

CHAPTER - 04

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemical bond

A chemical bond is an attraction that holds the constituent particles together in a chemical species.

KOSSEL-LEWIS ELECTRONIC THEORY OF CHEMICAL BONDING

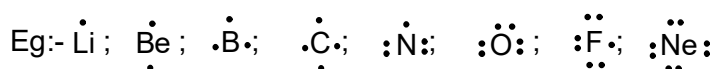
1. Lewis approach

Lewis pictured the atom in terms of

1. A positively charged "Kernel" [Nucleous + inner electrons] and
The outer shell that could accomodate a maximum of eight electrons.
2. When all the eight corners of the cube are occupied then an atom is said to have stable electronic configuraiton.
 - ▶ Cheaply noble gases which have 8 outer most electrons already have stable configuration while all other.

Lewis symbols

G.N. Lewis introduced a simple notation to represent valence electrons in an atom. These notations are called Lewis symbols or electron dot symbols. According to Lewis notatinos, the valence electrons are represented by dots around the symbol of the element.



Significance of Lewis dot symbols

The number of dots around the symbol represents the number of valence electrons. This number of valence electron helps to calculate the common or group valence of the element. **The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.**

2. Kossel approach

- ▶ Kossel, in relation to chemical bonding, drew attention to the following facts.
- ▶ In the periodic table, the highly electronegative halogen and the highly electropositive alkali metals are separated by the noble gases.

- ▶ The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
- ▶ The negative and positive ions thus formed attain stable noble gas electronic configurations.
- ▶ The noble gases have a particularly stable outer electronic configuration of eight.
- ▶ Negative and positive ions are stabilized by electrostatic attraction.

Octet Rule [Kossel and Lewis - 1916] (Electronic theory of chemical bonding)

According to octet rule, atoms of various elements take part in chemical combination in order to attain octet of electrons in their outermost shell.

Atoms generally achieve octet of electrons in two ways.

1. By the transfer of electron from one atom to another
2. By the mutual sharing of electron between the atoms.

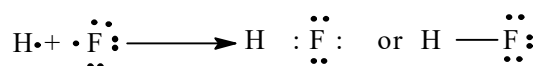
Covalent bond : (Lewis - Langmuir concept)

It is the bond formed by mutual sharing of electrons between two atoms so as to complete their octet or duplets.

Covalency : Of an element may be defined as the number of electrons contributed by its atom while forming covalent bond.

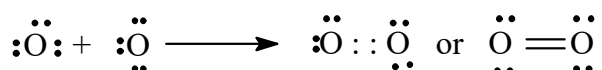
Types of covalent bond

1. **Single bond** : When two atoms share one electron pair, the bond formed is called single covalent bond.



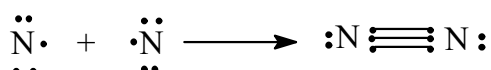
2. **Double bond** : When two atoms share two electron pairs, the bond formed is called double bond.

Eg: O₂ molecule



3. **Triple bond** : When two atoms share three electron pairs, the bond formed is called triple bond.

Eg: N₂ molecule



Double and triple bonds are together called multiple bond.

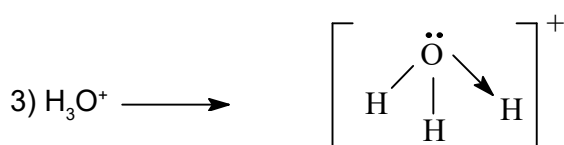
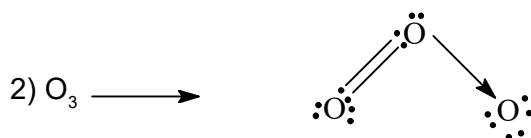
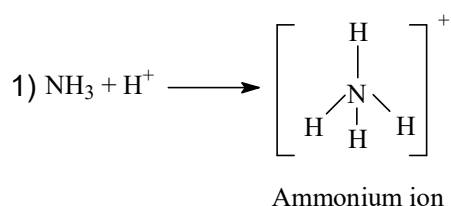
General characteristics of covalent compounds

1. Covalent compounds exist in all the three states (solid, liquid and gas)
2. Covalent compounds generally have low melting and boiling points because the molecules in covalent compounds are usually held together by weak vander waals forces.
3. They are generally soluble in organic solvents but insoluble in water.
4. They are generally bad conductors of electricity.

Co-ordinate bond or Dative bond

The bond formed between two atoms in which contribution of an electron pair is made by one atom out of them while the sharing is done by both (one side sharing).

Eg :

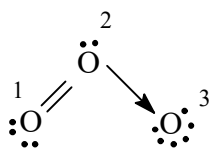


Formal charge

The charge possessed by an atom in a polyatomic ion or molecule considering its Lewis structure is called formal charge of that atom.

Formal charge = Total number of valence electron in the free atom – Total number of non bonding electron – $\frac{1}{2} \times \text{no. of bonding electrons}$.

Eg : O_3 molecule



$$\text{F.C. of O}_I = 6 - 4 - \frac{1}{2} \times 4$$

$$\text{F.C. of O}_{II} = 6 - 2 - \frac{1}{2} \times 6 = +1$$

$$\text{F.C. of O}_{III} = 6 - 6 - \frac{1}{2} \times 2 = -1$$

Limitations of Octet rule

1. **The incomplete octet of central atom:-** In some compounds, the number of electrons surrounding the central atom is less than eight.

Eg : BeH_2 , BCl_3 , BF_3 etc

2. **Odd Electron molecules:-** In molecules with an odd number of electrons like NO and NO_2 , the octet rule is not satisfied for all the atoms.

Eg: NO - $\text{:}\dot{\text{N}}=\ddot{\text{O}}\text{:}$



3. **The expanded octet :-** The octet rule is violated in the formation of compounds such as PCl_5 , SF_6 and IF_7 etc. In these molecules, the central atoms have more than eight electrons in their valence shells.

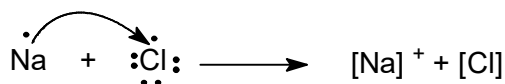
Eg : PCl_5 , SF_6 , IF_7 , SF_4 etc.

4. Formation of compounds by xenon and krypton
5. This theory does not account for the shape of molecules.
6. It does not explain the relative stability of the molecules.

Ionic or Electrovalent bond

An ionic bond or electrovalent bond is formed by the complete transference of one or more valence electrons of one atom to another. In this way both the atoms acquire electronic configuration of the nearest noble gas.

The atom which loses its valence electrons acquire positive charge and is known as cation or positive ion. The atom which gains electrons acquires negative charge and is called anion or -ve ion. These two oppositely charged ions then formed attracts each other by electrostatic force of attraction. The bond thus formed is known as ionic bond or electrovalent bond.

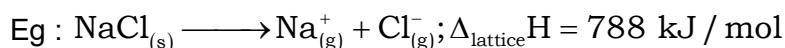


Factors favouring formation of ionic bond

1. Low ionisation energy of the electropositive atom
2. High negative electron gain enthalpy of the electronegative atom
3. High lattice energy of the compound formed
4. Difference in electronegativity between bonded atoms should be greater than 1.7

Lattice energy

It is the energy required to completely separate one mole of the solid ionic compound into constituent gaseous ions.



Factors affecting lattice energy

$$\text{L.E} \propto \frac{q^+ q^-}{r}$$

$q^+ \rightarrow$ charge on cation

$q^- \rightarrow$ charge on anion

$r = r_+ + r_- \rightarrow$ interionic distance

Partial covalent character in ionic compounds (Fajan's rule):

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a nearby anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

More distortion of anion, more will be polarisation, then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

- i. **Size of cation** : Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.
- ii. **Size of anion** : Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.
- iii. **Charge on cation** : Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.
- iv. **Charge on anion** : Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.
- v. **Pseudo inert gas configuration of cation** : Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert configuration.

Valence Bond Theory (VBT)

In valence bond theory, it is assumed that atoms with all their bonding electrons approach each other to form a molecule. This theory was first applied by Heitler and London in 1927 to the formation of the hydrogen molecule. It was further extended by Slater and Pauling.

According to the modern concept, the formation of bonds between atoms occur only if it is accompanied by decrease of energy. Thus, the tendency of atoms to acquire stability by lowering their potential energy is responsible for the formation of bond between them.

Let us consider two hydrogen atoms H_A and H_B lying far apart from each other, so that no interaction occurs between them. It is assumed that when the two atoms are far away from each other, that is the distance between H_A and H_B is infinity, the potential energy of the system is zero.

When the two atoms come closer, new attractive and repulsive forces begin to operate.

a. Attractive forces : Attractive forces operate between

i) Nucleus of one atom and its own electron i.e. $N_A - e_A$ and $N_B - e_B$

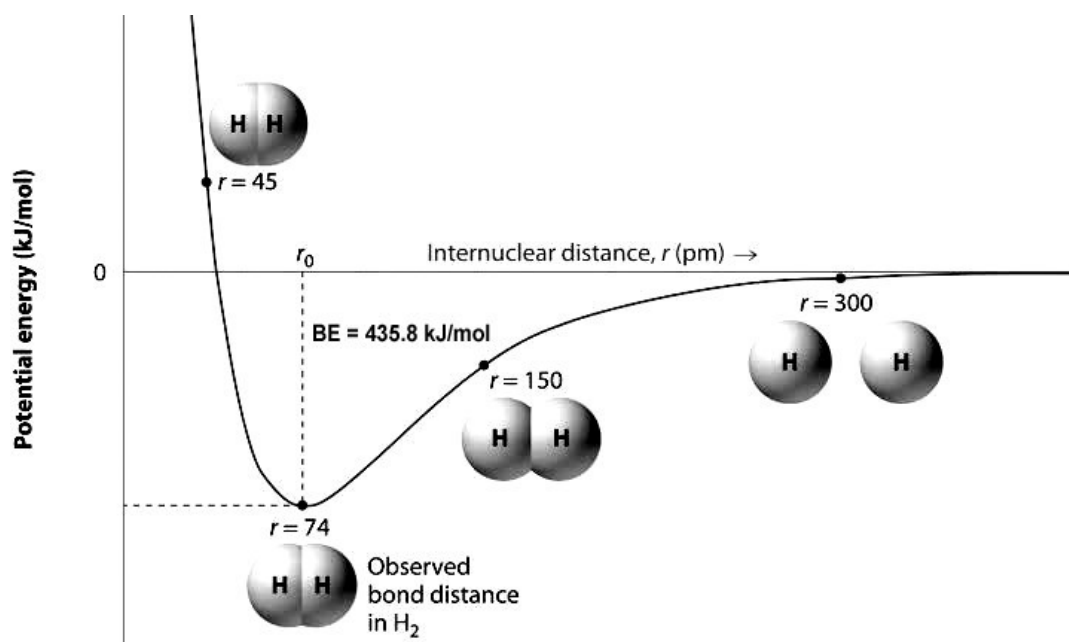
ii) Nucleus of one atom and electron of other atom .i.e, $N_A - e_B$ and $N_B - e_A$

b. Repulsive forces : Repulsive forces operate between

i) Electron of the two atoms i.e., $e_A - e_B$

ii) nuclei of the two atoms i.e., $N_A - N_B$

It has been found that in the beginning, the magnitude of attractive forces is greater than the repulsive forces. As a result, the two atoms go on approaching each other and the potential energy of the system goes on decreasing. Ultimately a stage is reached at which the total forces of attraction balance the forces of repulsion. At this stage the system will have minimum energy and the two hydrogen atoms are said to be bonded together resulting in the formation of H_2 molecule. The distance between the two nuclei in the molecule is called the bond length and it is found to be 74 pm (or 0.74 \AA) for H_2 . The potential energy changes taking place during the formation of H_2 molecule is shown graphically below.



The decrease in potential energy is accompanied by a release of energy when the H_2 molecule is formed from the two H atoms. That means heat is given out when a bond is formed. If a H_2 molecule ($H-H$) is to be broken, the process is endothermic or energy must be supplied.

Orbital overlap concept of covalent bond formation

In covalent bonding, there is a change in electron densities in the combining atoms. Accumulation of electron densities between the two nuclei results in bond formation. When two atoms approach, there is overlapping of electron waves.

The main ideas of orbital overlap concept of covalent bond formation are

- i. Covalent bonds are formed by overlapping of half filled atomic orbitals present in the valence shell of the atoms taking part in bonding.
- ii. The orbitals undergoing overlapping must have electrons with opposite spins
- iii. The strength of a covalent bond depends upon the extend of overlapping.

Overlapping of atomic orbitals

When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangement of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4 , NH_3 and H_2O , the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4 , NH_3 and H_2O molecules are tetrahedral, pyramidal and bent respectively.

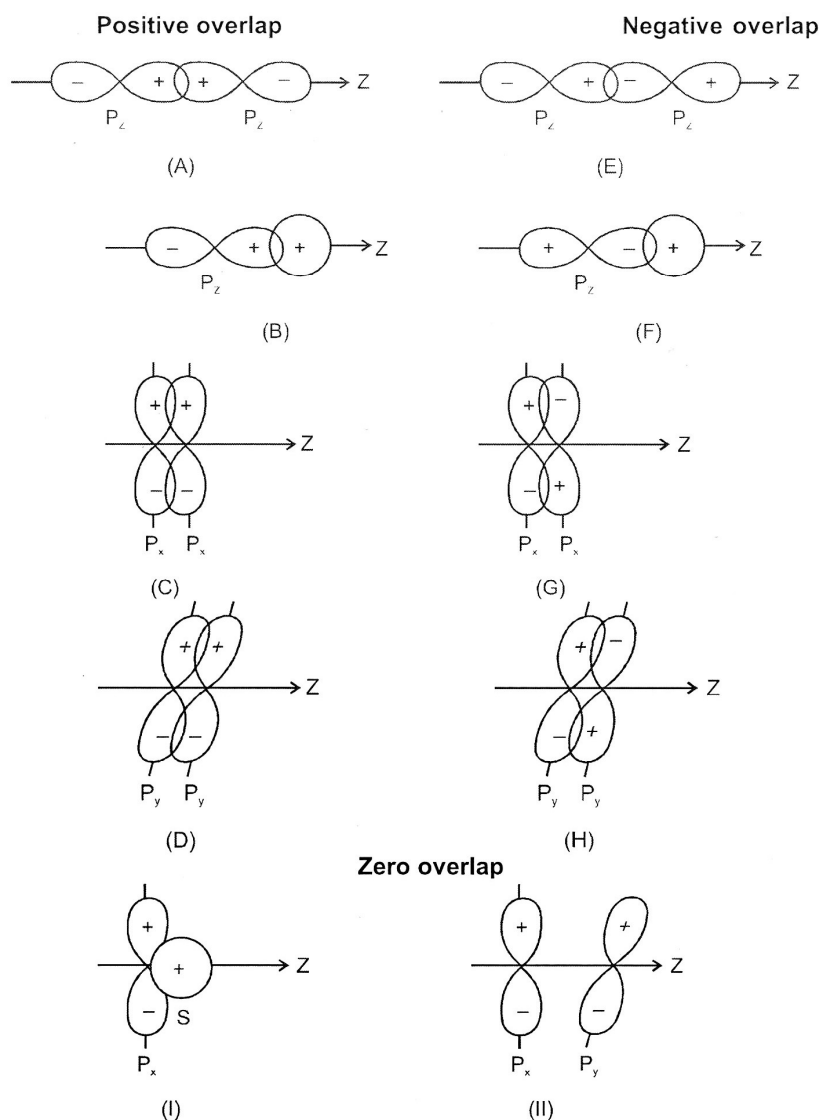


Figure : Positive , negative and zero overlaps of s and p atomic orbitals

TYPES OF COVALENT BONDS

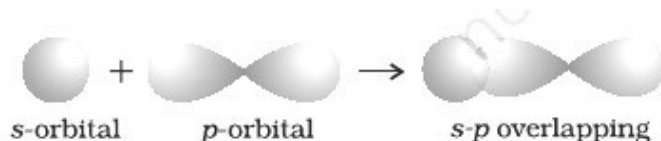
Sigma (σ) and pi (π) bonds

- a. **Sigma (σ) bond** : The bond formed by the axial (or head-on) overlap of atomic orbitals along the internuclear axis is known as (σ) bond. Sigma bond may be formed by any one of the following types of overlapping.
- i. **Overlapping of s-s orbitals** : Hydrogen molecule (H_2) formation is an example of 1s-1s overlap between two hydrogen atoms, resulting in the formation of a covalent bond.



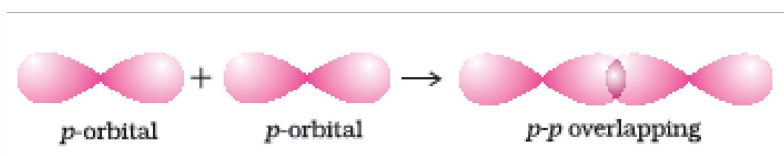
ii. **Overlapping of s-p orbitals**

The half filled s orbital of one of the two elements overlaps with the half-filled p-orbital of the other element resulting in the formation of a chemical bond. Examples of this type of s-p overlap are the formation of compounds HF, HCl etc. The general representation of an s-p orbital overlap can be made as shown.

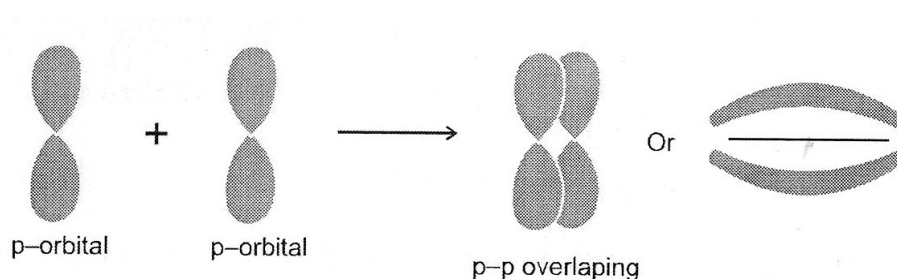


iii. **Overlapping of p-p orbitals**

The half filled p orbital of one of the two elements overlaps with the half filled p orbital of the other element resulting in the formation of a chemical bond. Examples of this type are the formation of compounds like F_2 , Cl_2 etc.



- b. **Pi (π) bond**: Covalent bond formed by the lateral or sidewise overlap of half-filled atomic orbitals is known as pi(π) bond. The atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.



Differences between sigma and pi bonds

σ bond	π bond
It is formed by axial overlap of s-s or s-p or p-p orbitals of two atoms	It is formed by lateral overlap of p-p orbitals
Extent of overlapping is quite large and hence σ bond is a strong bond	Overlapping is to a small extent and hence π bond is a weak bond
There can only be one σ bond between two atoms	There can be one or two π bonds between two atoms
Electron cloud is cylindrically symmetrical about the line joining the two nuclei	Electron cloud of π bond is unsymmetrical about the internuclear axis.
σ bond may involve the overlapping of hybrid orbitals. They determine the shape of the molecule	π bond usually involves the overlapping of pure orbitals. They do not determine the shape of molecules.

Hybridisation

It is defined as the intermixing of atomic orbitals of slightly different energy and shape so as to redistribute their energies, resulting in the formation of new set of orbitals of identical shape and similar energy. This explains why atoms like Be, B, C show a valency of 2, 3 and 4 respectively. The energy required for excitation is compensated by energy released during bond formation.

Characteristics of hybridisation

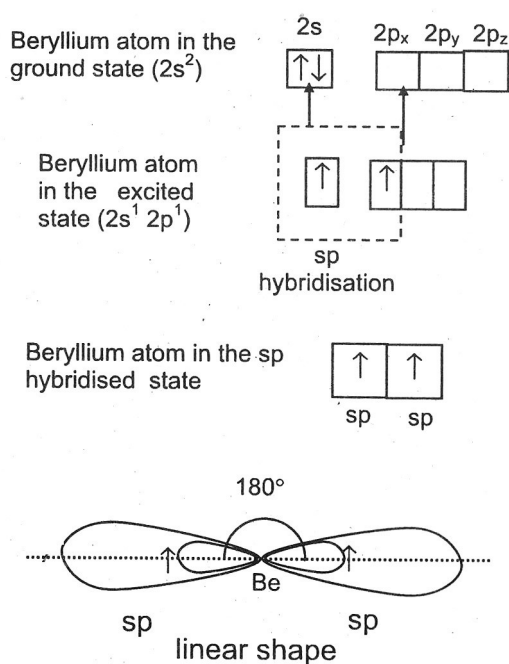
1. The number of hybrid orbitals formed is equal to the number of orbitals that get hybridised.
2. The hybrid orbitals are always equivalent in energy and shape.

- The hybrid orbitals are more effective in forming stable bonds than unhybridised atomic orbitals.
- The hybrid orbitals are directed in space in some preferred directions so as to have minimum repulsion between electron pairs. Therefore, the type of hybridisation indicates the geometry of the molecule.

Types of hybridisation

- sp hybridisation** : This involves one s and one p orbital of the valence shell of an atom resulting in the formation of two new equivalent hybridised orbitals. The sp hybrid orbitals have 50% s and 50% p character. The sp hybrid orbitals are linear and lie in the same line at an angle of 180° from each other.

Structure of BeCl_2 : In BeCl_2 , Cl–Be–Cl, the central Be atom uses both its valence electrons in forming 2σ bonds with the two chlorine atoms.

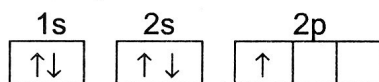


Each of these orbitals overlaps axially with half filled $3p$ orbitals of chlorine to form two Be–Cl bonds. Few other compounds which exhibit sp hybridization are BeF_2 , CO_2 , CH_3CN , HCN etc.

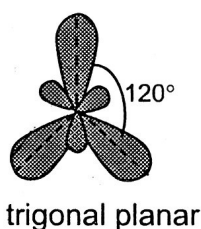
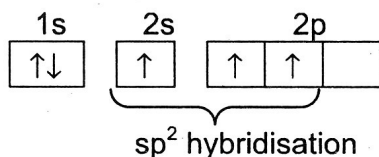
- sp^2 hybridisation** : This involves the mixing up of one s and two p orbitals of the valence shell of an atom to form three new equivalent orbitals. The three new equivalent sp^2 orbitals are formed with 33% s character and 67% p character. The three equivalent orbitals have a symmetrical distribution and are directed towards the corners of a trigonal planar structure at an angle of 120° from one another.

Structure of BCl_3 : In BCl_3 , the ground state electronic configuration of the central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the $2s$ electrons is promoted to vacant $2p$ orbital, as a result boron has three unpaired electrons. These three orbitals hybridise to form three sp^2 hybrid orbitals. The hybrid orbitals formed are oriented in a trigonal planar arrangement and overlap with the $3p$ orbitals of chlorine to form three B–Cl bonds.

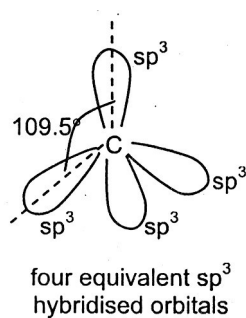
B (ground state)



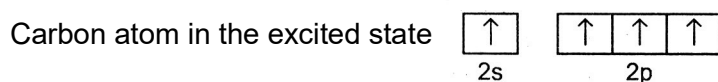
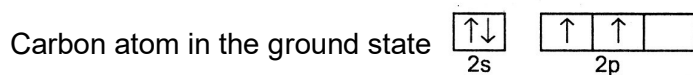
B (excited state)



3. **sp^3 hybridisation** : This involves the mixing up of one s and three p orbitals of the valence shell of an atom to form four new equivalent orbitals. Each sp^3 hybrid orbital has 25% s-character and 75% p-character. The four sp^3 hybrid orbitals are directed towards the four corners of a tetrahedron to minimise repulsion. The angle between the sp^3 hybrid orbitals is $109^\circ 28'$ or approximately 109.5° .

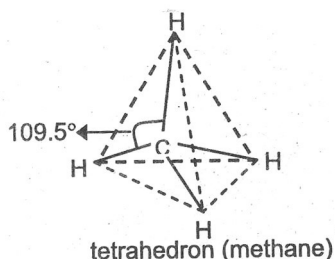


Structure of methane (CH_4)



Carbon atom after sp^3 hybridisation

↑	↑	↑	↑
sp^3	sp^3	sp^3	sp^3



In methane, the four sp^3 hybridised orbitals of carbon are directed towards the four corners of a regular tetrahedron with the carbon atom located at the centre and four hydrogen atoms at the corners.

Each of the four sp^3 hybrid orbitals on carbon is singly filled. In the formation of methane, each of these hybrid orbitals overlap with the half filled $1s$ orbital of hydrogen. This results in four C–H bonds and these single bonds are known as sigma (σ) bonds. The axes of the sp^3 orbitals are directed towards the four corners of a regular tetrahedron, with the carbon at the centre with H–C–H bond angle $109^\circ 28'$.

Energy is required for the promotion of a $2s$ electron to $2p$ orbital and for the hybridisation of the orbitals to give equivalent orbitals, but this is compensated by the release of energy in the formation of covalent bonds involving the sp^3 hybrid orbitals.

4. **sp^3d hybridisation** : When one s orbital, three p orbitals and one d orbital are involved in the hybridisation, it is called sp^3d hybridisation. For example, phosphorus in PCl_5 is sp^3d hybridised.

Structure of PCl_5 : The structure of PCl_5 shows that the central atom P uses all its five electrons from its valence shell ($3s^2 3p^3$) in forming the 5σ bonds with five chlorine atoms.

P atom in the ground state :

3s	3p	3d
↑↓	↑ ↑ ↑	

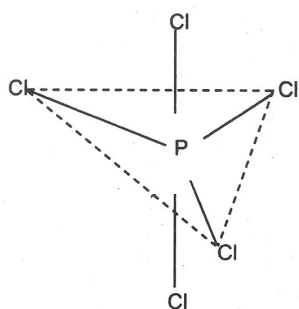
P atom in the excited state:

↑	↑ ↑ ↑	↑			
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↓
 sp^3d
hybridisation

The result is that there are five non-equivalent sp^3d hybrid orbitals with 2 axial orientations and 3 equatorial (lateral) orientations. sp^3d hybrid orbitals are singly occupied with electrons. They form five σ bonds with five p orbitals of five chlorine atoms.

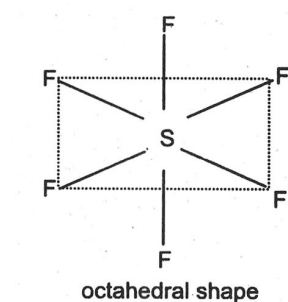
PCl_5 has a trigonal bipyramidal shape. Of the five bonds, three equatorial bonds are equal in length and two axial bonds are longer than the equatorial bonds. This is because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs. Axial bonds are less stronger than equatorial bonds.



5. **sp^3d^2 hybridisation:** It involves the mixing up of one s orbital three p orbitals and two d orbitals to give six hybridised orbitals. Sulphur hexafluoride (SF_6) is an example of a molecule where sulphur shows sp^3d^2 hybridisation.

Structure of SF_6 : In SF_6 , all the six valence electrons of sulphur are used up. There are six sp^3d^2 equivalent orbitals formed after hybridisation with no lone pair of electrons. Each of the six hybridised sp^3d^2 orbitals are singly filled before bonding.

Each one of these sp^3d^2 hybridised orbitals overlaps with p orbitals of six fluorine atoms to form SF_6 . The molecule has an octahedral shape.

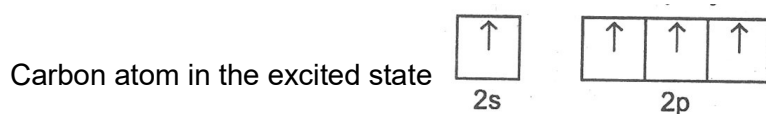


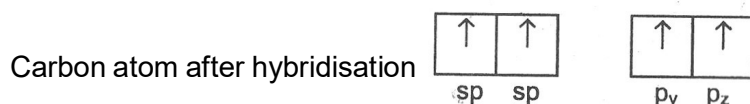
As the s-character in a hybrid orbital increases its electronegativity increases, since the s-electrons are more close to the nucleus.

Hybridisation	sp^3	sp^2	sp
% s-character	25%	33.3%	50%
Electronegativity order	$sp^3 < sp^2 < sp$		

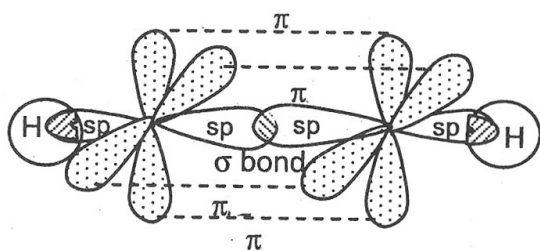
Structure of acetylene ($H-C \equiv C-H$)

Both the carbons in acetylene are sp hybridised.

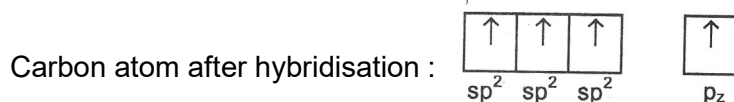
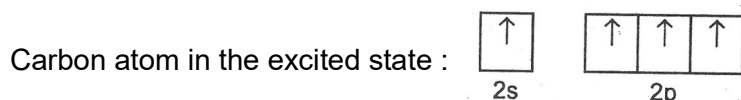




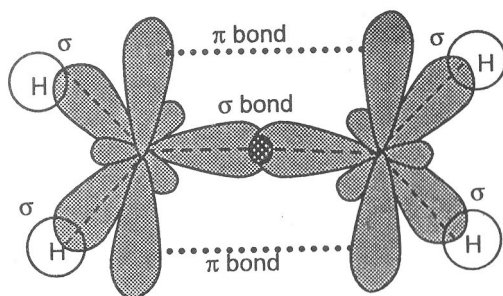
One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other to form C–C sigma bond. The other sp hybrid orbital of each carbon overlaps axially with 1s orbitals of hydrogen atoms to form C–H sigma bonds. Each of the two unhybridised orbitals (2p_y and 2p_z) of one carbon atom overlaps sidewise with similar orbitals of the other carbon atom to form two π bonds. Acetylene molecule is linear with bond angle of 180°.



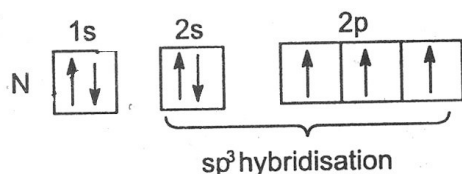
Structure of ethylen (CH₂ = CH₂): Both the carbons in ethylene are sp² hybridised.



The three sp² hybrid orbitals of carbon are oriented in a plane and are inclined at an angle of 120°. One sp² hybrid orbital of one carbon atom overlaps axially with sp² hybrid orbitals of the other carbon to form C–C sigma bond. The remaining two sp² hybrid orbitals of each carbon atom overlap axially with one s orbital of each carbon atom overlap axially with one s orbital of hydrogen to form C–H sigma bonds. The unhybridised two p orbitals (2p_z) of each carbon atom is oriented at right angles to the sp² hybridised orbitals. These unhybridised 2p_z orbitals of the two carbon atoms overlap sidewise to form a π bond. The π bond consist of two equal electron clouds distributed above and below the plane of other atom.

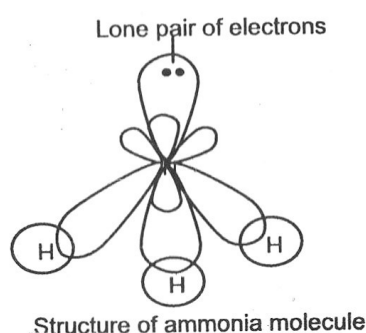


Structure of ammonia molecule (NH_3): The electronic configuration of nitrogen atom is $1s^1 2s^2 2p_x^1 2p_y^1 2p_z^1$. In the formation of NH_3 molecule, nitrogen undergoes sp^3 hybridisation in which one 2s and three 2p orbitals hybridise to form four sp^3 hybrid orbitals.

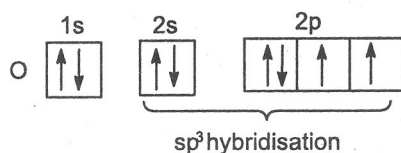


One of these hybrid orbitals contains a lone pair of electrons while the other three contain one unpaired electron each. The four sp^3 hybrid orbitals will be directed towards the corners of a tetrahedron. The three hybrid orbitals containing unpaired electrons overlap axially with half filled 1s orbitals of hydrogen to form three N–H sigma bonds. The lone pair of electrons do not participate in bond formation. Thus in ammonia, nitrogen is surrounded by three bond pairs and one lone pair of electrons. The lone pair of electrons repel the bond pairs strongly. As a result, the three N–H bonds move slightly closer. Thus the bond angle in ammonia decreases from 109.5° to 107° .

Since one of the tetrahedral positions is occupied by a lone pair, the shape of ammonia molecule is said to be pyramidal.



Structure of water molecule (H_2O): The electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. It contains two unpaired electrons. In the formation of H_2O molecule, oxygen undergoes sp^3 hybridisation in which 2s and three 2p orbitals hybridise to form four sp^3 hybrid orbitals.



Two of these hybrid orbitals contain lone pairs while the other two contain one unpaired electron each. These hybrid orbitals containing unpaired electrons overlap axially with half filled 1s orbitals of hydrogen to form two O–H sigma bonds. Thus in water, oxygen is surrounded by two lone pairs and two bond pairs of electrons. Since the lone pairs repel the bond pairs very strongly, the two O–H bonds move closer. Thus the bond angle in water is reduced to 104.5° .

Since two of the tetrahedral positions are occupied by lone pairs, water is said to be V-shaped (Bent)

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY :

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows:

- i. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- ii. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- iii. These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- iv. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- v. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- vi. Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

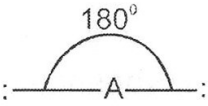
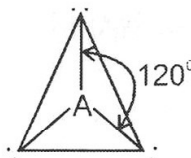
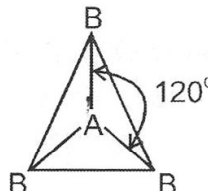
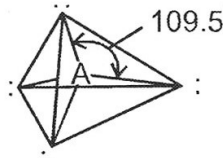
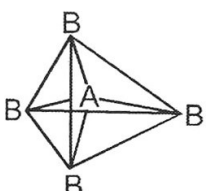
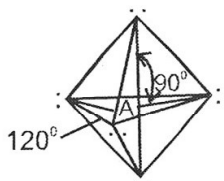
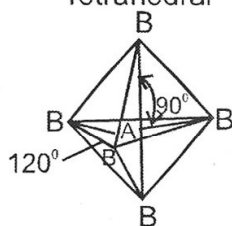
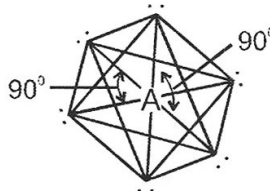
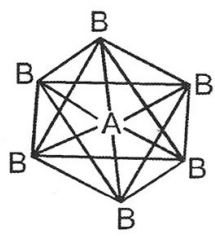
The repulsive interaction of electron pairs decreases in the order:

lone pair (ℓp) – lone pair (ℓp) > lone pair (ℓp) – bond pair (bp) > bond pair (bp) > bond pair (bp)

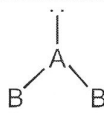
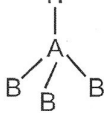
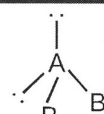
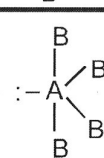
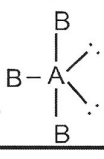
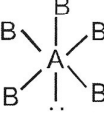

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsion. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom / ion has one or more lone pairs.

Shape (molecular geometry) of some simple molecules/ions with central atom/ion having no lone pairs of electrons (E).

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	 <p>Linear</p>	$B - A - B$ Linear	$BeCl_2, HgCl_2$
3	 <p>Trigonal planar</p>	 <p>Trigonal planar</p>	BF_3
4	 <p>Tetrahedral</p>	 <p>Tetrahedral</p>	CH_4, NH_4^+
5	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	PCl_5
6	 <p>Octahedral</p>	 <p>Octahedral</p>	SF_6

Shape (molecular geometry) of some simple molecules/ions with central atom/ions having one or more lone pairs of electrons (E).

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1		Bent	SO_2, O_3
AB_3E	3	1		Trigonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O
AB_4E	4	1		See saw	SF_4
AB_3E_2	3	2		T-shape	ClF_3
AB_5E	5	1		Square pyramidal	BrF_5
AB_4E_2	4	2		Square planar	XeF_4

Dipole moment

The degree of polar character in a polar covalent bond is given in terms of dipole moment. This is expressed as the product of the magnitude of the electric charge (Q) and the distance (r) between the positive and negative ends of the molecule.

Dipole moment is represented as μ ; $\mu = Q \times r$

Where μ - dipole moment, r - distance between two atoms

SI unit of dipole moment is coulomb meter (Cm). Dipole moment is usually expressed in Debye units (D)

$$1D = 3.33564 \times 10^{-30} \text{ Cm} = 1 \times 10^{-18} \text{ esu cm}$$

BOND PARAMETERS:

- Bond length** : The average distance between the centres of the nuclei of the two bonded atoms is called bond length.
 - ▶ For ionic compounds, the sum of ionic radius of cation and anion is called B.L.
 - ▶ For covalent compounds sum of covalent radius is called B.L.
- Bond Energy** : The amount of energy required to break one mole of bonds of a particular type. So as to separate them into gaseous atoms is called bond energy (B.E.)
- Bond order** : It is the number of covalent bonds between two atoms in a molecule. It is lobe noted that isoelectronic ions and molecules will have the same bond order.
Eg : NO^+ , CO and N_2 have the same bond order of 3.
- Bond angle** : It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule.

Molecular orbital theory

Molecular orbital theory was developed by Hund and Mulliken in 1932. The main ideas of this theory may be summed up as follows:-

- In molecules, electrons are present in new orbitals called molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of nearly same energies and proper symmetry.
- Molecular orbitals are associated with the nuclei of all the bonded atoms in a molecule. ie., a molecular orbitals is polycentric. (But an electron in an atomic orbital is under the influence of the nucleus of only one atom. ie, atomic orbitals are monocentric).
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. Among the new molecular orbitals formed, half are of lower energy than the combining atomic orbitals (called bonding molecular orbitals) and the other half are of higher energy than the combining atomic orbitals (called antibonding molecular orbitals)
- Like atomic orbitals, molecular orbitals are also filled in accordance with Pauli's exclusion principle, Hund's rule and Aufbau principle.

Linear Combinatin of Atomic Orbitals (LCAO)

According to wave mechanics, atomic orbital is expressed by wave function ϕ . Molecular orbitals are formed by linear combination of atomic orbitals which takes place by addition and subtraction of wave functions of individual atomic orbitals.

The method can be illustrated by considering the formation of hydrogen moleucle from two hdyrogen atoms A and B. Le the wave functions of the electrons in the atomic orbitals of the two atoms be ϕ_A and ϕ_B respectively. According to LCAO method, the wave functions of the two molecular orbitals formed are obtained by linear combination of ϕ_A and ϕ_B as shown below

$$\phi_{MO} = \phi_A \pm \phi_B$$

The two molecular orbitals σ and σ^* formed can be represented as

$$\varphi_{\text{BMO}} = \varphi_{\text{A}} + \varphi_{\text{B}}$$

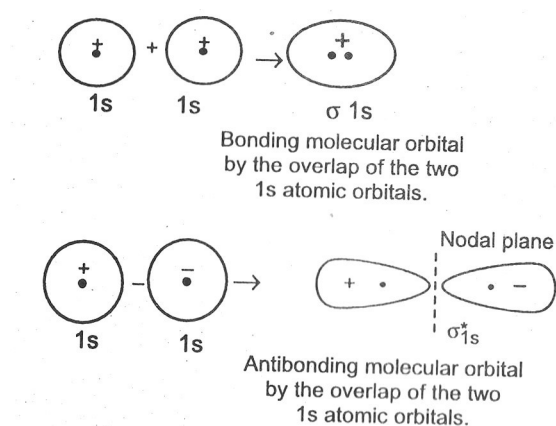
$$\varphi_{\text{AMO}} = \varphi_{\text{A}} - \varphi_{\text{B}}$$

The molecular orbital formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital formed by subtraction of atomic orbitals is called **antibonding molecular orbital**.

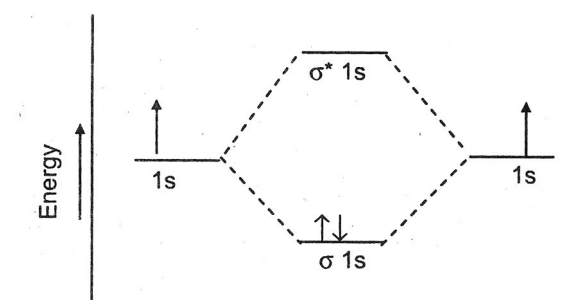
In bonding MO, the electron charge density between the two nuclei is high and therefore the repulsion between the nuclei is very low. Bonding molecular orbital, therefore, gets stabilised and bond formation is favoured.

In an antibonding MO, the electron charge density between the two nuclei is low and therefore the repulsion between the nuclei is high and hence the anti bonding molecular orbital is destabilized. Bond formation is not favoured in the anti bonding molecular orbital.

Combination of s-s atomic orbitals



Energy level diagram for $\sigma 1s$ bonding and $\sigma^* 1s$ antibonding molecular orbitals formed by the linear combination of 1s atomic orbitals of the two hydrogen atoms in a hydrogen molecule is shown below.



Difference between bonding and antibonding molecular orbitals

Bonding MO	Antibonding MO
1. Bonding MO is formed by the addition of atomic orbitals	1. Antibonding MO is formed by the subtraction of atomic orbitals
2. It has greater electron density in the region between the two nuclei of bonded atoms	2. It has less electron density in the region between the two nuclei
3. Its energy is less than the energy of the combining atomic orbitals	3. Its energy is more than the energy of the combining atomic orbitals
4. Electrons in bonding molecular orbitals result in attraction between atoms. Thus they favour bonding	4. Electrons in antibonding MO result in repulsion between atoms. So antibonding MO does not favour bonding

Conditions for combination of atomic orbitals

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The atomic orbitals must have the same symmetry about the molecular axis. Thus a $2p_z$ orbital can combine with $2p_z$ of another atom but not with the $2p_x$ or $2p_y$ of the second atom.
3. The atomic orbitals must overlap to maximum extent.

Types of molecular orbitals

There are different types of molecular orbitals called σ orbital, π orbital etc.

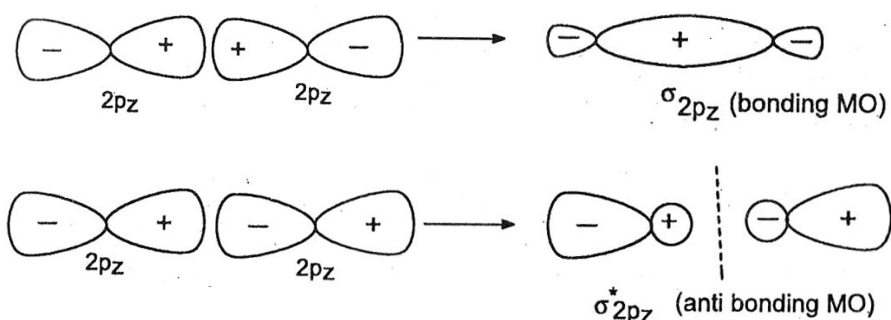
If two atomic orbitals overlap along the internuclear axis, the molecular orbital formed is called a sigma (σ) molecular orbital. Sigma molecular orbitals are symmetrical around the internuclear axis. For example, the molecular orbitals formed by the combination of two 1s orbitals are sigma molecular orbitals. Similarly 2s orbitals and $2p_z$ orbitals also combine to form σ molecular orbitals.

If two atomic orbitals overlap sidewise, the molecular orbitals formed is called pi (π) molecular orbital.

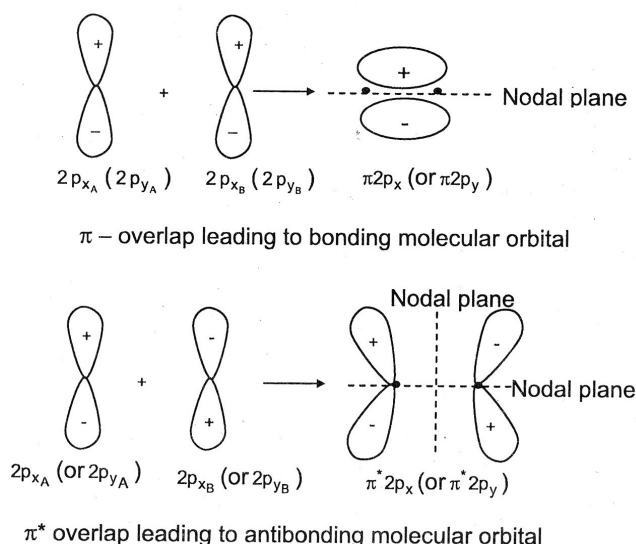
Pi (π) molecular orbitals are not symmetrical around the internuclear axis. For example, the molecular orbitals formed by two $2p_x$ orbitals are π molecular orbitals. Similarly, $2p_y$ orbitals also combine to form π molecular orbitals.

Molecular orbitals formed from p orbitals

By convention atoms form bonds along the z axis, $2p_z$ orbitals lie along the molecular axis. Therefore they overlap axially by addition and subtraction to form two σ molecular orbitals namely bonding and antibonding sigma molecular orbitals.



$2p_x$ and $2p_y$ overlap laterally to produce MO's which are called π MO's. Bonding and antibonding $\pi 2p_x$ and $\pi^* 2p_x$ molecular orbitals are formed respectively. In π -MO's the electron density is above and below the internuclear axis. There is zero electron density (nodal plane) on the line joining the two nuclei.



Similarly p_y orbitals also overlap laterally to form $\pi 2p_y$ and $\pi^* 2p_y$ molecular orbitals. $\pi 2p_x$ and $\pi 2p_y$ orbitals are degenerate (same energy orbitals) and $\pi^* 2p_y$ and $\pi^* 2p_x$ orbitals are also degenerate.

Energy level diagram for molecular orbitals

We have seen that 1s atomic orbitals of two form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. Similarly 2s orbitals give rise to $\sigma 2s$ and $\sigma^* 2s$. Molecular orbitals produced from 2p orbitals are $\sigma 2p_z$, $\sigma^* 2p_z$, $\pi 2p_x$, $\pi 2p_y$, $\pi^* 2p_x$ and $\pi^* 2p_y$. The energy levels of these orbitals have been determined from spectroscopic data.

The order is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

The order is slightly changed for lighter elements, Li_2 , Be_2 , B_2 , C_2 , N_2 . This is due to the mixing of $2s$ and $2p_z$ orbitals which have only slight difference in energy. The energy of the $\sigma 2p_z$ goes above $\pi 2p_x$ and $\pi 2p_y$. The modified order of energy levels for these elements is $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

Bond order : Bond order is defined as one half of the difference between the number of electrons in the bonding molecular orbitals (N_b) and that in the antibonding molecular orbitals (N_a)

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

If the number of electrons in the bonding and antibonding orbitals is the same, the bond order is zero and hence no bond formation occurs. Bond orders 1, 2 and 3 represent single, double and triple bonds respectively. The bond length decrease as bond order increase.

Magnetic properties from MOT

If all the molecular orbitals contain paired electrons, the molecule will be diamagnetic i.e., weakly repelled by external magnetic field and if one or more molecular orbitals contain unpaired electrons the molecule is paramagnetic.

BONDING IN SIMPLE HOMONUCLEAR DIATOMIC MOLECULES

1. Hydrogen molecule, H_2

Number of electrons in H_2 is $1 + 1 = 2$

The electronic configuration in $\text{H}_2 = \sigma 1s^2$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$$

There is a single bond, $\text{H}-\text{H}$

Molecule is stable and diamagnetic

2. Hydrogen molecule cation, H_2^+

No. of electrons = 1

Electronic configuration = $\sigma 1s^1$

$$\text{Bond order} = \frac{1}{2}(1 - 0) = \frac{1}{2}$$

H_2^+ is less stable because bond order is less than one. H_2^+ is paramagnetic.

3. Hydrogen molecule anion, H_2^-

No. of electrons = 3

Electronic configuration = $\sigma 1s^2 \sigma^* 1s^1$

$$\text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

Molecule is less stable and paramagnetic.

4. Boron molecule, B_2

No. of electrons = 10

Electronic configuration : $KK \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 \pi 2p_y^1$

$$\text{Bond order} = \frac{1}{2}(6 - 4) = 1$$

Molecule has two unpaired electrons. \therefore paramagnetic

5. Carbon molecule, C_2

No. of electrons = 12

Electronic configuration: $KK \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2$

$$\text{Bond order} = \frac{1}{2}(8 - 4) = 2$$

Molecule is stable and diamagnetic

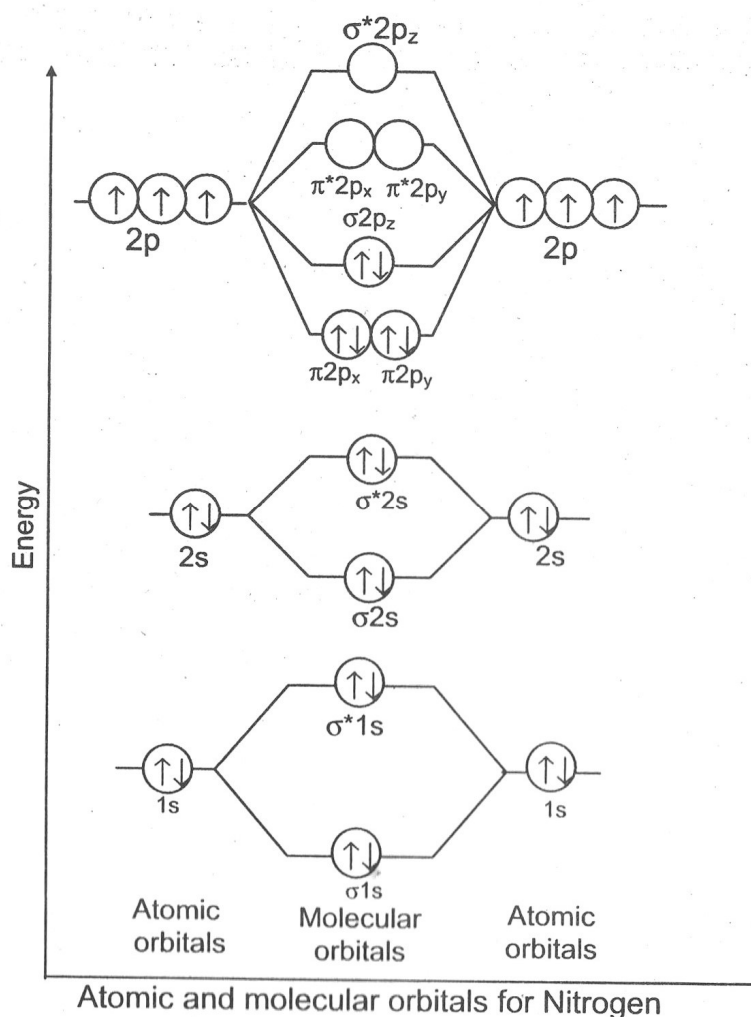
6. Nitrogen molecule, N_2

No. of electrons = 14

Electronic configuration : $KK \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$

$$\text{Bond order} = \frac{1}{2}(10 - 4) = 3$$

There is a triple bond. Bond energy is high (946 kJ mol^{-1}). Bond length is small. (110 pm). It is diamagnetic.



7. Oxygen molecule, O_2

Number of electrons = 16

Electronic configuration : $KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{1}{2}(10 - 6) = 2$$

There is a double bond in oxygen molecule. It has a short strong bond. It is to be specially noted that the molecule contains two unpaired electrons and therefore paramagnetic. According to VBT, O_2 molecule has only paired electrons and should be diamagnetic. Actually O_2 is paramagnetic. This was one of the earliest triumphs of MOT over VBT. Bond length = 121 pm.

Bond energy = 493 kJ mol⁻¹.

8. Super oxide ion (O_2^-)

O_2^- ion is formed by the combination of an oxygen atom with an oxygen ion O^- . There are 13 electrons in the molecular orbital of O_2^- , exclusive of the K shell.

$$O_2^- = KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^1$$

$$\text{Bond order} = \frac{1}{2}(10 - 7) = 1\frac{1}{2}$$

There is one unpaired electron and O_2^- is paramagnetic.

Properties of O_2 , N_2 and their ions related with bond order

Species	Bond order	Unpaired Electrons	Magnetic Property	Variation of Characteristic Properties
O_2	2	2	Paramagnetic	Bond length: $O_2 < O_2^- < O_2^{2-}$
O_2^-	1.5	1	Paramagnetic	Bond strength: $O_2 > O_2^- > O_2^{2-}$
O_2^{2-}	1	0	Diamagnetic	Magnetic moment: $O_2 > O_2^- > O_2^{2-}$
N_2	3	0	Diamagnetic	Bond length: $N_2 < N_2^+$
N_2^+	2.5	1	Paramagnetic	Bond strength: $N_2 > N_2^+$ Magnetic moment: $N_2 < N_2^+$

9. Fluorine molecule, F_2

No. of electrons = 18

$$\text{Electronic configuration} = KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$\text{Bond order} = \frac{1}{2}(10 - 8) = 1$$

10. Neon molecule, Ne_2

No. of electrons = 20

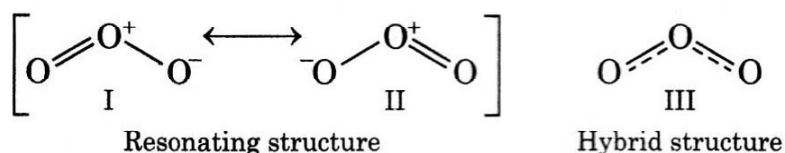
$$\text{Electronic configuration} = KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^2 \sigma^* 2p_z^2$$

$$\text{Bond order} = \frac{1}{2}(10 - 10) = 0$$

Since bond order is zero, molecule cannot exist. Ne exists as monoatomic molecule.

RESONANCE STRUCTURES

When a molecule can be represented by more than one Lewis formula, none of which is able to describe the molecule accurately, then the actual structure is a resonance hybrid of the various Lewis formulae (canonical forms). For example, ozone can be represented by two Lewis structures:



In structures I and II, the O = O bond length (121 pm) should be smaller than O – O (148 pm) bond length. But experiments have shown that both bonds are of equal length, 126 pm, which is intermediate between that of single and double bonds.

The actual structure of ozone is intermediate between structures I and II and is called a resonance hybrid. Structures I and II are called resonating structures, contributing structures or canonical forms.

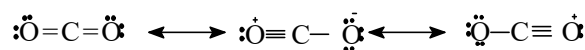
The resonance between canonical forms can be represented by a double headed arrow (\longleftrightarrow). Although it is not possible to draw the Lewis structure for the resonance hybrid, some idea can be drawn from the structure shown below, in which each oxygen-oxygen bond is intermediate between single and double bonds. The actual structure does not oscillate between the resonating forms and has its identity.

Rules for writing resonating structures

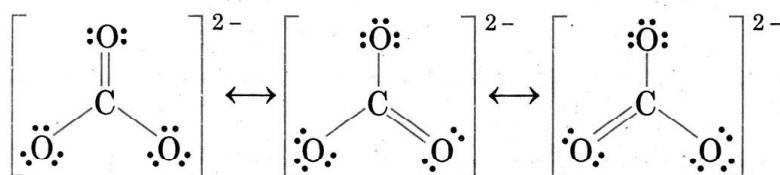
1. The contributing structures should have same arrangement of atoms. They should differ only in electronic arrangements.
2. The contributing structures should have same number of paired and unpaired electrons.
3. The contributing structures should have nearly same energy.
4. Contributing structures should be so written that negative charge (if appears) is on electronegative element and positive charge is on electropositive element.
5. In contributing structures, like charges should not reside on adjacent atoms.

RESONATING STRUCTURES OF SOME SPECIES

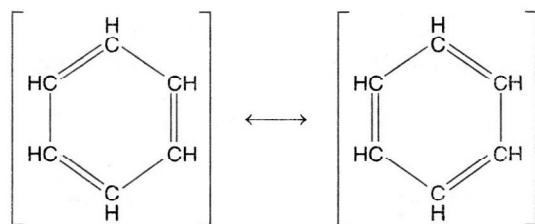
i) Carbon dioxide molecule (CO_2)



ii) Carbonate ion (CO_3^{2-})



iii) Benzene molecule (C_6H_6)

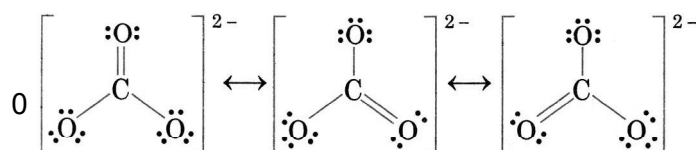


CHARACTERISTICS OF RESONANCE

1. Resonating structures are hypothetical and do not have real existence.
2. The actual molecule has a single structure which is a resonance hybrid of various canonical forms and as such it cannot be depicted by a single Lewis structure.
3. Bond lengths in hybrid structures are intermediate between the bond lengths in various resonating forms, e.g. C–C bond length in benzene molecule is 139 pm which is intermediate between C–C (154 pm) and C = C (134 pm).
4. Resonance hybrid is more stable, i.e., having lower energy than any of the resonating forms.
5. Canonical structures of similar energy contribute equally to the resonance hybrid. However, the structure with higher energy is less stable and makes lesser contribution to the resonance hybrid.
6. The difference in energy between the resonance hybrid and the most stable resonating form is called **resonance energy**.
7. Larger the value of resonance energy, greater will be the stability of the resonance hybrid.
8. Bond order of a particular bond in a molecule can be calculated from the resonating structure using the following formula:

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all resonating forms}}{\text{Total number of resonating forms}}$$

For calculating C–O bond order in CO_3^{2-} ion., let us consider bonds of C atom with a particular O atom in all the three resonating structures.



There is 1 bond in structure I, 1 bond in structure II and 2 bonds (double bond) in structure III. Thus

$$\text{C – O bond order} = \frac{1+1+2}{3} = 1.33.$$

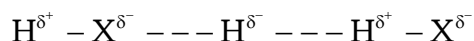
HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below:

$\text{---H}^{\delta+} - \text{F}^{\delta-} \text{---} \text{H}^{\delta+} - \text{H}^{\delta-} \text{---} \text{H}^{\delta+} - \text{F}^{\delta-}$. Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

Cause of formation of Hydrogen bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while 'X' attains fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as:

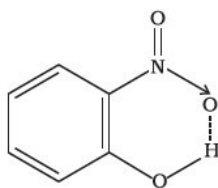


The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

Types of H-Bonds : There are two types of H-bonds

- i) Intermolecular hydrogen bond
- ii) Intramolecular hydrogen bond

1. **Intermolecular hydrogen bond** : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.
2. **Intramolecular hydrogen bond** : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.



Intramolecular hydrogen bonding in o-nitrophenol molecule.

Applications

1. To predict the boiling point of some compounds - hydrogen bonding increases the boiling point.
2. To predict the physical state of some compounds - H_2O is liquid while H_2S is gas.
3. To predict the existence of some compounds - KHF_2 exist but KHX_2 ($\text{X} = \text{Cl}, \text{Br}$ and I) does not.
4. Intermolecular hydrogen bonding decreases the volatility and increases viscosity and surface tension.
5. Intermolecular hydrogen bonding in ice gives it an open cage like structure. As a result ice has lower density than liquid H_2O .
6. Due to hydrogen bonding ethanol has higher boiling point than diethylether.