

## Module 1: Atomic and molecular structure Atomic structure Module1 (1 of 12)-MKM

### Introduction:

The size of atoms and molecules are very small. They exhibit behaviour that is quite outside our ordinary experiences. These molecular world particles must be treated by the methods of wave or quantum mechanics.

Structure of an atom is based on two approaches: Classical mechanics & Wave/Quantum mechanics

**Classical mechanics:** The development of science in real sense started in the year 1803 with Dalton's idea of atom that "atom is the smallest indivisible particle which aggregates to form matter." Much of the development in the modern atomic theory was based on two broad types of research performed during the late 1800s and early 1900s. Research first dealt with the more fundamental particles which form atom and also the approximate arrangement of these particles in an atom based on classical mechanics. The second broad area of research dealt with the interaction of matter with energy in the form of light, which led to a further detailed description of the arrangement of particles in atoms. This second approach is based on quantum mechanics.

Point of difference	Classical mechanics	Quantum mechanics
Applicable to	All macroscopic objects such as orbiting planets, a falling stone etc	All microscopic objects like electrons, atoms, molecules etc. Also applicable to macroscopic objects
Based on	Newton's law of motion which describe the motion of all macroscopic objects having essential a particle like behaviour	Schrodinger equation which incorporates wave-particle duality of matter as proposed by de-Broglie.

### Quantum mechanical model of atom:

After the failure of Bohr's atomic model, the scientists were looking for an atomic model which would incorporate, in itself the following:-

- (A) Concept of Bohr's atomic orbitals
- (B) De-Broglie's hypothesis
- (C) Heisenberg uncertainty principle

The latest quantum mechanical model of atom satisfies all the three requirements and is based on the dual nature of matter hypothesis.

The guiding equation of quantum mechanical model of atom is the Schrodinger's Wave equation.

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \Psi = 0$$

This model proposes the presence of electron waves probability in different regions around the nucleus rather than stationary orbits.

It is in accordance with de-Broglie's hypothesis of dual nature of matter as well as the Heisenberg uncertainty principle which elucidates that the position and momentum of a particle cannot be calculated simultaneously.

### **Difference between Bohr's atom and quantum mechanical atom.**

#### **Bohr's atomic model:**

- Scientist Neil's Bohr established an atomic model as he put forward his postulates.
- Bohr stated that electrons in an atom revolve around the nucleus in fixed stationary orbitals without the emission of radiation contrary to the electromagnetic wave theory.
- The orbital angular momentum of the revolving electron can be expressed as an integral multiple of  $\frac{n}{2} \pi$ . This is stated as quantisation of angular momentum.
- Bohr's atomic model does not take into consideration Heisenberg's Uncertainty principle or the wave nature of atom.
- Bohr's atomic model does not satisfy de-Broglie hypothesis of electron waves according to which, the wavelength of electron waves can be expressed as  $\lambda = h/mv$

### Heisenberg Uncertainty Principle:

According to this principle, it is impossible to know simultaneously the position and momentum of a particle.

If the uncertainty in measurement of position is  $\Delta x$  and uncertainty in momentum is  $\Delta p$ , then

$$\Delta x \cdot \Delta p \geq h/2\pi$$

$$\Delta x \cdot m\Delta v \geq h/2\pi$$

$$\Delta x \cdot \Delta v \geq h/2\pi m$$

Where  $h$  = plank's constant

The uncertainty product is significant in case of small particle like electron and negligible for large object like a stone.

The uncertainty product is negligible in case of large objects.

For moving ball of iron weighing 500g, the uncertainty expression assumes the form

$$\Delta x \cdot m\Delta v \geq h/2\pi$$

$$\Delta x \cdot \Delta v \geq h/2\pi m$$

$$\Delta x \cdot \Delta v \geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 500} = 5 \times 10^{-31} \text{ erg sec g}^{-1}$$

This is very small and thus negligible.

Therefore for large objects, the uncertainty of measurement is practically nil.

But for an electron of mass  $m = 9.109 \times 10^{-28} \text{ g}$ ,

The product of the uncertainty of measurements is quite large as:

$$\Delta x \cdot \Delta v \geq h/2\pi m$$

$$\geq \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.109 \times 10^{-28}}$$

$$= 0.3 \text{ erg sec g}^{-1} \text{ (approx)}$$

- The value is large enough in comparison with the size of the electron.
- If position is known quite accurately i.e.  $\Delta x$  is very small, the uncertainty regarding velocity  $\Delta v$  becomes immensely large and vice-versa.
- It is therefore very clear that the uncertainty principle is only important in considering measurements of small particles comprising an atomic system.

## De-Broglie Equation:

L. de-Broglie had arrived at his hypothesis with the help of Plank's quantum theory and Einstein's theory of relativity.

He derived relationship between the magnitude of the wavelength associated with the mass 'm' of a moving body and its velocity.

According to Plank's, the photon energy 'E' is given by the equation.

$$E = hv \text{ .....(i)}$$

Where  $h$  = plank's constant

$v$  = frequency of radiation

By applying Einstein's mass energy relationship, the energy associated with photon of mass 'm' is given as

$$E = mc^2 \text{ ..... (ii)}$$

Where  $c$  = velocity of radiation.

Comparing equation (i) and (ii)

$$mc^2 = hv = hc/\lambda \quad (v = c/\lambda)$$

$$\text{or } mc = h/\lambda \text{ .....(iii)}$$

where  $\lambda$  = wavelength of matter

$h$  = plank's constant

$m$  = mass

$c$  = velocity

$$\begin{aligned} \text{or } \text{mass} \times \text{velocity} &= h/\text{wavelength} \\ \text{momentum } (p) &= h/\text{wavelength} \\ \text{momentum } \alpha &1/\text{wavelength} \end{aligned}$$

The equation (iii) is called de-Broglie's equation and may be put in word as:-

- The momentum of a particle in matter is inversely proportional to wavelength; Plank's constant 'h' is the constant of proportionality.
- The wavelength of the waves associated with a moving material particle(matter wave) is called de-Broglie wavelength.
- The de-Broglie's equation is true for all particles, but it is only with very small particles, such as electrons, that the wave like aspect is of any significance.
- Large particles in motion though posses wavelength, but it is not measurable or observable.
- Let us, for instance consider de-Broglie's wavelength associated with two bodies and compare their values.

(a) For a large mass

Let us consider a stone of mass 100g moving with a velocity of 1000cm/sec. The de-Broglie's wavelength ' $\lambda$ ' will be given as follows

$$\begin{aligned}\lambda &= \frac{6.625 \times 10^{-27} \text{ erg}}{100 \times 1000} \\ &= 6.625 \times 10^{-32} \text{ cm}\end{aligned}$$

This is too small to be measure by any instrument and hence no significance.

(b) For a small mass

Let us consider an electron in a hydrogen atom. It has a mass =  $9.1091 \times 10^{-28}$  g and moves with a velocity  $2.188 \times 10^8$  cm/sec. The de-Broglie's wavelength ' $\lambda$ ' will be given as follows

$$\begin{aligned}\lambda &= \frac{6.625 \times 10^{-27} \text{ erg}}{9.1091 \times 10^{-28} \times 2.188 \times 10^8} \\ &= 3.32 \times 10^{-8} \text{ cm}\end{aligned}$$

The value is quite comparable to the wavelength of x-rays and hence detectable.

It is, therefore, reasonable to expect from the above discussion that everything in nature possesses both the properties of particle (or discrete units) and also the properties of waves (or continuity).

## Schrodinger's wave equation:-

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In order to provide sense and meaning to the probability approach, Schrodinger derived an equation known after his name as Schrodinger wave equation.

Calculation of the probability of finding the electron at various points in an atom was the main problem before Schrodinger.

His equation is the keynote of wave mechanics and is based upon the idea of the electron as “standing wave” around the nucleus.

The equation for the standing wave is:-

$$\Psi = A \sin 2\pi x/\lambda$$

Where  $\Psi$  = wave function (represents amplitude of wave)

$x$  = displacement in a given direction

$\lambda$  = wavelength

$A$  = constant

By differentiating the above equation twice w.r.t  $x$

$$d\Psi/dx = A \cdot 2\pi/\lambda \cos 2\pi x/\lambda \dots\dots\dots(i)$$

$$d^2\Psi/dx^2 = -4\pi^2/\lambda^2 \sin 2\pi x/\lambda \dots\dots\dots(ii)$$

$$\text{As, } A \sin 2\pi x/\lambda = \Psi \quad (A = \text{constant})$$

$$\text{So, } d^2\Psi/dx^2 = -4\pi^2/\lambda^2 \Psi \dots\dots\dots(iii)$$

$$\lambda^2 = -4\pi^2 \Psi / d^2\Psi/dx^2 \dots\dots\dots(iv)$$

The K.E of particle of mass ‘ $m$ ’ and velocity ‘ $v$ ’ is given by the relation,

$$\text{K.E} = \frac{1}{2} mv^2$$

$$= \frac{1}{2} mv^2/m \dots\dots\dots(v)$$

According to de-Broglie's equation

$$\lambda = h/mv$$

$$\lambda^2 = h^2/m^2v^2$$

$$m^2v^2 = h^2/\lambda^2$$

Substituting the value of  $m^2v^2$  in equation (v)

$$\text{K.E} = \frac{1}{2} h^2/m\lambda^2 \dots\dots\dots(vi)$$

Substituting the value of  $\lambda^2$  from equation (iv)

$$\begin{aligned} \text{K.E} &= -\frac{1}{2} m \cdot \frac{h^2}{4\pi^2} \Psi \cdot \frac{d^2 \Psi}{dx^2} \\ &= -\frac{h^2}{8\pi^2 m} \Psi \cdot \frac{d^2 \Psi}{dx^2} \end{aligned}$$

The total energy E of a particle is

$$E = \text{KE} + \text{PE} ; \text{KE} = E - \text{PE}$$

$$E - \text{PE} = -\frac{h^2}{8\pi^2 m} \Psi \cdot \frac{d^2 \Psi}{dx^2}$$

$$\frac{d^2 \Psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E - \text{PE}) \Psi$$

$$\frac{d^2 \Psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - \text{PE}) \Psi = 0$$

This is Schrodinger's equation in one dimension. It needs to be generalised for a particle whose motion is described by three space coordinate x, y and z.

Thus ,

$$\frac{d^2 \Psi}{dx^2} + \frac{d^2 \Psi}{dy^2} + \frac{d^2 \Psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - \text{PE}) \Psi = 0 \dots \dots \dots \text{(vii)}$$

**This is Schrodinger's wave equation.** This equation has several solutions. If PE term is known the total energy E and the corresponding wave function  $\Psi$  can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance.

Solutions that meet these requirements are only possible if E is given certain characteristic value called Eigen value.

As the eigen values correspond very nearly to the energy values associated with different Bohr-orbital, the Bohr's model may be considered as a direct consequence of wave mechanical approach.

$$\Delta^2 = \frac{d^2 \Psi}{dx^2} + \frac{d^2 \Psi}{dy^2} + \frac{d^2 \Psi}{dz^2} \text{ is laplacian operator.}$$

If V represents PE in equation (vii), it can be written as

$$\Delta^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

$$(-\frac{h^2}{8\pi^2 m} \cdot \Delta^2 + V) \Psi = E \Psi$$

$$H_{op} \Psi = E \Psi$$

Where,

$H_{op}$  = Hemiltonian operator

$$= -\frac{h^2}{8\pi^2 m} \Delta^2 + V$$

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

Schrodinger's equation is a second order differential equation and therefore has a large number of solutions. But only few values of wave function ( $\psi$ ) have physical significance. These are those values of  $\psi$  which correspond to certain definite (or discrete) values of total energy called *eigen values*. The corresponding wave function is referred to as *eigen function*.

The atomic orbital is the wave function  $\psi$  for an electron in an atom. Whenever an electron is described by a wave function, we say the electron occupies that orbital. There are many atomic orbital in an atom because many such wave functions are possible for an electron. These orbitals (or one electron orbital wave functions) form the basis of the electronic structure of atoms. All the information about the electron in an atom is stored in its orbital wave function ( $\psi$ ).

The wave function  $\psi$  as such has no physical significance except that it represents the amplitude of the wave. However, the square of the wave function ( $\psi^2$ ) is related to the probability of finding a particle with definite values of energy within a certain domain in space. This domain in space is between  $x$  and  $x + dx$  for a one-dimensional problem; an element of area for a two-dimensional problem ; and an element of volume for three-dimensional problem.

From the value of the square of the orbital wave function ( $\psi^2$ ) at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.

**Interpretation of  $\psi^2$  by Schrodinger:** In case of an electron, the value of  $\psi^2$  at any point around the nucleus gives a measure of the electronic charge density at that point.

**Interpretation of  $\psi^2$  by Max Born :** According to this statistical interpretation of electron wave function, the electron is still considered a particle and the value of  $\psi^2$  at any point is the probability of finding the electron at that point at a given instant.

### Q. What are the differences between orbital and orbit

Orbital	Orbit
Orbital is the three dimensional space around the nucleus in which the probability of finding the electron is maximum	Orbit is a well –defined circular path around the nucleus in which an electron revolves.
This concept is in accordance with the Heisenberg's uncertainty principle	This concept of orbit is not in accordance with the Heisenberg's uncertainty principle
Shapes of orbitals are different. For examples, s-orbital is spherical , p-orbital is dumb-bell shaped etc	All orbits are circular
An orbital cannot accommodate more than two electrons.	An orbit can accommodate $2n^2$ electrons, where $n$ represents the principal quantum number

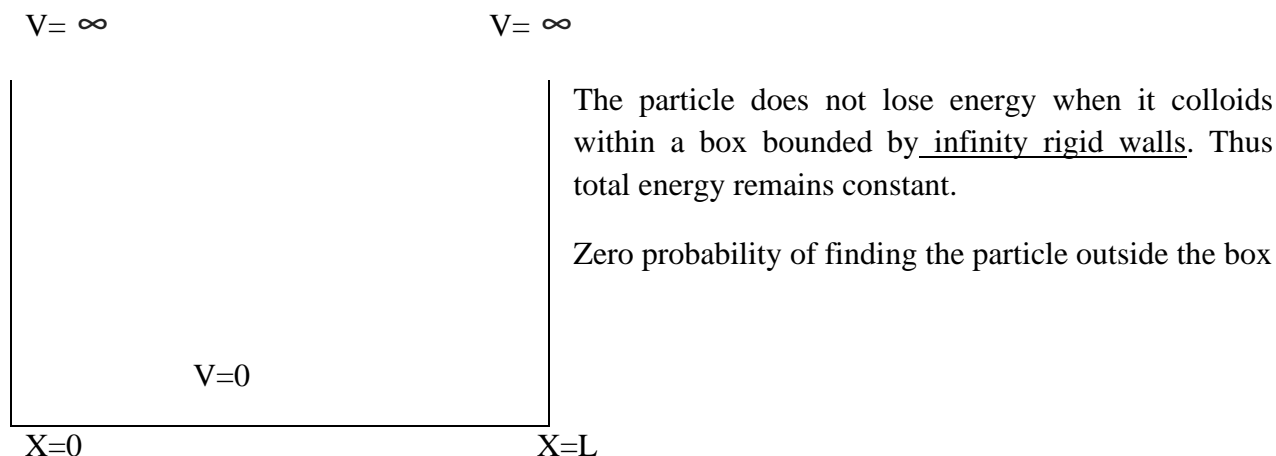


## The particle in a box:

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It is simplest application of the Schrodinger wave equation which can explain **energy quantization**, discrete or fixed value of energy.

Consider the motion of a particle of mass 'm' along 'x' axis and confined between the walls of the container of length L. Beyond L the potential energy (V)/(PE) is infinitely high and there will be zero probability of finding the particle



**Fig.1: A particle in a one dimensional box**

As  $V(x) = \infty$  for  $x < 0$  and  $x > L$

$$\Psi^2 = 0 \quad \text{for } x < 0 \text{ and } x > L$$

$$\Psi = 0 \quad \text{for } x < 0 \text{ and } x > L$$

Within box, the Schrodinger's wave equation

$$d^2 \Psi / dx^2 + 8\pi^2 m / h^2 (E - V) \Psi = 0$$

as  $V=0$  inside the box

[Potential energy (v) of the particle is constant inside the box and we take it zero for convenience]

$$d^2 \Psi / dx^2 + 8\pi^2 m / h^2 E \Psi = 0 \dots\dots\dots(1)$$

Now  $\Psi$  is zero at and outside  $x=0$  and  $x=L$ . So  $\Psi$  must be continuous in the region between  $x=0$  and  $x=L$ . On solving the differential equation (1) we get,

$$\Psi = A \sin 2\pi / h (2mE)^{1/2} x + B \cos 2\pi / h (2mE)^{1/2} x \dots\dots\dots(2)$$

Where A= maximum amplitude function of  $\Psi$   
B= constant

Now in order to satisfy the condition of  $\Psi = 0$  at  $x = 0$  the second term on RHS of equation (2) must be zero.

$$\Psi = A \sin 2\pi/h (2mE)^{1/2}x$$

On applying the other boundary condition of  $\Psi = 0$  at  $x = L$ , we get

$$\Psi = A [\sin 2\pi/h (2mE)^{1/2}L] = 0$$

As,  $A \neq 0$  ( $A = \text{max. amplitude function}$ )

$$\sin 2\pi/h (2mE)^{1/2}L = 0$$

$$2\pi/h (2mE)^{1/2}L = n\pi \dots\dots\dots(3)$$

Where,  $n = 1, 2, 3, 4, \dots$

On squaring equation (3) and rearranging

$$E_n = n^2 h^2 / 8mL^2 \dots\dots\dots (4)$$

Above equation gives eigen values of energy of the particle.  $n$  is called principal quantum number.

Thus a particle in a box possesses discrete values of energy (energy quantization).

$E=0$  is excluded because if at all the particle possesses zero energy inside the box then the wave function  $\Psi$  becomes zero which means particle no more exists inside the box.  
( $n=0$  not possible)

Thus particle can possess all values of energy given by equation (4) excluding zero value. From equation (4) it may be noted that as  $L$  increases, energy decreases. Quantum number ' $n$ ' also indicates number of nodes in the wave.

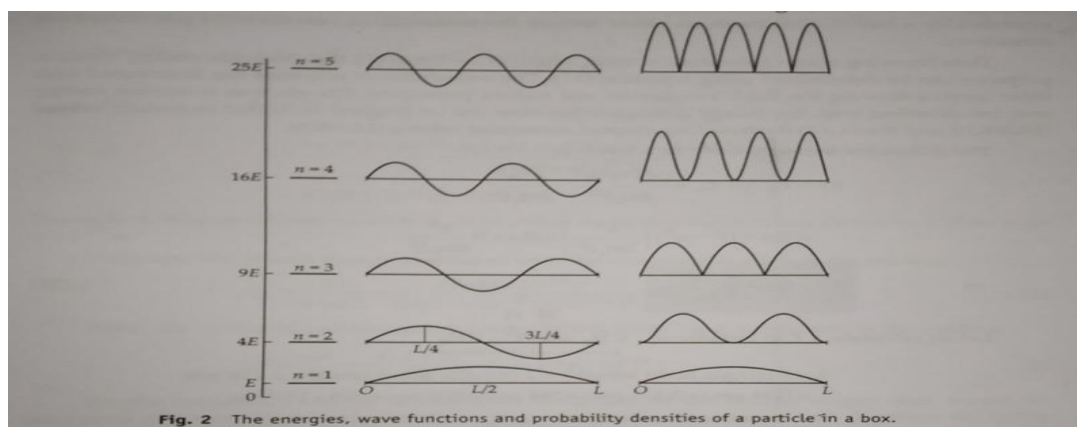
nodes = where no electron (particle) is present (nodes =  $n-1$ )

Where,

$n = 1$ , the number of nodes is equal to zero.

$n = 2$ , the number of nodes is equal to one.

$n = 3$ , there are two nodes and so on..



The value of energy is directly proportional to  $n^2$  and this rises rapidly as the number of nodes increases.

The lowest energy level  $n = 1$  is represented as :

$$E_1 = \frac{h^2}{8mL^2}$$

Consequently, the particle will possess minimum energy, which is known as zero point energy. The next higher values,

$$E_2 = \frac{4h^2}{8mL^2} = 4 \text{ times the minimum energy}$$

$$E_3 = \frac{9h^2}{8mL^2} = 9 \text{ times the minimum energy}$$

$$E_4 = \frac{16h^2}{8mL^2} = 16 \text{ times the minimum energy}$$

The following points can be concluded: -

- (i) The wave functions besides being zero at the walls of the box also have zero values at various points within the box. The number of times,  $\psi$  becomes zero is equal to  $(n-1)$ , where  $n$  is the quantum number. The point at which  $\psi = 0$  is known as the node of the wave function.
- (ii) The number of nodes of the function and energy associated with a wave function increases with  $n$ .
- (iii) The wave function may be Symmetric or Antisymmetric w.r.t. the centre of the box.

Function	Criteria	Examples of $\psi$ from particle in a box
Symmetric or Even	$\Psi(x) = \psi(-x)$	$\Psi_1, \Psi_3, \Psi_5$ -----
Antisymmetric or odd	$\Psi(x) = -\psi(-x)$	$\Psi_2, \Psi_4, \Psi_6$ -----

(iv) The probability density is not uniform at all positions. When  $n$  is small, probability density is more pronounced but when  $n$  is increased, the distribution becomes more and more uniform. For very high of  $n$ , the distribution is completely uniform. Thus, classical behaviour (that on an average, the particle spends equal amounts of time at all points) emerges when  $n$  becomes very large. This fact is in agreement with corresponding principle, which says that the prediction of quantum mechanics for a very large value of  $n$  are identical to those predicted by classical mechanics.

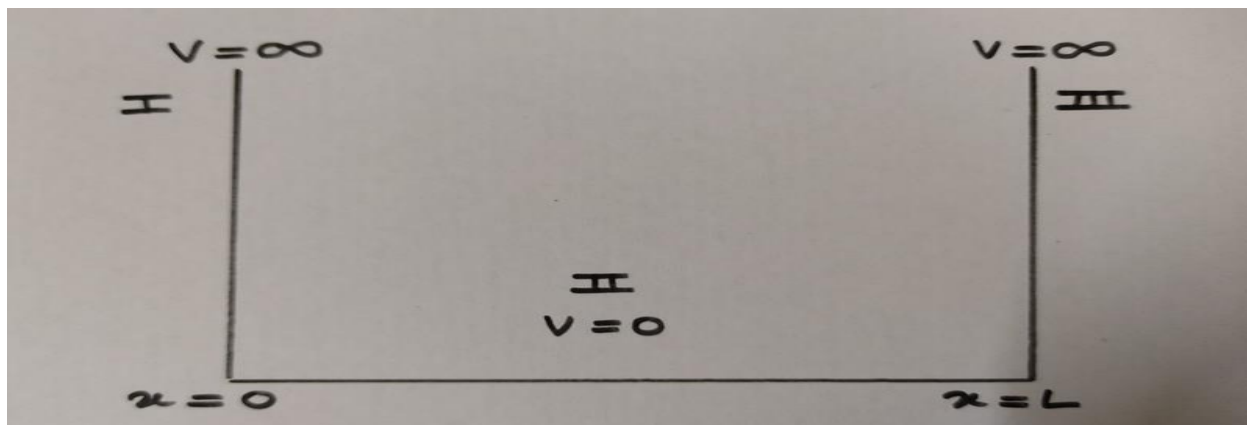
## Application of Schrodinger wave equation for conjugated dienes/molecules.

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The arrangement of alternating single-double bonds in an organic molecule that involves delocalized  $\pi$  electrons is called conjugated system.

Since there  $\pi$  electrons are mobile throughout the carbon atom skeleton containing the alternating double bonds, a very simple theoretical model can be applied to such a system in order to account for the energy of these electrons in the molecules.

If several  $\pi$  electrons are assumed as non- interacting and delocalized over the carbon atom skeleton, then the energetic of this system can be viewed as arising from the simple quantum mechanical model of one electron energy levels appropriate to the particle in the box model. Thus, potential energy of the electron is considered as constant throughout the length of the molecular box and then rising to infinity at each end of the conjugated portion of the molecules.



This quantum mechanical system by a particle of mass ( $m$ ) confined in a one dimensional box of length ( $L$ ). For the particle to be confined within region II, the potential energy outside region II is assumed to be infinite.

Thus, for region I and III (outside the box), the solution gives wave function  $\Psi$  zero. For region II, (inside the box).

$$-\frac{h^2}{2m} \cdot \frac{d^2 \Psi}{dx^2} = E\Psi$$

After solving Schrodinger wave equation, we can formulate energies

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Where

$n$  is the quantum number 1,2,3,4,.....

$L$  is the length of one dimensional molecular box

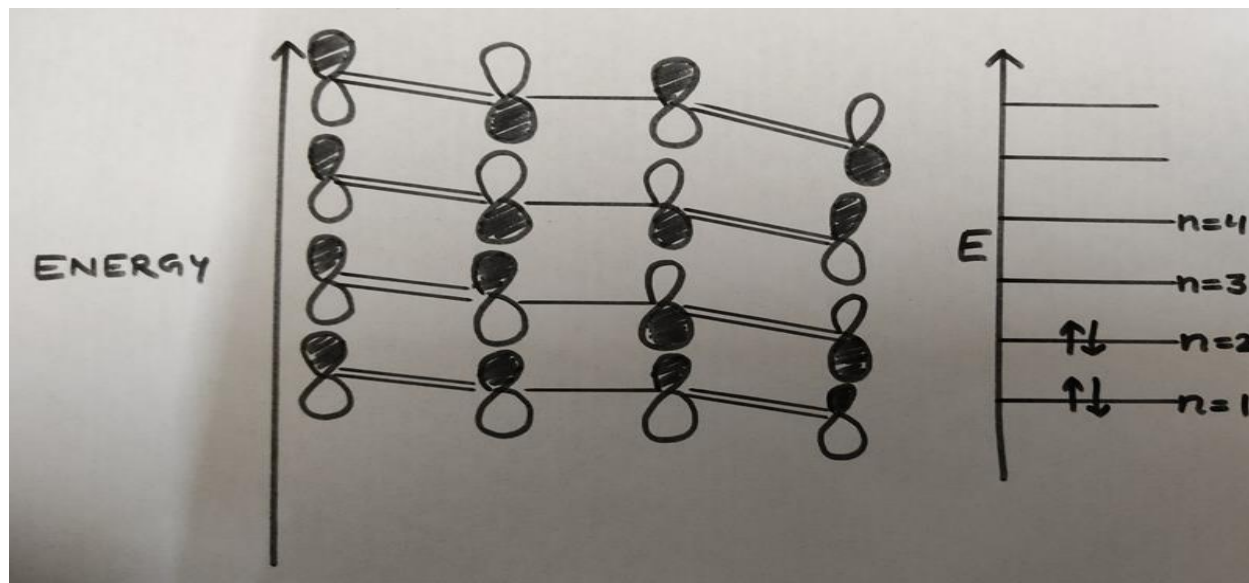
,m is the mass of particle (electron)

,h is Plank's constant.

For example: 1,3-Butadiene

Each C- atom is  $sp^2$  hybridized. These  $sp^2$  hybrid orbitals are used to form  $\sigma$ - bonds. Each C- atom has an unused 2p orbital and one electron, which are used in the formation of  $\pi$ - bond by sideways overlapping.

Thus, four 2p orbitals combine to form the following 4  $\pi$  orbitals, i.e 2  $\pi$  bonds.

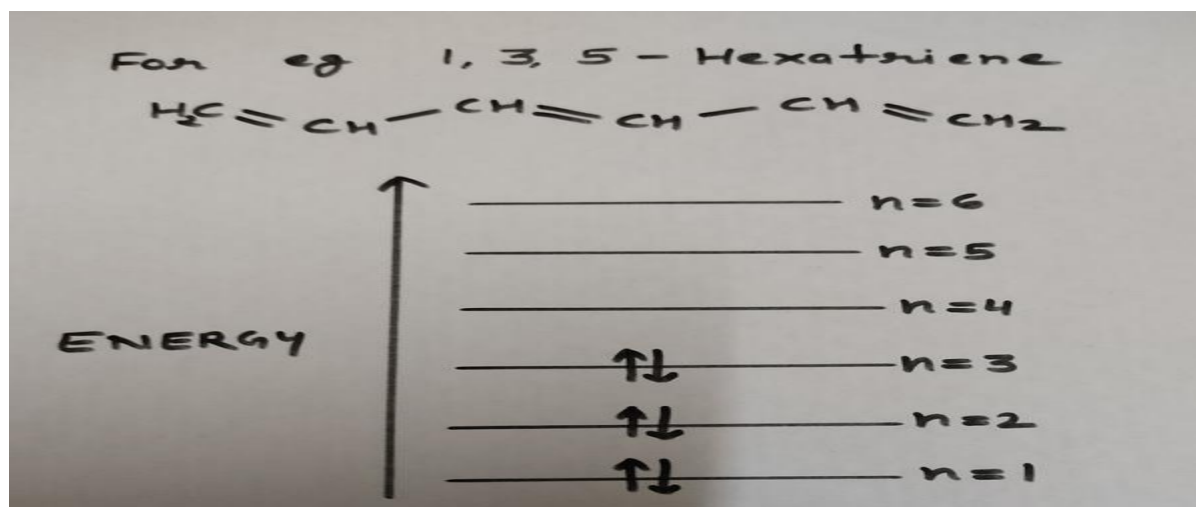


These  $\pi$  orbitals are arranged according to their energy. Thus, the  $\pi$  bonding orbitals at the bottom is lowest energy.

These  $\pi$  orbitals reveal a similarity to the particle in box wave functions. Thus one can use the simple particle in the box model to explain the complicated  $\pi$  orbitals in organic compounds which contain alternating single and double bonds.

Each of the  $\pi$  orbitals can accommodate 2 electrons. In 1, 3- butadiene there is 4 electrons so the second  $\pi$  orbitals are also filled. This is in accordance with the Pauli's exclusion principle.

Each wave function can be regarded as molecular orbital and its respective energy in the orbital energy. This allows the electronic structure for the  $\pi$  electrons in a conjugated molecule to be constructed according to Aufbau Principle.



Each C-atom is  $sp^2$  hybridized, and this contributes a p-orbital and one  $\pi$  electron to the system.

The lowest energy configuration called the electronic ground state corresponds to 6-electrons being in the lowest three orbitals.

Higher energy configurations are constructed by promoting an electron from highest filled orbital (HFO) to a higher, vacant orbital. This higher energy arrangement is called an electronically excited state. The lowest or first electronically excited state is achieved by promotion of an electron from the highest filled orbital to lowest unfilled orbital (LUO). The energy difference between these two states is given by

$$\Delta E = E_{\text{LUO}} - E_{\text{HFO}}$$

$$= \frac{h^2}{8mL^2} (n_{\text{LUO}}^2 - n_{\text{HFO}}^2)$$

The energy required for this electronic transition can be supplied by a photon of the appropriate frequency given by Planck's equation:

$$E = h\nu$$

$$E = hc/\lambda$$

Where,  $\lambda$  is the wavelength.

**Calculation of  $\Delta E$  between highest filled orbital and lowest unfilled orbital: -**

$$\begin{aligned}\Delta E &= E_{LVO} - E_{HFO} \\ \Delta E &= E_{n+1} - E_n \\ &= \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} \\ &= \left\{ (n+1)^2 - n^2 \right\} \left( \frac{h^2}{8mL^2} \right) \\ \Delta E &= (2n+1) \frac{h^2}{8mL^2}\end{aligned}$$

**Calculation of  $\Delta E$  in butadiene:**

CH2=CH-CH=CH2 ; Assume molecule is linear

The length of the box may be taken as the end to end distance of the molecule which is further extended by a half C-C distance on either side of the molecule, i.e another 154 pm is considered.

$$\begin{aligned}L &= 1 \text{ (single bond length)} + 2 \text{ (double bond length)} + 154 \text{ pm} \\ &= 154 \text{ pm} + 2 (135 \text{ pm}) + 154 \text{ pm} \\ &= 578 \text{ pm} \\ &= 578 \times 10^{-12} \text{ m}\end{aligned}$$

$$n = \text{number of } \pi \text{ electrons} / 2 = 4 / 2 = 2$$

$$\Delta E = (2n+1) \frac{h^2}{8mL^2}$$

$$\begin{aligned}&= (2 \times 2 + 1) (6.626 \times 10^{-34} \text{ JS})^2 / 8 (9.1 \times 10^{-31} \text{ kg}) (5.78 \times 10^{-10})^2 \\ &= 9.02 \times 10^{-19} \text{ J} \\ &= \Delta E / hc \\ &= 9.02 \times 10^{-19} \text{ J} / (6.626 \times 10^{-34} \text{ JS}) (3 \times 10^8 \text{ ms}^{-1}) \\ &= 4.54 \times 10^6 \text{ m}^{-1} \\ &= 4.54 \times 10^4 \text{ cm}^{-1} \quad [\text{Experiment value is } 4.61 \times 10^4 \text{ cm}^{-1}]\end{aligned}$$

## Chemical bonding and Molecular structure      Module1 (5 of 12)-MKM

*[Molecular Orbitals of diatomic molecules and plots of the multicentre orbitals. Equations for atomic and molecular orbitals. Energy level diagram of diatomics. Pi molecular orbitals of butadiene and benzene and aromaticity]*

“Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts”.

The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

Since the formation of chemical compounds takes place as a result of combination of atom of various elements in different ways, it raises many questions.

Why do atoms combine?

Why are only certain combinations possible?

Why do molecules possess definite shapes? Etc-

To answer such questions different theories and concept have been put forward from time to time.

- Kossel-Lewis Theory
- VSEPR Theory
- Valence Bond Theory (VBT)
- Molecular Orbital Theory(MOT)

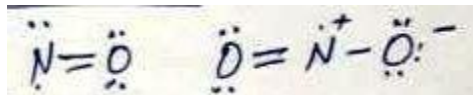
**Kossel- Lewis (1916) approach to chemical bonding.**

- Octet rule
- Covalent bond
- Formal charge

**Limitation of octet rule: -**

- Incomplete octet of the central atom  
 $\text{Cl-Li-Cl}$  ,  $\text{H:Be:H}$  ,  $\text{Cl:B:Cl}$

- Odd electron molecule



- The expanded octet  
 $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{H}_2\text{SO}_4$

**Ionic or electrovalent bond: -**

- Lattice enthalpy



Bond parameter: -

- Bond length
- Bond angle
- Bond enthalpy
- Bond order
- Resonance structure
- Polarity of bond, dipole moment

**VSEPR theory**

- Valence bond theory
- Orbital overlap concept

**Directional properties of bonds: -**

- Overlapping of atomic orbitals.

Types of overlapping and nature of covalent bond: -

1. Sigma bond ( $\sigma$ )
  - s-s overlapping
  - s-p overlapping
  - p-p overlapping
2. Pi bond ( $\pi$ )

**Molecular orbital theory:**

Molecular orbital theory (MOT) was developed by R.S Mulliken in 1932.

The salient features of this theory are:

- The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- While an electron in an atomic orbitals is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus an atomic orbital is mono centric while a molecular orbital is polycentric.
- The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as Bonding Molecular Orbital, while other is called Antibonding Molecular Orbital.
- The Bonding Molecular Orbital has lower energy and hence greater stability than the corresponding Antibonding Molecular Orbital. .
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- The molecular orbitals like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli's exclusion principle and Hund's rule.

**Differentiate between atomic and molecular orbital: -**

	Atomic orbitals	Molecular orbitals
1.	Their electron cloud extends around the nucleus of a single atom, i.e., atomic orbital is monocentric.	Their electron cloud extends around all the nuclei of bounded atoms in the molecule, i.e., a molecular orbital is polycentric. They are obtained by combining atomic orbitals of comparable energy.
2.	They are less stable	They are more stable.
3.	They have simple shapes.	They have complex shape.
4.	They are represented by s, p, d, f, etc	They are represented by $\sigma$ , $\sigma^*$ , $\pi$ , $\pi^*$ etc. They may be bonding or antibonding.

**Difference between bonding and antibonding orbitals:**

	Bonding Molecular orbitals	Anti-Bonding Molecular orbitals
1.	They are formed by the additive effect of atomic orbitals. $\Phi_b = \psi_1 + \psi_2$	They are formed by the subtractive effect of atomic orbitals. $\Phi_a = \psi_1 - \psi_2$
2.	The electrons present in the bonding orbitals result in an attraction between the two atoms	The electrons present in the antibonding orbitals (if any) result in an repulsion between the two atoms
3.	The electron density increases in the region between the nuclei of bonded atoms.	The electron density decreases in the region between the nuclei of atoms and it increases in the region away from the internuclear region. This is responsible for the instability of the bond.
4.	They are formed when the lobes of the combining orbitals have the same sign.	They are formed when the lobes of the combining orbitals have the opposite sign.
5.	These orbitals are represented by $\sigma$ and $\pi$ .	These orbitals are represented by $\sigma^*$ and $\pi^*$ .

**Difference between  $\sigma$  and  $\pi$  molecular orbitals:**

	$\sigma$ - molecular orbitals	$\pi$ - molecular orbitals
1.	It is formed by the overlap of atomic orbitals along the internuclear axis.	It is formed by the sideways overlap of atomic orbitals.
2.	Due to head on overlap, the overlapping is maximum.	Due to side way overlap, the overlapping is minimum.
3.	It consists of one electron cloud.	It consists of two electron clouds, one lying above and the other lying below a plane passing through the nuclei.
4.	Its electron cloud is symmetrical	Its electron cloud is unsymmetrical about

	about the internuclear axis.	the internuclear axis.
--	------------------------------	------------------------

1. When the two atomic orbitals overlap or combine, they lose their identity and form new orbitals. The new orbitals formed are called molecular orbitals.
2. Molecular orbitals give the electron probability distribution around a group of nuclei just as an atomic orbital gives the electron probability distribution around the single nucleus.
3. Only those atomic orbitals can combine to form molecular orbitals which have comparable energies and proper orientation.
4. The number of molecular orbital formed is equal to the number of combining atomic orbitals.
5. When two atomic orbitals combine, they form two new molecular orbitals called bonding molecular orbital and antibonding molecular orbital.
6. The bonding molecular orbital have lower energy and hence greater stability than the corresponding antibonding molecular orbital.
7. The bonding molecular orbitals are represents by  $\sigma$ ,  $\pi$  etc, whereas the corresponding antibonding molecular orbitals are represented as  $\sigma^*$ ,  $\pi^*$  etc.
8. The shapes of the molecular orbitals formed depend upon the type of combining atomic orbitals.
9. The filling of electrons in molecular orbitals takes place according to the Aufbau Principle, Pauli's exclusion principle, Hund's rule.

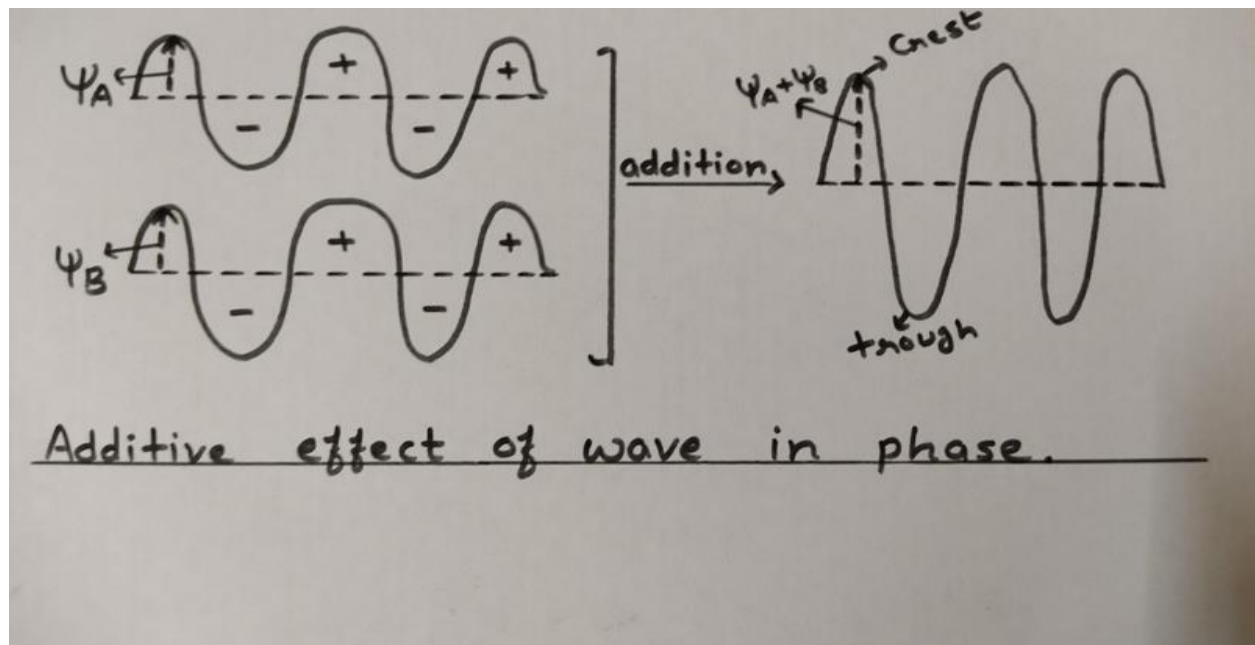
### Equation for atomic and molecular orbitals:

Linear combination of atomic orbitals (LCAO)

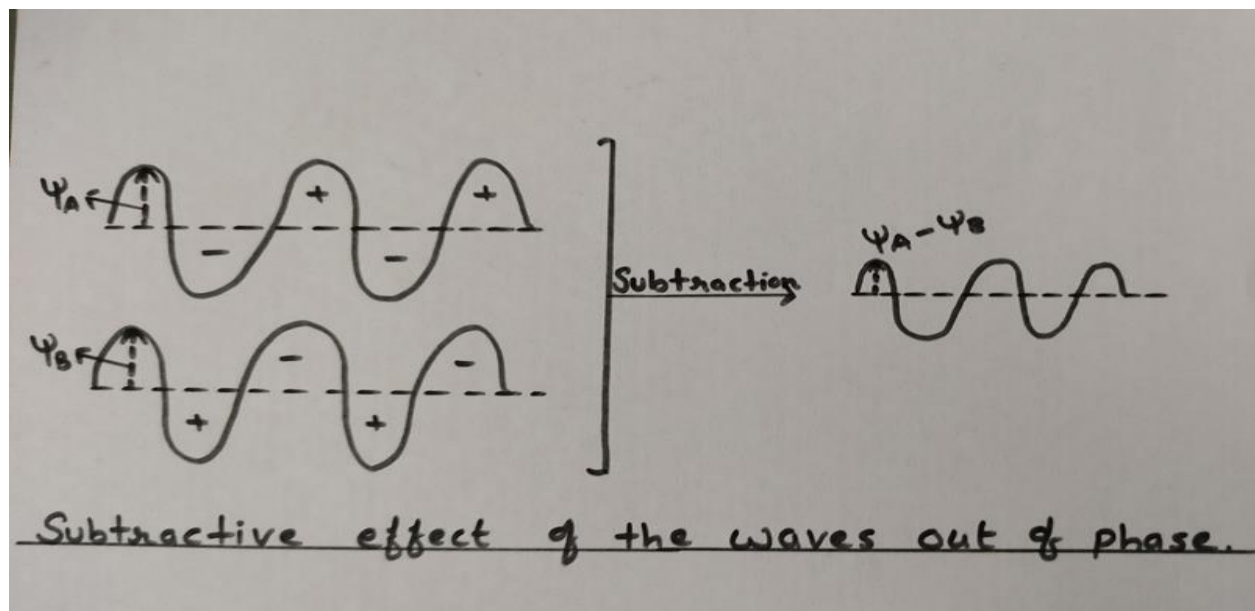
Consider two atoms A and B which have atomic orbitals described by the wave function  $\Psi_{(A)}$  and  $\Psi_{(B)}$ .

1. When the two waves are in phase (arrangement same) they add up  
$$\phi = \Psi_{(A)} + \Psi_{(B)} \quad \phi = \text{amplitude of the new wave}$$
2. When the two are out of phase, the waves subtracted from each other  
$$\phi' = \Psi_{(A)} - \Psi_{(B)}$$

### Additive effect of the wave in phase



### Subtractive effect of the waves out of phase



Probability density is given by the square of the wave function:

$$\begin{aligned}\Phi^2 &= (\Psi_{(A)} + \Psi_{(B)})^2 \\ &= \Psi_{(A)}^2 + \Psi_{(B)}^2 + 2\Psi_{(A)}\Psi_{(B)} \\ \Phi'^2 &= (\Psi_{(A)} - \Psi_{(B)})^2\end{aligned}$$

$$= \Psi_{(A)}^2 + \Psi_{(B)}^2 - 2 \Psi_{(A)} \Psi_{(B)}.$$

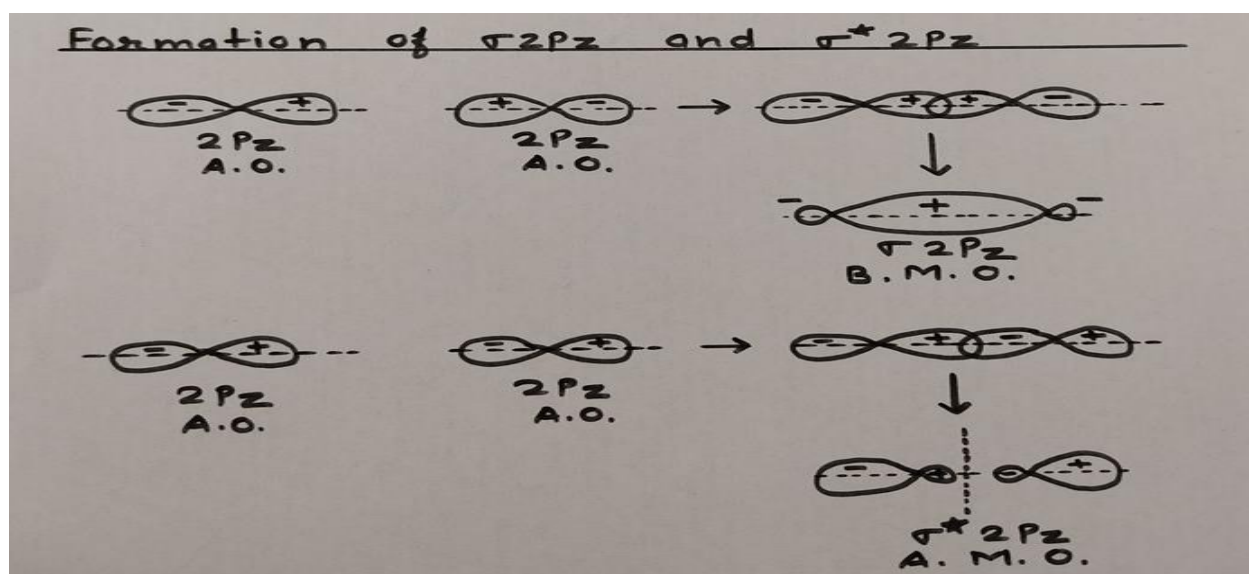
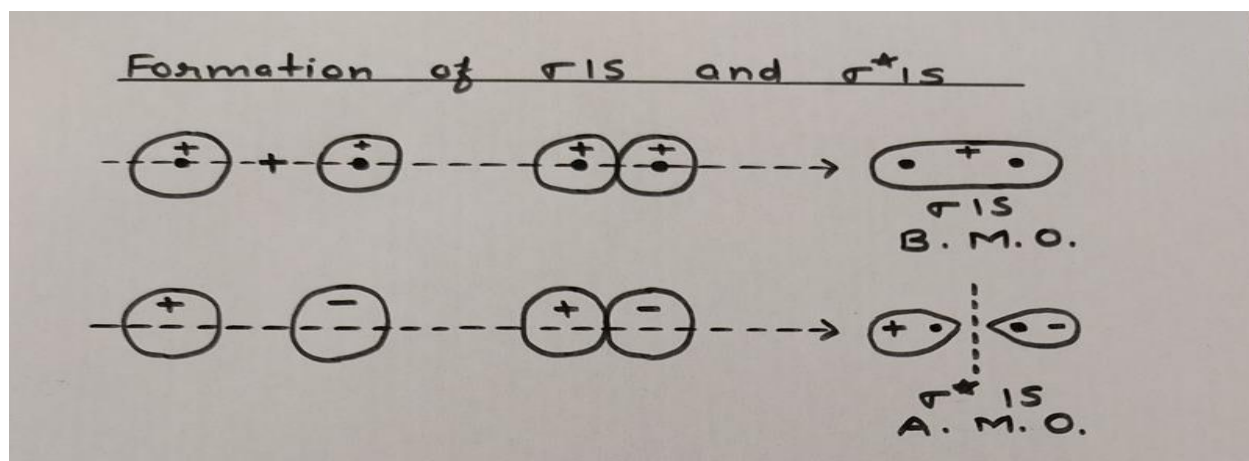
i.e,

$$\Phi^2 > \Psi_{(A)}^2 + \Psi_{(B)}^2$$

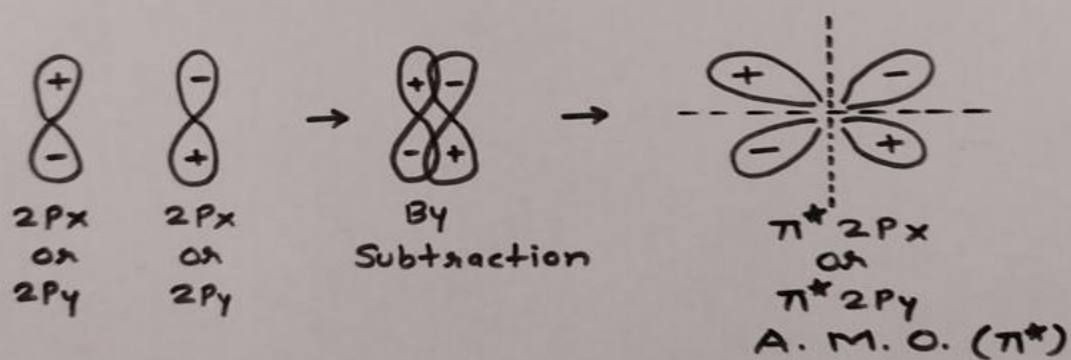
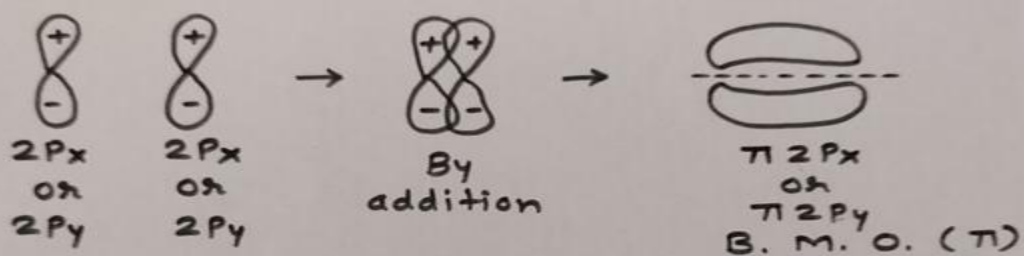
$$\Phi'^2 < \Psi_{(A)}^2 + \Psi_{(B)}^2$$

The molecular orbital formed by the additive effect of the atomic orbitals is called bonding molecular orbital. Most of the electron density is located between the nuclei of the bonded atoms in bonding molecular orbital.

The molecular orbital formed by the subtractive effect of the atomic orbitals is called antibonding molecular orbital. Most of the electron density is located away from the space between the nuclei of an antibonding molecular orbital and hence the repulsion between the nuclei is high.



## Formation of $\pi 2p_x$ and $\pi^* 2p_x$



## Energy level diagram of diatomic:

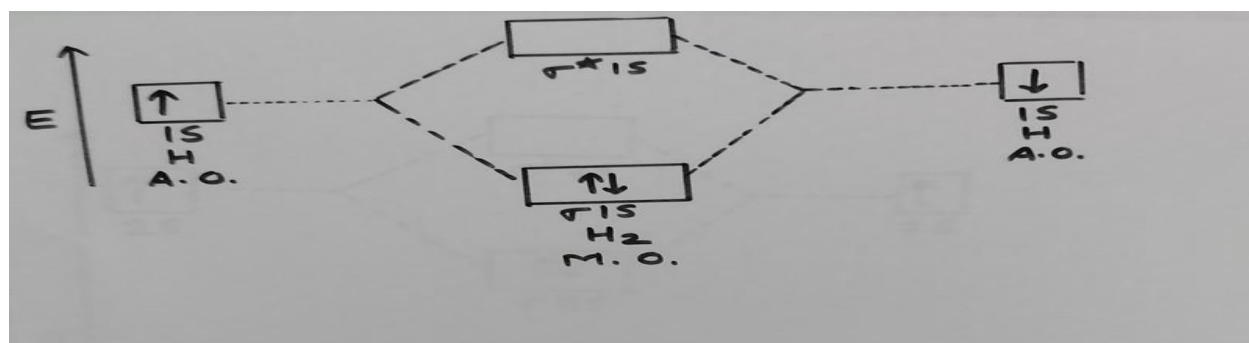
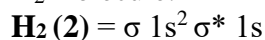
Module1 (7 of 12)-MKM

The filling of molecular orbital takes place according to:

- (a) **The Aufbau principle:** Molecular orbitals are filled in order of increasing energy.
- (b) **Pauli exclusive principle:** two electrons in the same orbital cannot have set of all the four Quantum numbers identical. It means maximum number of electrons in a orbital is two and they must have opposite spins.
- (c) **Hund's rule of maximum multiplicity:** Pairing of electrons in the molecular orbitals of same energy doesn't occur, until each of them has one electron each.

## Energy level diagrams of Homonuclear molecules:

H<sub>2</sub> molecule:



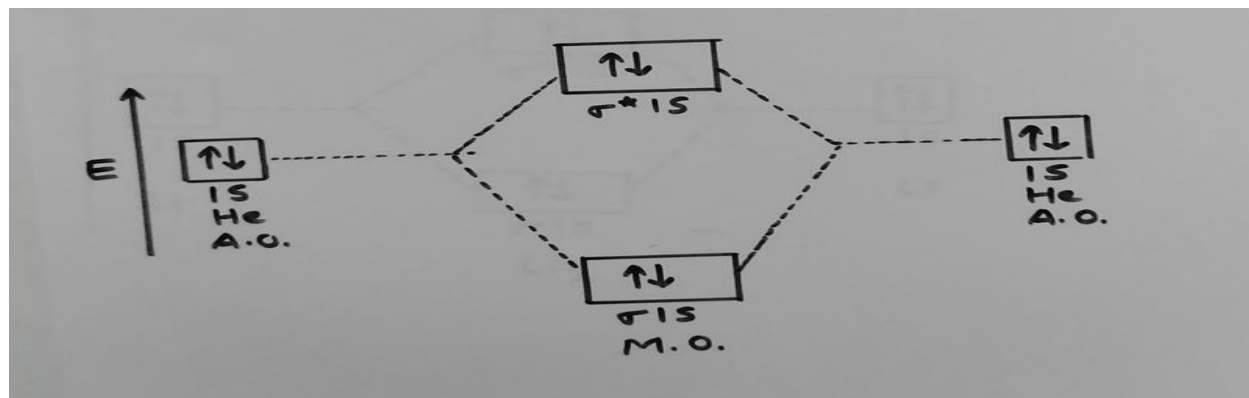
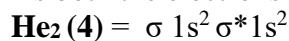
$$\begin{aligned}\text{Bond order} &= \text{Nb} - \text{Na}/2 \\ &= 2 - 0/2 = 1\end{aligned}$$

Where,

Nb = number of electrons in bonding molecular orbitals

Na = number of electrons in antibonding molecular orbitals

As both the electrons are paired it is diamagnetic.



$$\begin{aligned}\text{Bond order} &= \text{Nb} - \text{Na}/2 \\ &= 2 - 2/2 = 0\end{aligned}$$

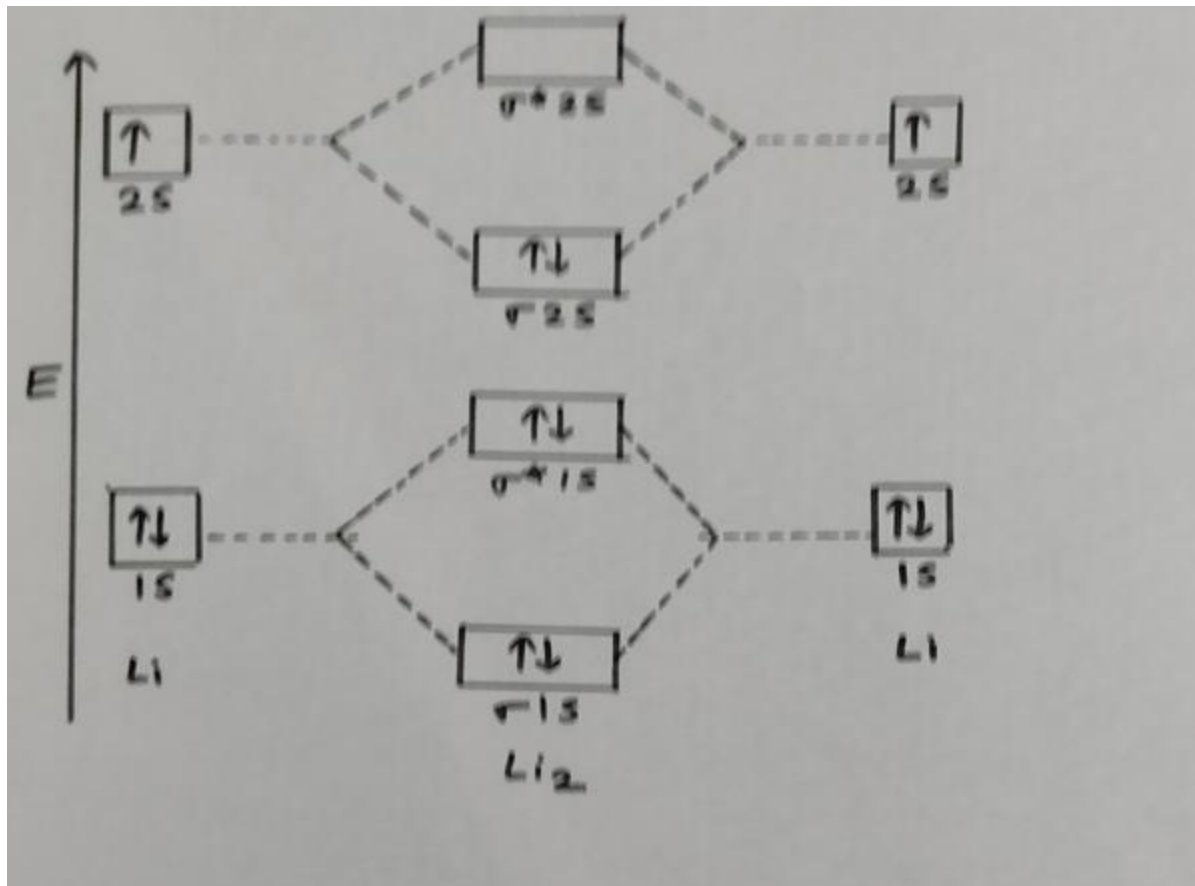
As bond order of He<sub>2</sub> molecule is zero, hence He<sub>2</sub> does not exist.



Li<sub>2</sub> molecule:

$$\text{Li}_2(6) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^0$$

$$\begin{aligned} \text{Bond order} &= \text{Nb} - \text{Na} / 2 \\ &= 4 - 2 / 2 = 1 \end{aligned}$$



$$\text{Be}_2(8) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$$

$$\begin{aligned} \text{Bond order} &= \text{Nb} - \text{Na} / 2 \\ &= 4 - 4 / 2 = 0 ; \text{Thus Be}_2 \text{ does not exist.} \end{aligned}$$

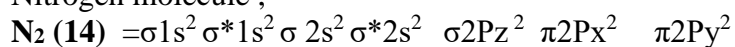
$$\text{B}_2(10) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 = \pi 2p_y^1 \sigma 2p_z \pi^* 2p_x = \pi^* 2p_y \sigma^* 2p_z$$

$$\begin{aligned} \text{Bond order} &= \text{Nb} - \text{Na} / 2 \\ &= 6 - 4 / 2 = 1 ; \text{Paramagnetic, due to unpaired electrons.} \end{aligned}$$

$$\text{C}_2(12) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z \pi^* 2p_x = \pi^* 2p_y \sigma^* 2p_z$$

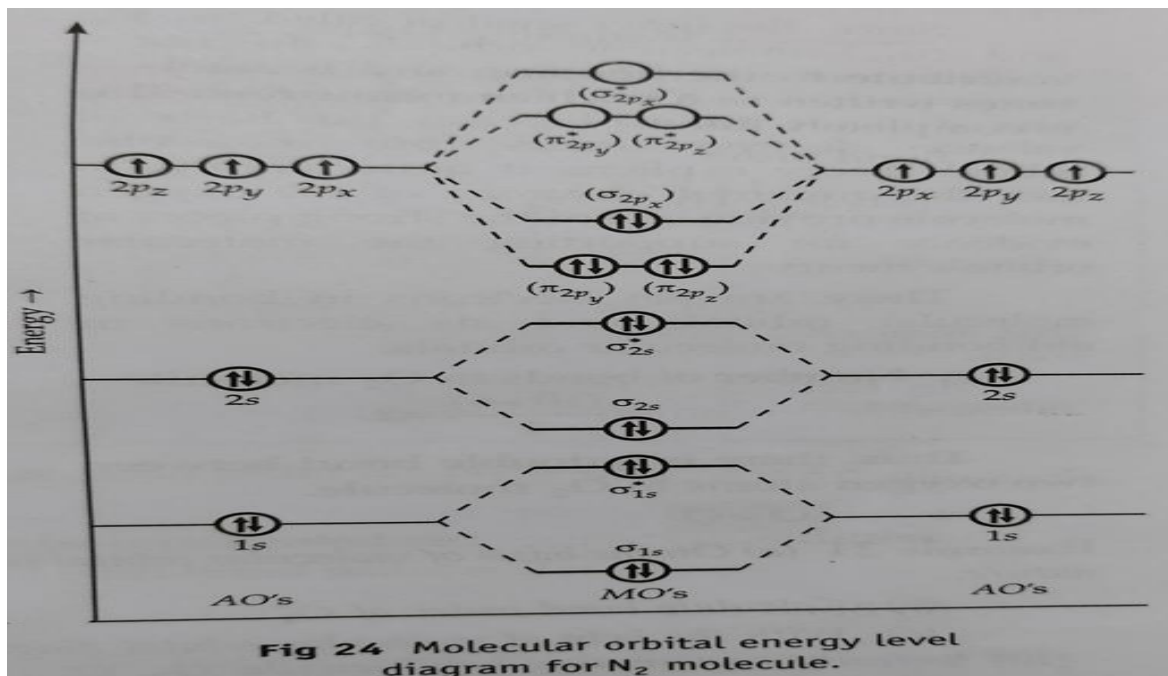
$$\begin{aligned} \text{Bond order} &= \text{Nb} - \text{Na} / 2 \\ &= 8 - 4 / 2 = 2 ; \text{Diamagnetic.} \end{aligned}$$

Nitrogen molecule ,



Bond order =  $N_b - N_a / 2$

$$= 10 - 4 / 2 = 3 \text{ bonds between two nitrogen atoms in N}_2 \text{ molecule, Diamagnetic}$$



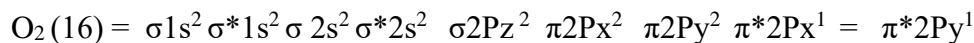
**Example 22** Write the electronic configurations of  $\text{N}_2$ ,  $\text{N}_2^+$ ,  $\text{N}_2^-$  and  $\text{N}_2^{2-}$ . Establish their stability order based on calculation of bond order. Also write their magnetic character.

**Solution**

Molecule (or Ion)	Electronic configuration	Bond order = $\frac{1}{2}(N_b - N_a)$	Magnetic behaviour
$\text{N}_2$	$K K(\sigma_{2s})^2 (\sigma_{2s}^*)^2 \left[ \begin{matrix} (\pi_{2p_y})^2 \\ (\pi_{2p_z})^2 \end{matrix} \right] (\sigma_{2p_x})^2$	$\frac{1}{2}(8 - 2) = 3.0$	Diamagnetic
$\text{N}_2^+$	$K K(\sigma_{2s})^2 (\sigma_{2s}^*)^2 \left[ \begin{matrix} (\pi_{2p_y})^2 \\ (\pi_{2p_z})^2 \end{matrix} \right] (\sigma_{2p_x})^1$	$\frac{1}{2}(7 - 2) = 2.5$	Paramagnetic
$\text{N}_2^-$	$K K(\sigma_{2s})^2 (\sigma_{2s}^*)^2 \left[ \begin{matrix} (\pi_{2p_y})^2 \\ (\pi_{2p_z})^2 \end{matrix} \right] (\sigma_{2p_x})^2 [(\pi_{2p_y}^*)^1]$	$\frac{1}{2}(8 - 3) = 2.5$	Paramagnetic
$\text{N}_2^{2-}$	$K K(\sigma_{2s})^2 (\sigma_{2s}^*)^2 \left[ \begin{matrix} (\pi_{2p_y})^2 \\ (\pi_{2p_z})^2 \end{matrix} \right] (\sigma_{2p_x})^2 \left[ \begin{matrix} (\pi_{2p_y}^*)^1 \\ (\pi_{2p_z}^*)^1 \end{matrix} \right]$	$\frac{1}{2}(8 - 4) = 2.0$	Paramagnetic

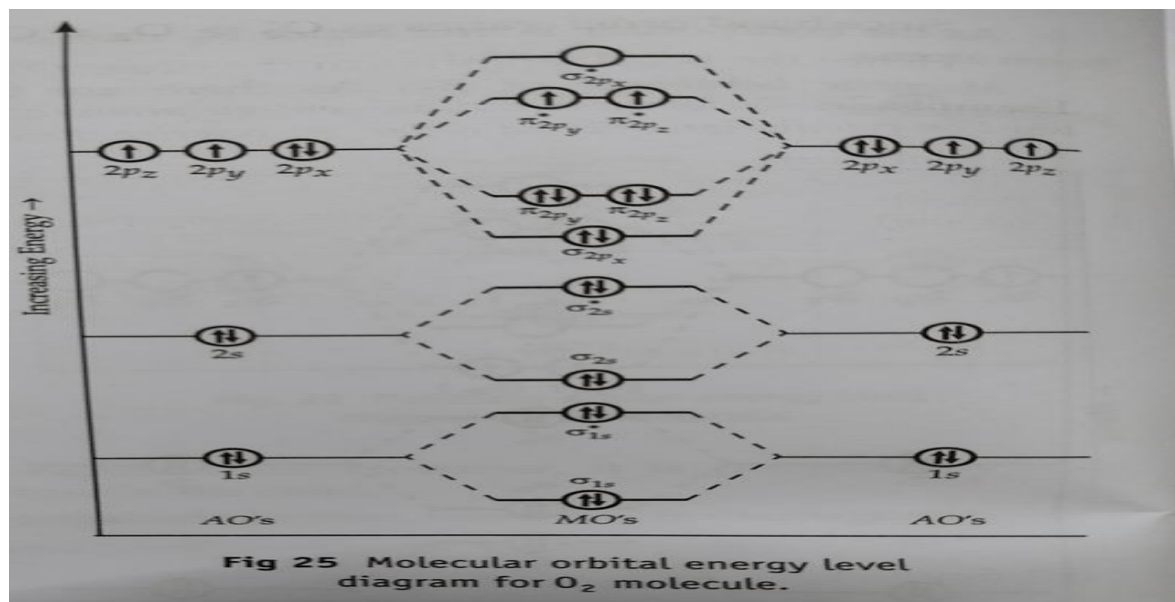
Now, stability order based on calculation of bond order is :  $\text{N}_2 > (\text{N}_2^+ = \text{N}_2^-) > \text{N}_2^{2-}$ .

Oxygen molecule



Bond order =  $\text{Nb} - \text{Na} / 2$

$$= 10 - 6 / 2 = 2 ; \text{Paramagnetic}$$



**Example 21** (a) On the basis of molecular orbital theory, prove that molecule of oxygen is paramagnetic in nature.

(b) Calculate bond order of  $\text{O}_2^+$

(c) With the help of molecular orbital diagram, arrange the following molecules/ions in order of their increasing bond lengths  $\text{O}_2$ ,  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$

(d) With the help of molecular orbital diagram, calculate the bond order of  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$ . Also write their magnetic character.

**Solution.**

Molecule	Electronic configuration	Bond order	Magnetic behaviour
$\text{O}_2^+$	$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2\left[\begin{smallmatrix}(\pi_{2p_y})^2 \\ (\pi_{2p_z})^2\end{smallmatrix}\right]\left[\begin{smallmatrix}(\pi_{2p_y}^*)^1 \\ (\pi_{2p_z}^*)^0\end{smallmatrix}\right]$	$\frac{1}{2}(8 - 3) = 2.5$	Paramagnetic
$\text{O}_2$	$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2\left[\begin{smallmatrix}(\pi_{2p_y})^2 \\ (\pi_{2p_z})^2\end{smallmatrix}\right]\left[\begin{smallmatrix}(\pi_{2p_y}^*)^1 \\ (\pi_{2p_z}^*)^1\end{smallmatrix}\right]$	$\frac{1}{2}(8 - 4) = 2$	Paramagnetic
$\text{O}_2^-$	$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2\left[\begin{smallmatrix}(\pi_{2p_y})^2 \\ (\pi_{2p_z})^2\end{smallmatrix}\right]\left[\begin{smallmatrix}(\pi_{2p_y}^*)^2 \\ (\pi_{2p_z}^*)^1\end{smallmatrix}\right]$	$\frac{1}{2}(8 - 5) = 1.5$	Paramagnetic
$\text{O}_2^{2-}$	$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2\left[\begin{smallmatrix}(\pi_{2p_y})^2 \\ (\pi_{2p_z})^2\end{smallmatrix}\right]\left[\begin{smallmatrix}(\pi_{2p_y}^*)^2 \\ (\pi_{2p_z}^*)^2\end{smallmatrix}\right]$	$\frac{1}{2}(8 - 6) = 1$	Diamagnetic

As the bond length is inversely proportional to bond order, so we can easily explain the gradation of the internuclear distances in the given series.

Since bond order varies as  $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$

Hence the bond length is in the order  $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$

**F<sub>2</sub> (18)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^1 = \pi^* 2P_y^1 \sigma^* 2P_z$   
 Bond order =  $N_b - N_a/2$   
 $= 10 - 8/2 = 1$  Diamagnetic.

**Ne<sub>2</sub> (20)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^2 = \pi^* 2P_y^2 \sigma^* 2P_z^2$

Bond order =  $N_b - N_a/2$   
 $= 10 - 10/2 = 0$

As bond order is zero, Ne<sub>2</sub> molecule does not exist.

**Question:** Compare the relative stability and indicate their magnetic properties of O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup> (superoxide), and O<sub>2</sub><sup>2-</sup> (peroxide).

**Answer: O<sub>2</sub> (16)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^1 = \pi^* 2P_y^1 \sigma^* 2P_z$   
 B.O =  $N_b - N_a/2 = 10 - 6/2 = 2$ , Paramagnetic.  
**O<sub>2</sub><sup>+</sup> (15)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^1 = \pi^* 2P_y \sigma^* 2P_z$   
 B.O =  $N_b - N_a/2 = 10 - 5/2 = 2.5$ , Paramagnetic.  
**O<sub>2</sub><sup>-</sup> (17)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^2 = \pi^* 2P_y^1 \sigma^* 2P_z$   
 B.O =  $N_b - N_a/2 = 10 - 7/2 = 1.5$ , Paramagnetic.  
**O<sub>2</sub><sup>2-</sup> (18)** =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2P_z^2 \pi 2P_x^2 = \pi 2P_y^2 \pi^* 2P_x^2 = \pi^* 2P_y^2 \sigma^* 2P_z$   
 B.O =  $N_b - N_a/2 = 10 - 8/2 = 1$ , Diamagnetic.

Bond order (decreasing order): -  
 $2.5 > 2 > 1.5 > 1$

Relative stability: -  
 $O_2^+ > O_2 > O_2^- > O_2^{2-}$

Greater the bond order, greater is the stability.

## Energy level diagrams of Hetero-atomic molecules

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The wave function describing a molecular orbital ( $\Psi_{AB}$ ) for a hetero-nuclear diatomic molecule can be obtained from LCAO.

$$\Psi_{AB} = \sum [C_A \Psi_A + C_B \Psi_B]$$

C = Constant; Measure of the extent of the contribution of the atomic orbitals

Here  $C_A \neq C_B$  because the electron distribution in the internuclear region is not symmetrical.

Let us assume that electro negativity of atom A is greater than the electro negativity of atom B. In this case  $\Psi_B > \Psi_A$  and atom A with wave function  $\Psi_A$  makes greater contribution to the bonding molecular orbital ( $\Psi_{AB}$ ) because it is having a lower energy and it lies close to the  $\Psi_{AB}$ .

Similarly atom B with wave function  $\Psi_B$  makes greater contribution to the antibonding molecular orbital ( $\Psi_{AB}^*$ ) because  $\Psi_B$  has higher energy and it lies close to  $\Psi_{AB}^*$ .

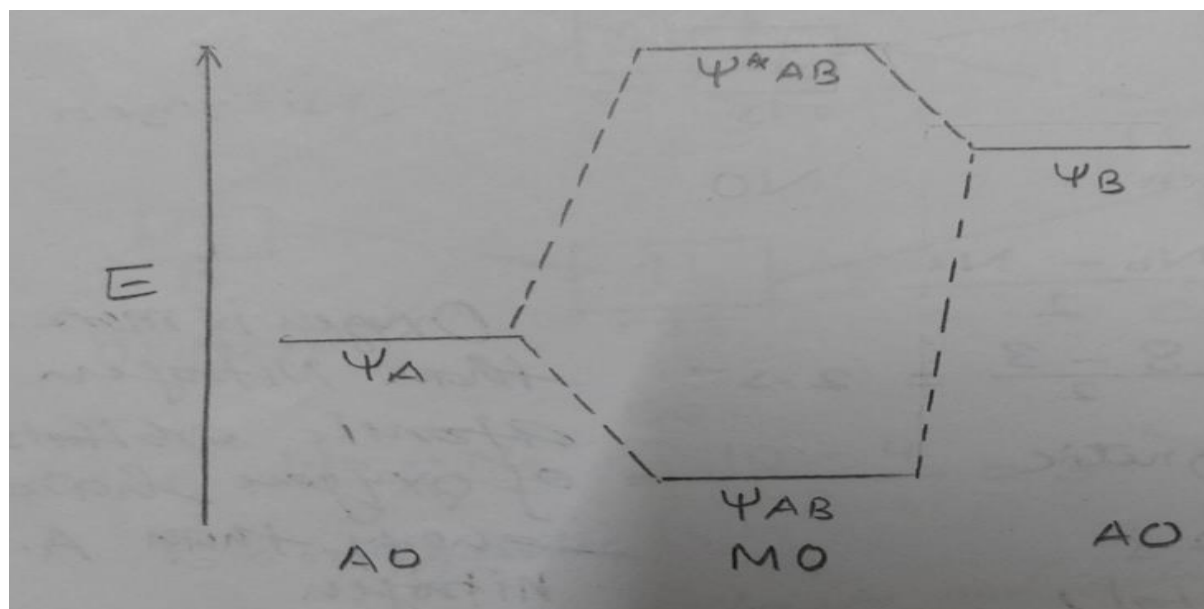


Fig: Energy level diagram for heteronuclear molecule

## Nitric oxide (NO) molecule:

(i) The molecular orbital electronic configuration of NO molecule is

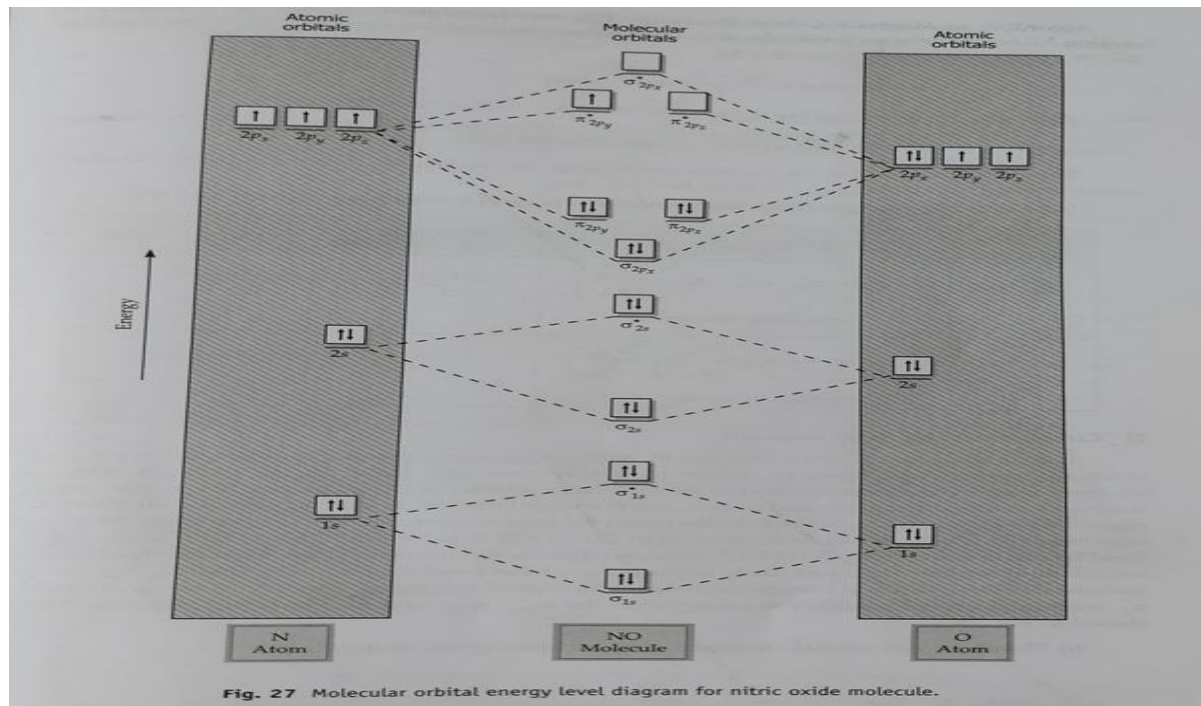
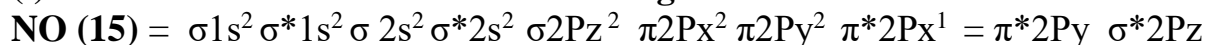


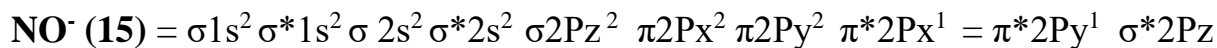
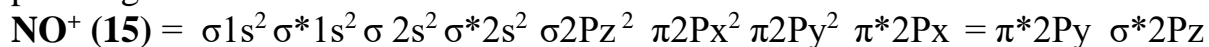
Fig. 27 Molecular orbital energy level diagram for nitric oxide molecule.

Oxygen is more electronegative than nitrogen hence atomic orbitals of oxygen have lower energy than atomic orbital of nitrogen.

(ii) Bond order of NO

$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na} / 2 \\ &= 10 - 5 / 2 = 2.5 \end{aligned}$$

NO molecule contains one unpaired electron in  $\pi^* 2p_x^1$  orbital so the molecule is paramagnetic



Bond order of  $\text{NO}^+$

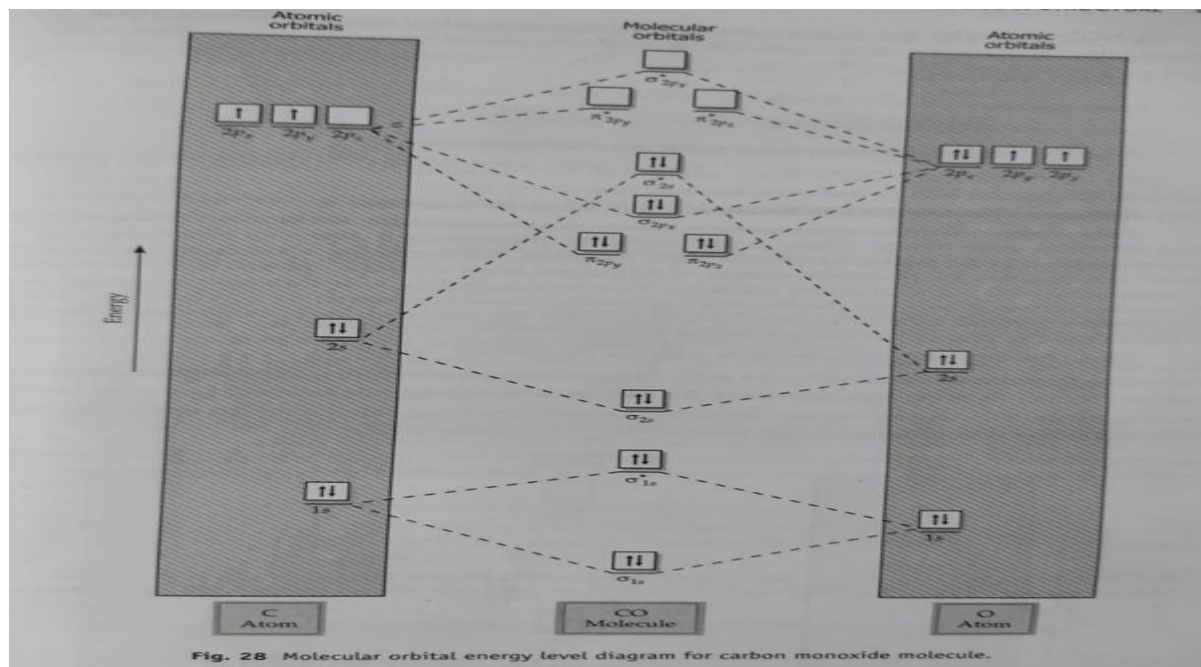
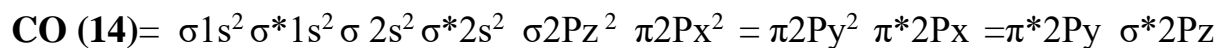
$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na} / 2 \\ &= 10 - 4 / 2 = 3 \end{aligned}$$

Bond order of  $\text{NO}^-$

$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na} / 2 \\ &= 10 - 6 / 2 = 2 \end{aligned}$$

## Carbon monoxide (CO) molecule:

(i) The molecular orbital electronic configuration of CO molecule is

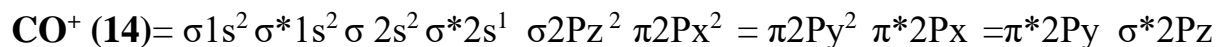


Oxygen is more electronegative than carbon hence atomic orbitals of oxygen have lower energy than atomic orbital of carbon.

(ii) Bond order of CO

$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na}/2 \\ &= 10 - 4/2 = 3 \end{aligned}$$

In the CO molecule, all the electrons are paired, so it is **diamagnetic molecule**.



Bond order of  $\text{CO}^+$

$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na}/2 \\ &= 10 - 3/2 = 3.5 \end{aligned}$$

**Bond order of  $\text{CO}^+ > \text{Bond order of CO}$**

Thus,  $\text{CO}^+$  molecule ion is more stable than CO molecule.

$\text{CO}^+$  has one unpaired electron in  $\sigma^* 2s^1$  orbital so it is a **paramagnetic**.



## HF molecule:

(i) The molecular orbital electronic configuration of HF molecule is

H -  $1s^1$

F -  $1s^2 2s^2 2p^5$

HF -  $1s^2 2s^2 [\sigma(sp)]^2 2p_x^2, 2p_y^2 [\sigma^*(sp)]$

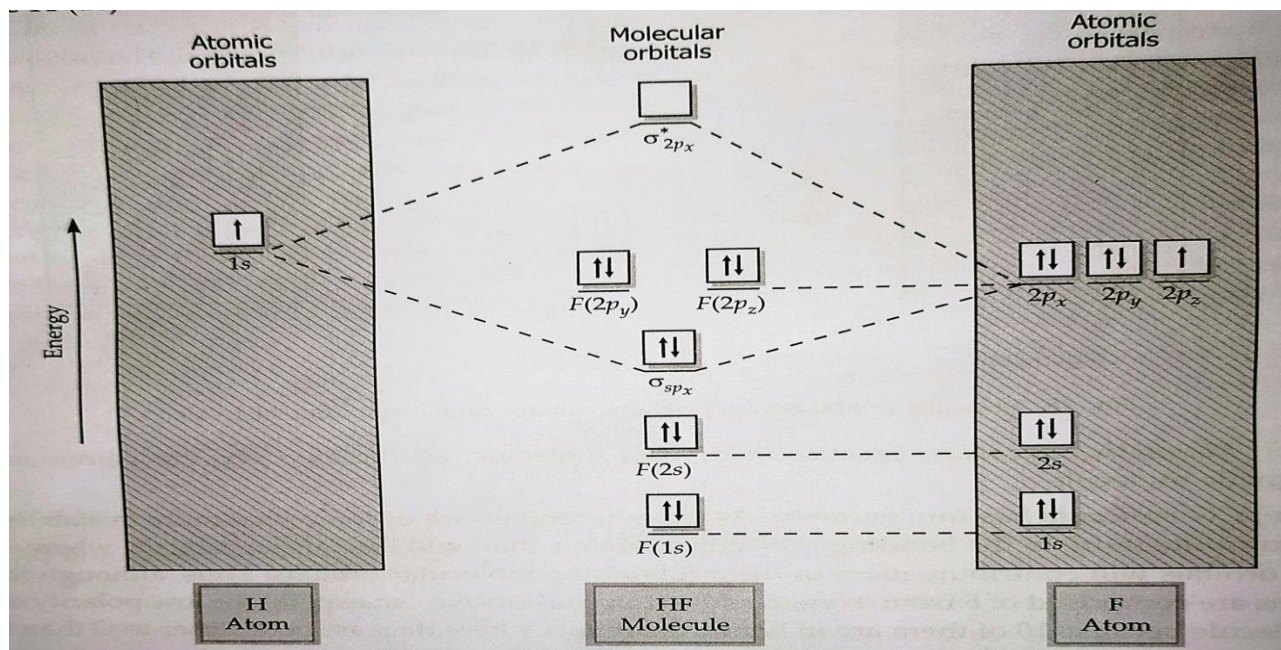


Fig: Molecular orbital energy level diagram of HF molecule

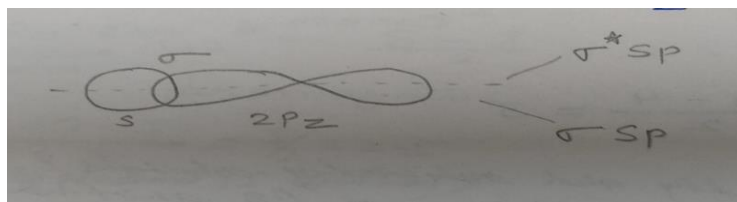
*Fluorine is more electronegative than Hydrogen hence atomic orbitals of Fluorine have lower energy than atomic orbital of Hydrogen.*

(ii) Bond order of HF

$$B.O = N_b - N_a / 2$$

$$= 2 - 0 / 2 = 1$$

Since all the molecular orbitals, (Whether non-bonding or bonding molecular orbitals) are completely filled, so HF molecule is diamagnetic.





## HCl Molecule:

(i) The molecular orbital electronic configuration of HF molecule is

HCl(18):  $1s^2 2s^2 2p^6 3s^2 [\sigma(sp)]^2 2P_x^2, 2p_y^2$

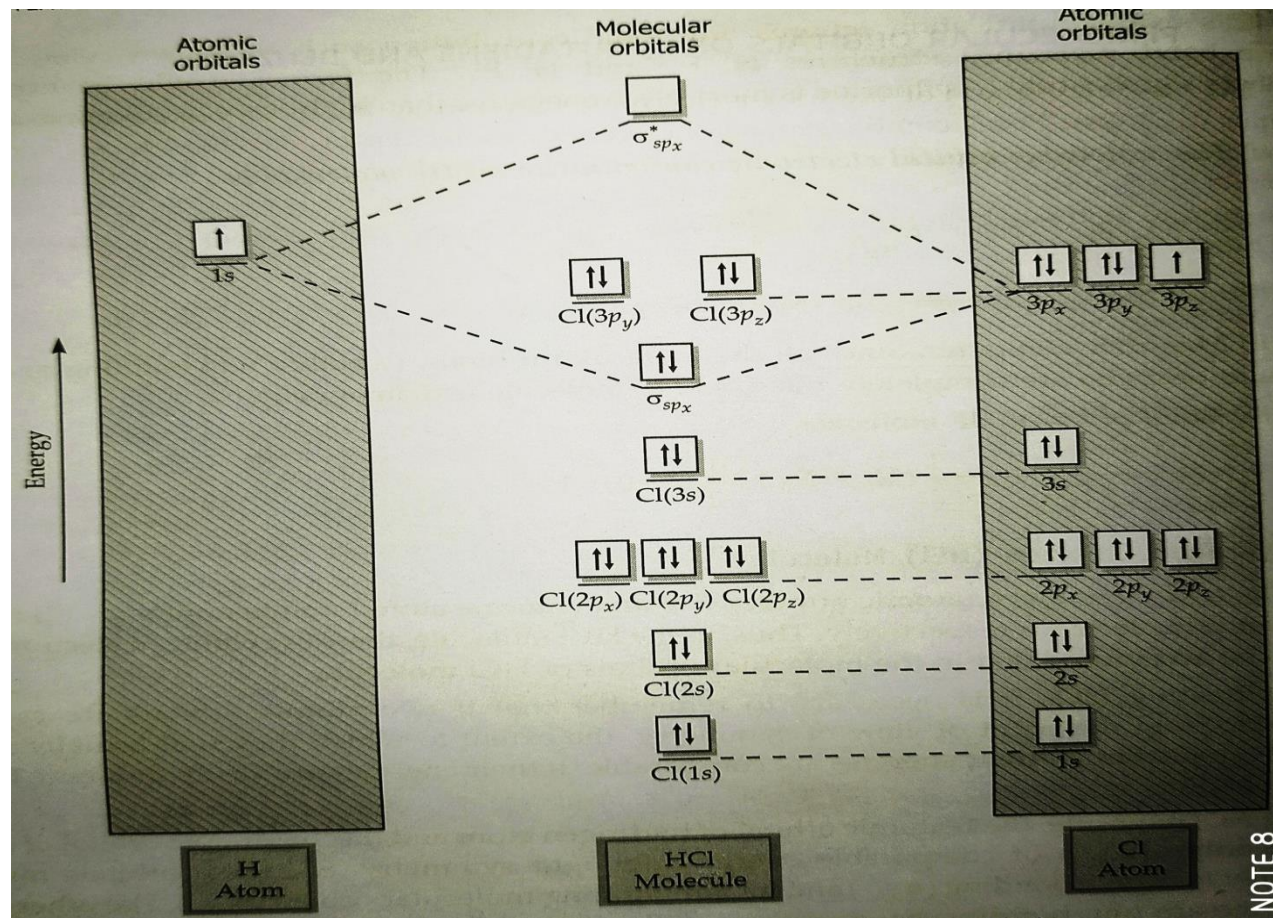


Fig: Molecular orbital energy level diagram of HCl molecule

*Chlorine is more electronegative than Hydrogen hence atomic orbitals of Chlorine have lower energy than atomic orbital of Hydrogen.*

(ii) Bond order of HCl

$$\begin{aligned} \text{B.O} &= \text{Nb} - \text{Na} / 2 \\ &= 2 - 0 / 2 = 1 \end{aligned}$$

Since all the molecular orbitals are completely filled, so HCl molecule is diamagnetic

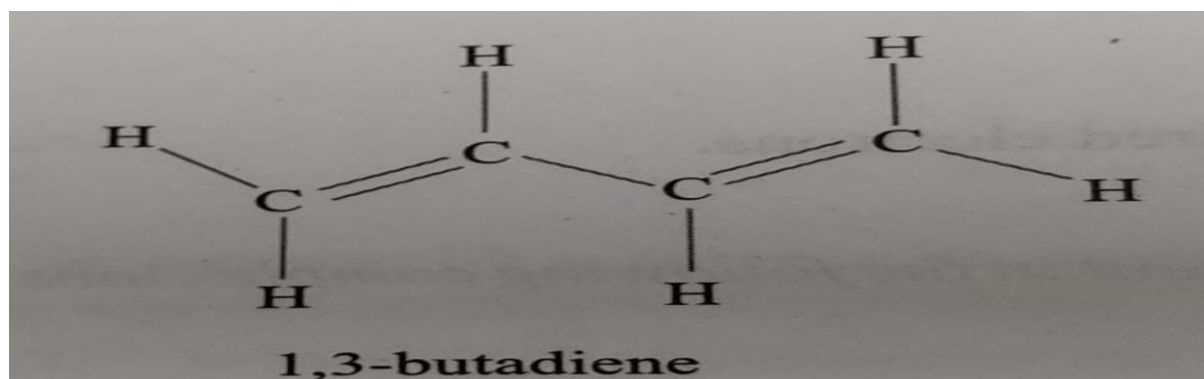
## Comparison of Valence bond and Molecular Orbital Theories

S.N	Valence Bond Theory (VBT)	Molecular Orbital Theory (MOT)
1	After the bond formation, the combining atoms in a molecule retain their identity. Bonding is explained with the help of atomic orbitals.	After the bond formation, the combining atoms in a molecule retain their identity. Bonding is explained with the help of Molecular orbitals.
2	Only the half filled atomic orbitals of the valency shell take part in bond formation	It considers all the electrons in the given atoms for the prediction of number of bonds per atoms.
3	The concept of resonance is applicable only to valence bond theory.	Resonance has no role in molecular orbitals.
4	It fails to explain paramagnetic character of O <sub>2</sub> molecule.	It explain the paramagnetic character of O <sub>2</sub> molecule
5	This theory finds difficulty in explaining the stability of one-and-three electron bonds having unpaired electrons.	The formation of one-electron bond and three –electron bonds can be easily explained by MOT

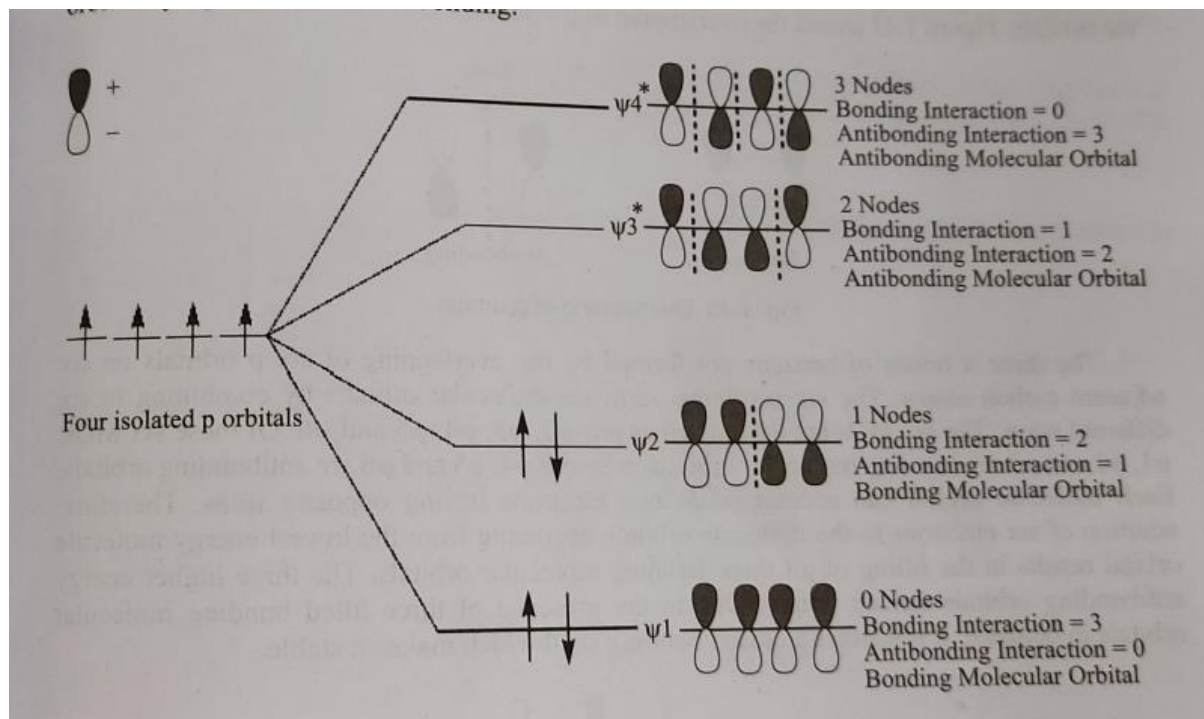
## Pi ( $\pi$ ) molecular orbitals of butadiene and benzene and aromaticity

### 1,3-Butadiene

The structure of 1,3-Butadiene consists of two conjugated double bonds. The structure has four  $sp^2$  hybridized C atoms. Each atom contributes a p atomic orbital consisting of one electron.



The combination of  $\pi$  molecular orbitals of two ethene molecules produces  $\pi$  molecular orbitals for which we need to make an in-phase combination and out-of-phase combination of  $\pi$  and  $\pi^*$  of ethene, respectively.



**Figure 1: Molecular Orbital of 1,3-butadiene**

Figure 1 represents the relative energies of  $\pi$  molecular orbitals of 1,3-butadiene, which is a derived compound of ethene. The energy of the p orbital of a C atom is denoted by the horizontal centre line. The orbitals lying below the horizontal line are bonding, whereas the orbitals above it are antibonding.

Each p orbital contributes one electron, resulting in the arrangement of four electrons from four p orbitals which combine in four different ways to form four molecular orbitals designated as  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$  and  $\psi_4$ .

- $\psi_1$  has bonding interaction between C1-C2, C2-C3, and C3-C4. Therefore, there exists 3 bonding interactions.
- $\psi_2$  has bonding interaction between C1-C2 and C3-C4 and antibonding interaction between C2-C3. Therefore, they have single bonding interaction. It is the highest occupied molecular orbital (HOMO).
- $\psi_3$  has bonding interaction between C2-C3 but antibonding interaction between C1-C2 and C3-C4. Therefore, they have a single antibonding interaction. It is the lowest unoccupied molecular orbital (LUMO).
- $\psi_4$  has antibonding interaction between C1-C2, C2-C3 and C3-C4. Therefore, they have 3 antibonding interaction.

Thus, out of four orbitals available,  $\psi_1$  and  $\psi_2$  are bonding molecular orbitals, whereas  $\psi_3$  and  $\psi_4$  are antibonding molecular orbitals. The p orbitals from which these orbitals are formed are at higher energy than the two bonding MOs, whereas the two antibonding MOs are higher in energy than the p orbitals. The energy in a molecular orbital increases with the rise in the number of nodes.

## Benzene:

### Molecular orbital theory of Benzene

The molecular orbital theory provides the fullest description of the benzene ring. It is based on spectroscopic and X-ray diffraction methods according to which benzene molecule is hexagonal planar structure. Each molecular orbital of benzene consists of a combination of the six p orbitals. Bonding interaction occurs when the orbitals line up in such a way that each lobe overlapping another p orbital has same sign. An orbital lining up with an opposite sign creates an antibonding interaction and a node between orbitals. Figure 1 shows the overlapping of p orbitals.

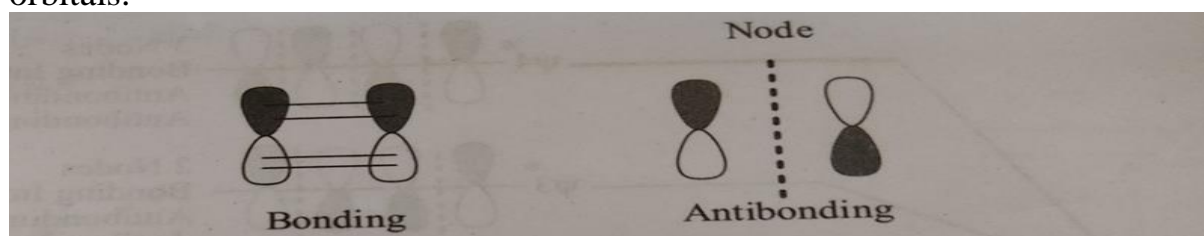


Figure 1: Overlapping of p orbitals

The three  $\pi$  bonds of benzene are formed by the overlapping of six p orbitals on six adjacent carbon atoms. The six p orbitals form six molecular orbitals by combining in six different ways. The six MOs are designated as  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ ,  $\psi_4$ ,  $\psi_5$  and  $\psi_6$ , of these six MOs,  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  are bonding molecular orbitals, whereas  $\psi_4$ ,  $\psi_5$  and  $\psi_6$  are antibonding orbitals.

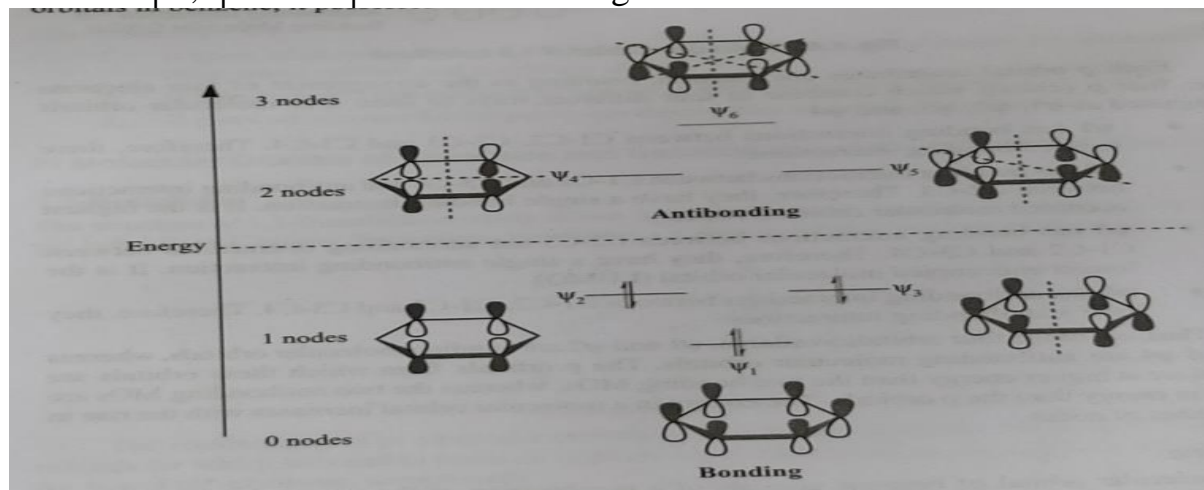


Figure 2 : Molecular Orbital of Benzene

Each molecule orbital can accommodate two electrons having opposite spins. Therefore addition of six electrons to the molecular orbitals beginning from the lowest energy molecule orbital result in the filling of all three bonding molecular orbitals. The three higher energy antibonding orbitals remain empty. Due to the presence of three filled bonding molecular orbitals in benzene, it possesses a closed bonding shell which makes it stable.

**Q.** Why is benzene extra-ordinary stable though it contains three double bonds?

**Answer:** Benzene is extra ordinary stable though it contains three double bonds because  $\pi$  electrons in benzene are delocalised. The absence of pure double bond in benzene accounts for the extraordinary stability. This also accounts for the reluctance of benzene to show addition reaction under normal conditions.





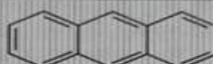
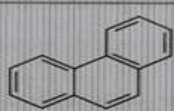






## Aromaticity

The necessary conditions for a molecule to be aromatic are;-

- (i) It should be planar (**Planarity**)
- (ii) The  $\pi$  electrons in the ring are completely delocalised (**Delocalisation**)
- (iii) It should contain  $(4n+2)$   $\pi$  electrons in the ring where  $n$  are an integer ( $n = 0, 1, 2, \dots$ ) [ $(4n+2)$   $\pi$  electrons/Huckel rule]

According to Huckel rule only those planar cyclic systems having conjugated double bonds display aromatic character which have  $(4n+2)$   $\pi$  electrons where  $n$  is integer and may be 0,1,2,3..... because such system possess substantial resonance energy. [ $n=0$   $\pi=2$  ;  $n=1$   $\pi=6$  ;  $n=2$   $\pi=10$ ..... ]

Aromatic Compound	Structure	$n$	$(4n+2)$ $\pi$ electrons
1. Benzene		1	6
2. Cyclopenta-dienyl anion		1	6
3. Cyclohepta-trienyl cation		1	6
4. Naphthalene		2	10
5. Anthracene		3	14
6. Phenanthrene		3	14
7. Pyrrole		1	6
8. Furan		1	6
9. Thiophene		1	6
10. Pyridine		1	6

## Crystal field theory and the energy level diagram for transition metal ions:

Crystal field theory was developed in 1930's by physicists and applied to transition metal ion in a crystal lattice, hence the name crystal –field theory. It assumes that the attraction between the central metal atom and the ligand in a complex is purely electrostatic. The central transition metal ion in the complex is regarded as cation of charge equal to the oxidation state. This is surrounded by ligands which have a lone pair of electrons. For neutral ligands such as  $\text{NH}_3$ , the negative end of the dipole in the ligand molecule is directed towards the metal ion. The electrons on the central transition metal are under the repulsive forces from those on the ligands. Thus the electrons occupy the d orbitals furthest away from the direction of approach of ligands. The free transition metal atom has d-orbitals of same energy that is degenerate. However, when a complex is formed the ligands destroy the degeneracy of these orbitals. On the basis of crystal field theory colour and magnetic properties of complexes can be easily explained.

The salient features of this theory are as follows:

1. The central metal cation remain surrounded by ligand which carry one or more lone pairs of electron.
2. The ionic ligands are regarded as point charge, whereas the neutral ligands are regarded as point dipoles.
3. The bonding between metal cation and ligands is purely electrostatic in nature.
4. The theory does not consider any orbital overlap.

### ***Grouping of d-orbitals in different crystal fields***

*Grouping of d-orbitals into two sets:*

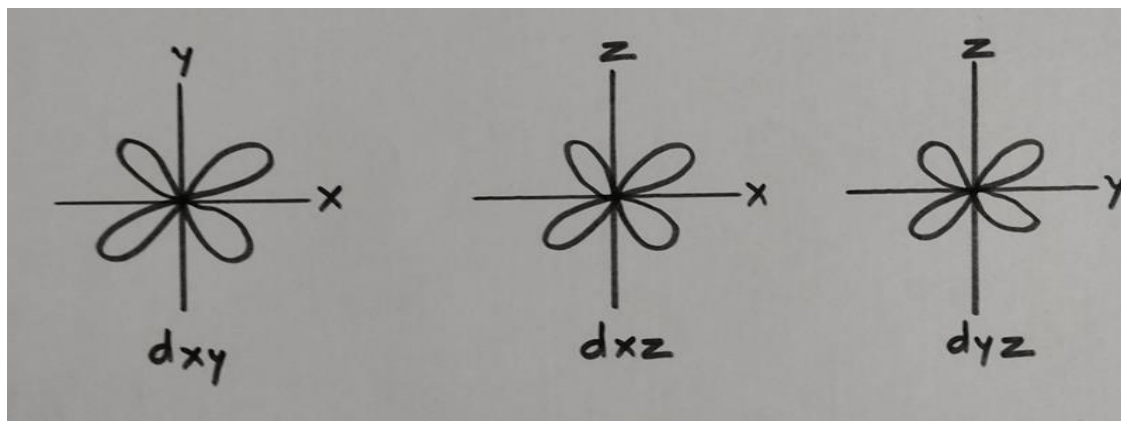
Based on the orientation of the lobes, five d- orbitals have been grouped as follows:-

**(i) eg set :**  $\text{dx}^2\text{-y}^2$  and  $\text{dz}^2$  have their lobes along the axes. They are also called axial orbitals. The letter 'e' in eg refers to doubly degenerate set.





(ii)  **$t_{2g}$  set:**  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals have lobes lying between the axes. They are also called non-axial orbitals. The letter 't' in  $t_{2g}$  refers to triply degenerate set.

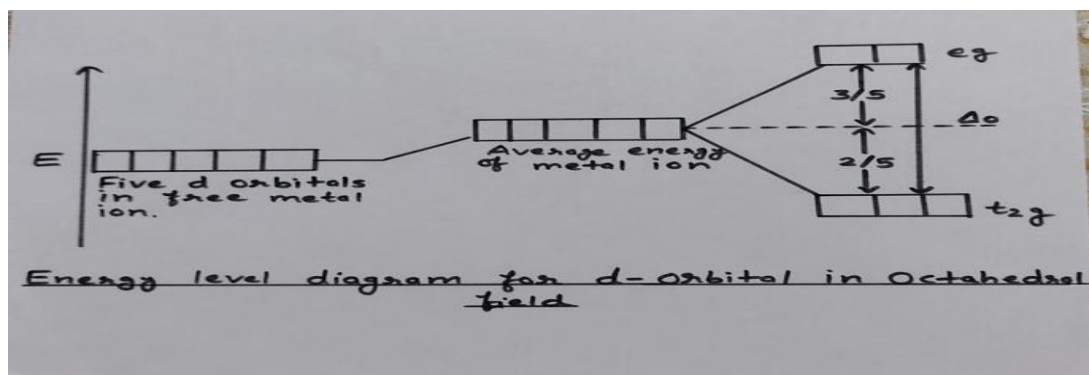


### Crystal field splitting of d- orbitals in octahedral complexes:

In an octahedral complex, the central metal ion is surrounded by six lone pairs of electrons. Two types of electrostatic interaction come into play:

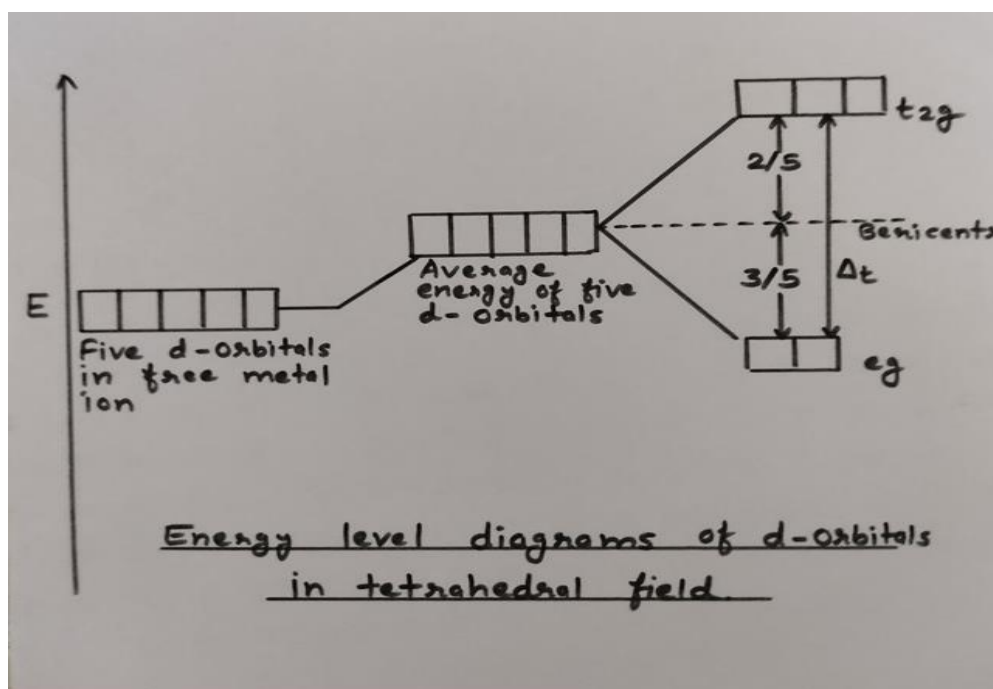
1. There is attraction between the positive metal ion and the negatively charged ligand. This force holds the ligands to the metal in complex.
2. There is electrostatic repulsion between the lone pairs in the ligands and the electrons in the d- orbitals of the metal. However the magnitude of this repulsion depends on the particular d- orbital involved.

As in octahedral complex, ligands approach along the axis, hence  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals experience more repulsion and their energy is increased while  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals experience less repulsion and their energy is less than  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.



### Crystal field splitting in tetrahedral complexes:

In tetrahedral complexes, the direction of approach of the four ligands does not coincide exactly with either the  $e_g$  or  $t_{2g}$  orbitals. However, the  $t_{2g}$  orbitals are nearer to the direction of the ligands than the  $e_g$  orbitals. Thus energy of  $t_{2g}$  set orbitals is increased and  $t_{2g}$  set orbitals have more energy than  $e_g$  orbitals.

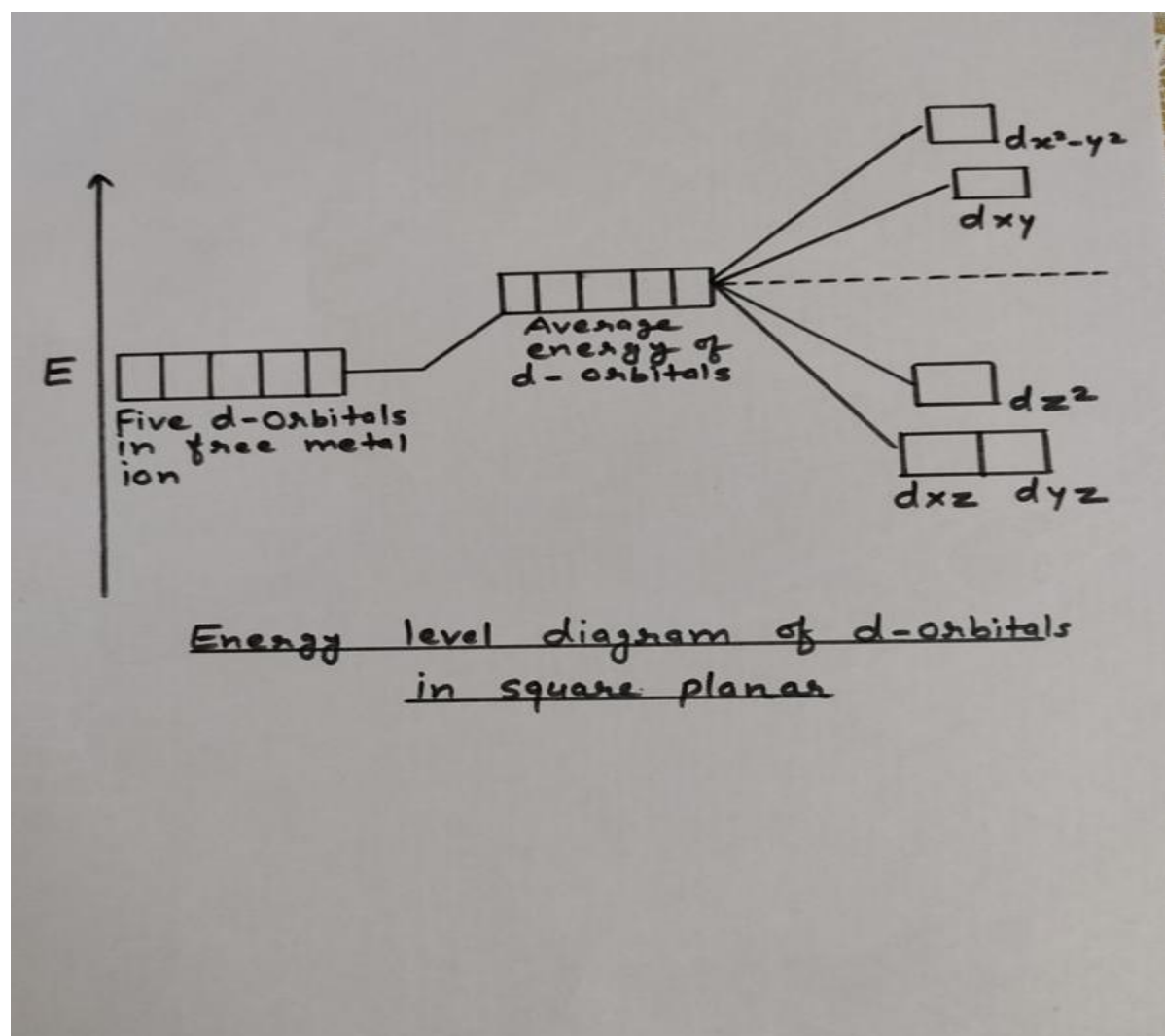


Crystal field splitting in tetrahedral complexes is quite lesser than in octahedral complexes, due to the following reasons:

1. There are only 4 ligands. So the ligand field is only  $4/9$  or  $2/3$  times, thus ligand field splitting is also  $2/3$  in size.
2. The direction of the orbitals does not coincide with that of ligands thus crystal field splitting is further reduced by  $2/3$ .

### Crystal field splitting in square planar complexes:

Four ligands in a square planar arrangement around the central ion would have the greatest influence on a  $dx^2-y^2$  orbital, so the energy of this orbital would be raised most. The  $dxy$  orbital lying in the same plane, but between the ligands will also have a greater energy. Though the effect will be lesser than that on the  $dx^2-y^2$  orbital. However, it is not possible to predict exactly the effect of the ligand field on the remaining orbitals, the effect on  $dxy$  and  $dx^2-y^2$  will be more than that on  $dxz$  and  $dyz$  orbitals.  $dxz$  and  $dyz$  orbitals are affected equally and thus remain degenerate.



### Magnetic properties of Transition metal compounds:

Electron is a charged particle and it has spin and orbital motion. Due to this motion electron creates a magnetic field and behave like a tiny magnet. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.

On the basis of magnetic properties, we can divide transition metal compounds into two types:

1. Paramagnetic substances:

These substances contain one or more unpaired electrons. The magnetic moment due to spin and orbital motion of such electrons get aligned parallel to the direction of external magnetic field applied. Such substances experience attraction in a magnetic field and show paramagnetic behaviour.

2. Diamagnetic substances:

These substances contain all the paired electrons. The effect of individual electrons are mutually compensated. Such substances experience repulsion in a magnetic field and thus show diamagnetic behaviour.

The effective magnetic moment ' $\mu_{\text{eff}}$ ' can be calculated by the formula.

$$\mu_{\text{eff}} = \sqrt{n(n+2)}$$

Bohr magneton (B.M), where  $n$  = number of unpaired electrons.

Q. Which complex has larger crystal field splitting?

- (i)  $[\text{Co}(\text{CN})_6]^{3-}$  or  $[\text{Co}(\text{CN})_6]^{3+}$
- (ii)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- (iii)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  or  $[\text{Rh}(\text{NH}_3)_6]^{3+}$

Answer:

- (i)  $[\text{Co}(\text{CN})_6]^{3-}$  [ $\text{CN}^-$  is more strong field ligand]
  - (ii)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  [CFSC  $\propto$  Charge on the metal]
  - (iii)  $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- [splitting of d-orbitals in ligand field in the order  $3d < 4d < 5d$ ]

## Band structure of solids and the role of doping on band structures

### Molecular Orbital Treatment of Metallic Bond (Band Theory)

This is the quantum mechanical treatment of the metallic bond and is similar to molecular orbital approach of covalent bond. Unlike simple covalent molecules during formation of metallic crystal, a very large number of atoms in the order of  $10^{23}$  or more are brought together so that their AOs undergo linear combination to form exactly same number of MOs. The energies of these MOs are so closely spaced that they appear to be a continuum known as quasi-continuous energy band. Hence, the name band theory. The MOs formed are delocalized, i.e., belong to the crystal as a whole. The progressive formation of a quasi-continuous band is shown in figure.1.

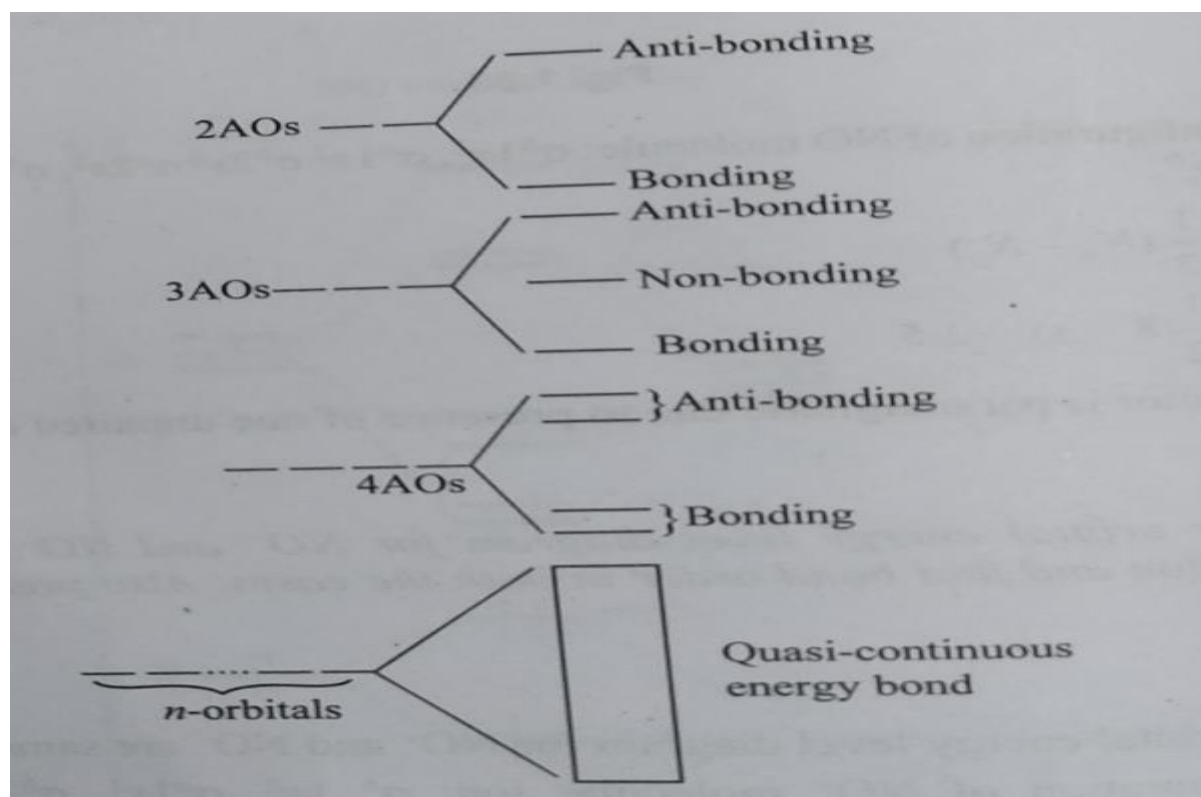


Figure1: Formation of MO band in metals

### For example: Li metals

The electronic configuration of Li is  $1s^2 2s^1 2p^0$ . When  $n$ -Li atoms close to form Li crystal, three energy bands are formed.

**1s band:** This band is formed by combination of large  $n$  of  $1s$  AOs of Li atoms and hence contains  $n$  number of energy levels. This band is completely filled and carries  $2n$  electrons. This is inner shell band and is not influenced by surrounding atoms, therefore narrow at equilibrium interatomic distance.

**2s band:** This band is formed by combination of  $2s$  orbitals of  $n$  atoms. This band has  $n$  levels. This band is half filled and contains  $n$ -electrons. The upper half is completely filled while the lower half remains vacant. This is valency band and is significantly influenced by surrounding atoms. It is quite spread out at equilibrium distance. Due to close spacing of energy levels, electrons can move to energy levels in upper half at room temperature.

**2p band:**  $n$  atoms of Li give  $3n$  levels in  $2p$  band.  $2s$  and  $2p$  levels are so close in energy that the bands overlap and the electrons of  $2s$  band gets additional energy levels differing slightly in energies to move about. The total capacity of this overlapped band is  $8n$  electron and is therefore  $1/8^{\text{th}}$  filled.

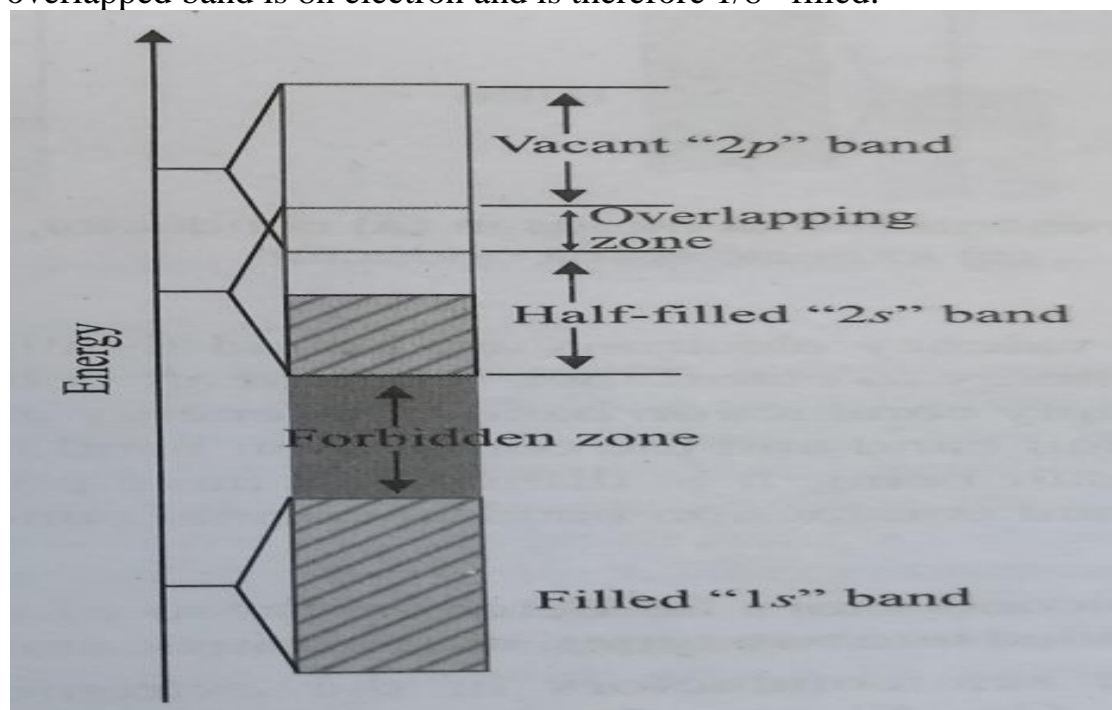


Fig2: Different band in Li metals

## Difference between Conductors, Insulators and Semiconductors on the basis of Band Theory:

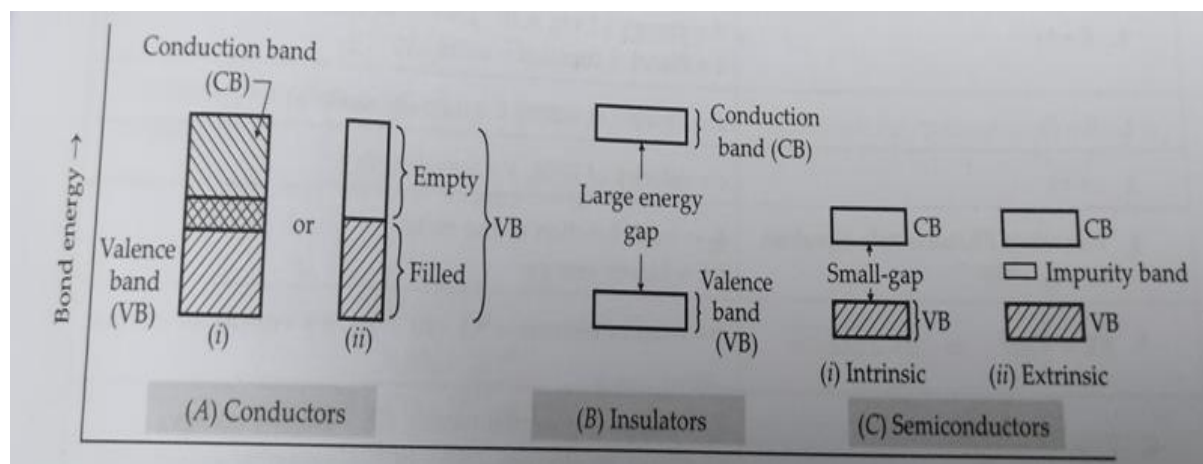


Figure1 : Energy band in (A) Conductor (B) Insulator and (C) Semi-conductor

With the help of molecular orbital theory, not only we can explain the properties of metals but also we can classify materials into three categories e.g conductors, Insulators and semi-conductor , depending on the energy gap between the valence and conduction bands.

In **Conductors** (metallic), either the valence and conduction bands overlap as in Mg [Fig.1(A) (i)] or the valence band is only partly full [Fig.1(A) (ii)]. As the filled and unfilled molecular orbitals are not separated by significant gap, perturbation can occur readily.

In **Insulators** (non-metallic elements), there is large band gap between the filled valence band and empty conduction band as in diamond. [Fig.1(B)] Therefore Electrons cannot be promoted from the valence band to conduction band where they could move freely.

**Semiconductors:** are of two types , intrinsic and extrinsic semiconductor. Intrinsic semiconductors (like Si or Ge) are having small energy gap between the filled valence band (VB) and empty conduction band (CB) see [Fig.1(C) (i)] sufficient to promote an electron from VB to CB. The hole left in the VB and the promoted electron in the CB increases with rise in temperature, thus conductivity of semiconductors increases with temperature. The conductance of semiconductors can also improved by doping. Doping means treatment of Si and Ge (typically semiconductors) with impurity atoms of Group (III) and Group (V) giving respectively **p-type and n-type** extrinsic semiconductors. Basically the band from the impurity lies in between the VB and CB , see [Fig.1(C) (ii)], so that electron may be easily excited from VB to impurity band and hence conductance increases.

Q1. How do you distinguish between a valence band and a conduction band.

Ans. The valence band is the highest band with electrons in it and the conduction band is the highest band with no electron in it.

Q2. Is the energy gap between an insulator is smaller or larger than the energy gap between a semiconductor?

Ans. Larger

Q3. What two methods bring conductivity to semiconductor?

Ans. (1) Electron transport or n-type

(2) Hole transport or p-type

	<b>n-type semiconductor</b>	<b>p-type semiconductor</b>
1.	Such a semiconductor is formed by doping Si or Ge with a pentavalent impurity	Such a semiconductor is formed by doping Si or Ge with a trivalent impurity.
2.	Has an excess of electrons.	Has an excess of electron holes.
3.	Conduction due to free electrons.	Conduction due to electron-holes.
4.	Conduction due to the movement of negative electric charge.	Conduction due to the movement of positive electric charge.



**Module 1: Atomic and molecular structure**

**[10 Lectures]**

Schrodinger equation. Particle in a box solutions and their applications for conjugated molecules. Molecular orbitals of diatomic molecules and plots of the multicentre orbitals. Equations for atomic and molecular orbitals. Energy level diagrams of diatomics. Pi-molecular orbitals of butadiene and benzene and aromaticity. Crystal field theory and the energy level diagrams for transition metal ions and their magnetic properties. Band structure of solids and the role of doping on band structures.

Q.1.	(A) Using Schrodinger Wave Equation derive expression for Wave Function, $\psi$ and the Energy, $E$ for the Particle in 1-D box. (B) What is $\psi$ ? What information is conveyed by $\psi$ and $\psi^2$ ?
Q.2.	(A) Derive Schrodinger wave equation for the wave mechanical model of an atom and discuss its application to hydrogen atom. (B) What is Difference between Bohr atom and the Quantum mechanical model?
Q.3	(A) What do you know about the dual character of matter? Derive de-Broglie Equation. (B) Write a note on Heisenberg Uncertainty Principle. How this Principle goes against Bohr's theory. (C) Describe application of Schrodinger wave equation for conjugated molecule.
Q.4	(A) With the help of Molecular Orbital theory, explain the paramagnetic character of Oxygen and diamagnetic character of nitrogen. (B) Calculate the bond order of $N_2^-$ , CO, NO and $O_2^+$ ? Explain the bond order in $N_2$ molecule
Q.5.	(A) Write the decreasing order of stability for the following: $H_2$ , $H_2^+$ , $H_2^-$ and justify. (B) Write down the electronic configuration, bond order and magnetic behaviour of NO, $NO^+$ and $NO^-$ . Draw the molecular Orbital diagram of NO molecule.
Q.6.	(A) Write Molecular Orbital Electronic Configuration, bond order, magnetic properties of HF and HCl. (B) Draw the molecular orbital diagram of HF and HCl.
Q.7	(A) What do you understand by LCAO? Discuss condition for combination of atomic Orbitals to form Molecular Orbital (M.O) (B) Write note on $(4n+2)$ rule.
Q.8.	(A) Draw Pi ( $\pi$ ) molecular orbitals of butadiene. (B) Draw Pi ( $\pi$ ) molecular orbitals of benzene.
Q.9	(A) Discuss the concept of aromaticity and mention which important cyclic Compounds exhibit it and why? (B) Write down the three important conditions for formation of metallic bond.
Q.10	(A) Describe and compare the splitting of d-orbitals under the influence of Octahedral and tetrahedral ligand fields. Draw energy level diagram. (B) Explain the magnetic properties of transition metal ions.

Q.11	(A) Discuss the main points of Crystal Field Theory (CFT). Show through a diagram, the splitting of d-orbitals in Octahedral and tetrahedral crystal fields. (B) Explain the splitting of d-orbitals under the influence of Square Planar ligand Field with the help of energy level diagram
Q.12.	(A) On the basis of VBT find the geometry and types of hybridization in the following complexes (i) $[\text{Fe}(\text{CN})_6]^{4-}$ (ii) $[\text{Cu}(\text{CN})_4]^{2-}$ (B) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ . Explain on the basis of CFT.
Q.13	(A) Explain the terms conductors, semiconductors and insulators on the basis of Band Theory/Molecular orbital theory. (B) Explain Intrinsic and extrinsic semiconductor with examples. (C) Discuss the electrical conductivity in n-type and p-type semiconductors.

### MCQs

- Q1 .Which of the following set of  $\Delta H$  and  $\Delta S$  values will lead to spontaneous reaction?  
 (a)  $\Delta H$  is positive and  $\Delta S$  is negative  
 (b)  $\Delta H$  is positive and  $\Delta S$  is positive (at low temperature)  
**(c)  $\Delta H$  is negative and  $\Delta S$  is positive**  
 (d)  $\Delta H$  is negative and  $\Delta S$  is negative (at high temperature)
- Q.2 which of the following have smallest ionic radius?  
**(a)  $\text{F}^-$**  (b)  $\text{O}^{2-}$  (c) H (d)  $\text{Cl}^-$
- Q.3. With the help of molecular orbital theory, predict which of the following species is Diamagnetic (a)  $\text{H}_2^+$  (b)  $\text{H}_2^-$  (c)  $\text{O}_2$  **(d)  $\text{O}_2^{+2}$**
- Q.4 which of the following is not a spontaneous process?  
 (a) Diffusion of a gas from higher pressure to lower pressure  
**(b) Flow of heat from lower to higher temperature**  
 (c) Precipitation of AgCl in the reaction of silver nitrate with sodium chloride  
 (d) The conversion of water from liquid to vapour at  $25^\circ\text{C}$
- Q.5 Which of the following has largest de-Broglie wavelength, provided all have Equal velocity? (a)  $\text{CO}_2$  molecule **(b) Electron** (c) Ammonia molecule (d) Proton
- Q.6. The species having bond order different from that in CO is  
 (a)  $\text{N}_2$  (b)  $\text{NO}^+$  (c)  $\text{CN}^-$  **(d)  $\text{NO}^-$**
- Q.7 which of the following has largest de-Broglie wavelength, provided all have equal velocity? (a)  $\text{CO}_2$  molecule **(b) Electron** (c) Ammonia molecule (d) Proton
- Q.8. Which of the following species doesn't exist under normal condition?  
 (a)  $\text{Li}_2$  (b)  $\text{Be}_2^+$  **(c)  $\text{Be}_2$**  (d)  $\text{B}_2$
- Q.9. To get an n-type semiconductor from silicon, it should be doped with a substance with valence----- (a) 2 (b) 1 (c) 3 **(d) 5**
- Q.10. The species having bond order different from that in CO is  
 (a)  $\text{N}_2$  (b)  $\text{NO}^+$  (c)  $\text{CN}^-$  **(d)  $\text{NO}^-$**
- Q.11.  $\psi^2 = 0$  represents  
**(a) a node** (b) an orbital (c) angular wave function (d) wave function
- Q.12 The species having bond order different from that in CO is  
**(a)  $\text{NO}^-$**  (b)  $\text{NO}^+$  (c)  $\text{CN}^-$  (d)  $\text{N}_2$

Q.13. which of the following shall form an octahedral complex?

(a)  $d^4$  (low spin) (b)  $d^8$  (high spin) (c)  **$d^6$  (low spin)** (d) all of these

Q.14. Silicon doped with electron-rich impurity forms-----.

(a) p-type semiconductor (b) **n-type semiconductor** (c) intrinsic semiconductor  
(d) insulator

Q.15. Silicon doped with Galium forms-

(a) **p-type semiconductor** (b) n-type semiconductor  
(c) Intrinsic semiconductor (d) Insulator