

SEMICONDUCTOR-PHYSICS

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UNIT-1

Ohm's law and its alternate form in Physics

If a potential difference V is applied across a solid, it establishes an electric field of magnitude E inside the solid such that

$$E = \frac{V}{L} \quad [\text{S.I unit of } E \text{ is } \text{Vm}^{-1}]$$

where L is the length of the solid along which charge carriers move. This electric field accelerates the charge carriers and causes a flow of electric current in the solid along its length such that $I = Q/t$ and the current density is given by

$$[\text{SI unit of } I \text{ is A}] \quad J = \frac{I}{A} = \frac{Q}{At} = \text{Charge flowing per unit time through an area } A \perp \text{ to direction of flow.}$$

When a reasonable electric current flows through a material, it is said to be conducting electricity. For a material to conduct electricity, it must contain large number of free (or mobile) charge carriers (e.g. free electrons or holes).

According to Ohm's law, the current flowing through a conductor is directly proportional to the potential difference applied across its ends (at a constant temperature) so that

$$I \propto V$$

$$\text{or } I = GV \quad [\text{S.I. unit of } G \text{ is ohm}^{-1} \text{ or mho}]$$

where G is a constant of proportionality and is called the conductance of the material. It is the inverse of resistance i.e. $G = 1/R$. Therefore,

$$I = \frac{V}{R} \quad \text{or} \quad V = IR \quad (\text{Ohm's Law})$$

Resistance is defined as the obstruction to the flow of current through a material. When electrons travel in vacuum, there is no obstruction to their motion and they travel along a straight line. So that

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

However, their motion is impeded (i.e. slowed down) due to collisions with atoms in a lattice while moving through a solid. This opposition to the electron motion in solids

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is the cause or source of electrical resistance. The electrical resistance R depends on size and shape of the solid and also on its physical properties which are material specific. In particular,

$$R = \rho l/A \quad [\text{S.I unit of } R \text{ is ohm}]$$

where l = length, A = area of cross-section and ρ = resistivity. Note that the resistivity ρ depends only on the material and not on the size and shape of the material.

The inverse of electrical resistivity is defined as electrical conductivity σ so that

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} \quad [\text{S.I. unit of } \sigma \text{ is ohm}^{-1}\text{m}^{-1}]$$

Substituting $R = V/I$ from Ohm's Law in the above equation, we get

$$\sigma = \frac{IL}{VA} = \frac{J}{E} \quad (\because J = \frac{I}{A} \text{ and } E = \frac{V}{L})$$

$$\text{i.e. } J = \sigma E$$

which is an alternate expression of Ohm's law in Physics.

Conductivity of Metals, Insulators and Semiconductors (at room temp)

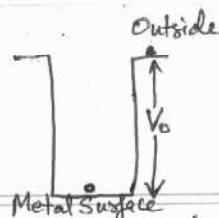
Metals \rightarrow Large Conductivity $\sim 10^8 \text{ S/m}$ at room temperature and are therefore called conductors.

Insulators \rightarrow Very low conductivity $\sim 10^{-12} \text{ S/m}$ at room temperature and are therefore bad conductors or insulators.

Semiconductors \rightarrow Their conductivity $\sim 10^{-4}$ to 10^{+4} S/m at room temperature, which is intermediate to those of conductors and insulators. They are therefore called semiconductors.

Free Electron Model of Solids - Electrical conduction is one of the important properties of solids. Experiments indicated that the valence electrons were involved in electrical conduction for case of metals & alloys. The free electron theory was therefore proposed. It underwent successive modifications to explain the electrical behaviour and distinction between these types of solids.

- (i) Classical Free Electron theory :-
- (ii) Quantum Free Electron theory :-
- (iii) Band Theory of Solids :-



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Free Electron Theory of Metals.

Classical Theory or Lorentz-Doude Theory

The main features of the theory are as below

1. It assumes that the atoms in a metal consist of positive ion cores and the valence electrons. Ion core consists of nucleus and all electrons except the valence electron.
2. The positive field of these ion cores is assumed to be constant throughout the metal. The force between valence electrons and ion cores is neglected i.e. the potential energy of electrons is taken as zero. So the valence electrons possess only kinetic energy and therefore behave as free electrons or conduction electrons. The mutual repulsion between the electrons is also neglected.
3. The behaviour of free electrons moving inside the metals is considered to be similar to that of atoms or molecules in a perfect gas.
4. The movement of conduction electrons is restricted to within the metallic crystal only, since the potential energy of an electron inside the metal is less than the potential energy of an identical electron just outside it. This potential energy difference, V_0 , serves as a potential barrier and stops the inner valence electrons from leaving the surface of the metal.
5. Thus, in free electron gas model, the movement of free electrons in a metal is equivalent to the movement of a free electron gas inside a "potential energy box".
6. At any temperature, the free electrons move in random directions inside the metal and their average velocity is zero. So there is no practical contribution to electrical and thermal conductivity in the absence of electric field or temperature gradient.
7. In the presence of electric field, the electrons are accelerated opposite to the direction of the field and therefore produce a current.
8. In thermal equilibrium, the free electrons obey Maxwell-Boltzmann statistics or classical laws of statistics.
9. Lorentz-Doude theory explains the electrical and thermal conductivities of metals. It can explain the Ohm's law.

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Thermal Motion of Free Electrons (When $E=0$)

In the absence of a potential difference across the ends of a material (ie $V=0$ or $E=0$), due to thermal energy at room temperature (Thermal energy $\propto kT$), the free electrons keep moving randomly in all directions in the crystal lattice. The average speed of the electrons during this thermal motion is very high and is of the order of 10^6 m/s. During their thermal motion, these free electrons suffer repeated collisions with the ion cores or other electrons and get deflected in random directions. Therefore, the direction of motion of each free electron changes in every collision and every electron moves along a zigzag path. Since all electrons move in random directions and because the sum total of random vectors is a null vector, therefore in the absence of Electric field, the thermal motion of free electrons does not cause flow of current through the metal. \therefore net displacement of an electron over a period of time is zero.

Drift Motion of Free Electrons (When Potential Difference is Applied)

When the ends of a piece of metal are connected to the terminals of a battery (ie when a potential difference is applied across the two ends of a long conductor) an electric field is set up inside it such that $E = V/l$. This electric field accelerates the electrons in a direction opposite to that of the electric field. Why?

$$\begin{aligned} \text{Charge on an electron is -ve i.e } &= -e \\ \text{Force on an electron due to electric field is } &\vec{F} = -e\vec{E} \\ \text{i.e } &m\vec{a} = -e\vec{E} \\ \text{or } &\boxed{\vec{a} = -\frac{e\vec{E}}{m}} \end{aligned}$$

i.e direction of acceleration is opposite to the direction of \vec{E} . However, the electron will not accelerate indefinitely but after a short period it collides with a +ve ion core inside the metal. At each collision its speed gets reduced considerably and gets slowed down. After the collision, it is again accelerated and again undergoes a collision and gets slowed down and this

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process is repeated. As a result of these collisions, a directional motion of electrons is set up inside the solid in a direction opposite to E . This motion is called "drift motion". The drift velocity gained by an electron due to acceleration is lost completely whenever a collision occurs. After that the electron gets accelerated again and loses its velocity at the next collision. The process is repeated and as a result of it the electron moves on an average with a "mean drift velocity" v_d . Thus the collisions play the role of a frictional force which obstructs the free motion of electrons inside the solid. The drift velocity is typically of the order of 10^{-2} m/s which is very small as compared to the thermal speed, 10^6 m/s. Thus, the motion of a free electron in the presence of electric field consists of a much slower directional drift motion superimposed over random zigzag thermal motion. Although the thermal motion of electrons does not contribute to the current in a solid, but the drift motion is directional and causes current flow in a conductor called "drift current" or "conduction current".

Mean Collision Time (τ) :-

The time elapsed between two successive collisions of the electron is not constant but varies. The average duration of time between two successive collisions is called "mean collision time" (τ) of the electron.

Mean Free Path (λ) :-

The average distance travelled by an electron between any two successive collisions is known as "mean free path" (λ) of the electron.

Relation between τ and λ :- $\lambda = \bar{v} \tau$

where \bar{v} = root mean square velocity of the electron.
 $= \sqrt{3kT/m}$

Mobility :- It is defined as the ratio of the drift velocity v_d of electrons to the electric field applied and is denoted by μ .

$$\boxed{\mu = \frac{v_d}{E}}$$

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Mobility indicates the ease with which electrons move inside a material in the presence of an electric field when a potential difference is applied across its ends.

$$\text{For metals} ; - \mu \approx 10^{-3} \text{ m}^2/\text{V.s}$$

$$\text{For semiconductors} ; - \mu \approx 10^{-1} \text{ m}^2/\text{V.s.}$$

[Note that mobility of electrons is larger in case of semiconductors as compared to conductors].

Relaxation Time

When the applied potential difference is switched off the drift velocity of electrons exponentially decays to zero with time as a result of collisions and thermal motion. Mathematically, this is expressed as

$$v_d(t) = v_d(0) e^{-t/\tau}$$

where $v_d(0)$ = drift velocity at the time $t=0$ when E is switched off.
 $v_d(t)$ = drift velocity at a time $t=t$ after E is switched off.

Note that, when $t=\tau$ we get $v_d(\tau) = v_d(0)/e$.

Therefore we see that in a time equal to τ , after switching off the potential difference or $E=0$, the value of drift velocity of electrons reduces to $1/e$ times the initial value when $E \neq 0$. This time is also known as the "relaxation time". So, relaxation time is defined as the time duration in which the drift velocity of an electron decays to $1/e$ of its initial value after the potential difference is switched off. It also represents the time taken by the electrons in a conductor to return from "non-equilibrium" drift motion to the "equilibrium" thermal motion after the applied electric field is switched off. Its value is of the order of 10^{-14} s which is extremely small.

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Expression of Drift Velocity (v_d)

When a potential difference V is applied across the ends of a conductor, an electric field \vec{E} is setup inside it such that

$$\vec{E} = \frac{V}{l}$$

where 'l' is the length of the conductor. Due to this electric field, the electrons experience a force \vec{F} given by

$$\vec{F} = -e\vec{E}$$

where ' $-e$ ' is the charge of the electron.

If \vec{v} is the velocity of free electron and τ is the average time between two successive collisions, the frictional force (due to collision of electrons with ion cores) opposing the continuous acceleration of the electron is given by

$$\vec{f} = -\frac{mv}{\tau} \quad (\text{momentum/time} = \text{force})$$

where the -ve sign indicates that the force of friction is opposite to the direction of motion of electrons. Using the Newton's second law (which is a law of Classical Physics), the equation of motion of the free electron can be written as

$$\vec{F}_{\text{tot}} = m \frac{d\vec{v}}{dt} \rightarrow \vec{F} + \vec{f} = m \frac{d\vec{v}}{dt}$$

$$\text{i.e. } m \frac{d\vec{v}}{dt} = -e\vec{E} - \frac{mv}{\tau} \quad (\because \vec{F} = -e\vec{E} \text{ & } \vec{f} = -\frac{mv}{\tau})$$

where 'm' is the mass of the electron. In the steady state, the electron attains a constant drift velocity v_d . Therefore, in this steady state,

$$\frac{d\vec{v}}{dt} = 0 \quad (\because \vec{v} \text{ is constant}).$$

So, in the steady state, the Newton's second law becomes

$$0 = -e\vec{E} - \frac{mv_d}{\tau}$$

$$\text{or } \frac{mv_d}{\tau} = -e\vec{E}$$

$$\text{or } \vec{v}_d = -\frac{e\vec{E}\tau}{m}$$

The -ve sign indicates that the drift velocity of electron is opposite to \vec{E} .

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Derivation of Ohm's Law :-

Let 'n' be the number of free electrons per unit volume of the conductor. It is also called the "free electron density" or "free electron concentration" in the solid.

$$n = \frac{N}{V}$$

where N = Total number of free electrons inside the solid

V = Total volume of the solid.

Now, if the solid is in the shape of a long rectangular block of length 'l' and cross-section area 'A', then

$$\text{Volume of solid, } V = A l$$

$$\text{Therefore } n = \frac{N}{A l} \Rightarrow N = n A l.$$

Now the total charge in the solid will be equal to the product of charge of one electron times the total number of electrons inside it. i.e

$$|Q| = e N = e n A l. (|Q| \equiv \text{magnitude of charge}).$$

By definition, the current flowing inside the solid will be charge upon time i.e

$$I = \frac{Q}{t} = \frac{e n A l}{t}$$

Now, the drift velocity of the electron inside the solid will be the distance travelled by the electron per unit time i.e.

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

So, we get

$$I = e n A v_d$$

Therefore, the current density of electrons in the solid is defined as

$$J = \frac{I}{A} = n e v_d$$

Substituting $v_d = |\vec{v}_d| = \frac{e E_z}{m}$ in the above equation, we get

$$J = ne \left(\frac{eE\tau}{m} \right) = \frac{ne^2 \sigma}{m} E = \sigma E \quad (\text{Ohm's Law}).$$

where σ = electrical conductivity of the solid.

i.e.
$$\sigma = \frac{ne^2 \tau}{m} = \frac{J}{E} = \frac{nev_1}{E} = ne\mu$$

where ' μ ' is the electron mobility. The above equation indicates that the electrical conductivity of a material mainly depends on the free electron density ' n ' inside it.

Metals \Rightarrow electron density is large \Rightarrow Conductivity is large

Insulators \Rightarrow electron density is very small \Rightarrow Conductivity is very low.

Thermal Conductivity :-

Heat conduction is the transfer of thermal energy from the hotter to the colder part of a material. The rate at which the heat is conducted depends on the temperature gradient and the material of the solid. The temperature gradient is defined as the change in temperature per unit length and is denoted by (dT/dx) .

Let us consider a metal bar of length x , whose ends are held at different temperatures. Let the cross-sectional area of the bar be equal to A . Then

$$\text{Heat Conducted through the bar } J = \frac{\Delta Q}{A \Delta t} \propto \frac{dT}{dx}$$

$$\text{or } J = \frac{\Delta Q}{A \Delta t} = -K \frac{dT}{dx}$$

Where J = thermal flux and K = thermal conductivity.

The -ve sign indicates that the heat flows from hotter end to the colder end of the solid. [The S.I unit of K are $\text{W m}^{-1}\text{K}^{-1}$].

Definition of Thermal Conductivity :-

Thermal conductivity is defined as the quantity of heat crossing per unit area per unit time across a unit temperature gradient in the body i.e. $K = Q \left[\frac{dT}{dx} \right]^{-1}$

Expression of Thermal Conductivity :-

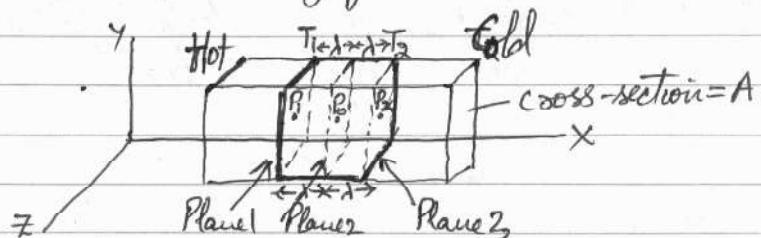
Free electrons also contribute to the conduction of heat energy in metals. In the "free electron model" the valence electrons behave like molecules of a perfect gas. At any given temperature T , an electron possesses a kinetic energy given by

$$E_k = \frac{1}{2} \times kT \times 3 \text{ (No. of degrees of freedom)}$$

$$\text{i.e } E_k = \frac{3}{2} kT \text{ where } k \equiv \text{Boltzmann constant} \\ = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Clearly, the electrons at the hotter end will have more kinetic energy than those at the colder end of the metal bar.

Now consider a uniform metal bar with the left end hotter than the colder right end i.e $T_1 > T_2$ in the figure below.



Therefore a temperature gradient exists along the x -axis. Let 'n' be the number density of electrons moving in all directions inside the metal. Along any one particular direction, only $n/6$ electrons will move as there are six directions of possible motion along the three axes. Now consider three planes of cross-section area A , namely P_1 , P_2 and P_3 which are equidistant from each other at a distance equal to mean free path of electrons. Let the temperatures of planes P_1 and P_2 be T_1 and T_2 respectively such that $T_1 > T_2$. Clearly, the number of electrons that will transfer from plane P_1 to P_2 per unit area per unit time will be $= \frac{n v}{6}$ where v is the velocity of the electrons.

Therefore, heat energy transferred per unit area per unit time from P_1 to P_2 will be $= \left(\frac{n v}{6}\right) \times \text{(kinetic energy of an electron)} = \frac{n v}{6} \times \frac{3 k T_1}{2} = \frac{n v k T_1}{4}$

Similarly the energy transferred by heat per unit area per unit time from P_2 to P_1 will be $= \frac{n v}{6} \times \frac{3 k T_2}{2} = \frac{n v k T_2}{4}$

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So net heat energy transferred from plane P₁ to P₂ per unit area per unit time will be

$$\frac{Q}{A\Delta t} = \frac{nve}{6} \times \frac{3k}{2} [T_1 - T_2] \quad (\because T_1 > T_2).$$

$$\text{i.e. } \boxed{\frac{Q}{A\Delta t} = \frac{nvek}{4} [T_1 - T_2]} \quad - (i)$$

Also from definition of thermal conductivity, we have

$$K = \frac{(Q/A\Delta t)}{(dT/dx)} \text{ or } \boxed{\frac{Q}{A\Delta t} = K \frac{dT}{dx}} \quad (\text{sign ignored})$$

Now $\boxed{\frac{dT}{dx} = \frac{T_1 - T_2}{2\lambda}}$. Substituting this equation above, we get,

$$\boxed{\frac{Q}{A\Delta t} = K \frac{[T_1 - T_2]}{2\lambda}} \quad - (ii)$$

Comparing the right hand sides of equations (i) and (ii) we get

$$\frac{K[T_1 - T_2]}{2\lambda} = \frac{nvek}{4} [T_1 - T_2]$$

$$\text{i.e. } \boxed{K = \frac{nvek\lambda}{2}} \quad [\text{S.I. units of } K \text{ are } \text{Wm}^{-1}\text{K}^{-1}]$$

which represents the expression for thermal conductivity of metals.

Wiedmann-Franz Law :-

Wiedmann-Franz law states that the ratio of thermal to electrical conductivity of a metal is proportional to absolute temperature and this ratio is constant for all metals at a given temperature. i.e.

$$\frac{K}{\sigma} \propto T$$

$$\text{i.e. } \frac{K}{\sigma T} = L$$

where L is a constant called the Lorenz number. Its S.I. units are Wohm/K^2 .

Temperature Dependence of Electrical Conductivity :- $\sigma = \frac{ne^2}{m} \Sigma$ and

$$\Sigma = \frac{1}{v} = \frac{\lambda}{\sqrt{3kT/m}} = \lambda \sqrt{\frac{m}{3kT}}. \text{ So } \sigma = \frac{ne^2\lambda}{m} \sqrt{\frac{m}{3kT}} \text{ i.e. } \sigma \propto \frac{1}{\sqrt{T}}. \text{ But}$$

experiments show that $\sigma \propto \frac{1}{T}$.

Derivation of Weidemann-Franz Law.

We know that for metals,

$$K = \frac{n v k \lambda}{2} = \frac{n v^2 k \sigma}{2} \quad (\because \lambda = v \tau)$$

and

$$\sigma = \frac{n e^2 \tau}{m}$$

$$\text{So } \frac{K}{\sigma} = \frac{(n v^2 k \tau / 2)}{(n e^2 \tau / m)} = \frac{mv^2 k}{2e^2}$$

$$\text{ie } \frac{K}{\sigma} = \left(\frac{1}{2} m v^2\right) \times \frac{k}{e^2} \quad - (i)$$

But we also know that the kinetic energy of an electron is given by

$$\frac{1}{2} m v^2 = \frac{3}{2} k T \quad - (ii)$$

Substituting (ii) in (i), we get.

$$\frac{K}{\sigma} = \left(\frac{3}{2} k T\right) \left(\frac{k}{e^2}\right)$$

$$\text{ie } \frac{K}{\sigma} = \frac{3}{2} \left(\frac{k}{e}\right)^2 T$$

$$\text{or } \frac{K}{\sigma T} = \frac{3}{2} \left(\frac{k}{e}\right)^2 = L.$$

Classical Value and Experimental Value of L :-

In classical free electron theory, the value of L is obtained by substituting values of $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ and $e = 1.6 \times 10^{-19} \text{ C}$ so that

$$L = \frac{3}{2} \left(\frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}}\right)^2 = 1.12 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$$

However, the experimental value is $L = 2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$ and is obtained using quantum theory as

$$L = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 = 2.45 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$$

* Means topic is not in syllabus

Advantages of Classical Free Electron Theory

1. It explains the Ohm's law
2. It explains high electrical and thermal conductivity of metals.
3. It explains Weisbachmann's Franz law.
4. It explains high lustre and complete opacity of metals.

Note - The opacity is due to high absorption of all the incident electromagnetic radiations by the electrons inside the metal which are set into forced oscillations. The electrons get excited to higher states and later return to the lower states or normal states by emitting the same amount of energy in all directions, thus producing metallic lustre.

Drawbacks of Classical Free Electron Theory :-

1. It could not explain the temperature dependence of resistivity for metals, insulators and semiconductors.
2. It could not explain the paramagnetic susceptibility of metals.
3. It could not explain the specific heat of metals at low temp.
4. It could not explain why multi-valent atoms have lower electrical conductivity.
5. It could not explain the classification of materials into conductors, semi-conductors and insulators due to energy gap between conduction and valence bands.
6. It could not explain the experimental values for mean free path of an electron. $\text{Classical} < \text{Experimental}$.

* Preliminary Reading for Quantum Mechanics :-

The Classical Mechanics and its laws are applicable only for studying the dynamics of macroscopic (large sized) systems. For atomic or subatomic (e.g. electrons) systems, the laws of Classical Mechanics do not provide a correct explanation of experimental observations. In such systems, one has to make use of Quantum Mechanics principles which are only applicable to microscopic (very small size) systems.

In order to study the dynamics of a system in Classical Mechanics, one has to start by solving the Newton's second law equation which is the fundamental equation in Classical Mechanics. Likewise, in order to study the dynamics and properties of microscopic systems in Quantum Mechanics, one has to start by solving the Schrodinger wave equation which is the fundamental equation in Quantum Mechanics.

In order to understand the origin of Schrodinger Wave Equation, we proceed as follows. We know that both matter as well as radiation possess "dual nature" i.e. sometimes they both behave as waves and sometimes as particles.

Example of Wave Nature of Radiation \Rightarrow Diffraction, Interference, etc.

Example of Particle Nature of Radiation \Rightarrow Photoelectric Effect, Compton Effect,

Example of Particle Nature of Electrons \Rightarrow Collision between two electrons

Example of Wave Nature of Electrons \Rightarrow Electron Diffraction from Crystals.

Therefore, all moving particles possess wave-like characteristics which explain the wave-nature associated with the moving particle. So, we have to associate a wave with every such moving particle. This wave is called the de-Broglie wave or matter wave, such that the wavelength of this wave is related to its momentum by the de-Broglie relation

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

where 'm' is the mass of the particle and v is its velocity.

Mathematically, a de-Broglie wave cannot be a plane wave [i.e. Sin wave or Cosine wave] because plane waves always extend from $-\infty$ to $+\infty$ in space i.e. they are completely delocalized in space whereas the particle (whose wave nature they are supposed to represent) occupy a finite region of space and do not extend from $-\infty$ to $+\infty$ i.e. the particles are always well defined in space. A matter wave

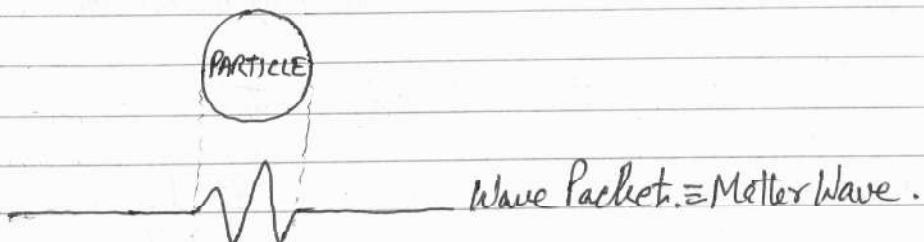
is therefore represented by a wave packet or a wave function or an eigenfunction which is a localized wave. Such a localized wave packet is formed by superimposition of infinite number of plane waves which differ only infinitesimally in their wavelengths and amplitudes such that after superimposition,

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of these plane waves, the resultant wave has a non-zero amplitude only in a finite region of space (where the particle is supposed to be present) and zero amplitude everywhere else. The most general expression of a wave packet is

$$\psi = \int_{-\infty}^{\infty} A(k) e^{ik(x-ct)} dk. \quad [\text{For one-dimensional Wave Packet}]$$

Graphical representation of one-dimensional wave packet is below



Note that the wave packet is non-zero i.e. it exists only where the particle exists and the wave packet is zero everywhere else. But the above expression of the wave packet implies that the wave packet ψ can be an imaginary or complex number and therefore ψ itself cannot be used as such to extract any information of the presence of particle. In fact the product of a complex number with its complex conjugate is always a real number. So

$$\psi\psi^* = |\psi|^2 \rightarrow \text{Always Real Number.}$$

In fact, $|\psi|^2$ represents the probability of finding the particle at a given point and time per unit volume i.e.

$|\psi|^2 \rightarrow$ Represents the Probability Density of the particle at given x and t .

In Quantum Mechanics, only those wave packets or wave functions are acceptable which obey the following Dirichlet conditions:

1. ψ must be single valued and continuous everywhere including at boundaries between two regions [Boundary Condition]
2. $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must be single valued and continuous everywhere [Boundary Condition]
3. $\int_{-\infty}^{\infty} |\psi|^2 dV = 1$ ie total probability of finding the particle must be equal to 1.

* Derivation of Time-Independent Schrodinger Wave Equation :-

Let us assume, for simplicity, that the expression of wave function is given by $\psi = A e^{i(kx - \omega t)}$ - (ii)

Now we know that $E = h\nu$ [Einstein Relation or Planck Relation]

$$\text{ie } E = h\nu \times \frac{2\pi}{\lambda} = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar} \quad \text{-(iii)}$$

Also we know that $p = \frac{\hbar}{\lambda}$ [de-Broglie Relation]

$$\text{ie } p = \frac{\hbar}{\lambda} \times \frac{2\pi}{\lambda} = \hbar k \Rightarrow k = \frac{p}{\hbar} \quad \text{-(iv)}$$

where $\hbar = \frac{h}{2\pi}$, $\omega = 2\pi\nu$ and $k = \frac{2\pi}{\lambda}$ by definition in Physics.

Substituting eqns (ii) and (iv) in eqn. (i) we get

$$\psi = A e^{\frac{i}{\hbar}(px - Et)}$$

Taking first order partial derivative of above equation w.r.t x , we get

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} A e^{\frac{i}{\hbar}(px - Et)} = \frac{ip}{\hbar} \psi$$

$$\text{or } -it \frac{\partial \psi}{\partial n} = p\psi \quad \text{ie } \left[-it \frac{\partial}{\partial n} \right] \psi = (p)\psi \quad \text{(iv)}$$

From eqn. (iv) we find that in Quantum Mechanics, momentum can be represented by a first order differential operator as

$$p \equiv -it \frac{\partial}{\partial n} \quad (\text{for one-dimension case})$$

Clearly, the operator for p^2 can be calculated as

$$p^2 \equiv p \times p = \left(-it \frac{\partial}{\partial n} \right) \left(-it \frac{\partial}{\partial n} \right) = -t^2 \frac{\partial^2}{\partial n^2}$$

ie the quantum mechanical operator for p^2 is given by

$$p^2 \equiv -t^2 \frac{\partial^2}{\partial n^2}$$

Schrodinger Equation Derivation.

These can be two types of particles in nature:

- (i) Free Particles
- (ii) Non-Free or Bound Particles.

Free Particles are those particles which do not experience any external forces or potential energy of such particles is always zero. For a free particle, the total energy is equal to its kinetic energy.

Non-Free Particles are those particles which are under the influence of an external force and therefore they have finite potential energy. Example:- An electron inside an atom is under the influence of the Coulomb force of the nucleus and therefore it has a potential energy. If the potential energy is -ve, the force is attractive and the particle is then bound to the system. For such a particle, the total energy is the sum of the kinetic and potential energies i.e.

$$E = E_k + V$$

The bracket is positioned above the equation $E = E_k + V$. It branches downwards into three arrows pointing to the right, each labeled with a component of energy:
 1. Potential Energy
 2. Kinetic Energy
 3. Total Energy

or

$$E = \frac{p^2}{2m} + V \quad (\because \text{Kinetic Energy} = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m})$$

The above equation is used to derive the Schrodinger Wave Equation in Quantum Mechanics as follows when the potential is time independent

- Multiply the above equation on the right hand side by the wave packet of the particle ψ .
- Replace the (p^2) with its operator $(-\hbar^2 \frac{\partial^2}{\partial x^2})$ in Quantum Mechanics

$$\text{i.e. } E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

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

$$\text{or } \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2} \psi = 0 \right] \Rightarrow \text{Schrodinger Wave Equation in Quantum Mechanics}$$

* Applications of Schrodinger Wave Equation :-

The Schrodinger wave equation can also be re-arranged as

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

The quantity on the left hand side in the brackets is called the Hamiltonian operator and can be denoted by H . So, we can write

$$H \psi = E \psi \quad (\text{Note that } H \text{ operator represents total energy of the particle.})$$

The above equation is called the Eigenvalue equation in Quantum Mechanics where E is the energy eigenvalue and ψ represents the wavefunction (also called the eigenfunction) of the particle corresponding to the Hamiltonian operator H . In most of the systems in Quantum Mechanics, we are required to calculate the expressions for energy eigenvalue E as well as the expression for eigenfunction ψ of the particle in the system and these are sufficient to explain the dynamics of the particle in the system.

Note that the Schrodinger Wave Equation given above can only be solved when the mathematical form (or expression) of the potential energy V of the particle is given to us. For example, in hydrogen atom

$$V = -\frac{Ze^2}{r}$$

Clearly the solution of Schrodinger wave equation will be simple and easy to compute if the mathematical expression of V is also simple. For complex potential energies, the solution of the Schrodinger Wave Equation is also complicated and difficult to obtain. To your surprise, the above expression of Coulomb potential energy for the electron in the hydrogen atom is not a simple potential and the solution of the Schrodinger wave equation for hydrogen atom is not a piece of cake (i.e. very difficult to obtain) and is a very complicated solution. Therefore, we have to use approximations for simpler potential energies which can ensure the following

- a) The potential is binding
- b) The solution of Schrodinger Equation is easy to obtain.

* Means not in syllabus

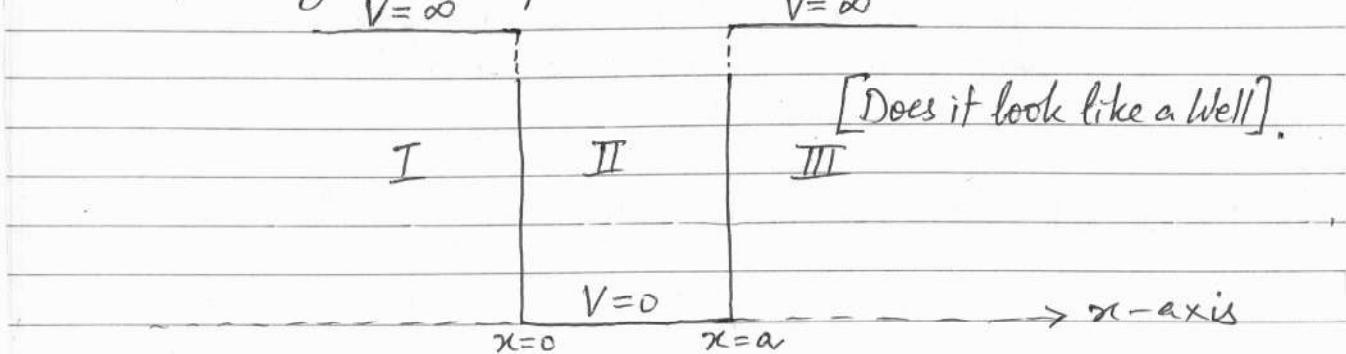
i.e. the potential should be simple and at the same time should be able to bind and confine the particle in space just as an electron is confined within the volume of the atom by the Coulomb potential energy. One such interesting potential is "infinite square well potential". The corresponding problem is called "particle in a box" problem. We now solve this problem first for the case of one-dimensional case and then for the three-dimensional case below.

* One-Dimensional Particle in Box Problem :-

Consider a particle (like an electron) moving along the x -axis under the influence of one-dimensional infinite square well potential which is given by

$$V = 0 \text{ for } 0 < x < a \\ = \infty \text{ everywhere else.}$$

Graphically, such a potential can be drawn as below



Note that the potential divides the x -axis into three regions I, II and III such that

Region I has $x < 0$ and $V = \infty$

Region II has $0 < x < a$ and $V = 0$

Region III has $x > a$ and $V = \infty$.

Also note that there are two boundaries, one at $x=0$ between region-I and region-II and the other boundary at $x=a$ between region-II and region-III. The boundaries are common to the regions on both its sides. Since the potential is different in the three regions, we will have to solve the Schrodinger equation individually for each of the three regions.

For Region -I :- The Schrodinger Wave Equation for this region is written as

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi_I}{\partial x^2} + E_I \psi_I = \infty \psi_I$$

The only solution to the above equation is $[\psi_I = 0]$ i.e. the wave function is zero in region -I.

So $|\psi_I|^2 = 0$ also. i.e. the probability density of finding the particle is zero in region -I. This means that the particle is not allowed in region -I.

For Region -III :- The Schrodinger Wave Equation for this region is also written as

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi_{III}}{\partial x^2} + E_{III} \psi_{III} = \infty \psi_{III}$$

implying that $\psi_{III} = 0$ and hence $|\psi_{III}|^2 = 0$ i.e the particle is not allowed in region -III also. So the particle, if at all, can only exist in region -II if $\psi_{II} \neq 0$. In that case, we say that the potential energy confines the particle motion only in the region -II between $0 \leq x \leq a$ and the particle is bound to that x -region. We check this now below.

For Region -II :- The Schrodinger Wave Equation for this region is written as

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi_{II}}{\partial x^2} + E_{II} \psi_{II} = 0$$

$$\text{i.e. } \frac{\partial^2 \psi_{II}}{\partial x^2} = -\frac{2mE_{II}}{\hbar^2} \psi_{II} = -k^2 \psi_{II} \quad (\text{let})$$

where we define $k^2 = \frac{2mE_{II}}{\hbar^2}$ - (ii)

The Schrodinger Wave Equation in region -II is now a simple mathematical equation of second order in x given by

$$\frac{\partial^2 \psi_{II}}{\partial x^2} = -k^2 \psi_{II} \quad \text{-(iii)}$$

It has a simple solution of the form

$$\psi_{II} = A \sin kx + B \cos kx \quad \text{-(iii)} \quad [\text{Verify this}]$$

where A and B are constants whose values are yet to be found.

To find the value of B , we use the first boundary condition for an acceptable wave function i.e. the wave function must be single valued and continuous everywhere including at the boundary between the different regions. Applying this condition at the first boundary at $x=0$ between the regions I and II we get

$$\psi_I(x=0) = \psi_{II}(x=0)$$

$$\text{i.e. } 0 = A \sin(0) + B \cos(0)$$

$$\text{i.e. } 0 = B \quad \boxed{B=0}$$

Substituting this value of $B=0$ in the solution of Schrödinger Wave Equation in Region-II we obtain

$$\boxed{\psi_{II} = A \sin kx}. - (iv)$$

Now applying the first boundary condition for acceptable wave function at the second boundary at $x=a$ between regions II and III we get

$$\psi_{II}(x=a) = \psi_{III}(x=a)$$

$$\text{i.e. } A \sin(ka) = 0$$

$$\text{or } \sin(ka) = 0$$

$$\text{or } ka = n\pi \quad \text{where } n=1, 2, 3, 4, \dots$$

$$\text{or } \boxed{k = \frac{n\pi}{a}} - (v) \quad [\text{Note that } n=0 \text{ is not allowed} \\ \because \text{it will imply } \psi_{II}=0 \text{ which is not acceptable}].$$

Comparing (iv) and (v) we obtain

$$\frac{2mE_{II}}{\hbar^2} = \frac{n^2\pi^2}{a^2}$$

$$\text{i.e. } \boxed{E_{II} = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2\hbar^2}{8mL^2}} - (vi) \quad (\because \hbar = \hbar/2\pi).$$

Likewise substituting (v) in (iv) we get

$$\boxed{\psi_{II} = A \sin \frac{n\pi x}{a}}$$

- (vii) [A more general solution
is $\psi_{II} = A e^{ikx} = A e^{inx/a}$]

To find the value of A , we use the third condition of acceptable wave function i.e.g.

$$\int_{-\infty}^{\infty} |\psi_{II}|^2 dx = 1$$

Since the particle can only exist in region-II, we need to carry out this integration only between the limits $x=0$ to $x=a$ i.e. we now have

$$^a \int |\psi_{II}|^2 dx = 1 \quad -(VIII)$$

Substituting eqn. (VII) in eqn (VIII) we get.

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

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

One can check easily that $\int_0^a \sin^2 \frac{n\pi x}{a} dx = \frac{a}{2}$

Therefore, we get $A^2 \left(\frac{a}{2}\right) = 1$ or $A = \sqrt{\frac{2}{a}}$ (IX)

Substituting (IX) in (VII) we get

$$\boxed{\psi_{II} = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \neq 0} - (IX) \boxed{\text{or } \psi_{II} = \sqrt{\frac{2}{a}} e^{in\pi x/a}}$$

Note that $\psi_{II} \neq 0$ and therefore $|\psi_{II}|^2 \neq 0$ in region-II. So there is a finite probability to find the particle in region-II and the particle is restricted to move only between $0 < x < a$ in region-II under the influence of the one-dimensional infinite square well potential energy. Hence the problem is referred to as "particle in one-dimensional box" problem. Also note that for the given problem, we have used the Schrodinger Wave Equation and the Dirichlet conditions to solve the expressions for energy eigenvalue and eigenfunction as

$$E = \frac{n^2 h^2}{8ma^2} \quad (n=1, 2, 3, \dots) \quad -(X)$$

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

Note that in the particle in box problem, the potential energy of the particle is zero in the region-II where it is confined.

So the particle is a free particle in this region. It is interesting to note that the energy of a freely moving particle in Quantum Mechanics is not allowed to have any possible range of continuous values but the energy of a free particle in Quantum Mechanics is quantized, i.e. it can have only certain specific values which are integral multiples of each other. For example,

$$E_1 = \frac{\hbar^2}{8ma^2} \text{ for } n=1 \text{ which is called the ground state energy}$$

$$E_2 = \frac{4\hbar^2}{8ma^2} \text{ for } n=2 \text{ which is called the first excited state energy}$$

and so on. In contrast, Classical Mechanics allows a free particle to have any energy

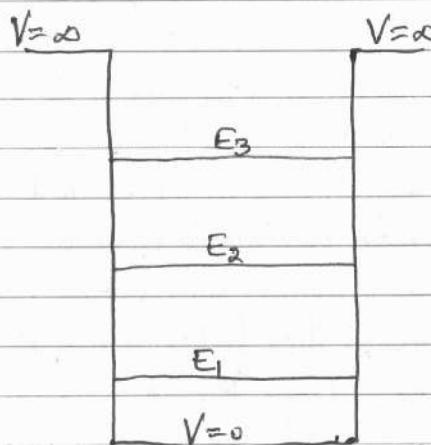
$$E = \frac{1}{2}mv^2$$

because there is no restriction on the velocity of a free particle in Classical Mechanics.

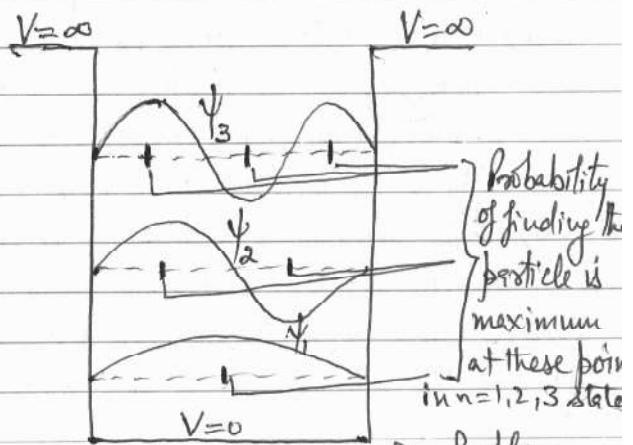
Note that "Quantization of Energy" is a characteristic of Quantum Mechanics. The word "Quantum" in fact means a "packet".

Note → **Photon** → It is defined as a quantum (or packet) of radiation energy.

Phonon → It is defined as a quantum (or packet) of vibrational energy.



Energy Levels in Particle in Box Problem



Eigenfunction in Particle in Box Problem

means

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(24)

* means not a part of syllabus

From the above two equations (xi) it is apparent that the allowed wave functions ψ and the allowed energy values E_n exist only for non-zero integral values of n . The number 'n' is called the "quantum number". Hence the energy spectrum consists of discrete energy levels (as shown above) where the spacing between the levels is determined by the values of quantum number 'n' and width of the box 'a'. It decreases with increase in 'a'. If 'a' is of the order of a few centimeters, the energy levels come very close to each other and form almost a continuum. But if 'a' has atomic dimensions, the spacing between the energy levels becomes appreciable and they become discrete.

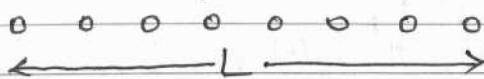
Quantum Free Electron Theory :- The free electron theory of solids was first modified in 1928 by Sommerfeld. It retains the key features of the classical free electron theory and included

- (i) the Pauli Exclusion Principle
- (ii) the Fermi-Dirac Statistics (Instead of Maxwell-Boltzmann Statistics for kinetic theory of gases)
- (iii) the Schrödinger equation approach (Instead of Classical Approach)
is used Quantum Mechanics to solve the problem rather than the Newton's second law equation of Classical Mechanics.

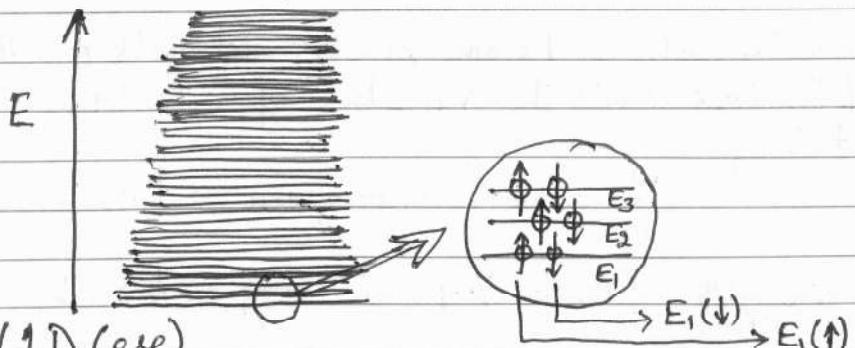
The main assumptions of this theory are as follows

- a) The energy of conduction electrons in a solid are quantized
 - b) The distribution of electrons in various allowed energy levels takes place according to Pauli Exclusion Principle
 - c) The electrons move in a constant potential $V=0$ inside the metal and are confined within defined boundaries.
 - d) Mutual interactions between electrons and ion cores and the repulsion between individual electrons are neglected so that the electrons move inside the metal with zero potential energy i.e. as free particles. [conductors]
 - e) The important feature of this model is that not all free electrons in metals are h.
- We now discuss the distribution of electrons among the allowed energy levels and determine the Fermi Energy and the total energy of all the electrons along with the density of states if the metal

is a one-dimensional crystal lattice as shown below



and the valence electrons in the atoms, all experience $V=0$ inside the lattice of length L . Clearly, the valence electrons will now behave as free electrons (or free particles) and experience a "one-dimensional infinite potential energy" inside the lattice i.e. they will behave as free particles in a one-dimensional box problem such that the length of box $= L = \text{length of the lattice}$. But since now, the value of L will be large (macroscopic), the energy levels will be very closely packed as shown below.



(i) Fermi Energy (1D Case)

The electrons are now distributed among the various possible energy levels starting from lowest energy state to higher energy states in accordance with the Pauli's exclusion principle which states that no two electrons can have all their quantum numbers identical i.e. each energy level can be occupied by two electrons with same value of ' n ' but different values of spin quantum number ' $s = \pm \frac{1}{2}$ '. Therefore, in a solid, an electron in a given energy state is characterized by two quantum numbers ' n ' and ' s ' where

$n \rightarrow$ principle quantum number $= 1, 2, 3, \dots$

and $s \rightarrow$ spin quantum number $= -\frac{1}{2} (\text{spindown}), +\frac{1}{2} (\text{spinup})$
Furthermore, different states may have different values (non-degenerate case) or the same value (degenerate case) of energy. In this nomenclature, each energy level with a given value of ' n ' is doubly degenerate i.e. the two electrons of opposite spin which are accommodated in each energy level have the same energy i.e. $E_1(\uparrow) = E_1(\downarrow)$. And the topmost filled energy level at OK is called Fermi level

and the energy corresponding to this level is called Fermi Energy represented by symbol E_F .

Clearly, if N is the total number of electrons in the linear metal lattice of length L , then for one-dimensional case we have

$$N = 2n_F$$

where $n_F \equiv$ principal quantum number of Fermi level.

With $n = n_F$, the energy eigenvalue expression for particle in 1-D box gives

$$E_F = \frac{\hbar^2}{2m} \left(\frac{n_F \pi}{L} \right)^2 = \frac{n_F^2 \pi^2 \hbar^2}{8mL^2} = \frac{n_F^2 \hbar^2}{8mL^2} = \frac{N^2 \hbar^2}{32mL^2}$$

Thus the value of Fermi Energy depends on the length (size) of the box and the number of electrons in it. For example, taking

$$\frac{N}{L} = 10^8 \text{ electrons/cm} = 1 \text{ electron/\AA} \quad [1\text{\AA} = \frac{10^{-10}}{10^8 \text{ cm}} \text{ m}]$$

we get $E_F = 7.4 \times 10^{-12} \text{ erg} = 4.8 \text{ eV}$

i.e. if we accommodate 10^8 electrons in 1 cm length of a one-dimensional metal lattice, the energy of the topmost filled energy level $E_F = 4.8 \text{ eV}$.

(iii) Total Energy :- The total energy E_0 of all the N electrons is calculated by adding up the energies of the individual electrons. For N electrons, the number of filled energy levels will be $N/2$ because each level can be occupied by two electrons with opposite spin. So we can write

$$E_0 = 2 \sum_{n=1}^{N/2} E_n$$

Here a factor of 2 appears because each level contains 2 electrons with equal energies. Using

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n \pi}{L} \right)^2 \text{ we get}$$

$$E_0 = 2 \times \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 \sum_{n=1}^{N/2} n^2 \quad \text{---(iv)}$$

(27)

$$\text{Since } \sum_{n=1}^{\infty} n^2 \approx \frac{1}{3} s^3 \text{ for } s \gg 1, \text{ so } \sum_{n=1}^{N/2} n^2 \approx \frac{1}{3} \left(\frac{N}{2}\right)^3$$

Substituting this in eqn (i) we get

$$E_0 = 2 \times \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \times \frac{1}{3} \left(\frac{N}{2}\right)^3 = \frac{1}{3} \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L}\right)^2 N$$

$$\text{i.e. } E_0 = \frac{1}{3} N E_F$$

Therefore the average kinetic energy of all the electrons at $T=0K$ will be

$$\bar{E} = \frac{E_0}{N} = \frac{1}{3} E_F$$

for a one-dimensional metal lattice.

(iii) Density of States :- The density of states is defined as the number of energy states present in a unit energy interval. It is denoted by $D(E)$ and is given by

$$D(E) = \frac{dN}{dE}$$

where dN represents the number of energy states present in the energy interval E and $E+dE$. Since each energy level can accommodate two electrons, the actual density of states will be twice the above value i.e.

$$D(E) = 2 \frac{dN}{dE}$$

Now, we already have

$$E = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 n^2 \quad \text{--- (i)} \quad \text{and} \quad \frac{1}{n} = \left(\frac{\hbar^2}{8mL^2 E}\right)^{1/2} \quad \text{--- (ii)}$$

$$\text{So } \frac{dE}{dN} = 2n \times \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 = \frac{\hbar^2 n}{4mL^2}$$

$$\therefore D(E) = 2 \times \frac{1}{\frac{dE}{dN}} = \frac{8mL^2}{\hbar^2 n} \quad \text{--- (iii)}$$

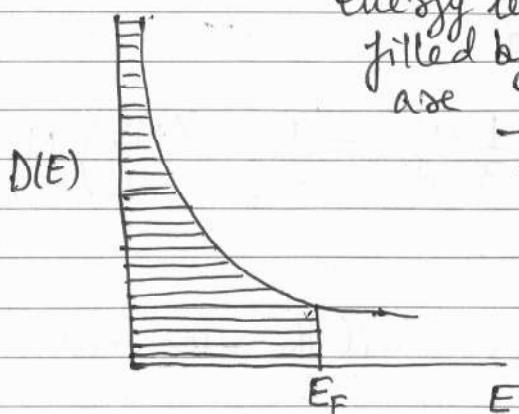
Substituting (ii) in (iii) we get

$$D(E) = \left(\frac{8mL^2}{\hbar^2 E}\right)^{1/2} = \frac{4L}{\hbar} \left(\frac{m}{2E}\right)^{1/2}$$

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28.

The plot of $D(E)$ vs E is shown below. It shows that all energy levels present below E_F are completely filled by electrons and all those above it are totally empty at 0 K temperature.



Thus, at 0 K, the Fermi Energy level divides or separates the filled energy levels from unfilled energy levels.

Quantum or Sommerfeld Free Electron Model in 3-D

Let us consider a specimen of a metal which is cubical in shape with side L . In the free electron model, the valence electrons move freely inside the metallic cube with $V=0$ and the restriction that they cannot escape out of the metal surface. This reduces the theory of conduction electrons in a metal to that of particles in a three dimensional cubical box of sides $= L$. Sommerfeld free electron model uses Schrödinger's Wave Equation to calculate the allowed energies for conduction electrons in a solid.

The three dimensional Schrödinger's Wave Equation for a free particle ($V=0$) in a cubical box of length L is written as

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = E \psi \quad [\text{Here } \psi = \psi(x, y, z)].$$

Note that here one has to take contributions for all three components of the momentum (p_x, p_y and p_z) of the free electrons and therefore include the corresponding quantum mechanical operators for $p_x^2/2m, p_y^2/2m$ and $p_z^2/2m$. Also in the three dimensional case, the total kinetic energy of the particle will be

$$E = E_x + E_y + E_z$$

where E_x = kinetic energy along x -axis

E_y = kinetic energy along y -axis

E_z = kinetic energy along z -axis.

Since x, y and z are independent variables, so we can write
 $\psi(x, y, z) = \phi(x)\phi(y)\phi(z)$

where $\phi(x), \phi(y)$ and $\phi(z)$ correspond to eigenfunctions for 1D cases along x -axis, y -axis and z -axis, i.e.

$$\phi(x) = \sqrt{\frac{2}{L}} \sin \frac{n_x \pi x}{L}; \quad \phi(y) = \sqrt{\frac{2}{L}} \sin \frac{n_y \pi y}{L}; \quad \phi(z) = \sqrt{\frac{2}{L}} \sin \frac{n_z \pi z}{L}.$$

Where n_x, n_y, n_z are three principal quantum numbers each of which must be non-zero positive integer i.e

$n_x, n_y, n_z \in 1, 2, 3, \dots$. So the total eigenfunction for the 3D-case becomes

$$\boxed{\psi(x, y, z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}} \quad \text{--- (i)}$$

Likewise, the total energy of the free particle in 3D-box will be

$$E = E_x + E_y + E_z \quad (\text{sum of kinetic energies along 3 axes})$$

Extending the expression for E in 1D-box case where

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

one obtains for the 3-D box case

$$E = E_x + E_y + E_z = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\text{i.e. } \boxed{E = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2)} \quad \text{--- (ii)}$$

From eqns (i) and (ii) we derive the following conclusions

- The three integers n_x, n_y and n_z (quantum numbers) are required to specify completely each energy state of the electron in 3D box problem. No quantum number can be equal to zero, otherwise $\psi(x, y, z) = 0$

which would mean that the electron cannot exist inside the box (or metal).

- b) The Energy of a given energy state depends on the sum of the squares of the quantum numbers n_x, n_y and n_z and not on their individual values.
- c) Several combinations of n_x, n_y, n_z may give different $\psi(n, y, z)$ values but of the same energy. Such energy states are said to be degenerate i.e. if several states have the same energy, they are said to be degenerate. For example $(n_x, n_y, n_z) = (1, 1, 2), (1, 2, 1), (2, 1, 1)$ have different values of $\psi(n, y, z)$ but in each case the energy value is exactly the same i.e.

$$E_{(1,1,2)} = E_{(1,2,1)} = E_{(2,1,1)} = \frac{6\hbar^2}{8ml^2}$$

These energy levels are therefore called three fold degenerate or triply degenerate. It can also be noted that the ground state $(n_x, n_y, n_z) = (1, 1, 1)$, as also several other states like $(n_x, n_y, n_z) = (2, 2, 2)$ are non-degenerate.

For a piece of metal of macroscopic dimensions, say 1cm^3 , the energy of the ground state ($n_x = n_y = n_z = 1$) is of the order of 10^{-15}eV and hence may be taken to be zero for all practical purposes. Also the maximum separation or spacing between successive energy levels is less than 10^{-6}eV and hence the energy levels are very closely spaced in their energy values and the distribution of energy spectrum may be regarded as almost continuous.

Since the energy levels are very close to each other, this leads to the concept of density of states which is defined as the number of energy states that lie in a unit energy interval.

Density of States (3D-case): - Mathematically, density of states is represented by $D(E)$ where

$$D(E) = \frac{dN}{dE}$$

where dN represents the number of energy states lying between the energy interval from E to $E+dE$. Since each energy level can accommodate two electrons (with opposite spin in accordance with Pauli Exclusion Principle), the actual density of states will be twice the above value, i.e.

$$\boxed{D(E) = 2 \frac{dN}{dE}} \quad - (i)$$

Now the energy of a free electron inside a metal (3D) is known to be

$$E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

The above expression can be rewritten as

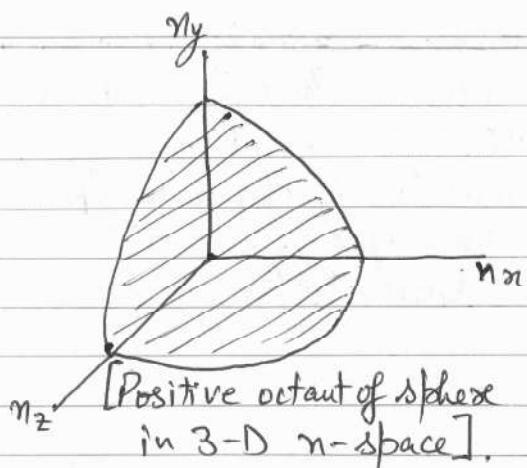
$$n_x^2 + n_y^2 + n_z^2 = \left(\frac{\sqrt{8mL^2 E}}{\hbar} \right)^2$$

The above equation represents the equation of a sphere of radius given by

$$\sqrt{\frac{8mL^2 E}{\hbar^2}}$$

in a 3-dimensional n -space with 1 axis n_x, n_y and n_z . [Note that eqn. of a sphere in 3-D actual space with 1 axes x, y, z is $x^2 + y^2 + z^2 = r^2$ where r is the radius of the sphere].

Note that every point in the n -space will have a fixed value of (n_x, n_y, n_z) and hence the different points in the n -space will represent different energy states of the electron inside the metal. Furthermore, the quantum numbers n_x, n_y, n_z can only have positive integral values, so the points corresponding to the allowed energy states for the electrons inside the metal can exist only in the positive octant of the sphere in n -space, i.e. the number of states of energy less than E must be equal to the volume of the positive octant of the sphere in n -space.



$$\text{i.e. } N = \frac{1}{8} \times \frac{4}{3} \pi R^3$$

$$\text{i.e. } N = \frac{1}{8} \times \frac{4}{3} \pi \left(\sqrt{\frac{8mE}{\hbar^2}} \right)^3$$

$$\text{i.e. } N = \frac{\pi}{6} \left(\frac{8mE}{\hbar^2} \right)^{3/2}$$

$$\text{i.e. } N = \frac{\pi L^3}{6} \left(\frac{8mE}{\hbar^2} \right)^{3/2}$$

i.e.
$$N = \frac{\pi V}{6} \left(\frac{8m}{\hbar^2} \right)^{3/2} E^{3/2}$$

\rightarrow Formula for No. of states with energy less than or equal to E

In terms of t we can rewrite the above expression as

$$N = \frac{V}{6\pi^2} \left(\frac{2m}{t^2} \right)^{3/2} E^{3/2} \quad (\because t = \hbar/2\pi)$$

Now, by definition, the density of states

$$D(E) = 2 \frac{dN}{dE} = 2 \times \frac{V}{6\pi^2} \left(\frac{2m}{t^2} \right)^{3/2} \times \frac{3}{2} E^{1/2}$$

i.e.
$$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{t^2} \right)^{3/2} E^{1/2} = \frac{4}{3}\pi V \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$
 - (iii)

\rightarrow Formula for Density of states for electrons in a 3-D metal lattice.

Fermi level and Fermi Energy (in 3D) :-

Let us consider the occupancy of allowed energy states at absolute zero temperature i.e. $T=0$ K. If we have to add electrons to the allowed energy states, first we will fill the ground state (with two electrons of opposite spin) and then the higher energy states (excited states) will be filled similarly, until the last electron in the metal is added at a level above which all other states are unoccupied.

This level is defined as the fermi level and is denoted by $E_F(0)$ at $T=0$ K. i.e. Fermi level is the top-most $E_F(0)$.

energy level filled with electrons at $T=0K$. In other words, the Fermi level $E_F(0)$ divides or separates the filled and empty energy states at $T=0K$. The energy of the Fermi level is called the Fermi Energy and is represented by $E_F(0)$ at $T=0K$.

To calculate the value of Fermi Energy $E_F(0)$ we have to first calculate the expression for the total number of electrons inside the metal. This can be done in two ways :

First Way :- From eqn (ii) we know that the total number of energy states in the metal with energy $\leq E$ is given by

$$N = \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2} = \frac{\pi V}{6} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}$$

Since every energy level can occupy two electrons, so total number of electrons in the energy states lying between energy $= 0$ to $E_F(0)$ will be at $T=0K$

$$N_e = 2N = 2 \times \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F(0)^{3/2} = \frac{2 \times \pi V}{6} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F(0)^{3/2}$$

or $N_e = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F(0)^{3/2} = \frac{8\pi V}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F(0)^{3/2}$ -(iv)

Second Way :- By definition of density of states, we have

$$D(E) = \frac{2dN}{dE} \cdot \text{So, at } T=0K, \text{ we obtain}$$

$$\text{or } dN = N_e = \int D(E) dE$$

Substituting the value of $D(E)$ from eqn (iii) in above eqn. we get

$$N_e = \int_0^{E_F(0)} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} dE$$

(34)

$$\text{i.e. } N_e = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{E_F(0)} E^{1/2} dE$$

$$\text{i.e. } N_e = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3} E_F^{3/2}(0)$$

$$\text{i.e. } N_e = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}(0) = \frac{8\pi V}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}(0)$$

—(v)

Derivation of Fermi Energy :- Using either eqn (iv) or (v)

we get on rearranging

$$E_F(0) = \left(\frac{3\pi^2 N_e}{V} \right)^{2/3} \frac{\hbar^2}{2m} = \left(\frac{3N_e}{8\pi V} \right) \frac{\hbar^2}{2m}$$

—(vi)

L Formula for Fermi Energy

Now, by definition, electron concentration (or electron density) in solids is defined as

$$n = \frac{N_e}{V}, \text{ so we can write the above}$$

expression for $E_F(0)$ as

$$E_F(0) = \left(3\pi^2 n \right)^{2/3} \frac{\hbar^2}{2m} = \left(\frac{3n}{8\pi} \right)^{2/3} \frac{\hbar^2}{2m}$$

—(vii)

L Formula for Fermi Energy

Also we know that if A is the Avogadro Number i.e.

$A = 6.023 \times 10^{23}$ particles/mol and ρ is the density of the substance in kg/m³ and W is the atomic weight of the element in grams then

$$\text{No. of particles or atoms in } W \text{ grams} = 6.023 \times 10^{23}$$

$$\text{No. of particles or atoms in } 1 \text{ gram} = \frac{6.023 \times 10^{23}}{W}$$

$$\text{No. of particles or atoms in } 1 \text{ kg} = \frac{6.023 \times 10^{23} \times 1000}{W}$$

$$\text{i.e. No. of atoms per 1 kg of material} = \frac{6.023 \times 10^{26}}{W}$$

So no. of atoms per unit volume of material ie $\frac{\text{Atoms}}{V}$ will be

$$\frac{\text{Atoms}}{V} = \frac{6.023 \times 10^{26} \times \rho}{W} = \frac{A \times \rho \times 1000}{W}$$

$$\text{i.e. } \frac{\text{Atoms}}{V} = \frac{1000 A \rho}{W}$$

For monovalent atoms, every atom contributes one electron to the metal. whereas for multivalent atoms, every atom contributes electrons = no. of valence electrons in the atom. Therefore, we can calculate the no. of electrons per unit volume of material, $n = Ne/V$ as

$$\frac{Ne}{V} = n = \frac{\text{Atoms}}{V} \times \frac{\text{No. of valence electrons in an atom}}{V}$$

$$\text{i.e. } \boxed{\frac{Ne}{V} = n = \frac{1000 A \rho}{W} \times \text{No. of valence electrons in an atom}}$$

The above expression can be substituted in eqns (vi) or (vii) to calculate the Fermi Energy of a metal if its density and atomic weight is given.

Note that the electron concentration for metals is of the order of $n \approx 10^{28}/m^3$ which gives $E_F(0) \approx 1.7 \text{ eV}$. This is something entirely different from Classical theory according to which the electrons should have zero energy at absolute zero temperature.

Variation of Fermi Energy With Temperature :-

Fermi Energy decreases with increase in temperature. An approximate relationship between Fermi Energy at a temperature $T \text{ K}$ and Fermi Energy at 0K , represented by $E_F(T)$ and $E_F(0)$ respectively is given by

$$E_F(T) = E_F(0) \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F(0)} \right)^2 \right]^{-\frac{1}{2}} \quad \text{(i)}$$

where $k = \text{Boltzmann constant}$
 $= 1.38 \times 10^{-23} \text{ J K}^{-1}$

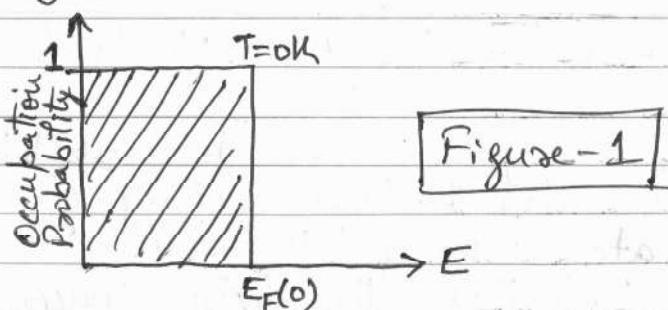
At room temperature (i.e $T=300\text{K}$), the value of the ratio

$$\frac{kT}{E_F(0)} = 0.015 \text{ for } E_F(0) = 1.7 \text{ eV. [for metals].}$$

Therefore, it follows that the temperature dependence of Fermi Energy is very slight and for all practical purposes (at room temperature) we can assume $E_F(T) \approx E_F(0)$ or $E_F(T) \leq E_F(0)$ and so at $T > 0K$ Fermi level no longer represents the top-most filled energy level as we shall see below.

Occupation Probability :-

From the definition of Fermi level at $T=0K$ (i.e. Fermi level is the top-most filled energy level at $T=0K$) we can say that the probability that a given energy state of energy between $0 \leq E \leq E_F$ is ~~filled~~ exactly equal to one. Graphically, this can be expressed as below



The shaded region in the figure signifies that all energy states below $E_F(0)$ are occupied (or filled) by electrons in the metal.

We now discuss the effect of temperature on the occupancy of energy levels, i.e. we will now study how the electrons are redistributed among the various energy levels in a conductor when the temperature becomes more than $0K$. It is apparent that for $T > 0K$, the Fermi level may not be the topmost filled level since some of the electrons from the filled energy levels may be excited to the higher empty levels by absorbing the thermal energy available at $T > 0K$.

Note that we cannot apply Maxwell-Boltzmann distribution to electrons in Quantum Mechanics because
a) they obey Pauli Exclusion Principle.

and b) They are indistinguishable particles.

The statistical distribution function applicable to quantum particles is the Fermi-Dirac distribution function and is represented by $f(E)$. Mathematically, it is expressed as

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

where $E_F \equiv E_F(T)$ is the fermi Energy at T K.
- (ii)

The fermi-dirac distribution function $f(E)$ basically denotes the occupation probability of an electron in an energy level E at any temperature T . One can check that for $T = 0K$

$$\text{and } \frac{(E-E_F)/kT}{e^{\infty}+1} = -\infty \text{ if } E < E_F \quad ; \text{ for } T=0K$$

$$\frac{(E-E_F)/kT}{e^{+\infty}+1} = +\infty \text{ if } E > E_F$$

$$\text{so that } f(E) = \frac{1}{e^{\infty}+1} = 1 \text{ for } E < E_F \quad ; \text{ for } T=0K$$

$$\text{and } f(E) = \frac{1}{e^{+\infty}+1} = 0 \text{ for } E > E_F$$

which is the same as expressed in Figure-1 before with $f(E) \equiv$ occupation probability. However, if we plot a similar figure at a temperature $T > 0K$ we get using eqn (ii)

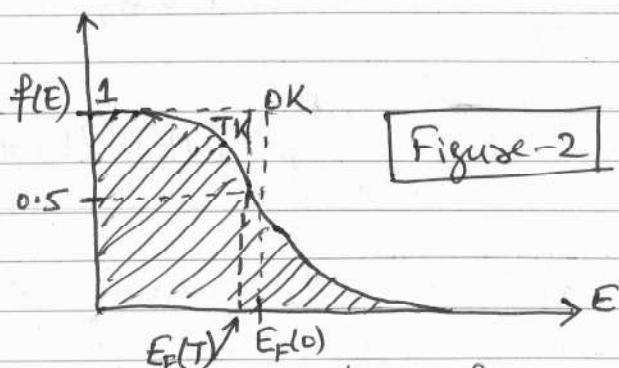


Figure-2

We note the following from the above figure :-

1. At $T > 0K$, $E_F(T) < E_F(0)$
2. At $T > 0K$, some energy states below $E_F(T)$ are empty and some energy states above $E_F(T)$ are filled due to excitation of electrons due to absorption of thermal energy.

c) At $E = E_F(T)$, $f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} = \frac{1}{2}$ i.e at $T > 0K$,

The Fermi level is defined as the energy level whose probability of finding the electron is exactly equal to 0.5.

d) For temperatures greater than 0K but less than the melting point of the metal [i.e practical temperatures for which $kT \ll E_F(0)$], the distribution function $f(E)$ loses its "step character" i.e Fermi level no longer separates the filled energy states from empty states. However, $f(E) \equiv \text{occupation probability}$ decreases gradually from 1 to 0 near $E_F(T)$ in contrast to the behaviour of $f(E)$ at 0K where is abruptly reduces from 1 to 0 at $E_F(0)$. This indicates that at $T > 0K$, some of the states below $E_F(T)$ are empty (orange region in Figure 14.2) while some others above it are filled by electrons (green region in Figure 14.2). This is because some of the electrons from the energy states below $E_F(T)$ gain thermal energy and get excited to the states above $E_F(T)$ and contribute to conduction in metals and only those free electrons are called conduction electrons.

Average kinetic energy of electron at $T=0K$

The average kinetic energy of an electron at a temperature T is given by

$$\bar{E} = \frac{1}{N_e} \int_0^{\infty} E D(E) f(E) dE$$

However, at $T=0K$, the maximum energy of electron = $E_F(0)$ and $f(E) = 1$ so that

$$\bar{E} = \frac{1}{N_e} \int_0^{E_F(0)} E D(E) dE.$$

Substituting the formula⁰ for density of states

$$D(E) = \frac{V}{2\pi^2} \left(\frac{g_m}{\hbar^2}\right)^{3/2} E^{1/2} \quad \text{in the above equation,}$$

we get

$$\bar{E} = \frac{1}{N_e} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{E_F(0)} E^{3/2} dE$$

$$\text{i.e. } \bar{E} = \frac{1}{N_e} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F(0) \times \frac{2}{5}$$

Now substituting the formula for $N_e = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F(0)$

in the above equation, we get .

$$\bar{E} = \frac{\frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F(0) \times \frac{2}{5}}{\frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F(0)} = \frac{3}{5} E_F(0)$$

$$\text{i.e. } \boxed{\bar{E} = \frac{3}{5} E_F(0)}$$

Failure of Quantum Free Electron Theory :-

- It failed to explain the distinction between conductors, insulators and semiconductors and the origin of energy gap in the conduction and valence bands.
- It could not explain why certain solids have a large number of free electrons and thus behave as good conductors while certain others have hardly any free electrons and are therefore insulators.
- It also could not explain the variation of resistivity with temperature for insulators and semiconductors.
- It could not explain the properties of semiconductors.

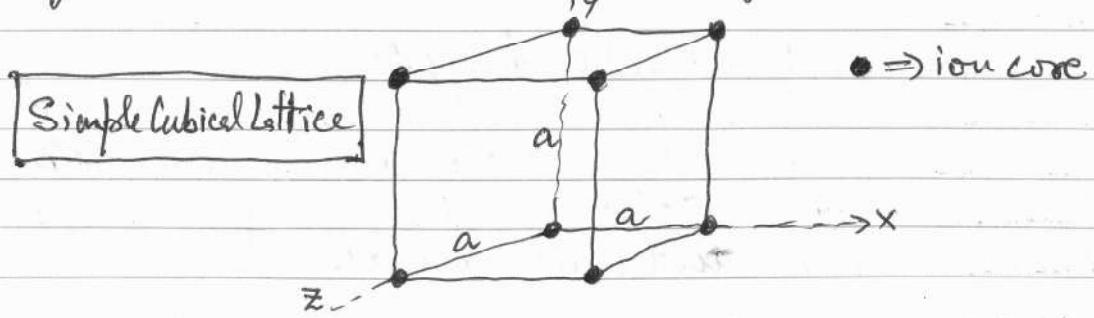
Important feature of Quantum Free Electron Theory :- The most important feature of this theory is that it destroys the notion of classical theory that all free electrons are conduction

electrons. According to this theory, only few free electrons whose energy lies in the interval $E_F(T) \pm kT$ in the vicinity of Fermi level contribute to the mechanism of conduction and only these free electrons are called conduction electrons.

Band Theory of Solids :-

The failure of the free electron model is due to the oversimplified assumption that a conduction electron in a metal experiences a constant $V=0$ potential due to the ion cores and hence is free to move about in the crystal; the motion being restrained only by the surface of the crystal.

In a solid metal, the ion cores are distributed periodically in 3 dimensional space at the lattice sites. For a simple cubic lattice, as shown below, the periodic distance of position of ion cores is equal to lattice constant 'a' for all the three axes (x -axis, y -axis and z -axis).



Note that the lattice constant 'a' equals the minimum distance between two successive ion cores in a cubical lattice along any of the three \perp axes. Now let us consider an isolated single ion core of charge ($+Ze$). The potential (Coulomb) energy of a free electron in its neighbourhood will be

$$V(r) = -\frac{Ze^2}{r} \text{ where } r \equiv \text{radial distance from center of the ion core.}$$

Graphically, the variation of V vs r in such a case can be depicted as below

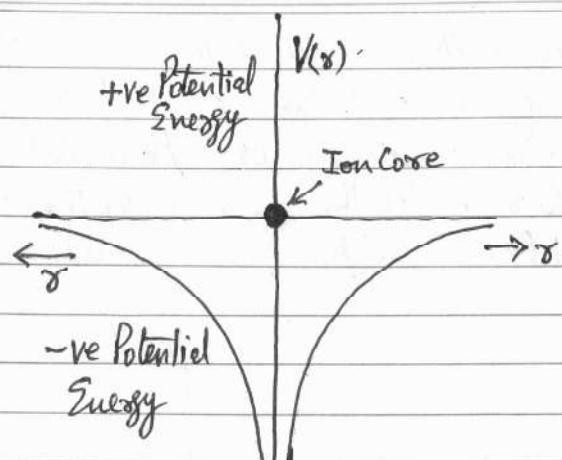


Figure-1:- Actual Coulomb Potential Energy for a single ion core

In order to find the allowed energies of electrons in solids, we have to solve the Schrödinger Wave Equation for an electron in a crystal lattice. Figure-2 shows the actual potential energy of a free electron in a one-dimensional periodic crystal lattice with lattice constant = a and length of lattice = L .

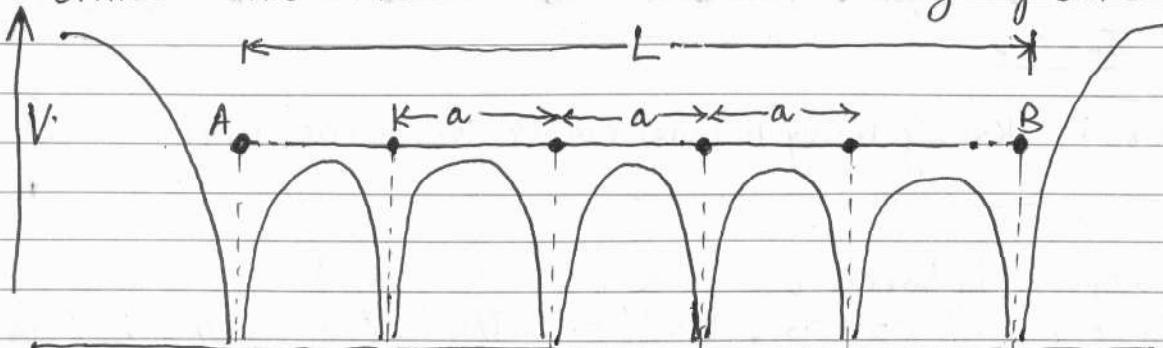


Figure-2:- Actual Potential Energy of a free electron in 1D lattice

Note that at the two end points of the lattice A and B, the potential energy energy V is very large and positive, so that the free electron remains confined or trapped always within the lattice and never escapes it.

Kronig-Penny Model :- - Kronig and Penny suggested a simplified rectangular well potential (of finite height) for every ion core in the lattice as shown below in figure 3.

$$V=V_0 \quad V=V_0 = \text{constant}.$$

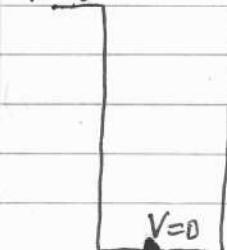


Figure 3:- Kronig-Penny Potential for a single ion core

Then, for a one dimensional periodic lattice with lattice constant = a , the potential energy of an electron will take the form of a periodic array of such rectangular potential wells with a period of $(a+b)$ where 'b' is the width of the potential barrier and each well has a depth V_0 . This is shown in Figure 4 below.

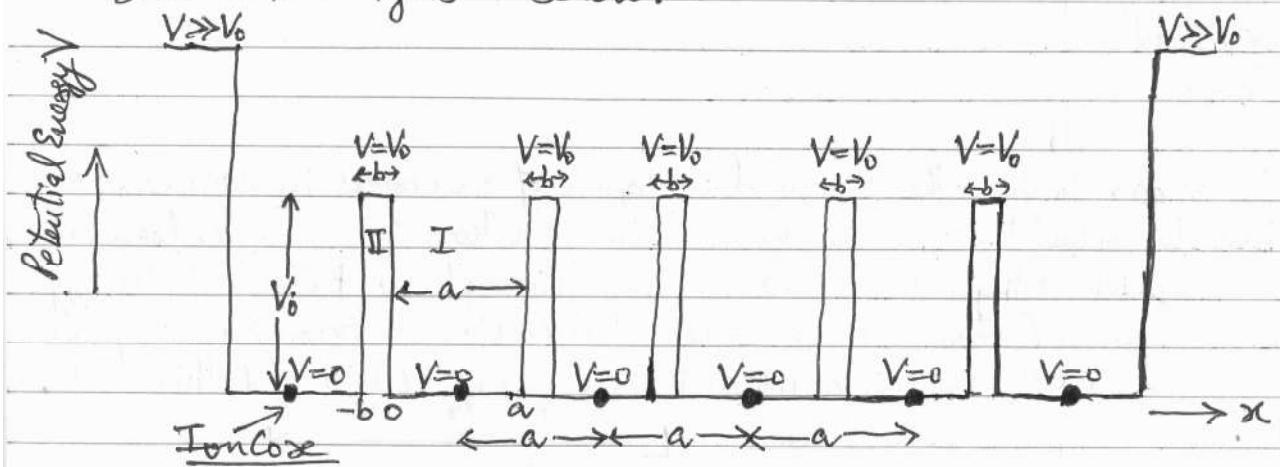


Figure 4:- Kronig Penny Potential energy for electron in 1D lattice

The regions between $0 \leq x \leq a$, $V = 0$ and for regions between $-b \leq x \leq 0$, $V = V_0 = \text{constant}$. Outside the boundary of the one-dimensional crystal $V \gg V_0$ so that the electron remains confined within the one-dimensional lattice.

Now the Schrodinger equation for these two regions can be written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{\hbar^2} E \psi = 0 \quad \text{for } 0 \leq x \leq a$$

and $\frac{\partial^2 \psi_{II}}{\partial x^2} + \frac{8m\pi^2}{\hbar^2} (E - V_0) \psi_{II} = 0 \quad \text{for } -b \leq x \leq 0$

We can rewrite the above equations as

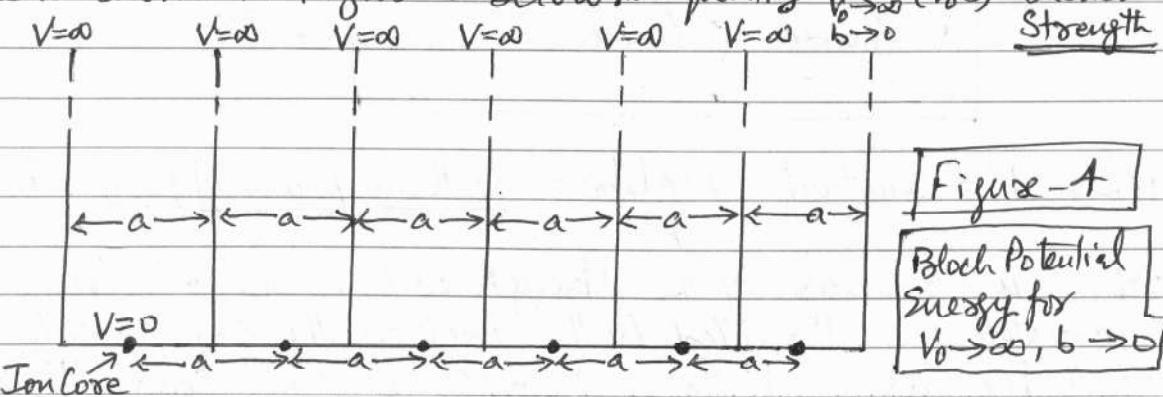
$$\frac{\partial^2 \psi_I}{\partial x^2} + \alpha^2 \psi_I = 0 \quad \text{for } 0 \leq x \leq a \text{ with } \alpha^2 = \frac{8\pi^2 m E}{\hbar^2}$$

and $\frac{\partial^2 \psi_{II}}{\partial x^2} + (-\beta^2) \psi_{II} = 0 \quad \text{for } -b \leq x \leq 0 \text{ with } \beta^2 = \frac{8\pi^2 m (V_0 - E)}{\hbar^2}$

— (i)

Kronig and Penney considered the simplest possibility when $V_0 \rightarrow \infty$ and $b \rightarrow 0$ but the product $(V_0 b)$ remains finite. Under these conditions, the model is simplified to the case of a series of infinitely deep potential wells (infinite square well potentials) separated by infinitely thin potential barriers.

This is shown in Figure 5 below. The quantity $\lim_{b \rightarrow 0} (V_0 b)$ is Barrier Strength



Now, the potential becomes periodic with distance = a i.e.

$$V(x) = V(x+a) \quad [\text{Periodic Potential for } V_0 \rightarrow \infty, b \rightarrow 0]$$

Bloch introduced a theorem known as [Bloch theorem] according to which the solution of the Schrödinger equation for a particle in a periodic potential is always a product of two functions

- i) a free particle wave function e^{ikx} for infinite square well potential (i.e. particle in 1D box problem wave function)
- and ii) a periodic wave function $U(x)$ that has the same period as the potential energy.

So if the potential repeats itself after a distance = a , i.e. if

$$V(x) = V(x+a+b)$$

then according to Bloch theorem, the solutions of the Schrödinger wave equations in regions I and II will be of the form

$$\boxed{\Psi(x) = U(x) e^{ikx} \text{ with } U(x) = U(x+a+b)} \quad -\text{(iii)}$$

↳ Bloch functions

The wave functions of the above type are called Bloch functions which change periodically with increasing values of x .

We substitute the Bloch wave functions of eqn (ii) into the Schrödinger equations (i) and solve them simultaneously using the boundary conditions for acceptable wave functions in Quantum Mechanics. This yields the following expression.

$$\boxed{P \frac{\sin da}{\alpha a} + \cos da = \cos ka} \quad - (iii)$$

where $P = \text{constant} = \frac{m a b V_0}{\hbar^2} = \underline{\text{scattering power of potential barrier}}$

which is a measure of the strength with which electrons in a crystal are attracted to the ions on the crystal sites.

Thus by varying P from 0 to ∞ we can cover the whole range for a completely free electron ($P=0$) to the completely bound electron ($P=\infty$) i.e. increasing the value of P has the physical meaning of binding the electron more strongly to a particular potential well.

Note that there are only two variables in eqn (iii) namely a and k . Also, the energy of the electron inside the potential well (region-I) is related to the variable a through the relation

$$\alpha^2 = \frac{2mE}{\hbar^2} \Rightarrow \boxed{E = \frac{\alpha^2 \hbar^2}{2m}}$$

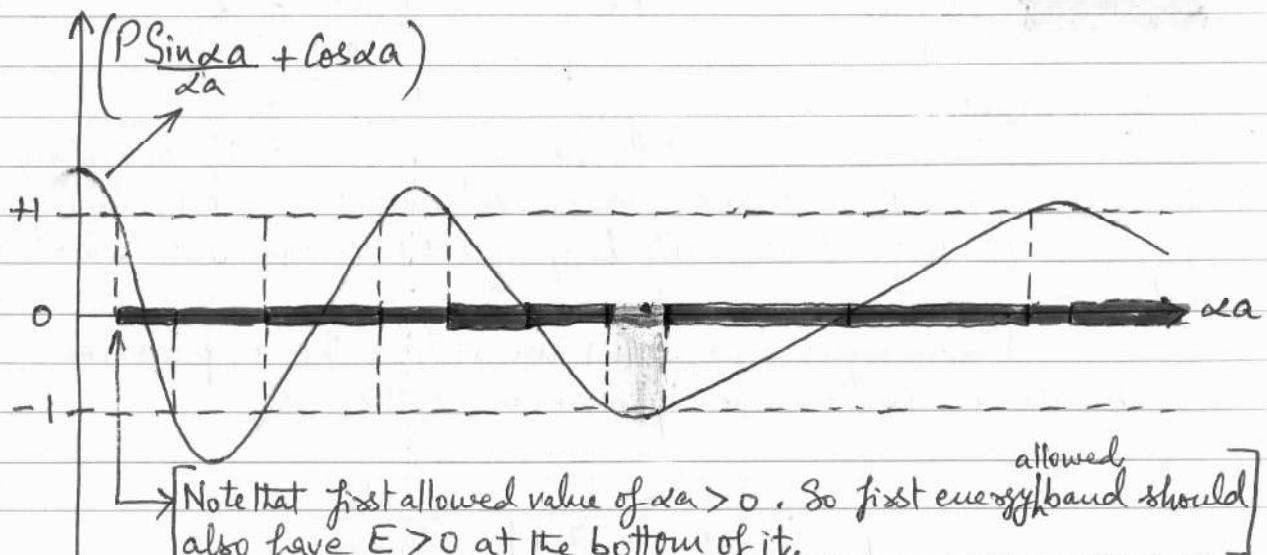
Now, since the RHS of eqn (iii) is equal to $\cos ka$, so it is bounded i.e. it can only assume values between +1 and -1. So only those values of the terms on RHS or LHS of eqn (iii) are allowed and correspond to the physical energy states of the electrons for which $\text{RHS} = \text{LHS}$ lie between +1 and -1.

To find the allowed values of energy E of electron inside the metal lattice, we require to find the allowed values of the variable α ($\propto \alpha a$). This is done by plotting the LHS of eqn (iii) vs (αa) for an arbitrary value of P .

Formation of Energy Bands :-

Case-I :- When P is not very large e.g. $P = 3\pi/2$

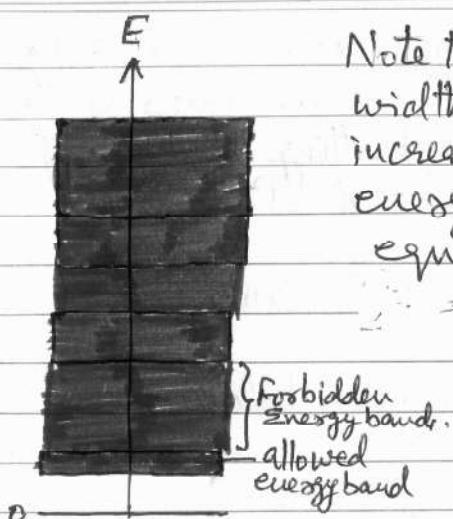
The plot of LHS of eqn (iii) vs. (αa) is shown below.



The allowed ranges of (αa) which correspond to physical energy states of the electron inside the metal lattice are highlighted by green color. The values of (αa) highlighted in red color are forbidden. Since the energy of the electron inside the metal lattice E is proportional to (αa) through the relation

$$E = \frac{(\alpha a)^2 \hbar^2}{2ma^2} = \frac{\alpha^2 \hbar^2}{2m} \quad (\text{iv})$$

therefore, the electron is allowed to have only certain ranges of energy corresponding to the allowed values of (αa) and other energies will be forbidden. Thus the motion of electrons in a periodic lattice is characterized by the formation of allowed bands separated by forbidden regions. This is highlighted in figure below.



Note that as the value of (αa) increases, the width of the allowed energy bands also increases and the width of the forbidden energy bands decreases. Note that in eqn (iii), when $\alpha a = \pm n\pi$, we obtain

$$\begin{aligned} \cos \alpha a &= \cos ka \\ \text{i.e. } ka &= \pm n\pi \\ \text{i.e. } k &= \pm \frac{n\pi}{a} = \alpha \end{aligned} \quad -(v)$$

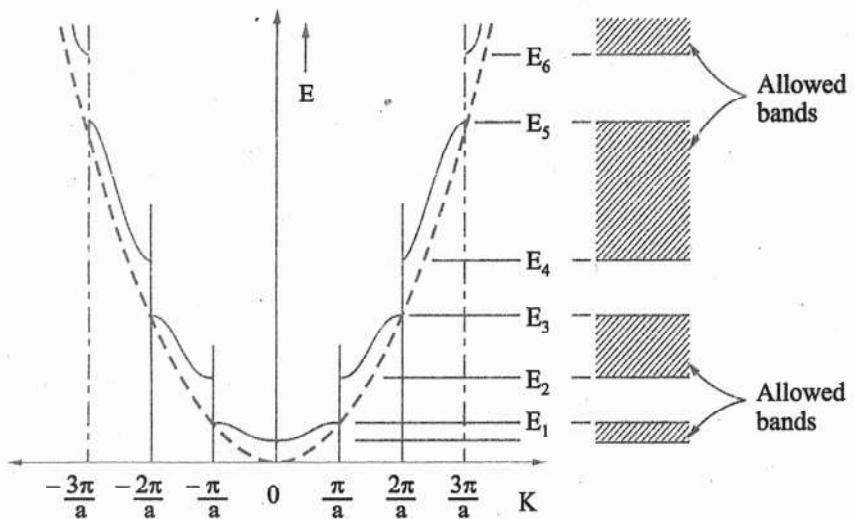
E-k Curves :-

These values of k or α represent the points of discontinuity in energy bands in the E - k curves for electrons in the crystal. This is because the RHS of eqn (iii) becomes ± 1 for values of $k = \pm \frac{n\pi}{a}$, where $n = 1, 2, 3, \dots$.

From eqns (iv) and (v) we obtain the expression for possible electron energies in a metal lattice as

$$E = \frac{\alpha^2 k^2}{2m} = \frac{k^2 h^2}{2m} = \frac{n^2 \pi^2 h^2}{2ma^2}$$

Therefore E vs k curve will be parabolic in nature, which is shown by the dotted line in the figure below.



From the graph we see that the lowest energy band which is allowed for electrons in the metal lattice has values of k extending from $k = -\frac{\pi}{a}$ to $k = +\frac{\pi}{a}$ (ie when $n=1$)

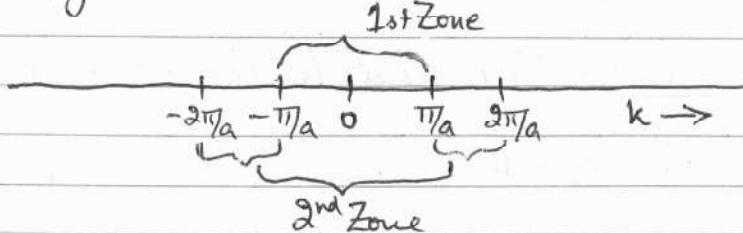
Therefore, the energy of the first energy band extends from

$$E_0 > 0 \text{ to } E_1 = \frac{\alpha^2 h^2}{2m} = \frac{k^2 h^2}{2m} \text{ where } k \text{ is free parameter}$$

This range or zone of allowed k values between $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ is called the first Brillouin Zone. After a break in the energy values called the forbidden region or zone, we get another allowed zone of energy values extending from

$$k = -\frac{\pi}{a} \text{ to } -\frac{2\pi}{a} \text{ and } k = +\frac{\pi}{a} \text{ to } +\frac{2\pi}{a}.$$

This zone is called the second Brillouin Zone. Hence the origin of allowed energy bands and forbidden gaps is clear from the above figure which represents $E-k$ diagram in Kronig-Penny model.



First two Brillouin Zones for 1D Metal Lattice

Case II :- P is very large :- It is known that P is a measure of potential barrier strength. If P is large, the LHS of eqn (iii) crosses +1 and -1 region at a steeper angle as shown in the Fig (a) below. Thus the allowed bands are narrower and the forbidden bands are wider.

Case III :- $P \rightarrow \infty$:- In this case a solution to eqn (iii) exists only if

$$\sin \alpha a = 0$$

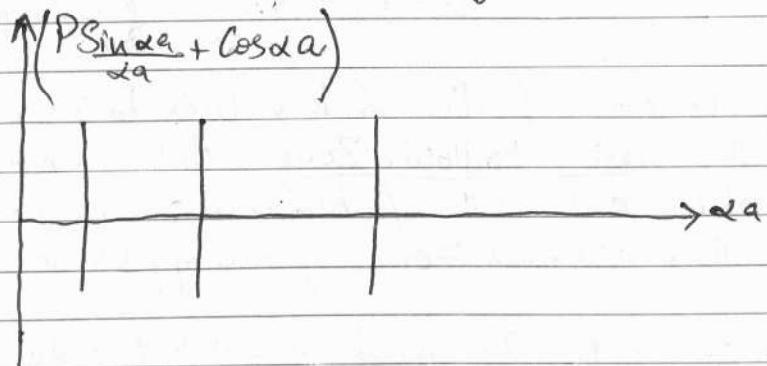
$$\text{i.e. } \alpha a = \pm n\pi \Leftrightarrow \alpha^2 = \frac{n^2 \pi^2}{a^2}$$

Hence

$$E = \frac{\alpha^2 h^2}{2m} = \frac{n^2 \pi^2 h^2}{2ma^2}$$

(48)

Here E becomes independent of the free variable k and can only have discrete values, similar to the energy levels of a particle in a 1D box problem. In such a case the LHS of eqn (iii) will intersect the (αa) axis at vertical lines only as shown in figure below.



Clearly, in the limit $P \rightarrow \infty$, the allowed energy bands reduce to discrete energy levels i.e. we are back to the case of discrete energy spectrum existing in isolated atoms (e.g. Bohr's atomic model of H-atom) where the electron is tightly bound to the atom.

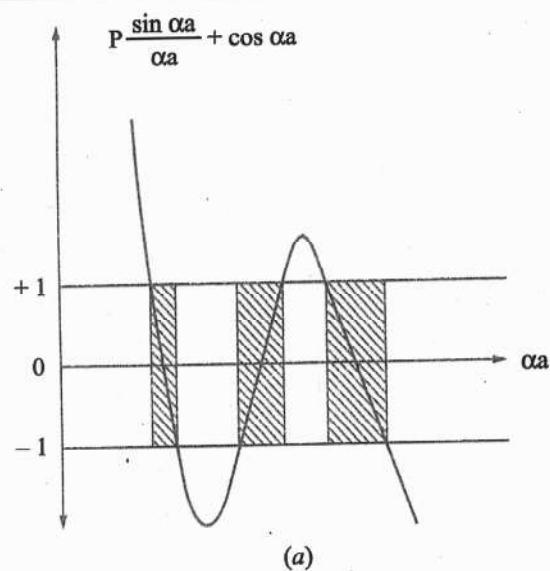
Case 4 :- $P \rightarrow 0$:- This leads to $\cos \alpha a = \cos ka$

$$\text{i.e. } \alpha = k$$

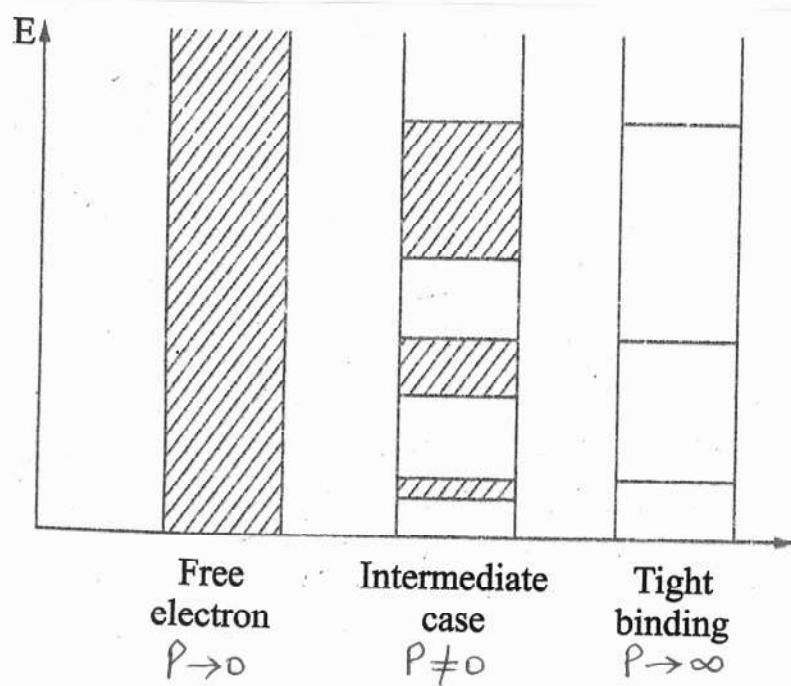
So that

$$E = \frac{k^2 h^2}{2m} \text{ which corresponds to all allowed}$$

parabolic values of E from 0 to ∞ $\because k$ is a free parameter in the model. This corresponds to a classical free particle for which all energies are allowed (i.e. no energy levels or forbidden regions exist at all). Clearly, in this case the plot of LHS of eqn(iii) vs (αa) is a cosine graph always within limits +1 to -1. The energy level structure for different degrees of binding (i.e. different values of P) are shown in the figure below.



(a)



Motion of Electrons in a 1D Periodic Potential :-

For a classical free particle, the mass of the electron is given by 'm' and is a constant of motion as long as it is moving at a speed, $v \ll c$ (speed of light). However, the mass of the electron inside a crystal (metal lattice) under the influence of a potential difference (of electric field) is not a constant of motion and is called the effective mass of the electron, which is represented by m^* . This is understood as follows. Inside the metal crystal, the moving electron has wave-like characteristics which are represented by its wave packet or wave function. This wave packet always travels with the speed of the particle. In quantum mechanics, a particle moving with a velocity v is equivalent to a wave packet moving with a group velocity v_g (=velocity of particle) defined as

$$v = v_g = \frac{dk}{dt} = \frac{t}{\hbar} \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \quad (\because E = \hbar\omega).$$

i.e. the velocity of the electron inside the metal is proportional to dE/dk i.e. slope of the $E-k$ curve. In the last topic on band theory of solids (i.e. Kronig-Penney Model), E is not proportional to k^2 ($\therefore E \propto k^2$ in Kronig-Penney Model) especially at the boundaries of the Brillouin Zones. This variation of E vs k is shown (for the first Brillouin Zone) in figure (a) below. The slope of this $E-k$ curve gives the velocity of the electron. This is plotted in figure (b) below.

Note that the points A and B are called the points of inflection on the $E-k$ curve [\therefore for these points $d^2E/dk^2 = 0$. Graphically, the points of inflection are the points on a curve where its curvature abruptly changes from convex to concave or vice-versa]. Note that the decrease of the electron velocity beyond the point B of inflection (with increase in E) and $v=0$ at the top of the energy band are entirely new features of band theory of solids, which do not appear at all in the behaviour of free electrons (in quantum theory of free electrons) or classical theory of free electrons.

It will be shown later that the effective mass of the electron depends on the nature of E_k -curve and mathematically it can be expressed as

$$m^* = \frac{\hbar^2}{\left[\frac{d^2 E}{dk^2} \right]}$$

The variation of the effective mass of the electron vs k is shown in the adjoining figure (c). Note that for a freely moving electron

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

so that $\frac{d^2 E}{dk^2} = \frac{\hbar^2}{m}$ so that $m^* = m$

\hookrightarrow for free electron

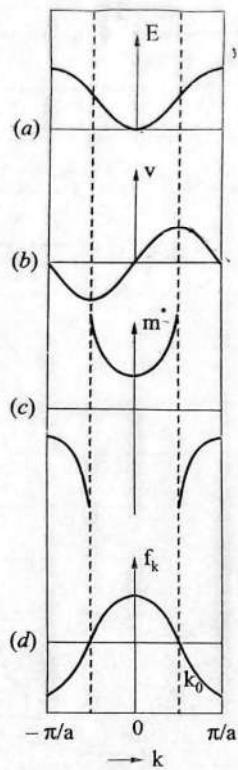


Fig. 6.50 Energy, effective mass and f_k as a function of K

one must replace m with m^* in the Schrodinger Wave Equations for Kronig-Penney Model and all its results.

Finally, the degree of freedom of an electron inside a metal crystal with periodic potential is defined as f_k such that

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \left[\frac{d^2 E}{dk^2} \right]$$

where f_k is the measure of the extent to which an electron in the state k is free. If m^* is large, f_k is small i.e. $m^* > m$ and electron behaves as a heavy particle and its motion gets restricted. When $f_k = 1$, $m^* = m$ and the electron behaves as a free electron. When m^* is small, f_k is large i.e. $m^* < m$ and the electron becomes lighter than a free electron and hence moves faster. The variation of f_k vs k is shown in figure (d) above. Note that $f_k > 0$ (or $m^* < m$) in the lower half of the energy band and $f_k < 0$ (or $m^* > m$) in the upper half of the energy band i.e. an electron behaves as a positively charged particle in the upper half of the energy band (when k is close to $\pm \pi/a$). Such particles are called 'holes'.

Effective Mass (Derivation) :-

Consider the effect of an applied electric field \vec{E} on the motion of an electron in the Brillouin zone. If v is the velocity of the electron and the field \vec{E} acts on it for a time dt , the increase in energy of the electron will be

$$dE = Fdx = eE dx = eE v dt \quad [\because dx = v dt] \\ - (i)$$

$$\text{We know that } v = \frac{1}{\hbar} \frac{dE}{dk} \quad - (ii)$$

Substituting (ii) in (i) we get

$$dE = \frac{eE}{\hbar} \left(\frac{dE}{dk} \right) dt$$

$$\therefore \frac{dk}{dt} = \frac{eE}{\hbar} \quad - (iii)$$

Now differentiating eqn (iii) w.r.t. we get the acceleration

$$a = \frac{dv}{dt} = \frac{1}{\hbar} \frac{d^2E}{dk^2} \left(\frac{dk}{dt} \right) \quad - (iv)$$

Substituting (iii) in (iv) we get

$$a = \frac{eE}{\hbar^2} \frac{d^2E}{dk^2} = \frac{F}{m^*}$$

Therefore, the effective mass of an electron moving in a crystal is given by

$$m^* = \frac{\hbar^2}{\left[\frac{d^2E}{dk^2} \right]}$$

Physical Significance of Effective Mass :- The concept of effective mass provides a satisfactory description of the charge carriers in crystals. In crystals, such as Alkali metals, which have partially filled energy band, the conduction takes place through electrons. However, in intrinsic semiconductor crystals for which the energy band is nearly full, the top-most electrons in the energy band have -ve effective mass and hence behave as positively charged particles that we call as holes.

Alternatively, the electron vacancies at top of energy band are also holes by nature as they have -ve mass and -ve charge so that the product ($m^*e \rightarrow +ve$)

No. of Possible Wave Functions in a Band :-

Consider a one-dimensional crystal of N lattice sites. The length of the lattice will then be $(L-a)$. Since the potential is periodic, so the wave function of the electron will also be periodic i.e.

$$\psi(x) = \psi(x+L).$$

Now from Bloch Theorem, we have

$$\begin{aligned}\psi(x) &= u(x) e^{ikx} \\ \psi(x+L) &= u(x+L) e^{ik(x+L)}\end{aligned}$$

-①

Also the modulating part of the wave function is periodic such that

$$u(x) = u(x+a) = u(x+2a) \dots = u(x+Na) = u(x+L)$$

-②

Substituting ② in ① we get.

$$e^{ikx} = e^{i(k+L)x} = e^{ikx} e^{ikL}$$

$$\text{i.e. } e^{ikL} = 1$$

$$\text{i.e. } kL = 2n\pi, n = \pm 1, \pm 2, \pm 3$$

$$\text{or } k = \frac{2n\pi}{L}$$

$$\text{or } n = \frac{kL}{2\pi}$$

So the no. of possible wave functions in the interval dk is

$$dn = \left(\frac{L}{2\pi}\right) dk$$

Hence total no. of possible states in a band will be

$$n = \int dn = \frac{L}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk \quad \left[\because -\frac{\pi}{a} \leq k \leq +\frac{\pi}{a} \text{ for 1st Brillouin Zone} \right]$$

$$\text{i.e. } n = \frac{L}{2\pi} \times \frac{2\pi}{a} = \frac{L}{a}$$

$$\text{i.e. } L = na$$

Also length of lattice, $L = Na$ from periodicity of lattice. Comparing the two we find, $n = N$ is the total number of possible states = no. of unit cells. Since each energy state can be occupied by two electrons of opposite spin, hence the total number of electrons in the band = $2N$.

(54).

Distinction between Metals, Insulators and Semiconductors :-

To distinguish between metals, semiconductors and insulators on the basis of band theory, let us consider an energy band which is filled with electrons upto a certain value k_1 ($< \pi/a$) as shown in figure below.

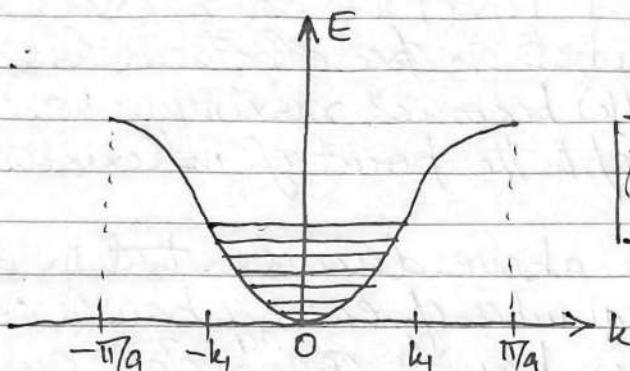


figure:- Energy band filled upto $k=k_1$

We need to find the effective number of free electrons present in this band as this will provide information about the conductivity of the band. Clearly, the total effective number of free electrons in a band

$N_{\text{eff}} = \text{sum total of } f_k \text{ (degree of freedom) of all electrons in the band}$

$$\text{i.e. } N_{\text{eff}} = \sum f_k$$

Now, the number of possible states in the interval dk for a one-dimension lattice of length L is

$$dn = \frac{L}{2\pi} dk \times 2 \quad (\text{since every state can be occupied by two electrons})$$

$$\therefore N_{\text{eff}} = \int_{-k_1}^{k_1} \frac{L}{2\pi} dk$$

$$\text{i.e. } N_{\text{eff}} = \frac{L}{\pi} \int_{-k_1}^{k_1} f_k dk$$

$$= \frac{2L}{\pi} \int_0^{k_1} k f_k dk \quad \left(\because f_k = \frac{m}{\hbar^2} \frac{d^2 E}{dk^2} \text{ is even function of } k \right)$$

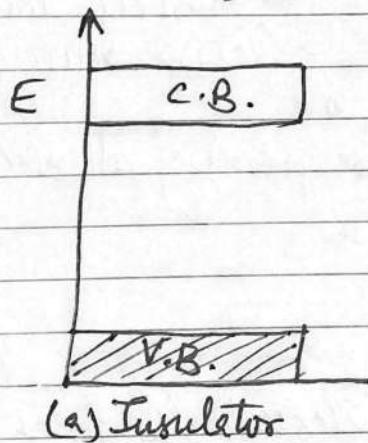
$$\therefore N_{\text{eff}} = \frac{2L}{\pi} \times \frac{m}{\hbar^2} \int_0^{k_1} \frac{d^2 E}{dk^2} dk$$

$$\text{i.e. } N_{\text{eff}} = \frac{2Lm}{\pi^2 h^2} \left(\frac{dE}{dk} \right)_{k=k_1}$$

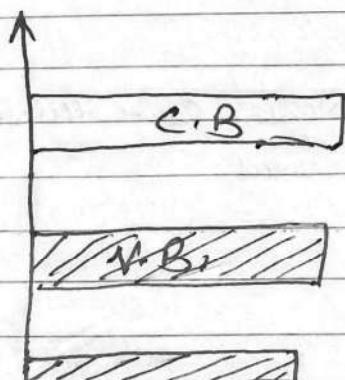
This gives the following results:-

- (i) The effective number of free electrons in a completely filled band is zero. This is because (dE/dk) i.e. slope of $E-k$ curve vanishes at top of the band (near $k = \pm \pi/a$).
- (ii) The effective number of free electrons has a maximum value when (dE/dk) becomes maximum i.e. when the band is filled upto the point of inflexion.

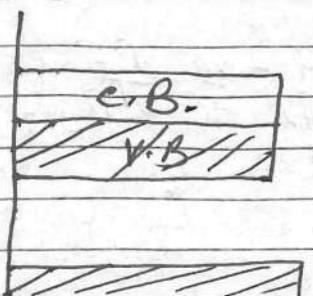
It follows from the above discussion that in a solid having a certain number of energy bands completely filled and all other bands completely empty, as shown in figure (a) below, will act as insulators.



(a) Insulator



(b) Semiconductor



On the other hand, a solid having a partially filled energy band has a metallic character as shown in figure (c).

Note that the situation shown in figure (a) can strictly occur ONLY at $T=0K$. For $T>0K$, some electrons from the topmost filled energy band (valence band) absorb thermal energy and get excited to next empty band (conduction band) where they participate in the conduction process. The number of such conduction electrons depends on the value of the forbidden gap between the valence band and the conduction bands. The larger the band gap, the smaller the number of free electrons and hence larger the tendency of the material to behave as an insulator. If band gap is small ($\approx 1\text{eV}$) the number of thermally excited electrons can be

appreciable even at ordinary temperatures and the material behaves as an intrinsic (i.e pure) semiconductor. At 0K, even these materials behave as insulators because electrons from the valence band cannot be thermally excited to the conduction band. Therefore, intrinsic semiconductors are insulators at 0K and all insulators may behave as semiconductors at temperatures sufficiently higher than 0K.

Conductors

1. Conduction band and valence band overlap. There is no forbidden band.
2. Large no. of free electrons are available for conduction. Holes are not present.
3. Electrical conductivity is very large.

Insulators

1. Forbidden gap is very large ($> 5\text{ eV}$)
2. Valence band is completely filled and conduction band is totally empty.
3. Electrical conductivity is very small.

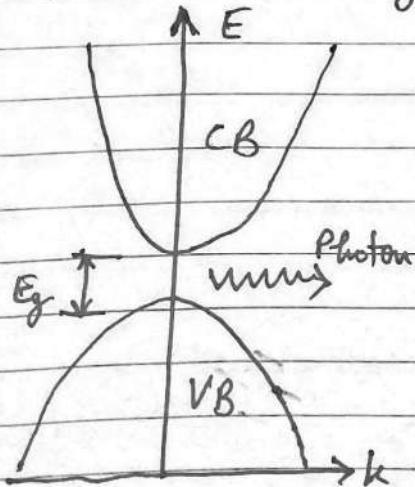
Semiconductors

1. Forbidden gap is small.
2. Valence band is partially empty and has holes. Conduction band is partially filled with free electrons.
3. Electrical properties lie between conductors and insulators.

Direct and Indirect Gap Semiconductors

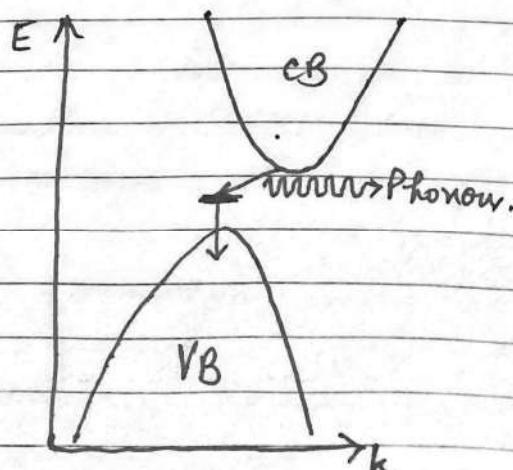
Direct Semiconductor

1. The top of valence band and the bottom of conduction band lies at the same value of k .



Indirect Semiconductor

1. The top of valence band and the bottom of conduction band lie at different values of k .



2. The de-excitation (or excitation) of electrons from C.B. to V.B (or vice-versa) takes place directly without the involvement of any intermediate energy state.
3. The electron transitions conserve the momentum and de-excitation leads to emission of light or photons.
4. These materials are usually alloy based like GaAs, CdS, etc.
5. These are used for making optoelectronic devices like LED, Solar Cells, Photodiode, Semiconductor laser, etc.
2. The de-excitation (or excitation) of electrons from C.B. to V.B (or vice-versa) takes place indirectly and an intermediate defect state is involved in the process.
3. The electron transitions do not conserve the momentum and de-excitation leads to emission of heat or phonons.
4. These materials are usually pure semiconductor based like Ge, Si.
5. These are used for making Zener diodes, rectifier diodes, transistors, etc.

Photon

1. It is a quantum of em or radiation energy
2. It travels with velocity of light i.e $v = c$.
3. Does not require a medium for propagation.

Phonon

1. It is a quantum of vibrational energy.
2. It behaves like a mechanical wave and $v < c$.
3. Requires a medium for propagation.

Solved Numericals.

Q1 Calculate the Fermi Energy for a one dimensional crystal lattice having 5×10^7 electrons/cm.

Aus.

$$E_F = \frac{\pi^2 n^2 \hbar^2}{2mL^2} = \frac{\hbar^2 \pi^2 (n)^2}{2m(L)^2}$$

Since every level can accommodate 2 electrons, so at $T=0K$

$$2n_F = N = \text{Total No. of electrons (free) in lattice.}$$

$$\text{So } E_F = \frac{\hbar^2 \pi^2 (N)^2}{2m(2L)} = \frac{\hbar^2 (N)^2}{8m(2L)} = \frac{\hbar^2 (N)^2}{32m(L)^2}$$

Given $\frac{N}{L} = 5 \times 10^7$ electrons/cm.

$$\text{Substituting. } \hbar = 6.6 \times 10^{-34} \text{ Js}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

we get

$$E_F = 3.7 \times 10^{-19} \text{ J} = 2.4 \text{ eV.}$$

Q2. Calculate the thermal energy acquired by a classical particle at temperature ~~equal to room temp.~~ equal to room temp.

Aus. Thermal Energy at $T K = kT$ ($k = 1.38 \times 10^{-23} \text{ JK}^{-1}$)
Room temperature = 300 K.

$$\begin{aligned} \therefore \text{Thermal Energy at } 300 \text{ K} &= 1.38 \times 10^{-23} \times 300 \text{ J} \\ &= \frac{1.38 \times 10^{-23} \times 300}{1.6 \times 10^{-19}} \text{ eV} \\ &= 0.025 \text{ eV.} \end{aligned}$$

Q3. The atomic radius of sodium is 1.86 \AA ($1 \text{ \AA} = 10^{-10} \text{ m}$). Calculate the Fermi Energy of sodium at ~~0K~~ = 0K.

Aus.

$$E_F(0) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

We know that (Na) has bcc structure. Total No. of atoms per unit cell = 2. Assuming every atom contributes one free electron in the lattice, we have

$$\text{No. of free electrons per unit cell} = 2.$$

$$\text{Volume of unit cell} = a^3 = \left[\frac{(4r)}{\sqrt{3}} \right]^3 = 7.93 \times 10^{-29} \text{ m}^3$$

\therefore for bcc diagonal length = $4r = \sqrt{3}a$

$$\therefore \frac{N}{V} = \frac{2}{7.93 \times 10^{-29}} = 2.52 \times 10^{28} \text{ electrons/m}^3$$

So $E_F(0) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$ $\therefore \hbar = 1.05 \times 10^{-34} \text{ Js}$

$$= \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \times (3\pi^2 \times 2.52 \times 10^{28})^{2/3}$$

$$= 4.98 \times 10^{-19} \text{ J}$$

$$\therefore E_F(0) = 3.11 \text{ eV.}$$

Q Determine the average energy and speed of electron at its mean energy at 0K, if the Fermi energy is 10 eV.

Ans:

$$E_F(0) = 10 \text{ eV.}$$

$$\therefore \text{Average energy } \boxed{\bar{E} = \frac{3}{5} E_F(0)} = \frac{3}{5} \times 10 \text{ eV} = 6 \text{ eV.}$$

$$\boxed{\frac{1}{2} m v^2 = \bar{E}} \Rightarrow v = \sqrt{\frac{2\bar{E}}{m}} = \sqrt{\frac{2 \times 6 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}}$$

$$\therefore v = 1.45 \times 10^6 \text{ m/s.}$$

Q There are 2.5×10^{28} free electrons in a given material per m^3 . Calculate the Fermi Energy and Fermi velocity.

Ans: $\frac{N}{V} = 2.5 \times 10^{28}$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \left[3\pi^2 \times 2.5 \times 10^{28} \right]^{2/3}$$

$$= 4.99 \times 10^{-19} \text{ J} = 3.12 \text{ eV.}$$

$$\boxed{v_F = \sqrt{\frac{2E_F}{m}}} = \sqrt{\frac{2 \times 4.99 \times 10^{-19}}{9.1 \times 10^{-31}}} = 1.05 \times 10^6 \text{ m/s.}$$

Q. The density of copper is 8940 kg/m^3 and its atomic weight is 63.55. Calculate the Fermi energy and average energy at 0K.

Ans: $\frac{N}{V} = \frac{6.02 \times 10^{23} \times 1000 \times 8940}{63.55} = 8.47 \times 10^{28}$

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \left(3\pi^2 \times 8.47 \times 10^{28} \right)^{2/3}$$

$$= 11.26 \times 10^{-19} \text{ J} = 7.04 \text{ eV}$$

$$\bar{E} = \frac{3}{5} E_F = \frac{3}{5} \times 7.04 \text{ eV} = 4.22 \text{ eV.}$$

Q. Aluminium metal crystallises in f.c.c. structure. If each atom contributes one free electron and the lattice constant $a = 4 \text{ \AA}$, find

(a) Fermi Energy (E_F)

(b) Fermi vector (k_F)

(c) Total kinetic energy of free electrons gas per unit volume at 0K.

Ans: In fcc. total atoms per unit cell = 4.

Volume of unit cell = $a^3 = 64 \times 10^{-30} \text{ m}^3$

So

$$\frac{N}{V} = \frac{4}{64 \times 10^{-30}} = 6.25 \times 10^{28}$$

$$(a) E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \times \left(3\pi^2 \times 6.25 \times 10^{28} \right)^{2/3}$$

$$= 9.2 \times 10^{-19} \text{ J} = 5.75 \text{ eV.}$$

$$(b) E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \text{ so } k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

i.e. $k_F = \left(3\pi^2 \times 6.25 \times 10^{28} \right)^{1/3} = 1.23 \times 10^{10} \text{ m}^{-1}$.

$$(c) \left[\text{Total kinetic energy of free electrons/volume at 0K} \right] = \left[\text{Average energy per electron at 0K} \right] \times \frac{N}{V}$$

$$= \frac{3}{5} E_F \times \frac{N}{V} = \frac{3}{5} \times 5.75 \times 6.25 \times 10^{28}$$

$$= 21.56 \times 10^{28} \text{ eV/m}^3$$

(61)

Q Calculate the drift velocity of electrons in a wire of diameter 0.9 mm carrying a current of 6 A. Assume that 4.5×10^{28} electrons/m³ are available for conduction.

Ans-

$$I = 6 \text{ A}$$

$$n = 4.5 \times 10^{28} \text{ electrons/m}^3$$

$$r = \frac{d}{2} = \frac{0.9 \times 10^{-3}}{2} = 4.5 \times 10^{-4} \text{ m.}$$

$$\text{Current Density, } J = \frac{I}{A} = \frac{I}{\pi r^2} = \frac{6 \text{ A}}{\pi \times (4.5 \times 10^{-4})^2} = 9.44 \times 10^6 \text{ A/m}^2$$

$$\text{Drift velocity, } v_d = \frac{J}{ne} = \frac{9.44 \times 10^6}{4.5 \times 10^{28} \times 1.6 \times 10^{-19}} = 1.31 \times 10^{-3} \text{ m/s.}$$

Q. The density of Cu is $8.92 \times 10^3 \text{ kg/m}^3$ and its atomic weight is 63.5. Calculate the current density if a current of 5 A is maintained in Cu wire of radius 0.7 mm. Assuming that only one electron per Cu atom takes part in conduction, calculate the drift velocity.

Ans-

$$n = \frac{N}{V} = \frac{6.02 \times 10^{23} \times 1000 \times 8.92 \times 10^3}{63.5} = 8.46 \times 10^{30} \text{ electrons/m}^3$$

$$J = \frac{I}{A} = \frac{I}{\pi r^2} = \frac{5}{\pi (0.7 \times 10^{-3})^2} = 3.25 \times 10^6 \text{ A/m}^2$$

$$v_d = \frac{J}{ne} = \frac{3.25 \times 10^6}{8.46 \times 10^{30} \times 1.6 \times 10^{-19}} = 2.4 \times 10^{-6} \text{ m/s.}$$

Q Find the mobility of electrons in Copper if there are 9×10^{28} valence electrons/m³ and the conductivity of Copper is $6 \times 10^7 \text{ mho/m.}$

Ans-

$$\sigma = ne\mu \quad \text{so } \mu = \frac{\sigma}{ne}$$

$$\text{i.e. } \mu = \frac{6 \times 10^7}{9 \times 10^{28} \times 1.6 \times 10^{-19}} = 4.16 \times 10^{-3} \text{ m}^2/\text{V.s.}$$

Q Find the relaxation time of conduction electrons in a metal if its resistivity is $1.54 \times 10^{-8} \Omega m$ and it has 5.8×10^{28} conduction electrons.

Aus-

$$\boxed{\frac{1}{\rho} = \sigma = \frac{e^2 n \tau}{m}}$$

$$\text{i.e. } \tau = \frac{m}{n e^2 \rho} = \frac{9.1 \times 10^{-31}}{1.54 \times 10^{-8} \times (1.6 \times 10^{-19})^2 \times 5.8 \times 10^{28}} \\ \text{i.e. } \tau = 3.9 \times 10^{-14} \text{ s.}$$

Q The electrical resistivity of Copper at $27^\circ C$ is $1.72 \times 10^{-8} \Omega m$. Calculate its thermal conductivity if the Lorenz number is $2.26 \times 10^{-8} W \Omega K^{-2}$. ($27^\circ C = 300 K$)

Aus-

$$\boxed{\frac{K}{\sigma T} = L} \therefore K = \frac{L T}{\rho} = \frac{2.26 \times 10^{-8} \times 300}{1.72 \times 10^{-8}} = 394 W m^{-1} K^{-1}$$

Q The thermal and electrical conductivities of Copper at $20^\circ C$ are $390 W/m^{-1} K^{-1}$ and $5.87 \times 10^7 \text{ mho/m}$. Calculate the Lorenz number.

Aus-

$$L = \frac{K}{\sigma T} = \frac{390}{5.87 \times 10^7 \times 293} = 2.267 \times 10^{-8} W \Omega K^{-2}$$

Q: A uniform Silver wire has a resistivity of $1.54 \times 10^{-8} \Omega m$ at room temperature. For an electric field of $1 V/cm$, calculate
 (a) relaxation time Given $n = 5.8 \times 10^{28} \text{ electrons/m}^3$.
 (b) drift velocity
 (c) mobility.

Aus-(a) $\boxed{\tau = \frac{m}{n e^2 \rho}} = \frac{9.1 \times 10^{-31}}{5.8 \times 10^{28} \times (1.6 \times 10^{-19})^2 \times 1.54 \times 10^{-8}} = 3.97 \times 10^{-14} \text{ s.}$

(b) $\boxed{V_d = \left(\frac{e E}{m}\right) \tau} = \frac{1.6 \times 10^{-19} \times 100 (V/m)}{9.1 \times 10^{-31}} \times 3.97 \times 10^{-14} = 0.7 \text{ m/s.}$

(c) $\boxed{\mu = \frac{V_d}{E}} = \frac{0.7}{100} = 0.7 \times 10^{-2} \text{ m}^2/V.s.$

(6)

- Q A Copper wire of length 0.5m and diameter 0.3mm has a resistance of 0.12Ω at 20°C. If the thermal conductivity of Copper is 390 W/m/K⁻¹, calculate the Lorenz number. Compare this value with the value predicted by classical free electron theory.

Aus: $\sigma = \frac{1}{\rho} = \frac{l}{AR} = \frac{l}{(\pi r^2)R} = \frac{0.5}{(\pi)(0.15 \times 10^{-3})^2 \times 0.12}$

i.e. $\sigma = 5.89 \times 10^7 \text{ mho/m.}$

$$L_{\text{classical}} = \frac{3}{2} \left(\frac{k}{e} \right)^2 = \frac{3}{2} \times \left(\frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \right)^2 = 1.12 \times 10^{-8} \text{ WΩK}^{-2}$$

$$L_{\text{expt}} = \frac{K}{\sigma T} = \frac{390}{5.89 \times 10^7 \times 293} = 2.26 \times 10^{-8} \text{ WΩK}^{-2}.$$

- Q Find the lowest energy of an electron confined in a 3-dimensional box of side 0.1nm each.

Aus: $E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$

For lowest energy, $n_x = n_y = n_z = 1$

$$\begin{aligned} E_{(1,1,1)} &= \frac{3\hbar^2}{8mL^2} = \frac{3 \times (6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.1 \times 10^{-9})^2} \\ &= 18.06 \times 10^{-18} \text{ J} \\ &= 112.9 \text{ eV.} \end{aligned}$$

- Q Calculate the occupation probability for an electron in an energy level kT above the Fermi energy.

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

$$\text{so } f(E) = \frac{1}{1+e} = \frac{1}{1+2.78} = \frac{1}{3.78} = 0.269.$$

(64)

- Q In a solid, consider the energy level lying 0.01 eV below the Fermi level. What is the probability of this level NOT being occupied by an electron.
 Given $(E_F - E) = 0.01 \text{ eV}$ and $kT = 0.026 \text{ eV}$ at $T = 300 \text{ K}$.

Ans: The probability of an energy level E to be occupied by electron at a temperature T is given by.

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}} = \frac{1}{1 + e^{-(0.01/0.026)}} = \frac{1}{1 + e^{-0.385}}$$

$$= 0.595$$

And probability of non-occupation will be

$$1 - f(E) = 1 - 0.595 = 0.405.$$

- Q. Show that the occupation probability at $E = E_F + \Delta E$ is equal to the non-occupation probability at $E = E_F - \Delta E$.

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

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

$$= 1 - \frac{e^{\Delta E/kT}}{e^{\Delta E/kT} + 1}$$

$$= \frac{e^{\Delta E/kT} + 1 - e^{\Delta E/kT}}{e^{\Delta E/kT} + 1}$$

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

Q Calculate the number of energy states available for the electrons in a cubical box of side 1 cm lying below an energy of 1 eV.

Ans- We know that

$$D(E) = 4\pi V \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{3/2}$$

$$N = \int_0^{1\text{eV}} D(E) dE = 4\pi V \left(\frac{2m}{\hbar^2} \right)^{3/2} \left[\frac{2}{3} E^{3/2} \right]_0^{1\text{eV}}$$

$$= \frac{8\pi V}{3} \left(\frac{2m}{\hbar^2} \right)^{3/2} (1\text{eV})^{3/2}$$

$$= \frac{8 \times \pi \times 10^{-6}}{3} \times \left[\frac{2 \times 9.1 \times 10^{-31}}{(6.62 \times 10^{-34})^2} \right]^{3/2} [1.6 \times 10^{-19}]^{3/2}$$

$$N = 4.5 \times 10^{21}$$

Q. For lithium, the Fermi Energy is 4.7 eV and $n = 4.6 \times 10^{28}/\text{m}^3$. Find the electron density for a metal with Fermi Energy 2.35 eV.

Ans: $E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

i.e. $E_F \propto n^{2/3}$ or $n \propto E_F^{3/2}$

$$\therefore \frac{n_{\text{metal}}}{n_{\text{Li}}} = \frac{E_{F_{\text{metal}}}^{3/2}}{E_{F_{\text{Li}}}^{3/2}}$$

So $n_{\text{metal}} = 4.6 \times 10^{28} \times \left(\frac{2.35}{4.7} \right)^{3/2} = 1.6 \times 10^{28}/\text{m}^3$.

Q. The Fermi level in Silver is 5.5 eV at 0K. Calculate the number of free electrons/volume and the probability of occupation for electrons with energy 5.6 eV in Silver at the same temperature.

Ans:
$$E_F(0) = \frac{k^2}{2m} (3\pi^2 n)^{2/3}$$

$$\text{i.e. } n = \left(\frac{2m E_F(0)}{k^2} \right)^{3/2} \frac{1}{3\pi^2}$$

$$= \frac{1}{3\pi^2} \times \left[\frac{2 \times 9.1 \times 10^{-31} \times 5.5 \times 1.6 \times 10^{-19}}{(1.05 \times 10^{-34})^2} \right]^{3/2}$$

$$= 5.84 \times 10^{28} \text{ m}^{-3}$$

Since $5.6 \text{ eV} > E_F$ at 0K, so no energy levels above $E_F = 5.5 \text{ eV}$ will be occupied at $T = 0 \text{ K}$ i.e. $f(E) = 0$.

Q. Fermi velocity of electron in a metal is $0.73 \times 10^6 \text{ m/s}$. Calculate the Fermi Energy and Fermi Temperature.

Ans:
$$\frac{1}{2} m v_F^2 = E_F \quad \Rightarrow \quad \frac{1}{2} \times 9.1 \times 10^{-31} \times (0.73 \times 10^6)^2 = 2.42 \times 10^{-19} \text{ J}$$

$$\text{i.e. } E_F = 1.51 \text{ eV.}$$

$$T_F = \frac{E_F}{k} = \frac{2.42 \times 10^{-19}}{1.38 \times 10^{-23}} = 1.75 \times 10^4 \text{ K.}$$

Q. Aluminium is an fcc crystal with lattice constant 4.05 \AA and the metal has 3 free electrons per atom. Calculate the Fermi Energy in eV for the metal. Also evaluate its electron occupational probability at $T = 300 \text{ K}$ for an energy value 0.1 eV higher than E_F .

(67)

Ans.

No. of atoms per unit cell in fcc = 4.

No. of free electrons/atom = 3

No. of free electrons/unit cell = $4 \times 3 = 12$.Volume of unit cell = $a^3 = (4.05 \times 10^{-10})^3 = 6.64 \times 10^{-29} \text{ m}^3$.

$$n = \frac{N}{V} = \frac{12}{6.64 \times 10^{-29}} = 1.8 \times 10^{29} / \text{m}^3$$

$$E_F = \frac{e^2}{2m} (3\pi^2 n)^{2/3} = \frac{(1.05 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \left[3 \times \pi^2 \times 1.8 \times 10^{29} \right]^{2/3}$$

$$\therefore E_F = 1.869 \times 10^{-18} \text{ J} = 11.66 \text{ eV.}$$

$$\text{Given } E - E_F = 0.1 \text{ eV}$$

$$kT = 1.38 \times 10^{-23} \times 300 = 0.026 \text{ eV.}$$

$$\begin{aligned} \therefore f(E) &= \frac{1}{1 + e^{(E-E_F)/kT}} = \frac{1}{1 + e^{0.1/0.026}} = \frac{1}{1 + e^{3.846}} \\ &= \frac{1}{1 + 46.8} = \frac{1}{47.8} = 0.021 \end{aligned}$$