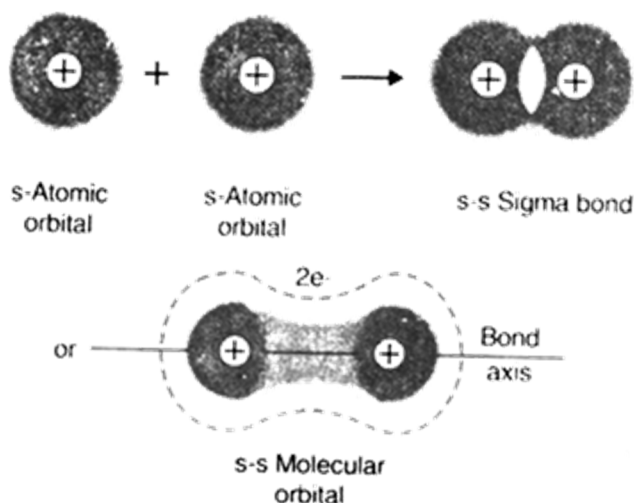


## Valence Bond Theory (VBT) of Covalent Bond

In order to explain how a covalent bond is formed **Heitler and London** in **1927** put forward a theory which is called *Valence Bond Theory (VBT)* or Atomic Postulate's of VBT. According to this theory;

- (i) An atomic orbital of the outermost shell of an atom containing one electron has a tendency to overlap with another atomic orbital of another atom containing one electron of opposite spin. This type of overlap 'gives rise to the formation' of a bond which is called *covalent bond*.



Thus;

According to atomic orbital theory a covalent bond between two atoms results by the *overlap of half-filled atomic orbitals* belonging to the outermost shell of these two atoms.

OR

The bond formed by the *overlap of two atomic orbitals* belonging to the outermost shell of two atoms and containing *two electrons of opposite spin* is called a covalent bond.

- (ii) The overlap of two atomic orbitals gives rise to a single *bond orbital* which is a *localized orbital* and is occupied by both the electrons.
- (iii) The two electrons that occupy the bond orbital have opposite spins.

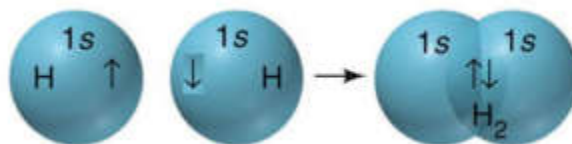
- (iv) Each electron occupies the entire bond orbital and hence may be considered to belong to both the atomic orbitals, *i.e.*, the electron pair present in the bond orbital now belongs to each of the two atomic orbitals.
- (v) As a result of overlapping there is maximum electron density somewhere between the two atoms.

***A large part of the bonding force of covalent bond results from the electrostatic attraction between the nuclei and the accumulated electron clouds between them.***

### **Extension of VB Theory**

The above theory was extended by *Pauling* and *Slater* in 1931. According to the extension of this theory;

- (i) The overlapping of orbitals involves a release of energy and hence the molecule formed has less energy and consequently is more stable than the isolated atoms. This implies that the formation of a covalent bond is always accompanied by the evolution of energy. The energy released as a result of overlapping of orbitals stabilizes the system. *The amount of energy released per mole at the time of overlapping of orbitals to form the covalent bond is termed as bond energy or stabilization energy. This means that this much energy is required to separate the atoms in a molecule, i.e. to break the bond.* The energy required to break the bond in the molecule is called *bond dissociation energy*. The overlapping of atomic orbitals stops at a point where the atomic nuclei of both the atoms have come close enough to exercise a repulsive force on each other. Here the force of repulsion exactly balances the force of merger or attraction. ***The equilibrium distance at which the two atomic nuclei are now held is called bond length.***
- (ii) Overlapping takes place only between those *valence-shell orbitals* which *have unpaired electrons*. The orbitals containing *paired electrons do not participate in overlapping process* and hence do not contribute to bond formation (figure 1).



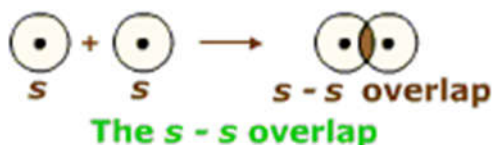
**Figure 1:** Overlap between valence shell/half filled shells (unpaired electrons)

- (iii) Between the two orbitals of the same energy or stability, the orbital which is non-spherical (e.g. dumb-bell shaped p-orbital) forms stronger bonds than that which is *spherically symmetrical* (e.g. s-orbital).
- (iv) A spherically symmetrical orbital does not show any preference in direction whereas the non-spherical orbitals tend to form a bond in the direction of maximum electron density within the orbital, i.e. along their axis.

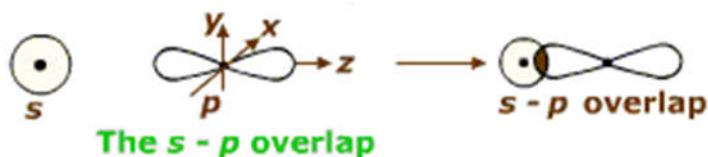
### Types of Overlap of Atomic Orbitals

Covalent bond between two atoms results by the following three types of overlap of atomic orbitals;

- (i) **s-s overlap.** In this type of overlap half-filled s-orbital of one atom overlaps with the half filled s-orbital of the other atom.

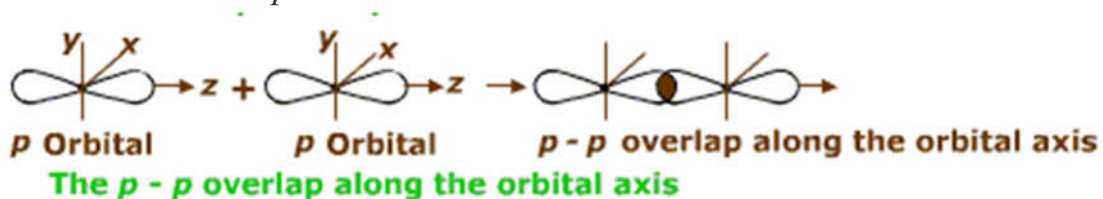


- (ii) **s-p overlap.** Here half-filled s-orbital of one atom overlaps with the half-filled p-orbital of the other atom.

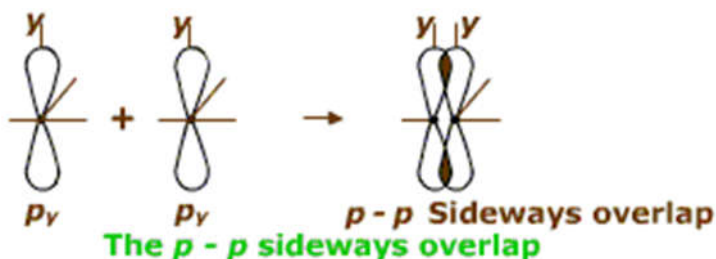


- (iii) **p-p overlap.** Here singly-filled p-orbital of one atom overlaps with the half-filled p-orbital of the other atom. Due to different spatial disposition of the p-orbital along the three Cartesian coordinate axis the two p-orbitals may overlap in any of the following two ways.

- (iv) ***p-p head-to-head overlap.*** This is also called head-on or end-on or end-to-end or linear overlap. Here the overlap of the two p-orbitals takes place along the line joining the nuclei of two atoms (called nuclear axis, bond axis or molecular axis) [Fig. 8.7 (c)]. Hence the name linear overlap.



- (v) ***p-p side-to-side overlap.*** This is also called side-wise or side-way or lateral overlap. Here the overlap of two p-orbitals takes place along a line perpendicular to the molecular axis. [Fig. 8.7 Cd)]. Hence the name lateral overlap.



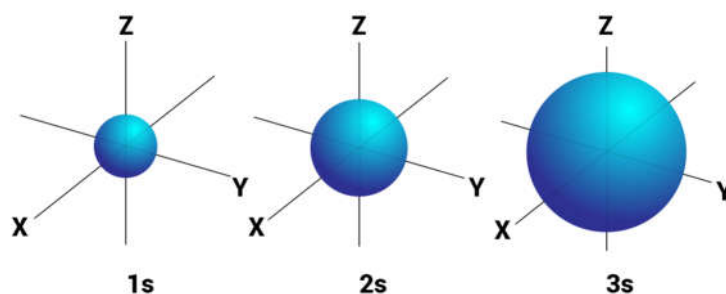
*This means that for this type of overlap the two p-orbitals must be held parallel to each other, i.e. the orbital axis should be parallel.*

### Strength of Covalent Bond-Effectiveness of overlap

The strength of a covalent bond can be predicted from the following general conclusions;

- (i) *In the covalent bond formation, greater the extent of overlapping of orbitals, greater is the energy released, i.e. the higher will be the strength of the covalent bond. This implies that the strength of a covalent bond is proportional to the extent of overlapping between the atomic orbitals and that for a bond to be stronger, greater should be the overlap which in turn shortens the distance between the nuclei. Thus a stronger bond has a shorter bond length.*

- (ii) *Bonding between two s-orbitals is weak particularly when two orbitals are of different energy (e.g. Li and K). Strongest bond between s-orbitals is between two 1s-orbitals of two H-atoms.*
- (iii) *A strong bond is given by the head-to-head overlap of two p-orbitals which are of the same energy. The bond is much weaker, if the orbitals have different principal quantum numbers and bond energy becomes zero as the distance between the two levels increases. For example, C-Br bond in bromobenzene is much weaker than C-F bond in fluorobenzene.*
- (iv) *The side-to-side overlap between two p-orbitals is much less effective and hence gives weak bond.*



**Figure:** Orbitals belonging to different energy levels (orbits)

### Types of Covalent Bond: Sigma ( $\sigma$ ) and Pi ( $\pi$ ) Bonds

Depending on the manner in which the two atomic orbitals overlap with each other, two main types of covalent bond are obtained. These are;

- (i) Sigma bond (also called a single bond) &
- (ii) Pi ( $\pi$ ) bond.

### Sigma ( $\sigma$ ) Bond

#### What is a Bond

A covalent bond which is formed between two atoms by the overlap of their half-filled atomic orbitals along the line joining the nuclei of both the atoms (i.e. along the nuclear axis, bond axis or molecular axis; as it is called) is called a  $\sigma$ -bond. In other words  $\sigma$ -bond is produced by the head-to-head overlap of the half-filled atomic orbitals of the two atoms.

## Characteristics of $\sigma$ -Bond.

$\sigma$ -bond formed as above has the following characteristics;

- (i) *The boundary surface of a-bond takes up an avoid shape.*
- (ii) *The electron cloud of this bond is symmetrical about the bond axis, i.e. the electron density in this bond is distributed symmetrically about the bond axis.*
- (iii) *This bond has two electrons which have opposite spins. Although these two electrons may be present anywhere in the bond, the probability of their finding is' maximum in the region between the two nuclei on the bond axis. Therefore they are attracted equally by the nuclei of both the atoms.*

How this bond is formed between two atoms can be understood by considering the formation of covalent bonds in the molecules like  $H_2$ , HF,  $H_2O$ ,  $NH_3$  and  $F_2$  on the basis of atomic orbital overlap theory of covalent bond described above.

## Molecules with $\sigma$ -Bonds formation

### 1. $H_2$ molecule (*s-s overlap*)

The two H-atoms of which  $H_2$  molecule is composed have  $1s$  orbital each which contains only one electron ( $H \rightarrow 1s^1$ ). These  $1s$  orbitals of both H-atoms approach each other closely and when they reach a point where the attractive forces (between electrons and nuclei) are balanced by the repulsive forces (between electrons and electrons, between the two nuclei), the potential energy becomes minimum, and hence they overlap and give rise to the formation of H-H  $\sigma$  bond. Since  $\sigma$ -bond is produced by the overlap of two s-orbitals, it is also called s-s  $\sigma$ -bond. Thus a  $\sigma$ -bond can be defined as Various steps for the formation of a  $\sigma$ -bond in  $H_2$  molecule are shown in Fig. 1111.

For reasons of space and convenience, a pictorial representation of the formation of a-bond is not always possible. Therefore in actual practice a single horizontal line (—) between the two linked atoms is used to depict a  $\sigma$ -bond.

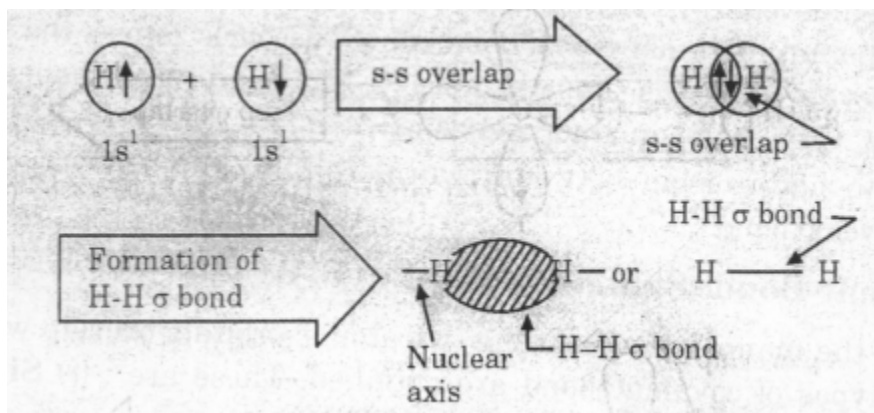


Fig.1111. Steps involved in the formation of H-H  $\sigma$ -bond in  $H_2$  molecule.

## 2. HF molecule (*s-p overlap*)

The half-filled  $1s$ -orbital of H-atom overlaps with half-filled  $2p_x$  orbital on F atom ( $F - (2s^2, 2p_x^1, 2p_y^2, 2p_z^2)$ ) to form H-F  $\sigma$ -bond. This bond has one large lobe and one small lobe (Fig. 1112). The other orbitals on F atom namely  $2s$ ,  $2p_y$ , and  $2p_z$ , being, completely filled, do not participate in the overlapping or bond formation process and, hence have not been shown in Fig. 1112. The resulting  $\sigma$ -bond is also symmetrical about the nuclear and has a nodal plane that stands perpendicular at the right angle axis but does not contain nuclear axis.

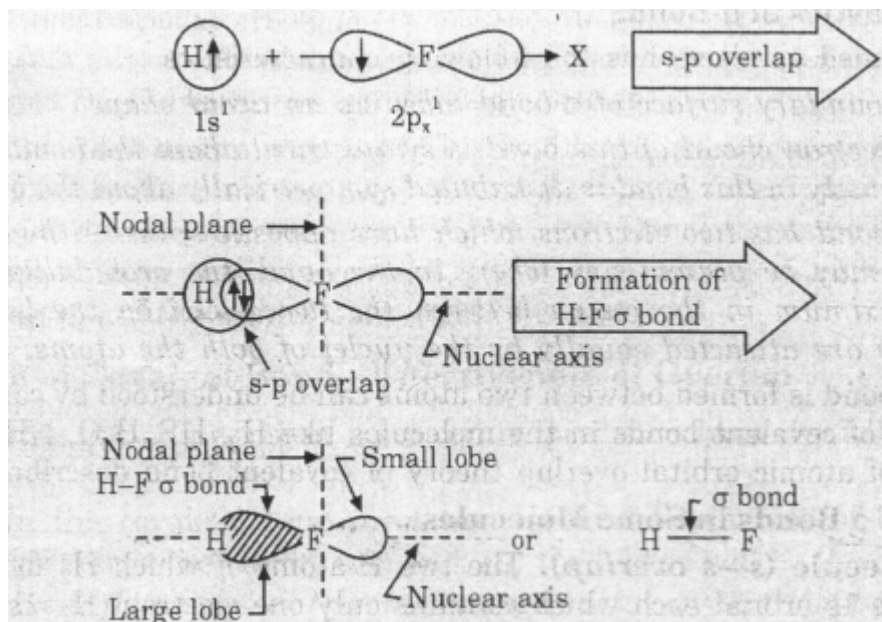


Fig. 1112. Steps involved in formation of H-F  $\sigma$ -bond in HF molecule.

### 3. H<sub>2</sub>O molecule (*s-p overlap*)

The valence shell configuration of O-atom viz.  $2s^2, 2p_x^1, 2p_y^2, 2p_z^1$  shows that it has two unpaired electrons. In the formation of H<sub>2</sub>O molecule the half-filled  $2p_x$  and  $2p_z$  orbitals overlap with half-filled  $2s$ -orbitals of two H-atoms and thus form two O-H  $\sigma$ -bond as shown in Fig 1113.

Since these O-H  $\sigma$ -bond are produced by *s-p* overlap, these bonds are also called *s-p<sub>x</sub>* and *s-p<sub>z</sub>* bonds. Now since  $2p_x$  and  $2p_z$  orbitals are at right angles to each other, an angle of  $90^\circ$  between two O-H  $\sigma$ -bond (i.e. H-O-H angle) is expected, but the actual angle is  $104.5^\circ$  instead of  $90^\circ$ . The increase in angle is due to the mutual electrostatic repulsion between the electron pairs constituting the two O-H bonds.  $2s$  and  $2p_y$  orbitals of O-atom, being completely filled, do not participate in the overlapping or bond formation process and hence have not been shown in Fig. 1113.

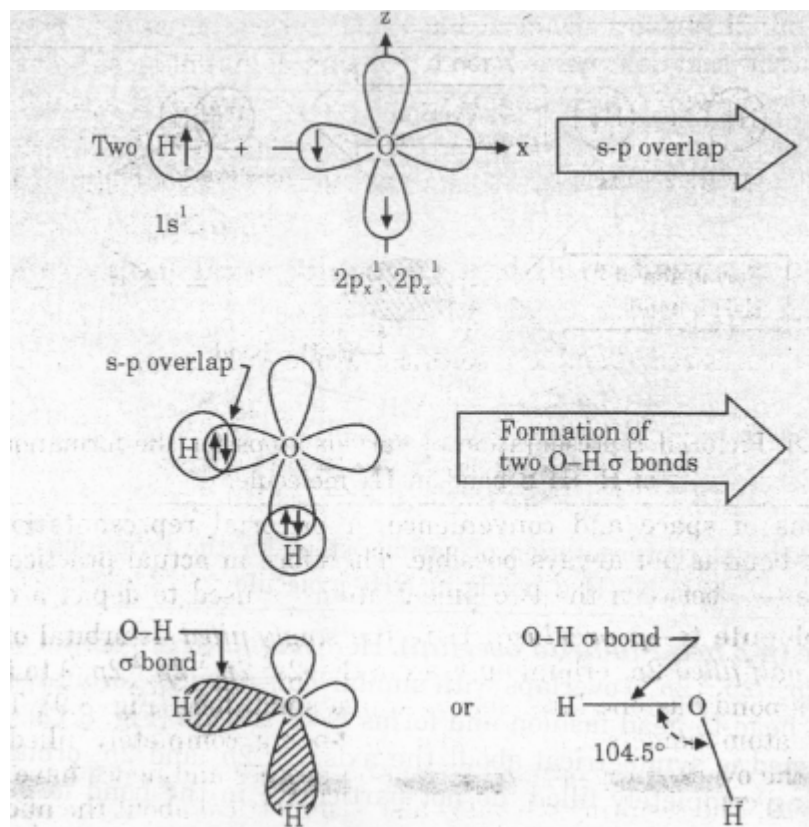


Fig. 1113. Steps involved in the formation of two O-H  $\sigma$ -bond in H<sub>2</sub>O molecule. '



#### 4. NH<sub>3</sub> molecule (s - p overlap)

The valence shell configuration of N-atom viz.  $2s^2, 2p_x^1, 2p_y^1, 2p_z^1$  shows that all its  $p$ - orbitals have unpaired electrons and hence overlap with singly-filled  $1s$ -orbitals of three H- atoms to form three s - p  $\sigma$  bonds (Fig. 4).  $2s$  orbital of N atom, being completely filled, has not been shown in the Figure. Due to mutual repulsion of the electron pairs constituting three NH  $\sigma$  bonds, the H-N-H angles are  $107^\circ$  instead of  $90^\circ$ .

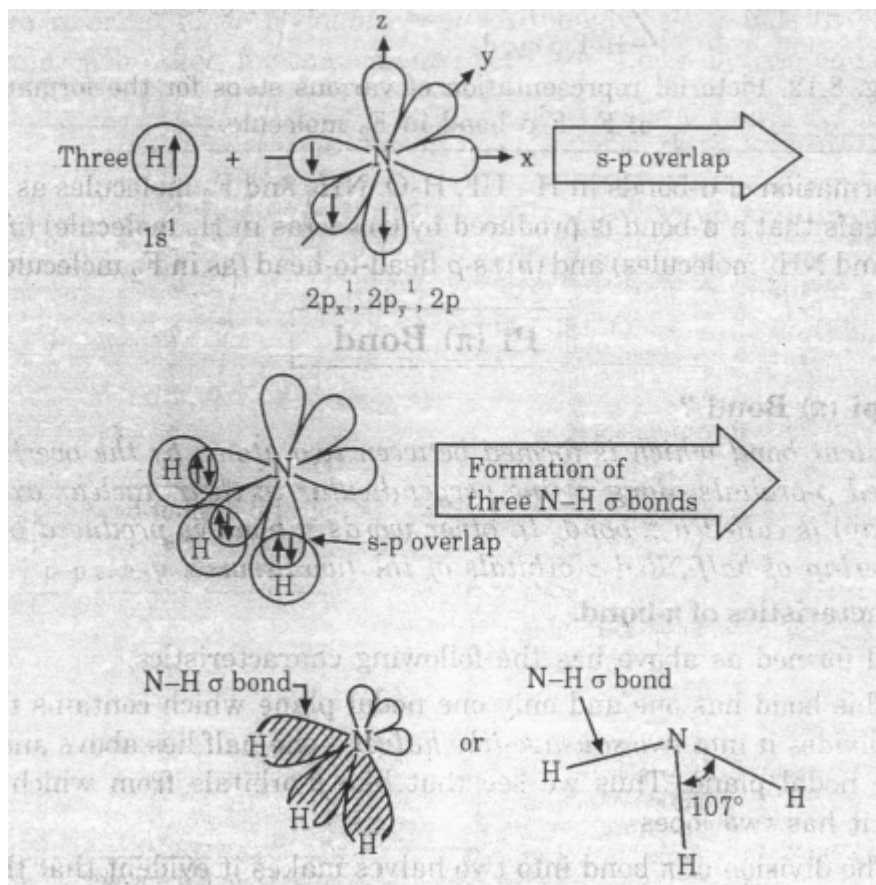


Fig. 4. Steps involved in the formation of N - H  $\sigma$  bond in NH<sub>3</sub> molecule

#### 5. F<sub>2</sub> molecule (p - p head-to-head overlap)

Here half-filled  $2p_x$  orbital on one F atom ( $F \sim 2s^2, 2p_x^1, 2p_y^2, 2p_z^2$ ) overlaps with similar half-filled  $2p_x$  orbital on the other F atom in a head-to-head fashion and forms F-F  $\sigma$  bond (Fig. 5), since the bond thus formed is 'symmetrical about the axis,  $2s$ ,  $2p_y$ , and  $2p_z$ ; orbitals of both F atoms, being completely filled, do not participate in the bond formation process and hence have not been shown in the Fig 5.

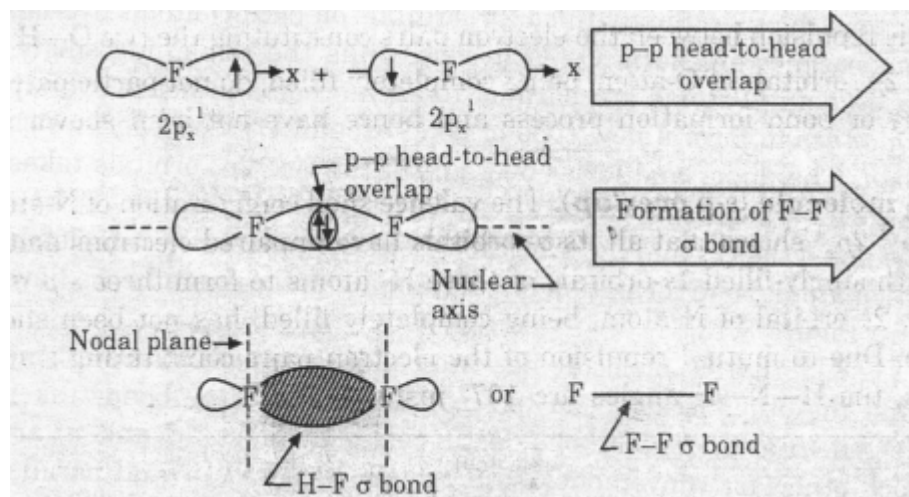


Fig. 5. Steps involved in the formation of F-F  $\sigma$  bond in  $F_2$  molecule

The  $\sigma$  bond formed has two nodal planes which are perpendicular to the nuclear axis but do not contain the nuclear axis. *The formation of  $\sigma$ -bonds in  $H_2$ ,  $H-F$ ,  $H_2O$ ,  $NH_3$  and  $F_2$  molecules as mentioned above reveals that a  $\sigma$ -bond is produced by;*

- (i) s - s (as in  $H_2$  molecule)
- (ii) s - p (as in HF,  $H_2O$  and  $NH_3$  molecules) and
- (iii) p - p head-to-head (as in  $F_2$  molecule) overlaps.

## Pi ( $\pi$ ) Bond

A covalent bond which is formed between two atoms by the *overlap of their singly-filled p-orbitals along' a line perpendicular to their nuclear axis (side-to side overlap)* is called a  $\pi$  bond. *In other words  $\pi$  bond is produced by the side-to-side overlap of half-filled p-orbitals of the two atoms.*

### Characteristics of $\pi$ -bond

It-bondformed as above has the following characteristics.

- (i) This bond has one and only one nodal plane which contains the nuclear axis and divides it into two *sausage-like halves-one* half lies above and the other below the nodal plane. Thus we see that like p-orbitals from which  $\pi$  bond is obtained, it has two lobes.

- (ii) The division of  $\pi$  bond into two halves makes it evident that the electron density of a  $\pi$  bond is concentrated above and below the plane of  $\sigma$  bond *i.e.* electron density of a  $\pi$  bond is unsymmetrical about the nuclear axis. This bond has an increased electron density in the inter-nuclear region, though not on the bond axis.

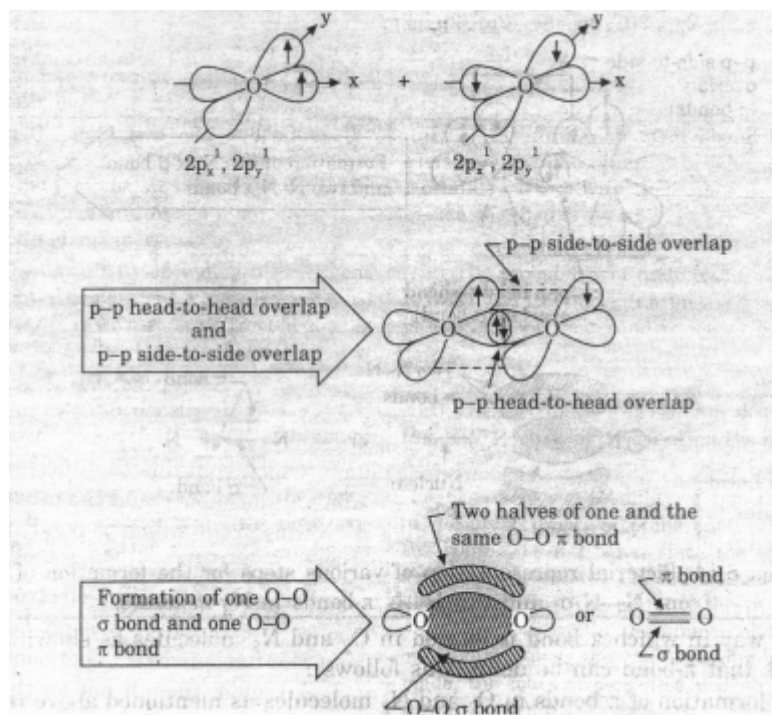
### ***Formation of $\sigma$ Bonds in $O_2$ and $N_2$ Molecules***

How this bond is formed can be understood by considering the formation of some simple molecules like  $O_2$  and  $N_2$  molecules.

#### **1. $O_2$ molecule (*p-p head-to-head and p-p side-to-side overlaps*)**

Valence shell configuration of O-atom *viz.*  $2s^2 2p_x^1 2p_y^1 2p_z^2$  shows that each of the O-atoms of  $O_2$  molecule has two singly filled p-orbitals namely  $2p_x$  and  $2p_y$  which are perpendicular to each other. Singly-filled  $2p_x$  orbitals on both O-atoms overlap in a *head-to-head manner* and form  $\sigma$  bond while the remaining singly filled  $2p_y$  orbitals on both a-atoms are parallel to each other and hence overlap in a *side-to-side manner* to form a new type of bond around  $\sigma$  bond which is called pi ( $\pi$ ) bond. The upper and lower overlaps of the two  $2p_y$  orbitals taken together constitute the  $\pi$  bond (Fig. 6).

Here it may be noted that  $2s$  and  $2p_z$  orbitals of both a atoms, being completely filled, do not participate in bond formation or overlapping process and hence have not been shown in Fig. 6. It is evident from Fig 6. that  $O_2$  molecule has two bonds one of which is a  $\sigma$ -bond ( $2p_x - 2p_x$  bond) and the other is  $\pi$ -bond ( $2p_y - 2p_y$  bond). Both the bonds taken together are referred to as a *double bond*. Although both bonds ( $\sigma$  and  $\pi$ ) are different from each other, for convenience both are shown by two equal parallel lines.



**Fig. 6.** Steps involved in the formation of one O-O  $\sigma$  and one O – O  $\pi$  bond in  $O_2$  molecule

## 2. $N_2$ molecule (*p-p head-to-head and side-to-side overlaps*)

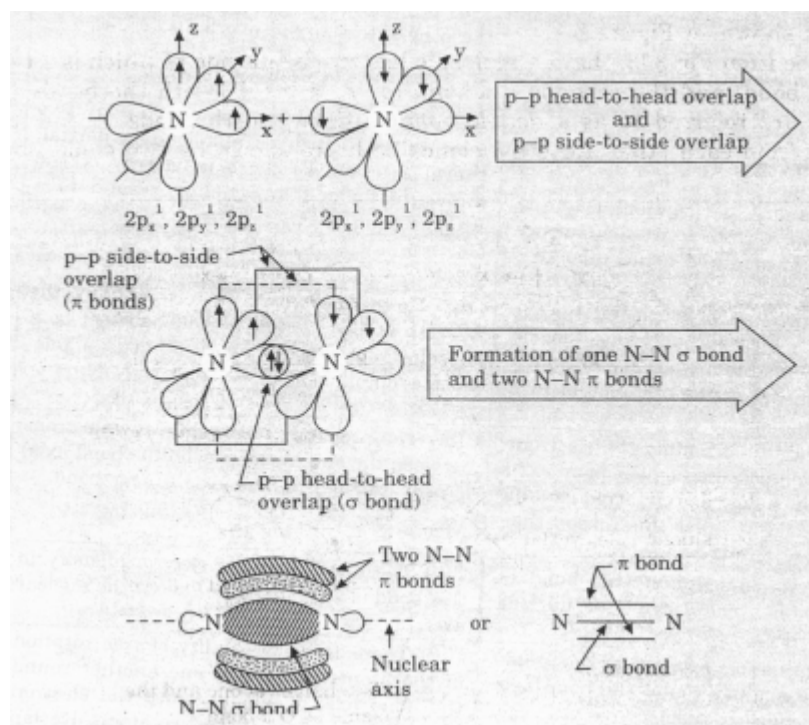
The valence-shell configuration of N atom *viz.*  $2s^2 2p_x^1, 2p_y^1, 2p_z^1$  shows that its all the three p-orbitals are singly-filled and hence will participate in the bond formation with other N-atom. Singly filled  $2p_x$  orbitals of both N atoms overlap in a *head to-head manner* and form N - N  $\sigma$ -bond ( $2p_x - 2p_x$  bond) while the remaining singly filled  $2p_y$  and  $2p_z$  orbitals of this N atom overlap with the similar p-orbitals of the other N atom in a *side-to-side manner* and form two N - N  $\pi$ -bonds ( $2p_y-2p_y$   $\pi_1$ -bond and  $2p_z - 2p_z$   $\pi_2$ -bond) as shown in Fig. 7.

Note that  $2s$  orbital, being completely filled does not participate in bond formation and hence has not been shown in the Figure 7. We learn from Fig. 7. that  $N_2$  molecule has three bonds one of which is a  $\sigma$ -bond ( $2p_x - 2p_x$   $\sigma$  bond) and the other two are  $\pi$ -bonds ( $2p_y - 2p_y$   $\pi$ -bond and  $2p_z - 2p_z$   $\pi$ -bond). All the three bonds taken together are referred to as a *triple bond*. The way in which  $\pi$  bond is formed

in  $O_2$  and  $N_2$  molecules as shown above suggests that 1t-bond can be defined as follows;

The formation of It bonds in  $O_2$  and  $N_2$  molecules as mentioned above reveals that if x-axis is assumed to be the molecular axis, n-bond is given by the side-to side overlap of;

- singly-filled  $p_y$ -orbital-of one atom with singly-filled  $p_y$ -orbital of the other atom ( $2p_y - 2p_y$  overlap).*
- singly-filled  $p_z$ -orbital of one atom with singly-filled  $p_z$ -orbital of the other atom ( $2p_z - 2p_z$  overlap).*



**Fig. 7.** Steps involved in the formation of one N – N  $\sigma$  and two N – N  $\pi$  bond in  $N_2$  molecule