

Inorganic Chemistry

M.S.C. / First Semester

(4) Lecturer

2020-2021

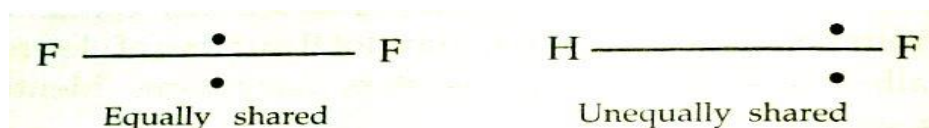
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Polarity of Covalent Bond:-

In all homonuclear diatomic molecules like hydrogen molecule (H_2), chlorine molecule (Cl_2), fluorine molecule (F_2) oxygen molecule (O_2), the electron pair or pairs is shared equally between the two atoms. This means that shared electrons are equally attracted to both the nuclei and therefore spend equal amounts of time near each nucleus. As a result. the molecule is neutral or non-polar.

When the heteronuclear diatomic molecule is considered the situation is not simple. **Electronegativity is defined as the tendency of an atom to attract electrons towards itself in a chemical bond.** Thus, in heteronuclear diatomic molecule, both the atoms joined by the covalent bond possess different electronegativity. As a result, the atom having higher value of electronegativity attracts the shared electron pair much more strongly than the other atom. For example, in HF the electron pair is more attracted towards F as it is more electronegative than hydrogen. Due to this, the fluorine end of the molecule appears negative and the hydrogen end positive. Such molecules having two oppositely charged poles are called polar molecules and the bond is said to be a polar covalent bond.



A covalent bond, in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond or a covalent bond between two dissimilar atoms is a polar covalent bond.

Two kinds of notation are used to indicate a polar covalent bond.



Polar covalent bonds may be thought of as being intermediate between the non-polar bonds and ionic and Bond polarity is described in terms of ionic character bonds.

Bond polarity is described in terms of ionic character which usually increases with increasing difference in the electronegativity (EN) between bonded atoms.

	H—F	H—Cl	H—Br	H—I
EN	2.1 4.0	2.1 3.0	2.1 2.8	2.1 2.5
Difference in EN	1.9	0.9	0.7	0.4

Ionic character decreases as the difference in electronegativity decreases

Pauling has estimated the approximate percentage of ionic character in various A-B covalent bonds from the $(X_A - X_B)$ values, i.e., electronegativity difference of the two atoms forming the covalent bond.

$X_A - X_B$	Percentage of ionic character	Nature of A—B bond
0	0	Purely covalent
0.1 to 0.8	0.5 – 15	Covalent
0.9 to 1.8	19 – 47	Polar covalent
1.9	50	50% ionic and 50% covalent
2 to 3.2	55–93	Ionic

Hanny and Smyth gave the following equation for calculating the percentage of ionic character in A-B bond on the basis of the values of electronegativity of the atoms A and B.

$$\text{Percentage of ionic character} = [16(X_A - X_B) + 3.5(X_A - X_B)^2]$$

This equation gives approximate calculation of percentage of ionic character, eg, 50% ionic character corresponds to $(X_A - X_B)$ equal to 2.1.

Example . Calculate the percentage of ionic character in Cs-Cl bond in CsCl molecule. The electronegativity values of Cs and Cl are 0.7 and 3.0 respectively.

Solution : $X_A - X_B = X_{Cl} - X_{Cs} = (3.0 - 0.7) = 2.3$

Percentage of ionic character in Cs-Cl bond

$$\begin{aligned} &= [16 \times 2.3 + 3.5 \times (2.3)^2] \\ &= [36.8 + 18.51] \\ &= 55.31 \end{aligned}$$

Hydrogen bonding:-

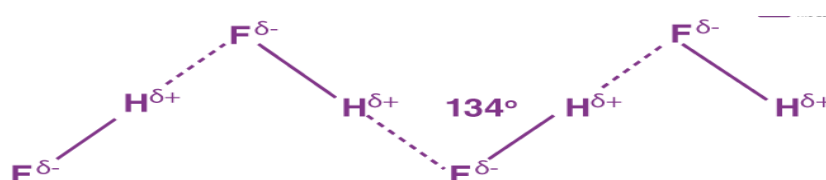
interaction involving a hydrogen atom located between a pair of other atoms having a high affinity for electrons; such a bond is weaker than an ionic bond or covalent bond but stronger than van der Waals forces. Hydrogen bonds can exist between atoms in different molecules or in parts of the same molecule. One atom of the pair (the donor), generally a fluorine, nitrogen, or oxygen atom, is covalently bonded to a hydrogen atom (—FH, —NH, or —OH), whose electrons it shares unequally; its high electron affinity causes the hydrogen to take on a slight positive charge. The other atom of the pair, also typically F, N, or O, has an unshared electron pair, which gives it a slight negative charge. Mainly through electrostatic attraction, the donor atom effectively shares its hydrogen with the acceptor atom, forming a bond. Because of its extensive hydrogen bonding, water (H_2O) is liquid over a far greater range of temperatures that would be expected for a molecule of its size. Water is also a good solvent for ionic compounds and many others because it readily forms hydrogen bonds with the solute. Hydrogen bonding is of two types.

1- Intermolecular hydrogen bonding :- this type of bonding results between the positive and negative ends of different molecules of same or different substances

Examples :-

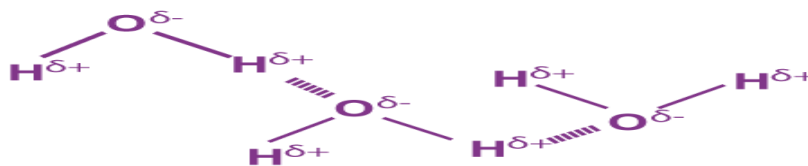
Hydrogen Bonding in Hydrogen fluoride

Fluorine having the highest value of electronegativity forms the strongest hydrogen bond.



Hydrogen Bonding in Water

A water molecule contains a highly electronegative oxygen atom linked to the hydrogen atom. Oxygen atom attracts the shared pair of electrons more and this end of the molecule becomes negative whereas the hydrogen atoms become positive.



Hydrogen Bonding in Ammonia

It contains highly electronegative atom nitrogen linked to hydrogen atoms.

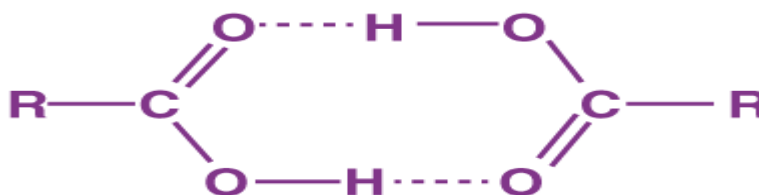


Hydrogen Bonding in Alcohols and Carboxylic acid

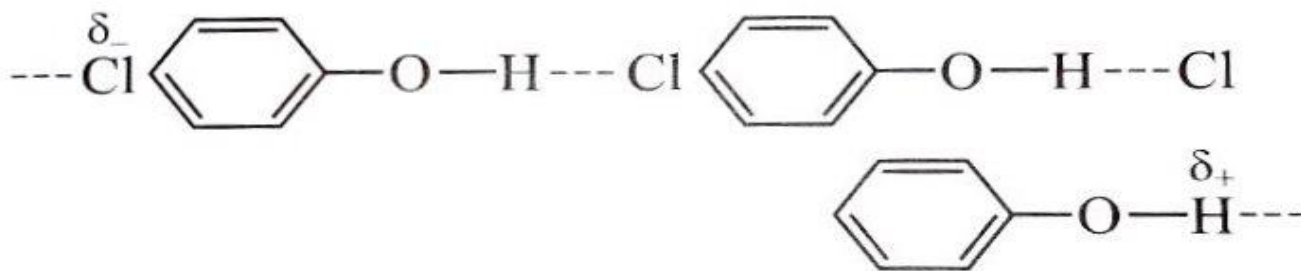
Alcohol is a type of an organic molecule which contains an -OH group. Normally, if any molecule which contains the hydrogen atom is connected to either oxygen or nitrogen directly, then hydrogen bonding is easily formed.



Hydrogen Bonding in Alcohols



Hydrogen Bonding in Carboxylic acid



Hydrogen Bonding in *p*-chlorophenol

This type of hydrogen bonding increases the boiling point of the compound and also its solubility in water. The increase in boiling point is due to association of several molecules of the compound.

Intermolecular hydrogen bond is also responsible for increase in the viscosity. Greater is the extent of hydrogen bonding more is the viscosity.



$$\eta = 1.2 \text{ C.P.}$$

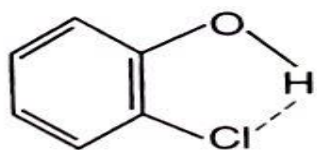


$$\eta = 17 \text{ C.P.}$$

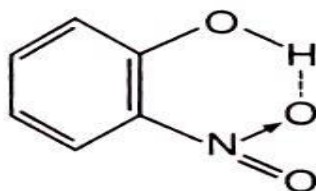


$$\eta = 1070 \text{ C.P.}$$

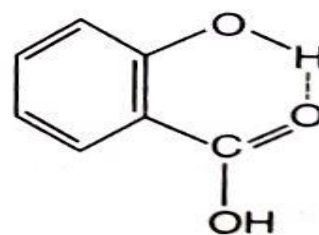
2- Intramolecular hydrogen bonding: This type of bonding results between hydrogen and an electronegative element both present in the same molecule. This type of bonding is generally present in organic compounds. Examples are *o*-chlorophenol, *o*-nitrophenol, *o*-hydroxy benzoic acid, etc.



o-Chlorophenol



o-Nitrophenol



o-Hydroxy benzoic acid

This type of bonding decreases the boiling point of the compound. The solubility of the compound also decreases.

Nature of Hydrogen Bond

- (i) Hydrogen bond is merely an electrostatic force rather than a chemical bond.
- (ii) Hydrogen bond never involves more than two atoms.
- (iii) Bond energy of hydrogen bond is in the range of 3 to 10 kcal/mole (10 to 40 kJ per mole), i.e., about 1/10 the energy of a covalent bond (strength 50-100 kcal/ mol).
- (iv) With the increase of electronegativity and decrease in size of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases. It is evident from the energies of hydrogen bonds in the three elements.



$$10 \text{ kcal mol} \quad 7 \text{ kcal mol} \quad 2 \text{ kcal mol}$$

- (v) All the three atoms in X-H--- X lie in the straight line.

MODERN CONCEPT OF COVALENT BOND

The Lewis or octet concept does not explain the following points:

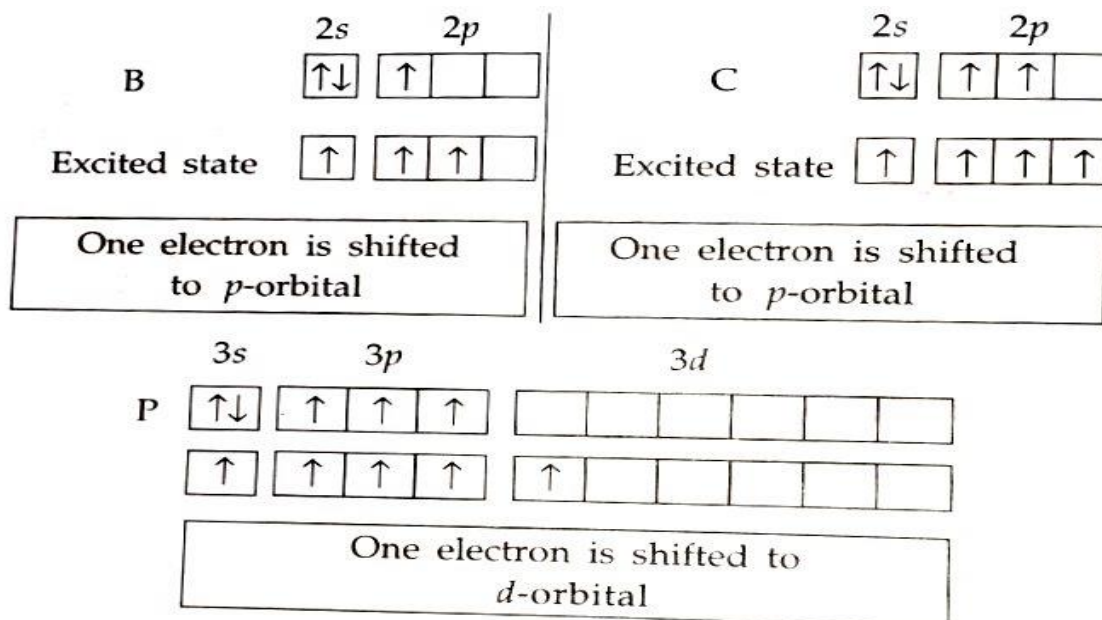
- (i) The cause of covalent bond formation.
- (ii) Nature of the forces operating between the atoms forming a covalent bond.
- (iii) Why different amounts of energies released during the formation of different molecules.
- (iv) Shape and geometry of molecules.
- (v) Why the molecules are stable in which central atoms have either less than 8 electrons or more than 8 electrons in the outermost shell.

To explain the above limitation, the following two theories based on quantum mechanics have been proposed

- (a) The valence bond theory and
- (b) Molecular orbital theory.

The valence bond theory: by Heitler and London, in 1927, to explain how a covalent bond is formed. This theory was extended by Pauling and Slater, in 1931. The main points of the theory are:

- (i) A covalent bond is formed by overlapping of atomic orbitals of valency shell of the two atoms.
- (ii) Only half filled atomic orbitals, i.e., orbitals singly occupied can enter into overlapping process. The resulting bond acquires a pair of electrons with opposite spins.
- (iii) The atoms with half filled orbitals must come closer to one another with their axes in proper directions for overlapping.
- (iv) As a result of overlapping, there is maximum electron density somewhere between the two atoms. A large part of bonding force comes into existence from the electrostatic attraction between the nuclei and the accumulated electron cloud between them.
- (v) Greater the overlapping, higher is the strength of the chemical bond. The amount of energy released per mole during overlapping is termed bond energy. This energy stabilises the system. Hence, the molecule formed has less energy and consequently more stability than the isolated atoms.
- (vi) Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell (valency shell). This point explains the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus, hexavalency of sulphur and heptavalency of halogens (Cl, Br, I) inspite of the fact that these atoms have paired orbital or orbitals in the valency shell.



(vii) Between two orbitals of the same stability (i.e., having same energy) one more directionally concentrated would form a stronger bond. **Dumb-bell shaped p-orbitals will form stronger bond as compared to spherically symmetrical s-orbital.** It is formed by head on or axial overlap.

(viii) Two types of bonds are formed on account of overlapping. These are (1) Sigma (σ) and (2) Pi (π) bonds.

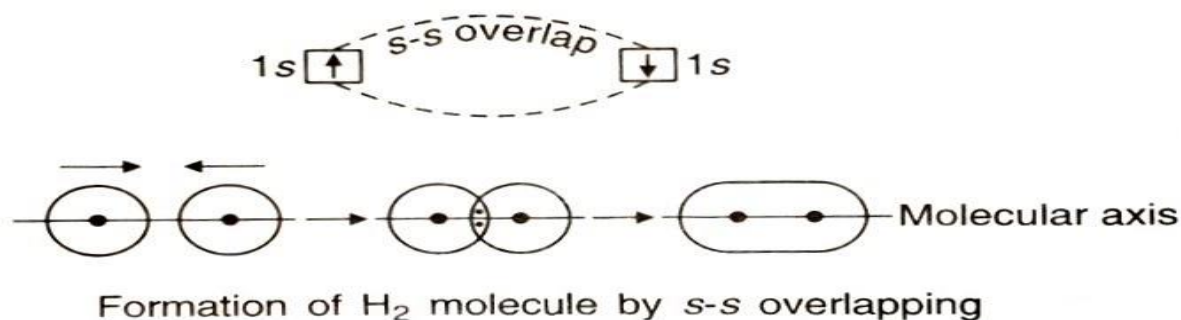
(1) Sigma (σ) Bond

A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma (σ) bond. In such a bond formation, maximum overlap is possible between electron clouds and hence, it is a strong bond. Electron cloud of this bond is symmetrical about the line joining the two nuclei of the two atoms. Sigma bond can, thus, be defined as: "**Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond.**" It is formed by head on or axial overlap.

Sigma bonds are formed by three types of overlapping:

(i) s-s overlapping (Formation of hydrogen molecule):

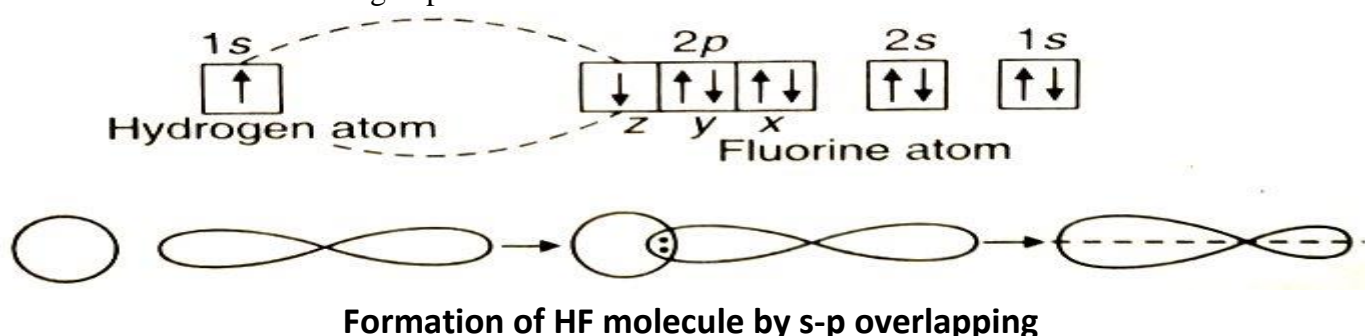
Each hydrogen atom has one electron in 1s-orbital which is spherical. 1s-orbital of both the hydrogen atoms approach each other closely and when they reach a point of maximum attraction by the two nuclei, they overlap and form a sigma bond.



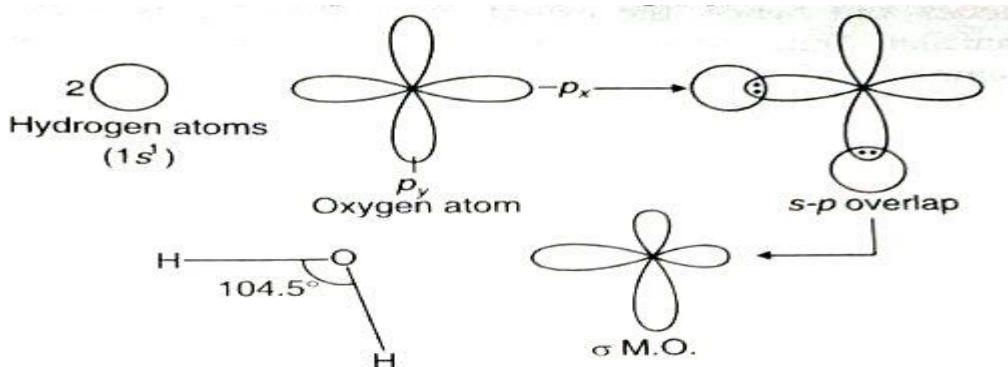
The bond has two electrons which have opposite spins. The probability of finding these electrons is maximum in the region between the two nuclei on the molecular axis. The electron density of the bond is distributed symmetrically about the molecular axis

(ii) s-p overlapping (Formation of HF, H₂O, NH₃ molecules) :

(a) Formation of HF molecule : In the formation of HF molecule the 1s-orbital of hydrogen overlaps with the p-orbital of fluorine containing unpaired electron.



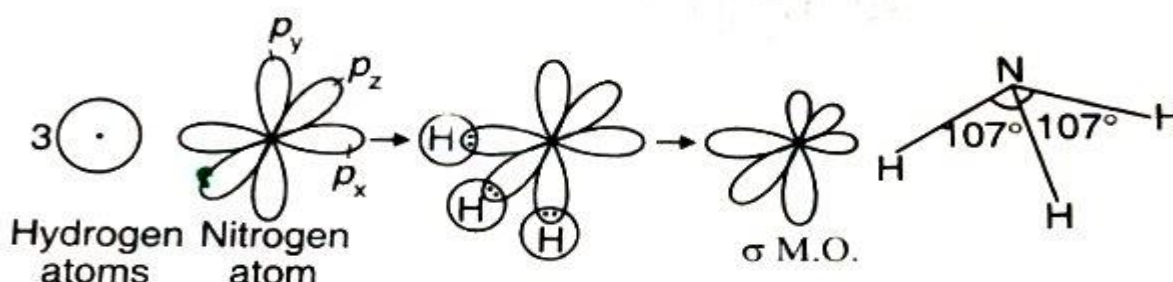
(b) Formation of water molecule: Oxygen atom has the configuration of valency shell $1s^2 2p_x^2, 2p_y^1 p_z^1$, i.e., it has two orbitals singly occupied. These two orbitals overlap with 1s orbital of two hydrogen atoms forming sigma bonds.



Formation of water molecule by S-p overlapping

Since the two orbitals of oxygen are at right angle to each other an angle of 90° is expected between two sigma bonds but actual bond angle observed is 104.5° .

(c) Formation of ammonia molecule: Nitrogen atom has the configuration of valency shell $2s^2 2p_x^1 2p_y^1 2p_z^1$, i.e., three singly occupied orbitals are present. These orbitals overlap with 1s-orbitals of three hydrogen atoms forming three sigma bonds.

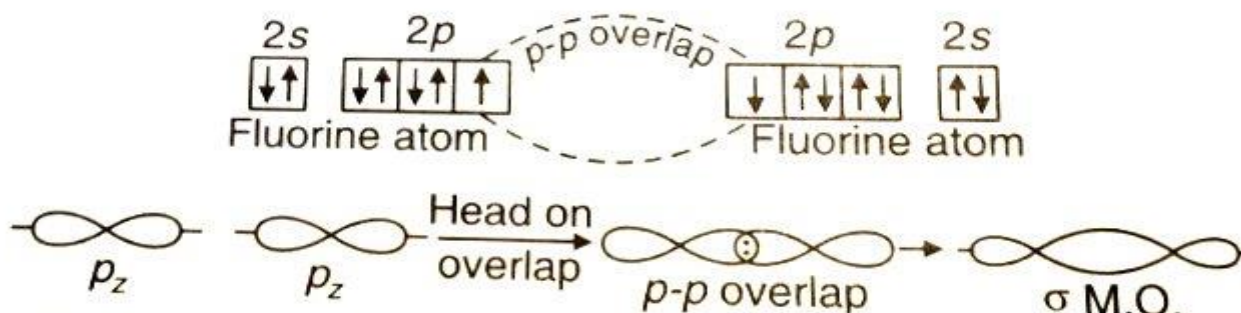


Formation of NH_3 molecule by s-p overlapping

Since the three orbitals of nitrogen are at right angle to each other, the expected angle between two sigma bonds should be 90° but actual bond angle observed is 107° .

(iii) p-p overlapping (Formation of fluorine molecule):

This is illustrated by the formation of fluorine molecule. The electronic configuration of fluorine atom is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$, i.e., one orbital is singly occupied. When p-orbitals of two fluorine atoms approach each other with their heads directly towards one another, they overlap and form a sigma bond.

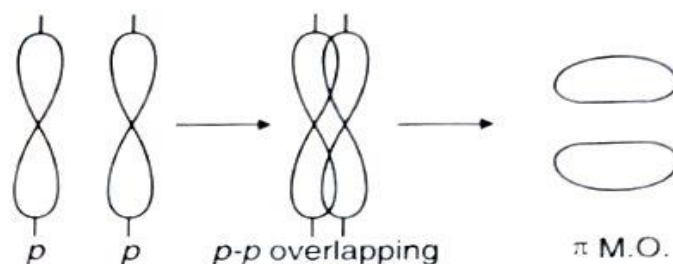


Formation of F_2 molecule by p-p overlapping

(2) Pi (π) Bond

π -bonds are formed by the sidewise or lateral overlapping of p-orbitals. The overlapping takes place at the side of two lobes and hence, the extent of overlapping is relatively smaller. Thus, π -bond is a weaker bond in

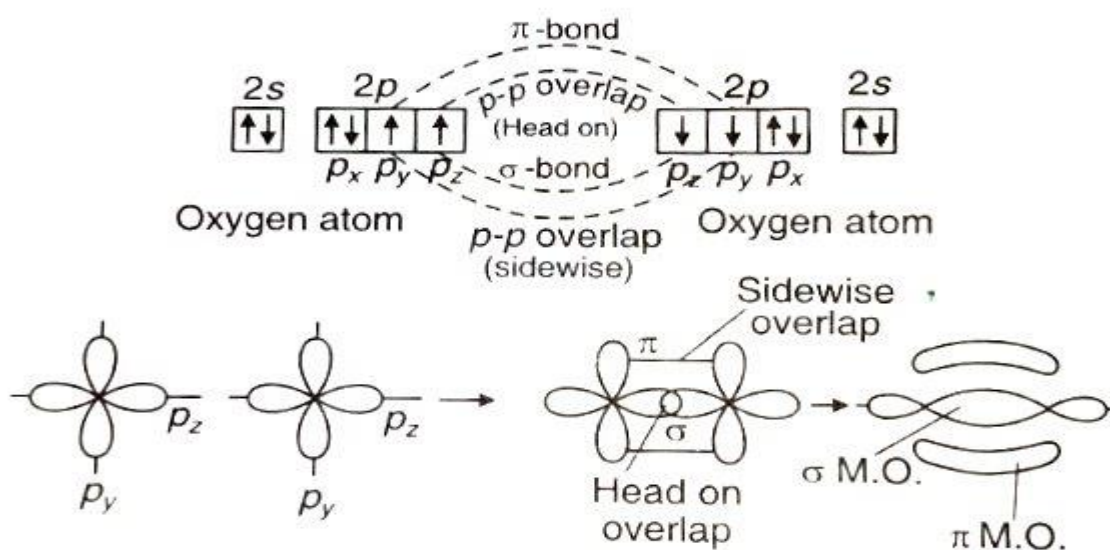
comparison to sigma bond. The molecular orbital is oriented above and below the plane containing nuclear axis.



Formation of π -bond

Formation of oxygen molecule :

Oxygen atom has two p -orbitals singly occupied in the valency shell. When two oxygen atoms approach each other, one set of p -orbitals experiences head on overlap forming a sigma bond while other set of p -orbitals overlaps sidewise to form a π -bond. Thus, oxygen molecule has one σ - and one π -bond.



Formation of O₂ molecule

Similarly, the formation of nitrogen molecule can be explained. It has one σ -bond and two π -bonds.

COMPARISON OF SIGMA (σ) AND PI (π) BOND

Sigma bond	Pi bond
1. The bond is formed by the overlap of orbitals along their axes (end to end overlap). It includes $s-s$, $s-p$ and $p-p$ overlapping.	The bond is formed by sidewise overlapping of orbitals (lateral overlapping). It includes $p-p$ overlapping.
2. It is a strong bond.	It is a weak bond.
3. Electron cloud is symmetrical about the line joining the two nuclei.	Electron cloud is unsymmetrical.
4. There can be free rotation of atoms around this bond.	Free rotation is not possible around this bond.
5. These are less reactive.	These are more reactive.
6. The shape of the molecule is determined by these bonds.	These bonds do not affect the shape of the molecule.
7. σ -electrons are referred as localized.	π -electrons are referred as mobile electrons.
8. σ -bond can have independent existence.	π -bond always exists along with a σ -bond.

All single bonds are sigma bonds. A double bond consists of one sigma and one pi-bond while a triple bond consists of one sigma and two pi-bonds.

(i) Bond energy increases from a single bond to a triple bond.

Bond energy : Single bond < Double bond < Triple bond

(ii) Bond strength increases from a single bond to a triple bond.

Bond strength: Single bond < Double bond < Triple bond

(iii) Bond length of a multiple bond (double or triple) is always shorter than the corresponding single bond.

Bond length : Single bond > Double bond > Triple bond

(iv) Reactivity of a multiple bond is always more than the single bond. This is due to the fact that π -electrons are mobile in nature.

Reactivity : Single bond < Double bond < Triple bond.