THEORIES OF BONDING IN METALS

Metals: Metals are elements that readily lose electrons to form positive ions (cations) and have metallic bonds. **(or) the electropositive elements are called metals.**

Characteristics of Metals:

Metals are elements that are typically **solid, lustrous, malleable, ductile, and good conductors** of heat and electricity. These properties arise due to the nature of **metallic bonding** — a sea of delocalized electrons shared among a lattice of metal cations.

1. Physical Characteristics:

a. Lustre (Shiny Appearance)

- Metals have a **bright, shiny surface** when freshly cut or polished.
- This is due to the **free electrons** reflecting light efficiently.
- Example: Silver and aluminum are highly lustrous.

b. High Density and Heavy Weight

- Most metals have **closely packed crystal lattices**, giving them high density.
- Exceptions: Alkali metals (like sodium and potassium) are light and soft.

c. High Melting and Boiling Points

- Strong metallic bonds require **high energy to break**, resulting in high melting and boiling points.
- Exception: Mercury is liquid at room temperature.

d. Hardness

- Most metals are **hard**, especially transition metals like iron, tungsten.
- Soft metals: Sodium, potassium (can be cut with a knife).

e. Malleability and Ductility

- **Malleability**: Can be hammered into sheets without breaking (e.g., gold, silver).

- **Ductility**: Can be drawn into wires (e.g., copper, aluminum).
- These arise due to **layers of atoms sliding over each other** without breaking metallic bonds.

f. Electrical Conductivity

- Metals are **excellent conductors of electricity** due to **free-moving electrons**.
- Silver is the **best conductor**, followed by copper and gold.

g. Thermal Conductivity

- Metals conduct heat well as free electrons **transfer energy** quickly through the lattice.

h. Sonority

- Metals produce a **ringing sound** when struck (they are sonorous).
- This property is used in making **bells and musical instruments**.

2. Mechanical Properties

a. Tensile Strength

- Metals can **withstand stretching forces** without breaking (e.g., steel is very strong)

b. Elasticity

- Metals like steel exhibit **elastic properties**—they can return to original shape after deformation within limits.

Metallic Bond:

Metals are believed to possess a special type of bond known as "metallic bond".
The electrostatic force of attraction that holds the two metal atoms in a metallic crystal is known as "Metallic bond".
The nature of metallic bonds is explained in terms of theories namely..

- Free electron theory
- Valence bond theory
- Molecular orbital theory (OR) Band theory

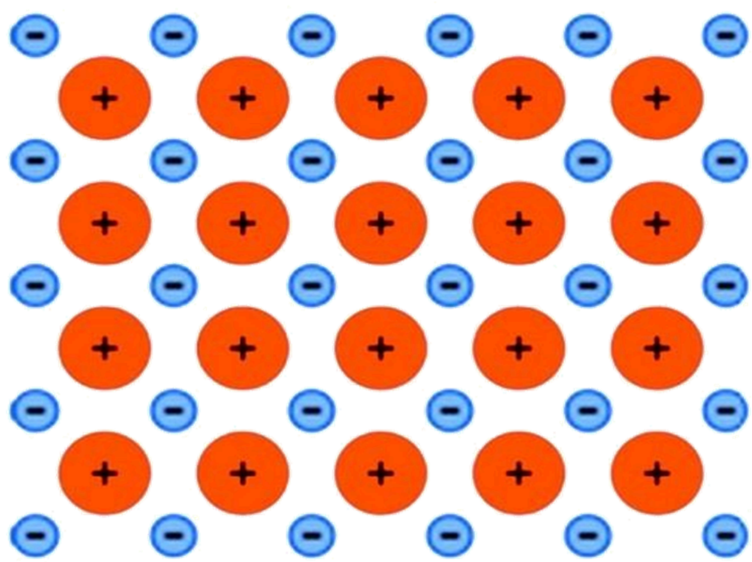
● Free Electron Theory of Metals

➔ **Introduction**

The **Free Electron Theory** was proposed by **Drude (1900)** and later modified by **Lorentz** and **Sommerfeld**. It explains the **electrical, thermal, and optical properties** of metals based on the behavior of **free electrons** inside a metal lattice.

➔ **Basic Assumptions of the Free Electron Theory:**

- According to this theory, metals because of their low ionization energies readily lose one or more valence electrons and form the positive metal ions called kernels.
- Thus, metallic lattice consists of rigid positive ions, which are assumed to be immersed in a sea of valence electrons or gas of electrons, which are in delocalized state.
- Hence it is also referred to as electron sea theory or electron gas theory.
- The force of attraction which binds a metal ion to a number of electrons within its sphere of influence is known as metallic bond.



Explanation of Metallic Properties Using Free Electron Theory

1. Electrical Conductivity

- When a voltage is applied, free electrons drift in the opposite direction of the electric field.

- This **drift of electrons** constitutes an **electric current**.
- The more free electrons in a metal, the better it conducts electricity.
- **Silver and copper** are good conductors because they have many free electrons.

2. Thermal Conductivity

- Free electrons **transfer kinetic energy** quickly from hot to cold regions.
- This explains why metals are **good conductors of heat**.

3. Metallic Lustre

- Free electrons **absorb and re-emit light**, giving metals a shiny appearance.

4. Malleability and Ductility

- The **electron cloud acts as a glue**, allowing metal ions to slide over each other without breaking the structure.
- This explains the **softness and shaping ability** of metals.

📉 Limitations of Classical Free Electron Theory (Drude Model)

1. **Fails to explain the temperature dependence** of electrical conductivity properly.
2. **Cannot explain** the different conductivities of different metals.
3. **Does not explain** why some metals are magnetic or non-conducting at certain conditions.
4. **Neglects quantum effects**—treats electrons classically.
5. **No explanation for specific heat values** at low temperatures.

Valence Bond Theory (VBT) of Metals

🔷 Introduction

This theory was proposed by Linus Pauling. It is also called resonance theory.

Valence Bond Theory (VBT) was originally developed to explain **bonding in molecules** by the **overlap of atomic orbitals**. Later, it was extended to explain the **metallic bonding** in solid metals.

According to VBT, in metals:

- **Atomic orbitals of adjacent atoms overlap**, forming a **giant lattice** of bonded atoms.
- Electrons are **delocalized** and move freely throughout the structure, explaining many metallic properties.

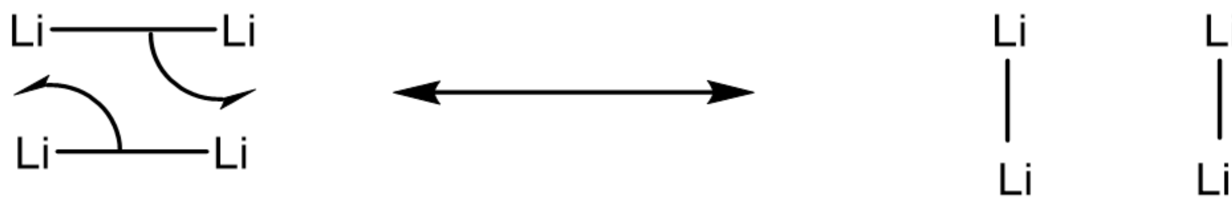
🔹 Assumptions of Valence Bond Theory for Metals:

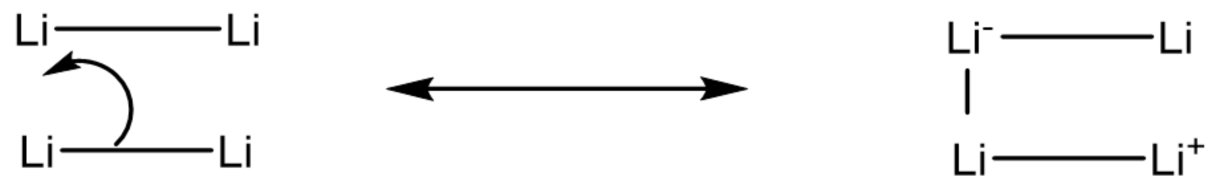
- **Metal atoms are closely packed in a crystal lattice**.
- The **outermost orbitals** (valence orbitals) of metal atoms **overlap with each other**.
- This overlapping results in the **delocalization of electrons** over many atoms.
- These delocalized electrons **hold the metal atoms together**, forming a strong **metallic bond**.
- According to this theory metallic bond is covalent in nature and the structure of metal involves resonance of covalent bonds between each atom and its nearest neighbour.

Ex: To explain this theory, let us consider the crystal lattice of lithium, the simplest metal.

- It has a body centered cubic structure.
- In this structure each lithium atom is surrounded by eight nearest lithium atoms and at a slightly greater distance it has six next nearest neighbours.
- Each lithium atom has one valence electron (2s1).
- So it can form a normal covalent bond with one of its nearest Li atoms.
- As Li is surrounded by eight Li atoms, there should be sixteen electrons to form the covalent bonds among all the atoms. However, only nine electrons are available from the nine Li atoms.
- Thus the bonding in Li metal is considered to be electron deficient.

- To overcome this problem Pauling suggested that, the bonding in metals is delocalized.
- The true state is a hybrid of several possible resonance structures, arising forms either synchronized resonance or unsynchronized resonance.





EXPLANATION OF METALLIC PROPERTIES

1. Metallic lustre:

When the light falls on a clean and smooth surface the valence electrons absorb energy and get excited into the nearest higher orbital, when these electrons return to the ground state and absorbed energy is released as visible light this emitted light ray is responsible for the metallic lustre.

2. Electrical conductivity:

The bonded electrons in the metallic bond neither belong to a positive bond nor they are localized between any two atoms so they are free to move and hence allow electrical conductivity

3. Malleability and Ductility:

Due to the uniform charge distribution between the positive ions when stress is applied the ions can change their position relative to their neighbouring atom without changing the internal environment.

LIMITATIONS:

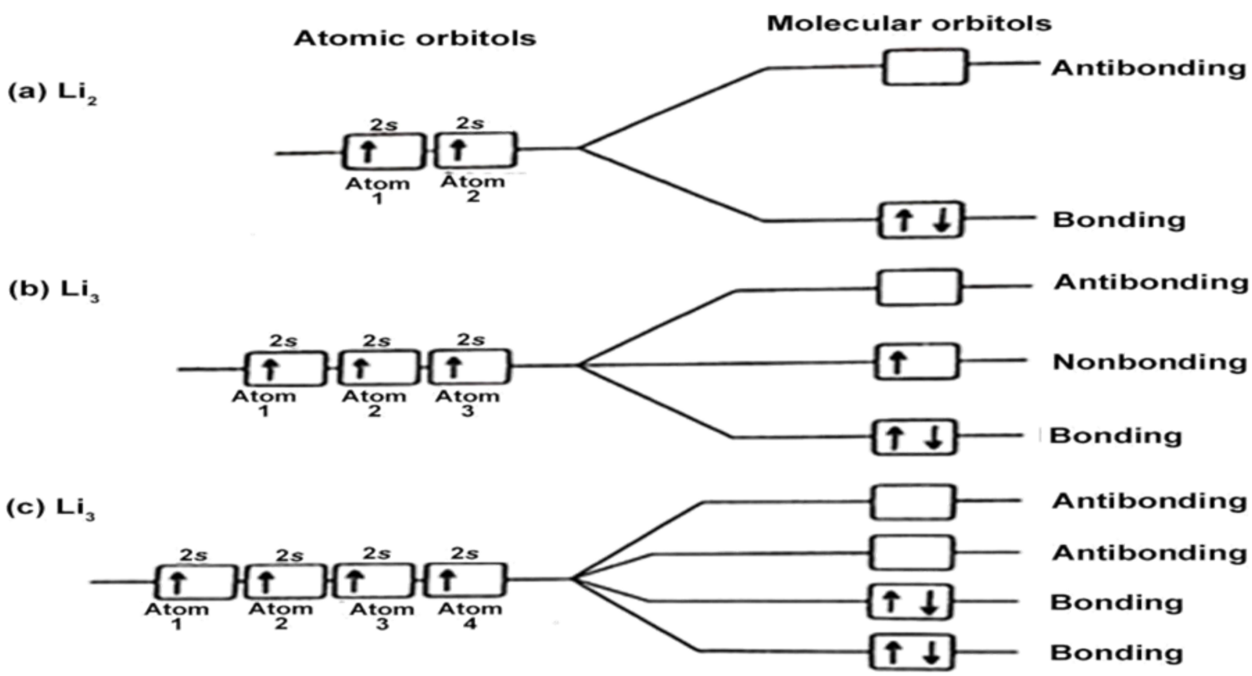
This theory does not explain

i) the conduction of heat in metals,

ii) retention of metallic properties in the liquid state or in solution.

Molecular orbital theory of bonding in metals (or) Band theory of solids

- According to molecular orbital theory a molecular orbital is formed by the linear combination of atomic orbitals(LCAO).
- The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
- When two atomic orbitals combine two molecular orbitals are formed. Out of these two the one having lower energy than the combining atomic orbitals is called bonding molecular orbital, while other having higher energy is called anti bonding molecular orbital.
- This concept can be extended to explain the metallic bonding and properties of metals.
- Let us consider the bonding in Li metal (one dimensional lattice involving a chain of Li atoms). The valence shell configuration of Li is $\mathbf{1s^2\ 2s^1}$



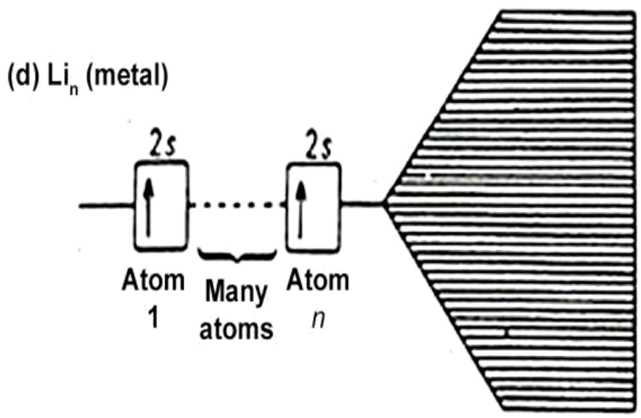
Likewise in the formation of Lin molecule, ‘n’ number of 2s orbitals of Li atoms interact and form ‘n’ number of molecular

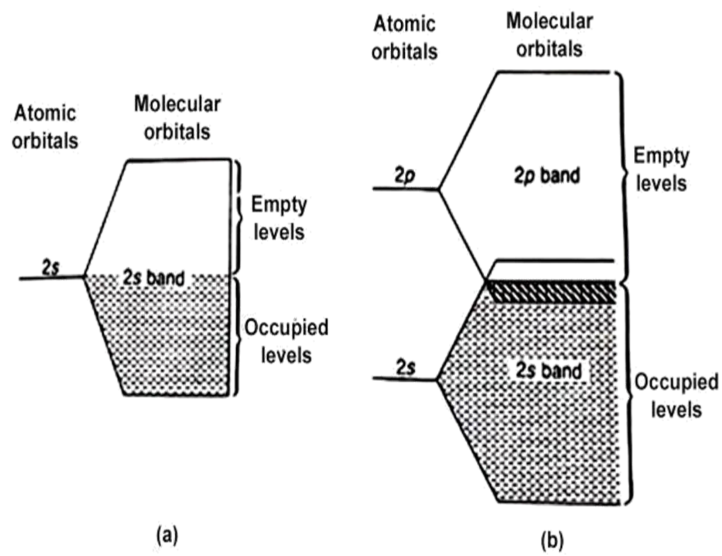
orbitals.

Out of these n/2 are bonding and n/2 are anti bonding molecular orbitals. The valence electrons of all the Li atoms (n), occupy all the n/2 bonding molecular orbitals

Thus, in Lin molecule, a series of closely spaced molecular orbital levels are formed giving rise to a continuous band (band related to 2s orbitals), hence molecular orbital theory is also called “band theory”

Half of the band is filled by the valence electrons of all Li atoms (n) and the remaining half of the band is vacant





Similarly, if the vacant 2p orbitals of Li atoms interact, they result in the formation of another continuous band called 2p band.

As the difference in energy between 2s and 2p orbitals is not much, the upper part of the 2s band and lower part of the 2p band merge to some extent.

The partially filled band or completely filled band that overlaps with an empty band is designated as a v**alence band.** The band into which the electrons jump is called **conduction band.**

Band Gap: The energy difference between the valence band and conduction band is called **band gap or forbidden gap.**

Classification Based on Band Theory:

On the basis of electrical conductivity solids can be divided into three types

- Conductors
- Insulators and
- Semiconductors.

Conductors:

The solids with conductivities ranging from 10^4 to10^7 ohm^{-1} m^{-1} are called conductors.

Metals having conductivities in the order of 10^7 ohm^{-1} m^{-1} are good conductors.

Metallic conduction is due to the movement of electrons.

In conductors there is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.So electrons can flow easily from valence band to conduction band under an applied electric field.

Insulators:

The solids with very low conductivities ranging from 10^{-20} to10^{-10} ohm^{-1} m^{-1} are called insulators.

In these substances the gap between filled valence band and conduction band is very large.

So electrons cannot jump from valence band to conduction band easily.

Semiconductors :

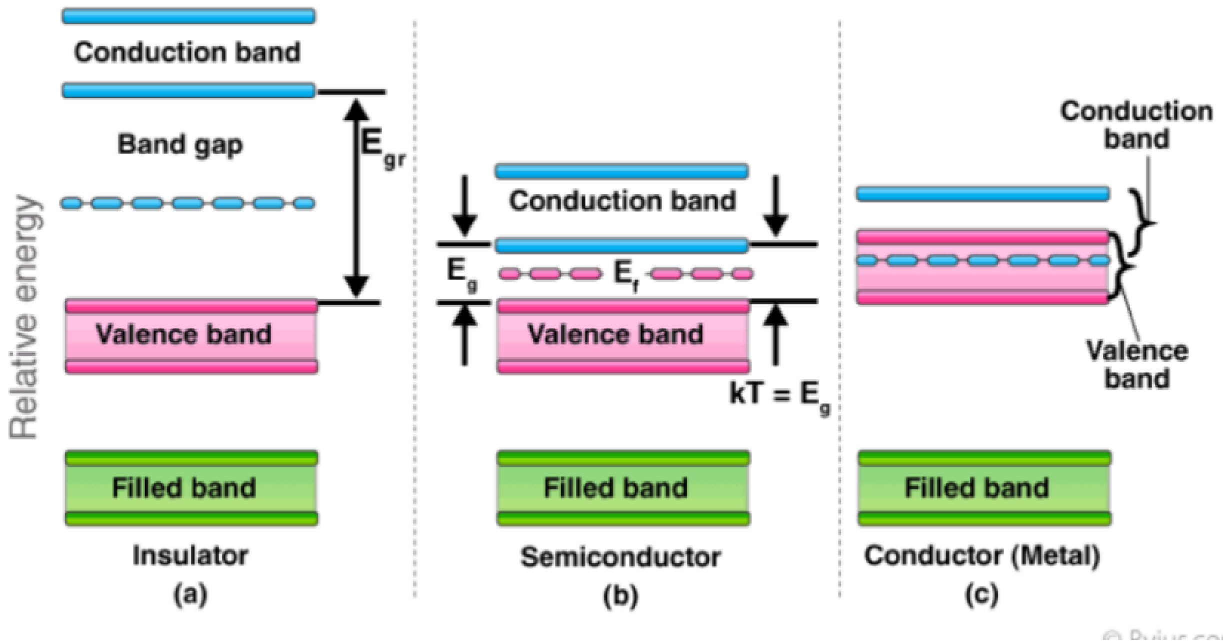
The solids with conductivities ranging from 10^{-6} to $10^4$$ohm^{-1}$ m^{-1} are called semiconductors.

In these, the gap between the valence band and the conduction and is intermediate between that of conductors and insulators.

Therefore some electrons may jump to the conduction band and show some conductivity.

With increase in temperature electrical conductivity of semiconductors increases.

This is because more electrons can jump from the valence band to the conduction band.


Conduction band
Band gap
E_{gr}
Relative energy
Valence band
Filled band
Insulator
(a)
Conduction band
E_g
E_f
Valence band
$kT = E_g$
Filled band
Semiconductor
(b)
Conduction band
Valence band
Filled band
Conductor (Metal)
(c)