

2 Bonding and Band theory of Solids

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Introduction

In crystalline solids atoms are arranged periodically, but question arises which force bound the atom together, gravitational, electrostatic, nuclear or weak forces.

Gravitational force bound the masses such as stars and planets. This force depend upon the mass the body. The nuclear forces bound nucleons (protons and neutrons). For binding the atom together electrostatic forces play important role. valence electrons are responsible for binding the atom together. In some crystals bond is form betⁿ the molecules even if the orbit is complete in atom. An attractive interatomic forces holds the atom together. This attractive force balance to the repulsive force and the crystal become stable. The energy of crystal is lower than that its free atom i.e. the crystal is more stable than that the collection of atoms. To separate these atoms from crystal energy is required. The amount of energy is required to pull the crystal apart into set of free atoms is called cohesive energy.

concept of Interatomic Forces

The forces between the atoms can be of two kinds: Attractive forces which keep the atoms together, and repulsive forces which come into play when the solid is compressed. The potential or stored internal energy of a material is the sum of the individual energies of the atoms plus their interaction energy.

When the atoms are all in the ground state and infinitely far apart so they do not interact each other to form a solid, the pot. energy is zero.

Since this is inversely proportional to some power of the distance of separation.

Assuming that the atom consist of moving electrical charges, one of the following two things can be happened.

As the atoms approach each other either they attract or repelled each other.

The P.E. due to attraction is negative, since the atoms do the work of attraction. The repulsive energy is positive, since external work must be done to bring the atoms together and it is inversely proportional to some power of the interatomic separation r . The net P.E. is the sum of both the terms. This may be consider by using following model.

Suppose two atoms A & B exert attractive and repulsive forces on each other such that the bonding force F betⁿ. the atoms may be represented as

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \quad \text{where } N > M \quad \text{--- (1)}$$

where r is the center to center spacing and A, B, M & N are constants characteristics of molecules. The first term represent the attractive force and the second term the repulsive force.

Near the equilibrium position the second term increases more rapidly for decreasing the value of r than the first term $N > M$

The equilibrium spacing r_0 of the given system is obtained as follows

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N}$$

At the equilibrium spacing

$$F(r) = 0 \quad \text{when } r = r_0$$

thus

$$0 = \frac{A}{r_0^M} - \frac{B}{r_0^N}, \quad \frac{A}{r_0^M} = \frac{B}{r_0^N}$$

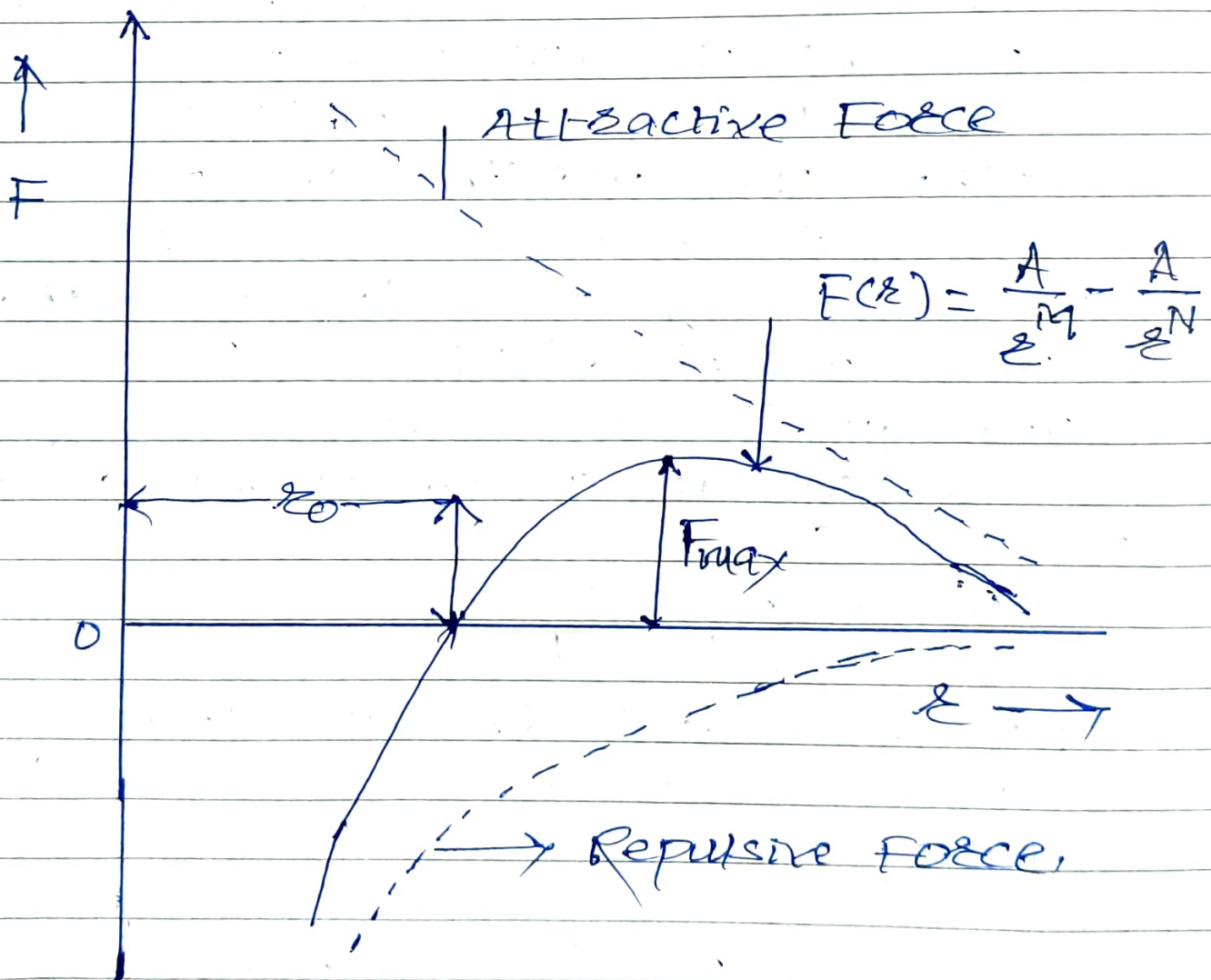
$$\frac{A}{r_0^M} = \frac{B}{r_0^N} \Rightarrow \frac{r_0^N}{r_0^M} = \frac{B}{A}$$

$$\sum_0^{N-m} = \frac{B}{A}$$

$$\sum_0^{N-m} \times \frac{1}{N-m} = \left(\frac{B}{A} \right)^{N-m}$$

$$\sum_0 = \left(\frac{B}{A} \right)^{\frac{1}{N-m}} \quad \text{--- (2)}$$

Fig. Variation of interatomic force with interatomic spacing.



Cohesive Energy and its calculations

The potential energy representing the interaction between two atoms varies greatly with the interatomic spacing and is obtained by integrating equation (1)

$$U(z) = \int F(z) dz$$
$$= \int \left[\frac{A}{z^M} - \frac{B}{z^N} \right] dz \quad \text{--- (1)}$$

$$= \int \left[A z^{-M} - B z^{-N} \right] dz$$

$$= A \frac{z^{-M+1}}{-M+1} - B \frac{z^{-N+1}}{-N+1} + C$$

$$= A \frac{z^{1-M}}{1-M} - B \frac{z^{1-N}}{1-N} + C$$

$$= - \left[\frac{A}{M-1} \right] \left[\frac{1}{z^{M-1}} \right] + \left[\frac{B}{N-1} \right] \left[\frac{1}{z^{N-1}} \right] + C$$

Let

$$a = \frac{A}{M-1} \quad b = \frac{B}{N-1}$$

$$m = M-1 \quad n = N-1$$

setting $U=0$ when $z=\infty$ we find $C=0$

$$U(z) = - \frac{a}{z^m} + \frac{b}{z^n} + C \quad \text{--- (2)}$$

$U=0, z=\infty \therefore C=0$ we get

$$0 = - \frac{a}{z^m} + \frac{b}{z^n}$$

$$0 = -\frac{a}{\infty^m} + \frac{b}{\infty^n} + C$$

$$\therefore C = 0$$

keeping $C = 0$ in eq. (2)

$$U(z) = -\frac{a}{z^m} + \frac{b}{z^n} \quad \text{--- (3)}$$

Here

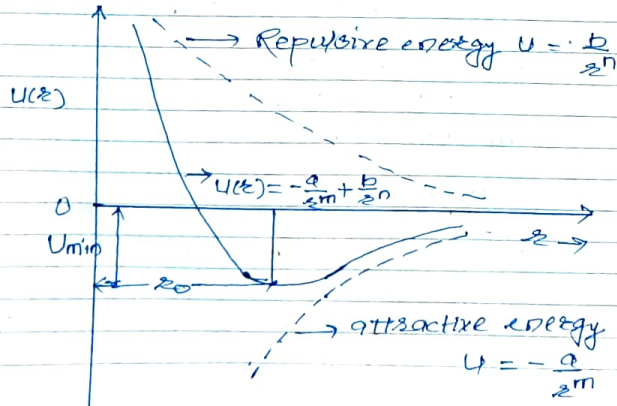
z - distance between centers of atom,

m, n - positive integers.

a - negative constant which deter-
-mine strength of attractive force

b - positive constant which
determine strength of repulsive
force.

The condition under which the parti-
-cles forms a stable lattice is that the
function $U(z)$ shows a minimum for
a finite value of z as shown in fig.
below. If this minimum exist then
the two atoms forms a stable lattice,
say a molecule.



The z_0 is the distance between two
atoms for this minimum $U(z)$ to
occur. This spacing z_0 is known
as equilibrium spacing of the system.

Calculation of Cohesive Energy

The energy corresponding to the equilibrium position ($r = r_0$) denoted by $U(r_0)$ is called binding energy or energy of cohesion of the molecule. This is the energy required to dissociate the two atoms of molecule into an infinite separation. This energy is also known as energy of dissociation. It is obtained as follows.

We know

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n}$$

$U(r)$ will be minimum when $r = r_0$
Thus,

$$U(r)_{\min} = -\frac{a}{r_0^m} + \frac{b}{r_0^n} \quad \text{--- (1)}$$

Hence

$$\left(\frac{dU}{dr}\right)_{r=r_0} = 0, \quad r = r_0$$

$$\left(\frac{dU}{dr}\right)_{r=r_0} = 0 = \frac{am}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

$$\frac{am}{r_0^{m+1}} = \frac{bn}{r_0^{n+1}}$$

$$\frac{r_0^{n+1}}{r_0^{m+1}} = \frac{bn}{am}$$

$$r_0^{n+1-m-1} = \frac{b}{a} \cdot \frac{n}{m}$$

$$r_0^{n-m} = \frac{b}{a} \cdot \frac{n}{m}$$

$$U(r_0) = -a r_0^{-m} + b r_0^{-n}$$

$$\frac{dU}{dr} = 0 \text{ at } r = r_0$$

$$= -a(-m)r_0^{-m-1} + b(-n)r_0^{-n-1}$$

$$= \frac{am}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

$$\frac{n}{z_0} \frac{-m}{z_0} = \left(\frac{b}{a}\right) \left(\frac{n}{m}\right)$$

multiply by z_0^m on both side we get

$$z_0^n = z_0^m \cdot \left(\frac{b}{a}\right) \cdot \left(\frac{n}{m}\right) \text{ --- (2)}$$

Substitute this value in equation (1)

$$U(z)_{\min} = -\frac{a}{z_0^m} + \frac{b}{z_0^m \left(\frac{b}{a}\right) \left(\frac{n}{m}\right)}$$

$$= -\frac{a}{z_0^m} + \cancel{a} \times \frac{a}{\cancel{b}} \cdot \frac{m}{n} \cdot \frac{1}{z_0^m}$$

$$= -\frac{a}{z_0^m} + \frac{m}{n} \frac{a}{z_0^m}$$

OR

$$= -\frac{a}{z_0^m} + \frac{m}{n} \cdot \frac{a}{z_0^m}$$

$$U(z)_{\min} = \frac{a}{z_0} \cdot \frac{m}{n} - \frac{a}{z_0^m}$$

$$= -\frac{a}{z_0^m} \left[1 - \frac{m}{n} \right] \text{ --- (3)}$$

$U(z)_{\min}$ is the amount of energy required to separate two atoms to an infinite distance, so this is called binding energy or cohesive energy of an atoms.

Ex - 4.4 eV energy is required to break one H-Cl bond.

Cohesive Energy and Types of Bonding

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The minimum potential energy required to separate the two atoms is called cohesive energy. The same amount of energy is released when the two such atoms brought closer to each other upto equilibrium distance.

Dissociation energy = Binding energy.

More stable the bond or more stable the crystal structure then amount of energy required to break bond is greater.

In crystal an atom is surrounded by more than one atom, which may be arranged such that they form different structure.

The most probable structure is that in which maximum amount of energy is released and that is a stable structure.

Valance electrons play very important role in bond formation for some crystals.

Valance electrons are present in unstable atoms. Tendency to complete octet rule is responsible for bond formation in some crystal. In this process some atom share electron, some gain or loose electrons and form atomic bond. In some crystal octet is complete but still the bond is form in the form of molecular bond. According to strength of bond or cohesive energy bonds are of two types they are primary bonds and secondary bonds.

The primary bond is the strong bond having cohesive energy in the range of $1 \rightarrow 10$ eV/atoms. This bond is interatomic

in nature due to valance electrons.

co-valent bond; ionic bond and metallic bond are the examples of inter-atomic ~~of~~ primary bonding.

Secondary bonds are intermolecular bond having cohesive energy in the range of $0.01 - 0.5$ eV/atom.

Van der waals and hydrogen bond are the examples of secondary bonds.

The ionic bond

Ionic bond is ~~from~~ the simplest type of chemical bonding and it is electrostatic in nature. It occurs between electropositive element (metal) and electronegative element (non-metal) eg - NaCl, MgO

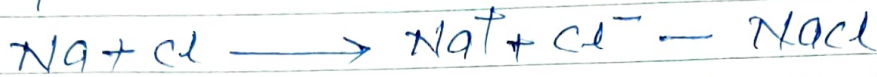
In ionic bond attractive force exist between a positive and negative ions, when they are brought close to each other. Ionic bonds are formed when the atoms involved in lose or gain electrons in order to stabilise their outer shell electronic configuration.

A typical example of an ionic bond is the bond between positive sodium ion and negative chlorine ion in sodium chloride.

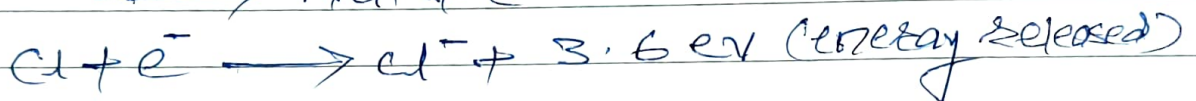
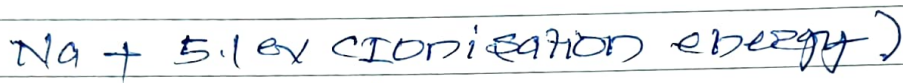
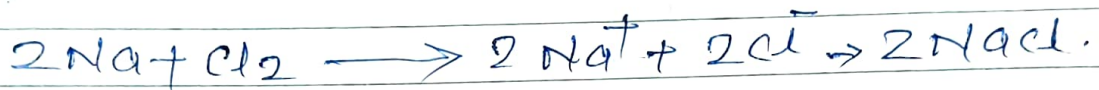
The sodium atom has following electronic configuration 2, 8, 1. This atom has low ionisation energy and hence easily lose an electron. The other atom chlorine, 2, 8, 7 has high electron affinity and strongly tend to acquire an electron.

Suppose a sodium atom and chlorine atom approach each other. The sodium atom give up its valance electron to the chlorine, each of the resulting ions then has a stable filled shell of outer electrons, and a strong electrostatic attraction is set up that bonds the Na^+ and Cl^- anion into a very

Stable molecule (NaCl) at the equilibrium spacing. This reaction is represented by

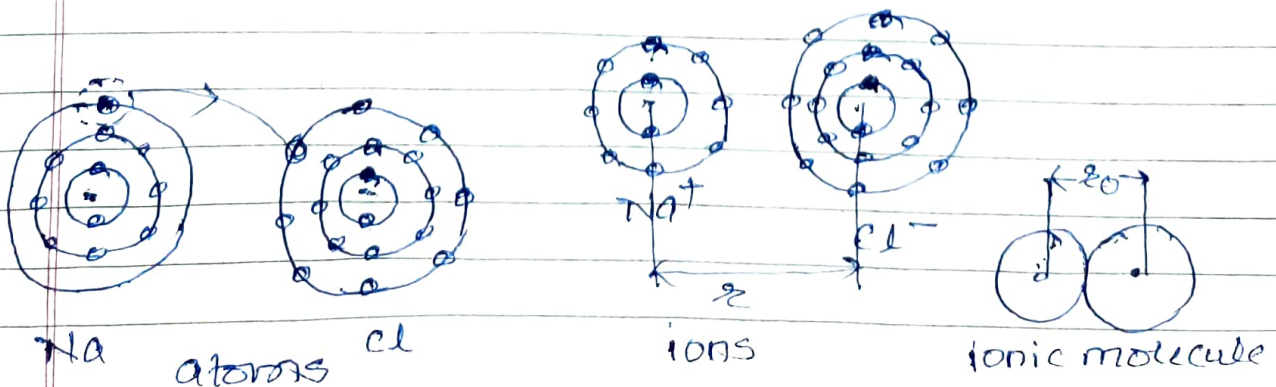


Since chlorine exist as molecule the chemical reaction must be written as



electron affinity

Thus net energy $5.1 - 3.6 = 1.5 \text{ eV}$ is spent in creating Na^+ & Cl^- ions. What happens when the electrostatic attraction between Na^+ & Cl^- bring them together to the equilibrium spacing $r_0 = 0.24 \text{ nm}$. At the equilibrium position the potential energy will be minimum and energy release in the formation of NaCl molecule is called bond energy of molecule. Schematic representation of formation of sodium chloride molecule.



Properties of ionic solids

- * All ionic compounds are rigid and crystalline in nature.
- * Ionic solids have high m.p and B.P.
The ionic bonds are fairly strong.
- * Pure dry ionic compound is insulator because non availability of free electrons, however in the solution they conduct electricity because movement of charge ions instead of free electrons.
- * Ionic solids are easily soluble in polar solvent like water but it is insoluble in non polar solvent like benzene (C_6H_6), carbon tetrachloride (CCl_4) etc.

Covalent Bond -

The covalent bond is formed by sharing a pair of valence electrons between like atoms rather than by electron transfer.

Eg. chlorine molecule, H_2 etc

In the outer shell of each atom of chlorine have seven electrons. Each atom would like to gain an electron, and thus form a stable octet. This can be done by sharing two electrons between pairs of chlorine atoms, thereby producing stable diatomic molecules. In other words, each atom contributes one electron for the sharing process.

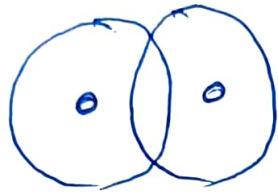
Fig. Molecular orbital formation from orbitals

(a) two isolated atomic orbitals

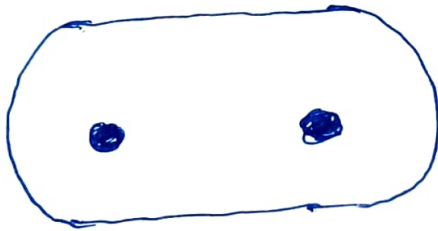
(b) overlap (c) the molecular orbital



(a)



(b)



(c)

✓ Consider another example of covalent bond in case H_2 molecules. When two isolated H atoms, each with its electron in the ground state '1s' orbital approach each other, the 1s clouds begin to overlap. Each electron is attracted to the other nucleus and the overlap increases. The two atomic orbitals merge into

2
a molecular orbital. Within the molecular orbital the two electrons are attached to both nuclei. When the repulsive force balance the attractive forces within a molecule results, having stability greater than that of the two isolated atoms.

The covalent bond is known as homopolar or electron-pair bonding. ✓

In the molecular orbital of H_2 , the two electrons are equally shared between the nuclei and can not be specifically identified with either nucleus.

Two shared electrons are more likely to be found between the two nuclei and thus the electron density is

relatively large.

The balance between attractive and repulsive force in the hydrogen molecule occurs at a separation of 0.074 nm . Hence some energy must be spent to break the covalent bond in hydrogen molecule into hydrogen atoms. About 4.5 eV energy is required to break one $\text{H}-\text{H}$ bond. Thus



~~The covalent bond in H_2 and Cl_2 is indicated as follows.~~

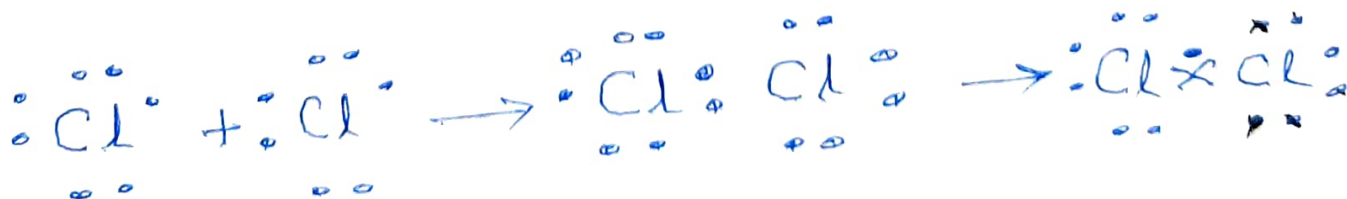
A covalent bond is usually indicated by showing two electrons between the symbols for the atoms

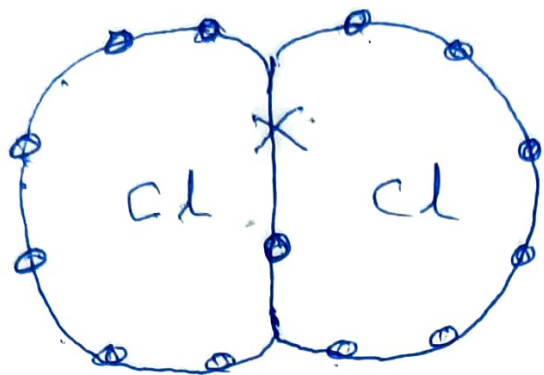


It is desired to make clear that one electron has come from each atom, they may be indicated as



• electron has come from the atom to the left and \times electron has come from the atom on the right. The actual bond generally represented as $\text{H}-\text{H}$ Thus,





In the chlorine molecule, each atom of chlorine has seven electrons in outer shell. When two atoms of chlorine tend to form chlorine molecule, one electron from each atom is shared with the other.

Properties of Covalent Bonds (Compounds)

- 1) The covalent compounds are mostly gases (Cl_2 , H_2 , O_2 , F_2 etc) and liquid (H_2O , HCl , HBr , HI , CH_4 etc) some compounds are Si , Ge , diamond, Graphite ^{solids} etc.
- 2) These crystals are hard and brittle
- 3) Having low m. P. and B. P. as compared to ionic solids
- 4) Due to lac of electrons most of covalent compounds are bad conductor of electricity
- 5) Soluble in non-polar solvent like benzene, carbon disulphide etc. but insoluble in polar solvents like water.

Prop. of metallic bond -

1. Due to weak bonding as compared to ionic and covalent so m.p. is moderate
2. Due to free electron cloud metallic crystals have high electrical and thermal conductivity
3. Incident energy is absorbed by free electrons so metals are opaque to light.
4. These solids have optical reflection and absorption coefficient.
5. Metals may be deformed easily because free electron gas acts as a lubricant to slide atomic layer

(ductile), (malleable)

Bond energy . 0.7 eV/atom
 melting point -39°C
 eg. Mercury.

Bond energy
 8.8 eV/atom
 m.p. 3610°C
 eg tungsten.

Metallic Bonding
 (Electron sea theory)

metallic bond - free moving electrons

Ionic bond NaCl \rightarrow non metal.

\downarrow metal

Covalent bond - Cl_2
 H_2 .

malleable - malle into different shape

ductile \rightarrow can pull wire
 (shape of wire)

eg copper.

m.p. & B.P. - High

(Free flow - Floating electrons)

luster -

Rigid

low ionisation energy (metal)

electron negativity low.

electron sea theory

Na⁺

K⁺

=

electron sea theory
 electron gas

Metallic Bond

In some respect metallic bond is similar to covalent bond. In covalent bond shared electrons are bound to particular atoms, but in metallic bond is formed partial sharing of valence electrons with atoms. These shared electrons are not bound to particular atom and are delocalized

having freedom to move anywhere in the space between positive ions core. Atoms in a metal share their electrons to form common cloud of electrons. These are called free electron gas. Atoms form bond with this common cloud of electrons to complete their octet.

Ex - If we consider the Lithium (Li) atom whose electronic configuration is $1s^2 2s^1$ (Li atomic number 3) means its valency is one and just requires one electron to complete its octet. So when two Lithium atoms come close together they form covalent bond but if third

lithium atom come near to this Li_2 molecule then it may also form bond without violating Pauli's exclusive principle so this bond is called unsaturated bond.

metallic bond is less directional than covalent bond

This is primary type of bonding having cohesive energy in the range $1-5 \text{ eV/atom}$. So this bond is weaker as compare to ionic and covalent bond.

Properties of Metallic bond.

1. Due to weak bonding as compared to ionic and covalent so melting point is moderate.
2. Due to free electron cloud, metallic crystal have high electrical and thermal conductivity.
3. Incident energy is absorbed by free electrons so metals are opaque to light.
4. These solids have high optical reflection and absorption coefficient.
5. Metals may be deformed easily because free electron gas acts as a lubricant to slide atomic layer.

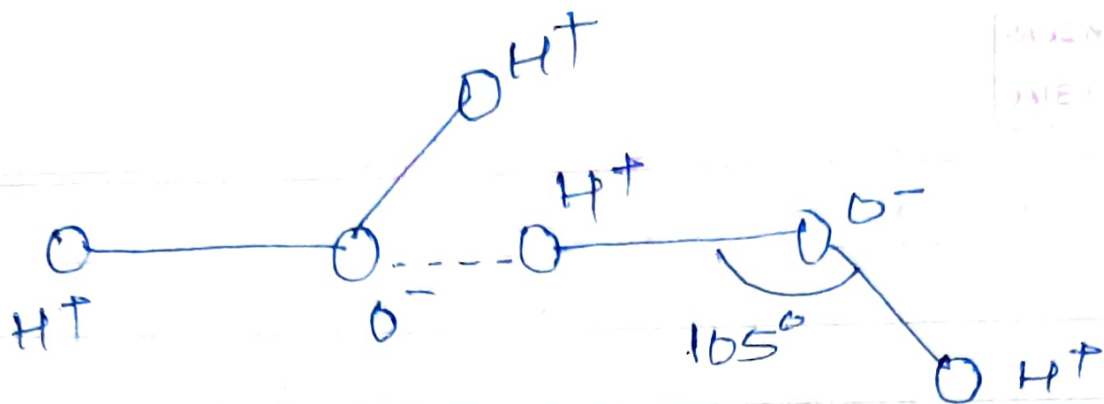
Secondary Bond.

Hydrogen Bond.

This is secondary type of bonding having cohesive energy in the range $0.1 \rightarrow 0.5$ eV/atom. This is also called as special type of dipole bond or molecular bond.

Ex - Hydrogen bond in water molecule

The covalent bond is formed between two oxygen and one hydrogen atom. In such a water molecule shared electron pair are more attracted towards the oxygen atom than hydrogen atom. So oxygen become more electronegative and hydrogen atom acquired more positive charge. So water molecule get polarised and behave like dipole. Number of such water dipoles are attracted towards each other. So this is also called as dipole bond. This bond is mainly formed due to improper shielding of electron: as shown in figure



Hydrogen bond play important role in the formation of ice and water. This bond is directional in characters. Similar type of bond is form in HF, HBr, HCl, SO₂ etc. When hydrogen atom bonded to relatively large atom such as oxygen, nitrogen, fluorine then hydrogen atom is not shielded properly by electrons and form permanent dipole which is responsible for dipole bond.

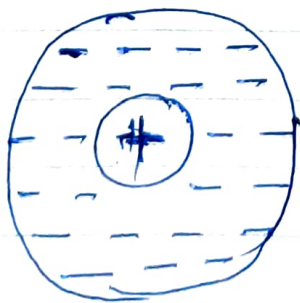
Van der Waal's Bond

This type of bond exist in inert atoms like He, Ne, Ar, Cr or molecule like O_2 , Cl_2 , CO_2 , CH_4 etc. In these atoms or molecules their outermost shell is completely filled, but still they form secondary type of bond with each other.

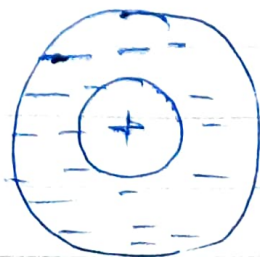
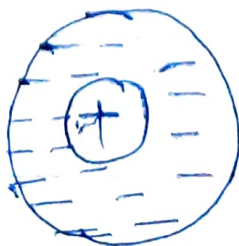
To understand this consider the examples of inert gases which are electrically neutral, not having tendency to share, loose or gain electron.

Fig.

Symmetrical electron cloud



Fluctuating dipoles



If the electrons distributed symmetrically then center of gravity of positive nucleus and negative charge electrons cloud coincides but when the electrons revolve around the nucleus their symmetry is get disturbed such that their center of gravity due to positive charge nucleus and negatively charge electron cloud is not matched and atom behave like fluctuating dipole. So two such dipoles attracts each other and form weak bond as shown in figure. Such a bond is called van der waals bond. To break this bond energy required is just $0.02 - 0.1$ eV/atoms. These solids have very low m.p & B.P. They get easily deformed and having weak mechanical strength. These materials are weak conductors of heat and electricity. This bond is also called dispersion bond. These materials are transparent to electromagnetic radiation.

The KRONIG-PENNY MODEL

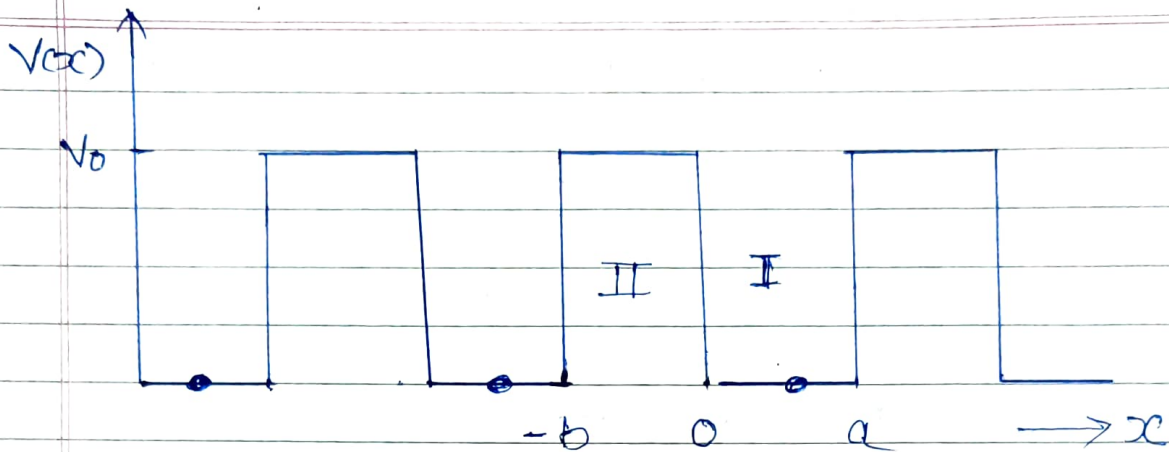


Fig. Ideal periodic square well potential suggested by Kronig and Penny

The properties of the behavior of electrons in one dimensional periodic potential given by Kronig and Penny in 1931. It has been assumed that the potential energy remains zero in the region $0 < x < a$ and potential energy remains V_0 in the region $-b < x < 0$. The Schrodinger equation for two regions are

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

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

Let the energy of electron is less than V_0 now putting

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

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

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

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

Now equation (1) & (2) can be written as

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

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad \text{FOR } -b < x < 0 \quad \dots \dots (4)$$

The solution of equation (3) & (4) should be Bloch function of the form

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

on differentiating we get

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

$$\frac{d^2\psi}{dx^2} = e^{ikx} (ik \cdot ik u(x)) + e^{ikx} ik \cdot \frac{du}{dx}$$

$$+ e^{ikx} ik \cdot \frac{du}{dx} + e^{ikx} \cdot \frac{d^2u}{dx^2}$$

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

putting these values in eqⁿ (3) & (4) we get

$$-k^2 e^{ikx} u(x) + 2ik e^{ikx} \frac{du}{dx} + e^{ikx} \frac{d^2u}{dx^2} + \alpha^2 e^{ikx} u(x) = 0$$

or

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

$$-k^2 e^{ikx} u(x) + 2iPk e^{ikx} \frac{du}{dx} + e^{ikx} \frac{d^2u}{dx^2} - \beta^2 e^{ikx} u(x) = 0$$

$$\frac{d^2u}{dx^2} + 2iPk \frac{du}{dx} - (\beta^2 + k^2) u(x) = 0$$

$$\text{for } -b < x < 0 \quad \text{----- (6)}$$

Now to solve above differential equation
Let us assume the solution of the form

$$u = e^{mx}$$

$$\frac{du}{dx} = m e^{mx} \quad / \quad \frac{d^2u}{dx^2} = m^2 e^{mx}$$

keeping these value in equation (5)

$$m^2 e^{mx} + 2iPk m e^{mx} + (\alpha^2 - k^2) e^{mx} = 0$$

$$m^2 + 2iPk m + (\alpha^2 - k^2) = 0$$

$$m = \frac{-2iPk \pm \sqrt{(-4k^2 - 4(\alpha^2 - k^2))}}{2}$$

$$= \frac{-2iPk \pm \sqrt{-4k^2 - 4\alpha^2 + 4k^2}}{2}$$

$$= \frac{-2iPk \pm \sqrt{-4\alpha^2}}{2}$$

2

$$= \frac{-2iK \pm 2i\alpha}{2}$$

$$= -iK \pm i\alpha$$

$$= \pm i\alpha - iK$$

$$m_1 = i(\alpha - K), \quad m_2 = -i(\alpha + K)$$

similarly on substituting in equation (6) we get

$$m^2 e^{mz} + 2iK m e^{mz} - (\beta^2 + K^2) e^{mz} = 0$$

$$m^2 + 2iKm - (\beta^2 + K^2) = 0$$

$$\beta > 0, -\beta < z < 0$$

So that

$$m = \frac{-2iK \pm \sqrt{-4K^2 - 4[-(\beta^2 + K^2)]}}{2}$$

$$= \frac{-2iK \pm \sqrt{-4K^2 + 4\beta^2 + 4K^2}}{2}$$

$$= \frac{-2iK \pm 2\beta}{2} = -iK \pm \beta$$

$$m = \pm \beta - iK$$

$$m_1 = (\beta - iK), \quad m_2 = -\beta - iK$$

$$m_2 = -(\beta + iK)$$

Hence the general solution is

$$u_1 = Ae^{m_1 x} + Be^{m_2 x} \quad \text{for } 0 < x < a$$

$$= Ae^{i(\alpha - k)x} + Be^{-i(\alpha + k)x} \quad \text{--- (7)}$$

Similarly

$$u_2 = ce^{m_1 x} + de^{m_2 x}$$

$$= ce^{(\beta - ik)x} + de^{-(\beta + ik)x} \quad \text{--- (8)}$$

where A, B, c & d are the constants which can be determined by applying boundary condition.

$$u_1(x=0) = u_2(x=0)$$

$$\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0}$$

$$Ae^{i(\alpha - k) \cdot 0} + Be^{-i(\alpha + k) \cdot 0}$$

$$= ce^{(\beta - ik) \cdot 0} + de^{-(\beta + ik) \cdot 0}$$

$$Ae^0 + Be^0 = ce^0 + de^0$$

$$A + B = c + d \quad \text{--- (a)}$$

$$\text{and } Ae^{i(\alpha - k)x} + Be^{-i(\alpha + k)x}$$

$$= ce^{(\beta - ik)x} + de^{-(\beta + ik)x}$$

$$\text{at } x=0$$

$$A e^{i(\alpha-k)x} - B e^{i(\alpha+k)x}$$

$$= C e^{i(\beta-ik)x} - D e^{i(\beta+ik)x}$$

or

$$i(\alpha-k)A - i(\alpha+k)B$$

$$= (\beta-ik)C - (\beta+ik)D$$

----- (10)

and because of the periodicity of the function $u(x)$ at the values $x=a$ must be equal to those value at $x=-b$

$$u_1(x)_{x=a} = u_2(x)_{x=-b}$$

$$\left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=-b}$$

$$\therefore A e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a}$$

$$= C e^{-(\beta-ik)b} + D e^{(\beta+ik)b}$$

----- (11)

$$A e^{i(\alpha-k)a} \cdot i(\alpha-k) + B e^{-i(\alpha+k)a} \cdot -i(\alpha+k)$$

$$= C e^{-(\beta-ik)b} \cdot -(\beta-ik) + D e^{(\beta+ik)b} \cdot (\beta+ik)$$

$$i(\alpha-k)A \cdot e^{i(\alpha-k)a} - i(\alpha+k)B e^{-i(\alpha+k)a}$$

$$= (\beta-ik)C e^{-(\beta-ik)b} + (\beta+ik)D e^{(\beta+ik)b}$$

----- (12)

Now these four equations 9, 10, 11, & 12 have the solution only if the determinant of coefficient vanishes

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

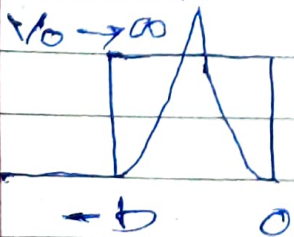
$$= 0 \quad \text{--- (13)}$$

This determinant after solving leads to the following equation.

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

$$= \cos k(a+b) \quad \text{--- (14)}$$

Equation (14) is complicated but a simplification is possible. Kronig-Penny consider the possibility that



as $b \rightarrow 0$ the $V_0 \rightarrow \infty$ but the product $V_0 b$ remains finite. Such a function is called delta function. Under these

circumstances,

$$\sinh \beta b \rightarrow \beta b$$

$$\cosh \beta b \rightarrow 1 \quad \text{as } b \rightarrow 0$$

Hence equation (14) becomes

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \cdot \beta b \sin \alpha a + \cos \alpha a = \cos \kappa a \quad (15)$$

Now

$$\beta^2 = \frac{2m}{\hbar^2} [V_0 - E], \quad \alpha^2 = \frac{2mE}{\hbar^2}$$

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

$$= \frac{2mV_0}{\hbar^2} - \frac{2mE}{\hbar^2} - \frac{2mE}{\hbar^2}$$

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

Since $V_0 \gg E$ then

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

Substituting this value in equation (15)

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

multiply & divide by αb

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

$$\left(\frac{mV_0 \alpha b}{\hbar^2} \right) \cdot \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos \kappa a$$

or

$$P \frac{\sin \alpha a + \cos \alpha a}{\alpha a} = \cos \alpha a \quad \text{--- (16)}$$

where $P = \frac{mV_0ab}{\hbar^2}$

the term V_0b is called barrier strength
the term $P = \frac{mV_0ab}{\hbar^2}$ in equation (16)

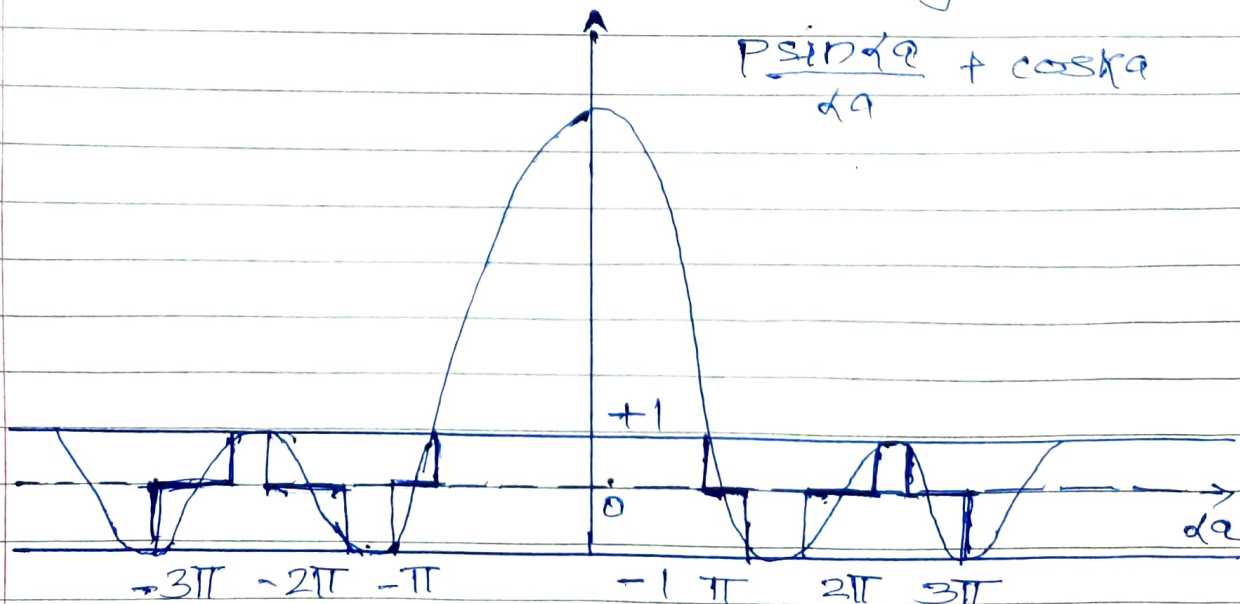
is some-time referred as scattering power of potential barrier.
It is a measure of the strength with which α electrons in a crystal are attracted to the ions on the crystal lattice sites.

also

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad E = \frac{\alpha^2 \hbar^2}{2m}$$

and $k = \frac{2\pi}{\lambda}$

The right hand side of equation (16) is bounded since it can assume values between +1 & -1. If we plot the left hand side of equation (16) against αa . The curve is shown in figure below



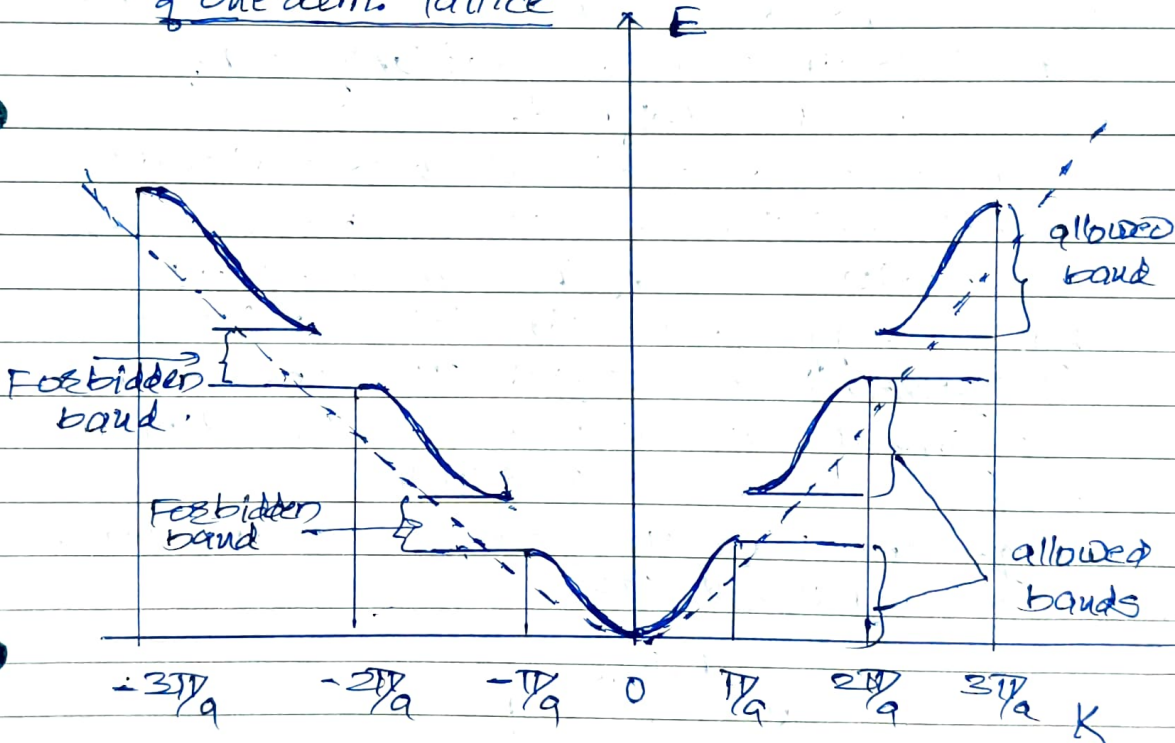
The following conclusion may be drawn from the above plot.

- 1) The energy spectrum consist of infinite number of allowed band separated by forbidden region.
- 2) when a is increases so the width of allowed band is increased and forbidden region becomes narrower.
- 3) when increasing value of P the width of allowed band decreases that is with increase the binding energy of electrons. when P is infinite the allowed energy band is infinitely narrow.

Bragg's zones

The electron moving in periodic potential lattice can have energy values only between allowed region or zones. It is possible to plot the total energy E of the electron versus the wave number or the propagation vector k and the plot is shown in figure

Fig. The relationship between energy (E) and wave number (k) of one dim. lattice



The right hand side of equation (16) in Kronig-Penney model becomes ± 1 for values of $k = \frac{n\pi}{a}$ and discontinuities

occur in the E versus k graph occur at $k = \frac{n\pi}{a}$ where n can take the

values of $\pm 1, \pm 2, \pm 3, \dots$. The dotted curve shows the free electron curve.

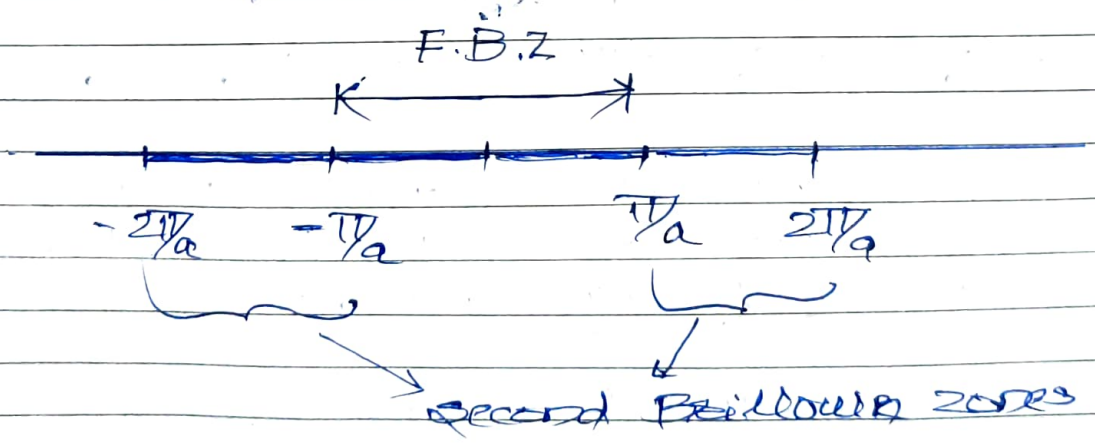
From the graph we see that the electron has allowed energy values in the region or zone extending

From $k = -\frac{\pi}{a}$ to $k = +\frac{\pi}{a}$

The zone is called First Brillouin zone. After a break in the energy values called the forbidden region or band or zone. We get another allowed zone of energy values in the region extending from $k = -\frac{\pi}{a}$ to $k = -\frac{2\pi}{a}$ and $k = +\frac{\pi}{a}$ to $k = +\frac{2\pi}{a}$. This zone is called second Brillouin zone. Similarly other zone can be defined.

In one dimensional monoatomic linear lattice a line representing the values of k is divided up by energy discontinuities into a segment of length $\frac{\pi}{a}$. These line segments are known as Brillouin zone.

Fig: The First two zones for one dimensional case.

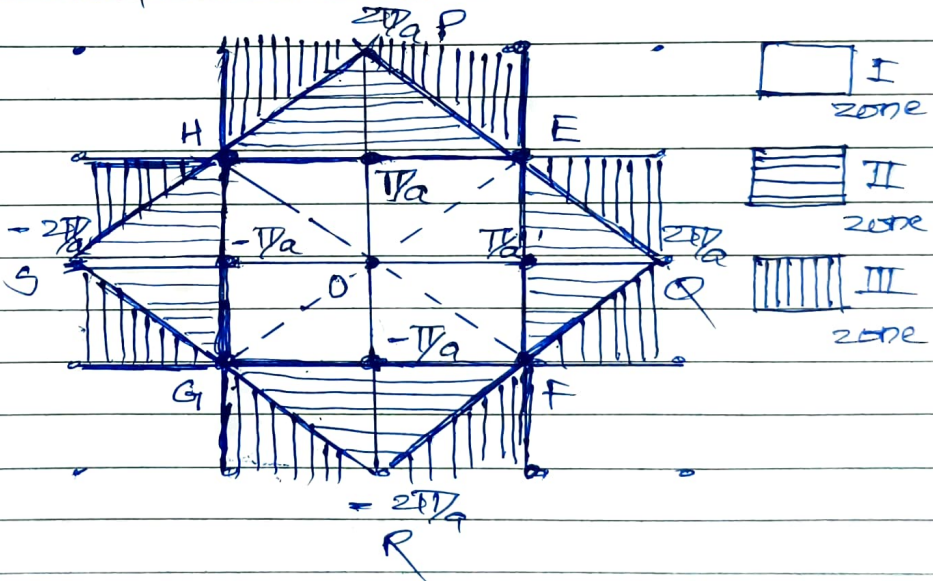


Although for many purposes only the first zone is sufficient but some time higher zone is desirable. The Brillouin zones are constructed from the plane which are perpendicular or bisectors of all

reciprocal lattice vectors that is we draw the vectors from origin to all other lattice points and then draw planes which bisect these vector perpendicularly. The first zone is the smallest volume about the origin enclosed by these planes and similarly the second zone is the volume between the first zone and next set of planes. For this consider two dimensional square lattice

Brillouin

Fig - The first three zones for two dimensional square lattice.



considering above different zones are constructed as follows

Take O as a origin and join O to a nearest lattice point take perpendicular bisectors of lattice vectors. These bisectors enclosed a square $EFGH$ is called first Brillouin zone. For second Brillouin zone again join the origin to next nearest lattice points. Take the mid points of E, F, G and H and draw perpendiculars

to these points. These perpendiculars -
-culars enclose a square PQRS

The area between PQRS and EFGH

represents second BELLOUIN ZONE

Similarly other zones can be
constructed.