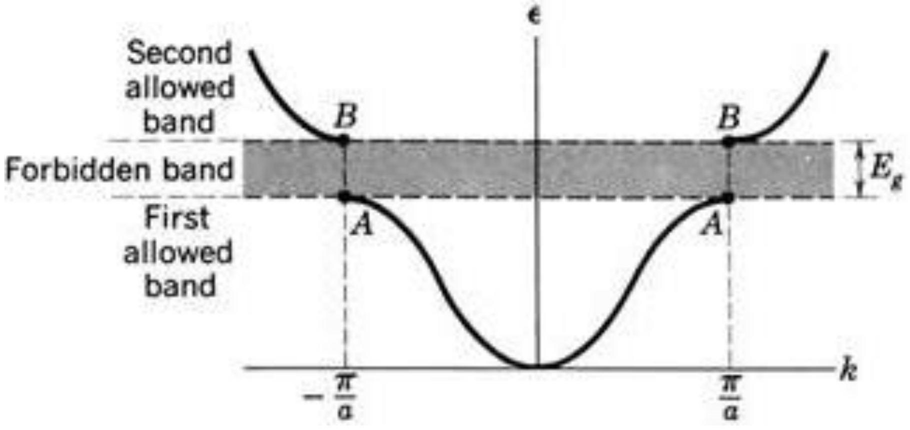
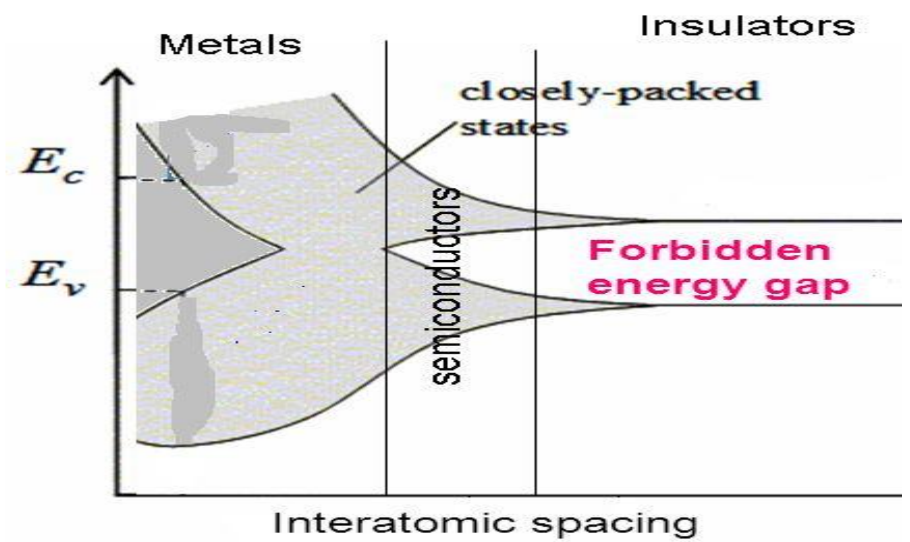
UNIT 5 SOLID STATE PHYSICS

LECTURE 3



One-electron approach



Atomistic approach

Lecture 1: Classical Free electron theory

Free electron gas

SOLID

→ **Amorphous**

→ **Crystalline**

1. Metal
(σ > 10^3S/cm or ρ < 10^{-3} Ω-cm)

2. Insulator
(σ < 10^{-8}S/cm or ρ > 10^8 Ω-cm)

3. Semiconductor
(10^{-8}S/cm < σ < 10^3S/cm or $10^8\Omega$-cm > ρ >10^{-3} Ω-cm)

- Metals posses hogh electrical conductivity; Ohm's law (1827) $J \, \alpha \, E \quad or\, J = \sigma E$
- Metals posses high thermal conductivity (**K)** Fourier's law (1822) $Q = \frac{T_1 - T_2}{2\lambda} K$
- Wiedemann –Franz law; $\frac{\sigma}{KT} = constant$
- Metals have positive temperature of resistivity ($\rho = \frac{1}{\sigma}$)

With the discovery of electron in 1897 these were explained by using classical free electron theory

Drude - Lorentz theory... Used classical mechanics (*Kinetic theory of gases*) and Maxwell-Boltzmann statistics with free electron concept

1. Electrical conductivity (**σ**) $\sigma = \frac{ne^2\lambda}{6kT}v$
2. Thermal conductivity (**K**) $K = \frac{nvk\lambda}{2}$
3. And their ratio **K/σ** - Wiedemann –Franz law $\frac{K}{\sigma T} = 3\left(\frac{k}{e}\right)^2$

J_d= nev J_d=σ E

$Q = \frac{T_1 - T_2}{2\lambda} K$

Ohms law

$$\sigma = \frac{ne^2\tau}{m} \qquad \rho = \frac{m}{ne^2\tau}$$

Fourier’s law

$$K = \frac{nv^2 k_B \tau}{2}$$

Drift current and diffusion current

Imp: Maxwell-Boltzmann distribution is a "sub-part" of Boltzmann's for which we focus only on the velocity distribution of the particles (KE) and applied for the classical system

Failures of Classical free electron theory

- Completely failed to explain the heat capacity (C_v) and the paramagnetic susceptibility of conduction electrons and its temperature dependence.
- $C_{v_{elec}} = \frac{3}{2} k_B N_A = 12.5$ a value 100 times greater than the experimentally obtained one. k_B Boltzmann's const. and N_A Avogadro number
- Could not explain the long mean path at low temperature.
- Unable to predict the correct dependence of resistance on the temperature.
- Could not explain why only some materials are metallic, insulator and semiconductors
- Why resistivity metal increases with temperature while it decreases in semiconductor and insulator?
- Why radiation does not affect the resistivity of metals but the resistivity of semiconductor decreases?
- Why resistivity of metal increases with impurity while that of semiconductor decreases?

- ✓ Furthermore it uses Maxwell-Boltzmann statistics which assume all free electron participate in the thermal conduction…. not right..
- ✓ The one near Fermi level participate and Fermi-Dirac statistics must be applied.. And so quantum theory comes to play its part

Hence the 2nd stage of development od solid state physics...

Sommerfeld free electron theory of metals

- ❖ Used the free electron theory of Drude' model
- ❖ But instead of Lorentz's Kinetic theory of gases and Maxwell-Boltzmann' statistics/distribution (truly classical concept) he used Fermi Dirac distribution and wave nature of electrons

In short considered, quantum mechanics, Schrodinger equation and Fermi-Dirac statistics/Distribution of fermions (electrons)

Lecture 2: Quantum Free Electron Theory

Free electron Fermi gas

Enrico Fermi
1901-1954

Arnold Sommerfeld
1858-1951

Sommerfeld's Quantum theory metals

- **F**ermi energy, Fermi level
- **F**ermi-Dirac distribution,
- **F**ermions- any particle that obey Fermi-Dirac distribution ..or..too deep into particle physics!!!..spin half particles.. E.g.. Electron, proton, neutron..

Arnold **Sommerfeld** who combined the classical **Drude model** with quantum mechanical Fermi–Dirac statistics and hence it is also known as the **Drude–Sommerfeld model**

The following assumptions of classical electron theory continue to be applicable in quantum free electron theory also.

a) The electrons travel in a constant potential inside the metal but stay confined within its boundaries.
b) Both the attraction between the electrons and the lattice ions, and the repulsion between the electrons themselves are ignored.

- ✓ But used Fermi–Dirac statistics instead of Maxwell-Boltzmann statistics

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

- ✓ Applied Schrodinger wave equation; found the solution and obtained the expression for Energy

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad \Rightarrow \quad E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$$

- ✓ Applied Pauli Exclusion principle : An energy level can accommodate a maximum of two electrons, one with spin up and the other one with spin down

1. The energy levels of the conduction electrons in metal are quantized.
2. The distribution of electrons : Fermi-Dirac distribution & Pauli exclusion principle.

✓ **Now we know about Fermi energy, Fermi level, work function, specific heat capacity of metals by considering the wave nature of electrons.**

The following assumptions apply to both the theories:

1. The valence electrons are treated as though they constitute an ideal gas.
2. The valence *electrons* can move freely throughout the body of the solid.
3. The *mutual* repulsion between the electrons, and the force of attraction between the *electrons* and ions are considered insignificant.

Difference between the two theories

Classical Free Electron Theory	**Quantum Free Electron Theory**
1. The free electrons, which constitute the electron gas can have continuous energy values.	1. The energy values of the free electrons are discontinuous because of which the energy levels are discrete.
1. It is possible that many electron may possess same energy.	1. The free-electrons obey the Pauli exclusion principle. Hence no two electrons can possess same energy.
1. The pattern of distribution of energy among the free electron obey Maxwell-Boltzmann statistics.	1. The distribution of energy among the free electrons is according to Fermi Dirac statistics which imposes a severe restriction on the possible way in which the electrons absorb energy from an external source.

Merits and demerits of quantum free electron theory

- ✓ Changed the concept of free electron or conduction electrons in metals
- ✓ Successfully explained thermal and electrical conductivity of metals
- ✓ Thermionic emission from metals explained
- ✓ Temperature dependence of conductivity explained
- ✓ **The theory explained experimentally observed electronic specific heat of metals**
  - ✓ **Only electrons near the fermi level participate in the conduction**
- ✓ Explained paramagnetic susceptibility

But failed to Explain

Ferromagnetism in metals
Why some materials are Metal, insulator and semiconductors?
Hall effect

This all are explained at the third stage of development “ **Band theory of solid**’ **developed by Bloch, Kroning-Penney** etc.. And that will be learned in this lecture

- ✓ From just metals to all type of materials (solids)

STAGE 3: Band Theory of Solid

Nearly free electron theory

There are two approaches to discuss the formation of energy bands in solids'

i) One-electron approach (electron –lattice interaction)

Behaviours of one electron in the potential field established by the lattice atom cores and modified by the presence of all the other free electrons. The permissible energy levels obtained for this electron using quantum mechanical Schrodinger wave equation represent allowed energy levels and the forbidden energy (band gap)

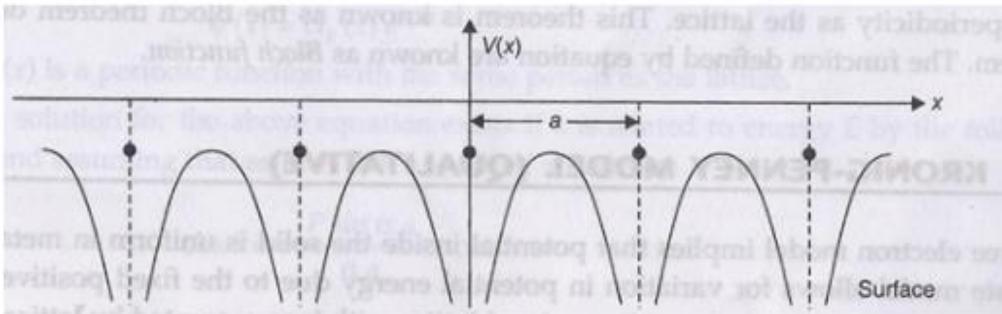
ii) Atomistic approach

Electrons are assumed to be tightly bound to the individual atoms. When atoms are brought together to form solids, the interaction between neighbouring atoms causes the electron energy levels of individual atoms splits into band of energies upon considering the Pauli's exclusion principle.

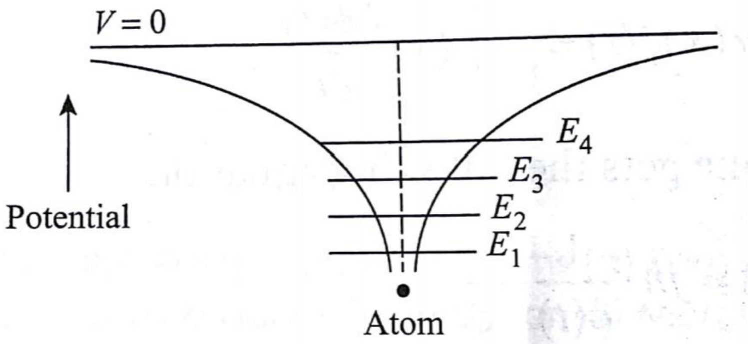
a. Band theory of solids- *One-electron approach*

1) Electron-ion interaction is considered
2) Periodic potential function of the lattice considered
3) Schrödinger wave equations- for electron in a periodic potential
4) Bloch function- solution of Schrödinger wave equation in a periodic potential- Bloch electrons
5) Kroning - Penning model- simplification of the periodic potential
6) E-k diagram- deviation from the parabolic behavior
7) Allowed and forbidden energy – concept of band gap and band overlap

We continue to treat valance electrons as independent (by neglecting e^--e^- interaction like in stage 1 and stage 2) but now we consider the electron-ion interaction. *Solid is a periodic arrangement of atoms….*

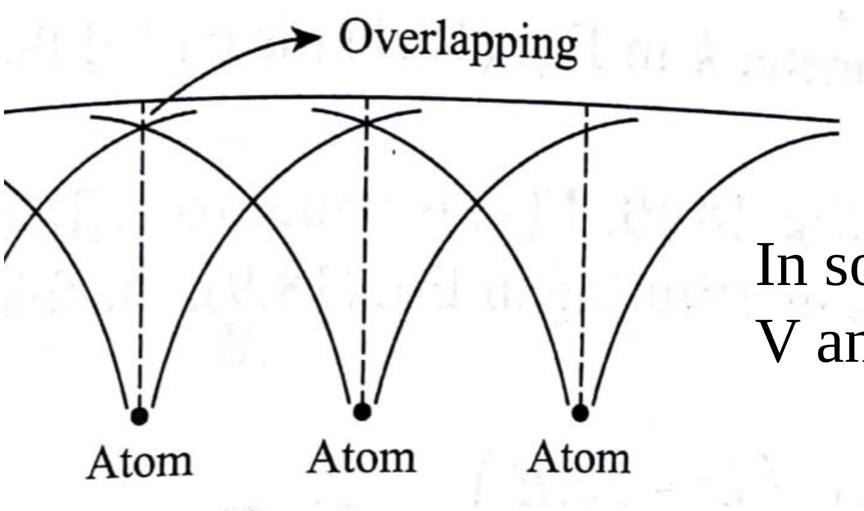


1. Free electron: Potential energy, **V=0**: Total energy is just the kinetic energy of the electron
   - ✓ This is the case for valance electron experience near the nucleus..
2. Not free when **$V=V_0$**; when electron is not in the well but at the barrier region, interaction with ion in the lattice considered.
   - ✓ This is what valance electron experience away from the nucleus
3. So electron wave experience a **periodicity in the potential** as it move through the lattice. ..This bring Bloch function to Schrödinger wave function

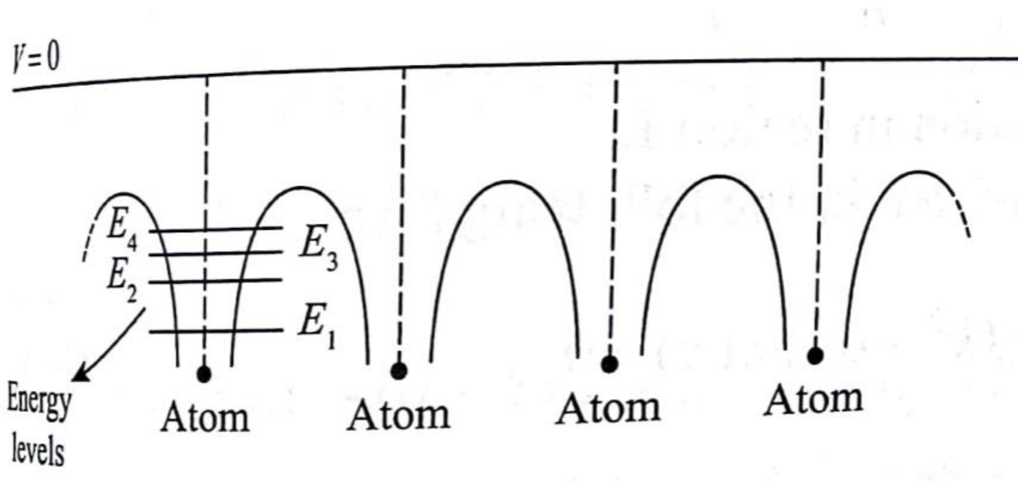


Non interacting atoms.. Energy levels are discrete.. Like we saw in the last class

Now imagine we are bringing atoms together.. And there is a periodicity in their positions.. A crystalline solid



In solid we get an overlapping potential V and is periodic function position..



Potential function of one dimensional array of atoms

Wave nature of electron (Quantum mechanics+ electron ion interaction, periodic potential)

Now we go back to the Schrödinger wave equation we learned in Unit 4 for the electron of mass **m** and total energy **E**

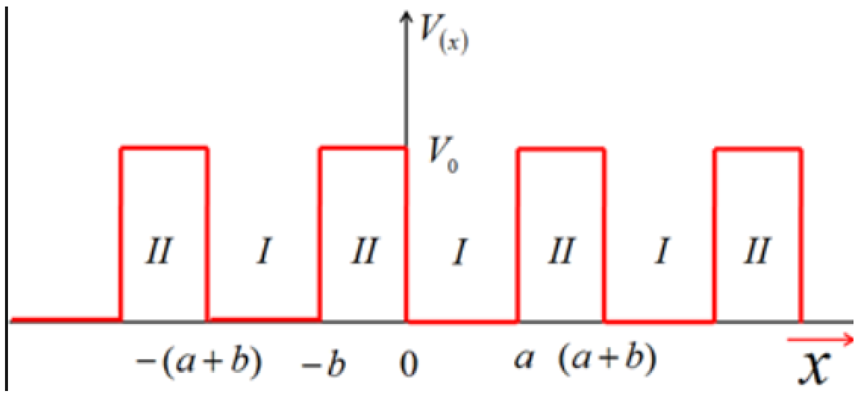
$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m\mathbf{E}}{\hbar^2}\psi = 0 \qquad \text{Eqn.1a}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\,\psi = 0 \qquad \text{Eqn.1b}$$

Kroning-Penney Model for the periodic potential

Simplified the problem by considering square well periodic potential

a) The energy of the electron is less than V_0
b) Solution of the above equation is Bloch function
c) Wave function and its derivative are continuous through out the crystal lattice
d) Product of the width and height of the potential is finite



At the bottom of the well ($0< x < a$) V is zero and electron is close to the nucleus
Out side of the well ($-b <x<0$) potential V is V_0, electron is away from the nucleus

Schrodinger equations for these two cases are given in eqn.1a and b

Block Theorem

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m\mathbf{E}}{\hbar^2}\psi = 0 \quad \text{Eqn.1a}$$

In 1928**, Felix Bloch** had the idea to take the quantum theory and apply it to solids. Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1927, Walter Heitler and Fritz London **discovered bands** very closely spaced orbitals with not much difference in energy

Solution for Equation 1a for V(x)=0, ψ, we have already seen

$$\psi(x) = e^{\pm ikx} \quad \text{Eqn.2}$$

$$\frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = E_k \quad \text{Eqn.3}$$

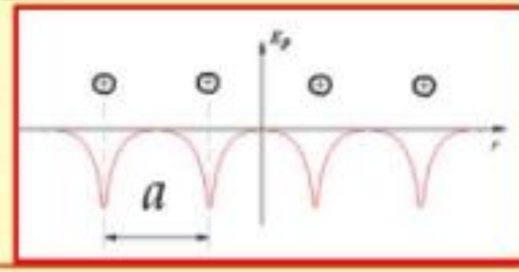
If the electron is moving through the periodic lattice, it experiences the periodic potential

$$V(x) = V(x+a) \quad \text{Eqn.4}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}[E - V(x)]\,\psi = 0 \quad \text{Eqn.5}$$

Solution of equation 5 is given by Bloch theorem…That is why the so called Bloch's theory of energy band in solids

Bloch Wavefunctions



- Bloch's Theorem states that for a particle moving in the periodic potential, the wavefunctions $\psi(x)$ are of the form

$$\psi(x) = u_k(x)e^{\pm ikx}, \text{ } where \; u_k(x) \textbf{ is a periodic function}$$

$$u_k(x) = u_k(x+a)$$

- $u_k(x)$ has *the periodicity of the atomic potential*
  - The exact form of *u(x)* depends on the potential associated with atoms (ions) that form the solid

With rigorous mathematical step they obtained the solution for Eq.5 as

$$P\frac{\sin \alpha a}{\alpha a} + \cos\alpha a = \cos Ka$$ Eqn.6

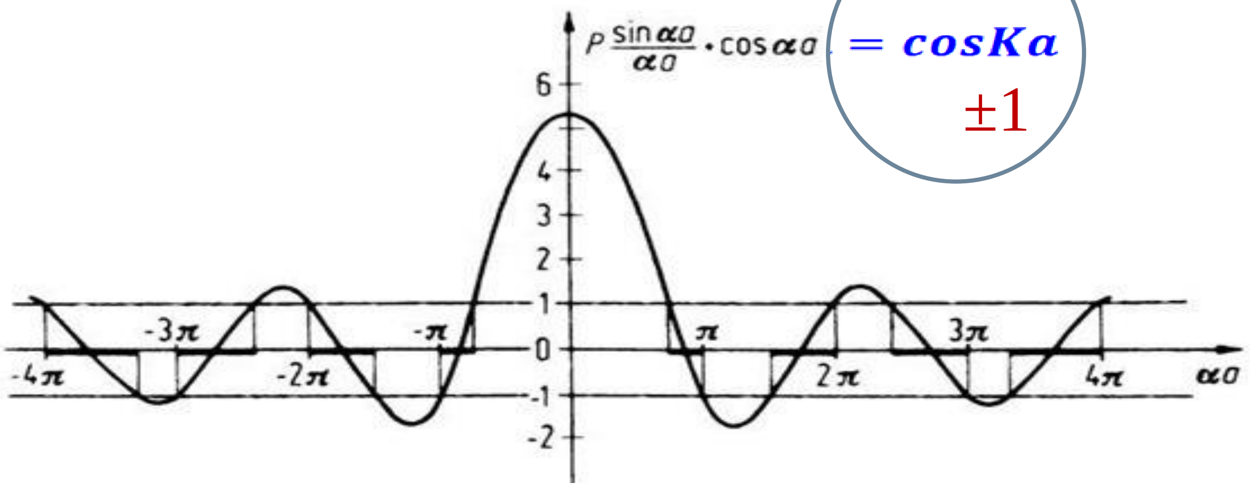
Equation 6 relates k, E and potential barrier; Gives a condition under which this Schrodinger wave equation has a solution

$$P = \frac{maV_0 b}{\hbar^2}$$ Eqn.7

Eqn.8 $$\alpha^2 = \frac{2mE}{\hbar^2}$$

P -Related to the Potential barrier

α -Related to the Energy



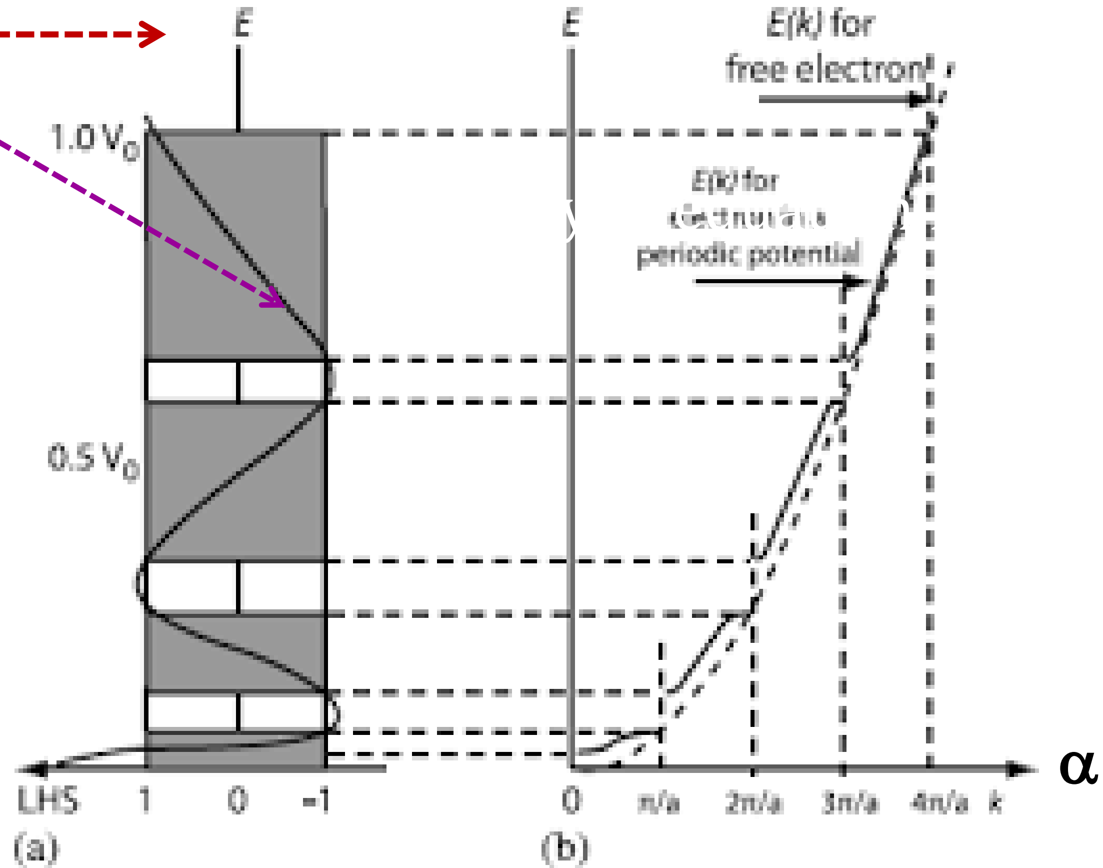
$= \cos Ka$

±1

Allowed values of the quantity on the y axis is within ±1, that restrict the energy values allowed for the Bloch electrons..

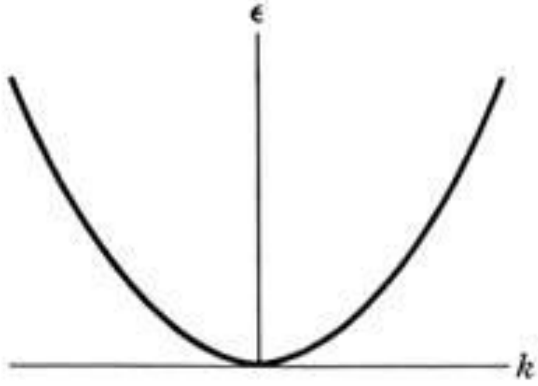
$$\alpha^2 = \frac{2mE}{\hbar^2} \dashrightarrow E = \frac{\alpha^2\hbar^2}{2m}$$

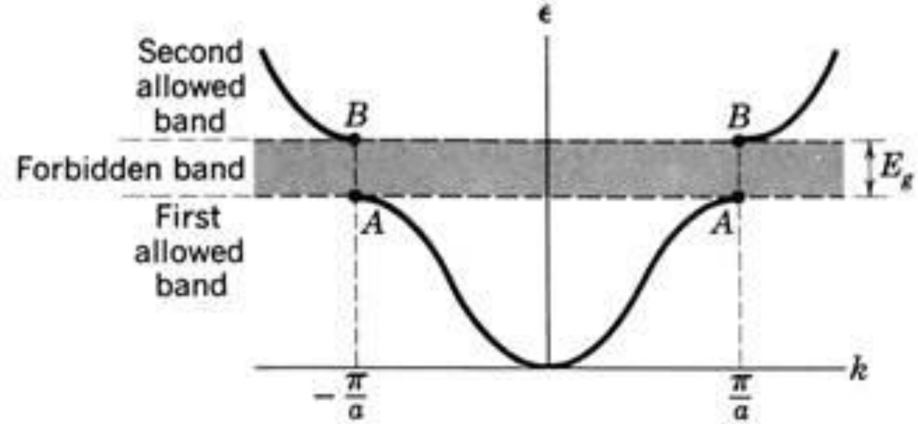
$$P\frac{\sin \alpha a}{\alpha a} + \cos\alpha a = \cos Ka$$



$\bar{e}$-energy in classical Physics

$\bar{e}$- energy in Quantum Physics





So periodic potential modulate the energy of the electron; it restrict the electron having a band of values and some energy is not allowed to possess in the lattice. **Origin of band gap in material come to exist**… **Now** we can distinguish metal, insulator and semiconductor ???

Kroning-Penney Model for the periodic potential uses

a) Square well potential function.
b) Linear potential function.
c) Continuous potential function.
d) None of the above.

Ans: A

To solve Schrödinger's wave equation of electrons in a periodic lattice which theorem is used

a) Stoke’s theorem
b) Divergence theorem
c) Gauss theorem
d) Bloch’s theorem

Ans: D

Periodic potential forbid the electron to have some energies in the lattice. State true or false

(a) True
(b) False

Ans: A

Band theory of solid consider

(a) Electron-electron interaction
(b) Electron-ion interaction
(c) Both (a) and (b)
(d) None of the above.

Ans: B

The wave function that satisfies the Schrödinger's wave equation in a period potential in a solid is known as

(a) Schrödinger function
(b) Block function
(c) Fourier function
(d) None of the above.

Ans: B

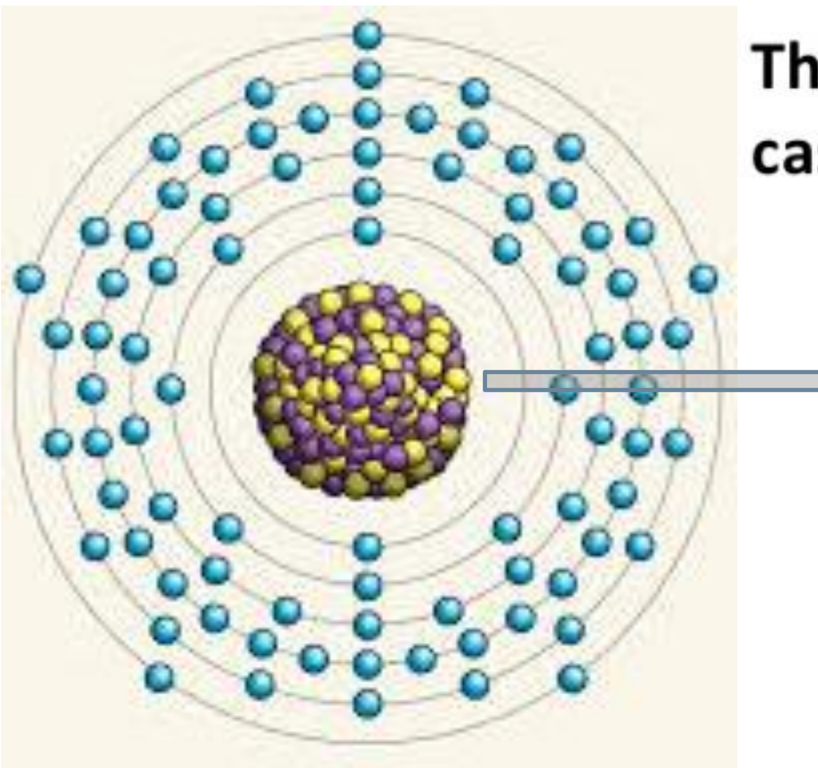
In Band theory of solid the electron moving through the periodic lattice is known as

(a) Block electron
(b) Positron
(c) Bound electron
(d) None of the above.

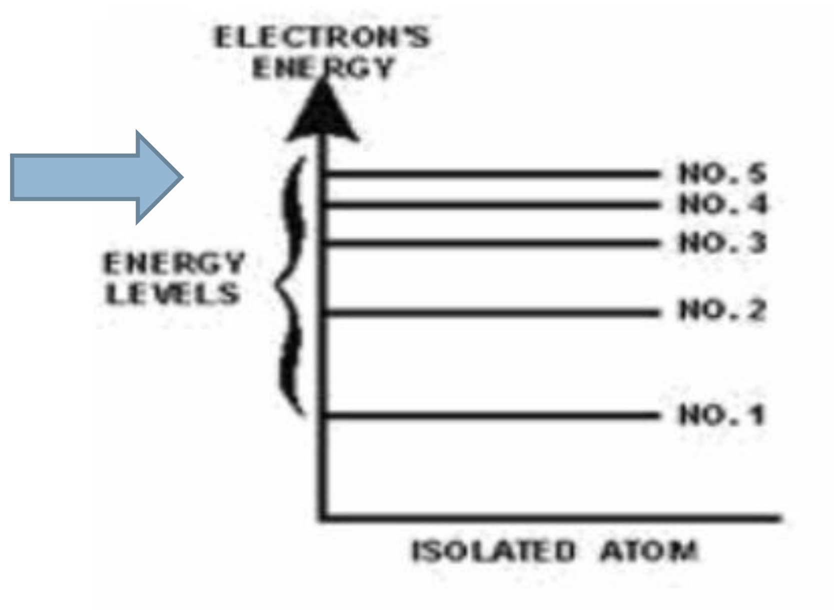
Ans: B

b. BAND THEORY OF SOLIDS- ATOMISTIC APPROACH

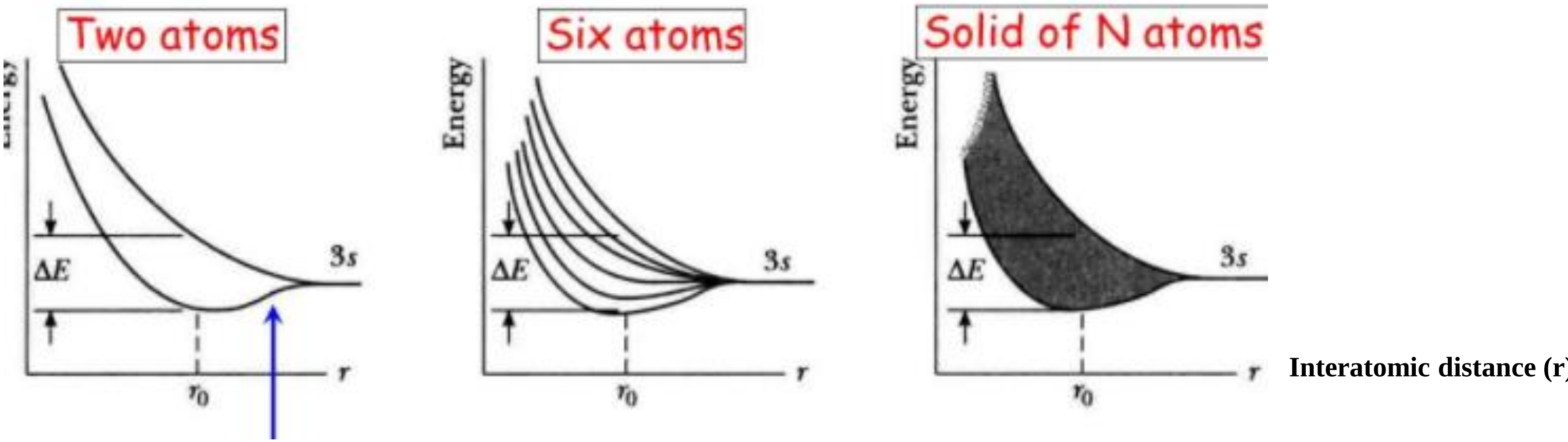
- Splitting of energy levels due Pauli’s exclusion principle- formation of band



There are discrete energy levels in the case of an isolated atom.



Now we will see what happens when atoms comes together to from solids



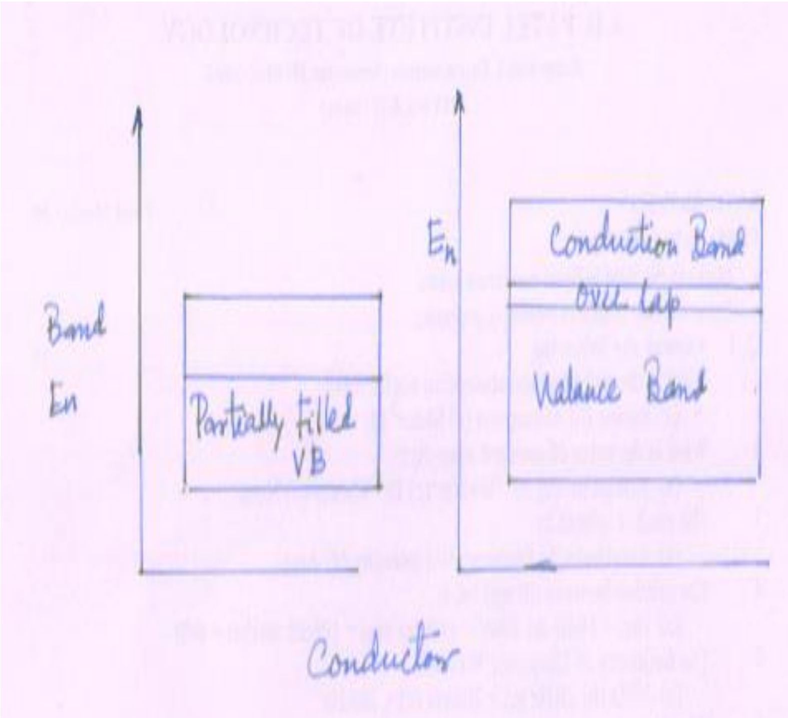
✓r_0 is the inter-atomic distance

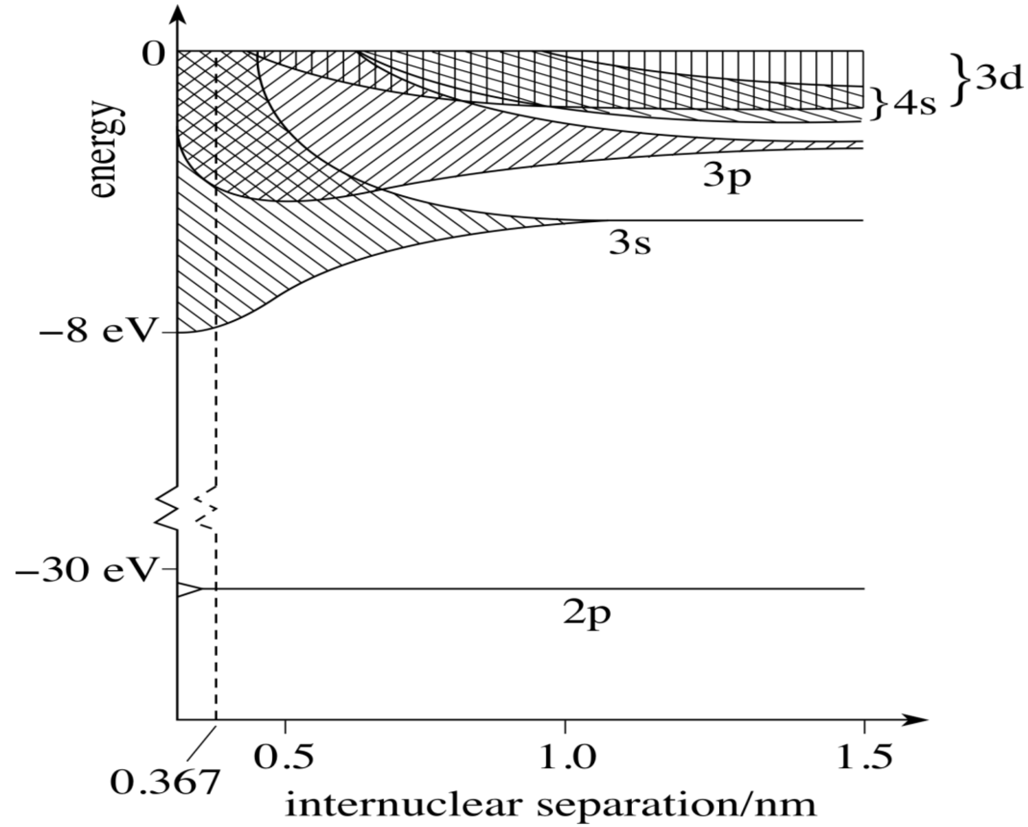
✓ Electrons with identical quantum numbers (1S, share the same band and 2S, 2P etc..)..like you all are in the same class☺

Splitting of discrete energy levels as two atoms come close to form solid due to Pauli's exclusion principle.

All discrete energy levels opens up.. But width ΔE increases towards higher levels (quantum numbers, or K,L,M,N etc.. Or s,p,d,f)

Metal



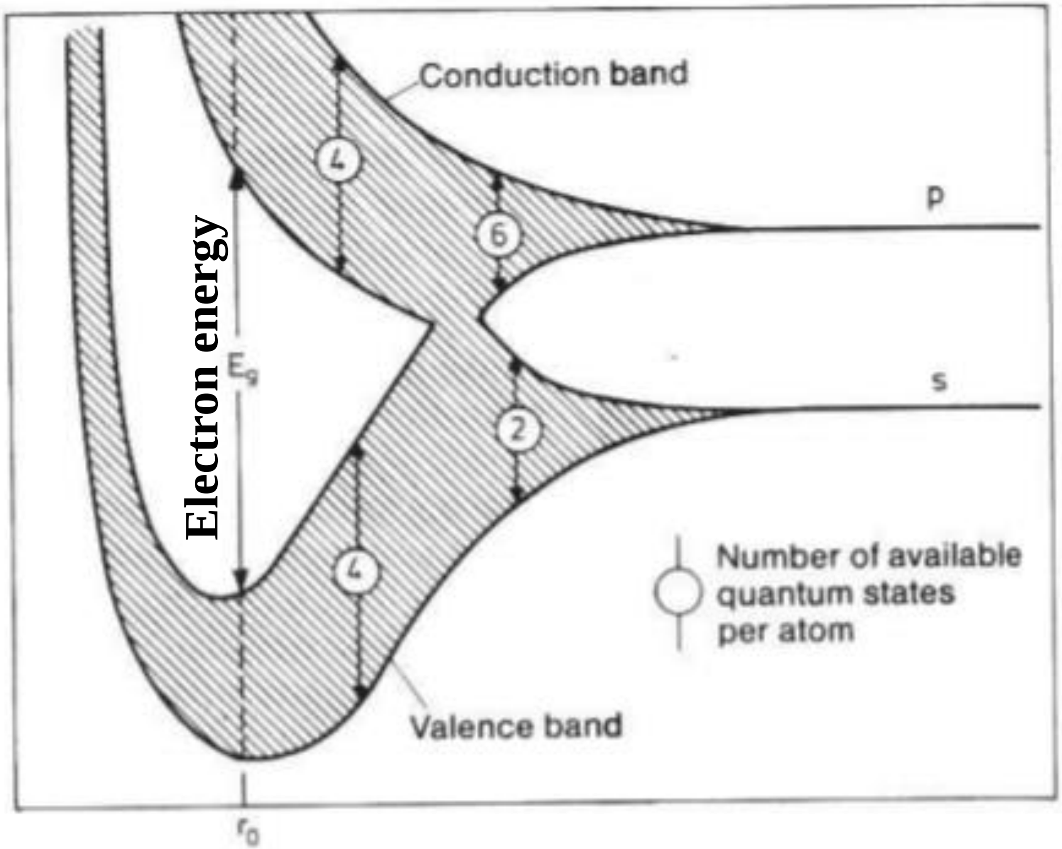


Li, Na, K etc..

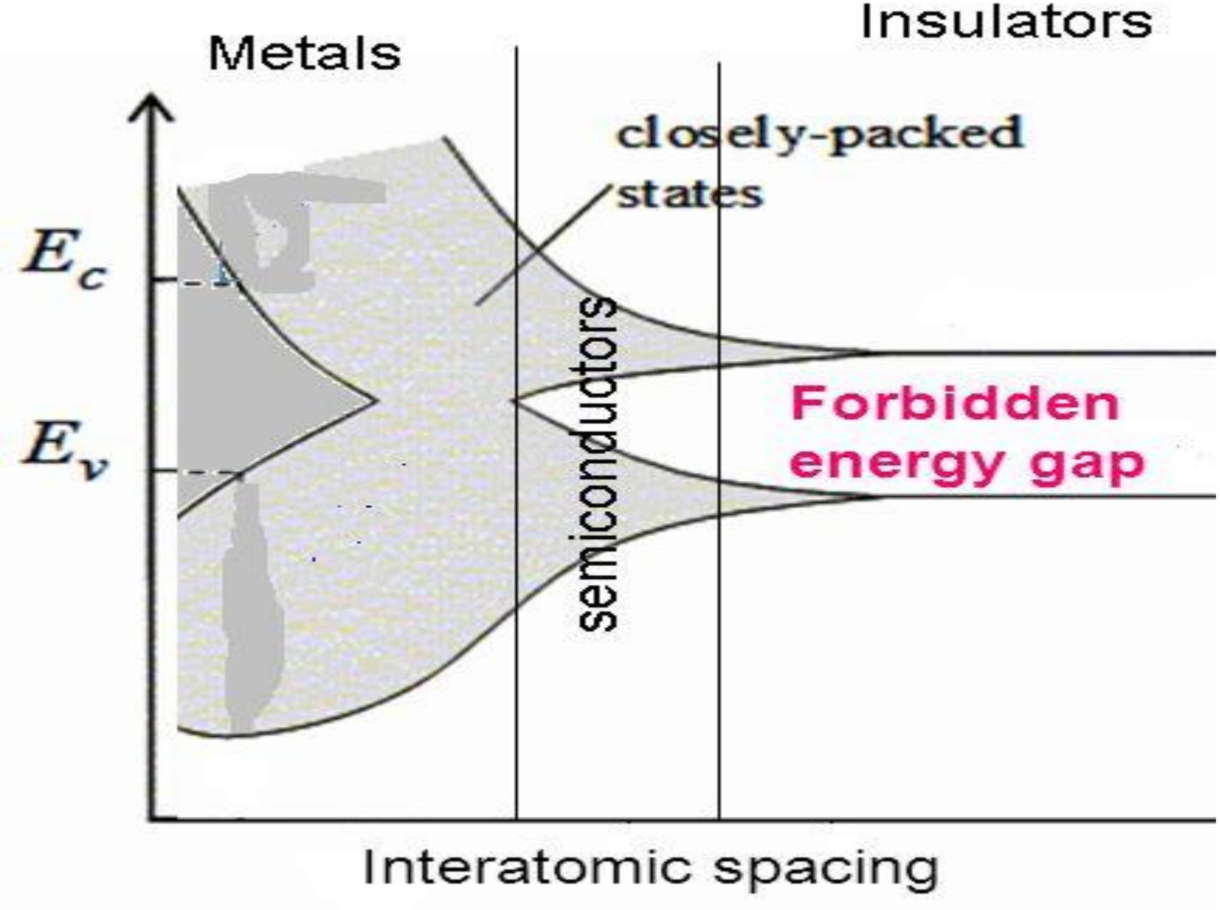
Partially filled Valance band / or Merging of bands

INSULATOR OR SEMICONDUCTOR

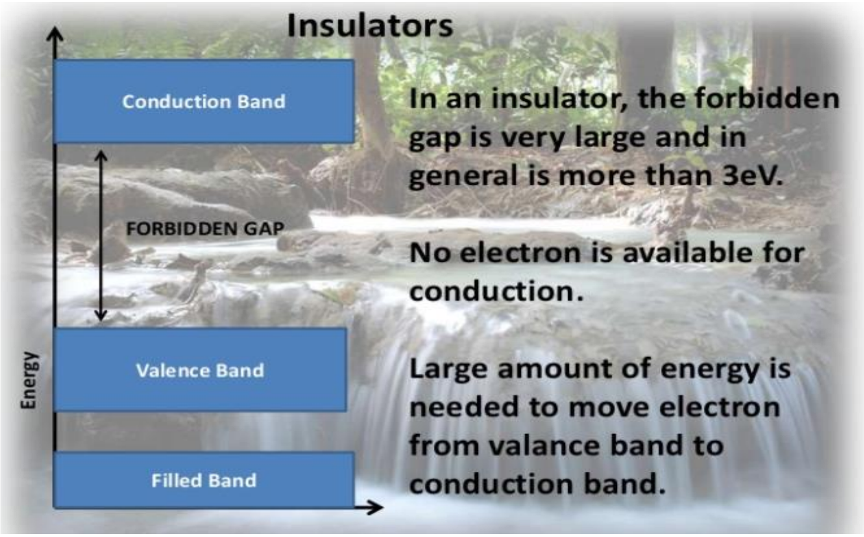
Formation of Band Gap

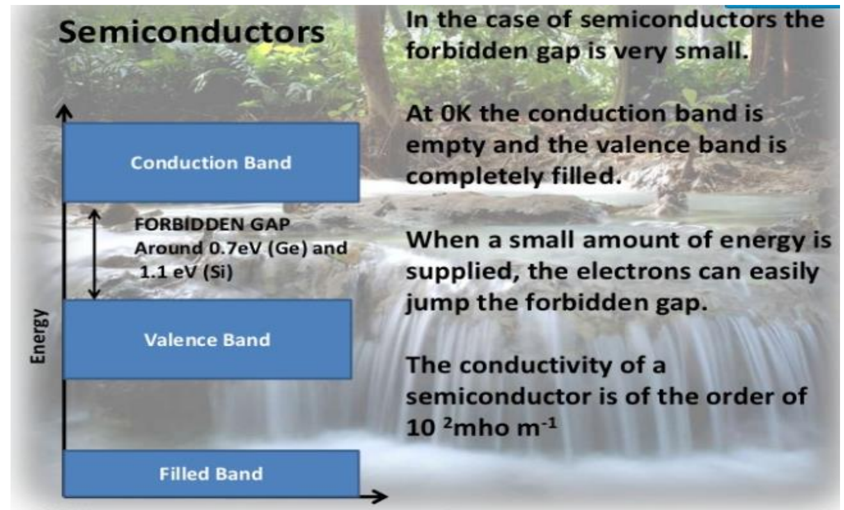


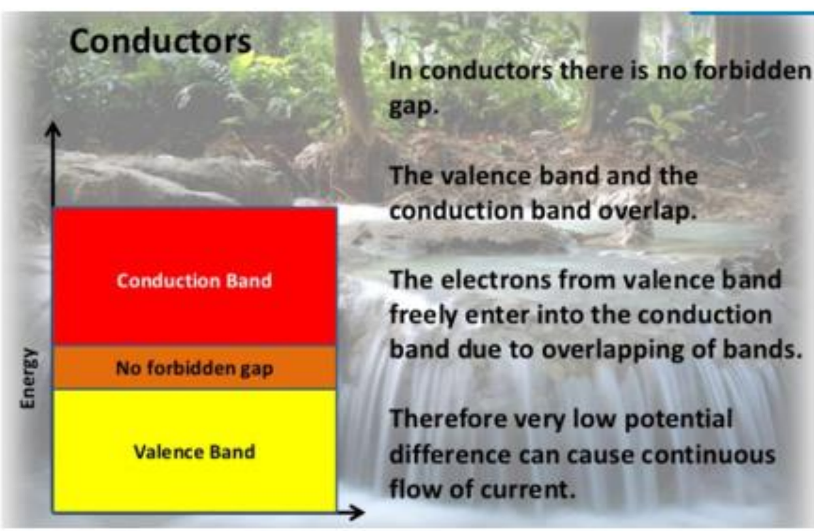
Interatomic distance


Insulators
Metals
closely-packed
states
E_c
E_v
semiconductors
Forbidden
energy gap
Interatomic spacing

Insulator, Semiconductor and Conductor in terms of the Band Gap







Insulator: $E_g > 3$ eV

Semiconductor: $0.5 < E_g < 3$ eV

Conductors: $E_g = 0$ eV

Energy band in solids are the consequence of

a) Ohm’s Law
b) Pauli’s exclusion principle
c) Heisenberg’s uncertainty principle
d) Bohr’s theory

Ans: B

The energy bands in solids are

a) Valence band
b) Conduction band
c) Forbidden band
d) All of the above

Ans: D

The band theory helps to visualise the difference between conductor, semiconductors and insulator by plotting available energies for an electron in a material. **State True or False**

True

PHY110 – ENGINEERING PHYSICS

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