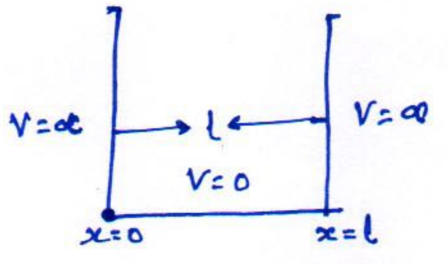
Solution of Schrödinger Wave equation for System

i.e "Particle in a One Dimensional Box."

This quantum mechanical Problem " Particle in a one dimensional Box represents translational motion. Here a particle of mass m is Confined to move in a One dimensional box of length l.

Let the Potential energy is inside everywhere in the box is Zero. While Out side the box the Potential energy is infinity. It is also assumed that the Particle is executing motion along X-axis.



The Schrödinger Wave equation for the particle inside the box may be written as,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{——} (1)$$

Inside Box V=0, eqn (1) may be written as

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

$$\text{or,} \quad \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad \text{——} (2)$$

Let $\frac{8\pi^2 m}{h^2}E = K^2$, where K^2 is a Constant independent of x.

Now eqn (2) may be written as.

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \quad \text{——} (3)$$

The solution of the equation (3) is

$$\psi(x) = A\sin Kx + B\cos Kx \quad \text{——} (4)$$

where A and B are Constants

From boundary Conditions, we have.

$\psi = 0$ at $x = 0$ and $x = l$

On Substituting the value in equation (4) we have

$$0 = A\times 0 + B\times 1$$

i.e $0 = B$ or $B = 0$

If $B = 0$, eqn (4) is as

$$\psi(x) = A\sin Kx \quad \text{——} (5)$$

On putting $\psi = 0$ and $x = l$ in equation (5) we have

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

$$0 = A \sin kl$$

Since A cannot be zero,

so, $\sin kl = 0$

or $kl = n\pi$

$$k = \frac{n\pi}{l} \quad \text{Where } n = 0, 1, 2, 3, 4 \ldots \quad (6)$$

Thus $n = 0$ is allowed but not acceptable since it will make ψ zero, everywhere inside the Box, so, the acceptable solution of equation (3) are

$$\psi_n(x) = A \sin \frac{n\pi x}{l} \quad \text{Where } n = 1, 2, 3 \ldots \quad (7)$$

Normalisation of the Wavefunction $\psi_n(x)$:—

We know from the condition of normalisation, we have,

$$\int_0^l \psi_n^2(x)\,dx = 1$$

or $$\int_0^l A^2 \sin^2 \frac{n\pi x}{l}\,dx = 1$$

or, $$A^2 \int_0^l \sin^2 \frac{n\pi x}{l}\,dx = 1$$

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

or, $$A^2 \int_0^l \frac{1}{2}\left(1 - \cos 2\frac{n\pi x}{l}\right) dx = 1$$

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

or, $$A^2 \left[\frac{l}{2} - 0\right] = 1$$

or, $$A^2 = \frac{2}{l}$$

or $$A = \sqrt{\frac{2}{l}}$$

Thus the normalised wavefunction for the Particle inside One dimensional Box is

$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \quad \text{———} \quad (8)$$

Where $n = 1, 2, 3 \ldots$

Energy of the Particle in One-dimensional Box —

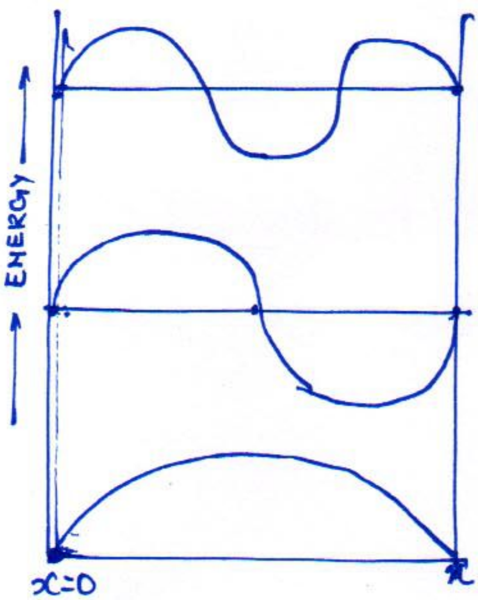
We have from the (2) and (6)

$$K^2 = \frac{8\pi^2 m}{h^2} E$$

$$\text{or} \quad \frac{n^2\pi^2}{l^2} = \frac{8\pi^2 m}{h^2} E$$

$$\text{or,} \quad E_n = \frac{n^2 h^2}{8ml^2} \quad (\text{where } n = 1, 2, 3 \cdots) \quad \text{—(9)}$$

Thus equation (9) gives the Energy of Particle in One-dimensional box.



$n=3$, $E_3 = \frac{9h^2}{8ml^2}$, $\psi_3 = \sqrt{\frac{2}{l}} \sin\frac{3\pi x}{l}$

$n=2$, $E_2 = \frac{4h^2}{8ml^2}$, $\psi_2 = \sqrt{\frac{2}{l}} \sin\frac{2\pi x}{l}$

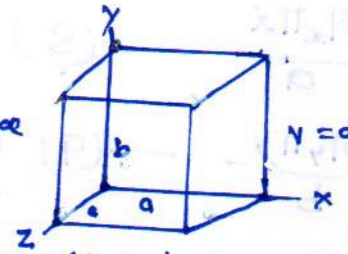
$n=1$, $E_1 = \frac{h^2}{8ml^2}$, $\psi_1 = \sqrt{\frac{2}{l}} \sin\frac{\pi x}{l}$

It is Obvious from the above facts about the nodes. So, there are $(n-1)$ nodes in ψ_n.

Particle in a three-dimensional box :—

Now consider the motion of a Particle of mass 'm' Confined to a three-dimensional box with dimensions a, b and c along X-, Y-, and Z-axes respectively.

The Potential energy of the particle is assumed to be Zero within the box and infinite outside the box and at the boundaries of the box.



Now, the Schrodinger's equation for the particle can be written as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0$$ [The Potential energy 'V' within the box is Zero]

$$\text{or, } \frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}E\psi=0 \quad \text{——— (1)}$$

Let $\psi(x,y,z)$ is the product of three functions X, Y and Z, which are functions of x, y and z respectively.

$$\text{i.e. } \psi(x,y,z)=X(x),\ Y(y),\ Z(z) \quad \text{——— (2)}$$

From equation (1) and (2) we have

$$YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0 \quad \text{—(3)}$$

On dividing equation (3) by XYZ, we have.

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}=0 \quad \text{—(4)}$$

In the above case the first term is the function of x only and is independent of y and z, Second term is the function of y only and it is independent of x and z, and the third term is a function of z only and independent of x and y. The fourth term is a constant.

If Energy E is written as the sum of three contributors associated with the three co-ordinates, then equation (4) can be separated in to three equations as,

$$\frac{\partial^2 X}{\partial x^2}+\frac{8\pi^2 m}{h^2}E_x X=0 \quad \text{——— (5)}$$

$$\frac{\partial^2 Y}{\partial y^2}+\frac{8\pi^2 m}{h^2}E_y, Y=0 \quad \text{——— (6)}$$

$$\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 m}{h^2}E_z, Z=0 \quad \text{——— (7)}$$

Where $E = E_x + E_y + E_z$

Now the Solutions of equation (5), (6) and (7) are given as follows,

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \quad \text{—— (8) where } n_x = 1, 2, 3, 4 \cdots\cdots$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \quad \text{—— (9) where } n_y = 1, 2, 3, 4 \cdots\cdots$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \quad \text{—— (10) where } n_z = 1, 2, 3, 4 \cdots\cdots$$

Now $\psi(x, y, z) = XYZ = \sqrt{\frac{8}{a,b,c}} \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{b} \cdot \sin \frac{n_z \pi z}{c}$ —— (11)

The box is Cubical, Hence.

$a = b = c$

So, the above eq^n (11) can be written as.

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{a} \cdot \sin \frac{n_z \pi z}{a} \quad \text{—— (12)}$$

Energy of Particle in three-dimensional box :—

The Solution of equations (5), (6) and (7) gives:

$E_x = \frac{n_x^2 h^2}{8ma^2}$, $E_y = \frac{n_y^2 h^2}{8mb^2}$, $E_z = \frac{n_z^2 h^2}{8mc^2}$, respectively

so, $E = E_x + E_y + E_z = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$

$$\text{or, } E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \quad \text{—— (13)}$$

For, a Cubical box $a = b = c$

$$\text{then, } E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{a^2} + \frac{n_z^2}{a^2}\right] \quad \text{—— (14)}$$

$$\text{Or } E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right] \quad \text{—— (15)}$$

The above eq^n is the energy expression of particle in three-dimensional box.

Degeneracy:— It is clear from eqn (15) that the total energy depends upon the sum of the squares of three quantum numbers.

It is clear that groups of different states in which each specified by a unique set of quantum numbers, can have the same energy. In such type of case, the energy levels are said to be degenerate.

Let us consider the energy level having energy

$$E = (1^2+2^2+3^2)\frac{h^2}{8ma^2}$$

$$= \frac{14h^2}{8ma^2}$$

There are six combinations of n_x, n_y and n_z which can give this value of energy.

n_x	1	1	2	3	2	3
n_y	2	3	1	1	3	2
n_z	3	2	3	2	1	1

This energy level is therefore six fold degenerate. It means the degeneracy is equal to 6. Particle in three dimension cubical box can show the degeneracy of energy levels fig. given below.