

Thus only the $2p_x$ orbital of fluorine atom has proper symmetry and energy to interact with the $1s$ orbital of the H-atom, giving one sigma bonding molecular orbital and one sigma antibonding molecular orbital. The $2p_y$ and $2p_z$ orbitals of fluorine yield non-bonding molecular (NB) orbitals at the same energies because of their symmetry they yield zero overlap with $1s$ orbital. These are actually unchanged atomic orbital of fluorine atom.

The MO is σ_x which is of σ -symmetry along the internuclear x -axis.

The molecular orbital diagram is shown in Fig. 2.49. The $2p_x$ orbitals of F are shown at a relatively lower energy state because of greater electronegativity of F. The energy difference 'e' between AOs corresponds to the extent of ionic character in HF which depends upon the difference in electronegativities between two atoms. The covalent character of bond is determined by the energy difference 'C' and would indicate the extent of overlap. The bond order in HF is 1. Therefore, the MO theory is able to predict the nature of the chemical bond to be expected from a molecule.

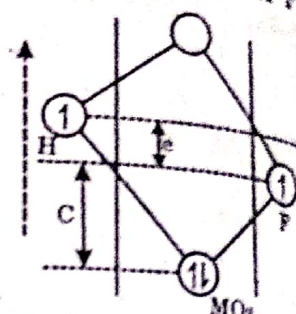


Fig. 2.49 Formation of HF

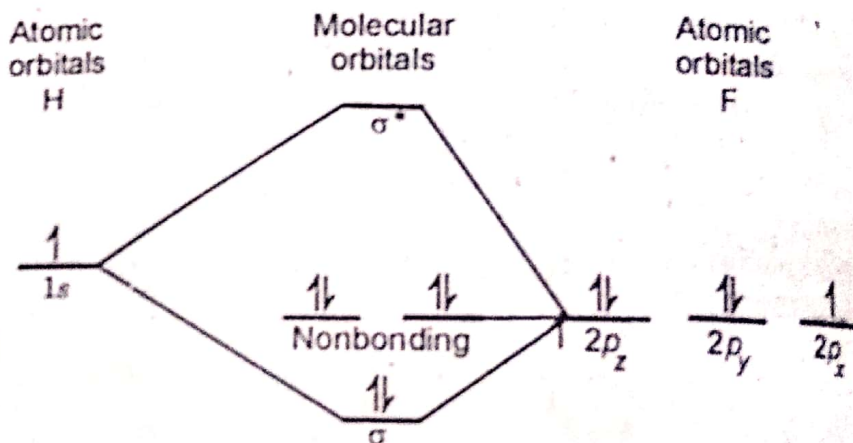
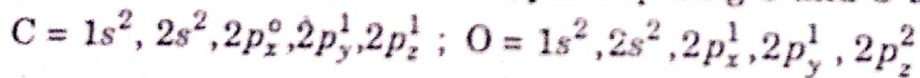


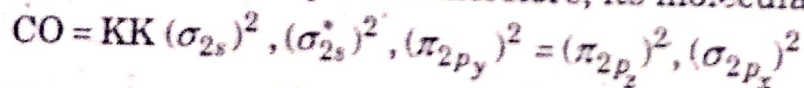
Fig. 2.50 Molecular orbital diagram for the $1s$ atomic orbital of hydrogen and the $2p$ atomic orbitals of fluorine in the HF molecule.

Carbon monoxide Molecule, CO

The electronic configurations of participating C and O atoms are:



Evidently CO molecule has 10 valence electrons: four from C atom ($2s^2p^2$) and six from O atom ($2s^2p^4$) and therefore, its molecular orbital configuration is



Thus its bond order is equal to $\frac{1}{2} (8-2) = 3$ showing that C and O atoms in CO molecule are linked together by one sigma (σ) and two pi (π) bonds.

A simplified diagram of the molecular orbitals derived from the $2s$ and $2p$ atomic orbitals is shown below in Fig 2.51. The oxygen atomic orbitals are lower in energy than those of carbon as a result of the greater Z_{eff} , but they are close enough in energy that we can construct a molecular orbital diagram similar to that of

homonuclear diatomic molecule. A major difference between homonuclear and heteronuclear diatomic molecule is that the molecular orbitals derived primarily from the $2s$ atomic orbitals of one element overlap significantly in energy with those derived from the $2p$ atomic orbitals of the other element. Thus we must consider the molecular orbitals derived from both these atomic orbitals. Further, because of the asymmetry of orbital energies, the bonding molecular orbitals are derived mostly from the oxygen atomic orbitals, whereas the antibonding molecular orbitals are derived mostly from the carbon atomic orbitals. Finally, there are two molecular orbitals whose energies are between those of contributing atomic orbitals. These orbitals, σ_{NB} , are defined as nonbonding, that is, they do not contribute significantly to the bonding. To determine the bond order of CO, the number of antibonding pairs (0) is subtracted from the number of bonding pairs (3), a calculation leading to the prediction of a triple bond. This very high bond energy of 1072 kJ mol^{-1} supports this prediction.

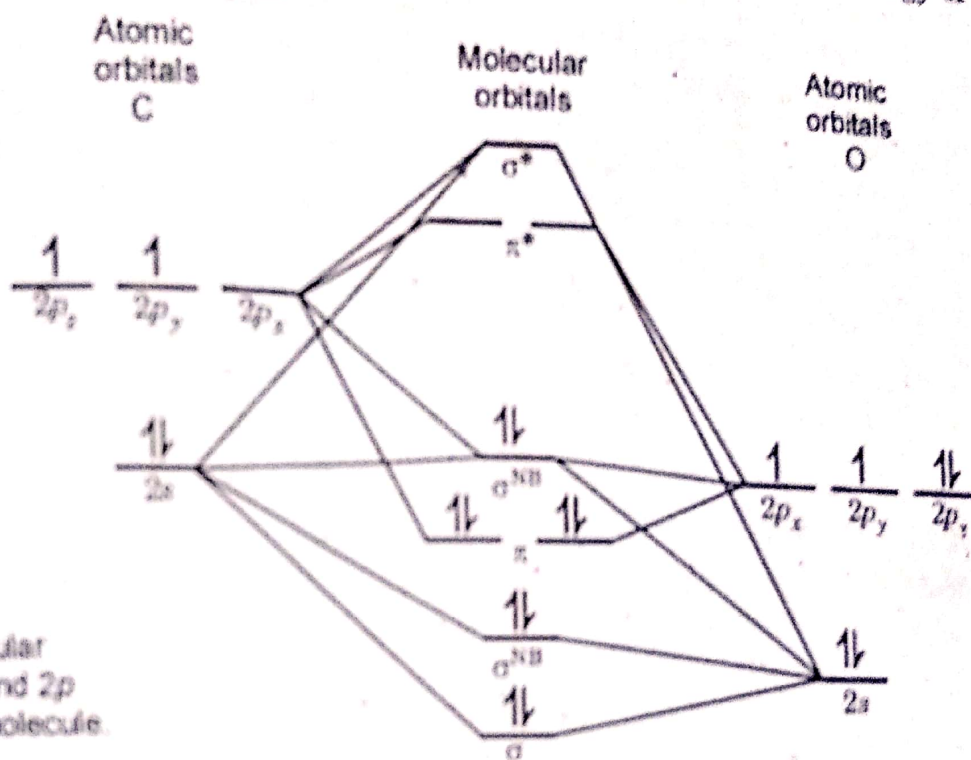
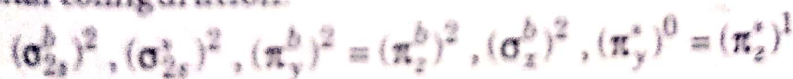


Fig 251 Simplified molecular orbital diagram for the $2s$ and $2p$ atomic orbitals of the CO molecule.

Nitric oxide molecule (NO). NO molecule has 11 electron in its valence shell: five from N-atom ($2s^2p^3$) and six from O atom ($2s^2p^4$). Thus it has the following molecular orbital configuration:



The bond order equal to $(8-3)/2 = 5/2$ shows that nitrogen and oxygen in the molecule are linked together by one σ and two π -bonds. σ -bond is due to the electron pair in σ_z^b molecular orbital and the two π -bonds are due to π_y^b and π_z^b molecular orbitals. One unpaired electron is present in π_x^* molecular orbital, which explains the paramagnetic character of NO. Thus, NO molecule has two 2-electron bonds and one 1-electron bond and can therefore be represented as $:\text{N} \equiv \dot{\text{O}}:$

This structure well accounts for the lower bond strength and larger bond length as compared with N_2 molecule. See Fig in oxides of nitrogen; NO.

2.17 Molecular Orbital Theory for Polyatomic molecules

Molecular orbital theory can also be used to develop bonding schemes for polyatomic molecules. However energy diagrams and the orbital shapes become more and more complex. In general, a molecular orbital in a polyatomic system extends over all the nuclei in a molecule. Indeed MOT forms the basis for most of the quantitative investigations of the properties of large molecules. Let us consider the simplest linear triatomic molecule: BeH_2 . Let us choose the x axis as the molecular axis. Note that only σ molecular orbitals can be formed because H atoms have only their $1s$ orbitals to use in bonding. These orbitals are themselves of σ character with respect to any axis that passes through the nucleus, and therefore they can contribute only to σ molecular orbitals. Then, on the Be atom, only the $2s$ and $2p_x$ orbitals can participate in bonding. The p_y and p_z orbitals, which have π character and zero overlap with any σ orbital, will not play a role in bonding in the BeH_2 molecule.

The $2s$ of Be can combine with the two $1s$ orbitals of the H atoms to form bonding and antibonding MO's, as is shown in Fig. 2.52.

The $2p_x$ orbital of Be also combines with the hydrogen $1s$ orbitals, as shown in Fig. 2.52 to form bonding and antibonding molecular orbitals. In these orbitals are out of phase with each other.

The important points to remember about these four σ molecular orbitals are as follows:

1. In each bonding MO, electron density is large and continuous between adjacent atoms, while in the antibonding MO's there is a node between adjacent pair of nuclei.
2. Electrons in MO's are *delocalized* over the whole extent of the MO.

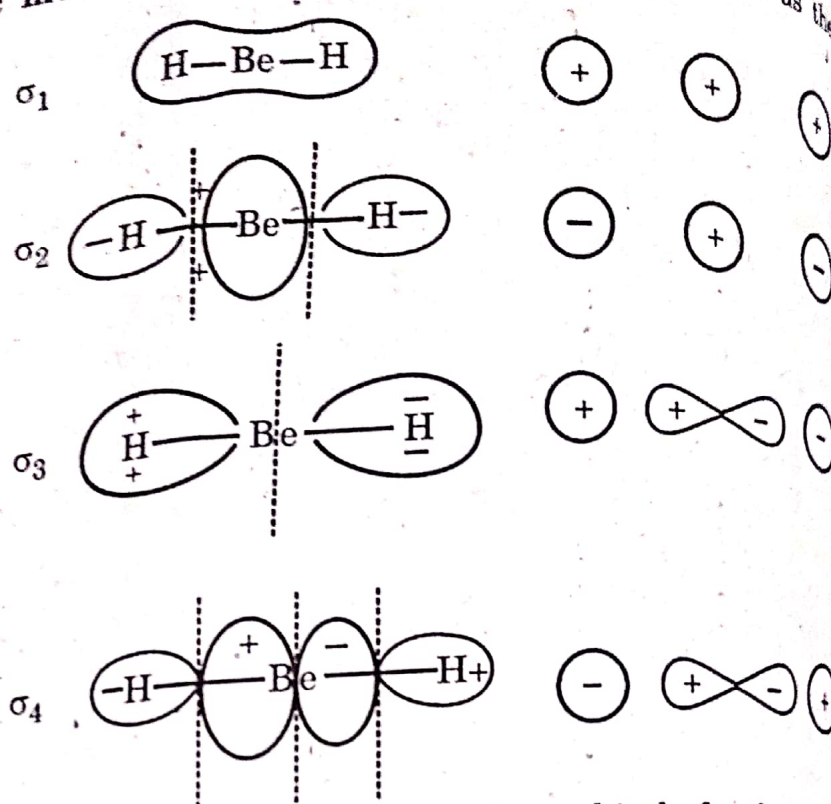


Fig. 2.52 The four σ molecular orbitals for the linear BeH_2 . The dashed vertical lines are nodal planes perpendicular to the molecular axis. Those p atomic orbitals of Be that are perpendicular to the molecular axis have nonbonding interactions with the hydrogen $1s$ orbitals.

The MO treatment of the bonding in BeH_2 can be represented in terms of an energy-level diagram as shown in Fig. 2.53. The main points here are that the $1s$ orbitals lie at much lower energy (-400 kJ/mol) than the $\text{Be } 2s$ orbital and that the p_y and p_z orbitals of Be remain completely unchanged into atomic orbitals, because they do not overlap with any other orbitals. The four valence electrons, $2s^2$ from Be and $1s$ from each H , occupy σ_1 and σ_2 . The total bond order of the Be-H bonds is two. Since each Be-H pair participates equally in the molecules, this is equivalent to saying that there are two equivalent Be-H single bonds.

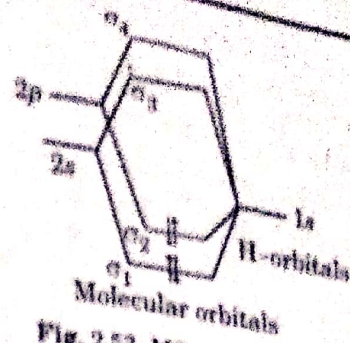


Fig. 2.53 MO energy level diagram for BeH_2 . The MO designations $\sigma_1 - \sigma_4$ correspond to those of above Fig. 2.52.

Structure of Water, H_2O

An analysis of the molecular orbitals for the H_2O molecule provides a good introduction to the way in which the symmetry of a molecule determines the forms of the molecular orbitals in a polyatomic system. There are three symmetry operations, which transform the nuclear framework of the water molecule into itself. For each symmetry operation, there is a corresponding symmetry element. The symmetry elements for the H_2O molecule are a two-fold axis of rotation C_2 and two planes of symmetry σ_1 and σ_2 . A rotation of 180° about the C_2 axis leaves the oxygen nucleus unchanged and interchanges the two hydrogen nuclei. A reflection through the plane labelled σ_1 leaves all the nuclear positions unchanged while a reflection through σ_2 interchanges the two protons. The symmetry operations associated with the three symmetry elements either leave the nuclear positions unchanged or interchange symmetrically equivalent (and hence indistinguishable) nuclei. Every molecular orbital for the H_2O molecule must, under the same symmetry operations, be left unchanged or undergo a change in sign.

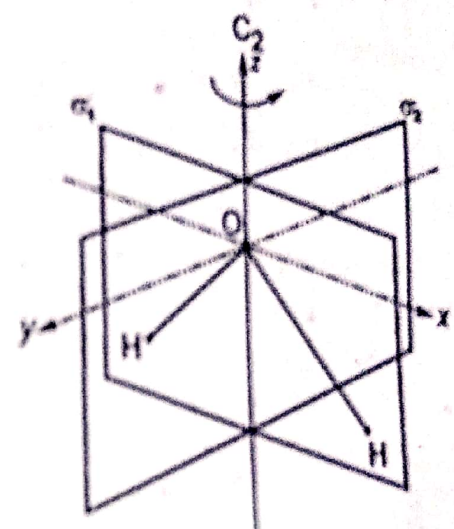


Fig. Symmetry elements for H_2O

We may use the symmetry transformation properties of the atomic orbitals on oxygen and hydrogen together with their relative orbital energy values to determine the primary atomic components of each molecular orbital in a simple MO approximation to the exact molecular orbitals. Only atomic orbitals which transform in the same way under the symmetry operations may be combined to form a molecular orbital of a given symmetry. The symmetry transformation properties of the atomic orbitals on oxygen and hydrogen are given in table. A value of $+1$ or -1 in a given orbital in the table indicates that the orbital is unchanged or changed in sign respectively by a particular symmetry operation.

Table: Symmetry Properties

Atomic orbitals on oxygen	Symmetry behavior under			Symmetry classification	Atomic orbitals on H	Symmetry behaviour under			Symmetry classification
	σ_2	σ_1	σ_2			σ_2	σ_1	σ_2	
1s	+1	+1	+1	a_1	$(1s_1 + 1s_2)$	+1	+1	+1	a_1
2s	+1	+1	+1	a_1	$(1s_1 - 1s_2)$	-1	+1	-1	b_1
$2p_z$	+1	+1	+1	a_1					
$2p_x$	-1	+1	-1	b_2					
$2p_y$	-1	-1	+1	b_1					

The 1s, 2s and $2p_z$ orbitals of oxygen are symmetric (i.e., unchanged) with respect to all three symmetry operations. They are given the symmetry classification a_1 . The $2p_x$ orbital, since it possesses a node in the σ_2 plane changes sign when reflected through the σ_2 plane or when rotated by 180° about the C_2 axis. It is classified as b_2 orbital. The $2p_y$ orbital is antisymmetric with respect to the rotation operator and to a reflection through the σ_1 plane. It is labelled b_1 .

The hydrogen 1s orbitals when considered separately are neither unchanged nor changed in sign by the rotation operator or by a reflection through the σ_2 plane. Instead both these operations interchange these orbitals. The hydrogen orbitals are said to be symmetrically equivalent and when considered individually they do not reflect the symmetry properties of the molecule. However, the two linear combinations $(1s_1 + 1s_2)$ and $(1s_1 - 1s_2)$ do behave in the required manner. The $(1s_1 + 1s_2)$ is symmetric under all three operations and is of a_1 symmetry while the $(1s_1 - 1s_2)$ is antisymmetric with respect to rotation operator and to reflection through the plane σ_2 and is of b_2 symmetry.

The molecular orbitals in H_2O molecule are classified as a_1 , b_1 or b_2 orbitals, as determined by their symmetry properties. In addition to the symmetry properties of the atomic orbitals we must consider their relative energies to determine which orbitals will overlap significantly and form delocalized molecular orbitals.

The 1s atomic orbital on oxygen possesses a much lower energy than any of the other orbitals of a_1 symmetry and should not interact significantly with them. The molecular orbital of lowest energy in H_2O should therefore correspond to an inner shell 1s atomic like orbital centered on the oxygen. This is the first orbital of a_1 symmetry and it is labeled $1a_1$. Notice that the orbital energy of the $1a_1$ molecular orbital is very similar to that for the 1s atomic orbital on oxygen.

symmetry on oxygen. This orbital will overlap with the $(1s_1 + 1s_2)$ combination of orbitals on the H atoms to form the $2a_1$ molecular orbital and is a binding orbital. Aside from the presence of the second proton, the general form and nodal structure of the $2a_1$ density distribution in the H_2O molecule is remarkably similar to the 2σ distributions in HF molecule.

Although the three 2p atomic orbitals are degenerate in the O atom, the presence of the two protons results in each 2p orbital experiencing a different potential field in the H_2O molecule. The nonequivalence of the 2p orbitals in the H_2O molecule is evidenced by all three possessing different symmetry properties. The three 2p orbitals will interact to different extents with the protons and their energies will differ.

The $2p_x$ orbital interacts with the protons and forms an orbital of b_2 symmetry by overlapping with the $(1s_1 - 1s_2)$ combinations of 1s orbitals on the hydrogens and the result is the $1b_2$ molecular orbital. The $1b_2$ orbital concentrates charge density along each O-H bond axis and draws the nuclei together. The charge density of $1b_2$ orbital binds all the three nuclei.

The $2p_z$ orbital may also overlap with the H 1s orbitals, the $(1s_1 + 1s_2)$ a_1 combination, and the result is the $3a_1$ molecular orbital. This orbital is concentrated along the z-axis and charge density is accumulated in both the bonded and non-bonded sides of the O nucleus. It exerts a binding force on the protons and an anti-binding force on the oxygen nucleus.

The $2p_y$ orbital is not of the correct symmetry to overlap with the hydrogen 1s orbitals. The $1b_1$ molecular orbital will be simply a $2p_y$ atomic orbital on the O, perpendicular to the plane of the molecule. The electronic configuration of the H_2O

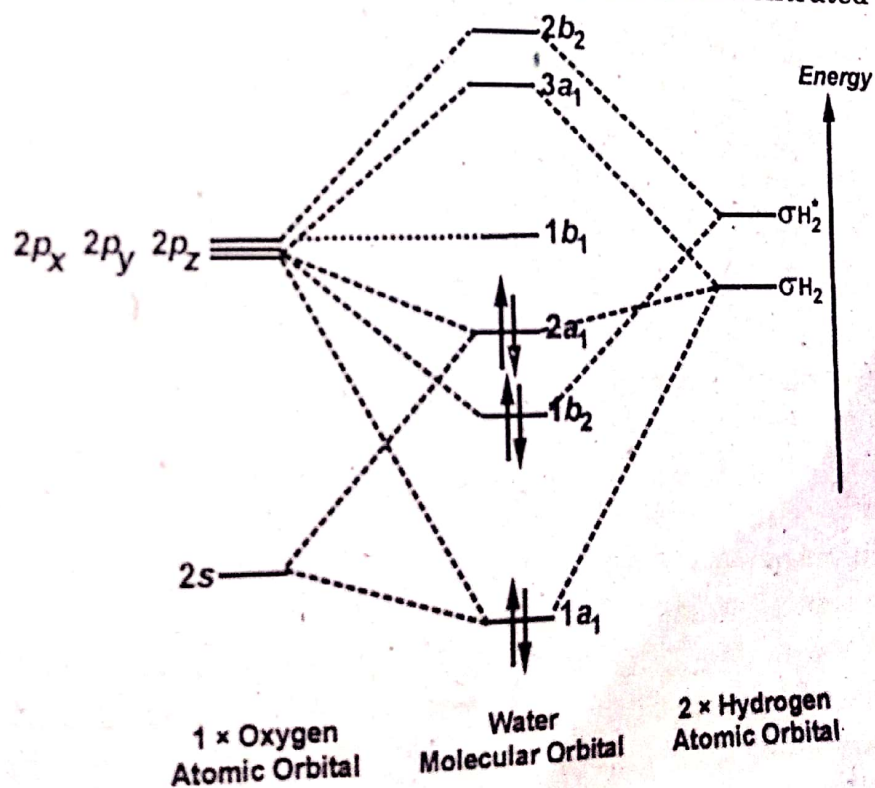


Fig. H_2O Molecule

molecular as determined by MOT is: $1a_1^2, 2a_1^2, 1b_2^2, 3a_1^2, 1b_1^2$

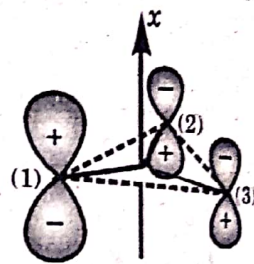
Trigonal planar Molecules: AB_3

An important and more general application of MO theory in polyatomic molecules deals with π bonding in planar systems. One important group of these symmetrical compounds of the general formula AB_3 , e.g., BF_3 , CO_3^{2-} and NO_3^- , then the π bond system will be formed entirely by the p_x atomic orbitals of the peripheral B atoms. The π -bond system must then have a node in the zy plane. Consistent with this, the MO approach involves overlap that encompasses the whole structure.

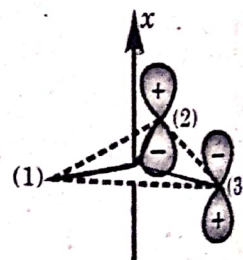
There are three linear combinations of p_x atomic orbitals from the peripheral B atoms of AB_3 . We shall not discuss the methods that are used to deduce these particular linear combinations, except to point out that these three particular linear combinations have been chosen to provide the best total, positive overlap with the atomic p_x orbital of the central atom A. These three linear combinations are termed **group orbitals** as shown in Fig. 2.54. The linear combinations [group orbitals (GO)] represented in the Fig. 2.54 arise from three distinct arrangements of the p_x atomic orbital at the vertices of the AB_3 triangle.

Only one group orbital of Fig. 2.54 has non-zero overlap with the p_x atomic orbital of the central atom A as shown in Fig. 2.55. The other two interactions are non-bonding (e.g., π_{2a} and π_{2b}) and the resultant MO's appear in the energy-level diagram of Fig. 2.56 with energy that are unchanged. One of the interactions shown in Fig. 2.55 is bonding and this leads to the π_1 molecular orbital shown in Fig. 2.56 as π_1^* .

$$(a) GO_1 = p_x(1) - p_x(2) - p_x(3)$$



$$(b) GO_2 = p_x(2) - p_x(3)$$



$$(c) GO_3 = p_x(1) + p_x(2) + p_x(3)$$

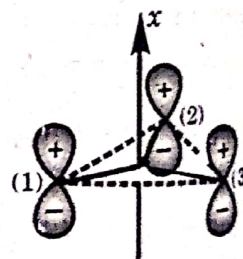


Fig. 2.54. Three combinations of p_x orbitals from the three outer B atoms of a planar AB_3 molecule. Each combination (called a group orbital) is multicentered and each is constructed to be used as a group in overlap with the p_x atomic orbital of the central atom A, as shown in Fig. 2.55.

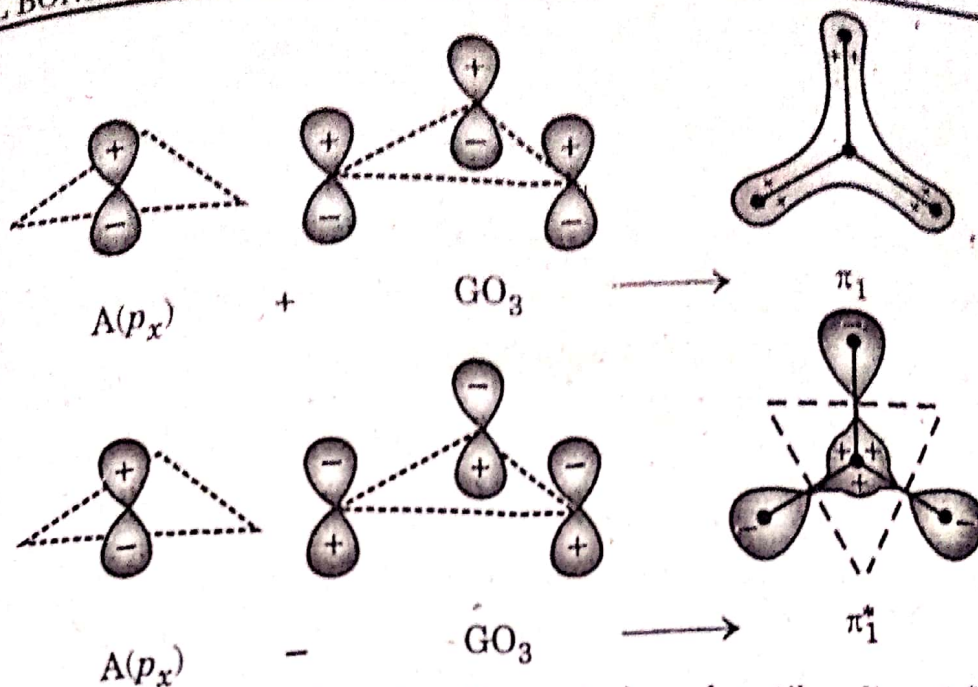


Fig. 2.55. Diagrams showing how bonding (π_1) and antibonding (π_1^*) molecular orbitals are formed in an AB₃ molecule using the p_x orbital of the central atom A and a group orbital (GO_3 of Fig. 2.54) from the outer atoms B. The MO's themselves, at the right, are viewed from above. The MO's change sign in the molecular plane, as do the p_x atomic orbitals from which they are formed. In addition, π_1^* has three nodal planes perpendicular to the molecular plane.

For each of the species BF₃, CO₃²⁻, or NO₃⁻, there are only 6 electrons to occupy the π molecular orbitals of Fig. 2.56 (The other 18 valence electrons occupy the various σ orbitals of the yz plane). The six π electrons are distributed as shown in Fig. 2.56. The 4 electrons in the two degenerate orbitals (π_{2a} and π_{2b}) neither contribute to nor detract the stability of the π bond system because they are nonbonding. Thus the π -bonding stability is provided entirely by the one electron pair in the π_1 molecular orbital. The total π bond order of one is equally distributed over the three equivalent AB regions so that the net π bond per AB group is one-third. The conclusion here is that one π bond is delocalized over three AB pairs.

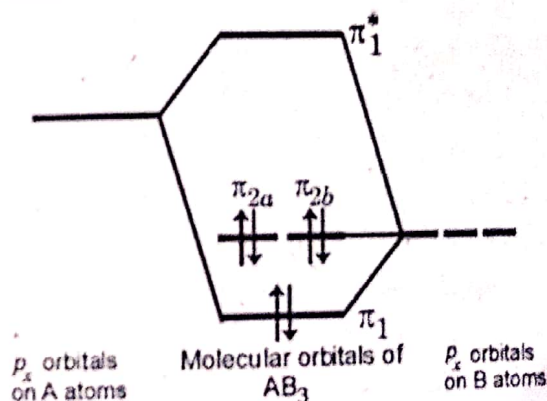


Fig. 2.56. The MO energy-level diagram for the p-bond system in a planar, symmetrical AB₃ molecule. The symbol π_1 and π_1^* correspond to those used in Fig. 2.55. The nonbonding orbitals π_{2a} and π_{2b} are essentially GO_1 and GO_2 of Fig. 2.54.

Example 2.3: What is the form of the wave function that describes a molecule in which an electron spends 90 per cent of its time in an orbital ψ_A on A and 10 percent in ψ_B on B in the polar molecule AB?

Solution. The wave function is written in the form: