SUBJECT - CHEMISTRY
CLASS - B.Sc (Hons) PART - III
PAPER - V
TOPIC - Three dimensional box,

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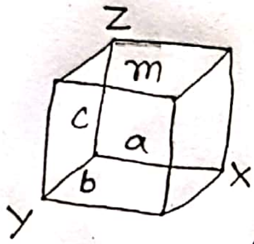
Q Derive the expression for energy of a particle in a three dimensional box.

Ans. A Particle in three dimensional box: Let us Consider a particle (electron) of mass m present in a three dimensional box. a, b and c are Side lengths along x, y and z directions. The P.E is zero everywhere inside the box and hence the Schrodinger equation is given as -



$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{-8\pi^2 m E\psi}{h^2}$$

This equation Can be Separated by putting

$$\psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}$$

or Simply $\psi = XYZ$

putting the value of ψ in the above equation, we get -

$$YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} = \frac{-8\pi^2 m E XYZ}{h^2}$$

Dividing throughout by XYZ, we get -

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\cdot\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial z^2} = \frac{-8\pi^2 m E}{h^2}$$

Since this equation must be true for all values of the Independent variables x, y, z therefore, the each term on LHS must be equal to a Constant.

$$\therefore \frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -K_x^2, \quad \frac{1}{Y}\cdot\frac{\partial^2 Y}{\partial y^2} = -K_y^2 \text{ and } \frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial z^2} = -K_z^2$$

where $K_x^2 = \frac{8\pi^2 m E_x}{h^2}$, $K_y^2 = \frac{8\pi^2 m E_y}{h^2}$, $K_z^2 = \frac{8\pi^2 m E_z}{h^2}$

and $E_x + E_y + E_z = E$ with $K^2 = K_x^2 + K_y^2 + K_z^2 = \frac{8\pi^2 m E}{h^2}$

Along x-direction, we have -

$$\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} = -K_x^2 \quad \text{or} \quad \frac{\partial^2 X}{\partial x^2} + K_x^2 X = 0$$

The general solution of this equation is given by

$$X = A \sin K_x x + B \cos K_x x$$

where A and B are arbitrary constants. Applying boundary conditions, $X = 0$ at $x = 0$, then $X = A \sin k_x \cdot x$ and from $X = 0$ at $x = a$, we have-

$$0 = A \sin K_x \cdot a$$

or $\sin K_x a = 0 = \sin n_x \pi$, $K_x a = n_x \pi$

or $K_x = \frac{n_x \pi}{a}$

Because the sin of angle is zero at any integral multiple of π. Here n_x is an integer, so we have-

$$X = A \sin \frac{n_x \pi}{a} \cdot x$$

A can be determined by applying normalisation condition -

$$\int_0^a A^2 \sin^2 a . x dx = 1$$

or $A^2 \int_0^a \sin^2 a \cdot x dx = 1$

or $A^2 \cdot \frac{a}{2} = 1$ $\quad\left[\because \int_0^a \sin^2 ax\, dx = \frac{a}{2}\right]$

$\therefore A = \sqrt{\frac{2}{a}}$; $\quad \therefore X = \sqrt{\frac{2}{a}} \cdot \sin \frac{n_x \pi}{a} \cdot x$

Similarly, $Y = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi}{b} y$

and $z = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi}{c} \cdot z$

In three dimensional box, the Complete eigen function, is given by -

$\because \psi = XYZ$

$\therefore \psi = \sqrt{\frac{8}{abc}} \cdot \sin \frac{n_x \pi}{a} \cdot x \ \sin \frac{n_y \pi}{b} \cdot y \ \sin \frac{n_z \pi}{c} \cdot z$

putting $K_x = n_x \pi / a$, we get -

$$\frac{8\pi^2 m E_x}{h^2} = k_x^2 = \frac{n_x^2 \pi^2}{a^2}$$

or $\frac{8mE_x}{h^2} = \frac{n_x^2}{a^2}$ $\quad \therefore E_x = \frac{n_x^2 h^2}{8ma^2}$

where n_x is an integer not excluding Zero as this value of n_x would make $X_{(x)}$ = Zero everywhere. The n_x is the quantum number along x direction Hence the total Kinetic Energy (E) of the electron in three dimensional box is given by -

$$E = E_x + E_y + E_z = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

where n_y and n_z are the quantum number along y and z axes respectively -

If the three dimensional box is cubical with Side a, then -

$$E = \frac{h^2}{8ma^2} \left(n_x^2 + n_y^2 + n_z^2 \right)$$

for a one dimensional box, the State of the System Could be specified by giving the value of the quantum number or the energy for a cubical box this is no longer true, because a given energy may be achieved by different Combinations of three quantum numbers n_x, n_y & n_z. The quantum number describe different States of the System but these states have the Same energy. Such an energy level is Called degenerate and the degeneracy is equal to the number of independent wave functions associated with a given energy level.