Valance bond Theory
VBT
Lec.2

Valence Bond Theory

Introduction

This theory was first put forward by Heitler and London in 1927. They gave a theoretical treatment to explain the formation of a covalent bond and energy changes taking place in H_2 molecule. This theory was further extended by Pauling and Slater (1931) to account for the directional characteristics of covalent bond.

Postulates of Pauling - Slater's theory

(*i*) This theory explains the formation and directional characteristics of covalent bond.

(*ii*) A covalent bond is formed by the overlap of pure atomic orbitals of the atoms between which the bond is being formed. The overlapping takes place only between those atomic orbitals which belong to the valance-shell of each atom and contain unpaired electrons with opposite spins. If the spins of the electrons are the same, orbitals, due to the repulsion between electrons, will increase the energy of the system and hence the system will become unstable, *i.e.*, no bond will be formed.

(*iii*) The atomic orbitals of the valence-shell which have paired electrons (completely-filled orbitals) donot participate in the overlapping process and hence donot contribute to the bond formation. The electron pairs in these orbitals are, therefore, called *non-bonding electron pairs* or *lone pairs* of electrons.

(*iv*) The orbitals overlapping together should have the same symmetry, *i.e.*, they should have proper orientation or alignment.

(*v*) Greater is the extent of overlapping between the atomic orbitals, greater is the strength of the resulted covalent bond, *i.e.*, strongest bonds are formed by the maximum overlap of atomic orbitals. Covalent bond formed by $s — s$ overlap is relatively weak, since *s*-orbitals have spherical distribution of electron density. On the other hand, covalent bond obtained by $p—s$ or $p—p$ overlap is relatively stronger, since *p*-orbitals are concentrated in a particular direction and their lobes are longer than the radius of the corresponding *s*-orbital. The relative strength of the covalent bonds obtained by $s—s$, $p—s$ and $p—p$ overlaps is as $s—s < p—s < p—p$.

(*vi*) Overlapping between atomic orbitals increases the electron density in the region between the nuclei of the combining atoms. This increased electron density holds the two atoms together and thus a bond is established.

(*vii*) Covalent bonds have directional characteristics. The direction of the covalent bond is that in which the overlapping orbitals have the greatest electron density. For example, since *p*-orbitals are directed towards the three axes, the bonds formed by their overlapping are also directed towards the three axes.

(*viii*) Energy is released when a covalent bond is formed. This energy can be used to unpair the paired electrons by trasfering them to the vacant orbitals having slightly higher energy and belonging to the same main energy level. For example when five P — Cl covalent bonds are formed in PCl_5 molecule, energy is released and this released energy is used to unpair the two paired electrons in 3*s* orbital of P-atom $\left(P = 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^0\right)$ by transfering one electron to the vacant 3*d* orbital. Thus this transfer gives 5 unpaired electrons $\left(P = 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1\right)$ which explains the pentacovalency of P-atom in PCl_5 molecule.

(*ix*) Depending on the way in which the atomic orbitals overlap together two types of covalent bonds are formed. These are *sigma* (σ) covalent bond and *pi* (π) covalent bond.

(*x*) The atoms whose atomic orbitals overlap together to form covalent bond donot lose their individual identity, *i.e.*, the atoms retain their individual identity.

(*xi*) According to this theory, an electron moves under the influence of only one nucleus of an atom.

(*xii*) Resonance also plays an important role in valence bond theory.

Sigma (σ) Bond

What is sigma(σ) bond?

A covalent bond which is formed between two atoms by the overlap of their two half-filled orbitals belonging to their valence-shell along a line joining the nuclei of both the atoms (*i.e.*, along the inter-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* (head-to-head overlap is also called *end-to-end overlap, head-on overlap, end-on overlap, axial overlap* or *linear overlap*) of the two half-filled orbitals belonging to the valence-shell of the two combining atoms. Thus if x-axis is assumed to be the molecular axis, then σ-bond is produced by $s - s$ overlap (as in H_2 molecule), $s - p_x$ overlap [as in NH_3, H_2O and HX (X = F, Cl, Br or I) molecules] and $p_x - p_x$ overlap (as in X_2 molecules). A sigma bond is also produced when two hybrid orbitals overlap together along the inter-nuclear axis.

Examples to show the formation of σ-bond

Here we shall see how σ-bond is formed in H_2, NH_3, H_2O, HF and F_2 molecules.

(*i*) *H_2 molecule* (*s—s overlap*). The electronic configuration of H-atom is $1s^1$. 1*s*-orbitals of both H-atoms which have one unpaired electron each overlap with each other along their axes and form one H—H σ-bond (Fig. 10.4).

Two 1*s*-orbitals on two H-atoms

H_2 molecule

Fig. 10.4: Formation of one σ-bond (H—H σ-bond) in H_2 molecule by the overlap of two 1*s*-orbitals (s—s overlap)

(*ii*) *NH_3 molecule* (*s—p overlap*). The valence-shell electronic configuration of N-atom is $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$. All the three *p*-orbitals on N-atom, each having one electron, overlap with three 1*s* orbitals of three H-atoms along their axes and form three N—H σ-bonds (Fig. 10.5). 2*s*-orbital of N-atom which has paired electrons

N-atom which has paired electrons does not participate in the overlapping process and hence the electron pair residing in 2*s*-orbital does not contribute to bond formation.

This pair of electrons is called *non-bonding electron pair* or *lone pair of electrons*. Thus NH_3 molecule has one lone pair of electrons on N-atom.

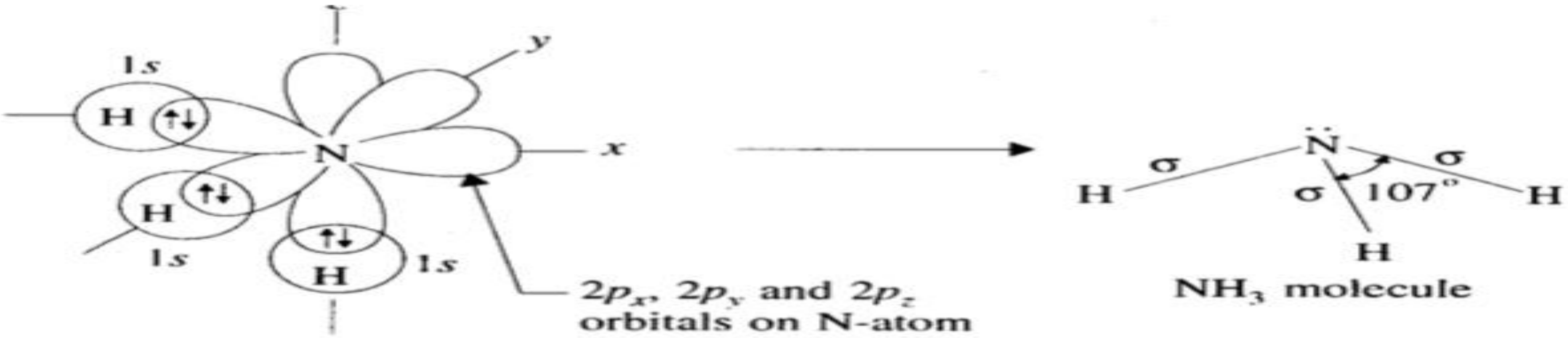

Fig 10.5: Formation of three σ-bonds (N—Hσ-bonds) in NH_3 molecule by three *s-p* overlaps. Two dots shown at N-atom represent a lone pair of electrons which is present in 2*s* orbital of N-atom.

(iii) H_2O molecule (s—p overlap). **The valence-shell configuration of O-atom is $2s^2$, $2p_x^1$,** $2p_y^2$, $2p_z^1$. Two 1*s*-orbitals on two H-atoms overlap with $2p_x$ and $2p_z$ orbitals (both having unpaired electron) along their axes and form two O—H σ-bonds (Fig. 10.6). The electron pairs in 2*s* and $2p_y$ orbitals reside as lone pairs of electrons on O-atom. Thus H_2O molecule has two lone pairs of electrons on O-atom.

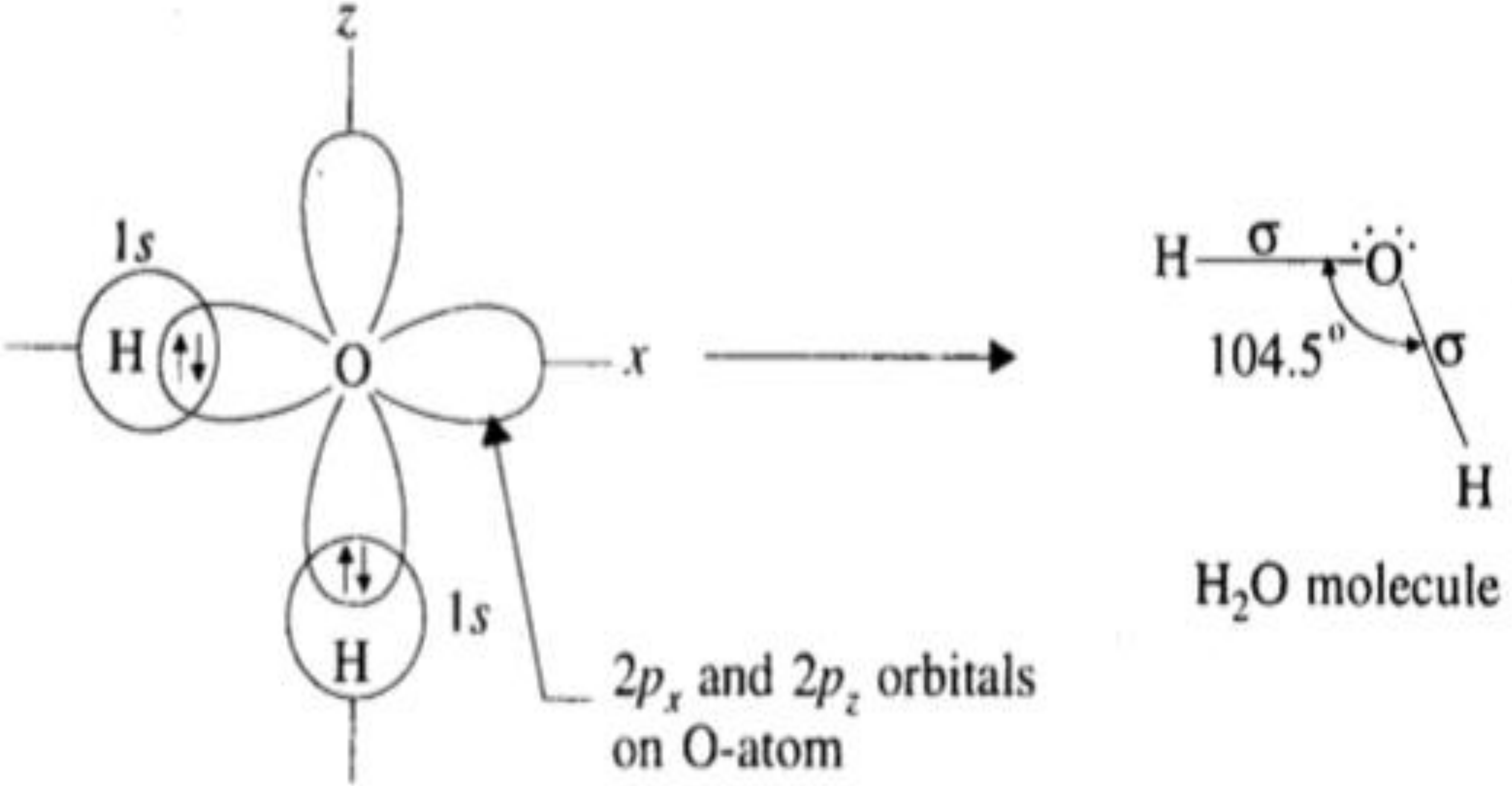

Fig. 10.6 : Formation of two σ–bonds (O—Hσ–bonds) in H_2O molecule by two *s*—*p* overlaps. O-atom has two lone pairs of electrons (shown by four dots)

Now since p_x and p_y orbitals are perpendicular to each other, each of the two H—O—H bond an-

(iv) HF molecule (s — p overlap). The valence-shell configuration of F-atom is $2s^2, 2p_x^1, 2p_y^2, 2p_z^2$. 1*s*-orbital of H-atom overlaps with the singly- filled $2p_x$ orbital on F-atom along the *x*-axis and gives rise to the

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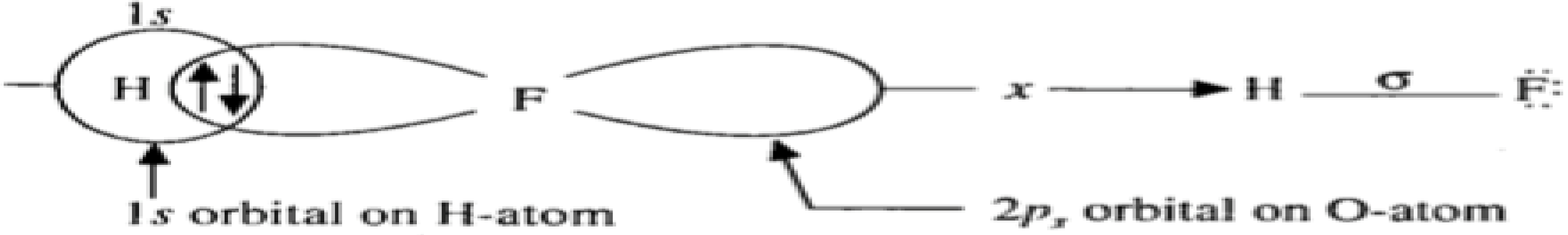


Fig. 10.7: Formation of one σ-bond (H—F σ-bond) in HF molecule. F-atom has three lone pairs of electrons (shown by six dots)

(*v*) *F_2 molecule (p—p overlap)*. The valence-shell configuration of F-atom is $2s^2$, $2p_x{}^1$ $2p_y{}^2$ $2p_z{}^2$. $2p_x$ orbitals (which have one unpaired electron) on two F-atoms overlap together along the *x*-axis and form one F—F σ-bond. The electron pairs in $2s$, $2p_y$ and $2p_z$ orbitals of both F-at-

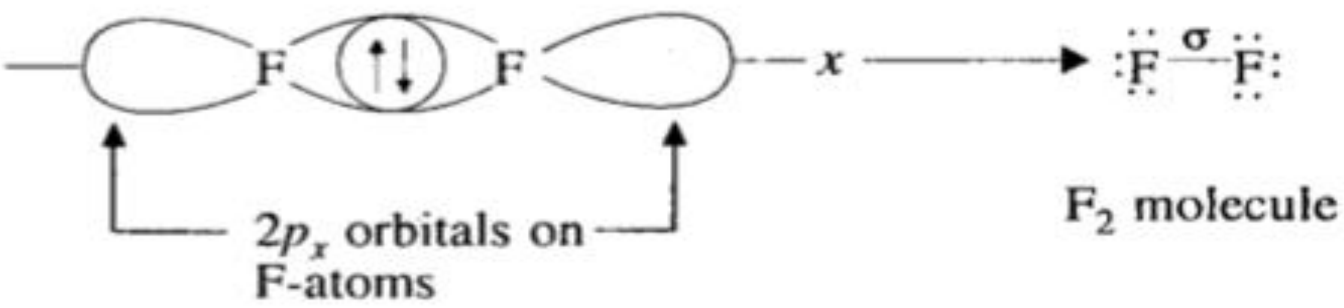


Fig. 10.8 : Formation of one σ-bond (F—F σ-bond) in F_2 molecule by *p-p* overlap. Each F-atom in F_2 molecule has three lone pairs of electrons.

Pi (π) Bond

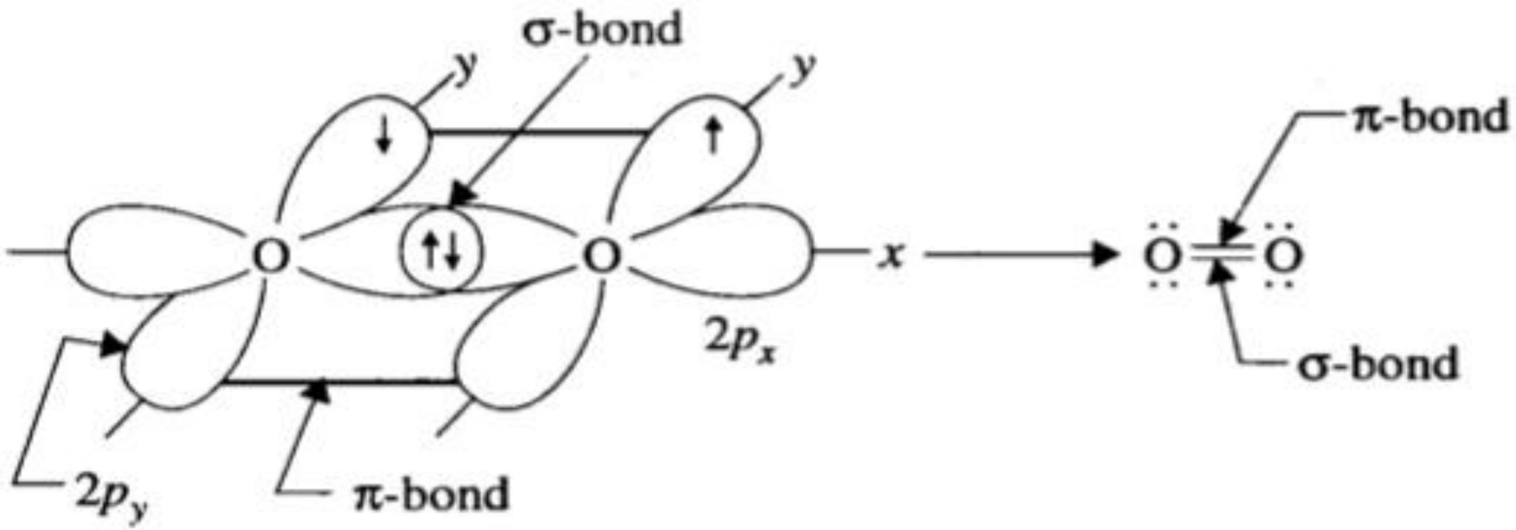
What is pi (π) bond?

A covalent bond which is formed between two atoms by the overlap of their two-half-filled orbitals belonging to their valence-shell along a line perpendicular to the inter-nuclear axis is called a π-bond. In other words, π-bond is produced by the *side-to-side overlap* (side -to-side overlap is also called *side-wise overlap,* or *lateral overlap*) of the two half-filled orbitals belonging to the valence-shell of the two combining atoms. Thus if x-axis is assumed to be the molecular axis, then π-bond is produced by $p_y - p_y$ and $p_z - p_z$ overlaps.

Examples to show the formation of π-bond

Here we shall see how π-bond is formed in O_2 and N_2 molecules.

O_2 *molecule*. The valence-shell configuration of O-atom is $2s^2, 2p_x^1\ 2p_y^1\ 2p_z^2$, showing that the atom has two half-filled p-orbitals namely $2p_x$ and $2p_y$. If x-axis is assumed to be the molecular axis, then the overlap between two $2p_x$ orbitals (each orbital has one unpaired electron) on two O-atoms along the x-axis gives rise to the formation



N_2 mlecule. The valence-shell electronic configuration of N-atom is $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$ showing that each of the three *p*-orbitals has one unpaired electron. If *x*-axis is assumed to be the molecular axis, then the overlap between two $2p_x$ orbitals on two N-atoms along *x*-axis produces N—N σ-bond. On the other hand, when two $2p_y$ orbitals on both N-atoms overlap together along a line perpendicular to *x*-axis, then N—N π bond is obtained. Similarly $2p_z - 2p_z$ overlap also gives another N—N π-bond. Thus N_2 molecule consists of three bonds (triple bond) one of which is a σ-bond and the other two are π-bonds. (Fig. 10.10). Each N-atom has one lone pair of electrons.

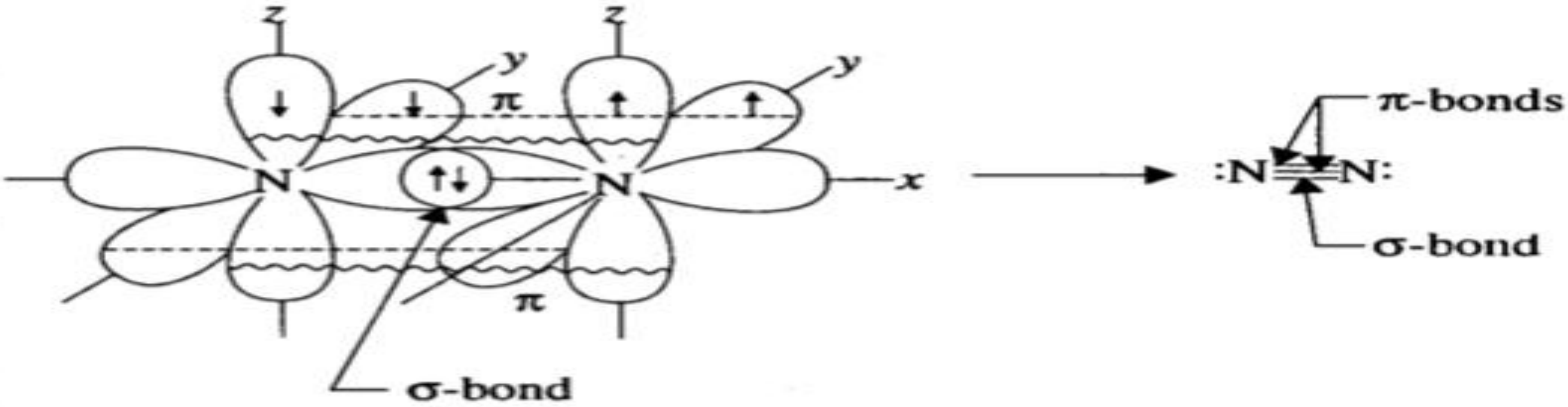


Fig. 10.10 : Formation of one σ-bond (N—N σ-bond) and two π-bonds (N—N π-bonds) in N_2 molecule by $2p_x - 2p_x$, $2p_y - 2p_y$ and $2p_z - 2p_z$ overlaps respectively.

Table 10.2: *Comparison between sigma (σ) and pi (π) bonds.*

	Sigma (σ) bond		Pi (π) bond
(i)	It is obtained when two pure atomic orbitals or hybrid orbitals overlap with each other along the inter-nuclear axis.	*(i)*	It is obtained when two pure atomic orbitals overlap with each other along a line perpendicular to the inter-nuclear axis.
(ii)	If x-axis is assumed to be the inter-nuclear axis (molecular axis), then s–s, s–p_x and $p_x - p_x$ overlaps produce σ-bond.	*(ii)*	If x-axis is assumed to be the inter-nuclear axis, then $p_y - p_y$ and p_z–p_z overlaps produce π-bond.
(iii)	σ-bond is a stronger bond, since the overlap of orbitals along the inter-nuclear axis takes place to a greater extent.	*(iii)*	π-bond is a weaker bond because the overlap of orbitals along a line perpendicular to the inter-nuclear axis does not take place to a greater extent. The already present σ-bond restricts the distance between the atoms.
(iv)	σ-bond determines the direction of the bond and bond length.	*(iv)*	It does not decide the direction of the bond but shortens the bond length due to multiple bonding.
(v)	σ-bond (or σ-molecular orbital) consists of one electron cloud, since the overlapping of orbitals in the formation of σ-bond takes place symmetrically along the inter-nuclear axis.	*(v)*	π-bond (or π-molecular orbital) consists of two electron clouds (electron lobes), since the overlapping of orbitals takes place above and below the inter-nuclear axis.
(vi)	There is free rotation of atoms about σ-bond.	*(vi)*	There cannot be a free rotation of atoms about π-bond, because a π-bond (or π-molecular orbital) consists of two electron clouds.
(vii)	s-orbitals take part in the formation of a σ-bond.	*(vii)*	s-orbitals never take part in the formation of a π-bond.
(viii)	One lobe of p-orbital taking part in the formation of a σ-bond stretches while the other lobe reduces in size.	*(viii)*	Both lobes of p-orbital taking part in π-bond formation remain of the same size.