

ELECTRON THEORY OF SOLIDS



**E content for Student of B. Sc Physics Honours
Part III (Paper- VII)
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Introduction to Electron Theory of Solids

The electrons in the outermost orbital of the atom which constitute the solid, determine its electrical properties. On the basis of electrical properties, solid can be broadly classified into insulators, semi conductors and conductors. The electron theory of solids (which is applicable to all solids both metals and non metals) aims to explain the structures and properties of solids through their electronic structure. It explains the electrical, thermal and magnetic properties of solids. The theory has been developed in three main stages.

- i) The classical free electron theory (CFET)
- ii) The quantum free electron theory (QFET)
- iii) The Zone theory or Band theory of solids.

The classical free electron theory

This theory was proposed to account for the electrical conduction in metals by Drude in 1900. It was extended by H.A. Lorentz in 1909. This theory was also known as **Free electron theory of metals**.

Metal atoms have one or more loosely bound valence electrons. Such electrons get detached easily even with small thermal energy. The detached electrons are neither shared nor acquired by any of the atoms of the metal. Hence they are free and just form a common pool.

The electrostatic interaction of detached electrons with the positive ion cores and with other electrons is assumed to be negligible. A consequence of this assumption is that the detached electrons can move freely everywhere within the confinements of the metal piece. Hence these electrons are called as free electrons or conduction electrons. When an electric field is applied, free electrons will experience slow drift motion in the positive direction of the field and produce a current in the metal.

Successes of Classical Free Electron Theory

- 1) It proved the validity of ohms law
- 2) It could give a satisfactory explanation to the mechanism of electrical current in conductors and thermal conductivity of metals.
- 3) It explains optical properties of metals.

It derives the relation between electrical conductivity and thermal conductivity.

Failures:

- 1) Temperature dependence of resistivity of metals could not be established correctly.
- 2) Heat capacity and paramagnetic susceptibility of conduction electrons could not be explained successfully.
- 3) It could not predict correct values to the mean free path of electrons.

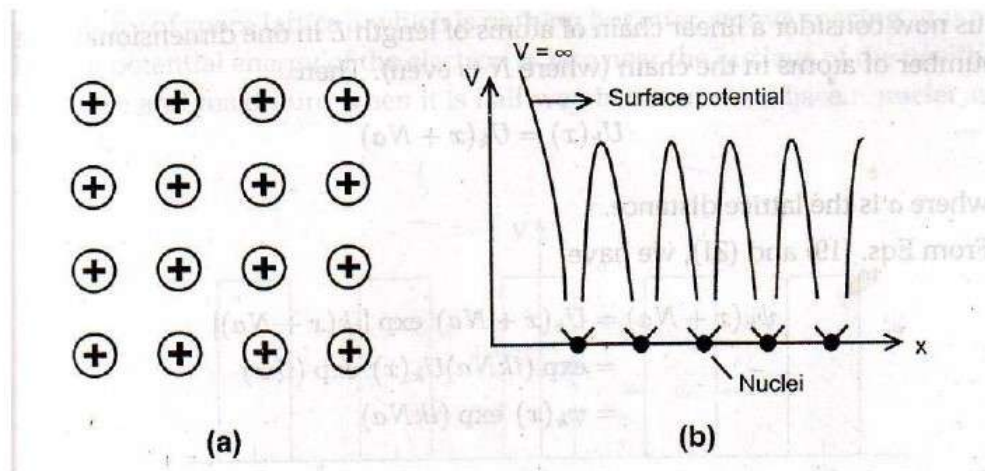
The electron quantum free theory

Sommerfeld developed this theory during 1928. He considered Drude's assumption on the free electrons as it is. In addition to that, he applied Pauli's exclusion principle to the electron gas and applied Fermi-Dirac statistics in place of Maxwell-Boltzmann statistics. The results of these modifications indicated that not all free electrons would contribute to the processes like electrical and thermal conductivities of metals. Rather only a small fraction of the free electron gas of the metal would participate in such properties.

Bloch's theorem

Crystalline solid consists of a lattice which is composed of a large number of ionic cores at regular intervals and the conduction electrons move throughout the lattice.

Let us consider the picture of the lattice in only one dimension, i.e., only an array of ionic cores along x-axis. If we plot the potential energy of a conduction electron as a position in the lattice, the variation of potential energy is as shown in figure. The potential is minimum at the positive ion sites and maximum between the two ions.



Periodic positive ion cores inside metallic crystals. b) One dimensional periodic potential in crystal.

The one dimension Schrodinger equation corresponding to this can be written as

$$\frac{d^2}{dx^2} + \frac{8\pi^2m[E-V(x)]}{\hbar^2} \psi = 0 \quad \rightarrow (1)$$

The periodic potential $V(x)$ may be defined by means of the lattice constant „a“ as

$$V(x) = V(x+a) \quad \rightarrow (2)$$

Bloch considered the solution as

$$\psi_k(x) = \exp(ikx)U_k(x) \quad \rightarrow (3)$$

Eqn (2) is known as Bloch function. $U_k(x)$ is periodic with the periodicity of the crystal lattice. The free electron wave is modulated by periodic function $U_k(x)$ is periodic with the periodicity of the crystal lattice. The free electron wave is modulated by periodic function $U_k(x)$. For a linear chain of atoms of length „L“ in one dimensional case with „N“ (= even) number of atoms in the chain,

$$U_{\mathbf{k}}(\mathbf{x}) = U_{\mathbf{k}}(\mathbf{x} + N\mathbf{a}) \quad \rightarrow (4)$$

From eqn (3) and eqn (4)

$$\begin{aligned} \Psi_{\mathbf{k}}(\mathbf{x} + n\mathbf{a}) &= U_{\mathbf{k}}(\mathbf{x} + N\mathbf{a}) e^{i\mathbf{k} \cdot (n\mathbf{a})} \\ &= e^{i\mathbf{k} \cdot N\mathbf{a}} U_{\mathbf{k}}(\mathbf{x}) e^{i\mathbf{k} \cdot \mathbf{x}} \\ &= \psi(\mathbf{e}) e^{i\mathbf{k} \cdot \mathbf{x}} \end{aligned} \quad \rightarrow (5)$$

This is referred to as Bloch condition.

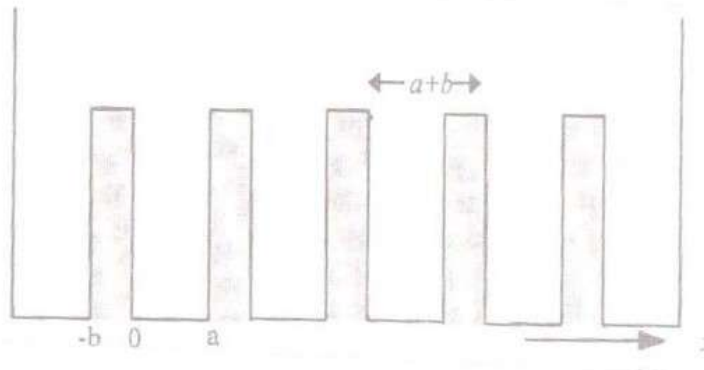
Now,

$$\begin{aligned} \psi_k(x+Na)\psi_k^*(x+Na) &= \psi_k(x)e^{(ikNa)}\psi_k^*(x)e^{(-ikNa)} \\ &= \psi_k(x)\psi_k^*(x)e^{(0)} \\ \Psi_k(x+Na)\Psi_k^*(x+Na) &= \Psi_k(x)\Psi_k^*(x) \end{aligned} \quad \rightarrow (6)$$

This means that the electron is not located around any particular atom and the probability of finding the electron is same throughout the crystal.

The Kronig-Penny Model

The periodic potential assumed by Kronig and Penny is shown in Figure. i.e., a series of rectangular wells of width „a” and are placed at a separation of b. in the regions where $0 < x < a$, the potential energy is zero and in regions such as $-b < x < 0$, the potential energy is V_0 .



One dimensional periodic potential assumed by Kronig and Penny

The main features of the model and its predictions can be explained qualitatively

Main features of the model

A. Schrodinger equation:

The dynamical behavior of electrons in the Kronig-Penny model is represented by the following Schrodinger equation,

$$\begin{aligned} \frac{d^2\psi}{dx^2} + \left[\frac{2m}{\hbar^2}\right] E\psi &= 0 && \text{for } 0 < x < a \\ \text{And} \\ \frac{d^2\psi}{dx^2} + \left[\frac{2m}{\hbar^2}\right] E - V \psi &= 0 && \text{for } -b < x < 0 \end{aligned} \quad \rightarrow (1)$$

Let us assume that total energy „E” of the electron under consideration is less than V_0 .

$$\text{Further, let us substitute } \alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \rightarrow (2)$$

Where α and β are real quantities.

Now Eq(1) becomes

$$\begin{aligned} \frac{d^2\psi}{dx^2} + \alpha^2\psi &= 0, && \text{for } 0 < x < a \\ \text{And} \\ \frac{d^2\psi}{dx^2} - \beta^2\psi &= 0, && \text{for } -b < x < 0 \end{aligned} \quad \rightarrow (3)$$

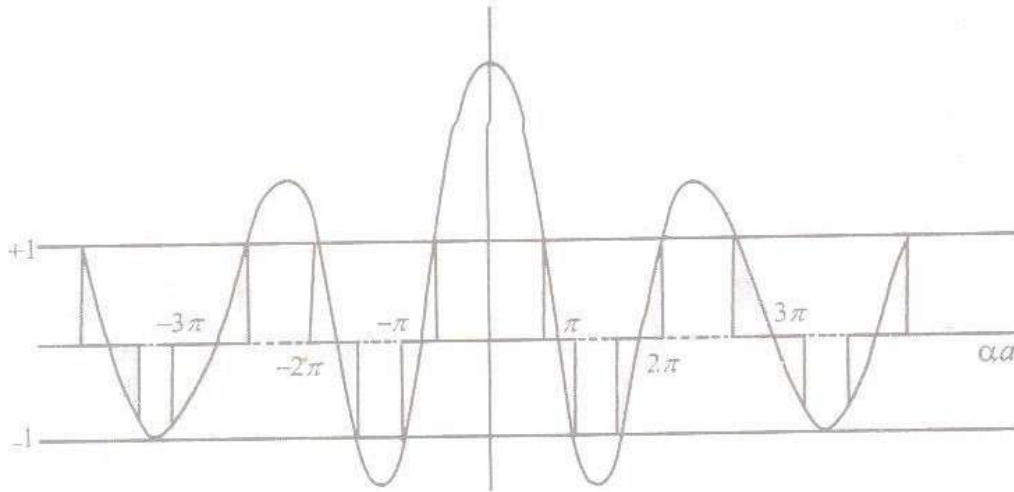
These equations can be solved with the help of block theorem. The final solution of eq (3) is given in the form of the following condition.

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a \quad \rightarrow (4)$$

Where $P = \frac{mbV_0}{\hbar^2} a$ is scattering power of the potential barrier and V_0 is barrier strength. That means, eq (3) will have a solution only when the condition (4) is satisfied.

Graph of αa versus $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$

For the best understanding of the meaning of eq(4), let us consider the plot of the condition(4) i.e. L.H.S versus αa . Since the values of $\cos k a$ on R.H.s of eq (4) lie between +1 and -1, αa (which is a measure of energy) can take only those values for which the total left hand side (L.H.S) value lies between -1 and +1. Other values are not allowed. This means that energy E is restricted to lie within certain ranges which form the allowed energy bands or zones.



Plot of the left hand side of eq (4) as a function of αa for $p = \frac{3\pi}{2}$. The solid and broken lines on the abscissa (αa - axis) correspond to allowed and forbidden energy regions of the energy spectrum respectively that are plotted in fig.

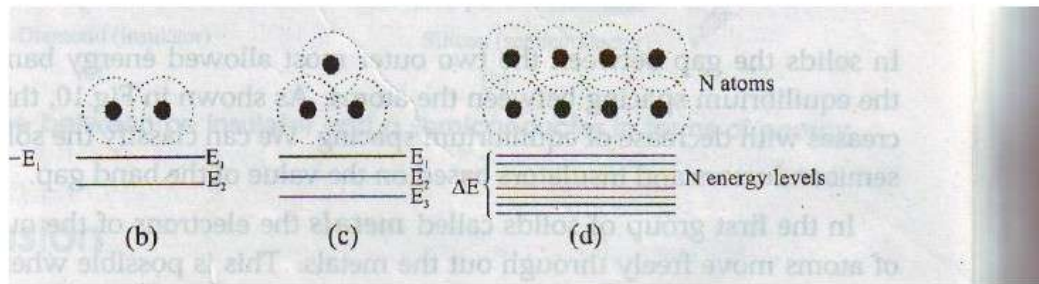
Conclusions of the graph

1. The energy spectrum consists of alternative regions of allowed and vacant bands. Forbidden band implies that the energy levels that lie in this region are not occupied by the electrons.
2. The allowed (shaded) bands are narrowest for low values of energy and become broader as energy increases, the unallowed (forbidden) bands becoming narrower.
3. a) For $P=0$ (i.e. on the extreme left), the whole energy spectrum is quasi-continuous. That is all allowed bands are joined together forming an almost continuum.
b) However, the width of a particular allowed band decreases with increase in the value of P . As $P \rightarrow \infty$, the allowed energy bands compress into simple energy levels and thus result in a line spectrum.

Origin of Energy band formation in solids

In an isolated atom, the electrons are tightly bound and have discrete, sharp energy levels [Figure]. When two identical atoms are brought closer, the outermost orbits of these atoms overlap and interact.

When the wave functions of the electrons of the different atoms begin to overlap considerably, the energy levels split into two

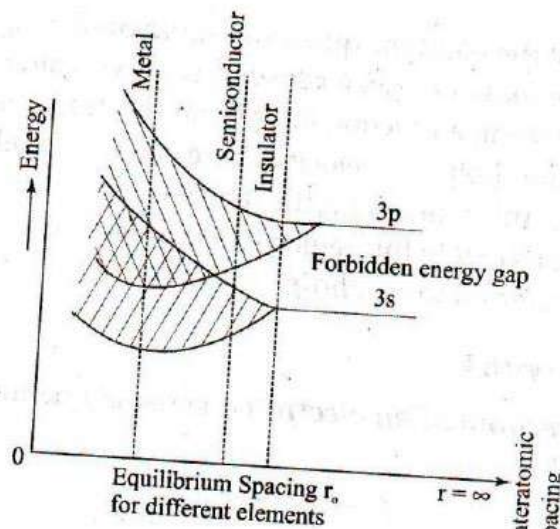


. Splitting of energy levels due to interatomic interaction

If more atoms are brought together, more levels are formed and for a solid of N atoms, each of the energy levels of an atom splits into N levels of energy [Figure].

The levels are so close together that they form an almost continuous band. The width of this band depends on the degree of overlap of the electrons of adjacent atoms and is largest for the outermost atomic electrons.

In a solid, many atoms are brought together that the split energy levels form a set of energy bands of very closely spaced levels with forbidden energy gaps between them. Overlapping of these atoms occurs for smaller equilibrium spacing r_0 .



. With decrease of interatomic spacing overlapping of energy bands take place

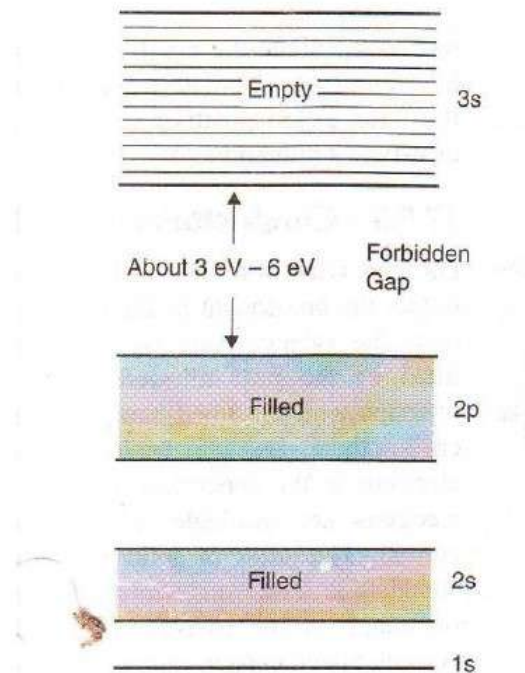
The band corresponding to outermost orbit is called conduction band and the next band is called valence band. The gap between these two allowed bands is called forbidden energy gap or band gap. According to the width of the gap between the bands and band occupation by electrons all solids can be classified broadly into three groups namely, conductors, semiconductors and insulators

Classification of materials into conductors, semiconductors and insulators

On the basis of band theory, solids can be broadly classified into three categories, viz, insulators, semiconductors and conductors. Their band structures can be as shown in figure.

Insulators

1. In case of insulators, the forbidden gap is very wide. Due to this fact electrons cannot jump from valence band to conduction band.
2. They have completely filled valence band and completely empty conduction band.
3. The resistivity of insulators is very high.
4. Insulators are bad conductors of electricity.

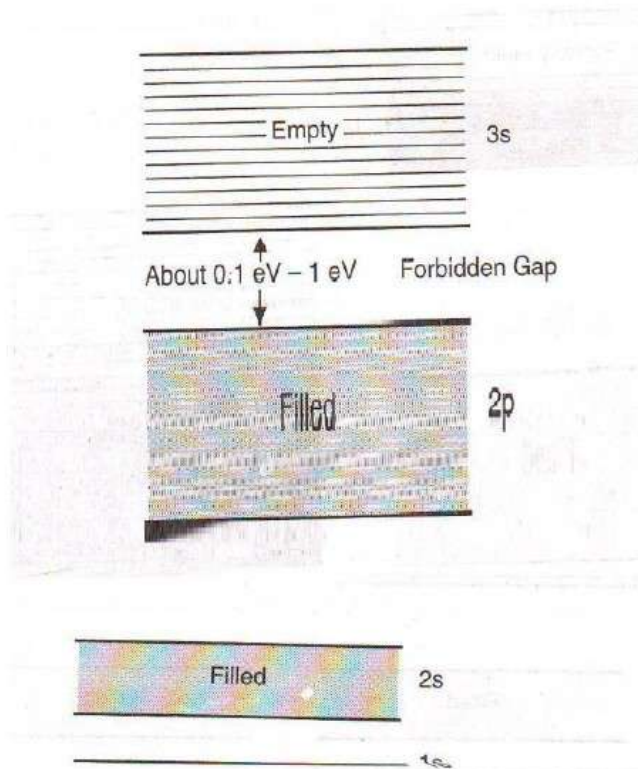


. Valence and conduction bands of insulator separated by large band gap

Semiconductors

1. In semiconductors, the band gap is very small (0.7 eV for germanium and 1.1 eV for silicon).
2. At 0k, there are no electrons in the conduction band and the valence band is completely filled. As the temperature increases, electrons from the valence band jump into conduction band.
3. The resistivity varies from 10^{-14} to $10^7 \Omega$ meter.

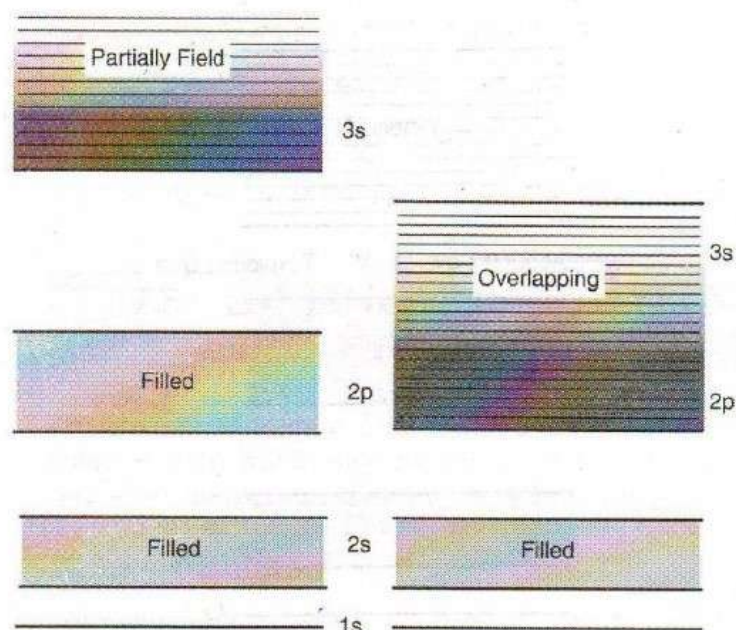
4. They have electrical properties between those of insulators and conductors.



. Valence and conduction bands of semiconductor separated by small band gap

Conductors

1. In case of conductors, there is no forbidden gap and the valence band conduction band overlaps each other.
2. Plenty of free electrons are available for electrical conduction.
3. They possess very low resistivity and very high conductivity values.
4. Metals like copper, iron etc. are best examples of conductors.



. Metals having (a) partially filled valence band and (b) overlap of completely filled valence band