

BAND Theory of SolidsRef. Solid state Physics
by Dekker.

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Date. /

In a solid one deals with a large no. of interacting particles, and consequently the problem of calculating the electronic wave fns and energy levels is extremely complicated. It is thus necessary to introduce a number of simplifying assumptions.

Assumptions: ① In the 1st place we will assume that the nuclei in the crystalline solid are at rest.

② The many electron problem can be solved by ~~approx~~ ~~matrix method~~ one electron approximation. In this approximation the total wave fn. for the system is given by a 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 the charge distribution of all other electrons.

Electron in Periodic Potential :-

Free electron in metal; For example let's take Na-atom.

Na-atom's 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 frequently observed 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 +ve ions cores at atomic sites.

(b) If there are N-atoms, each electron will move in the field of N singly charged +ve ions core plus (N-1) metallic electrons.

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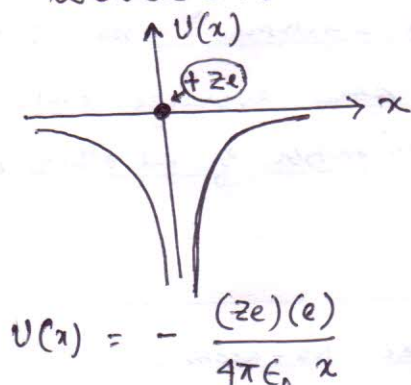
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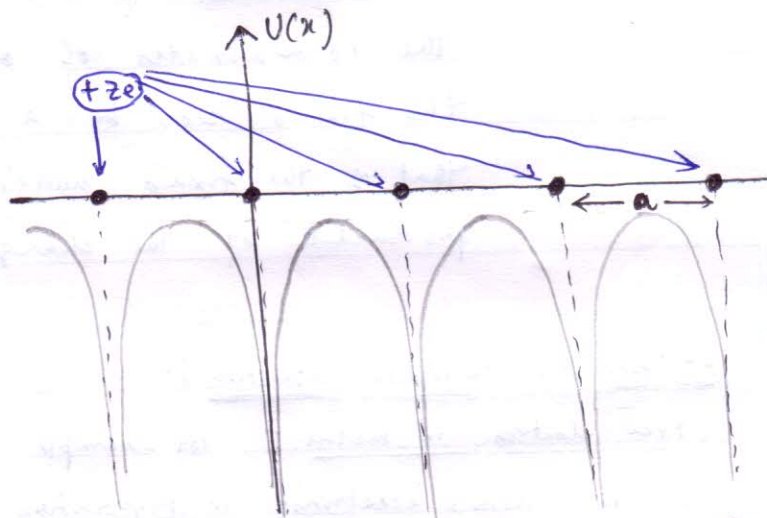
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Neglecting $e-e$ interaction we can claim that $(N-1)$ electrons are uniformly distributed over the crystal and for fairly large N values they can cancel the field due to N positive ions. So, any one electron can move in an approximately vanishing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

Periodic Potential :-



variation of potential energy with distance for an isolated atom.



variation of potential energy with distance for a 1D crystal (linear chain of ions)

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 QM is therefore justified. Our aim, here, is therefore 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. The pair $\{E, \psi(x)\}$ is determined by the following operator eigen-value equation:

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

The operator on the left-hand-side is known as the Hamiltonian of the system and the equation $\textcircled{1}$ 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 is an operator such that $T_a f(x) = f(x+a)$, then

a) H is periodic and

b) if $\psi(x)$ is an eigen fn. of H , then $(T_a \psi)$ is also an eigenfn. of H , H being the Hamiltonian of the system. $\Rightarrow H\{T_a \psi(x)\} = E\{T_a \psi(x)\}$

Proof: a) $V(x)$ is periodic $\therefore V(x) = V(x+a)$

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

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

and hence $H(x+a) = H(x)$ Proved.

b) let $\psi(x)$ be an eigen fn. of H

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

Now, $T_a \{H \psi(x)\} = T_a \{E \psi(x)\}$

$\Rightarrow H(x+a) \psi(x+a) = E \{T_a \psi(x)\}$ as $\psi(x+a) = T_a \psi(x)$

$\Rightarrow H(x) \{T_a \psi(x)\} = E \{T_a \psi(x)\}$ Proved.

Now, as $(T_a \psi)$ is an eigen fun. of H , it can be proportional to ψ .

lets 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~~ modulus, i.e., $\lambda = \exp(i\theta)$.

Proof: Let for a given energy $u_1(x)$ and $u_2(x)$ are two linearly independent solutions of Schrödinger equation, then for a potential of periodicity 'a', we can write

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

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

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

where M is called a transfer matrix for the potential.

[A differential eqn. of the 2nd order has only 2 independent solutions, and all other solutions are expressible as a linear combination of the independent solns.]

Now, any soln. $\psi(x)$ can be given by a linear combination of u_1 and u_2 . let

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

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

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

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

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

~~XXXXXXXXXXXXXXXXXXXX~~

$$\Rightarrow \lambda [A u_1(x) + B u_2(x)] = (A M_{11} + B M_{21}) u_1(x) + (A M_{12} + B M_{22}) u_2(x)$$

Hence upon comparison

$$\left. \begin{aligned} A M_{11} + B M_{21} &= \lambda A \\ A M_{12} + B M_{22} &= \lambda B \end{aligned} \right\}$$

for a nontrivial pair of solutions $\{A, B\}$ of this homogeneous system

$$\det \begin{vmatrix} M_{11} - \lambda & M_{21} \\ M_{12} & M_{22} - \lambda \end{vmatrix} = 0 \quad \rightarrow (2)$$

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

$$\text{From (1)} \quad \psi_1'' + \frac{2m}{\hbar^2} [E - V(x)] \psi_1 = 0 \Rightarrow \psi_1'' \psi_2 + \frac{2m}{\hbar^2} (E - V(x)) \psi_1 \psi_2 = 0$$

$$\psi_2'' + \frac{2m}{\hbar^2} [E - V(x)] \psi_2 = 0 \Rightarrow \psi_2'' \psi_1 + \frac{2m}{\hbar^2} (E - V(x)) \psi_2 \psi_1 = 0$$

$$\text{Subtraction: } (\psi_1'' \psi_2 - \psi_2'' \psi_1) = 0 \quad \rightarrow (3)$$

$$\text{Now, let's define } W = \psi_1 \psi_2' - \psi_1' \psi_2$$

$$\Rightarrow W' = \psi_1' \psi_2' + \psi_1 \psi_2'' - \psi_1'' \psi_2 - \psi_1' \psi_2'$$

$$= \psi_1 \psi_2'' - \psi_1'' \psi_2$$

$$= 0$$

[from eqn. (3)]

$$\Rightarrow W = \text{constant}$$

$$\Rightarrow W(x+a) = W(x)$$

$$\text{OR, } W(x) = W(x+a) = T_a W(x)$$

$$= T_a (\psi_1 \psi_2' - \psi_1' \psi_2)$$

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

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

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

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~~Q. 10 (a) (i)~~

$$W(x) = \lambda_1 \lambda_2 W(x)$$

$$\Rightarrow \boxed{\lambda_1 \lambda_2 = 1} \rightarrow \textcircled{4}$$

From Eqn. (2)

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

$$\Rightarrow (M_{11} - \lambda)(M_{22} - \lambda) - M_{12}M_{21} = 0$$

$$\Rightarrow M_{11}M_{22} - \lambda(M_{11} + M_{22}) + \lambda^2 - M_{12}M_{21} = 0$$

$$\Rightarrow \lambda^2 - (M_{11} + M_{22})\lambda + (M_{11}M_{22} - M_{12}M_{21}) = 0$$

$$\Rightarrow \lambda = \frac{1}{2} \left[(M_{11} + M_{22}) \pm \sqrt{(M_{11} + M_{22})^2 - 4(M_{11}M_{22} - M_{12}M_{21})} \right]$$

$$= \frac{1}{2} \left[(M_{11} + M_{22}) \pm \sqrt{M_{11}^2 + M_{22}^2 + 2M_{11}M_{22} - 4M_{11}M_{22} + 4M_{12}M_{21}} \right]$$

$$= \frac{1}{2} \left[(M_{11} + M_{22}) \pm \sqrt{(M_{11} - M_{22})^2 + 4M_{12}M_{21}} \right]$$

$$\Rightarrow \lambda = \frac{1}{2} \left[(M_{11} + M_{22}) \pm \sqrt{(M_{11} + M_{22})^2 - 4} \right]$$

we can show that
 $M_{11}M_{22} - M_{12}M_{21} = 1$

for certain ranges of energy E , viz., for those corresponding to $(M_{11} + M_{22})^2 < 4$, the two roots λ_1 and λ_2 will be complex, and since $\lambda_1 \lambda_2 = 1$, they will be conjugates.

In those regions of energy we may then write

$$\lambda_1 = e^{i\theta}$$

$$\lambda_2 = e^{-i\theta}$$

where, $\theta \rightarrow$ real quantity

The corresponding functions

$$\psi_1(x+a) = \lambda_1 \psi_1(x) = e^{i\theta} \psi_1(x)$$

$$\psi_2(x+a) = \lambda_2 \psi_2(x) = e^{-i\theta} \psi_2(x)$$

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

$$\begin{aligned} [\text{Hint: } \psi(x+a) &= \exp[iK(x+a)] \phi(x+a) \\ &= e^{iKa} (e^{iKx} \phi(x)) = e^{iKa} \psi(x)] \end{aligned}$$

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

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

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.*

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned} \Rightarrow e^{ika} [u_1(0) u_2'(0) - u_2(0) u_1'(0)] + e^{-ika} [u_1(a) u_2'(a) - u_2(a) u_1'(a)] \\ = [u_1(0) u_2'(a) + u_1(a) u_2'(0)] - [u_2(0) u_1'(a) + u_2(a) u_1'(0)] \end{aligned}$$

$$\Rightarrow e^{ika} \Delta_1 + e^{-ika} \Delta_2 = \Delta_2 - \Delta_1 \quad f_1 - f_2$$

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

$$\begin{aligned} \Delta (2 \cos ka) &= f_1 - f_2 \\ \Rightarrow \boxed{\cos ka = \frac{f_1 - f_2}{2\Delta} \quad \dots \quad [B]} \end{aligned}$$

It is to be noted that the r.h.s. is a function of the lattice periodicity a and free particle wave vector k .

• 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.

• IV 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

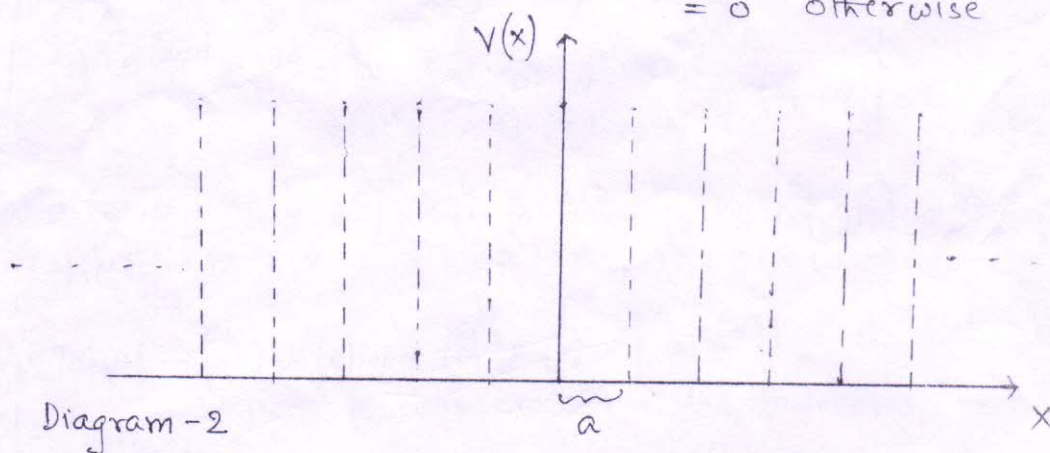


Diagram-2

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

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

$$\Rightarrow \left| \cos \left(ka - \tan^{-1} \frac{\Omega a}{ka} \right) \right| \leq \frac{1}{\sqrt{1 + \left(\frac{\Omega a}{ka} \right)^2}} \quad (D)$$

$$F(k) \leq G(k) \quad (D)$$

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

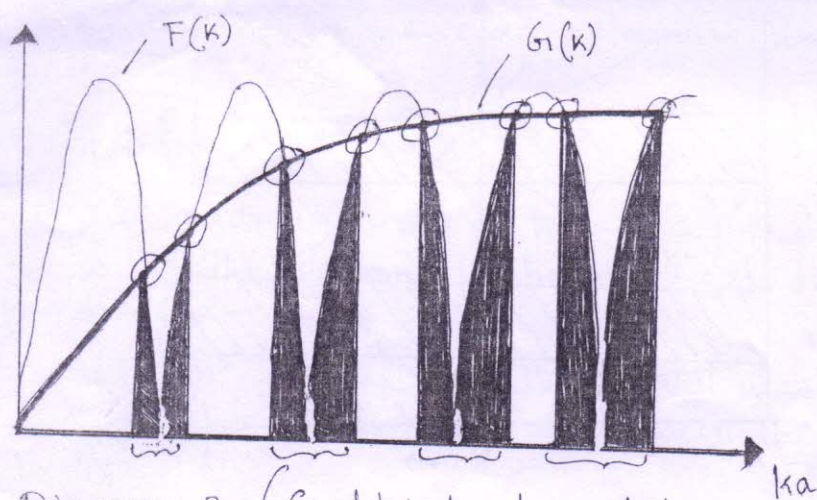


Diagram-3 (Graphical representation of band structure)

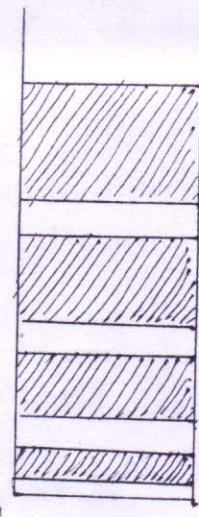


Diagram-4
Band-structure for Dirac-Comb.

Diagram-3 reveals the following facts

(i) The intersections of $F(k)$ and $G(k)$ 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 $\cos ka = \cos ka$. 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.

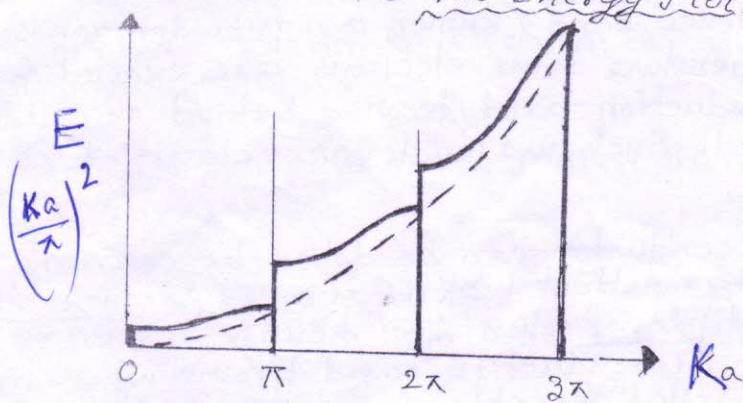


Diagram-5.

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 $-\pi \leq Ka \leq +\pi$ like the following

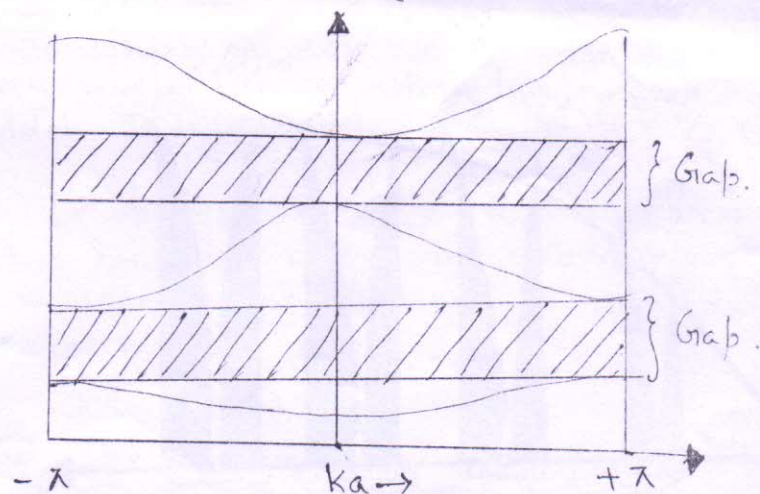


Diagram - 6.

• 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 attributive 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 'holes' 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

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

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 (in 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 ~~W~~ $v [E(k) - e\Phi]$, Φ being the externally applied electric potential. The total energy current,

$$\begin{aligned} W &= \sum v_n [E(k) - e\Phi] v(k) \\ &= \sum (1 - v_p) [E(k) - e\Phi] v(k) \\ &= \sum (E(k) - e\Phi) v(k) + \sum v_p (-E(k) + e\Phi) v(k) \end{aligned}$$

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

• 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 the 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~~ positive value of Hall coefficients for some ~~material~~ metal.