

UNIT-I (Energy Band in Solids)

Classical free Electron Theory

The theory developed by Drude & Lorentz in 1900 According to this theory metal contains free electrons responsible for the electrical conductivity and electrons obeys laws of classical mechanics.

Assumptions:

1. In metals, there are large number of free e^- which moves freely in all directions possible.
2. They move in straight lines until they collide with one another.
3. In metals, there must be atleast two types of particles, for the e^- being negatively charged & the metal is electrically neutral.
4. Positive charges are attached to much heavier particles which were considered to be immobile.
5. A single isolated atom, nucleus has eZ_a charge where Z_a = atomic number ; e = electronic charge around the nucleus - Z = weakly bound valence electrons ($Z_a - Z$) = relatively tightly bound to the nucleus called as "core electrons". Valence electrons are called as "conduction electrons".
6. Density of e^- gas can be calculated as

$$n = \frac{N}{V} = 6.023 \times 10^{23} \times \frac{P_m Z}{A}$$

where P_m = mass density ; A = Atomic mass; Z = no. of e^-/m^3
 P_m/A = moles/m³ ; N = Avogadro's number 6.023×10^{23} atoms/mole

(2)

7. Though there are strong $e^- - e^-$ & $e^- - \text{ion}$ interactions, with slight modifications, it was stated that

→ In absence of externally applied electromagnetic fields, every e^- moves freely and collides with other free e^- & or positive ion cores — Elastic Collision.

→ Neglection of $e^- - e^-$ interaction between collisions is "independent electron approximation". Correspondingly neglection of $e^- - \text{ion}$ interactions is "free e^- approximation".

→ In presence of externally applied electromagnetic fields, e^- acquiring some amount of energy from the field moves towards higher potential, acquiring constant velocity — "Drift Velocity"

8. Electron velocities in a metal obey Maxwell-Boltzmann distribution of velocities.

9. Probability of an e^- undergoing collision in any infinitesimal time interval of length dl is just dl/τ .

10. ' τ ' = Relaxation time, playing a vital role in metallic conduction.

11. Through collision, e^- acquire thermal equilibrium with their surroundings.

Merits / Advantages of classical free e- theory -

1. Verifies Ohm's law 2. Explains electrical & thermal conductivities of metals. 3. Explains optical properties of metals. 4. Explains ductility & malleability.

Demerits / Disadvantages of classical free e- theory -

1. fails to explain electrical conductivity of semiconductors and insulators.
2. fails to explain specific heat concept for metals.
3. fails to explain phenomena like photo-electric effect, Compton effect & black body radiation.
4. fails to explain temperature dependency of paramagnetic susceptibility & ferromagnetism.
5. fails to explain mean free path of electrons.

Quantum Free Electron Theory — Louis de Broglie suggested that "Matter also exhibits dual nature".

Considerations (i) Since light exhibit dual nature, matter also exhibit dual nature.

(ii) Waves associated with a moving material particle are called matter waves or de Broglie waves.

(iii) Based on above mentioned, de Broglie wave concept, moving e⁻ behaves as if it were a system of waves.

- (iv) Energy of an electron in a metal is quantized.
- (v) Electrons obey Pauli's Exclusive principle.
- (vi) In a given energy level, two states are there with spin up and spin down.
- (vii) Permissible energy levels of a free e^- are determined.
- (viii) Valence e^- travels around the potential ~~is~~ constantly inside the metal and are avoided to escape from the crystal by very high potential barriers.
- (ix) Electrons energy levels are discrete but as the space between the energy levels is very less & thus the Energy level distribution is continuous.

Merits:

- (i) Specific heat and paramagnetic susceptibility are in good agreement with experimental values.
- (ii) Experimental and theoretical values of Lorentz number ~~were agree~~ was agreed with each other.

Demerits:

- (i) Fails to explain why some crystals are having metallic properties & others do not have.
- (ii) Fails to explain why the atomic arrays in crystals including metals has certain structures & not others.

\rightarrow Maxwell's Boltzmann Statistics - Classical law

Postulates - (i) Associated particles are distinguishable
 (ii) Can have any spin (iii) Do not obey Pauli Exclusive principle
 (iv) Particles can have identical Energies.

$$\text{Equationally: } n_i = \frac{g_i}{e^{(\alpha + \beta E_i)}} \quad \text{--- (1)}$$

where n_i = Particles in number having energy E_i
 g_i = Number of energy states.

$$\alpha = -\frac{E_F}{kT} ; \beta = \frac{1}{kT}$$

where k = Boltzmann Constant; T = absolute temperature
 E_F = Fermi Energy.

Placing values of α, β in eqn (1)

$$n_i = \frac{g_i}{e^{(E_i - E_F)/kT}} \quad \text{--- (2)}$$

\Rightarrow Fermi-Dirac Statistics (Quantum law)

Postulates - (i) Applicable to the identical, indistinguishable particles of half spin.

- (ii) Obey's Pauli's Exclusive principle called fermions.
- (iii) Not more than one particles can be in quantum state.

~~Equationally:~~ $n_i = \frac{g_i}{e^{(\alpha + \beta E_i)} + 1} \quad \text{or} \quad n_i = \frac{g_i}{e^{(E_i - E_F)/kT} + 1}$

Note \rightarrow other terms names are same as classical law.

Classification of Electronic Materials:

(6)

Depending upon the number of valence electrons, the materials are classified as

(i) Valency $< 4 \Rightarrow$ Conductors / Metals.

(ii) Valency = 4 \Rightarrow Semiconductors.

(iii) Valency $> 4 \Rightarrow$ Insulators / Non-metals.

(i) Conductors - Valency of an atom in a material is < 4 . They have more free e⁻. They conduct electricity & thus have less resistivity.

Ex - Al, silver, Cu, Ag.

(ii) Semiconductor - Materials in which e⁻ flow partially. Have equal no. of particles (electrons) 4 in their outer most orbit. They do not conduct electricity at room temperature.

In addition of impurity, they conduct electricity. Resistivity lies between conductor & insulator.

Ex - Si, Germanium.

(iii) Insulator - Do not conduct electricity easily. Have more than 4 e⁻ in outermost shell. Has less number of free e⁻ as compared to semiconductors & conductor. Its resistivity is high. Ex - Wood, plastic, non-metals.

* Fermi Energy (E_F) :

"Fermi energy is the energy of states at which the probability of electron occupation is $1/2$ at any temperature above 0K . It is the maximum kinetic energy that a free electron can have at 0K . So the energy of the highest occupied level at absolute zero temp. is called Fermi Energy or Fermi Level". The Fermi Energy at 0K for metal is

$$E_F = \left[\frac{3N}{\pi} \right]^{2/3} \left(\frac{\hbar^2}{8m} \right) = \frac{\hbar^2}{8m} \left[\frac{3N}{\pi} \right]^{2/3}$$

when temperature increases the Fermi Energy or Level decreases.

Fermi-Dirac Distribution Function $f(E)$ & Effect of Temperature:

The distribution of electrons among the levels is usually described by the distribution function $f(E)$. It is defined as the probability of an electron occupying an energy level ' E '.

Free Electron gas Obey Fermi-Dirac statistics. Consider an assembly of fermions, ~~these~~ $M(E)$ are allowed quantum states in energy range between E & $E+dE$ and $N(E)$ are the number of particles, So the Fermi-Dirac Distribution function is

$$f(E) = \frac{N(E)}{M(E)} = \frac{1}{1 + e^{(E-E_F)/KT}} = \frac{1}{1 + e^{(E-E_F)/KT}}$$

Thus if level is certainly empty then $f(E)=0$, $f(E)$ has value between zero and unity.

The distribution function for electrons at absolute zero has different form :-

(i). When $E < E_F$ (i.e) for energy levels lying below E_F , $(E-E_F)$ is a negative quantity and hence

$$f(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1+0} = 1$$

So, All the levels below E_F are occupied by electrons.

(ii). When $E > E_F$ (i.e) for energy levels lying above E_F , $(E-E_F)$ is a positive quantity and hence

$$f(E) = \frac{1}{1 + e^{\infty}} = \frac{1}{1+\infty} = 0$$

So, All the levels above E_F are vacant.

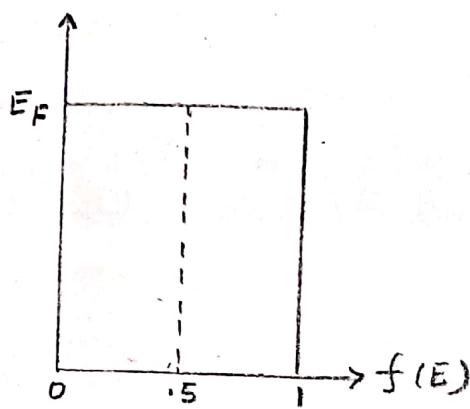
thus At absolute zero, all levels below E_F are completely filled and all levels above E_F are completely empty. The level that divides these two state is known as Fermi Energy level.

$$f(E) = \frac{1}{1+e^{\frac{E-E_F}{kT}}} = \frac{1}{1+1} = \frac{1}{2}$$

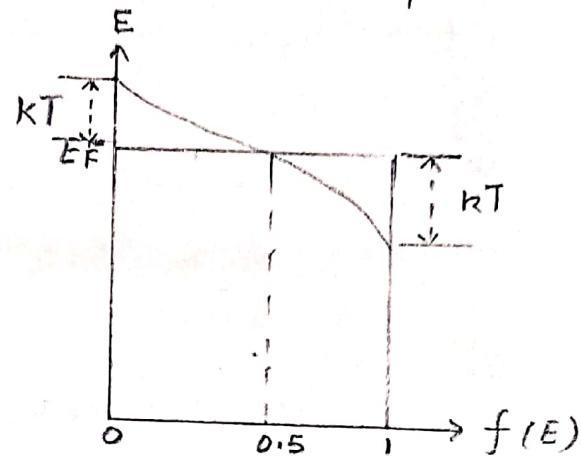
at all temperatures.

Thus the probability of finding an electron with energy equal to the fermi energy in a metal is $1/2$ at any temperature.

Fermi-Dirac E



(a) At $T=0K$



(b) When $T > 0K$

- (a) At $T=0$ all energy levels upto E_F are occupied & above E_F are empty.
- (b) At $T>0K$ some levels above E_F are filled & below E_F are partially empty.

* Semiconductors :
Semiconductors are materials whose electronic properties lies inbetween those of metals and insulators. These intermediate properties are determined by the crystal structure, bonding characteristics and electronic energy bands. They are a group of materials having conductivities between those of metals and insulators.

At room temperature semiconductor behave like insulators but when some energy like thermal energy given to it it behave like conductor.

* Classification :

According to the nature of current carriers, semiconductors are two

(i) Ionic Semiconductor : In this type of Semiconductor conduction takes place through the movement of ions and accomplished by mass transport.

(iii). Electronic Semiconductor : In this type conduction takes place through the movement of electrons and no mass transp is involved.

* According to the Structure of Semiconductor, it is of three type

(i). Amorphous Semiconductor : They have poor electrical charac

(ii). Poly-crystalline Semiconductor : They have better electrical characteristics and lower conductivity.

(iii). Single crystal Semiconductor : They have superior electrical characteristics and higher conductivity. They are mostly used

* According to the constituent atoms of Semiconductor

(i). Element Semiconductor : All the constituent atoms are of same kind i.e composed up of single species of atoms. Exp. Ge & Si

(ii). Compound Semiconductor : They are composed of two or more element. Exp. GaAs, AlAs.

* Intrinsic Semiconductor : When the semiconductor crystal is in pure form i.e free from any kind of impurity, the resultant crystal is known as Intrinsic Semiconductor.

* Extrinsic Semiconductor : When impurity atoms are added to the pure semiconductor then the resultant semiconductor is known as Extrinsic Semiconductor. The addition of impurity increases the carrier concentration and hence conductivity of conductor.

* Doping : The process of mixing impurity to the pure semiconductor crystal or others is known as doping.

Fermi Level : \Rightarrow The no. of free electrons per unit volume in an intrinsic semiconductor is

$$n = 2 \left(\frac{2\pi m_e k T}{h^2} \right)^{3/2} \exp \left(\frac{E_F - E_c}{k T} \right)$$

The no. of holes per unit volume in an intrinsic semiconductor is

$$p = 2 \left[\frac{2\pi m_h k T}{h^2} \right]^{3/2} \exp \left(\frac{E_v - E_F}{k T} \right)$$

Since $n = p$ in intrinsic semiconductor

$$2 \left(\frac{2\pi m_e k T}{h^2} \right)^{3/2} \exp \left(\frac{E_F - E_c}{k T} \right) = 2 \left(\frac{2\pi m_h k T}{h^2} \right)^{3/2} \exp \left(\frac{E_v - E_F}{k T} \right)$$

$$(m_e)^{3/2} \exp \left(\frac{E_F - E_c}{k T} \right) = (m_h)^{3/2} \exp \left(\frac{E_v - E_F}{k T} \right)$$

$$e^{2E_F/kT} = \left(\frac{m_h}{m_e} \right)^{3/2} \exp \left(\frac{E_v + E_c}{k T} \right)$$

Taking log on both sides

$$\frac{2E_F}{kT} = \frac{3}{2} \log_e \left(\frac{m_h}{m_e} \right) + \log_e \left[\exp \left(\frac{E_v + E_c}{k T} \right) \right]$$

$$\frac{2E_F}{kT} = \frac{3}{2} \log_e \left(\frac{m_h}{m_e} \right) + \left(\frac{E_v + E_c}{k T} \right)$$

$$E_F = \frac{3kT}{4} \log_e \left(\frac{m_h}{m_e} \right) + \left(\frac{E_v + E_c}{2} \right)$$

If we assume $m_h = m_e$

$$E_F = \frac{1}{2} (E_v + E_c)$$

$$(\log_e 1 = 0)$$



⇒ Electron in a periodic potential (field) of
a crystal - KRONIG-PENNEY MODEL

The below fig. shows the periodic potential well and barriers in a periodic arrangement.

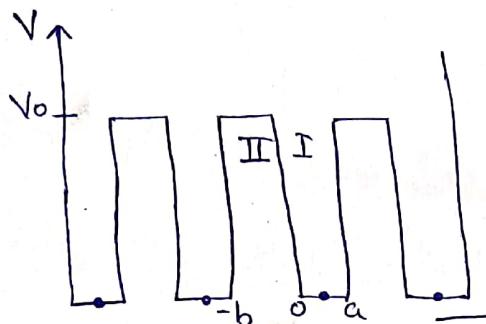


Fig-1- Though the fig is artificial but it shows

many features of the e- behaviour in a periodic lattice. The wave funcn associated with this model can be obtained by solving Schrödinger eqn for region I & II. The time independent Schrödinger eqn is shown as -

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \quad \text{for } (0 < x < a) \quad \text{--- (1)}$$

$$\text{and } \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V_0) \psi = 0 \quad \text{for } (-b < x < 0) \quad \text{--- (2)}$$

$$\text{let } \alpha^2 = \frac{8\pi^2 Em}{h^2} \quad \& \quad \beta^2 = \frac{8\pi^2 m}{h^2} (V_0 - E) \quad \text{as } E \ll V_0$$

Using Bloch theorem we have $\psi(x) = U_k(x) e^{ikx}$
planewave

Eqn ① & ② can be written as

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

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{for } -b < x < 0 \quad 28$$

Soln is appropriate for both the regions

$$\Psi(x) = U_k(x) e^{ikx} \quad \text{--- (3)}$$

$$\text{Now } \frac{d\psi}{dx} = e^{ikx} \frac{dU_k}{dx} + U_k e^{ikx} \cdot ik$$

$$\text{or } \frac{d^2\psi}{dx^2} = e^{ikx} \frac{d^2U_k}{dx^2} + ik e^{ikx} \frac{dU_k}{dx} + ik e^{ikx} \frac{dU_k}{dx}$$

modulated by a periodic function

$$-k^2 e^{ikx} U_k.$$

$$\text{or } \frac{d^2\psi}{dx^2} = -k^2 e^{ikx} U_k + 2ik e^{ikx} \frac{dU_k}{dx} + e^{ikx} \frac{d^2U_k}{dx^2}$$

Substituting the values of $\frac{d^2\psi}{dx^2}$ in eqn ① & ② we get -

$$\frac{d^2U_1}{dx^2} + 2ik \frac{dU_1}{dx} + (\alpha^2 - k^2)U_1 = 0 \quad \text{for } 0 < x < a \quad \text{--- (4)}$$

$$\frac{d^2U_2}{dx^2} + 2ik \frac{dU_2}{dx} + (\beta^2 - k^2)U_2 = 0 \quad \text{for } -b < x < 0 \quad \text{--- (5)}$$

where U_1 & U_2 represents the value of $U_k(x)$ in $0 < x < a$ & $-b < x < 0$.

On solving eqn ④ we get -

$$\frac{dU_1}{dx} = m e^{mx} \quad \& \quad \frac{d^2U_2}{dx^2} = m^2 e^{mx}$$

$$U_1 = e^{mx}$$



Substituting in eqn ④ we get -²⁹

$$\omega^2 e^{i\omega x} + 2ik e^{i\omega x} + (\alpha^2 - k^2) e^{i\omega x} = 0$$

$$\text{or } \omega^2 + 2ik\omega + (\alpha^2 - k^2) = 0$$

$$\omega = -ik \pm i\alpha$$

$$\text{or } \omega_1 = -ik + i\alpha = i(\alpha - k)$$

$$\& \omega_2 = -ik - i\alpha = -i(\alpha + k)$$

Thus, the general soln is

$$U_1 = Ae^{i\omega_1 x} + Be^{i\omega_2 x}$$

$$U_1 = Ae^{i(\alpha - k)x} + Be^{i(\alpha + k)x}$$

where A & B are const.

Similarly for eqn ⑤ we can write

$$U_2 = Ce^{(B-i\alpha)x} + De^{-(B+i\alpha)x}$$

where C & D are const.

A, B, C, D are constts that can be ~~applied~~
obtained by applying the boundary conditions. —

$$[U_1(x)]_{x=0} ; [U_2(x)]_{x=0} ; [U_1(x)]_{x=a}$$

$$[U_2(x)]_{x=-b}$$

$$\text{or } \left[\frac{dU_1(x)}{dx} \right]_{x=0} = \left[\frac{dU_2(x)}{dx} \right]_{x=0}$$

$$\left[\frac{dU_1(x)}{dx} \right]_{x=a} = \left[\frac{dU_2(x)}{dx} \right]_{x=-b}$$

Solving with these conditions, we get non-vanishing solutions, if the determinant of the coeff. A, B, C, D vanishes.

Note - K-P model demonstrates that a simple 1-D periodic potential ~~pot~~ yields energy bands as well as energy band gaps

$$A e^{(x-k)a} e^{i(x-k)a} - B i (x+k) e^{-i(x+k)a} \stackrel{30}{=} C (\beta - ik) e^{(\beta - ik)b} - D (\beta + ik) e^{-(\beta + ik)b}$$

On solving eqn ⑥ we get -

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

~~When~~ When $V_0 b$ remains infinite, function is delta function.

Now $\sinh \beta b \rightarrow \beta b$ & $\cosh \beta b \rightarrow 1$ if $b \rightarrow 0$

$$\text{i.e. } \frac{\beta^2 - \alpha^2}{2\alpha\beta} \beta b \sin \alpha a + \cos \alpha a = \cos k a \quad \text{--- ⑦}$$

$$\begin{aligned} \beta^2 - \alpha^2 &= \frac{8\pi^2 m}{h^2} (V_0 - E) - \frac{8\pi^2 m}{h^2} E \\ &= \frac{8\pi^2 m}{h^2} (V_0 - 2E) \end{aligned}$$

$$\text{Since } V_0 \gg E = \beta^2 - \alpha^2 = \frac{8\pi^2 m}{h^2} (V_0)$$

Substituting in eqn ⑦ we get -

$$\left(\frac{\beta^2 - \alpha^2}{2\alpha\beta h^2} \right) \beta b \sin \alpha a + \cos \alpha a = \cos k a$$

$$\text{where } P = \frac{m V_0 a b}{h^2}$$

$$\text{i.e. } \frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a.$$

Note $\rightarrow V_0$ = Barrier Strength, also called as scattering power of potential barrier.

i.e measure of strength with which e^- in a crystal are attached to the ions in the crystal lattice sites.

Now when $\sigma \rightarrow \infty$ we get

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$$\sin \alpha = 0$$

$$\text{or } \sin \alpha = \sin n\pi$$

$$\text{or } \alpha = n\pi$$

$$\text{or } \alpha^2 \alpha^2 = n^2 \pi^2$$

$$\text{or } \frac{8\pi^2 m E}{h^2} \alpha^2 = n^2 \pi^2$$

$$\text{or } E = E_m (\text{say}) = \frac{n^2 \pi^2 h^2}{8m \alpha^2}$$

The above eqn represent the energy levels of particle in 1-D box of atomic dimension.

when $\sigma \rightarrow 0$, eqn changes to

$$\cos \alpha = \cos k\alpha$$

$$\alpha = k\alpha$$

$$\alpha^2 = k^2$$

$$\text{or } \frac{8\pi^2 m E}{h^2} = k^2$$

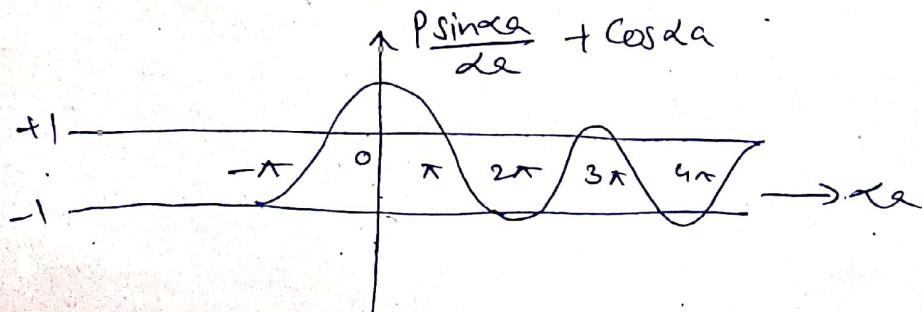
$$\text{or } E = \frac{h^2 k^2}{8\pi^2 m} \Rightarrow E = \frac{1}{2m} \left(\frac{\alpha \pi}{\lambda} \right)^2 \left(\frac{h^2}{4\pi^2} \right)$$

$$= \frac{h^2}{2m} \left(\frac{1}{\lambda} \right)^2 \text{ ie } \lambda^2 = (h/mv)^2$$

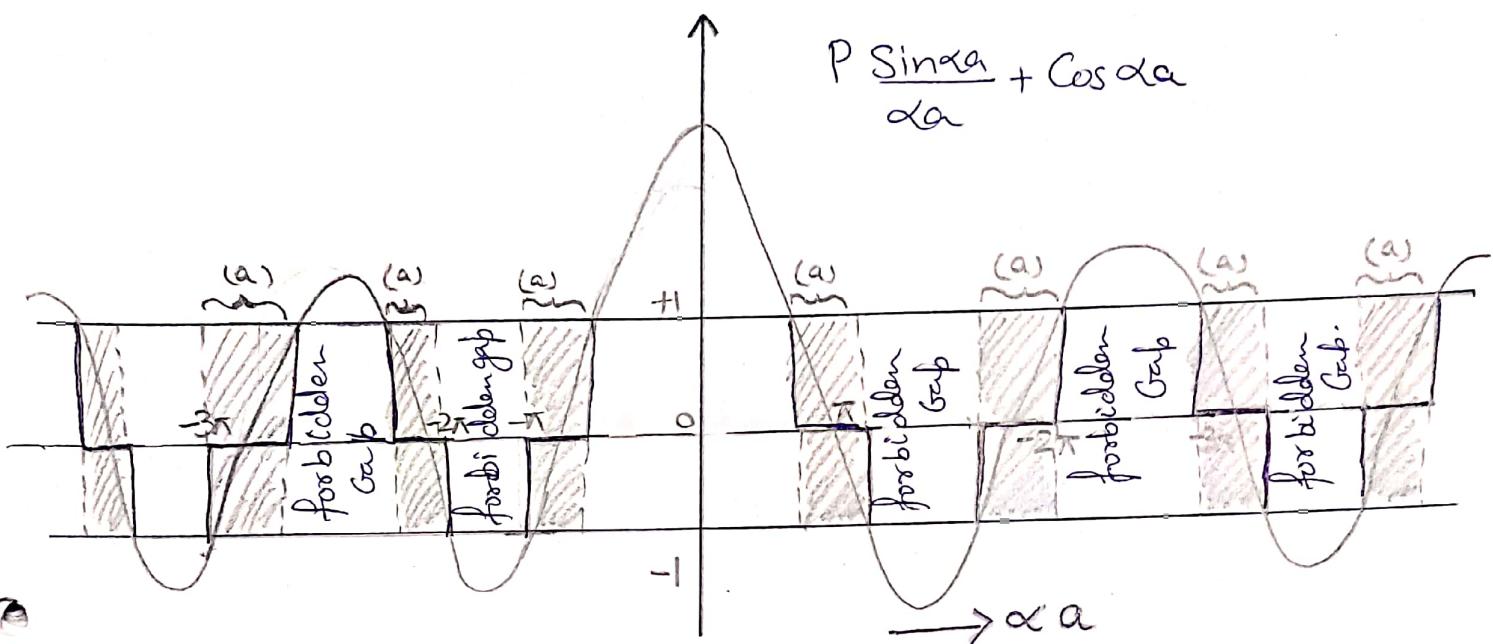
$$E = \frac{h^2}{2m} \left(\frac{m^2 v^2}{h^2} \right) = \frac{1}{2} mv^2. \text{ shows that}$$

allowed energy levels of e^- are continuous.

Note → Plot of $\frac{P \sin \alpha}{\alpha} + \cos \alpha = \cos k\alpha$ with $P = 3\pi/2$



P.T.O



E-K Diagram → Also called as band structure.

It shows the characteristics of a particular semiconductor material. It shows the relationship b/w the energy & momentum of available quantum mechanical states for e^- in the material. It tells us about the optical and electrical properties of the semiconductor or any material.

Why — To know the electronic behaviour of solids, to distinguish what the solid is (conductor, insulator, semiconductor) regarding energy gap. Can be used for band gap calculations, optical transitions & electron mobility, effective mass etc.

Physical Significance — In solid state, the stationary e^- states in solids are characterized by two invariant (conserved) quantities k (k_x, k_y, k_z) & energy E . k corresponds roughly to the momentum of free particles. $\hbar k$ is called the crystal momentum. E is sum of both kinetic & potential energy. These two are ^{not} independent of for free particles, they are related to each other and called as dispersion relation. Since momentum is \propto to velocity & $k \cdot E \propto v^2$. In free space, E depends on k^2 & thus is a parabola with its bottom at $k=0$.

The potential energy of free e^- is zero, that can be seen in E vs k diagram of solids.

Note - This is an important result based on Kronig-Penney model -

For a free particle, there are no potential barriers, so $V_0 = 0$ i.e. $\gamma_1 = 0$. We get now get -

$$\cos \alpha = \cos k\ell$$

$$\text{i.e. } \alpha = k\ell$$

$$\text{i.e. } \alpha^2 = \frac{2mE}{\hbar^2} = k^2$$

Since the particle has no potential energy, $k \cdot E$ is only the form. Thus we have.

~~$$k = \frac{\alpha^2 \cdot 2m}{\hbar^2} = \frac{2m \cdot k^2}{\hbar^2}$$~~

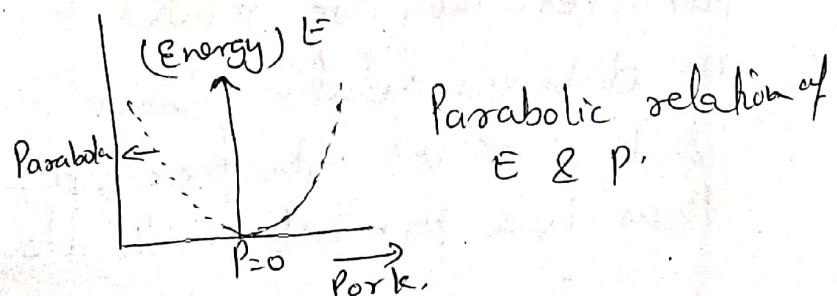
$$k = \sqrt{\frac{2m \cdot m v^2}{\hbar^2}} = k, \text{ or } \alpha = \sqrt{\frac{2m(\frac{1}{2}mv^2)}{\hbar^2}} = k$$

$$\text{or } \alpha^2 = \frac{p^2}{\hbar^2} = k. \quad p = \text{momentum of the particle}$$

$$\text{or } k = p/\hbar$$

$$\text{or } E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m} \quad \text{(A)}$$

From eqn (A) Energy & momentum (Cork)
 α is shown as



α or αa , parameter is related to the potential barrier. As it increases, the particle gets more & more tightly bound to the atom.

From eqn 8, $\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a - (B)$

L.H.S

R.H.S

The L.H.S. is a function of (αa) so we can write it as

$$f(\alpha a) = \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$$

Plot of ~~$\sin \alpha a / \alpha a$~~

Plot of $\tau, \sin \alpha a / \alpha a$ vs αa

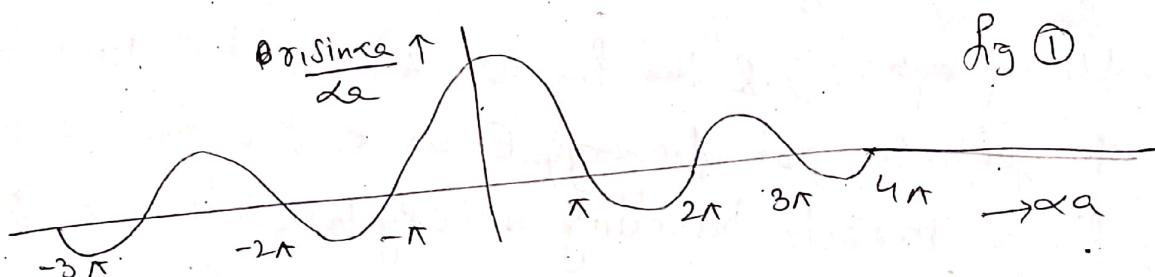


Fig 1

Fig 2

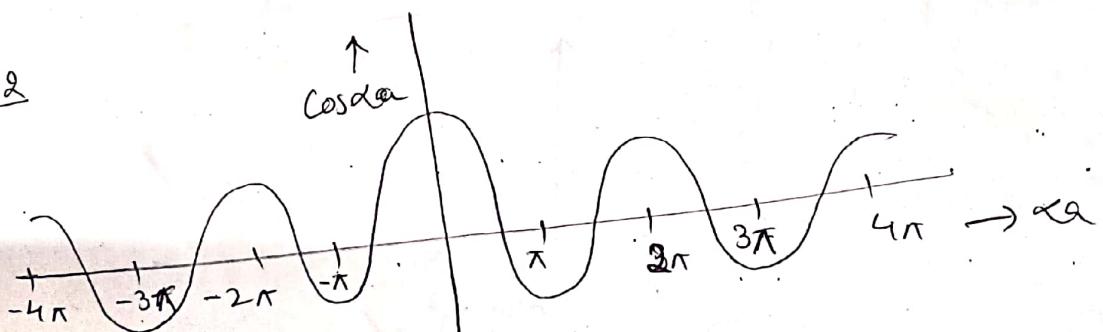
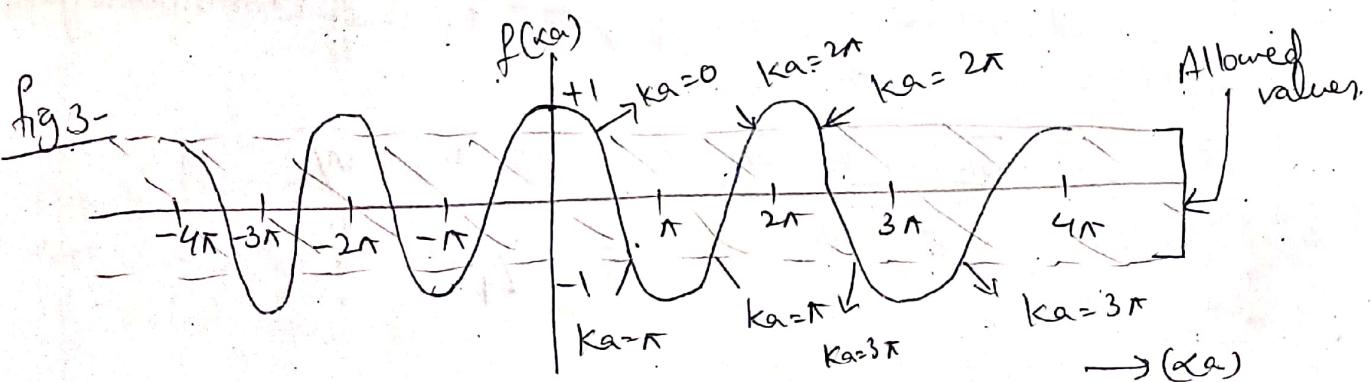


Fig 3-



Allowed values

On comparing eqn $P_1 \frac{\sin \alpha}{\alpha} + \cos \alpha = \cos k\alpha$

& $f(\alpha) = P_1 \frac{\sin \alpha}{\alpha} + \cos \alpha$ we get

$$f(\alpha) = \cos k\alpha. \quad \text{--- (C)}$$

The above eqn implies that $f(\alpha)$ must have values b/w $+1 \& -1$. Allowed values of $f(\alpha)$ for (α) in the range of $+1 \& -1$ is shown with shaded portion. Values of $(k\alpha)$ corresponding to allowed values of $f(\alpha)$ is shown in 3rd fig.

$$\alpha^2 = \frac{2mE}{\hbar^2} = k^2 \quad \text{--- (D)}$$

Using eqn (D) & ~~the~~ fig. ①, ②, ③, it is possible to generate plot of energy E as a function of k for a particle travelling in crystal lattice as shown in fig -

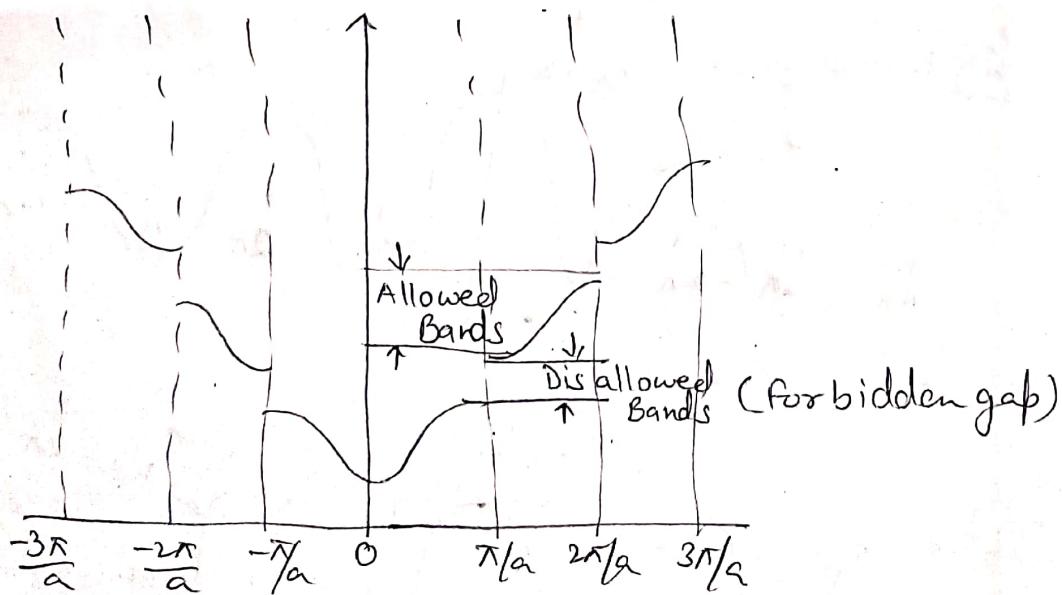


Fig (A)

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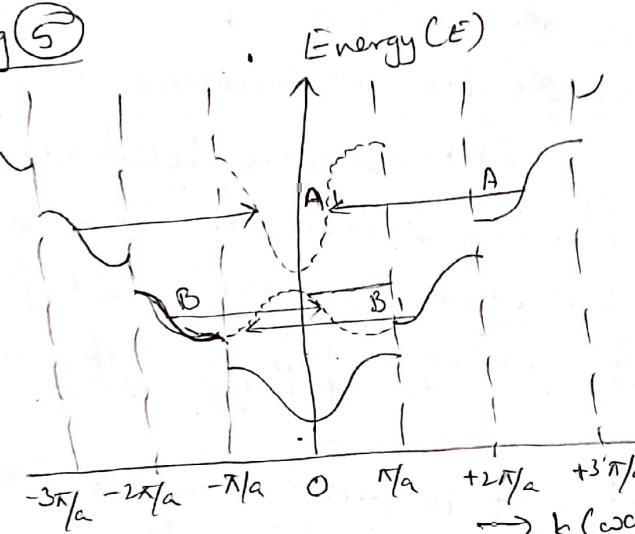
(5) This E-k plot gives the allowed & forbidden energy bands for a particle in ~~physic~~ crystal structure for different wave number values.

As cosine function is periodic-

$$\text{So } \cos(k_a) = \cos(k_a + 2\pi n) = \cos(k_a - 2\pi n)$$

where n is a positive integer.

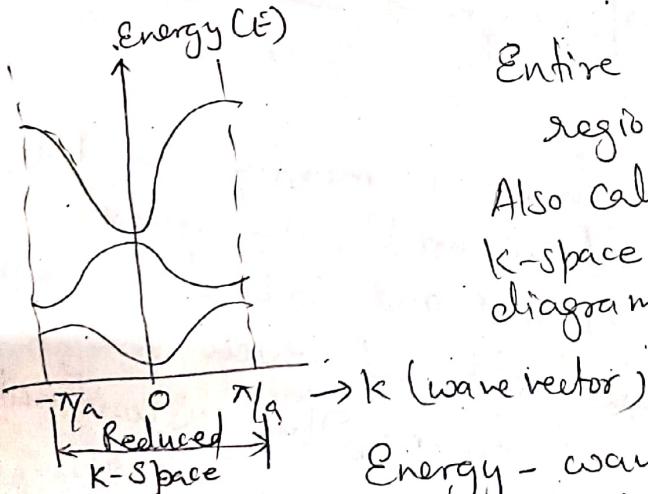
Fig (5)



Plot of energy Vs k .

fig - shows displaced portions with dotted curves. It does not effect the energy gap b/w allowed & forbidden bands. Though it helps in band gap visualization easier.

Fig (6)



Entire E-k plot within region $-\pi/a < k < \pi/a$.

Also called as reduced k-space or reduced zone diagram.

Energy - wave-number plot for region $-\pi/a < k < \pi/a$.

The different length segments of k in fig (5) are called Brillouin zones. Segment $-\pi/a < k < \pi/a$ is called first Brillouin zone. Sec. as $-\pi/a < k < -2\pi/a$ & $\pi/a < k < 2\pi/a$.

BRILLOUIN ZONES / KLEINER-SEITZ PRIMITIVE CELL

These are the set of points in k -space that can be reached from the origin without crossing plane.

Alternatively, it is defined as the set of points closer to the origin than to any other reciprocal lattice

Significance → Brillouin zone is nothing but they are the allowed energy regions of e^- in momentum/reciprocal space. In this region, e^- travelling will have wave like solutions. At these zone boundaries, the e^- suffers Bragg's diffraction & thus, no traveling wave like soln exist at zone boundaries. This diffraction originates the energy gap in crystals.

This is a representation of permissible values of k of e^- in one, two or three dimensions. It gives us the concept of origin of allowed & disallowed bands.

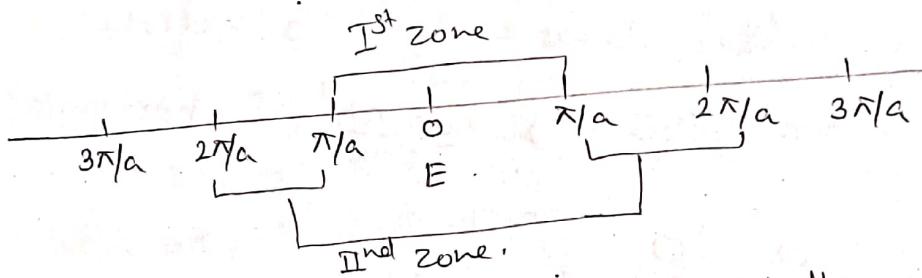
In 1-D — If an e^- is moving in 1-D periodic lattice. As a result, the energy spectrum contains allowed and forbidden regions. Considering the values of k , at which the discontinuities in E occur. The discontinuity occurs when the term $\frac{d}{dx} \sin kx + \cos kx$ reaches its maximum value i.e.

$$\cos(kx) = \pm 1$$

$$\text{or } k = \pm n \frac{\pi}{a} \quad \text{where } n = 1, 2, 3, \dots$$

At such values of k , the e^- momentum increases and as a result its energy increases, it jumps discontinuously from the top of one allowed band to the bottom of next. This region between the first & second values of k for which discontinuities occur is called the second Brillouin zone and so on.

for 1-D



The first two Brillouin zone in 1-D lattice

In 2-D - If the e^- is moving in 2-D square lattice, then let's consider-

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

low energy e^- will have long wavelength λ . without being diffracted they travel freely through a crystal. On the other hand, the more energetic e^- (near to the fermi level $E \approx E_F$) has comparable wavelength. They suffer Bragg's

diffraction law -

$$2a \sin \theta = n \lambda$$

where $n = 1, 2, 3, \dots$

where θ = angle of incidence of beam of e^- .

Replacing λ by K

$$|K| = \frac{2\pi}{\lambda}$$

from $n\lambda = 2a \sin\theta$ and $|K| = \frac{2\pi}{\lambda}$ — we get —

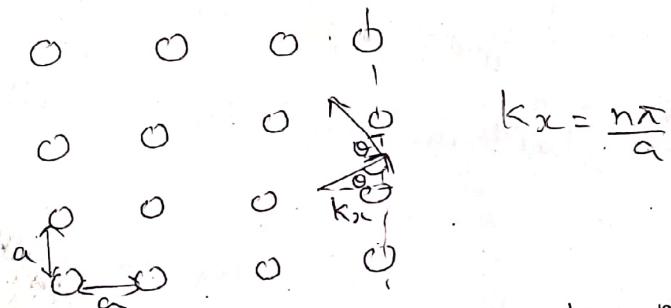
$$|K| = \frac{n\pi}{a \sin\theta} = k$$

k depends on angle of incidence θ .

Let us take the two dimensional lattice.

For vertical rows — k in x -direction

$$k_x = \frac{n\pi}{a} ; k_y = \frac{\pi n}{a} \text{ (for horizontal rows)}$$



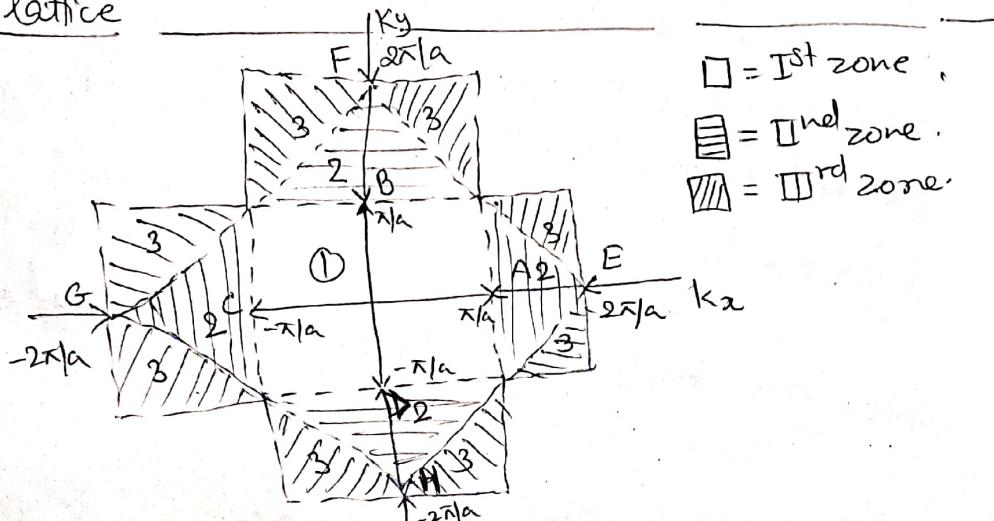
$$n_1 k_x + n_2 k_y = \frac{\pi}{a} (n_1^2 + n_2^2)$$

Hence

for first first zone, $n = \pm 1$,

$$k_x = \pm \frac{\pi}{a} \text{ & } k_y = \pm \frac{\pi}{a} \quad (\text{for } n_1 = \pm 1, n_2 = 0 \text{ & } n_1 = 0, n_2 = \pm 1)$$

⇒ fig ① first three Brillouin zones for a two dimensional lattice



- = Ist zone.
- = IInd zone.
- ▨ = IIIrd zone.

Now, to get the sketch we use integer values (41)

$$n_1 = +1; n_2 = +1 \rightarrow k_x + k_y = \frac{2\pi}{a} - (1)$$

$$n_1 = -1; n_2 = +1 \rightarrow -k_x + k_y = \frac{2\pi}{a} - (2)$$

$$n_1 = +1; n_2 = -1 \rightarrow k_x - k_y = \frac{2\pi}{a} - (3)$$

$$n_1 = -1; n_2 = -1 \rightarrow -k_x - k_y = \frac{2\pi}{a} - (4)$$

for two-dimensional case $k_x n_1 + k_y n_2 = \frac{\pi}{a} (n_1^2 + n_2^2)$

The above four set of equations, at 45° to the k_x & k_y axes passing through E, F, G, H or shown in fig (1). Similarly, for 3-D third zone n_1 & n_2 values will be given as $0, \pm 1, \pm 2$.

For three-dimension, the eqn is given as
 $n_1 k_x + n_2 k_y + n_3 k_z = \frac{\pi}{a} (n_1^2 + n_2^2 + n_3^2)$
gives complicated structure.

Direct & Indirect Band Gap

\Rightarrow Solution for $n_1 k_x + n_2 k_y = \frac{\pi}{a} (n_1^2 + n_2^2)$

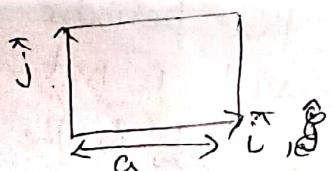
NOTE for first zone — $k_{xc} = k \sin \theta = \frac{n\pi}{a}$. (vertical)

for horizontal = $k_y = \frac{n\pi}{a}$

$k_{xc} = \pm \frac{\pi}{a}, k_y = \pm \frac{\pi}{a}$ for $n = \pm 1$.

let a square lattice

$$a_i = a_i^* \quad \& \quad b_j = b_j^*$$



corresponding primitive reciprocal lattice translations

$$\text{vectors } a^* = \frac{2\pi}{a} \hat{i}; b^* = \frac{2\pi}{a} \hat{j}$$

$$G (\text{the reciprocal lattice vector}) = n_1 a^* + n_2 b^* \\ = \frac{2\pi}{a} (n_1 i + n_2 j)$$

(10)

22

$$\text{Now } \mathbf{k}_0 = k_{xi} \hat{i} + k_{yj} \hat{j}$$

We have Bragg's condition $2\mathbf{k} \cdot \mathbf{G} + G^2 = 0$

$$2(k_{xi} + k_{yj}) \cdot \frac{2\pi}{a} (n_1 i + n_2 j) + \frac{4\pi^2}{a^2} (n_1^2 i^2 + n_2^2 j^2) = 0$$

$$\frac{4\pi}{a} (n_1 k_{xi} + n_2 k_{yj}) + \frac{4\pi^2}{a^2} (n_1^2 + n_2^2) = 0$$

for $i \cdot i - j \cdot j = 1 \text{ & } i \cdot j = 0$

$$\text{Thus } n_1 k_{xi} + n_2 k_{yj} = \frac{\pi}{a} (n_1^2 + n_2^2)$$

③ Use to calculate density of states. 24

12

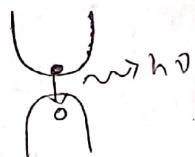
DIRECT & INDIRECT BAND GAP -

In direct band gap, the e^- & hole recombines to give a photon. This process is called radiative recombination. Also called as spontaneous emission. This happens when e^- in an excited state (conduction band) falls back into the valence band.

Ex- GaAs, GaAsP, InP.

Use- To make LEDs & lasers of different colours.

$e^- + \text{hole} \rightarrow h\nu$ (photon)

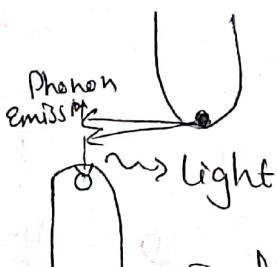


Direct Band gap

In an indirect band gap, when an excited e^- falls back into the valence band, it recombines with the hole that generates heat & is dissipated within the material. Ex- Si, Ge, GaP.

i.e. $e^- + \text{hole} \rightarrow \text{phonon}$.

(Non-radiative recombination)



Indirect Band gap

CONCEPT OF PHONONS²⁵ (Quantisation of 13 lattice Vibrations)

It is a definite discrete unit or quantum of vibrational mechanical energy. Phonons & electrons are the two elementary particles or excitations in solids. It is not a fundamental particle as it is a quantum of vibrational excitation in a crystal lattice.

So, localized traveling waves of atomic vibrations in solids, is called phonons, that are quantized with energy $\hbar\omega = h\nu$ where $\nu/\omega = \nu$, frequency of vibration of wave.

Ex → Sound moving through air, seismic waves, travels thousands of miles to reach seismograph detector that records earthquake event several minutes later.

Note - Phonons - are quantum of lattice vibration
Photons - Quantum of light energy.

As energy levels in harmonic oscillator are quantized -

The allowed energy levels in the harmonic oscillator are

$$E = (n + \frac{1}{2})\hbar\omega \quad \text{--- ①}$$

n = quantum number.

$$u = Ae^{i(q\vec{r} - \omega t)} = \text{normal vibrational mode in crystal with freq. } \omega.$$

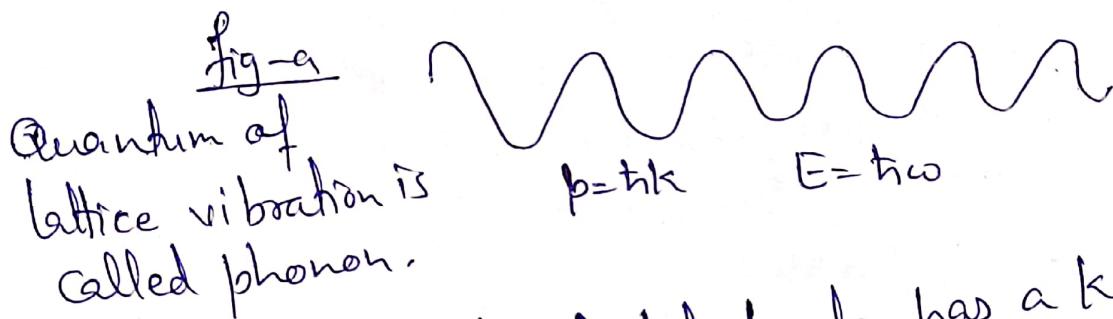
here the term $\frac{1}{2} \hbar \omega$ = zero point energy of the mode.

Phonons governs the thermal properties in semiconductors & insulators. They affects the thermal, electrical, optical & other properties of bulk material. They also have density of states $D(\text{PH})$ which is dimensional dependent & its electronic counterpart, affects some properties of solids.

Concept of Phonons - Contd.

We know $U_s = U e^{i(kxa - \omega t)}$ → ① (harmonic vibration of a particle)

Through the quantum properties of harmonic oscillator a quantum of energy as two is associated with the mode of frequency ω . U_s the amplitude vibration is associated with energy content of lattice mode vibration or lattice mode. This corresponds to an integral number of quanta. These quanta of lattice vibrations are known as 'phonons'.



A separate vibrational state mode has a known wave vector k and with an application of $p = \hbar k$. Thus, mechanical momentum of the whole specimen can arise in a rigid motion. The vibrational modes transport energy & are described by relative motion of individual atoms having average displacement as zero. Thus they don't contain a net momentum & quantity $\hbar k$ is not to be defined with linear momentum of conventional type.

However, during interaction, not only energy but $\hbar k$ should be conserved. Latter one is the crystal momentum.

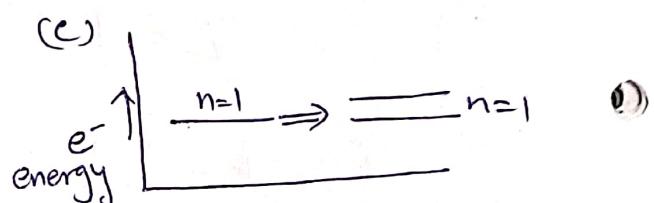
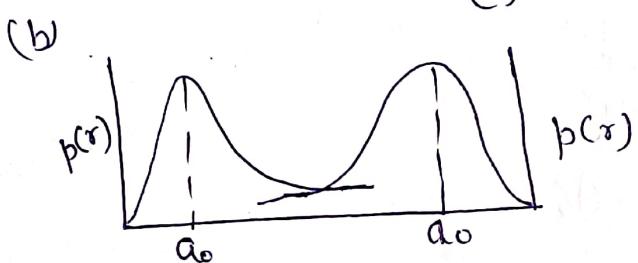
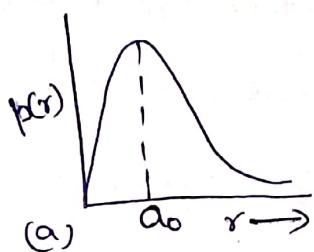
The laws followed by phonons while interacting are

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \quad \text{---} \quad ①$$

$$\hbar k_1 + \hbar k_2 = \hbar k_3 + \hbar G$$

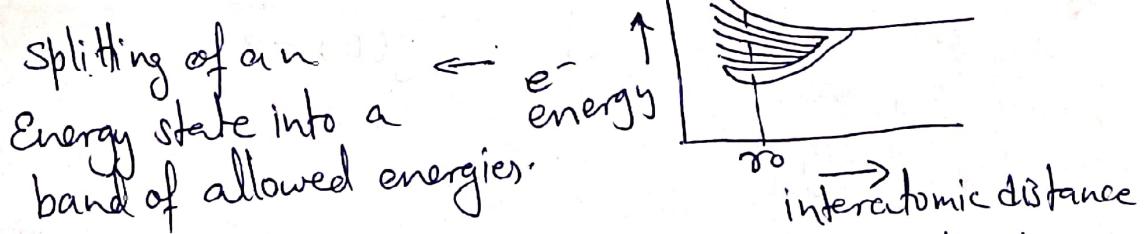
Energy Band in Solids -

For an atom of hydrogen, the probable density function, for a non interacting hydrogen atom (a single atom ~~to~~ with lowest e⁻ energy state) the fig is as follows -



Means that when two e⁻ interact, discrete quantized energy level splitting takes place in two discrete energy levels. This is in consistent with Pauli Exclusive principle

Consider an arrangement of hydrogen type atoms which are apart in starting & when they are pushed together, initial quantized energy level will split into a band of discrete energy levels, as shown in fig. -



At equilibrium interatomic distance, there is a band of allowed energies but within allowed band, energies are discrete.

However, since no $2e^-$ can have same quantum number, discrete energy must split into band of energies so that each e^- can occupy a distinct quantum state.

Now consider the arrangement in which atom contains more than 1e⁻. Consider that n=3 energy level. When the atoms are brought close to each other, outermost e⁻ in n=3 energy shell will begin to interact initially, so that this discrete energy level will break into band of allowed energies. In continuation n=2 will interact and split into a band of allowed energies & likely the innermost e⁻ will interact as shown in fig-

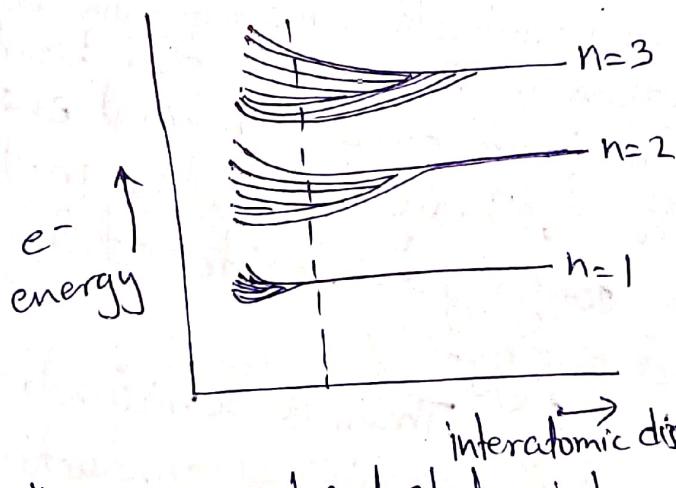


fig → Splitting of three energy band states into allowed band of energies.

Now, if the equilibrium interatomic distance is r_0 , then we have the bands of allowed energies which e⁻ may occupy separated by bands of forbidden energies. This is the theory of Energy-band theory of single-crystal materials.

Energy Band Structure of Semiconductor - Brillouin Zone

(Si & GaAs) -

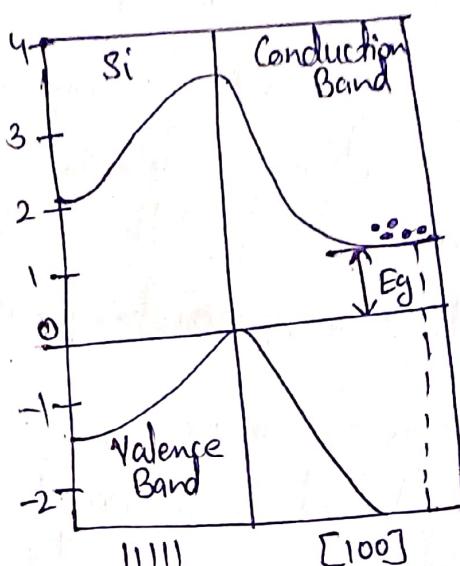
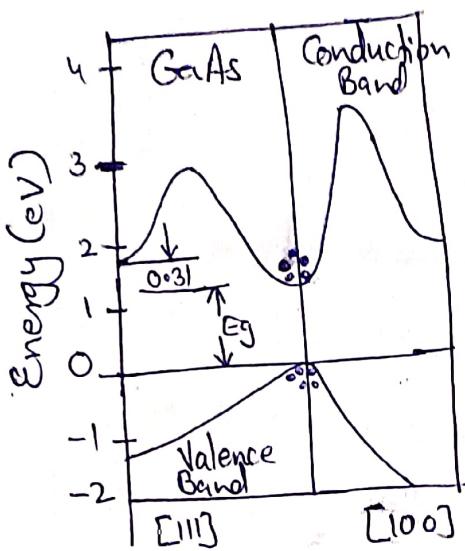


fig- Energy band structures of (a) GaAs and (b) Si

From fig (a) - the E versus k diagram for GaAs - Valence band maximum and conduction band minimum both occurred at $k=0$. Electrons in the conduction band tend to settle at the minimum conduction band energy ie maximum at $k=0$. Similarly, holes in the valence band tend to ~~congregate~~ reside at the upper most valence band energy.

Thus, a semiconductor with a property that having minimum conduction band energy and maximum valence band energy at the same k -value is called to be a direct band gap semiconductor. In other words it implies that, transition between two allowed bands, if it happens and there is no change in k -value (crystal momentum). This is helpful in optical properties of the material.

They are applicable in semiconductor laser & other optical devices.

On the other hand, in the fig 1(b), the maximum in the valence band energy occurs at $k=0$ but minimum of conduction band energy does not occur at $k=0$. Still, the difference between conduction & valence band energy is called as Band gap Energy (E_g). If such is the condition, in which minimum conduction band energy & maximum valence band energy does not occur at same k -values then ~~in~~ this type of semiconductor is known as Indirect Band-Gap Semiconductor. For such a case, indirect band gap transition material must contain such ~~transition~~ crystal field interaction so that crystal momentum is conserved.

Ex - Indirect Band Gap Semiconductor = Ge, GaP, AlAs, Si.

Direct Band Gap Semiconductor - GaAs, InGaAs, GaN, CdS, CdSe etc.



DENSITY OF STATES - Essentially, the number of different states at a particular energy level that e⁻ are allowed to occupy. i.e. the number of electron states per unit volume per unit energy.

It is essential for determining the carrier concentrations and energy distributions of carriers within a semiconductor.

Practical Applications - Quantum Well, Quantum wire and Quantum Dots-

To find $Z(E)$ - in energy range E to $E+dE$.

No. of electrons per unit volume in a given range of interest is given by $n = \int_{E_g}^{E} Z(E) F(E) dE$

where $Z(E) = \frac{\pi}{2} n^2 dn$ (in the energy range E to $E+dE$)

We have energy of particle as $E = \frac{n^2 h^2}{8mL^2}$ — (2)

$$\text{or } n^2 = \frac{E \cdot 8mL^2}{h^2} \quad (3)$$

$$\text{or } n = \sqrt{\frac{8mL^2 E}{h^2}} \quad (4)$$

Differentiate eqn (3) b.h.s.

$$2ndn = \frac{8mL^2 dE}{h^2}$$

$$dn = \left(\frac{8mL^2}{h^2} \right) \left(\frac{1}{2n} \right) dE$$

(2)

$$\text{or } \left(\frac{8mL^2}{h^2}\right) \cdot \frac{1}{2} \left(\frac{h^2}{8mL^2 \cdot E}\right)^{1/2} dE$$

$$dn = \frac{1}{2} \cdot \frac{dE}{(E)^{1/2}} \cdot \left(\frac{8mL^2}{h^2}\right)^{1/2} \quad \text{--- (5)}$$

Substitute dn & n^2 in eqn ① we get.

$$Z(E) dE = \frac{\pi}{4} \cdot \left(\frac{8mL^2}{h^2}\right) \cdot \frac{E}{E^{1/2}} \cdot \left(\frac{8mL^2}{h^2}\right)^{1/2} dE$$

$$\text{or } Z(E) dE = \frac{\pi}{4} \left(\frac{8mL^2}{h^2}\right)^{3/2} \cdot (E)^{1/2} dE$$

As per Pauli Exclusive principle, 2e⁻ of opposite spin can occupy each states & so, the number of energy state available is

$$Z(E) dE = 2 \cdot \frac{\pi}{4} \left(\frac{8mL^2}{h^2}\right)^{3/2} \cdot (E)^{1/2} dE$$

$$\text{or } Z(E) dE = 2 \cdot \frac{\pi}{4h^3} (8m)^{3/2} \cdot (E)^{1/2} dE$$

$$\text{or } Z(E) dE = 2 \cdot \frac{\pi}{4h^3} (8m)^{3/2} \cdot (L)^3 \cdot (E)^{1/2} dE$$

$$\text{Here } (8m)^{3/2} = 8m \cdot (8m)^{1/2}$$

$$\text{ie } Z(E) dE = 2 \cdot \frac{\pi}{4h^3} \cdot 8 \cdot (2m)^{3/2} \cdot (L)^3 \cdot (E)^{1/2} dE$$

$$\text{or } (4 \times 2)m \cdot [(4 \times 2)m]^{1/2}$$

$$\text{or } (4 \times 2)(m)^{3/2} \cdot (2)^{1/2}$$

$$\text{or } (4 \times 2) (2m)^{3/2}$$

$$\text{or } \frac{4\pi}{h^3} (2m)^{3/2} \cdot (L)^3 \cdot (E)^{1/2} dE$$



Fermi Surface

①

The surface in reciprocal space which separates occupied from unoccupied electron states at zero ~~top~~ temperature.

Its shape is derived from the periodicity and symmetry of the crystalline lattice and as ~~the~~ for the occupation of electronic energy bands. Its existence is the direct consequence of the pauli-exclusive principle.

In other words, fermi surface is the

surface of constant energy in k -space. It indicates that electrons behave similarly for any direction of motion.

Characteristics of Fermi Surface —

- 1) It represents the dynamic and inertial properties of conduction e⁻ in k -space.
- 2) Volume of fermi surface represents the number of conduction electrons.
- 3) It has spherical shape within first brillouin zone and non-spherical in higher zone.
- 4) It always meets the zone boundary at right angles along the line of intersection.
- 5) For spherical fermi surface (i.e for free e⁻ case)
The velocity of e⁻ is $v = \frac{e\hbar k}{m_0}$

Dated.

where v = proportional to and parallel to wave vector \vec{k} as shown in fig 1.

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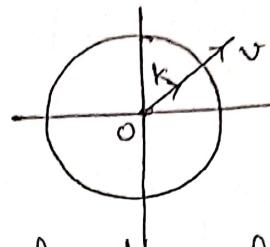


Fig 1 - velocity of a free e-.

For a case, other than free e- (for non-spherical fermi

surfaces, velocity is non-linear function of k ,

$$v = \frac{1}{\hbar} \nabla_k E(k)$$

where v = proportional to the gradient of the energy in k -space.

- 6) Fermi surface tells us many important properties of solids, such as heat capacity, pauli paramagnetism, electrical conductivity etc. of metals, semi-metals and doped semiconductors.

Note: Effect of temperature on fermi-surface :-

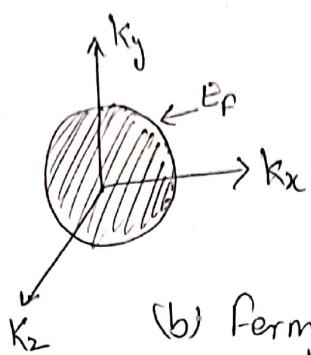
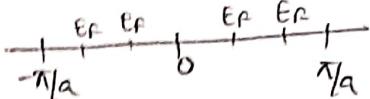
It has a very small effect of temperature and fermi-surface remains sharp even at room temperatures and at slightly high temperature.

With the concept of shape of fermi-surface, the linear response of a metal to an electric magnetic or thermal gradient is determined by the shape of fermi-surface because currents are due to the changes in the occupancy of states near the fermi surface.

$$\text{For free } e^- \quad E_n = \frac{k^2 h^2}{8m}$$

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③

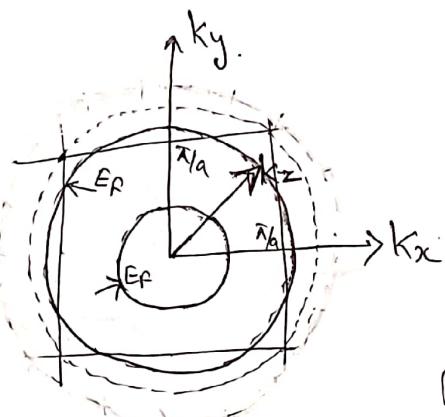


(a) Two points having fermi energy E_F , lying within the IBZ.

(b) Fermi circle with its center k_F as the centre of IBZ.

$\therefore BZ = \text{Brillouin Zone}$

(c) FS is the sphere with radius k_F and centre at the center of IBZ.



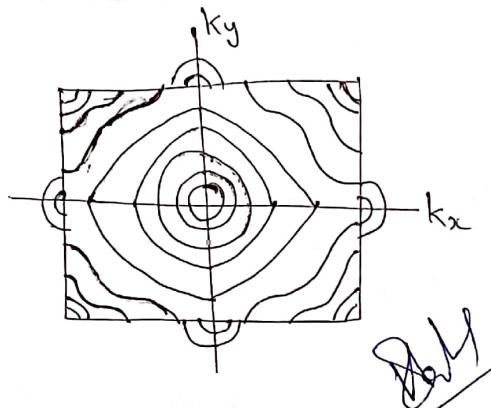
for nearly free e^- model,
no spherical ~~but~~ complicated
shapes are obtained as the
fermi surface and BZ boundaries
are close to each other due to
the effect of crystal potential.

With the increase of no. of valence electrons on the fermi surface gives the evolution of shape of constant Energy curve (fermi surface)

\therefore At the 1st BZ centre which has $k=0, E=0$,
when the n_e (no. of electrons) is small, only the states lying near the bottom of the band (1st BZ center)
are filled and the occupied volume is a circle / sphere in two dimensions (2D)

With further increase of e^- , the fermi volume gradually increases and thus the fermi surface starts deforming and loses its spherical shape near the zone boundary.

Fig 2.



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(4)

X — X — X



(1)

Schrodinger Time Independent Wave Equation

Let us consider a particle of mass 'm', moving with a velocity 'v'. The de Broglie wavelength associated with it is given by,

$$\lambda = \frac{h}{mv} \quad \dots \dots \dots \quad (1)$$

where $h = \text{Planck's constant} = 6.63 \times 10^{-34} \text{ Js}$

let Ψ be the wave function along x, y and z coordinate at any time 't'. The classical differential equation of a progressive wave moving with a wave velocity 'v' can be written as,

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} \quad \dots \dots \quad (2)$$

The solution of equation (2) is given by

$$\Psi = \Psi_0 e^{-i\omega t} \quad \dots \dots \dots \quad (3)$$

where $\Psi_0 = \text{Amplitude of the wave at the point } (x, y, z)$

$\omega = \text{Angular frequency of the wave}$

Differentiating eq.(3) with respect to 't',

$$\frac{\partial \Psi}{\partial t} = (-i\omega) \Psi_0 e^{-i\omega t}$$

Differentiating again with respect to 't',

$$\frac{\partial^2 \Psi}{\partial t^2} = (-i\omega)^2 \Psi_0 e^{-i\omega t} = -\omega^2 \Psi \quad \dots \dots \quad (4)$$

Substituting eqn.- (4) in eqn. (2),

$$\nabla^2 \Psi = -\left(\frac{\omega^2}{v^2}\right) \Psi \quad \dots \dots \dots \quad (5)$$

where $\nabla^2 = \text{Laplacian operator}$

$$\text{But } \omega = 2\pi f = 2\pi \left(\frac{v}{\lambda}\right) \text{ or } \frac{\omega}{v} = \frac{2\pi}{\lambda}$$

$$\text{or } \frac{\omega^2}{v^2} = \frac{4\pi^2}{\lambda^2} \quad \dots \dots \dots \quad (6)$$

(2)

Substituting eqn. (6) in eqn. (5),

$$\nabla^2 \psi = -\left(\frac{4\pi^2}{\lambda^2}\right) \psi \text{ or } \nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \quad \dots \dots \quad (7)$$

Substituting eqn. (1) in eqn. (7),

$$\nabla^2 \psi + \frac{4\pi^2}{\left(\frac{h}{mv}\right)^2} \psi = 0$$

$$\nabla^2 \psi + \frac{4\pi^2 m v^2}{h^2} \psi = 0 \quad \dots \dots \quad (8)$$

If 'E' is the total energy of the particle, 'V', the potential energy, then total energy of the particle is given by

$$E = PE + KE$$

$$E = V + \frac{1}{2} mv^2$$

$$E - V = \frac{1}{2} mv^2$$

$$2(E - V) = mv^2$$

Multiplying both sides by 'm',

$$2m(E - V) = m^2 v^2 \quad \dots \dots \quad (9)$$

Substituting eqn. (9) in eqn. (8),

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots \dots \quad (10)$$

This equation is known as Schrodinger's time independent wave equation.

For one-dimensional motion, the above equation becomes,

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots \dots \quad (11)$$

Introducing, $\hbar = \frac{h}{2\pi}$ in the above equation

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0 \quad \dots \dots \quad (12)$$

(3)

for three dimensions,

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

Schrodinger time dependent wave equation

Differentiating eqn-(3) with respect to 't',

$$\frac{\partial \psi}{\partial t} = (-i\omega) \psi e^{-i\omega t} = (-i\omega) \psi \quad \dots \dots \dots (13)$$

$$\text{But, } \omega = 2\pi f = 2\pi \left(\frac{E}{h}\right) \therefore \psi = \frac{E}{h} \quad \dots \dots \dots (14)$$

where E = energy of a photon

Substituting eqn.(14) in eqn.(13),

$$\frac{\partial \psi}{\partial t} = (-i) \left[2\pi \left(\frac{E}{h}\right) \right] \psi = -i \left(\frac{E}{h}\right) \psi = \frac{1}{\hbar} \left(\frac{E}{h}\right) \psi$$

$$\text{(or) } i\hbar \left(\frac{\partial \psi}{\partial t}\right) = E\psi \quad \dots \dots \dots (15)$$

Substituting the above equation in the time independent wave equation,

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \left[i\hbar \left(\frac{\partial \psi}{\partial t}\right) - V\psi \right] = 0$$

$$\nabla^2 \psi = -\frac{2m}{\hbar^2} \left[i\hbar \frac{\partial}{\partial t} - V \right] \psi$$

$$-\frac{\hbar^2}{2m} \cdot \nabla^2 \psi = \left[i\hbar \frac{\partial}{\partial t} - V \right] \psi$$

$$-\frac{\hbar^2}{2m} \cdot \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad \dots \dots \dots (16)$$

The above equation is known as Schrodinger time dependent wave equation.

from eqn.(16),

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V\right) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\text{(or) } H\psi = E\psi \quad \dots \dots \dots (17)$$

where, $H = -\frac{\hbar^2}{2m} \nabla^2 + V$ = Hamiltonian operator

$$(4) E = i\hbar \frac{\partial}{\partial t} = \text{Energy operator}$$

Application of Schrödinger Wave Equation to a Particle (Electron) Enclosed in a One Dimensional Potential Box.

Let us consider a particle (electron) $V = \infty$ of mass 'm' moving along x -axis, enclosed in a one dimensional potential box as shown in fig 1.

Since the walls are of infinite potential the particle does not penetrate out from the box.

Also, the particle is confined between the length 'l' of the box and has elastic collision with the walls.

Therefore, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.

\therefore we can say that outside the box and on the wall of the box, the potential energy V of the electron is ∞ .

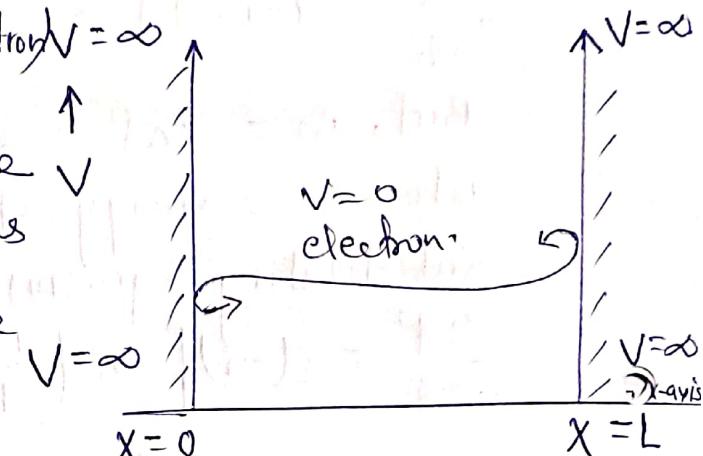
Inside the box the potential energy (V) of the electron is zero.

In other words, we can write the boundary condition as.

$$V(x) = 0 \text{ when } 0 < x < l$$

$$V(x) = \infty \text{ when } 0 \geq x \geq l$$

Since the particle cannot exist outside the box the wave function $\psi = 0$ when $0 \geq x \geq l$.



Length of the box \rightarrow

fig 1. Variation of potential energy of an electron in an one dimensional potential box.

(5)

To find the wave function of the particle within the box of length 'l', let us consider the Schrodinger one dimensional time independent wave equation (i.e.)

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

Since, the potential energy inside the box is zero (i.e. $V=0$). The particle has kinetic energy alone and thus it is named as a free particle (or) free electron.

∴ for a free particle (electron), the Schrodinger wave equation is given by,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \dots \dots \dots (1)$$

$$\frac{d^2\psi}{dx^2} + K^2 \psi = 0 \quad \dots \dots \dots (2)$$

$$\text{where } K^2 = \frac{2mE}{\hbar^2} \quad \dots \dots \dots (3)$$

Eqn. (2) is a second order differential equation, therefore it should have solution with two arbitrary constants.

∴ The solution of eqn(2) is given by

$$\psi(x) = A \sin kx + B \cos kx \quad \dots \dots \dots (4)$$

where A and B are called as arbitrary constants, which can be found by applying the boundary conditions.

(i.e.), $\psi(x) = 0$ when $x=0$ and $x=l$

Boundary condition (i) at $x=0$, potential energy $V=\infty$,

∴ There is no chance for finding the particle at the walls of the box, ∴ $\psi(x) = 0$

(6)

\therefore equation (4) becomes

$$0 = A \sin \alpha + B \cos \alpha$$

$$0 = 0 + B(1)$$

$$\therefore B = 0$$

Boundary condition (ii), at $x = l$, potential energy
 $V = \infty$.

∴ Therefore, there is no chance for finding the particle at the walls of the box, $\therefore \psi(x) = 0$

\therefore eqn. (3) becomes

$$0 = A \sin kl + B \cos kl$$

since $B = 0$ (from 1st boundary condition), we have

$$0 = A \sin kl$$

Since, $A \neq 0$;

$$\sin kl = 0$$

We know $\sin n\pi = 0$

Comparing these two equations, we can write

$$kl = n\pi$$

$$K = \frac{n\pi}{l} \quad \text{--- (5)}$$

Substituting the value of B and K in eqn. (4)
we can write the wave function associated
with the free electron confined in a one
dimensional box as

$$\psi_n(x) = A \frac{\sin n\pi x}{l} \quad \text{--- (6)}$$

Energy of the particle (electron)

We know from

$$K^2 = \frac{2mE}{h^2}$$

$$(7) \quad k^2 = \frac{8\pi^2 m E}{(h^2/4\pi^2)} \quad \left(\because h^2 = \frac{h^2}{4\pi^2} \right)$$

$$k^2 = \frac{8\pi^2 m E}{h^2} \quad \dots \dots \dots (7)$$

Squaring eqn. (5) we get

$$k^2 = \frac{n^2 \pi^2}{l^2} \quad \dots \dots \dots (8)$$

equating eqn. (7) and eqn. (8) we can write

$$\therefore \text{energy of the particle (electron)} E_n = \frac{n^2 h^2}{8ml^2} \dots (9)$$

\therefore from eqn. (9) and eqn. (6) we can say that, for each value of ' n ', there is an energy level and the corresponding wave function.

Thus, we can say that, each value of E_n is known as Eigen value and the corresponding value of ψ_n is called as Eigen function.

METHODS FOR CALCULATING BAND STRUCTURE

Properties of semiconductor materials are the fundamental part of solid-state physics and its related area of research. Investigation of band structure through computational methods are of great importance. Commonly used methods requires the use of complex algorithms and huge amount of computational power. In the adjoining section, several methods and their key properties are described in brief.

I- Tight-Binding Approximation -

- It uses atomic orbitals as basic wave functions.
- For ex - lithium, the free atom e⁻ moves in a potential well as shown in fig (a). It consists of discrete energy level series in its atomic spectrum represented as 1s, 2s, 2p etc. As lithium has 3e⁻, 2e⁻ are in 1s shell (completely occupied) and the third e⁻ in 2s shell (partially filled).
- If the lithium atom forms lithium molecule, each of 1s, 2s & 2p splits into two closely spaced levels, due to coupling of atoms.
- The amount of splitting depends strongly on the internuclear distance of the two atoms in a molecule. As strong is the perturbation, larger is the splitting.
- Splitting also depends on the atomic orbital. (i.e. $2p > 2s > 1s$)

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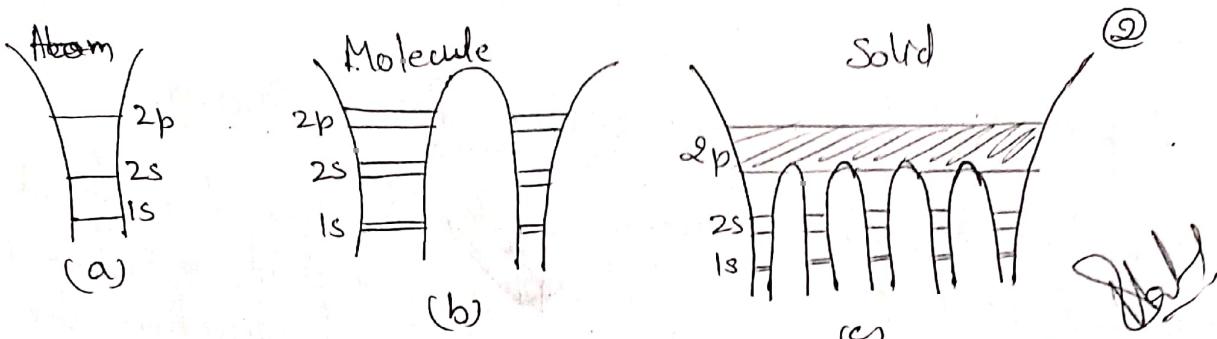


Fig- Evolution of energy spectrum of Li from (a) atom to a (b) Molecule to a (c) solid.

Here, 'Li' is a polyatomic molecule of an arbitrary number of atoms. Similarly, a 3-atom molecule, each atom splits into a triplet, 4 atom in quadruplet & so-on. Thus, the 1s, 2s, & 2p levels forms the energy bands as shown in figure (c). The separating area is known as energy bands (unoccupied by e^-). It is also inferred that higher the level / band, greater is the width. Slightly bound orbitals are slightly affected by perturbation.

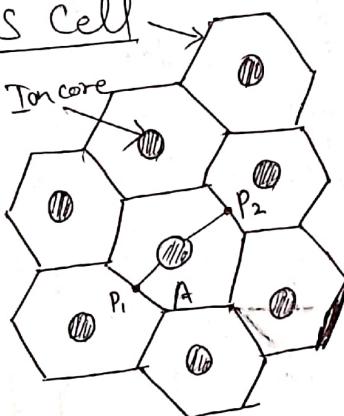
- This is also known as Linear Combination of atomic Orbitals (LCAO) approximation. It is beneficial to describe the inner electronic shells of atoms and relatively localized band of the shell.
- Not beneficial to describe the conduction of e^- themselves because, the free e^- theory is completely different to the nature of the localized atomic states.
- However, with this method, actual band structure can be reproduced including metals as solid, and it is possible to describe the ~~transport~~ transport properties of metals also.

⑨ Cellular Method (Wigner-Seitz Method) ③

Earlier in the TB method, it was found that it was useful for the calculations of actual bands and are comparable with experimental results.

The cellular method is the earliest method used in band calculations by Wigner and Seitz. It was applicable to alkali metals successfully. With the help of this method, crystal is divided into unit cells, with each cell having atom at its centre, as shown in figure 1 - kls cell.

DS



The WS-cell is constructed by drawing the planes/lines normal to the lines which connects atom A to its neighbors and "picking out" the volumes

enclosed by these planes.

By using the ~~Schrödinger~~ Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_k(r) = E(k) \psi_k(r) \quad \text{--- (1)}$$

solution is required for which an assumption is made that when e^- is in a particular cell, then it is influenced by the potential of the ion in that cell only. Other ions in other cells have negligible effect on the e^- considered. This is so

because each of these cell is occupied by another conduction e- which screens up the ion and thus the potential is reduced drastically. To verify the Block for $\Psi_k = e^{ikx} u_k$, u_k needs to be ~~periodic~~ periodic means it should be same on opposite faces of the cell.

Due to some problems to overcome it, WS cell was replaced by WS sphere of same volume as actual cell. Further, the conditions when implemented solved the equation numerically.

Shape of the wave function is the important feature. The wave function oscillates at the ion core & once it is outside the core, the function is constant (holds for 90% of cell volume) & thus, wave function behaves as plane wave for major portion of cell & as a result most of the crystal.

Thus we find that where the function is a plane wave, potential must be constant. So, the effective potential acting on e- is essentially constant except in the region at the ion core itself.

In view of e- motion in the crystal, it is concluded that e- moves in the constant potential across most of crystal. This method is greatly oversimplified & is not much in use.

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③ Augmented-plane Wave (APW) method - ⑤

It is a sounding method for calculating the band

structure in metals and has been used in the past few years.

We know that the effective crystal potential is constant in most of the spaces between the cores, APW method starts by assuming such potential as 'muffin-tin potential'. The potential is that of a free ion at the core and constant outside the core. In other words, outside the ion-core, function is a plane wave because the potential is constant there and inside the core, it is atom-like which is found by solving the appropriate free-atom Schrödinger equation.

④ Pseudopotential Method - An another popular method, which is distinguished by the ~~way~~ manner in which the wave function is chosen. Here, one needs a function which oscillates rapidly inside the core and runs smoothly as a plane wave in the remaining part of the open ~~space~~ space of Wigner-Seitz cell.

Theoretically, we know that the core e^- will not occupy the other atomic orbitals that are already occupied, avoiding the violation of Pauli-Exclusive principle. At core, rapid oscillations are there because atomic functions are appreciable. As a solution of appropriate Schrödinger wave equation, it is observed that, effective potential \leq real potential (on account of core levels).

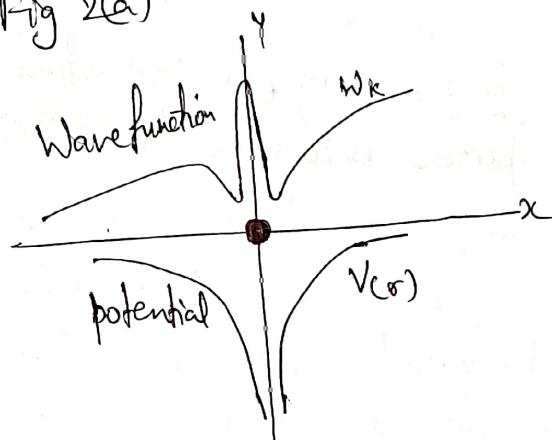
(V_{pseudo}) (V) Due to this, cancellation of crystal potential is there

leading to weak potential known as pseudopotential.

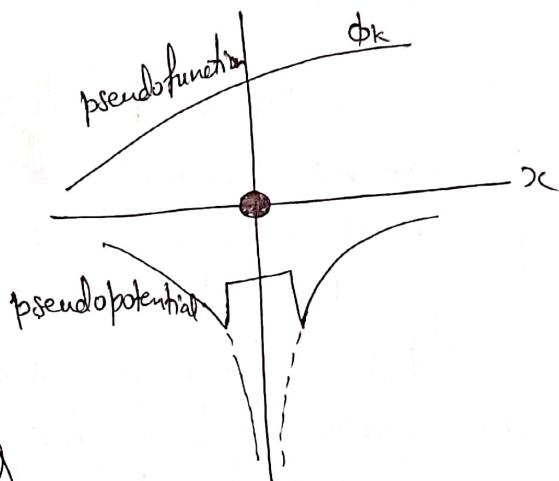
As V_{pseudo} is weaker than real potential,
the wave function is almost a plane wave, called
as pseudo function.

(b)

Fig 2(a)



(2b)



S.H

Fermi Surface of Copper - As an Example

The fermi surface of Copper (Cu) is non-spherical. It has 8 necks making contact with the hexagonal faces of 1st BZ. It is crystal's periodic potential that distorts the surface from the spherical shape and e- of same energy will have different momenta along different crystal directions.

Electron concentration in a monovalent metal with an FCC structure is

$$n = \frac{4}{a^3} \quad \text{--- ①}$$

Here electrons are 4 in a cube of volume a^3 .

Radius of free e- fermi sphere is

$$R_F = (3\pi^2 n)^{1/3} \\ = \left(3\pi^2 \frac{4}{a^3}\right)^{1/3} = \left(\frac{12\pi^2}{a^3}\right)^{1/2} \approx \frac{4.90}{a}$$

The distance between hexagonal faces is
(shortest distance across BZ) = $\left(\frac{2\pi}{a}\right)\sqrt{3}$

$\approx \frac{10.88}{a}$ which is some what larger than the diameter of the free e-s sphere

As we know that the zone boundary presence usually makes the band energy near the boundary to be less. ②

Thus, there is necking out of fermi surface to meet the closest (hexagonal) faces of the zone.

