A] Covalent bonding

Molecular orbital Theory [MOT]

- This theory was proposed by Hund and Mulliken in 1932.
- Accourding to this theory,
  " When atomic orbitals undergoes mixing, they loose their identity and forms new orbital is called as molecular orbitals. ~~This molecular orbitals belong to~~ molecule as a whole.
- This theory is more modern and rational.
- This theory use wave function (ψ) to discribe how electrons are distributed in molecule.

Postulates OR Important features of MOT

① The molecular orbitals ~~formed~~ are formed by combination of atomic orbitals.

② The atomic orbitals have nearabout same energy and proper symmetry.

③ The combination of atomic orbitals takes place accourding to LCAO method. [Liniar combination of Atomic orbitals methed]

④ When two atomic orbitals are ~~at~~ combine [mixed] then two molecular orbitals are formed.

⑤ one is of lower energy orbitals called as bonding molecular orbitals [BMO] other is of higher energy orbitals called Antibonding molecular orbitals [ABMO]

⑥ The no. of molecular orbitals formed is equal to no. of atomic orbitals mixed.

⑦ The shape of molecular orbitals depends upon the shape of combining atomic orbitals.

⑧ The distribution of electrons in the molecular orbitals are accourding to Paulis exclusion Principle, Hund's Rule and Aufbau principles.

LCAO approximation [LCAO method]

- Accourding LCAO method, the molecular orbitals are formed by Linear combination of atomic orbitals of atom.

- The molecular orbitals are formed (obtained) either by adding or by substracting wave functions (ψ) of atomic orbitals.

Consider two atoms A and B combine to form

molecule AB. Suppose ψ_A and ψ_B are the wave function of electrons in atomic orbitals.

- These two atomic orbitals can combine in two ways, either by addition or substraction.

$$\psi = \psi_A + \psi_B$$

This molecular orbitals is called as bonding m.o. ($\psi_{bonding}$)

$$\psi^* = \psi_A - \psi_B$$

This molecular orbital is called as antibonding m.o. ($\psi_{antibonding}$ OR ψ^*).

Formation of BMO & ABMO.

(A) ~~Bond~~ Formation of Bonding molecular orbitals [BMO]

① The ~~Bond~~ ~~or~~ BMO is formed by adding wave function ie $\psi_A + \psi_B$.

② During the formation of BMO, electron density ~~increases~~ between two combining nuclei. increases.

③ The new BMO has lower energy than corrosponding at. orbitals
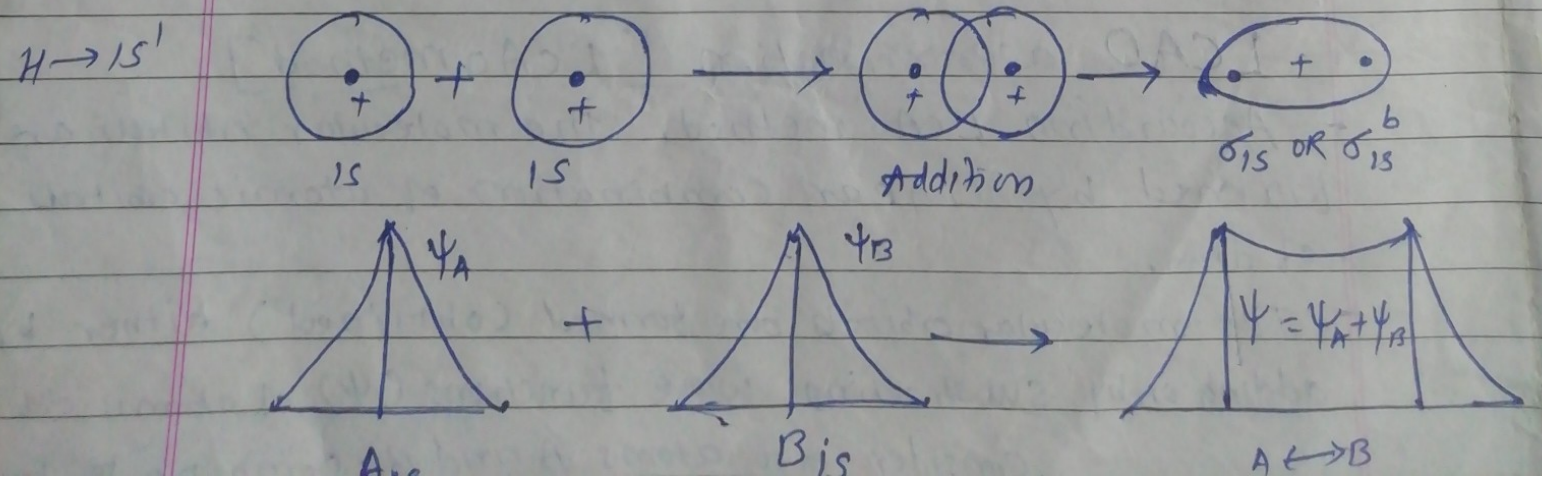
④ and ~~antibond~~ bond is formed between two atoms.

⑤ The energy of BMO is given by

$$E_{BMO} = E_0^* - \beta$$

E_0 is energy of atomic orbitals $\beta = const$.

eg

In case of Hydrogen (H_2) molecule, two Hydrogen atoms are involved in bonding. The formation of BMO is represented by electron density graph as.

$H \rightarrow 1s^1$

1s   1s   Addition σ_{1s} OR σ_{1s}^b

ψ_A + ψ_B $\psi = \psi_A + \psi_B$

A..   B is   A $\leftrightarrow$ B

(B) Formation of Antibonding molecular orbitals [ABMO]

(I) The ABMO is formed by substracting wave function.
ie $\psi_A - \psi_B$

(II) During the formation of ABMO, electron density between two combining nuclei decreases.

(III) The new ABMO has higher energy the corrosponding atomic orbitals.

(IV) This provides unfavavourable situation for formation of bonds.

(V) The energy of ABMO is given by

$$E_{ABMO} = E_0^° + \beta$$

where E_0 is energy of At. orbitals, $\beta = $ const.

eg. In case of Hydrogen (H_2) molecule, ABMO can be graphically represented by electron density.

1s   1s   substraction σ_{1s}^* or σ_{1s}^A

ABMO

A (1s)

B (1s)

σ_{1s}^*
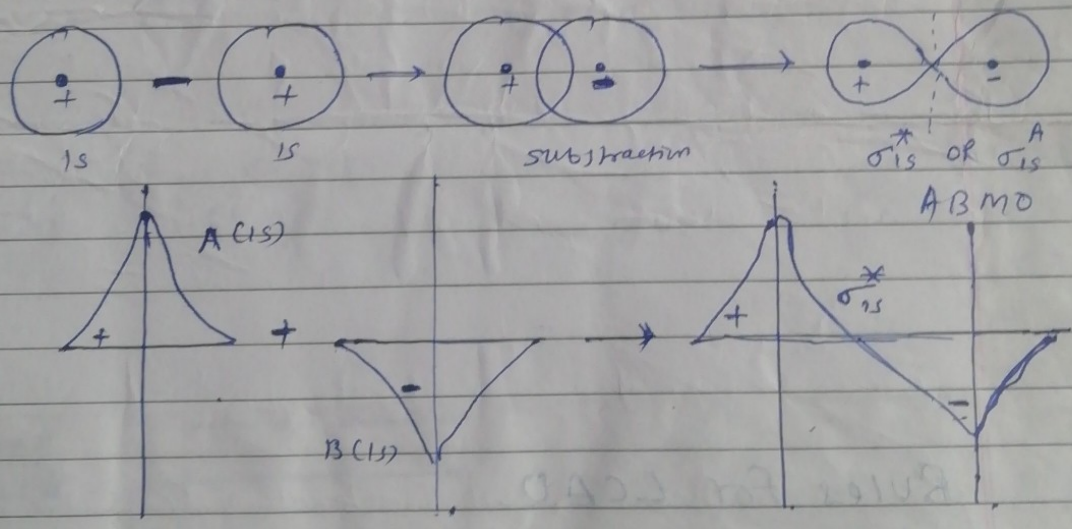
Extra shot.

not written in exam

The probability of finding an electron is given by Squaring wave functions.

$$\psi_{BMO}^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\psi_{ABMO}^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

From these eqn we can interprete that, the probability of finding the electron is more in BMO by a factor of $2\psi_A\psi_B$ while the probability of finding the e is less in ABMO by

a factor of $2\Psi_A\Psi_B$.

Therefore $\bar{e}$'s in BMO are present at the centre of two nuclei and gives more stability to the molecule.

Difference bet^n At. orbitals and molecular orbitals

Atomic orbitals	Molecular orbitals
i) Atomic orbitals are the region or space around the nucleus of an atom where there is a maximum probability of finding the electron.	i) Molecular orbital is the region or space around two or more nuclei where there is maximum probability of finding the electron
ii) Atomic orbitals are associated with atom.	ii) Molecular orbitals are associated with molecules and it is formed by combination of atomic orbitals.
iii) Atomic orbitals are monocentric	iii) Molecular orbitals are polycentric.

Difference between bonding and antibonding molecular orbital

BMO	ABMO
i) It is formed by LCAO method by addition of wave function i.e.($\Psi_A + \Psi_B$)	i) It Is formed by LCAO method by subtraction of wave function i.e. ($\Psi_A - \Psi_B$)
ii) It has lower energy than that of parent AO's.	ii) It has more energy than that of parent AO's
iii) It is stable	iii) It is unstable.
iv) Electron density lies (increase) in the region between two nuclei.	iv) Electron density lies away (decrease) from the internuclear region.
v) Actual bonding takes place.	v) No actual bonding is resulted
vi) There is a shielding of nuclear repulsion.	vi) Nuclear repulsion is not shielded.

Rules for LCAO

For the formation of molecular orbitals, the main conditions are

① Energy Rule:⇒

The energy of combining atomic orbitals must be same. or nearabout same.

② Extent of overlapping:-

The overlapping of atomic orbitals must be greater extent.

ie larger is the overlapping, stronger is the bond.

③ Symmetry Rule :

~~combining~~ combining

The symmetry of two atomic orbitals must be same. eg P_z or P_y orbital of one atom will not overlap with s-orbital of another atom, if the molecular axis is in X-direction and MO will not formed, because symmetry of s-orbital is not same as that of p-orbital.

s-orbital   P-orbital

permissible overlapping   NON permissible overlapping
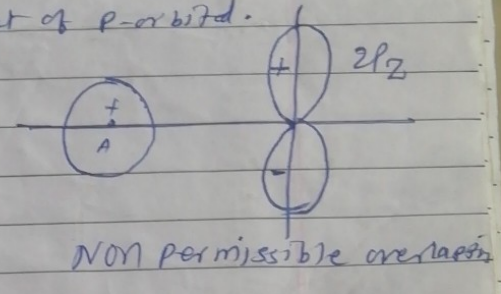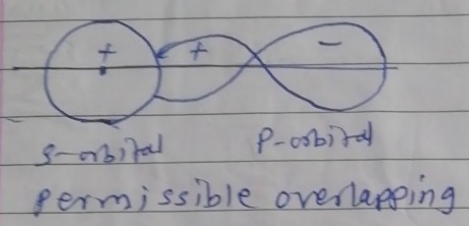
Molecular orbital energy level diagram.

When two atomic orbitals combined tougather then two molecular orbitals are formed. one is BMO and another is ABMO as

S.No	At-orbitals from which MO are formed	molecular orbitals	
		B MO	ABMO
1	IS orbitals of two atoms	σ_{1s}	σ^*_{1s}
2	2S orbitals of two atoms	σ_{2s}	σ^*_{2s}
3	2Px ———" ———	σ_{2Px}	σ^*_{2Px}
4	2Py ———" ———	π_{2Py}	π^*_{2Py}
5	2Pz ———" ———	π_{2Pz}	π^*_{2Pz}

The MO formed by combination of σ- symmetry AO's like 1s, 2s, 2Px are called as sigma (σ) molecular orbitals. The MO formed by π- symmetry orbitals like $2P_y$ & $2P_z$ are called as Pi (π) molecular orbitals. ABMO's are indicated with an asterisk ($*$) eg. σ^*_{1s}, σ^*_{2s}, π^*_{2Py}.
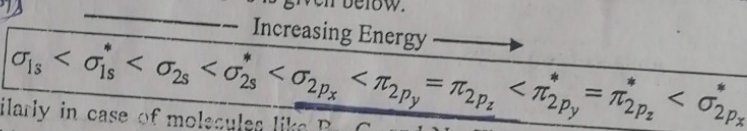
The formation of MO's are represented as,

PTO

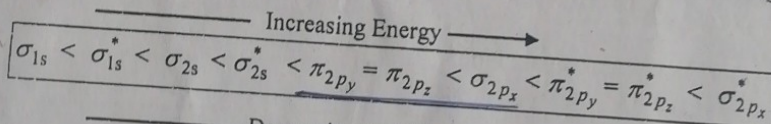**Fig 1.4: Diagrammatic represented of formation of various MO's**

Energy sequence of MO's in homonuclear diatomic molecules

Homonuclear diatomic molecules mean a molecule containing two atoms of same types of same elements eg. H_2, Cl_2, O_2, F_2 etc.

In case of homo nuclear diatomic moleculer of type O_2, Cl_2, O_2, F_2 etc. the atomic orbital involed inlinear combinging are $1s, 2s, 2p_x, 2p_y, 2p_z$, The energy sequence of various Mos formed by combination of AO' s is given below.

———— Increasing Energy ————→

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Similarly in case of molecules like B_2, C_2 and N_2. The energy sequence is slightly different and is given below.

———— Increasing Energy ————→

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$
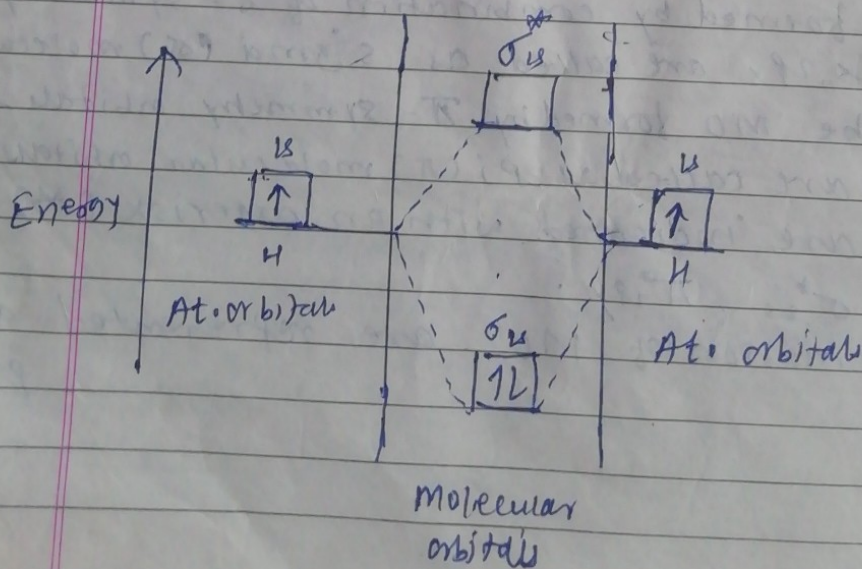
———— Decreasing Stability ————→

Energy level diagram

The distribution of electron in various molecular orbitals is similar to that of atomic orbitals i.e. according to *Aufbau* principle, Pauli's exclusion principle and Hund's rule.

In MO energy level diagram, the AO's and MO's can be represented as below.

Energy

At. orbital

At. orbital

Molecular orbitals

Concept of Bond order

The number of covalent bonds formed between two atoms in the molecule is called bond order or bond multiplicity.

- Bond order gives strength of covalent bond.
- Greater is the bond order, stronger is the covalent bond.
- Bond order is calculated by

$$\text{Bond order} = \frac{1}{2}\left[\frac{No.\ of\ \bar{e}s\ in\ BMO - No.\ of\ \bar{e}s\ in\ ABmo}{2}\right]$$

- Bond order of 1, 2, and 3 corrospends to single double and triple covalent bond.
- Bond order may be zero. This indicate that no covalent bond is formed.
- Sometimes bond order may be in fraction.

MO Structure of various molecules

① Structure of Hydrogen (H₂) molecule

- E.c. of Hydrogen is $1s^2$.
- When two hydrogen atoms combined tougather by LCAO method and formed two molecular orbitals σ_{1s} and σ^*_{1s}
- Total no. of $\bar{e}s$ in H₂ molecule is two.
- There two $\bar{e}s$ (one from each atom) goes to σ_{1s} MO
- Therefore E.c. of Hydrogen molecule is $\left[(\sigma_{1s})^2(\sigma^*_{1s})^0\right]$
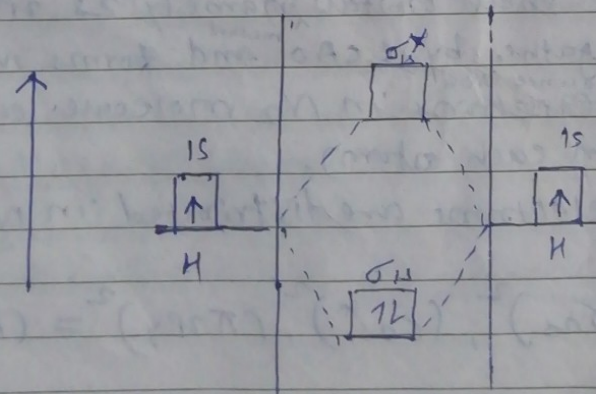
Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{2-0}{2} = 1$

Hydrogen atoms

As bond order is 1, This indicate. there is single covalent bond bet^n two

② Structure of helium (He₂) molecule

- E.C. of helium is $1s^2$
- When two helium atoms combined tougather by LCAO method and form two MO namely σ_{1s} and σ_{1s}^*.
- Total no. of electrons are 4 in He₂ molecule one 4
- There four electrons goes to σ_{1s} & σ_{1s}^*
- Therefore E.C. of He₂ molecule is $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$
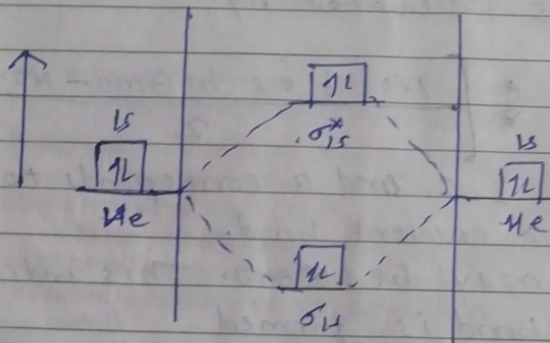
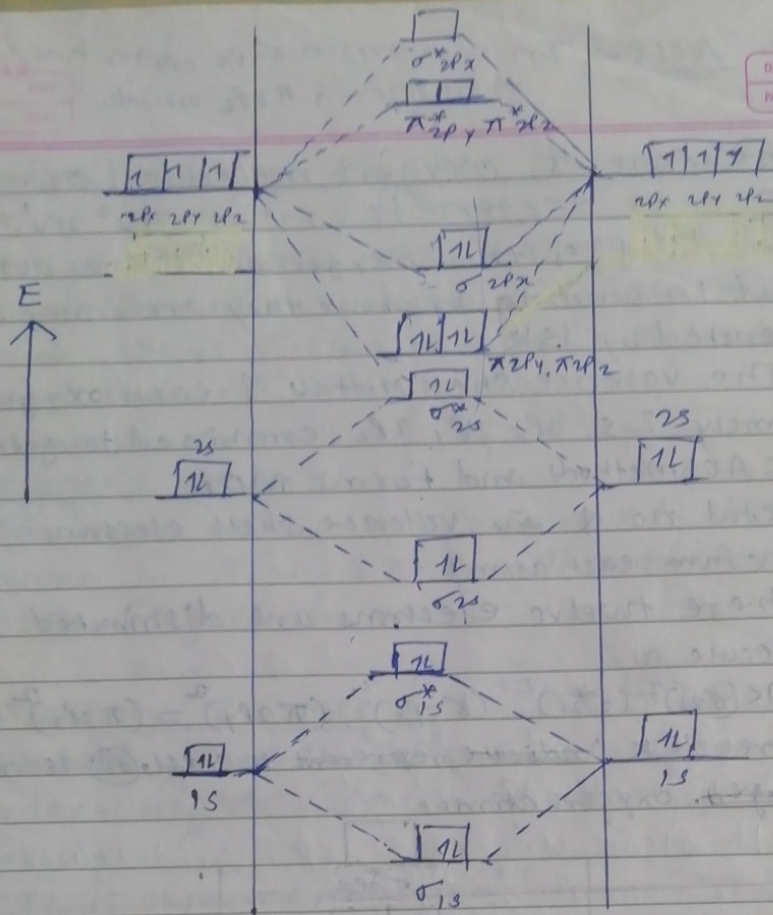- Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{2-2}{2} = 0$

As bond order is zero, this indicate that, NO covalent bond is formed between two He atoms. Therefore Helium exist in monoatomic state.

③ Structure of Nitrogen molecule

- E.C. of Nitrogen is $1s^2, 2s^2 2p_x^1, 2p_y^1, 2p_z^1$
- ~~When two~~ The $1s$ orbitals of two nitrogen atoms does not ~~toke~~ put in bonding because they are inner orbitals. Therefore they are denoted as KK.
- The valence shell orbitals of each nitrogen namely $2s, 2p_x, 2p_y, 2p_z$ combined tougather by LCAO method and forms MO.s.
- Total no. of valence shell electrons in N₂ molecule are 10 (~~each~~ five from each atom).
- These ten electrons are distributed in N₂ molecule as

$$\{ KK (\sigma_{2s})^2, (\sigma_{2s}^*)^2, (\pi 2p_y)^2 = (\pi 2p_z)^2 (\sigma_{2p_x})^2$$
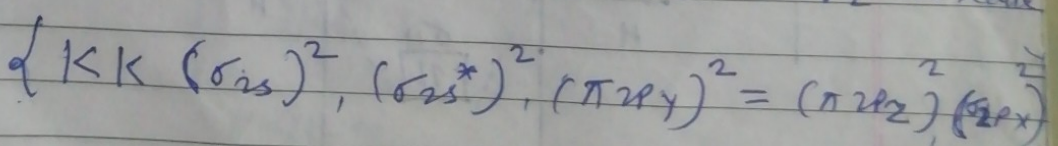
where KK represent K shells OR $1s$ orbital of both nitrogen

At. orbitals   Moleeular orbitals   At. Orbitals of Nitrogen
of Nitrogen   of Nitrogen.

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{10 - 4}{2} = \frac{6}{2} = 3$$

Bond order = 3

As bond order is three. This indicate that there are three bonds between nitrogen atoms. out of these three bonds. One bond is sigma bond and two bonds are π-bonds. Therefore nitrogen atoms are bonded by triple bond.
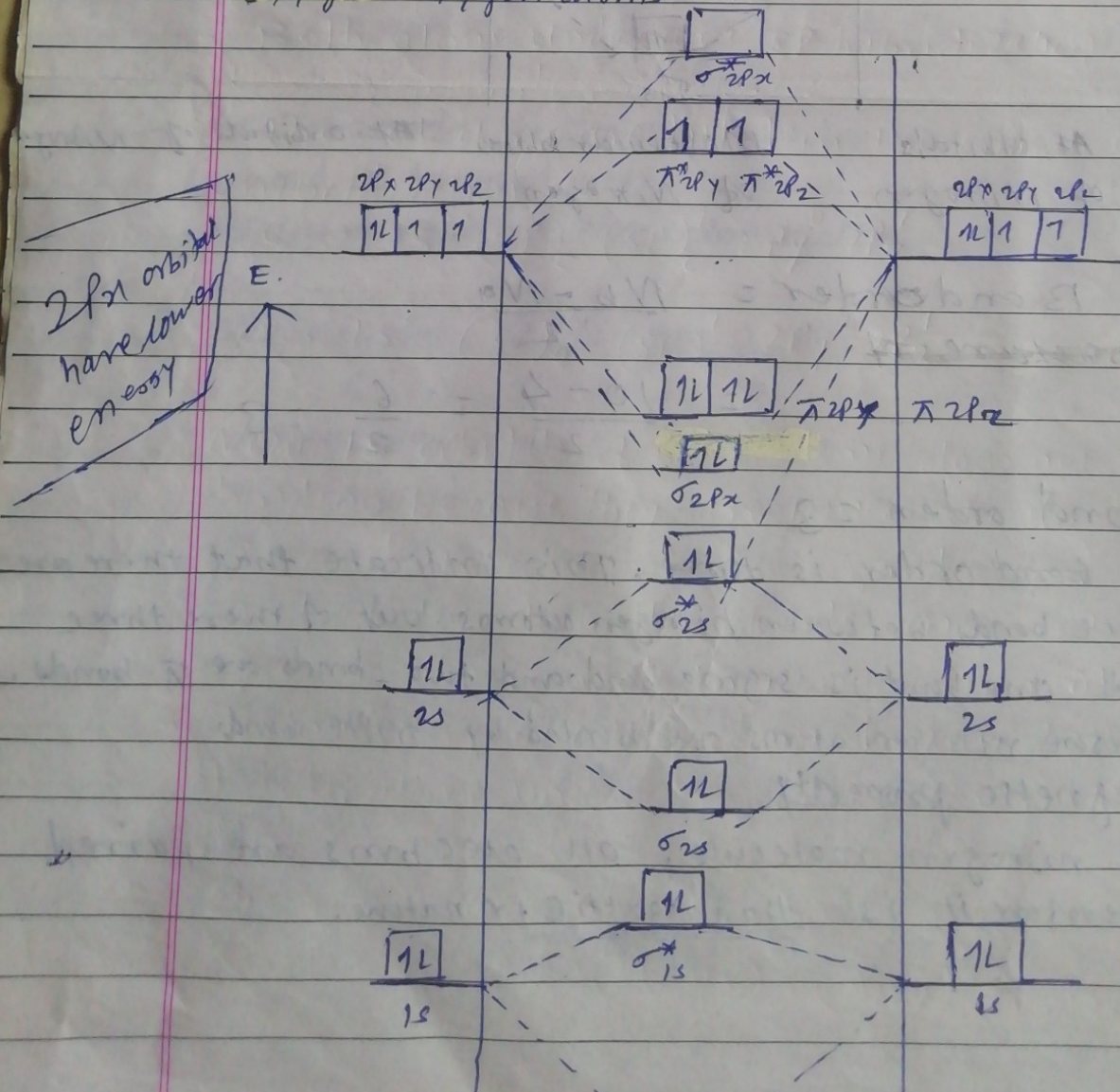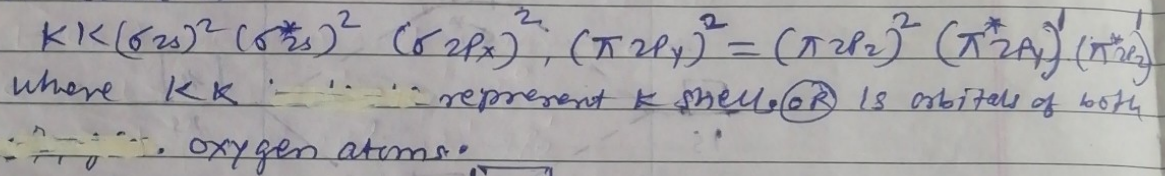
- Magnetic property

In nitrogen molecule, all electrons are paired. therefore it is <u>diamagnetic</u> in nature.

Imp. **Note →** "In case oxygen $\sigma 2px$ orbital has lower energy than $\pi 2py$ & $\pi 2p_2$ orbitals.

④ **Structure of oxygen molecule [O_2 molecule]**

- E.C. of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
- 1s orbital of two oxygen atom does not take part in bonding because they are inner orbitals and denoted by KK.
- The valence shell orbitals of each oxygen atom namely $2s, 2p_x, 2p_y, 2p_z$ combined tougether by LCAO methods and forms MOs.
- Total no. of the valence shell electrons are 12 (six from each atom)
- These twelve electrons are distributed in oxygen molecule as

$$KK (\sigma 2s)^2 (\sigma^*_{2s})^2 (\sigma 2p_x)^2, (\pi 2p_y)^2 = (\pi 2p_z)^2 (\pi^* 2p_y)^1 (\pi^* 2p_z)^1$$

where KK ‾‾‾‾ represent K shell. (OR) 1s orbitals of both ‾‾‾‾ oxygen atoms.

$2p_x$ orbital have lower enessy

E.

Bond order $= \dfrac{N_b - N_g}{2} = \dfrac{10-6}{2} = \dfrac{4}{2} = 2$

As bond order is 2. This indicate there are two bonds between two oxygen atoms. Out of these two bonds, one is σ-bond and one is π-bond. Therefore oxygen atoms are bonded by double bond.

(A) — **magnetic property**

In oxygen molecule, two unpaired electrons are present in π^*2p_y & π^*2p_z. Therefore oxygen molecule is **paramagnetic in nature**.

(B) — **Stability sequence of** $O_2^{2+} > O_2^{1+} > O_2 > O_2^{1-} > O_2^{2-}$

The stability of ions depends upon bond order. Higher is the bond order, greater is the stability.

— It is observed that, O_2^{2+} is most stable while O_2^{2-} is least stable. This can be explain as

— The +ive ions are formed by loss of $\bar{e}s$ while −ive ions are formed by gain of $\bar{e}s$.

— O_2^{2+} ions are obtained by loss of two $\bar{e}s$ from π^*2p_y & π^*2p_z orbitals therefore bond order increases while in case of O_2^{2-} ions are obtained by gain of two $\bar{e}s$ therefore bond order decreases as

The $\bar{e}s$ in σ_{1s} & σ_{1s}^* (**) does not consider in counting of BMO & ABMO

Species	No. of valence shell $\bar{e}s$ in BMO	No. of valence shell $\bar{e}s$ in ABMO	Bond order
O_2^{2+}	8	2	$\dfrac{8-2}{2} = 3$
O_2^{+}	8	3	$\dfrac{8-3}{2} = 2.5$
O_2	8	4	$\dfrac{8-4}{2} = 2$
O_2^{1-}	8	5	$\dfrac{8-5}{2} = 1.5$
O_2^{2-}	8	6	$\dfrac{8-6}{2} = 1$

Therefore order of stability of oxygen ions is

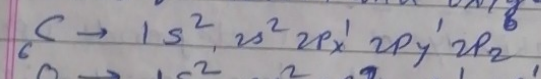$$O_2^{2+} > O_2^{+} > O_2 > O_2^{1-} > O_2^{2-}$$
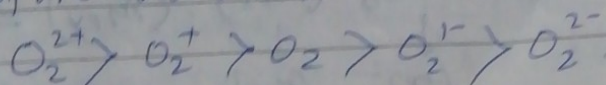
Molecular orbital structure of ~~hetroatomic~~
hetronuclear diatomic molecules

- In case of hetronuclear diatomic molecules, two different types of atoms are involved.
- These atoms do not have same energy or same symmetry.
- Due to this, some atomic orbitals does not take part in LCAO. Such orbitals are called as non bonding molecular orbital (NBMOs)

① Structure of carbon monoxide [CO] - Coulson's structure
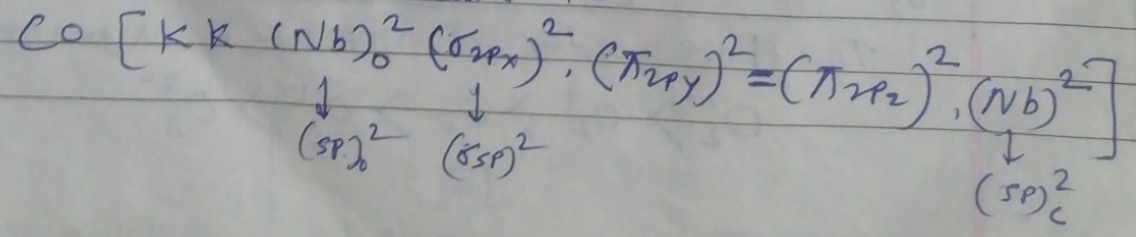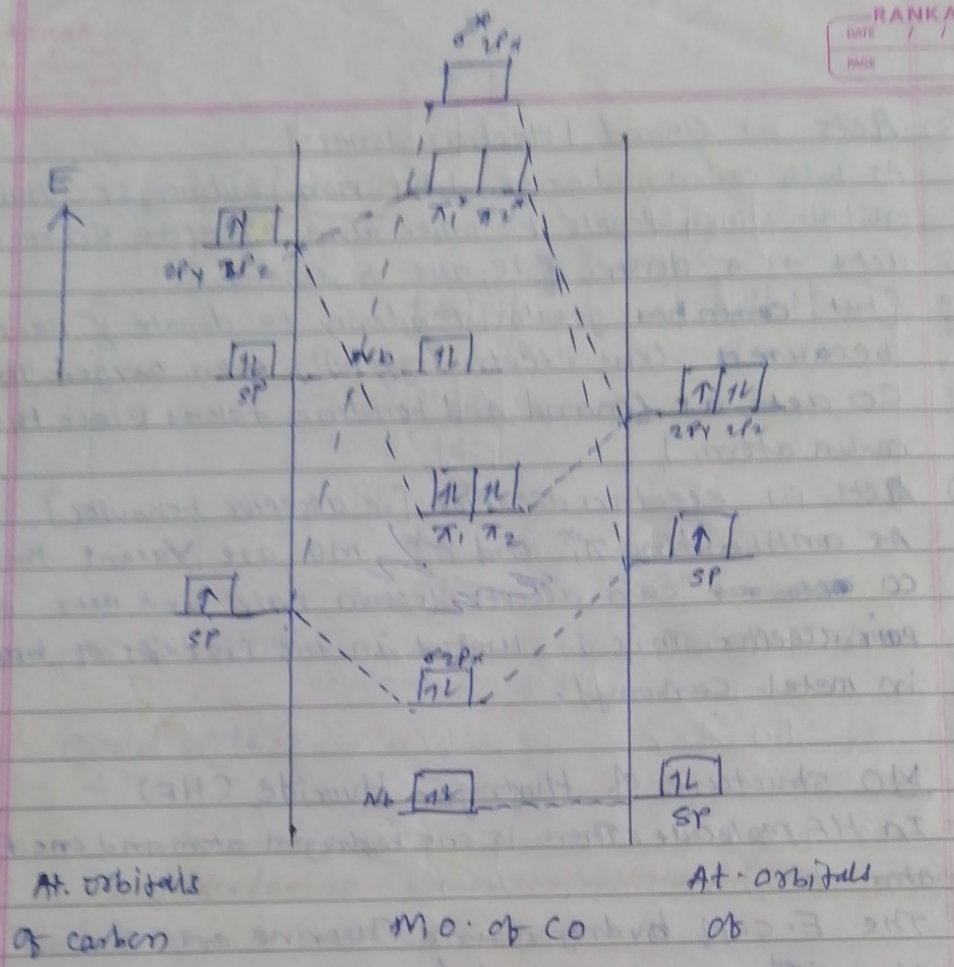- According Coulson's structure of CO is
- E.C. of carbon and oxygen are
  $_6C \rightarrow 1s^2, 2s^2 2P_x^1 2Py^1 2P_z$
  $_8O \rightarrow 1s^2, 2s^2 2P_x^2 2Py^1 2P_z^1$
- Both atoms undergoes sp hybridization and gives two sp hybride orbitals.
- The electrons are filled in the orbitals after hybridization as
  $_6C \rightarrow 1s^2 (SP)_c^2 (SP)_c^1 2Py^0 2P_z^1$
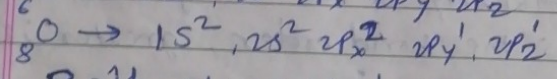
  $_8O \rightarrow 1s^2 (SP)_0^2 (SP)_0^1 2Py^2 2P_z^1$
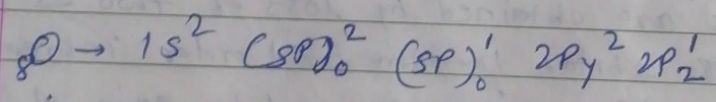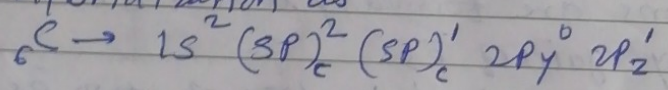
- NOW 1s orbitals of both atoms does not take part in bonding because they are inner orbitals.
- ~~2s and 2Px orbitals of carbon and oxygen~~
- Out of two hybride orbitals, one sp hybride orbitals of each atoms remain non bonding MO.
- Remaining one hybrid orbital, 2Py & 2P_z orbitals of both atoms undergoes linear combination & forms MO.
- E.C. of CO molecule is
  $CO [KK (Nb)_0^2 (\sigma_{2Px})^2, (\pi_{2Py})^2 = (\pi_{2P_z})^2, (Nb)^2]$
  $\downarrow \quad\quad \downarrow$
  $(SP)_0^2 \quad (\sigma_{SP})^2$
  $\downarrow$
  $(SP)_c^2$

At. orbitals
of carbon

M.O. of CO

At. orbitals
of oxygen

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$= \frac{6 - 0}{2} = 3$$

on the basis of MO structure, properties of CO are

① Presence of triple bond

As bond order is 3, this indicate that there are three bonds between carbon and oxygen atoms. out of these three bonds, one is σ-bond and two are π-bonds.

② Non polar Nature

The bonding electrons are more nearer to oxygen atom therefore excess nuclear charge on oxygen is partly neutralised. Therefore CO molecule is almost non-polar in nature (indicating low dipole moment ie 0.1 Debye)

③ **Acts as ligand [electron donar]**

As both carbon and oxygen have non-bonding sp hybride orbitals which donate to other atom therefore CO molecule acts as σ-donar. ie acts as ligand.

extra shot [but carbon has greater tendency to donate e^- pair because of low electronegativity than oxygen. Therefore CO acts as ligand and bonding takes place through carbon atom.]
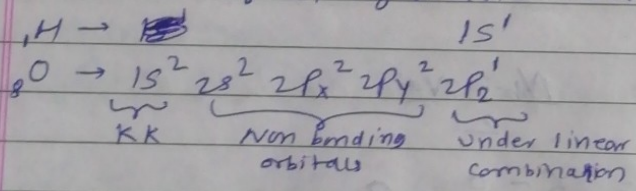
④ **Acts as electron acceptor [or acceptor behavior]**

As antibonding π_1^* and π_2^* MO are Vacant therefore CO can accept electron pair and acts as electron pair acceptor. This is useful in the process of back bonding in metal carbonyl.

② **MO structure of Hydrogen fluoride (HF)**

- In HF molecule, There is one hydrogen atom and one fluorine atom.
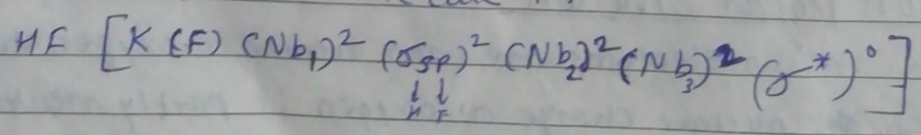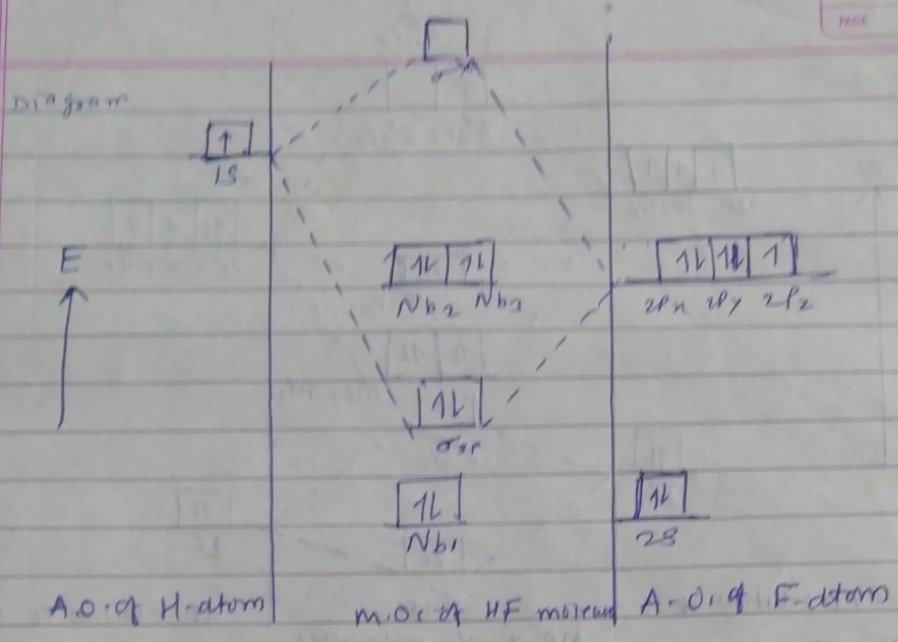
- The E.c. of hydrogen and fluorine are

$_1H \rightarrow$ $1s^1$

$_9O \rightarrow 1s^2\ 2s^2\ 2P_x^2\ 2Py^2\ 2P_2^1$

     KK   Non bonding   Under linear
                orbitals   combination

- Now 1s orbital of fluorine does not take part in bonding because it is inner orbital.

- The $2s, 2P_x, 2Py$ orbitals of fluorine remains nonbonding because these orbitals have comparable energy and symmetry and not available for linear combination with hydrogen atom.

- In HF, 1s orbital of hydrogen and $2P_z$ orbital of fluorine undergoes linear combination and forms two MOs namely σ and σ*. [Here z-axis is condisered as internuclear axis]
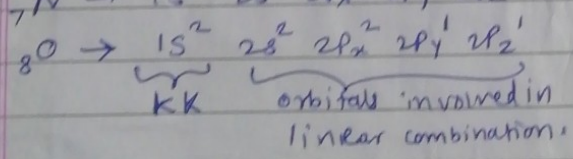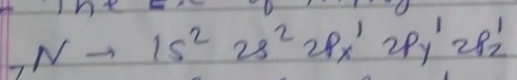
- E.c. of HF molecule is

HF $\left[K(F)\ (Nb_1)^2\ (\sigma_{sp})^2\ (Nb_2)^2\ (Nb_3)^2\ (\sigma^*)^0 \right]$

Diagram

E ↑

| $\uparrow$ | |
1S

| $\uparrow\downarrow$ | $\uparrow\downarrow$ |
Nb_2 Nb_3

| $\uparrow\downarrow$ | $\uparrow\downarrow$ | $\uparrow$ |
$2P_x$ $2P_y$ $2P_z$

| $\uparrow\downarrow$ |
σ_{rf}

| $\uparrow\downarrow$ |
Nb_1

| $\uparrow\downarrow$ |
$2S$

A.0 of H-atom   m.O of HF molecule   A·O·of F-atom

Bond order $= \dfrac{N_b - N_a}{2}$

$= \dfrac{2-0}{2} = 1$ ⚡

As bondorder is 1. This indicate that single covalent bond is present beth H & F.

③ __MO structure of nitric oxide [NO]__
- In NO molecule, There is one nitrogen atom and one oxygen atom.
- The E.C. of Nitrogen and oxygen are
$_7N \rightarrow 1S^2\ 2s^2\ 2P_x^1\ 2P_y^1\ 2P_z^1$
$_8O \rightarrow 1S^2\ 2s^2\ 2P_x^2\ 2P_y^1\ 2P_z^1$
  KK   orbitals involved in
       linear combination.

- Now 1S orbitals of Nitrogen and oxygen does not take part in bonding. because they are inner orbitals.
- The $2s, 2P_x, 2P_y, 2P_z$ orbitals of both atoms undergoes Linear combination and forms MOs.
- There are total 11 electrons [Five from nitrogen and six from oxygen] are arranged according to Aufbau Principle as

At. orbitals of Nitrogen atom

MO of NO molecules

At orbitals of oxygen atom
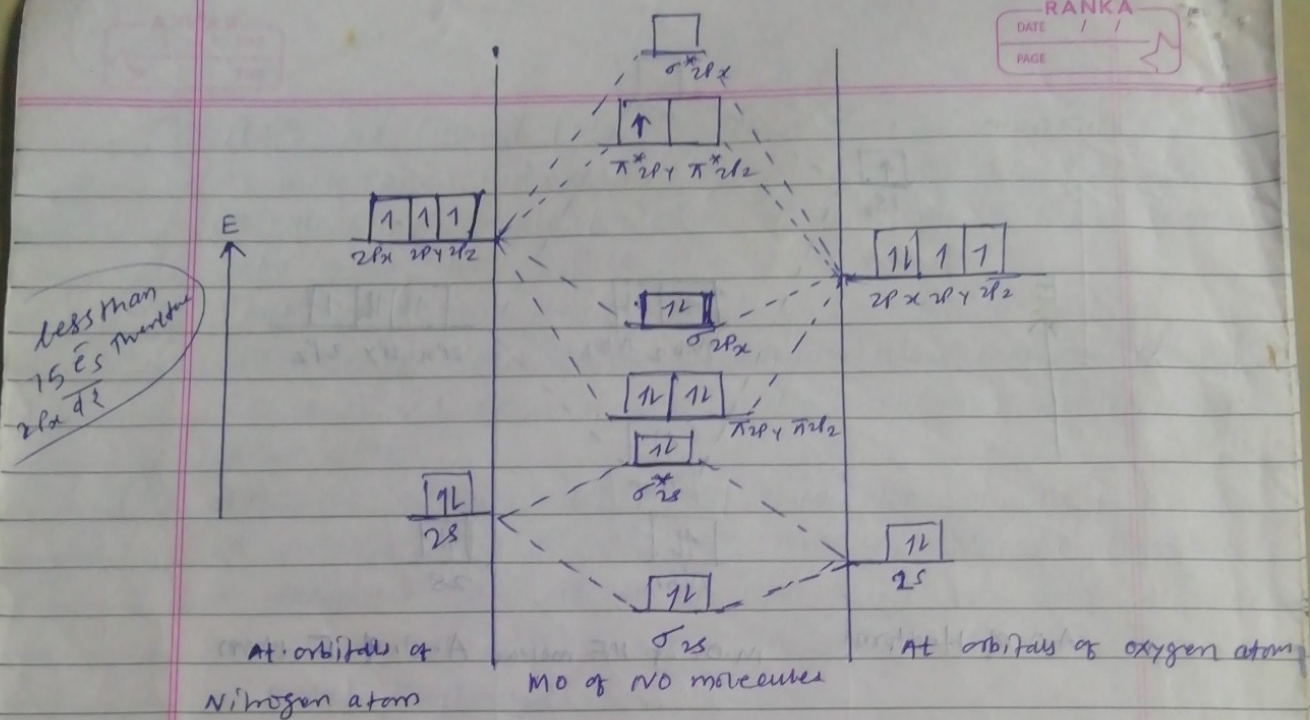
- Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{8 - 3}{2} = \dfrac{5}{2} = 2.5$

- As NO molecule contain unpaired $\bar{e}$, Therefore it is Paramagnetic.

Comparison of valence bond theory (VBT) and molecular orbital theory (MOT)

Similarities

i) Both the theories explain the nature of covalent bond and ~~hence both take into~~ consideration the sharing of electrons and pairing of electrons spins.

ii) Both the theories ~~take into~~ consideration the overlapping of atomic orbitals of comparable energy and same symmetry.

iii) Both the theories give an explanation for directional nature of covalent bond.

iv) Both the theories consider increase in electron density ~~as the criterion~~ bond formation. *during*

Differences

V B Theory	MO Theory
i) Atomic orbit are involved in bond formation and their identity is retained even after the molecules formed.	i) Molecular orbit are involved in bond formation and as soon as the MOs are formed, atomic orbits lose their identity.
ii) Atomic orbitals are monocentric i.e. electrons in atomic orbitals are under the influence of only one nucleus.	ii) Molecular orbitals are polycentric i.e. electrons in MOs are under the influence of more than one nucleus.
iii) Only unpaired electrons in valence shell take part in bonding.	iii) All the electrons in valence shall take part in bonding.
iv) It cannot explain the paramagnetic nature of O_2 molecule, properties of CO ~~and Spectra of molecules satisfactorily.~~	iv) It can explain satisfactorily the paramagnetic nature of O_2. Properties of CO and spectra of molecules
v) Bond order means the number of electron pairs shared between two atoms	v) Bond order is calculated as half the difference in number of electrons present in BMO and ABMO

less than 15 ē's multure
2Pα dξ