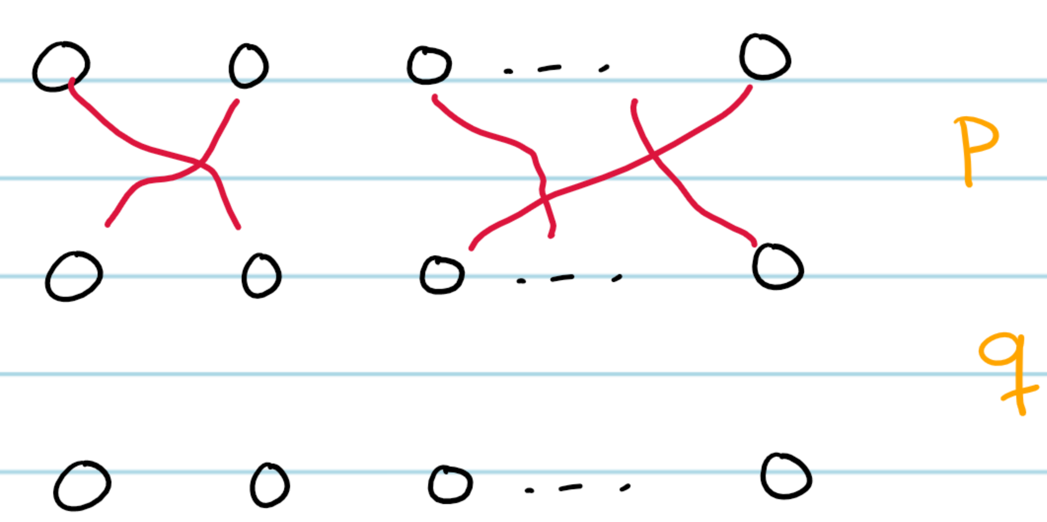
Some remarks

$\forall P \in D(S_n)$: $\quad PS = S$

$\quad PA = \text{Sign}(P)\, A.$

~Proof: $\forall\, q \in D(S_n) \;\exists\; p^{-1}q \in D(S_n)$: $P(p^{-1}q) = q$ → All the elements are generated.

There's a way to make the final configuration.



Similarly:

$PA = \text{Sign}(P)\, A$: Similar to the above, except

$$P \sum_{q} \text{Sign}(p^{-1}q)\; p^{-1}q = \sum_{q} \text{Sign}(p^{-1}q)\; q = \text{Sign}(P) \underbrace{\sum \text{Sign}(q)\, q}_{A}$$

$$S = \frac{1}{n!} \sum_{P \in D(S_n)} P \qquad A = \frac{1}{n!} \sum_{P \in D(S_n)} \text{Sign}(P)\, P$$

* $S^2 = S$ * $A^2 = A$ → They are projections.

- $S^2 = \frac{1}{n!} \sum_P P S = \frac{1}{n!} \sum_P S = \frac{n!}{n!} S = S.$

- $A^2 = \frac{1}{n!} \sum_P \text{Sign}(P)\, P A = \frac{1}{n!} \sum_P \text{Sign}(P)\, \text{Sign}(P)\, A = A$

Symmetric and Anti-Symmetric States:

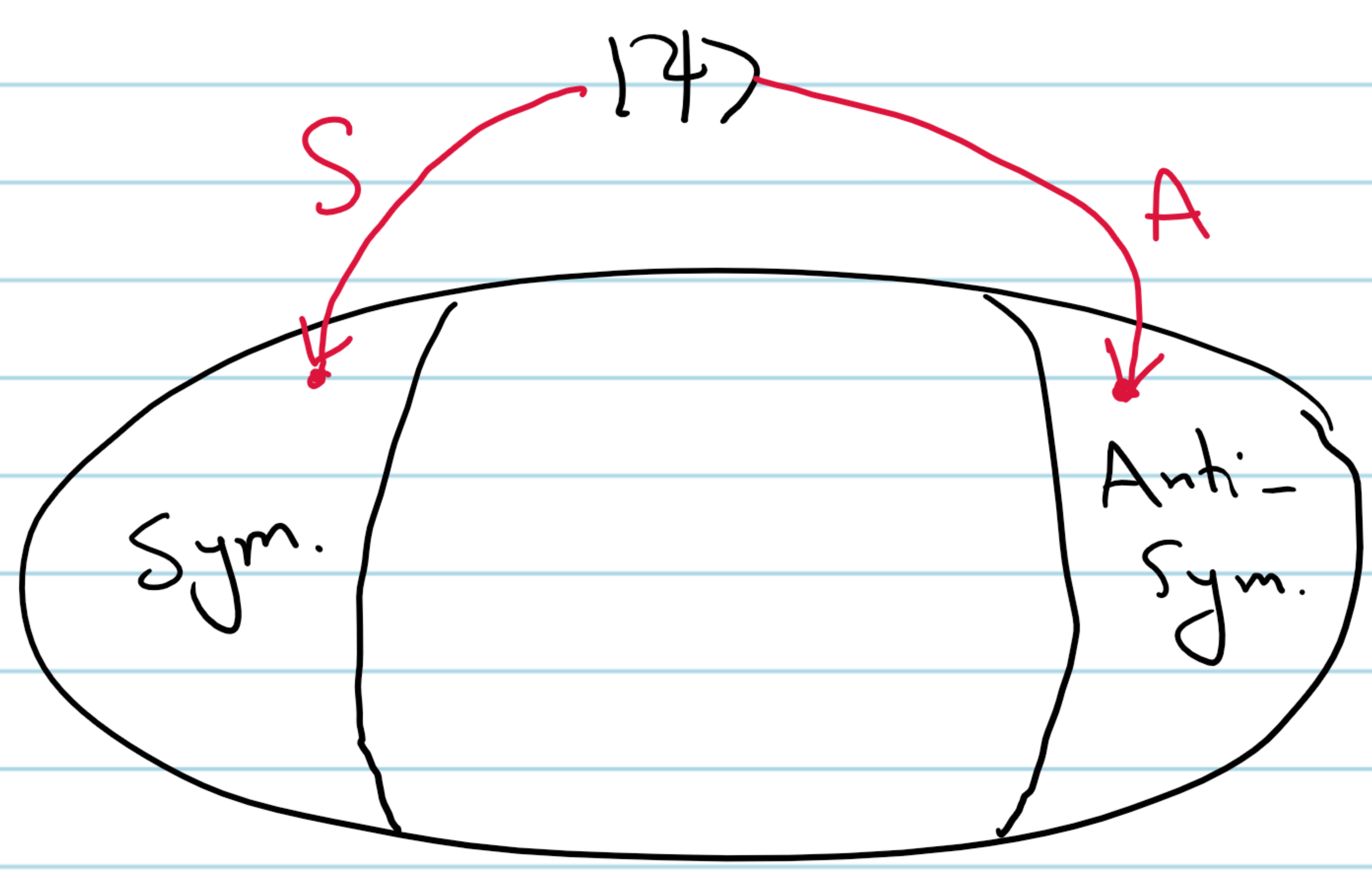
Claim: For any state $|\psi\rangle = |\psi_1\rangle|\psi_2\rangle \cdots |\psi_n\rangle$

$S|\psi\rangle$ gives a symmetric state and $A|\psi\rangle$ gives an anti-sym. State.

Proof: $\forall P \in D(S_n)$: $P(S|\psi\rangle) = S|\psi\rangle$ → Sym. State.

$\forall P \in D(S_n)$: $P(A|\psi\rangle) = \text{Sign}(P)(A|\psi\rangle)$ → Anti-sym. " .

S & A are the projective operators that project the state into the Sym & Anti-Sym sub-spaces.



Fermions & Bosons

Sym. States → Bosons ← Integer Spin

Anti- " . " → Fermions. ← Half- " "

Electron, quarks, .. spin $1/2$ → Fermions.

Photon , ... Spin 1 → Boson

For two Fermions, the state should be asymmetric, so

if $\psi_1 = \psi_2 \rightarrow |\tilde{\psi}_A\rangle = |\psi_1\rangle|\psi_1\rangle - |\psi_1\rangle|\psi_1\rangle = 0$ → Is not possible

Exclusion Principle ← For two fermions to occupy the exact same state.

Composite Particles

We need to figure out if they're Bosons or Fermions.

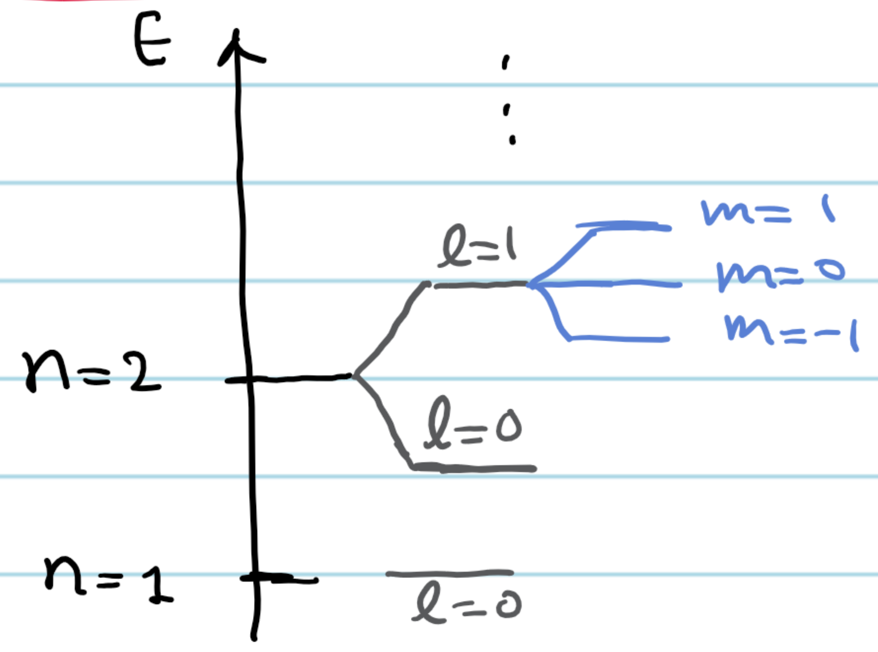
We use addition of angular momentum → j → Boson / Fermion

protons → Fermions

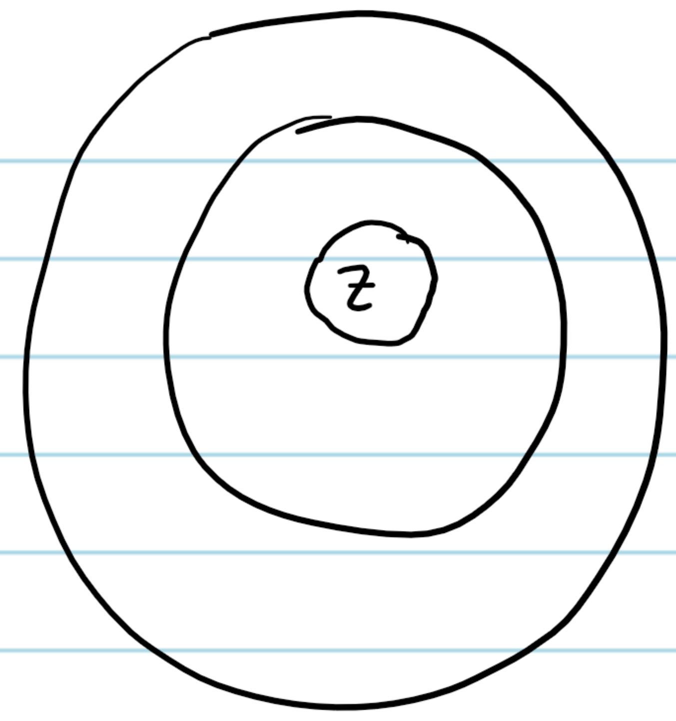
He^4 → Boson

He^3 → Fermion

Periodic Table



l:
0 → s
1 → p
2 → d
⋮



For atoms beyond H, i.e. $Z > 1$, this still gives a good approximation of the energy levels, but now there are multiple electrons that would fill up the levels.

(*) If electrons were Boson, what would be the ground state?

For each electron, ψ_{100} $(n=1, l=m=0)$ would be the lowest-energy level. For Bosons, this would be the state:

$$|\psi\rangle_{1..Z} = |\psi_{100}\rangle_1 |\psi_{100}\rangle \cdots |\psi_{100}\rangle_Z$$ → All of them would condensate in the GS: ψ_{100}.

But, electrons are Fermions. So, this state, since it is symmetric, is not acceptable.

Consider 2 electrons → He

$\chi \to$ spin: m_z

$$|\psi\rangle_{1,2} = \frac{1}{\sqrt{2}}\left(|\psi_{100}, \chi_1\rangle |\psi_{100}, \chi_2\rangle - |\psi_{100}, \chi_2\rangle |\psi_{100}, \chi_1\rangle\right)$$

$$= \frac{|\psi_{100}\rangle |\psi_{100}\rangle}{\sqrt{2}} \left(|\chi_1 \chi_2\rangle - |\chi_2 \chi_1\rangle\right)$$

→ So it would be possible to have two electron in ψ_{100}.

What about the Li? $\underline{Z=3}$

$m_z = \mp 1/2 \to$ Only two state with ψ_{100} is possible.

$\Rightarrow \psi_{100} \quad \psi_{200}$
(2) (1)

What is the state? 2 in 1s, 1 is 2s] But which one?

$$\det \begin{vmatrix} \psi_{100,\uparrow} & \psi_{100,\downarrow} & \psi_{200,\uparrow} \\ " & " & " \\ " & " & " \end{vmatrix} = \left[|\psi_{100,\uparrow}\rangle^A |\psi_{100,\downarrow}\rangle^B - |\psi_{100,\downarrow}\rangle^A |\psi_{100,\uparrow}\rangle^B \right] |\psi_{200,\uparrow}\rangle^C$$

$$+ |\psi_{100,\uparrow}\rangle^A \left(\text{Singlet}\,(B,C) \right)$$

$$- |\psi_{100,\downarrow}\rangle \; \text{Singlet}\,(A,C)$$

But, this is difficult, so we use a different notation

i.e. Occupation number / basis

(nl)[Occupation]

1 electron in $\psi_{100,\uparrow}$] $\to$ 2 electron in 1s $\boxed{\uparrow\downarrow}$ 1s
1 " " $\psi_{100,\downarrow}$] $(1s)^2$

1 " " $\psi_{200,\uparrow}$ $\to$ $(2s)^1$ $\boxed{\uparrow}$ 2s

We don't specify which electron is in which state, only that there's one in that state.

Spectroscopic Notation

$^{2S+1}L_J$, L = S, P, D...

Note: $\vec{J}, \vec{L}, \vec{S}, M = S_z + L_z$ → Makes a full set.

H: 1 electron $\begin{cases} l = 0 \\ s = 1/2 \end{cases}$ → $^2S_{1/2}$

He: 2 electron $\begin{cases} l = 0 : 0 \otimes 0 \to 0 \\ s = 0 : 1/2 \otimes 1/2 \to 1 \oplus 0 \end{cases}$ — $^1S_0$, $^3S_1$ (Not possible: $0 \otimes 1$ — sym, sym)

Li: $(1s)^2 (2s)^1$ ($(1s)^2$: spin 0) $\begin{cases} l = 0 \\ s = 1/2 \end{cases}$ → $^2S_{1/2}$

Be: $(1s)^2 (2s)^2$ $\begin{cases} l: 0 \otimes 0 - 0 \\ s: 1/2 \otimes 1/2 - 0 \oplus 1 \end{cases}$ — $^1S_0$ → The only Asym. State.

B: $(1s)^2 (2s)^2 (2p)^1$ $\begin{cases} l = 1 \\ s = 1/2 \end{cases}$ → $1 \otimes 1/2$ — $^2P_{1/2}$, $^2P_{3/2}$ → Two possibility.

Later, we'll learn that this is the lowest energy state. ($^2P_{1/2}$)

C: $(1s)^2 (2s)^2 (2p)^2$ $\begin{cases} l: 1 \otimes 1 = 0 \oplus 1 \oplus 2 \\ s: 1/2 \otimes 1/2 = 0 \oplus 1 \end{cases}$ →

l	s	j	
2 ⊗ 0 =		2	$^1D_2$
1 ⊗ 1 =		2 ⊕ 1 ⊕ 0	$^3P_0$, $^3P_1$, $^3P_2$
0 ⊗ 0 =		0	$^1S_0$

(the lowest energy state: $^3P_0$)

Note about 4s vs 3D.