**Introduction**

When we consider the mechanics of the objects which are directly observable or observable with the help of microscope, then classical physics is sufficient. The classical physics is based on the Newtonian mechanics and explain wide variety of phenomena prior to 1900 A.D. It could lead to useful results in kinetic theory of gas. Likewise Young in 1803 and Maxwell in 1864 derived their theory according to classical physics. However, the phenomena in the atomic scale could not be explained by the classical physics, it needs new physics called quantum mechanics. It should not be taken that quantum mechanics generally refer to microscopic world, but not to the macroscopic world. The laws of quantum physics are most general laws of nature.

* 1. **Inadequacy of classical mechanics and introduction of quantum mechanics**

When an electron moves round the nucleus, it is attracted by the positive charge of the nucleus. Hence it is accelerated towards the centre. According to classical physics, the accelerated charged particles loses its energy in the form of electromagnetic waves, therefore its velocity should decrease continuously until it collapses to the nucleus. This shows the instability of atom. No such things would happen, we observe the atoms are stable. Hence classical physics (or classical mechanics) fails to explain the stability of atom.

The classical mechanics also fails to explain the spectrum of hydrogen atom. According to classical theory, an excited atom of hydrogen emit electromagnetic radiations of all wavelengths continuously which should result the continuous spectra of all wavelength. But it is observed only the line spectra of certain wavelengths.

The other difficulties of classical mechanics are :

1. The spectral distribution of thermal radiation from a black body
2. The low-temperature specific heats of solids
3. Appearance of only five degree freedom in the motion of a free diatomic molecules at ordinary temperatures.
   1. **Planck’s idea and Quantum theory of radiation**

**Energy changes takes place discontinuously and discretely as an integral multiple of small unit of energy which is called a quantum.** An harmonic oscillator inside the enclosure absorbs energy from the radiation field and delivers it back to the field in quanta of 0,ε, 2ε,….etc where ε is a quantum of energy given by ε , where ν is frequency of oscillator.

Thus we can summarize the idea as **radiation is not emitted in continuous fashion but in discrete bundles of energy equal to hν. These bundles or packest of radiant energy are called photons**. **Energy of photon is given by E=hν.**

* 1. **De Broglie Hypothesis:**

A moving particle of whatever nature has wave properties associated with it. The wavelength which is associated with any moving particle is given by

Such waves associated with the matter particle is called matter waves or de Broglie waves. De Broglie assumed in the interference and diffraction phenomena, electron also follow wave nature. Thus, according to de-Broglie matter has dual nature i.e. particle as well as wave nature.

**The de Broglie Wavelength**

Energy of a photon is given by . ….. (i)

According to Einstein mass energy relation for photon of mass m,

, where p is the momentum. Hence …. (ii)

From equation (i) and (ii)

…..(iii)

According to de-Broglie, equation (iii) can be applied to a matter particle also. If m be the mass and be the velocity then equation (iii) becomes

……. (iv)

If be the kinetic energy of the particle, then

….(v)

From (iv) and (v)

…. (vi)

If a charge particle carrying charge q is accelerated through a potential difference V volt, then kinetic energy Hence corresponding de-Broglie wavelength

……………. (viii)

* 1. **Group Velocity**

Consider two waves moving along same direction along x axis with same amplitude differ by an amount in an angular frequency and an amount in wave number. They can be represented by two equations:

and

According to superposition principle , the resulting of these waves corresponding to a single wave which is called wave group or wave packets. The velocity with which this wave packet moves is called group velocity. Group velocity can also be understood as follows:

When large number of plane waves with slightly different wavelengths and frequencies travels in a dispersive medium, the observed velocity i.e. velocity with which the maximum amplitude of the group advances in the medium is called group velocity. It is the velocity at which the energy in the group is transmitted through the medium.

Now, the resultant displacement

Since and are small compare to ω and , hence and

. This is the resultant wave due to the superposition of two waves. Here second cosine term is the original wave and coefficient of this term is the amplitude. We can see that the amplitude varies with and t. The variation is called the modulation of the amplitude.

**Group velocity of de wave**

Let ω an K be the angular velocity and wavenumber of the de-Broglie waves associated with a particle of rest mass which is moving with velocity are given by

Or,

x

Or,

Hence group velocity:

.

This implies that wave group associated with moving particle travels with same velocity as of the particle.

**Relation between group velocity ( and wave velocity (or phase velocity):**

*The phase velocity of a monochromatic wave is the velocity at which a definite phase of the wave, such as crest or trough , is moved in a medium.*

We have group velocity, ,where we have used the relation

Or,

Also wave number .

Hence

Or, …. …… (i)

But

So equation (i) becomes

**Postulates of quantum mechanics**

In order to use wave equation and to obtain a quantitative description of matter on the atomic scale or nuclear scale such as the values of linear momentum, angular momentum, energy etc of a micro-particle, we have to formulate the quantum mechanics mathematically. The basic postulates of quantum mechanics are follow:

1. *Any state of a system can be described completely as possible by a wave-function ψ(r,t)*

The wave function depends on the coordinates of all the particles in the system and the time. For a single particle, the wave-function is a function of only of position **r** and time t and is written as ψ(**r, t)**  gives the complete knowledge of the behavior of the particle. Similarly. Ψ(r) gives the stationary state which is independent of time. Quantum mechanics assigns to every system a wave function ψ that contains implicitly everything that can be known about that system. gives the probability of finding a particle in the space with in r and .

1. Every physical observable is associated with a linear Hermitian operator.

The quantum mechanical operator for the total energy is

1. +V (time independent form)
2. (time dependent form)

where is called the Hermitian operator

We will define operators in the latter sections.

**Expectation value**

According to uncertainty principle, when we take measurement of a dynamical quantity say A of a particle for which the wave function is ψ, then we get different values of A during different trials. The most probable value of A is given by

, where is the operator associated with the quantity A , is the complex conjugate of the wave function ψ and is the small volume element. The quantity is called expectation value of the quantity A. If the wave function is not normalized ,then expectation will be:

The expectation value of an observable corresponds to that value which is obtained in the majority of the trials.

* 1. **Compton effect:**

It is an photon electron collision where energy of the photon is transferred to electron. The experiment was carried out by Compton where X-rays were incident on the material of low atomic number. Due this striking ,there is a change in wavelength of the scattered beam along with the change in its direction. So such scattering is also known as incoherent scattering where the wavelength are changed after scattering.

Let h be the energy of the incident photon and momentum be strikes on electron at rest, rest mass energy electron is , If m be the mass of electron and v be the velocity so that momentum of recoiling electron is mv and its equivalent energy is m. Let ϴ and φ be the direction of photon and recoiling electron with respect to original direction, as shown in figure (1.1).

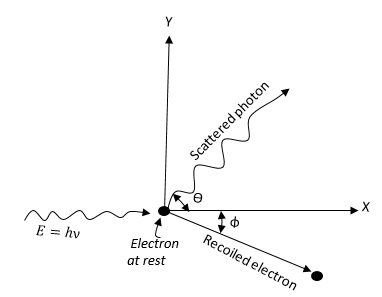
According to principle of conservation of energy:

……… (1)

Applying principle of conservation of momentum along x and y direction:

…. (2) along x direction

……… (3) along y direction

 From (2) , ….. (4)

From (3) ……………. (5)

Squaring and adding (4) and (5)

Or, …… (6)

From equation (1),

……. (7)

Subtracting (6) from (7)

Figure 1.1: Collision of photon with electron

……. (8)

Now, .

Or,

Or,

Or , ………. (9)

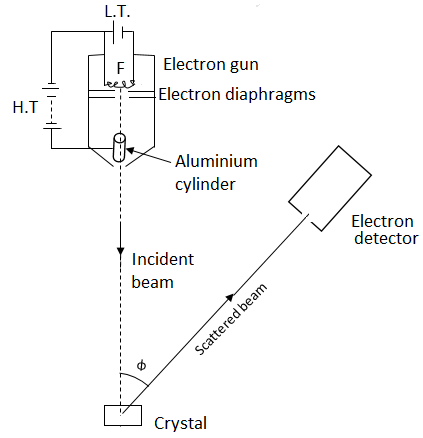
From (8) and (9) we get :

Or,

Or,

Or,

Figure 1.2: Experimental arrangement, showing diffraction of electron



**n**Or, ……. (10)

This is change in wavelength . The equation shows that change in wavelength depends only on the scattering angle ϴ, not with the nature of the scattering substance and wavelength of the incident radiations.

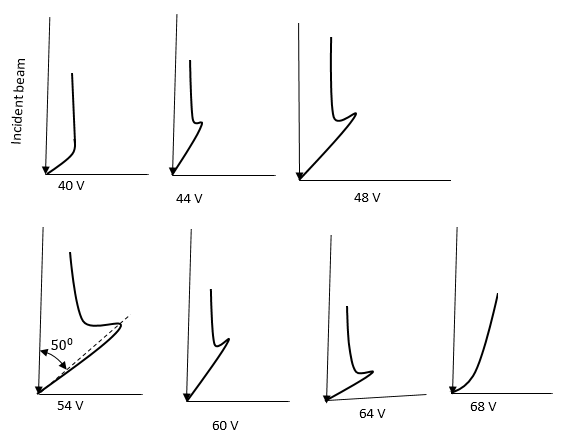
Cases:

1. When
2. When
3. When , which is maximum.

**Davisson and Germer’s experiment**

Diffraction is such phenomena which is possible only for wave . Davission and Germer’s experiment shows that electrons while diffracted through a crystal , behave as X-ray. This proves the wave nature of particle i.e. existence of de-Broglie wave.

**Experimental arrangement:**

Electrons are produced by heating filament(F) by a low tension battery . These electrons are accelerated through a potential difference V in the electron gun. The electron beam then falls normally on a large single crystal of nickel. The electrons are scattered in all directions by the atoms in the crystal. The detector receives the scattered electrons since it can be moved to any angle φ relative to the incident beam. The intensity of diffracted beam is plotted against the various angle φ. The method of plotting the curve is such that the intensity at any angle is proportional to the distance of the curve at that angle from the point of scattering. ****The observations are repeated for different accelerating voltages and the various curves are drawn.

The typical curves for electron intensity are shown in figure 1.3. The following are the conclusions drawn from the graphs:

Figure 1.3: different graphs showing the intensity curve

1. The graph remains fairly smooth till the accelerating voltage becomes 44 V when a spur (or bump) appears on the curve.
2. As the accelerating voltage is increased , the length of the spur increases.
3. The spur becomes maximum in the curve for 54 V at
4. As the accelerating voltage is further increased, the spur decreases in length and disappears finally at 68 V.

The reason of pronounced spur at with the accelerating voltage 54 V is the constructive interference of electron waves ,i.e. electron behaves as wave at that time, which are scattered towards the detector from regularly spaced planes in crystals of nickel.

**Calculation of Observed Wavelength**

According to de-Broglie’s theory, electron , when it behaves as a wave, its wavelength when accelerated through p.d. 54 V is

For electron, m= 9.1 and , h

, which is theoretical value.

Now we have scattered beam at angle of 500 , p.d. of 54V, we get constructive interference. For nickel target, for (111) reflecting plane

Applying the equation for plane reflecting grating:

d ,where n=1 for the first order, we get

= λ

, which is experimental value.

Thus, the experimental value is in close agreement with the theoretical value, which shows that the beam of electrons behaves like X-rays, gets diffraction at reflecting surfaces and has the wave like properties.

**Derivation of time – dependent form of Schrodinger equation**

The quantity that characterizes the de-Broglie waves is called the wave function. It is denoted by ψ. It may be a complex function. Let us assume that ψ is specified in the x direction by

………. (1)

[We can also take ]

Let f be the frequency , then and .

………… (2)

Let E be the total energy and p be the momentum of the particle, then and . Making these substitution

……………. (3)

Equation (3) is a mathematical description of the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the +x direction.

Differentiating equation (3) twice with respect to x

…………. (4)

Differentiating equation (3) with respect to t, we get

……………. (5)

At speed

Total energy ……… (6)

where V is the potential energy function of position x and time t.

Multiplying (6) by ψ

………… (7)

From equation (5) and (4)

……… (8)

……… (9)

Substituting (8) and (9) in equation (7)

Or, ….. (10)

Equation (10) is the time-dependent form of Schrodinger equation.

In three dimension,

**Schrodinger’s equation : Steady – state form**

When the force and hence V vary with the position particle only; then Schrodinger’s equation may be simplified by removing all reference to t

The one-dimensional wave function ψ of an unrestricted particle may be written as:

Or, …………..(1)

, where . …..(2)

Which shows that ψ is the product of a position dependent function and time dependent function

Differentiating equation (1) with respect to t:

…………. (3)

Differentiating equation (1) twice with respect to x ,we get :

…….. (4)

We have time dependent form of Schrodinger’s equation:

, . From equation (2) and (3) we get:

Or,

Or,

Or, ……… (5)

Equation (4) is the steady state form of Schrodinger’s equation, also called time independent form of equation.

In three dimension:

In general,

**Wave function**

The probability that a particle will be found at a given place in space at a given instant of time is characterize by the function This function can be either real or complex. The only quantity having a physical meaning is the square of its magnitude , where is the complex conjugate of ψ. The quantity P is the probability density. The probability of finding a particle in a volume is Further since the particle is found certainly somewhere in space,

……… (1)

The wave function satisfying equation (1) is called normalized wave function.

If for the interval are said to be orthogonal in the interval (a, b), while for wave function ψ,

and again for the whole volume V.

**Eigen functions and Eigen values**

Schrodinger’s time-independent equation is an example of a type of differential equation called an Eigen-value equation. In general

Where the function ψ is called Eigen-function of the operator , f is called Eigen- value.

**Equation of motion**

The time dependence of ψ is given by Schrodinger’s time dependent equation for a particle,

………. (1)

Where is the Hamiltonian operator.

Complex Conjugate of (1)

……. (2)

The expectation value of any observable associated with an operator in normalized state ψ is

………… (3). Taking derivation of equation (3) with respect to time

……….. (4)

From equation (1)

From equation (2)

Using these equations , (4) becomes:

Or, …………. (5)

As is Hermitian operator

………….. (6)

Or, ……………….. (7)

Here is called commutator of and .

Thus the rate of change of the expectation value of any dynamical variable A may be obtained as expectation value of

If the operator does not depend on time explicitly , then ……. (8)

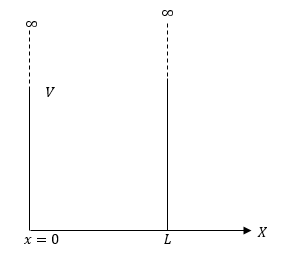
Equation (7) and (8) are called equation of motion in quantum mechanics. If then equation (8) becomes

Thus if the operator associated with a certain dynamical variable of the system commutes with the Hamiltonian of the system and does not depend up on time explicitly, then the dynamical variable called a constant of motion.

**Some application of Schrodinger wave equation**

1. **The particle in a box (infinite Square well potential):** Consider a particle moving inside a box along the x- direction. The particle is reflecting back and forth between the walls of the box. The box has infinite height at and , figure 1.4. The particle has a mass m and its position x at any instant is given by . The potential energy V of the particle is infinite on both sides of the box. The potential energy is zero between The boundary conditions imposed by the problem are:

is zero for since particle can not remain out side the box. Within the box , Schrodinger wave equation’s becomes



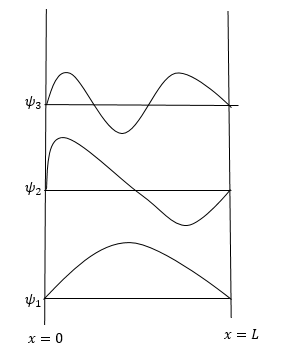


Figure 1.5

, where …..(\*)

The general solution of this equation is given by

……….. (1)

The boundary conditions are at and .

Since M where n is an integer , …..(\*\*)

Figure 1.4

……….. (2)

The energy of the particle [∵from (\*) and (\*\*)]

Or, ………….. (3)

For each value of n, there is an wave function given by equation (2). Each value of is called an eigen value and corresponding is called eigen function. Hence the energy values inside the box are discrete given by equation (3).

**Wave function**

hnyiyl.,The wave function corresponding to the particle inside the box is given by equation (2) after calculation of normalization constant M. Since particle can be found somewhere inside the box, hence

Or,

Or, 1

Or,

Hence the normalized wave function for the particle is given by

. The plot of this function for n=1 , n=2 and n=3 is shown in figure 1.5.

**Potential Step**

The potential function of a potential step is defined by

for

Suppose an electron of energy E move from left to right along positive direction of x axis . The time independent Schrodinger wave equation is

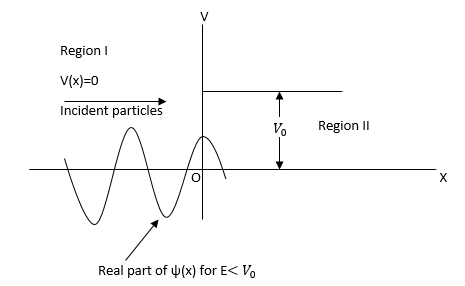


Figure 1.6

………………. (2)

For I region , we have Hence

……….. (3)

The solution of equation (3) is

……….(4) , where , A and B are constants. The first and second terms represents respectively incident and reflected particles. Schrodinger wave equation for II region is

………….. (4)

The solution of equation (4) is

……….(5)

Where , C and D are constant. The first term represents the transmitted wave, second terms represent a wave coming from + direction. Since for no particles can flow to left and D must be zero. So equation (5) becomes

……….. (6)

The continuity of ψ implies that at So from equation (4) and (5)

……… (7)

The continuity of implies

Hence

…………(8)

………….. (9)

Solving (7) and (9) we get

Or,

…………. (10)

Putting this value in equation (7) we get

Or, …………..(11)

Here B and C represents the amplitudes of reflected and transmitted beams respectively in terms of the amplitude of the incident wave. Now we can define

Reflectance R

Transmittance T

Two cases may arises:

1. (ii) E

Case (i) , is real. To find the value of T and R , we now derive the expression for current density in the II regions. The probability current is defined as

……….. (12)

; other terms are cancelled out.

……. (13)

Hence current in I region is equal to the difference between two terms incident wave and reflected wave

The probability current of incident beam …………. (14)

The probability current of the reflected beam ………..(15)

The expression for the probability current region II is

……. (16)

Equation (16) represents the transmitted current. The reflectance

, from equation (14) and (15) , we have

, from equation (10) we get

Also transmittance, .

From equation (16) and (14) we get:

, from equation (11) we get

Or,

**Case (ii)**  When E , is imaginary .

Hence and

The probability current in this case is given by

Substituting , we get

Thus the transmitted current is zero.

But the sum of transmittance and reflectance is one i.e.

**Barrier penetration problem**

Consider a beam of particles of kinetic energy E incident from left on a potential barrier of height V and width such that barrier height (V) is greater than the energy of the particle i.e. . On both side of the barrier, potential is . Hence potential is described as

(region II)

(region III) …………………… (1)

Let , and are the respective wave functions in regions I, II and III as indicated in the figure 1.7.

The corresponding Schrodinger equations are

For region I

For region II

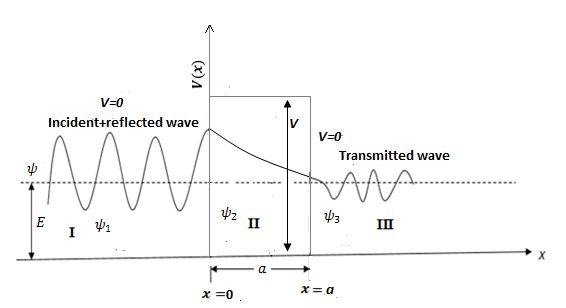
For region III

……………..(3)

Put and

Then the equations become

(Region I)



**Figure 1.7**

(Region II)

(Region III) ……………. (4)

The solutions are

(Region I)

(Region II)

(Region III)

………(4)

Where A is the amplitude of the wave incident on the barrier from the left; B is the amplitude of the reflected wave in region I; F is the amplitude of the wave, penetrating the barrier in region II; G is the amplitude of the reflected wave from the surface at in region II; C is the amplitude of the transmitted wave in region III and D is the amplitude of nonexistent reflected wave in region III, so putting D equal to zero we get the second equation in region III.

Since the probability density associated with a wave function is proportional to the square of the amplitude of the function, the barrier transmission coefficient and reflection coefficient at is

. In order to find out T and R , we have to apply boundary conditions:

…………. (5)

Or, …… (6)

At

⇨ F ………. (7)

And

………… (8)

Solving equations (7) from (8) (putting the value of G from equation (7) in equation (8)

Or,

Or,

Or, ………..(9)

………..(10)

Adding equation (5) and (6)

2A

Putting values of F and G from equations (9) and (10) we get

Or,

Or,

Or,

Or,

Or,

Or,

Or,

Or,

Or,

Or,

Or,

[∵]

Or,

Or,

Now , barrier transmission coefficient

…….(11)

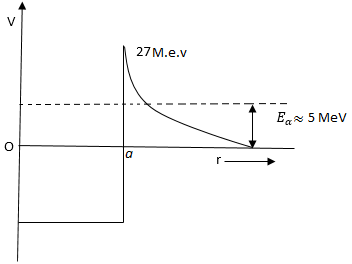
Now,

and

If is large, then

Then

**Figure 1.8**



…… (12)

The ratio is also called the “penetrability” of the barrier. It represents the probability that a particle incident on the barrier from one side will appear on the other side. In classical mechanics, such probability is zero since energy of the particle E is less than the barrier height V. But we have seen that there is a finite probability even small in quantum mechanics (equation 12). We can thus conclude that if a particle of energy E is incident on thin energy barrier of height V such that E, there is a finite probability of the particle penetrating the barrier. This phenomenon is called the tunnel effect. We will discuss this on the next § Gamow theory of α decay.

**Radioactive emission of particles: Gamow theory of α-decay**

α particle is identical with Helium nucleus and α decay is the process in which a nucleus loses an α particle and is converted into another nucleus with charge number less by two and mass number less by four. In general

, where is the parent nucleus losing α particle converting in to daughter nuclei , A and Z be the mass number and atomic number respectively.

From Rutherford’s scattering experiment , it was found that the force experienced by the α particle is a coulomb force down to a very small distance i.e. , from the centre of nucleus then coulomb force does not exist below this distance i.e. inside the nucleus (, where is radius of nucleus , figure 1.8 . There is strong nucleus attractive force inside.

Taking the radius of the radium nucleus to be , the Coulomb potential energy of an α particle outside the nucleus is 27.8 MeV. However, in the radioactive decay of radium, the α particle has an energy equal to 4.88 MeV. Now the question arises how it is possible for the α particle of 4.88 MeV energy go through a potential barrier of 27.8 MeV.

The difficulties of classical mechanics disappear in quantum mechanics. According to quantum mechanics, an electrostatic barrier though very high, can not completely reject the passage of wave through it. In quantum mechanics, a moving particle is regarded as a wave. Hence there is always certain probability of the particle penetrating through the barrier , however small energy may contain with it. The transmission coefficient T for ( see equation (12) will be . This explains why there is transmission of α-particle.

**Boundary conditions at the surface of infinite potentials (Infinite potential barrier)**

Consider a particle is moving from left to right in a region where potential is zero and after certain time , it reached to the region where potential becomes infinite as shown in figure below. The Schrodinger wave equation is

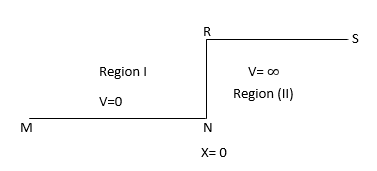


Figure 1.9

For the first region,

……… (1)

Or, , where

The general solution of equation (1) for x is

…….. (2)

The Schrodinger equation for the second region is

Or,

Or, …… (3) , where

The general solution of equation (3) is

……… (4)

For first term . So we have only second term which is well behaved part so

………….. (5)

The solution of equation (2) and (5) should be continuous as i.e. should be same as at .

Hence implies

…………… (6)

Similarly

⇨ …….(7)

From equation (7) we can see that as and B can not be infinite . Hence D should be zero.

which implies .

Thus at the surface of infinite potential, the wave function is zero.

The essential conditions that a physical meaningful solution or wave function ψ must satisfy are

1. must be finite.
2. must be continuous and single value
3. must be continuous and finite.

Linear Harmonic Oscillator

The one dimensional motion of a point mass attracted to a fixed centre by a force that is proportional to the displacement from that centre is called linear harmonic oscillator. It has great importance for the quantum mechanical treatment of the problems like vibrations of individual atoms in molecules and in crystals. The vibrations of electromagnetic field in a cavity can also be analyzed as the harmonic oscillator problem. Many complicated problems can be studied in terms of harmonic oscillator problem. It is one of the simplest problems for which discrete energy levels are obtained.

**Asymptotic behavior**

The force implies the potential energy in the linear harmonic oscillator

…………. (1)

Therefore Schrodinger equation in one dimension is

…….. (2)

To write it in dimensionless form, introduce a dimensionless independent variable μ . Then

and

Hence equation (2)becomes

……(3)

Let us choose ∝ such that or .

Also let, ……. (\*)

Hence equation (3) assumes the dimension form

…………. (4)

…………… (5)

where is a polynomial of finite order in μ. From equation (5)

in equation (4) we get:

Or,

Or, ………… (6)

**Energy levels**

We solve equation (6) using the power series method:

………… (7), where

…………. (7)

Or,

Substituting these values in equation (6)

……….. (8)

i.e. H(μ) to be solution of equation (6) , the coefficient of individual powers of μ must vanish separately i.e. equating to zero, the coefficients of various power of μ we get:

………………………………………………………………

…………………………………………………………………

………….. (9)

This gives

…………….. (10)

i.e implies that .

For arbitrary values of the energy parameter λ, the above series consists of infinite number of terms and does not corresponds to satisfactory wave function. For coefficient of the higher terms, i.e. as , equation (10) is

as . This ratio is same as that of the series as follows:

Here

Or, .

Thus behaves approximately as and the product will behave as in this region, thus making ψ(μ) unacceptable as a wave function for large . Thus the series (7) must terminate . This means that in equation λ must be equal to for the series to be terminated. Hence

, where 2r is an even integer, the index S be either 0 or 1 which implies λ is equal to . We can express both case in terms of a quantum number n such that

. From equation (\*) we get:

Or, ……. (11) ,where is the classical angular frequency of the oscillator.

**Zero Point energy** The energy levels given by equation (11) are discrete and have equal spacing, which is in agreement with the quantization rules of old quantum theory. When the finite value of ground state energy is . This is zero point energy The five lowest energy levels of a linear harmonic oscillator are shown in figure. It is seen that even in the lowest state, its energy greater than if it would have when it was at rest in its equilibrium position. The zero point energy is characteristic of quantum mechanics and is related to uncertainty principle.

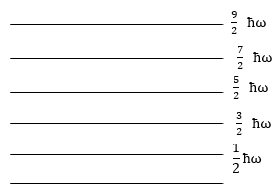


Figure 1.2 Energy level diagram of a linear harmonic oscillator

**Hermite Polynomial**

Since , equation (6) becomes

……… (12)

Hermite polynomials. To study the detailed properties of , we express in terms of generating function .

………… (13)

To show that satisfies that differential equations (12), we differentiate both sides of equation (13) first with respect to μ and then with respect to S.

From equation (13)

….. (14)

Or, …. (15)

From equation (14) and (15) equating equal powers of S on both side:

Replacing n by n-1 in equation (14) we get:

…………… (16)

From equation (15)

Or,

Or, ……... (17)

Differentiating equation (16) and (17) with respect to μ

Adding these two we get:

…… (18)

, putting

. Hence equation (18) becomes

Thus satisfies equation (12), so are hermite polynomials. For the function of the form , it is apparent that

hermite polynomial’s expression:

……… (19)

Putting , We obtain

Similarly

and and so on.

**Hermite Oscillator wave functions**

We have differential equation of linear harmonic oscillator

,where . The solution of this equation is given by

. The general solution is then

……..(20)

is called a normalization constant. To obtain the value of the constant, we start from the generating function

 Multiply both side by and then integrate with respect to μ from we get:

…………. (21)

Considering only left side

Or,

Now equation (21) becomes

…………… (23)

If equal powers of are equated in this series:

, If .

…....(#)

But, , if

By normalizing condition,

If we replace . we have normalization condition

, where we have used the wave function

Or, .

Hence using conditions (#) we get

Which gives

Hence equation (20) becomes

……… (23)

And from the second normalization constant we get:

….. (24)

where the value of ,where , f be the classical frequency of the oscillator with ω be its angular frequency, m be

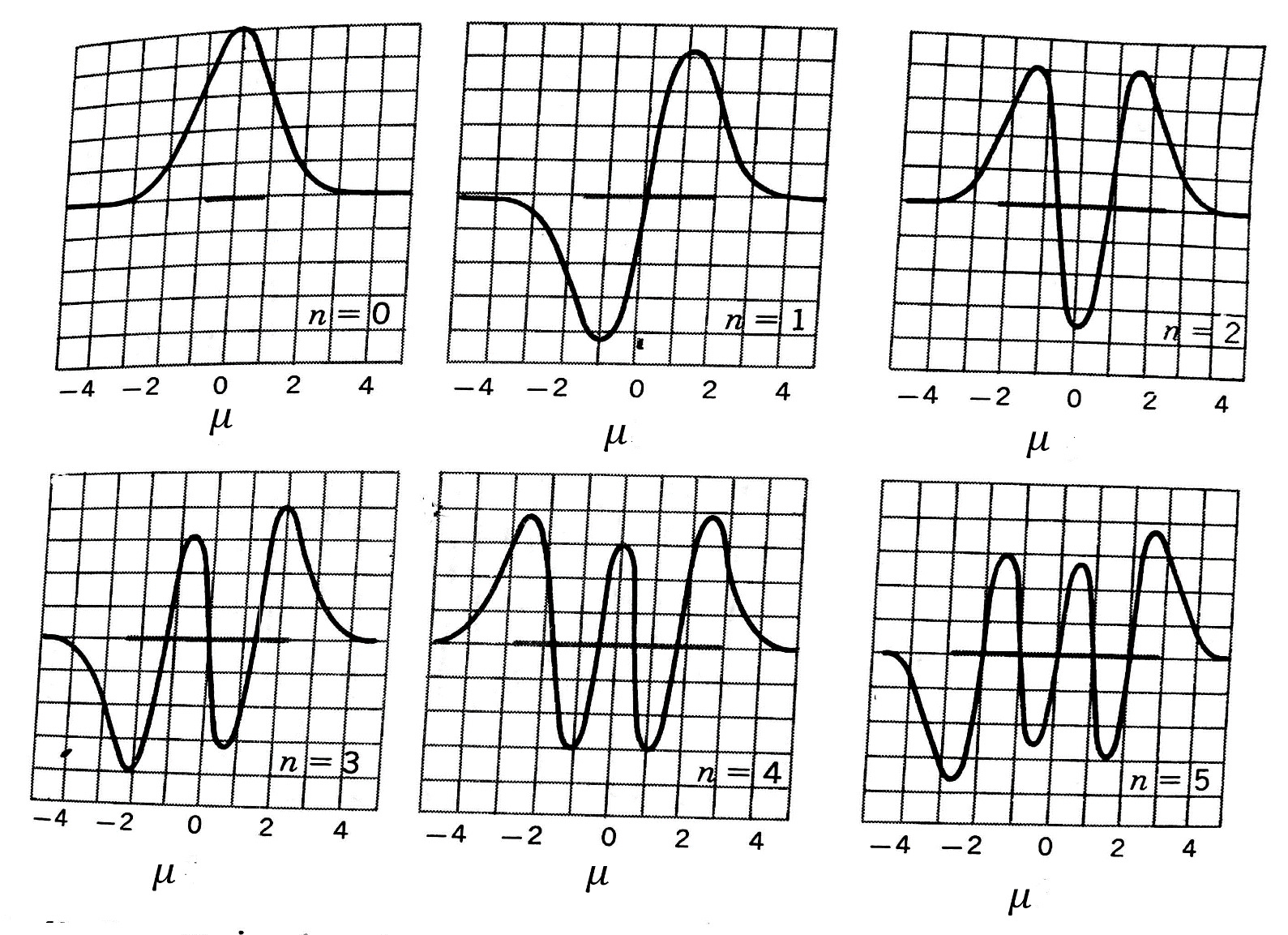


Figure 1.3 Figure 1.3: energy eigenstates for the first six states of the harmonic oscillator

*Source :* (Shiff, 1968)

the mass. .

Equation (23) and (24) give the nth wave function of linear harmonic oscillator.

**Physical interpretation of wave functions:**

Plots of first six harmonic-oscillator wave functions are shown in figure 1.3. The position probabilities densities associtated with these stationary wave functions do have little similarities to the corresponding densities for the classical harmonic oscillator. The probabilities densities for classical harmonic oscillator are proportional to is the amplitude of the classical oscillator . The agreement of classical with quantum probability densities occurs rapidly with increasing Figure 1.4 shows a plot of for where the dashed curve is for a classical harmonic oscillator of same total energy. The agreement between classical and quantum oscillator is somewhat good , on average , the principal discrepancy is the rapid oscillations in .

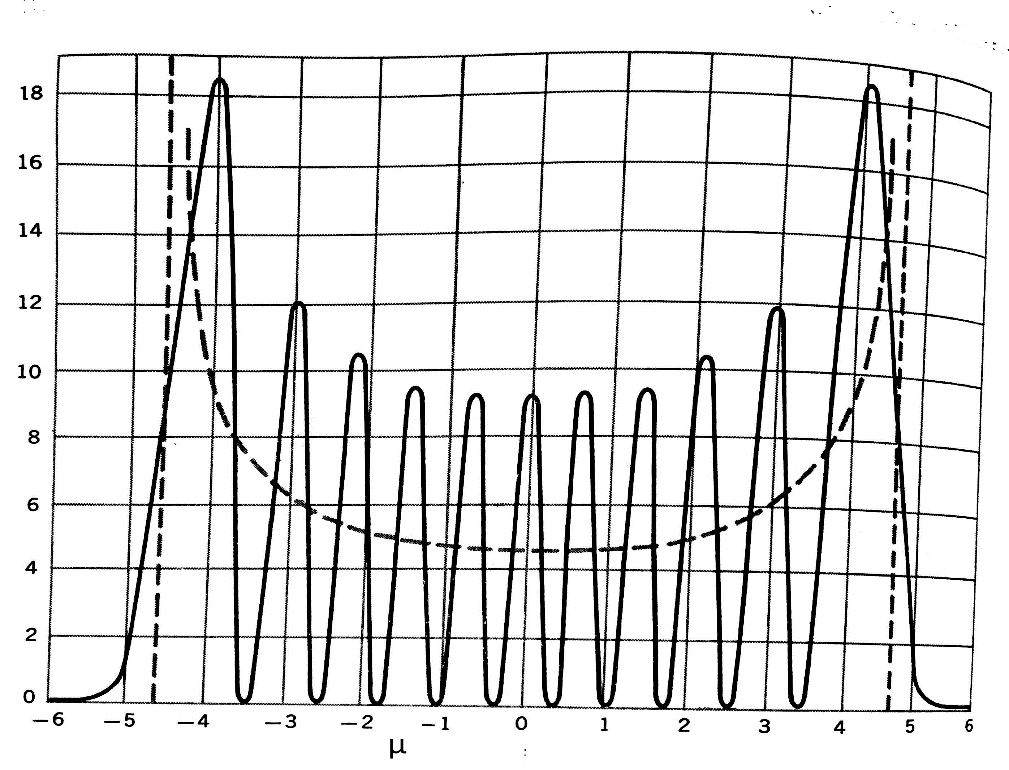


Figure 1.4: The position probability density for the state of a harmonic oscillator.

*Source :* (Shiff, 1968)

Hydrogen atom

In an hydrogen atom, there are two particles, nucleus and electron which are attracted with each other by a force called coulomb force and corresponding potential energy , r is the distance between nucleus and electron. For hydrogen atom while for singly charged helium ion, . Here , we use the method employed by Leonard I. Shiff[[1]](#footnote-1)

**Reduced mass: Reduction to equivalent one body problem:**

The Schrodinger wave equation for two particles of masses and is

…… (1)

Where are the Cartesian coordinates of and so on , T which signify total is written with E and ψ to indicate that these quantities refer to the complete system.

Now we define relative coordinates and and coordinates of the centre of mass X,Y and Z through

*, ,* and

MX , , where M be the total mass of the system. As the potential depends on the relative coordinates of two particles i.e. .

It can be shown that[[2]](#footnote-2)

….. (2)

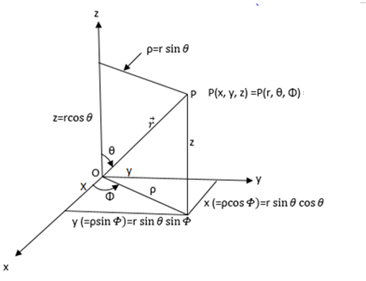
Where be the reduced mass of the system. Now we can define a equation

, where is the energy of the translation of centre of mass and E be the energy of interaction. Putting in equation (1) and using equation (2) we get:

…… (3)

This results two separate equations:

Figure1.5 The relation between rectangular and spherical polar coordinates of point P.



….. (4) and

……. (5)

Equation (4) applies to the translation of the centre of mass of the system. It gives the solution like that of a free particle of mass M and we are not going to consider it further. Equation (5) relates with the internal motion and contains potential energy term. Hence we take only equation (5) which can be written as :

Again, in spherical polar coordinates (figure 1.5)

The expression of in spherical polar coordinates is

Hence Schrodinger wave equation with spherically symmetric potential can be written in the spherical coordinate as

……. (6)

Putting this in equation (6) and multiply by and divide by we get:

…….. (7)

Second terms depends on and rest independent of φ. Hence the second terms should be equal to a constant say Hence

Or, ……………. (8)

Hence equation (8) becomes

……….(9)

Here first and fourth terms of this equation depend only on and second and third term only on . Therefore each part must be equal to a constant i.e.

So that we have,

………. (10)

And ………. (11)

Equation (8) , (10) and (11) are known as equations respectively. The complete solution of equation (6) depends on the solution of (8), (10) and (11).

**Solution of r equation or the radial equation**

Putting we get:

Now we introduce a dimensional independent variable or

Or, .

Putting these in the equation we get:

………. (12)

where for bound states i.e. .

…….. (13)

Choosing such that

i.e. ………… (13) (a)

Or, ………. (13)(b)

……… (14)

For large , the equation (14) has the form:

……….. (15)

The solution of equation (15) are:

and R…….. (16).

Only the second solution is satisfactory(vanishing for . The exact solution of equation (14) is of the form:

………….. (17)

where F(ξ) is the polynomial of finite order in . From equation (17):

Substituting this value in equation (14) we get

Since is not zero, the expression with in the square brackets is zero:

……….. (18)

Let …….. (18)\*

Then

L

. Then equation (18) becomes:

⇨ L=0 …….. (19)

Let L(ξ) . Then

………. (20)

From equation (20), putting the values of F(ξ), and in equation (18) we get:

Or,

Or, ……. (21)

Equating to zero, the coefficients of in equation (21) we get:

Since , equation (21) will be satisfied only when coefficient of is zero i.e.

Or,

This quadratic equation in s has two roots and . The boundary condition that be finite at requires we have to choose

Comparing now the coefficients of (putting we write:

……… (22)

If the series does not terminate , its dominant asymptotic behavior can be inferred from the coefficients of its higher terms:

This ration is the same as that of the series for with any finite value of n. Hence from equation (18)\* and from equation (17) we can see that behavior for L violates the boundary condition of R for large ξ, R should be zero for large ξ. H will diverge as which is physically unacceptable.

Hence the series must breakoff after finite number of terms, i.e. and higher terms are zero ,where highest power of ξ in L is This condition requires in equation (22) that :

. Putting

, where

Replacing by integer which is called the total quantum number. Hence

Since and can take on positive integer or zero values, n can have values 1,2…..

We have already consider in equation (13b) that

Or,

Replacing by n we get:

.

But .

Hence

…….. (23)

This energy value is in completely agreement with the old quantum theory and with experiment. Unlike the square well potential problem, the coulomb field problem yields to an infinite number of discrete energy levels extending from up to zero , for any finite value of z. This is due to the slow decrease in magnitude of the coulomb potential at large

The expression (23) is the energy of an atomic state of a hydrogen like atom which depend only on . But we have

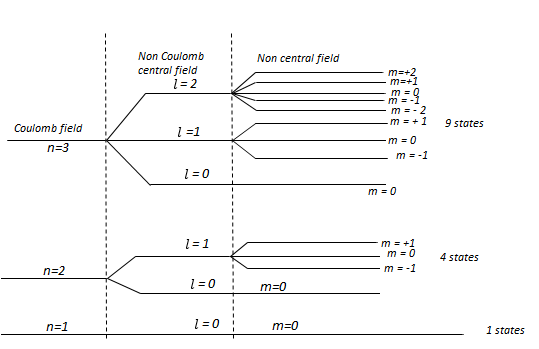


Figure 1.6: Different Eigen states of hydrogen or hydrogen like atoms.

, which implies that the given is satisfied for several combination of and implying that there are several possible wave functions for a given energy value i.e. for n fixed. When this occurs , the state is said to be degenerate . This is true for every value of

Since for each value of can vary from , and for each of these values, can vary from to . Hence the total degeneracy of the energy level is given by:

.

For

Hence we have only one state

For

For Figure 1.6 shows the different Eigen-states for hydrogen like atoms.

Now we derive the radial wave function.

From equation (19) we get:

Putting and replacing by we get;

………. (24)

Comparing it with the associated Laguerre equation :

We obtain ,

Hence we get the solution of r-equation as follows:

From equation (17)

and from equation (18)\* with . But is here ,we have seen that , it is associated Laguerre polynomial which is the required solution. Hence equation (17) now becomes

Putting the value of p and q we get:

………… (25)

Where N is the normalization constant which can be evaluated as

,where factor being included to convert the length into volume element.

Put Hence equation (25) now becomes:

………..

Hence equation (25) becomes

……. (26)

**Solution for equation:**

We have ϴ equation :

Put

Then

Or, ………..26 (a)

Or,

……….. 26 (b)

Writing equation 26 (a) and 26 (b) in equation:

……….. (27)

If , then

……….. (28)

Comparison of this equation with associated Legendre equation

: gives the solution, of equation (28) as

Where A is normalization constant, which is evaluated by normalizing Θ.

……….. (30)

Thus the solution is

……….. (31)

With

And

**Solution of**

The equation is

,

This is a second order differential equation whose solution is given by:

……… (32)

Where B is a arbitrary constant. The constant may be evaluated by normalizing i.e.

……. (33)

The function is single value function, which demands that

Or,

Or, ……… (34)

Equation (34) holds goods when we take Thus we can write

……..(35), where

The quantity is called the magnetic quantum number which possesses the integral nature.

**The radial and total wave function**

From equation 13 (a)

and putting the value of from equation (23) we get:

=

, where is the radius of first Bohr orbit.

Hence radial wave function from (25) and we get:

…… (36)

From equation (31), (35) and (36) , the complete solution of Schrodinger equation for a hydrogen like atoms is written as:

Or,

Or, …… (37), where subscripts has been written with total wave function to indicate that the wave function involves the quantum number

**The normal state of hydrogen atom**

For the ground state Hence the wave function becomes , from equation (37) we get:

Also, the radial wave function are obtained as:

**Ehrenfest’s theorem**

The classical equations are given by

and , where is the potential energy function.

These equations are the another form of Newton’s law of motion and are also valid in quantum mechanics provided we replace all the classical quantities by expectation values of their corresponding quantum mechanical operators. This is the concept of Ehrenfest’s theorem.

**Statement:**

It states that *the average motion of a wave packet agrees with motion of corresponding classical particle[[3]](#footnote-3).* Mathematically:

, where be the average values of position and momentum coordinates, V be the potential energy and m be the mass of the particle.

We can derive the Newton’s second law of motion from Schrodinger wave equation as follows.

Let be the position coordinate of mass m at time t. The rate of change of average value of position coordinate is calculated as

……. (i)

Time dependent Schrodinger equation is

…….. (ii)

Complex conjugate of time-dependent Schrodinger equation is:

Or,

Substituting the values of and in equation (i) we get:

…… (2)

The second integral can be integrated by:

…………. (3)

From Gauss-divergence theorem, we can transform first term in to an integral over a surface at infinity:

, where n denotes that the integral is taken over normal component of over the bounding surface S which goes up to infinity. The reason that vanishes at infinity :

Hence equation (3) becomes :

.

Again the first term vanishes according to Gauss divergence theorem as Hence we get:

………… (4)

Using equation (4), equation (2) can be written as

Or,

Similarly

And

Combining all components,

……. (5)

The time rate of change of X-component of momentum is given by:

Or,

From Gauss divergence theorem, second term is zero at great distance i.e. ψ is zero at .

s

. But

Hence we get: .

Similarly and .

Combining all of these equations, we get: .

In this way derive the second law motion from solving Schrodinger wave equation i.e. we use concept of quantum mechanics to get the second law of motion which is the classical concept.

**The Uncertainty Principle** When we go through the classical physics, the dynamical variable like position coordinates, components of momenta can be measured accurately at any time, with any arbitrary precision. The pairs like momentum and position, energy and time are called conjugate pairs. A careful behavior of the microphysical system like atoms, electrons, ions etc shows that the measurement of such pairs at a time , simultaneously is not possible with high degree of accuracy. There is always uncertainty in the measurement. The uncertainty relations between such pairs are derived by W.Heisenberg in 1927 and are known as uncertainty relations.

According to Heisenberg , there is always uncertainty in measuring simultaneously both the variables of a conjugate pair at a time. If be the uncertainty in position and momentum of the measurement then we have uncertainty relations

…………. (i) for position and momentum and for energy and time it is

, where ћ is called Planck’s constant.

Relations (i) and (ii) are called the Heisenberg’s uncertainty relations for pairs position-momentum and energy-time.

In quantum mechanics, a particle is described by a wave-packet and the uncertainty relations can be proved quantum mechanically. Here for one-dimensional wave- packet , the relation is according to the method employed by Powell[[4]](#footnote-4)

The uncertainty in position of a particle along X axis is defined by the relation

…………. (1)

where is the expectation value of . Since gives the probability that the position of a particle lies between Then average or expectation of is defined by the relation:

…. (2)

Similarly the uncertainty in momentum is given by

…… (3)

where expectation of the momentum is given by:

………. (4)

We present the proof for a wave function for which Then we can generalize the statement for functions with finite . To obtain the Heisenberg’s result , we consider the integral

. Integration by parts results:

, where we use

Since for , results first term is zero. Hence, we get

Or,

.

For normalized wave function ψ, we get . Hence we get

Equating the imaginary parts of both sides and then squaring the modulus of both the sides, we get[[5]](#footnote-5)

4 …… (5)

It is known that the magnitude of imaginary part of any complex number can never be greater than the magnitude of the number itself, hence

Hence equation (5) can be written as :

…….. (6)

Using Schwarz’s inequality[[6]](#footnote-6) , we get

.

Hence equation (6) can be written as:

Or,

Or, …… (7) where we used

Since we have assumed that , the equations (1) and (3) becomes:

……. (8) . Now using equation (7) and (8) we get:

Or, , which is the mathematical expression of Heisenberg’s uncertainty principle.

**Operator**

The minimum uncertainty with which two conjugate pairs of physical quantities can be measured is given by

for position and momentum and when we take energy and time , then we get:

where symbols have their usual meanings.

Due to this kind of uncertainty, physical variables in quantum theory are given in terms of their average values or probable values. The average of physical quantities can be determined with the help of suitable algebraic operators. When the operator operates on proper types of wave function, it gives the eigen value of the operator.

Any mathematical operation, differentiation, integration, division, multiplication, addition, subtraction etc can be represented by certain symbols known as operators.

Mathematically

When a operator operates on a function f(x), it changes in to another function g(x).

We now define linear operator, Hermitian operator and simultaneous Eigen functions as follows:

1. **Linear Operator:**  An operator is one which transforms one function in to another. For example, del operator (, differerential operator D etc.

An operator π is said to be linear if

and , where and are arbitrary functions, is a constant.

**Commutator :** Suppose A and B are two quantum operators. The commutators of these two operators is defined to be

. The two operators A and B are said to commute with each other when . If two operators commute then it is possible to measure both the variables associated with them simultaneously and accurately that means there is no uncertainty in measurement of either of them. While if two operators do not commute, converse would occur i.e. it is not possible to measure the variables associated with them accurately and simultaneously.

1. **Hermitian operator:** An operator D operating on any two functions is Hermitian if only if

.

linear combination of Hermitian operators itself be a Hermitian operator.

**Example 1: Prove that the eigen values of Hermitian operators are real**.

Proof: Let the Hermitian operator be D and , an eigen function belongings to the eigen value then eigen value equation:

………… (i)

………….(ii)

…….(iii)

As the operator is Hermitian

………(iv)

From (ii) and (iii) , equation (iv) becomes

Or,

Since

Or,

Hence eigen value is real.

**Orthogonal and Orthonormal functions**

Consider wave functions and . Then and are said to be mutually orthogonal in the interval if

, where . Now for a wave function ψ(), if the condition

, is satisfied then the wave function ψ(is said to be normalized in the interval (a, b). The functions which are orthogonal and also normalized are called orthonormal functions.

**Prove that any two eigen functions of a Hermitian operator belonging to different eigen values are orthogonal**

**Proof:** Let the Hermitian operator be D. Let the eigen-function be and with corresponding eigen values and . Hence eigen value equations are :

………(1)

and ………(2)

From equation (1)

………. (3)

But

[∵ D is a Hermitian operator]

……… (4)

From (3) and (4)

Or,

Or,

As , which means are orthogonal.

1. **Simultaneous Eigen functions; commutators**

If C and D are linear operators and ψ is a function satisfying both the equations

and …………… (1) , then ψ is a simultaneous eigen function of C and D , belonging to the Eigen values α and β, respectively.

if two if function ψ is simultaneous eigen function of the operator C and D, then it is also necessary that C and D must commute.

For example, let us take a non-relativistic free particle of energy and momentum The wave function

…………………… (2)

Satisfies simultaneous the equations

and .

Here is the Hamiltonian operator for a free particle.

Subtracting …….(3)

This equation shows that ψ is also an Eigen function of the operator , corresponding to the Eigen value zero. The equation (3) is necessary in order that ψ be a simultaneous Eigen function of C and D. Equation (3) is called the commutator of C and D and is written as

…………. (4)

Two operators satisfying the equation

, are said to be commute. .

Equation (3) is true for every ψ. Hence the Eigen function of commutating operator can always be considered in such a way that they are simultaneous Eigen functions.

1. **Simultaneous Measurement of Observables**

If two observables are simultaneously measurable in a particular state of a system, then the state function say ψ is an Eigen function of both the operators. If such condition occurs then observables are said to be compatible and also two operators commute. The two theorem indicate the connection between compatible observables and commuting operators.

**Theorem 1** Operators having common set of Eigen functions commute:

Proof: Consider two commuting operators C and D , the eigen value equation for C is

, (i) where we can take ………

Operating both side from left by D, we get

Since we have two operators C and D commute with each other (i.e.

That is is an eigen function of C with the same eigen value . If C has only non-degenerate eigen values , can differ from only by a multiplicative constant , (say). Hence ……. (ii)

From (i) and (ii) we can see that is a simultaneous eigen function of both C and D.

**Commutators** The operator is called the commutator of the operator and . The commutator satisfies the following rules:

If ,then the operators are said to commute.

**Theorem I** The necessary and sufficient condition that simultaneous eigen function exist for two operators and is that they commute.

**Problem I**  Show that the momentum operator commutes with the free particle Hamiltonian operator

Consider for a free particle i.e. potential applied on it V=0, then we get the Hamiltonian operator is obtained by using Schrodinger wave equation with i.e.

Hence the Hamiltonian operator in case of free particle is given by

, the momentum operator is given by

and

…….. (1)

In the same way

Or,

………….. (2)

From we get:

That means momentum of a free particle commutes with the Hamiltonian.

**Angular momentum operator**

The moment of linear momentum is called the angular momentum. If be the linear momentum of a particle about the origin at the position is

The operator associated with the linear momentum p is given by .

The angular momentum operator is

Let are the Cartesian coordinates and , and be components of orbital angular momentum along X, Y and Z axes, then

Let , be Cartesian components of

This leads to

Now,

,

Hence

Similarly, and

**Commutation relation of with components**

The total angular momentum is defined as

Now take

Now,

∵

Similarly and

Hence commutes with any of three components of the angular momentum operator. From these equations it is obvious that and commute so they have simultaneous eigen functions and hence they are simultaneously measurable.

**Parity operator**

It is one of a mathematical operator , denoted by . For a wave function ψ() of a variable parity operator

Thus the pairity operator make an inversion of the position coordinate through the origin.

**Properties of pairity operator:**

Parity operator is a linear operator.

To prove this, let us choose and are two wave functions. Then

Parity operator is Hermitian operator.

Let ψ(x) and φ(x) are two wave functions then

Let us change variable by , then

This relation shows that operator is Hermitian operator.

**Worked out examples**

1. A microscope, using photons, is employed to locate an electron in an atom within a distance of 0.2 . What is the uncertainty in the momentum of the electron located in this way? Also find the uncertainty in energy of electron in electron volt for this situation.

Solution: Here the uncertainty in position( ?

We have Heisenberg’s uncertainty relation . We can take

Or,

Now uncertainty in energy of the electron

1. Prove the nonexistence of electron in the nucleus on the basis of uncertainty principle.

Solution: We have uncertainty relation:

Or, , which implies that must at least equal to

. If electron lies inside the nucleus, then uncertainty in position must not greater than 2.

, where is the radius of the nucleus.

.

. Thus kinetic energy of the electron must at least equal to 95 MeV. But experiment shows that electrons emitted from β-decay is of the order 3 MeV. Hence it is concluded that electrons do not remain in the nucleus.

1. Find the normalization constant of the energy eigen function of the particle in a box of length L.

Solution: See 󠆖§ particle in a box. Answer:

1. Find the commutation relation between position and momentum.

Solution: Since . Let be a well defined wave function, then

Or, . Similarly .

But It is noted that since , it results that have common eigen functions and can be measured simultaneously with accuracy. Since it follows that both x and can not be measured both simultaneously with accuracy.

1. What are the eigen values of parity operator ?

Solution: Let ψ be any well behaved wave function and be the parity perator. Let α be the eigen value of the operator. We have eigen value equation:

……… (i)

Or,

………… (ii)

We have definition of parity operator :

Or,

………. (iii)

From equation (ii) and (iii) we get:

.

Hence eigen value of parity operator is If the eigen function ψ(x) has parity +1, then it is said to have even parity while for parity -1, the eigen function is said to have odd parity.

1. If the state function is given by . Find the eigen value of momentum operator.

Solution: Given .

Operating both side by momentum operator we get:

Comparing with the operator eigen value equation of a operator , we get eigen value of the momentum operator is equal to .

1. Explain whether energy and momentum can be measured simultaneously.

Solution: Consider ψ be the well behaved wavefunction, and are the energy and momentum operators of the particle, along x axis. Then we have , since eigen value of momentum operator is the momentum itself.

Now,

Since the momentum commutes with energy , so they can be measured simultaneously.

1. If is the angular momentum operator, find the commutator .

Solution: See § operator for the solution.

1. Write the momentum and time independent energy operators in quantum mechanics. Explain with proper theory, whether these physical quantities can be measured simultaneously.

Solution: we have momentum operator is,

(in one dimension) and time independent energy operator is

. In the case of free particle, i.e. Hence .

Now, we can prove that

Hence these observables can be measured simultaneously with high accuracy.

1. Calculate the probability density corresponding to .

Solution: The probability current density

………… (i)

, and .

Putting these values in equation (i) we get:

This is the expression of required probability current density for the given wave function.

1. The wave function of the hydrogen atom for 1s state is . Show that the wave function is normalized.

Solution: We have given the wave function

The normalized wave function satisfy the condition

……. (i)

In spherical polar coordinates, the volume element:

Hence equation (i) becomes

……… (2)

To solve this equation, put . Then .

Then

, where we have used .

Hence left hand side of equation (2) becomes:

= 2

Hence normalizing condition i.e. equation (1), is satisfied by the given wave function ψ. Hence ψ is the normalized wave function.

1. Calculate the average value of 1/r for an electron in the 1s state of the hydrogen atom.

Solution: The expectation value of 1/r is given by

……… (1)

The wave function for a 1s state electron is

Or, and also volume element in spherical coordinates is given by :

Hence equation (1) becomes :

1. A particle on a straight line is described by . Normalize it and explain where this particle is most likely found.

Solution: We have given wave function

and . Let M be the normalization constant. Then using normalization condition

Or,

Or,

Or,

Take

⇨ . Hence

. The integration gives :

Or,

This gives .

Then the normalized wave function will be

The maximum probability of finding particle at distance for which where P is the probability density equal to . Hence

Or, .

Or,

Or, .

Hence the particle will have maximum probability of finding at

1. Find the probability current density of the wave function in the region where the potential V

**Hint :** Use where and . The final result is obtained as

1. Compare the reflection coefficient with that of transmission coefficient in the case of a free electron moving towards a potential step of height 1 Kev if the energy of the particle is 1.5 kev.

Solution: Energy of the electron E and that of potential height . Hence . In this case,

Reflection coefficient and transmission coefficient where and .

Now

1. Normalize the harmonic oscillator wave function given by

Solution: see § linear harmonic oscillator.

1. Find the energy expectation value of particle described by the wave function moving between and .

Solution: We have wave function and . The normalization condition is

Or,

Or,

Or,

Hence wave function

The energy expectation value of the particle is given by

1. What is the significance of commutation relation in quantum mechanics ?

Hint: see § operator.

1. Explain the concept of probability density, normalization and expectation value in quantum mechanics.
2. Show that parity operator commutes with Hamiltonian of a system if the potential

Solution: Let be the Hamiltonian operator and be the parity operator. Then we can write

Then

…….. (i)

Similarly,

……… (ii)

From equation (i) and (ii) , we get:

Or, .

Hence the parity operator commutes with Hamiltonian of a system in the given condition

1. An electron of mass 9.1 is constrained to move in a 1-D potential well of width 1.5 Angstrom. Compare the energy values of electron in the ground state to second excited states if the walls of the well are impenetrable.

Solution: Given mass of an electron 9.1 , width of the well =1.5 Å

Here energy value of the electron inside the well is

For the ground state, , for the second excited, Then the ratio of energy is now

1. Estimate the de-Broglie wavelength of an electron of kinetic energy of 1 kilo electron volt.

Hint: Use , where h is Planck’s constant with energy joule. The answer is 0.3867 Å.

1. Under what circumstances is an atomic electron’s probability density distribution spherically symmetric? Why?

Solution: According to quantum mechanics, the wave function in spherical coordinate system is given by

.

Then the probability density

………. (i)

We have solution of equation in hydrogen atom is ( see § hydrogen atom)

Hence Hence equation (i) becomes

Hence the probability density P depends only on the radial probability and polar probability but not on the azimuthal coordinate ϕ. This results electron distribution is symmetric about z-axis.

1. Leonard I. Schiff ; Quantum mechanics , McGraw-Hill Company [↑](#footnote-ref-1)
2. S.L. Gupta(2002); Quantum Mechanics, Jai Prakash Nath and Co. [↑](#footnote-ref-2)
3. R.Murugeshan(2015), S.Chanda, New Delhi. [↑](#footnote-ref-3)
4. Powell, J. *Quantum mechanics*, New Delhi: Narosa Publishing house, 1998. [↑](#footnote-ref-4)
5. Murugeshan,R. *Modern Physics,* New Delhi: S.chand,2014. [↑](#footnote-ref-5)
6. Schwarz’s inequality: If a1, a2, a3…, aN and b1,b2, b3, ….. ,bN  be the two sets of N complex numbers, then Schwarz’s inequality is given by: [↑](#footnote-ref-6)