Quantum Mechanics(2017) Lecture Notes

Part-VII Identical Particles and Symmetrization Postulate

A One Semester Course of Lectures

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§1 Identical particles in quantum mechanics

§1.1 Indistinguishability of identical particles

In transition form classical to quantum mechanics one is forced to revise, or completely give up, many classical concepts. Some examples are

- Superposition principle is new for particles.
- Precise values for observables is given up. in general only probabilities can be computed.
- Not all observables can be measured simultaneously. Only those represented by a simultaneous commuting set can be measured simultaneously.

We shall see that for a system of two or more identical particles, the identity of individual particles looses its meaning in quantum mechanics; one can only talk about the system as a whole. We also need to introduce a new hypothesis about the states of a quantum mechanical system of several identical particles.

Classically it is always possible to distinguish two electrons because they are point particles having well defined positions. More importantly, this distinction can always be maintained at all times because each particle has a well defined trajectories which can be measured, and can also can be predicted if the interactions are known. This distinction between the electrons can be maintained at all times, also by, measuring the positions of each particle at successive times at regular intervals very accurately and doing this does not disturb their motion.

For a quantum mechanical system consisting of several identical particles we note the following.

- In the first place the particles cannot have well defined positions, only some probabilities can be assigned to different values of the position.
- At any given time, it is certainly possible to localize each particle with great accuracy.However, in general, the wave packets spread and it will not be possible to maintain the localization at later times. Thus when the particles come very close we would not be able to tell which particle was which one.
- The trajectories of particles do not have any meaning in quantum mechanics. One may attempt to follow the motion in quantum mechanics by measuring their positions very accurately at short intervals; but this exercise turns out to be useless for all practical purposes because it 'disturbs' the motion of the particles.

It is important to realize that inability to distinguish identical nature of particles is not due to some technical, theoretical or experimental, reasons. Even in principle a distinction between two identical particles cannot be maintained any thought experiment or any theoretical an analysis. Nor is this conclusion avoidable by improving upon the measuring apparatus. This surprising conclusion is more due to the structure of the quantum theory, rather than lack of a very accurate measuring apparatus. In some sense the nature of the conclusion is very similar to the uncertainty principle about impossibility of very precise simultaneous measurement of position and momentum. We , therefore, wish to conclude that even the possibility of being able to distinguish between two identical particles does not exist even in principle and that we should accept that they are **indistinguishable**.

In view of the above discussion, we abandon the attempts to distinguish between identical particles. We *assume* that in a quantum mechanical system of identical particles it is not possible to distinguish between any two identical particles; the individual particles loose their identity and we should refer to the system as a 'whole'.

This has far reaching consequences. for sake of definiteness, let us consider a system of two electrons and let their wave function be $\psi(\xi_1, \xi_2)$ where ξ_1, ξ_2 collectively denote the space as well as the spin variables of the two electrons. Then $\psi(\xi_2, \xi_1)$ will denote the state of two electrons obtained by exchanging the two electrons. If the two electrons are indistinguishable, this interchange of two electrons can have no effect on the state of the system as whole and thus the wave functions $\psi(\xi_1, \xi_2)$ and $\psi(\xi_2, \xi_1)$ must represent the same state and hence we must have

$$\psi(\xi_1, \xi_2) = \exp(i\alpha)\psi(\xi_2, \xi_1) \tag{1}$$

for some real α, as required by the first postulate. The above equation is valid for all ξ_1, ξ_2 and hence, replacing ξ_1 with ξ_2 and ξ_2 with ξ_1 we get

$$\begin{aligned} \psi(\xi_2, \xi_1) &= \exp(i\alpha)\psi(\xi_1, \xi_2) && (2) \\ &= \exp(i\alpha)\psi(\xi_2, \xi_3) && (3) \end{aligned}$$

and hence we conclude that

$$\exp(2i\alpha) = 1 \qquad \Rightarrow \qquad \exp(i\alpha) = 1 \tag{4}$$

Therefore, we arrive at an important conclusion that under exchange of all variables the wave function of two identical particles must be symmetric or antisymmetric.

$$\psi(\xi_2, \xi_1) = \pm\psi(\xi_1, \xi_2) \tag{5}$$

The symmetric or the antisymmetric nature Eq.(5), if enforced at initial time, will be preserved at all times. To see this let us introduce a permutation operator P_{12} by

$$P_{12}\psi(\xi_1, \xi_2) = \psi(\xi_2, \xi_1) \tag{6}$$

the Eq.(5) is just the statement that the state must be an eigenstate of the permutation operator. The Hamiltonian for two identical particles will be symmetric under exchange of ξ_1 and ξ_2 and hence commutes with P_{12} implying that the permutation operator is a constant of motion. Thus the wave function will remain an eigenfunction of P_{12} with the same eigenvalue at all times if it is chosen to be eigenfunction at initial time.

§1.2 Symmetrization postulate

hort Examples on illustrating use of symmetrization postulate for identical bosons in quantum mechanics.

We now introduce symmetrization postulate for a system of several identical particles. For a system of two identical particles wave function must be chosen to be symmetric or antisymmetric under exchange of space and spin variables, However, at this stage, theoretical considerations alone in non relativistic quantum mechanics, do not help us in deciding which one, symmetric or anti symmetric wave function is the correct choice for a given particle. An appeal to experiment does give an answer which is contained in the statement of the symmetrization postulate. Basically the symmetry property of the total wave function of a system of identical particles is tied to the spin of the particle. The symmetrization postulate states that

- For a system of **two** identical particles with integral spin bosons the total wave function must be symmetric under simultaneous exchange of all the variables such as the space and spin variables. For a system of two identical particles of half integral spin fermions the full wave function must be anti-symmetric under a simultaneous exchange of all the variables such as the space and spin variables.

  If ξ_1, ξ_2 denote the set of all variables such as, space and spin, of two identical particles. Then the symmetrization postulate states that the total wave function

$\psi(\xi_1, \xi_2)$ must be symmetric for bosons and antisymmetric for fermions under an exchange of ξ_1 and ξ_2.

$$\begin{aligned} \psi(\xi_2, \xi_1) &= +\psi(\xi_1, \xi_2) && (\text{ bosons}) && (7) \\ \psi(\xi_2, \xi_1) &= -\psi(\xi_1, \xi_2) && (\text{ fermions}) && (8) \end{aligned}$$

- The symmetrization postulate for a system of $n-$ identical particles sates that the total wave function must be symmetric simultaneous under exchange of variables ξ_j and ξ_k for every pair j, k, if the particles are bosons and the relation

  $$\psi(\xi_1, \cdot\xi_j \cdots, \xi_k, \cdots, \xi_n) = +\psi(\xi_1, \cdot\xi_k, \cdots, \xi_j, \cdots, \xi_n) \tag{9}$$

  should hold for all pairs AK. Similarly, for a system of $n-$ identical fermions the total wave function must be anti-symmetric under simultaneous exchange of variables ξ_j, ξ_k for every pair j, k

  $$\psi(\xi_1, \cdot\xi_j \cdots, \xi_k, \cdots, \xi_n) = -\psi(\xi_1, \cdot\xi_k, \cdots, \xi_j, \cdots, \xi_n) \tag{10}$$

  For a system of several identical bosons, the total wave function $\Psi(\xi_1, \cdots, \xi_n)$ remains unchanged under an arbitrary permutation of $\xi_1, \cdots, \xi_n$; where as for fermions the wave function remains unchanged under an even permutation but changes sign under an odd permutations.

We now give some explanatory remarks on the symmetrization postulate.

1. The postulate is a statement about the **full** wave function of the system of identical particles under a **simultaneous exchange of all** the variables. For example, there is no constraint on the space part (or the spin part) of the wave function alone need.

2. For composite systems such those consisting of both bosons and fermions, the symmetry rrequirementshold for every pair of identical bosons and identical fermions separately.

3. For a system consisting of several 'particles' which themselves could be bound state of bosons and fermions the postulate applies with spin interpreted to mean the total angular momentum at rest.

4. While for a system of two particles the symmetry property is restricted to symmetry or antisymmetry alone, for a system of many identical particles theoretical considerations allow existence of a variety of possibilities under permutation of variables. These choices, known generally as 'para-statistics', do not seem to play any role for real physical systems.

Our discussion of the symmetrization postulate will be incomplete if we do not mention the spin statistics connection contained in the postulates is contained the symmetrization postulate has been proved by Pauli and Luders within the framework of relativistic quantum field theory under very general assumptions such as relativistic invariance, micro causality and positivity of the Hamiltonian.

Here give two useful statements which will be needed repeatedly in this connection.

- ✍ When we add two, equal, angular momenta j the possible resulting values are $J = 2j, 2j-1, \cdots, 0$. Of these the state with the highest value, $J = 2j$, is symmetric under an exchange of the two particles, the next one, with $2j-1$ is antisymmetric; the states being alternately symmetric and antisymmetric as J takes on the values in descending order.

- ✍ For a two particle system, the effect of an exchange of the positions of the two particles is same as the parity on the wave function in the centre of mass frame. Therefore under an exchange of the space variables the space part of the wave function is symmetric for even ℓ and antisymmetric for odd ℓ.

§1.3 Illustrative Examples

)‖(**Short Examples 1** *Let us consider two particles interacting via a spherically symmetric potential $v(r)$ where r is the distance between the particles. We write the total wave function as*

$$\Psi_{\text{tot}}(\vec{r}, m_{s_1}, m_{s_2}) = \psi_{\text{space}}(\vec{r})\,\psi_{\text{spin}} \tag{11}$$

*If each particle has spin s the total spin has the values $S = 2s, 2s-1, 2s-2, \cdots 0$ with symmetry properties as given by rule $\star 1$). We shall see that for each value of total spin S only odd, or even, angular momentum ℓ values will be permitted when the particles are identical. We discuss four cases in the following.[**?**]*

(1a) When the two particle are not identical *there is no restriction symmetry of the total wave function. Therefore, all possible combination of ℓ and s values are permitted.*

(1b) When the two particles are identical fermions, *$2s =$ odd integer, the total wave function must be antisymmetric under an exchange of space and spin variables. Therefore, antisymmetric space wave functions ($\ell =$ odd) must be chosen with symmetric spin wave functions, $(S = 2s, 2s-2, \cdots)$. Also the space part of wave function must be symmetric, ($\ell =$ even) when the spin part of the wave function is antisymmetric $(S = 2s-1, 2s-3, \cdots)$.*

(1c) When the two particles are identical bosons, *$s =$ integer, the total wave function must be symmetric. Hence either both space and spin parts must be symmetric or both must be antisymmetric. Thus even ℓ values will correspond to total spin $S = 2s, 2s-2, \cdots$ and odd ℓ values will correspond to the total spin $S = 2s-1, 2s-3, \cdots$.*

(1d) In the special case of two identical spin zero *bosons, the total wave function is just the space part alone which must be symmetric and hence ℓ must be even. This give the statement that the spin and parity of a system of two identical spin zero bosons must both be even.*

(1e) All the cases of identical particles *are summarized by saying that*

$$(-1)^{\ell+2S} = 1 \tag{12}$$

or $\ell + 2S$ must be even.

Problem 1: Two identical spin s particles interact via a spherically symmetric potential $V(r)$ find the restrictions on allowed combinations of ℓ and $S_{\rm tot}$ where ℓ is the orbital angular momentum and $S_{\rm tot}$ is the total spin of the system.

Let us consider a system of two particles interacting via a central potential $V(|\vec{r_1} - \vec{r_2}|)$. In classical, as well as quantum, mechanics this two body problem is solved by changing the variables to the position of the center of mass $\vec{R}$ and relative coordinate $\vec{r}$. The problem then reduces free motion of the centre of mass and that of a particle of reduced mass μ moving in a potential $V(\vec{r})$. The Schrodinger equation for the two particle problem

$$H = \frac{\vec{p_1}^2}{2m} + \frac{\vec{p_2}^2}{2m} + V(|\vec{r_1} - \vec{r_2}|) \tag{13}$$

Here $\vec{r}_1 = (x_1, y_1, z_1)$, $\vec{r}_2 = (x_2, y_2, z_2)$, denote the position vectors of the nucleus and the electron respectively, and m_1 and m_2 are their masses. The Schrodinger equation for the an electron and a nucleus of charge Z is

$$-\frac{\hbar^2}{2m_1}\left(\frac{d^2}{dx_1^2} + \frac{d^2}{dy_1^2} + \frac{d^2}{dz_1^2}\right)\Psi - \frac{\hbar^2}{2m_2}\left(\frac{d^2}{dx_2^2} + \frac{d^2}{dy_2^2} + \frac{d^2}{dz_2^2}\right)\Psi + V(|\vec{r_1} - \vec{r_2}|)\Psi = \mathcal{E}\Psi$$

Introducing the centre of mass coordinate, $\vec{R} = (X, Y, Z)$, and the relative coordinate, $\vec{r} = (x, y, z)$ defined by

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r}_1 - \vec{r}_2 \tag{14}$$

the Schrodinger equation, in terms of the new variables, takes the form

$$-\frac{\hbar^2}{2M}\left(\frac{d^2}{dX^2} + \frac{d^2}{dY^2} + \frac{d^2}{dZ^2}\right)\Psi - \frac{\hbar^2}{2\mu}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\Psi + V(|\vec{r}|)\Psi = \mathcal{E}\Psi \tag{15}$$

If we now write the full wave function $\Psi(\vec{R}, \vec{r})$ as

$$\Psi(\vec{R}, \vec{r}) = U(\vec{R})u(\vec{r}),$$

and substitute it in the Schrodinger equation, the variables $\vec{R}, \vec{r}$ are separated and we would get the differential equations for $U(\vec{R}), u(\vec{r})$ given by

$$-\frac{\hbar^2}{2M}\left(\frac{d^2}{dX^2} + \frac{d^2}{dY^2} + \frac{d^2}{dZ^2}\right)U(\vec{R}) = E_{\rm cm}U(\vec{R}) \tag{16}$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)u(\vec{r}) + V(|\vec{r}|)u(\vec{r}) = Eu(\vec{r}) \tag{17}$$

where $M = m_1 + m_2$ is the total mass, μ is the reduced mass $\mu = \frac{(m_1 m_2)}{(m_1+m_2)}$, and $E_{\rm cm}, E$ are constants appearing from the process of separation of variables so that $E = E_{\rm cm} + E$. We shall now onwards take masses of the two particles to be equal. The equation (16)for $U(\vec{R})$, is a free particle equation and the centre of mass moves like a free particle. The equation (17) refers to the relative motion of the two particles. The Schrodinger equation (16) can be solved by separation of variables in polar coordinates r, θ, ϕ. The angular part of the wave function is given by a spherical harmonics $Y_{\ell m}(\theta, \phi)$ and the total wave function assumes the form

$$u(\vec{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi).$$

Note that the exchange of the two particle coordinates $\vec{r_1} \leftrightarrow \vec{r}_2$ is equivalent to parity operation $\vec{r} \to -\vec{r}$ and the total wave function $u(\vec{r})$ is symmetric for even ℓ values, antisymmetric for odd ℓ values:

$$u(\vec{r}) = (-1)^{\ell} u(\vec{r}). \tag{18}$$

If the two particles carry the same spin s, the total spin $S_{\rm tot}$ will have values from $2s$ to 0 in steps of 1. The spin wave function will be alternately symmetric and antisymmetric under the exchange of spin variables with the highest spin state with $2s$ being always symmetric under the exchange. For identical particles the total wave function must be symmetric for bosons and antisymmetric for fermions. This gives rise to restrictions on the allowed combinations of values of total spin $S_{\rm tot}$ and orbital angular momentum ℓ. For a spin half particle the restrictions are found in the table below. The last column gives allowed values of orbital angular momentum ℓ.

Total Spin	**1 (Triplet state)**	**0 (Singlet state)**
Spin wave function	Symmetric	Anti-symmetric
Total wave function	Anti-symmetric	Anti-symmetric
Space wave function	Symmetric	Anti-symmetric
Allowed values of ℓ	even only	odd only

§2 A First Look at He Atom Energy Levels

He atom energy levels: As an example of system of two identical particles we shall discuss He atom. The Hamiltonian for He atom is given by

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

If the electrostatic interaction, $e^2/|\vec{r}_1 - \vec{r}_2|$, between the two electrons is neglected as a first approximation, the hamiltonian becomes a sum of two hydrogen atom like hamiltonians. In this approximation the electronic states are described by quantum numbers (n_1, l_1, m_1) and (n_2, l_2, m_2) for the two electrons. Let u_1, u_2 denote corresponding H-atom wave functions. The space part of the wave function for the two electrons will be product wave function $u_1(\vec{r}_1)u_2(\vec{r}_2)$, which must be properly symmetrized or anti-symmetrized as discussed below.

In very many situations the total wave function is a product of a part describing space properties and a spin wave function. Thus we write

$$\Phi_{\text{total}} = \psi_{\text{space}}(\vec{r}_1, \vec{r}_2)\chi_{spin}(m_1, m_2)$$

where m_1, m_2 refer to the spin variables for the two electrons. As each electron carries spin 1/2, the total spin can take values 1 (triplet) and 0 (singlet). The values of total spin determines the symmetry property of spin wave function under an exchange of spin variables. It is known that spin wave function must be symmetric for $S = 1$ and antisymmetric for $S = 0$ states. The requirement that total wave function be antisymmetric (for 2 *electron* systems) fixes the symmetry property of the space part of the wave function as summarized in the table given below.

Spin State	Total Spin	Spin wave function	Space wave function
Triplet	$S = 1$	Symmetric	Antisymmetric
Singlet	$S = 0$	Antisymmetric	Symmetric

Therefore, out of the two combinations for the space wave function

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(u_1(\vec{r}_1)u_2(\vec{r}_2) \pm u_1(\vec{r}_2)u_2(\vec{r}_1)\right)$$

the symmetric combination ψ_+ should be used for the singlet states ($S = 0$) and the antisymmetric combination ψ_- should be used for triplet states ($S = 1$). The ground state corresponds to $n_1 = n_2 = 1$ $l_1 = l_2 = 0$ $m_1 = m_2 = 0$ and the antisymmetric combination ψ_- vanishes. Only the symmetric combination is nonzero. Thus the ground state is a singlet state; the same is true of all other states corresponding to electrons having identical (n, l, m) quantum numbers.

When the two electron states correspond to different (n, l, m) quantum numbers, both symmetric and antisymmetric combinations $\psi_{\pm}(\bar{r}_1, \bar{r}_2)$ are possible. However, the antisymmetric combination $\psi_{\pm}(\vec{r}_1, \vec{r}_2)$ vanishes when $\vec{r}_1 = \vec{r}_2$. Therefore, the probability that the two electrons will be found close to each other will be small for ψ_- (for triplet states, known as *ortho helium*) and large for ψ_+ (singlet states, known as *para helium*). Since the Coulomb interaction between two electrons is positive and is large when their separation is small, total Coulomb energy will be higher in singlet states as compared to its value in the triplet state. These predictions are in accordance with the results on energy levels of He atom derived from the spectrum of He atom.