US06CCHE22

Unit-1 Wave Mechanics

Wave Equation :

- If electrons have the wave properties then there must be a wave equation and a wave function to describe the electron waves just as the waves of light, sound and strings are described.
- Let us consider the motion of a string which is held fixed at two ends x = 0 and x = a. Upon certain kinds of vibrations a simple wave can be produced.
- If the wave travels in the y-direction, mathematically these motions can be described by functions of the form

$$y(x,t) = f(x)\,\phi(t) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where f(x) is independent of t and $\phi(t)$ is independent of x.

Such motions are called normal modes of vibration.

- The wave equation has the general form :

$$\frac{d^2y}{dx^2} = \frac{1}{c^2}\frac{d^2y}{dt^2} \ldots\ldots\ldots\ldots\ldots (2)$$

where c is called the wave velocity.

- Substituting for y from, Eq. (1) in Eq. (2)

$$\frac{c^2}{f(x)}\frac{d^2f(x)}{dx^2} = \frac{1}{\phi(t)}\frac{d^2\phi(t)}{dt^2} = -\omega^2 \ldots\ldots(3)$$

where $-\omega^2$ is constant.

- Separating x and t we get two differential equations:

$$\frac{d^2\phi(t)}{dt^2} + \omega^2\phi(t) = 0 \ldots\ldots\ldots\ldots(4)$$

$$\frac{d^2f(x)}{dx^2} + \frac{\omega^2 f(x)}{c^2} = 0 \ldots\ldots\ldots(5)$$

- The solution of equation (4) is given as:

$$\phi(t) = A \sin \omega t + B \cos \omega t \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where the A and B are constants determined from the boundary conditions, and **ω** is called the circular frequency which is related to the ordinary frequency

$\omega = 2\pi\nu$ ....(7)

- Equation (5) may therefore be written as :

$$\frac{d^2f(x)}{dx^2} + \frac{4\pi^2\nu^2}{c^2} f(x) = 0 \text{ ...... } (8)$$

- Putting $\lambda = c / \nu$ the solution of equation (8) becomes :

$$f(x) = A_1 \exp\left[+\frac{i2\pi x}{\lambda}\right] + A_2 \exp\left[-\frac{i2\pi x}{\lambda}\right] \text{ L..... } (9)$$

OR

$$f(x) = C \sin\frac{2\pi x}{\lambda} + D\cos\frac{2\pi x}{\lambda} \text{ .... } (9)$$

- Where A_1, A_2, C and D are constant.
- Let us consider Eq. (9) and impose the boundary conditions
  (i) f(x) = 0 at x = 0 and (ii) f(x) = 0 at x = a,
  where a is the length of the string.
  From the boundary condition (i), D = 0
  and from the condition (ii)

$$C \sin\frac{2\pi}{\lambda}a = 0$$

OR $$\sin\frac{2\pi a}{\lambda} = 0$$

OR $$\frac{2a}{\lambda} = n, \quad n = 1, 2, 3 \ldots \text{ ...... } (10)$$

Where n is positive integer.

Thus,

$$a = n\frac{\lambda}{2} \qquad \therefore \boxed{\lambda = \frac{2a}{n}}$$

- The normal modes are thus the stationary sine waves given by

$$f(x) = c\sin\frac{2\pi x}{\lambda}$$

but $\lambda = 2a/n$

$$\therefore f(x) = c \sin\frac{n\pi}{a}x \text{ .... } (11)$$

- The complete solution for a normal mode in a stretched string therefore from Eqs (1), (6), (7) and (11) is given by :

$$y(x,t) = f(x)\cdot\phi(t)$$

$$y(x,t) = C\sin\frac{n\pi}{cL}x\,(A\sin 2\pi\nu t + B\cos 2\pi\nu t) \quad \text{-------}(12)$$

- Equation (12) is an expression for the amplitude of waves generated during the normal modes of vibration in a stretched string. The same equation should represent the amplitude of a de Broglie wave associated with a moving particle. We are, primarily concerned here, with the time-independent or stationary waves. Therefore, the equation for a standing sine wave of wavelength (λ) is given by :

$$\psi = C\sin\frac{2\pi}{\lambda}x \quad \ldots\ldots\ldots\ldots\ldots(13)$$

where Ψ is the wave function and C is the amplitude of the wave

- Double differentiation of Eq. (13) with respect to x gives

$$\frac{d\psi}{dx} = C\cos\frac{2\pi x}{\lambda}\cdot\left(\frac{2\pi}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = -C\sin\frac{2\pi x}{\lambda}\cdot\left(\frac{2\pi}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= -\frac{4\pi^2}{\lambda^2}\cdot C\sin\frac{2\pi x}{\lambda}$$

$$\therefore\ \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\cdot\psi \quad \text{----------}(14)$$

- The kinetic energy T of a moving particle of mass m and velocity v is given by :

  $T = \frac{1}{2}mv^2 = m^2v^2/2m$ …………………………..(15)

- According to the de Broglie,

  $T = h^2/2m\lambda^2$ …………………………………………..(16)

- Substituting equation(14) in equation(16) we get :

$$T = -\frac{h^2}{8\pi^2 m} \cdot \frac{1}{\psi} \cdot \frac{d^2\psi}{dx^2} \quad \ldots\ldots\ldots (17)$$

- If the particle moves in a field whose potential energy is V, then

  E = K.E + P.E. = T + V

  $$T = E - V = -\frac{h^2}{8\pi^2 m} \cdot \frac{1}{\psi} \cdot \frac{d^2\psi}{dx^2} \quad \ldots\ldots\ldots (18)$$

  where E is the total energy. This is Schrödinger's equation for a particle in one dimension. It is usually written as

  $$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \ldots\ldots (19)$$

- In three dimensions this equation becomes:

  $$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \ldots\ldots (20)$$

Interpretation of Ψ and Heisenberg's Uncertainty Principle :

- In classical mechanics the square of wave amplitude associated with electromagnetic radiation is interpreted as a measure of the radiation intensity.This suggests that de Broglie waves are associated with electrons or any moving particle.
- Let the solution of wave equation (20) be a function **Ψ (x.y,z)**, called wave function. We may anticipate that some some physically observable property of the electron is connected to **Ψ^2 (x.y,z)** or more generally **Ψ^* (x.y,z).Ψ (x.y,z)** if **Ψ** is a complex wave function.
- For a system having electrons there are two ways in which **$|\Psi^2|$ or $|\Psi^*\Psi|$** can be interpreted. Either **$|\Psi^2|$** may be regarded as a measure of the the density of electrons or **$|\Psi^2|$dr** be interpreted as a measure of probability of finding the electrons in a small volume dr in a certain region between r and r + dr.
- This implies that if we know **Ψ** exactly we cannot say precisely where the electrons can be found. This destroys the classical concept of a precise trajectory (ગતિ પથ).
- Let us consider an electron of mass m_e with momentum P_x moving in a zero potential field along the x-direction only.The wave equation for such particle according to wave eq. Theory Is given by:

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2} p_x^2 \cdot \psi = 0 \quad \ldots\ldots (1)$$

Let, $k^2 = \frac{4\pi^2 p_x}{h^2}$ then,

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \ldots\ldots\ldots (2)$$

- The wave function **Ψ(x)** is given by either **exp (ikx)** or **exp (-ikx)**. We now ask whether the electron whose momentum is p_x can be found. The answer is given by:

  | Ψ^*(x) Ψ(x) | Which can be written as:

  Ψ^*(x) Ψ(x) = exp (ikx) exp (-ikx) = 1
- According to Born interpretation, this result implies that the probability of finding the electron in a region **dx** is situated. Thus quantum mechanics says that if any part of the space is inspected, the probability of finding the electron remains the same. In other words, if the momentum of a moving particle is precisely known, its position is totally uncertain.
- In 1927 Heisenberg derived a famous principle : In classical mechanics one can simultaneously determine as many properties of a system of any particle as one wishes, to any degree of accuracy. This is not true in wave mechanics.
- Suppose a tiny particle is at rest. We want to find its exact position by looking through a microscope. To see a particle we must hit the particle with photons. If the light has a wavelength **λ**, we cannot expect to determine the position within a distance shorter than **λ** because of diffraction. So **λ** is the order of the uncertainty in the measurement of position.
- But a photon of wavelength c has a momentum **| h/λ |** When a photon collides a particle it transfers this much momentum to the particle and the uncertainty in momentum is **| h/λ |**. The product of the uncertainties of the position and momentum is **λ (h/λ) = h**.
- According to more accurate treatment of Heisenberg, his principle states that :

If the momentum is known to lie within a range **Δp_x** along, say, the x-axis then the position of the particle on this axis must be uncertain to an extent of **Δx** where

$$\Delta p_x \cdot \Delta x \geq \frac{h}{4\pi} \quad \ldots\ldots\ldots\ldots (4)$$

❑ To accept the Born interpretation of the wave function. For this reason **$|\Psi^2|$** or **$|\Psi^*\Psi|$** may be called the probability function. Since the electron must be somewhere in space, the integration of **$|\Psi^2|$** or **$|\Psi^*\Psi|$** over all space must be unity, so that

$$\int \Psi^*(r)\,\Psi(r) = 1$$

Such wave functions are said to be normalised. For every system which is bound, every wave function must satisfy.

- **Properties of Ψ**

❑ The solution of Schrodinger wave equation gives several values of **Ψ**. It is not necessarily all of them that correspond to any physical or chemical reality. Such wave functions are therefore considered unacceptable. Acceptable wave functions are those which satisfy the following conditions:

1. Ψ is single valued, i.e. for each value of the variables x, y, z, there is only one value of the function Ψ. If one of the variables is an angle, say θ, then it requires that

   $$\Psi(\theta) = \Psi(\theta + 2n\pi) \qquad \text{where n is an integer.}$$

2. Ψ and its first derivative **$d\Psi/dx$** with respect to its variables are continuous, In other words, there must not exist any sudden changes in Ψ as its variables are changed.
3. For boundary states Ψ must vanish at infinity. If Ψ be a complex function, then $\Psi^*\Psi$ must vanish at infinity.

If above three conditions are satisfied the function Ψ is called well behaved wave function.

- **Operator concept in Quantum Chemistry :**
- **First (basic) Postulate of quantum mechanics :**

❑ To every physically measurable or observable quantity like position, velocity, linear momentum, angular momentum, energy, etc. of a system there corresponds an operator in quantum mechanics. This may be treated as one of the several basic postulates of quantum mechanics.

- An operator is a symbol for a certain mathematical procedure which transforms one function into another. For example, the operator of evaluating the derivative with respect to r is represented by the symbol d/dr. When this operator is applied to the function r we obtain a new function as :

$$\frac{d}{dx}(x^n) = nx^{n-1}$$

- A list of typical examples of different mathematical operations along with the results of the operations on the function, x^3 is given in Table.

Operation	Operator	Result of operation on x^3
Taking the square	$(\ )^2$	x^6
Taking the square root	$\sqrt{\ }$	$x^{3/2}$
Multiplication by a constant k	k	kx^3
Differentiation with respect to x	d/dx	$3x^2$
Integration with respect to x	$\int(\ )dx$	$x^4/4+c$

- (Operator) (function) = (Another function)
  Symbol of operator is : $(\hat{\ })$
  The function on which the operation is carried out is often called an operand.

- **Additional and Subtraction of Operators :**

  New operators can be constructed by adding and subtracting operators.If A and B are two different operators, then new operators can be defined as :

$$(\widehat{A + B})\,f = \hat{A}f + \hat{B}f$$

$$(\widehat{A - B})\,f = \hat{A}f - \hat{B}f$$

- where f is an operand. It is also true that

$$\widehat{A + B} = \hat{B} + \hat{A}$$

$$\widehat{A - B} = -\hat{B} + \hat{A}$$

Multiplication Operator :

- The consecutive operations with two or more operators on a function may be called the multiplication of operators. Let A and B represent two different operators and f, an operand. Then, the expression A B f means that the function f is first operated on with B to obtain a new function, f’ as

  $$\hat{B} f = f'$$

  Then f’ is operated on by A to obtain the final function f" as

  $$\hat{A} f' = f''$$

  So that

  $$\hat{A}\hat{B} f = f''$$

  The order of application of operators is always from right to left as they are written.

- If the same operator is applied several times in succession, it is written with a power. Thus

  $$\hat{A}\hat{A}f = \hat{A}^2 f$$

Linear Operator :

- If in operating on the sum of two functions an operator gives the same result as the sum of the operations on the two functions separately, then the operator is said to be linear. Thus the operator Â is linear if for any functions f and g we have :

  $$\hat{A}(f+g) = \hat{A}f + \hat{A}g$$

  And $\hat{A}cf = c\hat{A}f$ where c is a constant.

  The operation of taking square root is non-linear because

  $$\sqrt{f+g} \neq \sqrt{f} + \sqrt{g}$$

Commutator :

- Using any two operators Â and $\hat{B}$, it is possible to construct a new operator $\widehat{AB - BA}$, called the commutator of the two operators Â and $\hat{B}$ usually written as [A, B]. If these two operators commute then $[A, B] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$

- Thus the commutator means the multiplication with zero. Clearly, every operator commutes with itself or any power of it. Thus, for an operator Â,

$$\hat{A}\hat{A}^n - \hat{A}^n\hat{A} = 0$$

Vector Operator :

- Operators operating more than one variable are called vector operators. E.g. / x (differential operator) can operate on the function f(x, y, z) with variable x,y,z. An important group of operators are the vector operators. A vector operator ▽(del) is defined in Cartesian coordinates as :

$$\nabla = i\,\partial/\partial x + j\,\partial/\partial y + k\,\partial/\partial z$$

where **i, j, k** are unit vectors along the x,y and z axes. Operating on a scalar function ϕ, this operator generates a vector called the gradient of ϕ.

$$\nabla\phi = i\,\partial\phi/\partial x + j\,\partial\phi/\partial y + k\,\partial\phi/\partial z$$

Laplacian :

- In the quantum mechanics the Laplacian operator ∇^2 defined as

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

Second Postulate of Quantum Mechanics :

Another basic postulate or Law of Quantum Mechanics :

- "The only possible values that can be observed of a physical properties like angular momentum, energy etc. of a system are the eigenvalue λ, in the operator system.

i.e. $\hat{A}\Psi = \lambda\Psi$ ……………………………………(i)

Where, **Â** is the operator for physical quantity and Ψ is well behaved eigen wave function.

There are two types of operators that obey the eigen value relationship.

➢ Hermitian operator:

An operator **Â** is said to be Hermitian if,

$$\int \Psi_1^*.(\hat{A}\Psi_2)\,\partial\tau = \int(\hat{A}\Psi_1)^*.\Psi_2\,\partial\tau \text{ ………………….(ii)}$$

Where Ψ_1 and Ψ_2 are eigenfunctions of the operator **Â.**
Equation (ii) is a mathematical form of "turn-over rule".

* indicates the complex conjugate of the quantity immediately to its left. The hermitian operator is linear and it has real eigenvalue.

If **Â** is hermitian operator operating on eigenfunction Ψ, it gives eigenvalue 'a' then

$$\hat{A}\,\Psi = a\,\Psi \text{.....................................(iii)}$$

Multiplying both side of equation (iii) with Ψ^* and integrating over all space, we get

$$\int \Psi^* \hat{A}\, \Psi\, \partial\tau = a \int \Psi^* \Psi\, \delta\tau \text{ ....(iv)}$$

Taking the complex conjugate of every quantity in equation (3),

$$\hat{A}^* \Psi^* = a^* \Psi^* \text{ ....(v)}$$

and then multiplying both sides of eq.(v) with Ψ and integrating over the space,

$$\int \Psi\, \hat{A}^* \Psi^*\, \delta\tau = a^* \int \Psi^* \Psi\, \delta\tau \text{...................(vi)}$$

The left hand side of eq. (iv) and (vi) are equal according to the definition of a hermitian operator, so that

$$a \int \Psi^* \Psi\, \partial\tau = a^* \int \Psi^* \Psi\, \delta\tau \text{...................(vii)}$$

In other words, $a = a^*$ which is true only if a is real. This guarantees that any physical quantity represented by a hermitian operator is observable and physically measurable.

➢ Unitary operator :

A linear operator **Û** is said to be unitary operator

$$\int \Psi_1^*\, U^{-1}\, \Psi_2\, \delta\tau = \int \Psi_2\, \hat{U}^*\, \Psi_1^*\, \delta\tau \text{ ....(viii)}$$

where the operator U^{-1} is the inverse of **Û** such that $\hat{U}^{-1}\hat{U} = \hat{U}\,\hat{U}^{-1} = 1$ and , Ψ_1 and Ψ_2 are any two eigenfunctions of **Û** and the asterisk stands for the complex conjugate quantity.

Consider the equation :

$$\hat{U}\,\Psi = \lambda\,\Psi \text{ ....(ix)}$$

where λ is the eigenvalue. Then

$$\hat{U}^{-1}\,\hat{U}\,\Psi = \Psi = \lambda\,\hat{U}^{-1}\,\Psi \text{......................(x)}$$

Or $\hat{U}^{-1}\,\Psi = \lambda^{-1}\,\Psi$ ....(xi)

Inverse operator U-' has the same eigenfunction as U but with reciprocal cigen value. Multiplying both sides of Eq. (2.26) with y and integrating over all space

$$\int \Psi^*\, \hat{U}^{-1}\, \Psi\, \delta\tau = \lambda^{-1} \int \Psi^*\, \Psi\, \delta\tau \text{.............(xii)}$$

Taking the complex conjugate of Eq. (ix)

$$\hat{U}^* \Psi^* = \lambda^* \Psi^* \text{.....................................(xiii)}$$

Then, $\int \Psi \hat{U}^* \Psi^* \partial\tau = \lambda^* \int \Psi^* \Psi \partial\tau$..........(xiv)

R.H.S. of eq. (xii) and (xiv) are equal, so that

$$\lambda^{-1} = \lambda^* \quad \text{or} \quad \lambda^*\lambda = 1 \text{..................(xv)}$$

Thus eigenvalues of an unitary operator have modulus one.

Setting up of Operators for Different Observables :

It has been already mentioned that every dynamical variable is assigned a linear operator. According to classical mechanics, most dynamical variables may be expressed in terms of the position and momentum coordinates such as x, y, z, p_x, p_y, or p_z. The rule for setting up their quantum mechanical operators is simply to take the classical expressions and replace x, y, z, p_x, p_y, and p_z by the corresponding operators. Operators corresponding to positions along x, y and z axes are simply the multiplication by the variable itself. Operators for linear momenta may be found from the following considerations.

A beam of electrons travelling along the x-direction can be treated as a wave propagating along the x-axis. Taking these waves to be sinusoidal, the wave function may be written as :

$$\Psi = A \sin 2\pi x / \lambda \text{.................................(i)}$$

Where λ is the wavelength. An equivalent form for the time-independent wave is :

$$\Psi = C \exp [\pm \sin 2\pi i x / \lambda] \text{ ....(ii)}$$

Then $$\frac{\partial\psi}{\partial x} = \pm \frac{2\pi i}{\lambda} C \exp\left[\pm \frac{2\pi i}{\lambda} x\right] \text{....... (iii)}$$

$$= \pm \frac{2\pi i}{\lambda} \psi$$

Using de Broglie's relationship, i.e. $\lambda = h/P_x$, one may write

$$\hat{P}_x \psi = \pm \frac{h}{2\pi i} \cdot \frac{\partial\psi}{\partial x} \text{ .... (iv)}$$

Therefore, the operator corresponding to the linear momentum in the x-direction is written as :

$$\hat{P}_x = \frac{h}{2\pi i} \frac{\partial}{\partial x}$$

and $$\hat{P}_x^* = -\frac{h}{2\pi i} \cdot \frac{\partial}{\partial x} \text{ .... (v)}$$

Similarly for $\hat{P}_y$ and $\hat{P}_z$ one can write

$$\hat{P}_y = \frac{h}{2\pi i}\frac{\partial}{\partial y}\ , \quad P_z^* = -\frac{h}{2\pi i}\frac{\partial}{\partial z} \quad \text{........(vi)}$$

That the operator, say p_x, is hermitian is shown as follows :

$$\int_{-\infty}^{+\infty}\Psi_1^*\left[\frac{h}{2\pi i}\frac{\partial}{\partial x}\right]\Psi_2\, dx = \frac{h}{2\pi i}\Big[\Psi_1^*\Psi_2\Big]_{-\infty}^{+\infty} - \frac{h}{2\pi i}\int_{-\infty}^{+\infty}\Psi_2\frac{\partial \Psi_1^*}{\partial x}\, dx$$

The first term on the right hand side is zero since both Ψ_1 and Ψ_2 vanish at infinity. The second term on the right hand side can be written as :

$$\int_{-\infty}^{+\infty}\Psi_2\cdot\left[\frac{h}{2\pi i}\cdot\frac{\partial}{\partial x}\right]^*\Psi_1^*\, dx$$

Thus, the linear momentum operator is hermitian, hence linear momentum is observable.

The classical expression for the total energy of a single particle of mass m is called the hamiltonian, usually denoted by **H** and is given by :

$$\begin{aligned} H &= \frac{1}{2}mv^2 + V \\ &= \frac{m^2v^2}{2m} + V \\ &= \frac{p^2}{2m} + V \quad \text{............ (vii)} \end{aligned}$$

where **v** is the linear velocity, **P** the momentum, and **V** the potential energy of the particle. Written in terms of the components of the linear momentum **p, H** becomes :

$$H = \frac{P_x^2 + P_y^2 + P_z^2}{2m} + V \quad \text{...... (viii)}$$

The operator, say $\hat{P}_x^2$ is taken to mean that the corresponding operation P_x is to be repeated twice, so that ;

$$\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2$$

$$= \left[\frac{h}{2\pi i}\frac{\partial}{\partial x}\right]\left[\frac{h}{2\pi i}\frac{\partial}{\partial x}\right] + \left[\frac{h}{2\pi i}\frac{\partial}{\partial y}\right]\left[\frac{h}{2\pi i}\frac{\partial}{\partial y}\right]$$

$$+\left[\frac{h}{2\pi i}\frac{\partial}{\partial z}\right]\left[\frac{h}{2\pi i}\frac{\partial}{\partial z}\right]$$

$$= -\frac{h^2}{4\pi^2}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] = -\frac{h^2}{4\pi^2}\nabla^2 \quad \ldots\ldots(ix)$$

Substituting eq.(ix) in eq.(viii) ;

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \quad \ldots\ldots\ldots\ldots(x)$$

which can be proved to be hermitian and linear. If there are several particles then,

$$H = -\frac{h^2}{8\pi^2}\sum_i \frac{\nabla_i^2}{m_i} + V \quad \ldots\ldots\ldots\ldots(xi)$$

where m_i, is the mass of the **i**th particle and ∇^2_i is Laplacian operator containing the coordinates of **i**th particle.

Another important dynamical variable is the angular momentum. For a single particle moving around a fixed point, the angular momentum **L** is given by the vector product of **r** and **p** as :

L = r x p……………………………….(xii)

where **r** is the radius vector from a fixed point and **p**, the linear momentum vector. Both the vectors **r** and **p** can be written in terms of their components as :

$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$

$\mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z$…………………..(xiii)

where **i**, **j** and **k** are unit vectors along x, y and z axes. Therefore, in terms of the components of **r** and **p**, the angular momentum, **L** is

$\mathbf{L} = \mathbf{i}(yp_z - zp_y) + \mathbf{j}(zp_x - xp_z) + \mathbf{k}(xp_y - yp_x)$..........(xiv)

Replacing the **p's** by the corresponding quantum mechanical operators, the operators for the components of angular momentum are as follows:

$$\hat{L}_x = \frac{h}{2\pi i}\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$\hat{L}_y = \frac{h}{2\pi i}\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]$$

and

$$\hat{L}_z = \frac{h}{2\pi i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \quad \ldots\ldots(xv)$$

The total angular momentum is obviously given by

$$\mathbf{L} = \mathbf{i}L_x + \mathbf{j}L_y + \mathbf{k}L_z \text{ ………………………(xvi)}$$

However, more important in quantum mechanics, is the scalar product of **L** with itself,

$$\mathbf{LL} = \mathbf{L}^2 = \mathbf{L}^2_x + \mathbf{L}^2_y + \mathbf{L}^2_z \text{ .... (xvii)}$$

The angular momentum operators are usually expressed in spherical polar coordinates.

$$\hat{L}_x = \frac{h}{2\pi i}\left[-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right]$$

$$\hat{L}_y = \frac{h}{2\pi i}\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right]$$

$$\text{....(xviii)}$$

$$\hat{L}_z = \frac{h}{2\pi i}\frac{\partial}{\partial\phi}$$

$$\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Let us consider the component of angular momentum about z-axis. That this operator is hermitian can be shown as follows :

$$\int_0^{2\pi}\psi_2^*\left[\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right]\psi_1\,d\phi = \frac{h}{2\pi i}\left\{\left[\psi_2^*\psi_1\right]_0^{2\pi} - \int_0^{2\pi}\psi_1\frac{\partial\psi_2^*}{\partial\phi}\,d\phi\right\} \text{ ......(xix)}$$

Since the functions **$\Psi_1(\phi)$** & **$\Psi_2(\phi)$** must be single valued i.e. for any **(ϕ)**

$$\Psi_1(\phi) = \Psi(2\pi + \phi) \text{.....................................(xx)}$$

the first term on the right hand side of Eq. (xx) must vanish. Therefore, Eq. (xx) can be written as :

$$\psi_2^*\left[\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right]\psi_1\,d\phi$$

$$= -\frac{h}{2\pi i}\int_0^{2\pi}\psi_1\frac{\partial\psi_2^*}{\partial\phi}\,d\phi = \int_0^{2\pi}\psi_1\left[\frac{h}{2\pi i}\frac{\partial}{\partial\phi}\right]^*\psi_2^*\,d\phi \text{ ......(xxi)}$$

Because of the equivalence of L_x. L_y, and L_z an operator corresponding to any component of angular momentum is hermitian. So must also be hermitian. This shows that not only any component of angular momentum about any axis but also total angular momentum in a system is observable from the quantum mechanical view point.

- **Eigenvalues of $\hat{L}_z$:**

In accordance with the basic postulate embodied in Eq.$\hat{A}\Psi = \lambda\Psi$ the possible values of the component of angular momentum about z-axis, the axis of rotation, are given by the solution of equation

$$\hat{L}_z\psi = \lambda\psi$$

or
$$\frac{\partial\psi}{\partial\phi} = \frac{2\pi i}{h}\lambda\cdot\psi$$

or
$$\psi = \exp\left[\frac{2\pi i}{h}\lambda\phi\right]$$
$$= \cos[\frac{2\pi\lambda}{h}\phi + i\sin[\frac{2\pi\lambda}{h}\phi]$$

Since the function Ψ must be single valued, it follows from Eq. (xx) that :

$$\exp\left[\frac{2\pi i\lambda}{h}\phi\right] = \exp\left[\frac{2\pi i\lambda}{h}(\phi + 2\pi)\right]$$

$\exp(ik\phi) = \exp(ik[\phi + 2\pi])$ Where **$k = 2\pi\lambda / h$**

Or **$\exp(2\pi ik) = 1$**

In other word **$\cos(2\pi k) + i\sin(2\pi k) = 1$**

which is possible only if

$k = 0, \pm1, \pm2, \pm3, \ldots\ldots\ldots\ldots \pm n$

Or λ must be either zero or integral multiple of **$h/2\pi$**. This results in exactly what Bohr postulates about angular momentum of an electron in an atom. In other words, the component of angular momentum about any axis forms a discrete eigenspectrum. On the other hand, it can be shown that in the absence of any restrictions, the component of linear momentum along any axis forms a continuous eigenspectrum.

- ## Third Postulate of Quantum Mechanics :

According to the second postulate given by $\hat{A}\Psi = \lambda\Psi$ the given eigenvalue λ which a measurement of an observable characterised by an operator $\hat{A}$ may be written as :

$$\lambda = \frac{\hat{A}\psi}{\psi}$$

But this form of expression is not used in quantum mechanics, because it varies from place to place and cannot be equated to a constant λ. If, both the numerator and the denominator on the right hand side of above Eq. with Ψ^* and integrated over the entire space, we get :

$\int \Psi^* \hat{A} \Psi \, \partial\tau / \int \Psi^* \Psi \, \partial\tau$ no longer becomes a function of the coordinates (x,y,z). Thus it can be equal to the average value of the constant λ.

The third postulate may then be stated as follows:

“When a great many measurements of any observable represented by an operator $\hat{A}$ are made on a system characterised by a function Ψ, the average result obtained is given by :

$$\lambda = \frac{\int \psi^* \hat{A} \psi \, \partial\tau}{\int \psi^* \psi \, \partial\tau}$$

- ## Fourth Postulate of Quantum Mechanics :

The fourth postulate may be stated as follows:
The time development of a wave function is given by :

$$\frac{ih}{2\pi} \frac{\partial\psi}{\partial t} = \hat{H}\psi \qquad \text{..............(i)}$$

which is Schrödinger's equation where $\hat{H}$ is the hamiltonian operator. If we substitute $\hat{H} = -\frac{h^2}{8\pi^2 m} \nabla^2 + V$
in Eq. (i)

$$\left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V(x)\right]\psi = \frac{ih}{2\pi} \cdot \frac{\partial\psi}{\partial t} \qquad \text{(ii) ......(ii)}$$

The wave function Ψ is obviously a function of the space coordinates of a particle, i.e. x, y, z and time t. Using a collective symbol r for the space coordinates, x, y, z, Eq. (ii) can also be written as :

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial r^2}+V(r)\psi=\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} \quad ....(iii)$$

Where **V** the potential independent of time. Such an equation can be solved easily by assuming the separation of variables. Thus, the wave function Ψ may be factored into two functions, one depending only on **r** and the other on **t**.

$$\Psi(r,t) = \Psi(r)\,.\,\Psi'(t) \quad ....(iv)$$

$$\frac{\partial\psi(r,t)}{\partial r}=\psi'(t)\frac{\partial\psi(r)}{\partial r}$$

or $$\frac{\partial^2\psi(r,t)}{\partial r^2}=\psi'(t)\frac{\partial^2\psi(r)}{\partial r^2} \quad ......\ (v)$$

similarly

$$\frac{\partial\psi(r,t)}{\partial t}=\psi(r)\frac{\partial\psi'(t)}{\partial t} \quad ......\ (vi)$$

Using eq. (v) and (vi) in eq. (iii) we get,

$$-\frac{h^2}{8\pi^2 m}\psi'(t)\frac{\partial^2\psi(r)}{\partial r^2}+V(r)\psi(r)\psi'(t)$$
$$=\frac{ih}{2\pi}\psi(r)\frac{\partial\psi'(t)}{\partial t} \quad ....(vii)$$

Dividing eq. (vii) by $\psi(r)\,\psi'(r)$ we get,

$$\left[-\frac{h^2}{8\pi^2 m}\frac{1}{\psi(r)}\frac{\partial^2\psi(r)}{\partial r^2}+V(r)\right]$$
$$=\frac{ih}{2\pi}\frac{1}{\psi'(t)}\frac{\partial\psi'(t)}{\partial t} \quad ....(viii)$$

In eq. (viii) terms on the L.H.S. is independent of t and R.H.S. terms is independent of r.

Thus the variables r and t are separated and each side of the eq.(viii) may be equated to a constant, say E, giving:

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(r)}{\partial r^2} + V(r)\psi(r) = E\cdot\psi(r) \quad \text{......(ix(a))}$$

and $$\frac{ih}{2\pi}\frac{\partial\psi'(t)}{\partial t} = E\cdot\psi'(t) \quad \text{.....(ix(b))}$$

Suppose eq.(ix(a)) has the solution $\psi(r)$.
Eq(ix(b)) has obviously the following solution.

$$\psi'(t) = C\exp\left[-\frac{2\pi i}{h}E\cdot t\right] \quad \text{.......(x)}$$

So, the wave function $\psi(r,t)$ may be written as,

$$\psi(r,t) = \psi(r)\cdot C\exp\left[-\frac{2\pi i}{h}Et\right]$$

The constant C may be absorbed in $\psi(r)$ and we may write $\psi(r,t)$ as

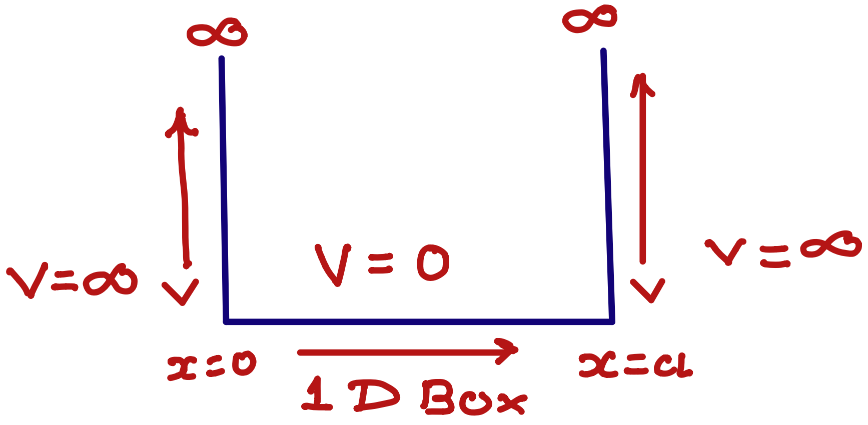
$$\boxed{\psi(r,t) = \psi(r)\cdot\exp\left[-\frac{2\pi i}{h}Et\right]}$$

Wave mechanics of some simple system with constant potential energy :

As an example, we consider the exact solution of Schrödinger's equation for a system of an electron confined in a box in which the potential energy is either zero or constant and infinite everywhere else outside the box. The mathematics is simple for this system but the results illustrate some important properties of quantum mechanical systems, such as quantisation of energy, quantum numbers, zero point energy, etc. In fact, this system provides the basis of the free electron approximation to molecular orbitals which we shall deal with in a later chapter.

One Dimensional Box :

Suppose an electron of mass $\mathbf{m_e}$ is constrained to move in the x-direction from **x = 0** to **x = a**. Outside this region(**0** to **a**) the potential energy, $\mathbf{V}$ is taken to be infinite, and within this region it is zero (because one electron possess wave nature so it can move).



Outside the box the Schrödinger equation is,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m_e}{h^2}(E-\infty)\psi = 0 \quad \text{......} \; (1)$$

This equation is satisfied if $\boldsymbol{\Psi}$ is zero at all points outside the box. In other words electron cannot be found at all outside the box.

Inside the box the wave equation is,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 me}{h^2} E\psi = 0 \quad \ldots\ldots\ldots (2)$$

Equation (2) may be written in the operator form

$$\hat{H}\psi = E\psi \quad \text{where } H = -\frac{h^2}{8\pi^2 me}\frac{d^2}{dx^2}$$

According to the third postulates of quantum mechanics, the mean value of **E** is observable and independent of the coordinate of the electron. Now we refer to **E** as the mean value of energy and assume,

$$\frac{8\pi^2 me}{h^2} E = k^2 \quad \ldots\ldots\ldots (3)$$

Where $\mathbf{k^2}$ is a constant independent of $\mathbf{x}$. Equation (2) can be written as :

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \ldots\ldots\ldots (4)$$

The solution of equation (4) is,

$$\Psi = C \cos kx + D \sin kx \quad \ldots\ldots\ldots (5)$$

In order to be a well-behaved wave function Ψ must be a continuous function of $\mathbf{x}$ in between $\mathbf{x = 0}$ to $\mathbf{x = a}$. While outside this Ψ must be **zero**.

From the boundary conditions,

(i) $\Psi = 0$**,** at $\mathbf{x = 0}$ hence from eq.(5) $\mathbf{C = 0}$ and

(ii) $\Psi = 0$ at $\mathbf{x = a}$, we have

$$D \sin ka = 0 \quad \ldots\ldots\ldots (6)$$

Or $\sin ka = 0$ or $ka = n\pi$ ……...…………(7)

$$n = 1,2,3,4,\ldots..$$

where $\mathbf{n}$ is called a quantum number which is either zero or a positive integer. Thus, the permitted solutions are

$$\psi_n = D \sin \frac{n\pi}{a} x \quad \ldots\ldots\ldots (8)$$

From Eqs (3) and (7), **E** is given as,

$$E = \frac{k^2h^2}{8\pi^2 me} = \frac{n^2h^2}{8mea^2} \quad \ldots\ldots (9)$$

If the potential energy inside the box is not zero but constant equal to say, **V**, then the energy spectrum is given by

$$E = \frac{n^2h^2}{8mea^2} + V \quad \ldots\ldots\ldots\ldots (10)$$

Although the value zero for **n** is permitted it is not acceptable because the function Ψ_n of Eq.(5) becomes zero; but an electron is assumed to be always present inside the box. Therefore, the lowest kinetic energy, called the zero-point energy, of an electron in a box is given by [substitute $n = 1$ in Eq. (9)].

$$E_{zero\,point} = \frac{h^2}{8mea^2} \quad \ldots\ldots (11)$$

This shows that the electron inside the box is not at rest even at **0 K**. Therefore, the position of the electron cannot be precisely known. Since only the mean value of the kinetic energy is known, the momentum of the electron is also not precisely known. The occurrence of the zero-point energy is therefore in accordance with the Heisenberg uncertainty principle.

If the walls of the box are removed and an electron is free to move without any restriction in a field whose potential energy may be assumed to be zero and in the eq. (2) and (5) **C,D & k^2** have any value, then the energy given by

$$E = \frac{k^2h^2}{8\pi^2 me} \quad \ldots\ldots\ldots\ldots (12)$$

This energy is not quantised in this case. Thus, when an electron is bound in a system it has quantised energy levels given by Eq. (9) or (10) and it leads to a discrete spectrum. On the other hand, a free electron moving without any restriction has the continuous energy spectrum. This qualitatively explains the occurrence of con tinuum in the atomic or molecular spectra on ionisation because an electron lost by an atom or molecule is free to move without any restriction.

Normalisation and Orthogonality :

The wave functions for the various states of an electron in a box are given by Eq. (8). The probability distribution is

$$|\psi_n^2| = D^2 \sin^2 \frac{n\pi}{a} x \quad \ldots\ldots\ldots(13)$$

The integral of this wave function over the entire space in the box must be equal to unity because there is only one electron and at all times it is somewhere in the box Therefore

$$\int_0^a |\psi_n^2|\, dx = \int_0^a D^2 \sin^2 \frac{n\pi}{a} x\, dx = 1$$

But, $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

so $$\int_0^a |\psi_n^2|\, dx = D^2\left[\frac{1}{2}\int_0^a dx - \frac{1}{2}\int_0^a \cos\frac{2n\pi}{a} x\, dx\right]$$

$$= D^2\left[a/2 - 0\right] = 1$$

or $$D = \sqrt{\frac{2}{a}} \quad \ldots\ldots\ldots(14)$$

Thus, the normalised wave function of an electron in a one-dimensional box is given by

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \quad \ldots\ldots\ldots(15)$$

Orthogonality :

Consider the normalised wave functions Ψ_n and $\Psi_{n'}$ corresponding to two different states of an electron in a box. It is found that for

$n \neq n'$ $$\int_0^a \psi_n \psi_{n'}\, dx = 0 \quad \ldots\ldots\ldots(16)$$

The wave functions for different states of this system are thus orthogonal. This can be shown as follows:

$$\int_0^a \psi_n \psi_{n'}\, dx = \frac{2}{a}\int_0^a \sin\frac{n\pi}{a} x \sin\frac{n'\pi}{a}\, dx$$

$$\left[\sin n\theta \cdot \sin n'\theta = \frac{1}{2}\left[\cos(n-n')\theta - \cos(n+n')\theta\right]\right.$$

$$= \frac{1}{a}\int_0^a \left[\cos(n-n')\pi\frac{x}{a} - \cos(n+n')\pi\frac{x}{a}\right]dx$$

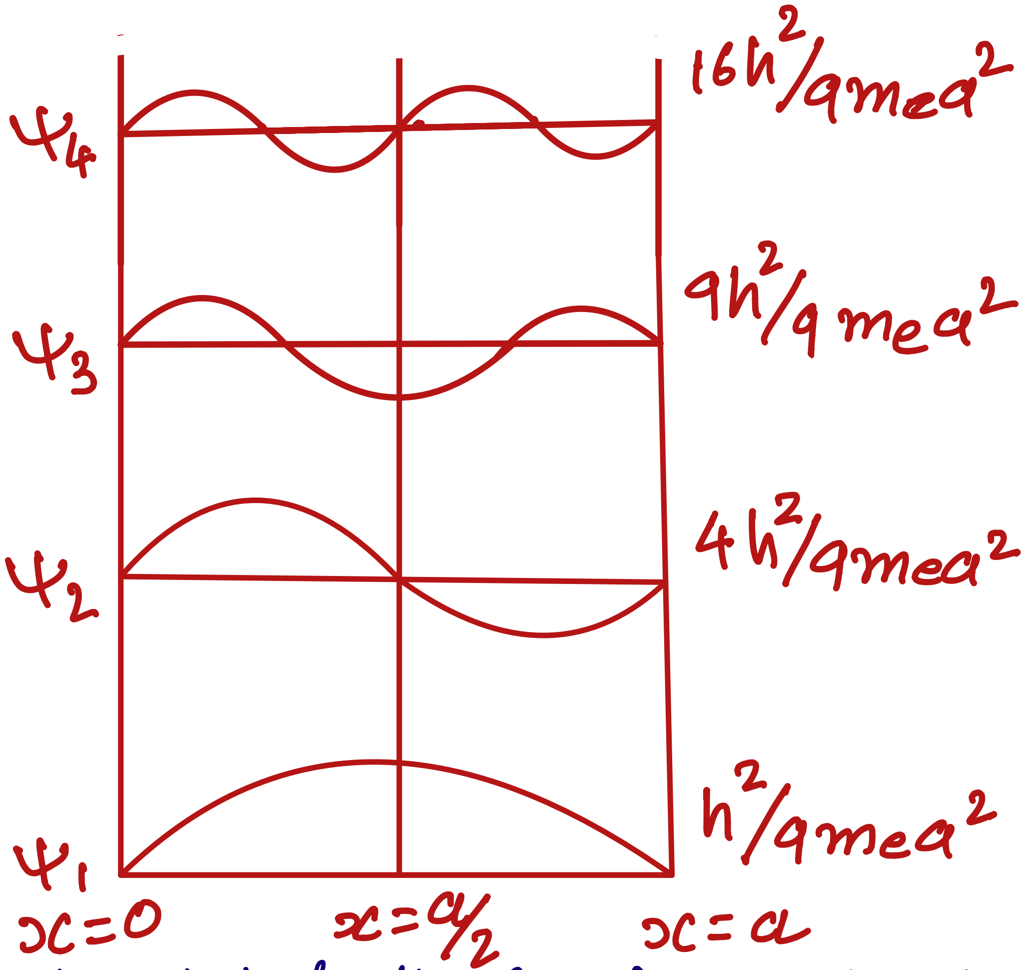
$$= \frac{1}{a\pi}\left[\frac{a}{(n-n')}\cdot\sin\frac{(n-n')\pi x}{a} - \frac{a}{(n+n')}\cdot\sin\frac{(n+n')\pi x}{a}\right]_0^a$$

$$= 0$$

Since the hamiltonian for an electron in a box is a hermitian operator, the wave function Ψ_n and $\Psi_{n'}$ corresponding to two different states should be orthogonal.

- **Characteristics of the Wave Functions :**

A few energy levels and the corresponding wave functions are shown graphically in figure. Imagine a one-dimensional mirror which is parallel to the walls of the box and situated at the centre of the box as shown by the dotted line in figure. It should be noted that the wave functions are alternately symmetrical and antisymmetrical with respect to reflection from such a mirror.



Energy levels and eigenfunctions for a few lowest levels of an electron in a 1-D Box of length a

Besides the points on the walls of the box, there are points inside the box where the wave function is zero. These points are called nodes. It is evident from the figure that as the quantum number **n** increases, the number of nodes on the wave increases. For example, the state whose wave function is $\boldsymbol{\Psi}_n$ has **(n - 1)** nodes inside the box. This type of behaviour is general for all systems. Increasing the number of nodes decreases the wavelength, which corresponds to increasing the kinetic energy.