Introduction: Materials having low electrical resistivity are known as conductors. Metals and their alloys come under this group of materials. In metals the valance electrons are loosely bound to their individual atoms. They become free and are responsible for the conduction of electricity and heat in metals. Free electron theory was proposed by Drude by assuming that the valance electrons become free in metals and move randomly within the molecule the same way as molecules in gas. The Drude-Lorentz theory could successfully explain the Ohm's law and high electrical conductivity of metals. But this theory failed to explain many properties about metallic behavior. Sommerfeld later proposed free electron model based on quantum theory by using Fermi-Dirac statistics. Free electron theory thus paved way to know the electrical behavior of solids.

Postulates of Classical Free Electron Theory of Metals [Drude-Lorentz theory]:

- According to this theory metals consist of positive ion cores and valence electrons. The ion cores are immobile and consist of positive nucleus and bound electrons.
- The valence electrons get detached from the parent atoms during the process of formation of metal and move randomly among these cores. Hence they are known as free electrons.
- The free electrons moving within the metal are supposed to be similar to the freely moving atoms in perfect gas.
- The free electrons keep moving randomly in all directions through the lattice structure of metal due to thermal energy. The free electrons during their random motion collide with fixed positive ions in the lattice and also among themselves. This motion of free electrons does not cause flow of current through the metal.
- The distribution of velocities of electron gas is in accordance with Maxwell's distribution for a gas. The random speed is a function of temperature. The total energy electron is the kinetic energy as the electron is free. The average kinetic energy of an electron is $\frac{3}{2}\mathrm{kT}$

  Here, k is Boltzmann constant, T is absolute temperature.
- When the electron field is applied across the metal across the metal, the free electrons acquire velocity and move in a direction opposite to that of electric field. This velocity acquired by free electron is drift velocity v_d.
- The number of collisions per second that electron makes with ion cores is proportional to the speed. The average collision time between two successive collisions is called mean collision time, $\tau = \frac{\lambda}{\overline{\upsilon}}$.here, $\overline{\upsilon}$ is rms velocity and λ is mean collision time.

Some basic definitions:

Drift velocity: It is defined as average velocity with which the free electrons get drifted towards the positive end of the conductor under the influence of external electric field. In the absence of external field the free electrons have random motions just like gas molecules in a container.

In the presence of electric field there is a net velocity associated with electrons called drift velocity v_d.

The electron experiences a Lorentz force F_L in the presence of applied electric field.

$$F_L = -eE$$

Due to this force, the electrons in a direction opposite to the field the frictional force is $F_R = m\frac{v_d}{\tau}$

At equilibrium, $F_L = F_R \Rightarrow m\frac{v_d}{\tau} = -eE \Rightarrow v_d = \frac{e\tau E}{m}$

Here, e is the charge of electron, τ is the average time between two successive collisions, m is the mass of electron.

RMS velocity: ***It is defined as the square root of average velocities squared of molecules in a gas*** $\bar{v} = \frac{3kT}{m}$ $\quad k = 1.38\times10^{-23}$ J/K is Boltzmann constant

Relaxation time τ_r :

It is the time taken by the free electrons of a metal to reach the equilibrium position from disturbed position by the application of external electric field.

$$v_d = v_0 e^{-(\tau/\tau_r)}$$

Here, v_0 is the initial velocity of electron before electric field is applied.

Electrical conductivity:

The electrical conductivity is ability of substance to allow the flow of electric current. From ohm's law the current density is $J = \sigma E$

The current density in terms of drift velocity is $J = nev_d$

Thus, electrical conductivity is $\sigma = \frac{nev_d}{E}$

Mobility of electrons μ :

Mobility of electrons is defined as the drift of electrons per unit electric field.

$$\mu = \frac{v_d}{E} \Rightarrow \sigma = ne\mu$$

Mobility indicates the ease with which electrons move in a solid. In metals μ decreases with increase in temperature and hence conductivity decreases.

Thermal conductivity: ***It is defined as the quantity of heat crossing per unit time per unit area and maintaining unit temperature difference across the body***.

Weidmann-Franz law: ***It is the ratio of thermal conductivity to electrical conductivity of a metal and is proportional to absolute temperature.***

$$\frac{K}{\sigma}\infty T \Rightarrow \frac{K}{\sigma T} = L$$ Here, L is Lorentz number

Merits of classical free electron theory:

- The free electron model is successful in explaining many physical properties of metals such as their high electrical, thermal conductivities, high luster etc.
- It verifies ohm's law
- It derives Weidmann-Franz law
- It explains optical properties of metals

Demerits of classical free electron theory:

- Classical free electron theory could not explain the classification of materials into conductors, insulators and semiconductors
- **Specific heat of solids:** according to free electron theory of metal, the energy gained by electrons due to absorption of heat is $E = \frac{3}{2}N_A kT$ Here, N_A is Avogadro number

$$C_v = \frac{dE}{dt} = \frac{3}{2}N_A k = \frac{3}{2}\left(6.023\times10^{26}\right)\left(1.38\times10^{-23}\right) = 12.5 \text{ KJ/MOL.K}$$

- ***The experimental value is hundred times less than this value. Classical free electron theory failed to explain this phenomenon.***
- **Temperature dependence on conductivity:** According to classical free electron theory the electrical conductivity is given by

  $$\sigma = \frac{ne^2\tau}{\sqrt{3mKT}} \Rightarrow \sigma = \infty \frac{1}{\sqrt{T}}$$

  But experimentally, $\sigma = \infty \frac{1}{T}$, So classical free electron theory failed to explain temperature dependence of electrical conductivity of metals.
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  Dependence of conductivity on electronic concentration: According to free theory of metals the electrical conductivity is directly proportional to free electron
  electron concentration $\sigma = ne\mu \Rightarrow \sigma \infty n$

  This relation shows monovalent metals should have lesser electrical conductivity compared to divalent and trivalent metals. But monovalent metals have higher electrical conductivity compared to divalent or trivalent metals. Free electron theory failed to explain this.
- ***The phenomenon such as photoelectric effect, Compton effect, Black body radiation, could not be explained by classical free electron theory.***
- ***According to classical free electron theory, the mean free path of electron in metals is*** 3A^0 ***but experimentally it is*** $50\ \text{A}^0$
- ***Classical free electron theory fails to explain Weidmann-Franz law at low temperatures.***
- ***Classical free electron theory failed to explain ferromagnetism.***

Quantum Free Electron Theory:

Quantum free electron theory was proposed by Sommerfeld. This theory was built on the basis of Pauli's exclusion principle and Fermi-Dirac statistics.

- This theory permits only few electrons to gain energy
- The distribution of electrons in various allowed energy levels in various energy levels takes place according to Pauli's exclusion principle.
- The electrons move in a constant potential inside metal and are confined within defined boundaries.
- Mutual attraction between electrons and lattice ions and repulsion between individual electrons may be ignored
- **Merits of Quantum Free Electron theory:**
  - The quantum free electron theory could explain the properties of conductors such as electrical conductivity, heat capacity, thermal conductivity in agreement with experimental values.
  - This theory explains photoelectric effect, Compton effect, black body radiation etc.
  - This theory succeeded in explaining temperature dependence of electrical conductivity $\sigma = \infty \frac{1}{T}$.
  - This theory put forward that there is no direct relation between electrical conductivity σ and electron concentration n.

Drawbacks of quantum free electron theory:

- This theory fails to explain the distinction between conductors, semiconductors and insulators.
- It also fails to explain the positive hall coefficient in case of some metals like zinc.
- According to this theory only two electrons are present and they are responsible for conduction which is not true.

Fermi energy:
Let the specimen of metal contain N free electrons. In a conductor at absolute zero temperature, the electrons fill the available states starting from the lowest energy level. Therefore, all energy levels with energy E less than a certain value $E_F(0)$ will be filled with electrons whereas all the levels with $E > E_F(0)$ will remain vacant. The energy $E_F(0)$ is known as Fermi energy and the corresponding energy level is known as Fermi level. The total number of free electrons is equal to the number of quantum states up to energy E_F

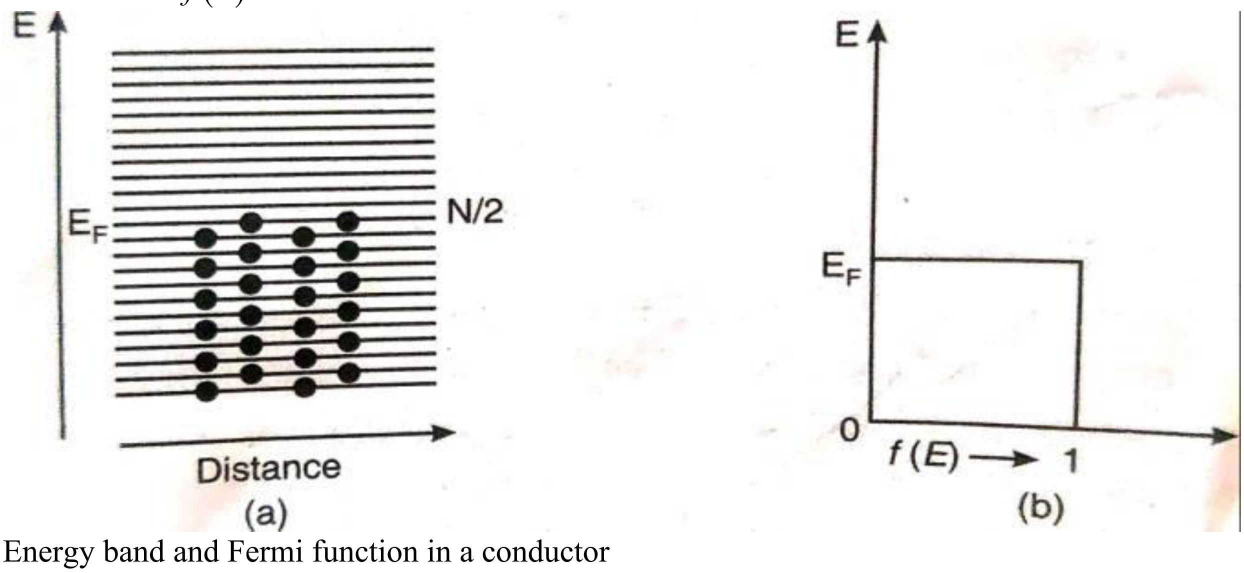
The Fermi energy in terms of electron concentration is

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

The Fermi energy of a metal depends only on the electron concentration in the metal.
Significance: Fermi energy levels are used to explain the flow of electrons when two metals are in contact, p-type and n-type semiconductors.
Fermi-Dirac distribution:
The electrons are distributed among the various energy levels in conduction band at a given temperature. The statistical distribution function applicable to quantum particles is the Fermi-Dirac distribution function.
The probability of an electron occupies an energy level E at thermal equilibrium is

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{KT}\right)}$$

The function $f(E)$ is known as Fermi factor.



Energy band and Fermi function in a conductor

Case 1: At $T = 0\text{K}$

At absolute zero electrons occupy energy levels in pairs starting from the bottom of band to the upper level E_F which is the uppermost filled energy level at 0K.

At $E < E_F$, $(\mathrm{E - E_F})$ is negative quantity

$$f(E) = \frac{1}{1+\exp-\left(\frac{E-E_F}{0}\right)} \Rightarrow \frac{1}{1+e^{-\infty}} = \frac{1}{1+0} = 1$$

$f(E) = 1$, Indicates that all energy levels lying below the level E_F.

At $E > E_F$, $(\mathrm{E - E_F})$ is postive quantity

$$f(E) = \frac{1}{1+\exp\left(\frac{E-E_F}{0}\right)} \Rightarrow \frac{1}{1+e^{\infty}} = \frac{1}{1+\infty} = 0$$

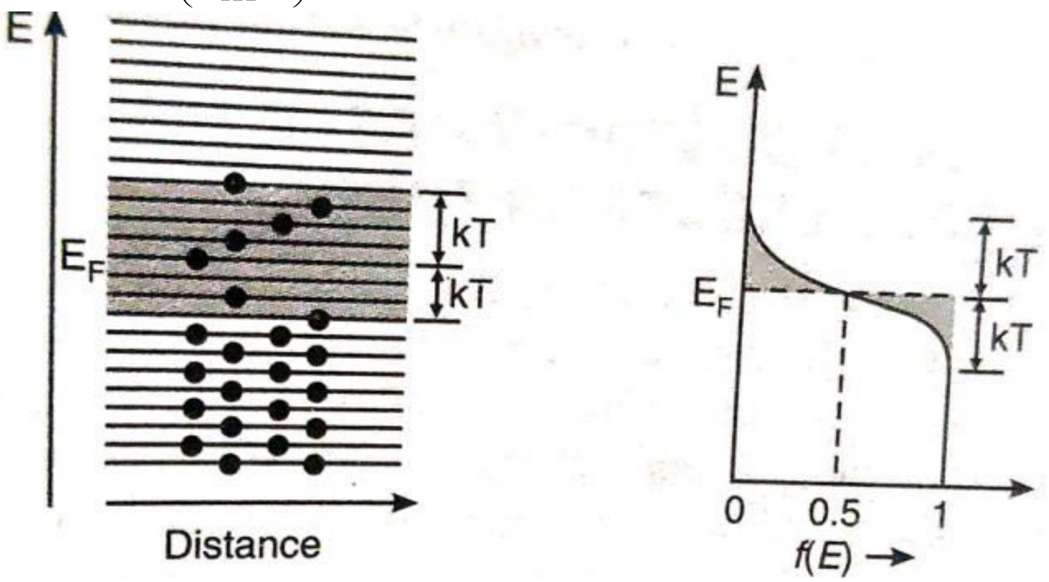
$f(E) = 0$, indicates that all energy levels lying above the level E_F are vacant at 0K

Case 2: At $T > 0\mathrm{K}$

On heating the conductor, electrons are excited to higher energy levels.

At $E = E_F$

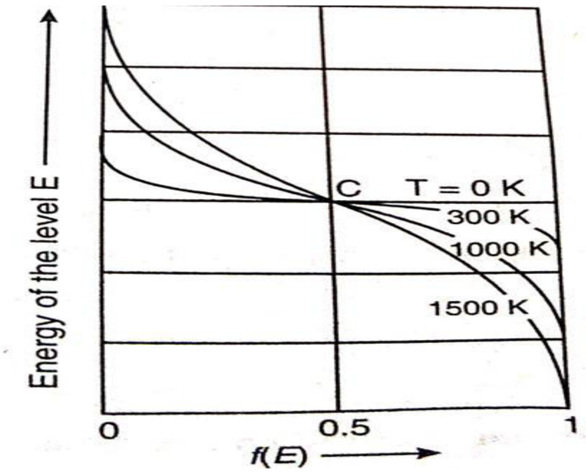
$$f(E) = \frac{1}{1+\exp-\left(\frac{E-E_F}{KT}\right)} \Rightarrow \frac{1}{1+e^{0/KT}} = \frac{1}{1+1} = \frac{1}{2}$$



Energy band and Fermi function in a conductor

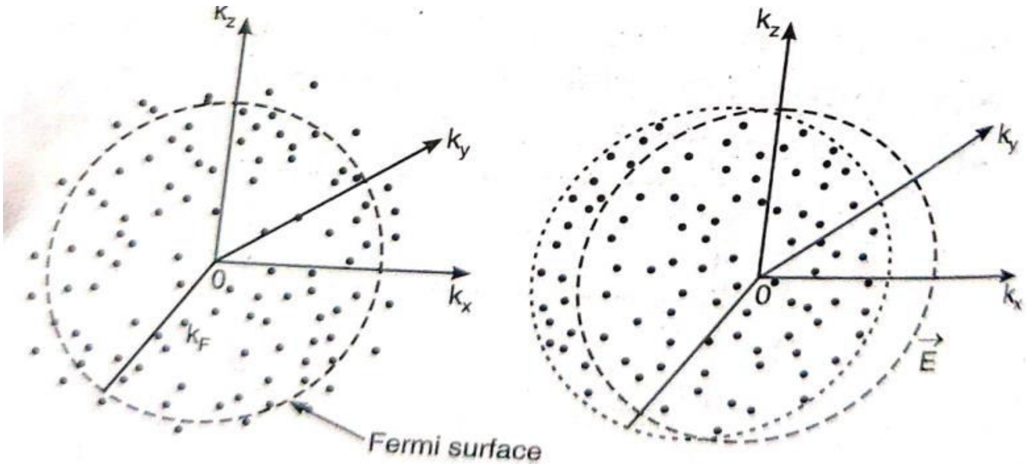
This implies that the probability of occupancy of Fermi level at any temperature above 0K is 50%.

The variation of Fermi-dirac distribution as a function of temperature is shown in figure. The probability of finding electron decreases below Fermi level and increases above Fermi level as temperature increases.



Electrical conductivity based on quantum free electron theory:

The conduction electrons occupy a particular energy state and possess momentum at $p = \hbar k$ if the momentum of electrons is plotted in k-space with Fermi surface it has both occupied and unoccupied states. Before the application of electric field, there is no current flow across the material as net momentum of electrons is zero.



Fermi Surface

When an electric field is applied, the electrons experience a force F .

$$F = \frac{dp}{dt} = -eE \Rightarrow \frac{d(\hbar k)}{dt} = -eE \Rightarrow \frac{\hbar(dk)}{dt} = -eE$$

This is the equation of motion of electron in the presence of electric field. Integrating above equation

$$\hbar(dk) = (-eE)dt \Rightarrow \int_0^t \hbar(dk) = (-eE)\int_0^t dt \Rightarrow k(t) - k(0) = \frac{-eEt}{\hbar} \Rightarrow \Delta k = \frac{-eEt}{\hbar}$$

At $t = \tau_F \Rightarrow \Delta k = -\frac{eE\tau_F}{\hbar}$

The electron density per unit volume near Fermi surface is

$$J = n(-e)v \Rightarrow -ne\frac{p}{m} \left(\because v = \frac{p}{m}\right)$$

$$J = \frac{-ne\hbar\Delta k}{m} \quad (\because p = \hbar\Delta k)$$

$$= \frac{-ne\hbar}{m}\left(\frac{-eE\tau_F}{\hbar}\right) = \frac{ne^2\tau_F}{m}E$$

The current density is $J = \sigma E$

$$\sigma E = \frac{ne^2\tau_F}{m}E \Rightarrow \sigma = \frac{ne^2\tau_F}{m}$$

The electrical conductivity of a metal depends largely on the population density of electrons near Fermi surface.

Q. No		Assignment questions	Marks	CO	RBT
1	A	Discuss the de-Broglie's hypothesis of duality of material particles? Also derive the wavelength expression.	7	CO4	Understand
	B	Use the Fermi distribution function to obtain the value of F(E) for $E - E_F = 0.01\,\text{eV}$ at 200 K	3	CO4	Apply
2	A	Explain in detail the classical free electron theory of metals.	7	CO4	Understand
	B	Calculate the wavelength associated with an electron with energy 2000 eV.	3	CO4	Apply
3	A	What are matter waves? Obtain the expression for wavelength of matter waves associated with electrons	7	CO4	Understand
	B	Calculate the wavelength associated with an electron raised to a potential 1600V	3	CO4	Apply
4	A	Derive the time independent Schrodinger wave equation.	7	CO4	Understand
	B	Calculate the Fermi energy of copper for the number of electrons per unit volume is 8.5×10^{28} atoms/m ^{3}	3	CO4	Apply
5	A	Derive the time dependent Schrodinger wave equation.	7	CO4	Understand
	B	Discuss the various drawbacks of classical free electron theory.	3	CO4	Understand
6	A	Describe in detail the properties of matter waves	7	CO4	Understand
	B	Calculate the Fermi energy of copper for the number of electrons per unit volume is 8.5×10^{28} atoms/m ^{3}	3	CO4	Apply
7	A	Calculate the de-Broglie wavelength associated with a neutron movingwith a velocity of 2000 m/s. (mass of neutron, m = 1.67 $\times10^{-27}$ kg ,Plank's constant $h = 6.626\times10^{-34}$ j−s)	4	CO4	Understand
	B	Explain the physical significance of wave function	6	CO4	Understand
8	A	Explicit the Fermi-Dirac distribution function in variation with temperature?	7	CO4	Understand
	B	Calculate the wavelength associated with an electron raised to a potential of 69V?	3	CO4	Apply
9	A	Describe the limitations of Wave function.	7	CO4	Understand
	B	An electron is bound in one dimensional infinite well of width1×10^{-10} m. Find the energy value of an electron in ground state and first two excited states?	3	CO4	Apply
10	A	Apply Schrodinger wave equation to the case of particle in a one dimensional potential box with neat diagrams.	7	CO4	Understand
	B	Prove that the energies particles in the potential box are quantized.	3	CO4	Understand

Q. No	Model Two Marks Questions	Marks	CO	RBT
1	Write any two limitations of wave function.	2	CO4	Remember
2	What are matter waves? Writes the Wavelength expression.	2	CO4	Remember
3	Explain the difference between a matter wave and an electromagnetic	2	CO4	Remember

	wave.			
4	Give any two properties of matter waves.	2	CO4	Remember
5	Derive the relation between wavelength and kinetic energy by using de-Broglie's hypothesis?	2	CO4	Understand
6	Explain any two merits of classical free electron theory?	2	CO4	Understand
7	Explain any two demerits of classical free electron theory?	2	CO4	Understand
8	Explain any two merits of quantum free electron theory?	2	CO4	Understand
9	Explain any two demerits of quantum free electron theory?	2	CO4	Understand
10	Calculate the de-Broglie wavelength associated with a particle of mass 0.05g moving with a velocity 200 m/s?	2	CO4	Apply
11	Calculate the de-Broglie wavelength associated with an electron subjected to potential difference of 1.25 kV?	2	CO4	Apply
12	Does the matter wave is associated with the particle at rest. Why?	2	CO4	Understand
13	A spectral line has wavelength $4000\,\mathrm{A}^0$ .calculate the frequency associated with it?	2	CO4	Apply
14	A spectral line has wavelength $5000\,\mathrm{A}^0$ .calculate the energy associated with it?	2	CO4	Apply
15	What will be the energy of gamma ray photon having wavelength $1\,\mathrm{A}^0$	2	CO4	Apply

1. **Use the Fermi distribution function to obtain the value of F(E)for** $E - E_F = 0.01\,\mathrm{eV}$ at $200\,\mathrm{K}$

Sol: Energy difference, $E - E_F = 0.01\,\mathrm{eV} = 0.01 \times 1.6 \times 10^{-19}$ J

Temperature, $T = 200\,\mathrm{K}$; Boltzmann constant, $k_B = 1.38 \times 10^{-23}$

The Fermi –Dirac distribution,

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} = \frac{1}{1 + \exp\left(\frac{0.01 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 200}\right)} = 0.355$$

2. **Calculate the Fermi energy of copper for the number of electrons per unit volume is** 8.5×10^{28} **atoms/m** ^{3}

Sol: The number of electrons per unit volume, $n = 8.5 \times 10^{28}$ atoms/m ^{3}

Fermi energy at 0K is, $E_F = 3.62 \times 10^{-19} (n)^{2/3} = 3.62 \times 10^{-19} \left(8.5 \times 10^{28}\right)^{2/3} = 7.05\,\mathrm{eV}$

3. ***An electron is bound in one dimensional infinite well of width*** 1×10^{-10} m***. Find the energy value of an electron in ground state and first two excited states?***

Sol: Length of potential well, $L = 1 \times 10^{-10}$ m

The energy corresponding to nth quantum state is,

$$E_n = \frac{n^2 h^2}{8mL^2} \Rightarrow E_1 = \frac{\left(6.626 \times 10^{-34}\right)^2}{8 \times \left(9.1 \times 10^{-31} \times \left(1 \times 10^{-10}\right)^2\right)} = 0.603 \times 10^{-17}\ \mathrm{J}$$

The energy in ground state in eV is, $E_1 = \dfrac{0.603 \times 10^{-17}\ \mathrm{J}}{1.6 \times 10^{-19}} = 37.68\,\mathrm{eV}$

For the first energy state, $n = 2$, $E_2 = 4E_1 = 4(37.68\,\mathrm{eV}) = 150.75\,\mathrm{eV}$

For the second energy state, $n = 3$, $E_3 = 9E_1 = 9(37.68\,\mathrm{eV}) = 339.12\,\mathrm{eV}$