UNIT – IV

7. BAND THEORY OF SOLIDS

Bloch Theorem: A crystalline solid consists of a lattice which is composed of a large number of ionic cores at regular intervals, and, the conduction electrons can move freely throughout the lattice.

Let the lattice is in only one-dimension ie only an array of ionic cores along x-axis is considered. If we plot the potential energy V of a conduction electron as a function of its position in the lattice, the variation of potential energy.

Since the potential energy of any body bound in a field of attraction is negative, and since the conduction electron is bound to the solid, its potential energy V is negative.

Further, as it approaches the site of an ionic core $V \rightarrow -\infty$. Since this occurs symmetrically on either side of the core, it is referred to as potential well. The width of the potential well b is not uniform, but has a tapering shape.

If V_0 is the potential at a given depth of the well, then the variation is such that

$b \rightarrow 0$, as $V_0 \rightarrow \infty$., and ,
The product $b\,V_0$ is a constant.

Now, since the lattice is a repetitive structure of the ion arrangement in a crystal, the type of variation of V also repeats itself. If a is the interionic distance, then , as we move in x-direction , the value of V will be same at all points which are separated by a distance equal to a.

ie $V(x) = V(x + a)$ where, x is distance of the electron from the core.

Such a potential is said to be a periodic potential.

The Bloch's theorem states that, for a particle moving in a periodic potential, the Eigen functions for a conduction electron are of the form,

$$\chi(x) = U(x) \cos kx$$

Where $U(x) = U(x + a)$

The Eigen functions are the plane waves modulated by the function U (x). The function U (x) has the same periodicity as the potential energy of the electron, and is called the modulating function.

In order to understand the physical properties of the system, it is required to solve the Schrödinger's equation. However, it is extremely difficult to solve the Schrödinger's equation with periodic potential described above. Hence the Kronig – Penney Model is adopted for simplification.

THE KRONIG -PENNEY MODEL:

It is assumed in quantum free electron theory of metals that the free electrons in a metal express a constant potential and is free to move in the metal. This theory explains successfully most of the phenomena of solids. But it could not explain why some solids are good conductors and some other are insulators and semi conductors. It can be understood successfully using the band theory of solids.

According to this theory, the electrons move in a periodic potential produced by the positive ion cores. The potential of electron varies periodically with periodicity of ion core and potential energy of the electrons is zero near nucleus of the positive ion core. It is maximum when it is lying between the adjacent nuclei which are separated by interatomic spacing. The variation of potential of electrons while it is moving through ion core is shown fig.

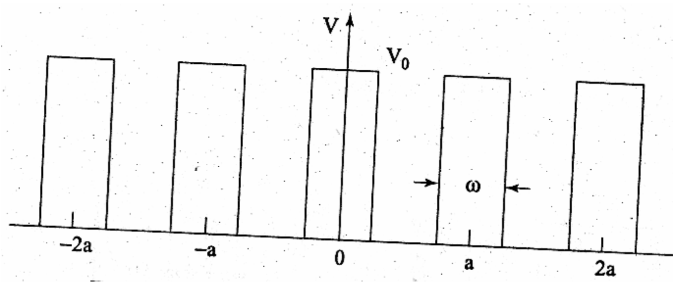


Fig. One dimensional periodic potential

$$V(x) = \{ 0, \text{ for the region } 0 < x < a$$
$$\{ V_0 \text{ for the region } -b < x < a \text{ ---------------------(1)}$$

Applying the time independent Schrödinger's wave equation for above two regions

$$d^2\Psi / dx^2 + 2mE\Psi/\hbar^2 = 0 \quad \text{for region } 0 < x < a \text{ -----------(2)}$$

and $$d^2\Psi / dx^2 + 2m(E - V)\Psi/\hbar^2 = 0 \quad \text{for region } -b < x < a \text{ -----------(3)}$$

Substituting $\alpha^2 = 2mE/\hbar^2$ ---------------(4)

$$\beta^2 = 2m(E - V)/\hbar^2 \text{ -----------(5)}$$

$$d^2\Psi / dx^2 + \alpha^2\Psi = 0 \quad \text{for region } 0 < x < a \text{ -----------(6)}$$

$$d^2\Psi / dx^2 + \beta^2\Psi = 0 \quad \text{for region } -b < x < a \text{ -----------(7)}$$

The solution for the eqn.s (6) and (7) can be written as

$$\Psi(x) = U_k(x)\, e^{ikx} \text{ ------------------(8)}$$

The above solution consists of a plane wave e^{ikx} modulated by the periodic function.

$U_k(x)$, where this $U_k(x)$ has the periodicity of the ion such that

$$U_k(x) = U_k(x+a) \text{ ------------------(9)}$$

and where k is propagating vector along x-direction and is given by $k = 2 \Pi / \lambda$. This k is also known as wave vector.

Differentiating equation (8) twice with respect to x, and substituting in equation (6) and (7), two independent second order linear differential equations can be obtained for the regions $0 < x < a$ and $-b < x < 0$.

Applying the boundary conditions to the solution of above equations, for linear equations in terms of A,B,C and D it can be obtained (where A,B,C,D are constants) the solution for these equations can be determined only if the determinant of the coefficients of A , B , C , and D vanishes, on solving the determinant.

$$(\beta^2 - \alpha^2 / 2 \alpha \beta)\sin h\beta b \sin \alpha a + \cos h\beta b \cos \alpha a = \cos k (a + b) \text{ ---------- ---- } (10)$$

The above equation is complicated and Kronig and Penney could conclude with the equation. Hence they tried to modify this equation as follows

Let V_o is tending to infinite and b is approaching to zero. Such that $V_o b$ remains finite. Therefore $\sin h\beta b \rightarrow \beta b$ and $\cos h\beta b \rightarrow 1$

$$\beta^2 - \alpha^2 = (2 m / \hbar^2) (V_o - E) - (2 m E / \hbar^2)$$

$$= (2 m / \hbar^2) (V_o - E - E) = (2 m / \hbar^2) (V_o - 2 E)$$

$$= 2 m V_o / \hbar^2 \qquad (\text{since } V_o >> E)$$

Substituting all these values in equation (10) it verities as

$$(2 m V_o / 2 \hbar^2 \alpha \beta) \beta b . \sin \alpha a + \cos \alpha a == \cos k a$$

$$(m V_o b a / \hbar^2) (\sin \alpha a / \alpha a) + \cos \alpha a == \cos k a$$

$$(P / \alpha a) \sin \alpha a + \cos \alpha a == \cos k a \qquad \text{-------------------}(11)$$

Where $P = [m V_o b a / \hbar^2]$ ------------------(12)

and is a measure of potential barrier strength.

The left hand side of the equation (11) is plotted as a function of α for the value of $P = 3 \Pi / 2$ which is shown in fig, the right hand side one takes values between -1 to +1 as indicated by the horizontal lines in fig. Therefore the equation (11) is satisfied only for those values of ka for which left hand side between ± 1.

From fig , the following conclusions are drawn.

1) The energy spectrum of the electron consists of a number of allowed and forbidden energy bands.
2) The width of the allowed energy band increases with increase of energy values ie increasing the values of αa. This is because the first term of equation(11) decreases with increase of αa.

$$(P / \alpha a) \sin \alpha a + \cos \alpha a == 3 \Pi / 2$$

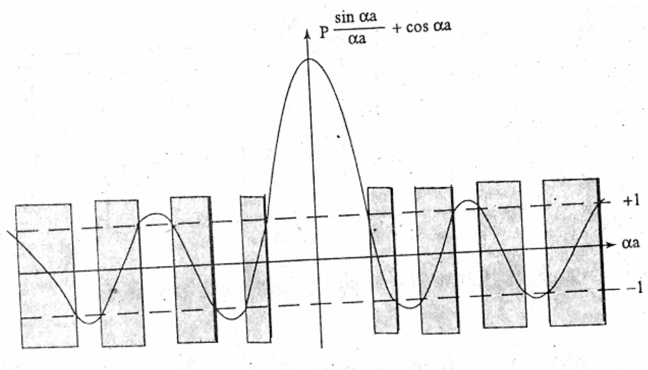


Fig Plot of $P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ versus αa.

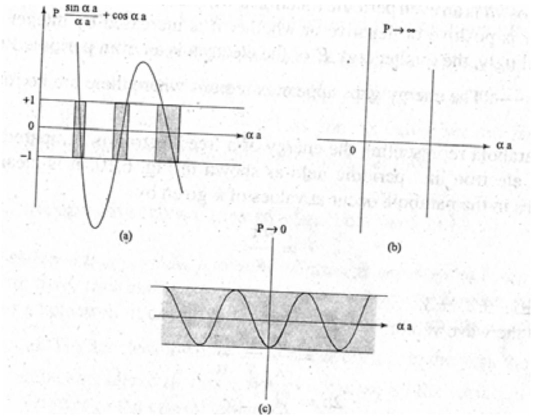


Fig. a) P=6pi b) p--> infinity c) p--> 0

3) With increasing P, ie with increasing potential barrier, the width of an allowed band decreases. As P→∞, the allowed energy becomes infinitely narrow and the energy spectrum is a line spectrum as shown in fig.

If P→∞, then the equation (11) has solution ie

$$\text{Sin } \alpha a = 0$$

$$\alpha a = \pm n \Pi$$

$$\alpha = \pm n \Pi / a$$

$$\alpha^2 = n^2 \Pi^2 / a^2$$

But $\alpha^2 = 2 m E / \hbar^2$

Therefore $2 m E / \hbar^2 = n^2 \Pi^2 / a^2$

$$E = [\hbar^2 \Pi^2 / 2 m a^2] n^2$$

$$E = n h^2 / 8 m a^2 \qquad (\text{ since } \hbar = h / 2 \Pi)$$

This expression shows that the energy spectrum of the electron contains discrete energy levels separated by forbidden regions.

4) When $P \to 0$ then

$$\cos \alpha a = \cos ka$$

$$\alpha = k , \quad \alpha^2 = k^2$$

but $\alpha^2 = 2\, m\, E / \hbar^2$

therefore $k^2 = (h^2 / 2\, m)\, (1 / \lambda^2) = (h^2 / 2\, m)\, (P^2 / h^2)$

$$E = P^2 / 2\, m$$

$$E = 1/2mv^2 \text{ ----------------(14)}$$

The equation (11) shows all the electrons are completely free to move in the crystal without any constraints. Hence , no energy level exists ie all the energies are allowed to the electrons and shown in fig(5). This case supports the classical free electrons theory.

$$[\, (P / \alpha a)\, \sin \alpha a + \cos \alpha a \,] , P \to 0$$

Velocity of the electron in periodic potential.:

According to quantum theory, an electron moving with a velocity can be treated as a wave packet moving with the group velocity v_g

$$v = v_g = d\omega / dk \text{ -----------------(1)}$$

where ω is the angular frequency of deBroglie wave and $k = 2\, \Pi / \lambda$ is the wave vector.

The energy of an electron can be expressed as

$$E = \hbar\, \omega \text{ ---------------------(2)}$$

Differentiating the equation (2) with respect to k

$$dE / dk = \hbar\, d\omega / dk \text{ -------------(3)}$$

from (1) & (3)

$$v_g = 1 / \hbar\, (dE / dk) \text{ -----------------(4)}$$

According to band theory of solids, the variations of E with k as shown in fig(1). Using this graph and equation (4), the velocity of electron can be calculated. The variation of velocity with k is shown in fig(2). From this fig, it is clear that the velocity of electron is zero at the bottom of the energy band. As the value of k increases, the velocity of electron increases and reaches to maximum at K=k.Further ,the increases of k, the velocity of electron decreases and reaches to zero at K= Π / a at the top of energy band.

Origin Of Energy Bands In Solids:

Solids are usually moderately strong, slightly elastic structures. The individual atoms are held together in solids by interatomic forces or bonds. In addition to these attractive forces, repulsive forces also act and hence solids are not easily compressed.

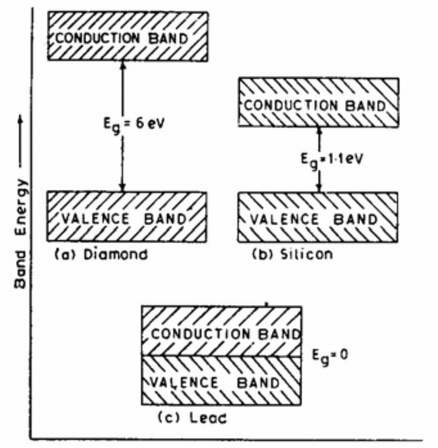
The attractive forces between the atoms are basically electrostatic in origin. The bonding is strongly dependent on the electronic structure of the atoms. The attraction between the atoms brings them closer until the individual electron clouds begin to overlap. A strong repulsive force arises to comply with Pauli’s exclusion principle. When the attractive force and the repulsive force between any two atoms occupy a stable position with a minimum potential energy. The spacing between the atoms under this condition is called equilibrium spacing.

In an isolated atom, the electrons are tightly bound and have discrete, sharp energy levels. When two identical atoms are brought closer , the outermost orbits of these atoms overlap and interact. When the wave functions of the electrons on different atoms begin to overlap considerably, the energy levels corresponding to those wave functions split. 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. 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 electrons of adjacent atoms and is largest for the outermost atomic electrons. In a solid many atoms are brought together so that the split energy levels form a set of bands of very closely spaced levels with forbidden energy gaps between them.

Classification Of Materials:

The electrons first occupy the lower energy bands and are of no importance in determining many of the electrical properties of solids. Instead, the electrons in the higher energy bands of solids are important in determining many of the physical properties of solids. Hence the two allowed energy bands called valence and conduction bands are required. The gap between these two allowed bands is called forbidden energy gap or band gap since electrons can’t have any energy values in the forbidden energy gap. The valence band is occupied by valence electrons since they are responsible for electrical, thermal and optical properties of solids. above the valence band we have the conduction band which is vacant at 0K. According to the gap between the bands and band occupation by electrons, all solids can be classified broadly into two groups.

In the first group of solids called metals there is a partially filled band immediately above the uppermost filled band .this is possible when the valence band is partially filled or a completely filled valence band overlaps with the partially filled conduction band.



In the second group of solids , there is a gap called band gap between the completely filled valence band and completely empty conduction band. Depending on the magnitude of the gap we can classify insulators and semiconductors.

Insulators have relatively wide forbidden band gaps. For typical insulators the band gap $E_g > 3$ eV. On the other hand , semiconductors have relatively narrow forbidden bands. For typical semiconductors $E_g \leq 1$ eV.

Effective mass of the electron: When an electron in a period potential is accelerated by an electric field (or) magnetic field, then the mass of the electron is called effective mass (m*).

Let an electron of charge 'e' and mass 'm' moving inside a crystal lattice of electric field E.

Acceleration $a = eE / m$ is not a constant in the periodic lattice of the crystal. It can be considered that its variation is caused by the variation of electron's mass when it moves in the crystal lattice.

Therefore Acceleration $a = eE / m^*$

Electrical force on the electron $F = m^* a$ --------------(1)

Considering the free electron as a wave packet , the group velocity v_g corresponding to the particle's velocity can be written as

$$v_g = dw / dk = 2 \Pi \, d\upsilon / dk = (2 \Pi / h) \, dE / dk \quad \text{------------------(2)}$$

where the energy $E = h \upsilon$ and $\hbar = h / 2 \Pi$.

Acceleration $a = d v_g / dt = (1 / \hbar) \, d^2E / dk \, dt = (1 / \hbar) (d^2E / dk^2) \, dk / dt$

Since $\hbar k = p$ and $dp / dt = F$,

$$dk / dt = F / \hbar$$

Therefore $a = (1 / \hbar^2) (d^2E / dk^2) F$

Or $F = (\hbar^2 / (d^2E / dk^2)) a$ -----------------------(3)

Comparing eqns . (1) and (3) we get

$$m^* = \hbar^2 / (d^2E / dk^2) \quad \text{---------------(4)}$$

This eqn indicates that the effective mass is determined by d^2E / dk^2 .

Questions:

1. Explain classical free- electron theory of metals.
2. Define electrical resistance
3. Give the basic assumptions of the classical free electron theory.
4. Explain the following: Drift velocity, mobility, relaxation time and mean free path.
5. Based on free electron theory derive an expression for electrical conductivity of metals.
6. Explain the failures of classical free theory.
7. Explain the salient features of quantum free electron theory.
8. Explain the Fermi- Dirac distribution for free electrons in a metal. Discuss its variation with temperature.
9. Explain the following i) Effective mass, ii) Bloch theorem.
10. Discuss the band theory of solids based on Kronig –Penney model. Explain the important features of this model.
11. Explain the origin of energy bands in solids.
12. Distinguish between metals, semiconductors and insulators.