Quantum theory (Modern theory) of covalent bond and overlapping.

(1) A modern Approach for covalent bond (Valence bond theory or VBT)

(i) Heitler and London concept.

(a) To form a covalent bond, two atoms must come close to each other so that orbitals of one overlaps with the other.

(b) Orbitals having unpaired electrons of anti spin overlaps with each other.

(c) After overlapping a new localized bond orbital is formed which has maximum probability of finding electrons.

(d) Covalent bond is formed due to electrostatic attraction between radii and the accumulated electrons cloud and by attraction between spins of anti spin electrons.

(e) Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high.

(ii) Pauling and slater extension

(a) The extent of overlapping depends upon: Nature of orbitals involved in overlapping, and nature of overlapping.

(b) More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high.

(c) Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy : $2s-2s < 2s-2p < 2p-2p$

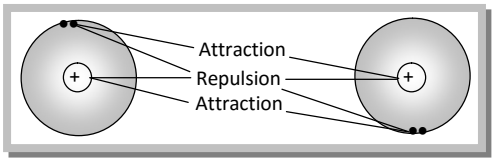
(d) s -orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, p -orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping.

(iii) Energy concept

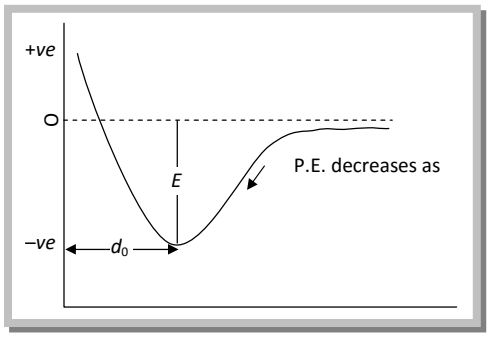
(a) Atoms combine with each other to minimize their energy.

(b) Let us take the example of hydrogen molecule in which the bond between two hydrogen atoms is quite strong.

(c) During the formation of hydrogen molecule, when two hydrogen atoms approach each other, two types of interaction become operative as shown in figure. The force of attraction between the molecules of one atom and electrons of the other atom. The force of repulsion between the nuclei of reacting atoms and electrons of the reacting atoms



(d) As the two hydrogen atoms approach each other from the infinite distance, they start interacting with each other when the magnitude of attractive forces is more than that of repulsive forces a bond is developed between two atoms.



(e) The decrease in potential energy taking place during formation of hydrogen molecule may be shown graphically (→)

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(f) The inter nuclear distance at the point O have minimum energy or maximum stability is called bond length.

(g) The amount of energy released (i.e., decrease in potential energy) is known as enthalpy of formation.

(h) From the curve it is apparent that greater the decrease in potential energy, stronger will be the bond formed and vice versa.

(i) It is to be noted that for dissociation of hydrogen molecule into atoms, equivalent amount of energy is to be supplied.

(j) Obviously in general, a stronger bond will require greater amount of energy for the separation of atoms. The energy required to cleave one mole of bonds of the same kind is known as the bond energy or bond dissociation energy. This is also called as orbital overlap concept of covalent bond.

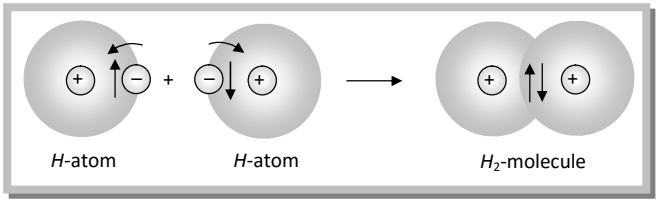
(2) Overlapping

(i) According to this concept a covalent bond is formed by the partial overlapping of two half filled atomic orbitals containing one electron each with opposite spins then they merge to form a new orbital known as molecular orbital.

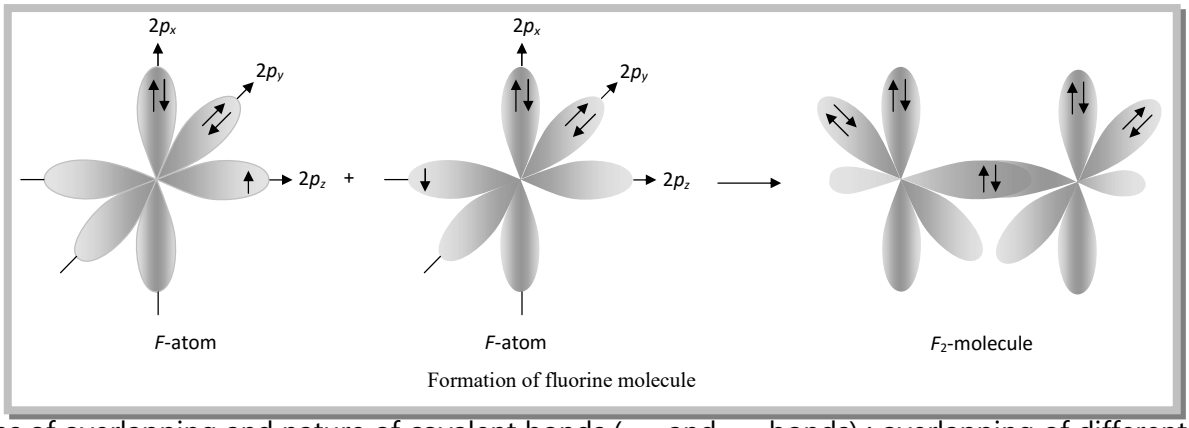
(ii) These two electrons have greater probability of their presence in the region of overlap and thus get stabilised i.e., during overlapping energy is released.

Examples of overlapping are given below :

Formation of hydrogen molecule : Two hydrogen atoms having electrons with opposite spins come close to each other, their s-orbitals overlap with each other resulting in the union of two atoms to form a molecule.



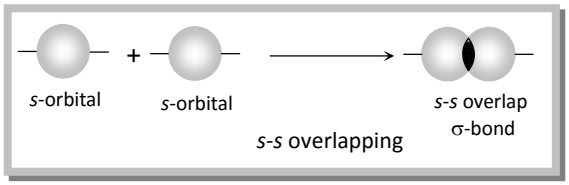
Formation of fluorine molecule : In the formation of F_2 molecule p-orbitals of each flourine atom having electrons with opposite spins come close to each other, overlapping take place resulting is the union of two atoms.



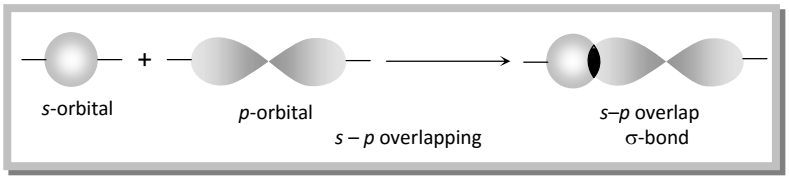
Formation of fluorine molecule

Types of overlapping and nature of covalent bonds (σ - and π - bonds) : overlapping of different type gives sigma (σ) and pi (π) bond. Various modes of overlapping given below :

s – s overlapping : In this type two half filled s-orbitals overlap along the internuclear axis to form σ-bond.



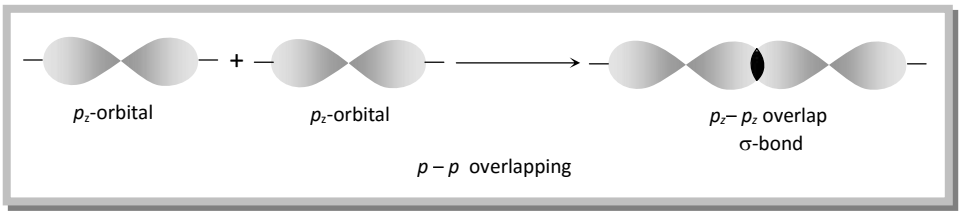
s-p overlapping : It involves the overlapping of half filled s-orbital of one atom with the half filled p-orbital of other atom This overlapping again gives σ-bond e.g., formation of H – F molecule involves the overlapping of 1s orbital of H with the half filled 2pz – orbital of Fluorine.



p-p overlapping : p-p overlapping can take place in the following two ways.

(i) When there is the coaxial overlapping between p-orbitals of one atom with the p-orbitals of the other then σ-bond formation take place e.g., formation of F2 molecule in which 2pz orbital

of one F atom overlap coaxially with the 2pz orbitals of second atom. σ-bond formation take place as shown below :



(ii) When p–orbitals involved in overlapping are parallel and perpendicular to the internuclear axis. This types of overlapping results in formation of pi bond. It is always accompanied by a σ bond and consists of two charge clouds i.e., above and below the plane of sigma bond. Since overlapping takes place on both sides of the internuclear axis, free rotation of atoms around a pi bond is not possible.

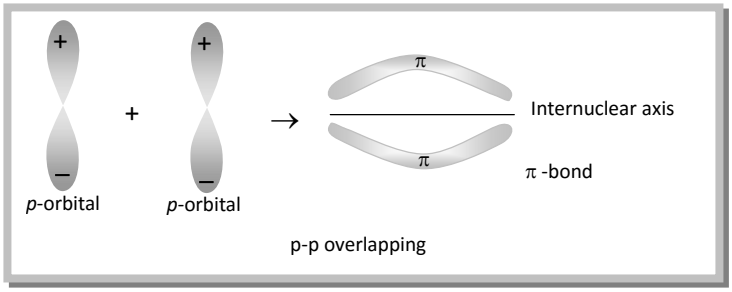


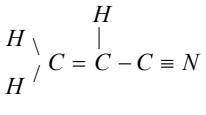
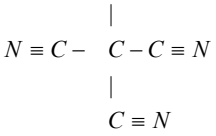
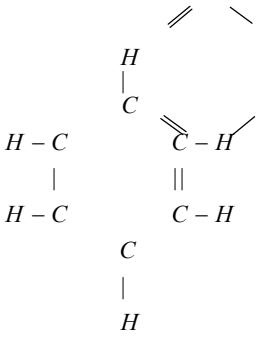
Table : Difference in σ and π bonds

Sigma (σ) bond	Pi (π) bond
It results from the end to end overlapping of two s-orbitals or two p-orbitals or one s and one p-orbital.	It result from the sidewise (lateral) overlapping of two p-orbitals.
Stronger	Less strong
Bond energy 80 kcals	Bond energy 65 kcals
More stable	Less stable
Less reactive	More reactive
Can exist independently	Always exist along with a σ-bond

The electron cloud is symmetrical about the internuclear axis.	The electron cloud is above and below the plane of internuclear axis.

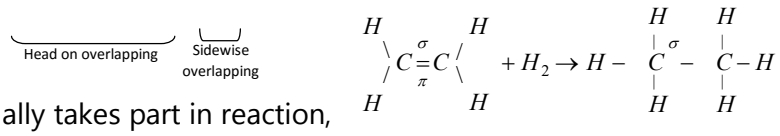
Important Tips

☞ To count the σ and π bonds in molecule having single, double and triple bond first we write its expanded structure.

ex. $\overset{\sigma}{H-H}$, $\underset{\pi}{\overset{\sigma}{O=O}}$, $\underset{2\pi}{\overset{\sigma}{N\equiv N}}$,  $(3\pi,6\sigma)$,  $(8\pi,8\sigma)$,  $(3\pi,12\sigma)$

All the single bonds are σ-bond. In a double bond, one will be σ and the other π type while in a triple bond, one will be σ and other two π.

The enolic form of acetone has 9σ, 1π and two lone pairs (enol form of acetone)



It is the π bond that actually takes part in reaction, but the shape of molecule is decided by σ-bond.

The number of sp2-s sigma bonds in benzene are 6.

When two atoms of the element having same spin of electron approach for bonding, the orbital overlapping and bonding both does not occur.

Head on overlapping is more stronger than lateral, or sidewise overlapping.

p-p > s-p > s-s > p-p