

QUANTUM MECHANICS

Phase velocity

A plane simple harmonic wave travelling in the positive x – direction is given by

$$y(x,t) = a \sin(\omega t - kx) \quad (1)$$

Where y is the displacement, a is amplitude, ω angular frequency, $k = \frac{2\pi}{\lambda}$ is known as propagation constant and λ the wavelength of the wave. From equation (1) the phase of the wave at position x and at time t is

$$\phi(x,t) = (\omega t - kx) \quad (2)$$

$$\therefore \frac{\partial \phi}{\partial t} = \omega - k \frac{\partial x}{\partial t}$$

For a constant phase, $\frac{\partial \phi}{\partial t} = 0 \therefore \omega - k \frac{\partial x}{\partial t} = 0 \Rightarrow \left(\frac{\partial x}{\partial t} \right)_{\phi \text{ constant}} = v_p = \frac{\omega}{k} \quad (3)$

$v_p = \frac{\omega}{k}$ is known as phase velocity.

Dispersive Medium

A medium in which the phase velocity v_p varies with wavelength λ or frequency f is known as dispersive medium. **e.g.** glass, water.

Nondispersive Medium

A medium in which the phase velocity of a wave is independent of wavelength or frequency is called as a nondispersive medium. **e.g.** Vacuum, stretched string for transverse mechanical waves



Group Velocity

When plane waves of different wavelengths travel simultaneously in the same direction along a straight line through a dispersive medium, i.e., a medium in which the phase velocity $v_p = \frac{\omega}{k}$ of a wave depends on its wavelength, successive groups of the waves are produced. **These wave - groups are also called wave – packets. Each wave – group travels with a velocity v_g called the group velocity. The group velocity is different from the phase velocity of a single wave.**

Group velocity
$$v_g = \frac{\partial \omega}{\partial k} = \frac{\omega_2 - \omega_1}{k_2 - k_1} \quad (4)$$

Relation between **phase velocity and group velocity**

$$v_g = v_p + k \frac{dv_p}{dk} \quad (5) ; \quad v_g = v_p - \lambda \frac{dv_p}{d\lambda} \quad (6)$$

Group velocity and refractive index of the medium

$$v_g = \frac{c}{n(\lambda) - \lambda \frac{dn(\lambda)}{d\lambda}} \quad (7)$$

Where $n(\lambda)$ is the refractive index of the medium which depends on wavelength.

$$v_p = \frac{\omega}{k} = f\lambda = \left(\frac{mc^2}{h}\right) \left(\frac{h}{mv}\right) = \frac{c^2}{v} \Rightarrow v_p \cdot v = c^2 \quad (8)$$

Where v is the velocity of the particle which must be less than velocity of light c , **De Broglie waves travel with group velocity $v_g < c$, which is the classical velocity of the particle.**



Example 1

In a certain medium, the wave number k and angular frequency ω are related by the dispersion relation $\omega^2 = c^2 k^2 (1 + \alpha k^2)$, where c and α are constants. If V_g is the group velocity and V_p is the phase velocity, then

(a) $V_p = V_g$ (b) $\frac{V_g}{V_p} = \frac{(1 + \alpha k^2)}{(1 + 2\alpha k^2)}$ (c) $V_p \cdot V_g = c^2$ (d) $V_p \cdot V_g = c^2 (1 + 2\alpha k^2)$

Solution

Given $\omega^2 = c^2 k^2 (1 + \alpha k^2)$ $\therefore \omega = ck(1 + \alpha k^2)^{1/2}$ (1) $V_p = \frac{\omega}{k} = c(1 + \alpha k^2)^{1/2}$ (2)

From (1) $V_g = \frac{\partial \omega}{\partial k} = c(1 + \alpha k^2)^{1/2} + ck \times \frac{1}{2}(1 + \alpha k^2)^{-1/2} (2\alpha k) = c(1 + \alpha k^2)^{1/2} + \frac{\alpha ck^2}{(1 + \alpha k^2)^{1/2}}$

$V_g = \frac{c(1 + \alpha k^2) + \alpha ck^2}{(1 + \alpha k^2)^{1/2}} = \frac{c(1 + 2\alpha k^2)}{(1 + \alpha k^2)^{1/2}}$ (3)

From (2) & (3) $V_p V_g = c(1 + \alpha k^2)^{1/2} \times \frac{c(1 + 2\alpha k^2)}{(1 + \alpha k^2)^{1/2}} = c^2 (1 + 2\alpha k^2)$ **Ans: (d)**

Uncertainty Principle

The principle states that for a particle in motion in smaller dimension, **it is impossible to determine both the position and the momentum simultaneously with perfect accuracy.** If Δx and Δp_x represent the inaccuracies / uncertainties with which the x – coordinate of position and the x – component of the momentum, then the following inequality must be satisfied.



JAM PHYSICS

QUANTUM MECHANICS AND RELATIVITY

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad \text{Position - Momentum} \quad (9)$$

Using the definition of standard deviation in statistics

$$\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2 \right]^{1/2} \quad \text{and} \quad \Delta p = \left[\langle p^2 \rangle - \langle p \rangle^2 \right]^{1/2} \quad (10)$$

Another form of uncertainty principle

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad \text{Energy - Time} \quad (11)$$

Where ΔE is the uncertainty in the energy and Δt the uncertainty in time.

Example 2

If a particle is represented by the normalized wave function

$$\psi(x) = \begin{cases} \frac{\sqrt{15}(a^2 - x^2)}{4a^{5/2}} & \text{for } -a < x < a \\ 0 & \text{otherwise} \end{cases} \quad \text{the uncertainty } \Delta P \text{ in its momentum is}$$

(a) $\frac{2\hbar}{5a}$ (b) $\frac{2\hbar}{2a}$ (c) $\frac{\sqrt{10}\hbar}{a}$ (d) $\frac{\sqrt{5}\hbar}{\sqrt{2}a}$

Solution

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

Given $\psi(x) = \frac{\sqrt{15}(a^2 - x^2)}{4a^{5/2}}$ for $-a < x < a$



$$\begin{aligned}\langle P \rangle &= \langle \psi | -i\hbar \frac{\partial}{\partial x} | \psi \rangle = \frac{15}{16a^5} \int_{-a}^a (a^2 - x^2) \left(-i\hbar \frac{\partial}{\partial x} \right) (a^2 - x^2) dx \\ &= \frac{15}{16a^5} (-i\hbar) \int_{-a}^a (a^2 - x^2) (-2x) dx = 0 \text{ (As the function given in the integral is odd)}\end{aligned}$$

$$\begin{aligned}\langle P^2 \rangle &= \int_{-a}^a \psi \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi dx \\ &= \frac{15}{16a^5} (-\hbar^2) \int_{-a}^a (a^2 - x^2) \frac{d^2}{dx^2} (a^2 - x^2) dx \\ &= -\frac{15\hbar^2}{16a^5} \int_{-a}^a (a^2 - x^2) (-2) dx = \frac{5\hbar^2}{2a^2}\end{aligned}$$

$$\therefore \Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{5\hbar^2}{2a^2} - 0} = \sqrt{\frac{5}{2}} \frac{\hbar}{a}$$

Ans: (d)

Wave function (ψ)

In water waves, the quantity that varies periodically is the height of the water surface. In sound waves, it is pressure. In light waves, electric and magnetic fields vary.

The quantity whose variations represent matter waves is called the wave function ψ . The wave nature associated with a moving particle is represented by a complex variable function $\psi(x, y, z, t)$ called the wave function. Therefore, it cannot have a direct physical meaning. The wave function ψ contains all information about the particle i.e., linear momentum, angular momentum, energy, etc., although ψ is a complex quantity, $\psi^* \psi = |\psi|^2$ is real and positive. The quantity $|\psi(x)|^2$ is proportional to the probability density (ρ) for finding the particle at x.



$\rho(x)dx = |\psi(x)|^2 dx$ gives the probability of finding the particle in an interval dx around x .

Normalization

The total probability of finding the particle described by ψ is, the integral of $|\psi|^2$ overall space. This must be finite – the particle is somewhere, i.e.,

$$\int_{-\infty}^{\infty} p d\tau = \int_{-\infty}^{\infty} |\psi|^2 d\tau = 1 \quad (12)$$

A wave function that obeys equation (12) is said to be normalized. Every acceptable wave function can be normalized by multiplying it by an appropriate constant.

$$|N|^2 \int_{-\infty}^{\infty} \psi^* \psi d\tau = 1 \quad (13)$$

Where N is the normalization constant.

Orthonormality condition

For a set of normalized wave function $\{\psi_i\}$, then

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n d\tau = \delta_{mn} \quad (14)$$

Where δ_{mn} is the Kronecker delta function defined through the equation

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \quad \text{Kronecker delta}$$



Equation (14) is known as **Orthonormality condition**

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n d\tau = 0 \quad \text{if } m \neq n \text{ orthogonal condition} \quad (15)$$

$$\int_{-\infty}^{\infty} \psi^* \psi d\tau = 1 \quad \text{if } m = n \text{ normalization condition} \quad (16)$$

Admissibility conditions ψ

1. ψ must be finite for all values of x,y,z.
2. ψ must be single valued, i.e. for each set of values of x,y,z, ψ must have only one value.
3. ψ must be continuous in all regions except in those region where the potential energy $V(x,y,z) = \infty$.
4. The partial derivatives $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}$ must be continuous everywhere.
5. ψ should be square integrable i.e. $\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = \text{finite quantity}$.

A wave function satisfying all these condition is known as well behaved function.

Probability current density

As the time changes from $t = 0$, the probability of finding the particle in some region of space may increase or decrease. If the probability increases in some region, then it should decrease in some other region such that total probability of finding the particle in the entire space should be equal to one. We can assume this as a flow of probability from one region to another region, like a fluid or current. Therefore, the probability flow satisfies the equation of continuity,



$$\text{ie., } \vec{\nabla} \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0 \quad (17)$$

$$\text{Where } \rho = \psi^* \psi \quad (18) \quad \text{and } \vec{J} = \frac{i\hbar}{2m} [\psi \nabla \psi^* - \psi^* \nabla \psi] \quad (19)$$

Here ρ probability per unit volume and it is known as position probability density, \vec{J} the probability current density.

Important Results

Probability current density = probability density \times velocity of the particle.

$$\vec{J} = (\psi^* \psi) \left(\frac{\hbar k}{m} \right) \quad (20)$$

Equation (20) is used to find the reflection coefficient and transmission coefficient in problems like finite step potential.

Example 3

Consider a system whose initial state at $t = 0$ is given in terms of 3 orthonormal state vectors

$$|\varphi_1\rangle, |\varphi_2\rangle, |\varphi_3\rangle \text{ as } |\psi(x, 0)\rangle = \frac{1}{\sqrt{2}} |\varphi_1\rangle + A |\varphi_2\rangle + \frac{1}{\sqrt{5}} |\varphi_3\rangle \text{ (A is real constant)}$$

- (a) Find the value of A so that $|\psi(x, 0)\rangle$ is normalized.
- (b) What are the probabilities for the system to be in $|\varphi_1\rangle, |\varphi_2\rangle, |\varphi_3\rangle$ states.
- (c) Find the state of the system at any time 't'.

Solution



$$(a) \langle \psi | \psi \rangle = 1 \Rightarrow c_1^2 + c_2^2 + c_3^2 = 1 \therefore \left(\frac{1}{\sqrt{2}}\right)^2 + A^2 + \left(\frac{1}{\sqrt{5}}\right)^2 = 1 \Rightarrow A^2 = \frac{3}{10} \Rightarrow A = \sqrt{\frac{3}{10}}$$

$$(b) \text{Probability for the system to be in } |\varphi_1\rangle = P_1 = c_1^2 = \frac{1}{2}$$

$$\text{Probability for the system to be in } |\varphi_2\rangle = P_2 = c_2^2 = \frac{3}{10}$$

$$\text{Probability for the system to be in } |\varphi_3\rangle = P_3 = c_3^2 = \frac{1}{5}$$

$$(c) |\psi(x, t)\rangle = \frac{1}{\sqrt{2}}|\varphi_1\rangle e^{-\frac{i}{\hbar}E_1t} + \sqrt{\frac{3}{10}}|\varphi_2\rangle e^{-\frac{i}{\hbar}E_2t} + \frac{1}{\sqrt{5}}|\varphi_3\rangle e^{-\frac{i}{\hbar}E_3t}$$

The Schrodinger Equation

The simplest type of wave is plane monochromatic wave described by the wave function

$$\psi(x, t) = Ae^{-i(\omega t - kx)} \quad (21)$$

Which represents a disturbance of amplitude A and wavelength $\lambda = \frac{2\pi}{k}$ travelling in the direction of its

wave vector \vec{k} with phase velocity $v_p = \frac{\omega}{k}$.

$$\therefore \omega = \frac{E}{\hbar} \text{ and } k = \frac{p}{\hbar} \quad (22) \quad ; \quad \psi(x, t) = Ae^{-\frac{i}{\hbar}(Et - px)} \quad (23)$$

Differentiating equation (23) with respect to t,

$$\frac{\partial \psi}{\partial t} = -\frac{iE}{\hbar}\psi \Rightarrow i\hbar \frac{\partial \psi}{\partial t} = E\psi \quad (24)$$



Differentiating equation (23) with respect to x,

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} \psi ; \frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \psi \Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = \frac{p^2}{2m} \psi \quad (25)$$

Since all speeds are small when compared to velocity of light, we may write

Total energy = Kinetic energy + Potential energy

$$E = \frac{p^2}{2m} + V(x, t)$$

$$\therefore E \psi = \frac{p^2}{2m} \psi + V(x, t) \psi \Rightarrow \frac{p^2}{2m} \psi = (E - V) \psi \quad (26)$$

From (25) and (26)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = (E - V) \psi \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (27)$$

In Three Dimensions

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (28)$$

Equation (27) and (28) are time **independent Schrodinger equations in one and three dimensions respectively.**

Time dependent Schrodinger equation

Total energy = Kinetic energy + Potential energy $E = \frac{p^2}{2m} + V(x, t)$

$$E \psi = \frac{p^2}{2m} \psi + V(x, t) \psi \text{ using (24)} \quad i\hbar \frac{\partial \psi}{\partial t} = \frac{p^2}{2m} \psi + V \psi \quad (29)$$

Equation (29) is the time dependent Schrodinger equation.



Ket and Bra Vectors

The physical state of a system is represented in quantum mechanics by elements of Hilbert space; these elements are called state vectors. Dirac denoted the state vector ψ by the symbol $|\psi\rangle$, which is called a ket vector, or simply ket. The conjugate of ket vector is known as Bra vector and is denoted by $\langle |$. Note: For every ket $|\psi\rangle$ there exists a unique bra $\langle\psi|$ and vice versa.

$$|\psi\rangle^* \leftrightarrow \langle\psi| \quad (30)$$

Scalar (inner) Product $(\phi, \psi) \rightarrow \langle\phi|\psi\rangle \quad (31)$

Two kets $|\psi\rangle$ and $|\phi\rangle$, are said to be orthonormal if they are orthogonal and if each one of them

has unit norm : $\langle\phi|\psi\rangle=0, \quad \langle\psi|\psi\rangle=1, \quad \langle\phi|\phi\rangle=1 \quad (32)$

Operators

An operator \hat{O} is a mathematical rule that when applied to a ket $|\psi\rangle$ transforms it into another ket $|\psi'\rangle$ of the same space and when it acts on a bra $\langle\phi|$ transforms it into another bra $\langle\phi'|$:

$$\hat{O}|\psi\rangle=|\psi'\rangle, \quad \langle\phi|\hat{O}=\langle\phi'| \quad (33)$$

Abstract ket, bra vectors and operators have no specific form but take up a particular form when bra and ket vectors are represented as state vector $\psi(x, y, z, t)$.



Examples of Operators

Energy operator : $E = i\hbar \frac{\partial}{\partial t}$

Momentum operator : $P = -i\hbar \frac{\partial}{\partial x}$; $\vec{P} = -i\hbar \vec{\nabla}$ in 3D

Expectation or Mean value

Expectation or mean value $\langle \hat{O} \rangle$ of an operator \hat{O} is defined by

$$\langle \hat{O} \rangle = \frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int_{-\infty}^{\infty} \psi^* \hat{O} \psi dv}{\int_{-\infty}^{\infty} \psi^* \psi dv} \quad (34)$$

where ψ is unnormalized wave function. **If the wave function is normalized, then**

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \hat{O} \psi dv \quad \text{Since } \langle \psi | \psi \rangle = 1.$$

Expectation values

For a normamised wave function

Position

$$\langle \hat{x} \rangle = \langle \psi | \hat{x} | \psi \rangle$$

Momentum

$$\langle \hat{P} \rangle = \langle \psi | -i\hbar \frac{\partial}{\partial x} | \psi \rangle$$



Expectation value of energy

The state of a system does not have to be represented by a single wave function; it can be represented by a superposition of two or more wave functions. **If $\psi_1, \psi_2, \psi_3, \dots$ separately satisfy the Schrodinger equation, then the general solution would be linear combination of all the particular solutions.**

$$|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle + c_3|\psi_3\rangle + \dots = \sum_i c_i |\psi_i\rangle \quad (35)$$

Where c_i are complex numbers.

The quantity $P = \left| \sum_i c_i |\psi_i\rangle \right|^2$ represents the probability for the superposition. If the states $|\psi_i\rangle$ are mutually orthogonal, the probability will be equal to the sum of the individual probabilities;

$$P = \left| \sum_i c_i |\psi_i\rangle \right|^2 = \sum_i |c_i|^2 = P_1 + P_2 + P_3 + \dots \quad (36)$$

Where $P_i = |c_i|^2$; P_i is the probability of finding the system in the state $|\psi_i\rangle$. If E_1, E_2, E_3, \dots are the eigen values of $\psi_1, \psi_2, \psi_3, \dots$ then the expectation values of energy of the system in the state $|\psi_i\rangle$ is

$$\langle E \rangle = \frac{P_1 E_1 + P_2 E_2 + P_3 E_3 + \dots}{P_1 + P_2 + P_3 \dots} \quad (37)$$

If $\{|\psi_i\rangle\}$ is an orthonormal set, then $P_1 + P_2 + P_3 \dots = 1$.



Example 4

The state $\frac{1}{\sqrt{6}}\psi_{-1} + \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{3}}\psi_2$ is a linear combination of three orthonormal eigen states of the operator \hat{O} corresponding to the eigen values -1, 1 and 2. The expectation value of \hat{O} for this state is

- (a) $\frac{2}{3}$ (b) $\sqrt{\frac{7}{6}}$ (c) 1 (d) $\frac{4}{3}$

Solution

Given $|\psi\rangle = \frac{1}{\sqrt{6}}\psi_{-1} + \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{3}}\psi_2$

Eigen values of ψ_{-1}, ψ_1 and ψ_2 corresponding to the operator \hat{O} are -1, 1, and 2.

$$\begin{aligned}\langle \hat{O} \rangle &= \langle \psi | \hat{O} | \psi \rangle = \frac{1}{6} \langle \psi_{-1} | \hat{O} | \psi_{-1} \rangle + \frac{1}{2} \langle \psi_1 | \hat{O} | \psi_1 \rangle + \frac{1}{3} \langle \psi_2 | \hat{O} | \psi_2 \rangle \\ &= \left(\frac{1}{6} \times -1 \right) \langle \psi_{-1} | \psi_{-1} \rangle + \left(\frac{1}{2} \times 1 \right) \langle \psi_1 | \psi_1 \rangle + \left(\frac{1}{3} \times 2 \right) \langle \psi_2 | \psi_2 \rangle = \frac{-1}{6} + \frac{1}{2} + \frac{2}{3} = 1 \quad \text{Ans (c)}\end{aligned}$$



The Infinite Square well potential – Particle in a Box

Consider a particle of mass m confined to move inside an infinitely deep **asymmetric potential well**

$$V(x) = 0 \quad \text{for } 0 \leq x \leq a$$

$$= \infty \quad \text{for } x < 0 \text{ and for } x > a$$
(38)

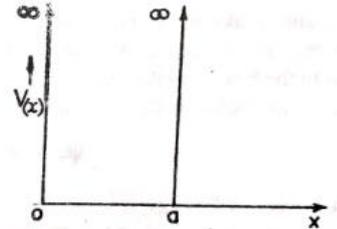


Figure 1

For $0 < x < a$, the one dimensional Schrodinger equation becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + k^2 \psi(x) = 0$$
(39)

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

(40)

The general solution of this equation is $\psi(x) = A \sin kx + B \cos kx$

The wave function vanishes at the walls $\psi(0) = \psi(a) = 0$: the condition $\psi(0) = 0$ gives $B = 0$, while

$\psi(a) = \sin(ka) = 0$ gives

$$ka = n\pi \quad \text{where } n = 1, 2, 3, \dots$$
(41)

From (40) and (41)

The energy of the particle

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2ma^2} n^2$$
(42)

The energy is quantized; only certain values are permitted. This is expected since the states of a particle which is confined to a limited region of space are bound states and the energy spectrum is

discrete. This is in sharp contrast to classical physics where the energy of the particle, given by $E = \frac{P^2}{2m}$

takes any value; the classical energy evolves continuously.



Since $B = 0$ and $k = \frac{n\pi}{a}$, $\psi_n(x) = A \sin\left(\frac{n\pi x}{a}\right)$. We can choose the constant A so that $\psi_n(x)$ is normalized :

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

Hence the eigen functions are
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad (43)$$

The first few functions are plotted in figure 2.

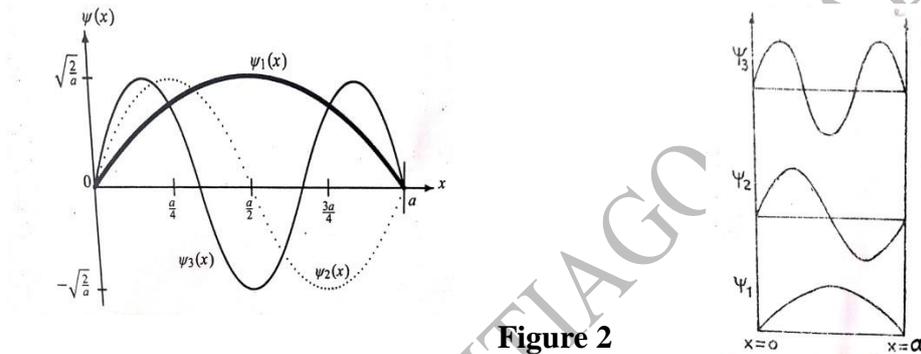


Figure 2

Example 5

Three identical spin $\frac{1}{2}$ particle of mass m are confined to a one dimensional box of length L , but are otherwise free. Assuming that they are non – interacting, the energies of the lowest two energy

eigenstates, in units of $\frac{\pi^2 \hbar^2}{2mL^2}$ are

- (a) 3 and 6 (b) 6 and 9 (c) 6 and 11 (d) 3 and 9

Solution

Pauli's exclusion principle allows only 2 electrons of opposite spin in a particular energy state.

So case 1: $n_1 = 1$ $n_2 = 2$

$$E = E_{n_1} + E_{n_2} = 1 \frac{\pi^2 \hbar^2}{2mL^2} + 2 \frac{4\pi^2 \hbar^2}{2mL^2} = \frac{9\pi^2 \hbar^2}{2mL^2}$$

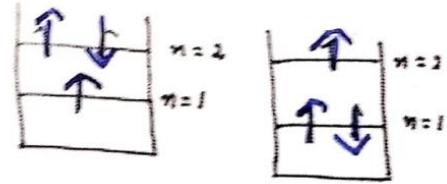


Figure 3

Case 2: $n_1 = 2$ $n_2 = 1$

$$E = 2 \frac{\pi^2 \hbar^2}{2mL^2} + 1 \frac{4\pi^2 \hbar^2}{2mL^2} = \frac{6\pi^2 \hbar^2}{2mL^2}$$

Ans: (b)

The Symmetric Potential

If the potential (38) is translated by a distance of $a/2$ along the $-ve$ x axis, it becomes a symmetric potential.

$$V(x) = 0 \text{ for } -a/2 \leq x \leq a/2$$

$$= \infty \text{ for } x \leq -a/2 \text{ and for } x > a/2$$

For symmetric potential $V(-x) = V(x)$, the wave function of bound states must be either even or odd parity. The wave function corresponding to the above potential can be written as follows:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \left[\frac{n\pi}{a} \left(x + \frac{a}{2} \right) \right] = \begin{cases} \sqrt{\frac{2}{a}} \cos \left(\frac{n\pi x}{a} \right) & (n = 1, 3, 5, \dots) \\ \sqrt{\frac{2}{a}} \sin \left(\frac{n\pi x}{a} \right) & (n = 2, 4, 6, \dots) \end{cases} \quad (44)$$

That is, the wave functions corresponding to odd quantum numbers $n = 1, 3, 5, \dots$ are symmetric,

$\psi(-x) = \psi(x)$, and those corresponding to even numbers $n = 2, 4, 6, \dots$ are antisymmetric,

$\psi(-x) = -\psi(x)$.

Particle in a Two Dimensional Box

The potential $V(x) = 0$ for $0 \leq x \leq a, 0 \leq y \leq b$,
 $= \infty$ other wise. (45)

The Schrodinger equation

$$\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} + \frac{2mE}{\hbar^2} \psi(x, y) = 0 \quad (46)$$

The normalized solution of the above equation

$$\psi(x, y) = \left[\sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \right] \left[\sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \right]; \quad n_x, n_y = 1, 2, 3, \dots \quad (48)$$

The total energy of particle $E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right]$ (49)

If $a = b$, $\psi(x, y) = \frac{2}{a} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right)$ (50)

$$E = \frac{\pi^2 \hbar^2}{2ma^2} [n_x^2 + n_y^2]$$



Particle in Three Dimensional Box

The potential $V(x) = 0$ for $0 \leq x \leq a$, $0 \leq y \leq b$, $0 \leq z \leq c$, (51)

The Schrodinger equation in this case

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (52)$$

The normalized solution of the above equation is

$$\psi(x, y, z) = \left[\sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \right] \left[\sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \right] \left[\sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \right]; \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \quad (53)$$

The energy of the particle

$$E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad (54)$$

For a particle in a cubic box of side 'a' is

Here $a = b = c$

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \quad (55)$$

$$E = \frac{\pi^2 \hbar^2}{2ma^2} [n_x^2 + n_y^2 + n_z^2] \quad (56)$$



Degeneracy

If there is more than one linearly independent wave function belonging to the same energy eigen value E, the energy level is said to be degenerate. If there are g linearly independent wave functions $(\psi_1, \psi_2, \dots, \psi_g)$ belonging to the same energy state, then the energy level is said to be g – fold degenerate.

For a particle in a cubical box, a number of energy – level with the corresponding quantum numbers and the degree of degeneracy are given in the following table

Energy level	Quantum numbers (n_x, n_y, n_z)	Degree of degeneracy
$\frac{3\pi^2\hbar^2}{2ma^2}$	(111)	Non – degenerate
$\frac{6\pi^2\hbar^2}{2ma^2}$	(211) , (121) , (112)	Three – fold degenerate
$\frac{9\pi^2\hbar^2}{2ma^2}$	(221) , (212), (122)	Three – fold degenerate
$\frac{11\pi^2\hbar^2}{2ma^2}$	(311) , (131), (113)	Three – fold degenerate
$\frac{12\pi^2\hbar^2}{2ma^2}$	(222)	Non – degenerate
$\frac{14\pi^2\hbar^2}{2ma^2}$	(123) ,(132), (213) (231), (312) ,(321)	six– fold degenerate

Note: consider a case where the energy of a particle $E_n = \frac{38\pi^2\hbar^2}{2ma^2}$

$$E_n = \frac{\pi^2\hbar^2}{2ma^2} [n_x^2 + n_y^2 + n_z^2] \quad \therefore \text{In this case } (n_x^2 + n_y^2 + n_z^2) = 38$$



$$n_x^2 + n_y^2 + n_z^2 = 6^2 + 1^2 + 1^2 \rightarrow 3 \text{ fold degenerate } (611), (161), (116)$$

$$= 2^2 + 3^2 + 5^2 \rightarrow 6 \text{ fold degenerate } (235), (253), (325), (352), (523), (532)$$

$$\therefore E_n = \frac{38\pi^2\hbar^2}{2ma^2} \text{ nine - fold degenerate}$$

Example 6

A particle of mass m is in a cubic box of size a . The potential inside the box

$(0 \leq x \leq a, 0 \leq y \leq a, 0 \leq z \leq a)$ is zero and infinite outside. If the particle is an eigen state of energy

$$E = \frac{84\pi^2\hbar^2}{2ma^2}, \text{ its wave function is:}$$

$$(a) \psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{3\pi x}{a}\right) \sin\left(\frac{5\pi y}{a}\right) \sin\left(\frac{6\pi z}{a}\right) \quad (b) \psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{7\pi x}{a}\right) \sin\left(\frac{4\pi y}{a}\right) \sin\left(\frac{3\pi z}{a}\right)$$

$$(c) \psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{4\pi x}{a}\right) \sin\left(\frac{8\pi y}{a}\right) \sin\left(\frac{2\pi z}{a}\right) \quad (d) \psi = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{2\pi y}{a}\right) \sin\left(\frac{3\pi z}{a}\right)$$

Solution

The energy of the particle in a cubic of side 'a' is $E = \frac{\pi^2\hbar^2}{2ma^2} [n_x^2 + n_y^2 + n_z^2]$

$$\therefore [n_x^2 + n_y^2 + n_z^2] \frac{\pi^2\hbar^2}{2ma^2} = \frac{84\pi^2\hbar^2}{2ma^2} \Rightarrow (n_x^2 + n_y^2 + n_z^2) = 84$$

$$\Rightarrow 4^2 + 8^2 + 2^2 = 84 \therefore \text{the possible value of } (n_x, n_y, n_z) = (4, 8, 2)$$

$$\therefore \text{The wave function of the particle } \psi_n = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{4\pi x}{a}\right) \sin\left(\frac{8\pi y}{a}\right) \sin\left(\frac{2\pi z}{a}\right)$$

Ans : (c)



One Dimensional Harmonic Oscillator

Consider a particle of mass m in a one dimensional harmonic potential. The harmonic potential is given by

$$V(x) = \frac{1}{2} kx^2 = \frac{1}{2} m\omega^2 x^2 \quad (57)$$

Where the angular frequency $\omega = \sqrt{\frac{k}{m}}$, k is the force constant. The Schrodinger equation in this case

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

The solution of the above equation can be expressed in terms of the Hermite polynomial

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-\frac{x^2}{2}} H_n(x) \quad (58)$$

Where $H_n(x)$ are the Hermite polynomial.

Rodrigue's formula $H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}) \quad (59)$

From this relation it is easy to calculate first few polynomials:

$$\begin{aligned} H_0(x) &= 1 & H_1(x) &= 2x \\ H_2(x) &= 4x^2 - 2 & H_3(x) &= 8x^3 - 12x \\ H_4(x) &= 16x^4 - 48x^2 + 12 & H_5(x) &= 32x^5 - 160x^3 + 120x \end{aligned}$$

The energy eigen values of the harmonic oscillator



$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad (n = 0, 1, 2, \dots) \quad (60)$$

The eigen values of total energy depend only on one quantum number. Therefore all the **energy levels of the oscillator are non degenerate (fig 4).**

The successive energy levels are equally spaced; the separation between two adjacent energy levels being $\hbar \omega$.

Zero Point Energy

when $n = 0$, $E_0 = \frac{1}{2} \hbar \omega$ zero point energy (61)

The zero point energy is the characteristic result of quantum mechanics. The zero point energy of the bound state systems cannot be zero, otherwise it would violate the Uncertainty Principle. The first few wave function of harmonic oscillator are given in figure (5)

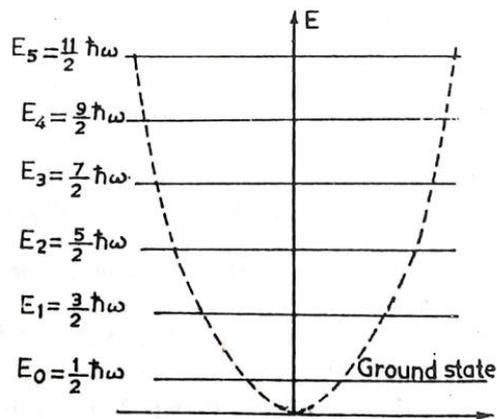


Figure 4

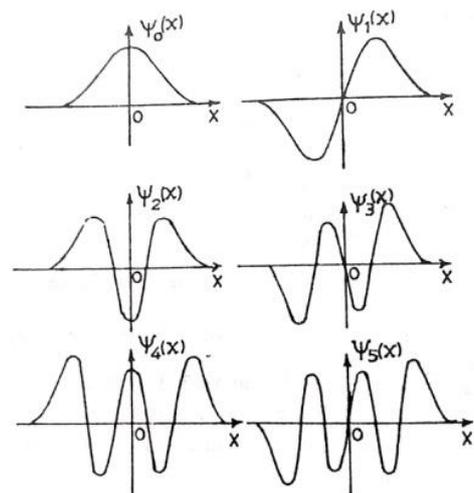


Figure 5

Example 7

The energy of a linear harmonic oscillator in third excited state is 4.1 eV. The frequency of vibration is _____.

Solution

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \Rightarrow E_3 = \left(3 + \frac{1}{2}\right) \hbar \omega = \frac{7}{2} \hbar \omega$$

$$\therefore \frac{7}{2} \hbar \omega = 4.1 \text{ eV} \Rightarrow \frac{7}{2} \hbar 2\pi f = 4.1 \text{ eV}$$

$$\therefore f = \frac{4.1 \text{ eV}}{7\pi \hbar} = \frac{4.1 \times 1.6 \times 10^{-19}}{7 \times 3.14 \times 1.054 \times 10^{-34}} \approx 0.28 \times 10^{15} = 2.8 \times 10^{14} \text{ Hz}$$

The Isotropic Three Dimensional Harmonic Oscillator

Consider a particle of mass m moving in a three dimensional isotropic oscillator potential

$$V(x, y, z) = \frac{1}{2} m \omega^2 x^2 + \frac{1}{2} m \omega^2 y^2 + \frac{1}{2} m \omega^2 z^2 \quad (62)$$

The Schrodinger equation

$$\nabla^2 \psi(x, y, z) + \frac{2m}{\hbar^2} [E - V(x, y, z)] \psi = 0 \quad (63)$$

The eigen energies corresponding to the potential can be expressed as

$$E_{n_x, n_y, n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \left(n_x + \frac{1}{2}\right) \hbar \omega + \left(n_y + \frac{1}{2}\right) \hbar \omega + \left(n_z + \frac{1}{2}\right) \hbar \omega = \left(n_x + n_y + n_z + \frac{3}{2}\right) \hbar \omega \quad (64)$$



With $n_x, n_y, n_z = 0, 1, 2, 3, \dots$. The degeneracy g_n of n^{th} excited state, which is equal to the number of ways the non negative integers n_x, n_y, n_z may be chosen to total to n , is given by

$$g_n = \frac{1}{2}(n+1)(n+2) \quad (65)$$

Where $n = (n_x + n_y + n_z)$.

The first few energy levels along with their degeneracies are given in the following table

n	E_{n_x, n_y, n_z}	$n_x n_y n_z$	g_n
0	$\frac{3}{2}\hbar\omega$	(000)	1
1	$\frac{5}{2}\hbar\omega$	(100),(010),(001)	3
2	$\frac{7}{2}\hbar\omega$	(200), (020),(002) (110),(101),(011)	6
3	$\frac{9}{2}\hbar\omega$	(300), (030),(003) (210),(201),(021) (120),(102),(012),(111)	10

The Potential Step

Another simple problem consists of a particle that is free everywhere, but beyond a particular point, say $x = 0$, the potential increases sharply (i.e., it becomes repulsive). A potential of this type is called a potential step.

$$V(x) = \begin{cases} 0, & x < 0 \\ V_0 & x \geq 0 \end{cases} \quad (66)$$



In this problem, we try to analyze the dynamics of a flux of particles (all having the same mass m and moving with same velocity) moving from left to the right. We are going to consider two cases, depending on whether the energy of particles is larger or smaller than V_0 Figure 6.

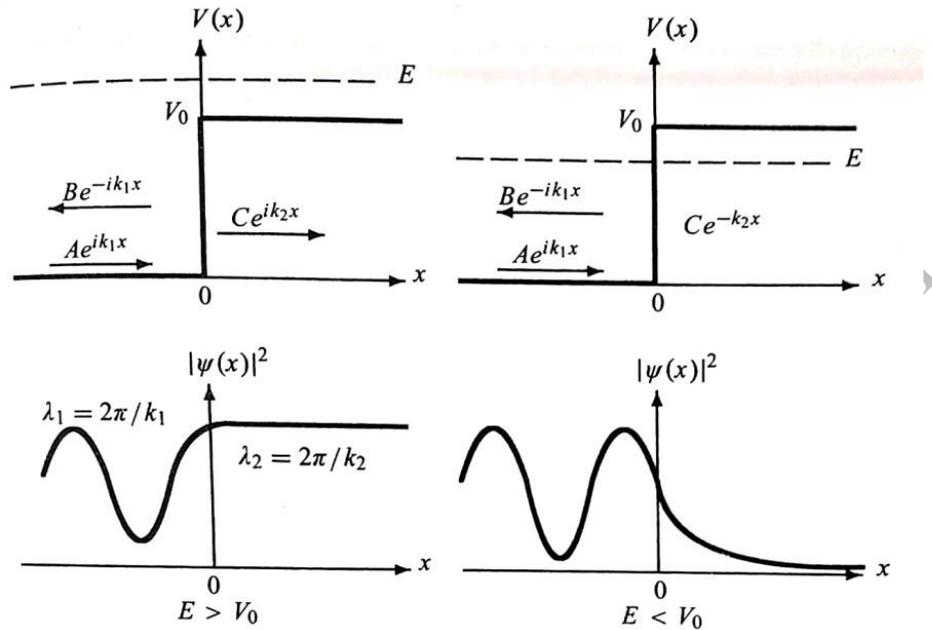


Figure 6

(a) Case $E > V_0$

The particles are free for $x < 0$ and feel a repulsive potential V_0 that starts at $x = 0$ and stays flat (constant) for $x > 0$. Let us analyze the dynamics of this flux of particles classically and then quantum mechanically. **Classically, the particles have sufficient energy to enter into the region $x \geq 0$, there will be total transmission.**

Quantum mechanically, the dynamics of the particle is regulated by the Schrodinger equation, which is given in these two regions by

$$\frac{\partial^2 \psi_1(x)}{\partial x^2} + k_1^2 \psi_1(x) = 0 \quad \text{where } k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad (67)$$

$$\frac{\partial^2 \psi_2(x)}{\partial x^2} + k_2^2 \psi_2(x) = 0 \quad \text{where } k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \quad (68)$$

The most general solutions to these two equations are plane waves:

$$\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \quad x < 0 \quad (69)$$

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \quad x \geq 0 \quad (70)$$

Since we are dealing with stationary states, the complete (time - dependent) wave function is obtained by multiplying equations (69) and (70) by $e^{-i\omega t}$.

$$\text{Thus for } x < 0 \quad \psi_1(x, t) = \psi_1(x)e^{-i\omega t} = Ae^{i(k_1x - \omega t)} + Be^{-i(k_1x - \omega t)} \quad (71)$$

Where $Ae^{i(k_1x - \omega t)}$ and $Be^{-i(k_1x - \omega t)}$ represent the incident and reflected waves respectively.

$$\text{For } x > 0 \quad \psi_2(x, t) = \psi_2(x)e^{-i\omega t} = Ce^{i(k_2x - \omega t)} + De^{-i(k_2x - \omega t)} \quad (72)$$

Where $Ce^{i(k_2x - \omega t)}$ represents the transmitted wave and since there is no reflected wave $D = 0$.

Continuity of ψ and $\frac{\partial \psi}{\partial x}$ at $x = 0$ gives us $A + B = C$

$$ik_1(A - B) = ik_2C$$

From which we readily obtain

$$B = \left(\frac{k_1 - k_2}{k_1 + k_2} \right) A \quad (73)$$



$$C = \left(\frac{2k_1}{k_1 + k_2} \right) A \quad (74)$$

Now Probability current density $J = \text{probability density} \times \text{velocity of particle}$

$$J_{\text{incident}} = \frac{\hbar k_1}{m} |A|^2 ; J_{\text{Reflected}} = \frac{\hbar k_1}{m} |B|^2 ; J_{\text{Transmitted}} = \frac{\hbar k_2}{m} |C|^2 \quad (75)$$

Thus, the reflection and transmission coefficients are given by

$$R = \frac{J_{\text{Ref}}}{J_{\text{inc}}} = \left| \frac{B}{A} \right|^2 ; T = \frac{J_{\text{trans}}}{J_{\text{inc}}} = \frac{k_2}{k_1} \left| \frac{C}{A} \right|^2 \quad (76)$$

Using (73) and (74)

$$R = \left(\frac{k_1 - k_2}{k_1 + k_2} \right)^2 ; T = \frac{4k_1 k_2}{(k_1 + k_2)^2} \quad (77)$$

From (77), we see that $R+T = 1$ as it indeed should be.

In contrast to classical mechanics, which states that none of the particles get reflected, equation (77) shows that the quantum mechanical reflection coefficient R is not zero: There are particles that get reflected inspite of their energies being higher than the step V_0 . This effect must be attributed to the **wave nature associated with moving particles.**

From equation (77) we see that as **E** gets smaller and smaller, **T** also gets smaller and smaller such that when **E = V₀** the transmission coefficient **T** becomes zero and **R = 1**.



On the other hand, when $E \gg V_0$, we have $\frac{k_2}{k_1} = \sqrt{1 - \frac{V_0}{E}} \approx 1$; hence $R = 0$ and $T = 1$. This is

expected since, when the incident particles have very high energies, the potential step is so weak that it produces not noticeable effect on their motion.

When $E < V_0$

Classically, when $E < V_0$ none of the particles will make it into the right side of barrier at $x = 0$,

i.e., There is total reflection of particles.

Quantum mechanically, the transmitted wave function $\psi_2(x) = Ce^{-k_2x}$, is zero, since $\psi_2(x)$ is purely real function $[\psi_2^*(x) = \psi_2(x)]$ and therefore

$$J_{\text{transmitted}} = \frac{\hbar k_2}{m} \left[\psi_2^*(x) \frac{d\psi_2(x)}{dx} - \psi_2(x) \frac{d\psi_2^*(x)}{dx} \right] = 0 \quad (78)$$

Hence, **the reflection coefficient R must be equal to 1.** It may be noted that although the transmission coefficient vanishes, the wave function is not zero in the region $x > 0$, i.e., There is finite probability of finding the particle in the classically forbidden region. The probability density $|\psi_2(x)|^2$ is proportional to e^{-2k_2x} is appreciable near $x = 0$ and falls exponentially to small values as x becomes large; the behaviour of the probability density is shown in figure (6).



Example 8

A particle of mass m and energy E moving in the positive x - direction, encounters a one – dimensional potential barrier at $x = 0$. The barrier is defined by $V = 0$ for $x < 0$, $V = V_0$ for $x \geq 0$ (V_0 is positive and $E > V_0$). The wave function of the particle in the region $x < 0$ is given by $Ae^{-ikx} + Be^{ikx}$. if $B/A = 0.4$, then E/ V_0 is

- (a) 29/40 (b) 49/40 (c) 69/40 (d) 79/40

Solution

The wave function of particle in the region $x < 0$ is $\psi = Ae^{-ikx} + Be^{ikx}$

Given $B/A = 0.4$, $E/ V_0 = ?$

$$\frac{B}{A} = \left(\frac{k - k_1}{k + k_1} \right) = \left(\frac{1 - \frac{k_1}{k}}{1 + \frac{k_1}{k}} \right) \quad \text{Where } k = \sqrt{\frac{2mE}{\hbar^2}} \text{ and } k_1 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}, \quad \therefore \frac{k_1}{k} = \sqrt{\frac{E - V_0}{E}} = \sqrt{1 - \frac{V_0}{E}}$$

$$\left| \frac{B}{A} \right|^2 = \frac{1 - \sqrt{1 - \frac{V_0}{E}}}{1 + \sqrt{1 - \frac{V_0}{E}}} = \frac{1 - x}{1 + x} \quad \text{where } x = \sqrt{1 - \frac{V_0}{E}}$$

$$\therefore 0.4 = \frac{1 - x}{1 + x} \Rightarrow 0.4(1 + x) = 1 - x \Rightarrow x = \frac{3}{7}$$

$$\therefore \sqrt{1 - \frac{V_0}{E}} = \frac{3}{7} \therefore 1 - \frac{V_0}{E} = \frac{9}{49} \therefore \frac{V_0}{E} = \frac{40}{49} \Rightarrow \frac{E}{V_0} = \frac{49}{40}$$

Ans: (b)

