INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 6

DATE:- 21, APRIL, 2021

TIME: (10.00A.M.)

Linear combination of atomic orbitals: (LCAO method):

Consider the two similar atoms H and H. These atoms are denoted as 1 and 2. Atomic orbital of atom 1 has wave function ψ_1 and atomic orbital of atom 2 has wave function ψ_2. When these atoms form a bond, the electrons originally in the atomic orbitals now occupy molecular orbitals. The molecular orbital is formed by a linear combination of the atomic orbitals ψ_1 and ψ_2 as

$$\Psi = N [C_1 \psi_1 + C_2 \psi_2]$$

Where Ψ is the wave function for the molecular orbital. N is the normalizing constant. The value of N is so selected that the probability of finding the electron in the whole space of the molecule is unity. C_1 and C_2 are the constants, whose values are so selected that they give a minimum energy for the molecular orbital wave function Ψ.

A wave function Ψ describes the probability of finding the electron and Ψ^2 describes the electron density. The two ways of combinations are

$\Psi_{(g)} = N\ [\psi_1 + \psi_2]$ and

$\Psi\ (u) = N\ [\psi_1 + (-\ \psi_2)]\ = N\ [\psi_1 - \psi_2]$

Thus, when a pair of atomic orbitals ψ_1 and ψ_2 combines they produce a pair of molecular orbitals $\Psi_{(g)}$ and $\Psi\ (u)$. Hence, the number of molecular orbitals produced must always be equal to the number of atomic orbitals taking part in combination. i.e. orbitals are not destroyed. Thus, such type of addition and subtraction of the wave functions of the atomic orbitals is called as LCAO principle.

In the MOT, wave functions are designated $\Psi_{(g)}$ and $\Psi\ (u)$. The letter 'g' stands for gerade (even) and the letter 'u' stands for ungerade (odd). The symbols g and u refer to the symmetry of the orbitals about its centre. The wave function is gerade, if the sign of Ψ remains unchanged when the orbital is reflected about its centre. While, the wave function is called ungerade, when the sign of Ψ is changed on the reflection of orbital about its centre.

The electron distribution in a MO can be obtained by squaring the wave function.

$$\Psi^2\,(g) = \Psi_1{}^2 + \Psi_2{}^2 + 2\,\Psi_1\,\Psi_2$$

$$\Psi^2\,(u) = \Psi_1{}^2 + \Psi_2{}^2 - 2\,\Psi_1\,\Psi_2$$

These two molecular orbitals differ by $2\,\Psi_1\,\Psi_2$. The wave function $\Psi_{(g)}$ increases the electron density between the nuclei by an amount $2\,\Psi_1\,\Psi_2$ and is therefore a bonding MO of lower energy. The wave function $\Psi_{(u)}$ decreases the electron density in between the nuclei by an amount $2\,\Psi_1\,\Psi_2$ and is therefore an anti-bonding MO of higher energy.

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 7
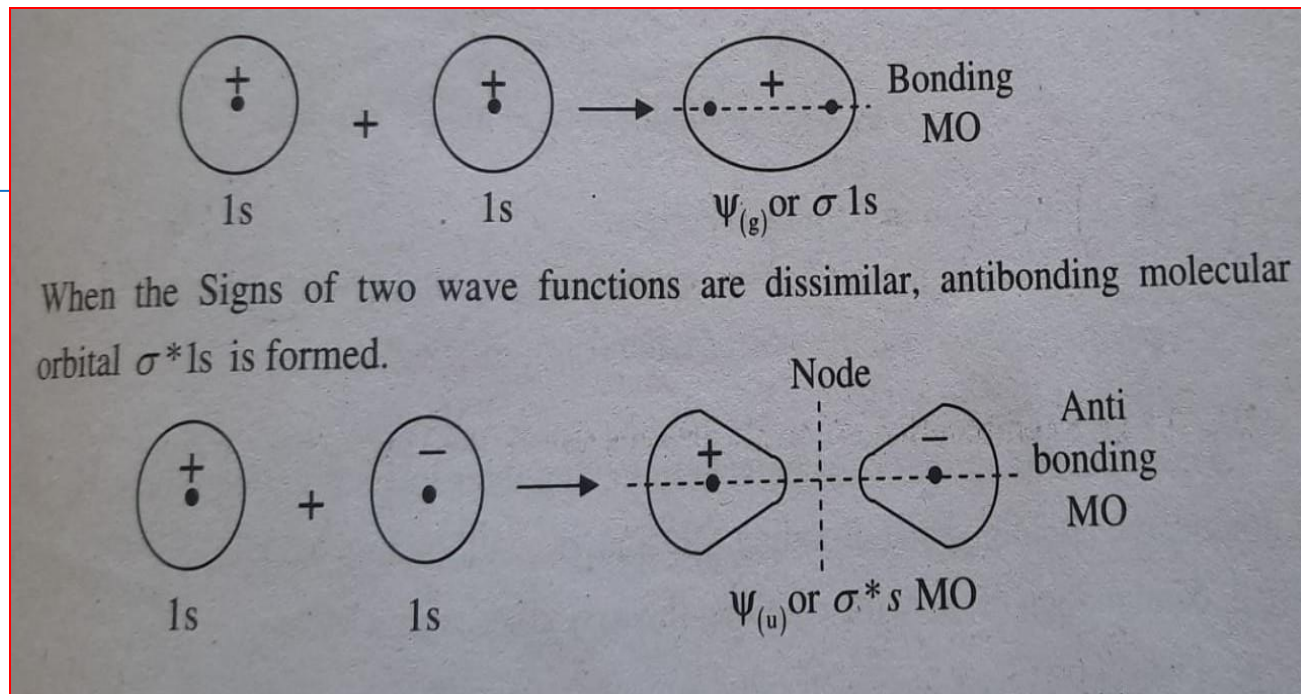
DATE:- 23, APRIL, 2021
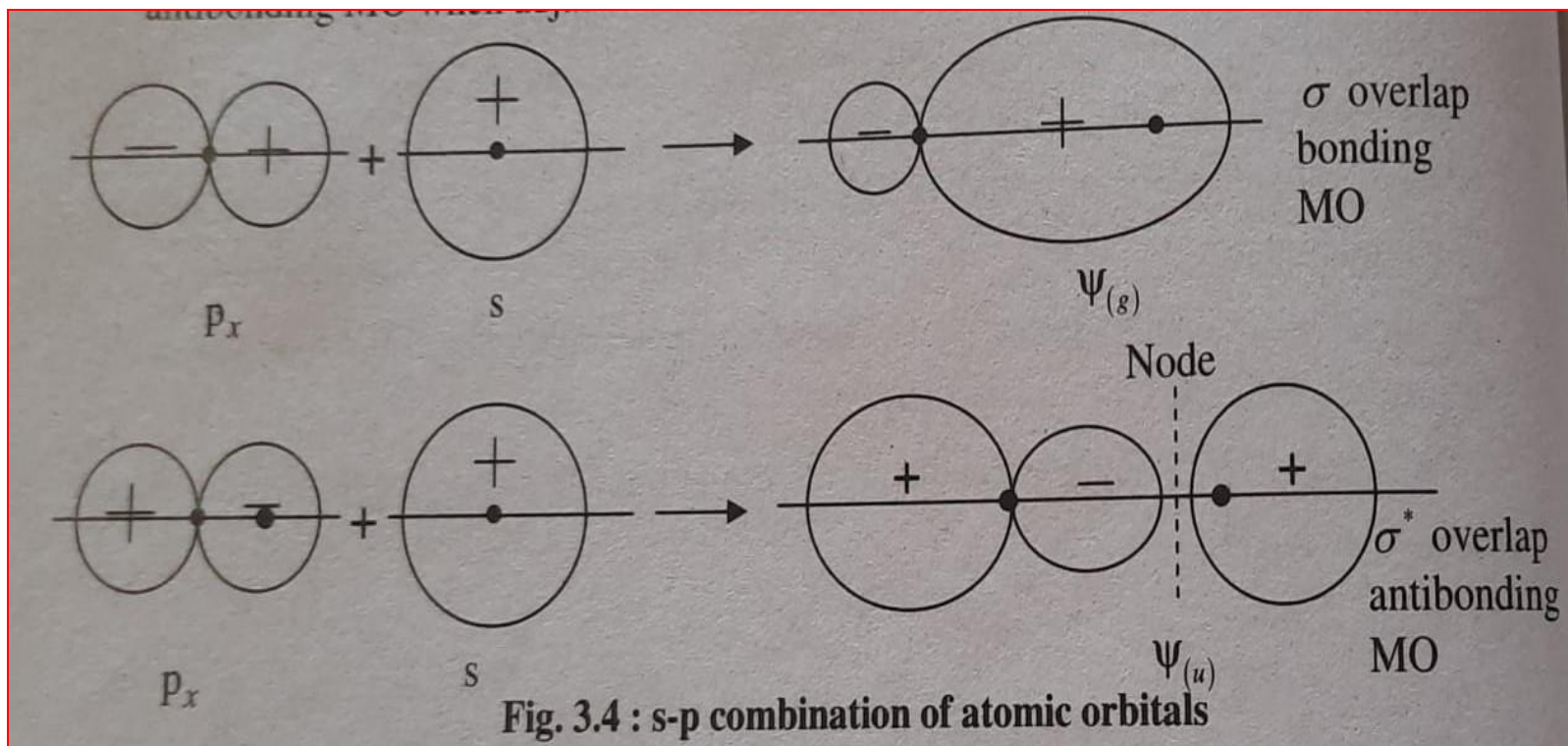
TIME: (9.00A.M.)

Types of combinations: -

•Combination of S-S orbitals: - The combination of S-orbital of one atom with the S-orbital of the other atom is called S-S combination. This overlap of orbitals occurs along the axis joining the nuclei produces σ-bond and σ-MO's. i.e. The pair of atomic orbitals combine to give a pair of MO's $\Psi_{(g)}$ and $\Psi_{(u)}$. When the adjacent lobes have same sign then bonding MO is formed. While, if the adjacent lobes have the opposite sign then anti-bonding MO is formed as follows:

1s + 1s →σ1s (BMO)

1s -1s →σ*1s (ABMO)

When the Signs of two wave functions are dissimilar, antibonding molecular orbital σ*1s is formed.

•Combination of S-P orbitals: - The combination of S-orbital of one atom with the P-orbital of the other atom is called S-P combination. This combination takes place only when the lobes of the P-orbitals are pointing along the axis joining the nuclei. This produces σ-bond and hence the σ-MO's.

s + p → Ψ$_{(g)}$ (BMO)
s - p → Ψ$_{(u)}$ (ABMO)

Fig. 3.4 : s-p combination of atomic orbitals

3) Combination of P-P orbitals: - The combination of P-orbital of one atom with the P-orbital of the other atom is called P-P combination. Overlap of orbitals along the axis joining the nuclei produces σ-bond and hence the σ-MO's. While, the lateral overlap of atomic orbitals produces π-bond and hence π-MO's.

a) Formation of σ-MO's: - The combination of two P-orbitals both of which have lobes pointing along the axis joining the nuclei produces σ-bond and hence the σ-MO's. Here x-axis has been assumed to be the molecular axis.

$P_x + p_x \rightarrow \sigma p_x$ or $\Psi(g)$ BMO

$P_x - p_x \rightarrow \sigma^* p_x$ or $\Psi(u)$ ABMO
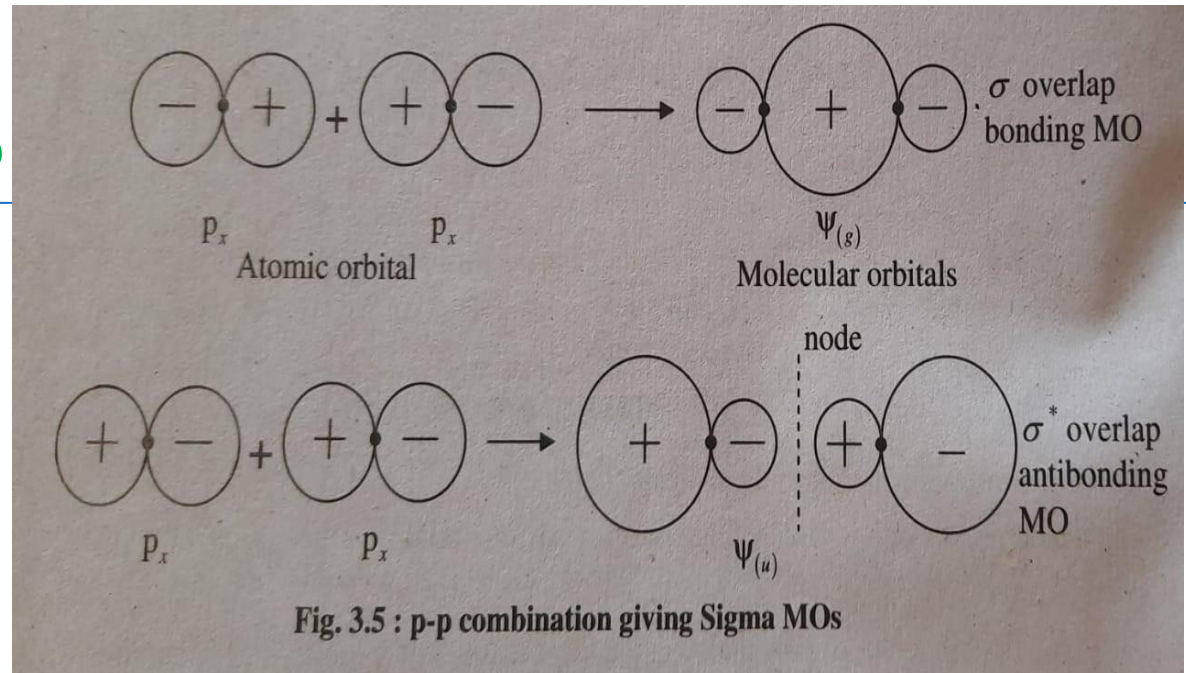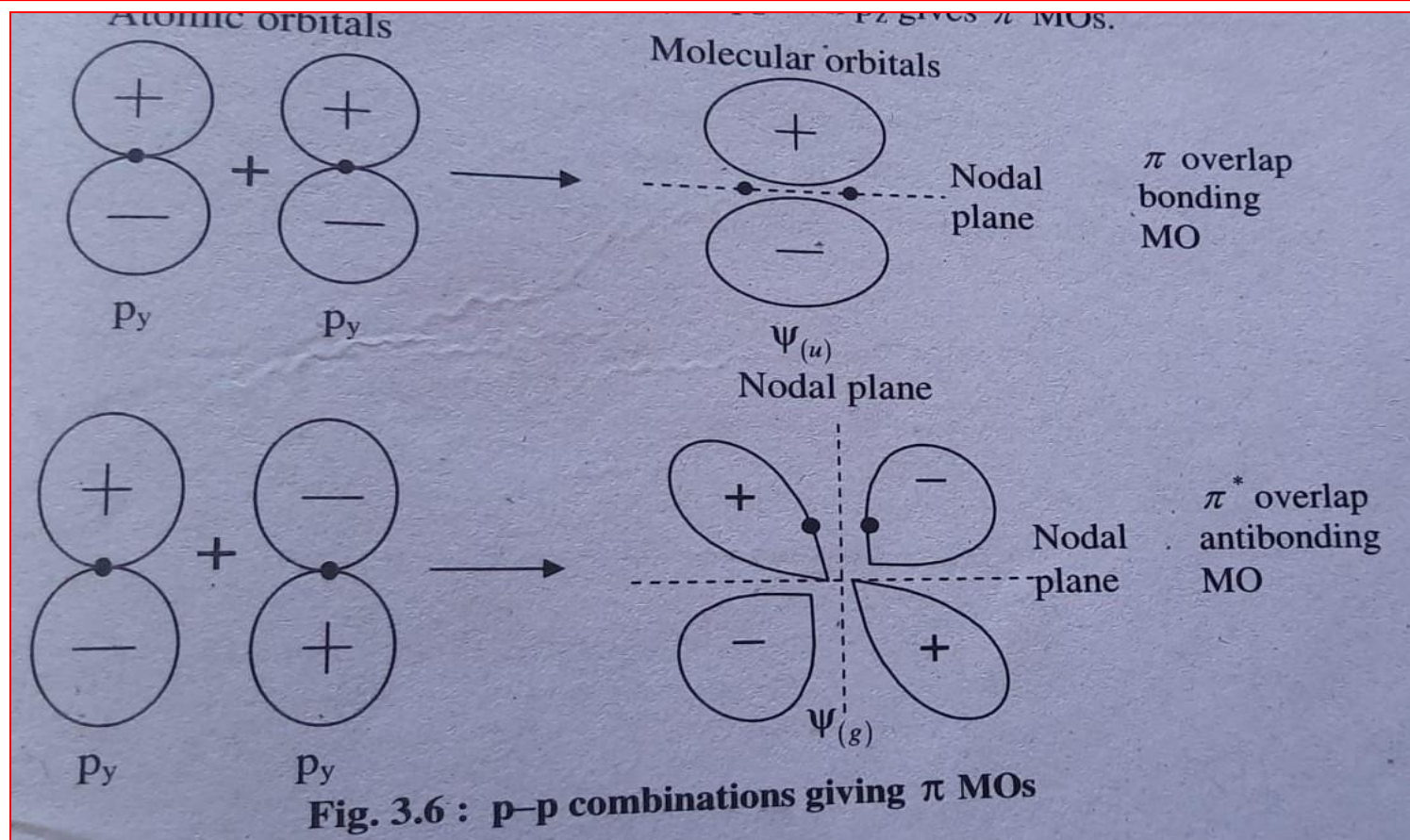

Fig. 3.5 : p-p combination giving Sigma MOs

b) Formation of π-MO's: - The combination of two P-orbitals both of which have lobes perpendicular to the axis joining the nuclei and hence overlaps laterally. This produces π-bond and hence the π-MO's.
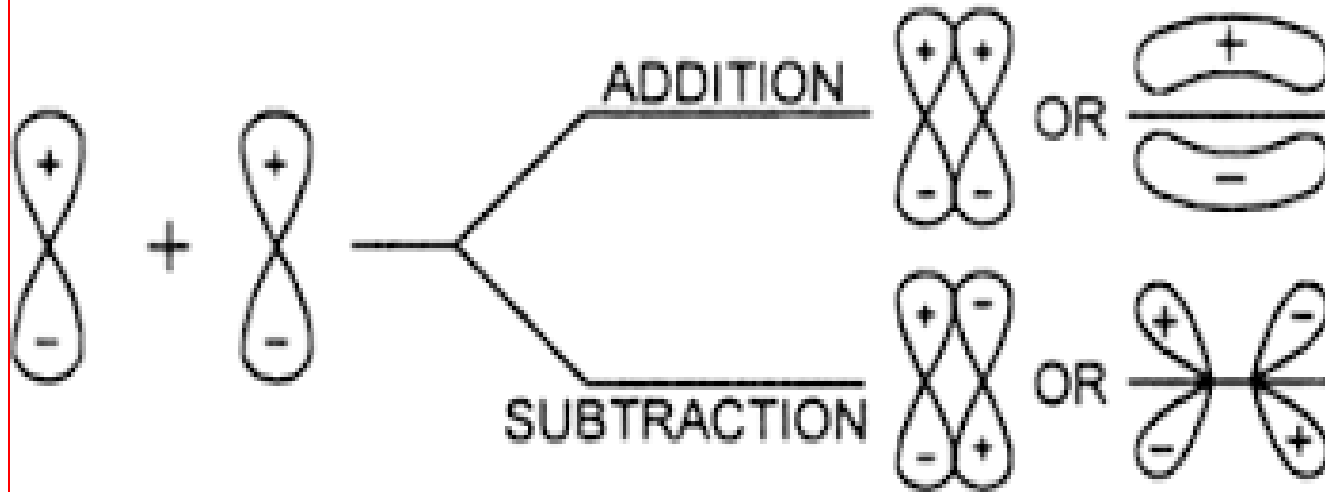
$p_y + p_y \rightarrow \pi p_y$ (BMO) similarly, $p_z + p_z \rightarrow \pi p_z$ (BMO)

$p_y - p_y \rightarrow \pi^* p_y$ (ABMO) similarly, $p_z - p_z \rightarrow \pi^* p_z$ (ABMO)

Fig. 3.6 : p–p combinations giving π MOs

Or

(ii) p_x and p_x combination.

•Combination of P and d-atomic orbitals: - The combination of P-orbital of one atom with the d-orbital of another atom is called P-d combination. The lateral overlap of atomic orbitals produces π-bond and hence π-MO's.

P_y or p_z + d → π-MO's

P_y or p_z - d → π*-MO's

Fig.3.7 : p-d combination of atomic orbitals
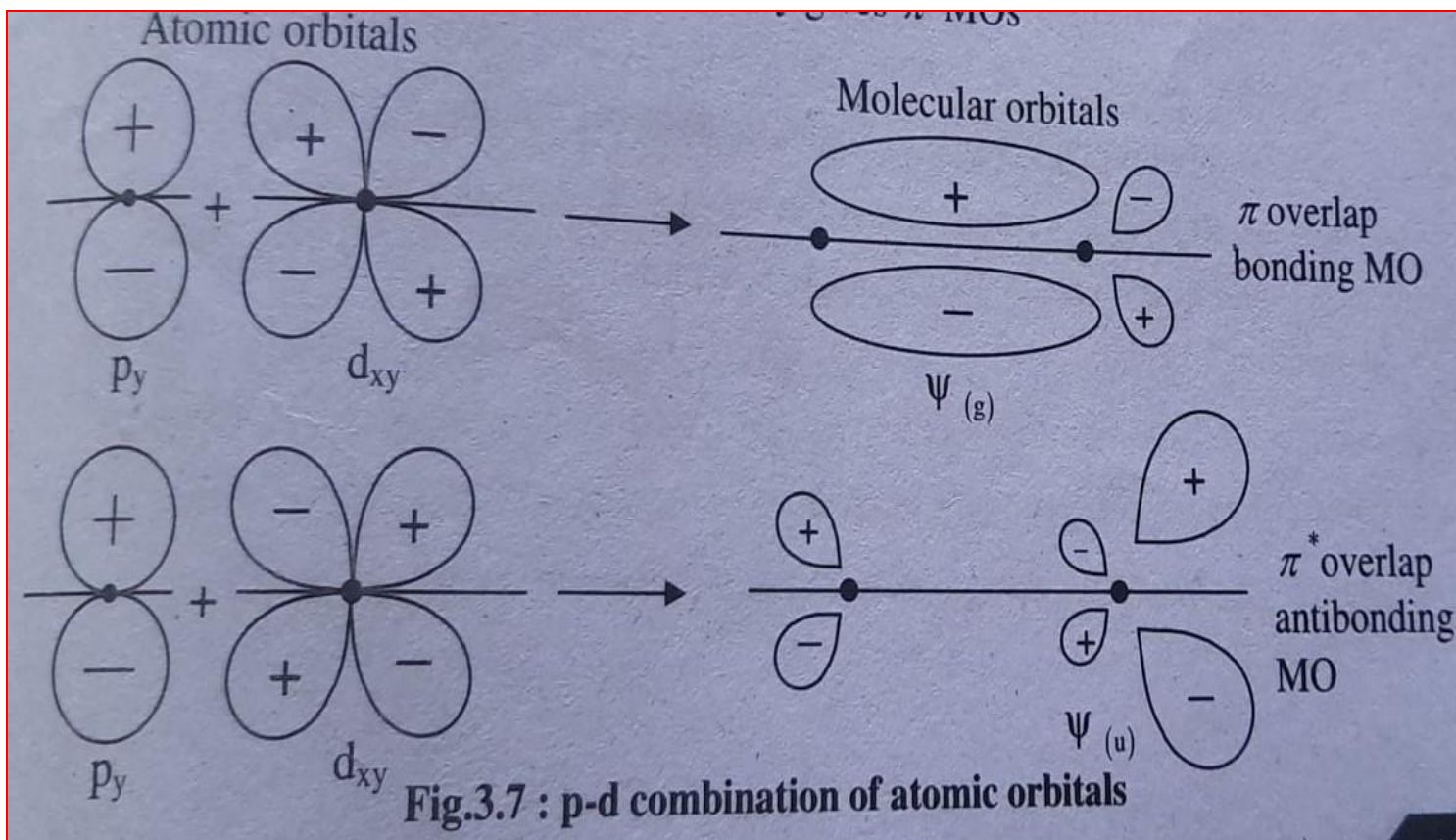
•Combination of d and d-atomic orbitals: - The combination of d-orbital of one atom with the d-orbital of another atom is called d-d combination. This produces one bonding MO denoted as δ and one antibonding MO denoted by δ^*. The formation of δ MO takes place by the overlap of two d_{xy} or two $d_{x^2-y^2}$ atomic orbitals. These δ MOs have two nodal planes along the molecular axis.

d + d $\rightarrow$ BMO and d - d $\rightarrow$ ABMO

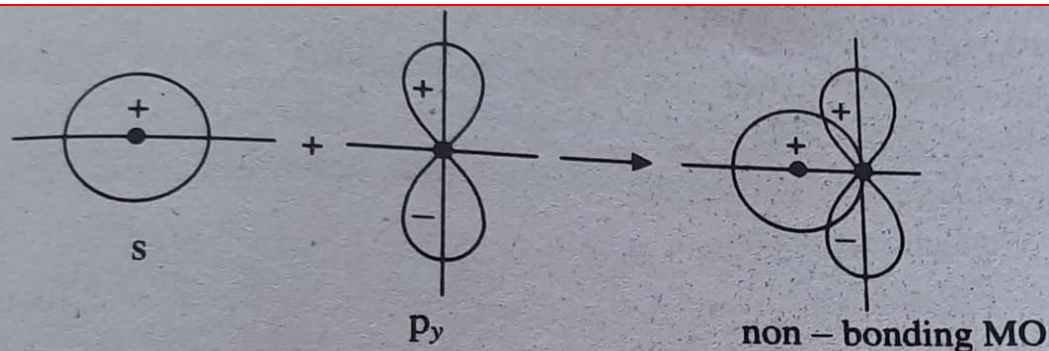Fig.3.8 : d-d combination of atomic orbitals
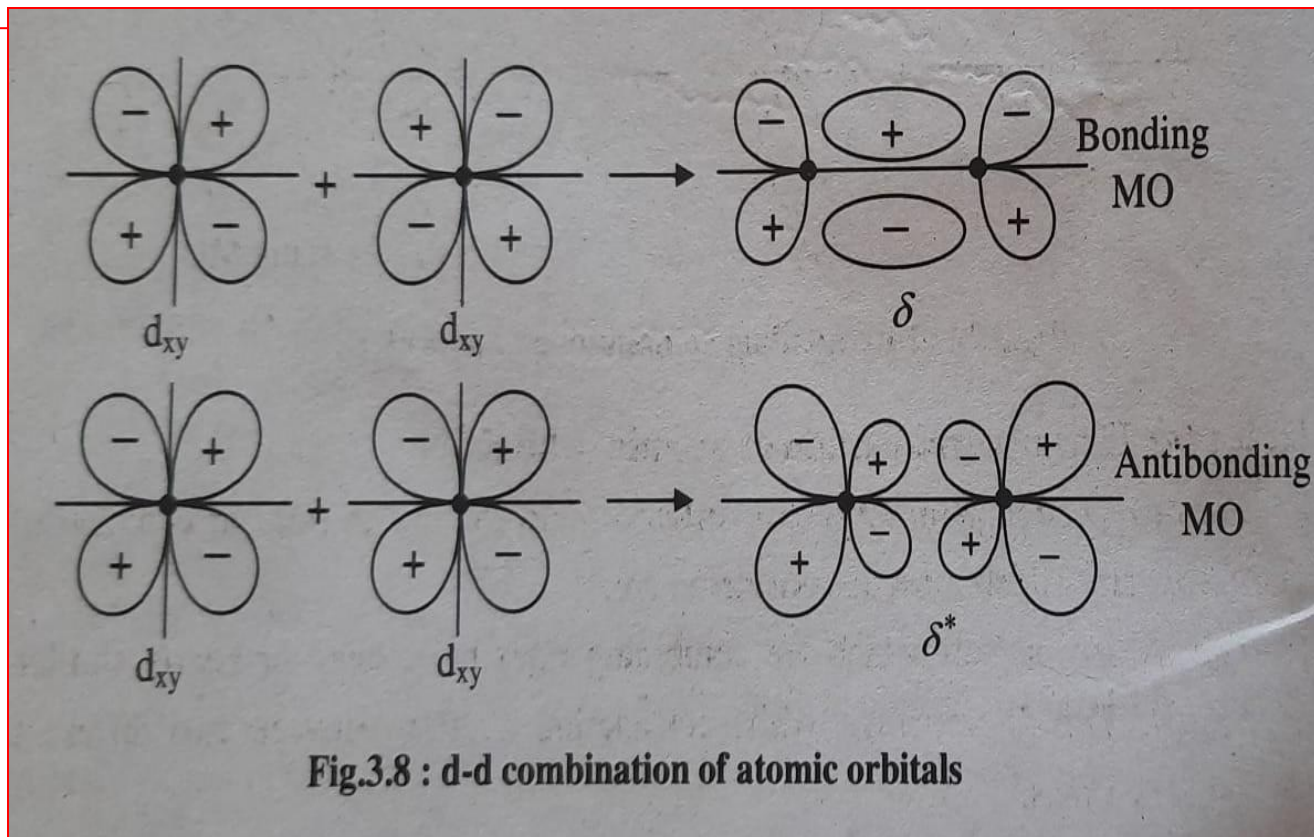
INORGANIC CHEMISTRY

CHAPTER- MOLECULAR ORBITAL THEORY

ONLINE LECTURE NO. 8

# DATE:- 28, APRIL, 2021

TIME: (10.00A.M.)

Non-bonding Molecular orbitals: - The orbitals which do not take part in bonding are called as non-bonding molecular orbitals. These orbitals of atoms are either very low in energy or they are not of proper symmetry, hence they are not used for bonding. So, they are called as non-bonding molecular orbitals. In these combinations any stabilization due to overlapping of '+' with '+' is destabilized by an equal amount of overlap of '+' with '—'.
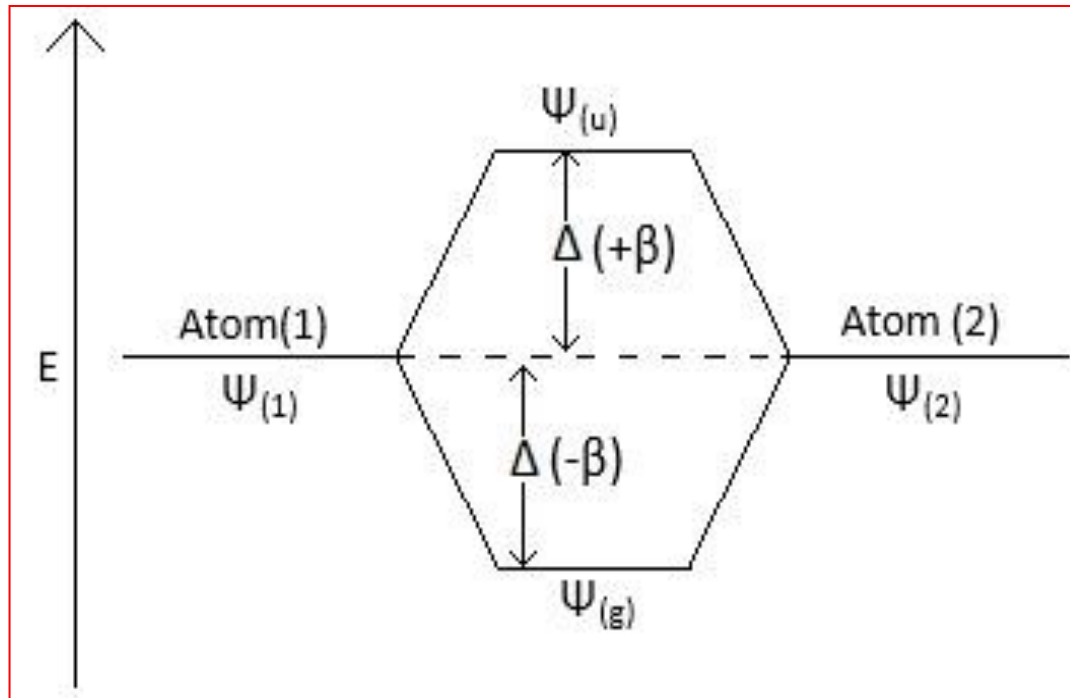

Fig. 3.9 : Non-bonding combination of s with P_y
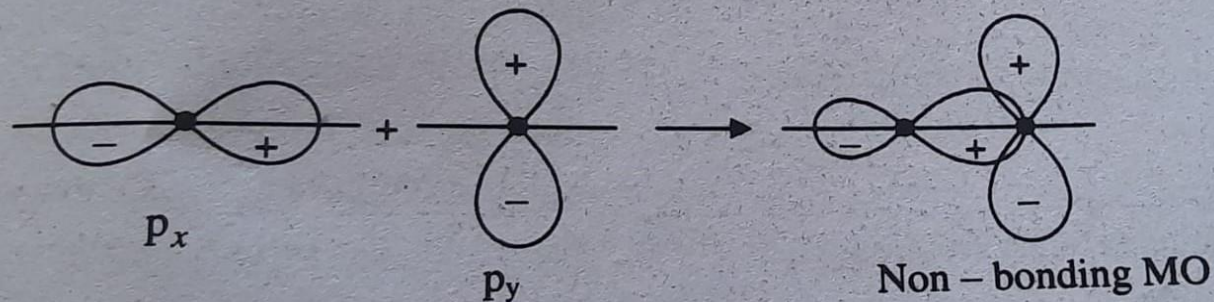
Fig.3.10 : Non-bonding combination of p_x with p_y

The MO energy level diagram: - In MO energy level diagram, the atomic orbitals of the combining atoms are shown to the two sides and the MO's formed are shown in the centre.

Δ or β represents the energies evolved or absorbed during formation of bonding and anti-bonding MO's respectively. The energy of the bonding MO is lower than that of the atomic orbital by an amount Δ or ($-\beta$) known as stabilization energy. Similarly, the energy of the anti-bonding MO is greater than that of the atomic orbital by an amount Δ or ($+\beta$) known as destabilization energy.

The decrease in energy is balanced by the same increase in energy. "The diagram representing the energies of atomic and MO's at a particular internuclear distance between the atoms is called as MO energy level diagram".

The order of energy of molecular orbitals has been determined mainly from spectroscopic data. The energy sequence of the MO's from Hydrogen upto Nitrogen (N_2) molecule is

$$\sigma 1S, \sigma^* 1S, \sigma 2S, \sigma^* 2S, \pi 2Py = \pi 2Pz, \sigma 2Px, \sigma^* 2Px, \pi^* 2Py = \pi^* 2Pz\ldots\ldots$$

This order is because for elements B, C and N the energy difference between 2s and 2p atomic orbitals is very small and hence they interact with one another.

Similarly, from Oxygen (O_2) to Neon (Ne_2) molecule, the sequence is

$$\sigma 1S, \sigma^* 1S, \sigma 2S, \sigma^* 2S, \sigma 2Px, \pi 2Py = \pi 2Pz, \pi^* 2Py = \pi^* 2Pz, \sigma^* 2Px \ldots\ldots$$
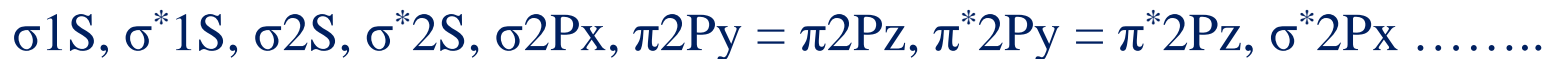
The combination of 2Px with 2Px orbitals of the two atoms gives $\sigma 2Px$ and $\sigma^* 2Px$ MO's. While, the combination of 2Py with 2Py and 2Pz with 2Pz of two atoms give $\pi 2Py$, $\pi^* 2Py$ and $\pi 2Pz$, $\pi^* 2Pz$ MO's respectively. The $\pi 2Py$ and $\pi 2Pz$ MO's have equal energies and are said to be doubly degenerate. Similarly, $\pi^* 2Py$ and $\pi^* 2Pz$ MO's are also doubly degenerate and are of equal energies.

Bond order or Bond Multiplicity: -

The number of bonds between the two combining atoms in the molecule is called the bond order.. The bond order in MO theory may be defined as "Half of the difference between the number of electrons in bonding MO's (N_b) and in anti-bonding MO's (N_a)".

Thus, Bond order = $\frac{1}{2}(Nb - Na)$

The electrons in bonding MO's help in the formation of bonds while, those in the anti-bonding MO's oppose it. It means that, there should always be more number of electrons in bonding MO's than in anti-bonding MO's for the formation of bond between the two atoms.

Characteristics of bond order: -

1) Bond order may be a whole number or a fraction.

2) If bond order is one, it indicates presence of single bond, while bond order two and three indicates presence of double and triple bonds respectively.

3) Fractional bond order indicates odd electron species.

4) If bond order is zero, the molecule does not exist.

5) Higher bond order gives shorter bond length and higher stability.

6) If $N_b > N_a$, the molecule is stable. The stability is due to net force of attraction.

7) If $N_b = N_a$ or $N_b < N_a$, the molecule does not exists. The net result is force of repulsion.

INORGANIC CHEMISTRY

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ORBITAL THEORY

ONLINE LECTURE NO. 9

DATE:- 30, APRIL, 2021

TIME: (9.00A.M.)

Magnetic property or Magnetism: -

The electrons in the molecule behave like tiny magnets. If the molecule contains one or more unpaired electrons, then it is called as paramagnetic. While, if the all the electrons are paired the molecule is called as diamagnetic.

Stabilization Energy: -

The stabilization energy can be calculated as:

S. E. = [Number of electrons in BMO] × (-β) + [Number of electrons in ABMO] × (+β)

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

The molecule with higher stabilization energy is more stable.

Rules for LCAO's: - There are three rules for LCAO's to form MO's. The MO's can be formed only when the following conditions are fulfilled:

1) The energies of combining atomic orbitals forming MO's must be nearly the same. e.g. 1S-orbital can combine with another 1S-orbital but not with 2S-orbitals.

2) The combining orbitals must be capable of overlapping and close enough for effective overlapping.

3) The combining orbital must have the same symmetry about the molecular axis. i.e. 2Px orbital will not combine with 2Py or 2Pz orbitals due to their different symmetries.

Rules for filling of electrons in MO's: -

1) The MO's are arranged in the increasing order of energies.

2) The MO with lowest energy is filled first.

3) Each MO can have maximum two electrons with opposite spins.

4) If there are two or more MO's at same energy levels, then pairing of electrons will occur only when each orbital of same energy has one electron.

Examples of MO treatment for homonuclear diatomic molecules: -

The molecules formed by combination of two atoms of the same element are called as homonuclear diatomic molecule. e. g. H_2, N_2, O_2, etc.

1) Hydrogen Molecule (H_2): - When two Hydrogen atoms combine together then Hydrogen molecule is formed. The electronic configuration of each Hydrogen atom (At. no. =1) is $1s^1$. So, there are (1 + 1 =2) two electrons in the Hydrogen molecule.

i. e. $H + H \rightarrow H_2$

$1e^- + 1e^- = 2e^-$

The linear combination of 1s atomic orbital of first H-atom with 1s atomic orbital of second H-atom gives two MO's, σ1s and σ*1s.

$1s + 1s \rightarrow σ1s$ and $1s - 1s \rightarrow σ*1s$

The bonding MO σ1s has lower energy than antibonding MO σ*1s. H_2 molecule contains two electrons. Both these electrons occupy lowest energy σ1s orbital. The molecular orbital electronic configuration of Hydrogen molecule is $σ1s^2$.

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

Fig. 3.13 : MO energy level diagram for H_2 molecule
(x- axis is internuclear axis)
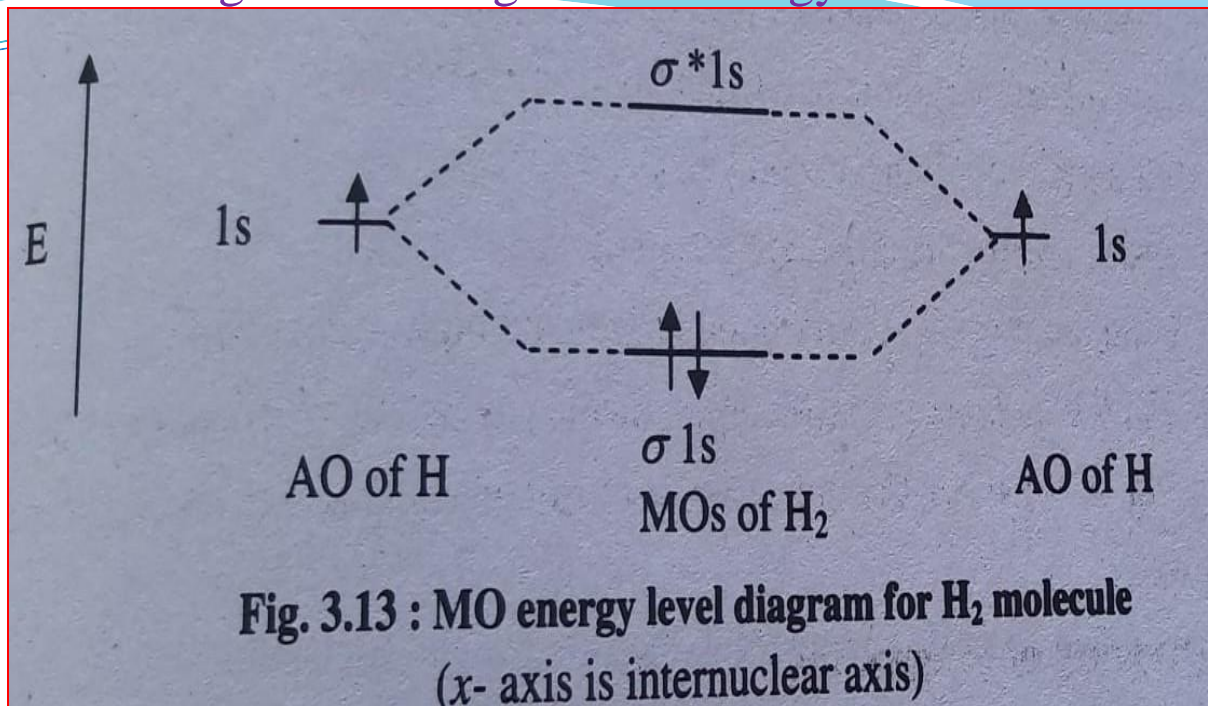
Bond order $= \frac{1}{2}$ (Nb—Na) $= \frac{1}{2}$ (2 − 0) $= \frac{1}{2}$ (2) $= 1$.

The bond order is one, which indicates the presence of single sigma bond between two H-atoms.

The molecule is diamagnetic, since both the electrons are paired.

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, the H_2 molecule exists and as the bond order is one, there should be single bond between two H-atoms. i. e. (H-H).

INORGANIC CHEMISTRY

CHAPTER- MOLECULAR

ORBITAL THEORY

ONLINE LECTURE NO. 10

DATE:- 5, MAY, 2021

TIME: (10.00A.M.)

2) Helium Molecule (He_2): - When two Helium atoms combine together then Helium molecule is formed. The electronic configuration of each Helium atom (At. no. =2) is $1s^2$. So, there are (2 + 2 =4) four electrons in the Helium molecule.

i. e. He + He → He_2

2e⁻ + 2e⁻ = 4e⁻

The linear combination of 1s atomic orbital of first He-atom with 1s atomic orbital of second He-atom gives two MO's, σ1s and σ*1s.

1s + 1s → σ1s and 1s – 1s → σ*1s

The bonding MO σ1s has lower energy than antibonding MO σ*1s. He_2 molecule contains four electrons, out of which two electrons occupy lowest energy σ1s orbital and remaining two electrons occupy σ*1s orbital. The molecular orbital electronic configuration of Helium molecule is $σ1s^2 σ*1s^2$.

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

Fig. 3.14 : MO energy level diagram for He_2 molecule
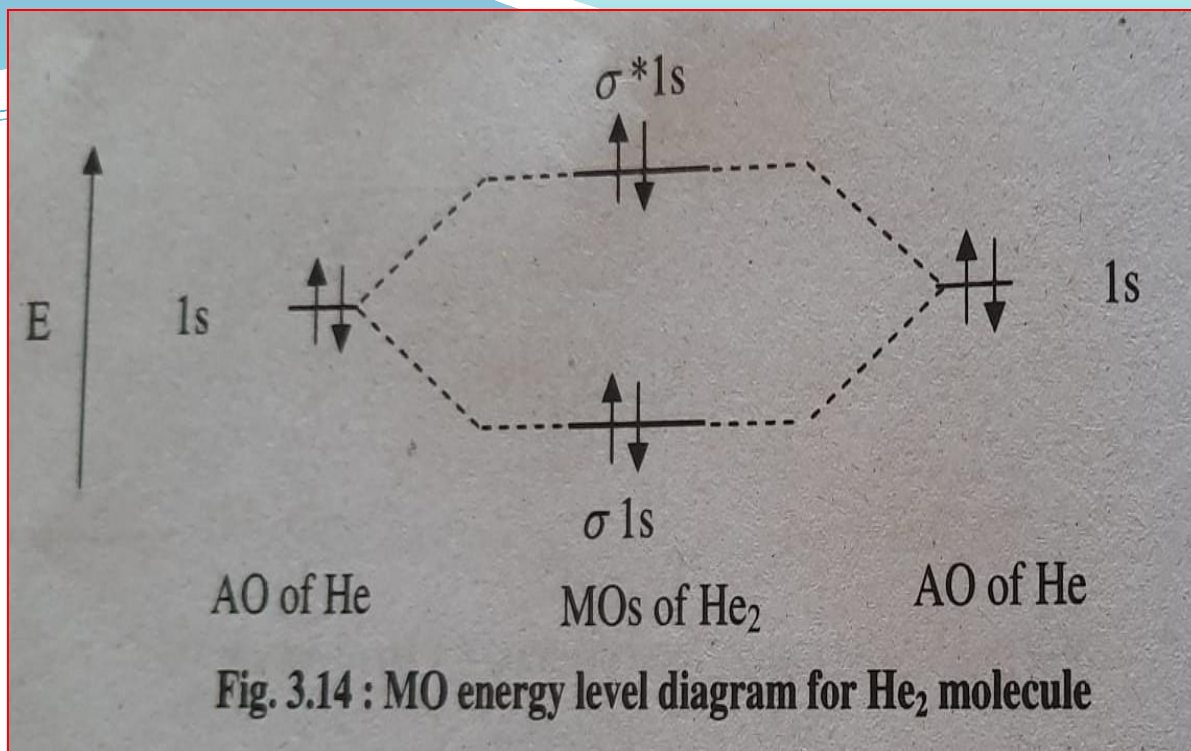
Bond order $= \frac{1}{2} (Nb - Na) = \frac{1}{2} (2 - 2) = \frac{1}{2} (0) = 0$

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

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

As the stabilization energy and bond order both are zero, indicates that He_2 molecule does not exists. Hence, Helium is a monoatomic

gas. Helium atom itself is stable according to duplet rule, and hence formation of

Helium molecule is not possible.

3) **Helium Molecule Ion (He_2^+):** - When Helium atom combines with Helium ion then Helium molecule ion is formed. The electronic configuration of Helium atom (At. no. =2) is $1s^2$, while the electronic configuration of Helium ion (He^+) is $1s^1$. So, there are (2 + 1 =3) three electrons in the Helium molecule ion.
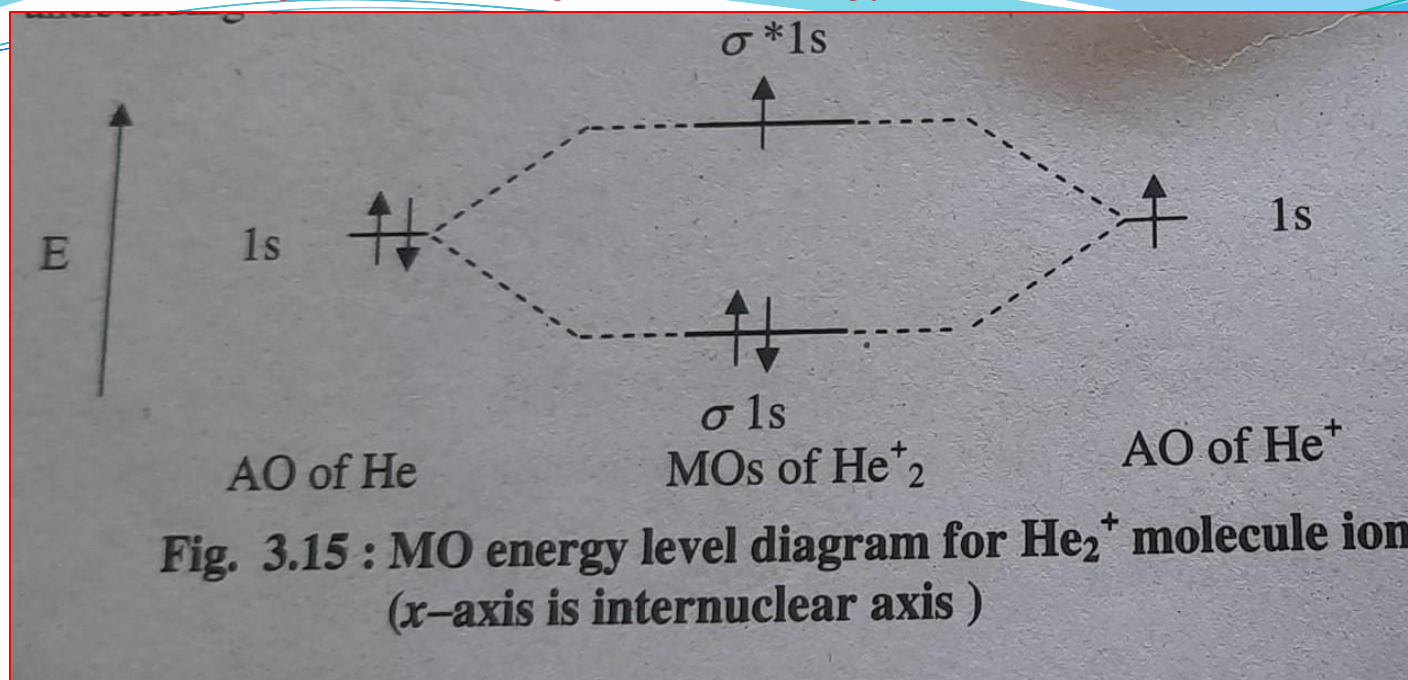
He →He^+ + e^- (Formation He^+ ion)

$2e^-$ → $1e^-$ + e^-

Now, He + He^+ → He_2^+

$2e^-$ + $1e^-$ = $3e^-$

The linear combination of 1s atomic orbital of He-atom with 1s atomic orbital of He^+ ion gives two MO's, σ1s and σ*1s.

1s + 1s → σ1s and 1s – 1s → σ*1s

The bonding MO σ1s has lower energy than antibonding MO σ*1s. He_2 molecule ion contains three electrons, out of which two electrons occupy lowest energy σ1s orbital and remaining one electron occupy σ*1s orbital. The molecular orbital electronic configuration of Helium molecule ion is σ$1s^2$ σ*$1s^1$.

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

Fig. 3.15 : MO energy level diagram for He_2^+ molecule ion
(x–axis is internuclear axis)

Bond order = $\frac{1}{2}$ (Nb—Na)= $\frac{1}{2}$ (2 − 1) = $\frac{1}{2}$ (1) = 0.5

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

$= 2 \times (-\beta) + 1 \times (+\beta) = -2 \beta + 1 \beta = - \beta$.

As the stabilization energy is negative and bond order is 0.5, indicates that He_2^+ molecule ion can exists but it is not very stable.

Similarly, as the He_2^+ molecule ion contains one unpaired electron ($\sigma*1s^1$) hence, it is paramagnetic.