Wave Equation:

(1) Schrodinger's Time Independent Wave Equation:

Let's start with de Broglie's hypothesis of matter waves.

when a particle of mass 'm' moving with velocity 'v', then it is always associated with matter wave having wavelength 'λ' as

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{--- (1)}$$

where, 'h' is Plank's constant

And 'p' is Momentum of moving particle.

Schrodinger's Wave Equation is the equation for these matter waves. ~~that~~ explain it's propagation / motion.

The wave equation for any simple 1D wave propagating along 'x' direction can be written as

$$\frac{d^2y}{dt^2} = v^2 \cdot \frac{d^2y}{dx^2} \quad \text{--- (2)}$$

where 'y' represents displacement of wave (or a wave variable associated with wave).

For a matter wave, it's wave-variable is known as a <u>wavefunction</u>.

Suppose, if we choose a quantum mechanical wavefunction for a matter wave in 1D is

$$\psi(x,t) = \psi_0 \, e^{i(kx-\omega t)} \quad \text{--- (3)}$$

where, ψ_0 is the amplitude of matter wave.

$\omega = 2\pi\nu$, angular frequency

And $k = \frac{2\pi}{\lambda}$, wave vector.

To set-ups Schrodinger's Wave Equation, we have to differentiate this wave function $\psi(x,t)$ two times with respect to 'x'. Note here the differentiation is a partial differention as $\psi(x,t)$ is a function of two variables 'x' and 't'.

$$\therefore \frac{\partial \psi(x,t)}{\partial x} = \psi_0 \cdot e^{i(kx-\omega t)} \cdot (ik)$$

$$\therefore \frac{\partial \psi(x,t)}{\partial x} = (ik)\,\psi(x,t) \quad \text{--- (4)}$$

And

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = (ik)\,\frac{\partial \psi(x,t)}{\partial x} \quad \text{--- (5)}$$

Let's substitute the value of $\frac{\partial \psi(x,t)}{\partial x}$ from eq^n (4) in to eq^n (5)

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} = (ik)\,(ik)\,\psi(x,t)$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} = i^2 k^2 \psi(x,t)$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} = -k^2 \psi(x,t)$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + k^2 \psi(x,t) = 0 \quad — (6)$$

As $K = \frac{2\pi}{\lambda}$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi(x,t) = 0 \quad — (7)$$

From de Broglie's Hypothesis

$$\lambda = \frac{h}{p}$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{4\pi^2 p^2}{h^2} \psi(x,t) = 0 \quad — (8)$$

Now, here we try to substitute the momentum 'p' of moving particle in terms of it's total energy, E.

And the total energy, E of the particle can be expressed as

E = Kinetic Energy + Potential Energy

i.e; $E = \frac{1}{2} m v^2 + V = \frac{p^2}{2m} + V \quad — (9)$

where, V is the potential Energy.

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Now let's simplify equation (9) for the value of p^2.

$$\therefore \frac{p^2}{2m} = E - V$$

$$\therefore p^2 = (E-V)\,2m \qquad (10)$$

$\therefore$ eq^n (8) becomes

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{4\pi^2}{h^2} \cdot 2m(E-V) \cdot \psi(x,t) = 0$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{2m(E-V)}{(h/2\pi)^2}\psi(x,t) = 0.$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\psi(x,t) = 0 \qquad (11)$$

This equation is known as Schrodinger Time Independent Wave Equation. Here, the potential energy V is independent on time or having a constant value.

In 3D, the above eq^n (11) takes the form,

$$\nabla^2 \psi(x,t) + \frac{2m(E-V)}{\hbar^2}\psi(x,t) = 0 \qquad (12)$$

where ∇^2 is known as Lapalacian Operator.

which is

$$\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

And '∇' is known as known as vector differential Operator.

And it is

$$\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}.$$

② Schrodinger's Time Dependent Wave Equation:

Schrodinger's Time Dependent Wave equation is applicable to all those cases for which the potential energy of particle explicitly depends on time.

Now, to set-up Schrodinger's Time Dependent Wave Equation we have to start with Time Independent Wave Equation which,

For 1D,

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\psi(x,t) = 0 \quad \text{--- ①}$$

To separate out, the terms for E and V, Let's multiply by $\left(-\frac{\hbar^2}{2m}\right)$ to eqn ①

$$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} - (E-V)\psi(x,t) = 0$$

$$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V\psi(x,t) = E\psi(x,t) \quad \text{--- ②}$$

In this equation ②, if we replace the term of $E\psi(x,t)$ in terms of Total Energy Operator, $\hat{E}$; then this same equation will become Schrodinger's Time Dependent Wave Equation.

Let's consider the quantum mechanical wavefunction $\psi(x,t)$ is as follows,

$$\psi(x,t) = \psi_0 e^{i(kx-\omega t)} \quad \text{— (3)}$$

Differentiate this eqn (3) partially with respect to 't'.

$$\therefore \frac{\partial \psi(x,t)}{\partial t} = \psi_0 e^{i(kx-\omega t)}(-i\omega)$$

$$\therefore \frac{\partial \psi(x,t)}{\partial t} = (-i\omega)\psi(x,t) \quad \text{— (4)}$$

From Plank's Quantum theory.

$$E = h\nu = h\nu \times \frac{2\pi}{2\pi} = \hbar\omega$$

i.e; $E = \hbar\omega$

$$\therefore \omega = \frac{E}{\hbar} \quad \text{—— (5)}$$

Let's substitute the value of ω from eqn (5) into eqn (4)

$$\therefore \frac{\partial \psi(x,t)}{\partial t} = \left(-i\frac{E}{\hbar}\right)\cdot \psi(x,t) \quad \text{— (6)}$$

Now, the term, $E\psi(x,t)$ from eq^n (6) is

$$E\psi(x,t) = -\frac{\hbar}{i}\frac{\partial \psi(x,t)}{\partial t}$$

If we multiply and divide by 'i' with right hand side of above equation, then

$$E\psi(x,t) = -\frac{i\hbar}{i^2}\frac{\partial \psi(x,t)}{\partial t}$$

$$\therefore E\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \quad \text{--- (7)}$$

From equation (7), we can define Total energy operator, $\hat{E}$ as

$$\hat{E} \equiv i\hbar\frac{\partial}{\partial t}$$

i.e. $$\boxed{\hat{E} = i\hbar\frac{\partial}{\partial t}} \quad \text{--- (8)}$$

From eq^n (7), if we substitute the value of $E\psi(x,t)$ in eq^n (2), then

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \quad \text{--- (9)}$$

This is the Schrodinger's Time Dependent wave Equation.

Applications of Schrodinger's Time Independent Wave Equation:

(1) Particle in a Rigid Box (Infinite Potential Well)

Let's consider a particle confined in a 1Dimensional (1D) Rigid Box of length "L". A rigid box means the potential experienced by particle at the walls is infinite and hence it is also known as infinite potential well. And if the particle is a <u>free particle</u>, then it's potential energy, $V = 0$.

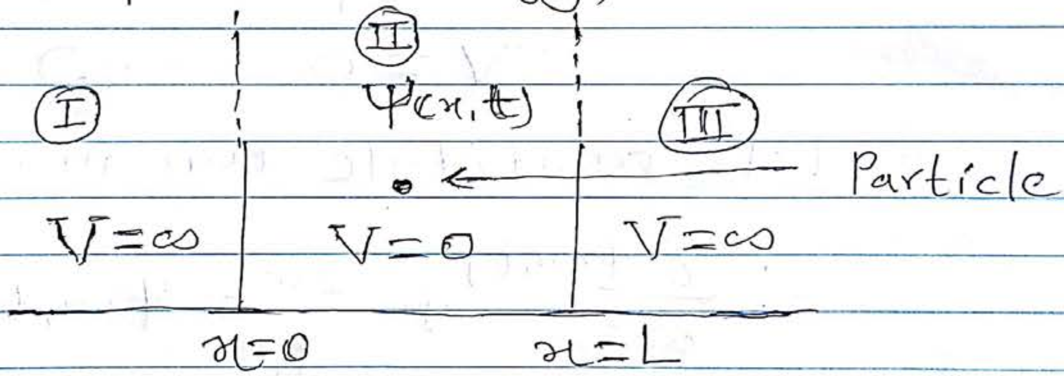

Fig. Free Particle in 1D Rigid Box of length 'L'.

Let's try to express this problem in the mathematical form
i.e;

$$V = 0 \quad ; \quad 0 < x < L$$
(for region II)

$$V = \infty \quad ; \quad 0 \geq x \geq L$$
(for egion I & III)

In fig., the region (II) is the region of rigid box, where a free particle is confined and the ~~matter~~ wavefunction of matter wave associated with this particle is represented as $\psi(x,t)$.

Now let's apply/use Schrodinger's Time Independent Wave Equation for this particle.

The equation is

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\psi(x,t) = 0 \quad \text{--- (1)}$$

For this free particle, as

$$V = 0 \quad \text{--- (2)}$$

Let's substitute this in equation (1)

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x,t) = 0 \quad \text{--- (3)}$$

substitute, $$\frac{2mE}{\hbar^2} = \phi^2 \quad \text{--- (4)}$$

$$\therefore \frac{\partial^2 \psi(x,t)}{\partial x^2} + \phi^2 \psi(x,t) = 0 \quad \text{--- (5)}$$

Equation (5), is a most general second order differential equation (identical with the case of harmonic oscillator), whose general solution can be written as

$$\psi(x,t) = A \sin \phi x + B \cos \phi x \quad \text{—} (6)$$

where 'A' and 'B' are arbitarary constant and there values can be determined from the boundary conditions of the problem.

For this case of particle in a rigid box, there are two boundaries which are at $x=0$ and ~~at~~ $x=L$.

As particle is confined in box only.

$\therefore$ at $x=0$; $\psi(x,t)=0$

Upon substituting this $(x=0)$ in eq^n (6)

$$\therefore \quad 0 = A \sin 0 + B \cos 0$$

$$\therefore \boxed{B=0} \quad \text{—} (7)$$

Substitute this value of 'B' from eq^n (7) in eq^n (6)

$$\therefore \psi(x,t) = A \sin \phi x \quad \text{—} (8)$$

The second boundary is at $x=L$

And

As $x=L$; $\psi(x,t)=0$

Now, upon substituting this $(x=L)$ in eq^n (8), then

$$0 = A \sin(\phi \cdot L)$$

Here, 'A' is an arbitarary const and, $A \neq 0$.

Therefore,

$$\therefore \sin(\phi \cdot L) = 0$$

$$\Rightarrow \phi \cdot L = n\pi \, , \text{ where } n \neq 0$$

$$\therefore \phi = \frac{n\pi}{L} \quad \text{—— (9)}$$

Upon substituting this value ϕ in eq^n (8), then the general solution becomes

$$\psi_n(x,t) = A \sin\left(\frac{n\pi \cdot x}{L}\right) \quad \text{—— (10)}$$

To find out the possible energy values of the particle, let's compare eq^n (9) and eq^n (4)

eq^n (4) is $\phi^2 = \dfrac{2mE}{\hbar^2}$

And from eq^n (9) $\phi^2 = \dfrac{n^2\pi^2}{L^2}$

$$\therefore \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$\therefore \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}} \quad \text{—— (11)}$$

This eq^n (11), will be used to find out all possible energy values of the particle confined in a 1D rigid box of length, L.

In the energy eq^n i.e,

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Here, 'n' is a quantization factor or we can say descritization factor. And $n \neq 0$ and can have all values like $n = 1, 2, 3, 4, 5, \ldots\ldots$ etc.

This indicates that, the particle will posses only certain descrete energies. For $n = 1$, the particle is said to be in a ground state and it's minimum possible energy will be.

As $n = 1$,

$$\therefore E_1 = \frac{1^2 h^2}{8mL^2} = \frac{h^2}{8mL^2} \quad \text{--- (12)}$$

For, 1st Excited state, $n = 2$

$$\therefore E_2 = \frac{2^2 h^2}{8mL^2} = 2^2 \cdot E_1 = 4E_1 \quad \text{--- (13)}$$

For, 2nd Excited state, $n = 3$

$$\therefore E_3 = 3^2 \cdot E_1 = 9 \cdot E_1 \quad \text{--- (14)}$$

In general, $E_n = n^2 \cdot E_1$ — (15)

This indicates that, the possible energies of this particle are either minimum energy (ground state energy/zero point energy) which is $\left(\frac{h^2}{8mL^2}\right)$ or it's n^2 multiples.

This is completely in contradication with the classical/Newtonian Mechanics results, where there is ~~no~~ usually no restrictions on the values of energies of the particle. It can either have zero value or any continuous values of energies upto some maximum limit.

Next important part of this problem is the possible quantum mechanical states of the particle. For that, consider equation (10), which is

$$\Psi_n(x,t) = A \sin\left(\frac{n\pi x}{L}\right) \quad — (10)$$

Here, we have to find out the value of A, from the normalization condition. which is

$$I = \int_{x=0}^{L} \Psi_n(x,t) \cdot \Psi_n^*(x,t)\, dx = 1 \quad — (16)$$

The complex conjugate of $\Psi_n(x,t)$ is

$$\Psi_n^*(x,t) = A \sin\left(\frac{n\pi x}{L}\right) \quad — (17)$$

$$\therefore I = |A|^2 \int_{x=0}^{L} \sin^2\left(\frac{n\pi x}{L}\right) dx \quad \text{--- (18)}$$

From the basic trigonometric identity

$$\sin^2\theta = \frac{1-\cos 2\theta}{2}$$

$$I = \frac{|A|^2}{2} \int_{x=0}^{L} \left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right] dx$$

$$= \frac{|A|^2}{2} \left[\int_{x=0}^{L} 1 \cdot dx - \int_{x=0}^{L} \cos\left(\frac{2n\pi x}{L}\right) dx\right]$$

$$= \frac{|A|^2}{2} \left[x \Big|_{x=0}^{L} - \frac{\sin\left(\frac{2n\pi x}{L}\right)}{\left(\frac{2n\pi}{L}\right)} \Bigg|_{x=0}^{L} \right]$$

$$= \frac{|A|^2}{2} \left[(L-0) - (0-0)\right]$$

$$I = \frac{|A|^2}{2} \cdot L \quad \text{--- (19)}$$

From eq^n (16) and (19)

$$\therefore \frac{|A|^2}{2} \cdot L = 1$$

$$\therefore |A|^2 = \frac{2}{L}$$

And $A = \sqrt{\frac{2}{L}}$ --- (20)

Equation (20) is the value of normalization constant; A.

Therefor equation (10) becomes

$$\psi_n(x,t) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right) \quad \text{— (21)}$$

This equation (21) is known as the normalized quantum mechanical state of the particle confined in 1 dimensional rigid box.

And the corresponding probability density equation eqⁿ is as follows.

$$|\psi_n(x,t)|^2 = \left(\frac{2}{L}\right) \sin^2\left(\frac{n\pi x}{L}\right) \quad \text{— (22)}$$

Now, lets consider the quantum mechanical state function for ground state $(n=1)$, first excited state $(n=2)$ and second excited state $(n=3)$, as follows.

$$\psi_1(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{1\cdot\pi x}{L}\right) \quad \text{— (23)}$$

$$\psi_2(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \quad \text{— (24)}$$

$$\psi_3(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) \quad \text{— (25)}$$

And corresponding probability densities are

$$|\psi_1(x,t)|^2 = \left(\frac{2}{L}\right) \sin^2\left(\frac{1\cdot\pi x}{L}\right) \quad \text{— (26)}$$

$$|\psi_2(x,t)|^2 = \left(\frac{2}{L}\right) \cdot \sin^2\left(\frac{2\pi x}{L}\right) \quad \text{— (27)}$$

$$|\psi_3(x,t)|^2 = \left(\frac{2}{L}\right) \cdot \sin^2\left(\frac{3\pi x}{L}\right) \quad \text{— (28)}$$

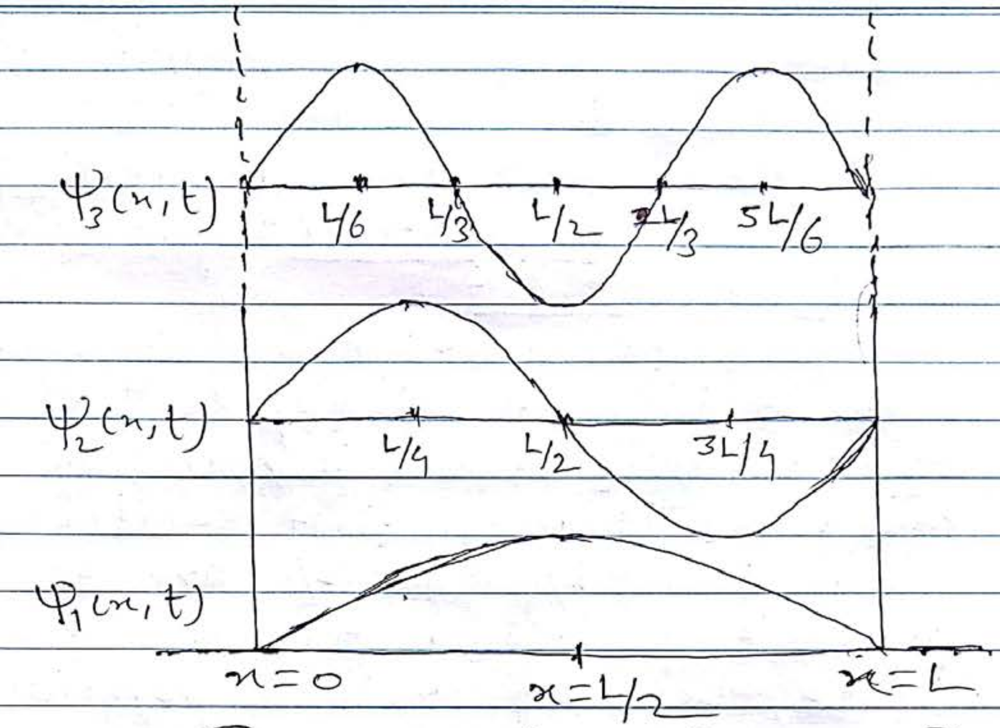

Fig. Ground State First Excited State and Second Excited state function for a particle in 1D Rigid Box.

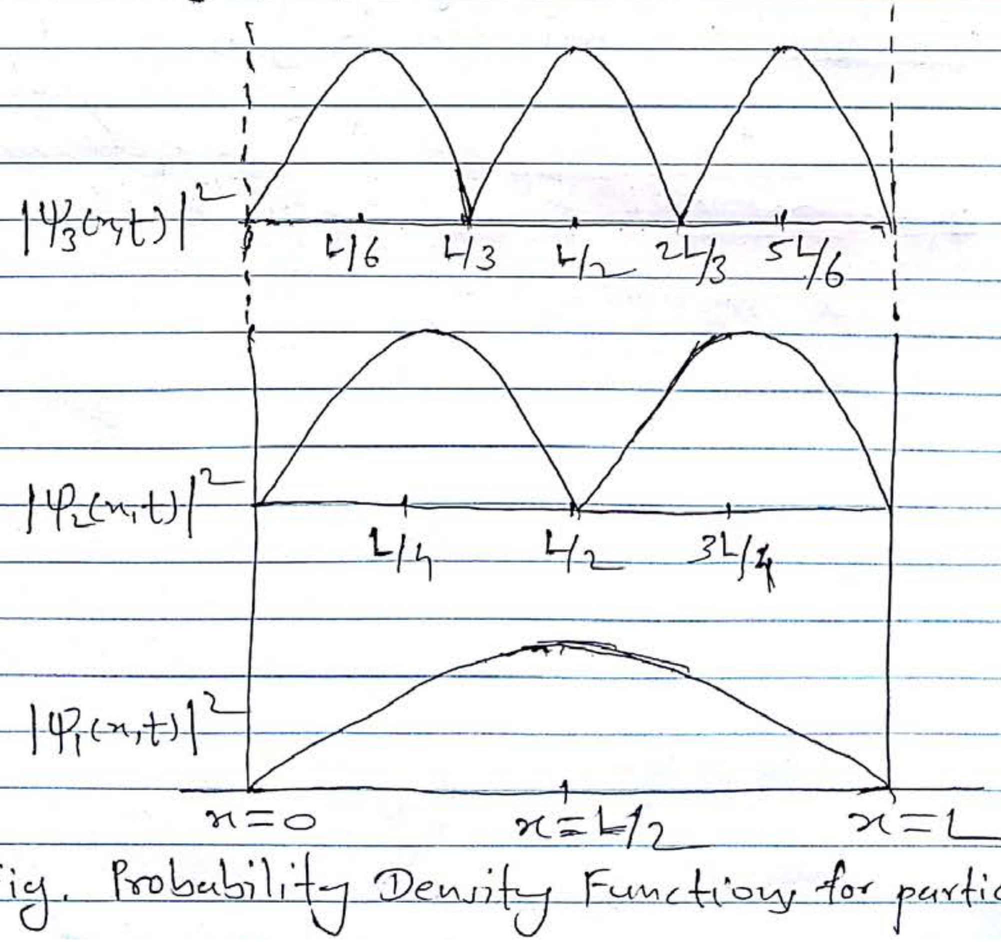

Fig. Probability Density Function for particle in 1D Rigid Box

From the probability density functions of particle confined in a 1D rigid box, It is clear that the probability of finding the particle at different places inside the box is different.

When the particle is in ground state, then it is most likely to be found at the middle of the box i.e; at $x = L/2$ and when it is in first excited state, then at $x = L/4$ and $3L/4$ are the most probabile positions. And for second excited state, the most probable positions are at $x = L/6$, $L/2$ and $5L/6$.

But according to the laws of classical mechanics, when the region of the box is homogeneous or same everywhere, then the probability of finding the particle at different places inside the box is always same.

Particle in a Non-rigid Box:
(Finite Potential Well)

In a non-rigid box, the potential energy experienced at the walls is finite.
i.e, $V = V_0$ at the walls

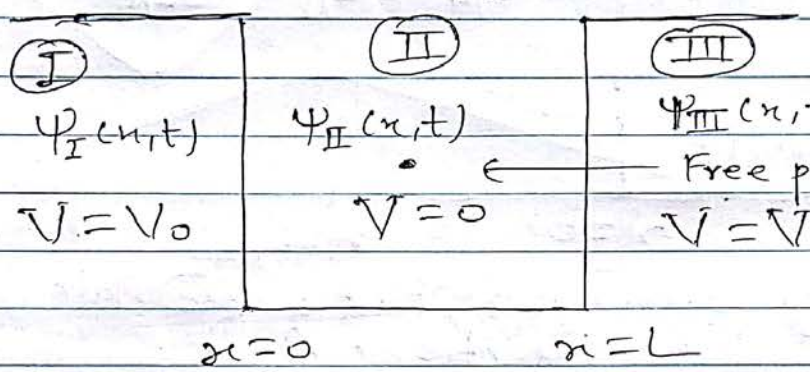

Fig. Particle confinide in a 1D Non-rigid box.

Here, we need to apply Schrodinger's time independent equation for all three regions and we have to solve it for $\psi_n(x,t)$ and E_n values of each of these regions. It is a very lengthy problem. Its derivation is not in our course, but only its comparision of the plots of states function and the probability density functions with the case of rigid box problem is the part of our course.

In these plots, only the change is the function get extended outside the box in region I and region III.

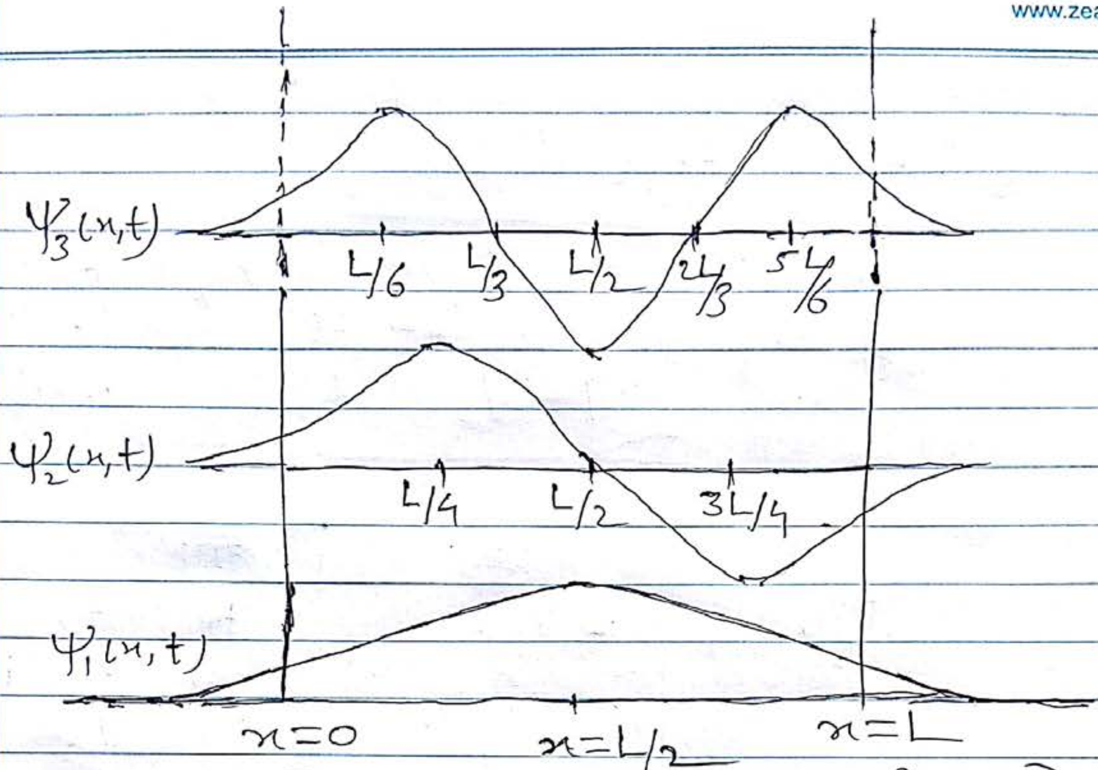

Fig. Ground state, First Excited State & second Excited states functions for a particle in 1D Non-rigid Box.

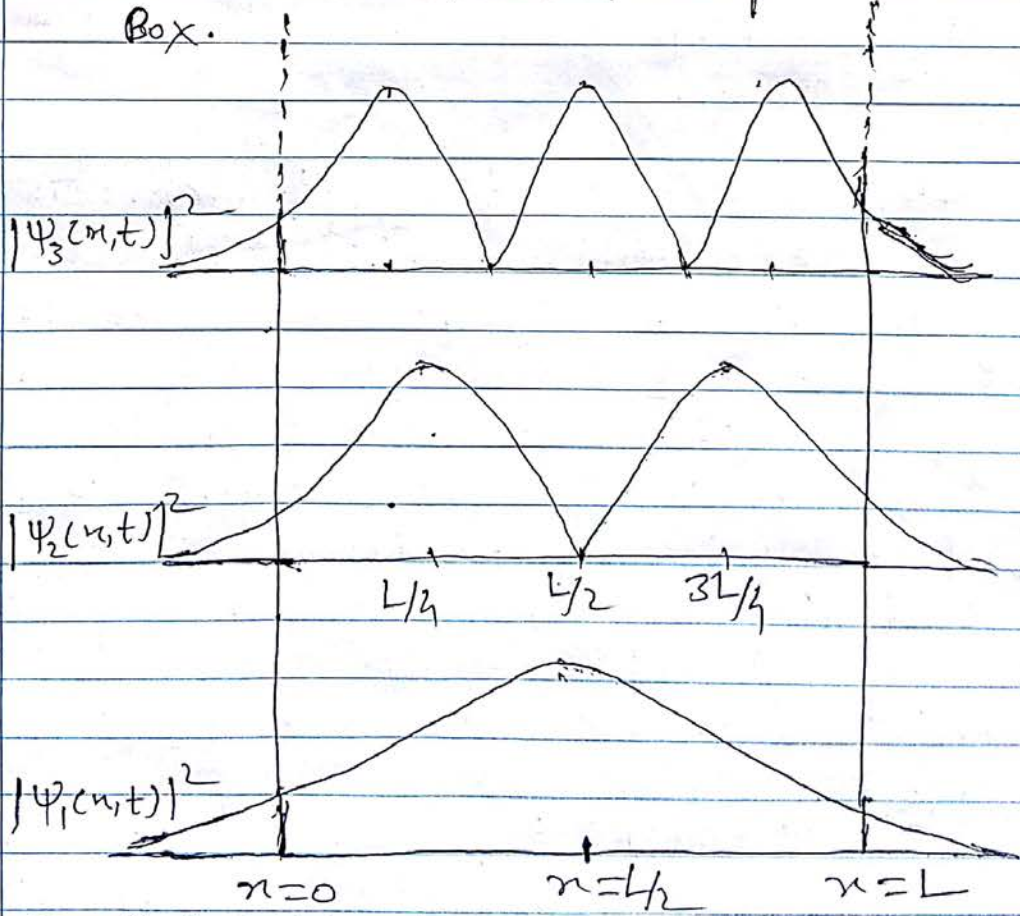

Fig. Probability density function for particle in 1D Non-rigid Box.

Tunneling Effect:

Tunneling effect is a quantum mechanical process by which a particle can pass through a potential energy barrier that is higher than the energy of the particle itself.

This effect will be observed in α-decay, scanning tunneling microscope, tunnel diode etc.

In case of α-decay, the α particles are getting emitted from radioactive nuclei. When we measure the kinetic energy of these α particle, it appears ~~in~~ to be in the range of 4 to 9 MeV. Whereas the coulombic barrier potential of the nucleus ~~nuc~~ is around 30 MeV. Thus here α-particles are tunneling through this huge barrier.

In scanning tunneling microscope, bais voltage is applied between a sharp conductive tip and a conductive sample. The distance between the tip and the sample is of the order of few angstroms therefore it develops a tunneling current due to the tunneling of electrons. The scanning tunneling microscope can operate in constan current mode and constant height mode.

In constant current mode operation of scanning tunneling microscope, the vertical motion of the tip can occure as per the nature of the sample and it can be used to determine the surface topography of the sample.

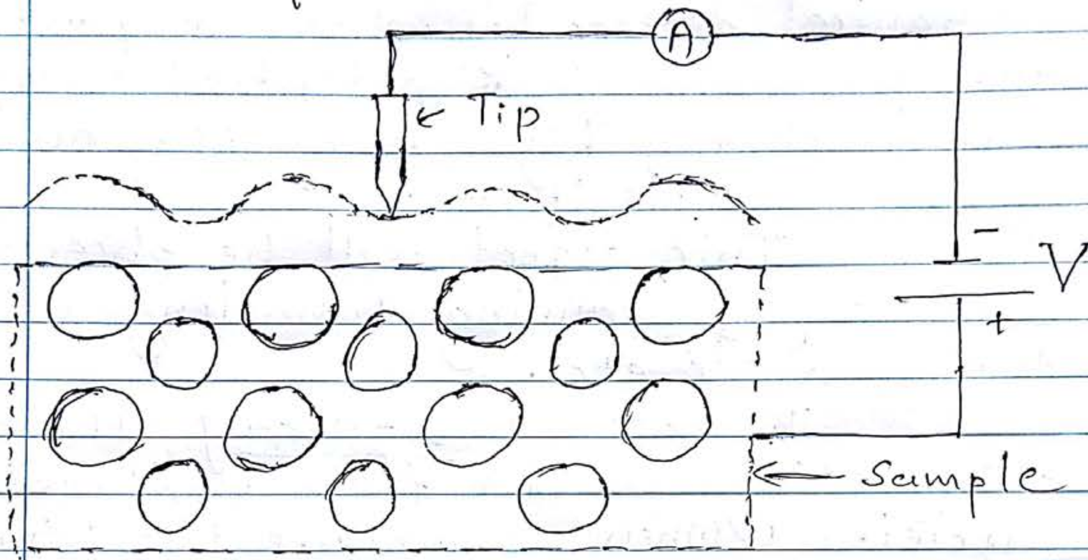

Fig. Constant Current Mode operation

Whereas in constant height mode operation of scanning tunneling microscope, the variation in tunnel current can be used to map the sample topography.

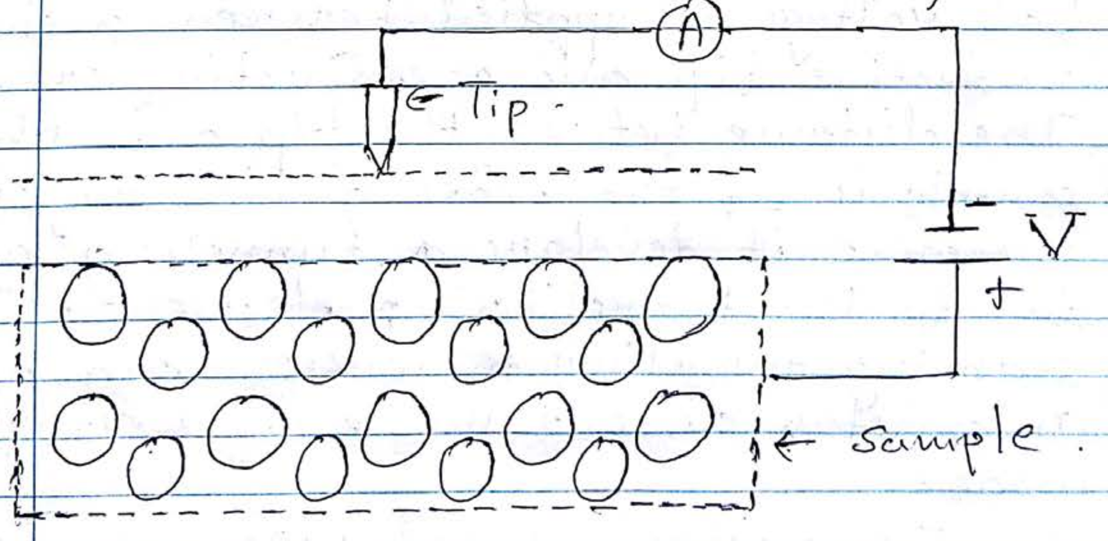

Fig. Constant Height Mode Operation

In tunnel diode, an electric current is produced because of the tunneling of electrons. It is a heavily doped p-n junction diode in which the electric current decrease the voltage increases.

It is fast switching device used in computers, high frequency oscillators etc.

Symbolically, it can be represented as