Chapter 01

Atomic and Molecular Structure

Atom:
"It is the smallest particle of element which cannot be further sub-divided and which can take part in all chemical changes. It may or may not be capable free existence".
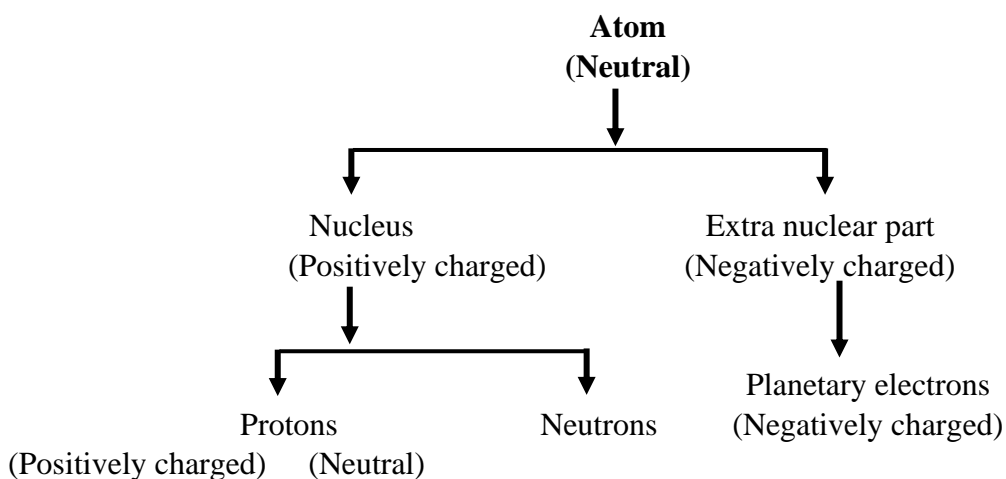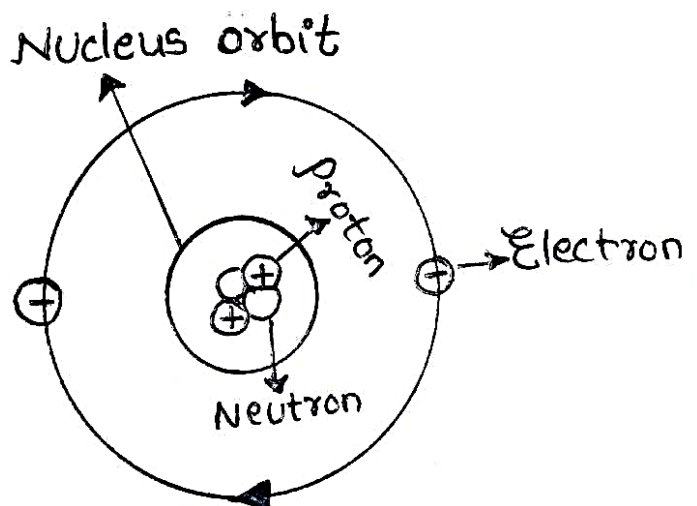Ex. H – atom, O – atom, N – atom etc.

Molecule:
"It is the smallest particle of an element or a compound that can exist in a free state and retain all its properties".
Ex. Cl_2, H_2O, H_2 etc.

Fundamental Particles of an Atom (Sub – atomic particles)

Atom
(Neutral)

Nucleus
(Positively charged)

Extra nuclear part
(Negatively charged)

Protons   Neutrons
(Positively charged)   (Neutral)

Planetary electrons
(Negatively charged)

Structure of Atom

Characteristic	Electron	Proton	Neutron
Discovered by	J. J. Thomson	Goldstein	Chadwick
	In 1896	In 1911	In 1932
Symbol	E	p	N
Location	Outside nucleus	Inside nucleus	Inside nucleus
Mass in amu	0.000555	1.007825	1.008665
charge	-1	+1	0

- **Concept of Shells (Main Energy Level), Sub- shells (Sub – sub energy level) and Orbitals:**
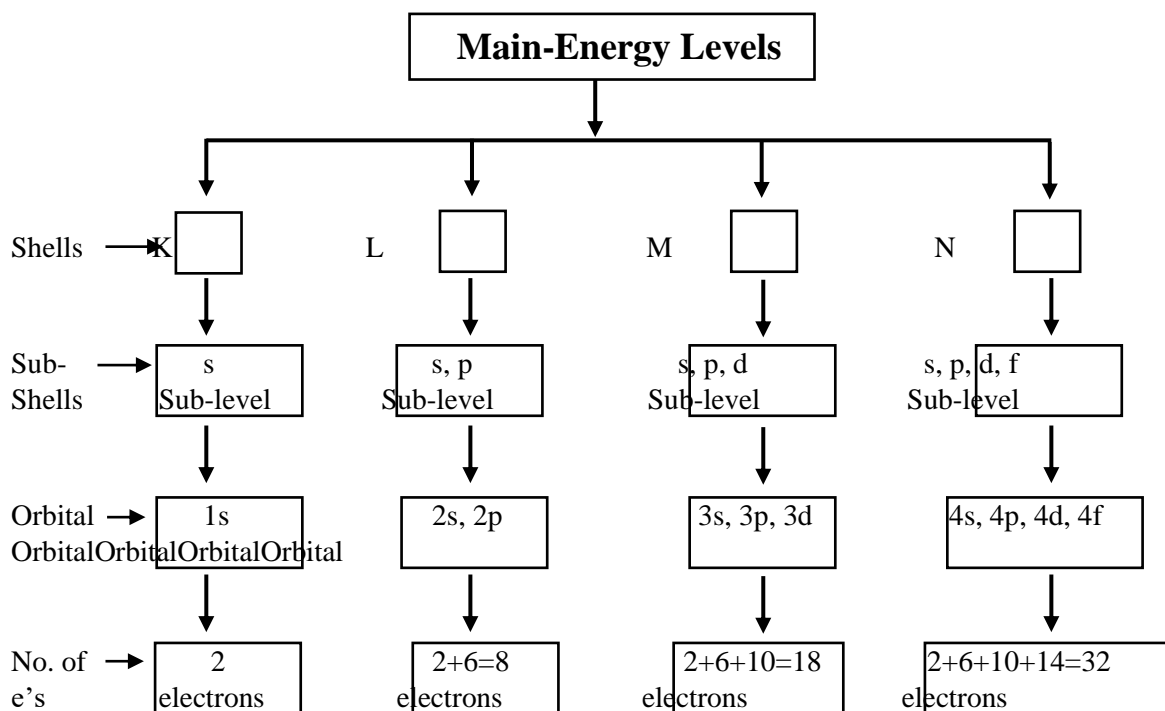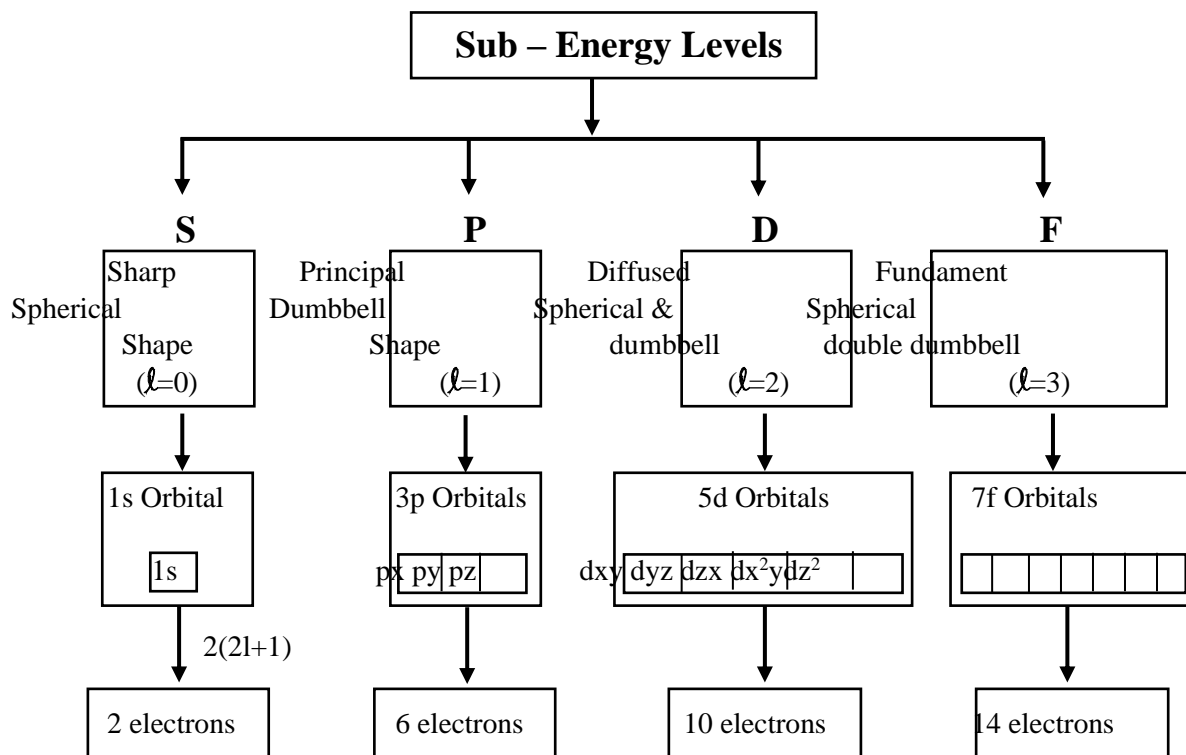
➢ **Shells (Main Energy Levels)**
Bohr's stationary orbits with definite amount of energy are called energy levels or energy states or Shells.

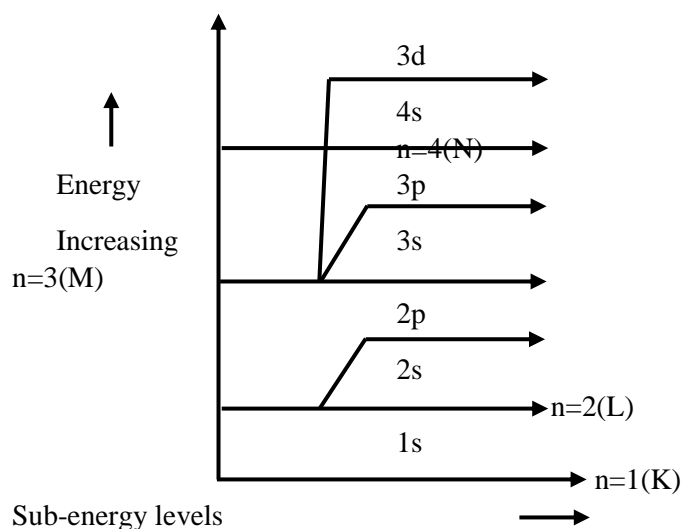| Shells	Orbit (n)	Max. no. of e's $(2n^2)$
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$

Partially charged nucleus
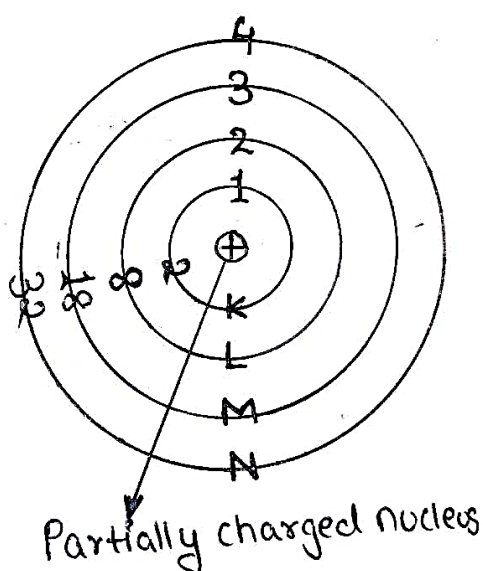
➢ **Sub-Shells (Sub-energy levels)**
The close grouping of a number of energy levels in the main energy level are called Sub-energy levels. They are denoted by s, p, d, and f

Sub – Energy Levels

S	P	D	F
Sharp Spherical Shape ($\ell=0$)	**Principal** Dumbbell Shape ($\ell=1$)	**Diffused** Spherical & dumbbell ($\ell=2$)	**Fundament** Spherical double dumbbell ($\ell=3$)
1s Orbital [1s]	3p Orbitals px py pz	5d Orbitals dxy dyz dzx dx²y dz²	7f Orbitals
2 electrons	6 electrons	10 electrons	14 electrons

$2(2l+1)$

Main-Energy Levels

	K	L	M	N
Shells				
Sub-Shells	s Sub-level	s, p Sub-level	s, p, d Sub-level	s, p, d, f Sub-level
Orbital Orbital Orbital Orbital Orbital	1s	2s, 2p	3s, 3p, 3d	4s, 4p, 4d, 4f
No. of e's	2 electrons	2+6=8 electrons	2+6+10=18 electrons	2+6+10+14=32 electrons

- **Graphical Representation of Sub-Shells**

- **Difference between Orbit and Orbital**

Sr. No.	ORBITS	ORBITALS
1.	Orbit is a fixed circular path described by a moving e⁻ around a nucleus.	Orbital is a 3 Dimensional region in space around the nucleus, where there is maximum probability of finding an electron.
2.	Maximum capacity of any orbit is $2n^2$ electrons, where n is the number of orbit.	Maximum capacity of any orbital is 2 electrons.
3.	Orbits are circular paths or elliptical in shape.	Orbitals have different geometrical shapes i.e. Spherical, dumbbell shaped.
4.	The position and velocity of a moving e⁻ in an orbit can be calculated with great accuracy.	The position and velocity of moving electron in an orbital can be determined in accordance with the uncertainty principle.
5.	The distance of the orbit from the nucleus for a given e⁻ is fixed.	It is not possible to know the exact distance of e⁻ from nucleus.
6.	The orbits are designated by the letters K, L, M, N etc.	The orbitals are designated by letters s, p, d, f etc.

- **What are Quantum Numbers? Explain them in detail.**

➤ **Quantum Numbers: -** "It may be defined as a set of four numbers (n, ℓ, m, s) with the help of which we can get complete information about all the electrons in an atom location, energy the type of orbital occupied shape and orientation of that orbital".

There are four quantum numbers:

1. Principal quantum number (n)
2. Azimuthal quantum number (ℓ)
3. Magnetic quantum number (m)
4. Spin quantum number (s)

1. Principal quantum number (n)

a) This number represents the main shell to which the electron belongs.
b) It determines the average distance of an element from the nucleus and its energy level.
c) It provides information about the energy of the principal shell.
d) It represents the size of the electron orbital higher the value of n, larger is the size of orbital and the energy of the orbital increases.
e) 'n' can have positive integral values 1, 2, 3, 4 corresponding to K, L, M, N etc.
f) Maximum number of electrons in a shell is given by $2n^2$.

Main energy level (n)	1	2	3	4
Letter designation	K	L	M	N
Maximum no. of electrons ($2n^2$)	2	8	18	32

2. Azimuthal quantum number (ℓ)

a) It is also called secondary, subsidiary quantum number.
b) It represents the sub-shells to which the electron belongs.

When

ℓ=0, 's' sub-shell

ℓ=1, 'p' sub-shell

ℓ=2, 'd' sub-shell

ℓ=3, 'f' sub-shell

c) It indicates the shape of the orbital i.e. whether the orbital is spherical, dumbbell shaped or some more complicated shape.
d) The value of 'ℓ' depends upon the value of 'n' hence l can have the values from 0 to (n-1)

ℓ= 0, 1, 2, 3 - - - - - (n-1)

When

n=1, ℓ=0

n=2, ℓ=0 &1

n=3, ℓ=0, 1 & 2

n=4, ℓ=0, 1, 2 & 3

e) This quantum number determines the angular momentum of an electron in a particular orbital.

$$L = \frac{h}{2\pi}\sqrt{l\,(l+1)}$$

Where

L = Angular momentum

h = Plank's constant

3. Magnetic quantum number (m)

a) It determines the orientation of the orbital relative to the magnetic field in which it is placed.

b) The values of 'm' depends on the value of 'ℓ'. For each value of l, the 'm' may have $(2\ell + 1)$ values.

These values range from $-\ell$ through zero to $+\ell$.

When $\ell = 0$, m = 0

$\ell = 1$, m = - 1, 0, + 1

$\ell = 2$, m = - 2, - 1, 0, + 1, + 2

$\ell = 3$, m = - 3, - 2, - 1, 0, + 1, + 2, + 3

4. Spin quantum number (s)

a) It indicates the direction in which the electron is spinning about its own axis.

b) The electron can spin clockwise ($\uparrow$) or anticlockwise ($\downarrow$), in two opposite directions.

c) Spin quantum numbers can have two possible values $+\frac{1}{2}$ and $-\frac{1}{2}$ depending on the direction of spin.

d) Only 2 electrons can be accommodated in the orbital with opposite spin ($\uparrow\downarrow$)
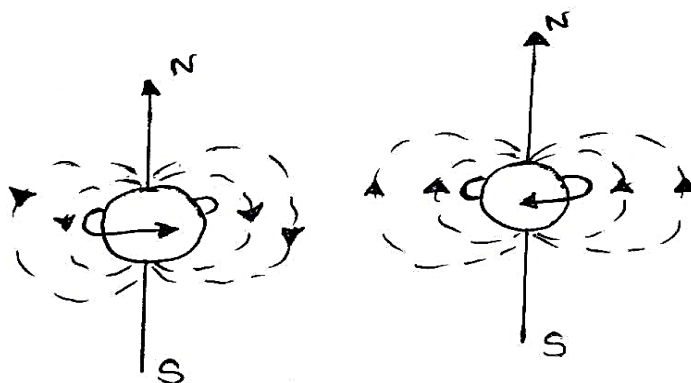
Permitted Values of Total Quantum Numbers.

Principal Q.N (n)		Azimuthal Q.N (ℓ)	Magnetic Q.N (m)	Spin Q.N (s)	Total no. of e's in shell
Value of N	Abbreviation	0 to (n - 1)	$2\ell + 1$		$2n^2$
1	K	$\ell = 0(s)$	m = 0	$\pm \frac{1}{2}$	2

2	L	$\ell = 0(s)$ $\ell = 1(p)$	m = 0 m = -1, 0, +1	± ½ ± ½	8
3	M	$\ell = 0(s)$ $\ell = 1(p)$ $\ell = 2(d)$	m = 0 m = - 1, 0, + 1 m = -2, -1,0, +1, +2	± ½ ± ½ ± ½	18
4	N	$\ell = 0(s)$ $\ell = 1(p)$ $\ell = 2(d)$ $\ell = 3(f)$	m = 0 m = - 1, 0, + 1 m = -2, -1,0, +1, +2 m = - 3,- 2, -1, 0, +1, +2, +3	± ½ ± ½ ± ½ ± ½	32

- **Explain the shapes of different types of atomic orbitals.**
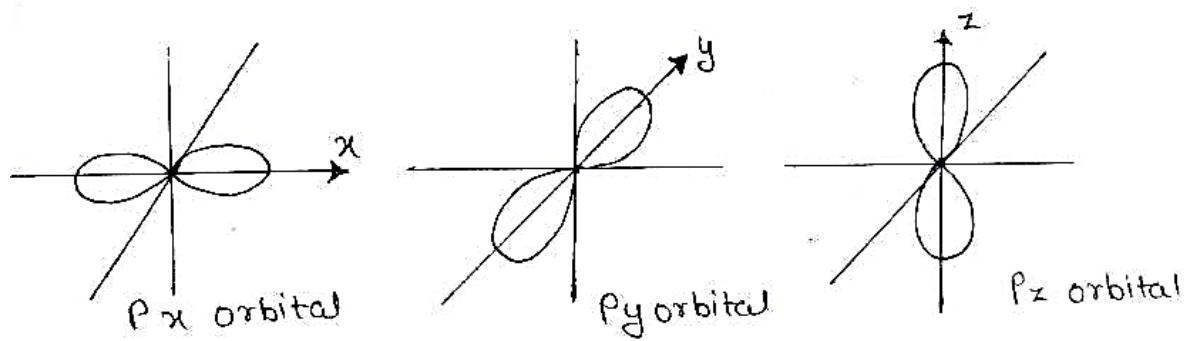
1. S - Orbital
   a) The lowest energy orbital of an atom is known as s – orbital.
   b) For s – orbital, ℓ= 0 and for ℓ= 0, m= 0

   Therefore s – orbital have only one orientation.
   c) S – Orbitals are spherically symmetrical about the nucleus.
   d) r
   e) In between 1s and 2s, there is a region where probability of finding the electron is zero. It is called as 'node'.
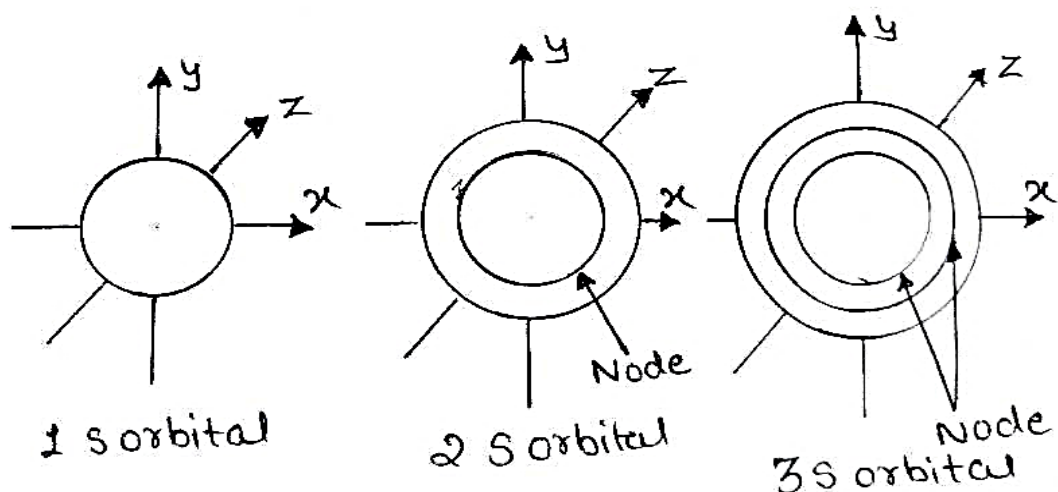
Increasing size of S – orbitals

2. <u>P – Orbitals</u>

a. For p – orbitals, $\ell = 1$ and for $\ell = 1$, m = +1, 0, -1
b. Thus p – orbitals have three orientations.
c. P – orbital is 'dumbbell' shaped consisting of two lobes.
d. Three p – orbitals px, py and pz are perpendicular to each other and oriented along x, y and z axes respectively in space.
e. They ae equivalent in energy in absence of magnetic field.
f. Orbitals, which differ in orientation but having equal energy, are called 'degenerate orbitals'.
g. The two lobes are separated by a plane having zero electron density such a plane is called 'nodal plane'.

Px orbital

Py orbital

Pz orbital

Nodal plane
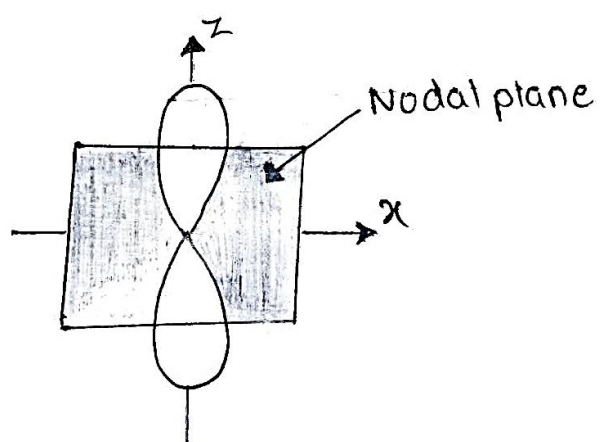
3. D - Orbitals

a. For d – orbitals, $\ell = 2$ and for $\ell = 2$, m = +2, +1, 0, -1, -2

b. Thus d – orbitals have five orientations.

c. They are designated as dxy, dyz, dzx,dx^2- y^2, dz^2.

d. They are equivalent in energy in absence of magnetic field, so they are also degenerate orbitals.

e. Out of five orbitals, the first three have double dumbbell shapein xy, yz and xz plane respectively.
The dx^2- y^{2}is also double dumbbell shaped lying along the x and y-axes.
The dz^{2}is dumbbell shaped with a doughnut shaped ring of high electron density around the nucleus in xy plane.
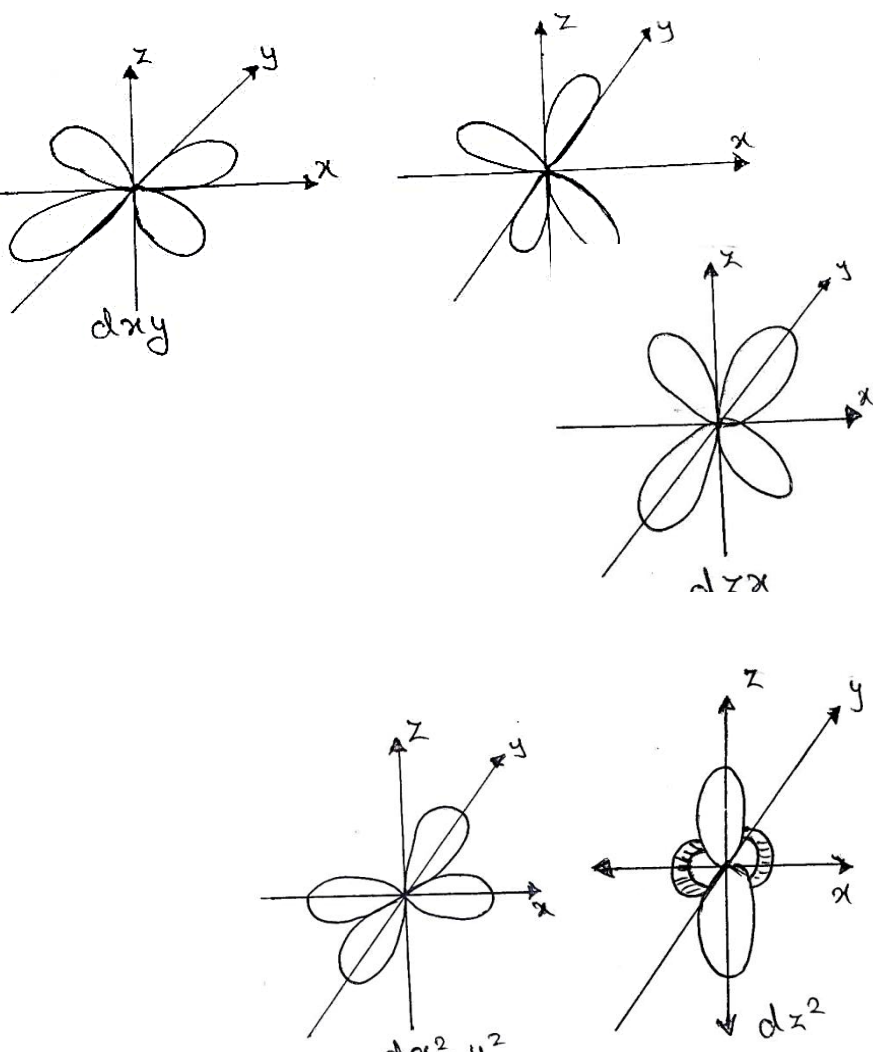
- **What does Electronic Configuration of an element means? Explain the rules to be followed for filling the electrons.**

  Electronic Configuration: The distribution of electrons in various orbitals of an atom is known as electronic configuration. It is written as $n\ell^x$, where n = shell number, ℓ = sub shell and x = no. of e's.
  E.g.: $3p^2$ where n = 3, ℓ = 1, x = 2

  Electronic configuration is mainly explained by following rules:
  1. Aufbau Principle
  2. Pauli's Exclusion Principle
  3. Hund's rule of maximum multiplicity.

  1. **Aufbau Principle**

     It states, "The electrons always enter the various orbitals in order of their increasing energies". According to Aufbau Principle, in the ground state of an atom, the orbital with lower energy is filled first before the filling of the orbital with higher energies.
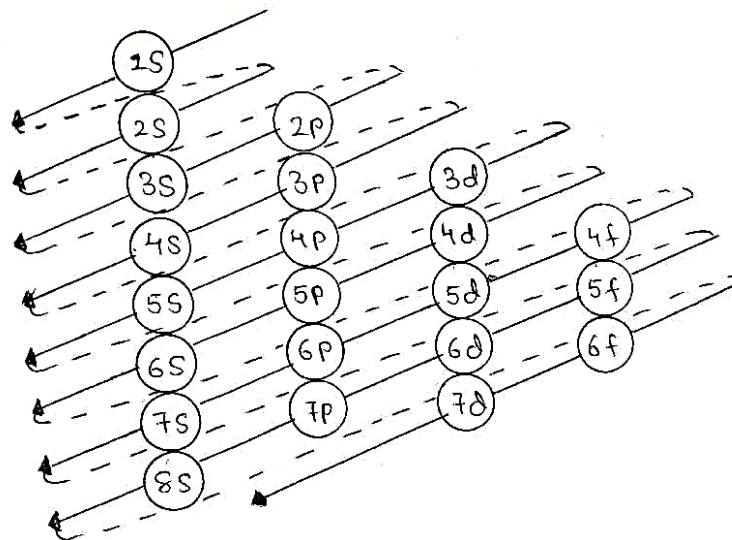
     The order of energy of different orbitals in an atom is given as:
     1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < 8s < 6f < 7d and so on.

  2. **Pauli's Exclusion Principle**

     It states, "No two electrons in a single atom can have the same set of four quantum numbers". Therefore, any orbital can have a maximum of only two electrons in opposite spin.
     E.g.: Consider He atom having atomic no. 2 and electronic configuration as $1s^2$.

| Electron	Quantum Number			
Number	n	ℓ	m	s
1st electron	1	0	0	+½
2nd electron	1	0	0	-½

It show that two electrons existing in the same orbital can have 3 quantum numbers same but the fourth will be different.

3. Hund's Rule of Maximum Multiplicity

It states, "No pairing takes place in degenerate orbitals until and unless each orbital is singly occupied".
When several orbitals of equal energy (degenerate orbitals) are available, the electrons first fill all the orbitals singly before pairing in any of these orbitals.
E.g.the configuration of four electrons occupying p – orbitals is
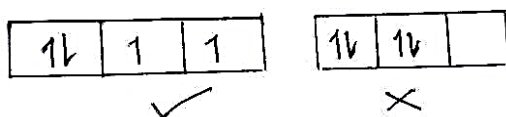
- **Write the electronic configuration of 30 elements of the periodic table.**

H (1) $-1s^1$

He (2) $- 1s^2$

Li (3) $-1s^2 2s^1$

Be (4) $-1s^2 2s^2$

B (5) $-1s^2 2s^2 2p^1$

C (6) $-1s^2 2s^2 2p^2$

N (7) $-1s^2 2s^2 2p^3$

O(8) $-1s^2 2s^2 2p^4$

F (9) $-1s^2 2s^2 2p^5$

N (10) $-1s^2 2s^2 2p^6$

Na (11) - $[Ne] 3s^1$

Mg (12) - $[Ne] 3s^2$

Al (13) - $[Ne] 3s^2 3p^1$

Si (14) - $[Ne] 3s^2 3p^2$

P (15) - $[Ne] 3s^2 3p^3$

S (16) - $[Ne] 3s^2 3p^4$

Cl (17) - $[Ne] 3s^2 3p^5$

Ar (18) - $[Ne] 3s^2 3p^6$

K (19) - $[Ar] 4s^1$

$\qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Ca [20] - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Sc [21] - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

Ti [22] - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

V [23] - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Cr [24] - $1s^2\,2s^22p^63s^23p^63d^54s^1$
Mn [25] - $1s^2\,2s^22p^63s^23p^63d^54s^2$
Fe [26] - $1s^2\,2s^22p^63s^23p^63d^64s^2$
Co [27] - $1s^2\,2s^22p^63s^23p^63d^74s^2$
Ni   [28] - $1s^2\,2s^22p^63s^23p^63d^84s^2$
Cu [29] - $1s^2\,2s^22p^63s^23p^63d^{10}4s^1$
Zn [30] - $1s^2\,2s^22p^63s^23p^63d^{10}4s^2$

Anomalies in electronic configuration

1. Cr (24)

Expected electronic configuration - $1s22s^22p^63s^23p^64s^23d^4$

Observed electronic configuration - $1s22s^22p^63s^23p^64s^13d^5$

The 3d orbital is not half filled. Hence, it is less stable. One 4s orbital e shifts to empty 3d orbital to make 4s and 4d orbitals half filled. Thus, Cr acquires stability as its electronic configuration becomes half-filled 4s and 3d.

2. Cu (29)

Expected electronic configuration - $1s^22s^22p^63s^24s^23d^9$

Observed electronic configuration - $1s^22s^22p^63s^24s^13d^1$

The 3d orbital is neither half-filled nor completely filled. Hence, it is less stable. One 4s electron shifts to one half-filled 3d orbital to make 4s half-filled and 3d completely filled. Thus Cu acquires stability as its electronic configuration become $4s^13d^{10}$. In this configuration, 3d orbital is completely filled and 4s orbital is half-filled which gives extra stability to Cu.

Molecular Orbital Theory (MOT)

It is a quantum mechanical approach in which the atomic orbitals combine to form new orbitals called molecular orbitals.

MOT was developed to explain:
➢ The formation of chemical bond.
➢ Relative bond strength.
➢ Paramagnetic or diamagnetic nature of molecules.

These properties were not explained by VBT (Valence bond theory). VBT explained stability of covalent bond and molecular geometrics. Therefore, this was the fundamental deficiency in VBT.

● **What is molecular orbital theory? Give its postulates.**

➢ The following are the main postulates of molecular orbital theory:

1. In the formation of a molecule, atoms come close to each other, interact and form bonds between them.
2. The number of MO formed is equal to the number of overlapping atomic orbitals.
3. The MO are formed by the mixing of atomic Orbitals of same energy levels and symmetry.

4. The atomic orbitals lose their identity after formation of molecular orbitals.
5. All the electrons present in the MO are considered to be moving under the influence of all the nuclei of the molecules.
6. Atoms have atomic orbitals with one nucleus whereas molecules have molecular orbitals with n nucleus. Therefore, atoms are monocentric while molecules are polycentric.
7. Molecular orbitals can be divided in 3 categories:
    a. Bonding molecular orbitals (BMO)
    b. Anti-bonding molecular orbitals (ABMO)
    c. Non-bonding molecular orbitals (NBMO)
8. BMO have lower energy than the corresponding anti-bonding molecular orbitals.
9. Each MO is described by a quantum mechanical wave function, which is associated with a set of quantum number.
10. Electrons fill up in the MOs in the same way as in atomic orbitals by following the rules like Aufbau principal, Pauli's exclusion principle and Hund's rule of maximum multiplicity.
11. The molecular orbitals for a molecule can be constructed by using LCAO (Linear combination of Atomic Orbitals) method.
12. The shape of MO formed depends on the type of combining atomic orbitals.
13. Inner Molecular orbital, which do not take part in bond formation, are called non-bonding MO.

- **Explain combination of atomic orbitals by LCAO method.**

1. According to quantum mechanics, the atomic orbitals can be expressed as wave functions (Ψ) which represent the amplitude of electron waves.
2. According to LCAO method, the molecular orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the molecule.
3. By combining the atomic orbitals A & B, we get two molecular orbitals:

    $\Psi b = \Psi A + \Psi B$

    $\Psi a = \Psi A - \Psi B$

    Where ΨA = atomic orbital of atom A

    ΨB = atomic orbital of atom B

    Ψb = wave functions of bonding molecular orbital

    Ψa = wave functions of anti-bonding molecular orbital
4. The MO with highest energy gives to a repulsive state and is called anti-bonding MO (Ψa).
5. The MO with lower energy gives rise to an attractive state and is called as bonding MO (Ψb)
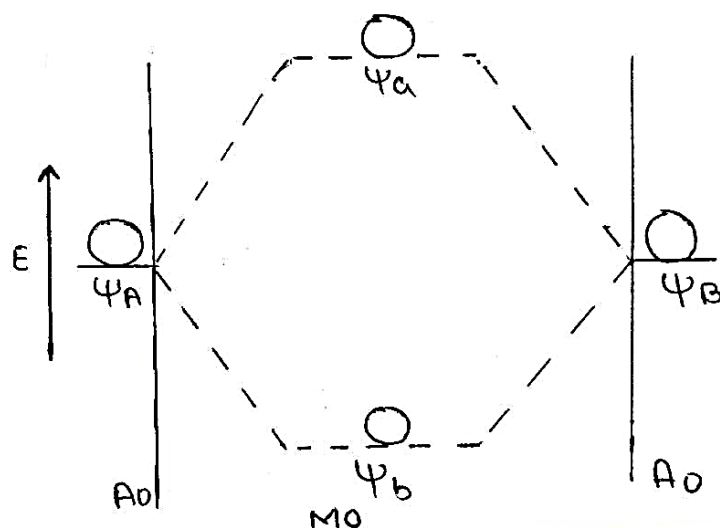
- **Explain the Bonding molecular orbitals and Anti-bonding molecular orbitals with example.**

  A wave has crest and trough, which is a property of wave function Ψ having positive and negative signs.
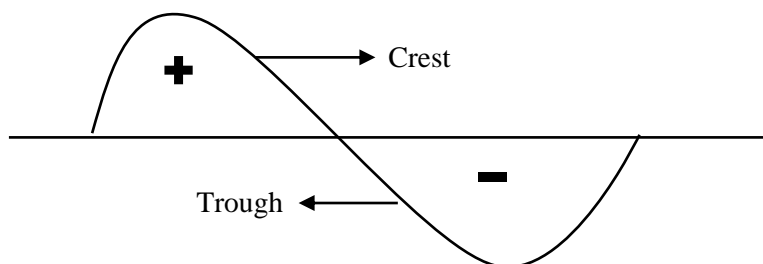

  Atomic orbitals combine and form the same number of molecular orbitals by either addition or subtraction of atomic orbitals.
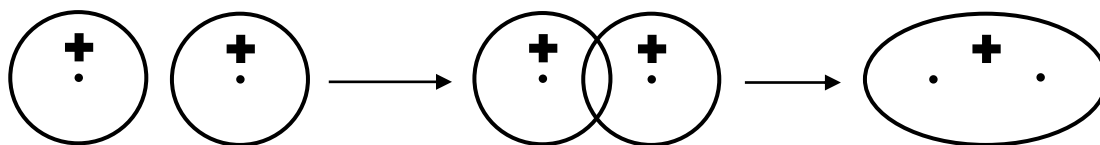
a) <u>**Bonding Molecular Orbitals (BMO)**</u>

  When the atomic orbitals with the same sign combine, their wave functions are in the same phase. This kind of combination gives rise to BMO.
  When combination of AO's takes place by addition, both the electron waves are on the positive side i.e. the same side or in same phase.
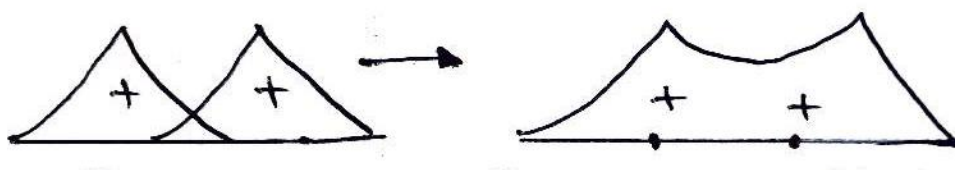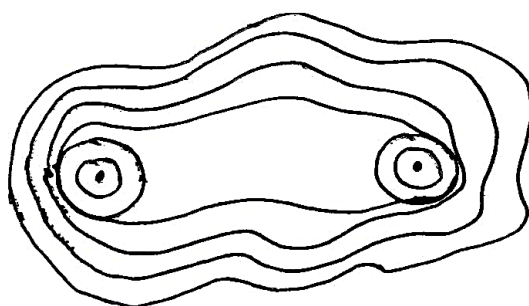

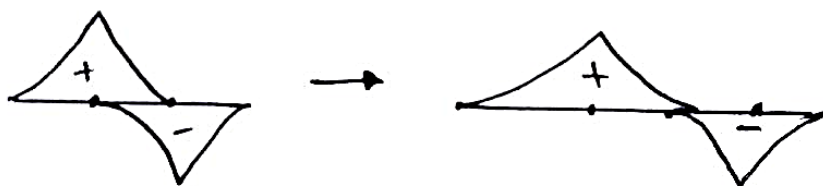**Combination of two 1S AO's by addition**

Formation of BMOs by addition of two AOs

In this molecular orbital, the region between the two uncle's is the place where there is over lap of the individual orbitals and hence there is greater probability of electrons density in the region.

b) <u>**Anti-bonding Molecular Orbitals (ABMO)**</u>

When the atomic orbitals with the opposite sign combine, their wave functions are out of phase. This kind of combination gives rise to anti-bonding molecular orbitals. They are designated as asterisk (*). When combination of AO's takes place by subtraction, their wave functions are in the opposite directions having wave functions of different signs or out of phase.

Combination of two 1S AO's by subtraction.
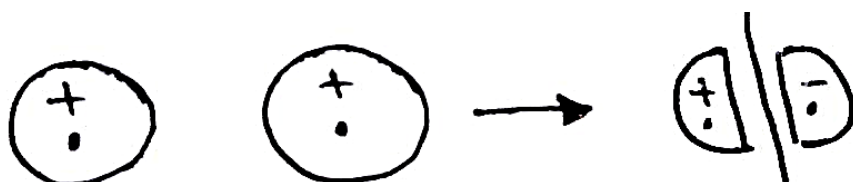
Formation of ABMOs by subtraction of two AOs.

In anti-bonding orbitals, the electrons are in those regions in space where they are not under the attraction of both the nuclei.

- **What are the conditions for the combination of atomic orbitals?**
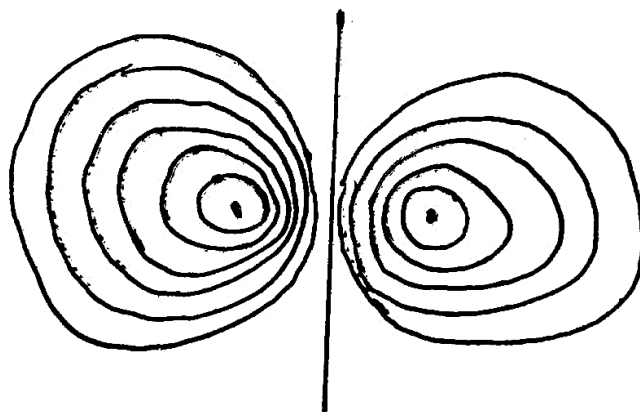
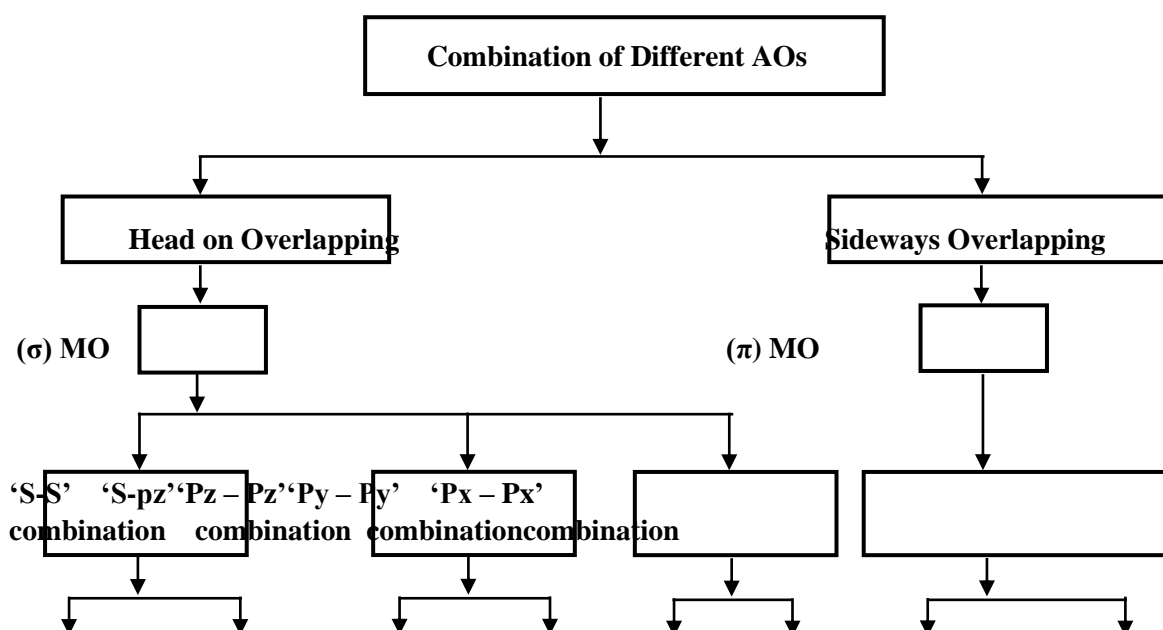 <u>**Conditions for the formation of molecular Orbitals**</u>

1. The energies of combining atomic orbitals should be same or nearly same.
   E.g.1s orbital can combine with another 1s orbital but not with 2s orbital, as 2s orbital is having higher energy than 1s orbital.

2. The combining atomic orbitals should possess same symmetry about the molecular axis.
   E.g.2pz orbital can combine with 2pz and not with 2px or 2py orbitals because of their different symmetries.

3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron density between the nuclei of molecular orbital.

- **What are sigma (σ) and pi (π) molecular orbitals?**
  <div align="center">**OR**</div>
  Sketch and describe the molecular orbital resulting from the combinations of different atomic orbitals.

1. Molecular orbitals of a diatomic molecule are designated as **σ**(sigma) and **π**(pi).
2. When two AOs overlap along the inter nuclear axis (head on collision), then the resulting molecular orbital is called **σ** (sigma) MO.
3. When two AOs overlap laterally (sideways), then the resulting MO is called **π**(pi) MO.

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                    ┌─────────────────────────────┐
                    │  Combination of Different AOs │
                    └─────────────────────────────┘
                                  │
            ┌─────────────────────┴──────────────────────┐
            │                                             │
   ┌──────────────────┐                          ┌──────────────────┐
   │ Head on Overlapping │                        │ Sideways Overlapping │
   └──────────────────┘                          └──────────────────┘
            │                                             │
   (σ) MO  ┌──────┐                             (π) MO   ┌──────┐
           └──────┘                                      └──────┘
            │                                             │
   ┌───────┬───────┬───────┐                   ┌───────┐
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‘S-S’   ‘S-pz’‘Pz – Pz’‘Py – Py’   ‘Px – Px’
combination   combination combinationcombination

σ1s / σ2s	σ*1s / σ*2s	σspz	σ*spz	σPz	σ*Pz	πPy = πPx	π*Py = π*Px	

a) S – S Combination of orbitals (1s with 1s / 2s with 2s)

1. The overlap is along inter nuclear axis.
2. Constructive overlapping forms σ1s / σ2s.
3. Destructive overlapping forms σ*1s / σ*2s.
4. The two BMOs formed are σ (1s) or σ (2s) and anti-bonding MOs are σ*(1s) or σ*(2s).
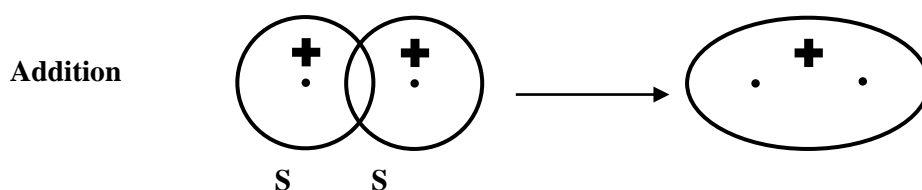
Bonding orbitals (σs)
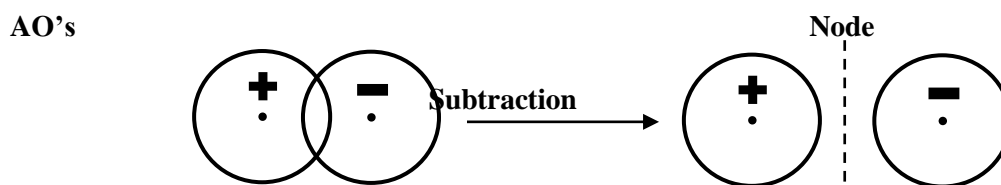
Anti-bonding orbitals (σ*s)

b) S – P Combination of orbitals (S- orbital with Pz orbital)

1) It is a coaxial overlap of S & pz orbitals.
2) S – Orbital can combine with p – orbital when the lobes of p – orbital are pointing along the axis joining the nuclei.
3) When same sign lobes overlap, BMO is formed (σsp) with an increased e⁻density between the nuclei.
4) When opposite sign lobes overlap, ABMO is formed (σ*sp) with reduced e⁻ density in between the nuclei.
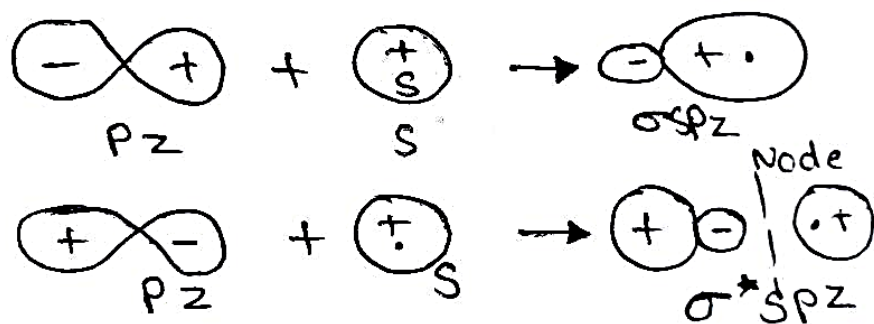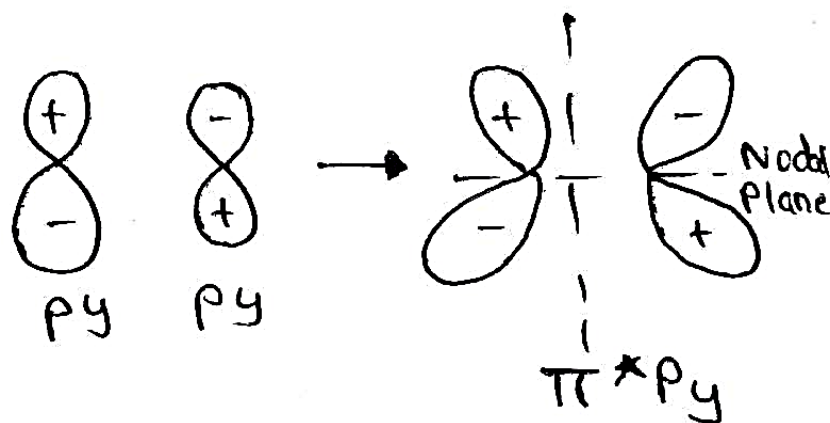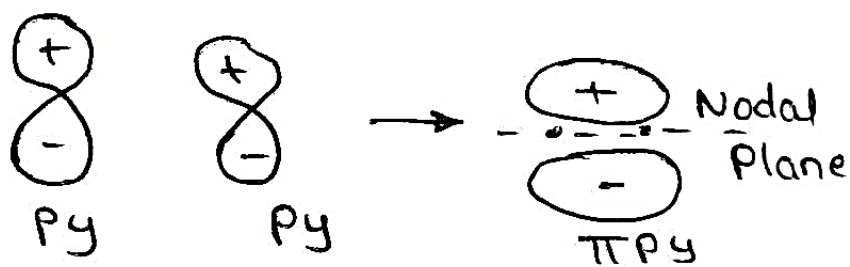
c) <u>Axial p – p combination of orbitals (Pz with Pz)</u>

1) It is axial overlap of pz-pz orbitals.
2) Lobes of combining orbitals point along the axis joining the nuclei.
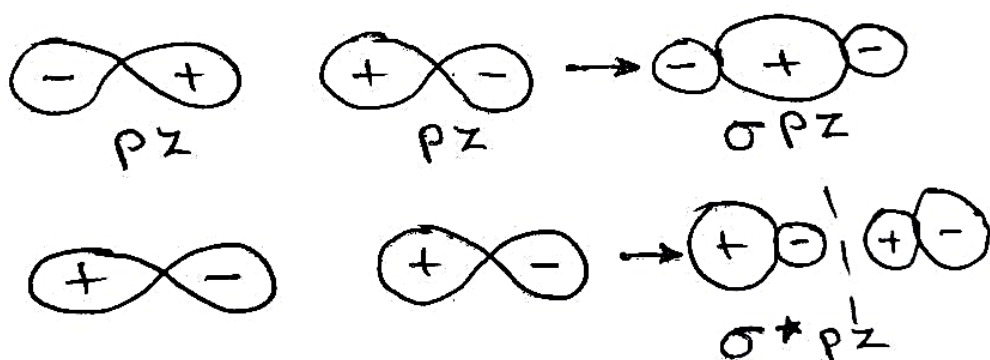
d) Side to side p-p combination (Py-Py / Px-Px)

1) It is side-to-side overlap of Py-Py or Px-Px.
2) Lobes of combining orbitals are perpendicular to the axis joining the nucleus.

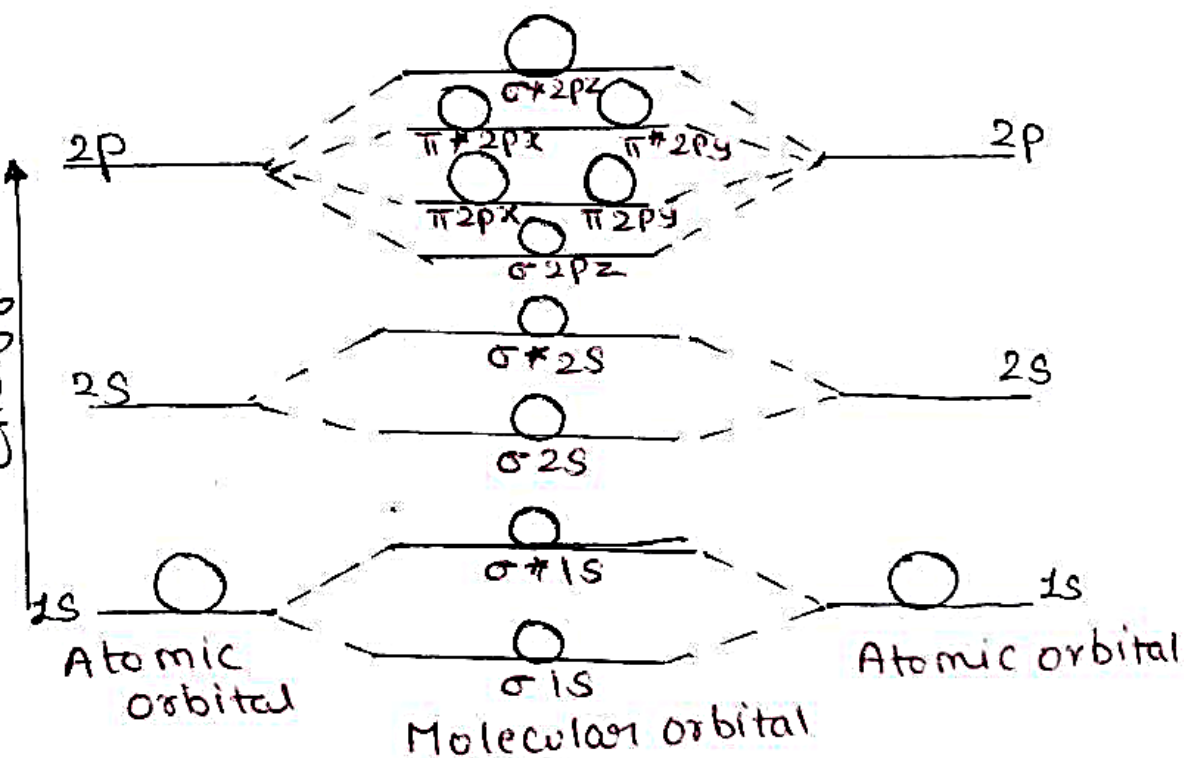- **Explain the formation of molecular orbitals in diatomic molecules.**
                                   OR
  Give the rules for writing MO electronic configuration.

1) To understand the physical and chemical properties of molecules, we should know how electrons are distributed in molecular orbitals.
2) The procedure for determining the electronic configuration of a molecule is same as the electronic configuration of atoms.
3) For writing the electronic configuration of a molecule, we should first arrange the MOs in the order of increasing energy.
4) The relative order of energy of MOs is:
   $(\sigma 1s <\sigma^*1s <\sigma 2s <\sigma^*2s <\sigma 2p_z <\pi 2p_x = \pi 2p_y <\pi^*2p_x = \pi^*2p_y <\sigma^*2p_z)$
5) The distribution of electrons in the molecular orbitals is on the basis of:

   a) **Aufbau principle:** Molecular orbitals are filled in order of increasing energy.

   b) **Pauli's exclusion principle:** Two electrons in the same orbital cannot have set of all the four quantum numbers identical. It means maximum two electrons can occupy a molecular orbital with opposite spin ( ).   ↑↓

   c) **Hund's rule of maximum multiplicity**: Pairing of electrons in the degenerate molecular orbitals does not occur until each of them has one e⁻ each.

6) Σ molecular orbital is more stable as compared to π molecular orbital.
7) The number of e⁻s in the MO is equal to the sum of all the e⁻s on the bonding atoms.
8) The e⁻s associated with bonding MO are known as bonding e⁻s and e⁻s in the anti-bonding orbital are known as anti-bonding e⁻s.

- **What are the atomic orbitals, which can combine for the formation of a diatomic molecule?**

Atomic Orbitals	Molecular Orbitals
$1s_A + 1s_B$	$\sigma 1s$
$1s_A - 1s_B$	σ^*1s
$2s_A + 2s_B$	$\sigma 2s$
$2s_A - 2s_B$	σ^*2s
$2p_{zA} + 2p_{zB}$	$\sigma 2p_z$
$2p_{zA} - 2p_{zB}$	σ^*2p_z
$2p_{yA} + 2p_{yB}$	$\pi 2p_y$
$2p_{xA} + 2p_{xB}$	$\pi 2p_x$
$2p_{yA} - 2p_{yB}$	π^*2p_y
$2p_{xA} - 2p_{xB}$	π^*2p_x

- **Give diagrammatic representation of the energy levels of the molecular orbitals in diatomic molecules.**

Molecular orbital energy diagram

- **What are the properties of a molecule that can be explained on the basis of molecular orbital energy diagram?**

The electronic configuration in the molecular orbital can explain certain facts and the properties observed for a molecule. The following properties can be explained:-

a) **Stability of the molecule:**

If Nb is the number of e⁻s present in BMO and Na is the number of e⁻s present in ABMO, then
1) If Nb is greater than Na i.e. Nb>Na – stable molecule.
2) If Nb is less than Na i.e. Na<Na – Unstable molecule.

b) **Bond order (BO):**

The bond order is defined as half the difference between the number of e-s present in the bonding and anti-bonding molecular orbitals. i.e.

Bonding order $(BO) = \frac{1}{2}(Nb - Na) = \frac{Nb - Na}{2}$

1) A positive BO means stable molecule.
2) A negative BO or zero BO means unstable molecule.

c) **Number and nature of bonds :**

1) The BO values of +1, +2, +3 indicates that the molecule is formed by joining of two atoms by a single, double or triple bond respectively.
2) Greater the value of BO, greater is the stability of the molecule.
3) Bond length is inversely proportional to BO.
4) Higher the bond order, higher is the dissociation energy.

d) **Magnetic nature** :

1) If the MO contains one or more unpaired electrons, the molecule is paramagnetic in nature. I.e. singly occupied () – paramagnetic.
2) If the MO does not have any unpaired electron i.e. if all electrons are paired, then the molecule is diamagnetic in nature. I.e. doubly occupied ( ) – diamagnetic.↑↓
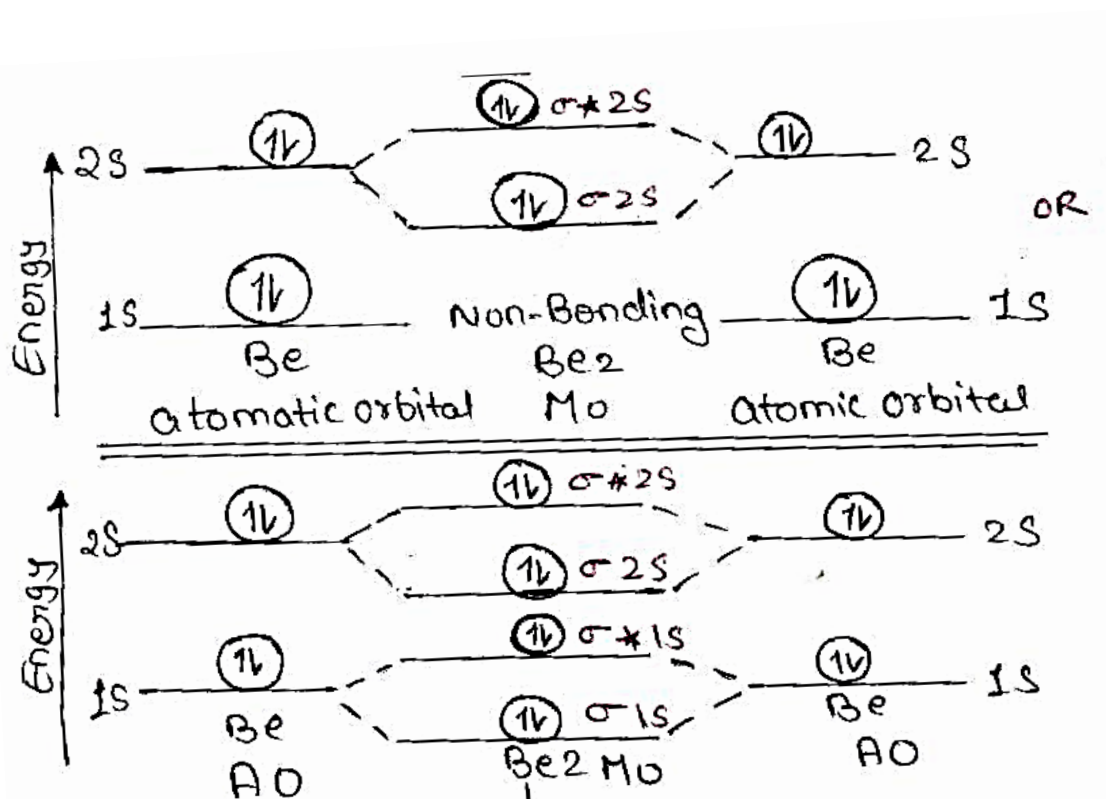
- **Explain in detail the MO diagram for the following Homo nuclear Diatomic molecules: (1) Be₂   (2) O₂**
                                OR
 **Explain on the basis of MOT, Why Be₂ molecule does not exist?**

1. Be molecule may be formed by the overlap of two Be atoms.
2. Each Be atoms have electronic configuration as $Be(4) = 1s^2 2s^2$.
3. Therefore, there are total of eight electrons from two Be atoms to be filled in the molecular orbitals.
4. The eight e-s are filled in four molecular orbitals i.e. σ1s, σ*1s, σ2s & σ*2s according to Aufbau principle and Pauli's exclusion principle.
5. MO electronic configuration of Be2 molecule = $σ1s^2 σ*1s^2 σ2s^2 σ*2s^2$
   Or Be₂ molecule = $kk\ σ2s^2\ σ*2s^2$
6. The inner shell of filled σ1s & σ*1s MOs do not take part in bond formation, i.e. they are non-bonding. So, sometimes it is written as KK that means K-shell is completely filled.
7. The remaining 2s orbitals of both Be atoms having 4 e-s will be filled in σ2s &σ*2s molecular orbitals.
8. The bond order (BO) of Be2 molecule $= \frac{Nb - Na}{2}$
$$= \frac{2-2}{2} = 0$$
9. Since the BO is zero, Be₂ is an imaginary, unstable non-existent molecule.
10. It indicates that formation of diatomic (Be₂) is not possible.

Energy diagram for Be and Be₂ molecular orbitals:

Upper diagram:
- 2S (Be atomic orbital, 1↓) — σ*2S (1↓) — 2S (Be atomic orbital, 1↓) — OR
- σ2S (1↓)
- 1S (Be atomic orbital, 1↓) — Non-Bonding (Be₂ MO, 1↓) — 1S (Be atomic orbital, 1↓)

Be atomic orbital — Be₂ Mo — Be atomic orbital

Lower diagram:
- 2S (1↓) — σ*2S (1↓) — 2S (1↓)
- σ2S (1↓)
- 1S (1↓) — σ*1S (1↓) — 1S (1↓)
- Be AO — σ1S (1↓) — Be AO
- Be₂ Mo

- **Explain the structure of O₂ molecule by MO theory. Show that O₂ is paramagnetic according to MO theory.**

1. O₂ molecule is formed by the overlap of two oxygen atoms each having electronic configuration as
   $O(8) = 1s^2 2s^2 2p^4$
2. Therefore, O₂ molecule has total 16 electrons to be filled in Mos.
3. As 1s orbitals are considered to be non-bonding, the 4 electrons of $\sigma 1s^2$ & $\sigma^* 1s^2$ are ignored.
4. The remaining 12 electrons are filled in MO.
5. The MO electronic configuration of O₂ molecule is
   $O_2 = KK\ \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$
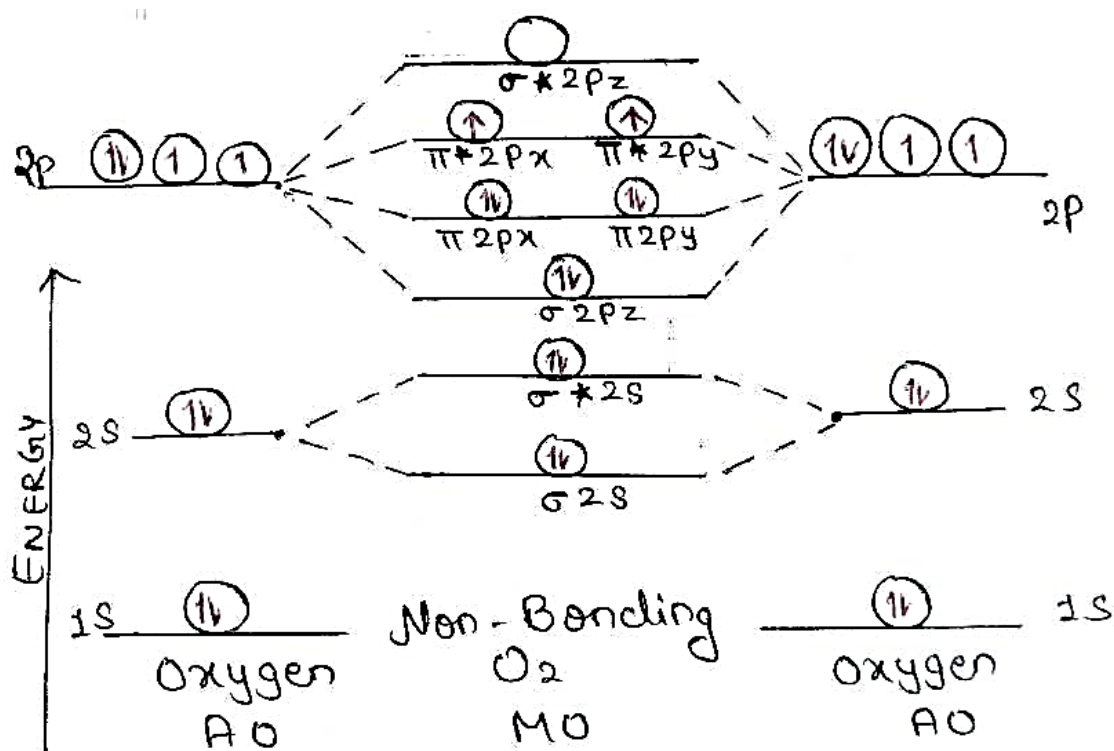
6) Bond order (BO) $= \dfrac{Nb - Na}{2} = \dfrac{8-4}{2} = 2$

7) Bond order of two suggests that O_2 molecule has double bond (0 - 0), one σ(sigma) and one π (Pi) bond between two O atoms.

8) The bond order of 2 also suggests that the O_2 molecule is quite stable.

9) Presence of two unpaired electrons in its π*2px and π*2py indicates that O_2 molecule is paramagnetic in nature.


- **Explain in detail the molecular orbital diagram of the hetero nuclear diatomic molecule (CO).**

➢ **Molecular orbital Diagram of CO molecule**

1. CO molecule is formed by the overlap of carbon and oxygen atom.
2. The electronic configuration of C & O are as follows:
   C (6) = $1s^2 2s^2 2p^2$
   O (8) = $1s^2 2s^2 2p^4$

3. There are total 14 electrons to be filled in MOs'
4. CO is hetero nuclear molecule in which oxygen is more electronegative than carbon. Therefor atomic orbitals of oxygen are at lower energy level than the atomic orbitals of carbon. As the bonding MOs are closer to oxygen AOs, they contribute more to the MOs' this unequal contribution of carbon and oxygen atoms to the MOs make CO molecule polar in nature.
5. Out of 14 electrons, four electrons are filled in non-bonding orbital i.e. σ1s & σ*1s as they are inner shells.
6. The remaining 10 electrons will be filled in MOs
7. The MO electronic configuration of CO is
   CO = KK σ2s² σ*2s²π*2px² = π*2py²σ2pz²
   Where KK ➝ the two non-bonding 1s orbital of C & O atoms.
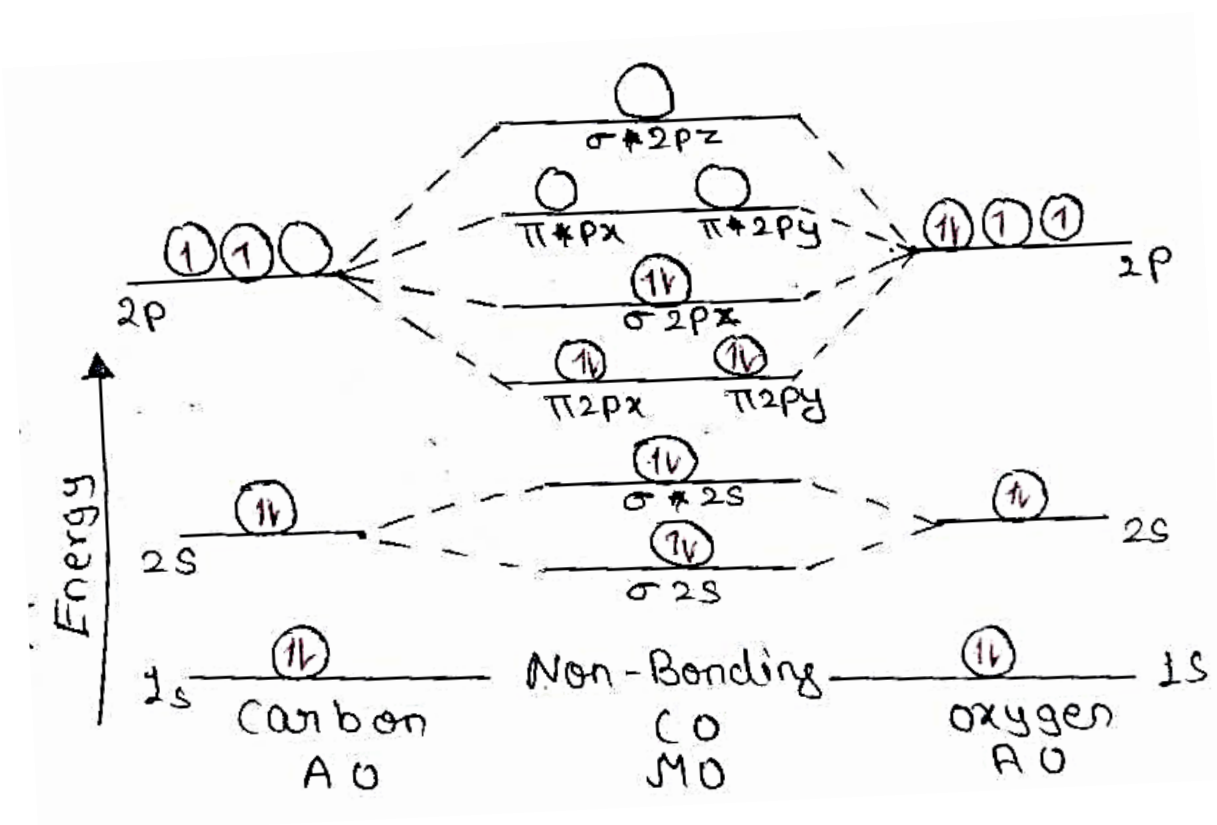
8. Bond order $= \dfrac{Nb-Na}{2} = \dfrac{8-2}{2} = 3$

9. The BO of three indicates that there is triple bond between C & O (C ≡ O), one sigma (σ) and two pi (π) bonds.
10. As BO is three, which is very high, CO is a very stable molecule.
11. As all the electrons are paired, CO is diamagnetic in nature.

   Note: Based on 14 electron rule, if the total number of e⁻s in a molecule is less than or equal to 14, then the $\sigma 2pz$ MO is higher in energy as compared to $\pi 2px$ and $\pi 2py$.
   Therefore, In MO diagram of CO, $\sigma 2pz$ is above than $\pi 2px = \pi 2py$.

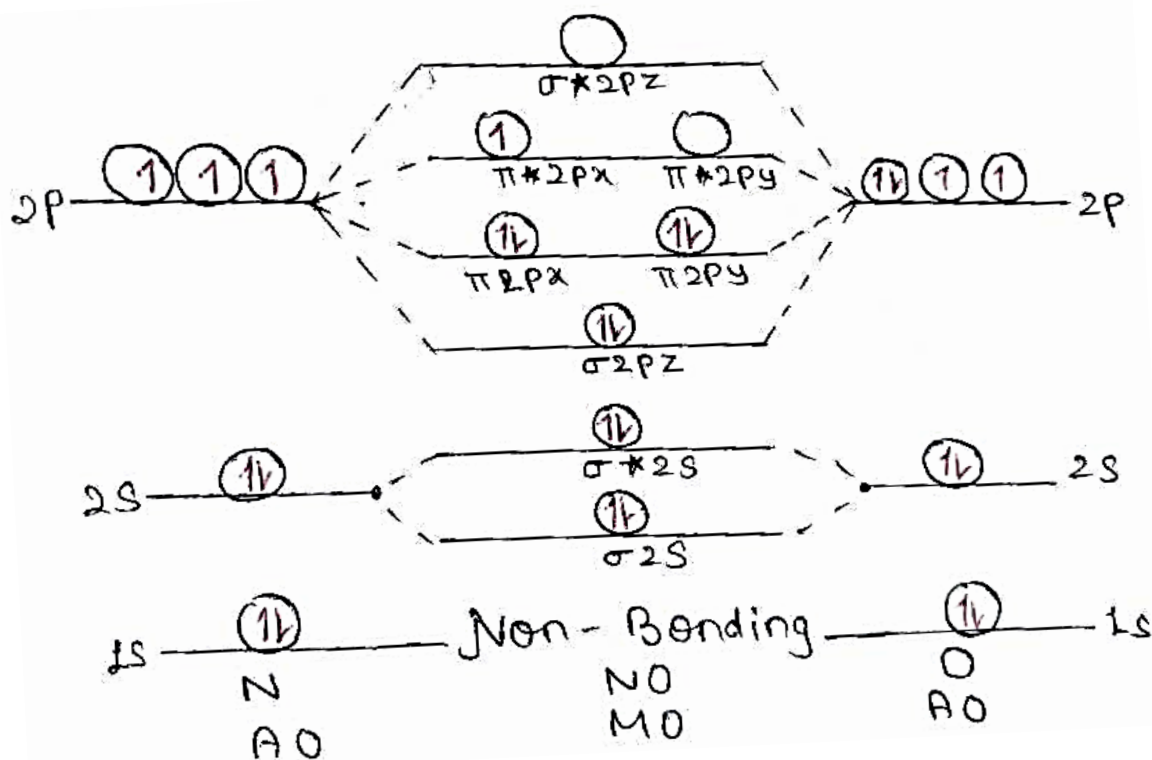- **Explain in detail the molecular orbital diagram for the hetero nuclear diatomic molecule (NO).**

➤ **Molecular orbital diagram of NO molecule**

1. NO molecule is formed by the overlap of Nitrogen and oxygen atoms.
2. The electronic configuration of N & O are as follows:
   $$N (7) = 1s^2 2s^2 2p^3$$
   $$O (8) = 1s^2 2s^2 2p^4$$
3. There are total 15 electrons to be filled in MOs'
4. NO is hetero nuclear molecule in which oxygen is more electronegative than N. Therefore, AOs of oxygen are at lower energy level than the AOs of nitrogen.
5. As the bonding MOs are closer to oxygen AOs, they contribute more to the MOs' this unequal contribution of N & O atoms to the MOs make NO molecule polar in nature.
6. Out of 15 electrons, four electrons form non-bonding orbital.
7. Remaining 11 electrons to be filled in MOs
8. The MO electronic configuration of NO is
   NO = KK $\sigma 2s^2$ $\sigma*2s^2$ $\sigma 2pz^2 \pi 2px^2 = \pi 2pz^2$ $\pi*2px^1$ or $\pi*2py^1$
   Where KK represents the two non-bonding 1s orbital of N & O atoms.

σ*2pz

π*2px   π*2py

2p ——— ①①①   2p

π2px   π2py

σ2pz

σ*2s

2s ——— ⑪   σ2s   2s

1s ——— ⑪   Non-Bonding   ⑪ ——— 1s

N
AO   NO
         MO   O
                  AO

9. Bond order (BO) = $\dfrac{Nb-Na}{2}$ = $\dfrac{8-3}{2}$ = 2.5

10. BO of 2.5 indicates that bond between N & O is between a double and triple bond.

11. Between N & O (N ≡O), one is sigma (σ) and one & half is Pi (π) bonds.

12. NO molecule is stable due to the presence of one unpaired e⁻ in antibonding MO that creates charge over both the atoms.

13. NO molecule is paramagnetic in nature due to the presence of one unpaired e⁻ in antibonding MO.

❖ NO⁺ is more stable than NO

Because BO of NO⁺ = 3. This leads to strengthening & shortening of bond length as a single bond is longer, double bond is shorter & triple bond is still shorter in length.

- **Differentiate between bonding and antibonding molecular orbitals.**

Bonding MO	Anti-bonding MO
1) Formed by addition overlap of atomic orbitals.	1) Formed by subtraction overlap of atomic orbitals.
2) Wave function of a bonding MO is given by $\Psi b = \Psi A + \Psi B$	2) Wave function of an anti-bonding MO is given by $\Psi a = \Psi A - \Psi B$
3) A BMO forms when the lobes of atomic orbitals have same sign.	3) A BMO forms when the lobes of atomic orbitals have different sign.
4) Possesses lower energy and hence is more stable than the overlapping atomic orbitals.	4) Possesses higher energy and hence is less stable than the overlapping atomic orbitals.
5) The e⁻ density between the two nuclei is maximum and results in less inter nuclear repulsion.	5) The e⁻ density between the two nuclei is nil and results in more inter nuclear repulsion.
6) Imparts stability to the molecule.	6) Imparts instability to the molecule.

- **Differentiate between sigma (σ) and pi (π) MOs.**

Sigma (σ) MO	Pi (π) MO
1) Formed by head on collision of AOs.	1) Formed by lateral overlap of AOs.
2) The lobes of the AOs are along the internuclear axis.	2) The lobes of the AOs are perpendicular to the internuclear axis.
3) The electron density along the internuclear axis is not zero ($\Psi^2 \neq 0$).	3) The electron density along the internuclear axis is zero ($\Psi^2 = 0$).
4) Σ BMOs are gerade (even) and σ*ABMOs are ungerade (uneven).	4) π BMOs are ungerade (uneven) and π*ABMOs are gerade (even).
5) Strength of overlapping is greater, therefore forms stronger bonds.	5) Strength of overlapping is less, therefore forms comparatively weaker bonds.