Sumedh

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- **Free electron theory of metals**

Theories

Classical free e^- theory	Quantum free e^- theory	zone / band theory
Drude & Lorentz	Sommerfield	Bloch
1900	1928	1928
electrical conductivity	move with const. potential	move in periodic potential in lattice
classical mechanics	Quantum laws	Band theory

- Classical free electron theory
- Postulates

Unit-1 Energy Bands in Solids

Classical Free Electron Theory :—

Postulates :-

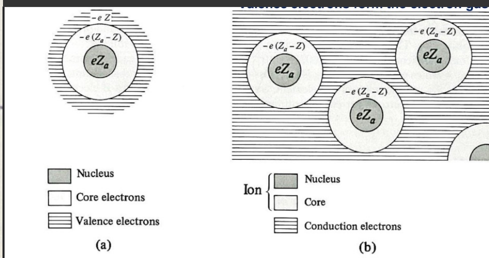
- In an atom electrons revolve around nucleus & metal consists of the ion core.
- ~~Force b/w val~~ Free e^- move in random directions & collide w the ions fixed to lattice & other free e^-s. All collisions are elastic (no energy transfer).
- when e^- field is applied, free e^- are accelerated in the direction opp. to direction of applied e^- field.

Success :

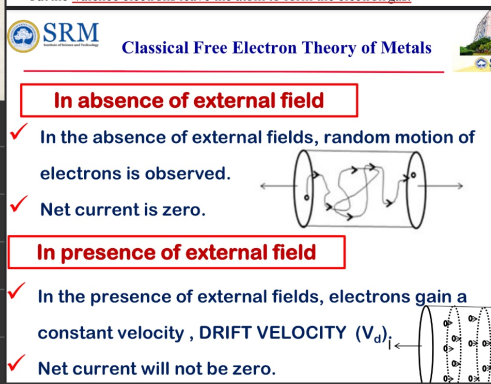
- Verifies Ohm's Law
- Explains Electrical & thermal conductivity of metal.
- Finds relation b/w " " " " " ".

Drawbacks :

- Electrical conductivity/semiconductors/insulators couldn't explained.
- Specific heat of metal is found to be 4.5 but experimental value is 3R.
- photoelectric, compton effect & black body radiation could'nt explained.



(a) Schematic picture of an isolated atom
(b) In a metal the nucleus and ion core retain their configuration in the free ... but the valence electrons leave the atom to form the electron gas.



Quantum free e⁻ theory :-

Postulates :

- e^- posses over wave nature
- allowed energy levels of e^- are quantized.
- distribution of e^-s in various energy levels obey Fermi-Dirac quantum statistics.

Merits :

- explains electrical/thermal conductivity.
- photoelectric effect & compton effect is explained.
- e^-s have wave motion.

Demerits :

- Fails to give diff b/w conductor/semi-conductor/insulator.
- Fails to explain charge transport properties of metals.

According to Quantum mechanics moving particles has some sort of wave motion

Then wavelength $\lambda = h/p$ (De-Broglie wavelength)

To characterize moving particle having wave motion-(ψ)-wavefunction is introduced

According to quantum theory of free electrons energy of a free electron is given by

$$E_n = n^2h^2/8mL^2$$

- According to quantum theory of free electrons the electrical conductivity is given by

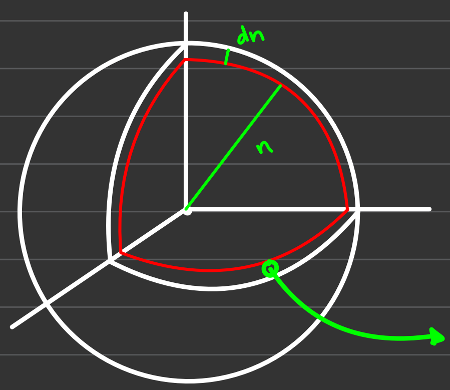
$$\sigma = ne^2T/m$$

- Density of states

The density of state is given by the number of energy levels per unit volume.

$$Z(E)\,dE = \frac{N(E)dE}{1}$$

Take a octant of a sphere



$n \longrightarrow E$
$n+dn \longrightarrow E+dE$

$$N(E)\,dE = (E+dE) - E$$

$$E = \frac{4}{3}\pi n^3 \quad ; \quad E+dE = \frac{4}{3}\pi(n+dn)^3$$

For Octant :-

$$E = \frac{1}{8}\frac{4}{3}\pi n^3 \quad ; \quad E+dE = \frac{1}{8}\frac{4}{3}\pi(n+dn)^3$$

$$\therefore \quad N(E)\,dE = (E+dE) - E$$

$$= \frac{1}{6}\pi(n+dn)^3 - \frac{1}{6}\pi n^3$$

$$= \frac{\pi}{6}\left(\cancel{n^3} + \cancel{dn^3}^{\,0} + 3n^2.dn + \cancel{3n\,dn^2}^{\,0} - \cancel{n^3}\right)$$

$$= \frac{\pi}{6}(3n^2.dn)$$

$$N(E)\,dE = \frac{\pi}{2}n\,(ndn)$$

We know that,

Energy of electron within a cube

$$E = \frac{n^2 h^2}{8 ma^2}$$

$$\therefore \quad n^2 = \frac{8 ma^2}{h^2} . E \quad ; \quad n = \left(\frac{8ma^2}{h^2} E \right)^{1/2}$$

diff n w.r.t E

$$2n . dn = \frac{8 ma^2}{h^2} . dE$$

Now,

$$N(E)\, dE = \frac{\pi}{2} n (ndn)$$

$$= \frac{\pi}{2} \left(\frac{8ma^2}{h^2} . E \right)^{1/2} . \left(\frac{8ma^2}{2h^2} . dE \right)$$

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

$\because$ each energy level provides 2 e^- states with opp spin we have,

$$N(E)\, dE = 2 \times \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} (E)^{1/2} . dE$$

$$N(E)\, dE = \frac{\pi}{2} \left(\frac{8ma^2}{h^2} \right)^{3/2} (E)^{1/2} . dE$$

$\because$ $N(E)\, dE = Z(E)\, dE$

$$\therefore \quad Z(E)\, dE = \frac{\pi}{2} \left(\frac{8ma^2}{h^2} \right)^{3/2} (E)^{1/2} dE$$

• Bloch theorem

Statement : The wave function of a e^- moving in a periodic 1-D lattice is of the form

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

e^{ikx} = wave function
$u(x)$ = periodic function

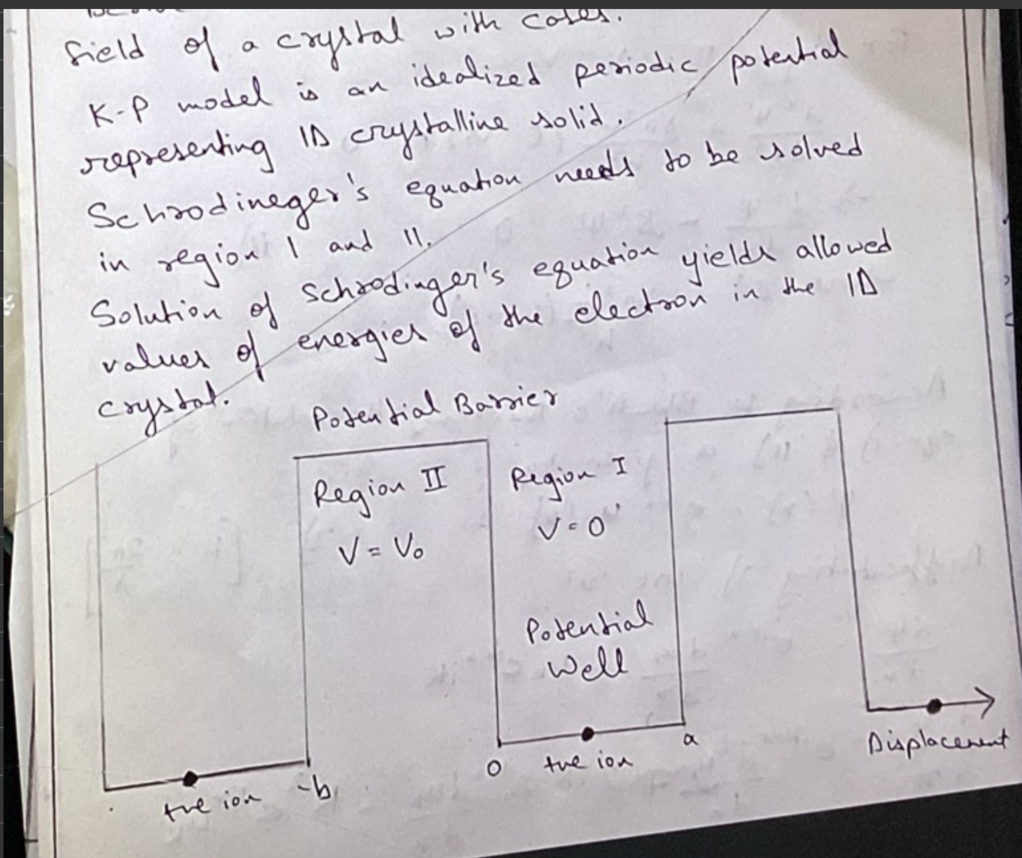
$u(x)$ has same periodicity as of the lattice

$$u(x) = u(x+a)$$

∴ Alternate statement

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

• Kronig - Penny Model


field of a crystal with cores.
K-P model is an idealized periodic potential representing 1D crystalline solid.
Schrodinger's equation needs to be solved in region I and II.
Solution of Schrodinger's equation yields allowed values of energies of the electron in the 1D crystal.

The schrodinger's time independant wave eq is given by

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

Region I ;

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

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{— (i)} \qquad \alpha^2 = \frac{8\pi^2 m E}{h^2}$$

Region II :-

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V_0)\psi = 0$$

$$\frac{d^2\psi}{dx^2} - \frac{8\pi^2 m}{h^2}(V_0-E)\psi = 0$$

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{— (ii)} \qquad \beta^2 = \frac{8\pi m^2}{h^2}(V_0-E)$$

Acc. to bloch thm

$$\psi(x) = e^{ikx}u_k(x) \quad \text{— (iii)}$$

$\frac{d^2x}{dy^2}$ w.r.t x

$$\frac{d\psi}{dx} = e^{ikx}\frac{du_k}{dx} + u_k e^{ikx}(ik)$$

$i \times i = -1$

$$\frac{d^2\psi}{dx^2} = e^{ikx}\cdot\frac{d^2u_k}{dx^2} + 2ike^{ikx}\cdot\frac{du_k}{dx} - k^2e^{ikx} \quad \text{— (iv)}$$

Sub (iii) & (iv) in (i)

$$\frac{d^2u_k}{dx^2} + 2ik\frac{du_k}{dx} + (\alpha^2-k^2)u_k = 0 \quad \text{— (v)}$$

Sub (iii) & (iv) in (ii)

$$\frac{d^2u_k}{dx^2} + 2ik\frac{du_k}{dx} - (\beta^2+k^2)u_k = 0 \quad \text{— (vi)}$$

The gen solⁿ of (v) & (vi) is

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

where $U_1 = U_k$ in $0<x<a$

$$U_2 = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x} \quad \text{— (viii)}$$

where $U_2 = U_k$ in $-b<x<0$

For Boundary Condⁿ

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

$$A+B = C+D$$

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

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

For Boundary Condition

$$[U_1(x)]_{x=a} = [U_2(x)]_{x=-b}$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \quad \text{— (x)}$$

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

$$i(\alpha-k)Ae^{i(\alpha-k)a} - i(\alpha+k)Be^{-i(\alpha-k)a} =$$
$$(\beta-ik)Ce^{-(\beta-ik)b} - (\beta+ik)De^{(\beta+ik)b} \quad \text{—— (xi)}$$

From (ix), (x), (xi), (xii), the coeff of A, B, C, D are taken in determinant $= 0$

$$\frac{P\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \quad \text{—(xii)}$$

When $P = 0$

$$\cos\alpha a = \cos ka$$
$$\alpha a = ka$$
$$\alpha = k$$
$$\alpha^2 = k^2$$
$$\frac{8\pi^2 m}{h^2} E = k^2 \qquad \hbar = h/2\pi$$

When $P = \infty$

$$\frac{P\sin\alpha a}{\alpha a} = \cos ka - \cos\alpha a$$

$$P\sin\alpha a = (\cos ka - \cos\alpha a)\,\alpha a$$
$$\sin\alpha a = \left(\frac{\quad}{\cancel{P}\,\infty}\right)$$

$$\sin\alpha a = 0$$
$$\alpha a = n\pi$$
$$\alpha^2 = \frac{n^2\pi^2}{a^2}$$
$$\frac{8\pi^2 m}{h^2} E = \frac{n^2\pi^2}{a^2}$$

$$E = \frac{n^2 \hbar^2}{8ma^2}$$

- ## Brillouin Zone

It is the representation of permissive of 'k' & e^-s in 1, 2, 3 dimension system. Thus the energy spectrum of e^-s moving in a periodic potential is divided into allowed and forbidden zones.

from KP model,

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

At $P \to \infty$ $\qquad \alpha = n\pi/a$

$P \to 0$ $\qquad k = n\pi/a$

But $k = 2\pi/\lambda$

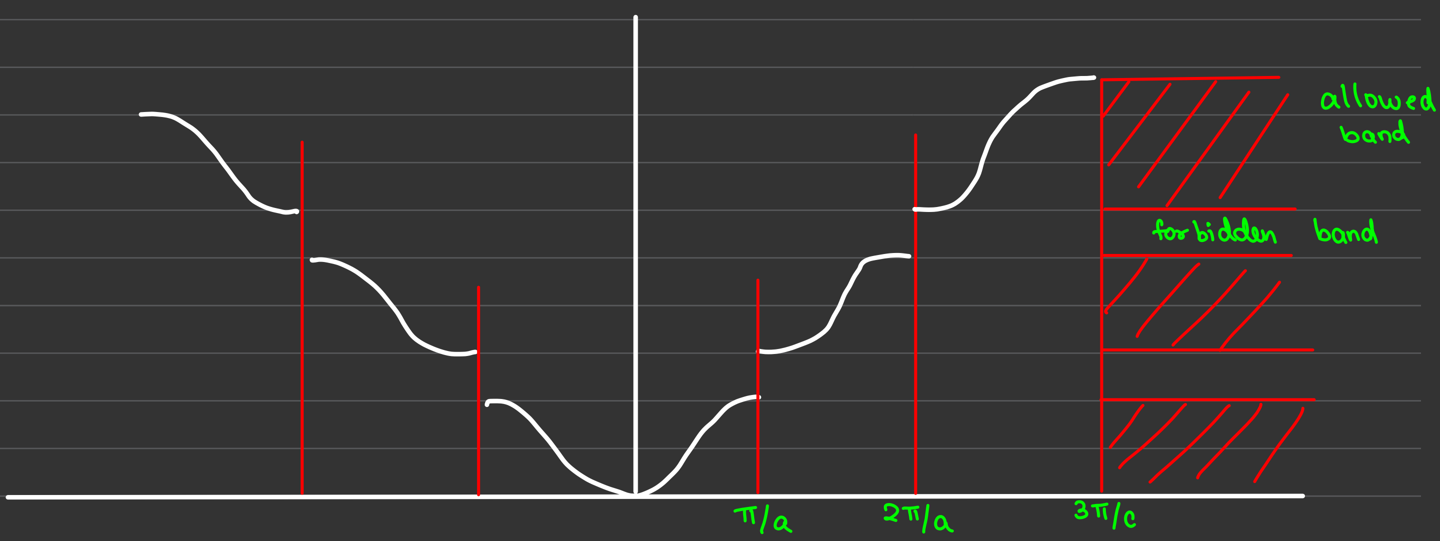
$$\frac{n\cancel{\pi}}{a} = \frac{2\cancel{\pi}}{\lambda}$$

$$2a = n\lambda$$

Bragg's law $\qquad 2a \sin\theta = n\lambda$

$$\sin\theta = 1 \; ; \; \theta = \pi/2$$

e^-s travelling through periodic array of atom in crystal gets diffracted when they satisfy bragg's law



1^{st} bro zone

$K = -\pi/a$ to π/a

2^{nd} Zone

$K = \pi/a$ to $2\pi/a$ & $-\pi/a$ to $-2\pi/a$

A discontinuity is energy of e^- b/w 1^{st} & 2^{nd} zone is called Forbidden zone.

- **E-K diagram**

The conventional band diagram show conventional energy only

E-K gives info about electrical & optical properties

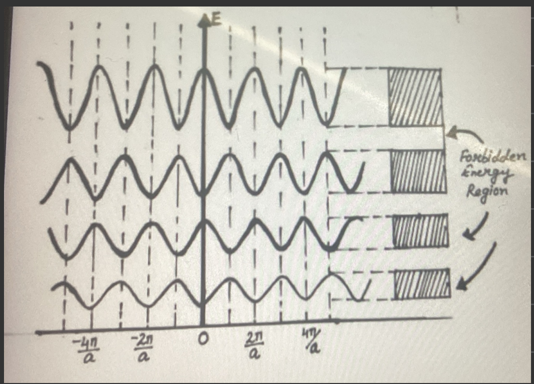
Show energy - momentum relation for available states of electron.

Obtained by schrodinger eq.

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

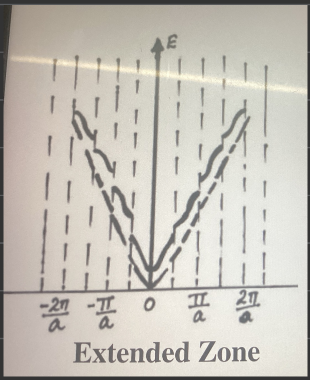
Types :-

① Periodic zone



Periodic repetition of allowed energy values of each allowed band, obtained by periodic repetition of the region of $-\pi/a < K < \pi/a$ thru K-space

② Extended zone

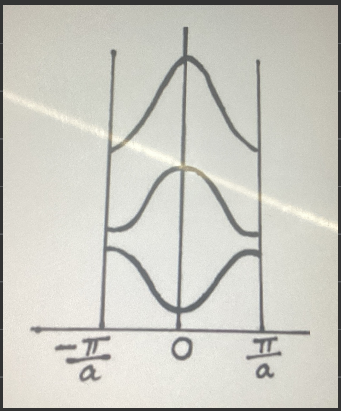


diff bands drawn in diff zones

discontinues at $K = \pm \frac{n\pi}{a}$

due to bragg's law of reflection at the edges of allowed bands

③ Reduced zone



distance is integral multiple of $2\pi/a$ so that they all fit within the interval $-\pi/a$ to π/a (1st bro)

1st zone is shown since EK diag. is periodic, it is sufficient to 1st zone.

Significance

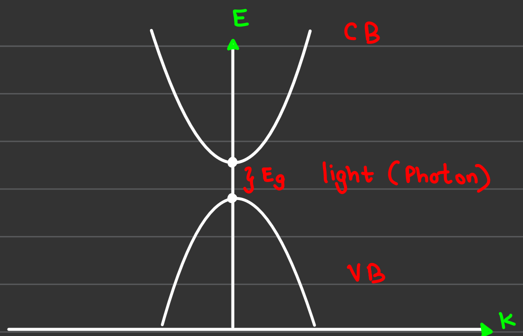
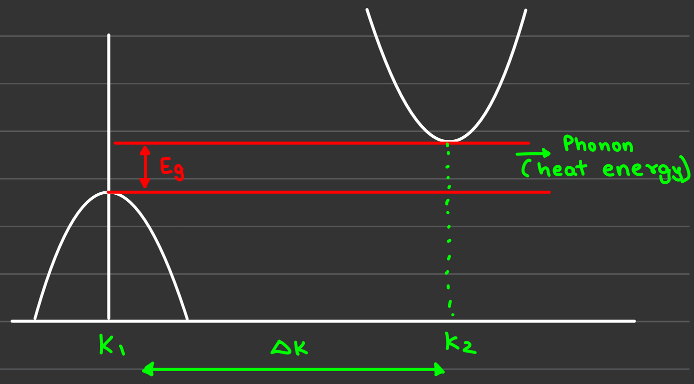
i) Shows direct vs indirect band gap

ii) demonstrates e⁻ hole mobility

iii) explains e⁻ (hole) effective mass

iv) Indicates the band gap E_g (diff in energy b/w valence & conduction band)

- Direct & Indirect band gap

Direct band gap	Indirect band gap
	
Maxima of VB & minima of CB have same momentum.	Maxima of VB & minima of CB occur at diff momentum
Momentum remains conserved & photon (light) is emitted	Momentum of is not conserved, to conserve it phonon (heat) is emitted.
direct band gap semicon	Indirect band gap semicon
efficiency is high	efficiency is low
Probablity of a radioactive recombination is high	is low
Used in LED & laser diodes	Used is amplifier, rectifier & transmittor

- **Phonons and Photons**

In quantum mechanical terms, phonons are a packet of waves that travel throughout the crystal with definite energy & momentum. It is derived from vibrations of atoms in a solid

Properties

i) Treated as quasi particle

ii) Carry heat, energy, momentum via packet of sound

iii) In crystal, heat energy ↓ when e^- collide, but in semicon at T ↓, e^- attract due to phonons

iv) Can travel from one object to another

Phonons	Photons
Quantized normal modes of lattic vibrations	Quantized normal modes of em waves
$E = \frac{h\nu}{\lambda}$	$E = \frac{hc}{\lambda}$
$P = \frac{h}{\lambda (A^\circ)}$	$P = \frac{h}{\lambda (\mu m)}$

- Fermi - dirac Statistics

Three types :-

i) Maxwell - boltzman :- spin of any type

$$f(E) = \frac{1}{e^{h\nu/kT}}$$

ii) Bose einstein : particles of zero or integral spin

$$f(E) = \frac{1}{e^{h\nu/kT} - 1}$$

iii) Fermi - dirac : half integral spin

$$\boxed{f(E) = \frac{1}{1 + e^{h\nu/kT}}}$$

fermi energy (E_F)

Energy of state where probab (ψ) = 1/2 at 0K

Max^m KE for free e^- at 0K

The highest occupied energy level

fermi - dirac distribution function f(E)

The distribution of e's among levels is described by f(E), ψ of of e^- is E

$$\therefore \quad f(E) = \frac{1}{1 + e^{(E-E_f)/kT}}$$

Case - 1 :- $T = 0K$

For energy level $E < E_f$

$$f(E) = \frac{1}{1+e^{(E-E_f)/k\cancel{T}0}} = \frac{1}{1+e^{-\Delta E/0}}$$

$$= \frac{1}{1+e^{-\infty}} = \frac{1}{1+1/e^{\infty}} = 1$$

Case - 2 :-

for energy level $E > E_f$

$$f(E) = \frac{1}{1+e^{(E-E_f)/kT}} = \frac{1}{1+e^{\Delta E/0}}$$

$$= \frac{1}{1+e^{\infty}} = 0$$

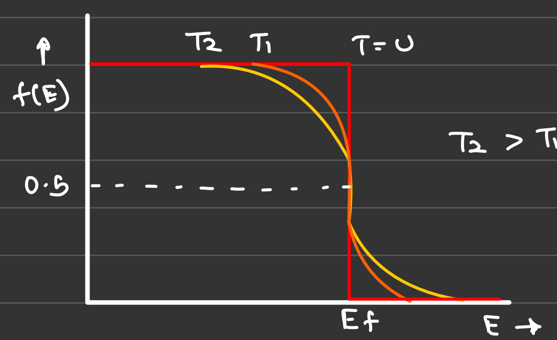
Case - 3 :- $T > 0K$

for $E = E_f$

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

$$= \frac{1}{1+e^{0}} = 1/2$$

Fermi - level



Difference between localized and delocalized wave functions

Localized function

- A localized wave function is one that is confined to a specific region of space.
- Herein, an electron bound to an atom is localized within a certain distance from the nucleus.
- The probability density of finding the electron is concentrated in a small region and the wave function decreases rapidly as we move away from the nucleus.

Delocalized function

- A delocalized wave function, on the other hand, is one that is spread out over a large region of space.
- Herein, an electron in a metal is delocalized over the entire metal, as the electron can be found anywhere in the metal with some probability.
- The probability density of finding the electron is not confined to a specific region, but is distributed over a large region of space.

Show that the sin(x) is an Eigenfunction of $\frac{d^2}{dx^2}$

$$\frac{d^2}{dx^2} \sin(x) = -\sin(x)$$

- sin (Kx) is an eigenfunction w double order derivative.

Derivative of sin function

$$-\frac{d}{dx} \sin(Kx) = -K\cos(Kx)$$

$$-\frac{d^2}{dx^2} \sin(Kx) = K^2 \sin(Kx)$$

↑ Eigen value.

Based on Schrodinger eqⁿ,

$$H\Psi = E\Psi$$

$$H = -\frac{h^2}{2m}\frac{d^2}{dx^2}$$ → Energy operator; Hamilton

$$E = \frac{h^2K^2}{2m}$$ → Energy eigenvalue; Energy

$$\Psi = \sin(Kx)$$

$$\therefore H\Psi = E\Psi$$

$$-\frac{h^2}{2m}\frac{d^2}{dx^2}\sin(Kx) = \frac{h^2K^2}{2m}\sin(Kx)$$

h → planck's const

m → mass.