

## Identical Particles and Spin

By identical particles we mean the particles like electrons which cannot be distinguished by means of any inherent property. Since otherwise they would not be identical in all respects. In classical mechanics identical particles do not lose their identity despite the identity of their physical properties due to the existence of sharply definable trajectories for individual particles can be followed during the course of an experiment. As an example of the classical mechanical particles consider the molecules in a gas at N.T.P.

$$\text{Molecular density} = 10^{25} \text{ mol/metre}^3$$

$$\text{Volume available for each particle} = 10^{-25} \text{ metre}^3$$

$$\text{Molecular radius} = 10^{-10} \text{ metre}$$

$$\text{Therefore the molecular volume} = \frac{4}{3} \pi r^3 = 10^{-30} \text{ metre}^3$$

(order of magnitude)

As the molecule is much smaller than the volume available for it we can, in principle, identify every molecule of the gas.

Hence the molecules (classical particles) are distinguishable.

In quantum mechanics a particle is described by a wave packet of finite size and spread and the exact specifications of the positions and momentum of the particle simultaneously is restricted by Heisenberg's uncertainty principle  $\Delta q \Delta p = h$ , therefore there is no way of keeping track of individual particles separately, specially, if they interact with each other to an appreciable extent, Hence in quantum mechanics the wave functions of the

particles overlap considerably. As a result the quantum mechanical particles can not be distinguished. As an example of the quantum particles consider the conduction electrons in metals.

The density of the electrons =  $10^{28}$  per metre<sup>3</sup> (order of magnitude). Therefore the volume available for each electron =  $10^{-28}$  metre<sup>3</sup>

$$\begin{aligned} \text{For a 1 eV electron momentum } p &= (2mE)^{1/2} \\ &= [2 \times (9.1 \times 10^{-31} \text{ kg}) (1 \times 1.6 \times 10^{-19} \text{ joule})]^{1/2} \\ &= 0.5 \times 10^{-24} \text{ kg-m/Sec} \end{aligned}$$

Therefore uncertainty in position of this electron

$$\begin{aligned} \Delta q &= \frac{h}{\Delta p} = \frac{6.6 \times 10^{-34} \text{ joule-sec}}{0.5 \times 10^{-24} \text{ joule sec/metre}} \\ &= 1.3 \times 10^{-9} \text{ metre} \end{aligned}$$

Therefore the volume of the conduction electron

$$\begin{aligned} &= \frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times (1.3 \times 10^{-9} \text{ metre})^3 \\ &= 10^{-27} \text{ metre}^3 \text{ (order of magnitude)} \end{aligned}$$

Comparing the volume of conduction electron to the volume available to it, we conclude that the electron wave function, overlap considerably in conduction electron cannot be identified separately and hence they are indistinguishable

Thus there are two general categories of particles

- (i) classical particles which are identical but distinguishable
- (ii) quantum particles which are identical and indistinguishable

It is to be noted that when quantum physics particles density is sufficiently low so that their uncertainty is small in comparison to the volume available to them, they are

obey classical statistics, otherwise we must use quantum statistics.

### Physical meaning of identity

Identical particles are those particles in a system for which the system remains unaltered by interchanging the particles. As each particle is described quantum mechanically by a wave packet, these particles can be distinguished from one another, only if their wave packets do not overlap. Similarly if particles have spin which are aligned in different positions in the process of any interaction, they can be identified from one another as a result of such interaction.

Thus the word identical in quantum mechanics is to describe the particles that can be substituted for each other under the most general possible circumstances with no change in physical situation of the system.

According to spin considerations, the particles can be distinguished from one another if they have different spin components. The component of spin along some particular axis remains unchanged during elastic collision.

### Symmetrical and Antisymmetrical wave functions:

The Schrodinger equation for  $n$  identical particles is written as

$$H(1, 2, \dots, n) \psi(1, 2, \dots, n, t) = i\hbar \frac{\partial}{\partial t} \psi(1, 2, \dots, n, t) \quad \dots (1)$$

where each of the numbers represents all the coordinates (positional and spin) of one of the particles. The Hamiltonian  $H$  is symmetric in its arguments due to the identity of particles. The identity of particles means that they can be substituted for each other without changing  $H$  or indeed any other observable.

There are two kinds of solutions of wave functions  $\psi$  of eqn. (1) that have symmetric properties of particular interest.

(i) Symmetric wave function  $\psi_s$ . A wave function is symmetric if the interchange of any pair of particles among its arguments leave the wave function unchanged.

(ii) Antisymmetric wave function  $\psi_A$ . A wave function is antisymmetric if the interchange of any pair of particles among its arguments changes the sign of the wave function.

It may now be pointed out that the symmetry character of a wave function does not change with time. If  $\psi_s$  is symmetric at a particular time  $t$  then  $H\psi_s$  is also symmetric and according to equation (1),  $\frac{\partial \psi_s}{\partial t}$  is symmetric at time  $t$ . Since  $\psi_s$  and  $\frac{\partial \psi_s}{\partial t}$  are symmetric at time  $t$ ,  $\psi_s$  at infinitesimally later time  $t+dt$  given by  $\psi_s + \frac{\partial \psi_s}{\partial t} dt$  is also symmetric. Such a step by step integration of the wave function

can in principle be continued for arbitrary large time intervals and  $\psi_s$  is seen to remain symmetric always.

Similarly if  $\psi_A$  is antisymmetric wave function at any time  $t$ , then  $H\psi_A$  and hence  $\frac{\partial \psi_A}{\partial t}$  are antisymmetric and the integration of the wave function  $\psi_A$  shows that  $\psi_A$  is always antisymmetric.

If  $P$  is an exchange operator, then we must have

$$P\psi_s(1,2) = \psi_s(2,1)$$

$$P\psi_A(1,2) = -\psi_A(2,1)$$

This symmetry property of the wave function has relationship with the spin of the particle. This relationship is listed here in the following postulates.

(1) The identical particles having having an integral spin quantum number are described by symmetric wave function

$$P\psi_s(1,2,3,\dots,r,\dots,s,\dots,n) = +\psi_s(1,2,3,\dots,s,\dots,r,\dots,n)$$

This class of particles i.e. the particles described by symmetric wave functions are known as Bose particles or Bosons and obey Bose-Einstein statistics. The examples of Bosons are photons (spin 1), neutral helium atoms in normal state ( $s=0$ ) etc.

(2) The identical particles having half odd integral spin quantum number are described by antisymmetric wave functions.

$$P\psi_A(1,2,\dots,r,\dots,s,\dots,n) = -\psi_A(1,2,\dots,s,\dots,r,\dots,n)$$

This class of particles i.e. the particles described by antisymmetric wave function obey Fermi-Dirac statistics and the

particles are known as Fermi-particles or Fermions. The examples of Fermions are electrons, protons, neutrons, muons (all spin  $1/2$ )

Construction of symmetric and Antisymmetric wave functions from unsymmetrised functions; Exchange degeneracy.

We shall now show that  $\Psi_s$  or  $\Psi_a$  can be constructed from a general unsymmetrized solution  $\Psi$  of eqn (1). If the arguments of the wave function  $\Psi$  are permuted in any way, then the resulting wave function is also a solution of eqn (1). This is because same permutation applied throughout eqn (1) does not impair its validity as it corresponds simply to a relabeling of the particles. Since  $H$  is symmetric, permuted  $H$  will be same as original  $H$  and the resulting equation is same as eqn (1) for the permuted  $\Psi$ . In this way  $n!$  solutions can be obtained from any one solution, each of which corresponds to one of the  $n!$  permutations of the  $n$  arguments of  $\Psi$ . Evidently any linear combination of these functions is also a solution of the wave equation (1). The sum of all these functions is symmetric (unsymmetrized) wave function  $\Psi_s$ . Since the interchange of any pair of particles changes any one of the component functions into another of them and the

wave function unchanged.

An antisymmetric unnormalised wave function can be constructed by adding together all the permuted wave functions that arise from the original solution by means of an even number of interchanges of pairs of particles and subtracting the sum of all the permuted wave functions that arise by means of an odd number of interchanges of pairs of particles in the original solution.

In the case where the Hamiltonian does not depend upon time, stationary state solution

$$\Psi(1, 2, \dots, n) = \phi(1, 2, \dots, n) e^{-i E_n t / \hbar} \dots (2)$$

can be found and the time independent Schrodinger's eqn. can be written as

$$H(1, 2, \dots, n) \phi(1, 2, \dots, n) = E \phi(1, 2, \dots, n) \dots (3)$$

There are  $n!$  solutions of this eqn. (eigen functions) derived from  $\phi(1, 2, \dots, n)$  by means of permutations of its arguments belonging to the same eigen value  $E$ . Any linear combination of these eigen functions is also an eigen function [i.e. solution of eqn (3)] belonging to eigen value  $E$ . Hence the system is degenerate\* and this type of degeneracy is called exchange degeneracy.

Let us now consider a two particles wave function  $\psi(1s_1, 2s_2)$ . For a two particles wave function, the Schrodinger's time independent equation is written as

The  $2! = 2$  solutions of this equation are  $\psi(1,2)$  and  $\psi(2,1)$ . The solutions correspond to a single energy state  $E$ .

The symmetric wave function can be written

$$\psi_s = \psi(1,2) + \psi(2,1) \quad \dots \quad (5)$$

and the antisymmetric wave function is written as

$$\psi_a = \psi(1,2) - \psi(2,1) \quad \dots \quad (6)$$

Similarly for a system of 3 particles, the schrodinger's equation as

$$H(1,2,3)\psi(1,2,3) = E\psi(1,2,3) \quad \dots \quad (7)$$

This eqn has  $3! = 6$  solutions corresponding to the same eigen values  $E$ . The six possible functions obtained by exchanging the indices of the particles are.

$$\psi(1,2,3), \psi(2,3,1), \psi(3,2,1), \psi(1,3,2), \psi(2,1,3), \psi(3,1,2)$$

Out of these six functions, those arising by an even number of interchanges of the pairs of particles in original wave function  $\psi(1,2,3)$  are

$$\psi(1,2,3), \psi(2,3,1), \psi(3,1,2)$$

and the functions arising by an odd number of interchanges of pairs of particles in original function  $\psi(1,2,3)$  are

$$\psi(1,3,2), \psi(2,1,3), \psi(3,2,1)$$

So the symmetric wave function can be written as

$$\psi_s = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(1,3,2) + \psi(2,1,3) + \psi(3,2,1) \quad \dots \quad (8)$$

and the antisymmetric wave function is

$$\psi_a = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(1,3,2) + \psi(2,1,3) + \psi(3,2,1) \quad \dots \quad (9)$$



Hence  $\psi_s$  and  $\psi_A$  are unnormalised wave functions.

Average value and quantum statistics:

The average value of any dynamical quantity  $p$  in state  $\psi$  is given by

$$\langle P \rangle = \frac{\int \psi^* P \psi d\tau}{\int \psi^* \psi d\tau}$$

where  $P$  is the operator corresponding to the dynamical quantity  $p$ . For example the operator  $p$  associated with energy  $E$  is  $i\hbar \frac{\partial}{\partial t}$  and the operator  $p$  associated with momentum  $p$  is  $\frac{\hbar}{i} \nabla$ .

If  $\psi$  is the normalised function, then

$$\int \psi^* \psi d\tau = 1, \text{ therefore}$$

$$\langle P \rangle = \int \psi^* P \psi d\tau.$$

The symmetric and antisymmetric normalised eigen functions lead to the following results

$$\langle P_s \rangle = \int \psi_s^* P \psi_s d\tau$$

$$\langle P_A \rangle = \int \psi_A^* P \psi_A d\tau$$

and

A little consideration shows that for symmetric solution an exchange of co-ordinates of particles leaves both  $\psi_s$  and  $\psi_s^*$  unaltered. Consequently  $\langle P_s \rangle$  remain unchanged. In the case of antisymmetric solution an exchange of co-ordinates changes the signs of both  $\psi_A$  and  $\psi_A^*$ . Consequently  $\langle P_A \rangle$  again remains unchanged. Therefore we conclude that any interchange of two particles leaves the average or the observed property of the system unaffected. Therefore from the quantum mechanical point of view the

similar particles can not be distinguished.

### Particle exchange operator:

The particle exchange operator  $P_{1,2}$  is defined by equation

$$P_{1,2} \psi(r_1, s_1; r_2, s_2) \equiv \psi(r_2, s_2; r_1, s_1) \dots (1)$$

The effect of this operator is to interchange the subscripts of the spin and position variables of the wave-function for particles 1 and 2. If the two particles are truly identical, then the Hamiltonian must be symmetric with respect to the position and spin of the identical particles. In other way, energy of the system will remain same if we merely relabel the particles.

### Eigen values and Eigen function of Particle Exchange Operator:

The eigen value equation for particle exchange operator is

$$P_{1,2} \psi(1,2) \equiv \alpha \psi(1,2) \dots (2)$$

where  $\alpha$  is eigen value of operator  $P_{1,2}$  in state  $\psi(1,2)$

operating again

$$\begin{aligned} P_{1,2}^2 \psi(1,2) &= P_{1,2} P_{1,2} \psi(1,2) = P_{1,2} \alpha \psi(1,2) \\ &= \alpha P_{1,2} \psi(1,2) = \alpha [\alpha \psi(1,2)] \end{aligned}$$

$$P_{1,2}^2 \psi(1,2) = \alpha^2 \psi(1,2) \dots (3)$$

From definition of particle exchange operator

$$P_{1,2}^2 \psi(1,2) = \psi(2,1)$$

Operating again  $P_{1,2}^2 \psi(1,2) = P_{1,2} \psi(2,1)$

$$P_{1,2}^2 \psi(1,2) = \psi(1,2) \dots (4)$$

Comparing (3) and (4) we note that

$$\alpha^2 = 1 \quad (\text{or}) \quad \alpha = \pm 1 \dots (5)$$

The eigen values of particle exchange operator are  $\pm 1$ , just they are for parity operator

The respective eigen functions of particle exchange operator corresponding to eigen values  $+1$  and  $-1$  are symmetric and antisymmetric

$$P_{12} \psi_s = \psi_s \quad \text{and} \quad P_{12} \psi_A = -\psi_A \quad \dots (b)$$

This may be seen as follows:

$$\psi_s = \psi(1,2) + \psi(2,1)$$

$$P_{12} \psi_s = P_{12} [\psi(1,2) + \psi(2,1)] \\ = \psi(2,1) + \psi(1,2) = \psi_s$$

$$\psi_A = \psi(1,2) - \psi(2,1)$$

$$P_{12} \psi_A = P_{12} [\psi(1,2) - \psi(2,1)] = \psi(2,1) - \psi(1,2) \\ = -[\psi(1,2) - \psi(2,1)] = -\psi_A$$

$$P_{12} \psi(1,2) = \psi(2,1)$$

$$P_{12} H(1,2) \psi(1,2) = H(2,1) \psi(2,1) \\ = H(1,2) \psi(2,1)$$

[Since Hamiltonian  $H$  is symmetric  
 $H(1,2) = H(2,1)$ ]

$$= H(1,2) P_{12} \psi(1,2)$$

$$[P_{12} H(1,2) - H(2,1) P_{12}] \psi(1,2) = 0$$

As  $\psi(1,2)$  is non-zero

$$P_{12} H(1,2) - H(1,2) P_{12} = 0$$

$$[P_{12}, H] = 0$$

Thus the particle exchange operator commutes with the Hamiltonian

## Distinguishability of Identical particles

The two identical particles can be distinguishable from each other if the sum of the probabilities of the individual wave functions in two states is equal to the probability derived by the symmetrised wave function

$$\begin{aligned} |\psi(1,2)|^2 + |\psi(2,1)|^2 &= |\frac{1}{\sqrt{2}}[\psi(1,2) \pm \psi(2,1)]|^2 \\ &= |\psi(1,2)|^2 + |\psi(2,1)|^2 \pm \\ &\quad 2 \operatorname{Re} \psi(1,2) \psi^*(2,1) \end{aligned}$$

where  $\operatorname{Re}$  denotes the real part of  $[\psi(1,2) \psi^*(2,1)]$ .

It is possible only when overlap of wave-function  $\psi(1,2)$  and  $\psi(2,1)$  is zero or  $2 \operatorname{Re} \{\psi(1,2) \psi^*(2,1)\} = 0$

Thus when the co-ordinates (space and spin) of two particles are not the same between exchange degenerate functions the interference term, i.e.  $2 \operatorname{Re} \psi(1,2) \psi^*(2,1)$  becomes zero and particle co-ordinates do not overlap.

Like this the identical particles can be distinguished by means of their position or their spin components. Such a situation implies in the case of two particles, that the wave-function  $\psi(1,2)$  is different from zero only when the co-ordinate 1 is in some region, A the co-ordinate 2 is in region B and A and B have no common domain. the co-ordinate probability density is given by (1). If now  $\psi(1,2)$  vanishes

whenever 1 is not A and 2 is not in B and A and B do not overlap, the bracket term in  $2 \operatorname{Re} \psi(1,2) \psi^*(2,1)$  is zero everywhere and (1) reduce to

$$|\psi(1,2)|^2 + |\psi(2,1)|^2 \quad \dots \quad (2)$$

Thus the probability density associated with either of the symmetrical wave functions  $\psi(1,2) \pm \psi(2,1)$  is the sum of the probability densities associated with  $\psi(1,2)$  and  $\psi(2,1)$  separately. This precise result will be obtained if the particles are not identical. Thus the interference effects between exchange degenerate wave-functions, represented by the bracket term in (1), disappear when the co-ordinates of the particles do not overlap.

### The Pauli's exclusion principle:

A particle during its motion in space reflects the properties of the statistics which it obeys. Consider two particles system which contains electrons in indistinguishable positions. Electrons are  $\frac{1}{2}$  spin particles and obey Fermi Dirac statistics. If they occupy the same position in space and have the same z-component of spin, it can be seen that the eigen function of exchange operator for a case will be

$$\begin{aligned} P_{12} \psi_A(r_1, s_1; r_2, s_2) &= -\psi_A(r_2, s_2; r_1, s_1) \quad \dots \quad (1) \\ &= \psi_A(r_1, s_1; r_2, s_2) \\ &= 0 \text{ if } \begin{cases} r_1 = r_2 \\ s_1 = s_2 \end{cases} \quad \dots \quad (2) \end{aligned}$$

The non existence of the wave-function under these conditions implies that there is zero probability that the particle will occupy the same point in space and have identical spin orientations.

eqn (2) is physical principle called Pauli exclusion principle which states that no two particles obeying Fermi statistic can exist in the same quantum state. This means that if there are two electron in one atomic orbit (angular momentum  $\pm 0$ ), they cannot have the same spin orientations. Then spins have to be oppositely directed.

The Pauli's Exclusion Principle from Slater's Determination:

In many particle problems a useful zero order approximation can be obtained by neglecting the interactions between the particles that make up the system under consideration. The approximation (unperturbed) Hamiltonian is equated to the sum of Hamiltonian function for the separate particles. Thus for a system of  $n$  particles

$$H_0(1, 2, \dots, n) = H_0'(1) + \dots + H_0'(n) \quad \dots (3)$$

and the approximate energy eigen function is a product of one particle eigen functions of  $H_0'$ .

$$\psi(1, 2, \dots, n) = \phi_0(1) \phi_0(2) \dots \phi_0(n) \dots (4)$$

$$E = E_a + E_b + \dots + E_k$$

$$H_0'(1) \phi_a(1) = E_a \phi_a(1) \text{ etc}$$

If the particles are electrons, an antisymmetric wave function must be constructed from the  $\psi$  given by (1). This is most easily expressed as determination of the  $\psi$ 's known as Slater's determinant.

$$\psi_A(1, 2, \dots, n) = \begin{vmatrix} \phi_a(1) & \phi_a(2) & \dots & \phi_a(n) \\ \phi_b(1) & \phi_b(2) & \dots & \phi_b(n) \\ \dots & \dots & \dots & \dots \\ \phi_k(1) & \phi_k(2) & \dots & \phi_k(n) \end{vmatrix} \dots (5)$$

The unnormalised  $\psi_A$  given in (5) is clearly an antisymmetric solution of the approximation wave equation.

$$(H_0 - E) \psi_A = 0 \dots (6)$$

Equation (5) has the interesting property that it vanishes if two or more of the  $\phi$ 's are same. For example if  $\phi_a(1) = \phi_b(1)$  or  $\phi_a(1) = \phi_a(2)$ , then determinant (3) will vanish. This is the special case of the general result that an antisymmetric wave function can not be constructed from a solution that is unaltered by the interchange of any pair of particles, thus the approximate Hamiltonian  $H_0$  has no solutions for which there is more than one electron in any one of the state  $a, b, k$ . This result is well known Pauli's exclusion principle which states that no two particles described by antisymmetric wave functions (or obeying Fermi Dirac statistic) can exist in the same quantum state.

Connection with statistical mechanics:

The unsymmetrised zero order solution in (4) can be used to construct a symmetric as well as an antisymmetric wave functions such as symmetric (unnormalised) function is the sum of all different permutations of the numbers  $1, 2, \dots, n$  among the one particle eigen functions  $\phi_a, \phi_b, \dots, \phi_n$ . This wave function is unique and can be specified simply by defining how many particles are in each of the states  $a, b$ .

The fundamental statistical difference between particles that are described by antisymmetric and by symmetric wave-functions is that number of the former type that can occupy any state is limited to 0 or 1 whereas any number  $(0, 1, 2, \dots)$  of the latter type of particles can occupy any state.

Hence the solution of large number of non-interacting (or weakly interacting) particles for which the states can be enumerated in these two ways form the subject matter of quantum statistical mechanics.

The particles that are described by antisymmetric wave functions are said to obey Fermi-Dirac statistics and are called Fermions. The examples of fermions are electrons, protons and neutrons.



The order class of particles which are described by symmetric wave functions obey Bose-Einstein statistics and are called bosons. The examples of bosons are  $\pi$ -mesons,  $\gamma$  rays (i.e. light quanta) etc. Further the aggregates of particles that are strongly bound to that they can be regarded as particles can be described either by symmetric or antisymmetric wave functions. For example the nucleus of helium atom is made up of two protons and two neutrons and an uncertain number of  $\pi$ -mesons, all these particles forming the helium nucleus are strongly bound-together. If we consider a number of helium nuclei which has no interactions or weak interactions so that the changes in internal motion of nuclei due to the interactions are negligible, then the motions of centres of gravity of nuclei can be thought of as the net effect of interchanges of two pairs of protons, two pairs of neutrons and a number of pairs of  $\pi$ -mesons. As the actual wave functions in protons and neutrons (fermions) is antisymmetric the resultant of first four interchanges leaves the approximate wave function unchanged and in  $\pi$ -mesons the symmetry of wave function is such that the latter interchanges (i.e. interchanges of  $\pi$ -mesons) have no effect. The extension of above reasoning gives the inference that the strongly bound particles.

which themselves interact weakly with each other (e.g. nuclei, atoms or molecules) obey Bose-Einstein statistics when each of them consists of even total number of electrons, protons and neutrons while they obey Fermi-Dirac statistics when each consists of an odd total number of these particles.

### Importance of Pauli exclusion principle:

The Pauli exclusion principle explains the classification of elements in periodic table. According to this principle no two fermions can exist in the same quantum state. According to this two electrons in one atomic orbit (angular momentum quantum numbers  $n, l, m_j$  same) can not have the same spin orientation (ie same spin quantum number) In other words the two electrons having same  $n, l$  and  $m_j$  have oppositely directed spins. Thus in each  $m_j$  state there can be maximum two electrons with anti-parallel spin combinations. Thus we have the following table for the number of electrons in an order.

Orbit	state	n	Quantum number	$m_j$	number of electrons	Total number of electrons
I	1s	1	0	0	2	with opposite spins 2
II	2s	2	0	0	2	
	2p	2	1	$\begin{bmatrix} +1 \\ 0 \\ -1 \end{bmatrix}$	$\begin{bmatrix} 2 \\ 2 \\ 2 \end{bmatrix}$	
						8

<u>III</u>	3s	3	0	0	2	2	18
	3p	3	1	+1	2		
				0	2	6	
				-1	2		
	3d	3	2	2	2		
				1	2		
				0	2		
				-1	2		
				-2	2	10	

Proceeding in a similar way we can show that the maximum number of electrons in  $n=4$  orbits is 32. In general the maximum number of electrons in an orbit specified by total quantum number  $n$  is  $2n^2$ .

The exclusion principle describes the group behaviour of all elementary particles having spin angular momentum quantum number  $s = \pm 1/2$  i.e. electrons, protons, neutrons etc. One of the most important consequences of Pauli exclusion principle is that interaction of identical particles having  $s = \pm 1/2$  are described by the new forces of non-dynamical character. To illustrate this we consider two electrons associated with de-Broglie waves  $e^{iP_1 x_1 / \hbar}$  and  $e^{iP_2 x_2 / \hbar}$  where  $x_1, x_2$  are the positions and  $P_1, P_2$  are momenta of electrons in a system of these electrons, the electrons can be distinguished since they may be interchanged without affecting any physical observable. As there are even number (2) of electrons, the wave function is antisymmetric which may be expressed as

$$\Psi_A = \frac{1}{\sqrt{2}} \left[ e^{i(P_1 x_1 + P_2 x_2)/\hbar} + e^{i(P_1 x_2 + P_2 x_1)/\hbar} \right]$$

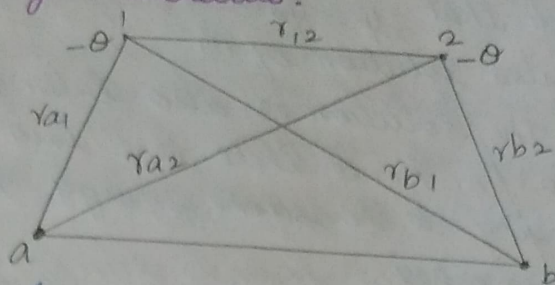
$\frac{1}{\sqrt{2}}$  being normalisation constant.

The probability of first electron to be found at  $x_1$  and second to be found  $x_2$  is given by

$$\Psi_A^* \Psi_A = 1 - \cos[(P_1 - P_2)(x_1 - x_2)/\hbar]$$

When the  $x_1 \rightarrow x_2$ , the probability density function  $\Psi_A^* \Psi_A$  vanishes. This signifies that there is some sort of repulsive force between electron in addition to the Coulomb repulsion. This repulsive force increases with decrease of difference in their momenta for a given separation between them. The principle also infers that when separation between atoms decreases to a value such that the electronic structures of atoms begins to overlap, then very strong repulsive forces come into play which account for very low compressibility of liquids and solids. Further it is due to the existence of this principle that the properties of electrons gas are quite different in many respects from those of an ordinary gas.

## Symmetric and Antisymmetric wave-functions of Hydrogen molecule:



When two ~~H~~ atoms meet a molecule is not always formed. The two atoms repel each other if the spins of two electrons are parallel ( $\uparrow\uparrow$ ) and two atoms attract each other if the spins of two electrons are antiparallel ( $\downarrow\uparrow$ ). The system consists of two hydrogen nuclei 'a' and 'b' and two electrons whose co-ordinates are denoted by symbols 1, 2:  $r_{12}$  the distance between two electrons 1 and 2.

For two electrons the Schrodinger equation becomes

$$\nabla_1^2 \psi + \nabla_2^2 \psi + \frac{2m}{\hbar^2} \left( E - V_1 - V_2 - \frac{e^2}{r_{12}} \right) \psi = 0 \dots (1)$$

Let us suppose the spinning of electrons is neglected. In order to solve (1) we neglect the term  $\frac{e^2}{r_{12}}$ . In other words we regard the electrons as moving independently of each other in an external potential field. Let total energy of the two electrons be  $E_a + E_b$ . We find a solution by putting  $\psi$  equal to the product of two functions eg

$$\psi = \psi_a(1) \psi_b(2) \dots (2)$$

Where  $\psi_a(1) = \psi_a(x_1, y_1, z_1)$  depends on the first electron only and  $\psi_b(2) = \psi_b(x_2, y_2, z_2)$  depends on the second electron only.

We have neglected the term  $\frac{e^2}{r_{12}}$  and we have described the state where the electron labelled No. 1 is in level  $a$  and the electron NO. 2 is in level  $b$ .

Physically, however, that two electrons are indistinguishable from each other. We therefore expect that  $\psi = \psi_a^{(2)} \psi_b^{(1)} \dots$  (3)

is also solution of (1)

The solution (3) also belongs to the energy  $E = E_a + E_b$ . Hence there are two wave-functions belonging to the same energy. It is the case of degeneracy.

From (2) and (3) we can build up more wave-functions belonging to the same energy. We may take any linear combination.

$$\psi_+ = \psi_a^{(1)} \psi_b^{(2)} + \psi_a^{(2)} \psi_b^{(1)} \dots (4a)$$

$$\psi_- = \psi_a^{(1)} \psi_b^{(2)} - \psi_a^{(2)} \psi_b^{(1)} \dots (4b)$$

$\psi_+$  does not change if we interchange 1 and 2. So  $\psi_+$  is symmetric wave-function.  $\psi_-$  changes its sign if 1 and 2 are interchanged. So  $\psi_-$  is antisymmetrical wave function. Now we have (2), (3) and (4a) as three symmetrical functions and (4b) as antisymmetrical wave-function

If we consider spin, we know that each electron has spin  $s_1 = s_2 = 1/2$ . The two spins then combine to give a resultant spin for the total system. The spin  $s$  can have the same directions ( $\uparrow\uparrow$ ) giving  $s=1$  and the spins can have the opposite directions ( $\uparrow\downarrow$ ) giving  $s=0$ .

The spin  $s=0$  corresponds to singlet and spins  $s=1$  corresponds to triplets.

For two electrons, there will be two spin functions  $\alpha(1)$  and  $\alpha(2)$ . The total spin wave function is the product of two such spin functions. In all, we have, for two electrons four spin functions:

	Electron 1	Electron 2
$\alpha(1) \alpha(2)$	$\uparrow$	$\uparrow$
$\beta(1) \beta(2)$	$\downarrow$	$\downarrow$
$\alpha(1) \beta(2)$	$\uparrow$	$\downarrow$
$\alpha(2) \beta(1)$	$\downarrow$	$\uparrow$

Each  $\alpha$  describes the spin  $+\frac{1}{2}$  and  $\beta$  describes the spin  $-\frac{1}{2}$ .

Since two electrons are indistinguishable from each other. So we choose linear combination of the four functions,  $\alpha(1)\alpha(2)$  and  $\beta(1)\beta(2)$  are already symmetrical.

Instead of  $\alpha(1)\beta(2)$  and  $\beta(2)\alpha(1)$  we choose  $\alpha(1)\beta(2) + \alpha(2)\beta(1)$  symmetrical function and  $\alpha(1)\beta(2) - \alpha(2)\beta(1)$  antisymmetrical function.

Now four spin function will be

$$\left. \begin{array}{l} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \beta(1)\beta(2) \end{array} \right\} \begin{array}{l} +1 \\ 0 \\ -1 \end{array} \quad \text{with } s=1$$

$$\left. \begin{array}{l} \alpha(1)\beta(2) - \alpha(2)\beta(1) \\ 0 \end{array} \right\} \quad \text{with } s=0$$

The complete wave-function of an electron is the product of the orbital wave-function multiplied by one of the spin functions.

According to Pauli exclusion principle only two products will be allowed.

$$\left[ \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) \right] \times \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right]$$

and

$$\left[ \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1) \right] \times \left[ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{array} \right]$$

Hence total wave-function of two electrons is always antisymmetrical in the electrons, because symmetric orbital functions will be associated with the anti-symmetric spin functions ( $s=0$  singlet) and anti-symmetric orbital function will be associated with symmetric spin function ( $s=1$ , triplet)

Total: Symmetry of Orbital Wave-functions and spin

Orbital	Spin	Total $s$
$\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)$	$\alpha(1)\beta(2) - \alpha(2)\beta(1)$	0 (singlet)
$\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)$	$\left[ \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{array} \right]$	1 (triplet)

## Spin Matrices and Eigen functions (general case)

Let the identical particles be represented by  $1, 2, \dots, n$ . The spin co-ordinates differ from the space co-ordinates in that they take on only  $(2s+1)$  values for a particle of spin  $s$ , instead of the infinite number of values that are taken by each space co-ordinate. The spin wave function of a particle is completely determined by the  $(2s+1)$  numbers.

A set of orthonormal one particle spin functions is given by the normalized eigen functions of the total angular momentum  $J$  and its components  $J_z$  matrices. The eigen functions are  $(2s+1)$  rows, one column that have zero in all position except one. For example if  $s = 3/2$ , the four spin eigen functions are easily seen to be

$$\psi(3/2) = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad \psi(1/2) = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \quad \psi(-1/2) = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \quad \psi(-3/2) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

and the corresponding eigen values of  $S_z$  are  $1/2\hbar$ ,  $3/2\hbar$ ,  $1/2\hbar$  and  $-3/2\hbar$  respectively

The orthonormality is demonstrated by multiplying the hermitian adjoint of one spin function into itself or another function.

$$[0100] \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = 1, \quad [0100] \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = 0, \text{ etc}$$



statistical weight or a priori probability

In some cases there is only one eigen function corresponding to each eigen value. In such cases the eigen state or the energy level is said to be non-degenerate. However in some other cases there are a number of eigen functions corresponding to a single eigen value. In these cases the eigen state is said to be degenerate. In the degenerate cases the number of eigen states for the particular energy state or level is called the degeneracy of that state.

Thus if  $g_i$  is the degeneracy for the eigen value  $E_i$ , then  $g_i$  is the number of eigen states for the  $i$ th eigen state having energy  $E_i$ .

Obviously for a non degenerate case  $g_i = 1$ . An important postulate of quantum statistics concerning the probability of eigen-states is that every eigen state possesses an equal a priori probability. According to this postulate the eigen state in quantum statistics is equivalent to the unit cell in the phase space of classical statistics. The degeneracy  $g_i$  is therefore often referred to as a priori probability or the statistical weight of the given eigen state.

### Density operator and Density matrix

A pure quantum state of a system is represented by a single eigen vector  $\psi_a$  or  $|\alpha\rangle$ ; but if the knowledge of the system is described by non-negative probabilities  $P_\alpha, P_\beta, \dots$  for being in states  $|\alpha\rangle, |\beta\rangle, \dots$ ; a statistical approach is necessary if the Theory of pure

states is inadequate. This can be developed in close analogy with the classical situation. A pure classical state is one that is represented by a single moving point in phase space, that have definite values of co-ordinates  $q_1, q_2, \dots, q_f$  and canonical momenta  $p_1, p_2, \dots, p_f$  at each instant of time.

On the other hand a statistical state can be described by a non-negative density function

$$f(q_1, \dots, q_f, p_1, \dots, p_f, t)$$

such that the probability that a system is found in the interval  $dq_1, \dots, dq_f, dp_1, \dots, dp_f$  at time  $t$  is

$$P(dq_1, \dots, dq_f, dp_1, \dots, dp_f)$$

The quantum analogue of the classical density function is known as the density operator and representation in the matrix form is known as the density matrix.

Consider an ensemble consisting of  $N$  systems in the normalised states  $\Psi_\alpha, \alpha=1, 2, 3, \dots, N$ . The expectation value of an observable  $f$  in this representation is given by.

$$\langle f \rangle = \int \Psi_\alpha^* \hat{f} \Psi_\alpha dq$$

$\hat{f}$  being operator associated with observable  $f$ .

If  $\Phi_n$ 's represent the orthonormal eigen functions, then a pure state  $\Psi_\alpha$  may be represented co-efficients of expansion of  $\Psi_\alpha$  into eigen vectors  $\Phi_n$ , i.e.

$$\Psi_\alpha = \sum_n C_n \Phi_n$$

$$\Psi_\alpha^* = \sum_n C_n^* \Phi_n^* \quad \dots (2)$$

so that eqn (1) takes the form

$$\langle f \rangle = \sum_m \sum_n C_m^* C_n \int \Phi_m^* \hat{f} \Phi_n dq$$

$$= \sum_m \sum_n C_m^* C_n \langle m | f | n \rangle \dots (3)$$

If the state is not specified completely, it may be represented by incoherent specified superposition of a number of pure states  $\psi^{(\alpha)}$  with statistical weight  $p^{(\alpha)}$ . to each pure state there corresponds a mean value  $\langle f \rangle_{\alpha}$ ; and the mean value of  $f$  for the incoherent superposition is given by the grand (or ensemble) average given by

$$\begin{aligned} \langle f \rangle &= \sum_{\alpha} p^{(\alpha)} \langle f \rangle_{\alpha} = \sum_{\alpha} p^{(\alpha)} \sum_m C_m^{*(\alpha)} C_n^{(\alpha)} \langle m | f | n \rangle \\ &= \sum_m \sum_n \langle m | f | n \rangle \sum_{\alpha} p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)} \dots (4) \end{aligned}$$

where  $0 < p^{(\alpha)} < 1$  and  $\sum_{\alpha} p^{(\alpha)} = 1 \dots (5)$

where  $p^{(\alpha)}$  represents the probability of finding the system in the state  $|\alpha\rangle$ ; when a measurement is made at random on the system.

For brevity let us write

$$\sum_{\alpha} p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)} = P_{mn}; \dots (6)$$

then eqn (5) takes the form

$$\langle f \rangle = \sum_n \sum_m P_{mn} \langle m | f | n \rangle = \sum_m \sum_n P_{nm} f_{mn} \dots (7)$$

The ensemble average of  $f$  is also represented by the ~~empirical~~ eqn

$$\bar{f} = \iint P(q, p) f(q, p) dq dp \dots (8)$$

where  $P$  is termed as the normalised density of distribution.

A comparison of eqn (7) and (8) shows that the integration over  $q$  and  $p$  has been replaced by a double sum over the quantum states. Thus the matrix  $P_{mn}$  plays a role analogous to that of the probability density  $P(q, p)$ . Therefore  $P$  is termed as the density matrix. whose matrix elements can be defined by eqn (6) as

$$P_{nm} = \sum_{\alpha} p^{(\alpha)} C_m^{*(\alpha)} C_n^{(\alpha)}$$

so that eqn (7) gives

$$\langle \hat{f} \rangle = \sum_m \sum_n P_{nm} f_{mn} = \sum_n (P^{\dagger})_{nm} \\ = \text{Trace}(P^{\dagger}) \dots (9)$$

where Trace stands for the sum of the diagonal elements of the matrix  $(P^{\dagger})$ . It is convenient to regard the density matrix as defined by equation (9) rather than by eqn (6).

Limitation on density matrix

(i) The condition that the expectation value of  $f$  is real for every Hermitian operator  $f$ , requires that  $P$  must also be hermitian

$$P_{nm} = P^{\dagger}_{mn} \dots (10)$$

(ii) The condition that the unit operator  $I$  has the expectation value 1, require that

$$\text{Trace}(P^{\dagger}) = \text{Trace}(P I) = \text{Trace}(P) = \sum_n P_{nn} = 1 \dots (11)$$

(iii) The condition that every operator with negative eigen values has a non-negative mean value, requires that  $P$  must be definitely positive. This means,

$$P_{nm} \geq 0 \dots (12)$$

(iv) The Hermitian matrix  $P$  by means of unitary transformations may be reduced to diagonal form

$$P_{ij} = \sum_n \sum_m U_{jn} P_{nm} U_{im}^{-1}$$

The conditions given by (11) and (12) require that

$$\sum_j P_j^2 \leq \left( \sum_j P_j \right)^2 = [\text{Trace}(P^2)] = 1$$

Thus we have in general  $\text{Trace}(P^2) =$

$$\sum_n \sum_m |P_{nm}|^2 \leq 1$$

This limits the value of every single element of the density matrix

# Time dependence of density matrix

Quantum mechanical analogue of Liouville's theorem:

Time dependent Schrodinger equation is

$$i\hbar \frac{\partial \psi_a}{\partial t} = H \psi_a \text{ where } \hbar = \frac{h}{2\pi} \dots (15)$$

$$\psi_a = \sum_k C_k^{(a)} \phi_k$$

We may write eqn (15) as

$$i\hbar \frac{\partial}{\partial t} \left( \sum_k C_k^{(a)} \phi_k \right) = H \sum_k C_k^{(a)} \phi_k$$

Multiplying above eqn by  $\phi_m^*$  and integrating over  $q$ , we get

$$i\hbar \sum_k \frac{\partial}{\partial t} \int C_k^{(a)} \phi_m^* \phi_k dq = \sum_k C_k^{(a)} \int \phi_m^* H \phi_k dq \dots (16)$$

$$i\hbar \frac{\partial}{\partial t} C_k^{(a)} \delta_{mk} = \sum_k C_k^{(a)} H_{mk} \dots (16)$$

$$\int \phi_m^* \phi_k dq = \delta_{mk}$$

$$\int \phi_m^* H \phi_k dq = H_{mk} = \langle m | H | k \rangle$$

$$i\hbar \frac{\partial C_m^{(a)}}{\partial t} = \sum_k C_k^{(a)} H_{mk} \dots (17)$$

The complex conjugate of above eqn is

$$i\hbar \frac{\partial C_m^{*(a)}}{\partial t} = \sum_k C_k^{*(a)} H_{mk}^* \dots (18)$$

From definition of density matrix in  $\phi_k$  representation

$$P_{nm} = \sum_a \rho^{(a)} C_m^{*(a)} C_n^{(a)} \dots (19)$$

Differentiating above equation with respect to time, we get

$$\frac{\partial P_{nm}}{\partial t} = \sum_a \rho^{(a)} \left[ C_m^{*(a)} \frac{\partial C_n^{(a)}}{\partial t} + C_n^{(a)} \frac{\partial C_m^{*(a)}}{\partial t} \right]$$

$$i\hbar \frac{\partial P_{nm}}{\partial t} = \sum_a \rho^{(a)} \left[ C_m^{*(a)} \left( i\hbar \frac{\partial C_n^{(a)}}{\partial t} \right) + C_n^{(a)} \left( i\hbar \frac{\partial C_m^{*(a)}}{\partial t} \right) \right]$$

Using (17) and (18), above eqn takes the form

$$i\hbar \frac{\partial P_{nm}}{\partial t} = \sum_a \rho^{(a)} \left\{ C_m^{*(a)} \sum_k C_n^{(a)} H_{mk} - C_n^{(a)} \sum_k C_m^{*(a)} H_{nk}^* \right\}$$

$$= \sum_k H_{nk} \sum_a \rho_a C_m^{*(a)} C_k^{(a)} - \sum_k \sum_a \rho_a C_n^{*(a)} C_k^{(a)} H_{mk}^*$$

$$= \sum_k (H_{nk} P_{km} - P_{nk} H_{mk}^*)$$

As  $H$  is Hermitian  $H_{mk}^* = H_{km}$

$$i\hbar \frac{\partial P_{nm}}{\partial t} = - \sum_k (P_{nk} H_{km} - H_{nk} P_{km})$$

$$= - (PH - HP)_{nm}$$

Using  $(PH - HP) = [P, H]$ ; the time dependence of density matrix is given by

$$i\hbar \frac{\partial P}{\partial t} = - [P, H]$$

This equation is analogous to Liouville's theorem of classical statistical mechanics