ENGINEERING PHYSICS

MODULE – 2

Modern Physics & Quantum Mechanics

Introduction to blackbody radiation spectrum- Wien's law, Rayleigh Jean's law, Stefan -Boltzmann law and Planck's law (qualitative), Deduction of Wien's law and Rayleigh Jeans law from Planck's law. Wave-Particle dualism, de Broglie hypothesis, de-Broglie wavelength. Heisenberg's uncertainty principle and its physical significance, Application of uncertainty principle-Non-existence of electron in the nucleus (relativistic case), Wave function Properties, Physical significance, Probability density, Normalization, Eigen values and Eigen functions. Time independent Schrödinger wave equation. Particle in a box- Energy Eigen values and probability densities, Numerical problems.

INTRODUCTION TO BLACK BODY RADIATION SPECTRUM:

BLACK BODY: A body which absorbs all the radiations incident on it is called a perfect black body. When radiations are allowed to fall on such a body, they are neither reflected nor transmitted. Such a body after absorbing the incident radiations gets heated and starts emitting radiations of all wavelengths. These radiations are known as black body radiations. In practice perfect black body does not exist. It is an ideal body. A surface coated with lamp black may be considered as perfectly black for all practical purposes.

DISTRIBUTION OF ENERGY IN THE BLACK BODY RADIATION SPECTRUM:

The distribution of energy among the different wavelength of thermal radiation of a black body is shown in the Fig. 2.1. The curves in the figure represent the variation of intensity of the radiation (or energy) with wavelength for different temperatures.

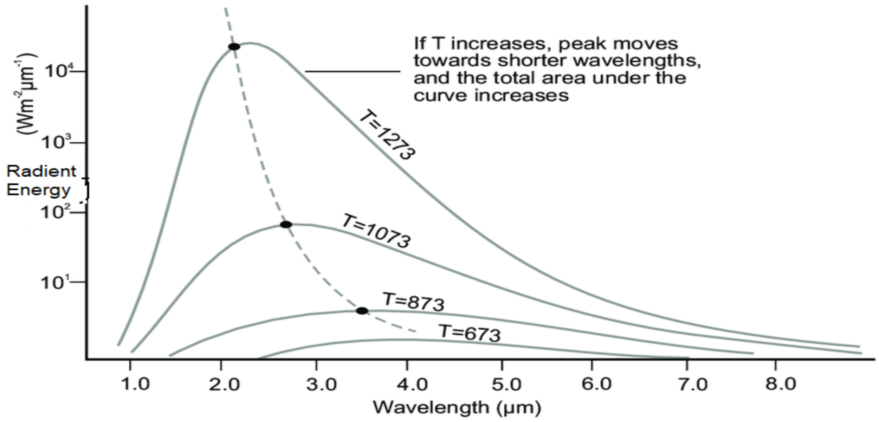


Fig. 2.1 Intensity distribution for a block body at different curves

It can be observed from the figure that,

1. At a given temperature the black body emits continuous range of wavelengths i.e., at a given temperature, the intensity of radiation increases with the wavelength and reaches the maximum value at a particular wavelength λ_m. Then it decreases with the increase in wavelength.
2. Energy at a definite wavelength increases with increase in temperature of the black body.
3. At a given temperature, the energy is not uniformly distributed in the radiation spectrum of the black body.
4. The wavelength λ_m at which maximum emission of energy takes place decreases (i.e., shifts towards the shorter wavelength) with increase in temperature. This is known as Wien's displacement law. $\lambda_m \mathrm{T} = \text{constant}$
5. The area under each curve represents the total energy emitted at a given temperature and it is found to be directly proportional to the fourth power of the absolute temperature i.e., $E \propto T^4$. It represents Stefan's fourth power law.

WIEN'S LAW:

According to Wien's law, the relation between the wavelength of emission and the temperature of the source is given by,

$$U_\lambda \, d\lambda = C_1 \lambda^{-5} e^{-(C_2/\lambda T)} d\lambda$$

where $U_\lambda \, d\lambda$ is the energy per unit area for wavelengths in the range λ & $\lambda + d\lambda$ and C_1 and C_2 are constants. This is called as Wien's energy distribution law.

Limitation of Wien's law:

It is found that Wien's law is applicable only for shorter wavelength. It failed to explain the gradual drop in the intensity of radiation whose wavelengths are more than the ones corresponding to the peak value.

RAYLEIGH – JEAN'S LAW:

Rayleigh and Jeans considered the black body radiator full of electromagnetic waves of all wavelengths between 0 and $\propto$. Using equipartition of energy principle Rayleigh and Jean derived the equation for the energy distribution as,

$$U_\lambda \, d\lambda = \frac{8\pi KT}{\lambda^4} d\lambda$$

$$or \qquad U_\lambda \, d\lambda = 8\pi \, KT \, \lambda^{-4} \, d\lambda$$

where K is the Boltzmann constant.

As per the above equation, the energy radiated by the black body is expected to decrease with increase in wavelength. Thus Rayleigh – Jeans law correctly predicts the fall of intensity towards the longer wavelength side.

Ultra-violet catastrope: Limitation of Rayleigh – Jeans law

According to Rayleigh – Jeans equation, the radiant energy decreases with the increasing wavelength i.e., the black body is predicted to radiate all the energy at very short wavelength side. But in actual practice a black body radiates mainly in the infrared or visible region of the electromagnetic spectrum and the intensity of radiation decreases down steeply for shorter wavelength as shown in the radiation curve. Thus Rayleigh – Jeans law fails to explain the lower wavelength side of the spectrum. The failure of the Rayleigh – Jeans law to explain the spectrum beyond the ultraviolet region towards the lower wavelength side of the spectrum is referred as **Ultraviolet Catastrophe.**

Stefan–Boltzmann Law

Radiation heat transfer rate, q [W/m^2], from a body (e.g. a black body) to its surroundings is proportional to the fourth power of the absolute temperature and can be expressed by the following equation:

$$q = \varepsilon \sigma T^4$$

where σ is a fundamental physical constant called the Stefan–Boltzmann constant, which is equal to 5.6697×10^{-8} W/m^2K^4.

The Stefan–Boltzmann constant is named after Josef Stefan (who discovered the Stefan-Boltzman law experimentally in 1879) and Ludwig Boltzmann (who derived it theoretically soon after).

PLANCK'S LAW

In order to explain the distribution of energy in the spectrum of a black body over the entire range of wavelength, Max Planck, a German physicist proposed in 1901 the quantum theory. According to this theory the surface of black body consists of a very large number of electrical oscillators. These oscillators emit or absorb energy as integral multiples of discrete packets of energy called quanta, $\Delta E = h\nu$ where h is a constant called Planck's constant ($h = 6.625 \times 10^{-34}$ Js) and ν is the frequency of radiation. The packets of energy are or photon.

i.e., $E = nh\nu$, n is an integer

Planck radiation law explains the thermal radiation emitted by the black body at different wavelength ranges and the equation governing the Planck's law is as follows.

$$U_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{h\nu/kT}-1}\right]d\lambda \text{ --------- (1)}$$

Planck's Hypothesis:

A black body consists of a large number of microscopic charge oscillators known as resonators. The energies of the resonators are quantized. When a black body absorbs or emits energy it will be as an integral multiple of the quanta, hν. The energy absorbed or emitted E = n hν where n is an integer

Deduction of Wien's law and Rayleigh -Jeans law from Planck's law

(1) Deduction of Wien's law from Planck's law:

Wien's law is true for the shorter wavelength.

For shorter wavelengths, $\nu = \frac{c}{\lambda}$ is large.

When ν is large, $e^{\frac{h\nu}{kT}}$ is very large.

ie $e^{\frac{h\nu}{kT}} >>> 1$

$\therefore (e^{\frac{h\nu}{kT}} - 1) \approx e^{\frac{h\nu}{kT}} = e^{\frac{hc}{\lambda kT}}$

Hence Planck's radiation equation (eqn 1) can be written as

$$U_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{hc/\lambda kT}}\right]d\lambda$$

$$= \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{C_2/\lambda T}}\right]d\lambda$$

$$= C_1 \lambda^{-5} e^{-(C_2/\lambda T)} d\lambda$$

where $C_1 = 8\pi hc$ and $C_2 = hc/k$

This is the Wien's law of radiation.

(2) Deduction of Rayleigh – Jeans law from Planck's law:

Rayleigh -Jeans law is true for longer wavelengths

For longer wavelengths, $\nu = c/\lambda$ is small. When ν is small $\frac{h\gamma}{kT}$ is very small.

Expanding $e^{\frac{h\nu}{kT}}$ as power series, we have

$$e^{\frac{h\nu}{kT}} = 1 + \frac{h\nu}{kT} + \left(\frac{h\nu}{kT}\right)^2 + \ldots.$$

$$= 1 + \frac{h\nu}{kT}$$

Since $\frac{h\nu}{kT}$ is very small, its higher power terms could be neglected.

$$\therefore \left(e^{\frac{h\nu}{kT}} - 1\right) = 1 + \frac{h\nu}{kT} - 1 = \frac{h\nu}{kT} = \frac{hc}{\lambda kT}$$

$\therefore$ Equation (1) becomes, $U_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{\frac{hc}{\lambda kT}}\right] d\lambda$

$U_\lambda \, d\lambda = \frac{8\pi kT}{\lambda^4} \, d\lambda$ This is Rayleigh – Jeans law.

DUAL NATURE OF MATTER:

Some of the properties of light (Energy) such as interference, diffraction and polarization can be explained by using wave nature and some other properties like photoelectric effect, Compton Effect, emission and absorption of radiations shows the particle nature (the radiation consists of small corpuscles known as photons). Thus, it is accepted that radiation has dual nature. Particle has mass, it occupies space, and it can move from one place to another, it gives energy when slowed down or stopped. Thus, the particle can be specified by mass, velocity, momentum energy and two particles cannot occupy the same space simultaneously. A wave as it travels, spreads occupying larger region of space. A wave is specified by wavelength, frequency, amplitude, intensity, phase and wave velocity.

De Broglie's concept of matter waves:

It is accepted that radiation has dual nature. In 1924 Louis de Broglie put forth the suggestion that matter, like radiation, has dual nature, i.e., matter which is made up of discrete particles, atoms, protons, electrons etc., might exhibit wave like properties under appropriate conditions. These waves associated with a moving material particle, are called matter waves.

"Every moving particle is associated with a set of waves known as matter waves."

The wavelength λ associated with a particle of mass 'm' moving with a velocity 'v' is called de Broglie wavelength and is given by

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

$h \rightarrow$ Planck's constant $\quad$ $p \rightarrow$ momentum of the particle

Expression for de Broglie wavelength in terms of energy of the particle:

Consider a particle of mass m moving with a velocity v. Let its kinetic energy be E.

$\therefore E = ½\, mv^2$

Multiplying by 'm' both sides,

$mE = ½\, m^2v^2$

$mE = \frac{p^2}{2}$ $\quad (\because mv = p)$

$p^2 = 2mE$

$p = \sqrt{2mE}$

De Broglie wavelength, $\lambda = \frac{h}{p}$

$$\boxed{\therefore \lambda = \frac{h}{\sqrt{2mE}}}$$

De Broglie wavelength associated with electrons:

Consider an electron of rest mass m and charge e, accelerated by a potential difference of V volt from rest to a velocity v. Then work done on the electron is W = eV

This work done is converted into kinetic energy of the electron.

$\therefore eV = \frac{1}{2}mv^2$ $\quad$ i.e., $\quad$ $v = \sqrt{\frac{2eV}{m}}$

But, $\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{\frac{m^2 2eV}{m}}} = \frac{h}{\sqrt{2meV}}$

$$\boxed{\therefore \lambda = \frac{h}{\sqrt{2meV}}}$$

de Broglie wavelength of electrons is given by

$h = 6.63 \times 10^{-34}$ Js, $m = 9.1 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V}} = \frac{12.27}{\sqrt{V}} \text{Å}$$

Characteristic properties of matter waves:

1. Matter waves are the waves that are associated with a moving particle. The wavelength λ and frequency γ of the waves are given by $\lambda = \frac{h}{p} = \frac{h}{mv}$ and $\gamma = \frac{E}{h}$ where h – Plank's constant, p and E are the momentum and energy of the particle respectively.
2. Lighter is the particle, greater is the wavelength associated with it.
3. Smaller is the velocity of the particle, greater is the wavelength associated with it.
4. The wave velocity or phase velocity of the matter waves is given by $V_{Phase} = \frac{C^2}{V_{group}}$

   Here V_{group} is same as the particle velocity, which is always lesser than the velocity of light C. Thus velocity of matter waves is always greater than C. This indicates that matter waves are not physical waves.
5. The velocity of matter waves depends on the velocity of material particle. i.e., it is not a constant, while the velocity of electromagnetic wave is constant.

Heisenberg's Uncertainty Principle:

In classical mechanics, a particle occupies a definite place in space and possess a definite momentum. By knowing the position and momentum of a particle at any given instant of time. It is possible to evaluate its position and momentum at any later stage and the trajectory of the particle could be continuously traced. But in quantum mechanics, since we are dealing with atomic scale, it is not possible to determine the position and momentum of a particle simultaneously with accuracy.

According to Heisenberg's uncertainty principle, it is impossible to determine simultaneously both the position and momentum of a particle with accuracy. The product of the uncertainties in the simultaneous determination of the position and momentum of a particle is equal to or greater than $\frac{h}{4\pi}$.

If Δp and Δx are the uncertainties in the momentum and position of a particle, then we can write the mathematical form of Heisenberg's uncertainty principle as

$\Delta p.\Delta x \geq \frac{h}{4\pi}$

According to this equation, an increase in the accuracy in the measurement of position means, a decrease in the value of Δx. As per the above equation, a decrement in the value of Δx, must simultaneously result in the proportionate increment in the value of Δp, since the right hand side of the above equation is a constant.

Heisenberg's uncertainty principle could also be expressed in terms of the uncertainties involved in the measurement of

a) Energy and time as $\Delta E.\Delta t \geq \frac{h}{4\pi}$

b) Angular momentum (L) and angular displacement (θ) is $\Delta L.\Delta\theta \geq \frac{h}{4\pi}$

Physical significance of Heisenberg's uncertainty Principle:

Uncertainty principle holds good for all the objects but this principle is significant for only microscopic particles. The energy of a photon is insufficient to make change in velocity or momentum of bigger particles when collision occurs between them.

The uncertainty principle formally limits the precision to which two complementary observables can be measured and establishes that observables are not independent of the observer. It also establishes that phenomena can take on a range of values rather than a single, exact value.

Application of Heisenberg's uncertainty Principle:

Non-existence of electron in the nucleus:

The typical nuclear size is of the order of 10^{-14}. If an electron is to exist inside the nucleus then the uncertainty in its position Δx should not exceed the size of the nucleus

i.e., $\Delta x \leq 5 \times 10^{-15}$ m. The uncertainty in the momentum of electron is $\Delta p \geq \frac{h}{4\pi.\Delta x}$

$$\Delta p \geq \frac{6.63\times10^{-34}}{4\times3.14\times5\times10^{-15}} = 1.1 \times 10^{-20} \text{ Ns}$$

Then the momentum of the electron must at least be equal to the uncertainty in the momentum i.e., $p = 1.1 \times 10^{-20}$ Ns

We have,

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}}; \quad m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$m_0 \rightarrow$ rest mass of the electron = $9.1\text{x } 10^{-31}$kg.

m $\rightarrow$ mass of the particle while its velocity is v,

Squaring we get

$$E^2 = \frac{m_0^2 c_0^4}{1 - \frac{v^2}{c^2}} = \frac{m_0^2 c^4}{\frac{c^2 - v^2}{c^2}} = \frac{m_0^2 c^6}{c^2 - v^2} \text{ ------ (1)}$$

Also $p = mv = \dfrac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$

Squaring, $$P^2 = \frac{m_0^2 v^2}{1 - \frac{v^2}{c^2}} = \frac{m_0^2 v^2}{\frac{c^2 - v^2}{c^2}} = \frac{m_0^2 v^2 c^2}{c^2 - v^2}$$

'×' by c^2 both sides, $$p^2c^2 = \frac{m_0^2 v^2 c^4}{c^2 - v^2} \text{ ------------------------------ (2)}$$

$$(1) - (2) \Rightarrow E^2 - p^2c^2 = m_0^2 c^4 \left(\frac{c^2 - v^2}{c^2 - v^2}\right)$$

$$E^2 = p^2c^2 + m_0^2c^4$$

$$= c^2 (p^2 + m_0^2c^2)$$

In order that the electron may exist within the nucleus, its energy e must be such that

$$E^2 \geq c^2 [p^2 + m_0^2c^2]$$

$E^2 \geq (3 \times 10^8)^2 \, [(1.1 \times 10^{-20})^2 + (9.1 \times 10^{-31})^2 \, (3 \times 10^8)^2]$

Or $E \geq 3.3 \times 10^{-12}$ J

$$E \geq \frac{3.3 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV}$$

Or $E \geq 20.6$ MeV

But during b decay the electrons ejected out of nucleus are observed to be processing energy between 3 to 4 MeV only. The electrons are pushed out of the nucleus since the do not have sufficient energy to stay inside the nucleus. Hence, we can say that electrons cannot exist inside the nucleus.

SCHRODINGER'S WAVE EQUATION

Schrodinger equation is the fundamental equation of Quantum mechanics. It is the wave equation in the variable ψ.Sound waves and waves in strings are described by the equations of Newtonian mechanics. Light waves are described by Maxwell's equations. Matter waves are described Schrodinger's equation. In 1925, Schrodinger used de Broglie's ideas to set up a mathematical theory to describe the dual nature of matter.

Wave function: The quantity that characterizes the de Broglie waves is called the wave function. It is usually represented by $\psi(x, y, z\ t)$ or $\psi(\vec{r}, t)$. It is a function of space variable and time.

PHYSICAL INTERPRETATION OF THE WAVE FUNCTION:

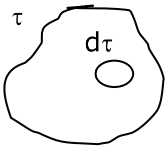


Fig. 2.2 Presence of electron in a certain region

In classical mechanics, the square of a wave amplitude associated with electromagnetic radiation is interpreted as a measure of radiation intensity. This suggests that we should make a similar interpretation for De Broglie waves associated with electron or any particle (Fig. 2.2). Hence if we consider a system of electrons and if ψ is the wave function associated with the system, then $|\psi^2|$ may be regarded as a measure of density of electrons. Also, if τ is a volume inside which an electron is known to be present, but where exactly the electron is situated inside τ is not known, and if ψ is the wave function associated with the electron, then the probability of finding the electron in a certain element of volume $d\tau$ of τ is equal to $|\psi|^2\, d\tau$. For this reason $|\psi|^2$ is called the probability function. Since the electron must be somewhere inside the volume τ, the integration of $|\psi|^2$ over the entire volume τ must be unity i.e., $\int |\psi|^2\, d\tau = 1$. This condition is known as **normalization condition**.

EIGEN FUNCTIONS & EIGEN VALUES

In order to find ψ, the Schrodinger's equation has to be solved. But since, it is a second order differential equation, there are several solutions. But all of them may not be the correct wave functions which we are searching for. We have to select only those functions which would correspond meaningfully to a physical system. Such wave functions are said to be acceptable wave functions and it has to satisfy the following conditions

1. ψ must be single valued and finite everywhere
2. ψ must be continuous and should have a continuous first derivative everywhere
3. The wave function must be normalized i.e., it has to satisfy the conditions $\int |\psi|^2\, d\tau = 1$

Such acceptable wave functions are called **Eigen functions**

Once the Eigen functions are known, they could be used in Schrodinger's equation to evaluate energy values. These values are called **Eigen values.**

Time independent Schrodinger's wave equation:

According to De Broglie's theory, a moving particle of mass 'm' is always associated with a wave whose wavelength is given by a $\lambda = \frac{h}{mv} = \frac{h}{p}$. If the particle has wave like properties, then there must be some sort of wave equation which describe the behavior of the particle.

Let x, y, z be the coordinates of the particle and ψ, the wave displacement for the de Broglie waves at any time t.

The classical differential equation for a wave motion is given by

$$\frac{\partial^2\psi}{\partial t^2} = v^2\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) \text{ ------------- } (*) \rightarrow \text{ for three dimensions}$$

Let us restrict our study to only one-dimensional case such that ψ is a function of 'x' only.

$\therefore$ Equation (*) becomes $\frac{d^2\psi}{dt^2} = v^2 \frac{d^2\psi}{dx^2}$ ----------- (1)

The solution of equation (1) is given by

$$\psi = Ae^{-i\omega t} \text{ --------------------------------------- } (2)$$

where A is the amplitude and ω is the angular frequency of the wave. Differentiating equation (2) w.r.t 't' twice

$$\frac{d\psi}{dt} = -i\omega Ae^{-i\omega t}$$

$$\frac{d^2\psi}{dt^2} = -i\omega(-i\omega)Ae^{-i\omega t}$$

$= i^2\omega^2\psi$ (Using equation (2)) $\qquad [\because i^2 = -1]$

$= -\omega^2\psi$ ---------------------------- (3)

Substituting the value of $\frac{d^2\psi}{dt^2}$ in equation (1), we get $-\omega^2\psi = v^2\frac{d^2\psi}{dx^2}$

$$-\frac{\omega^2}{v^2}\psi = \frac{d^2\psi}{dx^2}$$

$$\text{or } \frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi = 0 \text{ ------------------- } (4)$$

But $\omega = 2\pi\nu$ Also $v = \nu\lambda$ (using $v = f\lambda$)

Substituting for ω & v in equation (4) $\quad \frac{d^2\psi}{dx^2} + \frac{4\pi^2\nu^2}{\nu^2\lambda^2}\psi = 0$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0$$

Using de Broglie wavelength equation $\lambda = \frac{h}{mv}$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}m^2v^2\psi = 0 \text{ ------------- } (5)$$

Consider a particle moving in an electric field. Then, it will have a potential energy (V) also, in addition to kinetic energy.

The total energy of particle, E = kinetic energy + Potential energy

$$\text{i.e., } E = \frac{1}{2} mv^2 + V \quad \text{or} \quad \frac{1}{2} mv^2 = E - V$$

Multiplying by m on both sides,

$$\frac{1}{2} m^2v^2 = m\,(E - V) \text{ or } m^2v^2 = 2m\,(E - V) \text{ ----------- } (6)$$

Substituting equation (6) in equation (5)

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}\, 2m\,(E - V)\psi = 0$$

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

This is the time independent Schrodinger wave equation in one dimension

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

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

Application of Schrodinger Wave Equation

I. Particle in one dimensional potential well of infinite height (or particle in a box)

Consider a free particle of mass 'm' confined to a box of width 'L' with infinitely high walls (Fig. 2.3). The condition for particle motion is

1. The particle moves along x – axis between x = 0 and x = L

2. The particle is a free particle i.e., not subjected to any external force.

Therefore, the potential energy (V) is zero inside the box.

i.e. V = 0 for 0 < x < L. The potential outside the box is infinite.

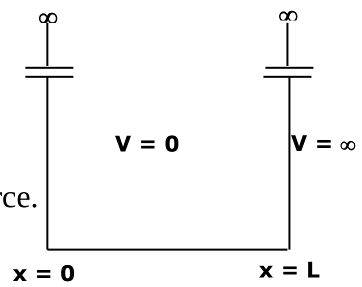


Fig. 2.3 Potential well

3. The value of the wave function ψ outside the box is zero. i.e., $\psi = 0$ which means that the particle cannot be found outside the box

The Schrodinger equation for a particle in one dimension is

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

Outside the box, the equation becomes

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

Inside the box the equation becomes

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

Let $\frac{8\pi^2 mE}{h^2} = k^2$ ---------------------- (2)

$\therefore$ Equation (1) becomes, $\frac{d^2\psi}{dx^2} + k^2\psi = 0$ ------------- (3)

The solution of Equation (3) is given by

$\psi = A \cos kx + B \sin kx$ ------------- (4)

where A and B are the constants depending on the boundary condition

Applying the boundary conditions

1. At $x = 0$, $\psi = 0$ $\qquad$ $\cos 0 = 1$ $\quad$ $\sin 0 = 0$

   Hence equation (4) becomes $0 = A \cos 0 + B \sin 0$

   $\therefore A = 0$ ------------ (5)

2. At $x = L$, $\psi = 0$

   $\therefore$ Equation (4) becomes, $0 = A \cos kL + B \sin kL$

   But $A = 0$ from equation (5)

   $\therefore 0 = B \sin kL$

   B need not be equal to zero

   $\therefore \sin kL = 0$ ------------ (6)

   We have

Sin 0 = 0, Sin π = 0, Sin 2π = 0, Sin 3π = 0…

$\sin n\pi = 0$ ------------- (7), $n = 0, 1, 2, 3\ldots$

Comparing equation (6) and (7)

$n\pi = kL$ or $k = \frac{n\pi}{L}$ ----------- (8)

Substituting the value of A and k in equation (4)

$\psi = B \sin \frac{n\pi}{L} x$ -------------- (9)

To evaluate B in equation (9) we have to perform the normalization of the wave function. Since the particle is inside the box, the probability of finding the particle is 1. Hence

$$\int_0^L \psi^2\, dx = 1$$

$$\int_0^L B^2 \sin^2 \frac{n\pi}{L} x\, dx = 1 \qquad \text{But } \sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$$

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

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

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

$$\frac{B^2}{2}\left[[x]_0^L - \left[\frac{L}{2n\pi}\sin\frac{2n\pi}{L}x\right]_0^L\right] = 1 \qquad \text{Using } \int \cos n\theta\, d\theta = \frac{\sin n\theta}{n}$$

$$\frac{B^2}{2}\left[L - 0 - \frac{L}{2n\pi}\sin\frac{2n\pi L}{L} - 0\right] = 1$$

$$\frac{B^2}{2}\left[L - \frac{L}{2n\pi}\sin 2n\pi\right] = 1 \qquad (\sin 2n\pi = 0)$$

$$\therefore \frac{B^2 L}{2} = 1 \Rightarrow B^2 = \frac{2}{L} \text{ or } B = \sqrt{\frac{2}{L}} \text{ ----------- (10)}$$

$\therefore$ Equation (9) becomes, $\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$ ---------- (11)

From equation (2) $\frac{8\pi^2 mE}{h^2} = k^2$ Now $k = \frac{n\pi}{L}$

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{L^2}, \qquad E = \frac{n^2h^2}{8mL^2} \text{ --------------- (12)}$$

This equation gives the allowed values of energy for different value of n.

The particle has discrete energy levels.

For n = 1 $E_1 = \frac{h^2}{8mL^2}$ and wave function $\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x$

For n = 2 $E_2 = \frac{4h^2}{8mL^2}$ and wave function $\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x$

For n = 3 $E_3 = \frac{9h^2}{8mL^2}$ and wave function $\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi}{L} x$

These values of energy are called Eigen values of energy. The energy corresponding to n = 1 is called the ground state energy (or zero point energy). The other energies are called excited states

Case (i): When n = 1 (ground state) (Fig. 2.4)

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi}{L} x$$

$\psi_1 = 0$ when x = 0 and x = L

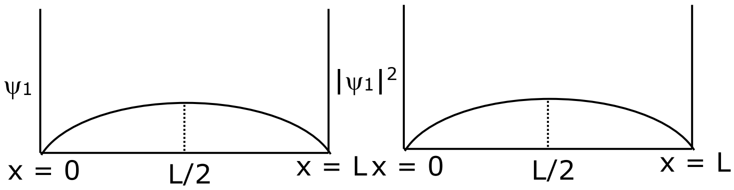
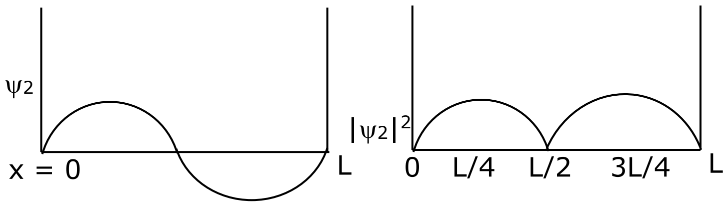


Fig. 2.4 Plots of wave function and probability, n=1

ψ_1 is maximum at $x = \frac{L}{2}$ ($\because$ sin 90 = 1) $\Rightarrow$ the particle is not found near the walls and the probability of finding the particle is maximum at the central region and energy in the ground state is $E_1 = \frac{h^2}{8mL^2}$

Case (ii): n = 2 (1st excited state, Fig. 2.5)



$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x$$

$\psi_2 = 0$, when $x = 0, \frac{L}{2}, L$

Fig. 2.5 Plots of wave function and probability, n=2

ψ_2 is max for $x = \frac{L}{4}$ and $\frac{3L}{4} \Rightarrow$ In the 1st excited state the particle cannot be observed either at the walls or at the center. The particle is most likely to be found at $x = \frac{L}{4}$ and $\frac{3L}{4}$ and energy in the 1st excited state is 4 times the zero-point energy

i.e., $E_2 = \frac{4h^2}{8mL^2}$

Case (iii): n = 3 (2nd excited state) (Fig. 2.6

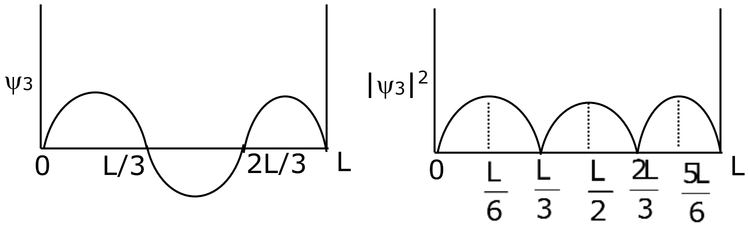


Fig. 2.6 Plots of wave function and probability, n=3

$\psi_3 = \sqrt{\frac{2}{L}}\ \sin \frac{3\pi}{L} x$

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

ψ_3 is max for $x = \frac{L}{6}, \frac{L}{2}, \frac{5L}{6}$

$\Rightarrow$ The particle is most likely to be present at $x = \frac{L}{6}, \frac{L}{2}$ and $\frac{5L}{6}$

Energy in the 2nd excited state is 9 times the zero-point energy i.e. $E = \frac{9h^2}{8mL^2}$ (Fig. 2.7)

II. Case of a free particle:

Schrodinger's wave equation for a particle of mass m, total energy E and potential energy V is written as

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

Free particle means, it is not under the influence of any kind of field or force. Thus it has zero potential energy i.e., V = 0. Hence Schrodinger's becomes

$$\therefore \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \qquad \therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

The solution of this equation is given by

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

Since the particle is free, the constants A, B and K can take any value. That is energy of a free particle is not quantized and it is given by $E = \frac{h^2k^2}{8\pi^2 m}$

Graphical representation of E_n, $\psi_n(x)$ and $P_n(x)$ for n = 1, 2 & 3 quantum states

Eigen values	**Eigen functions**	**Probability densities**
$E_n = \frac{n^2h^2}{8mL^2}$	$\psi_n(x) = \sqrt{2/L}\,sin\left(\frac{n\pi x}{L}\right)$	$P_n(x) = \left(\frac{2}{L}\right) sin^2\left(\frac{n\pi x}{L}\right)\,dx$

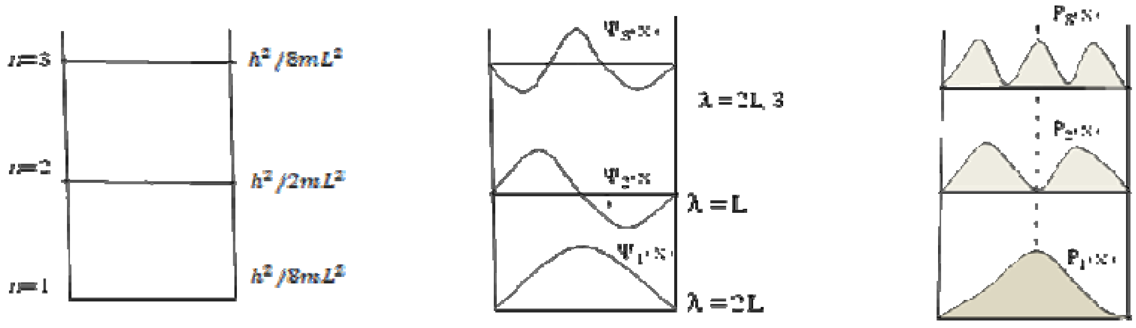


Fig. 2.7 Graphical representation of energy, wavefunction and probability

QUESTION BANK

1. Define black body? Explain the black body radiation spectrum.
2. Discuss Wien's radiation law & Rayleigh Jean's law. Mention their drawbacks.
3. What is Planck's radiation law? Show that Planck's radiation equation reduces to Wien's radiation law & Rayleigh Jeans' law under certain conditions.
4. What is the significance of blackbody radiation spectrum?
5. Explain De-Broglie's hypothesis.
6. What are matter waves? Mention their characteristic properties.
7. Define phase velocity & group velocity.
8. State & explain Heisenberg's uncertainty principle. Give its physical significance.
9. Show that electrons cannot exist in the nucleus of an atom based on Heisenberg's uncertainty principle.
10. What is a wave function? Explain the properties of wave function.
11. Write the physical significance of wave function.
12. Set up time independent one-dimensional Schrödinger's wave equation.
13. Write down the condition for a normalized wave function.
14. What are Eigen values & Eigen functions?
15. Find the Eigen functions & Eigen values for a particle in one dimensional potential well of infinite height & discuss the solutions.