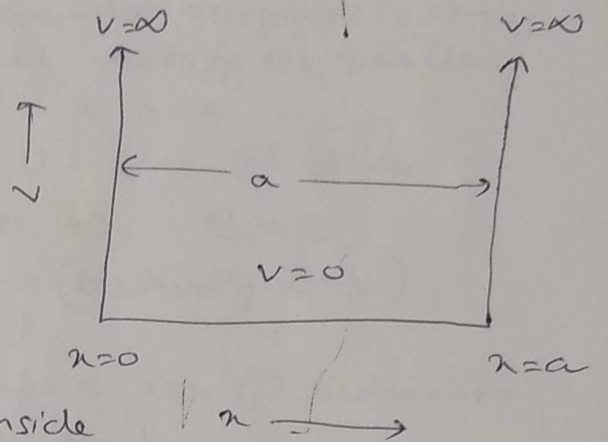
Particle in a 1-Dimensional Box:- This is the simplest application of the Schrodinger wave eqn. to the translational motion of a particle (electron, atom or molecule) in space. The results obtained can explain as to why the energies ~~are~~ are quantized i.e. can have only discrete values unlike the classical mechanics according to which the energy associated with motion of a particle can vary continuously i.e. can have any values.

Here a particle of mass 'm' is confined to move in one dimensional box of length 'a' having infinitely high walls. It is assumed for the sake of simplicity the potential energy of the particle is zero every where inside the box i.e.



$$V(x) = 0$$

In order that the particle may remain within the box, it is essential to assume that the potential energy outside the walls is very high i.e. $V(x) = \infty$ so that as soon as the particle reaches the wall it is reflected back into the box.

Now, the Schrodinger wave eqn. for one dimension is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}[E - V]\psi = 0 \quad \text{——— (1)}$$

where ψ is function of x coordinate only.

As outside the box $V = \infty$, $\therefore$ outside the box eqn. (1) become

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

Neglecting E in comparison to ∞ the above eqn reduced to

$$\frac{d^2\psi}{dx^2} - \infty\psi = 0 \quad \text{or} \quad \frac{d^2\psi}{dx^2} = \infty\psi$$

$$\text{or} \quad \psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} = 0$$

Hence outside the box $\psi = 0$. This is another way of saying that particle cannot be found outside the box i.e. it is confined within the box.

For the particle within the box, $V = 0$

$\therefore$ Schrodinger wave eqn. (1) takes the form

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

As for the given state of system, the energy E is constant

∴ we put $\frac{8\pi^2 m}{h^2} E = k^2$ —③
where k^2 is constant independent of x.
∴ eqn ② becomes $\frac{d^2\psi}{dx^2} + k^2\psi = 0$ —④
A general solution for this differential eqn. is given by
$$\psi = A \sin kx + B \cos kx \quad —⑤$$
where A & B are constants
Depending upon the values of A & B & k, ψ can have many values. But all the values are not acceptable. Only those values of ψ are acceptable which satisfy the boundary condition i.e. $\psi = 0$ at $x = 0$ & $x = a$
∴ Putting $\psi = 0$ when $x = 0$ eqn. ⑤ becomes
$$0 = A \sin 0 + B \cos 0 \Rightarrow B = 0$$
∴ when $x = 0$ eqn ⑤ becomes (by putting $B = 0$)
$$\psi = A \sin kx \quad —⑥$$
Now putting $\psi = 0$ when $x = a$ eqn ⑥ reduces to
$$0 = A \sin ka \quad \text{or} \quad \sin ka = 0$$
The eqn. holds good only when the values ka are integral multiple of π i.e.
$$ka = n\pi \quad —⑦$$
where n is an integer i.e. $n = 0, 1, 2, 3 \ldots$. However the value $n = 0$ may be excluded bcz it makes $k = 0$ & hence $\psi = 0$ for any value of a b/w 0 & a i.e. within the box. But this is not true bcz the particle is always assumed to be present within the box.
from eqn. ⑦ $k = \frac{n\pi}{a}$ —⑧
substituting the value in eqn. ⑥
$$\boxed{\psi = A \sin\left(\frac{n\pi x}{a}\right)} \quad —⑨ \quad n = 1, 2, 3, \ldots$$
This gives expression for eigenfunction ψ
from ③ the expression for energy is
$$E = \frac{k^2 h^2}{8\pi^2 m} = \frac{n^2 \pi^2 h^2}{8\pi^2 m a^2}$$
$$\therefore \boxed{E = \frac{n^2 h^2}{8ma^2}} \quad —⑩ \quad n = 1, 2, 3, \ldots$$
eqn ⑨ & ⑩ are solns. for Schrodinger's wave eqn. for a particle in 1-D box. However the eqn. ⑨ contains undermined constant A. Its value can be obtained by normalization of wave which is as follows.

Determination of Orthonormal Set :- The eigenfunction are said to form ortho-normal set if

$$\int \psi_n^* \psi_m \, d\tau = \begin{cases} 0 & \text{if } n \neq m \\ 1 & \text{if } n = m \end{cases}$$

They are orthogonal when $\int \psi_n^* \psi_m \, d\tau = 0$

& normalized when $\int \psi_n^* \psi_n \, d\tau = \phi$

where ψ_n^* is complex conjugate of ψ_n.

Determination of A :- Since the total probability of finding the particle within the box is 1, therefore the normalization of ψ required.

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

substituting the value of ψ $(=\psi^*)$ from eqn (9)

$$\int_0^a A \sin\left(\frac{n\pi x}{a}\right) \cdot A \sin\left(\frac{n\pi x}{a}\right) dx = 1$$

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

$$A^2 \int_0^a \left\{ \frac{1 - \cos \frac{2n\pi x}{a}}{2} \right\} dx = 1$$

$$\frac{A^2}{2} \left[\int_0^a \left(1 - \cos \frac{2n\pi x}{a}\right) dx \right] = 1$$

$$\frac{A^2}{2} \left[|x|_0^a - \left| \frac{\sin \frac{2n\pi x}{a}}{\frac{2n\pi}{a}} \right|_0^a \right] = \phi$$

$$\frac{A^2}{2} \left[(a - 0) - \frac{a}{2n\pi} \{ \sin 2n\pi - \sin 0 \} \right] = \phi$$

$$\frac{A^2}{2}[a-0] = 1 \Rightarrow A^2 = \frac{2}{a} \Rightarrow A = \sqrt{\frac{2}{a}}$$

Hence normalized wave function for the particle in 1-D box are

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)} \quad n = 1, 2, 3 \ldots$$

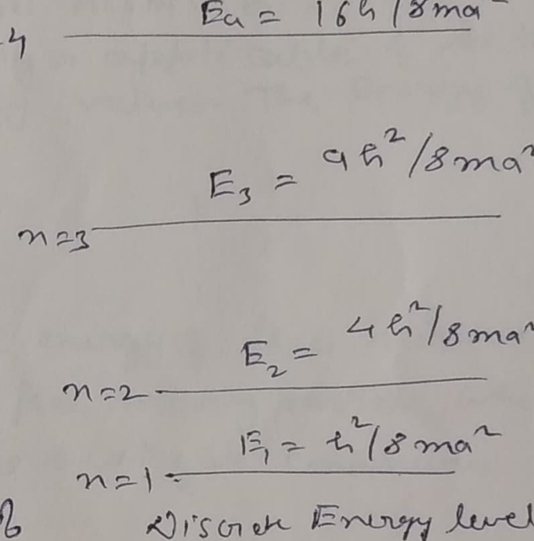
Unit of ψ for 1-D box is $cm^{-1/2}$

Some Important Results from the study of particle in 1-D Box :-

1) Quantization of Energy :- Since n can have only integral values equal to 1, 2, 3 etc. therefore from expression $E = \frac{n^2 h^2}{8ma^2}$ follows that energy E associated with the motion of particle in a box can have only discrete values. i.e. the energy is quantized.

The integer n is called quantum number of the particle.

Further putting $n = 1, 2, 3, \ldots$ etc. the discrete energy levels obtained for particle of mass 'm' confined in the box of length 'a' is shown in the figure. It is important to note that as quantum number n increases the separation b/w them increases. It may also be noted that separation of energy levels also depends upon the box length 'a'. As 'a' increases i.e. the space available to a particle increases energy quanta become smaller & energy levels move closer together. If the box length become very large, the quantization disappears & there is smooth transition from quantum behaviour to classical behaviour. This is called correspondence principle given by Bohr.



Discrete Energy level of particle in 1-D box.

2) Existence of Zero point energy (Z.P.E) :-

Since $\psi(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$

$$E = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3 \ldots$$

The value of $n = 0$ is not permitted bcz the function $\psi(x)$ then become zero, But the particle is always present in the box. There the acceptable values of $n = 1, 2, 3 \ldots$

Now when $n=1$ $E_1 = \frac{h^2}{8ma^2}$

This implies that minimum energy possesed by the particle is not zero, but has definite value. This is called zero point energy. This means that particle in the box is not at rest even at 0K. Thus the position of particle cannot be determined precisely. Similarly, linear momentum also cannot be precisely determined. Thus occurence of Z.P.E is in accordance with Heisenberg's uncertainity principle

3) Non-quantization of energy for a particle or Free particle without boundary condition :- If the walls of box are removed the particle is free to move in a field whose potential energy values have no restriction. Then the boundary condition are no longer applicable & so the constants A, B & k have any values. The energy of particles is then given by

$$E = \frac{k^2 h^2}{8\pi^2 m}$$

As k can have any value, the energy of free particle is not quantized. In other words, free moving particle, which may be an e̅n, has no restrictions & will give continuous energy spectrum.

Q:- why $n=0$ is not acceptable

Q:- What is Z.P.E. Is it accordance with uncertainity principle

Q:- What happened if the walls of 1-D box is suddenly removed?

Q:- Show that the wave function for particle in 1-D box is normalized.

A:- For wave function to be normalize $\int_0^a \psi^2 dx = 1$

$$\therefore \frac{2}{a}\int_0^a \sin^2 \frac{n\pi x}{a}\, dx = \frac{2}{a}\cdot\int_0^a \left[\frac{1-\cos\frac{2n\pi x}{a}}{2}\right] dx$$

$$= \frac{1}{a}\left[x\Big|_0^a - \frac{\sin\frac{2n\pi x}{a}}{\frac{2n\pi}{a}}\Bigg|_0^a\right] = \frac{1}{a}[a-0-0]$$

$$=1$$

Hence the wave function is normalized.