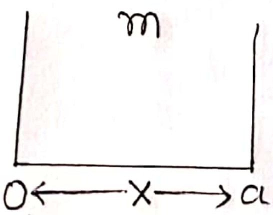
SUBJECT - CHEMISTRY
CLASS - B.Sc (Hons) PART - III
PAPER - V
TOPIC - Particle in a one dimensional box
Dr Hari Mohan prasad Singh
Department of Chemistry
Dr. L.K.V.D College Tajpur Samastipur

Q1 Derive the expression for the energy of a particle in a one dimensional box and discuss its main consequences.

Ans Let us consider a particle (electron) of mass m confined to move a distance 'a' along x-axis in one dimensional box. For values of x between 0 and a the particle is completely free and hence P.E is taken as zero. At boundaries, however, the particle is constrained by an infinite potential wall over which there is no escape, thus P.E = ∞ when x = a or 0.



Now applying one dimensional schrodinger equation to the particle in one dimensional box. we get -

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} \cdot E\psi = 0$$

The general solution of this equation is $\psi = A \sin kx + B \cos kx$

where $k^2 = \frac{8\pi^2 mE}{h^2}$ and A & B are arbitrary constants.

or $k = \frac{2\pi}{h}(2mE)^{1/2}$ $\left[\because E = \frac{p^2}{2m} \quad \therefore p = \sqrt{2mE}\right]$

To have $\psi = 0$, at $x = 0$, the cosine function must vanish, a condition that requires $B = 0$. Thus -

$\psi = A \sin kx$

To have $\psi = 0$ at $x = a$, we must have -

$0 = A \sin ka$

If $A = 0$ then $\psi = 0$ everywhere and this is not an acceptable Solution

$\therefore \; \sin ka = 0 = \sin n\pi$

or $\quad ka = n\pi$

$\therefore \; k = \frac{n\pi}{a} \quad \therefore \; k^2 = \frac{n^2\pi^2}{a^2} \quad \cdots (1)$

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

Hence the wave function for a particle in one dimensional box is given by -

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

The Constant A can be evaluated by applying normalisation condition. i.e

$$\int \psi^2 dx = 1$$

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

or $\quad \frac{A^2}{2} \int_0^a \left[1 - \cos \frac{2n x}{a} x \right] dx$

or $\quad \frac{A^2}{2} \left[\int_0^a dx - \int_0^a \cos \frac{2n\pi}{a} dx \right]$

or $\quad \frac{A^2}{2} [a - 0] = 1$

or $\quad A^2 \cdot \frac{a}{2} = 1 \qquad \therefore \; A = \sqrt{\frac{2}{a}}$

Hence the Complete wave function for a particle in one dimensional box is given by -

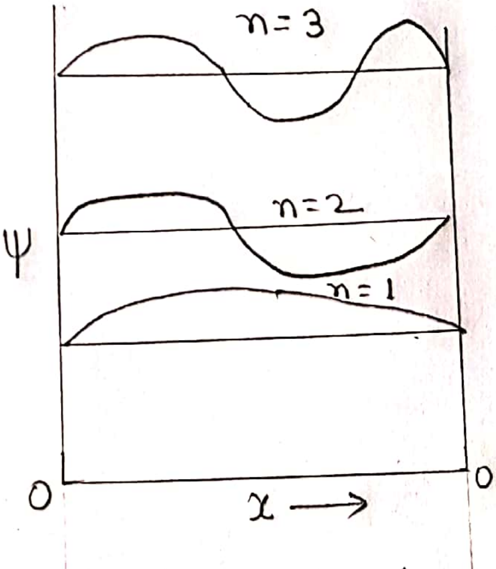
$$\psi = \sqrt{\frac{2}{a}} \cdot \sin \frac{n x}{a} \cdot x \quad -- \quad (3)$$

Now putting the value of k^2 in equation (1), we get -

$\because \; \frac{n^2\pi^2}{a^2} = k^2 = \frac{(8\pi^2 m E)}{h^2}$

or $\quad \frac{n^2}{a^2} = \frac{8mE}{h^2} \quad$ or $\quad E = \frac{n^2 h^2}{8 m a^2} \quad \cdots \quad (4)$

This is the expression for kinetic energy of a particle in one dimensional box. we see that a particle in a box Cannot have zero energy



because the lowest energy for $n=1$ is $h^2/8ma^2$. A particle moving between two points on a line Can have only the energies given by this equation for integral values of n, whereas a perfectly free particle Can have any energy. Such discrete energy levels are characteristic of Solutions of Schrodinger equation for bound particle. It is again Clear that more localised is the motion of the particle, the higher will be its kinetic energy as $E \propto 1/a$, so the delocalisation of electrons in Conjugated Systems enhances the Stability of the Compound the integer n is a typical quantum number, which Now appears quite naturally and without any adhoc assumptions its function is to specify the number of nodes in the electron wave. when $n=1$, There is no node when $n=2$, there is a node in the centre of the box, when $n=3$, there are two nodes etc the value of the energy depends directly on n^2 and, therefore, rises rapidly as the number of nodes increases.