Notes

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC 105

Paper Title: Physical Chemistry

Unit: Quantum Chemistry (Section B)

Module Name: Particle in One-dimensional Box

Module No: 36

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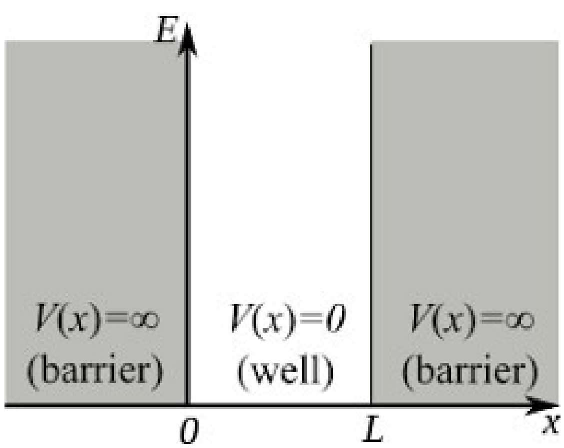
Particle in one dimensional box

Particle is subjected to a potential energy function that is infinite everywhere along the x axis except for the line segment of length l where the potential energy is zero.

Consider a particle of mass m confined in a box of length a and moving along x direction. The walls of the box represent regions of high potential energy so that particle cannot escape outside. Potential energy inside the box is zero.



The schrodinger equation is given by

$$H\psi\ (x) = E\psi\ (x)$$ ---(1) where H= T(x)+V(x) ---(2)

$$T(x) = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$ ----(3)

Substituting in equation (1)

$$\left\{-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + V(x)\right\}\psi\ (x) = E\psi\ (x)$$ ---------(4)

transfering E ψ to rhs and dividing by $8\pi^2 m/h^2$ and region I & III, V(x)= ∞,

ψ (x) =0, Probability of finding electron in region I, III are zero.

$$\left\{\frac{d^2\ \psi(x)}{dx^2} + \frac{8\pi^2\ m(E - \infty)\psi(x)}{h^2}\right\} = 0$$ **----(5)**

For the particle inside the box x lies between 0 and a and pE is zero.

$$\left\{\frac{d^2\ \psi(x)}{dx^2} + \frac{8\ \pi^2\, mE\psi(x)}{h^2}\right\} = 0$$

$\partial^2\ \psi(x)/\partial x^2 + k = 0$ let $K^2 = 8\ \pi^2\ mE\ /\ h^2$

$\partial^2\ \psi(x)/\partial x^2 + K^2\ \psi = 0$

The general solution for this equation is **ψ= A sinkx+B cos kx** where A and B are arbitrary constants whose values can be determined by applying boundary conditions.

1) **Ψ =0 at x= 0**
   0= A sink0+B cos k0
   B =0
   ψ= A sinkx

   2) Ψ =0 at x= a

Either A =0 or sinka=0

If A =0 Ψ is 0 everywhere which is not possible sinka=0

Sin nπ =0 ka = nπ k = nπ/a n=1,2,3,4,……

The wave function for particle inside the box becomes ψ= A sin(nπx/a)

$$k = n\pi/a \qquad k^2 = 8\pi^2 mE / h^2$$

$$n^2\pi^2/a^2 = 8\pi^2 mE / h^2$$

$$E = n^2 h^2/8m a^2$$

Thus for a particle moving between two points on a line energy is quantized.

To find out the value of A

$$\int_0^a \psi^*\psi dx=1$$

This is called normalization of function.

In general $\int_{-\infty}^{+\infty} |\psi^2| dx=1$, when ψ satisfies this condition, it is said to be normalized.

$$\int_0^a A^2 \sin^2(n\pi x/a) \, dx=1 \qquad \sin^2(n\pi x/a) = ½[1-\cos(2 n\pi x/a)]$$

$$= A^2 \int_0^a [½ -½\cos(2 n\pi x/a)]dx$$

$$= A^2 \int_0^a ½dx - \int_0^a ½\cos(2 n\pi x/a)dx$$

$$= A^2 [x/2]_0^a -[½\sin (2 n\pi x/a]_0^a$$

$$= A^2 [a/2] -[½\sin (2 n\pi a/a]$$

$$= A^2 [a/2] -[0]$$

$$A = (2/a)^{1/2}$$

The normalized wave function is given by $\psi_n= (2/a)^{1/2} \sin(n\pi x/a)$.

Energy of the particle is given as

$$E_n = n^2h^2/8ma^2$$

The equation gives allowed or permissible values of energy corresponding to different values of n.n is called as quantum no and can assume only integral values.The particle may have certain discrete values of E .These are the eigenvalues for E

When n=1 $E = h^2/8ma^2$

This implies that the minimum energy possessed by the particle is not zero but a definite value. This is called zero point energy. This can be concluded as particle will have only certain discrete values of energy. So in the box there is an infinite sequence of discrete energy levels. The energy of the particle is quantized in the box and cannot change in a continuous manner. These permissible values depend upon n and not on x. These are called eigen values.

When n=1 $E_1 = h^2/8ma^2$ **When n=3** $E_3 = 9h^2/8ma^2$

When n=2 $E_2 = 4\,h^2/8ma^2$ **When n=4** $E_4 = 16\,h^2/8ma^2$

$E_2 - E_1 = 3\,h^2/8ma^2$ **similarly** $E_3 - E_2 = 5\,h^2/8ma^2$

This shows that the energy difference between consecutive energy levels is not constant.

$\psi_n = (2/a)^{1/2} \sin(n\pi x/a)$.

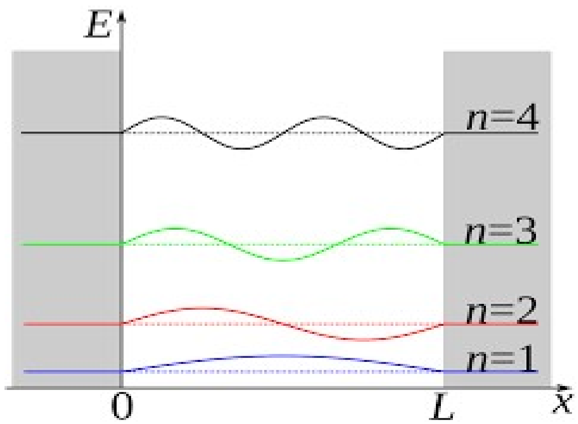
When n=1 $\psi_1 = (2/a)^{1/2} \sin(\pi x/a)$.

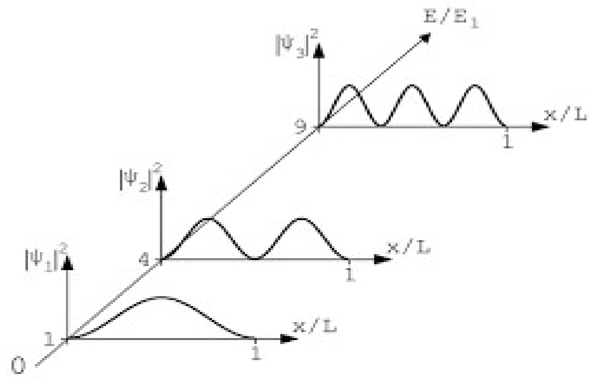
When n=2 $\Psi_2 = (2/a)^{1/2} \sin(2\pi x/a)$.

When n=3 $\Psi_3 = (2/a)^{1/2} \sin(3\pi x/a)$.

$\Psi^2_n = (2/a) \sin^2(n\pi x/a)$.

The plots of ψ_n **and** Ψ^2_n against x are shown in the figure





From the plots of $\boldsymbol{\psi_n}$ **and** $\boldsymbol{\Psi^2_n}$ against x, it is observed that the quantum states have **nodes**. At a node there is zero probability of finding the particle.

The $\mathbf{n}^{th}$ quantum state has n−*1* nodes.The number of nodes increases with the energy of the quantum state.It is also observed that Ψ_n may be positive or negative, but $\Psi^2{}_n$ is always positive.