QUANTUM MECHANICS

Prerequisites

Knowledge of derivatives and integration

Introduction to Quantum Mechanics

Quantum mechanics is one of the most important intellectual achievement of the 20th century. This sophisticated field in physics has refined our understanding of the nature, particularly in the nanometer length scale down to atomic and subatomic level and has profound implications in chemistry, materials science, optics, and electronics. The existence of orbitals and energy levels in atoms can only be explained using quantum mechanics. It can aptly explain the behaviours of insulators, semi-conductors and conductors, as well as that of giant magneto-resistance. It can explain the quantization of light and both its corpuscular and wave nature.

Quantum mechanics has found myriad of applications in photonics, quantum electronics, and micro-electronics, nanotechnology and many more emerging technologies. Therefore, it is of extreme importance that scientists and engineers learn quantum mechanics.

Historical background

A series of experiments during the late nineteenth century, with puzzling and paradoxical results, proved impossible to be explained by the classical physics of mechanics and electromagnetism; and needed radically new concepts of theoretical physics. These experiments fell roughly into three categories:

1. *The Corpuscular (particle-like) Behaviour of Light Waves*
     Black-body radiation, the photoelectric effect, the Compton effect.
2. *The Stability of the Atom*
   Why doesn't the electron fall into the nucleus as predicted by classical electromagnetic
     theory? What is the origin of atomic spectra?
3. *The Wave-like Behaviour of Particles*
     Electron diffraction

The emergence of quantum mechanics was an attempt to explain these phenomena and it has proved itself to be immensely accurate.

In the following sections we shall discuss these with considerable details.

Black-body radiation

All bodies give out radiation consistent with the temperature it is at. For example, at room temperature, humans give out infra red (IR) radiation. This is the reason that militaries use IR goggles to spot people at night. At around 1000°C, bodies give out visible light, which is how conventional light bulbs function. When electromagnetic radiation is incident on a substance, some of it will be absorbed, some reflected and some transmitted. A substance can be imagined and constructed that absorbs all radiation incident on it as long as it cooler than its surroundings. This substance will also emit radiation as long as it is hotter than its surroundings. Such a substance is referred to as a "Black body". Graphite, as a material, comes close to satisfying this description. The figure below shows the schematic of the blackbody designed by Kirchoff. The arrows indicate that radiation entering the body will get absorbed by the internal surfaces of the body. Kirchhoff's law, states that the emissivity of a body which is in thermal equilibrium with its surrounding is equal to the absorptivity of the body.
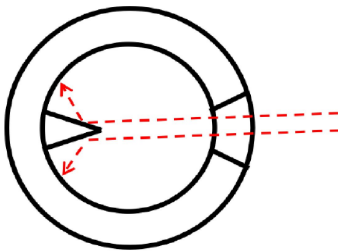
In general, electromagnetic radiation emitted by a blackbody comes out over a range of wavelengths, however it is not emitted with uniform intensity across all wavelengths. The maximum intensity of the radiation occurs at one wavelength and the intensity decreases for all other wavelengths. The spectral distribution of the radiation emitted by blackbody is shown in figure below.
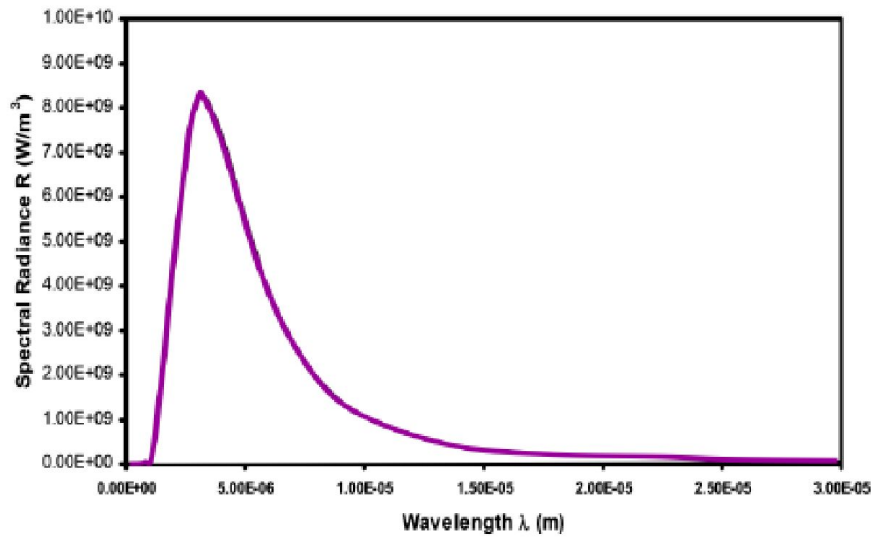
The spectral radiance plotted on the y-axis represents power per unit area per unit wavelength and is therefore represented by $W/m^2/m = W/m^3$, which is the unit shown on the y-axis. The area under the curve represents intensity (I), which is power per unit area.

Mathematically, $I = \int_0^\infty R(\lambda)\, d\lambda$

There are two observations that can be made about blackbody radiation:

1) As temperature T of the body increases, intensity of the radiation from the body increases.

2) Higher the temperature, lower is the wavelength of the most intense part of the spectrum.

These two observations are represented by the figure below:

Spectral radiance (W/m³)
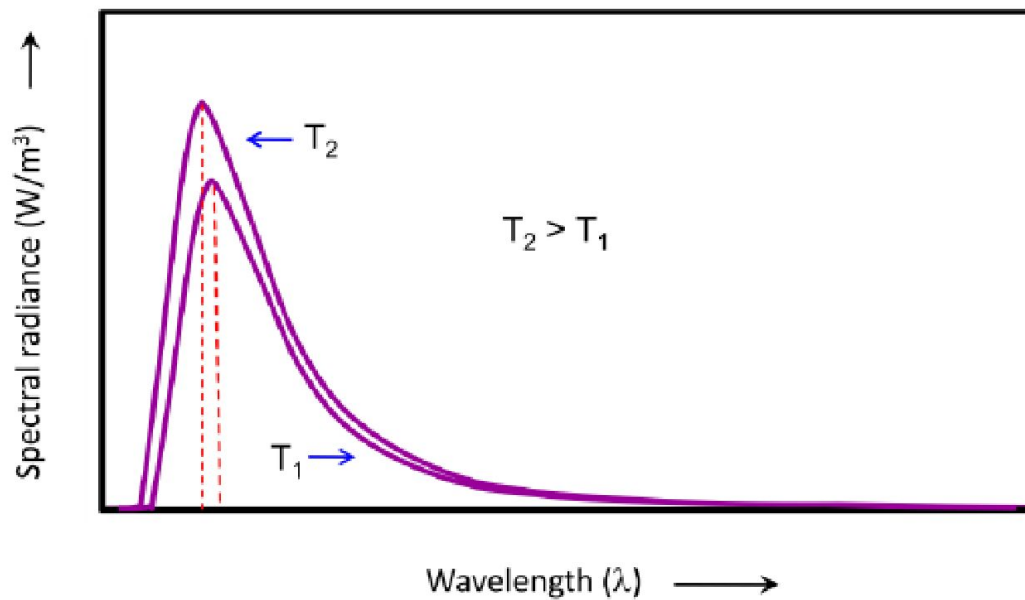
Wavelength (λ)

From this figure, it is evident that at the higher temperature T_2, the area under the curve, and hence intensity, has increased relative to the curve at T_1. Also, at the higher temperature T_2, the wavelength corresponding to the maximum intensity (identified using the red dotted lines in the figure), has decreased relative to that at T_1.

These two trends in blackbody radiation, can be mathematically stated in the form of two laws:

Stefan Boltzmann Law:

Josef Stefan based on experimental facts suggested that the total emissive power of a blackbody (I) is proportional to the fourth power of the absolute temperature.

$$I(T) = \sigma T^4$$

Here,

I is the total amount of radiation emitted by an object per square meter (W m^{-2})
σ is a constant called the Stefan-Boltzmann constant (5.67 x 10-8 Wm^{-2}K^{-4})
T is the absolute temperature of the body (in K)

Wein's displacement law

The variation of blackbody radiation with temperature shows that as the temperature increases the most intense part of the spectrum shifts towards the shorter wavelength. This is given by Wein's law

$$\lambda_{max} T = constant = 2898 \ \mu mK$$

The scientific challenge that remained was to determine the exact form of the spectral radiance, or power per unit area at a particular wavelength, R (λ).

Several researchers worked to determine the form of R (λ). One of the early attempts, looked at the matter-radiation interaction in a classical manner, i.e. assumed an equipartition of energy, wherein all modes available to the solid through which it could absorb energy, participated in the process equally. This led to the law known as the Rayleigh-Jean law, which provides an equation for the spectral radiance as follows:

$$R(\lambda, T) = \frac{8\pi kT}{\lambda^4}$$

At higher values of λ, this led to a good match between theory and experiment. However as λ decreases, the theory predicts an ever increasing spectral radiance – a prospect dubbed as "Ultraviolet catastrophe". Common experience shows that this does not occur – bodies do not spontaneously release infinite energy. Therefore the Rayleigh-Jean law comprehensively fails at lower wavelengths. The mismatch between theory and experiment is shown in the schematic in figure below.
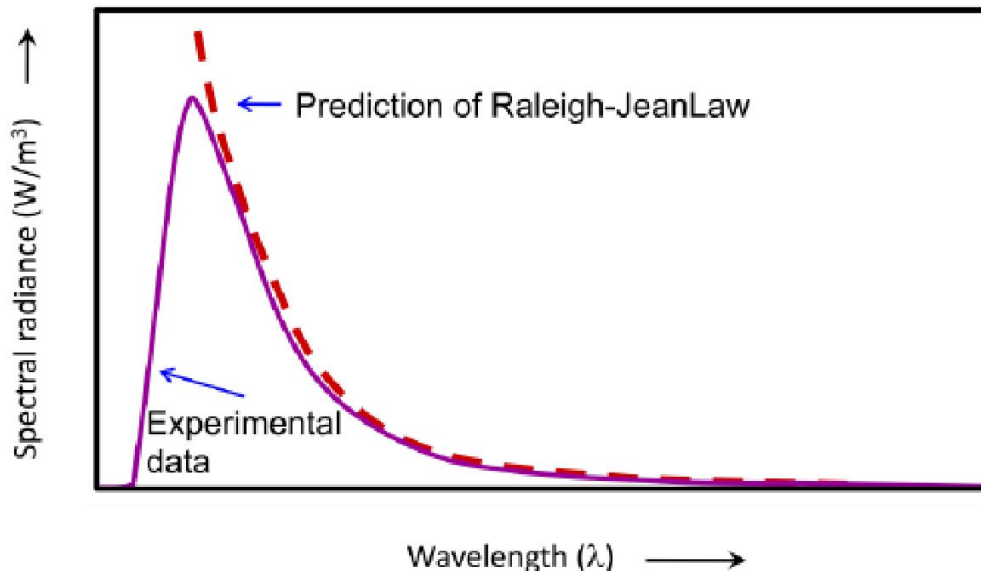
Hence, classical wave theory of radiation is not able to predict blackbody radiation. In order to explain these facts Max Planck (1901) gave a theory called Planck's quantum theory of radiation. The various postulates of quantum theory of radiations are as follows:

A radiation has energy. As light and heat are radiations, they are also associated with energy.

Radiant energy is not emitted or absorbed continuously but discontinuously in the form of small packets called photons. Photon is not a material body but is considered to be a massless packet of energy.

The energy E of a photon is related to the frequency of radiation, n; the two being related as E = hν where h is planck's constant.

Whenever a body emits or absorbs energy, it does so in whole number multiples of photons, i.e., E = nhν where n = 1, 2, 3 etc.

de Broglie's Hypothesis

From the study of black body radiation, photo electric effect and Compton effect it was necessary to assign particle like properties to radiation. The amount of energy associated with the radiant particle or photon is

$$E = h\upsilon = \frac{hc}{\lambda} \tag{1}$$

where h, c, υ and λ are Planck's constant, speed of light, frequency and wavelength, respectively, and since $\upsilon\lambda = c$. Eqn. (1) proves that the radiation has particle like nature described by photons and, at the same time, wave like nature described by wavelength λ.

Louis de Broglie asserted that this dual property is not merely confined to photon or radiation, it can be attributed to any material particle. For his hypothesis de Broglie relied on the special theory of relativity and old quantum theory. These waves that arise out of matter particles are known as matter waves.

The energy E and momentum p of the photon is related by

$$p = \frac{E}{c} = \frac{h\upsilon}{c} = \frac{h}{\lambda}$$

The wavelength of a photon is therefore specified by its momentum according to the relation

$$\lambda = \frac{h}{p} \tag{2}$$

de Broglie asserted that the nature is symmetric. Therefore, what is applicable to photon can also be applied to any other particle.

For a particle of mass m moving with a velocity v, the momentum is given by $p = mv$. So the wavelength associated with the material particle is

$$\lambda = \frac{h}{mv} \tag{3}$$

Where m = relativistic mass = $\frac{m_0}{\sqrt{(1-\frac{v^2}{c^2})}}$, m_0 being the rest mass.

λ in Eqn. (3) is called de Broglie wavelength.

Davisson-Germer Experiment (*Experimental verification of de Broglie hypothesis*)

Clinton Davisson and Lester Germer in the USA and G.P. Thompson in the UK independently confirmed de Broglie's hypothesis experimentally. Davisson and Germer studied the diffraction of electron beam using nickel crystal. If the electrons are accelerated by a potential difference of V volts it gains a kinetic energy given by

$$\tfrac{1}{2}mv^2 = eV \tag{4}$$

Where v is the velocity attained by the electrons and $v \ll c$, c being the speed of light. The de Broglie wavelength of the electron is

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{(2meV)}} \tag{5}$$

Here we put the value of v from Eqn. 4. Thus we get λ in terms of voltage V.
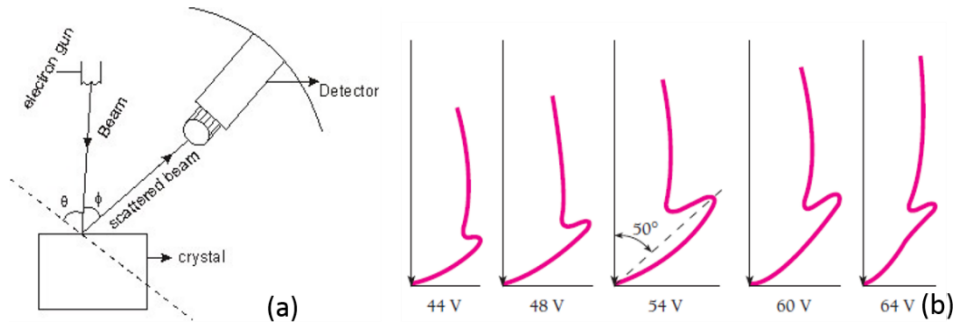

Fig.

The experimental arrangement is shown in Fig. (a). The electrons from a hot tungsten electron gun are collimated and incident normally on the crystal surface. The intensities of the electron beam scattered in all directions by the atoms of the crystal, which are arranged in a regular periodic fashion, were measured as a function of the angle of scattering. The results are shown in

polar diagram (Fig.   ). The length of the radius vector is proportional to the intensity of the scattered beam and the angle of the radius vector and the Y-axis is the angle of scattering. Experimental results shows that the length of the peak increases until it reaches a maximum at $\phi = 50°$ for $V = 54$ V. This can be explained as follows.
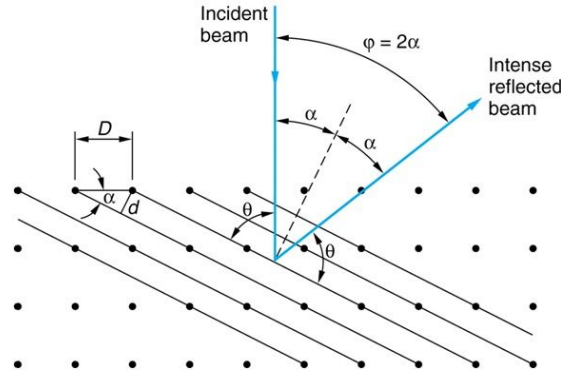

Fig.

The planes are shown in Fig.   , where D is the distance between the consecutive atoms and d is the inter-planar separation. The Bragg's condition for constructive interference is

$$n\lambda = 2d\ sin\theta = 2d\ sin\ (90°\text{-}\alpha) = 2d\ cos\ \alpha \tag{6}$$

Again, from Fig. .

$$d = Dsin\ \alpha \tag{7}$$

Combining Eqns. 6 and 7, we get

$$n\lambda = 2D\ sin\ \alpha.cos\ \alpha = D\ sin\ 2\alpha$$

In terms of ϕ

$$n\lambda = D\ sin\ \phi \tag{8}$$

From x-ray data it is known that for nickel $D = 2.15$ Å. Therefore, for 54 V electron at $\phi = 50°$ and in the first order (i.e. n = 1)

$$\lambda = 2.15\ \text{Å. Sin } 50° = 1.65\ \text{Å}$$

Further, with V = 54 V and standard values of the constants Eqn. 5 can be used to obtain the wavelength of electron as $\lambda = 1.66$ Å. The remarkably close agreement between the two results proves the validity of de Broglie hypothesis.

Heisenberg's uncertainty Principle (in presentation)

<u>Wave-function</u>

The determination of wave-function Ψ, representing the de-broglie wave of a particle is the principle concern of quantum mechanics. While the wave-function Ψ (**r**, t) is not a measurable quantity by itself, the square of its absolute magnitude $|\Psi|^2$ at any particular place and time is proportional to the probability of finding the particle at that place and time. The magnitude of wave-function is large in regions where the probability of finding the particle is high and vice-versa. The linear and angular momentum, energy are other quantities that can be extracted from the wave-function Ψ. The wave-function can be real or imaginary while its probability density $|\Psi|^2$ is always a real positive quantity.

The probability of finding a particle between the co-ordinates x_1 and x_2 is equal to the integral of probability density over that region.

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx$$

<u>Probability interpretation of wave-function by Max Born</u>

Born proposed 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.

<u>Well-behaved wave-functions</u>

A wave-function Ψ is well-behaved (i.e., capable of yielding meaningful results) if it satisfies the following conditions:

1. **Ψ must be finite and continuous at all points in space.**

All its first and second-order partial derivatives must also be finite and continuous everywhere. If Ψ is infinite, it would imply an infinitely large probability of finding the particle in that region which would be in violation to the uncertainty principle. Also, since Ψ is related to a physical quantity, it cannot have a discontinuity at any point.

2. **The function must be single-valued;**

i.e. at any point in space, the function $\int \Psi^* \Psi$ must have only one numerical value. This is because any physical quantity can have only one value at a point.

3. **Ψ must be normalizable,**

i.e., Ψ must go to zero as x, y, z tends to $\pm\infty$ in order that $\int_{-\infty}^{\infty} |\Psi|^2 dV = finite\ number$.

4. **The wave functions must be orthogonal. i.e.,** $\int_{-\infty}^{\infty} \Psi_i^* \Psi_j\ dV = 0\ when\ i{\neq}j$.

In the next section, we obtain Schrödinger's equation, the fundamental equation of quantum mechanics, analogous to the second law of motion of Newtonian mechanics. The solution of the Schrödinger's equation should not only describe the corpuscular and wavelike behaviour of particles like electrons and protons but must also be in complete agreement with the uncertainty principle. Hence, the trajectory of the particle is described by the wave-function Ψ (**r**, t).

Schrödinger's equation: Time-Dependent Form for a free particle

A free particle of total energy E and momentum p moving in the +x direction can be described by the wave-function Ψ of a place monochromatic wave. The expression for Ψ is given by

$$\Psi(x, t) = A \exp exp\ \left(\tfrac{i}{\hbar}(px - Et)\right)\ (1)$$

where A = amplitude of displacement of the wave

$\hbar$ = reduced Planck constant (h/2π) = 1.05457 x 10^{-34} J.s

The energy E and momentum p of the particle are related to its wave-vector k and frequency ω by the relations

$p = \hbar k = \hbar\ \tfrac{2\pi}{}$, $E = \hbar\omega$

Differentiating Eq. (1) once with respect to time gives,

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

or

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

Differentiating Eq. (1) twice with respect to x gives,

$$-i\hbar \frac{\partial \Psi(x,t)}{\partial x} = p\Psi(x, t) \qquad\qquad (3)$$

$$-\hbar^2 \frac{\partial^2 \Psi(x,t)}{\partial x^2} = p^2 \Psi(x,t) \tag{4}$$

Dividing both sides of Eq. (4) by (1/2m), we obtain,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{p^2}{2m} \Psi(x,t) \tag{5}$$

Now the energy E and momentum p of a free non-relativistic particle of mass m are related by the expression

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{6}$$

As the particle is free, there are no boundary conditions to be applied to the particle motion and hence there are no restrictions on wave-vector k. As a result, the particle can possess any value of energy or the energy is not quantized. Thus, a freely moving particle possesses a continuous
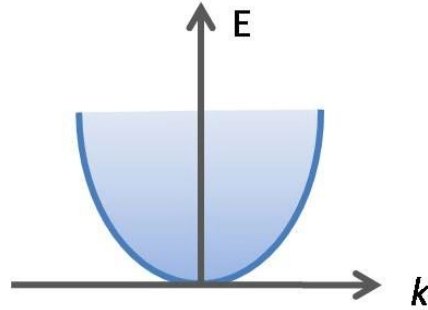
energy spectrum as given in the adjoining figure.

Substituting Eq. (2) and Eq. (5) in Eq. (6), we obtain the one-dimensional time dependent Schrödinger equationfor a free non-relativistic particle given below

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \tag{7}$$

From Eq. (2) and Eq. (3), it is evident that E and p can be represented by the following operators

$$E = i\hbar \frac{\partial}{\partial t} , \quad \text{Total-energy operator}$$

$$p = -i\hbar \frac{\partial}{\partial x} \text{ Linear Momentum Operator}$$

An operator describes the operation to be carried out on the quantity following it. Thus, Eq. (7) can also be written in the form

$$E\Psi(x,t) = \frac{p^2}{2m} \Psi(x,t) \tag{8}$$

The three-dimensional form of time dependent Schrödinger equation for a free non-relativistic particle is obtained as follows

The initial expression for Ψ in three dimensions is given by

$$\Psi(r,t) = A \exp\exp\left(\frac{i}{\hbar}(p.r - Et)\right)$$

(9)

$$= A \exp\exp\left(\frac{i}{\hbar}(p_x x + p_y y + p_z z - Et)\right)$$

(10)

Differentiating Eq. (10) once with respect to time gives

$$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi \tag{11}$$

Similarly, differentiating Eq. (10), twice with respect to the co-ordinates x, y and z of the free non-relativistic particle yields

$$-\hbar^2\frac{\partial^2\Psi}{\partial x^2} = p_x^2\Psi \tag{12}$$

$$-\hbar^2\frac{\partial^2\Psi}{\partial y^2} = p_y^2\Psi \tag{13}$$

$$-\hbar^2\frac{\partial^2\Psi}{\partial z^2} = p_z^2\Psi \tag{14}$$

Substituting Eqns. (11-14) in the expression for energy E in three dimensions given by

$$E = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

yields

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right] = -\frac{\hbar^2}{2m}\nabla^2\Psi \tag{15}$$

Thus,the three-dimensional form of time dependent Schrödinger equation for a free non-relativistic particle.

The operator representation for the components E and p in the three-dimensional case is given by

$$E = i\hbar\frac{\partial}{\partial t}\ , \qquad \text{Total-energy operator} \tag{16}$$

$$p = -i\hbar\nabla \qquad \text{Linear Momentum Operator} \tag{17}$$

Here, $\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$

Schrödinger's equation : Time-Dependent Form for particle in a field

In this section, we obtain Schrödinger's equation for a particle moving in an external potential field. Let the potential energy function V(**r**, t) characterize this external field. Then, according to classical mechanics, the total energy of the particle in this external field is given by

$$E = \frac{p^2}{2m} + V(r,t) \tag{18}$$

Substituting Eq. (16) and Eq. (17) in Eq. (18), we obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \right] \tag{19}$$

The above equation is the three-dimensional time dependent Schrödinger equation for particle in a field.

Eq. (19) is usually written as

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \tag{20}$$

where $H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m} \nabla^2 + V$

is known as the Hamiltonian operator.

The corresponding one-dimensional equation is

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right] \Psi(x,t) \tag{21}$$

Example:

A particle limited to the x axis has wave-function = ax between x = 0 and x = 1; while = 0 elsewhere, (a) Find the probability that the particle can be found between x = 0.45 and x = 0.55, (b) Find the expectation value of the particle's position.

Solution:

(a) The probability is

(b) The expectation value is =

Time Independent Schrödinger's equation

When the potential energy of a particle just depends on the position of the particle and is independent of time, then the time dependent Schrödinger's equation given by

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right] \Psi(x,t) \tag{29}$$

can be simplified by removing all reference to t. This is done by using the method of separation of variables.

$$\Psi(x,t) = (x)\,T(t) \tag{30}$$

Substituting Eq. (30) in Eq. (29) and dividing the entire expression by Eq. (29), we get

$$\frac{i\hbar}{T(t)}\frac{dT}{dt} = \frac{1}{(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2(x)}{dx^2} + V(x)(x) \right] \tag{31}$$

It is observed that in the above equation, LHS is a function of time alone while RHS is a function of space alone; hence, each side must be equal to a constant. Let that constant be E.

Hence, $\quad \frac{i\hbar}{T(t)}\frac{dT}{dt} = E \quad \therefore T(t) = e^{\frac{-iEt}{\hbar}} \tag{32}$

and $\frac{1}{(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2(x)}{dx^2} + V(x)(x) \right] = E$

$$\therefore \left[-\frac{\hbar^2}{2m}\frac{d^2(x)}{dx^2} + V(x)(x) \right] = E(x) \tag{33}$$

Hence, on substituting Eq. (32) in Eq. (30), the solution is obtained as

$$\Psi(x,t) = (x)\,e^{\frac{-iEt}{\hbar}} \tag{34}$$

Now, Eq. (33) can be written as

$$\therefore H(x) = E(x)$$

$$where\ H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{35}$$

represents the Hamiltonian operator and E is the energy eigenvalue. Eq. (33) represents the time independent Schrödinger equation. A state is called stationary if it is represented by the wave-function given by Eq. (34). The probability density of such states are time independent and as a result the eigenvalues of the Hamiltonian, which represent the energy levels of the system are also time independent.

The general solution of Eq. (29) can be written in the form

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{\frac{-iE_nt}{\hbar}} \tag{36}$$

where $\psi_n(x)$ are the eigenfunctions of H and E_n are the corresponding eigenvalues while c_n are constants which can be determined from the form of $\Psi(x, 0)$.

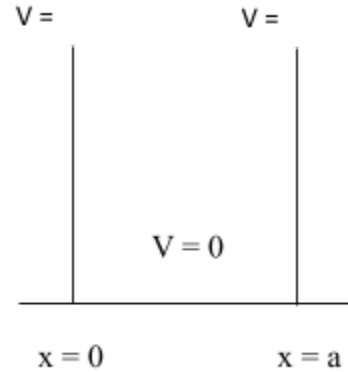**Solutions of Schrödinger's equation:**

I.   *Particle in a one-dimensional infinitely deep potential well*

Consider a particle of mass m in a one-dimensional infinitely deep potential well given by potential energy function of the form

V(x) = 0 for 0 < x < a

    = ∞ for x < 0 and x > a

Calculate the eigenfunction and the corresponding eigenvalues

of the particle.

Solution:

Boundary conditions for wave-function ψ is

$$\psi(x = 0) = \psi(x = a) = 0 \tag{I}$$

Consider the one-dimensional time-independent Schrödinger

equation for particle in a field

$$\left[-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) \right] = E\psi(x) \tag{II}$$

For 0 < x < a, Eq. (II) becomes

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

or $\frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$

or $\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0$ where $k^2 = \frac{2mE}{\hbar^2}$ (III)

The general solution of the Eq. (III) is

$$(x) = A \sin kx + B \cos \cos kx \qquad \text{(IV)}$$

Imposing the boundary condition (I) in Eq. (IV) we obtain

$$(x = 0) = 0 = A \sin \sin (k.0) + B \cos \cos (k.0) \therefore B = 0 \qquad \text{(V)}$$

and $(x = a) = 0 = A\sin(ka)$ $\qquad \text{(VI)}$

Hence, either $A = 0$ or $ka = n\pi$, $n = 1, 2, 3, \ldots$

The condition $A = 0$ or $n = 0$ leads to the trivial solution of vanishing everywhere. Hence, the allowed energy levels are given by

$$E_n = \frac{2n^2\hbar^2}{2ma^2} \quad \text{(VII)}$$

The spacing between the energy levels is not constant and $E_n \propto n^2$, where n denotes the number of state.Eq. (VII) indicates that a particle confined in a certain region can have only certain, discrete values of energy. Thus, the energy becomes quantized due to confinement of the particle. The energy E_1 is called the zero-point energy. The zero-point energy is the consequence of the uncertainty principle. If the energy of the particle is zero, its momentum is also zero. Then according to uncertainty principle, the position of the particle would become infinite and the particle cannot be confined to the box. Therefore, the particle cannot have zero energy.

The eigenfunctions corresponding to the above energy eigenvalues is given by

$$_n = A \sin \sin kx = A \sin \sin \sqrt{\frac{2mE_n}{\hbar^2}}\, x \qquad \text{(VIII)}$$
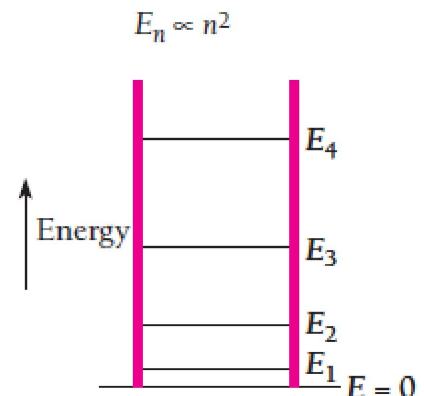
Substituting Eq. (VII) in Eq. (VIII), we obtain

$$_n = A\sin \frac{n\pi x}{a} \qquad \text{(IX)}$$

To find the constant A in the above equation, we normalize the wave-function in Eq. (IX)

$$\int_{-\infty}^{\infty} |_n|^2 dx = 1 \quad \text{(Normalization Condition)}$$

$$\int_{0}^{a} |_n|^2 dx = A^2 \int_{0}^{a} \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

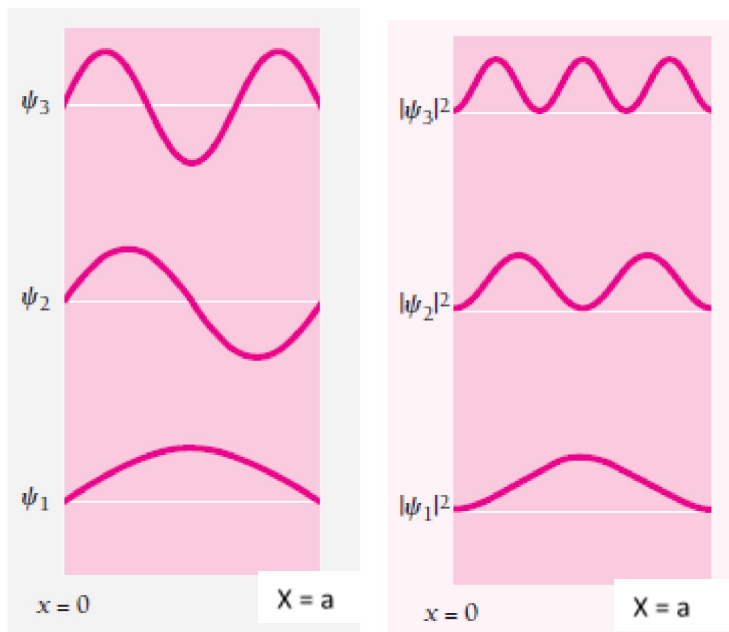$$\therefore \frac{A^2}{2} \int_{0}^{a} \left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right] dx = 1$$

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

$$\therefore A^2 \left(\frac{a}{2}\right) = 1 \text{ which gives } A = \sqrt{\frac{2}{a}}$$

Hence, the normalized wave-functions for a particle in a one-dimensional infinitely deep potential well is given by

$$_n = \sqrt{\frac{2}{a}} \, sin\frac{n\pi x}{a} \text{ where n} = 1, 2, 3, \ldots \ldots \qquad \text{(X)}$$

The wave-functions and probability densities at different energy levels for particle in a one-dimensional infinitely deep potential well is given below.

II.   *Particle trapped in a three-dimensional box*

For particle trapped in a three-dimensional square box of length a, the energy eigenvalues are given by

$$E = E_x + E_y + E_z = \left(n_x^2 + n_y^2 + n_z^2\right) \frac{^2\hbar^2}{2ma^2} \qquad \text{(I)}$$

The corresponding eigenfunction in three dimensions is given by

$$\psi = \psi_x \psi_y \psi_z = \left(\sqrt{\tfrac{2}{a}}\right)^3 \sin\sin\tfrac{n_x\pi x}{a} \;\sin\sin\tfrac{n_y\pi y}{a} \;\sin\sin\tfrac{n_z\pi z}{a} \qquad\qquad\qquad (II)$$

Example: Find the probability that a particle trapped in a box L wide can be found between 0.45L and 0.55L for the ground and first excited states.

Solution: Probability =

For the ground state, i.e., n = 1, Probability = 0.198 = 19.8%

For the first excited state, i.e., n = 2, Probability = 0.0065 = 0.65%