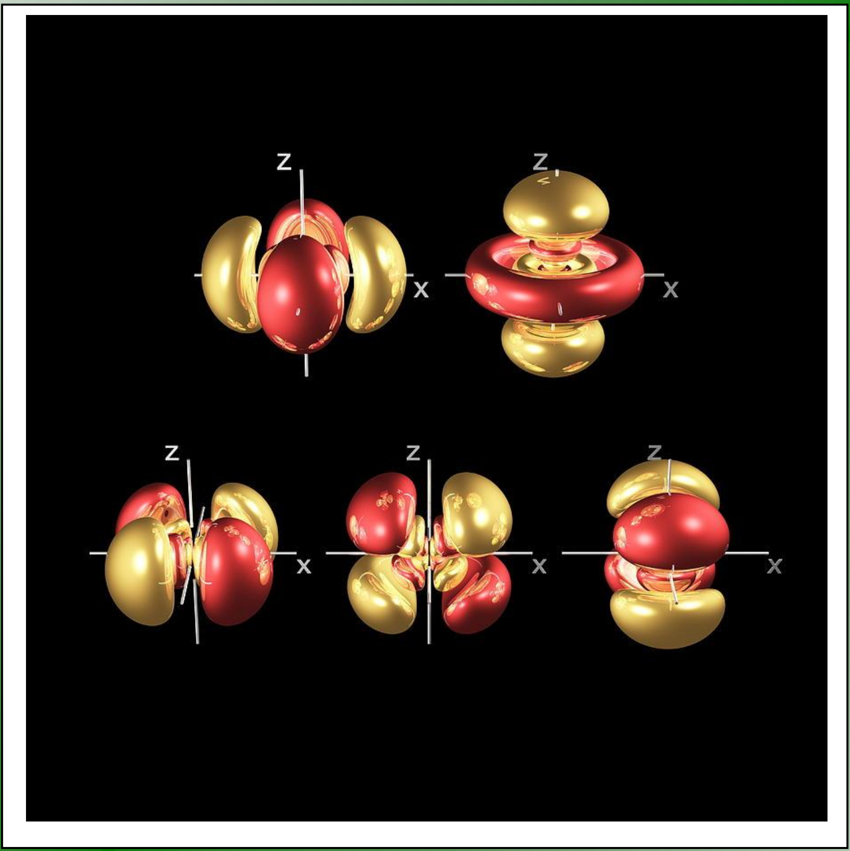
KARNATAKA STATE OPEN UNIVERSITY

Mukthagangothri, Mysore – 570 006

M.Sc. PHYSICS

(SECOND SEMESTER)



COURSE –MP 2.2

Quantum Mechanics-1

M.Sc. PHYSICS

SECOND SEMESTER

Course: MP 2.2

QUANTUM MECHANICS-1

Course Design

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PRELUDE

In spite of the successful explanation of multitude of phenomena by Classical Mechanics and Electrodynamics, a large group of natural phenomena remains unexplained by Classical Physics. It is possible to find examples in various branches of physics, why only Physics, in all branches of science. Though sometimes it is thought that the Classical Mechanics satisfactorily describes the phenomena related to macroscopic objects and the difficulty arises only in case of microscopic particles, even the physics of macroscopic bodies (solids, liquids, and gases) is not completely understood on the basis of Classical Mechanics when it comes to the consistent explanations for the structure and stability of condensed matter, for the energy of cohesion of solids, for electrical and thermal conductivity, specific heat of molecular gases and solids at low temperatures, and for phenomena such as superconductivity, ferromagnetism, super fluidity, quantum crystals, and neutron stars. Nuclear Physics and elementary particle physics require definitely new theoretical foundations in order to describe the structure of atomic nuclei, nuclear spectra, nuclear and the stability of nuclei, and similarly in order to make predictions concerning the size and structure of elementary particles, their mechanical and electromagnetic properties and their interactions. Even in Electrodynamics and Optics there are effects which cannot be understood with the help of classical theories, for example, the blackbody radiation and the photoelectric effect.

All of these phenomena can be understood and can be well explained by quantum theories. Thus it is very much necessary to study and understand the Quantum Mechanics. With this in view, the fundamentals of Quantum Mechanics have been thoroughly studied in the post-graduate level.

In the present book an attempt has been made to introduce the fundamentals of Quantum mechanics. The authors have tried to present the ideas in a lucid style so that the post-graduate students of Karnataka State Open University can go through the same and understand the basics on their own.

For the sake of understanding the syllabus this book of Quantum Mechanics has been divided into four blocks. The first block deals with fundamental concepts of Quantum Mechanics without which one cannot swim in the ocean of Quantum Mechanics. They can be called as basic / foundation principles of Quantum Mechanics. It starts with the understanding of a special experiment called Stern-Gerlach experiment – but of course not just the one that has been studied in the graduation level – but the sequential one which involves several fascinating results which will make one to think in a new dimension. These basic ideas can be followed under the umbrella of Vector algebra – Linear vector space!

The second block deals with Quantum dynamics. Yes, we know what is meant by dynamics. Here we can understand the way in which one can study the behavior of particles not only as a function of space but also as a function of time! Starting from the setting up the Schrödinger equation for the wave function, one can study the linear harmonic oscillator problem and even move over to study the two body problem

The third block is dedicated to the study of the theory of angular momentum wherein one can study the commutation relations; Spin half systems, finite rotations, Eigen values and eigenstates of angular momentum, addition of angular momentum and then various symmetries.

The fourth and the final block is named as Approximation methods in which perturbation theory and the Variational methods are discussed in detail.

This SLM has adopted such a method so that the material helps the individuals to understand the underlying principles and get a good flavor of the subject and also get motivated to study other reference books in order to go to the depth of the subject.

Unit 1: The Stern-Gerlach experiment, kets, bras and operators, base kets and matrix representations.

Structure:

1.0 Objectives:

After studying this unit you will be able to understand the following aspects:

- The Sequential Stern-Gerlach experiment
- The Operators used in Quantum mechanics
- The Bra and Ket notations used for vectors
- The Matrix representation theory used in Quantum mechanics

1.1 Introduction:

Several experimental evidences conclusively demonstrated that light was an electromagnetic phenomenon. But the understanding of the emission and absorption of radiation by matter posed some difficulties. However this difficulty was partially resolved by making some ad-hoc assumptions regarding the structure of matter. It was assumed that atoms and molecules, which constitute matter, consist of electron oscillators, begin to oscillate under the influence of some external source of excitation. Since the oscillating electron is an accelerated charged particle, it radiates electromagnetic radiation.

Therefore, when electromagnetic wave is incident on such an atomic oscillator, electrons are set into forced oscillations, which in turn emit electromagnetic waves of frequency equal to that of the incident wave. To explain the phenomenon of absorption it was assumed that some kind of dissipative force of viscous type, whose exact origin was not known at that time, act on atomic oscillator. The transformation of incident electromagnetic energy into other form on account of dissipative forces causes loss of energy. At the end of 19th century, like classical mechanics, the electromagnetic theory of radiation was regarded as the ultimate theory of radiation. At this time when the classical physics was at the peak of its accomplishments, some physicists were facing problems that could not be understood within the framework of classical physics. Some of the most outstanding problems among them were (i) the explanation of line spectrum emitted by elements in gaseous state (ii) the photoelectric effect, (iii) the distribution of energy in the spectrum of a black body. Probably, the understanding of these phenomena indicated a different aspect of the nature of radiation. In other words, the understanding of phenomena associated with interaction of radiation with matter requires a fundamental change in our concepts regarding the nature of radiation and the structure of matter. The theory, which regards radiation as stream of particles (called quanta) is called quantum theory of radiation.

Classical Mechanics Vs Quantum Mechanics

Classical Mechanics: the goal of classical mechanics is to determine the position of a particle at any given time **x(t).** Once we know **x(t)** then we can compute the velocity **v_x=dx/dt,** the momentum **P_x=mv_x** the kinetic energy $T = P_x^2 / 2m,$ or any dynamical variable.

Classical Equation of Motion: Newton's Laws for a particle under the influence of potential **V(x)** are as follows:

$$F_x = ma_x = \frac{dp_x}{dt} = -\frac{dV(x)}{dx} \quad with \quad P_x = \frac{dx}{dt}$$

To determine **x(t)** one must solve the Newton's equation

$$m\frac{d^2x(t)}{dt^2} = -\frac{dV(x)}{dx}$$

With the appropriate initial conditions (typically the position and velocity at **t =0)**

Quantum Mechanics: In Quantum Mechanics the situation is much different. In this case we are looking for the particles' wave function $\psi_{(x,t)}$ which is the solution of Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t} -------- > Schrödinger's\, Equation$$

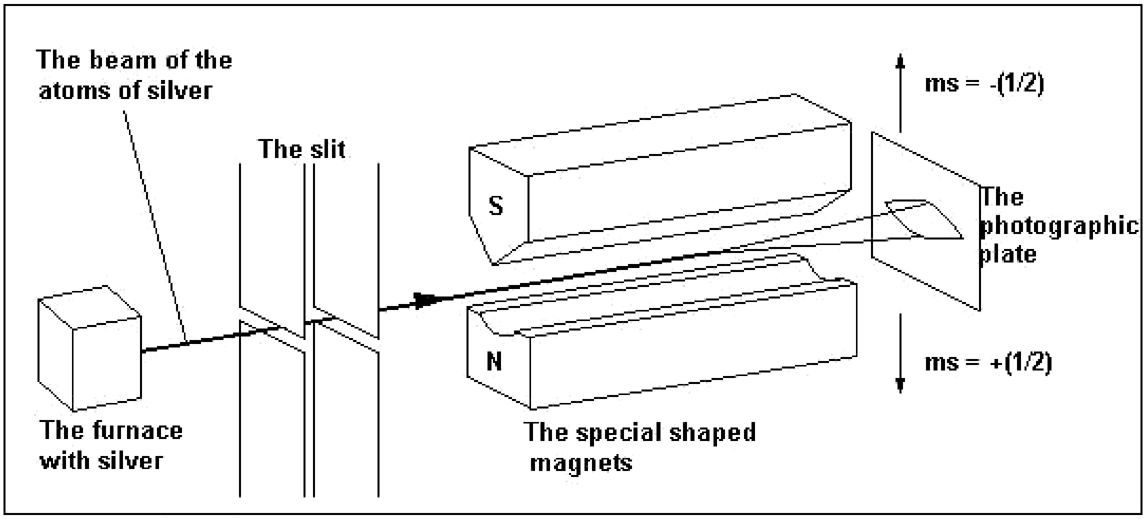
$$where\, i = \sqrt{-1} \;\; and$$
$$\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34}\; J.s$$

The wave function is a complex function and Schrödinger's equation is analogous to Newton's equation. Given suitable initial conditions (typically $\psi_{(x,0)}$), one can solve Schrodinger's equation for $\psi(x,t)$ for all future times just as in classical physics, Newton's equation determines **x(t)** for all future times.

1.2 Stern-Gerlach Experiment:

The theory of spatial quantization of the spin moment of the momentum of electrons of atoms situated in the magnetic field needed to be proved experimentally. In 1920 (two years before the theoretical description of the spin was created) Otto Stern and Walter Gerlach observed it in the experiment they conducted.

The atoms of silver from the source which was the furnace with boiling silver were lead to the vacuum space. There the flat beam of those atoms was created. Then the beam got into non-homogeneous magnetic field and incident a photographic plate. Using classical physical laws we would expect the single picture of the beam on the plate, whereas, the beam of atoms passing through non-homogenous magnetic field undergoes splitting. That is why Otto Stern and Walter Gerlach received the two lines on the photographic plate.

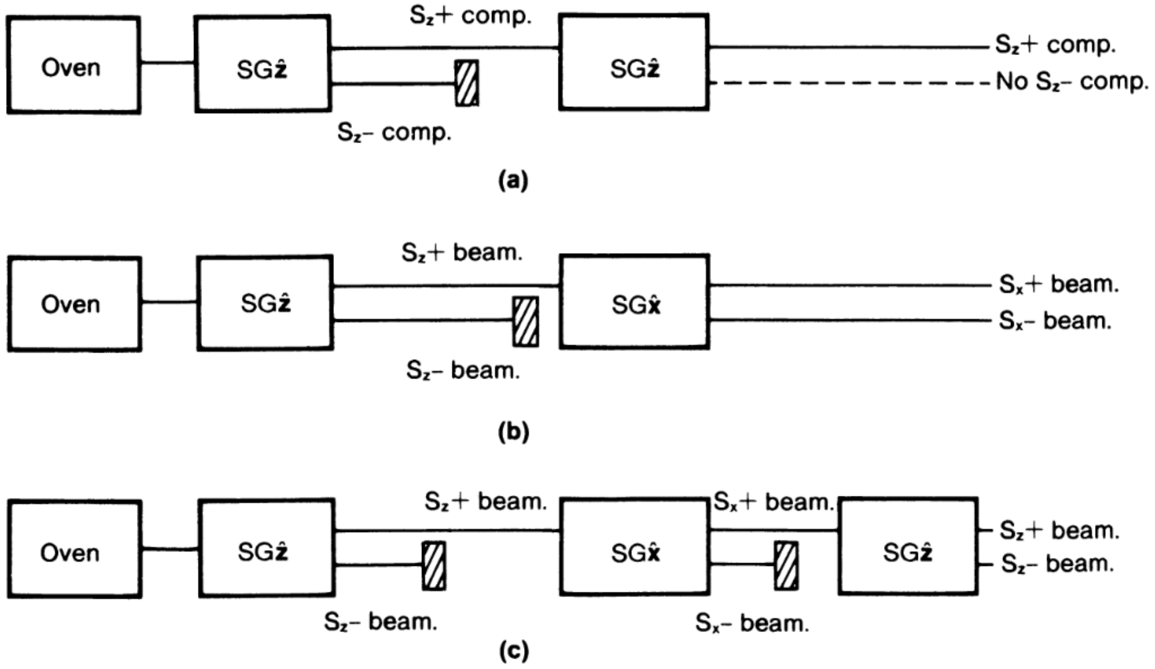


The phenomena can be explained with the spatial quantization of the spin moment of momentum. In atoms the electrons are located in such way that in the each next pair of electrons there is one of the upward spin and one of the downward spin. So the whole spin of such pair is equal zero. But in the atom of silver on the outer shell there is a single electron whose spin is not balanced by any electron.

The circulation causes some magnetic dipole moment (it's like it was a very small magnet). There is a force moment in the magnetic field influencing the dipole that is turning it until its position is the same as the direction of the field B. There is some other force influencing the dipole in the field. When the dipole is directed the same as the magnetic field then the dipole is pulled by that force in to the space of a strongest field. But if the dipole is directed opposite to the fields direction is pulled by that force out from the space of a strongest field.

So the atom of silver having one electron on the outer shell can be pulled in or out the space of a strongest magnetic field, which depends on the value of the magnetic spin quantum number. When the spin of the electron is equal +1/2 the atom is pulled out and when the spin is equal -1/2 the atom is pulled in. So during passing through the non-homogenous magnetic field the beam of the atoms of silver undergoes splitting into the two beams. Each of them consists of atoms which outer electrons are of the same spin.

Let us now consider **a sequential Stern-Gerlach experiment**. By this we mean that the atomic beam goes through two or more SG apparatuses in sequence.



Sequential Stern-Gerlach experiments.

The first arrangement we consider is relatively straightforward. We subject the beam coming out of the oven to the arrangement shown in Figure 1.3a, where SG$_z$ stands for an apparatus with the inhomogeneous magnetic field in the z-direction, as usual. We then block the S$_z$ — component coming out of the first SG$_z$ apparatus and let the remaining S$_z$ + component be subjected to another SG$_z$ apparatus. This time there is only one beam component coming out of the second apparatus—just the S$_z$ + component. This is perhaps not so surprising; after all if the atom spins are up, they are expected to remain so, short of any external field that rotates the spins between the first and the second SG$_z$ apparatuses.

In the second case; The S_z + beam that enters the second apparatus (SG_x) is now split into two components, an S_x + component and an S_x -component, with equal intensities.

In the third case: It is observed experimentally that two components emerge from the third apparatus, not one; the emerging beams are seen to have both an S_z + component and an S_z — component.

This is a complete surprise because after the atoms emerged from the first apparatus, we made sure that the S_z - component was completely blocked.

How is it possible that the S_z — component which, we thought, we eliminated earlier reappears?

How to explain the observed effect?

This can be explained by using the analogy with the polarization triple filter experiment. It is reasonable to represent the S_x + state by a vector, which we call a ket in the Dirac notation which we have already discussed earlier. We denote this vector by;

$\left|S_x;+\right\rangle$ and write it as a linear combination of two base vectors, $\left|S_z;+\right\rangle$ and $\left|S_z;-\right\rangle$ which corresponds to the S_z + and the S_z – states , respectively. So we may conjecture.

$$\left|S_x;+\right\rangle \overset{?}{=} \frac{1}{\sqrt{2}}\left|S_z;+\right\rangle + \frac{1}{\sqrt{2}}\left|S_z;-\right\rangle ------------(1)$$

$$\left|S_x;-\right\rangle \overset{?}{=} -\frac{1}{\sqrt{2}}\left|S_z;+\right\rangle + \frac{1}{\sqrt{2}}\left|S_z;-\right\rangle ------------(2)$$

Thus the unblocked component coming out of the second ($SG_{\hat{x}}$) apparatus of Fig 1.3c is to be regarded as a superposition of S_z + and S_z – in the sense of equation (1). It is for this reason that two components emerge from the third ($SG_{\hat{z}}$) apparatus.

Applying this with the analogy of circularly polarized light, we see that if we are allowed to make the coefficients preceding base kets complex, there is no difficulty in accommodating the S_y ± atoms in our vector space formalism:

$$\left|S_y;-\right\rangle \overset{?}{=} \frac{1}{\sqrt{2}}\left|S_z;+\right\rangle + \frac{1}{\sqrt{2}}\left|S_z;-\right\rangle ------------(3)$$

We thus see that the two-dimensional vector space needed to describe the spin states of silver atoms must be a complex vector space; an arbitrary vector in the vector space is written as a linear combination of the base vectors $\left|S_z\ ;\pm\right\rangle$ with, in general, complex coefficients. The fact that the necessity of complex numbers is already apparent in such an elementary example is rather remarkable.

1.3 Operators in Quantum mechanics:

An operator is a rule or an instruction which transforms a function into another function. Liner operators play a very important role in quantum mechanics. If $\hat{Q}$ is an operator and f(x) is an arbitrary function then the action of $\hat{Q}$ on f(x) is represented as

$$\hat{Q}f(x) = \lambda g(x) --------------(1)$$

Where g(x) is another function and λ is constant. A linear operator is one which satisfies the following two conditions:

$$\hat{Q}(f_1 + f_2 + --)\hat{Q}f_1 + \hat{Q}f_2 + --------------(2)$$

$$\hat{Q}(cf) = c\hat{Q}f \quad where\ \ c\ \ is\, an\ arbitary\, constant$$

Algebra of Operators:

(i) The sum and difference of two operators $\hat{P}\ and\ \hat{Q}$ are defined by equations

$$\left(\hat{P} + \hat{Q}\right) f(x) = \hat{P}f(x) + \hat{Q}f(x)$$

$$\left(\hat{P} - \hat{Q}\right) f(x) = \hat{P}f(x) - \hat{Q}f(x)$$

(ii) The product of two operators $\hat{P}\ and\, \hat{Q}$ is defined by equation

$$\hat{P}\hat{Q}f(x) = \hat{P}\left[\hat{Q}f(x)\right]$$

In above equation we first operate on f(x) with the operator on the right of the operator product and then we take the resulting function and operate on it with the operator on the left of the operator product

(iii) The operators are said to be equal if

$$\hat{P}f(x) = \hat{Q}f(x)$$

(iv) The operator $\hat{I}$ (multiplication by 1) is the unit operator.

(v) The operator $\hat{O}$ (multiplication by 0) is the null operator.

(vi) The square of an operator is defined as the product of the operator with itself.

$$\hat{Q}^2 = \hat{Q}\hat{Q}$$

The nth power of an operator is defined to mean applying the operator n times in succession.

(vii) Operators obey associative law of multiplication

$$\hat{P}(\hat{Q}\hat{R}) = (\hat{P}\hat{Q})\hat{R}$$

An important difference operator algebra and ordinary algebra is that numbers obey commutative law of multiplication but operators do not necessarily do so. That is $\hat{P}\hat{Q} = \hat{Q}\hat{P}$ are not necessarily equal operators.

(viii) We defined the commutator $\left[\hat{P}, \hat{Q}\right]$ of operator $\hat{P}\, and\, \hat{Q}$ as operator $\hat{P}\hat{Q} - \hat{Q}\hat{P}$

$$\left[\hat{P}, \hat{Q}\right] = \hat{P}\hat{Q} - \hat{Q}\hat{P}$$

If $\hat{P}\hat{Q} - \hat{Q}\hat{P}$ the $\left[\hat{P}, \hat{Q}\right]$=0 and we say that $\hat{P}\ and\ \hat{Q}$ commute.

Operators of some Dynamical variables:

The wave function of a free particle moving in three dimensional spaces is given by

$$\psi = (x, y, z, t) = A\mathrm{e}^{\left\{-\frac{i}{\hbar}\left(Et - p_x x - p_y y - p_z z\right)\right\}} ------(4)$$

Partial derivative of ψ *with respect to x is*

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p_x \psi \ \ or \ -i\hbar \frac{\partial \psi}{\partial x} = p_x \psi$$

$$-i\hbar \frac{\partial \psi}{\partial y} = p_y \psi$$

$$-i\hbar \frac{\partial \psi}{\partial z} = p_z \psi$$

similarly,

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi -------(5)$$

A close look at the above equation reveals that the dynamical variables p_x, p_y, p_z *and* E are in some sense related to the differential operator $-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}\ and\ \ i\hbar\frac{\partial}{\partial t}\ respectively.$

Let us list out few dynamical variables and their corresponding operators:

p_x	$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$
p_y	$\hat{P}_y = -i\hbar \frac{\partial}{\partial y}$
p_z	$\hat{P}_z = -i\hbar \frac{\partial}{\partial z}$
p	$\hat{P} = -i\hbar\nabla$
E	$\hat{E} = i\hbar \frac{\partial}{\partial t}$
$Kinetic\, enrgy\, T = \frac{p^2}{2m}$	$\hat{T} = \frac{\hbar^2}{2m}\nabla^2$

The Hamiltonian (Total Energy) function of a mechanical system is given by;

$$H = \frac{p^2}{2m} + V$$

Its corresponding operator is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V -------(6)$$

For a conservative system the total energy is represented by the Hamiltonian function H expressed in terms of the position coordinates and conjugate momenta. Hence the energy operator is given by

$$\hat{H} \rightarrow -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}\; and\;\; not\;\;\; i\hbar\frac{\partial}{\partial t}$$

There is no operator for time.

In view of the equation (5), the time independent Schrödinger's equation can be written as

$$\hat{H}\psi = E\psi --------(7)$$

$$or\; -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi -----------(8)$$

which is an eigen value equation.

Angular momentum operator: In classical mechanics the angular momentum of a particle is given by

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_x = yp_z - zp_y, L_y = zp_x - xp_z, L_z = xp_y - yp_x$$

The operators corresponding to these variables are

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial x} \right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) ------------(9)$$

Notice the kind of symmetry in the expression for operator L_x. By carrying a cyclic permutation of *x, y, z* (i.e., replacing *x* by *y, y* by *z, z* by *x*) we can get operator of $\hat{L}_y$ *and* $\hat{L}_z$.

The Eigen value equation:

In general, each physical quantity is represented by a linear operator and for each operator one can set up an equation of the type

$$\hat{Q}u_q = qu_q$$

i.e., the effect of the operator is to multiply the function u_q by constant factor q. is an Eigen value equation. The solutions of above equation satisfying the set of conditions can be found not for all values but for selected values of parameter q. These special values of the parameter q are called the Eigen (characteristic) values of the operator $\hat{Q}$ and the functions u_q which satisfy the above equation are called the Eigen (characteristic) functions of the operator.

When a system is in an eigenstate u_q of $\hat{Q}$ the dynamical variables Q has a definite value equal to the Eigen value q. That is the uncertainty in the value of Q is zero if the system is in one the Eigen states of $\hat{Q}$ and the physical quantity Q is said to be quantized. The meaning of equation (3.7.1) is that if the system is in the eigen state u_q the measurement of the quantity Q will yield only one number q . The set of all Eigen values of $\hat{Q}$ forms a spectrum called eigen value spectrum. The spectrum may be discrete or continuous or partly discrete and partly continuous. If there exists only one Eigen function belonging to a given eigen value is said to be non –degenerate. It may happen that several Eigen functions may belong to a single eigen value. Then this eigen value is said to be degenerate. if u_q and v_q belong to the same eigen value q , then their linear combination $c_1u_q+c_2v_q$, for all values of c_1 and c_2 is also an eigen function belonging to the same eigen value.

$$\hat{Q}\left(c_1u_q+c_2v_q\right)=c_1\hat{Q}u_q+c_2\hat{Q}v_q=q(c_1u_q+c_2v_q)$$

Thus a degenerate eigen value corresponding to an number of eigen function the totality of eigen functions belonging to a degenerate eigen value forms a linear space called eigen space. The set of all eigen functions belonging to a given degenerate eigen value is closed under linear combination. This implies that any linear combination of members of the set of eigen functions it is always possible to choose a subset of linearly independent eigen functions say u_{q1} , $u_{q2}\ldots\ldots u_{qr}$ such that any eigen function belonging to the eigen value q can be expressed uniquely as linear combination of the type $(c_1u_{q1}+c_2u_{q2}+\ldots\ldots\ldots..+c_ru_{qr})$ with suitable co efficients c_1, $c_2\ldots.c_r$.

The set of independent function $u_{q1},u_{q2}\ldots\ldots\ldots u_{qr}$ is said to span the linear space and this set of functions is said to form the basis functions of the space. The number r is characteristic of the space. This means that out of infinite number of eigen functions belonging to a given degenerate eigen value there exists only a definite number say r of linearly independent functions. This number r is called the degree of degeneracy and the eigen value is said to be r-fold degenerate

Operators simplified:

Operators

An operator on a linear vector space defines a relationship between two vectors

Ex- $\hat{A}X=Y$

Operators

An operator on a linear vector space defines a relationship between two vectors

Ex- $\hat{A}X=Y$

If $\hat{A}$ is a rotation operator it rotates the vector X to result in the vector Y. $\hat{A}$ has a meaning only with reference to a set of vectors. The space on which $\hat{A}$ is defined i.e., set of vectors X for which $\hat{A}$ has meaning is called the domain of $\hat{A}$. The set of vectors Y which can be expressed as Y= $\hat{A}$X is called the range of $\hat{A}$. In a linear vector space if X_1 and X_2 are in the domain of $\hat{A}$ then $(c_1x_1+c_2x_2)$ is also in domain of $\hat{A}$.

An operator $\hat{A}$ is said to be linear if

$$\hat{A}\,(C_1X_1+C_2X_2)=C_1(\hat{A}X_1)+C_2(\hat{A}X_2)$$

Is anti linear if

$$\hat{A}\left(C_1X_1+C_2X_2\right)=C_1^*\left(\hat{A}X_1\right)+C_2^*\left(\hat{A}X_2\right)$$

Ex- differential operator d/dx is a linear operator

$$\frac{d}{dx}\left[C_1 f_1(x)+C_2 f_2(x)\right]=C_1\frac{df_1}{dx}+C_2\frac{df_2}{dx}$$

$$Squaring\ in\ a\ non-linear\ operator$$

$$Sq(C_1X_1+C_2X_2)\neq SqC_1X_1+SqC_2X_2$$

$$Null\ operator: \hat{O}X=0$$

$$Unity\ opertor: \hat{I}X=X\quad or\ \hat{I}X=X$$

$$equality: \hat{A}=\hat{B}\ if\ \hat{A}X=\hat{B}X$$

$$\hat{A}>\hat{B}\quad if\ (X,\hat{A}X)>(X,\ \hat{B}X)$$

$$Sum: \hat{C}=\hat{A}+\hat{B}\ \ if\ \hat{C}X=\hat{A}X+\hat{B}X$$

$$\Pr oduct: \hat{C}=\hat{A}\hat{B}\quad if\ \ \hat{C}X=\hat{A}(\hat{B}X)$$

$$In\ general\ \hat{A}\,\&\,\hat{B}\ do\ not\ commute\ i.e.,\hat{A}\hat{B}=\hat{B}\,\hat{A}$$

$$Example:-consider\ \hat{A}\equiv x\ \ \&\ \hat{B}\equiv\frac{d}{dx}$$

$$Then\ \ \hat{A}\hat{B}f(x)=x\frac{df}{dx}$$

$$\hat{B}\hat{A}f(x)=\frac{d}{dx}xf(x)=\frac{dx}{dx}f+x\frac{df}{dx}=f+x\frac{df}{dx}$$

$$i,e\ \hat{B}\hat{A}f(x)=f+\hat{A}\hat{B}f(x)=(1+\hat{A}\hat{B})f$$

$$i.e(\hat{A}\hat{B}-\hat{B}\hat{A})\ f(x)=-\hat{1}f(x)$$

$$i.e\ x\frac{d}{dx}-\frac{d}{dx}x=-\hat{1}$$

$$or\ \frac{d}{dx}x-x\frac{d}{dx}=\hat{1}$$

$$Power: \hat{A}^2=\hat{A}\hat{A};\ \hat{A}^2X=\hat{A}(\hat{A}X)$$

$$\hat{A}^n=\hat{A}\hat{A}^{n-1}=\hat{A}\hat{A}\hat{A}-----\hat{A}(n\ factors)$$

$$Inverse: If\ \ \hat{A}\hat{B}=\hat{B}\hat{A}=\hat{1}\ \ then\ they\ are\ said\ to\ be\ receprocal\ of\ each\ other\ i.e.,\hat{B}=\hat{A}^{-1}$$

An operator for which an inverse exists is said to be non singular where as one for which no inverse exits is called singular

$$\left(\hat{A}\hat{B}\hat{C}\right)^{-1} = \hat{C}^{-1}\hat{B}^{-1}\hat{A}^{-1}$$

Function : function of an operator can be formed by combining the operations of addition and multiplication

i.e., $\hat{F} \equiv a\frac{d^2}{dx^2} + b\frac{d}{dx} + c\hat{1}$

is a function of the differential operator $\frac{d}{dx}$.

Function of a liner operator is a linear operator i.e.,

$$\hat{F}\left[c_1 f_1(x) + c_2 f_2(x)\right] = c_1(\hat{F}f_1) + c_2(\hat{F}f)$$

Eigen values and Eigen vectors of an operator:

$We\,have\,\hat{A}X = Y$

But there may be some vector X with the property $\hat{A}X = \alpha X$ where α is scalar. Then X is called an eigen vector (eigen function) of $\hat{A}$ belonging to the eigen value α .The equation is called as eigen value equation for $\hat{A}$.

In general, a linear operator will have several eigenvalues and eigen vectors.

i.e $\hat{A}X_k = \alpha_k X_k$

The set $\{\alpha_k\}$ *of all eigen values taken together consistute the spectrum of the operator*

The eigen values may be discrete, continuous or partly discrete and partly continuous. An eigen vector belongs to only one eigen value.

But several linearly independent eigen vectors may belong to the same eigen value. In this case the eigen value is said to be degenerate, and the number of linear independent eigen vectors is called the **degree of degeneracy.**

In general, a linear operator will have several eigen values and eigen vectors.

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The set $\{\alpha_K\}$ of all eigen values taken together constitute the spectrum of the operator. The eigen values may be discrete, continuous or party discrete or partly continuous.

An eigen vector belongs to only one eigen value. But several linear independent eigen vectors may belong to the same eigen value. In this case the eigen value is said to be degenerate. And the number of linearly independent eigen vectors is called the degree of degeneracy.

Ex- consider the operator $\frac{-d^2}{dx^2}$

We have the eigen value equation $\frac{-d^2}{dx^2}\phi(x) = E\phi(x)$

$$i.e\left(-\frac{d^2}{dx^2} - E\right)\phi(x) = 0$$

The two linearly independent eigen vectors for this case are:

$$\phi_p(x) = e^{ipx} \;\; and \quad \phi_{-p}(x) = e^{-ipx} \;\; where\, P^2 = E.$$

Here both the eigen vectors belong to same eigen value E. Hence E is 2 fold degenerate. If p is continuous, then the eigen value is continuous.

Eigen value of the square of an operator is the square of the eigen value of the operator.

If $\hat{A}X = \alpha X ; \hat{A}^2 X = \hat{A}(\hat{A}X) = \hat{A}(\alpha X) = \alpha(\hat{A}X) = \alpha^2 X$

<u>Hermitian operator :</u>

An operator $\hat{A}$ is said to be Hermitian or self adjoint if

$$\hat{A} = \hat{A}^\dagger$$

$$\alpha\; anti-Hermitian \;\; if \;\; \hat{A} = -\hat{A}^\dagger$$

Properties of Hermitian operators:

1) The eigen values are real.
2) Eigen vectors belonging to different eigen values are orthogonal.
3) Set of all eigen vectors of a bounded Hermitian operator forms a complete set.

Unitary operator:

A linear operator $\hat{U}$ is unitary if it preserves the Hermitian character of an operator under a similarity transformation.

Similarity transformation of an operator $\hat{A}$ by a non – singular operator $\hat{S}$ is defined as $\hat{A} \rightarrow \hat{A}' = \hat{S}\hat{A}\hat{S}^{-1}$.

Thus the condition for $\hat{U}$ to be unitary is that ,

$$\left(\hat{U}\hat{A}\hat{U}^{-1}\right)^{\dagger} = \hat{U}\hat{A}\hat{U}^{-1}$$

Where $\hat{A}^{\dagger} = \hat{A}$

1.4 Bra and Ket notation for vectors:

Consider the scalar product (X,Y). Here we have a prefactor and a postfactor. Thus we have a space of post factors. A vector in the prefactor space is denoted by a bra {< | } and a vector in the post factor space is denoted by a ket | > . Thus X and Y in (X,Y) can be written as $\langle x | and | y \rangle$ respectively and scalar product of Y by X as $\langle X | Y \rangle$.

i.e $(X,Y) \equiv \langle X | Y \rangle = \langle Y | X \rangle^*$

Thus prefactor space is called as bra-space and post factor space is called as ket space.

Also we have $| X \rangle^* = \langle X | \; and \, \langle Y | = | Y \rangle^*$.

Thus the two spaces are not independent of each other. They are said to be dual to each other. Or they are said to have dual correspondence. Every vector in one space has its image in the other space.

Ket space	Bra space
$\vert X \rangle$	$\langle X \vert$
$c \vert X \rangle$	$\langle X \vert C^*$
$\vert Z \rangle = \vert X \rangle + \vert Y \rangle$	$\langle Y \vert + \langle X \vert = \langle Z \vert$
$\vert Y \rangle = \hat{A} \vert X \rangle$	$\langle X \vert \bar{\hat{A}} = \langle Y \vert$

Here we have:

Orthonormality condition; $\langle u_i | u_j \rangle = \delta_{ij}$

Completeness condition: $\sum |u_j\rangle\langle u_j| = \hat{1}$

Projection operator; $\hat{\pi}_j = |u_j\rangle\langle u_j|$

Matrix representation theory:

Representation theory:

Consider an orthogonal basis $\left[|u_j\rangle\right]_N$ in an N-dimensional space. Any vector in this space can be expanded in terms of the vector $|u_j\rangle$

Thus, if $|X\rangle$ *and* $|Y\rangle$ are some arbitrary vectors,

We have

$$|X\rangle = \sum_{j=1}^{N} x_j |u_j\rangle$$

$$|Y\rangle = \sum_{j=1}^{N} y_j |u_j\rangle$$

Consider a vector $|Z\rangle$ *such that*

$$|Z\rangle = a|X\rangle + b|Y\rangle \qquad with\, |Z\rangle = \sum_{j=1}^{N} z_j |u_j\rangle$$

$$then\ Z_j = ax_j + by_j$$

$$and\ \langle X|Y\rangle = \sum_{j=1}^{N} x^*{}_j y_j$$

Thus in place of abstract vectors $|X\rangle, |Y\rangle$ one can use their ordered expansion co efficients or components.

$$[x] \equiv [x_1, x_2, \ldots\ldots\ldots\ldots\ldots x_N]$$
$$and\, [y] \equiv [y_{1,} y_{2,} \ldots\ldots\ldots\ldots y_N]$$

They are called as the representation of the vectors.

Thus we can write,

[Z]=a[x] + b[y]

Or $[Z_1,Z_2$-------------$Z_N]=[ax_1+by_1;ax_2+by_2$…………$ax_N + by_N]$

This representation depends on the basis. Change of basis will change the representatives also. But with respect to a given basis, the representation [x] corresponding to $\left|X\right\rangle$ is unique.

Thus we say that the $\left|X\right\rangle$ is represented by [x] in the representation defined by the basis $\left[\left|u_j\right\rangle\right]_N$.

The basis vectors themselves are represented by $[u_1]$, $[u_2]$-----------$[u_N]$

Where
$$\begin{aligned}&[u_1]\equiv[1,0,0........................0]\\&[u_2]\equiv[0,1,0........................0]\\&\vdots\\&[u_N]\equiv[0,0,0,.....................1]\end{aligned}$$

The representative [x] of a ket vector $\left|X\right\rangle$ can be written in the form of a column matrix x;

$$i.e.,\left|X\right\rangle\to[X]\to x\equiv\begin{bmatrix}x_1\\x_2\\x_N\end{bmatrix}$$

whereas representative of the bra vector $\left\langle X\right|$ is represented by a row matrix;

$$\left\langle X\right|\to x^*\equiv[x_1^*,x_2^*...........x_N^*]$$

Then we have vector addition; Z=ax+by and scalar product; $x^\dagger y$ matrix product .

The unit vector are represented by

$$u_1=\begin{bmatrix}1\\0\\0\\.\\.\\0\end{bmatrix},u_2=\begin{bmatrix}0\\1\\0\\.\\.\\0\end{bmatrix}.............................u_N=\begin{bmatrix}0\\0\\0\\.\\.\\1\end{bmatrix}$$

Then we have

Orthonormality condition $\langle u_i | u_j \rangle \rightarrow u_i^\dagger u_j = \delta_{ij}$

Completeness relation (condition) $\sum_j |u_j\rangle\langle u_j| = \sum_j u_j u_j^\dagger = I$

The operator equation $\hat{A}|X\rangle = |Y\rangle$

Is represented by the matrix equation Ax = y

Since both x and y are (Nx1) matrices, A must be an (N X N) matrix. Thus an operator in an N-dimensional space is represented by a square matrix of the order N.

The properties of the linear operators thus follow from the properties of the square matrices.

This scheme of representing vectors and operators by matrices is called as Matrix representation.

Matrix elements of $\hat{A}$:

Consider the equation $|Y\rangle = \hat{A}|X\rangle$

Expanding $|Y\rangle$ *and* $|X\rangle$ *in terms of unit vectors* $|u_i\rangle$

$$we\,get: \sum_{i=1}^{N} y_i |u_i\rangle = \hat{A}\sum_{K=1}^{N} x_k |u_k\rangle = \sum_{k=1}^{N} x_k \hat{A}|u_k\rangle$$

Taking the scalar product of equation with $|u_j\rangle$ *we have*

$$\sum_{i=1}^{N} y_i |u_i\rangle\langle u_j| = \sum_{k=1}^{N} \langle u_j|\hat{A}|u_k\rangle x_k$$

$$y_i = \sum_{k=1}^{N} \langle u_j|\hat{A}|u_k\rangle x_k \text{ -----------(1)}$$

$$But\,we\,have\; y_j = A_{jk} x_k \text{ ----------(2)}$$

comparing (1) & (2) *we see that*

$$A_{jk} \equiv \langle u_j|\hat{A}|u_k\rangle \text{ --------------(3)}$$

i.e., the $\mathrm{j_k^{th}}$ matrix element of the matrix A that represents the operator $\hat{A}$ in the representation defined by the basis $\left[|u_j\rangle\right]_N$ is the scalar product of the vector $\hat{A}|u_k\rangle$ by the vector $|u_j\rangle$.

If $\hat{A}$ is one of the complete set of commuting operator that define the basis then

$$\hat{A}|u_k\rangle = \alpha_k |u_k\rangle \text{ ----------(4)}$$

$$So\,that\; A_{jk} = \langle u_j|u_k\rangle \alpha_k \text{ -----(5)}$$

$$i.e\; A_{jk} = \delta_{ij}\alpha_k \text{ ------------(6)}$$

Thus A is diagonal. That is, an operator is represented by a diagonal matrix in a representation defined by its own eigen vectors (Eigen values of a diagonal matrix are its diagonal elements)

Thus we have

$x' = (U')^{\dagger} U x = S^{\dagger} x$

$i.e.,\ x' = s^{\dagger} x \quad and \quad x = Sx'$

$Consider\ linear\ transformation\ |Y\rangle = \hat{A}|X\rangle$

$which\ is\ represented\ by\ the\ matrix\ equation\ \ y = Ax\ and\ y' = A'x' ------(4)$

$in\ representations\ \ U\ and\ \ U'\ respectively$

$From\ (2)\ \ we\ \ have\ \ \ x = Sx^{1}\ and\ y = Sy'$

$$sy' = ASx'$$

Using this (3) becomes $or\ y' = (S^{\dagger} AS)x' ----------(5)$

$$Comparing\ (4)\ and\ (5)\ we\ get;\ A' = S^{\dagger} AS\ ------(6)$$

Equations (1),(2), and (6) represent the transformation laws for vectors and operators under change of basis. Thus change of basis corresponds to a unitary transform it can be seen that $U'A^{1}U'^{\dagger} = UAU^{\dagger}$ i.e., product $(UAU^{\dagger})$ is invariant under change of basis.

1.6 Let us sum up:

Classical mechanics fails to explain several observed phenomena. Though it explains everything that is exhibited by macroscopic particles, it fails to do so when applied to the case of micro-particles. Hence understanding the physics in the light of quantum mechanics plays a vital role.

Micro-particles such as electrons exhibit matter waves. They even exhibit the existence of wave packets. The Stern-Gerlach experiment provides concrete proof for the existence of “Spin” for the Quantum-mechanical particle. The sequential Stern-Gerlach experiment shows that there are spin states which can be represented as linear combinations of each other.

Operators play an important role in quantum mechanics. For every physical observable there exists an operator which when operates on the state function, gives the various values of that observable.

The state vectors can be represented using Bra and Ket notations. The matrix representation theory shows that there is a correspondence with the linear vector space.

1.7 Key words:

The Stern-Gerlach experiment
Operators
Linear vector space
Ket and Bra notation of vectors

Matrix representation theory

1.8 Problems

Ex-1 obtain expression for the following operators

$$(i)\left(\frac{d}{dx}+x\right)^2,(ii)\left(x\frac{d}{dx}\right)^2,(iii)\left(\frac{d}{dx}(x)\right)^2$$

$So\ln:$

$$(i)\left(\frac{d}{dx}+x\right)^2\psi=\left(\frac{d}{dx}+x\right)\left(\frac{d}{dx}+x\right)\psi$$

$$=\left(\frac{d}{dx}+x\right)\left(\frac{d\psi}{dx}+x\psi\right)$$

$$=\frac{d^2\psi}{dx^2}+2x\frac{d\psi}{dx}+(x^2+1)\psi$$

$$\therefore \qquad \left(\frac{d}{dx}+x\right)^2=\frac{d^2}{dx^2}+2x\frac{d}{dx}+x^2+1$$

$$(ii)\left(x\frac{d}{dx}\right)^2\psi=\left(x\frac{d}{dx}\right)\left(x\frac{d}{dx}\right)\psi=\left(x\frac{d}{dx}\right)\left(x\frac{d\psi}{dx}\right)$$

$$=x\left(\frac{d\psi}{dx}+x\frac{d^2\psi}{dx^2}\right)$$

$$=x\frac{d\psi}{dx}+x^2\frac{d^2\psi}{dx^2}$$

$$\left(x\frac{d}{dx}\right)^2 = x^2\frac{d^2}{dx^2} + x\frac{d}{dx}$$

$$(iii)\left(\frac{d}{dx}x\right)^2\psi = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\right)\psi = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\psi\right)$$

$$= \frac{d}{dx}x\left(\psi + x\frac{d\psi}{dx}\right)$$

$$= \frac{d}{dx}\left(x\psi + x^2\frac{d\psi}{dx}\right)$$

$$= \psi + x\frac{d\psi}{dx} + 2x\frac{d\psi}{dx} + x^2\frac{d^2\psi}{dx^2}$$

$$\left(\frac{d}{dx}x\right)^2 = x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1$$

Ex-2: Find the value of constant A which makes the function exp(- λ x^2) an eigen function of the operator $\left(\frac{d^2}{dx^2} - Ax^2\right)$. What is the corresponding eigen value?

Soln: Eigen value equation of the given operator is

$$\left(\frac{d^2}{dx^2} - Ax^2\right)\mathrm{e}^{(-\lambda x^2)} = q\,\mathrm{e}^{(-\lambda x^2)},\ q\ \ is\ \ eigen value$$

$$(-2\lambda + 4\lambda^2 x^2 - Ax^2)\,\mathrm{e}^{(-\lambda x^2)} = q\,\mathrm{e}^{(-\lambda x^2)}$$

The function $\mathrm{e}^{(-\lambda x^2)}$ *will be an eigen function of the given operator if* $(4\lambda^2 x^2 - Ax^2 - 2\lambda)$ *is independant of x.That is the coefficient of* x^2 *must vanish. Thus,*

$$4\lambda^2 - A = 0 \quad or \quad A = 4\lambda^2$$

The expression for operator now becomes

$$\left(\frac{d}{dx^2} - 4\lambda^2 x^2\right)$$

The eigen value equation is

$$\left(\frac{d}{dx^2} - 4\lambda^2 x^2\right)\mathrm{e}^{(-\lambda x^2)} = q\,\mathrm{e}^{(-\lambda x^2)}\ \ where\, q\, is\, eigen\, value$$

$$= -2\lambda\,\mathrm{e}^{(-\lambda x^2)}$$

$\therefore -2\lambda$ *is the eigen value of the given operator*

Example -3

The vectors in a three dimensional complex vector space are defined by

$$\left|A\right\rangle = \begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} \left|B\right\rangle = \begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix}$$

$Let\, a = 6+5i$

$(a)\, Compute\;\; a\left|A\right\rangle, a\left|B\right\rangle, and\; a(\left|A\right\rangle + \left|B\right\rangle).Show\; that\;\; a(\left|A\right\rangle + \left|B\right\rangle) = a(\left|A\right\rangle + a\left|B\right\rangle).$

$(b)\, Find\; the\; inner\; products \left\langle A \mid B\right\rangle, \left\langle B \mid A\right\rangle$

(a)

$$a\left|A\right\rangle = (6+5i)\begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} = \begin{pmatrix} (6+5i)2 \\ (6+5i)(-7i) \\ (6+5i)1 \end{pmatrix} = \begin{pmatrix} 12+10i \\ 35-42i \\ 6+5i \end{pmatrix}$$

$$a\left|B\right\rangle = (6+5i)\begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix} = \begin{pmatrix} (6+5i)(1+3i) \\ (6+5i)4 \\ (6+5i)8 \end{pmatrix} = \begin{pmatrix} -9+23i \\ 24+20i \\ 48+40i \end{pmatrix}$$

$$\Rightarrow a\left|A\right\rangle + a\left|B\right\rangle = \begin{pmatrix} 12+10i \\ 35-42i \\ 6+5i \end{pmatrix} + \begin{pmatrix} -9+23i \\ 24+20i \\ 48+40i \end{pmatrix}$$

$$= \begin{pmatrix} 12+10i+(-9+23i) \\ 35-42i+(24+20i) \\ 6+5i+(48+40i) \end{pmatrix} = \begin{pmatrix} 3+33i \\ 59-22i \\ 54+45i \end{pmatrix}$$

$Now\, adding\; the\, vectors\;\; first, we\, have$

$$\left|A\right\rangle + \left|B\right\rangle = \begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} + \begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix} = \begin{pmatrix} 2+1+3i \\ -7i+4 \\ 1+8 \end{pmatrix} = \begin{pmatrix} 3+3i \\ 4-7i \\ 9 \end{pmatrix}$$

$$\Rightarrow a(\left|A\right\rangle + \left|B\right\rangle) = (6+5i)\begin{pmatrix} 3+3i \\ 4-7i \\ 9 \end{pmatrix} = \begin{pmatrix} (6+5i)(3+3i) \\ (6+5i)(4-7i) \\ (6+5i)9 \end{pmatrix}$$

$$= \begin{pmatrix} 18+15i+18i-15 \\ 24+20i-42i+35 \\ 54+45i \end{pmatrix} = \begin{pmatrix} 3+33i \\ 59-22i \\ 54+45i \end{pmatrix} = a\left|A\right\rangle + a\left|B\right\rangle$$

(b) First we compute $\left\langle A \mid B\right\rangle$. To form the dual vector of $\left|A\right\rangle$, we compute the complex conjugate of its elements and then transpose the result to form a row vector .

$$\left|A\right\rangle^* = \begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} = \begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} \Rightarrow \left|A\right\rangle = (2\ 7i\ 1)$$

and so the inner product is

$$\left\langle A\middle|B\right\rangle = (2\ 7i\ 1)\begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix} = 2(1+3i)+7i(4)+1(8) = 10+34i$$

Now we compute $\left\langle B\middle|A\right\rangle$*. The complex conjugate of* $\left|B\right\rangle$ *is given by*

$$\left|B\right\rangle^* = \begin{pmatrix} 1+3i \\ 4 \\ 8 \end{pmatrix}^* = \begin{pmatrix} 1-3i \\ 4 \\ 8 \end{pmatrix}$$

Now we transpose this to get dual vector

$$\left|B\right\rangle = (1-3i \quad 4 \quad 8)$$

and so the inner product is

$$\left\langle B\middle|A\right\rangle = (1-3i \quad 4 \quad 8)\begin{pmatrix} 2 \\ -7i \\ 1 \end{pmatrix} = (1-3i)(2)+(4)(-7i)+(8)(1) = 2-6i+8 = 10-34i$$

Notice that $\left\langle B\middle|A\right\rangle = \left\langle A\middle|B\right\rangle$ a result that holds in general for the inner product in a complex vector space. We now list this and other important properties of the inner product

1.9 Questions for self study:

1. Give an account of the failure of classical mechanics.
2. Discuss the sequential Stern-Gerlach experiment and comment on its results.
3. List out various operators used in Quantum mechanics.
4. Distinguish between ket space and bra space.
5. Give the matrix representation theory in quantum mechanics.

1.10 References for further study:

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Unit 2: Measurements, observables and the un-certainty relations, compatible and incompatible observables, change of basis.

Structure:

2.0 Objectives:

After studying this unit you will be able to understand the following aspects;

- Heisenberg uncertainty principle
- Compatible and incompatible observables
- Change of basis

2.1 Introduction:

The dual nature of matter and radiation requires profound changes in our concepts built on the basis of common sense and everyday experience. The formulation of classical mechanics implies that the position and momentum of a particle are assumed to have well defined values and can be determined simultaneously with perfect accuracy. But the 'wave-particle duality' compels us to abandon the idea of simultaneous determination of position and momentum with perfect accuracy. Whenever we do some measurement, there is always some uncertainty associated with it. This plays an important role in the understanding of Physics in the light of Quantum mechanics. Now let us move further in order to understand this idea of uncertainty principle.

2.2 Heisenberg's Uncertainty principle or Principle of indeterminacy:

In 1927 Werner Heisenberg, a German physicist, enunciated that *it is impossible to determine both position and momentum simultaneously with perfect accuracy. If* Δx *is the uncertainty in position and* Δp_x *is the uncertainty in the corresponding momentum then*

$$\Delta P_x . \Delta x \geq \hbar$$

Similarly if ΔE is the uncertainty in energy and Δt is uncertainty in time then

$$\Delta E . \Delta t \geq \hbar$$

It is evident that if we try to measure the position of particle with utmost accuracy i.e., $\Delta x \to 0$, the corresponding uncertainty in momentum becomes very large i.e., $\Delta P_x \to \infty$ and vice versa.

Let us illustrate the above assertion. Consider a particle having well-defined momentum $P_x (= \hbar k)$. Such a particle has well defined k or λ and is represented by a sinusoidal (monochromatic wave) has no beginning and end i.e., it is infinitely long; its amplitude is constant for all values space co ordinates x and therefore the particle may be anywhere between $x = -\infty \ to \ +\infty$. Thus the position of the particle is completely uncertain $(\Delta x \to \infty)$.

Now consider a particle having well-defined position $(\Delta x \to 0)$. A wave packet having very small extension in space describes such a particle. Fourier's transform of this wave packet shows that it is formed by superposition of a very large number of waves having continuous distribution of k or λ within a large of Δk . Thus the uncertainty in k or p is very large $\left(\Delta k \to \infty\right)$

A particle with well-defined momentum p is described by a sinusoidal wave extending from $x = -\infty$ to $+\infty$. Here $\Delta p \to 0$ but $\Delta x \to \infty$

Fig. 2.1

Thus a particle with relatively small uncertainty in momentum has large uncertainty in position. A sinusoidal wave has well defined frequency and so is its energy$\left(E = \hbar\omega\right)$. A particle described this e wave also has well defined energy E and therefore ΔE =0. In order to see the constancy of amplitude of such a sinusoidal wave which exits from $t = -\infty \; to \; +\infty$, we have to look for a very long time . Therefore the uncertainty in time is infinite$\left(\Delta t \to \infty\right)$.

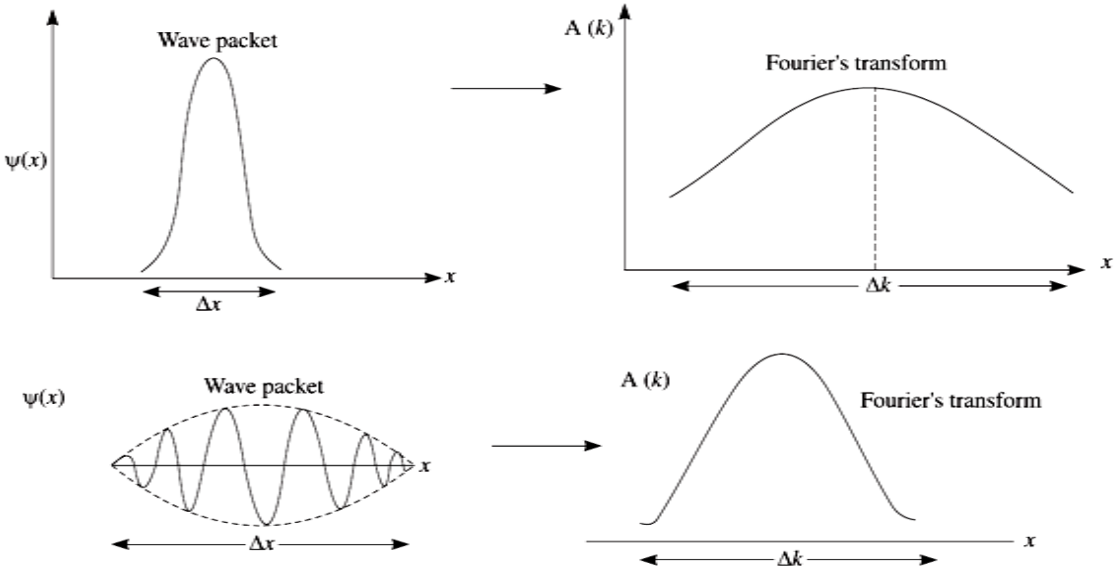

Fig 2.2 Some wave packets and their Fourier's transforms, $\Delta x \Delta k \simeq 1$

Consider a particle, which is described by a wave packet as shown in fig (2.8.2). The Fourier's transform of the wave packet is also shown adjacent to it. Let Δx be the spread of the wave packet in space and Δk the spread in propagation constant. It can be shown by standard mathematical technique that

$$\Delta x \Delta k \geq 1$$

Since $p = \hbar k$ and $\Delta p = \hbar \Delta k$ we have

$$\Delta Px \Delta x \geq \hbar$$

It should be carefully noted that the uncertainties in measurement of position and momentum are not because of inadequacies in our measuring instruments. Even with ideal instrument we can never in principle do better. This principle is the fundamental law of nature. The indeterminism is inherent in the very structure of matter. The momentum and position don't assume well-defined values simultaneously.

Notice that it is the smallness of Planck's constant that makes the uncertainty principle insignificant in macroscopic world. In microscopic world the consequences of uncertainty principle cannot be ignored.

2.3 Compatible and incompatible observables:

Two observed which can be measured simultaneously and precisely without influencing each other are called Compatible. The operators of such observable commute i.e $\left[\hat{P}, \hat{Q}\right] = 0$. On the other hand two observables are such that the determination of one observable introduces an uncertainty in the other they are called incompatible. The operators of incompatible observed do not commute. That is $\left[\hat{P}, \hat{Q}\right] \neq 0$

Assume that two physical quantities Q and R can simultaneously have definite values when the system is in a common state ψ_n. The wave function ψ_n of the state in which the quantity Q has a value q_n and the quantity R the value r_n must satisfy two equation simultaneously

$$\hat{Q}\psi_n = q_n \psi_n$$
$$\hat{R}\psi_n = r_n \psi_n$$

The product of operators is determined by the condition

$$\Pi \psi_n = \left(\hat{Q}\hat{R}\right)\psi_n = \hat{Q}\left(\hat{R}\psi_n\right) = q_n r_n \psi_n$$

Thus:

$$\left(\hat{R}\hat{Q}\right)\psi_n = \hat{R}\left(\hat{Q}\psi_n\right) = \hat{R}(q_n \psi_n) = r_n q_n \psi_n$$

Hence:

$$\Pi = \hat{Q}\hat{R} = \hat{R}\hat{Q}$$

$$\hat{Q}\hat{R} - \hat{R}\hat{Q} = 0$$

Thus **if two quantities can simultaneously have definite values then (*i*) their operators have common eigen functions and (*ii*) their operators commute.**

In general, the product of operators is non-commuting *i.e.*,

$$\hat{Q}\hat{R} \neq \hat{R}\hat{Q}$$

This can be verified taking the example of the operators

$$\hat{Q} = \frac{\partial}{\partial x} \ \ and \ \ \hat{R} = x$$

$$\left(\hat{Q}\hat{R}\right)\psi = \frac{\partial}{\partial x}\left(x\psi\right) = x\frac{\partial \psi}{\partial x} + \psi$$

$$\left(\hat{R}\hat{Q}\right)\psi = x\frac{\partial \psi}{\partial x}$$

Operators $\hat{Q}$ and $\hat{R}$ for which the condition

$$\hat{Q}\hat{R} = \hat{R}\hat{Q}$$

is observed are said to be *commutative operators*. If this condition is not satisfied, the operators are said to be non-commutative. Operators, which satisfy the condition

$$\hat{Q}\hat{R} = -\hat{R}\hat{Q}$$

are called *anti-commutative operators*.

2.4 Change of basis:

We know that the matrices representing vectors and operators on the basis (representation). If the basis (or representation) is changed, the matrices are also changed for the same set of vectors and operators. Thus we have to find a relationship between matrices which represent the same set of vectors and operators in different representations (bases).

Let $[u_i\rangle]_N$ & $[u'_i\rangle]_N$ be two orthonormal bases in a Hilbert space. Since both sets are complete, vectors of one set can be expanded in terms of vectors in the other set.

$\left| u'_j \right\rangle = \sum_{k=1}^{N} \left| u_k \right\rangle s_{kj}$ with j=1,2,3……………………..N

S$_{kj}$ are the expansion co-efficients, which are the matrix elements of an (N X N) matrix S which represents transformation from the representation $[|u_i\rangle]$ to $[|u'_i\rangle]$

i.e., S$_{ij}$ = $\left\langle u_i \middle| u'_j \right\rangle$

It can be seen that $S^{\dagger}S = I = SS^{\dagger}$ and $S = U^{\dagger}U'$

The expansion of an arbitrary vector $\left| X \right\rangle$ in terms of the basis vector is

$$\left| X \right\rangle = \sum_{i=1}^{N} x_i \,|u_i\rangle = \sum_{j=1}^{N} x'_j \,|u'_j\rangle$$
$$or \quad Ux = U'x'$$

Where x & x' are two column matrices representing $\left| X \right\rangle$ in representation of U&U' respectively.

Co ordinate representation:

$$\hat{x} = x; \hat{p}_x = -i\hbar \frac{d}{dx}$$

Momentum representation:

$$\hat{x} = i\hbar \frac{d}{dp_x}; \hat{P}_x = P_x$$

$$\& \left\langle P_x \middle| x \right\rangle = c\ e^{\{-\left(\frac{i}{\hbar}\right) P_x x\}}$$

Where c = c*= $\frac{1}{\sqrt{2\pi\hbar}}$

$$Also, \quad u_j(p) = (2\pi\hbar)^{\left(3/2\right)} \int u_j(r)\, \mathrm{e}^{\left\{\left(\frac{-i}{\hbar}\right) p.r\right\}}\, d^3 r$$

$$\& \quad u_j(r) = (2\pi\hbar)^{\left(-3/2\right)} \int u_j(p)\, \mathrm{e}^{\left\{\left(\frac{i}{\hbar}\right) p.r\right\}}\, d^3 p$$

Thus $u_j(p)$ and $u_j(r)$ are Fourier transforms of each other

Matrix elements $A_{jk} = \int u_j^*(r)\hat{A}(r)u_k(r)d^3r$

2.5 Let us sum up:

Simultaneous, precise measurement of position and momentum of a quantum-mechanical particle is not possible according to un-certainty principle. There is always some uncertainty associated with the measurement of any physical quantity. We have understood the implications of this principle. Also, we have understood differentiation between compatible and incompatible observables and also the manner in which change of basis is undertaken in the field of Quantum mechanics.

2.6 Key words

- Uncertainty
- Position
- Momentum
- Compatible observable
- Incompatible observable
- Basis

2.7 Problems:

Example 1. Show that the wavelength of electron accelerated through a potential difference V is given by

$$\lambda = \frac{h}{\sqrt{2me^{V}}} = \frac{12.3}{\sqrt{V(volt)}}\ \text{Å}$$

Solution. The kinetic energy of electron T=$\frac{p^2}{2m} = eV$

And $p = \sqrt{2mT} = \sqrt{2meV}$

Therefore $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mT}} = \frac{h}{\sqrt{2meV}}$

Substituting m = $9.1\text{x}10^{-31}$ kg, e =$1.6\text{x}10^{-19}$C, h = 6.6 x 10^{-34} Js, we have,

$$\lambda = \frac{12.3}{\sqrt{V}} X10^{-10} m = \frac{12.3}{\sqrt{V}} \mathring{A}$$

For other charged particles appropriate values of *m* and charged *q* should be substituted in the above equation.

Example-2 Obtain expression for the wavelength of a particle moving with relativistic speed.

Solution The relativistic momentum of a particle

$$p = \frac{m_0 v}{\sqrt{1 - v^2/c^2}}$$

$$\therefore \lambda = \frac{h}{p} - \frac{h(1 - v^2/c^2)^{1/2}}{m_0 v} = \frac{h}{m_0 c} \frac{\left(1 - v^2/c^2\right)^{1/2}}{(v/c)}$$

The momentum *p* of a relativistic particle can also be expressed as follows:

$$E^2 = p^2 c^2 + (m_o c^2)^2 = (T + m_0 c^2)^2$$

$$p = \frac{\sqrt{T(T + 2m_0 c^2)}}{c}$$

Hence $\lambda = h/p$

$$= \frac{hc}{\sqrt{T(T + 2m_0 c^2)}} = \frac{h}{\sqrt{2m_0 T}} \frac{1}{\sqrt{1 + T/2m_0 c^2}}$$

$$= \frac{h}{\sqrt{2m_0 T}} \left(1 + \frac{T}{2m_0 c^2}\right)^{-1/2}$$

If the particle under consideration is an electron accelerated through a potential difference of V volt, its de Broglie wavelength is given by

$$\lambda = \frac{h}{\sqrt{2m_0 eV}} \left(1 + \frac{eV}{2m_0 c^2}\right)^{-1/2}$$

Example-3 Find the de Broglie wavelength of (i) electron moving with velocity 1000 m/s (ii) an object of mass 100 gm moving with the same velocity.

Solution (i) de Broglie wavelength of electron

$$\lambda = \frac{h}{mv} = \frac{6.63X10^{-34}\,Js}{\left(9.1X10^{-31}kg\right)\left(1000\,m/s\right)} = 7285X10^{-10}\,m$$

(ii) de Broglie wavelength of object

$$\lambda = \frac{h}{mv} = \frac{6.63X10^{-34}\,Js}{\left(0.1kg\right)\left(1000\,m/s\right)} = 8.63X10^{-36}\,m$$

Owing to extremely short wavelength of the object, its wave behavior cannot be demonstrated.

Example-4 An object has a speed of 10000 m/s accurate to 0.01%. With what fundamental accuracy can we locate its position if the object is (a) a bullet of mass of 0.05kg (b) an electron?

Solution momentum of bullet $p = mv = (0.05kg)\ (1000m/s) = 50kg\ m/s$

Uncertainty in momentum $\Delta p = 50X\,0.0001 = 5X10^{-3}kg$ m/s

Minimum uncertainty in position

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.054X10^{-34}\,Js}{5X10^{-3}Kg\,m/s} = 2.1X10^{-31}m$$

Momentum of electron

$P = mv = (9.1\ X\ 10^{-31}\ kg)(1000\ m/s) = 9.1\ X\ 10^{-28}\ kg\ m/s$

Uncertainty in momentum

$\Delta p =$ 9.1 x 10^{-28} x 0.0001= 9.1 x 10^{-32} kg m/s

Uncertainty in position

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.054X10^{-34}\,Js}{9.1X10^{-32}kg\,m/s} = 0.115m$$

The uncertainty in bullet’s position is so small that it is far beyond the possibility of measurement. Thus, we see that for macroscopic objects like bullet the uncertainty principle practically sets no limits to the measurement of conjugate dynamic variables position and momentum. For electron uncertainty in its position is very large, nearly 10^7 times the dimensions of atom. Thus for microscopic objects such as electron the uncertainty in their position is significant and cannot be overlooked.

Example-5 The position and momentum of 1 keV electrons are measured simultaneously. If its position is located within 1Å what is the percentage uncertainty in its momentum? Is this consistent with the binding energy of electron in atom?

Solution The uncertainty in position of electron

$$\Delta p \geq \frac{h}{\Delta x} = \frac{1.054 X 10^{-34} \, Js}{10^{-10} \, m} = 1.054 X 10^{-24} \, kg \, m/s$$

The momentum of electron inside the atom is at least equal to p=1.054x 10^{-24} kg m/s the corresponding kinetic energy is

$$T = \frac{p^2}{2m} = \frac{(1.054 X 10^{-24} \, kg \, m/s)^2}{2 X 9.1 X 10^{-31} \, kg} = 0.061 X 10^{-17} \, J = 3.8 eV$$

The ionization potential of atoms is of this order and hence the uncertainty in momentum is consistence with the binding energy of electrons in atoms.

2.8 Questions for self study

1. Write a note on Heisenberg’s uncertainty principle.
2. List out various uncertainty relations that are encountered.
3. State and prove Heisenberg’s uncertainty principle.
4. Distinguish between compatible and incompatible observables.
5. Describe the formalism of change of basis.

2.9 References for further study

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UNIT 3: Position, momentum and translation. Momentum as generator of translations. The canonical commutation relations, wave functions in position and momentum space.

Structure:

3.0 Objectives:

After studying this unit you will be able to understand the following aspects;

- Position, Momentum and Translation.
- Momentum as generator of translations.
- The canonical commutation relations.
- Wave functions in position and momentum space.

3.1 Introduction:

Momentum operator:

In quantum mechanics, momentum (like all other physical variables) is defined as an operator, which "acts on" or pre-multiplies the wave function $\psi(r, t)$ to extract the momentum eigenvalue from the wavefunction: the momentum vector a particle would have when measured in an experiment. The momentum operator is an example of a differential operator.

At the time quantum mechanics was developed in the 1920s, the momentum operator was found by many theoretical physicists, including Neil's Bohr, Arnold Sommerfeld, Erwin Schrödinger, and Eugene Wigner.

Origin from De Broglie plane waves

The momentum and energy operators can be constructed in the following way.

In One dimension:

Starting in one dimension, using the plane wave solution to Schrödinger's equation:

$\psi = e^{i\left(kx-\omega t\right)}$ Starting in one dimension using the plane wave solution to Schrödinger's equation:

The first order partial derivative with respect to space is

$$\frac{\partial \psi}{\partial x} = ike^{i(kx-\omega t)} = ik\psi$$

By expressing k from the de-Broglie relation: $p = \hbar k$

The formula for the derivative of ψ becomes: $\frac{\partial \psi}{\partial x} = i\frac{p}{\hbar}\psi$

This suggests the operator equivalence: $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

Hence the momentum value p is a scalar factor, the momentum of the particle and the value that is measured, is the eigenvalue of the operator. Since the partial derivative is a linear operator, the momentum operator is also linear, and because any wavefunction can be expressed as a superposition of other states, when this momentum operator acts on the entire superimposed wave, it yields the momentum eigenvalues for each plane wave component, the momenta add to the total momentum of the superimposed wave.

In three dimensions:

The derivation in three dimensions is the same, except the gradient operator Del is used instead of one partial derivative. In three dimensions, the plane wave solution to Schrödinger's equation is: $\psi = e^{i(\vec{k}.\vec{r}-\omega t)}$

and the gradient is

$$\begin{aligned}\nabla\psi &= e_x\frac{\partial\psi}{\partial x}+e_y\frac{\partial\psi}{\partial y}+e_z\frac{\partial\psi}{\partial z}\\ &= ik_x\psi e_x+ik_y\psi e_y+ik_z\psi e_z\\ &= \frac{i}{\hbar}\left(p_xe_x+p_ye_y+p_ze_z\right)\psi\\ &= \frac{i}{\hbar}\hat{p}\psi\end{aligned}$$

where e_x, e_y, e_z are the unit vectors for the three spatial dimensions, hence

$$\hat{p}=-i\hbar\nabla$$

This momentum operator is in position space because the partial derivatives were taken with respect to the spatial variables.

Definition (position space)

For a single particle with no electric charge and no spin, the momentum operator can be written in the position basis as:

$$\hat{p}=-i\hbar\nabla$$

where ∇ is the gradient operator, ħ is the reduced Planck constant, and i is the imaginary unit.

In one spatial dimension this becomes:

$$\hat{p}=\hat{p}_x=-i\hbar\frac{\partial}{\partial x}$$

This is a commonly encountered form of the momentum operator, though not the most general one. For a charged particle q in an electromagnetic field, described by the scalar potential φ and vector potential A, the momentum operator must be replaced by:

$$\hat{p}=-i\hbar\nabla-q\vec{A}$$

Where the canonical momentum operator is the above momentum operator:

$$\hat{p} = -i\hbar\nabla$$

This is of course true for electrically neutral particles also, since the second term vanishes if q is zero and the original operator appears.

Fourier transform

One can show that the Fourier transform of the momentum in quantum mechanics is the position operator. The Fourier transform turns the momentum-basis into the position-basis. The following discussion uses the Bra-ket notation:

$$\left\langle x \,|\, \hat{p} \,|\, \psi \right\rangle = -i\hbar \frac{d}{dx}\psi(x)$$

The same applies for the Position operator in the momentum basis:

$$\left\langle p \,|\, \hat{x} \,|\, \psi \right\rangle = i\hbar \frac{d}{dp}\psi(p)$$

and other useful relations:

$$\left\langle p \,|\, \hat{x} \,|\, p' \right\rangle = i\hbar \frac{d}{dp}\delta(p - p')$$
$$\left\langle x \,|\, \hat{p} \,|\, x' \right\rangle = -i\hbar \frac{d}{dx}\delta(x - x')$$

where δ stands for Dirac's delta function.

Derivation from infinitesimal translations

The translation operator is denoted by T(ε), where ε represents the length of the translation. It satisfies the following identity:

$$T\left(\varepsilon\right)\left|\psi\right\rangle = \int dx T\left(\varepsilon\right)\left|x\right\rangle\left\langle x\middle|\psi\right\rangle$$

which becomes

$$\int dx \mid x+\varepsilon\rangle\left\langle x-\varepsilon\middle|\psi\right\rangle = \int dx \mid x\rangle\psi\left(x-\varepsilon\right)$$

Assuming the function ψ to be analytic (i.e., differentiable in some domain of the complex plane), one may expand in a Taylor series about *x*:

$$\psi\left(x-\varepsilon\right) = \psi(x) - \varepsilon\frac{d\psi}{dx}$$

Thus for infinitesimal values of ε:

$$T(\varepsilon) = 1 - \varepsilon\frac{d\psi}{dx} = 1 - \frac{i}{\hbar}\varepsilon\left(-i\hbar\frac{d}{dx}\right)$$

As it is known from classical mechanics, the momentum is the generator of translation, so the relation between translation and momentum operators is:

$$T\left(\varepsilon\right) = 1 - \frac{i}{\hbar}\varepsilon\hat{p}$$

Thus

$$\hat{p} = -i\hbar\frac{d}{dx}$$

3.2 COMMUTATOR:

The operator $\hat{Q}\hat{R} - \hat{R}\hat{Q}$ formed from the operators $\hat{Q}$ *and* $\hat{R}$ is called the '***commutator*** of the given operators' and is designated by the symbol $\left[\hat{Q},\hat{R}\right]$ i.e

The commutator of commuting operator is zero.

3.3 Commutation relation:

Linear operators obey following commutations rules:

$$\left[\hat{A},\hat{B}\right]=-\left[\hat{B},\hat{A}\right]$$

$$\left[\hat{A},\hat{B}\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]$$

$$\left[\hat{A}\hat{B},\hat{C}\right]=\left[\hat{A},\hat{C}\right]\hat{B}+\hat{A}\left[\hat{B},\hat{C}\right]$$

Some commutation relations of quantum mechanical operators:

1.$\left[\hat{x},\hat{y}\right]=\left[\hat{y},\hat{z}\right]=\left[\hat{z},\hat{x}\right]=0$

$$\left[\hat{x},\hat{y}\right]=\hat{x}\hat{y}-\hat{y}\hat{x}=xy-yx=0$$

2.$\left[\hat{x},\hat{p}_x\right]=\left[\hat{y},\hat{p}_y\right]=\left[\hat{z},\hat{p}_y\right]=i\hbar$

$$\left[\hat{x},\hat{p}_x\right]\psi=\left(\hat{x}\hat{p}_x-\hat{p}_x\hat{x}\right)\psi=-i\hbar\left(x\frac{\partial\psi}{\partial x}-\frac{\partial(x\psi)}{\partial x}\right)$$

$$=-i\hbar\left(x\frac{\partial\psi}{\partial x}-\psi-x\frac{\partial\psi}{\partial x}\right)=i\hbar\,\psi$$

3.$\left[\hat{x},\hat{p}_x\right]=\left[\hat{y},\hat{p}_y\right]=\left[\hat{z},\hat{p}_y\right]=0$

$$\left[\hat{x},\hat{p}_y\right]\psi=\left(\hat{x}\hat{p}_y-\hat{p}_y\hat{x}\right)\psi=-i\hbar\left(x\frac{\partial\psi}{\partial y}-\frac{\partial(x\psi)}{\partial y}\right)=0$$

4. $\left[\hat{p}_x,\hat{p}_y\right]=\left[\hat{p}_y,\hat{p}_z\right]=\left[\hat{p}_z,\hat{p}_x\right]=0$

$$\left[\hat{p}_x,\hat{p}_y\right]\psi=\left(\hat{p}_x\hat{p}_y-\hat{p}_y\hat{p}_x\right)\psi=\left(-i\hbar\right)^2\left(\frac{\partial}{\partial x}\frac{\partial\psi}{\partial y}-\frac{\partial}{\partial y}\frac{\partial\psi}{\partial x}\right)=0$$

5.$\left[\hat{H},\hat{p}\right]=0$

$$\left[\hat{H},\hat{p}\right]\psi=\left(\hat{H}\hat{p}-\hat{p}\hat{H}\right)\psi$$

$$=\left\{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)+i\hbar\frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\right\}\psi$$

$$=i\frac{\hbar^3}{2m}\left(\frac{\partial^3\psi}{\partial x^3}-\frac{\partial^3\psi}{\partial x^3}\right)=0$$

6.$\left[\hat{L}_x,\hat{x}\right]=0,\left[\hat{L}_y,\hat{y}\right]=0,\left[\hat{L}_z,\hat{z}\right]=0$

$$\left[\hat{L}_x,\hat{x}\right]\psi=\left(\hat{L}_x\hat{x}-\hat{x}\hat{L}_x\right)\psi=-i\hbar\left\{\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)x\psi-x\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\psi\right\}$$

Inspection of above formulas shows that a component of the angular momentum and the corresponding coordinate can have simultaneously definite values.

$$7.\left[\hat{L}_x,\hat{y}\right]=i\hbar z,\qquad \left[\hat{L}_y,\hat{z}\right]=i\hbar x,\left[\hat{L}_z,\hat{x}\right]=i\hbar y$$

$$\left[\hat{L}_x,\hat{y}\right]\psi=\left(\hat{L}_x\hat{y}-\hat{y}\hat{L}_x\right)\psi$$

$$=-i\hbar\left\{\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)y\psi-y\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\psi\right\}$$

$$=-i\hbar\left\{y^2\frac{\partial\psi}{\partial z}-zy\frac{\partial\psi}{\partial y}-z\psi-y^2\frac{\partial\psi}{\partial z}+yz\frac{\partial\psi}{\partial y}\right\}$$

$$=i\hbar z\psi$$

Inspection of these formulas shows that the component L_x and the coordinate y (or z) cannot be determined simultaneously. The same holds for L_y and the coordinate z (or x) and also for L_z and the coordinate x (or y).

$$8.\left[\hat{L}_x,\hat{p}_x\right]=0\qquad \textit{similar results hold for other similar commutators}$$

$$\left[\hat{L}_x,\hat{p}_x\right]\psi=\left(\hat{L}_x\hat{p}_x-\hat{p}_x\hat{L}_x\right)\psi$$

$$=(-i\hbar)^2\left\{\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\frac{\partial\psi}{\partial x}-\frac{\partial}{\partial x}-\left(y\frac{\partial\psi}{\partial z}+z\frac{\partial\psi}{\partial y}\right)\right\}=0$$

$$9.\left[\hat{L}_x,\hat{p}_y\right]=i\hbar\hat{p}_z\ \textit{similar results hold for other components}$$

$$\left[\hat{L}_x,\hat{p}_y\right]\psi=\left(\hat{L}_x\hat{p}_y-\hat{p}_y\hat{L}_x\right)\psi$$

$$=(-i\hbar)^2\left\{\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\frac{\partial\psi}{\partial y}-\frac{\partial}{\partial y}\left(y\frac{\partial\psi}{\partial z}-z\frac{\partial\psi}{\partial y}\right)\right\}$$

$$=(-i\hbar)^2\left\{y\frac{\partial^2\psi}{\partial y\partial z}-z\frac{\partial^2\psi}{\partial y^2}-y\frac{\partial^2\psi}{\partial z\partial y}-\frac{\partial\psi}{\partial z}+z\frac{\partial^2\psi}{\partial y^2}\right\}$$

$$=(-i\hbar)^2\left(-\frac{\partial\psi}{\partial z}\right)$$

$$=i\hbar\left(-i\hbar\frac{\partial\psi}{\partial z}\right)$$

$$=i\hbar\hat{p}_z\psi$$

10. $\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z,\left[\hat{L}_{y,}\hat{L}_z\right]=i\hbar\,\hat{L}_x,\left[\hat{L}_{z,}\hat{L}_x\right]=i\hbar\,\hat{L}_y$

$$\left[\hat{L}_x,\hat{L}_y\right]=\hat{L}_x\hat{L}_y-\hat{L}_y\hat{L}_x=\hat{L}_x\left(\hat{z}\hat{p}_x-\hat{x}\hat{p}_z\right)-\left(\hat{z}\hat{p}_x-\hat{x}\hat{p}_z\right)\hat{L}_x$$
$$=\hat{L}_x\hat{z}\hat{p}_x-\hat{L}_x\hat{x}\hat{p}_z-\hat{z}\hat{p}_x\hat{L}_x+\hat{x}\hat{p}_z\hat{L}_x$$

Since $\hat{L}_x$ commutes both with $\hat{x}$ and $\hat{p}_x$ we can interchange the operators $\hat{L}_x$ and $\hat{x}$ in the second term and also the operators $\hat{p}_x$ and $\hat{L}_x$ in the third term. The result is

$$\left[\hat{L}_x,\hat{L}_y\right]=\hat{L}_x\hat{z}\hat{p}_x-\hat{x}\hat{L}_x\hat{p}_z-\hat{z}\hat{L}_x\hat{p}_x+\hat{x}\hat{p}_z\hat{L}_x$$

Let us combine the first term with the third one and the second term with the fourth one

$$\left[\hat{L}_x,\hat{L}_y\right]=\left(\hat{L}_x\hat{z}-\hat{z}\hat{L}_x\right)\hat{p}_x-\hat{x}\left(\hat{L}_x\hat{p}_z-\hat{p}_z\hat{L}_x\right)$$
$$=\left(i\hbar y\right)\hat{p}_x-\hat{x}\left(i\hbar\hat{p}_y\right)$$
$$=i\hbar\left(\hat{y}\hat{p}_x-\hat{x}\hat{p}_y\right)$$
$$=i\hbar\hat{L}_z$$

By carrying out two successive cyclic permutation on $\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z$ We can get the remaining two results.

11. $\left[\hat{L}^2,\hat{L}_x\right]=0,\ \left[\hat{L}^2,\hat{L}_y\right]=0,\left[\hat{L}^2,\hat{L}_z\right]=0$

$$\left[\hat{L}^2,\hat{L}_x\right]=\left(\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2\right)\hat{L}_x-\hat{L}_x\left(\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2\right)$$
$$=\hat{L}_x^3+\hat{L}_y^2\hat{L}_x+\hat{L}_z^2\hat{L}_x-\hat{L}_x^3-\hat{L}_x\hat{L}_y^2+\hat{L}_x\hat{L}_z^2$$

Using the commutation relation $\hat{L}_x\hat{L}_y-\hat{L}_y\hat{L}_x=i\hbar\hat{L}_z$ we can transform the second and fifth term as follows

$$\hat{L}_y^2\hat{L}_x-\hat{L}_x\hat{L}_y^2=\hat{L}_y\hat{L}_y\hat{L}_x-\hat{L}_x\hat{L}_y\hat{L}_y$$
$$=\hat{L}_y\left(\hat{L}_x\hat{L}_y-i\hbar\hat{L}_z\right)-\left(\hat{L}_y\hat{L}_x-i\hbar\hat{L}_z\right)\hat{L}_y$$
$$=-i\hbar\left(\hat{L}_y\hat{L}_z+\hat{L}_z\hat{L}_y\right)$$

Using the relation $\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z = i\hbar\hat{L}_y$ we can perform a similar transformation of the third and sixth terms.

$$\begin{aligned}\hat{L}_z^2\hat{L}_x - \hat{L}_x\hat{L}_z^2 &= \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z\hat{L}_z \\ &= \hat{L}_z\left(\hat{L}_x\hat{L}_z - i\hbar\hat{L}_y\right) - \left(\hat{L}_z\hat{L}_x - i\hbar\hat{L}_y\right)\hat{L}_y \\ &= -i\hbar\left(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z\right)\end{aligned}$$

Making use of these transformations we get

$$\left[\hat{L}^2, \hat{L}_x\right] = 0$$

We conclude that only the square of the vector L and one of its projections onto the coordinate axes can be determined simultaneously. The other two projections are indeterminate (except when all three components are zero). Consequently, all that we can know about the vector L is its "length" and the angle it makes with a certain axis. The direction of the vector L, however, does not lend itself to determination. The operators, which commute, can have simultaneous eigen states.

3.4 The Position and Momentum Representations

In this section we revert to the space f of the wave functions of a particle. To every wave function $\psi\left(\vec{r}\right)$ we corresponds a ket $\left|\psi\right\rangle$ belongs to the space ε_r. This correspondence is linear and the scalar product of two kets coincides with that of the corresponding wave function

$$\left\langle\phi\middle|\psi\right\rangle = \int\phi^*(\vec{r})\psi(\vec{r})d^3r \text{ ---------------------} (1)$$

ε_r can thus be regarded as the space of the states of a particle. We now proceed to study two particularly important representations in this space called the position and momentum representations.

(a) Definition

We know that two bases in the space f : $\left\{\varepsilon_{r_0}(\vec{r})\right\}$ *and* $\left\{v_{p_0}(\vec{r})\right\}$. These bases do not consist of the functions belonging to the space f :

$$\varepsilon_{r_0}(\vec{r}) = \delta\left(\vec{r} - \vec{r}_0\right)$$

$$v_{p_0}(\vec{r}) = \left[2\pi(h/2\pi)\right]^{-3/2} e^{\frac{i}{(h/2\pi)}\vec{p}_0.\vec{r}}$$

However any function of the space f can be expanded in either of the bases. We therefore associate a ket to each of the function of these bases

$$\varepsilon_{r_0}(\vec{r}) \Leftrightarrow |\vec{r}_0\rangle$$
$$v_{p_0}(\vec{r}) \Leftrightarrow |\vec{p}_0\rangle$$

With respect to these bases $\left\{\varepsilon_{r_0}(\vec{r})\right\} and \left\{v_{p_0}(\vec{r})\right\}$ of f, we define two representation in ε_{r_0} the position representation $|\vec{r}_0\rangle$ and the momentum representation $|\vec{p}_0\rangle$. A basis vector of the first of this representation is characterized by three continuous indices x_0, y_0, and z_0 which are simply the co ordinates of a point in the three dimensional space. For the second representation the three indices are components of an ordinary vector

(b) Orthonormality Relation

Let us consider $\langle\vec{r}_0|\vec{r}_0'\rangle$ According to the definition of the scalar product in ε_r we have

$$\langle\vec{r}_0|\vec{r}_0'\rangle = \int \varepsilon_{r_0}(\vec{r})\varepsilon_{r_0'}(\vec{r})\, d^3r = \delta(\vec{r}_0 - \vec{r}_0') \text{---------}(2)$$

Similarly

$$\langle\vec{p}_0|\vec{p}_0'\rangle = \int v_{r_0}(\vec{r})v_{r_0'}(\vec{r})\, d^3r = \delta(\vec{p}_0 - \vec{p}_0') \text{---------}(3)$$

The bases that we have just defined can be regarded as orthonormal in a large sense.

(c) Closure Relation

The fact that set $|\vec{r}_0\rangle$ or $|\vec{p}_0\rangle$ constitutes a base in ε_r can be expressed by an appropriate closure relation. this can be written in the same way as where we now do the summation over three indices. we thus have the following fundamental relation.

(i) $\int|\vec{r}_0\rangle\langle\vec{r}_0|d^3r_0 = I$

(ii) $\int|\vec{p}_0\rangle\langle\vec{p}_0|d^3p_0 = I$ $3(a)$

(d) Components of Ket

Let us consider any ket $\left|\psi\right\rangle$ corresponding to the wave function $\psi(\vec{r})$. The closure relation given above enables us to write it in one of the two forms:

$$\left|\psi\right\rangle = \int \left|\vec{r}_0\right\rangle\left\langle\vec{r}_0\right|\psi d^3 r_0$$

$$\left|\psi\right\rangle = \int \left|\vec{p}_0\right\rangle\left\langle\vec{p}_0\right|\psi\rangle d^3 p_0$$

We can calculate the co efficients

$$\left\langle\vec{r}_0\right|\psi\left.\right\rangle = \int \varepsilon^*_{r_0}(\vec{r})\psi(\vec{r})d^3 r$$

$$\left\langle\vec{p}_0\right|\psi\left.\right\rangle = \int v^*_{p_0}(\vec{r})\psi(\vec{r})d^3 r$$

We thus find that

$$\left.\begin{array}{l} \left\langle\vec{r}_0\right|\psi\left.\right\rangle = \psi(\vec{r}_0) \\ \left\langle\vec{p}_0\right|\psi\left.\right\rangle = \bar{\psi}(\vec{p}_0) \end{array}\right\} \text{---------}(4)$$

Where $\bar{\psi}(\vec{p})$ is the Fourier transformation of $\psi(\vec{r})$

The value $\psi(\vec{r}_0)$ of the wave function at the point $\vec{r}_0$ thus out to be the component of the ket $\left|\psi\right\rangle$ along the basis vector $\left|\vec{r}_0\right\rangle$ of the position representation $\left\{\left|\vec{r}_0\right\rangle\right\}$ .The wave function (in the momentum space) $\bar{\psi}(\vec{p})$ can be similar interpreted.

For $\left|\psi\right\rangle = \left|\vec{p}_0\right\rangle$, the relation (4) gives

$$\left\langle\vec{r}_0\right|\vec{p}_0\left.\right\rangle = v_{p_o}(\vec{r}_0) = \left[2\pi(h/2\pi)\right]^{-3/2} e^{\frac{1}{(h/2\pi)}\vec{p}_0.\vec{r}_0}$$

For $\left|\psi\right\rangle = \left|\vec{r}\,'_0\right\rangle$ the result is quite in agreement with the Orthonormality relation

$$\left\langle\vec{r}_0\right|\vec{r}\,'_0\left.\right\rangle = \varepsilon_{r'_0}(\vec{r}_0) = \delta(\vec{r}_0 - \vec{r}\,'_0)$$

Now that we have again interpreted the wave function $\psi(\vec{r})$ and its Fourier transform $\psi(\vec{p})$ we shall write $\left|\vec{r}\right\rangle$ and $\left|\vec{p}\right\rangle$ in place of $\left|\vec{r}_0\right\rangle$ and $\left|\vec{p}_0\right\rangle$, for the basis vectors of the two representations under study. Nevertheless $\vec{r}$ and $\vec{p}$ are here always considered as the two sets of continuous indices {x,y,z} and {p_x,p_y,p_z} respectively.

Note: – Let us consider an orthonormal base $\{u(\vec{r})\}$ in the space f. To very $u(\vec{r})$ we associate a ket $|u_i\rangle$ of the space ε_r The set $\{u(\vec{r})\}$ constitutes an orthonormal base in ε_r it therefore satisfies the closure relation

$$\sum|u_i\rangle\langle u_i| = I \text{------------------} (5)$$

Let us take the matrix elements on both sides of (5) between $|\vec{r}\rangle and |\vec{r}'\rangle$

$$\sum_i \langle\vec{r}|u_i\rangle\langle u_i|\vec{r}'\rangle = \langle\vec{r}|I/\vec{r}'\rangle = \langle\vec{r}|\vec{r}'\rangle$$

From (2) *and* (4), *this equation becomes*

$$\sum_i u_i(\vec{r})u_i^*(\vec{r}') = \delta(\vec{r}-\vec{r}')$$

The closure relation in the base $\{u_i(\vec{r})\}$ is thus simply another form, in the representation $\{|\vec{r}\rangle\}$ of the vectorial closure relation (5)

(e) Scalar Product of Two Vectors

We have defined the scalar product of two ket of ε_r as the same for the corresponding wave functions in f. It can be seen that is reproduced if we substitute the closure relation between $\langle\phi| and |\psi\rangle$:

$$\langle\phi|\psi\rangle = \int\langle\phi|\vec{r}\rangle\langle\vec{r}|\psi\rangle d^3r$$

And substitute (5) for the components $\langle\vec{r}|\psi\rangle and \langle\vec{r}|\phi\rangle$

If we use the momentum representation $\{|\vec{p}\rangle\}$, we obtain an important relation of the Fourier transformations:

$$\begin{aligned}\langle\phi|\psi\rangle &= \int\langle\phi|\vec{p}\rangle\langle\vec{p}|\psi\rangle d^3r \\ &= \int\bar{\phi}^*(\vec{p})\bar{\psi}(\vec{p})d^3p \qquad (6)\end{aligned}$$

(f) Change from a Representation $\{|\vec{r}\rangle\}$ to a Representation $\{|\vec{p}\rangle\}$

A change from one representation to another involves the numbers:

$$\langle\vec{r}|\vec{p}\rangle = \langle\vec{p}|\vec{r}\rangle^* = (2\pi\hbar)^{-3/2}e^{i/\hbar\,\vec{p}.\vec{r}} \qquad (7)$$

A given ket $|\psi\rangle$ is represented by $\langle\vec{r}\,|\psi\rangle=\psi(\vec{r})\,in\,the\,representation\left\{|\vec{r}\rangle\right\}and\,by\langle\vec{p}\,|\psi\rangle=\bar{\psi}(\vec{p})$ in the representation. $\left\{|\,\vec{p}\rangle\right\}$. From the formulae we already know that $\psi(\vec{r})\,and\,\bar{\psi}(\vec{p})$ are related by the Fourier transformation It is form this that we got our formulae for a change of representation.

$$\langle\vec{r}\,|\psi\rangle=\int\langle\vec{r}\,|\,\vec{p}\rangle\langle\vec{p}\,|\psi\rangle d^3p$$

or

$$\psi(\vec{r})=(2\pi\hbar)^{-3/2}\int e^{\frac{i}{\hbar}\vec{p}.\vec{r}\bar{\psi}(\vec{p})d^3p}$$

Inversely

$$\langle\vec{p}\,|\psi\rangle=\int\langle\vec{p}\,|\vec{r}\rangle\langle\vec{r}\,|\psi\rangle d^3r$$

or

$$\bar{\psi}(\vec{p})=(2\pi\hbar)^{-3/2}\int e^{\frac{i}{\hbar}\vec{p}.\vec{r}\,\psi(\vec{r})d^3r}$$

We can easily change the matrix elements

$$\left\langle\vec{r}'\middle|\hat{A}\,|\,\vec{r}\right\rangle=A(\vec{r}',\vec{r})$$

of an operator $\hat{A}$ in the representation $\left\{|\vec{r}\rangle\right\}$ to the matrix elements

$$\left\langle\vec{p}'\middle|\hat{A}\,|\,\vec{p}\right\rangle=A(\vec{p}',\vec{p})$$

$of\ the\,same\,operator\,in\,the\,represenation\left\{|\,\vec{p}\rangle\right\}$

$$A(\vec{p}',\vec{p})=(2\pi\hbar)^{-3}\int d^3r\int e^{\frac{i}{\hbar}(\vec{p}.\vec{r}-\vec{p}'.\vec{r}')}A(\vec{r}',\vec{r})\,d^3r'$$

$A\,similar\,\exp ression\,gives\,us\,the\,change\ \,from\,A(\vec{p}',\vec{p})\,to\,A(\vec{r}',\vec{r})$

(g) The Operators $\hat{R}\,and\,\hat{P}$

Let $|\psi\rangle$ by any ket of $\delta_r\,and\langle\vec{r}\,|\psi\rangle=\psi(\vec{r})=\psi(x,y,z)$ the corresponding wave function. By definition of the operator $\hat{X}$:

$$|\psi'\rangle=\hat{X}\,|\psi\rangle$$

The ket $|\psi'\rangle$ is represented in the base $\left\{|\vec{r}\rangle\right\}$ the operator $\hat{X}$ coincides with the operator of multiplication with x. Although we characterize $\hat{X}$ as an operator transforming the wave functions, it is very much an operator acting in the space ε_r . In the same way, we introduce two more operators $\hat{Y}$ *and* $\hat{Z}$. We thus define the three operators $\hat{X}$, $\hat{Y}$ *and* $\hat{Z}$ by the formula

$$\left.\begin{aligned}\left\langle \vec{r}\,\middle|\,\hat{X}\,|\psi\right\rangle &= x\langle\vec{r}\,|\psi\rangle\\ \left\langle \vec{r}\,\middle|\,\hat{Y}\,|\psi\right\rangle &= y\langle\vec{r}\,|\psi\rangle\\ \left\langle \vec{r}\,\middle|\,\hat{Z}\,|\psi\right\rangle &= z\langle\vec{r}\,|\psi\rangle\end{aligned}\right\}\text{.....(8)}$$

where the numbers x,y,z are precisely the three indices for the ket $|\vec{r}\rangle$. $\hat{X},\hat{Y}$ *and* $\hat{Z}$ will be considered as the “components” of a “vector operator” $\hat{R}$.

The operators $\hat{X},\hat{Y},\hat{Z}$ can be very conveniently employed in the representation $\{|\vec{r}\rangle\}$. For example to calculate the matrix elements $\left\langle\phi\middle|\hat{X}\,|\psi\right\rangle$ all that we have to do is to insert the closure relation between $\langle\phi|$ *and* $\hat{X}$ and use the formulae

In the same way we can define the vector operator $\hat{P}$ by its components $P_{x.}P_y,P_z$ whose action in the representation $\{|\vec{p}\rangle\}$ is given by

$$\begin{aligned}\left\langle \vec{p}\,\middle|\,\hat{P}_x\,|\psi\right\rangle &= P_x\langle\vec{p}\,|\psi\rangle\\ \left\langle \vec{P}\,\middle|\,\hat{p}_y\,|\psi\right\rangle &= P_y\langle\vec{p}\,|\psi\rangle\\ \left\langle \vec{P}\,\middle|\,\hat{P}_z\,|\psi\right\rangle &= P_z\langle\vec{p}\,|\psi\rangle\text{---------------(9)}\end{aligned}$$

Where $P_{x.}P_y,P_z$ are the three indices for the ket $|\vec{p}\rangle$.

Let us now see how the operator $\hat{P}$ acts in the representation $\{|\vec{r}\rangle\}$. All that we have now to do is to use the closure relation 3(a) and the matrix for the change of base (7)

$$\begin{aligned}\left\langle \vec{r}\,\middle|\,\vec{P}_x\,|\psi\right\rangle &= \int\langle\vec{r}\,|\,\vec{p}\rangle\langle\vec{p}\,|\,\vec{p}_x\,|\,\psi\rangle d^3p\\ &= -(2\pi\hbar)^{-3/2}\int e^{\frac{i}{\hbar}\vec{p}.\vec{r}}\,p_x\psi(\vec{p})d^3p\text{---------------------(10)}\end{aligned}$$

We have recognized the Fourier transformation of $p_x\,\psi(\vec{p}),i.e., -i\hbar\frac{\partial}{\partial x}\psi(\vec{r})$ according to the properties of the Fourier transformation). Thus,

$$\left\langle \vec{r}\,\middle|\,\vec{P}_x\,|\psi\right\rangle = -i\hbar\nabla\langle\vec{r}\,|\psi\rangle$$

In the representation $\{|\vec{r}\rangle\}$ the operator $\hat{P}$ coincides with the differential operator $-i\hbar\nabla$ applied to the wave functions. In the representation $\{|\vec{r}\rangle\}$ the calculation of a matrix elements such as $\langle\phi|\vec{P}_x|\psi\rangle$ can be done as follows

$$\begin{aligned}\langle\phi|\vec{P}_x|\psi\rangle &= \int\langle\phi|\vec{r}\rangle\langle\vec{r}|\vec{P}_x|\psi\rangle d^3r\\ &= \int\phi^*(\vec{r})\left[-i\hbar\frac{\partial}{\partial x}\right]\psi(\vec{r})\,d^3r\end{aligned}$$

We can also calculate the commutation between the operators $\hat{X},\hat{Y},\hat{Z},\hat{P}_x,\hat{P}_y,\hat{P}_z$ in the representation $\{|\vec{r}\rangle\}$ for example $|\psi\rangle$ and for all kets of the base $|\vec{r}\rangle$ we conclude that

$$\begin{aligned}\langle\vec{r}|\left[\hat{X},\hat{P}_x\right]|\psi\rangle &= \langle\vec{r}|\left(\hat{X}\hat{P}_x-\hat{P}_x\hat{X}\right)|\psi\rangle\\ &= x\langle\vec{r}|\hat{P}_x|\psi\rangle+i\hbar\frac{\partial}{\partial x}\langle\vec{r}|\hat{X}|\psi\rangle\\ &= -i\hbar x\frac{\partial}{\partial x}\langle\vec{r}|\psi\rangle+i\hbar\frac{\partial}{\partial x}x\langle\vec{r}|\psi\rangle\\ &= i\hbar\langle\vec{r}|\psi\rangle\end{aligned}$$

As this calculation is valid for any ket $|\psi\rangle$ and for all kets of the base $|\vec{r}\rangle$ we conclude that

$$\left[\hat{X},\hat{P}_x\right]=i\hbar \qquad (11)$$

In the same way we can find all other commutation relations between the components of $\hat{R}\,and\,\hat{P}$ We give these results here

$$\left.\begin{aligned}\left[\hat{R}_{i,}\hat{R}_j\right]&=0\\ \left[\hat{P}_{i,}\hat{P}_j\right]&=0\\ \left[\hat{R}_{i,}\hat{R}_j\right]&=i\hbar\,\delta_{ij}\end{aligned}\right\}----(12)$$

$where\,i,\,j=1,2,3\,and\,\hat{R}_1,\hat{R}_2,\hat{R}_3\,\&\,\hat{P}_1,\hat{P}_{2,}\hat{P}_3\,denote\,respectively\,\hat{X},\hat{Y},\hat{Z}\,and\,\hat{P}_{x,}\hat{P}_y,\hat{P}_z$

(h) Operator $\hat{R}$ and functions of $\hat{R}$ in $\{|\vec{r}\rangle\}$

Let us calculate the matrix elements of the operator $\hat{X},\hat{Y},\hat{Z}$ in the representation $\{|\vec{r}\rangle\}$. Using the Orthonormality relation (2), we get atonce:

$$\left.\begin{aligned}(\vec{r}\mid\hat{X}\mid\vec{r}'\rangle &= x\delta(\vec{r}-\vec{r}')\\(\vec{r}\mid\hat{Y}\mid\vec{r}'\rangle &= y\delta(\vec{r}-\vec{r}')\\(\vec{r}\mid\hat{Z}\mid\vec{r}'\rangle &= z\delta(\vec{r}-\vec{r}')\end{aligned}\right\}----(13)$$

These three equations can be combined into a single equation:

$$(\vec{r}\mid\hat{R}\mid\vec{r}'\rangle = \vec{r}\,\delta(\vec{r}-\vec{r}') \qquad (14)$$

The matrix elements of a function $\hat{R}$ can also be similarly written as:

$$(\vec{r}\mid F\left(\hat{R}\right)\mid\vec{r}'\rangle = F\left(\vec{r}\right)\delta(\vec{r}-\vec{r}')$$

(i) Operator $\hat{P}$ and Function of $\hat{P}$ in $\left\{|\vec{r}\rangle\right\}$

Let us calculate the matrix elements $\langle\vec{r}\mid\hat{P}_x\mid\vec{r}'\rangle$

$$\begin{aligned}(\vec{r}\mid\hat{P}_x\mid\vec{r}'\rangle &= \int\langle\vec{r}\mid\hat{P}_x\mid\vec{r}'\rangle\left\langle\vec{p}\middle|\vec{r}'\right\rangle d^3p\\&= \int p_x\left\langle\vec{r}\mid\vec{p}\right\rangle\left\langle\vec{p}\middle|\vec{r}'\right\rangle d^3p\\&= (2\pi\hbar)^{-3}\int p_x e^{\frac{i}{\hbar}\vec{p}.(\vec{r}-\vec{r}')}d^3p\\&= \left[\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}p_x e^{\frac{i}{\hbar}p_x(x-x')}dp_x\right]\times\\&\qquad\left[\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}e^{\frac{i}{\hbar}p_y(y-y')}dp_y\right]\times\\&\qquad\qquad\left[\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}e^{\frac{i}{\hbar}p_z(z-z')}dp_z\right]------------(15)\end{aligned}$$

If we now use the integral form of the “delta function” and its derivatives we get

$$\langle\vec{r}\mid\hat{P}_x\mid\vec{r}'\rangle = -i(h/2\pi)\delta(x-x')\ \delta(y-y')\delta(z-z') \qquad (16)$$

The matrix elements of the other components of $\hat{P}$ can be obtained in the same way.

We can also calculate the matrix elements of a function $G(\hat{P})$ of the operator $\hat{P}$ **:**

$$\langle\vec{r}\,|\,G(\hat{P})\,|\,\vec{r}'\rangle = \int\langle\vec{r}\,|\,G(\vec{P})\,|\,\hat{P}\rangle\left\langle\hat{P}\middle|\vec{r}'\right\rangle d^3p$$

$$= (2\pi\hbar)^{-3}\int G(\vec{P})e^{\frac{i}{\hbar}\vec{p}.(\vec{r}-\vec{r}')}d^3p$$

$$= \left[(2\pi\hbar)\right]^{-3/2} G\left(\vec{r}-\vec{r}'\right)----------------------(17)$$

where $\tilde{G}(\vec{r})$ is the Fourier transform of the function $G(\vec{P})$:

$$G(\vec{r}) = \left(2\pi\hbar\right]^{-3/2}\int e^{\frac{i}{\hbar}\vec{p}.\vec{r}\,G(p)d^3p}$$

(j) Schrodinger's equation in Representation $\left\{\left|\vec{r}\right\rangle\right\}$

We have deduced Schrodinger's equation in the form

$$i\left(h/2\pi\right)\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

Using the representation of state vectors we can write this equation in the form

$$i\left(h/2\pi\right)\frac{d}{dt}\left|\psi(t)\right\rangle = \hat{H}\,|\,\psi\rangle \qquad (18)$$

We will now show that in the representation $\left\{\left|\vec{r}\right\rangle\right\}$**,** it has the same form. In the representation $\left\{\left|\vec{r}\right\rangle\right\}$ the wave function $\psi\left(\vec{r},t\right)$ is defined by

$$\psi\left(\vec{r},t\right) = \left\langle\vec{r}\left|\psi(t)\right.\right\rangle$$

For a spinless particle in the potential $V(\vec{r})$, the Hamiltonian has the form

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{R}) \qquad (19)$$

Projecting (18) on $\left|\vec{r}\right\rangle$ we get :

$$i\left(h/2\pi\right)\frac{\partial}{\partial t}\langle\vec{r}\,|\psi(t)\rangle = \frac{1}{2m}\left\langle\vec{r}\,|\hat{P}^2\middle|\psi(t)\right\rangle + \left\langle\vec{r}\,|V(\hat{R})\middle|\psi(t)\right\rangle$$

We know that

$$\frac{\partial}{\partial t}\langle\vec{r}\,|\psi(t)\rangle = \frac{\partial}{\partial t}\psi(\vec{r},t)$$

$$\left\langle\vec{r}\,|V(\hat{R})\middle|\psi(t)\right\rangle = V(\vec{r})\psi(\vec{r},t)$$

The matrix element $\left\langle\vec{r}\,|\hat{P}^2\middle|\psi\right\rangle$ can be calculated using the representation $\{|\vec{r}\rangle\}$ with $\hat{P}$ acting as $-i\hbar\nabla$

$$\left\langle\vec{r}\,|\hat{P}^2\middle|\psi(t)\right\rangle = \left\langle\vec{r}\,|\left(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2\right)\middle|\psi(t)\right\rangle$$

$$= -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z,t)$$

$$= -\hbar^2\nabla^2\psi(\vec{r},t) \qquad (20)$$

The schrodinger equation thus becomes

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right]\psi(\vec{r},t) \qquad (21)$$

(k) Operator $\hat{P}$ and function of $\hat{P}$ $\{|\vec{p}\rangle\}$

As in section *h* above, we obtain the following corresponding relations:

$$\langle\vec{p}\,|\,\hat{p}\,|\,\vec{p}'\rangle = \vec{p}\delta(\vec{p}-\vec{p}')$$

$$\langle\vec{p}\,|G\left(\hat{p}\right)|\,\vec{p}'\rangle = G(\vec{p})\delta(\vec{p}-\vec{p}')$$

(l) Operator $\hat{R}$ and function of $\hat{R}$ in $\{|\vec{p}\rangle\}$

Following the arguments of section *i* above, we obtain the following corresponding relation

$$\langle\vec{p}\,|\,\hat{X}\,|\,\vec{p}'\rangle = i\hbar\delta'(p_x-p'_x)\delta(p_y-p'_y)\delta(p_z-p'_z)$$

and

$$\langle\vec{p}\,|F(\hat{R})|\,\vec{p}'\rangle = (2\pi\hbar)^{-3/2}\bar{F}(\vec{p}-\vec{p}')$$

with

$$\bar{F}(\vec{p}) = (2\pi\hbar)^{-3/2}\int e^{-\frac{i}{\hbar}\vec{p}.\vec{r}}F(\vec{r})d^3r$$

(m)Schrodinger's equation in Representation $\{|\vec{p}\rangle\}$

Let us introduce the wave function in representation $\{|\vec{p}\rangle\}$ as:

$$\bar{\psi}(p,t)=\langle\vec{p}|\psi(t)\rangle$$

We then use equation (18) to look for an equation which gives the time evolution of $\bar{\psi}(\vec{p},t)$ projecting (18) on the ket $|\vec{p}\rangle$ we get:

$$i\hbar\frac{\partial}{\partial t}\langle\vec{p}|\psi(t)\rangle=\frac{1}{2m}\langle\vec{p}\,|\,\hat{p}^2|\psi(t)\rangle+\langle\vec{p}\,|V(\hat{R})|\psi(t)\rangle$$

For the three members of this equation we have:

$$\frac{\partial}{\partial t}\langle\vec{p}|\psi(t)\rangle=\frac{\partial}{\partial t}\bar{\psi}(\vec{p},t)$$
$$\langle\vec{p}\,|\,\hat{p}^2\,|\psi(t)\rangle=\vec{p}^2\bar{\psi}(\vec{p},t)$$

The matrix element $\langle\vec{p}\,|V(\hat{R})|\,\psi(t)\rangle$ can be calculated as follows

$$\langle\vec{p}\,|V(\hat{R})|\,\psi(t)\rangle=\int\langle\vec{p}\,|V(\hat{R})|\,\vec{p}'\rangle\langle\vec{p}'|\psi(t)\rangle d^3p'$$

$$\langle\vec{p}\,|V(\hat{R})|\,\psi(t)\rangle=(2\pi\hbar)^{-3/2}\int\bar{V}(\vec{p}-\vec{p}')\bar{\psi}(p',t)d^3r$$

where $\bar{V}(\vec{p})$ *is the Fourier transform of* $V(\vec{r})$

$$\bar{V}(\vec{p})=(2\pi\hbar)^{-3/2}\int e^{-\frac{i}{\hbar}\vec{p}.\vec{r}}\,V(\vec{r})\,d^3r$$

The schrodinger equation in representation $\{|\vec{p}\rangle\}$ *thus is*

$$i\hbar\frac{\partial}{\partial t}\bar{\psi}(\vec{p},t)=\frac{\vec{p}^2}{2m}\bar{\psi}(\vec{p},t)+(2\pi\hbar)^{-3/2}\int\bar{V}(\vec{p}-\vec{p}')\bar{\psi}(p',t)d^3p'$$

3.5 Let us sum up

In this section we have understood about commutator, properties of commutators and few important commutation relations. Also, we were able to see how wave functions look like in position space and momentum space.

3.6 Key words

Commutator ,Commutation relation, Wave function, Position space, Momentum space

3.7 Questions for self study

- Discuss the properties of commutators used in Quantum mechanics with examples.
- Discuss five commutation relations used in Quantum mechanics.
- Write the wave function in position space and momentum space.

3.8 Problems

Examples 2.20

Suppose $\psi(x) = \frac{1}{\sqrt{a}}\ for - a \le x \le a$ Find the momentum space wave function $\phi(p)$

SOLUTION

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(x) e^{-ipx/\hbar} dx$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-a}^{+a} \frac{1}{\sqrt{a}} e^{-ipx/\hbar} dx$$

$$= \frac{1}{\sqrt{2\pi\hbar a}} \int_{-a}^{+a} e^{-ipx/\hbar} dx$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{\hbar}{-ip} \right) e^{-ipx/\hbar} \Big|_{-a}^{a}$$

$$= \frac{1}{\sqrt{2\pi\hbar a}} \frac{2\hbar}{p} \left(\frac{e^{-ipa/\hbar} - e^{-ipa/\hbar}}{2i} \right)$$

$$= \sqrt{\frac{2a}{\pi\hbar}} \frac{\sin\left(pa/\hbar\right)}{\left(pa/\hbar\right)} = \frac{2a}{\sqrt{\pi\hbar}} = \sin c\left(pa/\hbar\right)$$

3.9 References for further study

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UNIT 4:

Momentum operator in position eigen values and eigen functions, Gaussian wave packets.

Structure:

4.0 Objectives

After studying this unit you will be able to understand the following aspects;

What is a wave packet? What is the mathematical description of the wave packet? What is the significance of the study of these wave packets? What is their role in quantum mechanics?

4.1 Introduction

4.1.1 Quantum Particles

Just as light waves sometimes exhibits particle-like properties, it turns out that massive particles sometimes exhibit wave-like properties. For instance it is possible to obtain a double-slit interference pattern from a stream of mono-energetic electrons passing through two closely spaced narrow slits. Now the effective wavelength of the electrons can be determined by measuring the width of the light and dark bands in the interference pattern it is found that

$$\lambda = \frac{h}{p} \qquad (1)$$

The same relation is found for the other types of particles. The above wavelength is called the de Broglie wavelength, after Louis de Broglie who first suggested that particles should have wave-like properties in 1923. Note that the de Broglie wavelength is generally pretty small for instance that of an electron is

$$\lambda_e = 1.2\times10^{-9}\left[E(eV)\right]^{-1/2} m \qquad (2)$$

where the electron energy is conveniently measured in units of electron- volts (eV). (An electron accelerated from rest through a potential difference of 1000V acquire an energy of 1000 eV and so on) The de Broglie wavelength of proton is

$$\lambda_p = 1.9\times10^{-11}\left[E(eV)\right]^{-1/2} m \qquad (3)$$

Given the smallness of the de Broglie wavelengths of common particles it is actually quite different to do particle interference experiments. In general in order to perform an effective interference experiment, the spacing of the slits must not be too much greater than the wavelength of the wave. Hence particle interference experiments require either very low energy particles (since $\lambda \propto E^{-1/2}$) or very closely spaced slits. Usually the “slits” consist of crystals, which act a bit like diffraction grating with a characteristic spacing of order the inter-atomic spacing (which is generally about 10^{-9} m).

Equation (1) can be rearranged to give

$$p = \hbar k \qquad (4)$$

For the case of a particle moving the three dimensions the above relation generalize to give

$$\vec{p} = \hbar\vec{k} \qquad (5)$$

Where $\vec{p}$ is the particles vector momentum and $\vec{k}$ its wave vector. It follows that the momentum of a quantum particle and hence its velocity is always parallel to its wave vector.
Then, the expression for energy can be derived as:

$$E = \hbar\omega, \qquad (6)$$

For particle waves, the dispersion relation is: then yield the following dispersion relation for such waves:

$$\omega = \frac{\hbar k^2}{2m} \qquad (7)$$

Now we saw earlier that a plane wave propagates at the so called phase velocity

$$v_p = \frac{\omega}{k}$$

However according to the above dispersion relation a particle plane wave propagates at

$$v_p = \frac{p}{2m}$$

This is only half of the classical particle velocity. Does this imply that the dispersion relation (7) is incorrect? Let us investigate further.

4.1.2 Wave Packets

The above discussion suggests that the wavefunction of massive particle of momentum p and energy E, moving in the positive x-direction can be written

$$\psi(x,t) = \bar{\psi} e^{i(kx - \omega t)} \qquad (8)$$

$where\, k = p/\hbar > 0\, and\, \omega = E/\hbar > 0\, where\, \omega\, and\, k$ are linked via the dispersion relation (7). Expression (8) represents a plane wave whose maxima and minima propagate in the positive x-direction with the phase velocity $v_p = \omega/k$. As we have seen this phase velocity is only half of the classical velocity of a massive particle.

From before the most reasonable physical interpretation of a wavelength is that $\left|\psi(x,t)\right|^2$ is proportional to the probability density of finding the particle at position x at time t. However the modulus squared of the wavefunction (8) is $|\bar{\psi}|^2$, which depends on neither *x* nor *t*. In other words this wave function represents a particle which is equally like to be found anywhere on the x-axis at all times. Hence the fact that maxima and minima of the wave function propagates at a phase velocity which does not correspond to the classical particle velocity does not have any real physical consequences.

So how can we write the wave function of a particle which is localized in x: i.e a particle which is more likely to be found at some positions on the x-axis than at others? It turns out that we can achieve this goal by forming a linear combination of plane waves of different wave numbers.

$$\psi(x,t) = \int_{-\infty}^{\infty} \bar{\psi}(k) e^{i(kx-\omega t)} dk. \qquad (9)$$

Here $\bar{\psi}(k)$ represents the complex amplitude of plane waves of wave number k in this combination. In writing the above expression, we are relaying on the assumption that particle waves are superposable: i.e., it is possible to add two valid wave solutions to form a third valid wave solution. The ultimate justification for this assumption is that particle waves satisfy a different wave equation which is linear in Ψ. This is indeed the case. Incidentally a plane wave which varies as exp [i(kx-ωt)] and has negative k (but positive ω) propagates in the negative x-direction at the phase velocity $\omega/|k|$. Hence the superposition (9) includes both forward and backward propagating waves.

Now there is useful mathematical theorem known as Fourier's theorem which states that if

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \bar{f}(k) e^{ikx} dk,$$

then

$$\bar{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx,$$

Here $\bar{f}(k)$ is known as the Fourier transformation of the function f(x). We can use Fourier's theorem to find the k-space function $\bar{\psi}(k)$ which generates any given x-space wave function $\psi(x)$ at a given time.

For instance suppose that at t = 0 the wave function of our particle takes the form

$$\psi(x,0) \propto \exp\left[ik_0 x - \frac{(x-x_0)^2}{4(\Delta x)^2}\right] \qquad (10)$$

Thus the intial probability density of the particle is written

$$|\psi(x,0)|^2 \propto \exp\left[-\frac{(x-x_0)^2}{2(\Delta x)^2}\right] \qquad (11)$$

This particular probability distribution is called a Gaussian distribution and is plotted in Fig 4.1. It can be seen that a measurement of the particle's position is most likely to yield the value $x_{0,}$ and very unlikely to yield a value which differs from x_0 by more than 3Δx. Thus eqn (11) is the wave function of a particle which is initially localized around $x=x_0$ in some region whose width is of order Δx. This type of wave function is known as a wave packet.

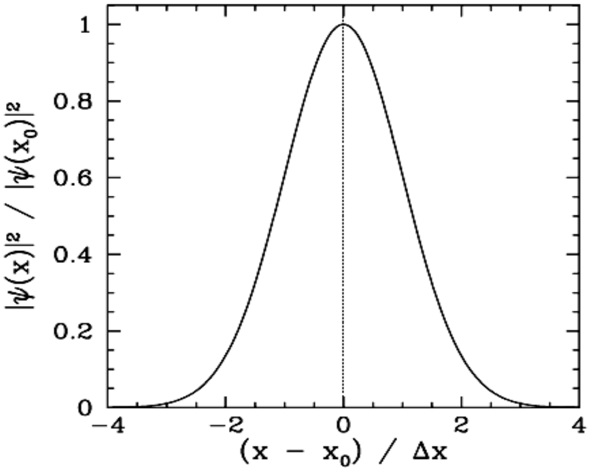

Fig 4.1: A Gaussian probability distribution in x-space

Now , according to Eq (9)

$$\psi(x,0) = \int_{-\infty}^{\infty} \bar{\psi}(k)e^{ikx}dk.$$

Hence we can employ Fourier's theorem to invert this expression to give

$$\bar{\psi}(k) \propto \int_{-\infty}^{\infty} \psi(x,0)e^{-ikx}$$

Making use of equation (11) *we obtain*

$$\bar{\psi}(k) \propto e^{-i(k-k_0)x_0} \int_{-\infty}^{\infty} \exp\left[-i(k-k_0)(x-x_0) - \frac{(x-x_0)^2}{4(\Delta x)^2}\right] dx.$$

Changing the variable of integration to $y = (x - x_0)/(2\Delta x)$, *this reduces to*

$$\bar{\psi}(k) \propto e^{-ikx_0} \int_{-\infty}^{\infty} \exp\left[-i\beta y - y^2\right] dy,$$

where $\beta = 2(k - k_0)\,\Delta x$. *The above equation can be rearranged to give*

$$\bar{\psi}(k) \propto e^{-ikx_0 - \beta^2/4} \int_{-\infty}^{\infty} e^{-(y-y_0)^2} dy$$

Where $y_0 = -i\beta/2$. The integral now just reduces to a number as can easily be seen by making the change of variables $z = y - y_0$ Hence we obtain

$$\bar{\psi}(k) \propto \exp\left[-i\,k\,x_o - \frac{(k-k_0)^2}{4(\Delta k)^2}\right], \qquad (12)$$

where

$$\Delta k = \frac{1}{2\Delta x}$$

Now if $|\psi(x)|^2$ is proportional to the probability density of a measurement of the particle's position yielding the value x then it stands to reason that $|\bar{\psi}(k)|^2$ is proportional to the probability density of a measurement of a particle's wave number yielding the value k. (Recall that $p = \hbar k$, so a measurement of a particle's wave number k is equivalent to a measurement of the particle's momentum p) According to Equation (12)

$$|\bar{\psi}(k)|^2 \propto \exp\left[-\frac{(k-k_0)^2}{2(\Delta k)^2}\right] \qquad (13)$$

Note that this probability distribution is a Gaussian in k-space. See equation (11) and Fig 4.1. Hence a measurement of k is most likely to yield the value k_0 and very unlikely to yield a value which differs from k_0 by more than 3Δk. incidentally a Gaussian is the only mathematical function in x-space which has the same form as its Fourier transformation in K-space.

We have just that Gaussian probability distribution of characteristic width Δx in x-space [see Eq (11)] transforms to Gaussian probability distribution of characteristic width Δk in k-space [see Eq- (13)]

Where

$$\Delta x \Delta k = \frac{1}{2} \tag{14}$$

This illustrates an important property of wave packets. Namely if we wish to contribute a packet which is much localized in x-space (i.e., if Δx is small) then we need to combine plane waves with a very wide range of different k-values (i.e., Δk will be large). Conversely if we only combine plane waves whose wave numbers differ by a small amount (i.e., if Δk is small) then the resulting wave packet will be very extended in x-space (i.e., Δx will be large)

4.1.3 Evolution of Wave Packets

We have seen in Equation in Eq (10) , how to write the wave function of a practice which is initially localized in x-space. But how does this wave function evolve in time? Well, according to Eq(8) we have

$$\psi\left(x,t\right) = \int_{-\infty}^{\infty} \bar{\psi}\left(k\right) e^{i\phi(k)} dk \tag{15}$$

where

$$\phi(k) = kx - \omega(k)t. \tag{16}$$

The function $\bar{\psi}(k)$ is obtained by Fourier transforming the wave function at t=0. Now according to Eqn (13), $\left|\bar{\psi}(k)\right|$ is strongly peaked around k=k_0. Thus it is a responsible approximation to Taylor expand ϕ(k) about k_0. Keeping terms up to second order in k-k_0 we obtain

$$\psi(x,t) \propto \int_{-\infty}^{\infty} \bar{\psi}(k) \exp\left[i \left\{ \phi_0 + \phi_0' \left(k - k_0\right) + \frac{1}{2} \phi_0'' \left(k - k_0\right)^2 \right\} \right] \tag{17}$$

where

$$\phi_0 = \phi(k_0) k_0 x - \omega_0 t,$$

$$\phi_0' = \frac{d\phi(k_0)}{dk} = x - v_g t$$

$$\begin{aligned}
&\phi_0'' = \frac{d^2\phi(k_0)}{dk^2} = -\alpha t \\
&\textit{with} \\
&\omega_0 = \omega(k_0) \\
&v_g = \frac{d\omega(k_0)}{dk} \\
&\alpha = \frac{d^2\omega(k_0)}{dk^2}
\end{aligned} \tag{18}$$

Substituting from Equation (12) rearranging and then changing the variable of integration to $y = (k - k_0)/(2\Delta k)$ we get

$$\psi(x,t) \propto e^{i\left(k_0 x - \omega_o t\right)} \int_{-\infty}^{\infty} e^{i\beta_1 y - (1+i\beta_2)y^2}\, dy,$$

$$\begin{aligned}
&\textit{where} \\
&\beta_1 = 2\Delta k(x - x_0 - v_g t) \\
&\beta_2 = 2\alpha(\Delta k)^2 t,
\end{aligned}$$

Incidentally Δk=1/(2Δx), where Δx is the initial width of the wave packet. The above expression can be rearranged to give

$$\psi(x,t) \propto e^{i\left(k_0 x - \omega_o t\right) - \left(1+i\beta_2\right)\beta^2/4} \int_{-\infty}^{\infty} e^{-(1+i\beta_2)(y-y_0)^2}\, dy,$$

where $y_0 = i\beta/2$ *and* $\beta = \beta_1/\left(1 + i\beta_2\right)$. *Again changing the variable of integration to*

$z = (1 + i\beta_2)^{1/2}\,(y - y_0)$

$$\psi(x,t) \propto \frac{\exp\left[\, i(k_0 x - \omega_0 t) - (x - x_0 - v_g t)^2 \left\{1 - i2\alpha(\Delta k)^2 t\right\} / (4\sigma^2)\right]}{\left[1 + i2\alpha(\Delta k)^2 t\right]^{1/2}} \tag{19}$$

where

$$\sigma^2(t) = (\Delta x)^2 + \frac{\alpha^2 t^2}{4(\Delta x)^2} \tag{20}$$

Note that the above wave function is identical to our original wave function at t=0 This justifies the approximation which we made earlier by Taylor expanding the phase factor ϕ(k) about $k=k_0$.

According to Eq (10), the probability of our particle as a function of time is written

$$|\psi(x,t)|^2 \propto \sigma^{-1}(t)\exp\left[-\frac{(x-x_0-v_g t)^2}{2\sigma^2(t)}\right]$$

Hence the probability distribution is a Gaussian of characteristic width σ which peaks at $x = x_0 + v_g t$. Now the most likely position of our particle coincides with the peak of the distribution function, thus the particle's most likely position is given by

$$x = x_0 + v_g t$$

It can be seen that the particle effectively moves at the uniform velocity

$$v_g = \frac{d\omega}{dk}$$

which is known as the group velocity. In other words a plane wave travels at the phase velocity $v_p = \omega / k$, where as a wave packet travels at the group velocity $v_g = d\omega/dt$ Now it follows from the dispersion relation for particle waves that

$$v_g = \frac{p}{m}$$

However it can be seen from Equation that this is identical to the classical particle velocity. Hence the dispersion relation turns out to be consistent with classical physical after all as soon as we realize that individual particles must be identified with wave packets rather than plane waves. In fact a plane wave is usually interpreted as a continuous stream of particles propagating in the same direction as the wave

According to equation (20) the width of our wave packet grows as time progresses. Indeed it follows from equation (7) and (18) that characteristic time for a wave packet of original width Δx to double in spatial extent is

$$t_2 \sim \frac{m(\Delta x)^2}{\hbar}$$

For instance if an electron is originally localized in a region of atomic scale (i.e., $\Delta x=10^{-10}$ m) then the doubling time is only about 10^{-16} s. Evidently, particle wave packets (for freely moving particles) spread very rapidly

Note from the previous analysis that the rate of spreading of a wave packet is ultimately governed by the second derivative of $\omega(k)$ with respect to k. This is why a functional relationship between ω and k is generally known as a dispersion relation: i.e., because it governs how wave packets disperse as time progresses. However for the special case where ω is a linear function of k the second derivative of ω with respect to k is zero and hence there is no dispersion of wave pockets. i.e., wave packets propagate without changing shape. Now the dispersion wave relation for light waves is linear in k. It follows that light pulses propagates through a vacuum without spreading. Another property of linear dispersion relations is that the phase velocity $v_p = \omega / k$ and the group velocity $v_g = d\omega/dt$ identical. Thus both plane light waves and light pulses propagates through a vacuum at the characteristic speed c = $3\text{x}10^8$ m/s. Of course the dispersion relation for particle waves is not linear in k. Hence particle plane waves and particle wave packets propagate at different velocities and particle wave packets also gradually disperse as time progresses.

4.2 Momentum Operator in Position space:

4.2.1.Definition (Position space)

For a single particle with no electric charge and no spin the momentum operator can be written in the position basis as

$$\hat{p} = -i\hbar\nabla$$

$where\,\nabla\; is\, the\, gradnient\, operator\,,$

$\hbar\, is\, the\, reduced\; Planks\, cons\tan t$

$i = is\, the\, imaginary\, unit$

In one special dimension this becomes,

$$\hat{p} = \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

This is a commonly encountered form of the momentum operator through not the most general one. For a charged particle q in an electromagnetic field, described by the scalar potential φ and vector potential A, the momentum operator must be replaced by

$$\hat{p} = -i\hbar\nabla - q\vec{A}$$

where the canonical momentum operator is the above momentum operator

$$\hat{p} = -i\hbar\vec{\nabla}$$

This is of course true for electrically neutral particles also since the second term vanishes if q is zero and the original operator appears.

4.2.2 Description of Quantum Particle: Wave Packets

Free Particle

Let us consider a particle whose potential energy at every point of the space is zero has a constant value. There is thus no force acting on the particle and we call it a free particle With $\vec{V}(r,t) = 0$ Schrodinger's time- dependant wave equation becomes

$$(i\hbar)\frac{\partial}{\partial t}\psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) \qquad (21)$$

This equation has the possible solutions of the form

$$\psi(\vec{r},t) = Ae^{i(\vec{k}.\vec{r}-\omega t)}$$

Where A is a constant. The wave vector $\vec{k}$ and ω are interconnected

$$\omega = \frac{\hbar\vec{k}^2}{2m} \qquad (22)$$

This relation implies that the energy E and momentum $\vec{p}$ of a free particle satisfy the relation

$$E = \frac{p^2}{2m} \qquad (23)$$

it is obvious that

$$|\psi(\vec{r},t)|^2 = |A|^2$$

which means that a plane wave of this type represents a particle having a uniform probability of presence throughout the space. According to superposition principle all linear combinations of the wave satisfying (22) are also the solution of equation (21) such a combination can be written in the form

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}}\int g(\vec{k})e^{i(\vec{k}.\vec{r}-\omega(k)t)}.d^3k \qquad (24)$$

Here d^3H is by definition an infinitesimal volume element in $\vec{k}$ -space : $dk_x\, dk_y\, dk_z$. The factor g(k) which may be complex must be sufficiently regular to ensure of the integral.

A wave function of the type (24) obtained by superposition of plane waves is called a three dimensional wave packet. For simplification we often use a one dimensional wave packet for study. Such a wave packet is obtained by the superposition of plane waves propagating to 0x: the wave function now depends only on x and t :

$$\psi\left(x,t\right)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}g\left(k\right)w^{i\left(kx-\omega\left(k\right)t\right)}dk \qquad (25)$$

If we choose the wave packet at the instant t = 0, the wavefunction is given by

$$\psi\left(x,0\right)=\frac{1}{\sqrt{2\pi}}\int\ g(k)e^{ikx}dk \qquad (26)$$

We observe that g(k) is simply the Fourier transform of $\psi(x,0)$:

$$\left(k\right)=\frac{1}{\sqrt{2\pi}}\int\psi\left(x,0\right)e^{ikx}dx \qquad (27)$$

It is to be noted that the formula (26) is not limited to the case of free particles it remains valid whatever be the potential. Thus the consequences that we are going to study are perfectly general

4.2.3 Form of the Wave Packets at a given instant

Let us suppose that $\left|g\left(k\right)\right|$has the form shown in figure 4.2 it shows a peak with maximum at $k=k_0$ and its (at half of the maximum height) is Δk. in order to understand the behavior of the wave function ψ(x,0) we consider a particularly simple case: we consider the wave function ψ(x,0) which in fact consists of a superposition of an infinite number of plane waves e^{ikx} to be a sum of three plane waves only. We suppose the wave vectors of these plane waves to be $k_0 k_0-\frac{\Delta k}{2} and\, k_0+\frac{\Delta k}{2}$ and let their amplitudes be respectively proportional to 1, ½, and ½ we then have

$$\psi\left(x\right)=\frac{g\left(k_0\right)}{\sqrt{2\pi}}\left[e^{ik_0x}+\frac{1}{2}e^{i\left(k_0-\frac{\Delta k}{2}\right)x}+\frac{1}{2}e^{i\left(k_0+\frac{\Delta k}{2}\right)x}\right]$$

$$=\frac{g\left(k_0\right)}{\sqrt{2\pi}}=e^{ik_0x}\left[1+\cos\left(\frac{\Delta k}{2}x\right)\right] \qquad (28)$$

We see that $\left|\psi\left(x\right)\right|$is maximum for x = 0. This is due to the fact that as *x* approaches the value 0, the three waves are in phase and interfere constructively as shown in fig 4.3. As we get farther from x=0 the waves get out of phase with respect to each other and $\left|\psi\left(x\right)\right|$ decreases. Completely destructive interference takes place when the phase difference between

e^{ik_0x} *and* $e^{i\left(k_0\pm\Delta k/2\right)x}$ *equals* $\pm\pi : \psi\left(x\right)$ *vanishes for* $x=\pm\frac{\Delta x}{2}, \Delta x$ being given by $\Delta x.\Delta k = 4\pi$

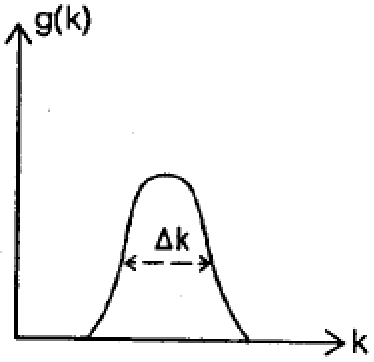

Fig 4.2

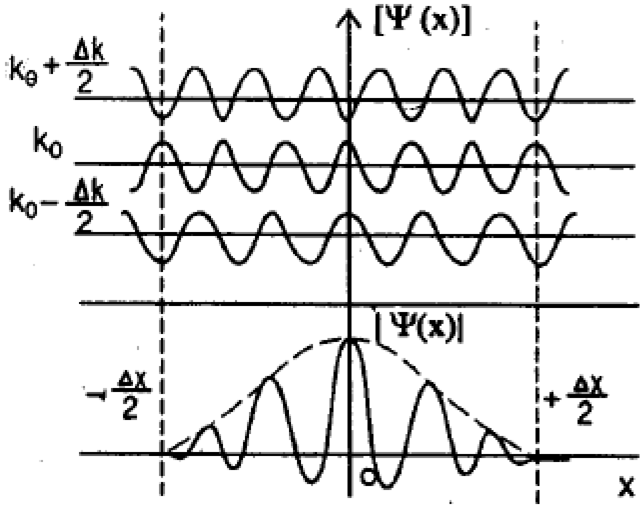

Fig 4.3

Let us now return to the general wave packet of the form (26). Its form is also the result of interference between the various plane waves. $\left|\psi\left(x\right)\right|$ will be maximum when the plane waves undergo a constructive interference.

Let the argument of the function $g(k)$ *be* $\alpha(k)$:

$$g\left(k\right)=\left|g\left(k\right)\right|e^{i\alpha\left(k\right)}$$

Let $\alpha(k)$ vary fairly regularly in the interval $\left[k_0-\frac{\Delta k}{2}, k_0+\frac{\Delta k}{2}\right]$ where $\left|g\left(k\right)\right|$ is appreciable; for very small values of Δk we can expand $\alpha(k)$ around $k=k_0$:

$$\alpha\left(k\right)\cong\alpha\left(k_0\right)+\left(k-k_0\right)\left[\frac{d\alpha}{dk}\right]_{k=k_0}$$

In view of this we can rewrite (26) in the form:

$$\psi\left(x,0\right)\cong\frac{e^{i\left[k_0x+\alpha\left(k_0\right)\right]}}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\left|g\left(k\right)\right|e^{i\left(k-k_0\right)\left(x-x_0\right)}dk \qquad (29)$$

$$where\, x_0=-\left[\frac{d\alpha}{dk}\right]_{k=k_0} \qquad (30)$$

The form (29) is quite suitable to study the variation of *x*: when $|x-x_0|$ is large, the function of k to be integrated oscillates a large number of times in the interval Δk. We find that the successive oscillations cancel each other and the integral takes a negligible value (fig 4.4(a)). In other words for a value of *x* fixed away from x_0 the phase of the various waves constituting ψ(x, 0) vary rapidly in the region Δk and these waves tend to destroy each other by interference. On the contrary if $x \approx x_0$ the function to be integrated is practically without any oscillations and $\left|\psi(x,0)\right|$ is maximum fig4.4b

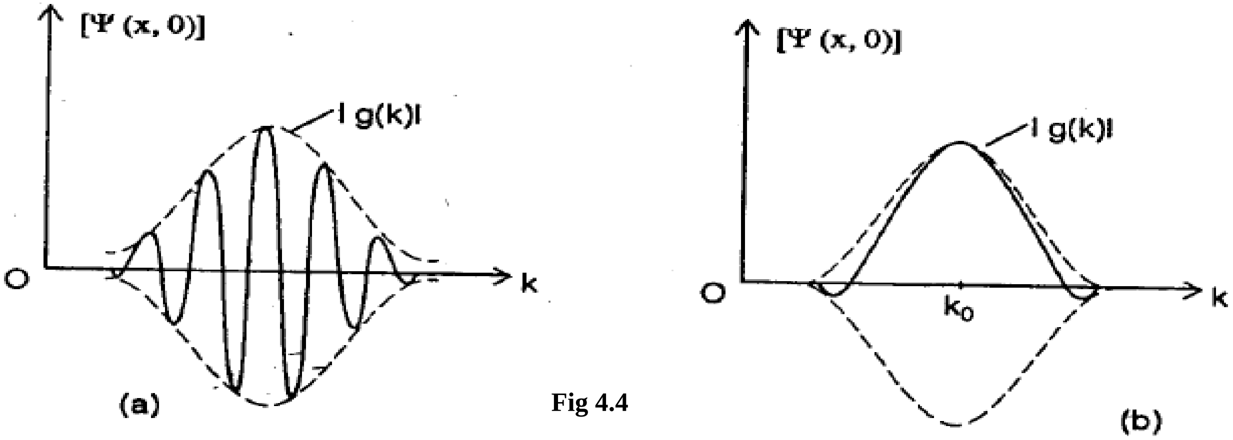

Fig 4.4

The position $x_m(0)$ of the wave packet is then

$$x_m(D) = x_0 = -\left[\frac{d\alpha}{dk}\right]_{k=k_0} \qquad (31)$$

As the value of x gets away from the value x_0, $\left|\psi(x,0)\right|$ *decreases: this decrease becomes appreciable if* $e^{i(k-k_0)(x-x_0)}$ *oscillates nearly once as k travels the region* Δk, *that is to say, when –*

$$\Delta k.(x-x_0) \approx 1 \qquad (32)$$

If Δx *is the width of the wave packet we have*

$$\Delta k.\Delta x \geq 1 \qquad (33)$$

We thus arrive at a classical result between the widths of two functions which are the Fourier transformation of each other. The important fact is that the product **$\Delta x.\Delta k$** has a lower limit; the exact value of this lower limit of course depends on how the widths Δx and Δk are defined.

A wave packets such as (25) then represents the state of a particle having practically no chance (zero probability) to be present at t = 0 outside a region of width approximately Δx centred around x_0

4.2.4Time Dependence of a Free Wave Packet:

Consider a wave packet of a free particle described by (25). A particular plane wave $e^{i(kx=\omega t)}$ propagates along the x- direction with a velocity

$$V_\phi(k) = \frac{\omega}{k} \qquad (34)$$

Since it depends on ***x*** and ***t*** only through the factor $\left(x - \frac{\omega}{k}t\right)$.

$V_\phi(k)$ is called the phase velocity of the plane wave.

We know that for an electromagnetic wave propagating in vacuum V_ϕ is independent of k and equal to the speed of light ***c***. All the waves constituting a wave packet move with the same velocity so that the resultant wave packet also progresses at the same velocity ***c*** without getting deformed. On the other hand we also know that it is not so in a dispersive medium for which the phase velocity is given by

$$V_\phi(k) = \frac{c}{n(k)} \qquad (35)$$

n(k) is the refractive index of the medium and varies with wavelength.

In present situation under study we have a dispersive medium, because in view of the relation (22) the phase velocity is

$$V_\phi(k) = \frac{\hbar k}{2m} \qquad (36)$$

We shall presently see that when the various waves have different phase velocities the maximum x_m of the wave packet does not move with the average phase velocity $\frac{\omega_0}{k_0} = \frac{\hbar k_0}{2m}$ contrary to what one would expect.

As above we again start with an attempt to understand qualitatively happens for a wave packet before taking up a general case. Let us therefore again consider a superposition of the three waves of the relation (28) for any time t, $\psi(x,t) is\, given by$

$$\psi(x,t)=\frac{g(k_0)}{\sqrt{2\pi}}\left\{e^{i(k_0x-\omega_0t)}+\frac{1}{2}e^{i\left[\left(k_0-\frac{\Delta k}{2}\right)x-\left(\omega_0-\frac{\Delta\omega}{2}\right)t\right]}+\frac{1}{2}e^{i\left[\left(k_0+\frac{\Delta k}{2}\right)x-\left(\omega_0+\frac{\Delta\omega}{2}\right)t\right]}\right\}$$

$$=\frac{g(k_0)}{\sqrt{2\pi}}e^{i(k_0x-\omega_0t)}\left[1+\cos\left(\frac{\Delta k}{2}x-\frac{\Delta\omega}{2}t\right)\right] \qquad (37)$$

We thus see that the maximum of $|\psi(x,t)|$, which at t = 0was at x = 0, is now at a point given by

$$x_m(t)=\frac{\Delta\omega}{\Delta k}t \qquad (38)$$

and not at the point

$$x=\frac{\omega_0}{k_0}t$$

This result is physically explained in the fig 4.5 below.

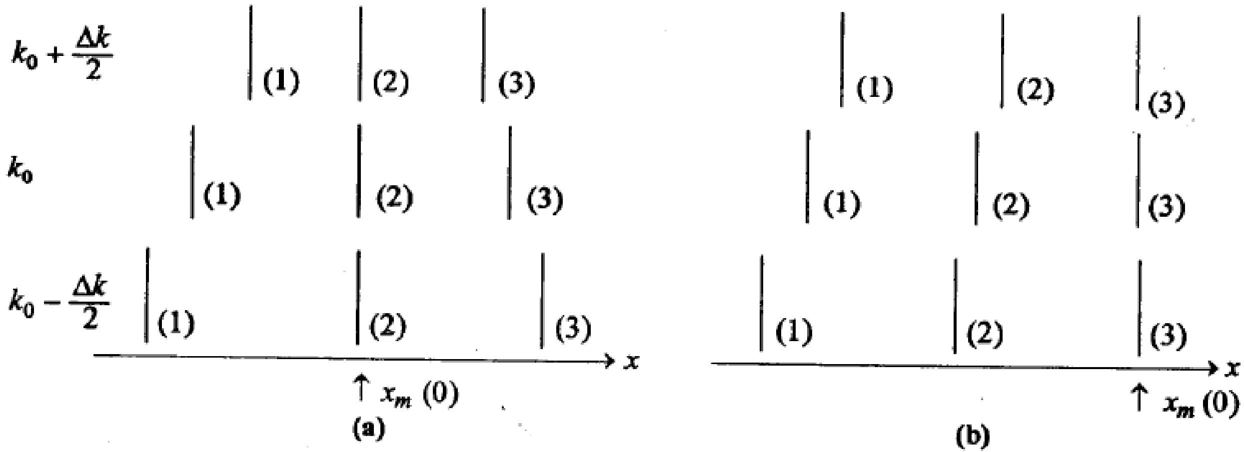

Fig 4.5

In the part (a) of this figure are shown the position of the three adjacent maximum (1),(2),(3) for each of the real parts of the three waves at t=0; the maxima indicated by (2) coincide at *x = 0* giving a constructive interference at this point which there corresponds to the position of the maximum of $|\psi(x,0)|$. As the phase velocity increases with k (relation 36) the maximum (3) of the wave $\left(k_0+\frac{\Delta k}{2}\right)$will slowly overtake that the wave (k_0) which in turn overtakes that of the wave $\left(k_0-\frac{\Delta k}{2}\right)$. At the end of certain time we will have the situation shown in part (b) of the figure: now these are maximum indicated by (3) which coincide and give the position of the maxima $x_m(t) of\ |\psi(x,t)|$ it is clear from the figure that $x_m(t)$ is not equal to $\frac{\omega_0}{k_0}t$ and a simple calculation will reproduce the formula (38).

The displacement of the centre of the wave packet (25) can be obtained in a similar way by applying the method of the “stationary phase. We can note that the form of the wave packet of free waves indicates that to change ψ(x, 0) to ψ(x, t) it is only necessary to change g(k) to $g(k)e^{-i\omega(k)t}$ the reasoning of the earlier paragraphs remains valid under a replacement of the argument α(k) of g(k) by :

$$\alpha(k)-\omega(k)t$$

The condition (31) *thus gives*

$$x_m(t)=\left[\frac{d\omega}{dk}\right]_{k=k_0} t-\left[\frac{d\alpha}{dk}\right]_{k=k_0}$$

We thus again arrive at the result (38) *the velocity of the maximum of the wave packet is*

$$V_s(k_0)=\left[\frac{d\omega}{dk}\right]_{k=k_0} \tag{39}$$

V_g (k_0) is called the group velocity of the wave packet. In view of the law of dispersion (22) we obtain; the following relation between the group velocity and the phase velocity:

$$V_s(K_o)=\frac{\hbar K_0}{m}=2V_\phi(k_0) \tag{40}$$

This result is important as it enables us to have a classical description of the free particles whenever we have a situation in which such a description is valid.

4.3 Let us sum up

From this chapter we have understood regarding the following concepts:

What is a wave packet? What is the mathematical description of the wave packet? What is the significance of the study of these wave packets? What is their role in quantum mechanics?

4.4 Key words:

Wave packet, Wave-packet duality, Fourier theorem, Fourier integral, Gaussian wave packet, Wave velocity, Phase velocity.

4.5 Questions for self study

What is a wave packet? What is the mathematical description of the wave packet?

What is the significance of the study of these wave packets? What is their role in quantum mechanics?

Discuss the wave packet concept in quantum mechanics.

Discuss the time dependence of free wave packet.

4.6 Problems

See problems on normalization of a wave function given in the next chapter.

4.7 References for further study

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UNIT 5: Time evolution and the Schrödinger equation. Spin precession, the Schrödinger and Heisenberg picture.

Structure:

5.0 Objectives

After studying this unit you will be able to understand the following aspects;

Introductory ideas regarding the Schrödinger equation in one dimension and three dimensions, Later the concept of time evolution operator is introduced. One gets an idea about the Schrödinger picture and the Heisenberg picture.

5.1 Introduction

Schrödinger equation:

The wave function of a particle moving in x-direction is represented as

$$\psi(x,t) = Ae^{-i(\omega t - k_x x)} = Ae^{i(k_x x - \omega t)} \quad ...(1)$$

The wave attributes k_x (= $2\pi/\lambda$) and ω (= $2\pi\nu$) are related to the particle attributes p_x and E as

$$p_x = \hbar k_x, \qquad E = \hbar\omega \quad ...(2)$$

In terms of p_x and E the wave function $\psi(x, t)$ can be expressed as

$$\psi(x,t) = A\exp\left\{-i\left(\frac{Et}{\hbar} - \frac{p_x x}{\hbar}\right)\right\} \quad ...(3)$$

From Eqn. (3)

$$\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\psi$$

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \quad ...(4)$$

Similarly,

$$\frac{\partial\psi}{\partial x} = \frac{ip_x}{\hbar}\psi$$

$$-i\hbar\frac{\partial\psi}{\partial x} = p_x\psi \quad ...(5)$$

Differentiating Eqn. (5) again with respect to x, we have

$$-i\hbar\frac{\partial^2\psi}{\partial x^2} = p_x\frac{\partial\psi}{\partial x} = i\frac{p_x^2}{\hbar}\psi$$

$$-\hbar^2\frac{\partial^2\psi}{\partial x^2} = p_x^2\psi \quad ...(6)$$

For a non-relativistic free particle the total energy E of the particle moving in x-direction is equal to its kinetic energy T.

$$\mathrm{E} = \mathrm{T} = \frac{p_x^2}{2m}$$

Multiplying both sides of above equation by ψ, we have

$$\mathrm{E}\psi = \frac{p_x^2}{2m}\psi \qquad \text{...(7)}$$

Making use of Eqns. (4) and (6) we can write Eqn. (7) as

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} \qquad \text{...(8)}$$

This equation is known as *time-dependent Schrödinger for a free particle.*

If the particle is moving in a force field described by potential energy function V, its total energy is

$$\mathrm{E} = \frac{p_x^2}{2m} + \mathrm{V}(x)$$

and the Schrödinger equation is

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \mathrm{V}\psi} \qquad \text{...(9)}$$

If the particle is free to in three dimensions, it is represented by wave function

$$\psi(x, y, z, t) = \mathrm{A}\exp\left\{-i\left(\omega t - k_x x - k_y y - k_z z\right)\right\}$$

$$= \mathrm{A}\exp\left\{-\frac{i}{\hbar}\left(Et - p_x x - p_y y - p_z z\right)\right\} \qquad \text{...(10)}$$

From Eqn. (10), we have

$$i\hbar\frac{\partial\psi}{\partial t} = \mathrm{E}\psi \qquad \text{...(11)}$$

$$-i\hbar\frac{\partial\psi}{\partial x} = p_x\psi \quad \text{and} \quad -\hbar^2\frac{\partial^2\psi}{\partial x^2} = p_x^2\psi \qquad \text{...(12)}$$

$$-i\hbar\frac{\partial\psi}{\partial y} = p_y\psi \quad \text{and} \quad -\hbar^2\frac{\partial^2\psi}{\partial y^2} = p_y^2\psi \qquad \text{...(13)}$$

$$-i\hbar\frac{\partial\psi}{\partial z} = p_z\psi \quad \text{and} \quad -\hbar^2\frac{\partial^2\psi}{\partial z^2} = p_z^2\psi \qquad \text{...(14)}$$

Total energy of the particle is

$$\mathrm{E} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x, y, z) \qquad \text{...(15)}$$

Making use of Eqns. (11) and (12, 13, & 14) we can write Eqn. (15) as

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \mathrm{V}\psi$$

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + \mathrm{V}\psi} \qquad \text{...(16)}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian operator. Eqn. (16) is known as the **time-dependent Schrödinger equation** of a particle in three dimensions.

Stationary State: Time- independent Schrodinger Equation: When the potential energy V is independent of time, the wave function ψ(x, t) may be written as product of two wave functions, of which one is functional of *x* and the other is function of *t* only.

$$\psi(x,t)=\psi(x)f(t) \qquad (17)$$

Substituting equation (16) in (10) and dividing the resulting equation throughout by ψ(x) f(t) we find

$$i\hbar\frac{1}{f(t)}\frac{df}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} + V \qquad (18)$$

The left hand side of eqn(18) is function of time t only and the right hand is function of x only. Since x and t are independent of each other, this equality can hold only if each side is equal to the same constant. Each side has the dimensions of energy, so we write the separation constant as E.

The separation constant E is a number and represents the total energy of the particle. Therefore

$$i\hbar \frac{1}{f(t)} \frac{df}{dt} = \mathrm{E} \qquad \text{...(19)}$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi}{dx^2} + \mathrm{V} = \mathrm{E} \qquad \text{...(20)}$$

Eqn. (19) can be expressed as

$$\frac{df}{dt} - \frac{E}{i\hbar} f = 0,$$

which integrates to

$$f(t) = \mathrm{C}\exp\left(-\frac{i\mathrm{E}t}{\hbar}\right) \qquad \text{...(21)}$$

where C is constant of integration. A particle whose state is described by wave function

$$\psi(x,t) = \psi(x).\, e^{-iEt/\hbar}$$

is said to be in stationary state because its probability density $\Psi^*(x,t)\Psi(x,t)$ or $|\Psi(x,t)|^2$ is independent of time.

The time independent Schrödinger equation can be expressed as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \mathrm{V}\psi = \mathrm{E}\psi \qquad \text{...(22)}$$

or $$\boxed{\hat{\mathrm{H}}\psi = \mathrm{E}\psi} \qquad \text{...(23)}$$

where $$\hat{\mathrm{H}} = \frac{\hat{p}^2}{2m} + \mathrm{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathrm{V}$$

is *Hamiltonian operator*, an operator representing the total energy of the particle. Eqn. (22) can also be written as

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(\mathrm{E}-\mathrm{V})\psi = 0} \qquad \text{...(24)}$$

[For a system whose potential energy V is a function of coordinates only, the total energy remains constant with time i.e., E is conserved. For such a system, the classical mechanical Hamiltonian function turns out to be the total energy in terms of coordinates and conjugate momenta].

The time-dependent Schrödinger equation can be written as

$$\hat{H}\psi(x,t) = \hat{E}\psi(x,t)$$

where $$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V} \quad \text{and} \quad \hat{E} = i\hbar\frac{\partial}{\partial t}.$$

5.2 Physical Significance of Wave Function ψ

It is natural to ask the question regarding the physical significance of the wave function ψ. For a vibrating string, it represents the displacement of the string from equilibrium position; in case of electromagnetic waves it represents the electric or magnetic field at the point under consideration. But there is no physical quantity with which the wave function ψ of matter wave may be associated. Just as the concepts of electric and magnetic field are abstraction to explain the interaction between electrical charges, the concept of wave function ψ is an abstraction to describe the dynamics of microscopic particles. But such an interpretation of ψ is of little significance.

In 1926 Max Born suggested a useful statistical interpretation of wave function, which was inspired by Einstein's concept of wave like behavior of particle like photons. According to Einstein the propagation of photon in space is described by Maxwell's equation involving electric field E (x, y, z, t) and magnetic field B (x, y, z, t). The magnitude of field E and B provides the probability of the location of the photon. In the region where E and B are large, the likelihood of finding the photon is also large and vice-versa. It is therefore reasonable to associate a probability function P with wave amplitude E**.** The probability function P (x, y, z, t) expresses the likelihood of finding the photon and is related to the wave amplitude E (x,y,z,t) as

$$P(x,y,z,t) = |E(x,y,z,t)|^2$$

According to Born, the wave function ψ(x,y,z,t) is analogous to the electric field E and Einstein's interpretation can be utilized to provide a physical meaning to the wave function associated with the material particles. The probability of finding a particle at (x,y,z) at time t is given by $|\psi(x,y,z,t)|^2$ or $\psi\,\psi^*$ where ψ^* is the complex conjugate of ψ. The probability of finding the particle in a volume element dxdydz centered around the point (x,y,z) is given by

$$|\psi(x,y,z,t)|^2\, dxdydz \quad \text{or} \quad \psi\,\psi^* dxdydz.$$

Thus $|\psi|^2$ is the probability density and ψ itself is called as the probability amplitude.

Since the probability of finding the particle somewhere in the universe is unity, we have:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi\psi^{*}dx\,dy\,dz=1 \qquad (25)$$

5.3 Normalization of the Wave function

Now the probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. The probability of a measurement of *x*

$$P_{x\in-\infty:\infty}(t)=\int_{-\infty}^{\infty}\left|\psi\,(x,t)\right|^{2}dx \qquad (26)$$

However a measurement of x must yield a value between -∞ and +∞, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}=1$,

$$\int_{-\infty}^{\infty}\left|\psi(x,t)\right|^{2}dx=1 \qquad (27)$$

Which is generally known as the normalization condition for the wave function

For example suppose that we wish to normalize the wave function of a Gaussian wave packet, centered on $x=x_0$ and of characteristic width σ :

$$\psi(x)=\psi_0 e^{-(x-x_0)^2/(4\sigma^2)} \qquad (28)$$

In order to determine the normalization constant ψ_0 we simply substitute Eq. (28) into Eq. (27) to obtain

$$\left|\psi_0\right|^2\int_{-\infty}^{\infty}e^{-(x-x_0)^2/(2\sigma^2)}dx=1 \qquad (29)$$

Changing the variable of integration to $y=(x-x_0)/(\sqrt{2}\,\sigma)\, we\, get$

$$\left|\psi_0\right|^2\sqrt{2}\sigma\int_{-\infty}^{\infty}e^{-y^2}dy=1$$

However,

$$\int_{-\infty}^{\infty}e^{-y^2}dy=\sqrt{\pi}$$

Which implies that;

$$\left|\psi_0\right|^2=\frac{1}{\left(2\pi\sigma^2\right)^{1/2}} \qquad (30)$$

Hence, a general normalized Gaussian wavefunction takes the form

$$\psi(x) = \frac{e^{i\phi}}{\left(2\pi\sigma^2\right)^{1/4}} e^{-\left(x-x_0\right)^2/4\sigma^2} \qquad (31)$$

where ϕ is an arbitrary real phase-angle.

Now, it is important to demonstrate that if a wave function is initially normalized then it stays normalized as it evolves in time a according to Schrödinger's equation. If this is not the case then the probability interpretation of the wave function is untenable, since it does not make sense for the probability that a measurement of *x* yields any possible outcome (which is manifestly unity) to change in time. Hence we required that

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\psi(x,t)|^2\,dx = 0, \qquad (32)$$

for wavefunctions satisfying Schrodinger's equation. The above equation gives

$$\frac{d}{dt}\int_{-\infty}^{\infty} \psi^*\,\psi\,dx = \int_{-\infty}^{\infty}\left(\frac{\partial\psi^*}{\partial t}\,\psi + \psi^*\,\frac{\partial\psi}{\partial t}\right)\,dx = 0. \qquad (33)$$

Now, multiplying Schrödinger's equation by $\psi^*/(i\,\hbar)$, we obtain

$$\psi^*\,\frac{\partial\psi}{\partial t} = \frac{i\,\hbar}{2\,m}\,\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \frac{i}{\hbar}\,V\,|\psi|^2.$$

The complex conjugate of this expression yields

$$\psi\,\frac{\partial\psi^*}{\partial t} = -\frac{i\,\hbar}{2\,m}\,\psi\,\frac{\partial^2\psi^*}{\partial x^2} + \frac{i}{\hbar}\,V\,|\psi|^2$$

[since $(A\,B)^* = A^*\,B^*$, $A^{**} = A$, and $i^* = -i$]. Summing the previous two equations, we get

$$\frac{\partial\psi^*}{\partial t}\,\psi + \psi^*\,\frac{\partial\psi}{\partial t} = \frac{i\,\hbar}{2\,m}\left(\psi^*\,\frac{\partial^2\psi}{\partial x^2} - \psi\,\frac{\partial^2\psi^*}{\partial x^2}\right) = \frac{i\,\hbar}{2\,m}\,\frac{\partial}{\partial x}\left(\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right).$$

Thus,

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = \frac{i\hbar}{2\,m}\left[\psi^*\,\frac{\partial\psi}{\partial x} - \psi\,\frac{\partial\psi^*}{\partial x}\right]_{-\infty}^{\infty} = 0.$$

The above equation is satisfied provided

$$|\psi| \to 0 \quad \text{as} \quad |x| \to \infty.$$

However this is an necessary condition for the integral on the left-hand side Eq.(27) to converge. Hence we conclude that all wave functions which are *square integrable* [i.e., are such that the integral in Eq (27) converges] have the property that if the normalization condition (27) is satisfies at one instant in time then it is satisfied at all subsequent times.

It is also possible to demonstrate via very similar analysis to above that

$$\frac{dp_{x\in a:b}}{dt} + j(b,t) - j(a,t) = 0 \qquad (36)$$

Where

$$j(x,t) = \frac{i\hbar}{2m}\left(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right)$$

is known as the probability current. Note that *j* is real. Equation (36) is a *probability conservation equation*. According to this equation the probability of a measurement of x lying in the interval a to b evolves in time due to the difference between the flux of probability into the interval [i.e., j(a, t)] and that our of the interval [i.e., j(b, t)]. Here we are interpreting j(x, t) as the flux of probability in the +x- direction at position *x* and time *t.*

Note finally that not all wave function can be normalized according to the scheme set out in equation (4.4) for instance a plane wave function

$$\psi(x,t) = \psi_0 e^{i(kx-\omega t)}$$

Is not square integrable and thus cannot be normalized. For such wavefunctions, the best we can say is that

$$P_{x\in a:b(t)} \propto \int_a^b |\psi(x,t)|^2\,dx \qquad (4.21)$$

In the following all wave functions are assumed to be square integrable and normalized unless otherwise stated.

5.4 Quantum Dynamics

Variation of expectation value of an operator i.e., $\langle \hat{A} \rangle$ can be due to;

i) Change of state vector ψ with time, but $\hat{A}$ remaining unchanged (Schrodinger picture).

ii) Change of $\hat{A}$ with time, ψ remaining constant (Heisenberg picture)

iii) Change of both ψ & $\hat{A}$ with time (interaction picture).

Time evolution operator & Schrodinger Picture:

Dynamical Postulate: Corresponding to every quantum mechanical system, there exists a family of lower operators $\hat{U}(t,t_0)$ defined on the infinite distance. Hilbert space of the system which describe the evolution of the state vector from time t_0 to time t;

$$\psi(t)=\hat{U}(t,t_0)\psi(t_0)$$

Here $\hat{U}$ is called the time evolution operator

Some of its properties are:

$$\hat{U}(t_0,t_0)=\hat{I}$$

$$\hat{U}(t_0,t)\hat{U}(t,t_0)=\hat{I}$$

$$\hat{U}(t,t_0)\hat{U}(t_0,t)=\hat{I}$$

$$U^{\dagger}(t,t_0)=\hat{U}^{-1}(t,t_0)$$

$$U^{-1}(t,t_0)=\hat{U}(t_0,t)$$

We have $\psi(t)=\hat{U}(t,t_0)\psi(t_0)$ (38)

So that $\hat{U}(t_1,t)\hat{U}(t,t_0)=\hat{U}(t_1,t_0)$ (39)

i.e., $\hat{U}(t,t_1)\hat{U}(t_1,t_0)=\hat{U}(t,t_0)$ (40)

Putting $t_1=t-\delta t$ *where* δt *is infinitesimal, we have;*

$$\hat{U}(t,t_0)=\hat{U}(t,t-\delta t)\hat{U}(t-\delta t,t_0) \qquad (41)$$

$\hat{U}(t,t-\delta t)$ *is an infinitesimal operator (unitary) and can be written as:*

$$\hat{U}(t,t-\delta t)=\hat{I}-\left(\frac{i}{\hbar}\right)\delta t\,\hat{H}(t) \qquad (42)$$

where the Hermitian operator $\hat{H}(t)$ is called the generator of the infinitesimal unitary transformation $\psi(t-\delta t)\rightarrow\psi(t)$.

Using (42), (41) becomes;

$$\hat{U}(t,t_0) = \hat{U}(t-\delta t,t_0) - \left(\frac{i}{\hbar}\right)\delta t\,\hat{H}(t)\hat{U}(t-\delta t,t_0)$$

$$i.e.,\ \frac{U(t,t_0) - \hat{U}(t-\delta t,t_0)}{\delta t} = -\left(\frac{i}{\hbar}\right)\hat{H}(t)\hat{U}(t-\delta t,t_0)$$

$$Taking\ the \lim it\quad \delta t \to 0\ we\ get$$

$$\frac{\partial\hat{U}(t,t_0)}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{H}(t)\hat{U}(t,t_0)$$

$$i.e.,\quad i\hbar\frac{\partial\hat{U}(t,t_0)}{\partial t} = \hat{H}(t)\hat{U}(t,t_0)$$

Integrating this with respect to t between the limits t_0 and t we get

$$\int_{t_0}^{t} d\hat{U}(t',t_0) = -\left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\hat{H}(t')\hat{U}(t',t_0)\,dt'$$

$$i.e.,\ \hat{U}(t,t_0) = \hat{I} - \left(\frac{i}{\hbar}\right)\int_{t_0}^{t}\hat{H}(t')\hat{U}(t',t_0)\,dt'$$

$$i.e.,\quad i\hbar\frac{\partial\hat{U}(t,t_0)}{\partial t} = \hat{H}(t)\hat{U}(t,t_0)\psi(t_0)$$

$$i.e.,\ i\hbar\frac{\partial\psi(t)}{\partial t} = \hat{H}(t)\psi(t) \qquad (43)$$

This is the equation of motion for the state vector and is known as the time dependent Schrodinger equation

5.5 Heisenberg picture: Heisenberg's equation of motion:

Here we shall write the state vector and operator as ψ_H *and* $\hat{A}_H$. In this case ψ_H is time independent and $\hat{A}_H$ depends on time

Let us define

$$\psi_H(t) \text{ by } \psi_H(t) = \hat{U}^{-1}(t,t_0)\psi(t)$$

$$\text{Since it is time independent } \psi_H(t) = \psi(t_0)$$

$$(\psi \text{ is the state vector in Schrodinger picture})$$

$$\text{The relation between the operator in Heisenberg and Schrodinger picture is}$$

$$\hat{A}_H(t) = U^{-1}(t,t_0)\hat{A}\hat{U}(t,t_0)$$

$$= U^{\dagger}(t,t_0)\hat{A}\hat{U}(t,t_0)$$

$$\text{Thus } \frac{d\hat{A}_H}{dt} = \frac{\partial U^{\dagger}}{\partial t}\hat{A}\hat{U} + U^{\dagger}\hat{A}\frac{\partial \hat{U}}{\partial t}$$

$$\text{But we know that } \quad i\hbar\frac{\partial \hat{U}}{\partial t} = \hat{H}(t)\hat{U}(t,t_0)$$

$$\therefore \frac{\partial \hat{U}}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{H}\hat{U} \text{ and } \quad \frac{\partial \hat{U}^{\dagger}}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{U}^{\dagger}\hat{H}$$

$$\therefore \frac{d\hat{A}_H}{dt} = \left(\frac{i}{\hbar}\right)\left\{\hat{U}^{\dagger}\hat{H}\hat{A}\hat{U} - \hat{U}^{\dagger}\hat{A}\hat{H}\hat{U}\right\}$$

$$= \left(\frac{i}{\hbar}\right)\left\{U^{\dagger}\hat{H}\hat{U}\hat{U}^{\dagger}\hat{A}\hat{U} - \hat{U}^{\dagger}\hat{A}\hat{U}\hat{U}^{\dagger}\hat{H}\hat{U}\right\}$$

$$= \left(\frac{i}{\hbar}\right)\left(\hat{H}_H\hat{A}_H - \hat{A}_H\hat{H}_H\right)$$

$$= -\left(\frac{i}{\hbar}\right)\left[\hat{H}_H, \hat{A}_H\right]$$

$$\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}_H\right] \qquad (44)$$

$$\text{If } \hat{A}_H \text{ explicitly depends on time then}$$

$$\frac{d\hat{A}_H}{dt} = \frac{\partial \hat{A}_H}{\partial t} + \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}_H\right] \qquad (45)$$

Equation (44) and (45) are called as Heisenberg's equation of motion for the operator $\hat{A}_H$.

In Heisenberg picture the equation of motion for the expectation value $\left\langle \hat{A}_H \right\rangle$ is given by

$$\frac{d}{dt}\left\langle \hat{A}_H \right\rangle \equiv \frac{d}{dt}\left\langle \psi_H \left| \hat{A}_H(t) \right| \psi_H \right\rangle$$

$$= \left\langle \psi_H \left| \frac{d\hat{A}_H}{dt} \right| \psi_H \right\rangle$$

$$= \left\langle \frac{1}{i\hbar}\left[\hat{A}_{H,} \hat{H}_H \right] \right\rangle if \ \hat{A}_H \ has \ no \ \exp licit \ \ dependance \ on \ time \ and$$

$$\frac{d\left\langle \hat{A}_H \right\rangle}{dt} = \left\langle \frac{\partial \hat{A}_H}{\partial t} \right\rangle + \left\langle \frac{1}{i\hbar}\left[\hat{A}_{H,} \hat{H}_H \right] \right\rangle if \ \hat{A}_H \ has \exp lict \ dependence \ on \ time$$

Equations of motion for expectation values in the Heisenberg and Schrödinger picture are the same

5.6 Let us sum up

In this section we have considered ideas regarding the Schodinger equation in one dimension and three dimensions. Also we have understood the physical significance of the wave function. Later the concept of time evolution operator is introduced. Also, we gained the idea about the Schodinger picture and the Heisenberg picture.

5.7 Key words

Wave function, One dimension, Three dimension, Schodinger equation, Time evolution, Schodinger picture, Heisenberg picture.

5.8 Problems

Example1

Suppose $\psi(x,t) = A(x - x^3)e^{-iEt/\hbar}$. Find V(x) such that the Schrodinger equation is satisfied

Solution:

The wave function is written as a product:

$$\Psi(x,t) = \Phi(x)\exp(-iEt/\hbar)$$

Therefore it is not necessary to work with the full Schrödinger equation. Recalling the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Phi(x)}{\partial x^2} + V(x)\Phi(x) = E\Phi(x)$$

We set $\Phi(x) = A(x - x^3)$ and solve to find V. The right-hand side is simply:

$$E\Phi(x) = EA(x - x^3)$$

To find the form of the left-side of the equation, we begin by computing the first derivative:

$$\frac{\partial\Phi(x)}{\partial x} = \frac{\partial}{\partial x}\left[A(x - x^3)\right] = A(1 - 3x^2)$$

For the second derivative, we obtain:

$$\frac{\partial^2\Phi(x)}{\partial x^2} = \frac{\partial}{\partial x}\left(A(1 - 3x^2)\right) = -6Ax, \Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\Phi(x)}{\partial x^2} = \frac{\hbar^2}{2m}6Ax$$

Putting this in the left-side of the time-independent Schrödinger equation and equating this to $EA(x - x^3)$ gives:

$$\frac{\hbar^2}{2m}6Ax + V(x)A(x - x^3) = EA(x - x^3)$$

Now subtract $(\hbar^2/2m)6Ax$ from both sides:

$$V(x)A(x - x^3) = EA(x - x^3) - \frac{\hbar^2}{2m}6Ax$$

Dividing both sides by $A(x - x^3)$ gives us the potential:

$$V(x) = E - \frac{\hbar^2}{2m}\frac{6x}{(x - x^3)}$$

Example 2

The wave function for a particle contined to $0 \le x \le a$ in a ground state was found to be

$$\Psi(x) = A\sin(\pi x/a)$$

where A is the normalization constant. Find A and determine the probability that the particle is found in the interval $\frac{a}{2} \le x \le \frac{3a}{4}$.

SOLUTION

Normalization means that:

$$\int_{-\infty}^{\infty} |\psi|^2\, dx = 1$$

The wavefunction is zero outside of the interval, $0 \le x \le a$, therefore we only need to consider

$$\int_0^a |\psi|^2\, dx = \int_0^a A^2 \sin^2\left(\frac{\pi x}{a}\right) dx = A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx$$

We use the trigometric identity $\sin^2 u = (1 - \cos 2u)/2$ to rewrite the integrand:

$$A^2 \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = A^2 \int_0^a \frac{1 - \cos\left(\frac{2\pi x}{a}\right)}{2} dx$$

$$= \frac{A^2}{2}\int_0^a dx - \frac{A^2}{2}\int_0^a \cos\left(\frac{2\pi x}{a}\right) dx$$

The first term can be integrated immediately:

$$\frac{A^2}{2}\int_0^a dx = \frac{A^2}{2}x\Big|_0^a = A^2\frac{a}{2}$$

For the second term, let $u = (2\pi x)/a, \Rightarrow du = (2\pi)/a\, dx$ and:

$$\int_0^a \cos\left(\frac{2\pi x}{a}\right) dx = \frac{a}{2\pi}\int_0^{2\pi} \cos(u) du = \frac{a}{2\pi}\sin(u)\Big|_0^{2\pi}$$

$$\frac{a}{2\pi}\left[\sin(2\pi) - \sin(0)\right] = 0$$

And so, only the first term contributes and we have:

$$\int_0^a |\psi|^2\, dx = \frac{A^2}{2}a = 1$$

Solving for the normalization constant A, we find:

$$A = \sqrt{\frac{2}{a}}$$

and the normalized wavefunction is:

$$\psi(x) = \sqrt{\frac{2}{a}}\sin(\pi x/a)$$

The probability that the particle is found in the interval $a/2 \leq x \leq 3a/4$ is given by:

$$P\left(\frac{a}{2} \leq x \leq \frac{3a}{4}\right) = \int_{\frac{a}{2}}^{\frac{3a}{4}} |\psi(x)|^2\, dx = \int_{\frac{a}{2}}^{\frac{3a}{4}} \left(\frac{2}{a}\right) \sin^2\left(\frac{\pi x}{a}\right) dx$$

$$= \left(\frac{2}{a}\right) \int_{\frac{a}{2}}^{\frac{3a}{4}} \frac{1-\cos(2\pi x)}{2} dx$$

$$= \frac{1}{a}\int_{\frac{a}{2}}^{\frac{3a}{4}} dx - \frac{1}{a}\int_{\frac{a}{2}}^{\frac{3a}{4}} \cos\left(\frac{2\pi x}{a}\right) dx$$

$$= \frac{1}{a}x\bigg|_{\frac{a}{2}}^{\frac{3a}{4}} - \frac{1}{2\pi}\sin\left(\frac{2\pi x}{a}\right)\bigg|_{\frac{a}{2}}^{\frac{3a}{4}}$$

$$= \frac{1}{a}\left[\frac{3a}{4} - \frac{a}{2}\right] - \frac{1}{2\pi}\left[\sin\left(\frac{6\pi}{4}\right) - \sin(\pi)\right]$$

$$= \frac{1}{a}\left[\frac{a}{4}\right] - \frac{1}{2\pi}\sin\left(\frac{3\pi}{2}\right)$$

$$= \frac{1}{4} + \frac{1}{2\pi} = \frac{\pi + 2}{4\pi} = 0.41$$

Example 3.

Find an A and B so that

$$\Phi(x) = \begin{cases} A & \text{for } 0 \leq x \leq a \\ Bx & \text{for } a \leq x \leq b. \end{cases}$$

is normalized.

SOLUTION

$$\int_{-\infty}^{\infty} |\Phi(x)|^2\, dx = \int_0^a A^2 dx + \int_a^b B^2 x^2 dx$$

$$= A^2 x\big|_0^a + \frac{B^2(x^3)}{3}\ \big|_a^b = A^2 a + \frac{B^2(b^3 - a^3)}{3}$$

Using $\int_{-\infty}^{\infty} |\Phi(x)|^2\, dx = 1$, we obtain:

$$A^2 a + \frac{B^2(b^3 - a^3)}{3} = 1, \Rightarrow A^2 = \left(\frac{1}{a}\right)\left(1 - \frac{B^2(b^3 - a^3)}{3}\right)$$

As long as $\int_{-\infty}^{\infty} |\Phi(x)|^2\, dx = 1$ is satisfied, we are free to arbitrarily choose one of the constants as long as it's not zero. So we set $B = 1$:

$$A^2 = \left(\frac{1}{a}\right)\left(1 - \frac{(b^3 - a^3)}{3}\right), \Rightarrow A = \sqrt{\frac{1}{a}\left(1 - \frac{(b^3 - a^3)}{3}\right)}$$

EXAMPLE 4.

Normalize the wave function

$$\psi(x) = \frac{C}{x^2 + a^2}$$

SOLUTION

We start by finding the square of the wavefunction:

$$|\psi(x)|^2 = \frac{C^2}{(x^2 + a^2)^2}$$

To compute $\int |\psi(x)|^2\, dx$, we will need two integrals which can be found in integration tables. These are:

$$\int \frac{du}{u^2 + a^2} = \frac{1}{a}\tan^{-1}\frac{u}{a} \text{ and } \int \frac{du}{(u^2 + a^2)^2} = \frac{1}{2a^2}\left(\frac{u}{u^2 + a^2}\right) + \int \frac{du}{u^2 + a^2}$$

We begin by using the second of these:

$$\Rightarrow \int_{-\infty}^{\infty} |\psi(x)|^2\, dx = C^2 \int_{-\infty}^{\infty} \frac{dx}{(x^2 + a^2)^2}$$

$$= \frac{C^2}{2a^2}\left(\left.\frac{x}{x^2 + a^2}\right|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \frac{dx}{x^2 + a^2}\right)$$

Where the first term is to be evaluated at $\pm\infty$. Consider the limit as $x \to \infty$:

$$\lim_{x\to\infty} \frac{x}{x^2 + a^2} = \lim_{x\to\infty} \frac{1}{2x} = 0$$

where L'Hopitals rule was used. Similarly, for the lower limit we find:

$$\lim_{x\to-\infty} \frac{x}{x^2 + a^2} = \lim_{x\to-\infty} \frac{1}{2x} = 0$$

So we can discard the first term altogether. Now we can use $\int (du)/(u^2 + a^2) = (1/a)\tan^{-1}(u/a)$ for the remaining piece.

$$\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = \frac{C^2}{2a^2}\int_{-\infty}^{\infty} \frac{dx}{x^2 + a^2} = \frac{C^2}{2a^2}\left(\frac{1}{a}\right)\tan^{-1}\left.\frac{x}{a}\right|_{-\infty}^{\infty}$$

$$= \lim_{u\to\infty} \frac{C^2}{2a^3}\left[\tan^{-1}(u) - \tan^{-1}(-u)\right]$$

$$= \frac{C^2}{2a^3}\left[\frac{\pi}{2} - \left(-\frac{\pi}{2}\right)\right] = \frac{C^2}{2a^3}\pi$$

Again we recall that the normalization condition is:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$$

therefore, setting our result equal to one we find that:

$$\frac{C^2}{2a^3}\pi = 1 \Rightarrow C = \sqrt{\frac{2a^3}{\pi}}$$

And so, the normalized wavefunction is:

$$\psi(x) = \sqrt{\frac{2a^3}{\pi}} \frac{1}{x^2 + a^2}$$

5.9 Questions for self study

Discuss the time evolution operator and its properties in quantum mechanics.

Discuss the time evolution operator and its significance in quantum mechanics.

Distinguish between Schodinger picture and Heisenberg picture.

5.10 References for further study

- Introduction to Modern Physics by R.B.Singh, Vol1, 2nd Edn.

UNIT 6: The Heisenberg equation of motion, free particles, Ehrenfest's theorem.

Structure:

6.0 Objectives:

After studying this unit you will be able to understand the following aspects;

- Heisenberg equation of motion
- Expectation value
- Ehrenfest's theorem

6.1 Introduction:

In quantum mechanics we have come across several types of equations which describe the motion of quantum mechanical particles. In this section we shall discuss the Heisenberg equations of motion which is based on Heisenberg picture. Also, we shall discuss the expectation value of an observable and the method of arriving at it. Later we shall discuss the Ehrenfest's theorem in case of the position coordinate and the momentum coordinate.

6.2 Heisenberg equation of motion:

Here we shall write the state vector and operator as ψ_H *and* $\hat{A}_H$. In this case ψ_H is time independent and $\hat{A}_H$ depends on time

Let us define

$$\psi_H(t) \ \ by \ \ \psi_H(t) = \hat{U}^{-1}(t,t_0)\psi(t)$$

$$Since \ it \ is \ time \ independent \ \ \psi_H(t) = \psi(t_0)$$

$$(\psi \ is \ the \ state \ vector \ in \ Schrodinger \ picture)$$

$$The \ relation \ between \ the \ operator \ in \ Heisenberg \ and \ Schrodinger \ picture \ is$$

$$\hat{A}_H(t) = U^{-1}(t,t_0)\hat{A}\hat{U}(t,t_0)$$

$$= U^{\dagger}(t,t_0)\hat{A}\hat{U}(t,t_0)$$

$$Thus \frac{d\hat{A}_H}{dt} = \frac{\partial U^{\dagger}}{\partial t}\hat{A}\hat{U} + U^{\dagger}\hat{A}\frac{\partial \hat{U}}{\partial t}$$

$$But \ we \ know \ that \quad i\hbar\frac{\partial \hat{U}}{\partial t} = \hat{H}(t)\hat{U}(t,t_0)$$

$$\therefore \frac{\partial \hat{U}}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{H}\hat{U} \ \ and \ \ \frac{\partial \hat{U}^{\dagger}}{\partial t} = -\left(\frac{i}{\hbar}\right)\hat{U}^{\dagger}\hat{H}$$

$$\therefore \frac{d\hat{A}_H}{dt} = \left(\frac{i}{\hbar}\right)\left\{\hat{U}^{\dagger}\hat{H}\hat{A}\hat{U} - \hat{U}^{\dagger}\hat{A}\hat{H}\hat{U}\right\}$$

$$= \left(\frac{i}{\hbar}\right)\left\{U^{\dagger}\hat{H}\hat{U}\hat{U}^{\dagger}\hat{A}\hat{U} - \hat{U}^{\dagger}\hat{A}\hat{U}\hat{U}^{\dagger}\hat{H}\hat{U}\right\}$$

$$= \left(\frac{i}{\hbar}\right)\left(\hat{H}_H\hat{A}_H - \hat{A}_H\hat{H}_H\right)$$

$$= -\left(\frac{i}{\hbar}\right)\left[\hat{H}_H, \hat{A}_H\right]$$

$$\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}_H\right] \qquad (1)$$

$$If \ \hat{A}_H \ \text{exp} \ licitly \ depends \ on \ time \ then$$

$$\frac{d\hat{A}_H}{dt} = \frac{\partial \hat{A}_H}{\partial t} + \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}_H\right] \qquad (2)$$

Equation (1) and (2) are called as Heisenberg's equation of motion for the operator $\hat{A}_H$.

6.3 Expectation value:

When the wave function ψ of a system is not an Eigen function of operator $\hat{Q}$ representing an observable Q of the system then the measurement of Q with identical systems will give various possible values. The expectation value of observable Q is equal to the average value of the results of these measurements.

The expectation value of a physical quantity Q represented by operator $\hat{Q}$ is defined by

$$\langle \mathrm{Q} \rangle = \int \psi^* \hat{\mathrm{Q}} \psi d\tau$$

Where ψ is the state of the system. If the wave function ψ is not normalized the expectation value is given by

$$\langle \mathrm{Q} \rangle = \frac{\int \psi^* \hat{\mathrm{Q}} \psi d\tau}{\int \psi^* \psi d\tau}$$

The expectation values of the physical quantities x, p_x, p, E etc., with respect to the state ψ are calculated from the following equation respectively

$$\langle x \rangle = \int \psi^* x \psi d\tau$$

$$\langle p_x \rangle = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi d\tau$$

$$\langle p \rangle = \int \psi^* \left(-i\hbar \nabla \right) \psi d\tau$$

$$\langle \mathrm{E} \rangle = \int \psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \psi \, d\tau$$

$$\left\langle \frac{p^2}{2m} \right\rangle = \int \psi^* \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \psi d\tau$$

$$\langle \mathrm{V} \rangle = \int \psi^* \mathrm{V} \psi d\tau$$

Since $\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle$ we have

$$\langle E \rangle = \int \psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi d\tau + \int \psi^* V \psi d\tau.$$

6.4 Ehrenfest's theorem:

The theorem states that the classical equation of motion viz

$$\frac{dx}{dt} = \frac{P_x}{m}; \qquad \frac{dp_x}{dt} = -\frac{\partial V}{\partial x} = F_x$$

are valid in Quantum mechanics if we replace the physical quantities such as x, p_x by their expectation values. Thus the Quantum equations of motion are;

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m}$$

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

In other words, the expectation value of physical quantities obeys classical equations of motion.

Proof: The time derivative of expression value of position coordinate x is

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

$$= \int \psi^* x \frac{\partial \psi}{\partial t} d\tau \quad + \quad \int \frac{\partial \psi^*}{\partial t} x \psi d\tau$$

All changes in x with time are being determined by the change in ψ therefore there is no term like $\frac{\partial x}{\partial t}$ in above equation. This is how Schrödinger mechanics works.

Substituting the values $\frac{\partial \psi}{\partial t}$ *and* $\frac{\partial \psi^*}{\partial t}$ of obtained from Schrödinger equation into the above equation, we have;

$$\frac{d}{dt}\langle x\rangle = \int \psi^* x \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right) + \int -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*\right) x\psi d\tau$$

$$= \frac{1}{i\hbar}\int \frac{-\hbar^2}{2m}\left(\psi^* x\nabla^2\psi - \nabla^2\psi^* x\psi\right) d\tau$$

$$= \frac{i\hbar}{2m}\int \left[\psi^* x\nabla^2\psi - (\nabla^2\psi^*)(x\psi)\right] d\tau$$

$$= \frac{i\hbar}{2m}\int \psi^* x\nabla^2\psi d\tau - \mathrm{I}$$

where

$$\mathrm{I} \;=\; \frac{i\hbar}{2m}\int (\nabla^2\psi^*)(x\psi) d\tau$$

Making use of the identity

$$\nabla.(\varphi\mathbf{A}) = \nabla\varphi.\mathbf{A} + \varphi\nabla.\mathbf{A}$$

We can write

$$\nabla.(x\psi\nabla\psi^*) = \nabla x\psi.\nabla\psi^* + x\psi\nabla^2\psi^* \qquad \ldots(a)$$

Interchanging $x\psi$ and ψ^*, we obtain

$$\nabla.(\psi^*\nabla x\psi) = \nabla\psi^*.\nabla(x\psi) + \psi^*\nabla^2(x\psi) \qquad \ldots(b)$$

In view of (a) we have

$$\mathrm{I} \;=\; \frac{i\hbar}{2m}\int\left\{\nabla.(x\psi\nabla\psi^*) - \nabla x\psi\cdot\nabla\psi^*\right\}d\tau$$

$$= \frac{i\hbar}{2m}\left\{\int (x\psi\nabla\psi^*)\cdot ds - \int \nabla x\psi\cdot\nabla\psi^* d\tau\right\}$$

Where use of divergence theorem has been made to transform the volume integral into surface integral. The surface integral vanishes because $\psi \to 0\, as\, x \to \infty. So$

$$\mathrm{I} \;=\; \frac{i\hbar}{2m}\int\left(-\nabla x\psi\cdot\nabla\psi^*\right)d\tau$$

Making use of (*b*), we have

$$\mathbf{I} = \frac{i\hbar}{2m}\int[\psi^*\nabla^2(x\psi) - \nabla\cdot(\psi^*\nabla x\psi)]d\tau$$

$$= \frac{i\hbar}{2m}\int\psi^*\nabla^2(x\psi)d\tau - \frac{i\hbar}{2m}\int\psi^*\nabla(x\psi)\cdot ds$$

$$= \frac{i\hbar}{2m}\int\psi^*\nabla^2(x\psi)d\tau + 0 \quad \text{(The surface integral again vanishes)}$$

Thus we have:

$$\frac{d}{dt}\langle x\rangle = \frac{i\hbar}{2m}\int\left[\psi^* x\nabla^2\psi - \psi^*\nabla^2 x\psi\right]d\tau$$

$$= \frac{i\hbar}{2m}\int\psi^*\left(x\frac{d^2\psi}{dx^2} - \frac{d^2}{dx^2}(x\psi)\right)d\tau$$

$$= \frac{i\hbar}{2m}\int\psi^*\left(x\frac{d^2\psi}{dx^2} - x\frac{d^2\psi}{dx^2} - 2\frac{d\psi}{dx}\right)d\tau$$

$$= \frac{i\hbar}{2m}\int\psi^*\left(-2\frac{d\psi}{dx}\right)d\tau$$

$$= \frac{1}{m}\int\psi^*\left(-i\hbar\frac{d}{dx}\right)\psi d\tau$$

$$= \frac{1}{m}\langle p_x\rangle$$

Similarly,

$$\frac{d}{dt}\langle p_x\rangle = \frac{d}{dt}\int\psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right)d\tau$$

$$= -i\hbar\int\left(\psi^*\frac{\partial}{\partial x}\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\frac{\partial\psi}{\partial x}\right)d\tau$$

Substituting the value of $\frac{\partial\psi}{\partial t}$ and $\frac{\partial\psi^*}{\partial t}$ from Schrödinger equation, we obtain

$$\frac{d}{dt}\langle p_x\rangle = \frac{\hbar^2}{2m}\int\left(\psi^*\frac{\partial}{\partial x}\nabla^2\psi - \nabla^2\psi^*\frac{\partial\psi}{\partial x}\right)d\tau - \int\left(\psi^*\frac{\partial}{\partial x}(V\psi) - V\psi^*\frac{\partial\psi}{\partial x}\right)d\tau$$

$$= \frac{\hbar^2}{2m}\int\left(\psi^*\frac{\partial}{\partial x}\nabla^2\psi - \psi^*\frac{\partial}{\partial x}\nabla^2\psi\right)d\tau -$$

$$\int\left(\psi^*\frac{\partial}{\partial x}(V\psi) - V\psi^*\frac{\partial\psi}{\partial x}\right)$$

$$= -\int\psi^*\left(\frac{\partial}{\partial x}(V\psi) - V\frac{\partial\psi}{\partial x}\right)d\tau$$

$$= \int\psi^*\left(-\frac{\partial V}{\partial x}\right)\psi d\tau$$

$$= \left\langle -\frac{\partial V}{\partial x}\right\rangle$$

6.5 Let us sum up:

After studying this unit you we have understood the following aspects;

- Heisenberg equation of motion
- Expectation value
- Ehrenfest's theorem

6.6 Key words:

Heisenberg equation of motion, Expectation value, Ehrenfest's theorem

6.7 Problems:

Example 1.

A particle m a one dimensional box $0 \le x \le a$ is in the ground state. Find $\langle x\rangle$ *and* $\langle p\rangle$

SOLUTION
The wave function is:

$$\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$$

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{\infty}\psi^*(x)x\psi(x)dx = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)(x)\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)dx\\ &= \frac{2}{a}\int_0^a x\left(\sin\left(\frac{\pi x}{a}\right)\right)^2 dx\\ &= \frac{2}{a}\int_0^a x\left(\frac{1-\cos\left(\frac{2\pi x}{a}\right)}{2}\right)dx\\ &= \frac{2}{a}\int_0^a xdx - \frac{1}{a}\int_0^a x\cos\left(\frac{2\pi x}{a}\right)dx\end{aligned}$$

integrating the first term yields:

$$\int_0^a xdx = x^2/2\Big|_0^a = a^2/2$$

The second term can be integrated by parts, giving

$$\begin{aligned}\int_0^a x\cos\left(\frac{2\pi x}{a}\right)dx &= a^2/4\pi^2\cos(2\pi x/a) + a/2\pi x\sin\left(\frac{2\pi x}{a}\right)\Bigg|_0^a\\ &= a^2/4\pi\ [\cos 2\pi - \cos 0] = 0\end{aligned}$$

And so, we find that:

$$\langle x\rangle = \frac{1}{a}\int_0^a xdx = \left(\frac{1}{a}\right)x^2/2\Bigg|_0^a = a/2$$

To calculate $\langle p\rangle$, we write p as a derivative operator:

$$\begin{aligned}\langle P\rangle &= \int_{-\infty}^{\infty}\psi^*(x)p\psi(x)dx\\ &= \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\left(-ih\frac{d}{dx}\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\right)dx\\ &= -ih\frac{2}{a}\left(\frac{\pi}{a}\right)\int_0^a \sin\frac{\pi x}{a}\cos\frac{\pi x}{a}dx\end{aligned}$$

You may already know this integral is zero, but we can calculate it easily so we proceed.

Let $u = \sin\left(\frac{\pi x}{a}\right)$, then $du = \left(\frac{\pi}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx$. This gives:

$$\int u du = u^2/2, \Rightarrow$$

$$\int_{-\infty}^{\infty} \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx = (1/2)\left(\sin\left(\frac{\pi x}{a}\right)\right)^2\Big|_0^a$$

$$= (1/2)\left[(\sin(\pi))^2 - (\sin(0))^2\right] = 0$$

And so, for the ground state of the particle in a box, we have found:

$$\langle p \rangle = 0$$

Example 2.

$$\psi(x) = A\left(ax - x^2\right) \text{ for } 0 \le x \le a$$

(a) Normalize the wavefunction

(b) Find $\langle x \rangle$, $\langle x^2 \rangle$ and Δx

SOLUTION

(a) The wavefunction is real. So $\psi^*\psi = \psi^2$ and we have:

$$\begin{aligned}
\int \psi^2 dx &= \int_0^a A^2(ax - x^2)^2 dx = A^2 \int_0^a a^2x^2 - 2ax^3 + x^4 dx \\
&= A^2\left[a^2(x^3/3) - ax^4/2 + x^5/5\right]\Big|_0^a \\
&= A^2\left[a^5/3 - a^5/2 + a^5/5\right] \\
&= A^2\left[10a^5/30 - 15a^5/30 + 6a^5/30\right] \\
&= A^2a^5/30, \Rightarrow A = \sqrt{30/a^5}
\end{aligned}$$

,

(b)

$$\begin{aligned}
\langle x \rangle &= \int x^2\psi^2 dx = (30/a^5)\int_0^a x(ax - x^2)^2 dx \\
&= (30/a^5)\int_0^a a^2x^3 - 2ax^4 + x^5 dx \\
&= (30/a^5)\left[a^2\left(x^4/4\right) - 2a\left(x^5/5\right) + x^6/6\right]\Big|_0^a \\
&= (30/a^5)\left[a^6/4 - 2a^6/5 + a^6/6\right] \\
&= (30/a^5)(a^2/60) = \frac{a}{2}
\end{aligned}$$

$$
\begin{aligned}
\langle x^2\rangle &= \int x^2\psi^2 dx = (30/a^5)\int_0^a x^2\left(ax-x^2\right)^2 dx \\
&= (30/a^5)\int_0^a a^2x^4 - 2ax^5 + x^6 dx \\
&= (30/a^5)\left[a^2\left(x^5/5\right) - 2a\left(x^6 + x^7/7\right)\right]\Big|_0^a \\
&= (30/a^5)\left[a^7/5 - 2a^7/6 + a^7/7\right] \\
&= \frac{2a^2}{7}
\end{aligned}
$$

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2} = \sqrt{\frac{2a^2}{7} - \left(\frac{a}{2}\right)^2} = \sqrt{\frac{2a^2}{7} - \frac{a^2}{4}} = \frac{a}{\sqrt{28}}$$

6.8 Questions for self study:

1. Arrive at the Heisenberg equation of motion. Narrate its importance.
2. What do you mean by Expectation value? Narrate the method of finding the value of Expectation value of an observable.
3. State and prove Ehrenfest's theorem for the position coordinate.
4. State and prove Ehrenfest's theorem for the momentum coordinate.

6.9 References for further study:

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4. E.Merzbacher, Quantum mechanics, John Wiley, New York

5. Richtmyer, Kennard and Lauritsen, Introduction to Modern Physics

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7. Quantum mechanics by Gupta and Kumar.

UNIT-7: Simple harmonic oscillator, Schrödinger wave equation, Solution by operator and differential equation approach.

Structure:

- 7.0 Objectives.
- 7.1 Introduction.
- 7.2 Schrodinger's wave equation for linear harmonic oscillator.
- 7.3 Solution by differential equation approach.
- 7.4 Solution by operator method.
- 7.5 Let us sum up.
- 7.6 Key words.
- 7.7 Question for self Study.
- 7.8 Reference for further study.
- 7.9 Problems.

7.0 Objectives.

After studying this unit you will be able to understand the following aspects: Introduction to harmonic oscillator, Schrodinger's wave equation for linear harmonic oscillator solution by differential equation approach and solution by operator method.

7.1 Introduction: Simple harmonic oscillator

The classical Hamiltonian of a simple harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}Kx^2 \qquad (1)$$

Where k>0 is the so called force constant of the oscillator. Assuming that the quantum mechanical Hamiltonian has the same from as the classical Hamiltonian, the time independent Schrödinger equation for a particle of mass m and energy E moving in a simple harmonic potential becomes

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}Kx^2 - E\right)\psi \qquad (2)$$

Let $\omega = \sqrt{K/m}$ where ω is the oscillator’s classical angular frequency of oscillation. Furthermore,

$$y = \sqrt{\frac{m\omega}{\hbar}}\,x \qquad (3)$$

and

$$\varepsilon = \frac{2E}{\hbar\omega} \qquad (4)$$

Equation (2) *reduces to*

$$\frac{d^2\psi}{dy^2} - \left(y^2 - \varepsilon\right)\psi = 0 \qquad (5)$$

We need to find solutions to the above equation which are bounded at infinity: i.e., solutions which satisfy the boundary condition $\psi \to 0 \quad as \ |y| \to \infty$.

Consider the behavior of the solution to eqn (5) in the limit $|y| \gg 1.$ As is easily seen, in this limit the equation simplifies somewhat to give

$$\frac{d^2\psi}{dy^2} - y^2\psi \simeq 0$$

The approximation solutions to the above equation are:

$$\psi(y) = A(y)e^{\pm y^2/2} \qquad (7)$$

where A(y) is a relatively slowly varying function of *y*. Clearly if ψ(y) is to remain bounded as |y|→∞ then we must chose the exponentially decaying solution. This suggests that we should write

$$\psi(y) = h(y)e^{-y^2/2} \qquad (8)$$

where we would expect *h(y)* to be an algebraic rather than an exponential function of *y*.

Substituting Eq. (8) into Eq. (5) we obtain

$$\frac{d^2h}{dy^2} - 2y\frac{dh}{dy} + (e-1)h = 0 \qquad (9)$$

Let us attempt a power-law solution of the form

$$h(y) = \sum_{i=0}^{\infty} c_i y^i \qquad (10)$$

Inserting this test solution into Eq. (9) and equating the co-efficient of y^i, we obtain the recursion relation

$$c_{i+2} = \frac{(2i - \varepsilon + 1)}{(i+1)(i+2)} c_i \qquad (11)$$

Consider the behavior of *h(y)* in the limit |y|→∞. The above recursion relation simplifies to

$$c_{i+2} \cong \frac{2}{i} c_i \qquad (12)$$

Hence at larger |y|, when the higher powers of *y* dominate, we have

$$h(y) \approx C \sum_j \frac{y^{2j}}{j!} \approx Ce^{y^2} \qquad (13)$$

It follows that $\psi(y) = h(y)$ exp(-y^2/2) varies as exp(y^2/2) as |y|→∞. This behavior is unacceptable, since it does not satisfy the boundary condition ψ→0 as |y|→∞. The only way in which we can prevent ψ from blowing up |y|→∞ is to demand that the power series (10) terminate at some finite value of i. this implies from the recursion relation (11)that

$$\varepsilon = 2n + 1 \qquad (14)$$

Where *n* is a non negative integer. Note that the number of terms in the power series (!0) is n+1. Finally using Eq. (4) we obtain

$$E = (n + 1/2)\hbar\omega \qquad (15)$$
$$for \;\; n = 0, 1, 2.........$$

Hence, we conclude that a particle moving in a harmonic potential has quantized energy levels which are *equally spaced*. The spacing between successive energy levels is $\hbar$ ω where ω is the classical oscillation frequency. Furthermore, the lowest energy the lowest energy state (n = 1) possesses the finite energy (1/2) $\hbar$ ω. This is sometimes called zero-point energy. It is easily demonstrated that the (normalization) wavefunction of the lowest energy state takes the form

$$\psi_0(x) = \frac{e^{-x^2/2d^2}}{\pi^{1/4}\sqrt{d}} \qquad (16)$$
$$where \;\; d = \sqrt{\hbar / m\omega}$$

Let $\psi_n = (x)$ be an energy eigenstate of the harmonic oscillator corresponding to the eigenvalue

$$E_n = \left(n + 1/2\right)\hbar\omega \qquad (17)$$

Assuming that ψ_n are properly normalized (and real), we have

$$\int_{-\infty}^{\infty} \psi_n \psi_m dx = \delta_{nm} \qquad (18)$$

Equation (5) *can be written*

$$\left(-\frac{d^2}{dy^2} + y^2\right)\psi_n = \left(2n+1\right)\psi_n \qquad (19)$$

where $x = dy$, *and* $d = \sqrt{\hbar / m\omega}$. *it is helpful to define the operators*

$$a_{\pm} = \frac{1}{\sqrt{2}}\left(\mp\frac{d}{dy} + y\right) \qquad (20)$$

As is easily demonstrated, these operators satisfy the commutation relation

$$\left[a_{+,} a_{-}\right] = -1 \qquad (21)$$

u sin *g these operators Eq*(19) *can also written in the forms*

$$a_+ a_- \psi_n = n\psi_n \qquad (22)$$

$$a_+ a_- \psi_n = \left(n+1\right)\psi_n \qquad (23)$$

The above two equations imply that

$$a_+ \psi_n = \sqrt{n+1}\,\psi_{n+1} \qquad (24)$$

$$a_- \psi_n = \sqrt{n}\,\psi_{n-1} \qquad (25)$$

We conclude that a_+ and a_- are raising and lowering operators, respectively for the harmonic oscillator: i.e., operating on the wavefunction with a_+ causes the quantum number *n* to increase by unity and vice versa. The Hamiltonian for the harmonic oscillator can be written in the form

$$H = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right) \qquad (26)$$

From which the result

$$H\psi_n = \left(n + 1/2\right)\hbar\omega\psi_n = E_n\psi_n \qquad (27)$$

is readily deduced. Finally, Eq. (18), (24) and (25) yield the useful expression

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_m x \psi_n dx &= \frac{d}{\sqrt{2}}\int_{-\infty}^{\infty} \psi_n \left(a_+ + a_-\right)\psi_n dx \\ &= \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{m}\,\delta_{m,n+1} + \sqrt{n}\,\delta_{m,n-1}\right) \qquad (28) \end{aligned}$$

Linear Harmonic Oscillator:

A study of a linear harmonic oscillator is particularly important in Physics. In its simplest form it represents the case of a particle moving in a potential which depends only on x and has the form:

$$V(x) = \frac{1}{2}kx^2 \qquad (29)$$

where k is a real positive constant. The particle is attracted towards the equilibrium position by the restoring force:

$$F = -\frac{dV}{dx} = -kx$$

The force is thus proportional to the displacement from the mean position. We know that classically such a force results in the sinusoidal oscillations of the particle describe by an equation of the type

$$x = A\cos\left(\omega t + \varphi\right)$$

with the angualr frequency ω given by

$$\omega = \sqrt{\frac{k}{m}} \qquad (30)$$

A large number of physical systems are described by such of the harmonic oscillator among these are the vibrations of atom in a molecule oscillations of atoms or ions in a crystal lattice surface vibrations of spherical atomic nuclei electromagnetic field etc:,

A detailed study of the harmonic oscillator is thus of prime importance in quantum mechanics Moreover it represents a quantum system for which the Schrodinger equation can be rigorously solved.

7.2 Schrodinger's Equation for a Harmonic Oscillator:

The classical Hamiltonian for a particle described a linear simple harmonic motion is the sum of its kinetic and potential energies. Thus,

$$H_{cl} = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where p is the momentum of the particle. The quantum mechanical Hamiltonian is obtained by substituting the corresponding operator in the above equation. We thus get

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2$$

$$= \frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \qquad (31)$$

$$where\ \hat{p} = -i\hbar\frac{d}{dx}; \hat{x} = x, and\ k = m\omega^2$$

The time independent Schrodinger equation is thus

$$\hat{H}\psi = E\psi \qquad (32)$$

where E is the total energy of the particle

Substituting for $\hat{H}$ *from* (31) *we get*

$$\left(-\frac{\hbar^2}{2m}.\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)\psi = E\psi$$

or

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2 x^2\right)\psi = 0 \qquad (33)$$

To solve this equation we introduce dimensionless variables

$$\xi = x\sqrt{\frac{m\omega}{\hbar}}\ and\ \lambda = \frac{2E}{\hbar\omega} \qquad (34)$$

Eqn(33) *then becomes*:

$$\frac{d^2\psi}{d\xi^2} + \left(\lambda - \xi^2\right)\psi = 0 \qquad (35)$$

Asymptotic Behavior (Energy Eigen values):

From equation (34) it is clear that for every large values of ζ we have λ become negligible compared to ζ^2 Eqn (35) thus becomes

$$\frac{d^2\psi}{d\xi^2} - \xi^2\psi = 0 \qquad (36)$$

The corresponding solution for the wave function is therefore of the form

$$\exp\left(\pm\frac{\xi^2}{2}\right) \qquad (37)$$

However we must ensure the realistic condition that ψ vanishes for $\zeta=\pm\infty$. We must therefore retain only the solution with negative sign in 37. We thus write the solution of (35) in the form

$$\psi\left(\xi\right)=H\left(\xi\right)\exp\left(-\frac{\xi^2}{2}\right) \qquad (38)$$

Substituting this into (35) we get

$$H''\left(\xi\right)-2\xi H'\left(\xi\right)+\left(\lambda-1\right)H\left(\xi\right)=0 \qquad (39)$$

Where the primes indicates differentiation w.r.t ζ. We look for a solution in the form of a power series of the type

$$H\left(\xi\right)=a_0+a_1\xi+a_2\xi^2+a_3\xi^3 \qquad (40)$$

On substituting for $H\left(\xi\right), H'\left(\xi\right) and\ H''\left(\xi\right),\ eqn(39)\ becomes$

$$\begin{aligned}&1.2a_2+2.3a_3\xi+3.4a_4\xi^2+4.5a_5\xi^3+..........\\&-2a_1\xi-2.2a_2\xi^2-2.3a_3\xi^3-...................\\&+(\lambda-1)a_0+(\lambda-1)a_1\xi+(\lambda-1)a_2\xi^2+(\lambda-1)a_3\xi^3+.......=0\end{aligned}$$

In order for this series to vanish for all values of ζ (i.e for H(ζ) to be a solution of (39) the coefficient of individual powers of ζ must vanish separately Thus

$$\begin{aligned}&1.2a_2+(\lambda-1)a_0=0\\&2.3a_3+(\lambda-1-2.1)a_1=0\\&3.4a_4+(\lambda-1-2.2)a_2=0\\&4.5a_5+(\lambda-1-2.3)a_3=0\\&-----------------\\&-----------------\end{aligned}$$

which leads to the recursion formula for the coefficient of ζ^l

$$\left(l+1\right)\left(l+2\right)a_{1+2}+\left(\lambda-1-2.1\right)a_l=0$$

$$a_{l+2}=-\frac{\left(\lambda-1-2l\right)}{\left(l+1\right)\left(l+2\right)}a_l \qquad (41)$$

In order to ensure that ψ(ζ) vanishes for ζ= ±∞ the series (40) must be limited*. Let us suppose that the series breaks at the nth power of ζ. Thus a_{n+2}must be zero. This is evidently the case if in (41) we have

$$\lambda=2n+1 \qquad (42)$$

---

*Note: As *l* become large the recursion formula (41) gives $a_{l+2}=\frac{2}{l}a_l$. The series (40) behaves like exp(ζ^2)

The wave function ψ(ζ) then becomes according to (38)

$$\psi(\xi) = \exp(\xi^2).\exp(-\xi^2/2)$$

$$= \exp\left(\frac{\xi^2}{2}\right)$$

which is a result that we have already discarded. To show that ratio of the coefficient of ζ^{1+2} and ζ^1 in exp (ζ^2) is also $2/l$, we have

$$\exp\left(\xi^2\right) = l + \xi^2 + \frac{\xi^4}{2!} + ... + \frac{\xi^1}{(1/2)!} + \frac{\xi^{1+2}}{\left[(l+2)/2\right]} + ...$$

from which the required ratio is

$$\frac{(l/2)!}{\left[(l/2)+1\right]!} = \frac{1}{(l/2)+1} = \frac{2}{l}\left(1+\frac{2}{l}\right)^{-1} = \frac{2}{l} \quad \textit{for large values of } l$$

where n is an integer. Substituting for λ from (34) we have for the allowed energy values of the oscillator

$$E_n = (n + 1/2)\hbar\omega \qquad (43)$$

n is called the quantum number of the corresponding state of the oscillator. E_n are called the energy eigen values of the harmonic oscillator.

7.3 Discussion

According to Planck's original ideas the energies of a liner oscillator are quantized as $n\hbar\omega$ so that the lowest energy state has zero energy for n=0. However the present result (43) shows that all the energy levels are displaced upwards by an amount $\frac{1}{2}\hbar\omega$. The ground state energy of the oscillator corresponding to n=0 is:

$$E_0 = \frac{1}{2}\hbar\omega$$

which is called the zero-point energy of the oscillator. Thus even in its lowest state the system is not deprived of all its energy. Such an existence of zero point energy which has led to an improved agreement with experimental result is an important success of quantum mechanics

Figure (1) shows the various energy levels of a harmonic oscillator

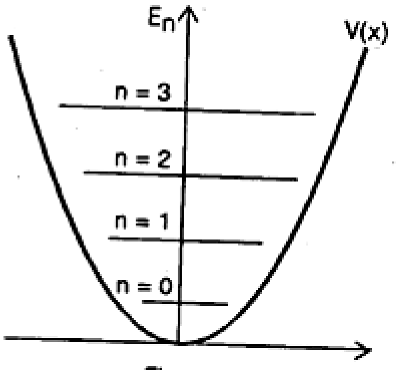

Fig (1)

Harmonic Oscillator Wave Function :

The solutions of equation (35) are the Eigen functions of the harmonic oscillator from (38) we can write them in the form

$$\psi_n(x) = H_n(\xi)\exp\left(-\frac{\xi^2}{2}\right)$$

As we have found $\lambda = 2n+1$, the function $H_n(\xi)$ satisfy the following relation which is evident from (39)

$$H_n''(\xi) - 2\xi H_n^1(\xi) + 2nH_n(\xi) = 0 \qquad (44)$$

This is the equation satisfied by the Hermite polynomials. Thus the Eigen functions of a harmonic oscillator are expressed through Hermite polynomials.

The normalized oscillator wave function can be written as

$$\psi_n(x) = N_n H_n(\xi)\exp\left(-\frac{\xi^2}{2}\right) \qquad (45)$$

where N_n is the normalizing constant. This constant can be evaluated from the usual normalizing condition

$$\int_{-\infty}^{+\infty} \psi_m(x)\psi_n(x)\,dx = 1 \qquad (46)$$

where $\psi_m(x) = \psi_n^*(x)$

Now

$$\int_{-\infty}^{+\infty} \psi_m(x)\psi_n(x)\,dx = \frac{N_m N_n}{\sqrt{a}}\int_{-\infty}^{+\infty} H_m(\xi)H_n(\xi)e^{\xi^2}\,d\xi \qquad (47)$$

where $\alpha = \frac{m\omega}{\hbar}$ *and* $x\sqrt{\alpha} = \xi$

The generating function for Hermite polynomials is

$$S\left(\xi,s\right)=\sum_{n}\frac{H_n\left(\xi\right)s^n}{n!}=e^{\xi^2-\left(s-\xi\right)^2}$$

$$T\left(\xi,t\right)=\sum_{m}\frac{H_m\left(\xi\right)t^m}{m!}=e^{\xi^2-\left(t-\xi\right)^2}$$

$$Then\int_{-\infty}^{+\infty}S.T.e^{-\xi^2}.d\xi=\sum_{n}\sum_{m}s^nt^m\int_{-\infty}^{+\infty}\frac{H_n\left(\xi\right)H_m\left(\xi\right)}{n!m!}e^{-\xi^2}d\xi$$

$$=\int_{-\infty}^{+\infty}e^{\left(-s^2-t^2+2s\xi+2t\xi-\xi^2\right)}d\xi$$

$$=e^{2st}\int_{-\infty}^{+\infty}e^{\left(-\xi-s-t\right)^2}d\left(\xi-s-t\right)$$

$$=e^{2st}\sqrt{\pi}$$

We thus have

$$\sum_{n}\sum_{m}s^nt^m\int_{-\infty}^{+\infty}\frac{H_n\left(\xi\right)H_m\left(\xi\right)}{n!m!}e^{-\xi^2}d\xi=\sqrt{\pi}\,e^{2st}$$

$$=\sqrt{\pi}\left(1+2st+\frac{2^2s^2t^2}{2!}+......+\frac{2^ns^nt^n}{n!}\right)$$

Equating the coefficient of s^nt^m in the two equal series expansions, we have

$$\frac{1}{n!m!}\int_{-\infty}^{+\infty}H_n\left(\xi\right)H_m\left(\xi\right)e^{-\xi^2}d\xi=0$$

If however m = n, we have, on comparing the coefficients of s^nt^n

$$\int_{-\infty}^{+\infty}H_n\left(\xi\right)H_m\left(\xi\right)e^{-\xi^2}d\xi=\sqrt{\pi}.2^n.n!$$

This result combined with (46) and (47) gives value of the normalizing constant

$$N_n=\left[\sqrt{\frac{\alpha}{\pi}}.\frac{1}{2^n.n!}\right] \qquad (48)$$

$For\ this\ value\,N_n$

$$\int\ \psi_m^*\psi_n dx=\delta_{mn} \qquad (49)$$

Thus the harmonic oscillators are Hermite orthogonal functions which can be normalized with constant N_n

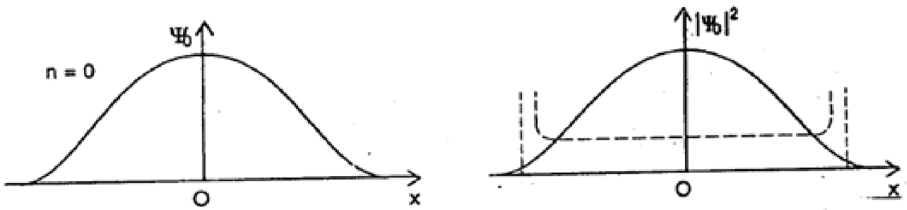

Fig: 2(a)

The normalized wave function fro n=0,`1,2 and 10 shown graphically in fig (2). The correspondence probability distribution are also shown as variations of $|\psi^2|$. The dotted curves show the classical probability densities.

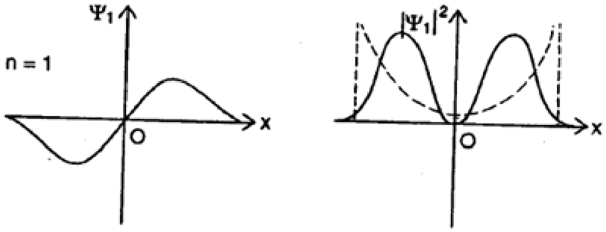

Fig: 2(b)

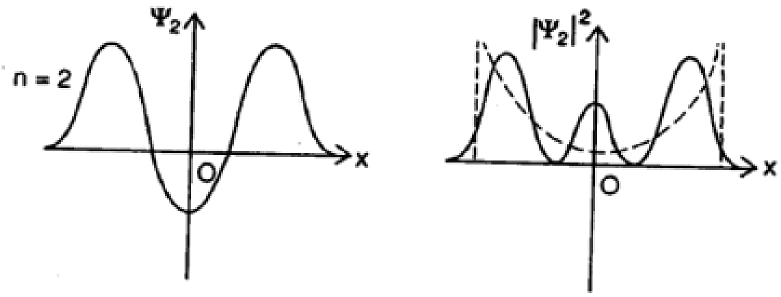

Fig: 2(c)

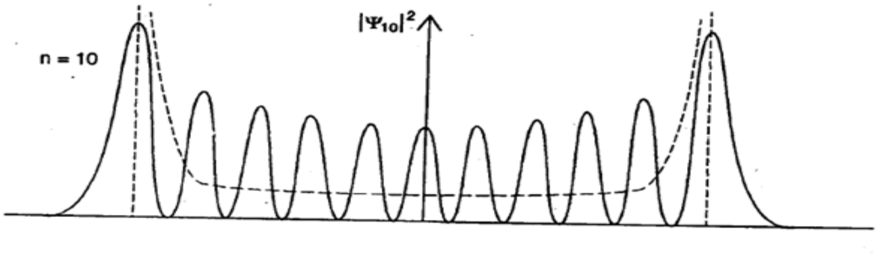

Fig: 2(d)

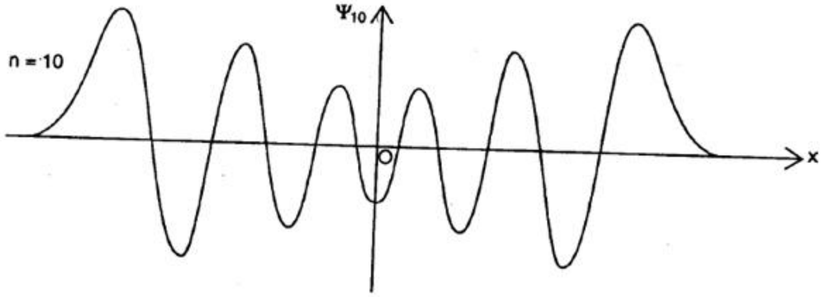

Fig: 2(e)

7.4 Linear harmonic oscillator- Operator method

We know proceed to solve the harmonic oscillator problem using an entirely different method based on operators and algebra alone. Consider the following operators defined in terms of the position and momentum operators.

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right)$$

$$a^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$$

We can rewrite the Hamiltonian using these operators and then solve the Eigen vector/Eigen values problem in an algebraic way. An important part of working with these operators is to determine their commutator.

Example 1:

Derive the commutator $\left[a, a^{+}\right]$.

Solution:

To find this commutator we rely on [x, p]=i $\hbar$

$$\left[a,a^{\dagger}\right]=\left[\sqrt{\frac{m\omega}{2\hbar}}\left(x+\frac{ip}{m\omega}\right).\sqrt{\frac{m\omega}{2\hbar}}\left(x-\frac{ip}{m\omega}\right)\right].$$

$$=\frac{m\omega}{2\hbar}\left[\left(x+\frac{ip}{m\omega}\right).\left(x-\frac{ip}{m\omega}\right)\right]$$

$$=\frac{m\omega}{2\hbar}\left\{[x,x]-\frac{i}{m\omega}[x,p]+\frac{1}{m\omega}[p,x]+\frac{1}{m^2\omega^2}[p,p]\right\}$$

$$Since\,[x,x]=[p,p]=0 \text{ this simplifies to}$$

$$\left[a,a^{\dagger}\right]=\frac{m\omega}{2\hbar}\left\{-\frac{i}{m\omega}[x,p]+\frac{1}{m\omega}[p,x]\right\}$$

$$=\frac{i}{2\hbar}\left\{-[x,p]+[p,x]\right\}$$

$$=\frac{i}{2\hbar}\left\{-[x,p]-[x,p]\right\}$$

$$=\frac{-i}{\hbar}[x,p]=\frac{-i}{\hbar}(i\hbar)=1$$

$$\Rightarrow\left[a,a^{\dagger}\right]=aa^{\dagger}-a^{\dagger}a=1$$

Example 2:

Show that the harmonic oscillator Hamiltonian can be written in the form

$$H=\hbar\omega\left(a^{\dagger}a+\frac{1}{2}\right)$$

Solution:

We begin writing the position and momentum in terms of $a, a^{\dagger}$. Notice that

$$a+a^{\dagger}=\sqrt{\frac{m\omega}{2\hbar}}\left(x+\frac{ip}{m\omega}\right)+\sqrt{\frac{m\omega}{2\hbar}}\left(x-\frac{ip}{m\omega}\right)=\sqrt{\frac{m\omega}{2\hbar}}x$$

and so the position can be written as

$$x=\sqrt{\frac{\hbar}{2m\omega}}\left(a+a^{\dagger}\right)$$

The harmonic oscillator Hamiltonian contain the square of x*. Squaring this term we find*

$$x^2=\frac{\hbar}{2m\omega}\left(a+a^{\dagger}\right)=\frac{\hbar}{2m\omega}\left(a^2+aa^{\dagger}+a^{\dagger}a+\left(a^{\dagger}\right)^2\right)$$

Now we write the momentum operator in *terms of* $a, a^{\dagger}$ *.consider*

$$a - a^{\dagger} = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right) + \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$$

$$= \sqrt{\frac{m\omega}{2\hbar}}\frac{ip}{m\omega} = i\frac{1}{\sqrt{2\hbar m\omega}}p$$

And so we can write momentum as

$$p = -i\sqrt{\frac{\hbar m\omega}{2}}\left(a - a^{\dagger}\right), \Rightarrow$$

$$\frac{p^2}{2m} = -\frac{\hbar m\omega}{4m}\left(a^2 - aa^{\dagger} - a^{\dagger}a + \left(a^{\dagger}\right)^2\right)$$

Now we can insert terms into the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

$$= -\frac{\hbar\omega}{4}\left[a^2 - aa^{\dagger} - a^{\dagger}a + \left(a^{\dagger}\right)^2\right] + \frac{m\omega^2}{2}\left(\frac{\hbar}{2m\omega}\right)\left[a^2 + aa^{\dagger} + a^{\dagger}a + \left(a^{\dagger}\right)^2\right]$$

Notice that

$$\frac{m\omega^2}{2}\left(\frac{\hbar}{2m\omega}\right) = \frac{\hbar\omega}{4}$$

Therefore $a^2, \left(a^{\dagger}\right)^2$ terms cancel. This leaves

$$H = \frac{\hbar\omega}{4}\left[2aa^{\dagger} + 2a^{\dagger}a\right] = \frac{\hbar\omega}{2}\left[aa^{\dagger} + a^{\dagger}a\right]$$

Now we use the commutation relation

$\left[a, a^{\dagger}\right] = aa^{\dagger} - a^{\dagger}a = 1$ *to write* $aa^{\dagger} = 1 + a^{\dagger}a$*, and we have*

$$H = \frac{\hbar\omega}{4}\left[1 + 2a^{\dagger}a\right] = \hbar\omega\left(a^{\dagger}a + \frac{1}{2}\right)$$

some other importent commutation relations are

$$\left[H, a\right] = -\omega a, \left[H, a^{\dagger}\right] = \hbar\omega a^{\dagger}$$

7.4(a) Number states of the Harmonic oscillator:

Now that we have expressed the Hamiltonian in terms of the operators $a, a^{\dagger}$ we can derive the energy Eigen states. We being by stating the Eigen values

$$H\left|E_n\right\rangle = E_n\left|E_n\right\rangle$$

To simplify notation, we set $\left|E_n\right\rangle = \left|n\right\rangle$.*We have already seen that*

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right), \quad n = 0,1,2...........$$

Using the form of the Hamiltonian written in terms of $a, a^\dagger$, we find that

$$H\left|n\right\rangle = \hbar\omega\left(a^\dagger a+\frac{1}{2}\right)\left|n\right\rangle = \hbar\omega\left(a^\dagger a\left|n\right\rangle\right)+\frac{\hbar\omega}{2}\left|n\right\rangle$$

However we know that

$$H\left|n\right\rangle = E_n\left|n\right\rangle = \hbar\omega\left(n+\frac{1}{2}\right)\left|n\right\rangle$$

Equating this to the above we have

$$\hbar\omega\left(a^\dagger a\left|n\right\rangle\right)+\frac{\hbar\omega}{2}\left|n\right\rangle = \hbar\omega n\left|n\right\rangle+\frac{\hbar\omega}{2}\left|n\right\rangle$$

Now divide throughout by $\hbar\omega$ and subtract the common term ½|n> from both sides giving

$$a^\dagger a\left|n\right\rangle = n\left|n\right\rangle$$

This shows that the energy Eigen state is an eigenstate of $a^\dagger a$ with eigenvalue *n.* The operator $a^\dagger a$ is called the *number operator.*

7.5 Let sum up

In this section we have understood the method of solving the Schroedinger equation in case of linear harmonic oscillator using the differential equation approach and operator approach

7.6 Key words

Linear harmonic oscillator, Ladder operator, Number operator, Energy eigen state, Energy eigen value.

7.7 Question for self study

1. Arrive at the energy eigen values and eigen function of the linear harmonic oscillator by differential equation approach.

2. Arrive at the energy Eigen values and eigen function of the linear harmonic oscillator by operator method.
3. Write note on ladder operator.
4. Write a note on number operator.

7.8 Problems

1. Calculate the zero point energy of a system consisting of a mass of 1g connected to a fixed point by a spring which is stretched by 1 cm by a force of 0.1 N the particle being constrained to move only along x-axis

   HINT: zero point energy= $\frac{1}{2}\hbar\omega_0$

   $\omega_0 = \sqrt{(k/m)}$

   $Ans: 5.25\times 10^{-33}\ joule$

2. The energy of a linear harmonic oscillator in third excited state is 0.1eV. Find the frequency of vibration.

7.9 References for further study

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Unit-8: Spherically symmetric potentials, hydrogen atom, two body problem, energy eigenstates and eigen values

Structure:

8.0 Objectives

1. After Studying this unit you will be able to understand the following aspects;
2. What is meant by central potential?
3. What is meant by radial equation?
4. What is the form of wave equation in case of hydrogen atom?
5. How to solve the wave equation in case of hydrogen atom?
6. How to find the Eigen function and Eigen values in case of hydrogen atom?

8.1 Introduction

In this chapter we shall investigate the interaction of a non-relativistic particle of mass m and energy E with various so called central potentials. V(r) where $r = \sqrt{x^2 + y^2 + z^2}$ is the radial distance from the origin. It is of course most convenient to work in spherical polar co ordinates –r, θ,φ-during such an investigation. Thus we shall be searching for stationary wavefunctions ψ(r,θ,φ) which satisfy the time independent Schrodinger equation

$$H\psi = E\psi \qquad (1)$$

where the Hamiltonian takes the standard non-relativistic form

$$H = \frac{p^2}{2m} + V(r) \qquad (2)$$

8.2 Radial Equation

Now we have seen that the Cartesian components of the momentum P can be represented as

$$P_r = -i\hbar \frac{\partial}{\partial x_i} \qquad (3)$$

For i=1,2,3, where $\boldsymbol{x_1 \equiv x}$, $\boldsymbol{x_2 \equiv y}$, $\boldsymbol{x_3 \equiv z}$, and $\boldsymbol{r \equiv (x_1, x_2, x_3)}$. Likewise it is easily demonstrated from the above expression and the basic definitions of the spherical polar coordinates that the radial component of the momentum can be represented as

$$P_r \equiv \frac{P.r}{r} = -i\hbar \frac{\partial}{\partial r} ------------(4)$$

Recall that the angular momentum vector, **L,** is defined

$$L = r \times p. ----------------(5)$$

This expression can also be written in the following form:

$$L_i = \in_{ijk} x_j Pk. --------------(6)$$

Here the €$_{ijk}$ (where i,j,k all run from 1 to 3) are elements of the so called totally anti-symmetric tensor. The values of the various elements of this tensor are determined via a simple rule:

$$\in_{ijk} = \begin{cases} 0 & if\ i,j,k\ not\ all\ different \\ 1 & if\ i,j,k\ are\ cyclic\ permutation\ of\ 1,2,3 \\ -1 & if\ i,j,k\ are\ anti-cyclic\ permutation\ of\ 1,2,3 \end{cases} \quad -------------(7)$$

Thus $\in_{123} = \in_{231} = 1, \in_{321} = \in_{132} = -1\ and\ \in_{112} = \in_{131} = 0$ etc. Equation (6) also makes use of the Einstein summation convention, according to which repeated indices summed (from 1 to 3). For instance, $a_i b_i = a_1 b_1 + a_2 b_2 + a_3 b_3$. Making use of this convention as well as Eq(7) it is easily seen that equation (5) and (6) are indeed equivalent.

Let us calculate the value of L^2 using equation (6). According to our new notation L^2 is the same as $L_i L_i$. Thus, we obtain

$$L^2 = \in_{ijk} x_j P_k \in_{ilm} x_l p_m = \in_{ijk} \in_{ilm} x_j p_k x_l p_m -----(8)$$

Note that we are able to shift the position of $\in_{ilm}$ because its elements are just numbers and therefore commute with all of the x_i and the p_i now it is easily demonstrated that

$$\in_{ijk}\in_{ilm} \equiv \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl} ------------(9)$$

Here δ_{ij} is the usual *Kronecker delta*, whose elements are determined according to the rule

$$\delta_{ij} = \begin{cases} 1 & if\ i\ and\ j\ the\ same \\ 0 & if\ i\ and\ j\ different ------------(10) \end{cases}$$

It follows from equation (8) and (9) that

$$L^2 = x_i p_j x_i p_j - x_i p_j x_j p_i . -------------(11)$$

Here we have made use of the fairly self-evident result that $\delta_{ij}\, a_i b_j \equiv a_i b_i$. We have also been careful to preserve the order of the various terms on the right hand side of the above expression since the x_i and p_i do not necessarily commute with one another.

We now need to rearrange the order of the terms on the right-hand side of equation (11) we can achieve this by making use of the fundamental commutation relation for the x_i and the p_i

$$[x_i , p_j] = i\hbar\delta_{ij} ---------------------(12)$$

Thus

$$\begin{aligned} L^2 &= x_i\left(x_i p_j - [x_{i,} p_j]\right)p_j - x_i p_j\left(p_i x_j + [x_{j,} p_i]\right) \\ &= x_i x_i p_j p_i - i\hbar\delta_{ij} x_i p_j - x_i p_j p_i x_j - i\hbar\delta_{ij} x_i p_j \\ &= x_i x_i p_j p_j - x_i p_i p_j x_j - 2i\hbar x_i p_{i,} ---------------(13) \end{aligned}$$

Here we have made use of the fact that $p_j p_i = p_i p_j$, since the p_i commute with one another. Next

$$L^2 = x_i x_i p_j p_j - x_i p_i\left(x_j p_j - [x_j , p_j]\right) - 2i\hbar x_i p_i -----------(14)$$

Now according to (12)

$$[x_{j,} p_j] \equiv [x_1 p_1] + [x_2 , p_2] + [x_3 , p_3] = 3i\hbar ---------------(15)$$

Hence we obtain

$$L^2 = x_i x_i p_j p_j - x_i p_i x_j p_j + i\hbar x_i p_i ------------------(16)$$

When expressed in more conventional vector notation the above expression becomes

$$L^2 = r^2 p^2 - (\vec{r}.\vec{p})^2 + i\hbar\vec{r}.\vec{p} ---------------------------(17)$$

Note that if we had attempted to derive the above expression directly from equation (5) using standard vector identities then we would have the final term on the right hand side. This term originates from the lack of commutation between the x_i and p_i operators in quantum mechanics. Of course standard vector analysis assumes that all terms commute with one another.

Equation (17) can be rearranged to give

$$p^2 = r^{-2}\left[\left(\vec{r}.\vec{p}\right)^2 - i\hbar\vec{r}.\vec{p} + L^2\right] ------------------------(18)$$

Now

$$\vec{r}.\vec{p} = rp_r = -i\hbar r\frac{\partial}{\partial r} ------------------------------(19)$$

where use has been made of equation (4) Hence we obtain

$$p^2 = -\hbar^2\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right] ------------------------(20)$$

Finally the above equation can be combined with equation (2) to give the following expression for the Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right) + V(r) ------------------------------(21)$$

Let us now consider whether the above Hamiltonian commutes with the angular momentum operators L_z and L^2. Recall that L_z and L^2 are represented as differential operators which depend solely on the angular spherical polar co ordinates, θ and φ and do not contain the radial polar co ordinates r. thus any function of r or any differential operator involving r (but not θ and φ) will automatically commutes with $L^2$and L_z . Moreover L^2 commutes both with itself and with L_z it is therefore clear that the above Hamiltonian commutes with both L_z and L^2

Now if two operators commute with one another then they possess simultaneous eigenstates. We thus conclude that for a particle moving in a central potential the eigenstates of the Hamiltonian are simultaneous eigenstates of L_z and L^2. Now we have already found the simultaneous eigenstates of L_z and L^2 they are the spherical harmonics $Y_{l,m}(\theta,\varphi)$ it follows that the spherical harmonics are also eigenstates of the Hamiltonian. This observation leads us to the following separable form for the stationary wavefunction

$$\psi(r,\theta,\varphi) = R(r)Y_{l,m}(\theta,\varphi) ------------------(22)$$

It immediately follows from the fact that L_z and L^2 both obviously commute with R(r) that

$$L_z\psi = m\hbar\psi \text{ ------------ } (23)$$

$$L^2\psi = l(l+1)\hbar^2\psi \text{ ---------- } (24)$$

Recall that the quantum numbers m and l are restricted to take certain values

Finally making use of equation (1), (21) and (24) we obtain the following differential equation which determines the radial variation of the stationary wave function.

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+2\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)R_{n,l}+VR_{n,l} = E\,R_{n,l} \text{ ---------- } (25)$$

Here we have labeled the function R(r) by two quantum numbers n and l. the second quantum number *l* is of course related to the eigenvalues of L^2. [Note that azimuthal quantum number m does not appear in the above equation, and therefore does not influence either the function R(r) or the energy E] As we shall see the first quantum number n is determined by the constant that the radial wave function de square integrable.

8.3 Infinite spherical potential

Consider a particle of mass m and energy E > 0 moving in the following simple central potential

$$V(r) = \begin{cases} 0 & for\, 0 \le r \le a \\ \infty & otherwise \end{cases} \text{ ------------------ } (26)$$

Clearly the wave function ψ is only non –zero in the region $0 \le r \le a$ within this region it is subjected to the physical boundary conditions that it be well behaved (i.e., square integrable) at r=0 and that it be zero at r=a writing the wave function in the standard form

$$\psi(r,\theta,\varphi) = R_{n,l}(r)Y_{l,m}(\theta,\phi) \text{ ---------------------- } (27)$$

We deduce that the radial function $R_{n,l}(r)$ satisfies

$$\frac{d^2R_{n,l}}{dr^2}+\frac{2}{r}\frac{dR_{n,l}}{dr}+\left(k^2-\frac{l(l+1)}{r^2}\right)R_{n,l} = 0 \text{ ------------------ } (28)$$

In the region $0 \le r \le a$ where

$$k^2 = \frac{2mE}{\hbar^2} \text{ ---------------------- } (29)$$

Defining the scaled radial variable *z* = *kr*, the above differential equation can be transformed into the standard form

$$\frac{d^2R_{n,l}}{dz^2}+\frac{2}{z}\frac{dR_{n,l}}{dz}+\left[1-\frac{l(l+1)}{z^2}\right]R_{n,l} = 0 \text{ --------- } (30)$$

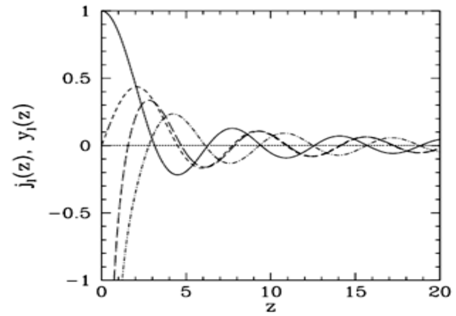


Figure (1)

The above figure (1) shows the first few spherical Bessel function. The solid short dashed long-dashed and dot- dashed curves shows $j_o(z)$, $j_1(z)$, $y_0(z)$, and $y_1(z)$ respectively

The two independent solutions to this well known second order differential equation are called spherical Bessel function and can be written

$$j_l(z) = z^l \left(-\frac{1}{z}\frac{d}{dz}\right)^l \left(\frac{\sin z}{z}\right) \text{---------------}(31)$$

$$y_l(z) = -z^l \left(-\frac{1}{z}\frac{d}{dz}\right)^l \left(\frac{\cos z}{z}\right) \text{---------------}(32)$$

Thus the first few spherical Bessel functions take the form

$$j_0(z) = \frac{\sin z}{z} \text{-------------------------}(33)$$

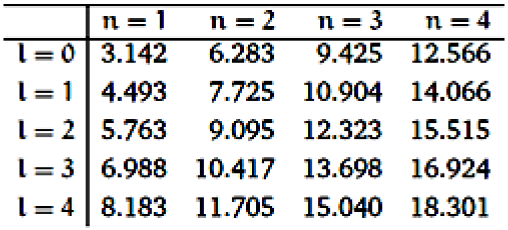
$$j_1(z) = \frac{\sin z}{z} - \frac{\cos z}{z} \text{--------------------}(34)$$

$$y_0(z) = -\frac{\cos z}{z} \text{-----------------------}(35)$$

$$y_1(z) = -\frac{\cos z}{z^2} - \frac{\sin z}{z} \text{--------------------}(36)$$

These functions are also plotted in fig (1). It can be seen that the spherical Bessel functions are oscillatory in nature passing through zero many times. However the $y_l(z)$ functions are badly behaved (i.e., they are not square integrable) at z=0 whereas the $j_l(z)$

Table 1: First few zeros of the spherical Bessel function $j_l(z)$



	n = 1	n = 2	n = 3	n = 4
l = 0	3.142	6.283	9.425	12.566
l = 1	4.493	7.725	10.904	14.066
l = 2	5.763	9.095	12.323	15.515
l = 3	6.988	10.417	13.698	16.924
l = 4	8.183	11.705	15.040	18.301

function are well behaved everywhere. It follows from our boundary condition at r=0 that the $y_l(z)$ are unphysical and that radial wave function $R_{n,l}(r)$ is thus proportional to $j_l(k,r)$ only. In order to satisfy the boundary condition at r=a [i.e $R_{n,l}(a)=0$] value of k must be chosen such that $z=ka$ corresponding to one of the zeros of $j_l(z)$. Let us denote the nth zero of $j_l(z)$ as $z_{n,l}$ it follows that

$$ka = z_{n,l} \text{------------------------------} (37)$$

for n=1,2,3…..

Hence from (29) the allowed energy levels are

$$E_{n,l} = z_{n,l}^2 \frac{\hbar^2}{2ma^2} \text{-----------------------------} (38)$$

The first values of $z_{n,l}$ are listed in Table (1) it can be seen that $z_{n,l}$ is an increasing function of both n and *l* .

We now in a position to interpret the three quantum numbers-n,1 and m- which determine the form of the wave function specified in Equation (27) The azimuthal quantum number m determines the number of nodes in the wave function as the azimuthal angle φ varies between 0 and 2π. Thus m=0 corresponds to no nodes, m=1 to single node m=2 to two nodes etc, Likewise the polar quantum number l determines the number n determines the number of node in the wave function as the polar angle θ varies between 0 and π. Again l=0 corresponds to no nodes l=1 to a single node, etc. finally the radial variable r varies between 0 and 1 (not counting any nodes at r=0 or r=a). Thus n=1 corresponds to no nodes n=2 to a single node n=3 to two nodes etc. Note that for the case of an infinite potential well the only restrictions on the values that the various quantum numbers can take are that n must be positive integer, l must be a non negative integer and m must be an integer lying between –l and l. Note further that the allowed energy levels (38) only depend on the values of the quantum numbers n and l. finally it is easily demonstrated that the spherical Bessel functions are mutually orthogonal.

$$\int_0^a j_l(z_{n,l}r/a) j_l(z_{n,l}r/a) r^2 dr = 0 \text{----------------------} (39)$$

When $n \neq n^1$ Given that the $Y_{l,m}$ (θ,φ) are mutually orthogonal this ensure that wave function (27) corresponding to distinct sets of values of the quantum numbers *n, l* and *m* are mutually orthogonal.

8.4 The Hydrogen atom:

A hydrogen atom consists of an electron of charge –*e* and mass m_e and a proton of charge +*e* and mass m_p moving in the Coulomb potential

$$V(r) = -\frac{e^2}{4\pi e_0 |\vec{r}|} -------------------(40)$$

where $\vec{r}$ is the position vector of the electron with respect to the proton. Now this two-body problem can be converted into an equivalent one-body problem. In the latter problem, a particle of mass

$$\mu = \frac{m_e m_p}{m_e + m_p} ---------------(41)$$

Moves in the central potential

$$V(r) = -\frac{e^2}{4\pi e_0 r} ----------------(42)$$

Note however that since $m_e/m_p \cong 1/1836$ the difference between m_e and μ is very small. Hence in the following, we shall write neglect this difference entirely.

Writing the wave function in the usual form

$$\psi(r,\theta,\phi) = R_{n,l}(r) Y_{l,m}(\theta,\phi) ----------(43)$$

Also the radial function $R_{n,l}(r)$ satisfies

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right)R_{n,l} - \left(\frac{e^2}{4\pi \in_0 r} + E\right)R_{n,l} = 0 --------(44)$$

Let $r = a\,z$; with

$$a = \sqrt{\frac{\hbar^2}{2m_e(-E)}} = \sqrt{\frac{E_0}{E}}a_0 ----------------------------(45)$$

where E_o and a_0 are defined in equation (57) and (58) respectively. Here it is assumed that $E<0$, since we are only interested in bound states of the hydrogen atom. The above differential equation transforms to

$$\left(\frac{d^2}{dz^2}+\frac{2}{z}\frac{d}{dz}-\frac{l(l+1)}{z^2}+\frac{\xi}{z}-1\right)R_{n,l}=0---------------(46)$$

where

$$\xi=\frac{2m_e ae^2}{4\pi\in_0\hbar^2}=2\sqrt{\frac{E_0}{E}}------------------------(47)$$

Suppose that $R_{n,l}(r)=Z(r/a)\exp(-r/a)$. It follows that

$$\left(\frac{d^2}{dz^2}+2\frac{d}{dz}-\frac{l(l+1)}{z^2}+\frac{\xi}{z}\right)Z=0----------------------(48)$$

We now need to solve the above differential equation in the domain z=0 to z=∞ subjected to the constraint that $R_{n,l}(r)$ be square integrable.

Let us look for a power law solution of the form

$$Z(z)=\sum_k c_k z^k ----------------------(49)$$

Substituting this solution into equation (48), we obtain

$$\sum_k c_k\left\{k(k-1)z^{k-2}-2kz^{k-1}-l(l+1)z^{k-2}+\xi z^{k-1}\right\}=0$$

Equating the coefficients of z^{k-2} gives the recursion relation

$$c_k\left[k(k-1)-l(l+1)\right]=c_{k-1}\left[2(k-l)-\xi\right]------------(51)$$

Now the power series (49) must terminates at small k at some positive value of k otherwise Z(z) behaves unphysically as z→0 [i.e., it yields an $R_{n,l}(r)$that is not square integrable as r→0]. From the above recursion relation this is only possible if $[k_{min}(k_{min}-1)-l(l+1)]=0$, where the first term in the series is $C_{k_{min}}z^{k_{min}}$. There are two possibilities: $k_{min}=-l$ or $k_{min}=l+1$. However the former possibility predicts unphysical behavior of Z(z) at z=0. Thus we conclude that $k_{min}=l+1$. Note that since $R_{n,l}(r)\simeq Z(r/a)\big/(r/a)\simeq\left(r/a\right)^l$ at small r, there is a finite probability of finding the electron at the nucleus for an *l* =0 state, whereas there is zero probability of finding the electron at the nucleus for an *l* >0 state [i.e., $|\psi|^2=0$ at r=0 except when *l*=0].

For large values of z, the ratio of successive co efficients in the power series (49) is

$$\frac{c_k}{c_{k-1}}=\frac{2}{k}----------------------------(52)$$

According to (51) this is the same as the ratio of successive co efficients in the power series

$$\sum_k \frac{(2z)^k}{k!} \text{------------------------------------}(53)$$

which converges to exp(2z). We conclude that Z (z)→exp(2z) as z→∞. It thus follows that $R_{n,l}(r) \sim Z\left(r/a\right)\left(\frac{e^{(r/a)}}{(r/a)}\right) \to \frac{e^{(r/a)}}{(r/a)}$ as r→∞. This does not correspond to physically acceptable behavior of the wave function since ∫ |ψ|^2 dV must be finite. The only way in which we can avoid this un physical behavior is if the power series terminates at some maximum value of k. according to the recursion relation this is only possible if

$$\frac{\xi}{2} = n \text{------------------------------}(54)$$

where n is an integer and the last term in the series is $c_n z^n$. Since the first term in the series is $c_{l+1}\ z^{l+1}$, it follows that *n* must be greater than *l* otherwise there are no terms in the series at all. Finally it is clear from equation (47) and (54) that

$$E = \frac{E_0}{n^2} \text{-----------------------------}(55)$$

and

$$a = na_0 \text{-----------------------------}(56)$$

where

$$E_0 = -\frac{m_e e^4}{2(4\pi \in_0)^2 \hbar^2} = -\frac{e^2}{8\pi \in_0 a_0} = -13.6eV \text{--------}(57)$$

and

$$a_0 = \frac{4\pi \in_0 \hbar^2}{m_e e^2} = 5.3 \times 10^{-11} m \text{------------------}(58)$$

Here E_0 is the energy of so called ground state (or lowest energy state) of the hydrogen atom and the length a_0 is known as the Bohr radius. Note that $|E_0| \sim \alpha^2\ m_e c^2$, where $\alpha = e^2/(4\pi\varepsilon_0 \hbar\ c) \cong 1/137$ is the dimensionless fine structure constant. The fact that $|E_0| << m_e c^2$ is the ultimate justification for our non relativistic treatment of the hydrogen atom.

We conclude that the wave function of a hydrogen atom takes the form

$$\psi_{n,l,m}(r,\theta,\varphi) = R_{n,l}(r) Y_{l,m}(\theta,\varphi) \text{-----------------}(59)$$

Here the $Y_{l,m}(\theta,\varphi)$ are the spherical harmonics and $R_{n,l}(z=r/a)$ is the solution of

$$\left(\frac{1}{z^2}\frac{d}{dz}z^2\frac{d}{dz}-\frac{l(l+1)}{z^2}+\frac{2n}{z}-1\right)R_{n,l}=0-------------(60)$$

which varies as z^l at small z. Furthermore the quantum number n, *l* and m can only take values which satisfy the inequality

$$|m|\le l\le n--------------------------------(62)$$

Where n is a positive, *l* is a non negative integer and m an integer

Now, we expect the stationary states of the hydrogen atom to be orthonormal: i.e.,

$$\int\psi^*_{n',l',m'}\psi_{n,l,m}dV=\delta_{nn'}\delta_{u'}\delta_{mm'}-----------------(62)$$

Where dV is a volume element and the integral is over all space. Of course dV= r^2 dr dΩ, where dΩ, is an element of solid angle. More over we already know that the spherical harmonics are orthonormal i.e.,

$$\oint Y^*_{l',m'}Y_{l,m}d\Omega=\delta_{ll'}\ \delta_{mm'}----------------------(63)$$

It thus follow that the radial wave function satisfies the orthonormality constraint

$$\int_0^\infty R^*_{n',l}R_{n,l}\ r^2dr=\delta_{nn'}--------------------------(64)$$

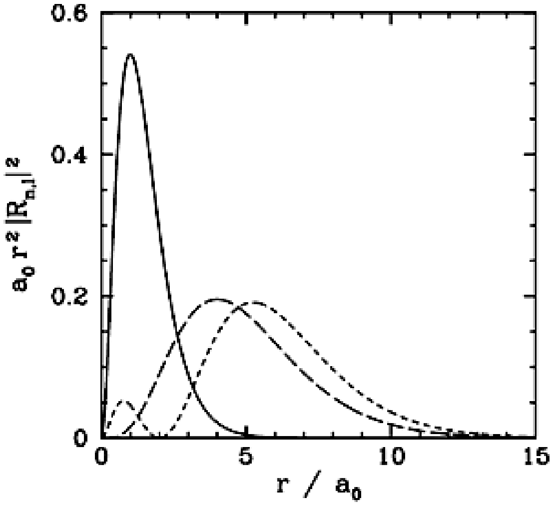


Figure (2) The $a_o r^2 \left|R_{n,l}(r)\right|^2$ *plotted* **as a function of r/a₀. The solid short-dashed, and long-dashed curves correspond to n, l=1, 0, and 2,0 and 2,1 respectively**

The first few radial wave functions for the hydrogen atom are listed below

$$R_{1,0}(r) = \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right) ----------------------------(65)$$

$$R_{2,0}(r) = \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right) -------------------(66)$$

$$R_{2,1}(r) = \frac{2}{\sqrt{3}(2a_0)^{3/2}} \left(\frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right) --------------------(67)$$

$$R_{3,0}(r) = \frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \exp\left(-\frac{r}{3a_0}\right) ---------------(68)$$

$$R_{3,1}(r) = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) \exp\left(-\frac{r}{3a_0}\right) -----------------(69)$$

$$R_{3,1}(r) = \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3a_0}\right) -------------------(70)$$

These function are illustrated in figure (2) and (3)

Given the (properly normalized) hydrogen wave function (59) plus our interpretation of $|\psi|^2$ as a probability density we can calculate

$$\left\langle r^k \right\rangle = \int_0^\infty r^{2+k} \left|R_{n,l}(r)\right|^2 dr ---------------------(71)$$

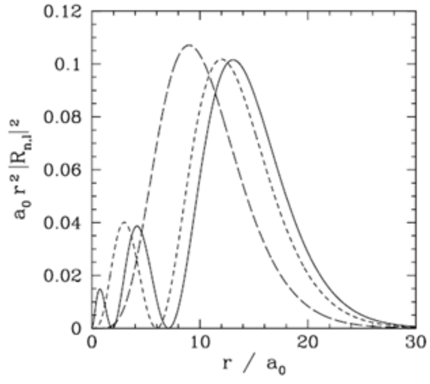


Figure 3: the a_0 r^2 $\left|R_{n,l}(r)\right|^2$ plotted as a function of r/a_0. The solid short-dashed and long-dashed curves correspond to n,l=3,0 and 3,1 and 3,2 respectively

where the angle brackets denote an expectation value. For instance it can be demonstrated (after much tedious algebra) that

$$\left\langle r^2 \right\rangle = \frac{a_0^2 n^2}{2}\left[5n^2 + 1 - 3l(l+1)\right] - - - - - - - (72)$$

$$\left\langle r \right\rangle = \frac{a_0}{2}\left[3n^2 - l(l+1)\right] - - - - - - - - - - - - - (73)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0} - - - - - - - - - - - - - - - - - - - (74)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l+1/2\right) n^3 a_0^2} - - - - - - - - - - - - - - (73)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l\left(l+1/2\right)\left(l+1\right) n^3 a_0^2} - - - - - - - - - - - (76)$$

According to equation (55) the energy levels of the bound states of a hydrogen atom only depend on the radial quantum number n. it turns out that this is a special property of a 1/r potential. For a general central potential V(r) the quantized energy levels of a bound- state depends on both n and l.

Fact that the energy levels of a hydrogen atom only depends on *n* and not on *l* and *m* implies that the energy spectrum of a hydrogen atom is highly degenerate: i.e., there are many different states which possess the same energy. According to the inequality (61) (and the fact that *n,l* and *m* are integers) fro a given value of *l* there are 2*l*+l different allowed values of m (i.e., –*l*,-*l*+1…..*l*-l,*l*). Likewise for a given value of *n* there are *n* different allowed values of *l* (i.e., 0, 1,……….., n-1). Now all states possessing the same value of *n* have the same energy (i.e., they are degenerate). Hence the total number of degenerate states corresponding to a given value of *n* is

$1+3+5+$---------------$+2(n-1)+1=n^2$-----------------------------(77)

Thus the ground state (n=1) is not degenerate the first excited state (n=2) is four fold degenerate the second excited state (n=3) is nine- fold degenerate etc. [Actually when we take into account the two spin states of an electron the degeneracy of the nth energy level becomes $2n^2$].

The eigen functions $\psi(r,\theta,\varphi)$ depend on three quantum numbers: *n,l,m*. We give below some of these normalized function obtained by combining the expressions for $Y_j^m\left(\theta,\varphi\right) and\ R_{nl}(r)$:

Table I

n	l	m	$\psi_{nlm}(r,\theta,\phi)$	$R_{nl}(r)$
1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	$2\left(\frac{Z}{a_0}\right)^{3/2} . e^{-Zr/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$	
2	1	± 1	$\mp\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}.\sin\theta . e^{\pm i\phi}$	

Fig 4 shows the radial dependence of the wave function for the few energy levels, while the angular dependence is shown in fig 5. In every direction (θ,φ) we calculate $\left|y_l^m(\theta,\phi)\right|^2$; we thus obtain a surface of revolution around the z-axis. For *l*=0 this surface is a sphere with O as centre; but becomes more complex for higher values of *l*.

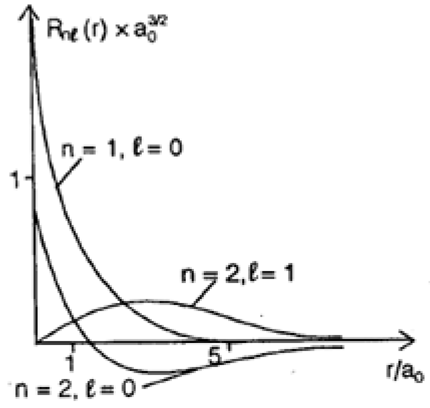


Fig. 4

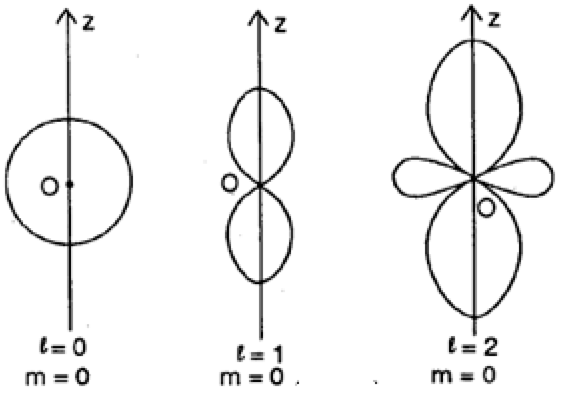


Fig.5

8.5 Let us sum up

We have understood the following concepts: the central potential, the radial equation wave equation in case of hydrogen atom, The method of solving the equation in case of hydrogen atom the eigen function and eigen values in case of hydrogen atom.

8.6 Key words

Central potential, spherically symmetric potential, radial equation, hydrogen atom wave equation.

8.7 Question for self study

What is meant by central potential?

What is meant by radial equation?

Write down the wave equation in case of hydrogen atom?

Discuss the method of solving the wave equation in case of hydrogen atom?

Discuss the eigen functions and eigen values in case of hydrogen atom?

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Unit-9: Rotation and angular momentum commutations relations, Spin ½ system and finite rotations

Structure:

9.0 Objectives:

After studying this unit you will be able to understand

- Rotations of angular momentum.
- Commutation relation.
- Spin ½ systems and
- Finite rotations

9.1 Introduction

The study of angular momentum and related topics is very important in modular physics. It is essential to understand angular momentum to understand molecular, atomic and nuclear spectroscopy: angular momentum considerations play an important role in scattering and collision problems as well as in boundary state problems further more angular momentum concepts have important generalizations iso-spin in nuclear physics Su(3), SU(2) and U(1) in particle physics and so on.

9.2 Contents of the Unit:

a. Rotations and angular momentum commutation relations.

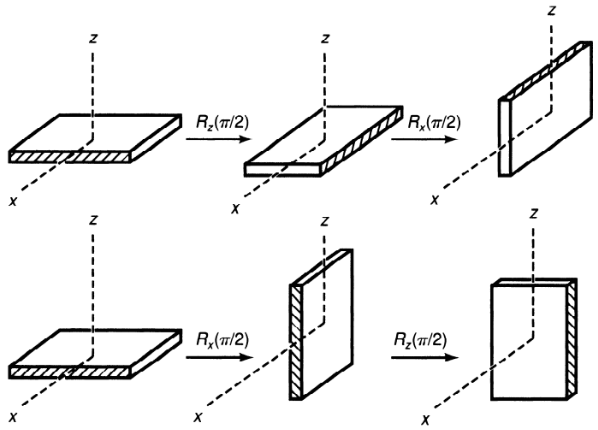
- i) Finite versus infinitesimal rotations
- ii) Infinite rotation in QM

b. Spin ½ system and finite rotations**.**

9.2.1. Rotations and angular momentum commutation relations:-

i) Finite Versus infinitesimal rotations:

We recall from elementary physics that rotations about the same axis commute, where as rotations about different axis followed by a 60^o rotation about the same z-axis is obviously equivalent to a 60^o rotation followed by a 30^o rotation both 90^0 rotation about the z-axis denoted by $R_z(\pi/2)$ followed by a 90^0 rotation about the x-axis denoted by $Rx(\pi/2)$ compare this with a 90^0 rotation about the x-axis followed by a 90^0 rotation about the z-axis. The net results are different as shown in the figure



First we have rotations out quantitatively the manner in which rotations about different axis fail to commute. Let us first see how to represent rotation in three dimensions by 3 X 3 real, orthogonal matrices. Consider a vector V with components V_x, V_y, V_z. When we rotate the three components becomes some other set of numbers $V_x^{'}, V_y^{'}\, and\, V_z^{'}$. The old and new components are related via a 3 X 3 orthogonal matrix R.

$$\begin{pmatrix} V_x^{'} \\ V_y^{'} \\ V_z^{'} \end{pmatrix} = (R) \begin{pmatrix} V_x \\ V_y \\ V_z \end{pmatrix} ----------- (1a)$$

$$RR^T = R^T R = 1 ------------ (1b)$$

where the superscript T stands for a transpose of matrix. It is a property of orthogonal matrices that

$$\sqrt{V_x^2 + V_y^2 + V_z^2} = \sqrt{V_x^{'2} + V_y^{'2} + V_z^{'2}} ---------- (2)$$

is automatically satisfied

To be definite, we consider a rotation about the z-axis by angleθ. The convention we follow throughout our discussion is that a rotation operation affects a physical system itself as in the above fig while the coordinate axis remains unchanged. The angle θ is taken to be positive ($+^{ve}$) when the rotation in question is counter clockwise in the x-y plane as viewed from the positive -side. If we associate a right handed screw with such a rotation, a +ve φ- rotation around the z-axis means that the screw is advancing in the +ve z-direction with this convention we easily verify that

$$R_z(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} -------- (3)$$

$If\ we\, want\, to\, write\, an$ inf $initesimal\ form\, of\ R_z$

$$R_z(\in)=\begin{pmatrix} 1-\frac{\in^2}{2} & -\in & 0 \\ \in & 1-\frac{\in^2}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}----------(4)$$

Where terms of order E^3 *and higher are ignored. Likewise we have*

$$R_x(\in)=\begin{pmatrix} 1 & 0 & 0 \\ 1 & 1-\frac{\in^2}{2} & -\in \\ 0 & \in & 1-\frac{\in^2}{2} \end{pmatrix}-----------(5a)$$

and

$$R_y(\in)=\begin{pmatrix} 1-\frac{\in^2}{2} & 0 & \in \\ 0 & 1 & 0 \\ -\in & 0 & 1-\frac{\in^2}{2} \end{pmatrix}------------(5b)$$

which may be read from equation (4) by cyclic permutations of x,y,z that is $x \to y$, $y \to z$, $z \to x$. Let us now compare the effect of a y-axis rotation followed by an x-axis rotation with that of an x-axis rotation with that of an x-axis rotation followed by a y-axis rotation elementary matrix manipulations lead to

$$R_x(\in)\,R_y(\in)=\begin{pmatrix} 1-\frac{\in^2}{2} & 0 & \in \\ \in^2 & 1-\frac{\in^2}{2} & -\in \\ -\in & \in & 1-\frac{\in^2}{2} \end{pmatrix}------------(6a)$$

and

$$R_y(\in)R_x(\in)=\begin{pmatrix} 1-\frac{\in^2}{2} & \in^2 & \in \\ 0 & 1-\frac{\in^2}{2} & -\in \\ \in & \in & 1-\in \end{pmatrix}--------------(6b)$$

From (6a) and (6b) we have the first important result; infinitesimal rotations about different axes do commute if terms of order $\in^2$ and higher are ignored. The second and even more important result concerns the manner in which rotations about different axis fail to commute when terms of order $\in^2$ are kept

$$R_x(\in)R_y(\in)-R_y(\in)R_x(\in)=\begin{pmatrix} 0 & -\in^2 & 0 \\ \in^2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$=R_z\left(\in^2\right)-1----------------------(7)$$

where all terms of order higher than $\in^2$ have been ignored throughout this derivation. We also have

$1=R_{any}(0)$--(8)

where 'any' stands for any rotation axis. Thus the final result can be written as

$$R_x(\in)R_y(\in)-R_y(\in)R_x(\in)=R\left(\in^2\right)-R_{any}(0)--------(9)$$

This is an example of the commutation relations between rotation operations about different axis which we will use later in deducing the angular momentum commutation relations in quantum mechanics.

ii. Infinitesimal rotations in Quantum Mechanics:

So far we have not used quantum mechanical concepts. The matrix R is just a 3X3 orthogonal matrix acting on a vector **V** written in column matrix form. We must now understand how to characterize rotations in Quantum Mechanics.

Because rotation affects physical systems, the state ket corresponding to a rotated system is expected to look different from the state ket corresponding to the original unrotated system. Given a rotation operation R characterized by a 3X3 orthogonal matrix R, we associate an operator D(R) in the appropriate ket space such that

$$|\alpha\rangle_R = D(R)|\alpha\rangle ---------(10)$$

Where $|\alpha\rangle_R$ *and* $|\alpha\rangle$ stand for the kets of the rotated and original system respectively. Note that the 3X3 orthogonal matrix R acts on a column matrix made up of the three components of a classical vector, while the operator D(R) acts on state vector in ket space. The matrix representation of D(R), which we will study in great detail in the subsequent sections, depends on the dimensionality N of the particular ket space in question. For N=2 appropriate for describing a spin ½ system with no other degree of freedom, D(R) is represented by a 2X2 matrix. For a spin 1 system, the appropriate is a 3X3 unitary matrix and so on.

To construct the rotation operator D(R) it is again fruitful to examine first its properties under an infinitesimal rotation. We can almost guess how we must proceed by analogy. In both translations and time evolution, the appropriate infinitesimal operator could be written as

$$U_\in = 1 - iG\in --------------(11)$$

with a Hermitian operator G. Specifically

$$G \to \frac{p_x}{\hbar}, \in \to dx' ------------(12)$$

For an infinitesimal displacement dx' in the x-direction

$$G \to \frac{H}{\hbar}, \in \to dt -------(13)$$

For an infinitesimal time evolution with time displacement *dt*. We know from classical mechanics that angular momentum is the generator of rotation in much the same way as momentum and Hamiltonian are the translation and time evolution, respectively. We therefore define the angular momentum operator J_k in such a way that the operator for an infinitesimal rotation around the k^{th} axis by angle dφ can be obtained by letting

$$G \to \frac{J_k}{\hbar}, \qquad \in \to d\varphi ------------- (14)$$

in eqn (11) with J_k taken to be Hermitian, the infinitesimal rotation operator is guaranteed to be unitary and reduces to the identity operator in the limit dφ→0. More generally, we have,

$$D\left(\hat{n}, d\varphi\right) = 1 - i\left(\frac{\vec{J}.\hat{n}}{\hbar}\right) d\varphi --------\left(15\right)$$

for a rotation about the direction characterized by a unit vector $\hat{n}$ by an infinitesimal angle dφ.

A finite rotation can be obtained by compounding successively infinitesimal rotations about the same axis. For instance, if we are interested in a finite rotation about the z-axis by angle φ we consider

$$\begin{aligned} D_z\left(\varphi\right) &= \lim_{N\to\infty}\left[1 - i\left(\frac{J_z}{\hbar}\right)\left(\frac{\varphi}{N}\right)\right]^N \\ &= \exp\left(\frac{-iJ_z\varphi}{\hbar}\right) \\ &= 1 - \frac{iJ_z\varphi}{\hbar} - \frac{J_z^2\varphi^2}{2\hbar^2} + ----------- (16) \end{aligned}$$

In order to obtain the angular momentum commutation relations, we need one more concept. As considered earlier for every rotation R represented by a 3X3 orthogonal matrix R there exits a rotation operator D(R) in the appropriate ket space we further postulate that D(R) has the same group properties as R;

$$Identity: R.1 = R \Rightarrow D(R).1 = D(R) ---------- (17a)$$

$$Closure: R_1 R_2 = R_3 \Rightarrow D(R_1)\,D\left(R_2\right) = D\left(R_3\right) ----- \left(17b\right)$$

$$Inverse: RR^{-1} = 1 \Rightarrow D(R)\,D^{-1}\left(R\right) = 1 -------- \left(17c\right)$$
$$R^{-1}R = 1 \Rightarrow D^{-1}(R)\,D(R) = 1$$

$$Associativity: R_1(R_2R_3) = \left(R_1R_2\right)R_3 = R_1R_2R_3 ----- (17d)$$
$$\Rightarrow D\left(R_1\right)\left[D(R_2)D\left(R_3\right)\right]$$
$$\Rightarrow \left[D\left(R_1\right)D\left(R_2\right)\right]D\left(R_3\right)$$
$$= D\left(R_1\right)D\left(R_2\right)D\left(R_3\right)$$

Let us now return to the fundamental commutation relations for rotation operations (9) written in terms of the R matrices. Its rotation operator analogue would read

$$\left(1-\frac{iJ_x \in}{\hbar}-\frac{J_x^2 \in^2}{2\hbar^2}\right)\left(1-\frac{iJ_y \in}{\hbar}-\frac{J_y^2 \in^2}{2\hbar^2}\right)-\left(1-\frac{iJ_y \in}{\hbar}-\frac{J_y^2 \in^2}{2\hbar^2}\right)\left(1-\frac{iJ_x \in}{\hbar}-\frac{J_x^2 \in^2}{2\hbar^2}\right)$$
$$=1-\frac{iJ_z \in^2}{\hbar}-1----------------\left(18\right)$$

Terms of order $\in$ automatically drop out equating terms of order $\in^2$ on both sides of (18) we obtain

$$\left[J_{x,}J_y\right] = i\hbar J_z ------------ (19)$$

Repeating this kind of argument with stations about other axis we obtain $\left[J_i, J_j\right] = i\hbar \in_{ijk} J_k -------\left(20\right)$ known as the fundamental commutation relations of angular momentum.

9.2.2. Spin ½ system and finite rotations

Rotations operator for Spin -1/2

The above number, N of dimensions in which the angular momentum commutation relations (20) are realized is N=2.

The operators for S_x, S_y, and S_z are defined by

$$S_x=\left(\frac{\hbar}{2}\right)\left\{\left(|+\rangle\langle-|\right)+\left(|-\rangle\langle+|\right)\right\}$$
$$S_y=\left(\frac{i\hbar}{2}\right)\left\{-\left(|+\rangle\langle-|\right)+\left(|-\rangle\langle+|\right)\right\}$$
$$S_z=\left(\frac{\hbar}{2}\right)\left\{\left(|+\rangle\langle+|\right)-\left(|-\rangle\langle-|\right)\right\}-------------(21)$$

satisfy commutation relations (20) with J_k replaced by S_k. It is not a priori obvious that nature takes advantage of the lowest dimensional realization of equation (20) but numerous experiments- from atomic spectroscopy to nuclear magnetic resonance, suffice to convince us that this is in fact the case.

Consider a rotation by a finite angle φ about the z-axis. If the ket of a spin ½ system before rotation is given by $|\alpha\rangle$ the ket after rotation is given by

$$|\alpha\rangle_R=D_z\left(\varphi\right)|\alpha\rangle---------------(22)$$

with

$$D_z\left(\varphi\right)=\exp\left(\frac{-iS_z\varphi}{\hbar}\right)-------------(23)$$

To see that this operator really rotates the physical system, let us see its effect on $<S_x>$ under rotation this expectation value changes as follows

$$\langle S_x\rangle\rightarrow_R\langle\alpha\,|\,S_x\,|\,\alpha\rangle_R=\left\langle\alpha\,|\,D_z^+\left(\varphi\right)S_xD_z\left(\varphi\right)|\,\alpha\right\rangle-------(24)$$

we must therefore compute

$$\exp\left(\frac{iS_z\varphi}{\hbar}\right)S_x\exp\left(\frac{-iS_z\varphi}{\hbar}\right)------------------(25)$$

Let us evaluate this in two ways:

<u>Derivation 1</u>:- Here we use the specific form of S_z given by (21). We then obtain for (25)

$$\left(\frac{\hbar}{2}\right)\exp\left(\frac{iS_z\varphi}{\hbar}\right)\left\{\left(|+\rangle\langle-|\right)+\left(|-\rangle\langle+|\right)\right\}\exp\left(\frac{-is_z\varphi}{\hbar}\right)$$
$$=\left(\frac{\hbar}{2}\right)\left(e^{i\varphi/2}\,|+\rangle\langle-|e^{i\varphi/2}+e^{-i\varphi/2}\,|-\rangle\langle+|e^{-i\varphi/2}\right)$$
$$=\frac{\hbar}{2}\left[\left\{\left(|+\rangle\langle-|\right)+\left(|-\rangle\langle+|\right)\right\}\cos\varphi+i\left\{\left(|+\rangle\langle-|\right)-\left(|-\rangle\langle+|\right)\right\}\sin\varphi\right]$$
$$=S_x\cos\varphi-S_y\sin\varphi------(26)$$

Derivation 2:- Alternatively we many use formula

$$\exp(iG\lambda)A\exp(-iG\lambda)=A+i\lambda[G,A]+\left(\frac{i^2\lambda^2}{2!}\right)\big[G,[G,A]\big]$$

$$+------+\left(\frac{i^n\lambda^n}{n!}\right)\Big[G,\big[G,[G,........]G,A\big]-----\Big]+----(25)$$

To evaluate eqn (25)

$$\exp\left(\frac{iS_z\varphi}{\hbar}\right)S_x\exp\left(\frac{-iS_z\varphi}{\hbar}\right)=S_x+\left(\frac{i\varphi}{\hbar}\right)\underbrace{\left[S_{z,}S_x\right]}_{i\hbar S_y}$$

$$+\left(\frac{1}{2!}\right)\left(\frac{i\varphi}{\hbar}\right)^2\underbrace{\left[S_z\underbrace{\left[S_{z,}S_x\right]}_{i\hbar S_y}\right]}_{\hbar^2 S_x}+\left(\frac{1}{3!}\right)\left(\frac{i\varphi}{\hbar}\right)^3\Big[S_z,\big[S_z,[S_{z,}S_x]\big]\Big]+-----$$

$$=S_x\left[1-\frac{\varphi^2}{2!}+------\right]-S_y\left[\varphi-\frac{\varphi^3}{3!}+-------\right]$$

$$=S_x\cos\varphi-S_y\sin\varphi---------------(27)$$

Notice that in derivation (2) we used only the commutation relations for $S_{i.}$ So this method can be generalized to rotations of systems with angular momentum higher than ½.

For spin ½ both methods give

$$\langle S_x\rangle\rightarrow_R\langle\alpha|S_x|\alpha\rangle_R=\langle S_x\rangle\cos\varphi-\langle S_y\rangle\sin\varphi-------(28)$$

where the expectation value without subscripts is understood to be taken w.r.t the unrotated system.

Similarly

$$\langle S_y\rangle\rightarrow\langle S_y\rangle\cos\varphi+\langle S_x\rangle\sin\varphi------(29)$$

As for the expectation value of S_z, there is no change because S_z commutes with $D_z(\varphi)$.

$$\langle S_z\rangle\rightarrow\langle S_z\rangle---------(30)$$

Relations (28), (29) and (30) are quite reasonable. They show that rotation operator (23) when applied to the state ket does rotate the expectation value of S around the z-axis by angle φ. In other words, the expectation value of the spin operator behaves as though it were a classical vector under rotation.

$$\langle S_k\rangle\rightarrow\sum_l R_{k.l}\langle S_l\rangle----------(31)$$

where R_{kl} are the elements of the 3X3 orthogonal matrix R that specifies the rotation in question. It should be clear from our derivation (2) that this property is not restricted to the spin operator of spin ½ systems. In general we have,

$$\langle J_k \rangle \rightarrow \sum_l R_{k.l} \langle J_l \rangle ----------(32)$$

Under rotation where J_k are the generators of rotations satisfying the angular momentum commutation relations (20).

9.2.3. Commutation relations of angular momentum with components:-

The total angular momentum is defined by

$$J^2 = J_x^2 + J_y^2 + J_z^2 ----------(33)$$

We can derive the commutation relation of J^2 with components J_x, J_y, J_z

Let us take

$$\left[J^2, J_x\right] = \left[J_x^2 + J_y^2 + J_z^2, J_x\right]$$

$$= \left[J_x^2, J_x\right] + \left[J_y^2, J_x\right] + \left[J_z^2, J_x\right] ----------(34)$$

$$\text{We know that } \left[ab, c\right] = a[b, c] + \left[a, c\right]b$$

$$\text{So}\left[J_x^2, J_x\right] = \left[J_x J_{x,} J_x\right] - J_x\left[J_x, J_x\right] + \left[J_x J_x\right] J_x$$

$$= 0$$

$$\left[J^2, J_x\right] = \left[J_y^2, J_x\right] + \left[J_z^2, J_x\right]$$

$$= J_y\left[J_{y,} J_x\right] + \left[J_{y,} J_x\right] J_y + J_z\left[J_x, J_x\right] + \left[J_z J_x\right] J_z$$

$$= J_y(-i\hbar J_z) + \left(-i\hbar J_z\right) J_y + J_z\left(i\hbar J_y\right) + \left(i\hbar J_y\right) J_z$$

$$= 0$$

$$\therefore \left[J^2, J_x\right] = 0 ----------------------(35)$$

$$\left[J^2, J_y\right] = 0 ------------------------(36)$$

$$\left[J^2, J_z\right] = 0 ------------------------(37)$$

9.2.4.Ladder Operators J_+ and J_- :

Now, let us define the new operators

$$\left.\begin{aligned} J_+ &= J_x + iJ_y \\ J_- &= J_x - iJ_y \end{aligned}\right\} -------------(38)$$

Commutation relation of J_z with J_+ and J_-

$$[J_z, J_+] = [J_z, J_x + iJ_y]$$
$$= [J_z, J_x] + i[J_z, J_y] = [J_z, J_x] - i[J_y, J_z]$$
$$= i\hbar J_y - i(i\hbar J_x)$$
$$\left\{ \sin ce\ [J_z, J_x] = i\hbar J_y and [J_y, J_z] = i\hbar J_y and [J_y, J_z] = i\hbar J_x \right\}$$
$$= i\hbar J_y + \hbar J_x - \hbar[J_x + iJ_y]$$
$$= \hbar\, J_+ -------------------(39)$$

And similarly,

$$[J_z, J_-] = [J_z, J_x - iJ_y]$$
$$= \begin{bmatrix} J_z, \\ J_x \end{bmatrix} - i(-i\hbar J_x)$$
$$= i\hbar J_y - \hbar J_x$$
$$= -\hbar J_- ----------------(40)$$

Or we can write (39) and (40) in compact form as

$$[J_z, J_\pm] = \hbar J_\pm -------------(41)$$
$$[J_+, J_-] = [J_x + iJ_{y,} J_x - iJ_y]$$
$$= [J_x, J_x] - [J_x, J_y] + i[J_y, J_x] + [J_y, J_y]$$
$$= 0 - i[J_x, J_y] = -i[J_x, J_y] \neq 0$$
$$= -2i[J_x, J_y] = -2i[i\hbar J_z]$$
$$= 2\hbar J_z ----------------(42)$$

Commutation relations of J^2 with J_+ and J_-

$$[J^2, J_+] = [J^2, J_x + iJ_y]$$
$$= [J^2, J_x] + i[J^2, J_y]$$
$$[J^2, J_+] = 0 + 0 = 0 \qquad (43)$$

$$Similarly \quad \left[J^2, J_-\right] = \left[J^2, J_x - iJ_y\right]$$

$$= \left[J^2, J_x\right] - i\left[J^2, J_y\right] = 0 \qquad (44)$$

$$Combining\,(43)\,in\,(44)\,we\,have$$

$$\left[J^2, J_\pm\right] = 0 ------------------ (45)$$

9.3 Let us sum up

So we have learnt the rotations of angular momentum commutation relations, spin ½ systems and some more commutation relations of angular momentum components.

9.4 Key words

Angular momentum, spin, commutation relation, rotations.

9.5 Question for Self study

1. Discuss the rotations of angular momentum?
2. Explain infinitesimal rotations QM?
3. Discuss the rotations of spin -1/2 system?
4. P.T $[J^2, J_x] = 0$
5. Evaluate the brackets $[J_z\ J_\pm]$, $[J_+, J_-]$ and $[J^2, J_\pm]$.

9.6 References for further study:

- Modern Quantum Mechanics by J.J.Sakurai, Addison Wesley Publications.

Unit-10: Eigen values and Eigen states of angular momentum.

Structure:

10.0 Objectives:

After studying this unit you will be able to understand

- The Eigen values of J^2 and J_z.
- Matrix elements of Angular momentum operators.
- Eigen functions of J^2 and J_z

10.1 Introduction

Till now we have discussed angular momentum rotations and its commutation relations. Now we will see what are the eigenvalues and eigenfunctions of J^2 and J_z and derive the expression for matrix elements of angular momentum operators while are first obtained in 1926 by M.Born, W Heisenberg and P. Jordan.

10.2 Contents:

(a) Eigen values of J^2 and J_z

(b) Eigen values of J_+ and J_-

(c) Eigen Values of J_x and J_y

(d) Explicit form of the angular momentum matrices.

(e) Eigen functions of J^2 and J_z .

a) Eigen values of J^2 and J_z:

As J^2 and J_z commutate, they possess simultaneous Eigen functions. If *a* and *b* are Eigen values of operators J^2 and J_z in the state $|\psi\rangle$ then Eigen value equation of J^2 and J_z in the state $|\psi\rangle$ are

$$J^2|\psi\rangle = a|\psi\rangle \text{-------------------------}(1)$$

$$J_z|\psi\rangle = b|\psi\rangle \text{-------------------------}(2)$$

Now let us operate by ladder operators $J_+=J_x+iJ_y$ and $J_-=J_x-iJ_y$, then we have

$$JzJ_+|\psi\rangle = \left\{\left[J_{z,}J_+\right] + J_+J_z\right\}|\psi\rangle$$

$$\left\{Since\left[J_{z,}J_+\right] = J_zJ_+ - J_+J_z\right\}$$

$$= \left[J_zJ_+\right]|\psi\rangle + J_+b|\psi\rangle$$

$$= \hbar\, J_+|\psi\rangle + J_+\, b|\psi\rangle$$

$$\left\{Since\left[J_zJ_+\right] = \hbar J_+ \;\; and \;\; J_z|\psi\rangle = b|\psi\rangle\right\}$$

$$i.e.,\; J_zJ_+|\psi\rangle = \left(b+\hbar\right)J_+|\psi\rangle --------------(3)$$

This equation shows that J$_+$ has eigen value (b+$\hbar$) in the state J$_+$ $|\psi\rangle$. Thus the operation of J$_+$ on ψ increase the eigen value of J$_+$ by an amount $\hbar$

Operating again by J$_+$ on J$_+|\psi\rangle$ then we have

$J_+ J_+ |\psi> = J_+^2|\psi>$

$$\text{So that } J_zJ_+^2|\psi\rangle = J_zJ_+\left(J_+|\psi\rangle\right)$$

$$\left\{\left[J_z, J_+\right] + J_+J_z\right\}J_+|\psi\rangle$$

$$= \left(\hbar\, J_+ + J_+J_z\right)J_+|\psi\rangle$$

$$= \hbar\, J_+^2|\psi\rangle + J_+J_zJ_+|\psi\rangle$$

$$= \hbar\, J_+^2|\psi\rangle + J_+(b+\hbar)\,J_+|\psi\rangle \quad u\sin g\,(3)$$

$$= \left(b+2\hbar\right)J_+^2|\psi\rangle -------------(4)$$

This equation shows that J$_z$ has a eigen value (b+2$\hbar$) in the state $J_+^2|\psi\rangle$. Thus the operator of J$_+$ on $|\psi\rangle$ each time simply means the increase in eigen value of J$_z$ by $\hbar$ each time. Hence in general we may write

$$J_zJ_+^n|\psi\rangle = \left(b+n\hbar\right)J_+^n|\psi\rangle --------------(5)$$

And similarly for J$_-$ operator we write

$$J_zJ_-^n|\psi\rangle = \left(b-n\hbar\right)J_-^n|\psi\rangle --------------(6)$$

These two equations show that there is a discrete spectrum for the eigen values of J$_Z$ depending on the integer n. The eigen values are

n=-n,…….n=-2, n=-1, n=0, n=1, n=2………..n = n

$$\left(b-n\hbar\right)...........\left(b-2\hbar\right),\left(b-\hbar\right),b,\left(b+\hbar\right)...............\left(b+n\hbar\right)$$

Thus we see that as *n* tends from -∞ to +∞, the eigen values of J$_z$ tend from -∞ to ∞.

As angular momentum of a system is finite, therefore eigenvalues of J^2 is finite i.e a is finite

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

i.e., $J_z^2 \le J^2$ therefore the eigen values of J_z must be finite and hence terminated after certain terms so that inequality $J_z^2 \le J^2$ may hold good. Hence we terminate this series of eigen values like

$$J_z J_+^{l+1}\left|\psi\right\rangle = 0 \ \ and \ \ J_z J_-^{k+1}\left|\psi\right\rangle = 0 ----------------(7)$$

i.e., maximum and minimum values of integers are *l* and *k* respectively defined by (7)

Therefore the eigen values of J_z are restricted to the region

n=-k,………..n=-1, n=0, n=1…….n = *l*.

$$\left(b-k\hbar\right)................\left(b_{-}\hbar\right),b,\left(b+\hbar\right)...........\left(b+l\hbar\right)$$

Now we have

$$J_+ = J_x + iJ_y, J_- = J_x - iJ_y$$
$$J_-J_+ = \left(J_x - iJ_y\right)\left(J_x + iJ_y\right) = J_x^2 + J_y^2 + i\left[J_x J_y\right]$$
$$or\ J_x^2 + J_y^2 = J_-J_+ - i\left(i\hbar J_z\right)$$
$$J_x^2 + J_y^2 = J_-J_+ + \hbar J_z ----------------(8a)$$

Similarly if we start with J_+J_- we get

$$J_x^2 + J_y^2 = J_+J_- - \hbar J_z ----------(8b)$$
$$J^2 = J_x^2 + J_y^2 + J_z^2 = \left(J_x^2 + J_y^2\right) + J_z^2$$
$$= J_z^2 + J_-J_+ + \hbar J_z \qquad (u\sin g\,(8a)) ------------(9a)$$
$$J^2 = J_z^2 + J_+J_- - \hbar J_z \quad (u\sin g\,(8b)) -----------(9b)$$

Now let us find eigen values of J^2 in terms of J_z

Since $[J_z, J^2]=0$. Therefore J_z and J^2 have the same eigen function i.e., if $J_+^l\left|\psi\right\rangle$ is an eigen function of J_z , it will be also for J^2

$$Hence\ J^2 J_+^l\left|\psi\right\rangle = \left(J_z^2 + J_-J_+ + \hbar J_z\right)J_+^l\left|\psi\right\rangle$$
$$= J_z^2 J_+^l\left|\psi\right\rangle + J_-J_+J_+^l\left|\psi\right\rangle + \hbar J_z J_+^l\left|\psi\right\rangle$$

Using equation (5) and (7)

$$J^2 J_+^l|\psi\rangle = J_z J_z J_+^l|\psi\rangle + J_- J_+^{l+1}|\psi\rangle$$
$$= \left\{(b+l\hbar)(b+l\hbar)+\hbar(b+l\hbar)\right\} J_+^l|\psi\rangle ----------(10)$$
$$= (b+l\hbar)(b+l\hbar+\hbar) J_+^l|\psi\rangle$$

This equation gives the eigen values for J^2

$$Again\ \ J^2 J_-^k|\psi\rangle = \left(J_z^2 + J_+J_- - \hbar J_z\right) J_-^k|\psi\rangle$$
$$= \left\{(b-k\hbar)^2 + 0 - \hbar(b-k\hbar)\right\} J_-^k|\psi\rangle$$
$$= (b-k\hbar)(b-k\hbar-\hbar) J_-^k|\psi\rangle ---------------(11)$$

Equating two eigen values given by (10) and (11) of J^2, which represent eigen values of “a”, We have,

$$a = (b+l\hbar)(b+l\hbar+\hbar) = (b-l\hbar)(b-k\hbar-\hbar) -----------(12)$$

Solving for b we get $b = \frac{\hbar}{2}(k-l)$

And therefore from (12), we have

$$a = \hbar^2\left(\frac{k+l}{2}\right)\left\{\frac{(k+l)}{2}+1\right\}$$

where $\left(\frac{k+l}{2}\right)$ and $\left(\frac{k-l}{2}\right)$ are necessarily integers.

Now we substitute $\left(\frac{k+l}{2}\right) = j$; so that

$$\left.\begin{aligned} a &= j(j+1)\hbar^2 \\ b &= \frac{\hbar}{2}(k-l) \end{aligned}\right\}$$

Since $\left(\frac{k+l}{2}\right) = j$; thus

$$\left.\begin{aligned} K_{\max} &= 2j; \qquad K_{\min} = 0 \\ l_{\max} &= 2j; \qquad l_{\min} = 0 \end{aligned}\right\}$$

Therefore when $k = k_{\max} = 2j, l = l_{\min} = 0$; we have $j_{\max} = j$

and when $k = k_{\min} = 0, l = l_{\max} = 2j$; we have $j_{\min} = -j$

Thus eigen values *b* may be expressed as

$$-j\hbar,\left(-j+1\right)\hbar,.......2\hbar,-\hbar,0,\hbar,2\hbar,........(j-1)\hbar,\ j\hbar \qquad (15)$$

Therefore J$_z$ have eigen values from $-\,j\hbar, to + j\hbar$ i.e., the total values are (2j+1). Thus we define b = m$_z$. Where m$_z$ have these all (2j+1) values and it is called magnetic quantum number

Hence eigen values of J^2 and J$_z$ are respectively;

$$\left.\begin{array}{l} j\left(j+1\right)\hbar^2 \\ and \ \ m_z\hbar^2 \end{array}\right\}----------------------(16)$$

Equation (16) represents the eigen values of J^2 and J$_z$. The matrix elements of J$_z$ which is diagonal in above representation are determined by equation

$J_z\psi\left(jm\right) = m_z\psi(jm) \quad whence\ if\ \ \psi\left(jm\right)$ are normalized.

$$\left\{\psi\left(j'm'\right) = J_z\psi\left(jm\right)\right\} = \left\langle j'm' \,|\, Jz \right| j_m \rangle$$
$$= m_z\hbar\delta_{mm'}\delta_{jj'}$$

(b) Eigen values of J_+ and J_-:

If we represent a state function $\psi\left(r, j, m\right)$ where j and m are angular and magnetic quantum number respectively then eigen value equation of operator J$_+$ is

$$J_\pm\psi\left(r, j, m\right) = N_\pm\psi\left(r, j, m\pm1\right)-----------(17)$$

Where N$_\pm$ is eigen value of J$_\pm$, J$_+$ being is raising and J$_-$ the lowering operator

We have; $J_\pm^*\psi^*\left(r, j, m\right) = N^*{}_\pm\,\psi^*\left(r, j, m\pm1\right)$

So that

$$\psi^*\left(r, j, m\pm1\right)\psi\left(r, j, m\pm1\right) = \frac{1}{N_\pm^*N_\pm}\,J_\pm^*\psi^*\left(r, j, m\right)J_\pm\psi\left(r, j, m\right)$$
$$= \frac{1}{|\,N_\pm\,|^2}\,J_\pm J_\pm\psi^*\left(r, j, m\right)\psi\left(r, j, m\right)$$
$$= \frac{1}{|\,N_\pm\,|^2}\left[J^2 - J_z\left(J_z \pm \hbar\right)\right]\psi^*\left(r, j, m\right)\times\psi\left(r, j, m\right)$$

Now applying normalization condition

$$\int\psi^*\psi\ d\tau = 1$$

we get

$$1=\frac{1}{|N_\pm|^2}\left[j(j+1)\hbar^2-m_z\hbar(m_z\pm\hbar)\right]$$

$$or\ N_\pm=\hbar\sqrt{j(j+1)-m_Z(m_z\pm1)}\ e^{i\delta}---------(18)$$

where δ is arbitrary real number and is phase factor. Thus we have some useful derivation from (17) and (18) by taking $e^{i\delta}=1$.

From (17), $J_\pm\psi(r,j,m)=N_\pm\psi^*(r,j,m\pm1)$

Then the equation (17) becomes

$$J_+\psi(r,j,m)=\hbar\sqrt{j(j+1)-m_z(m_z+1)}\ \ \psi(r,j,m+1)----------(19)$$

$$J_-\psi(r,j,m)=\hbar\sqrt{\left[j(j+1)-m_z(m_z-1)\right]}\ \ \psi(r,j,m-1)---------(20)$$

or in more simplified form (19) and (14) can be written as

$$J_+\psi(jm)=\hbar\sqrt{\left[(j-m)-(j+m+1)\right]}\ \ \psi(j,m+1)-------------(21)$$

$$J_-\psi(jm)=\hbar\sqrt{\left[(j+m)\ \ (j-m\ \ +1)\right]}\ \ \psi(j,m-1)-------------(22)$$

The matrix elements of J_+ and J_- are

$$\langle j'm'|J_+|jm\rangle=\langle j'm'|jm+1\rangle\hbar\sqrt{(j-m)(j+m+1)}-----------(23)$$

$$or\quad \langle j'm'|J_+|jm\rangle=\hbar\sqrt{(j-m)(j+m+1)}\,\delta_{jj'}\delta_{m'm+1}$$

Similarly;

$$\langle j'm'|J_-|jm\rangle=\hbar\sqrt{(j-m)(j-m+1)}\,\delta_{jj'}\delta_{m'm-1}--------------(24)$$

(c) ***<u>Eigen values of J_x ang J_y:</u>***

The matrix elements or eigen values of J_x and j_y can be determined by following equation

$$\left.\begin{aligned}J_+&=J_x+iJ_y\\J_-&=J_x-iJ_y\end{aligned}\right\}$$

Hence,

$$\left.\begin{aligned}J_x&=\frac{1}{2}(J_++J_-)\\J_y&=\frac{1}{2i}(J_+-J_-)=-\frac{1}{2}i(J_+-J_-)\end{aligned}\right\}---------(25)$$

$$and\ also\ J_+^\dagger = J_-$$

$$\therefore \langle j'm'|J_x|jm\rangle = \langle j'm'|\frac{1}{2}(J_+ + J_-)|jm\rangle$$

$$= \frac{1}{2}\langle j'm'|(J_+ + J_-)|jm\rangle$$

$$= \frac{1}{2}\langle j'm'|J_+|jm\rangle + \langle j'm'|J_-|jm\rangle$$

$$from\ equations\ (23)\ and\ (24)\ we\ get$$

$$\langle j'm'|J_x|jm\rangle = \frac{1}{2}\hbar\sqrt{\left[(j-m)(j+m+1)\right]}\,\delta_{j'j}\,\delta_{m'm+1}$$

$$+\frac{1}{2}\hbar\sqrt{\left[(j+m)(j-m+1)\right]}\,\delta_{j'j}\,\delta_{m'm-1} ------------- (26)$$

$$in\ another\ form$$

$$J_x\psi(jm) = \frac{1}{2}\hbar\sqrt{\left[(j-m)(j+m+1)\right]}\,\psi(j,m+1)$$

$$+\frac{1}{2}\hbar\sqrt{\left[(j+m)(j-m+1)\right]}\,\psi(j,m-1) -------- (27)$$

Similarly, the matrix elements of J$_y$ are as follows:

$$\left\langle j'm'|J_y\right|jm\rangle = \langle j'm'|-\frac{1}{2}i(J_+ - J_-)|jm\rangle$$

$$= -\frac{1}{2}i\langle j'm'|J_+|jm\rangle + \frac{1}{2}i\langle j'm'|J_-|jm\rangle$$

$$= \frac{-i\hbar}{2}\sqrt{(j-m)(j+m+1)}\,\delta_{j'j}\,\delta_{m'm+1} + \frac{i\hbar}{2}\sqrt{(j+m)(j-m+1)}\,\delta_{j'j}\delta_{m'm-1} -------- (28)$$

or in more simplified form

$$J_y\psi(jm) = -\frac{i}{2}\hbar\sqrt{(j+m)(j+m+1)}\psi(j,m+1) + \frac{i}{2}\hbar\sqrt{(j+m)(j-m+1)}\psi(j,m-1)$$

If we consider $J' = J$, then Eqns (26) and (28) will reduce to

$$\langle jm'|J_x|jm\rangle = \frac{1}{2}\hbar\sqrt{\left[(j-m)(j+m+1)\right]}\,\delta_{jj}\,\delta_{m'm+1}$$

$$+\frac{1}{2}\hbar\sqrt{\left[(j+m)(j-m+1)\right]}\,\delta_{jj}\,\delta_{m'm-1} ----------- (29)$$

and

$$\left\langle jm'|J_y\right|jm\rangle = \frac{-i\hbar}{2}\sqrt{(j-m)(j+m+1)}\,\delta_{jj}\,\delta_{m'm+1}$$

$$+\frac{i\hbar}{2}\sqrt{(j+m)(j-m+1)}\,\delta_{jj}\delta_{m'm-1}$$

$$But\ \delta_{jj} = 1; then$$

$$\langle jm'|J_x|jm\rangle = \frac{1}{2}\hbar\sqrt{\left[(j-m)(j+m+1)\right]}\ \delta_{m'm+1}$$

$$+\frac{1}{2}\hbar\sqrt{\left[(j+m)(j-m+1)\right]}\ \delta_{m'm-1}------------(30)$$

$$If\ m' = m+1;\ \delta_{m'm+1} = 1$$
$$and\ m' = m-1;\ \delta_{m'm-1} = 1$$

The matrix element of J$_x$ will be finite. But if $m' \neq m+1; \delta_{m'm-1} = 0\ \ and\ \ m' \neq m-1, \delta_{m'm-1} = 0$ and hence the matrix elements of J$_x$ will be zero.

Similarly,

$$\left\langle jm'\middle|J_y|\ jm\right\rangle = -\frac{i}{2}\hbar\sqrt{(j-m)(j+m+1)}\,\delta_{m'm+1}$$

$$+\frac{i}{2}\hbar\sqrt{(j+m)(j-m+1)}\,\delta_{m'm-1}----------------(31)$$

If $m' \neq m\pm1$; the matrix elements of J$_x$ will be zero and if $m' = m\pm1$, elements will be finite. Hence if $m' = m+1$ we get

$$\left\langle j, m+1\middle|J_x|\ j_m\right\rangle = \frac{1}{2}\hbar\sqrt{(j-m)(j+m+1)}-------(32a)$$

$$If\ m' = m-1$$

$$\left\langle j, m-1\middle|J_x|\ j_m\right\rangle = \frac{1}{2}\hbar\sqrt{(j+m)(j-m+1)}-------(32b)$$

All other elements (for which $m' \neq m\pm1,$) will be zero. Similarly the matrix elements of J$_y$ can be written as

$$If\ m' = m+1, we\ get$$

$$\left\langle j, m+1|\ J_y\middle|jm\right\rangle = -\frac{i\hbar}{2}\sqrt{(j-m)(j+m+1)}---------(33a)$$

$$and\ if\ m' = m-1$$

$$\left\langle j, m-1|\ J_y\middle|jm\right\rangle = +\frac{i\hbar}{2}\sqrt{(j+m)(j-m+1)}---------(33b)$$

***<u>(d)Explicit form of the angular momentum matrices</u>*:**

The matrices of J^2 and J$_z$ are diagonal $\left\{J_z = m_z\hbar\ \ \ and\ \ \ J^2 = j(j+1)\hbar^2\right\}$

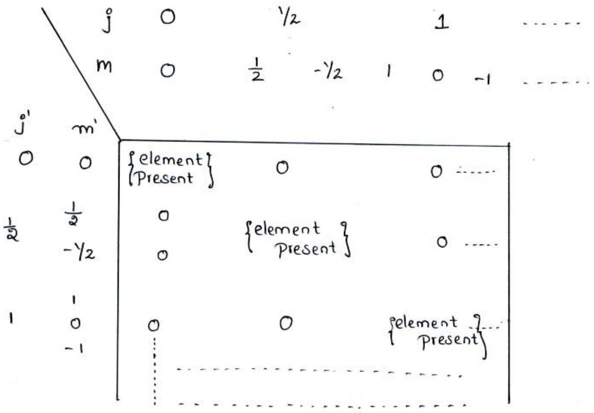
The value of magnetic quantum number m_z varies from –j to +j and total values of m_z will be (2j+1). Hence the dimensions of these diagonal matrices will be (2j+1) X (2j+1) i.e., (2j+1) rows and (2j+1) columns.

$$J_z = \hbar \begin{bmatrix} j & 0 & 0 & 0 \\ 0 & j-1 & 0 & 0 \\ 0 & 0 & j-2 & 0 \\ 0 & 0 & 0 & -j \end{bmatrix}$$

Diagonal matrix

$$J^2 = \hbar^2 \begin{bmatrix} j(j+1) & 0 & 0 & 0 \\ 0 & j(j-1) & 0 & 0 \\ 0 & 0 & j(j+1) & 0 \\ 0 & 0 & 0 & j(j+1) \end{bmatrix} \text{diagonal matrix}$$

Each of matrices J_z , J^2 has the form



Hence J_z and J^2 matrices contain only principal diagonal terms.

The matrix elements of J_+ are given by

$$\langle j'm' | J_+ | jm \rangle = \hbar\sqrt{(j-m)(j+m+1)}\,\delta_{jj'}\,\delta_{m'm+1}$$

The non–vanishing matrix elements of J_+ *are given by*

$$\langle j, m+1 | J_+ | jm \rangle = \hbar\sqrt{(j-m)(j+m+1)}$$

$$\sin ce \quad \delta_{jj} = 1;\ \delta_{m+1,m+1} = 1$$

And all other elements of J_+ will be zero. *m* will take values depending on value of j.

For given j; *m* will take values from *–j* to *+j* with a difference of 1.

$m = -j, -j+1, -j+2, ------ j-2, j-1, j$

and moreover J_+ *and* J_- *should satisfy the condition*

$[J_+, J_-] = 2\hbar J_z$

$[J_z, J_+] = \hbar J_+$

and $[J_z, J_-] = -\hbar J_-$

According to the matrices for J_+ and J_- will be of the form

	j	0	1/2	1	
	m	0	1/2 -1/2	1 0 -1	....
j'	m'				
0	0	0	{element present}	0	0
1/2	1/2 -1/2	0	0	{element present}	0
1	1 0 -1	0	0	0	{element present} ......
		0	0	0	0 ......

i.e., J_+ matrix will contain only upper diagonal terms and

	j	0	1/2	1	2
	m	0	1/2 -1/2	1 0 -1	2 1 0 -1 -2
j'	m'				
0	0	0	0	0	0 ......
1/2	1/2 -1/2	{element present}	0	0	0 ......
1	1 0 -1	0	{element present}	0	0 ......
2	2 1 0 -1 -2	0	0	{element present}	0 ......
	......	......	.....	.....	....

That is J_- matrix will contain only lower diagonal terms.

Problems:

1. Find the angular momentum matrices for $J = \frac{1}{2},\ j = 1$ *and* $j = \frac{3}{2}$

$Solution:$

$$(i)\ j=\frac{1}{2}, m=\frac{1}{2}, -\frac{1}{2}$$

$$J^2=\hbar^2 j(j+1)=\frac{1}{2}\hbar^2\left(\frac{1}{2}+1\right)=\frac{3}{2}\hbar^2$$

Matrices with angular momentum number *j* is (2j+1) by (2j+1) matrices

Here j=1/2, therefore J^2 matrices is 2 X 2 matrix

$$J^2=\hbar^2\begin{pmatrix}\frac{3}{4} & 0\\ 0 & \frac{3}{4}\end{pmatrix}$$

$$and\ J_z=m_z\hbar$$

$$=\begin{cases}\frac{1}{2}\hbar\ for\ m_z=\frac{1}{2}\\ -\frac{1}{2}\hbar\ for\ m_z=-\frac{1}{2}\end{cases}$$

$$J_z=\hbar\begin{pmatrix}\frac{1}{2} & 0\\ 0 & -\frac{1}{2}\end{pmatrix}$$

$Also$

$$J_+=\hbar\sqrt{(j-m)(j+m+1)}$$

i.e., only upper diagonal terms appear and rest of elements is zero.

$$J_+=\hbar\sqrt{\left(\frac{1}{2}-\frac{1}{2}\right)\left(\frac{1}{2}+\frac{1}{2}+1\right)}\quad for\ j=\frac{1}{2}; m=\frac{1}{2}$$
$$=0$$

$$J_+=\hbar\sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}+\frac{1}{2}+1\right)}\quad for\ j=\frac{1}{2}; m=-\frac{1}{2}$$
$$=\hbar$$

$$\therefore J_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

$and\ J_- = \hbar\sqrt{(j+m)(j-m+1)}$ *i.e., only diagonal terms appear and all the best elements are zero*

$$= \begin{cases} \hbar & for\ j = \frac{1}{2}, m = \frac{1}{2} \\ 0 & for\ j = \frac{1}{2}, m = -\frac{1}{2} \end{cases}$$

$$J_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

(ii) *Simialrly for* $j = 1, m = 1, 0, -1$

$$J^2 = \hbar^2 \begin{bmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{bmatrix}, \qquad J_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$J_+ = \hbar \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}, \qquad J_- = \hbar \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix}$$

(iii) *For* $j = \frac{3}{2};\ J^2 = \hbar^2 \begin{bmatrix} \frac{15}{4} & 0 & 0 & 0 \\ 0 & \frac{15}{4} & 0 & 0 \\ 0 & 0 & \frac{15}{4} & 0 \\ 0 & 0 & 0 & \frac{15}{4} \end{bmatrix}$

$$J_z = \hbar \begin{bmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{bmatrix}$$

$$J_+ = \hbar\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{bmatrix}; \qquad J_- = \hbar\begin{bmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix}$$

(e) Eigen functions of J^2 and J_z:

We have seen that J^2 and J_z commute with each other therefore the simultaneous eigen function of J^2 and J_z can be constructed.

The eigen value equation of J^2 and J_z are

$$\left.\begin{array}{l} J^2\psi = j\left(j+1\right)\hbar\psi \\ J_z\psi = m\hbar\psi \end{array}\right\} ------(34)$$

where *m* takes values from *–j* to *+j* with a difference of unity

we have also noticed while finding the eigen values of J^2 and J_z that the eigen function of J^2 and J_z may be constructed by repeated application of operators J_+ and J_- where

$$J_+ = J_x + iJ_y \text{ and } J_- = J_x - iJ_y$$

With the condition that

$$\left.\begin{array}{l} J_+\psi_j^j = 0 \text{ and } J_-\psi_j^j = 0 \\ \text{where}\, \psi_j^j = J_\pm^j\psi \end{array}\right\} --------(35)$$

10.3 Let us sum up:

This unit has dealt with very fundamental, required concepts of Quantum Mechanics like the eigen values and the derivation of angular momentum using ladder operators and the eigen functions of these operators in detail.

10. 4 Questions for self study:

1. Derive the eigen values of the operators L2 and Lz.

2. Express the components of angular momenta and L2 operators in spherical coordinate system.

3. Obtain the eigenfunctions of L^2 and L_z

10.5 References for further study:

1. Modern Quantum Mechanics by J.J.Sakurai
2. Introduction to Quantum Mechanics by D.J.Griffiths
3. Introduction to Quantum Mechanics by ArulDhas

Unit-11: Addition of two angular momentum Clebsch- Gordan co-efficients and their symmetries

Structure:

11.0 Objectives:

After studying this unit you will be able to understand

- Addition of angular momenta.
- Clebsch Gordan coefficients (C-G coefficients)
- Recursion relation of C-G Co-efficients
- Examples of the addition of two angular momenta.

11.1 Introduction

Addition of angular momentum is very important in the study of atomic spectra, structure of nuclei etc. In this unit we are going to first understand the general problem of the addition of two angular momenta and later we are going to consider the particular examples.

11.2 Contents of the Unit

a) Addition of general angular momentum.

b) Clebsch- Gordan coefficient

c) Selection rules

d) Recursion relations.

e) Computation of Clebsch-Gordan co-efficient

a) **Addition of angular momenta:**

Addition of angular momenta is very important in the study of atomic spectra, structure of nuclei. Let us consider two non interacting systems having angular momenta J_1 and J_2 and eigen kets $|j_1m_1\rangle$ and $|j_2m_2\rangle$ respectively. That is

$$J_1^2|j_1m_1\rangle = j_1(j_1+1)\hbar^2|j_1m_1\rangle --------------(1a)$$

$$J_{1z}|j_1m_1\rangle = m_1\hbar|j_1m_1\rangle ------------------(1b)$$

and

$$J_2^2|j_2m_2\rangle = j_2(j_2+1)\hbar^2|j_2m_2\rangle ------------(2a)$$

$$J_{2z}|j_2m_2\rangle = m_2\hbar|j_2m_2\rangle ----------------(2b)$$

where $m_1 = j_1, j_1-1, ----------- j_1;\ m_2 = j_{2,} j_2-1, ----- j_2$

Since the two systems are non interacting,

$$[J_{1,}J_2] = 0 \quad and\left[J_1^2, J_2^2\right] = 0 ---------------(3)$$

and therefore the operator $J_1^2, J_{1z}, J_2^2, J_{2z}$ form a complete set with simultaneous eigen kets $|j_1m_1,\ j_2m_2\rangle$ which is a product of $|j_1m_1\rangle$ and $|j_2m_2\rangle$ for given values of j_1 and j_2

$$|j_1m_1,\ j_2m_2\rangle = |j_1m_1\rangle\,|j_2m_2\rangle = |m_1m_2\rangle -------------(4)$$

Since m_1 and m_2 can respectively have $(2j_1+1)$ *and* $(2j_2+1)$ orientations, the subspace with definite values of j_1 and j_2 will have $(2j_1+1)$ *and* $(2j_2+1)$ dimensions.

b. Clebsch- Gordan coefficient

For the total angular momentum vector $J=J_1+J_2$

$$J \times J = i\hbar J ----------------(5)$$

$$Also\ \ it\ \ follows\ that$$

$$\left[J^2, J_z\right] = 0; \left[J^2, J_1^2\right] = \left[J^2, J_2^2\right] = 0 --------(6)$$

The orthonormal eigen kets of J^2 and J_z be $\left| jm \right\rangle$. Since J^2 commutes with J_z , J_1^2 and J_2^2 ,they form another complete set and their simultaneous eigenkets will be $\left| j_1 j_2 j\, m \right\rangle$. For given values of j_1 and j_2, $\left| j_{1,} j_{2,} j\, m \right\rangle = \left| j, m \right\rangle$. The completeness of the known kets $\left| m_1 m_2 \right\rangle$ allows us to express the unknown kets $\left| j, m \right\rangle$ as a linear combination of $\left| m_1 m_2 \right\rangle$

$$\left| jm \right\rangle = \sum_{m_1, m_2} C_{j_1 m m_1 m_2} \left| m_1 m_2 \right\rangle -------------(7)$$

The coefficients of this linear combination are called Clebsch- Gordon coefficients or Wigner coefficient or vector coupling coefficient. Multiplying equation (7) with the $\left\langle m_1 m_2 \right|$.

$$\left\langle m_1 m_2 \right| jm \rangle = C_{j\ m m_1 m_2} ----------------(8)$$

Substituting this value of the co efficient in equation (7) we have

$$\left| jm \right\rangle = \sum_{m_1, m_2} \left| m_1 m_2 \right\rangle \left\langle m_1 m_2 \right| jm \rangle -------------(9)$$

As the co efficient $\left\langle m_1 m_2 \right| jm \rangle$ relates two orthogonal bases, they form a unitary matrix formed by these elements, $m_{1,}m_2$ labeled as the rows and *j, m* labeled as the columns. The parameters j_1 and j_2 are not appearing explicitly in the co efficients as we are working for definite values of j_1 and j_2. In the strict sense, the coefficients would be $\left\langle j_1 m_{1,} j_2 m_2 \right| j_1 j_2\, jm \rangle$.

The inverse of equation (9) is given by

$$\left| m_1 m_2 \right\rangle = \sum_{j,m} \left\langle jm \right| m_1 m_2 \rangle \left| jm \right\rangle --------(10)$$

where the summation over m is from $-j$ to j and j is from $|j_1-j_2|$. The unitary character of Clebsch- Gordon co efficients is expressed by the equation

$$\sum_{j,m}\langle m_1m_2\,|\,jm\rangle\left\langle jm\middle|m_1'm_2'\right\rangle=\left\langle m_1m_2\middle|m_1'm_2'\right\rangle=\delta m_1m_1'\delta m_2m_2'-----(11a)$$

and

$$\sum_{m_1,m_2}\left\langle jm\middle|m_1\,m_2\right\rangle\langle m_1m_2\,|\,j'm'\rangle=\langle jm\,|\,j'm'\rangle=\delta_{jj'}\delta_{mm'}----------(11b)$$

$$where\left\langle jm\middle|m_1m_2\right\rangle=\langle m_1m_2\,|\,jm\rangle^*----------(11c)$$

c. <u>Selection Rules</u>:

Operating equation (9) from left by J_z , we have

$$J_z\,|\,jm\rangle=\sum_{m_1,m_2}(J_{1z}+J_{2z})\,|\,m_1m_2\rangle\langle m_1m_2\,|\,jm\rangle$$

or

$$m\hbar\,|\,jm\rangle=\sum_{m_1,m_2}(m_1+m_2)\,\hbar\,|m_1m_2>\langle m_1m_2\,|\,jm\rangle$$

Replacing $|\,jm\rangle$ using equation (9) and rearranging we get

$$\sum_{m_1,m_2}(m-m_1-m_2)|m_1m_2\rangle\langle m_1m_2\,|\,jm\rangle=0----------(12)$$

which is valid only if the coefficient of each term vanishes separately. This leads to one of the rules of vector atom model, that is

$m=m_1+m_2$---(13)

We shall next find out how the various m and j values arise from the values of m_1 and m_2. For given values of j_1 and j_2; m_1 can have values from j_1 to $-j_1$ and m_2 from j_2 to $-j_2$ in integral steps. Since $m=m_1+m_2$, the possible values of m are j_1+j_2, j_1+j_2-1, j_1+j_2-2,-----------(j_1+j_2). The largest value (j_1+j_2) can occur only once when $m_1=j_1$ and $m_2=j_2$. The value of j corresponding to this m value is also (j_1+j_2). The next largest value of m is (j_1+j_2-1) which can occur in two ways $m_1=j_1$, $m_2=j_2-1$ or $m_1=j_1-1$ or $m_2=j_2$. This gives rise to the two known $|m_1m_2>$ kets $|j_1,j_2-1>$ and $|j_1-1,j_2>$ leading to two linearly independent $|j,m>$ combinations. We can have $m=j_1+j_2-1$ when $j=(j_1+j_2)$ or (j_1+j_2-1) as can be seen from the following when $j=j_1+j_2$, m can have the values j_1+j_2-1, j_1+j_2-2,------------- $-[j_1+j_2-1]$. Thus $m=j_1+j_2-1$ can result from $j=(j_1+j_2)$ or (j_1+j_2-1). This process is continued and the results are summarized as shown in table

Values of *j* and *m* for different values of m_1 and m_2

m_1	m_2	m	j
j_1	j_2	j_1+j_2	j_1+j_2
j_1	j_2-1	j_1+j_2-1	j_1+j_2
j_1-1	j_2		j_1+j_2-1
j_1	j_2-2		j_1+j_2
j_1-1	j_2-1	j_1+j_2-2	j_1+j_2-1
j_1-2	j_2		j_1+j_2-2
$\vdots$	$\vdots$	$\vdots$	
j_1	j_2-k		j_1+j_2
j_1-1	j_2-k+1	j_1+j_2-k	j_1+j_2-1
j_1-2	j_2-k+2		j_1+j_2-2
$\vdots$	$\vdots$	$\vdots$	$\vdots$
j_1-k	j_2		j_1+j_2-k
$\vdots$	$\vdots$	$\vdots$	$\vdots$

The smallest value of j occurs for

$J_1-k=-j_1$ or $j_2-k=-j_2$

That is when $k=2j_1$ or $2j_2$ the smallest value of j is then

$j_1+j_2-2j_1=j_2-j_1$ or $j_1+j_2-2j_2=j_1-j_2$

In otherwords the permitted values of j are

$(j_1+j_2),(j_1+j_2-1), (j_1+j_2-2)$---------------$|j_1-j_2|$--------------------(14)

Which is the triangle rule of the vector atom model.

Recursion relations

Recursion relations connecting Clebsh Gordon coefficient would be very useful in evaluating explicit expressions for them. Operating equation (9) from left by J_- and replacing J_- by $J_1 \pm J_2$ on the RHS we get

$$J_-|jm\rangle = \sum_{m_1'm_2'} (J_{1-}+J_{2-})\left|m_1'm_2'\right\rangle\left\langle m_1'm_2'\right|jm\rangle$$

Using equation

$$\langle j'm'|J_-|jm\rangle = [j(j+1)-m(m-1)]^{1/2}\hbar\delta_{jj'}\delta_{m',m-1}$$

$$[j(j+1)-m(m-1)]^{1/2}\hbar|j,m-1\rangle$$

$$= \sum_{m_1',m_2'}\left[j_1(j_1+1)-m_1'\left(m_1'-1\right)\right]^{1/2}\hbar\left|m_1'-1,m_2'\right\rangle$$

$$\left\langle m_1'm_2'\right|jm\rangle$$

$$+\sum_{m_1',m_2'}\left[j_2(j_2+1)-m_2'\left(m_2'-1\right)\right]^{1/2}\hbar\left|m_1',m_2'-1\right\rangle$$

$$\left\langle m_1'm_2'\right|jm\rangle$$

Multiplying both sides by $\langle m_1m_2|$ we get $[j_1(j_1+1)-m(m-1)]^{1/2}\langle m_1m_2|j,m-1\rangle$

$$=[j_1(j_1+1)-m_1(m_1+1)]^{1/2}\langle m_1+1,m_2|jm\rangle$$
$$+[j_2(j_2+1)-m_2(m_2+1)]^{1/2}\langle m_1,m_2+1|jm\rangle \text{---------------}(15)$$

Repeating the procedure with J_+ in the place of J_-

$$=\left[\, j_1\left(j+1\right)-m\ \ \left(m\ \ +1\right)\right]^{1/2}\left\langle m_1, m_2 \,|\, jm+1\right\rangle$$

$$=\left[\, j_1\left(j_1+1\right)-m_1\left(m_1+1\right)\right]^{1/2}\left\langle m_1-1, m_2 \,|\, jm\right\rangle$$

$$+\left[\, j_2\left(j_2+1\right)-m_2\left(m_2-1\right)\right]^{1/2}\left\langle m_1, m_2-1 \,|\, jm\right\rangle \text{----------------}(16)$$

Equations (15) and (16) are the recursion relations required for the computation of the Clebsch- Gordon coefficients.

e. Computation of Clebsch-Gordon Coefficients:

The Clebsch-Gordon Coefficient matrix $\langle m_1 m_2 \,|\, jm\rangle$ has ($2j_1+1$) ($2j_2+1$) rows and columns. However it breaks up into smaller matrices depending on the value of m. It can be seen from table that there will be a 1 *X* 1 sub-matrix for which $m=j_1+j_2$ and $j=j_1+j_2$. Then there will be a 2 *X* 2 sub-matrix for which $m=j_1+j_2-1$ and $j=j_1+j_2$ or $j=j_1+j_2-1$. The rank of these matrices increases by unity until a maximum is reached and remains in that level for one or more sub matrices, thereafter it decreases by unity until the last 1 *X* 1 sub matrix is reached. For convenience the first 1 *X* 1 sub matrix is selected as +1 that is

$$\left\langle j_1, j_2 \,|\, j_1+j_2, j_1+j_2\right\rangle = +1 \quad \text{-------------------------------}(17)$$

To compute the next 2 *X* 2 sub matrix set $m_1=j_1$, $m_2=j_2-1$, $j=j_1+j_2$ and $m=j_1+j_2$ in equation (15). On simplification we get,

$$\left(j_1+j_2\right)^{1/2}\left\langle j_1, j_2-1 \middle| \left(j_1+j_2\right), \left(j_1+j_2-1\right)\right\rangle = j_1^{1/2}\left\langle j_1 j_2 \,|\, j_1+j_2, j_1+j_2\right\rangle$$

Using the results in equation (17)

$$\left\langle j_1, j_2-1 \middle| j_1+j_{2,} j_1+j_2-1\right\rangle = \left(\frac{j_2}{j_1+j_2}\right)^{1/2} \text{------------------}(18)$$

Proceeding on similar lines with $m_1=j_1-1$, $m_2=j_2$; $j=j_1+j_2$ and $m=j_1+j_2$ in equation (15) we have

$$\left\langle j_1-1, j_2 \,|\, j_1+j_{2,} j_1+j_2-1\right\rangle = \left(\frac{j_1}{j_1+j_2}\right)^{1/2} \text{------------------}(19)$$

Equation (18) and (19) give two of the elements for which j=j_1+j_2 and m=j_1+j_2-1. The other two elements $\left\langle j_1, j_2 -1 \middle| j_1 + j_{2,} -1, j_1 + j_2 -1 \right\rangle and \left\langle j_1 -1, j_2 \,|\, j_1 + j_2 -1,\ j_1 + j_2 -1 \right\rangle$

are evaluated using the Unitary nature of the transformation matrix, equation (11). While evaluating these elements it is the practice to take the element having the form $\left\langle j_{1,} j - j_1 \,|\, jj \right\rangle$ which involves the highest value of m_1 as real and positive.

Using equation (11b), we get

$$\left\langle j_1 + j_{2,}\ j_1 + j_2 -1 \middle| j_{1,} j_2 -1 \right\rangle \left\langle j_1, j_2 -1 \middle| j_1 + j_2 -1, j_1 + j_2 -1 \right\rangle$$
$$+\left\langle j_1 + j_{2,} j_1 + j_2 -1 \middle| j_1 -1, j_2 \right\rangle \left\langle j_1 -1, j_2 \,|\, j_1 + j_2 -1, j_1 + j_2 -1 \right\rangle = 0$$

Since $\langle jm | m_1 m_2 \rangle = \langle m_1 m_2 \,|\, jm \rangle^*$, the above equation reduces to

$$\left(\frac{j_2}{j_1 + j_2}\right)^{1/2} \langle j_1, j_2 -1 | j_1 + j_2 -1, j_1 + j_2 -1 \rangle + \left(\frac{j_1}{j_1 + j_2}\right)^{1/2} \langle j_1 -1, j_2 \,|\, j_1 + j_2 -1, j_1 + j_2 -1 \rangle = 0$$

Use of the convention that the first element is real and positive gives

$$\left\langle j_1, j_2 -1 \middle| j_1 + j_2 -1, j_1 + j_2 -1 \right\rangle = \left(\frac{j_1}{j_1 + j_2}\right)^{1/2} \text{-----------------------------------}(20)$$

and

$$\left\langle j_1 -1, j_2 \,|\, j_1 + j_2 -1, j_1 + j_2 -1 \right\rangle = -\left(\frac{j_2}{j_1 + j_2}\right)^{1/2} \text{---------------------------------}(21)$$

The next sub matrix is 3 *X* 3 may be obtained in the same way. Using equation (15), (18) and (19) we can get three elements for where j=j_1+j_2 and m=j_1+j_2-2. Another three elements corresponding to j=j_1+j_2-1 and m=j_1+j_2-1 are obtained using equation (20) (21) and (15). Equation (11b) is used to obtain the normalized set of coefficients that are orthogonal to the other six. As in the 2 *X* 2 case, the element $\left\langle j_{1,} j_2 -2 \middle| j_1 + j_2 -2, j_1 + j_2 -2 \right\rangle$ is selected as positive. The results of 2 X 2 and 3 X 3 sub matrix are shown in the following tables. The recursion relation equation (16) can also be used for computing Clebsch-Gordon coefficient, if we start from the other end corresponding to j=j_1+j_2 and m= -(j_1+j_2)

Table (2a) Clebsch – Gordon co efficient for $\left|m_1 m_2\right\rangle = \left|j_1 + j_2 - 1\right\rangle$ *and* $\left|j_1 - 1, j_2\right\rangle$

m_1	**m_2**	$\left\lvert jm\right\rangle$	
		$\left\lvert j_1 + j_2 - 1, j_1 + j_2 - 1\right\rangle$	$\left\lvert j_1 + j_2, j_1 + j_2 - 1\right\rangle$
j_1	j_2-1	$\left(\frac{j_2}{j_1 + j_2}\right)^{1/2}$	$\left(\frac{j_1}{j_1 + j_2}\right)^{1/2}$
j_1-1	J_2	$\left(\frac{j_1}{j_1 + j_2}\right)^{1/2}$	$-\left(\frac{j_2}{j_1 + j_2}\right)^{1/2}$

Table (2b) Clebsch Gordon coefficients for $\left|m_1 m_2\right\rangle = \left|j_1 + j_2 - 2\right\rangle, \left|j_1 - 1, j_2 - 1\right\rangle$ *and* $\left|j_1 - 2, j_2\right\rangle$

m_2		$\left\lvert jm\right\rangle$		
		$\left\lvert j_1 + j_2, j_1 + j_2 - 2\right\rangle$	$\left\lvert j_1 + j_2 - 1, j_1 + j_2 - 2\right\rangle$	$\left\lvert j_1 + j_2 - 2, j_1 + j_2 - 2\right\rangle$
j_1	j_2-2	$\left[\frac{j_2(2j_2 - 1)}{(j_1 + j_2)A}\right]^{1/2}$	$\left[\frac{j_1(2j_2 - 1)}{(j_1 + j_2)B}\right]^{1/2}$	$\left[\frac{j_1(2j_1 - 1)}{AB}\right]^{1/2}$
j_2-1	j_2-1	$\left[\frac{4j_1 j_2}{(j_1 + j_2)A}\right]^{1/2}$	$\frac{j_1 - j_2}{[(j_1 + j_2)B]^{1/2}}$	$-\left[\frac{(2j_1 - 1)(2j_2 - 1)}{AB}\right]^{1/2}$
j_1-2	j_2	$\left[\frac{j_1(2j_1 - 1)}{(j_1 + j_2)A}\right]^{1/2}$	$-\left[\frac{j_2(2j_1 - 1)}{(j_1 + j_2)B}\right]^{1/2}$	$\left[\frac{j_2(2j_2 - 1)}{AB}\right]^{1/2}$

11.3 Problems:

Obtain the Clebsch- Gordon Coefficient for a system having j_1=1and j_2=1/2 .

Solution: The system has two angular momenta with j_1=1and j_2=1/2. The allowed values of j are 3/2 and 1/2. For j=3/2, m=3/2, ½, -1/2, -3/2 and for j=1/2, m=1/2 and -1/2. The number of $\left|jm\right\rangle$ eigenstates is thus six and the 6 X 6 matrix reduces to two 1 X 1 and two 2 X 2 matrices. The details of which are given in the table 3. The elements

$$\left\langle 1,\frac{1}{2}\middle|\frac{3}{2},\frac{3}{2}\right\rangle\left\langle 1,-\frac{1}{2}\middle|\frac{3}{2},\frac{1}{2}\right\rangle,\left\langle 0,\frac{1}{2}\middle|\frac{3}{2},\frac{1}{2}\right\rangle\left\langle 1,-\frac{1}{2}\middle|\frac{1}{2},\frac{1}{2}\right\rangle \quad and \quad \left\langle 0,\frac{1}{2}\middle|\frac{1}{2},\frac{1}{2}\right\rangle$$

Are easily obtained by the help of equation (17) to equation (21) and are listed in the table evaluation of the remaining elements are done as follows:

(i) For $\left\langle 0,-\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle$:

Setting $j=\frac{3}{2}, m=\frac{1}{2}, m_1=0 \; and \; m_2=-\frac{1}{2}$ in equation (15) we get

$$2\left\langle 0,-\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle = 2^{1/2}\left\langle 1,-\frac{1}{2}\middle|\frac{3}{2},\frac{1}{2}\right\rangle + \left\langle 0,\frac{1}{2}\middle|\frac{3}{2},\frac{1}{2}\right\rangle$$

Substituting the two coefficients on the right side from table (3), we have

$$\left\langle 0,-\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle = \sqrt{2/3}$$

(ii) **For** $\left\langle -1,\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle$:

Setting $j=\frac{3}{2}, m=\frac{1}{2}, m_1=-1 \; and \; m_2=\frac{1}{2}$ in equation (15) and proceeding as in the previous case, we have

$$2\left\langle -1,\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle = 2^{1/2}\left\langle 0,\frac{1}{2}\middle|\frac{3}{2},\frac{1}{2}\right\rangle$$

$$or \; \left\langle -1,\frac{1}{2}\middle|\frac{3}{2},-\frac{1}{2}\right\rangle = 1/\sqrt{3}$$

(iii) **For** $\left\langle 0,-\frac{1}{2}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle$:

Setting $j=\frac{1}{2}, m=-\frac{1}{2}, m_1=0 \; and \; m_2=-\frac{1}{2}$ in equation (15) we get $\frac{1}{\sqrt{3}}$

(iv) **For** $\left\langle -1,\frac{1}{2}\middle|\frac{1}{2},-\frac{1}{2}\right\rangle$:

Again setting $j=\frac{1}{2}, m=\frac{1}{2}, m_1=-1 \, and \, m_2=\frac{1}{2}$ in equation (15) we get $-\sqrt{2/3}$

The last two coefficients could be evaluated by following the procedure used for the derivation of equation (20) and (21). Obviously, the last element

$$\left\langle -1,-\frac{1}{2} \middle| \frac{3}{2},-\frac{3}{2} \right\rangle = 1$$

Table (3) Clebsch- Gordon coefficient for j_1=1 and j_2=1/2

m_1	**m_2**	$\vert j,m\rangle$					
		$\vert 3/2, 3/2\rangle$	$\vert 3/2, 1/2\rangle$	$\vert 1/2, 1/2\rangle$	$\vert 3/2, -1/2\rangle$	$\vert 1/2, -1/2\rangle$	$\vert 3/2, -3/2\rangle$
1	½	1					
1	-½		$1/\sqrt{3}$	$\sqrt{2/3}$			
0	½		$\sqrt{2/3}$	$-1/\sqrt{3}$			
0	-½				$\sqrt{2/3}$	$\sqrt{1/3}$	
-1	½				$\sqrt{1/3}$	$-\sqrt{2/3}$	
-1	-½						1

11.4 Let us sum up

We have studies the addition of angular momentum Clebsch- Gordon coefficient selection rules recursion relations and computation of Clebsch Gordon coefficient and also one example.

11.5 Key words

Angular momentum, addition, Clebsch- Gordon coefficients etc.

11.6 Question for Self study

1) Explain the addition of angular momentum.
2) What are Clebsch-Gordon co efficients? Explain their significance
3) Explain the recurrence relation of Clebsch-Gordon co efficients.
4) Explain how the Clebsch-Gordon coefficients can be computed.
5) How many angular momentum states arise for a system with two angular momentum j_1=1 and j_2-1/2? Specify the states,

11.7 References

- Modern Quantum Mechanics by J.J. Sakurai,
- Introduction to Quantum Mechanics by Griffiths.
- Quantum Mechanics by Thankappan

Unit-12: Symmetry in quantum mechanics –Symmetries, conservation laws and degeneracy. Discrete symmetries, parity and time reversal symmetry

Structure:

12.0 Objectives

After studying this unit you are going to understand

- Symmetry transformations.
- Conservation law of linear momentum.
- Conservation of energy.
- Conservation of angular momentum.
- Parity conservation.
- Time reversal.

12.1: Introduction

Symmetry plays an important role in understanding numerous phenomena in physics. By considering the symmetries of a physical system one can obtain certain constants of motion. These constants of motion reveal lot of information regarding the system under consideration. So let us find out the connection between some of the important symmetry operations and the associated conservation laws.

12.2: Contents of the unit:

a. Symmetry transformations.
b. Translation in space: conservation of linear momentum.
c. Translation in time: conservation of Energy
d. Rotation in space: conservation of Angular momentum.
e. Space inversion: parity conservation.
f. Time reversal.

(a) Symmetry transformations:

A unitary transformation is said to be infinitesimal if the associated unitary operator is very close to a unit operator. We can then write

$$U = I + i \in G -------------(1)$$

where I is the unit operator, $\in$ is a real arbitrary small parameter and G is a Hermitian operator

$$U^{\dagger}U = (I - i \in G^{\dagger})(I + i \in G) \cong I + i \in (G - G^{\dagger}) ----------(2)$$

Since $\in$ is small, the term in $\in^2$ is neglected.

For U to be unitary:

$G - G^{\dagger} = 0 \;\; or \quad G = G^{\dagger}$--(3)

The operator G is called the generator of the infinitesimal unitary transformation.

If the infinitesimal unitary transformation is performed, the transformed wave function is given

$\psi' = \psi + \delta\psi = (I + i \in G)\psi$ −−−−−−−−(4)

In the case of a dynamical variable the transformed operator

$$\begin{aligned} A' &= UAU^{\dagger} = (I + i \in G)A(I - i \in G) \\ &= A + i \in (GA - AG) \\ &= A + i \in [G, A] \text{−−−−−−−−−−−−−(5)} \end{aligned}$$

A dynamical variable A is said to be invariant under a unitary transformation

$If \;\; A' = UAU^{\dagger} = A$ −−−−−−−−−−−−(6)

It follows from equation (5) that this condition is satisfied if

[G, A]=0 -------------------------------------(7)

That is, dynamically variables that commute with the generator G of the infinitesimal unitary transformation are said to be invariant under the transformation concerned.

A particular case of interest is when A=H, the Hamiltonian of the system. The condition then reduce to

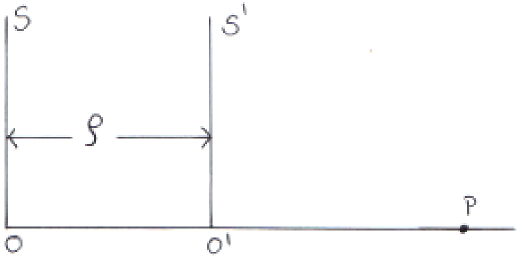
[G, H]=0------------------------------------(8)

Since G commutes with the Hamiltonian, it is a constant of motion. Consequently, observables proportional to G will also be constant of motion. A transformation that leaves the Hamiltonian invariant is called a symmetry transformation. Thus, the existence of symmetry transformation conserves probabilities and preserves the Hermitian nature of the operator also.

The symmetries associated with geometrical operations like displacement, rotation and inversion in space and time called geometrical symmetries are the important space-time symmetries one considers normally. Out of these, the displacement in space and time rotations in space come under continuous symmetry and those associated with space inversion and time reversal come under discrete symmetry.

(b) **Translation in space- conservation of linear momentum**:

Consider a particle in one dimension. We shall find out the effect of transformation on its wave function in the Schrödinger picture. Let S and S' be two reference frames with S' shifted from S by ρ and x and x' be the co ordinates of a point P with respect to S and S' respectively as shown in figure



Two reference frames S and S' shifted by ρ

ψ and ψ' be the form of a typical wave function S and S'. We shall assume that the physical properties of an isolated system will not change by a translation of the system by an arbitrary amount ρ. Hence for the physical point P.

$$\psi(x) = \psi'(x')\, and\, x' = x - \rho \qquad ------(9)$$

$$Therefore \qquad \psi'\left(x-\rho\right) = \psi(x)$$

$$or \quad \psi'(x) = \psi\left(x+\rho\right) ----------(10)$$

where ρ is infinitesimal expanding equation (10) we get

$$\psi'(x) = \psi(x) + \rho\frac{\partial\psi(x)}{\partial x} = \left(1 + i\rho G_x\right)\psi(x) \qquad ----(11)$$

$$where\, G_x = -i\frac{\partial}{\partial x} = -\frac{i\hbar}{\hbar}\frac{\partial}{\partial x} - \frac{P_x}{\hbar} \qquad ----------(12)$$

As ψ(x) and $\psi'(x)$ are the wave functions of the same physical state referred to S and S', they can be taken as expressing the same physical state in terms of the two different bases in the Hilbert space . The wave function ψ(x) is transformed to $\psi'(x)$ by the action of the operator is G_x on ψ(x). Therefore, G_x is often referred to as the generator of infinitesimal translation in the *x*-direction. In the view of equation (12), the momentum operator between the generator of the infinitesimal translation in space denoting the position eigen state for a particle at the coordinate *x* measured from O and O' respectively by $|x\rangle \, and \, |x\rangle'$

$$\psi(x)=\langle x|\psi\rangle \quad and \quad \psi'(x)='\langle x|\psi\rangle ------(13)$$

$$where \quad '\langle x|\psi\rangle=\left[1+\frac{i\rho p_x}{\hbar}\right]\psi(x)$$

$$=\left[1+\frac{i\rho p_x}{\hbar}\right]\langle x|\psi\rangle$$

$$=\langle x|\left(1+\frac{i\rho p_x}{\hbar}\right)|\psi\rangle ---------------(14)$$

$$\therefore \, '\langle x|=\langle x|\left(1+\frac{i\rho p_x}{\hbar}\right) --------------(15)$$

Taking conjugates

$$|x'\rangle=\left(1-\frac{i\int p_x}{\hbar}\right)|x\rangle -----------------(16)$$

which is the relation connecting the basis states $|x\rangle$ and $|x\rangle'$ defined with respect to S and the translate from S' respectively.

Translation through some finite distance ρ could be regarded as a succession of N infinitesimal translation. Equation (16) then gives

$$|x\rangle'=\lim_{N\to\infty}\left(1-\frac{i\rho p_x}{\hbar}\right)^N|x\rangle$$

$$=\sum_{N=0}^{\infty}\frac{(-1)^N}{N!}\left(\frac{i\rho p_x}{\hbar}\right)^N|x\rangle$$

$$=\exp\left(-\frac{i\rho p_x}{\hbar}\right)^N|x\rangle -------(17)$$

$$and \quad '\langle x|=\langle x|\exp\left(-\frac{i\rho p_x}{\hbar}\right) -----(18)$$

The corresponding relation between the wave function of a physical state $|\psi\rangle$ is given by

$$\psi'(x)='\langle x|\psi\rangle=\langle x\left|\exp\left({i\rho p_x}/{\hbar}\right)\right|\psi\rangle$$

$$=\exp\left({i\rho p_x}/{\hbar}\right)\psi(x)$$

Generalization to three dimensions is straight forward:

$$\psi'(r) = \exp\left(\frac{i\vec{\rho}.\vec{P}}{\hbar}\right)\psi(r) ------------(19)$$

where $\vec{P}$ is the momentum of the particle. For an *n*- particle system, the form of the equation will be the same as equation (19) but $\vec{P}$ stands for $\vec{p}_1 + \vec{p}_2 + \vec{p}_3 + \vec{p}_4 + ... + \vec{p}_n$. From a generalization of equation (16), the unitary infinitesimal translation operator is given by

$$U_T = I - \frac{i\vec{\rho}.\vec{p}}{\hbar}$$

It follows immediately

$$\begin{aligned} H' &= U_T H U_T^{\dagger} \\ &= \left(I - \frac{i\vec{\rho}.\vec{P}}{\hbar}\right) H \left(I + \frac{i\vec{\rho}.\vec{P}}{\hbar}\right) \\ &= H - \frac{i\rho}{\hbar}\left[P, H\right] ----------- (20) \end{aligned}$$

Hence, invariance of the Hamiltonian under translation in space requires that the linear momentum operator P must commute with H. This implies that the linear momentum operator P must commute with H and this in turn implies that the linear momentum of the system is conserved.

(c)Translation in time - conservation of Energy:

For an infinitesimal time translation τ, in the similar way,

$$\begin{aligned} \psi'(x,t) &= \psi(x, t+\tau) = \psi(x,t) + \tau\frac{\partial\psi}{\partial t} \\ &= \psi(x,t) + \frac{i}{\hbar}\tau\left(-i\hbar\frac{\partial}{\partial t}\right)\psi(x,t) \\ &= \left[1 + i\tau\left(\frac{-H}{\hbar}\right)\right]\psi(x,t) ----------(21) \end{aligned}$$

Consequently, (-H/ $\hbar$) may be defined as the generator of time translations on quantum mechanical wave functions.

The unitary operator corresponding to infinitesimal displacement τ in time of the system is given by

$$U = I - \frac{i\tau H}{\hbar} ---------------(22)$$

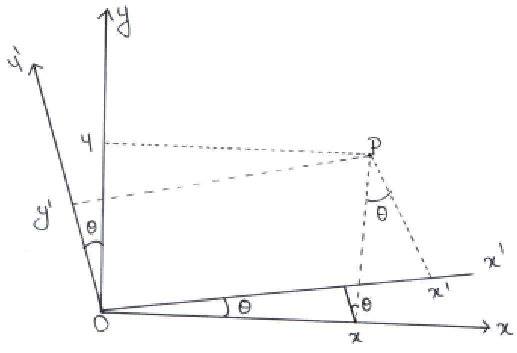
where H is the Hamiltonian, which is independent of time. The invariance of the Hamiltonian under translation in time requires that

$$H' = UHU^{\dagger} = H \quad or \quad UH = HU ---------------(23)$$

It is obvious from the form of U that it commutes with H as it is independent of time. The time independence of H means that the total energy of the system is conserved. Thus the total energy of the system is conserved if the system is invariant under translation in time. If H depends on time, it will not be invariant under translation in time.

(d) Rotation in space: Conservation of angular momentum:-

Let OXYZ (s-frame) and $OX'Y'Z'(S'\ frame)$ be two coordinate systems. The system $OX'Y'Z'$ is rotated anticlockwise through an angle θ about the z- axis. A point P whose coordinates with respect to the two systems are connected by the relations



$x' = x\cos\theta + y\sin\theta$; $y' = -x\sin\theta + y\cos\theta; z' = z$ −−−−−−−(24) ; when θ is infinitesimal cosθ→1 and sinθ→θ. Then

$$x' = x + y\theta;\ \ y' = -x\theta + y;\ \ z' = z \qquad ------------(25)$$

The wave function at a physical point P has a definite value independent of the system of coordinate. Therefore, the form of the wave function in S and S' are related by

$$\psi'(r') = \psi(r) ------------(26)$$

Substituting for x', y', z' from equation (25) we have

$$\psi'\left(x+y\theta,\ -x\theta+y,\ z\right)=\psi(x,y,z)---------(27)$$

For convenience, replacing ***x*** by ***x-yθ*** and ***y*** by ***y+xθ*** on both sides

$$\psi'(x,y,z)=\psi(x-y\theta,y+x\theta,z)$$
$$=\psi(x,y,z)+\theta(-y\frac{\partial\psi}{\partial x}+x\frac{\partial\psi}{\partial y})$$
$$=\psi(x,y,z)+\frac{i\theta}{\hbar}\left[x\left(-i\hbar\frac{\partial}{\partial y}\right)-y\left(-i\hbar\frac{\partial}{\partial x}\right)\right]\psi(x,y,z)$$

Since the operator associated with L_Z is:

$$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$$

We have $\psi'(r)=\left(1+\frac{i\theta}{\hbar}L_Z\right)\psi(r)-------------(29)$

Thus $L_z/\hbar$ is the generator of infinitesimal rotation about the z-axis for rotation about any arbitrary axis

$$\psi'(r)=\left(1+\frac{i\theta}{\hbar}\hat{n}.\vec{L}\right)\psi(r)-------------(30)$$

here **n** is the unit vector along the arbitrary axis

Rotation through a finite angle θ can be considered as a succession of N infinitesimal rotation each one through an angle θ/N proceeding as in the case of translation in space. We get the rule for the transformation of the wave function between the basis states $\left|r\right\rangle$ of position referred to S and $\left|r\right\rangle'$ referred to the rotation frame S'.

$$\psi'(r)=\exp\left(i\theta\frac{\hat{n}.\vec{L}}{\hbar}\right)\psi(r)---------(31)$$

Equation (31) can be written in terms of $\left|r\right\rangle$ and $\left|r\right\rangle'$ as below:

$$'\langle r|\psi\rangle = \langle r\left|\exp\left(i.\theta\frac{n.L}{\hbar}\right)\right|\psi\rangle$$

or

$$|r\rangle' = \exp\left(-i\theta\frac{n.L}{\hbar}\right)|r\rangle -------------- (32)$$

For an n particle system the angular momentum, operator L is the sum of angular momentum operator of the individual particles. The unitary operator corresponding to an infinitesimal rotation θ about an arbitrary axis ***n*** is given by :

$$U_R(n,\theta) = I + \frac{i\theta}{\hbar}\hat{n}.\vec{J} --------- (33)$$

where **J** is total angular momentum for H to be invariant under the transformation, H' must equal H

$$\begin{aligned} H' &= U_R H U_R^\dagger \\ &= \left(I + \frac{i\theta}{\hbar}n.j\right)H\left(I - \frac{i.\theta}{\hbar}\hat{n}.\vec{J}\right) \\ &= H + \frac{i\theta}{\hbar}n.\left[J,H\right] ------------- (34) \end{aligned}$$

This is, the condition for invariance of H requires that [J,H]=0. Thus conservation of total angular momentum is a consequence of the rotational invariance of the system.

(e) Space Inversion: Parity Conservation:-

We have so far discussed the continuous symmetry operations. We now consider discrete symmetry transformations, the reflection through the origin. This operation is called space inversion or parity operation. Associated with such an operation, there is a unitary operator called the parity operator, which is usually denoted by the letter P. For a single particle wave function ψ(r) parity operator P is defined by

$$\hat{P}\psi(r) = \psi(-r) ---------- (35)$$

For a system of several particle

$$\hat{P}\psi(r_{1,}r_{2,}r_{3,}.............r_n) = \psi(-r_{1,}-r_{2,}.............-r_n) \qquad (36)$$

It follows from equation (35) that

$$\hat{P}^2\psi(r) = \hat{P}\psi(-r) = \psi(r) ---------- (37)$$

It is evident from equation (37) that ψ(r) is an eigen function of $\hat{P}^2$ with eigen value 1 and therefore the eign values of $\hat{P}$ are -1 or +1. That is., the eigen functions either change sign (odd parity) or do not change sign (even parity) under inversion. Denoting the eigen functions corresponding to even and odd eigen states by ψ_+(r) and ψ_-(r) we have

$$\hat{P}\psi_+(r) = \psi_+(-r) = \psi_+(r) ------(38a)$$

and

$$\hat{P}\psi_-(r) = \psi_-(-r) = -\psi_-(r) ------(38b)$$

The eigen states ψ_+(r) and ψ_-(r) are orthogonal, therefore

$$\langle\psi_+(r)|\psi_-(r)\rangle = 0 -------------- (39)$$

It can easily be proved that the parity operator $\hat{P}$ is Hermitian and unitary. That is.,

$$\hat{P} = \hat{P}^\dagger \quad and \quad \hat{P}\hat{P}^\dagger = \hat{P}^\dagger\hat{P} = 1 \text{-------------------------}(40)$$

The effect of the parity operator $\hat{P}$ on observables **r, p** and **L** can easily be obtained with the help of equation

$$\hat{P}r\psi(r) = -r\psi(-r) = -rp\psi(r)$$
$$\hat{P}r = -rp \quad or \quad \hat{P}r\hat{P}^\dagger = -r\hat{P}\hat{P}^\dagger = -r --------- (41)$$

Similar considerations give

$$\hat{P}p\hat{P}^\dagger = -p \quad and \quad \hat{P}L\hat{P}^\dagger = L \text{ ----------------------------}(42)$$

If the parity operator $\hat{P}$ leaves the Hamiltonian H invariant i.e., $\hat{P}H\hat{P}^\dagger = H,$ then we say that the system has space inversion symmetry and the parity operator commutes with the Hamiltonian. In other words, the parity is conserved. If the weak nuclear interaction is neglected the parity operator commutes with the Hamiltonian of atomic and nuclear systems. It is now well established that in strong interactions parity is conserved. However it is not conserved that in beta decay, decay of π^+ or π^- meson etc. They are called by the weak interactions.

(f)Time Reversal:

Another important discrete transformation is one in which the time is reversed $t' = t$. Denoting the wave function after time reversal by $\psi'(r,t')$, we have

$$\psi'(r,t') = T\,\psi(r,t); \qquad t' = -t ---------- (43)$$

where **T** is the operator that effects the transformation. Let **A** be a time independent operator associated with an observable and A' be its transform.

Consider the equation

$$A\psi = \phi \qquad (44)$$

$$Then\;\; \phi' = TA\psi = TAT^{-1}\tau\psi = (TAT^{-1})\tau\psi$$

$$= (TAT^{-1})\psi'$$

$$or$$

$$\phi' = A'\psi' \;\; where\; A' = TAT^{-1} ---------- (45)$$

We shall now investigate the effect of the T operator on observables to the inconformity with the time reversal invariance in Classical Mechanics. We require that the position operator **r** be left unchanged and the momentum operator shall change sign under time reversal.

Mathematically,

$$r' = TrT^{-1} = r; \qquad p' = TPT^{-1} = -p; \qquad L' = TLT^{-1} = -L .... (46)$$

We now evaluate the fundamental commutation relation

$$\left[x', p_x'\right]$$

$$\left[x', p_x'\right] = \left[TxT^{-1}, Tp_xT^{-1}\right]$$

$$By\;\; virtue\;\; of\;\; equation\,(46)$$

$$TxT^{-1} = x \;\; and \quad Tp_xT^{-1} = -p_x$$

$$\therefore \left[x', p_x'\right] = \left[x, -p_x\right] = -i\hbar ------------- (47)$$

The value of $\left[x', p_x'\right]$ commutator can be also be written as

$$\left[x', p_x'\right] = T\left[x, p_x\right]T^{-1} = T(i\hbar)T^{-1} ---------(48)$$

From equation (47) and (48) we have

$$T(i\hbar)T^{-1} = -i\hbar ----------------------(49)$$

which is possible only if T operating on any number changes it into its complex conjugate. Hence, T is not a linear operator. An operator **A** is said to be anti-linear if

$$A[c_1\psi_1(x) + c_2\psi_2(x)] = c_1^* A\psi_1 + c_2^* A\psi_2 ----------(50)$$

Let us now investigate the effect of time reversal $(t \to t' = -t)$ in the time dependent Schrödinger equation.

$$i\hbar\frac{\partial}{\partial t}\psi(r,t) = H\psi(r,t) ---------------(51)$$

of a particle moving in a time independent particle V(r). Since $r' = r \quad and \quad p' = p,$ the Hamiltonian operator for a particle under time reversal is invariant. Hence,

[T, H]=0--- (52)

Operating equation (51) from left by T and noting [T, H] =0

$$T\left[i\hbar\frac{\partial}{\partial t}\psi(r,t)\right] = HT\psi(r,t) ------------------(53)$$

In view of the T(i$\hbar$)=-i$\hbar$T, eqn (53) reduces to

$$-i\hbar\frac{\partial}{\partial t'}\psi'(r,t') = H\psi(r,t') \quad or \quad i\hbar\frac{\partial\psi'}{\partial t}(r,t')$$
$$= H\psi'(r,t') ------------------------------(54)$$

Thus the Schrödinger equation satisfied by the time reversed function $\psi(r,t')$ has also the same form as the original one.

As the non linear operator T performs the time reversal and complex conjugation it is possible to consider it as the product of a linear operation **U** and a complex conjugation operator **K**,

T = UK --(55)

To ensure the norm of ψ' and ψ equal, the linear operator U has to be unitary

$$\left\langle\psi\middle|\psi^{-1}\right\rangle = \langle UK\psi|UK\psi\rangle$$
$$= \left\langle K\psi\,|U^{\dagger}U\middle|K\psi\right\rangle$$
$$= \left\langle K\psi\middle|K\psi\right\rangle = \langle\psi|\psi\rangle^{*} = \langle\psi|\psi\rangle ------------------(56)$$

The above simplification is possible only if $UU^{\dagger}=1$, $\langle\psi|\psi\rangle^{*}=\langle\psi|\psi\rangle$, since the norm is real. Since U is unitary and K is anti-unitary the time reversal operator T is anti-unitary under time reversal for the position operator **r** to remain unchanged and the momentum operator to change sign, the operator U should be reduce to the unit operator.

It may be noted that the time reversal invariance of the Schrödinger equation results only if the commentator [T,H]=0. At one time it was thought that all Hamiltonians satisfied the time reversal invariance condition. However,, now it is established that Hamiltonian corresponding to weak nuclear interaction is not time reversal invariant.

12.3 Problems:

(1) Prove that the parity of spherical harmonics $Y_{l,m}(\theta,\varphi)$ is $(-1)^l$.

Solution:- When a vector **r** is reflected through the origin, we get the vector –**r**. In spherical polar coordinates, this operation corresponds to the following change in the angles θ and φ leaving **r** unchanged; θ→(π-θ) and φ→(φ+π)

$$We\;\; have\;\;\; Y_{l,m}(\theta,\phi) = c\,P_l^m\,(\cos\theta)\exp(im\phi)$$
$$c\;\; is\;\; constant$$
$$\therefore Y_{l,m}(\pi-\theta,\phi+\pi) = c\,P_l^m\left[\cos(\pi-\theta)\exp\left[im(\phi+\pi\right]\right]$$
$$= cP_l^m(-\cos\theta)\exp(im\phi)\,emp\,(im\pi)$$
$$= cP_l^m(\cos\theta)\,(-1)^{l+m}\exp(im\phi)\,(-1)^m$$
$$= (-1)^l\,Y_{l,m}(\theta,\phi)$$

During simplification we have used the result $P_n^m(-x) = (-1)^{n+m}\,P_n^m(x)$. That is., the parity of spherical harmonics is given by $(-1)^l$.

(2) **If $\psi_+(r)$ and $\psi_-(r)$ are the eigen function of the parity operator belonging to even and odd eigen states, show that they are orthogonal.**

Solution: From definition we have

$$\hat{P}\psi_+(r) = \psi_+(r) \quad and \quad \hat{P}\psi_-(r) = -\psi_-(r)$$

$$then \qquad \langle \psi_+(r)|\psi_-(r)\rangle = \langle \psi_+(r)\big|\hat{P}\hat{P}\,|\,\psi_-(r)\rangle$$

Here we have used the resultant $\hat{P}^2$ =1 since $\hat{P}$ is Hermitian

$$\langle \psi_+(r)|\psi_-(r)\rangle = \langle \hat{P}\psi_+(r)\big|\hat{P}\,|\,\psi_-(r)\rangle = -\langle \psi_+(r)|\psi_-(r)\rangle$$

$$\therefore \langle \psi_+(r)|\psi_-(r)\rangle = 0$$

$$Hence \;\; \psi_+(r) \;\; and \;\; \psi_-(r) \;\; are \;\; orthogonal$$

12.4 Let us sum up

We have learnt about the symmetries in quantum mechanics. Continuous symmetries will lead to certain conservation laws such as conservation of linear momentum, angular momentum energy etc. Whereas, discrete symmetries lead to conservation of parity and time reversal in quantum mechanics.

12.5 Key words

Symmetry, conservation laws, parity, time reversal.

12.6 Question for self study

(1) What is symmetry transformation? Prove that a symmetry transformation conserves probabilities.
(2) Explain how the momentum operator becomes the generator of infinitesimal transformation space.
(3) Conservation of angular momentum is a consequence of the rotational invariance of the system. substantiate
(4) Explain the effect of parity operator on the observables **r, p** and **L**
(5) Why time reversal operator is not linear?
(6) Discuss the effect of time reversal in the time dependent Schrödinger equation.
(7) Prove that the parity operator is Hermitian and Unitary
(8) Show that the time reversal operator operating on any number changes it into its complex conjugates.

12.7 Further reference:

- Introduction to Quantum Mechanics by Griffiths By Sakurai

Unit-13: Identical particle- Indistiguishability exchange symmetry, exchange degeneracy, spin and statistics, permutation symmetry.

Structure:

13.0 Objectives

After studying this unit you will be able to understand:

- Symmetrical and anti-symmetrical wave function.
- Exchange degeneracy.
- Particle exchange operator.
- Distinguishability of identical particles.
- The Pauli's exclusion principle
- connection with statistical mechanics etc

13.1 Introduction

By identical particles, we mean the particle 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 since each particle can be followed during the course of an experiment.

In Quantum Mechanics, a particle is described by a wave packet of finite size and shape and the exact specification of the position and momentum of the particle simultaneously is restricted by Heisenberg's uncertainty principle $\Delta q \Delta p \approx \hbar$. 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 cannot be distinguished.

There are two general categories of particles:

(a) Classical Particles which are identical but distinguishable.
(b) Quantum Particles which are identical and indistinguishable.

It is to be noted that, when quantum particle density is sufficiently low so that their uncertainty is small in comparison to the volume available to them they also obey classical statistical otherwise we must use Quantum Mechanics.

13.2 Contents:

a) Physical meaning of identity.
b) Symmetrical and anti symmetrical wave functions.
c) Exchange degeneracy.
d) Particle exchange operator.
e) Distinguishability of identical particles.
f) The Pauli's exclusion principle.
g) Connection with statistical Mechanics

(a) 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.

(b) Symmetrical and anti symmetric wave function.

The Schrödinger equation for n identical particles is written as

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

where each of the numbers represents all the co ordinates (positional and spin) of one of the particles. The Hamiltonian H is symmetrical 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 ψ of equation (1) that have symmetric properties of particular interest.

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

(ii) Anti symmetric wave function Ψ_A: A wave function is anti-symmetric if the inter change 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 Ψ_s is symmetric at a particular time t then HΨ_s is also symmetric and according to equation (1), $\partial\psi_S/\partial t$ is symmetric at time t, since Ψ_s and $\partial\psi_S/\partial t$ are symmetric at time t, ψ_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 ψ_s is seen to remain symmetric always.

Similarly if Ψ_A is anti symmetric wave function at any time *t*, then Hψ_A and hence $\partial\psi_A/\partial t$ are anti symmetric and the integration of the wave function ψ_A shows that Ψ_A is always anti symmetric.

If $\hat{P}$ is an exchange operator then we must have

$$\hat{P}\psi_S(1,2)=\psi_S(2,1)$$
$$\hat{P}\psi_A(1,2)=-\psi_A(2,1)$$

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

1. The identical particles having an integral spin quantum number are described by symmetric wave function i.e.,

$$\hat{P}\psi_S(1,2,3,........r......s....n)=+\psi_S(1,2,3,.......s...r.......n)$$

This class of particles i.e., the particles described by symmetric wave function are known as Bose particles or Bosons and obey Bose-Einstein statistics. The example of Bosons are photons (spin1), neutral helium atoms in normal state (S = 0) etc.

2. The identical particles having half integral spin quantum number are described by anti symmetric wave function i.e.,

$$\hat{P}\psi_A(1,2,........r......s....n)=-\psi_A(1,2,.......s...r.......n)$$

These clans of particles i.e., the particles described by anti symmetric wave function obey Fermi-Dirac statistics and the particles are known as Fermi-particles or Fermions. The examples of Fermions are electrons, protons, neutrons etc.

(c) Exchange Degeneracy:-

We now show that ψ_s and ψ_A can be constructed from general unsymmetrized solution ψ of equation (1).

If the arguments of the wave function ψ are permuted in any way, then the resulting wave function is also a solution of equation (1). This is because same permutation applied throughout equation (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 equation (1) for the permuted ψ. 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 ψ.

An anti-symmetric unnormalized 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 function 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 solutions

$$\psi_A(1,2,..........n) = \varphi(1,2,.......n)e^{-iE_n t/\hbar} \qquad ------(2)$$

can be formed and the time independent Schrodinger Equation can be Written as

$$H(1,2,..........n)\varphi(1,2,.......n) = E\varphi(1,2...........n) \qquad ------(3)$$

There are n! Solutions of this equation (eigen function) derived from φ(1,2,……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 equation (3)) belonging to eigen value E. Hence the system degenerate and this type of degeneracy is called 'exchange degeneracy'.

Let us now consider a two particle wave function $\psi(1S_1, 2S_2)$. For a two particle wave function the Schrödinger's time independent equation is written as

H(1,2) ψ(1,2) = Eψ(1,2)---------------------------------(4)

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

The symmetric wave function can be written as

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

and the anti-symmetric wave function is written as

$$\psi_A = \psi(1,2) - \psi(2,1) ---------------(6)$$

Similarly, for a system of 3 particles the Schrodinger equation is

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

This equation has 3!=6 solutions corresponding to the same eigen value 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 $\psi(1,2,3)$

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

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

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

So the symmetric wave function can be written as

$$\psi_s = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(1,3,2) + \psi(2,1,3)$$
$$+\psi(3,2,1) \text{-------------------} (8)$$

and the anti-symmetric wave function is

$$\psi_A = \psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2) - \left\{\psi(1,3,2) + \psi(2,1,3) + \psi(3,2,1)\right\} \text{----} (9)$$

Here ψ_A and ψ_s are unnormalized wave function.

The average value of any dynamical quantity P in state ψ 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 and the $i\hbar \frac{\partial}{\partial t}$ operator P associated with momentum p is $\frac{\hbar}{i}\nabla$

If ψ is the normalized function, then

$$\int \psi^* \psi \, d\tau = 1$$
$$\therefore \langle p \rangle = \int \psi^* p \psi \, d\tau \text{-----------} (10)$$

The symmetric and anti symmetric normalized eigen functions lead to the following results

$$\langle P_s \rangle = \int \psi_s^* p \psi_s \, d\tau$$
$$and \, \langle P_A \rangle = \int \psi_A^* P \psi_A \, d\tau$$

For symmetric solution, an exchange of coordinates of particles leaves both ψ_s and ψ_s^* unaltered. So, $\langle P_s \rangle$ remains unchanged. In the case of anti-symmetric solution, an exchange of co ordinates changes the signs of both ψ_A and ψ_A^*. So $\langle P_A \rangle$ again remains unchanged. Therefore we conclude that any interchange of two particles leave the average or the observed property of the system unaffected.

(d)**Particle exchange Operator:-**

The particle exchange operator P_{12} is defined by equation

$$P_{12}\psi(r_1 s_1; r_2 s_2) \equiv \psi(r_2 s_2; r_1 s_1) \text{------------} (11)$$

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 functions of particles exchange operators

The eigen value equation for particle exchange operator is

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

Where α is eigen value of operators P_{12} in state $\psi(1,2)$

Operating again

$$P_{12}^2\psi(1,2) = P_{12}P_{12}\psi(1,2) = P_{12}\alpha\psi(1,2) = \alpha P_{12}\psi(1,2) = \alpha\left[\alpha\psi(1,2)\right]$$

$$i.e\, P_{12}^2\psi(1,2) = \alpha^2\psi(1,2) -----------(13)$$

From definition of particle exchange operator

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

Operating again

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

$$i.e.,\ P_{12}^2\psi(1,2) = \psi(1,2) -------(14)$$

$$Comparing\ (13)\ and\ (14)\ we\ note\ that\ \alpha^2 = 1\ or\ \alpha = \pm 1-----(15)$$

i.e., the eigen values of particle exchange operator are ±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 anti symmetric.

$$i.e.,\ P_{12}\psi_s = \psi_s\ \ and\ \ P_{12}\psi_A = -\psi_A\ \ -----------(16)$$

This may be seen as follows:

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

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

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

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

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

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

$$= -\left[\psi(2,1) - \psi(1,2)\right] = -\psi_A$$

Such an interchange operator applied twice brings the particles back to their original configuration and hence produces no change in the wave function

Commutation relation with Hamiltonian:

We have

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

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

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

$$i.e., \left[P_{12}H(1,2) - H(1,2)P_{12}\right]\psi(1,2) = 0$$

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

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

$$i.e\left[P_{12,}H\right] = 0$$

Thus the particle exchange operator commutes with the Hamiltonian

(e) Distinguishability of identical particle:

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

i.e., if

$$\left|\psi(1,2)\right|^2 + \left|\psi(2,1)\right|^2 = \left|\left\{\psi(1,2) \pm \psi(2,1)\right\}\right|^2$$

$$= \left|\psi(1,2)\right|^2 + \left|\psi(2,1)\right|^2 \pm 2\,\mathrm{Re}\,\psi\left[(1,2)\psi^*(2,1)\right] ----(17)$$

where Re denotes the real part of $\left[(1,2)\psi^*(2,1)\right]$

It is possible only when overlap of wave function ψ(1,2) and ψ(2,1) is zero or $2\,\mathrm{Re}\left[\psi(1,2)\psi^*(2,1)\right]$=0

Thus, when coordinates (space and spin) of two particles are not the same between exchange degenerate functions, the interference term i.e., $2\,R_e\psi\left[(1,2)\psi^*(2,1)\right]$becomes zero and particle coordinates 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 ψ(1,2) is different from zero only when the co ordinate 1 is in same 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 (17) . If now ψ(1, 2) vanishes whenever 1 is not in A and 2 is not in B and A and B do not overlap, the bracket term i.e., $2\,\mathrm{Re}\left[\psi(1,2)\psi^*(2,1)\right]$ is zero everywhere and reduces to

$$\left|\psi(1,2)\right|^2 + \left|\psi(2,1)\right|^2$$

Thus, the probability density associated with either of the symmetrized wave function $\psi(1,2) \pm \psi(2,1)$ 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 exchanges of degenerate wave functions represented by the bracket term in (17) disappear when the co ordinates of the particle do not overlap.

(f) The Pauli's exclusion Principle:

A particle, during its motion in space reflects the properties of the statistics which it obeys. Consider two particle systems which contain electrons in indistinguishable positions. Electrons are ½ 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 functions of exchange operator for a case will be

$$\begin{aligned} P_{12}\psi_A\left(r_1,s_1;r_{2,}s_2\right) &= -\psi_A\left(r_{2,}s_2;r_1,s_1\right) \\ &= \psi_A\left(r_1,s_1;r_{2,}s_2\right) ------(18) \\ &= 0\, if \begin{cases} r_1 = r_2 \\ s_1 = s_2 \end{cases} ---------(19) \end{aligned}$$

The non existence of the wave function under these conditions implies that there is zero probability that the particle will occupy the same point and have identical spin orientations. Equation (19) is the physical principle called 'Pauli's exclusion principle' which states that- "no two particles obeying Fermi statistics can exist in the same quantum state". This means that if there are two electrons in one atomic orbit (angular momentum L_θ), they cannot have the same spin orientation. Then spin 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 approximate (unperturbed) Hamiltonian is equated to the sum of Hamiltonian function for the separate particles. Thus, for a system of *n* particles-

$$H_0\left(1,2..........n\right) = H_0^{'}\left(1\right) + H_0^{'}\left(2\right) + --------H_0^{'}(n) ----\left(20\right)$$

and the approximate energy eigen function is a product of one particle eigen function of $H_0^{'}$

$$\psi\left(1,2,.....n\right) = \varphi_a\left(1\right)\varphi_b\left(2\right)......................\varphi_k(n) \qquad ----(21)$$

$$with\;\; E = E_a + E_b + ------ + E_k$$

$$H_0^{'}(1)\varphi_a\left(1\right) = E_a\varphi_a\left(1\right) \quad etc.$$

If the particles are electrons, an anti-symmetric wave function must be constructed from the ψ given by (21). This is most easily expressed as determinant of φ's known as Slater's determinant

$$\psi_A\left(1,2....n\right)=\begin{vmatrix} \varphi_a(1) & \varphi_a(2) & ---- & \varphi_a(n) \\ \varphi_b(1) & \varphi_b(2) & ---- & \varphi_b(n) \\ ---- & ---- & ---- & ---- \\ \varphi_k(1) & \varphi_k(2) & ---- & \varphi_k(n) \end{vmatrix} \qquad (22)$$

The un normalized ψ_A given in equation (22) is clearly an anti-symmetric solution of the approximate wave equation $\left[H_0-E\right]\psi_A=0$ (23)

Equation (22) has the interesting property that it vanishes if two or more of the φ's are same. For example if $\varphi_a(1)=\varphi_b(1)$ or $\varphi_a(1)=\varphi_a(2)$, then determinant will vanish. This is the special case of the general result that an anti-symmetric wave function cannot 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 states a, b…...k. This result is the well known 'Pauli's exclusion principle' which states that no two particles described by anti-symmetric wave functions can exist in the same quantum state.

(g)Connection with statistical Mechanics:

The unsymmetrized zero solution in (21) can be used to construct a symmetric as well as an anti-symmetric wave function. Such a symmetric function is the sum of all different permutations of the numbers 1,2…....n among the one particle eigen functions φ_a , φ_b …….φ_n. This wave function is unique and can be specified simply by defining how many particles are there in each of the states a, b,....... The fundamental statistical difference between particles that are described by anti-symmetric and by symmetric wave function is that number of the former type that can occupy any state is limited to 0 or 1 whereas any number (0,1,2....) 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 from the subject matter of quantum statistical mechanics.

The particles that are described by anti-symmetric wave functions are said to obey Fermi- Dirac statistics and are called Fermions. The examples of fermions are- electrons, protons and neutrons. The other particles which are described by symmetric wave function obey Bose-Einstein statistics and are called Bosons. The examples of bosons are π- mesons, photons (i.e., light quanta) etc. Further the aggregates of particles that are strongly bound so that they can be regarded as particles and can be described either by symmetric or anti symmetric wave functions. For example the nucleus of helium atom is made up of two photons and two neutrons and an uncertain number of π-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 changes in internal motion of nuclei due to these interactions are negligible, then the motions of centers of gravity of nuclei can be described approximately by symmetric wave functions. The interchange of a pair of helium nuclei can be thought of as the net effect of interchange of two pairs of neutron (fermions) is anti symmetric, the resultant of first four interchanges leaves the approximate wave function unchanged and in π- mesons the symmetry of wave function is such that the latter interchanges (i.e., interchanges of π mesons) have no effect. The extension of above reasoning gives the inference that the strongly bound particles which themselves interact weakly with each other (ex: nuclei, atoms, 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.

13.3 Let us sum up:

We have understand the symmetrical and anti symmetrical functions exchange symmetry particle exchange operator distinguishability of identical particles the Pauli’s exclusion principle and its connections with statistical mechanics.

13.4 Key words

Wave function, symmetrical and anti symmetrical wave function degeneracy, identical particles etc.

13.5 Question for self study

1. Define symmetric and anti symmetric wave function?
2. What is exchange degeneracy?
3. What is meant by symmetric and anti symmetric wave function? How can the behaviour of particles be distinguished in system having symmetric and anti symmetric wave function?
4. Write a short note on the Pauli’s exclusion principle?
5. Define particle exchange operator and show that if eigen values are ± 1
6. Show that the indistinguishability of similar particles implies that admissible wave functions must obey symmetry restrictions w.r.t interchange of particles.

13.6 Further reference:

- Advanced Quantum Mechanics by J.J.Sakurai.

Unit-14: Stationary state perturbation theory, first and second orders, degenerate and non-degenerate cases.

Structure:

14.0 Objectives

14.1 Introduction

14.2 Contents:

- a : Basic concepts
- b: Non degenerate energy levels
- c: Anharmonic oscillator: first order correction
- d: Degenerate energy levels.
- e: Effect of electric field on the n=2 state of hydrogen.

14.3 Let us sum up

14.4 Questions for self study

14.5 Further references

14.0 Objectives

After studying the unit you will be able to understand

- Basic concepts of the perturbation theory.
- Energy corrections to non-degenerate energy levels and examples.
- Energy corrections to the degenerate energy levels and examples.

14.2Introduction

We have already considered in earlier discursion some of the systems for which the Schrödinger equation is exactly solvable. For example, Harmonic oscillator, finite potential well, infinite square well potential, Hydrogen atom etc. But the potential energy of most of the real systems is different from those which have been considered and an exact solution is not possible for them. Therefore different approximation methods are considered to obtain approximate solution of the systems. Perturbation method is one such method.

14.2 Contents:

a : Basic concepts
b: Non degenerate energy levels
c: The ground state of helium.
d: Effect of electric field on the ground state of hydrogen.
e: Degenerate energy levels.
f: Effect of electric field on the n=2 state of hydrogen.
g: Spin orbit interaction.
h: Worked examples.

(a) **Basic concepts:**

In the time independent perturbation approach a known solution of a system whose Hamiltonian is only slightly different from that of system under consideration is used as the starting point.

The Hamiltonian operator H representing the total energy of the system can be written as

$H=H^0+H^1$-----------------------------------(1)

Where H^0 is called the unperturbed Hamiltonian whose non degenerate eigen values ($E_n^0, n = 1,2 - - - - -$) and eigen functions ψ_n^0 are named to be known and the time independent operator H^1 called the perturbation is small. These functions $\psi_n^0, n = 1,2 - - - - -$ form a complete orthonormal basis.

These correspond to the eigen value equation

$$H^0\psi_n^0 = E_n^0\psi_n^0 \qquad n = 1, 2 - - - - - - - - - - - - (2)$$

Our aim here is to solve the Schrödinger equation:

$$H\psi_n = E_n\psi_n - - - - - - - - - - - - - - - - - - (3)$$

The Hamiltonian H of the perturbed system is

$$H = H^0 + \lambda H^1 - - - - - - - - - - - - - - - - - - (4)$$

as the parameter λ changes from 0 to 1, the Hamiltonian changes from H^0 to H and the eigen function from ψ_n^0 and ψ_n . We can therefore expand E_n and ψ_n in terms of the parameter λ as

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + - - - - - - - - - - - - - - - - - (5)$$
$$\psi_n = \psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + - - - - - - - - - - - - - - - - - (6)$$

where the terms independent of λ are known as zero order terms (unperturbed ones), those in λ are first order, those in λ^2 second order and so on. Thus $E_n^{(1)}$ *and* $\psi_n^{(1)}$ are respectively the first order correction to the energy and wave function $E_n^{(2)}$ *and* $\psi_n^{(2)}$ the respective second order correction and so on. Substituting these in equation (3), we get

$$(H^0 + \lambda H^1)\left(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + - - - - - - - - - - -\right)$$
$$= \left(E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + - - - - - - -\right)\left(\psi_n^0 + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + - - - - - -\right)$$

or

$$\left(H^0 - E_n^0\right)\psi_n^0 + \lambda\left(H^1\psi_n^0 + H^0\psi_n^{(1)} - E_n^{(1)}\psi_n^0 - E_n^0\psi_n^{(1)}\right)$$
$$+ \lambda^2\left(H^1\psi_n^{(1)} + H^0\psi_n^{(2)} - E_n^{(2)}\psi_n^0 - E_n^0\psi_n^{(1)} - E_n^0\psi_n^{(2)}\right) = 0 ....(7)$$

Since λ is arbitrary, the co efficient of each power of λ must vanish separately and therefore we have

$$H^0\psi_n^0 = E_n^0\psi_n^0 \text{------------------------------}(8)$$
$$H^1\psi_n^0 + H^0\psi_n^{(1)} = E_n^{(1)}\psi_n^0 + E_n^0\psi_n^{(1)} \text{----------------------}(9)$$
$$H^1\psi_n^{(1)} + H^0\psi_n^{(2)} = E_n^{(2)}\psi_n^0 + E_n^{(1)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(2)} \text{----------------}(10)$$

As we are interested only up to second order we neglect equations beyond equation (10), equation (8) is identical to equation (2) as expected since it reflects to perturbation of zero order.

(b) Non degenerate energy levels:

First we shall consider perturbations on energy levels that are non degenerate. For convenience we shall use the wave function itself to label the states.

First order correction to the energy:-

Multiplying equation (9) from the left by $\langle\psi_n^0|$ we get

$$\langle\psi_n^0|H'|\psi_n^0\rangle + \langle\psi_n^0|H^0|\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^0\rangle + E_n^0\langle\psi_n^0|\psi_n^{(1)}\rangle \text{------}(11)$$

Since H^0 is Hermitian, the second term on the left reduces to $E_n^0\langle\psi_n^0|\psi_n^1\rangle$ and equation (11) gives

$$E_n^{(1)} = \langle\psi_n^0|H'|\psi_n^0\rangle \text{----------------}(12)$$

In simplified form, equation (12) can be written as

$$E_n^{(1)} = \langle n|H'|n\rangle \text{-------------------}(13)$$

which is often referred to as matrix elements

First order correction to wave function:

The First order correction to the wave function is written as a linear combination of the unperturbed wave functions of the system.

$$\psi_n^{(1)} = \sum_{t=1}^{\infty} a_i\psi_i^0 \text{-----------------------------}(14)$$

Substitution of equation (14) in equation (9) and multiplication from the left by $\langle\psi_m^0|$ gives

$$\left\langle \psi_m^0 \middle| H' | \psi_n^0 \right\rangle + \sum_{l=1}^{\infty} a_l E_l^0 \left\langle \psi_m^0 \middle| \psi_l^0 \right\rangle = E_n^{(1)} \left\langle \psi_m^0 \middle| \psi_n^0 \right\rangle + \sum_{l=1}^{\infty} a_l E_n^0 \left\langle \psi_m^0 \middle| \psi_l^0 \right\rangle$$

$$or \quad \left\langle \psi_m^0 \middle| H' | \psi_n^0 \right\rangle + a_m E_m^0 = a_m E_n^0$$

$$a_m = \frac{\left\langle \psi_m^0 \middle| H' | \psi_n^0 \right\rangle}{E_n^0 - E_m^0} = \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0} \text{-----------------------------}(15)$$

All the ***a***’s except a_n in equation (14) can be calculated using equation (15). The coefficient a_n is found to be zero from the normalization condition $\langle \psi_n | \psi_n \rangle = 1$. It follows that

$$\psi_n^{(1)} = \sum_m \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0} \left| \psi_m^0 \right\rangle \text{-----------------------------------}(16)$$

Consequently the energy and wave function corrected to first order are

$$E_n = E_n^0 + \langle n | H' | n \rangle \text{---------------------------------------}(17)$$

$$and$$

$$\psi_n = \psi_n^0 + \sum_m{}' \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0} \left| \psi_m^0 \right\rangle \text{-----------------------------------}(18)$$

where the prime on the sum means that state m = n should be excluded.

Second order correction to the energy:

The same procedure is used to obtain the second order correction to the energy from equation (10). Multiplying equation (10) from left by $\left\langle \psi_n^0 \right|$ and using the Hermitian nature of H^0 , we get

$$\left\langle \psi_n^0 \middle| H' | \psi_n^{(1)} \right\rangle = E_n^{(2)} \left\langle \psi_n^0 \middle| \psi_n^0 \right\rangle + E_n^{(1)} \left\langle \psi_n^0 \middle| \psi_n^{(1)} \right\rangle \qquad (19)$$

The form of $\psi_n^{(1)}$, equation (16) suggests that the second term on the right vanishes therefore

$$E_n^{(2)} = \left\langle \psi_n^0 | H' | \psi_n^{(1)} \right\rangle \qquad (20)$$

$$E_n^{(2)} = \sum_m{}' \frac{\left\langle \psi_m^0 | H' \middle| \psi_n^0 \right\rangle \left\langle \psi_n^0 | H' \middle| \psi_m^0 \right\rangle}{E_n^0 - E_m^0} = \sum_m{}' \frac{\langle m | H' | n \rangle \langle n | H' | m \rangle}{E_n^0 - E_m^0} \text{----------}(21)$$

If H' is Hermitian $\langle n|H'|m\rangle = \langle m|H'|n\rangle^*$ Then

$$E_n^{(2)} = \sum_m{}' \frac{|\langle m|H'|n\rangle|^2}{E_n^0 - E_m^0} \text{------------------------} (22)$$

Since $|\langle m|H'|n\rangle|^2$ is always positive, the sign of the correction is determined by the denominator. The 2nd order correction in energy in level *n* due to levels for which $E_n^0 > E_m^0$ is positive whereas that due to levels for which $E_n^0 < E_m^0$ is negative.

Second order correction to the wave function:

The second order correction to the wave function $\psi_n^{(2)}$ is written as a linear combination of the unperturbed wave function of the system

$$\psi_n^{(2)} = \sum_k b_k \psi_k^0 \text{------------------------------} (23)$$

Substitution of equation (23) in equation (10) and multiplication from left by $\langle \psi_l^0|$ gives

$$\sum_m{}' a_m \langle l|H'|m\rangle + \sum_k b_k \langle l|H^0|k\rangle = E_n^{(2)}\langle l|n\rangle + \sum_m{}' a_m E_n^{(1)}\langle l|m\rangle + \sum_k b_k E_n^0 \langle l|k\rangle$$

The first term on the right is zero. Rearranging we get:

$$b_l(E_l^0 - E_n^0) = E_n^{(1)} a_l - \sum_m{}' a_m \langle l|H'|m\rangle$$

Substituting the values of the *a*'s and $E_n^{(1)}$, we have

$$b_l = \frac{\langle n|H'|n\rangle\langle l|H'|n\rangle}{\left(E_l^0 - E_n^0\right)\left(E_n^0 - E_l^o\right)} - \sum_m{}' \frac{\langle m|H'|n\rangle\langle l|H'|m\rangle}{\left(E_n^0 - E_m^0\right)\left(E_l^0 - E_n^o\right)}$$

$$= \sum_m{}' \frac{\langle m|H'|n\rangle\langle l|H'|m\rangle}{\left(E_n^0 - E_m^0\right)\left(E_n^0 - E_l^o\right)} - \frac{\langle n|H'|n\rangle\langle l|H'|n\rangle}{\left(E_n^0 - E_l^o\right)^2} \text{---------------} (24)$$

The normalization condition of the wave function shows that the coefficient b_n is zero. It follows that the energy and wave function of the system corrected to second order in the perturbation is

$$E_n = E_n^0 + \langle n \mid H' \mid n \rangle + \sum_m{}' \frac{\left|\langle n \mid H' \mid m \rangle\right|^2}{E_n^0 - E_m^0} \text{------------} (25)$$

and

$$\psi_n = \psi_n^0 + \sum_m{}' a_m \psi_m^0 + \sum_l{}' b_l \psi_l^0 \text{----------------} (26)$$

where the coefficient a_m and b_l are given by equation (15) and (24) respectively. The prime on the sum again signifies the omission of the states m=n or $l=n$ as the case may be.

c. Anharmonic oscillator: first order correction

Consider a particle of mass *m* subjected to a one dimensional potential

$$V(x) = \frac{1}{2} m\omega^2 x^2 + bx^4 \text{-----------------------} (27)$$

where ω is the angular frequency and *b* is a small parameter independent of *x*. If b were zero, the potential would correspond to that of a harmonic oscillator. The inclusion of the term bx^4 in the potential changes the system from a harmonic oscillator to an anharmonic oscillator. We calculate the first order correction to the ground state energy which is given by

$$E^{(1)} = \langle 0 \mid bx^4 \mid 0 \rangle \text{---------------} (28)$$

In terms of creation ($a^\dagger$) and annihilation (a) operators

$$x = \left(\frac{\hbar}{2m\omega} \right)^{1/2} \left(a + a^+ \right) \text{----------------} (29)$$

and $$E^{(1)} = b \left(\frac{\hbar}{2m\omega} \right)^2 \left\langle 0 \left| \left(a + a^+ \right)\left(a + a^+ \right)\left(a + a^+ \right)\left(a + a^+ \right) \right| 0 \right\rangle \text{----} (30)$$

when expanded, the expression on the right will have 16 terms with four factors of a or $a^\dagger$ or both. A product operator like $a^\dagger a a^\dagger a$ gives zero for the matrix element since $a|0\rangle = 0$. Also in a product operator like $aa^\dagger a^\dagger a^\dagger$, the number of *a*'s and $a^\dagger$ are unequal. In such a case $aa^\dagger a^\dagger a^\dagger |0\rangle$ will be different from $|0\rangle$ leading to zero value for $\langle 0 | aa^\dagger a^\dagger a^\dagger | 0 \rangle$.Hence the two non-vanishing terms in the present case will be $\langle 0 | aaa^\dagger a^\dagger | 0 \rangle$ *and* $\langle 0 | aa^\dagger aa^\dagger | 0 \rangle$. The relations:

$$a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle \quad and \quad a|n\rangle = \sqrt{n}\,|n-1\rangle \text{------------} (31)$$

Then the corrected ground state energy is

$$E_0 = \frac{1}{2}\hbar\omega + 3b\left(\frac{\hbar}{2m\omega}\right)^2 ----------(34)$$

d. Degenerate energy levels:

The unperturbed wave function ψ_n^0 is a unique one in the non degenerate case. When degeneracy exists, a linear combination of the degenerate wave functions can be taken as the unperturbed wave function. For simplicity, consider a case in which E_n^0 is twofold degenerate. Let ψ_n^0 and ψ_l^0 be eigen functions corresponding to eigen values $E_n^0 = E_l^0$ and a linear combination of the two be

$$\varphi = C_n\psi_n^0 + C_l\psi_l^0 -------------------(35)$$

where C_n and C_l are constants.

First order corrections:

Replacing ψ_n^0 in equation (9) by φ we get

$$H'\left|C_n\psi_n^0 + C_l\psi_l^0\right\rangle + H^0\left|\psi_n^{(1)}\right\rangle = E_n^{(1)}\left|C_n\psi_n^0 + C_l\psi_l^0\right\rangle + E_n^0\left|\psi_n^o\right\rangle ----------(36)$$

Multiplying equation (36) from left by $\left\langle\psi_n^0\right|$ we have

$$C_n\langle\psi_n^0|H'\left|\psi_n^0\right\rangle + C_l\left\langle\psi_n^0|H'\right|\psi_l^0\rangle + \left\langle\psi_n^0|H^0\right|\psi_n^{(1)}\rangle = C_nE_n^{(1)} + E_n^0\left\langle\psi_n^0\middle|\psi_n^{(1)}\right\rangle -------(37)$$

Since H^0 is Hermitian

$$\left\langle\psi_n^0|H^0\middle|\psi_n^{(1)}\right\rangle = E_n^0\left\langle\psi_n^0\middle|\psi_n^{(1)}\right\rangle --------------(38)$$

And equation (37) reduces to

$$\left(H'_{nn} - E_n^{(1)}\right)C_n + H'_{nl}C_l = 0 -----------------(39)$$

Operating equation (36) from left by $\left\langle\psi_l^0\right|$ we have

$$H'_{lm}C_n + \left(H'_{ll} - E_n^{(1)}\right)C_l = 0 -------------------(40)$$

Equation (39) and (40) together form a set of simultaneous equations for the coefficient C*n* and C*l*. A nontrivial solution of these equations exists only if the determinants of the coefficients vanish.

$$\begin{vmatrix} H'_{nn} - E_n^{(1)} & H'_{nl} \\ H'_{ln} & H'_{ll} - E_n^{(1)} \end{vmatrix} = 0 ------------- (41)$$

This is called the scalar equation and its solutions are

$$E_{n\pm}^{(1)} = \frac{1}{2}\left(H'_{nn} + H'_{ll}\right) \pm \frac{1}{2}\left[\left(H'_{nn} - H'_{ll}\right)^2 + 4\,|\,H'_{nl}\,|^2\right]^{(1/2)}$$

Now the corrected energies are

$$E_n = E_n^0 + E_{n+}^{(1)} \text{ and } E_l = E_n^0 + E_{n-}^1 ------------- (43)$$

Both the energies will be real as the diagonal matrix elements H'_{nn} and H'_{ll} of the Hermitian operator H^1 are real. if $H'_{nn} = H'_{ll}$ and $H'_{nl} = 0, E_{n+} = E_{n-}$ and the degeneracy is not removed in the first order.

When the two roots of equation (41) are distinct, each can be used to calculate the ratio c_n/c_l either from equation (39) or from equation (40). The normalization condition $C_n^2 + C_l^2 = 1$ allows us to calculate the values of C_n and C_l. The values of C_n and C_l thus determined gives the desired linear combination associated with the level $E_n^0 + E_{n-}^{(1)}$ can also be evaluated.

e. Effect of electric field on the n=2 state of hydrogen:

The first excited state (n=2) of hydrogen atom is four fold degenerate since it has the (*l,m*) values (0,0), (1,0), (1,1) (1,-1). As before, let the electric field E be applied along the +ve z-axis which interacts with the electric dipole moment giving the perturbing Hamiltonian $H' = eEz = erE\cos\theta$. The four degenerate states may conveniently be specified by the quantum number (*n l m*) as

$$|nlm\rangle : |200\rangle, |210\rangle, |211\rangle, |21-1\rangle$$

As the state is four fold degenerate, the application of the perturbation theory for degenerate states requires the evaluation of sixteen matrix element of H^1 . Of these, the four diagonal elements are zero since they correspond to the same parity (H^1 is of odd parity). The off diagonal matrix elements between states of different *m* values (10 in numbers) are zero since

$$\int_0^{2\pi} \exp\left[i\left(m'-m\right)\phi\right]d\phi = 0 \quad if \quad m' \neq m$$

The remaining two matrix elements $\langle 200|H'|210\rangle$ *and* $\langle 210|H'|200\rangle$ are the only non vanishing ones. These can be evaluated using the values of

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^{3/2}}\left(2-\frac{r}{a_0}\right)\exp\left(\frac{-r}{2a_0}\right)----------(44)$$

$$and \quad \psi_{210} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^{3/2}}\frac{r}{a_0}\exp\left(\frac{-r}{2a_0}\right)\cos\theta--------(45)$$

$$\therefore \langle 200|H'|210\rangle = \frac{eE}{32\pi a_0^4}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(2-\frac{r}{a_0}\right)r^2\exp\left(\frac{-r}{a_0}\right)\cos^2\theta \; r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{eE}{16\, a_0^4}\int_0^{\pi}\cos^2\theta\sin\theta\, d\theta\int_0^{\infty}\left(2r^4-\frac{r^5}{a_0}\right)\exp\left(\frac{-r}{a_o}\right)dr$$

Using standard integrals we have

$$\langle 200|H'|210\rangle = -3eEa_o ------------------(46)$$

$$similarly, \; \langle 210|H'|200\rangle = -3eEa_o -------------(47)$$

The perturbation matrix is therefore

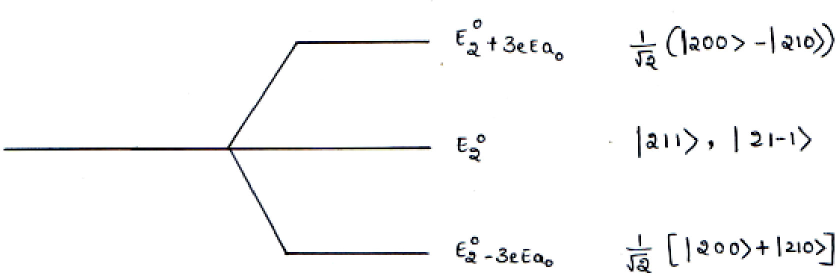
$$H' = \begin{array}{c|cccc|}
\underset{\downarrow}{(n\,l\,m)} \rightarrow & (200) & (210) & (211) & (21-1) \\
(200) & 0 & -3eEa_o & 0 & 0 \\
(210) & -3eEa_o & 0 & 0 & 0 \\
(211) & 0 & 0 & 0 & 0 \\
(21-1) & 0 & 0 & 0 & 0
\end{array} -------------48$$

The secular determinant is then

$$= \begin{vmatrix} -E_2^{(1)} & -3eEa_o & 0 & 0 \\ -3eEa_o & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} ---------------(49)$$

The four roots of this determinantal equation are 3eEa$_0$, -3eEa$_0$, 0 and 0. The states $|200\rangle$ and $|210\rangle$ are affected by the electric field whereas the states $|211\rangle$ and $|21-1\rangle$ are not. The four fold degeneracy is thus lifted partially eigen states corresponding to these eigen values can be evaluated using equations (39) or (40) and the normalization condition for the coefficients for the eigen value 3eEa$_0$, from equation (39) C$_n$/C$_l$ = -1 and the condition $C_n^2 + C_l^2 = 1$ gives $C_n = 1/\sqrt{2}$ and $C_l = -1/\sqrt{2}$. The eigenstate corresponding to the eigenvalues 3eEa$_0$ is then $\frac{(|200\rangle - |210\rangle)}{\sqrt{2}}$.In a similar way the eigen states of the eigen value -3eEa$_0$ is $\frac{(|200\rangle - |210\rangle)}{\sqrt{2}}$

The energy field along with the eigenstates of the n=2 state of the hydrogen atom in an electric field E along the z- direction is as shown.



The hydrogen atom in the first excited states thus possesses a permanent electric dipole momentum of magnitude 3ea$_0$ with three different orientations, one state parallel to the external electric field, one state antiparallel to the field and two states with zero component along the field. The states $|211\rangle$ and $|21-1\rangle$ do not possess dipole moments and therefore do not have a first order interaction with the field.

14.3 Let us sum up:

We have discussed the stationary state perturbation theory for both first and second orders. We have discussed in detail the degenerate and non degenerate cases and their examples for the two cases separately.

14.4 Questions for self study:

1. Explain briefly the principle of time-independent perturbation theory.

2. Explain the first order and second order correction to the energy and wavefunction for the non-degenerate for the non-degenerate energy levels?

3. Discuss the first order correction for the anharmonic oscillator.

4. Discuss the first order correction for degenerate energy levels.

5. Discuss the effect of electric field on the n = 2 state of hydrogen.

14.5 Further references:

- Quantum Mechanics by Aruldhas
- Introduction to Quantum Mechanics by D.J.Griffiths

Unit-15: Variational methods, ground state of helium atom, semi classical methods, sudden approximation, adiabatic expansion

Structure:

15.0 Objectives:

After studying this unit you will be able to understand

- The variational methods
- The example of ground state of helium atom
- Semi classical methods
- Sudden and adiabatic approximation.

15.1 Introduction

There are many problems in Quantum Mechanics which cannot be conveniently solved either by direct solution of wave equation or by the use of perturbation theory. The Helium atom is one such system. No direct method of solving the wave equation has been found for this atom and the application of perturbation theory is unsatisfactory because the first order approximation is not accurate enough, which is why the method conveniently used for such systems is 'Variation method'. The Variation method is especially applicable for the interest in chemical problems. In special cases, Variation method can be extended to the state of the system other than lowest one. The variation method may also be applied to the lowest state of the given resultant angular momentum and of given electron spin multiplicity.

15.2 Contents of the units:

e) The Variation method.
f) Physical applications of variation method.
    iii) Ground state of helium.
    iv) Zero point energy of one dimensional Harmonic oscillator.
g) Adiabatic approximation
h) Sudden approximation.
i)

a) The variation method:

The expectation value of energy in normalized state ψ is given by

$$\langle E\rangle = \int \psi^* H\psi d\tau ------(1)$$

If we choose the wave function ψ as variable function then the integral (1) is known as variational integral and gives an upper limit to the energy E_0 of the lowest state of the system. The function ψ is the variation function and its choice may be quite arbitrary but more wisely it is chosen such that E approaches more closely to E_0.

If the variation function ψ equals the function ψ_0 of the lowest states then energy E will be equal to E_0 i.e.,

$$\langle E\rangle = \int \psi_0^* H \psi_0 d\tau = E_0 ---------(2)$$

If $\psi \neq \psi_0$ then by expansion theorem ψ may be expanded in terms of a complete set of orthonormal function $\varphi_0, \varphi_{1,} \varphi_2 -----$ obtaining

$$\psi = \sum_n a_n \varphi_n \qquad with \qquad \sum_n a_n a_n^* = 1 and\ H\varphi_n = E_n \varphi_n \qquad (3)$$

Substituting this in equation (1) we get

$$\langle E\rangle = \sum_n a_n^* a_m \int \varphi_n^* H \varphi_m d\tau ------(4)$$

$$But\ H\varphi_m = E_m \varphi_m$$

$$we\ have\ \ \langle E\rangle = \sum_n a_n^* a_m \int \varphi_n^* E_m \varphi_m d\tau$$

$$= \sum_n a_n^* a_m E_m \int \varphi_n^* \varphi_m d\tau$$

$$= \sum_n a_n^* a_m E_m \delta_{nm}$$

$$\therefore \langle E\rangle = \sum_n a_n^* a_m E_n \quad \begin{bmatrix} \sin ce\ \delta_{nm} = 1 & for\ m = n \\ = 0 & for\ m \neq n \end{bmatrix}$$

$$\sum_n |a_n|^2 E_n -------(5)$$

Subtracting ground state energy E_0 from both sides we get

$$\langle E\rangle - E_0 = \sum_n |a_n|^2 (E_n - E_0) ---------(6)$$

As $|a_n|^2$ is positive and $E_n \geq E_0$ (always) for all values of *n*; therefore right hand side is positive or zero. Thus, we have proved that <E> is always an upper limit to E_0 i.e.,

$$\langle E\rangle \geq E_0 -------(7)$$

This theorem is the basis of the variation method for the calculation of the approximate eigen values of the system. If we choose a number of wave functions ψ_1,ψ_2,ψ_3 .... and calculate the values E_1,E_2,E_3........ corresponding to the them, then each of these values of E is greater than the energy E_0 so that the lowest one is the nearest to E_0. Often the functions ψ_1,ψ_2,ψ_3............are only distinguished by having different values of some parameter λ, the process of minimizing E w.r.t this parameter may then be carried out in order to obtain the best approximation to E_0, which, from the trial function ψ is so chosen that it involves the variation parameter which may vary considerably with E_0

Ex: in the case of Helium atom this method has been applied with great success

If function ψ is not normalized, equation (1) can be written as

$$\langle E\rangle = \frac{\langle\psi\,|\,H\,|\psi\rangle}{\langle\psi|\psi\rangle}\,or\,\frac{\int\psi^* H\psi d\tau}{\int\psi^*\psi d\tau}-----------(8)$$

Evaluating the integral on R.H.S of equation (1) or (8) with a trial function ψ that depends on the number of parameters and varying these parameters until the expectation value of the energy is minimum so that

$$E\left(\lambda_1,\lambda_{2,}------\lambda_n\right)=\frac{\left\langle\psi\left(\lambda_1,\lambda_2-----\lambda_n\right)|\,H\,|\,\psi\left(\lambda_1,\lambda_{2,}------\lambda\right)\right\rangle}{\langle\psi|\psi\rangle}.....................(9)$$

These parameters are such that the expectation values of the energy take a value

$$\frac{\partial E}{\partial\lambda_1}=0,\frac{\partial E}{\partial\lambda_2}=0-----\frac{\partial E}{\partial\lambda_n}=0$$

Application to the excited state:

The variation method can also be used to calculate an upper limit for one of the higher energy level if the trial function is orthogonal to the eigen function of all the lower states. Taking the energy levels in ascending series $E_0,E_1.E_2$........ then if ψ is orthogonal to φ_i for i=0,1,.........*n*, it is easily seen from (3) that the corresponding coefficient a_i are zero and an inequality can be obtained from (5).

The technique of choosing the trial function for evaluation of energy for any excited state is that- this function must be orthogonal to the eigen functions of all the lower states (arranged in ascending order of energy). For nth excited state the trial function is chosen to be of the form

$$\psi = \chi - \sum_{n=0}^{n-1} a_n \int \varphi_n^* \chi d\tau -----(10)$$

χ is an arbitrary function and $\varphi_n^{'} s\left(i.e., \ \varphi_0, \varphi_1, \varphi_2 ....\varphi_{n-1}\right)$ represent the eigen functions of lowest *n* states. If we expand ψ in the complete set of $\varphi_n^{'} s$ we find that

$a_n = 0 \quad for \quad n = 0,1,2.........n-1$

$we\,have$

$$\langle E \rangle = \int \psi^* H \psi d\tau = \langle \psi | H | \psi \rangle \geq E_n -------(11)$$

This equation gives an upper limit to the energy of the n^th^ state. There are several cases in which such a situation may arise. The simplest example is a one dimensional problem in which independent variable *x* goes from -∞ to +∞ and the potential function is an even function of *x* : i.e.,

V(-*x*)=V(*x*)

The wave function belonging to the lowest level of such a system is always an even function of *x* i.e.,

$\varphi_0(-x) = \varphi_0(x)$

while the φ_1 is an odd function. i.e.,

$\varphi_1(-x) = -\varphi_1(x)$

Therefore if we choose an even function for ψ, we can only say that $E \geq E_0$, but if it is an odd function, a_0 will be zero and the relation $E \geq E_1$ will hold. For such a problem, the variation method may be used to obtain the lowest energy levels.

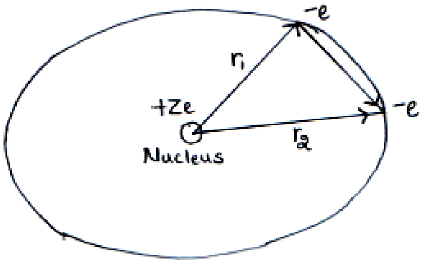
(b)Physical applications of Variation method:

(i)Ground state of Helium (He): We use the variation method with a simple trial function to obtain an upper limit for the energy of the ground state of the helium atom. The helium atom consists of a nucleus of charge +2e and two electron each of charge “-e”.

If we consider the nucleus at rest, the Hamiltonian will be

$$H = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)$$

$$-2e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{r_{12}} - - - - - - (12)$$



where ∇_1^2 *and* ∇_2^2 and Laplacian operators for the first and second electrons at a distance r_1 and r_2 from the nucleus, $r_{12}=|r_2-r_1|$ is the distance between two electrons. If the interaction energy e^2/r_{12} between two electrons were not present, the ground state eigen function of Helium would be product of two normalized hydrogen like wave functions $u_{100}(r_1)$ $u_{100}(r_2)$ given by

$$\psi\left(r_1, r_2\right) = u_{100}(r_1)\, u_{100}\left(r_2\right) = \frac{z^3}{\pi a_0^3} e^{-\left(z/a_0\right)\left(r_1+r_2\right)}$$

$$with \quad z = 2 \quad and \quad a_0 = \frac{\hbar^2}{me^2}$$

We shall use $\psi(r_1,r_2)$ as a trial function and treat z to be the variation parameters so that it is not necessarily equal to 2.

The expectation value of Hamiltonian *H* is the sum of expectation values of Kinetic energy and potential energy individually.

$$H = K.E + P.E$$

$$= T + V + \text{int}\,eracting\, energy\left(i.e\,\frac{e^2}{r_{12}}\right) of\ electrons$$

$$then \quad \langle H\rangle = \langle T\rangle + \langle V\rangle + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

Now the expectation values of hydrogen like atoms (having one electron) with Z-atomic number in general are

$$\langle T\rangle = \frac{z^2e^2}{2a_0}, \langle V\rangle = \frac{-2ze^2}{a_0} \quad \sin ce \quad \frac{1}{r_1} = \frac{z}{a_0}$$

But helium atom in ground state has two electrons, so it will be twice of hydrogen like atoms. i.e.,

$$\langle T\rangle = \frac{2z^2e^2}{2a_0} = \frac{z^2e^2}{a_0} -------(13)$$

and

$$\langle V\rangle = -2\times\frac{2ze^2}{a_0} = \frac{-4ze^2}{a_0} -----(14)$$

Hence

$$\langle H\rangle = \frac{z^2e^2}{a_0} - \frac{4ze^2}{a_0} + \left\langle \frac{e^2}{r_{12}} \right\rangle ------(15)$$

Electron interaction energy:

The expectation value of the interaction energy between the electrons is

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \iint \psi^*\left(r_{1,}r_2\right)\frac{e^2}{r_{12}}\psi\left(r_1,r_2\right)d^3r_1d^3r_{2,}$$

$$= \left(\frac{z^2}{\pi a_0^3}\right)^2 e^2 \iint \frac{1}{r_{12}} e^{-(2z/a_0)(r_1+r_2)}\, d^3r_1d^3r_2$$

Substituting

$$\frac{2z}{a_0}r_1 = \rho_1 \;\; and \quad \frac{2z}{a_0}r_2 = \rho_{2,}\; \frac{2z}{a_0}r_{12} = \rho_{12}$$

$$we\;\; get\; \left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{ze^2}{32\pi^2 a_0}\iint \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d^3\rho_1 d^3\rho_2$$

Solving the spherically symmetric integral with the knowledge of electrostatics as in perturbation theory, we get,

$$\therefore \left\langle \frac{\theta^2}{r_{12}} \right\rangle = \frac{ze^2}{32\pi^2 a_0} 20\pi^2$$

$$= \frac{5ze^2}{8a_0} -------------(16)$$

The expectation value of Hamiltonian (15) for the trial function is

$$\langle H\rangle = \frac{e^2z^2}{a_0} - \frac{4e^2z}{a_0} + \frac{5e^2z}{8a_0} = \frac{e^2}{a_0}\left(z^2 - \frac{27}{8}z\right)$$

Differentiating with respect to z and for minimum <H>

$$\frac{\partial\langle H\rangle}{\partial Z}=\frac{\partial}{\partial z}\left\{\frac{e^2}{a_0}\left(z^2-\frac{27}{8}z\right)\right\}=0$$

$$this\, gives\, z=\frac{27}{16}=1.69$$

Thus the lowest upper limit for the ground state energy of helium atom obtained with trial function

$$=\frac{e^2}{a_0}\left[\left\{\frac{27}{10}\right\}^2-\frac{27}{8}-\frac{27}{16}\right]=-\left\{\frac{27}{16}\right\}^2\frac{e^2}{a_0}=-2.85\frac{e^2}{a_0}---(17)$$

Using perturbation method, the ground state energy of helium atom comes out -2.85 e^2/a_0 where

$$a_0=\frac{\hbar^2}{m_0e^2}$$

The hydrogenetic wave functions give the best energy value when z =27/16 rather than 2. It indicates that each electron screen the nucleus from the other electron, therefore the effective nuclear charge being reduced (i.e., $2-\frac{27}{16}=\frac{5}{16}$) by of an electronic charge.

Hence "effective charge" in the nucleus is less than 2

(ii*) Zero point energy of one Dimensional harmonic oscillator:*

The one dimensional harmonic oscillator is simply a point mass *m* executing simple harmonic motion in one dimension.

The Hamiltonian of the system is:

$$H=\frac{P_x^2}{2m}+\frac{1}{2}kx^2$$

where k is force constant given by $k=m\omega_c^2,\omega_c$ being angular frequency of free oscillations and

$$P_x=\frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$H=\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}m\omega_c^2\,x^2------------(18)$$

We choose a trial wave function $\psi(x)$ which satisfies the following condition

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi^* H \psi dx = \min imum -------(19)$$

$$subjected\ to \int_{-\infty}^{\infty} \psi^* \psi dx = 1 \ \ (normalisation\ \ condition)$$

The normalization condition for real ψ means that ψ(x) must be an even function of *x*. More over as the integral must be convergent; $|\psi|^2 \rightarrow 0$ as $x \rightarrow \pm\infty$. These properties suggest the simplest function

$$\psi(x) = Ae^{-\alpha x^2} ------(20)$$

Where A is a constant and α is a variation parameter. Then the equation (3) provides

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = \int_{-\infty}^{\infty} A^* e^{-\alpha x^2} Ae^{-\alpha x^2} dx = 1$$

or

$$|A|^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = 1$$

or

$$|A|^2 \sqrt{\frac{\pi}{2\alpha}} = 1$$

This gives $|A| = \left(\frac{2\alpha}{\pi}\right)^{1/4}$

Choosing undetermined phase factors to be zero, we may write

$$A = \left(\frac{2\alpha}{\pi}\right)^{1/4} ------------(21)$$

Now

$$H\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega_c^2 x^2 \right] Ae^{-\alpha x^2}$$

$$= -\frac{A\hbar^2}{2m}\left[\left(4\alpha^2 - \frac{m^2\omega_c^2}{\hbar^2}\right)x^2 - 2\alpha\right]e^{-\alpha x^2}$$

Equation (19), for expectation value of energy gives

$$\langle E\rangle = \int_{-\infty}^{+\infty} Ae^{-\alpha x^2}\left[-\frac{A\hbar^2}{2m}\left\{\left(4\alpha^2-\frac{m^2\omega_c^2}{\hbar^2}\right)x^2-2\alpha\right\}\right]e^{-\alpha x^2}dx$$

$$= -\frac{A^2\hbar^2}{2m}\int_{-\infty}^{+\infty}\left\{\left(4\alpha^2-\frac{m^2\omega_c^2}{\hbar^2}\right)x^2-2\alpha\right\}e^{-2\alpha x^2}dx$$

$$= -\frac{A^2\hbar^2}{2m}\left(4\alpha^2-\frac{m^2\omega_c^2}{\hbar}\right)\int_{-\infty}^{+\infty}x^2e^{-2\alpha x^2}dx+\frac{A^2\hbar^2}{2m}.2\alpha\int_{-\infty}^{+\infty}e^{-2\alpha x^2}dx$$

Using the standard integrals

$$\int_{-\infty}^{+\infty}e^{-2\alpha x^2}dx=\sqrt{\frac{\pi}{2\alpha}}$$

$$and\int_{-\infty}^{+\infty}x^2e^{-2\alpha x^2}dx=\frac{1}{2}\sqrt{\frac{\pi}{(2\alpha)^3}}=\frac{1}{4\alpha}\sqrt{\frac{\pi}{2\alpha}}$$

we get

$$\langle E\rangle=-\frac{A^2\hbar^2}{2m}\left[4\alpha^2-\frac{m^2\omega_c^2}{\hbar^3}\right].\frac{1}{4\alpha}\sqrt{\frac{\pi}{2\alpha}}+\frac{A^2\hbar^2}{2m}.2\alpha\sqrt{\frac{\pi}{2\alpha}}$$

$$=\frac{A^2\hbar^2}{2m}\sqrt{\frac{\pi}{2\alpha}}\left[-\alpha+\frac{m^2\omega_c^2}{4\hbar^2\alpha}+2\alpha\right]$$

$$As\ A^2=\sqrt{\frac{2\alpha}{\pi}}\quad we\ \ have,$$

$$\langle E\rangle=\frac{\hbar^2}{2m}\left[\alpha+\frac{m^2\omega_c^2}{4\hbar^2\alpha}\right]$$

$$=\frac{\hbar^2\alpha}{2m}+\frac{m\omega_c^2}{8\alpha}------------------(22)$$

$$For\ \min imum\langle E\rangle,\frac{\partial\langle E\rangle}{\partial\alpha}=0$$

$$\frac{\partial\langle E\rangle}{\partial\alpha}=\frac{\partial}{\partial\alpha}\left[\frac{\hbar^2}{2m}\alpha+\frac{m\omega_c^2}{8\alpha}\right]=0$$

$$i.e\frac{\hbar^2}{2m}-\frac{m\omega_c^2}{8\alpha}=0$$

This gives

$$\alpha=\frac{m\omega_c^2}{2\hbar}-----------------(23)$$

Substituting this value of α in equation (22), we have minimum energy

$$\langle E\rangle = \frac{\hbar^2}{2m}\frac{m\omega_c^2}{2\hbar} + \frac{m\omega_c^2}{8\left(\frac{m\omega_c}{\hbar}\right)} = \frac{\hbar\omega_c}{4} + \frac{\hbar\omega_c}{4} = \frac{1}{2}\hbar\omega_c -----(24)$$

This is well known expression for zero point energy of harmonic oscillator. The required function of the oscillator in ground state will be given by

$$\psi(x) = Ae^{-\alpha x^2} = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$$

$$= \left(\frac{2}{\pi}\frac{m\omega_c}{2\hbar}\right)^{1/4} e^{-m\omega_c x^2/2\hbar}$$

$$i.e.,\ \psi(x) = \left(\frac{m\omega_c}{\pi\hbar}\right)^{1/4} e^{-m\omega_c x^2/2\hbar} ----------------(25)$$

(c) Adiabatic Approximation:

The adiabatic approximation the perturbation is turned on very slowly. In this approximation we expect on physical grounds that solution of the Schrödinger equation can be approximated by means of stationary eigen functions of instantaneous Hamiltonian so that a particular eigen function at one time goes over continuously into corresponding eigen function at a later time.

Let us try to solve Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = H(t)\psi -----------(26)$$

where H(t) varies slowly with time. Under this condition we may expect that a good approximation should be given by solving equation(9) at each instant of time under the assumption that H is constant and is equal to instantaneous value $H'(t')$ where t' is the time at which H is required. The stationary state wave function is obtained by setting t'=t = constant and would satisfy the equation

$$H(t')\psi_n(r,t') = E_n(t')\psi_n(r,t') ------------(27)$$

The approximation solution is

$$\psi_n = \varphi_n(t)\exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right) -----------(28)$$

In general

$$\psi_n = \sum_n a_n(t)\varphi(t)\exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right] ------(29)$$

substituting this value in (26) *we get*

$$i\hbar\left[\sum_n\left(a_n(t)\varphi_n(t) + a_n\frac{\partial\varphi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\} + \sum_n a_n\varphi_n E_n\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\}\right]$$

$$= H\sum_n a_n\varphi_n\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\}$$

$$= \sum_n a_n\varphi_n E_n\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\}$$

or

$$i\hbar\sum_n\left(a_n\varphi_n + a_n\frac{\partial\varphi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\} = 0$$

or

$$\sum_n\left(a_n\varphi_n + a_n\frac{\partial\varphi_n}{\partial t}\right)\exp\left\{-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right\} = 0$$

Multiplying by $\varphi_f^*\exp\left\{\frac{i}{\hbar}\int_0^t E_f(t')dt'\right\}$ and integrating over all space, we get

$$\int\sum_n a_n\varphi_n\varphi_f^*\exp\left\{-\frac{i}{\hbar}\int_0^t\left(E_n - E_f\right)dt'\right\}d\tau + \sum_n a_n\int\varphi_f^*\frac{\partial\varphi_n}{\partial t}\exp\left\{-\frac{i}{\hbar}\int_0^t\left(E_n - E_f\right)dt'\right\}d\tau = 0$$

Using condition of Orthonormality we get,

$$a_f = -\sum_n a_n\int\varphi_f^*\frac{\partial\varphi_n}{\varphi t}\exp\left\{-\frac{i}{\hbar}\int_0^t\left(E_n - E_f\right)\right\}d\tau$$

$$= -\sum_n a_n\int\varphi_m^*\frac{\partial\varphi_n}{\partial t}d\tau.\exp\left\{-\frac{i}{\hbar}\int_0^t\left(E_n - E_f\right)dt'\right\} ------(31)$$

$$\text{Evaluation of } \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau = \left\langle \varphi_f \middle| \varphi_n \right\rangle$$

$$\text{we have } H(t)\varphi_n(t) = E_n(t)\varphi_n(t) -----------------(32)$$

$$\text{Differentiating } (32) \text{ with respect to } t \text{ we get}$$

$$\frac{\partial H}{\partial t}\varphi_n + H\frac{\partial \varphi_n}{\partial t} = \frac{\partial t_n}{\partial t}\varphi_n + E_n\frac{\partial \varphi_n}{\partial t}$$

$$\text{Multiplying by } \varphi_f^* \text{ and integrating over all space, we get}$$

$$\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau + \int \varphi_f^* H \frac{\partial \varphi_n}{\partial t} d\tau = \frac{\partial E_n}{\partial t}\int \varphi_f^* \varphi_n d\tau + E_n \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau$$

$$\text{As } \int \varphi_f^* \varphi_n d\tau = 0 \text{ and } H \text{ is Hermitian, we get}$$

$$\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau + \int \left(H\varphi_f\right)^* \frac{\partial \varphi_n}{\partial t} d\tau = E_n \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau$$

$$\text{As } H\varphi_f = E_m \varphi_f$$

$$\therefore \int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau + E_f \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau$$

$$= E_n \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau$$

$$\text{i.e., } \left(E_f - E_n\right)\int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau = -\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau$$

$$\text{This gives } \int \varphi_f^* \frac{\partial \varphi_n}{\partial t} d\tau = -\frac{\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau}{E_f - E_n} ------(33)$$

$$= \frac{\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau}{E_n - E_f} \quad (\text{for } n \neq f)$$

$$\text{Substituting this value in } (31) \text{ we get}$$

$$a_f = -\sum_{n \neq f} a_n \frac{\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau \exp\left(-\frac{i}{\hbar}\int_0^t \left(E_n - E_f\right) dt'\right)}{E_n - E_f}$$

or

$$a_f = -\sum_{n \neq f} a_n \frac{\left(\int \varphi_f^* \frac{\partial H}{\partial t}\varphi_n d\tau\right)\exp\left(-\frac{i}{\hbar}\left(E_n - E_f\right) dt'\right)}{E_n - E_f}$$

We now apply the method of variation of constants.

Let the system start with $a_k=1$ and $a_n=0$ for $n \neq k$.

Solving this by successive approximations,

$$a_f = \frac{\left\langle f \,|\, \frac{\partial H}{\partial t} \middle| k \right\rangle}{E_k - E_f} \exp\left\{ -\frac{i}{\hbar}\left(E_k - E_f\right)t \right\} ------- (35)$$

$$where \left\langle f \,|\, \frac{\partial H}{\partial t} \middle| k \right\rangle = \int \varphi_f^* \frac{\partial H}{\partial t} \varphi_k d\tau$$

To evaluate the matrix element, we can neglect the slow change of $\left(\frac{\partial H}{\partial t}\right)_{fk}$ and integrate eqn (35), so that

$$a_f = -\frac{\left\langle f \,|\, \frac{\partial H}{\partial t} \middle| k \right\rangle}{E_k - E_f} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}\left(E_k - E_f\right)t} dt$$

$$or$$

$$a_f = -\frac{i\hbar}{\left(E_k - E_f\right)^2} \left\langle f \,|\, \frac{\partial H}{\partial t} \middle| k \right\rangle \left\{ \exp\left(-\frac{i}{\hbar}\left(E_k - E_f\right)t \right) - 1 \right\}$$

$$But\, E_k - E_f = \hbar\omega_{fk} \qquad (36)$$

$$a_f = \frac{1}{i\hbar\omega_{fk}^2} \left\langle f \,|\, \frac{\partial H}{\partial t} \middle| k \right\rangle \left\{ \exp\left(-i\omega_k t\right) - 1 \right\} ------- (37)$$

The total probability in the interval 0 to *t* is given by

$$\left|a_f\right|^2 = \frac{\left| \left\langle f \middle| \frac{\partial H}{\partial t} \,|\, k \right\rangle \right|^2}{\hbar^2 \omega_{fk}^4}$$

$$The\ condition\ that\ \left|a_k\right|^2 << 1\ requires$$

$$\frac{1}{\hbar\omega_{fk}^2} \left| \left\langle f \middle| \frac{\partial H}{\partial t} \,|\, k \right\rangle \right| << 1$$

Thus for adiabatic approximation $\left| \left\langle f \middle| \frac{\partial H}{\partial t} \,|\, k \right\rangle \right|$ should be enough, but should be appreciable.

<u>(d) Sudden approximation</u>:

The sudden approximation occurs when the Hamiltonian changes approximately during a very short but finite interval of time t_o. Sudden approximation consists of the change in Hamiltonian discontinues on different times. Let t_o be the duration and to consider sudden approximations, we again consider equation (35)

i.e.,

$$a_f = \frac{\left\langle f \mid \frac{\partial H}{\partial t} \middle| k \right\rangle}{E_k - E_f} \exp\left\{ -\frac{i}{\hbar}\left(E_k - E_f\right)t \right\} ------(38)$$

In the sudden approximation, the variation of $\left(\frac{\partial H}{\partial t}\right)$ cannot be neglected so

$$a_f = \int_0^{t_0} \frac{\left\langle f \mid \frac{\partial H}{\partial t} \middle| k \right\rangle}{\left(E_k - E_f\right)} \exp\left\{ -\frac{i}{\hbar}\left(E_k - E_f\right)t \right\} dt$$

$$= \left\{ \frac{\langle f \mid H(t) | k \rangle}{\left(E_k - E_f\right)} \exp\left(-\frac{i}{\hbar}\left(E_k - E_f\right)t \right) \right\}_0^{t_0}$$

$$-\int_0^{t_0} \frac{\langle f \mid H(t) | k \rangle}{\left(E_k - E_f\right)} \exp\left(-\frac{i}{\hbar}\left(E_k - E_f\right)t \right)\left(-\frac{i}{\hbar}\left(E_k - E_f\right)t \right) dt -----(39)$$

The condition of sudden approximation, by the help of uncertainty relation $\Delta E\ \Delta t \approx \hbar$ is expressed (since $\Delta t = t_0$ is very small) as

$$\frac{\hbar}{\Delta E} >> t_0 ---------(40)$$

The physical interpretation of this condition is that of the energy of the system changes by an amount ΔE. In a time t_0 which is much less than the characteristic time associated with energy change, then the state of the system remains unaltered and so $\langle f \mid H(t) | k \rangle = 0$; so equation (39) becomes

$$a_f = \frac{i}{\hbar}\int_0^{t_0} \langle f \mid H(t) | k \rangle \exp\left\{ -\frac{i}{\hbar}\left(E_k - E_f\right)t \right\} dt --------(41)$$

If ω_k is the angular frequency of the transitions from initial state f then

$$\omega_{fk} = \frac{E_f - E_k}{\hbar} \quad \textit{so that we may write}$$

$$a_f = \frac{i}{\hbar}\int_0^{t_0} \langle f \mid H(t) | K \rangle e^{i\omega_{fk} t} dt -------(42)$$

When perturbation is switched on suddenly H(t) changes instantaneously in time Δt which is small compared to period $\left(\omega_{fk}\right)^{-1}$ so that the factor $e^{i\omega_{fk}t}$ in the above integral changes a little and hence can be taken outside the integral, then we get

$$a_f = \frac{i}{\hbar} e^{i\omega_{fk}t} \int_0^{t_0} \left\langle f \,|\, H(t) \middle| K \right\rangle dt$$

$$= \frac{i}{\hbar} e^{i\omega_{fk}t} \left\langle f \,|\, H(t_0) - H(o) \middle| k \right\rangle t_0$$

$$= \frac{it_0}{\hbar} e^{i\omega_{fk}t} \left\langle f \,|\, H' \middle| k \right\rangle ----------(43)$$

where $H' = H(t_0) - H(o)$ and may be taken as the maximum value of interaction during its sudden switch on.

Therefore, sudden probability of transition from state k to state f will be given by:

$$\left|a_f\right|^2 = \frac{t_0^2}{\hbar^2} \left|\left\langle f \,|\, H' \middle| k \right\rangle\right|^2 = \frac{\left|\left\langle f \,|\, H' \middle| k \right\rangle\right|^2}{\hbar^2 \omega_{fk}^2} ------(44)$$

This equation may be used to evaluate the probability for transition under the influence of sudden perturbation which is sufficiently small so that the perturbation theory may be applied.

15.3: Let us sum up:

After studying this unit, we have understood the variational principle, examples of this method, ground state of helium atom and zero point energy of one dimensional harmonic oscillator. We have also learnt the adiabatic and sudden approximation method.

15.4 Key words:

variational method, adiabatic approximation and sudden approximation.

15.5 Questions for self study:

1. Discuss the variational method for obtaining approximate energies. Use it to find the ground state energy of helium atom.
2. Discuss the general theory of the variational principle. Show that this method can be used to obtain the zero point energy of one dimensional harmonic oscillator.
3. Write a short note on

   a. adiabatic approximation
   b. sudden approximation

4. Give an account of adiabatic and sudden approximations.

15.6 References for further study:

1. Modern Quantum Mechanics by J.J.Sakurai
2. Introduction to Quantum Mechanics by D.J.Griffiths
3. Introduction to Quantum Mechanics by ArulDhas

Unit-16 Time dependent potentials interaction picture, two state problems, time dependent perturbation theory, constant and harmonic perturbations and Fermi's golden rule, applications to interactions with classical radiation field.

Structure:

16.0 Objectives:

After studying this unit you will be able to understand.

- The time dependent potentials
- Interaction picture
- Two state problems
- Time dependent perturbation
- Fermi- golden rule
- Classical radiation field etc.

16.1 Introduction

In the last two units we have considered the Hamiltonians that do not contain time explicitly. Actually, in nature there are many quantum mechanical systems of importance with time dependence. So we have to consider these potentials and find out the solutions of such problems.

16.2 Contents of the unit:

h) Time dependent potentials
i) Interaction picture.
j) Two state problems.
k) Time dependent perturbation theory.
l) Transition probability.
m) Harmonic perturbation.
n) Application to interactions with the classical radiation field.

a) **Time dependent potentials:-**

Let us consider Hamiltonian H such that it can be split into two parts.

$H=H_0+V(t)$..................(1)

where H_0 does not contain time explicitly. The problem $V(t)=0$ is assumed to be solved in the sense that the energy eigenkets |n> and the energy eigenvalues E_n defined by

$$H_0|n\rangle = E_0|n\rangle ----------------(2)$$

are completely known. We may be interested in situations where initially only one of energy eigen states of H_0 - for example $|i\rangle$ – is populated. As time goes on however states other than $|i\rangle$ are populated because with V(t)≠0 we are no longer dealing with stationary problems; the time evolution operator is no longer as simple as $e^{-iHt/\hbar}$ when H itself involves time. Quite generally the time- dependent potential V(t) can cause transitions to states other than $|i\rangle$. The basic equation we address is- what is the probability as a function of time for the system to be formed in $|n\rangle$ with n≠i ?

More generally we are interested in how an arbitrary state ket changes as time goes on where the total Hamiltonian is the sum of H_0 and V(t). Suppose at t=0, the state ket of physical system is given by

$$|\alpha\rangle = \sum_n c_n(0)|n\rangle - - - - - - - - - - - - - - (3)$$

We wish to find $C_n(t)$ *for* $t > 0$ *such that*

$$|\alpha, t_0 = 0; t\rangle = \sum_n C_n(t) e^{-iE_n t/\hbar} |n\rangle - - - - - - (4)$$

where the ket on the left stands for the state ket in the Schrödinger picture at *t* of a physical system whose state ket at t=0 was found to be $|\alpha\rangle$.

(b) **The interaction picture: -**

Let us consider a physical system such that its state ket coincides with $|\alpha\rangle$ at t=t_0, where t_0 is often taken to be zero. At a later time we denote the state ket in the Schrödinger picture by $|\alpha, t_0; t\rangle_s$, where the subscripts S reminds us that we are delaying with the state ket of the Schrödinger picture.

We now define

$$|\alpha, t_0; t\rangle_t = e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_s - - - - - - - - - (5)$$

where $|\ \rangle$, stands for a state ket that represents the same physical situation in the interaction picture at t=0, $|\ \rangle_t$ evidently coincides with $|\ \rangle_S$. For operator (representing observables) we define observables in the interaction picture as

$$A_I = e^{-iH_0 t/\hbar} A_s \, e^{-iH_0 t/\hbar} -------------(6)$$

In particular,

$$V_I = e^{-H_0 t/\hbar} V e^{-iH_0 t/\hbar} ----------------(7)$$

where V without a subscript is understood to be the time independent potential in the Schrödinger picture. We know the connection between the Schrödinger and the Heisenberg picture

$$|\alpha\rangle_H = e^{+iHt/\hbar} |\alpha, t_0 = 0; t\rangle_s -----------(8)$$

$$A_H = e^{iHt/\hbar} A_s \, e^{-iHt/\hbar} ---------------(9)$$

The basic difference between (8) and (9) on the one hand and (6) and (7) on the other is that H rather than H_0 appears in the exponential.

We now derive the fundamental differential equation that characterized the time evolution of a state ket in the interaction picture. Let us take the time derivative (5) with the full H given by (1)

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_t = i\hbar \frac{\partial}{\partial t} \left(e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_s \right)$$

$$= -He^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_s + e^{iH_0 t/\hbar} \left(H_0 + V \right) |\alpha, t_0; t\rangle_s$$

$$= e^{iH_0 t/\hbar} V \; e^{-iH_0 t/\hbar} \; e^{iH_0 t/\hbar} |\alpha, t_0; t\rangle_s ------------(10)$$

We thus see

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_t = V_I \, |\alpha, t_0; t\rangle_I ----------------(11)$$

which is a Schrödinger- like equation with the total H replaced by V_I. In other words $|\alpha, t_0; t\rangle_I$ would be a ket fixed in time if V_I were absent. We can also show for an observable A (that does not contain time *t* explicitly in Schrödinger picture) that

$$\frac{dA_I}{dt} = \frac{1}{i\hbar} \left[A_I, H_0 \right] -------------(12)$$

which is a Heisenberg like equation with H replaced by H_0.

The interaction picture or Dirac picture is intermediate between the Schrödinger picture and the Heisenberg picture. This is shown in the table

	Heisenberg picture	**Interaction picture**	**Schrodinger picture**
State ket	No change	Evolution determined by V_I	Evaluation determined by H
Observable	Evolution determined By H	Evolution determined by H_0	No change

In the interaction picture we continue using $|n\rangle$ as our base kets. Thus, we expand $|\ \rangle_t$ as follows

$$|\alpha,t_0;t\rangle_t = \sum_n c_n(t)\,|\,n\rangle \qquad (13)$$

With t$_0$ set equal to 0, we see that the C$_n$ (t) appearing here are the same as the c$_n$(t) introduced earlier in equation (4) as can easily be verified by multiplying both sides of equal (4) by $e^{iH_o t/\hbar}$ using equation (2). We are finally in a position to write the differential equation for C$_n$(t). Multiplying both sides of equation (11) by $\langle n|$ from the left we obtain

$$i\hbar\frac{\partial}{\partial t}\langle n|\alpha,t_0;t\rangle_I = \sum_m \langle n|V_I\,|\,m\rangle\langle m|\alpha,t_0;t\rangle_I$$

This can also be written using

$$\left\langle n\left|e^{iH_0t/\hbar}\,V(t)\,e^{-iH_0t/\hbar}\,|\,m\right.\right\rangle = V_{nm}(t)\,e^{i(E_n-E_m)t/\hbar}$$

$$and\; C_n(t) = \langle n|\alpha,t_0;t\rangle_t$$

$$From\;\; eqn\; (13) -$$

$$i\hbar\frac{d}{dt}c_n(t) = \sum_m V_{nm}e^{i\omega_{nm}t}c_m(t) \qquad (15)$$

$$where$$

$$\omega_{nm} = \frac{(E_n - E_m)}{\hbar} = -\omega_{mn} \qquad (16)$$

Explicitly

$$i\hbar\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} \vdots = \begin{pmatrix} V_{11} & V_{12}e^{i\omega_{12}t} & . & . \\ V_{21}e^{i\omega_{121}t} & V_{22} & . & . \\ ' & . & V_{33} & . \\ . & . & . & . \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ \vdots \end{pmatrix} \qquad (17)$$

This is the basic coupled differential equation that must be solved to obtain the probability of finding $\langle n|$ as a foundation of *t*.

(c)Time dependent two state problems:

Exact solvable problems with time independent potentials are rather rare. In most cases we resort to perturbation expansion to solve the coupled differential equation (17), as we will discuss in the next section. There is however a problem of enormous practical importance which can be solved exactly as a two state problem with a sinusoidal oscillating potential.

The problem is defined by

$$H_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| \qquad \textit{with } (E_2 > E_1)$$
$$V(t) = \gamma e^{i\omega t}|1\rangle\langle 2| + \gamma e^{-i\omega t}|2\rangle\langle 1| \qquad (18)$$

Where γ and ω are real and positive. In the language of equation (14) and (15) we have

$$V_{12} = V_{21}^* = \gamma e^{i\omega t}$$
$$V_{11} = V_{22} = 0 \qquad (19)$$

We thus have a time dependent potential that connects the two energy eigen states of H_0. In other words we can have a transition between the two states $|1\rangle \Leftrightarrow |2\rangle$.

An exact solution to this problem is available. If initially at t=0 only the lower level is populated so that

$$C_1(0) = 1 \quad \textit{and} \quad C_2(0) = 0 \qquad (20)$$

Then the probability for being found in each of the two states is given by (Rabi's formula)

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + (\omega-\omega_{21})^2/4}\sin^2\left\{\left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}\right]^{1/2} t\right\} \qquad (21a)$$

$$|c_1(t)|^2 = 1 - |c_2(t)|^2 \qquad (21b)$$

where,

$$\omega_{21} = \frac{(E_2 - E_1)}{\hbar} \qquad (22)$$

Let us now find $|c_2|^2$. We see that the probability for finding the upper state E_2 exhibits oscillatory time dependence with angular frequency two times that of

$$\Omega = \sqrt{\left(\frac{\gamma^2}{\hbar^2}\right) + \frac{(\omega-\omega_{21})^2}{4}} \qquad (23)$$

The amplitude of oscillation is very large when

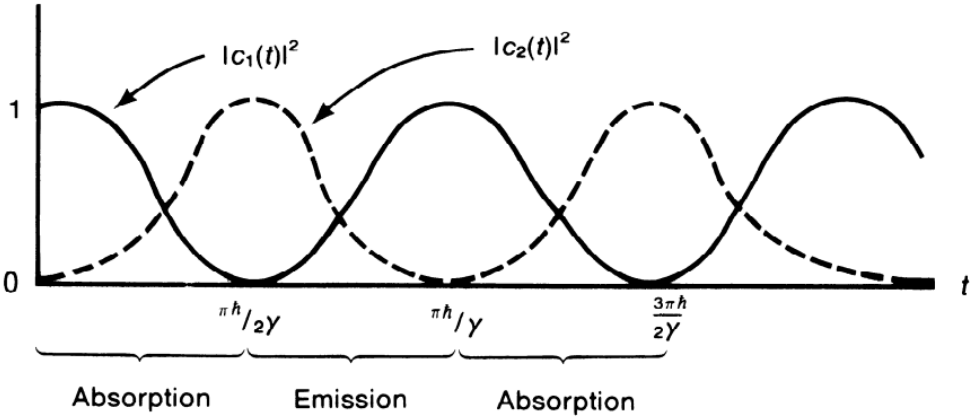
$$\omega \cong \omega_{21} = \frac{(E_2 - E_1)}{\hbar} \qquad (24)$$

That is when the angular frequency of the potential usually due to an externally applied electric field or magnetic field is nearly equal to the angular frequency characteristic of the two state systems. Equation (24) is therefore known as the resonance condition

It is very interesting to look at (21a) and (21b) a little closely exactly at resonance:

$$\omega = \omega_{21}, \Omega = \frac{\gamma}{\hbar} \qquad (25)$$

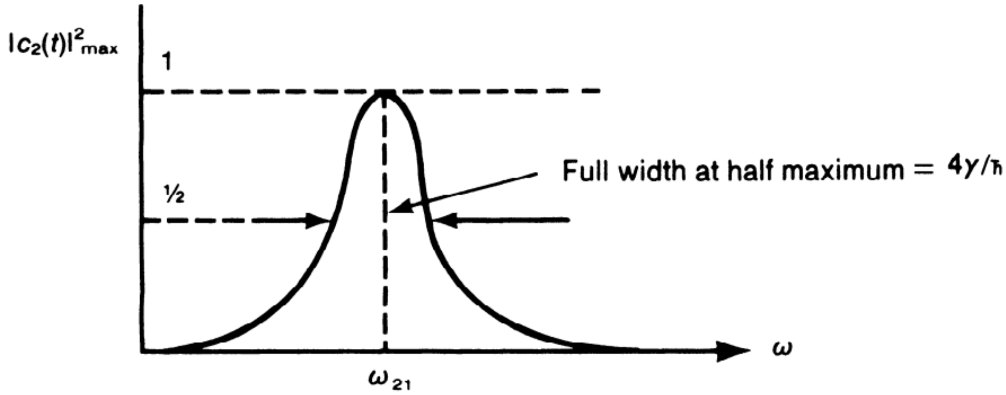
We can plot $\left|C_1(t)\right|^2 and \left|C_2(t)\right|^2$ as a function of t: it's shown in figure



From the time t=0 to $t = \pi\hbar/2\gamma$, the two level system absorbs energy from the time dependant potential $V(t) : \left|C_1(t)\right|^2$ decreases from unity as $\left|C_2(t)\right|^2$ grows. At $t = \pi\hbar/2\gamma$, only the upper state is populated. From $t = \pi\hbar/2\gamma$ to $t = \pi\hbar/\gamma$, the system gives up its excess energy to V(t) ; $|c_2|^2$ decreases and $|c_1|^2$ increases .

This absorption emission cycle is repeated indefinitely as is also shown in above figure. So, V(t) can be regarded as a source or sink of energy; put in another way V(t) can cause a transition from $|1\rangle$ to $|2\rangle$ (absorption) or from $|2\rangle$ to $|1\rangle$ (emission). We will come back to this point of view when we discuss emission and absorption of radiation.

The absorption-emission cycle takes place even away from resonance. However, the amplitude of oscillation for $|2\rangle$ is now reduced. $\left|C_2(t)\right|^2_{\max}$ is no longer 1 and $\left|C_1(t)\right|^2$ does not go down all the way to 0. In the following figure,



We plot $\left|C_2(t)\right|^2_{\max}$ as a function of ω. This curve has a resonance peak centred around $\omega=\omega_{21}$ and the full width at half maxima is given by $4\gamma/\hbar$. It is worth noting that the weaker the time-dependent potential (γ small) the narrower the resonance peak.

(d)Time dependent perturbation theory:

Dyson Series:

With the exception of a few problems like the two level time- dependent problems of the previous section, exact solutions to the differential equation for $C_n(t)$ are usually not available. We must be content with approximate solution equation (17) obtained by perturbation expansion

$$C_n(t) = C_n^{(0)} + C_n^{(1)} + C_n^{(2)} + ------------(26)$$

where $C_n^{(0)}, C_n^{(1)}$........... signify amplitudes of first order, second order and so on in the strength parameter of the time dependent potential. The iteration method used to solve this problem is similar to what we did in time independent perturbation theory. If initially only the state *i* is populated, we approximate C_n on the right hand side of differential equation (17) by $C_n^0 = \delta_{ni}$ (independent of *t*) and relate it to the time derivative of $C_n^{(1)}$, integrate the differential equation to obtain the differential equation for $C_n^{(2)}$ and so on. This is how Dirac developed time dependent perturbation theory in 1927.

Instead of working with $C_n(t)$ we propose to look at the time evolution operator $U_t(t,t_0)$ in the interaction picture, which we will define later. We obtain a perturbation expansion for $U_t(t,t_0)$ and at the very end we relate the matrix elements of U_I to $C_n(t)$. If we are interested only in solving simple problems in non relativistic quantum mechanics, all this might look superfluous;

however the operator formalism we develop is very powerful because it can immediately be applied to more advanced problems such as relativistic quantum field theory and many body theory.

The time evolution operator in the interaction picture is defined by

$$\left|\alpha,t_0;t\right\rangle_t = U_I\left(t,t_0\right)\left|\alpha,t_0;t_0\right\rangle_I \qquad (27)$$

Differential equation (11) for the state ket of the interaction picture is equivalent to

$$i\hbar\frac{d}{dt}U_I\left(t,t_0\right)=V_I\left(t\right)U_I\left(t,t_0\right) \qquad (28)$$

We must solve this operator differential equation subject to the initial condition

$$U_I\left(t,t_0\right)|_{t=t_0}=1 \qquad (29)$$

First let us note that the differential equation together with the initial condition is equivalent to the following integral equation

$$U_I\left(t,t_0\right)=1-\frac{i}{\hbar}\int_{t_0}^{t}V_I\left(t'\right)U_I\left(t',t_0\right)dt' \qquad (30)$$

We can obtain an approximation solution to this equation by iteration

$$U_I\left(t,t_0\right)=1-\frac{i}{\hbar}\int_{t_0}^{t}V_I\left(t'\right)\left[1-\frac{i}{\hbar}\int_{t_0}^{t'}V_I\left(t''\right)\ddot{U}_I\left(t'',t_0\right)dt''\right]dt'$$

$$=1-\frac{i}{\hbar}\int_{t_0}^{t}dt'V_I\left(t'\right)+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}dt^1\int_{t_0}^{t'}dt'V_I\left(t'\right)V_I\left(t''\right)+------+\left(\frac{-i}{\hbar}\right)^n\int_{t_0}^{t}dt'\int_{t_0}^{t'}dt''----$$

$$\times\int_{t_0}^{t^{(n-1)}}dt^n\,V_I\left(t'\right)V_I\left(t''\right)--------V_I\left(t^{(n)}\right)+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(31)$$

This series is known as the Dyson series. Setting aside the difficult question of convergence we can complete $U_I(t,t_0)$ to any finite order of perturbation theory.

(e)Transition probability:-

Once $U_I(t,t_0)$ is given, we can predict the time development of any state ket for example if the initial state at t=0 is one of the energy eigenstates of H_0; then to obtain the initial state ket at a later time, all we need to do is multiply by $U_I(t,0)$;

$$\left|i,t_0=0;t\right\rangle_I = U_I\left(t,o\right)|\,i\rangle$$

$$=\sum_n\left|n\right\rangle\left\langle n\right|U_I\left(t,0\right)|\,i\rangle----------------------(32)$$

In fact, $\langle n|U_I(t,0)|i\rangle$ is nothing more than what we called $C_n(t)$ earlier.

We earlier introduced the time evolution operator $U(t,t_0)$ in the Schrödinger picture. Let us now explore the connection between $U(t,t_0)$ and $U_I(t,t_0)$

$$|\alpha,t_0;t\rangle_I = e^{iH_0t/\hbar}|\alpha,t_0;t\rangle_S$$
$$= e^{iH_0t/\hbar}U(t,t_0)|\alpha,t_0;t\rangle_S$$
$$= e^{iH_0t/\hbar}U(t,t_0)e^{-iH_0t_0/\hbar}|\alpha,t_0;t\rangle_I \text{-------}(33)$$

So, we have

$$U_I(t,t_0) = e^{iH_0t/\hbar}U(t,t_0)e^{-iH_0t_0/\hbar} \text{-------}(34)$$

Let us now look at the matrix element of $U_I(t,t_0)$ between energy eigen states of H_0;

$$\langle n|U_I(t,t_0)|i\rangle = e^{i(E_nt-E_it_0)/\hbar}\langle n|U(t,t_0)|i\rangle \text{------------}(35)$$

We have $\langle n|U(t,t_0)|i\rangle$ is defined to be the transition amplitude. Hence our $\langle n|U_I(t,t_0)|i\rangle$ here is not quite the same as the transition amplitude defined earlier. However the transition probability defined as the square of the modulus of $\langle n|U(t,t_0)|i\rangle$ is the same as the analogous quantity in the interaction picture

$$|\langle n|U_I(t,t_0)|i\rangle|^2 = |\langle n|U(t,t_0)|i\rangle|^2 \text{------------}(36)$$

If the matrix elements of U_I are taken between initial and final states that are energy eigen states- for example between $|a'\rangle$ and $|b'\rangle$ (eigen kets of A and B respectively) where $[H_0,A]\neq 0$ and or $[H_0,B]\neq 0$ we have in general

$$|\langle b'|U_I(t,t_0)|a'\rangle| \neq |\langle b'|U(t,t_0)|a'\rangle|$$

as the reader may easily verify in problems where the interaction picture is found to be useful. The initial and final states are usually taken to be H_0 eigen states. Otherwise all that is needed is to expand $|a'\rangle$ and $|b'\rangle$ and so on in terms of the energy eigen kets of H_0

Coming back to $|\langle n|U_I(t,t_0)|i\rangle|$ we illustrate by considering physical situation where at $t=t_0$, the system is known to be in state $|i\rangle$. The state ket in the Schrödinger picture $|i,t_0;t\rangle_S$ is then equal to $|i\rangle$ up to a phase factor. In applying the interaction picture it is convenient to choose the phase factor at $t = t_0$ so that

$$\left|i,t_0;t_0\right\rangle_S = e^{-iE_it_o/\hbar}\,|\,i\rangle -----------------(37)$$

which means that in the interaction picture we have the simple equation

$$\left|i,t_0;t_0\right\rangle_I = \left|i\right\rangle -----------------(38)$$

At a later time we have

$$\left|i,t_0;t_0\right\rangle_I = U_I\left(t,t_0\right)|\,i\rangle -------------(39)$$

Comparing this with the expansion

$$\left|i,t_0;t_0\right\rangle_I = \sum_n C_n\left(t\right)|\,n\rangle -------------(40)$$

We see

$$C_n\left(t\right) = \left\langle n\right|U_I\left(t,t_0\right)|\,i\rangle -------------(41)$$

We now use the perturbation expansion for $U_I(t,t_0)$. We can also expand $C_n^{(t)}$ where $C_n^{(1)}$ is first order in $V_n(t)$, $C_n^{(2)}$ is second order in $V_I(t)$ and so on. Comparing the expansion of both sides of (41), we obtain,

$$C_n^{(0)}\left(t\right) = \delta_{ni}\left(independent\ of\ t\right)$$

$$C_n^{(1)}\left(t\right) = -\frac{i}{\hbar}\int_{t_0}^{t}\left\langle n\right|V_I\left(t'\right)|\,i\rangle dt'$$

$$= -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'}V_{ni}\left(t'\right)dt' ---------------(42)$$

$$C_n^2\left(t\right) = \left(\frac{-i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{i\omega_{nm}t'} V_{nm}\left(t'\right) e^{i\omega_{mi}t''}{}''V_{mi}\left(t''\right)$$

where we have used

$$e^{i\left(E_n-E_i\right)t/\hbar} = e^{i\omega_{ni}t} --------------------(43)$$

The transition probability for $\left|i\right\rangle \rightarrow \left|n\right\rangle$ with n≠i is obtained by

$$P\left(i\rightarrow n\right) = \left|C_n^{(1)}\left(t\right) + C_n^{(2)}\left(t\right) + -----\right|^2 \qquad (44)$$

Constant Perturbation

As an application of (42), let us consider a perturbation turned on at t=0;

$$V\left(t\right) = \begin{cases} 0 & for\quad t<0 \\ V\left(independent\ of\ t\right) & for\quad t\geq 0 \end{cases} ---------(45)$$

Even though the operator V has no explicit dependence on time, it is in general made up of operators like ***x, p*** and ***S***. Now suppose at t=0 we have only $\left|i\right\rangle$, with t_0 taken to be zero.

We obtain

$$C_n^{(0)} = C_n^{(0)}(0) = \delta_{in}$$

$$C_n^{(1)} = \frac{-i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni}t'} dt'$$

$$= \frac{V_{ni}}{E_n - E_i}\left(1 - e^{i\omega_{ni}t}\right) \text{-------------} (46)$$

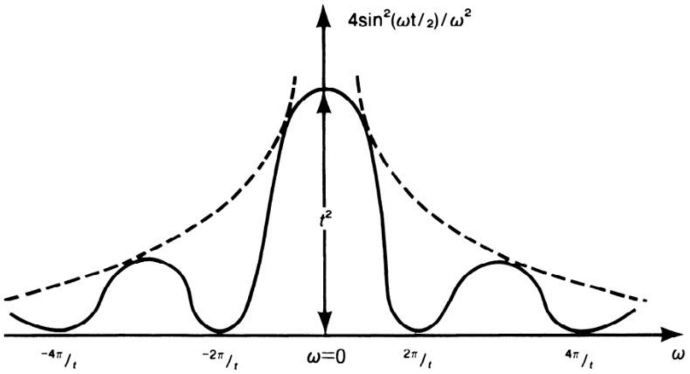
or

$$\left|C_n^{(1)}\right|^2 = \frac{\left|V_{ni}\right|^2}{\left|E_n - E_i\right|^2} \quad \left(2 - 2\cos\omega_{ni}t\right)$$

$$= \frac{4\left|V_{ni}\right|^2}{\left|E_n - E_i\right|^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] \text{-------} (47)$$

The probability of finding $\left|n\right\rangle$ depends not only on $\left|V_{ni}\right|^2$ but also on the energy difference (E_n-E_i), so let us try to see how equation (47) looks as a function of E_n. In practice we are interested in this way of looking at (47) when there are many states with $E \sim E_n$, so that we can talk about a continuum of final states with nearly the same energy. To this end we define $\omega \equiv \frac{E_n - E_i}{\hbar}$ ------------- (48)

and plot of $\frac{4\sin^2\left(\omega t/2\right)}{\omega^2}$ as a function of ω for fixed *t*, the time interval during which the perturbation has been show on the below figure.



We see that the height of the middle peak cantered around ω=0, is t^2 and the width is proportional to 1/t . As *t* becomes large, $\left|C_n^{(1)}(t)\right|^2$ is appreciable only for those states that satisfy

$$t \sim \frac{2\pi}{|\omega|} = \frac{2\pi\hbar}{|E_n - E_i|} -------------(49)$$

If we call Δt the time interval during which the perturbation has been turned on, a transition with appreciable probability is possible only if

$$\Delta t\,\Delta E \sim \hbar ------------------(50)$$

where by ΔE we mean the energy change involved in a transition with appreciable probability. If Δt is small, we have a broader peak and as a result we can tolerate a fair amount of energy non conservation. On the other hand if the perturbation has been on for a very long time, we have a very narrow peak and approximate energy conservation is required for a transition with appreciable probability. Note that this uncertainty relation is fundamentally different from the ***x-p*** uncertainty relation. There, ***x*** and ***p*** are both observables. In contrast, time in non- relativistic quantum mechanics is a parameter not an observable.

For those transitions with exact energy conservation $E_n=E_i$, we have

$$\left|C_n^{(1)}(t)\right|^2 = \frac{1}{\hbar^2}|V_{ni}|^2 t^2 ----------(51)$$

The probability of finding $|n\rangle$ after a time interval *t* is quadratic, not linear, in the time interval during which V has been ON. This may appear intuitively unreasonable. In a realistic situation where our formalism is applicable, there is usually a group of final states all with nearly the same energy as the energy of the initial state $|i\rangle$. In other words, a final state forms a continuous energy spectrum in the neighbourhood of E_i.

Let us calculate the total probability -that is, the transition probabilities summed over final states with $E_n \approx E_i$;

$$\sum_{n,E_n\approx E_i} \left|C_n^{(1)}\right|^2 -----------------(52)$$

It is customary to define the density of final states as the number of states within energy interval (E, E+dE) as

$$\rho(E)\,dE ---------------(53)$$

We can then write (52) as

$$\sum_{n,E_n \approx E_i} \left|C_n^{(1)}\right|^2 \Rightarrow \int dE_n \rho\left(E_n\right)\left|C_n^{(1)}\right|^2$$

$$= 4\int \sin^2\left[\frac{\left(E_n - E_i\right)t}{2\hbar}\right]\frac{\left|V_{ni}\right|^2}{\left|E_n - E_i\right|^2}\rho\left(E_n\right)dE_n ---------(53)$$

As t→∞ we can take advantage of

$$\lim_{t\to\infty}\frac{1}{\left|E_n - E_i\right|^2}\sin^2\left[\frac{\left(E_n - E_i\right)t}{2\hbar}\right] = \frac{\pi t}{2\hbar}\delta\left(E_n - E_i\right)-------(54)$$

Which follows from $\lim_{\alpha\to\infty}\frac{1}{\pi}\frac{\sin^2 \alpha x}{\alpha x^2} = \delta\left(x\right)----------(55)$

It is now possible to take the average of $\left|V_{ni}\right|^2$ outside the integral sign and performed the integration with the δ function

$$\lim_{t\to\infty}\int dE_n \rho\left(E_n\right)\left|C_n^{(1)}\left(t\right)\right|^2 = \left(\frac{2\pi}{\hbar}\right)\left|\overline{V}_{ni}\right|^2 \rho\left(E_n\right)t \mid E_n = E_i --------------(56)$$

Thus the total transition probability is proportional to *t* for large values of E, which is the quite reasonable. Notice that the linearity in *t* is a consequence of the fact that the total transition probability is proportional to the area under the peak in the earlier figure where height varies as t^2 and the width varies as 1/t.

It is conventional to consider the transition rate- that is the transition probability per unit time. Equation (56) tells us that the total transition rate defined by

$$\frac{d}{dt}\left(\sum_n\left|C_n^{(1)}\right|^2\right)----------------(57)$$

is constant in *t* for large *t*, calling equation (57) $\omega_{i\to[n]}$, where [n] stands for a group of final states with energy similar to *i* we obtain

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\left|\overline{V}_{ni}\right|^2 \rho\left(E_n\right)_{E_n = E_i} ----------(58)$$

Independent of *t*, provided the first order time independent perturbation theory is valid. This formula is called Fermi’s Golden rule. We can also write (58) as

$$\omega_{i\to n} = \left(\frac{2\pi}{\hbar}\right)\left|V_{ni}\right|^2 \delta\left(E_n - E_i\right)--------(59)$$

(f) Harmonic Perturbation:-

We now consider a sinusoidally varying time dependent potential commonly referred to as harmonic perturbation;

$$V(t) = \gamma e^{i\omega t} + \gamma^{\dagger} e^{-i\omega t} ------------------(60)$$

where γ may still depend on ***x, p, s*** and so on. Let us assume that only one of the eigen states of H_0 is populated initially. Perturbation (58) is assumed to be turned ON at t=0. So,

$$C_n^{(1)} = \frac{-i}{\hbar}\int_0^t \left(\gamma_{ni} e^{i\omega t'} + \gamma_{ni}^{\dagger} e^{-i\omega t'}\right) e^{i\omega_{ni} t'} dt'$$

$$= \frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{ni})t}}{(\omega+\omega_{ni})} + \frac{1-e^{i(\omega_{ni}+\omega)t}}{(-\omega+\omega_{ni})}\gamma_{ni}^{\dagger}\right] --------(61)$$

The only change needed was

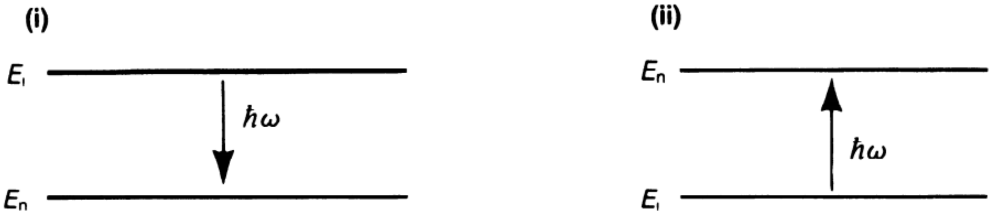
$$\omega_{ni} = \frac{E_n - E_i}{\hbar} \to \omega_{ni} \pm \omega ------62$$

$$So \;\; as \;\; t \to \infty \left|C_n^{(1)}\right|^2 \; is \;\; appreciable \;\; only \;\; if \;\; \omega_{ni} + \omega \approx 0 \;\; or \;\; E_n \approx E_i - \hbar\omega -----(63)$$

$$\omega_{ni} - \omega \approx 0 \;\; or \;\; E_n \approx E_i + \hbar\omega ------------(64)$$

Clearly, whenever the first term is important because of equation (63) and (64), the second term is unimportant and vice versa. We see that, we have no energy conservation condition satisfied alone rather the apparent lack of energy conservation is compensated by the energy given out to or energy taken away from the external potential V(t)

Pictorially it can be shown as in figure



(i) Stimulated emission: Quantum-mechanical system gives up $\hbar\omega$ to V (possible only if initial state is excited). (ii) Absorption: Quantum mechanical system receives $\hbar\omega$ from V and ends up as an excited state.

In the first case the quantum mechanical system gives up energy $\hbar\omega \;\; to \; V;$ this is clearly possible only if the initial state is excited. In the second case the quantum mechanical system receives energy $\hbar\omega$ from V and end Y as an excited state. Thus a time dependent perturbation can be regarded as an inexhaustible source or sink of energy.

We will use Fermi's Golden rule, we have

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\left|\bar{\gamma}_{ni}\right|^2 \rho\left(E_n\right)\Big|_{E_n=E_i-\hbar\omega} --------------\left(65\right)$$

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\left|\gamma^{\dagger}_{ni}\right|^2 \rho\left(E_n\right)\Big|_{E_n=E_i+\hbar\omega}$$

or more commonly

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\begin{Bmatrix}\left|\gamma_{ni}\right|^2 \\ \left|\gamma^{\dagger}_{ni}\right|^2\end{Bmatrix}\delta_{\left(E_n-E_i\pm\hbar\omega\right)} --------------(66)$$

Note also that

$$\left|\gamma_{ni}\right|^2 = \left|\gamma^{\dagger}{}_{ni}\right|^2 ------------------------\left(67\right)$$

which is a consequence of

$$\left\langle i\,|\,\gamma^{\dagger}\middle|\,n\right\rangle = \left\langle n\,|\,\gamma\,|\,i\right\rangle^{*} ---------------------\left(68\right)$$

Combining (65) *and* (67) *we have,*

$$\frac{\text{emission rate for } i\to\left[n\right]}{\text{density of final states for }\left[n\right]} = \frac{\text{absorption rate for } n\to\left[i\right]}{\text{density of final states for}\left[i\right]} ------\left(69\right)$$

where in the absorption case we let i stand for final states. Equation (69) which expresses symmetry between emission and absorption is known as 'detailed balancing'.

(g) Interactions with the classical radiation field:-

Absorption and stimulated emission

We apply the formalism of time dependent perturbation theory to the interactions of atomic electron with the classical radiation field. By a classical radiation field, we mean the electronic or magnetic field derivable from a classical radiation field.

The basic Hamiltonian with $|A|^2$ omitted is

$$H = \frac{\vec{P}^2}{2m_e} + e\varphi(x) - \frac{e}{m_e C}.\vec{A}.\vec{P}---------------(70)$$

Which is justified if

$$\vec{\nabla}.\vec{A} = 0 \qquad (71)$$

Specifically, we work with a monochromatic field of the plane wave for

$$\vec{A} = 2A_0\, \hat{\in} \cos\left(\frac{\omega}{c}\hat{n}.\vec{x} - \omega t\right)-------------(72)$$

where $\hat{\in}$ *and* $\hat{n}$ are the (linear) polarization and propagation directions. Equation (72) obviously satisfies (71) because $\hat{\in}$ is perpendicular to the propagation direction $\hat{n}$. We write

$$\cos\left(\frac{\omega}{c}\hat{n}.x - \omega t\right) = \frac{1}{2}\left[e^{i(\omega/c)\hbar.x - i\omega t} + e^{-i(\omega/c)\hat{n}.x + i\omega t}\right]-----(73)$$

And treat $(e/m_e c)\vec{A}.\vec{P}$ as time dependent potential where we express A in (72) as:

$$A = A_0\, \hat{\in}\left[e^{i(\omega/c)\hat{n}.x - i\omega t} + e^{-(\omega/c)\hat{n}.x + i\omega t}\right]------------(74)$$

Comparing this result with equation (60) we see that the $e^{-i\omega t}$ term in

$$-\left(\frac{e}{m_e c}\right)\vec{A}.\vec{P} = -\left(\frac{e}{m_e c}\right)A_0\, \hat{\in}.\vec{p}\left[e^{i(\omega/c)\hat{n}.x - i\omega t} + e^{-(\omega/c)\hat{n}.x + i\omega t}\right]----------(75)$$

is responsible for absorption, while the $e^{i\omega t}$ term is responsible for stimulated emission

Let us now treat the absorption case in detail

We have

$$\gamma_{ni}^{\dagger} = -\frac{eA_0}{m_e c}\left(e^{i(\omega/c)(\hat{n}.x)}\, \hat{\in}.\vec{p}\right)_{ni}-------(76)$$

and

$$\omega_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2}{m_e^2 c^2}|A_o|^2 \left|\langle n|e^{i(\omega/c)(\hat{n}.x)}\, \hat{\in}.\vec{p}|i\rangle\right|^2 \delta\left(E_n - E_i - \hbar\omega\right)-----------(77)$$

The meaning of the δ-function is clear. If $|n\rangle$ forms a continuum, we simply integrate with $\rho(E_n)$. But even if $|n\rangle$ is discrete because, $|n\rangle$ cannot be a ground state; its energy is not infinitely sharp; there may be a natural broadening due to a finite lifetime, there can also be a mechanism for broadening due to collision. In such cases we regard $\delta\left(\omega-\omega_{ni}\right)\ as:$

$$\delta\left(\omega-\omega_{ni}\right)=\lim_{\gamma\to 0}\left(\frac{\gamma}{2\pi}\right)\frac{1}{\left[\left(\omega-\omega_{ni}\right)^2+\gamma^2/4\right]}----------(78)$$

Finally, the incident electromagnetic wave itself is not perfectly monochromatic. In fact there is always a finite frequency width

We derive an absorption cross section as:

(Energy/unit time) absorbed by the atom (i→n)

Energy flow of the radiation field

For the energy flow (energy per area per unit time) classical electromagnetic theory gives us

$$Cu=\frac{1}{2\pi}\frac{\omega^2}{c}\left|A_o\right|^2-----------(80)$$

$$where\ \ we\ \ have\ \ used$$

$$u=\frac{1}{2}\left(\frac{E_{\max}^2}{8\pi}+\frac{B_{\max}^2}{8\pi}\right)--------(81)$$

$$For\ energy\ density\ (energy\ \ per\ unit\ volume)\ with$$

$$E=-\frac{1}{c}\frac{\partial}{\partial t}A,\quad B=\nabla\times A-------(82)$$

Putting everything together, we get

$$\sigma_{abs}=\frac{\hbar\omega\left(2\pi/\hbar\right)\left(e^2/m_e^2c^2\right)\left|A_0\right|^2\left|\langle n|e^{i(\omega/c)(\hat{n}.\vec{x})}\ \hat{\in}.\vec{p}|i\rangle\right|^2\delta\left(E_n-E_i-\hbar\omega\right)}{\left(1/2\pi\right)\left(\omega^2/c\right)\left|A_0\right|^2}$$

$$=\frac{4\pi^2\hbar}{m_e^2\omega}\left(\frac{e^2}{\hbar c}\right)\left|\langle n|e^{i(\omega/c)(\hat{n}.\vec{x})}\ \hat{\in}.\vec{p}|i\rangle\right|^2\delta\left(E_n-E_i-\hbar\omega\right)----------(83)$$

Equation (83) has the correct dimension $\left[1/\left(M^2/T\right)\right]\left[M^2L^2/T^2\right]T=L^2$. If we recognize that $\alpha\ =e^2/\hbar c\approx 1/137$ and $\delta\left(E_n-E_i-\hbar\omega\right)=\left(1/\hbar\right)\delta\left(\omega_{ni}-\omega\right)$ where $\delta\left(\omega_{ni}-\omega\right)$ has time dimension T.

16.3 Let us sum up:

After studying this unit you will be in a position to understand the time dependent potential, interaction picture, two state problems and the time dependent perturbation, Fermi's golden rule and applications to interactions with classical radiation fields.

16.4: Questions for self study:

1. Discuss briefly the time dependent perturbation theory and derive the expression for the transition probability to a group of states per unit time.
2. Write a short note on Fermi-Golden rule.
3. Derive Fermi-Golden rule for constant perturbation that acts for a short interval of time.
4. Show that the first order effect of the time dependent perturbation, varying sinusoidally in time leads to the emission or absorption of energy.
5. Discuss the application of the time dependent perturbation to the interactions with the classical radiation field with respect to absorption and stimulated emission.
6. Derive the principle of detailed balance starting from the harmonic perturbation.
7. Write a note on Interaction picture of the time dependent potentials.

16.5 References:

1. Modern Quantum Mechanics by J.J.Sakurai
2. Introduction to Quantum Mechanics by D.J.Griffiths
3. Introduction to Quantum Mechanics by ArulDhas