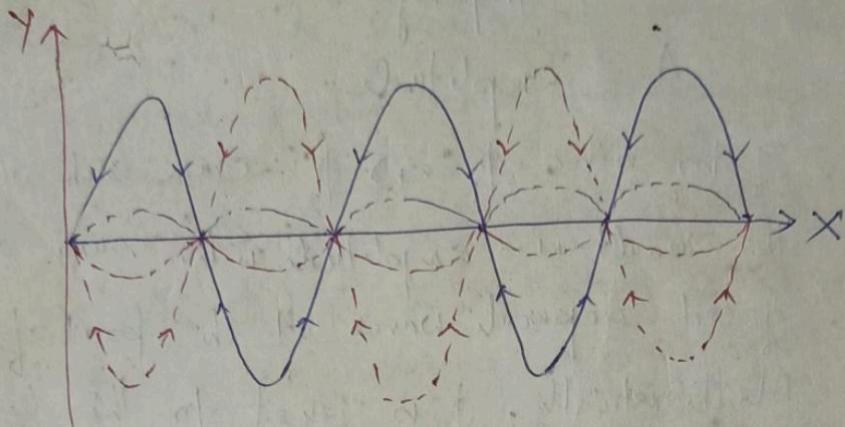


Quantum Mechanics

(1) Description of Waves



Standing Harmonic Wave.

Let us consider a wave propagating in X -direction. This is called the progressive wave. This motion can be described by a differential equation

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{c^2} \left(\frac{\partial^2 \phi}{\partial t^2} \right) \quad \dots \quad (i)$$

The value ϕ is the amplitude function and is a measure of the variation of displacement along the Y -axis at a particular distance x along the X -axis, c is the velocity of wave and in time. This is a 2D order differential equation. This equation has many solutions and one of them is in terms of sine function

$$\phi = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right) \quad \dots \quad (ii)$$

(1) Ans

Show λ = wavelength

ν = frequency

A = amplitude

If two waves ϕ_1 and ϕ_2 cross each other, the resultant amplitude is the sum of the amplitudes of each separate waves at the point of crossing.

Mathematically, ϕ is equal to the linear combinations of two separate functions ϕ_1 and ϕ_2 .

$$\phi = a_1 \phi_1 + a_2 \phi_2 \quad \dots \quad (iii)$$

Where a_1 and a_2 are arbitrary constants.

This equation (iii) is an example of the principle of superposition. According to this principle, any linear combination of the solutions of the wave equation is also a solution. Eqn(ii) represent a plane wave travelling from left to right. An equivalent wave, travelling in the opposite direction, is given by

$$\phi = A \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right)$$

When two waves of the form of eqn (ii) travel with equal speed but in opposite directions, then their resultant amplitude by the principle of superposition will be

$$\phi = A \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right) + A \sin 2\pi \left(\frac{x}{\lambda} + \nu t \right)$$

$$\phi = 2A \sin 2\pi \frac{x}{\lambda} \cos 2\pi \nu t \quad \dots \quad (iv)$$

(2)

The new resultant wave, which does not move either forward or backward, is known as the standing wave or a stationary wave. All waves whose amplitude function can be factorised into a factor independent of space coordinates and factor independent of time, are called standing waves.

An electron in an atom can be described by considering standing wave.

From eqn(iv), we get that ϕ vanishes irrespective of the value of t , for the points at which

$$\sin 2\pi \frac{x}{\lambda} = 0 \quad \text{i.e. at } x = 0, \frac{\lambda}{2}, \frac{2\lambda}{2}, \dots, \frac{n\lambda}{2}$$

These points are called nodes (minimum amplitude). The midway between two nodes are the position of maximum amplitude, or antinodes.

(2) The Schrodinger Time-independent Wave

Equation:

Let us consider an electron moving in along x -axis and behaving like a standing wave.

The amplitude function of this wave can be written as —

$$\phi(x, t) = 2A \sin \frac{2\pi x}{\lambda} \cos 2\pi \nu t$$

$$= \psi(x) f(t) = \psi(x) \cos 2\pi$$

(2) min.

λ = wavelength, ν = frequency, A = amplitude
where $\psi(x) = 2A \sin \frac{2\pi x}{\lambda}$ and is a function
of x -coordinate only.

$f(t) = \cos 2\pi \nu t$, is a function of t only.

These two functions are independent of each other.

Diff. eqn (i),

$$\frac{\delta^2 \phi}{\delta x^2} = \cos 2\pi \nu t \cdot \frac{d^2 \psi(x)}{dx^2} \quad \text{--- (i)}$$

$$\frac{\delta^2 \phi}{\delta t} = -\psi(x) \cdot 2\pi \nu \sin 2\pi \nu t$$

$$\frac{\delta^2 \phi}{\delta t^2} = -\psi(x) \cdot 4\pi^2 \nu^2 \cos 2\pi \nu t \quad \text{--- (ii)}$$

Substituting these values in eqn (i), we get -

$$\cos 2\pi \nu t \cdot \frac{d^2 \psi(x)}{dx^2}$$

A progressive wave is described by the differential eqn,

$$\frac{\delta^2 \phi}{\delta x^2} = \frac{1}{c^2} \left(\frac{\delta^2 \phi}{\delta t^2} \right) \quad \text{--- (iv)}$$

Substituting the values of $\frac{\delta^2 \phi}{\delta x^2}$ and $\frac{\delta^2 \phi}{\delta t^2}$ from eqn (ii) and (iii) to eqn (iv), we get -

$$\cos 2\pi \nu t \cdot \frac{d^2 \psi(x)}{dx^2} = -\frac{1}{c^2} \psi(x) \cdot 4\pi^2 \nu^2 \cos 2\pi \nu t$$

$$\text{or, } \frac{d^2 \psi(x)}{dx^2} = -\frac{1}{c^2} 4\pi^2 \nu^2 \psi(x) \quad \text{--- (v)}$$

This is a wave equation independent of time.

Since, $c = \lambda v$

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

From de Broglie's eqn,

$$\lambda = \frac{h}{mv} \quad (\text{for micro-particles})$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2 m^2 v^2}{h^2} \psi(x) \quad \text{--- (vii)}$$

Now, the total energy (E) is the sum of K.E. (T) and P.E. (V), for an electron.

$$\therefore E = T + V$$

$$T = \frac{1}{2}mv^2 = (E-V).$$

$$mv^2 = 2(E-V)m$$

Substituting in eqn(vii), we get -

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

This is the famous Schrodinger equation for a single particle of mass m moving in one dimension.

(2) ~~contd.~~

For three dimensions, it is given by

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (ix)}$$

where ψ and V are functions of coordinates

x, y, z and ψ is known as the wave function

for one-particle system, the Schrödinger wave eqn is generally written as

$$-\frac{h^2}{8\pi^2 m} \left[\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \right] \psi + V \psi = E \psi \quad \text{--- (x)}$$

(3) The Wave Function

The wave function ψ is a sort of amplitude function. In classical mechanics, the square of wave amplitude, associated with the electromagnetic radiation, is proportional to the intensity of radiation. Hence the square of the absolute value of ψ is a measure of the intensity or particle density.

But the present accepted idea of ψ in quantum mechanics is based on the uncertainty principle. According to this principle, it is not possible to simultaneously measure the position and momentum of a microparticle such as electron, precisely. So, the idea of particle

(4)

density or intensity of light has no place in quantum mechanics.

According to Born, $|\psi|^2$ should be treated as proportional to the probability of finding a particle at a point at any given moment. Since the probability of finding a particle at a point in space must be real, more generally, $\psi^* \psi$ is taken as the measure of the probability of finding a particle at any point, if ψ is a complex function. The function ψ^* is the complex conjugate of ψ and their product will always be a real non-negative quantity.

e.g. Let $\psi = a + ib$

where, $i = \sqrt{-1}$. The square of this quantity will always be imaginary. The complex conjugate of ψ is

$$\psi^* = a - ib$$

so that the product

$\psi^* \psi = a^2 + b^2$, is a real non-negative quantity. If ψ is a real function, then $\psi = \psi^*$.

Generally, the probability of finding a particle in a certain volume element, $dx dy dz$

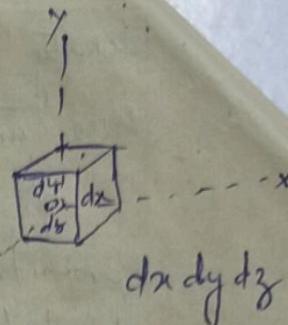
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is expressed as $|\psi|^2 dxdydz$

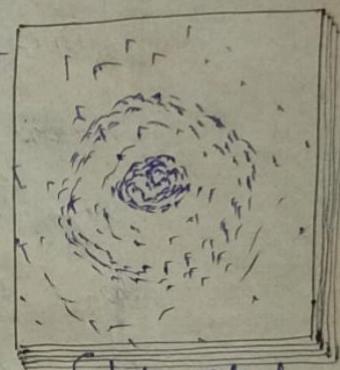
or. $|\psi|^2 dxdydz$ and

probability of finding a particle
per unit volume, is

represented by $|\psi|^2$ and is known as
probability density.



Suppose we have an electron bound to the nucleus of an atom. The position of the electron ~~at~~ any instant - could be specified by taking a 3-d photograph. Since the electron is continuously in motion, a photograph taken a fraction of second later would reveal the electron in a new position. If we take thousands of such photographs and combine them, we shall get something like the electron cloud which shows that the electron is present in some particular region for longer time where the number of dots are more.



Electron Cloud.

So, we can say that probability of finding an electron at that particular region is maximum. The density of the charge cloud at any point corresponds to the probability density and is given by the square of wave function $|\psi|^2$.

The Born postulate for one-dimensional system is given by —

"If the wavefunction of a particle has a value ψ at any point x , the probability (P) of finding the particle between x and $x+dx$ (i.e. within the infinitesimal distance element dx) is proportional to $|\psi|^2 dx$. i.e."

$$P \propto |\psi|^2 dx \quad \dots \dots \text{(i)}$$

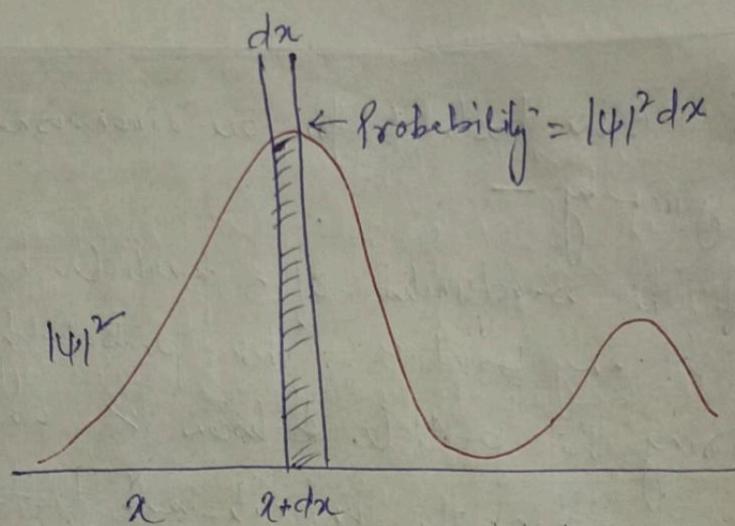
For a particle moving in a three dimensional space the wavefunction ψ at a point r is a function of (x, y, z) . Its probability, in terms of Born postulate is stated as —

If the wavefunction of a particle has a value ψ at some point r with coordinates (x, y, z) , the probability (P) of finding the particle between x and $x+dx$, y and $y+dy$ and z and $z+dz$ (i.e. within the volume element $d\tau = dx dy dz$) is proportional to $|\psi|^2 dx dy dz$. i.e.

$$P \propto |\psi|^2 dx dy dz = |\psi|^2 d\tau \dots \text{(ii)}$$

The probability $|\psi|^2$ is a real and non-negative quantity, but wave function ψ may be +ve, -ve or even complex.

(5) contd



The probability density $|ψ|^2$.

(4) Properties of Wave Function.

The Schrodinger equation is a second order differential equation and therefore, it has an infinite number of solutions, but only a few of these solutions have any physical or chemical significance.

The physical interpretation of $|ψ|^2 d\tau$ as a measure of the probability of finding a particle in the volume element $d\tau$ implies that it must obey certain mathematical conditions.

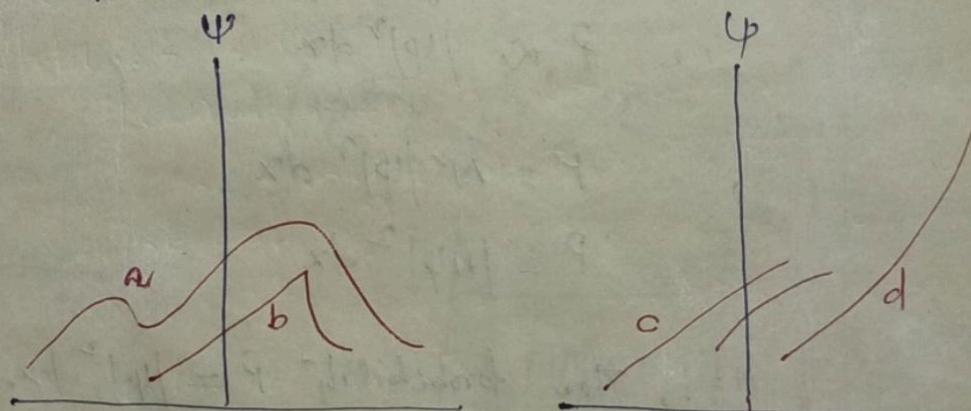
We require that

- (i) $ψ$ must be single valued
- (ii) $ψ$ and its first-derivative must be continuous.

(6)

(iii) Ψ must be finite for all physically possible values of x, y, z in the sense that $\int \Psi^* \Psi d\tau$ exists.

Ψ must be single-valued since the probability density of a particle at a point (x, y, z) must be unique. It cannot be infinite at any point, otherwise the probability density will be infinite. The requirement of continuity implies that there must not exist any sudden change in Ψ when the variables are changed. When a wave function satisfies these three conditions, the function is called a well-behaved function.

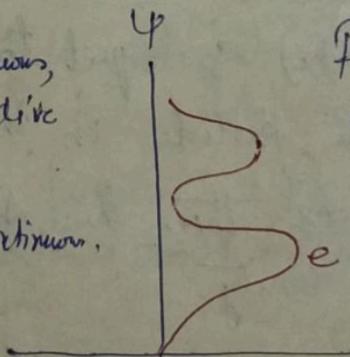


Function 'a' is continuous and its first derivative is also continuous.

Function 'b' is continuous, but its first derivative has a discontinuity.

Function 'c' is discontinuous.

Function 'd' approaches infinity and function 'e' is multivalued.



(5) contin.

(5) Normalised and Orthogonal Functions:

(a)

Let us consider the Schrodinger equation

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

If ψ is a solution of this equation, $N\psi$ is also a solution of the equation, where N is any constant factor. Since ψ occurs in every term of the Schrodinger equation, the multiplication by a constant factor does not affect the equation and wavefunction ~~is~~ anyway. This freedom to vary ψ by a constant factor makes it possible to convert proportionality sign into equality sign.

$$\text{r.e. } P \propto |\psi|^2 dx$$

$$\therefore P = N^2 |\psi|^2 dx$$

$$P = |N\psi|^2 dx \quad \text{--- (ii)}$$

If $N=1$, then probability $P = |\psi|^2 dx$ and

if $N \neq 1$, then $P = |N\psi|^2 dx$. If $|\psi|^2 dx$

($= \psi^* \psi dx$) is equal to the probability of finding the particle in the infinitesimal distance element dx , then the sum of such probabilities must be unity.

This can be expressed as

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1 \quad \dots \dots \dots \text{(iii)}$$

When a wave function satisfies the above relation, it is said to be normalised function. If $N \neq 1$, then ψ is not normalised. Since N is an arbitrary constant, we can choose its value in such a way that the total ~~prob~~ probability over the whole space becomes unity.

We assume $(N\psi)$ to be a normalised function. If the new function $(N\psi)$ is to be normalised it must meet the requirement

$$\int_{-\infty}^{\infty} (N\psi)^* (N\psi) \, dx = 1$$

or,

$$N^2 \int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

or,

$$N = \left[\frac{1}{\int_{-\infty}^{\infty} \psi^* \psi \, dx} \right]^{1/2} \quad \dots \dots \text{(iv)}$$

where N is called the normalisation constant. From the value of the integral in eqn(iv), we can find N which may be used to obtain the normalised function $(N\psi)$.

For three dimensional system, the condition for normalisation is

(x) conti-

$$\int_{-\infty}^{\infty} \psi^* \psi d\tau = 1 \quad [d\tau = \text{volume element}] \quad (v)$$

and the normalisation constant

$$N = \left[\frac{1}{\int_{-\infty}^{\infty} \psi^* \psi d\tau} \right]^{1/2} \quad (vi)$$

The normalisation condition (iii) implies that the particle is likely to be found in every region of a given volume, whatever may be the location of the region in space, and the sum of the probabilities of the particle in all the regions in space must be equal to 1.

(b) If ψ_i and ψ_j are the two acceptable wavefunctions of a given system then these functions are said to be mutually orthogonal if

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 0 \quad \text{if } i \neq j \quad (vii)$$

For three dimensional systems, it takes the form,

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau = 0, \quad i \neq j \quad (viii)$$

(8)

The orthogonality condition (viii) in terms of vector algebra means that the scalar product of the function-vectors ψ_i, ψ_j , vanishes. This is possible only if these vectors are completely independent of one another. Likewise in quantum mechanics, orthogonal functions are completely independent functions and one cannot be expressed in terms of others.

When ψ_i and ψ_j of a system satisfy the condition of orthogonality, i.e.

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau = 0, \quad i \neq j$$

and that of normalisation i.e.

$$\int_{-\infty}^{\infty} \psi_i^* \psi_i d\tau = 1, \quad i = j$$

then these functions are said to be orthonormal implying that the functions are normalised and at the same time also orthogonal.

(6) Translational Motion: A Free Particle.

By a free particle, we mean a particle of mass m , not under the action of any force. The potential energy of such a particle is taken to be zero for convenience and the total energy is therefore entirely kinetic. The Schrödinger equation for such a system in one-dimension is given by

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

This is a second-order linear differential equation and its general solution in exponential form is

$$\psi = A \exp\left[i\left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} x\right] + B \exp\left[-i\left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} x\right]$$

Substituting $\frac{8\pi^2 m E}{h^2} = k^2$, we get

$$\psi = A \exp(ikx) + B \exp(-ikx) \quad \dots \quad (ii)$$

where A and B are arbitrary constants. For the probability of finding a particle to remain finite as x goes to infinity, the necessary condition is that the energy, E must be positive. Otherwise, if $E < 0$, then the first term in (ii) will be infinite as x approaches minus infinity,

(7)

and the second term becomes infinite as x approaches plus infinity. Thus, the restriction on the energy of a free particle is

$$E > 0$$

Under such restrictions, the arbitrary constants A and B can now have any values. Therefore, for the free particle, energy is not quantised and it can have any value greater than zero, and the energy spectrum will be continuous. This conclusion is in agreement with the observed spectra of an atom.

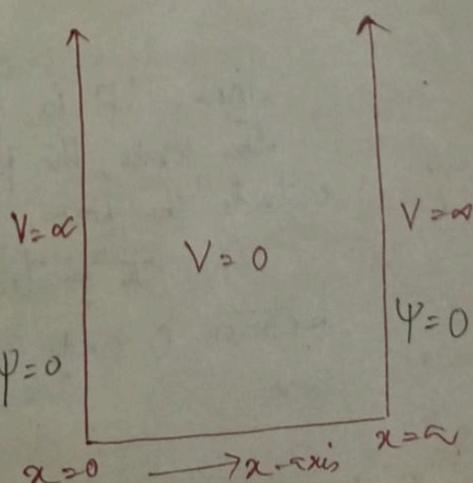
The dissociation of an electron from the atom and the radioactive emission of alpha rays and beta rays are some of the examples of free particles. Classically, the waves associated with the free particle are progressive in nature.

(7)

Translational Motion : A particle in ∞

One-dimensional Box

Let us consider a particle of mass m confined in a box of length a , and moving along the x -direction.



9) contd

The 'walls' of the box are formed by the potential barriers (which represent the regions of high potential energy). The potential energy V , at the boundaries (walls) is so high that the particle cannot escape. Therefore, the potential energy outside the box will be infinite but inside the box its value is zero.

Since the potential energy V , is infinite outside the box, the Schrodinger equation for this region will be

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (\Sigma - \infty) \psi = 0 \quad \dots \dots \text{(i)}$$

$[\because V = \infty]$

For finite values of energy Σ , we can write

$$\frac{d^2\psi}{dx^2} = \infty \psi \quad \dots \dots \text{(ii)}$$

$$\text{or, } \psi = \frac{1}{\infty} \frac{d^2\psi}{dx^2} = 0 \quad \dots \dots \text{(iii)}$$

Thus, ψ is zero at all points outside the box. In other words, the particle cannot be found at all outside the box, because $\psi^* \psi$ is zero.

For the particle inside the box, x lies between 0 and a , and the potential energy V , is zero.

(10)

Therefore, the Schrodinger equation for the particle inside the box will be

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

Let-

$$k^2 = \frac{8\pi^2 m}{h^2} E \quad \dots \dots \quad (v)$$

where k is a constant, and is independent of x .

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

The general solution of this equation is

$$\psi = A \sin kx + B \cos kx \quad \dots \dots \quad (vii)$$

Since A and B are arbitrary constants, we shall have infinite number of solutions. But only those solutions which satisfy the appropriate boundary conditions should be considered as acceptable.

The boundary conditions for this problem are,

ψ is zero at $x=0$ and $x=L$.

Thus, at the point $x=0$, eqn (vii) becomes,

$$0 = A \sin k \cdot 0 + B \cos k \cdot 0$$

$$= B$$

$$\therefore B = 0$$

As a result of this boundary condition, eqn (vii) reduces to,

$$\psi = A \sin kx \quad \dots \dots \quad (viii)$$

(10) contd.

At the other wall, i.e. at $x = a$, the wave function ψ must again go to zero. Therefore, at that, the wave function ψ becomes

$$0 = A \sin k a$$

either, $A = 0$ or $\sin k a = 0$

If $A = 0$, then the wavefunction ψ will be zero everywhere and this is not an acceptable solution. Therefore,

$$\sin k a = 0 = \sin n \pi$$

$$\therefore k a = n \pi$$

$$\therefore k = \frac{n \pi}{a} \quad \dots \dots \quad (ix)$$

where n is an integer, having values $0, 1, 2, \dots$

Therefore, the wavefunction for the particle inside the box becomes

$$\psi_n = A \sin \left(\frac{n \pi}{a} x \right) \quad \dots \dots \quad (x)$$

Substituting the value of k from eqn (ix) in eqn (v), the translational kinetic energy of the particle is given by

$$E_n = \frac{n^2 h^2}{8 m a^2} ; \quad n = 1, 2, \dots \quad \dots \dots \quad (xi)$$

As a result of boundary conditions, the energy (xi) is restricted to a quantised value. Thus, we find quantization of energy is a consequence of the boundary conditions.

Since a particle is assumed to be always present inside the box, the lowest energy of a particle in a box is obtained by substituting $n=1$ in eqn (xi) and this energy is known as the zero point energy.

$$\therefore E_{\text{zero-point}} = \frac{\hbar^2}{8ma^2} \quad (\text{xii})$$

We know that a classical particle has zero kinetic energy at 0K , at its lowest energy state. However, quantum mechanically, the minimum kinetic energy is taken as $\frac{\hbar^2}{8ma^2}$. This is explained as follows —

(i) Firstly, this is in accordance with the uncertainty principle, $\Delta x \Delta p_x \geq \frac{\hbar}{4\pi}$. If the energy is zero, then momentum becomes exactly zero. Under such condition, the uncertainty in position becomes infinite. But since the particle is inside the box, the maximum uncertainty in position can never be greater than the length, a , of the box. Hence the energy cannot be zero even at the lowest energy state.

(ii) Secondly, if $E=0$, then $k^2=0$ and consequently, $\psi = A \sin kx = 0$ everywhere within the box. This means that the probability density $|\psi|^2$ is also zero everywhere and there

(1) contd...

exist no state at all. This goes against our initial assumption that the particle lies inside box. Hence $E = 0$ is not acceptable.

Factors Influencing the Energy

(a) Considering eqn (xi), we find the translational kinetic energy E_N decreases as the length a of the box increases and as $a \rightarrow 0, E \rightarrow \infty$. The energy difference between two successive energy levels is

$$\Delta E = E_{n+1} - E_n = \frac{(2n+1)h^2}{8ma^2} \quad \text{--- (xi)}$$

As 'a' increases and becomes large, this difference becomes negligible. The particle may then treated as a free particle whose energy is not quantised, but continuous. Since E is small, the translational energy of an atom or a molecule is found to be quantised.

(b) The second factor which influences the energy or energy difference ΔE is the mass of the particle. Thus, if a small particle like electron is confined to a box of atomic dimensions, then ΔE is appreciable and is quantised. But for a particle of large mass moving in a space of large dimension, then E or ΔE is negligibly small to be detected. Hence such particle will not have quantised energy value.

(12)

Normalization of the Wave function.

The value of constant A is calculated by normalising the wavefunction Ψ . The probability that the particle is somewhere between $x=0$ and $x=a$ is unity because at all the times, it is somewhere in the box.

Therefore,

$$\int_0^a \Psi_n^* \Psi_n dx = \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$$

$$\text{But } \sin^2 \frac{n\pi x}{a} = \frac{1}{2} \left(1 - \cos \frac{2n\pi x}{a} \right)$$

$$\text{So, } \int_0^a \Psi_n^* \Psi_n dx = A^2 \left[\frac{1}{2} \int_0^a dx - \frac{1}{2} \int_0^a \cos \frac{2n\pi x}{a} dx \right] \\ = A^2 \left[\frac{a}{2} - 0 \right] = 1 \\ A = \left(\frac{2}{a} \right)^{1/2} \quad \dots \quad (\text{iv})$$

Thus, the normalised wavefunction of a particle in a one-dimensional box is given by

$$\Psi_n = \left(\frac{2}{a} \right)^{1/2} \sin \frac{n\pi x}{a} \quad \dots \quad (\text{v})$$

Orthogonality of the wavefunctions:

Ψ_n represents a whole set of wavefunctions, each characterised by a particular value of energy and quantum number n . Let us consider two different wavefunctions Ψ_i and Ψ_j

(12) conti--

corresponding to two different states of a particle in a box. Then the integral,

$$\int_0^a \psi_i^* \psi_j dx = \int_0^a \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{m_i \pi x}{a}\right) \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{m_j \pi x}{a}\right) dx$$

$$\text{Let } \frac{\pi x}{a} = \mu \quad \therefore dx = \left(\frac{a}{\pi}\right) d\mu$$

$$\mu = 0 \text{ when } x=0, \quad \mu = \pi \text{ when } x=a$$

$$\therefore \int_0^a \psi_i^* \psi_j dx = \left(\frac{2}{a}\right) \int_0^\pi \sin(x_i \mu) \cdot \sin(x_j \mu) d\mu \left(\frac{a}{\pi}\right)$$

$$\text{Since, } \sin x_i \mu \cdot \sin x_j \mu = \frac{1}{2} [\cos(x_i - x_j) \mu - \cos(x_i + x_j) \mu]$$

$$\begin{aligned} \therefore \int_0^a \psi_i^* \psi_j dx &= \frac{2}{a} \cdot \frac{a}{\pi} \cdot \frac{1}{2} \left[\int_0^\pi \cos(x_i - x_j) \mu d\mu \right. \\ &\quad \left. - \int_0^\pi \cos(x_i + x_j) \mu d\mu \right] \\ &= \frac{1}{\pi} \left[\frac{1}{(x_i - x_j)} \sin(x_i - x_j) \mu - \frac{1}{(x_i + x_j)} \sin(x_i + x_j) \mu \right]_0^\pi \end{aligned}$$

[since $\sin n\pi = 0$, for integral values of n] (xvi)

Thus, we have, $\int_0^a \psi_i^* \psi_j dx = 0$; $i \neq j$... (xvii)

The wavefunctions for different states of the system are thus orthogonal to each other and in general, solutions of the Schrodinger equation

(13)

for a system corresponding to different energy values are always orthogonal. Both the normalised and the orthogonal character of a set of wavefunction can be combined by writing -

$$\int \psi_i^* \psi_j dx = \delta_{ij} \quad \dots \quad (\text{Kronecker Delta})$$

where δ_{ij} is called the Kronecker Delta and is defined by

$$\delta_{ij} = 0, \text{ when } i \neq j$$

$$\delta_{ij} = 1, \text{ when } i = j$$

Therefore, the wavefunctions are orthonormal.

Probability of finding the particle

Classically, the probability of finding a particle is the measure of the time spent by the particle at a certain location, which is, in turn, the measure of the velocity of the particle. The particle will travel from one end of the box to the other end with uniform velocity. Hence the probability of finding a particle is uniform throughout the box.

Quantum mechanically, the probability of finding a particle $P(x)$ over an infinitesimal distance is given by

(b) contd.

$$P(x) = \left|4\eta\right|^2 dx \\ = \left(\frac{2}{a}\right) \sin^2 \frac{n\pi x}{a} dx$$

and the probability density

$$\left|4\eta\right|^2 = \frac{2}{a} \sin^2 \frac{n\pi x}{a} \quad \text{--- (ix)}$$

For this probability density to be maximum,

$$\frac{\sin^2 \frac{n\pi x}{a}}{a} \text{ must be equal to 1.}$$

This is possible only if

$$\sin^2 \frac{n\pi x}{a} = \sin^2 \left(n' + \frac{1}{2}\right)\pi, \quad n' = 0, 1, 2$$

$$\text{or, } \frac{n\pi x}{a} = \frac{(2n'+1)}{2}\pi$$

$$x = a \left(\frac{2n'+1}{2n}\right)$$

That is, at $x = \frac{a}{2n}, \frac{3a}{2n}, \frac{5a}{2n}, \frac{7a}{2n}$, etc. $P(x)$ is

maximum.

Hence for a state $\eta=1$, the most probable position of the particle is $\frac{a}{2}$, because the next higher positions are outside the box.

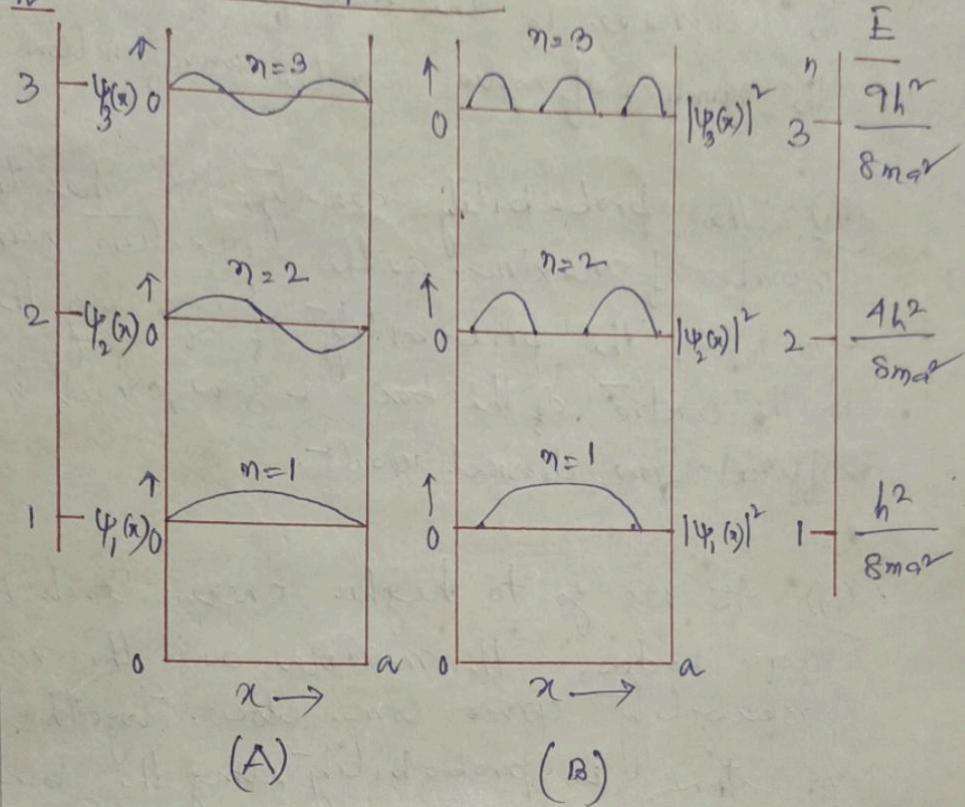
For $\eta=2$, the most probable positions are at $x = \frac{a}{4}, \frac{3a}{4}$

$$\eta=3, \quad x = \frac{a}{6}, \frac{3a}{6}, \frac{5a}{6}$$

$$\eta=4, \quad x = \frac{a}{8}, \frac{3a}{8}, \frac{5a}{8}, \frac{7a}{8}$$

(14)

Graphical Interpretation

(A) Wavefunction ψ

(B) Probability density function $|\psi|^2$ for the lowest three energy levels of a particle in a box.

From the examination of these graphs, it is found that

- (i) The wavefunctions are alternately symmetrical and antisymmetrical with respect to the reflection from a mirror placed at the centre of the box.
- (ii) Besides the points at the boundaries of the box, there are points inside the box where wavefunction is zero. These points are called nodes. With

(i) contd -

The increase in the value of quantum number,
the number of nodes on the wavefunction increases.

(ii). The probability density, $|\Psi|^2$ has the same number of maxima as the quantum number n . For $n=2$, the probability of finding the particle in the centre of the box is zero, which is quite different from classical result.

(iv) As we go to higher energy levels with more nodes, the maxima and the minima of probability curves come closer together and the variations in probability along the box ultimately becomes undetectable. For higher quantum numbers, we approach the classical results of uniform probability density. This is in agreement with the Bohr Correspondence principle.

According to this principle, the quantum mechanical results must be equal to that of classical mechanics when the quantum number describing the system becomes very large.

For macroscopic bodies, quantum mechanics give the same results as classical mechanics.

[An ~~as~~ electron bound to an atom is similar to a particle in a one-dimensional box].