CHEMICAL BONDING

4.2.1 Valence Bond Theory :

Valence bond theory was postulated by Heitler and London. This was extented later by Pauling and Slater to explain the shapes of the molecules as well as the directions of the bonds in them . It is based on the overlapping and hybridisation of atomic orbitals.The important postulates of this theory are as follows

1. A covalent bond is formed by the overlap of two atomic orbitals.

2. The overlapping orbitals contain unpaired electrons of opposite spins.

3. Each of the bonded atoms retains its own atomic orbitals. But the electron pair in the overlapping orbitals is shared by both atoms.

4. Greater the extent of overlap orbitals , stronger is the bond formed.

5. As the atomic orbitals are directional , the bonds that result due to the overlap of orbitals are also directional. This gives the definite geometry to the covalent molecule.

6. The increased electron density due to the overlap of atomic orbitals of the two atoms is along the internuclear axis and keeps two atoms attracted to each other. This gives stability to the molecule.

Limitations : 1. Valence bond theory explains about valence electrons of the bonded atoms.It does not explain about role of other electrons.

2. It does not explains the paramagnetism of molecule like oxygen.

3. It does not explain bond order.

4.2.2 Hybridisation :

" The intermixing of atomic orbitals of almost equal energies of an atom resulting in the formation of equal number of identical orbitals" is called as Hybridisation. The different types of hybridisation as below

SP Hybridisation : One s orbital and one p orbital mix to form two 'sp' hybrid orbitals, they have 50% s and 50% p character .Geometry of sp hybridisation molecule is linear and bond angle is 180°.

Ex : $BeCl_2$, C_2H_2 , BeF_2

SP^2 Hybridisation : One s orbital and two p orbitals mix to form three sp^2 hybrid orbitals, they have 33% s and 66% p character .Geometry of sp^2 hybridisation molecule is Trigonal planar and bond angle is 120°.

Ex : BCl_3 , $CH_2=CH_2$

SP^3 Hybridisation : One s orbital and three p orbitals mix to form four sp^3 hybrid orbitals, they have 25% s and 75% p character .Geometry of sp^3 hybridisation molecule is Tetrahydral and bond angle is 109°28'.

Ex : CH_4 , NH_3 ,H_2O , F_2O

SP^3d Hybridisation : One s orbital and three p orbitals and one d orbital mix to form five sp^3d hybrid orbitals.Geometry of sp^3d hybridisation molecule is Trigonal bipyramidal and bond angle is 90°, 120°.

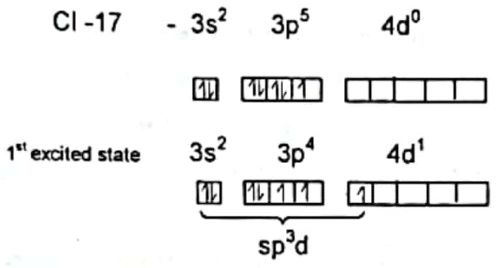
Ex : PCl_5 ,PF_5

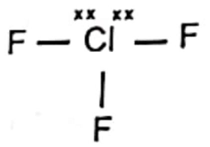
SP^3d^2 Hybridisation : One s orbital and three p orbitals and two d orbitals mix to form six sp^3d^2 hybrid orbitals. Geometry of sp^3d^2 hybridisation molecule is Octahedral and bond angle is 90°.

Ex : SF_6

4.2.3 Structure of ClF_3 :

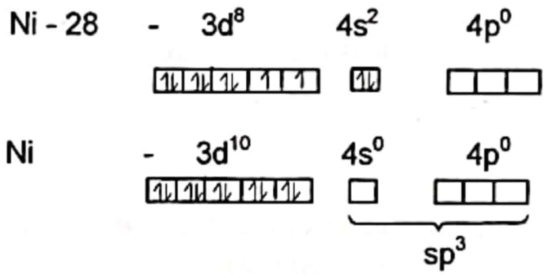
In ClF_3 the central atom Cl undergo sp^3d hybridisation, out of the five SP^3d hybrid orbitals, three contain unpaired electrons which overlaps directly with the three p-orbitals of fiuorine atoms to form 3 σ - bonds. The un used two pairs of electrons form the two equitorial positions of the trigonal bipyramidal. The structure of ClF_3 is Trigonal bipyramid (or) T- Shape.

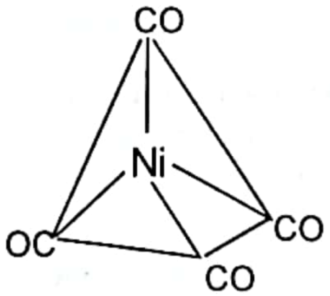




4.2.4 Structure of $Ni(CO)_4$:

In Nickel carbonyl central atom nickel undergo sp^3 hybridisation.
Ni (28) - $3d^8$ $4s^2$ $4p^0$. The $4s^2$ electrons entered to 3d orbital to give stable configuration $3d^{10}$ $4s^0$ $4p^0$. Now the vacent 4s and 4p orbitals undergo sp^3 hybridisation to give four vacent sp^3 hybrid orbitals. These accept lone pairs from four carbon monoxide molecules to form coordinate covalent bonds. Hence the structure is Tetrahydral.





Tetra hydral

4.2.5 Molecular Orbital Theory : Molecular orbital theory was developed by Hund and Mulliken. The sailent features of this theory are :

1. Electrons of atoms are present in atomic orbitals where as electrons of molecules are present in molecular orbitals.
2. The number of molecular orbitals formed will be equal to the number of atomic orbitals combining.
3. When two atomic orbitals are combine , two molecular orbitals are formed. One is known as Bonding molecular orbital while the other is called Antibonding molecular orbital.
4. The bonding molecular orbital has lower energy and hence greater stability than the anti bonding molecular orbital.
5. Atomic orbitals are monocentric i.e influenced by only one nucleous while molecular orbitals are poly centric. i.e influenced by two nuclei.
6. The filling of electrons in molecular orbital is similar to that of atomic orbitals i.e in according to Hund's rule, Pauli's exclusion principle and Aufbau principle.

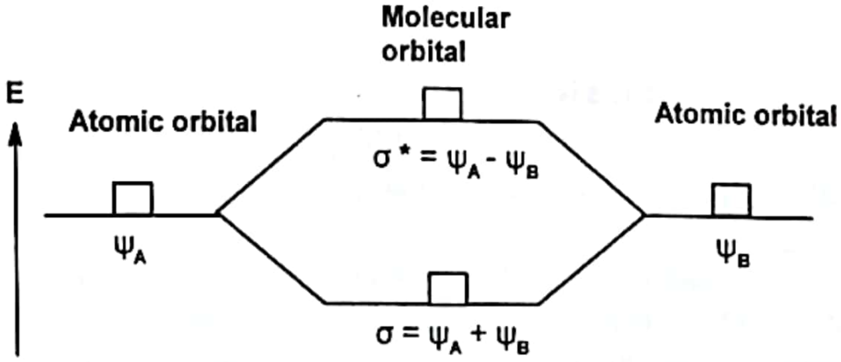
Linear Combination of Atomic Orbitals :

According to wave mechanics , the atomic orbitals can be expressed by wave functions (ψ) which represent the amplitude of the electron waves. These are solutions of Schrodinger wave equation.It is difficult to solve for many electron systems. Therefore a method is known as Linear Combination of Atomic Orbitals (LCAO) has been adopted.

Consider a homonuclear diatomic molecule, hydrogen which consists of two hydrogen atoms A and B. Each hydrogen atom in ground state has one electron in 1s orbital.The atomic of these atoms may be represented by the wave functions ψ_A and ψ_B.The formation of molecular may be discribed by the linear combination of atomic orbitals as shown by $\psi_{MO} = \psi_A \pm \psi_B$

Therefore the two molecular orbitals σ and σ^* are formed as $\sigma = \psi_A + \psi_B$ and $\sigma^* = \psi_A - \psi_B$

The molecular orbital σ formed by the $\sigma = \psi_A + \psi_B$ is called Bonding molecular orbital while molecular orbital σ^* formed by $\sigma^* = \psi_A - \psi_B$ is called antibonding molecular orbital.



Bond Order : It is defined as half of the difference between the number of electrons present in the bonding and anti bonding orbitals.

Bond Order (B.O) = 1/2 [N_b- N_a]

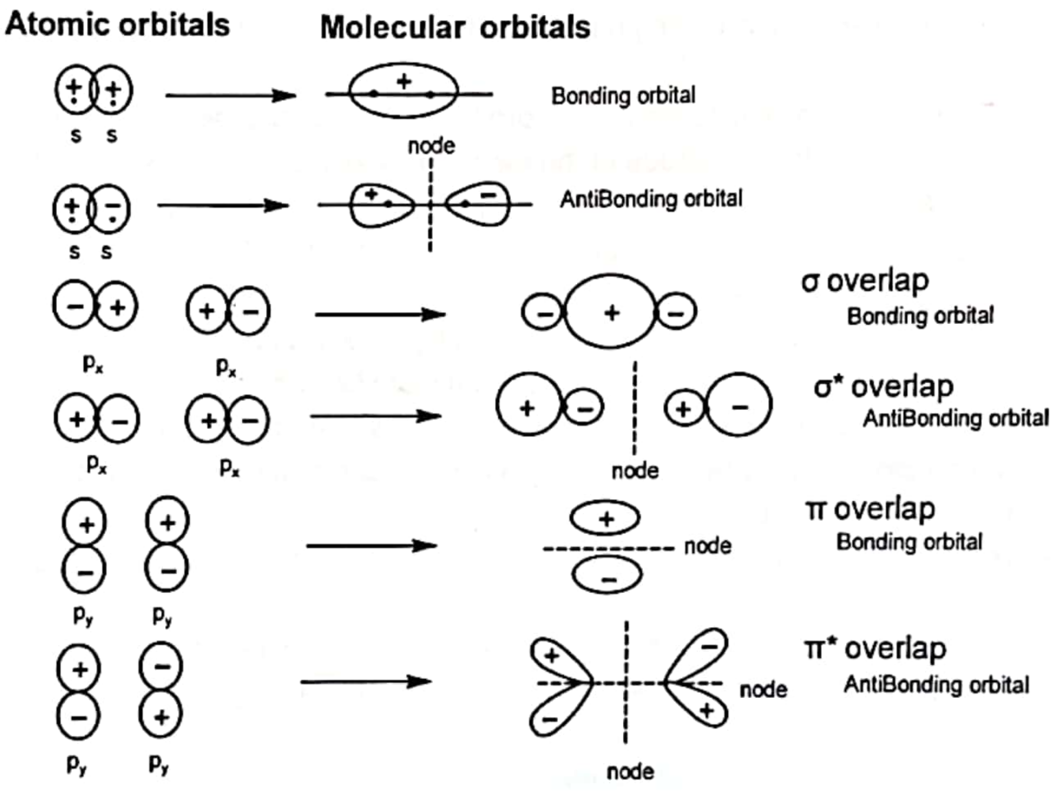
N_b = no of bonding electrons
N_a = no of antibonding electrons

If $N_b > N_a$ then the molecule would be stable.
If $N_b = N_a$ then the molecule is unstable and does not exist.

Bond order values 1 , 2, 3 corresponds to single , double, triple bonds resply. Bond order is directly proportional to Bond dissociation energy and Bond order is inversely proportional to Bond length.

Magnetic nature : If all the molecular orbitals in a molecule are doubly occupied , the substance is diamagnetic. If one or more molecular orbitals are singly occupied the substance is paramagnetic.

Linear combination of various atomic orbitals give following molecular orbitals



The energy order of molecular orbitals is :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$

$\pi 2p_y$, $\pi 2p_z$ and $\pi^* 2p_y$, $\pi^* 2p_z$ have same energy.

Conditions for LCAO :

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must overlap to the maximum extent.
3. The combining atomic orbitals must have the same symmetry about the molecular axis.

Molecular Orbital diagrams :

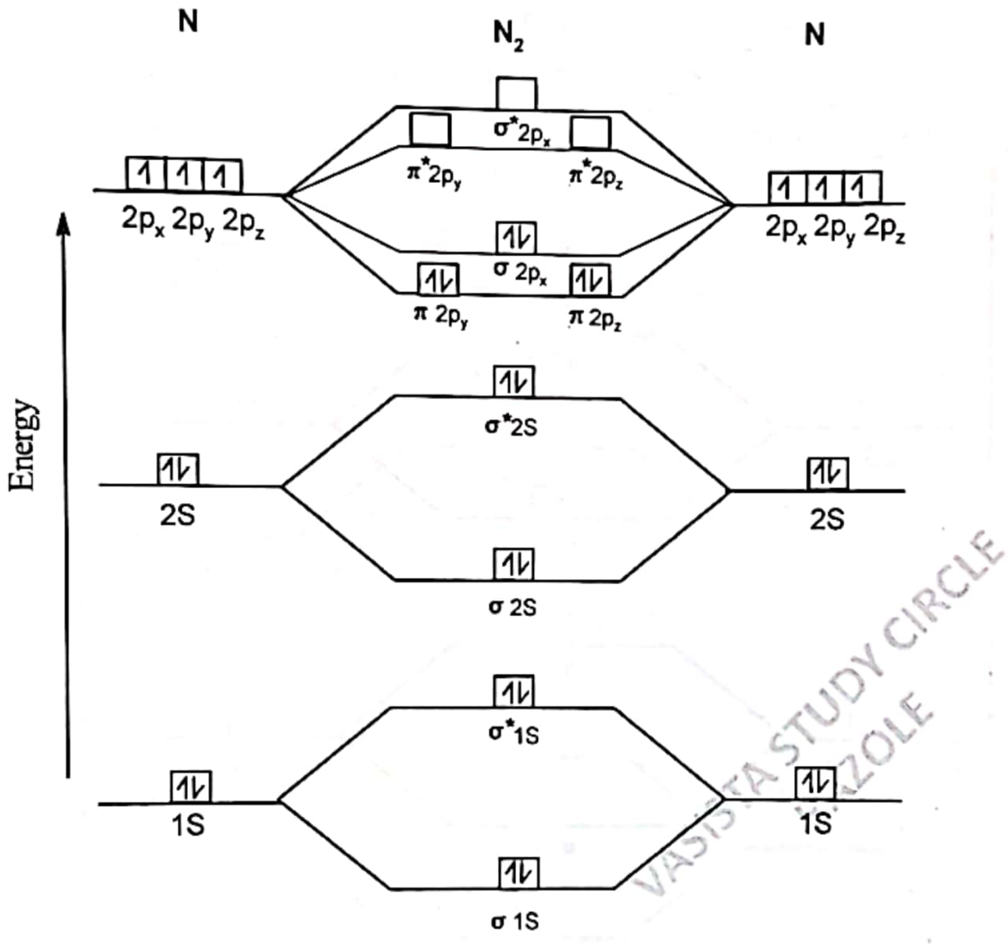
1. N_2 :

1. Atomic number of Nitrogen - 7
2. Electronic configuration of Nitrogen - $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1 2p_z^1$
3. Total number of electrons in N_2 - 7 + 7 = 14
4. Molecular orbital configuration of N_2 -

   $\sigma\ 1s^2\ \sigma^*\ 1s^2\ \sigma\ 2s^2\ \sigma^*\ 2s^2 \pi\ 2p_y^2\ \pi\ 2p_z^2\ \sigma\ 2p_x^2$
5. Number of bonding electrons (n_b) - 10
6. Number of Anti bonding electrons (n_a) - 4
7. Bond Order = $n_b - n_a / 2$ = 10 - 4 / 2 = 3

A triple bond exist between two nitrogen atoms, and it as no unpaired electrons , so it is a diamagnetic molecule.

The molecular orbital energy diagram for N_2 molecule is represented as in below



2. O_2 :

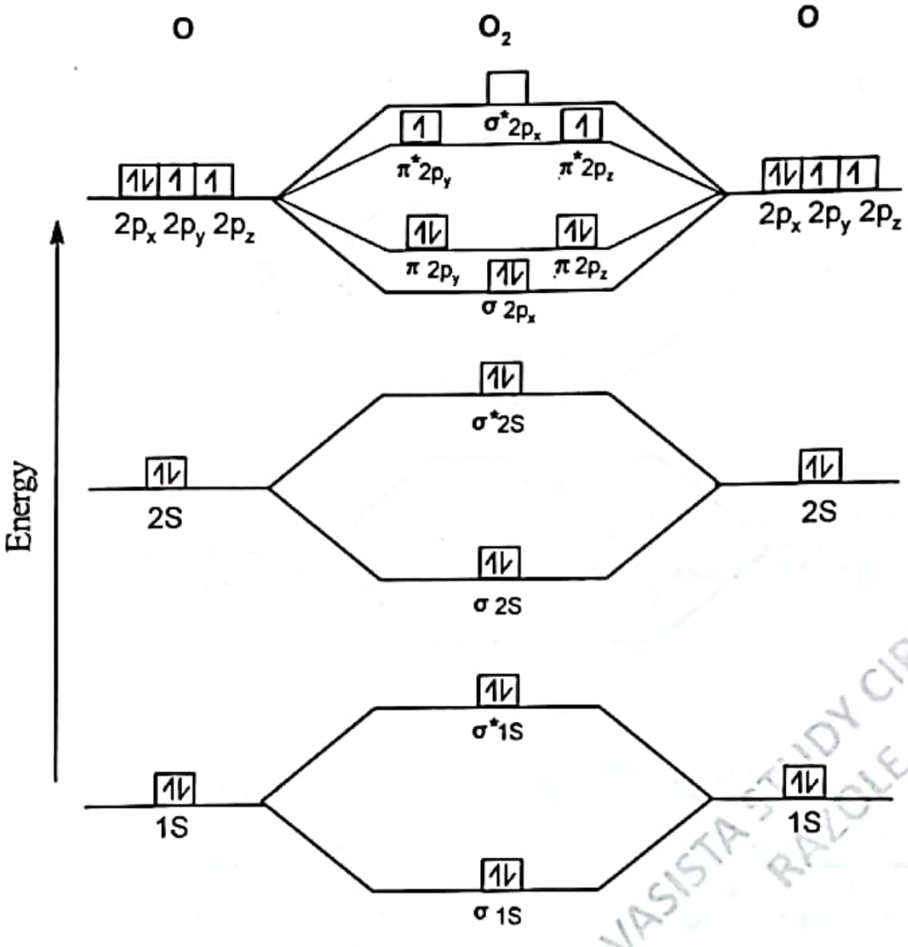
1. Atomic number of Oxygen - 8
2. Electronic configuration of Oxygen - $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
3. Total number of electrons in O_2 - 8 + 8 = 16
4. Molecular orbital configuration of O_2 -

$$\sigma\ 1s^2\ \sigma^*\ 1s^2\ \sigma\ 2s^2\ \sigma^*\ 2s^2\ \sigma\ 2p_x^2\ \pi\ 2p_y^2\ \pi\ 2p_z^2\ \pi^*\ 2p_y^1\ \pi^*\ 2p_z^1$$

5. Number of bonding electrons (n_b) - 10
6. Number of Anti bonding electrons (n_a) - 6
7. Bond Order = $n_b - n_a / 2$ = 10 - 6 / 2 = 2

A double bond exist between two oxygen atoms, and it contais un paired electrons , so it is a paramagnetic molecule.

The molecular orbital energy diagram for O_2 molecule is represented as in below



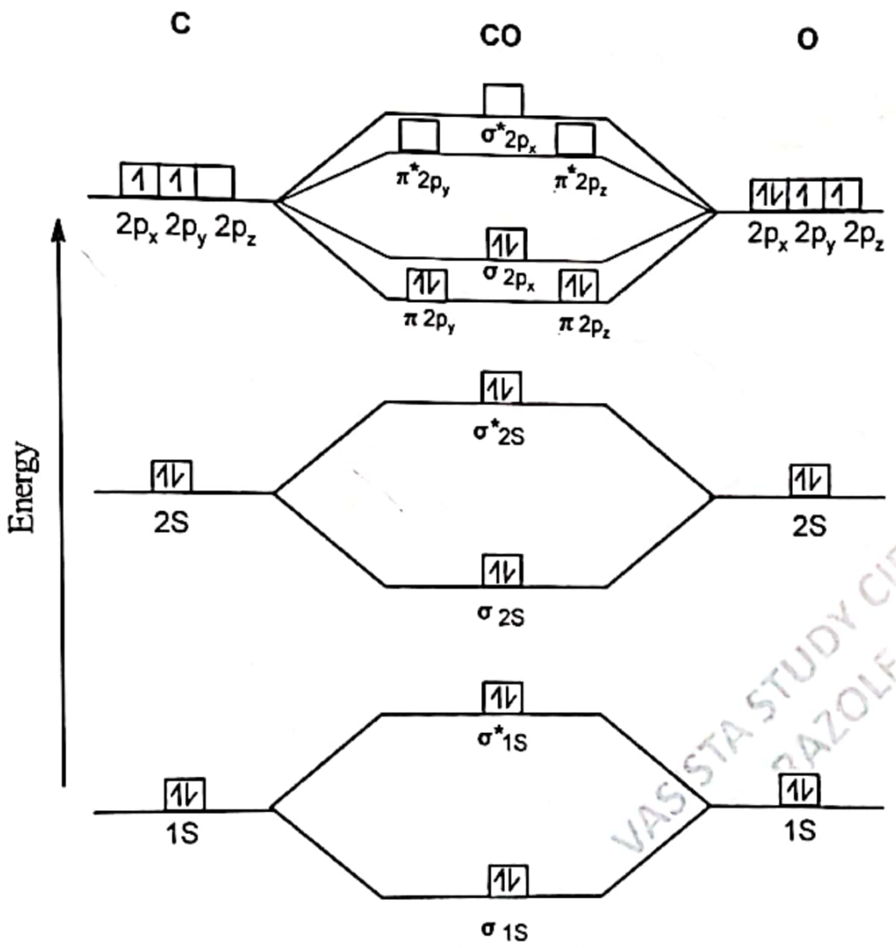
3. CO (Carbon monoxide) :

1. Atomic number of Carbon - 6
2. Electronic configuration of Carbon - $1s^2 2s^2 2p_x^1 2p_y^1$
3. Atomic number of Oxygen - 8
4. Electronic configuration of Oxygen - $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
5. Total number of electrons in CO - 6 + 8 = 14
6. Molecular orbital configuration of CO -

   $\sigma 1s^2 \, \sigma^* 1s^2 \, \sigma 2s^2 \, \sigma^* 2s^2 \, \pi 2p_y^2 \, \pi 2p_z^2 \, \sigma 2p_x^2$
7. Number of bonding electrons (n_b) - 10
8. Number of Anti bonding electrons (n_a) - 4
9. Bond Order = $n_b - n_a / 2 = 10 - 4 / 2 = 3$

A triple bond exist between carbon and oxygen. It is isoelectronic with N_2. It does not contain unpaired electrons, so it is a diamagnetic molecule.

The molecular orbital energy diagram for CO molecule is represented as in below



4. NO (Nitric oxide) :

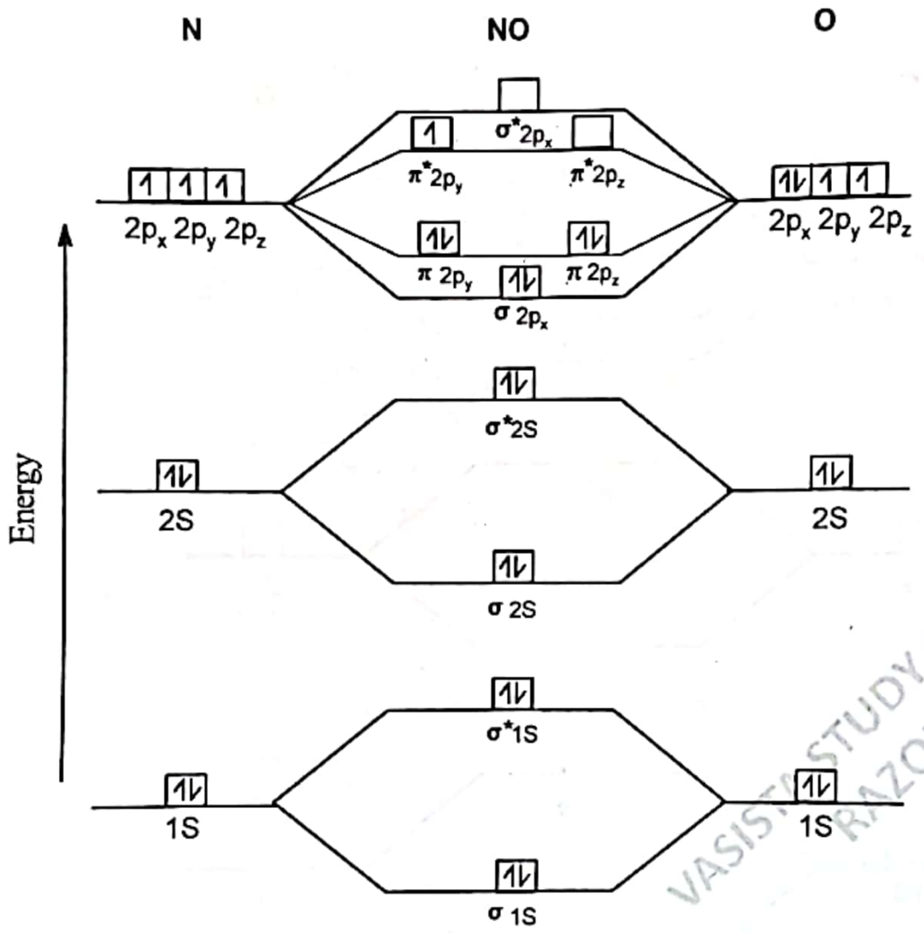
1. Atomic number of Nitrogen - 7
2. Electronic configuration of Ntrogen - $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$
3. Atomic number of Oxygen - 8
4. Electronic configuration of Oxygen - $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$
5. Total number of electrons in NO - 7 + 8 = 15
6. Molecular orbital configuration of NO -

$$\sigma\,1s^2\ \sigma^*\,1s^2\ \sigma\,2s^2\ \sigma^*\,2s^2\ \sigma\,2p_x^2\,\pi\,2p_y^2\ \pi\,2p_z^2\ \pi^*\,2p_y^1$$

7. Number of bonding electrons (n_b) - 10
8. Number of Anti bonding electrons (n_a) - 5
9. Bond Order = $n_b - n_a / 2$ = 10 - 5 / 2 = 2.5

NO molecule exist , but unstable. It contain unpaired electron, so it is a para-magnetic molecule.

The molecular orbital energy diagram for NO molecule is represented as in below



4.2.7 Differences between Valence bond theory and Molecular orbital theory :

V. B. T	M. O. T
1. Atomic orbitals are monocentric.	1. Molecular orbitals are polycentric.
2. Can not explains excited states.	2. Explains excited states in a molecule
3. Does not explains bond order .	3. Explains bond order , odd electron bond
4. Does not explains para magnetism of oxygen.	4. Explains para magnetism of oxygen.
5. Resonance plays an important role.	5. Resonance has no place in MOT