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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – I - Condensed Matter Physics – SPHA5301

1. CRYSTAL BINDING

Forces between the atoms

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. For example a crystal of sodium chloride is more stable than a collection of free Na and Cl atoms. This implies that the Na and Cl atoms attract each other, i.e. there exist an attractive **interatomic force,** which holds the atoms together. This also implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy which is required to pull the crystal apart into a set of free atoms is called the *cohesive energy* of the crystal.

Cohesive energy = energy of free atoms – crystal energy

Magnitude of the cohesive energy varies for different solids from 1 to 10 eV/atom, except inert gases in which the cohesive energy is of the order of 0.1eV/atom. The cohesive energy controls the melting temperature .

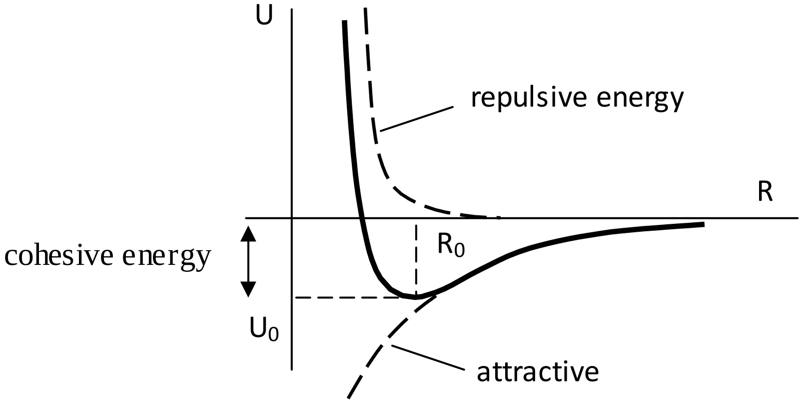

Fig.1

(Solid Curve is Resultant energy)

A typical curve for the potential energy (binding energy) representing the interaction between two atoms is shown in Fig.1. It has a minimum at some distance $R=R_0$.

Potential energy increases due to repulsion and decreases due to attraction.

For $R>R_0$ the potential decreases gradually, approaching 0 as R□ □, while for $R<R_0$ the potential increases very rapidly, tending to infinity at $R=0$. Since the system tends to have the lowest possible energy, it is most stable at $R=R_0$, which is *the equilibrium interatomic distance*. The corresponding energy U_0 is the cohesive energy.

A typical value of the equilibrium distance is of the order of a few angstroms (e.g. 2-3Å), so that the forces under consideration are short range.

The interatomic force is determined by the gradient of the potential energy (U), so that

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If we apply this to the curve in Fig.1, we see that $F(R)<0$ for $R>R_0$. This means that for large separations the force is *attractive,* tending to pull the atoms together. On the other, hand $F(R) > 0$ for $R<R_0$, i.e. the force becomes *repulsive* at small separations of the atoms, and tends to push the atoms apart. The repulsive and attractive forces cancel each other exactly at the point R_0, which is the point of equilibrium.

The attractive interatomic forces reflect the presence of bonds between atoms in solids, which are responsible for the stability of the crystal. There are several types of bonding, depending on the physical origin and nature of the bonding force involved. The four main types are: Van der Waals (or molecular) bonding, ionic bonding, covalent bonding and metallic bonding.

Although the nature of the attractive energy is different in different solids, the origin of the repulsive energy is similar in all solids. The origin of the repulsive force is mainly due to the Pauli exclusion principle. The elementary statement of this principle is that two electrons cannot occupy the same orbital. As ions approach each other close enough, the orbits of the electrons begin to overlap, i.e. some electrons attempt to occupy orbits already occupied by others. This is, however, forbidden by the Pauli exclusion principle. As a result, electrons are excited to unoccupied higher energy states of the atoms. Thus, the electron overlap increases the total energy of the system and gives repulsive contribution to the interaction.

Born Haber Cycle

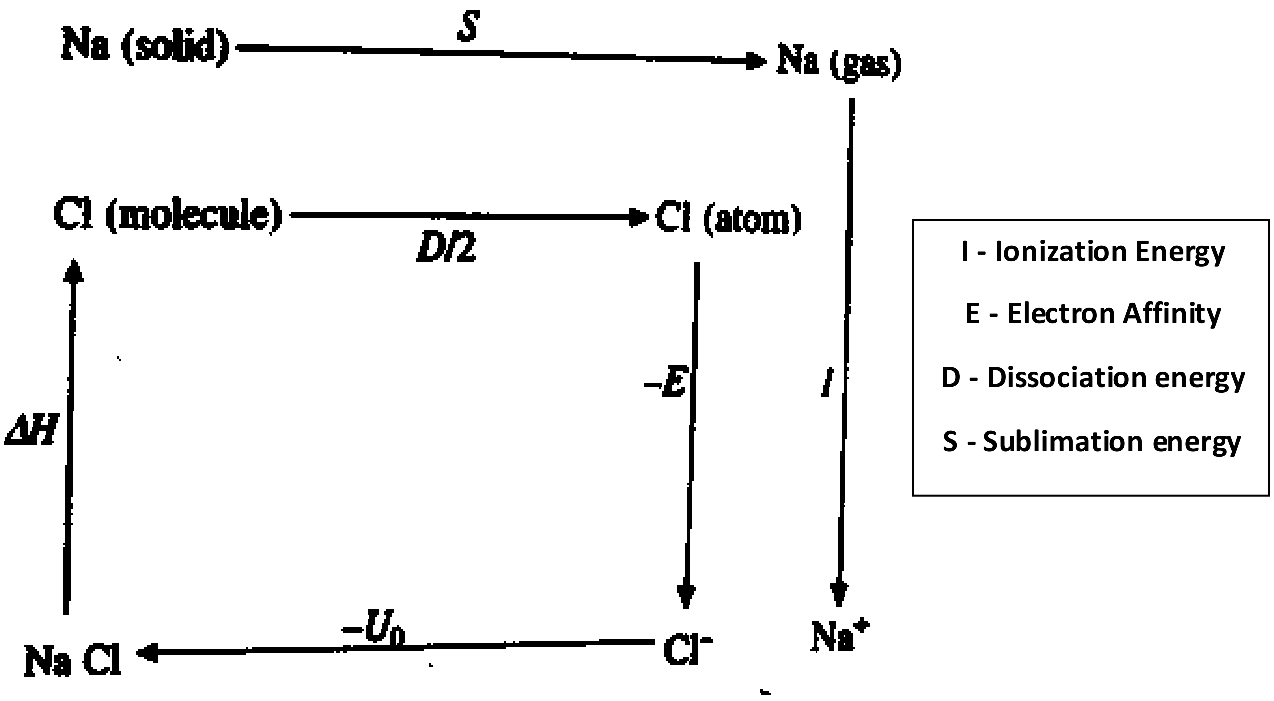


Fig. 2 Born Haber Cycle

The compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

Lattice Energy is a type of potential energy that may be defined in two ways.

In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction.

The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Unit: kJ/mol.

There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy and heat of formation.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive.
- **Sublimation energy** is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.

Born Haber Cycle Process:

Step 1:

In first stage, the solid sodium and chlorine molecules are dissociated into constituent atoms. The solid sodium is vaporized by applying an energy equal to the sublimation energy (S), while chlorine molecule is dissociated by supplying an energy equal to dissociation energy (D). (D/2 per Cl atom).

Step 2:

In second stage, the gaseous sodium and chlorine atoms are ionized. This requires Ionization energy (I) to remove an electron (outermost) from a Na atom. When this energy is added to Cl atom, energy equivalent to electron affinity (E) is released.

Step 3:

In third stage two ions (Na^+ and Cl^-) are allowed in the lattice and lattice energy (U_0) is released.

Step 4:

In fourth stage, it is return back to the starting point by breaking the lattice into solid sodium and Cl molecules by supplying heat of dissociation (ΔH).

Hence $S + D/2 + I - E - U_0 + \Delta H = 0$; $S + D/2 + I - E + \Delta H = U_0$

Calculate Lattice Energy for Nacl:

$S = 108.8 \times 10^3$ J/mol; $D = 242.8 \times 10^3$ J/mol; $I = 494 \times 10^3$ J/mol; $E = 364.2 \times 10^3$ J/mol and $\Delta H = 410.2 \times 10^3$ J/mol ?

Hence $U_0 = 770 \times 10^3$ J/mol

Remarks:

The distance between the ions increases and the lattice energy is reduced. The melting and hardness of the crystal fall progressively or coefficient of thermal expansion and compressibility increases.

Bonding in Solids

- A **chemical bond** is a lasting attraction between atoms, ions or molecules that enables the formation of chemical compounds.
- The bond may result from the electrostatic force of attraction between oppositely charged ions as in ionic bonds or through the sharing of electrons as in covalent bonds.

The strength of chemical bonds varies considerably; there are "strong bonds" or "primary bonds" and "weak bonds" or "secondary bonds" such as Vander waals and Hydrogen bond.

- The three **primary bonds are**
- ☐ • **Covalent Bonds**
  (Sharing of electrons)
- ☐ • **Metallic Bonds**
  (free nature of valence electrons)
- ☐ • **Ionic Bonds**
  (Transfer of electrons)

The two **secondary bonds are**

- ☐ **Hydrogen**
- ☐ **Vander Waals Bond or Molecular bond**

Ionic bonding

- An ionic bonding is the attractive force existing in between a positive ion and a negative ion.
- These ions are formed when the atoms of different elements involved in loss or gain of electrons in order to stabilize their outer shell electron configuration.
- Electro positive elements readily give up electrons and are usually group I or II elements.
- Eg. Na, K and Ba
- Electro negative elements readily take up electrons and are typically group VI or VII elements
- Eg. Cl,Br and O

Formation of Ionic bond:

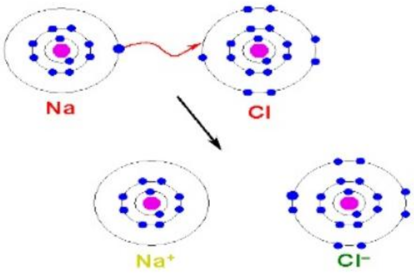


Fig.3. Ionic bonding in NaCl

Let us consider a molecule of NaCl . When neutral atoms of Na and Cl are brought close together the outer valence electron of Na gets transformed to the chlorine atom to acquire a stable electronic configuration. Eg. NaCl, KCl, KBr etc.,

Properties of Ionic solids:

- Ionic solids are crystalline in nature
- They are hard and brittle
- They have high melting and boiling point
- Solids are good insulator of electricity
- They are soluble in polar solvents and insoluble in non polar solvents .

Covalent Bonding

- In covalent bonding the stable arrangement of electrons in an outer shell is achieved by a process of sharing of valence electrons rather than electron transfer and usually takes place in non metal elements.

- Such sharing results lowering of potential energy of the system

- When two atoms are involved in the bond formation process and they share a single pair of electrons and they are known as single covalent bond.
- When two atoms are involved in the bond formation process and they share two or three pair of electrons results in double or triple bond.
- A Covalent bond is formed not only due to overlap of either pure 's' orbital or 'p' orbital, but also due to overlap of 's' and 'p' orbital. such bonding is called **hybrid bonding**.

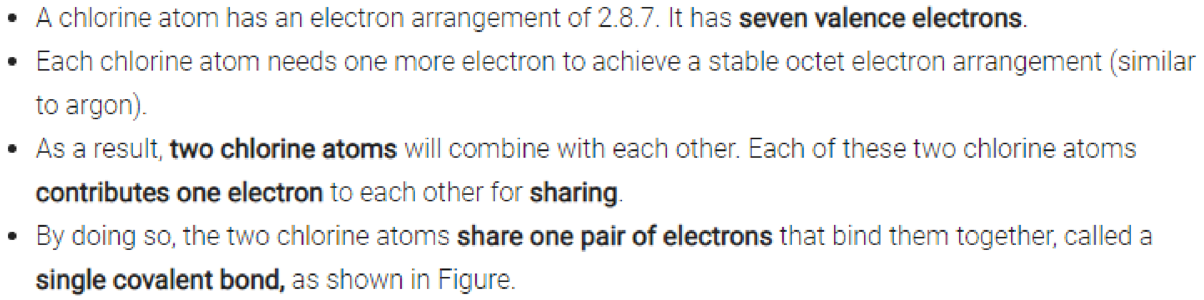
  Eg. Cl_2, H_2O, HCl, Carbon, NH_3

  <u>sp^3 bonding/ hybrid bonding</u>

  To explain the tetrahedron arrangement in diamond, we note that each C atom has four electrons in the second shell: two 2s electrons and two 2p electrons ($2s^2 2p^2$). The s states are spherically symmetric, whereas the p states represent charge distributions lying along x, y, and z coordinates. The energy difference between these states is not very big. It appears that it energetically favourable to excite one of the s electrons to p states so that the electronic configuration becomes $2s^2p^3$.

<u>Formation of covalent bond:</u>

<u>(i) single covalent bond:</u>



- A chlorine atom has an electron arrangement of 2.8.7. It has **seven valence electrons**.
- Each chlorine atom needs one more electron to achieve a stable octet electron arrangement (similar to argon).
- As a result, **two chlorine atoms** will combine with each other. Each of these two chlorine atoms **contributes one electron** to each other for **sharing**.
- By doing so, the two chlorine atoms **share one pair of electrons** that bind them together, called a **single covalent bond,** as shown in Figure.

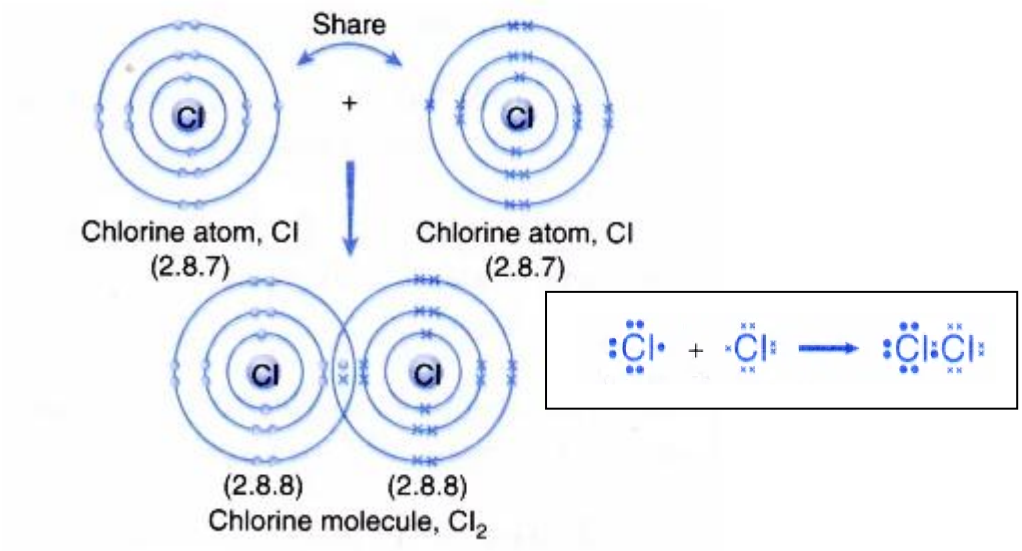


Fig. 4 Covalent Bonding

(ii) Two single covalent bond:

Formation of a water molecule, H_2O

- An oxygen atom has an electron arrangement of 2.6. It has **six valence electrons**.
- Each oxygen atom needs two more electrons to achieve a stable octet electron arrangement (similar to neon).
- A hydrogen atom has an electron arrangement of 1 and **one valence electron**.
- Each hydrogen atom needs one more electron to achieve a stable duplet electron arrangement (similar to helium).
- As a result, **two hydrogen atoms** will combine with **one oxygen atom** through the **sharing** of electrons. Each of the two hydrogen atoms **contributes one electron** and one oxygen atom **contributes two electrons** for **sharing**.
- By doing so, one oxygen atom is bonded to each of the two hydrogen atoms by a **shared pair of electrons** so that all the three atoms achieve in **stable noble gas electron arrangements**, as shown in Figure.

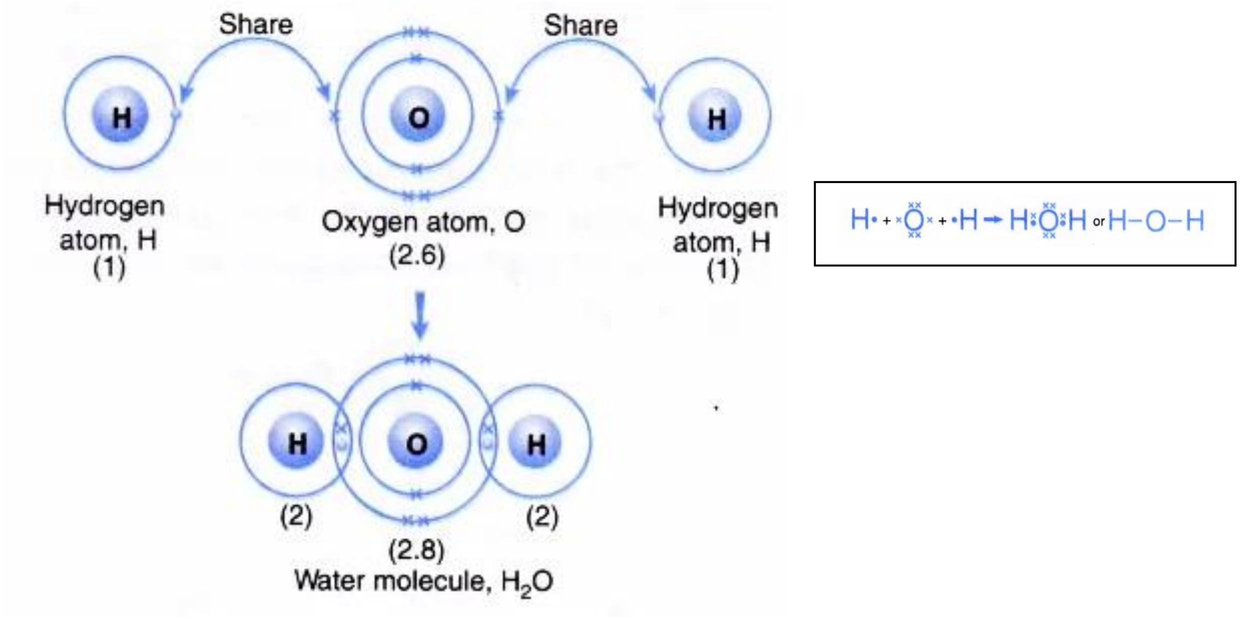


Fig. 5. H_2O bonding

Properties of Covalent bond

- Covalent bonds are directional
- Covalent solids are hard and brittle ; crystalline in nature
- When compared to ionic solids they have low melting and boiling point.

- Pure covalent solids are insulators
- It will become semiconductor upon doping.

METALLIC BONDING

- The valence electrons from all the atoms belong to the crystal are free to move throughout the crystal.
- The crystal may consider as on array of positive metal ions embedded in a cloud or sea of free electrons. This type of bonding is called metallic bonding.
- Eg. Cu, Ag, Al etc.,

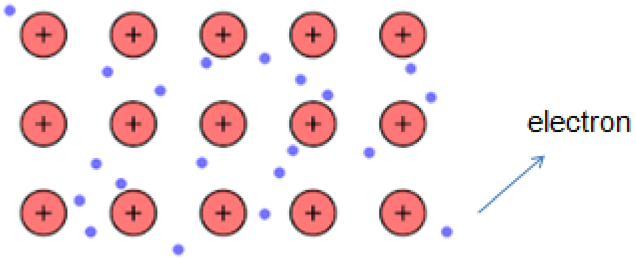


Fig. 6 Metallic Bonding

Formation of metallic bond:

In **metallic bonds**, the valence electrons from the s and p orbitals of the interacting metal atoms delocalize. That is to say, 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.

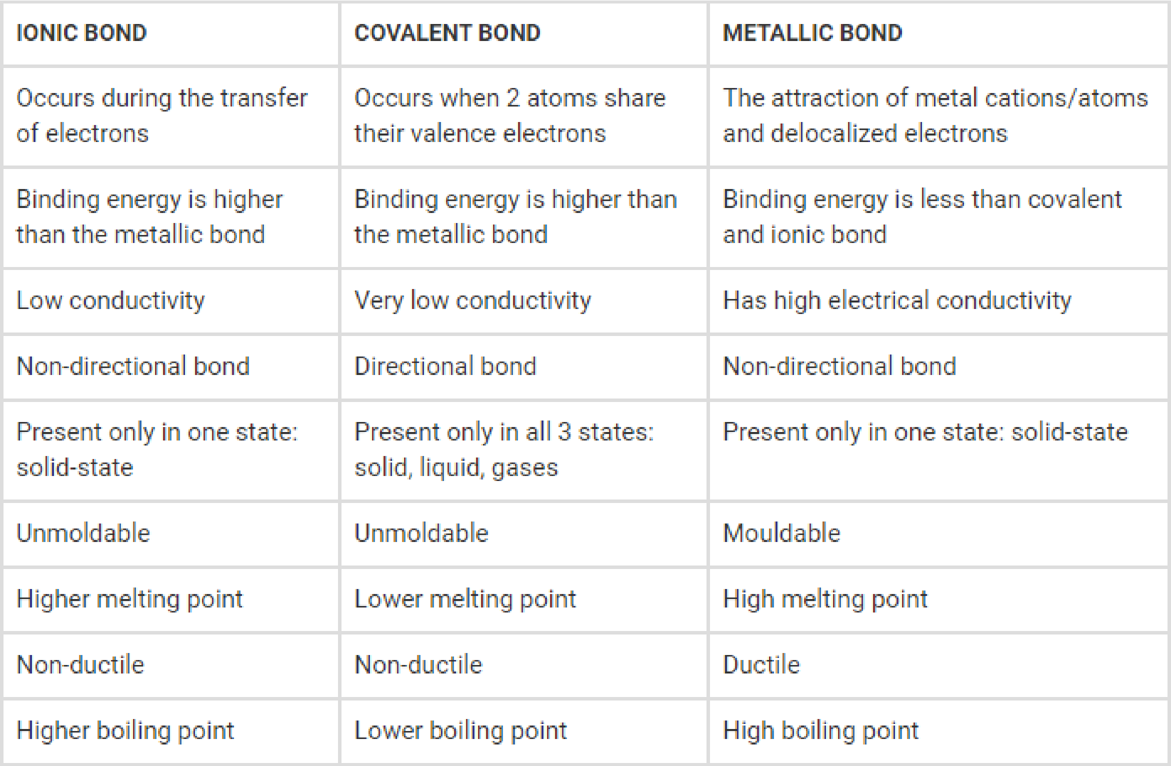
Metallic bonding is a type of chemical **bonding** that rises from the electrostatic attractive force between conduction electrons (in the **form** of an electron cloud of delocalized electrons) and positively charged metal ions.

Properties of metallic bond / metallic solids

- The metallic bond is weaker than the ionic and the covalent bonds.
- Non directional
- • Metals are good conductors of electricity when solid, or liquid. The delocalized electrons are able to move under an electric field.
- • Metals are good conductors of heat. The delocalized electrons disperse heat more quickly.

- • Metals are malleable and ductile, not brittle. The cations are able to slide past each other and still retain their attraction to the electron sea.
- Metallic solids are not soluble in polar and non polar solvents

- **Table 1- Difference Between Ionic bond, Covalent bond, and Metallic bond**



IONIC BOND	COVALENT BOND	METALLIC BOND
Occurs during the transfer of electrons	Occurs when 2 atoms share their valence electrons	The attraction of metal cations/atoms and delocalized electrons
Binding energy is higher than the metallic bond	Binding energy is higher than the metallic bond	Binding energy is less than covalent and ionic bond
Low conductivity	Very low conductivity	Has high electrical conductivity
Non-directional bond	Directional bond	Non-directional bond
Present only in one state: solid-state	Present only in all 3 states: solid, liquid, gases	Present only in one state: solid-state
Unmoldable	Unmoldable	Mouldable
Higher melting point	Lower melting point	High melting point
Non-ductile	Non-ductile	Ductile
Higher boiling point	Lower boiling point	High boiling point

What is Hydrogen Bonding?

- In a molecule, when a hydrogen atom is linked to a highly electronegative atom, it attracts the shared pair of electrons more and so this end of the molecules becomes slightly negative while the other end becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called the **hydrogen bond.**
- Hydrogen bonding is a special class of attractive intermolecular forces that arise due to the dipole-dipole interaction between a hydrogen atom that is bonded to a highly electronegative atom and another highly electronegative atom while lies in the vicinity of the hydrogen atom. For example, in water molecules (H_2O), hydrogen is covalently bonded to the more electronegative oxygen atom. Therefore, hydrogen bonding arises in water molecules due to the dipole-dipole interactions between the hydrogen atom of one water molecule and the oxygen atom of another H_2O molecule.

Here, the location of the bond pair of electrons in the O-H bond is very close to the oxygen nucleus (due to the large difference in the electronegativities of oxygen and hydrogen). Therefore, the oxygen atom develops a partial negative charge (-δ) and the hydrogen atom develops a partial positive charge (+δ). Now, hydrogen bonding can occur due to the electrostatic attraction between the hydrogen atom of one water molecule (with +δ charge) and the oxygen atom of another water molecule (with -δ charge). Thus, hydrogen bonds are a very special class of intermolecular attractive forces that arise only in compounds featuring hydrogen atoms bonded to a highly electronegative atom. Hydrogen bonds are mostly strong in comparison to normal dipole-dipole and dispersion forces. However, they are weak compared to true covalent or ionic bonds.

The conditions for hydrogen bonding are:

1. The molecule must contain a highly electronegative atom linked to the hydrogen atom. The higher the electronegativity more is the polarization of the molecule.
2. The size of the electronegative atom should be small. The smaller the size, the greater is the electrostatic attraction.

Eg. HF, H_2O and carboxylic acid etc.,

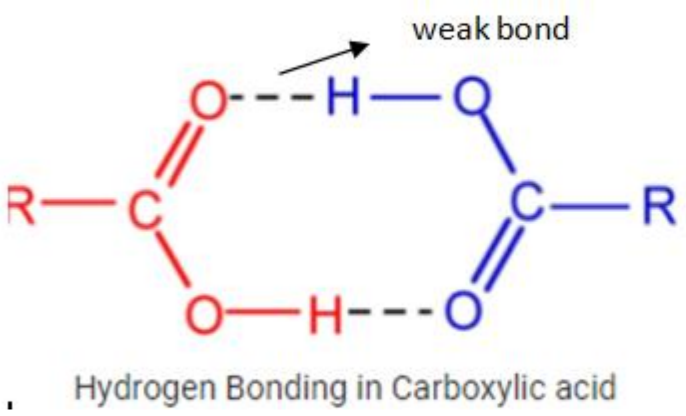


Fig. 7 Hydrogen Bonding

Properties of Hydrogen Bonding

- **Solubility:** Lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecule.
- **Volatility:** As the compounds involving hydrogen bonding between different molecules have a higher boiling point, so they are less volatile.
- **Viscosity and surface tension:** The substances which contain hydrogen bonding exists as an associated molecule. So their flow becomes comparatively difficult. They have higher viscosity and high surface tension.
- **The lower density of ice than water:** In the case of solid ice, the hydrogen bonding gives rise to a cage-like structure of water molecules. As a matter of fact, each water

molecule is linked tetrahedral to four water molecules. The molecules are not as closely packed as they are in a liquid state. When ice melts, this case like structure collapses and the molecules come closer to each other. Thus for the same mass of water, the volume decreases and density increases. Therefore, ice has a lower density than water at 273 K. That is why ice floats**.**

Van Der Waals Bonding

Secondary bonds are weak in comparison to primary bonds.

They are found in most materials, but their effects are often overshadowed by the strength of the primary bonding.

Secondary bonds are not bonds with a valence electron being shared or donated. They are usually formed when an uneven charge distribution occurs, creating what is known as a dipole (the total charge is zero, but there is slightly more positive or negative charge on one end of the atom than on the other).

These dipoles can be produced by a random fluctuation of the electrons around what is normally an electrically symmetric field in the atom.

Once a random dipole is formed in one atom, an induced dipole is formed in the adjacent atom. This is the type of bonding present in N_2 molecules, and is known as Van Der Waals Bonding.

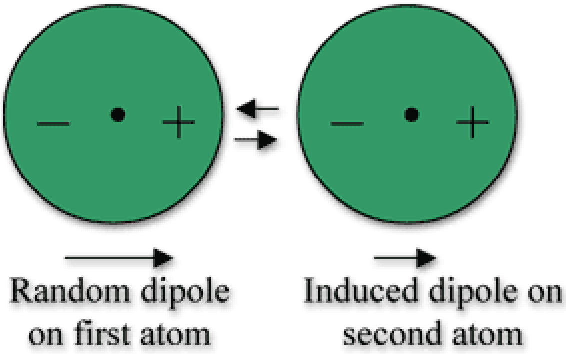


Fig.8. Vander waals Bonding

Secondary bonding may also exist when there is a permanent dipole in a molecule due to an asymmetrical arrangement of positive and negative regions.

Molecules with a permanent dipole can either induce a dipole in adjacent electrically symmetric molecules, and thus form a weak bond, or they can form bonds with other permanent dipole molecules.

Properties:

- The main **characteristics of van der Waals** forces are: They are weaker than normal covalent and ionic **bonds**.
- **Van der Waals** forces are additive and cannot be saturated.
- They have no directional characteristic.
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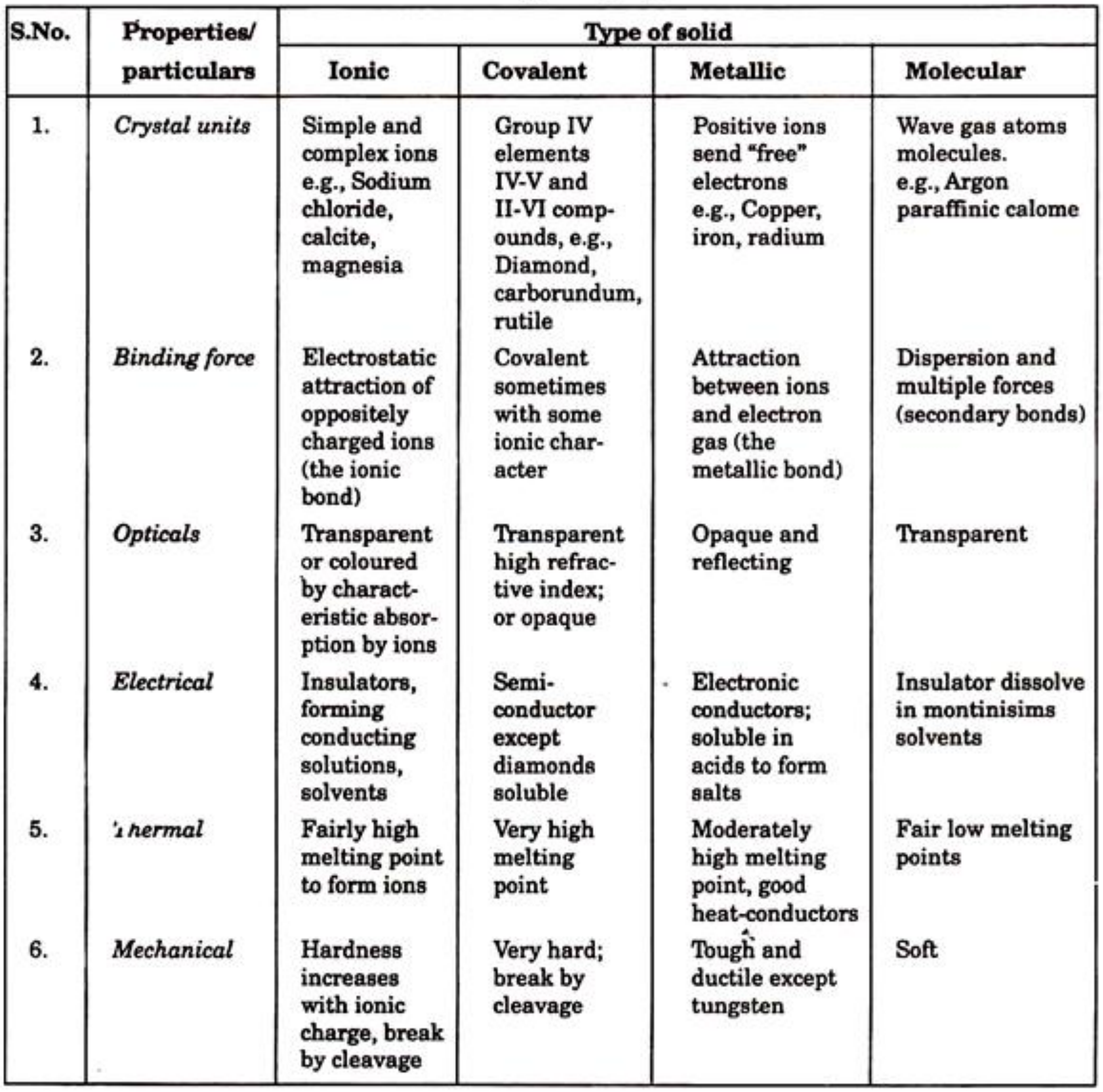
Table 2



S.No.	Properties/ particulars	Type of solid			
		Ionic	Covalent	Metallic	Molecular
1.	*Crystal units*	Simple and complex ions e.g., Sodium chloride, calcite, magnesia	Group IV elements IV-V and II-VI compounds, e.g., Diamond, carborundum, rutile	Positive ions send "free" electrons e.g., Copper, iron, radium	Wave gas atoms molecules. e.g., Argon paraffinic calome
2.	*Binding force*	Electrostatic attraction of oppositely charged ions (the ionic bond)	Covalent sometimes with some ionic character	Attraction between ions and electron gas (the metallic bond)	Dispersion and multiple forces (secondary bonds)
3.	*Opticals*	Transparent or coloured by characteristic absorption by ions	Transparent high refractive index; or opaque	Opaque and reflecting	Transparent
4.	*Electrical*	Insulators, forming conducting solutions, solvents	Semi-conductor except diamonds soluble	Electronic conductors; soluble in acids to form salts	Insulator dissolve in montinisims solvents
5.	*Thermal*	Fairly high melting point to form ions	Very high melting point	Moderately high melting point, good heat-conductors	Fair low melting points
6.	*Mechanical*	Hardness increases with ionic charge, break by cleavage	Very hard; break by cleavage	Tough and ductile except tungsten	Soft

IMPERFECTIONS IN CRYSTALS

INTRODUCTION

In an ideal crystal, the atomic arrangement is perfectly regular and continuous throughout. But real crystals are never perfect; lattice distortion and various imperfections, irregularities or defects generally present in them. The mechanical, electrical and magnetic properties of engineering crystalline solids, particularly metals and alloys, are affected by the imperfections in the crystals.

If atoms in the solid are not arranged in a perfectly regular manner, it is called defects in crystals.

CLASSIFICATION OF IMPERFECTIONS (Defects)

The various types of structural imperfections or defects in crystals are classified as follows:

1. Point defects (or) Zero dimensional defects
a. Vacancies
i. Schottky defect
ii. Frenkel defect
b. Interstitial atoms
c. Extrinsic defects (Impurities)
i. Substitutional Impurity
ii. Interstitial Impurity
2. Line defects (or) one dimensional defect
a. Edge dislocation
b. Screw dislocation
3. Surface defects (or) Plane defects (or) two dimensional defects
a. Grain boundaries
b. Tilt boundaries
c. Twin boundaries
d. Stacking faults

Point defects

Point defect is also called zero dimensional imperfections. In a crystal lattice, point defect is one which is completely local in its effect, e.g. a vacant lattice site. The introduction of point defect into a crystal increases its internal energy as compared to that of the perfect crystal. They change the electrical resistance of a crystal.

Point defects are created during crystal growth and application of thermal energy, mechanical stress or electric field. Further they are created by irradiating the crystal by x-ray, microwaves and light.

Different types of point defects are described below.

a. Vacancies

A vacancy is the simplest point defect in a crystal. This refers to a missing atom (or) a vacant atomic site. Such defects may arise either from imperfect packing density crystallization process or from thermal vibration of atoms at high temperature.

Vacancy may also occur if an atom leaves its own site and dissolved interstitially into the structures. The vacancies may be single or deviancies or trivacancies and so on.

Vacancies are classified into two types as follows.

(i) Schottky defect
(ii) Frenkel defect

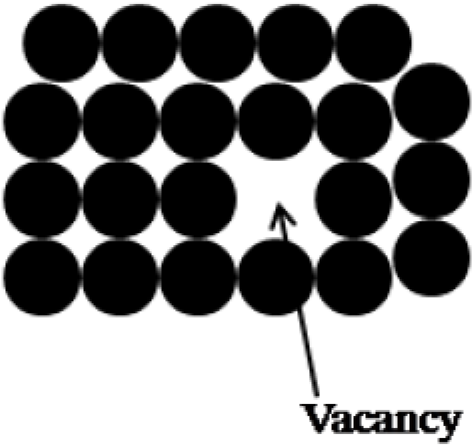


Fig. 9. Point defect

(i) Schottky defects

Schottky vacancies refer to the missing of anion and cation. In general the missing of pair of ions in ionic crystal is called schottky defect. This defect is the combination of one cation vacancy and one anion vacancy. The concentration of Schottky defect decreases the density of the crystal. This type of point defect is dominant in alkali halides.

Consider an ionic crystal having equal number of positively and negatively charged ions.

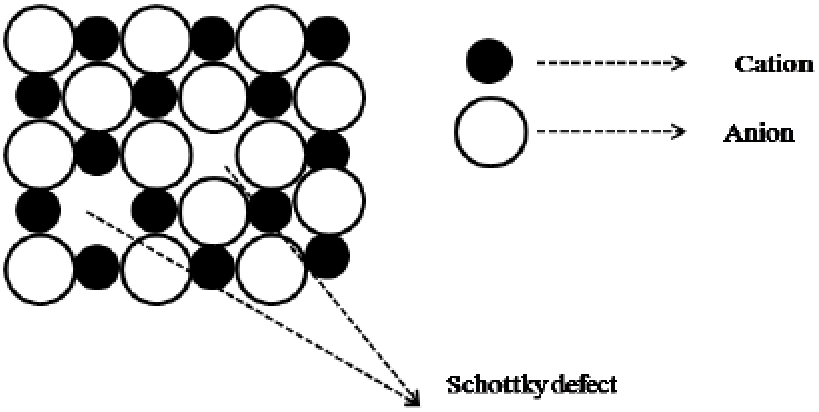


Fig. 10. Schottky defect

(ii) Frenkel defects

Frenkel vacancies refer to the shift of cation from the regular site to interstitial site. As cations are generally the smaller ions, it is possible for them to get displaced into

the void space present in the lattice. The concentration of Frenkel defects does not change the density of the crystal and the overall electrical neutrality of the crystal. The point defect in silver halides and calcium fluoride are of the Frenkel type.

Extrinsic vacancies (Impurities)

This is a defect in which a foreign atom occupies a regular lattice site. Foreign atoms generally have atomic radii and electronic structures differing from those of the host atoms and therefore act as centers of distortion. Basically there are two types of impurity defects.

(a) Substitutional impurity

It refers to a foreign atom substitutes or replaces a parent atom in the lattice.
Example: In the case of semiconductor technology, Aluminum and phosphorus doped in silicon are substitutional impurities in the crystal.

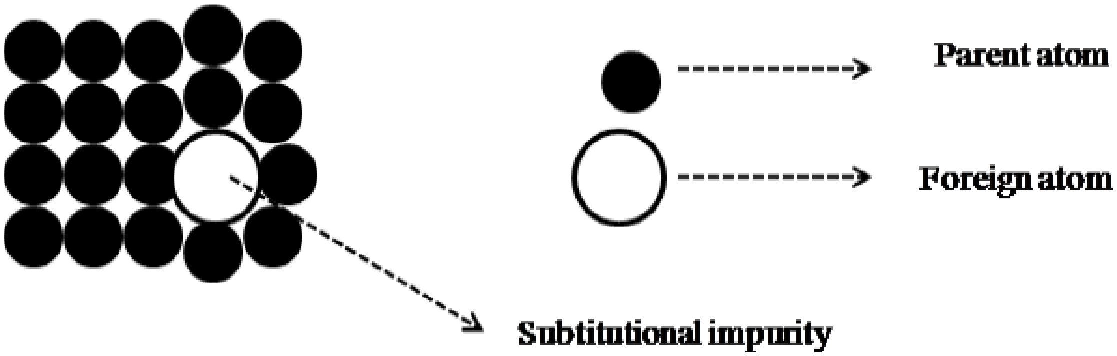


Fig. 11 Substitutional defect

(b) *Interstitial impurity*

It is a small sized atom occupying the void space in the parent crystal, without dislodging any of the parent atoms from their sites. An atom can enter the interstitial or void space only when it is substantially smaller than the parent atom.
Example: Presence of carbon in iron.

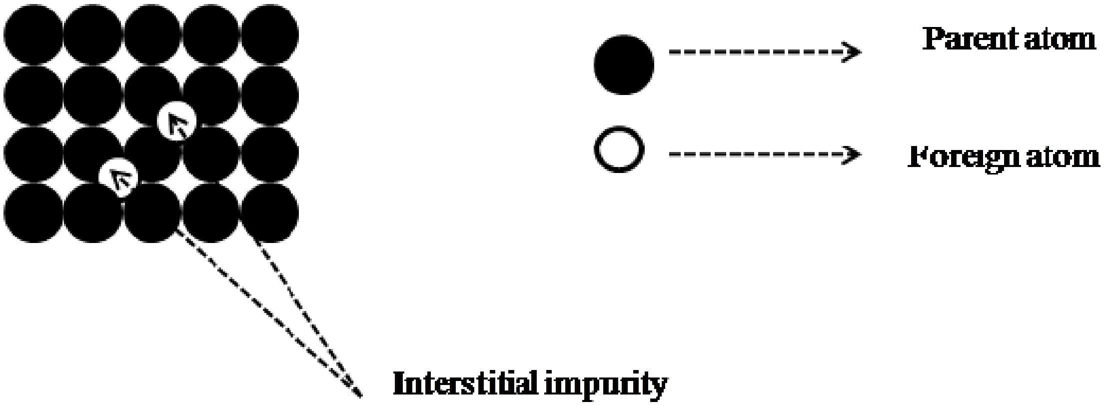


Fig. 12 Interstitital impurity

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DEPARTMENT OF PHYSICS

UNIT – II - Condensed Matter Physics – SPHA5301

LATTICE DYNAMICS

Born–von Karman boundary conditions are periodic **boundary conditions** which impose the restriction that a wave function must be periodic on a certain Bravais lattice.

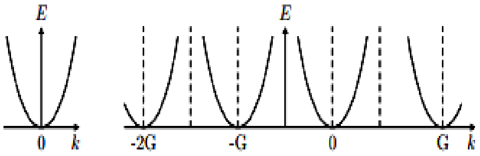

Fig.1

The reciprocal lattice has extraordinary consequences for the electronic motion, even before we "switch on" the lattice potential. Instead of dealing with just one electron dispersion relationship $E(\mathbf{k})$ there must be an infinite number of equivalent dispersion relationships (see Figure 2.1) such that $E(\mathbf{k}) = E(\mathbf{k}+\mathbf{G})$ for all $\mathbf{G}$ (*c.f.* Equation 2.2). However, the k-space periodicity also implies that all information will be contained in the primitive unit cell of the reciprocal lattice, known as *the first Brillouin zone.*[3] The first Brillouin zone has a k-space volume

$$V_{k3} = \mathbf{A}_1.\mathbf{A}_2 \times \mathbf{A}_3. \tag{2.7}$$

We need to derive a suitable set of functions with which we can describe the motion of the electrons through the periodic potential; "motion" implies that we do not want standing waves. The functions should reflect the translational symmetry properties of the lattice; to do this we use *Born–von Karman periodic boundary conditions.*

We choose a plane wave

$$\phi(\mathbf{r}) = \mathrm{e}^{\mathrm{i}(\mathbf{k}.\mathbf{r}-\omega t)} \tag{2.8}$$

subject to boundary conditions which include the symmetry of the crystal

$$\phi(\mathbf{r}+N_j\mathbf{a}_j) = \phi(\mathbf{r}), \tag{2.9}$$

where $j = 1,\ 2,\ 3$ and $N = N_1N_2N_3$ is the number of primitive unit cells in the crystal; N_j is the number of unit cells in the jth direction.

The boundary condition (Equation 2.9) implies that

$$\mathrm{e}^{\mathrm{i}N_j\mathbf{k}.\mathbf{a}_j} = 1 \tag{2.10}$$

for $j = 1,\ 2,\ 3$. Comparing this with Equation 2.4 (and the discussion that follows it) suggests that the allowed wavevectors are

$$\mathbf{k} = \sum_{j=1}^{3} \frac{m_j}{N_j}\mathbf{A}_j. \tag{2.11}$$

Each time that all of the m_j change by one we generate a new state; therefore the volume of k-space occupied by one state is

$$\frac{\mathbf{A}_1}{N_1} \cdot \frac{\mathbf{A}_2}{N_2} \times \frac{\mathbf{A}_3}{N_3} = \frac{1}{N} \mathbf{A}_1 . \mathbf{A}_2 \times \mathbf{A}_3 . \tag{2.12}$$

Comparing this with Equation 2.7 shows that *the Brillouin zone always contains the same number of k-states as the number of primitive unit cells in the crystal.* This fact will be of immense importance later on (remember it!); it will be a key factor in determining whether a material is an insulator, semiconductor or metal.

PHONONS: Quantization of Lattice Vibrations

According to the quantum theory, electromagnetic energy (light) comes in packets of energy we call **photons**. Since there is energy in lattice vibrations as well, this energy will also be quantized, and we will call these packets of vibrational energy: **phonons**.

1. Energy of phonons:

From the **quantum theory**, the energy of a harmonic oscillator (PE=½kx² put into Schrodinger's Equation) is calculated to be:

$E_{HO} = (n+\frac{1}{2})\hbar\omega$ (recall that $\hbar = h/2\pi$; ω is the angular frequency).

As in the previous sections we will use **Ω for the frequency of vibration in the solid** to distinguish it from the **ω for the frequency of vibration of an E&M wave**.

Note that even with n=0 there is still a non-zero energy!

From the equipartition of energy theorem, the energy should be equally divided (on average) between each way of having energy (between each degree of freedom). For a harmonic oscillator (mass on a spring), we can have both kinetic energy ($\frac{1}{2}mv^2$) and potential energy ($\frac{1}{2}kx^2$). Thus, the time average (denoted by < >) of the energy is:

$$\langle E_{total}\rangle = (n+\tfrac{1}{2})\hbar\omega = \langle KE + PE\rangle = \langle KE\rangle + \langle PE\rangle ,$$

and from equipartition of energy: $\langle KE\rangle = \langle PE\rangle$, we have

$$\langle E_{total}\rangle = 2\langle KE\rangle , \quad \text{or} \quad \langle KE\rangle = \tfrac{1}{2}\langle E_{total}\rangle = \tfrac{1}{2}(n+\tfrac{1}{2})\hbar\Omega .$$

Inelastic Neutron Scattering

One of the great advantages of neutrons as a probe in condensed matter physics is that they can be used to measure details of atomic and molecular motions by using so-called inelastic neutron scattering (**INS**), in which the neutron exchanges energy with the atoms in a material. When a neutron is scattered by a crystalline solid, it can absorb or emit an amount of energy equal to a quantum of phonon energy, hν. This gives rise to inelastic coherent scattering in which the neutron energy before and after the scattering differ by an amount, hν (i.e. **energy transfer**). In most solids ν is a few terahertz (THz), corresponding to phonon energies of a few meV (1 THz corresponds to an energy of 4.18 meV). Because neutrons used for INS also have energies in the meV range, scattering by a phonon causes an appreciable fractional change in the neutron energy, allowing accurate measurement of phonon frequencies. For INS, the neutron has different velocities, and thus different wavevectors, before and after it interacts with the sample. To determine the phonon energy and the scattering vector, **Q**, we need to determine the neutron wavevector before ($\mathbf{k}_i$, i = *initial*) and after ($\mathbf{k}_f$, f = *final*) the scattering event. Several different methods are available but the workhorse instruments for this type of measurement are called triple-axis spectrometers.

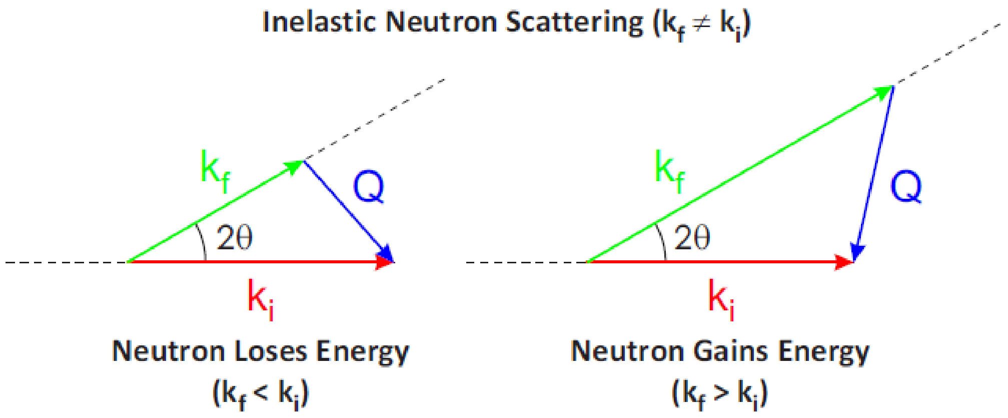

Fig.2

The three-axis spectrometer (**TAS**) can be considered the mother of all crystal spectrometers and they are the most versatile instruments for performing INS experiment. They allow for a controlled access to both the momentum $\mathbf{Q} = \mathbf{k_i} - \mathbf{k_f}$ as well as energy transfer $\hbar\omega = E_i - E_f$. During an TAS experiment (see Fig. 4) an incident neutron beam of well defined wavevector $\mathbf{k_i}$ is selected from the white spectrum of the neutron source by the monochromator crystal (first axis). The monochromatic beam is then scattered from the crystalline sample (second axis). The intensity of the scattered beam with wavevector kf is reflected by the analyzer crystal (third axis) onto the neutron detector (^{3}He-tube), thereby defining the energy transfer $\hbar\omega$ as well.

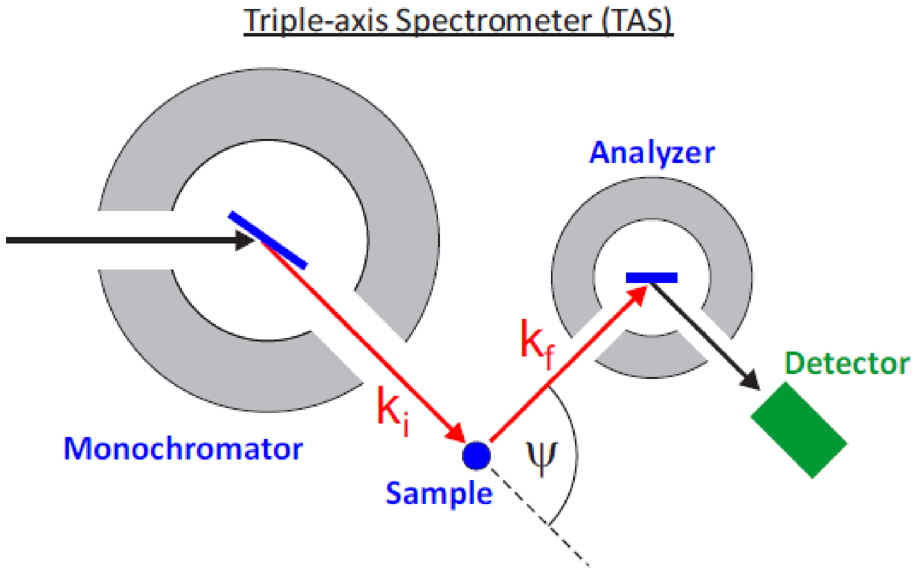

Fig. 3

Mono atomic Chain- Lattice Vibration

Lattice vibrations give the key to many temperature dependent properties of solids. If we know the quantum mechanical energy eigenvalues of these vibrations, we can easily model thermodynamic quantities such as the Gibbs energy and the heat capacity. If we also know the eigenfunctions corresponding to the eigenvalues, we can calculate, e.g. the vibrational displacements of the atoms and connect that to properties such as the electrical resistivity. In applications to materials science the temperature is often so high that a *classical description* agrees very well with the more fundamental *quantum mechanical approach*. We therefore start with a brief comparison of these two descriptions.

Linear chain with one atomic species

To describe the lattice vibrations of crystals, we consider first linear chains of equal atoms (present section), then linear chains with a basis of different atoms (Section 9.2), and finally general three-dimensional structures (Section 9.3). This sequence of increasing sophistication is adopted because some physical concepts are better illustrated in one-dimensional situations, where notations and technicalities can be kept at the minimal level.
So, we begin by considering a one-dimensional chain, of lattice constant a, formed by a (large) number N of atoms of mass M. We indicate by un the longitudinal displacement of the nth atom from the equilibrium position tn=na, at a particular time (see Figure 9.1). We denote by E0({un}) the total ground-state energy of the interacting electronic-nuclear system, with the *nuclei fixed in the positions* Rn=na+un. The ground state of the crystal is supposed to be non-degenerate for all configurations {un} of interest.

$$M \ddot{s}_n = -f(s_n - s_{n+1}) + f(s_{n-1} - s_n)$$

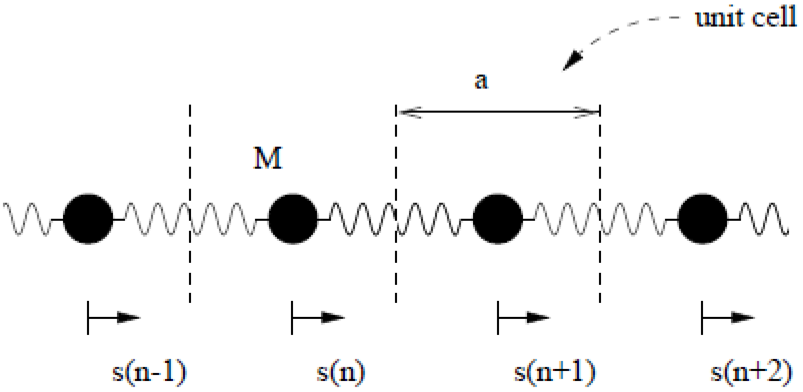

Fig.4

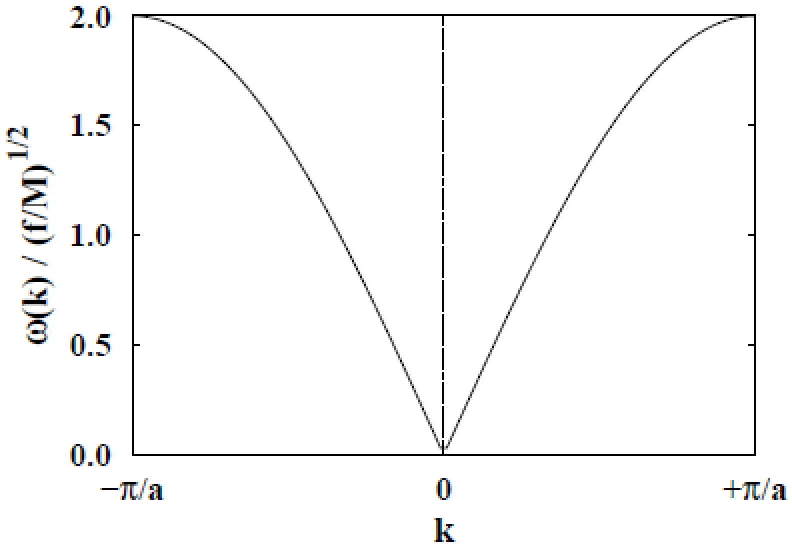

Fig.5 Dispersion Curve

$$s_n = \frac{1}{\sqrt{M}} c e^{i(kan-\omega t)} \quad ,$$

yielding

$$\omega^2 M = f\left(2 - e^{-ika} - e^{ika}\right) \quad .$$

Solving for ω, one therefore obtains

$$\omega(k) = 2\sqrt{\frac{f}{M}}\left|\sin\left(\frac{ka}{2}\right)\right| \quad ,$$

Linear chain with two atomic species

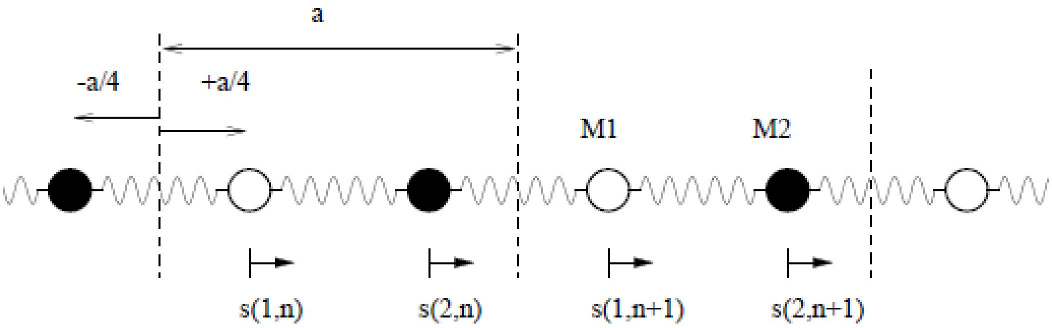

Fig.6

where there are two different atomic species in the linear chain, i.e. the basis in the unit cell is two. The equations of motion for the two atoms follow as a direct generalization of eqn.

A *phonon* is the quantum of energy associated with a lattice vibration or elastic wave. To exemplify this concept, we consider a set of *N* identical ions of mass *m* distributed along a monatomic 1D Bravais lattice whose translation vector is R→=naz^, with *n* being an integer and *a* denoting the distance between two adjacent ions. The vibrational motion is assumed here to be confined to the *z*-direction (along the chain).
Let u_n be the displacement of the ion that oscillates from its equilibrium position $z = na$ along the linear chain (see Fig. 1.5). The number *N* is taken to be sufficiently large that end effects can be ignored (i.e. the chain is effectively infinite). Assuming that only neighboring ions interact, Newton's equation of motion for the *n*th ion yields.

Linear monatomic chain with nearest neighbour interactions

To show the essential aspects of the lattice vibrations in the linear chain, we suppose that the only relevant inter-atomic interactions occur between nearest neighbour atoms; in other words, we assume that the only force constants different from zero are D_{nn}, D_{nn+1} and D_{n-1n}.

$$\begin{aligned} M_1\,\ddot{s}_n^{(1)} &= -f\left(s_n^{(1)} - s_n^{(2)} - s_{n-1}^{(2)}\right) \\ M_2\,\ddot{s}_n^{(2)} &= -f\left(s_n^{(2)} - s_{n+1}^{(1)} - s_n^{(1)}\right) \quad . \end{aligned}$$

Hence, also the same wave-like ansatz should work as before

$$\begin{aligned} s_n^{(1)} &= \frac{1}{\sqrt{M_1}} c_1 e^{i\left(k(n-\frac{1}{4})a-\omega t\right)} \\ s_n^{(2)} &= \frac{1}{\sqrt{M_2}} c_2 e^{i\left(k(n+\frac{1}{4})a-\omega t\right)} \quad . \end{aligned}$$

This leads to

$$\begin{aligned} -\omega^2 c_1 &= -\frac{2f}{\sqrt{M_1M_2}} c_1 + \frac{2f}{\sqrt{M_1M_2}} c_2 \cos\left(\frac{ka}{2}\right) \\ -\omega^2 c_2 &= -\frac{2f}{\sqrt{M_1M_2}} c_2 + \frac{2f}{\sqrt{M_1M_2}} c_1 \cos\left(\frac{ka}{2}\right) \quad , \end{aligned}$$

i.e. in this case the frequencies of the two atoms are still coupled to each other. The eigenvalues follow then from the determinant

$$\left| \begin{array}{cc} \frac{2f}{\sqrt{M_1M_2}} - \omega^2 & -\frac{2f}{\sqrt{M_1M_2}} \cos\left(\frac{ka}{2}\right) \\ -\frac{2f}{\sqrt{M_1M_2}} \cos\left(\frac{ka}{2}\right) & \frac{2f}{\sqrt{M_1M_2}} - \omega^2 \end{array} \right| = 0 \quad ,$$

which yields the two solutions

$$\begin{aligned} \omega_\pm^2 &= f\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm f\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}\sin^2\left(\frac{ka}{2}\right)} \\ &= \frac{f}{\widetilde{M}} \pm f\sqrt{\frac{1}{\widetilde{M}^2} - \frac{4}{M_1M_2}\sin^2\left(\frac{ka}{2}\right)} \quad , \end{aligned}$$

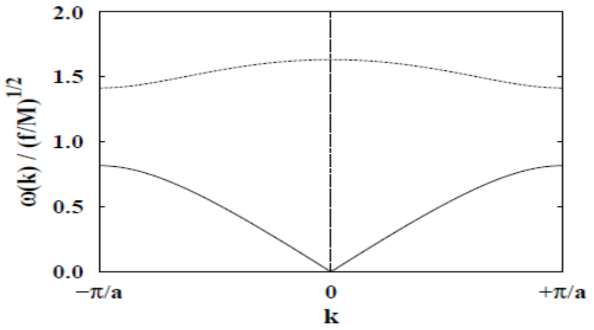

Fig. 7

To describe the lattice vibrations of crystals, we consider first linear chains of equal atoms(present section), then linear chains with a basis of different atoms(Section 2), and finally general three-dimensional structures (Section 3). This sequence of increasing sophistication is adopted because some physical concepts are better illustrated in one-dimensional situations, where notations and technicalities can be kept at the essential.

So, we begin by considering a one-dimensional chain, of lattice constant *a*, formed by a (large) number *N* of atoms of mass *M*. We indicate by u_n the (longitudinal) displacement of the *n*-th atom from the equilibrium position $t_n = na$, at a particular time(see Fig. 1). We denote by $E_0(\{u_n\})$ the total ground-state energy of the crystal Hamiltonian, with the *nuclei fixed in the positions* $R_n = na + u_n$; the energy $E_0(\{u_n\})$ is also called *static lattice energy*. The ground state of the crystal is supposed to be non-degenerate for all configurations $\{u_n\}$ of interest.

Phonon specific heat

A phonon is the quantum mechanical description of an elementary vibrational motion in which a lattice of atoms or molecules uniformly oscillates at a single frequency. In classical mechanics this designates a normal mode of vibration. Normal modes are important because any arbitrary lattice vibration can be considered to be a superposition of these *elementary* vibration modes (cf. Fourier analysis). While normal modes are wave-like phenomena in classical mechanics, phonons have particle-like properties too, in a way related to the wave–particle duality of quantum mechanics.

High temperature limit (Dulong-Petit law)

In the high temperature limit and can therefore expand the exponential in the denominator in eq.

$$\begin{aligned}
c_V^{\text{vib}}(T \to \infty) &= \frac{\partial}{\partial T} \int_0^\infty d\omega\, g(\omega) \left[\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right] \hbar\omega \\
&= \frac{\partial}{\partial T} \int_0^\infty d\omega\, g(\omega) \left[\frac{1}{(1 + \frac{\hbar\omega}{k_B T} + \ldots) - 1} \right] \hbar\omega \\
&= \int_0^\infty d\omega\, g(\omega) \frac{\partial}{\partial T} (k_B T) \\
&= 3k_B M/V \;=\; \text{constant} \quad ,
\end{aligned}$$

That we recover it in this limit is simply a consequence of the fact that at such high temperatures the quantized nature of the vibrations does not show up anymore. Energy can be taken up in a quasi-continuous manner and we arrive at the classical result that each degree of freedom yields *kBT* to the energy of the solid.

Low temperature limit (Debye approximation)

The vibrational term here is only the **low temperature limit** of the **Debye** specific **heat** expression; the full expression includes an integral which must be evaluated numerically. It produces good agreement with the transition to the Dulong and Petit **limit** athigh **temperatures**.

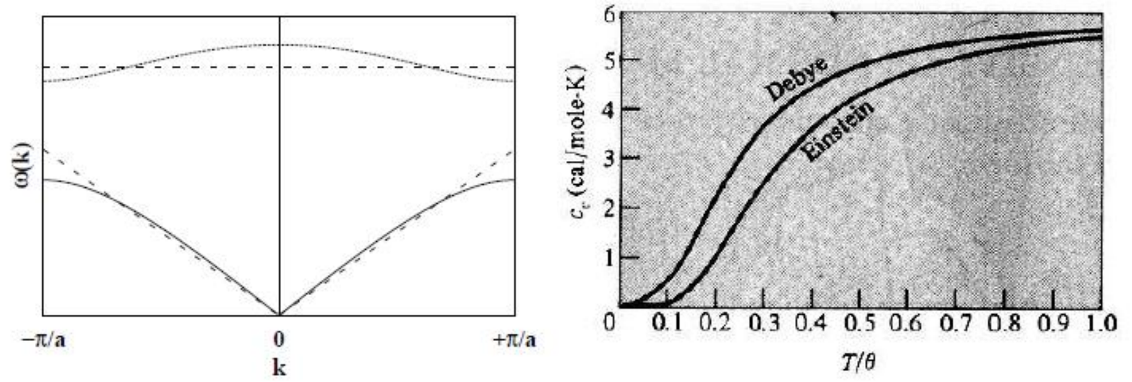

Fig.8

Anharmoniceffectsincrystals

Anharhominicity in Phonons Discussion till now confined to harmonic approximation – potential energy of lattice vibrations had only quadratic terms. We learnt that the lattice waves are normal modes – phonons do not interact with each other; they do not change with time. Its consequences are: 1. The heat capacity becomes T independent for T>TD. 2. There is no thermal expansion of solids. 3. Thermal conductivity of solids is infinite Conditions not fulfilled in real crystals. Way out: Include higher order terms in potential energy. with c,g and f >0 This is equivalent to having three or more phonon processes in the Hamiltonian. They can lead to processes like:

$$\alpha = \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P \quad .$$

This can be expressed in terms of the bulk modulus, *B*,

$$\frac{1}{B} = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad ,$$

as

$$\alpha = \frac{1}{3B}\left(\frac{\partial P}{\partial T}\right)_V \quad .$$

Since we know that pressure, *P*, can be expressed as

$$P = -\left(\frac{\partial U}{\partial V}\right)_T \quad ,$$

Normal and Umklapp process

In crystalline materials, **Umklapp scattering** (also **U-process** or **Umklapp process**) is a scattering process that results in a wave vector (usually written k) which falls outside the first Brillouin zone. If a material is periodic, it has a Brillouin zone, and any point outside the first Brillouin zone can also be expressed as a point inside the zone. So, the wave vector is then mathematically transformed to a point inside the first Brillouin zone. This transformation allows for scattering processes which would otherwise violate the conservation of momentum: two wave vectors pointing to the right can combine to create a wave vector that points to the left. This non-conservation is why crystal momentum is not a true momentum.

Examples include electron-lattice potential scattering or an anharmonic phonon-phonon (or electron-phonon) scattering process, reflecting an electronic state or creating a phonon with a momentum k-vector outside the first Brillouin zone. Umklapp scattering is one process limiting the thermal conductivity in crystalline materials, the others being phonon scattering on crystal defects and at the surface of the sample.

Figure 1 schematically shows the possible scattering processes of two incoming phonons with wave-vectors (k-vectors) k_1 and k_2 (red) creating one outgoing phonon with a wave vector k_3 (blue). As long as the sum of k_1 and k_2 stay inside the first Brillouin zone (grey squares), k_3 is the sum of the former two, thus conserving phonon momentum. This process is called normal scattering (N-process).

With increasing phonon momentum and thus larger wave vectors k_1 and k_2, their sum might point outside the first Brillouin zone (k'_3). As shown in Figure 2, k-vectors outside the first Brillouin zone are physically equivalent to vectors inside it and can be mathematically transformed into each other by the addition of a reciprocal lattice vector G. These processes are called Umklapp scattering and change the total phonon momentum.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – III - Condensed Matter Physics – SPHA5301

3.Band Theory of Solids

Applications of Uncertainty Principle

Calculation of energy of particle in 1D box:

Consider a particle of mass ‘m’ moving along the x-axis between the two rigid walls of the well with x = 0 and x = a.

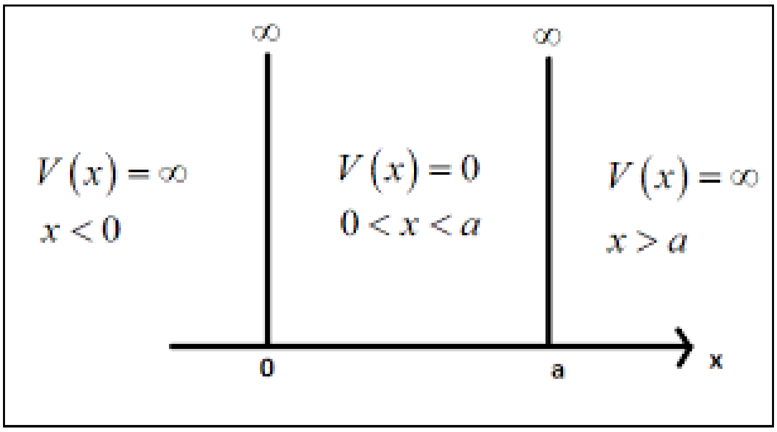

Fig.1.8 Particle in a box

When the force acting on the particle between the walls is zero, its potential energy is constant in this region and it is duly taken to be zero. As the walls are assumed to be rigid, the force acting on the particle abruptly increases from zero to finite value at the boundaries and hence the potential energy of the particle becomes infinitely large at x = 0 and x = a.

Thus, potential function V(x) is expressed as

$$V(x) = 0 \text{ for } 0 < x < a$$

$$V(x) = \infty \text{ for } 0 \geq x \geq a$$

This potential function is known as square well potential.

The particle cannot move out of the box. Also, it cannot exist on the walls of the box. So its wave function Ψ is 0 for $x \leq 0$ and $x \geq a$ and for zero potential the Schrodinger equation can be written as:

$$\frac{d^2\Psi}{dx^2} + \frac{2mE}{\hbar^2}\Psi = 0 \qquad \text{... (1)}$$

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \qquad \text{... (2)}$$

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

The general solution of equation (2) is

$$\Psi(x) = A\,\sin kx + B\cos kx \qquad \dots (3)$$

Applying the boundary conditions $\Psi(x) = 0$ at x = a and x = 0, one gets $k = \frac{n\pi}{a}$ where n = 1, 2, 3, ... and B = 0.

Thus the wave function associated with the electron is:

$$\Psi_n = A\sin\left[\frac{n\pi x}{a}\right] \qquad \dots (4)$$

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2h^2}{8ma^2} \qquad \dots (5)$$

This equation gives the energy of the particle in the nth energy state.

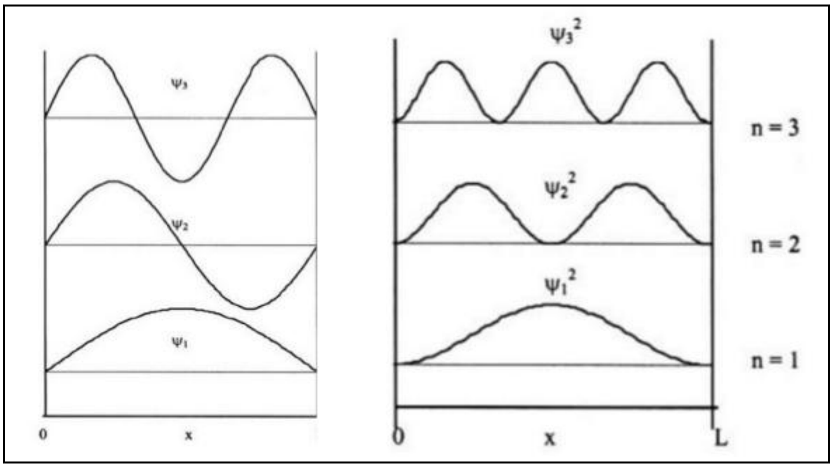

Fig.1 Energy levels and wave functions

The particle in the box cannot possess any arbitrary amount of energy. Rather, it can have discrete energy values specified by the equation (5). In other words, its energy is quantised.

Each value of E_n is called as eigen value and the corresponding Ψ_n is called eigen function.

Problems

1. Calculate the minimum energy of an electron can possess in an infinitely deep potential will of width 4nm.

   Given:

   a = 4nm; n = 1 (for minimum energy)

Solution:

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

$$E = \frac{1^2(6.625 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}(4 \times 10^{-9})^2}$$

$$E = 3.7639 \times 10^{-21}\,J \; or \; E = 0.0235\,eV$$

2. An electron is trapped in a one-dimensional box of length 0.1nm. Calculate the energy required to excite the electron from its ground state to the sixth excited state.

   Given:

   a = 0.1 nm; n = 1 (for ground energy)

Solution:

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

$$E = \frac{1^2(6.625 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}(0.1 \times 10^{-9})^2}$$

$$E = 6.0223 \times 10^{-18}\,J$$

For sixth state, n = 6

$$E = \frac{6^2(6.625 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}(0.1 \times 10^{-9})^2}$$

$$E = 2.1680 \times 10^{-16}\,J$$

The energy required to excite the electron from its ground state to the sixth excited state is
$E = E_6 - E_1$

$$E = 2.1680 \times 10^{-16} - 6.0223 \times 10^{-18}$$

$$E = 2.1078 \times 10^{-16}\,J$$

$$E = 1317\,eV$$

3. If the uncertainty in position of an electron is 4 X 10^{-10} m, calculate the uncertainty in its momentum.

Solution:

$$\Delta p_x\,\Delta x \approx h$$

$$\Delta p_x \approx \frac{h}{\Delta x} \approx \frac{6.6 \times 10^{-34}}{4 \times 10^{-10}}$$

$$= 1.65 \times 10^{-24}\,kg\,\frac{m}{sec}$$

ORIGIN OF ENERGY BANDS

Generally solid consists of more number of atoms and each atom consists of the central nucleus of positive charge around which small negatively charged particles called electrons revolve in different paths or orbits. An Electrostatic force of attraction between electrons and the nucleus holds up electrons in different orbits.

An isolated atom possesses discrete energies of different electrons. If two isolated atoms are brought to very close proximity, then the electrons in the orbits of two atoms interact with each other. So, that in the combined system, the energies of electrons will not be in the same level but changes and the energies will be slightly lower and larger than the original value. So, at the place of each energy level, a closely spaced two energy levels exists. If ‘N’ number of atoms are brought together to form a solid and if these atoms’ electrons interact and give ‘N’ number of closely spaced energy levels in the place of discrete energy levels, it is known as bands of allowed energies/band. Between the bands of allowed energies, a small region does not allow any energy levels. Such regions are called forbidden energy band/ energy gap (E_g). The allowed bands of energies and forbidden bands of energies are present alternatively one after another for the electrons of a solid**.**

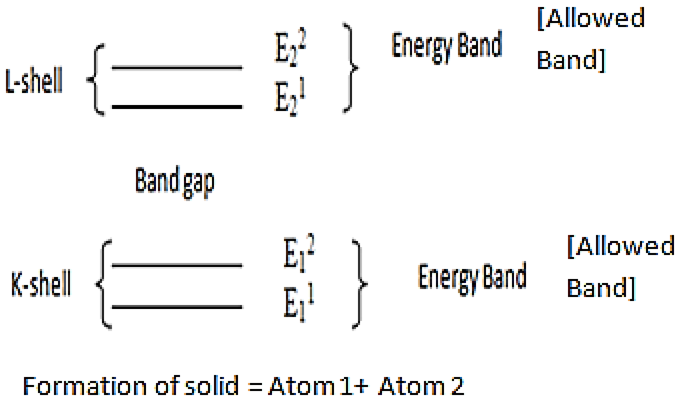

Fig. 2 Band formation in solids

When two atoms of equal energy levels are brought closer together, the k shell energy levels of individual atoms lie in the energy level E_1 and splits into E_1^1 and E_1^2 become as **energy band.** Similarly for L-shell energy levels lies in the energy level E_2 and splits into E_2^1 and E_2^2. Similarly when three atoms are brought together, the energy levels are in K – shell and L-shell are E_1^1 , E_1^2 and E_2^1, E_2^2 respectively. Similarly for K, L,M and N shells are E_1^1 , E_1^2,E_1^3 , E_1^4 and E_2^1, E_2^2, E_2^3, E_2^4 respectively. These type of transformations from the original energy levels into two (or) more energy levels is known as energy level splitting.

In example Lithium atom consists of 3 electrons. Among them the two electrons are in the same energy state (1s) and the other one is in the higher energy state (2s). In a solid of lithium contains N number of atoms, the lower energy level forms a band of 2N electrons occupying N different energy levels are shown in Fig.2.4. The higher energy level can form a band of 2N electrons (completely filled). But only N numbers of electrons are present in the next energy level. Therefore the band is half-filled band. The unoccupied band of the solid corresponds to the un occupied excitation level of the isolated atom.

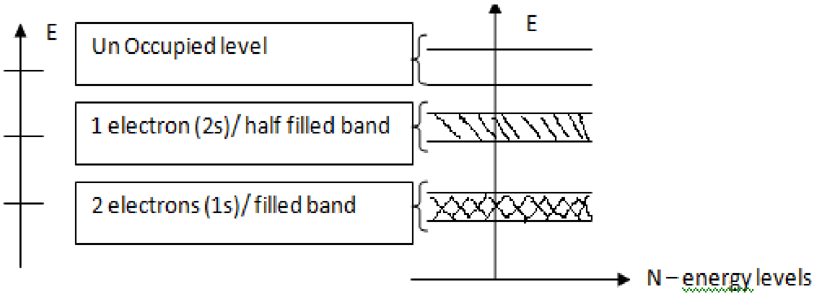

Fig.3 (a) Isolated atom and (b) Solid of N atoms

The width of the energy band depends on the relative freedom of electrons in the crystal. The electrons in lower filled energy (closely bounded with nucleus) band do not have any freedom to move in the crystal. The electrons in half filled energy level (loosely bound with nucleus) are free to move inside the crystal. Generally the half-filled band is called **valence band** and the upper unoccupied (unfilled) band is called **conduction band**. In between the valence band and conduction the gap is known as energy gap

The differences between metals, semiconductors and insulators can be made based on (i) the width of the energy gap (ii) number of effective electrons (The availability of number of free electrons that participate in electrical conduction per unit volume when an electric field is applied. These free electrons are called **effective electrons**).

BAND STRUCTURE OF CONDUCTOR, SEMICONDUCTORS, INSULATORS, HALF METALS AND SEMI METALS

Conductors:

In case of conductors, there is no forbidden band and the valence band and conduction band overlap each other (Fig). Low resistive materials and it is about $10^{-8}\Omega$m are generally called as conducting materials. These materials have high electrical and thermal conductivity. The conducting property of a solid is not a function of total number of the electrons in a metal and it is about the number of free/valence electrons called as conduction electrons. Hence in metals the electrical conductivity depends on the number of free electrons. Here, plenty of free electrons are available for electric conduction. The electrons from valence band freely enter in the conduction band due to overlapping of bands.

Examples: Iron, Copper etc.,

Semiconductors:

In semiconductors, the forbidden band is very small (Fig.). Germanium and silicon are the best examples of semiconductors. In Germanium the forbidden band is of the order of 0.7eV while in case of silicon, the forbidden gap is of the order of 1.1eV. Actually, a semi-conductor material is one whose electrical properties lie between insulators and good conductors. At 0°K, there are no electrons in conduction band and the valence band is completely filled. When a small amount of energy is supplied, the electrons can easily jump from valence band to conduction band due to minimum energy gap. For example, when the temperature is increased, the forbidden band is decreased so that some electrons are liberated into the conduction band. In semi-conductors, the conductivities are of the order of 10^2 ohm-meter.

Examples: Silicon, Germanium etc.,

Insulator

In case of insulators, the forbidden energy band is wide (Fig.). Due to this fact, electrons cannot jump from valence band to conduction band. In insulators, the valence electrons are bound very tightly to their parent atoms. For example, in case of materials like glass, the valence band is completely filled at 0K and the energy gap between valence band and conduction band is of the order of 6 eV. Even in the presence of high electric field, the electrons do not move from valence band to conduction band. When a very large energy is supplied, an electron may be able to jump across the forbidden gap. Increase in temperature enables some electrons to go to the conduction band. This explains why certain materials which are insulator become conductors at high temperature. The resistively of insulators is of the order of 10^7 ohm-meter.

Examples: Wood, Glass etc.,

At absolute zero (0K) the energy levels are completely occupied by electrons up to a certain level. Above that the energy levels are completely unoccupied by electrons. This highest level which is completely filled by electrons is called **Fermi level**. In conductor the Fermi level lies in the permitted band (since the valence and conduction band overlap without an energy gap). In Semiconductor the Fermi level lies in the small energy gap. In Insulator the Fermi level lies exactly in the middle of energy gap.

The **Fermi energy** (E_F) is described as the highest energy that the electrons assumes at a temperature of 0 K (Fig.2.5). The Fermi energy is the difference in energy, mostly kinetic. To put this into perspective one can imagine a cup of coffee and the cup shape is the electron band; as one fills the cup with the liquid the top surface increases. This can be compared to the Fermi energy because as electrons enter the electron band the Fermi energy increases. The Semiconductors act differently than the above stated analogy.

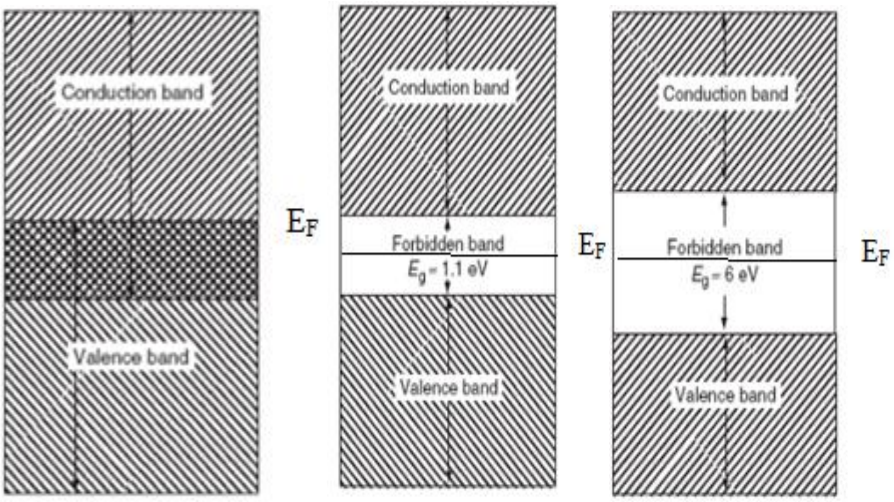

Fig. 4 (a) Conductor (b) Semiconductor (c) Insulator

BLOCH THEOREM

Based on band theory, the solids are again classified into conductor, semiconductor and insulator. The free electron theory explained about the electrical conductivity and thermal conductivity of solids but it fails to clearly explain about the difference in between the conductor, insulator and semiconductor. Hence the Bloch theorem is used to explain as follows:

In order to understand the difference between the conductors and insulators, it is necessary to incorporate the variation of potential inside the crystal due to the presence of positive ion cores in the free electron model. It gives the realistic idea about to assume the potential inside the metallic crystal to be periodic with the periodicity of the lattice shown in Fig.

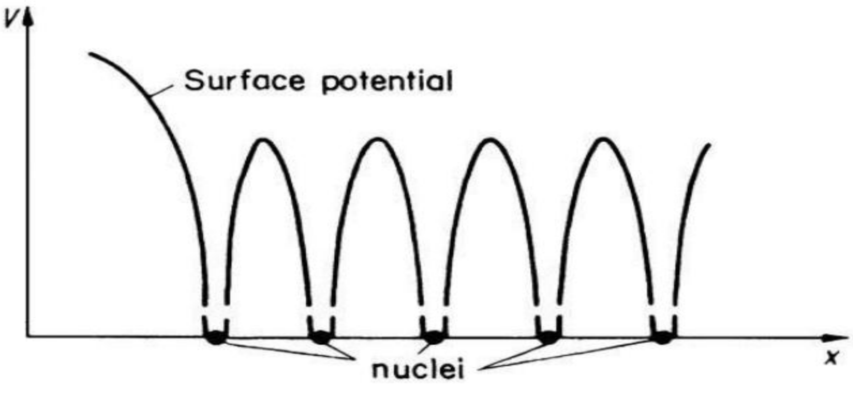

Fig. 5 One dimensional periodic potential in a crystal

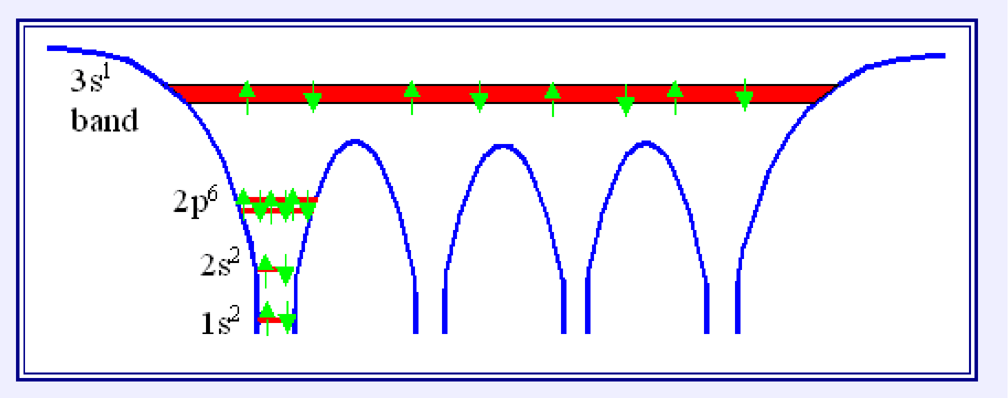

Fig.6

Suppose an electron passes along X-direction in a one-dimensional crystal having periodic potentials:

$$V(x) = V(x + a)$$

where '*a*' is the periodicity of the potential.

The Schrödinger wave equation for the moving electron in a constant potential (V) is:

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

The solution for Equation (1) is of the form:

$$\psi(x) = e^{iKx}\, u_k(x) \qquad (2)$$

where $u_k(x) = u_k(x + (N)\, a)$ (3)

Eqn. (3) represents periodic function and e^{ikx} represents plane wave. The above statement is known as Bloch theorem and Eqn. (3) is called **Block function.**

The Bloch function has the property:

$\psi(x + a) = \exp\,[ik\,(x + (N)a)]$

$u_k(x + a) = \psi(x) \exp ik(N)a$ (4)

or $\psi(x + a) = Q\psi\,(x)$ where $Q = \exp ik(N)a$ (5)

This is frequently referred as Bloch condition.

If exp $ik(N)a$ = 1; KNa = 2πn : Hence K = 2πn **/ L (Because L= Na)**

The total number of allowed k- values in first zone is

Length of the first zone/ Length of the unit spacing = (2π/a) / (2π/L) = L/a = N.

Kronig Penny Model:

Proof: Suppose g(x) and f(x) are two real independent solutions for the Schrödinger's equation (1), then f($x + a$) and g($x + a$) are also solutions of the above equation so that:

$f(x + a) = \alpha_1 f(x) + \alpha_2 g(x)$

$g(x + a) = \beta_1 f(x) + \beta_2 g(x)$ (6)

where α_1, α_2, β_1 and β_2 are the real functions of energy (E).

The solution for Schrödinger wave equation is of the form:

$\psi(x) = \mathrm{A} f(x) + \mathrm{B}\, g(x)$ (7)

where A and B are constants and

$\psi(x + a) = \mathrm{A} f(x + a) + \mathrm{B}\, g(x + a)$ (8)

Substituting Eqn (6) in Eqn (8), we have:

$\psi(x + a) = \mathrm{A}[\alpha_1 f(x) + \alpha_2 g(x)] + \mathrm{B}[\beta_1 f(x) + \beta_2 g(x)]$

$= [\mathrm{A}\alpha_1 + \mathrm{B}\beta_1] f(x) + [\mathrm{A}\alpha_2 + \mathrm{B}\beta_2] g(x)$ (9)

From the property of Bloch function, Eqn. (5) can be written as using Eqn. (7), we have:

$\psi(x + a) = Q\psi(x) = Q\mathrm{A}f(x) + Q\mathrm{B}g(x)$ (10)

Comparing Equations (9) and (10), we have:

$\mathrm{A}\alpha_1 + \mathrm{B}\beta_1 = Q\mathrm{A}$

and $\mathrm{A}\alpha_2 + \mathrm{B}\beta_2 = Q\mathrm{B}$ (11)

In Eqn. (11), A and B have non-vanishing values only if the determinant of the coefficients of A and B is equal to zero.

i.e. $$\begin{vmatrix} \alpha_1 - Q & \beta_1 \\ \alpha_2 & \beta_2 - Q \end{vmatrix} = 0$$

or $Q^2 - (\alpha_1 + \beta_2) Q + \alpha_1\beta_2 - \alpha_2\beta_1 = 0$ (12)

From the above equation, we can show $\alpha_1\beta_2 - \alpha_2\beta_1 = 1$ Then the Eqn.(12) becomes:

$Q^2 - (\alpha_1 + \beta_2)Q + 1 = 0$ (13)

The above quadratic equation has two roots say Q_1 and Q_2. So, we have two values for $\psi(x)$ i.e., $\psi_1(x)$ and $\psi_2(x)$. Also note that $Q_1\, Q_2 = 1$. For certain values of energy corresponding to $(\alpha_1 + \beta_2)^2 < 4$, the two roots are complex and can be written as:

$$Q_1 = e^{iKa} \quad \text{and} \quad Q_2 = e^{-iKa} \tag{14}$$

The wave functions $\psi_1(x)$ and $\psi_2(x)$ can be represented as $\psi_1(x + a) = e^{\,ika}\, \psi_1(x)$ and

$$\psi_2(x + a) = e^{-iKa}\, \psi_2(x) \tag{15}$$

For other regions of energy corresponding to $(\alpha_1 + \beta_2)^2 > 4$, the roots Q_1 and Q_2 are real and reciprocal to each other. These two roots corresponding to Schrödinger's equation of the type:

$$\psi_1(x) = e^{\mu x}u(x) \quad \text{and} \quad \psi_2(x) = e^{-\mu x}u(x) \tag{16}$$

(μ is a real quantity)

Mathematically, the above solutions are sound but not accepted as wave functions describing elections. This leads to the energy spectrum of an electron in a periodic potential consists of allowed and forbidden energy regions or bands.

Requirements for An Acceptable Wavefunction

1. The wave function **ψmust be continuous**. All its **partial derivatives must also becontinuous** (partial derivatives are$\left(\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y} \text{etc.}\right)$ This makes the wave function"smooth".
2. The wave function ψ must be **quadratically integrable**. This means that the integral $\int\psi^*\psi\,\mathrm{d}\tau$must exist.
3. Since $\int\psi^*\psi d\tau$ is the probability density, **it must be single valued**.
4. The wave functions must form an **orthonormal set**. This means that
    - the wave functions must be **normalized.**

      $\int_{-\infty}^{\infty} \psi_i * \psi_i \mathrm{d}\tau = 1$
    - the wave functions must be **orthogonal**.

      $\int_{-\infty}^{\infty} \psi_j * \psi_j \mathrm{d}\tau=0$

$\int_{-\infty}^{\infty} \psi_j * \psi_j \mathrm{d}\tau = \delta_{ij}$ where $\delta_{ij} = 1\, when i = j$; $\delta_{ij} = 0\, when i \neq j$

Δijis called Kronecker delta

5. The wave function must be **finite everywhere**.
6. The wave function must satisfy the **boundary conditions** of the quantum mechanical system it represents.

HEISENBERG UNCERTAINTY PRINCIPLE

Uncertainty principle, also called **Heisenberg uncertainty principle** or **indeterminacy principle**, statement, articulated (1927) by the German physicist Werner Heisenberg, that the position and the velocity of an object cannot both be measured exactly, at the same time, even in theory. The very concepts of exact position and exact velocity together, in fact, have no meaning in nature.

The uncertainty principle is alternatively expressed in terms of a particle's momentum and position. The momentum of a particle is equal to the product of its mass times its velocity. Thus, the product of the uncertainties in the momentum and the position of a particle equals $h/(4\pi)$ or more, where h is Planck's constant, or about 6.6×10^{-34} joule-second. It is impossible to know the precise position and momentum. This relationship also applies to energy and time, in that one cannot measure the precise energy of a system in a finite amount of time. Uncertainties in the products of "conjugate pairs" (momentum/position) and (energy/time) were defined by Heisenberg as having a minimum value corresponding to Planck's constant divided by 4π. More clearly:

$$\Delta p * \Delta x \geq \frac{h}{4\pi}$$

$$\Delta t * \Delta E \geq \frac{h}{4\pi}$$

Where Δ refers to the uncertainty in that variable.

Qualitatively this principle states that "the order of magnitude of the product of the uncertainties in the knowledge of two variables must be at least Planck's constant h". Considering the position and momentum is the pair of physical variables, we have

$$\Delta p \, \Delta x \approx h \quad \text{... (1)}$$

where Δp is the uncertainty in determining the momentum and

Δx is the uncertainty in determining the position of the particle.

Similarly, we have

$$\Delta E \, \Delta t \approx h \quad \text{... (2)}$$

$$\Delta J \, \Delta \theta \approx h \quad \text{... (3)}$$

where ΔE and Δt are uncertainties in determining the energy and time while ΔJ and $\Delta\theta$ uncertainties in determining the angular momentum and angle.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – IV - Condensed Matter Physics – SPHA5301

4.ATOMIC MOLECULAR STRUCTURE

The Hydrogen molecule:

We are now in a position to discuss the electronic structure of the simplest molecule: H2. For the low-lying electronic states of H_2, the BO approximation is completely satisfactory, and so we will be interested in the electronic Hamiltonian.

BO approximation (Born Oppenheimer) :

The **Born-Oppenheimer Approximation** is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.

$$\hat{H}_{el} = -\tfrac{1}{2}\nabla_1^{\,2} - \tfrac{1}{2}\nabla_2^{\,2} + \frac{1}{R_{AB}} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} + \frac{1}{r_{12}}$$

where “1” and “2” label the two electrons and “A” and “B” label the two nuclei.

a. Minimal Atomic Orbital Basis

The most natural basis functions are the atomic orbitals of the individual Hydrogen atoms. If the bond length is very large, the system will approach the limit of two non-interacting Hydrogen atoms, in which case the electronic wavefunction can be well approximated by a product of an orbital on atom “A” and an orbital on atom “B” and these orbitals will be exactly the atomic orbitals (AOs) of the two atoms. Hence, the smallest basis that will give us a realistic picture of the ground state of this molecule must contain two functions: ^1s_A and $^1s_{B.}$ These two orbitals make up the minimal AO basis for H2. For finite bond lengths, it is advisable to allow the AOs to polarize and deform in response to the presence of the other electron (and the other nucleus).

b. Molecular Orbital Picture

We are now in a position to discuss the basic principles of the molecular orbital (MO) method, which is the foundation of the electronic structure theory of real molecules. The first step in any MO approach requires one to define an effective one electron Hamiltonian, (hˆ$_{\text{eff})}$. To this end, it is useful to split the Hamiltonian into pieces for electrons “1” and “2” separately and the interaction:

$$\hat{h}(1) \equiv -\tfrac{1}{2}\nabla_1^{\,2} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_B|} \qquad \hat{h}(2) \equiv -\tfrac{1}{2}\nabla_2^{\,2} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|}$$

$$\hat{V}_{12} \equiv \frac{1}{r_{12}}$$

The full Hamiltonian is then

$$\hat{H}_{el} = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12} + \frac{1}{R_{AB}}$$

The matrix representation,

of $\hat{h}$ in the minimal basis is:

$$\begin{pmatrix} \langle 1s_A|\hat{h}|1s_A\rangle & \langle 1s_A|\hat{h}|1s_B\rangle \\ \langle 1s_B|\hat{h}|1s_A\rangle & \langle 1s_B|\hat{h}|1s_B\rangle \end{pmatrix} \equiv \begin{pmatrix} \varepsilon & h_{AB} \\ h_{AB} & \varepsilon \end{pmatrix}$$

where we made use of the average one electron (onsite) energy:

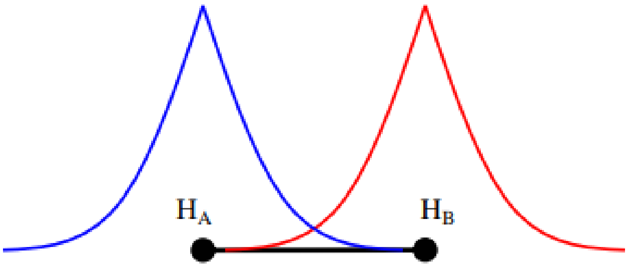
$$\varepsilon \equiv \langle 1s_A|\hat{h}|1s_A\rangle = \langle 1s_B|\hat{h}|1s_B\rangle$$

and the off-diagonal coupling (often called a "hopping integral"):

$$h_{AB} \equiv \langle 1s_A|\hat{h}|1s_B\rangle = \langle 1s_B|\hat{h}|1s_A\rangle .$$

We can immediately diagonalize this matrix; the eigenvalues are $\varepsilon_\pm = \varepsilon \pm h_{AB}$ and the eigenstates are:

$$|\phi_+\rangle \propto \tfrac{1}{\sqrt{2}}\left(|1s_A\rangle + |1s_B\rangle\right) \qquad |\phi_-\rangle \propto \tfrac{1}{\sqrt{2}}\left(|1s_A\rangle - |1s_B\rangle\right)$$



The eigenstates of the effective one-electron Hamiltonian are called molecular orbitals (just as the basis functions are called atomic orbitals). They are one-electron functions that are typically delocalized over part (or all) of the molecule. As a first step, we need to normalize these MOs. This is more complicated than it might at first appear, because the AOs are ***not orthogonal***. For example, as the atoms approach each other, the two AOs might look like the picture at right. However, if we define the ***overlap integral*** by

$$S \equiv \langle 1s_A|1s_B\rangle ,$$

we can normalize the MOs:

$$\langle\phi_+|\phi_+\rangle = \tfrac{1}{2}\left(\langle 1s_A|1s_A\rangle + \langle 1s_B|1s_A\rangle + \langle 1s_A|1s_B\rangle + \langle 1s_B|1s_B\rangle\right) = 1 + S$$
$$\langle\phi_-|\phi_-\rangle = \tfrac{1}{2}\left(\langle 1s_A|1s_A\rangle - \langle 1s_B|1s_A\rangle - \langle 1s_A|1s_B\rangle + \langle 1s_B|1s_B\rangle\right) = 1 - S$$

These eigenfunctions merely reflect the symmetry of the molecule; the two hydrogen atoms are equivalent and so the eigenorbitals must give equal weight to each 1s orbital. So our "choice" of the one electron Hamiltonian actually does not matter much in this case; any one-electron Hamiltonian that reflects the symmetry of the molecule will give the same molecular orbitals.

$|\phi_+\rangle$ is usually denoted $|\sigma\rangle$ while $|\phi_-\rangle$ is denoted $|\bar{\sigma}\rangle$

The second step in MO theory is to construct a single determinant out of the MOs that corresponds to the state we are interested in. For the purposes of illustration, let us look at the lowest singlet state built out of the molecular orbitals. Hence,

$$|\Phi_{MO}\rangle = \left| |\sigma\rangle |\bar{\sigma}\rangle \right|$$

First, we decompose the wavefunction into spatial and spin parts and note that the spin part is normalized:

$$\left|\langle\sigma|\langle\bar{\sigma}\|\hat{H}_{el}\|\sigma\rangle|\bar{\sigma}\rangle\right| = \langle\sigma(1)|\langle\sigma(2)|\hat{H}_{el}|\sigma(1)\rangle|\sigma(2)\rangle\langle\Phi_{spin}|\Phi_{spin}\rangle$$

$$= \langle\sigma(1)|\langle\sigma(2)|\hat{H}_{el}|\sigma(1)\rangle|\sigma(2)\rangle$$

Then, we note that $\hat{H}_{el} = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12} + 1/R_{AB}$ and

$$\langle\sigma(1)|\langle\sigma(2)|\hat{h}(1)|\sigma(1)\rangle|\sigma(2)\rangle = \langle\sigma(1)|\hat{h}(1)|\sigma(1)\rangle\langle\sigma(2)|\sigma(2)\rangle$$

$$= \langle\sigma(1)|\hat{h}(1)|\sigma(1)\rangle \equiv \varepsilon_\sigma$$

$$\langle\sigma(1)|\langle\sigma(2)|\hat{h}(2)|\sigma(1)\rangle|\sigma(2)\rangle = \langle\sigma(2)|\hat{h}(2)|\sigma(2)\rangle\langle\sigma(1)|\sigma(1)\rangle$$

$$= \langle\sigma(2)|\hat{h}(2)|\sigma(2)\rangle \equiv \varepsilon_\sigma$$

$$\langle\sigma(1)|\langle\sigma(2)|\hat{V}_{12}|\sigma(1)\rangle|\sigma(2)\rangle \equiv J_{\sigma\sigma}$$

Taken together, these facts allow us to write:

$$\langle\Psi_{MO}|\hat{h}_1|\Psi_{MO}\rangle = \langle\Psi_{MO}|\hat{h}_1|\Psi_{MO}\rangle + \langle\Psi_{MO}|\hat{h}_2|\Psi_{MO}\rangle + \langle\Psi_{MO}|\hat{V}_{12}|\Psi_{MO}\rangle + \frac{1}{R_{AB}}$$

$$= 2\varepsilon_\sigma + J_{\sigma\sigma} + \frac{1}{R_{AB}}$$

Each of the first two terms is energy of a single electron (either 1 or 2) in the field produced by the nuclei (hˆ) while the third is the average repulsion of the two electrons. Note that the second and third terms are both positive, so binding has to arise from the one-electron piece. This is the MO energy for the ground state of H2.

Central Field Approximation

The basic difficulty in solving the Schrödinger equation stems from the fact that the interelectron repulsion is too larger an effect to be treated as a perturbation. 2*Nijijer*<Σ

→ It is that the inter electron repulsion contains a large spherically symmetric component. Thus it is possible to construct a potential energy function which is a spherically symmetric. ()*iUr*

→ One electron operator is a good approximation to the actual potential energy of the ith electron in the field of the nucleus and the other electrons. The Hamiltonian may be written as,

$$H = H^* + H_1$$

$$where\ H^* = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}U(r_i)$$

$$where\ \sum_i U(r_i) = -\sum_{i=1}^{N}\frac{Ze^2}{r_i} + \left\langle\sum_{i<j}^{N}\frac{e^2}{r_{ij}}\right\rangle$$

$$and\ H_1 = \sum_{i<j}^{N}\frac{e^2}{r_{ij}} - \left\langle\sum_{i<j}^{N}\frac{e^2}{r_{ij}}\right\rangle \qquad \text{Non-Spherical part only}$$

In which $\left\langle\sum_{i<j}^{N}\frac{e^2}{r_{ij}}\right\rangle$ is the average over a sphere of the electron repulsion.

It is therefore independent of the angular coordinates, then becomes the Hamiltonian which contains the non spherical part of the electron repulsions, whereas contains the K.E, P.E in the field of the nucleus, and the spherical average electron repulsion energy. $1H$ $*H$
This is Known as central field approximation. The advantage of this approach is that, it is assumed that contains most of the inter electron repulsion, the remaining term is small enough to be treated as a perturbation.$*H$ $1H$

$$H^*\Phi = \left\{ -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} U(r_i)\right\}\Phi = E\Phi$$

is a product of single electron wave function . When is allowed to operate on a product wave function, it operates on each of the in turn, since the coordinates of each of electrons are independently variable. So, the equation reduced to a set of simultaneous equation, one for each electron. Φ $_i\phi$ $^*H$ $\Phi_i\phi N$

$$H_1^*\phi_1 = E_1\phi_1 \quad ; \quad H_2^*\phi_2 = E_2\phi_2 \quad ; \quad \dots.$$

$$H^* = \sum_{i=1}^{N} H_i^* \quad ; \quad E = \sum_i E_i$$

Each is hydrogen type orbitals except radial part. These orbitals are called central field orbitals. $_i\phi$

The symmetric wavefunction remains same even we interchange the indices 1 and 2
On the other hand antisymmetric wavefunction changes sign if we interchange indices 1 and 2.

This is required because of the indistinguishability of identical particles like electrons. In Classical mechanics, identical particles are distinguishable, because it is possible to define the individual particles in terms of their space coordinate and time.

However, in Quantum mechanics, this is not possible. So, identical particles are always considered to be indistinguishable.
For two electrons system, when the two electrons are interchanged, then the wavefunctions are related with a phase factor as

$$\text{Thus, } e^{-2i\varphi} = 1$$

$$\text{So } e^{i\phi} = \pm 1 \text{ and thus, } \Phi(r_1, r_2) = \pm\,\Phi(r_2, r_1)$$

The “+” sign is for symmetric state and “-“ sign is for antisymmetric state.
This shows that the wavefunction should be either symmetric or antisymmetric with respect to the interchange of the electrons.
If the two electrons are in the symmetric or antisymmetric state in a system, then these electrons remain in that state for all time unless it disturbed by external perturbation.

Hartree's method of Self Consistent field for N-electron system

- For the Schrödinger equation to be analytically solvable, the variables must be separable - the variables are the coordinates of the electrons.
- To separate the variables in a way that retains information about electron-electron interactions, the electron-electron term must be approximated so it depends only on the coordinates of one electron.
- Such an approximate Hamiltonian can account for the interaction of the electrons in **an average way**.
- The exact one-electron eigenfunctions of this approximate Hamiltonian then can be found by solving the Schrödinger equation.
- These functions are the best possible **one-electron functions**.
- The Hartree method is used to approximate the **wavefunction** and the energy of a quantum multi-electron system in a stationary state.
- This approximation assumes that the exact N-body wave function of the system can be approximated by a product of single-electron wavefucntions.
- In principle, the Hartree-Fock technique enables us to calculate all the states and their energies for any atom in the periodic table.
- However, the computational effort required increases rapidly with the number of electrons since the size of the Slater determinant scales with the square of the number of single-electron states involved.

The best single electron atomic wave functions are the self consistent field (SCF) functions introduced by Hartree (1927).

To obtain these, we start with a set of approximate single electron functions. Using of these except the ith function, the average field due to their charge clouds is calculated. N

This constitutes the potential field in which the ith electron moves. Solution of the ith equation gives an improved wave function . $J\varphi'$

This is repeated for each of the electrons, giving first improved, single electron wave functions. N

These are then used to calculate a set of second improved wave functions, and so on; the process is continued until no further improvement is registered.

In other words, the electrons are supposed to move in a potential which they themselves generate. This is the reason it is known as Self Consistent

The calculated energy of the atom is the sum of the energies of the individual electrons, minus the coulomb repulsion energy averaged over all pairs of electron wave functions, since this gets included twice over for each pair of electrons & , once in calculation and once in . The energy of each of the SCF/AO's, is found to be a function

When the central field orbital is multiplied by a spin function which is or , we have a one-electron, central field spin orbital.

$\psi_{n\ell m_\ell m_s} = \Phi_{n\ell m_\ell}(r)\,\chi(m_s)$ Characterized by the four quantum nos. n, ℓ, m_ℓ, m_s.

Finally the spin orbitals may be organized into an antisymmetric N-electron wavefunction in order to satisfy the requirements of the Pauli principle.

$$\psi(\lambda_1, \lambda_2, \ldots, \lambda_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\lambda_1) & \psi_2(\lambda_1) & .. & \psi_N(\lambda_1) \\ \psi_1(\lambda_2) & \psi_2(\lambda_2) & .. & \psi_N(\lambda_2) \\ .. & .. & .. & .. \\ .. & .. & .. & .. \\ \psi_1(\lambda_N) & \psi_2(\lambda_N) & .. & \psi_N(\lambda_N) \end{vmatrix}$$

in which $\psi_i(\lambda_i)$ are spin orbitals.

in which are spin orbitals.

The distribution of electrons with and are known as configuration. Electrons in orbitals with same and are said to be equivalent.

Example: He atom

Hamiltonian $H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$

In zeroth order approximation; ignore ${e^2}/{r_{12}}$ term.

So, $$H^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_2}$$
$$= H_1 + H_2$$

Eigen functions of H_0, $\Phi(1,2) = \phi_a(1)\phi_b(2)$

This is the product wavefunction with the electron coordinates replaced by 1 & 2.

Eigen values, $E_0 = E_a + E_b$

Next part is to introduce the inter electronic repulsion term as a perturbation.

$$E_{ee} = \int \Phi(1,2) \left|\frac{e^2}{r_{12}}\right| \Phi(1,2)\, d\tau$$
$$= \int \phi_a(1)\phi_b(2) \left|\frac{e^2}{r_{12}}\right| \phi_a(1)\phi_b(2)\, d\tau$$

So the total Energy of the system $E = (E_a + E_b) + E_{ee}$

- It is helps to predict that exact solutions to the multi-electron Schrödinger equation would consist of a family of multi-electron wavefunctions, each with an associated energy eigenvalue.
- These wavefunctions and energies would describe the ground and excited states of the multi-electron atom, just as the hydrogen wavefunctions and their associated energies describe the ground and excited states of the hydrogen atom. We would predict quantum numbers to be involved, as well.
- The fact that electrons interact through their electron-electron repulsion means that an exact wavefunction for a multi-electron system would be a single function that depends simultaneously upon the coordinates of all the electrons; i.e., a multi-electron wavefunction:
- $|\psi(r1,r2,\cdots ri)\rangle$
- Unfortunately, the electron-electron repulsion terms make it impossible to find an exact solution to the Schrödinger equation for many-electron atoms.
- **What is meant by LCAO (Linear Combination of Atomic orbitals)?**

  The Linear combination of atomic orbitals which is also known as LCAO is an approximate method for representing molecular orbitals. It's more of a superimposition method where constructive interference of two atomic wave function produces a bonding molecular orbital whereas destructive interference produces non-bonding molecular orbital.
- **Conditions to be satisfied:** The conditions that are required for a linear combination of atomic orbitals are as follows:

  Same Energy of combining orbitals –
- The combining atomic orbitals must have same or nearly same energy. This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine as they have appreciable energy difference.
- **Same symmetry about the molecular axis –**
- combining atoms should have same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have same energy but still, the $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom but cannot combine with $2p_x$ and $2p_y$ orbital as they have a different axis of symmetry. In general, the z-axis is considered as the molecular axis of symmetry

- **Proper Overlap between the atomic orbitals** – The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.
- The condition can be understood by two simple requirements. For the formation of proper molecular orbital, proper energy and orientation are required. For proper energy, the two atomic orbitals should have the same energy of orbitals and for the proper orientation, the atomic orbitals should have proper overlap and the same molecular axis of symmetry.
- Covalent bonds and linear combination of atomic orbitals
- Consider two atoms next to each other.
- Since different orbitals of an atom are separated in energy, we consider one orbital per atom
- That the atoms are sufficiently far apart, so that the shape of the orbitals or the energy of the orbitals doesn't change much.
- **Bonding** molecular **orbitals** are formed by in-phase combinations of atomic wave functions, and electrons in these **orbitals** stabilize a molecule. **Antibonding** molecular **orbitals** result from out-of-phase combinations of atomic wave functions and electrons in these **orbitals** make a molecule less stable.

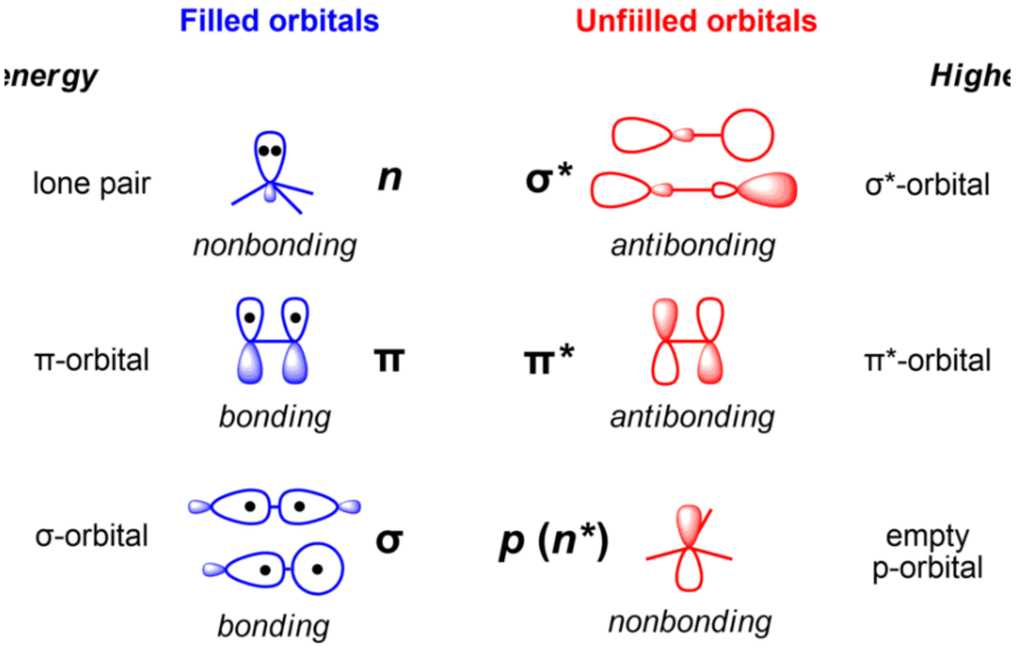


Fig. 1

Hybridization

- Hybridization is defined as the concept of mixing two atomic orbitals with the same energy levels to give a degenerated new type of orbitals. This intermixing is based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process, provided they have equal energy.
- During the process of hybridization, the atomic orbitals of similar energy are mixed together such as the mixing of two 's' orbitals or two 'p' orbital's or mixing of an 's' orbital with a 'd' orbital.
- What are hybrid orbitals?
- The hybrid orbitals can be defined as the combination of standard atomic orbitals resulting in the formation of new atomic orbitals.
- a 'p' orbital or 's' orbital with a 'd' orbital.

Important points about hybridisation

1)Only those orbitals which have approximately equal energies and belong to the same atom or ion can undergo hybridisation.

2)Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed.

3)It is not necessary that all the half filled orbitals must participate in hybridisation. Even completely filled orbitals with slightly different energies can also participate.

4)Hybridisation never take place in isolated atoms but it occurs only at the time of bond formation.

5)One can tell the shape of a molecule by knowing the kind of hybridisation involved.

6)The bigger lobe of the hybrid orbital always have positive sign while the smaller lobe on the opposite side has negative sign.

Types of Hybridisation

- Based on the types of orbitals involved in mixing, the hybridization can be classified as sp3, sp2, sp, sp3d, sp3d2, sp3d3. Let us now discuss the various types of hybridization, along with their examples.

1) sp Hybridization

- sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals.** It forms linear molecules **with an angle of 180°**

- This type of hybridization involves the mixing of one ‘s’ orbital and one ‘p’ orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital.

- sp hybridization is also called **diagonal hybridization.**

- Each sp hybridized orbital has an equal amount of s and p character, i.e., **50% s and p character.**

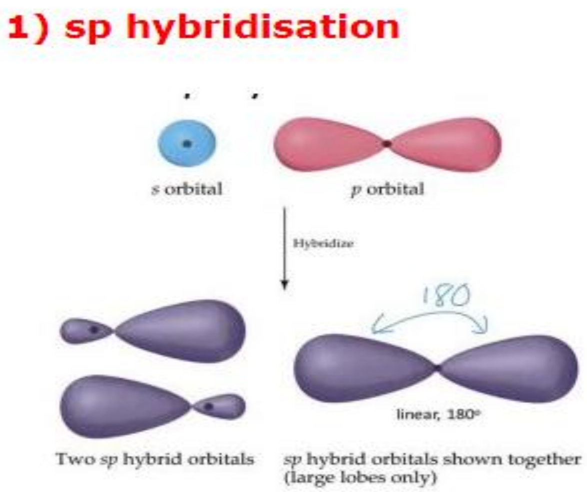


Fig. 2

Examples of sp Hybridization:

All compounds of beryllium like BeF_2, BeH_2, $BeCl_2$

All compounds of carbon-containing triple Bond like C_2H_2.

- **sp^2 hybridisation** is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called **sp^2 hybrid orbitals.**

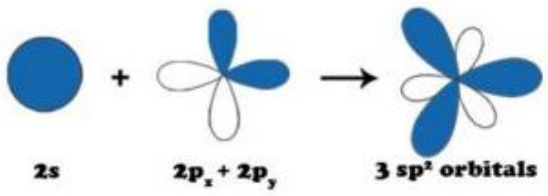
- sp^2 hybridization is also called **trigonal hybridization.**

- It involves mixing of one ‘s’ orbital and two ‘p’ orbital’s of equal energy to give a new hybrid orbital known as sp^2.

- A mixture of s and p orbital formed in trigonal symmetry and is **maintained at 120^0**.

- All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has **33.33% s character and 66.66% ‘p’ character.**

- The molecules in which the central atom is linked to 3 atoms and is sp2 hybridized have a triangular planar shape



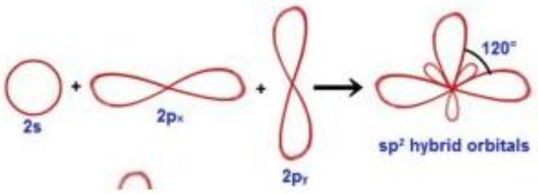
- 

Fig. 3

- Examples of sp^2 Hybridization
- All the compounds of Boron i.e. BF_3, BH_3
- All the compounds of carbon containing a carbon-carbon double bond, Ethylene (C_2H_4)
- **sp^3 Hybridization**
- When one ‘s’ orbital and 3 ‘p’ orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization or sp^3**. The new orbitals formed are called **sp^3 hybrid orbitals.**
- These are directed towards the four corners of a regular tetrahedron and make **an angle of 109°28’** with one another.
- The angle between the sp3 hybrid orbitals is 109.28^0
- Each sp^3 hybrid orbital has **25% s character and 75% p character.**
- Example of sp^3 hybridization: ethane (C_2H_6), methane.

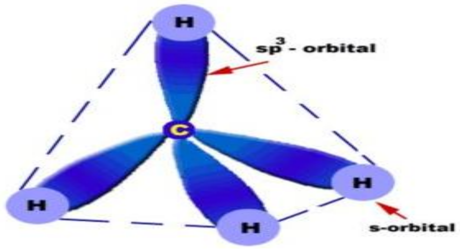
- 

Fig.4

Heitler and London Theory

- **Valence Bond Theory**
- Heitler and London introduced this theory. This is primarily based on the concepts of atomic orbitals, electronic configuration of elements, the overlapping of atomic orbitals, hybridization of atomic orbitals.
- The overlapping of atomic orbitals results in the formation of a chemical bond. The electrons are localized in the bond region due to overlapping.
- Valence bond theory describes the electronic structure of molecules.
- The theory says that electrons fill the atomic orbitals of an atom within a molecule.
- It also states that the nucleus of one atom is attracted to the electrons of another atom.
- It is a theory which describes chemical bonding.
- VBT states that the overlap of incompletely filled atomic orbitals leads to the formation of a chemical bond between two atoms.
- The unpaired electrons are shared and a hybrid orbital is formed.
- **Postulates of Valence Bond Theory**
- The overlapping of two half-filled valence orbitals of two different atoms results in the formation of the covalent bond.
- The overlapping causes the electron density between two bonded atoms to increase. This gives the property of stability to the molecule.
- In case the atomic orbitals possess more than one unpaired electron, more than one bond can be formed and electrons paired in the valence shell cannot take part in such a bond formation.
- Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule.
- The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.
- A covalent bond is directional. Such a bond is also parallel to the region of overlapping atomic orbitals.

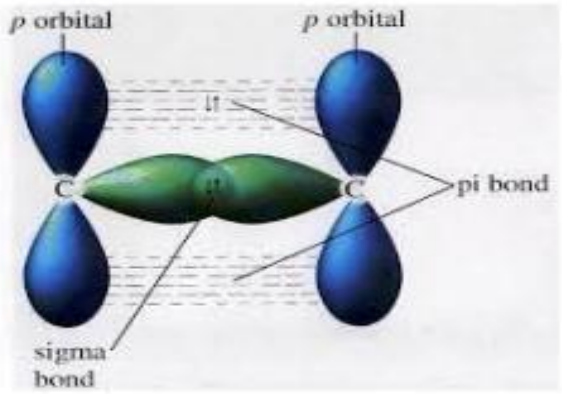
- Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond and a **pi bond**. The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis is known as a **sigma bond.**
- Based on the overlapping of orbitals, how many types of covalent bonds are formed and what are they?
- Answer: Based on the overlapping of orbitals, two types of covalent bonds are formed. These are known as sigma(σ) and pi(π) bonds.
- **Sigma bonds** are formed by the end-to-end overlap of atomic orbitals along the inter-nuclear axis known as a head-on or axial overlap. End-on overlapping is of three types, they are s-s overlapping, s-p overlapping and p-p overlapping.
- A **pi bond** is formed when atomic orbitals overlap in a specific way that their axes remain parallel to each other and perpendicular to the internuclear axis.
- 

Fig.5

- **Applications of Valence Bond Theory**
- The maximum overlap condition which is described by the valence bond theory can explain the formation of covalent bonds in several molecules.
- This is one of its most important applications. For example, the difference in the length and strength of the chemical bonds in H_2 and F_2 molecules can be explained by the difference in the overlapping orbitals in these molecules.
- The covalent bond in an HF molecule is formed from the overlap of the 1s orbital of the hydrogen atom and a 2p orbital belonging to the fluorine atom, which is explained by the valence bond theory.

- **Limitations of Valence Bond Theory**
- It fails to explain the tetravalency of carbon.
- No insight offered on the energies of the electrons.
- The theory assumes that electrons are localized in specific areas.
- It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- No distinction between weak and strong ligands.

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UNIT – V - Condensed Matter Physics – SPHA5301

5.Fermi surface

The Fermi surface is defined as the surface of constant energy EF in K- space inside which all the states are occupied by the valence electron, while all the states lying outside it are empty at zero temperature. The effect of temperature on the Fermi surface is very slight and the surface remains sharp even at room temperature or higher. The shape of the Fermi surface is determined by the geometry of the energy contours in a zone. For a free electron, the Fermi surface is a sphere of radius KF when it lies well within the first Brillouin zone.
However, non spherical and complicated shaper are observed when the Fermi surface and Brillouin zone are close to or touch one another under the effect of pseudo potential $Veff$ (r). Hence, a study of the shape of the Fermi surface and its proximity of the Brillouin zone is used to determine the properties of solids, such as heat capacity, pauli's paramagnetism , electrical conductivity, etc. Fig shows the evolution of the shape of constant energy curve (fs) as the number of electrons are gradually increased. The kinetic energy of a free electron in K - space is given by the parabolic eqn.

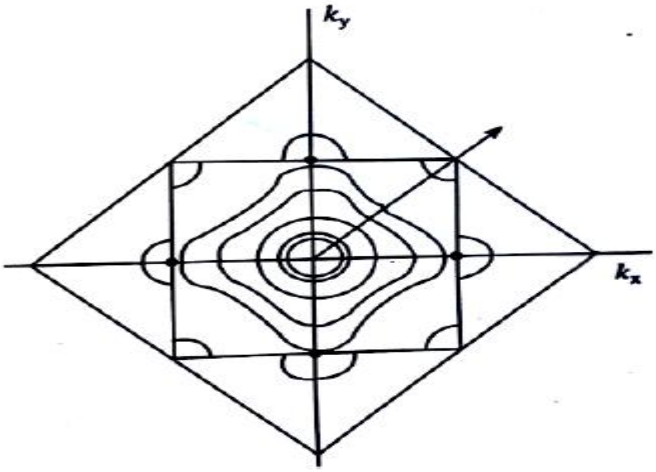

Fig.1 –Fermi Surface

$$E_{(k)} = \frac{\hbar^2 k^2}{2m}$$

The center of the first BZ (where K=0) is a minimum energy position, E = 0. This implies that for K =0 all the states are empty inside the brillouin zone. For small number of valence electrons, only the states lying near the bottom of the band (ie. the centre of the first BZ) are filled and the occupied volume is a sphere of radius KF . As the number of valence electrons is increased, more and more states are occupied and so the Fermi volume gradually expands. The Fermi surface begins to deform and loses its spherical shape near the zone boundary. The degree of distortion depends on (i) how near is the Fermi surface to the zone boundaries, (ii) the magnitude of the effective pseudo potential.

Characteristics of Fermi surfaces

1. The Fermi surface represents the dynamic and inertial properties of conduction electron in K- space.
2. The volume of the Fermi surface represents the number of conduction electrons.
3. The Fermi surface has spherical shape within the first brillouin zone and non- spherical in higher zones.

4. The Fermi surface always meets the zone boundary at right angles along the line of intersection.
5. For a spherical Fermi surface, the velocity of for a free electron is v = $\hbar K$
6. For non- spherical Fermi surfaces, under periodic potential, the velocity of electron is a non linear function of K.
7. Study of Fermi surface gives to know the important properties of solids, such as heat capacity, pauli's paramagnetism, electrical conductivity etc.

Harrison's method of constructing Fermi surface
Extended zone scheme

Harrison's method is based on a weak pseudo potential $Veff$ (r) . The effect of this potential causes the energy discontinuities ΔE as well as distortion in the Fermi surface at the zone boundaries. Therefore, if $Veff$ (r) is made arbitrarily low , the energy discontinuities and the distortion in the Fermi surface can be removed. By taking arbitrarily low pseudo potential, we can describe the Fermi sphere of any radius KF from the centre of the first Brillouin zone which will cross a whole nmber of zone boundaries without distortion. This representation is an example of extended zone scheme. Thus, using Harrison's method, let us construct Fermi surface for some simple lattice in two and three dimensions.

Fermi surfaces in two dimension (square lattice)

Consider a square lattice of lattice periodicity 'a'. In order to know the size of the Harrison's Fermi circle, let us consider the following cases of increasing electron concentration.

(a) Monovalent metal

The area of a first Brillion zone corresponding to a square lattice of parameter 'a' is given by A = $4\pi2/a2$. In a monovalent lattice, there is only one electron per unit cell. Thus only half the area in the first BZ will be occupied, and the rest will be vacant. The area of the Fermi circle (2D) equal to $\pi KF2$ must be equal to half the area of the first Brillouin zone.

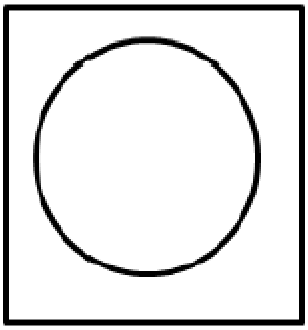

Fig.2

$$\pi K_F^2 = \frac{1}{2}\,\frac{4\pi^2}{a^2} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

$$K_F = \sqrt{\frac{2}{\pi}}\left(\frac{\pi}{a}\right) = 0.798\,\frac{\pi}{a}\ldots\ldots\ldots(2)$$

K_F – Radius of Fermi circle.
Where π/a is the distance of the zone boundary from the centre of the zone. Since the value A k_f lies between $0<k_f< \pi/a$, the Fermi circle lies well within the first BZ as shown in fig Hence the Fermi surface remains undistorted.

(b) Divalent metal

If the atom of the metal is divalent in a square lattice, then from the same argument as given above

$$\pi K_F^2 = \frac{2}{2}\,\frac{4\pi^2}{a^2}\text{.........}(3)$$

$$K_F = \frac{2}{\sqrt{\pi}}\left(\frac{\pi}{a}\right) = 1.228\ {}^{\pi}/_{a}\text{.....................}(4)$$

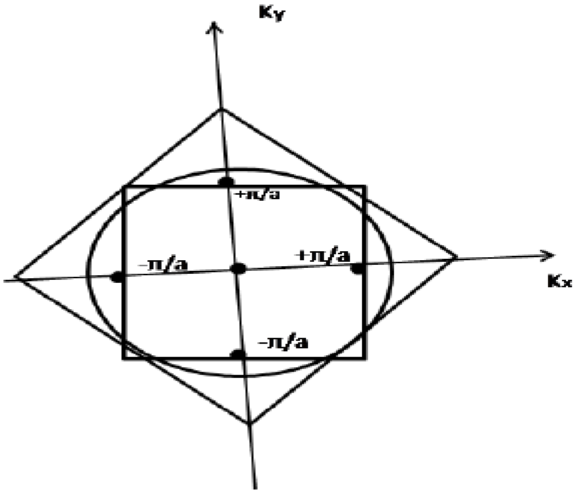

Fig. 3

Distance of the first Brillouin zone boundary from the centre is equal to (π/a) and the corner of the first zone from the centre in equal to 2 π/a = 1.414 ……(5)
From eqn (3) and (4) , we have ,$\pi/a < kf < 1.414\ \pi/a$

This implies that a circle of radius KF will go beyond the first zone boundary but will remain inside the corner of the first Brillouin zone as shown in fig. If we translate the pieces of Fermi circle shown in fig through a distance 2(π/a) along kx and ky axes , we can construct closed curves around the corner and the boundaries of the first BZ as shown in the figure in a periodic zone scheme.
In fig 4, the constant energy curves surround empty areas and are known as first zone holes and the constant energy curves in fig 5 surround the areas filled with electron and are known as the second zone electrons.

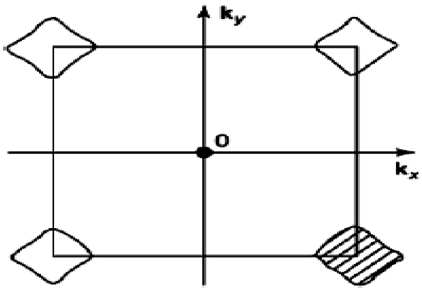

Fig. 4

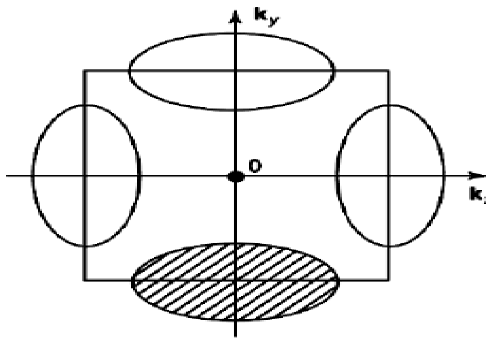

Fig. 5

(c) Trivalent metal

For the trivalent metal, the radius of the Fermi circle is found to be

$$\pi k_f^2 = \frac{3}{2}\,\frac{4\pi^2}{a^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$K_F = \sqrt{\frac{6}{\pi}}\left(\frac{\pi}{a}\right) = 1.38\,\frac{\pi}{a}\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

It means that $\pi/a < K_F < 1.414\ \pi/a$, which shows that the radius of the Fermi circle is still smaller than the distance of the corner of the first zone from the centre. Hence, the nature of the Fermi surface will be similar to the divalent case. The only difference will be that the size of the first zone holes will be smaller and the size of the second zone electrons bigger.

Effect of magnetic field on Fermi surface: electron orbit

In the absence of collision, the equation of motion of an electron in a magnetic field is given by

$$\hbar\left(\frac{dk}{dt}\right) = e(v \times B)$$

Where e (v×B) is Lorentz force experienced by the electrons moving with velocity V in a magnetic field B. In metals, since V is perpendicular to Fermi surface in K space, the force is parallel to the Fermi surface and perpendicular to both v and B. The component of K parallel to B is therefore constant. So that electron orbit in K space is obtained by taking the intersection of the Fermi surface with a plane normal to B. The shape of the electron orbit in k space depends on the shape of the Fermi surface and the orientation of the external magnetic field.

Let us consider two closely spaced electron orbits in k space with energies E and E+ dE as shown in fig . The shape of the electron orbit in r- space can be obtained by integrating eqn(1).

$$\mathrm{K} = \frac{e}{\hbar}(\mathrm{r}\times B)$$

This shows that the electron orbit in r- space is similar in shape with the K space orbit but differs by a scale factor of $\hbar/eB$ and rotation of $\pi/2$. The period of electron orbit in a magnetic field is obtained as

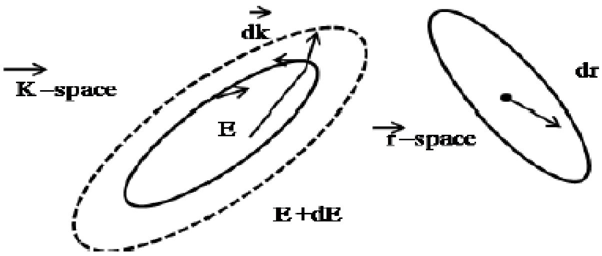

Fig.6

$$T = \oint dt = \oint \frac{dr}{V} \ldots\ldots\ldots\ldots(3)$$

The velocity of an electron in a band of energy E in K space is given by

$$V = \frac{dr}{dt} = \frac{1}{\hbar}\frac{dE(k)}{dk} = \frac{1}{\hbar}\frac{dE}{dk_{\cdot}} \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where $dk_{\cdot}$ is the normal distance in k space. Eqn (3) becomes

$$T = \hbar \oint dr.\frac{dk_{\cdot}}{dE} = \frac{\hbar^2}{eB}\oint \frac{|dk \times dk_{\cdot}|}{dE}$$

$$= \frac{\hbar^2}{eB}.\frac{dA_k}{dE} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

A is the area of the orbit in K space .
Therefore, the cyclotron frequency is ω_c,

$$\frac{2\pi}{T} = \frac{2\pi eB}{\hbar^2}.\frac{dE}{dA_k} \ldots\ldots\ldots(6)$$

Cyclotron frequency is also given by ωc = v/r = eB/mc
Where mc is the cyclotron effective mass and can be determined by comparing eqn (5) and (6) cyclotron effective mass mc is

$$\frac{\hbar^2}{2\pi}.\frac{dA_k}{dE}.$$

Fermi surface in metals: construction of Fermi surface of metals

The procedure for constructing the Fermi surface in metal consists the following steps.
1. For a given metal lattice, construct the corresponding reciprocal lattice.
2. Near each reciprocal lattice point, construct a unit cell (brillouin zone) by the Wigner Seitz method.
3. For the given parameters of the Brillouin zone and valence of the metal, determine the radius of the Fermi sphere KF . A sphere of this radius is drawn from the centre of the extended zone.
4. The Fermi surface formed by the intersection of the Fermi sphere is classified by the rules. For constructing Fermi surface in 3D for metals having simple crystal structures, first we have to develop a formula connecting KF and the dimension of the brillouin zones.

Electron orbit, hole orbit and open orbit

The three types of orbits in a magnetic field are shown in fig 1.14. The three orbits are (1)electron orbit (2) hole orbit (3) open orbit. The first two orbits are closed orbits and are traversed in opposite manner. Because, particles of opposite charge moving in the magnetic field in opposite direction. Electrons in holes like orbits move in a magnetic field with a positive charge. The third orbit is not closed. The particle on reaching the zone boundary at A is instantly recoils back to B. such an orbit is called an open orbit. Open orbits have an important effect on the magneto resistance. Orbits that enclose filled states are electron orbits. Orbits that enclose the empty states are called hole orbits. Orbits that move from zone to zone without closing are open orbits.

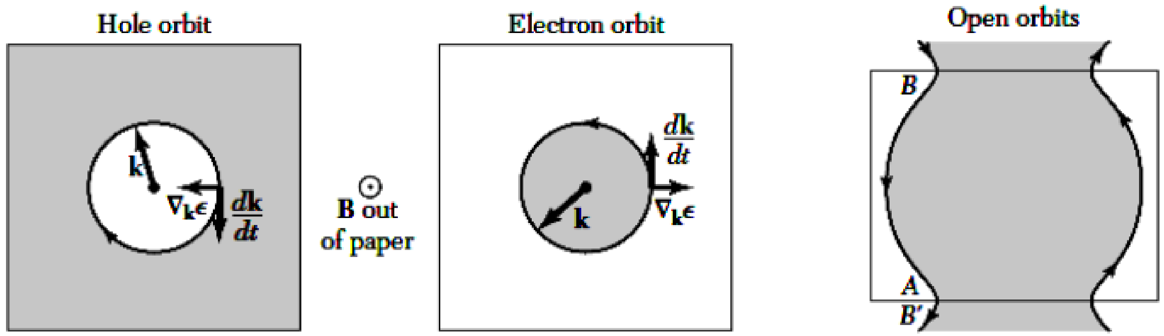

Fig. 7

De-Hass-van alphen effect (dHvA effect)

When a metal is placed in a magnetic field, the electrons do not move in straight path but rotate in quantized orbits around the Fermi surface in a plane perpendicular to the field. Based on this concept, de Hass and van Alphen discovered that, at low temperatures the diamagnetic susceptibility of pure bismuth as a function of magnetic field in high fields exhibits periodic oscillations. This effect is called as de Hass van Alphen effect.

This effect has been developed successfully in determining the external cross- sectional area of the Fermi surface. The basic idea of the de Hass van Alphen effect involves the quantization of electron orbits in a constant magnetic field applied in the Z- direction on such a way that the flux through the orbit.

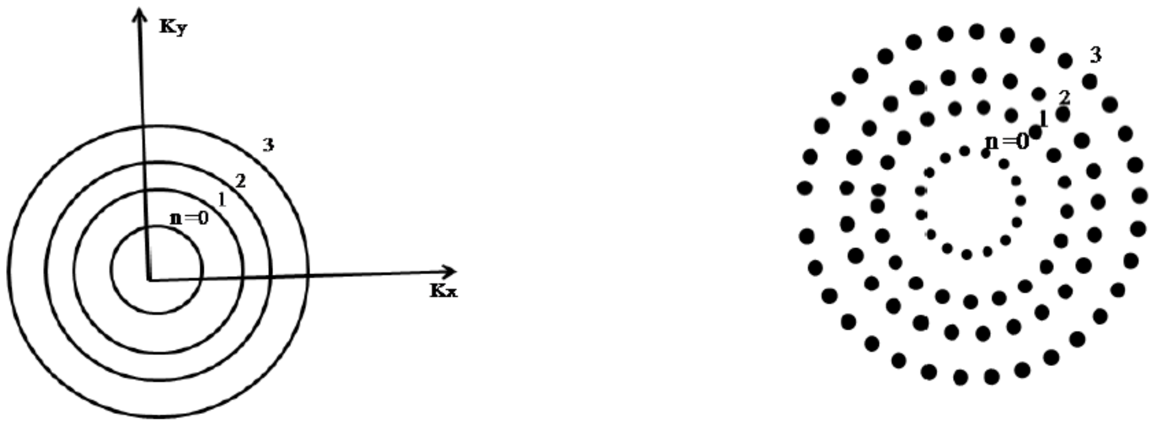

Fig.8 a and b

The Bloch theorem is still applicable to KZ component of K, but not to KX and KY. Therefore the stationary allowed values specified by the square lattice of points are taken as shown in fig 8(a). They move round on one or other set of quantized circular orbits shown in fig 8(b). Each of these circular orbits has a considerable degree of degeneracy. When a magnetic field is applied along KZ direction, it confines electrons to orbits of quantization area and these orbits lie on a set of coaxial cylinders of axis KZ. On the application of magnetic field, the energy levels which are condensed in this way are termed as Landau levels. When the magnetic field is increased, the allowed area of the orbit increases. So that the cylinders which correspond to the Landau level expand in cross section. Near the Fermi surface, the nearest cylinder expands in areas with increasing field, cylinder crosses the Fermi energy and so the corresponding landau level becomes empty. The electrons then distribute themselves on other parts of the Fermi surface. The critical field at which this happens is obtained as

$$1/B = 2\pi e/\hbar A\ (n + \nu)$$

If ν Landu levels are below the Fermi energy, ($\nu - 1$) levels will be below it. If ν is very large, the new state of the electron gas with ($\nu - 1$) levels below EF becomes equivalent to the earlier situation and, therefore the process repeats as field is increases further. The effect of this procession of Landau level through the Fermi level as the magnetic field is increased gives the periodic fluctuation of the energy of the electron about the zero filed. The magnetic moment is the rate of change of free energy with field. Therefore the magnetization and the susceptibility vary periodically with 1/B. The period is $\delta(1/B) = 2\pi e/\hbar A$
Thus the period of oscillations is inversely proportional to the cross- sectional area of the Fermi surface in a plane perpendicular to the magnetic field. The external area of the Fermi surface normal to the direction of applied field is measured using the above equation.

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