

Free electron theory

The word “free” means two important assumptions.

- The mutual interactions between electrons are ignored.
- The interactions between electrons and ions (nucleons) are ignored.

Classical Theory :

A metal is assumed as the structure of 3-dimensional array of ions in between which, there are free moving valence electrons confined to the body of the material. Such freely moving electrons cause electrical conduction under an applied field and hence referred to as conduction electrons.

The electric potential due to the ionic cores is taken to be essentially constant throughout the body of the metal and the effect of repulsion between the electrons is considered insignificant.

The electric current in a metal due to an applied field is a consequence of the drift velocity in a direction opposite to the direction of the field.

The free electrons are treated as equivalent to gas molecules and they are assumed to obey the laws of kinetic theory of gases.

In the absence of the electric field, the energy associated with each electron at a temperature T is given by $3/2 kT$, where k is a Boltzmann constant.

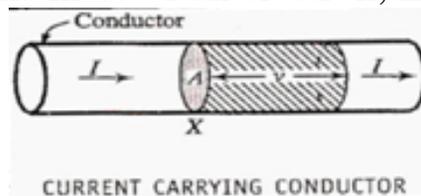
This energy is related to the kinetic energy of the electron.

$$3/2 kT = \frac{1}{2} m v_{th}^2$$

Where v_{th} is the thermal velocity same as root mean square velocity of gas molecule.

Expression for electrical conductivity in metals.

Consider the motion of an electron in a conductor in an influence of an electric field. If e is the charge, m is the mass of an electron, E is the electric field.



The force on an electron is

$$F = eE$$

Also from Newton's laws of motion $F = ma$

$$\Rightarrow ma = eE$$

$$\Rightarrow a = \frac{eE}{m}$$

$$\Rightarrow \frac{dv}{dt} = a = \frac{eE}{m}$$

$$\Rightarrow dv = \frac{eE}{m} dt$$

$$\Rightarrow \int dv = \frac{eE}{m} \int dt$$

$$\Rightarrow V = \frac{eE}{m} t + c$$

if $t \rightarrow 0$ then $v \rightarrow 0$;

$$\therefore c = 0$$

$$\therefore V = \frac{eE}{m} t$$

If the time of traverse is taken to be collision time ' τ ' and ' v ' is taken as average velocity $\langle v \rangle$

$$\therefore \text{Average velocity } \langle v \rangle = \frac{eE}{m} \tau$$

According to Ohm's Law $J = \sigma E$; where ' J ' is the current density.

$$\text{But } J = \frac{I}{A} \text{ Where 'I' is the current and}$$

'A' is the area of cross section of the conductor

$$\text{Therefore } \sigma = \frac{I}{EA}$$

Velocity = distance travelled by electron in unit time = v

\therefore Volume sweep in unit time = $A v$

Let e = the charge on the electron

' n ' = the number of electron per unit volume

$\therefore nAV$ = the number of electron per unit time crossing the given point

\therefore Then quantity of the charge crossing the given point in the conductor per unit time =

$$I = A v n e$$

$$\sigma = \frac{I}{EA} = \frac{nevA}{EA} = \frac{nev}{E} = \frac{ne eE \tau}{E m} = ne^2 \tau / m$$

Basic Terms :

- Drift velocity (v_d):* The velocity of electrons in the steady state in an applied electric field is called drift velocity.
- Relaxation time (τ_r):* From the instant of sudden disappearance of an electric field across a metal, the average velocity of the conduction electrons decays exponentially to zero, and the time required in this process for the average velocity to reduce to $(1/e)$ times its value is known as Relaxation time.
- Mean free path (λ):* The average distance travelled by the conduction electrons between successive collisions with lattice ions.

d) *Mean collision time* (τ): The average time that elapses between two consecutive collisions of an electron with the lattice points is called mean collision time.

$$\tau = \lambda/v$$

where 'λ' is the mean free path,

$v \approx v_{th}$ is velocity same as combined effect of thermal & drift velocities.

Failure of classical free electron theory :

Electrical and thermal conductivities can be explained from classical free electron theory. but it fails to account the facts such as specific heat, temperature dependence of conductivity and dependence of electrical conductivity on electron concentration.

Specific heat: The molar specific heat of a gas at constant volume is $C = \frac{3}{2} R$

As per the classical free electron theory, free electrons in a metal are expected to behave just as gas molecules.

Thus the above equation holds good equally well for the free electrons also.

But experimentally it was found that, the contribution to the specific heat of a metal by its conduction electrons = $C_v = 10^{-4} RT$

which is for lower than the expected value.

On the other hand , according to the free electron theory the specific heat is independent of temperature whereas experimentally specific heat is proportional to temperature.

Temperature dependence of electrical conductivity:

Experimentally, electrical conductivity σ is inversely proportional to the temperature T.

$$\sigma_{exp} \propto 1/T$$

According to the assumptions of classical free electron theory

$$\frac{3}{2} kT = \frac{1}{2} m v_{th}^2$$

$$\Rightarrow v_{th}^2 = \frac{3kT}{m}$$

$$\Rightarrow v_{th} = \sqrt{\frac{3kT}{m}}$$

$$\Rightarrow v_{th} \propto \sqrt{T}$$

The mean collision time 'τ' is inversely proportional to the thermal velocity.

$$\tau \propto 1/v_{th}$$

$$\propto 1/\sqrt{T}$$

$$\text{But } \sigma = ne^2 \tau / m$$

$$\therefore \sigma \propto \tau$$

$$\Rightarrow \sigma \propto \tau$$

$$\Rightarrow \sigma \propto 1/\sqrt{T}$$

\therefore the experimental value is not agreeing with the theory.

Dependence of electrical conductivity on electron concentration:

According to the Free electron theory

$$\sigma = \frac{I}{EA} = \frac{nevA}{EA} = \frac{nev}{E} = \frac{ne eE \tau}{E m} = ne^2 \tau / m$$

$\therefore \sigma \propto n$

But experimental value is not agreeing with the theory. let us take an example of zinc and cadmium which are divalent metals. Their electrical conductivities are $1.09 \times 10^7 / \Omega\text{m}$ and $0.15 \times 10^7 / \Omega\text{m}$. These are much lesser than that of monovalent metals copper and silver. The values of which are $5.88 \times 10^7 / \Omega\text{m}$ and $6.3 \times 10^7 / \Omega\text{m}$ respectively. The electron concentrations for zinc and cadmium are $13.1 \times 10^{28} / \text{m}^3$ and $9.28 \times 10^{28} / \text{m}^3$ which are much higher than that for copper and silver, the values of which are $8.45 \times 10^{28} / \text{m}^3$ and $5.85 \times 10^{28} / \text{m}^3$ respectively. Hence the classical free electron theory fails to explain the dependence of σ on electron concentration.

Quantum free electron theory

The following assumptions of classical free electron theory holds good in quantum free electron theory also.

- ✓ The electrons travel with a constant potential inside the metal but confined within its boundaries.
- ✓ The attraction between the electrons and the lattice ions and the repulsion between the electrons themselves are ignored.

The following assumptions are introduced in quantum free electron theory

- ✓ The energy values of the conduction electrons are quantized.
- ✓ The allowed energy values are realized in terms of a set of energy values.
- ✓ The distribution of electrons in the various allowed energy levels occur as per Pauli's exclusion principle.

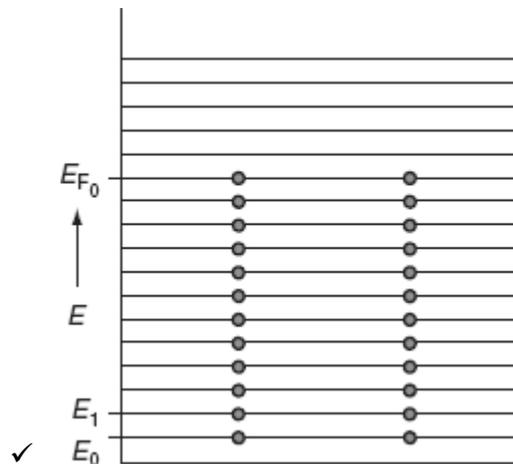
Fermi energy level

According to the Quantum theory quantization leads to discrete energy levels. The electrons are distributed among these energy levels according to Pauli's

exclusions principle i.e., it allows a maximum number of two electrons with spins in opposite directions in any energy level. The pair of electrons, one with spin up and the other with spin down occupy the lowest energy level. The next pair occupies the next level. This process goes on until all the electrons in the metal occupy their position.

The highest energy level that can be occupied by an electron at 0 K is called Fermi energy level. It is denoted by E .

When the metal is not under the influence of an external field, all the levels above the Fermi energy level are empty; those lying below are completely filled.



Fermi – Dirac Distribution:

The electrons in the energy levels which are below the Fermi level cannot absorb the energy above absolute zero temperature. When the material is at a temperature higher than 0K, it receives thermal energy from surroundings so, electrons are thermally excited. As a result, they move into the higher energy levels which are unoccupied at 0K. Though the excitations are random, the distributions of electrons in various energy levels will be systematically governed by a statistical function at the steady state.

The occupation obeys a specified statistical distribution. This distribution is called Fermi – Dirac distribution law.

According to this distribution law, the probability $F(E)$ that a given energy state E is occupied at a temperature T is given by

$$f(E) = 1/e^{(E-E_f)/KT} + 1$$

Here $f(E)$ is called Fermi – Dirac probability function.

It indicates that the fraction of all energy state (E) occupied under thermal equilibrium ‘ K ’ is Boltzmann constant.

$f(E)$ is called the fermi factor.

Fermi factor is the probability of occupation of a given energy state for a material in thermal equilibrium.

At $T = 0K$,the nature of F D Statistics is

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/K_B \times 0]} = 1 \text{ for } E < E_F$$

$$= 0 \text{ for } E > E_F$$

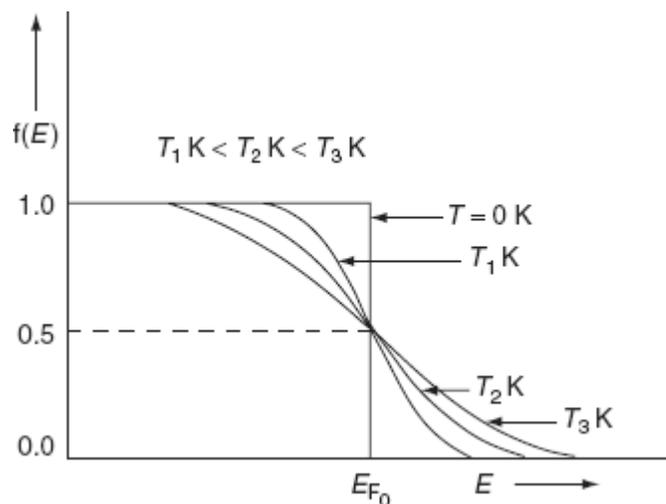
At $T > 0K$,the nature of F D Statistics is

$$f(E) = \frac{1}{1 + \exp(E - E_F)/K_B T} < 1 \text{ for } E < E_F$$

$$> 0 \text{ for } E > E_F$$

$$= \frac{1}{2} \text{ for } E = E_F$$

The dependence of Fermi factor on temperature and energy is as shown in the figure.



Success of Quantum free electron theory

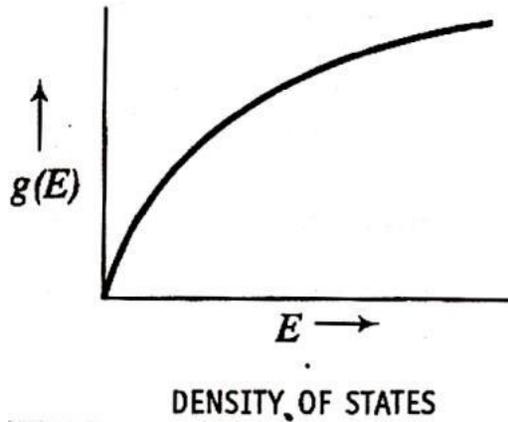
Density of states.

There are large numbers of allowed energy levels for electrons in solid materials. A group of energy levels close to each other is called as energy band. Each energy band is spread over a few electron-volt energy ranges. In 1mm^3 volume of the material, there will be a more than a thousand billion permitted energy levels in an energy range of few electron-volts.

therefore, the energy values appear to be virtually continuous over a band spread.

To represent it technically , it is stated as density of energy levels.

The dependence of density of energy levels on the energy is denoted by $g(E)$. The graph shows variation of $g(E)$ versus E .



It is called density of states function. It is the number of allowed energy levels per unit energy interval in the band associated with material of unit volume. In an energy band as E changes $g(E)$ also changes.

Success of quantum free electron theory

Quantum free electron theory has successfully explained following observed experimental facts where as the classical free electron theory failed.

1. **Specific heat:** According to classical free electron theory all the conduction electron are capable of observing the heat energy as per Maxwell Boltzmann statistics which results in large value of specific heat. According to quantum free electron theory, it is only those electron that are occupying energy levels close to E_F , which are capable of observing the heat energy to get excited to higher energy levels .

Hence only a small percentage of the conduction electrons are capable of receiving the thermal energy input, thus the specific heat value becomes very small for the metal.

According to quantum free electron theory, it can be shown

$$C_v = \frac{2K}{E} RT \text{ where } E = E_F = 5 \text{ eV (say)}$$

$$\therefore \frac{2K}{E} = 10^{-4}$$

$$\therefore C_v = 10^{-4} RT \text{ which is close to experimental value.}$$

2. **Temperature depends on electrical conductivity.**

Electrical conductivity σ is proportional to $\frac{1}{T}$ but not $1/\sqrt{T}$ which is as follows:

$$\text{Electrical conductivity } \sigma = ne^2 \tau / m^*$$

Where m^* is called effective mass of an electron.

According to quantum free electron theory $\tau = \lambda / V_F$

$$\therefore \sigma = ne^2 \lambda / V_F m^*$$

According to quantum free electron theory E_F and v_F are independent of temperature.

The dependence of λ & T may be explained as follows

Conduction electrons are scattered by the vibrating ions of the lattice. The vibration occurs such that the displacement of ions takes place equally in all directions.

If 'r' is the amplitude of vibrations then the ions can be considered to present effectively a circular cross section of area πr^2

That area blocks the path of the electron irrespective of direction of approach. Since the vibrations cover larger area of cross section should scatter more number of electrons, it results in the reduction of mean free path of the electron.

$$\lambda \propto 1/ \pi r^2$$

Since, The energy of vibrating body is proportional to the square of amplitude. And The energy of ions is due to the thermal energy.

Since, The thermal energy is proportional to the temperature 'T'.

Thus, We can write $r^2 \propto T$

$$\lambda \propto 1/T$$

$$\therefore \sigma \propto 1/T$$

Thus $\sigma \propto 1/T$ is correctly explained by quantum free electron theory.

3. Electrical conductivity and electron concentration:

Aluminium and gallium which have three free electrons per atom have lower electrical conductivity than that of copper and silver, which have only one free electron per atom.

As per quantum free electron the electrical conductivity is

$$\sigma = ne^2 \lambda / V_F m^*$$

The value of n for aluminium is 2.13 times higher than that of copper. But the value of λ/v_f for copper is about 3.73 times higher than that of aluminium. Thus the conductivity of copper exceeds that of aluminium.

Drawbacks of Quantum free electron theory :

(1) Lorentz Number : The Lorentz number in the Quantum free electron theory is given by $L = (\pi^2 / 3)(K/e)^2$

Here K is Boltzmann constant and e is charge of electron

But, the observed Lorentz number is greater than the theoretical value as calculated from the above expression.

Actually, it is found that the Lorentz number vary with temperature.

When metals are heated, the positive ions cores vibrate about their mean position and generate photons. The Phonons along with the free electrons carry some of the heat supplied to the metal.

This must be the cause of large difference between observed and theoretical Lorentz number.

(2) Conductivity : According to Quantum free electron theory, the conductivity of a metal is $\sigma = \mu n e$

where μ is the mobility of electron, n is the free electron concentration and e is the electron charge.

According to the above equation, polyvalent metals like Aluminum (Al) should be more conductive than mono valent metals like copper (Cu). But experimentally it is not so.

(3) Hall coefficient: According to the free electron theory, the hall coefficients for all metals is negative where as there are certain metals like Be, Cd, Zn for which the Hall coefficient is + ve

(4) Free electron theory could not explain why certain substances behave as insulators and some other substances as semiconductors, in spite of they have free electrons in them.

Numerical :

1. At what temperature we can expect 1% probability that an energy level 0.5eV above Fermi energy level will be occupied.
2. The Fermi level in potassium is 2.1eV. What are the energies for which the probabilities of occupancy at 300K are 0.99 and 0.5?
3. Calculate the Fermi energy of electron of mass 9.1×10^{-31} kg, given that density = 1.9×10^3 kg/m³, Avogadro number = 6.02×10^{26} and atomic weight = 132.9×10^{-3} kg/mol for monovalent metals.
4. Calculate the probability of an electron occupying an energy level 0.02 eV above the Fermi level at 200K, in a material
5. The Fermi level for a metal is 3.1eV, calculate the energies for which the probability of occupancy at 300K are 98% and 50%.

