

Band Theory of Solids

§ 1. Introduction. In a solid one deals with large number of interacting particles and consequently the problem of calculating the electronic wave functions and energy levels is extremely complicated. It is thus necessary to introduce a number of simplifying assumptions. First we shall assume that the nuclei in the crystalline solid are at rest. In an actual crystal this of course, is never the case, but the influence of nuclear motion on the behaviour of electrons may be treated as a perturbation of the case in which they are assumed to be at rest. Even with this assumption, we are still left with a many electron problem which can be solved only by approximate methods. In the case of solids, the most important approximate method which has been applied extensively is one electron approximation. In this approximation that total wave function is given by the combination of wave functions each of which involves the co-ordinates of only one electron. In other words the field seen by a given electron is assumed to be that of the fixed nuclei plus some average field produced by charge distribution of all other electrons. An extreme case of the one-electron approximation is Sommerfeld's theory of metals.

Within the framework of one electron approximation there are two different approaches—

1. Heitler-London or valence bond scheme—which is applicable when the atoms are far apart.
2. Bloch approach—which is applicable when an electron is considered to belong to the crystal as a whole rather than to the particular atom.

The problem as outlined above involves essentially that of the behaviour of an electron in a potential which has the periodicity of the crystals. We shall see later on that this leads to a natural distinction between metals, insulators, and semi-conductors.

Before discussing the actual problem it will be useful to discuss electronic motion in a constant and periodic potential and propagation of waves in a continuous and periodic structure.

§ 2. Density of States : Consider fig. 1 to show a diagrammatic representation of states of different momenta. Let the momentum p have the components p_x, p_y, p_z in three dimensional space. Then the vector from origin to the point (p_x, p_y, p_z) indicates the momentum in magnitude and direction. This space is called *momentum space*. A spherical surface of radius p centred on the origin will consist of all points having equal energy $p^2/2m$ and is therefore a *constant energy surface*. The quantity $g(\epsilon)$ is called density of states such that $g(\epsilon) d\epsilon$ represents the number of possible states with kinetic energy between ϵ and $\epsilon + d\epsilon$, of course, the classical values of $g(\epsilon)$ will be different from that of quantum values. If a free electron in potential box is considered classical then all points of fig. 1 represent possible states because the allowed values of p are distributed continuously and $g(\epsilon)$ is infinite. But the number of points

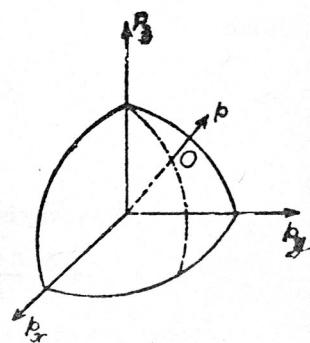


Fig. 1. Momentum Space

representing energies between ϵ and $\epsilon + d\epsilon$ will be proportional to the volume of the space between spherical surfaces of radii p and $p + dp$ i.e., $\pi p^2 dp$

$$g(\epsilon) = \frac{1}{2\pi^2} \cdot \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot \epsilon^{1/2} \quad \dots(2.1)$$

This is not infinite but becomes infinite when $\hbar \rightarrow 0$, i.e., in the classical limit which is never possible.

The expression (2.1) can be proved by referring to the wave nature of electrons which shows that a sum of electrons of momentum p can be treated as a wave train of wave length λ given by

$$\lambda = \frac{\hbar}{p} \quad \dots(2.2)$$

In general, the motion of electrons can be calculated by solving

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V] \psi = 0 \quad \dots(2.3)$$

in which E is the total energy, V is the potential energy which is usually a function of (x, y, z) and describes the field in which the electron is supposed to be moving, ψ is wavefunction, the knowledge of which constitutes the knowledge of the electron's state of motion.

In order to find the motion of an electron we must concern ourselves with the potential energy function V which describes the field in which the electron is moving e.g., Coulomb field $V = \frac{Ze^2}{r}$ in one electron problem. We then solve the equation for ψ subjecting to boundary condition of the problem. In this case, $V = -W$ because in one electron problem the nucleus and the remaining electrons are considered as one core. The boundary conditions that determine the allowed values of λ , hence also of p and therefore finally of $g(\epsilon)$.

Let the potential box be cubic of side L , then the solution of eqn. (2.3) representing the plane wave can be written as

$$\psi = ce^{ikr} = c \exp [i(k_x x + k_y y + k_z z)] \quad \dots(2.4)$$

where c is a complex number giving wave amplitude and phase, and k is a vector pointing in the direction of propagation of the wave and having magnitude $2\pi/\lambda$. The most suitable boundary condition which may be fit is that ψ is periodic with period L parallel to the axes. Then there would be an integral number of wavelengths in the distance L . If this condition is imposed the function is said to obey 'periodic boundary conditions', which satisfy if

$$k_x = \frac{2\pi}{L} n_x, \quad k_y = \frac{2\pi}{L} n_y, \quad k_z = \frac{2\pi}{L} n_z \quad \dots(2.5)$$

where n_x, n_y, n_z are $0, \pm 1, \pm 2, \dots$

and we have from (2.2),

$$p_x = \frac{\hbar}{L} n_x, \quad p_y = \frac{\hbar}{L} n_y, \quad p_z = \frac{\hbar}{L} n_z \quad \dots(2.6)$$

since

$$p = \frac{\hbar}{\lambda} \quad \text{and} \quad \lambda = \frac{L}{n}$$

The physical meaning of this boundary condition is that volume L^3 is to be regarded as one section of very large solid subdivided into identical cubical blocks lying side by side. It should be noted that it has nothing to do with unit cell. It simply implies that electron motion is identical in every subdivision.

The block L^3 typifies as infinitely large solid through which any particular electron wave stretches to infinity in the direction of its own k .

From (2.5) it follows that the possible values of p are not continuously variable as in the classical case. The states represented in fig. 1 are separated points and the quantum values of p are separated by $\hbar/2\pi$ which is very small as compared to the momentum p itself; so that a sphere of radius p will contain a large number of lattice cubes. So, the number of lattice points (states) within a radius

$$p = \frac{\text{vol. of the sphere}}{\text{vol. of one small cube}} = \frac{\frac{4}{3}\pi p^3}{\frac{h^3}{L^3}} = \frac{4\pi p^3 L^3}{h^3}$$

$$\text{So the number of states with momentum } p \text{ to } p + dp = \frac{4\pi p^2 L^3 dp}{h^3} \quad \dots(2.7)$$

$$\text{Number of states per unit volume} = \frac{4\pi p^2 dp}{h^3} \quad \dots(2.8)$$

Putting $p = (2m\epsilon)^{1/2}$, we get

$$= \frac{4\pi (2m\epsilon) (2m)^{1/2} \frac{1}{2} \epsilon^{1/2}}{h^3} = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \epsilon^{1/2} \times 2.$$

The above expression has been multiplied by 2 for the fact that each state is double in the sense that each value of momentum can be associated with either of two opposite directions of the spin.

An alternative way of dealing with the boundary conditions would be to consider a finite solid of volume L^3 but to regard potential barrier so large as to prevent completely the escape of electrons. Then whatever the electron waves may be inside the box would have to decrease to zero at the walls.

For above states given by (2.4), (2.5), (2.6) the allowed kinetic energies are

$$\epsilon = \frac{p^2}{2m} = \frac{h^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(2.9-a)$$

$$\text{and total energies} \quad E = \frac{h^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) - W \quad \dots(2.9-b)$$

Discussion of fig. 1 often refers to phase space. Phase space is a six dimensional space having three momentum co-ordinates and three position co-ordinates of a particle. Volume of a phase space is a quantity obtained by multiplying three lengths and three momenta together. A point in the phase space will represent the state of an electron which has a given p and is at a given position. Uncertainty relation does not permit p and (x, y, z) to be specified simultaneously, established experimentally in Solid State Physics in Mossbauer effect. A quantum state must be regarded not as a point in phase space but as a small volume. The size of the volume denotes the uncertainty in the state. Let this small volume be q . Now the volume of phase space occupied by electron states with momentum p to $p + dp$ is the product of $4\pi p^2 dp$ of momentum space and L^3 of ordinary space. The number of states in this range of momentum is therefore $4\pi L^3 p^2 dp/q$. Comparing this with (2.7) we get $q = h^3$. Thus each quantum state must be allotted a volume h^3 of phase space.

§ 3. k -space : The wave vector k gives the direction of the Bloch or Sommerfeld waves. Its magnitude is $2\pi/\lambda$. Each electron will have its own k and its own energy.

Consider a set of three Cartesian axes labelled k_x, k_y, k_z and situated parallel to the x, y, z axes of ordinary space, fig. 2. The three new axes define k -space. Obviously the distance from the origin to some point in k -space represents a wave vector k .

Sommerfeld waves have a particularly simple relation between k and p i.e. $p = \hbar k$. Therefore for the free electrons of the Sommerfeld model, k -space and momentum space are practically identical; they differ by a scale factor only. Spherical surfaces, in k -space, centred on the origin, will consist of points representing states of the same energy.

$$E = \frac{\hbar^2 k^2}{2m} W. \quad \dots(3.1)$$

For electrons in a periodic potential the constant energy surfaces may be quite different from spheres.

For elastic waves in a continuous medium the frequency is inversely proportional to the wavelength i.e., there exists a linear relationship between frequency and wave number (or wave vector). This implies that a velocity of propagation is independent of the wavelength. Furthermore, there exists no upper limit for the frequency of the vibrational modes in a continuous medium. When one considers the modes of vibration in a lattice of discrete mass points which form a periodic structure, two characteristic features appear :

1. There exist allowed frequency bands, separated by forbidden regions.
2. The frequency is no longer proportional to a wave number but a periodic function of the wave number.

Returning now to the motion of electrons, we have

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

and the kinetic energy of the electrons is

$$E_{\text{kin}} = E - V = \frac{1}{2} mu^2 = \frac{p^2}{2m} \quad \dots(3.2)$$

where

$$p = mu = h/\lambda.$$

The wave number ($1/\lambda$) for a free electron is given by (mu/h). Sometimes it is customary to multiply the wave number by 2π and represent $(2\pi/\lambda) = k$.

$$\text{So, } E_{\text{kin}} = \frac{p^2}{2m} = \frac{h^2}{2m \lambda^2} = \frac{h^2 k^2}{8\pi^2 m} = \frac{\hbar^2 k^2}{2m}. \quad \dots(3.3)$$

This quantity k for free electron is a vector whose magnitude is given by

$$k = \frac{2\pi}{\lambda} = 2\pi \frac{mu}{h} = \frac{mu}{\hbar}. \quad \dots(3.4)$$

Here λ is the wavelength associated with the electron and p is the momentum of the electron ; of course, the potential energy has been assumed zero. In this case there is no upper limit to the energy i.e. energy spectrum is quasi continuous, quasi because the limited dimensions of the potential box produce closely spaced but discrete energy levels.

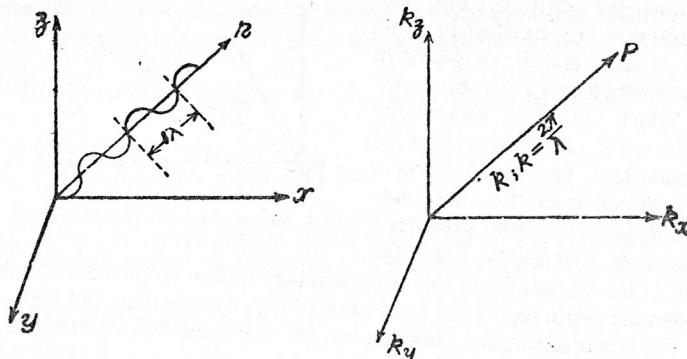


Fig. 2. k -space and ordinary space. The wave-vector k of a wave of wavelength λ proceeding through ordinary space in the direction r is represented in k -space by the point P .

In an assembly of free electrons the state of any one electron may be described in terms of its k value and the diagrams in the so called k -space can be drawn in which three rectangular coordinates k_x , k_y , k_z represent the components of the wave number k in the direction of the coordinate axis, fig. 3. Free electrons represented by points near the origin of the k space have low wave number and low momenta and hence low velocities, whereas a point far from the origin represents an electron of high wavenumber and high velocities.

For free electron, the direction OP, where P is the wave number of a given electron is the direction of the electron with velocity u .

As the energy of the free electron is given by the relation

$$E_{\text{kin}} = \frac{\frac{h^2 k^2}{2}}{8 \pi^2 m}, \quad \dots(3.5)$$

it is evident that a graph between $E(k)$ and k should be periodic (parabolic) of the form shown in fig. 4, since the energy is independent of the direction of k .

Thus we arrive at the following two important results which will be derived later on.

1. There exist allowed energy bands separated by forbidden bands.
2. The functions $E(k)$ are periodic in k .

§ 4. Bloch Wave. Consider fig. 5 in which crystal cells are shown diagrammatically. Let $V(r)$ be the potential energy of an electron at position r . Let r' be the corresponding point in another cell. Then $V(r) = V(r')$. A vector joining any point r , with a corresponding one r' is called a translation vector R . If a_1, a_2, a_3 are three primitive vectors defining the edges of unit cell; then R can be written as :

$$R_m = m_1 a_1 + m_2 a_2 + m_3 a_3 \quad \dots(4.1)$$

where m is any integer. The repetitive nature of the potential energy can be expressed by ;

$$V(r + R_m) = V(r). \quad \dots(4.2)$$

The problem of the possible electron states must be in wave mechanical form. It was Bloch who in 1928 showed that the solutions are of the form

$$\psi_k = u_k(r) e^{ikr} \quad \dots(4.3)$$

or

$$\psi_k(x) = u_k(x) e^{ikx}$$

in one dimension. Functions like this are called *Bloch functions*. k , the wave factor must be a real quantity otherwise ψ would not remain finite as $r \rightarrow \pm \infty$, $u_k(r)$ is a function of r which has the same periodicity as the lattice, i.e.,

$$u_k(r + R_m) = u_k(r) \quad \dots(4.4)$$

In general, there will be a different $u_k(r)$ for each E , we may refer to ψ_k as a wave propagated in the direction of k , having an amplitude which is modulated with the period of lattice. A similarity between Bloch function and Sommerfeld's waves is the fact that they travel in the direction of k undiminished in

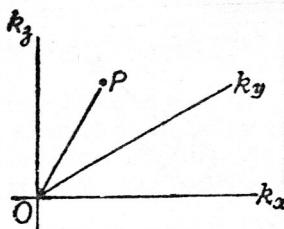


Fig. 3. Position of free electron in k -space.

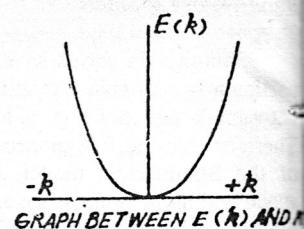


Fig. 4.

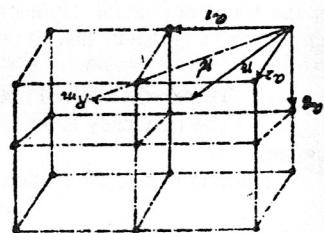


Fig. 5. Primitive vectors a_1, a_2, a_3 of a unit cell of a crystal and the translation vector R_m . The R_m shown here is $1a_1 + 0a_2 + 0a_3$.

amplitude. They cannot by themselves therefore, describe any resistance to the motion of electrons. It is an important result of the theory that in a perfectly periodic potential, the electron waves travel unhindered through the crystal.

§ 5. Bloch Theorem: The Schrodinger equation for an electron moving in one dimensional periodic potential is

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad \dots(5.1)$$

where $V(x)$ is the potential at a distance x from the origin which is assumed to vary periodically in space with an interval equal to the lattice constant a i.e., the potential at x and that at $(x + a)$ is the same i.e., in other words

$$V(x) = V(x + a) \quad \dots(5.2)$$

The Schrodinger equation is then —

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0.$$

The solution of this theorem exists in the form

$$\psi = e^{\pm ikx} \cdot u_k(x) \quad \dots(5.3)$$

where

$$u_k(x) = u_k(x + a).$$

In other words the solutions are plane waves modulated by the function $u_k(x)$ which has the same periodicity as the lattice. This theorem is known as *Bloch Theorem*. Functions of the type (5.3) are called *Bloch functions*. Before giving the proof of this Bloch theorem we first give the property of Bloch function,

$$\psi(x) = e^{ikx} \cdot u_k(x)$$

$$\psi(x + a) = e^{ik(x+a)} u_k(x + a) = e^{ikx} u_k(x)$$

$$u_k(x + a) = u_k(x).$$

Thus the Bloch function has the property

$$\psi(x + a) = Q \psi(x)$$

where

$$Q = e^{\pm ikx} \quad \dots(5.4)$$

Now it is quite obvious that if we can show that the equation (5.1) with the property (5.4) has the solutions as Bloch functions then the theorem will be proved.

Since the equation (5.1) is the differential equation of the second order so it has two independent solutions and all other solutions are expressible as a linear combination of the independent ones. Suppose $f(x)$ and $g(x)$ are two real independent solutions of the equation. Then, since $f(x + a)$ and $g(x + a)$ are the solutions of Schrodinger equation we have—

$$f(x + a) = \alpha_1 f(x) + \alpha_2 g(x)$$

$$g(x + a) = \beta_1 f(x) + \beta_2 g(x)$$

$$\dots(5.5)$$

where α and β are real functions of E .

Then the solution of Schrodinger equation is

$$\psi(x) = Af(x) + Bg(x).$$

Then according to (5.4) we have

$$\psi(x + a) = (A\alpha_1 + B\beta_1)f(x) + (A\alpha_2 + B\beta_2)g(x).$$

Now in view of the property (5.5), we should choose A and B such that

$$A\alpha_1 + B\beta_1 = QA$$

$$A\alpha_2 + B\beta_2 = QB$$

$$\dots(5.6)$$

Thus, we have obtained the property

$$\psi(x+a) = Q \cdot \psi(x).$$

Since equations (5.6) have non-vanishing values for A and B only if the determinant of their coefficients vanish

$$\begin{vmatrix} \alpha_1 - Q & \beta_1 \\ \alpha_2 & \beta_2 - Q \end{vmatrix} = 0 \quad \text{or} \quad Q^2 - (\alpha_1 + \beta_2)Q + \alpha_1\beta_2 - \alpha_2\beta_1 = 0. \quad \dots(5.7)$$

Now in order to show that $\alpha_1\beta_2 - \alpha_2\beta_1 = 0$, we consider in the following manner :

Since $f(x)$ and $g(x)$ are the two independent solutions of Schrodinger equation, then we have

$$-\frac{\hbar^2}{2m} \frac{d^2 f(x)}{dx^2} + V(x) \cdot f(x) = E \cdot f(x). \quad \dots(5.8)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 g(x)}{dx^2} + V(x) \cdot g(x) = E \cdot g(x). \quad \dots(5.9)$$

and

Multiplying (5.8) and (5.9) by $g(x)$ and $f(x)$ respectively and subtracting, we get

$$-\frac{\hbar^2}{2m} \left[g(x) \cdot \frac{d^2 f(x)}{dx^2} - f(x) \cdot \frac{d^2 g(x)}{dx^2} \right] = 0. \quad \dots(5.10)$$

Since $\frac{\hbar^2}{2m}$ is not zero, therefore, we have

$$g(x) \cdot \frac{d^2 f(x)}{dx^2} - f(x) \cdot \frac{d^2 g(x)}{dx^2} = 0.$$

which on integration yields

$$W(x) = g(x) \cdot \frac{d f(x)}{dx} - f(x) \cdot \frac{d g(x)}{dx} = \text{constant}. \quad \dots(5.11)$$

This is known as *Green's identity* and W is known as *Wronskian* of the two solutions which in this case is constant. Hence it must have the same value at x and $x+a$, i.e.

$$W(x) = W(x+a). \quad \dots(5.12)$$

$$W(x+a) = g(x+a) \cdot \frac{d f(x+a)}{dx} - f(x+a) \cdot \frac{d g(x+a)}{dx}$$

Substituting for $f(x+a)$ and $g(x+a)$ from (5.5), we get

$$\begin{aligned} W(x+a) &= \{\beta_1 f(x) + \beta_2 g(x)\} \frac{d}{dx} (\alpha_1 f(x) + \alpha_2 g(x)) - \{\alpha_1 f(x) + \alpha_2 g(x)\} \frac{d}{dx} (\beta_1 f(x) + \beta_2 g(x)) \\ &= \left\{ \beta_1 f(x) + \beta_2 g(x) \right\} \left\{ \alpha_1 \cdot \frac{d f(x)}{dx} + \alpha_2 \cdot \frac{d g(x)}{dx} \right\} - \left\{ \alpha_1 f(x) + \alpha_2 g(x) \right\} \cdot \left\{ \beta_1 \cdot \frac{d f(x)}{dx} + \beta_2 \cdot \frac{d g(x)}{dx} \right\} \\ &= \alpha_1 \beta_1 f(x) \cdot \frac{d f(x)}{dx} + \alpha_2 \beta_1 f(x) \cdot \frac{d g(x)}{dx} + \beta_2 \alpha_1 g(x) \cdot \frac{d f(x)}{dx} + \beta_2 \alpha_2 g(x) \cdot \frac{d g(x)}{dx} \\ &\quad - \alpha_1 \beta_1 f(x) \cdot \frac{d f(x)}{dx} - \alpha_1 \beta_2 f(x) \cdot \frac{d g(x)}{dx} - \alpha_2 \beta_1 g(x) \cdot \frac{d f(x)}{dx} - \alpha_2 \beta_2 g(x) \cdot \frac{d g(x)}{dx} \end{aligned}$$

$$\text{or } W(x+a) = \alpha_1 \beta_2 \left\{ g(x) \cdot \frac{d f(x)}{dx} - f(x) \cdot \frac{d g(x)}{dx} \right\} - \alpha_2 \beta_1 \left\{ g(x) \cdot \frac{d f(x)}{dx} - f(x) \cdot \frac{d g(x)}{dx} \right\}$$

$$= (\alpha_1 \beta_2 - \alpha_2 \beta_1) \left\{ g(x) \cdot \frac{df(x)}{dx} - f(x) \cdot \frac{dg(x)}{dx} \right\}$$

From (5.11) we have

$$W(x+a) = (\alpha_1 \beta_2 - \alpha_2 \beta_1) W(x).$$

Since $W(x+a) = W(x)$ we get

$$\alpha_1 \beta_2 - \alpha_2 \beta_1 = 1 \quad \dots(5.13)$$

Substituting this value of (5.13) in (5.7), we get

$$Q^2 - (\alpha_1 + \beta_2) Q + 1 = 0 \quad \dots(5.14)$$

or $Q^2 - \mu Q + 1 = 0 \quad \text{where } \mu = \alpha_1 + \beta_2.$

Here $\alpha_1 + \beta_2$ is a real function of E . The two roots of this equation are Q_1 and Q_2 , given by

$$Q_1 = \frac{\mu + \sqrt{(\mu^2 - 4)}}{2} \quad \text{and} \quad Q_2 = \frac{\mu - \sqrt{(\mu^2 - 4)}}{2}$$

such that $Q_1 Q_2 = 1$. Thus there are two functions $\psi_1(x)$ and $\psi_2(x)$ which exhibit the property (5.4).

The following cases are of special interest —

Case I. For the regions of energy in which $\mu < 2$ or ($\mu^2 < 4$), the two roots are complex and since $Q_1 Q_2 = 1$ they will be conjugate. In these regions of energy we may write

$$Q_1 = e^{ika} \text{ and } Q_2 = e^{-ika} \quad \dots(5.15)$$

and the corresponding wave functions $\psi_1(x)$ and $\psi_2(x)$ must satisfy the relation

$$\psi_1(x+a) = e^{ika} \psi_1(x) \quad \text{and} \quad \psi_2(x+a) = e^{-ika} \psi_2(x)$$

or in general, $\psi(x+a) = e^{\pm ika} \psi(x)$ $\dots(5.16-a)$

Such wave functions as already mentioned are called *Bloch functions* and are generally in the form

$$\psi(x) = e^{\pm ikx} \cdot u_k(x) \quad \text{where} \quad u_k(x) = u_k(x+a). \quad \dots(5.16-b)$$

These have the property

$$\psi(x+a) = e^{\pm ik(x+a)} \cdot u_k(x+a) = e^{\pm ikx} e^{\pm ika} \cdot u_k(x) = e^{\pm ika} \cdot \psi(x) \quad \dots(5.17)$$

which gives the same form as in (5.16-a).

Hence it is concluded that if Schrodinger equation

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

has solutions of the property

$$\psi(x+a) = e^{\pm ika} \psi(x),$$

then the solution can be written as Bloch function

$$\psi(x) = e^{\pm ikx} \cdot u_k(x) \quad \text{where} \quad u_k(x) = u_k(x+a).$$

Case II. When $\mu > 2$ or ($\mu^2 > 4$) the two roots Q_1 and Q_2 are real and reciprocals of each other. Their solutions do not represent a wave function and thus there are no electronic states in the energy region corresponding to Q_1 and Q_2 .

This leads to the concept that the energy spectrum of an electron in a periodic potential consists of allowed and forbidden energy regions of bands. The regions corresponding to complex values of μ represent the allowed energy bands while those for the real values of μ correspond to the forbidden energy bands.

Now to study the details of this phenomenon we shall consider the motion of electrons in a simple one-dimensional periodic potential suggested by Kronig and Penney.

§ 6. Kronig-Penney Model : The essential feature of the behaviour of electronic potential may be studied by considering a periodic rectangular well structure in one dimension, which was first discussed

by Kronig and Penney in 1931. It is assumed here that the potential energy of an electron, when it moves in one dimensional perfect crystal lattice, is represented in the form of rectangular walls as shown in the fig. 6. The period of the potential is $(a + b)$. In regions where $0 < x < a$, the potential energy is assumed to be zero and in the regions $-b < x < 0$, the potential energy is V_0 .

Though this is a highly artificial model but it is a model for which the Schrodinger equation can be solved explicitly in terms of elementary functions. The Schrodinger equation for the two regions can be written as

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi = 0 \quad \text{for } 0 < x < a \quad \dots(6.1)$$

and

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{for } -b < x < 0 \quad \dots(6.2)$$

Let the energy E of the electrons under consideration be less than V_0 , then let us put

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \dots(6.3)$$

where α and β are real quantities. The two equations then become

$$\frac{d^2 \psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{for } 0 < x < a \quad \dots(6.4)$$

$$\frac{d^2 \psi}{dx^2} - \beta^2 \psi = 0 \quad \text{for } -b < x < 0 \quad \dots(6.5)$$

Now from the Bloch theorem the solution of wave equation for a periodic potential will be of the form of a plane wave modulated with the periodicity of the lattice of the form

$$\psi = e^{ikx} \cdot u_k(x) \quad \dots(6.6)$$

where $u_k(x)$ is the periodic function in x with period $(a + b)$.

Since

$$\psi = e^{ikx} \cdot u_k(x)$$

So,

$$\frac{d\psi}{dx} = i k \cdot e^{ikx} \cdot u_k(x) + e^{ikx} \cdot \frac{du}{dx}$$

$$\frac{d^2 \psi}{dx^2} = -k^2 \cdot e^{ikx} \cdot u_k(x) + i k e^{ikx} \frac{du}{dx} + i k \cdot e^{ikx} \cdot \frac{du}{dx} + e^{ikx} \frac{d^2 u}{dx^2}$$

$$= -k^2 \cdot e^{ikx} \cdot u_k(x) + 2i k \cdot e^{ikx} \frac{du}{dx} + e^{ikx} \frac{d^2 u}{dx^2}$$

Substituting these values in (6.4) and (6.5), we get

$$\frac{d^2 \psi}{dx^2} + 2i k \cdot \frac{du}{dx} + (\alpha^2 - k^2) u = 0 \quad \text{for } 0 < x < a \quad \dots(6.7)$$

and

$$\frac{d^2 \psi}{dx^2} + 2i k \cdot \frac{du}{dx} + (\beta^2 + k^2) u = 0 \quad \text{for } -b < x < 0 \quad \dots(6.8)$$

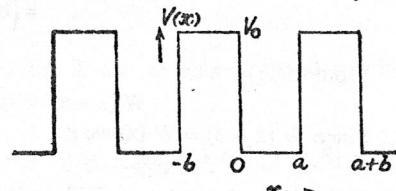


Fig. 6

Now to solve these differential equations assume the solution of the form

$$\text{so that } \frac{du}{dx} = m e^{mx}; \quad \frac{d^2 u}{dx^2} = m^2 e^{mx}$$

which on substituting in (6.7), gives

$$m^2 e^{mx} + 2ik.m e^{mx} + (\alpha^2 - k^2) e^{mx} = 0 \quad \text{or} \quad m^2 + 2ik.m + (\alpha^2 - k^2) = 0 \quad \text{for } 0 < x < a$$

$$\text{so that } m = \frac{-2ik \pm \sqrt{\left\{ (-4k^2 - 4\alpha^2 + k^2) \right\}}}{2} = -ik \pm i\alpha$$

$$\text{i.e. } m_1 = i(\alpha - k) \quad \text{and} \quad m_2 = -i(\alpha + k).$$

Hence the general solution is

$$u_1 = A e^{m_1 x} + B e^{m_2 x} \quad \dots(6.9)$$

$$u_2 = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x} \quad \dots(6.10)$$

Similarly,

where A, B, C, D are constants. These constants are so chosen that they satisfy the conditions of continuity and periodicity of wavefunctions. Now because of continuity at $x = 0$ the two wave-functions and their derivatives must have the same value at $x = 0$,

$$\text{i.e. } u_1(x)_x=0 = u_2(x)_x=0$$

$$\text{or } \left(\frac{du_1}{dx} \right)_{x=0} = \left(\frac{du_2}{dx} \right)_{x=0} \quad \text{or} \quad A + B = C + D \quad \dots(6.11)$$

$$\text{and } i(\alpha - k) A - i(\alpha + k) B = (\beta - ik) C - (\beta + ik) D \quad \dots(6.12)$$

and because of periodicity of function U(x), the values at $x = a$ must be equal to those at $x = -b$.

$$u_1(x)_x=a = u_2(x)_x=-b \quad \text{and} \quad \left(\frac{du_1}{dx} \right)_{x=a} = \left(\frac{du_2}{dx} \right)_{x=-b}$$

$$\text{or } A e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a} = C e^{-(\beta-ik)b} + D e^{(\beta+ik)b} \quad \dots(6.13)$$

$$\text{and } i(\alpha - k) A e^{i(\alpha-k)a} - i(\alpha + k) B e^{-i(\alpha+k)a} = (\beta - ik) C e^{-(\beta-ik)b} - (\beta + ik) D e^{(\beta+ik)b} \quad \dots(6.14)$$

Now these four equations (6.11) to (6.14) have a solution only if the determinant of the coefficients of A, B, C, D vanishes, i.e.,

$$\begin{vmatrix} 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) \\ e^{i(\alpha-k)a} & e^{-i(\alpha+k)a} \\ i(\alpha - k) e^{i(\alpha-k)a} & -i(\alpha + k) e^{-i(\alpha+k)a} \\ & -1 \\ & -(\beta - ik) & (\beta + ik) \\ & -e^{-(\beta-ik)b} & -e^{(\beta+ik)b} \\ & -(\beta - ik) e^{-(\beta-ik)b} & (\beta + ik) e^{(\beta+ik)b} \end{vmatrix} = 0$$

This determinant on solving leads to the following equation

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b. \sin \alpha a + \cosh \beta b. \cos \alpha a = \cos k(a+b) \quad \dots(6.15)$$

In order to express the relation in a more simplified form Kronig and Penney suggested delta functions such that $V_0 \rightarrow \infty$ and $b \rightarrow 0$ but the product $V_0 b$ or $\beta^2 b$ remains finite. Such a function is known as *delta function*. Within this limit equation (6.15) reduces to

$$\frac{\beta b}{2\alpha} \cdot \sin \alpha a + \cos \alpha a = \cos k a \quad \dots(6.16)$$

between when $b \rightarrow 0$, $\sinh \beta b \rightarrow \beta b$; $\cosh \beta b \rightarrow 1$

Equation (6.16) is further written as

$$P \cdot \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a. \quad \dots(6.17)$$

where the quantity P is defined by the expression

$$P = \frac{\beta^2 a b}{2} = \frac{2 m V_0 a b}{2 \hbar} = \frac{m V_0 a b}{\hbar^2} \quad \dots(6.18)$$

since V_0 tends to infinity i.e. P is a measure of the quantity $V_0 b$, which is the area of the potential barrier.

The physical significance of this quantity is that if P is increased, the area of the potential barrier is increased and the given electron is bound more strongly to a particular potential well. When $P \rightarrow 0$, the potential barrier becomes very weak which means that electrons are free electrons. In this case we obtain from equation (6.17),

$$\alpha a = ka \quad \text{or} \quad \alpha = k$$

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

$$\text{Hence } E = \frac{k^2 \hbar^2}{2m} = \frac{\hbar^2 k^2}{8\pi m} \quad \dots(6.19)$$

which resembles the result obtained by considering the Sommerfeld model of a metal.

If a graph of the function $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$ is plotted against αa for $P = 3\pi/2$, a curve as shown in

fig. 7 is obtained. Since $\alpha = \sqrt{\left(\frac{2m E}{\hbar^2}\right)}$ the abscissa αa is a measure of energy and by finding the value of αa at any point, the energy represented by the function at that point is calculated. The values of αa satisfying equation (6.17) are obtained by drawing a line parallel to αa axis at a distance $\cos ka$ from it and if we vary ka continuously from 0 to π i.e. $\cos ka$ from +1 to -1, we obtain all possible values of αa and hence that of energy.

These possible values of αa are drawn heavily in fig. 7. The following important conclusions can be drawn from the diagram.

1. The energy spectrum consists of an infinite number of allowed energy bands separated by intervals in which there are no energy levels. These are known as *forbidden regions*.

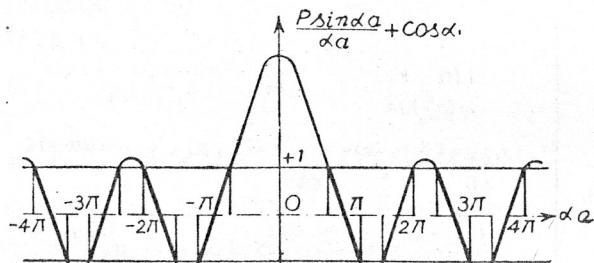


Fig. 7. Graph showing the function $[(P \sin \alpha a)/\alpha a] + \cos \alpha a$ plotted against αa for $P = 3\pi/2$.

The boundaries of the allowed ranges of αa correspond to the values of $\cos ka = \pm 1$ or $ka = n\pi$ i.e.

$$k = \frac{n\pi}{a}$$

2. When αa increases the first term on the left side of (6.17) decreases so the width of allowed energy bands is increased and forbidden regions become narrower.

3. The width of allowed band decreases with the increasing value of P i.e., with increasing the binding energy of electrons. When P is infinite, the allowed energy bands are infinitely narrow and are independent of k because when $P \rightarrow \infty$, the allowed energy ranges of αa reduce to points given by

$$\alpha a = \pm n\pi \quad \text{or} \quad \alpha = \pm \frac{n\pi}{a} \quad \text{or} \quad \alpha^2 = \frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$\text{or} \quad E = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \dots(6.20)$$

i.e., E is independent of k .

The energy levels in this case are discrete and the electron is completely bound. It is caught between the potential wells and moves only in one cell of width a .

Hence we conclude that in one dimensional problem for the limiting case the spectrum of permissible energy values is found to consist of continuous regions separated by finite intervals. By varying the quantity P i.e. $V_0 b$ from 0 to ∞ we pass from the case of free to that of bound electrons and can thus study the changes in the allowed and forbidden ranges of energy and the wave function.

From (6.17) it is also possible to obtain the energy E as a function of the wave number k which leads to the following conclusion.

The discontinuities in the E vs k curve occur at $k = (n\pi/a)$ where $n = 1, 2, 3, \dots$

These k values define boundaries of the I, II etc. Brillouin zones. From $k = \pi/a$ to $-\pi/a$ there exists the first Brillouin zone. The second zone consists of two parts : one from $+\pi/a$ to $+2\pi/a$ and the second from $-\pi/a$ to $-2\pi/a$.

Each portion of the curve may be called a band. The characteristics of the curves are that :

1. They are horizontal at the top and bottom.
2. They are parabolic near the top and the bottom with curvatures in opposite directions.
3. (d^2E/dk^2) is positive in the lower portion of the band and negative for the upper portion.

§ 7. Origin of Energy Gap :

In order to consider physically the reason of forbidden bands, consider first the simple problem of a linear lattice of lattice constant a . The low energy portions of the band structure are shown in fig. 9 (a) and in fig. 9 (b) for electrons which are nearly free but with energy gap at $k = \pm \pi/a$.

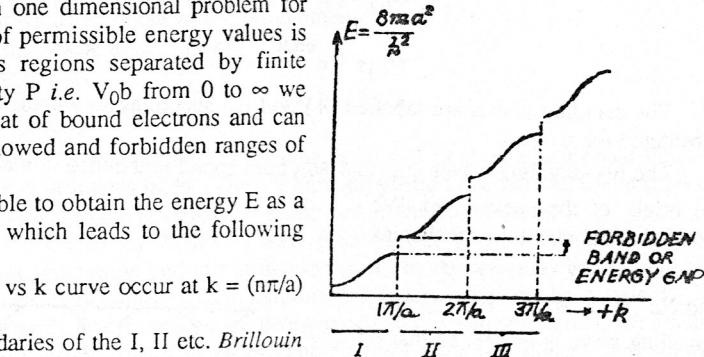


Fig. 8. E as a function of wave no k .

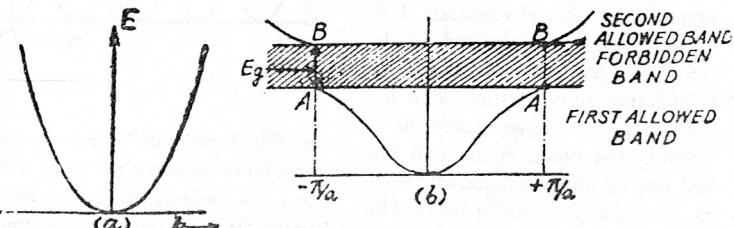


Fig. 9. (a) Plot of E versus k for free electron.

(b) Plot of E versus wave vector k for an electron in a monatomic linear lattice of lattice constant a . The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm \pi/a$.

The Bragg condition, $(K + G)^2 = k^2$, for diffraction of a wave vector k becomes in one dimension

$$k = \pm \frac{1}{2}G = \pm \frac{n\pi}{a} \quad \dots(7.1)$$

where $G = \pm (2n\pi/a)$ is a reciprocal lattice vector. The first reflection and the first energy gap occur at $k = \pm \pi/a$, other energy gaps occur for other values of integer n in (7.1)

The reflection at $k = \pm \pi/a$ arises because the wave reflected from one atom in the linear lattice interferes constructively with the wave from a nearest neighbour atom. The phase difference between the two reflected waves is just $\pm 2\pi$ for these two values of k . The region in k space between $-\pi/a$ and $+\pi/a$ is called first Brillouin zone.

At $k = \pm \pi/a$ the wave functions are not the travelling waves $e^{i\pi x/a}$ and $e^{-i\pi x/a}$ of the free electron model. We shall show that the solutions of these particular values of k are made up equally of waves travelling to the right and to the left. The solutions are standing waves. This can be understood in the following manner : When the Bragg condition is satisfied, a wave travelling in one direction is soon Bragg-reflected and then travels in opposite direction. Each subsequent Bragg reflection reverses the direction of travel again. The only time-independent situation is formed by standing waves. We can form two different standing waves from the travelling waves $e^{i\pi x/a}$ and $e^{-i\pi x/a}$.

$$\begin{aligned}\psi_{(+)} &\propto \left(e^{i\pi x/a} + e^{-i\pi x/a} \right) = 2 \cos \frac{\pi x}{a} \\ \psi_{(-)} &\propto \left(e^{i\pi x/a} - e^{-i\pi x/a} \right) = 2 \sin \frac{\pi x}{a}.\end{aligned} \quad \dots(7.2)$$

The standing waves are labelled (+) and (-) according to whether they are even or odd when $-x$ is substituted for x .

The two standing waves $\psi_{(+)}$ and $\psi_{(-)}$ correspond in a lattice to the different values of energy. This is the origin of the energy gap. We recall that in quantum mechanics the probability density ρ of a particle is $|\psi|^2$. For a pure travelling wave $\psi \propto e^{ikx}$, so that $\rho \propto e^{-2ikx}$, $e^{-2ikx} = 1$, a constant. But ρ is not constant for linear combination of plane waves. Consider linear combinations $\psi_{(\pm)}$ in (7.2); for $\psi_{(+)}$ we have $\rho \propto \cos^2 \pi x/a$. Fig. 10 (a) indicates the variation of the electrostatic P.E. of the conduction electron in the field of positive ion cores of monatomic linear lattice. The ion cores bear a positive charge, as in forming the metal each atom has lost one or more valence electrons to form the conduction band. The potential energy of an electron in the field of a positive ion is negative. In fig. 10 (b) we sketch

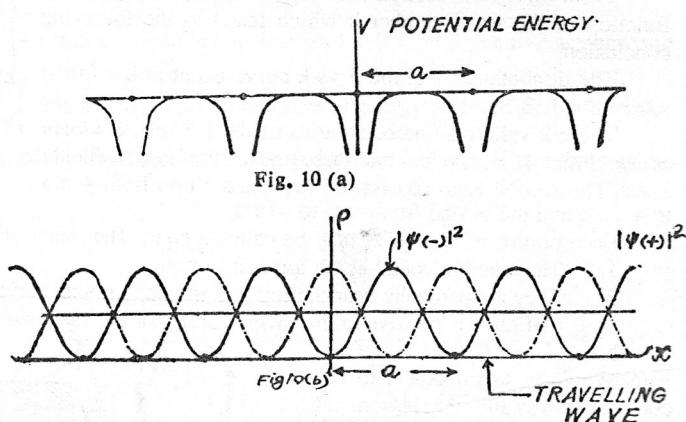


Fig. 10 (a) Variation of P.E. of conduction electron in the field of ion cores of linear lattice. (b) Distribution of probability density ρ in the lattice for $|\psi_{(-)}|^2 \propto \sin^2 \pi x/a$; $|\psi_{(+)}|^2 \propto \cos^2 \pi x/a$, and for a travelling wave. The wave function $\psi_{(+)}$ piles up lowering the P.E. in comparison with the average potential energy seen by travelling wave. The wave function $\psi_{(-)}$ piles up charge in the region, between the ions and removes it from the ion cores, thereby raising the P.E. in comparison with that seen by travelling wave.

the distribution of electron density corresponding to the standing waves ψ_+ , ψ_- and to travelling wave.

The travelling wave e^{ikx} distributes electrons uniformly over the line : standing wave $\psi_- \propto \sin \pi x/a$ distributes electrons preferentially midway between the ion cores; and the standing wave $\psi_- \propto \cos \pi x/a$ distributes electrons on the ion cores, where the potential energy is lowest." On calculating the average value of potential energy over the three charge distributions, we expect to find the potential energy of ψ_+ lower than that of a travelling wave, whereas the potential energy of ψ_- is higher than that of travelling wave. If the potential energy of ψ_+ and ψ_- differ by an amount E_g , we have an energy gap of width E_g between the two solutions at $k = \pi/a$ or between the two at $k = -\pi/a$. In fig. 9 (b) the wave function at A will be ψ_+ and the wave function at B will be ψ_- .

§ 8. Brillouin Zones. We have seen in the Kronig Penney model that the energy discontinuities in a monatomic one dimensional lattice occur when the wave number k satisfies the relation $k = n \pi/a$, where n is any positive or negative integer. Thus it is the value of wave number which is important for the energy discontinuities.

In one dimensional monatomic lattice a line representing the value of k is divided up by energy discontinuities into segments of length π/a as shown in fig. 11. These line segments are known as Brillouin zones; the segment.

$$-\pi/a < k < \pi/a$$

is the first Brillouin zone, the two segments

$$-\pi/a < k < \pi/a \quad \text{and} \quad \pi/a < k < 2\pi/a$$

form the second Brillouin zone and so on.

All the results for a one dimensional periodic field apply equally to two or three dimensional fields if we keep the other one or two of the coordinates fixed. (The axes are supposed to be parallel to the sides of the square in two dimensional crystal and to the three axes of a unit cell in three dimensions).

The zone description was introduced by Brillouin who pointed out that many important and characterised features of electron propagation in periodic structures could be described by considering the positions, in k -space, of the boundaries of zones, these positions are independent of the details of the electron lattice interaction but are mainly determined by the geometry of the crystal structure. Each crystal structure gives rise to its own characteristic Brillouin zones. The first zone for two dimensional simple square lattice will be a square ABCD the boundaries of which will be given by the relations

$$k_x = \pm \pi/a ; \quad \pm k_y = \pi/a$$

The boundaries of the second zone are given by the relations

$$\pm k_x = \pm k_y = \pi/a$$

This is represented in the diagram by EFGH. The same principle applies to three dimensional crystal structure. The first Brillouin zone of the simple cubic lattice is a cube of edge $2\pi/a$.

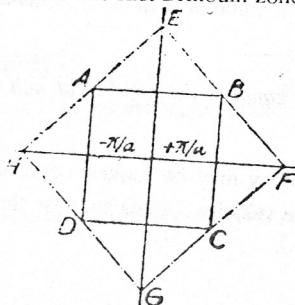


Fig. 12. Brillouin zones in two dimensional simple square lattice

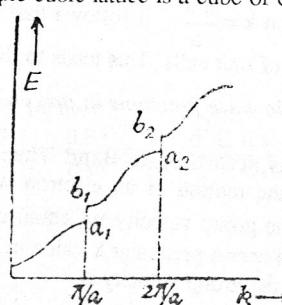


Fig. 13. Relation between E and k for one direction of k space.

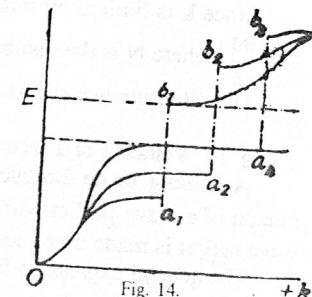


Fig. 14.

The meaning of these wave number diagrams is that if we start at the origin of k-space and consider a series of states with continuously increasing k , then E varies continuously with k as long as k lies within the zone, but when k reaches the surface of the zone, there is an abrupt increase in energy. The explanation of this abrupt increase of energy has already been discussed previously. For any one direction in k space the relation between E and k is of the same general form as already studied but the position and magnitude of the gaps, $a_1 b_1, a_2 b_2 \dots$ depend upon the direction concerned. This gives the possible type of Brillouin zone.

(1) Zones do not Overlap :

Here the energies of states at the top of the first band i.e., a_r may for all directions be less than the energy of any state for any direction at any bottom of the second band i.e., as in fig. 14.

(2) Zones Overlap :

Here the energy gap E_g is present at the top of the first band for any direction but some of the states at the top of first band i.e., a_r have energy values higher than those of the lowest state situated at the bottom of the second zone i.e., b_r . This condition of affairs is shown in fig. 15.

§ 9. Number of Possible Wave Functions per Band .

So far we have assumed the crystal to be infinite, but now it will be essential to consider the consequences of imposing boundary conditions. For it, consider a linear crystal of length L and the boundary conditions may be taken as

$$\psi(x + L) = \psi(x) \quad \dots (9.1)$$

Now making use of the Bloch functions

$$e^{ik(x+L)} u_k(x+L) = e^{ikx} u_k(x)$$

and because of the periodicity of u_k we have

$$u_k(x+L) = u_k(x)$$

The boundary conditions thus require,

$$k = \frac{2\pi n}{L} \quad \dots (9.2)$$

where $n = \pm 1, \pm 2, \dots$

The number of possible wave functions (or k -values) in the range dk is

$$dn = \frac{L}{2\pi} dk. \quad \dots (9.3)$$

Since k is limited by relation $k = \frac{n\pi}{a}$, it follows that the maximum value of n in (9.2) is given by $\frac{L}{2a} = \frac{N}{2}$ where N is the number of unit cells. This leads to the conclusion—

The total number of possible wave functions in any energy band is equal to the number of unit cells N .

§ 10. Velocity of Electrons according to Band Theory.

According to de Broglie, the motion of an electron with a velocity v may be looked upon as the motion of a wave packet with the group velocity v_G equal to the particle velocity. Let us suppose that the wave packet is made up of states near a particular k value in a single band.

The general expression for the group velocity is

$$v = v_G = \frac{d\omega}{dk}$$

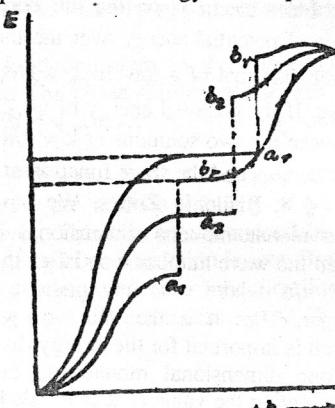


Fig. 15.

according to wave mechanical theory, where ω is the angular frequency of de Broglie wave and is related to the energy of the particle by the relation,

$$E = \hbar \omega \quad \text{or} \quad \omega = \frac{E}{\hbar}.$$

Thus

$$v = \frac{1}{\hbar} \cdot \frac{dE}{dk} \quad \dots(10.1)$$

But

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{and} \quad \frac{dE}{dk} = \frac{\hbar k}{m}.$$

$$\therefore v = \frac{\hbar k}{m}, \quad \dots(10.2)$$

i.e. the velocity of free electrons is proportional to k .

Now on the band theory the energy versus k curve is shown in fig. 16. Because it is a symmetrical curve having points of inflexion at M and N, the value of (dE/dk) is different for different portions of the curve.

Since the curve is horizontal at A, O and B we have for these portions $(dE/dk) = 0$. At the points N and M, (dE/dk) is the maximum but negative at M and positive at N. The velocity versus k curve can therefore be obtained from

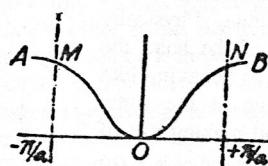


Fig. 16 E versus k curve

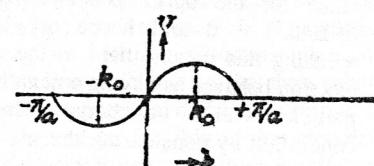


Fig. 17 Velocity versus k curve

the E versus k diagram which is of the type as shown in fig. 17. It is important to note here that the absolute value of velocity reaches a maximum for $k = k_0$ where k_0 corresponds to the point of inflection in the $E - k$ diagram and beyond this point the velocity decreases with the increasing energy which is quite different in behaviour from that of free electrons.

§ 11. Influence of Electric Field. To study the influence of an electric field ϵ on the motion of an electron in one dimensional periodic field, let us consider that the Brillouin zone under consideration contains only one electron which is initially in the state- k . When the field ϵ acts on the electron for a time dt , the electron gains certain energy dE which is the work done on the electron by the electric field in the time dt i.e.,

$$dE = e\epsilon v \cdot dt = e\epsilon \left(\frac{1}{\hbar} \cdot \frac{dE}{dk} \right) \cdot dt \quad \dots(11.1)$$

because

$$v = \frac{1}{\hbar} \cdot \frac{dE}{dk}.$$

Now

$$dE = \frac{dE}{dk} \cdot dk$$

which gives

$$\frac{dk}{dt} = \frac{e\epsilon}{\hbar}$$

... (11.2)

Now if 'a' be the acceleration of the electron, we have

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

Substituting for $\frac{dk}{dt}$ in the above expression we get

$$a = \frac{e\epsilon}{\hbar^2} \cdot \frac{d^2 E}{dk^2} \quad \dots(11.3)$$

For free electron, we have

$$a = \frac{e\epsilon}{m} \quad \dots(11.4)$$

These two expressions (11.3) and (11.4) suggest that on the band theory, the electron behaves as if it had an *effective mass* m^* equal to $m^* = \frac{\hbar^2}{d^2 E / dk^2}$

(Note that if energy is given by $E = (\hbar^2 k^2 / 2m^*)$, the same expression for m^* can be obtained). The effective mass is thus determined by $(d^2 E / dk^2)$. This shows that since for the lower positions of the $E-k$ curve $(d^2 E / dk^2)$ is + ve, m^* is + ve and it will have a - ve value for the upper position. At the points of inflection, $(d^2 E / dk^2) = 0$ and hence m^* becomes infinite. Physically speaking this means that in the upper half of the band the electron behaves as having a negative mass or as behaving like particles with + ve charges. One can arrive at the same conclusion by considering the $v-k$ curve and making use of (11.2) i.e. $(dk/dt) = (eE/\hbar)$ Suppose an electron starts at $k = 0$: when an electric field is applied, the wave vector increases linearly with time. Until the velocity reaches its maximum value, the electron is accelerated by the field; beyond the maximum the same field produces a decrease in v , i.e., the mass must become negative in the upper part of the band.

Sometimes it is convenient to introduce a factor

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \cdot \frac{d^2 E}{dk^2}.$$

This factor f_k determines the extent upto which the electron in a k -state is a 'free electron'. If m^* is large, f_k is small, i.e., the particle behaves as a heavy particle. When $f_k = 1$ then electron behaves as a free electron.

§ 12. Distinction between Metals, Insulators, and Intrinsic Semi-conductors :

The distinction between metals, insulators and intrinsic semiconductors can be made on the basis of band theory. For this, let us consider a particular energy band filled with electrons upto a certain value k , as shown in fig. 19. As far as the influence of an external electric field is concerned, we shall be interested in knowing that with how many 'free' electrons the N electrons in the band are equivalent? If we could know the answer to this question, it would be possible to draw conclusions regarding conductivity associated with this band. The effective number of the "free" electrons in the band according to preceding discussion is

$$N_{\text{eff}} = \sum f_k \quad \dots(12.1)$$

where summation extends over occupied states in the band.

The number of states in the range dk for one dimensional lattice of length L is

$$dn = \frac{L}{2\pi} dk. \quad \dots(12.2)$$

In the shaded region of fig. 19, i.e., within limits $-k_1$ to $+k_1$.

$$N_{\text{eff}} = \frac{L}{2\pi} \int_{-k_1}^{k_1} f_k dk \quad \dots(12.3)$$

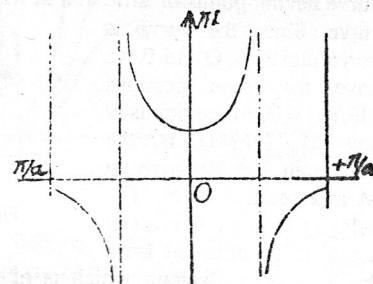


Fig. 18. $m^* - k$ curve.

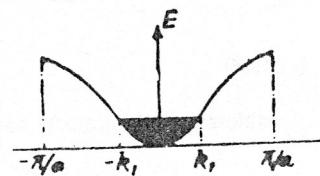


Fig. 19. Energy band filled upto state k_1 .

Since two electrons occupy each of the state, the term on the right hand side of equation (12.3) is to be multiplied by 2. Hence,

$$\begin{aligned} N_{\text{eff}} &= \frac{L}{\pi} \int_{-k_1}^{k_1} f_k dk \\ &= \frac{2 L m}{\pi \hbar^2} \int_0^{k_1} \frac{d^2 E}{dk^2} dE \quad \text{or} \quad N_{\text{eff}} = \frac{2 L m}{\pi \hbar^2} \left[\frac{dE}{dk} \right]_{k=k_1} \end{aligned} \quad \dots(12.4)$$

From this expression the following important conclusions can be drawn —

1. The effective number of electrons in a completely filled band vanishes, because (dE/dk) vanishes at the top.

2. The effective number of electrons reaches to maximum value corresponding to the point of inflexion, where (dE/dk) is maximum.

From the above discussion it follows that *a solid for which any zone or any allowed band which has electrons in it is completely full, the other bands being completely empty, is an insulator*. In a completely full zone for every electron state with vector k there is a corresponding one with $-k$. Consequently a full-zone cannot show preponderance of electron waves in any preferred direction which means that there cannot be any electric current. The substance behaves as an insulator under ordinary potential differences inspite of the fact that the electrons are free to move through the crystal. The reason for this is that electrical conductivity requires not merely freedom of motion of the individual electrons but also the possibility of giving a swarm of electrons as a whole, a resultant velocity in the direction of the field which can only happen if there are unoccupied states into which the electrons can pass when the field is applied. From the above approach of wave mechanics it is clear that if all the states in the first zone are filled and there is a gap before the next zone the probability of an electron passing from a state in the first zone to one in the second zone is negligibly small - instead it suffers Bragg reflection in the lattice. Hence as all the states in first zone are occupied, the applied field can produce no change in the motion of the electrons as a whole and no current can be carried. On the other hand, a solid *containing an energy band which is incompletely filled has metallic character* and on the older theory can be called to have free electrons. It will be evident that this situation can occur only at absolute zero, when the crystal is in the lowest energy state. At temperatures other than zero, some of the electrons from the upper filled band will be excited to the next empty band called *conduction band* and the conduction becomes possible. If the energy gap is of the order of several e.v., the solid will remain an *insulator*. For example in the case of diamond the forbidden energy gap is about 7 e.v. But for a smaller forbidden gap say 1 e.v. the number of thermally excited electrons will be appreciable and in this case we can speak of *intrinsic semiconductor*. The examples of this case are Germanium and Silicon. As a matter of fact, all intrinsic semiconductors are insulators at $T = 0$ and all insulators may be regarded as semiconductors at $T > 0$. Thus it is quite obvious from these arguments that conductivity of semiconductors increases with increasing temperature while the conductivity of metals decreases with increasing temperature.

§ 13. Direct Experimental Evidence for Band Structure :

The band theory as a whole is supported mostly by indirect evidence but for more or less direct evidence of the band structure of the energy levels we require :

1. That the existence of the energy gaps ΔE between allowed bands should be somewhat confirmed.
2. We should get some experimental confirmation of the fact that allowed bands are partly full in metals and completely full in insulators.

Study of resistivity variation with temperature, light absorption and photo-conductivity in semiconductors and insulators indicate the existence of energy gap ΔE .

Confirmation of (2) comes from soft X-ray spectroscopy. Let us consider X-ray emission first, using the energy level diagram 20 (a). 'A' represents the energy level of a core electron say 1s (K-shell) state.

Such core levels are sharp. Suppose a suitable bombardment in an X-ray tube removes the core electron. The level can be filled from the electrons in the higher 'allowed' band which is shown partly full.

For $v > v_2$, there will be no emission; since there are no levels in higher band from where transition can take place at v_2 , sudden emissions of all transitions will take place which therefore becomes the emission edge. $v_1 < v < v_2$ will correspond to the emission band; for $v < v_1$ there will be no emission because again there are no possible transition levels. The observed emission band width therefore measures the extent to which the allowed band is full.

Now consider the absorption of X-rays by the same substance. Fig. 20 (b) shows that for $v < v_2$ there should be no absorption; at $v = v_2$ there should be an 'absorption edge'; at $v > v_2$ there should be an 'absorption band'. Absorption therefore also gives the evidence for the existence of the unfilled levels in the allowed band.

Absorption and emission edges coincide in frequency in metals.

Emission bands for non-metals are different from metals and are what can be expected from full zones. They have no sharp emission edges.

Emission bands in metals are also not perfectly sharp as transitions from filled to unfilled levels occur in metals over a region proportional to kT at the Fermi levels. As a consequence, the width of the emission edge also varies with temperature.

PROBLEMS

- Show that if in the potential model used in connection with the Kronig - Penney calculation, V_0 is allowed to become infinitely large and b is allowed to approach zero, such that the product $P = -(\beta^2 ab/2)$ remains fixed, ten allowed energy values are given by the solution of equation

$$\frac{P \sin a \alpha}{\alpha a} + \cos \alpha a = \cos K a$$

Also show that this leads to allowed and forbidden energy bands.

In § 6, while discussing Kronig - Penney model, it has been shown that equations (6.11) to (6.14) have non-vanishing solutions, if and only if

$$\frac{-\alpha^2 + \beta^2}{2\alpha\beta} \sin \alpha a \sin \beta b + \cos \alpha a \cos \beta b = \cos K(a+b) \quad (\text{Eqn. 6.15})$$

Within energy range $0 < E < V_0, \pm \beta$ is imaginary and putting $\beta = iy$. Noting that $\cos ix = \cos hx$ and $\sin ix = \sin hx$. Eqn. (6.15) can be written as

$$\frac{\gamma^2 - \alpha^2}{2\alpha\gamma} \sin h\gamma b \sin \alpha a + \cos h\gamma b \cos \alpha a = \cos K(a+b)$$

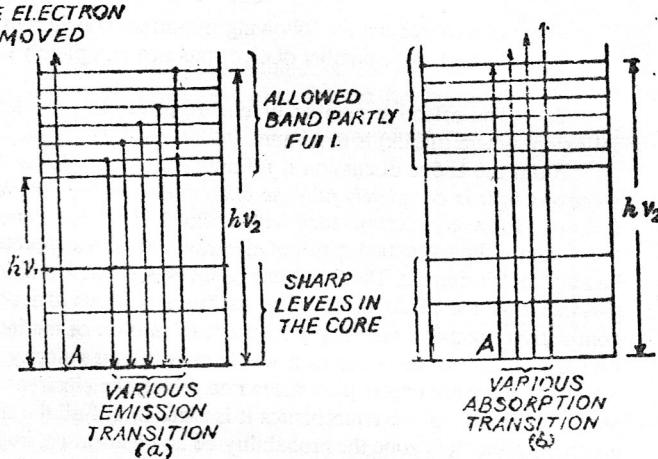


Fig. 20. Transitions in Soft X-ray Spectroscopy.

Substituting

$$\gamma^2 - \alpha^2 = \frac{2m V_0}{\hbar^2}$$

Since $b \rightarrow 0 \sin h \gamma b \rightarrow \gamma b$ and $\cos h \gamma b \rightarrow 1$ in equation (1), we have

$$\frac{2m V_0}{\hbar^2 \cdot 2\alpha \gamma} \cdot \gamma b \cdot \sin \alpha a + \cos \alpha a = \cos K a$$

$$\left(\frac{2m V_0 b}{\alpha \hbar^2} \right) \cdot \sin \alpha a + \cos \alpha a = \cos K a$$

Since $V_0 \rightarrow \infty$, neglecting E in β in comparison to V_0 , we have

$$P = -\frac{\beta a b}{2} = \frac{m V_0 b}{\hbar^2} \cdot a$$

$$\frac{m V_0 b}{\hbar^2} = \frac{P}{a}$$

We get

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos K a$$

or

The plot of $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$ against αa is shown in fig. (7). Since α^2 is proportional to the energy E, the abscissa is a measure of energy. Furthermore, the right hand side can accept values between -1 and +1 only as indicated by horizontal line, fig. (7).

Thus, the energy spectrum of electrons consists of a number of allowed energy bands separated by forbidden regions.