CHEMICAL BONDING AND MOLECULAR STRUCTURE

VALENCE BOND THEORY

VALENCE BOND THEORY

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 limitations 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: This theory was presented by Hitler 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.

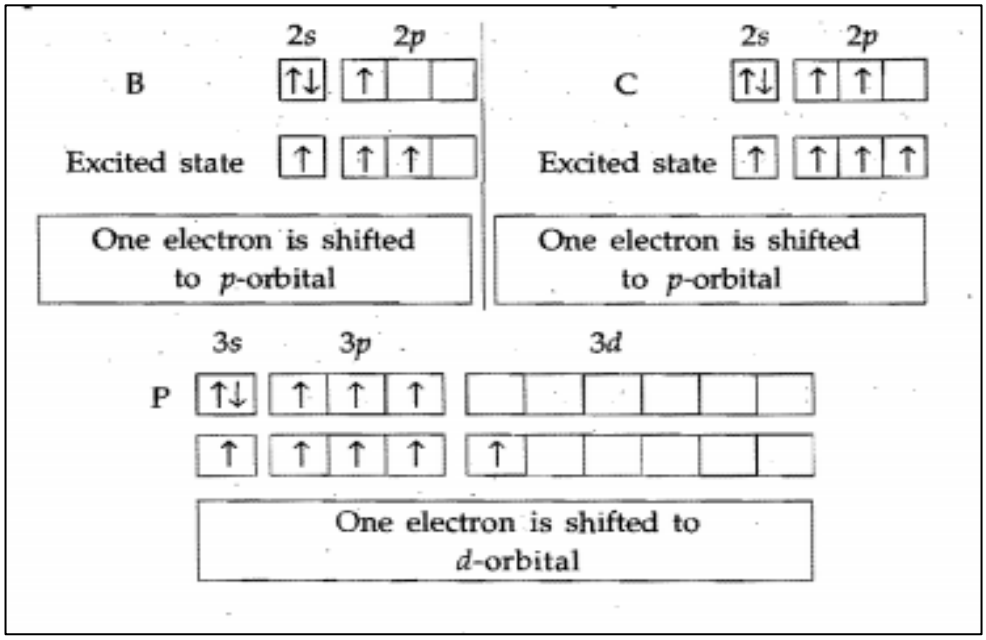
(iii) The atoms with half-filled orbitals must come closer to one another with their axes in proper directions for overlapping.

(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 stabilizes 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 trivialness of boron, tetravalency of carbon, Penta valency of phosphorus, hex valency of sulphur and heat a valency of halogens (CI, Br, I) inspire 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 (a) Sigma (σ) and (b) Pi (π) bonds.

(a) 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 Is-orbital which is spherical. Is-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.

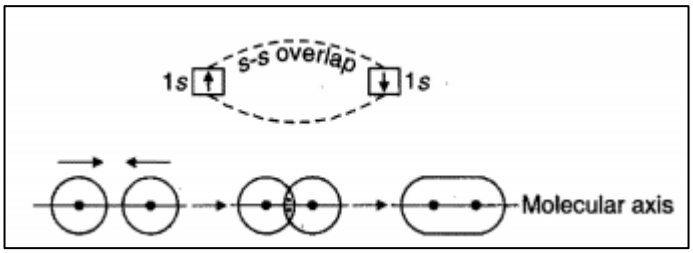


Fig: formation of H2 molecule by s-s **overlapping**

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, H20, 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.

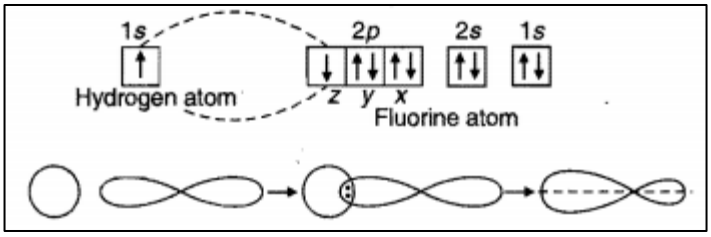


Fig: formation of HF molecule by s-p overlapping

(b) Formation of water molecule: Oxygen atom has the configuration of valency shell Is2 2pz2 ply Axl, i.e., it has two orbitals singly occupied. These two orbitals overlap with 1s-orbital of two hydrogen atoms forming sigma bonds.

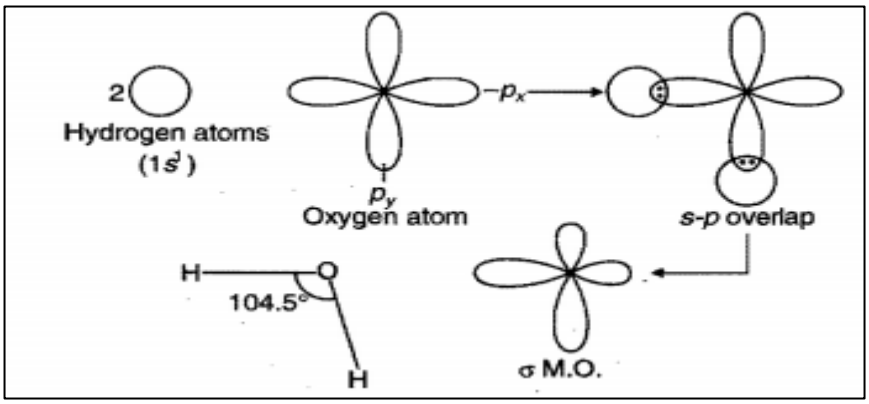


Fig: formation of water molecule by s-p overlapping

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 shell2s2 2Pxl 2py1 2pzl, i.e., three singly occupied orbitals are present. These orbitals overlap with Is-orbitals of three hydrogen atoms forming three sigma bonds.

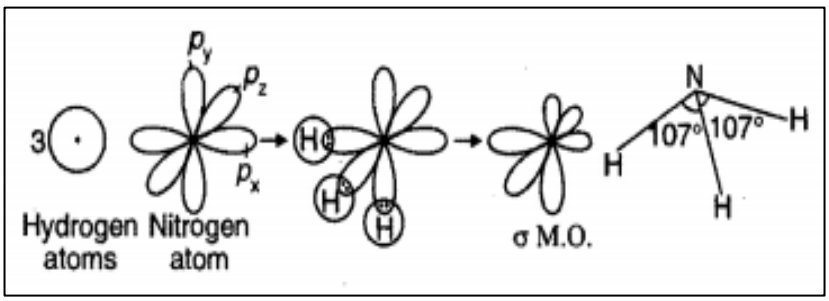


Fig: formation of NHs molecule by s-p overlapping

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 1; 2s22pi 2pl 2pz*l,* 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.