

- 0. Introduction: Two historical facts

(i) Drude's inference from cathod ray: The enormous range of values of resistivity (the difference is almost 30 orders of magnitude found between the resistivity of noble metals and some synthetic polymer) has ever been a simple though intriguing observation. The first major breakthrough was due to a suggestion regarding cathode ray by Drude, who held that "as the properties of cathode rays are independent of the metal used in the filament, they seem to be contained in all metallic solids". The constituent of cathode rays, the electrons were later regarded as independently moving electrons in metals and was held responsible for its conduct. Drude's classical model involving independent electron approximation (neglecting electron-electron interaction) and free-electron approximation (neglecting electron-ion interaction) and its subsequent modification by Sommerfeld, however, failed to explain so many observations, to name a few as follows:

- a. Positive values of Hall-coefficient of some metals (Al, In) indicating that current carrier can have **POSITIVE charge**.
- b. The intermediate value of Lorentz number (due to Wiedemann-Franz law) between two extremes of temperature was hardly predictable.
- c. The temperature dependence of DC electrical conductivity is not so immediate from Drude's model and sometime frustratingly exotic for certain materials.
- (ii) Wave propagation in lattice structure: The failure of Drude theory involving electrons as classical particles demanded a wave-theoretic replacement especially with the emergence of quantum mechanics. The propagation of elastic wave (sound wave) and light was quite rigorous understood by people like, Newton, Euler, Bernoulli, Cauchy, Laplace and many others. In solids the elastic wave propagation was explained by considering the vibration of matter particles forming a continuum. By the end of 19th century, it had been well appreciated that due to the periodic arrangements of atoms (objects) certain modes or frequencies that are bound to be eliminated and certain other ...

^{for waves}
through the lattice structure under consideration and the fact majority depends upon both the system's dimension and degrees of freedom. Later it was the work of Brillouin which brought this fact to its quantum mechanical ramifications.

• I. Electrons in Periodic Potential.

• (i) Free electron in metal: Na-atom as a case in point

The Na-atom with its electronic configuration — $1s^2 2s^2 2p^6 3s^1$ reveals the fact that the $3s$ electron (called the valence electron) is easily ionizable while the 1st 10 electrons (called the core electrons) are tightly bound — a characteristic frequent in metallic atoms. At this point we make the following two assumptions: —

• a. The valence electrons called the metallic electrons move over the crystal leaving behind the positive ion core at atomic sites.

• b. If there are N -atoms, each electron will move in the field of N singly charged positive ion core plus $N-1$ metallic electrons.

Neglecting electron-electron interaction we can claim $N-1$ electrons are uniformly distributed over the crystal and for fairly large N value they can cancel the field due to N positive ions. So any one electron can move in an approximately vanishing field. Such free electrons in crystal lattice are treated by both Drude and Sommerfeld under different contexts. The failure or inadequacy of their theory led us to a purely quantum mechanical theory of electrons as wave propagating in a so called periodic potential.

• Periodic Potential: Considering a linear chain of ions as representative of a model of linear one dimensional solid the following figure resembles the individual atomic potential as the ion is approached closely and flattening off in the region between ions.

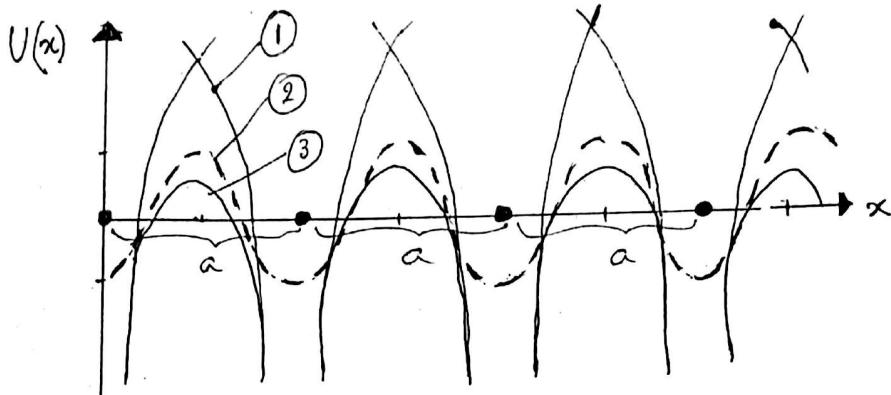


Diagram - 1.

- ① → The potential for single isolated ions.
- ② → Structure of the periodic potential along a line between planes of ions. a being the period.
- ③ → Potential along the line of ions.

The solid circles indicate ionic sites at equilibrium.

- (ii) The Quantum Mechanics in Periodic Structure

Since the scale of periodicity of the potential (10^{-9} cm) is comparable with the de Broglie wavelength of a free electron the application of quantum mechanics is therefore justified. Our aim, here, is to determine the wave function and energy eigen value of an electron in a periodic potential in one dimension.

- Axiom - 1: A quantum mechanical particle is characterized by a stationary state of energy E , known as energy eigen value and a function $\psi(x)$, known as wave function or energy eigen function where the pair $\{E, \psi(x)\}$ is determined by the following operator eigen-value equation:

$$\left[-\frac{d^2}{dx^2} + \frac{2m}{\hbar^2} V(x) \right] \psi(x) = E \psi(x) - \frac{2mE}{\hbar^2} \psi(x) - [1]$$

The operator on the left-hand-side is known as the Hamiltonian of the system and the equation (eqn - [1]) is known as time-independent Schrödinger equation.

For a periodic potential the following theorem on Hamiltonian H is immediate.

• Theorem-1: If $v(x)$ is a periodic function with period a and T_a be an operator such that $T_a f(x) = f(x+a)$, then

(i) H is periodic and

(ii) if $\psi(x)$ is an eigenfunction of H , then $T_a \psi$ is also an eigenfunction

H being the Hamiltonian of the system.

Proof: (i) As $v(x)$ is periodic $v(x) = v(x+a)$

$$\text{Now } H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\text{Let } x' = x+a, \text{ then } \frac{d^2}{dx^2} = \frac{d^2}{dx'^2}$$

$$\text{and hence } H(x+a) = H(x)$$

(ii) Let $\psi(x)$ be an eigenfunction of H . Then

$$H\psi(x) = E\psi(x)$$

$$\text{Now } T_a H \psi(x) = H(x+a) \psi(x+a) = H(x) T_a \psi(x)$$

$$\Rightarrow E(T_a \psi(x)) = H(T_a \psi(x))$$

$$\Rightarrow \boxed{H(T_a \psi) = E(T_a \psi) \dots \dots [2]}$$

Hence, $(T_a \psi)$ is an eigenfunction of H .

Now as $T_a \psi$ is an eigenfunction of H , it can be proportional to ψ . Let's write $T_a \psi = \lambda \psi$. To determine λ we can use the following theorem due to Floquet.

• Theorem-2: If in a periodic lattice with $v(x) = v(x+a)$ and $T_a \psi = \lambda \psi$, then λ is a complex number of unit modulus i.e., $\lambda = e^{i\phi}(i\theta)$.

Proof: If $u_1(x)$ and $u_2(x)$ are two linearly independent solutions of Schrödinger equation, then for a potential of periodicity 'a' the solution from the left hand side and that from the right hand side are related by

$$\begin{pmatrix} u_1(x+a) \\ u_2(x+a) \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} u_1(x) \\ u_2(x) \end{pmatrix}$$

where M is called a transfer matrix for the potential.

Now any solution $\psi(x)$ can be given by a linear combination of u_1 & u_2 . Let,

$$\psi(x) = A u_1(x) + B u_2(x)$$

$$\text{Hence, } \psi(x+a) = A u_1(x+a) + B u_2(x+a)$$

$$= A(M_{11} u_1(x) + M_{12} u_2(x))$$

$$+ B(\cancel{M_{21} u_1(x)})$$

$$+ B(M_{21} u_1(x) + M_{22} u_2(x))$$

$$= (A M_{11} + B M_{21}) u_1(x) + (A M_{12} + B M_{22}) u_2(x)$$

$$\text{Now, } \psi(x+a) = T_a \psi = \lambda \psi$$

Hence, upon comparison

$$A M_{11} + B M_{21} = \lambda A \quad \{$$

$$A M_{12} + B M_{22} = \lambda B \}$$

For a nontrivial pair of solutions $\{A, B\}$ of the homogeneous system

$$\det \begin{vmatrix} M_{11} - \lambda & M_{21} \\ M_{12} & M_{22} - \lambda \end{vmatrix} = 0$$

The two values of $\lambda \{ \lambda_1, \lambda_2 \}$ thus obtained leads to 2 functions $\psi_1(x)$ and $\psi_2(x)$.

Now let's define a quantity $w = \psi_1 \psi_2' - \psi_1' \psi_2$. As ψ_1 & ψ_2 are eigenfunctions of H also (for a given energy)

$$w' = \psi_1 \psi_2'' + \psi_1' \psi_2'' - \psi_1' \psi_2' - \psi_1'' \psi_2$$

$$= 0 \quad (\text{due to Schrödinger's eqn.})$$

$$w = \text{const}$$

$$\text{Hence, } w(x+a) = w(x)$$

$$\text{On the other hand, } w(x+a) = T_a w(x)$$

$$= \psi_1(x+a) \psi_2'(x+a)$$

$$- \psi_2(x+a) \psi_1'(x+a)$$

$$= \lambda_1 \psi_1 \lambda_2 \psi_2' - \lambda_2 \psi_2 \lambda_1 \psi_1'$$

$$= \lambda_1 \lambda_2 (\psi_1(x) \psi_2'(x) - \psi_2(x) \psi_1'(x))$$

Hence $\lambda_1, \lambda_2 = 1$.
 Now for $|\lambda| > 1$ or $|\lambda| < 1$ the amplitude of ψ will give runaway solution for $x \rightarrow \pm\infty$. Hence $|\lambda| = 1$ i.e.;
 $\lambda_{1,2} = \exp(\pm i\theta)$; $\theta \in \mathbb{R}$

Remark: The above theorem appreciates the fact that while passing through periodic potential, the wave function adopts a phase factor. This type of phase modification will eventually lead us to what is known as Bloch theorem.

✓ III. Bloch Theorem (1-D)

In view of the above discussion let's choose $\theta = Ka$ for some K , ' a ' being the periodicity as usual. For obvious reason θ can be identified with some angle and hence K (which has the dimension $1/a$) can be regarded as some sort of wave vector.

Now for any integer n

$$\psi(x+na) = T_a^n \psi(x) = \exp(inka) \psi(x)$$

And this is possible when

$$\psi(x) = \exp(iKx) \phi(x)$$

$\phi(x)$ being periodic i.e; $\phi(x+a) = \phi(x)$

$$[\text{Hint: } \psi(x+a) = \exp[iK(x+a)] \phi(x+a)$$

$$= e^{ika} (e^{ikx} \phi(x)) = e^{ika} \phi(x)]$$

Hence we can conclude the following theorem due to Bloch.

Theorem-3: If the potential $V(x)$ is periodic with the periodicity of the lattice (a'), then the solution $\psi(x)$ of the wave equation

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

is of the form: $\boxed{\psi(x) = \exp(iKx) \phi(x)}$ for a given E . where, $\phi(x)$ is a periodic function i.e.,

$$\phi(x) = \phi(x+a)$$

Remark: The wavefunction $\psi(x)$ is called Bloch wave function.

Now one can calculate the energy spectrum of the Bloch electron.

We consider two forms of $\psi(x)$

$$\psi(x) = A u_1(x) + B u_2(x) \quad \dots \dots \dots \text{(a)}$$

$$\text{In view of Bloch theorem } \psi(x) = e^{ika} \psi(x-a) \quad \dots \dots \dots \text{(b)}$$

$$\text{i.e. } \psi(x) = e^{ika} [A u_1(x-a) + B u_2(x-a)] \quad \dots \dots \dots \text{(b)}$$

Now at $x=a$ comparing (a) and (b)

$$A u_1(a) + B u_2(a) = e^{ika} [A u_1(0) + B u_2(0)] \quad \dots \dots \dots \text{(c)}$$

Differentiating (a) and (b) and equating at $x=a$

$$A u'_1(a) + B u'_2(a) = e^{ika} [A u'_1(0) + B u'_2(0)] \quad \dots \dots \dots \text{(d)}$$

Hence, for a non-trivial solution for this homogeneous system

$$\det \begin{vmatrix} u_1(a) - e^{ika} u_1(0) & u_2(a) - e^{ika} u_2(0) \\ u'_1(a) - e^{ika} u'_1(0) & u'_2(a) - e^{ika} u'_2(0) \end{vmatrix} = 0$$

$$\Rightarrow e^{ika} [u_1(0) u'_2(0) - u_2(0) u'_1(0)] + \bar{e}^{ika} [u_1(a) u'_2(a) - u_2(a) u'_1(a)] \\ = [u_1(0) u'_2(a) + u_1(a) u'_2(0)] - [u_2(0) u'_1(a) + u_2(a) u'_1(0)]$$

$$\Rightarrow e^{ika} \Delta_1 + \bar{e}^{ika} \Delta_2 = \cancel{\Delta_3} \cancel{\Delta_4} f_3 - f_2$$

Let's define $\Delta = u_1(x) u'_2(x) - u_2(x) u'_1(x)$

$\Delta' = 0$ due to Schrödinger equation.

Hence $\Delta = \text{const} \Rightarrow \Delta_1 = \Delta_2 = \Delta_0$ (say)

Hence the above equation gives

$$\Delta (2 \cos ka) = f_1 - f_2$$

$$\Rightarrow \boxed{\cos ka = \frac{f_1 - f_2}{2\Delta}} \quad \dots \dots \dots \text{[B]} \checkmark$$

It is to be noted that the r.h.s. is a function of the lattice

• Remark: 1. Equation - B can be satisfied only if the right hand side is ≤ 1 . At this point we conclude that there are only certain energy intervals which satisfy the condition alternating with intervals which do not. We therefore do not obtain sharp energy levels but an alternating sequence of allowed and forbidden energy bands.

2. Equation - B reveals a relation between ' K ' and ' k ' and the left hand side restrict the arbitrariness of the free particle k values—a fact that will be rigorously explained in the following model.

• The Kronig-Penney Model (Qualitative)

(i) Let us consider a potential function like the following.

$$V = \frac{\hbar^2}{m} \Omega \sum_{n=-\infty}^{+\infty} V_n(x)$$

where $V_n(x) = \delta(x + na) = 1$ for $x = \pm na$

$= 0$ otherwise

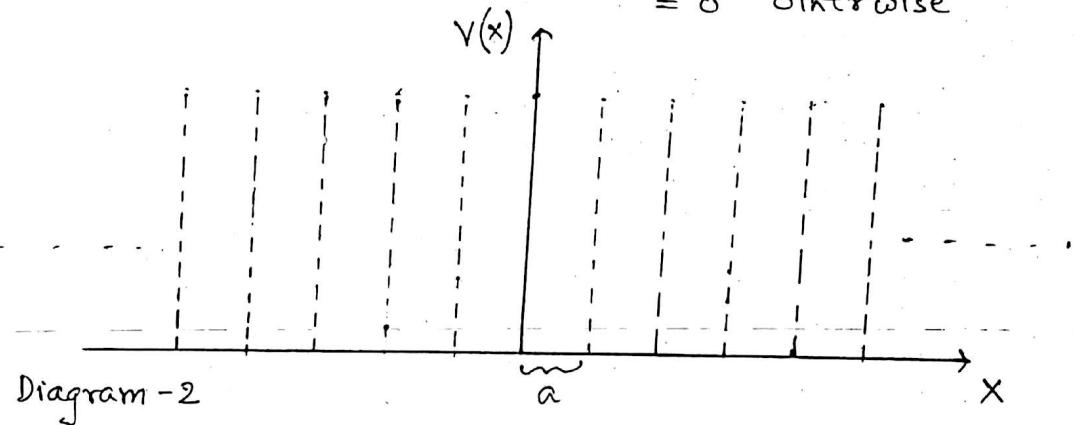


Diagram-2

A similar analysis like the previous section for such a potential (known as Dirac comb) give us the following K - k relation:

$$\cos ka = \cos ka + \frac{\Omega}{k} \sin ka$$

This means

$$\left| \cos ka + \frac{\Omega}{k} \sin ka \right| \leq 1$$

$$\Rightarrow \boxed{\left| \cos \left(ka - \tan^{-1} \frac{\Omega a}{ka} \right) \right| = \frac{1}{\sqrt{1 + (\Omega a/ka)^2}} \quad \dots (P)}$$

$$F(k) = G(k) \quad \dots (D)$$

The plot of left and right hand side of the equation D is given below.

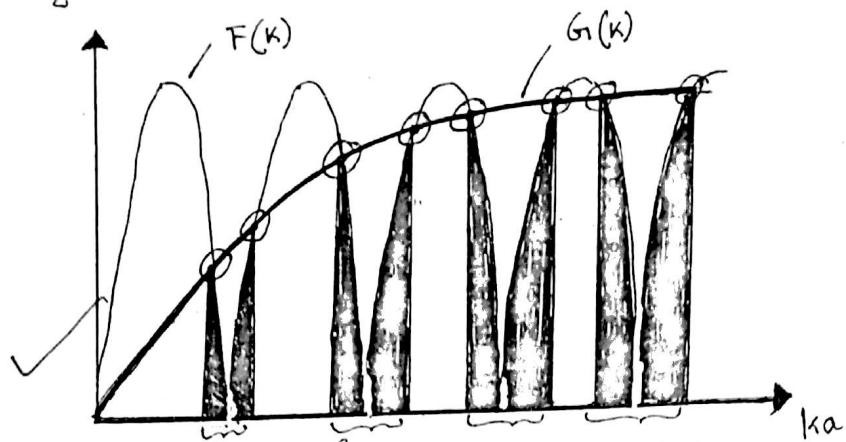


Diagram - 3 (Graphical representation of band structure)

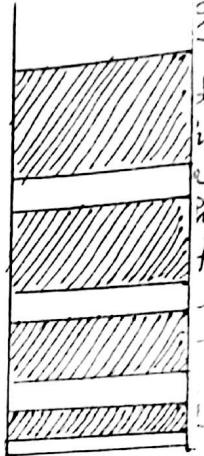


Diagram - 4
Band-structure for
Dirac-Comb.

Diagram - 3 reveals the following facts

(i) The intersections of $F(k)$ and $G_1(k)$ are given by the circles, the square-bracketed region on ka axis gives the allowed value of k for the equation-D to hold. The upper band limits appear at integral multiples of π where $\cos ka = \cos k\alpha$. The regions other than the bracketed one imply the existence of band gap.

(ii) Both in view of diagram - 3 and 4 we see that the bands become broader with increasing energy so that the spectrum approaches (but never quite reaches) the continuum. Even at the highest energies there always remain forbidden zones above the upper band limits at $ka = n\pi$.

The Energy Plot.

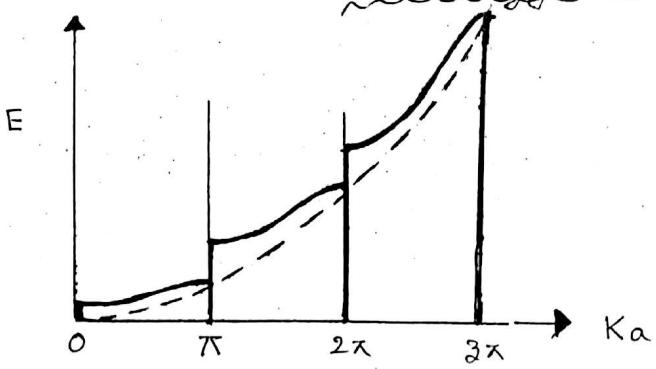


Diagram - 5 reveals the fact that

- (i) The energy value is monotonously growing from band to band
- (ii) The broken line implies the parabola of free particle energies.

Diagram - 5 can be represented in a reduced interval $-\pi \leq k_a \leq +\pi$ like the following

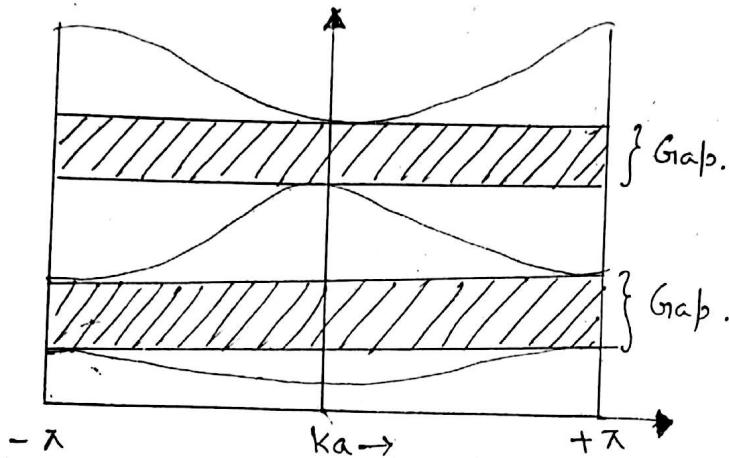


Diagram - 6.

Conductor / Semiconductor / Insulator

Reinvoking the electronic configuration of Na atom if we consider the periodic potential structure due to the ion core, the 3s electrons do not appear to be localized at any particular atom and a continuous energy band is thus formed. The allowed values of energy for these electrons are virtually independent of position in the crystal. This is typical to metallic solids where the continuation of band structure is argued as an overlap of conduction and valence band. Some of such configurations are classified as semimetals (Bi) when the number of carriers is too small.

The absence of such overlap region is attributable of non-metallic behavior which predominates insulators where large gap exists between the conduction and valence band. In such a situation almost no electron is available in the conduction band even at sufficiently low temp high temperature.

On the other hand, there are materials where gap between conduction and valence band (known as forbidden zones) is such that at finite temperature some electrons are excited from the valence band to conduction band leaving behind so called 'hole' in the valence band. Such materials are classified as intrinsic semiconductor.

Intrinsic semiconductor can be doped by carriers in a controllable way. The resultant material is called extrinsic semiconductor — called donor when the impurity level are situated near the bottom of the conduction band providing extra electrons contrary to what is called acceptor (near the top of the valence band) providing holes.

IV Effective Mass.

In a typical one-dimensional situation one can expand the band energy near an extremum like the following

$$E(k) = E_0 + \frac{\partial E}{\partial k} \Big|_0 k + \frac{\partial^2 E}{\partial k^2} \Big|_0 \frac{k^2}{2} + \dots$$

The quantity $m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$ is called the effective mass of the system particle. It has the following properties.

(i) m^* differs from the actual mass m because it arises due to interaction between the particle and the lattice

(ii) m^* is positive and nearly constant for states lying near the bottom of an energy band, negative for states lying near the top of a band and even infinite at some energy in the interior of a band.

The Concept of hole.

As the electronic velocity is group velocity (for a quantum mechanical matter-wave consideration)

$$v = \frac{dE}{dp} = \frac{1}{\hbar} \frac{dE}{dk}$$

$$\text{As } E(k) = E(-k) \quad v(k) = -v(-k)$$

Hence, for a completely filled band both k and $-k$ states are filled by particles and hence the total current in presence of a small external field vanishes

$$\sum v_k = 0 \Rightarrow J = -e \sum v_k = 0$$

For a partially filled band, however, the total current is determined by the difference in filled states with k and $-k$. If the occupation factor of electron is v_n , the same that of hole is

$$v_p = 1 - v_n$$

and J can be expressed as

$$J = -e \sum v_n v(k) = e \sum v_p v(k)$$

So, we can express the current of a partly filled band as the current of holes with charge $e > 0$.

Let us define energy current $\mathbf{J} = [E(\mathbf{k}) - e\Phi] \mathbf{v}(\mathbf{k})$, Φ being the externally applied electric potential. The total current,

$$\begin{aligned} J &= \sum n_n [E(\mathbf{k}) - e\Phi] v(\mathbf{k}) \\ &= \sum (1 - n_p) [E(\mathbf{k}) - e\Phi] v(\mathbf{k}) \\ &= \sum (E(\mathbf{k}) - e\Phi) v(\mathbf{k}) + \sum n_p (-E(\mathbf{k}) + e\Phi) v(\mathbf{k}) \end{aligned}$$

Hence the hole can be considered as particle with energy $-E(\mathbf{k})$ and hence a negative effective mass.

• V Conclusion

The whole idea of band theory relies on the fact that it is possible to consider the motion of a quantum mechanical particle through an infinitely extended periodic lattice by assuming the following facts

- (i) The periodic lattice provides a periodic potential structure.
- (ii) The particle moves like almost a free particle with a modified wave vector and an effective mass.
- (iii) The presence of periodic potential structure restricts the values of wave vector and hence energy while allowing the particle to move through it.

In physics the emergence of energy bands in solid has grossly been explained in the light of scattering of wave obeying Schrödinger equation & involving various Hamiltonian operator. The potential or interaction terms appearing in Hamiltonian give the energy bands of the relevant system.

Finally, the idea of energy bands in solid explains the origin of conductivity in solids and classifies them accordingly. Not only that it also explains some of the behavior of solids quite alien to Drude model. For example the concept of majority carrier (hole/electron) explains the negative to positive value of Hall coefficient for some material metal.

The dispersion relation for a one dimensional crystal of lattice constant a is given by

$$E(k) = E_0 - \alpha - 2\beta \cos ka, \quad E_0, \alpha, \beta \text{ const.}$$

- (i) Find the value of k for which the velocity of the electron is maximum. What the maximum value of v .
- (ii) Find the difference between the top and the bottom of the energy band.
- (iii) Obtain the effective mass m^* of the electron at the bottom & at the top of the band.

$$(i) v = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{1}{\hbar} [2\beta a \sin ka]$$

Let $k = k_0$ for $v = v_{\max}$

$$\frac{dv}{dk} = \frac{1}{\hbar} [2\beta a^2 \cos ka] = 0 \Rightarrow \cos ka = \left(\frac{2n+1}{2}\right)\frac{\pi}{2}$$

$$k = \left(\frac{2n+1}{2}\right)\frac{\pi}{2a} = k_0$$

$$v_{\max} = \frac{2\beta a}{\hbar}$$

$$(ii) E_{\text{Top}} = E_0 - \alpha - 2\beta(-1) = E_0 - \alpha + 2\beta$$

$$E_{\text{bottom}} = E_0 - \alpha - 2\beta$$

$$\text{Band gap} = 4\beta$$

$$(iii) m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}} = \frac{\hbar^2}{[2\beta a^2 \cos ka]}$$

$$\text{at the top } \cos ka = -1 \quad m^* = -\frac{\hbar^2}{2\beta a^2}$$

$$\text{at the bottom } \cos ka = 1 \quad m^* = \frac{\hbar^2}{2\beta a^2}$$