Sigma *(σ)* 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 σ-bond. In other words σ-bond is produced by the head-to-head overlap of the half-filled atomic orbitals of the two atoms.

Characteristics of σ-Bond.

σ-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_20, NH_3 and F2 on the basis of atomic orbital overlap theory of covalent bond described above.

Molecules with σ-Bonds formation
1. H_2 molecule *(s-s overlap)*

The two H-atoms of which H_2 molecule is composed have Is orbital each which contains only one electron (H $1s^1$). These Is 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 σ bond. Since σ-bond is produced by the overlap of two s-orbitals, it is also called *s-s* σ-bond. Thus a σ-bond can be defined as Various steps for the formation of a a-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 σ-bond.

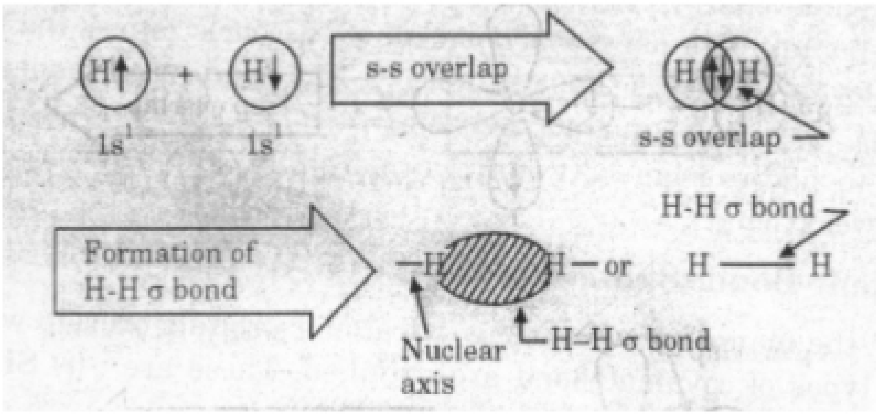


Fig.1111. Steps involved in the formation of H-H· σ-bond in H2 molecule.

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

The half-filled Is-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 σ-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 arid, hence have not been shown in Fig. 1112. The resulting σ-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.

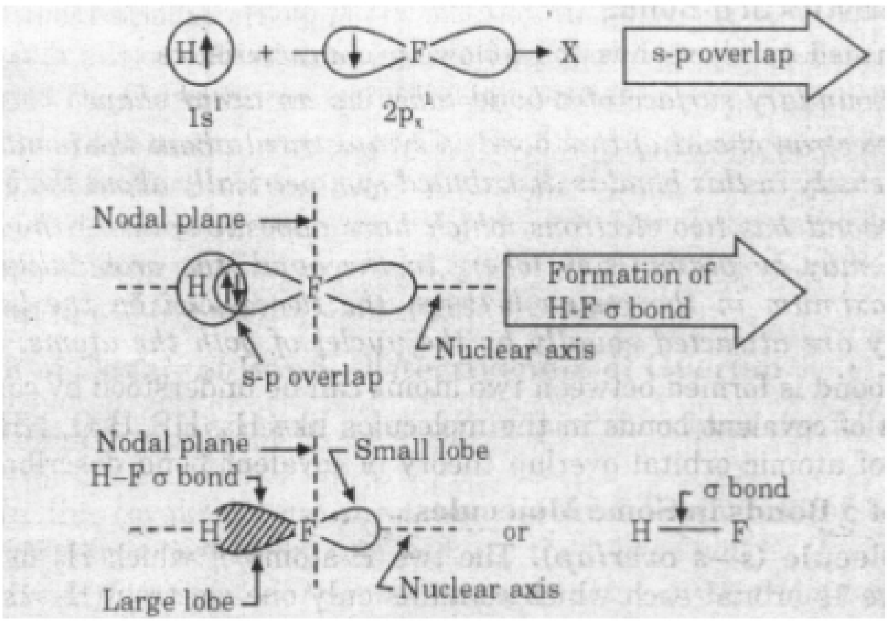


Fig. 1112. Steps involved in formation of H-F σ-bond in HF molecule.

3. $H_2$0 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 H20 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 σ-bond as shown in Fig 1113.

Since these O-H σ-bond are produced by s-p overlap, these bonds are also called s-p_x and s-p_z bonds. Now since $2p_x$ and $2p_z$ orbitals are at right angles to each other, an angle of 90° between two O-H σ-bond i.e. H-O-H angle) is expected, but the actual angle is 104.5°instead of 90°. 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.

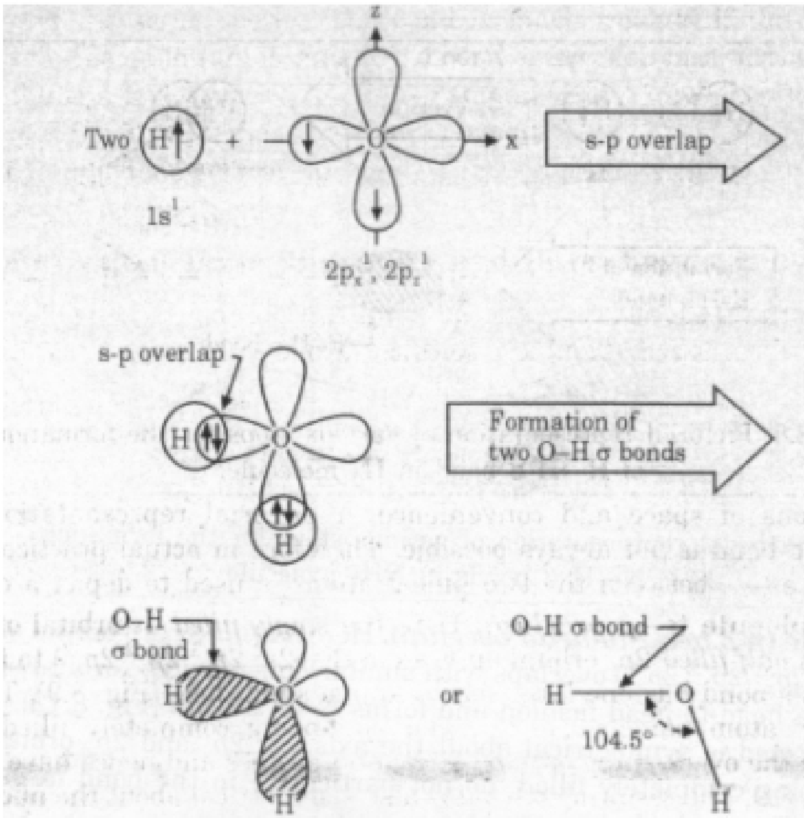


Fig. 1113. Steps involved in the formation of two O-H σ-bond in H_2O molecule. '

4. NH_3 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 σ 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 *σ* bonds, the H-N-H angles are 107° instead of 90°.

Pi (π) Bond

What is pi (π) 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 π bond. In other words π bond is produced by the side-to-side overlap of half-filled p-orbitals of the two atoms.

Characteristics of π-bond.

π-bond formed 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 π bond is obtained, it has two lobes.

(*ii*) The division of π bond into two halves makes it evident that the electron density of a π bond is concentrated above and below the plane of σ bond *i.e.* electron density of a π 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 π 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.* $2s^2\ 2p_x1\ 2p_y^1\ 2p_z^2$ 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 O—O σ bond while the remaining singly-filled $2p_y$ orbitals on both O-atoms are parallel to each other and hence overlap in a *side-to-side manner* to form a new type of bond around O—O σ bond which is called *pi* (π) *bond*. The upper and lower overlaps of the two $2p_y$ orbitals taken together constitute the π bond (Fig. 8.13).

Here it may be noted that $2s$ and $2p_z$ orbitals of both O atoms, being completely filled, do not participate in bond formation or overlapping process and hence have not been shown in Figure 8.13.

We see from Fig 8.l3. that O_2 molecule has two bonds one of which is a σ-bond (p_x–p_x σ bond) and the other is a π-bond (p_y–p_y π bond). Both the bonds taken together are referred to as a *double bond*. Although both bonds (σ and π) are different from each other, for convenience both are shown by two equal parallel lines.

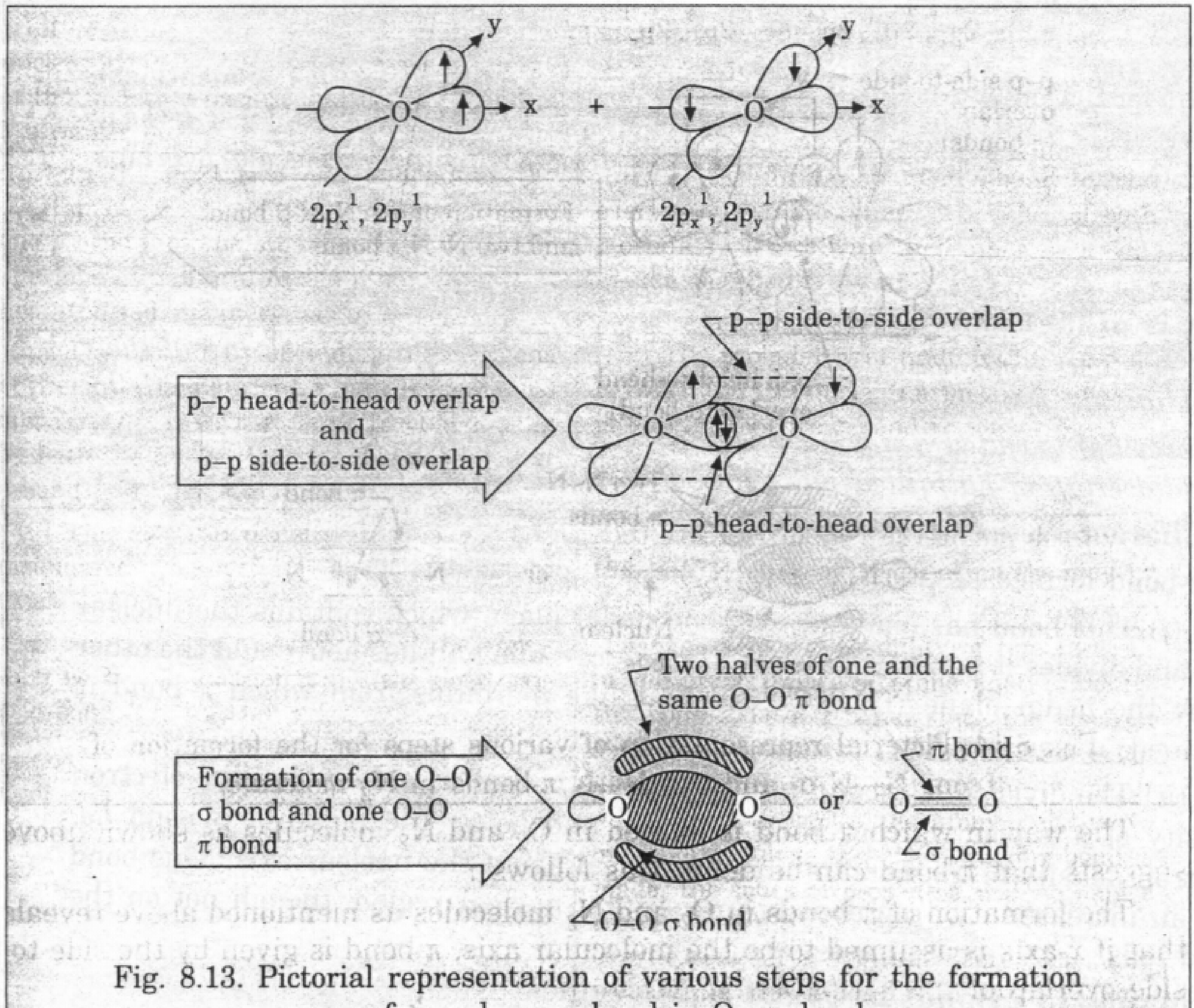


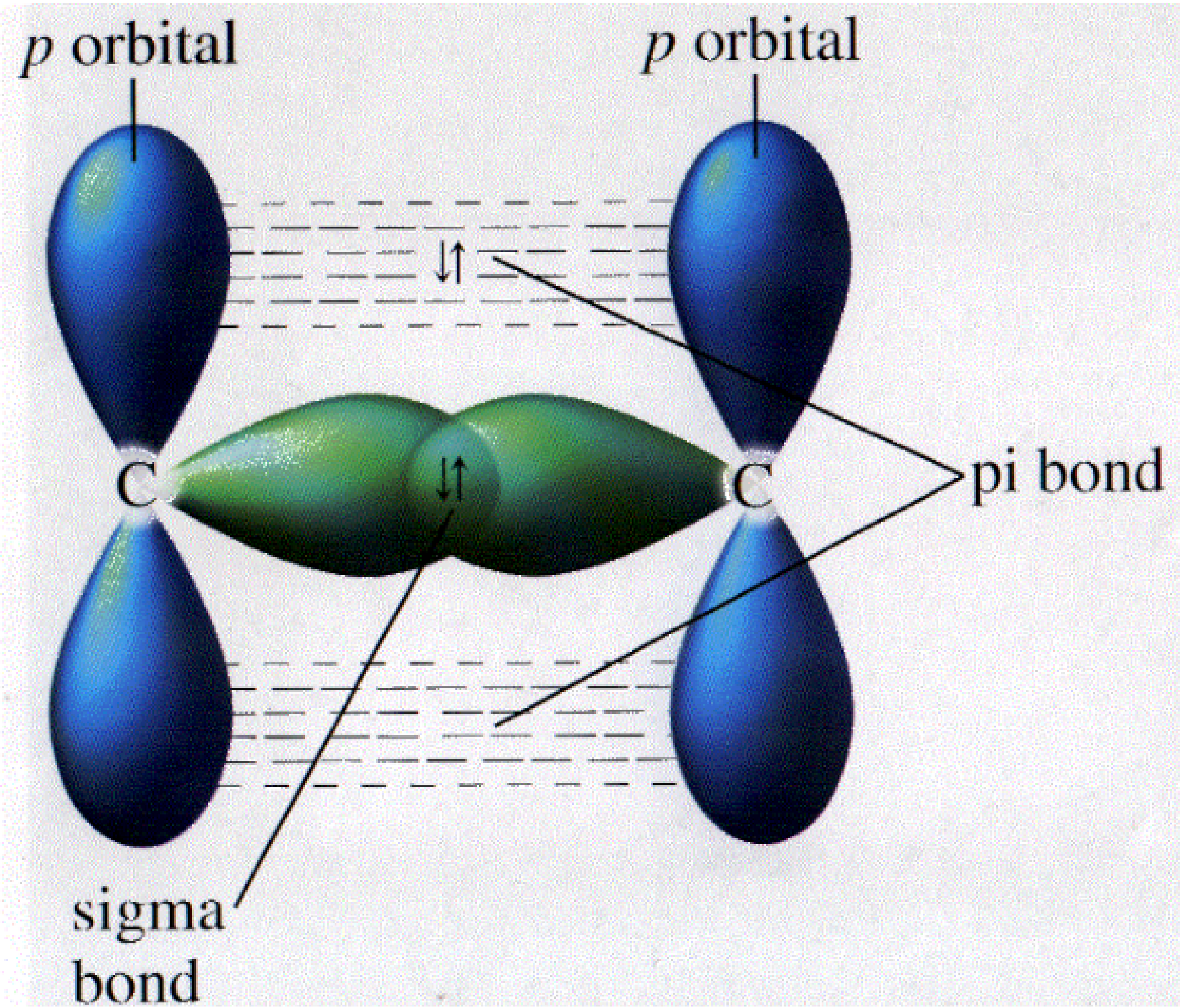
Fig. 8.13. Pictorial representation of various steps for the formation one of σ and one π bond in O_2 molecule.

2. N_2 molecule (*p–p head-to-head and p–p 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

Comparison of σ- and π-Bonds

The distinguishing features of a σ-bond from a π-bond are given in the following Table :

σ-Bond	π-Bond
(*i*) A σ-bond obtained by the *head-to-head* overlap *i.e.* (overlap of orbitals along the nuclear axis) of : (*a*) two *s*-orbitals on two different atoms (*s–s* overlap). (*b*) one *s*-orbital of one atom with *p*-orbital of the other atom (*s–p* overlap). (*c*) two *p*-orbitals on two different atoms (*p–p* overlap).	(*i*) If *x*-axis is assumed to be the nuclear axis, π-bond is given by the *side-to-side* overlap (*i.e.* overlap of orbitals along a line perpendicular to the nuclear axis) of : (*a*) p_y orbital of one atom with p_y orbital of the other atom (*p_y–p_y overlap*). (*b*) p_z orbital of one atom with p_z orbital of the other atom (p_z–p_z overlap).
(*ii*) Since the extent of overlapping of orbitals along the nuclear axis is relatively greater than the extent of overlapping of orbitals along a line perpendicular to the nuclear axis, there is *more* decrease in energy of the molecule formed and hence σ-bond is a stronger bond.	(*ii*) Since the side-wise overlap of two *p*-orbitals which gives a π-bond is partial, there is lesser *decrease* in energy of the molecule formed and hence π-bond is a weaker bond.
(*iii*) In the formation of a σ-bond by the overlap of two *p*-orbitals, only one lobe of one *p*-orbital of one atom overlaps with only one lobe of *p*-orbital of the other atom in a head-to-head manner.	(*iii*) In the formation of a π-bond by the overlap of two *p*-orbitals, both lobes of both *p*-orbitals overlap with each other in a side-to-side manner.
(*iv*) The probability of finding the electrons between the two nuclei (*i.e.* on the bond axis) is *maximum*, since they are attracted equally by both the nuclei. It is for this reason that σ-bond is a very strong bond.	(*iv*) The probability of finding the electrons between the two nuclei (*i.e.* on the bond axis) is *poor* and hence π-bond is a poor bond.
(*v*) The electron density in this bond is distributed *symmetrically* about the nuclear axis.	(*v*) The distribution of electron density in this bond is *unsymmetrical* about the nuclear axis.
(*vi*) There can be *free rotation* of the atoms relative to one another round the bond axis of σ-bond (*i.e.* nuclear axis).	(*vi*) There is no possibility of free rotation of the atoms relative to one another round the bond axis of π-bond, since the electron clouds of *p*-orbitals of the two atoms overlap above and below the plane of the atoms. If an attempt to rotate the atoms relative to one another along the bond axis of π-bond is made, the lobes of *p*-orbitals will no longer remain co-planar and the extent of overlapping of *p*-orbitals decreases, thus weakening the π-bond still further. This property of *restricted rotation* in case of π-bond is very useful in explaining the phenomena of *cis-trans isomerism* (*geometrical isomerism*).



p orbital
p orbital
C
C
pi bond
sigma
bond