VIVEKANANDA COLLEGE
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NAAC ACCREDITED 'A' GRADE

Topic: MO THEORY

Course Title: CC-2-4-TH

Paper: 4

Unit: L-1

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Name of the Teacher: R Mondal

Name of the Department: Chemistry

Theoretical basis of MO theory in view wave mechanics,

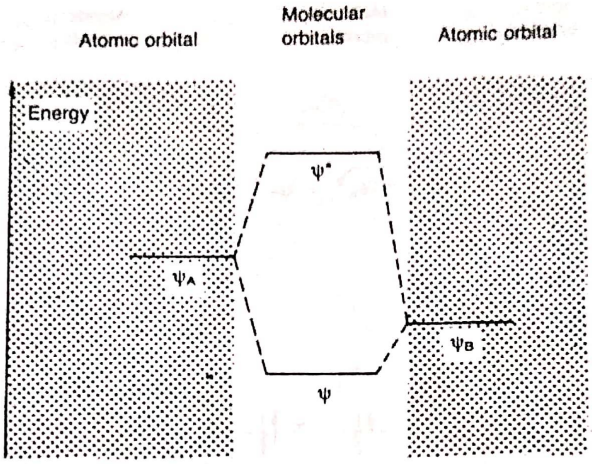

Figure 4.30 The relative energy levels of atomic orbitals and molecular orbitals for a heteronuclear diatomic molecule AB.

The problem is that in many cases the order of MO energy levels is not known with certainty. Thus we will consider first some examples where the two different atoms are close to each other in the periodic table, and consequently it is reasonable to assume that the order of energies for the MOs are the same as for homonuclear molecules.

NO molecule

The nitrogen atom has 2 + 5 = 7 electrons, and the oxygen atom has 2 + 6 = 8 electrons, making 15 electrons in the molecule. The order of energy levels of the various MOs are the same as for homonuclear diatomic molecules heavier than C_2, so the arrangement is:

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2,\ \sigma 2p_x^2,\ \begin{cases} \pi 2p_y^2, \\ \pi 2p_z^2, \end{cases}\ \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{cases}$$

This is shown in Figure 4.31.

The inner shell is non-bonding. The bonding and antibonding 2*s* orbitals cancel, and a σ bond is formed by the filled $\sigma 2p_x^2$ orbital. A π bond is formed by the filled $\pi 2p_z^2$ orbital. The half-filled $\pi^* 2p_y^1$ half cancels the filled $\pi 2p_z^2$ orbital, thus giving half a bond. The bond order is thus $2\frac{1}{2}$, that is in between a double and a triple bond. Alternatively the bond order may be worked out as (bonding − antibonding)/2, that is $(10 - 5)/2 = 2\frac{1}{2}$. The molecule is paramagnetic since it contains an unpaired electron. In NO there is a significant difference of about 250 kJ mol^{-1} in the energy of the AOs involved, so that combination of AOs to give MOs is less effective than in O_2 or N_2. The bonds are therefore weaker than might be expected. Apart from this the molecular orbital pattern (Figure 4.31)

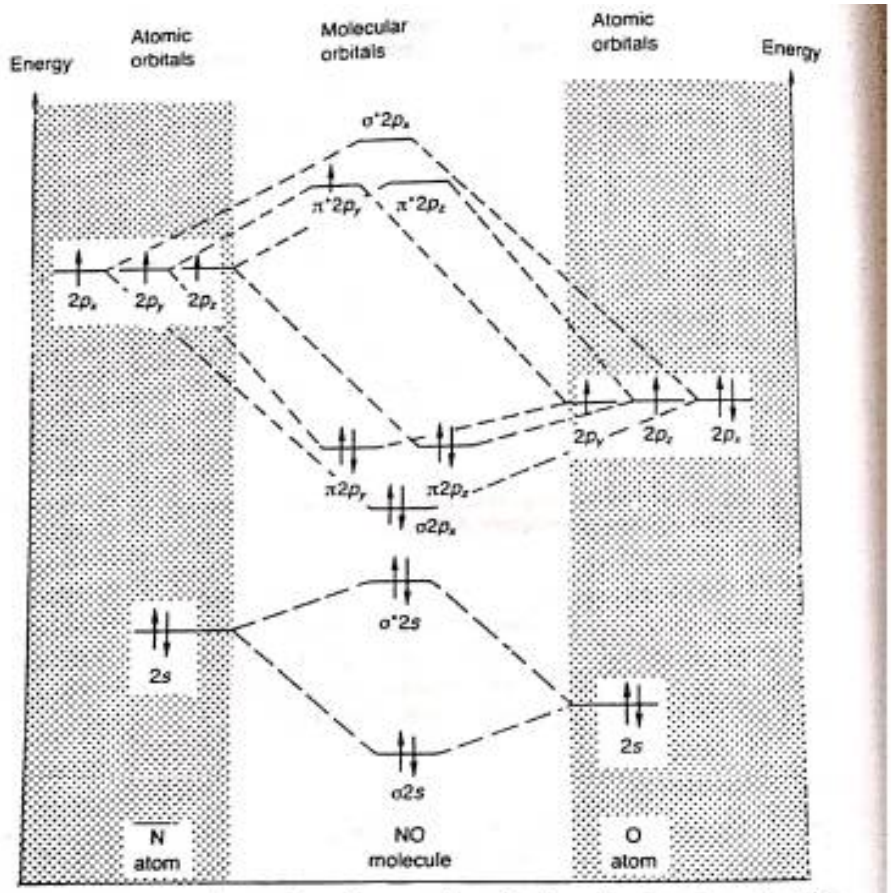

Figure 4.31 Electronic configuration, atomic orbitals and molecular orbitals for nitric oxide. (This diagram is essentially the same as that for homonuclear diatomic molecules such as N_2, O_2 or F_2. The difference is that the atomic energy levels of N and O are not the same. The $\sigma 1s$ and $\sigma^* 1s$ MOs are omitted for simplicity.)

is similar to that for homonuclear diatomic molecules. Removal of one electron to make NO^+ results in a shorter and stronger bond because the electron is removed from an antibonding orbital, thus increasing the bond order to 3.

CO molecule

The carbon atom has 2 + 4 = 6 electrons, and the O atom has 2 + 6 = 8 electrons, so the CO molecule contains 14 electrons. In this case we are rather less certain of the order of energies of the MOs, since they are different for C and O. Assume the order is the same as for light atoms like C: