Matter is made up of one or different type of elements. Under normal condition no other atoms exist independent in nature except noble gases. However, a group of atoms having same properties is known as molecules.

The attractive forces holding these atoms together is known as chemical bond.

Chemical bonding and molecular structure is a concept for understanding how atoms combines to form the molecular compounds.

Why do atoms combine?

Why only specific combinations are possible?

Why molecules posses certain molecular shape?

To answer this many theories and concepts are there – Kossel Lewis approach, Valence shell electron pair theory, valance bond theory, Molecular orbital theory.

Kossel-Lewis Approach to Chemical Bonding:

The Kossel-Lewis approach is an early explanation of how chemical bonds form between atoms.

Lewis Contribution:

Lewis pictured the atoms in term of positive charged “Kernel” (the nucleus plus inner electron) and the outer shells having a maximum of eight electrons.

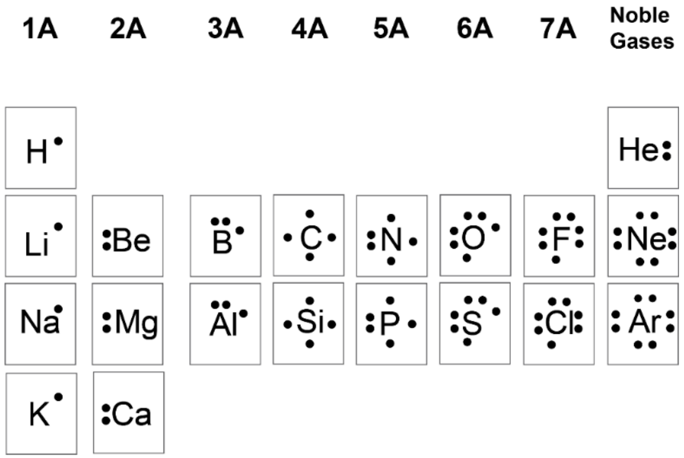
Lewis proposed that atoms are most stable when they have 8 electrons in their outermost shell (like noble gases)

To achieve this stable configuration, atoms either lose, gain, or share electrons. This is called the octet rule.

He assumed that each of the eight electrons will occupy the corner of a cube surrounding the kernel. (Sodium – outermost shell has only one electron so it will occupy one corner, electrons of noble gases will occupy all corners). Lewis postulated that the arrangement of these electrons achieves the stable octet when they are linked with chemical bonds.

Example; NaCl: Transfer of electron from Na to Cl, giving Na^+ and Cl^- . So, each atoms attains a stable outer octet of electrons.

Lewis Symbols: In the formation of a molecules only outer shell electrons take part in chemical combinations and they are known as valence electrons. Lewis gave simple notations to represent valence electrons in an atom. These notations are known as Lewis Symbols or electron-dot structures. Example:



Kossel Contribution:

Kossel explained the formation of ionic bonds (electrovalent bonds) based on the transfer of electrons from one atom to another.

Ionic bond: Forms when a metal loses electrons and a non-metal gains those electrons.

Metals (like sodium) tend to lose electrons and form positive ions (cations). Non-metals (like chlorine) tend to gain electrons and form negative ions (anions).

Octet Rule:

So, Kossel and Lewis in 1916 developed a theory of chemical combinations between atoms known as electronic theory of chemical bonding. According to this theory “the atoms may combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of electrons in order to have an octet in valence shell” is known as octet rule.

Significance of Octet Rule

1. Predicts Chemical Bonding
2. Explains Molecular Structures
3. Reactivity Trends
4. Basis of Valency

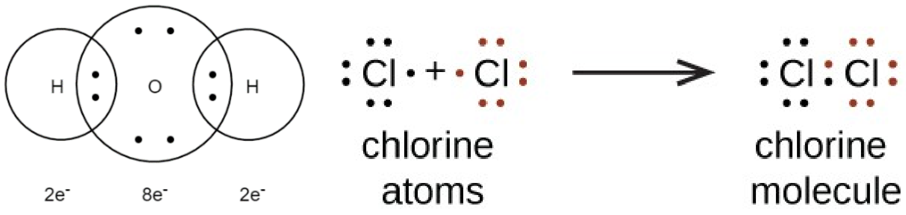
Limitations of Octet Rule

1. Incomplete Octets: Some elements (like hydrogen, lithium, and beryllium) cannot have eight electrons around them. For example: Hydrogen forms bonds with just 2 electrons (H_2).
2. Expanded Octets: Elements in the 3rd period and beyond (like phosphorus, sulfur, chlorine) can have more than eight electrons around them due to available d-orbitals. Example: PCl_5 and SF_6 have expanded octets.
3. Odd-Electron Molecules: Some molecules have an odd number of electrons, making it impossible for every atom to have an octet. Example: NO (Nitric oxide) has 11 valence electrons.
4. Doesn't Explain Transition Metals: The octet rule is not applicable to transition metals and f-block elements since their bonding involves d- and f-orbitals.

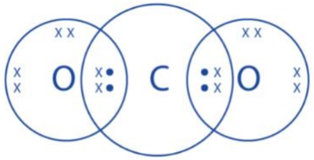
Covalent Bond: Lewis-Langmuir (1919) Theory:

According to Lewis the atoms combine by sharing electrons in such a way that each atom attains the electron configuration of the nearest noble gas, which is typically 8 electrons in the outer shell (the octet rule). A covalent bond is formed when two atoms share one or more pairs of electrons. This sharing allows both atoms to attain a stable configuration. Langmuir applied Lewis's concept to explain the formation of molecules. He explained that molecules are composed of atoms that are held together by electron-pair bonds. Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. Langmuir provided insights into multiple bonding (double and triple bonds) by explaining that atoms can share more than one pair of electrons to achieve a full octet.

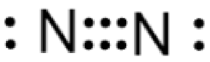
Example: (Single Bond)

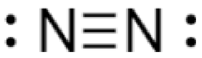


Double Bond:



Triple Bond:





Bond Length: The average distance between the nuclei of two bonded atoms in a molecule.

Bond Angle: The angle formed between two adjacent bonds on the same atom.

Bond Enthalpy: The energy required to break one mole of a specific bond in a molecule in the gaseous state.

Bond Order: The number of chemical bonds between a pair of atoms.

Resonance Structure:

Resonance structures are different possible arrangements of electrons (specifically π-electrons or lone pairs) in a molecule that cannot be represented by a single Lewis structure. They collectively describe the true delocalized electron distribution in the molecule.

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory)

The VSEPR theory helps predict the geometry (shape) of molecules based on the repulsion between the electron pairs (both bonding pairs and lone pairs) surrounding a central atom.

Main Postulates of VSEPR Theory:

- Electron Pair Repulsion: The shape of a molecule depends on the number of valence shell electron pairs around the central atom. These pairs can be either bond pairs (involved in forming bonds with other atoms) or lone pairs (non-bonded pairs of electrons).

Key Point: The electron pairs repel each other because they have negative charges, which pushes them apart.

- Minimizing Repulsion: Electron pairs will arrange themselves to be as far apart as possible to minimize the repulsion between them. This arrangement dictates the shape of the molecule.
- Bonded and Non-Bonded Pairs: There is a distinction between bonded pairs (involved in a bond) and non-bonded (lone) pairs: Lone pairs exert more repulsion than bond pairs, because they are localized closer to the central atom.As a result, lone pairs take up more space, causing bond angles to reduce compared to a molecule with only bond pairs.

Order of Repulsive Interaction:
The strength of repulsion between electron pairs follows this order:

- Lone pair – Lone pair (strongest repulsion)
- Lone pair – Bond pair
- Bond pair – Bond pair (weakest repulsion)

This means that if a molecule has lone pairs, they will compress the angles between the bond pairs, distorting the shape of the molecule.

Valence Bond Theory (VBT)

- The valence bond theory explains how atoms form bonds by overlapping their atomic orbitals. When two atoms come close enough, their atomic orbitals overlap, and electrons in these orbitals pair up to form a covalent bond.

- Heitler and London (1927) first proposed VBT, which was later developed by Linus Pauling.

- According to VBT, a bond is formed when the overlap of atomic orbitals allows electrons from two different atoms to pair up, forming a bonding orbital. The strength of this bond depends on the extent of overlap—the greater the overlap, the stronger the bond.

- VBT also discusses the bond dissociation enthalpy and bond lengths, which are determined by how close the atoms are when their orbitals overlap optimally.

Bonding and Antibonding Orbitals:

- Bonding orbitals result from constructive overlap, which means the orbitals merge in a way that lowers the energy and stabilizes the molecule.
- Antibonding orbitals result from destructive overlap, which raises the energy and makes the molecule unstable.

VBT provides a qualitative explanation for the formation of bonds and the shapes of molecules, though it has limitations in explaining certain molecular behaviors.

Forces of Attraction and Repulsion in H_2 Molecule

- Attractive Forces: These forces tend to bring the two atoms (or their nuclei) closer together, reducing the potential energy of the system.
- Repulsive Forces: These forces work against the attractive forces, pushing the atoms apart due to repulsion between like charges (nuclei repelling nuclei, or electrons repelling electrons).

This page explains that in the formation of the hydrogen molecule (H_2), both types of forces (attraction and repulsion) are present. As the two hydrogen atoms approach each other, the attractive forces between their nuclei and electrons increase, and the repulsive forces start to play a role as the atoms come too close.

Bond Enthalpy: Bond enthalpy is defined as the energy released when a bond is formed (in this case, 435.8 kJ/mol for H_2). Conversely, this energy is required to dissociate the molecule.

Orbital Overlap Concept

- The formation of a hydrogen molecule is explained in terms of orbital overlap, where the atomic orbitals of the two hydrogen atoms merge slightly.

- The extent of this overlap determines the strength of the covalent bond between the atoms.

What are Directional Properties?

- Covalent bonds (formed by the sharing of electrons between atoms) are directional in nature. This means that bonds are not formed randomly; they have specific orientations in space depending on the type of orbitals involved.
- The spatial arrangement of these bonds determines the shape and geometry of molecules like methane (CH_4), ammonia (NH_3), and water (H_2O).

For example:

- Methane (CH_4): The C-H bonds point in such a way that the molecule adopts a tetrahedral shape.
- Ammonia (NH_3): The bonds form a pyramidal structure.
- Water (H_2O): The shape becomes bent (angular) due to the lone pairs and bond repulsion.

What is Orbital Overlap?

When two atoms approach each other to form a covalent bond, their atomic orbitals overlap to share electrons. The degree and type of overlap determine the strength and type of the bond formed.

- Greater overlap results in a stronger bond because more electron density is concentrated between the two nuclei.
- Poor overlap leads to weaker bonds or no bond at all.

Types of Orbital Overlap

1. **Sigma (σ) Bond**

- A sigma (σ) bond is formed by the head-on (end-to-end) overlap of orbitals along the internuclear axis (the line connecting the nuclei of the two bonding atoms).
- It is the strongest type of covalent bond because the electron density is directly between the two nuclei, providing maximum overlap.

Types of Sigma Bond Overlaps:

- s-s Overlap: Two s-orbitals from two atoms overlap.
  Example: H_2 molecule (overlap of 1s orbitals of two H atoms).
- s-p Overlap: One s-orbital overlaps with one p-orbital.
  Example: HCl molecule (overlap of H's 1s orbital with Cl's 3p orbital).
- p-p Overlap (along the axis): Two p-orbitals overlap end-to-end along the internuclear axis.
  Example: Formation of sigma bonds in molecules like F_2.

2. **Pi (π) Bond**

- A pi (π) bond is formed by the sideways (parallel) overlap of two p-orbitals. The electron density in a π bond is concentrated above and below the plane of the nuclei.
- Pi bonds are weaker than sigma bonds because the overlap is less extensive.
- Example of Pi Bond:

  In a double bond (e.g., C_2H_4 or ethene), there is one sigma bond along the internuclear axis and one pi bond formed by the sideways overlap of p-orbitals.

  In a triple bond (e.g., N_2), there is one sigma bond and two pi bonds formed by the sideways overlap of two sets of p-orbitals.

Positive, Negative, and Zero Overlap

- Positive Overlap: When the phases (wave functions) of two orbitals are in phase, constructive interference occurs, forming a strong bond.
- Negative Overlap: When the phases are out of phase, destructive interference occurs, leading to a weaker bond or no bond.
- Zero Overlap: If the orbitals approach at the wrong angle or orientation, no effective overlap occurs, and no bond is formed.

Importance of Orbital Overlap in Bond Formation

- Bond Strength: Greater overlap (as in sigma bonds) results in stronger bonds, which makes the molecule more stable.
- Molecular Geometry: The type of orbital overlap also determines the geometry of molecules. For example, the tetrahedral structure of CH_4 is a result of sp^3 hybrid orbitals overlapping with hydrogen's 1s orbitals.
- Restricted Rotation: Pi bonds restrict the free rotation of atoms around the bond axis, giving rise to different isomers (like cis- and trans-isomers in alkenes).

2. **Strength of Sigma and Pi Bonds**

- The strength of a covalent bond depends on the extent of overlap between the orbitals. A sigma bond is stronger because the overlap is greater compared to a pi bond.
- A molecule like ethene (C_2H_4) has both sigma and pi bonds. The sigma bond forms along the internuclear axis, while the pi bond forms above and below this axis.

Hybridization: Hybridization is the concept introduced by Linus Pauling to explain the shapes of polyatomic molecules like methane (CH_4), ammonia (NH_3), and water (H_2O). It involves the mixing or intermixing of atomic orbitals of nearly the same energy to form new orbitals called hybrid orbitals.

Process of Hybridization:

- Atomic orbitals of the same atom, but with slightly different energies, mix together to redistribute their energy.
- The result is the formation of a new set of orbitals known as hybrid orbitals.
- Hybrid orbitals are used in bonding and are more stable than pure atomic orbitals.

Salient Features of Hybridization:

1. The number of hybrid orbitals formed is always equal to the number of atomic orbitals that undergo hybridization.
2. Hybrid orbitals are always equivalent in shape and energy.
3. Hybrid orbitals are more effective in forming stable bonds due to better overlap with other orbitals, which increases the bond strength.
4. These orbitals are directed in specific directions in space, which minimizes repulsion between electron pairs and leads to a stable arrangement, determining the geometry of the molecule.

Conditions for Hybridization:

1. Valence Orbitals: Only the orbitals in the valence shell of an atom undergo hybridization.
2. Nearly Equal Energy: The orbitals that participate in hybridization must have almost equal energy.
3. Electron Promotion: It is not necessary for an electron to be promoted to higher energy levels before hybridization. In some cases, hybridization can occur without any electron promotion.
4. Fully Filled Orbitals: Hybridization can occur even with fully filled orbitals.

Types of Hybridization:

1. **sp Hybridization:**
   - Orbitals Involved: One s orbital and one p orbital.
   - Hybrid Orbitals Formed: Two sp hybrid orbitals.
   - Characteristics: Each sp hybrid orbital has 50% s-character and 50% p-character. This results in a linear arrangement with a bond angle of 180°.
   - Example: $BeCl_2$ (Beryllium Chloride): In $BeCl_2$, the ground state configuration of beryllium is $1s^2\ 2s^2$. One of the 2s electrons is promoted to the vacant 2p orbital, and these orbitals hybridize to form two sp orbitals, resulting in a linear molecule with bond angles of 180°.

2. **sp^2 Hybridization:**
   - Orbitals Involved: One s orbital and two p orbitals.
   - Hybrid Orbitals Formed: Three sp^2 hybrid orbitals.
   - Characteristics: Each sp^2 orbital has 33% s-character and 67% p-character, which leads to a trigonal planar structure with bond angles of 120°.
   - Example: BCl_3 (Boron Trichloride): The ground state configuration of boron is $1s^2\ 2s^2\ 2p^1$. One of the 2s electrons is promoted to the 2p orbital, and three orbitals (one 2s and two 2p) hybridize to form sp^2 orbitals. These orbitals form a trigonal planar arrangement with bond angles of 120°.

3. **sp^3 Hybridization:**
   - Orbitals Involved: One s orbital and three p orbitals.
   - Hybrid Orbitals Formed: Four sp^3 hybrid orbitals.
   - Characteristics: Each sp^3 orbital has 25% s-character and 75% p-character. This results in a tetrahedral geometry with bond angles of 109.5°.

- Example: CH_4 (Methane): In methane, the carbon atom undergoes sp^3 hybridization, resulting in four hybrid orbitals directed towards the corners of a tetrahedron. The bond angles between the hydrogen atoms are 109.5°.
- Example: NH_3 (Ammonia): In ammonia, nitrogen undergoes sp^3 hybridization, but one of the hybrid orbitals contains a lone pair. This lone pair leads to slight compression of the bond angle to 107° from the ideal tetrahedral angle.
- Example: H_2O (Water): In water, oxygen undergoes sp^3 hybridization, but two of the four hybrid orbitals contain lone pairs of electrons. This leads to a further compression of the bond angle to 104.5°.

d-Orbital Participation in Hybridisation:

- In third-period elements and beyond (like P, S), 3d orbitals become available for hybridisation.
- These elements can use d-orbitals along with s and p orbitals to form different molecular geometries.

Energy Compatibility:

The energy of 3d orbitals is comparable to the energies of 3s and 3p orbitals.This makes combinations like sp3 d or sp3 d^2 hybridization possible.

Electronic Configuration of Phosphorus (Z = 15):

- Ground State: 1s2 2s2 2p6 3s2 3p3
- In the ground state, phosphorus has 5 valence electrons: 2 in 3s and 3 in 3p orbitals.
- Excited State: One of the 3s electrons is promoted to a 3d orbital. This gives phosphorus 5 unpaired electrons, making it capable of forming five bonds.

Hybridisation in PCl^5:

- Orbitals Involved: One 3s, three 3p, and one 3d orbital combine to form five sp3^33d hybrid orbitals.
- Molecular Geometry: The shape of PCl^5 is trigonal bipyramidal.
- Angles: 120° between atoms in the equatorial plane.
- 90° between axial and equatorial atoms.

Bond Formation in PCl^5 :

- Each of the five sp3 d hybrid orbitals overlaps with the orbitals of chlorine atoms to form sigma bonds.
- PCl5_55 thus has five covalent bonds, resulting in a trigonal bipyramidal structure.

Electronic Configuration of Sulfur (Z = 16):

- Ground State:1s2 2s2 2p6 3s2 3p4 Sulfur has 6 valence electrons: 2 in 3s and 4 in 3p orbitals.
- Excited State:Two electrons from 3p orbitals are promoted to 3d orbitals. This creates 6 unpaired electrons, allowing sulfur to form 6 covalent bonds.

Hybridisation in SF^6 : :

- Orbitals Involved: One 3s, three 3p, and two 3d orbitals combine to form six sp3^33d2^22 hybrid orbitals.
- Molecular Geometry: The shape of SF6_66 is octahedral.
- Bond Angle: 90° between all adjacent bonds.

Bond Formation in $SF^{6:}$

- Each sp3^33d2^22 hybrid orbital overlaps with the 2p orbital of a fluorine atom, forming six sigma bonds.
- The result is a highly symmetrical octahedral structure.

Molecular Orbital Theory (MOT)

- Proposed by Friedrich Hund and Robert Mulliken, Molecular Orbital Theory (MOT) explains chemical bonding by treating electrons as belonging to molecular orbitals spread across the entire molecule, rather than being confined to individual atoms.
- MOT provides a more accurate understanding of bonding compared to the Valence Bond Theory (VBT), especially for molecules with delocalized electrons (e.g., O2_22, NO, etc.).

Key Concepts of MOT:

1. Molecular Orbitals (MO): When two atomic orbitals overlap, they combine to form two molecular orbitals:
   - Bonding Molecular Orbital (BMO): Formed by constructive interference of atomic orbitals, resulting in lower energy and increased stability.
   - Antibonding Molecular Orbital (ABMO): Formed by destructive interference, resulting in higher energy and decreased stability. It is denoted with a star symbol (e.g., σ^*, π^*).
2. Distribution of Electrons: Just like atomic orbitals, molecular orbitals are filled according to the Aufbau principle, Pauli exclusion principle, and Hund's rule.

Formation of Molecular Orbitals:

The wave functions of two combining atomic orbitals (ψA and ψB) interact in two ways:

1. **Constructive Interference:** ($\psi=\psi A+\psi B$)

- This results in a bonding molecular orbital with high electron density between the nuclei.
- Increased electron density leads to a stronger bond and lower energy.

2. **Destructive Interference:** ($\psi=\psi A-\psi B$)

- This results in an antibonding molecular orbital with low or zero electron density between the nuclei (a node).
- Antibonding orbitals are higher in energy and reduce bond strength.

Advantages of Molecular Orbital Theory:

1. Explains Paramagnetism: MOT correctly predicts the paramagnetic nature of O2_22, which VBT fails to explain.
2. Delocalization of Electrons: Molecular orbitals extend over the entire molecule, giving a better description of molecules with delocalized electrons (like benzene).
3. Accurate Bonding Insights:MOT provides a quantitative way to determine bond order, stability, and magnetic properties.

Limitations of Molecular Orbital Theory:

1. Complex Calculations: The formation and energy levels of molecular orbitals involve complicated quantum mechanical calculations.
2. Less Intuitive: Compared to VBT, MOT is less intuitive, especially for beginners, as it requires understanding of wave functions and constructive/destructive interference.

Hydrogen Bonding: Hydrogen bonding is a type of intermolecular or intramolecular attraction between a hydrogen atom covalently bonded to a highly electronegative atom (such as O, N, or F) and another electronegative atom with a lone pair of electrons.

Types of Hydrogen Bonding:

1. **Intermolecular Hydrogen Bonding:** Occurs between hydrogen and electronegative atoms in different molecules. Example: Water (H_2O) molecules bonding with each other.
2. **Intramolecular Hydrogen Bonding:** Occurs between hydrogen and electronegative atoms within the same molecule. Example: Ortho-nitrophenol (where the hydrogen bond forms within the molecule).