

(37) Identical Particles

Until now we have discussed ^(for the most part) the QM of single particle systems. We will now look at ^{the} more realistic situation of multi-particle states.

Consider a system of $N=2$ particles (spin included).

Suppose for the moment that we know ~~the~~ ^a ~~the~~ basis for each particle in isolation. Let \mathcal{H}_1 and \mathcal{H}_2 be ~~the~~ ^{the} Hilbert spaces ^{for each particle}. The combined two-

particle system lives in (a subspace of) the direct

(or tensor) product $\mathcal{H}_1 \otimes \mathcal{H}_2$. If the two

particles are identical these two ^{individual} Hilbert spaces are actually the same space, $\mathcal{H}_1 = \mathcal{H}_2 \equiv \mathcal{H}$. A set of

basis states of this two particle system of identical

particles is $\{|\alpha_1, \alpha_2\rangle\}$ where $\{|\alpha_i\rangle\}$ is a complete set of states in \mathcal{H} . Here, $|\alpha_i\rangle$ are the states for

particles 1 and 2 resp.

Q: Is the state $|\alpha_2, \alpha_1\rangle$ different in any essential way from $|\alpha_1, \alpha_2\rangle$?

A: NO. The reason is that all possible operators (i.e. observables) are symmetric under the exchange

of the labels, e.g. the Hamiltonian is

$$H = H_1 + H_2 + H_{12}$$

and it is invariant under the permutation or exchange (i.e. two particle exchanges) ($1 \leftrightarrow 2$) of the particle labels, i.e.

$$\Rightarrow \langle \alpha_1, \alpha_2 | H | \beta_1, \beta_2 \rangle = \langle \alpha_2, \alpha_1 | P_{12}^\dagger H P_{12} | \beta_2, \beta_1 \rangle$$

$$\text{where } P_{12} | \beta_2, \beta_1 \rangle = | \beta_1, \beta_2 \rangle$$

$$P_{12} | \alpha_2, \alpha_1 \rangle = | \alpha_1, \alpha_2 \rangle$$

$$\text{Note: } (P_{12}^\dagger = P_{12}^{-1} \text{ see below})$$

$$\Rightarrow P_{12}^{-1} H P_{12} = H \quad (\text{by symmetry}) \Rightarrow$$

$$\langle \alpha_1, \alpha_2 | H | \beta_1, \beta_2 \rangle = \langle \alpha_2, \alpha_1 | H | \beta_2, \beta_1 \rangle$$

The same applies to all observables.

$$\text{Since } P_{12}^{-1} H P_{12} = H \Rightarrow H P_{12} = P_{12} H \Rightarrow [H, P] = 0$$

\Rightarrow we can choose the eigenstates of H to be also eigenstates of P .

$$\text{But } P_{12} | \alpha_1, \alpha_2 \rangle = | \alpha_2, \alpha_1 \rangle \quad \text{and} \quad P_{12}^2 | \alpha_1, \alpha_2 \rangle = P_{12} | \alpha_2, \alpha_1 \rangle = | \alpha_1, \alpha_2 \rangle$$

$$\Rightarrow P_{12}^2 = I \Rightarrow P_{12}^\dagger = P_{12}^{-1}$$

$$\text{If } P_{12} | \alpha_1, \alpha_2 \rangle = \lambda | \alpha_1, \alpha_2 \rangle \Rightarrow P_{12}^2 | \alpha_1, \alpha_2 \rangle = | \alpha_1, \alpha_2 \rangle$$

(i.e. $| \alpha_1, \alpha_2 \rangle$ is an eigenvector)

$$\Rightarrow \lambda^2 = 1 \Rightarrow \lambda = \pm 1$$

(Note: this rule may be violated in two dimensions).

⇒ The eigenstates of P_{12} are either symmetric
or antisymmetric under exchange. (not pairwise
 permutations).

Postulate: Any state of a set of N identical
 particles should be physically equivalent to a state
 obtained by (any) number of pair-wise permutations.

⇒ The states of a general QM system are either
symmetric or antisymmetric under pairwise permutations.

Particles ~~which~~ whose states are symmetric under
exchange are called bosons and particles
 whose states are antisymmetric under exchange are
 called fermions. Note: Antisymmetry \Leftrightarrow Pauli Principle.

There is a fundamental prpl. of QM (which
 actually ~~is~~ is inherent to Relativistic Quantum Field Theory)
 called the Spin-Statistics Theorem which states

that: particles with $1/2$ -integer spin are fermions
integer spin are bosons.

In reality this means that we have two types of
 Q.Mechanics. The term statistics derives from their
 origin in counting states in Statistical Physics.

Fermions: electrons, protons, neutrons, quarks, He₃ nuclei...

Bosons: photons, gluons, pions, phonons, spin-waves, etc.
He₄ atoms...

N-particle States

From the above considerations it follows that we must construct N-particle states in such a way that they are either symmetric or antisymmetric under pair-wise permutations or exchanges. If we have

a group of N objects we can define a ~~permutation~~ permutation by ~~the~~ constructing an algorithm that generates any sequence of N objects from a standard one (say 1 2 3 ... N)

Thus, a permutation of N elements is denoted by

$$\begin{pmatrix} 1 & 2 & 3 & \dots & N \\ \downarrow & \downarrow & \downarrow & & \downarrow \\ a_1 & a_2 & a_3 & \dots & a_N \end{pmatrix} \quad \text{which tells us what is the label$$

assigned to each object. It is easy to show that all permutations can be constructed ~~as~~ ^{as} a sequence of ~~pairwise~~ ^{pairwise} permutations.

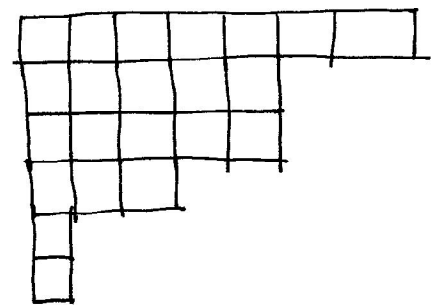
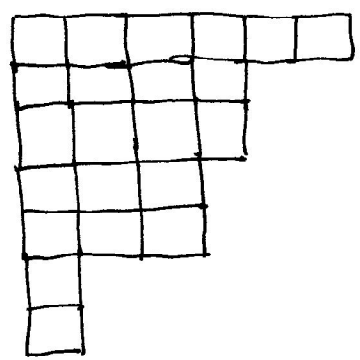
Permutations form a group: S_N

Thus the states can be arranged (or classified) according to their transformation properties under permutations \Rightarrow we are constructing representations of S_N . In practice this is achieved by noting that the ~~set~~ ^{set of} N objects can be partitioned into several ^{sub}sets with N_1, \dots, N_k elements s.t. $N = N_1 + N_2 + \dots + N_k$ (for some k)

We ~~know~~ ^{already} two operations: ~~total~~ total symmetrization and total antisymmetrization. But there are more types.

Suppose we pick $N=22$. Two partitions are $6 + 4 + 4 + 3 + 3 + 1 + 1$ and $7 + 5 + 5 + 3 + 1 + 1$

1st
2nd
:
:
:
:
:



Young Tableaux

(i.e. the wave function)

~~we now pick the state and symmetrize it w.r.t. the variables in each ~~row~~ row separately. Then we antisymmetrize w.r.t. variables in \neq rows (i.e. ~~along~~ along one column). Then we further antisymmetrize what's left after fixing the variables in the first column and continue until all are done.~~

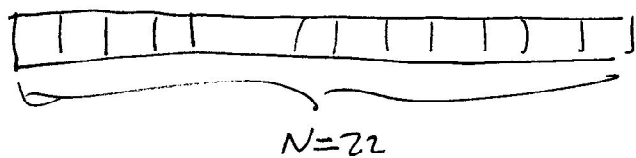
We now pick the state, i.e. its wavefunction, and symmetrize it w.r.t. the variables on each row separately. Next we antisymmetrize w.r.t. the variables on the first column. We continue by antisymmetrizing w.r.t. the variables on the second column and so on until we are done.

The states produced by this method are neither symmetric nor antisymmetric. Also the wave functions thus generated are not all linearly independent but there are methods to construct an appropriate set of basis states (see Messiah)

\Rightarrow each Young diagram determines a symmetry of a type of wave function w.r.t. permutations.

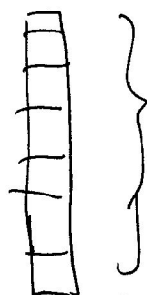
\Rightarrow to each energy level we associate a Young diagram which determines the symmetry of the state under permutation. This is possible since $[\hat{P}_{ij}, \hat{H}] = 0$ (however $[\hat{P}_{ij}, \hat{P}_{kl}] \neq 0$ in general)

Notice that



is fully symmetric

and



is fully antisymmetric.

The main point is that the representations of S_N are in one-to-one correspondence with the Young Tableaux.

Imagine now, that we are looking at a problem

with several particles with spin out in a system

without spin orbit interaction. \Rightarrow H does not

depend explicitly on spin. We can then write

the wave function in a factorized form

$$\Psi(r_1, \sigma_1, \dots, r_N, \sigma_N) = \Psi_0(r_1, \dots, r_N) \chi_S(\sigma_1, \dots, \sigma_N)$$

\uparrow
orbital

\uparrow
spin.

If the particles are fermions (e.g. electrons)

$$\Rightarrow P_{ij} \Psi(r_1, \sigma_1, \dots, r_i, \sigma_i, \dots, r_j, \sigma_j, \dots, r_N, \sigma_N) = - \Psi(r_1, \sigma_1, \dots, r_j, \sigma_j, \dots, r_i, \sigma_i, \dots, r_N, \sigma_N)$$

\Rightarrow either $\Psi_0(r_1, \dots, r_N)$ is symmetric and $\chi_S(\sigma_1, \dots, \sigma_N)$ is antisymmetric

or Ψ_0 is antisymmetric and χ_S is symmetric.

For the orbital wave function permutation reduces to inversion since the center of mass factorizes (and it is symmetric) and the relative coordinate $\vec{r}_{ij} \rightarrow + \vec{r}_{ji} = -\vec{r}_{ij}$ under permutation.

Example: two fermions ^{interacting through a pair} ~~in~~ central potential:

$$\Psi_0(r_1, r_2) = \Psi_{CM}(R_{CM}) \underset{\text{also}}{\varphi}(\vec{r})$$

relative orbital angular momentum

$$\varphi_{\text{even}}(-\vec{r}) = (-1)^l \varphi_{\text{even}}(\vec{r})$$

The spin wave functions have either $S=0$ or $S=1$

\uparrow singlet \uparrow triplet

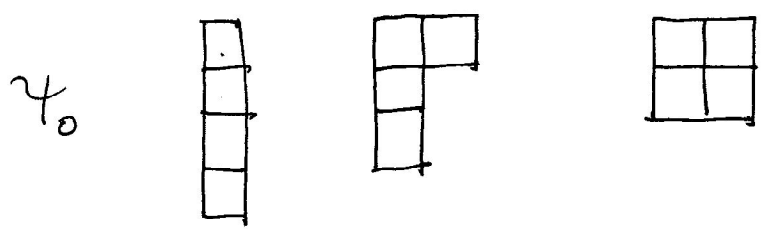
Since χ_{singlet} is antisymmetric
 χ_{triplet} is symmetric

→ the allowed states have

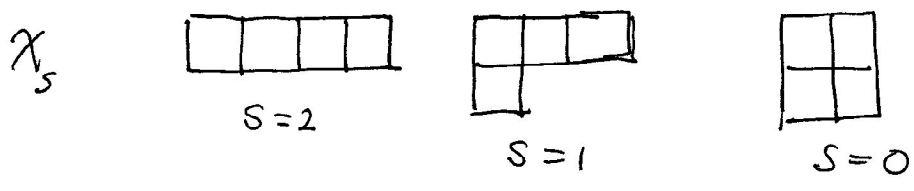
- (a) l even (Ψ_0 symmetric) and $S=0$ (χ_S odd)
- (b) l odd (Ψ_0 odd) and $S=1$ (χ_S even)

→ Not all states are allowed.

Another example: $N=4$ particles



(other orbital functions cannot be antisymmetrized by multiplication with a spin wave function)
 (Fock condition, see Hammermesh's book on group theory)



(because for $S=1/2$ we cannot have more than two rows)

Exchange Interactions and Spin

Consider first a problem with two spins $1/2 \vec{S}_1$ and \vec{S}_2 .

The operator

$$P_{12} = \frac{1}{2} \left(1 + \frac{4}{\hbar^2} \vec{S}_1 \cdot \vec{S}_2 \right) \text{ exchange the spins.}$$

Indeed, since $\vec{S} = \vec{S}_1 + \vec{S}_2$ and $2 \vec{S}_1 \cdot \vec{S}_2 = \vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2$

$$\Rightarrow \frac{4}{\hbar^2} \vec{S}_1 \cdot \vec{S}_2 = \frac{2}{\hbar^2} (S(S+1) - \frac{3}{2}) \text{ acting on states } |S, M\rangle$$

$$\Rightarrow P_{12} = \frac{1}{2} + S(S+1) - \frac{3}{2} = S(S+1) - 1$$

$$\Rightarrow P_{12} |0,0\rangle = -1 |0,0\rangle \leftarrow \text{antisymmetric}$$

$$P_{12} |1, M\rangle = +1 |1, M\rangle \leftarrow \text{symmetric}$$

$$\Rightarrow P_{12} |\uparrow\uparrow\rangle = |\uparrow\uparrow\rangle \quad P_{12} |\downarrow\downarrow\rangle = |\downarrow\downarrow\rangle$$

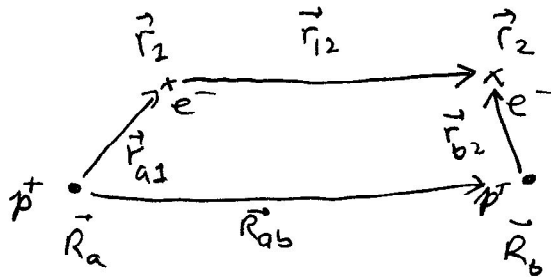
$$P_{12} |\uparrow\downarrow\rangle = |\downarrow\uparrow\rangle$$

$$P_{12} |\downarrow\uparrow\rangle = |\uparrow\downarrow\rangle$$

Consider now the Hydrogen molecule. Let \vec{R}_a and \vec{R}_b be the (fixed) nuclei (protons) with $|\vec{R}_{ab}| \gg a_0$

Let H be the ~~interaction~~ Hamiltonian (Heitler and London)

$$H = \left(\frac{\vec{p}_1^2}{2m} - \frac{e^2}{r_{1a}} + \frac{\vec{p}_2^2}{2m} - \frac{e^2}{r_{2b}} \right) + \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right)$$



$$\vec{R}_{ab} \equiv \vec{R}_b - \vec{R}_a$$

$$\vec{r}_{ij} \equiv \vec{r}_j - \vec{r}_i$$

$$r_{ij} = |\vec{r}_{ij}| = r_{ji}$$

Let $\Psi_I(\vec{r}_1, \vec{r}_2)$ be the ^{orbital} wave function of the electrons, and E will choose at first

$$\Psi_I(r_1, r_2) = \varphi_a(r_1) \varphi_b(r_2)$$

where

$$\left(\frac{p_1^2}{2m} - \frac{e^2}{r_{1a}} \right) \varphi_a(r_1) = E_0 \varphi_a(r_1)$$

$$\left(\frac{p_2^2}{2m} - \frac{e^2}{r_{2b}} \right) \varphi_b(r_2) = E_0 \varphi_b(r_2)$$

i.e. each electron in the same state of its hydrogen atom. (\Rightarrow even though the energies are the same, the wave functions are different, these are \neq states!)

But $\Psi_{II}(r_1, r_2) = \varphi_a(r_2) \varphi_b(r_1) = \Psi_I(r_2, r_1)$

is just as good a wave function.

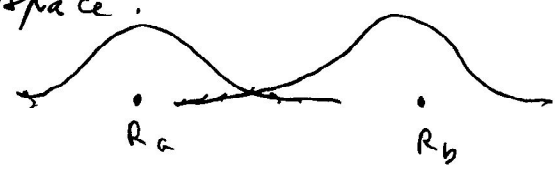
Let us construct the wave functions

$$\Psi_S(r_1, r_2) = \frac{1}{\sqrt{2}} (\Psi_I(r_1, r_2) + \Psi_{II}(r_1, r_2)) = \frac{1}{\sqrt{2}} (\varphi_a(r_1) \varphi_b(r_2) + \varphi_a(r_2) \varphi_b(r_1))$$

$$\Psi_A(r_1, r_2) = \frac{1}{\sqrt{2}} (\varphi_a(r_1) \varphi_b(r_2) - \varphi_b(r_1) \varphi_a(r_2))$$

We will diagonalize H in this subspace.

First we define



$$1 = \int d^3r |\varphi_a(r)|^2 = \int d^3r |\varphi_b(r)|^2$$

(overlap) $k = \int d^3r \varphi_a^*(r) \varphi_b(r)$ (overlap) (we will take $k \in \mathbb{R}$)

(Coulomb) $V = \int d^3r_1 \int d^3r_2 |\Psi_I|^2 \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) = \langle I | H_{int} | I \rangle$
 $= \int d^3r_1 \int d^3r_2 |\Psi_{II}|^2 \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2b}} \right) = \langle II | H_{int} | II \rangle$

(exchange) $U = \int d^3r_1 \int d^3r_2 \Psi_I^* \Psi_{II} \left(\frac{e^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2a}} \right) = \langle I | H_{int} | II \rangle$
 (I will also take $U = U^*$)

The normalization of the wave functions are

$$\int d^3r_1 \int d^3r_2 |\Psi_{S,A}|^2 = 1 \pm |k|^2, \quad \int d^3r_1 \int d^3r_2 \Psi_{S,A}^* \Psi_{A,S} = 0$$

\Rightarrow we will work with unnormalized wave functions

$$\tilde{\Psi}_{S,A} = \frac{1}{\sqrt{1 \pm |l|^2}} \frac{1}{\sqrt{2}} [\varphi_a(r_1) \varphi_b(r_2) \pm \varphi_b(r_1) \varphi_a(r_2)]$$

$$\Rightarrow \int d^3r_1 \int d^3r_2 \tilde{\Psi}_{S,A}^* H_0 \tilde{\Psi}_{S,A} = 2E_0$$

$$\int d^3r_1 \int d^3r_2 \tilde{\Psi}_{S,A}^* H_0 \tilde{\Psi}_{A,S} = 0$$

$$\int d^3r_1 \int d^3r_2 \tilde{\Psi}_{S,A}^* H_{\text{int}} \tilde{\Psi}_{S,A} = \frac{V \pm \frac{U \pm U^*}{2}}{1 \pm |l|^2}$$

$$\int d^3r_1 \int d^3r_2 \tilde{\Psi}_{S,A}^* H_{\text{int}} \tilde{\Psi}_{A,S} = \pm \frac{1}{2} \frac{(U^* - U)}{\sqrt{1 - |l|^4}}$$

and we have the effective 2×2 H_{eff} ($U = U^*, l = l^*$)

$$H_{\text{eff}} = \begin{bmatrix} 2E_0 + \frac{V+U}{1+l^2} & 0 \\ 0 & 2E_0 + \frac{V-U}{1-l^2} \end{bmatrix}$$

\Rightarrow The new eigenvalues are

$$E_{\pm} = 2E_0 + \frac{V \pm U}{1 \pm l^2} \quad \text{with } (+) \leftrightarrow \Psi_S \\ (-) \leftrightarrow \Psi_A$$

Note: If $|\vec{R}_{ab}| \gg a_0 \Rightarrow E_+ - E_- \rightarrow 0$ since $U \rightarrow 0$ and $l \rightarrow 0$.

According to our general ppls. the actual wave function is a product of the orbital and sp wave functions.

Since the e^- are fermions the total wave function must be antisymmetric under exchange.

\Rightarrow we have the states

$$\Psi_S(r_1, r_2) \chi_{S=0}(\sigma_1, \sigma_2) \longleftrightarrow E_+$$

$$\Psi_A(r_1, r_2) \chi_{S=1}(\sigma_1, \sigma_2) \longleftrightarrow E_-$$

$$\begin{aligned} \text{Since } E_{\pm} &= 2E_0 + \frac{V \pm U}{1 \pm l^2} \\ &= 2E_0 + \frac{(V \pm U)(1 \mp l^2)}{1 - l^4} \end{aligned}$$

$$\Rightarrow E_{\pm} = \left(2E_0 + \frac{V - Ul^2}{1 - l^4} \right) \pm \frac{U - Vl^2}{1 - l^4}$$

and \oplus corresponds to the state with $S = 0$

\ominus " " " " $S = 1$

The operator $P_{12} = \frac{1}{2} \left(1 + \frac{4}{\hbar^2} \vec{S}_1 \cdot \vec{S}_2 \right)$ is diagonal in
($\sigma_1 \leftrightarrow \sigma_2$ exchange) this basis

$$\text{and } P_{12} \chi_{S=0} = - \chi_{S=0}$$

$$P_{12} \chi_{S=1} = + \chi_{S=1}$$

$$\Rightarrow \text{Hoff} = \left(2E_0 + \frac{V - Ul^2}{1 - l^4} \right) \mathbb{I} + \frac{Vl^2 - U}{1 - l^4} P_{12}$$

$$\text{Hoff} = 2E_0 + \frac{1}{1 - l^4} \left(\left(\frac{1 + l^2}{2} \right) V - \left(\frac{1}{2} + l^2 \right) U \right) - J_{12} \vec{S}_1 \cdot \vec{S}_2$$

where
$$J_{12} = -\frac{2}{\hbar^2} \left(\frac{V e^2 - U}{1 - e^4} \right)$$

For the 1s state of Hydrogen (Heitler and London) found that $J_{12} < 0 \Rightarrow$ ground state is a singlet.

H-L found that the triplet state has an energy greater than two unbound atoms \Rightarrow no triplet bound state ("antibonding")

\Rightarrow The bound state is a singlet,
[for a detailed discussion see D. Matt's].

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Scattering of Identical Particles

Let us turn now to the problem of scattering of two identical particles.

(A) Bosons

Consider two spinless bosons (e.g. α particles). The wave functions for two α -particles look like

$$\psi(\vec{r}_1, \vec{r}_2) = e^{\frac{i}{\hbar} \vec{p} \cdot (\vec{r}_1 + \vec{r}_2)/2} \psi(\vec{r})$$

where $\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$ is the CM and \vec{r} is

the relative coordinate. Clearly

$$\psi_{CM}(\vec{R}) = e^{\frac{i}{\hbar} \vec{p} \cdot \vec{R}} \quad \text{is symmetric under exchange.}$$

For $\psi(\vec{r})$ to be symmetric it is necessary that

$$\psi(\vec{r}) = \psi(-\vec{r}) \quad \Rightarrow \quad l \text{ must be even.}$$

Neglecting symmetry, the scattered wave functions

are (asymptotically) of the form

$$e^{i\vec{k} \cdot \vec{r}} + f(\theta) \frac{e^{ikr}}{r}$$

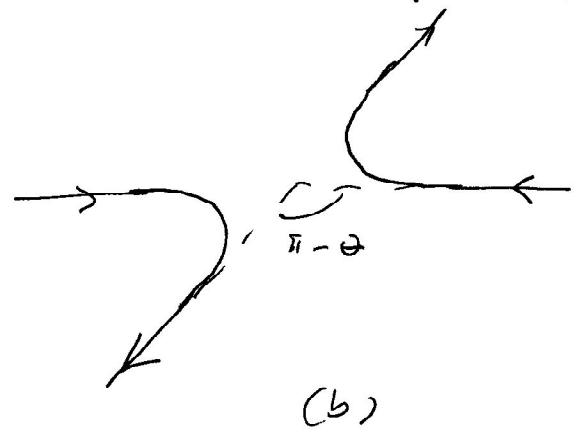
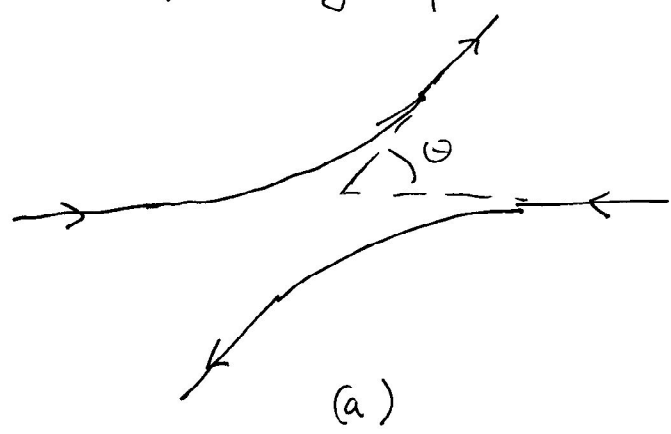
\Rightarrow symmetrizing

$$\psi(\vec{r}) = (e^{i\vec{k} \cdot \vec{r}} + e^{-i\vec{k} \cdot \vec{r}}) + (f(\theta) + f(\pi - \theta)) \frac{e^{ikr}}{r}$$

since under $\vec{r} \rightarrow -\vec{r}$, $\theta \rightarrow \pi - \theta$

for distinguishable particles ->

$f(\theta)$ is the scattering amplitude. The fact that we get two terms simply means that the following processes have the same amplitude



Diff. Cross section: $\frac{d\sigma}{d\Omega} = |f(\theta) + f(\pi - \theta)|^2$

$$= |f(\theta)|^2 + |f(\pi - \theta)|^2 + 2 \operatorname{Re}(f^*(\theta) f(\pi - \theta))$$

\uparrow \uparrow \uparrow
 (a) (b) exchange
 for distinguishable particles contribution.

If $\theta = \frac{\pi}{2} \Rightarrow f(\theta) = f(\pi - \theta) = f(\frac{\pi}{2})$

$\Rightarrow \left. \frac{d\sigma}{d\Omega} \right|_{\theta = \frac{\pi}{2}} = 4 |f(\frac{\pi}{2})|^2$ \leftarrow indistinguishable

and $\left. \frac{d\sigma}{d\Omega} \right|_{\theta = \frac{\pi}{2}} = 2 |f(\frac{\pi}{2})|^2$ \leftarrow distinguishable

Partial waves:

$$f(\theta) = \sum_l i^l P_l(\cos\theta) (2l+1) f_l$$

$$\Rightarrow f(\theta) + f(\pi-\theta) = 2 \sum_{\text{even } l} i^l (2l+1) P_l(\cos\theta) f_l$$

since $P_l(\cos(\pi-\theta)) = P_l(-\cos\theta) = (-1)^l P_l(\cos\theta)$

(B) Fermions : now we have to account for spin. Take two electrons

$$s=1/2 \Rightarrow \Psi(\vec{r}_1, s_1, \vec{r}_2, s_2) = e^{\frac{i}{\hbar} \vec{P} \cdot \vec{R}} \underbrace{\Psi(\vec{r}_1 - \vec{r}_2) \chi(s_1, s_2)}_{\text{Spin part}}$$

$$\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$$

Two cases: (i) Spin singlet $S=0$ $\chi_{0,0}(s_1, s_2)$ is antisymmetric

$\Rightarrow \Psi(\vec{r}_1 - \vec{r}_2)$ must be symmetric

$$\Rightarrow \Psi(\vec{r}) = (e^{i\vec{k} \cdot \vec{r}} + e^{-i\vec{k} \cdot \vec{r}}) + (f(\theta) + f(\pi-\theta)) \frac{e^{ikr}}{r}$$

(as for bosons)

$$\Rightarrow \left(\frac{d\sigma}{d\Omega} \right)_{\text{singlet}} = |f(\theta) + f(\pi-\theta)|^2$$

$S=0 \Leftrightarrow$ Same predictions as for bosons.

(ii) Spin triplet: $S=1 \Rightarrow \chi_{1,1}(s_1, s_2)$ is symmetric

$\Rightarrow \Psi(\vec{r})$ must be antisymmetric.

$$\Rightarrow \psi(\vec{r}) \sim (e^{i\vec{k}\cdot\vec{r}} - e^{-i\vec{k}\cdot\vec{r}}) + (f(\theta) - f(\pi-\theta)) \frac{e^{i\vec{k}\cdot\vec{r}}}{r}$$

$$\begin{aligned} \Rightarrow \left(\frac{d\sigma}{d\Omega} \right)_{\text{triplet}} &= |f(\theta) - f(\pi-\theta)|^2 \\ &= |f(\theta)|^2 + |f(\pi-\theta)|^2 - 2 \operatorname{Re} (f(\theta) f(\pi-\theta)^*) \end{aligned}$$

Now we notice that for $\theta = \frac{\pi}{2}$

$$f(\theta) - f(\pi-\theta) = f\left(\frac{\pi}{2}\right) - f\left(\frac{\pi}{2}\right) = 0 !$$

We get no scattering of electrons at $\theta = \frac{\pi}{2}$ if the electrons are in a $s > 1$ state!

For an unpolarized beam we get the average

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{\text{unpol.}} &= \frac{3}{4} \left(\frac{d\sigma}{d\Omega} \right)_{\text{triplet}} + \frac{1}{4} \left(\frac{d\sigma}{d\Omega} \right)_{\text{singlet}} \\ &= |f(\theta)|^2 + |f(\pi-\theta)|^2 - \operatorname{Re} [f(\theta) f(\pi-\theta)^*] \\ &\xrightarrow{\theta \rightarrow \frac{\pi}{2}} |f\left(\frac{\pi}{2}\right)|^2 \end{aligned}$$