Syllabus : UNIT-IV : Quantum Mechanics and Free electron theory

Quantum Mechanics: Dual nature of matter – Heisenberg's Uncertainty Principle – Significance and properties of wave function – Schrodinger's time independent and dependent wave equations– Particle in a one-dimensional infinite potential well.

Free Electron Theory: Classical free electron theory (Qualitative with discussion of merits and demerits) – Quantum free electron theory – electrical conductivity based on quantum free electron theory - Fermi-Dirac distribution - Density of states - Fermi energy.

UNIT IV : Quantum Mechanics

Introduction:

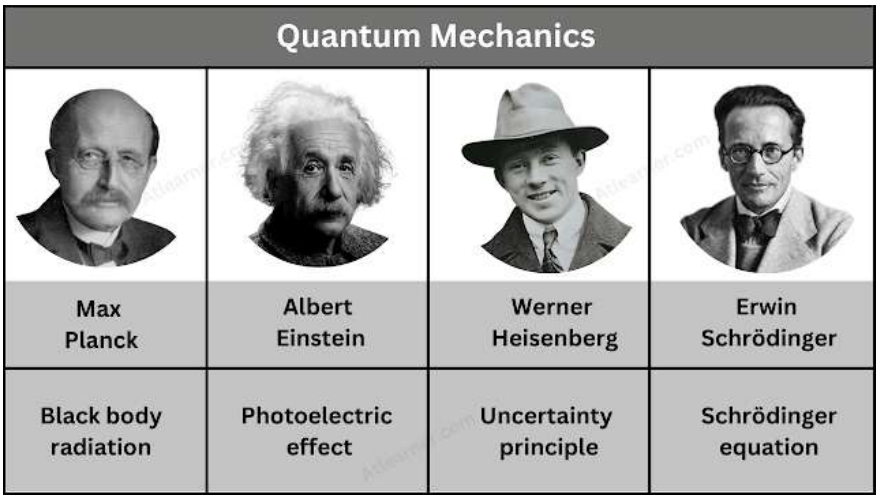
Mechanics, the study of behaviour of objects, under the action of force, occupies a special position among all branches of physics.

Classical mechanics:

- Classical mechanics deals with the motion and behavior of **macroscopic particles**.
  E.g., Motion of planets

Quantum mechanics:

- Quantum mechanics deals with the motion and behavior of **microscopic particles** or microscopic world, that is the world inside the atom.
- This branch of physics emerged at the beginning of the 20th century, as a response to the limitations of classical physics.
  E.g., Motion of Electrons



Particle:

If a certain amount of quantity occupies a certain space then it becomes a particle.

Characteristics:

- Mass
- Velocity
- Momentum
- Energy

Wave:

Spreading of disturbance in a medium.

Characteristics:

- Amplitude
- Time period
- Frequency
- wavelength
- Phase and Intensity

de- Broglie (Hypothesis) concept of dual nature:

The waves associated with a material particle are called as matter waves.

De-Broglie wavelength:

From the theory of light, considering a photon as a particle the tot

energy of the photon is given by

$$E = mc^2. \xrightarrow{\hspace{2cm}} \quad (1)$$

Where m is the mass of the particle

c is the velocity of light

Figure .1 Motion of particle (Electron)

Considering the photon as a wave, the total energy is given by

$$E = h\gamma \xrightarrow{\hspace{2cm}} \quad (2)$$

Where h is the Planck's constant

Γ is the frequency of the radiation.

From equations (1) and (2)

$$E = mc^2 = h\gamma \xrightarrow{\hspace{2cm}} \quad (3)$$

de-Broglie suggested that the equation 3 can be applied both for photons and material particles. If m is the mass of the particle and v is the velocity the particle, then

Momentum $p = mv$

$$p = mc$$

$$h\nu = pc$$

$$\therefore \quad p = \frac{h\nu}{c} \text{ since } \frac{c}{\nu} = \lambda$$

We can write $p = \frac{h}{\lambda}$

Or the wavelength $\lambda = \frac{h}{p} \xrightarrow{\hspace{2cm}} 4$

$$\lambda = \frac{h}{mv} \qquad \text{-------5}$$

de-Broglie wavelength in terms of energy:

$$E = \frac{1}{2}mv^2$$

$$m^2v^2 = 2Em$$

We know $$mv = \sqrt{2Em}$$

$$\boxed{\therefore \lambda = \frac{h}{\sqrt{2mE}}} \quad \text{——} \quad \mathbf{6}$$

de-Broglie wavelength in terms of Voltage:

If a charged particle of charge ’e’ is accelerated through a potential difference ‘V’

Then the Kinetic Energy of the particle = $\frac{1}{2}mv^2$

Also we know energy = eV $\qquad$ ———————— **8**

Equating 7 and 8, we get,

$$\frac{1}{2}mv^2 = eV$$

Multiplying by ‘m’ both sides, we get

$$m^2v^2 = 2meV$$

Or $$mv = \sqrt{2meV} \qquad \text{————————} \quad \mathbf{9}$$

Substituting 9 in 5, we get

de-Broglie wavelength

$$\boxed{\lambda = \frac{h}{\sqrt{2meV}}} \qquad \text{——————} \quad \mathbf{10}$$

$$\lambda = \frac{12.26}{\sqrt{V}}$$

Wave velocity:

We know that

$$E = h\nu \text{ and } E = mc^2$$

$$h\nu = mc^2$$

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

The wave velocity is given by

$$\omega = \nu\,\lambda$$

$$\omega = \frac{mc^2}{h} \cdot \frac{h}{mv}$$

$$\therefore \ \omega = \frac{c^2}{V}$$

Thus matter waves travel faster than velocity of light.

Properties of de-Broglie waves / Matter waves :

- Matter waves are produced by the motion of the particles and are independent of the charge.
- They can travel through vacuum and do not require any material medium for their propagation.
- The smaller the velocity of the particle, the longer is the wavelength of the matter wave associated with it.
- The lighter the particle, the longer is the wavelength of the matter wave associated with it.
- The velocity of matter waves depends on the velocity of the material particle and it is not a constant quantity.
- Matter waves are not electromagnetic waves, they are pilot waves guiding the particle.
- The velocity of matter waves is greater than the velocity of light.

Heisenberg uncertainty principle:

In 1927, Heisenberg proposed a very interesting principle, which is direct consequence of the dual nature of matter, known as uncertainty principle.

According to Heisenberg uncertainty principle, it is impossible to determine accurately and simultaneously the values of position and momentum of a particle at any time.

If Δx is the error (uncertainty) in measuring position,
Δp is the error (uncertainty) in measuring momentum;

Then according to this principle

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

$$\Delta E.\ \Delta t \geq \frac{h}{4\pi}$$

Where ΔE and Δt are the uncertainties in determining the energy and time

Application of uncertainty principle:

- It is verified Nonexistence of Electrons inside the nucleus.
- It is also verified Existence of protons and neutrons inside the nucleus
- It is calculated binding energy of electron in an atom
- Emitted radiation of excited atom is confirmed by this principle.

Physical significance of wave function:

According to Heisenberg uncertainty principle tells us that we cannot detect the particle nature and wave nature at the same time.

The amplitude of the wave tells us about the probability of finding particle in space at a particular instant. A large wave amplitude means a large probability of finding the particle at that position.

Mathematically, to explain it, scientists introduced a new physical quantity called wave function.

Wave function:

It is a mathematical tool used in quantum mechanics to describe any physical system, and it is denoted by 'ψ'.

- It is variable quantity i.e., associated with a moving particle at any position (x,y,z) and at any time t and it relates probability of a finding the particle at that point and at that time.

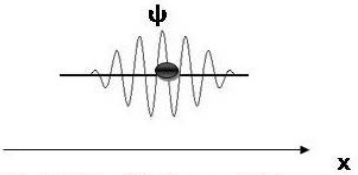


Fig: Probability of finding particle in space

- It must be well behaved, that is single valued and continuous everywhere.
- It usually complex quantity and individually it has no meaning.

- According Max born $\psi\ \psi^{*}=|\psi|^{2}$ is a real and positive, it has physical meaning.

- It represents the probability of finding the particle in the state ψ.

- Since the wave function is a complex quantity, it may be expressed in the form of

$$\Psi_{(x,y,z)} = (a+ib)$$

Where a, b are real function of the variables (x,y,z,t) and $i=\sqrt{-1}$.

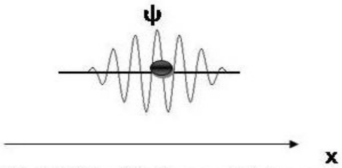


Fig: Probability of finding particle in space

- The complex conjugate of ψ is given by

$$\Psi^{*}{}_{(x,y,z)} = (a-ib)$$

Multiplying the above two equations, we have

$$\Psi\ \Psi^{*} = (a+ib)\,(a-ib) = a^{2}+b^{2}$$

According to Max born

$$P = \Psi\ \Psi^{*} = \left|\psi_{(x,y,z)}\right|^{2} = a^{2}+b^{2}$$

Thus the product of ψ and ψ^{*} is real and positive if $\psi\neq 0$ and is known as **probability density of the particle associated with the de-Broglie wave**

- The probability of finding the particle in a volume dv=dx.dy.dz is given by

$$\text{Probability (p)} = |\psi|^{2} dx\ dy\ dz$$

- For the total probability of finding the particle somewhere is (space).

$$P = \iiint |\psi|^{2}\ dx\ dy\ dz = 1$$

- A wave function ψ satisfying the above relation is called a normalized wave function.

- For motion of a particle in one dimensional, the quantity

  P dx = $|\psi|^2$dx is the probability of finding the particle over a small distance dx at position x.

Schrodinger wave equation:

The equation that describes the wave nature of a particle in mathematical form is known as Schrodinger's wave equation.

There are two types of Schrodinger wave equations they are

1) Time independent wave equation and

2) Time dependent wave equation

Schrodinger time dependent wave equation:

Schrodinger time dependent wave equation is derived from Schrodinger time independent wave equation.

The solution of classical differential equation of wave motion is given by

$$\psi(x, y, z, t) = \psi_0(x, y, z)e^{-i\omega t} \quad \dots (1)$$

Differentiating eqn (1) with respect to time t, we get out

$$\frac{\partial\psi}{\partial t} = -i\,\omega\,\psi_0\,e^{-i\omega t} \quad \dots (2)$$

$$\frac{\partial\psi}{\partial t} = -i\,(2\pi\nu)\,\psi_0\,e^{-i\omega t} \quad (\because \omega = 2\pi\nu)$$

$$\frac{\partial\psi}{\partial t} = -2\pi i\nu\psi \quad \dots (3)$$

$$(\because \psi = \psi_o e^{-i\omega t})$$

$$\frac{\partial\psi}{\partial t} = -2\pi i\frac{E}{h}\psi \quad \left(\because E = h\nu \text{ or } \nu = \frac{E}{h}\right)$$

$$\frac{\partial\psi}{\partial t} = -i\frac{E}{\frac{h}{2\pi}}\psi = -i\frac{E}{\hbar}\psi \quad \left[\because \hbar = \frac{h}{2\pi}\right]$$

$$\frac{\partial\psi}{\partial t} = -i\frac{E}{\hbar}\psi \quad \dots (4)$$

Multiplying i on both sides in eqn (4), we have

$$i\frac{\partial\psi}{\partial t} = -i\times i\left(\frac{E}{\hbar}\right)\psi = -i^2\left(\frac{E}{\hbar}\right)\psi$$

$$i\frac{\partial\psi}{\partial t} = \frac{E}{\hbar}\psi \qquad [\because\ i\times i = i^2 = -1]$$

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi \qquad \dots (5)$$

Schroedinger time independent wave equation is

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

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

$$\Rightarrow \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \dots (7)$$

$$\text{or} \quad \boxed{H\psi = E\psi} \qquad \dots (8)$$

where $H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$ is Hamiltonian operator

$E = i\hbar\frac{\partial}{\partial t}$ is energy operator.

The eqn (7) is known as **Schrodinger time dependent wave equation.**

Schrodinger one dimensional Time independent wave equation

Consider a particle of mass m moving with velocity v along the x-direction. It is associated with a wave. The displacement of the wave is given be the wave function Ψ.

For steady state wave motion, Ψ is a function of x-coordinate only for one dimensional motion.

A one dimensional wave equation for the steady wave associated with a particle is given by

$$\psi(x) = A\sin\frac{2\pi x}{\lambda}$$

Where A is amplitude and λ is wave length.

Differentiating w. r. t. X we get $\frac{d\psi}{dx} = A\frac{2\pi}{\lambda}\ cos\frac{2\pi x}{\lambda}$

$$\frac{d^2\psi}{dx^2} = -4\frac{\pi^2}{\lambda^2}Asin\frac{2\pi x}{\lambda}$$

$$-\frac{4\pi^2}{\lambda^2}\psi \quad ---- (2)$$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{4\pi^2\psi}{\lambda^2}=0 \qquad (3)$$

This is the classical wave equation in terms of wavelength.

We know that debroglie wavelength is given by

$$\lambda = \frac{h}{mv} \rightarrow \ (4)$$

Substituting equation (4) in (3), we get

$$\frac{\partial^2\psi}{\partial x^2}+\frac{4\pi^2m^2v^2}{h^2}\ \psi=0 \ \rightarrow(5)$$

If E is the total energy of a particle, 'V' is the potential energy and $\frac{1}{2}mv^2$ is the kinetic energy; then

Total energy (E) =P.E+K.E

$$E = V+\frac{1}{2}mv^2$$

(Or) $E-V=\frac{1}{2}mv^2$

$$2(E-V) = mv^2$$

Multiplying by 'm' on both sides in the above equation, we get

$$2m\,(E-V) = m^2\,v^2 \ \rightarrow \ (6)$$

Substituting equation (6) in (5) we get $\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2m}{h^2}(E-V)\ \psi=0 \rightarrow (7)$

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2m}{\hbar^2}(E-V)\ \psi=0 \rightarrow (8)$$

Where $\hbar = \frac{h}{2\pi}$ is called plank's reduced constant.

This equation is known as Schrodinger time independent one-dimensional wave equation.

For 3dimensional:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2m}{h^2}(E-V)\ \psi=0$$

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

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ is called Laplace operator.

Application of Schrodinger time independent wave equation – Particle in one dimensional box or well:

Let us consider a particle of mass '*m*' moving with velocity '*v*' along x-direction and is confined between to infinite potential rigid walls, so that the particle has no chance of escaping from them. Therefore, the particle bounces back and forth between two walls as shown in fig.

Let the potential energy of electron inside the box is constant and can be taken as zero for simplicity.

From fig , we consider two regions :

(i) Outside the box
(ii) Inside the box

Outside the box:
The particle cannot exist outside and on the walls of the box; therefore the probability of finding the electron outside the wall is zero and the potential energy is∞.

$\psi(x)=0$
$V(x) = \infty$ When $x \leq 0$ and $x \geq l$

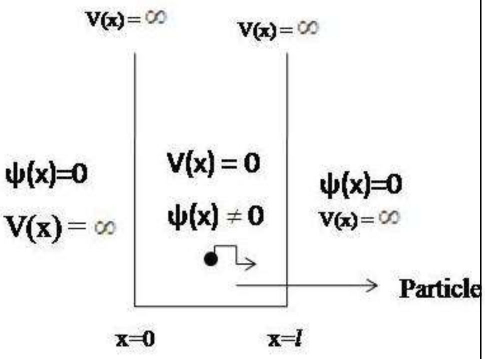


Fig : Particle in one dimensional box

Inside the box:
The particle exists inside the box; therefore the probability of finding the electron inside the box is no equal zero and the potential energy is zero.

$\psi(x) \neq 0$ When $x>0$ and $x< l$
$V(x) = 0$

To calculate the probability of finding particle within the box , let us consider one dimensional time independent Schrödinger wave equation

$$\text{i.e., } \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V(x))\psi = 0 \longrightarrow (1)$$

Inside the box, the potential energy $V(x) = 0$
Therefore, equation (1) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0$$

$$\text{(Or) } \frac{d^2\psi}{dx^2} + k^2\psi = 0 \longrightarrow (2)$$

$$\text{Where } k^2 = \frac{8\pi^2 mE}{h^2} \longrightarrow (3)$$

Equation (2) is a second order differential equation; therefore it should have solution with two arbitrary constants.

∴ The solution for equation (2) is given by

$$\Psi(x) = A\sin Kx + B\cos Kx \longrightarrow (4)$$

Where A and B are called as arbitrary constants, which can be found by applying the boundary conditions.

Boundary Condition at x=0:

At x = 0, the probability of finding the electron is zero, i.e., $\psi(x) = 0$

Equation (4) becomes

$O = A \sin K(0) + B \cos K(0)$

$O = 0 + B$

$$B=0 \longrightarrow (5)$$

Boundary Condition at x=*l*:

At x = *l*, the probability of finding the electron is zero, i.e., $\psi(x) = 0$

Equation (4) becomes

$O = A \sin K(l) + B \cos K(l)$

$O = A \sin K(l) + (0) \cos K(l)$ [Since B = 0]

$A \sin K(l) = 0$

Since $A \neq 0$; $\sin K(l) = 0 \longrightarrow (6)$

We know that, $\sin n\pi = 0 \longrightarrow (7)$

Comparing these two equations, we can write

$K(l) = n\pi$

$$K = \frac{n\pi}{l} \longrightarrow (8)$$

$$k^2 = \frac{n^2\pi^2}{l^2} \longrightarrow (9)$$

Substituting the values of '*B*' and '*K*' in equation (4),
Equation (4) becomes

$$\Psi_n(x) = A\sin\frac{n\pi x}{l} \longrightarrow (10)$$

This equation represents the wave function associated with moving free electron inside the box.

Normalization of the wave function:

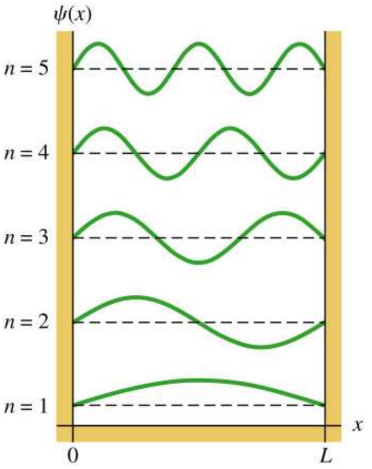
It is the process by which the probability (P) of finding the particle or electron inside the box can be done.

The total probability that the particle is somewhere in the box must be unity

$$\text{i.e .,}\ P = \int_0^l |\psi_n(x)|^2 \longrightarrow (11)$$

[Since the particle present inside the box between the length 0 to *l,* then the limits are chosen between 0 to *l*]

Substituting equation (10) in equation (11), we get



$$P= \int_0^l A^2 \mathrm{Sin}^2 \frac{n\pi x}{l}\, dx = 1$$

$$A^2 \quad \int_0^l \mathrm{Sin}^2 \frac{n\pi x}{l} \quad dx \quad = \quad 1$$

[Since $\mathrm{Sin}^2 x = \frac{1-C}{2}$]

$$A^2 \quad \int_0^l \frac{\frac{1-Cos2n\pi x}{2}}{l} \quad = \quad 1$$

[Since $\int \frac{Cosn\pi x}{l} = \frac{\frac{Sinn\pi x}{l}}{\frac{n\pi}{l}}$]

$$\frac{A^2}{2} \int_0^l \frac{1-Cos2n\pi x}{l}\, dx = 1$$

$$\frac{A^2}{2} \int_0^l \frac{1-Cos2n\pi x}{l}\, dx = 1$$

$$\frac{A^2}{2} [\int_0^l dx - \int_0^l \frac{Cos}{l}\, dx] =1$$

$$\frac{A^2}{2}[l] - \frac{A^2}{2}\left[\frac{\frac{Sin2n\pi l}{l}}{\frac{2n\pi}{l}}\right] = 1 \quad \longrightarrow (12)$$

Since Sin nπ = 0, Sin 2nπ is also= 0

Equation (13) can be written as

$$\frac{A^2}{2}[l] = 1$$

$$A^2 = \frac{2}{l}$$

$$\boxed{A= \sqrt{\frac{2}{l}}} \quad \longrightarrow \quad (13)$$

Substituting the values of '*A*' in equation (10),

$$\Psi_n(x) = \sqrt{\frac{2}{l}}\, \mathrm{Sin} \frac{n\pi x}{l} \quad \longrightarrow (14)$$

Each value of wave function is known as Eigen function .The various Eigen functions of an electron enclosed in a1D box as shown in fig.

Case 1: If n=1, then $\Psi_1(x)$ has two nodes at x=0 and x= *l.*

Case 2: If n=2, then $\Psi_2(x)$ has two nodes at x=0 and $x= \frac{l}{2}$ *and* $x = l$.

Case 3: If n=3, then $\Psi_3(x)$ has three nodes at x=0 and $x= \frac{l}{3}$ *and* $x = \frac{2l}{3}$ *and* $x = l$. Therefore $\Psi_n(x)$ has (n+1) nodes.

Probability of the location of the particle:

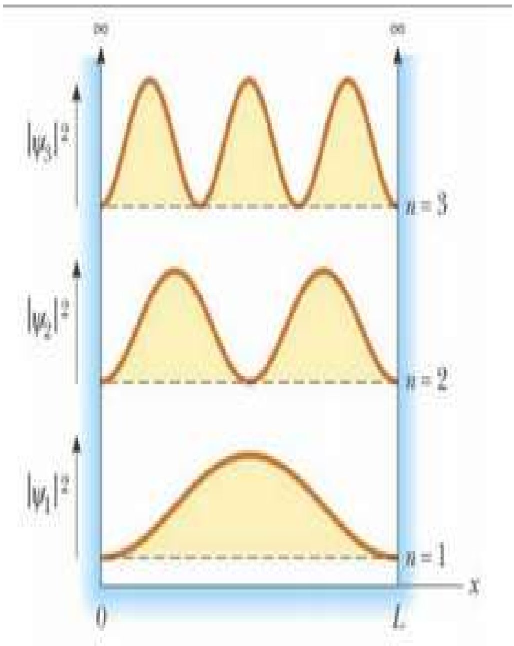
The probability of finding a particle over a small distance *dx* at x is given by

$$P(x)\,dx = |\psi_n(x)|^2 dx$$

$$P(x)\,dx = \frac{2}{l}\,\mathrm{Sin}^2\frac{n\pi x}{l}$$

Thus, the probability density for one dimensional motion is

$$P(x) = \frac{2}{l}\,\mathrm{Sin}^2\frac{n\pi x}{l}$$



The probability density is maximum when $\frac{n\pi x}{l} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$

$$x = \frac{l}{2n}, \frac{3l}{2n}, \frac{5l}{2n} \ldots\ldots$$

Case 1: If n=1, then the probability of position of the particle is at $x = \frac{l}{2}$

Case 2: If n=2 then the probability of position of the particle is at $x = \frac{l}{4}$ and $\frac{3l}{4}$.

Case 3: If n=3, then the probability of position of the particle is at $x = \frac{l}{6}$ and $\frac{3l}{6}$ and $\frac{5l}{6}$. these positions are shown in fig.

Energy of the Particle:

From the equations (3) & (9)

$$k^2 = \frac{8\pi^2 mE}{h^2} \longrightarrow (3)$$

$$k^2 = \frac{n^2\pi^2}{l^2} \longrightarrow (9)$$

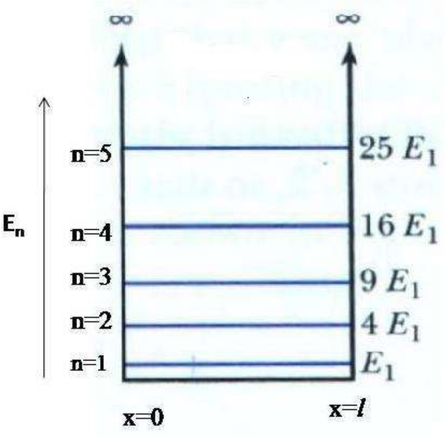
$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{l^2}$$

$$E_n = \frac{n^2h^2}{8m\ ^2} \longrightarrow (10)$$

This is an expression for the energy of the particle.

Each value of E_n is known as Eigen value.

The various Eigen values of an electron enclosed in a 1D box as shown in fig

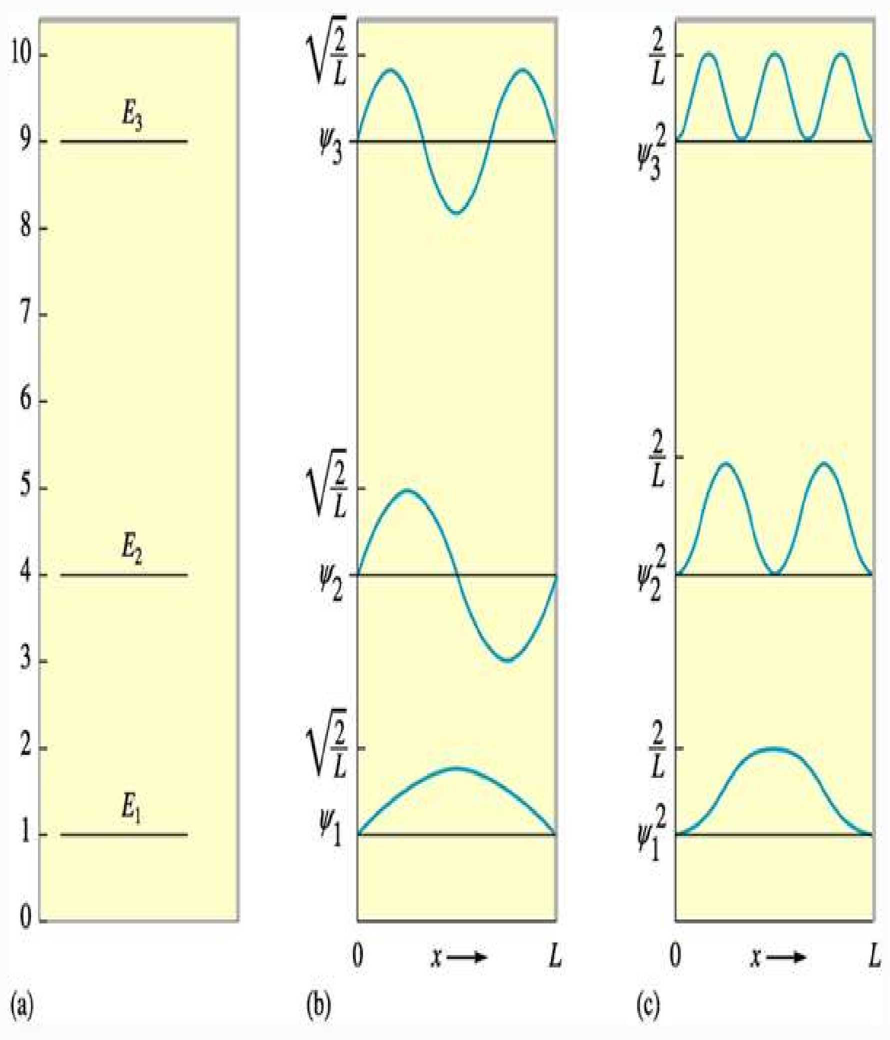


Case 1: If n=1, then $E_1 = \frac{h^2}{8ml^2}$.

Case 2: If n=2, then then $E_2 = \frac{4h^2}{8ml^2} = 4E_1$

Case 3: If n=3, then $E_3 = \frac{9h^2}{8ml^2} = 9E_1$ and so on. Therefore, energy levels of electron are discrete.

THE EIGEN VALUE, WAVEFUNCTION AND PROBABILITY DENSITY OF THE PARTICLE IN A ONE DIMENSIONAL BOX



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

$$\psi(x) = \sqrt{\frac{2}{L}} \cdot \sin\frac{n\pi x}{L}$$

$$P(x)dx = \frac{2}{L} Sin^2 \, n\pi x/_{L} \, dx$$

UNIT IV: Free electron theory

Conducting materials have high electrical and thermal conductivity. The conducting property of a solid is due to the **number of valence electrons** so called Free electrons or Conduction electrons. Hence in metals, the electrical conductivity depends on the number of free electrons.

The electron theory of metals explains the following concepts such as

- ✓ Structural, electrical and thermal properties of materials
- ✓ Elasticity, cohesive force in solids
- ✓ Behaviour of conductors, semiconductors, insulators etc

"The study of behavior of free electrons and various properties such as electrical, thermal and magnetic properties etc., in a solid is known as free electron theory of solids."

The electron theory of solids has been developed in three main stages.

Classical free electron theory:

- It is a macroscopic theory, proposed by Drude and Lorentz in 1900.
- This theory explains the **free electrons in lattice** and it obeys the laws of classical mechanics.

Quantum free electron theory:

- It is a microscopic theory, proposed by Sommerfeld in 1928.
- This theory is explained with the concept that the **electron moves in a constant potential** and it obeys the Quantum laws.

Brillouin Zone theory or Band theory:

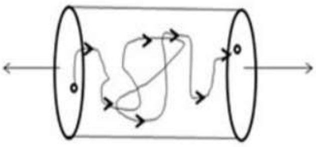
- This theory is proposed by Bloch in 1928.
- It is explained with the concept that the **electron moves in a periodic potential.**
- This theory used to describe and analyze the electron energy in the band energy structure of crystals.

The classical Free Electron Theory of Metals:

Postulates :

In the absence of electric field:

- The free electrons in the metals moves freely in the boundaries of the metal, similar to the gas molecules moving in a vessel.
- The forces between the conduction electrons and the core is neglected and the total energy of the electron is assumed to be purely kinetic energy.

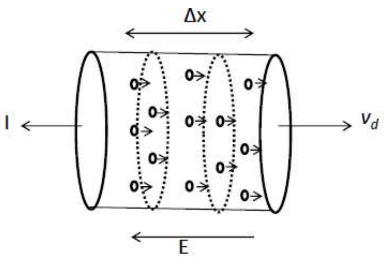


Random motion of electrons

- The free electrons move randomly in all directions. The free electrons collide with each other and also with the lattice elastically.

In the presence of electric field:

- The free electron moves in the direction opposite to that of the electric field
- It obeys classical kinetic theory of gases and the electron velocities in the metal obey the Maxwell-Boltzman statistics



Directed motion of electrons

Definitions :

Drift Velocity (V_d):

The average velocity acquired by the free electron in a particular direction due to the application of electric field is called drift velocity.

Mobility (μ):

Drift velocity acquired by the free electron per unit electric field (E) applied to it.

$$\mu = \frac{V_d}{E}$$

Relaxation time (τ_r):

It is the time taken by the free electron to reach its equilibrium position from its disturbed position, in the presence of applied field.

$$\tau_r = \frac{l}{v_d}$$

Let l is distance travelled by the electron

Collision time(τ_c):

It is the average time taken by a free electron between two successive collisions.

$$\tau_c = \frac{\lambda}{v}$$

Where λ is mean free path

Mean free path (λ):

The average distance travelled between two successive collision is called mean free path

$$\lambda = \bar{c}\,\tau_c$$

Where $\bar{c}$ is the root mean square velocity of the electron

Current Density(J): The current flowing through the solid per unit area.

$$J = \frac{I}{A}$$

Success of Classical Free Electron Theory:

- Explains the concept of resistance in metals
- Verifies Ohm's law

- Explains high electrical and thermal conductivity of metals
- Establishes relation between electrical and thermal conductivities of metals (Wiedemann–Franz law)

$$k/\sigma = L.T$$

- where, k is thermal conductivity, σ is electrical conductivity, L is Lorentz number, T is temperature (in K)
- Explains optical properties of metals

Drawbacks of Classical Free Electron Theory:

Classical theory failed to explain:

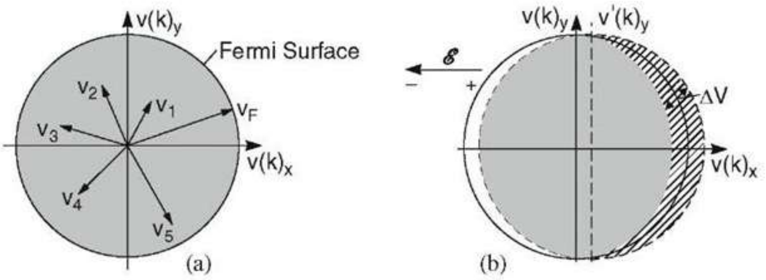
- Photoelectric effect, Compton effect, black body radiation, Ferromagnetism and paramagnetism etc.
- Electrical conductivity of non metals such as semiconductors and insulators.
- Specific heat of metals.
- Thermal conductivities at low temperature
- Theoretical and experimental values of mean free path does not coincide

Postulates of Quantum Free Electron Theory:

- The valance electrons are free in a metal piece and they are moving in a **uniform potential**
- Only Fermi level electrons are responsible for electrical, thermal conductivity.
- It obeys the laws of **Fermi-Dirac statistics** instead of Maxwell-Boltzmann statistics.
- This theory explains by taking into account the **quantum theory and Pauli's exclusion** principle.

Quantum Free Electron Theory- Electrical conductivity

- The Free electrons will have discrete energy states (or) levels in a metal.
- The occupation (or) distribution of electrons among these energy levels will be governed by Pauli's exclusion principle.
- The highest energy level occupied by electrons at absolute zero temperature is known as "Fermi energy level" (E_F). Above Fermi energy level all energy levels are empty. i.e., at 0K all the energy levels below Fermi energy level are filled by free electrons. So they possess different energies and velocities or momentums.
- The different velocities of these free electrons of a metal can be represented in velocity space as shown fig.
- At 0K, free electrons present in Fermi energy level possess maximum velocity represented by V_F.
- We assume a sphere of radius V_F, at the origin of velocity space as shown in fig.

- At 0K, all points inside the Fermi sphere are occupied.
- Each point inside the sphere from the origin represents the velocity of a free electron.
- The vectors joining different points inside the sphere from the origin represent velocity vectors.
- 

    - Fig: Displacement of Fermi sphere under applied electric field.

The relation between momentum P and wave vector k is given by

$$p = \hbar k$$

$$mv = \hbar k$$

$$v = \left(\frac{\hbar k}{m}\right) \quad \text{———} \quad (1)$$

$$a = \frac{dv}{dt} = \frac{\hbar}{m}\frac{dk}{dt} \quad \text{———} \quad (2)$$

Force on the electron in the applied field E is given by

$$F = eE$$

$$ma = eE$$

$$m\frac{\hbar}{m}\frac{dk}{dt} = eE$$

$$dk = \frac{eE\,dt}{\hbar} \quad \text{———} \quad (3)$$

Integrating the above eq. we get $\int_0^t dk = k_t - k_0 = \frac{eEt}{\hbar}$ ——— (4)

Let the mean collision time and mean free path of electron at fermi surface then $\tau_f = \frac{\lambda_f}{v_f}$ ——— (5)

$on\ fermi\ surface\ t = \tau_f$ and $k_t - k_0 = \Delta k$

$$\Delta k = \frac{eE\tau_f}{\hbar} = \frac{eE}{\hbar}\left(\frac{\lambda_f}{v_f}\right) \quad \text{———} \quad (6)$$

$J = n\,e\,\Delta v$ where Δv is the change in velocity ——— (7)

$$From\ eq\ (1)\ \Delta v = \frac{\hbar\,\Delta k}{m} \quad \text{———} \quad (8)$$

Substitute eq (8) in eq (7)

$J = ne\frac{\hbar\,\Delta k}{m^*}$ where m^* is the effective mass of electron ——— (9)

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Substitute eq (8) in eq (7)

$$J = ne\, \frac{\hbar\, \Delta k}{m^*} \text{ where } m^* \text{ is the effective mass of electron} \quad \text{———} \quad (9)$$

Substitute eq (6) in eq (9)

$$J = \frac{ne\, \hbar}{m^*}\left[\frac{eE}{\hbar}\left(\frac{\lambda_f}{v_f}\right)\right]$$

$$\sigma\, E = \frac{n\, e^2\, \tau_f\, E}{m^*}$$

$$\sigma = \frac{n\, e^2\, \tau_f}{m^*} \quad \text{———} \quad (10)$$

Eq. (10) represents the electrical conductivity

Merits of Quantum Free Electron Theory:

- It explains the electrical and thermal conductivity of metals
- The phenomena of thermionic emission can be explained by this theory.
- Temperature dependence of conductivity of metals can be explained by this theory
- It explains the specific heat of metals
- It explains the magnetic susceptibility of metals

Drawbacks of Quantum Free Electron Theory:

- It is unable to explain the metallic properties exhibited by only certain crystals.
- It is unable to explain why the atomic arrays in metallic crystals should prefer certain structures only.

Fermi-Dirac distribution:

Fermi-Dirac (F-D) distribution describes the behavior of free electron gas, taking into account the **quantum theory** and **Pauli's exclusion principle**.

As shown in fig. **Quantum theory**, the electrons will have discrete energy levels.

According to **Pauli's exclusion principle**, only two electrons will be occupied by each energy level.

- At absolute zero temperature, two electrons occupy the ground state and two into each state of next higher energy levels.

"The highest energy level occupied by electrons at absolute zero temperature (T=0 K) is known as Fermi energy level (E_F)".

- The Fermi energy level separates the occupied states from unoccupied states.

The probability of the occupation of an energy level E by an electron at temperature T is given by

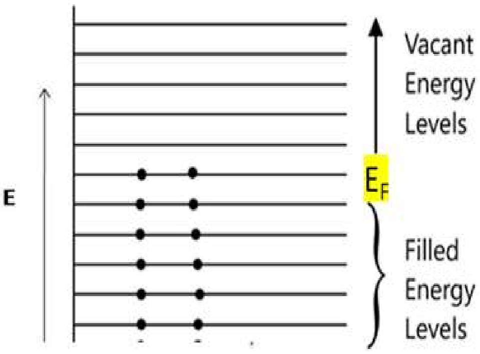


Fig: Distribution of free electrons in various energy levels at 0K.

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

Where F(E) is the Fermi Dirac distribution function and K_B is the Boltzmann's constant.

Effect of Temperature on Fermi-Dirac Distribution Function:

Figure shows the plots of the distribution function against energy at different temperatures. The special features of the plots are discussed below

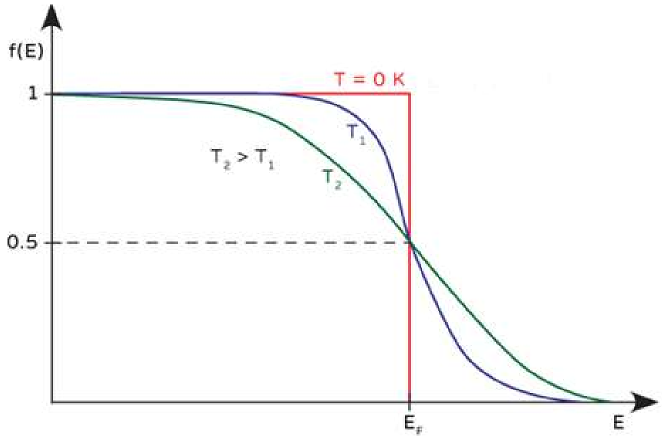


Fig. Variation of Fermi distribution function with energy

$$f\,(E) = \frac{1}{1 + e^{\left(\frac{E_f - E_f}{K_B T}\right)}} = \frac{1}{1 + e^{o}}$$

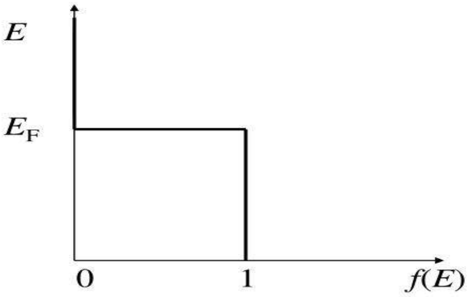
$$= \frac{1}{1+1} = \frac{1}{2}$$

Thus, **at finite temperature**, the probability of occupancy of **the Fermi level is ½** .

Fermi-Dirac distribution: Consider $T \rightarrow 0$ K

For $E > E_F$: $$f(E > E_F) = \frac{1}{1+\exp(+\infty)} = 0$$

For $E < E_F$: $$f(E < E_F) = \frac{1}{1+\exp(-\infty)} = 1$$



Thus, at absolute zero temperature **F(E) is a step function**. All the states with energies up to E_F are filled with electrons and the states with **energies greater than E_F are empty.**

Density of states (DOS):

The density of states (DOS) of a system describes the proportion of states are to be occupied by the system at each energy.

The density of states is defined as

$$D(E) = \frac{N(E)}{V}$$

Wheree N(E) Delta E is the no. of states in the system of volume V whose energies lie in the range E+dE

"The density of states gives the number of allowed electron (or hole) states per volume at a given energy. It can be derived from basic quantum mechanics"

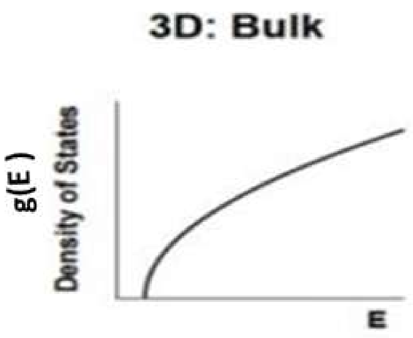
Density of states (DOS) in 3-D, 2-D, 1-D:

For a 0-D structure i.e., for nanoparticles, the permitted energy values are not continuous but form **discrete bunches of electrons** as shown in fig.e. (because of confined condition for electrons). In real quantum dots, however, the size distribution leads to a broadening of the lines.

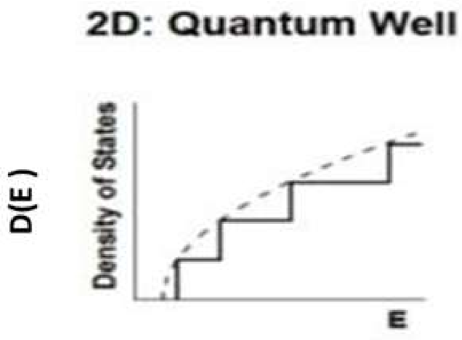
For a **1-D structure**, i.e., for a quantum wire, the DOS **variation is not smooth** as in the case of 3-D structure not even constant over the subband also. The density hits peaks at energy values decreases rapidly (fig.c.)

For **2-D structure**, the DOS is denoted as D(E) varies **as step-function**. If the thickness of the 2-D materials increased, more sub bands will be created which results in decrease of the step width.

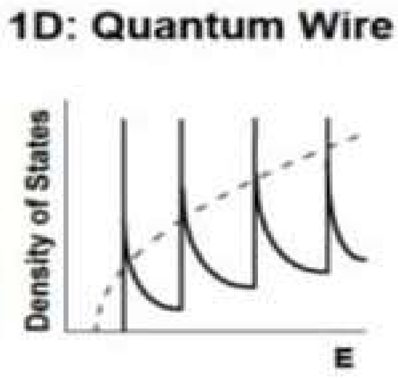
If the thickness increase continues, then the material reaches **3ds**, the innumerable steps would be seen merged into an envelope of **parabolic variation for DOS**.



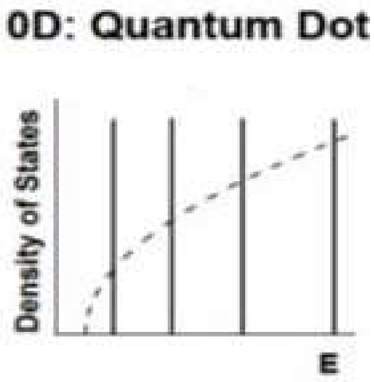
(a)



(b)



(c)



(e)

References: Text Books:

1. Engineering Physics by V Rajendran, K Thyagarajan, McGraw Hill.
2. Solid State Physics by G V Rao.
3. Engineering Physics by G. Senthil Kumar, VRB Publishers.
4. Solid State Physics by S.O. Pillai