Unit 1
Quantum Mechanics

Basics of Quantum Mechanics

Why Quantum Physics?

The three theories, namely Newtonian mechanics, thermodynamics and Maxwell's electromagnetic theory together constitute the classical physics.

The classical physics is based on:

1) The physical quantities can take any value.
2. An object can be isolated from its environment and treated as an independent quantity for the investigation.

Classical mechanics (Newton's mechanics) and Maxwell's equations (electromagnetics theory) can explain MACROSCOPIC phenomena such as motion of billiard balls or rockets.

Basics of Quantum Mechanics

There are a few phenomena which classical mechanics failed to explain such as Stability of atom, spectral series of hydrogen atom (line spectra), black body radiation, photoelectric effect etc.

Failures of Classical mechanics led to the **Need of Quantum mechanics**

Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and flow of the electrons in a semiconductor.

QUANTUM MECHANICS is a collection of postulates based on a huge number of experimental observations.

Basics of Quantum Mechanics

1) According to Planck's hypothesis in 1900, the radiating body consists of an enormous number of atomic oscillators vibrating at all possible frequencies and that each oscillator emits or absorb energy in discrete portions.

2) This discrete portions cannot be further subdivided.

Einstein extended Planck's hypothesis.
. An electromagnetic wave having a frequency ν contains identical photons, each photon having an energy $h\nu$

Photoelectric effect:
$h\nu = \mathrm{K.E} + \mathrm{W}$

$\boldsymbol{K.E} = h\nu - \mathrm{W}$

In 1921 A. Einstein received Nobel Prize

De BROGLIE HYPOTHESIS

Light can exhibit both kind of nature of waves and particles so the light shows wave particle duality nature. So the particle electron should also show wave nature.

In some cases like interference ,diffraction and polarization it behaves as a wave while in other cases like photoelectric effect and Compton effect it behaves as a particle (photon)

Not only light but every materialistic particle such as electron, proton or even heavier object exhibits wave particle duality nature.

De Broglie proposed that a moving particle whatever its nature has waves associated with it these waves are called matter waves.

De BROGLIE HYPOTHESIS

Consider a particle of mass m. According to Einstenin's mass energy relation.

$$E = mc^2 \qquad \text{--- (1)}$$

where E is energy and c is the velocity of light. According to Planck's quantum theory

$$E = h\nu \qquad \text{--- (2)}$$

where h is Planck's constant and ν is frequency of oscillations of photon particle. E is energy of photon.

From equation (1) and (2)

$$E = mc^2 = h\nu$$

$$c = \nu\lambda$$

$$\nu = c/\lambda$$

$$mc^2 = h \times \frac{c}{\lambda}$$

$$\lambda = \frac{h}{mc} \qquad v \simeq c$$

$$\lambda = \frac{h}{\text{momentum}}$$

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

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

This equation is known as De-Broglie's wavelength of matter waves.

De BROGLIE HYPOTHESIS

De-Broglie wavelength associated with an accelerated charged particle

If a charged particle, say an electron is accelerated by a potential difference of V volts, then its kinetic energy is given by $K.E. = eV$.

Or $$\frac{1}{2}m\upsilon^2 = eV$$

$\therefore$ $$\upsilon = \sqrt{\frac{2eV}{m}}$$

Then the electron wavelength is given by

$$\lambda = \frac{h}{m\upsilon} = \frac{h}{m} \cdot \sqrt{\frac{m}{2eV}}.$$

$\therefore$ $$\lambda = \frac{h}{\sqrt{2emV}}$$

De BROGLIE HYPOTHESIS

De Broglie Wavelength expressed in terms of K.E.

If a particle has kinetic energy K.E., then $K.E. = \frac{1}{2}m\upsilon^2 = \frac{m^2\upsilon^2}{2m} = \frac{p^2}{2m}$

or $$p = \sqrt{2m(K.E.)}$$

$\therefore$ $$\lambda = \frac{h}{\sqrt{2m(K.E.)}}$$

Properties of matter waves

1. Lighter is the particle, greater is the wavelength associated with it, because $\lambda = \frac{h}{m\,v}$.

2. Smaller is the velocity of the particle greater is the wavelength associated with it.

3. When velocity is zero, then wavelength is infinity. (Wave becomes indeterminate. It shows that waves are generated by the motion of particles.)

4. When velocity is infinity then λ (wavelength) becomes zero.

$$\lambda = \frac{h}{\infty} \Rightarrow \lambda = 0$$

5. The velocity of matter waves depends on the velocity of material particle. Material particle's velocity is not constant while the velocity of electromagnetic waves is constant.

Properties of matter waves

6. The velocity of matter waves is greater than the velocity of light.

Here, $E = h\nu$

By Einstein's relation

$$E = mc^2$$

$$\therefore \quad h\nu = mc^2$$

$$\nu = \frac{mc^2}{h}$$

The wave velocity $\omega = \nu \times \lambda$

$$= \frac{mc^2}{h} \times \frac{h}{mv}$$

$$\omega = \frac{c^2}{v}$$

Here, v cannot exceed the velocity of light.

Therefore $\omega >> c$

Problems

Obtain an expression for the de Broglie wavelength associated with an electron accelerated through V volts. Also find the wavelength for 100v and 54V

Solution: The k.E. Acquired by the electron accelerated through V volts is

$(½)mv^2 = eV$

$mv^2 = 2eV$

$m^2v^2=2meV$

$mv= \sqrt{2meV}$ or $p = \sqrt{2meV}$ ------(1)

$\lambda= h/p$ or $\lambda = h/\sqrt{2meV}$ ($h= 6.625 \times 10^{-34}$ J-s, $m=9.1 \times 10^{-31}$kg, $e= 1.6 \times 10^{-19}$ C

Using all these values $\lambda = (12.27 /\sqrt{V})$ AU

For v=100V , $\lambda = 1.227$ AU

For v=54V $\lambda = 1.67$AU

Problems

Calculate the de Broglie wavelength of an electron moving with speed 1/10 th of the velocity of light.

m = 9.1×10^{-31}kg, h= 6.625×10^{-34} J-s, c = 3×10^{8}m/s

$V = c/10 = 3 \times 10^{7}$ m/s

$P = mv = 2.73 \times 10^{-23}$kg-m/s

$\lambda = h/p = 2.43 \times 10^{-11}$ m

$\lambda = 0.243$ AU

Find the De broglie wavelength of neutron whose K.E. is 1eV.

Given: mass of neutron = 1.676×10^{-27}kg

k.E. of neutron = 1ev

k.E. of neutron = $1 \times 1.6 \times 10^{-19}$ J

$(½)\ mv^2 = 1.6 \times 10^{-19}$ J

$V^2 = (2 \times 1.6 \times 10^{-19}\ J) / m = 1.9093 \times 10^8$

$V = 1.38 \times 10^4$ m/s

$\lambda = h / mv = 0.286$AU

Physical Significance of Wave Function and Probability Density Interpretation

- We know there is a wave associated with a moving particle and the motion of a particle is guided by the wave group.
- The mathematical function which describes wave group is the wave function ψ.
- As the particle moves under the action of external forces the wave function changes with time.

Thus, the variable quantity characterizing the De Broglie wave is called as wave function and it is denoted by the symbol ψ (x,y,z,t).

- ψ describes the wave as a function of position and time.
- The wave function usually contains all the information which the uncertainty principle allows us to know about the associated particle. But the wave function ψ itself has no physical interpretation, as it may be positive, negative or complex.

Physical Significance of Wave Function and Probability Density Interpretation

- ψ has no direct physical significance, as it is not an observable quantity. In general, ψ is a complex-valued function.
- According to Heisenberg uncertainty principle, we can only know the probable value in a measurement.
- The probability cannot be negative. Hence ψ cannot be a measure of the presence of the particle at the location (x, y, z).
- This difficulty is solved by taking $|\psi|^2 = \psi\,\psi^*$. This quantity is called probability density.
- The product of ψ and its complex conjugate is having physical significance and it represents the probability of finding the particle in a volume dxdydz.
- A probability interpretation of the wave function was given by Max Born in 1926.
- He suggested that ***the square of the magnitude of the wave function $|\psi|^2$ evaluated in a particular region represents the probability of finding the particle in that region.***

Physical Significance of Wave Function and Probability Density Interpretation

Probability, P, of finding the particle in an infinitesimal volume *dV (= dx dy dz) is* proportional to $|\psi(x, y, z)|^2 \, dx\, dy\, dz$ *at time t.*

$$P \propto |\psi(x,y,z)|^2 \, dV$$

$|\psi|^2$ is called the **probability density and** ψ **is the probability amplitude.**

Since the particle is certainly somewhere in the space, the probability *P = 1 and the* integral of $|\psi|^2 dV$ *over the entire space must be equal to unity. That is*

$$\int_{-\infty}^{+\infty} |\psi|^2 \, dV = 1$$

The wave function ψ is in general a complex function. But the probability must be real.

Physical Significance of Wave Function and Probability Density Interpretation

Therefore to make probability a real quantity, ψ is to be multiplied by its complex conjugate ψ^*

$$\int_{-\infty}^{+\infty} \psi\psi^* \, dV = 1$$

Thus, ψ has no physical significance but $|\psi|^2$ gives the probability of finding the particle in a particular region..

The above condition on ψ is known as normalisation condition. the wave function that satisfies above condition is called normalised wave function.

Physical Significance of Wave Function and Probability Density Interpretation

How to normalise a wave function?

If the wave function is not normalised in order to normalise the wave function it is multiplied by some arbitrary constant and then the integral is evaluated over the entire space.

The normalisation procedure is as follows:

If ψ is not normalised wave function then multiply it by some constant A. Then evaluate the integral and equate it to unity and calculate the constant A called normalisation constant i.e.

$$\int A\psi\,(A\psi)^*\,dV = 1$$

Or $$AA^*\int \psi\,\psi^*\,dV = 1$$

As A is real constant, we get

$$|A|^2\int \psi\,\psi^*\,dV = 1$$

This gives normalisation constant as

$$|A|^2 = 1 / \left(\int\psi\,\psi^*\,dV\right)$$

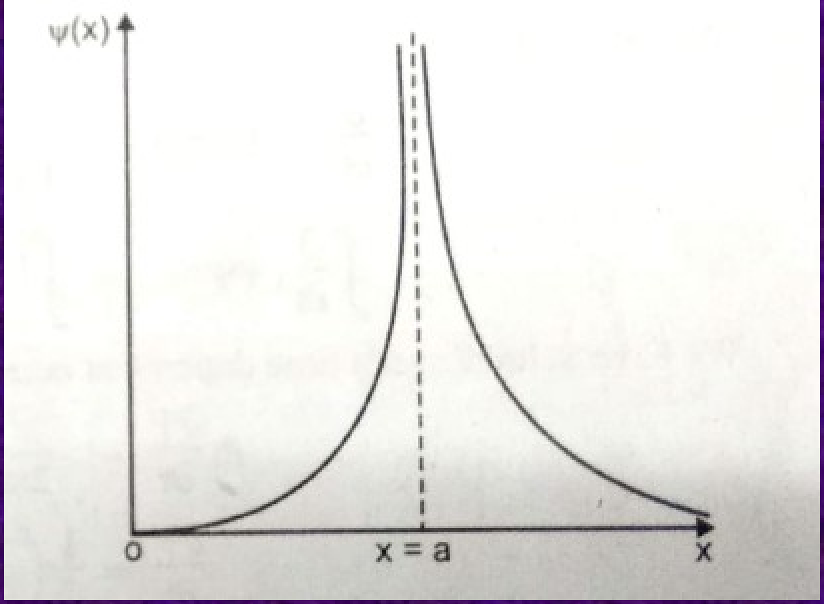
The normalisation constant can be positive square root of above equation.

Requirements of wave function

Conditions to be satisfied by ψ – function

1) ψ *function must be finite:* The wave function must be finite everywhere.

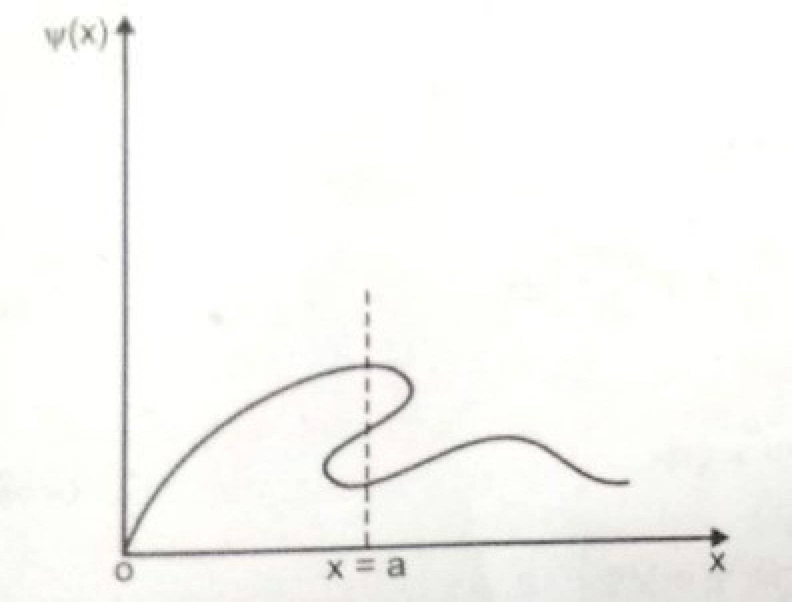
It must remain finite for all values of x, y, z. If ψ is infinite, it would imply an infinitely large probability of finding the particle at that point.



Not finite at x=a

Requirements of wave function

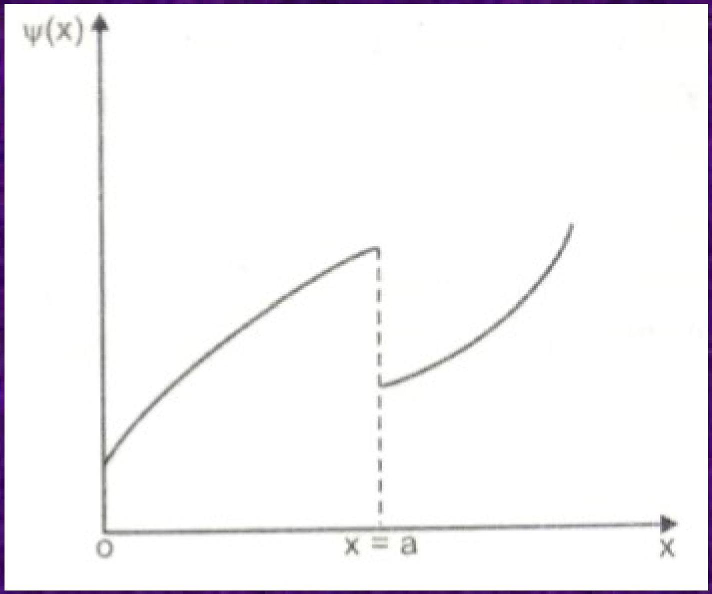
2) ψ function must be single–valued: The function related to a physical quantity cannot have more than one value at that point. If it has more than one value at a point,it means that there is more than one value of probability of finding the particle at that point.



Not single valued

Requirements of wave function

3) ψ function must be continuous: **ψ function** should be continuous across any boundary. Since ψ is related to a physical quantity, it cannot have a discontinuity at any point. Therefore, the wave function ψ and its space derivatives should be continuous across any boundary. Since ψ is related to a real particle, it cannot have a discontinuity at any boundary where potential changes.

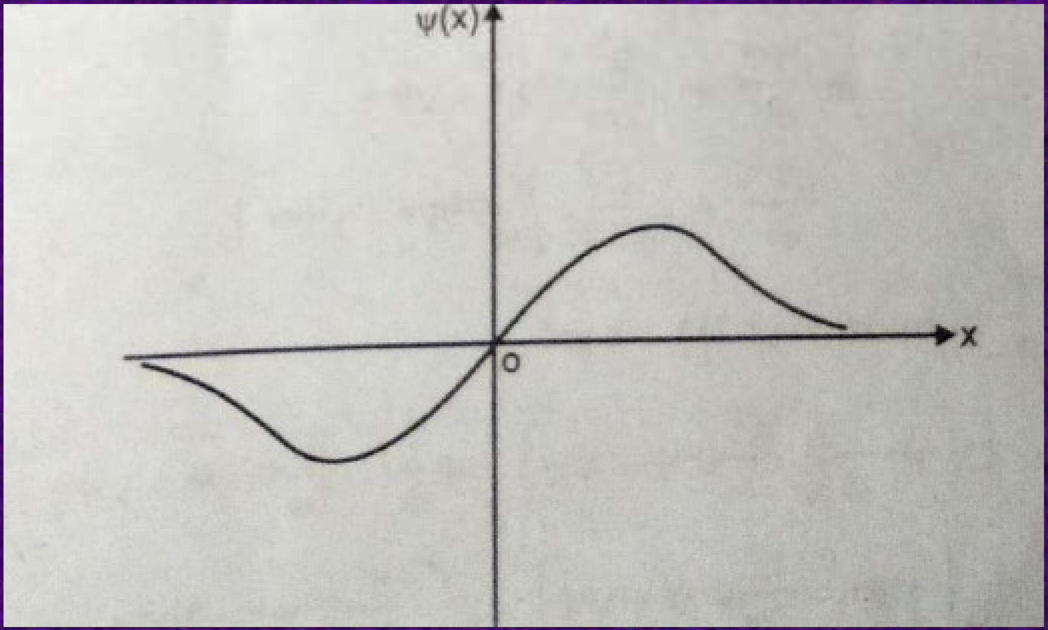


Discontinuous at x=a

Well-behaved Wave Functions

4) ψ function must be normalised:

$$\int_{-\infty}^{+\infty} \psi\psi^{*} dV = 1$$



Well behaved wave function

Schrodingers time dependent wave equation

In order to obtain Schrödinger wave equation, we will start with an equation of a wave propagating along +X axis. The general equation for the wave motion of a particle is given by

$$y = Ae^{i(kx - \omega t)}$$

In quantum mechanics, the wave function Ψ corresponds to the variable y of general wave motion. However, Ψ itself is not a measurable quantity, and may, therefore, be complex. For this reason, we assume that Ψ for a particle moving freely along $+x$ axis is specified by

$$\Psi = Ae^{i(kx - \omega t)} \qquad \ldots(2.1)$$

The de Broglie – Einstein postulates are

$$\lambda = \frac{h}{p} \quad \text{and} \quad E = h\nu$$

We can write above equations as

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k \qquad (\because\ k = 2\pi/\lambda)$$

Schrodingers time dependent wave equation

and $$E = h\nu = \frac{h}{2\pi} 2\pi\nu = \hbar\omega \qquad (\because \ \omega = 2\pi\nu)$$

Therefore,

$$k = \frac{p}{\hbar} \text{ and } \omega = \frac{E}{\hbar}$$

Using these in equation (2.1), we get

$$\Psi = A\, e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}$$

or $$\Psi = Ae^{\frac{i}{\hbar}(px - Et)} \qquad \ldots(2.2)$$

Equation (2.2) represents the wave equivalent of a free particle of total energy E and momentum p moving in the $+x$ direction. Equation (2.2) is true only for the particles moving freely. But we are interested in situations where the motion of particle is constrained by some restrictions. We wish to obtain differential equation for the wave function Ψ, which can be solved in specific situations. This equation is called Schrödinger's equation.

Differentiating equation (2.2) w. r. t. x we get

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} Ae^{\frac{i}{\hbar}(px - Et)} \qquad \ldots(2.3)$$

Schrodingers time dependent wave equation

Again differentiating above equation with respect to x, we get

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} Ae^{\frac{i}{\hbar}(px - Et)}$$

$$\therefore \quad \frac{\partial^2\Psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\Psi \qquad \ldots(2.4)$$

Therefore, from the above equation, we get

$$p^2\Psi = -\hbar^2 \frac{\partial^2\Psi}{\partial x^2} \qquad \ldots(2.5)$$

Differentiating equation (2.2) with respect to t, we get

$$\frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar} Ae^{\frac{i}{\hbar}(px - Et)}$$

or

$$\frac{\partial\Psi}{\partial t} = -\frac{iE}{\hbar}\Psi$$

Above equation can be written as

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = E\Psi$$

or

$$E\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad \ldots(2.6)$$

Schrodingers time dependent wave equation

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When speed of the particle is small compared to the velocity of light, the total energy E of a particle is the sum of kinetic energy $p^2/2m$ and potential energy V(x).

$$E = \frac{p^2}{2m} + V \qquad \ldots(2.7)$$

Multiplying equation (2.7) on both sides by Ψ, we get

$$E\Psi = \frac{p^2\Psi}{2m} + V\Psi \qquad \ldots(2.8)$$

Substituting $p^2\Psi$ and EΨ from equations (2.5) and (2.6) in equation (2.8), we get

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \qquad \ldots(2.9)$$

Equation (2.9) was first obtained by Schrödinger in 1926 and, therefore, called Schrödinger's wave equation. This is Schrödinger's *time dependent equation*. Equation (2.9) is a one-dimensional equation, since it is for motion along X-direction.

Schrodingers time dependent wave equation

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In two dimensions, the equation (2.9) can be written as

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2}\right) + V\Psi \qquad \ldots(2.10)$$

where $\Psi = \Psi(x, y, t)$

In three dimensions, the equation (2.9) can be written as

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}\right) + V\Psi$$

or

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad \ldots(2.11)$$

where

$$\Psi = \Psi(x, y, z, t)$$

and

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

Schrodingers time independent wave equation

In number of situations the potential energy of a particle is independent of the time explicitly and depends on the position only. In such situations Schrödinger's equation is simplified by removing the time dependent part.

We have one-dimensional Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi \qquad \text{...(2.12)}$$

where $\Psi = \Psi(x, t)$

This equation can be solved by separation of variables method.

Let $$\Psi(x, t) = \psi(x)\,\phi(t) \qquad \text{...(2.13)}$$

Using equation (2.13) in (2.12), we get

$$i\hbar \frac{\partial \psi\phi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi\phi}{\partial x^2} + V\psi\phi$$

$$\therefore \quad i\hbar\psi \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2m}\phi\frac{\partial^2 \psi}{\partial x^2} + V\psi\phi$$

Dividing above equation throughout by $\psi\phi$, we get

$$i\hbar \frac{1}{\phi}\frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2} + V \qquad \text{...(2.14)}$$

Schrodingers time independent wave equation

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The right side of above equation is function of x only and the left side is function of t only. This is possible only when both sides are equal to some constant, say E. We denote this constant as energy E because first term on RHS is kinetic energy and second term is potential energy. Thereore,

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2\psi}{\partial x^2} + V = E \qquad \text{...(2.15)}$$

and

$$i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t} = E \qquad \text{...(2.16)}.$$

Schrodingers time independent wave equation

Equation (2.15) can be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \ldots(2.17)$$

This is Schrödinger's *one dimensional time independent equation*. Since the differential equation does not involve the time variable 't', the solution ψ also does not depend upon time t. Hence the equation is also called *steady state equation*.

In three dimensions (x, y, z), Schrödinger's time independent equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

$$\text{or} \quad \nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \ldots(2.18)$$

where $\psi = \psi(x, y, z)$ and $\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$

Schrodingers time independent wave equation

- **Solution of time part equation:**

Equation (2.16) can be written as

$$\frac{1}{\phi}\frac{\partial\phi}{\partial t} = \frac{1}{i\hbar}E$$

Since ϕ depends only on 't', we have

$$\frac{1}{\phi}\frac{d\phi}{dt} = -\frac{i}{\hbar}E$$

$$\therefore \qquad \frac{d\phi}{\phi} = -\frac{i}{\hbar}Edt$$

On integration we get,

$$ln\,(\phi) = -\frac{i}{\hbar}E\,t + ln\,A$$

where A is a constant.

$$\therefore \qquad \phi = A\,e^{-\frac{iE}{\hbar}t}$$

Ignoring the multiplicative constant A, we write

$$\Psi\,(x, t) = \psi\,(x)\,e^{-\frac{iE}{\hbar}t}$$

Operators in quantum mechanics

The wave function for one-dimensional motion of a free particle along x-axis is given as

$$\Psi(x,t) = A\, e^{\frac{i}{\hbar}(px - Et)}$$

Differentiating equation (2.2) with respect to x we get

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} A\, e^{\frac{i}{\hbar}(px - Et)}$$

or
$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} \Psi$$

∴
$$p\Psi = \frac{\hbar}{i} \frac{\partial \Psi}{\partial x}$$

or
$$p\Psi = -i\hbar \frac{\partial \Psi}{\partial x} \qquad \ldots(2.28)$$

Differentiating $\Psi(x, t)$ with respect to t, we get

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} A\, e^{\frac{i}{\hbar}(px - Et)}$$

or
$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$$

∴
$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = E\Psi$$

or
$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \ldots(2.29)$$

Operators in quantum mechanics

Equation (2.28) indicates that there is an association between the dynamical quantity p and the differential operator $-i\hbar\frac{\partial}{\partial x}$. That is the effect of multiplying $\Psi(x, t)$ by p is the same as the operating the differential operator $-i\hbar\frac{\partial}{\partial x}$ on $\Psi(x, t)$. This differential operator $\left(-i\hbar\frac{\partial}{\partial x}\right)$ is called *momentum operator*. It can be written as

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} \qquad \ldots(2.30)$$

As it is related to variable x, we have

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

Corresponding components of momentum operators for y and z variables are

$$\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$$

and

$$\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

From equation (2.29), a similar association can be found between dynamical variable E and the differential operator $i\hbar\frac{\partial}{\partial t}$. Thus,

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \qquad \ldots(2.31)$$

Eigen Functions and Eigen Values

Let ψ be the well behaved function of the state of the system and an operator operates on this function such that

$$\hat{A}\,\psi(x) = a\,\psi(x)$$

where $\hat{A}$ is an operator

$\psi(x)$ is the eigen function

a is eigen value of operator $\hat{A}$

For example,

$$\frac{d^2}{dx^2}e^{4x} = 16e^{4x}$$

where $\frac{d^2}{dx^2}$ is operator

e^{4x} is the eigen function

16 is eigen value.

Expectations Values

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The expectation value of any dynamical variable is given by

$$\langle f \rangle = \int \psi^* f \psi \, dx$$

Thus expectation value of position of particle is given by

$$\langle x \rangle = \int \psi^* x \psi \, dx$$

In order to obtain expectation value of momentum p and energy E corresponding operators are used.

$$\langle p \rangle = \int \psi^* \hat{p} \psi \, dx$$

$$\langle p_x \rangle = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, dx$$

$$\langle p_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, dx$$

For energy

$$\langle E \rangle = \int \psi^* \hat{E} \psi \, dx$$

$$= \int \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dx$$

$$= i\hbar \int \psi^* \frac{\partial \psi}{\partial t} \, dx$$

Problems

1) Find eigen value of the operator $\frac{d^2}{dx^2}$ for eigen function $e^{-i\alpha x}$.

Solution: $\frac{d}{dx}(e^{-i\alpha x}) = -i\alpha e^{-i\alpha x}$

$$\frac{d^2}{dx^2}(-i\alpha e^{-i\alpha x}) = -i\alpha \cdot -i\alpha e^{-i\alpha x}$$

$$= i^2\alpha^2 e^{-i\alpha x}$$

$$= -\alpha^2 e^{-i\alpha x}$$

$$\frac{d^2}{dx^2}(e^{-i\alpha x}) = -\alpha^2 e^{-i\alpha x}$$

$-\alpha^2$ is the eigen value.

2) The eigen function for momentum operator is e^{ikx}. Find eigen value.

Solution: $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

$$-i\hbar\frac{\partial}{\partial x}e^{ikx} = -i\hbar \cdot ik e^{ikx}$$

$$= -i^2\hbar k e^{ikx}$$

$$= \hbar k e^{ikx}$$

$\hbar k$ is the eigen value.

Example 4 : *Consider the wave function of a particle*

$$\Psi(x) = A\left(1 - \frac{x}{a}\right) \text{ for } a/2 < x < a$$

Find the normalisation constant A and also obtain $\langle x \rangle$.

Solution:

$$|\psi(x)|^2 = |A|^2\left(1 - \frac{x}{a}\right)^2 = |A^2|\left(1 - \frac{2x}{a} + \frac{x^2}{a^2}\right)$$

We have

$$\int_{a/2}^{a} |\psi(x)|^2 \, dx = 1$$

$$\therefore \quad |A|^2 \int_{a/2}^{a}\left(1 - \frac{2x}{a} + \frac{x^2}{a^2}\right) dx = 1$$

$$|A|^2\left[x - \frac{x^2}{a} + \frac{x^3}{3a^2}\right]_{a/2}^{a} = 1$$

$$|A|^2\left[a - \frac{a^2}{a} + \frac{a^3}{3a^2} - \left(\frac{a}{2} - \frac{a^2}{4a} + \frac{a^3}{24a^2}\right)\right] = 1$$

$$|A|^2\left(\frac{a}{24}\right) = 1$$

$$\therefore \quad |A| = \sqrt{\frac{24}{a}}$$

$$\therefore \quad \psi(x) = \sqrt{\frac{24}{a}}\left(1 - \frac{x}{a}\right)$$

Expectation value of x is given as

$$\langle x \rangle = \int_{a/2}^{a} x\,|\psi(x)|^2\,dx$$

$$\langle x \rangle = |A|^2 \int_{a/2}^{a} x\left(1 - \frac{2x}{a} + \frac{x^2}{a^2}\right) dx$$

$$= \frac{24}{a} \int_{a/2}^{a} \left(x - \frac{2x^2}{a} + \frac{x^3}{a^2}\right) dx$$

$$= \frac{24}{a}\left[\frac{x^2}{2} - \frac{2x^3}{3a} + \frac{x^4}{4a^2}\right]_{a/2}^{a}$$

$$= \frac{24}{a}\left[\frac{a^2}{2} - \frac{2a^3}{3a} + \frac{a^4}{4a^2} - \left(\frac{a^2}{8} - \frac{2a^3}{24a} + \frac{a^4}{64a^2}\right)\right]$$

$$= \frac{24}{a}\left[\frac{a^2}{2} - \frac{2a^3}{3a} + \frac{a^4}{4a^2} - \frac{a^2}{8} + \frac{2a^3}{24a} - \frac{a^4}{64a^2}\right]$$

$$= \frac{24}{a}\, a^2\left[\frac{1}{2} - \frac{2}{3} + \frac{1}{4} - \frac{1}{8} + \frac{2}{24} - \frac{1}{64}\right]$$

$$\langle x \rangle = 0.625\, a$$

Example 5 : *Normalise the wave function*

$$\Psi(x) = A\, e^{-x^2/2a^2 + ikx}$$

The range of x is from $-\infty$ to $+\infty$.

Solution : If A is the normalisation constant, then $\int \Psi\Psi^* \, dx = 1$

$$\therefore \quad \int_{-\infty}^{\infty} A\, e^{-x^2/2a^2 + ikx} \; A^*\, e^{-x^2/2a^2 - ikx} \, dx = 1$$

or

$$|A|^2 \int_{-\infty}^{\infty} e^{-x^2/a^2} \, dx = 1$$

We have the general integral $\int_{-\infty}^{\infty} e^{-\beta x^2} \, dx = \sqrt{\frac{\pi}{\beta}}$

Therefore,

$$|A|^2 \sqrt{\frac{\pi}{1/a^2}} = 1$$

$$|A|^2\, a\sqrt{\pi} = 1$$

$$\therefore \quad |A| = \frac{1}{\sqrt{a}\, \pi^{1/4}}$$

$$\psi(x) = \frac{1}{\sqrt{a}\, \pi^{1/4}}\, e^{-x^2/2a^2 + ikx}$$

Example 10 : *A wave function of a free particle moving in the range $-\infty$ to $+\infty$ is given by*

$$\psi(x) = x\, e^{-\alpha x^2}$$

Normalise the wave function.

Solution : In order to normalise the wave function, multiply the rhs by constant A.

$\therefore$

$$\psi(x) = A\, x\, e^{-\alpha x^2}$$

Condition for normalisation is

$$\int |\Psi|^2\, dx = 1 \quad \text{or} \quad \int \Psi\Psi^*\, dx = 1$$

$$\therefore \quad \int_{-\infty}^{\infty} A\, x\, e^{-\alpha x^2}\, A^*\, x\, e^{-\alpha x^2}\, dx = 1$$

$$\therefore \quad AA^* \int_{-\infty}^{\infty} x^2\, e^{-2\alpha x^2}\, dx = 1$$

or

$$|A|^2 \int_{-\infty}^{\infty} x^2\, e^{-2\alpha x^2}\, dx = 1$$

We have the general integral $\int_{-\infty}^{\infty} x^2\, e^{-\beta x^2}\, dx = \frac{1}{2\beta}\sqrt{\frac{\pi}{\beta}}$

Thus,

$$\int_{-\infty}^{\infty} x^2\, e^{-\alpha x^2}\, dx = \frac{1}{2(2\alpha)}\sqrt{\frac{\pi}{(2\alpha)}}$$

$$\therefore \quad |A|^2 \frac{1}{2(2\alpha)}\sqrt{\frac{\pi}{(2\alpha)}} = 1$$

$$|A|^2 = 4\alpha\sqrt{\frac{2\alpha}{\pi}}$$

or

$$A = 2\left(\frac{2\alpha^3}{\pi}\right)^{1/4}$$

$$\therefore \quad \psi(x) = 2\left(\frac{2\alpha^3}{\pi}\right)^{1/4} x\, e^{-\alpha x^2/2}$$

Numericals

A particle is limited to move on x-axis has the normalised wavefunction given by..

$$\Psi(x) = ax \quad \text{for} \quad 0 \le x \le 1$$
$$= 0 \quad \text{at all other points.}$$

What is the probability that particle is found between x=0.45 and x=0.55 ?

Solution: Probability $P = \int_{0.45}^{0.55} |\Psi|^2 dx$

$$P = \int_{0.45}^{0.55} (ax)^2 dx$$

$$= a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55}$$

$$= 0.0251\, a^2$$

Numericals

Problem : A wave function of the free particle in the range -∞ to +∞ is given by
$\psi = A\, e^{-\alpha x^2/2}$

Normalise the wave function given by $\psi = Ae^{\frac{-\alpha x^2}{2}}$ (Given : $\int_{-\infty}^{\infty} e^{-\beta x^2}\,dx = \sqrt{\frac{\pi}{\beta}}$)

Solution: Condition for normalization is

$$\int_{-\infty}^{+\infty} |\psi|^2\,dx = 1 \quad \text{or} \quad \int_{-\infty}^{+\infty} \psi\,\psi^* = 1$$

$$\therefore \int_{-\infty}^{+\infty} A\, e^{-\frac{\alpha x^2}{2}}\; A^*\, e^{-\frac{\alpha x^2}{2}}\,dx = 1$$

$$A A^* \int_{-\infty}^{+\infty} e^{-\alpha x^2}\,dx = 1$$

$$\text{or} \quad |A|^2 \int_{-\infty}^{+\infty} e^{-\alpha x^2}\,dx = 1$$

$$|A|^2 \sqrt{\frac{\pi}{\alpha}} = 1 \qquad \left[\because \int_{-\infty}^{+\infty} e^{-\beta x^2}\,dx = \sqrt{\frac{\pi}{\beta}}\right] \text{ Given}$$

$$|A|^2 = \sqrt{\frac{\alpha}{\pi}}$$

$$A = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\therefore \boxed{\psi(x) = \left(\frac{\alpha}{4}\right)^{1/4} e^{-\frac{\alpha x^2}{2}}}$$

Motion of a free particle

Suppose the particle is moving with constant potential i.e
V(x) = constant.

Then the force acting on the particle F = -dV/dx = 0

Because force is called as negative gradient of potential.

Thus the particle is free particle so to predict the quantum mechanical behaviour of a free particle, we have to solve the schrodingers time independent wave equation

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

With V = 0, we get

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \ldots(4.1)$$

Let $k^2 = \frac{2mE}{\hbar^2}$

$$\therefore \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots(4.2)$$

Motion of a free particle

- The solution of equation 4.2 are eigen functions. The possible solutions of equation 4.2 are e^{-ikx} and e^{ikx}

Suppose $\Psi = e^{-ikx}$

$$\frac{d\Psi}{dx} = -ik\,e^{-ikx}$$

$$\frac{d^2\Psi}{dx^2} = -k^2 e^{-ikx}$$

$$\frac{d^2\Psi}{dx^2} = -k^2\Psi$$

Substitute in eq^n 4.2

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0$$

$$\cancel{-k^2\Psi} + \cancel{k^2\Psi} = 0$$

So value of Ψ satisfy the eq^n 4.2

The solution of the time part is given by

$\phi(t) = e^{-iEt/\hbar}$ Since we have $E = \hbar\omega$

There fore $\phi(t) = e^{-i\omega t}$

The wave function is

$$\Psi(x,t) = \psi(x)\,\phi(t)$$

$$\Psi(x,t) = e^{ikx}\,e^{-i\omega t} = e^{i(kx-\omega t)} \quad \text{--------4.3}$$

$$\Psi(x,t) = e^{-ikx}\,e^{-i\omega t} = e^{-i(kx+\omega t)} \quad \text{--------4.4}$$

Equation 4.3 represents wave propagating along +x direction and

Equation 4.4 represents wave propagating along –ve x direction

Motion of a free particle

- Let us consider equation 4.3 and Let A is the normalization constant

$$\Psi\ (x,t) = A\ e^{i(kx-\omega t)}$$

$$\Psi^*\ (x,t) = A^*\ e^{-i(kx-\omega t)}$$

$$\Psi\ \Psi^* = A\ A^* = e^{i(kx-\omega t)}\ e^{-i(kx-\omega t)}$$

$\Psi\ \Psi^* = A\ A^* =$ Constant (This probability density)

There is difficulty in the normalisation of free partcile wave function. According to normalisation condition

$$\int_{-\infty}^{\infty} \Psi^*\Psi\, dx = AA^* \int_{-\infty}^{\infty} dx = 1$$

$$AA^* \int_{-\infty}^{\infty} dx = 1$$

$$A\ A^*\ [x]_{-\infty}^{\infty} = 1$$

$$A\ A^*\ \infty = 1$$

A A* is the amplitude of the wave. There fore the probability of finding the particle will be very small everywhere.

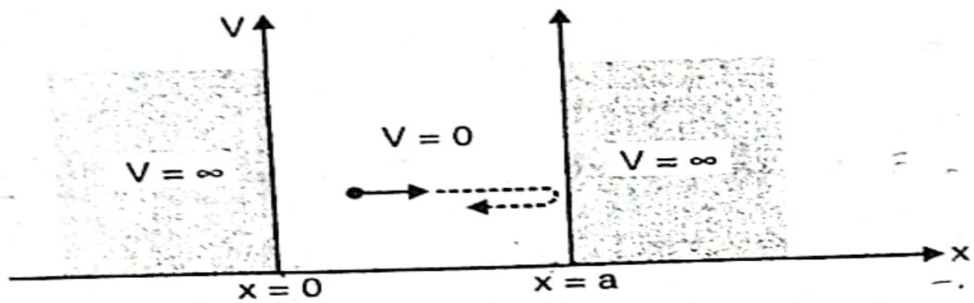
Particle in an infinite deep potential well (Rigid box)

•

Let us consider one-dimensional motion along X-axis of a particle between two points $x = 0$ and $x = a$. The particle is free to move between 0 and a. But it cannot cross to the left of $x = 0$ and to the right of $x = a$. This situation is represented by the potential function V given by

$$V = \infty \qquad x \leq 0$$
$$V = 0 \qquad 0 < x < a$$
$$V = \infty \qquad x \geq a$$

A partcile moving under the influence of infinite square well potential is often called a particle in one dimensional rigid box



In the region within the potential well, the time-independent Schrödinger's equation can be solved to obtain eigen values of energy and corresponding eigen functions.

Schrödinger's time independent equation is given as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \ldots(4.6)$$

Particle in an infinite deep potential well (Rigid box)

In the region $0 < x < a$, above equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \ldots(4.7)$$

Let

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \qquad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots(4.8)$$

The general solution of this equation may be written as

$$\psi(x) = A \sin kx + B \cos kx \qquad \ldots(4.9)$$

where A and B are arbitrary constants and can be obtained by using the boundary conditions on ψ.

Out side the region $0 < x < a$ the wave function $\psi(x) = 0$

Also, at the boundaries of the potential well, $\psi(x) = 0$

Therefore, at $x = 0$, $\psi(x) = 0$, which gives

$$B = 0$$

Using in equation (4.9), we get

$$\psi(x) = A \sin(kx) \qquad \ldots(4.10)$$

At $x = a$, $\psi(x) = 0$, which gives

$$A \sin(ka) = 0$$

Particle in an infinite deep potential well (Rigid box)

Thus we choose k such that sin ka = 0. This is possible only if

$$ka = n\pi \qquad \text{where } n = 1, 2, 3, 4, 5, \ldots$$

or

$$k = \frac{n\pi}{a} \qquad \ldots(4.11)$$

∴

$$\psi(x) = A \sin\left(\frac{n\pi}{a}x\right) \qquad \ldots(4.12)$$

Since we have $k^2 = \frac{2mE}{\hbar^2}$, therefore,

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

Thus, we get energy eigen value

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Since energy E depends on index 'n', we may write

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad \ldots(4.13)$$

where n = 1, 2, 3, 4

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2} \qquad \ldots(4.14)$$

$$E_2 = 4\frac{\pi^2\hbar^2}{2ma^2} = 4E_1$$

$$E_3 = 9\frac{\pi^2\hbar^2}{2ma^2} = 9E_1$$

The energy spectrum is shown in Fig. 4.2.

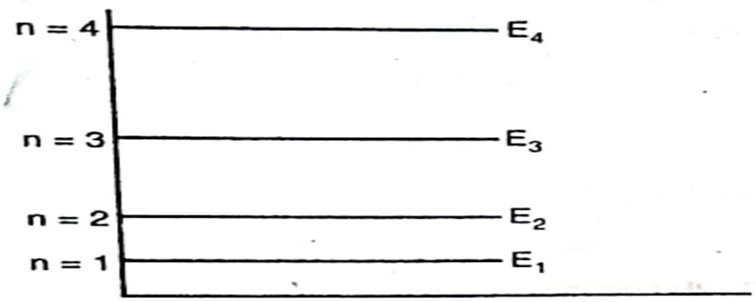


Fig. 4.2 : Energy spectrum

Wave functions :

The wave functions are given by the equation (4.12). As it is characteristic of n we may write

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) \qquad \ldots(4.15)$$

As the particle is confined to move between $x = 0$ and $x = a$, the condition for normalisation is

$$\int_0^a |\psi_n(x)|^2 \, dx = 1$$

$$\therefore \quad \int_0^a |A|^2 \sin^2\left(\frac{n\pi}{a}x\right) dx = 1$$

$$|A|^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = 1 \qquad \ldots(4.16)$$

We have $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$, therefore, equation (4.16) becomes

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

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

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

$$\frac{|A|^2}{2}\left[x - \frac{\sin\left(\frac{2n\pi}{a}x\right)}{\frac{2n\pi}{a}}\right]_0^a = 1$$

$$\frac{|A|^2}{2}a = 1$$

$$\therefore \qquad |A| = \sqrt{\frac{2}{a}}$$

Thus, on normalisation we get

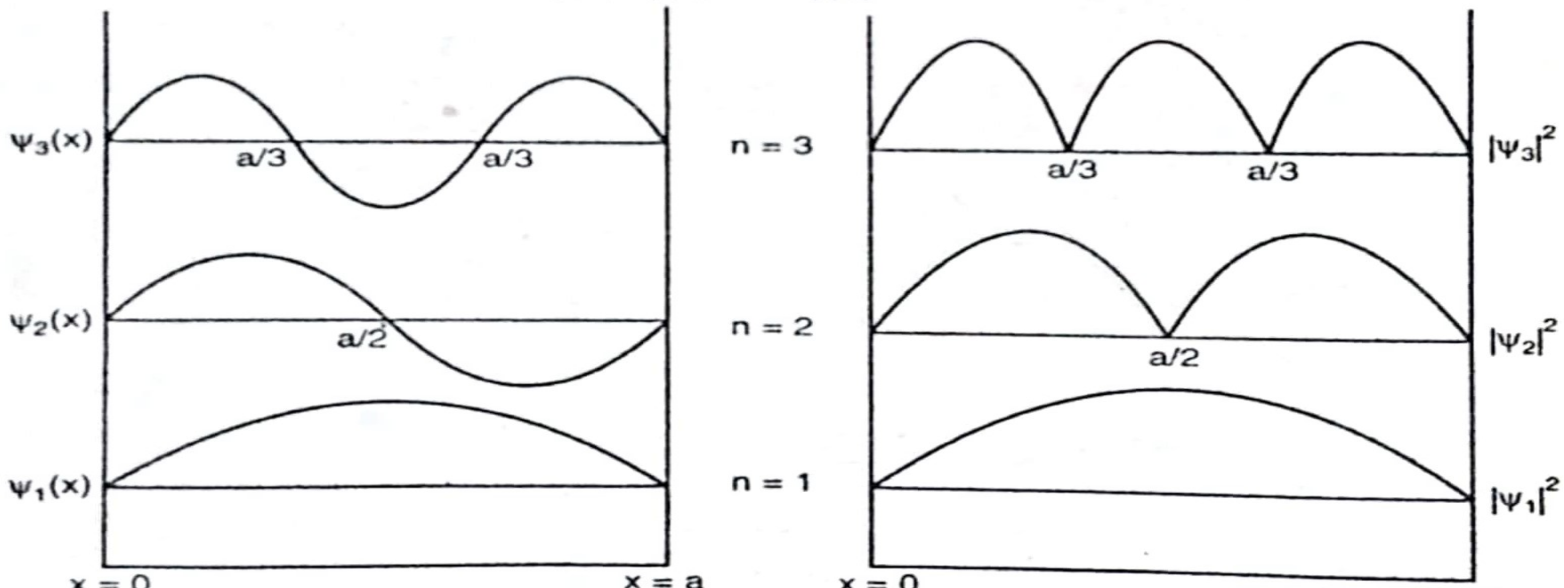
$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \qquad \ldots(4.17)$$

This is the wave function corresponding to energy eigen value E_n.

The ground state function (n = 1) is:

$$\psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right) \qquad \ldots(4.18)$$

In Fig. 4.3 (*a*) and the first three wave functions ψ_1, ψ_2 and ψ_3 are shown and in Fig. 4.3 (b) corresponding probability densities $|\psi_1|^2$, $|\psi_2|^2$ and $|\psi_3|^2$ are shown



(a) wave functions (b) probability densities

Fig. : 4.3

Particle in a finite deep potential well (Non rigid box)

The square well potential is shown in the Fig. 4.5.
It may be mathematically expressed as

$$
\begin{aligned}
V &= V_0 & x &\le -a \\
V &= 0 & -a &< x < a \\
V &= V_0 & x &\ge a
\end{aligned}
$$

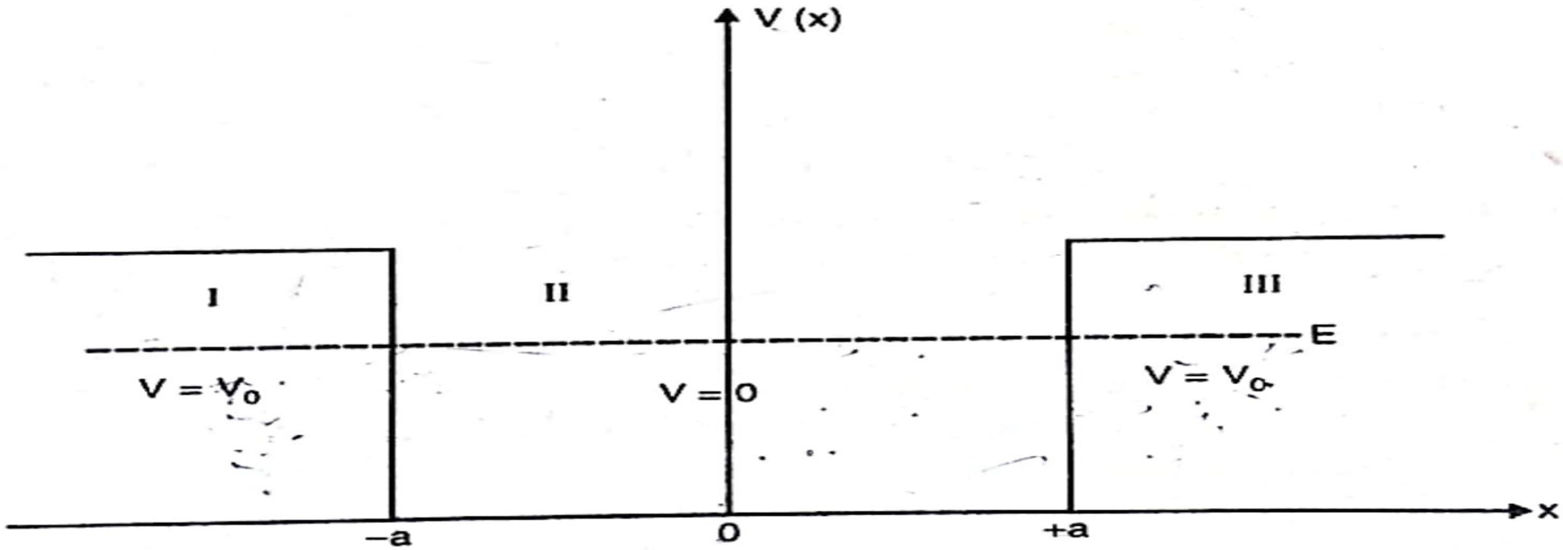


Fig. 4.5 : Finite potential well potential

If the particle has total energy $E < V_0$, Then according to classical mechanics particle may be in the region II only ($-a < x < a$). Because in the region I and III the momentum $P = (\sqrt{2m(E-V_0)}$ will be imaginary and it is not possible. Thus the particle is permanently in the region II with momentum of constant magnitude $P = (\sqrt{2mE})$. If $E > V_0$ then only particle can go in the region I and III

Particle in a finite deep potential well (Non rigid box

Case I : $E < V_0$

Let us first consider the case $E < V_0$.

We have one dimensional time independent Schrödinger's equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad \text{...(4.42)}$$

In region I, $V = V_0$. Since $E < V_0$, we may write equation (4.42) as follows

$$\frac{d^2\psi_1}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi_1 = 0 \quad \text{...(4.43)}$$

In region II, Schrödinger's equation is

$$\frac{d^2\psi_2}{dx^2} + \frac{2mE}{\hbar^2}\psi_2 = 0 \quad \text{...(4.44)}$$

In region III, Schrödinger's equation is

$$\frac{d^2\psi_3}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi_3 = 0 \quad \text{...(4.45)}$$

Let

$$k^2 = \frac{2mE}{\hbar^2} \quad \text{...(4.46)}$$

and

$$\alpha^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \text{...(4.47)}$$

Particle in a finite deep potential well (Non rigid box

With above two equations, equations (4.43), (4.44) and (4.45) become

$$\frac{d^2\psi_1}{dx^2} - \alpha^2\psi_1 = 0 \qquad \ldots(4.48)$$

$$\frac{d^2\psi_2}{dx^2} + k^2\psi_2 = 0 \qquad \ldots(4.49)$$

and

$$\frac{d^2\psi_3}{dx^2} - \alpha^2\psi_3 = 0 \qquad \ldots(4.50)$$

The general solution of equation (4.48) is given by

$$\psi_1(x) = C\,e^{\alpha x} + D\,e^{-\alpha x} \qquad \ldots(4.51)$$

In region I, $\psi_1(x)$ should vanish as $x \to -\infty$. From equation (4.51), we get $e^{-\alpha x} \to \infty$ as $x \to -\infty$. Therefore, to get acceptable solution in region I we must set $D = 0$ in equation (4.51). Hence

$$\psi_1(x) = C\,e^{\alpha x} \qquad \ldots(4.52)$$

The general solution of equation (4.49) is given by

$$\psi_2(x) = A \sin kx + B \cos kx \qquad \ldots(4.53)$$

The general solution of equation (4.50) is given by

$$\psi_3(x) = F\,e^{\alpha x} + G\,e^{-\alpha x}$$

In region III, $\psi_3(x)$ should vanish as $x \to \infty$. However, we get $e^{\alpha x} \to \infty$ as $x \to \infty$. Therefore, to get acceptable solution in region III we must have $F = 0$. Hence,

$$\psi_3(x) = G\,e^{-\alpha x}$$

Numericals

Example 14 : *An electron is trapped in an infinitely deep potential well 3.0 A^0 in length. If the electron is in the ground state, what is the probability of finding it within 1.0 A^0 of the left hand wall ?*

Solution : The eigen function for the particle in a deep potential well of width a is given as

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right) \qquad \text{for } 0 < x < a$$

The ground state wave function is

$$\psi_0(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{\pi}{a}x\right)$$

The probability of finding the particle in the region from 0 to $a/3$ *i.e.* up to the distance 1/3rd of total width from the left wall is

$$p(x) = \int_0^{a/3} |\psi_0(x)|^2\,dx$$

$$= \int_0^{a/3} \frac{2}{a}\sin^2\left(\frac{\pi}{a}x\right)dx$$

$$p(x) = \frac{2}{a}\int_0^{a/3} \sin^2\left(\frac{\pi}{a}x\right) dx$$

We have $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$, therefore, equation (4.16) becomes

$$\therefore \quad p(x) = \frac{2}{a}\int_0^{a/3} \frac{1}{2}\left[1 - \cos\left(\frac{2\pi}{a}x\right)\right] dx$$

$$= \frac{1}{a}\int_0^{a/3} \left[1 - \cos\left(\frac{2\pi}{a}x\right)\right] dx$$

$$= \frac{1}{a}\int_0^{a/3} \left[dx - \cos\left(\frac{2\pi}{a}x\right) dx\right]$$

$$= \frac{1}{a}\left[x - \frac{\sin\left(\frac{2\pi}{a}x\right)}{\frac{2\pi}{a}}\right]_0^{a/3}$$

$$= \frac{1}{a}\left[\frac{a}{3} - \frac{a}{2\pi}\sin\left(\frac{2\pi}{a}\frac{a}{3}\right)\right]$$

$$= \left[\frac{1}{3} - \frac{1}{2\pi}\sin\left(\frac{2\pi}{3}\right)\right]$$

$$= 0.3333 - 0.1370$$

$$= 0.1963$$

$$\therefore \quad p(x) = 19.63\ \%$$

Numericals

.

1) An electron is trapped in a rigid box of width 1 Å. Find its lowest energy level and momentum. Hence find energy of 5th level.

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

$$P = \frac{h}{2L}$$

As P= ħk= (h/2π)x(nπ/L) and n= 1 ∴ P= h/2L

E_0 lowest energy level for the value of n = 1.

$$E_0 = \frac{(1)^2 \times (6.63\times10^{-34})^2}{8\times9.1\times10^{-31}\times(1\times10^{-10})^2}$$

$$E_0 = 6\times10^{-18} \text{ Joule}$$

$$1\text{ eV} = 1.6\times10^{-19}\text{ J}$$

$$E_0 = \frac{6\times10^{-18}}{1.6\times10^{-19}}\text{ eV}$$

$$E_0 = 38 \text{ eV}$$

$$P = \frac{h}{2L}$$

$$= \frac{6.63\times10^{-34}}{2\times1\times10^{-10}}$$

$$= 3.315\times10^{-24} \text{ m/s}$$

$$E_5 = \frac{(5)(66.63\times10^{-34})^2}{8\times9.1\times10^{-31}\times(1\times10^{-10})^2}$$

$$E_5 = 937.5 \text{ eV}$$

Numericals

2) Lowest energy of an electron trapped in a infinite potential well is 38 electron Volt. Calculate the width of the well.

$$E = \frac{n^2 h^2}{8 m L^2}$$

$$L^2 = \frac{n^2 h^2}{8 m E}$$

$$L = \sqrt{\frac{n^2 h^2}{8 m E}}$$

$$n = 1$$

$$L = \frac{h}{\sqrt{8 m E}}$$

$$L = \frac{6.63 \times 10^{-34}}{\sqrt{8 \times 9.1 \times 10^{-31} \times 38 \times 1.6 \times 10^{-19}}}$$

$$L = 9.965 \times 10^{-11} \text{ m}$$

$L = 0.9965$ Å is width of well.

Numericals

- 3) A small object of mass 1 μg is confined to move between two rigid walls separated by a distance of 1mm.

    (a) Calculate the minimum speed of the object

    (b) If the speed is 3 x10^8 m/s, find the corresponding value of n.

Sol: (a)

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

We have

$$a = 1.00 \text{ mm} = 1 \times 10^{-3} \text{ m}$$

$$m = 1.00 \text{ μg} = 1 \times 10^{-6} \text{ g} = 10^{-9} \text{ kg.}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-sec}$$

$$\therefore \quad E_1 = \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 10^{-9} \times (10^{-3})^2}$$

$$= 5.486 \times 10^{-53} \text{ J}$$

The particle has only the kinetic energy, since V = 0.

$$E_1 = \frac{1}{2} m v^2$$

$$v = \sqrt{\frac{2E}{m}} = \left(\frac{2 \times 5.486 \times 10^{-53}}{10^{-9}}\right)^2$$

$$= 3.31 \times 10^{-22} \text{ m/s}$$

Numericals

(b) Let the particle be in level n with speed $v = 3 \times 10^6$ m/sec.

We have
$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$\therefore \quad \frac{1}{2}mv^2 = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

or
$$n^2 = \frac{m^2a^2v^2}{\pi^2\hbar^2}$$

or
$$n = \frac{m\,a\,v}{\pi\,\hbar}$$

$$= \frac{10^{-9} \times 10^{-3} \times 3 \times 10^6}{3.14 \times 1.055 \times 10^{-34}}$$

$$= 0.905 \times 10^{28}$$

$$\therefore \quad n = \mathbf{9 \times 10^{27}}$$

n is very high, so the particle cannot be treated quantum mechanically.

Numericals

4) Determine the probability that a particle trapped in a rigid box of length L can be found between 0.45L and 0.55L for ground and first excited state.

Given : $\psi = \sqrt{(2/L)}\ (\sin(n\pi x/L))$

Solution :

$$P = \int_{0.45L}^{0.55L} |\psi|^2\, dx$$

$$= \frac{2}{L}\int_{0.45L}^{0.55L} \left(\sin^2 \frac{n\pi}{L} x\right) dx$$

$$= \frac{2}{L}\int_{0.45L}^{0.55L} \frac{1}{2}\left[1 - \cos\left(\frac{2n\pi}{L} x\right)\right] dx$$

$$= \frac{1}{L}\int_{0.45L}^{0.55L} \left[dx - \cos\left(\frac{2n\pi}{L} x\right) dx\right]$$

$$= \frac{1}{L}\left[x - \frac{\sin\left(\frac{2n\pi}{L} x\right)}{\frac{2n\pi}{L}}\right]_{0.45L}^{0.55L}$$

$$= \frac{1}{L}\left[x - \frac{L}{2n\pi}\sin\left(\frac{2n\pi}{L}x\right)\right]_{0.45L}^{0.55L}$$

$$= \left[\frac{x}{L} - \frac{1}{2n\pi}\sin\frac{2n\pi}{L}x\right]_{0.45L}^{0.55L}$$

For Ground state $n=1$

$$P = 0.198$$

For 1st excited state $n=2$

$$P = 0.0065$$

Numericals

. 5) Ruby laser emits light of wavelength 693.4 nm. If the light is due to transition from n=2 to n=1 state of an electron in one dimensional rigid box, find the width of the box.

Solution : The energy in the n^{th} level is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

When electron jumps from n = 2 to n = 1, the energy difference is

$$E_2 - E_1 = 4\frac{\pi^2\hbar^2}{2ma^2} - \frac{\pi^2\hbar^2}{2ma^2} = 3\frac{\pi^2\hbar^2}{2ma^2}$$

This energy difference is emitted in the form of photon with frequency ν. Then

$$E_2 - E_1 = h\nu$$

$\therefore$

$$h\nu = 3\frac{\pi^2\hbar^2}{2ma^2}$$

or

$$\frac{hc}{\lambda} = 3\frac{\pi^2\hbar^2}{2ma^2}$$

or

$$a^2 = \frac{3\pi^2\hbar^2\lambda}{2mhc}$$

Since $h = \frac{\hbar}{2\pi}$, we get

$$a = \frac{3h\lambda}{8mc}$$

Given :

$$\lambda = 693.4 \text{ nm} = 693.4 \times 10^{-9} \text{ m}$$
$$c = 3 \times 10^8 \text{ m/sec}$$
$$m = 9.1 \times 10^{-31} \text{ kg}$$
$$h = 6.625 \times 10^{-34} \text{ J-sec}$$

$\therefore$

$$a^2 = \frac{3 \times 6.625 \times 10^{-34} \times 693.4 \times 10^{-9}}{8 \times 9.1 \times 10^{-31} \times 3 \times 10^8}$$
$$= 63.1 \times 10^{-20} \text{ m}^2$$

$\therefore$

$$a = 7.94 \times 10^{-10} \text{ m} = \mathbf{7.94\ A^\circ}$$

Numerical

- Find the probability that a particle trapped in one dimensional rigid box L wide can be found between 0.45 L and 0.55 L for ground state and first excited state.

solution: Probability $P(x) = \int_{x_1}^{x_2} |\psi_n|^2 dx$

$$P(x) = \left(\sqrt{\frac{2}{L}}\right)^2 \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx$$

$$P(x) = \frac{2}{L} \int_{x_1}^{x_2} \frac{1}{2}\left[1 - \cos\left(\frac{2\pi n x}{L}\right)\right] dx$$

$$P(x) = \frac{1}{L} \int_{x_1}^{x_2} \left[dx - \cos\left(\frac{2n\pi x}{L}\right)\right] dx$$

$$P(x) = \frac{1}{L}\left[x - \frac{\sin\left(\frac{2n\pi x}{L}\right)}{\frac{2n\pi}{L}}\right]_{x_1}^{x_2}$$

$$P(x) = \left[\frac{x}{L} - \frac{1}{2n\pi}\sin\left(\frac{2n\pi x}{L}\right)\right]_{x_1}^{x_2}$$

$x_1 = 0.45L$ & $x_2 = 0.55L$

for $n = 1$, $P(x) = 0.198$ or 19.8% for ground state

for $n = 2$, $P(x) = 0.0065$ or 0.65% for 1^{st} excited state

Numerical

Example 3 : *A proton is confined to move in a one-dimensional box of width 0.200 nm. (a) Find the lowest possible energy of the proton. (b) What is the lowest possible energy of an electron confined to the same box ?*

When particle is confined to one dimensional rigid box, the energy eigen value is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

(a) If the particle is in n = 1 *i.e.* in the ground state, it has the lowest energy. Thus,

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

We have $a = 0.200 \text{ nm} = 0.200 \times 10^{-9} \text{ m} = 2 \times 10^{-10} \text{ m}$

For proton, $m = 1.66 \times 10^{-27}$ kg

$\hbar = 1.055 \times 10^{-34}$ J-s

$$\therefore \quad E_1 = \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 1.66 \times 10^{-27} \times (2 \times 10^{-10})^2}$$

$$= 0.826 \times 10^{-21} \text{ J}$$

$$= 5.16 \times 10^{-3} \text{ eV}$$

Numerical

(b) Now let us work out the problem for electron

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2},$$

We have

$$a = 0.200 \text{ nm} = 0.2 \times 10^{-9} \text{ m}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}$$

$$\therefore \quad E_1 = \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31} \times (2 \times 10^{-10})^2}$$

$$= 0.1507 \times 10^{-17} = 1.507 \times 10^{-18} \text{ J}$$

$$= 9.42 \text{ eV}$$

Numerical

Example 1 : *The wave function for a particle in infinite potential well is given as*

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) \qquad \text{where } 0 \le x \le a. \text{ Find } \langle x \rangle \text{ and } \langle p_x \rangle$$

Solution : A is normalization constant and it is easy to show that its value is $A = \sqrt{\frac{2}{a}}$

$$\therefore \qquad \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

(a) Expectation value of x is given as

$$\langle x \rangle = \int_0^a x\,|\psi_n(x)|^2\,dx$$

$$\langle x \rangle = \int_0^a x\,|A|^2 \sin^2\left(\frac{n\pi}{a}x\right)\,dx$$

$$= \frac{2}{a}\int_0^a x \sin^2\left(\frac{n\pi}{a}x\right)\,dx$$

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

Numerical

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

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

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

$$= \frac{1}{a}\left(\left.\frac{x^2}{2}\right|_0^a - \int_0^a x\cos\left(2\frac{n\pi}{a}x\right) dx\right)$$

Integrating second term by parts, we get

$$\int_0^a x\cos\left(2\frac{n\pi}{a}x\right) dx = x\,\frac{\sin\left(2\frac{n\pi}{a}x\right)}{2n\pi/a} - \int_0^a \cos\left(2\frac{n\pi}{a}x\right) dx$$

Numerical

$$= \left[x \frac{\sin\left(2\frac{n\pi}{a}x\right)}{2n\pi/a} - \frac{\sin\left(2\frac{n\pi}{a}x\right)}{2n\pi/a} \right]_0^a = 0$$

This gives $\int_0^a x \cos\left(2\frac{n\pi}{a}x\right) dx = 0$

$\therefore$ $$\langle x\rangle = \frac{1}{a}\frac{a^2}{2}$$

or $$\langle x\rangle = \frac{a}{2}$$

(b) Expectation value of p_x is given as

$$\langle p_x\rangle = \int_0^a \psi_n^*\left(-i\hbar\frac{d}{dx}\right)\psi_n\, dx$$

Numerical

$$<p_x> = -i\hbar \int_0^a \psi_n^* \frac{d\psi}{dx} dx$$

$$= -i\hbar \frac{2}{a} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \frac{d}{dx} \sin\left(\frac{n\pi}{a}x\right) \; dx$$

sin2θ = 2sinθ cosθ

$$= -i\hbar \frac{2}{a}\frac{n\pi}{a} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \cos\left(\frac{n\pi}{a}x\right) \; dx$$

$$= \frac{-i\hbar n\pi}{a^2} \int_0^a \sin\left(\frac{2n\pi}{a}x\right) dx$$

$$= \frac{i\hbar n\pi}{a^2}\left[\frac{\cos\left(\frac{2n\pi}{a}x\right)}{2n/\pi}\right]_0^a$$

$$<p_x> = 0$$

Thanks