Chapter – III : Applications of Quantum Mechanics :-

Unit – III

Introduction :-

The problem of motion of particle on atomic scale is studied in quantum mechanics by solving schrodinger wave eqn. In this chapter schrodinger wave equation and its various forms, which are required to describe particles motion under different constraints are presented along with various necessary concepts like expectation values, operators etc. Quantum mechanical treatement is employed to solve the problem of particle moving in a one and three dimensional box. Further the problem of harmonic oscillator is discussed.

The particle in one dimensional box : Energy quantization :-

The problem of a particle bounding back and forth between the walls of a box is solved in this article as an application of quantum mechanics. steady state schrodinger equation is set for the particle such that its solution satisfies all existing boundary conditions. schrodinger equation is solved to know the solution and possible energy eigen values of the particle in the box.

Let us consider that the motion of freely moving particle of mass m along x-axis is restricted in the region or box formed by walls at $x = 0$ and $x = a$, it is assumed that there is no energy loss even after it colloids with wall of box. Thus total energy of the particle is constant within the box. It is obvious that in present situation, potential energy is infinite on both sides of the box, while V is constant say zero inside region of the box is shown in fig.

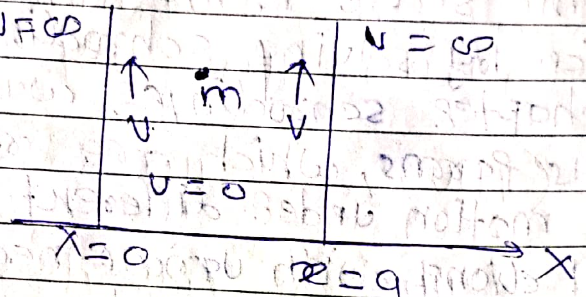


Fig ① : particle in a box

i.e –

$V(x) = \infty$; for $x \leq 0$ and $x \geq a$
$V(x) = 0$; for $0 \leq x \geq a$ } – ①

The motion of particle is limited to region inside the box, the value of wave function ψ is zero. In region outside the box. i.e – $\psi = 0$. in region for which $x \leq 0$ or $x \geq a$. since the particle cannot have infinite energy, so we may restrict our problem to find wave function ψ of a particle moving in box with finite energy.

The schrodinger steady state form for the particle is given by

$$\nabla^2\psi + \frac{2m}{\hbar^2}[E-V]\psi = 0 \quad \text{--- (ii)}$$

But Here only x-axis

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}[E-V]\psi = 0 \quad \text{--- (iii)}$$

Applying boundary condition from eqn ①

i.e $V(x) = 0$, for $0 \leq x \geq a$, we have.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad --- \text{(iv)}$$

since ψ is function of x only in this problem $\frac{\partial^2 \psi}{\partial x^2}$ may be replaced by $\frac{d^2\psi}{dx^2}$; this, eqn (iv) becomes.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad --- \text{(v)}$$

Let $\frac{2mE}{\hbar^2} = k^2$, then eqn (v) changes to.

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

The soln of eqn (vi) is of the form of $\sin kx$ or $\cos kx$. The general soln is given by.

$$\psi(x) = A \sin kx + B \cos kx \quad -- \text{(vii)}$$

where A and B are constants. The values of these constants can be obtained by applying the boundary condition of the problem. The particle cannot penetrate the walls. hence $\psi = 0$ at $x = 0$ and $\psi = 0$ at $x = a$. These are the boundary condition. Applying these conditions, we have.

$$0 = A \sin 0 + B \cos 0, \text{ ie.}$$

$$\psi(x) = A \sin kx \qquad \text{ie } B = 0.$$

$$0 = A \sin ka$$

$\therefore \psi(x) = 0$ when $x = a$

Here, either $A = 0$ or $\sin ka = 0$ but because if $A = 0$, the entire function will zero as $B = 0$.

$$\therefore \sin ka = 0 \quad \text{or}$$

$$\therefore ka = n\pi \quad [n, 0, 1, 2, 3, \ldots]$$

$$K = \frac{n\pi}{a} \quad \text{--- (viii)}$$

From eqn (vii) and (viii), we get

$$k^2 = \frac{n^2\pi^2}{a^2}$$

$$\& \; k^2 = \frac{2mE}{\hbar^2} \quad \therefore k = \frac{\sqrt{2mE}}{\hbar}$$

$$\therefore \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$\boxed{E = \frac{n^2\pi^2\hbar^2}{2ma^2}} \quad \text{--- (ix)}$$

$$\text{or } \hbar = h/2\pi \quad \therefore \hbar^2 = \frac{h^2}{4\pi^2}$$

$$\therefore E = \frac{n^2\pi^2 h^2}{8\pi^2 ma^2} = \frac{n^2h^2}{8ma^2}$$

$$\boxed{\therefore E = \frac{n^2h^2}{8ma^2}} \quad \text{--- (x)}$$

This equation (x) implies that the energy of the particle can have only certain values which are known as eigen values. These are specified represented as E_n instead of E.

The integer n corresponding to energy eign value E_n is called as its quantum number. It may be also noted that the particle in box cannot have zero energy. This result is arisen due to fact that the wave function is finite and exist some where in box at all time. If the particles have zero energy then the wave function ψ would be zero everywhere in the box. Therefore energy of particle in box is quantised.

⊛ The particle in a box : wave function and momentum quantization :-

The constant A of eqn (viii) i.e.

$$k = \frac{n\pi}{a} \quad \text{--- (I)}$$

Now the wave function becomes.

$$\psi(x) = A \sin kx$$

$$\therefore \psi(x) = A \cdot \sin \frac{n\pi x}{a} \quad \text{--- (II)}$$

Now applying this normalization condition is -

$$\int_0^a |\psi(x)|^2 dx = 1$$

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

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

$$A^2 \int_0^a \frac{1}{2}\left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right] \cdot dx = 1$$

$$\frac{A^2}{2}\left[x - \frac{a}{2\pi n}\sin\frac{2n\pi x}{a}\right]_0^a = 1$$

$$\frac{A^2 a}{2} = 1 \quad \text{or} \quad A^2 = \frac{2}{a}$$

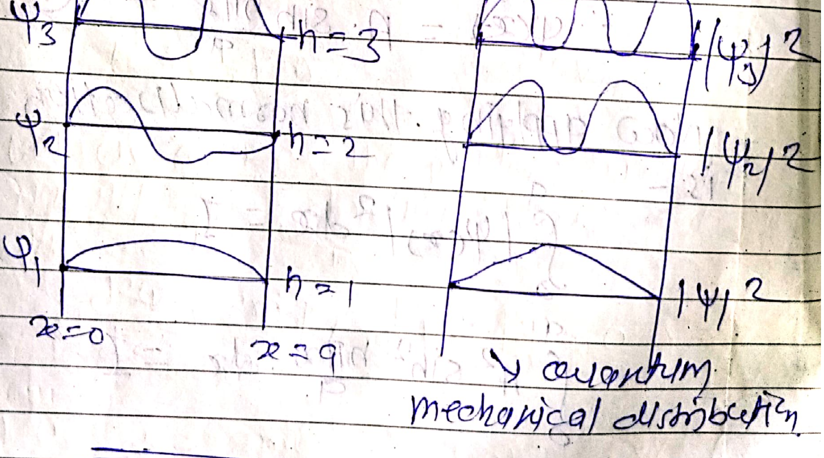
$$A = \sqrt{2/a} \quad \text{--- (iii)}$$

put this value in eqn (ii), we get

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}}\cdot\sin\frac{n\pi x}{a}} \quad \text{--- (iv)}$$

eqn (iv) gives the wave function of the particle enclosed in infinite deep potential well.

The normalised wave functions ψ_1, ψ_2 & ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$ & $|\psi_3|^2$ are plotted in figure (2)



∴ momentum -

$$\Delta p\cdot\Delta x \geq h/2\pi \qquad [\because \Delta x = a]$$

$$\Delta p \geq \frac{h}{2\pi a}$$

$$\Delta E = \frac{\Delta p^2}{2m} \geq \frac{h^2}{8\pi^2 m a^2}$$

The Harmonic oscillator :-

From classical mechanics, we know that when restoring force acting on particle is directly proportional to the displacement of the particle, the particle executes simple harmonic motion. Examples are the small amplitude oscillation of a pendulum, vertical oscillation of a mass supported by an ideal spring, atoms in molecules and crystals, etc. The importance of this particular force law extends far beyond such simple cases. So we consider the problem of linear harmonic oscillator quantum mechanically. For simple harmonic motion.

$$f(x) \propto x$$

$$f(x) = -Kx \quad \text{--- (i)}$$

where K is constant know as force per unit displacement. Again -

$$f(x) = ma = m\frac{d^2x}{dt^2} \quad \text{--- (ii)}$$

From eqn (i) & (ii), we get

$$m\frac{d^2x}{dt^2} = -Kx$$

$$\therefore m\frac{d^2x}{dt^2} + Kx = 0$$

$$\frac{d^2x}{dt^2} + \frac{K}{m}x = 0 \quad \text{--- (iii)}$$

This is classical eqn of S.H.M. The potential energy function $V(x)$ is given by -

$$f(x) = -Kx = -\frac{dV(x)}{dx}$$

$$dV(x) = Kx \cdot dx$$

on integration, we get.

$$V(x) = \frac{1}{2}kx^2 \quad --- (iv)$$

The plot of V Vs x is a parabola as shown in figure.

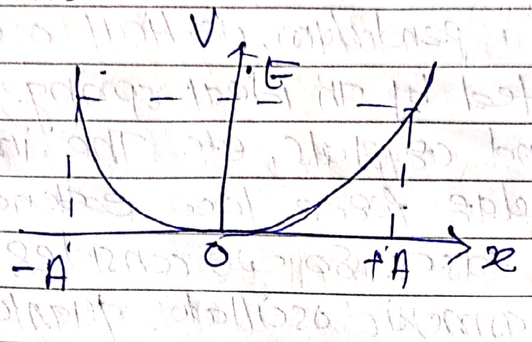


Fig (2)

Now the particle may be described in parabolic potential well. If E be the total energy of the particle then the particle oscillates back and forth between - $x = -A$ and $x = +A$, The amplitude A is determined by energy E, such that.

$$E = \frac{1}{2}kA^2 \quad --- (v)$$

Let us consider the problem quantum mechanically. The schrodinger wave eqn of harmonic oscillator is -

$$\frac{d^2\varphi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]\varphi = 0$$

(iii)

Let us $\alpha = \frac{2mE}{\hbar^2}$ and $\sqrt{\frac{mk}{\hbar^2}} = \beta$ — (vi)

$$\frac{d^2\varphi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{\cancel{2}m}{\hbar^2}\cdot\frac{1}{\cancel{2}}kx^2\right)\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \frac{mk}{\hbar^2} x^2\right]\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} + (\alpha - \beta^2 x^2)\varphi = 0 \quad \text{---} (vii)$$

Let us introduce a dimensionless independent variable ξ such that.

$$\xi = \sqrt{\beta}\cdot x \qquad \therefore x = \frac{\xi}{\sqrt{\beta}}$$

$$\frac{d^2}{dx^2} = \beta \frac{d^2}{d\xi^2} \quad \text{---} (viii)$$

put this value in eqn (vii), we get

$$\beta \cdot \frac{d^2\varphi}{d\xi^2} + \left(\alpha - \beta^2 \frac{\xi^2}{\beta}\right)\varphi = 0$$

$$\boxed{\frac{d^2\varphi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\varphi = 0} \quad \text{---} (ix)$$

The solution of eqn (ix) can be expressed in terms of Hermite polynomial $H_n(\xi)$

The general soln of eqn (ix) is -

$$\varphi(\xi) = C H_n(\xi) e^{-\xi^2/2} \quad \text{----} (x)$$

The soln is acceptable only for $n = 0, 1, 2 ...$
The restriction on n gives a corresponding restriction on E. In this case, we have -

$$\frac{\alpha}{\beta} = (2n+1)$$

$$\frac{2mE/\hbar^2}{\sqrt{2m/\hbar^2}} = (2n+1) = 2\left(n+\frac{1}{2}\right)$$

$$\frac{2mE}{\hbar^2 \times \frac{\sqrt{mk}}{\hbar}} = 2\left(n+\frac{1}{2}\right)$$

$$E = \left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}} \quad \text{--- (xi)}$$

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad \text{--- (xii)}$$

This frequency of oscillator.

$$\therefore E = \left(n+\frac{1}{2}\right)\hbar\omega \quad \text{--- (xiii)}$$

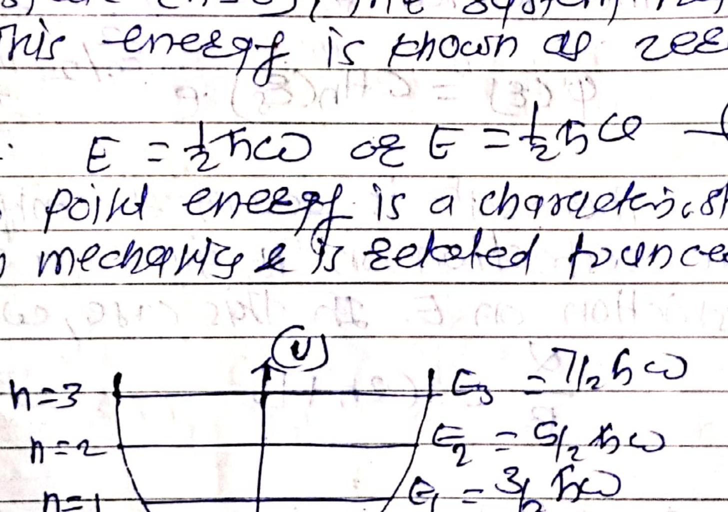
where $n = 0, 1, 2, ----$

eqn (xiii) shows that wave mechanical oscillator can take only certain discrete energies separated by intervals $\hbar\omega$, where ω is the frequency of classical oscillator and h is plancks constant.

The energy levels of harmonic oscillator according to quantum mechanics are shown in figure (2). The energy levels are equally spaced & quantised. It is obvious that even in the lowest state ($n=0$), the system has energy ($\frac{1}{2}\hbar\omega$). This energy is known as zero point energy.

$$\therefore E = \frac{1}{2}\hbar\omega \text{ or } E = \frac{1}{2}\hbar\omega \quad \text{--- (xiv)}$$

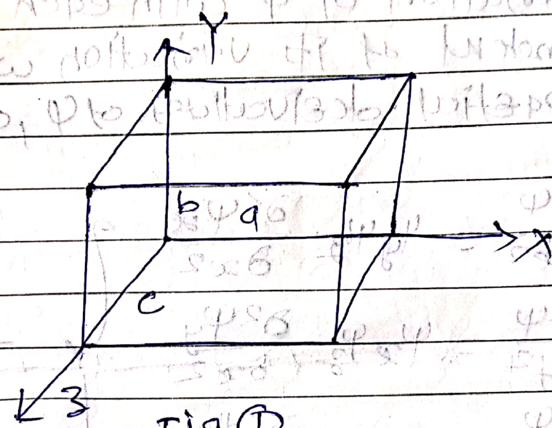
Zero point energy is a characteristic of quantum mechanics & is related to uncertainty principle.



Fig(2): Energy levels of linear Harmonic oscillator

The particle in a Three dimensional :-

Let us consider the case of a single particle i.e. a gas molecule of mass m, confined within a rectangular box with edges parallel to X, Y, & Z axes as shown in fig (1). Let the sides of rectangular box be a, b and c respectively. The particle can move freely within the region $0<x<a$, $0<y<b$ and $0<z<c$ i.e inside the box where potential V is zero as shown in figure (1)



(2)

Fig (1)

[∵ a = b = c]

$$\left.\begin{aligned} V(x,y,z) &= 0 \quad 0<x<a \\ V(x,y,z) &= 0 \quad 0<y<a \\ V(x,y,z) &= 0 \quad 0<z<a \end{aligned}\right\} \quad \text{--- (1)}$$

The potential rises suddenly to have large value at the boundaries i.e the potential outside the box is infinite.

The schrodinger wave equation inside the box is :-

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}E\psi = 0 \quad \text{--- (2)}$$

Thus, the wave function ψ represents motion in three-dimensional. Hence ψ is function of three variable x, y, z i.e

$$\psi = \psi(x,y,z) \quad \text{--- (3)}$$

If ψ_x, ψ_y & ψ_z are three independent wave functions representing particle's motion along x, y, & z directions. Then ψ in three dimensions can be represented as product of ψ_x, ψ_y & ψ_z.

i.e. $\psi(x,y,z) = \psi_x(x)\,\psi_y(y)\,\psi_z(z)$ --- (4)

or simply $\psi = \psi_x \psi_y \psi_z$. ——— (4)

The variation of ψ with each co-ordinates is independent of its variation with the others. Taking partial derivatives of ψ, we get.

$$\left.\begin{aligned}\frac{\partial^2\psi}{\partial x^2} &= \psi_y\psi_z \cdot \frac{\partial^2\psi_x}{\partial x^2}\\ \frac{\partial^2\psi}{\partial y^2} &= \psi_x\psi_z \cdot \frac{\partial^2\psi_y}{\partial x^2}\\ \frac{\partial^2\psi}{\partial z^2} &= \psi_x\psi_y \cdot \frac{\partial^2\psi_z}{\partial z^2}\end{aligned}\right\} \text{——— (5)}$$

Now we substitute these partial derivatives together with values of ψ in eqn (2) and obtain.

$$\psi_y\psi_z \frac{\partial^2\psi_x}{\partial x^2} + \psi_x\psi_z \frac{\partial^2\psi_y}{\partial y^2} + \psi_x\psi_y \cdot \frac{\partial^2\psi_z}{\partial z^2} + \frac{2mE}{\hbar^2}\psi_x\psi_y\psi_z = 0 \text{ --- (6)}$$

Dividing through by $\psi_x\psi_y\psi_z$, we get

$$\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} + \frac{1}{\psi_y}\cdot\frac{\partial^2\psi_y}{\partial y^2} + \frac{1}{\psi_z}\cdot\frac{\partial^2\psi_z}{\partial z^2} + \frac{2mE}{\hbar^2} = 0$$

——— (7)

Let $\frac{2mE}{\hbar^2} = k_x^2 + k_y^2 + k_z^2$ ——— (8)

Therefore eqn (7) becomes.

$$\therefore \frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2}+\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2}+\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2}+k_x^2+k_y^2+k_z^2=0$$

$$\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2}+\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2}+\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2}=-k_x^2-k_y^2-k_z^2 \quad \text{--- (9)}$$

since terms on LHS seperately varies with independent variables x, y & z respectively and therefore can be equated to respective constant terms on RHS. Thus we have three eqn as–

$$\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2}=-k_x^2 \quad \text{--- (10a)}$$

$$\frac{1}{\psi_x}\frac{\partial^2\psi_y}{\partial y^2}=-k_y^2 \quad \text{--- (10b)}$$

$$\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2}=-k_z^2 \quad \text{--- (10c)}$$

$$\therefore \frac{\partial^2\psi_x}{\partial x^2}=-k_x^2\psi_x$$

$$\therefore \frac{\partial^2\psi_x}{\partial x^2}+k_x^2\psi_x=0 \quad \text{--- (11a)}$$

$$\text{–lly.}\quad \frac{\partial^2\psi_y}{\partial y^2}+k_y^2\psi_y=0 \quad \text{--- (11b)}$$

$$\&\quad \frac{\partial^2\psi_z}{\partial z^2}+k_z^2\psi_z=0 \quad \text{--- (11c)}$$

The general soluation of eqn (11a) will be a sine function of the orbitary amplitude, frequency and phase ie.

$$\psi_{(x)}=A.\sin(Bx+C) \quad \text{--- (12)}$$

where A, B & C are constant whose values are determined boundary condition.

The probabiluty of finding the partical at the walls will be zero ie.

$$|\psi_x|^2=0 \quad \text{when } x=0 \;\&\; x=a$$

$\psi(x) = 0$ when $x = 0$ & $x = a$

Using these boundary condition in eqn (12), we have.

$$0 = A \sin(0 + c) \quad \text{i.e. } A \neq 0$$

$$\therefore \sin c = 0 \quad \& \quad 0 = A \sin(Ba + c)$$

$$\therefore \sin Ba = 0 \quad \text{or} \quad Ba = n_x \pi$$

$$B = \frac{n_x \pi}{a}$$

where n_x is a positive integer.

$$\psi(x) = A \sin \frac{n_x \pi x}{a} \quad \text{---} (13)$$

Now Applying the normalization condition between $x = 0$ to $x = a$, we have.

$$\int_0^a |\psi(x)|^2 . dx = 1$$

$$\int_0^a \left| A \sin \frac{n_x \pi x}{a} \right|^2 . dx = 1$$

$$A^2 \int_0^a \sin^2\left(\frac{n_x \pi x}{a}\right) . dx = 1$$

$$\therefore A^2 \frac{a}{2} = 1 \quad \text{or} \quad A = \sqrt{\frac{2}{a}}$$

$\therefore$ put this value in eqn (13), we get

$$\psi(x) = A \sin \frac{n_x \pi x}{a}$$

$$\psi(x) = \sqrt{\frac{2}{a}} . \sin \frac{n_x \pi x}{a} \quad \text{---} (14)$$

$||^y$

$$\psi(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \quad \text{---} (15)$$

$$\psi_z(z) = \sqrt{\frac{2}{c}}\ \sin\frac{n_z \pi c}{c} \quad \text{--- (16)}$$

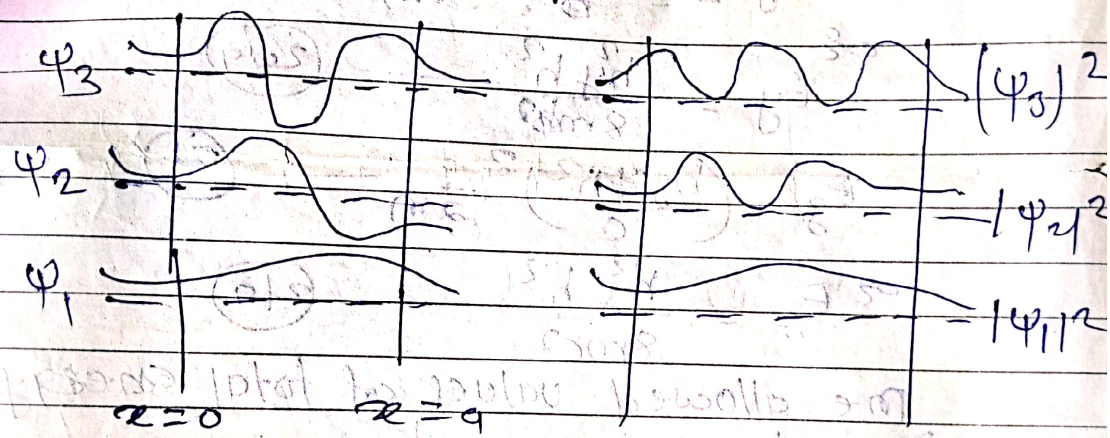
The complete wavefunction $\psi_x \psi_y \psi_z$ has the form

$$\psi(x,y,z) = \sqrt{\frac{2}{a}}\ \sin\frac{n_x \pi x}{a}\ \sqrt{\frac{2}{b}}\ \sin\frac{n_y \pi y}{b}$$

$$\sqrt{\frac{2}{c}}\ \sin\frac{n_z \pi c}{c}$$

$$= \frac{2\sqrt{2}}{\sqrt{abc}}\ \sin\frac{n_x \pi x}{a}\ \sin\frac{n_y \pi y}{b}\ \sin\frac{n_z \pi c}{c} \quad \text{--- (17)}$$

The wavefunction of a particle in finite box and its probability are shown in fig (2)



From eqn (14), we have.

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\left(\frac{n_x \pi}{a}\right)^2 \sqrt{\frac{2}{a}}\ \sin\frac{n_x \pi x}{a}$$

$$= -\left(\frac{n_x \pi}{a}\right)^2 \psi(x) \quad \text{--- (18)}$$

substituting the value of eqn (18) in eqn (119), we have.

$$-\left(\frac{n_x \pi}{a}\right)^2 \psi(x) + k_x^2 \psi(x) = 0$$

$$\text{since } k_x^2 = \frac{2mE_x}{\hbar^2}$$

$$\therefore -\left(\frac{n_x\pi}{a}\right)^2\psi(x) + \frac{2mE_x}{\hbar^2}\psi(x) = 0$$

$$-\left(\frac{n_x\pi}{a}\right)^2\psi(x) = -\frac{2mE_x}{\hbar^2}\psi(x) = 0$$

$$\therefore E_x = \frac{\hbar^2}{2m}\left(\frac{n_x\pi}{a}\right)^2$$

$$E_x = \left(\frac{n_x\pi\hbar}{a}\right)^2 \cdot \frac{1}{2m} \quad \text{--- (19)}$$

or. $$E_x = \frac{n_x^2 h^2}{8ma^2} \quad \text{--- (19a)}$$

Hly.

$$E_y = \left(\frac{n_y\pi\hbar}{b}\right)^2 \cdot \frac{1}{2m} \quad \text{--- (20)}$$

or

$$E_y = \frac{n_y^2 h^2}{8mb^2} \quad \text{--- (20a)}$$

$$E_z = \left(\frac{n_z\pi\hbar}{c}\right)^2 \cdot \frac{1}{2m} \quad \text{--- (21)}$$

or $$E_z = \frac{n_z^2 h^2}{8mc^2} \quad \text{--- (21a)}$$

The allowed values of total energy are given by -

$$E = E_x + E_y + E_z$$

$$E = \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \quad \text{--- (22a)}$$

or

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \quad \text{--- (23)}$$

where n_x, n_y, n_z denote any set of three positive numbers.

When the box is a cube i.e. $a = b = c$ then

$$E = \frac{\hbar^2\pi^2}{2ma^2}\left[n_x^2 + n_y^2 + n_z^2\right] \quad \text{--- (24)}$$

or

$$E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right] \quad \text{--- (25)}$$

with $n_x, n_y, n_z = 1, 2, 3, \ldots$

The end