

## Structure and Bonding models

### planck's quantum Theory :

photo electric effect : When a beam of light of suitable frequency is allowed to incidence on the surface of a metal, the electrons are ejected from the surface of the metals.

- In 1900, Max planck proposed a theory of radiation to explain black body radiation and photo electric effect.

While analysing the light emitted by heated objects. He discovered that the emitted light is non-continuous and is in the form of defined energy packets. These small packets of energy are known as quanta or photons. The energy of the photon is directly proportional to the frequency of the radiation.

$$E \propto \nu$$

Where,

$$E = h\nu$$

$E$  = energy of photon

$\nu$  = frequency of radiation

$h$  = planck's constant

$$\therefore \nu = \frac{c}{\lambda} \quad E = \frac{hc}{\lambda}$$

$$6.626 \times 10^{-34} \text{ ergs} \cdot \text{sec}$$

$$6.626 \times 10^{-34} \text{ Joules} \cdot \text{sec}$$

The above equation says that a wave of higher frequency (or) lower wave length will be more energetic and vice versa.

→ For example the violet light of high frequency has more energy whereas as red light of low energy will exhibit less frequency.

### Dual nature of matter :

Bohr's model of the atom has the following two inherent defects.

- (i) The simultaneous assignments of an exact position and definite momentum to a given electron which is contradictory to Heisenberg uncertainty principle.
- (ii) principle of quantization of angular momentum for which no justification was made by bohr.

→ De-Broglie pointed out in 1924 that radiation including, visible light, infrared, ultra violet and x-rays behave like waves in propagation experiment based on interference and diffraction. These experiments conclusively proved the wave nature of these radiation.

- Radiation behave like a particle in interaction experiment which include black body radiation, photo electric effect and crompton effect.
- Hence radiation have a dual nature i.e wave and particle nature. In other words, matter also possesses particle as well as wave character.
- Wave is specified by its frequency, wave length, phase, amplitude etc.
- While a particle is specified by its mass, velocity, energy etc.

De-Broglie hypothesis :

In 1924, De-Broglie suggested that, waves sometimes behave like particles and conversely particles can have wave like characteristic properties. Therefore particles like electrons, protons, neutrons, atoms or molecules have waves associated with them known as matter waves (or) de-broglie waves.

(or)

According to de-Broglie's hypothesis all the matter particles like electrons, protons, neutrons, atoms

should have not only the particle nature but also the wave properties.

### De-Broglie wavelength :

According to Planck's and Einstein theories the energy of a photon whose frequency  $\nu$ ,

$$E = h\nu \quad \nu = \frac{c}{\lambda}$$

$$E = \frac{hc}{\lambda} \rightarrow ①$$

According to Einstein mass-energy relation,

$$E = mc^2 \rightarrow ②$$

Hence from eq ① and ②

$$mc^2 = \frac{hc}{\lambda}$$

$$mc = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

If we consider the case of a material particle of mass  $m$  moving with velocity ' $v$ ' then,

$$\lambda = \frac{h}{mv} \quad p = mv$$

$$\boxed{\lambda = \frac{h}{p}}$$

$$\lambda = \frac{h}{p} \quad \lambda = \text{wave length}$$

$m$  = mass of the  $e^-$

$h$  = planck's constant

$p$  = movement of  $e^-$

The above equation indicates the de-broglie wave-length of matter waves.

### Heisenberg uncertainty Principle :

one of the important consequences of dual nature of matter is the uncertainty principle developed by Heisenberg in 1926. The Heisenberg uncertainty principle states that, it is impossible to determine simultaneously both the position and momentum of a microscopic particle like an electron with accuracy.

- multiplying together the errors in measurements of position and momentum has to give a number greater than or equal to half of constant called ( $\frac{h}{2}$ ).

$$\therefore \Delta x \cdot \Delta p \geq \frac{h}{2}$$

$$\hbar = \frac{h}{2\pi}$$

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{4\pi}$$

$$\Delta x \cdot m \Delta v \geq \frac{\hbar}{4\pi}$$

Where,

$\Delta x$  = uncertainty in position

$\Delta p$  = uncertainty in momentum

$m$  = mass of electron

$h$  = planck's constant.

Schrodinger Equation :

In 1926 Erwin schrodinger developed a new model of the atom.

In the schrodinger wave equation, electrons are treated as a wave motion in three dimensional space around the nucleus having nodes and quantized energies.

If  $\psi$  (psi) is the amplitude or wave function of a wave moving in a three - dimentional space with a velocity of ' $v$ ' and frequency ' $\nu$ '.

The wave equation is,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 v^2 \psi = 0 \rightarrow ①$$

According to de-broglie's equation,

$$\lambda = \frac{h}{mv}$$

$$\frac{1}{\lambda} = \frac{mv}{h} \quad \boxed{\frac{1}{\lambda} = v}$$

$$v = \frac{mv}{h}$$

$v$  value is substituted in eq ①

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \left(\frac{mv}{h}\right)^2 \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \frac{m^2 v^2}{h^2} \psi = 0 \rightarrow ②$$

$$\text{kinetic Energy } h \cdot E = \frac{1}{2} mv^2$$

$$2 \text{ K.E} = mv^2$$

Multiply 'm' both side

$$2 m \text{ K.E} = m^2 v^2$$

These K.E value is substitute in Eq ②

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + 4\pi^2 \frac{2mk \cdot E}{h^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m k \cdot E}{h^2} \psi = 0$$

Total energy  $E = k \cdot E + p \cdot E(v)$

$$k \cdot E = E - V$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

simply  $\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$

This is known as the schrodinger equation.

Here,  $\nabla^2 = \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$

$m$  = mass of electron

$V$  = potential energy ( $p \cdot E$ )

$E$  = Total energy

$h$  = planck's constant

## Significance of $\psi$ and $\psi^2$ :

- $\psi$  is the amplitude (maximum displacement) of the wave and is called the wave function.
- It takes a positive value above the axis and negative value below the axis and becomes zero while crossing / intercepting the axis.
- $\psi$  is a state function but it has no physical significance, it only represents the amplitude of electron wave.
- The  $\psi^2$  gives the probability function, which describes the probability of finding an electron around the nucleus. and the point where the value of  $\psi^2$  is maximum is called the orbital.
- The value of  $\psi^2$  is always positive. The value of  $\psi^2$  at different points within the atom, it is possible to find out the orbital of the electron.

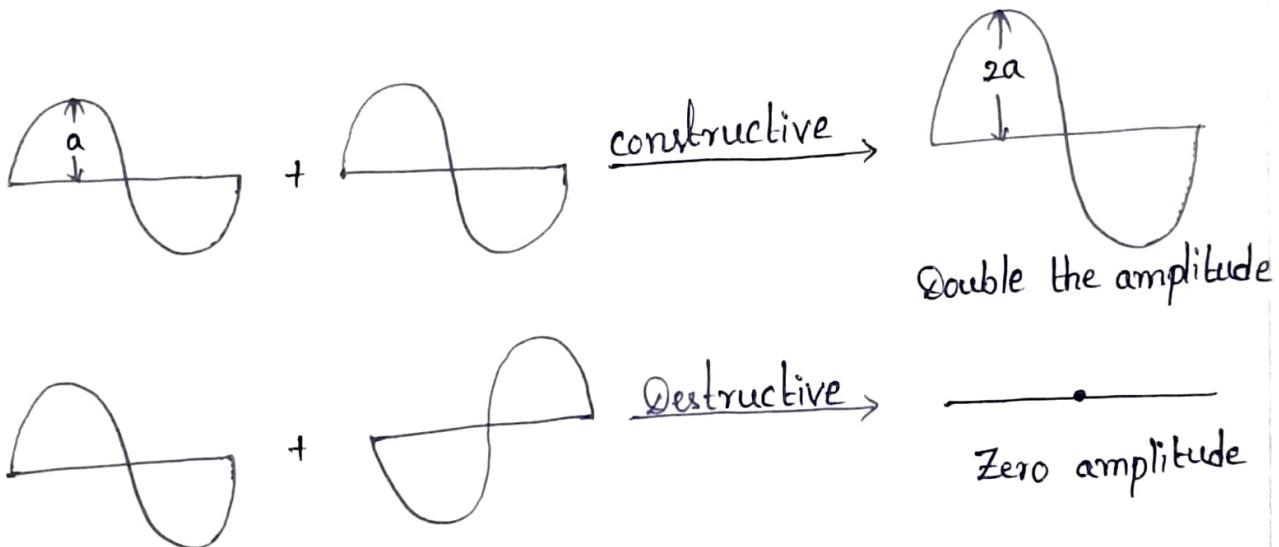
## molecular orbital Theory (MOT)

- Hund and Mullikan were proposed the molecular orbital theory.
- According to this theory, all the atomic orbitals of the participating atoms get mixed up to give equal number of new orbitals is called molecular orbitals.
- The molecular orbitals are polycentric, the probability of finding electron is maximum.
- The molecular orbitals are of varying energies and are arranged in the order of increasing energy levels as in the case of atomic orbitals.
- The molecular orbitals follow the same rules as the atomic orbitals.

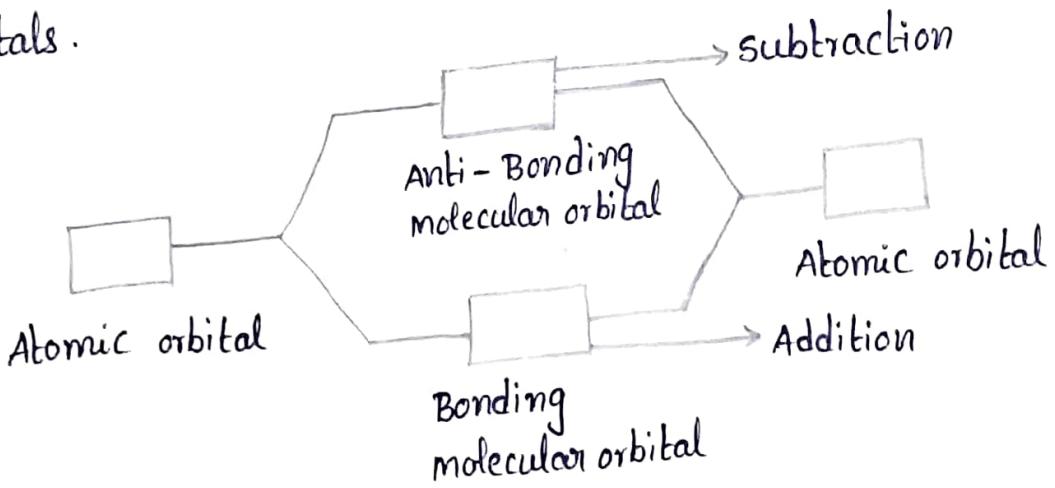
## Linear combination of atomic orbitals (LCAO) method :

- Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of bonded atoms.
- According to the LCAO method, the linear combination of atomic orbitals can take place either by adding (constructive) or subtracting (destructive) the wave function of the atomic orbitals.

- If the two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wave length.
- If they combine destructively to produce the wave with zero amplitude.



- The molecular orbital formed as a result of constructive interference is known as Bonding molecular orbitals.
- The molecular orbital formed as a result of destructive interference is called Anti-Bonding molecular orbitals.



If  $\Psi_A$  and  $\Psi_B$  represent wave functions (amplitude) of the electron waves of the atomic orbitals of two atoms A and B.

ii) When two waves are combine constructively, the waves are added so that the wave function of new wave i.e bonding molecular orbital ( $\Psi_b$ ) is

$$\Psi_b = \Psi_A + \Psi_B$$

$$\Psi_b^2 = (\Psi_A + \Psi_B)^2$$

$$= \Psi_A^2 + \Psi_B^2 + 2\Psi_A \Psi_B$$

$$\Psi_b^2 = \Psi_A^2 + \Psi_B^2$$

iii) when the two waves are combine destructively the waves are subtracted from each other so that the wave function of the new wave i.e anti-bonding molecular orbital ( $\Psi_a$ ) is,

$$\Psi_a = \Psi_A - \Psi_B$$

$$\Psi_a^2 = (\Psi_A - \Psi_B)^2$$

$$= \Psi_A^2 + \Psi_B^2 - 2\Psi_A \Psi_B$$

$$\Psi_a^2 < \Psi_A^2 + \Psi_B^2$$

- where  $\psi_b^2$  and  $\psi_a^2$  are probable electron density of bonding and anti-bonding molecular orbitals.
- The probability of finding the electron in the bonding molecular orbital increases while it decreases in an-anti-bonding molecular orbital.
- The energy of the bonding molecular orbital is always lower than the energy of the atomic orbitals and anti-bonding molecular orbitals also.
- The energy of the anti-bonding molecular orbital is always higher than the energy of the atomic orbitals and bonding molecular orbitals.
- so that bonding molecular orbital is more stable and anti-bonding molecular orbital is less stable.
- $\sigma, \pi, \delta$  etc are used to represent bonding molecular orbitals and  $\sigma^*, \pi^*, \delta^*$  etc are used to denote anti-bonding molecular orbitals.

### Salient features of molecular orbital Theory :

- (1) The number of the molecular orbitals produced is equal to the number of atomic orbitals combined.
- (2) When two atomic orbitals combine, they form two molecular orbitals. one of which is called bonding

molecular orbitals and other is called anti-bonding molecular orbital. These are formed by addition and subtraction of wave functions.

- (3) The electrons normally seek the lowest energy molecular orbitals i.e bonding molecular orbitals available to them in a molecule.
- (4) Bonding molecular orbitals have energy lower than the combining atomic orbitals while anti-bonding molecular orbital have higher energy than combining atomic orbitals.
- (5) obeying pauli exclusion principle , each molecular orbital accommodates a maximum of two electrons in it.
- (6) obeying Hund's rule , electrons enter in the molecular orbitals of identical energies singly before they pairup.
- (7) molecular orbitals are filled to increase energies starting with the orbital of minimum energy (Aufbau principle).
- (8) shapes of molecular orbitals formed depend on the type of combining orbitals.

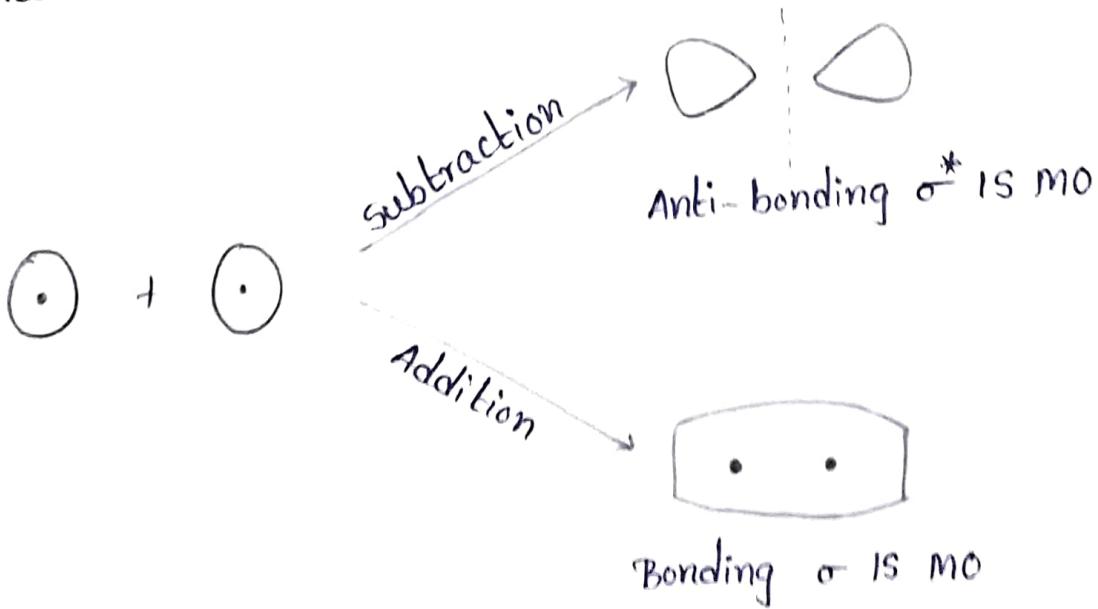
## Types of combination of Atomic orbitals :

When two atomic orbitals combine along the internuclear axis, the molecular orbitals formed are called  $\sigma$  and  $\sigma^*$  molecular orbitals and when overlap sideways (lateral) the molecular orbitals formed are known as  $\pi$  and  $\pi^*$  molecular orbitals.

### II S-S combination of orbitals :

on the linear combination of 1s atomic orbitals of two atoms formed two molecular orbitals.

- When the addition of wave functions  $\sigma$  1s molecular orbital is formed, while subtraction of wave functions  $\sigma^*$  1s molecular orbital is formed.
- similarly the combination of two 2s orbitals forms two molecular orbitals  $\sigma$  2s and  $\sigma^*$  2s



(2) P-P combination of orbitals:

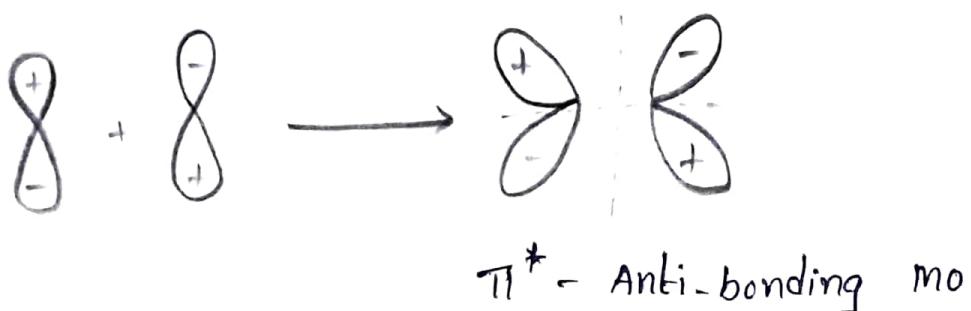
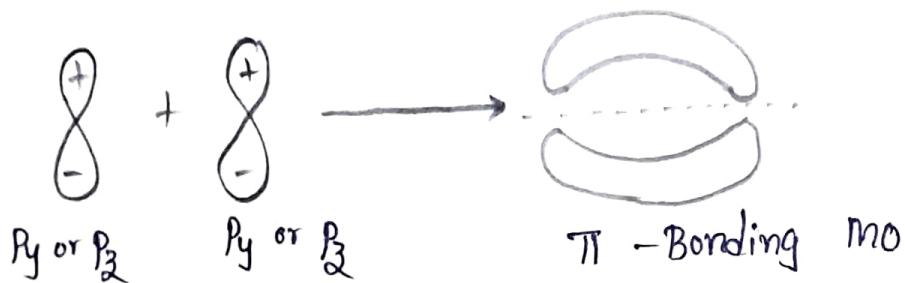
(a) End-to-End combination of p-p orbitals:

The combination of two  $p_x$  atomic orbitals will yield a bonding or anti-bonding  $\sigma$  molecular orbitals.



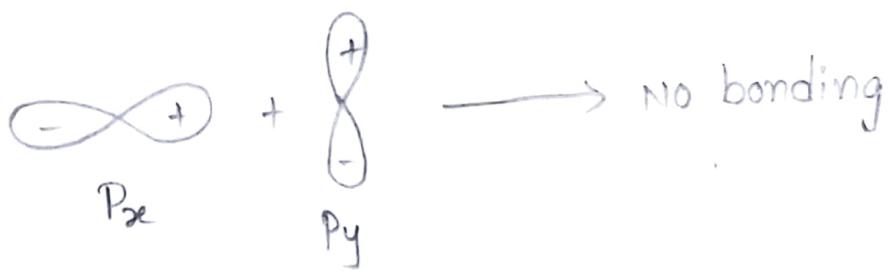
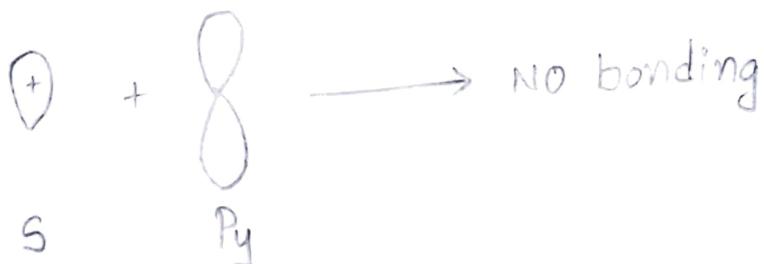
(b) side-by-side combination of p-p orbitals:

overlapping of two 'p' orbitals situated perpendicular to the internuclear axis ( $p_y, p_z$ ) gives rise  $\pi$ -bonding molecular orbital and also  $\pi^*$ -anti-bonding molecular orbital.



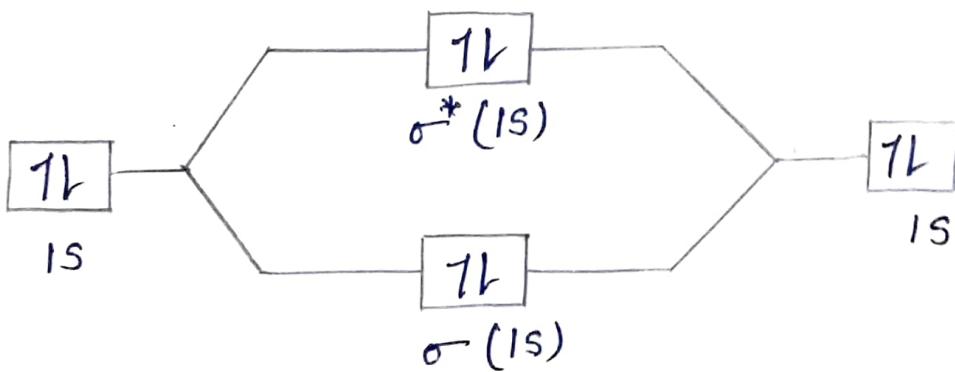
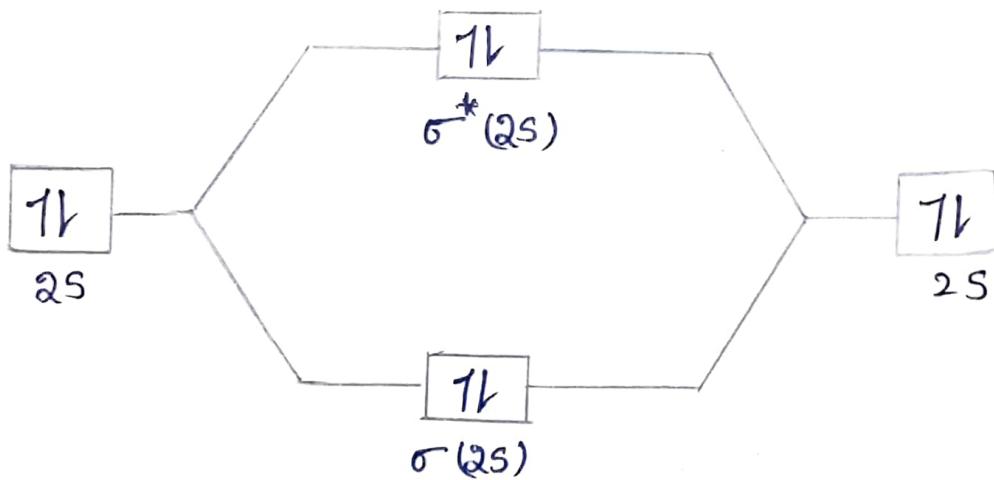
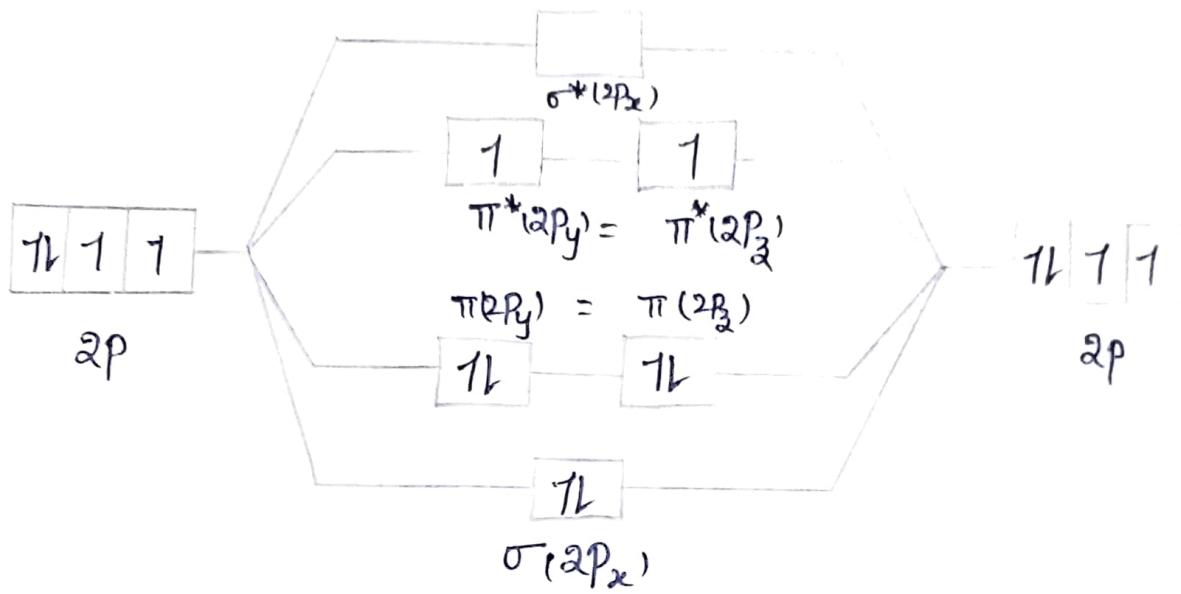
(3) Non-Bonding Combination of orbitals :

When the combination of two atomic orbitals brings no change in over all energy , then the situation is called no-bonding.



Homo-molecule : ( $O_2$ )

'O' - 8 - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>



'O'

$O_2$

'O'

• Bond order =  $\frac{1}{2} [ \text{No. of Bonding electrons} - \text{No. of Anti-Bonding } e^- ]$

$$\text{B.O.} = \frac{1}{2} [N_b - N_a]$$

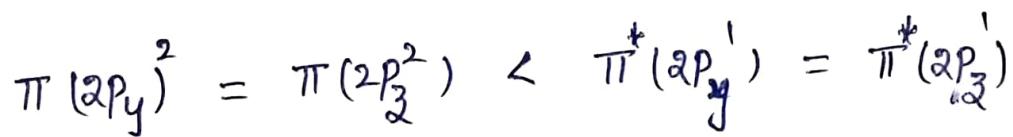
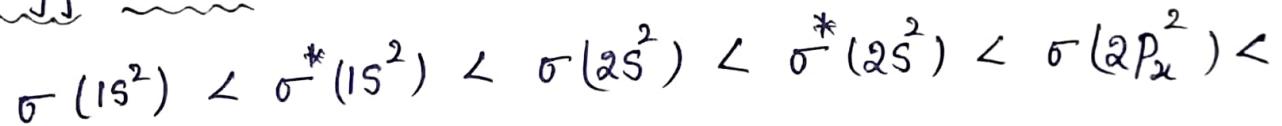
$$= \frac{1}{2} [10 - 6]$$

$$= \frac{1}{2} [4] = 2 [O=O]$$

magnetic property :

The molecule is paramagnetic nature due to the presence of unpaired electrons.

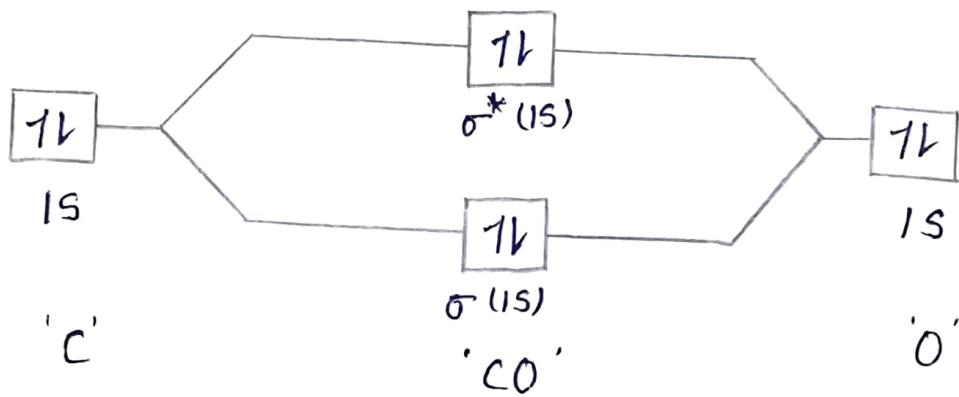
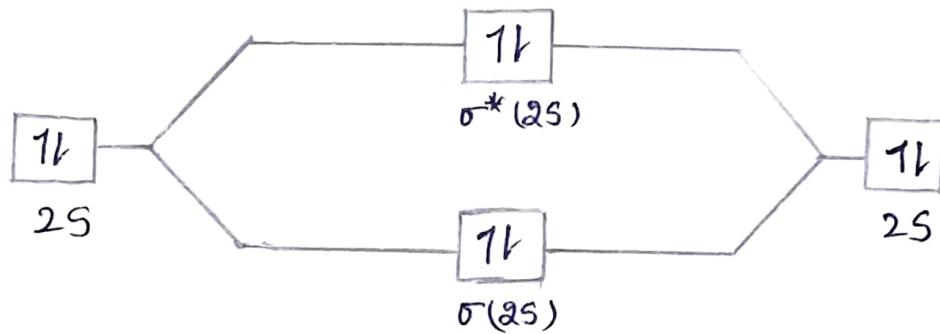
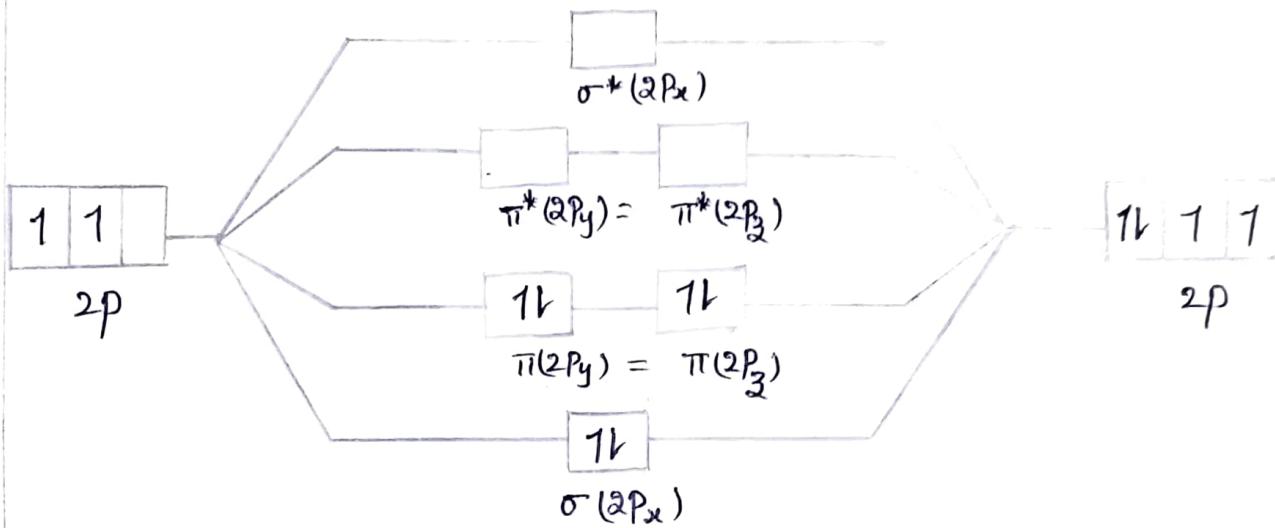
Energy Level :



Hetero - molecules : (CO)

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

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



Bond order =  $\frac{1}{2} \left[ \frac{\text{No. of Bonding electrons}}{\text{No. of Anti-Bonding electrons}} - 1 \right]$

$$\text{B.O.} = \frac{1}{2} [N_b - N_a]$$

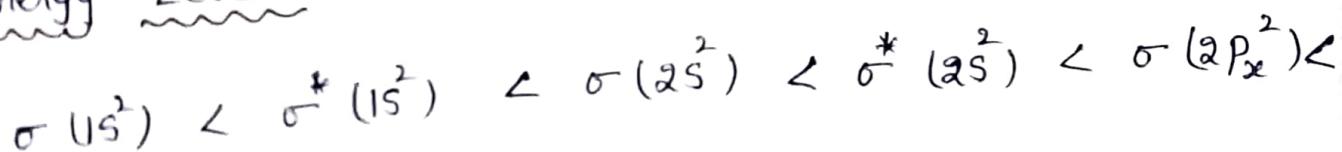
$$= \frac{1}{2} [10 - 4] = \frac{1}{2} [6]$$

$$= 3 [C \equiv O]$$

magnetic property:

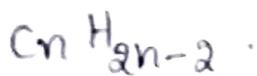
The molecule is diamagnetic properties because there is no unpaired electrons.

Energy Level:



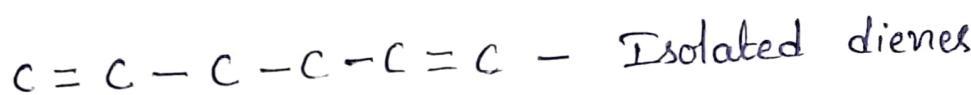
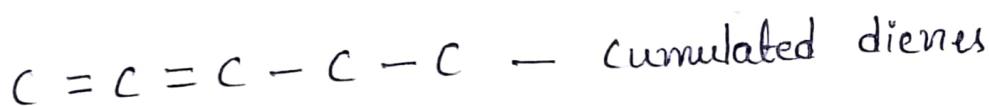
$\pi$ -molecular orbitals of 1,3 Butadiene:

- Alkenes with two double bonds are called alkadienes. They are represented by the general formula

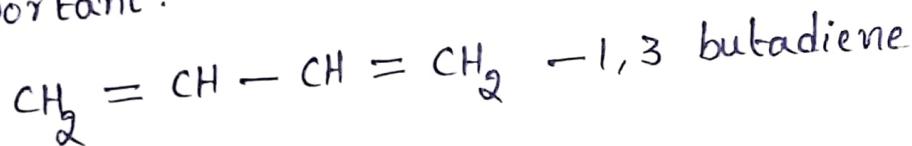


- If the two double bonds are adjacent to each other they are called cumulated dienes.

- If the two double bonds are separated by single bond they are called conjugated dienes.
- If the two double bonds are separated by more than one single bond they are called as isolated dienes.



- out of these compounds the conjugated dienes are the most important.

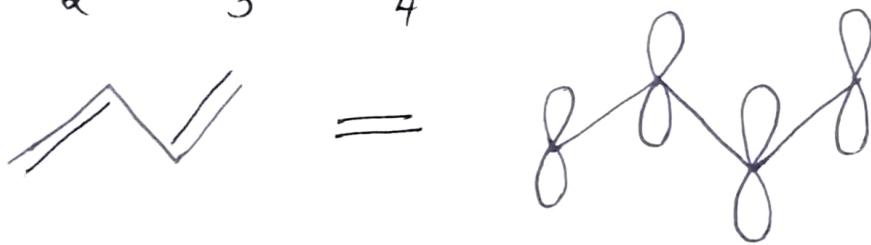


- 1,3 butadiene contains two double bonds that are conjugated.

- It is built from 4  $sp^2$  hybridised 'c' atoms each contributing a p atomic orbital containing 1 electron. The pi electron density will be delocalized between carbons 1 and 2 and 3 and 4.

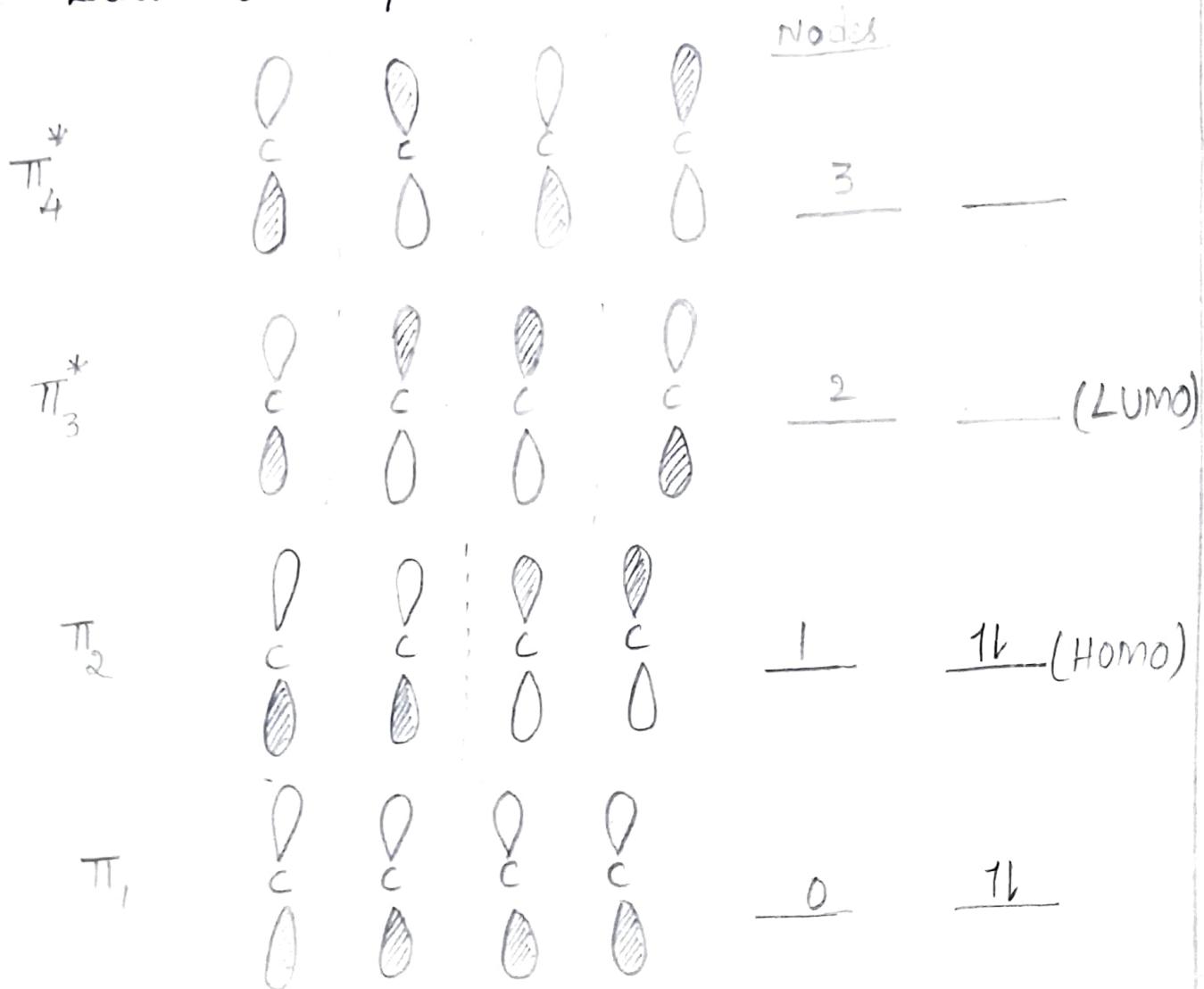
- there are four adjacent carbon atoms involved in the pi-system and the combination of a p orbital from each of these atoms will result in four pi molecular orbitals it referred to

$\pi_1, \pi_2, \pi_3^*, \pi_4^*$

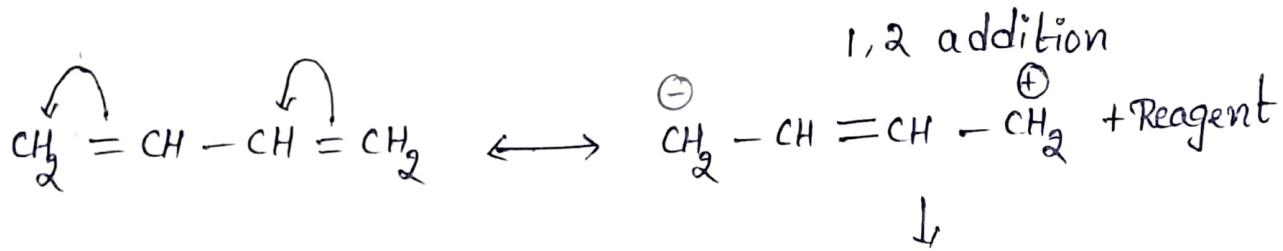
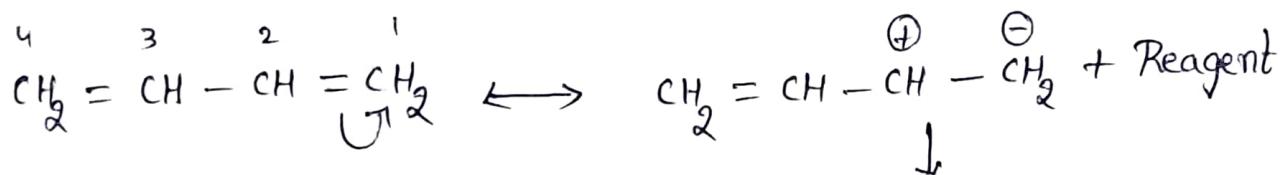
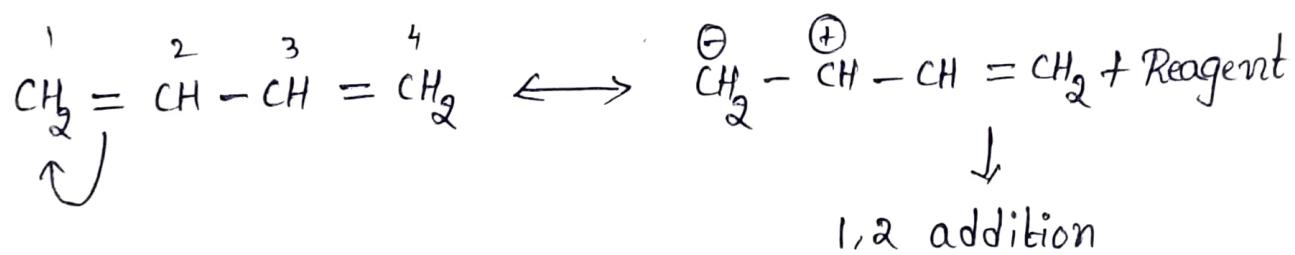


$\pi_1$  and  $\pi_2$  are bonding molecular orbitals and are occupied in the ground state with  $\pi_2$  being the highest occupied molecular orbital (HOMO).

$\pi_3^*$ ,  $\pi_4^*$  are anti-Bonding molecular orbitals and are unoccupied in the ground state with  $\pi_3^*$  being the lowest unoccupied molecular orbital (LUMO).



- So the presence of pi bond in 1,3-Butadiene.  
so the addition reaction take place in two ways.

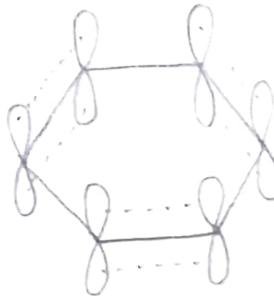
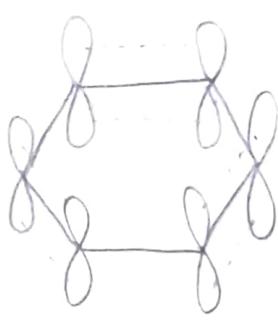


- Low temperature 1,2 addition is takes place and  
high temperature 1,4 addition.

### $\pi$ - Molecular orbitals of Benzene :

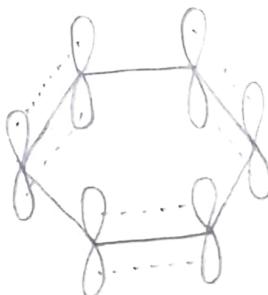
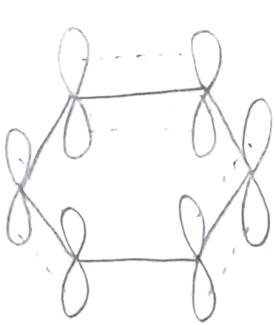
$\pi$  structure of benzene can be described by using molecular orbital approach. with the help of x-ray diffraction measurements it is known that benzene consists of a planar hexagon of six carbon atoms having all carbon - carbon (C-C).

- bonds equal in length  $1.39\text{ \AA}$  and C-C-C bond angle  $120^\circ$  each.
- That it is known that all the carbon atoms in the benzene ring are in the state of  $sp^2$  hybridisation.
- The two  $sp^2$  orbitals of each carbon overlap with  $sp^2$  orbitals of adjacent carbon atom to form  $sp^2 - sp^2$  bonds. This is a planar hexagon.
- The third  $sp^2$  orbital of each carbon overlap with s-orbital of hydrogen to form  $sp^2 - s$  bond.



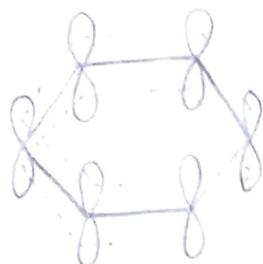
- There will be continuous p-orbital overlap around the benzene ring. Therefore  $6\pi$  electrons are now said to be completely delocalized and can move freely about the six positive carbon nuclei.

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- There will be continuous p-orbital overlap around the benzene ring. Therefore  $6\pi$  electrons are now said to be completely delocalized and can move freely about the six positive carbon nuclei.

- As a result of delocalisation benzene gets stability.



delocalization  $\rightarrow$   $\text{C}_6\text{H}_6$   
of 6  $\pi$  electrons

- In benzene 6 pi orbitals are participated so the 6 pi molecular orbitals are formed. It referred as  $\pi_1^+$ ,  $\pi_2$ ,  $\pi_3$ ,  $\pi_4^*$ ,  $\pi_5^*$ ,  $\pi_6^*$ . In this three orbitals are bonding molecular orbitals and three orbitals are anti-bonding molecular orbitals.

