Chapter 8

Identical Particles

Two particles are *identical* if all their intrinsic properties (mass, spin, charge, magnetic moment, etc.) are the same and therefore no experiment can distinguish them. Of course, two identical particles can have different momentum, energy, angular momentum. For example all electrons are identical, all protons, all neutrons, all hydrogen atoms are identical (the possible excitation states viewed as energy, momentum, etc.)

8.1 Identical particles in Classical Mechanics

We can assign a labeling of the particles and follow through. Results are labeling independent.

As shown in Fig.8.2 we have two cases:

- Case 1: Assume we solve the dynamics and find

$$\begin{aligned} \mathbf{r}_1(t) &= \mathbf{r}(t) \qquad \text{with} \qquad \mathbf{r}(t_0) = \mathbf{r}_0 \\ \mathbf{r}_2(t) &= \mathbf{r}'(t) \qquad \text{with} \qquad \mathbf{r}'(t_0) = \mathbf{r}'_0 \end{aligned}$$

- Case 2: Since the particles are identical the Hamiltonian must make this clear

$$H(\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2) = H(\mathbf{r}_2, \mathbf{p}_2; \mathbf{r}_1, \mathbf{p}_1) \tag{8.1.1}$$

  This time, when we solve

$$\begin{aligned} \mathbf{r}_1(t) &= \mathbf{r}'(t) \qquad \text{with} \qquad \mathbf{r}'(t_0) = \mathbf{r}'_0 \\ \mathbf{r}_2(t) &= \mathbf{r}(t) \qquad \text{with} \qquad \mathbf{r}(t_0) = \mathbf{r}_0 \end{aligned}$$

The two descriptions are equivalent. We can follow the particles and the particle that started at $\{\mathbf{r}_0, \mathbf{p}_0\}$ will be at $\mathbf{r}(t)$, while the one that started at $\{\mathbf{r}'_0, \mathbf{p}'_0\}$ will be at $\mathbf{r}'(t)$.

In conclusion, we choose one labeling, just as if the particles were different. Follow through without regard to other possible labeling.

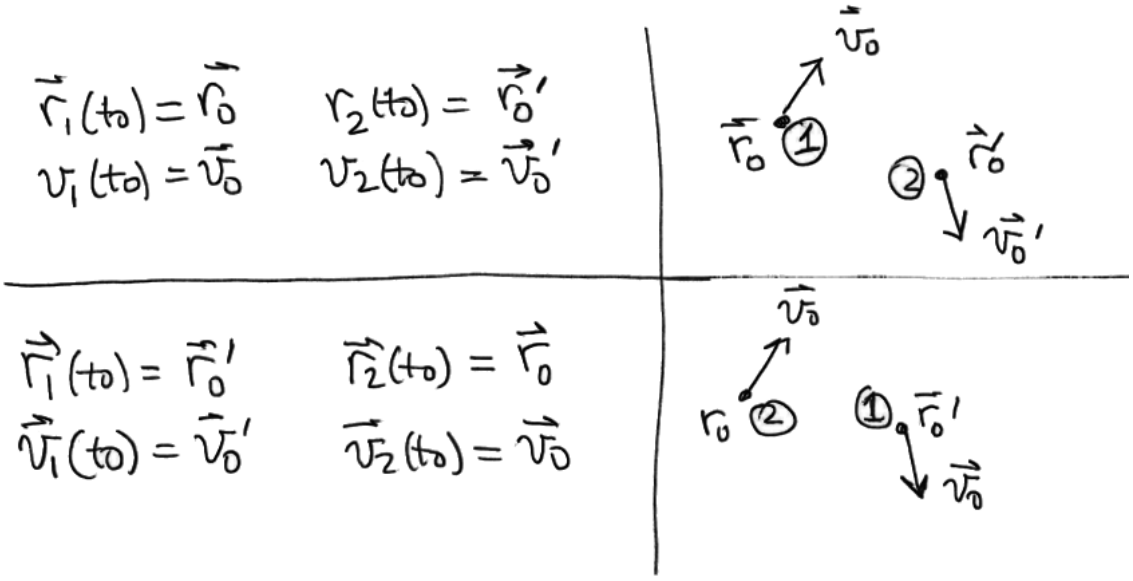


Figure 8.1: Example of two different ways of labeling the initial state

8.2 Identical particles in Quantum Mechanics

8.2.1 Exchange degeneracy

If we cannot follow particles once they overlap and/or collide, we can't know what alternative took place.
Question: How to write kets for the initial and final states?

Simpler case to see the complications Let there be two spin-1/2 particles. Consider only their spin[1], one is $|+\rangle$, the other $|-\rangle$. Recall tensor product $|v_i\rangle_{(1)} \otimes |v_j\rangle_{(2)}$ describing particle 1 in state v_i and particle 2 in state v_j. More briefly $|v_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \equiv |v_i\rangle \otimes |v_j\rangle$ with the understanding that the first ket is for particle 1 and the second for particle 2. What is the state of the two spin 1/2 particles?

$$|+\rangle_{(1)} \otimes |-\rangle_{(2)} \qquad \text{or} \qquad |-\rangle_{(1)} \otimes |+\rangle_{(2)} \tag{8.2.1}$$

A priori either one! This, despite the fact that in our conventions for inner products these two states are orthogonal! Can we declare these states to be physically equivalent and thus solve the ambiguity? No. If the two states above are equivalent we would have to admit that even the states

$$|\psi\rangle = \alpha|+\rangle \otimes |-\rangle + \beta|-\rangle \otimes |+\rangle \tag{8.2.2}$$

[1] in this approximation we could say that they are static and very close to each other, even on top of each other

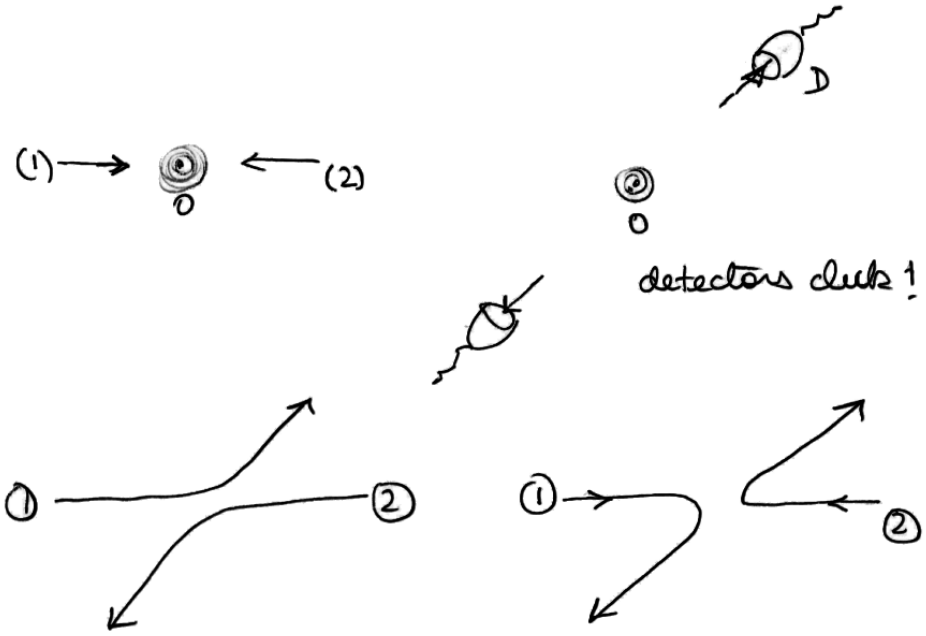


Figure 8.2: Example of two different processes involving identical particles. In principle, in quantum mechanics it is impossible to tell which one happened.

with $|\alpha|^2 + |\beta|^2 = 1$ for normalization, are equivalent. This ambiguity in the specification of a state of identical particles is called *exchange degeneracy*.
What is the probability to find these particles in the $|+,\chi\rangle \otimes |+,\chi\rangle$ state?
This states is

$$\begin{aligned} |\psi_0\rangle &= \frac{1}{\sqrt{2}}\Big(|+\rangle_{(1)} \ + \ |-\rangle_{(1)}\Big) \otimes \frac{1}{\sqrt{2}}\Big(|+\rangle_{(2)} \ + \ |-\rangle_{(2)}\Big) \\ &= \frac{1}{2}\Big(|+\rangle_{(1)} \otimes |+\rangle_{(2)} \ + \ |+\rangle_{(1)} \otimes |-\rangle_{(2)} \ + \ |-\rangle_{(1)} \otimes |+\rangle_{(2)} \ + \ |-\rangle_{(1)} \otimes |-\rangle_{(2)}\Big) \end{aligned} \tag{8.2.3}$$

the probability is

$$\Big|\langle\psi_0|\psi\rangle\Big|^2 = \Big|\frac{1}{2}(\alpha+\beta)\Big|^2 \tag{8.2.4}$$

thus a tremendous ambiguity because the chosen values of α, β matter!
Three particle degeneracy; 3 different eigenstates $|a\rangle, |b\rangle, |c\rangle$ give the following combinations

$$\begin{aligned} &|a\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |c\rangle_{(3)}\,, && |a\rangle_{(1)} \otimes |c\rangle_{(2)} \otimes |b\rangle_{(3)}\,, \\ &|b\rangle_{(1)} \otimes |c\rangle_{(2)} \otimes |a\rangle_{(3)}\,, && |b\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |c\rangle_{(3)}\,, \\ &|c\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |b\rangle_{(3)}\,, && |c\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |a\rangle_{(3)}\,. \end{aligned}$$

8.2.2 Permutation operators

Two particle systems

Consider the case when the vector space V relevant to the particles is the same for both particles, even though the particles may be *distinguishable*. Call the particles 1 and 2. Consider the state in which particle one is in state u_i and particle 2 in state u_j

$$|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \ \in V \otimes V \tag{8.2.5}$$

Since the particles are possibly distinguishable note that

$$|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \neq |u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \,. \tag{8.2.6}$$

Define $\hat{P}_{21}$ the linear operator on $V \otimes V$ such that

$$\hat{P}_{21}\Big[|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)}\Big] \equiv |u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \,. \tag{8.2.7}$$

note that

$$\hat{P}_{21}\hat{P}_{21} = \mathbb{1} \,, \tag{8.2.8}$$

i.e. $\hat{P}_{21}$ is its own inverse. Claim

$$\boxed{\hat{P}_{21}^\dagger = \hat{P}_{21} \,, \text{ Hermitian}} \tag{8.2.9}$$

Proof: First of all let's recall that for a generic operator $\hat{O}$, the adjoint of $\hat{O}$ is defined s.t.

$$\langle\alpha|\hat{O}^\dagger|\beta\rangle = \langle\beta|\hat{O}|\alpha\rangle \tag{8.2.10}$$

In our case, not writing the subscript labels,

$$\langle u_k| \otimes \langle u_\ell|\hat{P}_{21}|u_i\rangle \otimes |u_j\rangle = \langle u_k| \otimes \langle u_\ell|\Big(|u_j\rangle \otimes |u_i\rangle\Big) = \delta_{kj}\delta_{\ell i}$$
$$\langle u_k| \otimes \langle u_\ell|\hat{P}_{21}^\dagger|u_i\rangle \otimes |u_j\rangle = \Big(\langle u_i| \otimes \langle u_j|\hat{P}_{21}|u_k\rangle \otimes |u_\ell\rangle\Big)^* = \Big[\langle u_i| \otimes \langle u_j|\big(|u_\ell\rangle \otimes |u_k\rangle\big)\Big]^* = \Big[\delta_{i\ell}\delta_{jk}\Big]^* = \delta_{kj}\delta_{\ell i}$$

hence

$$\hat{P}_{21}^\dagger = \hat{P}_{21} \qquad \checkmark \,. \tag{8.2.11}$$

Because of (8.2.8) we also have that $\hat{P}_{21}$ is unitary:

$$\hat{P}_{21}^\dagger\hat{P}_{21} = \hat{P}_{21}\hat{P}_{21} = \mathbb{1} \,. \tag{8.2.12}$$

Given a generic state $|\psi\rangle$ it is not clear a priori what would it be its behaviour under the action of $\hat{P}_{21}$, hence to make our life easier we want to rewrite a generic state $|\psi\rangle$ in

terms of eigenstates of $\hat{P}_{21}$.
We can define two eigenstates of $\hat{P}_{21}$ with the following properties

$$\begin{aligned} \hat{P}_{21}|\psi_S\rangle &= |\psi_S\rangle && \text{Symmetric state} \\ \hat{P}_{21}|\psi_A\rangle &= -|\psi_A\rangle && \text{Antisymmetric state} \end{aligned}$$

and two operators $\hat{S}$ and $\hat{A}$

$$\hat{S} \equiv \frac{1}{2}(\mathbb{1} + \hat{P}_{21})\,, \qquad \hat{A} \equiv \frac{1}{2}(\mathbb{1} - \hat{P}_{21})\,. \tag{8.2.13}$$

Note that $\hat{S}$ and $\hat{A}$ are such that

$$\begin{aligned} \hat{P}_{21}\hat{S} &= \frac{1}{2}(\hat{P}_{21} + \hat{P}_{21}\hat{P}_{21}) = \frac{1}{2}(\hat{P}_{21} + \mathbb{1}) = \hat{S} \\ \hat{P}_{21}\hat{A} &= \frac{1}{2}(\hat{P}_{21} - \hat{P}_{21}\hat{P}_{21}) = \frac{1}{2}(\hat{P}_{21} - \mathbb{1}) = -\hat{A} \end{aligned}$$

Therefore, given a generic state $|\psi\rangle$ we have that

$$\begin{aligned} \hat{P}_{21}\hat{S}|\psi\rangle = \hat{S}|\psi\rangle \qquad &\Longrightarrow \qquad \hat{S}|\psi\rangle \text{ is symmetric} \\ \hat{P}_{21}\hat{A}|\psi\rangle = -\hat{A}|\psi\rangle \qquad &\Longrightarrow \qquad \hat{A}|\psi\rangle \text{ is anti-symmetric.} \end{aligned}$$

Because of this, the Hermitian operators $\hat{S}$ and $\hat{A}$ are called *symmetric/antisymmetric projectors*. From a mathematical point of view $\hat{S}$ and $\hat{A}$ are orthogonal projectors[2] and satisfy

$$\hat{S}^2 = \hat{S}\,, \qquad \hat{A}^2 = \hat{A}\,, \qquad \hat{S} + \hat{A} = \mathbb{1}\,, \qquad \hat{S}\hat{A} = \hat{A}\hat{S} = 0\,. \tag{8.2.15}$$

Action on operators Let $B(n)$ be an operator acting on the n-th vector space, i.e.

$$\begin{aligned} B(1)|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= \Big(B|u_i\rangle\Big)_{(1)} \otimes |u_j\rangle_{(2)} \\ B(2)|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= |u_i\rangle_{(1)} \otimes \Big(B|u_j\rangle\Big)_{(2)} \end{aligned}$$

then the action of $\hat{P}_{21}$ on $B(1)$ is

$$\begin{aligned} \hat{P}_{21}B(1)\hat{P}_{21}^\dagger|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} &= \hat{P}_{21}B(1)|u_j\rangle_{(1)} \otimes |u_i\rangle_{(2)} \\ &= \hat{P}_{21}\Big(B|u_j\rangle\Big)_{(1)} \otimes |u_i\rangle_{(2)} = |u_i\rangle_{(1)} \otimes \Big(B|u_j\rangle\Big)_{(2)} = B(2)|u_i\rangle \otimes |u_j\rangle \end{aligned} \tag{8.2.16}$$

[2] A projector $P : V \to U \subset V$ is *orthogonal* if $V = \ker P \oplus \text{range } P$, with $\ker P \perp \text{range } P$. Take $v \in V$, then

$$v = \underbrace{Pv}_{\text{range}P} + \underbrace{v - Pv}_{\ker P} = u + w \tag{8.2.14}$$

where $w \in \ker P$, $u = Pv \in \text{range}P$, then $\ker P \perp \text{range}P$ because

$$\langle w, u\rangle = \langle w, Pv\rangle = \langle P^\dagger w, v\rangle = \langle Pw, v\rangle = \langle 0, v\rangle = 0$$

hence

$$\boxed{\hat{P}_{21}B(1)\hat{P}_{21}^{\dagger} = B(2)} \tag{8.2.17}$$

Similarly we have

$$\hat{P}_{21}B(2)\hat{P}_{21}^{\dagger} = B(1) \tag{8.2.18}$$

and if we consider a generic operator $\hat{\Theta}(1,2)$, then

$$\boxed{\hat{P}_{21}\hat{\Theta}(1,2)\hat{P}_{21}^{\dagger} = \hat{\Theta}(2,1)}\,. \tag{8.2.19}$$

Note that if $\hat{\Theta}(1,2) = \hat{\Theta}(2,1)$ we say $\hat{\Theta}(1,2)$ is *symmetric*. If an operator is symmetric then

$$\begin{aligned} 0 &= \hat{P}_{21}\hat{\Theta}(1,2)\hat{P}_{21}^{\dagger} - \hat{\Theta}(1,2) \\ 0 &= \hat{P}_{21}\hat{\Theta}(1,2) - \hat{\Theta}(1,2)\hat{P}_{21} \\ 0 &= [\hat{P}_{21}, \hat{\Theta}(1,2)] \end{aligned} \tag{8.2.20}$$

$$[\hat{P}_{21}, \hat{\Theta}(1,2)] = 0 \iff \hat{\Theta} \text{ is symmetric}\,. \tag{8.2.21}$$

N particle systems

In a N particle system we can define $N!$ permutation operators $\hat{P}_{i_1,\ldots,i_N}$, with $\hat{P}_{12\ldots N}$ being the identity. For a 3-particle system, for example, the operator P_{npq} acting on a state has the effect of

$$\hat{P}_{npq} \qquad \text{means} \qquad \begin{aligned} n &\to 1 \qquad & n-\text{th state moved to position 1} \\ p &\to 2 \qquad & p-\text{th state moved to position 2} \\ q &\to 3 \qquad & q-\text{th state moved to position 3} \end{aligned}$$

e.g.

$$\hat{P}_{231}|u_i\rangle_{(1)} \otimes |u_j\rangle_{(2)} \otimes |u_k\rangle_{(3)} = |u_j\rangle_{(1)} \otimes |u_k\rangle_{(2)} \otimes |u_i\rangle_{(3)} \tag{8.2.22}$$

You should check that its inverse is $\hat{P}_{312}$, so that

$$\hat{P}_{231}\hat{P}_{312} = \mathbb{1}\,. \tag{8.2.23}$$

More formally we can define a *permutation* of N numbers by the function α that maps the standard ordered integers $1, \ldots, N$ into some arbitrary ordering of them

$$\alpha : [1, 2, \ldots, N] \to [\alpha(1),\, \alpha(2),\, \ldots,\, \alpha(N)] \tag{8.2.24}$$

and associate it with a permutation operator

$$\hat{P}_{\alpha} \equiv \hat{P}_{\alpha(1),\,\alpha(2),\,\ldots,\,\alpha(N)} \tag{8.2.25}$$

$$\hat{P}_{\alpha}|u_1\rangle_{(1)} \otimes \cdots \otimes |u_N\rangle_{(N)} = |u_{\alpha(1)}\rangle_{(1)} \otimes \cdots \otimes |u_{\alpha(N)}\rangle_{(N)} \tag{8.2.26}$$

For example

$$\hat{P}_{3142}|u_1\rangle_{(1)} \otimes |u_2\rangle_{(2)} \otimes |u_3\rangle_{(3)} \otimes |u_4\rangle_{(4)} = |u_3\rangle_{(1)} \otimes |u_1\rangle_{(2)} \otimes |u_4\rangle_{(3)} \otimes |u_2\rangle_{(4)} \tag{8.2.27}$$

or

$$\hat{P}_{3142}|a\rangle_{(1)} \otimes |b\rangle_{(2)} \otimes |c\rangle_{(3)} \otimes |d\rangle_{(4)} = |c\rangle_{(1)} \otimes |a\rangle_{(2)} \otimes |d\rangle_{(3)} \otimes |b\rangle_{(4)} \tag{8.2.28}$$

The set of all permutations of N objects forms the *symmetric group* S_N and it has $N!$ elements. For S_3 we have 6 elements or the 6 permutation operators:

$$\underbrace{\hat{P}_{123}}_{\mathbb{1}} \overset{\text{cyclic}}{\to} \hat{P}_{312} \overset{\text{cyclic}}{\to} \hat{P}_{231}\,, \quad \underbrace{\hat{P}_{132} \overset{\text{cyclic}}{\to} \hat{P}_{213} \overset{\text{cyclic}}{\to} \hat{P}_{321}}_{\substack{\text{these are } \textit{transpositions},\\ \text{a permutation in which only}\\ \text{2 particles are exchanged}\\ \text{without affecting the rest}}}$$

$\hat{P}_{132}$ is a transposition in which the states of the second and third particles are exchanged while the first particle is left unchanged. For transpositions we sometimes use the notation where we just indicate the two labels that are being transposed. Those two labels could be written in any order without risk of confusion, but we will use ascending order:

$$\begin{aligned} (12) &\equiv P_{213} \\ (13) &\equiv P_{321} \\ (23) &\equiv P_{132} \end{aligned} \tag{8.2.29}$$

While all permutations that are transpositions are Hermitian (see the proof for $\hat{P}_{21}$ that easily generalizes), general permutations are not Hermitian. It is intuitively clear that any permutation can be written as product of transpositions: any set of integers can be reordered into any arbitrary position by transpositions (in fact by using transpositions of consecutive labels). The decomposition of a permutation into a product of transpositions is not unique, but it is unique (mod 2). Hence we have that every permutation is either *even* or *odd*. A permutation is said to be even if it is the product of an even number of transpositions, and it is said to be odd if it is the product of an odd number of transpositions.

Since transposition operators are and unitary any permutation is a unitary operator. All transpositions are also Hermitian, but an arbitrary product of them is not hermitian because the transpositions do not necessarily commute.

In fact, the Hermitian conjugate of a permutation is its inverse, which is a permutation of the same parity. This is clear from writing $\hat{P}_\alpha$ as a product of transpositions P_{t_i}:

$$\begin{aligned} \hat{P}_\alpha &= \hat{P}_{t_1}\hat{P}_{t_2}\ldots\hat{P}_{t_k} \\ \hat{P}_\alpha^\dagger &= \hat{P}_{t_k}^\dagger\ldots\hat{P}_{t_2}^\dagger\hat{P}_{t_1}^\dagger = \hat{P}_{t_k}\ldots\hat{P}_{t_2}\hat{P}_{t_1} \end{aligned} \tag{8.2.30}$$

and therefore

$$\implies \hat{P}_\alpha\hat{P}_\alpha^\dagger = \mathbb{1} \tag{8.2.31}$$

Theorem 8.2.1. *The number of even permutations is the same as the number of odd permutations*

Proof. Consider the map that multiplies any permutation by (12) from the left (12) : $P_{\text{even}} \to P_{\text{odd}}$ so that if $\sigma \in P_{\text{even}}$ then $(12)\sigma \in P_{\text{odd}}$. This map is one to one

$$(12)\sigma = (12)\sigma' \implies \sigma = \sigma' \,, \tag{8.2.32}$$

by multiplying from the left by (12), which is the inverse of (12). This map is also surjective or onto:for any $\beta \in P_{\text{odd}}$, we have $\beta = (12)\underbrace{(12)\beta}_{\in P_{\text{even}}}$. □

$A\backslash B$	$\hat{P}_{312}$	$\hat{P}_{231}$	(23)	(12)	(13)
$\hat{P}_{312}$	$\hat{P}_{231}$	$\mathbb{1}$	(12)	(13)	(23)
$\hat{P}_{231}$	$\mathbb{1}$	$\hat{P}_{312}$	(13)	(23)	(12)
(23)	(13)	(12)	$\mathbb{1}$	$\hat{P}_{231}$	$\hat{P}_{312}$
(12)	(23)	(13)	$\hat{P}_{312}$	$\mathbb{1}$	$\hat{P}_{231}$
(13)	(12)	(23)	$\hat{P}_{231}$	$\hat{P}_{312}$	$\mathbb{1}$

Table 8.1: $A \cdot B$ matrix for S_3.

Complete symmetrizer and antisymmetrizer

Permutation operators do not commute, so we can't find complete basis of states that are eigenstates of all permutation operators. It is possible, however, to find some states that are simultaneous eigenvectors of all permutation operators.

Consider N particles, each with the same vector space. Let $\hat{P}_\alpha$ be an arbitrary permutation, then

$$\begin{aligned} \text{Symmetric state } |\psi_S\rangle \ : \quad & \hat{P}_\alpha|\psi_S\rangle = |\psi_S\rangle \quad \forall\alpha \\ \text{Antisymmetric state } |\psi_A\rangle \ : \quad & \hat{P}_\alpha|\psi_A\rangle = \epsilon_\alpha|\psi_A\rangle \end{aligned}$$

where

$$\epsilon_\alpha = \begin{cases} +1 & \text{if } \hat{P}_\alpha \text{ is an even permutation} \\ -1 & \text{if } \hat{P}_\alpha \text{ is an odd permutation} \end{cases} \tag{8.2.33}$$

In the total Hilbert space $V^{\otimes N} \equiv \underbrace{V \otimes \cdots \otimes V}_{N}$, we can identify a subspace $\text{Sym}^N V \subset V^{\otimes N}$ of symmetric states and a subspace $\text{Anti}^N V \subset V^{\otimes N}$ of antisymmetric states. Can we construct projectors into such subspaces?

Yes!

$$\hat{S} \equiv \frac{1}{N!}\sum_\alpha \hat{P}_\alpha \qquad \text{and} \qquad \hat{A} \equiv \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha \tag{8.2.34}$$

where we sum over all $N!$ permutations. $\hat{S}$ is called the *symmetrizer* and $\hat{A}$ is called the *antisymmetrizer*.

$$\text{Claim:} \qquad \hat{S} = \hat{S}^\dagger \qquad \hat{A} = \hat{A}^\dagger \tag{8.2.35}$$

Hermitian conjugation of $\hat{P}_\alpha$ gives $\hat{P}_\alpha^{-1}$ which is even if $\hat{P}_\alpha$ is even and odd if $\hat{P}_\alpha$ is odd. Thus Hermitian conjugation just rearranges the sums, leaving them invariant.
Moreover

$$\hat{P}_{\alpha_0}\hat{S} = \hat{S}\hat{P}_{\alpha_0} = \hat{S} \tag{8.2.36}$$

$$\hat{P}_{\alpha_0}\hat{A} = \hat{A}\hat{P}_{\alpha_0} = \epsilon_{\alpha_0}\hat{A} \tag{8.2.37}$$

Proof. Note that $\hat{P}_{\alpha_0}$ acting on the list of permutations simply rearranges the list, given two permutations $P_{\gamma_1} \neq P_{\gamma_2}$ then $\hat{P}_{\alpha_0}P_{\gamma_1} \neq \hat{P}_{\alpha_0}P_{\gamma_2}$, hence

$$\hat{P}_{\alpha_0}\hat{S} = \hat{P}_{\alpha_0}\frac{1}{N!}\sum_\alpha \hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{1}{N!}\sum_\beta \hat{P}_\beta = \hat{S} \qquad \checkmark \tag{8.2.38}$$

analogously

$$\begin{aligned}\hat{P}_{\alpha_0}\hat{A} &= \hat{P}_{\alpha_0}\frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \underbrace{\epsilon_{\alpha_0}\epsilon_{\alpha_0}}_{=1}\hat{P}_{\alpha_0}\hat{P}_\alpha \\ &= \frac{\epsilon_{\alpha_0}}{N!}\sum_\alpha \epsilon_\alpha\epsilon_{\alpha_0}\hat{P}_{\alpha_0}\hat{P}_\alpha = \frac{\epsilon_{\alpha_0}}{N!}\sum_\beta \epsilon_\beta \hat{P}_\beta = \epsilon_{\alpha_0}\hat{A} \qquad \checkmark\end{aligned} \tag{8.2.39}$$

□

Finally they are projectors

$$\boxed{\hat{S}^2 = \hat{S}\,, \qquad \hat{A}^2 = \hat{A}\,, \qquad \hat{S}\hat{A} = \hat{A}\hat{S} = 0} \tag{8.2.40}$$

$$\hat{S}^2 = \frac{1}{N!}\sum_\alpha \hat{P}_\alpha\hat{S} = \frac{1}{N!}\sum_\alpha \hat{S} = \frac{1}{N!}N!\,\hat{S} = \hat{S} \qquad \checkmark \tag{8.2.41}$$

$$\hat{A}^2 = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{P}_\alpha\hat{A} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\epsilon_\alpha\hat{A} = \frac{1}{N!}\sum_\alpha \hat{A} = \frac{1}{N!}N!\,\hat{A} = \hat{A} \qquad \checkmark \tag{8.2.42}$$

$$\hat{A}\hat{S} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{P}_\alpha\hat{S} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha\hat{S} = \frac{\hat{S}}{N!}\sum_\alpha \epsilon_\alpha = 0 \qquad \checkmark \tag{8.2.43}$$

Since, as explained before there are equal numbers of even and odd permutations, i.e. $\sum_\alpha \epsilon_\alpha = 0$.
Note that

$$\hat{S}|\psi\rangle \in \mathrm{Sym}^N V \quad \text{since} \quad \hat{P}_\alpha\hat{S}|\psi\rangle = \hat{S}|\psi\rangle \;\forall\,\alpha \tag{8.2.44}$$

and analogously

$$\hat{A}|\psi\rangle \in \mathrm{Anti}^N V \quad \text{since} \quad \hat{P}_\alpha\hat{A}|\psi\rangle = \epsilon_\alpha\hat{A}|\psi\rangle \;\forall\,\alpha \tag{8.2.45}$$

Hence, they are, as claimed, projectors into the symmetric and antisymmetric subspaces:

$$\hat{S} : V^{\otimes N} \to \mathrm{Sym}^N V\,, \qquad \hat{A} : V^{\otimes N} \to \mathrm{Anti}^N V \tag{8.2.46}$$

Example: $N = 3$ For S_3 we have 6 elements or the 6 permutation operators:

$$\hat{P}_{123} = \mathbf{1}\,,\ \hat{P}_{312}\,,\ \hat{P}_{231}\,,\ \hat{P}_{132}\,,\ \hat{P}_{213}\,,\ \hat{P}_{321}$$

In this case the symmetrizer and antisymmetrizer operators $\hat{S}$ and $\hat{A}$ are

$$\hat{S} = \tfrac{1}{6}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231} + \hat{P}_{132} + \hat{P}_{213} + \hat{P}_{321}) \tag{8.2.47}$$

$$\hat{A} = \tfrac{1}{6}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231} - \hat{P}_{132} - \hat{P}_{213} - \hat{P}_{321}) \tag{8.2.48}$$

Note that

$$\hat{S} + \hat{A} = \tfrac{1}{3}(\mathbf{1} + \hat{P}_{312} + \hat{P}_{231}) \neq \mathbb{1} = \hat{P}_{123} \tag{8.2.49}$$

This is a manifestation of the fact that in general for $N > 2$, we have

$$\mathrm{Sym}^N V \oplus \mathrm{Anti}^N V \subset V^{\otimes N} \tag{8.2.50}$$

i.e. in principle, the N-particle Hilbert space is not spanned by purely symmetric or antisymmetric states.
We define $\Theta(1, 2, \ldots, N)$ to be a *completly symmetric observable* if

$$[\Theta(1, 2, \ldots, N), \hat{P}_\alpha] = 0 \quad \forall\alpha \tag{8.2.51}$$

8.3 The symmetrization postulate

In a system with N identical particles the states that are physically realized are not arbitrary states in $V^{\otimes N}$, but rather they are totally symmetric (*i.e.* belong to $\mathrm{Sym}^N V$), in which case the particles are said to be *bosons*, or they are totally antisymmetric (*i.e.* belong to $\mathrm{Anti}^N V$) in which case they are said to be *fermions*.

Comments:

1. The above is a statement of fact in 3D. Alternative possibilities can happen in worlds with 2 spatial dimensions (anyons)

2. The postulate describes the statistical behaviour of bosons and of fermions

3. Spin-statistics theorem from Quantum Field Theory shows that bosons are particles of integer spins (0, 1, 2, ...) while fermions are particles of half-integer spin (1/2, 3/2 , ...)

4. The symmetrization postulate for elementary particles lead to a definite character, as bosons or fermions, for composite particles, which in turn obey the symmetrization

postulate. Take for example two hydrogen atoms

p = proton is a fermion (spin 1/2)
e = electron is a fermion (")

The system is made by 4 particles and its total wavefunction is $\Psi(p_1, e_1; p_2, e_2)$. Since the two electrons are identical particles of spin 1/2, the wavefunction must be anti-symmetric under the exchange $e_1 \leftrightarrow e_2$

$$\Psi(p_1, e_2; p_2, e_1) = -\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.1}$$

Exactly the same argument applies to the protons,

$$\Psi(p_2, e_1; p_1, e_2) = -\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.2}$$

Therefore under the simultaneous exchange

$$\Psi(p_2, e_2; p_1, e_1) = +\Psi(p_1, e_1; p_2, e_2)\,. \tag{8.3.3}$$

The exchange in (8.3.3) corresponds to $p_1 \leftrightarrow p_2$ *and* $e_1 \leftrightarrow e_2$, an exchange of the two hydrogen atoms! Since the wavefunction is symmetric under this exchange, (8.3.3) shows that the hydrogen atom is a boson!

5. The symmetrization postulate solves the exchange degeneracy problem.

   Say $|u\rangle \in V^{\otimes N}$ represents mathematically a state. Let $V_{|u\rangle} \equiv \text{span}\left\{\hat{P}_\alpha|u\rangle\,, \forall\alpha\right\}$. Depending on $|u\rangle$ the dimension of $V_{|u\rangle}$ can go from 1 to $N!$. This dimensionality, if different from one, is the degeneracy due to exchange.

   The exchange degeneracy problem (*i.e.* the ambiguity in finding a representative for the physical state in $V_{|u\rangle}$) is solved by the symmetrization postulate by showing that $V_{|u\rangle}$ contains, up to scale, a single ket of $\text{Sym}^N V$ and a single ket of $\text{Anti}^N V$.

Proof. Suppose we have two states $|\psi\rangle$, $|\psi'\rangle \in V_{|u\rangle}$ that both happen to be symmetric: $|\psi\rangle$, $|\psi'\rangle \in \text{Sym}^N V$. We can write them as

$$|\psi\rangle = \sum_\alpha c_\alpha P_\alpha|u\rangle \quad \text{and} \quad |\psi'\rangle = \sum_\alpha c'_\alpha P_\alpha|u\rangle \tag{8.3.4}$$

with c_α, c'_α some coefficients. Then, since $|\psi\rangle \in \mathrm{Sym}^N V$

$$|\psi\rangle = \hat{S}|\psi\rangle = \hat{S}\sum_\alpha c_\alpha P_\alpha |u\rangle = \sum_\alpha c_\alpha \hat{S} P_\alpha |u\rangle = \sum_\alpha c_\alpha \hat{S}|u\rangle = \hat{S}|u\rangle \sum_\alpha c_\alpha \,. \tag{8.3.5}$$

Analogously

$$|\psi'\rangle = \hat{S}|u\rangle \sum_\alpha c'_\alpha \,. \tag{8.3.6}$$

Hence $|\psi\rangle \propto |\psi'\rangle$, the states are the same up to scale. □

6. Building antisymmetric states.

Constructing the three-particle state $\hat{A}|u\rangle$ with $|u\rangle \in V^{\otimes 3}$ given by

$$|u\rangle = |\varphi\rangle_{(1)} \otimes |\chi\rangle_{(2)} \otimes |\omega\rangle_{(3)} \tag{8.3.7}$$

The claim is that the antisymmetric state is constructed by a determinant:

$$\hat{A}|u\rangle = \tfrac{1}{3!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha |\varphi\rangle_{(1)} \otimes |\chi\rangle_{(2)} \otimes |\omega\rangle_{(3)} = \tfrac{1}{3!}\begin{vmatrix} |\varphi\rangle_{(1)} & |\varphi\rangle_{(2)} & |\varphi\rangle_{(3)} \\ |\chi\rangle_{(1)} & |\chi\rangle_{(2)} & |\chi\rangle_{(3)} \\ |\omega\rangle_{(1)} & |\omega\rangle_{(2)} & |\omega\rangle_{(3)} \end{vmatrix} \tag{8.3.8}$$

When writing the products in the determinant one must reorder each term to have the standard order $|\cdot\rangle_{(1)} \otimes |\cdot\rangle_{(2)} \otimes |\cdot\rangle_{(3)}$. You can confirm you get the right answer. Now do it generally. Recall the formula for the determinant of a matrix

$$\det \hat{B} = \sum_\alpha \epsilon_\alpha B_{\alpha(1),1} B_{\alpha(2),2} \ldots B_{\alpha(N),N} \tag{8.3.9}$$

Let $|\omega\rangle$ be a generic state $\in V^{\otimes N}$

$$|\omega\rangle = |\omega_1\rangle_{(1)} |\omega_2\rangle_{(2)} \ldots |\omega_N\rangle_{(N)} \tag{8.3.10}$$

then

$$\hat{P}_\alpha |\omega\rangle = |\omega_{\alpha(1)}\rangle_{(1)} |\omega_{\alpha(2)}\rangle_{(2)} \ldots |\omega_{\alpha(N)}\rangle_{(N)} \tag{8.3.11}$$

so that

$$\hat{A}|\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha |\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha |\omega_{\alpha(1)}\rangle_{(1)} |\omega_{\alpha(2)}\rangle_{(2)} \ldots |\omega_{\alpha(N)}\rangle_{(N)} \,. \tag{8.3.12}$$

If we define a matrix

$$\omega_{ij} \equiv |\omega_i\rangle_{(j)} \tag{8.3.13}$$

then

$$\hat{A}|\omega\rangle = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \omega_{\alpha(1),1} \omega_{\alpha(2),2} \ldots \omega_{\alpha(N),N} = \frac{1}{N!}\det(\omega) \tag{8.3.14}$$

i.e.

$$\hat{A}|\omega\rangle = \frac{1}{N!}\begin{vmatrix} |\omega_1\rangle_{(1)} & |\omega_1\rangle_{(2)} & \dots & |\omega_1\rangle_{(N)} \\ |\omega_2\rangle_{(1)} & |\omega_2\rangle_{(2)} & \dots & |\omega_2\rangle_{(N)} \\ \vdots & & & \vdots \\ |\omega_N\rangle_{(1)} & \dots & \dots & |\omega_N\rangle_{(N)} \end{vmatrix} \tag{8.3.15}$$

8.4 Occupation numbers

Consider a system of N identical particle. Basis states in $V^{\otimes N}$ take the form

$$|u_i\rangle_{(1)} \otimes \dots |u_p\rangle_{(N)} \tag{8.4.1}$$

where the one-particle states form an orthonormal basis of V:

$$V = \text{span}\{|u_1\rangle, |u_2\rangle, \dots\} \tag{8.4.2}$$

By applying $\hat{S}$ or $\hat{A}$ to the full set of states in $V^{\otimes N}$ we obtain all physical states in $\text{Sym}^N V$ and $\text{Anti}^N V$. But many different states in $V^{\otimes N}$ can give rise to the *same* state in $\text{Sym}^N V$ and $\text{Anti}^N V$ after the application of the projectors.

To distinguish basis states in $V^{\otimes N}$ that after application of $\hat{S}$ or $\hat{A}$ are linearly independent, define the *occupation number*. We assign a set of occupation numbers to a basis state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$. An occupation number is an integer $n_i \geq 0$ associated with each vector in V:

$$\underset{n_1}{|u_1\rangle}, \ \underset{n_2}{|u_2\rangle}, \ \dots, \ \underset{n_k}{|u_k\rangle}, \ \dots \tag{8.4.3}$$

We define n_k to be the number of times that $|u_k\rangle$ appears in the chosen basis state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$. Thus, by inspection of the state $|\cdot\rangle \otimes \cdots \otimes |\cdot\rangle$ we can read all the occupation numbers $n_1, n_2, \cdots$. It should be clear that the action of a permutation operator on a basis state in $V^{\otimes N}$ will not change the occupation numbers.

Two basis states in $V^{\otimes N}$ with the same occupation numbers can be mapped into each other by a permutation operator; they lead to the same state in $\text{Sym}^N V$ and to the same state (up to a sign) in $\text{Anti}^N V$. Two basis states in $V^{\otimes N}$ with different occupation numbers cannot be mapped into each other by a permutation operator. They must lead to different states in $\text{Sym}^N V$ and to different states in $\text{Anti}^N V$, unless they give zero.

Given the occupation numbers of a basis state, we denote the associated basis state in $\text{Sym}^N V$ as follows

$$|n_1, n_2, \dots\rangle_S \qquad\qquad n_i \geq 0 \tag{8.4.4}$$

Explicitly

$$|n_1,\, n_2,\, \ldots\rangle_S \;\equiv\; c_S\, \hat{S}\, \underbrace{|u_1\rangle \ldots |u_1\rangle}_{n_1 \text{ times}} \otimes \underbrace{|u_2\rangle \ldots |u_2\rangle}_{n_2 \text{ times}} \otimes \ldots \tag{8.4.5}$$

where c_S is a constant that is used to give the state unit normalization. More briefly we write

$$|n_1,\, n_2,\, \ldots\rangle_S \;\equiv\; c_S\, \hat{S}\, |u_1\rangle^{\otimes n_1} \otimes\; |u_2\rangle^{\otimes n_2} \otimes \ldots \tag{8.4.6}$$

where $|u_i\rangle^{\otimes n_i}$ is equal to 1 when $n_i = 0$ These states form an orthonormal basis in $\mathrm{Sym}^N V$:

$${}_S\langle n_1',\, n_2',\, \ldots | n_1,\, n_2,\, \ldots\rangle_S = \delta_{n_1,n_1'}\delta_{n_2,n_2'} \ldots \tag{8.4.7}$$

The space $\mathrm{Sym}^N V$ relevant to identical bosons is spanned by all the states

$$|n_1,\, n_2,\, \ldots\rangle \qquad \text{with } \sum_k n_k = N \tag{8.4.8}$$

The space $\mathrm{Anti}^N V$ relevant to identical fermions is spanned by all the states

$$|n_1,\, n_2,\, \ldots\rangle_A \qquad \text{with } \sum_k n_k = N \;\text{ and }\; n_k \in \{0,1\}\,, \tag{8.4.9}$$

since occupation numbers cannot be greater than one (any state with an occupation number two or larger is killed by $\hat{A}$). We have

$$|n_1,\, n_2,\, \ldots\rangle_A \;\equiv\; c_A\, \hat{A}\, |u_1\rangle^{\otimes n_1} \otimes\; |u_2\rangle^{\otimes n_2} \;\otimes \ldots \tag{8.4.10}$$

where c_A is a constant that is used to give the state unit normalization. These states form an orthonormal basis in $\mathrm{Anti}^N V$.

8.5 Particles that live in $V \otimes W$

A particle may have space degrees of freedom, described by a vector space V and spin degree of freedom associated with W. Suppose we have a state than of 2 such particles described in $(V \otimes W)^{\otimes 2}$ for example

$$|\psi\rangle = |v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)} + \ldots \tag{8.5.1}$$

This ψ should belongs either to $\mathrm{Sym}^2(V \otimes W)$ or to $\mathrm{Anti}^2(V \otimes W)$. The permutation operator here that exchange particles 1 and 2 is

$$\hat{P}_{3412}|\psi\rangle = \hat{P}_{3412}\Big(|v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)}\Big) = |v_j\rangle_{(1)} \otimes |w_j\rangle_{(1)} \otimes |v_i\rangle_{(2)} \otimes |w_i\rangle_{(2)} \tag{8.5.2}$$

Wanto to express this in terms of $\mathrm{Sym}^2 V$, $\mathrm{Anti}^2 V$, $\mathrm{Sym}^2 W$, $\mathrm{Anti}^2 W$.
Why? Because it is possible: for any state

$$\ldots \overset{W}{|a\rangle} \ldots \overset{W}{|b\rangle} = \frac{1}{2}\underbrace{\Big(\ldots |a\rangle \ldots |b\rangle + \ldots |b\rangle \ldots |a\rangle\Big)}_{\in \mathrm{Sym}^2 W} + \frac{1}{2}\underbrace{\Big(\ldots |a\rangle \ldots |b\rangle - \ldots |b\rangle \ldots |a\rangle\Big)}_{\in \mathrm{Anti}^2 W} \tag{8.5.3}$$

Thus we can assume we work with simultaneous eigenstates of $\hat{P}_{3214}$, which exchanges the V states, and of $\hat{P}_{1432}$, which exchanges the W states. Note that

$$\hat{P}_{3412} = \hat{P}_{3214}\hat{P}_{1432} \tag{8.5.4}$$

where the order is not important since $[\hat{P}_{3214}, \hat{P}_{1432}] = 0$.
The eigenvalues are

$\hat{P}_{3214}$	$\hat{P}_{1432}$	$\hat{P}_{3412}$
1	1	1
-1	-1	1
1	-1	-1
-1	1	-1

This means that

$$\mathrm{Sym}^2(V \otimes W) \simeq \left(\mathrm{Sym}^2 V \otimes \mathrm{Sym}^2 W\right) \oplus \left(\mathrm{Anti}^2 V \otimes \mathrm{Anti}^2 W\right) \tag{8.5.5}$$

$$\mathrm{Anti}^2(V \otimes W) \simeq \left(\mathrm{Sym}^2 V \otimes \mathrm{Anti}^2 W\right) \oplus \left(\mathrm{Anti}^2 V \otimes \mathrm{Sym}^2 W\right) \tag{8.5.6}$$

where with $\simeq$ we indicate

$$|v_i\rangle_{(1)} \otimes |w_i\rangle_{(1)} \otimes |v_j\rangle_{(2)} \otimes |w_j\rangle_{(2)} \simeq |v_i\rangle_{(1)} \otimes |v_j\rangle_{(1)} \otimes |w_i\rangle_{(2)} \otimes |w_j\rangle_{(2)} \,. \tag{8.5.7}$$

The generalization to 2 particle belonging to $(U \otimes V \otimes W)$ is simple, for 3 or more particle is more complicated.

Example. Two electrons with spin wavefunction

$$\Psi(\mathbf{x_1}, m_1; \mathbf{x_1}, m_2) = \phi(x_1, x_2) \cdot \chi(m_1, m_2) \qquad \hat{S}_z = m\hbar \tag{8.5.8}$$

χ can be some normalized state in the space spanned by the triplet and the singlet. The probability $\mathrm{d}P$ to find one electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1}$ and in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2}$ is

$$dP = |\phi(\mathbf{x_1}, \mathbf{x_2})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.9}$$

Assume for simplicity that the electrons are non interacting so that the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{x_1}} + V(\mathbf{x_1}) - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{x_2}} + V(\mathbf{x_2})\right]\Psi = E\Psi \tag{8.5.10}$$

is separable, so there is a solution of the form $\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2})$ with

$$\int \mathrm{d}^3\mathbf{x}\,|\psi_A(\mathbf{x})|^2 = 1\,, \qquad \int \mathrm{d}^3\mathbf{x}\,|\psi_B(\mathbf{x})|^2 = 1\,, \qquad \int \mathrm{d}^3\mathbf{x}\,\psi^*_A(\mathbf{x})\psi_B(\mathbf{x}) = \alpha_{AB} \neq 0 \tag{8.5.11}$$

By Schwarz's inequality $|\langle u, v\rangle| \leq \sqrt{\langle u, u\rangle}\sqrt{\langle v, v\rangle}$ we have

$$\int \mathrm{d}^3\mathbf{x}\, \psi_A^*(\mathbf{x})\psi_B(\mathbf{x}) = |\langle \psi_A, \psi_B\rangle| \leq \sqrt{|\langle \psi_A, \psi_A\rangle|}\sqrt{|\langle \psi_B, \psi_B\rangle|} \implies \boxed{|\alpha_{AB}| \leq 1} \tag{8.5.12}$$

But then must build

$$\phi_\pm(\mathbf{x_1}, \mathbf{x_2}) = \frac{N_\pm}{\sqrt{2}}\big(\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}) \pm \psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})\big) \tag{8.5.13}$$

with $N_\pm$ a real normalization constant.

Take the following combination of ϕ and χ:

$\phi_+ \cdot \chi_{\text{singlet}}$	so that the total wavefunction is antisymmetric
$\phi_- \cdot \chi_{\text{triplet}}$	any of the 3 states of the triplet

Again, the probability to find one electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1}$ and in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2}$ is

$$\begin{aligned}\mathrm{d}P_\pm &= |\phi_\pm(\mathbf{x_1}, \mathbf{x_2})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ &= \frac{N_\pm}{\sqrt{2}}\Big\{|\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})|^2 \pm \underbrace{2\Re\big[\psi_A^*(\mathbf{x_1})\psi_A(\mathbf{x_2})\psi_B^*(\mathbf{x_2})\psi_B(\mathbf{x_1})\big]}_{\text{Exchange density}}\Big\}\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2}\end{aligned} \tag{8.5.14}$$

If we take the case $\mathbf{x_1} = \mathbf{x_2} = \mathbf{x}$, we get

$$\begin{aligned} &\mathrm{d}P_\pm = N_\pm\Big\{|\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2 \pm |\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2\Big\}\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ \implies\ &\mathrm{d}P_+ = 2N_\pm|\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2\mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \qquad (8.5.15) \\ &\mathrm{d}P_- = 0 \qquad (8.5.16)\end{aligned}$$

Recall that P_+ is associated with the singlet, while P_- with the triplet. Therefore electrons avoid each other in space when they are in the triplet state. In the singlet states there is enhanced probability to be at the same point.
Note that normalization requires

$$\begin{aligned}1 &= \frac{N_\pm^2}{2}\int \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2}\left\{|\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})|^2 \pm 2\Re\big[\psi_A^*(\mathbf{x_1})\psi_A(\mathbf{x_2})\psi_B^*(\mathbf{x_2})\psi_B(\mathbf{x_1})\big]\right\} \\ &= \frac{N_\pm^2}{2}\left\{1 + 1 \pm 2\Re\left[\int \mathrm{d}^3\mathbf{x_1}\,\psi_A^*(\mathbf{x_1})\psi_B(\mathbf{x_1})\int \mathrm{d}^3\mathbf{x_2}\,\psi_B^*(\mathbf{x_2})\psi_A(\mathbf{x_2})\right]\right\} \\ &= N_\pm^2\Big\{1 \pm \Re\left[\alpha_{AB}\cdot\alpha_{AB}^*\right]\Big\} \\ &= N_\pm^2\Big(1 \pm |\alpha_{AB}|^2\Big) \implies \boxed{N_\pm = \frac{1}{\sqrt{1 \pm |\alpha_{AB}|^2}}}\end{aligned} \tag{8.5.17}$$

So

$$\mathrm{d}P_+ = \frac{2}{1 \pm |\alpha_{AB}|^2} |\psi_A(\mathbf{x})\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.18}$$

to be compared with

$$\mathrm{d}P_D = |\psi_A(\mathbf{x})|^2 |\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \tag{8.5.19}$$

for distinguishable particles.
Since from (8.5.12) we have $|\alpha_{AB} < 1|$, then

$$\mathrm{d}P_+ \geq \mathrm{d}P_D \tag{8.5.20}$$

Assume $\psi_A(\mathbf{x})$ is nonzero only in a region R_A, $\psi_B(\mathbf{x})$ is nonzero only in a region R_B and $R_A \cap R_B = 0$, then

$$\alpha_{AB} = \int \mathrm{d}^3\mathbf{x}\, \psi_A^*(\mathbf{x})\psi_B(\mathbf{x}) = 0 \tag{8.5.21}$$

since ψ_A requires $\mathbf{x} \in R_A$ and ψ_B requires $\mathbf{x} \in R_B$. Therefore in this case $N_\pm = 1$.
Then the probability to find an electron in $\mathrm{d}^3\mathbf{x_1}$ around $\mathbf{x_1} \in R_A$ and another in $\mathrm{d}^3\mathbf{x_2}$ around $\mathbf{x_2} \in R_B$ is

$$\begin{aligned}\mathrm{d}P_\pm &= \Big\{ |\psi_A(\mathbf{x_1})\psi_B(\mathbf{x_2}|^2 + |\cancel{\psi_A(\mathbf{x_2})\psi_B(\mathbf{x_1})}|^2 \pm 2\Re\big[\psi_A^*(\mathbf{x_1})\cancel{\psi_A(\mathbf{x_2})}\psi_B^*(\mathbf{x_2})\cancel{\psi_B(\mathbf{x_1})}\big] \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} \\ &= |\psi_A(\mathbf{x})|^2 |\psi_B(\mathbf{x})|^2 \mathrm{d}^3\mathbf{x_1}\mathrm{d}^3\mathbf{x_2} = \mathrm{d}P_D \end{aligned} \tag{8.5.22}$$

it is the probability density for distinguishable particles.
Therefore, there is no need to symmetrize or antisymmetrize the wavefunction of non overlapping localized particles.

8.6 Counting states and distributions

E_i energy of the i-th level, d_i degeneracy of the i-th level. Assume we have N particles and we want to place N_1 particles in level 1, ..., N_i particles in level i (E_i, d_i). Let's call $Q(N_1, N_2, \dots)$ the number of ways to do this.

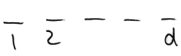
8.6.1 Distinguishable particles (Maxwell Boltzman)

Split N into $N_1, N_2, \dots$ in $\frac{N!}{N_1!N_2!\dots}$ ways (imagine putting them on a line $\underbrace{\dots}_{N_1}\underbrace{\dots}_{N_2}$ after drawing one ball at a time). Placing N_i particles in d_i slots gives $(d_i)^{N_i}$ ways, therefore

$$\boxed{Q(N_1, N_2, \dots) = N! \prod_i \frac{(d_i)^{N_i}}{N_i!}} \qquad \text{Maxwell Boltzman}$$

8.6.2 Identical fermions

Splitting the N states into groups for identical particles can only be done in one way



$N_i < d_i$

how many ways to place them?

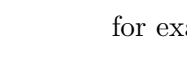
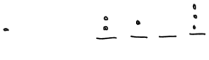
$$d_i \text{ choose } N_i = \frac{d_i}{N_i!(d_i - N_i)!}$$

$$\implies Q(N_1, N_2, \dots) = \prod_i \frac{d_i}{N_i!(d_i - N_i)!}$$

8.6.3 Identical bosons

N_i particles!

N_i balls and $(d_i - 1)$ bars,

for example:  

How many ways to order the $N_i + d_i - 1$ objects? $(N_i + d_i - 1)!$ but we must divide by the irrelevant permutations, hence

$$Q(N_1, N_2, \dots) = \prod_i \frac{(N_i + d_i - 1)!}{N_i!(d_i - 1)!} \tag{8.6.1}$$

This is for bosons:
$Q(N_1, N_2, \dots)$ counts the number of ways to have N particles and fixed energy $E = \sum_i N_i E_i$. Want to find the values of $N_1, N_2, \dots$ that are most likely.
Want to maximize $Q(N_1, N_2, \dots)$ under the constraint that $N = \sum_i N_i$ and $E = \sum_i N_i E_i$.
Maximizing Q is the same as maximizing $\ln Q$ and using lagrange multipliers

$$f(N_1, N_2, \dots) = \ln Q(N_1, N_2, \dots) + \alpha(N - \sum_i N_i) + \beta(E - \sum_i N_i E_i) \tag{8.6.2}$$

Do the fermion one, using Q_F from (8.6.1) we have

$$\ln Q_F = \sum_i \ln d_i! - \ln N_i! - \ln(d_i - N_i)! \tag{8.6.3}$$

Since all these quantities d_i, N_i are large we can use the Stirling approximation

$$\ln n! \simeq n \ln n - n \tag{8.6.4}$$

so that

$$\ln Q_F = \sum_i d_i \ln d_i \cancel{-d_i} - N_i \ln N_i \cancel{+N_i} - (d_i - N_i)\ln(d_i - N_i) \cancel{+d_i - N_i} = \sum_i d_i \ln d_i - N_i \ln N_i - (d_i - N_i)\ln(d_i - N_i) \tag{8.6.5}$$

Minimizing w.r.t. to N_i without constraints,

$$\frac{\mathrm{d}}{\mathrm{d}N_i} \ln Q_F = -\ln N_i \cancel{-1} + \ln(d_i - N_i) \cancel{+1} = \ln\left(\frac{d_i - N_i}{N_i}\right). \tag{8.6.6}$$

so that, adding the lagrange multipliers, we have

$$\frac{\partial f}{\partial N_i} = \ln\left(\frac{d_i - N_i}{N_i}\right) - \alpha - \beta E_i \implies \frac{d_i - N_i}{N_i} = e^{\alpha + \beta E_i} \implies d_i = N_i\left(e^{\alpha+\beta E_i} + 1\right)$$

$$\implies N_i = \frac{d_i}{e^{\alpha+\beta E_i} + 1} \tag{8.6.7}$$

α and β can be calculated using the equations $\sum_i N_i = N$ and $\sum_i N_i E_i = E$:

$$\alpha \equiv -\frac{\mu(T)}{k_B T}, \qquad \beta \equiv \frac{1}{k_B T} \quad \text{definition of temperature} \tag{8.6.8}$$

then

$$N_i = \frac{d_i}{e^{\frac{E_i - \mu(T)}{k_B T}} + 1} \tag{8.6.9}$$

The expected occupation number $n \sim \frac{N_i}{d_i}$ for a single state is

$$\boxed{n = \left(e^{\frac{E-\mu(T)}{k_B T}} + 1\right)^{-1}} \qquad \text{Fermi-Dirac distribution}$$

For bosons we have

$$\boxed{n = \left(e^{\frac{E-\mu(T)}{k_B T}} - 1\right)^{-1}} \qquad \text{Bose-Einstein distribution}$$

Since $n \geq 0$ we need $E > \mu$ for all energy levels $\mu < E_i \ \forall i$. For an ideal gas $\mu(T) < 0 \ \forall T$, i.e. $\alpha > 0$

For fermions

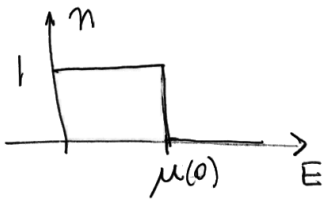


Figure 8.3: Occupation number for a state as a function of the energy for a system of identical fermions in the $T \to 0$ limit. $\mu(T=0) = E_F$is called the *Fermi energy*.

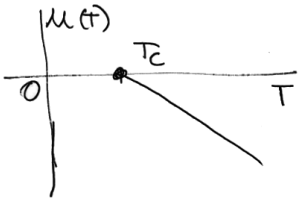


Figure 8.4: Chemical potential μ as a function of the temperature for a system of identical bosons. T_C, the *critical temperature* is defined to be the temperature such that $\mu(T_C) = 0$ and it's the temperature for Bose-Einstein condensation

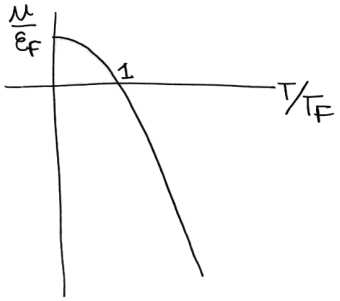


Figure 8.5: Chemical potential μ as a function of the temperature for a system of identical fermions.

Aside from statistical mechanics

$$\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V} \qquad \text{keeping constant entropy may require lowering the energy} \qquad (8.6.10)$$

Suppose we add a particle with no energy to the system. S will increase (more ways to

divide up the total energy) for this not to happen, must reduce the energy.

$$\begin{aligned} \mathrm{d}E(V,S) &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \\ &= \mathrm{d}(TS) - S\mathrm{d}T - P\mathrm{d}V \\ \mathrm{d}\underbrace{(E-TS)} &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \end{aligned} \tag{8.6.11}$$

$$F(T,V) = E - TS\,. \tag{8.6.12}$$

μ is an intensive quantity, and in terms of F we have

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} \qquad \begin{array}{c}\text{Adding a particle changes}\\ \text{the energy and the entropy}\end{array} \tag{8.6.13}$$

8.06 Quantum Physics III
Spring 2018