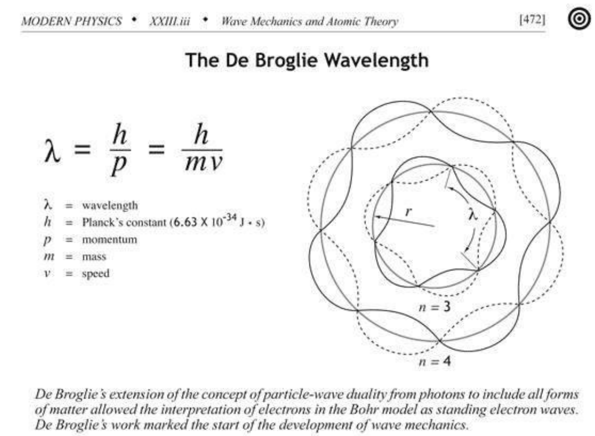
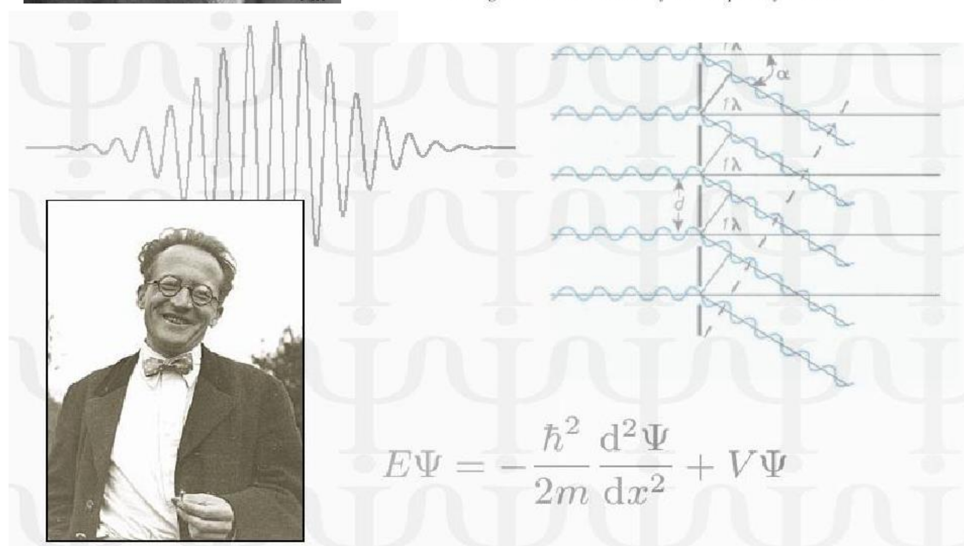
QUANTUM MECHANICS

UNIT II
Quantum Mechanics
Lecture-6



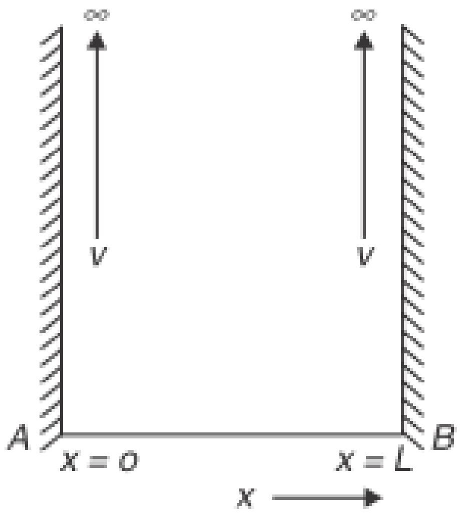


APPLICATIONS OF SCHRÖDINGER WAVE EQUATION

Particle in a One-Dimensional Box.

$V = 0$ for $0 \leq x \leq L$

$V = \infty$ for $x < 0$ and $x > L$



Application of Schrodinger Wave Equation Contd…

The Schrödinger wave equation for the particle is given by

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

- Schrodinger wave equation in one dimension can be written as

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

Inside the box, $V = 0$, therefore the above equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Let $2mE/\hbar^2 = k^2$, then Eq. (23.63) takes the form

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

The general solution of Eq. (23.64) can be given as

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

Problem of the particle in the box Contd..

- The values of A and B can be determined by applying the boundary conditions.
- Since this particle cannot penetrate the walls and cannot exist outside the box, the probability of finding the particle (i.e., ψ) will be zero outside the box.
- Hence, $\psi = 0$ at $x = 0$ and $\psi = 0$ at $x = L$
- Applying these boundary conditions to we get
- $0 = A \sin 0 + B \cos 0$ (because at $x = 0$, $\psi = 0$)
- or $B = 0$

Problem of the particle in the box Contd..

- Using the value of B =0 in the above equation we get $\psi = A \sin kx$
- Using the boundary condition, $\psi = 0$ at $x = L$, we get $A \sin kL = 0$
- In the above equation, either A is zero or sin kL is zero.
- Since A is the amplitude of the wave, $A \neq 0$. Hence, we get

$$\sin kL = 0$$

or $$kL = n\pi \qquad (n = 0, 1, 2, 3, \ldots$$

or $$k = \frac{n\pi}{L}$$

Now, the wave function ψ can be given as

$$\psi(x) = A \sin \frac{n\pi x}{L}$$

Problem of the particle in the box Contd..

We have assumed that

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

Again, from Eq. (23.66), we have

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

or $$E_n = \frac{n^2h^2}{8mL^2}$$ (using E_n for E in general and $\hbar = h / 2\pi$)

$$= \frac{h^2}{8m}\left[\frac{n^2}{L^2}\right]$$

where $n = 1, 2, 3.$

Problem of the particle in the box Contd..

- It is clear from this expression that the particle has only discrete sets of values of energy, i.e., the energy of the particle is quantised.

The discrete energy levels of the particle in deep potential box have been shown in Fig.

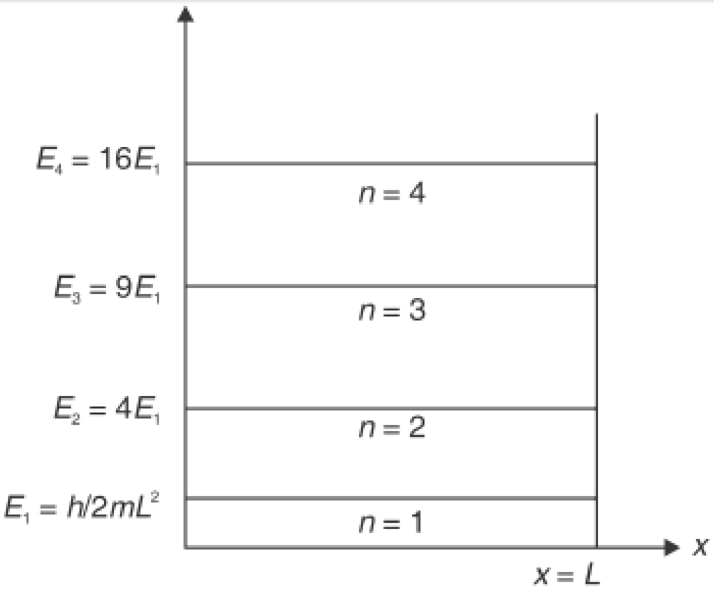
$$E_1 = \frac{h^2}{8mL^2} \quad \text{for } n = 1$$

$$E_2 = \frac{4 \cdot h^2}{8mL^2} = 4E_1 \quad \text{for } n = 2$$

$$E_3 = 9\frac{h^2}{8mL^2} = 9E_1 \quad \text{for } n = 3$$

$$E_4 = 16\frac{h^2}{8mL^2} = 16E_1 \quad \text{for } n = 4$$

$$\vdots \quad \vdots$$



Problem of the particle in the box Contd..

We still require the exact value of constant A. To find the value of constant A, we apply normalization condition,

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1$$

Using the boundary conditions of our problem, we can write

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

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

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

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

or $$\frac{A^2}{2} \left[x - \frac{L}{2\pi n} \sin \frac{2n\pi x}{L}\right]_0^L = 1$$

or $$\frac{A^2}{2} L = 1$$

or $$A = \sqrt{\frac{2}{L}}$$

Using the value of A we get

$$\Psi(x) = \sqrt{\frac{2}{L}} \, \mathrm{Sin} \, \frac{n\pi x}{L}$$

Probability Density Distribution

The first three normalized wave functions ψ_1, ψ_2, and ψ_3 along with their corresponding probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^3$ are shown in Figs. 23.7 (a) and (b).

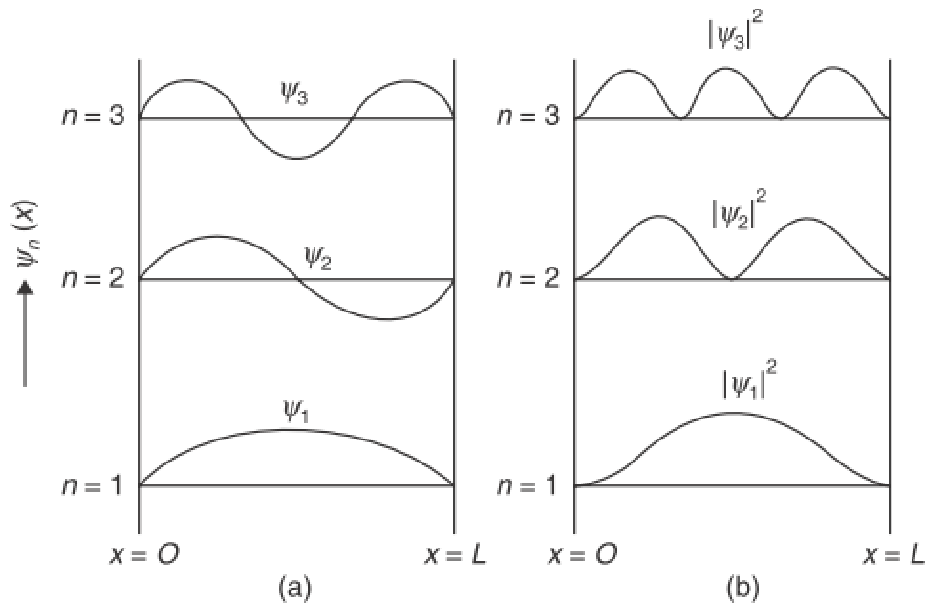


Fig. 23.7 Wave function and probability density of a particle inside an infinite potential well

Physical Interpretation of Probability Density Distribution

For physical interpretation of probability density distribution, let us consider three conditions corresponding to n = 1, 2, and 3, respectively.

Condition I: When $n = 1$

This is the condition of ground state where particle is normally found.

$$E_1 = \frac{h^2}{8mL^2} = E_0$$

For this state, ψ (eigenfunction) is expressed as

$$\psi_1 = \sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{\pi x}{L}\right)$$

At $x = 0$ and $x = L$, $\psi_1 = 0$. But at $x = L/2$, ψ_1 has the maximum value.

A plot of ψ_1 versus x is shown in Fig. 23.8(a) and the plot of $|\psi_1|^2$ versus x is shown in Fig.

Physical Interpretation of Probability Density Distribution

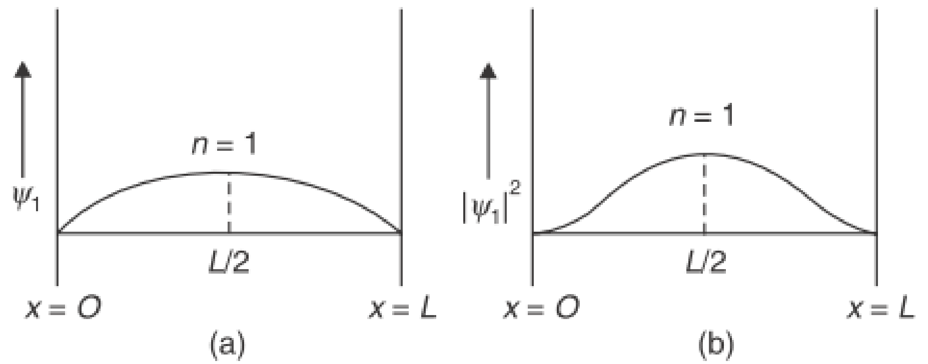


Fig. 23.8 Plot showing the variation in ψ_1 and $|\psi_1|^2$ against x

- From Fig. 23.8(b), it is clear that the probability of finding the particle inside the box is maximum at x = L/2, while it is zero at x = 0 and x = L.

- We can conclude that in ground state, the probability of finding the particle is maximum at central region, while it is minimum at the walls of the box.

Condition II: When n = 2

- This condition is known as first excited state . In this case, the energy of the particle can be given as

$$E_2 = \frac{4h^2}{8mL^2} = 4E_0$$

In this condition, wave function ψ^2 can be given as

$$\psi^2 = \sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{2\pi x}{L}\right)$$

From the above expression, it is clear that ψ^2 is zero for $x = 0$, $L/2$, and L. But it is maximum at $x = L/4$ and $x = 3L/4$.

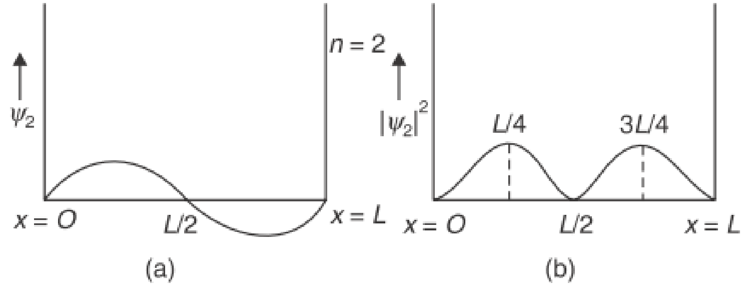


Fig. 23.9 Variation in ψ_2 and $|\psi_2|^2$ against x

The variation in ψ_2 and probability density $|\psi_2|^2$ with x is shown in Fig. 23.9. It is clear from this figure that particle is observed neither at the walls nor at the centre of the box. The maximum probability of finding the particle is either at $x = L/4$ or $3L/4$.

Condition III: When n = 3

Similar to above conditions, we can obtain the expression of energy for the second excited state which can be given as

$$E_3 = \frac{9h^2}{8mL^2} = 9E_0$$

and corresponding eigenfunction in this state can be given as

$$\psi_3 = \sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{3\pi x}{L}\right)$$

$$\psi_3 = 0 \text{ for } x = 0, \frac{L}{3}, \frac{2L}{3}, \text{ and } L$$

ψ_3 has maximum values for $x = L/6, L/2,$ and $5L/6$. The variation in ψ_3 and $|\psi_3|^2$ versus x is shown in Fig. 23.10

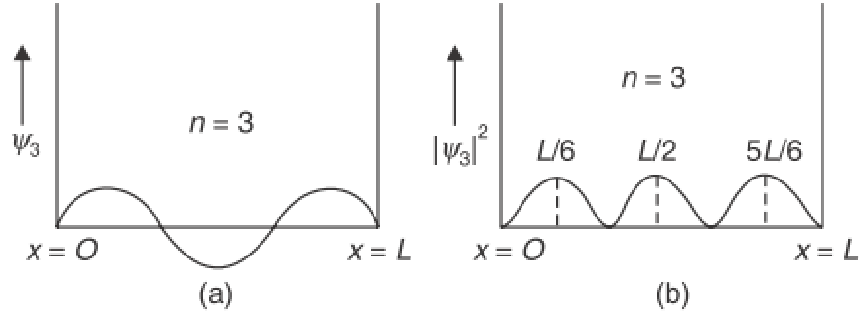


Fig. 23.10 Variation in eigenfunction and probability density versus *x*

It is clear from Fig. 23.10 that the particle is most likely to be found at the locations $x = L/6, L/2,$ or $5L/6$. This means that particle is found neither at the walls nor at the centre of the box.

Find the energy of an electron moving in one-dimension in an infinitely high potential box of width 1 Å. (Mass of the electron is 9.1×10^{-31} kg and $h = 6.63 \times 10^{-34}$ Js.)

Solution

From the expression of energy of a particle in a deep potential box of width L, we have

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

where $n = 1, 2, 3, ...$

Particle is generally found in the ground state, which occurs corresponding to $n = 1$.

Hence,

$$E = \frac{h^2}{8mL^2}$$

$$= \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1 \times 10^{-10})^2}$$

$$= \frac{43.96 \times 10^{-68}}{72.8 \times 10^{-51}}$$

$$= 6.038 \times 10^{-18} \text{ J}$$

$$= \frac{6.038 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 37.74 \text{ eV}$$

Find the probabilities of finding a particle trapped in a box of length L in the region from 0.45L to 0.55L for the ground state and the first excited state.

Solution

If a particle is trapped in a box of length L, then the wave function can be given as

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Now, the probability of finding the particle between $0.45L$ to $0.55L$ can be given as

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

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

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

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

For $n = 1$, we have

$$P = \frac{1}{L}\left[\left(0.55L - \frac{L}{2\pi}\sin(1.10\pi)\right) - \left(0.45L - \frac{L}{2\pi}\sin(0.90\pi)\right)\right]$$

$$= \left[\left(0.55 - \frac{1}{2\pi}\sin 198^\circ\right) - \left(0.45 - \frac{1}{2\pi}\sin 162^\circ\right)\right]$$

$$= (0.55 - 0.45) - \frac{1}{2\pi}(\sin 198^\circ - \sin 162^\circ)$$

$$= 0.10 - \frac{1}{2\pi}(\sin 198^\circ - \sin 162^\circ)$$

$$= 0.10 - (-0.0984)$$

$$= 0.1984$$

$$= 19.84\%$$

Similarly, for the first excited state (for $n = 2$), the above calculation gives the value of probability as $P = 0.65\%$.

Assignment Based on this Lecture

- Describe the problem of the particle in a box.
- Obtain the expression of wave function ψ and energy for a particle in a box.
- Explain the Physical interpretation of probability distribution of a particle.

A particle is in motion along a line between $x = 0$ and $x = a$ with zero potential energy. At points for which $x < 0$ and $x > a$, the potential energy is infinite. The wave function for the particle in the nth state is given by

$$\psi_n = A \sin \frac{n\pi x}{a}$$

Find the expression for the normalized wave function.