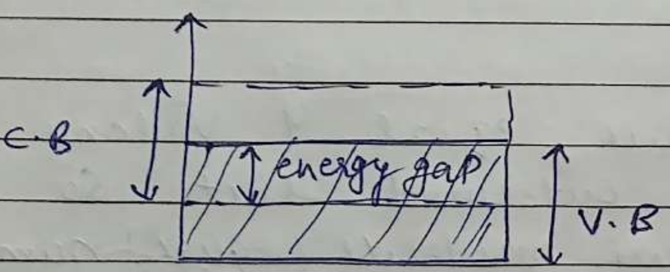
Unit-1 Electronic Materials

1. Types of Electronic Material

→ Metal / conductor
→ Non Metal / Insulator
→ Semiconductor

Metals → If the Valency of an atom in a material is < 4, then those material are called Metals / Conductor.
This type of materials have more free electron so can easily conduct electricity and hence less resistivity.
e.g. Aluminium, silver, copper, sodium.

Energy band diagram of Metal →
As conductor have large number of free electron and easily conduct electricity. So the valence band and Conduction band are overlap each other.



Non-Metals → The Valency of an atom in a material is more than 4 in their outermost orbit. Hence they have less number of free electron. So This type of material do not conduct electricity.

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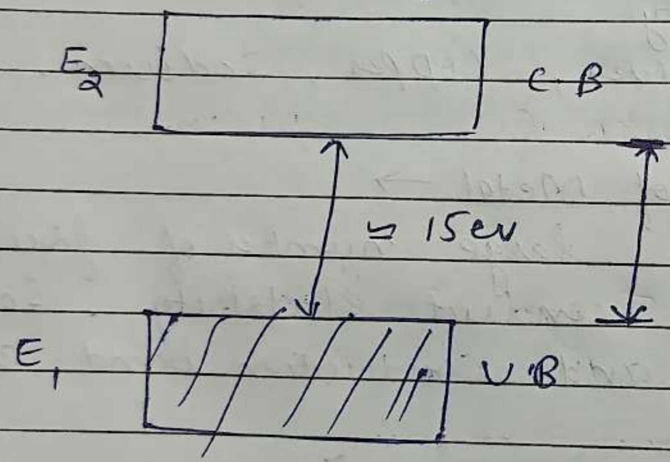
Therefore resistivity is high as compared to Metals
eg. Wood, Plastic etc

Energy band diagram of Non-Metal →

As these material have more than 4 Valence electron. Therefore less number of free electron and do not conduct electricity. Hence energy difference between valence band and conduction band is very high (≃ 15eV).

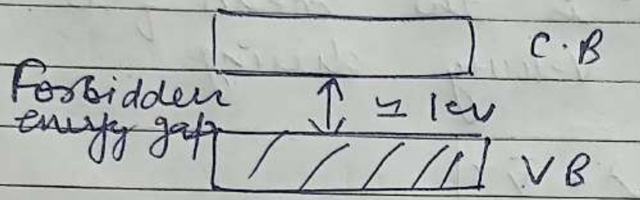


$E_2 - E_1$ = energy difference or Forbidden energy gap

Semiconductor →

These material have equal 4 Valence electron in their outermost orbit so these material have moderate (equal) number of free electron. Hence do not conduct electricity at room Temperature. But if impurity is add to it then it will conduct electricity. Its resistivity lies between conductor and insulator
eg. Silicon & germanium

Energy band diagram of Semiconductor →
In this case the energy gap between Valence band and conduction band is very less ($\simeq$ 1ev) Therefore conduct electricity if impurity is add or temperature is raised



(2.) Free Electron Theory

Classical Free electron   Quantum Free electron.

Classical Free electron Theory :→
In 1900, Drude and Lorentz developed this theory. According to this theory, metal contains free electron which are responsible for electrical conductivity and electron obey laws of Classical Mechanics

Assumptions
① electron are freely to move similar as gas molecule inside a container. Therefore Potential on electron is zero.
② electron are responsible for conductivity
③ Electron always move in a straight line inside a material but in the presence of electric field the trajectory

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of electron is developed.

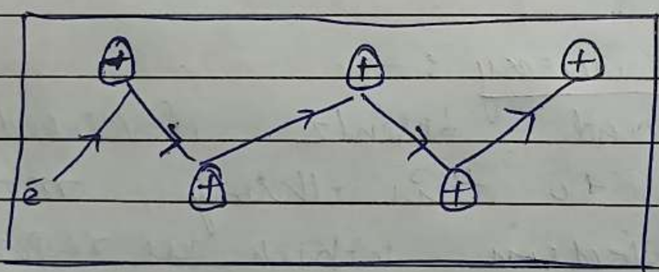
(4) Electron Velocity in a metal obey Maxwell Boltzmann statistics

(5) In the absence of field, the energy of electron at temperature T is given by $\frac{3}{2}KT$.

(6) If τ is the average relaxation time before collision & λ is the mean free path then average velocity during collision will be

$$\bar{v} = \frac{\lambda}{\tau} \Rightarrow \boxed{\lambda = \bar{v}\tau}$$

(7) electron get thermal equilibrium by each collision. After one collision the velocity is directly proportional to surrounding temperature.



<u>Derivation of electrical conductivity from Classical free e^- theory</u>

When electric field is applied, the force on an electron is $-qE$ — (1)

and also from classical Law $F = m\frac{dv}{dt}$ — (2)

equate equation (1) & (2)

$$-qE = m\frac{dv}{dt} \quad \text{— (3)}$$

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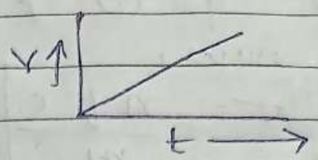
$$\frac{dv}{dt} = -\frac{q}{m} E$$



$$\frac{dv}{dt} \propto E$$

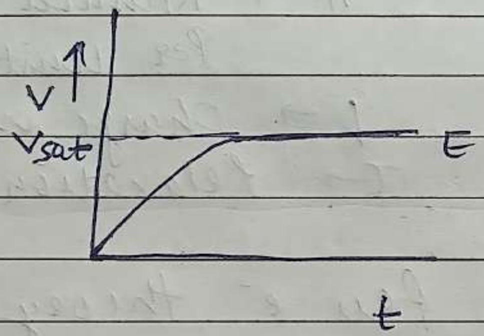
Therefore As E increases, $\frac{dv}{dt}$ increases which is not possible

Now, some damping factor must be added in equation ③

$$m\frac{dv}{dt} + \gamma V_{sat} = -qE$$

Due to damping, at saturation value $\frac{dv}{dt} \to 0$

Therefore $V_{sat} = -\frac{q}{\gamma} E$



Now from kinetic theory of gases, drude drive a formula for V_{sat} which are given by →

$$V_{sat} = -\frac{qE\tau}{m}$$

Put in this equation

Also $J = -nq\,V_{sat}$

Current density

$$= -nq\left[-\frac{qE\tau}{m}\right]$$

$$J = \left(\frac{nq^2\tau}{m_e}\right)E \quad \text{——} ④$$

Also from Ohm Law in Vector form

$$J = \sigma E \quad \text{——} ⑤$$

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Compare eq. (4) & (5)
We have,

$$\boxed{\sigma = \frac{nq^2\tau}{m}}$$

This is the electrical conductivity for electron inside a metal.

As $\rho = \frac{1}{\sigma}$

Therefore $\boxed{\rho = \frac{m}{nq^2\tau}}$

Resistivity

$m \rightarrow$ mass of electron
$n \rightarrow$ Number of electron Per Unit Volume
$q \rightarrow$ Charge on electron
$\tau \rightarrow$ Relaxation time

Failure of Classical free e^- theory

(1) It fails to explain electrical conductivity of Semiconductor and insulators.

(2) It fail to explain specific heat of Metal
According to drude specific heat of metal is independent of Temperature but experimentally specific heat decreases at low Temperature

(3) Hall coefficient (R_H)

$$R_H = -\frac{1}{nq}$$

Drude model is Successful for R_H of Li, Na, K, Cs But for Be, I, Mg it fails

(4) Magneto resistance

According to drude $\rho_{MR} = \frac{m}{nq^2\tau}$ (Independent of E)

But experimentally $\rho_{MR} \propto E$

(5) According to drude theory

$$\rho \propto \frac{1}{\sqrt{T}}$$

But experimentally $\rho \propto \frac{1}{T}$

Quantum free electron Theory →

Quantum free electron theory was proposed by Sommerfeld. It overcomes many drawbacks of classical Theory. Sommerfeld explained them by choosing fermi dirac statistics instead of Maxwell - Boltzmann statistics. He developed this theory by applying the principles of Quantum mechanics.

- According to Sommerfeld electron is Quantum partille and show Quantum behaviour

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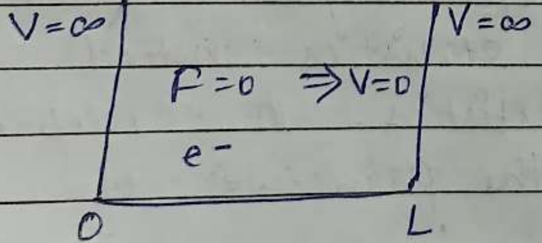
- According to Kinetic theory of gases, if Temperature of Metal is at 0 Kelvin, then Kinetic energy and Velocity of electron will be zero
But
According to Sommerfeld at 0 kelvin temperature of Metal the energy and Velocity of electron will not zero. The energy will be in the range and energy Value of free electron are quantized.

- According to Sommerfeld, Valence electron move freely in a constant potential with in boundaries of metal and Prevented from escaping the metal at the boundaries.

- To find the energy Values of electron Schrodinger time independent wave equation is applied.



According to Schrodinger wave equation →

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

As $V=0$ (Inside the box)

Therefore,
$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}E\right)\psi = 0 \quad —(2)$$

Put $K^2 = \frac{2mE}{\hbar^2}$ —(3)

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Equation (2) becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

Solution of above second order differential equation is $\rightarrow$

$$\psi = A \sin kx + B \cos kx \quad \text{— (4)}$$

Now, To find the values of A & B we have to use Boundary conditions

(i) at $x=0$ $\quad \psi = 0$

(ii) at $x=L$ $\quad \psi = 0$

using eq (i) in eq (4) we have $B=0$

Now equation (4) become $\psi = A \sin kx$

Apply (ii) Boundary conditions we have $0 = A \sin kL$

$(As \cdot A \neq 0)$

So, $0 = \sin kL$

$$\sin n\pi = \sin kL$$

$$n\pi = kL$$

$$K = \frac{n\pi}{L}$$

$$k^2 = \frac{n^2\pi^2}{L^2} \quad \text{— (5)}$$

On comparing (5) & (3) we have

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$\boxed{E = \frac{n^2\pi^2\hbar^2}{2mL^2}} \quad \text{where } n = 1, 2, 3 \text{ —}$$

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(Energy - Momentum diagram)

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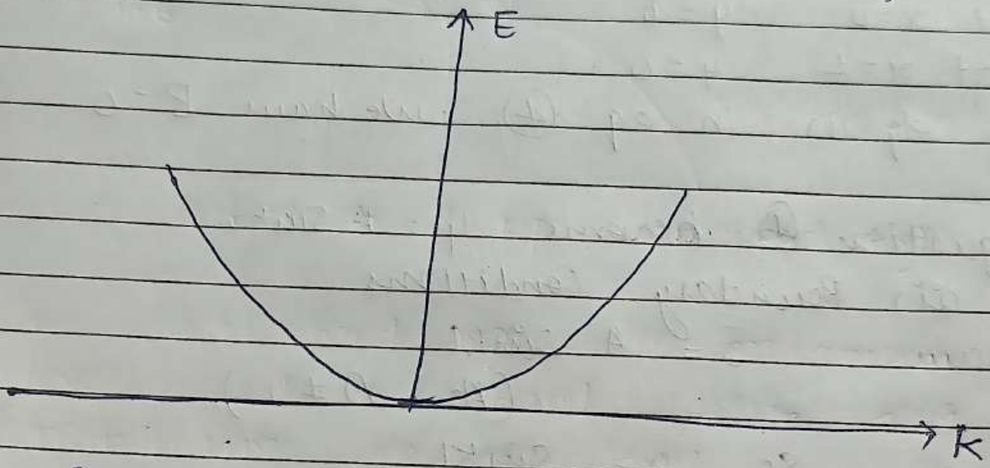
E-k diagram for free - electron theory

using equation (3) we have,

$$k^2 = \frac{2mE}{\hbar^2}$$

ie $E \propto k^2$ (same as parabola equation $y = kx^2$)



(3) Bloch Theorem (Electron in periodic Potential)

Instead of considering zero or uniform constant potential as explain in free electron theory (Classical as well Quantum free electron theory). Bloch consider that this constant potential assumption is over simplified.

According to Bloch, In actual crystal the potential due to positive ion is quite complicated but for reasonable approximation it can be taken as periodic potential.

Bloch approximation are called Quasi free

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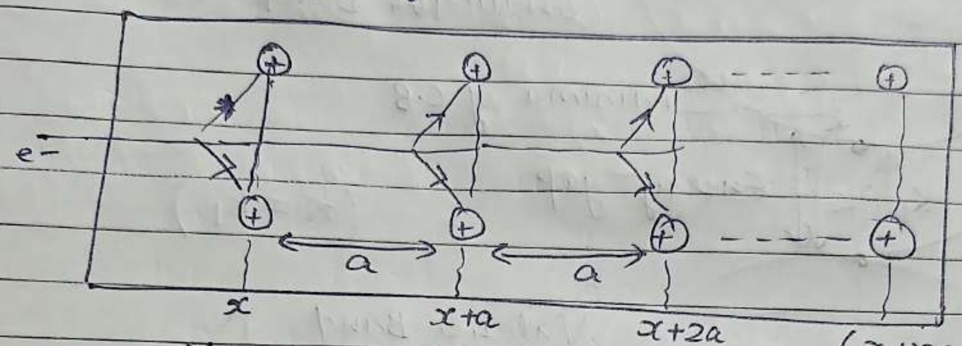
electron approximation.
Bloch consider the variation of potential inside the metallic crystal with in the periodicity of lattice.



$V(x) = V(x+a) = V(x+2a) -- V(x+na)$

According to Schrodinger wave equation

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

As $V = V(x)$ so

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

where $V(x) = V(x+a) = V(x+2a) - V(x+na)$

The solution of equation (1) is

Bloch Theorem $$\boxed{\psi(x) = U_k(x)\, e^{ikx}} \quad - (2)$$

In equation (2) $U_k(x)$ is Bloch function and it is also periodic so

$$U_k(x) = U_k(x+a) --- U_k(x+na) - (3)$$

From eq. (2) & (3) we can also write

$$\psi(x+a) = U_k(x+a)\, e^{ik(x+a)} \quad - (4)$$

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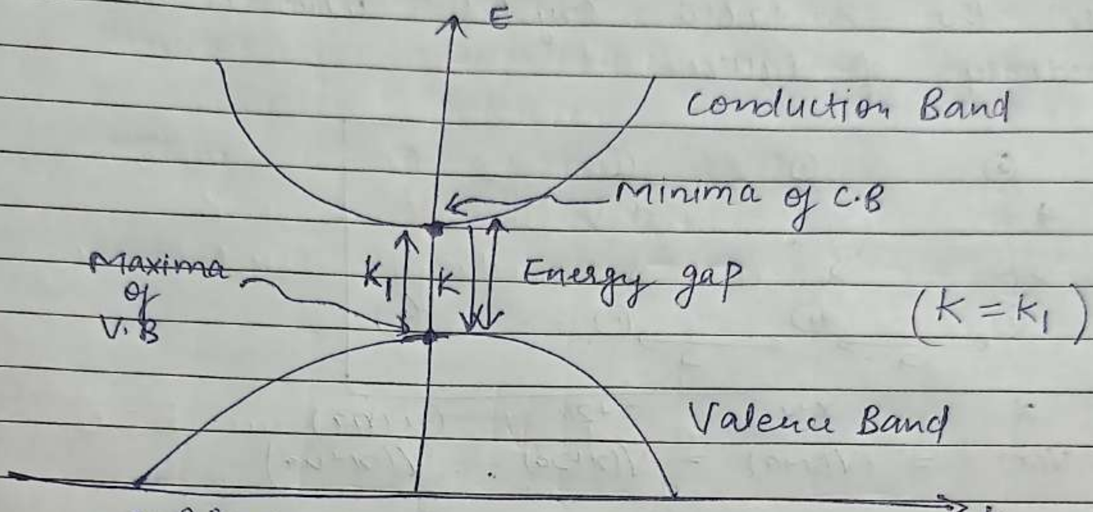
(4) Direct and Indirect Band gap Semiconductors



(Direct band gap Semiconductor)

→ In Direct Band gap, the maximum energy level of Valence Band align with the minimum energy level of Conduction Band with respect to momentum.

→ During recombination, the energy release in the form of light. So it is called radiative recombination

→ The efficiency of Direct band gap Semiconductor is higher Therefore they are always preferred for making optical sources eg. LED

→ examples of direct Band gap Semiconductor → Gallium Arsenide (GaAs)

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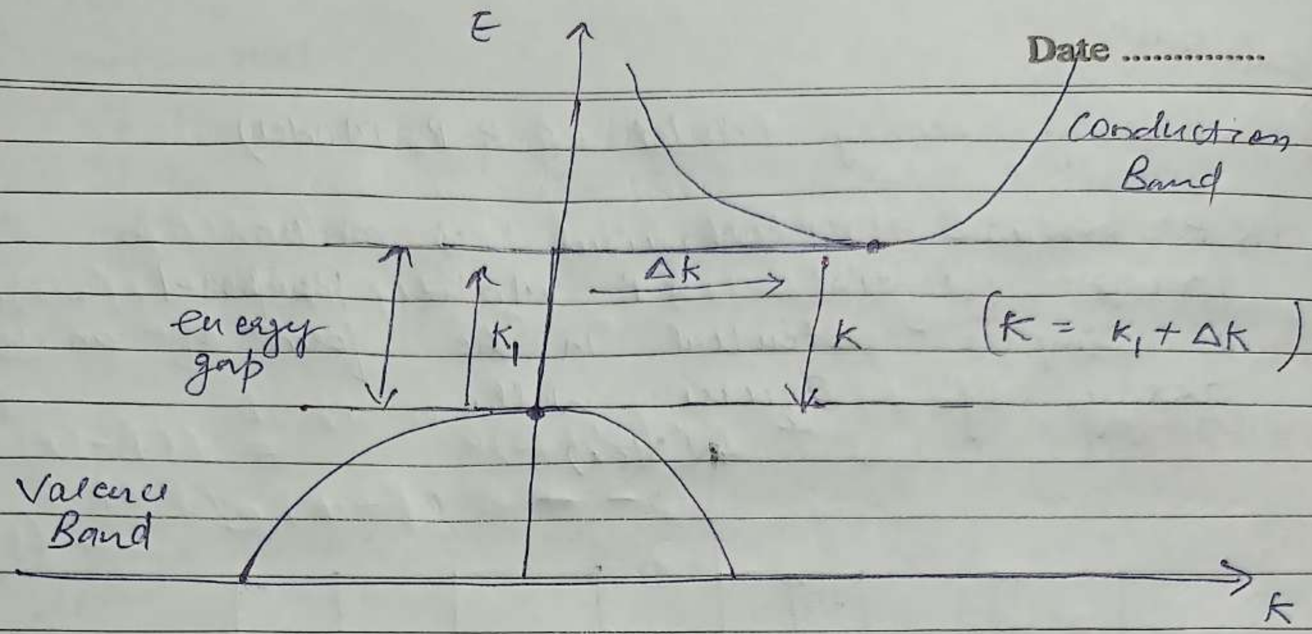
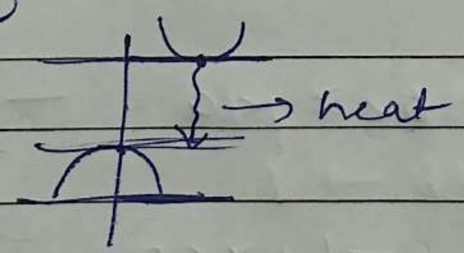


→ In Indirect Band gap, the maximum energy level of Valence Band and minimum energy level of conduction Band are misalign with respect to momentum.

→ During recombination, the energy release in the form of heat. so it is called non-radiative recombination.

→ The efficiency of Indirect Band gap Semiconductors is lower as heat is emitted during recombination of electron from C.B to hole in V.B.



They are used in Switches, Circuits, gates

→ examples of Indirect Bandgap Semiconductors [Silicon (Si), germanium (Ge)]

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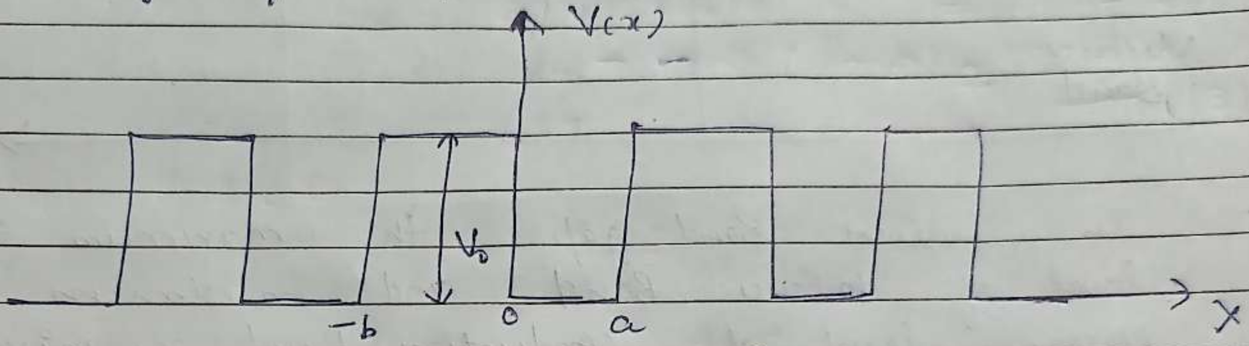
(5) Kroning - Penney Model (K-P Model)

K-P explain the behaviour of electron in periodic potential. K-P Model Proposed a simpler potential in the form of an array of square well.



$$\begin{cases} V=0 & \text{if } 0<x<a \\ V=V_0 & \text{if } -b<x<0 \end{cases}$$

The Schroding wave equation for both regions will be

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V_0)\psi = 0 \quad -(1)$$

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

Let $\frac{2mE}{\hbar^2} = \alpha^2$ $\qquad \frac{2m}{\hbar^2}(V_0 - E) = \beta^2$

Then eq. (1) & (2) becomes

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \qquad \text{if } 0<x<a \quad -(A)$$

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \qquad \text{if } -b<x<0 \quad -(B)$$

According to Bloch theorem

$$\psi(x) = U_k(x)\, e^{ikx} \quad -(3)$$

& $U_k(x) = U(x + \underline{a+b})$

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Now differentiate equation (3) we get

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

Again differentiate

$$\frac{d^2\psi}{dx^2} = ike^{ikx}\frac{du}{dx} + e^{ikx}\frac{d^2u}{dx^2} + \left(i^2k^2 e^{ikx}\right)u + (ike^{ikx})\frac{du}{dx}$$

$$\frac{d^2\psi}{dx^2} = e^{ikx}\frac{d^2u}{dx^2} + 2ik e^{ikx}\frac{du}{dx} - k^2 e^{ikx} u$$

put this value in eq. (A) & (B)
we have,

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} + (\alpha^2 - k^2)u = 0 \quad , \quad 0<x<a \quad -(4)$$

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} - (\beta^2 + k^2)u = 0 \quad , \quad -b<x<0 \quad -(5)$$

general solution of eq (4) & (5) are

$$u_1 = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x} \quad , \quad 0<x<a \quad -(6)$$

$$u_2 = C e^{(\beta-ik)x} + D e^{-(\beta+ik)x} \quad , \quad -b<x<0 \quad -(7)$$

using Boundary conditions

$$\left.\begin{aligned} (u_1)_{x=0} &= (u_2)_{x=0} \\ \left(\frac{du_1}{dx}\right)_{x=0} &= \left(\frac{du_2}{dx}\right)_{x=0} \end{aligned}\right] \quad - (8)$$

$$\left.\begin{aligned} (u_1)_{x=a} &= (u_2)_{x=-b} \\ \left(\frac{du_1}{dx}\right)_{x=a} &= \left(\frac{du_2}{dx}\right)_{x=-b} \end{aligned}\right] \quad - (9)$$

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Now we have four equations

$$A+B = C+D \quad \text{—— (10)}$$

$$Ai(\alpha-k) - Bi(\alpha+k) = C(\beta-ik) - D(\beta+ik) \quad \text{—— (11)}$$

$$Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b} \quad \text{—— (12)}$$

$$Ai(\alpha-k)e^{i(\alpha-k)x} - Bi(\alpha+k)e^{i(\alpha+k)b} = C(\beta-ik)e^{(\beta-ik)b} - D(\beta+ik)e^{(\beta+k)b} \quad \text{—— (13)}$$

Choose A B C D

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

$$\left(\frac{\beta^2+\alpha^2}{2\alpha\beta}\right)\sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos k(a+b) \quad \text{—— (14)}$$

If $V_0 \to \infty$, $b \to 0$

If $b \to 0$ $\quad \sinh\beta b \to \beta b$

$\cosh\beta b \to 1$

Therefor equation (14) becomes

$$\left(\frac{\beta^2+\alpha^2}{2\alpha}\right) b \sin\alpha a + \cos\alpha a = \cos ka \quad \text{—— (15)}$$

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As $\alpha^2 = \frac{2mE}{\hbar^2}$ $\beta^2 = \frac{2m}{\hbar^2}(V_0 - E)$

$\alpha + \beta^2 = \frac{2mV_0}{\hbar^2}$

Put in eq (15) We get

$\frac{mV_0 b}{\alpha \hbar^2} \sin\alpha a + \cos\alpha a = \cos ka$

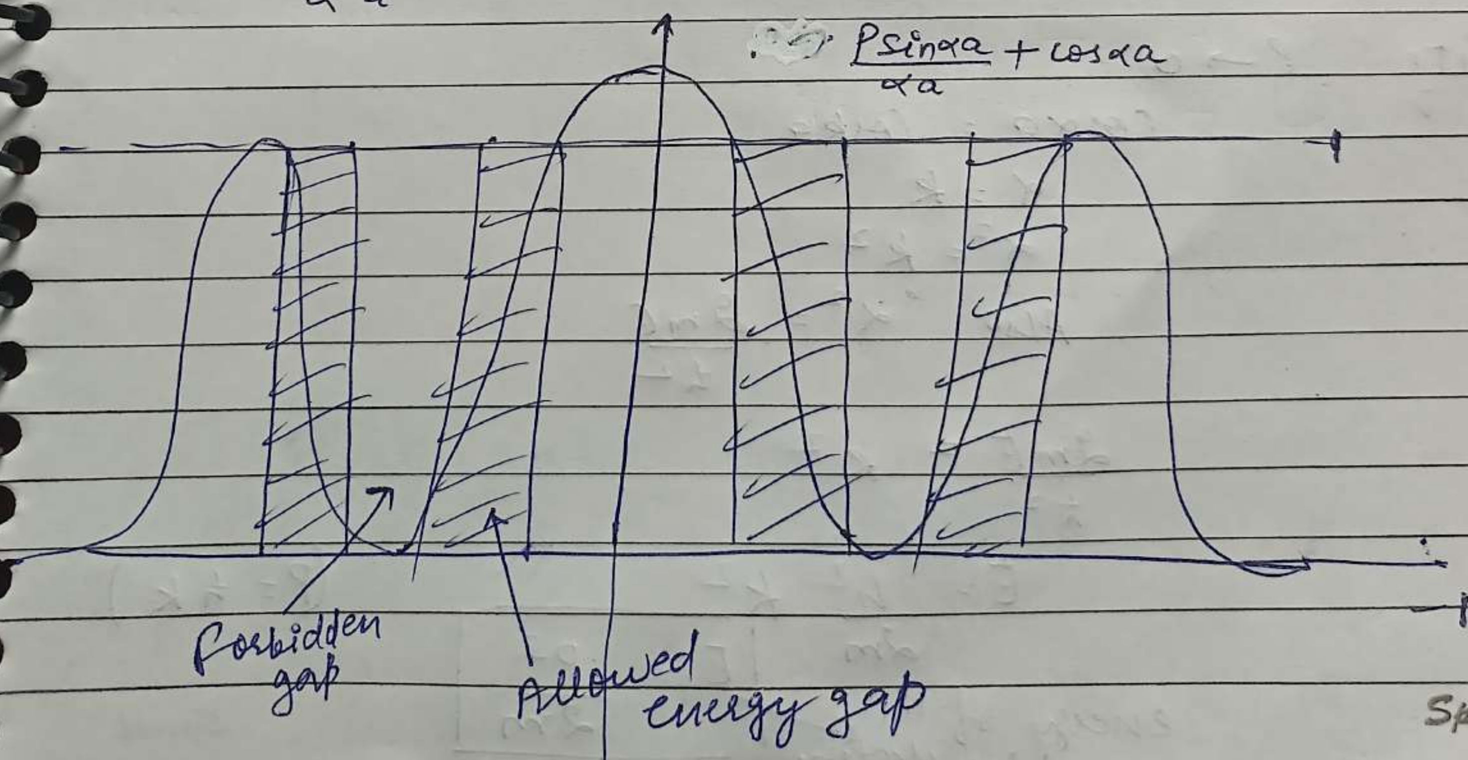
$\left(\frac{mV_0 ab}{\alpha a \hbar^2}\right) \sin\alpha a + \cos\alpha a = \cos ka$

$\left(\frac{mV_0 ab}{\hbar^2}\right) \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

↓ Put P

$P = \frac{mV_0 ab}{\hbar^2}$

$P \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \underline{\cos ka}$ — (16)



barrier strength → $V_0 b$

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Conclusions →

(i) If $P \to \infty$, the barrier strength increases and width of allowed energy band becomes narrow

So, $\sin \alpha a = 0$

$$\sin \alpha a = \sin n\pi$$

$$\alpha a = n\pi$$

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

$$\alpha^2 = \frac{n^2\pi^2}{a^2}$$

Also $\alpha^2 = \frac{2mE}{\hbar^2}$

on comparing the value of α^2, we have

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

Same as energy of electron in a box (from Sommerfeld theory)

energy of bound electron

(ii) If $P \to 0$

$$\cos \alpha a = \cos ka$$

$$\alpha = k$$

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

Also $\alpha^2 = \frac{2mE}{\hbar^2}$

$$\frac{2mE}{\hbar^2} = k^2$$

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

$(P = \hbar k)$

$$\boxed{E = \frac{P^2}{2m}}$$

energy of free electron

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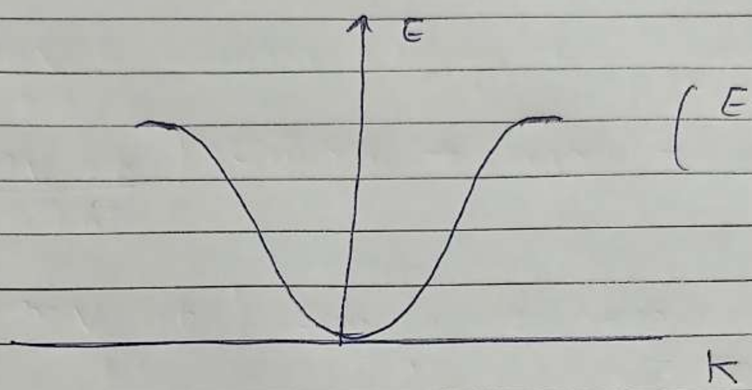
E-k diagram & Brillouin zone for band Theory →

As $\cos ka = \pm 1$

$ka = n\pi$

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



(E-k diagram for band theory)

For First Brillouin zone $n=1$ $k = \pm \frac{\pi}{a}$

— Second — $n=2$ $k = \pm \frac{2\pi}{a}$