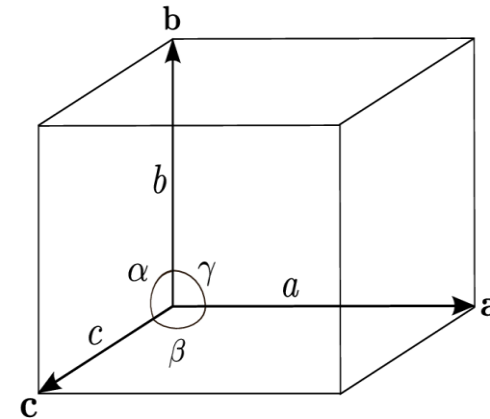


# Solid State Physics

The smallest group of symmetrically aligned atoms which can be repeated in an array to make up the entire crystal is called a unit cell. Bravais Lattice refers to the 14 different 3-dimensional configurations into which atoms can be arranged in crystals.

## Different types of Bravais Lattices



### 1. Cubic Systems

In Bravais lattices with cubic systems, the following relationships can be observed.

$$a = b = c \text{ and } \alpha = \beta = \gamma = 90^\circ$$

### 2. Orthorhombic Systems

The Bravais lattices with orthorhombic systems obey the following equations:

$$a \neq b \neq c \text{ and } \alpha = \beta = \gamma = 90^\circ$$

### 3. Tetragonal Systems

In tetragonal Bravais lattices, the following relations are observed:

$$a = b \neq c \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ$$

### 4. Monoclinic Systems

Bravais lattices having monoclinic systems obey the following relations:

$$a \neq b \neq c \quad \text{and} \quad \beta = \gamma = 90^\circ \text{ and } \alpha \neq 90^\circ$$

### 5. Triclinic System

There exists only one type of triclinic Bravais lattice, which is a primitive cell. It obeys the following relationship.

$$a \neq b \neq c \quad \text{and} \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$$

### 6. Rhombohedral System

Only the primitive unit cell for a rhombohedral system exists. Its cell relation is given by:

$$a = b = c \quad \text{and} \quad \alpha = \beta = \gamma \neq 90^\circ$$

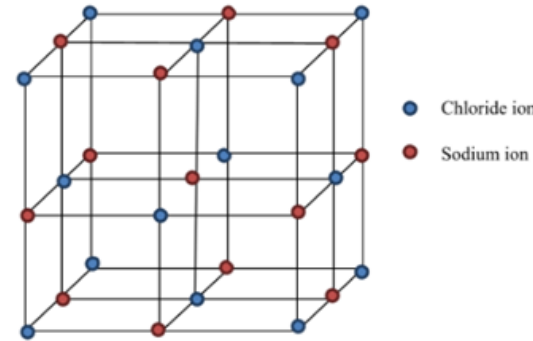
### 7. Hexagonal System

The only type of hexagonal Bravais lattice is the simple hexagonal cell. It has the following relations between cell sides and angles.

$$a = b \neq c \quad \text{and} \quad \alpha = \beta = 90^\circ \text{ and } \gamma = 120^\circ$$

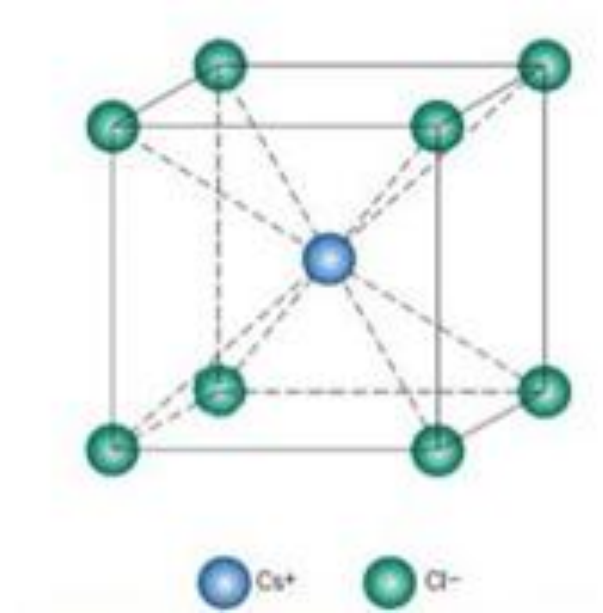
## NaCl structure

NaCl crystal has FCC structure with  $\text{Na}^+$  ion and  $\text{Cl}^-$  ion as shown in the figure.



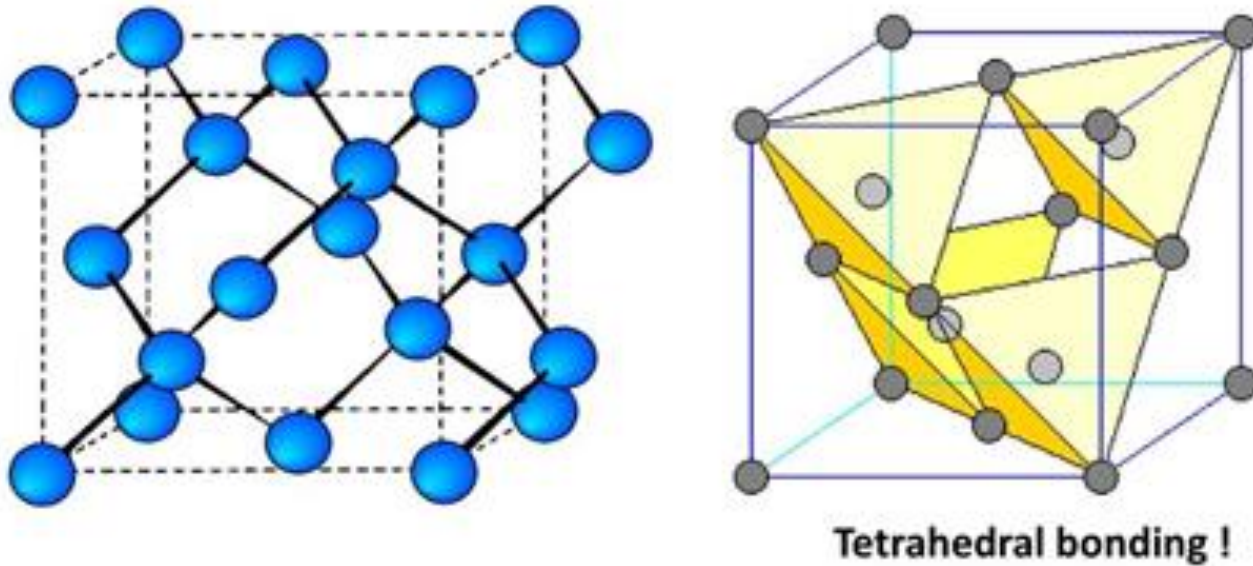
- Each chloride ion is surrounded by six sodium ions which are disposed towards the corners of a regular octahedron.
- The structure of sodium chloride consists of eight ions a unit cell, four are  $\text{Na}^+$  ions and the other four are  $\text{Cl}^-$  ions.
- In this structure, each corner ion is shared between eight-unit cells, each ion a face of the cell by two cells, each ion on a edge by four cells and the ion inside the cell belongs entirely to that unit cell.

## CsCl structure



- It has BCC structure
- Coordination number 8
- The anions are located at each of the corners of a cube, with single cation at the center.
- Interchange of anions with cations produces the same crystal structure.

# Diamond structure



- It has FCC structure
- Coordination number 4
- Numbers of atoms in unit cell 8
- There are eight carbon atoms at the corner, creating a cube.
- The six carbon atoms in the faces create an octahedron.
- The four internal carbon atoms lie at  $\frac{1}{4}$  of the distance along body diagonal forming a tetrahedron.

- **Crystal bonding**

### **Ionic bonding**

In ionic bonding atoms transfer electrons, forming ions. Positively and negatively charged ions attract each other in giant ionic lattices.

Ionic compounds have high melting points, are hard & brittle, soluble in water and conduct electricity when molten or in solution. e.g. sodium chloride.

the bond formed by the complete transfer of valence electron to attain stability.

leads to the formation of two oppositely charged ions – positive ions known as cations and negative ions known as anions.

The presence of two oppositely charged ions results in a strong attractive force between them. This force is an ionic or electrovalent bond.

form between atoms with large differences in electronegativity.

The compound formed by the electrostatic attraction of positive and negative ions is called an ionic compound.

## Covalent Bond

It is formed by equal sharing of electrons from both the participating atoms. The pair of electrons participating in this type of bonding is called shared pair or bonding pair.

are also termed as molecular bonds.

### Properties of Covalent Bond

Does not result in the formation of new electrons. The bond only pairs them.

Are very powerful chemical bonds that exist between atoms.

Normally contains the energy of about ~80 kilocalories per mole (kcal/mol).

Rarely break spontaneously after it is formed.

Are directional where the atoms that are bonded showcase specific orientations relative to one another.

Most compounds having covalent bonds exhibit relatively low melting points and boiling points.

Compounds with covalent bonds usually have lower enthalpies of vaporization and fusion.

Compounds formed by covalent bonding don't conduct electricity due to the lack of free electrons.

Covalent compounds are not soluble in water.

- **Polar Covalent Bond**

This type of covalent bond exists where the unequal sharing of electrons occurs due to the difference in the electronegativity of combining atoms.

More electronegative atom will have a stronger pull for electrons.

The electronegative difference between the atoms is greater than zero and less than 2.0.

The shared pair of electrons will be closer to that atom.

### **Nonpolar Covalent Bond**

It is formed whenever there is an equal share of electrons between atoms.

The electronegativity difference between two atoms is zero.

It occurs wherever the combining atoms have similar electron affinity (diatomic elements).



## **Metallic bond**

A metallic bond is a type of chemical bond formed between positively charged atoms in which the free electrons are shared among a lattice of cations.

Metallic bonds are seen in pure metals and alloys and some metalloids.

In metallic bonds, the valence electrons from the s and p orbitals of the interacting metal atoms delocalize.

Instead of orbiting their respective metal atoms, they form a “sea” of electrons that surrounds the positively charged atomic nuclei of the interacting metal ions.

Properties of metal having metallic bonding :

- They are malleable.
- They are ductile
- Have high melting and boiling point
- Have high electrical and thermal conductivity
- Metals tend to be shiny or display metallic luster.

## **Van der Waals Bond**

Van der Waals forces are weak intermolecular forces that are dependent on the distance between atoms or molecules. These forces arise from the interactions between uncharged atoms/molecules.

- Following are the characteristics of Van Der Waal forces.
- These forces are additive.
- They are weaker than ionic, covalent bonds.
- Van Der Waals forces are not directional.
- They work in a short range. The interaction increases when molecules are closer.
- These forces are independent of temperature. The only exception is dipole-dipole interaction.

## **Free electron theory**

The classical free electron theory was proposed by Drude and Lorentz in 1900. This theory said that metals with free electrons obey the laws of classical mechanics.

Assumptions used in classical free electron theory

1. The valence electrons contained in an atom, are free to move about the whole volume of the metal, as the molecules of a perfect gas move in a container.
2. The free electrons of the atoms move in a random direction. While doing so they collide with either positive ions fixed to the lattice or the other free electrons of the atom. But there is no loss of energy as all the collisions are elastic in nature.
3. The momentum of free electrons of the atoms obeys the laws of the classical kinetic theory of gases.

4. The velocity with which the free electrons are moving in metal also obeys classical Maxwell-Boltzmann distribution of velocities.
5. When the electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of the applied electric field.
6. There is no mutual repulsion among the electrons. So that they move in all directions with all possible velocities.
7. In the absence of the field, the energy associated with an electron

$$\frac{3}{2} kT = \frac{1}{2} mv^2$$

Where T is the temperature, k is the Boltzmann constant, m is the mass of the electron and v is the velocity.

## **Ohm's law** [from the CFT Model]

Consider a current carrying conductor of length  $l$ , area of cross section  $A$  and free electron density be “ $n$ ” electrons/ $m^3$ . When we applied potential  $V$  across the conductor then electric field  $E$  is produced, in the influence of electric field electrons are moving in opposite direction to the field by the Drift velocity due to which the current  $I$  flows through it. Electric force experienced by electron

$$F = -e.E$$

$$|F| = e.E$$

If the mass of an electron be “ $m$ ” and acceleration of it between two consecutive collision be “ $a$ ” then by second law of motion

$$F = m.a$$

Comparing above two forces

$$m.a = e.E$$

$$a = e. \frac{E}{m}$$

the average drift speed of electron

$$v_d = a \cdot \tau = e \cdot \frac{E}{m} \cdot \tau$$

the electron mobility is defined as the drift velocity per unit applied electric field.

Electron mobility  $\mu = \frac{v_d}{E} = \frac{e \tau}{m}$

And current density,  $J = e v_d n = e \cdot \frac{E}{m} \cdot \tau \cdot n \cdot e = \frac{n e^2 \tau}{m} \cdot E$

Since  $J = \sigma \cdot E$

$$\sigma = \frac{n e^2 \tau}{m}$$

and resistivity

$$\rho = \frac{1}{\sigma} = \frac{m}{n e^2 \tau} = \frac{1}{n e} \frac{m}{e \tau}$$

and

$$\sigma = n e \frac{e \tau}{m} = n e \mu$$

the resistivity depends only on material parameters and not on any particular shape or size of the sample.

Since potential  $V = E \cdot \text{length}$ , and current  $I = \text{current density}(J) \cdot \text{area}(A)$

$$\frac{V}{I} = \frac{E \cdot L}{J \cdot A} = \frac{E \cdot L}{\frac{n e^2 \tau}{m} \cdot E \cdot A} = \frac{m}{n e^2 \tau} \frac{L}{A} = \frac{\rho \cdot L}{A}$$

For the given shape and size of the material  $\frac{\rho \cdot L}{A} = \text{constant}$  or  $\frac{V}{I} = \text{constant} (R)$

i.e. current flowing through the conductor is directly proportional to potential difference across it, which is ohm's law.

**Thermal conductivity:** Thermal conductivity is the property of the material that indicates its ability to conduct heat. The thermal conductivity of this metal is, like electrical conductivity, determined largely by the free electrons. Suppose now that the metal has different temperatures at its ends. The electrons are moving slightly faster at the hot end and slower at the cool end.

Consider a region of metal filled with an electron gas. The rate of flow of heat through a metal slab is proportional to the temperature gradient across the slab and its cross-sectional area.

$$Q = \eta A \frac{dT}{dx} \quad \text{And heat current density,} \quad J = \frac{Q}{A} = \eta \frac{dT}{dx} \quad 1$$

Let  $n$ - be the number of electrons per unit volume.

$V_{\text{rms}}$ - be the thermal speed.

$l$  – be the mean free path between the collisions.

$U$  – be the thermal energy at the central plane region.

$\frac{dU}{dx}$  –be the gradient of thermal energy from  $T + dT$  to  $T$ .

Then thermal energy of electron at a plane  $l$  away from the central plane towards hot side will be  $U + \frac{dU}{dx} \cdot l$  and toward the cold side is  $U - \frac{dU}{dx} \cdot l$

Since number of free electrons crossing per unit area per unit time in all ( $\pm$ ) direction =  $nv_{\text{rms}}$ .

In average only one sixth of them are in motion in a particular direction so, number of free electrons

crossing per unit area per unit time in one particular direction =  $\frac{1}{6} nv_{\text{rms}}$

Therefore, the current density  $J$  in +ve x-direction is

$$J^+ = \frac{1}{6} nv_{\text{rms}} \left( U + \frac{dU}{dx} \cdot l \right)$$

the current density  $J$  in - ve x-direction is

$$J^- = \frac{1}{6} nv_{\text{rms}} \left( U - \frac{dU}{dx} \cdot l \right)$$

Net current density  $J = J^+ - J^-$

$$= \frac{1}{6} nv_{\text{rms}} \left( \frac{dU}{dx} \cdot l + \frac{dU}{dx} \cdot l \right)$$

$$J = \frac{1}{3} nv_{\text{rms}} \frac{dU}{dx} \cdot l.$$



Now amount of heat required to raise the temperature of 1mole of substance by 1K, molar specific heat

$$C_V = \frac{dU}{dT} \cdot N_A \quad \text{and} \quad dU = \frac{C_V}{N_A} \cdot dT$$

So, 
$$J = \frac{nv_{rms} l C_V}{3N_A} \cdot \frac{dT}{dx} \quad 2$$

Comparing eq 1, 2 we get

$$\eta = \frac{nv_{rms} l C_V}{3N_A}$$

since  $l = \tau \cdot v_{rms}$

Therefore, 
$$\eta = \frac{n v_{rms}^2 \tau C_V}{3N_A} \quad \text{or} \quad \eta = \frac{n v_{rms}^2 \tau R}{2N_A} \quad [ C_V = \frac{3}{2} R ]$$

$$\eta = \frac{1}{2} n v_{rms}^2 \tau K_B \quad [ \frac{R}{N_A} = K_B ]$$

which is expression for thermal conductivity..

## Wiedemann–Franz law

It states that the ratio of the electronic contribution of the thermal conductivity ( $\kappa$ ) to the electrical conductivity ( $\sigma$ ) of a metal is proportional to the temperature (T).

Since thermal conductivity

$$\eta = \frac{1}{2} n v_{rms}^2 \tau K_B$$

electrical conductivity

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

therefore,

$$\begin{aligned}\frac{\eta}{\sigma} &= \frac{mv_{rms}^2 K_B}{2e^2} = \frac{1}{2} m v_{rms}^2 \frac{K_B}{e^2} \\ &= \frac{3}{2} K_B T \cdot \frac{K_B}{e^2} = \frac{3}{2} T \cdot \frac{K_B^2}{e^2} \\ \frac{\eta}{\sigma} &= \frac{3}{2} \left( \frac{K_B}{e} \right)^2 \cdot T\end{aligned}$$

$$\frac{\eta}{\sigma} = L \cdot T$$

Where,  $L = \frac{3}{2} \left( \frac{K_B}{e} \right)^2 = \frac{3}{2} \left( \frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \right)^2$   
 $= 1.12 \times 10^{-8} \text{ W} \cdot \Omega \text{K}^{-2}$  is called Lorentz number.

## **Limitations of classical theory:**

It fails to explain the electric specific heat and the specific heat capacity of metals.

It fails to explain superconducting properties of metals.

It fails to explain new phenomena like photo-electric effect, Compton effect, Black body radiation, etc.

It fails to explain electrical conductivity of semiconductors or insulators.

Ferromagnetism could not be explained by this theory.

Susceptibility of magnetic material has found greater theoretical value than the experimental value.

## **Quantum Mechanical Free Electron Model [QMFE]**

Many of the difficulties encountered by the classical free electron model were removed with the advent of quantum mechanics. In 1928, A. Sommerfeld modified the free electron model in two important ways:

The electrons must be treated quantum mechanically. This will quantize the energy spectrum of the electron gas.

The electrons must obey Pauli's exclusion principle; that is, no two electrons can have the same set of quantum numbers.

As a result of these modifications, when we put an electron gas in a solid, we begin by putting the electrons in the lowest energy states available, while obeying the exclusion principle, until we have used all the available electrons. This is to be contrasted with the classical free electron gas in which Arnold Sommerfeld (1868-1951).

The assumptions of the Drude model:

The valence electrons are free to move through the solid.

Aside from collisions with the ions, the electrostatic interaction between the electrons and the lattice ions is ignored.

The interaction between the electrons is also neglected.

In one dimensional infinite potential well, the energy eigen value is given by

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

And the wave function  $\psi(x) = A \sin kx$

For three dimensions

$$E_n = \frac{(n_x^2 + n_y^2 + n_z^2) \hbar^2 \pi^2}{2mL^2}$$

And the wave function  $\psi(x,y,z) = A \sin k_1 x \cdot A \sin k_2 y \cdot A \sin k_3 z$ .

## Fermi Energy

The highest energy level that an electron can occupy at the absolute zero temperature is known as the Fermi Level. The Fermi level lies between the valence band and conduction band because at absolute zero temperature the electrons are all in the lowest energy state. Due to the lack of sufficient energy at 0 Kelvin, the Fermi level can be considered as the sea of fermions (or electrons) above which no electrons exist. The highest energy level in the conduction band filled up with electrons at absolute is called Fermi level and the energy corresponding to the Fermi level is called Fermi energy.

As electron energy in one dimensional potential well is

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

At fermi level  $n = n_f$ , the fermi energy

$$E_F = \frac{n_f^2 \hbar^2 \pi^2}{2mL^2} = \frac{\hbar^2}{2m} \left( \frac{\pi n_f}{L} \right)^2 = \frac{\hbar^2 K_F^2}{2m}$$

Where,  $K_F = \frac{\pi n_f}{L}$  is the fermi wave vector. And the sphere of radius  $K_F$  in E-k space is called fermi sphere. Eq 1 shows that E-k curve is parabolic as shown in figure.



At  $T = 0K$ , the electron occupies the lowest quantum state to save energy. In other words, the quantum states  $E \leq E_F$  are occupied while the states with  $E > E_F$  are empty.

Since,  $E_F = \frac{\hbar^2 K_F^2}{2m}$ , this means the states with momentum.  $K \leq K_F$  are empty. In other words, in the k-space the occupied states form a sphere with radius  $K_F$ . This sphere is called Fermi sphere.

Total volume of the Fermi sphere is  $\frac{4}{3} \pi K_F^3$

Each quantum state occupies the volume  $\left(\frac{2\pi}{L}\right)^3$ , which comes from uncertainty relation.

So, the total number of quantum states  $= \frac{\frac{4}{3} \pi K_F^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V K_F^3}{6\pi^2}$

Since there are 2 electrons per state, so total number of occupied electrons in the sphere is

$$N = 2 \cdot \frac{V K_F^3}{6\pi^2} \quad \& \quad K_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

$$E_F = \frac{\hbar^2 K_F^2}{2m} = \frac{\hbar^2}{2m} \cdot \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

This shows that  $E_F$  does not depend upon temperature and number of electrons but depends upon  $\frac{N}{V}$  only.

If  $v_F$  is the velocity of the electron at the Fermi surface then,  $v_F = \frac{\hbar K_F}{m} = \frac{\hbar}{m} \cdot \left(\frac{3\pi^2 N}{V}\right)^{1/3}$



# Density of States

The density of states is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. Bulk properties such as specific heat, paramagnetic susceptibility, and other transport phenomena of conductive solids depend on this function. DOS calculations allow one to determine the general distribution of states as a function of energy and can also determine the spacing between energy bands in semi-conductors.

The density of states is once again represented by a function  $g(E)$  which this time is a function of energy and has the relation  $g(E) dE$  = the number of states per unit volume in the energy range:  $(E, E + dE)$  .

As electron energy in one dimensional potential well is

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

In three-dimensional quantum space  $n^2 = n_x^2 + n_y^2 + n_z^2$

The number of energy states within the sphere of radius  $n$  is given by

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

$$N = \frac{4\pi V}{3h^3} \cdot (2m)^{3/2} \cdot (E)^{3/2}$$

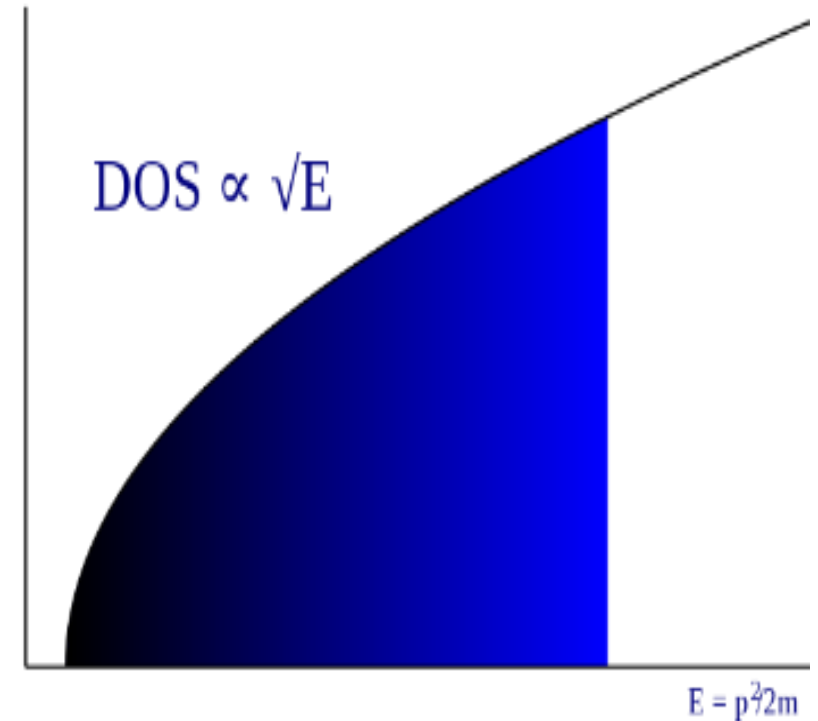
The density of state function is given by

$$g(E) = \frac{dN}{dE} = \frac{3}{2} \cdot \frac{4\pi V}{3h^3} \cdot (2m)^{3/2} \cdot (E)^{1/2}$$

$$g(E) = \frac{2\pi V}{h^3} \cdot (2m)^{3/2} \cdot (E)^{1/2}$$

$$g(E) = C \cdot (E)^{1/2}$$

$$\text{where } C = \frac{2\pi V}{h^3} \cdot (2m)^{3/2}$$



## Fermi-Dirac distribution

The Fermi-Dirac distribution applies to fermions, particles with half-integer spin which must obey the Pauli exclusion principle. Mathematically the probability of finding an electron in the energy state  $E$  at the temperature  $T$  is expressed as :

$$F(E) = \frac{1}{1 + \exp^{\frac{(E-E_F)}{KT}}}$$

$E$  – energy of electron,

$E_F$ - Fermi energy,

$T$  – absolute temperature,

$K$  – Boltzmann constant =  $1.38 \times 10^{-23}$  J/K

At fermi level  $E = E_F$

$$F(E) = \frac{1}{1 + \exp^{\frac{(E-E_F)}{KT}}} = \frac{1}{1 + \exp^0} = \frac{1}{1+1} = \frac{1}{2}$$

This means the fermi level at which the electron to be present exactly 50% of the time.

## Bloch's Theorem

A theorem that specifies the form of the wave functions that characterize electron energy levels in a periodic crystal.

Eigen function of the wave equation for a periodic potential are the product of plane wave  $e^{(i \mathbf{k} \cdot \mathbf{r})}$  and a function  $u_{\mathbf{k}}$  with periodicity of the crystal lattice.

i.e.  $\Psi(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \cdot e^{(i \mathbf{k} \cdot \mathbf{r})}$  1

Thus the solution of the Schrodinger wave equation  $\frac{d^2 \psi_k}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi_k = 0$  is given by

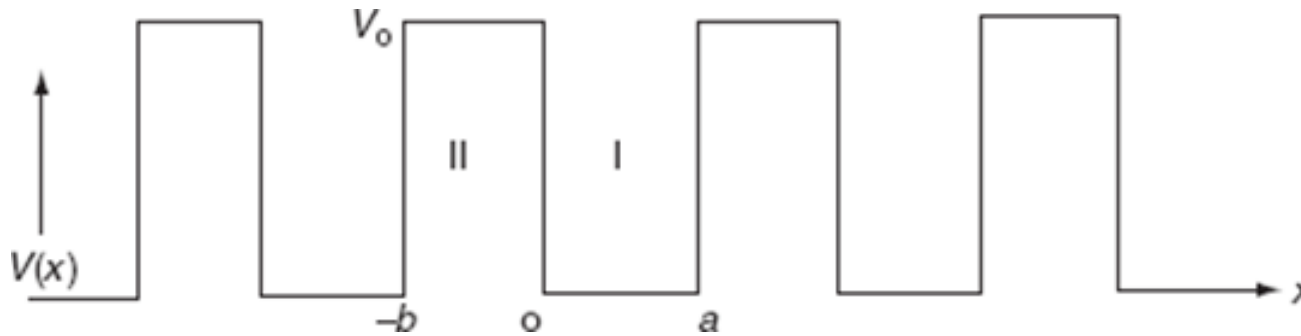
$$\Psi(x) = u_k(x) \cdot e^{i k x} \quad 2$$

For  $V(x) = V(x + a)$  and  $u_k(x) = u_k(x + a)$ . The function represented by eq 2 is called Bloch theorem. So, for a particle moving in a periodic potential with period  $a$ , and potential  $V(x)$ ,  $V(x+a)$ ,  $V(x+2a)$ ,...

$$\Psi(x + a) = e^{\pm i k(x+a)} \cdot u_k(x) = e^{\pm i k x} \cdot e^{\pm i k a} \cdot u_k(x) = [e^{\pm i k x} \cdot u_k(x)] \cdot e^{\pm i k a} = e^{\pm i k a} \cdot \Psi(x)$$

## THE KRONIG-PENNEY MODEL:

Kronig and Penney examined the behavior of electrons in a periodic potential by considering a relatively simple and one-dimensional model. It is assumed that the potential energy of an electron has the shape of a square well as shown in fig. The period of potential is (a+b)



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

The Schrodinger equations for two cases are-

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{for } 0 < x < a \quad 1$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V_0] \psi = 0 \quad \text{for } -b < x < 0 \quad 2$$

If  $V_0 > E$  and  $\alpha, \beta$  are real quantities then equations (1) and (2) will become-

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{for } 0 < x < a \quad 3$$

$$\frac{d^2\psi}{dx^2} + \beta^2 \psi = 0 \quad \text{for } -b < x < 0 \quad 4$$

$$\text{where } \alpha^2 = \frac{2m}{\hbar^2} E$$

$$\text{And } \beta^2 = \frac{2m}{\hbar^2} [V_0 - E]$$

Since the potential is periodic, so the solution of eq. (3) and (4) must be of the form of Bloch functions i.e.

$$\Psi(x) = u_k(x) e^{ikx}$$

Where  $u_k(x)$  is the periodic function  $x$  with period  $(a+b)$

$$\text{since, } \frac{d\psi}{dx} = ik e^{ikx} u_k(x) + e^{ikx} \frac{du}{dx}$$

Therefore, equations (3) and (4) can be written as-

$$\frac{d^2u}{dx^2} + 2ik \frac{du}{dx} + (\alpha^2 - k^2)u = 0 \quad \text{for } 0 < x < a \quad 5$$

$$\frac{d^2u}{dx^2} + 2ik \frac{du}{dx} - (\beta^2 - k^2)u = 0 \quad \text{for } -b < x < 0 \quad 6$$

The solutions of these equations are,

$$u_1 = A e^{i(\alpha-k)x} + B e^{-i(\alpha-k)x} \quad \text{for } 0 < x < a \quad 7$$

$$u_2 = C e^{i(\beta-ik)x} + D e^{-i(\beta+ik)x} \quad \text{for } -b < x < 0 \quad 8$$

where A, B, C and D are constants.

These constants can be determined in such a way that the wave function  $\Psi$  and its derivative  $\frac{d\psi}{dx}$  are single valued and continuous.

$$u_1(0) = u_2(0), \quad \& \quad u_1(a) = u_2(-b)$$

$$\left. \frac{du_1}{dx} \right|_{x=0} = \left. \frac{du_2}{dx} \right|_{x=0} \quad 9$$

$$\left. \frac{du_1}{dx} \right|_{x=a} = \left. \frac{du_2}{dx} \right|_{x=-b} \quad 10$$

Using these boundary conditions in equations (7) and (8) we get,

$$A + B = C + D$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik)$$

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

$$Ai(\alpha - k)e^{i(\alpha - k)a} - Bi(\alpha + k)e^{-i(\alpha + k)a} = C(\beta - ik)e^{-(\beta - ik)b} - D(\beta + ik)e^{(\beta + ik)b}$$

These equations have non-zero solutions if the determinant of the coefficients A, B, C and D vanishes. That is-

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) & (\beta - ik) & (\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{-(\beta - ik)b} & e^{(\beta + ik)b} \\ i(\alpha - k)e^{i(\alpha - k)a} & -i(\alpha + k)e^{-i(\alpha + k)a} & (\beta - ik)e^{-(\beta - ik)b} & -(\beta + ik)e^{(\beta + ik)b} \end{vmatrix} = 0 \quad (11)$$

On expanding this determinant and after simplification, we get-

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \cdot \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a + b) \quad \dots (12)$$



In order to make the situation more simple, Kronig and Penney considered the height of the potential barrier is very large. i.e  $V_0 \rightarrow \infty$  and simultaneously the width of the barrier is very small  $b \rightarrow 0$  but the product  $V_0 b$  or  $\beta_2 b$  remains finite.

Within such limit,  $\lim_{\beta b \rightarrow 0} \frac{\sin \beta b}{\beta b} = 1$

equation (12) reduces to-

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

$$P \cdot \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad 13$$

Where the quantity P is defined as,

$$P = \frac{\beta^2 ab}{2} = \frac{2mV_0 ab}{2\hbar^2} = \frac{mV_0 ab}{\hbar^2} \quad 14$$

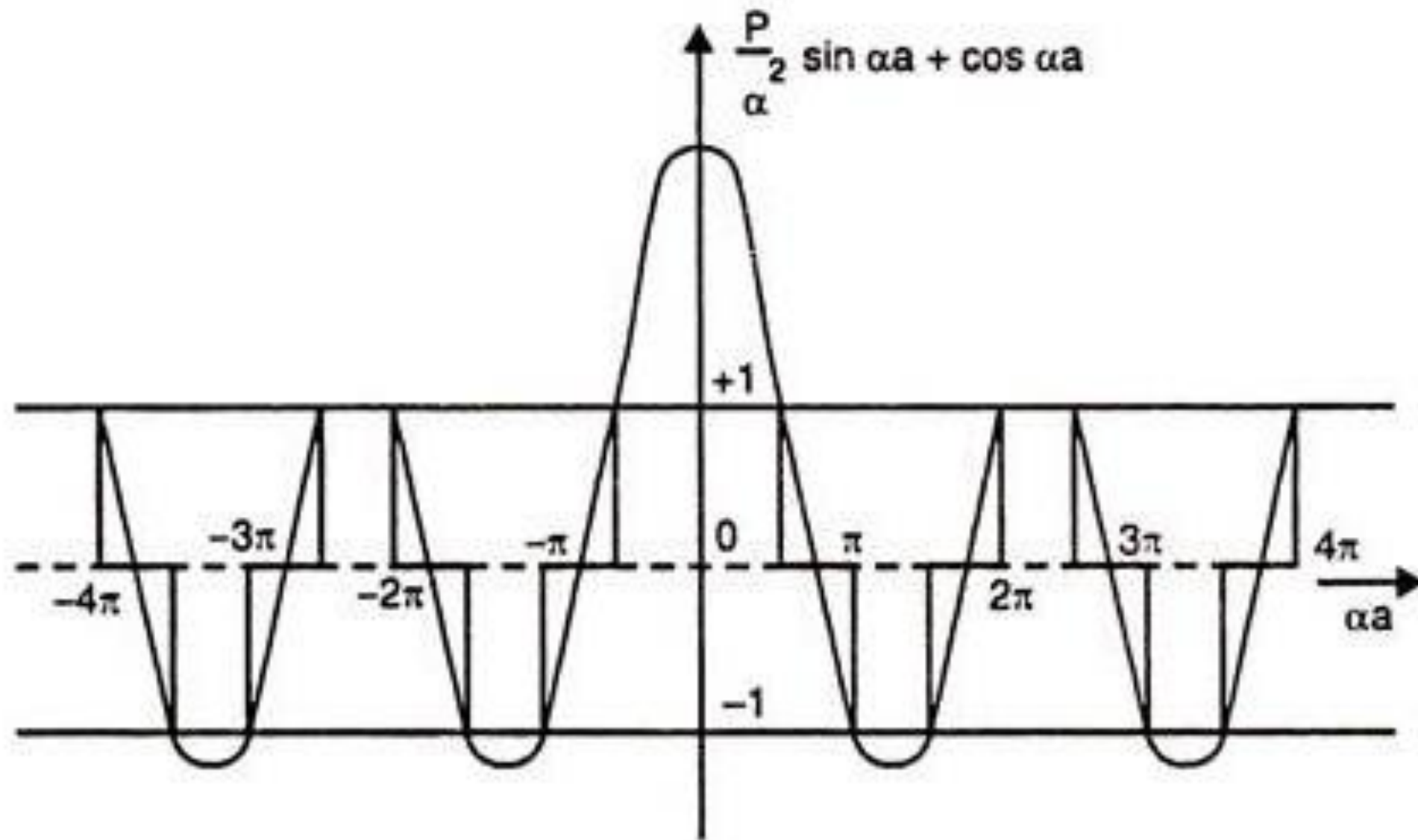
Since  $V_0 b$  measures the area of the potential well. So, if  $P$  increased, the area of the potential barrier is increased and the given electron is bound more strongly to a particular barrier is increased and the given electron is bound more strongly to a particular well. when  $P \rightarrow 0$ , the potential becomes very weak which means that electron are free. i.e. at  $P \rightarrow 0$

$$\cos \alpha a = \cos ka \quad \text{or} \quad \alpha = k$$

$$k^2 = \alpha^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad E = \frac{\hbar^2 k^2}{2m} \quad \text{is energy of free electron.}$$

From eq 13,  $\cos ka$  lies between +1 to -1. so,  $|\frac{P}{\alpha a} \sin \alpha a + \cos \alpha a| \leq 1$ . such value of  $\alpha a$ , represents wave like solution of the form  $\Psi(x) = u_k(x) \cdot e^{i k x}$  and are allowed values. The other values of  $\alpha a$  are not allowed.

The plot of  $|\frac{P}{\alpha a} \sin \alpha a + \cos \alpha a|$  as a function of  $\alpha a$  is shown in figure below.



**Plot of  $(P/\alpha a) \sin \alpha a + \cos \alpha a$  as a function of  $\alpha a$  using  $P = (3\pi/2)$ .**

The conclusions from the above figure are given below.

1. The energy spectrum of the electrons consists of energy bands allowed and forbidden.
2. The width of the allowed energy region or band increases with increasing values of energy.
3. Width of the allowed energy band decreases with the increasing the value of  $P$ . when  $P \rightarrow \infty$ , the allowed region becomes infinitely narrow and independent of  $k$ .

For  $P = 0$  the is energy spectrum is quasi-continuous and at  $P \rightarrow \infty$ , the energy spectrum is a line spectrum. For the intermediate value of  $P$ , the position and width of the allowed and forbidden bands are obtained by drawing a vertical line.

If one solves the radial part of the Schrodinger equation for the hydrogen atom, one obtains the radial part of the eigenfunction for the 1s state as  $\psi_{1s} = e^{\frac{-r}{r_0}}$

As two H atoms approach each other, the atomic wavefunction overlap. this overlapping of the wavefunction produces two new wavefunctions with different energies and hence different quantum numbers, the two eigenfunctions can overlap either in phase forming symmetric eigenfunction  $\psi_s = C (\psi_A + \psi_B)$  or in out of phase forming an antisymmetric eigenfunction  $\psi_a = C (\psi_A - \psi_B)$ .

## **Tight-Binding Approximation**

This method was first proposed by Bloch and also known as linear combination of atomic orbitals(LCAO).

The tight binding method is a semi-empirical method that is primarily used to calculate the band structure and single-particle Bloch states of a material.

The semi-empirical tight binding method is simple and computationally very fast.

This approximation is quite good for the inner electrons of the atoms, but it is not a good description of the conduction electrons themselves.

It is used to describe the d-bands of the transition metals and valance bands of diamond like and inner gas crystals.

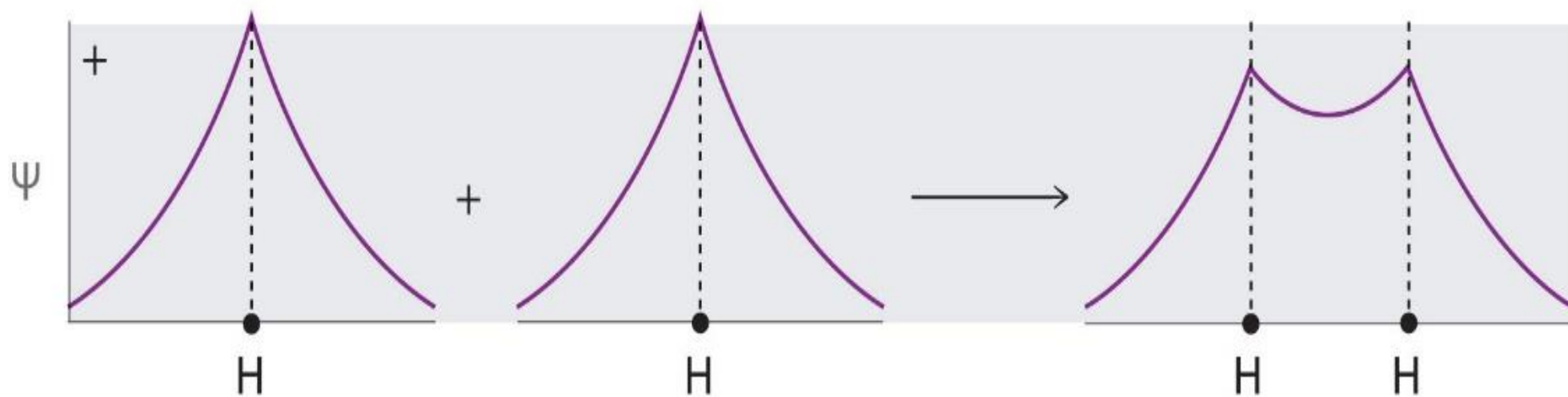
If one solves the radial part of the Schrodinger equation for the hydrogen atom, one obtains the radial part of the eigenfunction for the 1s state as  $\psi_{1s} = e^{-r/r_0}$ .

As two H atoms approach each other, the atomic wavefunction overlap. this overlapping of the wavefunction produces two new wavefunctions with different energies and hence different quantum numbers, the two eigenfunctions can overlap either in phase forming symmetric eigenfunction  $\psi_s = C (\psi_A + \psi_B)$  or in out of phase forming an antisymmetric eigenfunction  $\psi_a = C (\psi_A - \psi_B)$ .

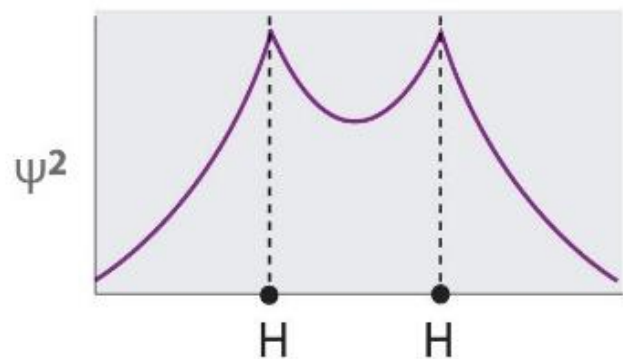
The figure given below shows that the probability function  $\psi_s^2$  is in the large region between two nuclei so the electron spends more time between both nuclei. In this region, it is under the attractive influence of both protons at once. The binding energy of the electron resulting from the presence of the two protons will be more negative than if it was only under the influence of one of them. Thus, when two atoms are brought together, two separate energy levels are formed from each level of the isolated atom. The physical reason for this effect is the differing ways that the electrons interact with the ions in the symmetric and antisymmetric states.

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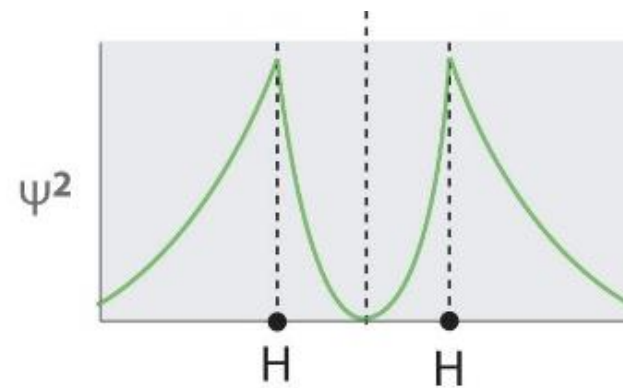




Combined wave function



Bonding probability density



Anti - bonding probability density

## Effective mass

In a crystal, the electron is moving under the influence of other electrons, the periodic potential of the lattice, and Phonons. Interaction of electrons with all of the above three modifies its mass, which is known as effective mass.

$$\text{Since } v_g = \frac{d\omega}{dk} = \frac{d}{dk} \left( \frac{E}{\hbar} \right) = \frac{1}{\hbar} \frac{dE}{dk} \quad 1$$

When electric field  $\varepsilon$  is applied to accelerate electron then work done  $dw$  on a particle is energy of the particle increases by the electric field at time  $dt$ ,

$$dE = F \cdot dx = F \cdot v_g \cdot dt$$

$$F = \frac{1}{v_g} \frac{dE}{dt} = \frac{1}{\left( \frac{1}{\hbar} \frac{dE}{dk} \right)} \cdot \frac{dE}{dt} = \hbar \cdot \frac{dk}{dt} \quad 2$$

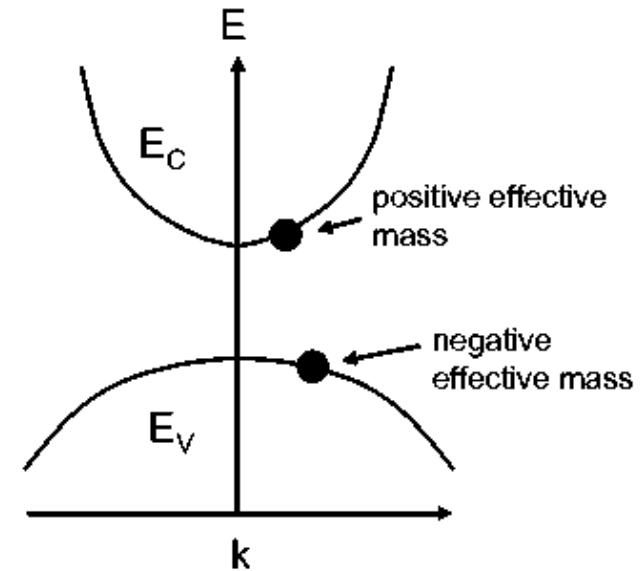
$$F = m^* a = m^* \frac{dv_g}{dt} = m^* \frac{d}{dt} \left( \frac{1}{\hbar} \frac{dE}{dk} \right) = m^* \frac{d}{dk} \left( \frac{1}{\hbar} \frac{dE}{dk} \right) \frac{dk}{dt} \quad 3$$

$$F = m^* a = m^* \frac{1}{\hbar} \frac{dE^2}{dk^2} \frac{dk}{dt} \quad 4$$

from 2, 4

$$\hbar \cdot \frac{dk}{dt} = m^* \frac{1}{\hbar} \frac{dE^2}{dk^2} \frac{dk}{dt} \quad 5$$

$$m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}} \text{ is the expression of effective mass}$$



E-k diagram with different surface curvatures for conduction band and valence band

The effective mass is determined by the radius of curvature of the E-k curve at a given energy level, i.e. the effective mass varies with k value. When the E-k curve is concave as the shape of conduction band, the effective electron mass is positive, whereas, when it is convex as the shape of valence band, the effective electron mass is negative. This means that an electron in the valence band will be accelerated by the field as if it is a positively charged particle and mass.

## **Distinguish between metals, semiconductors and insulators on the basis of band theory**

**Valance band** - The band of energy occupied by the valance electrons is called the valence band. The electrons in the outermost orbit of an atom are known as valance electrons. This band may be completely or partially filled. An electron can be moved from one valance band to the conduction band by the application of external energy.

**Conduction band** The band of energy occupied by the conduction electrons is called the conduction band. This is the uppermost band; all electrons in the conduction band are free. The conduction band is empty for insulators and partially filled for conductors.

**Forbidden Energy Gap or Forbidden band** The gap between the valance band and conduction band on the energy level diagram is known as the forbidden band or energy gap. Electrons are never found in the gap. Electrons may jump back and forth from the bottom of the valance band to the top of the conduction band. But they never come to rest in the forbidden band.

**Conductors** - There is no forbidden gap and the conduction band and valence band are overlapping each other between and hence electrons are free to move about. Examples are Ag, Cu, Fe, Al, Pb .... They have high electrical conductivity. So, in general, the electrical resistivity of the conductor is very low and it is of the order of  $10^{-6} \Omega \text{ cm}$ . Due to the absence of the forbidden gap, there is no structure for holes. The total current in the conductor is simply a flow of electrons. For conductors, the energy gap is of the order of 0.01 eV.

**Semiconductors** - Semiconductors are materials whose electrical resistivity lies between insulator and conductor. Examples are silicon (Si), and germanium (Ge) ....The resistivity of semiconductors lies between  $10^{-4} \Omega \text{ cm}$  to  $10^3 \Omega \text{ cm}$  at room temperature. At low temperature, the valence band is all most full and conduction band is almost empty. The forbidden gap is very small equal to 1 eV. Semiconductor behaves like an insulator at low temperature. The most commonly used semiconductor is silicon and its band gap is 1.21 eV and germanium band gap is 0.785 eV.

**Insulators** – In an insulator, the valence band is full but the conduction band is totally empty. So, free electrons from the conduction band are not available. In insulator the energy gap between the valence and conduction band is very large and it is approximately equal to 5 eV or more. Hence electrons cannot jump from valence band to the conduction band. So, very high energy is required to push the electrons to the conduction band. The electrical conductivity is extremely small. The resistivity of insulator lie between  $10^3$  to  $10^{17} \Omega \text{ m}$ , at room temperature □ Examples are plastics, paper

