STRUCTURE OF ATOM - V

Molecular Orbital Theory :-

(1927 - 28 : Hund and Mulliken. 1929 - Lennard Jones)

In Molecular Orbital (MO) Theory, it is assumed that each electron in a molecule is described by a certain wavefunction ψ. This wavefunction describes the electron in the molecule and hence it is called a molecular orbital.

These orbitals are polycentric and the electrons are supposed to move over all the nuclei in the molecule and not in range of a particular nucleus. Each of these orbitals represents a state at which the square of the molecular wavefunction (MO) is a measure of the probability of finding the electron at any point. Each MO is associated with a definite energy and the total energy of the molecule is the sum of energies of all the occupied molecular orbitals, ignoring the mutual interaction between the electrons.

It is imagined that the total number of electrons present in a molecule are fed into the available MO's in an increasing order of energy, as per Pauli's exclusion principle. The shape and energy of these orbitals can be obtained from the solutions of molecular Schrödinger equation.

The basic principles of the MO treatment are thus analogous to those used for atomic orbitals.

Just as the simple harmonic waves are combined when they are superposed to form another wavefunction (principle of superposition), the MO may be obtained by taking linear combination of atomic orbitals, called LCAO.

If ϕ_a and ϕ_b are the AO's on atoms A and B respectively, then MO's (ψ) are written as —

$$\psi_1 = C_a \phi_a(1) + C_b \phi_b(1)$$

$$\psi_2 = C_a \phi_a(2) + C_b \phi_b(2) \qquad \cdots (i)$$

Where C's are arbitrary constants chosen to give lowest-energy value of the molecular orbital and electrons 1 and 2 are placed with AO's ϕ_a and ϕ_b.

In general, if $\phi_1, \phi_2, \phi_3, \ldots, \phi_n$ be the atomic orbitals on atoms $1, 2, 3, \ldots, n$, respectively, then MO are written as

$$\psi_i = \sum_{j}^{a} c_j \psi_j \qquad \cdots (ii)$$

The total molecular wave function can be written as the product of all MO's, i.e.

$$\psi = \psi_1 \cdot \psi_2 \cdot \psi_3 \cdots \psi_n \qquad \cdots (iii).$$

MO Treatment of the Homonuclear Diatomic Molecules:

In the case of homonuclear diatomic molecules, in addition to $1s$ orbitals, $2s$, $2p$ and $3d$ orbitals are also involved in the formation of MO's. But all the combinations of AO's do not lead to the formation of an MO. The AO's taking part in the formation of MO's should fulfill the following requirements:—

(i) The AO's forming the MO should have similar energy.

(ii) The AO's should overlap to a considerable extent so that the bond becomes stronger.

(iii) The signs of the wavefunctions of the overlapping portions of the orbitals must be the same. (Same symmetry).

When two AO's combine, two MO's are formed — a bonding orbital and an antibonding orbital.

When the overlap between two atomic orbitals takes place along the internuclear axis and is symmetrical about it, the bond is called a σ (sigma) bond. eg. Two $1s$ hydrogen orbitals form a σ bond.

But in case of p-orbitals, two types of bonds are formed.

when the lobes of the two p-orbitals are along the internuclear axis, a σ-bond is formed. On the other hand, if the lobes of p-orbitals are perpendicular to the internuclear axis, they can form, π (Pi) bonds. Since p-orbitals in an atom are mutually perpendicular, if two sets of p-orbitals overlap, then one will be a σ-bond and the other two will be π-bonds.

A π-bond is weaker than a σ-bond since the net accumulation of charges along the internuclear axis is maximum in case of a σ-bond. The antibonding orbitals of both σ and π types are generally designated with an asterisk (*).

The designation of molecular orbitals are σ, π, etc. is based on the value of the angular momentum component along the z-axis. The component of the MO angular momentum for an electron along the internuclear axis (z-axis) is $\frac{\lambda h}{2\pi}$, where $\lambda = M_L = 0, \pm 1, \pm 2, \pm 3, \ldots$

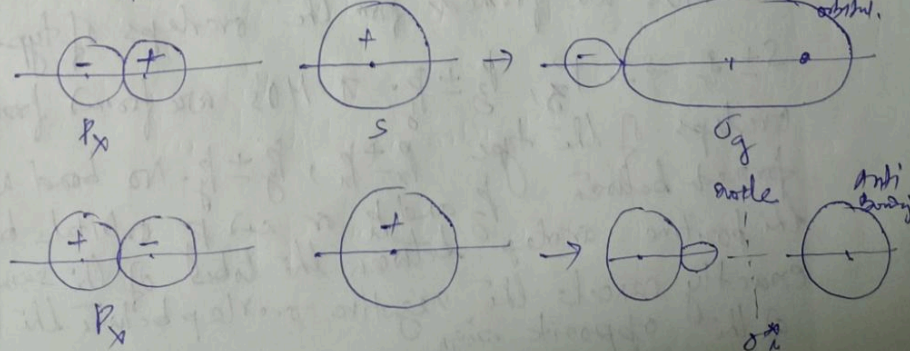| value of quant. no. : (λ)	0	1	2	3
Designation of orbit. (φ)	σ	π	δ	φ

Inversion :

Starting from any point of a the molecule, exactly similar points are encountered by proceeding in a straight-line on the other side of the centre, then the molecule is said to possess a centre of symmetry. Such a process is known as inversion.
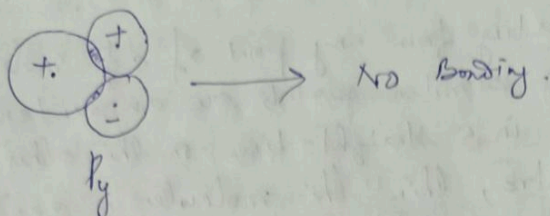
When the inversion causes no change in the sign of the wavefunction ψ (MO), the orbital is represented by g (eg. σ_g, π_g, etc.) and if inversion causes a change in sign of the wavefunction, the orbital is denoted by u (ungerade, eg. σ_u, π_u, etc.)

In general, a sigma MO is of type g-type, thus σ_g and a π-MO is of u-type, thus π_u.

Shapes of Molecular Orbitals :-

AO   MO

P_x S   Bonding orbital. σ_g
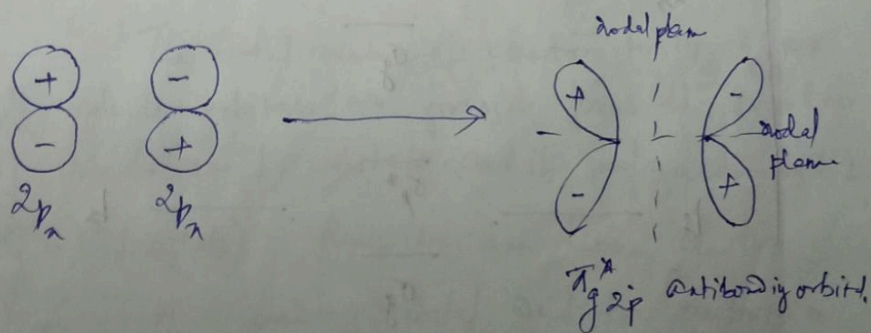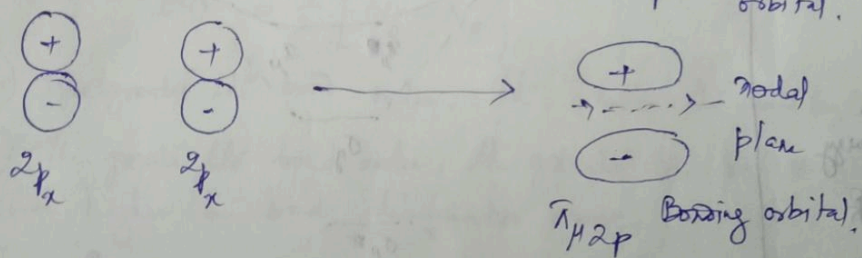
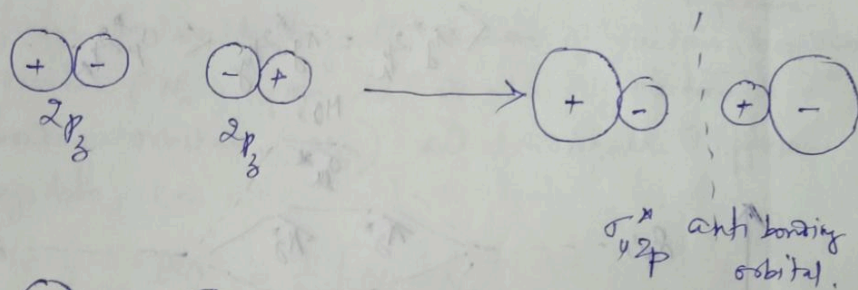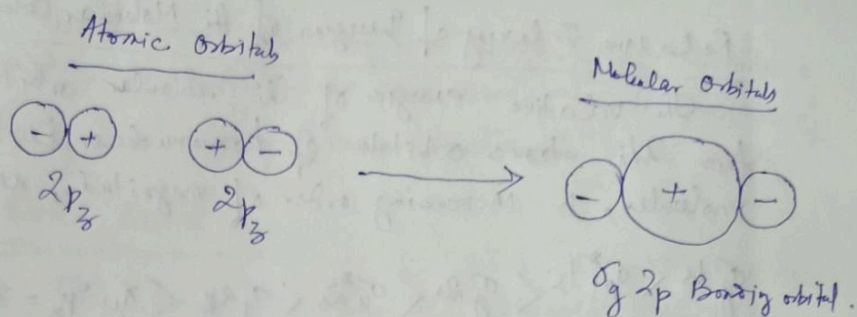P_x Anti Bonding σ_u^{*}

P_y

s-orbital overlaps with a p-orbital (P_z) along with the internuclear axis forming a σ-bond. However, s-orbital does not form molecular orbitals with P_x and P_y orbitals, i.e., with a p-orbital which is perpendicular to the internuclear axis, because, in one region the amplitudes of the orbitals interfere constructively, while in the other region they interfere destructively to an exactly equivalent extent. As a result, the net accumulation of electron density in one region (i.e. positive overlap) is compensated by its disappearance from the other (i.e. negative overlap). Therefore, the overlap integral S_{ab} is zero and hence the orbitals are said to be orthogonal.

Now, if we take the internuclear axis as the z-axis, σ-MO's are formed from the overlaps of type

$s \pm s$, $s \pm P_z$, $P_z \pm P_z$. π MO's are formed from the overlaps of the type $P_x \pm P_x$, $P_y \pm P_y$. No bond will be formed between P_z and P_x or and P_y orbitals because the positive overlap between the lobes of the same sign exactly cancels the negative overlap between the lobes of the opposite sign.

Atomic Orbitals   Molecular Orbitals

$2p_z$ $2p_z$ $\longrightarrow$ $\sigma_g 2p$ Bonding orbital.

$2p_z$ $2p_z$ $\longrightarrow$ $\sigma_u^* 2p$ anti bonding orbital.

$2p_x$ $2p_x$ $\longrightarrow$ nodal plane

$\pi_u 2p$ Bonding orbital.

nodal plane

$2p_x$ $2p_x$ $\longrightarrow$ nodal plane

$\pi_g^* 2p$ antibonding orbital.

Relative Ordering of Energies of the Molecular Orbitals:

The relative energies of the molecular orbitals formed from the atomic orbitals of homonuclear diatomic molecules, in increasing order of magnitude, are

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \sigma_g 2p_z < \pi_u 2p_x = \pi_u 2p_y$$

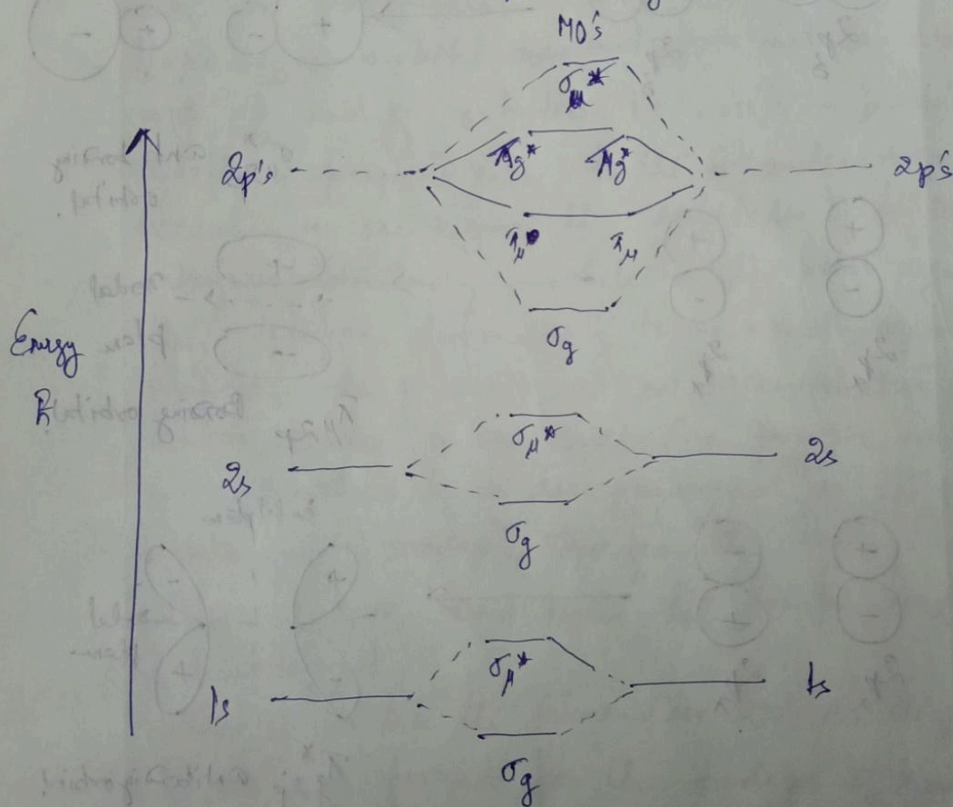$$< \pi_g^* 2p_x = \pi_g^* 2p_y < \sigma_u^* 2p_z \quad --- (i)$$

MO's

Fig: Energy level diagram for a homonuclear diatomic molecule.

For diatomic molecules upto nitrogen (N_2), this order is slightly changed. For such cases, only the position of $\sigma_g 2p_z$ and $\pi_u 2p$ are interchanged in the series.

Bond order :

The bond order gives the strength of a bond. In a diatomic molecule, the bond order is found by subtracting the number of electrons in antibonding orbitals (N_a) from the number of electrons in the bonding orbitals (N_b) and dividing the difference by two, i.e.,

$$BO = \frac{1}{2}\left[N_b - N_a\right]$$

i) The greater the bond order, the shorter the bond length.

ii) The greater the bond order, the greater the bond strength and higher the bond dissociation energy.

He_2 : The total number of electrons in He_2 is four. Its molecular orbitals are formed from the overlap of two helium 1s orbitals and its configuration will be $\left(\sigma_g 1s\right)^2 \left(\sigma_u^* 1s\right)^2$. Here, we see there are two electrons in the bonding orbital and two electrons in the antibonding orbitals. The latter electrons cancel the effect of the bonding electron. Its bond order is zero. Therefore, the He_2 molecules does not exist under normal conditions.

Li_2 : Its electronic configuration is

$$2 Li \, (1s^2 2s^1) \longrightarrow Li_2 \left[(\sigma_g 1s)^2 (\sigma_M^* 1s)^2 (\sigma_g 2s)^2 \right]$$
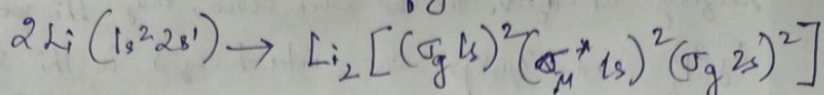
Since the bonding associated with $(\sigma_g 1s)^2$ electrons is cancelled by antibonding effect of $(\sigma_M^* 1s)^2$, the bonding between the two lithium atoms results from the pairing of only 2s orbitals. Writing $(\sigma_g 1s)^2 (\sigma_M^* 1s)^2$ equal to KK, indicating the two undisturbed K shells, the ground state of lithium molecule can be written as $Li_2 [KK (\sigma_g 2s)^2]$.

Bond order for Li_2 molecule is 1 and is stable. However, it is less stable than the H_2 molecule.

N_2 : It has fourteen electrons. Its electronic configuration is

$$(\sigma_g 1s)^2 (\sigma_M^* 1s)^2 (\sigma_g 2s)^2 (\sigma_M^* 2s)^2 (\pi_M 2p_x = \pi_M 2p_y)^4 (\sigma_g 2p_z)^2$$
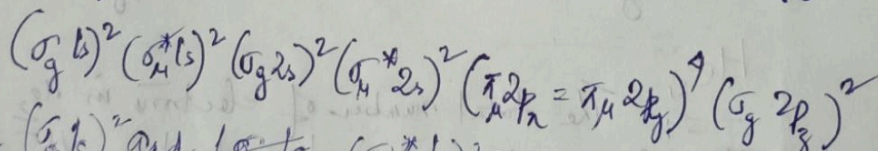
The $(\sigma_g 1s)^2$ and $(\sigma_g 1s)^2 (\sigma_M^* 1s)^2$ are cancelled by their antibonding counterparts. Therefore, the bonding orbitals, which are not cancelled by the corresponding antibonding orbitals are $(\sigma_g 2p_z)^2 (\pi_M 2p_y)^4$. Therefore, the net number of bonds in nitrogen molecule is three — one sigma and two pi-bonds. Its bond order is 3.
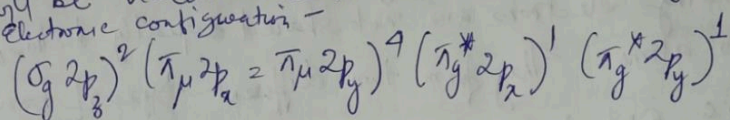
$$B.O. (N_2) = \frac{10-4}{2} = \frac{6}{2} = 3$$

$$B.O. (N_2^+) = \frac{10-3}{2} = \frac{7}{2} = 3.5 \checkmark$$

$$B.O. (N_2^-) = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

O_2: — The O_2 molecule has two more electrons than the N_2 molecule. These two electrons will go to antibonding π_g^* orbitals. Since the energies of the two π_g^* MO's are same, by Hund's Rule, one electron will be accomodated in each antibonding orbital.
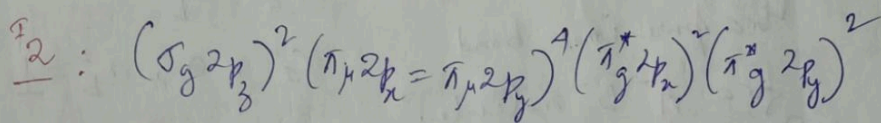
Electronic configuration —

$$(\sigma_g 2p_z)^2 (\pi_\mu 2p_x = \pi_\mu 2p_y)^4 (\pi_g^* 2p_x)^1 (\pi_g^* 2p_y)^1$$
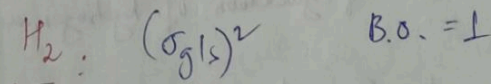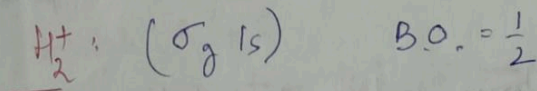
Bond order is 2. $\qquad \left(\because \dfrac{6-2}{2} = 2 \right)$

It is a stable molecule and its stability is decreased if one electron is added to the molecule, while the removal of an electron strenghtens the bond in terms of bond order.

Since the electrons in the last two orbitals are having parallel spin, this gives rise to the ~~paras~~ **paramagnetic character** of oxygen molecule.

$\overline{2}^{\mathcal{I}}$: $(\sigma_g 2p_z)^2 (\pi_\mu 2p_x = \pi_\mu 2p_y)^4 (\pi_g^* 2p_x)^2 (\pi_g^* 2p_y)^2$

B.O. = 1

H_2^+: $(\sigma_g 1s)$ $\qquad$ B.O. = $\dfrac{1}{2}$

H_2: $(\sigma_g 1s)^2$ $\qquad$ B.O. = 1

(GA)

Molecular Orbital (MO) Treatment of the Heteronuclear Diatomic Molecules :-

By applying $\angle CAO-MO$ theory to diatomic molecules, it is found that MO's are not symmetric with respect to the plane bisecting the internuclear axis. Moreover, bonding electrons are not shared equally between the two atoms. They form two different types of bonds — ionic and polar bonds.

It is given by —

$$\psi_{MO} = c_a \phi_a + c_b \phi_b$$

where c_a and c_b are coefficients. The square of any one of these coefficients gives the fraction of the atomic orbital involved in bond formation, i.e. the proportion of ϕ_a in the bond formation is c_a^2 and that of ϕ_b is c_b^2.
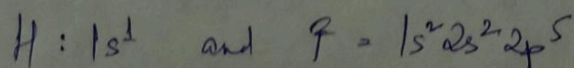
For a pure covalent bond, $c_a^2 = c_b^2$

For a pure ionic bond , $c_a^2 = 0 , c_b^2 = 1$

for a $A^+ B^-$ molecule.

So, a heteronuclear diatomic molecule will be polar in nature.

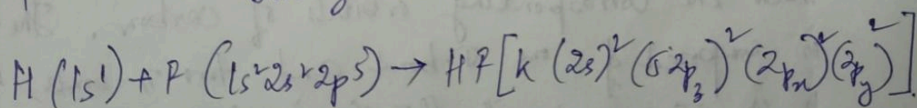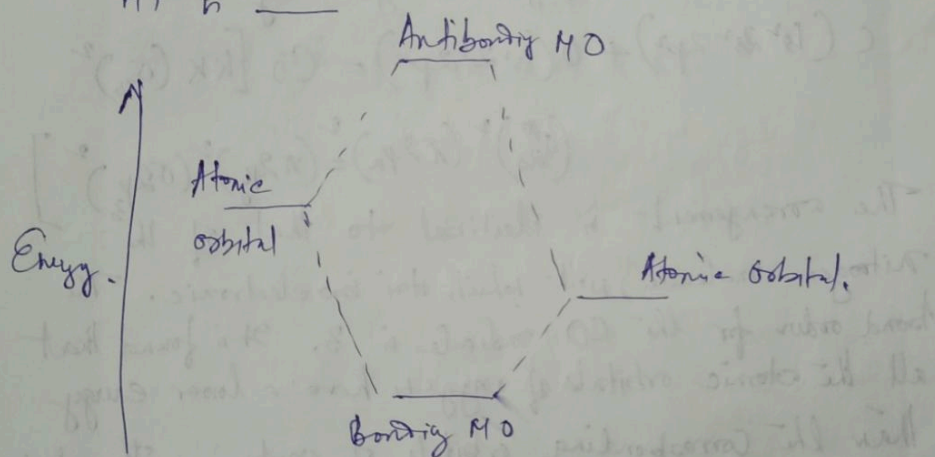(i) <u>HF</u> :- The electronic configuration of hydrogen and fluorine are —

$$H : 1s^1 \quad \text{and} \quad F = 1s^2 2s^2 2p^5$$

The MO describing the H–F bond must be formed from a Linear Combination of a $1s_H$ orbital

with one of the fluorine AO's.

From the spectroscopic studies, it is found that the energies of 1s and 2s electrons in fluorine are low, compared to $1s_H$ orbitals, but the energy of 2p orbital of fluorine is close to that of $1s_H$ orbital. We may consider the overlapping of the $2p_z$ orbital of fluorine with the $1s_H$ orbital. The basic energy level diagram of a heteronuclear diatomic molecule HF is ____

Antibonding MO

Atomic
orbital

Energy.

Atomic orbital.

Bonding MO

$$H\,(1s^1) + F\,(1s^2 2s^2 2p^5) \rightarrow HF\left[k\,(2s)^2\left(\sigma 2p_z\right)^2\left(2p_x\right)^2\left(2p_y\right)^2\right].$$

As a result of the overlapping, a σ bond will be formed. $2p_x$, $2p_y$ orbitals are the non-bonding orbitals in HF.
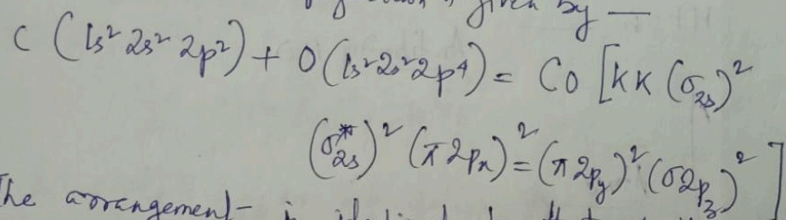
Calculation shows that its bonding MO has the form $[0.45\,(1s_H) + 0.82\,(2p_z)]$. Therefore, the proportion of $1s_H$ orbitals, involved in the formation of MO, is $(0.45)^2/[(0.45)^2 + (0.82)^2] = 0.23$ and
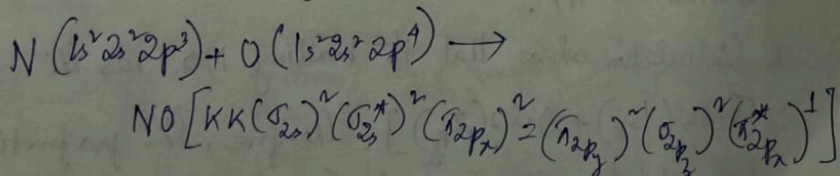
the proportion of the $2p_z$ orbital is 0.77. In other words, an electron occupying a MO will spend 77% of its time near the fluorine atom, thus justifying the polar nature of the HF molecule.

(ii) <u>CO</u> : The configuration is given by —

$$C\left(1s^2\,2s^2\,2p^2\right) + O\left(1s^2 2s^2 2p^4\right) = CO\left[KK\,(\sigma_{2s})^2\right.$$

$$\left.(\sigma_{2s}^{*})^2\,(\pi\,2p_x)^2 = (\pi\,2p_y)^2\,(\sigma 2p_z)^2\right]$$

The arrangement is identical to that of the nitrogen molecule, with which it is isoelectronic. The bond order for the CO molecule is 3. It is found that all the atomic orbitals of oxygen have a lower energy than the corresponding orbitals of carbon. The molecule is composed of one σ-bond and two π-bonds, which is in agreement with the Lewis electron structure: $C\equiv O$.

(iii) <u>NO</u> : The molecule of NO has 15 electrons and its electronic configuration is

$$N\left(1s^2 2s^2 2p^3\right) + O\left(1s^2 2s^2 2p^4\right) \longrightarrow$$

$$NO\left[KK(\sigma_{2s})^2(\sigma_{2s}^{*})^2(\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma_{2p_z})^2 (\pi_{2p_x}^{*})^1\right]$$

Its electronic configuration is like that of CO

with the extra electron in the antibonding $\pi^*_{2p_x}$ orbital.

This single electron gives rise to paramagnetism in NO. The antibonding orbital $\pi^*_{2p_x}$ weakens the bonding between nitrogen and oxygen and consequently, the bond in NO is weaker than that in the CO molecule.

The bond order of NO is 2.5.