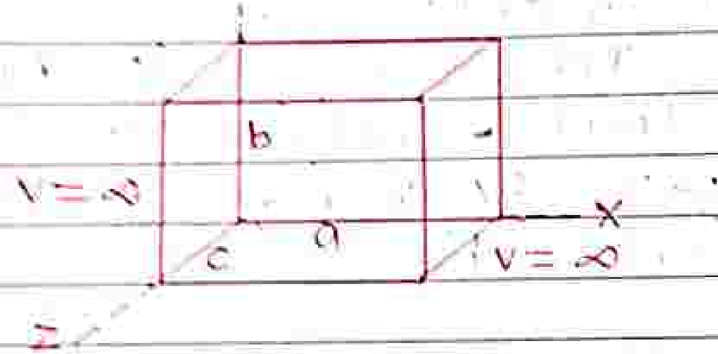
Dr. Amarendra Kumar
Deptt. of Chemistry
Jain College, Arrah

PARTICLE IN A THREE - DIMENSIONAL BOX

Let us consider the motion of a particle of mass m confined to a three - dimensional box with dimensions a, b, c along x, y and z - axes. The potential energy of the particle is assumed to be zero within the box and is infinite (∞) outside the box and its boundaries.



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

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-0)\psi = 0 \quad (\because V = 0 \text{ within the box})$$

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

i.e.

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

from eq^n (1) and (2) we get.

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

Dividing eq^n (3) by XYZ, we get

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

from eq^n (4) the first term is the function of x only and is independent of y and z. The second term is function of y only and is independent of x and z and the third term is function of z only and is independent of x and y. The fourth term is constant.

If energy E is written as the sum of three contributions associated with the three co-ordinates.

Then equation (1) can be seperated into three equations as

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

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

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

Where $E = E_x + E_y + E_z$

The Solutions of eqn (5), (6) and (7) are given as

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \qquad (8)$$

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

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \qquad (9)$$

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

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \qquad (10)$$

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

Now,

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

for a cubical box,
where $a = b = c$
we can write

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

Energy of a particle in a three-dimensional box ⇒

Solutions of equation (5), (6) and (7) gives

$$E_x = \frac{n_x^2 h^2}{8ma^2}$$

$$E_y = \frac{n_y^2 h^2}{8mb^2} \quad \text{and}$$

$$E_z = \frac{n_z^2 h^2}{8mc^2}$$

so,

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

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,
where $a = b = c$ then

$$\boxed{E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]}$$