INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 11

DATE:- 7, MAY, 2021

TIME: (9.00A.M.)

4) Boron Molecule (B_2): - When two Boron atoms combine together then Boron molecule is formed. The electronic configuration of each Boron atom (At. no. = 5) is $1s^2\ 2s^2\ 2P_x^1 2P_y^0\ 2P_z^0$. There are two energy levels in each Boron atom. So, there are totally (5 + 5 = 10) ten electrons in the Boron molecule.

i. e. $B + B \rightarrow B_2$

$5e^- + 5e^- = 10e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of first B-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of second B-atom gives ten MO's, σ1s, σ*1s, σ2s, σ*2s, $\sigma 2P_x$, $\sigma^* 2P_x$, $\pi 2P_y$, $\pi^* 2P_y$, $\pi 2P_z$, $\pi^* 2P_z$ as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Boron molecule is

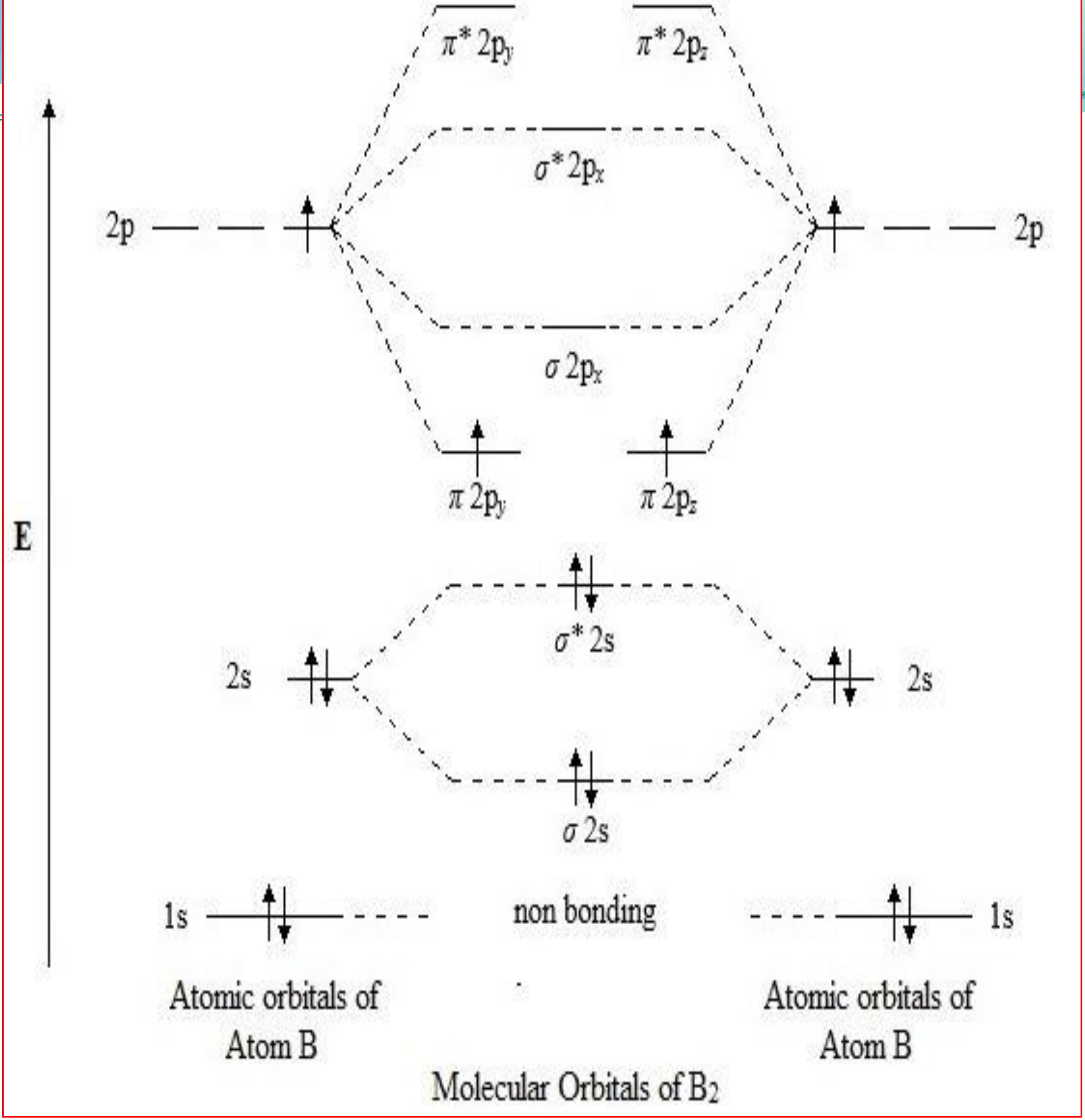
$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2P_y{}^1 = \pi 2P_z{}^1, \sigma 2P_x, \sigma^*2P_x, \pi^*2P_y = \pi^*2P_z$.

But, according to MOT, only the atomic orbitals from valence shell are involved in bonding. The inner atomic orbitals do not take part in bonding. Hence, neglecting inner shell ($1s^2$) electrons in both Boron atoms, the MO electronic configuration can also be written as

$B_2 = [KK(\sigma 2s)^2(\sigma^*2s)^2(\pi 2P_y)^1 = (\pi 2P_z)^1]$, Where KK represents inner shells.

Due to the interaction between 2s and 2P atomic orbitals, $\sigma 2P_x$ has higher energy than $\pi 2P_y$ and $\pi 2P_z$ MO's. Since the $\pi 2P_y$ and $\pi 2P_z$ orbitals are degenerate, they occupy single electron each with parallel spins according to Hund's rule.

These MO's are arranged according to their increasing energy as shown below.



MO Energy level diagram of B_2 Molecule

Bond order = $\frac{1}{2}(Nb—Na) = \frac{1}{2}(4-2) = \frac{1}{2}(2)$

= 1.

It contains a single π-bond. i. e. As the π-bond is very weak, its bond energy is also less. Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 4 \times (-\beta) + 2 \times (+\beta) = -4\beta + 2\beta = -2\beta$.

As the stabilization energy is negative, indicates that B_2 molecule can exists.

Similarly, as the B_2 molecule contains two unpaired electrons $[\pi 2P_y^1$ and $\pi 2P_z^1]$ hence, it is paramagnetic.

5) Nitrogen Molecule (N_2):- When two Nitrogen atoms combine together then Nitrogen molecule is formed. The electronic configuration of each Nitrogen atom (At. no. =7) is $1s^2\ 2s^2\ 2P_x^1 2P_y^1\ 2P_z^1$. So, there are totally (7 + 7 =14) fourteen electrons in the Nitrogen molecule.

i. e. $N + N \rightarrow N_2$

$7e^- + 7e^- = 14e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of first N-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of second N-atom gives ten MO's, $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2P_x$, $\sigma^* 2P_x$, $\pi 2P_y$, $\pi^* 2P_y$, $\pi 2P_z$, $\pi^* 2P_z$ as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

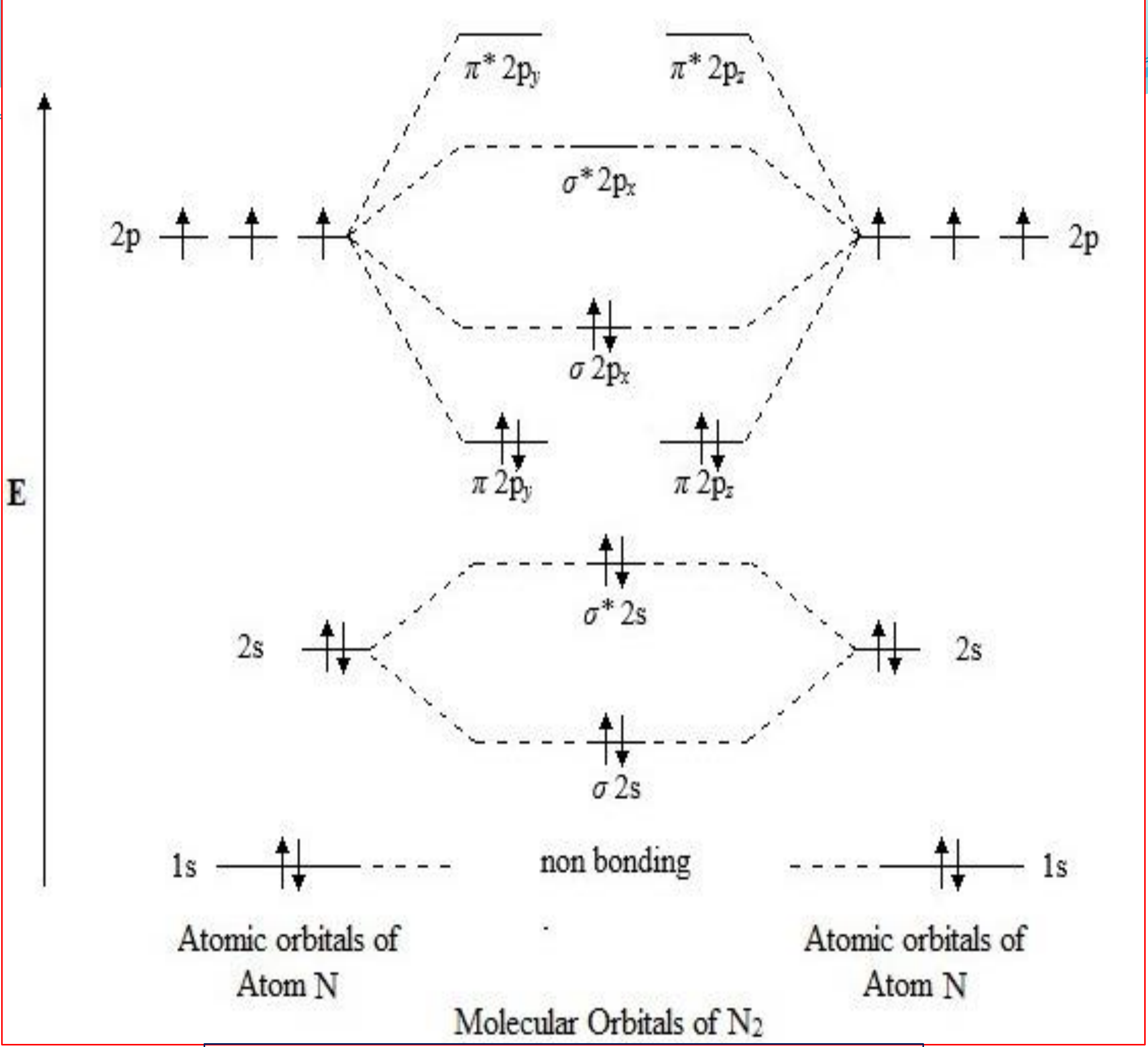
The molecular orbital electronic configuration of Nitrogen molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2P_y{}^2 = \pi 2P_z{}^2, \sigma 2P_x{}^2, \sigma^* 2P_x, \pi^* 2P_y = \pi^* 2P_z.$

The inner atomic orbitals do not take part in bonding. Hence, neglecting inner shell ($1s^2$) electrons in both Nitrogen atoms, the MO electronic configuration of Nitrogen molecule is $N_2 = [KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2P_y)^2 = (\pi 2P_z)^2\ (\sigma 2Px)^2]$, Where KK represents inner shells.

Due to the interaction between 2s and 2P atomic orbitals, $\sigma 2P_x$ has higher energy than $\pi 2P_y$ and $\pi 2P_z$ MO’s.

These MO’s are arranged according to their increasing energy as shown below.



Mo Energy level diagram of N_2 molecule

Bond order $= \frac{1}{2}(Nb - Na) = \frac{1}{2}(8-2) = \frac{1}{2}(6) = 3.$

It contains a triple bond ($N \equiv N$), out of which one is σ-bond and two are π-bonds.

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 2 \times (+\beta) = -8\beta + 2\beta = -6\beta.$

Due to higher bond order and higher stabilization energy, N_2 molecule is highly stable and is chemically inert. The bond between two Nitrogen atoms will break during thundering.

Since all the electrons are paired, Nitrogen molecule is diamagnetic.

6) Oxygen Molecule (O_2):- When two Oxygen atoms combine together then Oxygen molecule is formed. The electronic configuration of each Oxygen atom (At. no. =8) is $1s^2\ 2s^2\ 2P_x^2 2P_y^1\ 2P_z^1$. So, there are totally (8 + 8 =16) sixteen electrons in the Oxygen molecule.

i. e. $O + O \rightarrow O_2$

$8e^- + 8e^- = 16e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of first O-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of second O-atom gives ten MO's, $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2P_x$, σ^*2P_x, $\pi 2P_y$, π^*2P_y, $\pi 2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^*1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^*2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^*2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^*2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^*2P_z$

The molecular orbital electronic configuration of Oxygen molecule is

$\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2P_x{}^2$, $\pi 2P_y{}^2 = \pi 2P_z{}^2$, $\pi^* 2P_y{}^1 = \pi^* 2P_z{}^1$, $\sigma^* 2P_x$.

The inner atomic orbitals do not take part in bonding. Hence, neglecting inner shell ($1s^2$) electrons in both Oxygen atoms, the MO electronic configuration of Oxygen molecule is

O_2 = $[KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\pi^* 2P_y)^1 = (\pi^* 2P_z)^1]$, Where KK represents inner shells.

Since, the energy difference between 2s and 2P orbitals in Oxygen atom is large; there is no interaction between 2s and 2P atomic orbitals. Hence, $\sigma 2P_x$ has lower energy than $\pi 2P_y$ and $\pi 2P_z$ MO's.

These MO's are arranged according to their increasing energy as shown below.

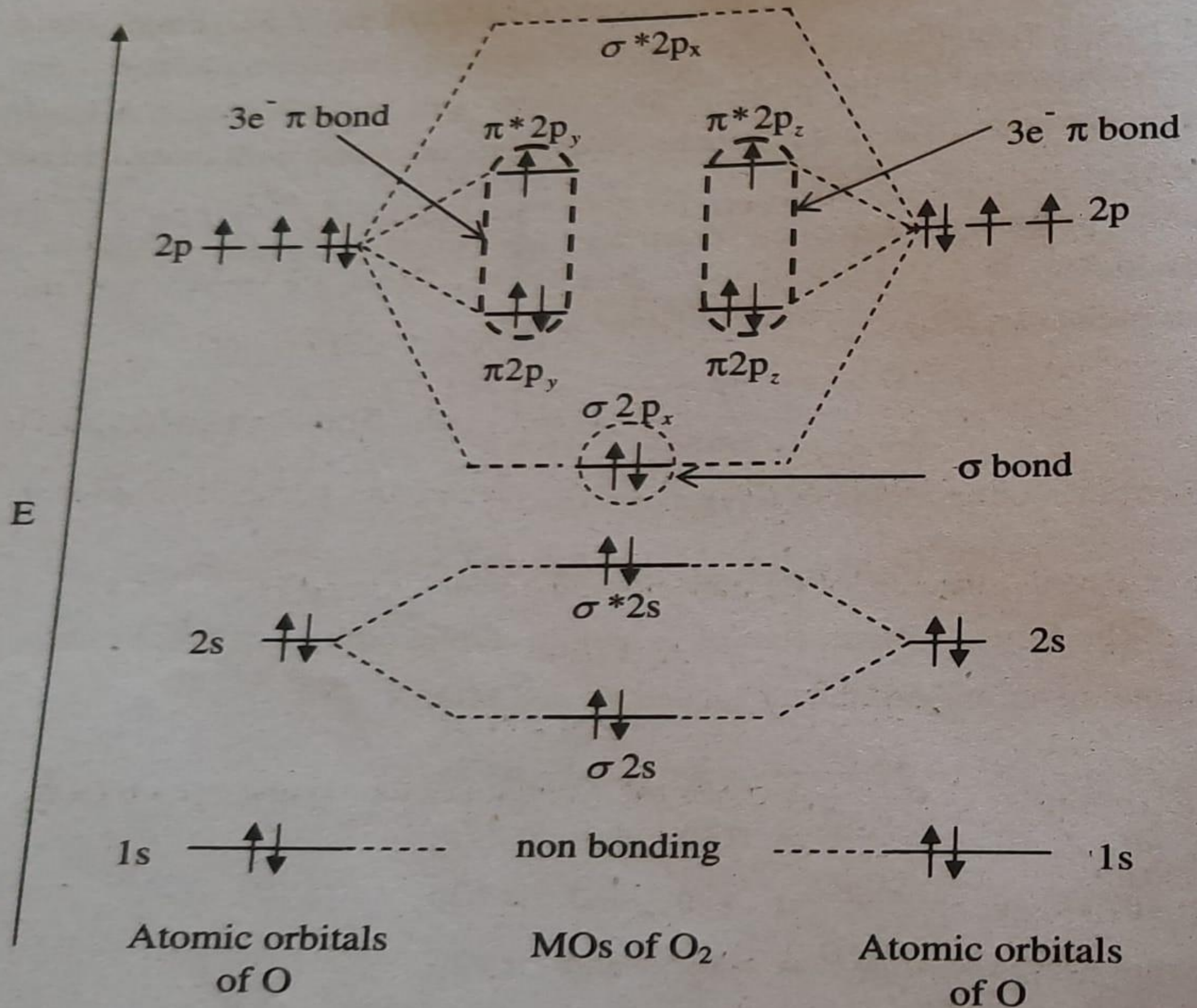


Fig. 3.18 MO energy level diagram for O_2 molecule. (x- axis is internuclear axis)

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 4) = \frac{1}{2}(4) = 2.$

It contains a double bond ($O = O$), out of which one is σ-bond and other is π-bonds.

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 4 \times (+\beta) = -8\beta + 4\beta = -4\beta.$

As the stabilization energy is negative, indicates that O_2 molecule exists.

The reactivity of O_2 molecule is due to the presence of unpaired electrons in π^*2P_y and π^*2P_z. Due to these two unpaired electrons, O_2 molecule is paramagnetic.

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 12

DATE:- 12, MAY, 2021

TIME: (10.00A.M.)

6) Oxygen Molecule (O_2):- When two Oxygen atoms combine together then Oxygen molecule is formed. The electronic configuration of each Oxygen atom (At. no. =8) is $1s^2\ 2s^2\ 2P_x^{\,2} 2P_y^{\,1}\ 2P_z^{\,1}$. So, there are totally (8 + 8 =16) sixteen electrons in the Oxygen molecule.

i. e. $O + O \rightarrow O_2$

$8e^- + 8e^- = 16e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of first O-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of second O-atom gives ten MO's, σ1s, σ*1s, σ2s, σ*2s, $\sigma 2P_x$, $\sigma^* 2P_x$, $\pi 2P_y$, $\pi^* 2P_y$, $\pi 2P_z$, $\pi^* 2P_z$ as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Oxygen molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2P_x{}^2, \pi 2P_y{}^2 = \pi 2P_z{}^2, \pi^* 2P_y{}^1 = \pi^* 2P_z{}^1, \sigma^* 2P_{x.}$

The inner atomic orbitals do not take part in bonding. Hence, neglecting inner shell ($1s^2$) electrons in both Oxygen atoms, the MO electronic configuration of Oxygen molecule is

$O_2 = [KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\pi^* 2P_y)^1 = (\pi^* 2P_z)^1]$, Where KK represents inner shells.

Since, the energy difference between 2s and 2P orbitals in Oxygen atom is large; there is no interaction between 2s and 2P atomic orbitals. Hence, $\sigma 2P_x$ has lower energy than $\pi 2P_y$ and $\pi 2P_z$ MO's.

These MO's are arranged according to their increasing energy as shown below.

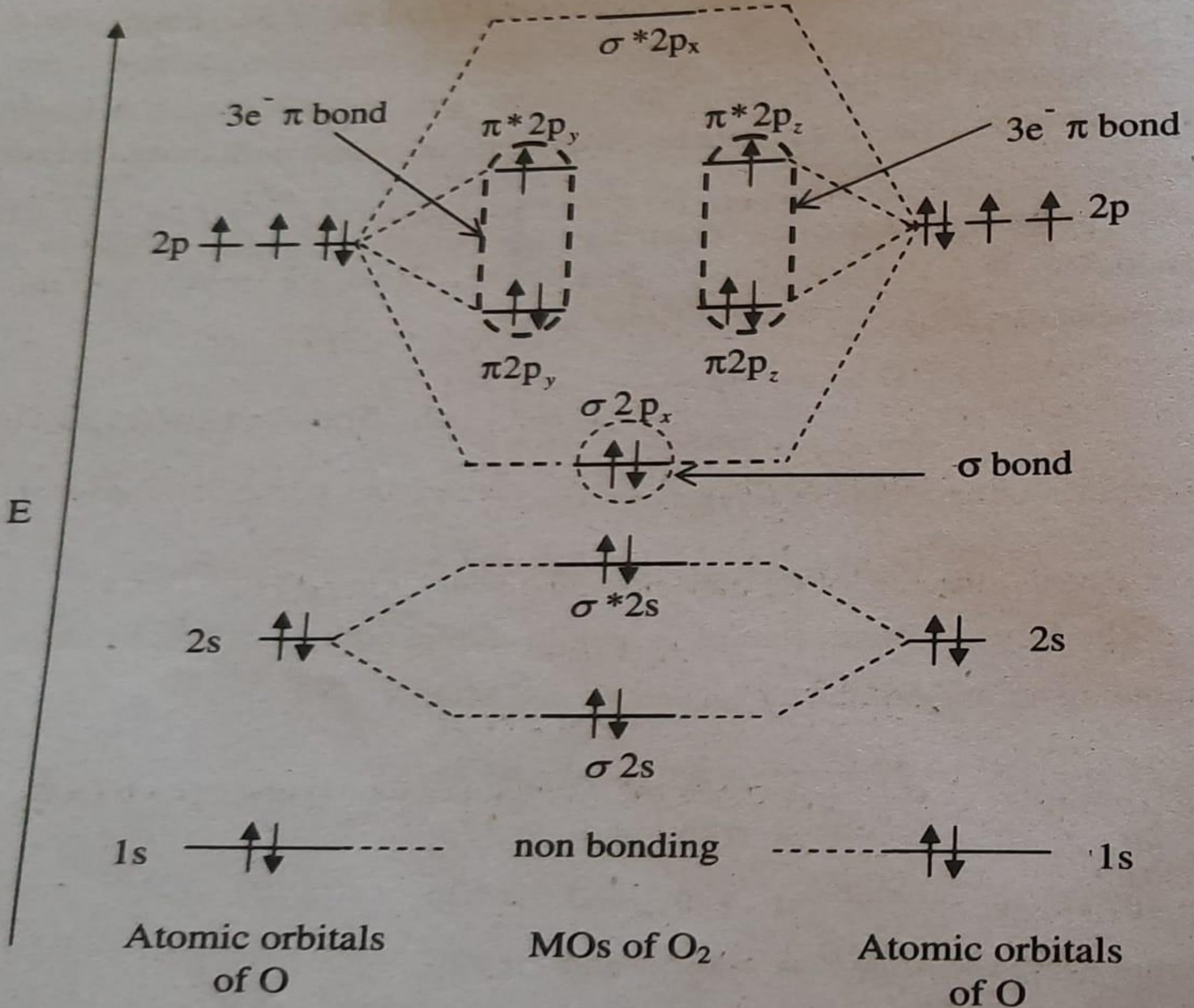


Fig. 3.18 MO energy level diagram for O_2 molecule. (x- axis is internuclear axis)

Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-4) = \frac{1}{2}(4) = 2$.

It contains a double bond ($O{=}O$), out of which one is σ-bond and other is π-bonds.

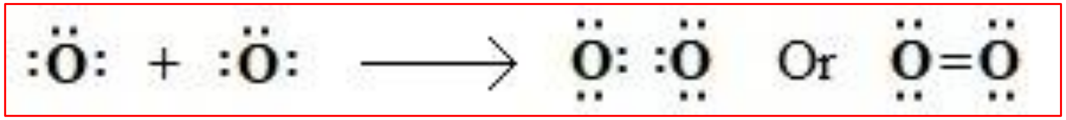
Stabilization Energy = S. E. $= [N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 4 \times (+\beta) = -8\,\beta + 4\,\beta = -4\beta$.

As the stabilization energy is negative, indicates that O_2 molecule exists.

The reactivity of O_2 molecule is due to the presence of unpaired electrons in π^*2P_y and π^*2P_z. Due to these two unpaired electrons, O_2 molecule is paramagnetic.

Paramagnetism of O_2 molecule: - 1) It is very difficult to explain the paramagnetism of O_2 molecule with the help of VBT. The Valence bond theory assumes the sharing and pairing of electrons between the two Oxygen atoms for the completion of the octet configuration of each Oxygen atom in the O_2 molecule. This can be represented as, $(O \rightarrow 1s^2, 2s^2, 2Px^2.2Py^1 2Pz^1)$



Thus, VBT can predict the presence of double bond correctly but not the presence of two unpaired electrons.

- MO theory gives a very simple explanation for the presence of two unpaired electrons and hence paramagnetism of O_2 molecule.
- The distribution of electrons in the MO configuration of O_2 molecule is $[KK(\sigma 2s)^2(\sigma^* 2s)^2 (\sigma 2Px)^2 (\pi 2P_y)^2 = (\pi 2P_z)^2 (\pi^* 2P_y)^1 = (\pi^* 2P_z)^1]$

According to MOT, O_2 molecule contains two unpaired electrons in $(\pi^* 2P_y)^1(\pi^* 2P_z)^1$. This is according to Hund’s rule, which states that, “If several orbitals of equal energy are available then electrons are singly filled first and then pairing starts”. Because of these two unpaired electrons, O_2 molecule is paramagnetic according to MOT.

7) Superoxide ion (O_2^- ion): -

When Oxygen atom combines with Oxygen ion then Superoxide molecule ion is formed. The Oxygen ion can be formed from the Oxygen atom by the gain of one electron. The electronic configuration of Oxygen atom (At. no. = 8) is $1s^2\ 2s^2\ 2P_x^2 2P_y^1\ 2P_z^1$, while the electronic configuration of Oxygen ion (O^-) is $1s^2\ 2s^2\ 2P_x^2 2P_y^2\ 2P_z^1$. So, there are totally (8 + 9 =17) seventeen electrons in the Superoxide molecule ion.

i. e. $O + e^- \rightarrow O^-$ (Formation of O^- ion)

$O + O^- \rightarrow O_2^-$ or $O_2 + e^- \rightarrow O_2^-$

$8e^- + 9e^- = 17e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of O-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of Oxygen ion give ten MO's, $\sigma1s$, σ^*1s, $\sigma2s$, σ^*2s, $\sigma2P_x$, σ^*2P_x, $\pi2P_y$, π^*2P_y, $\pi2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^{*}1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^{*}2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^{*}2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^{*}2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^{*}2P_z$

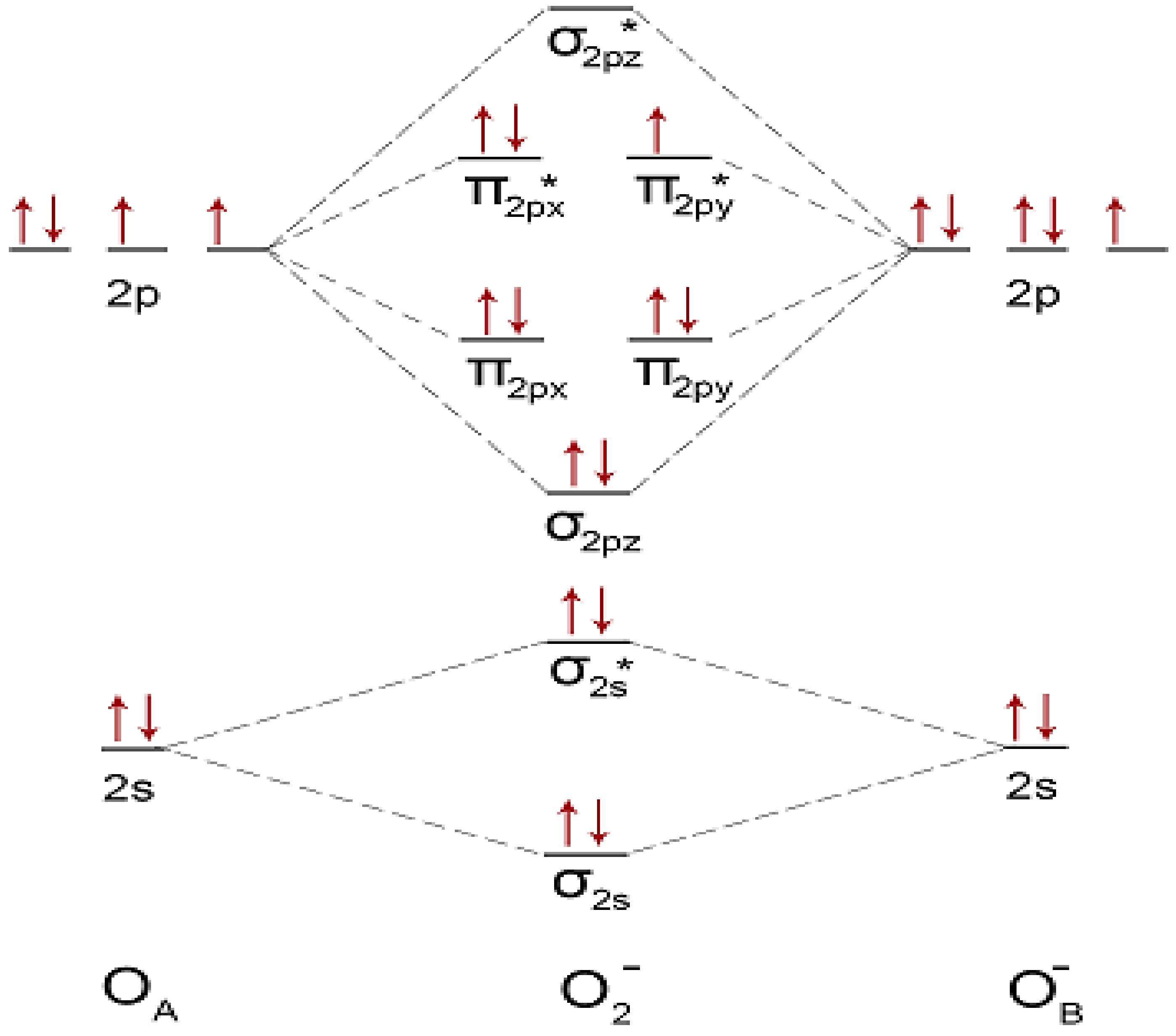
The molecular orbital electronic configuration of Superoxide Oxygen molecule ion is

$\sigma 1s^2, \sigma^{*}1s^2, \sigma 2s^2, \sigma^{*}2s^2, \sigma 2P_x^{\,2}, \pi 2P_y^{\,2} = \pi 2P_z^{\,2}, \pi^{*}2P_y^{\,2} = \pi^{*}2P_z^{\,1}, \sigma^{*}2P_{x.}$

Or, $O_2^- = [KK(\sigma 2s)^2(\sigma^{*}2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\pi^{*}2P_y)^2 = (\pi^{*}2P_z)^1]$, Where KK represents inner shells.

Since, the energy difference between 2s and 2P orbitals in Oxygen atom and ion is large, so there is no interaction between 2s and 2P atomic orbitals. Hence, $\sigma 2P_x$ has lower energy than $\pi 2P_y$ and $\pi 2P_z$ MO's.

Neglecting inner energy level electrons (1s AO's of O-atom and O^- ions and $\sigma 1s^2$, $\sigma^{*}1s^2$ MO's), these MO's are arranged according to their increasing energy as shown below:


σ_{2pz}^*
π_{2px}^*
π_{2py}^*
2p
2p
π_{2px}
π_{2py}
σ_{2pz}
σ_{2s}^*
2s
2s
σ_{2s}
O_A
O_2^-
O_B^-

Bond order = $\frac{1}{2}(\text{Nb}—\text{Na}) = \frac{1}{2}(8-5) = \frac{1}{2}(3) = 1.5$

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 5 \times (+\beta) = -8\beta + 5\beta = -3\beta$.

As the stabilization energy is negative, indicates that O_2^- molecule ion exists.

As the Superoxide molecule ion contains one unpaired electron in $\pi^*2P_z^1$ hence, the Superoxide (O_2^-) molecule ion is paramagnetic.

The bond order has decreased from 2 in O_2 molecule to 1.5 in O_2^- molecule ion. The bond length of O_2^- has increased to 0.126 nm as compared to bond length of O_2 molecule (0.121 nm). Similarly, as the bond order decreases, the bond energy also decreases.

8) Peroxide ion (O_2^{-2} ion): -

When two Oxygen ions combine together then Peroxide molecule ion is formed. The Oxygen ion can be formed from the Oxygen atom by the gain of one electron. The electronic configuration of each Oxygen ion (O^-) is $1s^2\ 2s^2\ 2P_x^2 2P_y^2\ 2P_z^1$. There are only nine electrons in each Oxygen ion. So, there are totally (9 + 9 =18) eighteen electrons in the Peroxide molecule ion.

i. e. $O + e^- \rightarrow O^-$ (Formation of O^- ion)

$O^- + O^- \rightarrow O_2^{-2}$ or $O_2 + 2\ e^- \rightarrow O_2^{-2}$

$9e^- + 9e^- = 18e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of one Oxygen ion with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of other Oxygen ion give ten MO's, $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2P_x$, $\sigma^* 2P_x$, $\pi 2P_y$, $\pi^* 2P_y$, $\pi 2P_z$, $\pi^* 2P_z$ as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

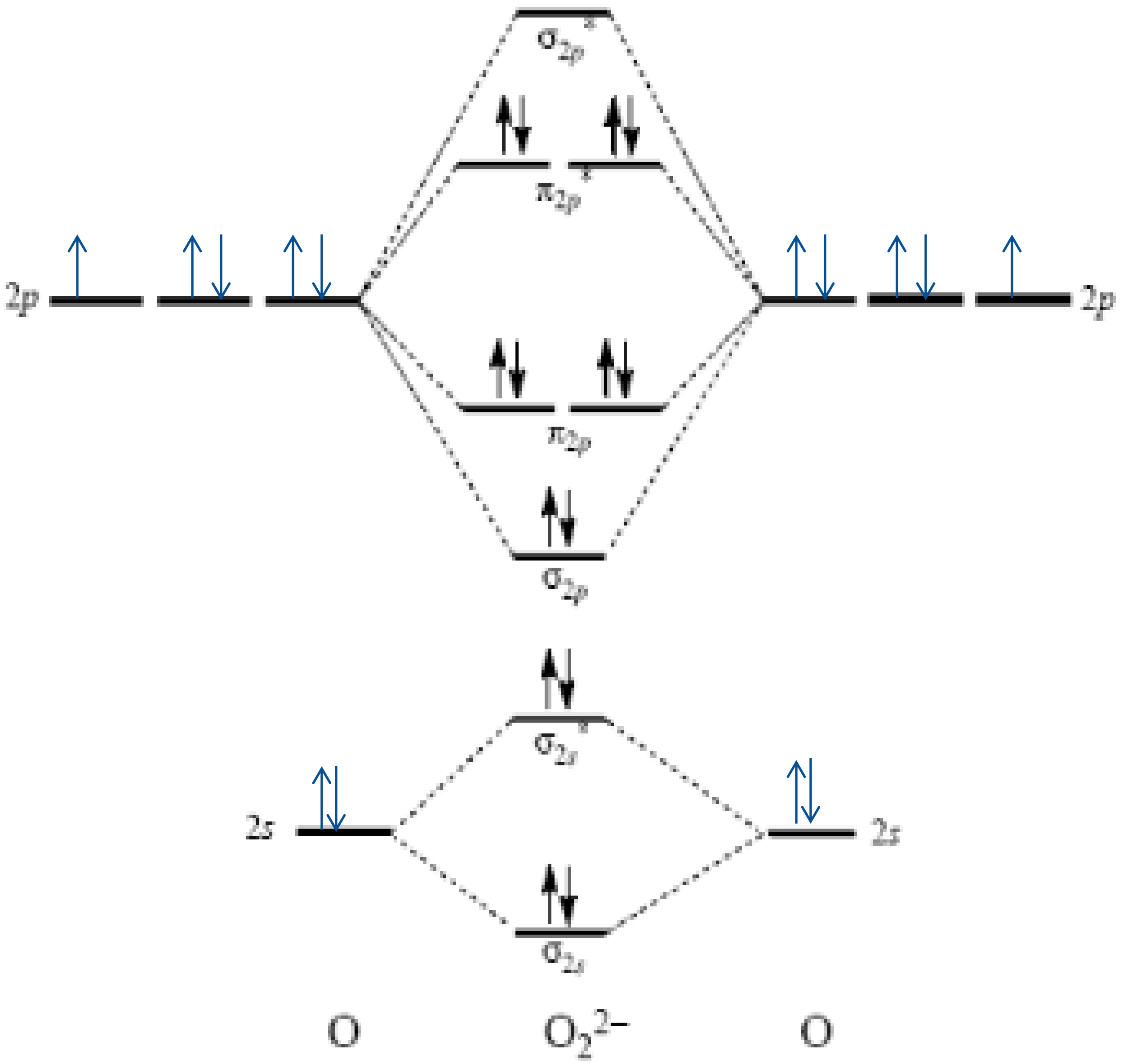
The molecular orbital electronic configuration of Peroxide molecule ion is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2P_x^{\ 2}, \pi 2P_y^{\ 2} = \pi 2P_z^{\ 2}, \pi^* 2P_y^{\ 2} = \pi^* 2P_z^{\ 2}, \sigma^* 2P_{x.}$

Or, $O_2^{-2} = [KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\pi^* 2P_y)^2 = (\pi^* 2P_z)^2]$, Where KK represents inner shells.

Since, the energy difference between 2s and 2P orbitals in Oxygen ions is large, so there is no interaction between 2s and 2P atomic orbitals. Hence, $\sigma 2P_x$ has lower energy than $\pi 2P_y$ and $\pi 2P_z$ MO's.

Neglecting inner energy level electrons (1s AO's of both O^- ions and $\sigma 1s^2, \sigma^* 1s^2$ MO's), these MO's are arranged according to their increasing energy as shown below.


σ*2p
π*2p
2p
2p
π2p
σ2p
σ*2s
2s
2s
σ2s
O
O2 2−
O

Bond order = $\frac{1}{2}(Nb—Na) = \frac{1}{2}(8-6) = \frac{1}{2}(2) = 1.$

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 6 \times (+\beta) = -8\,\beta + 6\,\beta = -2\beta.$

As the stabilization energy is negative, indicates that O_2^{-2} molecule ion exists.

As the Peroxide molecule ion does not possess any unpaired electron hence, the Peroxide (O_2^{-2}) molecule ion is diamagnetic.

The bond order has decreased from 2 in O_2 molecule to 1 in O_2^{-2} molecule ion. The bond length of O_2^{-2} ion has increased to 0.149 nm as compared to bond length of O_2 molecule (0.121 nm). Similarly, as the bond order decreases, the bond energy also decreases.

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 13

DATE:- 14, MAY, 2021

TIME: (9.00A.M.)

Examples of MO treatment for heteronuclear diatomic molecules:-

Molecules formed by combination of atoms of two different elements are called as heteronuclear diatomic molecules. e. g. HCl, CO, NO, etc.

The formation of MO's in heteronuclear diatomic molecules can be considered by adopting same general principles as applied for homonuclear diatomic molecules. The MO's are considered by forming LCAO on the two atoms. The formation of heteronuclear diatomic molecules differs from homonuclear diatomic molecules in the following respect.

1) The combining atoms have different electronegativities and hence the energies of the AO’s of these elements are not same.

2) In heteronuclear diatomic molecules the contribution of AO’s towards MO’s is not identical. This is due to the difference in the electronegativity of two elements.

3) The MO’s are not symmetric with respect to a plane perpendicular to and bisecting the internuclear (molecular) axis.

4) Greater the difference between the two combining AO’s, lesser is the interaction (overlapping) between them, hence lesser is the bonding effect.

5) The order of energies of MO’s are the same as for homonuclear diatomic molecules.

1) Carbon monoxide (CO) molecule: -

When Carbon atom combines with Oxygen atom then Carbon monoxide molecule is formed. The electronic configuration of Carbon atom (At. no. = 6) is $1s^2\ 2s^2\ 2P_x^1\ 2P_y^1\ 2P_z^0$ while, the electronic configuration of Oxygen atom (At. no. = 8) is $1s^2\ 2s^2\ 2P_x^2\ 2P_y^1\ 2P_z^1$. So, there are totally (6 + 8 =14) fourteen electrons in the Carbon monoxide molecule.

i. e. $C + O \rightarrow CO$

$6e^- + 8e^- = 14e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of C-atom with corresponding1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of O-atom give ten MO's, $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2P_x$, σ^*2P_x, $\pi 2P_y$, π^*2P_y, $\pi 2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Carbon monoxide molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2P_y{}^2 = \pi 2P_z{}^2, \sigma 2P_x{}^2, \sigma^* 2P_{x,}\ \pi^* 2P_y = \pi^* 2P_z.$

Or, $CO = [KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\sigma 2Px)^2]$, Where KK represents inner shells.

In CO molecule, Oxygen is more electronegative than Carbon and hence, the atomic orbitals of Oxygen atom will be at a lower energy level than the corresponding atomic orbitals of Carbon atom. Thus, atomic orbitals of Carbon and Oxygen do not contribute equally to the MO’s formed from them.

CO is isoelectronic (Having same number of electrons) with N_2 molecule. Isoelctronic species have similar MO's and similar molecular structure.

Hence, neglecting inner shell ($1s^2$) electrons in both Carbon and Oxygen atoms, These MO's are arranged according to their increasing energy as shown below.

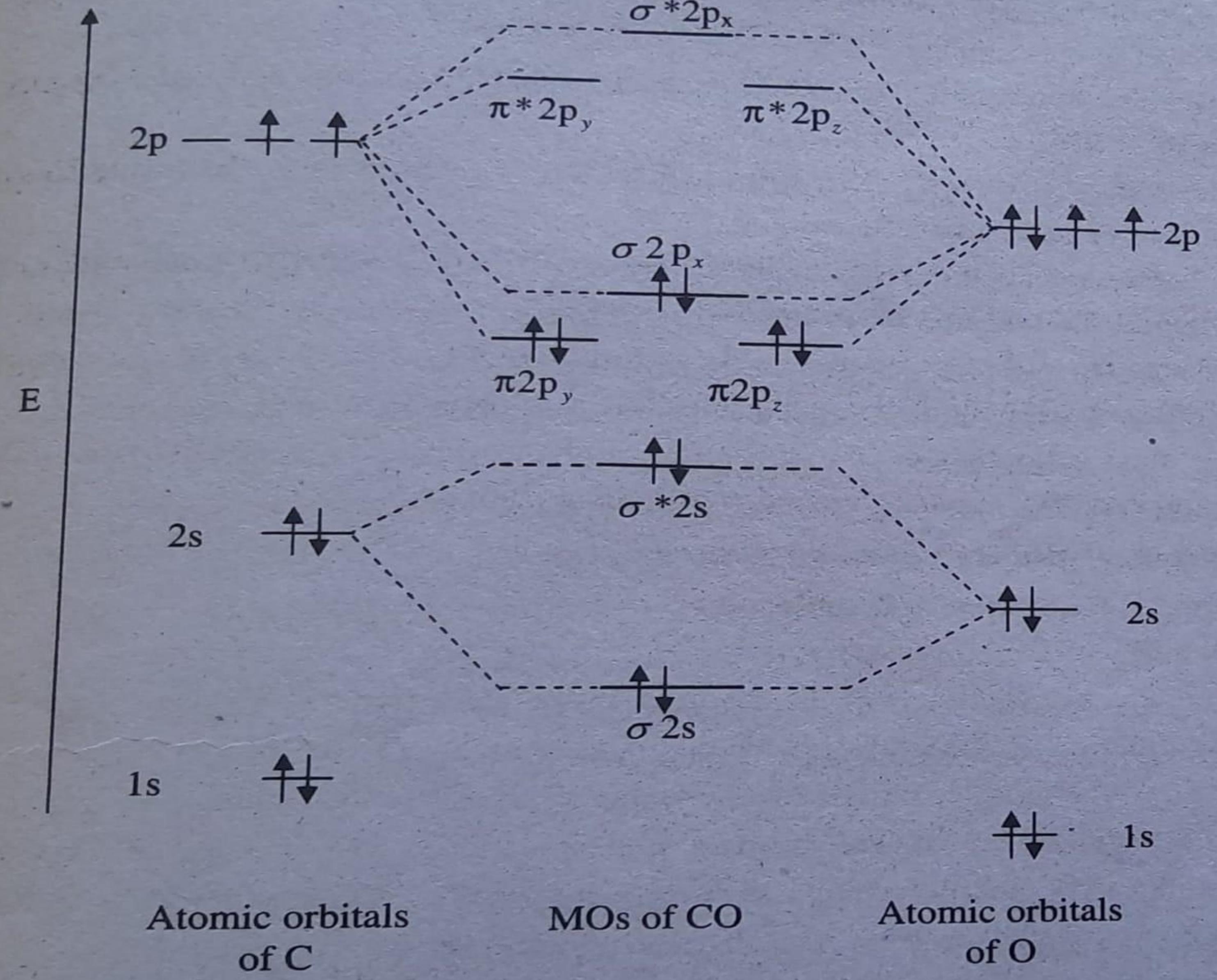


Fig. 3.19 : MO energy level diagram for CO molecule.
(*x*–axis is internuclear axis)

Bond order = $\frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) = \frac{1}{2}(6) = 3.$

It contains a triple bond (C ≡ O), out of which one is σ-bond and two are π-bonds.

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 2 \times (+\beta) = -8\beta + 2\beta = -6\beta.$

As the stabilization energy is negative, indicates that CO molecule exists.

Since all the electrons are paired, Carbon monoxide molecule is diamagnetic.

Polarity of Carbon monoxide molecule: -

The electronegativity of O-atom is more than that of C-atom. Due to this, contribution of AO’s towards MO’s is not identical.

The AO’s of Oxygen atom are close to bonding MO’s with respect to energy. Hence, Oxygen orbitals contribute more to bonding MO’s than Carbon orbitals. The atomic orbitals of Carbon are close to antibonding MO’s with respect to energy. Hence, Carbon orbitals contribute more to antibonding MO’s. Due to these eight electrons in bonding MO’s are close to Oxygen than to Carbon. Hence, Oxygen atom acquires slightly negative charge and Carbon acquires slight positive charge. So, CO molecule is polar but its polarity is less.

2) Nitric oxide (NO) molecule: -

When Nitrogen atom combines with Oxygen atom then Nitric oxide molecule is formed. The electronic configuration of Nitrogen atom (At. no. = 7) is $1s^2\ 2s^2\ 2P_x^{\ 1}\ 2P_y^{\ 1}\ 2P_z^{\ 1}$ while, the electronic configuration of Oxygen atom (At. no. = 8) is $1s^2\ 2s^2\ 2P_x^{\ 2}\ 2P_y^{\ 1}\ 2P_z^{\ 1}$. So, there are totally (7 + 8 =15) fifteen electrons in the Nitric oxide molecule.

i. e. $N + O \rightarrow NO$

$7e^- + 8e^- = 15e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of N-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of O-atom give ten MO's, $\sigma1s$, σ^*1s, $\sigma2s$, σ^*2s, $\sigma2P_x$, σ^*2P_x, $\pi2P_y$, π^*2P_y, $\pi2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Nitric oxide molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2Px^2, \pi 2Py^2 = \pi 2P_z{}^2, \pi^* 2P_y{}^1 = \pi^* 2P_z, \sigma^* 2P_x.$

Or, NO = $[KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ \pi^* 2P_y{}^1]$, Where KK represents inner shells.

In NO molecule, Oxygen is more electronegative than Nitrogen and hence, the atomic orbitals of Oxygen atom will be at a lower energy level than the corresponding atomic orbitals of Nitrogen atom. Thus, atomic orbitals of Nitrogen and Oxygen do not contribute equally to the MO's formed from them.

Hence, neglecting inner shell ($1s^2$) electrons in both Nitrogen and Oxygen atoms, these MO's are arranged according to their increasing energy as shown below.

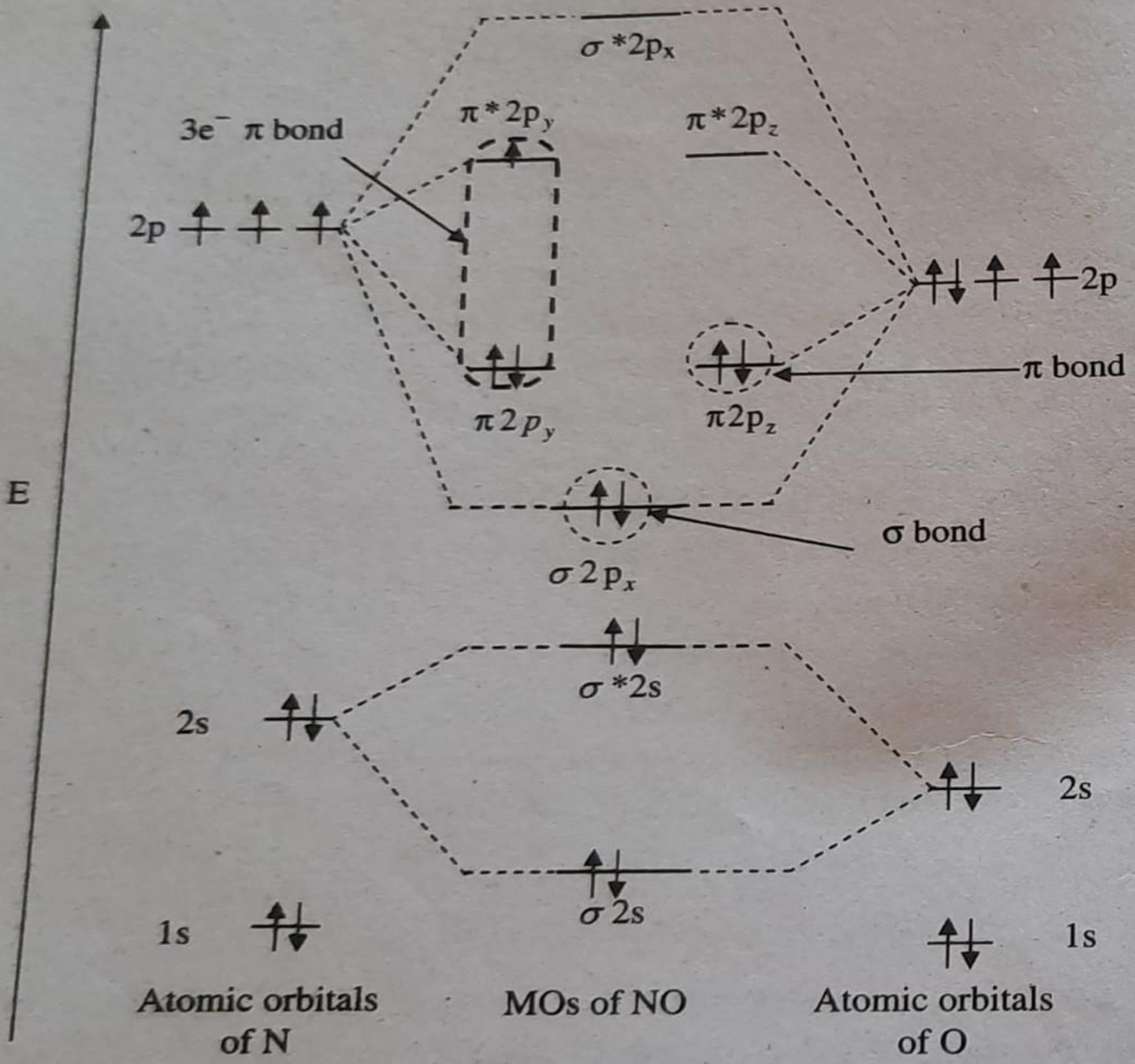
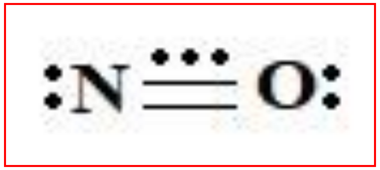


Fig. 3.20 : MO energy level diagram for NO molecule.
(x–axis is internuclear axis)

Bond order = $\frac{1}{2}(Nb - Na) = \frac{1}{2}(8-3) = \frac{1}{2}(5) = 2.5$

The bond order is 2.5, which indicates presence of one σ-bond, one π-bond and one three electron bond. The structure of NO molecule can be represented as



Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 3 \times (+\beta) = -8\,\beta + 3\,\beta = -5\beta$.

As the stabilization energy is negative, indicates that NO molecule exists, but it is less stable than N_2 molecule.

Since, the NO molecule contains one unpaired electron in $(\pi^*2P_y)^{1,}$ hence, it is paramagnetic.

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 14

DATE:- 19, MAY, 2021

TIME: (10.00A.M.)

Examples of MO treatment for heteronuclear diatomic molecules:-

Molecules formed by combination of atoms of two different elements are called as heteronuclear diatomic molecules. e. g. HCl, CO, NO, etc.

The formation of MO's in heteronuclear diatomic molecules can be considered by adopting same general principles as applied for homonuclear diatomic molecules. The MO's are considered by forming LCAO on the two atoms. The formation of heteronuclear diatomic molecules differs from homonuclear diatomic molecules in the following respect.

1) The combining atoms have different electronegativities and hence the energies of the AO’s of these elements are not same.

2) In heteronuclear diatomic molecules the contribution of AO’s towards MO’s is not identical. This is due to the difference in the electronegativity of two elements.

3) The MO’s are not symmetric with respect to a plane perpendicular to and bisecting the internuclear (molecular) axis.

4) Greater the difference between the two combining AO’s, lesser is the interaction (overlapping) between them, hence lesser is the bonding effect.

5) The order of energies of MO’s are the same as for homonuclear diatomic molecules.

1) Carbon monoxide (CO) molecule: -

When Carbon atom combines with Oxygen atom then Carbon monoxide molecule is formed. The electronic configuration of Carbon atom (At. no. = 6) is $1s^2\ 2s^2\ 2P_x^1\ 2P_y^1\ 2P_z^0$ while, the electronic configuration of Oxygen atom (At. no. = 8) is $1s^2\ 2s^2\ 2P_x^2\ 2P_y^1\ 2P_z^1$. So, there are totally (6 + 8 =14) fourteen electrons in the Carbon monoxide molecule.

i. e. $C + O \rightarrow CO$

$6e^- + 8e^- = 14e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of C-atom with corresponding1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of O-atom give ten MO's, $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2P_x$, σ^*2P_x, $\pi 2P_y$, π^*2P_y, $\pi 2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Carbon monoxide molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2P_y^{\,2} = \pi 2P_z^{\,2}, \sigma 2P_x^{\,2}, \sigma^* 2P_{x,}\ \pi^* 2P_y = \pi^* 2P_z.$

Or, CO = $[KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ (\sigma 2Px)^2]$, Where KK represents inner shells.

In CO molecule, Oxygen is more electronegative than Carbon and hence, the atomic orbitals of Oxygen atom will be at a lower energy level than the corresponding atomic orbitals of Carbon atom. Thus, atomic orbitals of Carbon and Oxygen do not contribute equally to the MO's formed from them.

CO is isoelectronic (Having same number of electrons) with N_2 molecule. Isoelctronic species have similar MO's and similar molecular structure.

Hence, neglecting inner shell ($1s^2$) electrons in both Carbon and Oxygen atoms, These MO's are arranged according to their increasing energy as shown below.

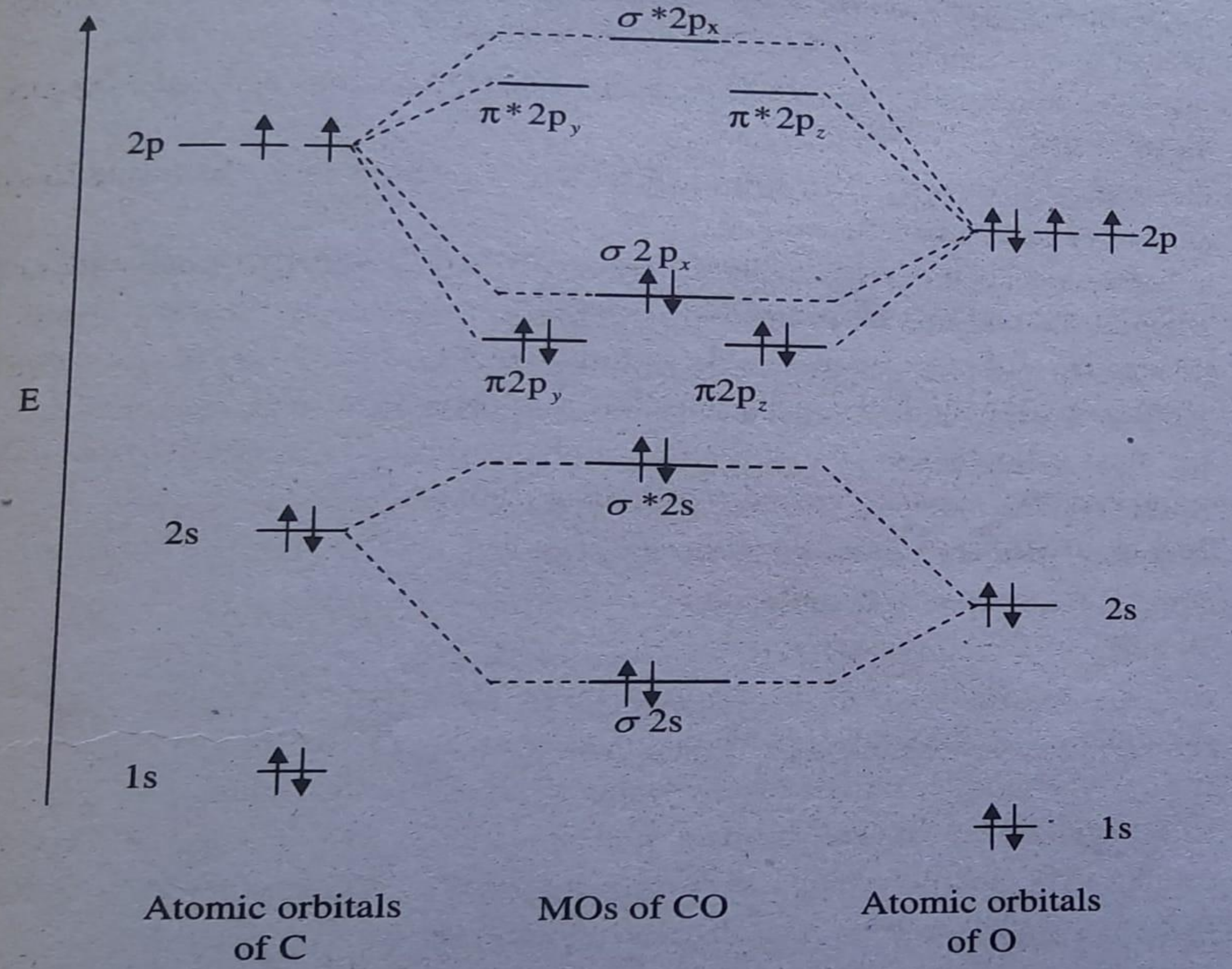


Fig. 3.19 : MO energy level diagram for CO molecule.
(x–axis is internuclear axis)

Bond order = $\frac{1}{2}(Nb - Na) = \frac{1}{2}(8 - 2) = \frac{1}{2}(6) = 3.$

It contains a triple bond ($C \equiv O$), out of which one is σ-bond and two are π-bonds.

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 2 \times (+\beta) = -8\beta + 2\beta = -6\beta.$

As the stabilization energy is negative, indicates that CO molecule exists.

Since all the electrons are paired, Carbon monoxide molecule is diamagnetic.

Polarity of Carbon monoxide molecule: -

The electronegativity of O-atom is more than that of C-atom. Due to this, contribution of AO’s towards MO’s is not identical.

The AO’s of Oxygen atom are close to bonding MO’s with respect to energy. Hence, Oxygen orbitals contribute more to bonding MO’s than Carbon orbitals. The atomic orbitals of Carbon are close to antibonding MO’s with respect to energy. Hence, Carbon orbitals contribute more to antibonding MO’s. Due to these eight electrons in bonding MO’s are close to Oxygen than to Carbon. Hence, Oxygen atom acquires slightly negative charge and Carbon acquires slight positive charge. So, CO molecule is polar but its polarity is less.

2) Nitric oxide (NO) molecule: -

When Nitrogen atom combines with Oxygen atom then Nitric oxide molecule is formed. The electronic configuration of Nitrogen atom (At. no. = 7) is $1s^2\ 2s^2\ 2P_x^{\ 1}\ 2P_y^{\ 1}\ 2P_z^{\ 1}$ while, the electronic configuration of Oxygen atom (At. no. = 8) is $1s^2\ 2s^2\ 2P_x^{\ 2}\ 2P_y^{\ 1}\ 2P_z^{\ 1}$. So, there are totally (7 + 8 =15) fifteen electrons in the Nitric oxide molecule.

i. e. $N + O \rightarrow NO$

$7e^- + 8e^- = 15e^-$

The linear combination of 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of N-atom with corresponding 1s, 2s, $2P_x$, $2P_y$ and $2P_z$ (Five) atomic orbitals of O-atom give ten MO's, $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2P_x$, σ^*2P_x, $\pi 2P_y$, π^*2P_y, $\pi 2P_z$, π^*2P_z as follows:

$1s + 1s \rightarrow \sigma 1s$ and $1s - 1s \rightarrow \sigma^* 1s$

$2s + 2s \rightarrow \sigma 2s$ and $2s - 2s \rightarrow \sigma^* 2s$

$2P_x + 2P_x \rightarrow \sigma 2P_x$ and $2P_x - 2P_x \rightarrow \sigma^* 2P_x$

$2P_y + 2P_y \rightarrow \pi 2P_y$ and $2P_y - 2P_y \rightarrow \pi^* 2P_y$

$2P_z + 2P_z \rightarrow \pi 2P_z$ and $2P_z - 2P_z \rightarrow \pi^* 2P_z$

The molecular orbital electronic configuration of Nitric oxide molecule is

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2Px^2, \pi 2Py^2 = \pi 2P_z{}^2, \pi^* 2P_y{}^1 = \pi^* 2P_z, \sigma^* 2P_x.$

Or, NO = $[KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma 2Px)^2\ (\pi 2P_y)^2 = (\pi 2P_z)^2\ \pi^* 2P_y{}^1]$, Where KK represents inner shells.

In NO molecule, Oxygen is more electronegative than Nitrogen and hence, the atomic orbitals of Oxygen atom will be at a lower energy level than the corresponding atomic orbitals of Nitrogen atom. Thus, atomic orbitals of Nitrogen and Oxygen do not contribute equally to the MO's formed from them.

Hence, neglecting inner shell ($1s^2$) electrons in both Nitrogen and Oxygen atoms, these MO's are arranged according to their increasing energy as shown below.

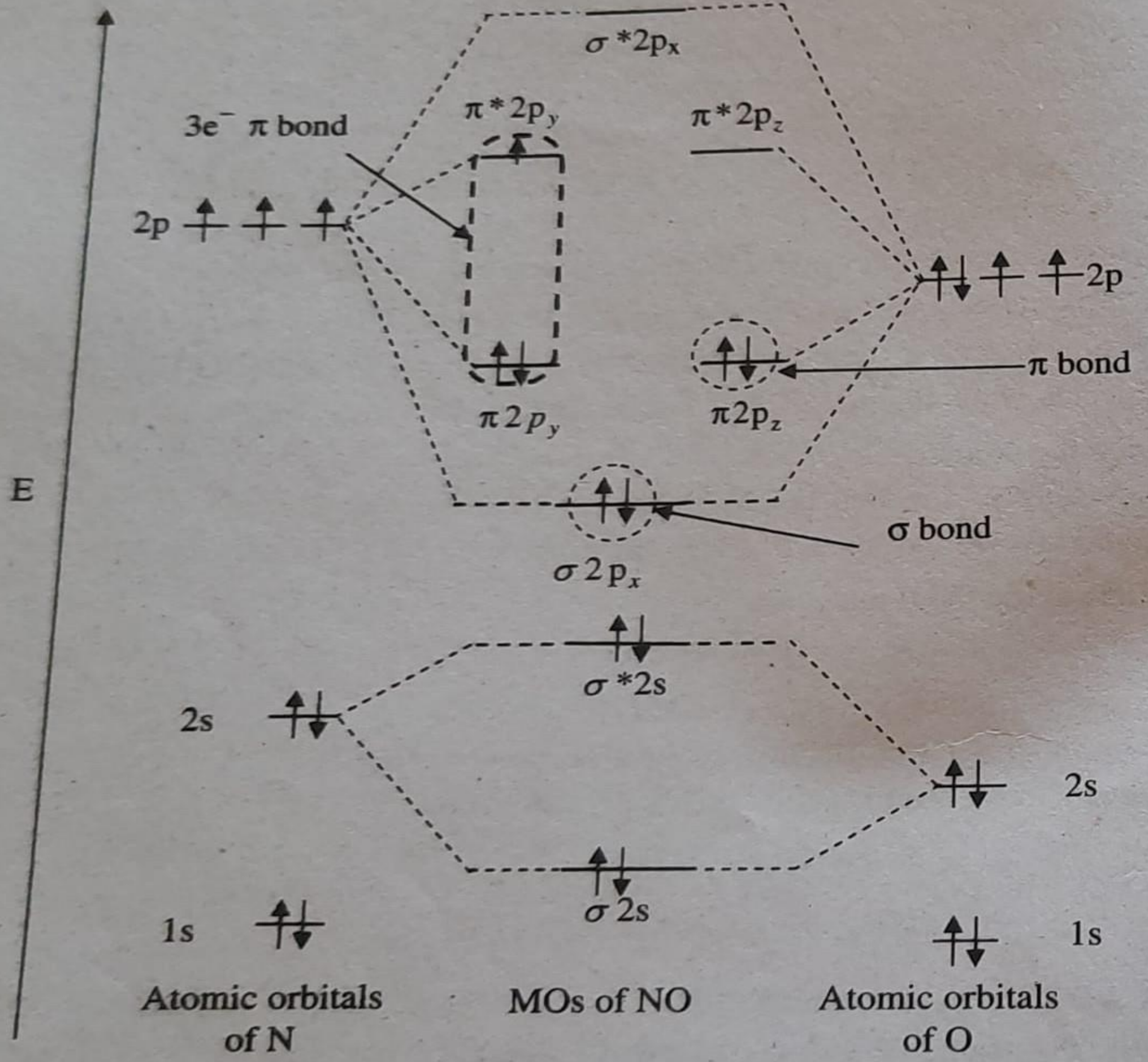
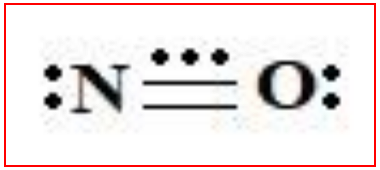


Fig. 3.20 : MO energy level diagram for NO molecule.
(x–axis is internuclear axis)

Bond order = $\frac{1}{2}(Nb—Na) = \frac{1}{2}(8-3) = \frac{1}{2}(5) = 2.5$

The bond order is 2.5, which indicates presence of one σ-bond, one π-bond and one three electron bond. The structure of NO molecule can be represented as



Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 8 \times (-\beta) + 3 \times (+\beta) = -8\beta + 3\beta = -5\beta$.

As the stabilization energy is negative, indicates that NO molecule exists, but it is less stable than N_2 molecule.

Since, the NO molecule contains one unpaired electron in $(\pi^*2P_y)^{1,}$ hence, it is paramagnetic.

3) Hydrogen Chloride (HCl) molecule: -

When Hydrogen atom combines with Chlorine atom then Hydrogen Chloride molecule is formed. The electronic configuration of Hydrogen atom (At. no. = 1) is $1s^1$ while, the electronic configuration of Chlorine atom (At. no. = 17) is $1s^2\ 2s^2\ 2P^6\ 3s^2\ 3P_x^{\ 2}\ 3P_y^{\ 2}\ 3P_z^{\ 1}$. The energy levels of the AO's of these two atoms are not identical. Similarly, there is a large difference in electronegativities of these elements. Chlorine is more electronegative than Hydrogen atom. It is experimentally observed that the energies of filled $1s^2\ 2s^2\ 2P^6\ 3s^2$ orbitals of Chlorine atom are very low than the energy of 1s atomic orbital of Hydrogen. Therefore, $1s^2\ 2s^2\ 2P^6\ 3s^2$ orbitals of Chlorine atom cannot take part in bonding. Only 3P orbitals ($3P_x$, $3P_y$ and $3P_z$) of Chlorine atom are of suitable energy and can overlap with 1s orbital of H-atom. If we assume H-Cl axis as the X-axis, then only the 3Px orbital of Cl- atom is of correct symmetry, pointing along the H-Cl axis. Thus, out of three 3P orbitals, the $3P_y$ and $3P_z$ orbitals are perpendiculars to the x-axis will be non-bonding. This is because they will give zero overlap.

Thus, only $3P_x$ orbital of Chlorine will be the most suitable to give the effective overlap. Hence, the bonding in HCl molecule is mainly due to the overlap of 1s orbital of H-atom with $3P_x$ orbital of Cl-atom.

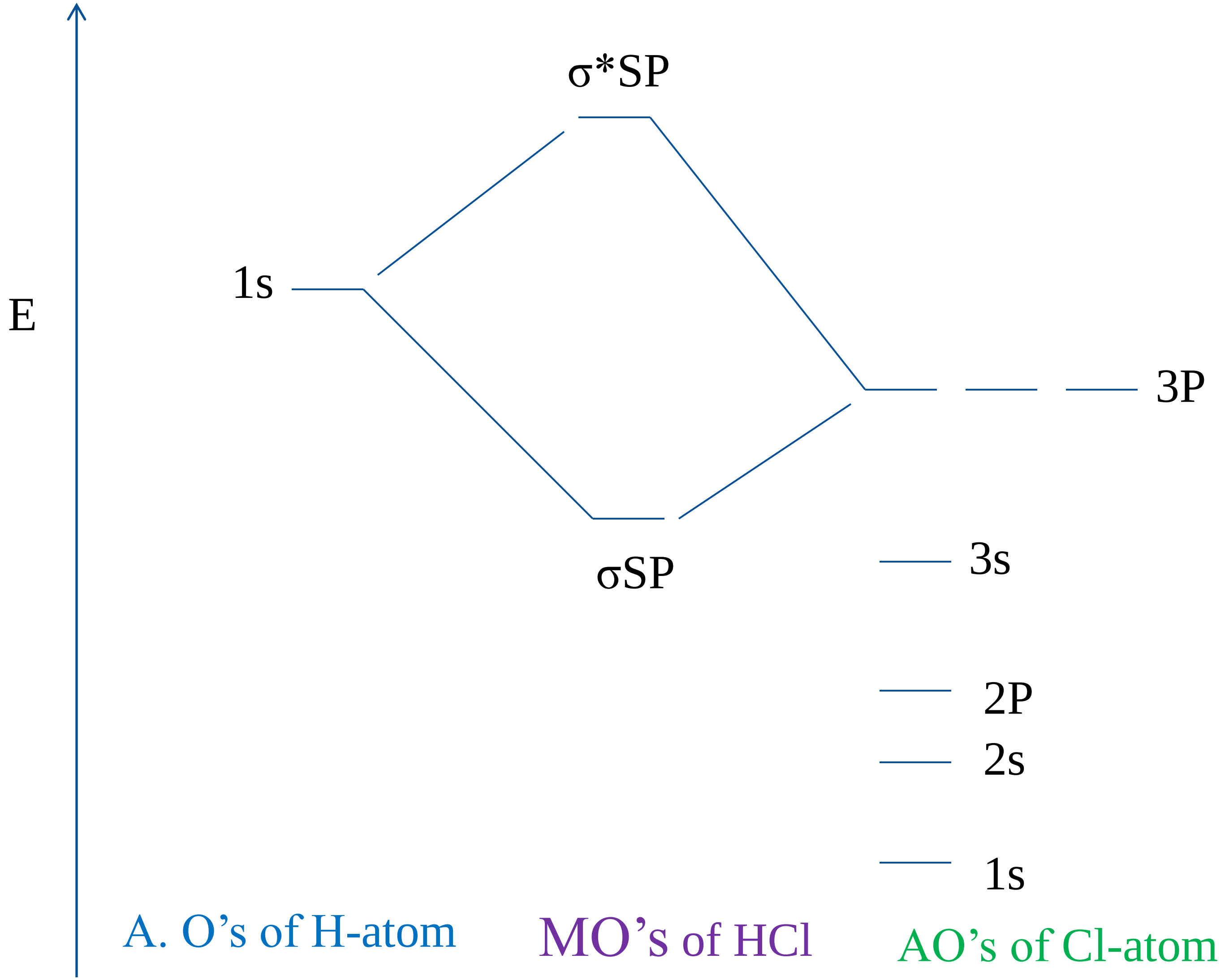
$H + Cl \rightarrow HCl$

$1e^- + 1e^- \rightarrow 2e^-$

So, after neglecting the nonbonding electrons, there are only (1 +1 =2) two electrons in the Hydrogen Chloride molecule.

The linear combination of 1s orbital of H-atom with $3P_x$ orbital of Cl-atom forms two MO's, one is bonding σsp and the other is antibonding σ*sp as shown below:

$1s + 3P_x \rightarrow \sigma sp$ and $1s - 3P_x \rightarrow \sigma^* sp$



σ*SP

E

1s

3P

σSP

3s

2P

2s

1s

A. O’s of H-atom

MO’s of HCl

AO’s of Cl-atom

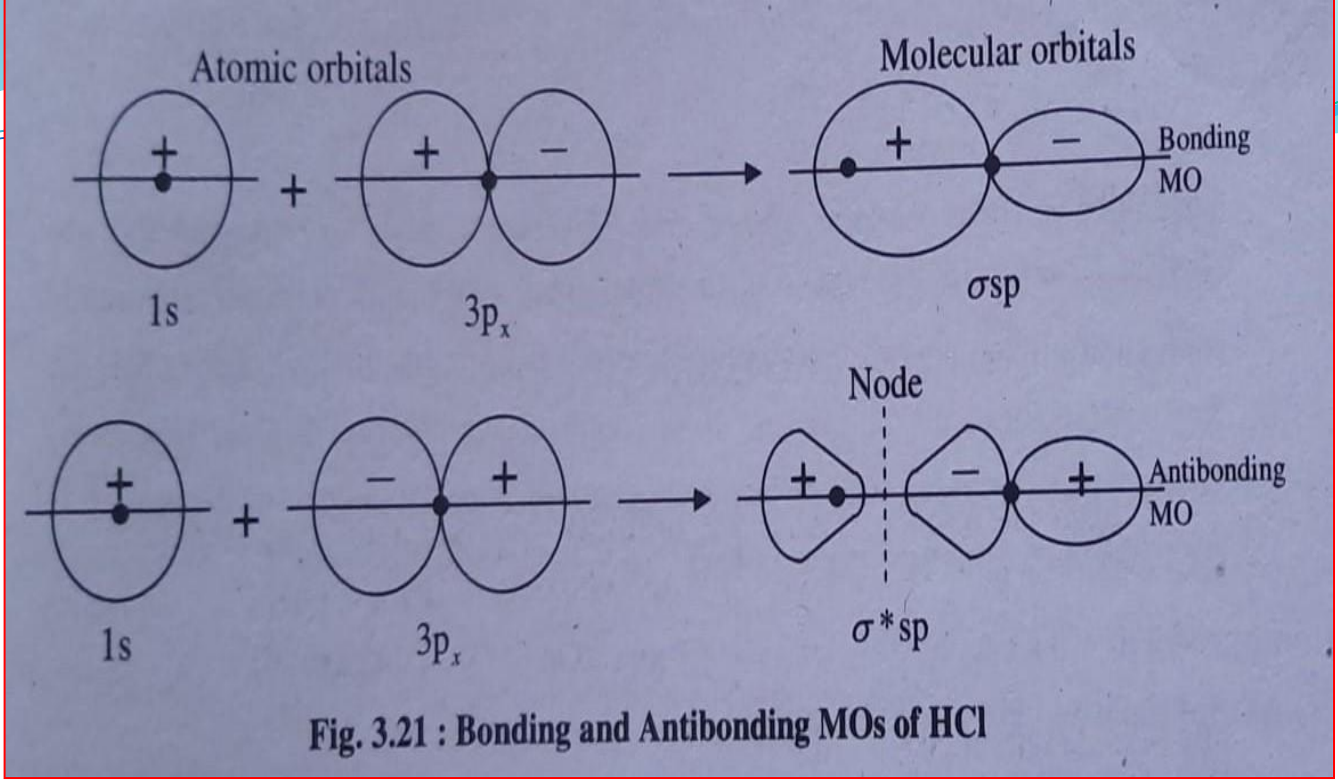


Fig. 3.21 : Bonding and Antibonding MOs of HCl

The molecular orbital electronic configuration of HCl molecule is

$[KL\ (3s^2)\ (3P_y{}^2)\ (3P_z{}^2)\ (\sigma sp^2)]$ or σsp^2

Where, K and L stand for first and second shell of Chlorine atom respectively.

In HCl molecule, Chlorine is more electronegative than Hydrogen and hence, the atomic orbitals of Chlorine atom will be at a lower energy level than the corresponding atomic orbitals of Hydrogen atom. Thus, atomic orbitals of Chlorine and Hydrogen do not contribute equally to the MO’s formed from them.

These MO’s are arranged according to their increasing energy as shown below:

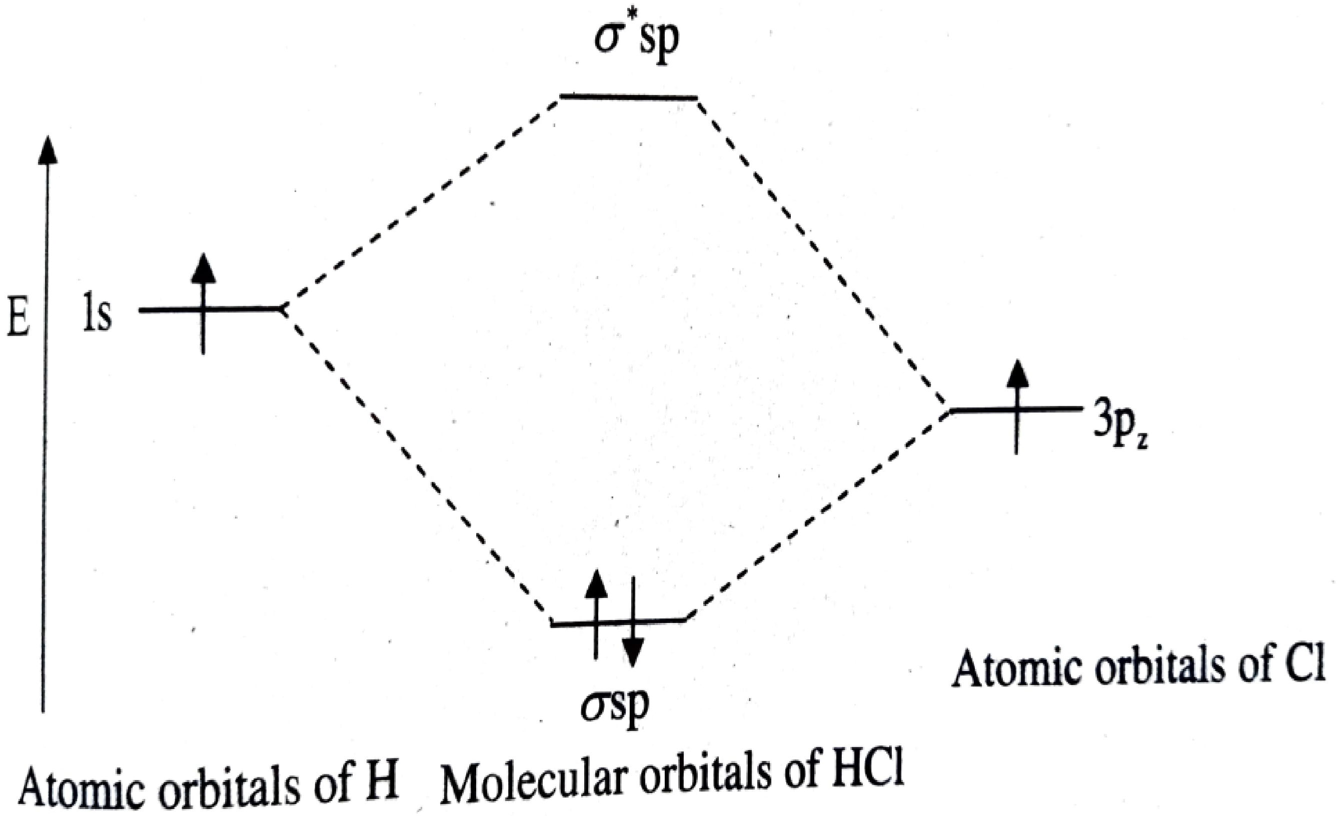


Fig. 3.22 : MO energy level diagram for HCl molecule
(x –axis is internuclear axis)

Bond order = $\frac{1}{2}(Nb - Na) = \frac{1}{2}(2 - 0) = \frac{1}{2}(2) = 1.$

The bond order is 1, which indicates presence of one σ-bond in HCl.

Stabilization Energy = S. E. = $[N_b] \times (-\beta) + [N_a] \times (+\beta)$

$= 2 \times (-\beta) + 0 \times (+\beta) = -2\beta.$

As the stabilization energy is negative, indicates that HCl molecule is stable.

Since, all the electrons in HCl molecule are paired hence, it is diamagnetic.

Polarity of HCl molecule: -

Chlorine is more electronegative than Hydrogen and the electronegativity difference is very large. Due to this atomic orbital of Cl atom is nearer to bonding σsp MO with respect to energy. The electrons in the bonding MO are much more localized on Chlorine atom which makes Chlorine slightly negatively charged and Hydrogen slightly positively charged. This causes charge separation in HCl making it polar $H^{+\delta}$- $Cl^{-\delta}$.

Comparison between VBT and MOT: -

Similarities: - 1) Both theories explains the nature and formation of the covalent bonds in the various types of molecules.

2) For the covalent bond formation orbital overlap is necessary in both the theories.

3) Both consider the sharing of electrons between the nuclei, which concentrate the electron density between the nuclei and develops the attraction between them.

4) Both consider the directional character of the covalent bond.

5) Both theories consider that the bond is formed only when the AO's of the atoms possess a) Nearly similar energy b) Suitable symmetry and c) Good overlap with each other.

6) Both consider that the Aufbau principle, Hund's rule and Pauli's exclusion principle are used for filling the electrons in the AO's and MO's.

7) Both the theories predict the non existence of He_2 and Ne_2 molecules

Difference between VBT and MOT: -

VBT	MOT
1) The AO’s simply overlap to form a bond.	1) The AO’s overlap and combine to form MO’s to form a bond.
2) The AO’s are monocentric.	2) The MO’s are polycentric.
3) Electron pairs are localized between the two nuclei.	3) Electrons are delocalized over all nuclei.
4) Atoms retain their individual character in the molecule.	4) Atoms lose their individual character in the formation of MO’s.
5) It is simple and qualitative.	5) It is quantitative.
6) It fails to explain the magnetic property of molecule.	6) It is used to explain the magnetic property of molecule.
7) Only half filled orbitals from valency shell take part in bonding.	7) All the atomic orbitals (Filled, half filled or vacant) from valency shell take part in bonding.
8) It cannot predict the stability of molecule.	8) It predicts the stability of molecule.
9) It fails to explain the existence of odd molecule ions. E. g. H_2^+, He_2^+, etc.	9) It explains the existence of odd molecule ions. E. g. H_2^+, He_2^+, etc.
10) It fails to explain paramagnetism in O_2 molecule.	10) It explains the paramagnetism in O_2 molecule.
11) The MO wave function is the product of atomic wave functions. i.e. $\Psi_{MO} = \Psi_A \times \Psi_B$	11) The MO wave function is the algebraic sum of atomic wave functions. i.e. $\Psi_{MO} = \Psi_A \pm \Psi_B$

Distinction between Bonding and Antibonding MO's: -

Bonding MO	Antibonding MO
1) Formed by addition overlap of AO's.	1) Formed by subtraction overlap of AO's.
2) Electron density concentrated between the nuclei.	2) Electron density lies away from nuclei.
3) Nuclear repulsion is shielded.	3) Nuclear repulsion is not shielded.
4) Lower in energy than parent atomic orbitals.	4) Higher in energy than parent atomic orbitals.
5) More stable than corresponding AO's.	5) Stability is less than corresponding AO's.
6) Favours bond formation.	6) Loss of bonding takes place.
7) Electrons in bonding MO increase bond order.	7) Electrons in antibonding MO decrease bond order.
8) No node between the nuclei.	8) A nodal plane is present between the nuclei perpendicular to the bonding axis.

Comparison between atomic orbital and Molecular orbital: -

1) Both atomic and molecular orbitals can accommodate maximum two electrons with opposite spins.

2) Both have different energies and get arranged according to their energy in the atom or molecule.

3) Both have different shapes and size.

4) Filling of electrons in AO’s and MO’s follow Aufbau’s principle, Pauli’s exclusion principle and Hund’s rule of maximum multiplicity.

Difference between Atomic orbitals and Molecular orbitals: -

Atomic orbitals	Molecular orbitals
1) Atomic orbitals are self existing.	1) MO's are formed by combination of AO's.
2) AO's are monocentric.	2) MO's are polycentric.
3) AO's are denoted by s, p, d, f etc.	3) MO's are denoted by σ, σ*, π, π*, δ etc.
4) These are of single type.	4) These are of two types, Bonding and antibonding.
5) It belongs to single atom.	5) It belongs to whole molecule.
6) It has simple shape.	6) It has complex shape.

Difference between σ and π MO's: -

σ MO's	π MO's
1) Formed by axial overlap of AO's which are pointing along the internuclear axis.	1) Formed by lateral overlap of AO's which are perpendicular to the line joining the nuclei.
2) The electron density is concentrated between the two nuclei.	2) The electron density is zero between the two nuclei.
3) All σ-bonding MO's are symmetric about the internuclear axis.	3) These have no symmetry about the internuclear axis.
4) All σ*-antibonding MO's are unsymmetric.	4) All π*-antibonding MO's are symmetric.

Limitations of MOT: -

1) According to MOT, the inner completely filled shells do not participate in bonding. This may be wrong.

2) It involves mixing of orbitals rather than hybridization.

3) MOT do not consider resonance concept of bonding.

4) For polyatomic molecules, it fails to explain the contribution of atomic orbitals to the mixed atomic orbitals.

5) The theory requires the knowledge of symmetry and group theory.