Lesson 3: Chemical Bond Theories & Types of crystal

Lesson objective :

By the end of this lesson, you will be able to:

- Name two chemical bond theories.
- Explain the valence bond theory.
- Distinguish the Lewis model and the valence bond model.
- Discuss the overlapping of orbitals in covalent bond formation.
- Explain hybridization show the process of hybridization involved in some covalent molecules.
- Draw hybridization diagrams for the formation of space,sp2,sp3,sp3d and sp3d2 hybrids.
- Suggest the kind of hybrid orbitals on the basis of the electron structure of the central atom
- Predict the geometrical shapes of some simple molecules on the basis of hybridization and the nature of electron pairs
- Discuss the hybridization involved in compounds containing multiple bonds.
- Explain bond length and bond strength
- Explain molecular orbital theory.
- Describe molecular orbital using atomic orbitals.
- Describe bonding and anti bonding molecular orbitals.

Brainstorming questions

1. List four physical characteristics of a solid metal?

2. Briefly account for the following relative values?

A. Lithium boils at 1317 °C and melts at 179 °C. The boiling point is
about 1138 °C higher than its melting point.
B. The melting point of Li and Be are 180 °C and 1287 °C, respectively.
C. The melting point of sodium is 89 °C, whereas that of potassium is 63 °C.

key terms/Concepts

- Valance bond theories
- Molecular orbital theory
- Hybridization
- Crystals

Valence Bond Theory suggests that covalent bonds are formed when atomic orbitals overlap and share electrons. It focuses on the idea that electrons reside in atomic orbitals localized around each atom before bonding occurs.

2. 4 Chemical Bonding Theories

A. Valance bond Theory (V BT)

B. Molecular bond theory (MOT)

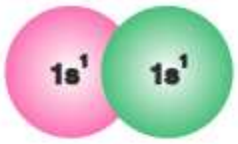
2.4.1 Valance bond Theory

- The VBT was proposed by Heitler and London to explain the formation of covalent bond quantitatively using quantum mechanics.
- Later on, Linus Pauling improved this theory by introducing the concept of hybridization.

The main postulates of this theory are as follows:

- A covalent bond is formed by the overlapping of two half filled valence atomic orbitals of two different atoms.
- The electrons in the overlapping orbitals get paired and confined between the nuclei of two atoms.
- The electron density between two bonded atoms increases due to overlapping. This confers stability to the molecule.
- Greater the extent of overlapping, the stronger is the bond formed.
- As the two atoms are brought more closely together, however, the repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction and the bond become unstable.

For each bond, then, there is a condition of optimal orbital overlap that leads to a maximum bond strength (bond energy) at a particular internuclear distance (bond length).



atomic orbital overlap & Bondind in H2

The s orbital is spherical, but p and d orbitals have particular orientations.
Thus, in p & d orbitals, more electron density is in one direction than in another.
The bond involving p or d orbitals will tend to be oriented in the direction that maximizes overlap
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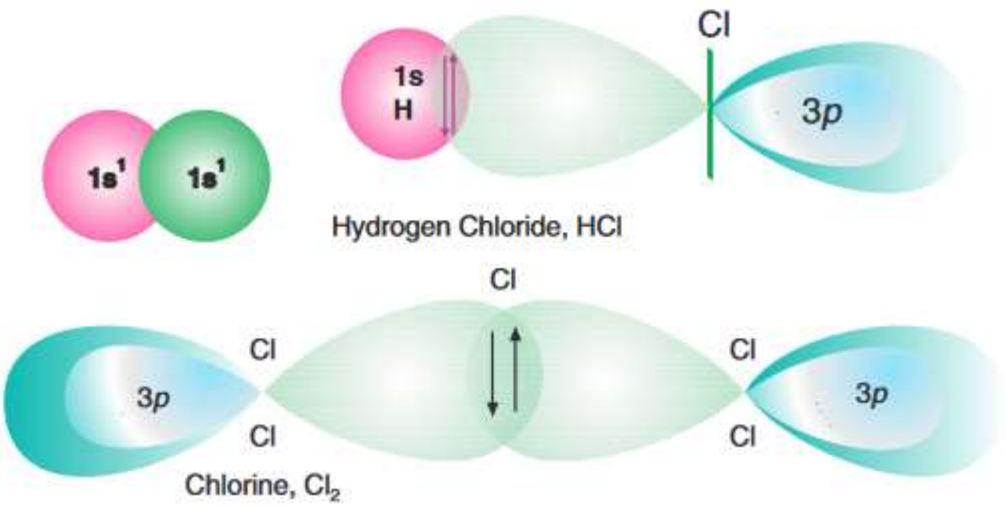
S-S, S-P, P-P orbital overlap& spin paring in 3D molecules



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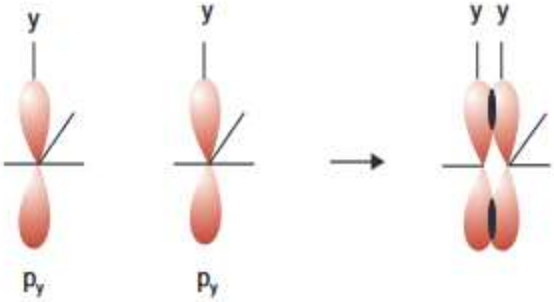
Pi-bond

- The covalent bond formed by sidewise overlapping of atomic orbitals is called π-bond.
  In π- bond, the electron density is present above and below the inter-nuclear axis.
  It is relatively a weaker bond than sigma bond since the electrons are not strongly attracted by the nuclei of bonding atoms



Orbital Hybridization

- The old version of valence bond theory is limited to diatomic molecules only.

- For example, the covalent bond in H_2, O_2, Cl_2, N_2, HCl, etc. molecule can be explained by the orbital overlapping of the two atoms.
- However, it could not explain the structures and bond angles of molecules with more than three atoms.
- E.g. It could not explain the structures and bond angles of H_2O, NH_3 etc.
- In order to explain the structures and bond angles of molecules,
- Linus Pauling modified the valence bond theory using hybridization concept.
- Definition: Orbital hybridization is the intermixing of two or more atomic orbitals of similar energy to give identical and degenerate new type of orbitals.
- Only atomic orbitals of same atom with almost same energy can participate in the hybridization.

  The completely-filled or half-filled or even empty orbitals can undergo hybridization.

  The combination of orbitals belonging to different atoms is called bonding.

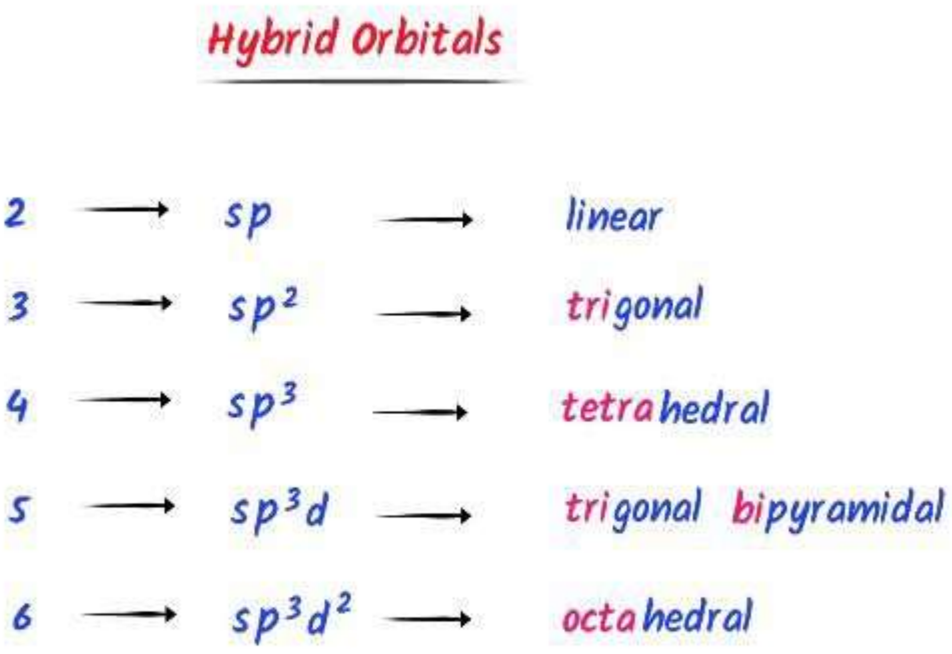
  The new orbitals that are formed due to hybridization are known as hybrid orbitals, which have mixed characteristics of atomic orbitals.

  The shapes of hybrid orbitals are identical. Usually they have one big lobe associated with a small lobe on the other side.

  The hybrid orbitals are degenerate i.e., they have similar energy.

  The number of hybrid orbitals formed are exactly equal to the number of atomic orbitals intermixed.
- Example: If three atomic orbitals hybridize, the number of hybrid orbitals formed will be equal to 3.
- The bond angles in the molecule are equal to or almost equal to the angles between the hybrid orbitals forming the σ bonds.

  The shape of the molecule is determined by the type of hybridization, number of bonds formed by them and the number of lone pairs



Hybrid Orbitals

2 → sp → linear

3 → sp^2 → trigonal

4 → sp^3 → tetrahedral

5 → sp^3d → trigonal bipyramidal

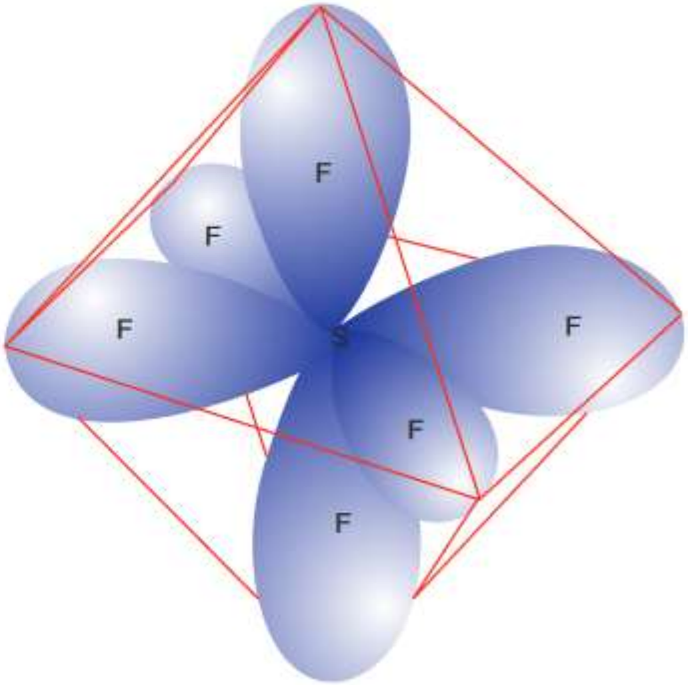
6 → sp^3d^2 → octahedral

Easytrick to find hybridization of central atom

- Hybridorbital=lonepair+number of surrounding ato
  Identify the hybridization of the central atom

SF6 CH4, PCl,

CO2 ,S02, BF4- SF4 , SF6 ,CO32- NH4+, CH4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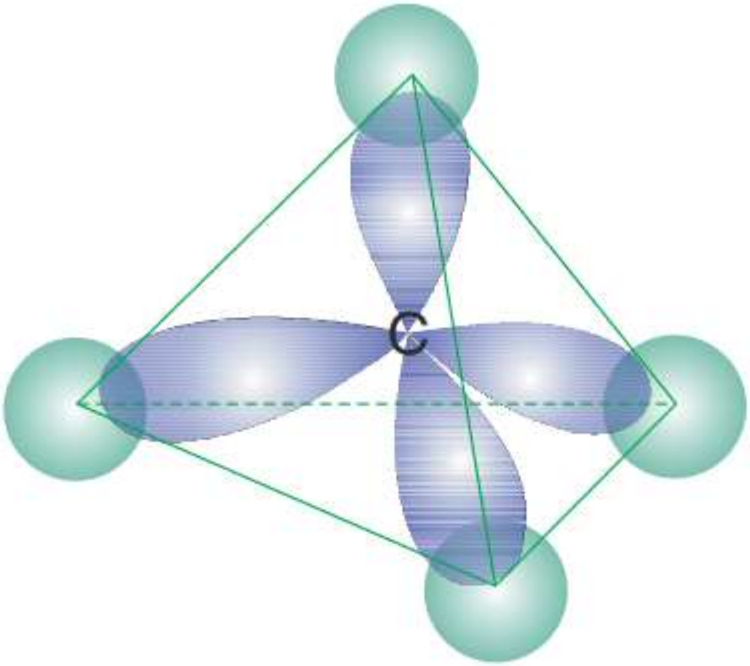
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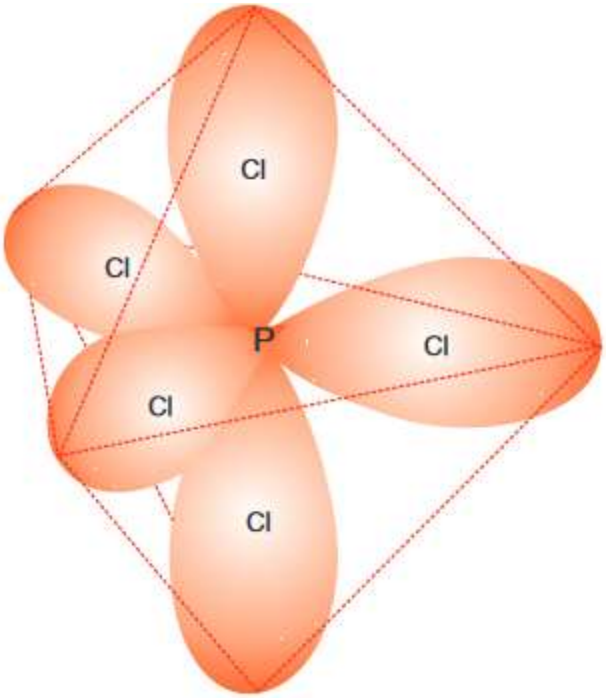


Eg, SF_6= Sp^3d^2 = number of set of electron =6

2.4.2 Molecular Orbitals Theory

The molecular orbital theory assumes that when atoms come together, their orbitals not only overlap, but are also simultaneously transformed into new orbitals.
These new orbitals, called molecular orbitals (MOs) These play the same role for molecules that atomic orbitals play for atoms.
Note that atomic orbitals are the allowed states for an electron moving in the field of one nucleus, whereas molecular orbitals are the allowed states for an electron moving in the field of several nuclei (atoms present in the molecules).
In MOT two molecular orbital result from the combination of atomic Orbital.

A) Bonding molecular orbital (BMO):

- Is the combination of atomic orbitals is additive, it results in forms bonding molecular orbitals
- AOA + AOB = BMOAB
- where: AO is atomic Orbital and BMO is a bonding molecular orbital.
- The energy of BMO is lower than the energy of atomic orbital in an isolated atom.
- The electron density is concentrated b/n the two nuclei.
- Formation of BMO is exothermic process and stabilizes the molecule.

b) Anti Bonding molecular orbital (ABMO)

- Is formed by subtraction of atomic orbital that overlap.
- AOA – AOB = (ABMO)*AB

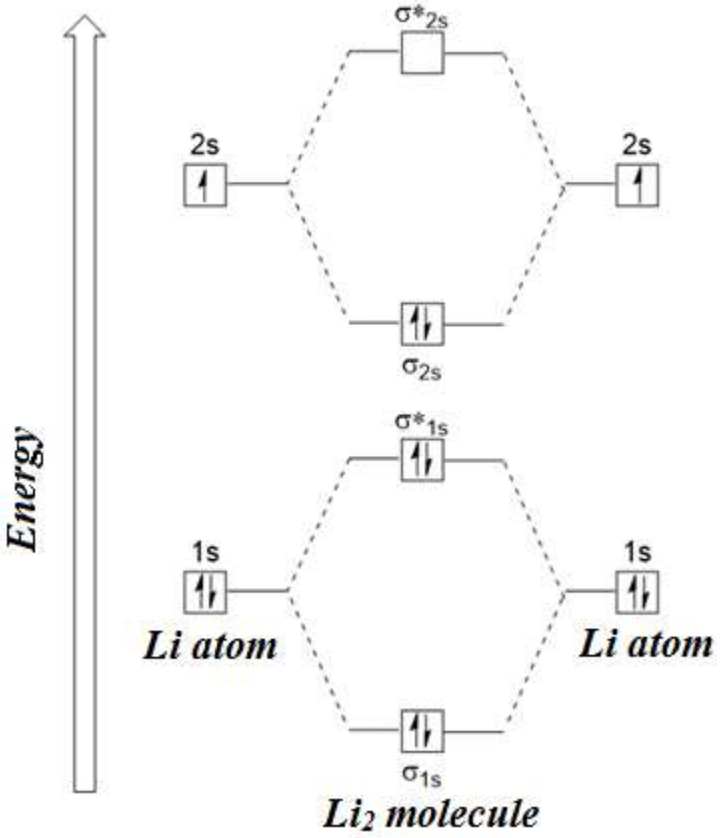
- This combination forms an antibonding MO, which has a node between the nuclei, a region of zero electron density.
- The energy of ABMO is higher than the energy of isolated atomic orbital electronic configuration in MOT depends on:

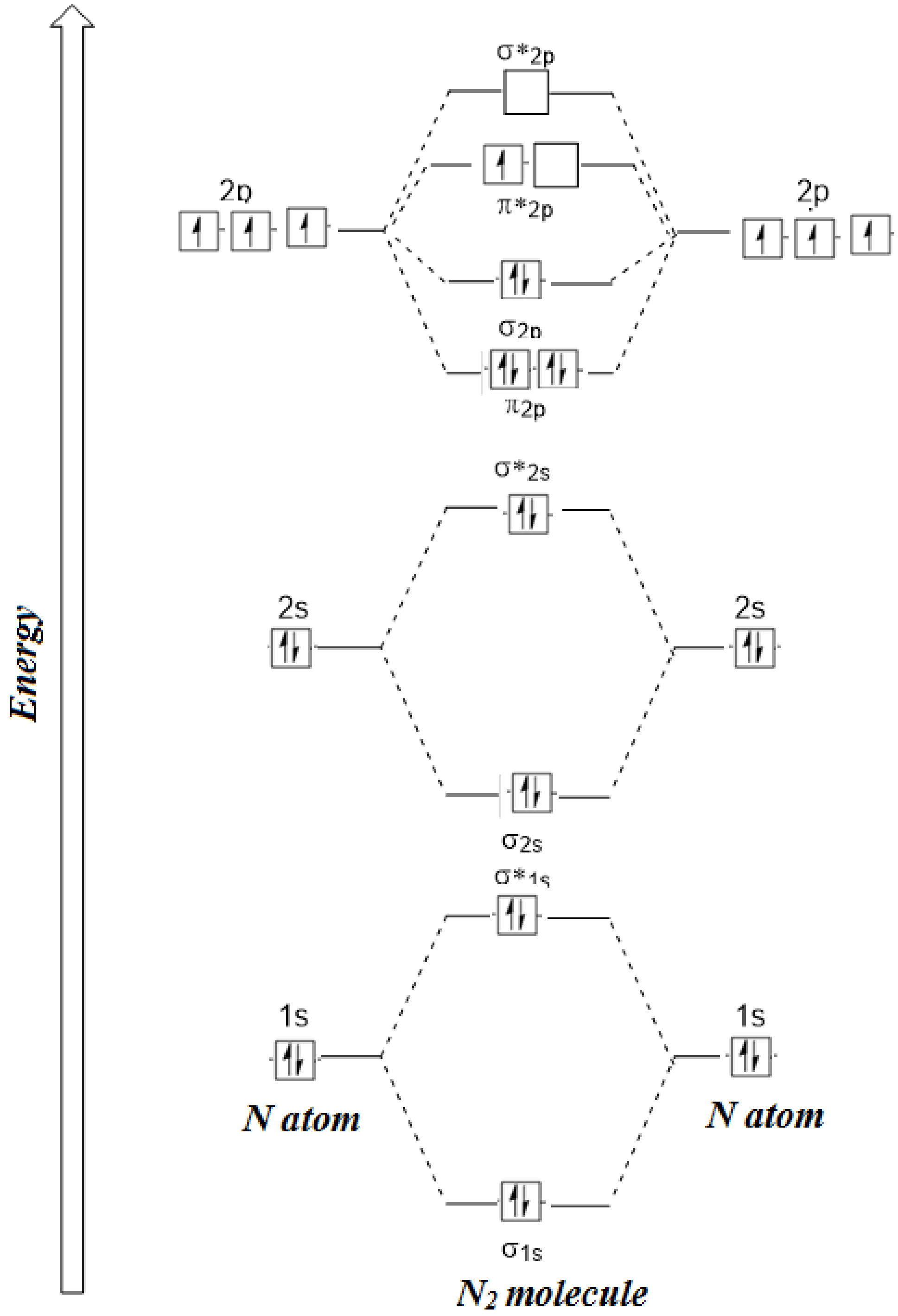
- I)The Aufbau Principle:
  ii) Pauel’s Exclusion Principle:
- each molecular orbital can contain a maximum of two electrons with opposite spin.
  iii) Hund’s rule:
- if the molelecules Homouclear diatomic molecules (Molecules made from atoms of atomic number 8-10) (for O2, F2, and Ne2).
  -There is no interaction between 2s and 2p orbitals and the BMO resulted from head-on overlap of 2p atomic orbitals (δ2px) is lower in energy than that of p- Mos resulted from sidewise overlapping (л2py & л2py). In this case, δ- overlap is stronger than л- overlap.

δ1s, δ*1s, δ2s, δ*2s, δ2px, л2py,//*2pz л* 2py //*2pz, δ* 2px , δ3s , δ*3s, …
example: Write the molecular orbital electron configuration of O2 molecule.

- example: Write the molecular orbital electron configuration of O2 molecules
- δ1s2 , δ_1s2 , δ2s2 , δ_2s2, δ2p2x, л2p2y , л* 2p1y л2p2z л* 2p1z
- Homonuclear diatomic molecules (Molecules made from atoms of atomic number less than 8) (for N2, C2, and B2).
  In this cases, interactions take place between the 2s and 2p atomic orbitals that are strong enough to swap the ordering of the σ2p and π2p molecular orbitals.
  The MO electron configuration becomes
- δ1s, δ*1s, δ2s, δ*2s, л2py, δ2px, л* 2py , δ* 2px ,
- The MO electron configurations can be indicated by the energy diagram.
  Example 1: Draw the MO electron configuration Energy diagram for Li2 molecules
  Energy diagrams of Molecular Orbitals .

Energy diagrams


Energy
σ*2s
2s
2s
σ2s
σ*1s
1s
1s
Li atom
Li atom
σ1s
Li2 molecule



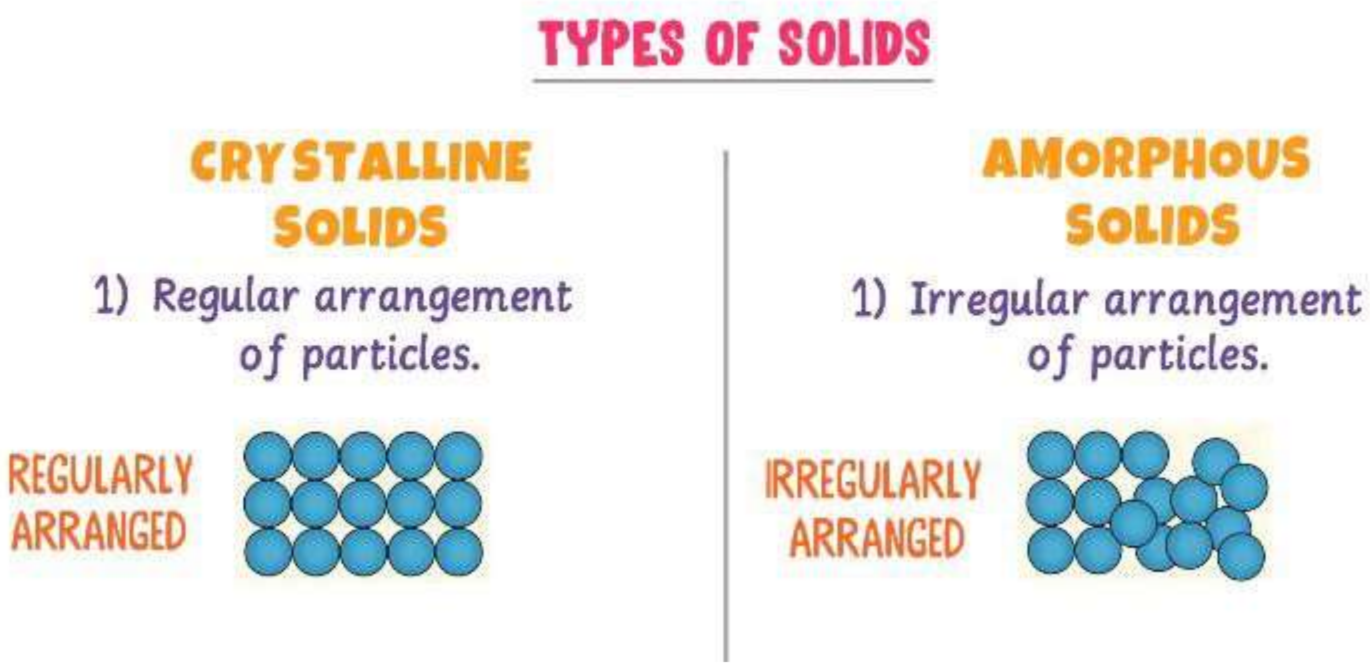
Bond Order of Molecules
Bond order (B.O.): is the number of bonding electron pairs between two atoms with in a covalent molecule.
BO = (electron in BMO- es in AMO)/2

- Molecules with bond order ½ or greater will be stable with respect to their atoms.
  Molecules with bond order zero will be unstable.
  The greater the bond order the more stable the molecule
- Example 1: Determine the bond order and stability of He2
  Total electron = 2+2=4
  Electronic configuration = δ1s2, δ*1s2
  Bond order = ½ (# e- in BMO – # e- in ABMO)/2
  Bond order = (2 -2) /2= 0
  Magnetic property

- One of the advantages of molecular orbital theory over valence bond theory is its ability to explain the magnetic properties of covalent molecules.
  If the electronic configuration of a molecule contains unpaired electron(s), the molecule is said to be paramagnetic.
  If the electronic configuration of a molecule contains all electrons paired, the molecule is said to be diamagnetic.
  Example: Write the MO electron configuration of O2- molecule ion, calculate bond order, determine stability and its magnetic property.
  Solution
- the ion has 17 electrons
- O2- = 17 e-s = δ1s2 , *δ1s2 , δ2s2 ,* δ2s2 , δ2p2x, л2p2y , *л2p2y , л2p2z* л2p1z
- BO= 1.5 so its stable
- paramagnetic because there is no unpaid electron .

Types Of Solids

- Depending On the arrangement of atoms,there are two types of solids
- Crystalline
- Amorphous



NB all crystals are solids,but not all solids are Crystals Types Of Solid

Types of crystals

1. IONIC Crystals

- Ioniccrystalsconsistofionsheldtogetherbyionicbonds
- Thestructureofanioniccrystaldependsonthechargesonthecation, anion and on their radii.
- Thepropertiesofionicsolidsaredirectconsequencesofthestronginterionic forces, which create a high lattice energy.
- Ionic solids have high melting points,an indication of the strong attraction force holding the ions together.

2.Molecular crystals

- Contains molecules
- Molecular solids are made up of discrete molecules that interact via intermolecular forces.
- Variouscombinationsof dipole-dipole, dispersion and hydrogen-bonding forces

3. Covalent network crystals

- In This Type Of Crystalline Solids,separate particles are not present. Instead,strong covalent bonds link the atoms together throughout the network of covalent solid.
- As a consequence of the strong bonding, all these substances have extremely high melting and boiling points, but their conductivity and hardness depend on the nature of their bonding.
- Eg. graphite and diamond

4. Metallic crystals

- The strong metallic bonding forces hold individual atoms together in metallic solids.
- Bonding in metals can be explained as a network of positive ions immersed in a sea of electrons.
- That Is,the electrons in the valence shell of the metal atoms are highly delocalized.
- For This Reason,metals are very good conductors of electricity.

Lesson 3: Summary

Chemical Bonding Theories:

Chemical Bonding Theories: VBT focuses on localized bonds formed by overlapping atomic orbitals, while MOT describes bonding using molecular orbitals formed by combining atomic orbitals across the molecule.

1. V**alence Bond Theory (VBT)**:

- **Concept**: VBT describes chemical bonding as the overlap of atomic orbitals between atoms to form covalent bonds.
- **Key Points**:

- Covalent bonds are formed by the overlap of atomic orbitals (s, p, d) from adjacent atoms.
- Predicts bond angles and shapes using hybridization (sp^3, sp^2, sp…….).
- Explains localized bonding and bond strengths. Examples include sigma (σ) and pi (π) bonds.

2. Molecular Orbital Theory (MOT)

- **Concept**: MOT describes chemical bonding as the interaction of atomic orbitals across an entire molecule to form molecular orbitals.
- **Key Points**:
  - Molecular orbitals are formed by the linear combination of atomic orbitals (LCAO) across the molecule.
  - Predicts bond order, magnetic properties, and electronic transitions.
  - Considers both bonding and antibonding orbitals. Examples include sigma (σ) and pi (π) molecular orbitals.

Types of Crystals:

Crystals are solid materials with a highly ordered arrangement of atoms, ions, or molecules in a repeating pattern called a crystal lattice. The main types of crystals are Ionic crystals are held together by electrostatic forces, covalent network crystals by strong covalent bonds, metallic crystals by delocalized electrons, molecular crystals by weak forces, and amorphous solids lack long-range order.

1.Ionic Crystals

- **Composition**: Composed of positively and negatively charged ions held together by electrostatic forces (ionic bonds), **Examples**: Sodium chloride (NaCl), potassium nitrate (KNO_3).

Properties:

- Brittle, high melting points, conduct electricity in molten or aqueous state.

2. **Covalent Network Crystals**

- **Composition**: Atoms are bonded together by strong covalent bonds extending throughout the crystal . Examples: Diamond (C), quartz (SiO_2).

Properties:

- Very hard, high melting points, poor conductivity of electricity.

3. **Metallic Crystal**s

- **Composition**: Metal atoms packed closely together in a sea of delocalized electrons. Examples: Copper (Cu), iron (Fe).

Properties:

- High electrical conductivity, malleability, ductility.

4. **Molecular Crystal**

- **Composition**: Molecules held together by weak van der Waals forces or hydrogen bonding. **Examples**: Ice (H_2O), sugar ($C_{12}H_{22}O_{11}$)

Properties:

- Soft, lower melting points, often transparent.

Amorphous Solids

- **Composition**: Lack long-range order in atomic arrangement. **Examples**: Glass, certain plastics.

- **Properties**: Lack of distinct melting points, isotropic (no directional properties).
  Hybridization:
  Hybridization is a concept in chemistry where atomic orbitals mix to form new hybrid orbitals suitable for bonding.

  Hybridization involves mixing atomic orbitals to form new hybrid orbitals that optimize bonding in molecules.
- Hybrid orbitals allow atoms to maximize bonding and minimize repulsion by achieving optimal overlap with neighboring atoms
  Types of Hybridization
- **sp Hybridization**: Occurs when one s orbital and one p orbital mix to form two sp hybrid orbitals. Example: $BeCl_2$.
- **sp² Hybridization**: Occurs when one s orbital and two p orbitals mix to form three sp² hybrid orbitals. Example: BF_3.
- **sp³ Hybridization**: Occurs when one s orbital and three p orbitals mix to form four sp³ hybrid orbitals. Example: CH_4.
  Applications:
- Predicts molecular geometry, bond angles, and the nature of bonds in molecules.
  Sigma (σ) Bond:
- Sigma bonds are formed by the head-on overlap of atomic orbitals along the internuclear axis.and are stronger, allowing free rotation.
  Pi (π) Bond
- **Pi (π) bonds** result from sideways overlap of p orbitals and are weaker, restricting rotation.
- Pi bonds are formed by the sideways overlap of p orbitals above and below the internuclear axis.
  Characteristics of sigma bond
- Stronger and more stable than pi bonds.
- Allows free rotation around the bond axis.
- Exists in all types of covalent bonds: single, double, and triple bonds.
- **Examples**: C-C single bond in ethane (C_2H_6), C-H bond in methane (CH_4).
  Characteristics Pi (π) Bond
- Weaker and less stable than sigma bonds.
- Results from the overlap of unhybridized p orbitals.
- Restricts rotation around the bond axis.
- **Examples**: C=C double bond in ethene (C_2H_4), C≡C triple bond in ethyne (C_2H2)
- Understanding hybridization, sigma bonds, and pi bonds is essential for predicting molecular geometry, bond strengths, and reactivity in organic and inorganic chemistry. These concepts help explain the diversity of molecular structures and properties observed in chemical substances.