Explanation is based on half filled and completely filled d orbital.

1.7   The Molecular Orbital Theory

- The Molecular Orbital Theory was put forth in the 1930s by F Hund and R.S. Mulliken and later it was developed by J.E. Lennard-Jones and Charles Coulson.

- Earlier to this valence bond theory was also proposed by Linus Pauling. The two theories reflect distinctly different conceptual approaches to the basic structural model of a molecule. For example, according to VBT only the half filled atomic orbitals of one atom overlaps with the half filled atomic orbital of the other atom resulting in the formation of a covalent bond. Their completely filled atomic orbitals remain intact. But in MOT, the nuclei of the two atoms lie at appropriate distance so that all the atomic orbitlas of one atom overlap with all the atomic orbital of the other atom provided the overlapping orbitals are of the same symmetry.

- The resulting polynuclear molecular orbitals contain all the electrons of the molecule, which move along the entire molecule under the influence of all the nuclei. Thus according to MOT molecule is supposed to have orbitals of varying energy levels in the same way as an isolated atom has. These orbitals are called molecular orbitals.

- Pauli's exclusion principle, Hund's rule of maximum multiplicity and Aufbau principle hold for the molecule just as they do for an atom. Each MO can accommodate maximum of two electrons with opposite spins.

- If a molecule has 'n' electrons, then the combined configuration wave function of the system would be given by,

$$\psi = \psi_1 \cdot \psi_2 \cdot \psi_3 \dots \psi_n$$

Where, ψ_1, $\psi_2 \dots \psi_n$ etc are one-electron molecular orbital wave function.

- MO's are formed by the linear combination of atomic orbitals. Total number of MO's formed is equal to the total number of AO's combined to form the molecule. Addition overlap of atomic orbitals give bonding molecular orbitals (BMO) (ψ_+). It's energy (E_+) is lower, than that of either of the atomic orbitals. Also, the subtraction overlap give anti bonding molecular orbital (ABMO) (ψ_-) and its energy E_- is higher than that of either of the atomic orbitals.

- The extent of lowering of energy of the BMO is approximately equal to the extent of increase of energy of the ABMO, as shown in Fig. 1.7.1.
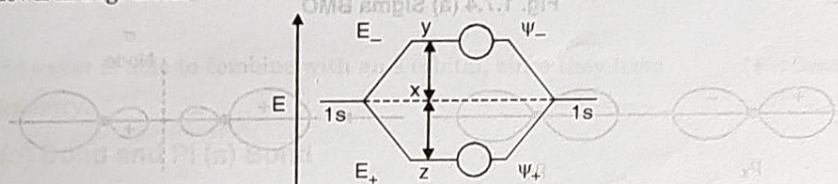

Fig. 1.7.1 : Energies of BMO and ABMO (more precisely XZ < XY)

1.7.1　Combination of Atomic Orbitals to form Molecular Orbitals

There are two methods of combination of atomic orbitals. One is by the additive combination while the second one is by the subtractive combination. Let as discuss this with few examples.

(a)　Combination of s-s atomic orbitals

- Linear additive combination gives a BMO. It is also called sigma (σ) orbital. It is symmetrical about the molecular axis.

- While linear subtractive combination give a ABMO and it is designated as σ^*

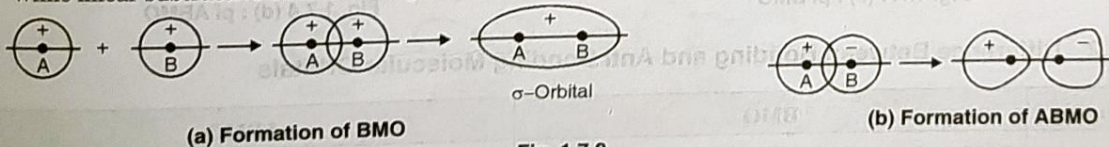(a) Formation of BMO　　　　　　　　　　　　(b) Formation of ABMO

Fig. 1.7.2

(b)　Combination of s-p orbitals

- One s orbital may combine with a p-orbital provided that the lobes of p orbital are along the axis joining the nuclei. Additive combination gives BMO with an increased electron density between the nuclei.
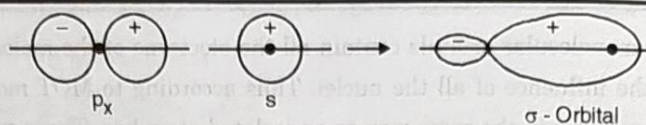
p_x s σ - Orbital

Fig. 1.7.3 (a) Sigma MO

- While linear subtractive combination give an ABMO and the designated by σ^*
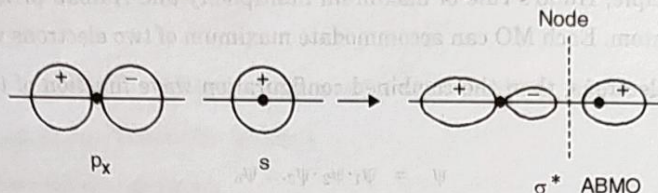

Node

p_x s σ^* ABMO

Fig. 1.7.3 (b) : Sigma ABMO

(c) Combination of p-p orbitals

- Consider first the combination of two p-orbitals which both have lobes pointing along the axis joining the nuclei. BMO and ABMO are produced by additive and subtractive combination of atomic orbitals.
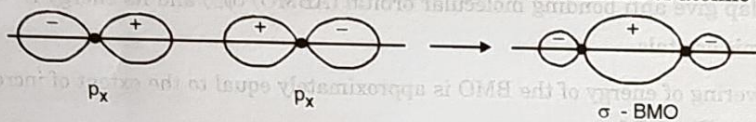

p_x p_x σ - BMO

Fig. 1.7.4 (a) Sigma BMO

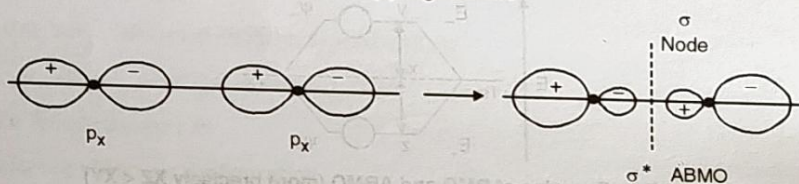

p_x p_x σ^* Node   ABMO

Fig. 1.7.4 (b) : Sigma ABMO

- Two p-orbitals having lobes perpendicular to the axis joining the nuclei, can also combine resulting π bonding and π^* antibonding MOs.
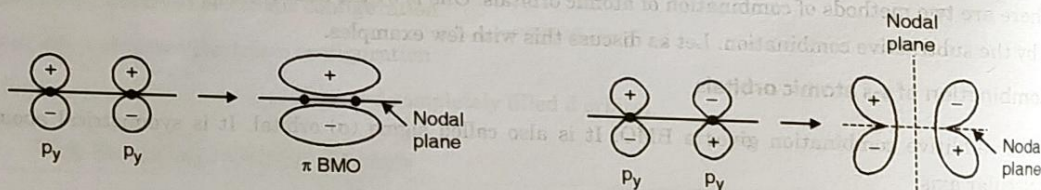

P_y P_y π BMO   Nodal plane

Fig. 1.7.4 (c) : pi BMO

Nodal plane

P_y P_y π^* ABMO   Nodal plane

Fig. 1.7.4 (d) : pi ABMO

1.7.2 Difference Between Bonding and Anti Bonding Molecular Orbitals

| Sr. No.	BMO	ABMO
1.	BMO is formed by additive linear combination of atomic orbitals	ABMO are formed by subtractive linear combination of atomic orbitals.
2.	Energy of BMO is lower than that of atomic orbitals from which it is formed.	It has higher energy than the AOs from which it is formed.

Sr. No.	BMO	ABMO
3.	BMO is stabilized by high electron density in between the nuclei, thus repulsion between nuclei is minimized.	ABMO is destabilized by low electron density in between the nuclei, thus repulsion between nuclei is very high.
4.	Electrons in BMO favour bond formation.	Electrons in ABMO oppose bond formation.

1.7.3 Conditions for the Combination of Atomic Orbitals

Not all atomic orbitals combine to give molecular orbitals. These are few limitations for this combination, which are as follows.

1. The energy of AOs involved should not differ much from one another. For example in formation of homonuclear diatomic molecule, 1s – orbital of one atom does not combine with 2s orbital of another atom of the same element. In case of hetero nuclear diatomic molecules of the type AB, such combination may be possible if the energy difference between the two combining atomic orbitals is not very high.

2. Atomic orbitals combine only if they overlap to a considerable extent. With increased overlap, electron charge density between the two nuclei is also increased, thereby minimizing their mutual repulsion.

3. The Atomic orbitals should have same symmetry about the molecular axis. For example p_x and p_y orbital does not combine with an s- orbital as they have different symmetry. Since (+ +) overlap is cancelled by (+ –) overlap.

   A p_z orbital however is able to combine with an s orbital, since they have the same symmetry.
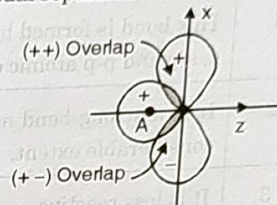
(++) Overlap

(+ –) Overlap

1.7.4 Sigma (σ) Bond and Pi (π) Bond

A covalent bond is formed by the overlapping of atomic orbitals. This overlapping can take place either along the axes of orbitals or perpendicular to their axes. Thus it gives rise to two types of bonds σ - and π - bonds.

(a) Sigma (σ) bond

Bond formed by end to end overlapping of AOs is known as σ - bond. Such a bond is formed by the overlapping of s-s, s-p or p-p orbitals along their axes. This is a strong bond because the overlapping is maximum.
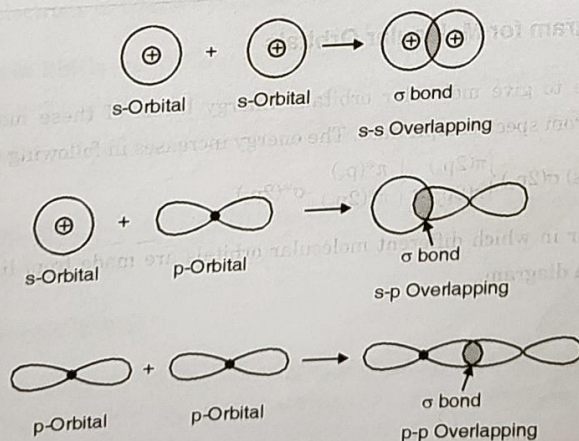
s-Orbital + s-Orbital → σ bond
s-s Overlapping

s-Orbital + p-Orbital → σ bond
s-p Overlapping

p-Orbital + p-Orbital → σ bond
p-p Overlapping

Fig. 1.7.5 : Formation of σ bonds

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(b) pi bond

The bond formed as a result of sideways overlapping of p-p orbitals is known π - bond. Because of partial overlapping pi bond is weak.
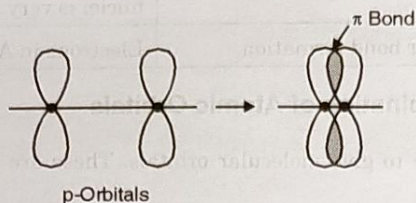

Fig. 1.7.6 : Formation of pi bond

1.7.5 Difference between σ and π - Bonds

Sr. No.	σ Bond	π Bond
1.	This bond is formed by end to end overlapping of s-s, s-p and p-p atomic orbitlas.	This bond formed by the sideways or partial overlapping of p-p atomic orbitals.
2.	It is a strong bond as atomic orbitals overlap to a considerable extent.	It is a weak bond as atomic orbitals overlap to a little extent.
3.	It is less reactive.	It is more reactive.
4.	There can be only one σ-bond between two atoms.	There can be more than one π-bond between two atoms.
5.	The electron cloud of σ-bond is symmetrical about the molecular axis.	The electron could of π- bond is unsymmetrical
6.	Shape of the molecules is determined by these bonds.	Shape of the molecule is not affected by these bonds.

1.7.6 Energy Level Diagram for Molecular Orbitals

Atomic orbitals combine to give molecular orbitals. Energy levels of these molecular orbitals have been determined experimentally from spectroscopic data. The energy increases in following order.

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

Following is the manner in which different molecular orbitals are made from linear combination of atomic orbitals and represented in a diagram.
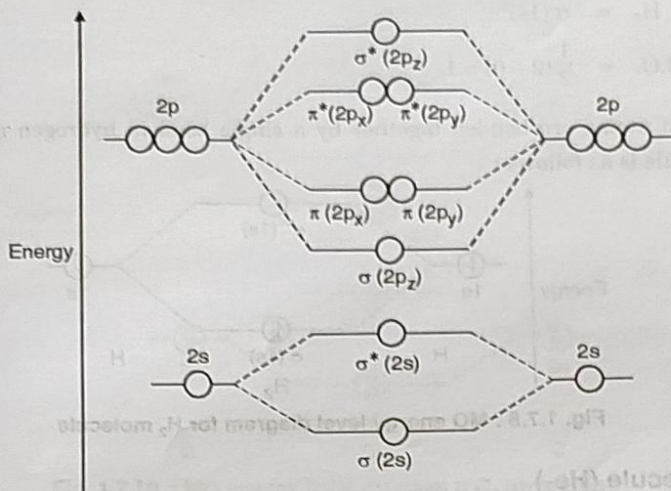
Fig. 1.7.7 : Energy levels of different Molecular orbitals

1.7.7 Rules for Adding Electrons to MOs

Pauli's exclusion principle, Hund's Rule of maximum multiplicity and Aufban principle hold for the molecule just as they do for an atom.

(i)　The molecular orbital with lowest energy is filled first.

(ii)　The maximum number of electrons in a MO cannot exceed two and two electrons must be of opposite spins.

(iii)　If there are two molecular orbitals at the same energy level, pairing of electrons will occur only after each orbital of the same energy is filled with one electron.

Bond order :

− Bond order of a molecule is related with the stability of the molecule. It is calculated from the number of electrons in bonding and anti bonding molecular orbital as follows.

$$B.O. = \frac{1}{2} \text{ [number of electrons in BMOs} - \text{number of electrons in ABMOs]}$$

− If number of electrons in BMOs and ABMOs are the same the bond order is zero i.e. no bond is formed. The bond order of 1,2 and 3 corresponds to single, double and triple bond, respectively.

− Bond order of a molecule is directly proportional to its bond dissociation energy and inversely proportional to it's bond length.

1.7.8 Molecular Orbital Energy Level of Homonuclear Diatomic Molecules

Few examples are listed as follows :

1.7.8 (A)　Hydrogen Molecule (H₂)

− It is formed by the combination of two H atoms. Each H atom has one electron in its 1s orbital. Hence two electrons to be accommodated is MOs. Electronic configuration of H_2 molecule is,

$$H_2 = \sigma(1s)^2$$

And
$$B.O. = \frac{1}{2}(2-0) = 1$$

- Hence, two hydrogen atoms are bonded together by a single bond in hydrogen molecule. MO energy level diagram of H_2 molecule is as follows :
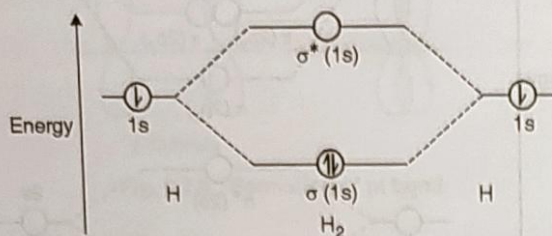

Fig. 1.7.8 : MO energy level diagram for H_2 molecule

1.7.8 (B)　Helium Molecule (He_2)

- It is formed by the combination of two He atoms. Each atom has two electrons in its 1s orbital. Hence four electron to be accommodated in MOs. Electronic configuration of He_2 is as follows.

$$He_2 = \sigma(1s)^2, \sigma^*(1s)^2 \text{ and}$$

$$B.O. = \frac{1}{2}(2-2) = 0$$

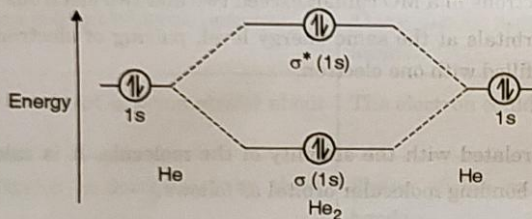- Zero bond order indicates that the molecule does not exist. MO energy level diagram is as follows.

Fig. 1.7.9 : MO energy level diagram of He_2 molecule

1.7.8 (C)　Carbon Molecule (C_2)

- Its electronic configuration is $1s^2\, 2s^2\, 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C_2 molecule, there will be evidently 8 electrons to be accommodated in the molecular orbitals of C_2.

$$C_2 : KK\, \sigma(2s)^2 \sigma^*(2s)^2 \begin{cases} \pi(2p_x)^2 \\ \pi(2p_y)^2 \end{cases}$$

$$\text{and Bond order} = \frac{1}{2}(6-2) = 2$$

- Since C_2 molecule does not have any unpaired electron. It is diamagnetic as observed experimentally. M.O. energy level diagram is as follows.
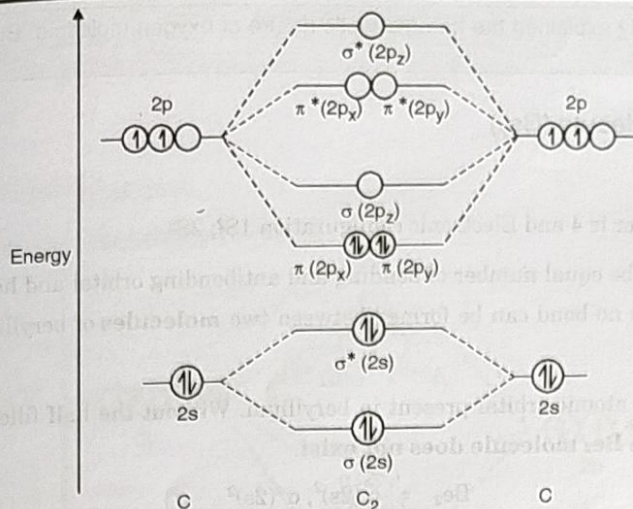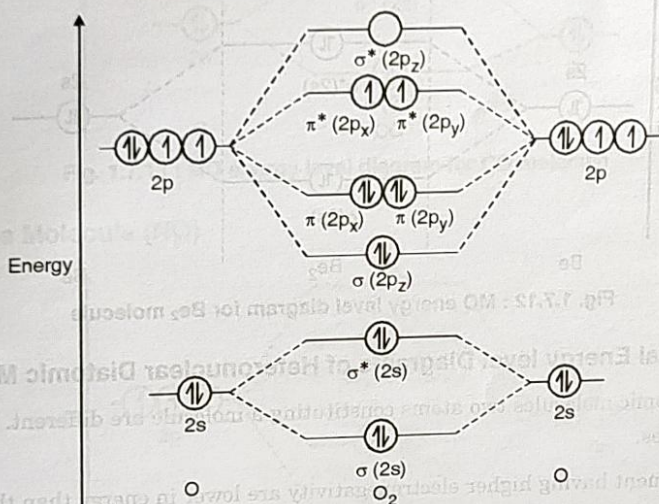
Fig. 1.7.10 : MO energy level diagram if C_2 molecule

1.7.8 (D) Oxygen Molecule (O_2)

Fig. 1.7.11 : MO energy level diagram of Oxygen molecule

- The electronic configuration of oxygen is $1s^2\ 2s^2\ 2p^4$. In the formation of O_2 molecule, 12 outer electrons to be accommodated in MOs, four of these electrons fill the $\sigma(2s)$ and $\sigma^*(2s)$ MOs. Six of these (3 pairs) go into these BMOs which is $\sigma(2p_z)$, $\pi(2p_x)$ and $\pi(2p_y)$. Now all BOMs are filled, the remaining two electrons go into the π^* $(2p_x)$ and $\pi^*(2p_y)$ ABMOs. Since both these orbitals are of equal energy the electron will be distributed themselves one-one in each orbital. Due to two unpaired electron in its ABMOs oxygen molecule is paramagnetic. The electronic configuration of oxygen molecule is.

- $O_2 : KK\ \sigma\ (2s)^2\sigma^*\ (2s)^2\ (2p_z)^2 \begin{cases} \pi\ (2p_x)^2 & \pi^*\ (2p_x)^1 \\ \pi\ (2p_y)^2 & \pi^*\ (2p_y)^1 \end{cases}$

- Bond order is $= \frac{1}{2}(8-4) = 2$

- Molecule thus contain a double bond

Note : MO theory successfully explained the paramagnetic nature of oxygen molecule. But valence bond theory was failed in explaining this.

1.7.8 (E) Beryllium Molecule (Be₂)

$-$ It is Diatomic molecule.

$-$ Berylliums atomic number is 4 and Electronic configuration $1S^2; 2S^2$

$-$ In case of **Be₂** there will be equal number of bonding and antibonding orbital and hence bond order comes out to be zero. Which means no bond can be formed between two **molecules** of beryllium and hence **Be₂** cannot exist.

$-$ There is no singly filled atomic orbital present in beryllium. Without the half filled orbital, the overlapping is **not** possible, therefore **Be₂** molecule does not exist.

$$Be_2 = \sigma(2s)^2, \sigma^*(2s)^2$$
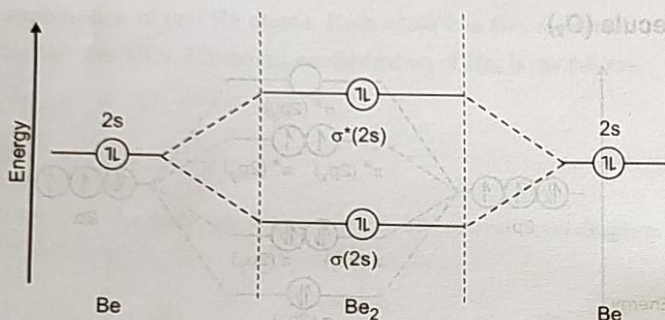
And
$$B.O. = \frac{1}{2}(2-2) = 0$$

Fig. 1.7.12 : MO energy level diagram for Be₂ molecule

1.7.9 Molecular Orbital Energy level Diagrams of Heteronuclear Diatomic Molecules

$-$ In heteronuclear diatomic molecules two atoms constituting a molecule are different. With difference in their electronegativity values.

$-$ Atomic orbitals of element having higher electronegativity are lower in energy than the corresponding AOs of the elements of lower electronegativity. Due to this energy difference the bonding and anti bonding molecular orbitals will receive different contributions from AOs of both the elements.

$-$ The BMO will receive more contribution from AOs of the elements of higher electronegativity and would be closer to it, in energy than the ABMOs which would be closer to the elements with lower electronegativity. Hence MO diagrams of heteronuclear diatomic molecules are not symmetrical as in case of homonuclear diatomic molecule. Let us discuss this with few examples as follows.

1.7.9 (A) Carbon Monoxide Molecule (CO)

$-$ The electronic configurations of C and O atoms are $1s^2\ 2s^2\ 2p^2$ and $1s^2\ 2s^2\ 2p^4$ respectively. Total ten electrons of outer shell are to be accommodated in the MOs of CO molecule. In MO energy level diagram BMOs are near to oxygen because its electronegativity is higher than that of carbon and ABMOs are near to carbon. The electronic configuration of CO molecule is.

CO : KK $\sigma(2s)^2 \sigma^*(2s)^2 \begin{cases} \pi(2p_x)^2 \\ \pi(2p_y)^2 \end{cases} \sigma(2p_z)^2$
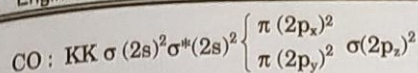
And B.O. $= \dfrac{1}{2}(8-2) = 3$

Thus CO contains total three bonds in it

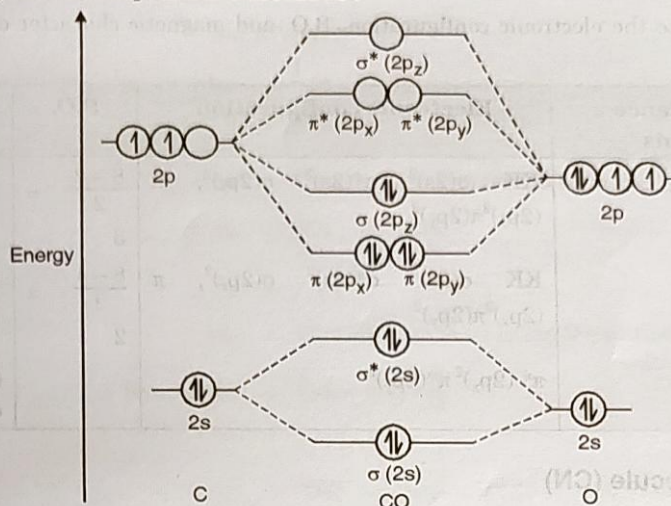MO energy level diagram cam be presented as follows :

Fig. 1.7.13 : MO energy level diagram for CO molecule
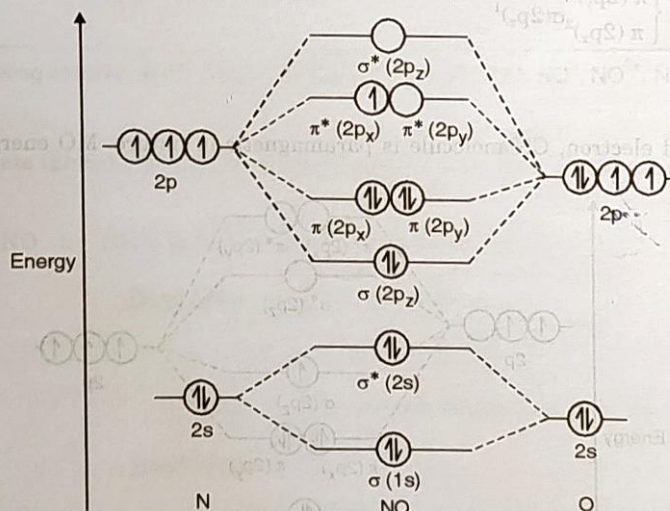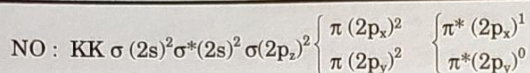
1.7.9　(B) Nitric Oxide Molecule (NO)

Fig. 1.7.14 : MO energy level diagram for NO molecule

- The electronic configuration of N and O atoms are $1s^2\ 2s^2\ 2p^3$ and $1s^2\ 2s^2\ 2p^4$ respectively. There are 5 electrons in the outer shell of nitrogen and 6 electrons in the outer shell of oxygen. Thus a total of 11 outer electrons has to be accommodated in the molecular orbitals of NO molecule. The electronic configuration of NO molecule is,

$$NO : KK\ \sigma\ (2s)^2\sigma^*(2s)^2\ \sigma(2p_z)^2 \begin{cases} \pi\ (2p_x)^2 \\ \pi\ (2p_y)^2 \end{cases} \begin{cases} \pi^*\ (2p_x)^1 \\ \pi^*(2p_y)^0 \end{cases}$$

The B.O. in this case is $= \dfrac{1}{2}(8-3) = 2\dfrac{1}{2}$

- Presence of anti bonding electrons makes the NO molecule less stable than the N_2 molecule. Also because of one unpaired electron this molecule is paramagnetic in nature. MO energy level diagram is as follows.

Similarly we can write the electronic configuration, B.O. and magnetic character of NO^+ and NO^- ions as follows.

Species	No. of valence electrons	Electronic configuration	B.O.	Magnetic character
NO^+	14	$KK\quad \sigma(2s)^2\quad \sigma^*(2s)^2\quad \sigma(2p_z)^2,\quad \pi$ $(2p_x)^2\pi(2p_y)^2$	$\dfrac{8-2}{2} = 3$	Diamagnetic
NO^-	16	$KK\quad \sigma(2s)^2\quad \sigma^*(2s)^2\quad \sigma(2p_z)^2,\quad \pi$ $(2p_x)^2\pi(2p_y)^2$ $\pi^*\ (2p_x)^2\ \pi^*(2p_y)^2$	$\dfrac{8-4}{2} = 2$	Paramagnetic (Two unpaired electrons)

1.7.9 (C) Cyanide Molecule (CN)

- The electronic configuration of carbon and nitrogen atoms are $1s^2\ 2s^2\ 2p^2$ and $1s^2\ 2s^2\ 2p^3$ respectively. Total nine valence electrons are to be accommodate in MOs as follows.

$$CN : KK\ \sigma\ (2s)^2\sigma^*(2s)^2 \begin{cases} \pi\ (2p_y)^2 \\ \pi\ (2p_x)^2 \end{cases} \sigma(2p_z)^1$$
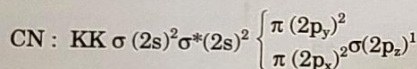
$$B.O. = \frac{1}{2}\ [7-2] = 2\frac{1}{2}$$

- Since it has one paired electron, CN molecule is paramagnetic in nature. MO energy level diagram can be made as follows.
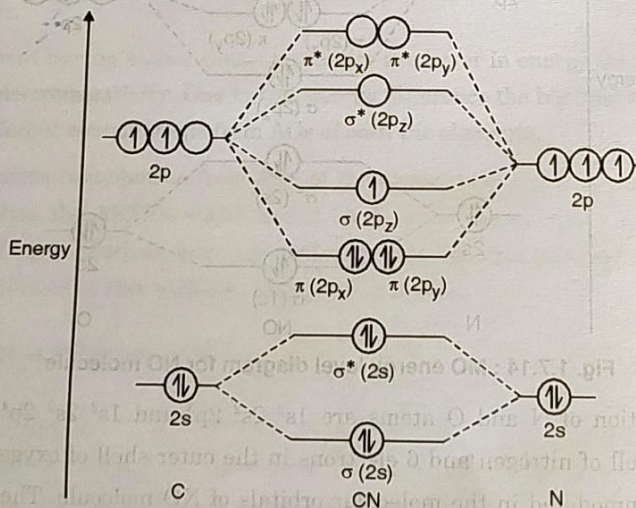

Fig. 1.7.15 : MO energy level diagram for CN molecule

1.8　Solved Examples

Ex. 1.8.1 :　Of the species O_2^+, O_2, O_2^-, O_2^{2-} which would have the maximum bond strength ?

Soln. :

Higher bond orders are associated with shorter bond lengths and higher bond strengths. We will first calculate the bond orders for the various species from their electronic configurations : First of all let us start with oxygen molecule.

O_2 : KK $\sigma(2s)^2\sigma^*(2s^2)$ $\sigma(2p_z)^2\pi(2p_y)^2$ $\pi(2p_x)^2\pi^*(2p_y)^1\pi^*(2p_y)^1$

$$\therefore \text{Bond order} = \frac{1}{2}(8-4) = 2$$

Then, In case of ;

O_2^+ :　One electron is removed from the antibonding $\pi^*(2p_y)$ ABMO

$$\therefore \text{Bond order} = \frac{1}{2}(8-3) = 2\frac{1}{2}$$

but, In case of;

O_2^- = One electron is added to the antibonding $\pi^*(2p_x)$ MO

$$\therefore \text{Bond order} = \frac{1}{2}(8-5) = 1\frac{1}{2}$$

also, in case of ;

O_2^{2-} :　Two electrons are added to the outermost ABMO

$$\therefore \text{Bond order} = \frac{1}{2}(8-6) = 1$$

Since O_2^+ has the highest bond order, it has the shortest bond length and hence the maximum bond strength.

Ex. 1.8.2 :　Of the following species, which has the shortest bond length : NO, NO^+, NO^{2+}, NO^- ?

Soln. :

We shall first calculate the band orders for the given species from their electronic configurations. Let us start with NO molecule.

NO :　KK $\sigma(2s)^2\sigma^*(2s)^2$ $\sigma(2p_z)^2\pi(2p_x)^2\pi(2p_y)^2\pi^*(2p_x)^1$

$$\therefore \text{Bond order} = \frac{1}{2}(8-3) = 2\frac{1}{2}$$

But, in case of;

NO^+ :　One electron is removed from the antibonding $\pi^*(2p_x)$ orbital.

$$\therefore \text{Bond order} = \frac{1}{2}(8-2) = 3$$

In, NO^{2+} = One electron is removed from the antibonding $\pi^*(2p_x)$ MO and the other electron is removed from the bonding $\pi(2p_y)$ MO.

$$\therefore \text{Bond order} = \frac{1}{2}(7-2) = 2\frac{1}{2}$$

NO^- : One electron is added to the antibonding $\pi^*(2p_x)$ orbital.
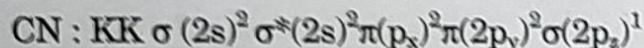
$$\text{Bond order} = \frac{1}{2}(8-4) = 2$$

Evidently, the species NO^+ has the highest bond order and thus has the shortest bond length.

Ex. 1.8.3 : Compare the bond energy, bond length and magnetic character of CN and CN^- species with the help of molecular orbital theory.

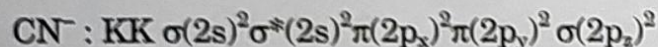**Soln. :** In order to compare bond energy and bond length,

We shall first calculate bond orders for these species from their electronic configurations.

CN has 13 electrons and its electronic configuration is

$CN : KK \ \sigma \ (2s)^2 \sigma^*(2s)^2 \pi(p_x)^2 \pi(2p_y)^2 \sigma(2p_z)^1$

$$\text{Bond order} = \frac{1}{2}(7-2) = 2\frac{1}{2}$$

CN^- : In this case, one electron is added to $\sigma(2p_z)$ MO so that its electronic configuration is

$CN^- : KK \ \sigma(2s)^2 \sigma^*(2s)^2 \pi(2p_x)^2 \pi(2p_y)^2 \ \sigma(2p_z)^2$

$$\text{Bond order} = \frac{1}{2}(8-2) = 3$$

Since CN^- has a higher bond order, it has larger bond energy and smaller bond length than CN. Further since there is one unpaired electron in $\sigma(2p_z)$ MO of CN, it will be paramagnetic. But CN^- is evidently diamagnetic.