CHAPTER

3

Particle in a Box

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Particle in One Dimensional Box:

In this problem a particle of mass is placed in a one dimensional box of length l particle is free to move. Box have infinite walls.

It is assumed that the potential energy of particle is zero every where inside the Box i.e.

V(x) = 0.

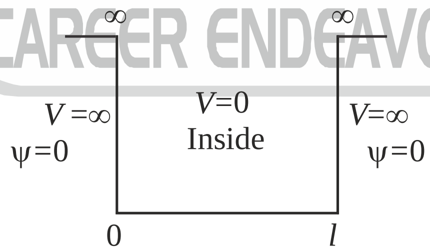
The time-independent one-dimension Schrodinger equation will be

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

Outside the box, equation (1) takes the form.

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

Neglecting E is comparison to ∞ , we have.



$$\frac{d^2\psi}{dx^2}=\infty\,\psi \;\; or \;\; \psi=\frac{1}{\infty}\frac{d^2\psi}{dx^2}$$

That is $\psi=0$ outside the box. This means that the particle cannot exist outside the region $0<x<l$.

Within the box, the schrodinger equation for the motion of the particle takes the form.

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

$$\frac{d^2\psi}{dx^2}+\alpha^2\psi=0 \qquad ...(2)$$

where, $\alpha^2=\frac{8\pi^2 mE}{h^2}$ ...(3)

A general solutioin of equation (2) is given by.

$$\psi = A\sin(\alpha x) + B\cos(\alpha x) \qquad ...(4)$$

Where A and B are constant.

Boundary conditions :

(1) $\psi(x) = 0$ at $x = 0$

$$0 = A\sin(\alpha\ 0) + B\cos(\alpha\ 0)$$

The above expression will be true only when $B = 0$, thus the wavefunction as given by equation (4) becomes.

$$\psi = A\sin(\alpha\, x) \qquad ...(5)$$

(2) $\psi(x) = 0$ at $x = \ell$, then

$$0 = A\sin(\alpha l)$$

The above expression will be true only where $\alpha\, l$ is an integral multiple of π that is,

$$\alpha\, l = n\pi \qquad ...(6)$$

When n can have only integral values of 1, 2, 3, ... and is known as quantum number. A value of $n = 0$ is eliminated since it leads to $\alpha = 0$ i.e. $\psi(x) = 0$ every where within the box. Substituting α from equation (6) in equation (5) we get.

$$\psi = A\sin\left(\frac{n\pi x}{l}\right) \qquad ...(7)$$

Now from equation (3) we have.

$$\alpha^2 = \frac{8\pi^2 mE}{h^2} \Rightarrow E = \frac{\alpha^2 h^2}{8\pi^2 m} = \frac{n^2 h^2}{8m\ell^2} \qquad ...(8)$$

Energy of a particle in 1-D box is quantized.

So energy difference between the two sucessive energy levels will be

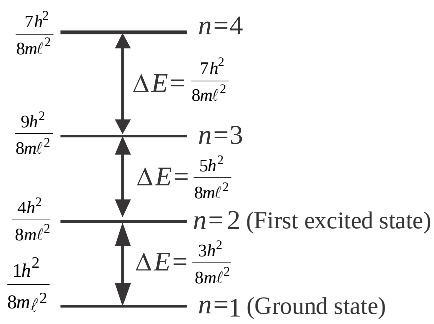
$$\Delta E = E_{n+1} - E_n$$

$$\Rightarrow \qquad \Delta E = \frac{(n+1)^2 h^2}{8ml^2} - \frac{n^2 h^2}{8ml^2} = \frac{[(n+1)^2 - n^2]h^2}{8ml^2} = \frac{(2n+1)\, h^2}{8ml^2}$$

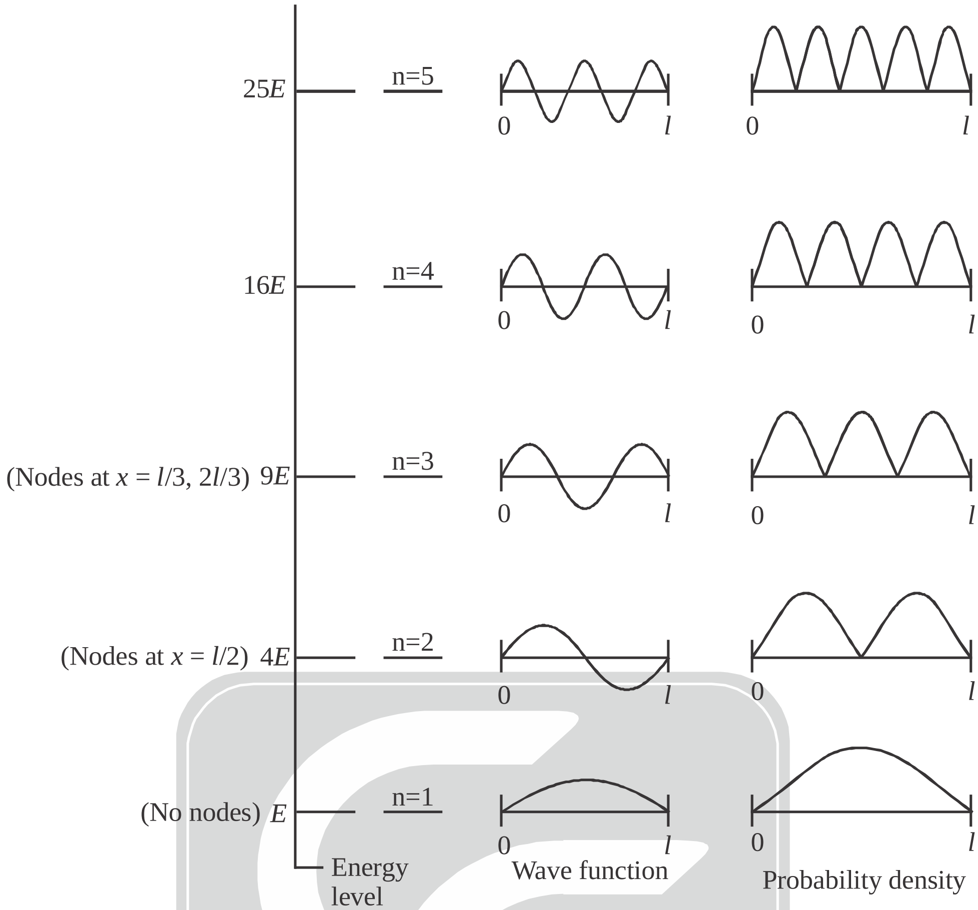
Zero point energy (Ground state energy):

$$E_{n=1} = \frac{h^2}{8m\ell^2}$$

Energy Level Diagram in 1-D box:



Graph of Wave Functions and Probability :



Particle in a symmetric 1-D box from –*l* to +*l* :

Consider a free particle is confined to move in 1D box of length $-l$ to l.

$$V = 0 \qquad \text{inside the box}$$
$$V = \infty \qquad \text{else where}$$

Schrodinger wave equation for 1-D box is

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

Or, $$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad (\because V = 0)$$

Or, $$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$\because \qquad \psi = A\sin kx + B\cos kx \qquad \text{... (1)}$

Boundary conditions:

(i) For first $\psi = 0,\ x = -\ell$

$$0 = -A\sin k\ell + B\cos k\ell \qquad \text{... (2)} \qquad \begin{bmatrix} \because \quad \sin(-\theta) = -\sin\theta \\ \text{and } \cos(-\theta) = +\cos\theta \end{bmatrix}$$

(ii) $\psi = 0,\ x = +\ell$

$$0 = A\sin k\ell + B\cos k\ell \qquad \text{... (3)}$$

From (ii) and (iii)

(2) + (3) $\qquad 2B\cos k\ell = 0 \ \Rightarrow B\cos k\ell = 0$ i.e. $B = 0$ or $\cos k\ell = 0$

(2) – (3) $\qquad -2A\sin k\ell = 0 \Rightarrow A\sin k\ell = 0$ i.e. $A = 0$ or $\sin k\ell = 0$

Possible solutions:

(a) $A = 0, \cos k\ell = 0 \Rightarrow k\ell = n\frac{\pi}{2} \Rightarrow k = \frac{n\pi}{2\ell} (n = 1, 3, 5, ...)$

So, $\psi(x) = B\cos\left(\frac{n\pi x}{2\ell}\right) \quad (n = 1, 3, 5......)$

(b) $B = 0, \sin k\ell = 0 \Rightarrow k\ell = n\frac{\pi}{2} \Rightarrow k = \frac{n\pi}{2\ell} \quad (n = 2, 4, 6, ...)$

So, $\psi(x) = A\sin\left(\frac{n\pi x}{2\ell}\right) \quad (n = 2, 4, 6......)$

For normalised function, $\int_{-\ell}^{\ell} \psi^2 dx = 1$

$$\Rightarrow \quad \int_{-\ell}^{+\ell} A^2 \sin^2 \frac{n\pi x}{2\ell} dx = 1 \qquad \left[\text{Let } \frac{n\pi}{2\ell} = z\right]$$

$$\Rightarrow \quad A^2 \int_{-\ell}^{+\ell} \left[\frac{1 - \cos 2zx}{2}\right] dx = 1$$

$$\Rightarrow \quad A^2 \left[\int_{-\ell}^{+\ell} \frac{\ell}{2} dx - \frac{1}{2}\int_{-\ell}^{+\ell} \cos 2zx\right] = 1$$

$$\Rightarrow \quad A^2 \int_{-\ell}^{+\ell} \frac{1}{2} dx = 1 \qquad \left[\frac{1}{2}\int_{-\ell}^{+\ell} \cos 2zx = 0\right]$$

$$\Rightarrow \quad A^2 \times \frac{1}{2}[x]_{-\ell}^{+\ell} = 1 \Rightarrow A^2 \times \frac{1}{2} \times [2\ell] = 1 \Rightarrow A^2 = \frac{1}{\ell} \Rightarrow A = \sqrt{\frac{1}{\ell}}$$

Similarly for, $\int_{-\ell}^{+\ell} B^2 \cos^2 \frac{n\pi x}{2\ell} dx = 1 \Rightarrow \quad B = \sqrt{\frac{1}{\ell}}$

Therefore, $\psi_{\text{normalized}} = \frac{1}{\sqrt{\ell}} \sin \frac{n\pi x}{2\ell}$ (n = 2, 4, 6, ...)

$\psi_{\text{normalized}} = \frac{1}{\sqrt{\ell}} \cos \frac{n\pi x}{2\ell}$ (n = 1, 3, 5, ...)

And for these function energy is $\boxed{E = \frac{n^2 h^2}{32 m \ell^2}}$

SOLVED PROBLEMS

1. A particle in a 1-D box of length L has eigenstates $\psi_n(x)$ with energies E_n. Consider two initial states of the particle at time t = 0: case (1) $\psi(x,t=0)=\psi_n$ (arbitrary n), and case (2) $\psi(x,t=0)=\psi_n+\psi_m$ (arbitrary n and m; $n \neq m$). The probability to find the particle at a specific position within the box:
(a) Varies with time for case 1 but not for case 2
(b) Is time dependent for both cases
(c) Is time independent for both cases
(d) Varies with time for case 2 but not for case 1

Soln. Case (1): $\psi(x,t=0)=\psi_n=\phi_n e^{-iE_nt/\hbar}$

Probability density = $\psi_n\psi_n^*$

$=\phi_n e^{-iE_nt/\hbar}\cdot\phi_n^* e^{iE_nt/\hbar}$

$=\phi_n\phi_n^*$ (Independent of time)

Case (2): $\psi(x,t=0)=\psi_n+\psi_m$

Probability density = $(\psi_n+\psi_m)(\psi_n+\psi_m)^*$

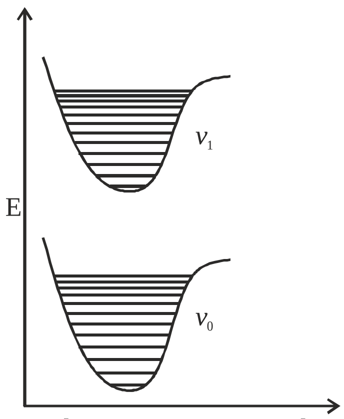
$=(\phi_n e^{-iE_nt/\hbar}+\phi_m e^{-iE_mt/\hbar})\cdot(\phi_n^* e^{iE_nt/\hbar}+\phi_m^* e^{iE_mt/\hbar})$

$=\phi_n\phi_n^*+\phi_n\phi_m^* e^{-it/\hbar(E_n-E_m)}+\phi_n\phi_n^* e^{-i\hbar t(E_m-E_n)}+\phi_m\phi_m^*$ (Time dependent)

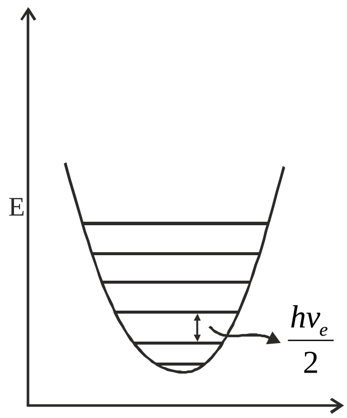
Correct option is (d)

2. Given three system, A, B and C what could be they if the spacing between the neighbouring energy levels in A decreases with increasing energy, while that for B is constant, and that for C increases with increasing energy?
(a) A = particle in a one-dimensional box, B = harmonic oscillator, C = electron in hydrogen atom
(b) A = electron in hydrogen atom, B = harmonic oscillator, C = particle in a one-dimensional box
(c) A = particle in a one-dimensional box, B = electron in hydrogen atom, C = harmonic oscillator
(d) A = electron in hydrogen atom, B = particle in a one-dimensional box, C = harmonic oscillator

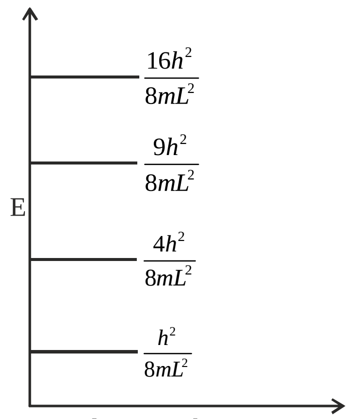
Soln.



Electronic Energy Levels



Harmonic Oscillator Energy Levels

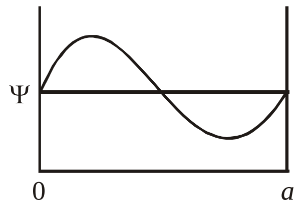


Particle in 1-D box Energy Levels

Space between neighbouring energy level decrease because as vibrational quantum number increase ΔE value decrease for upper level in electronic transition	Space between neighbouring energy level remain constant because harmonic oscillator difference in energy between two levels is independent of vibrational quantum number	Space between neighbouring energy level increase as principal quantum number value increase in 1-D box
$\Delta E = h\nu_e[1-2x_e(1+v)]$	$\Delta E = h\nu_e$	$\Delta E = \dfrac{(2n+1)h^2}{8mL^2}$

Correct option is (b)

3. Plot the graph of a wave function having energy $\dfrac{0.5\,h^2}{ma^2}$.



Soln. $\dfrac{n^2h^2}{8m\,a^2} = \dfrac{0.5h^2}{m\,a^2}$ $\Rightarrow\ n^2 = 4,\ \Rightarrow n = 2$

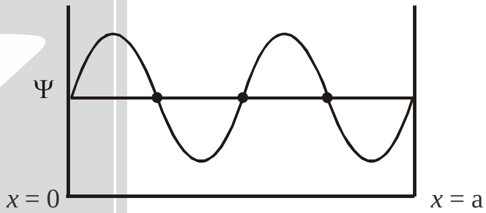
This corresonds to first excited state having 1 nodes at $x = \dfrac{a}{2}$

4. If a electron escaped in a 1-D box of length 1Å having energy 608.4 eV, plot it's graph.

Soln. $\dfrac{n^2h^2}{8m\ell^2} = 608.4\times1.6\times10^{-19}$ *Joule*

$$\therefore \qquad n^2 = \frac{608.4\times1.6\times10^{-19}\times8\times9.1\times10^{-31}\times\left(10^{-20}\right)}{\left(6.62\times10^{-34}\right)^2} = 16.17$$

$$\therefore \qquad n = \sqrt{16.17} \approx 4$$



5. Consider a ball of mass 1 g moving with a speed 1 cm s^{-1} in a one dimensional box of edge length equal to 10 cm.

(1) Calculate its kinetic energy and the number n corresponding to this kinetic energy.

(2) If the ball is to be promoted to the next higher qunatum level, then how much of energy is required ? Formthe obtained value justify that the kinetic energy of a larger mass varies in a continuous manner and can be calculated from the classical mechanical laws of Newton.

Soln. **(1)** Kinetic energy of the ball = $\left(\dfrac{1}{2}\right)\text{mv}^2 = \left(\dfrac{1}{2}\right)(10^{-3}\,\text{kg})(10^{-2}\,\text{ms}^{-1})^2 = 0.5\times10^{-7}\ \text{kg m}^2\ \text{s}^{-2} = 0.5\times10^{-7}$ J.

Since, $$E_n = n^2\left\{\frac{h^2}{8l^2m}\right\}$$

Therefore, $$n^2 = \frac{E_n}{(h^2/8\,l^2m)} = \frac{E_n(8l^2m)}{h^2} = \frac{(0.5\times10^{-7}\,J)(8)(10^{-1}\,m)^2(10^{-3}\,kg)}{(6.626\times10^{-31}\,Js)^2} = 9.11\times10^{58}$$

$$\boxed{n = 3.02\times10^{29}}$$

(2) Now, $$\Delta E = E_{n+1} - E_n = (2n+1)\left(\frac{h^2}{8\,l^2\,m}\right)$$

$$= \left(2\times3.02\times10^{29}+1\right)\left\{\frac{(6.626\times10^{-34}\,Js)^2}{8\times(10^{-1}\,m)^2(10^{-2}\,kg)}\right\} = 3.32\times10^{-34}\ \text{J}.$$

6. An electron is confined in a 1-D box of length of 1Å. If electron falls from first excited state to ground state, what energy it will emitt?

Soln. Length of box, $\ell = 1\text{Å} = 10^{-10}$ m

Energy of 1st excited state, $E_1 = \frac{1^2\, h^2}{8m\ell^2} = \frac{h^2}{8m\ell^2}$

Energy of 2nd excited state, $E_2 = \frac{2^2 h^2}{8m\ell^2} = \frac{4h^2}{8m\ell^2}$

$$\therefore \qquad \Delta E = E_2 - E_1 = (4-1)\frac{h^2}{8m\ell^2} = (3\times 37.6)eV = 112.8\, eV$$

7. A ball of mass 1 gm confined to move in 1-D box of length 0.1 m with a velocity of 0.01 m/s. Calculate the n (principle quantum number). Is quantization is possible?

Soln. We know the energy of 1-D box = It's kinetic energy.

$$\therefore \qquad \frac{n^2h^2}{8m\ell^2} = \frac{1}{2}mv^2 \qquad \Rightarrow n^2 = \frac{4m^2v^2\ell^2}{h^2} = \frac{4\times(10^{-3})^2\times(0.01)^2\times(0.1)^2}{(6.627\times10^{-34})^2} = 9.13\times10^{57}$$

$$\therefore \qquad n \approx 9\times10^{28}$$

Quantum number n is very very large. It is not possible to calculate the difference between successive energy level. So, **it is not possible to observe quantization in the energy level .**