

# **Unit-I**

## **ATOMIC AND MOLECULAR STRUCTURE**

Presented  
by

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## **UNIT I - ATOMIC AND MOLECULAR STRUCTURE**

Schrodinger Equation – Introduction – Derivation – Particle in a box solution – Applications for Conjugated Molecules – Forms of The Hydrogen Atom Wave Functions – Plots of These Functions to Explore their Spatial Variations. Molecular Orbitals of Diatomic Molecules- Homonuclear – Heteronuclear Diatomic Molecules- Equations for Atomic Orbital – Equation for Molecular Orbitals – Energy Level Diagrams of Diatomic. Introduction – Explanation –  $\pi$ -molecular Orbitals Of Butadiene –  $\Pi$ -molecular Orbitals Benzene – Aromaticity – Introduction – Explanation – Crystal Field Theory – Introduction – Explanation – Energy Level Diagrams for Transition Metal Ions – Magnetic Properties Of Transition Compounds

# **UNIT I - ATOMIC AND MOLECULAR STRUCTURE**

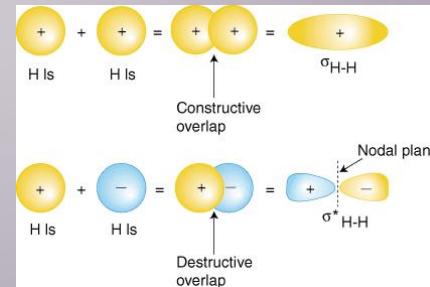
❖ Atom

❖ Molecules

❖ Examples

# Molecular Orbital Theory (MOT)

- ✓ When atoms combine to form molecules, their individual atomic orbital lose their identity and forms new orbitals called Molecular Orbital Theory (MOT)



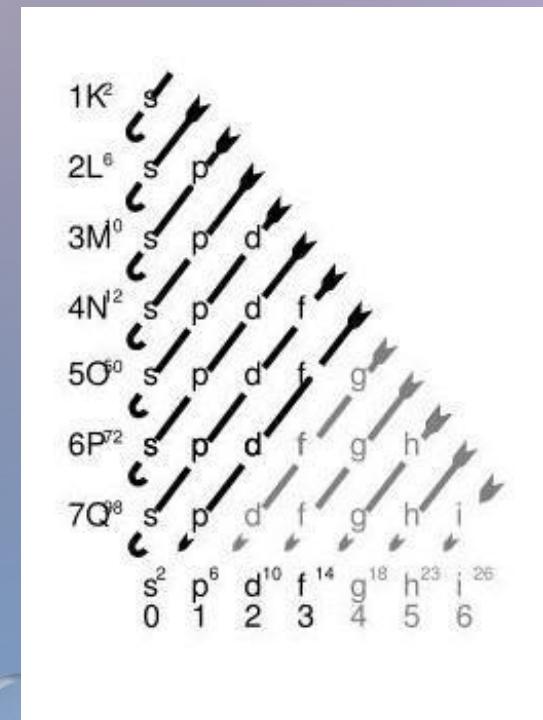
- ✓ The Shape of molecular orbitals depend up on the shapes of combining atomic orbitals.
- ✓ The number of molecular orbitals formed is same as the number of combining atomic orbitals Half the number of molecular orbitals formed will have lower energy than corresponding atomic orbital, while remaining orbitals will have higher energy
- ✓ Molecular orbital with lower energy is called bonding molecular orbital.
- ✓ Molecular orbital with higher energy is called anti-bonding molecular orbital
- ✓ The bonding orbitals are represented as  $\sigma$  (sigma) and  $\pi$  (pi)  
4
- ✓ The anti-bonding orbitals are represented as  $\sigma^*$  and  $\pi^*$ .

- ✓ The electrons in a molecule are accommodated in the newly formed molecular orbital. The filling of the electrons in orbitals follows Aufbau's, pauli's exclusion principle and Hund's rule.

### Rules for Filling of Molecular Orbitals

- ✓ **Aufbau Principle** – This principle states that those molecular orbital which have the lowest energy are filled first.

$1s^2 2s^2 2p_{10}^6 3s^2 3p_{18}^6 4s^2 3d_{30}^{10} 4p_{36}^6 5s_{38}^2 4d_{48}^{10} 5p_{54}^6 6s_{56}^2 4f_{70}^{14} 5d_{80}^{10} 6p_{86}^6 7s_{88}^2 5f_{102}^{14} 6d_{112}^{10} 7p_{118}^6$



- ✓ **Pauli's Exclusion Principle** – According to this principle each molecular orbital can accommodate maximum of two electrons having opposite spins.
- ✓ **Hund's Rule** – This rule states that in two molecular orbitals of the same energy, the pairing of electrons will occur when each orbital of same energy consist one electron.

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
H	1	1				$1s^1$
He	2	1↓				$1s^2$
Li	3	1↓	1			$1s^2 2s^1$
Be	4	1↓	1↓			$1s^2 2s^2$
B	5	1↓	1↓	1		$1s^2 2s^2 2p^1$

- ✓ Bond order gives the number covalent bonds between two combined atoms. The bond order is calculated as follows

$$Bond\ Order = \frac{N_b - N_a}{2}$$

Where

$N_b$  = Total number of electrons present in the bonding molecular orbitals.

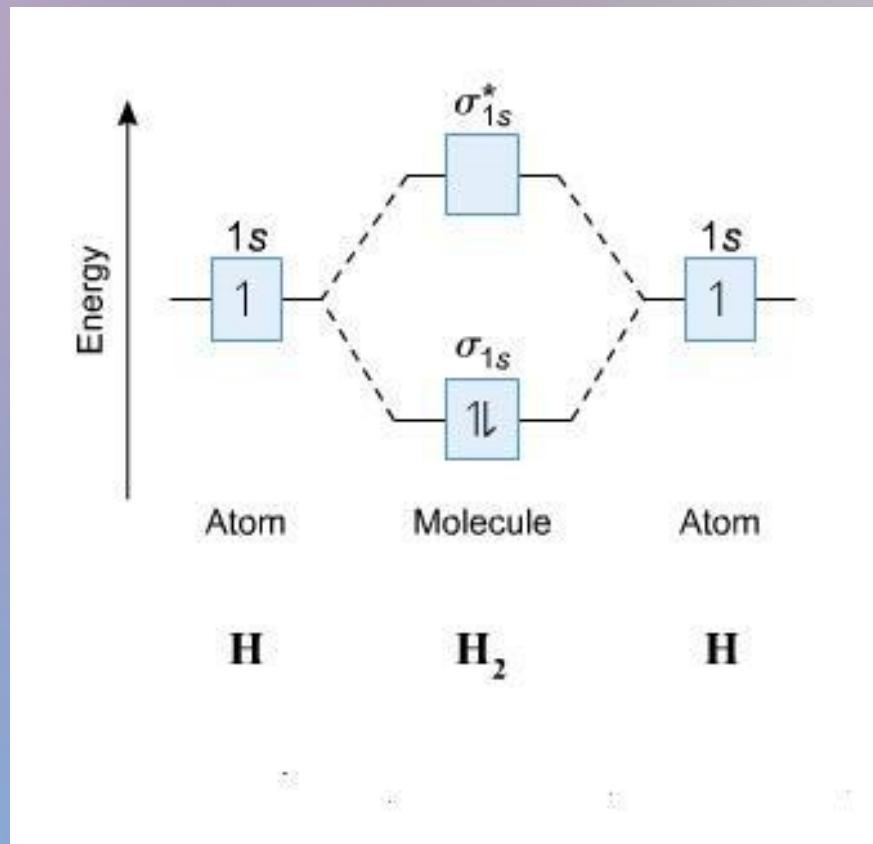
$N_a$  = Total number of electrons present in the anti-bonding molecular orbitals

Bond order is zero, indicate that the molecule doesn't exist.

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

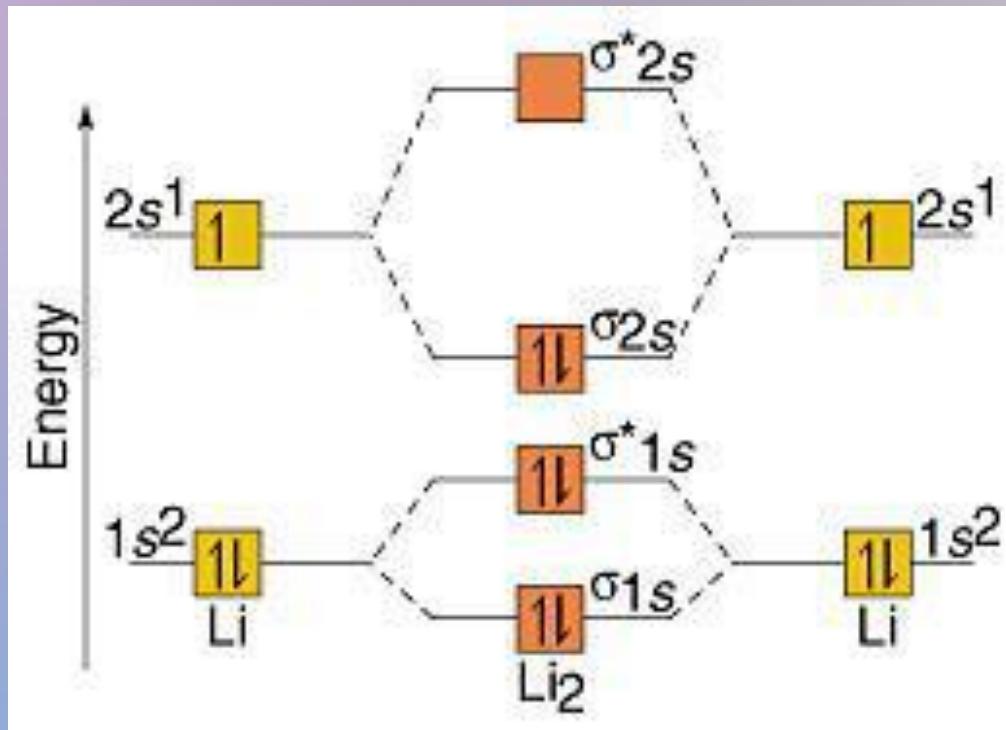
# Bonding in some homonuclear diatomic molecules

MO Diagram of H<sub>2</sub> molecule

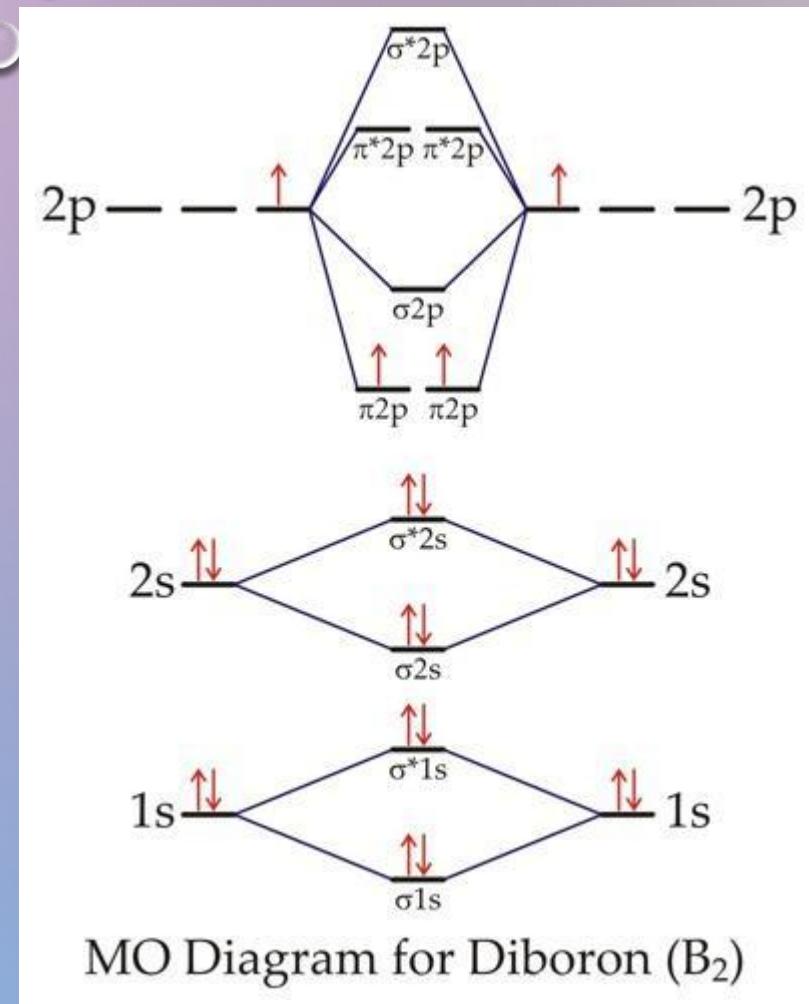


- ✓ Electronic configuration of H atom 1s<sup>1</sup>
- ✓ Electronic configuration of H<sub>2</sub> molecule 1s<sup>2</sup>
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{2 - 0}{2} = 1$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

## MO Diagram of $\text{Li}_2$ molecule



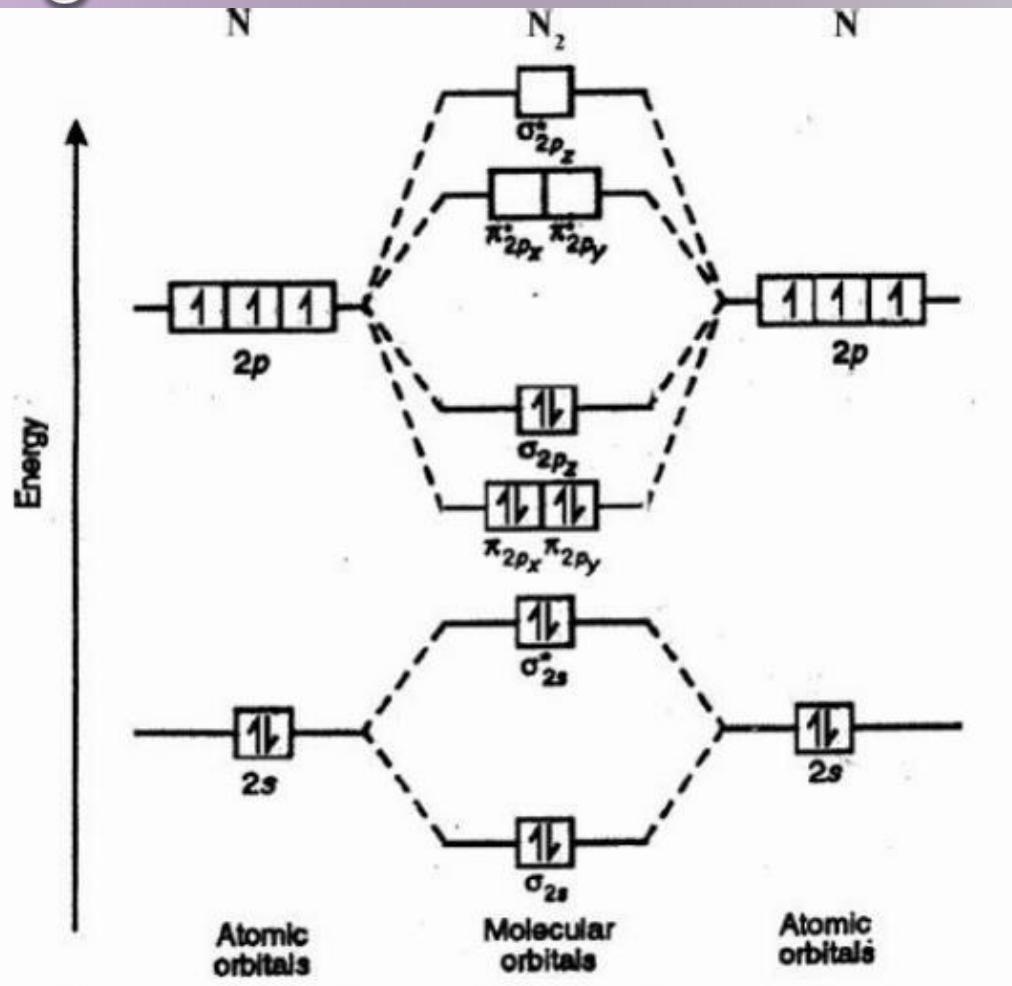
- ✓ Electronic configuration of Li atom  $1s^2 2s^1$
- ✓ Electronic configuration of  $\text{Li}_2$  molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$
- ✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{4 - 2}{2} = 1$
- ✓ Molecule has no unpaired electron hence it is diamagnetic



## MO Diagram of B<sub>2</sub> molecule

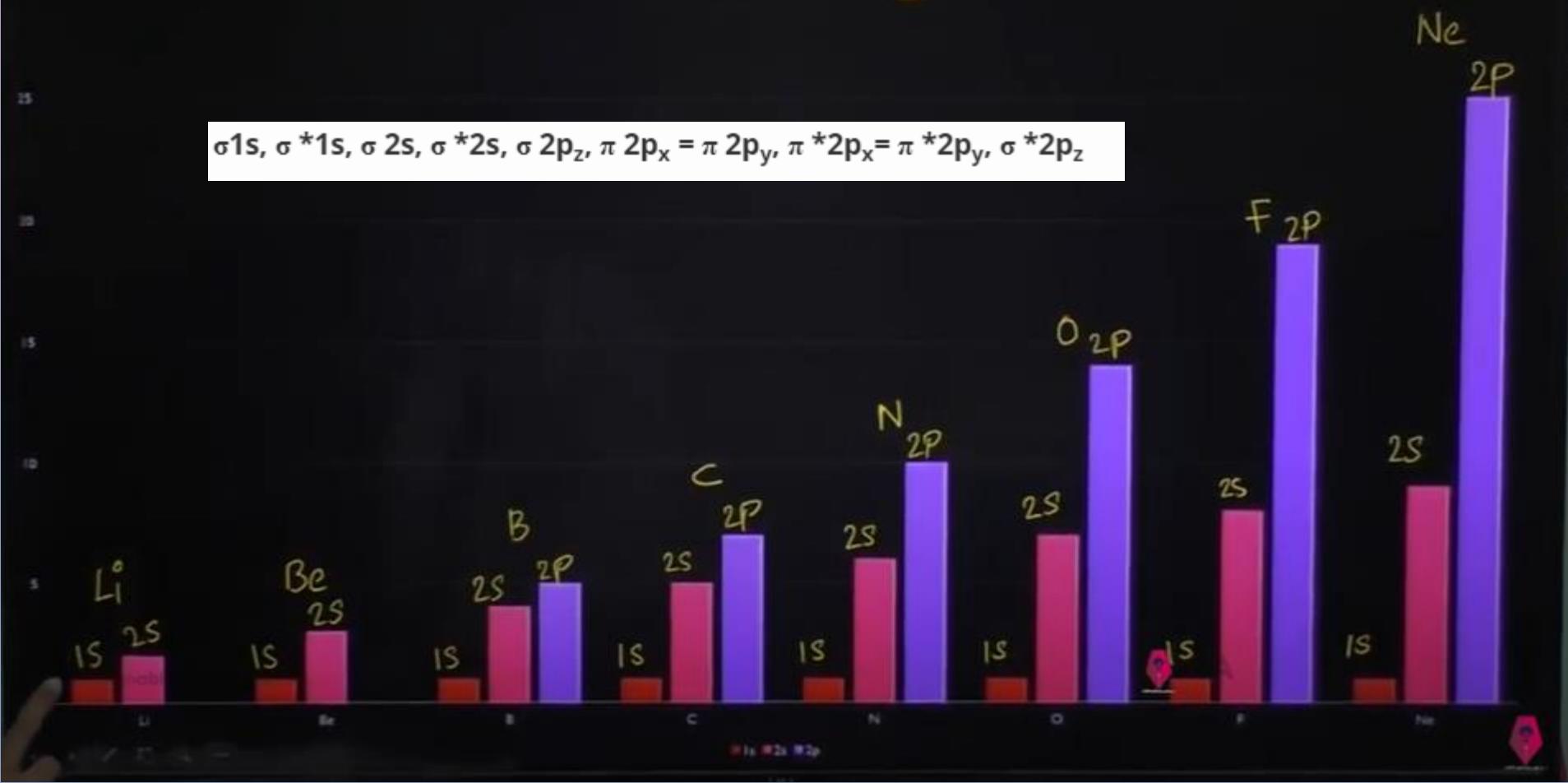
- ✓ Electronic configuration of B atom  $1s^2 \ 2s^2 \ 2p_1$
- ✓ Electronic configuration of B<sub>2</sub> molecule  $\sigma 1s^2 \ \sigma^* 1s^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \pi^1_{2px} \ \pi^1_{2py}$
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{6-4}{2} = 1$
- ✓ Molecule has two unpaired electron hence it is paramagnetic

## MO Diagram of N<sub>2</sub> molecule

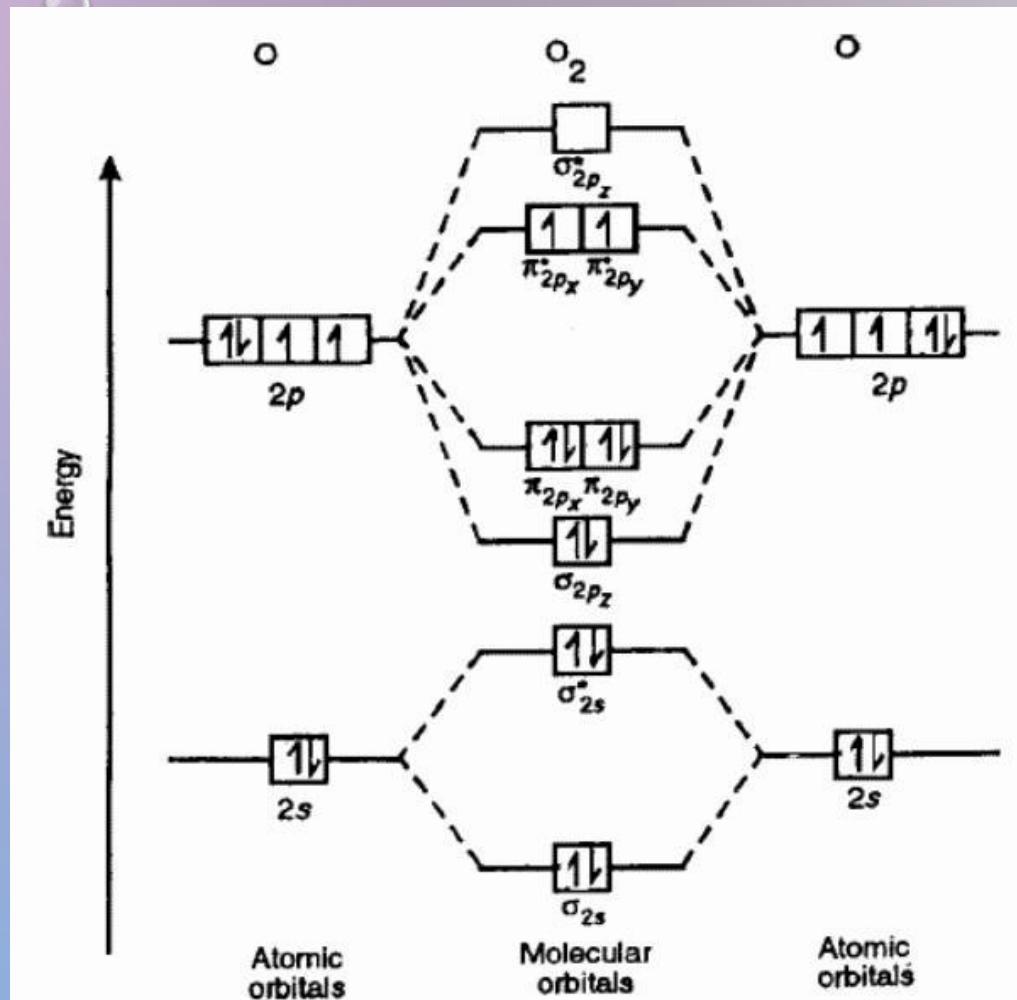


- ✓ Electronic configuration of N atom  $1s^2\ 2s^2\ 2p^3$
- ✓ Electronic configuration of N<sub>2</sub> molecule  $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi^2_{2p_x}\ \pi^2_{2p_y}\ \sigma^2_{2p_z}$
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{10 - 4}{2} = 3$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

## Difference of Energy between 2s and 2p



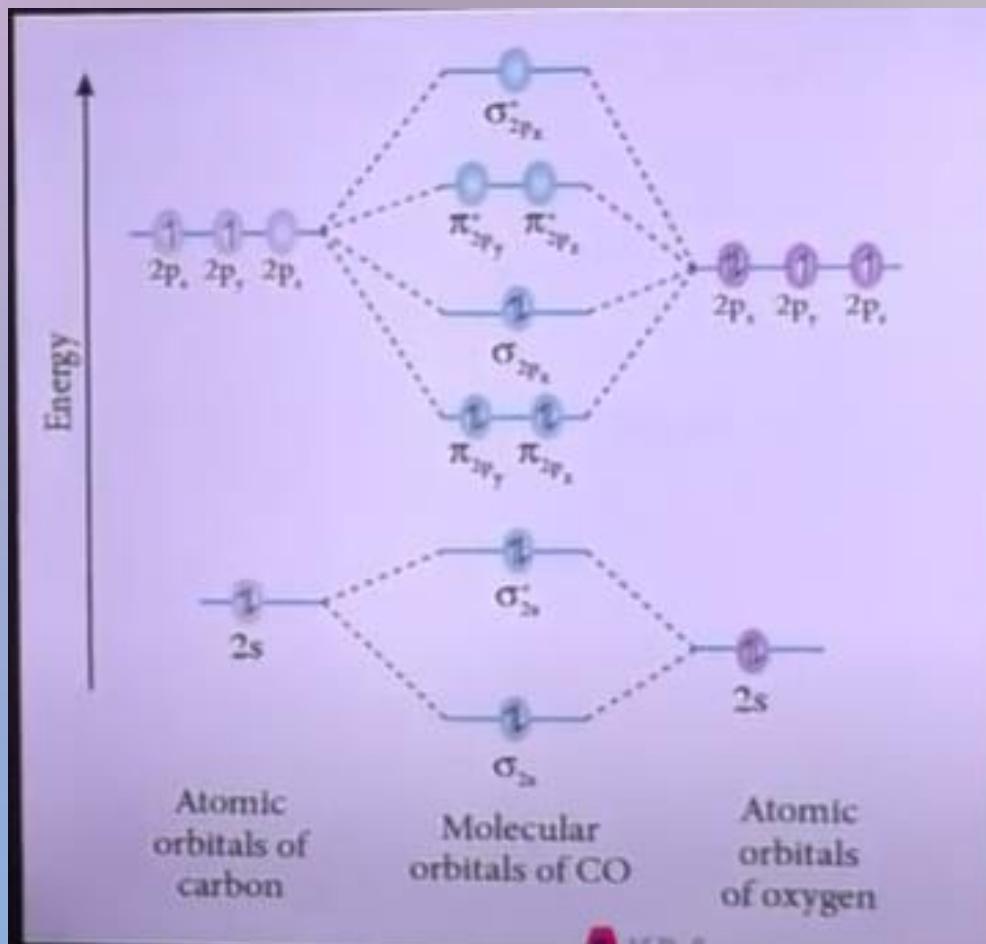
## MO Diagram of O<sub>2</sub> molecule



- ✓ Electronic configuration of O atom  $1s^2\ 2s^2\ 2p^4$
- ✓ Electronic configuration of O<sub>2</sub> molecule  $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi^2_{2p_x}\ \pi^2_{2p_y}\ \sigma^2_{2p_z}\ \pi^{*1}_{2p_x}\ \pi^{*1}_{2p_y}$
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{10 - 6}{2} = 2$
- ✓ Molecule has two unpaired electron hence it is paramagnetic

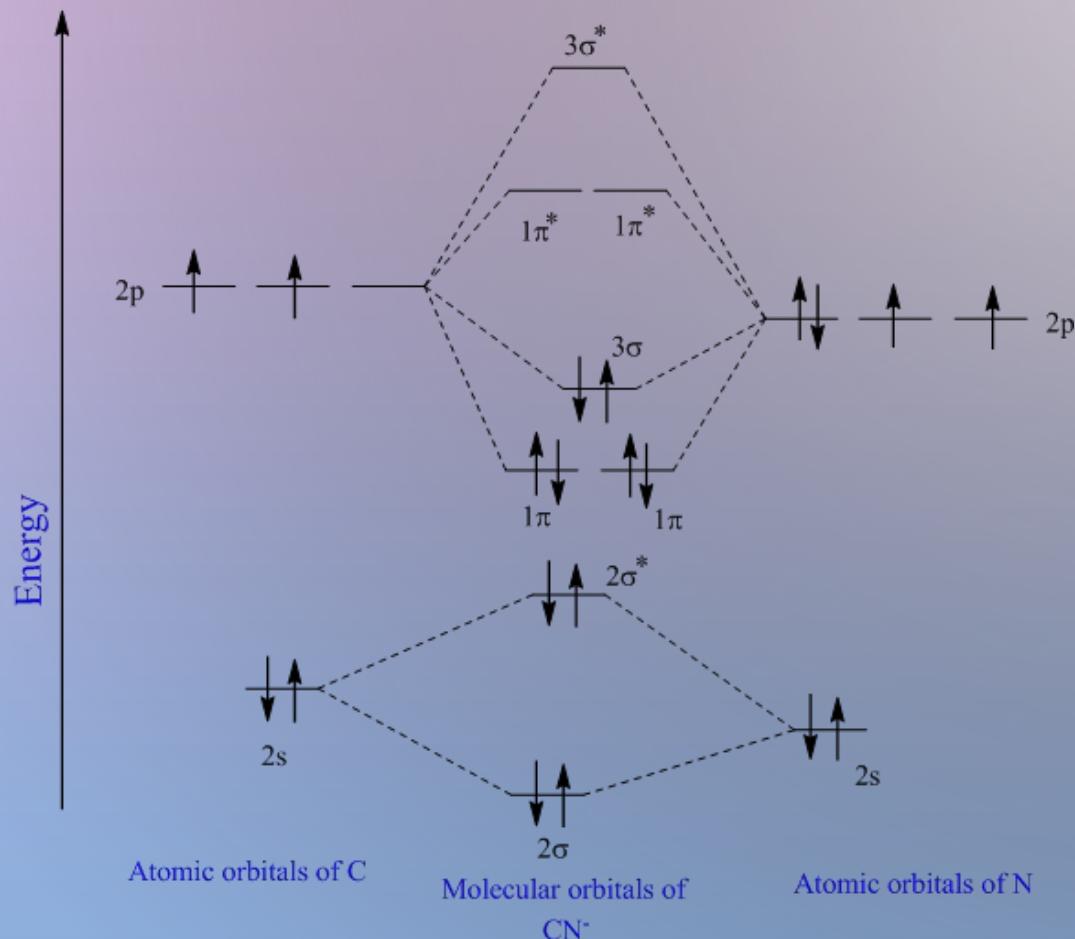
# Bonding in some heteronuclear diatomic molecules

## MO Diagram of CO molecule



- ✓ Electronic configuration of C atom  $1s^2 2s^2 2p^2$
- ✓ Electronic configuration of O atom  $1s^2 2s^2 2p^4$
- ✓ Electronic configuration of CO molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi^2 2p_x \pi^2 2p_y \sigma^2 2p_z$
- ✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{10 - 4}{2} = 3$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

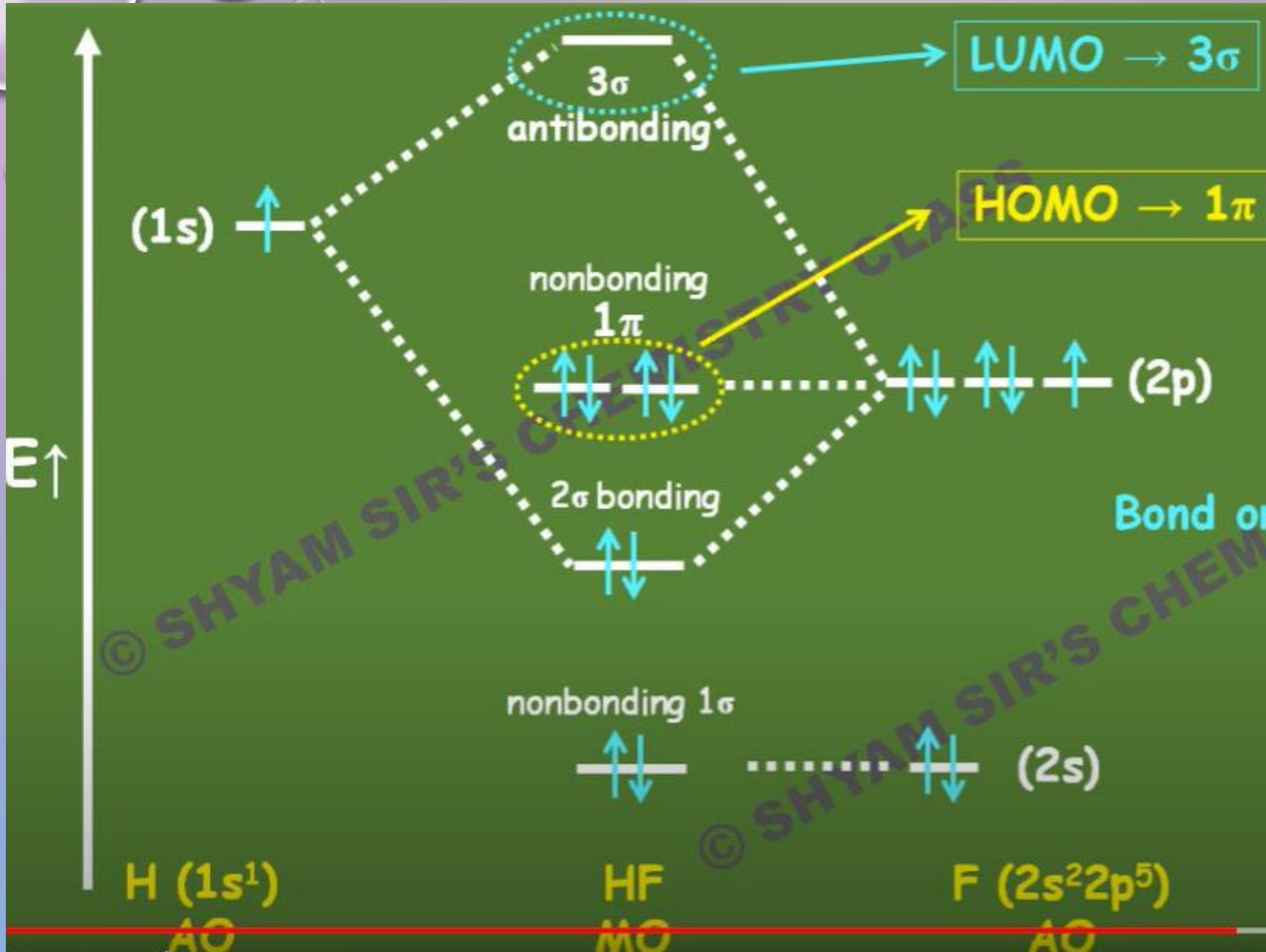
## MO Diagram of CN<sup>-</sup> molecule



- ✓ Electronic configuration of C atom  $1s^2 2s^2 2p^2$
- ✓ Electronic configuration of N<sup>-</sup> atom  $1s^2 2s^2 2p^4$
- ✓ Electronic configuration of CN<sup>-</sup> molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi^2_{2px} \pi^2_{2py} \sigma^2_{2pz}$
- ✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{10 - 4}{2} = 3$
- ✓ Molecule no unpaired electron hence it is diamagnetic

## MO diagram for HF molecule:

1. The energy of orbitals:  $1s(H) = -13.6 \text{ eV}$        $2s(F) = -40.2 \text{ eV}$   
 $2p_x = 2p_y = 2p_z (F) = -18.6 \text{ eV}$
2. It is clear from above data that energy of  $1s$  AO of F  $\ll -40.2 \text{ eV}$   
Hence, we will exclude  $1s$  AO of F in the MO diagram of HF due to extreme mismatch of energy
3.  $2s$  AO of F has much lower energy than  $1s$  AO of H atom. So, this will remain as nonbonding near F atom.
4. Three  $2p$  AOs have same energy.  $2p_z$  AO of F will combine with  $1s$  AO of H atom because they both have right symmetry to combine (in both cases  $m=0$ ). Whereas, in case of  $2p_x$  and  $2p_y$  AOs the value of  $m=+1$  and  $-1$ , respectively.



- ✓ Electronic configuration of H atom  $1s^1$

Hydrogen 

- ✓ Electronic configuration of F atom  $1s^2 2s^2 2p^5$

$1\downarrow$	$1\downarrow$	$1\downarrow$	$1\downarrow$	$1$
1s	2s	2p		

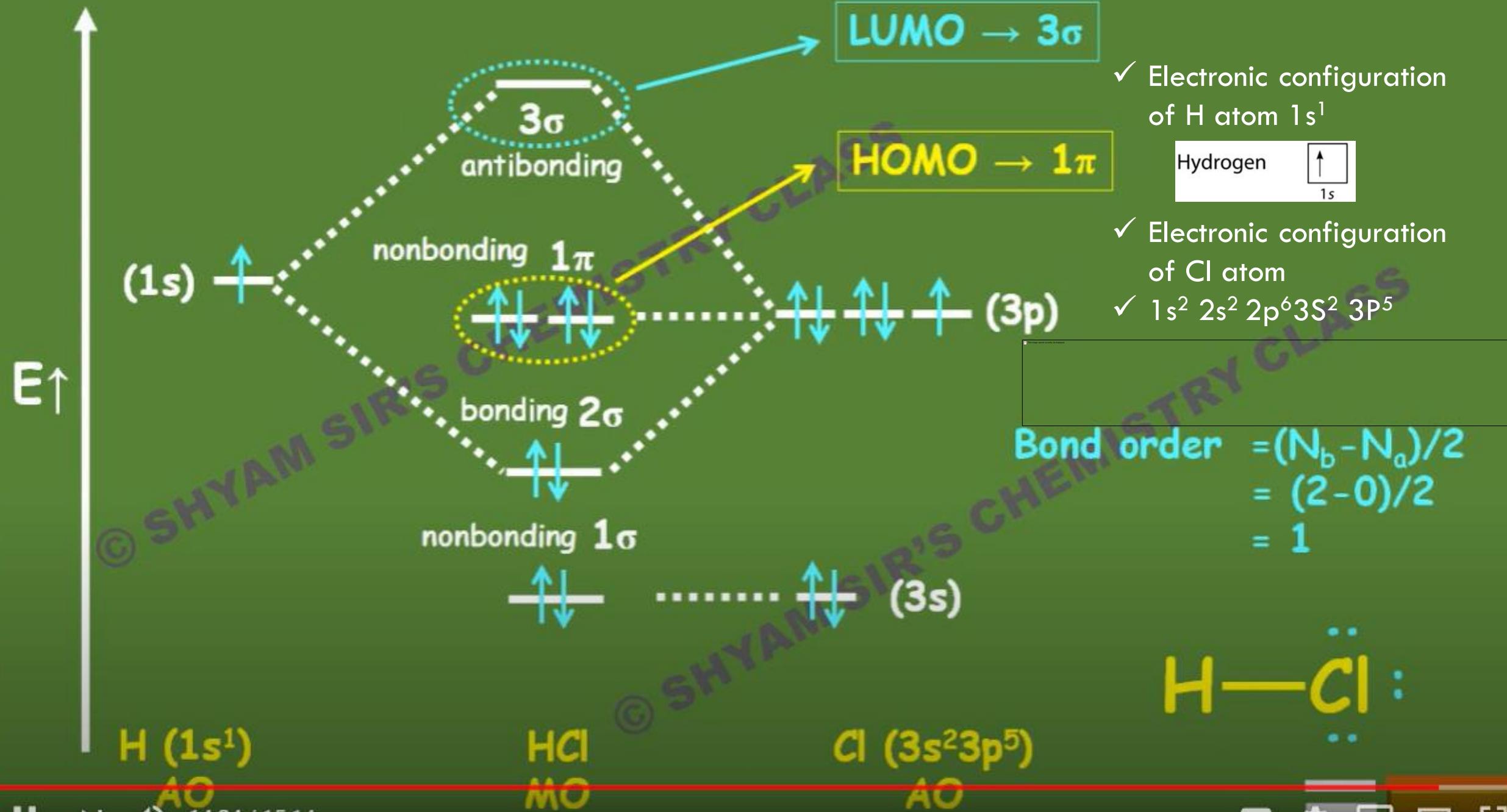
Bond order  $= (N_b - N_a)/2$   
 $= (2 - 0)/2$   
 $= 1$

$1\sigma^2 2\sigma^2 1\pi^4$

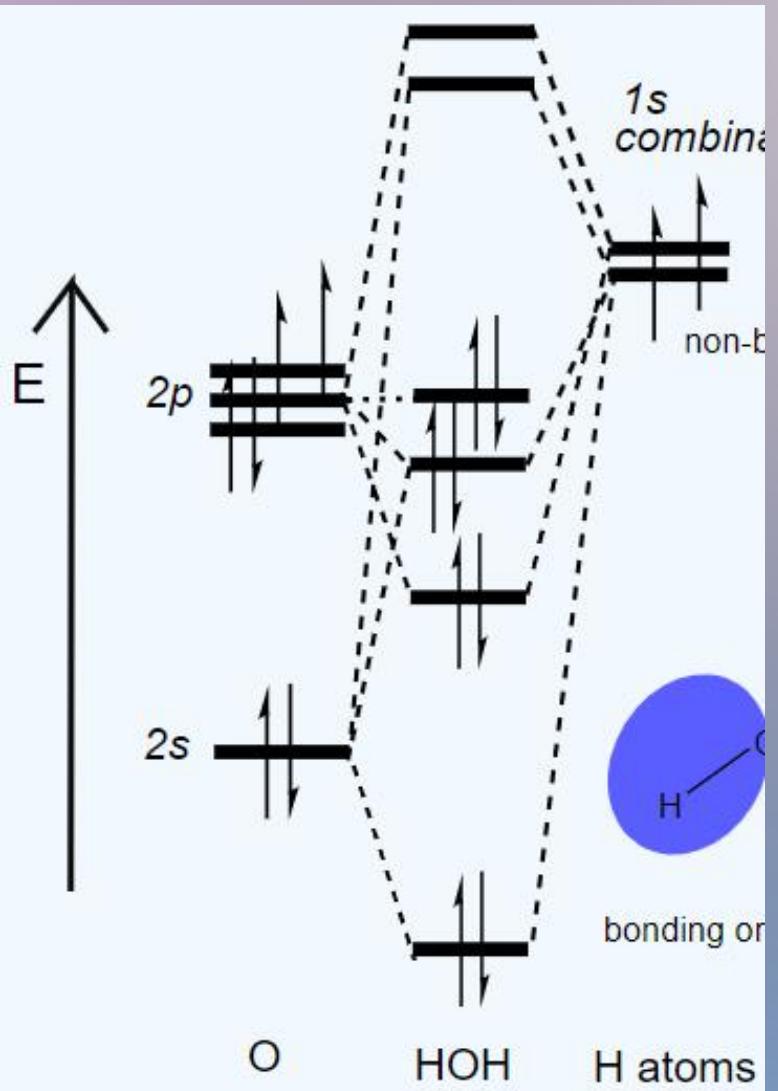


## MO diagram for HCl molecule:

1. The energy of orbitals:  $1s(H) = -13.6 \text{ eV}$        $3s(Cl) = -25.2 \text{ eV}$   
 $3p_x = 3p_y = 3p_z (Cl) = -13.7 \text{ eV}$
2. For our convenience we can consider 3s AO of Cl atom remains as nonbonding.
3.  $3p_z$  AO of Cl will combine with  $1s$  AO of H atom to produce one bonding and one antibonding molecular orbitals.
4. Whereas,  $3p_x$  and  $3p_y$  AOs remains as nonbonding.

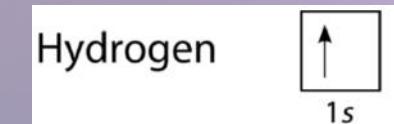


## MO Diagram of H<sub>2</sub>O molecule

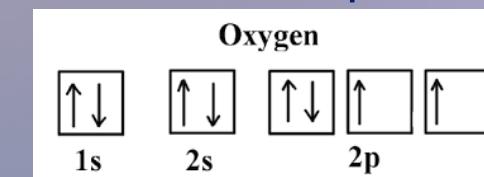


✓ Energy 1s (H) = -13.6 eV  
2s (O) = -38.3 eV  
2P (O) = -18 eV

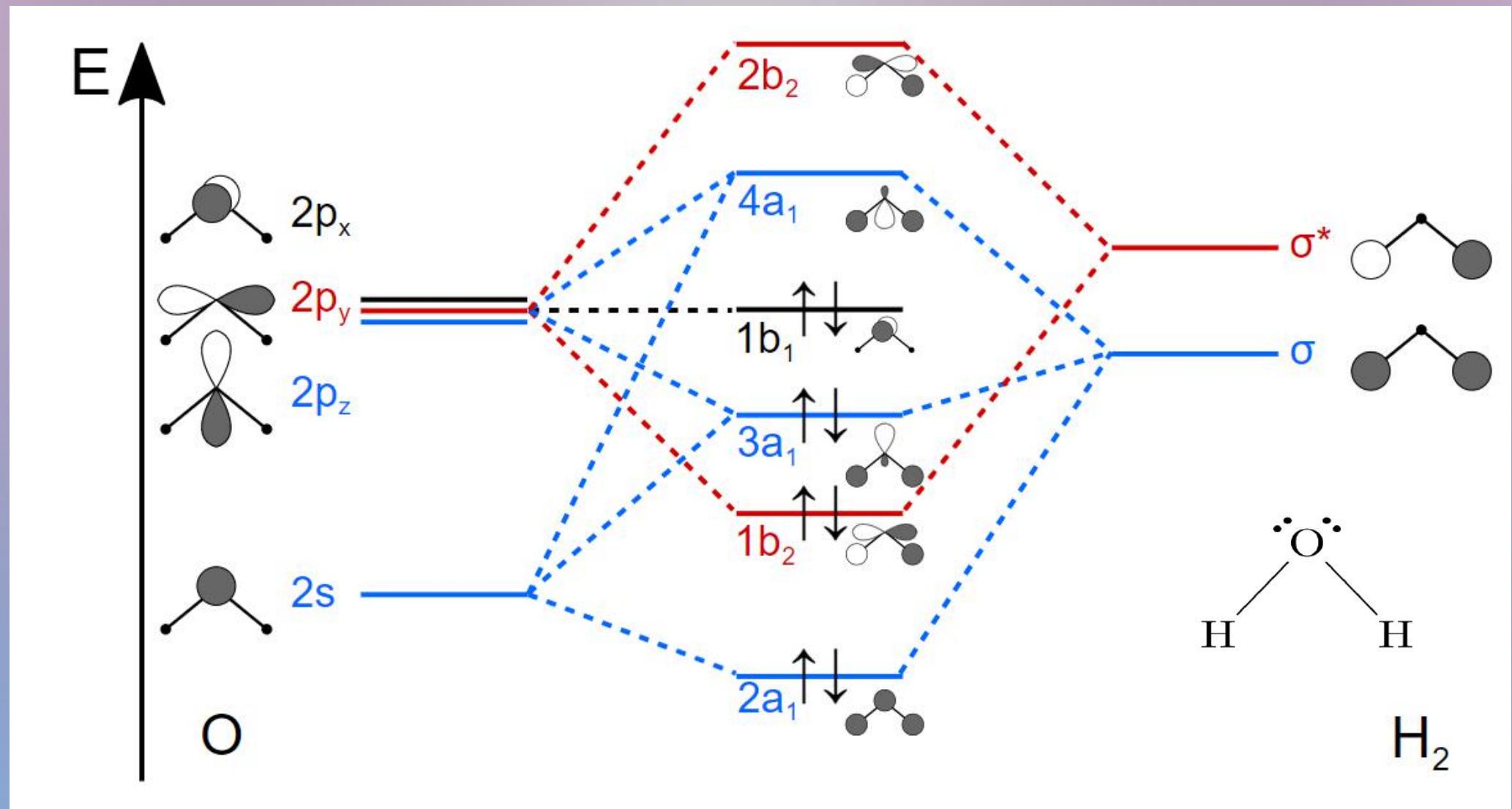
✓ Electronic configuration of H atom  $1s^1$



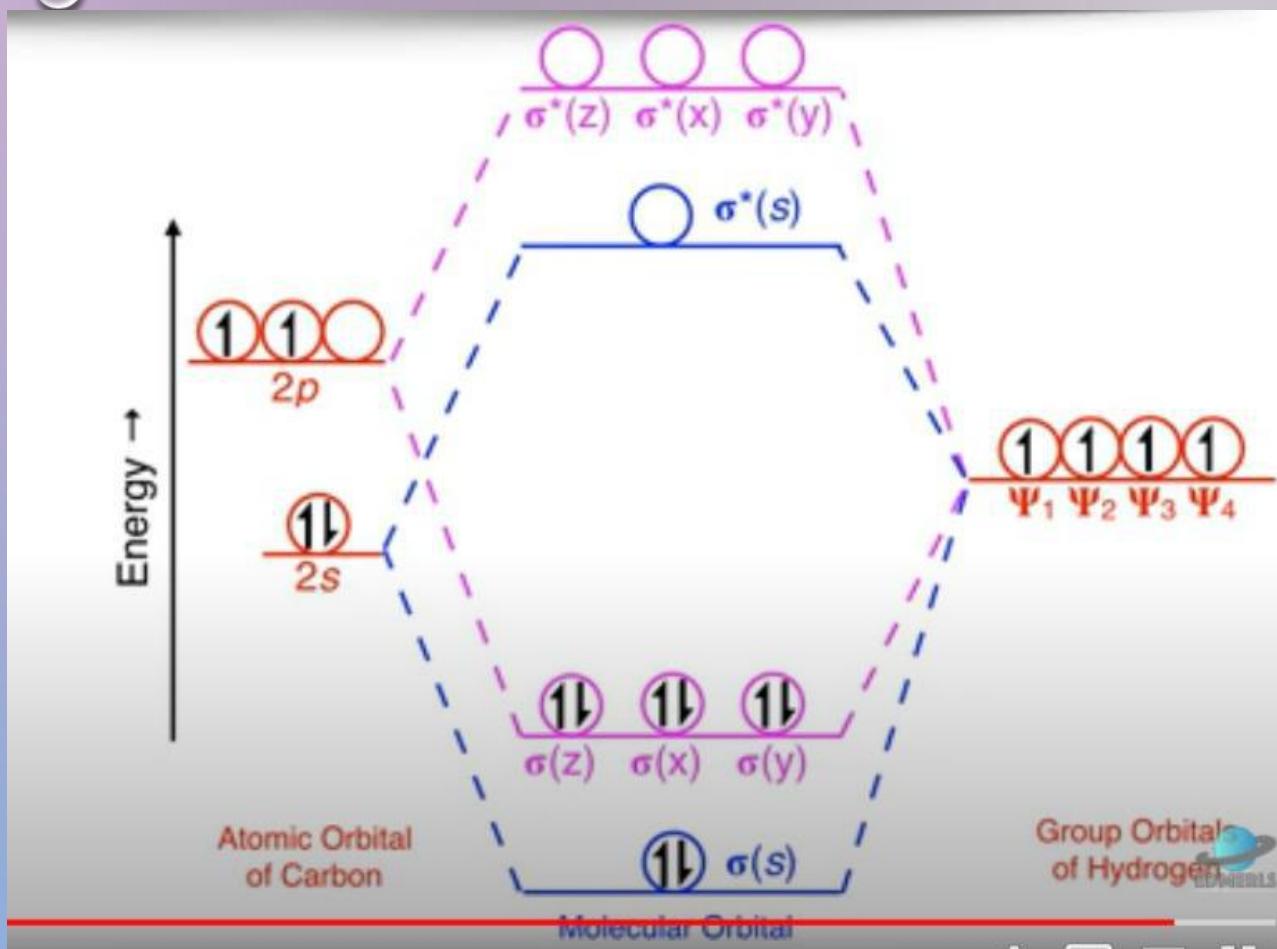
✓ Electronic configuration of O atom  $1s^2 2s^2 2p^4$



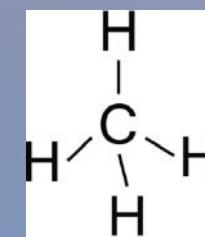
✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{4 - 0}{2} = 2$



# MO Diagram of CH<sub>4</sub> molecule



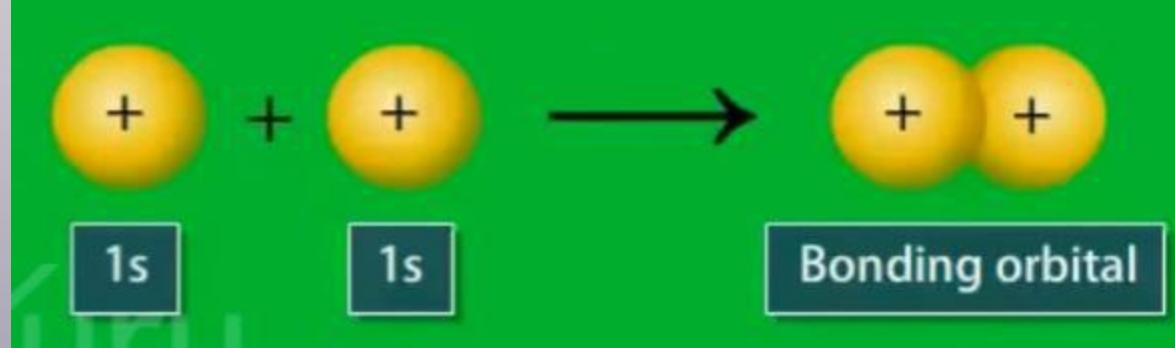
- ✓ Energy 1s (H) = -13.6 eV  
2s (C) = -19.5 eV  
2P (C) = -10.7 eV
- ✓ Electronic configuration of H atom 1s<sup>1</sup>
- ✓ Electronic configuration of C atom 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{8 - 0}{2} = 4$



## Atomic and Molecular Orbital

According to Schrodinger's wave equation an atomic orbital can be represented in terms of its wave function  $\Psi$

If for two atoms A and B each containing one electron their wave functions are represented by  $\Psi_A$  and  $\Psi_B$  respectively,

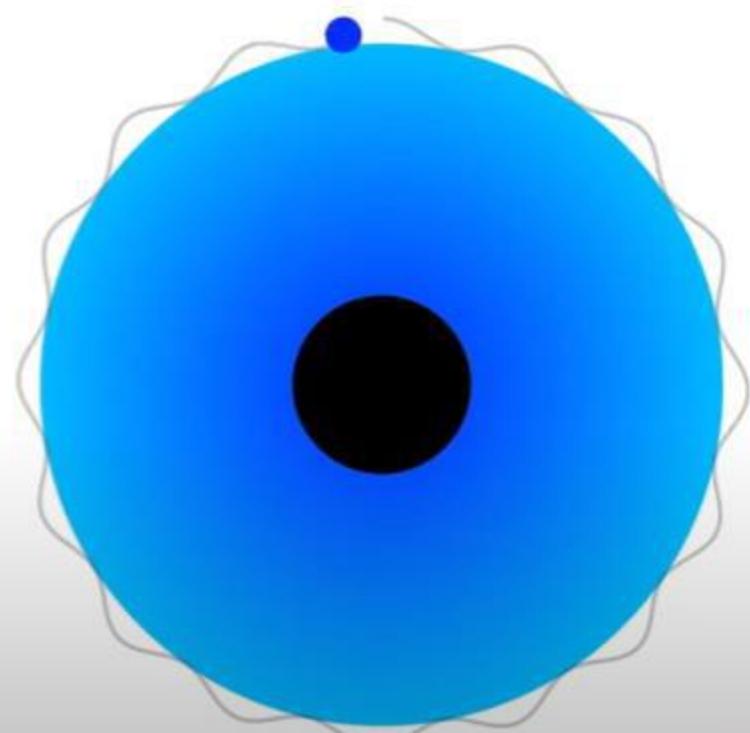


As electrons have dual nature of particle and wave.  
They can be considered as moving in atom in the form  
of a wave represented as  $\Psi$ .

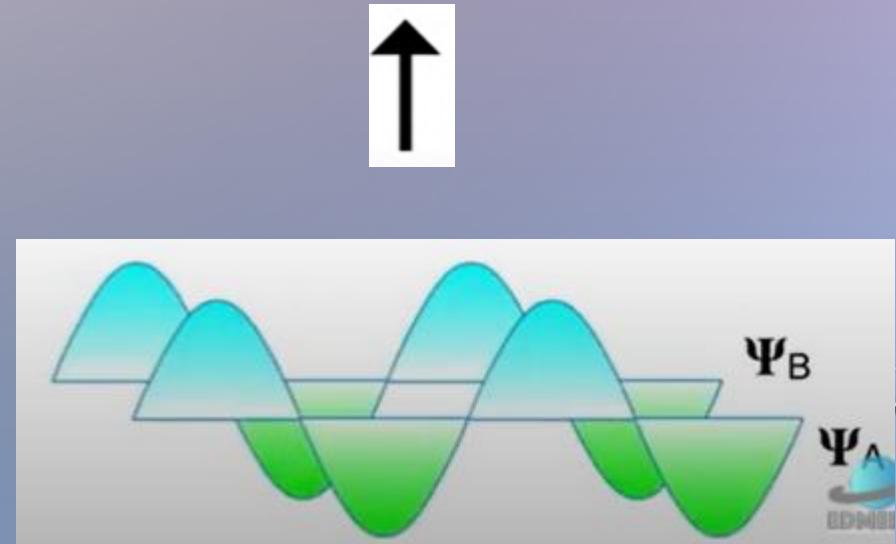
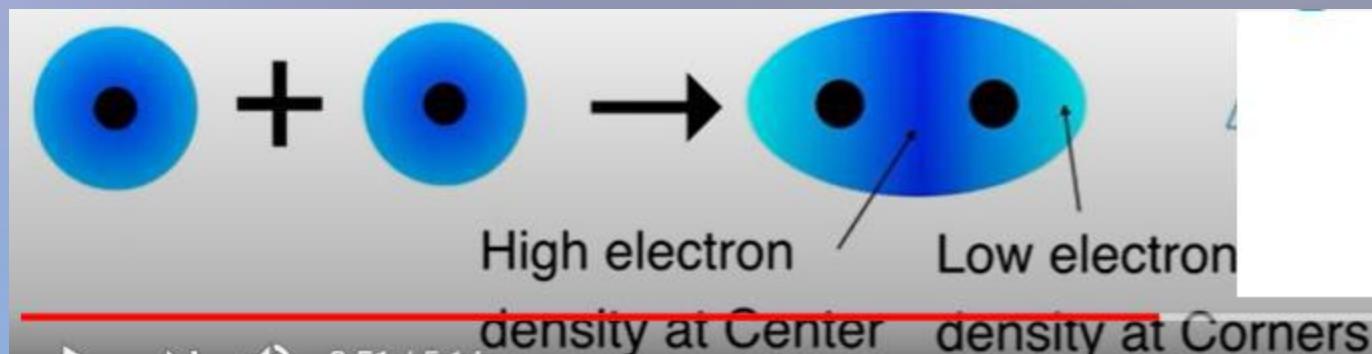
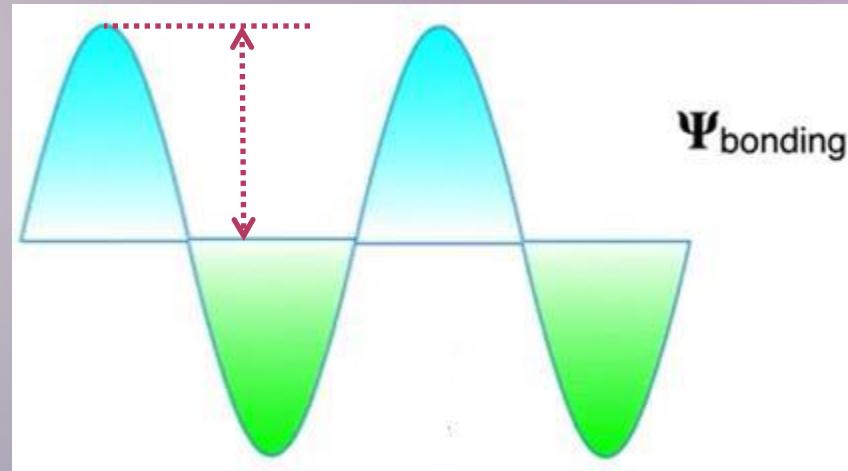
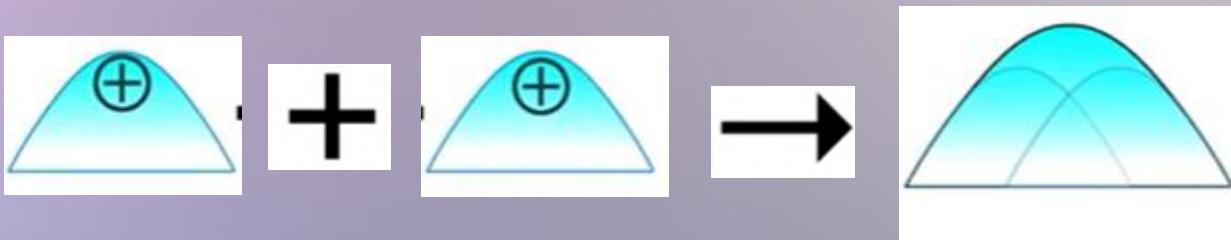
Let us consider  $\Psi_A$  is the wave function of electron of  
atom A and  $\Psi_B$  is wave function of electron of atom B.

∴ wave function of Bonding molecular orbital will be  
given by  $\Psi_{\text{bonding}} = \Psi_A + \Psi_B$

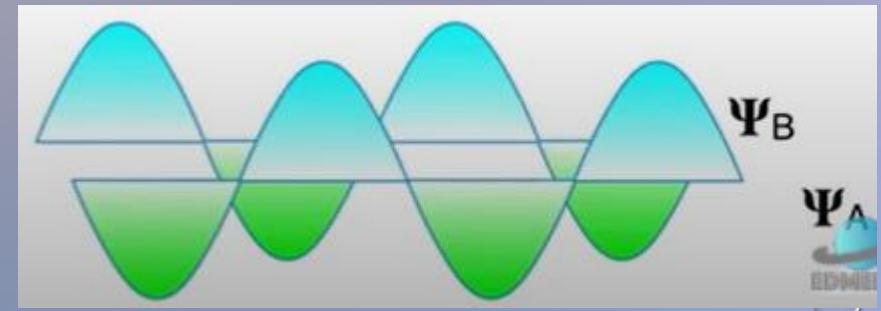
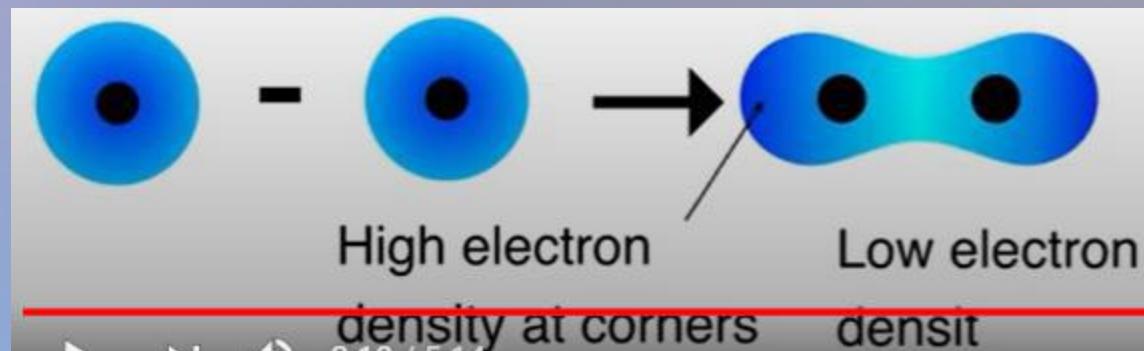
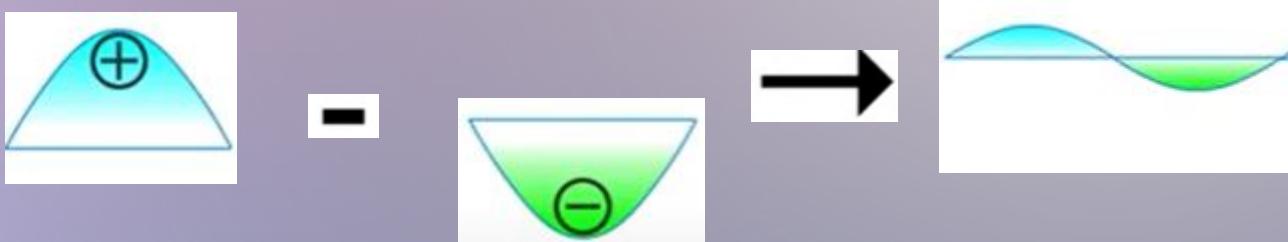
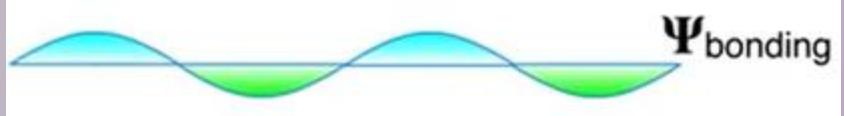
And wave function of Antibonding molecular orbital will  
be  $\Psi_{\text{antibonding}} = \Psi_A - \Psi_B$



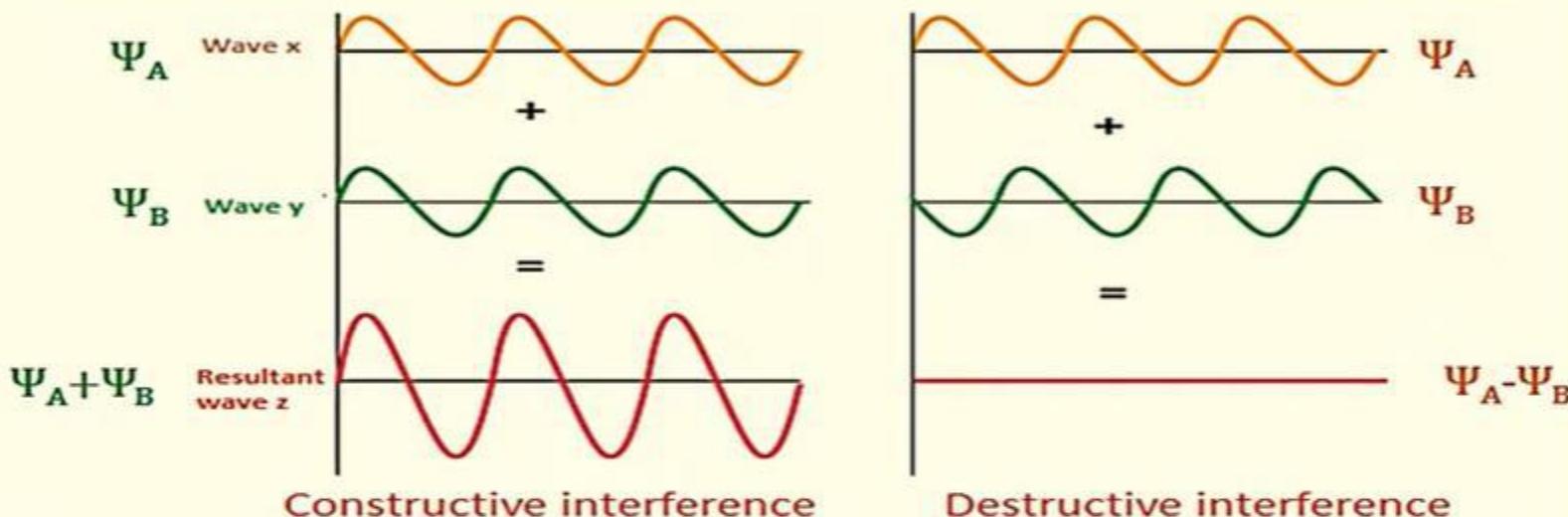
$$\Psi_{\text{bonding}} = \Psi_A + \Psi_B$$



$$\Psi_{\text{antibonding}} = \Psi_A - \Psi_B$$

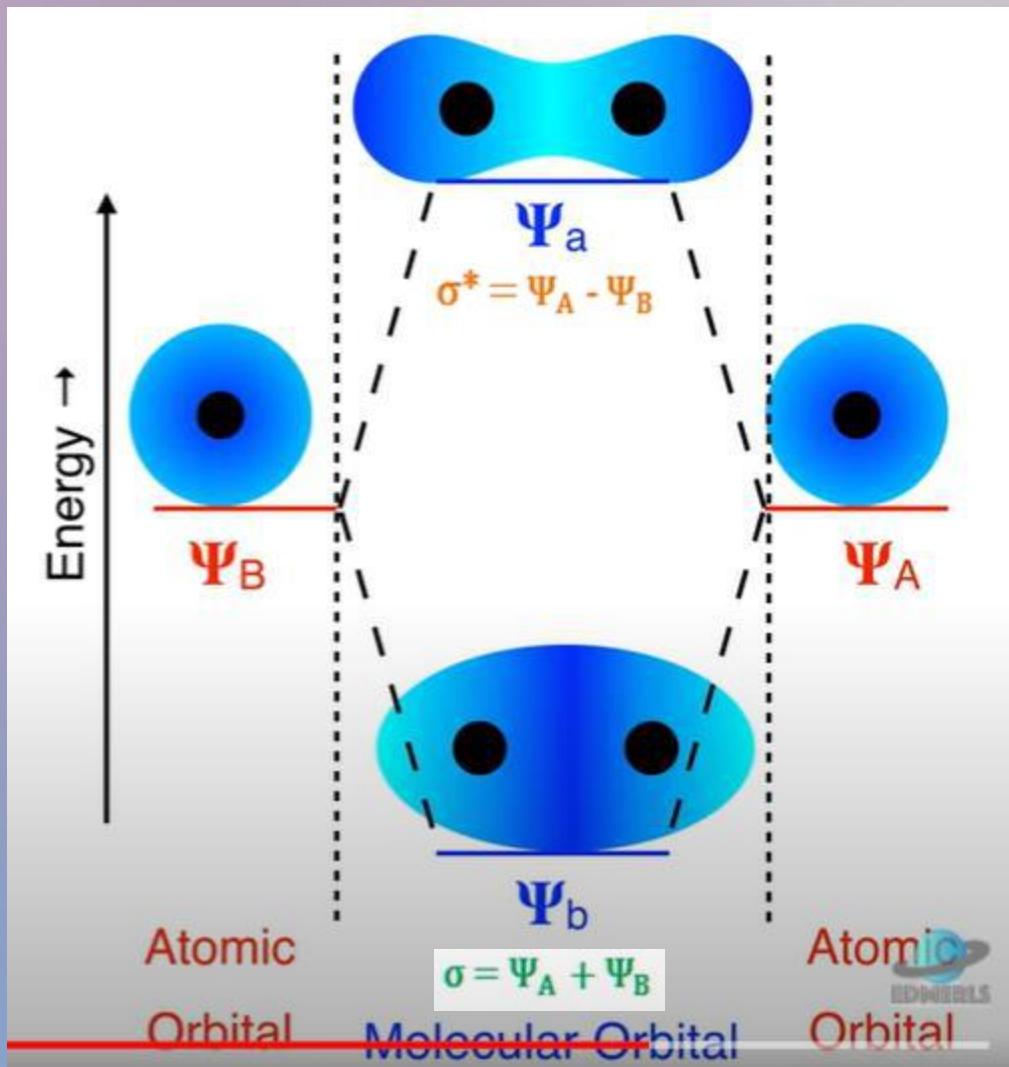


- Linear Combination of Atomic Orbitals Two AOs (A & B) combine to form an MO, the wave functions ( $\Psi_A$  &  $\Psi_B$ ) are combined both 'in phase' ( $\Psi_A + \Psi_B$ ) & 'out of phase' ( $\Psi_A - \Psi_B$ )



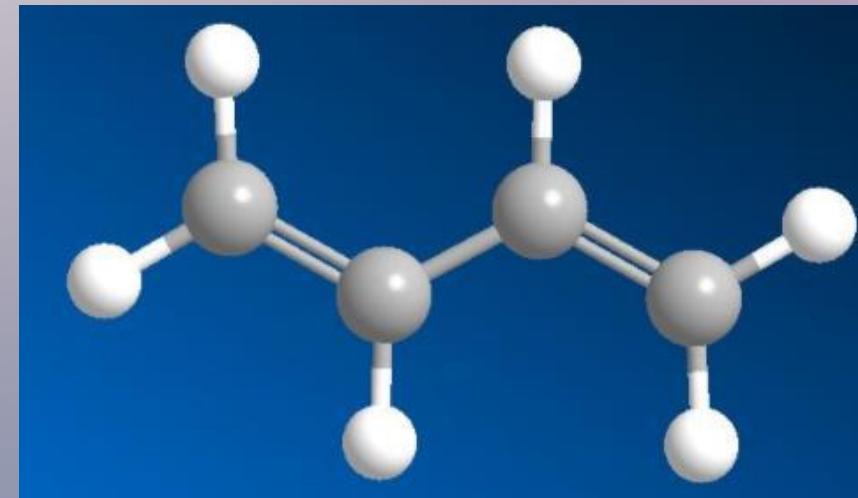
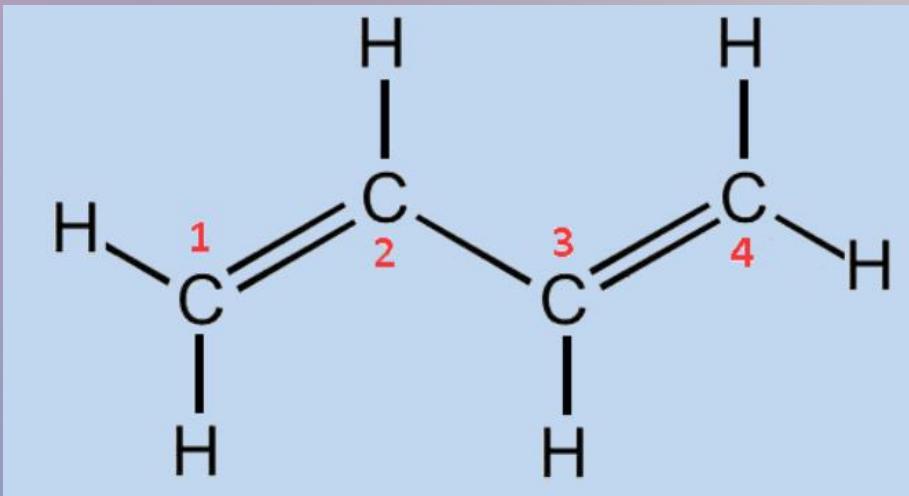
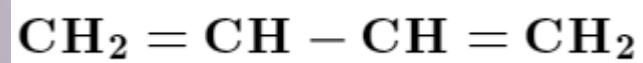
- The two electron waves of the bonding atoms reinforce each other due to constructive interference (symmetric combination), thus forming bonding MO.
- The electron waves cancel each other due to destructive interference (anti-symmetric combination), forming antibonding MO.
- The electron density in a bonding MO is located between the nuclei of the bonded atoms; so repulsion between the nuclei is very less while in case of an antibonding MO, most of the electron density is located away from the space between the nuclei.





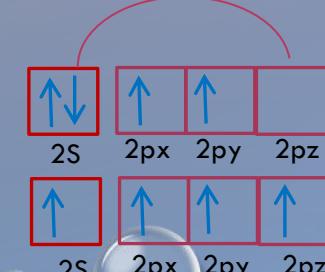
$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

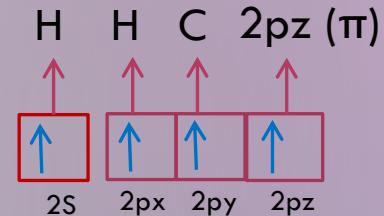
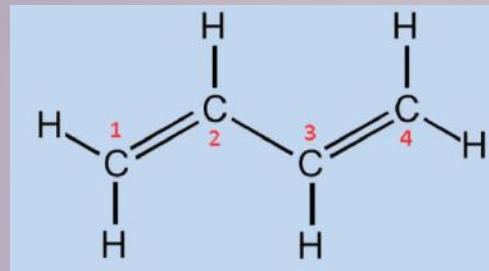
## $\pi$ Molecular Orbital of Butadiene



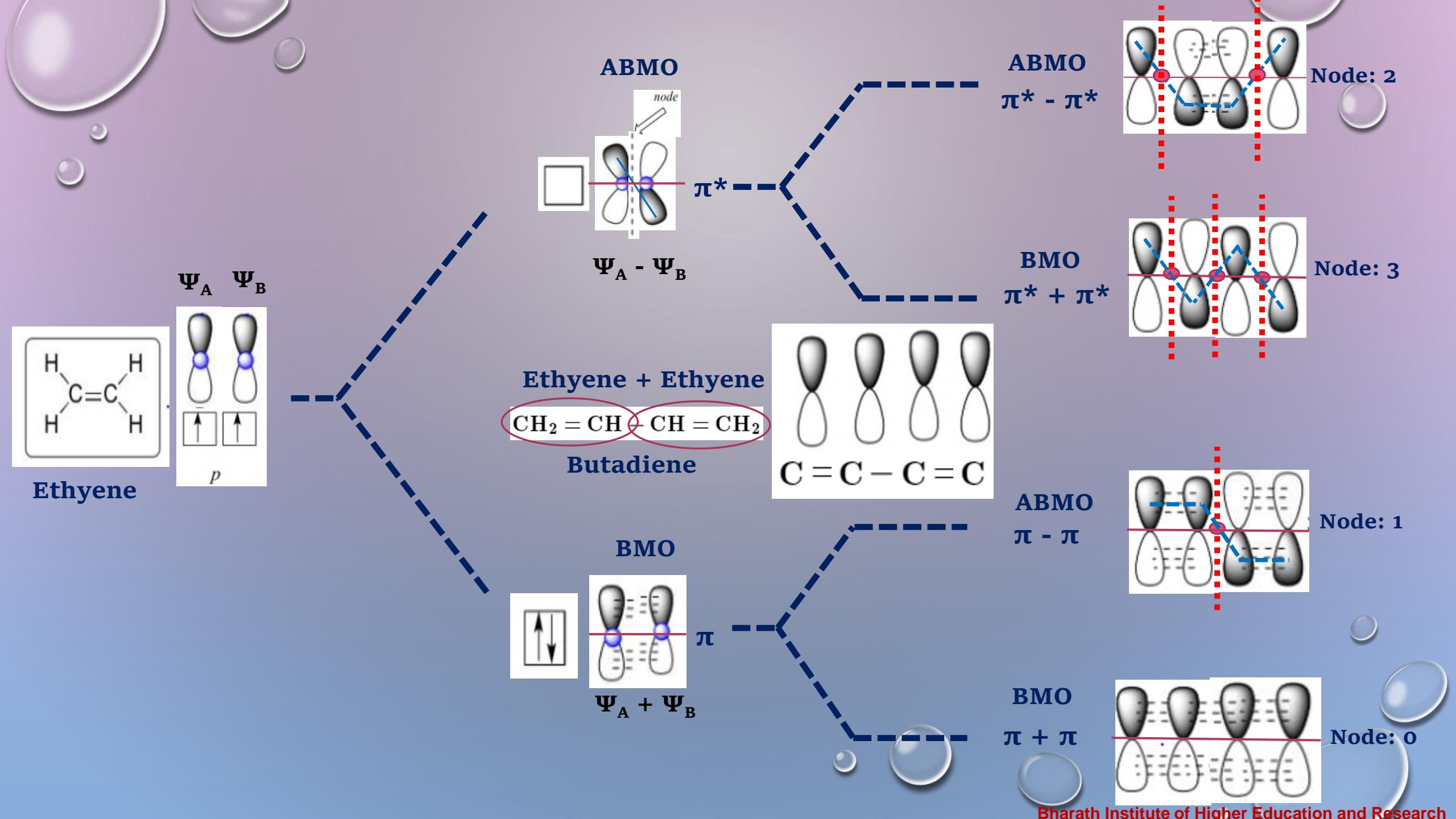
Electronic configuration of C atom  $1s^2 2s^2 2p^2$

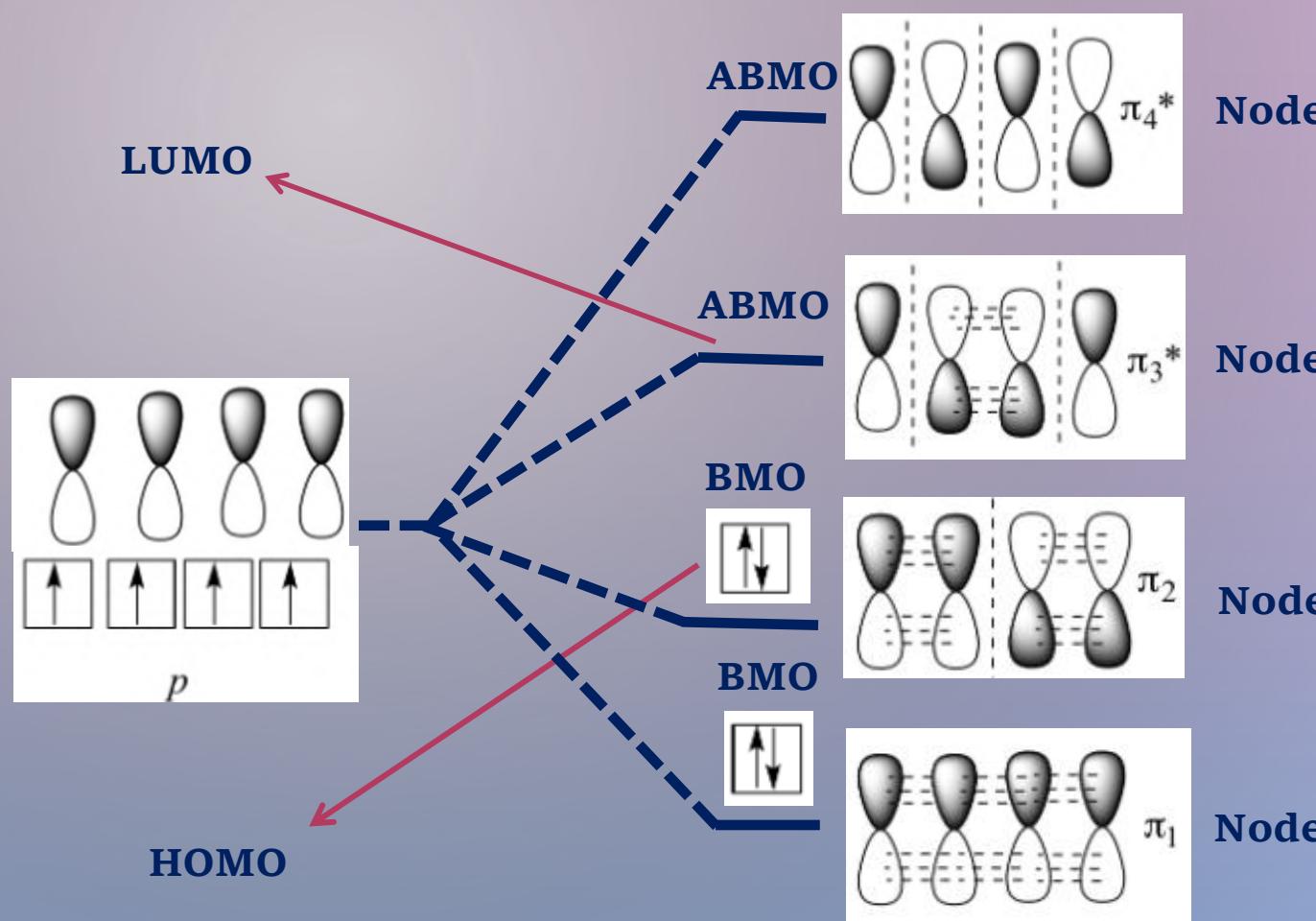
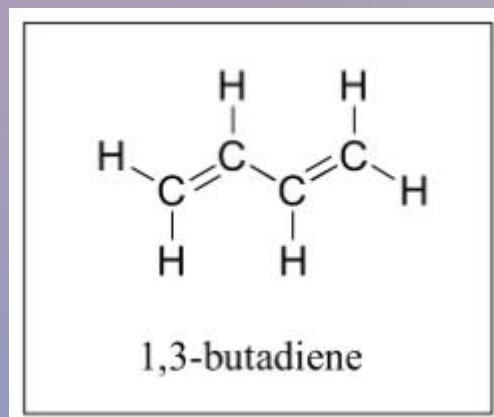
${}_6\text{C}$   
 ${}_6\text{C}^*$





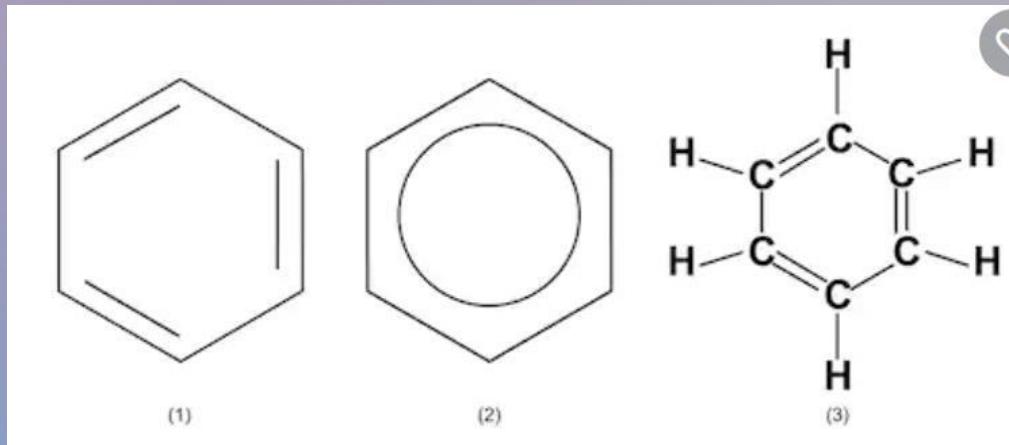
- Butadiene contains two double bonds and they are conjugated.
- Every carbon atom undergoes SP<sub>2</sub> hybridisation and forms strong  $\sigma$  – bonding with hydrogens and adjacent carbon atom.
- The unhybridized fourth Pz orbital containing one electron of each carbon atom undergo molecular bonding by overlapping, forming molecular orbital above and below the carbon atom.



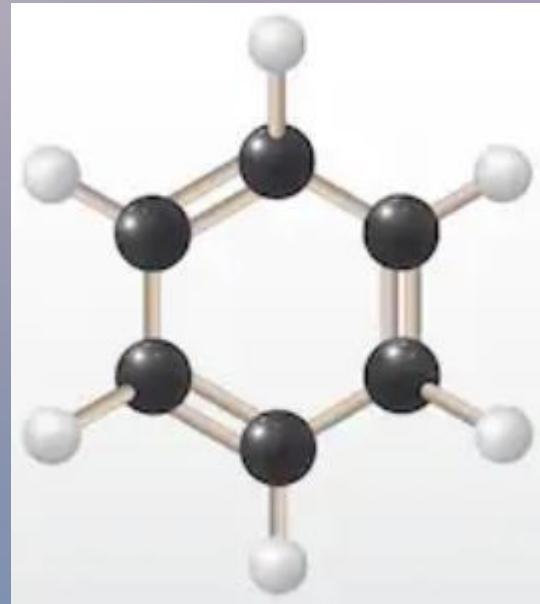


## Aromaticity and $\pi$ Molecular Orbital of Benzene

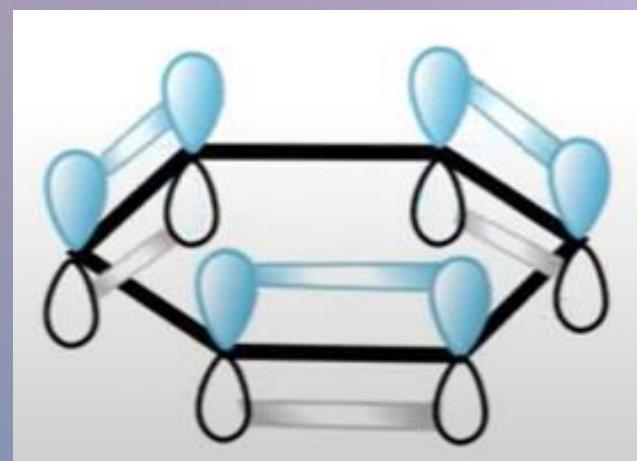
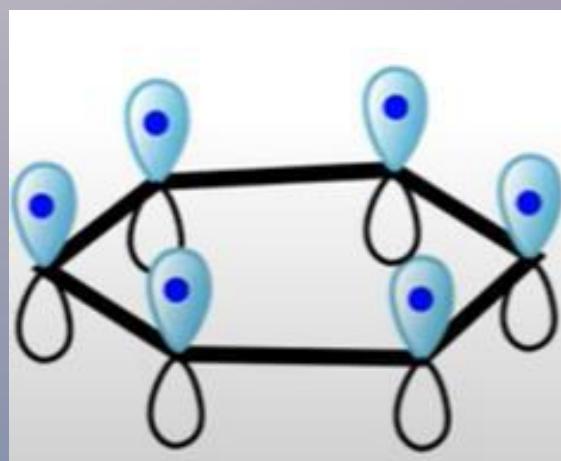
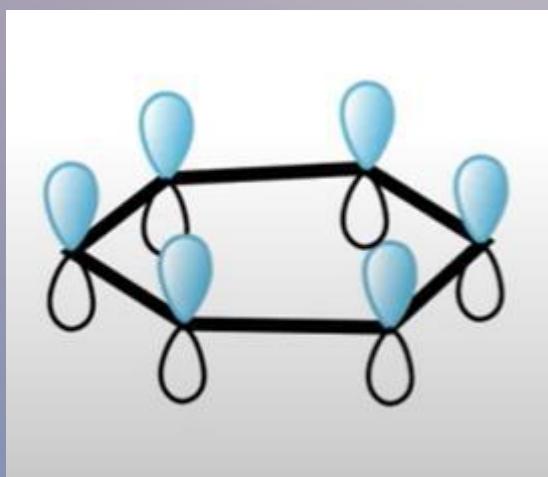
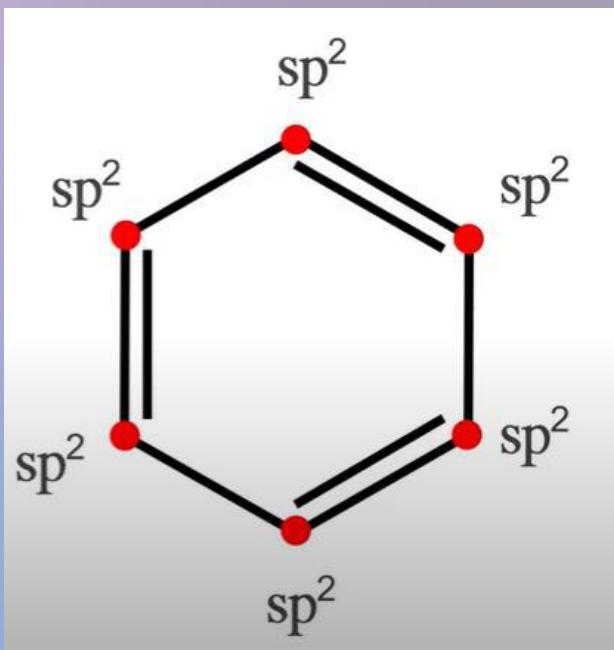
Molecular formula of benzene is  $C_6H_6$



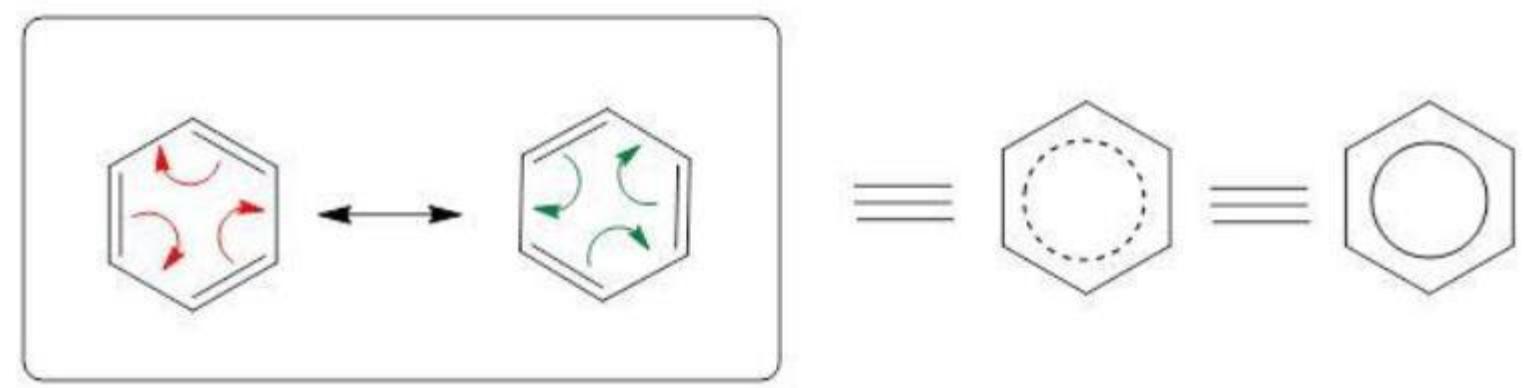
Structure of benzene



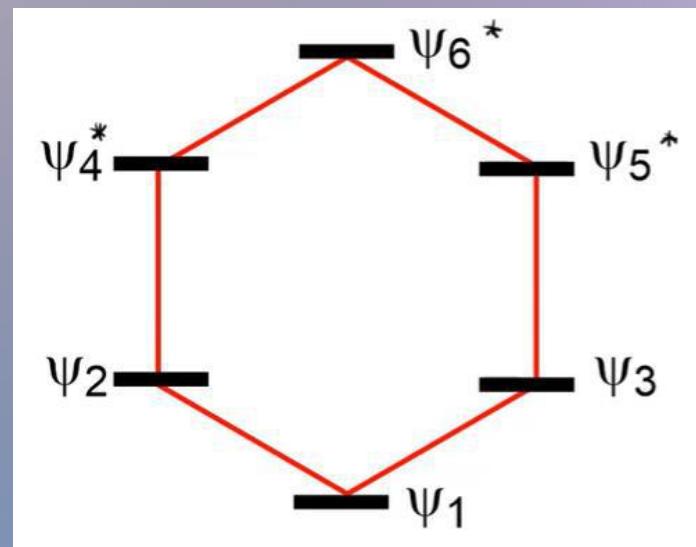
- In Benzene all the carbon atoms are  $SP^2$  hybridized.
- Each  $SP^2$  hybridized carbon atom contains unhybridized p orbital.
- Each unhybridized p orbital contains one electron.
- These six unhybridized p orbitals overlap to form three  $\pi$  bonds



- The alternative double bonds in benzene are in continuous delocalization, i.e., benzene exhibits resonance
- There are six  $2p_z$  atomic orbitals in benzene. These combine to form  $\pi$  molecular orbitals.
- Among these, three are bonding molecular orbitals ( $\Psi_1$ ,  $\Psi_2$  &  $\Psi_3$ ), and three are anti-bonding orbitals ( $\Psi_4^*$ ,  $\Psi_5^*$  &  $\Psi_6^*$ )



**Resonance structure of benzene**

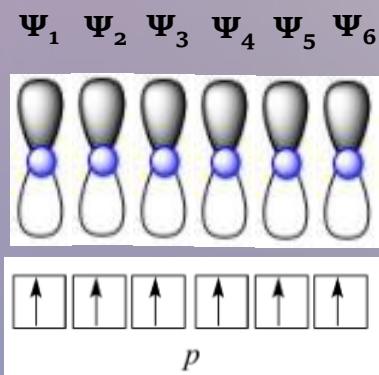
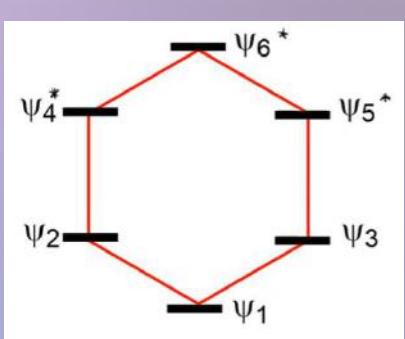


➤ The anti-bonding molecular orbital with highest energy is  $\Psi_6^*$ .

➤ It has three nodal planes

➤ The next higher energy orbitals are  $\Psi_4^*$ ,  $\Psi_5^*$  anti-bonding molecular orbitals.

➤ These are degenerate and gave two nodal planes

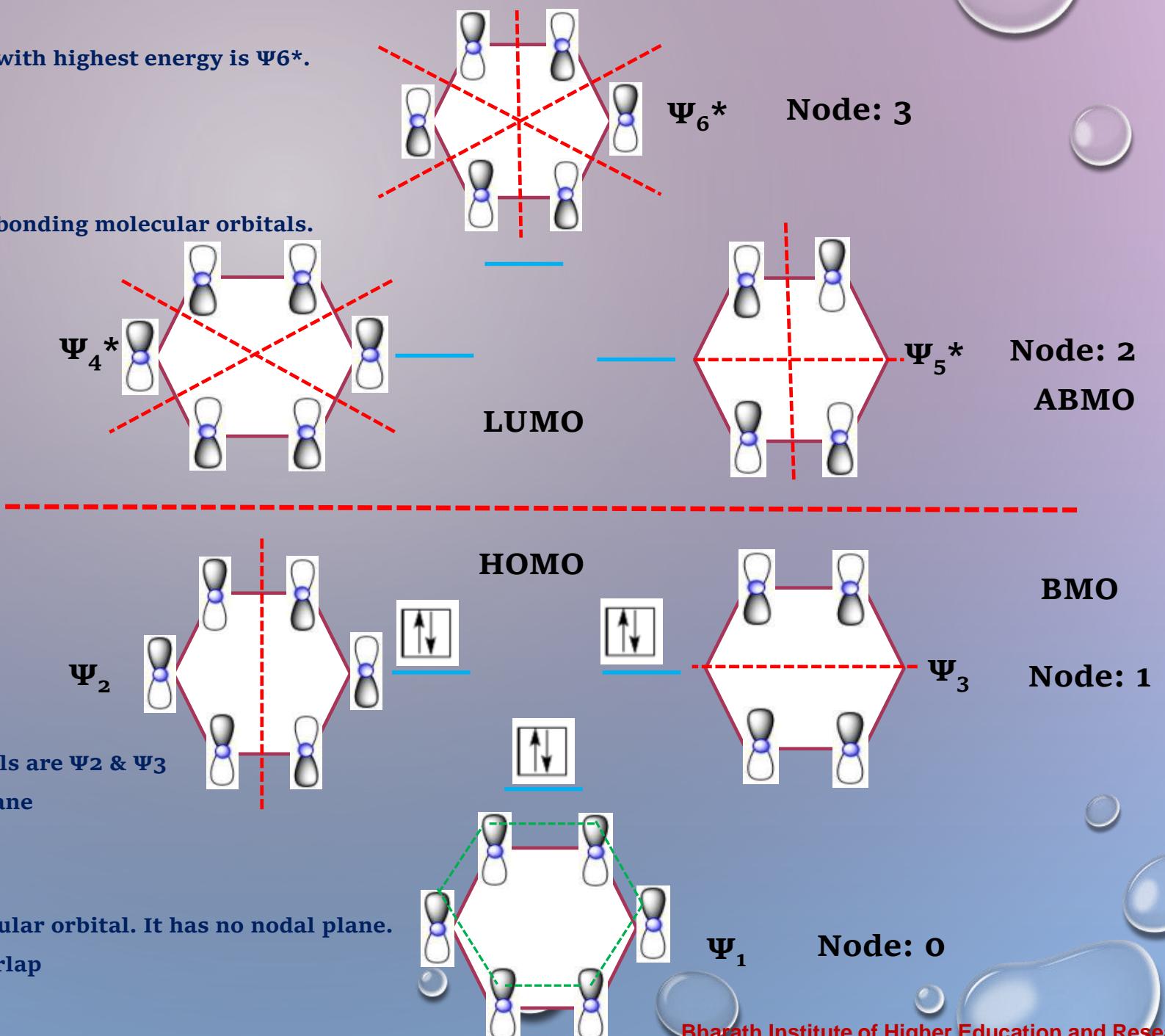


➤ The next higher energy bonding molecular orbitals are  $\Psi_2$  &  $\Psi_3$

➤ These two are degenerate and have one nodal plane

➤ The lowest Molecular orbital is the  $\Psi_1$  bonding molecular orbital. It has no nodal plane.

➤ All the six  $2p_z$  orbitals are in the same phase and overlap



## SCHRODINGER WAVE EQUATION

Schrodinger wave equation is one of the basic equations in quantum mechanics. It can be used for both macroscopic and microscopic particles. Schrodinger derived this mathematical equation to describe the dual nature of waves and also to extend the idea of waves. He has incorporated the expression for De Broglie wavelength into the general classical wave equation to form his wave equation. This equation describes the motion of the atomic particles like electrons in atom or metal. There are two forms of Schrodinger wave equation

1. Time dependent wave equation
2. Time independent wave equation

## Schrodinger Time dependent wave equation

According to classical mechanics if 'x' is the position of the particle moving with the velocity 'v' then the displacement of the particle at time 't' is given by

$$Y = A e^{-i\omega(t-x/v)}$$

where  $\omega$  is the angular frequency of the particle.

Similarly, in Quantum Mechanics the wave function  $\Psi(x, t)$  represents the position  $x$  of a moving particle at any time 't' and is given by

$$\Psi(x, t) = A e^{-i\omega(t-x/v)} \quad (1)$$

We know the angular frequency  $\omega = 2\pi\nu$

$\therefore$  Equation (1) becomes as

$$\Psi(x, t) = A e^{-2\pi i(\nu t - vx/v)} \quad (2)$$

We know  $E = h\nu$

$$\text{Or } v = \frac{E}{h} \quad (3)$$

Also, if ‘v’ is the velocity of the particle behaving as a wave, then the frequency  $\nu = \frac{v}{\lambda}$   
(or)  $\frac{\nu}{v} = \frac{1}{\lambda}$  (4)

substituting equation (3) and (4) in equation (2) we get

$$\Psi(x, t) = A e^{-2\pi i \left( \frac{E}{\hbar} t - \frac{x}{\lambda} \right)} (5)$$

If ‘p’ is the momentum of the particle behaving as a wave, then the de – Broglie wavelength is given by

$$\lambda = \frac{\hbar}{mv} = \frac{\hbar}{p} (6)$$

substituting equation (6) in (5) we get

$$\begin{aligned} \Psi(x, t) &= A e^{-2\pi i \left( \frac{Et}{\hbar} - \frac{px}{\hbar} \right)} \\ (\text{or}) \quad \Psi(x, t) &= A e^{\frac{-2\pi i}{\hbar} (Et - px)} \end{aligned} (7)$$

We can write

$$\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)} \quad (8)$$

where  $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}$  Js is called reduced Planck's constant.

Differentiating equation (8) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A e^{\frac{-i}{\hbar}(Et - px)} (ip/\hbar) \quad (9)$$

Differentiating once again partially with respect to 'x' we get

$$\frac{\partial^2 \Psi}{\partial x^2} = A e^{\frac{-i}{\hbar}(Et - px)} \left( \frac{i^2 p^2}{\hbar^2} \right) \quad (10)$$

Since  $\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)}$  and  $i^2 = -1$ , we can write

$$\frac{\partial^2 \Psi}{\partial x^2} = \Psi(x, t) \cdot \left( \frac{-p^2}{\hbar^2} \right)$$

$$(\text{or}) p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \quad (11)$$

Differentiating equation (8) partially with respect to 't' we get

$$\frac{\partial \Psi}{\partial t} = A e^{\frac{-i}{\hbar}(Et - px)} (-iE/\hbar)$$

(or)  $\frac{\hbar}{-i} \frac{\partial \Psi}{\partial t} = E \Psi$

$$[\Psi(x, t) = A e^{\frac{-i}{\hbar}(Et - px)}]$$

(Or)  $E\Psi = i\hbar \frac{\partial \Psi}{\partial t}$

(12)

A particle can behave as wave only under motion. So, it should be accelerated by a potential field (V) and kinetic energy.

**Total Energy = Potential Energy + Kinetic Energy**

Therefore the total energy  $E = V + \frac{mv^2}{2}$       **Multiply and Divide by m**

$$E = V + \frac{m^2 v^2}{2m}$$

$$E = V + \frac{p^2}{2m} \quad (p=mv)$$

$$E\Psi = V\Psi + \frac{p^2}{2m}\Psi$$

(13)

Substituting equations (11) and (12) in equations (13), we get,

$$i\hbar \frac{\partial \Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad (14A)$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{\partial \Psi}{\partial t} - V\Psi = 0 \quad (14B)$$

equation (14) represents the **Schrödinger's one dimensional time dependent wave equation**. It is called time dependent wave equation because here the wave function  $\Psi(x, t)$  depends both on position  $x$  and time  $t$ .

For a free particle, the potential energy  $V=0$  and the equation (14B) becomes

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{\partial \Psi}{\partial t} = 0 \quad (14C)$$

The equation (14C) represents **Schrödinger's one dimensional time dependent wave equation for a free particle**.

Similarly, the three dimensional form of above equation is written as

$$\frac{\hbar^2}{2m} \nabla^2 \Psi + i\hbar \frac{\partial \Psi}{\partial t} - V\Psi = 0 \quad (15)$$

where  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is the Laplacian operator

The equation (15) represents Schrödinger's three dimensional time dependent wave equation.

$$\frac{\hbar^2}{2m} \nabla^2 \Psi + i\hbar \frac{\partial \Psi}{\partial t} = 0 \quad (15A)$$

The equation (15A) represents Schrödinger's three dimensional time dependent wave equation for a free particle.

Equation (15) can be written as

$$E\Psi = H\Psi$$

where  $\Psi(x, t) = \Psi(x, y, z, t)$

where Hamiltonian operator  $H = V - \frac{\hbar^2}{2m} \nabla^2$

## Schrodinger Time Independent wave equation

We know that from equation (8), the splitting of RHS of this equation can be separated into two parts, viz, (1) Time dependent factor and (2) Time independent factor.

Therefore  $\Psi(x, t) = A e^{\frac{-iEt}{\hbar}} \cdot e^{\frac{ipx}{\hbar}}$

Or  $\Psi(x, t) = A \psi(x) e^{\frac{-iEt}{\hbar}}$  (16)

Where  $\psi(x)$  represents the time independent wave function i.e.  $\psi(x) = e^{\frac{ipx}{\hbar}}$

Differentiating equation (16) partially with respect to 't' we get

$$\frac{\partial \Psi}{\partial t} = A \psi(x) e^{\frac{-iEt}{\hbar}} \left( \frac{-iE}{\hbar} \right)$$
 (17)

$$\Psi(x, t) = A \psi(x) e^{\frac{-iEt}{\hbar}}$$

Differentiating equation (16) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A e^{\frac{-iEt}{\hbar}} \frac{\partial \psi(x)}{\partial x} \quad (18)$$

Differentiating equation (18) partially with respect to 'x' we get

$$\frac{\partial^2 \Psi}{\partial x^2} = A e^{\frac{-iEt}{\hbar}} \frac{\partial^2 \psi(x)}{\partial x^2} \quad (19)$$

From the equation (14A) the Schrödinger one dimensional time dependent wave equation is

$$i \hbar \frac{\partial \Psi}{\partial t} = V \Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

by substituting equations (17), (18) and (19) in above equation, we get

$$i \hbar A \psi(x) e^{\frac{-iEt}{\hbar}} \left( \frac{-iE}{\hbar} \right) = V A \psi(x) e^{\frac{-iEt}{\hbar}} - \frac{\hbar^2}{2m} A e^{\frac{-iEt}{\hbar}} \frac{\partial^2 \psi(x)}{\partial x^2} \quad (20)$$

$$(or) i\hbar \left( \frac{-iE}{\hbar} \right) \psi = V \psi - \frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2}$$

$$(or) - (i)^2 E \psi = V \psi - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

After simplification of the equation (20), we get

$$E \psi(x) = V \psi(x) - \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \quad \dots\dots(21)$$

Equation (21) is modified and then written as

$$(or) \quad E\psi - V\psi = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

$$(or) \quad \frac{\partial^2 \psi}{\partial x^2} = \frac{-2m}{\hbar^2} [E\psi - V\psi]$$

$$(or) \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E\psi - V\psi] = 0$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} (E-V) \psi(x) = 0 \quad (22)$$

Equation (22) is called as **Schrödinger's one dimensional time independent wave equation.**

For a free particle, the potential energy  $V=0$  and the equation (22) becomes

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad (23)$$

Equation (23) is called as **Schrödinger's one dimensional time independent wave equation for a free particle.**

Similarly the **three dimensional Schrödinger time independent wave equation** can be written as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (\mathbf{E} - \mathbf{V}) \psi = 0 \quad (24)$$

For a free particle, the potential energy  $V=0$  and the equation (23) becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} \mathbf{E} \psi = 0 \quad (25)$$

where  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is the Laplacian operator

Equation (25) is called as **Schrödinger's three dimensional time independent wave equation for a free particle.**

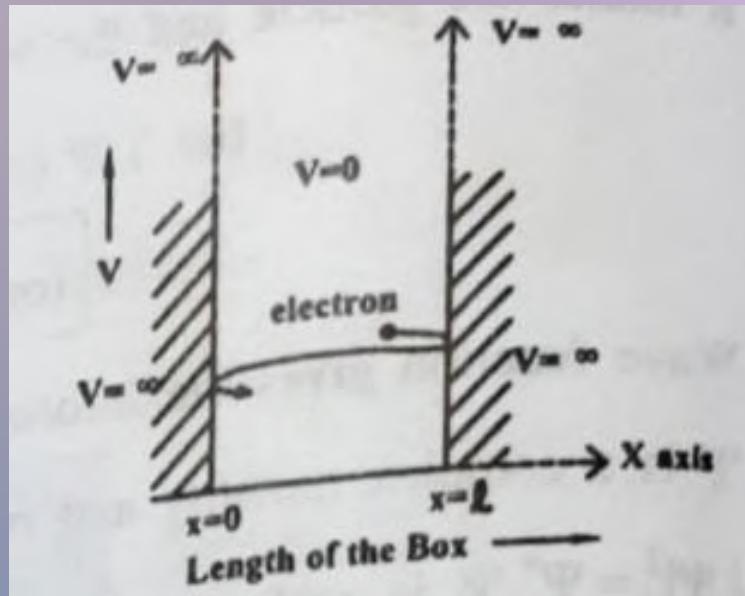
## Particle in a box solution

- Let us consider a particle (electron) of mass ‘m’ moving along with x-axis, enclosed in one dimensional potential box as shown in Figure
- Since the walls are of infinite potential the particle does not penetrate out from the box.
- Also, the particle is confined between the length ‘ $\ell$ ’ of the box and has elastic collisions with the walls. Therefore, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.
- We can say that outside the box and on the wall of the box, the potential energy  $V$  of the electron is  $\infty$ .
- Inside the box the potential energy ( $V$ ) of the electron is zero.

In other words we can write the boundary condition as

$$V(x) = 0 \text{ when } 0 < x < l$$

$$V(x) = \infty \text{ when } 0 \geq x \geq l$$



- Since the particle cannot exist outside the box the wave function  $\psi = 0$  when  $0 \geq x \geq \ell$
  - To find the wave function of the particle within the box of length ‘ $\ell$ ’, let us consider the Schrodinger one dimensional time independent wave equation

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

- Since the potential energy inside the box is zero [i.e,  $V=0$ ], the particle has kinetic energy alone and thus it is named as free a free particle or free electron

∴ For free electron, the Schrodinger wave equation is given by

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} E \Psi = 0$$

(or)

## Where

$$k^2 = \frac{2mE}{\hbar^2}$$

Equation (1) is a second order differential equation, therefore, it should have solution with two arbitrary constants

The solution for equation (1) is given by

Where A and B are called as arbitrary constants, which can be found by applying the boundary conditions.

i.e.,  $V(x) = \infty$  when  $x = 0$  and  $x = \ell$

**Boundary condition (i) at  $x = 0$ , potential energy  $V = \infty$ ,**  $\therefore$  There is no chance for finding the particle at the walls of the box,

$$\therefore \psi(x) = 0$$

$\therefore$  Equation (3) becomes

$$0 = A \sin 0 + B \cos 0$$

$$0 = \mathbf{0} + B(1)$$

$$\therefore B = 0$$

**Boundary condition (ii) at  $x = \ell$ , potential energy  $V = \infty$ .**  $\therefore$  there is no chance for finding the particle at the walls of the box,  $\therefore \psi(x) = 0$

$\therefore$  Equation (3) becomes

$$0 = A \sin Kl + B \cos kl$$

Since  $B = 0$  (1<sup>st</sup> Boundary condition), we have

$$0 = A \sin kl$$

Since  $A \neq 0$ ;  $\sin kl = 0$

We know  $\sin n\pi \equiv 0$

Comparing these two equations, we can write

$$kl = n\pi$$

Where n is an integer

Substituting the value of B and k in equation (3) we can write the wave function associated with the free electron confined in a one dimensional box as

$$\psi(x) = A \sin kx + B \cos kx$$

## Energy of the particle (electron)

We know from equation (2)

$$k^2 = \frac{2mE}{\hbar^2}$$

$$k^2 = \frac{2mE}{h^2/4\pi^2}$$

(or)

Squaring equation (4) we get

Equating equation (6) and equation (7), we can write

$$\frac{8\pi^2 m E}{\hbar^2} = \frac{n^2 \pi^2}{l^2}$$

∴ Energy of the particle (electron)

$$E_n = \frac{n^2 h^2}{8ml^2} \quad \dots \dots \dots \quad (8)$$

From equations (8) and (5) we can say that, for each value of 'n', there is an energy level and the corresponding wave function. Thus we can say that, each value of  $E_n$  is known as Eigen value and the corresponding value of  $\psi_n$  is called as Eigen function.

# Energy Level of an electron

For various values of 'n' we get various energy values of the electron. The lowest energy value or ground state energy value can be got by

Substituting  $n = 1$  in equation (8)

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

When  $n = 1$  we get

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

Similarly we can get the other energy values

i.e., when  $n = 2$  we get

$$E_2 = \frac{4h^2}{8ml^2} = 4E_1$$

when  $n = 3$  we get

$$E_3 = \frac{9h^2}{8ml^2} = 9E_1$$

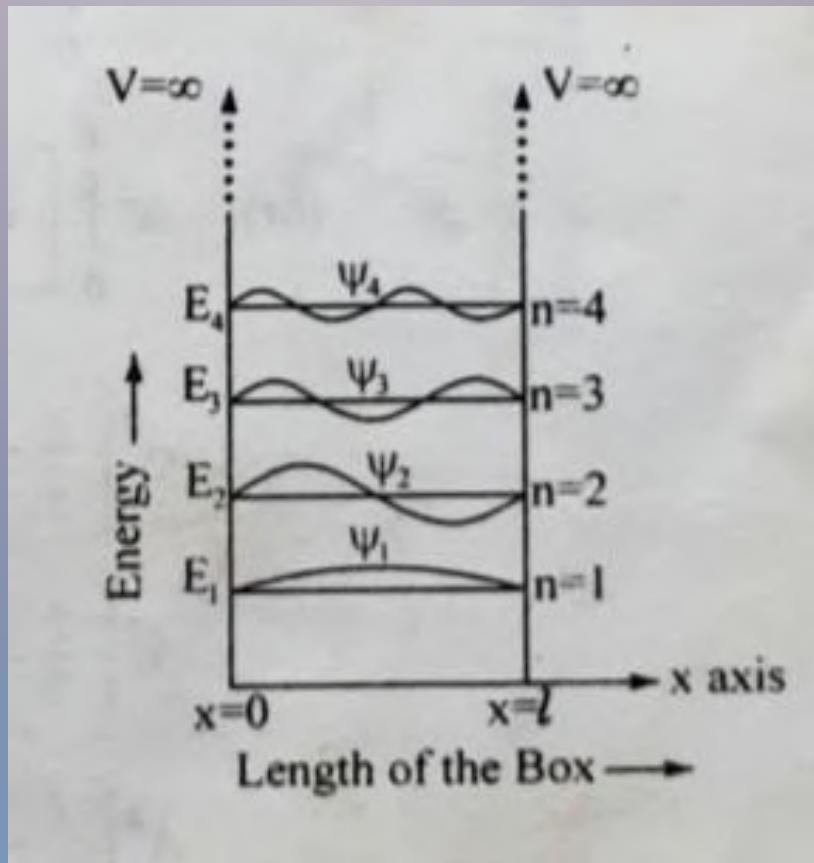
when  $n = 4$  we get

$$E_4 = \frac{16h^2}{8ml^2} = 16E_1$$

∴ in general we can write the energy Eigen function as

$$E_n = n^2 E_1 \quad \dots \quad (9)$$

- It is found from the energy levels  $E_1, E_2, E_3$  etc., the energy levels of an electron are discrete
- The various energy Eigen values and their corresponding Eigen function of an electron enclosed in one dimensional box is shown in Figure.



## Normalisation of the wave function

- Normalisation: It is the process by which the probability (P) of finding the electron inside the box can be done
- We know that the total probability (P) is equal to 1 means there is a particle inside the box  
∴ For a one dimensional potential box of length ' $\ell$ ', the probability

$$P = \int_0^\ell |\psi|^2 dx = 1 \quad (\text{Since the particle is present inside the wall between the length } 0 \text{ to } \ell \text{ the limits are chosen between } 0 \text{ to } \ell) \dots\dots\dots(10)$$

Substituting equation (5) in equation (10), we get

$$\Psi = A \sin \frac{n\pi x}{l} \quad \dots\dots\dots(5)$$

$$P = \int_0^l A^2 \sin^2 \frac{n\pi x}{l} dx = 1$$

$$A^2 \int_0^l \left[ \frac{1 - \cos \frac{2n\pi x}{l}}{2} \right] dx = 1$$

$$A^2 \left[ \frac{x}{2} - \frac{1}{2} \frac{\sin \frac{2n\pi x}{l}}{2n\pi/l} \right]_0^l = 1$$

$$A^2 \left[ \frac{l}{2} - \frac{1}{2} \frac{\sin \frac{2n\pi l}{l}}{2n\pi/l} \right] = 1$$

$$A^2 \left[ \frac{l}{2} - \frac{1}{2} \frac{\sin 2n\pi}{2n\pi/l} \right] = 1$$

We know  $\sin n\pi = 0 \therefore \sin 2n\pi = 0$

$\therefore$  Equation (11) can be written as

$$\frac{A^2 l}{2} = 1$$

$$A^2 = \frac{2}{l}$$

$$A = \sqrt{\frac{2}{l}}$$

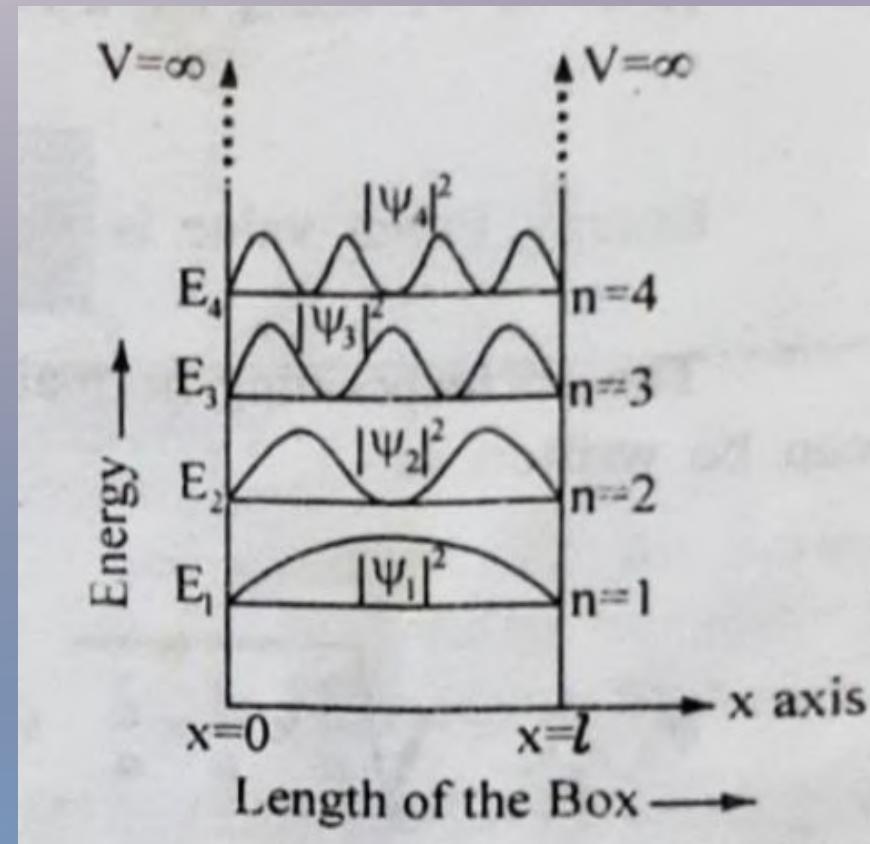
Substituting the value of 'A' in equation (5)

$$\psi_n(x) = A \sin \frac{n\pi x}{l}$$

The normalised wave function can be written as

$$\psi_n = \sqrt{2/l} \sin \frac{n\pi x}{l}$$

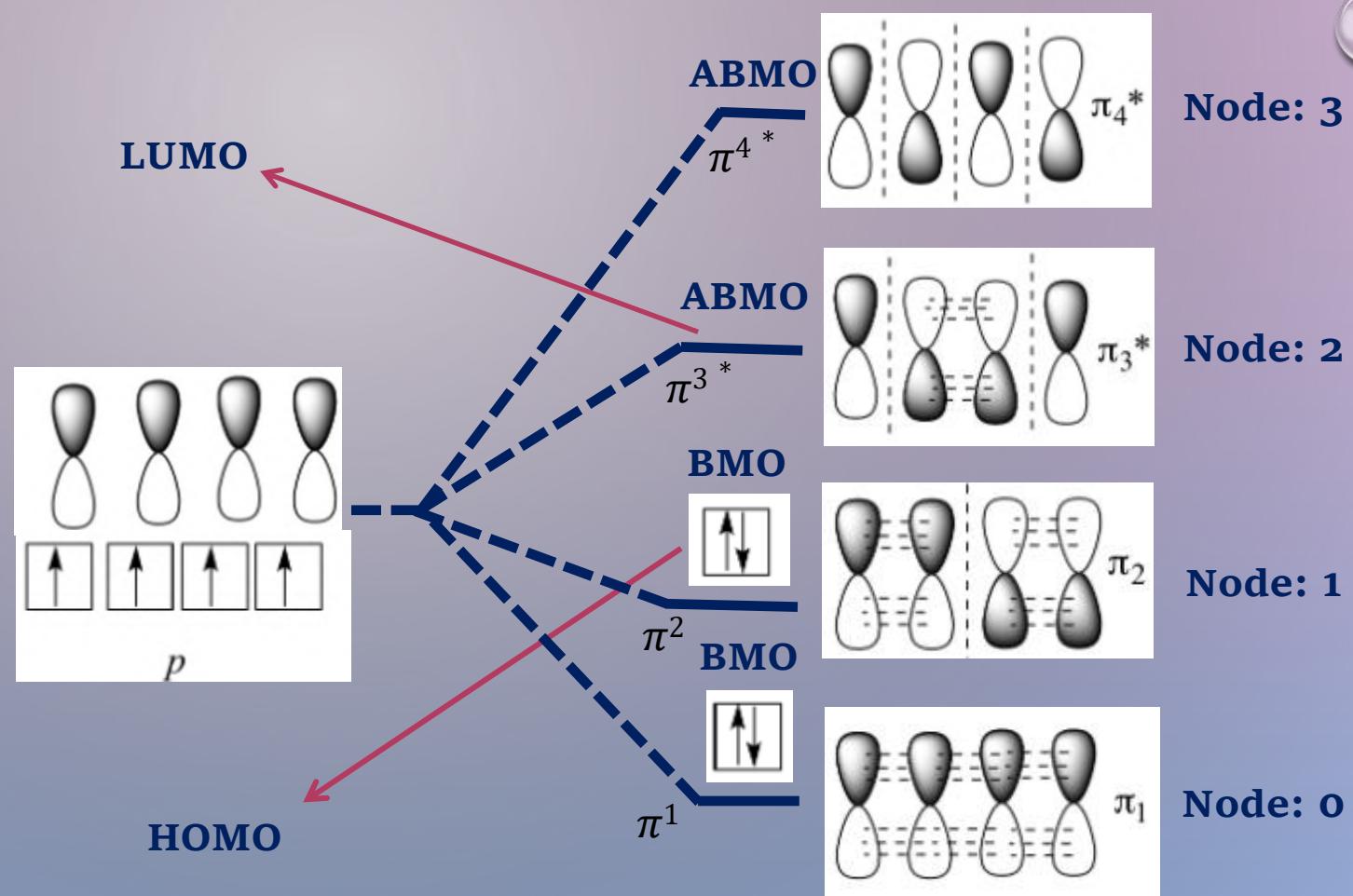
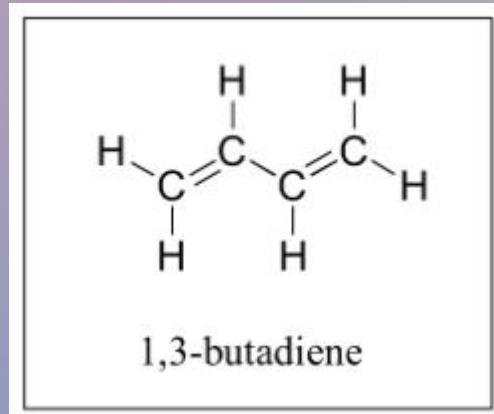
The normalised wave function and their energy values are as shown in Figure



## APPLICATIONS FOR CONJUGATED MOLECULES

### Calculation of $\Delta E$ of the conjugated molecules

- $\Delta E$  means the energy difference between HOMO represented by (n) and LUMO represented by (n+1) in case of conjugated molecules as polyenes can be studied by the application on particle in a box
- Polyenes – compounds having several conjugated single and double bonds
- Eg  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
- $\pi$  Electron of molecule can be correlated with the system a particle in one dimensional box
- Thus knowing the mass of electron (m) and length of the 1 D box ( $\ell$ )



- The electron energy level can be determined using equation (1)

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

- Where  $n = 1, 2, 3, \dots$
- $n$  = quantum number of particle
- $E$  = Energy associated with the motion of a particle in a box
- $h$  = plank's constant
- $m$  = mass of electron
- $\ell$  = length of molecule

### Energy between HOMO and LUMO

$$(a + b)^2 = a^2 + b^2 + 2ab$$

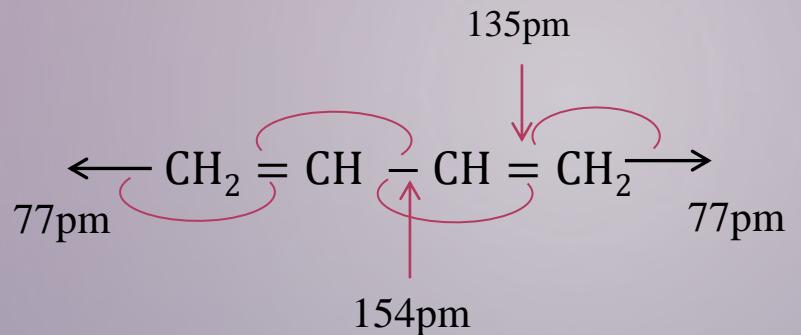
$$(n + 1)^2 = n^2 + 1^2 + 2n(1)$$

$$(n + 1)^2 - n^2 = n^2 + 1 + 2n - n^2$$

$$(n + 1)^2 - n^2 = 2n + 1$$

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= \frac{(n + 1)^2 h^2}{8ml^2} - \frac{n^2 h^2}{8ml^2} \\ &= [(n + 1)^2 - n^2] \frac{h^2}{8ml^2} \\ \Delta E &= (2n + 1) \frac{h^2}{8ml^2}\end{aligned}$$

## Length of the molecule



$$\begin{aligned}\text{Length of the box} &= 1 \times (\text{single bond length}) + 2 \times (\text{double bond length}) + 154\text{pm} \\ &= 1 \times 154\text{pm} + 2 \times 135\text{pm} + 154\text{pm} \\ &= 154 \times 2 + 135 \times 2 \\ &= 308 + 270 \\ &= 578 \text{ pm} \\ &= 578 \times 10^{-12} \text{ m}\end{aligned}$$

$$n = \frac{\text{Total number of electron}}{2}$$

$$n = \frac{4}{2} = 2$$

$$\text{Mass of electron} = 9.11 \times 10^{-31} \text{ kg}$$

$$\text{Plank's constant} = 6.626 \times 10^{-34} \text{ J Sec}$$

$$\begin{aligned}\Delta E &= (2n + 1) \frac{h^2}{8ml^2} \\ &= (2(2) + 1) \frac{(6.626 \times 10^{-34} \text{ J Sec})^2}{8 \times 9.11 \times 10^{-31} \text{ kg} \times (578 \times 10 - 12 \text{ m})2}\end{aligned}$$

$$= \frac{5 (43.90 \times 10^{-68}) \text{ J}^2 \text{ sec}^2}{8 \times 9.11 \times 10^{-31} \text{ kg} \times (5.78 \times 10 - 10 \text{ m})2}$$

$$= \frac{5 (43.90 \times 10^{-68})}{8 \times 9.11 \times 10^{-31} \times 33.40 \times 10^{-20}} \frac{\text{J}^2 \text{ sec}^2}{\text{kg m}^2}$$

$$= \frac{5 (43.90 \times 10^{-68})}{8 \times 9.11 \times 10^{-31} \times 33.40 \times 10^{-20}} \frac{J^2 \text{ sec}^2}{\text{kg m}^2}$$

$$= \frac{219.50 \times 10^{-68+31+20}}{8 \times 9.11 \times 33.4} \frac{J^2}{\text{kg m}^2/\text{sec}^2}$$

$$= \frac{219.50 \times 10^{-17}}{2434.192} \frac{J^2}{J}$$

$$= 0.090173 \times 10^{-17} J$$

$$\Delta E = 9.02 \times 10^{-19} J$$

# CRYSTAL FIELD THEORY (CFT)

## PERIODIC TABLE

The following table lists the elements of the periodic table, categorized by group and row:

<b>1</b> <b>H</b> Hydrogen																			<b>2</b> <b>He</b> Helium																	
<b>3</b> <b>Li</b> Lithium	<b>4</b> <b>Be</b> Beryllium																			<b>9</b> <b>F</b> Fluorine	<b>10</b> <b>Ne</b> Neon															
<b>11</b> <b>Na</b> Sodium	<b>12</b> <b>Mg</b> Magnesium																			<b>5</b> <b>B</b> Boron	<b>6</b> <b>C</b> Carbon	<b>7</b> <b>N</b> Nitrogen	<b>8</b> <b>O</b> Oxygen	<b>17</b> <b>Cl</b> Chlorine	<b>18</b> <b>Ar</b> Argon											
<b>19</b> <b>K</b> Potassium	<b>20</b> <b>Ca</b> Calcium	<b>21</b> <b>Sc</b> Scandium	<b>22</b> <b>Ti</b> Titanium	<b>23</b> <b>V</b> Vanadium	<b>24</b> <b>Cr</b> Chromium	<b>25</b> <b>Mn</b> Manganese	<b>26</b> <b>Fe</b> Iron	<b>27</b> <b>Co</b> Cobalt	<b>28</b> <b>Ni</b> Nickel	<b>29</b> <b>Cu</b> Copper	<b>30</b> <b>Zn</b> Zinc	<b>31</b> <b>Ga</b> Gallium	<b>32</b> <b>Ge</b> Germanium	<b>33</b> <b>As</b> Arsenic	<b>34</b> <b>Se</b> Selenium	<b>35</b> <b>Br</b> Bromine	<b>36</b> <b>Kr</b> Krypton																			
<b>37</b> <b>Rb</b> Rubidium	<b>38</b> <b>Sr</b> Strontium	<b>39</b> <b>Y</b> Yttrium	<b>40</b> <b>Zr</b> Zirconium	<b>41</b> <b>Nb</b> Niobium	<b>42</b> <b>Mo</b> Molybdenum	<b>43</b> <b>Tc</b> Technetium	<b>44</b> <b>Ru</b> Ruthenium	<b>45</b> <b>Rh</b> Rhodium	<b>46</b> <b>Pd</b> Palladium	<b>47</b> <b>Ag</b> Silver	<b>48</b> <b>Cd</b> Cadmium	<b>49</b> <b>In</b> Indium	<b>50</b> <b>Sn</b> Tin	<b>51</b> <b>Sb</b> Antimony	<b>52</b> <b>Te</b> Tellurium	<b>53</b> <b>I</b> Iodine	<b>54</b> <b>Xe</b> Xenon																			
<b>55</b> <b>Cs</b> Cesium	<b>56</b> <b>Ba</b> Barium	<b>57-71</b>	<b>72</b> <b>Hf</b> Hafnium	<b>73</b> <b>Ta</b> Tantalum	<b>74</b> <b>W</b> Tungsten	<b>75</b> <b>Re</b> Rhenium	<b>76</b> <b>Os</b> Osmium	<b>77</b> <b>Ir</b> Iridium	<b>78</b> <b>Pt</b> Platinum	<b>79</b> <b>Au</b> Gold	<b>80</b> <b>Hg</b> Mercury	<b>81</b> <b>Tl</b> Thallium	<b>82</b> <b>Pb</b> Lead	<b>83</b> <b>Bi</b> Bismuth	<b>84</b> <b>Po</b> Polonium	<b>85</b> <b>At</b> Astatine	<b>86</b> <b>Rn</b> Radon																			
<b>87</b> <b>Fr</b> Francium	<b>88</b> <b>Ra</b> Radium	<b>89-103</b>	<b>104</b> <b>Rf</b> Rutherfordium	<b>105</b> <b>Db</b> Dubnium	<b>106</b> <b>Sg</b> Seaborgium	<b>107</b> <b>Bh</b> Bohrium	<b>108</b> <b>Hs</b> Hassium	<b>109</b> <b>Mt</b> Meitnerium	<b>110</b> <b>Ds</b> Darmstadtium	<b>111</b> <b>Rg</b> Roentgenium	<b>112</b> <b>Cn</b> Copernicium	<b>113</b> <b>Nh</b> Nihonium	<b>114</b> <b>Fl</b> Flerovium	<b>115</b> <b>Mc</b> Moscovium	<b>116</b> <b>Lv</b> Livermorium	<b>117</b> <b>Ts</b> Tennessine	<b>118</b> <b>Og</b> Oganesson																			
																			<b>57</b> <b>La</b> Lanthanum	<b>58</b> <b>Ce</b> Cerium	<b>59</b> <b>Pr</b> Praseodymium	<b>60</b> <b>Nd</b> Neodymium	<b>61</b> <b>Pm</b> Promethium	<b>62</b> <b>Sm</b> Samarium	<b>63</b> <b>Eu</b> Europium	<b>64</b> <b>Gd</b> Gadolinium	<b>65</b> <b>Tb</b> Terbium	<b>66</b> <b>Dy</b> Dysprosium	<b>67</b> <b>Ho</b> Holmium	<b>68</b> <b>Er</b> Erbium	<b>69</b> <b>Tm</b> Thulium	<b>70</b> <b>Yb</b> Ytterbium	<b>71</b> <b>Lu</b> Lutetium			
																			<b>89</b> <b>Ac</b> Actinium	<b>90</b> <b>Th</b> Thorium	<b>91</b> <b>Pa</b> Protactinium	<b>92</b> <b>U</b> Uranium	<b>93</b> <b>Np</b> Neptunium	<b>94</b> <b>Pu</b> Plutonium	<b>95</b> <b>Am</b> Americium	<b>96</b> <b>Cm</b> Curium	<b>97</b> <b>Bk</b> Berkelium	<b>98</b> <b>Cf</b> Californium	<b>99</b> <b>Es</b> Einsteinium	<b>100</b> <b>Fm</b> Fermium	<b>101</b> <b>Md</b> Mendelevium	<b>102</b> <b>No</b> Nobelium	<b>103</b> <b>Lr</b> Lawrencium			

s – block elements

<b>1</b>	<b>H</b>	Hydrogen
<b>3</b>	<b>Li</b>	Lithium
<b>4</b>	<b>Be</b>	Beryllium
<b>11</b>	<b>Na</b>	Sodium
<b>12</b>	<b>Mg</b>	Magnesium
<b>19</b>	<b>K</b>	Potassium
<b>20</b>	<b>Ca</b>	Calcium
<b>21</b>	<b>Sc</b>	Scandium
<b>22</b>	<b>Ti</b>	Titanium
<b>23</b>	<b>V</b>	Vanadium
<b>24</b>	<b>Cr</b>	Chromium
<b>25</b>	<b>Mn</b>	Manganese
<b>26</b>	<b>Fe</b>	Iron
<b>27</b>	<b>Co</b>	Cobalt
<b>28</b>	<b>Ni</b>	Nickel
<b>29</b>	<b>Cu</b>	Copper
<b>30</b>	<b>Zn</b>	Zinc
<b>37</b>	<b>Rb</b>	Rubidium
<b>38</b>	<b>Sr</b>	Strontium
<b>39</b>	<b>Y</b>	Yttrium
<b>40</b>	<b>Zr</b>	Zirconium
<b>41</b>	<b>Nb</b>	Niobium
<b>42</b>	<b>Mo</b>	Molybdenum
<b>43</b>	<b>Tc</b>	Technetium
<b>44</b>	<b>Ru</b>	Ruthenium
<b>45</b>	<b>Rh</b>	Rhodium
<b>46</b>	<b>Pd</b>	Palladium
<b>47</b>	<b>Ag</b>	Silver
<b>48</b>	<b>Cd</b>	Cadmium
<b>49</b>	<b>In</b>	Indium
<b>50</b>	<b>Sn</b>	Tin
<b>51</b>	<b>Sb</b>	Antimony
<b>52</b>	<b>Te</b>	Tellurium
<b>53</b>	<b>I</b>	Iodine
<b>54</b>	<b>Xe</b>	Xenon
<b>55</b>	<b>Cs</b>	Cesium
<b>56</b>	<b>Ba</b>	Barium
<b>57-71</b>	<b>Hf</b>	Hafnium
<b>72</b>	<b>Ta</b>	Tantalum
<b>73</b>	<b>W</b>	Tungsten
<b>74</b>	<b>Re</b>	Rhenium
<b>75</b>	<b>Os</b>	Osmium
<b>76</b>	<b>Ir</b>	Iridium
<b>77</b>	<b>Pt</b>	Platinum
<b>78</b>	<b>Au</b>	Gold
<b>79</b>	<b>Hg</b>	Mercury
<b>80</b>		
<b>81</b>	<b>Tl</b>	Thallium
<b>82</b>	<b>Pb</b>	Lead
<b>83</b>	<b>Bi</b>	Bismuth
<b>84</b>	<b>Po</b>	Polonium
<b>85</b>	<b>At</b>	Astatine
<b>86</b>	<b>Rn</b>	Radon
<b>87</b>	<b>Fr</b>	Francium
<b>88</b>	<b>Ra</b>	Radium
<b>89-103</b>	<b>Rf</b>	Rutherfordium
<b>104</b>	<b>Db</b>	Dubnium
<b>105</b>	<b>Sg</b>	Seaborgium
<b>106</b>	<b>Bh</b>	Bohrium
<b>107</b>	<b>Hs</b>	Hassium
<b>108</b>	<b>Mt</b>	Meitnerium
<b>109</b>	<b>Ds</b>	Darmstadtium
<b>110</b>	<b>Rg</b>	Roentgenium
<b>111</b>	<b>Cn</b>	Copernicium
<b>112</b>		
<b>113</b>	<b>Nh</b>	Nihonium
<b>114</b>	<b>Fl</b>	Flerovium
<b>115</b>	<b>Mc</b>	Moscovium
<b>116</b>	<b>Lv</b>	Livermorium
<b>117</b>	<b>Ts</b>	Tennessee
<b>118</b>	<b>Og</b>	Oganesson

# Transition elements

The position of d-block elements are in between s block and p block elements in periodic table. These d-block elements are called transition elements because they exhibit transitional behavior between s and p elements.

d – block elements

<b>5</b>	<b>B</b>	Boron	<b>6</b>	<b>C</b>	Carbon	<b>7</b>	<b>N</b>	Nitrogen	<b>8</b>	<b>O</b>	Oxygen	<b>9</b>	<b>F</b>	Fluorine	<b>10</b>	<b>Ne</b>	Neon
<b>13</b>	<b>Al</b>	Aluminum	<b>14</b>	<b>Si</b>	Silicon	<b>15</b>	<b>P</b>	Phosphorus	<b>16</b>	<b>S</b>	Sulfur	<b>17</b>	<b>Cl</b>	Chlorine	<b>18</b>	<b>Ar</b>	Argon
<b>31</b>	<b>Ga</b>	Gallium	<b>32</b>	<b>Ge</b>	Germanium	<b>33</b>	<b>As</b>	Arsenic	<b>34</b>	<b>Se</b>	Selenium	<b>35</b>	<b>Br</b>	Bromine	<b>36</b>	<b>Kr</b>	Krypton
<b>49</b>	<b>In</b>	Indium	<b>50</b>	<b>Sn</b>	Tin	<b>51</b>	<b>Sb</b>	Antimony	<b>52</b>	<b>Te</b>	Tellurium	<b>53</b>	<b>I</b>	Iodine	<b>54</b>	<b>Xe</b>	Xenon
<b>81</b>	<b>Tl</b>	Thallium	<b>82</b>	<b>Pb</b>	Lead	<b>83</b>	<b>Bi</b>	Bismuth	<b>84</b>	<b>Po</b>	Polonium	<b>85</b>	<b>At</b>	Astatine	<b>86</b>	<b>Rn</b>	Radon
<b>113</b>	<b>Nh</b>	Nihonium	<b>114</b>	<b>Fl</b>	Flerovium	<b>115</b>	<b>Mc</b>	Moscovium	<b>116</b>	<b>Lv</b>	Livermorium	<b>117</b>	<b>Ts</b>	Tennessee	<b>118</b>	<b>Og</b>	Oganesson

f – block elements

<b>57</b>	<b>La</b>	58	<b>Ce</b>	59	<b>Pr</b>	60	<b>Nd</b>	61	<b>Pm</b>	62	<b>Sm</b>	63	<b>Eu</b>	64	<b>Gd</b>	65	<b>Tb</b>	66	<b>Dy</b>	67	<b>Ho</b>	68	<b>Er</b>	69	<b>Tm</b>	70	<b>Yb</b>	71	<b>Lu</b>
	Lanthanum		Cerium		Praseodymium		Neodymium		Promethium		Samarium		Europium		Gadolinium		Terbium		Dysprosium		Holmium		Erbium		Thulium		Ytterbium		Lutetium
<b>89</b>	<b>Ac</b>	90	<b>Th</b>	91	<b>Pa</b>	92	<b>U</b>	93	<b>Np</b>	94	<b>Pu</b>	95	<b>Am</b>	96	<b>Cm</b>	97	<b>Bk</b>	98	<b>Cf</b>	99	<b>Es</b>	100	<b>Fm</b>	101	<b>Md</b>	102	<b>No</b>	103	<b>Lr</b>
	Actinium		Thorium		Protactinium		Uranium		Neptunium		Plutonium		Americium		Curiom		Berkelium		Californium		Einsteinium		Fermium		Mendelevium		Nobelium		Lawrencium

# CRYSTAL FIELD THEORY (CFT)

- CFT discovered by Van Vleck & Brethe in 1935
- It explains clearly about colors and magnetic properties
- This theory was originally used to explain ionic crystal, later on used to explain the properties of transition metals and complexes
- Bond between metal and Ligand 100% purely ionic due to electrostatic attraction between electron deficiency metal and electron rich ligand.
- Metal and Ligand considered as a point charges (or)
- For neutral metal and ligands considered as electric dipole
- All the d-orbitals are degenerate in nature (equal energy or same energy),  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$ ,  $d_z^2$

## Electrostatics force

Electrostatic forces are attractive or repulsive forces between particles that are caused by their electric charges

## Hypothetical Steps

When ligand approaches to metal ion

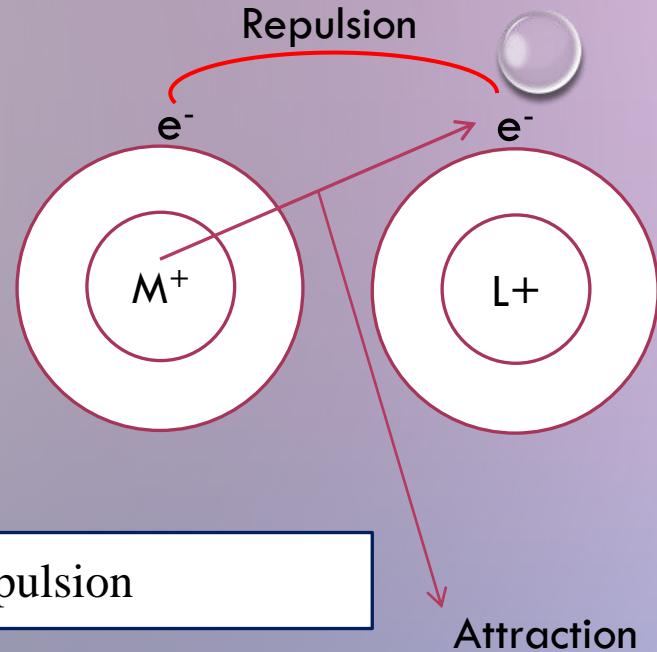
Ligand approaches to d-orbitals of metal  
of metal

Force of attraction

Decrease Energy

Force of repulsion

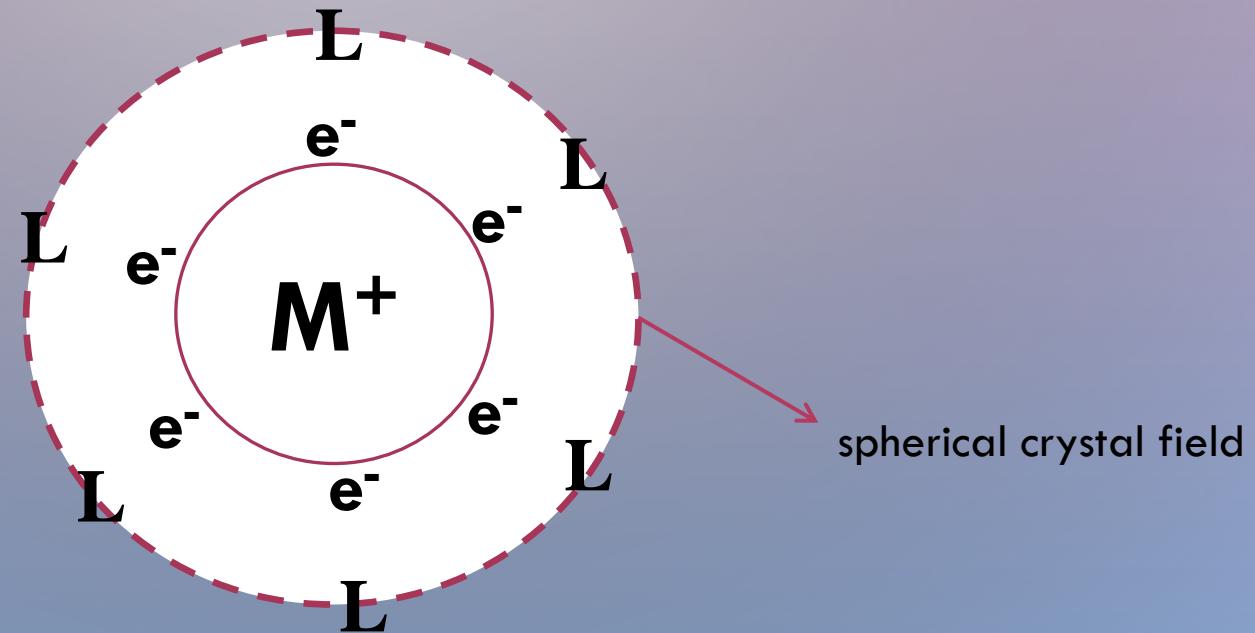
Increase Energy



## Hypothetical steps

### Step 1

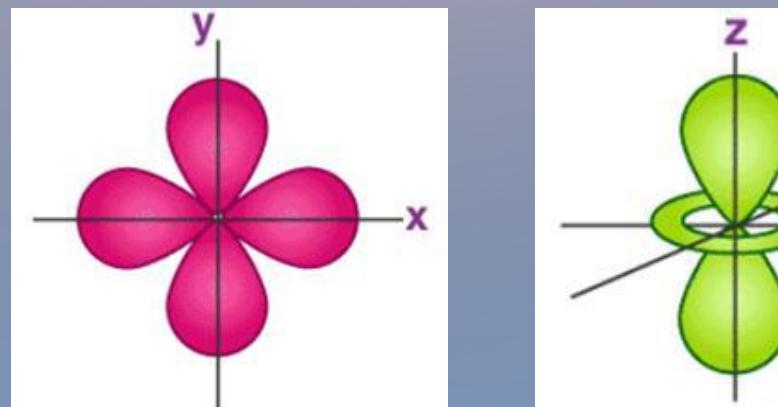
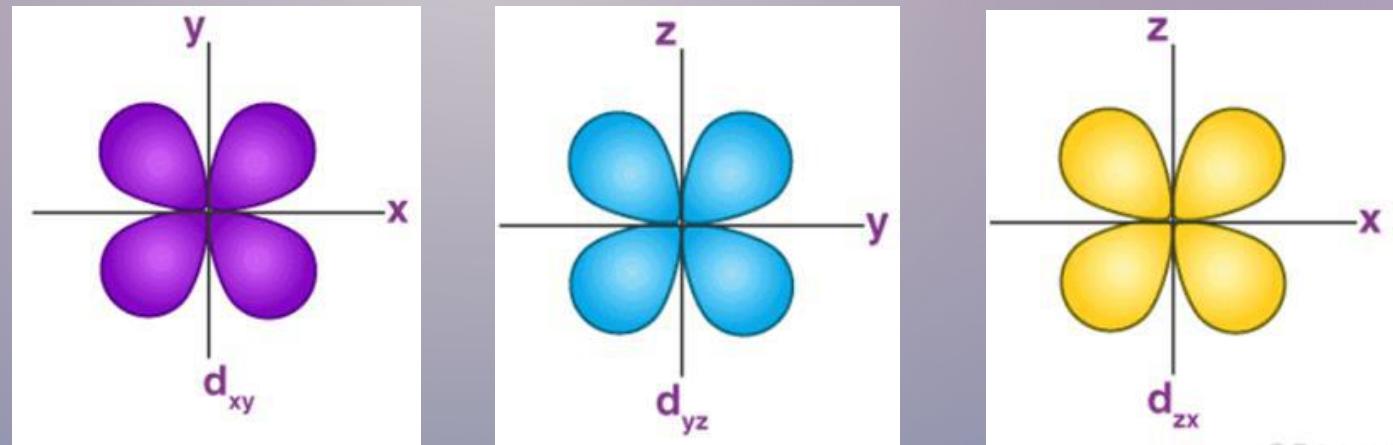
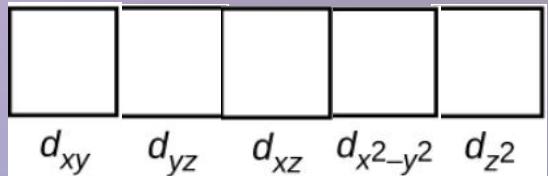
In isolated gas state all five d-orbitals degenerate and ligands forms a spherical field of negative charges around metal.



## Step 2

Shapes and orientation of five d-orbitals in metal ion

**d-orbitals**



$$d_{x^2-y^2}$$

$$d_{z^2}$$

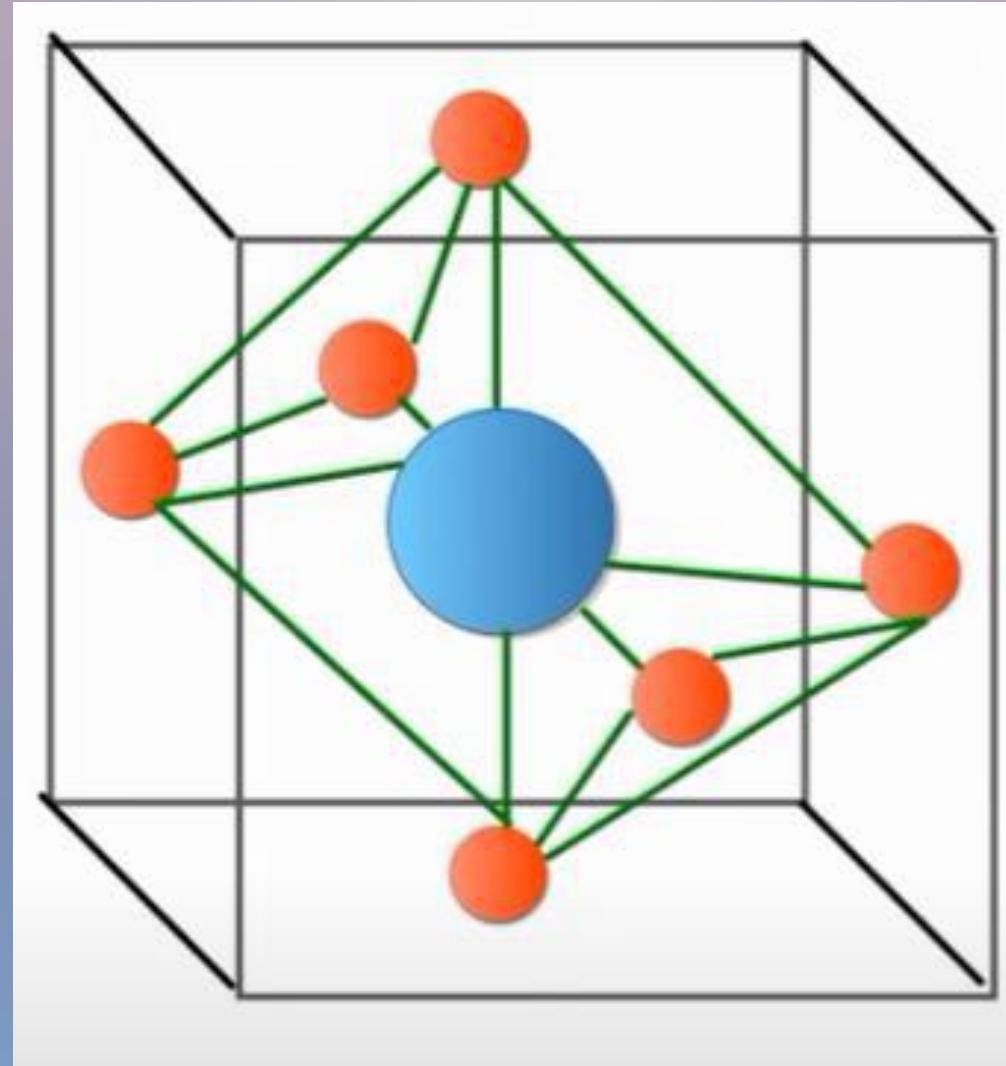
## Crystal Field Theory



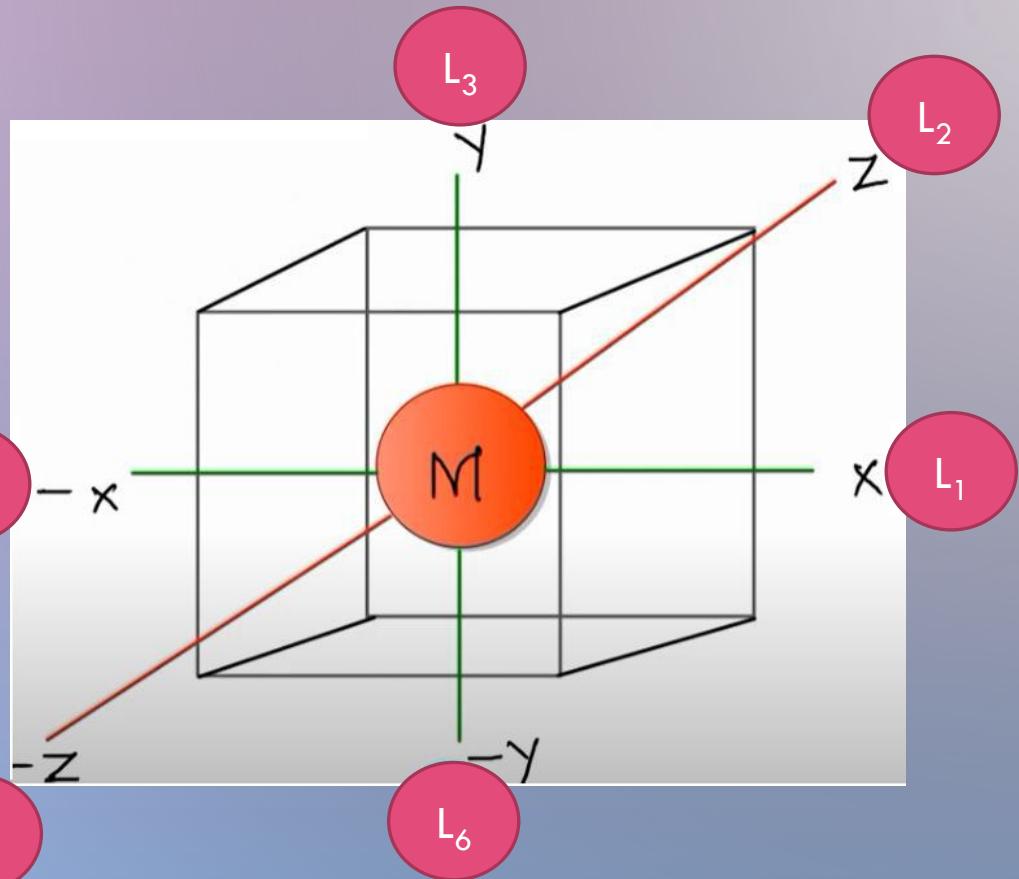
Octahedral Splitting

Tetrahedral Splitting

# Octahedral Splitting



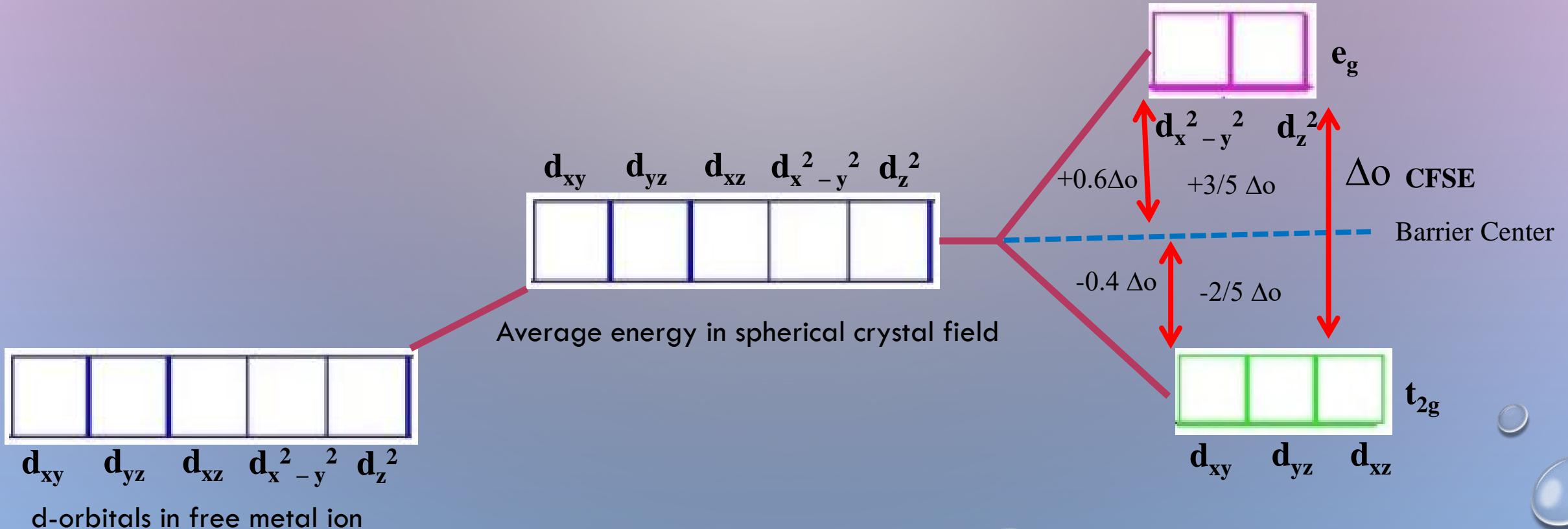
# Octahedral Splitting

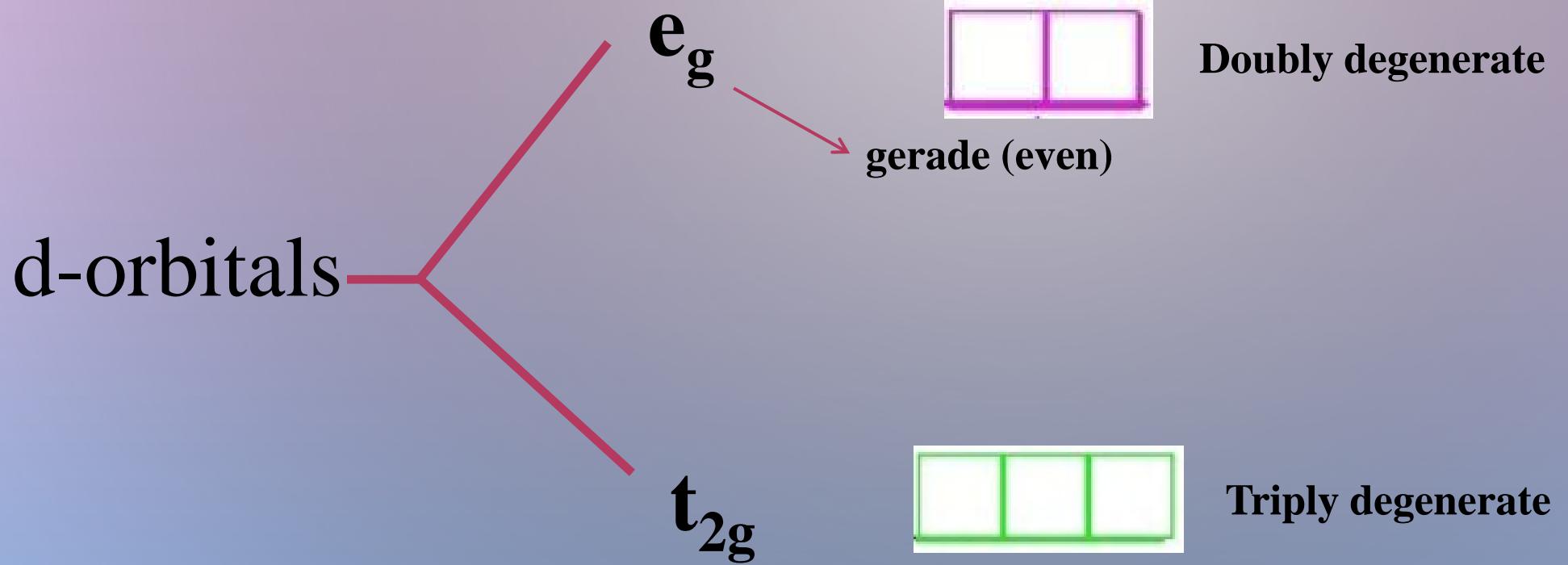


- $d_x^2 - y^2$ ,  $d_z^2$  (along the axis) experiences strong repulsion and energy increases than  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$
- Therefore d-orbitals undergoes splitting called as Crystal field splitting

### Step 3

- Up to this complex formation not favored, however when the ligands approaches further, there will be attractive force between negative charged ligand and positive charged metal due to this, energy decreases.
- According to Aufbau principle, electrons are filled in the lower energy orbital.

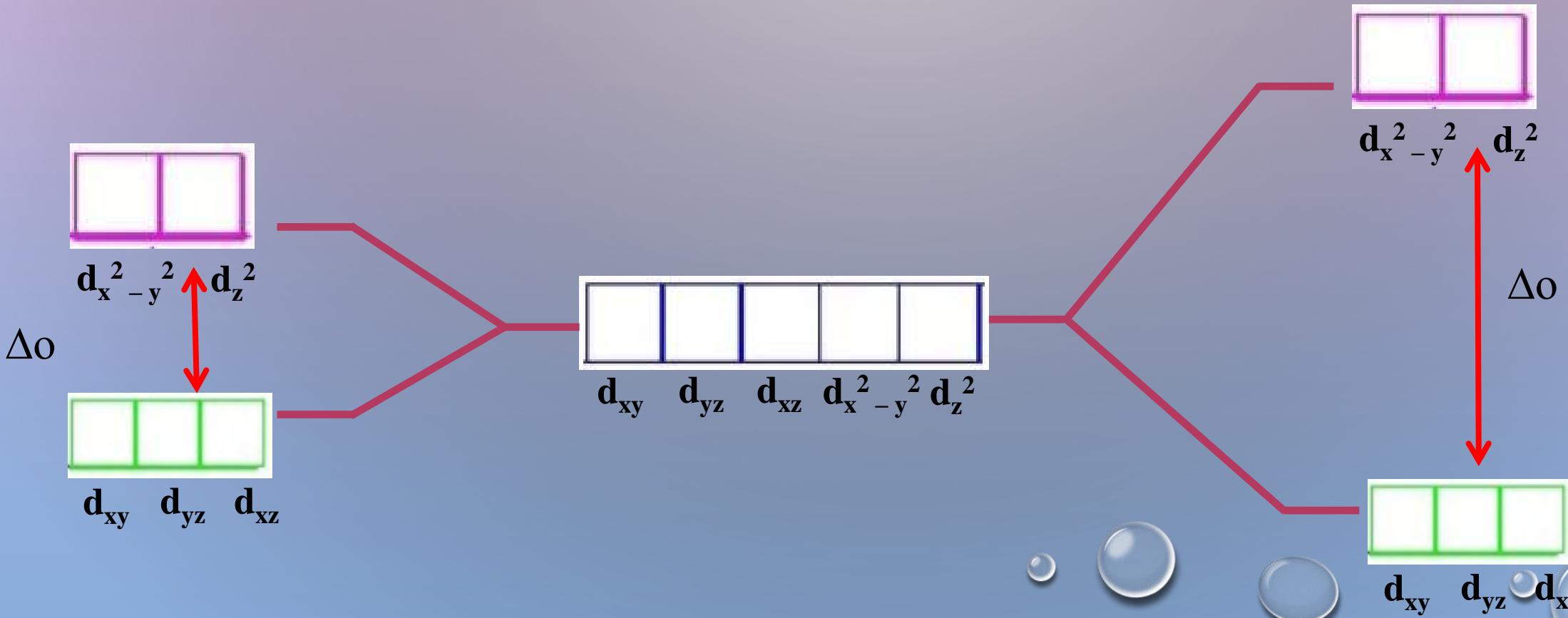




## Tricks to identify weak ligands and strong ligands

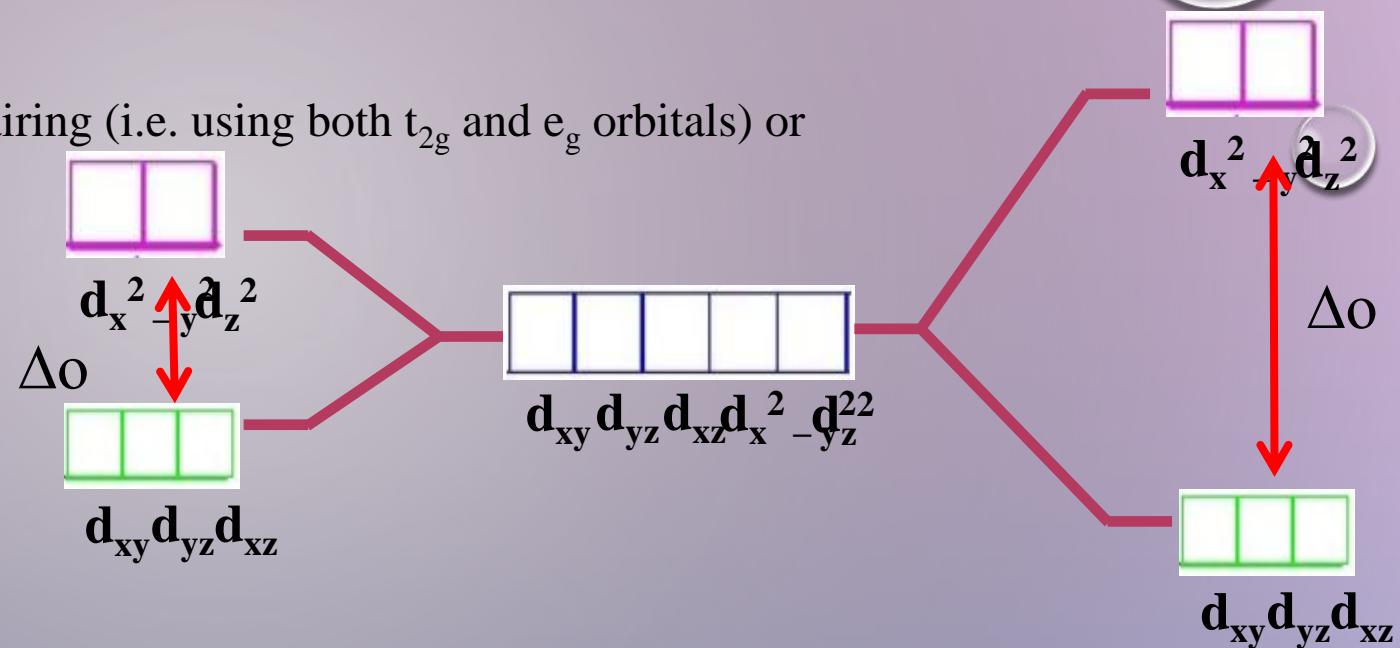
Ligands in which donor atoms are **Halogens, Oxygen or Sulphur - Weak Ligands**

Ex; F, Cl, Br, I, OH, SCN, C<sub>2</sub>O<sub>4</sub><sup>-</sup>



**There are two ways to place electrons:**

1. Singly to the fullest extent possible before pairing (i.e. using both  $t_{2g}$  and  $e_g$  orbitals) or
2. First pairs in  $t_{2g}$  then only goes to  $e_g$  orbitals



The decision is made based on whether  $\Delta o$  is greater or less than the pairing energy (PE): energy of electron-electron repulsion.

### When $\Delta o$ is small, $\Delta o < PE$

- Electrons are placed singly with parallel spins to the fullest possible extent in  $t_{2g}$  orbitals and  $e_g$  orbitals.
- This arrangement of electrons gives the maximum number of unpaired electrons (high spin).

### When $\Delta o$ is large, $\Delta o > PE$

- Electrons are paired in lower energy  $t_{2g}$  orbitals,  $e_g$  orbitals are not both occupied until  $t_{2g}$  orbitals are filled.
- This arrangement of electrons gives the minimum number of unpaired electrons (low spin).

## Super tricks to write electronic configuration of d-block elements

3d

1	2	3	X	5	6	7	8	X	10
1	2	3	5	5	6	7	8	10	10

4d

1	2	X	4	5	5	7	8	10	10
1	2	4	5	5	7	8	10	10	10

5d

1	2	3	4	5	6	7	X	9	10
1	2	3	4	5	6	7	9	10	10

S.No	3d Elements	Electronic configuration
1	$^{21}\text{Sc}$	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>
2	$^{22}\text{Ti}$	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>
3	$^{23}\text{V}$	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>
4	$^{24}\text{Cr}$	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>
5	$^{25}\text{Mn}$	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>
6	$^{26}\text{Fe}$	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>
7	$^{27}\text{Co}$	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>
8	$^{28}\text{Ni}$	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>
9	$^{29}\text{Cu}$	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
10	$^{30}\text{Zn}$	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>

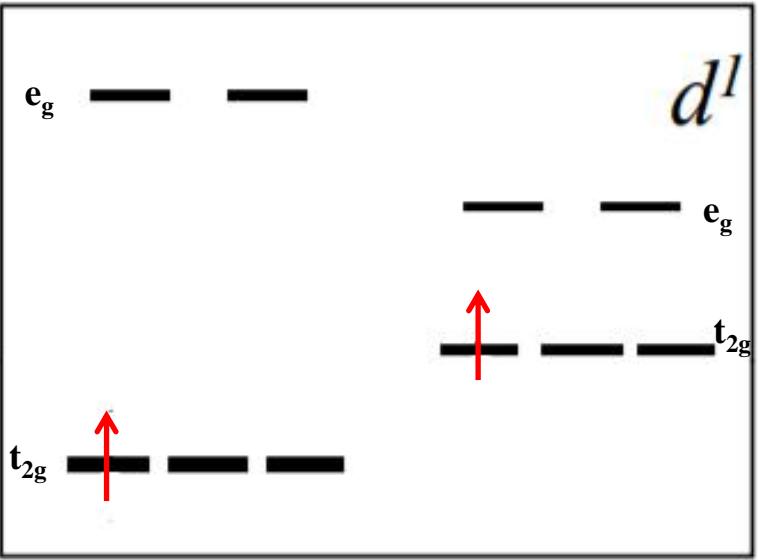
3d	4, 9
4d	3, 6, 9
5d	8

$$^{21}\text{Sc} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$$

# Distribution of Electrons in an Octahedral Complex

Strong field

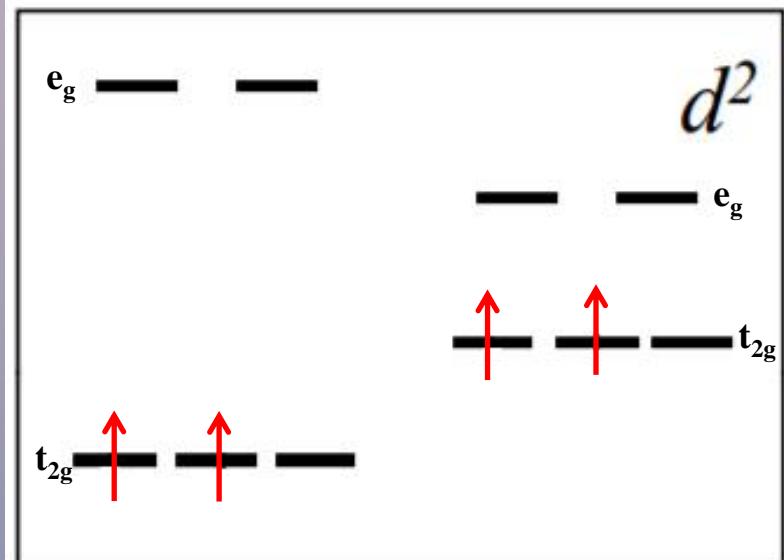
Weak field



$$\text{For } d^1, \text{ CFSE} = 1 \times 0.4 = \mathbf{0.4 \Delta_o}$$

Strong field

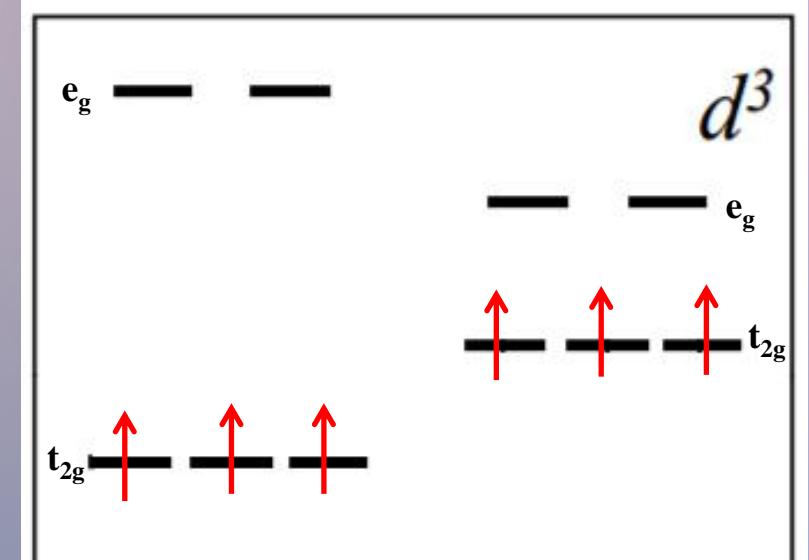
Weak field



$$\text{For } d^2, \text{ CFSE} = 2 \times 0.4 = \mathbf{0.8 \Delta_o}$$

Strong field

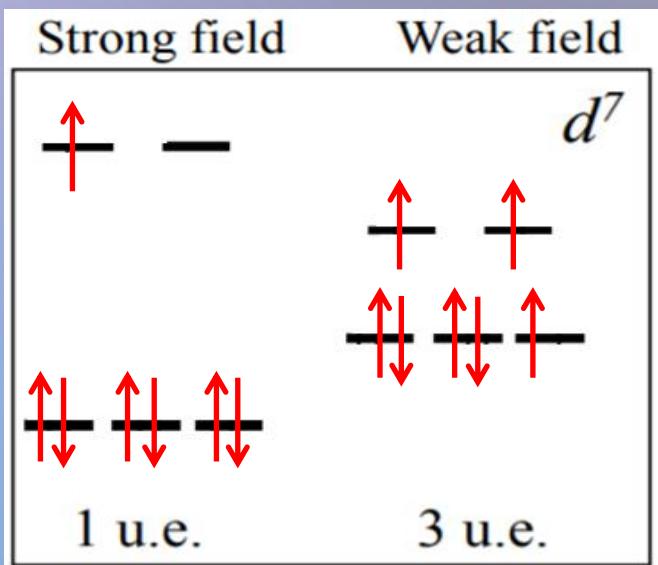
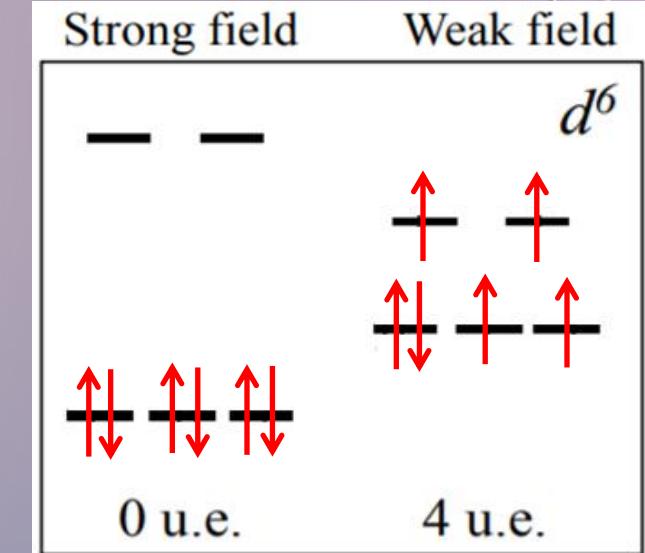
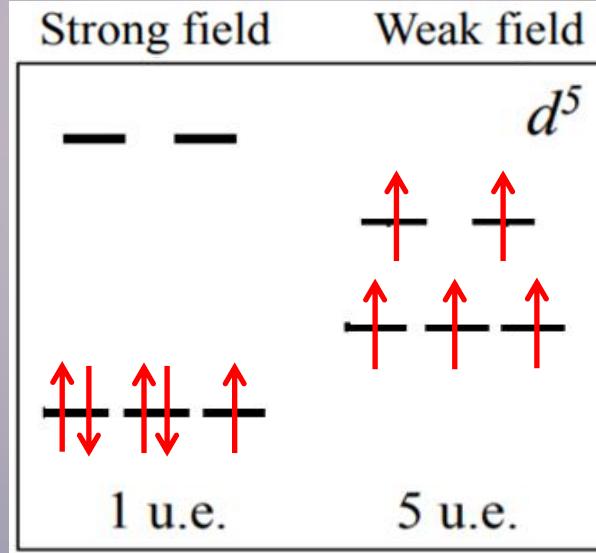
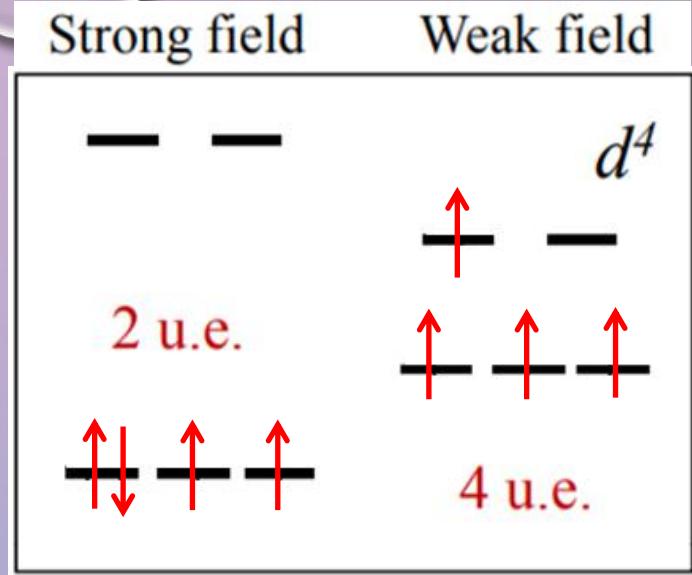
Weak field



$$\text{For } d^3, \text{ CFSE} = 3 \times 0.4 = \mathbf{1.2 \Delta_o}$$

$$\text{For the } d^1 \text{ system, CFSE} = (1 \times 0.4) - (0 \times 0.6) = 0.4 \Delta_o$$

There are two possibilities for metal ions having  $d^4$  –  $d^7$  electronic configuration. Depending on the ligands and the metal they could be high-spin or low-spin complexes.



- $d^4$  system, CFSE =
- For High spin,  $(3 \times 0.4) - (1 \times 0.6) = 0.6 \Delta_o$
- For Low spin,  $4 \times 0.4 = 1.6 \Delta_o$
  
- $d^5$  system, CFSE
- For High spin,  $(3 \times 0.4) - (2 \times 0.6) = 0 \Delta_o$
- For Low spin,  $5 \times 0.4 = 2.0 \Delta_o$

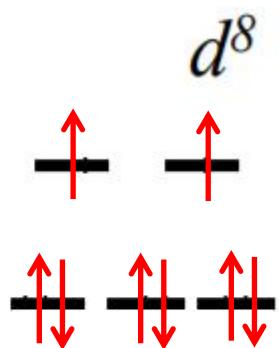
- $d^6$  system, CFSE =
- For High spin,  $(4 \times 0.4) - (2 \times 0.6) = 0.4 \Delta_o$
- For Low spin,  $6 \times 0.4 = 2.4 \Delta_o$
  
- $d^7$  system, CFSE
- For High spin,  $(5 \times 0.4) - (2 \times 0.6) = 0.8 \Delta_o$
- For Low spin,  $(6 \times 0.4) - (1 \times 0.6) = 1.8 \Delta_o$

Strong field



2 u.e.

Weak field



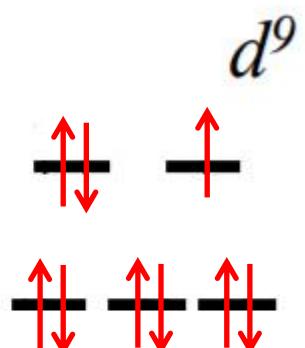
2 u.e.

Strong field



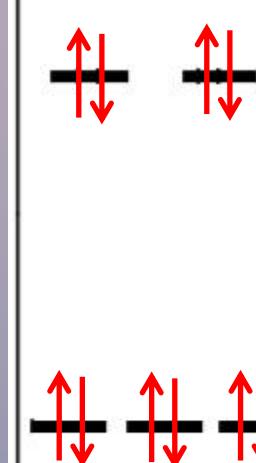
1 u.e.

Weak field



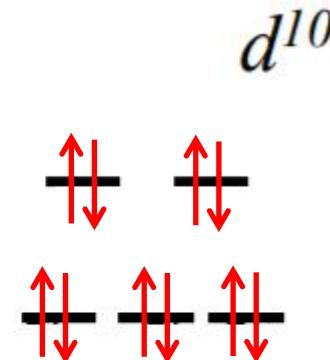
1 u.e.

Strong field



0 u.e.

Weak field



0 u.e.

$$\text{For } d^8, \text{CFSE} = (6 \times 0.4) - (2 \times 0.6) = 1.2 \Delta_0$$

$$\text{For } d^9, \text{CFSE} = (6 \times 0.4) - (3 \times 0.6) = 0.6 \Delta_0$$

$$\text{For } d^{10}, \text{CFSE} = (6 \times 0.4) - (4 \times 0.6) = 0.0 \Delta_0$$

## Distribution of Electrons in an Octahedral Complex

	<u>High-spin</u>	<u>Low-spin</u>
$d^1$	$t_{2g}^1 e_g^0$ $0.4 \Delta_o$	$t_{2g}^1 e_g^0$ $0.4 \Delta_o$
$d^2$	$t_{2g}^2 e_g^0$ $0.8 \Delta_o$	$t_{2g}^2 e_g^0$ $0.8 \Delta_o$
$d^3$	$t_{2g}^3 e_g^0$ $1.2 \Delta_o$	$t_{2g}^3 e_g^0$ $1.2 \Delta_o$
$d^4$	$t_{2g}^3 e_g^1$ $0.6 \Delta_o$	$t_{2g}^4 e_g^0$ $1.6 \Delta_o$
$d^5$	$t_{2g}^3 e_g^2$ $0.0 \Delta_o$	$t_{2g}^5 e_g^0$ $2.0 \Delta_o$
$d^6$	$t_{2g}^4 e_g^2$ $0.4 \Delta_o$	$t_{2g}^6 e_g^0$ $2.4 \Delta_o$
$d^7$	$t_{2g}^5 e_g^2$ $0.8 \Delta_o$	$t_{2g}^6 e_g^1$ $1.8 \Delta_o$
$d^8$	$t_{2g}^6 e_g^2$ $1.2 \Delta_o$	$t_{2g}^6 e_g^2$ $1.2 \Delta_o$
$d^9$	$t_{2g}^6 e_g^3$ $0.6 \Delta_o$	$t_{2g}^6 e_g^3$ $0.6 \Delta_o$
$d^{10}$	$t_{2g}^6 e_g^4$ $0.0 \Delta_o$	$t_{2g}^6 e_g^4$ $0.0 \Delta_o$

Example. Consider two different iron compounds:  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$

### Figure out the oxidation number of Fe

$$x + 0 = +3$$

$$x = +3$$

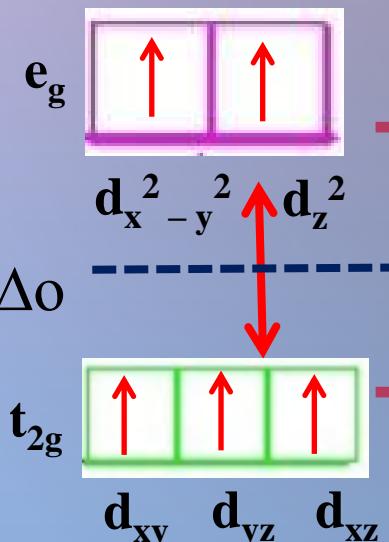
### Electronic configuration

$${}^{26}\text{Fe} = 1\text{s}^2, 2\text{s}^2, 2\text{p}^6, 3\text{s}^2, 3\text{p}^6, 4\text{s}^2, 3\text{d}^6$$

$$= [\text{Ar}] 3\text{d}^6, 4\text{s}^2$$

$$\text{Fe}^{3+} = [\text{Ar}] 3\text{d}^5, 4\text{s}^0$$

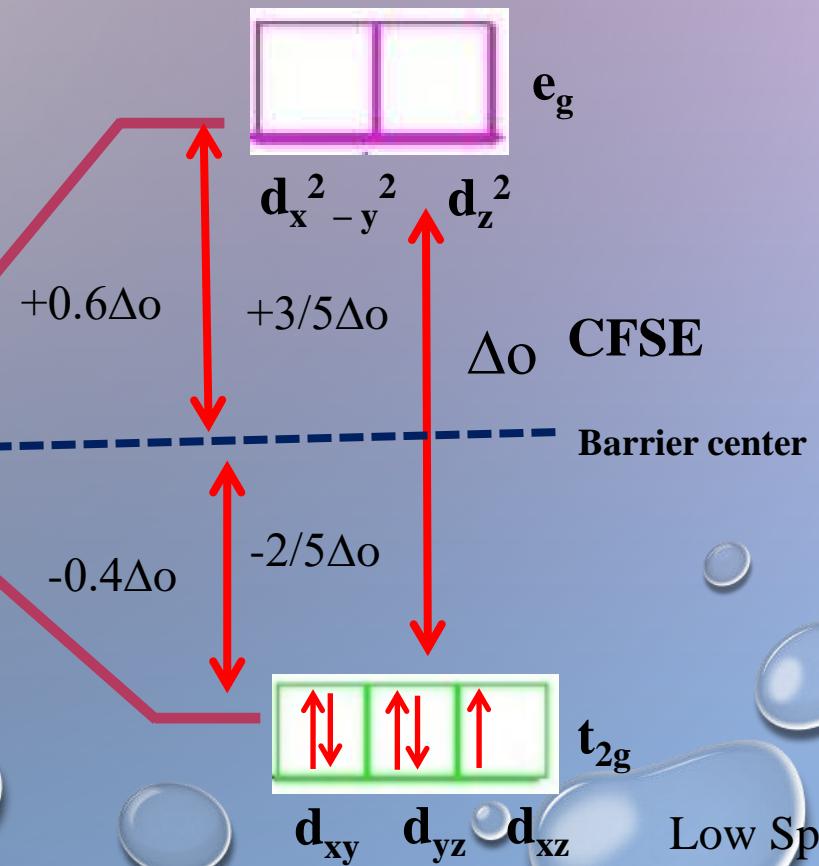
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  Weak ligand



High Spin

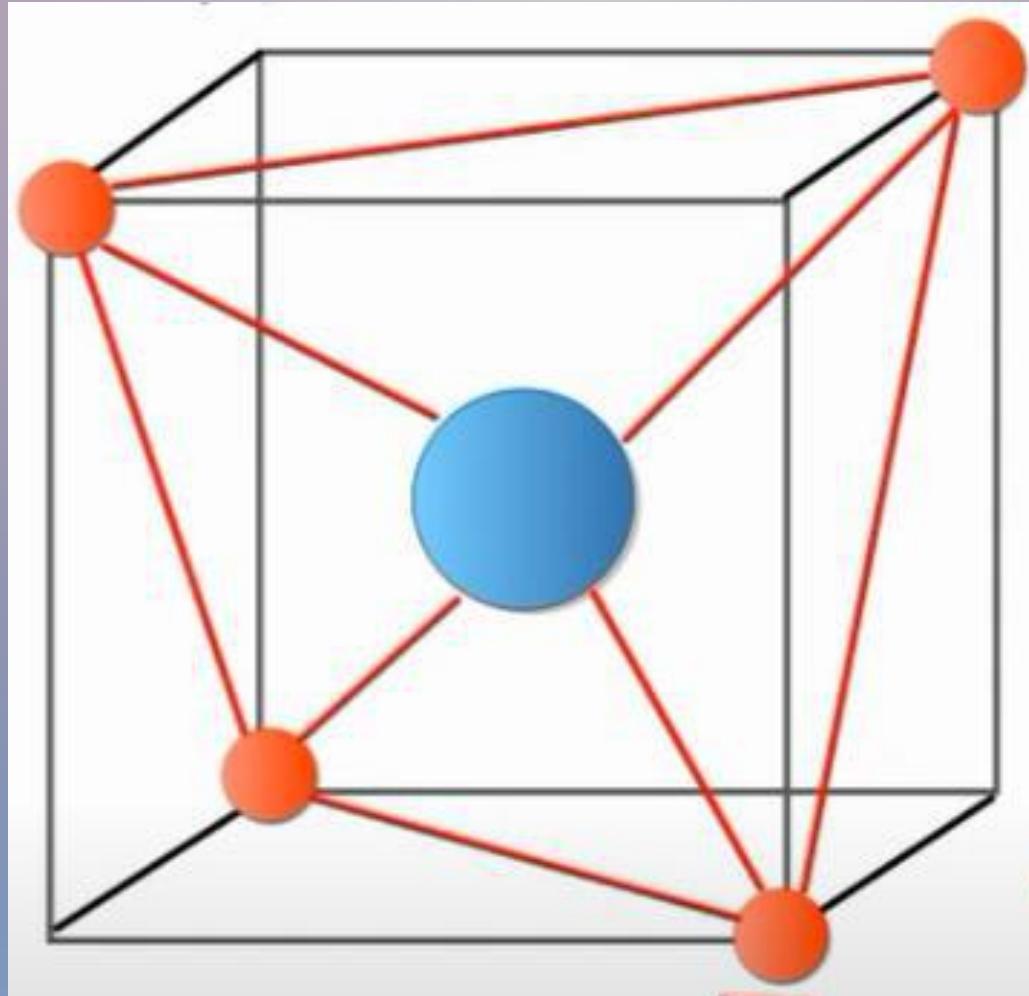
- CFSE =
- For High spin,  $(3 \times 0.4) - (2 \times 0.6) = 0 \Delta_o$
- For Low spin,  $5 \times 0.4 = 2.0 \Delta_o$

$[\text{Fe}(\text{CN})_6]^{3-}$  Strong ligand

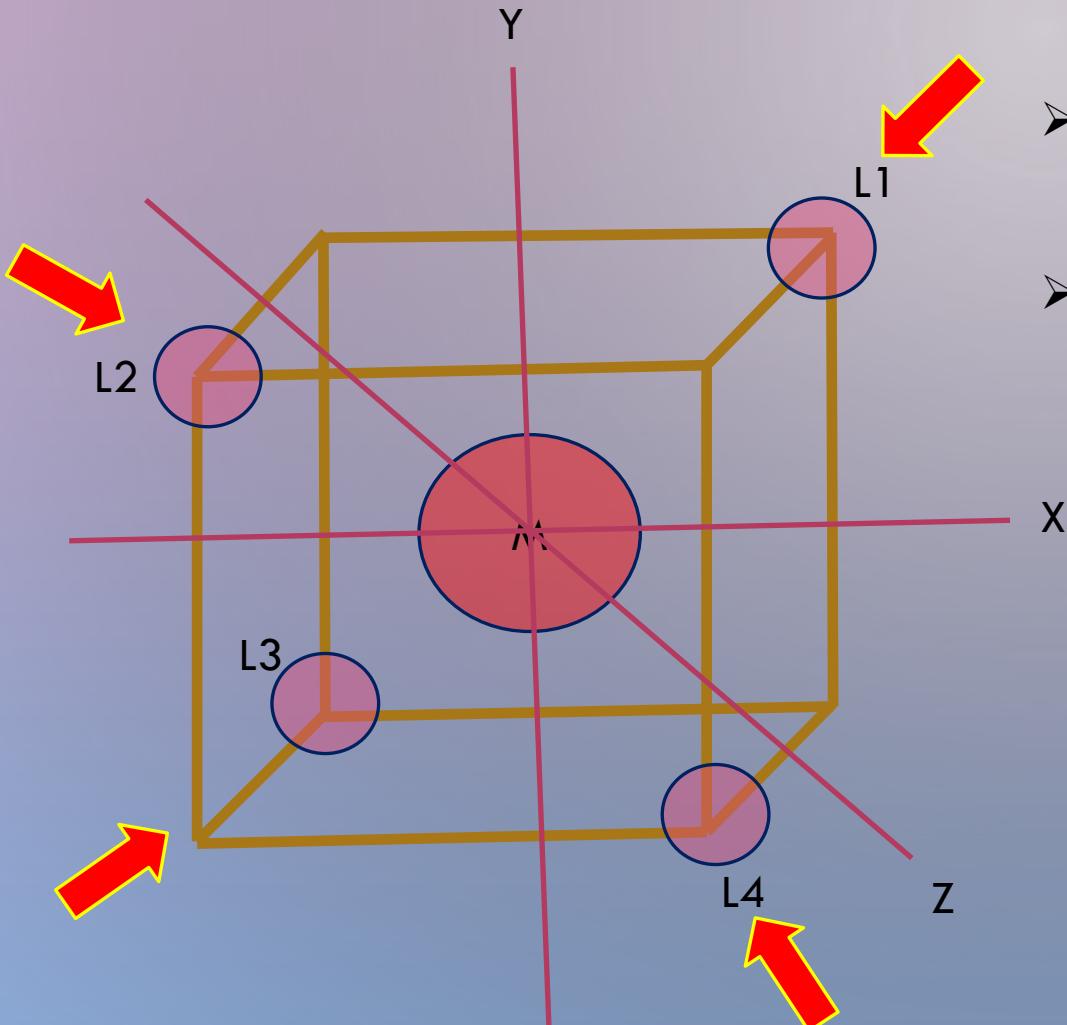


Low Spin

# Tetrahedral Splitting

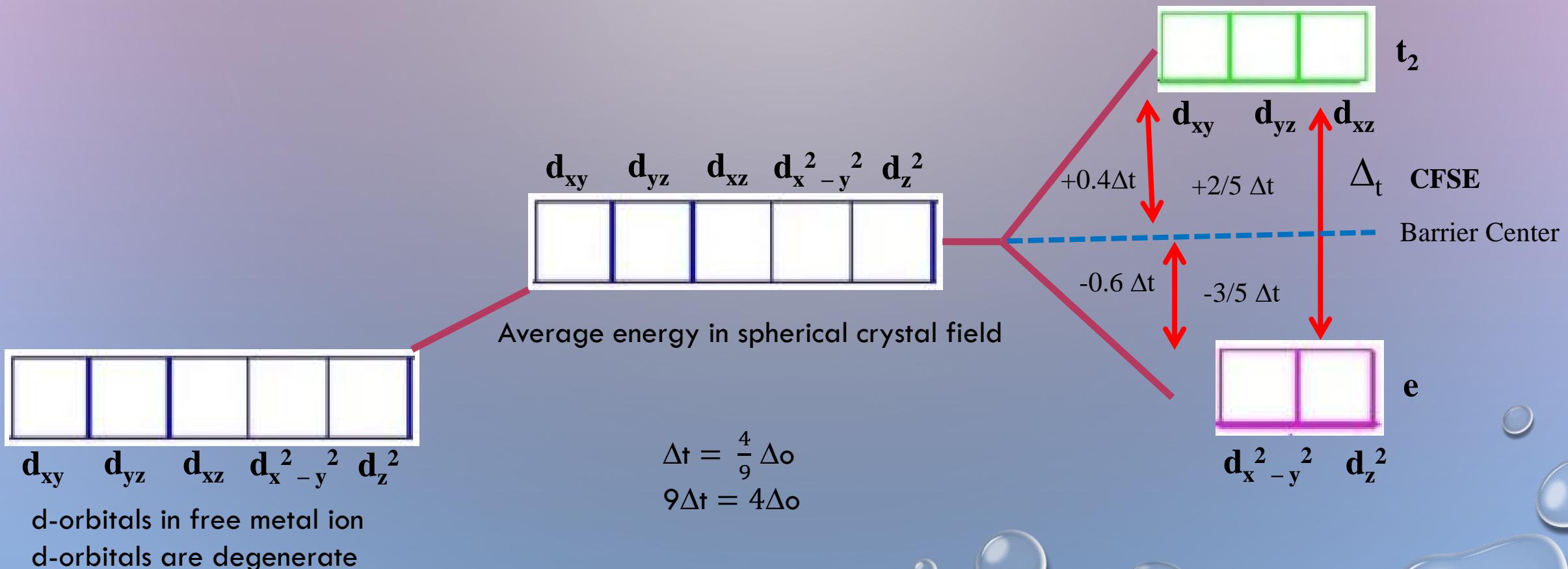


Tetrahedral structure



- $d_{xy}, d_{yz}, d_{xz}$  (between the axis) experiences strong repulsion and energy increases than  $d_x^2 - y^2, d_z^2$
- Therefore d-orbitals undergoes splitting called as Crystal field splitting

- Up to this complex formation not favored, however when the ligands approaches further, there will be attractive force between negative charged ligand and positive charged metal due to this, energy decreases.
- According to Aufbau principle, electrons are filled in the lower energy orbital.



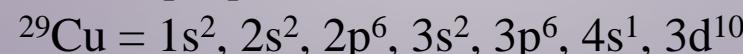
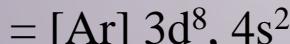
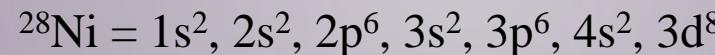
Example. Consider two different compounds:  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{Cl})_4]^{2-}$

### Figure out the oxidation number of Ni & Cu

$$x + (-4) = -2$$

$$x = +2$$

### Electronic configuration

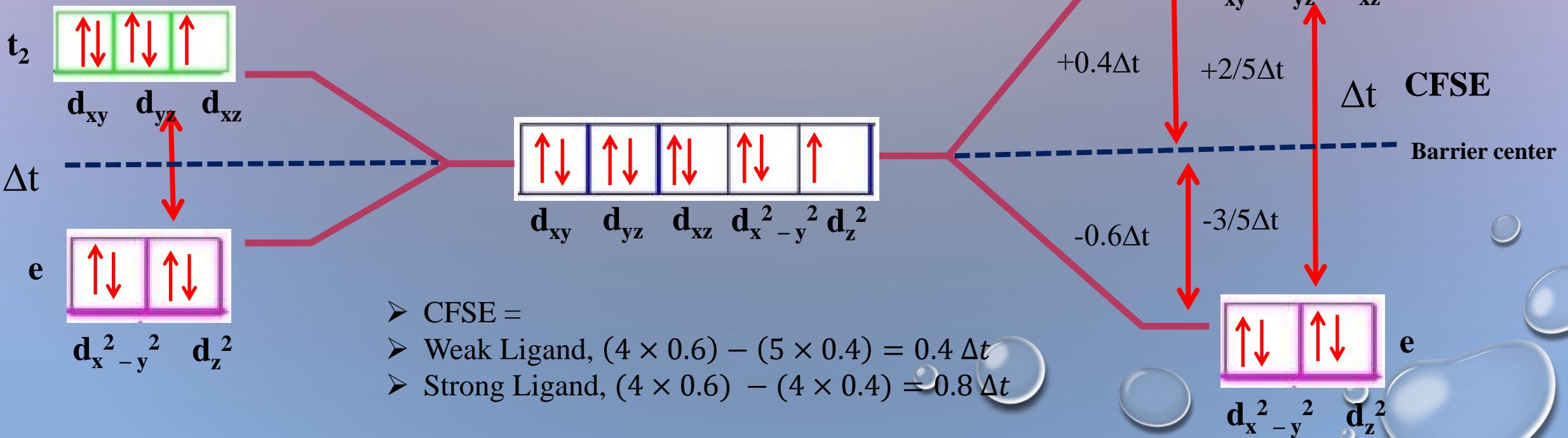


If  $\Delta_t < \text{PE}$ , 3<sup>rd</sup> and 4<sup>th</sup> electron (up to d<sup>4</sup>) will enter 'e' then electron will enter t<sub>2</sub>

$[\text{Ni}(\text{CN})_4]^{2-}$  Strong ligand

If  $\Delta_t > \text{PE}$ , 3<sup>rd</sup> electron will enter t<sub>2</sub>

$[\text{Cu}(\text{Cl})_4]^{2-}$  Weak ligand



- CFSE =
- Weak Ligand,  $(4 \times 0.6) - (5 \times 0.4) = 0.4 \Delta t$
- Strong Ligand,  $(4 \times 0.6) - (4 \times 0.4) = 0.8 \Delta t$

## Distribution of Electrons in a Tetrahedral Complex

Tetrahedral splitting is seldom large enough to result in pairing of the electrons.  
As a result, low-spin tetrahedral complexes are not common.

$d^1$	$e^1 t_2^0$	$0.6 \Delta_t$
$d^2$	$e^2 t_2^0$	$1.2 \Delta_t$
$d^3$	$e^2 t_2^1$	$0.8 \Delta_t$
$d^4$	$e^2 t_2^2$	$0.4 \Delta_t$
$d^5$	$e^2 t_2^3$	$0.0 \Delta_t$
$d^6$	$e^3 t_2^3$	$0.6 \Delta_t$
$d^7$	$e^4 t_2^3$	$1.2 \Delta_t$
$d^8$	$e^4 t_2^4$	$0.8 \Delta_t$
$d^9$	$e^4 t_2^5$	$0.4 \Delta_t$
$d^{10}$	$e^4 t_2^6$	$0.0 \Delta_t$

## **Unit-II**

# **FUNDAMENTALS AND APPLICATIONS OF SPECTROSCOPY**

Presented by

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## **UNIT II - FUNDAMENTALS AND APPLICATIONS OF SPECTROSCOPY**

Spectroscopy – General Introduction and Explanation; Types of Spectroscopy – Basic Concepts and Principles of Electronic Spectroscopy, Rotational Spectroscopy And Vibrational Spectroscopy – Applications of Rotational And Vibrational Spectroscopy of Diatomic Molecules – Selection Rules – Nuclear Magnetic Resonance Spectroscopy – Introduction, Principle, Instrumentation And Applications.

# WHAT IS SPECTROSCOPY ?

SPECTRO/SCOPY

SPECTRO  
SCOPY

- RADIATION  
- MEASUREMENT

## ANALYTICAL CHEMISTRY

- Analytical chemistry is concerned with the identification of a substance, the elucidation of its structure and quantitative analysis of its composition.
- It is an interdisciplinary branch of science which deals with various disciplines of chemistry such as inorganic, organic, physical, industrial and biochemistry

## SPECTROSCOPY

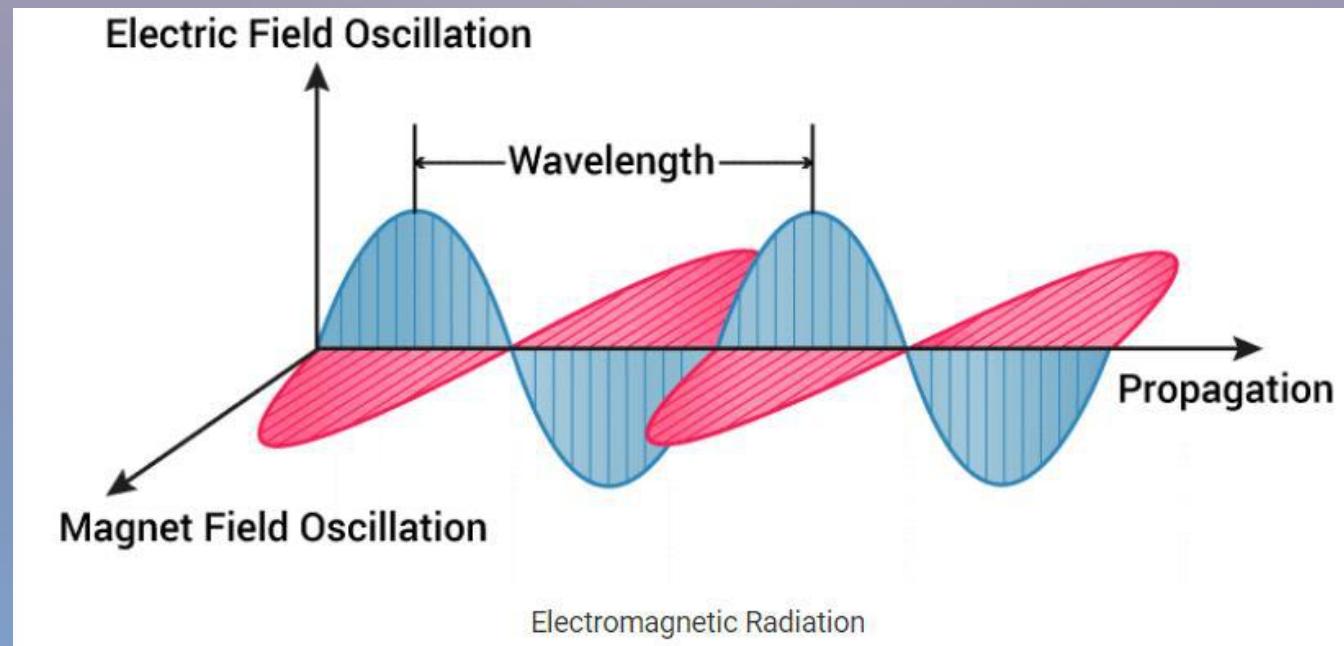
- It is a branch of Science
- It deals with the interaction of electromagnetic radiation with matter

# Spectroscopy

- Most powerful tool for study of
  - Atomic structure &
  - Molecular structure

## Electromagnetic radiation (EMR)

It is the stream of energy particles called photons or quanta moving in the direction of propagation and is perpendicular to both the electric field as well as magnetic field



- Wave like picture relates the wavelength ( $\lambda$ ) of light to its speed (C) and frequency (v)

$$\lambda = cv$$

$$v = c/\lambda$$

- A result usually associated with the particle-like picture relates energy and frequency

$$E = hv$$

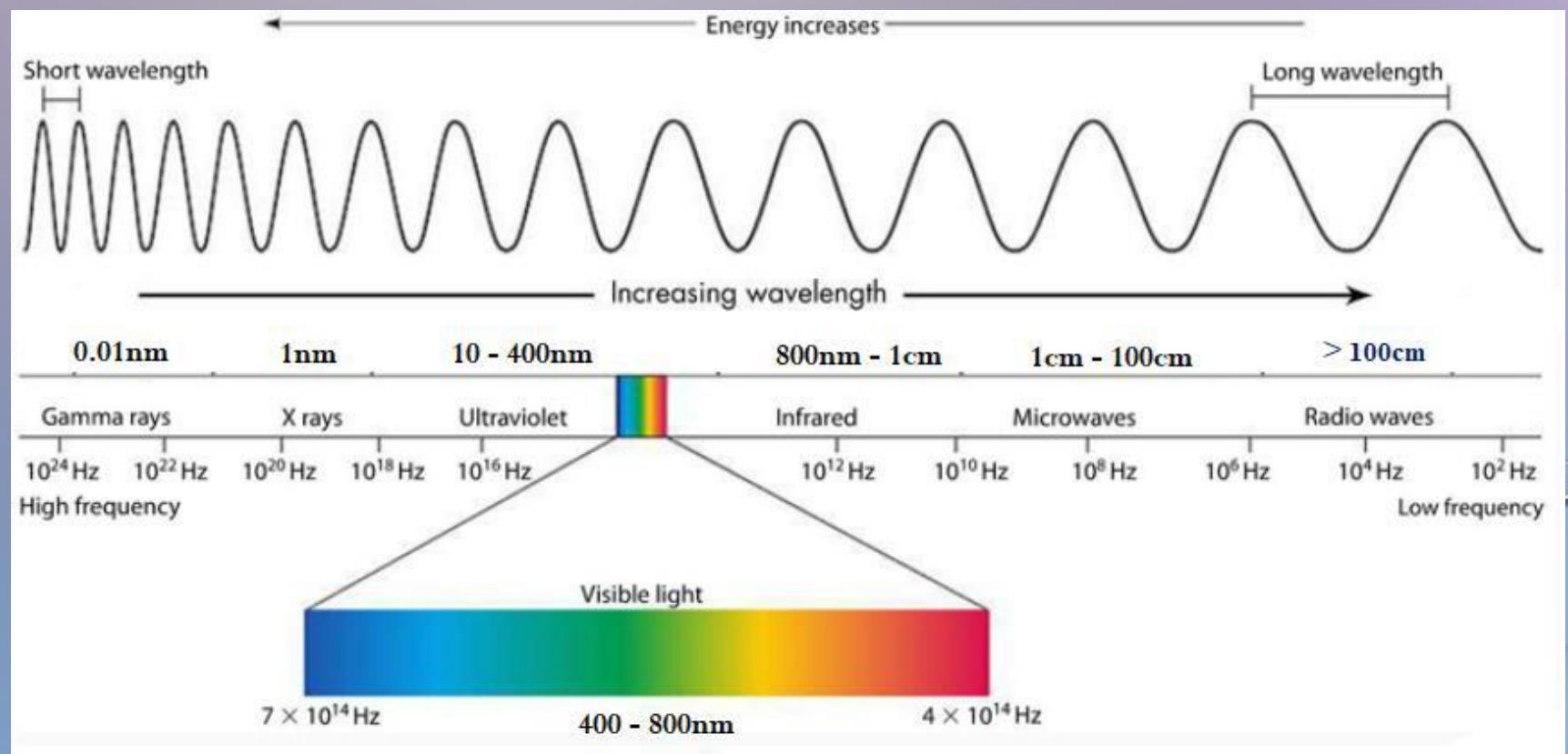
$$E = h c/\lambda$$

### Types of electromagnetic radiation

- Gamma radiation
- X-ray radiation
- UV-visible radiation
- IR-radiation
- Micro wave radiation
- Radio wave radiation

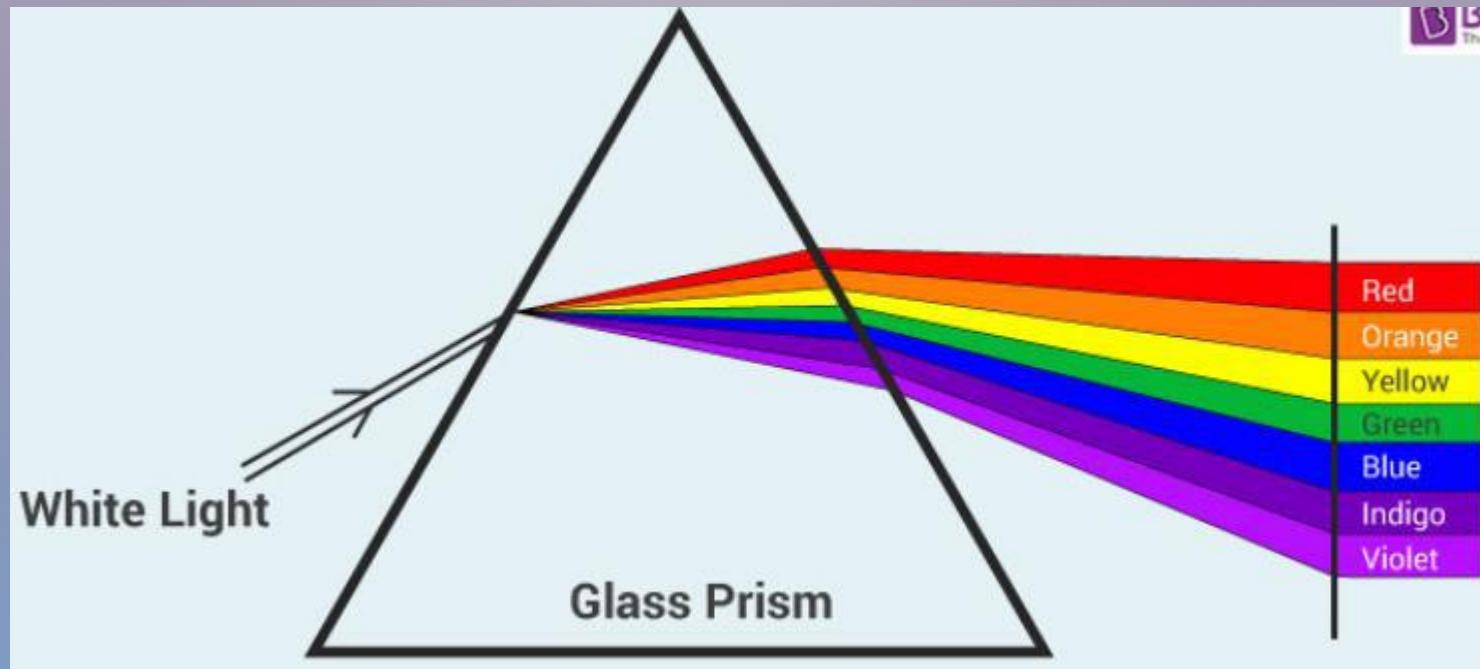
## Electromagnetic (EM) spectrum

- The arrangement of all types of electromagnetic radiation in order of their increasing wavelength or decreasing frequency is known as complete electromagnetic spectrum
- The EM spectrum shows that decreasing range of frequencies from Gamma rays (Highest frequency) to Radio waves (Lowest frequency)
- The EM spectrum shows that an Increasing Wavelength range from gamma rays (Lowest wave length) to Radio wave(Highest wavelength)

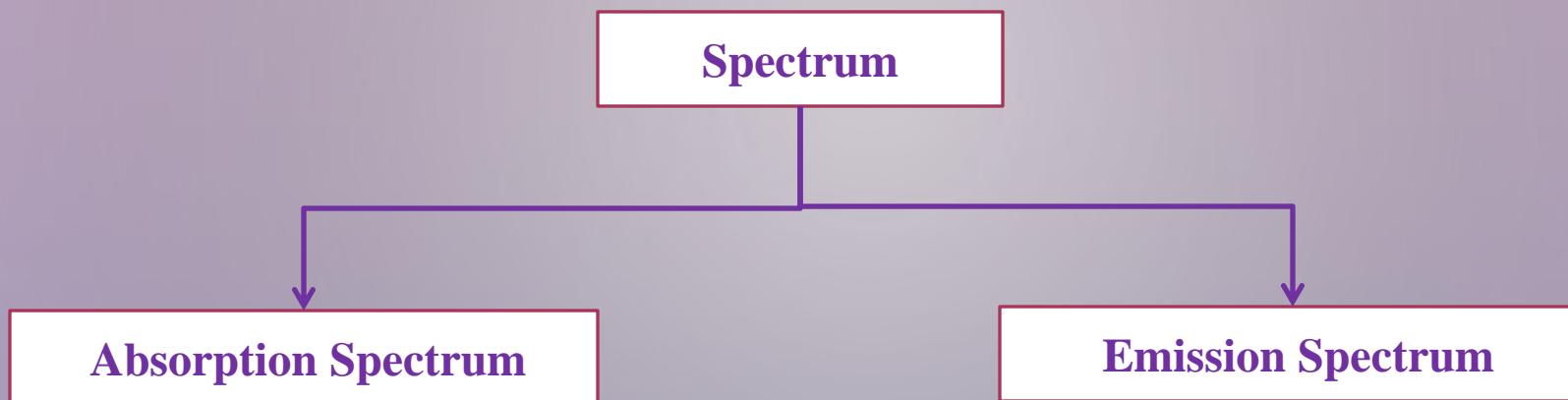


## SPECTRUM

- The analysis of a composite radiation into different frequency or wavelength is called spectrum
- First Spectrum is discovered by Isaac Newton
- Isaac Newton first applied the word *spectrum* to describe the rainbow of colors that combine to form white light.

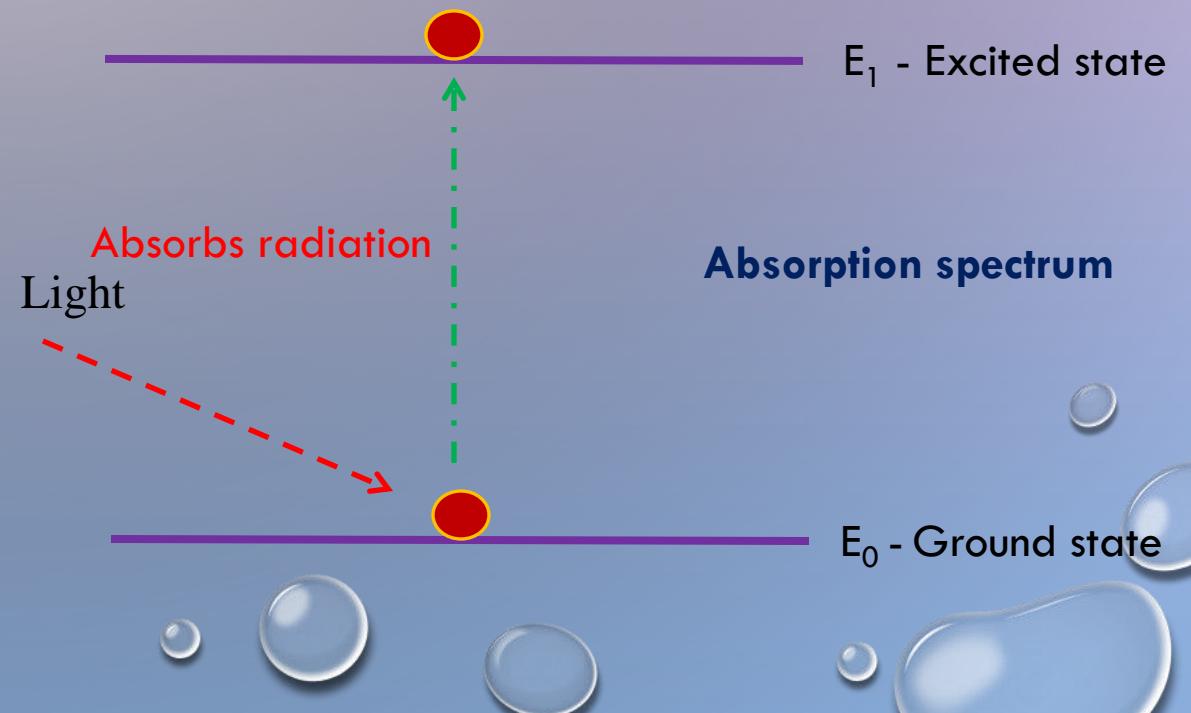


## TYPES OF SPECTRUM



### Absorption spectrum

When electromagnetic radiation interacts with atoms and molecules of matter, the electrons in these atoms may absorb energy and jump to a higher energy state

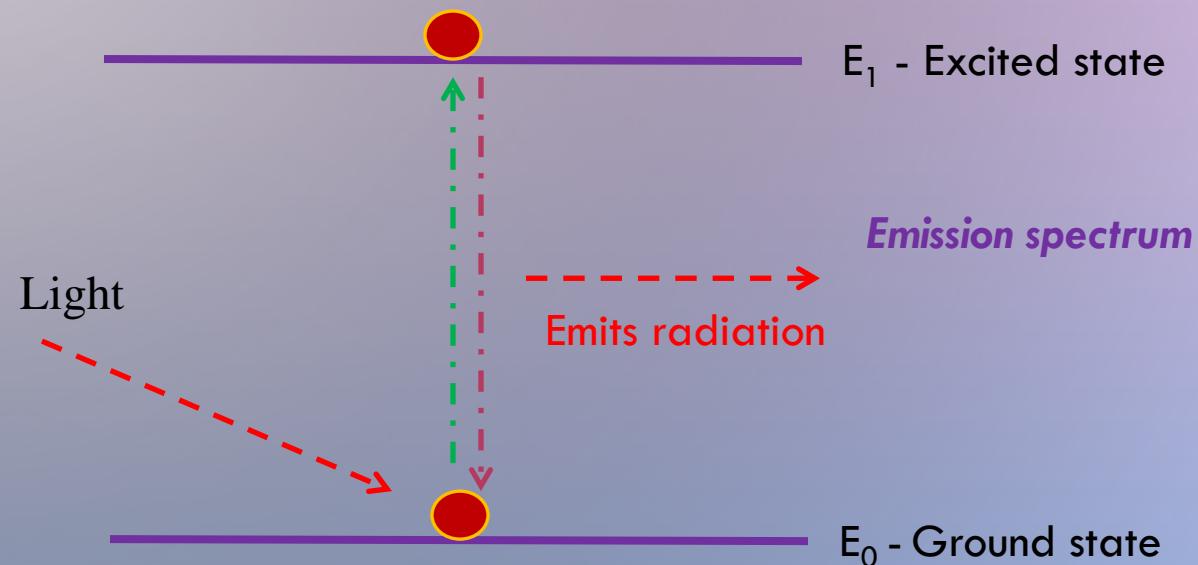


## Emission Spectrum

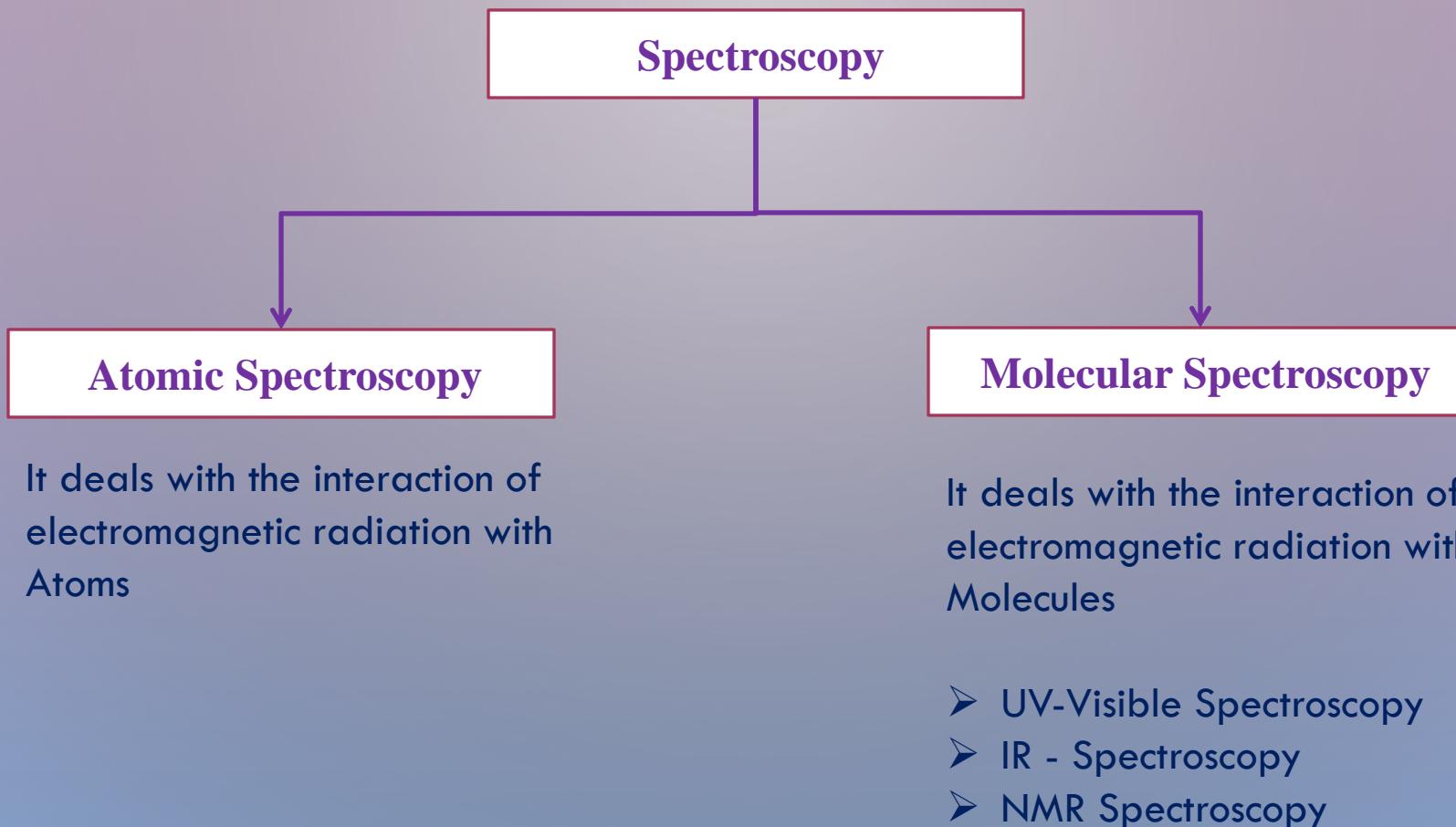
When electromagnetic radiation interacts with atoms and molecules of matter, the electrons in these atoms may absorb energy and jump to a higher energy state, losing their stability.

In order to regain their stability, they need to move from the higher energy state to the previous lower energy state. These atoms and molecules emit radiation in various regions of the electromagnetic spectrum.

This spectrum of radiation emitted by electrons in the excited atoms or molecules is known as an **emission spectrum**.



# Types of Spectroscopy



# **UV-Visible Spectroscopy**

# Interaction of EMR with matter

## Electronic Energy Level

- At room temperature the molecules are in the lowest energy level  $E_0$
- When the molecules absorb UV-Visible light from EMR, one of the outermost/lone pair electron is promoted to higher energy state such as  $E_1$ ,  $E_2$ ,  $E_3$ ..... $E_n$ , etc is called as electronic transition and
- The difference is  $\Delta E = h\nu = E_n - E_0$ , where  $n = 1, 2, 3, \dots$

# Lambert's law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation ( $-dl$ ) with thickness of the medium ( $dx$ ) is directly proportional to the intensity of incident light ( $I$ )

Let  $I$  be the intensity of incident radiation

$dx$  be the thickness of the medium

Then

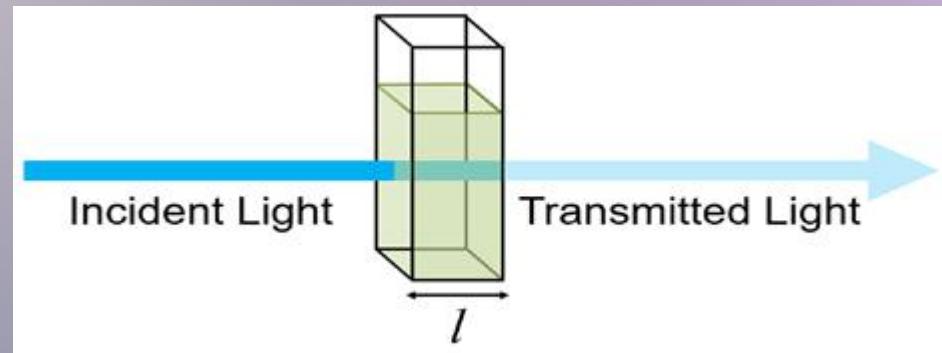
$$-\frac{dI}{dx} \propto I$$

$$-\frac{dI}{dx} = KI$$

Integrate equation between limit  $I = I_0$  at  $x = 0$  and  $I = I$  at  $x = l$

$$-\int_{I_0}^I \frac{dI}{I} = K \int_0^l dx$$

$$\ln \frac{I}{I_0} = Kl$$



$$2.303 \log \frac{I}{I_0} = Kl$$

$$\log \frac{I}{I_0} = \frac{K}{2.303} l$$

$$\log \frac{I}{I_0} = A$$

Absorbance

$$\frac{K}{2.303} = \epsilon$$

Absorption coefficient

$$A = \epsilon \cdot l$$

Lambert's law

The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette

## Beer's law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation ( $-dl$ ) with thickness of the medium ( $dx$ ) is directly proportional to the intensity of the incident light ( $I$ ) as well as concentration of the solution ( $C$ ).

Let  $I$  be the intensity of incident radiation

$dx$  be the thickness of the medium, then

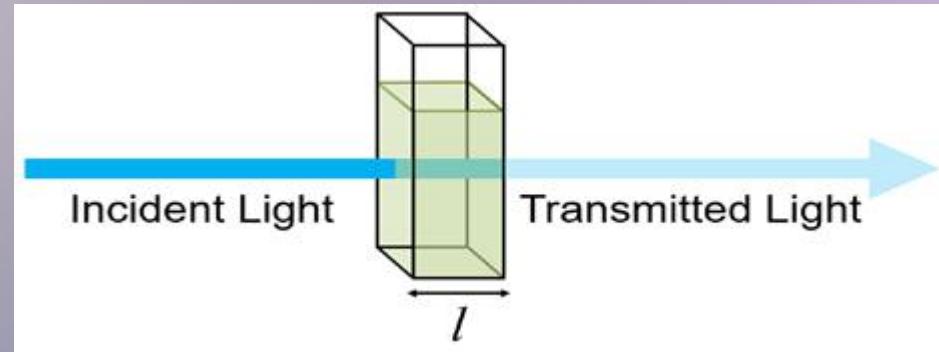
$$-\frac{dI}{dx} \propto CI$$

$$-\frac{dI}{dx} = KCI$$

Integrate equation between limit  $I = I_0$  at  $x = 0$  and  $I = I$  at  $x = l$

$$-\int_{I_0}^I \frac{dI}{I} = KC \int_0^l dx$$

$$\ln \frac{I}{I_0} = KCl$$



$$2.303 \log \frac{I}{I_0} = KCl$$

$$\log \frac{I}{I_0} = \frac{K}{2.303} cl$$

$$\log \frac{I}{I_0} = A \quad \text{Absorbance}$$

$$\frac{K}{2.303} = \varepsilon \quad \text{Molar extinction coefficient}$$

$$A = \varepsilon \cdot c \cdot l \quad \text{Beer's law}$$

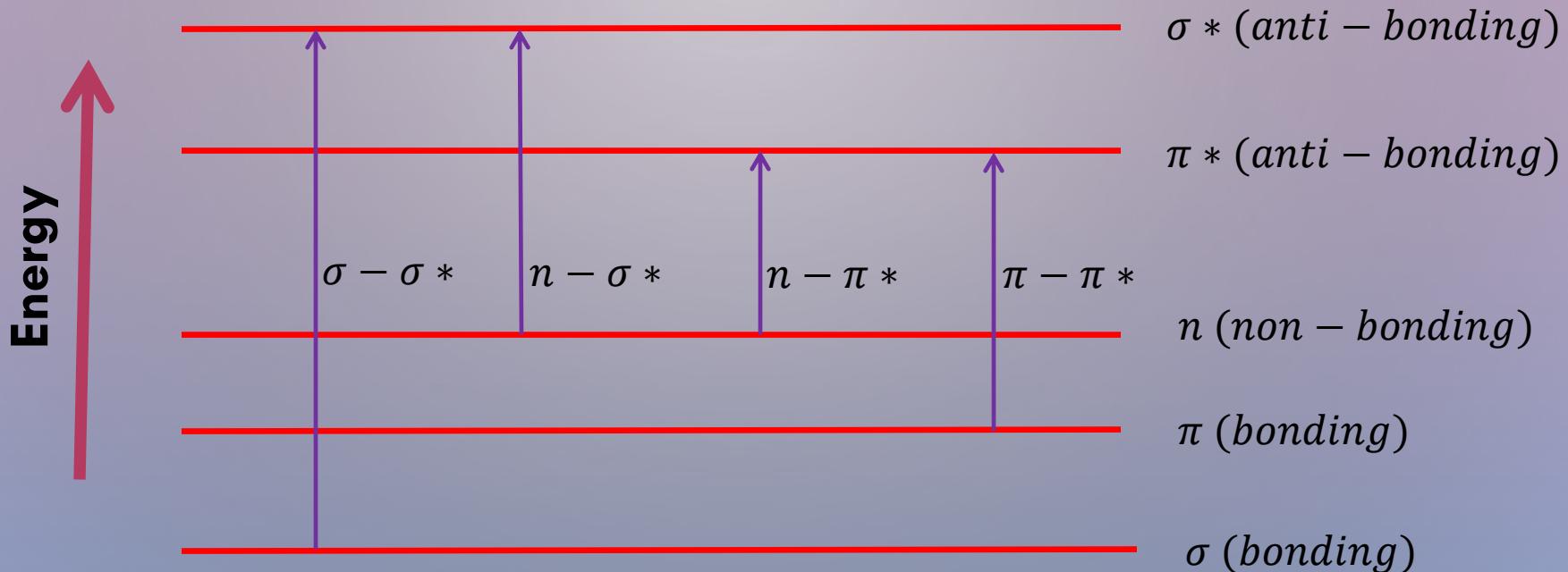
- The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment.
- The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette

## Principle of UV-visible Spectroscopy

- The UV radiation region extends from 10 nm to 400 nm and the visible region extends from 400 nm to 800 nm
- Near UV region: 200 nm to 400 nm
- Far UV region : below 200 nm
- Far UV Spectroscopy studied under vacuum condition
- The common solvent used for preparing the sample to be analyzed is either ethyl alcohol or hexane

# Electronic Transitions

The possible electronic transitions can graphically shown as



The possible electronic transitions are

1.  $\sigma - \sigma^*$  transition
2.  $n - \sigma^*$  transition
3.  $\pi - \pi^*$  transition
4.  $n - \pi^*$  transition

## 1. $\sigma - \sigma^*$ transition

- This transition is possible only in saturated compound
- $\sigma$  electron from bonding orbital is excited to corresponding anti-bonding orbital  $\sigma^*$
- The energy required is large for this transition
- e.g. Methane ( $\text{CH}_4$ ) has C – H bond only and undergo  $\sigma - \sigma^*$  transition and shows absorbance maxima at 125nm

## 2. $n - \sigma^*$ transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and Halogens are capable of  $n - \sigma^*$  transition
- An electron from non-bonding orbital is promoted to anti-bonding orbital  $\sigma^*$
- These transitions usually requires less energy than  $\sigma - \sigma^*$  transition
- The number of organic functional groups with  $n - \sigma^*$  peaks in UV region is small (150-250nm)

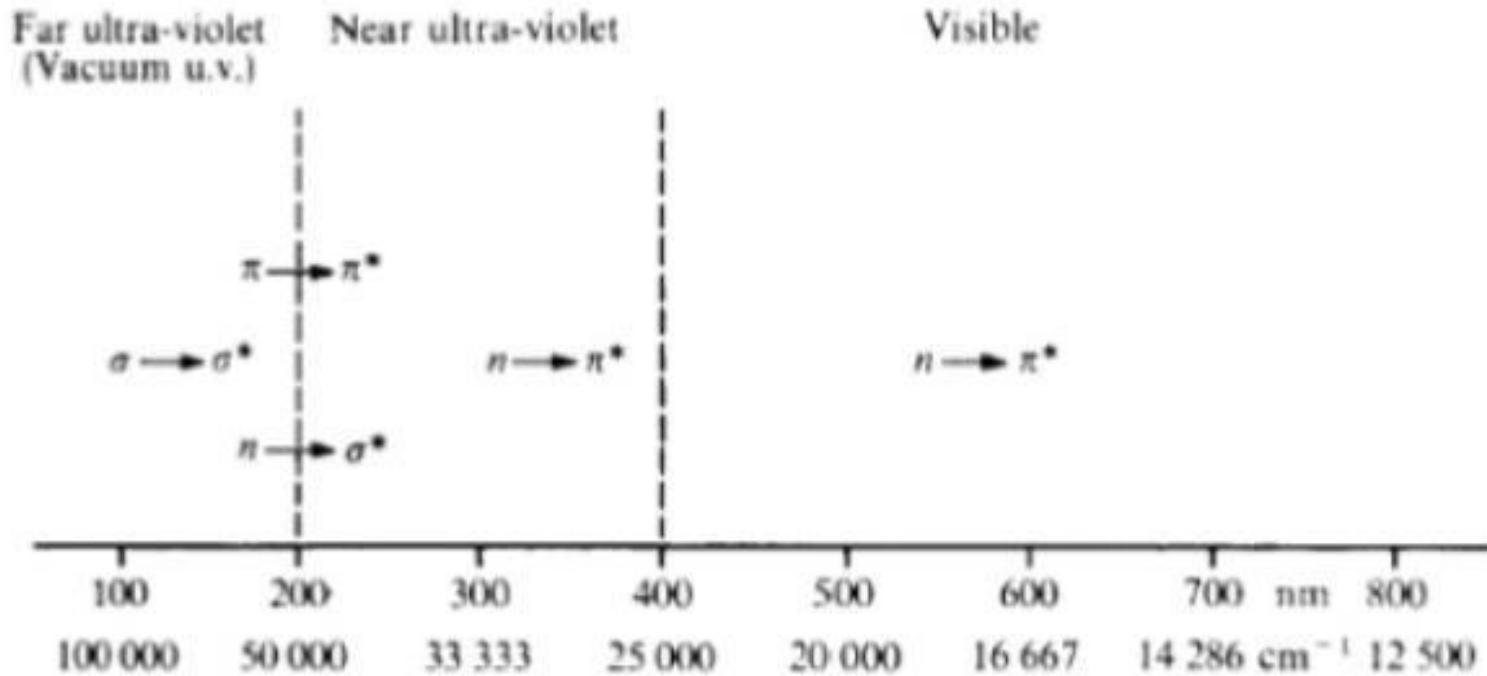
### 3. $\pi - \pi^*$ transition

- Compound containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compound etc undergo  $\pi - \pi^*$  transition
- $\pi$  electron in a bonding orbital is excited to corresponding anti-bonding orbital  $\pi^*$
- The energy required is large for this transition
- e.g. Alkenes generally absorb in the region 175 to 205nm

### 4. $n - \pi^*$ transition

- Compounds containing double bond involving hetero C=O, C  $\equiv$  N, N=O undergo  $n - \pi^*$  transition
- An electron from non-bonding orbital is promoted to anti-bonding orbital  $\pi^*$
- $n - \pi^*$  transitions requires minimum energy and show absorption at longer wavelength around 300 nm

## The region of the electronic spectrum



The regions of the electronic spectrum and the types of transitions that occur in each.

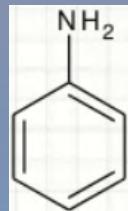
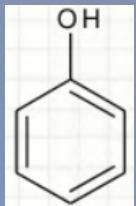
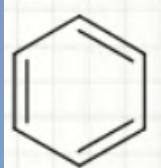
# Important terms used in UV-visible Spectroscopy

## Chromophore

- The part of a molecule responsible for imparting color, are called as chromophore (or)
- The functional groups containing multiple bonds capable of absorbing radiations above 200nm due to  $n - \pi^*$  &  $\pi - \pi^*$  transitions
- e.g.  $\text{NO}_2$ ,  $\text{N}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$  etc

## Auxochrome

- It is a group which itself does not act as a chromophore but when attached to a chromophore, it shifts the adsorption towards longer wavelength along with an increase in the intensity of absorption.



## Absorption and Intensity shifts

- Bathochromic shift (Red shift)
- Hypsochromic Shift (Blue shift)
- Hyperchromic effect
- Hypochromic effect

## Bathochromic shift (Red shift)

- When absorption maxima of a compound shifts to longer wavelength, it is known as Bathochromic shift or red shift
- The effect is due to presence of an auxochrome or by the change of solvent
- e.g. an auxochrome group like  $-\text{OH}$ ,  $-\text{OCH}_3$  causes absorption of compound at longer wave length

## Hypsochromic Shift (Blue shift)

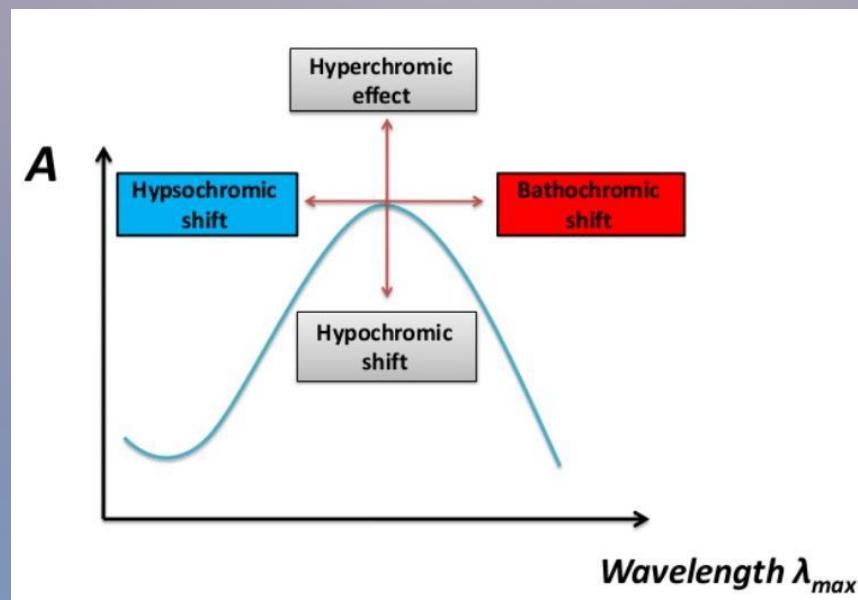
- When absorption maxima of a compound shifts to shorter wavelength, it is known as Hypsochromic shift or blue shift
- The effect is due to presence of a group causes removal of conjugation or by the change of solvent

## Hyperchromic effect

When absorption intensity of a compound is increased, it is known as hyperchromic effect

## Hypochromic effect

When absorption intensity of a compound is decreased, it is known as hypochromic effect

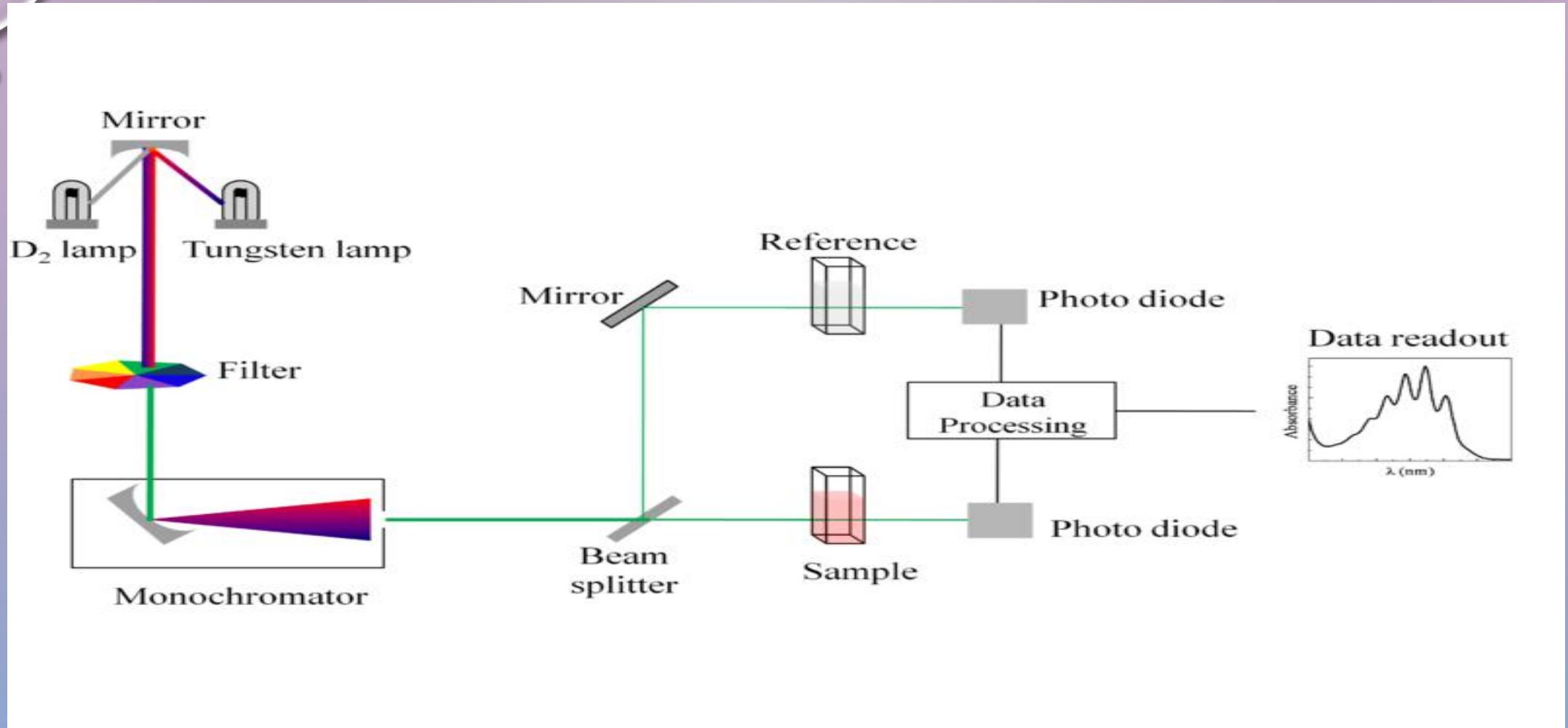


## Instrumentation of UV-visible Spectroscopy

- Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample moves from one energy state to another energy state.
- UV-visible spectroscopy is type of absorption spectroscopy in which light of UV-visible region 100 to 700 ( UV region 100-400 nm and Visible region 400-700nm) is absorbed by the molecule which results in the excitation of the electrons from the ground state to higher energy state.



## Instrumentation of UV-visible Spectroscopy



Instrumentation of UV-visible Spectroscopy

## **Source**

### **Requirements of an ideal sources**

- It should be stable
- It should emit light of continues spectrum of high and uniform intensity over the entire wavelength region in which its used
- It should provide incident light of sufficient intensity for the transmitted energy to be detected at the end of optic path
- It should not show fatigue on continued used

### **Source for UV region**

#### **Hydrogen lamp or Deuterium Lamp**

- In hydrogen discharge lamp pair of electrodes is enclosed in a glass tube (provided with silica or quartz window for UV radiation to pass through) filled with hydrogen gas
- When current is passed through these electrodes maintained at high voltage, discharge is electrons occurs which excites hydrogen molecules which in turn case emission of UV radiations in near UV region

## **Source of Visible region**

### **Tungsten halogen lamp**

- The bulbs contain a filament of tungsten fixed in evacuated condition and then filled with inert gas
- The filament can be heated up to 3000K, beyond this tungsten starts sublimation
- Sublimated from the tungsten reacts with iodine to form Tungsten-Iodine complex
- Which migrates back to the hot filament where it decomposes and tungsten get deposited

### **Mirror**

- These are used to reflect, focus or collimate light beams in spectrophotometer
- To minimize the light loss, mirrors are aluminized on their front surface

### **Slits**

- It is an important device in resolving polychromatic in to monochromatic radiation
- To achieve this, entrance slit and exit sit are used
- The width of slit plays an important role in resolution of polychromatic radiation

## **Monochromators**

It is device used to isolate the radiation of the desired wavelength from wavelength of continues spectra

Following types of monochromatic devices are used

- Filters
- Prisms
- Gratings

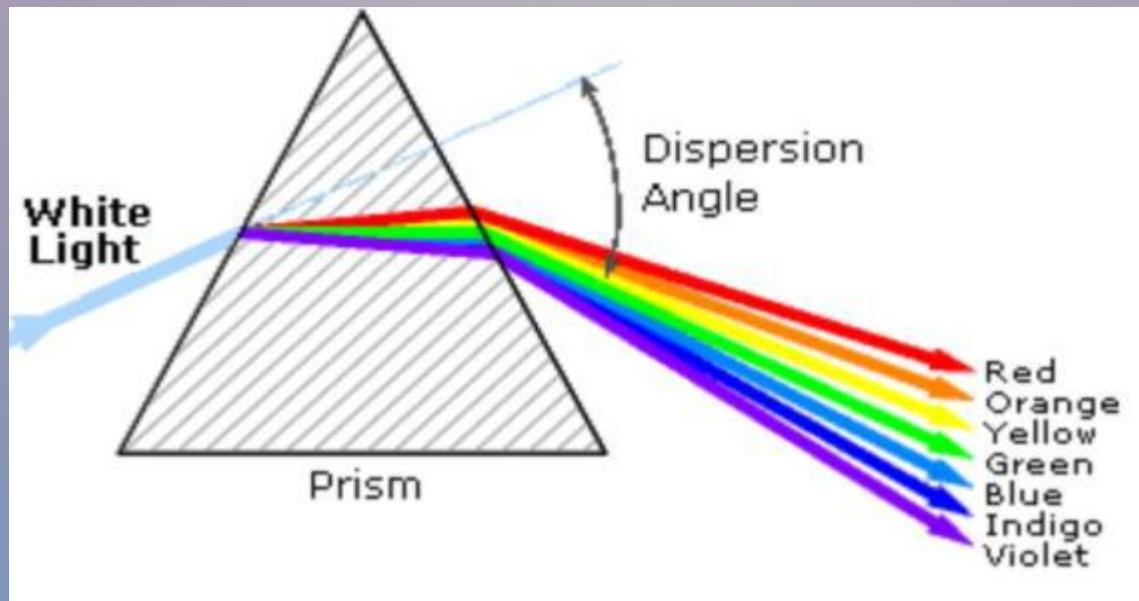
### **Filters**

It works by selective absorption of unwanted radiation and transmits the radiation (narrow band of radiation) which is required

e.g. Glass and gelatin filters

## Prisms

- It is made of quartz or fused silica
- When light is passed through glass prism, dispersion of polychromatic light in rainbow occurs. Now by rotation of the prism different wavelength of spectrum can be made to pass through in exit slit on the sample
- The effective wavelength depends on the dispersive power of prism material and the optical angle of the prism

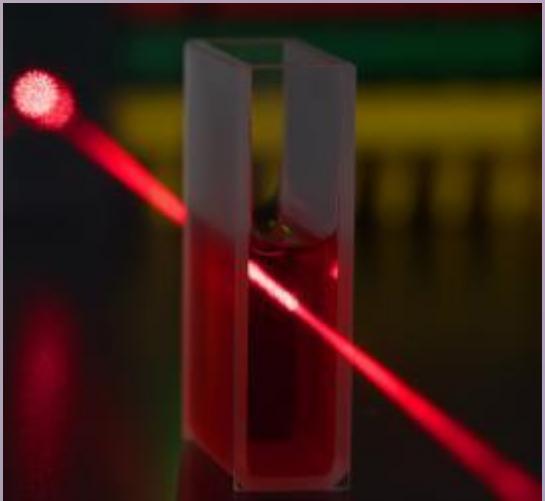


## Gratings

Finely grooved highly reflective surface (diffraction)

## Sample holder/Cuvettes

- The cells or cuvettes are used for handing liquid samples
- It may either be rectangular or cylindrical in nature
- It is made of quartz or fused silica



## Detectors

- Device which converts light energy in to electrical signals, that are displayed on readout devices
- The transmitted radiation falls on the detector which determines the intensity of radiation absorbed by sample

## Types of detectors

- Barrier layer/photovoltaic cell
- Phototubes/photo emissive tube
- Photomultiplier tube

## **Requirements of an ideal detector**

- It should give quantitative response
- It should have high sensitivity and low noise level
- It should have a short response time
- It should provide signal or response quantitative to wide spectrum of radiation received

## **Amplifier**

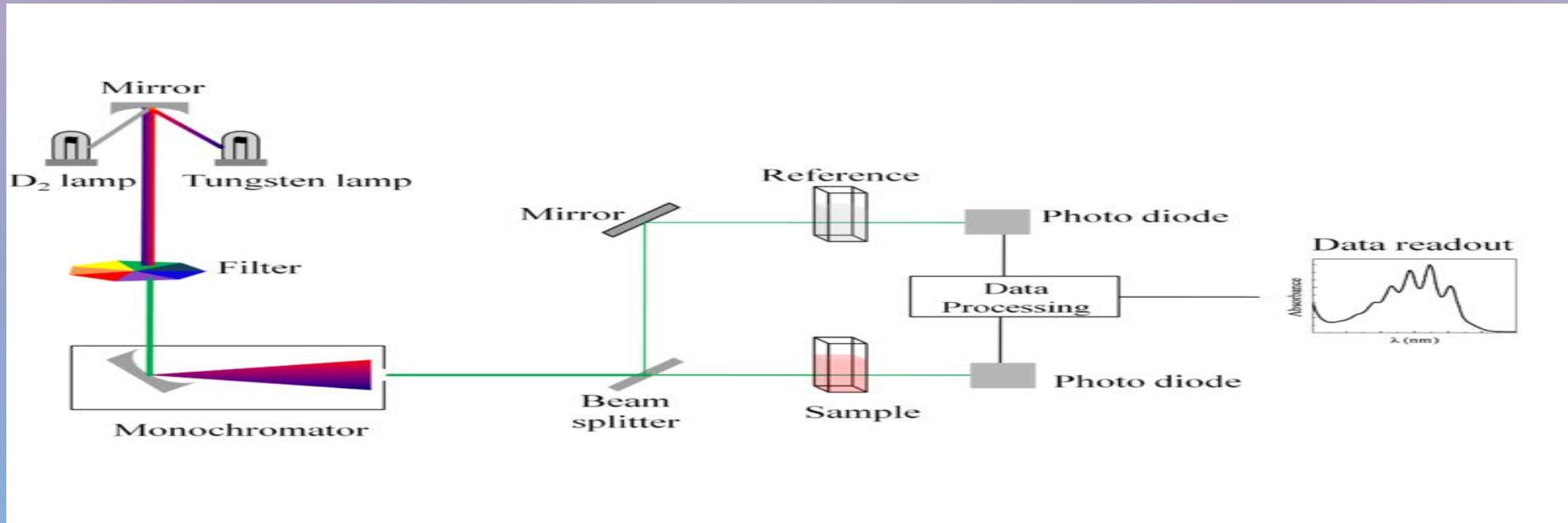
- The alternating current generated in the photocells is transferred to the amplifier
- The amplifier is coupled to a small servometer
- Generally current generated in the photocells is very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals

## **Recording devices**

- Most of the time amplifier is coupled to a pen recorder which is connected to the computer
- Computer stores all the data generated and produces the spectrum of the desired compound

## Working:

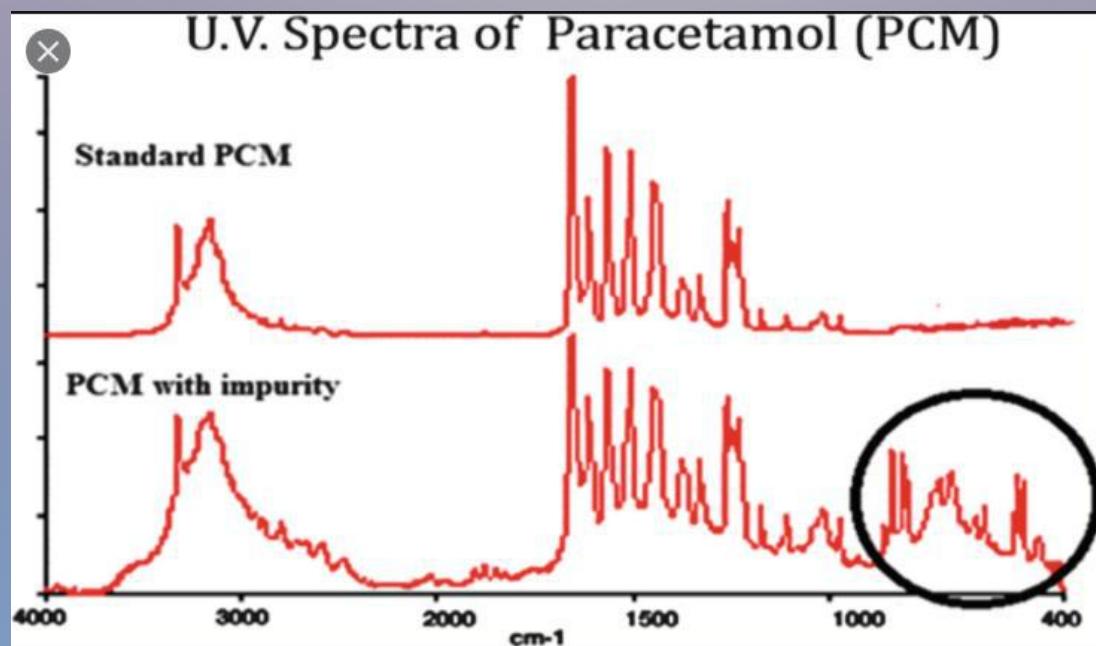
The radiation from the source is passed through the monochromator where it splitted into two equal beams, one half is passed into the sample cell and another half is passed into the reference cell containing solvent. The detector will measure the comparison of intensities of beam of light. If the sample absorbs light then the intensity of sample beam is less than the intensity of reference beam. It will be recorded as a signal in recorder. The instruments gives output graph



# Applications of UV-visible Spectroscopy

## 1. Detection of Impurities

UV absorption spectroscopy is one of the best method for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw materials. By also measuring the absorbance at specific wavelength, the impurities can be detected



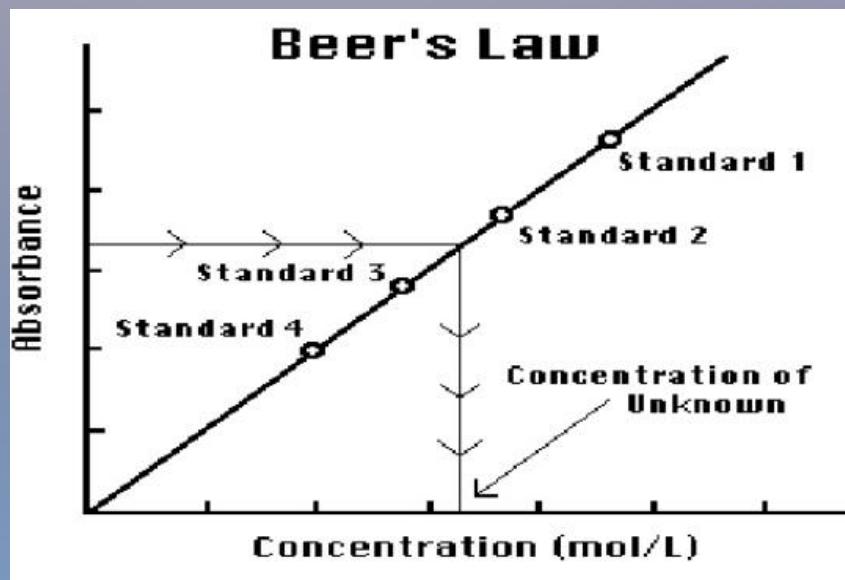
## 2. Structure elucidation of organic compounds

- UV-spectroscopy is useful in the structure elucidation of organic molecules, the presence or absence of unsaturation, the presence of hetero atoms
- From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc

## 3. Quantitative analysis

UV absorption spectroscopy can be used for the quantitative determination of compounds that absorbs UV radiation. This determination is based on Beer's law

$$A = \epsilon cl$$



#### 4. Qualitative analysis

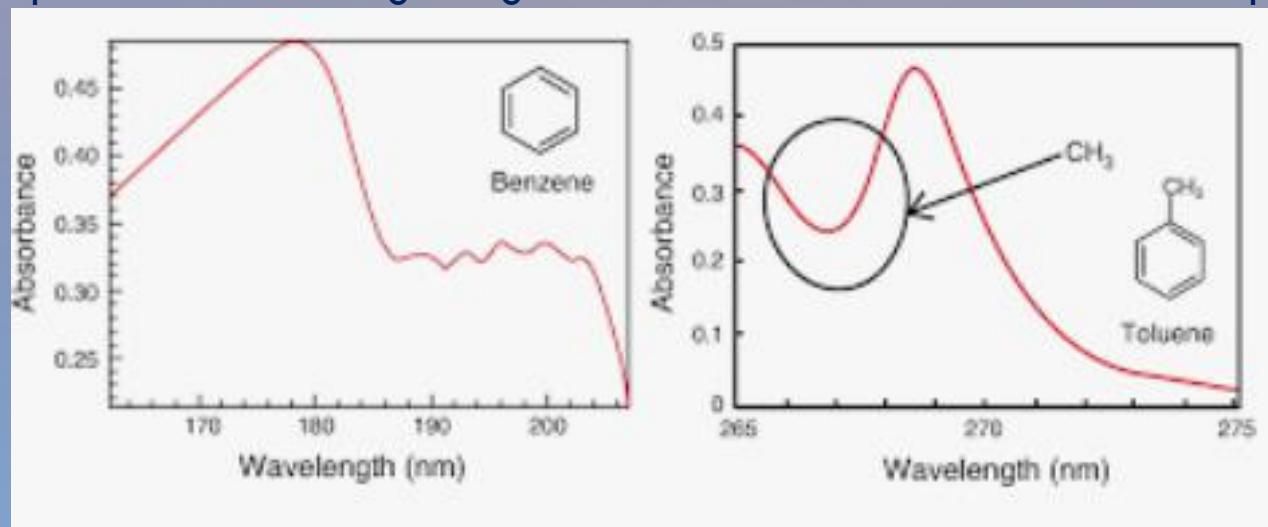
UV absorption spectroscopy can characterize those type of compounds which absorbs UV radiation. Identification is done by comparing the absorption spectrum with spectra of known compounds

#### 5. Chemical Kinetics

Kinetics of the reaction can also be studied using UV Spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed

#### 6. Detection of Functional groups

- This technique is used to detect the presence or absence of functional group in the compound
- Absence of a band at particular wavelength regarded as an evidence for absence of particular group

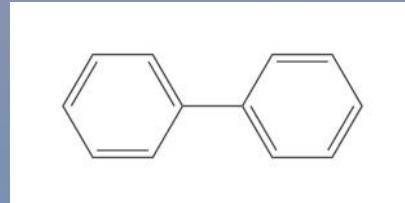
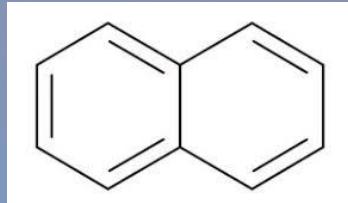


## 7. Quantitative analysis of pharmaceutical substances

Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength

## 8. Examination of polynuclear hydrocarbons

- Benzene and polynuclear hydrocarbons have characteristic spectra in ultraviolet and visible region. Thus identification of polynuclear hydrocarbon can be made by comparison with the spectra of known polynuclear compounds.
- Polynuclear hydrocarbons are the hydrocarbon molecule with two or more closed rings; examples are naphthalene  $C_{10}H_8$ , with two benzene rings side by side, or diphenyl  $(C_6H_5)_2$ , with two bond connected benzene rings as known as polycyclic hydrocarbon

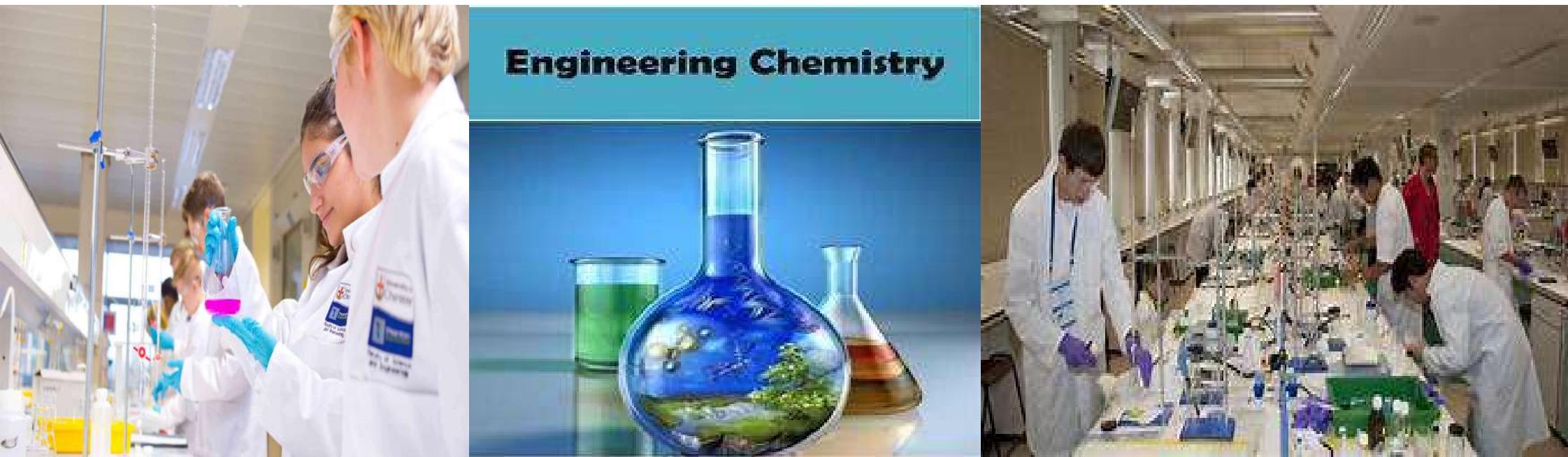


## **9. Molecular weight determination**

- Molecular weight of the compounds can be determined spectrophotometrically by preparing the suitable derivatives of these compounds
- For example, if we want determine the molecular weight of amine then it is converted in to amine picrate. Then known concentration of amine picrate is dissolved in a litre of solution and its optical density is measured at  $\lambda_{\text{max}} 380\text{nm}$

## **10. As HPLC detector**

UV-visible spectrophotometer may be used as a detector for HPLC



# **ENGINEERING CHEMISTRY**

## **SEC-E & F**

**Dr. Sivasankaran**

**Mb. No.:7397575840**

**Associate Professor**

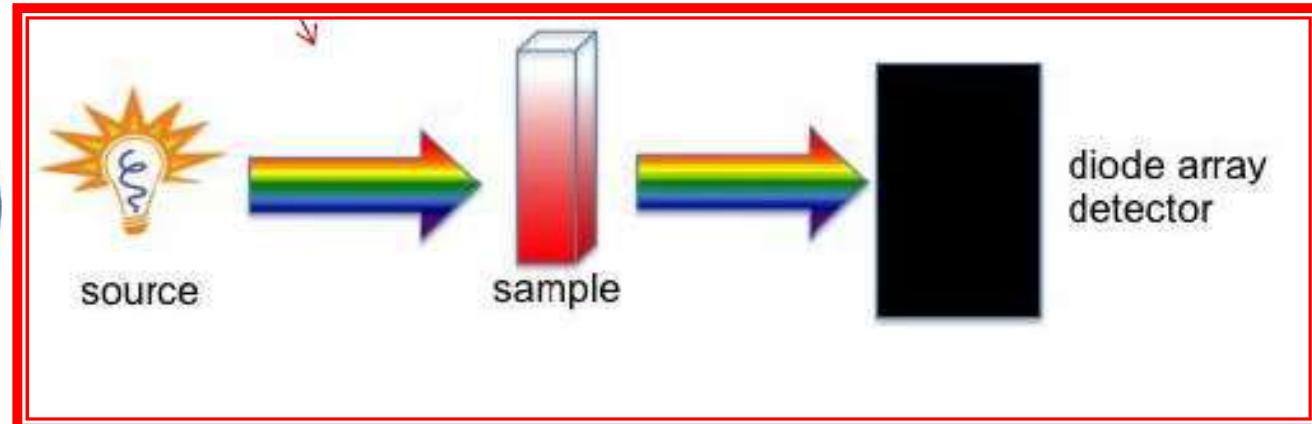
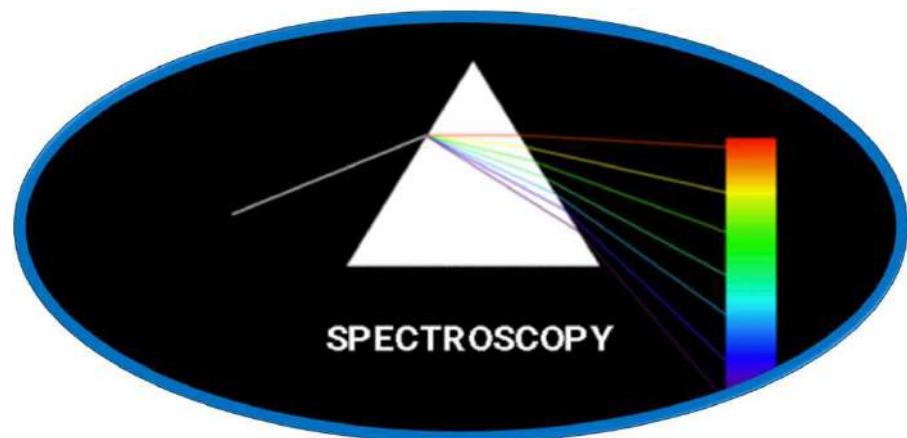
**Department of Chemistry**

**BIHER, Chennai, India**

## UNIT II

# FUNDAMENTALS AND APPLICATIONS OF SPECTROSCOPY

- ❖ Spectroscopy – General introduction and Explanation;
- ❖ Types of Spectroscopy – Basic concepts and Principles of Electronic spectroscopy, Rotational spectroscopy and Vibrational spectroscopy.
- ❖ Applications of rotational and vibrational spectroscopy of diatomic molecules – Selection rules.
- ❖ Nuclear magnetic resonance spectroscopy – Introduction, principle, Instrumentation and applications.



**Spectroscopy:** It is a technique that uses the interaction of energy with a sample to perform an analysis.

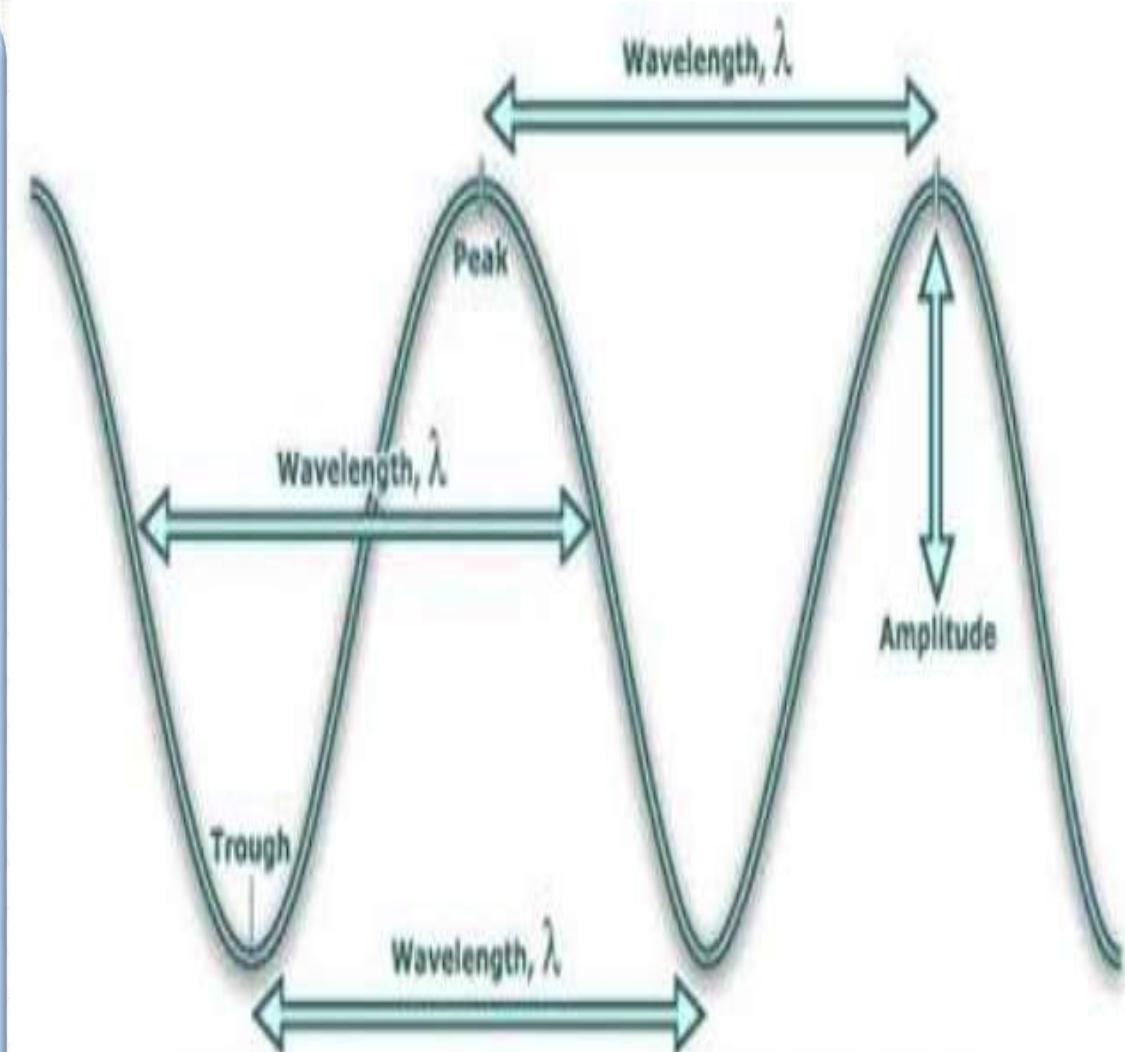
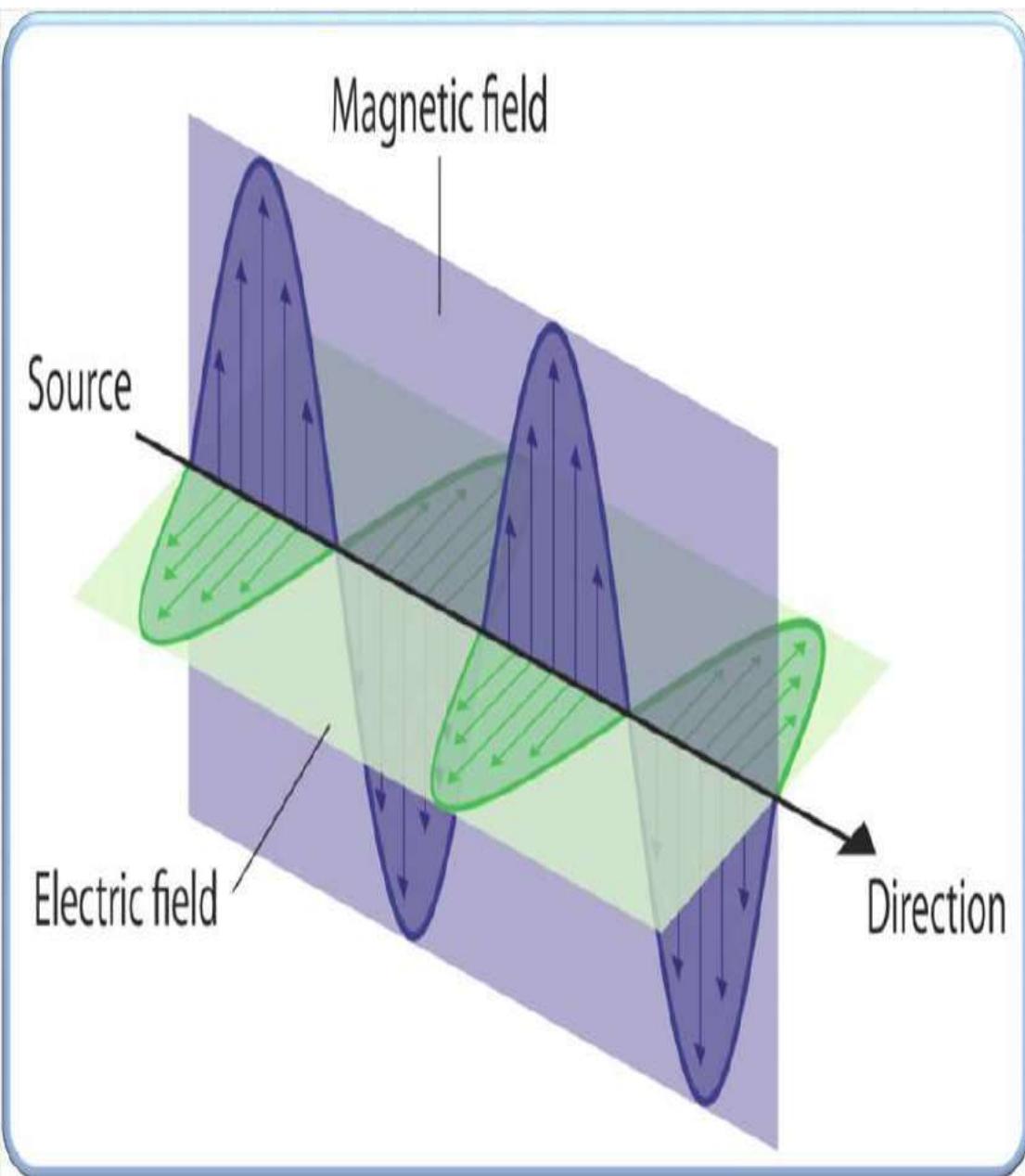
**Spectrum:** The data that is obtained from spectroscopy is called a Spectrum. A spectrum is a plot of the intensity of energy detected versus the wavelength (or mass or momentum or frequency, etc.) of the energy.

**What Information Is Obtained:** A spectrum can be used to obtain information about atomic and molecular energy levels, molecular geometries, chemical bonds, interactions of molecules, and related processes. Often, spectra are used to identify the components of a sample (qualitative analysis). Spectra may also be used to measure the amount of material in a sample (quantitative analysis).

**What Instruments Are Needed:** Several instruments are used to perform spectroscopic analysis. In simplest terms, spectroscopy requires an energy source (commonly a laser, but this could be an ion source or radiation source) and a device for measuring the change in the energy source after it has interacted with the sample (often a spectrophotometer or interferometer).

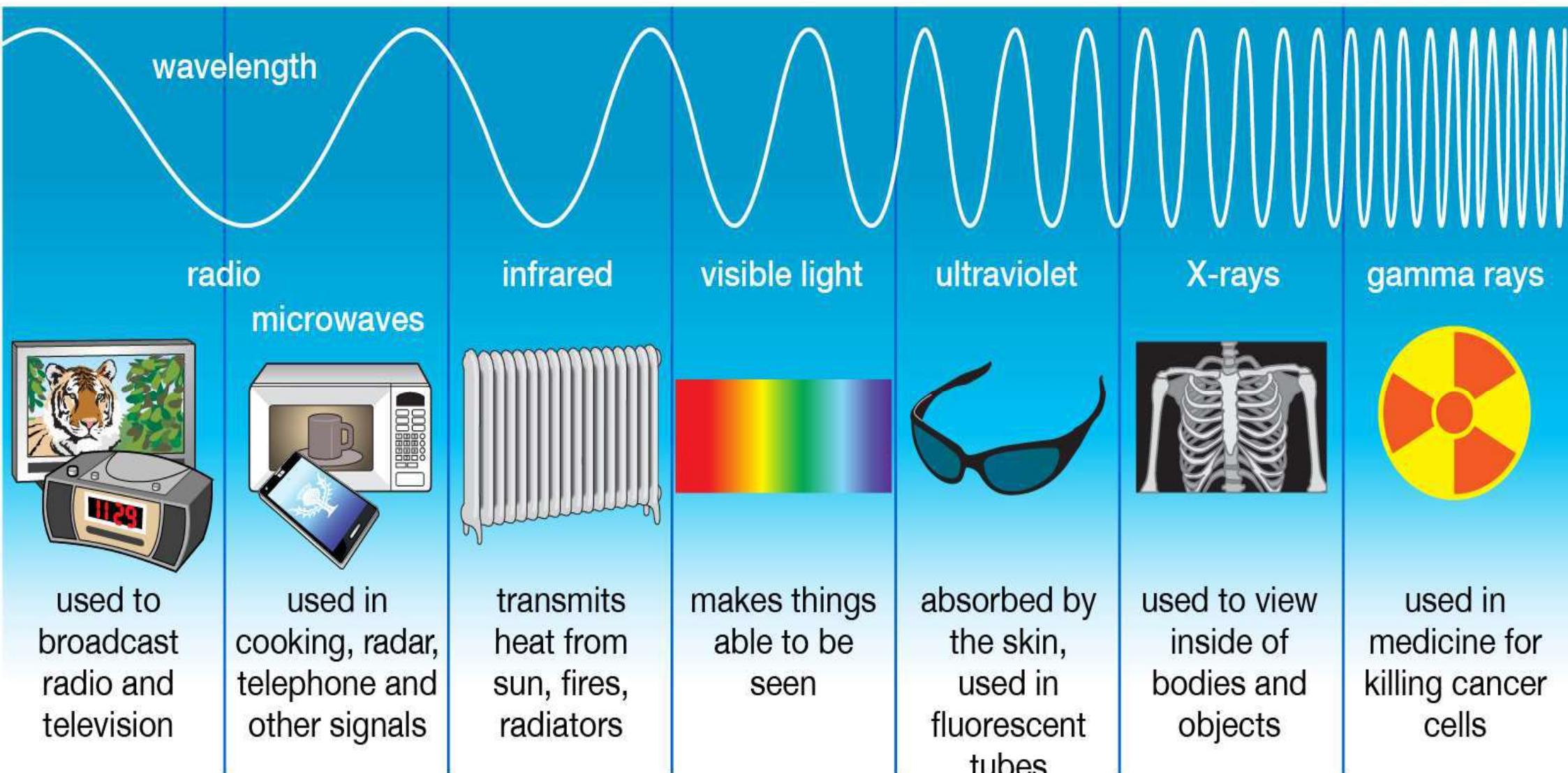
## **ELECTROMAGNETIC RADIATION (EMR)**

- ❖ Electromagnetic radiation consist of discrete packages of energy which are called as photons.
- ❖ A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.
- ❖ Frequency ( $\nu$ ): It is defined as the number of times electrical field radiation oscillates in one second.
- ❖ The unit for frequency is Hertz (Hz).  $1 \text{ Hz} = 1 \text{ cycle per second}$
- ❖ Wavelength ( $\lambda$ ): It is the distance between two nearest parts of the wave in the same phase i.e. distance between two nearest crest or troughs.
- ❖ The relationship between wavelength & frequency can be written as:  $c = \nu \lambda$
- ❖ As photon is subjected to energy, so  $E = h \nu = h c / \lambda$ ;  $E \propto 1/\lambda$
- ❖  $\nu \propto 1/\lambda$ , frequency  $\propto 1/\text{wavelength}$  and energy  $\propto 1/\text{wavelength}$ .



$$\text{Speed of wave, } v = \text{frequency, } f \times \text{wavelength, } \lambda$$

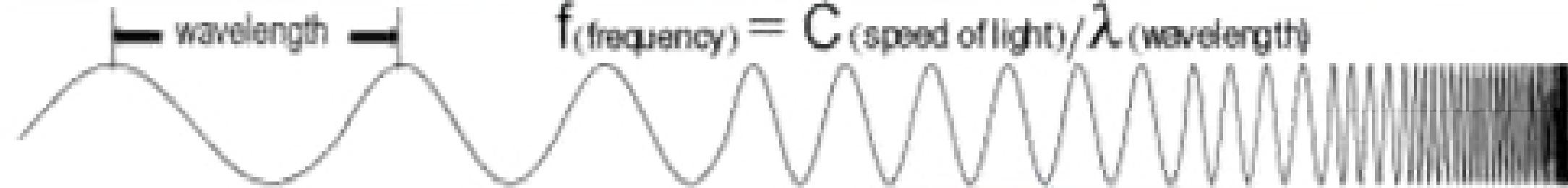
# Types of Electromagnetic Radiation



## INTERACTION OF EMR WITH MOLECULE

non-ionizing

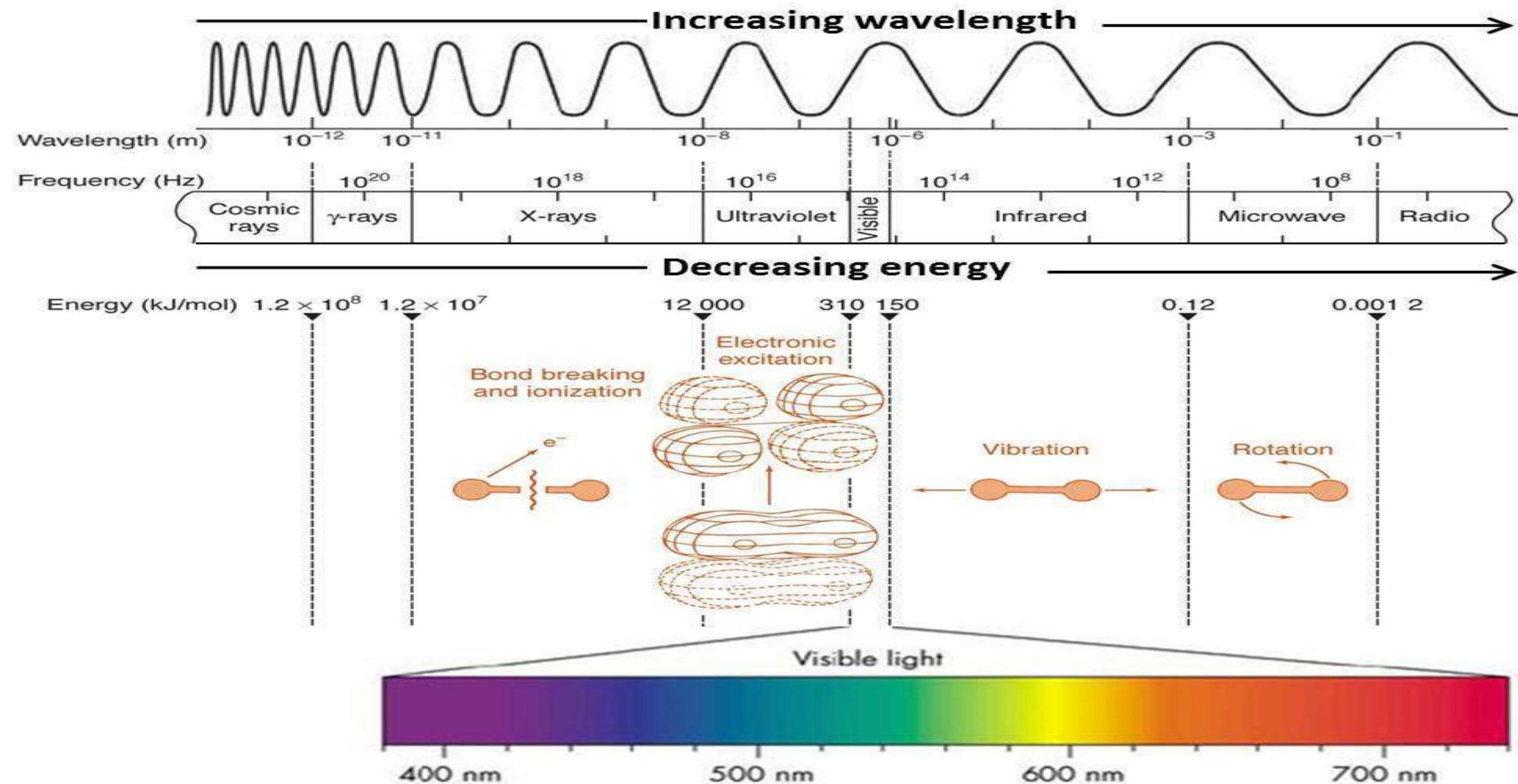
ionizing



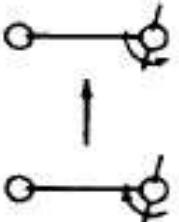
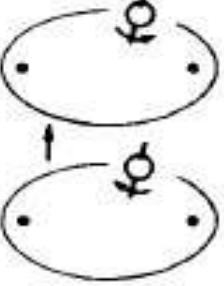
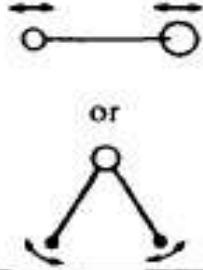
### EMF Sources



# INTERACTION OF EMR WITH MOLECULE



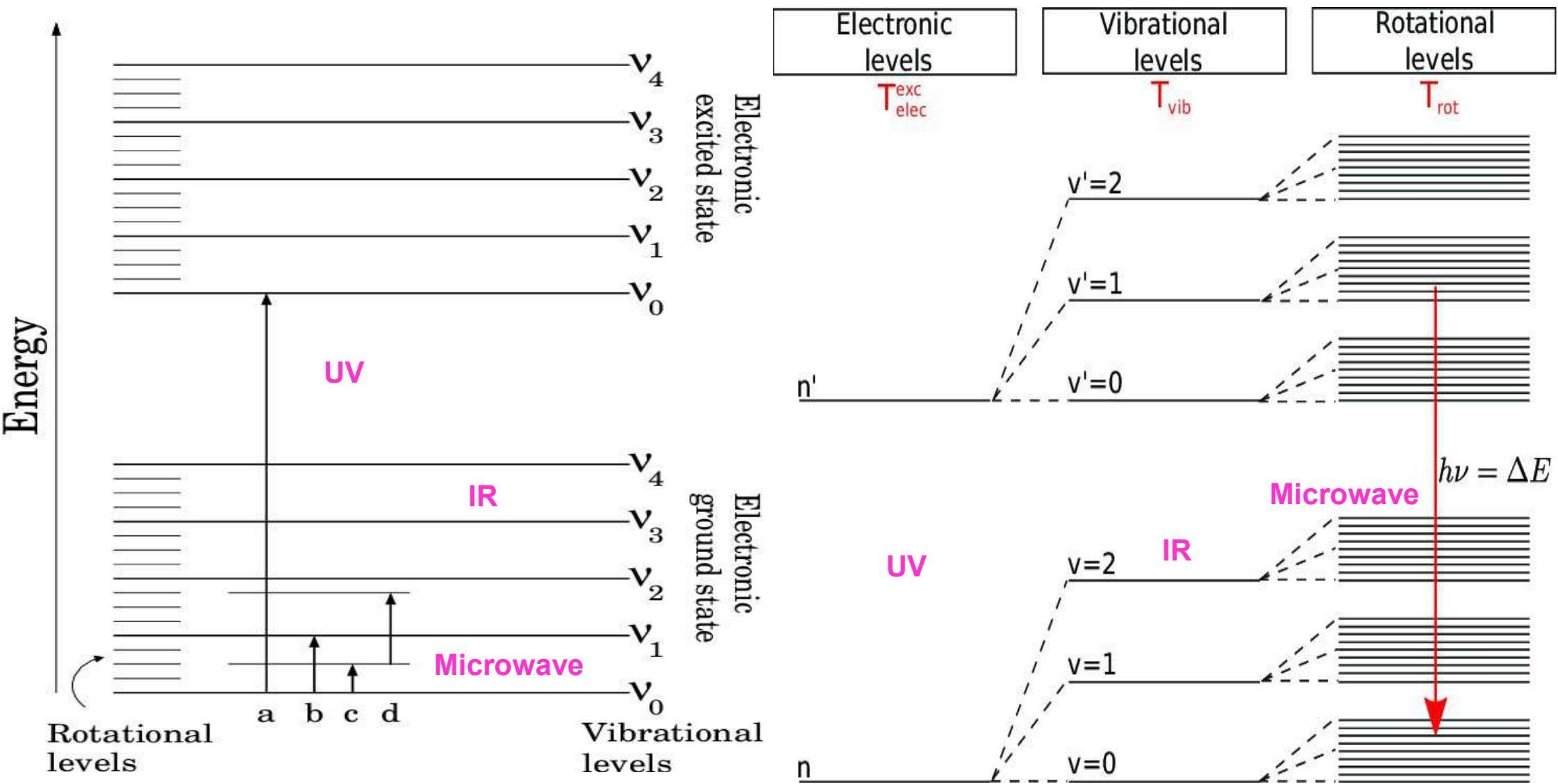
# INTERACTION OF EMR WITH MOLECULE

Change of spin	Change of orientation	Change of configuration	Change of electron distribution			Change of nuclear configuration
<b>Radio Wave</b>						
N.m.r.	E.s.r.	Microwave	Infra-red	Visible and ultra-violet	X-ray	$\gamma$ -ray
			 or 			
$10^{-2}$	1	100	$10^4$	$cm^{-1}$	$10^6$	Wavenumber $10^8$
10 m	100 cm	1 cm	100 $\mu$ m	1 $\mu$ m	10 nm	Wavelength 100 pm
$3 \times 10^6$	$3 \times 10^8$	$3 \times 10^{10}$	$3 \times 10^{12}$	$3 \times 10^{14}$	Hz	$3 \times 10^{16}$ Frequency $3 \times 10^{18}$
$10^{-3}$	$10^{-1}$	10	$10^3$	$10^5$	joules/mole	$10^7$ Energy $10^9$

## **VARIOUS ENERGY LEVEL OF MOLECULE**

- 1. Electronic Energy level:** At room temperature the molecules are in the lowest energy levels  $E_0$ . When the molecules absorb UV-visible light from EMR, one of the lowest level electron is promoted to higher energy state such as  $E_1$ ,  $E_2$ , ...  $E_n$ , is called as electronic transition and the difference is as:  $\Delta E = h \nu = E_n - E_0$  where ( $n = 1, 2, 3, \dots$  etc).  $\Delta E = 35$  to  $143$  kcal/mole.
- 2. Vibrational Energy Levels:** These are less energy level than electronic energy levels. The spacing between energy levels are relatively small i.e.  $\Delta E = 0.01$  to  $10$  kcal/mole.
- 3. Rotational Energy Levels:** These energy levels are quantized & discrete. The spacing between energy levels are even smaller than vibrational energy levels.  $\Delta E < 0.01$  kcal/mole.
- 4. Spin Energy Levels:** These energy levels are quantized & discrete. The spacing between energy levels are even smaller than rotational energy levels.
- 5.  $\Delta E_{\text{Electronic}} > \Delta E_{\text{Vibrational}} > \Delta E_{\text{Rotational}} > \Delta E_{\text{Spin}}$**

# SCHEMATIC ENERGY LEVEL DIAGRAM

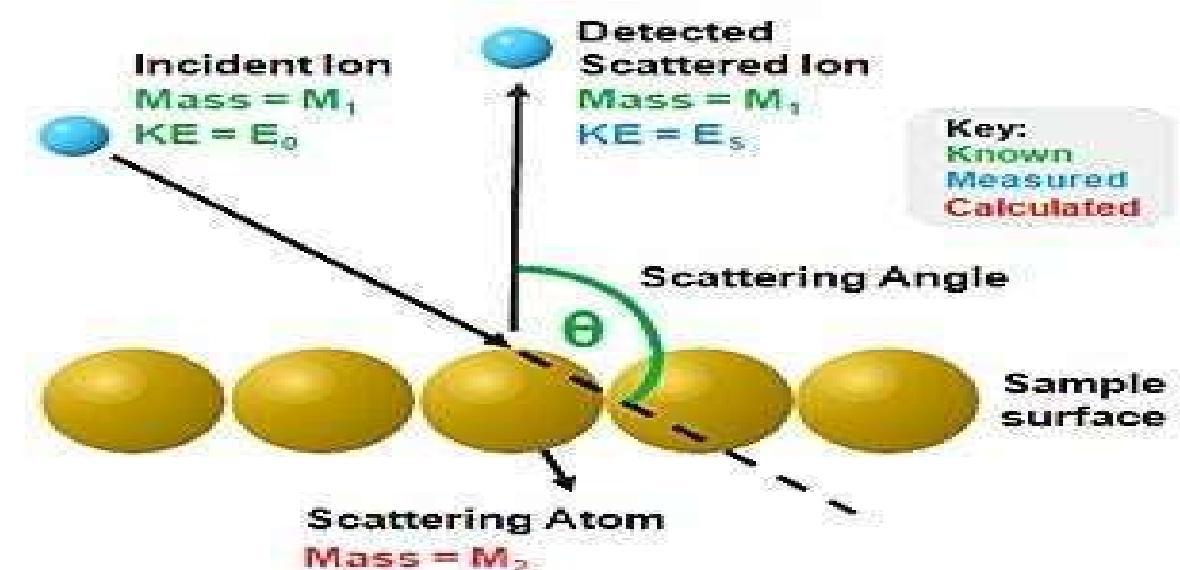
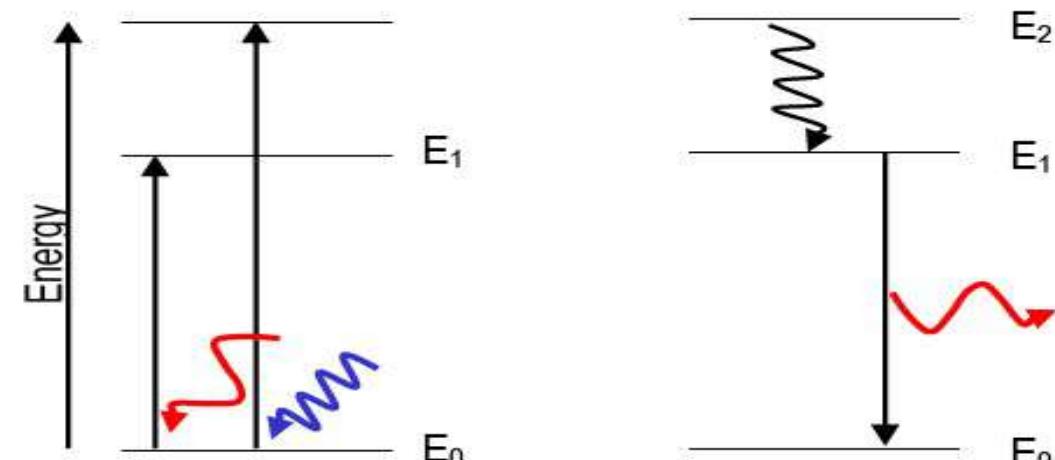
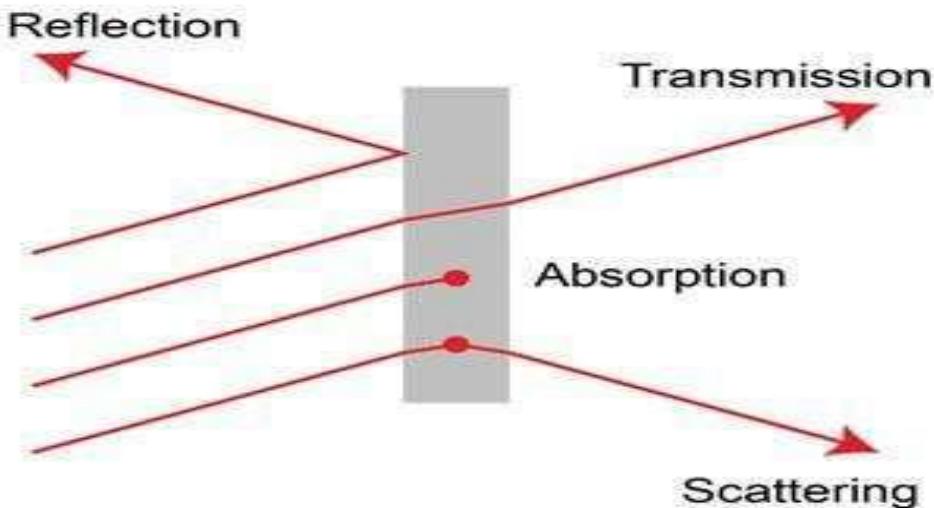


# **Types of Energy Transitions in Each Region of the Electromagnetic Spectrum**

<b>REGION</b>	<b>ENERGY TRANSITIONS</b>
X-ray	Bond-breaking
UV/Visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radio Frequency (NMR)	Nuclear and Electronic Spin

# INTERACTION OF EMR WITH MATTER/MOLECULE

- **Absorption** - Light is absorbed
- **Emission**- Light is emitted or released
- **Transmission**- Light is allowed to pass through
- **Reflection**- Light is reflected or bounced away
- **Scattering**- Light is dispersed



## **Types of Spectroscopy**

- 1. Atomic Absorption Spectroscopy:** Energy absorbed by the sample is used to assess its characteristics. Sometimes absorbed energy causes light to be released from the sample, which may be measured by a technique such as fluorescence spectroscopy.
- 2. Electron Spectroscopy/ UV-Visible:** Electronic spectroscopy provides vital information about molecular structure such as nature of chemical bonds, functional groups, isomerism, tautomerism, and extent of conjugation in organic compounds. Electronic spectra arise due to the absorption of energy by the molecule in the ultraviolet region and make transitions between the electronic energy levels.
- 3. Infrared Spectroscopy:** Absorption of this lower energy radiation causes vibrational and rotational excitation of group of atoms within the molecule. The characteristic absorptions used for identification of functional groups and this method is sometimes called as molecular fingerprint. Although frequently used to identify materials, infrared spectroscopy also may be used to quantify the number of absorbing molecules.

**Laser Spectroscopy:** Absorption spectroscopy, fluorescence spectroscopy, Raman spectroscopy, and surface-enhanced Raman spectroscopy commonly use laser light as an energy source. Laser spectroscopies provide information about the interaction of coherent light with matter. Laser spectroscopy generally has high resolution and sensitivity.

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** Absorption in the low-energy radio-frequency part of the spectrum causes excitation of nuclear spin states. NMR spectrometers are tuned to certain nuclei (e.g.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  &  $^{31}\text{P}$ ). For a given type of nucleus, high-resolution spectroscopy distinguishes and counts atoms in different locations in the molecule.

**Fourier Transform Spectroscopy:** This is a family of spectroscopic techniques in which the sample is irradiated by all relevant wavelengths simultaneously for a short period of time. The absorption spectrum is obtained by applying mathematical analysis to the resulting energy pattern.

**Electron Paramagnetic Spectroscopy:** This is a microwave technique based on splitting electronic energy fields in a magnetic field. It is used to determine structures of samples containing unpaired electrons.

**Gamma-ray Spectroscopy:** Gamma radiation is the energy source in this type of spectroscopy, which includes activation analysis and Mossbauer spectroscopy.

**Raman Spectroscopy:** Raman scattering of light by molecules may be used to provide information on a sample's chemical composition and molecular structure.

**Mass Spectrometry:** A mass spectrometer source produces ions. Information about a sample may be obtained by analysing the dispersion of ions when they interact with the sample, generally using the mass-to-charge ratio.

**X-ray Spectroscopy:** This technique involves the excitation of inner electrons of atoms, which may be seen as x-ray absorption. An x-ray fluorescence emission spectrum may be produced when an electron falls from a higher energy state into the vacancy created by the absorbed energy.

# UV-VISIBLE SPECTROSCOPY

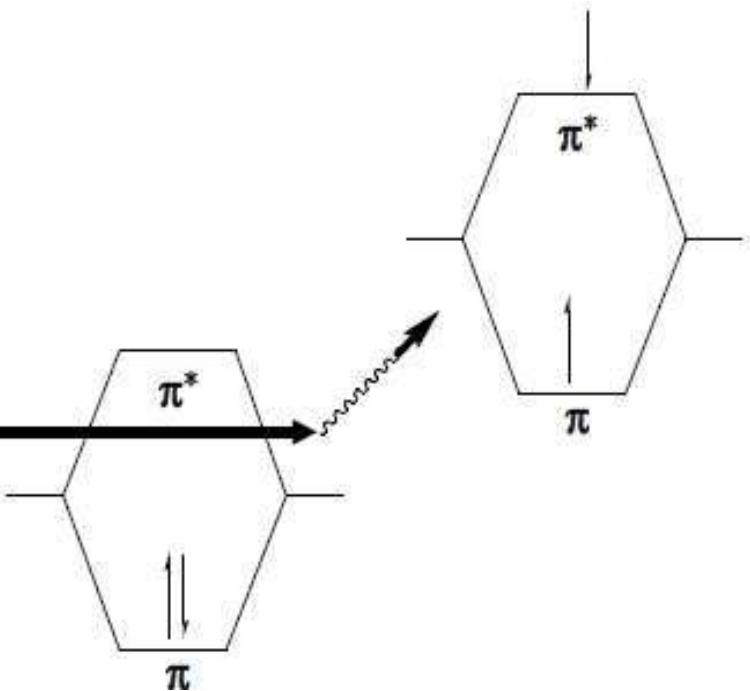
## Content

- ❖ PRINCIPLE OF UV-VISIBLE SPECTROSCOPY
- ❖ TYPES OF ELECTRONIC TRANSITION
- ❖ TERMS USED IN UV-VISIBLE SPECTROSCOPY
- ❖ ABSORPTION AND INTENSITY SHIFT
- ❖ WOODWARD-FEISER RULE
- ❖ ABSORPTION LAWS
- ❖ INSTRUMENTATION
- ❖ APPLICATIONS

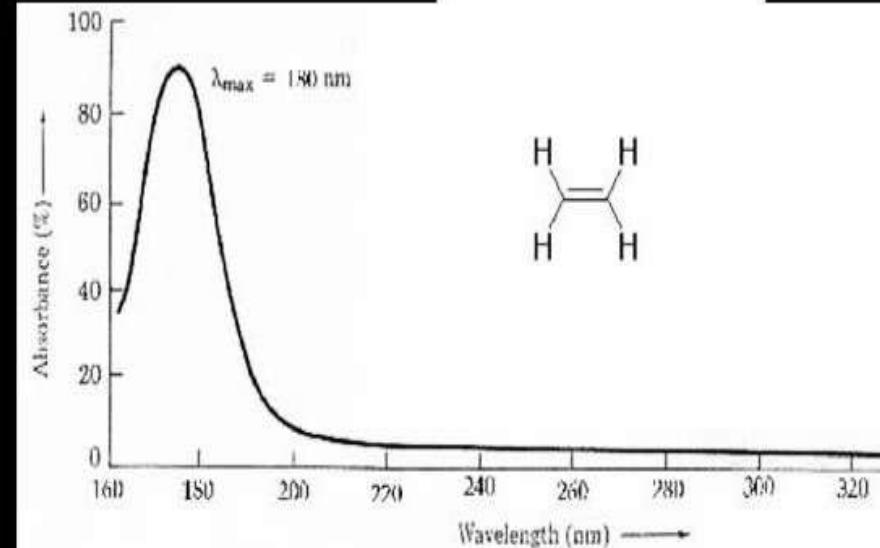


## **PRINCIPLES OF UV ABSORPTION SPECTROSCOPY**

- The UV radiation region extends from 10 nm to 400 nm.
- Near UV Region: 200 nm to 400 nm.
- Far UV Region: below 200 nm to 10 nm.
- Far UV spectroscopy is studied under vacuum condition.
- The visible radiation region extends from 400 nm to 800 nm.
- In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation.
- If a particular electronic transition matches with the energy of a certain band of UV, it will be absorbed and the remaining UV light passes through the sample and is observed.
- From this residual radiation a spectrum is obtained with “gaps” at these discrete energies – this is called an *absorption spectrum*.



# UV-vis Spectrum of Ethylene



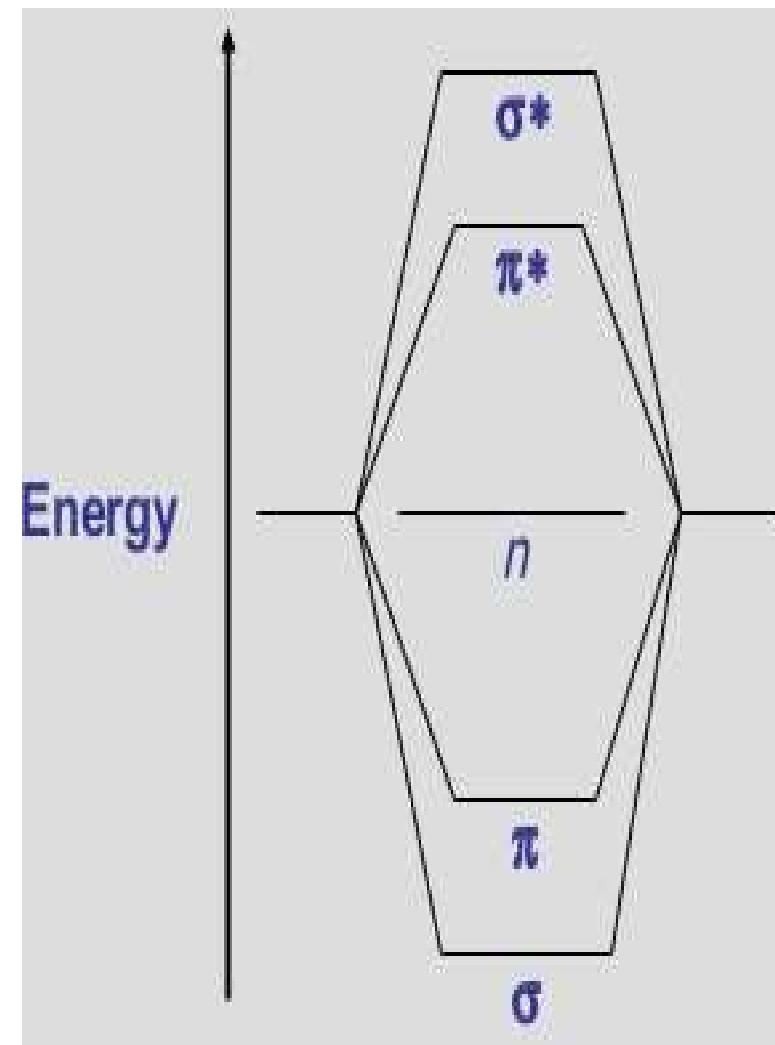
1. The lowest energy transition is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).
2. The electrons are present in ground state (HOMO,  $\pi$  orbitals), when we irradiate with light UV radiation these electrons were excited from the HOMO to the LUMO ( $\pi^*$  orbital) and the resulting species is known as excited state or anti-bonding state.

## **WHY WE NEED TO STUDY UV SPECTROSCOPY**

1. Detection of Functional group
2. Detection of Impurities
3. Qualitative Analysis
4. Quantitative Analysis
5. Identification conjugations
6. Identification of Chromophores and Auxochromes
7. Drugs with chromophoric reagent

## MO DIAGRAM OF DIATOMIC MOLECULES

1. The lowest energy transition is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).
3. The lowest energy occupied orbitals are typically the  $\sigma$  and the corresponding anti-bonding  $\sigma^*$  orbital is of the highest energy.
4.  $\pi$ -orbitals are of somewhat higher energy, and their complementary anti-bonding orbital  $\pi^*$  somewhat lower in energy than  $\sigma^*$ .
5. Unshared pairs lie at the energy of the original atomic orbital and these electrons are called non-bonding electrons, most often this energy is higher than  $\pi$  and  $\sigma$  orbitals and lower than  $\pi^*$  and  $\sigma^*$

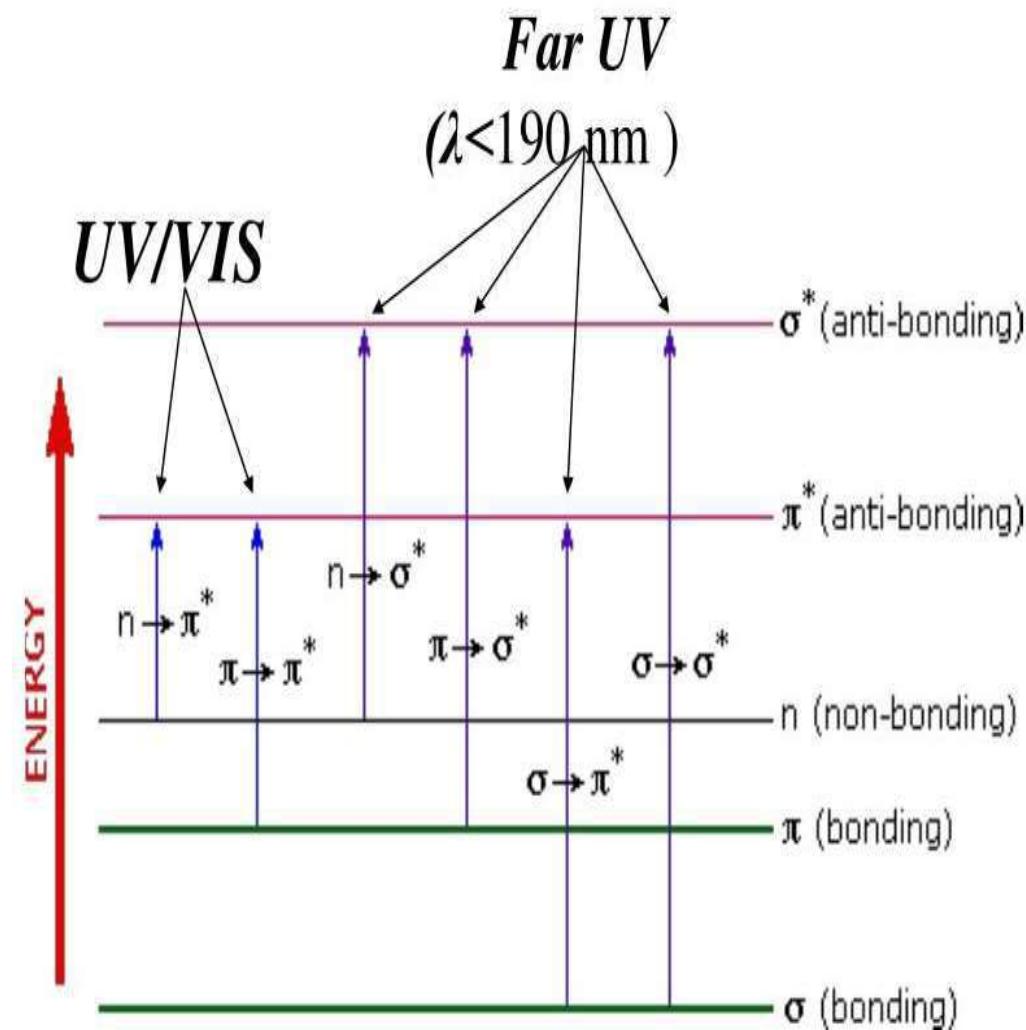


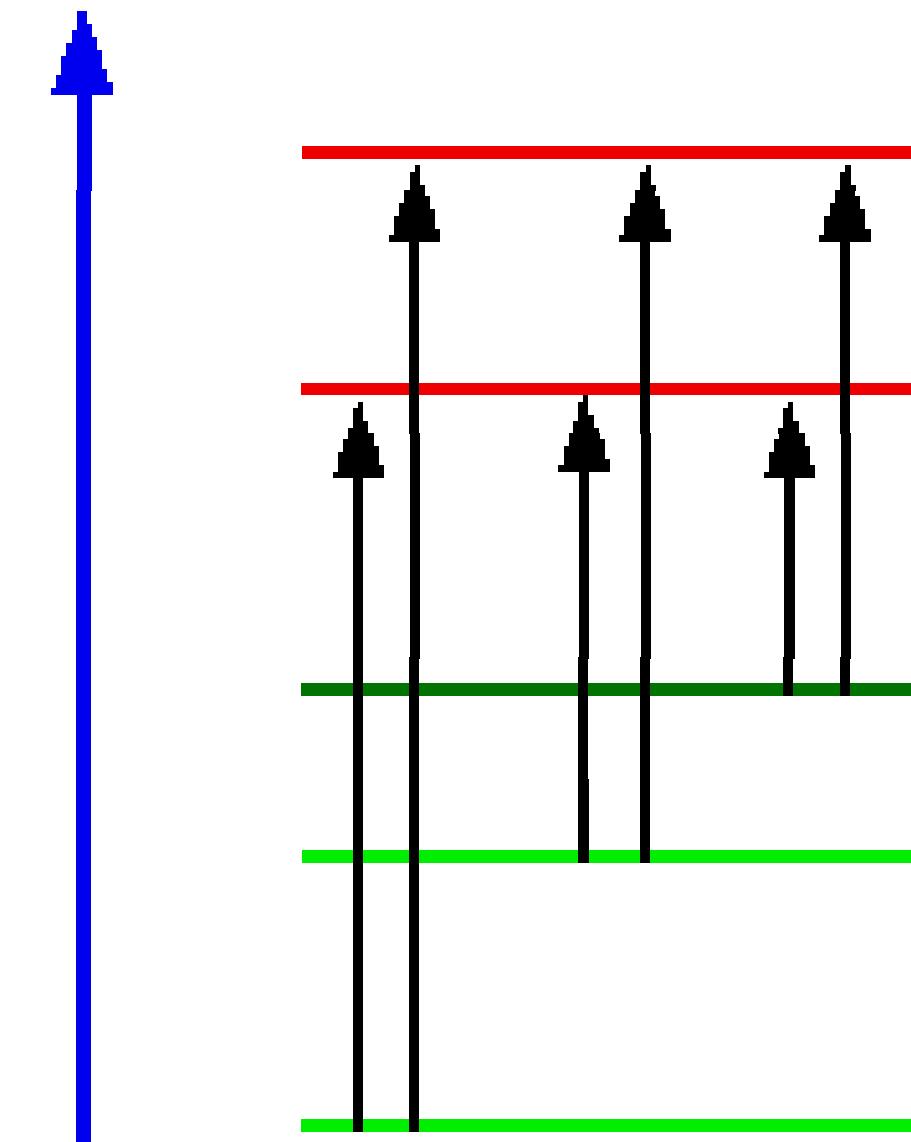
**MO diagram of diatomic molecules**

## THE POSSIBLE TYPE OF ELECTRONIC TRANSITIONS

In UV-Vis spectroscopy the electrons undergo transitions involving  $\sigma$ ,  $\pi$  and  $n$  electrons. There are six type of transitions are possible. They are

1.  **$\sigma \rightarrow \sigma^*$  transition**, In alkanes & single bond compounds like  $H_2$ ,  $Li_2$ ,  $CH_4$ .
2.  **$n \rightarrow \sigma^*$  transition**, In oxygen, Nitrogen, Sulfur, halogen containing single bond compounds.
3.  **$\pi \rightarrow \pi^*$  transition**, In alkenes, alkynes, carbonyl like unsaturated compounds,  $B_2$ ,  $C_2$ ,  $CO$ ,  $CN$ .
4.  **$n \rightarrow \pi^*$  transition**, Carbonyls, Nitriles like oxygen, Nitrogen, Sulfur containing double bond (unsaturated) compounds.
5.  **$\sigma \rightarrow \pi^*$  transition**, Carbonyls
6.  **$\pi \rightarrow \sigma^*$  transition**,





$\sigma^*$  (anti-bonding)

These are normally empty

**LUMO**

$\pi^*$  (anti-bonding)

$\eta$  (non-bonding)

These contain lone pairs

**HOMO**

$\pi$  (bonding)

These contain normal bonding pairs of electrons

$\sigma$  (bonding)

energy

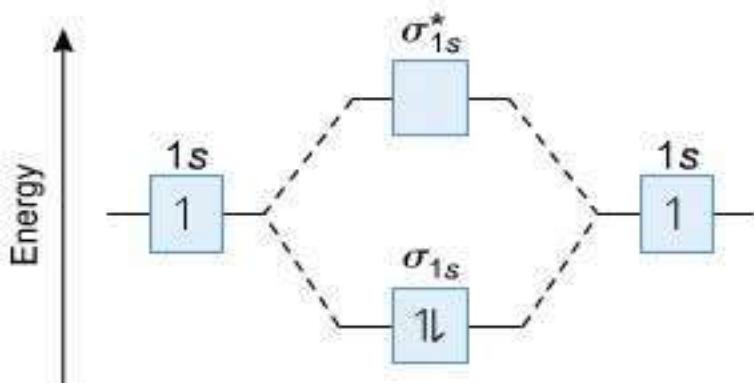
## TYPE OF ELECTRONIC TRANSITIONS

1.  **$\sigma \rightarrow \sigma^*$  Transition:**  $\sigma$  electron from orbital is excited to corresponding anti-bonding orbital  $\sigma^*$ . • The energy required is large for this transition. e.g. Methane ( $\text{CH}_4$ ) has C-H bond only and can undergo  $\sigma \rightarrow \sigma^*$  transition and shows absorbance maxima at 125 nm.
2.  **$n \rightarrow \sigma^*$  transition:** Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of  $n \rightarrow \sigma^*$  transition. These transitions usually requires less energy than  $\sigma \rightarrow \sigma^*$  transitions. The number of organic functional groups with  $n \rightarrow \sigma^*$  peaks in UV region is small 150 – 250 nm.
3.  **$\pi \rightarrow \pi^*$  transition:**  $\pi$  electron in a bonding orbital is excited to corresponding anti-bonding orbital  $\pi^*$ . Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, undergo  $\pi \rightarrow \pi^*$  transitions. e.g. Alkenes generally absorb in the region 170 to 205 nm.
4.  **$n \rightarrow \pi^*$  transition:** An electron from non-bonding orbital is promoted to anti-bonding  $\pi^*$  orbital. Compounds containing double bond involving hetero atoms ( $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{N}=\text{O}$ ) undergo such transitions.  $n \rightarrow \pi^*$  transitions require minimum energy and show absorption at longer wavelength around 300 nm.
5.  **$\sigma \rightarrow \pi^*$  transition:** Carbonyls.
6.  **$\pi \rightarrow \sigma^*$  transition:** These electronic transitions are forbidden transitions & are only theoretically possible.

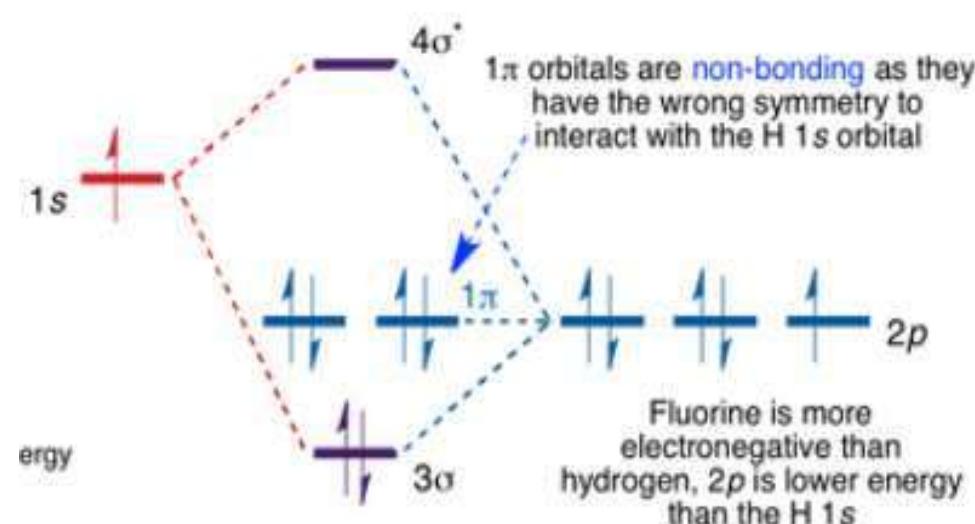
Table illustrates the type of transition and the resulting maximum wavelength.

Molecule	Transition	$\lambda_{\text{max}}$ (nm)
Ethane	$\sigma \rightarrow \sigma^*$	135
Methanol	$\sigma \rightarrow \sigma^*$	150
	$\pi \rightarrow \sigma^*$	183
Ethylene	$\pi \rightarrow \pi^*$	175
Benzene	$\pi \rightarrow \pi^*$	254
Acetone	$\pi \rightarrow \pi^*$	290

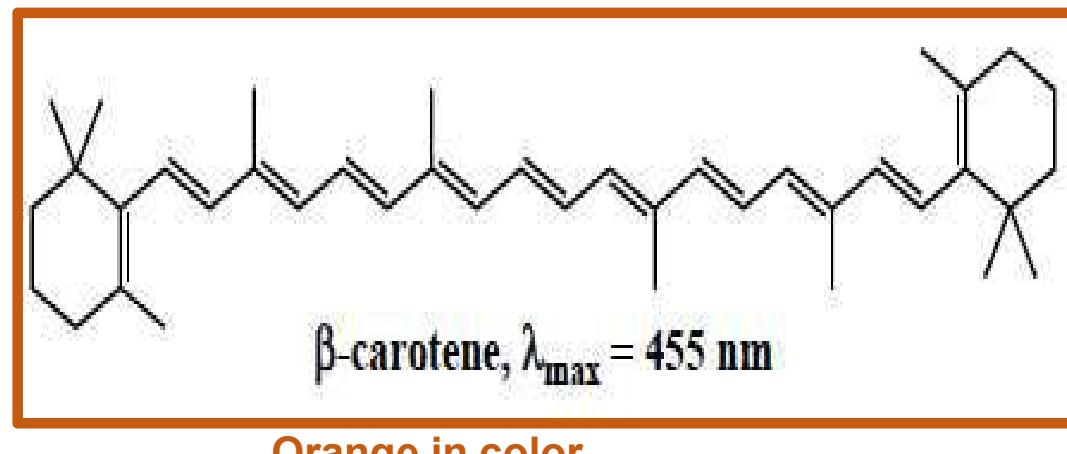
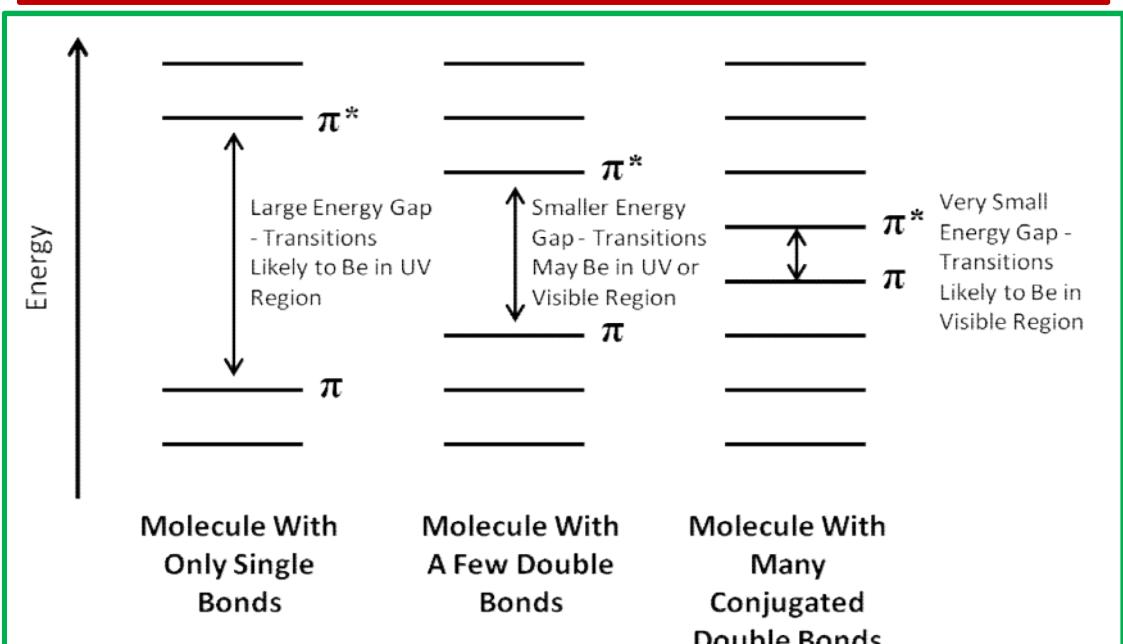
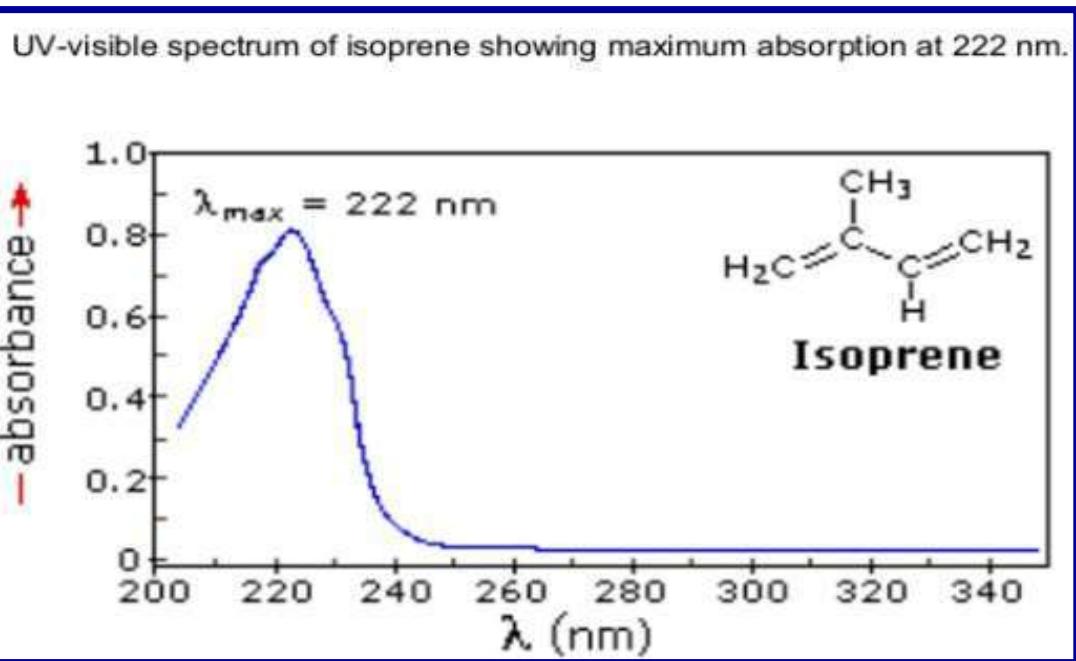
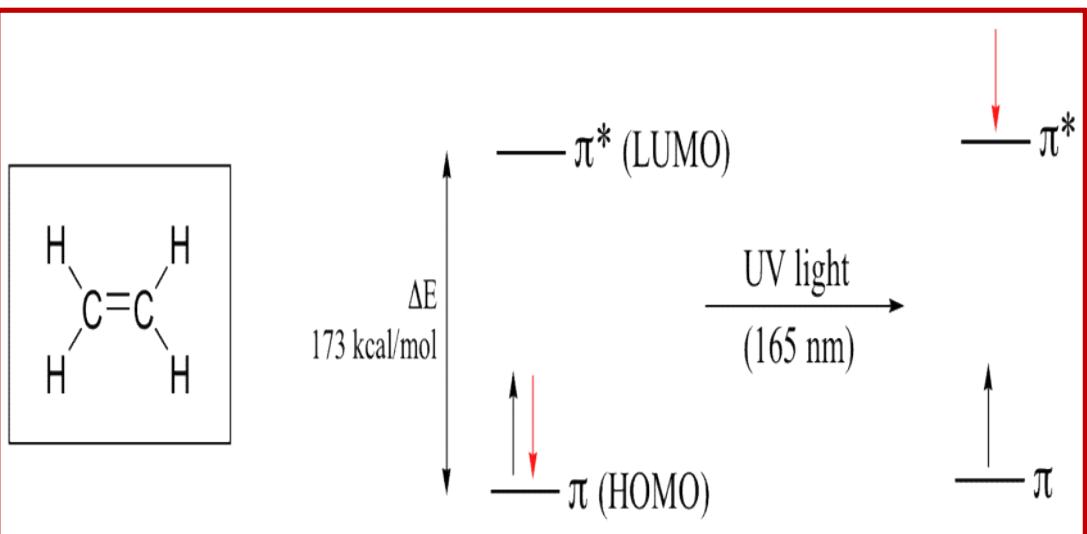
## 1. $\sigma-\sigma^*$ , H<sub>2</sub> molecule



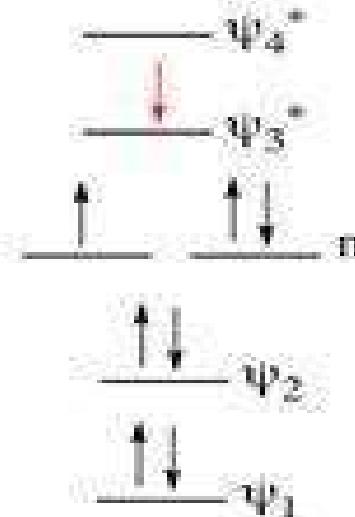
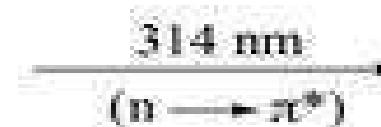
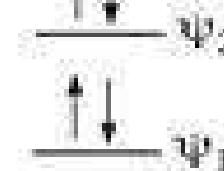
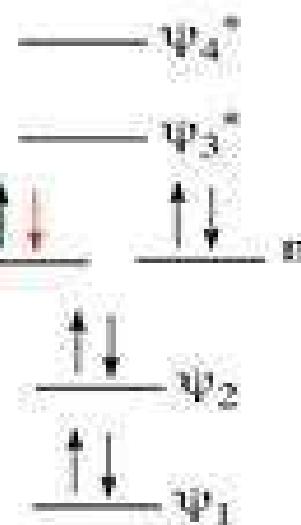
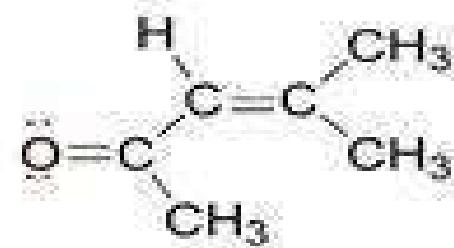
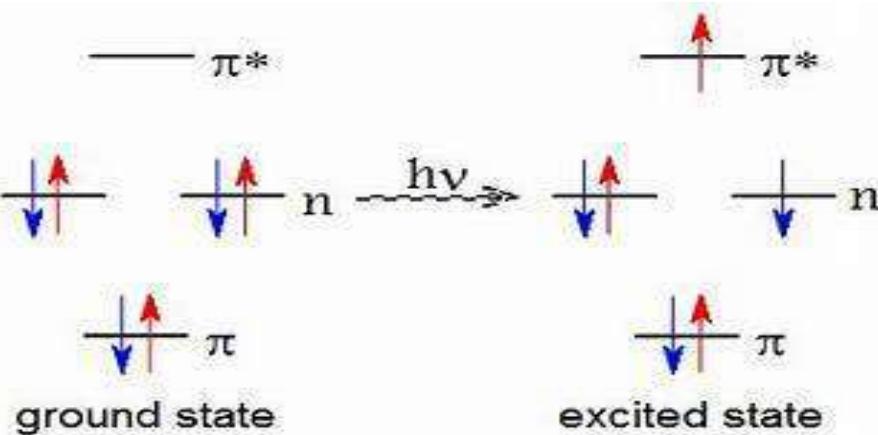
## 2. n- $\sigma^*$ , H-F molecule



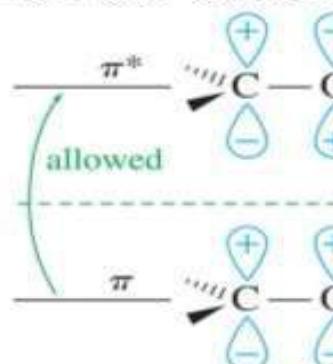
### 3. $\pi \rightarrow \pi^*$ transition



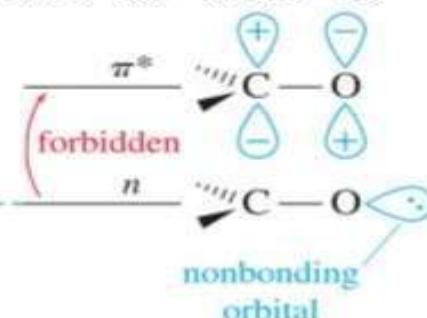
## **3. $\pi \rightarrow \pi^*$ transition & 4. $n \rightarrow \pi^*$ transition of Carbonyl compounds**



# Electronic Transitions of the C=O



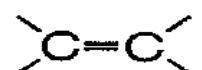
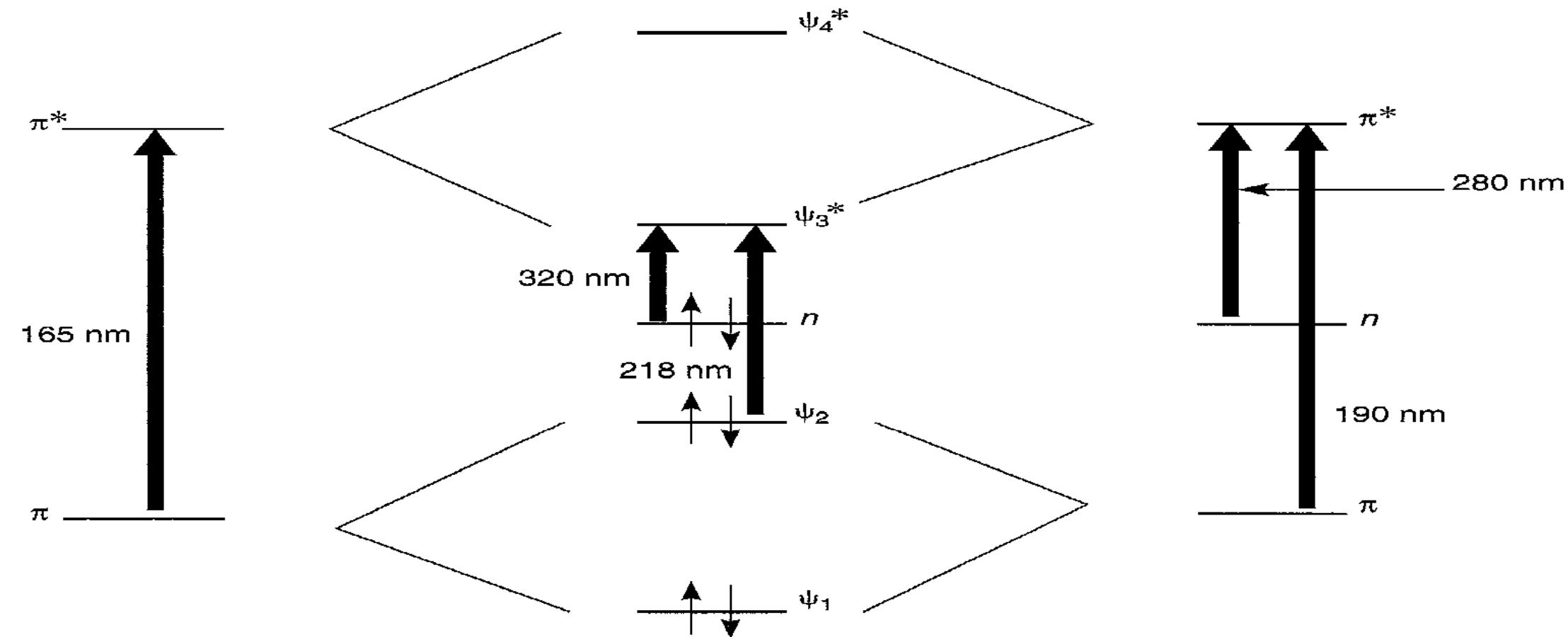
"allowed" transition  
 $\varepsilon \equiv 5000\text{--}200,000$



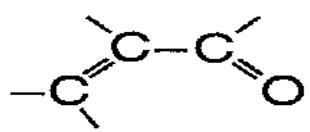
"forbidden" transition  
 $\varepsilon \equiv 10-200$

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- Small molar absorptivity.
  - “Forbidden” transition occurs less frequently.



Alkene



Enone



Carbonyl

# **TERMS USED IN UV / VISIBLE SPECTROSCOPY**

## **CHROMOPHORE**

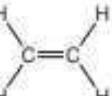
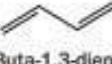
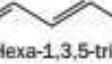
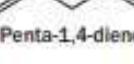
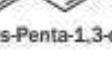
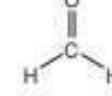
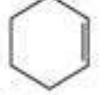
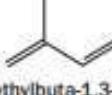
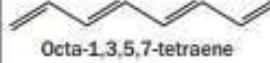
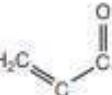
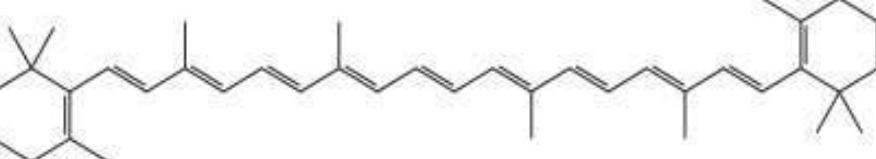
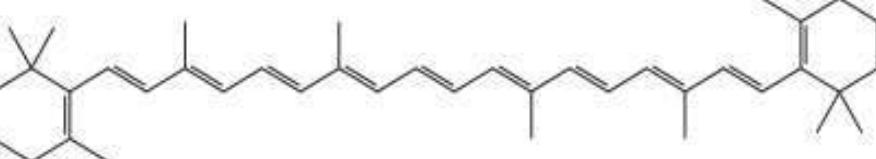
- ❑ Chromophore is a Greek word. Chroma = “colour” & phoros = “bearer”
- ❑ The part of a molecule responsible for imparting colour, are called as chromophores, i.e., the functional groups containing multiple bonds capable of absorbing radiations in the UV or visible region due to  $n \rightarrow \pi^*$  &  $\pi \rightarrow \pi^*$  transitions. Eg:  $\text{NO}_2$ ,  $\text{N}=\text{O}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{S}$ , etc.
- ❑ Compound containing chromophore is Chromogen.
- ❑ The chromophores are two types they are,
- ❑ **Independent Chromophores:** Single functional group (chromophore) is sufficient to import colour to the compound. Eg: Azo group  $-\text{N}=\text{N}-$ , Nitroso group  $-\text{NO}$ .
- ❑ **Dependent Chromophore:** More than one chromophore is required to produce colour to the compound. Eg: Acetone having one ketone group is colourless where as diacetyl have two ketone group is yellow in colour.

## TYPICAL ABSORPTIONS OF SIMPLE ISOLATED CHROMOPHORES

Class	Transition	$\lambda_{\max}$ (nm)	$\log \epsilon$	Class	Transition	$\lambda_{\max}$ (nm)	$\log \epsilon$
R-OH	$n \rightarrow \sigma^*$	180	2.5	R-NO <sub>2</sub>	$n \rightarrow \pi^*$	271	<1.0
R-O-R	$n \rightarrow \sigma^*$	180	3.5	R-CHO	$\pi \rightarrow \pi^*$	190	2.0
R-NH <sub>2</sub>	$n \rightarrow \sigma^*$	190	3.5		$n \rightarrow \pi^*$	290	1.0
R-SH	$n \rightarrow \sigma^*$	210	3.0	R <sub>2</sub> CO	$\pi \rightarrow \pi^*$	180	3.0
R <sub>2</sub> C=CR <sub>2</sub>	$\pi \rightarrow \pi^*$	175	3.0		$n \rightarrow \pi^*$	280	1.5
R-C≡C-R	$\pi \rightarrow \pi^*$	170	3.0	RCOOH	$n \rightarrow \pi^*$	205	1.5
R-C≡N	$n \rightarrow \pi^*$	160	<1.0	RCOOR'	$n \rightarrow \pi^*$	205	1.5
R-N=N-R	$n \rightarrow \pi^*$	340	<1.0	RCONH <sub>2</sub>	$n \rightarrow \pi^*$	210	1.5

- To interpretate UV – visible spectrum following points should be noted:
- Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.
- Non-conjugated carbonyl group compound give a weak absorption band in the 200 – 300 nm region.
- When double bonds are conjugated in a compound of alkenes and carbonyls the  $\lambda_{\text{max}}$  is shifted to longer wavelength which are accessible in UV spectrophotometer.

TABLE 15-1  $\lambda_{\text{max}}$  for the Longest-Wavelength UV–Vis Absorptions of a Variety of Organic Compounds<sup>a</sup>

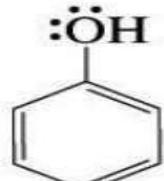
Compound	$\lambda_{\text{max}}$ (nm)	Compound	$\lambda_{\text{max}}$ (nm)	Compound	$\lambda_{\text{max}}$ (nm)
Alkanes and cycloalkanes	<150				
	161		217		256
Ethene		Buta-1,3-diene		Cyclohexa-1,3-diene	
	177		223		274
Hex-1-ene		cis-Penta-1,3-diene		Hexa-1,3,5-triene	
	178		223.5		280
Penta-1,4-diene		trans-Penta-1,3-diene		Methanal (Formaldehyde)	
	182		224		290
Cyclohexene		2-Methylbuta-1,3-diene (Isoprene)		Octa-1,3,5,7-tetraene	
	185		239		340
Hex-1-yne		Cyclopentadiene		Propenal (Acrolein)	
	455			Beta-Carotene	

## AUXOCHROME

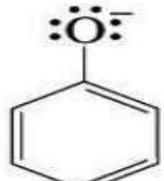
- The functional groups with non-bonding electrons which does not itself act as a chromophore but when it attached to a chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of absorption. It is a colour enhancing group.
- The effect is due to its ability to extend the conjugation of a chromophore by sharing the non-bonding and bonding electrons. Eg: -OH, -NH<sub>2</sub>, -SH, -CO<sub>2</sub>H, -SO<sub>3</sub>H



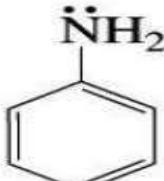
**benzene**  
**255 nm**



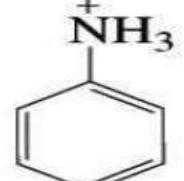
**phenol**  
**270 nm**



**phenolate ion**  
**287 nm**



**aniline**  
**280 nm**



**anilinium ion**  
**254 nm**

# ABSORPTION & INTENSITY SHIFTS

## 1. Bathochromic Shift (Red Shift):

When absorption maxima ( $\lambda_{\max}$ ) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.

## 2. Hypsochromic Shift (Blue Shift):

When absorption maxima ( $\lambda_{\max}$ ) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

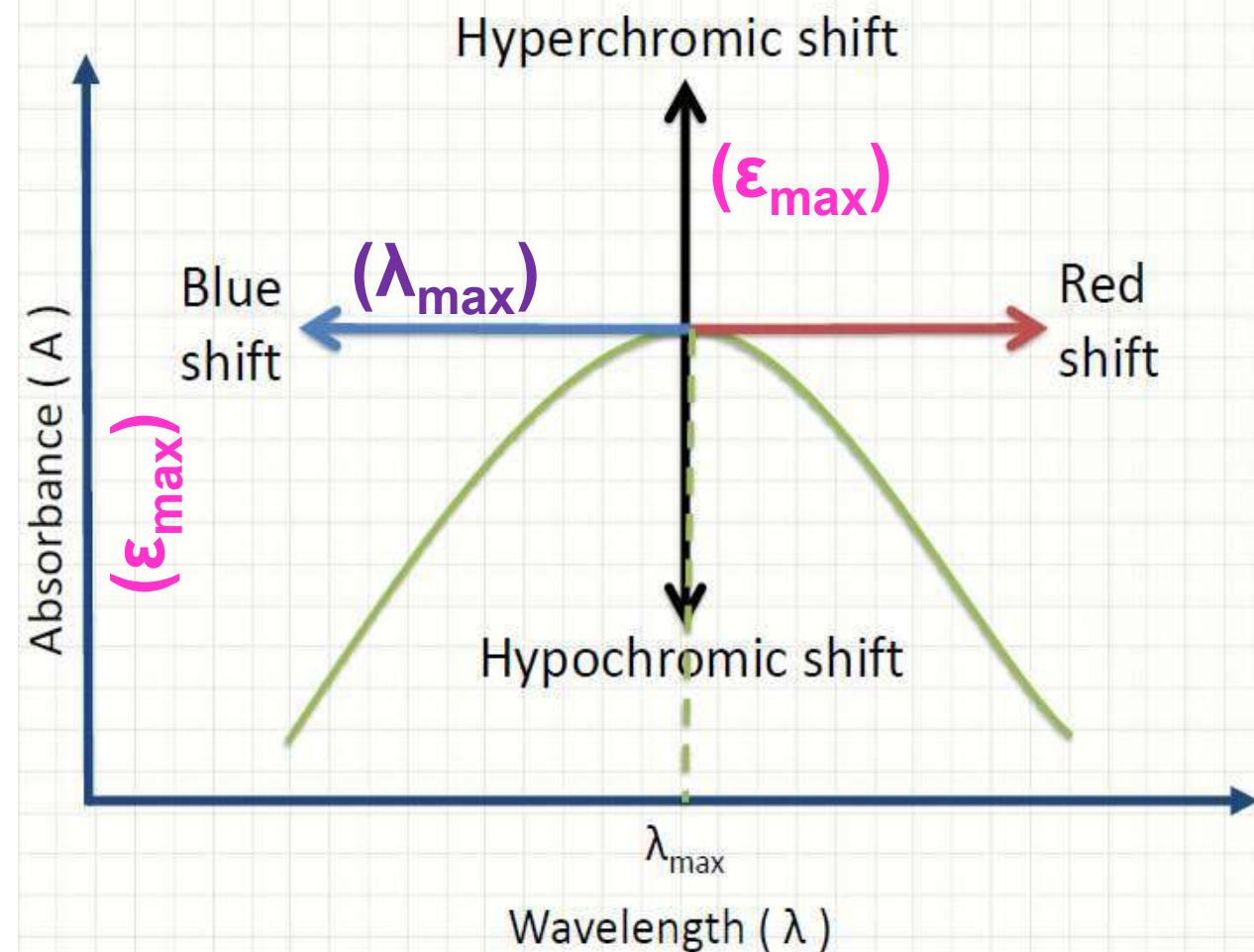
## 3. Hyperchromic Effect:

When absorption intensity ( $\epsilon_{\max}$ ) of a compound is increased, it is known as hyperchromic shift.

## 4. Hypochromic Effect:

When absorption intensity ( $\epsilon_{\max}$ ) of a compound is decreased, it is known as hypochromic shift.

## Shifts and Effects

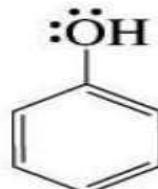


**1. Bathochromic Shift (Red Shift):** When absorption maxima ( $\lambda_{\text{max}}$ ) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.

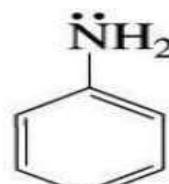
- The effect is due to presence of an auxochrome or by the change of solvent.
- An auxochrome group like  $-\text{OH}$ ,  $-\text{NH}_2$  causes absorption of compound at longer wavelength.



benzene  
255 nm

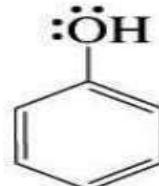


phenol  
270 nm

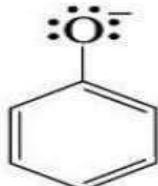


aniline  
280 nm

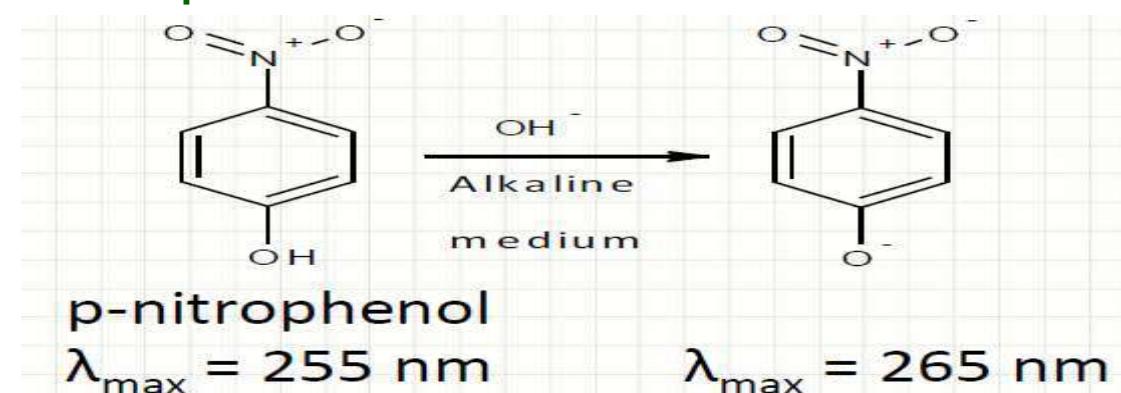
- In alkaline medium, phenol & p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



phenol  
270 nm

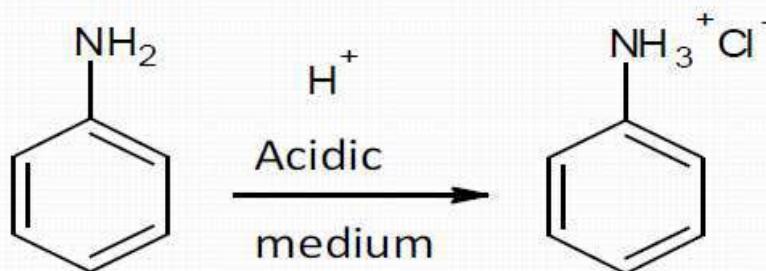


phenolate ion  
287 nm



**2. Hypsochromic Shift (Blue Shift):** When absorption maxima ( $\lambda_{\max}$ ) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.
- Aniline shows blue shift in acidic medium, it loses conjugation. Eg: Primary, Secondary & Tertiary amines



Aniline

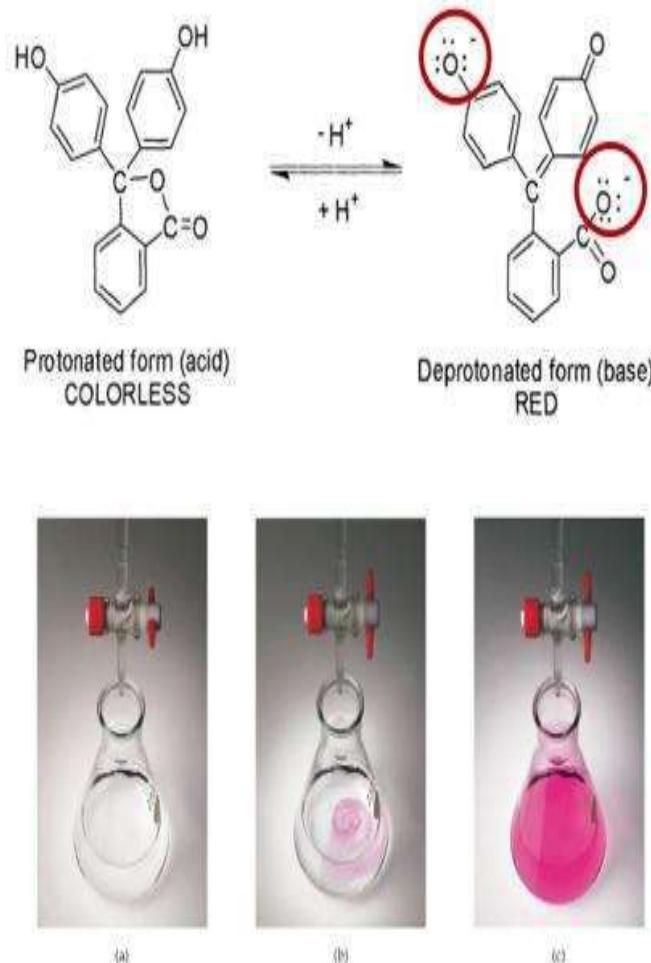
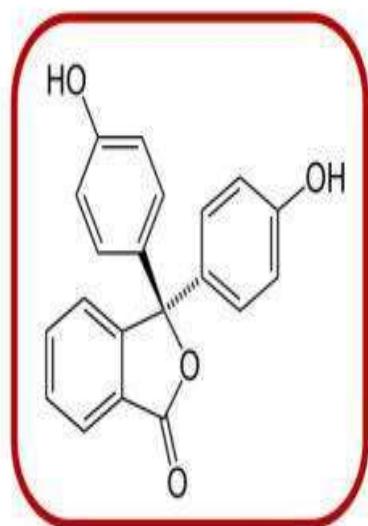
$$\lambda_{\max} = 280 \text{ nm}$$

$$\lambda_{\max} = 265 \text{ nm}$$

Effect of solvent		
Transition	Solvent	Shift
$\pi \rightarrow \pi^*$	Polar	Bathochromic shift
	Non-Polar	Hypsochromic shift
$n \rightarrow \pi^*$	Polar	Hypsochromic shift
	Non-Polar	Bathochromic shift

# Acid/Base Indicators and Resonance Energy

- Example: Phenolphthalein **Bathochromic Shift**



## Hypsochromic Shift

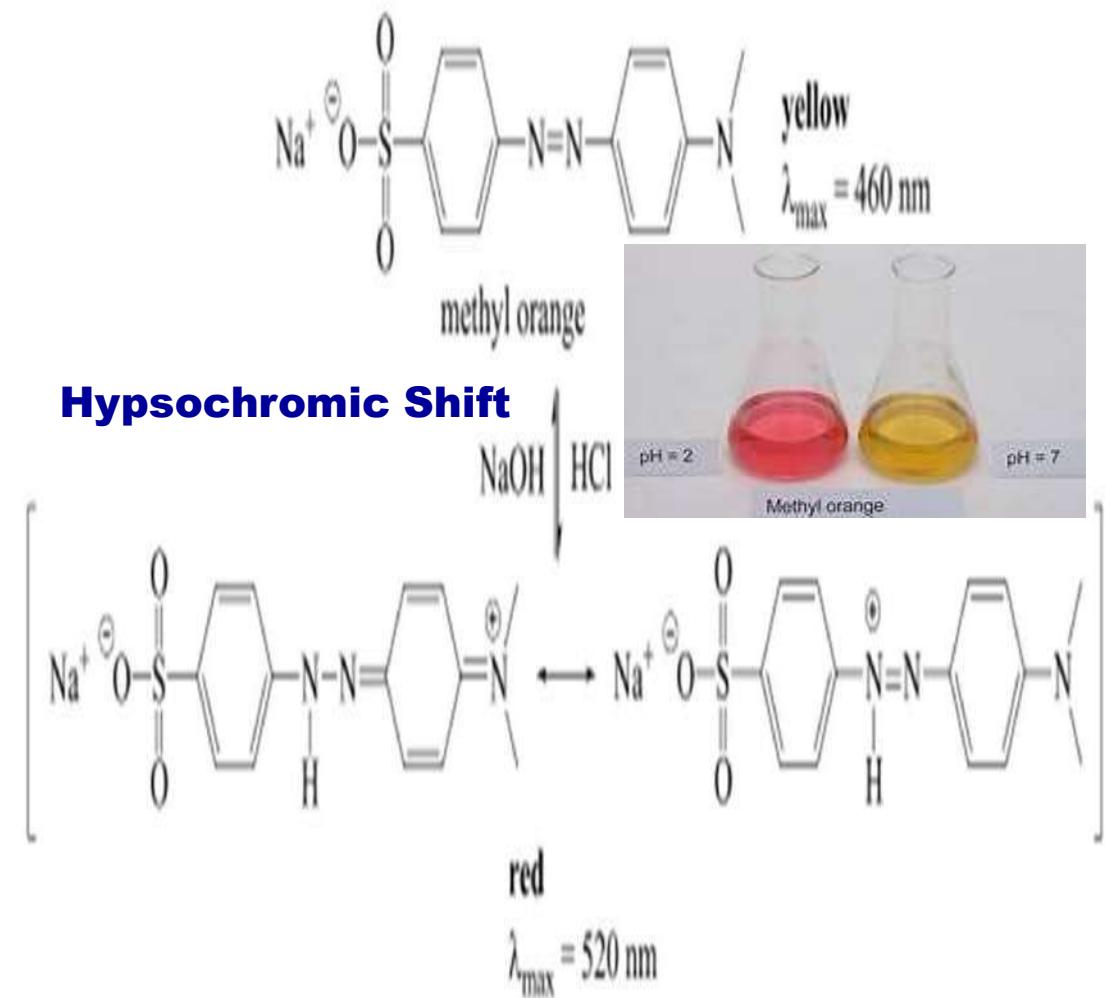
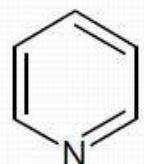


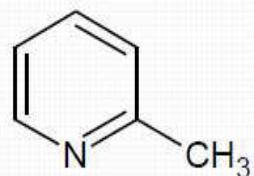
Figure 1. Acidic and basic forms of methyl orange.

**3. Hyperchromic Effect:** When absorption intensity ( $\epsilon_{\max}$ ) of a compound is increased, it is known as hyperchromic shift.

- ❖ If auxochrome introduces to the compound, the intensity of absorption increases.
- ❖ While Changing the solvent affects the absorption intensity ( $\epsilon_{\max}$ ) changes.
- ❖ Eg: 2-Methyl pyridine shows increase absorption intensity ( $\epsilon_{\max}$ ).



Pyridine  
 $\lambda_{\max} = 257 \text{ nm}$   
 $\epsilon = 2750$

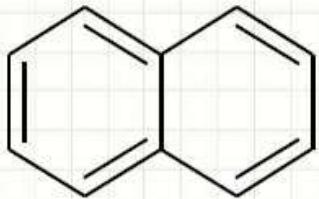


2methylpyridine  
 $\lambda_{\max} = 260 \text{ nm}$   
 $\epsilon = 3560$

Absorption characteristics of 2-methylpyridine			
Solvent	$\lambda_{\max}$	$\epsilon_{\max}$	
Hexane	260	2000	
Chloroform	263	4500	
Ethanol	260	4000	
Water	260	4000	
Ethanol - HCl (1:1)	262	5200	

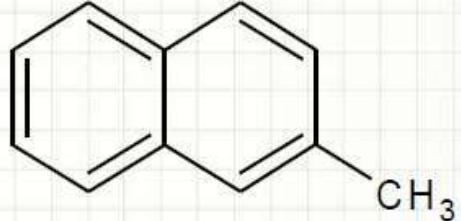
**4. Hypochromic Effect:** When absorption intensity ( $\epsilon_{\max}$ ) of a compound is decreased, it is known as hypochromic shift.

✓ Eg: 2-Methyl Naphthalene shows decreased absorption intensity ( $\epsilon_{\max}$ ).



Naphthalene

$\epsilon = 19000$



2-methyl naphthalene

$\epsilon = 10250$

# TYPES OF ABSORPTION BANDS

## 1) K - Band

- ❖ K-Bands originate due to  $\pi-\pi^*$  transition from a compound containing a conjugated system
- ❖ Such type of bands arise in compounds like dienes, polyenes and enones etc.

Compound	Transition	$\lambda_{max}(\text{nm})$	$\epsilon_{max}$
Acetophenone	$\pi-\pi^*$	240	13,000
1,3-butadiene	$\pi-\pi^*$	217	21,000

## 2) R-Band

- ❖ R-Band transition originate due to  $n-\pi^*$  transition of a single chromophoric group and having atleast one lone pair of electrons on the hetero atom
- ❖ These are less intense with  $\epsilon_{max}$  value below 100

Compound	Transition	$\lambda_{max}(\text{nm})$	$\epsilon_{max}$
Acetone	$n-\pi^*$	270	15
Acetaldehyde	$n-\pi^*$	293	12

### 3) B-Band

- Such type of bands arise due to  $\pi-\pi^*$  transition in aromatic or hetero-aromatic molecules.
- Benzene shows absorption peaks between 230-270nm. When a chromophoric group is attached to the benzene ring, the B-Bands are observed at longer wavelengths than the more intense K-Bands.

Compound	Transition	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}}$
Benzene	$\pi-\pi^*$	255	215
Phenol	$\pi-\pi^*$	270	1450

## 4) E-Band

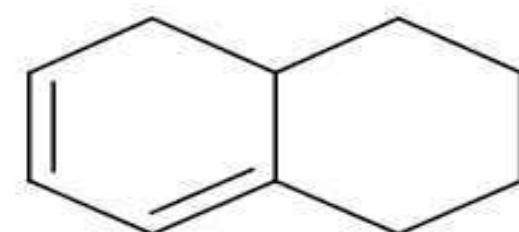
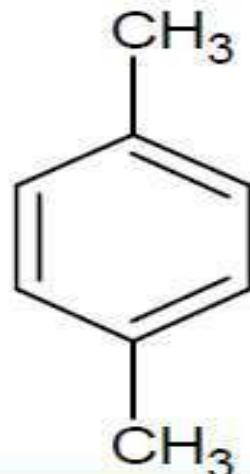
- ❖ E-Band originate due to the electronic transitions in the benzenoid systems of three ethylenic bonds which are in closed cyclic conjugation.
- ❖ These are further characterized as E<sub>1</sub> and E<sub>2</sub> bands
- ❖ E<sub>1</sub> band which appear at shorter wavelength is usually more intense than the E<sub>2</sub> band for the same compound which appears at longer wavelength.

Compound	E <sub>1</sub> Band	E <sub>1</sub> Band	E <sub>2</sub> Band	E <sub>2</sub> Band
	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}}$	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}}$
Benzene	184	50,000	204	79,000
Naphthalene	221	133,000	286	9,300

## Woodward Fieser Rule



- It is used for calculating the absorption maxima
  - Woodward (1941) gives certain rule for correlating  $\lambda_{\text{max}}$  with the molecular structure
  - These rules are modified by Scott & Feiser.
  - This rule for calculating  $\lambda_{\text{max}}$  in conjugated dienes, trienes, polyenes.
- ❖ **Homoannular dienes:-**  
cyclic dienes having conjugated double bonds in the same ring.
- e.g.



## **Woodward Fieser rule for $\alpha,\beta$ -unsaturated Carbonyl compounds**

Woodward-Fieser rules can be extended to calculate the  $\lambda_{\text{max}}$  of  $\alpha,\beta$ -unsaturated carbonyl compounds. In a similar manner to Woodward rules for dienes discussed previously, there is base value to which the substituent effects can be added and the  $\lambda_{\text{max}}$  can be calculated using the formula:

$$\lambda_{\text{MAX}} = \text{BASE VALUE} + \sum \text{SUBSTITUENT CONTRIBUTIONS} + \sum \text{OTHER CONTRIBUTIONS}$$



## **BASE VALUES FOR DIFFERENT FUNCTIONAL GROUPS:-**

### **KETONES**

- If it is a acyclic compound =215nm
- If 6 membered ring system =215 nm
- If 5 membered ring system =202 nm

### **ALDEHYDES**

- If it is a acyclic compound =210 nm
- If 6 membered ring system =215 nm
- If 5 membered ring system =202nm

### **CARBOXYLICACID AND ESTER**

- If compound is carboxylicacid or ester =197nm

# The parent values and increment for different substituents / groups

- (A) Parent value :-

1) Homo annular conjugated diens	$\lambda$ 253 nm
2) Hetero annular conjugated diens Acyclic conjugated diens	$\lambda$ 214 nm
3) Acyclic conjugated diens	$\lambda$ 214 nm
4) Butadiene system open chain (Acyclic)	$\lambda$ 217 nm
5) Acyclic triens	$\lambda$ 245 nm

- (B) Increment :-

1) Each alkyl substitution or ring residue	$\lambda$ + 5 nm
2) Exocyclic double bond	$\lambda$ +5 nm
3) Double bond extending conjugation	$\lambda$ +30 nm

- (C) Auxochromes :-

-O- alkyl	$\lambda$ +6 nm	-N(alkyl) <sub>2</sub>	$\lambda$ +60 nm
-S-alkyl	$\lambda$ +30 nm	-OCOCH <sub>3</sub>	$\lambda$ 0 nm
-Cl, -Br	$\lambda$ +5 nm		

## Woodward-Fieser Rules for Dienes UV-Vis Absorption Maxima

Parent

Homoannular diene  $\lambda = 253 \text{ nm}$

Heteroannular diene  $\lambda = 214 \text{ nm}$   $= 217$  (acyclic)

Increments for:

Double bond extending conjugation 30

Alkyl substituent or ring residue 5

Exocyclic double bond 5

Polar groupings:

-OC(O)CH<sub>3</sub> 0

-OR 6

-Cl, -Br 5

-NR<sub>2</sub> 60

-SR 30

Example



Heteroannular diene 214

4 alkyl substituents (4x5) 20

exocyclic double bond 5

239 nm



## **APPLICATION OF WOODWARDFIESER RULE FOR AROMATIC COMPOUNDS**

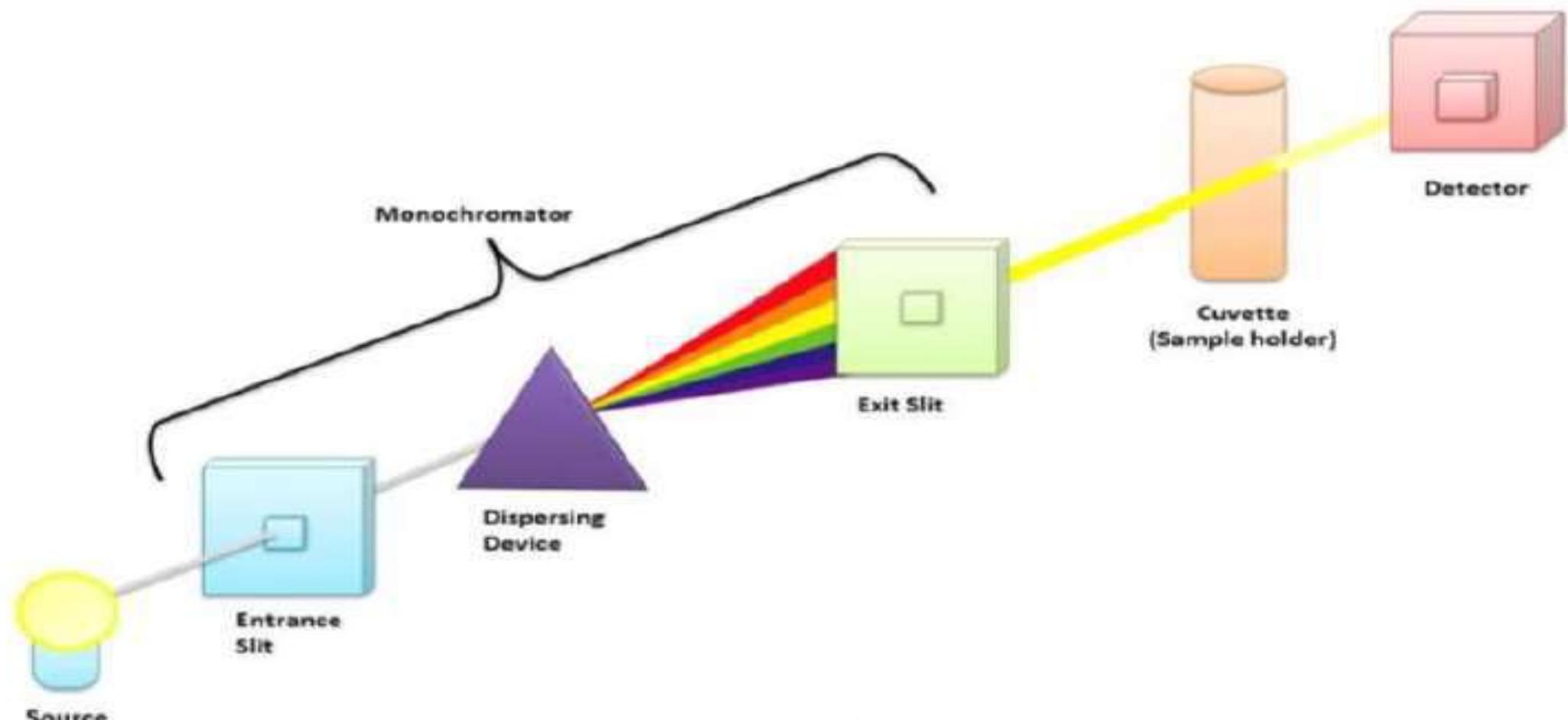
### **1.BASE VALUES :-**

- Ar COR=246nm
- Ar CHO=250nm
- Ar CO<sub>2</sub>H=230nm
- Ar CO<sub>2</sub>R=230nm
- Alkyl groups or ring residues in ortho and meta positions=3nm
- Alkyl groups or ring residue in Para position=10nm

# Instrumentation

## Components of UV-Visible spectrophotometer

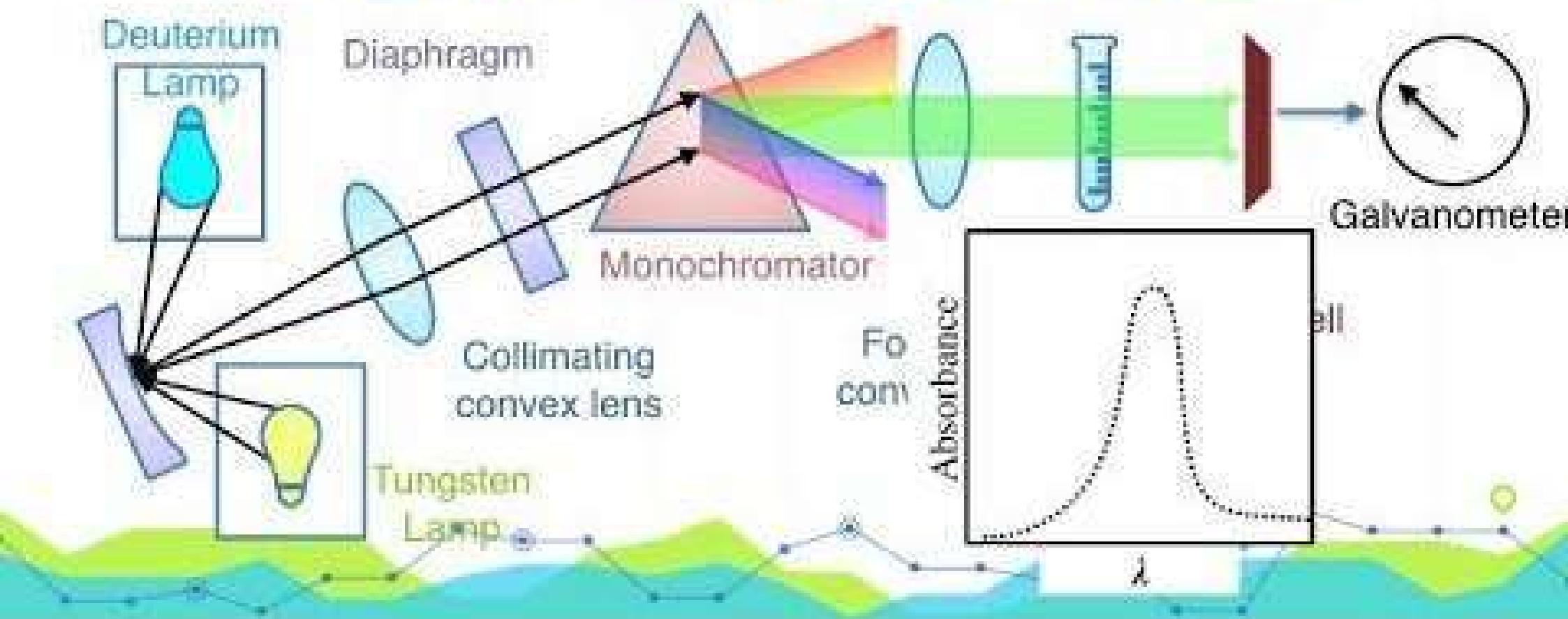
- Source
- Filters & Monochromator
- Sample compartment
- Detector
- Recorder



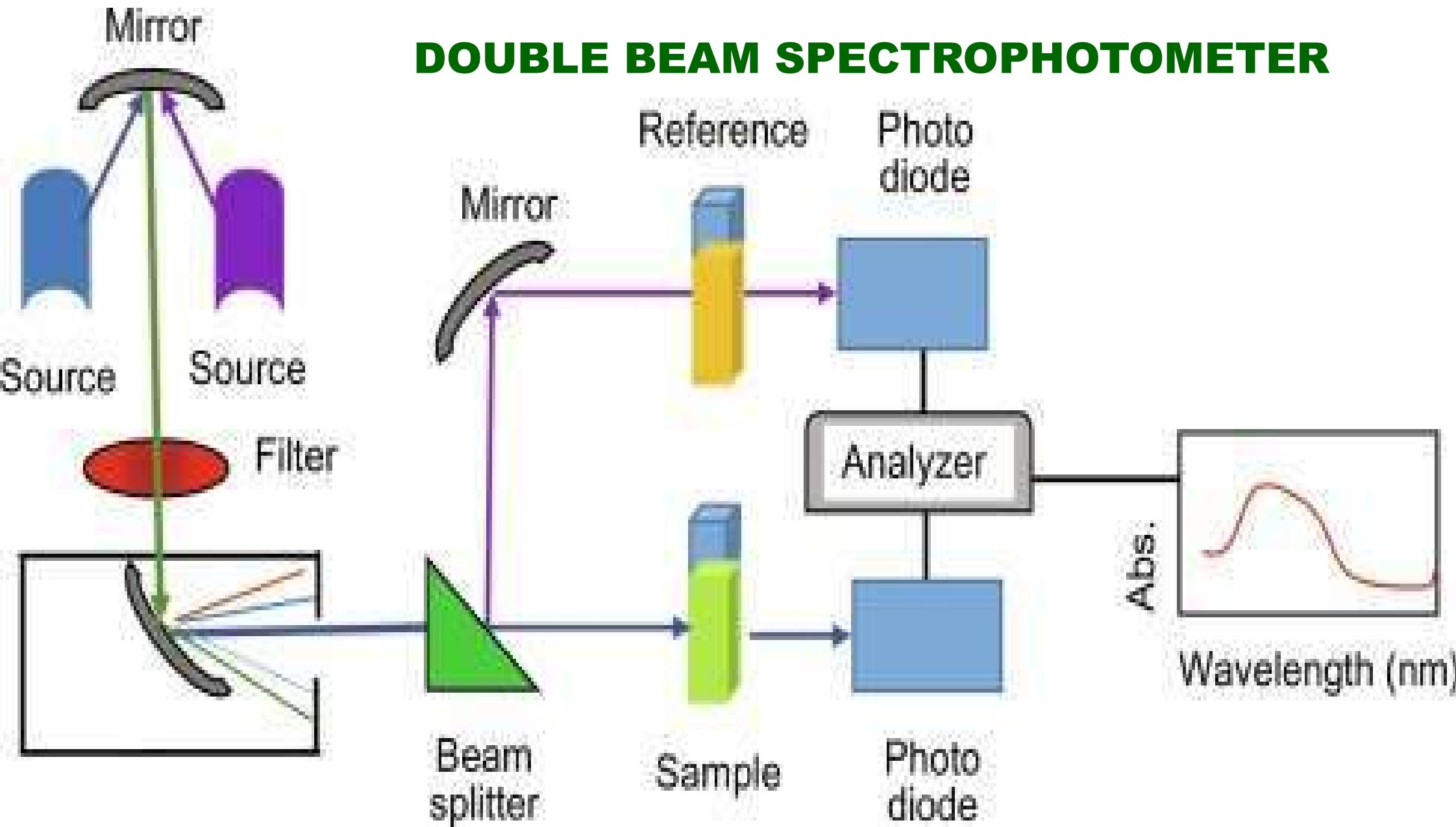
Representative Diagram of a Simple UV-Visible Spectrophotometer

Spectroscopy

# SINGLE BEAM SPECTROPHOTOMETER.

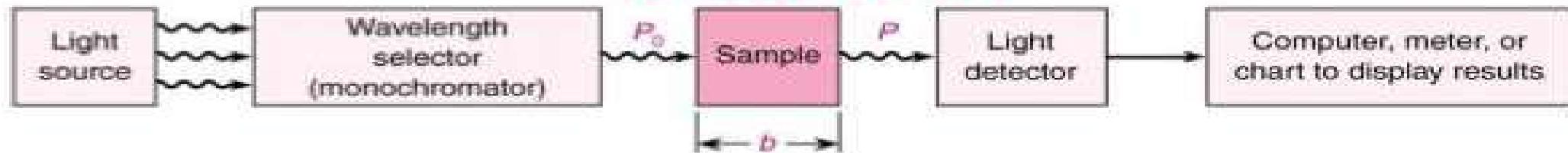


## DOUBLE BEAM SPECTROPHOTOMETER

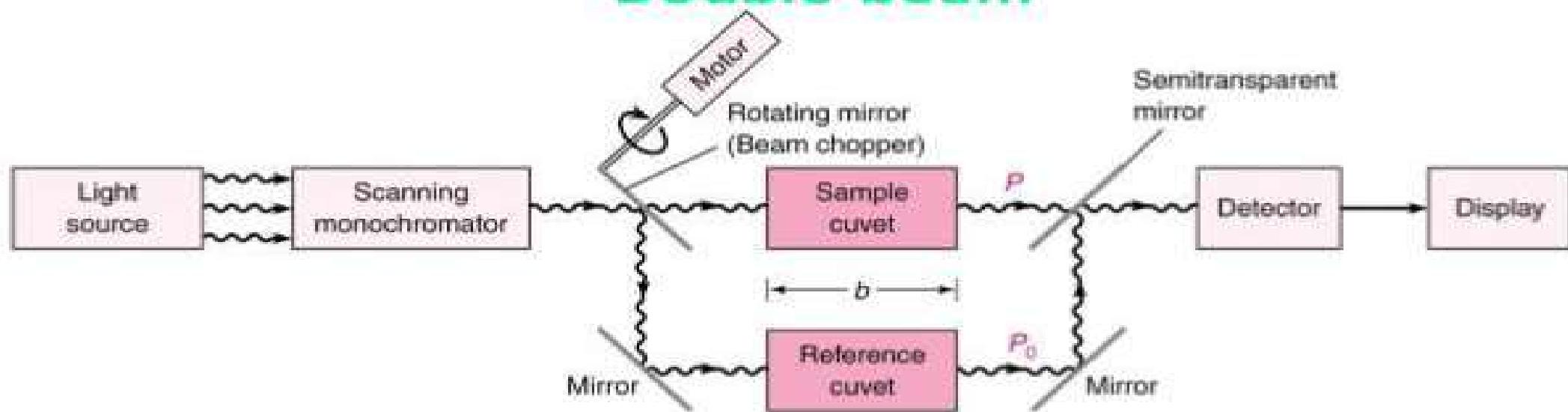


# The Spectrophotometer

## Single-beam



## Double-beam



# LIGHT SOURCES

***Various UV radiation sources are as follows***

- a. Deuterium lamp
- b. Hydrogen lamp
- c. Tungsten lamp
- d. Xenon discharge lamp
- e. Mercury arc lamp



***Various Visible radiation sources are as follow***

- a. Tungsten lamp
- b. Mercury vapour lamp
- c. Carbonone lamp

# **Wavelength Selectors**

- Wavelength selectors output a limited, narrow, continuous group of wavelengths called a *band*.

Two types of wavelength selectors:

- A) **Filters**
- B) **Monochromators**

## **A) Filters -**



Two types of filters:

- a) **Interference Filters**
- b) **Absorption Filters**

## B. Monochromators

- Wavelength selector that can continuously scan a broad range of wavelengths.
- Used in most scanning spectrometers including UV, visible, and IR instruments.

**PRISM TYPE**

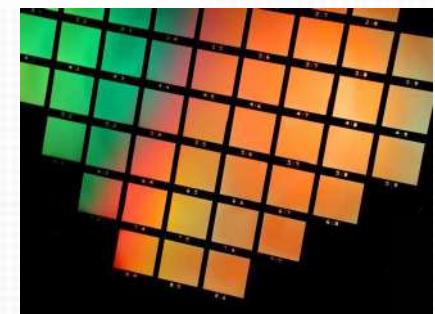
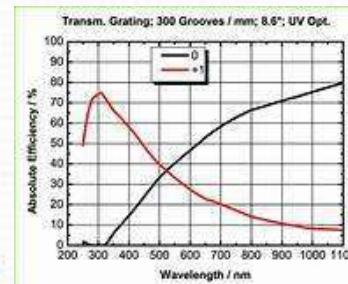
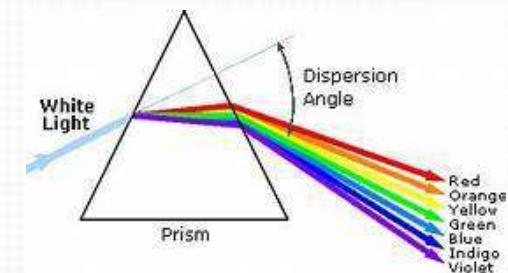
**Refractive type**

**Reflective type**

**GRATING TYPE**

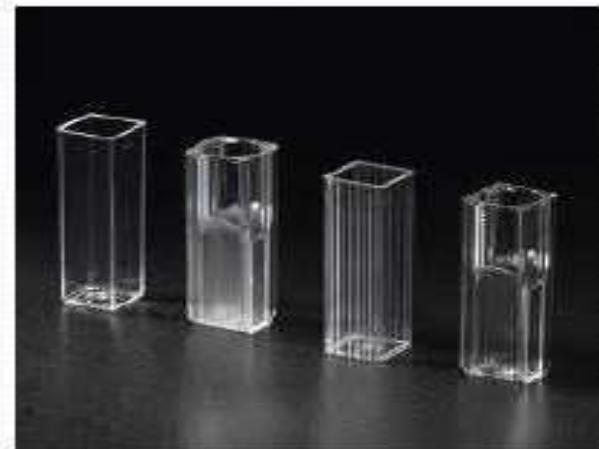
**Diffraction type**

**Transmission Type**



# SAMPLE COMPARTMENT

- Spectroscopy requires all materials in the beam path other than the analyte should be as transparent to the radiation as possible.
- The geometries of all components in the system should be such as to maximize the signal and minimize the scattered light.
- The material from which a sample cuvette is fabricated controls the optical window that can be used.
- Some typical materials are:
- Optical Glass - 335 - 2500 nm
- Special Optical Glass – 320 - 2500 nm
- Quartz (Infrared) – 220 - 3800 nm
- Quartz (Far-UV) – 170 - 2700 nm



# Detectors

- After the light has passed through the sample, we want to be able to detect and measure the resulting light.
- These types of detectors come in the form of transducers that are able to take energy from light and convert it into an electrical signal that can be recorded, and if necessary, amplified.
- **Three common types of detectors are used**
  - ✓ Barrier layer cells
  - ✓ Photo emissive cell detector
  - ✓ Photomultiplier

# SUMMARY

- Types of source, sample holder and detector for various EM region

REGION	SOURCE	SAMPLE HOLDER	DETECTOR
Ultraviolet	Deuterium lamp	Quartz/Fused silica	Phototube, PM tube, diode array
Visible	Tungsten lamp	Glass/Quartz	Phototube, PM tube, diode array

## **ABSORPTION LAWS**

Beer Lamberts Law:

$$A = \epsilon b c$$

A=absorbance

$\epsilon$  =molar absorbtivity with units of L /mol.cm

b=path length of the sample (cuvette)

c =Concentration of the compound in solution,  
expressed in mol /L

# ABSORPTION LAWS

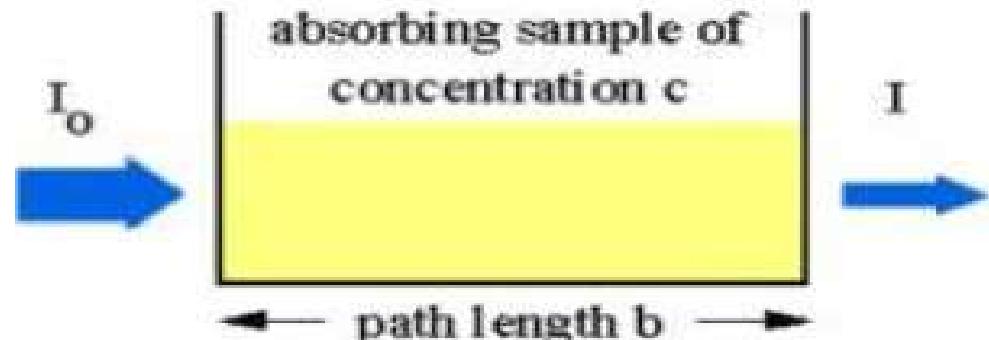
## Lambert's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

Let  $I$  be the intensity of incident radiation.

$x$  be the thickness of the solution.

Then



$$-\frac{dI}{dx} \propto I$$

$$\text{So, } -\frac{dI}{dx} = KI$$

Integrate equation between limit

$I = I_0$  at  $x = 0$  and

$I = I$  at  $x = 1$ ,

We get,

$$\ln \frac{I}{I_0} = -KI$$

$$2.303 \log \frac{I}{I_0} = -Kl$$

$$\log \frac{I}{I_0} = -\frac{K}{2.303} l$$

Where,  $\log \frac{I_0}{I} = A$       Absorbance

$$\frac{K}{2.303} = E$$
      Absorption coefficient

$$A = E.l$$
      Lambert's Law

## Beer's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

Let  $I$  be the intensity of incident radiation.

$x$  be the thickness of the solution.

$C$  be the concentration of the solution.

Then

$$-\frac{dI}{dx} \alpha C \cdot I$$

$$\text{So, } -\frac{dI}{dx} = K' C \cdot I$$

Integrate equation between limit

$I = I_0$  at  $x = 0$  and

$I = I$  at  $x=1$ ,

We get,

$$\ln \frac{I}{I_0} = -K' C \cdot l$$

$$2.303 \log \frac{I_0}{I} = K \cdot C \cdot l$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} C \cdot l$$

Where,  $\log \frac{I_0}{I} = A$

Absorbance

$$\frac{K}{2.303} = E$$

Molar extinction  
coefficient

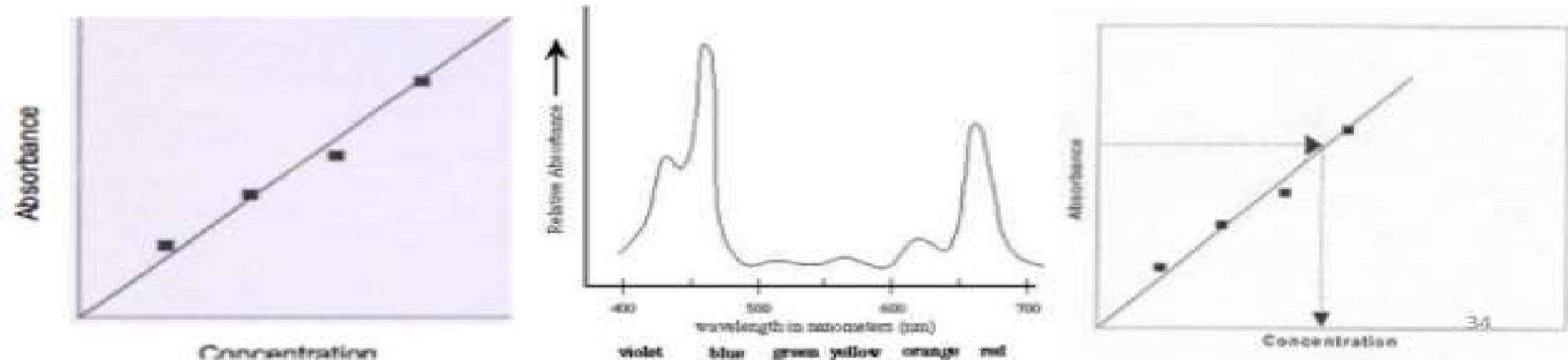
$$A = E \cdot C \cdot l$$

Beer's Law

# APPLICATIONS:

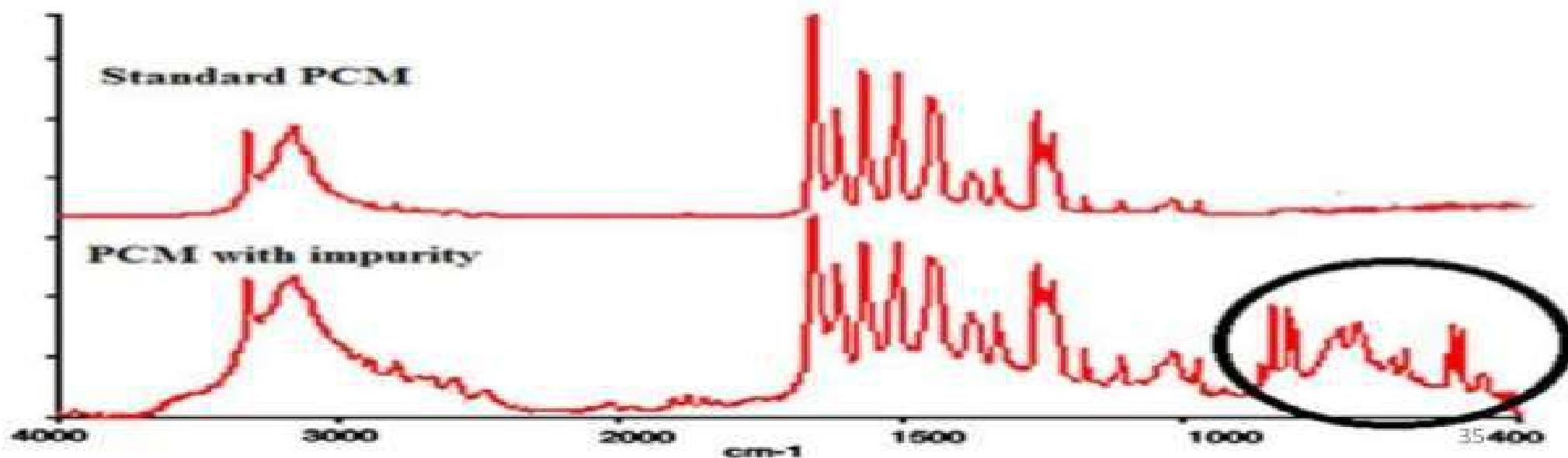
## 1. *Measurement of Concentration:*

- Prepare samples
- Make series of standard solutions of known concentrations
- Set spectrophotometer to the  $\lambda$  of maximum light absorption
- Measure the absorption of the unknown, and from the standard plot, read the related concentration



## **2. Detection of impurities:**

- UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules
- Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material

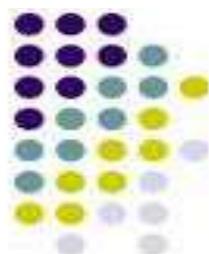


### ***3. Elucidation of the structure of Organic Compounds:***

- From the location of peaks and combination of peaks UV spectroscopy elucidate structure of organic molecules:
  - the presence or absence of unsaturation,
  - the presence of hetero atoms

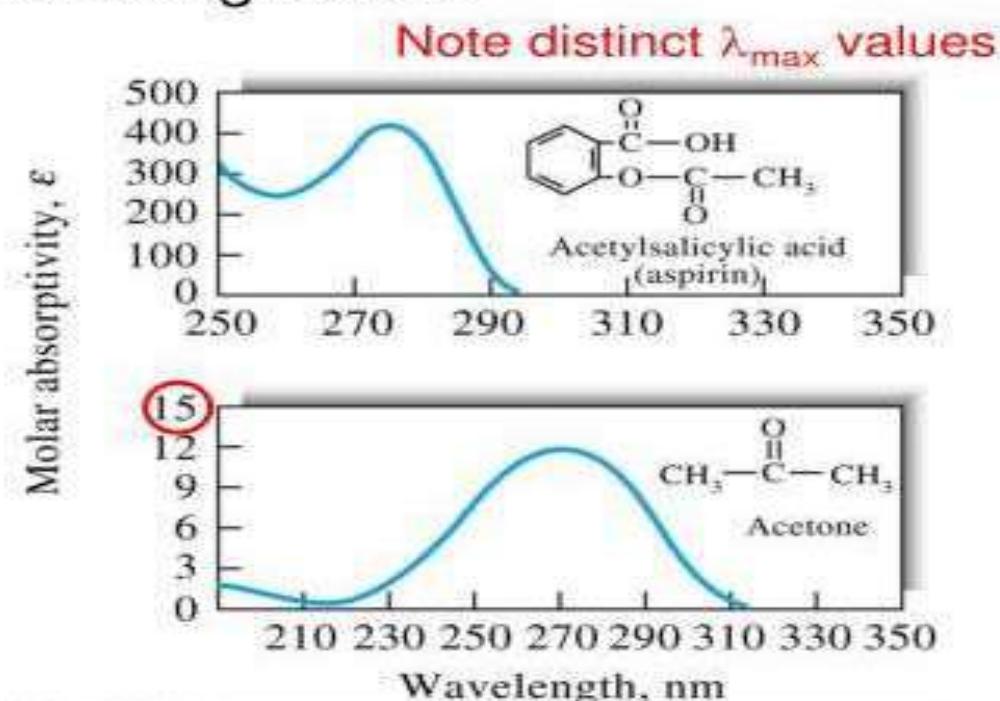
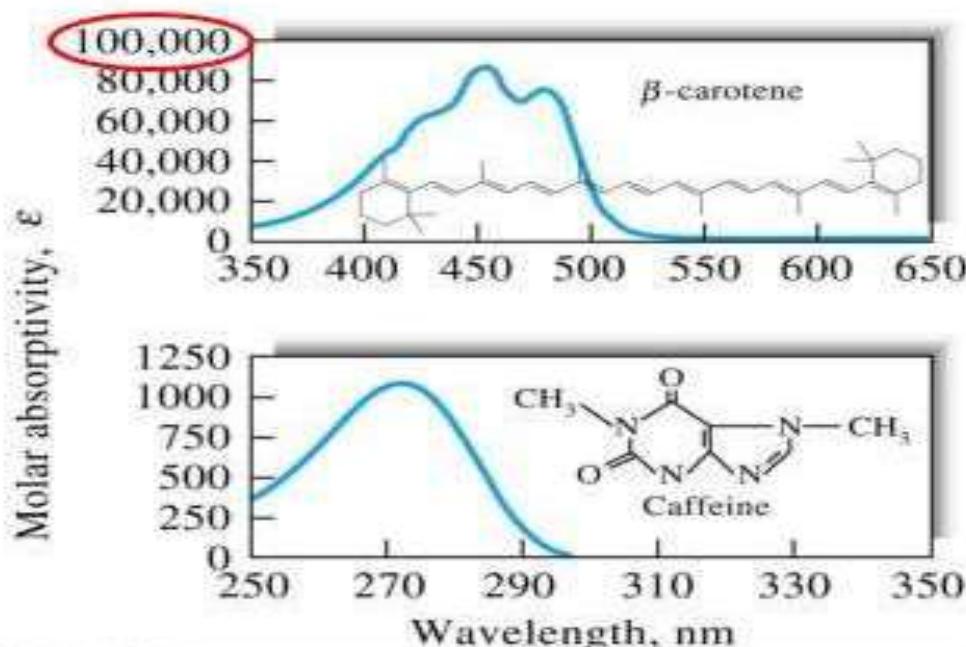
### ***4. Chemical Kinetics:***

- Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed



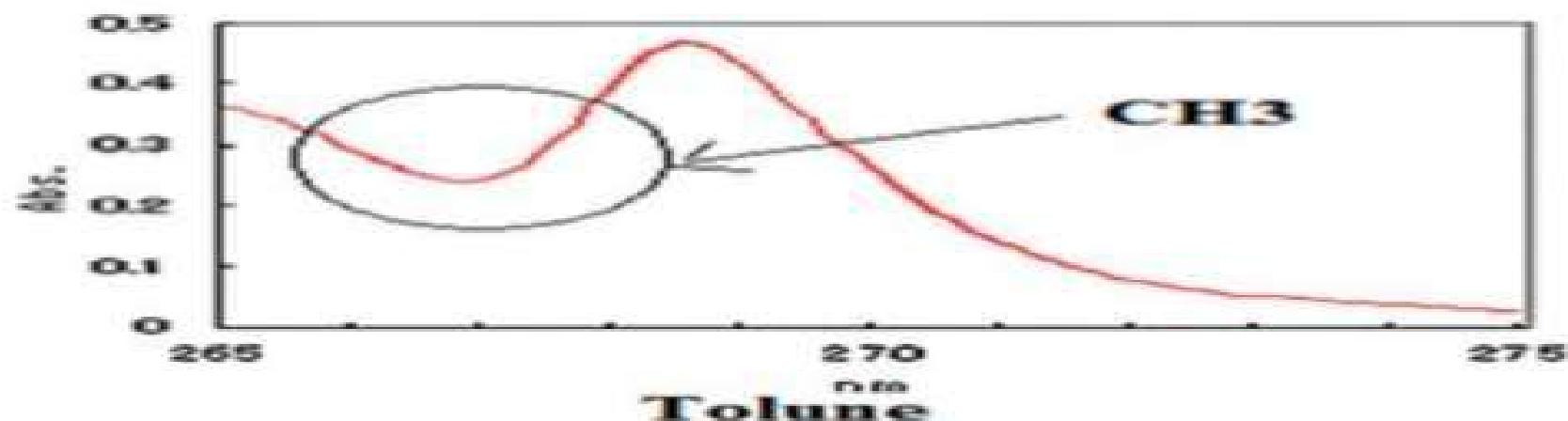
## Absorption signatures of various organic functional groups, continued

- Conjugation causes shift to longer wavelength
- $\pi \rightarrow \pi^*$  transitions more 10-100x or more intense than  $n \rightarrow \pi^*$
- Nonbonding electrons of heteroatoms in saturated compounds can give UV absorbance signature.



## **5. Detection of Functional Groups:**

- Absence of a band at particular wavelength regarded as an evidence for absence of particular group



## **6. Molecular weight determination:**

- Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.
- For example, if we want to determine the molecular weight of amine then it is converted in to *amine picrate*

# Crystal Field Theory

This theory considers only **electrostatic interactions** between the central metal ion (C.M.A.) and the ligand.

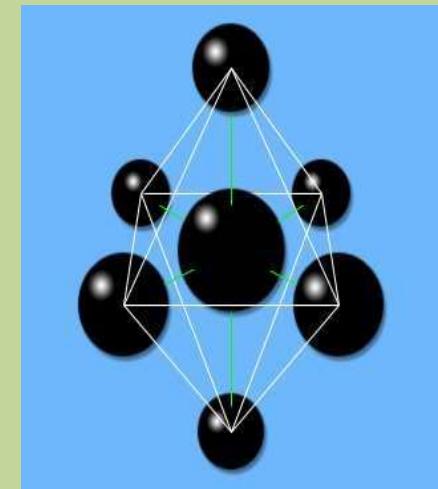
It considers the ligands and the C.M.A. as point charges:

**C.M.A. = +ve point charges**

**Ligands = - ve point charges**

Attractive forces = decreases energy

Repulsive forces = increases energy



To form a complex compound with the -ve charged ligand molecules approach the C.M.A.

Crystal field theory (CFT) explains many important properties of transition-metal complexes, including their colours, magnetism, structures, stability, and reactivity

# FEATURES OF CRYSTAL FIELD THEORY

- CFT assume that bonds between central metal atom or ion and ligands are purely ionic
- Examples of central metal atoms are Cu<sup>+</sup>, Mg<sup>2+</sup>, Ca etc.
- Ligands are of three types positive, neutral, and negative.

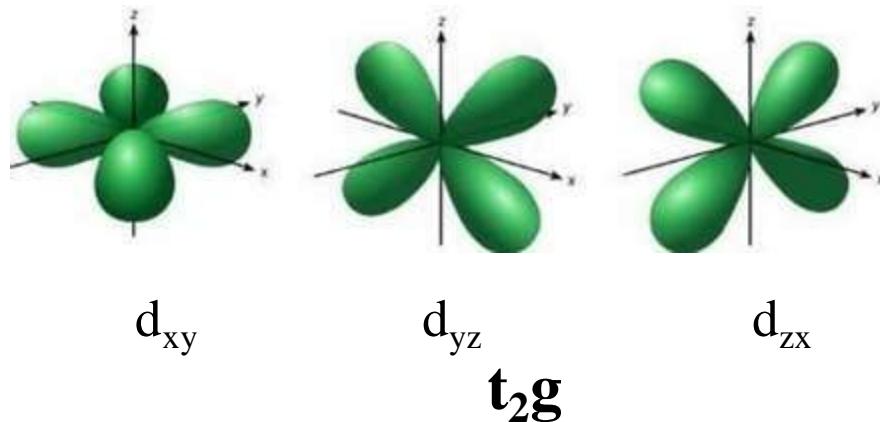
Examples of :-

- -ve ligands : F<sup>-</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, CN<sup>-</sup>
- +ve ligands : NO<sup>+</sup>
- Neutral : NH<sub>3</sub>, H<sub>2</sub>O

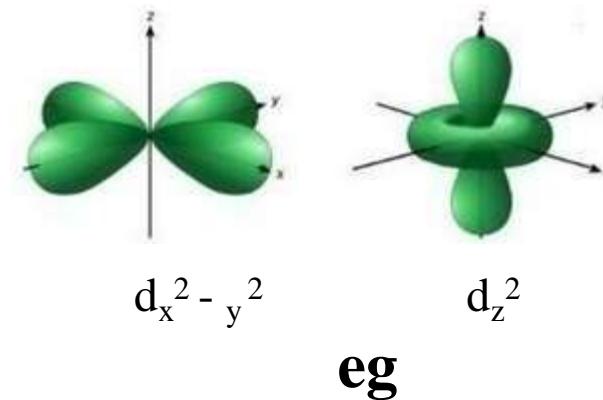
The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are **degenerate**.

$d_{xy}$	$d_{yz}$	$d_{zx}$	$d_x^2 - y^2$	$d_z^2$
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Lobes lying between the axis

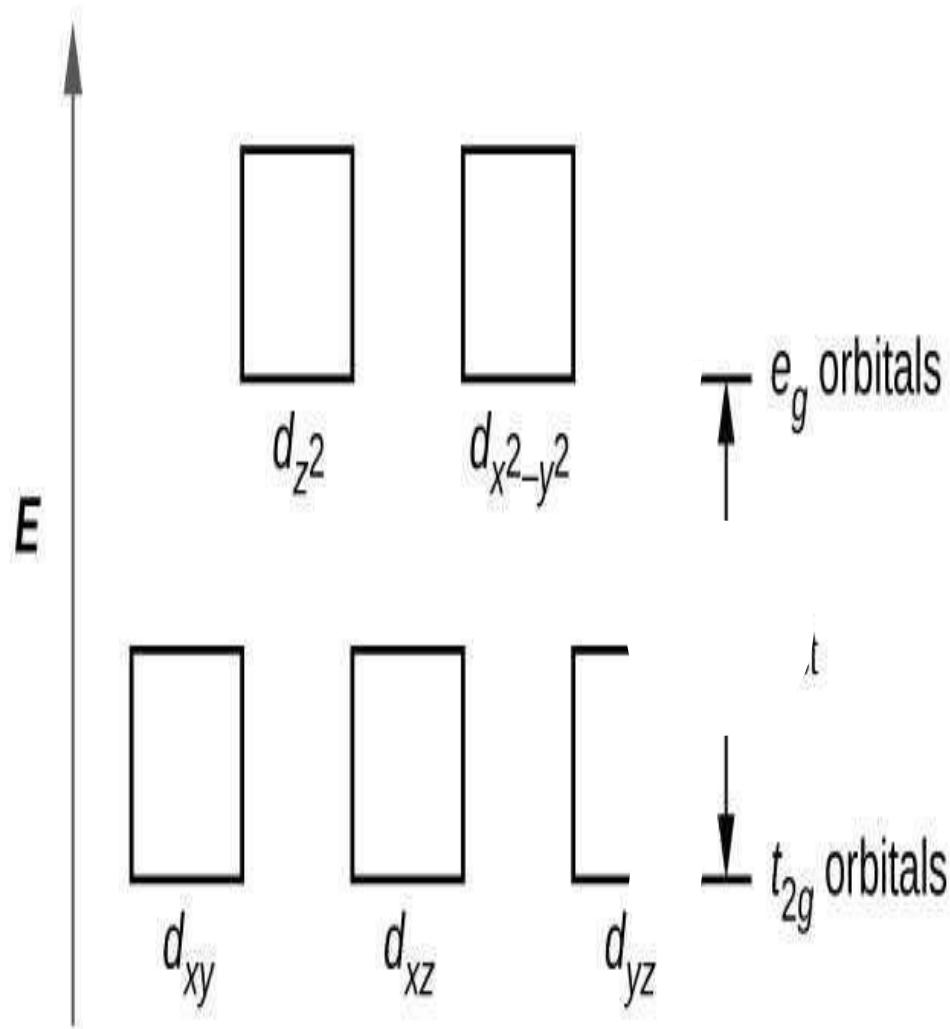


Lobes lying along the axis



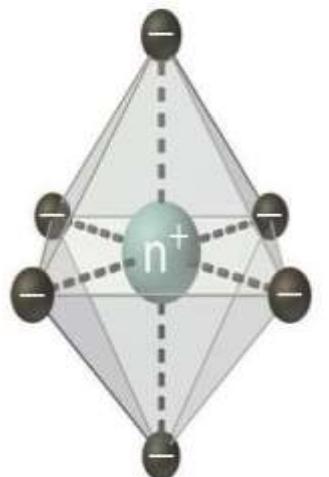
the  $e_g$

- while, the  $t_{2g}$  has  $d_{xy}$ ,  $d_{yz}$   $d_{zx}$  having electrons in BETWEEN the xy, yz and zx axes
- the energies of these two groups  $e_g$  &  $t_{2g}$  depend on their orientations in space



- d-orbitals are degenerate
- **BUT**, when ligands get attached and are uniformly distributed; their energy gets higher
- **IF**, the ligands are oriented at the axes i.e. x, y and z, the degeneracy gets removed and the d-orbitals split into two groups [  $e_g$  &  $t_{2g}$  ]

Negative charges distributed uniformly over surface of a sphere

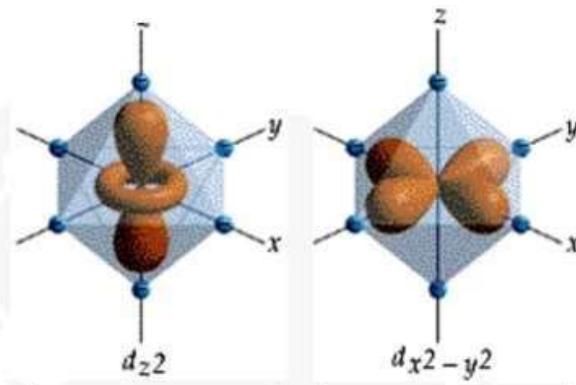
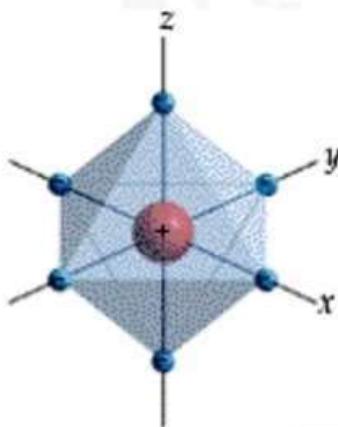


Negative charges located at vertices of an octahedron

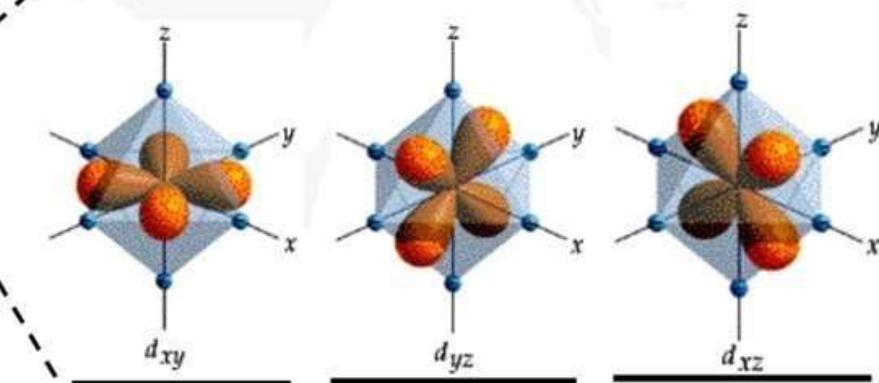
# Crystal Field splitting

Splitting of d orbital into two different set of orbitals in presence of the repulsive field created by the approaching ligands .

Ligands  
approach  
metal



d-orbitals pointing directly at axis are affected most by electrostatic interaction



d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

# CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEX

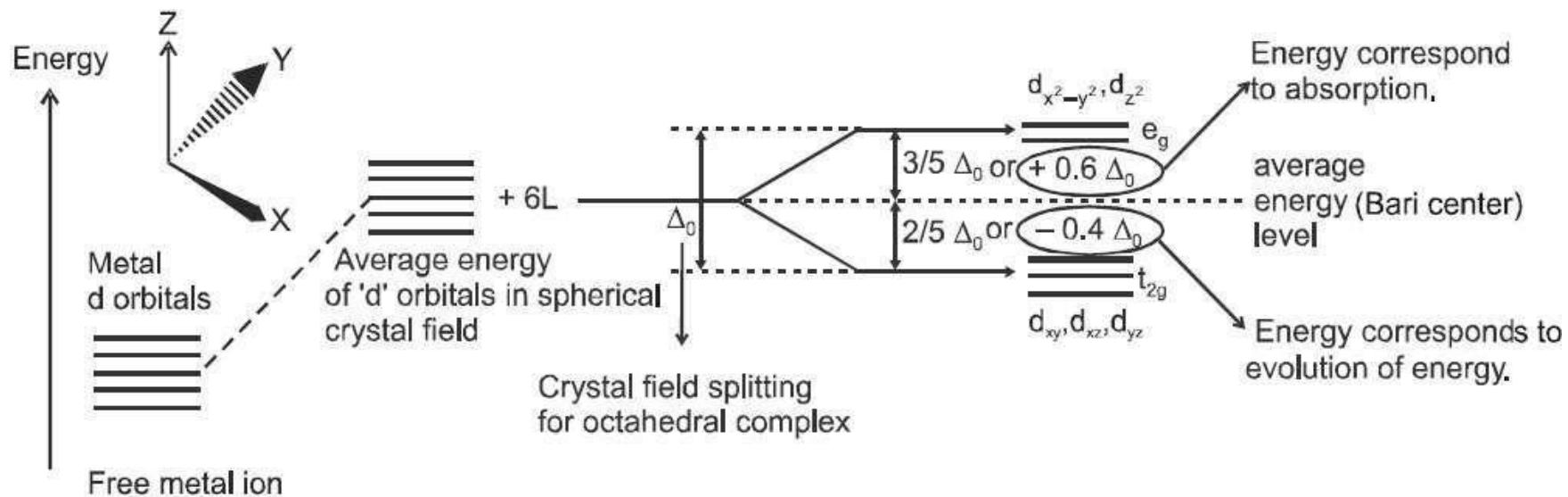


Figure showing crystal field splitting in octahedral complex.

# CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEX

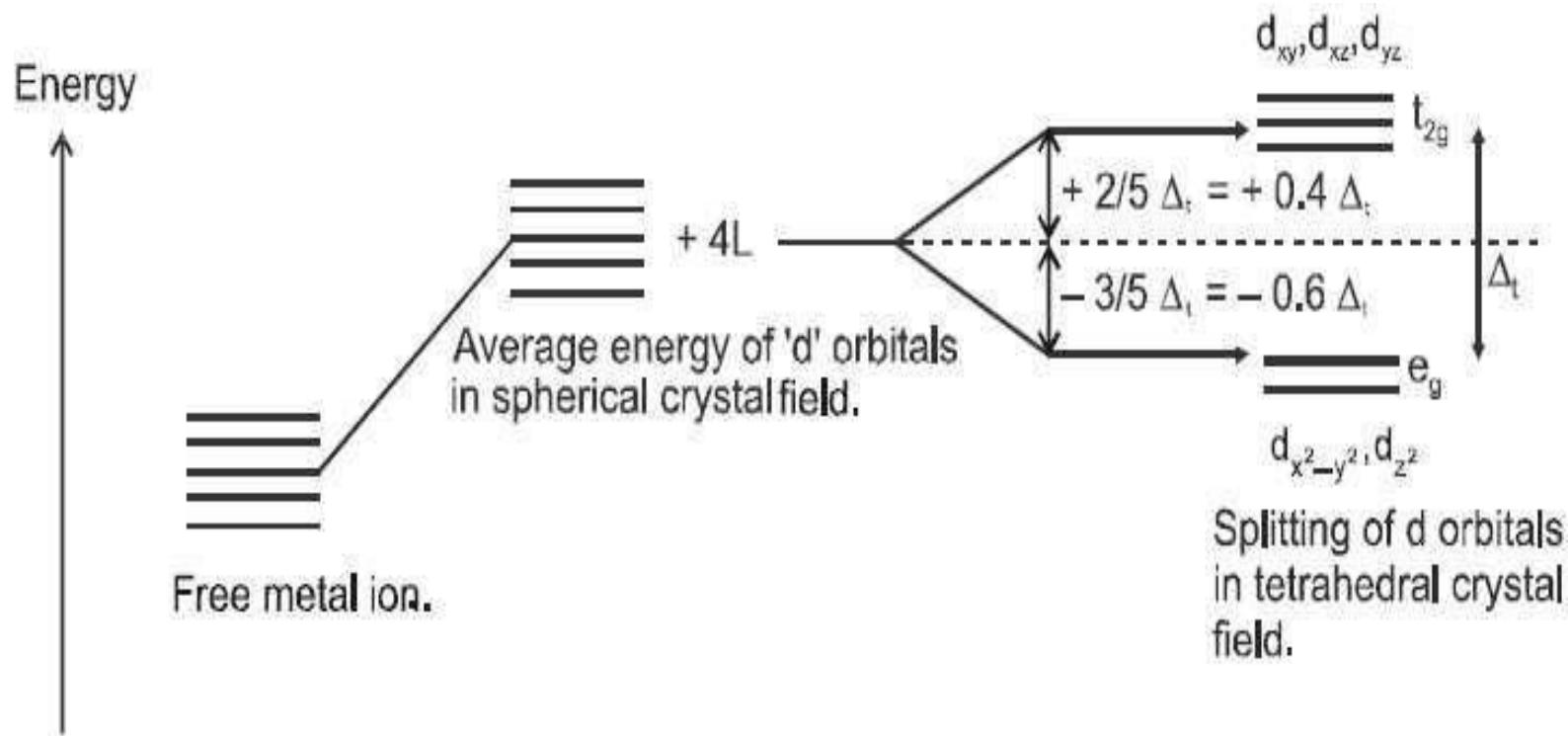


Figure showing crystal field splitting in tetrahedral complex.

$$\Delta_t = \frac{4}{9} \Delta_o.$$

In general, ligands can be arranged in a series in the orders of increasing field strength as given below:  
 $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

The two possibilities are :

- (i) If  $\Delta_0 < P$       weak field ligands and form high spin complexes.
- (ii) If  $\Delta_0 > P$       strong field ligands and form low spin complexes.

## COLOUR IN COORDINATION COMPOUNDS

According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands.

# Factors affecting CFSE

**nature of the metal ion**

CFSE  $\propto$  principle quantum no. Of metal

**oxidation state of metal**

CFSE  $\propto$  oxidation state of C.M.A.

**nature of the ligands**

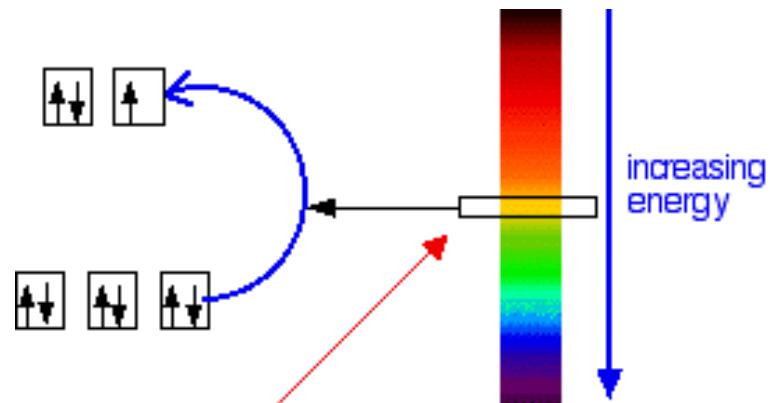
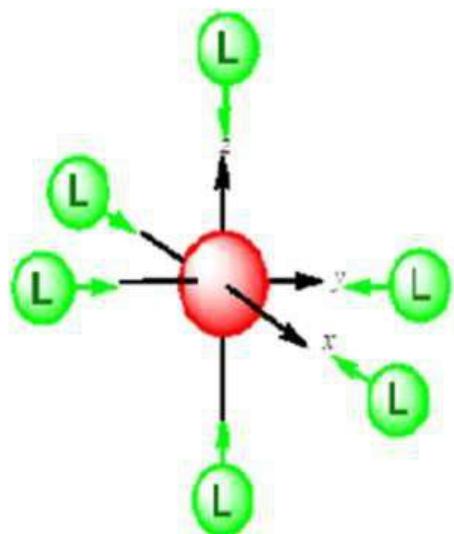
CFSE  $\propto$  strength of ligand

**nature of the complex**

Octahedral complex > tetrahedral complex

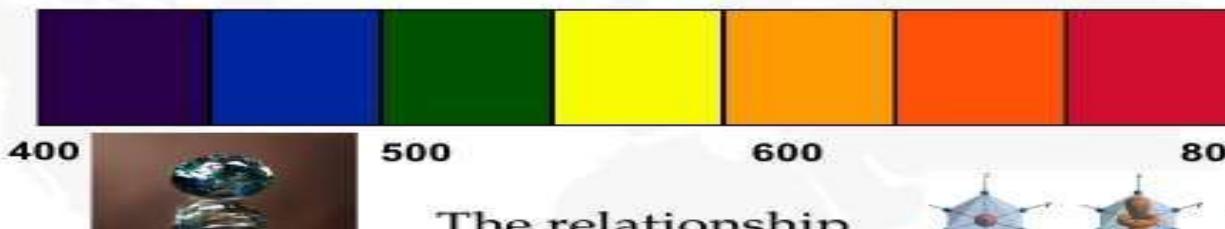
# Limitations of crystal field theory

- (1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, px, py and pz orbitals).
- (2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why  $\text{H}_2\text{O}$  is a stronger ligand than  $\text{OH}^-$  in the spectrochemical series.
- (3) Account to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.
- (4) The CFT cannot account for the  $\pi$ -bonding in complexes.
- (5) The theory failed to explain color in compound having  $d^0$  configuration  
For ex.  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$

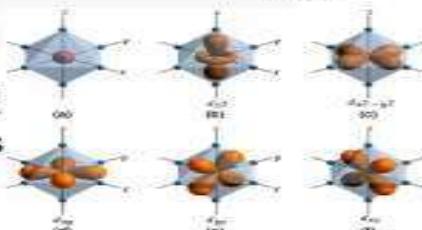


The energy of this particular colour is just right to promote the electron.

## Crystal Field Theory

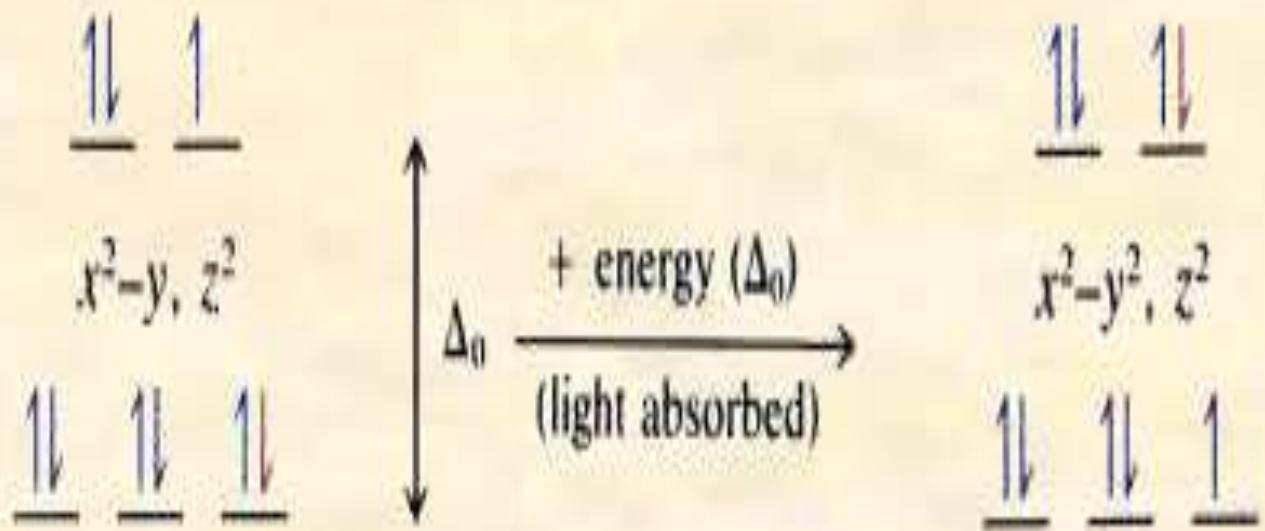


The relationship between colors and complex metal ions



# APPEARANCE OF COLOURS

- The striking colours that these metal complexes show are because of the d-d transition of electrons in the d-orbitals
- Involves the jumping of electrons from lower energy orbitals and their subsequent jumping back
- Jumping occurs when electrons get excited
- In case of colour properties, excitation is caused by photons of visible light
- A photon of light can excite and can cause jumping, ***if*** its energy is equal to the **crystal field splitting energy ( $\Delta_o$ )** (CFSE)
- **CFSE** is the difference in energy between the two sets of d-orbitals
- Energy is absorbed and then released, respectively



ground state  $\text{Cu}^{2+}$

excited state  $\text{Cu}^{2+}$

Thank you



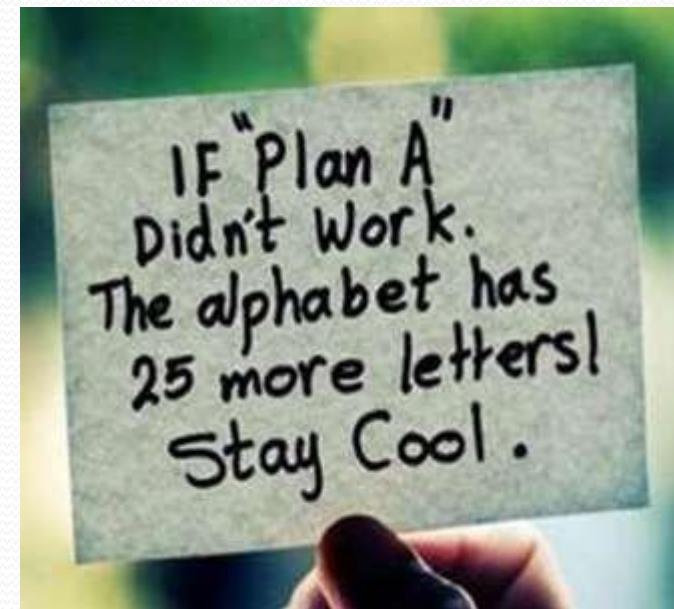
# PLANNING



# Contents

- Nature
- Importance and purpose of planning process
- Steps in Planning and Planning Premises
- Types of plans
- Objectives
- Decision Making
- Types of planning
- Hierarchy of plans

❖ **Planning** (also called **forethought**) is the process of thinking about and organizing the activities required to achieve a desired goal.



- ❖ “If you don't have daily objectives, you qualify as a dreamer.” - **Zig Ziglar**
- ❖ “Planning is deciding in advance what is to be done. It involves the selection of objectives, policies, procedures and programs from alternatives” - **M E Harley**
- ❖ “Planning is a trap laid down to capture the future” - **Allen**
- ❖ “If you don't know where you are going, how can you expect to get there?” - **Basil S. Walsh**

# Nature or Features or Characteristics of Planning

- ❖ **Planning is goal oriented**
  - Plans are made in order to seek certain predetermined goals.
- ❖ **Planning is a primary function**
  - “Planning provides the basic foundation from which all future management functions arise”
- ❖ **Planning is a thinking process**
  - Involves imagination, foresight and sound judgement.

## ❖ **Planning is flexible**

- Planning should not be rigid.

## ❖ **Planning is all-pervasive**

- Planning is an on-going activity at all levels of an organizational hierarchy, right from CEO to first line managers.

## ❖ **Planning is a continuous process**

- Planning involves continuous assessment and reassessment of the resources, directions, opportunities and problems of the organization while converting them to achieve goals.

## ❖ **Planning involves choice**

- Planning always involves choices among various alternatives.
- If there is only one way of doing something, there is no need for planning, planning arises only when there are alternatives available.

## ❖ **Planning is rational**

- Planners should be objective and unemotional in their approach to planning.
- Aim would be to achieve efficiency and effectiveness while optimally deploying resources.

## ❖ **Planning is an integrated process**

- Plans are structured in a logical way such that every lower level plan serves as a means to accomplish higher level plans.
- Plans are inter-related, interdependent and mutually supportive.

## ❖ **Planning is futuristic**

- Planning attempts to peep into the future, analyses it and prepare for it.

# Importance and Purpose of Planning

- ❖ **Planning provides direction**
  - Planning provides clear sense of direction and purpose of activities of an organization.
- ❖ **Planning minimizes risk and uncertainty**
  - In fast changing organizations, planning based on hard facts and data help managers to reduce risk and uncertainties.
- ❖ **Planning ensures co-ordination**
  - Planning helps to establish co-ordinated efforts from various divisions, departments and people.

## ❖ **Planning leads to economy**

- Planning helps accomplish an optimal utilization of physical and human resources, leading towards cost reduction, higher efficiency and productivity which lead to better economy.

## ❖ **Planning facilitates decision-making**

- Planning helps in providing guidelines and thus facilitate decision-making.

## ❖ **Planning reduces overlapping and wastage of efforts**

- Planning avoids duplication of efforts, and overlapping of tasks and responsibilities, reducing wastage.

## ❖ **Planning encourages innovation and creativity**

- Planning helps to remain competitive.
- Innovation and creativity are like ‘trump cards’ in competitive world.

## ❖ **Planning facilitates control**

- Control is key to success of any organization, and in order to control there has to be a plan.

## ❖ **Planning improves morale**

- If Employees participate in planning process it boosts their morale and develops a broad mentality and thinking of achieving organizational goals.

# Steps in Planning

Step 1: To establish objectives which are verifiable

Step 2: To establish planning premises

Step 3: To determine alternative course of action

Step 4: To evaluate the alternatives and select the best Step 5:

To formulate derivative plans

Step 6: To secure co-operation and participation of all employees

Step 7: To measure and control the progress through follow-up

# Steps in Planning

## **Step 1: To establish objectives which are verifiable**

- ❖ Identify goals of the organization
- ❖ Internal(Financial position of company, human resources available, manufacturing facility, company image, etc.) and external environment(Government rules and regulations, Socio-economic condition of the society, competition level, suppliers reliability) of the organization has to be studied

## **Step 2: To establish planning premises**

- ❖ Planning premises are assumptions of future market conditions which become the basis for current planning process.
- ❖ Planning premises usually relate to cost and availability of raw materials, labour, power, product demands, population trends, technology growth, government policies etc.

## **Step 3: To determine alternative course of action**

- ❖ Search and list all possible alternatives in order to be compared and analytically evaluated.

## **Step 4: To evaluate the alternatives and select the best**

- ❖ Select most suitable and best course of action.
- ❖ Alternatives have to be compared and evaluated with respect to their expected contribution to organizational goals.
- ❖ Evaluation and selection is often done with the help of quantitative techniques and operations research.

## **Step 5: To formulate derivative plans**

- ❖ Management has to formulate derivative plans or secondary plans to support the basic plan.
- ❖ Derivative plans are sub plans or departmental plans.
- ❖ For Example, if the production plan of TATA MOTORS is to produce a million of Nano's in the next five years, the derivative plans would be plans for various departments like fabrication, forging, casting, purchase, assembly etc.

## **Step 6: To secure co-operation and participation of all employees**

- ❖ Involving employees in planning process enhances their co-operation and participation.
- ❖ Continuous suggestions, complaints and criticisms must be solicited from the employees.

## **Step 7: To measure and control the progress through follow-up**

- ❖ Continuous evaluation of plans help in identifying recurring mistakes and avoiding them in future.

# Planning Premises

- ❖ Planning premises are assumptions of future market conditions which become the basis for current planning process.
- ❖ Planning premises have to be established even before planning.
- ❖ To establish planning premises means to forecast future business conditions under which a plan has to operate.
- ❖ Planning premises provide bedrock upon which the plans are based.

# Classification of Planning Premises

1. Internal and External premises
2. Tangible and Intangible premises
3. Controllable, Semi-controllable and Uncontrollable premises

## **Internal premises**

- ❖ Internal premises are those factors which exist within organization and are generally under the control of management.
- ❖ Internal premises include – men, money, machinery, materials and methods.

## **External premises**

- ❖ External premises are those factors which exist outside the purview of the organization and are generally not under the control of the management.
- ❖ External premises include government policies, general economy of country, technological trends, climatic conditions etc.

# Tangible and Intangible Premises

## Tangible premises

- ❖ Tangible premises are those which are quantifiable in nature.
- ❖ For Example, production quality, quality standards, capital required, machinery to purchase.
- ❖ These info. Is needed for planning and are quantifiable and measurable in nature.

## Intangible premises

- ❖ Intangible premises are those which are abstract and non-quantifiable in nature.
- ❖ For Example, company image, brand loyalty, political situation etc., are needed for planning but are qualitative in character.

# **Controllable, Semi-controllable and Uncontrollable Premises**

## **Controllable premises**

- ❖ Controllable premises are those factors which are said to be completely under the control of management.
- ❖ For Example, Managerial policies, rules and regulations etc.

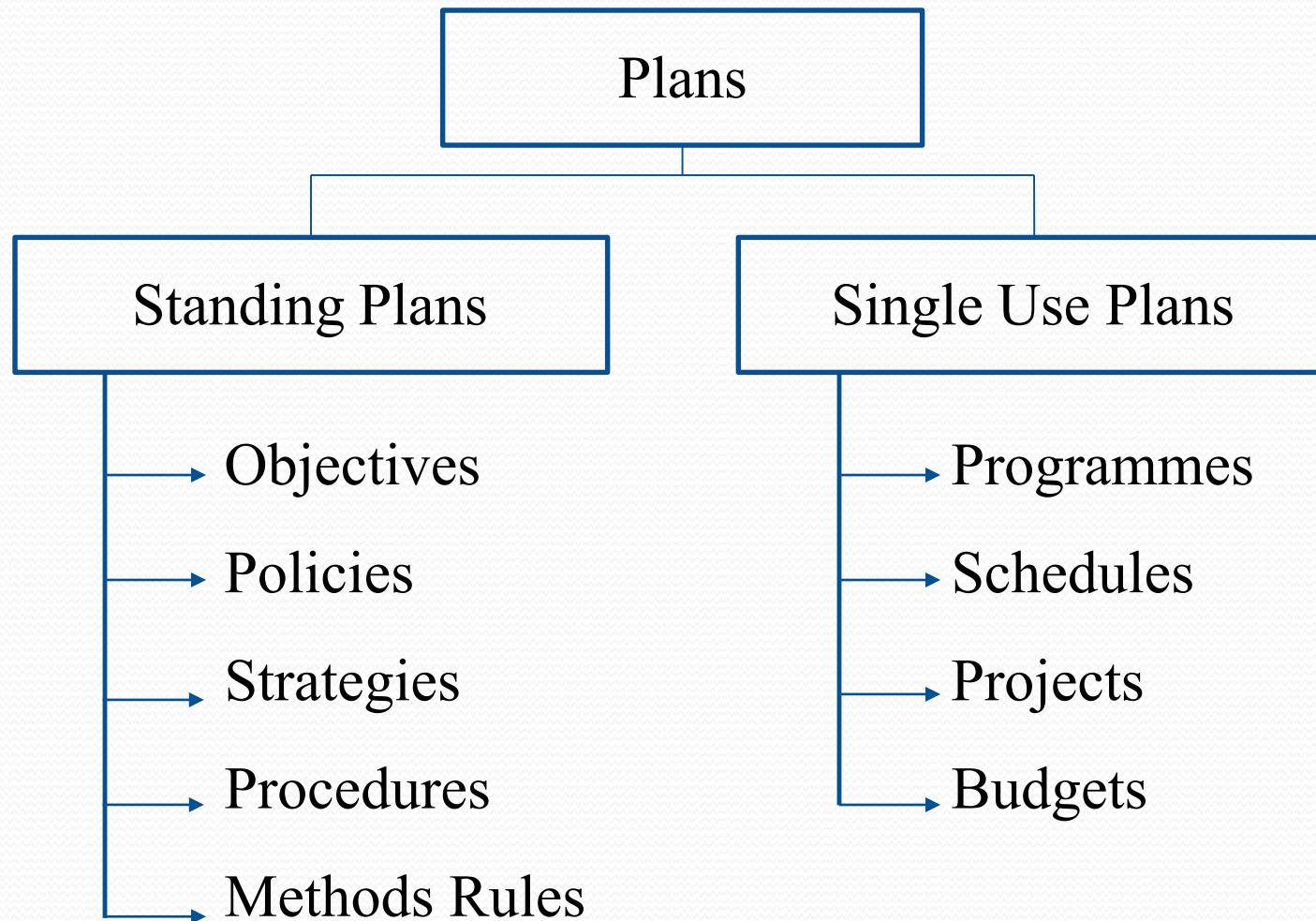
## **Semi-controllable premises**

- ❖ Controllable premises are those which management has partial control.
- ❖ For Example, workers attitude and efficiency, firms pricing policy, firms marketing programs, raw materials etc.

## **Uncontrollable premises**

- ❖ Internal premises are those factors over which management has absolutely no control.
- ❖ For Example, Natural calamities, new inventions, wars, strikes imposition of emergency, government etc.

# Types of Plans



# Objectives

- ❖ Objectives, goals, aims, purposes, missions are the terms with same meaning.
- ❖ Objectives are goals or end-points towards which all business activities are directed.
- ❖ Objectives or goals are the desirable end results planned by the management or administration and expected to be achieved by the organization.
- ❖ Objectives are the products of specific, concrete thinking, they commit employees and organization to verifiable accomplishments.

# Characteristics of Objectives

## i. Objectives are multiple in nature

- Organizations have multiple objectives due to many areas of business operations where organizations try to set their goals.
- Key areas for setting objectives of performance are;
  - Market Standing of the company
  - Innovation achieved by the company
  - Productivity in various parameters
  - Physical and financial resources

- Managerial performance and development
  - Worker performance and attitude
  - Fulfillment of public responsibility
- Objectives are always multiple in nature in order to get a right balance.

## **ii.Objectives have a hierarchy**

- we have corporate objectives of the total enterprise at the top, followed by divisional or departmental objectives, then each section and finally individual objectives. Objectives at all levels serve as an end and as a means.

### **iii. Objectives form a network**

- Objectives of the organization across various dept. and along the hierarchy are all inter-related and independent.

### **iv. Objectives may be long-range or short-range**

- Long range objectives are vague. For Example, survival and growth of the company, diversification plans, expansion plan etc.
- Short range objectives are specific and definite. For Example, Profit maximization, inventory control, ensuring adequate cash flows etc.

## **v. Objectives are either tangible or intangible**

- Objectives could be tangible which means they could be quantifiable. For Example, productivity, profitability etc.
- Objectives could be intangible which means they are qualitative in nature and cannot be quantified. For Example, Workers morale, company image etc.

## **vi.Objective have priority**

## **vii.Objectives some times clash with each other**

# Importance or Advantages of Objectives

- ❖ Objectives provide directions to the individual efforts and activities of an organization.
- ❖ Provide strong basis for determining policies, procedures, strategies, programs, budgets and other plans.
- ❖ Help in effective delegation of authority.
- ❖ Serve as standards for the evaluation of actual performance.
- ❖ Help in coordinating the efforts of various departments and people.
- ❖ Help in achieving personal goals

# Policies

- ❖ Policies are guidelines set up by the company for managerial decision making.
- ❖ ‘A policy is a verbal, written or implied overall guide setting up boundaries that supply the general limits and directions in which managerial actions will take place’.
- ❖ For Example,
  - Policy of recruiting only MBA’s from top 10 institutes.
  - Policy of promotion of in-house employees.
  - Policy on selling goods only for cash and not credit.

# Strategies

- ❖ Strategies specify the route taken to achieve company objectives and policies.
- ❖ Strategy comprises of;
  - a course of action
  - a commitment of resources
  - a detailed blue print of all moves, initiatives, responses with timing concern.
- ❖ Strategy is a unified and critical plan of action to achieve a goal

## Strategies Cont.

- ❖ A Strategy is a master plan for moving the organization towards its objectives through the complex and volatile environment of market forces.
- ❖ Strategy involve innovation and creativity.
- ❖ For Example;
  - Strategy for wining an approval in the board meeting.
  - Strategy to make the best use of media coverage.
  - Strategy to convince the lecturer that he should let you free in the class! etc.

# Procedures

- ❖ Procedures are action guidelines which specify how particular activity has to take place.
- ❖ Procedures provide chronological step-by-step sequence of required actions in order to achieve a certain goal or policy.
- ❖ A procedure lays down the manner and method by which work is to be performed in a standard or uniform way.
- ❖ Procedure ensures higher than average level performance, which results in work simplification and eliminates duplication of efforts.

# Procedures Cont.

- ❖ A good procedure should be;
  - Purposeful and functional
  - In written form
  - Simple and clear
  - Flexible
  - Exposed to periodic review
- ❖ For Example;
  - Procedure for recruitment of employees.
  - The CET procedure for engineering admission.
  - Procedure for processing customer complaints.

# Methods

- ❖ Methods are basically sub-units of procedure.
- ❖ Break-up of each steps of a procedure into sub-steps.
- ❖ Methods indicate the simplified and standardized techniques to be employed in carrying out a particular task in the best way.
- ❖ Methods are products of research, experimentation and analysis.
- ❖ For Example;
  - Method of conducting a written test for recruitment.
  - Method employed for failure analysis.
  - Method employed for distracting the professor.

# Rules

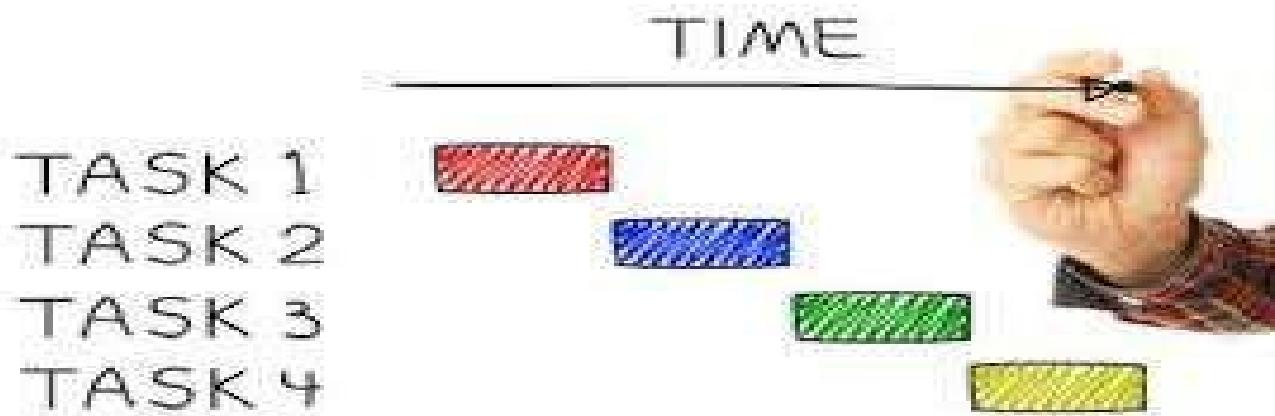
- ❖ Rules are standard guidelines which specify what is good and what is bad for an employee/organization.
- ❖ Rules are always established to direct or restrict action in order to govern the behavior of individuals.
- ❖ Rules if violated are viewed seriously and penalties are imposed.
- ❖ For Example;
  - Rule of ‘No Smoking’
  - Rule of formal dressing
  - Rule of not using cell phones in academic promises.

# Programmes

- ❖ A program is a precise plan which lays down the operations to be carried out to accomplish a given work.
- ❖ Program is aggregate of several related action plans that have been designed to accomplish a mission within specified time.
- ❖ A program is a comprehensive plan that includes a complex set of goals, procedures, methods, strategies etc.
- ❖ For Example;
  - Program of organizing an international seminar.
  - An Expansion program for a company.

# Schedules

- ❖ Schedules are time-tables which clearly specify when, what and where each element of work is carried out.
- ❖ Aim of scheduling is to plan the sequences of work so that all units of work can be systematically arranged towards their completion by due date.



# Projects

- ❖ Project is small program. Several projects may also make up a program.
- ❖ Projects are individual portions of a general program which clear-cut and relatively distinct.
- ❖ For Example;
  - A Software project part of a larger program.
  - SPSS Project work
  - Demolition Project as part of a encroachment-removal program.

# Budgets

- ❖ A Budget is a written plan of future activities of the company in monetary terms.
- ❖ Budgets are managerial tools for planning, programming, and controlling business activities.
- ❖ Budget defines the anticipated cost of attaining an objective.
- ❖ For Example;
  - Sales Budget
  - Production Budget
  - Advertising Budget

# Budgets Cont.

- ❖ General features of budget are:
  - It is statement in terms of money.
  - It is prepared for a definite future period.
  - It is prepared in advance.
  - It gives an overall view of the business in terms of sales, production and expenditure.
  - It helps in anticipation and control of financial requirements of different branches of business.

# Decision Making

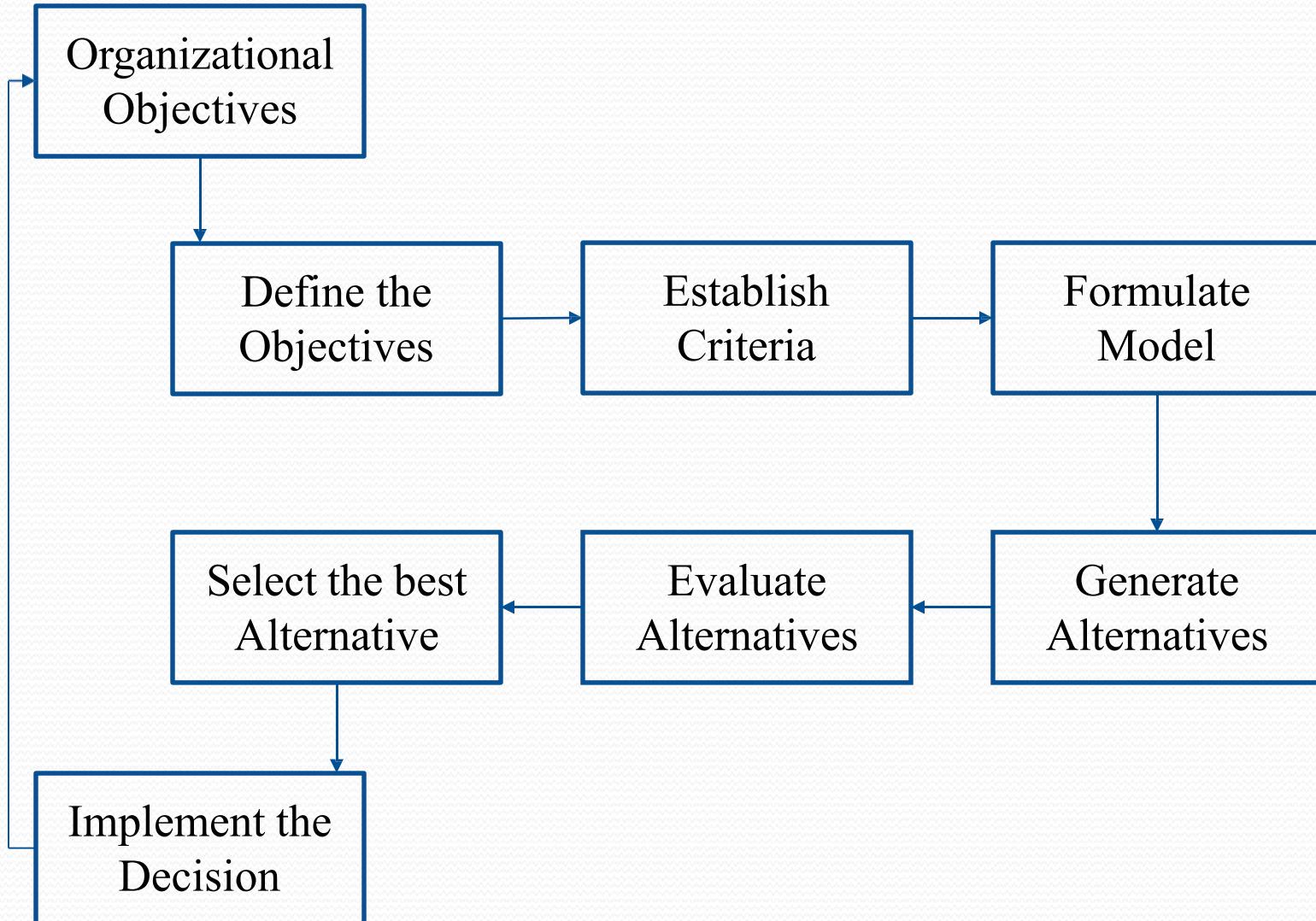
- ❖ In an organization decisions are routinely taken in operations, marketing, maintenance, R & D, transportation, finance, human resource etc.
- ❖ Decision making is the cognitive process leading to the selection of a course of action among alternatives.
- ❖ Every decision making process produces a final choice. It can be an action or an opinion.



# Characteristics of Decision Making

- ❖ Decision making is goal oriented
- ❖ Decision making involves alternatives
- ❖ Decision making is an analytical intellectual process
- ❖ Decision making is a continuous activity
- ❖ Decision making is an all pervasive function
- ❖ Decision making is situational and dynamic.

# Decision Making Process



# Decision Making Process

- ❖ To define the problem and parameters influencing it
- ❖ To establish criteria for decision making
- ❖ To formulate a model considering all decision variables
  - Physical model – architects idea of a building
  - Computer Model – CAD model of cars and machines
  - Mathematical Models – Forecasting  
model, simplex model, transportation model etc.
  - Verbal Models – Words and description

# Decision Making Process

- ❖ To generate alternatives solution by varying parameters
  - By varying the values of the parameters several alternatives can be framed.
- ❖ Evaluate all alternatives – Selecting the course of action that best satisfies the criteria
- ❖ Select the best alternatives
- ❖ Implement the decision and monitor the result.

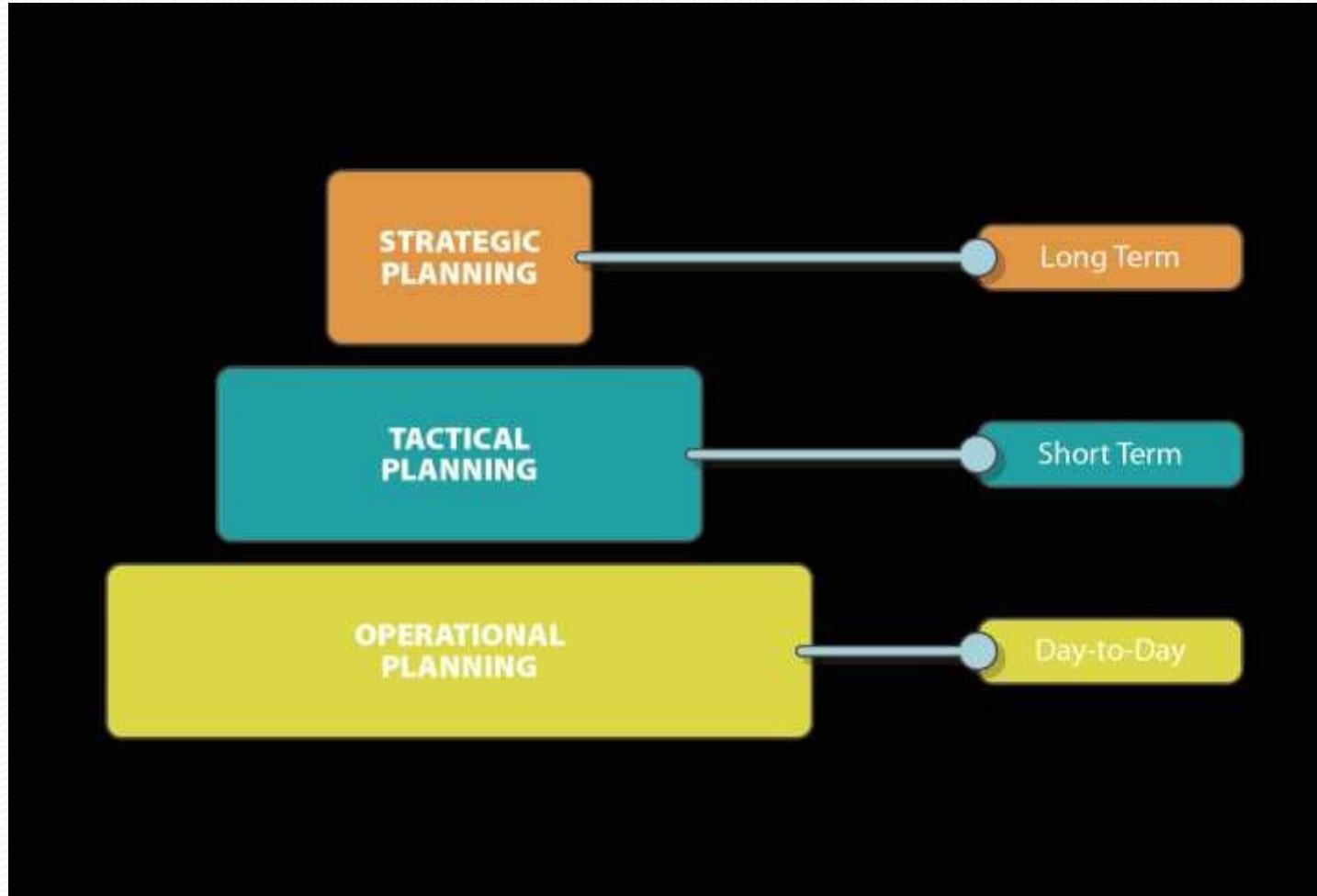
# Decision Methodology

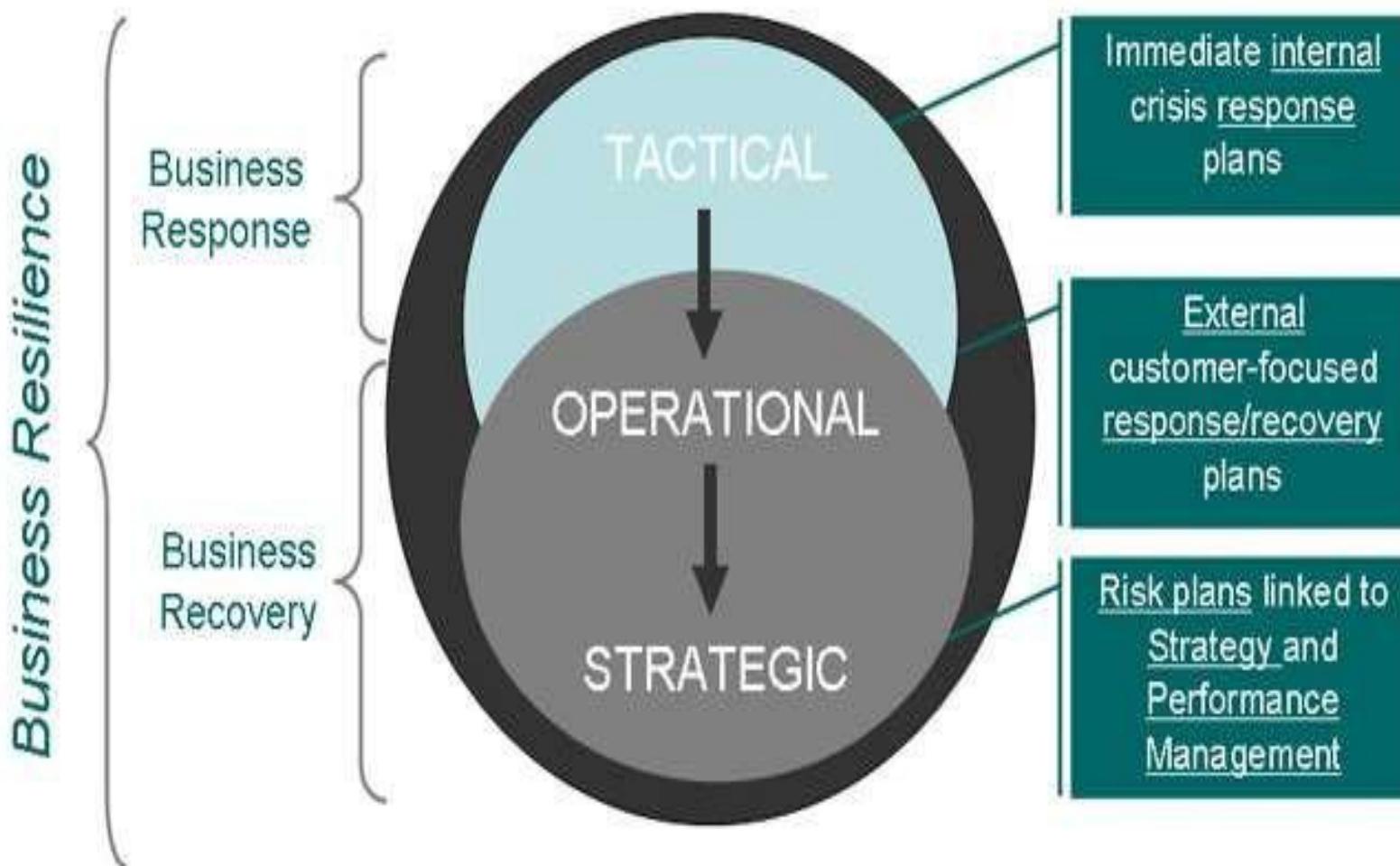
- ❖ Engineers and managers are expected to use a number of quantitative technique to serve as basis for decision making.
- ❖ Type of quantitative technique depends on nature of variables influencing the problem.
- ❖ In some cases,
  - All information about decision variables are known
  - Some information about decision variables are known
  - No information about decision variables are known

# Several Quantitative Techniques

- ❖ Variables with complete certainty
  - For Example: Break-even analysis, Scheduling, Linear and Non-linear programming, Dynamic programming, Cost benefit analysis etc.
- ❖ Variables with risk and partial certainty
  - For Example: Forecasting, Simulation, theory, Queueing Decision trees, Regression, Aggregate planning etc.
- ❖ Variables with extreme uncertainty
  - For Example: Game theory, Flip of coin, Astrology etc.

# Types of Planning





Strategic Planning	Tactical Planning	Operational Planning
Long range plans	Intermediate range plans	Short range plans
Time Frame: 3 or more years	Time Frame: 2-3 years	Time Frame: one year
Responsibility of top Management	Responsibility of middle management	Responsibility of lower level management
Concerned with objectives, policies, programmes	Concerned with procedures, projects and strategies	Concerned with schedules and methods
Responsible for overall progress of the company	Responsible for integrating the work of various department of the organization	Responsible for covering day-to-day operation and implementing internal goals
Focus on planning and forecasting	Focus on co-ordination	Focus on directing and controlling

# STRATEGIC X TACTICAL X OPERATIONAL



## Strategic Planning

- Why and When?
- Entrepreneur: President, Partners, Directors.
- Long Term. More Comprehensive.



STRATEGIC



## Tactical Plan

- Where and How?
- Administrator: Manager, Coordinator.
- Medium-term. Link between levels.



TACTICAL



## Operational Plan

- What?
- Technical: Executor.
- Short Term. Specific.

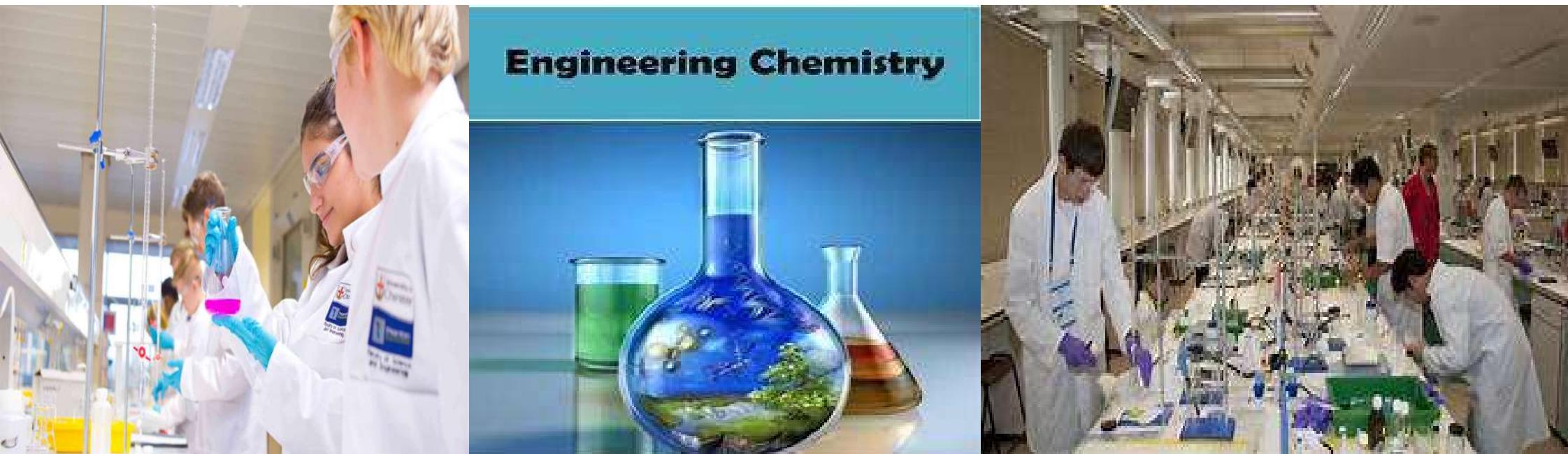


OPERATIONAL

# Hierarchy of Plans



# Thank you



# **ENGINEERING CHEMISTRY-SEC-E**

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# **ENGINEERING CHEMISTRY SYLLABUS**

## **UNIT I - ATOMIC AND MOLECULAR STRUCTURE**

Structure of Atom – Introduction- Schrodinger equation - Derivation – Particle in a box solution – Plots of these functions to explore their spatial variations - Forms of the hydrogen atom wave functions. Orbitals and Quantum Numbers.

Atomic orbital – Equation for molecular orbitals – Energy level diagrams of diatomic molecular orbital. Molecular orbitals of diatomic molecules- Homonuclear – Heteronuclear diatomic molecules.

Introduction – Explanation –  $\pi$ -molecular orbitals of butadiene- Applications for conjugated molecules . Aromaticity –  $\pi$ -molecular orbitals benzene.

Crystal field theory – Introduction – Explanation – Energy level diagrams for transition metal ions – Magnetic properties of transition compounds.

# **UNIT I - ATOMIC AND MOLECULAR STRUCTURE**

## **HISTORY & EARLY STUDY OF ATOMS**

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter.

According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible.

The word ‘atom’ has been derived from the Greek word ‘a-tomio’ which means ‘uncut-able’ or ‘non-divisible’. These earlier ideas were mere speculations and there was no way to test them experimentally.

These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

# DALTON'S ATOMIC THEORY

- ❖ The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. Dalton's atomic theory stated that,
- ❖ All matter is made up of tiny, indivisible particles called atoms.
- ❖ All atoms of a specific elements are identical in mass, size, and other properties. However, atoms of different element exhibit different properties and vary in mass and size.
- ❖ Atoms can neither be created nor destroyed. Furthermore, atoms cannot be divided into smaller particles.
- ❖ Atoms of different elements can combine with each other in fixed or whole number ratios in order to form compounds.
- ❖ Atoms can be combined in chemical reactions to form molecules or compounds



Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully.

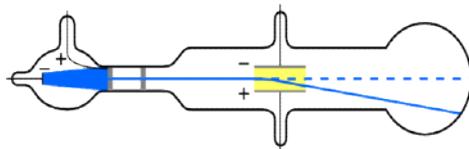
However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged.

## DEFINITION OF ATOM

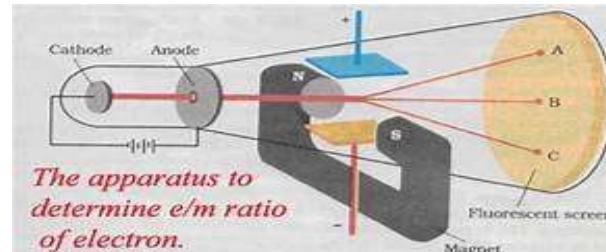
An atom is the smallest unit quantity of an element that is capable of existence, either alone or in chemical combination with other atoms of the same or another element. The fundamental particles of atom are composed of proton, electron and neutron.

## DISCOVERY OF ELECTRON

In 1897, British physicist J.J. Thomson discovered, in the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles ("corpuscles"), suggesting that the cathode rays consist of negatively charged particles, called today as electrons.



Cathode ray tube



J.J. Thompson  
1856-1940

- Discovered electron 1897 – Cathode Ray Experiment
- Plum Pudding model 1904
  - Electrons in a soup of positive charges
- Discovered isotopes 1913

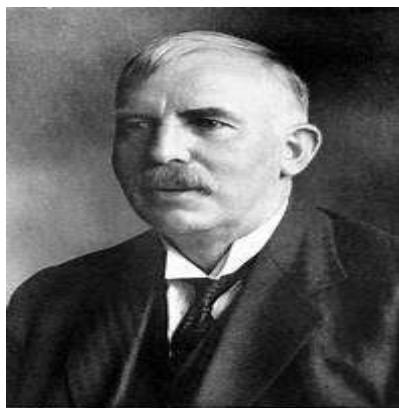


He also measured the ratio of electrical charge ( $e$ ) to the mass of electron ( $m_e$ ) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other to the path of electrons.

In 1906 Thomson won Nobel Prize "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases".

## DISCOVERY OF PROTON

The discovery of protons stated in 1815, William Prout, English chemist suggested that all atoms are made up of hydrogen atoms (which he referred to as protyles). German physicist Eugen Goldstein in 1886 discovered, canal rays from electrical discharge carried out in the modified cathode ray tube led to the discovery of carrying positively charged particles. The smallest and lightest positive ion was obtained from hydrogen and was called proton. The discovery of the proton is credited to Ernest Rutherford, who proved that the nucleus of the hydrogen atom is present in the nuclei of all other atoms in the year 1917.



Rutherford

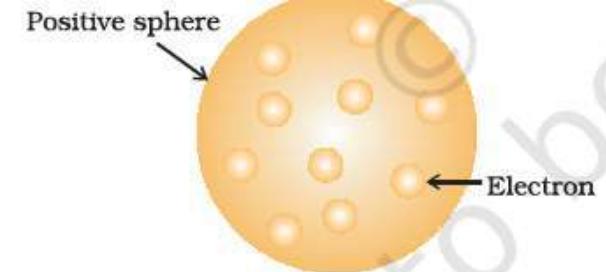
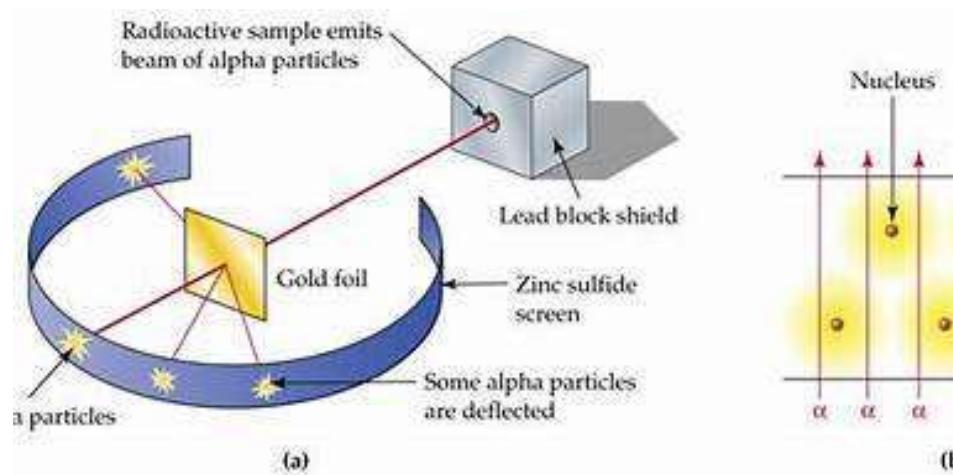


Fig. 2.4 Thomson model of atom

Plum Pudding model

In 1908 Rutherford and Soddy are awarded the Nobel Prize for discovery of element transmutations.

## DISCOVERY OF NEUTRON

Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. In 1932, Chadwick carried out a series of experiments with a cloud chamber filled with different gases, H, He, N, Ar and with different windows, Li, Be, C. He exposes the chamber to the new radiation particles and observes the range of recoiling nuclei. From the large range of the recoils (even for heavy elements), he identifies the new radiation as neutrons, the particle having the mass equal to the mass of a proton.

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	$-1.602176 \times 10^{-19}$	-1	$9.109382 \times 10^{-31}$	0.00054	0
Proton	p	$+1.602176 \times 10^{-19}$	+1	$1.6726216 \times 10^{-27}$	1.00727	1
Neutron	n	0	0	$1.674927 \times 10^{-27}$	1.00867	1

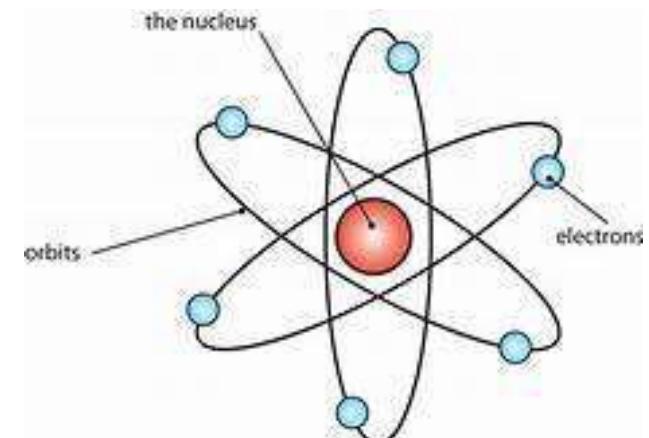
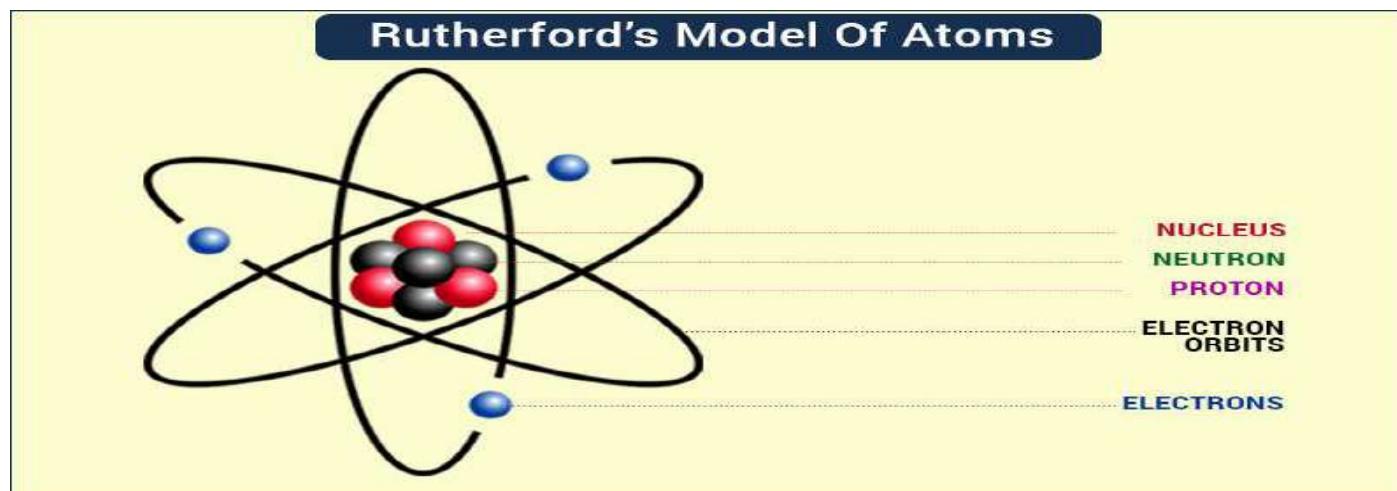


1935 Chadwick receives Nobel Prize for discovering neutron

# ATOMIC MODEL

Rutherford proposed the nuclear model of atom, on the basis of observations and conclusions from his results.

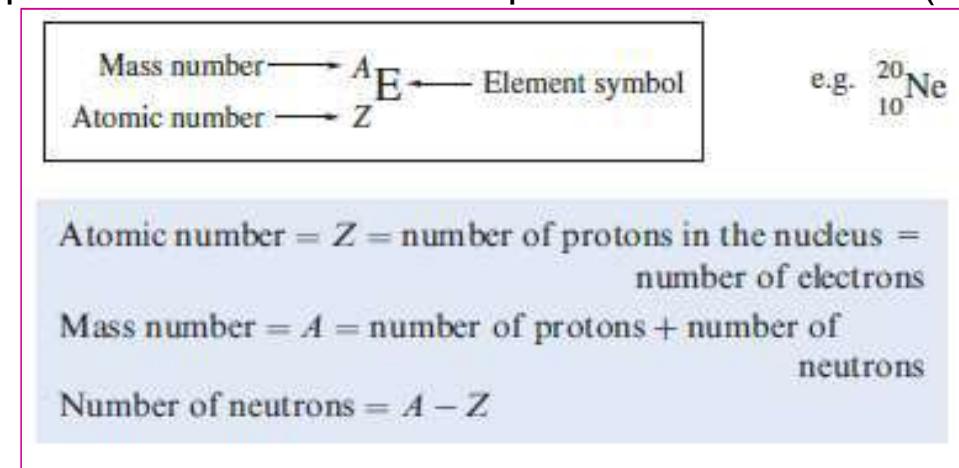
- The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus.
- The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.
- Electrons and the nucleus are held together by electrostatic forces of attraction.



# ATOMIC NUMBER & MASS NUMBER

The presence of positive charge on the nucleus is due to the protons in the nucleus. The charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number ( $Z$ ).

Mass number ( $A$ ) of the nucleus is due to protons and neutrons in the nucleus are collectively known as nucleons. A shorthand method of showing the atomic number and mass number of a nuclide along with its symbol,  $E$ , is:



## ISOTOPES

Nuclides of the same element possess the same number of protons and electrons but may have different mass numbers, the number of neutrons may vary, are called isotopes. Isotopes can be separated by mass spectrometry. E.g.: C ( $^{12}_6\text{C}$  and  $^{13}_6\text{C}$ ) and O ( $^{16}_8\text{O}$ ,  $^{17}_8\text{O}$  and  $^{18}_8\text{O}$  ).

## ISOBARS

Isobars are the atoms with same mass number but different atomic number. E.g.:  $^{14}_6\text{C}$  and  $^{14}_7\text{N}$ .

## **FAILURE OF RUTHERFORD MODEL & DUAL NATURE OF ELECTRON**

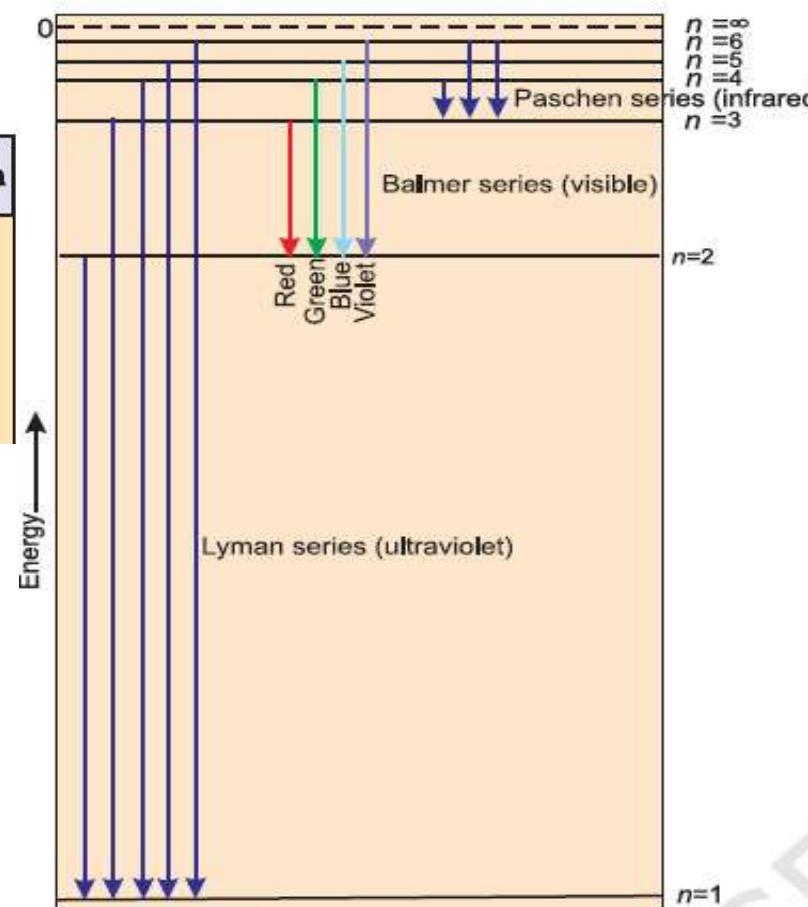
Rutherford model cannot explain the stability of an atom. According to the electromagnetic theory of Maxwell, when charged particles accelerated should emit electromagnetic radiation. Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will continue to shrink. But this does not happen. It also did not say anything about distribution of the electrons around the nucleus and the energies of these electrons.

Neils Bohr improved the model proposed by Rutherford and it has two developments which played a major role in the formulation of Bohr's model of atom. They are:

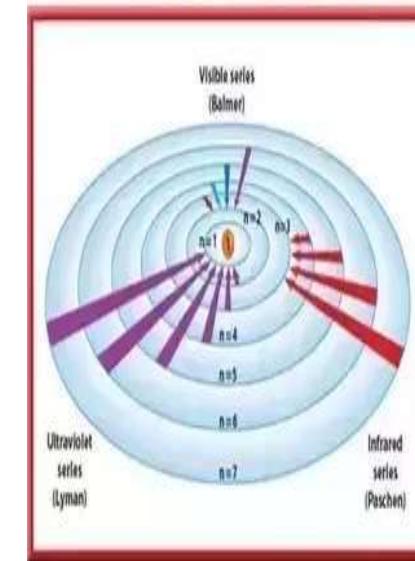
1. According to Max Planck and Albert Einstein theory, "electromagnetic radiation possess dual character both wave and particle like properties". The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

2. Experimental results regarding atomic spectra. When an electric discharge is passed through a sample of H<sub>2</sub> molecules, it dissociate into atoms. The electron in a particular excited H atom may be promoted to one of the high energy levels. These states are transient and the electron falls back to a lower energy state, emitting energy. The stationary states for electron are numbered  $n = 1, 2, 3, \dots$ . These integral numbers are known as Principal quantum numbers.

Series	$n_1$	$n_2$	Spectral Region
Lyman	1	2,3,...	Ultraviolet
Balmer	2	3,4,...	Visible
Paschen	3	4,5,...	Infrared
Brackett	4	5,6,...	Infrared



### Bohr's Atomic Model of Hydrogen



- Bohr - electrons exist in energy levels AND defined orbits around the nucleus.
- Each orbit corresponds to a different energy level.
- The further out the orbit, the higher the energy level

Bohr was awarded the Nobel Prize in Physics in 1922.

## **LIMITATIONS OF BOHR'S MODEL**

Bohr's atomic model explains the stability and line spectra of hydrogen atom.

But It fails to account for the finer details doublet using spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons.

Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

It could not explain the ability of atoms to form molecules by chemical bonds.

One need a better theory which can explain the salient features of the structure of complex atoms. Many attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of new atomic model were :

- ❖ De Broglie dual behaviour of matter
- ❖ Heisenberg uncertainty principle

## **DE BROGLIE DUAL BEHAVIOUR OF MATTER**

In 1924, Louis de Broglie argued that if light were composed of particles and yet showed wave-like properties, the same should be true of electrons and other particles. This phenomenon is referred to as **wave-particle duality**. The de Broglie relationship combines the concepts of classical mechanics with the idea of wave-like properties by showing that a particle with momentum  $mv$  associated the wave of wavelength  $\lambda$ .

$$\lambda = h/mv \text{ where } h \text{ is the Planck constant}$$

( $m$  = mass and  $v$  = velocity of the particle)



*Louis de Broglie was awarded the Nobel Prize in Physics in 1929.*

# THE UNCERTAINTY PRINCIPLE

If an electron has wave-like properties, it becomes impossible to know exactly both the momentum and position of the electron at the same time. This is a statement of Heisenberg's uncertainty principle. In order to solve this problem, it has been used the probability of finding the electron in a given volume of space  $\psi^2$ .

The probability of finding an electron at a given point in space is determined from the function  $\psi^2$ ;  $\psi$  is the wave function.



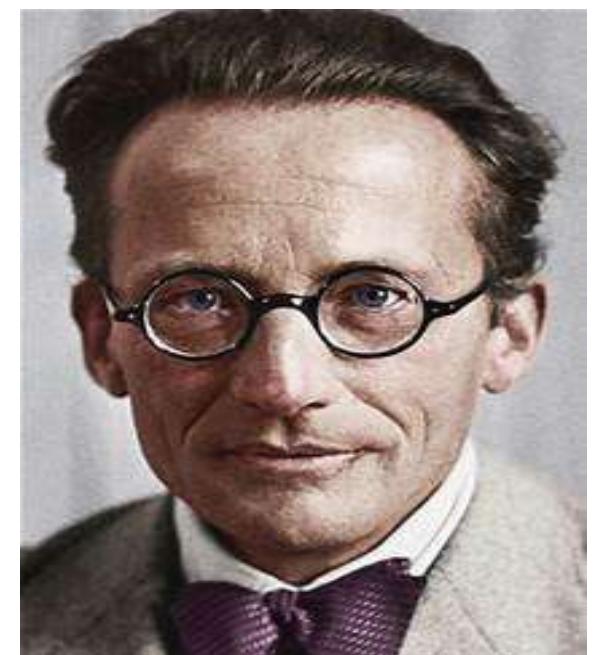
*Heisenberg was awarded the Nobel Prize in Physics in 1932.*

## SCHRÖDINGER WAVE EQUATION

Heisenberg & Louis de Broglie dual behaviour of electron, an Austrian physicist Erwin Schrödinger developed his legendary equation by making the use of wave-particle duality and classical wave equation. [Schrödinger wave equation](#) is a mathematical expression describing the energy and position of the electron in space and time, taking into account wave nature of the electron inside an atom.

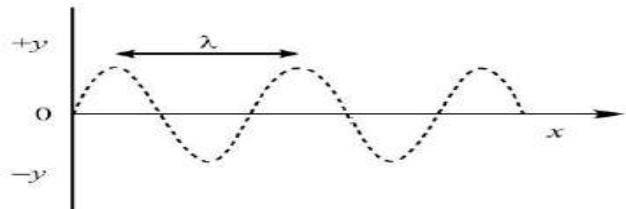
$$\begin{aligned}\widehat{H}\psi &= E\psi \\ \widehat{H} &= -\frac{\hbar^2}{8\pi^2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \\ \left[\frac{-\hbar^2}{8\pi^2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi &= E\psi \\ \frac{-\hbar^2}{8\pi^2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi &= E\psi \\ \frac{-\hbar^2}{8\pi^2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi - E\psi &= 0 \\ \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{\hbar^2}(E - V)\psi &= 0\end{aligned}$$

*Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933*



## SCHRÖDINGER WAVE EQUATION: ONE DIMENTIONAL BOX

The Schrödinger wave equation may be represented in several forms, in order to understand the concept involved, consider a wave traveling in a string along the  $x$ -axis with velocity  $v$  and it examines its application to the motion of a particle in a one-dimensional box gives the form of the Schrödinger wave equation that is appropriate for motion in the  $x$  direction:



The wave motion in a string.

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

where  $m$  = mass,  $E$  = total energy and  $V$  = potential energy of the particle.

Now let us rewrite the Schrödinger equation for the specific case of the particle in the one-dimensional box where  $V = 0$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m E}{h^2}\psi \quad \frac{d^2\psi}{dx^2} = -k^2\psi \quad \text{where } k^2 = \frac{8\pi^2 m E}{h^2}$$

## SCHRÖDINGER WAVE EQUATION: PARTICLE IN BOX

$\psi = A \sin kx + B \cos kx$ . where A and B are constants. When  $x = 0$ ,  $\sin kx = 0$  &  $\cos kx = 1$ ; hence,  $\psi = B$  when  $x = 0$ . However, the boundary condition stated that  $\psi = 0$  when  $x = 0$ , and this is only true if  $B = 0$ .

Rewriting the above equation:  $\psi = A \sin kx$ ;  $\psi = 0$ .

Since the probability,  $\psi^2$ , that the particle will be at points between  $x = 0$  and  $x = a$ ; a cannot be zero. The particle must be somewhere inside the box, the last equation is only valid if:  $Ka = n\pi$ ; where  $n = 1, 2, 3 \dots$ ; n cannot be zero as this would make the probability,  $\psi^2$ , zero meaning that the particle would no longer be in the box. Combining the last two equations gives:

$$\psi = A \sin \frac{n\pi x}{a}$$

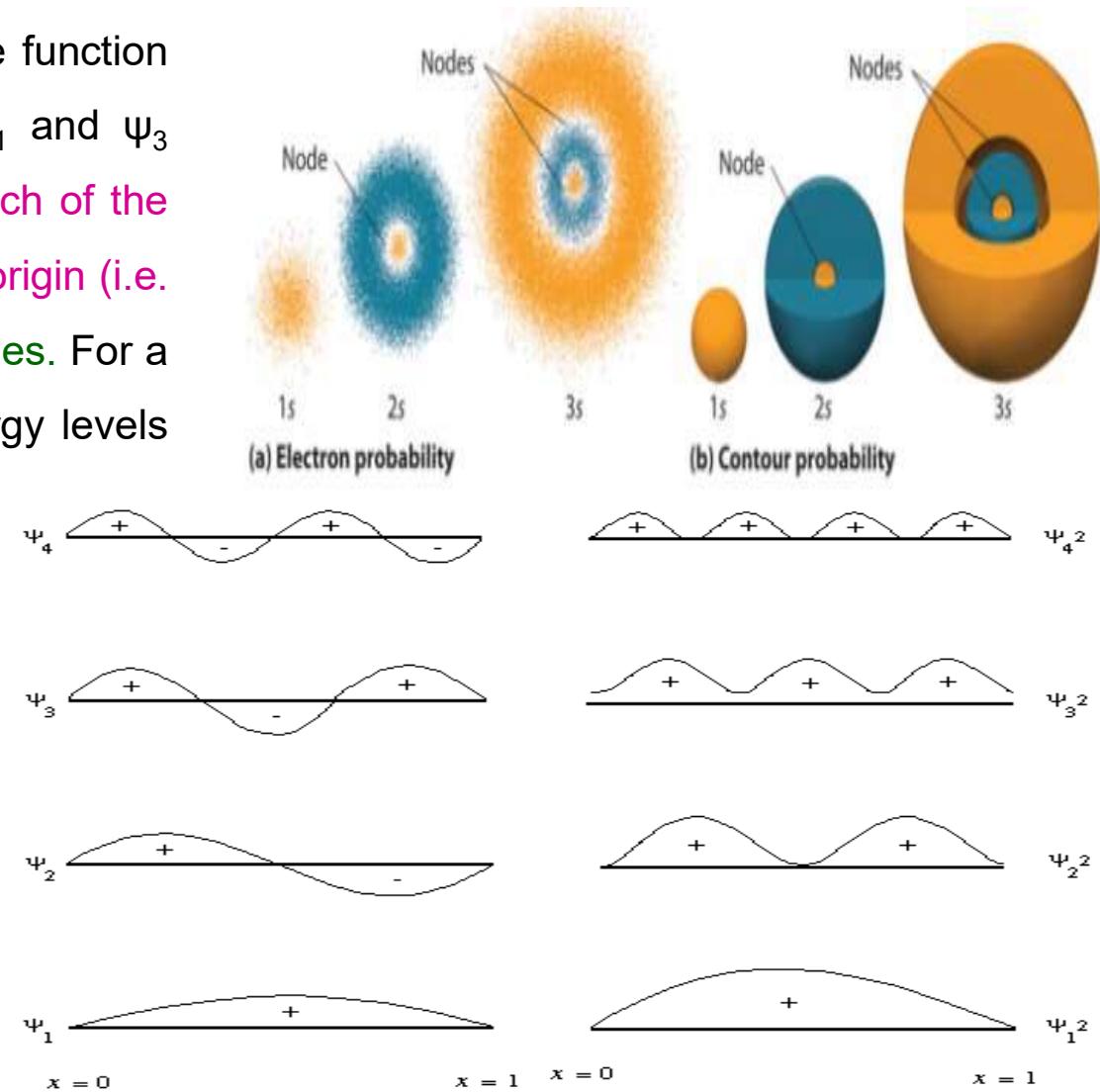
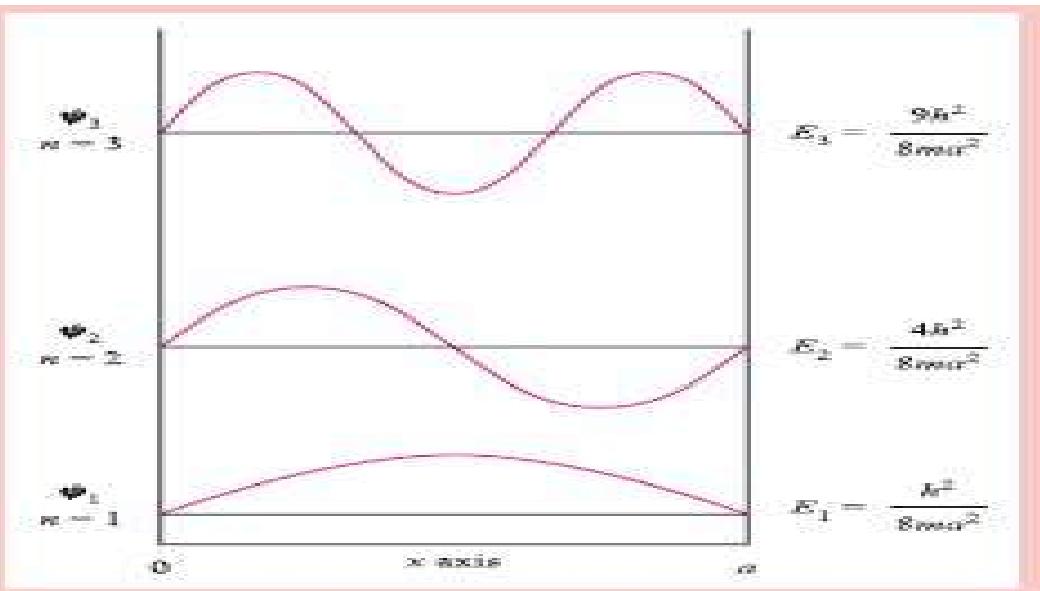
$$k^2 = \frac{8\pi^2 m E}{h^2}$$

$$E = \frac{k^2 h^2}{8\pi^2 m} = \frac{n^2 h^2}{8ma^2}$$

where  $n = 1, 2, 3 \dots$ ; n is the quantum number determining the energy of a particle of mass m confined within an one dimensional box of width a. So, the limitations placed on the value of  $\psi$  have led to quantized energy levels, the spacing of which is determined by m and a.

# PLOTS OF WAVE FUNCTIONS

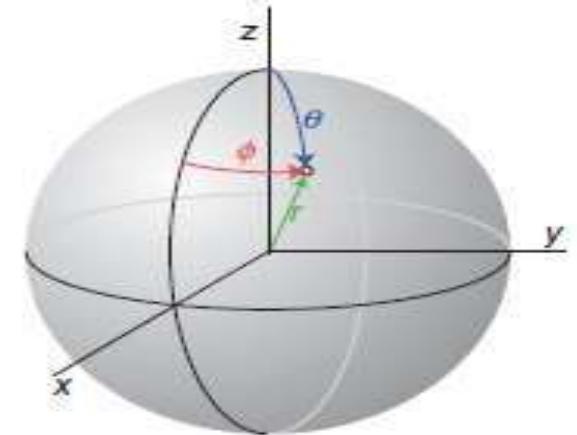
The resultant motion of the particle is described by wave function  $\psi_2$  has a wavelength of  $a$ , while wave functions  $\psi_1$  and  $\psi_3$  possess wavelengths of  $a/2$  and  $2a/3$  respectively. Each of the waves in the diagram has an amplitude of zero at the origin (i.e. at the point  $a = 0$ ); points at which  $\psi = 0$  are called nodes. For a given particle of mass  $m$ , the separations of the energy levels vary according to  $n^2$ , i.e. the spacing's are not equal.



# SOLUTION OF SCHRÖDINGER EQUATION & SPATIAL VARIATIONS

Solving the wave equation, gives the conclusion of,

- The wave function is a solution of the Schrödinger equation and describes the behaviour of an electron in a region of space called the atomic orbital.
- We can find energy values that are associated with particular wave functions.
- The quantization of energy levels arises naturally from the Schrödinger equation
- A wave function  $\psi$  is a mathematical function that contains detailed information about the behaviour of an electron.
- An atomic wave function  $\psi$  consists of a radial component,  $R(r)$ , and an angular component,  $A(\theta, \phi)$ . The region of space defined by a wave function is called an atomic orbital.



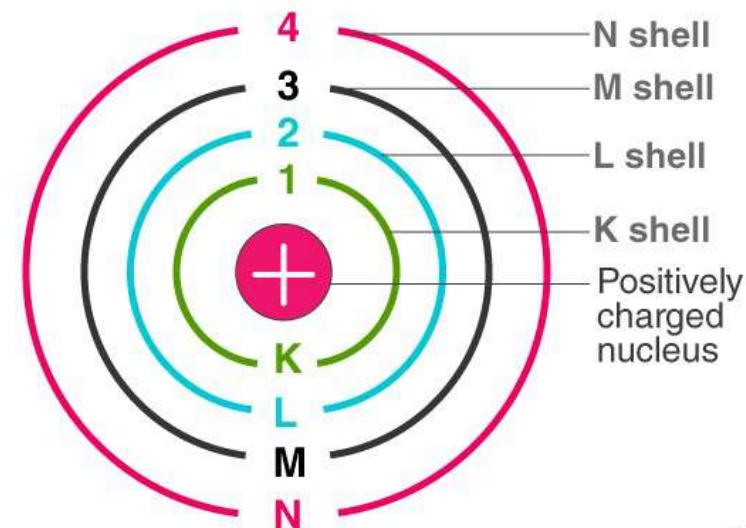
**Figure 1.7** Spherical polar coordinates:  $r$  is the radius,  $\theta$  (theta) the colatitude, and  $\phi$  (phi) the azimuth.

# FORMS OF HYDROGEN ATOM WAVE FUNCTION

## ATOMIC ORBITALS AND QUANTUM NUMBERS PRINCIPAL QUANTUM NUMBER

An atomic orbital is usually described in terms of three integral quantum numbers  $n$ ,  $l$  and  $m_l$ . The principal quantum number,  $n$ , already encountered in the Bohr model of the hydrogen atom. The principal quantum number is a positive integer with values lying between the limits  $1 \leq n \leq \infty$ ; The principal quantum number determines the size and to large extent the energy of the orbital. The principal quantum number also identifies the shell and are represented by the following letters.

$n =$	1	2	3	4	.....
Shell =	K	L	M	N	.....



# **ORBITAL QUANTUM NUMBER [(AZIMUTHAL QUANTUM NUMBER (m)]**

Two more quantum numbers,  $l$  and  $m_l$ , appear when the angular part of the wave function is solved. The quantum number  $l$  is called the orbital quantum number (Azimuthal quantum number) and has allowed values of 0, 1, 2 . . . ( $n-1$ ). The value of  $l$  determines the shape and symmetries of the atomic orbital, and the orbital angular momentum of the electron. Atomic orbital most commonly encountered as s, p, d and f of these four types of orbitals. Each shell consists of one or more subshells or sub-levels. The number of sub-shells in a principal shell is equal to the value of  $n$ .

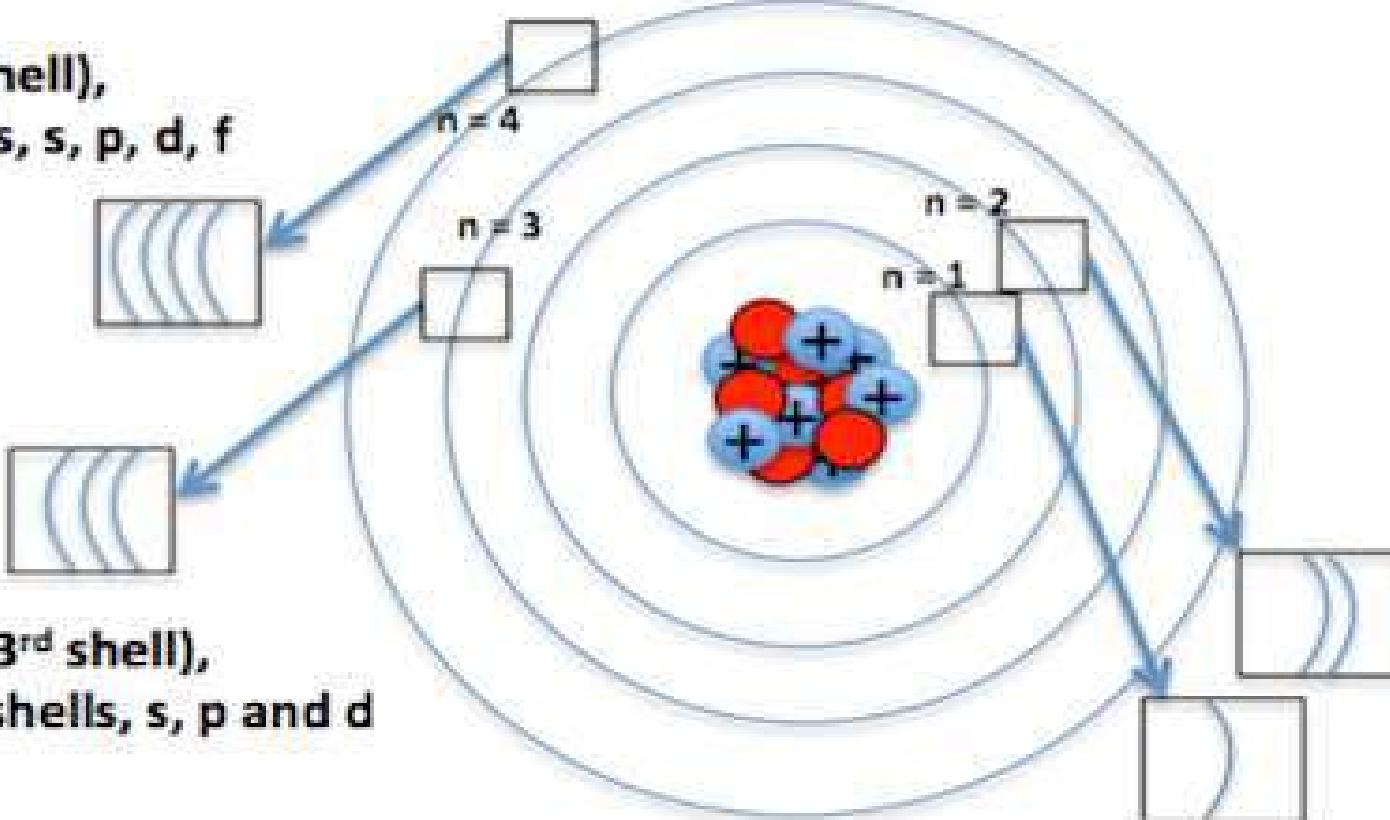
For example in the first shell ( $n = 1$ ), there is only one sub-shell which corresponds to  $l = 0$ .

There are two sub-shells ( $l = 0, 1$ ) in the second shell ( $n = 2$ ).

Three ( $l = 0, 1, 2$ ) in third shell ( $n = 3$ ) and so on.

Value for $l$ :	0	1	2	3	4	5	.....
notation for	s	p	d	f	g	h	.....
sub-shell							

$n = 4$  (4<sup>th</sup> shell),  
3 subshells, s, p, d, f



$n = 3$  (3<sup>rd</sup> shell),  
3 subshells, s, p and d

$n = 2$  (2<sup>nd</sup> shell),  
2 subshells, s and p

$n = 1$  (1<sup>st</sup> shell),  
1 subshell, s

## Shells and Subshells

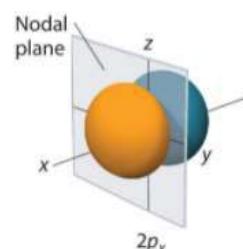
# MAGNETIC ORBITAL QUANTUM NUMBER ( $m_l$ )

Magnetic orbital quantum number ' $m$ ' gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. It gives the information about the directionality of an atomic orbital and has integral values between  $+l$  and  $-l$ . For any sub-shell (defined by ' $l$ ' value)  $2l+1$  values of  $m_l$  are possible. An orbital described by the quantum numbers  $n = 2$ ,  $l = 1$ ,  $m_l = 3$  is an orbital in the  $p$  sub-shell of the second shell. The following chart gives the relation between the subshell and the number of orbitals associated with it.

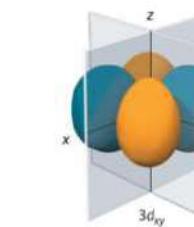
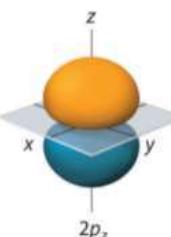
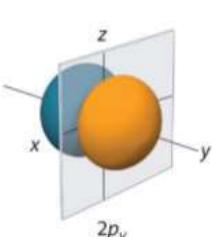
Value of $l$	0	1	2	3	4	5
Subshell notation	$s$	$p$	$d$	$f$	$g$	$h$
number of orbitals	1	3	5	7	9	11



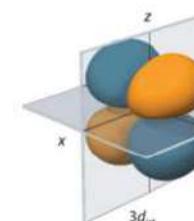
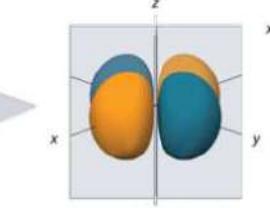
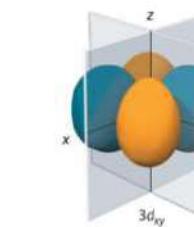
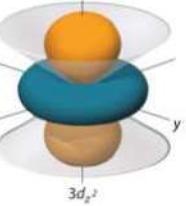
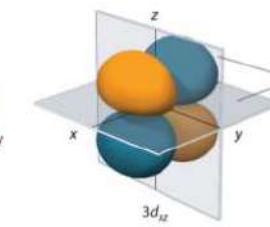
**s - Orbitals**



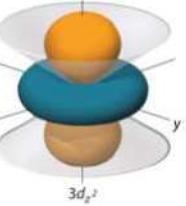
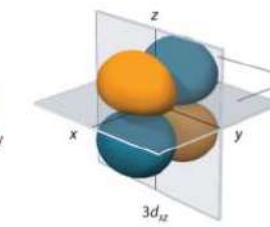
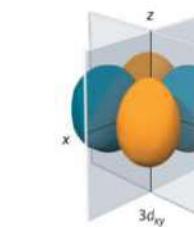
**$p$  - Orbitals**



**$d$  - Orbitals**

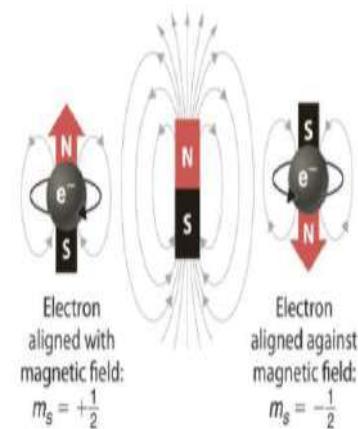


**$d$  - Orbitals**

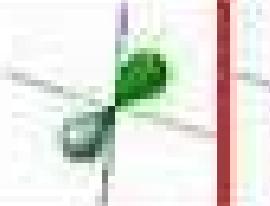
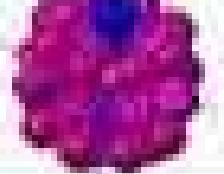


## ELECTRON SPIN QUANTUM NUMBER ( $m_s$ )-

In 1925, George Uhlenbeck and Samuel Goudsmit proposed the fourth quantum number known as the electron spin quantum number ( $m_s$ ). An electron spins around its own axis and it has the spin angular momentum, which is a vector quantity, will have two orientations relative to the axis. These two orientations are distinguished by the spin quantum numbers  $m_s$  which can take the values of  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . An orbital cannot hold more than two electrons and these two electrons should have opposite spins.



## SHAPE OF s, p, d, f ORBITALS

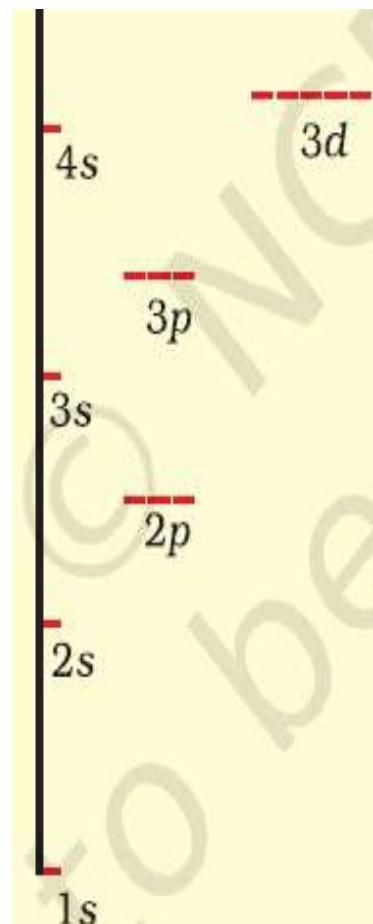
SET	INDIVIDUAL ORBITALS				COLLECTIVE
s					
p					
d					
f					

## ENERGIES OF s, p, d, f ORBITALS

The energy of an electron in a hydrogen atom determined by the principal quantum number. Thus the energy of the orbitals in hydrogen atom increases as follows :  $1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$ .

In a multi-electron atom, orbitals with the same value of  $n$  but different values of  $l$ , the sub-shells are not degenerate. It follows  $(n+l)$  rule.

The  $(n+l)$  rule says that the lower the value of  $(n + l)$  for an orbital, the lower is its energy. If two orbitals have the same value of  $(n + l)$ , the orbital with lower value of  $n$  will have the lower energy



Orbital	Value of $n$	Value of $l$	Value of $(n + l)$	
<b>1s</b>	1	0	$1 + 0 = 1$	
<b>2s</b>	2	0	$2 + 0 = 2$	
<b>2p</b>	2	1	$2 + 1 = 3$	$2p \text{ } (n=2)$ has lower energy than
<b>3s</b>	3	0	$3 + 0 = 3$	$3s \text{ } (n=3)$
<b>3p</b>	3	1	$3 + 1 = 4$	$3p \text{ } (n=3)$ has lower energy than
<b>4s</b>	4	0	$4 + 0 = 4$	$4s \text{ } (n=4)$
<b>3d</b>	3	2	$3 + 2 = 5$	$3d \text{ } (n=3)$ has lower energy than
<b>4p</b>	4	1	$4 + 1 = 5$	$4p \text{ } (n=4)$

Arrangement of Orbitals with Increasing Energy on the Basis of  $(n+l)$  Rule

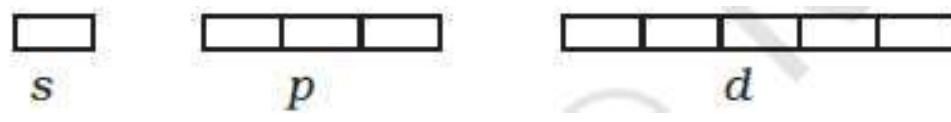
# ELECTRONIC CONFIGURATION OF ATOMS

Every element is different. The number of protons determines the identity of the element. The number of electrons determines the charge. All chemistry is done at the electronic level i.e., electrons are very important.

Electronic configuration is the arrangement of electrons in an atom.

These electrons fill in the atomic orbitals.

The electronic configuration of different atoms can be represented as mention below as box. Each orbital of the subshell is represented by a box and the electron is represented by an arrow ( $\uparrow$ ) a positive spin or an arrow ( $\downarrow$ ) a negative spin.



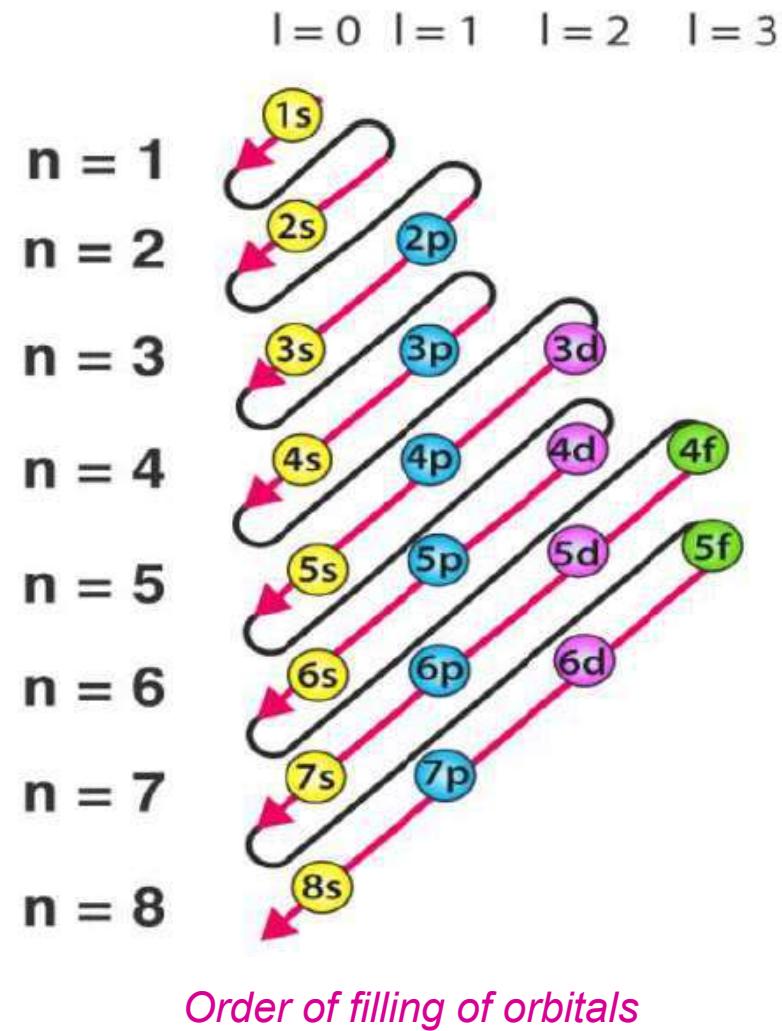
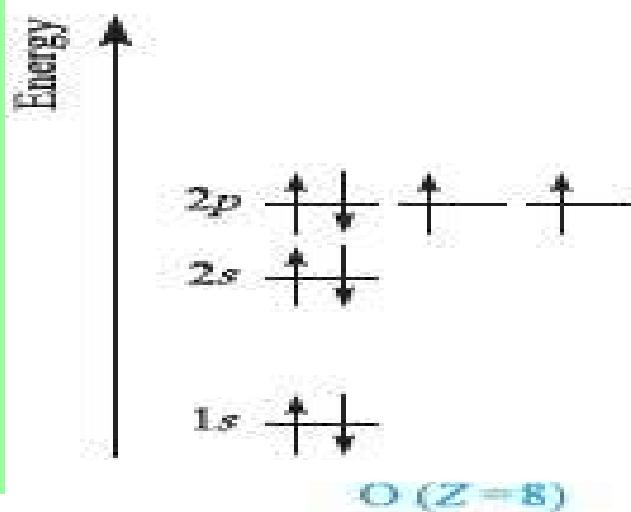
Orbital diagram

- H = 1s<sup>1</sup>
- He = 1s<sup>2</sup>
- Li = 1s<sup>2</sup> 2s<sup>1</sup>
- Be = 1s<sup>2</sup> 2s<sup>2</sup>
- B = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>1</sup>
- C = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>
- N = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>
- O = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>
- F = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>
- Ne = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup>

## FILLING OF ORBITALS: AUFBAU PRINCIPLE

The filling of electrons into the orbitals of different atoms takes place according to the *aufbau* principle which is based on the Hund's rule of maximum multiplicity, the Pauli's exclusion principle, and the relative energies of the orbitals. The word '*aufbau*' in German means 'building up'.

Orbitals are filled in order of energy, the lowest energy orbitals being filled first.

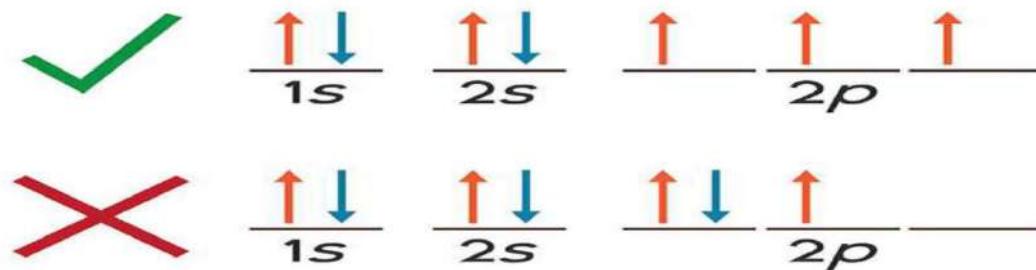


## FILLING OF ORBITALS: *HUND'S RULE*

This rule deals with filling of electrons in the orbitals belonging to the same subshell of the equal energy called as degenerate orbitals.

Pairing of electrons in a set of degenerate orbitals does not take place until each orbital in the set contains one electron i.e., it is singly occupied because orbitals in a degenerate set have parallel spins, i.e. they have the same values of  $m_s$ .

Within a sublevel, place one electron per orbital before paring them.  
Its like Empty Bus Seat rule.



Robert S. Mulliken, who was awarded the 1966 Nobel Prize in chemistry he would have gladly shared the Nobel prize with Hund

## **FILLING OF ORBITALS: PAULI EXCLUSION PRINCIPLE**

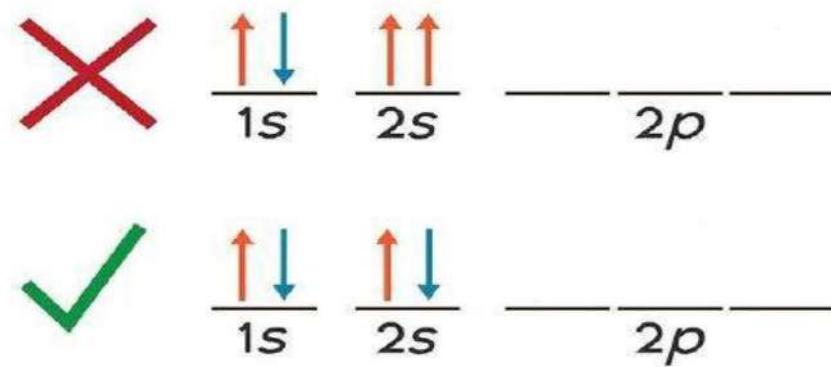
No two electrons in an atom may have the same set of four quantum numbers ( $n$ ,  $l$ ,  $m_l$  and  $m_s$ ). It follows that each orbital can accommodate a maximum of two electrons with different  $m_s$  values (different spins-spun-paired). The maximum number of electrons in the shell with principal quantum number  $n$  is equal to  $2n^2$ .

n =	1	2	3	4	.....
Shell =	K	L	M	N	.....

For K shell n = 1,  $2(1)^2 = 2(1) = 2$

For L shell  $n = 2$ ,  $2(2)^2 = 2(4) = 8$

For M shell  $n = 3$ ,  $2(3)^2 = 2(9) = 18$



Pauli won Nobel Prize in Physics 1945

# EFFECTIVE NUCLEAR CHARGE

Shielding of the outer shell electrons from the nucleus decreases by the inner shell electrons, and the net positive charge experienced by the outer electrons is known as effective nuclear charge ( $Z_{\text{eff}}$  e). Energies of the orbitals in the same subshell decrease with increase in the atomic number ( $Z_{\text{eff}}$ ).

## Slater's rules

Effective nuclear charges,  $Z_{\text{eff}}$ , experienced by electrons in different atomic orbitals may be estimated using Slater's rules. It is based on experimental data for electron promotion and ionization energies.

$$Z_{\text{eff}} = Z - S, \text{ where } Z = \text{nuclear charge, } S = \text{screening (or shielding) constant.}$$

1. The electronic configuration of the element write in the order of groupings: (1s), (2s, 2p), (3s, 3p), (3d ), (4s, 4p), (4d ), (4f ), (5s, 5p). Electrons in any group higher in the sequence contribute less of S.
2. Consider a particular electron in an ns or np orbital:
  - Each of the other electrons in the (ns, np) group contributes  $S = 0.35$ .
  - Each of the electrons in the (n-1) shell contributes  $S = 0.85$ .
  - Each of the electrons in the (n-2) or lower shells contributes  $S = 1.00$ .

# ELECTRONIC CONFIGURATION OF ELEMENTS

The distribution of electrons into orbitals of an atom is called its electronic configuration. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily. The electronic configuration of different atoms can be represented as mention below as box. each orbital of the subshell is represented by a box and the electron is represented by an arrow ( $\uparrow$ ) a positive spin or an arrow ( $\downarrow$ ) a negative spin.

• H = 1s <sup>1</sup>
• He = 1s <sup>2</sup>
• Li = 1s <sup>2</sup> 2s <sup>1</sup>
• Be = 1s <sup>2</sup> 2s <sup>2</sup>
• B = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>
• C = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>
• N = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
• O = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>
• F = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>
• Ne = 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>

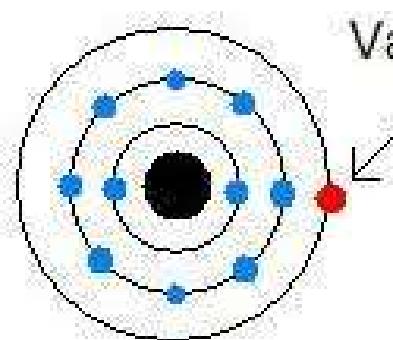
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# VALENCE AND CORE ELECTRONS

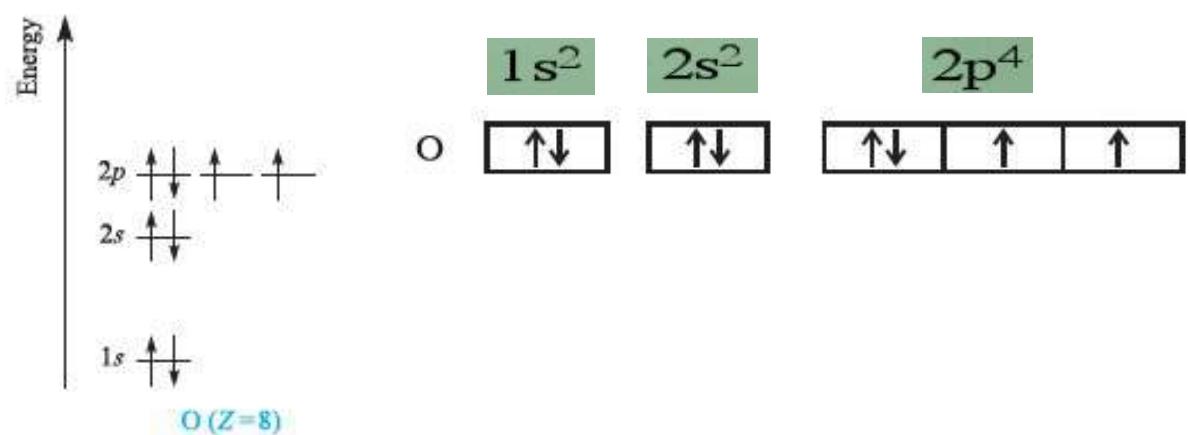
The configuration of the outer or valence electrons is of particular significance. These electrons determine the chemical properties of an element. Electrons that occupy lower energy quantum levels are called core electrons.

The core electrons shield the valence electrons from the nuclear charge, resulting in the valence electrons experiencing only the effective nuclear charge,  $Z_{\text{eff}}$ .

For an element of low atomic number, the core and valence electrons are readily recognized by looking at the ground state electronic configuration. That of oxygen is  $1s^22s^22p^4$ . The core electrons of oxygen are those in the  $1s$  atomic orbital; the six electrons with  $n = 2$  are the valence electrons.



Rest are core electrons.



# Periodic table of the elements

period	group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1*	H																He	
2	1		Li	Be														Ne	
3	2	Na	Mg																
4	3	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	B	C	N	O	F
5	4	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Si	P	S	Cl	Ne
6	5	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Sn	Sb	Te	I	Br	Kr
7	6	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
lanthanoid series		58	59	60	61	62	63	64	65	66	67	68	69	70	71				
actinoid series		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
		90	91	92	93	94	95	96	97	98	99	100	101	102	103				
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

\*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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# **CHEMICAL BONDING AND MOLECULAR STRUCTURE**

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule.

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 atoms of various elements in different ways, it raises many questions.

- Why do atoms combine?
- Why are only certain combinations possible?
- Why do some atoms combine while certain others do not?
- Why do molecules possess definite shapes?

# **CHEMICAL BONDING AND THEORY**

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

The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table.

Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

- ❖ Kössel-Lewis Approach,
- ❖ Valence Shell Electron Pair Repulsion (VSEPR) Theory,
- ❖ Valence Bond (VB) Theory
- ❖ Molecular Orbital (MO) Theory
- ❖ Crystal Field Theory

## KÖSSEL-LEWIS APPROACH

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus and the inner electrons) and the outer shell that could accommodate a maximum of eight electrons.

*Lewis Symbols:* In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. G.N. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols. For example, the Lewis symbols for the elements of second period are as under:

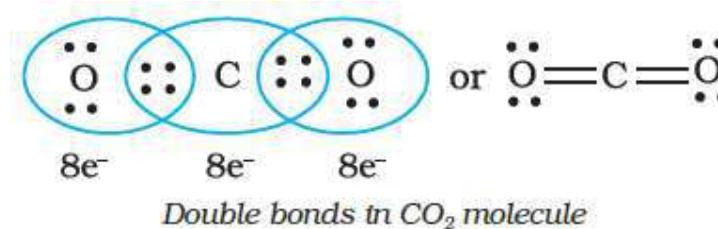
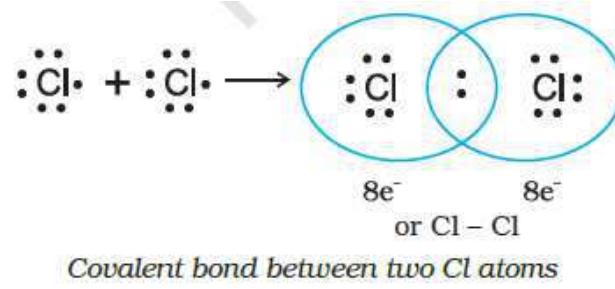


The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond. The electrovalence is thus equal to the number of unit charge on the ion.

**Octet Rule:** Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule.

# OCTECT RULE

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term covalent bond. According to this theory, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.



# Formal Charge

Formal charge (F.C.)on an atom in a Lewis Structure = total number of valence electrons in the free atom — total number of non bonding (lone pair) Electrons — (1/2) total number of bonding(shared) electrons

Molecule/Ion	Lewis Representation
H <sub>2</sub>	H : H*
O <sub>2</sub>	:O:O:
O <sub>3</sub>	O <sup>+</sup>   O <sub>-</sub> : O <sub>-</sub>
NF <sub>3</sub>	:F: N: F: :F: :F:
CO <sub>3</sub> <sup>2-</sup>	$\left[ \begin{array}{c} \vdots & \vdots \\ \text{:O:} & \text{C} & \text{:O:} \\ \vdots & \vdots \end{array} \right]^{2-}$
HNO <sub>3</sub>	O <sup>+</sup> : N : O : H :O: :O:

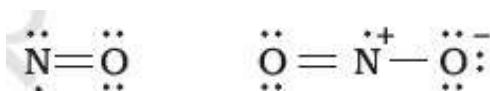
## The Lewis Representation

# LIMITATIONS OF THE OCTET RULE

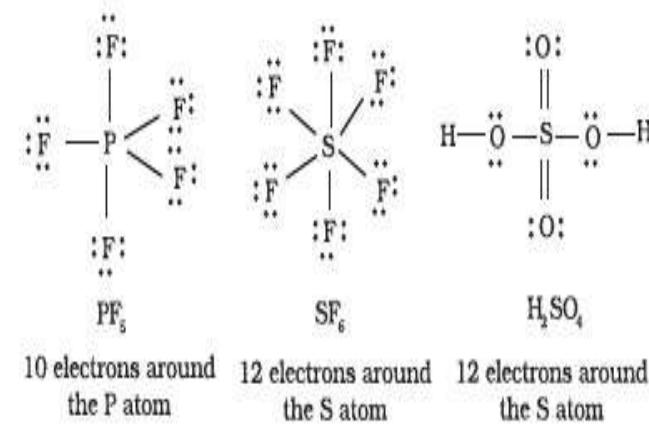
The octet rule, though useful, is not universal. It is useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

***The incomplete octet of the central atom:*** In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Ex: LiCl, BeH<sub>2</sub> and BCl<sub>3</sub>.

***Odd-electron molecules:*** In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO<sub>2</sub>, the octet rule is not satisfied for all the atoms.



***The expanded octet:*** Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Ex: PF<sub>5</sub>, SF<sub>6</sub>, H<sub>2</sub>SO<sub>4</sub> and (d-block elements) coordination compounds.



## **OTHER DRAWBACKS OF THE OCTET THEORY**

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like  $\text{XeF}_2$ ,  $\text{KrF}_2$ ,  $\text{XeOF}_2$  etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

## **IONIC OR ELECTROVALENT BOND**

The ionic bonds will be formed more easily between elements having low ionization enthalpies and elements having high electron gain enthalpy. The qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state.

**Lattice Enthalpy:** The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. lattice enthalpy plays a key role in the formation of ionic compounds.

## BOND PARAMETERS

**Bond length:** It is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques. The covalent radius is measured as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule.

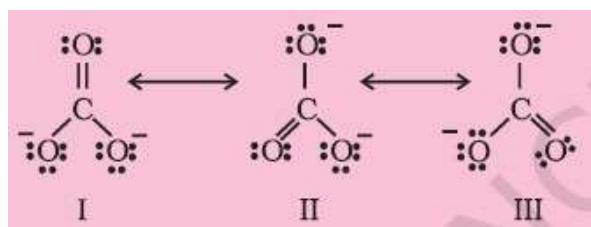
**Bond Angle:** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.

**Bond Enthalpy:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

**Bond Order:** In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. Isoelectronic molecules and ions have identical bond orders; for example,  $F_2$  and  $O_2^{2-}$  have bond order 1 and  $N_2$ ,  $CO$  and  $NO^+$  have bond order 3.

A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases.

**Resonance Structures:** Whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure and resonance averages the bond characteristics as a whole.



**Polarity of Bonds:** The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character. In case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond. The molecule possesses the dipole moment which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge.

## FAJANS RULE

All the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character.

The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules:

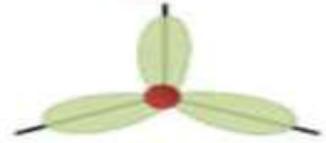
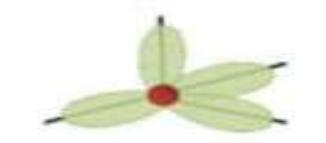
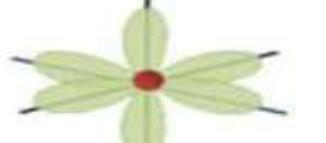
- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration of transition metals, is more polarising than the one with a noble gas configuration,  $ns^2\ np^6$ , typical of alkali and alkaline earth metal cations. The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond.

# **VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY**

VSEPR theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957). The main postulates of VSEPR theory are as follows:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

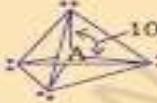
VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

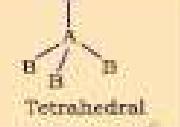
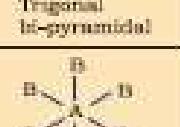
Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 Lone Pair	2 Lone Pairs	3 Lone Pairs	4 Lone Pairs
2	Linear	 Linear				
3	Trigonal planar					
4	Tetrahedral					
5	Trigonal bipyramidal					
6	Octahedral					
						

VSEPR theory divides molecules into two categories

1. Molecules in which the central atom has no lone pair and

2. Molecules in which the central atom has one or more lone pairs

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2		$B-A-B$ Linear	$BeCl_2, HgCl_2$
3		$B-A-B$ Trigonal planar	$BF_3$
4		$B-A-B$ Tetrahedral	$CH_4, NH_4^+$
5		$B-A-B$ Trigonal bipyramidal	$PCl_5$
6		$B-A-B$ Octahedral	$SF_6$

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
$AB_3E$	2	1		Bent	$SO_3$
$AB_3E$	3	1		Trigonal pyramidal	$NH_3$
$AB_3E_2$	2	2		Bent	$H_2O$
$AB_3E$	4	1		See saw	$SF_4$
$AB_3E_2$	3	2		T-shape	$ClF_3$
$AB_3E$	5	1		Square pyramidal	$BrF_3$
$AB_3E_2$	4	2		Square planar	$XeF_4$

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB <sub>2</sub> E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB <sub>3</sub> E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between ip-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
AB <sub>2</sub> E <sub>2</sub>	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB <sub>4</sub> E	4	1	(a)	See-saw	In (a) the lp is present at axial position so there are three lp-bp repulsions at 90°. In (b) the lp is in an equatorial position, and there are two lp-bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a tilted square or a see-saw.
			(b)		(More stable)

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB <sub>3</sub> E <sub>2</sub>	3	2	(a)	T-shape	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable (T-shaped).
			(b)		
			(c)		

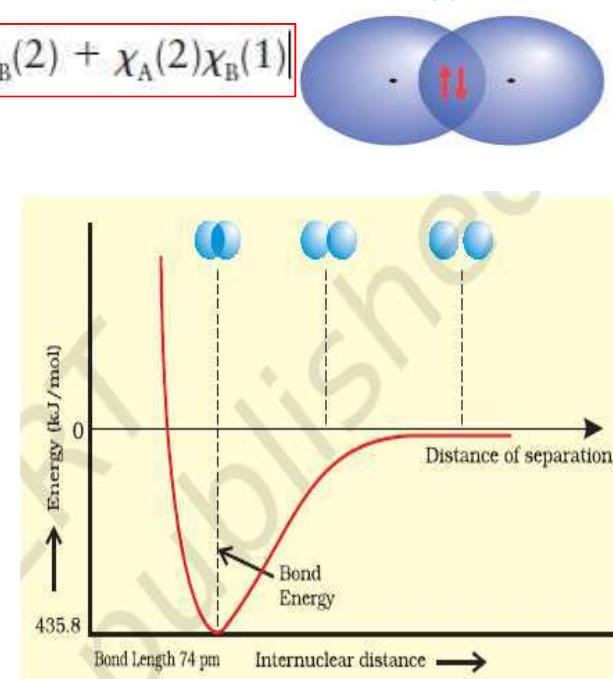
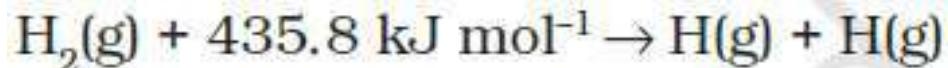
VSEPR theory gives the geometry of simple molecules theoretically, but it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

## VALENCE BOND THEORY

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. The **valence bond theory (VB theory)** of bonding was the first quantum mechanical theory of bonding to be developed. Valence bond theory considers the interaction of atomic orbitals on separate atoms as they are brought together to form a molecule. In valence bond theory, the wavefunction of an electron pair is formed by superimposing the wavefunctions for the separated fragments of the molecule; a molecular potential energy curve shows the variation of the molecular energy with internuclear separation.

$$\psi = \chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1)$$

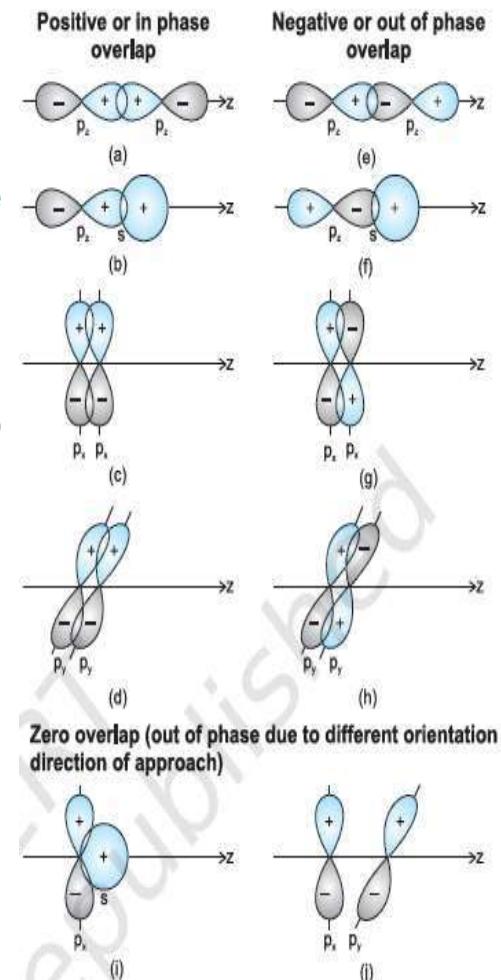
Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. Energy gets released when the bond is formed between two hydrogen atoms, that is called bond enthalpy. The hydrogen molecule is more stable than that of isolated hydrogen atoms.



## ORBITAL OVERLAP CONCEPT

Formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. According to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

**Directional Properties of Bonds:** VB theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals. When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space.



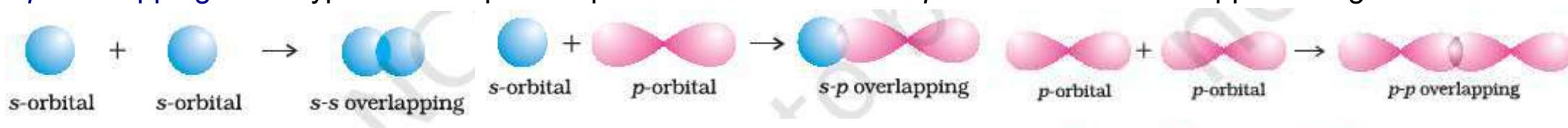
**Types of Overlapping and Nature of Covalent Bonds:** The covalent bond may be classified into two types depending upon the types of overlapping: (i) Sigma ( $\sigma$ ) bond, and (ii) pi ( $\pi$ ) bond.

**Sigma ( $\sigma$ ) bond :** This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of these types of combinations of atomic orbitals.

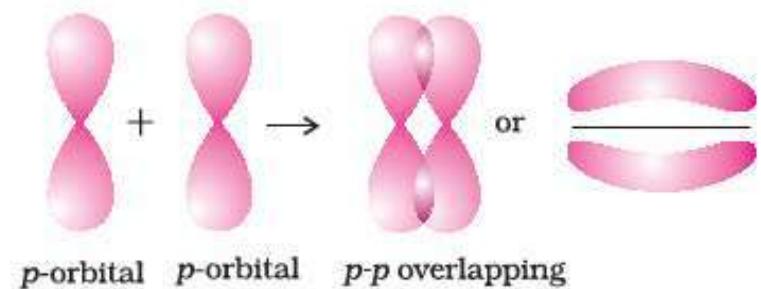
**s-s overlapping :** In this case, there is overlap of two half filled s-orbitals along the internuclear axis.

**s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.

**p-p overlapping :** This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



**pi ( $\pi$ ) bond :** In the formation of p bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



**Strength of Sigma and pi Bonds:** Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond.

## HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  etc., Pauling introduced the concept of hybridisation. The atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new  $sp_3$  hybrid orbitals.

**SALIENT FEATURES OF HYBRIDISATION:** The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

### **IMPORTANT CONDITIONS FOR HYBRIDISATION**

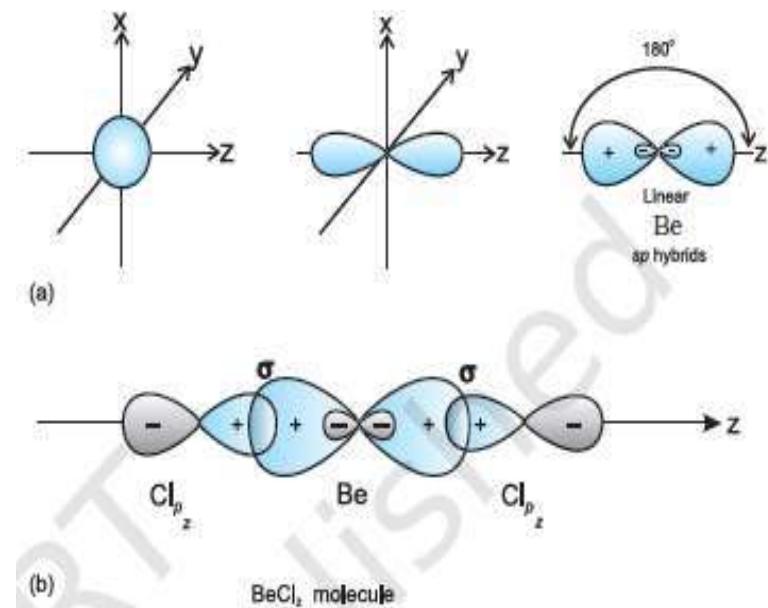
- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

## TYPES OF HYBRIDISATION

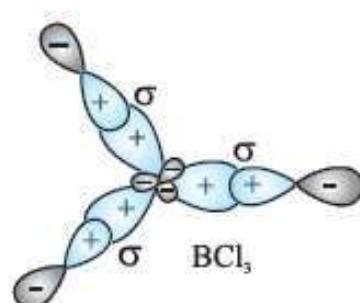
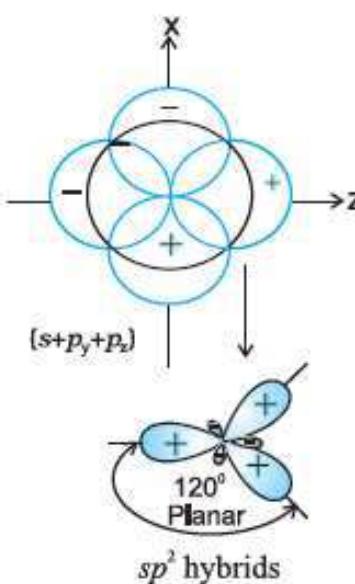
There are various types of hybridisation involving *s*, *p* and *d* orbitals. The different types of hybridisation are

(I) *sp hybridisation*: This type of hybridisation involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals. The suitable orbitals for *sp* hybridisation are *s* and *pz*, if the hybrid orbitals are to lie along the *z*-axis. Each *sp* hybrid orbital has 50% *s*-character and 50% *p*-character. Such a molecule in which the central atom is *sp*-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation. Example of molecule having *sp* hybridisation  $\text{BeCl}_2$ .

The ground state electronic configuration of Be is  $1s^22s^2$ . In the excited state one of the 2s-electrons is promoted to vacant 2*p* orbital to account for its bivalence. One 2s and one 2*p*-orbital gets hybridised to form two *sp* hybridised orbitals. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of  $180^\circ$ . Each of the *sp* hybridised orbital overlaps with the 2*p*-orbital of chlorine axially and form two Be-Cl sigma bonds.



(II)  $sp^2$  hybridisation: In this hybridisation there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridised orbitals. For example, in  $BCl_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^22s^22p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital as a result boron has three unpaired electrons. These three orbitals (one  $2s$  and two  $2p$ ) hybridise to form three  $sp^2$  hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with  $2p$  orbitals of chlorine to form three B-Cl bonds. Therefore, in  $BCl_3$ , the geometry is trigonal planar with  $Cl-Cl$  bond angle of  $120^\circ$ .



$B(1,1,-1)$

$C(-1,1,1)$

$D(-1,-1,-1)$

$A(1,-1,1)$

$\theta$

$a \cdot b = ||a|| ||b|| \cos\theta$

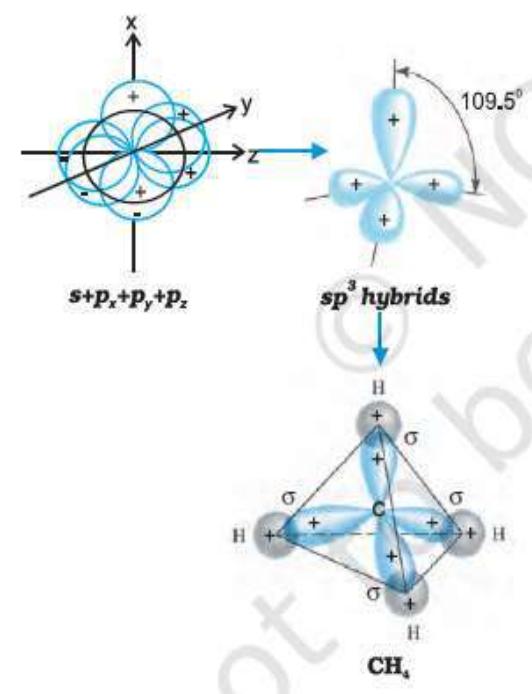
$\cos\theta = \frac{a \cdot b}{||a|| ||b||}$

$= \frac{\begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}}{\sqrt{1^2+1^2+1^2} \cdot \sqrt{1^2+1^2+1^2}}$

$= \frac{1 \times 1 + (-1) \times 1 + 1 \times (-1)}{\sqrt{3} \cdot \sqrt{3}}$

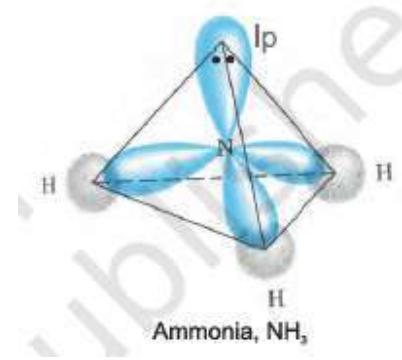
$= -\frac{1}{3}$

$\therefore \theta = \arccos\left(-\frac{1}{3}\right) \approx 109.47^\circ$

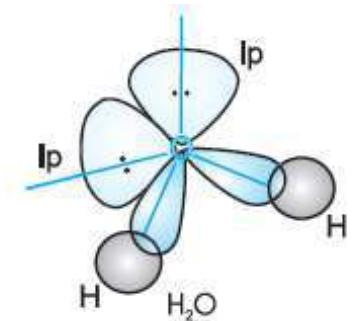


(III) *sp<sup>3</sup> hybridisation:* This type of hybridisation can be explained by taking the example of CH<sub>4</sub> molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp<sup>3</sup> hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp<sup>3</sup> hybrid orbital. The four sp<sup>3</sup> hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp<sup>3</sup> hybrid orbital is 109.5°.

The structure of NH<sub>3</sub> molecule can also be explained with the help of sp<sup>3</sup> hybridisation. The force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107° from 109.5°. The geometry of such a molecule will be pyramidal.

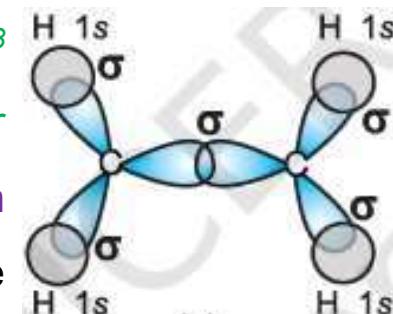


In H<sub>2</sub>O these four sp<sup>3</sup> hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° and the molecule thus acquires a V-shape or angular geometry.

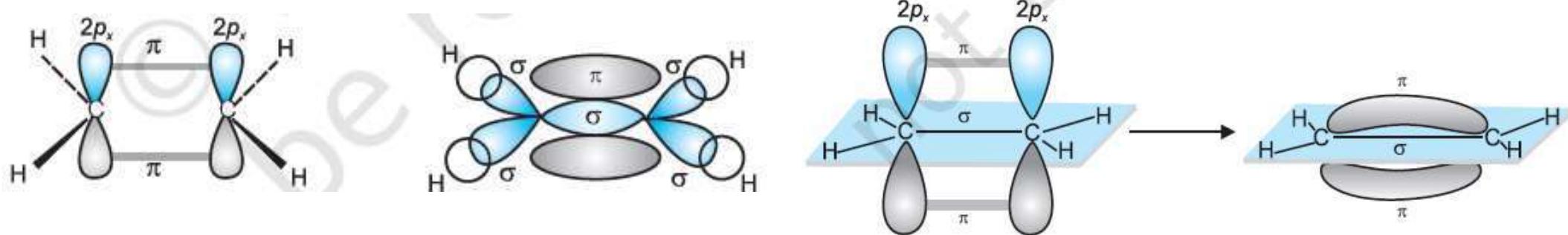


## ***sp<sup>3</sup>, sp<sup>2</sup> & sp HYBRIDISATION OF CARBON ATOM***

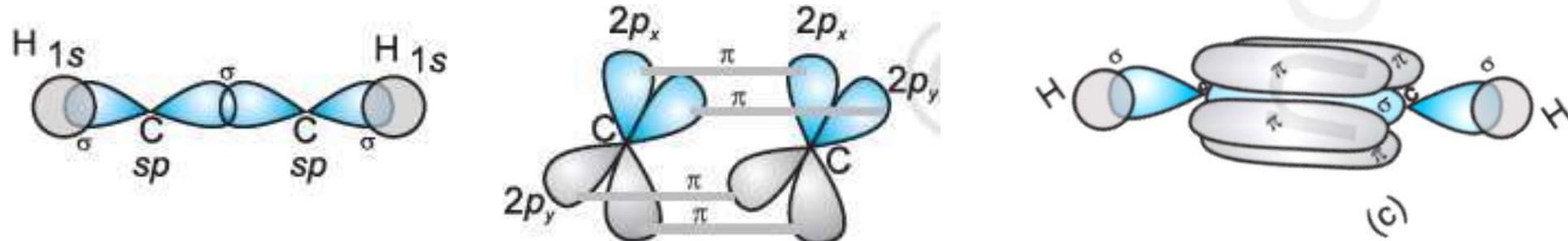
*sp<sup>3</sup> Hybridisation in C<sub>2</sub>H<sub>6</sub> molecule:* In ethane molecule both the carbon atoms assume sp<sup>3</sup> hybrid state. One of the four sp<sup>3</sup> hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp<sup>3</sup>-sp<sup>3</sup> sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp<sup>3</sup>-s sigma bonds with hydrogen atoms. Therefore in ethane C-C bond length is 154 pm and each C-H bond length is 109 pm.



*sp<sup>2</sup> Hybridisation in C<sub>2</sub>H<sub>4</sub>:* In the formation of ethene molecule, one of the sp<sup>2</sup> hybrid orbitals of carbon atom overlaps axially with sp<sup>2</sup> hybridised orbital of another carbon atom to form C-C sigma bond. While the other two sp<sup>2</sup> hybrid orbitals of each carbon atom are used for making sp<sup>2</sup>-s sigma bond with two hydrogen atoms. The unhybridised orbital (2px or 2py) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak pi bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms. Thus, in ethene molecule, the carbon-carbon bond consists of one sp<sup>2</sup>-sp<sup>2</sup> sigma bond and one pi ( $\pi$ ) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C-H bond is sp<sup>2</sup>-s sigma with bond length 108 pm. The H-C-H bond angle is 117.6° while the H-C-C angle is 121°.



**sp Hybridisation in  $C_2H_2$**  : In the formation of ethyne molecule, both the carbon atoms undergo *sp*-hybridisation having two unhybridised orbital *i.e.*,  $2p_y$  and  $2p_x$ . One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled s orbital of hydrogen atoms forming  $\sigma$  bonds. Each of the two unhybridised *p* orbitals of both the carbon atoms overlaps sidewise to form two *pi* bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two *pi* bonds.



## HYBRIDISATION OF ELEMENTS INVOLVING *d*-ORBITALS

The elements present in the third period contain *d* orbitals in addition to *s* and *p* orbitals. The energy of the  $3d$  orbitals are comparable to the energy of the  $3s$  and  $3p$  orbitals. The energy of  $3d$  orbitals are also comparable to those of  $4s$  and  $4p$  orbitals. As a consequence the hybridisation involving either  $3s$ ,  $3p$  and  $3d$  or  $3d$ ,  $4s$  and  $4p$  is possible. However, since the difference in energies of  $3p$  and  $4s$  orbitals is significant, no hybridisation involving  $3p$ ,  $3d$  and  $4s$  orbitals is possible. The important hybridisation schemes involving *s*, *p* and *d* orbitals are summarised below:

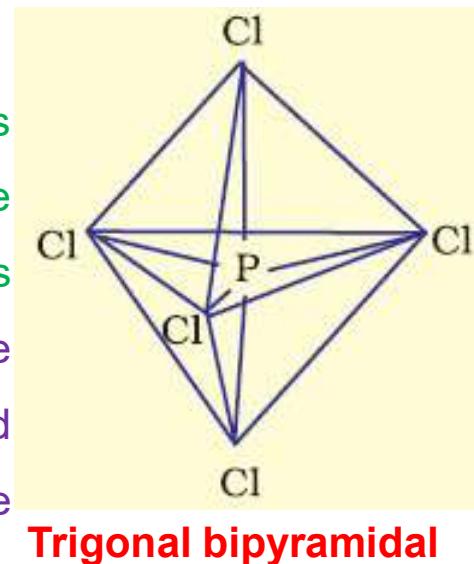
<b>Shape of molecules/ ions</b>	<b>Hybridisation type</b>	<b>Atomic orbitals</b>	<b>Examples</b>
Square planar	$dsp^2$	$d+s+p(2)$	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{Cl})_6]^{2-}$
Trigonal bipyramidal	$sp^3d$	$s+p(3)+d$	$\text{PF}_5$ , $\text{PCl}_5$
Square pyramidal	$sp^3d^2$	$s+p(3)+d(2)$	$\text{BrF}_5$
Octahedral	$sp^3d^2$ $d^2sp^3$	$s+p(3)+d(2)$ $d(2)+s+p(3)$	$\text{SF}_6$ , $[\text{CrF}_6]^{3-}$ , $[\text{Co}(\text{NH}_3)_6]^{3+}$

**Formation of  $\text{PCl}_5$  ( $sp^3d$  hybridisation):** The ground state and the excited state outer electronic configurations of phosphorus ( $Z=15$ ) are represented below.

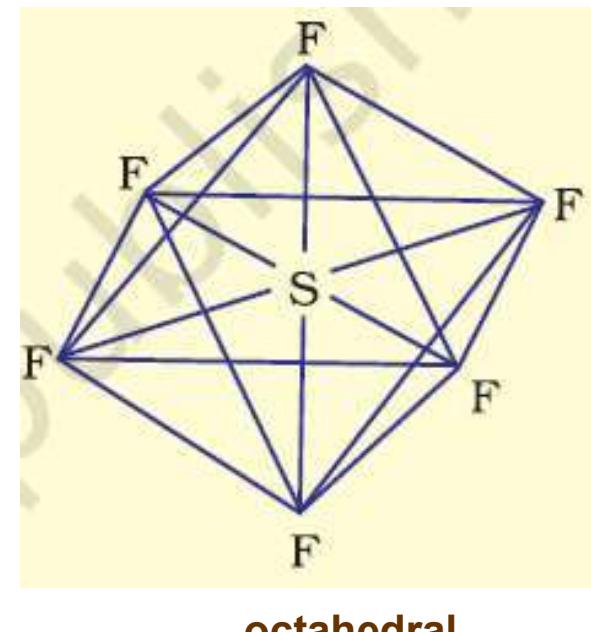
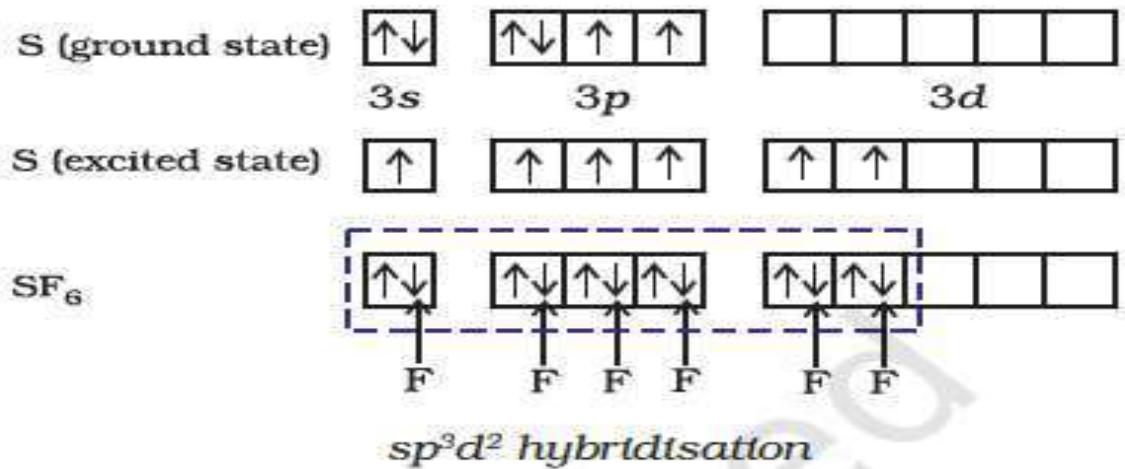
P (ground state)	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	$\square\square\square$
	3s	3p	3d
P (excited state)	$\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow$
$\text{PCl}_5$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\uparrow$	$\uparrow\downarrow$
	Cl	Cl Cl Cl Cl	Cl

Now the five orbitals (i.e., one s, three p and one d orbital) are available for hybridisation to yield a set of five  $sp^3d$  hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal. All the bond angles in trigonal bipyramidal geometry are not equivalent. In  $\text{PCl}_5$  the five  $sp^3d$  orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P–Cl sigma bonds.

Three P–Cl bond lie in one plane and make an angle of  $120^\circ$  with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds—one lying above and the other lying below the equatorial plane, make an angle of  $90^\circ$  with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes  $\text{PCl}_5$  molecule more reactive.



*Formation of  $SF_6$  ( $sp^3d^2$  hybridisation):*



## DRAWBACKS OF VB THEORY

VB theory works on the premise that electrons are paired wherever possible, the model predicts that  $O_2$  is diamagnetic. One of the notable failures of VB theory is its inability to predict the observed paramagnetism of  $O_2$ .

## **MOLECULAR ORBITAL THEORY**

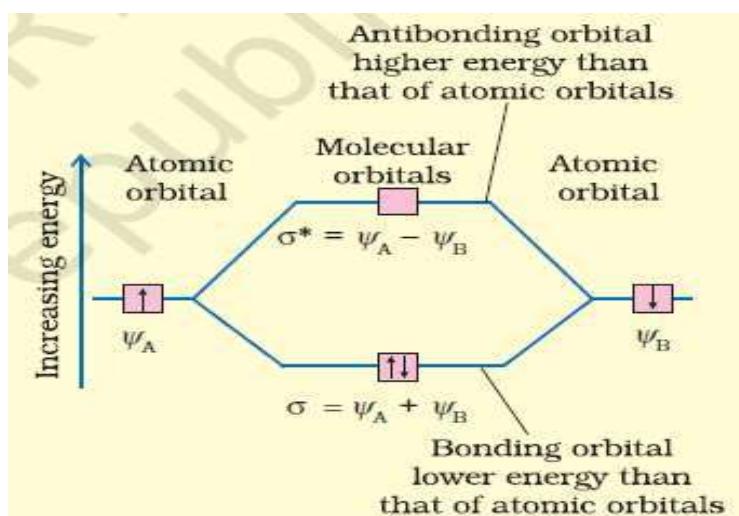
Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

- (i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- (ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- (iii) Electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
- (iv) 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 the other is called antibonding molecular orbital.
- (v) The bonding molecular orbital has lower energy and greater stability than the corresponding antibonding molecular orbital.
- (vi) 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 a molecular orbital.
- (vii) The molecular orbitals are filled like atomic orbitals in accordance with the *aufbau* principle obeying the Pauli's exclusion principle and the Hund's rule.

## LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave functions ( $\psi$ ) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. Molecular orbitals were obtained from linear combination of atomic orbitals (LCAO).

Homonuclear diatomic hydrogen molecule consisting of two hydrogen atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  and  $\psi_B$ . Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals.



$$\psi_{MO} = \psi_A \pm \psi_B$$

$$\sigma = \psi_A + \psi_B$$

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

Two molecular orbitals  $\sigma$  and  $\sigma^*$  are formed

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called antibonding molecular orbital.

## **CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS**

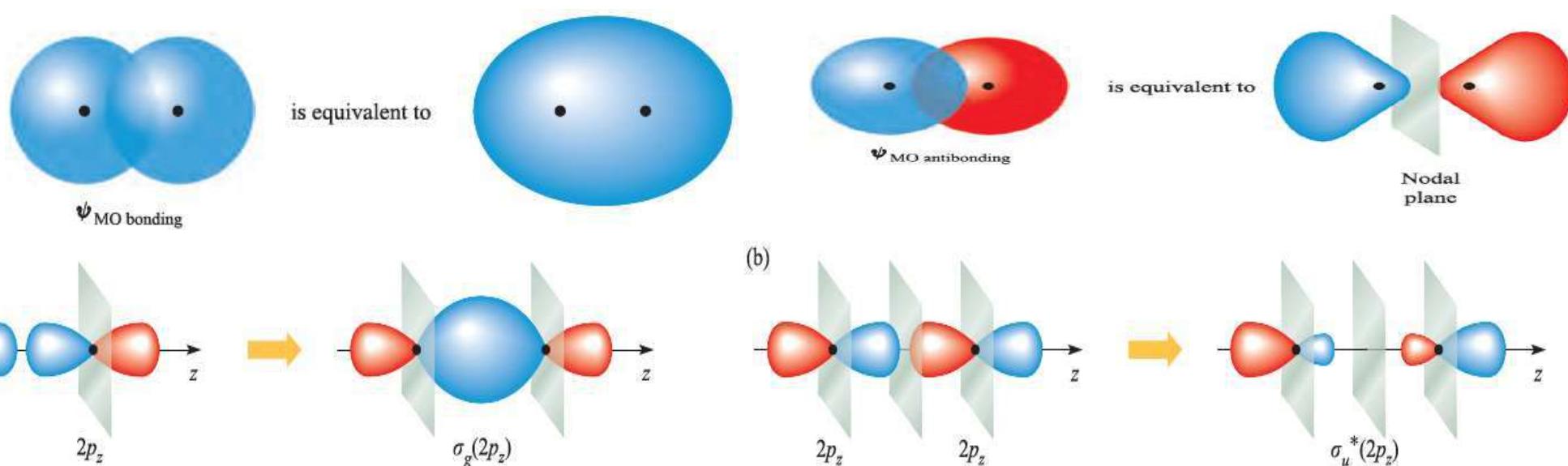
The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. **This is not true if the atoms are very different.**
2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2pz orbital of one atom can combine with 2pz orbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries.
3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

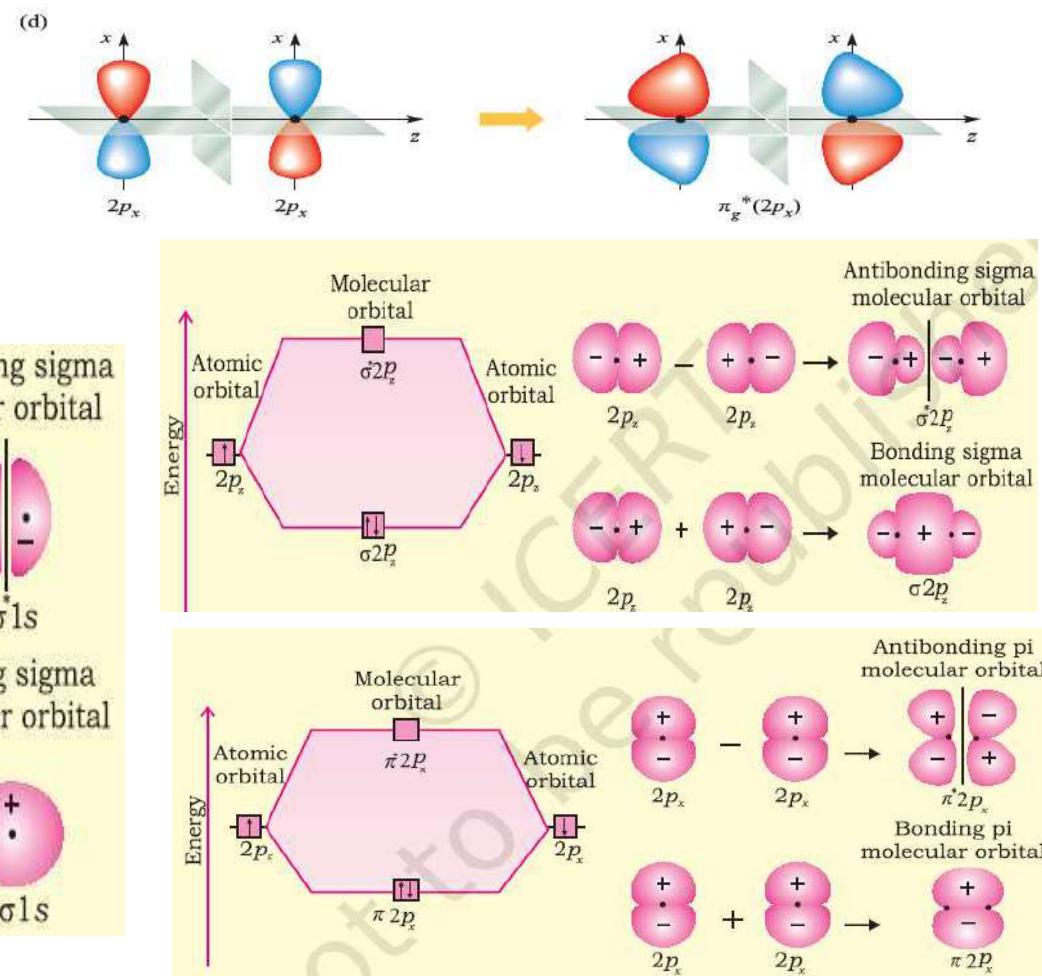
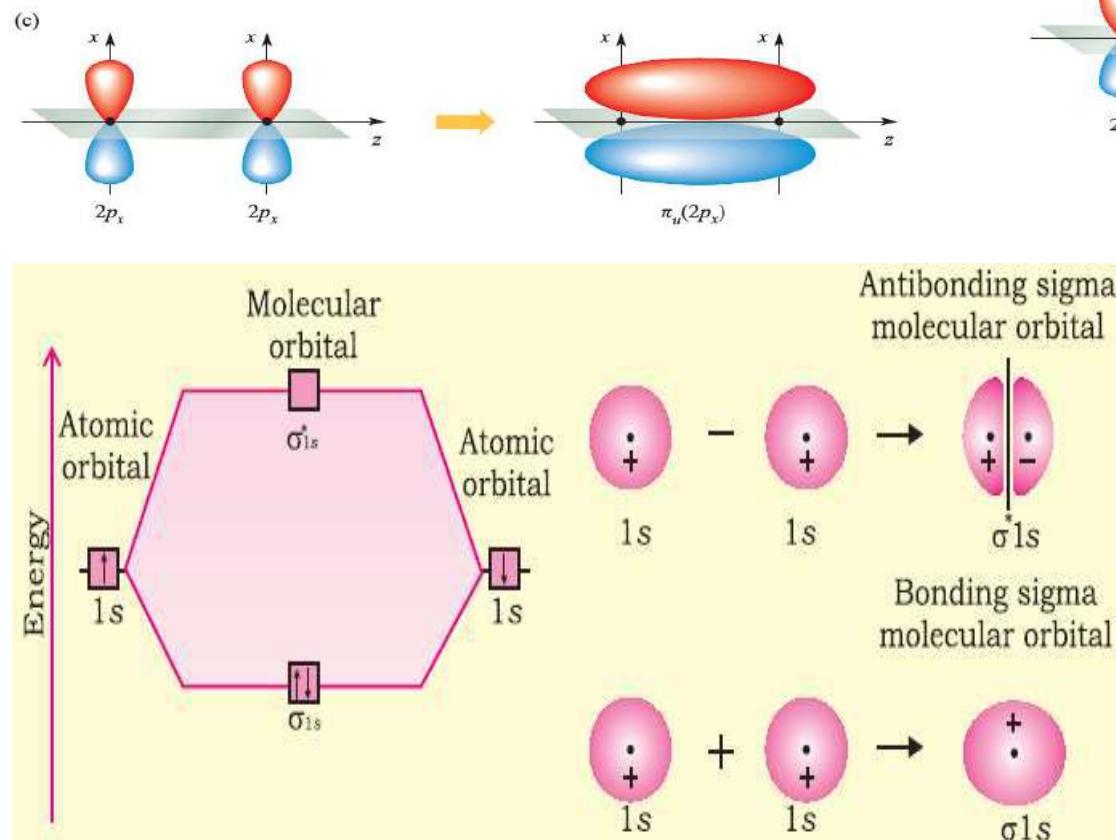
## TYPES OF MOLECULAR ORBITALS

Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta), etc.

In this nomenclature, the sigma ( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis while pi ( $\pi$ ) molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the  $\sigma$  type and are designated as  $\sigma 1s$  and  $\sigma^* 1s$ . If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of  $2p_z$ - orbitals of two atoms also produces two sigma molecular orbitals designated as  $\sigma 2p_z$  and  $\sigma^* 2p_z$ .



Molecular orbitals obtained from  $2px$  and  $2py$  orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as  $\pi$  and  $\pi^*$ . A  $\pi$  bonding MO has larger electron density above and below the internuclear axis. The  $\pi^*$  antibonding MO has a node between the nuclei.



## ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS

1s atomic orbitals on two atoms form two molecular orbitals designated as  $\sigma 1s$  and  $\sigma^* 1s$ . In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

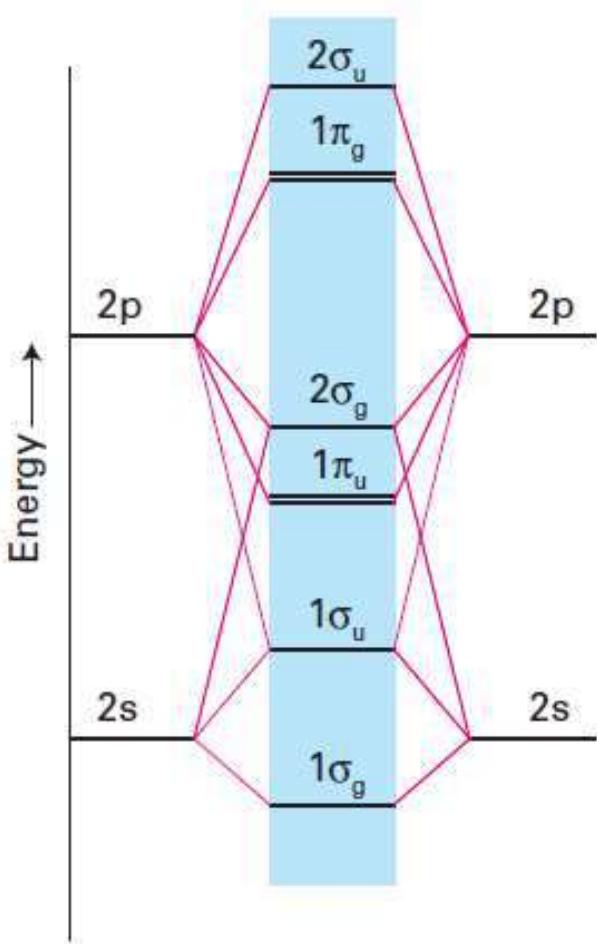
Antibonding	MOs	$\sigma^* 2s$	$\sigma^* 2p_z$	$\pi^* 2p_x$	$\pi^* 2p_y$
Bonding	MOs	$\sigma 2s$	$\sigma 2p_z$	$\pi 2p_x$	$\pi 2p_y$

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

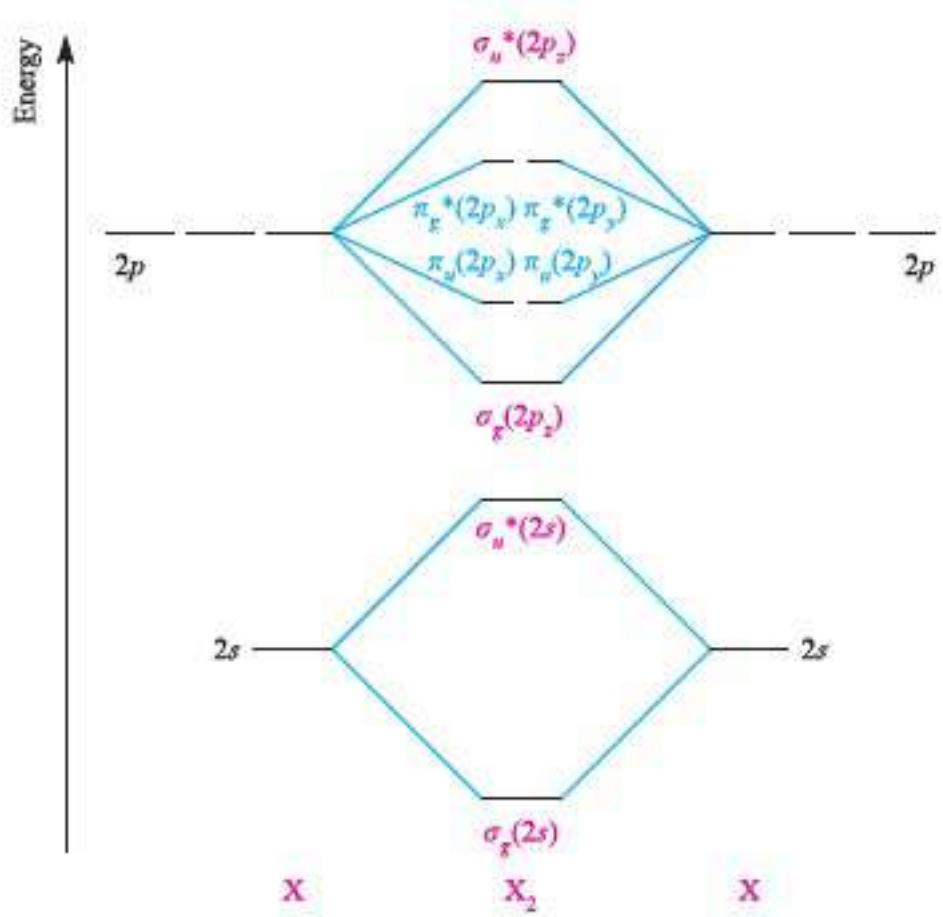
The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$ ,  $N_2$ . For instance, it has been observed experimentally that for molecules such as  $B_2$ ,  $C_2$ ,  $N_2$ , etc. the increasing order of energies of various molecular orbitals is

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

The important characteristic feature of this order is that the energy of  $\sigma 2p_z$  molecular orbital is higher than that of  $\pi 2p_x$  and  $\pi 2p_y$  molecular orbitals.



The molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules from Li<sub>2</sub> to N<sub>2</sub>. 2s & 2p orbitals mixing



The molecular orbital energy level diagram  
2s & 2p energy gap is higher than 1.0 eV.  
Without orbital mixing

## ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. Electronic configuration of the molecule gives important information about the molecule.

*Stability of Molecules:*  $N_b$  is the number of electrons occupying bonding orbitals and  $N_a$  the number occupying the antibonding orbitals,

- (i) Molecule is stable if  $N_b$  is greater than  $N_a$ , and
- (ii) Molecule is unstable if  $N_b$  is less than  $N_a$

*Bond order:* Bond order is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) =  $\frac{1}{2} (N_b - N_a)$

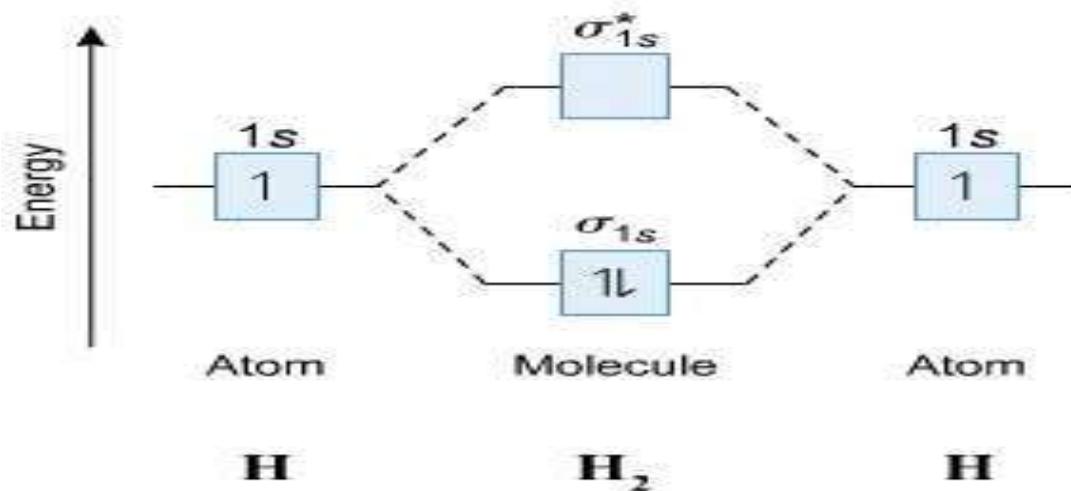
*Nature of the bond:* Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively as studied in the classical concept.

*Bond-length:* The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. *The bond length decreases as bond order increases.*

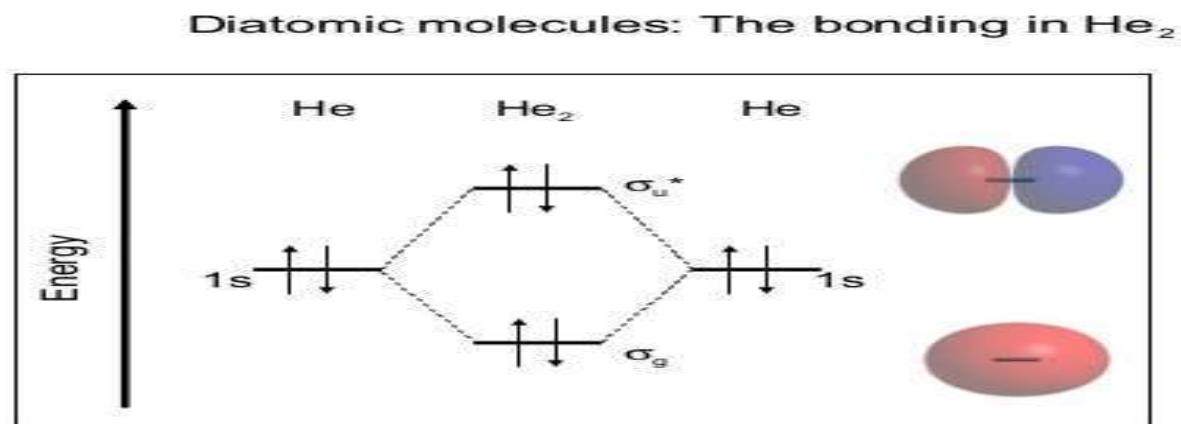
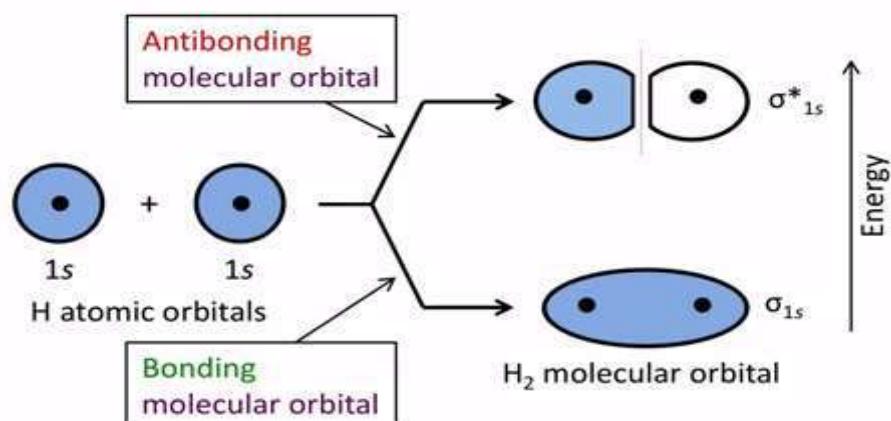
*Magnetic nature:* If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). *However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O<sub>2</sub> molecule.*

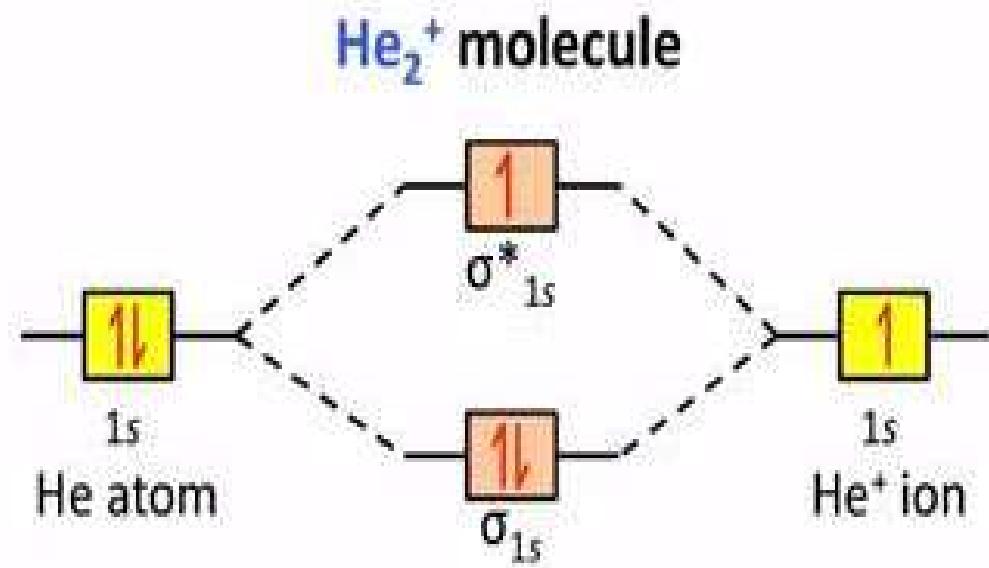
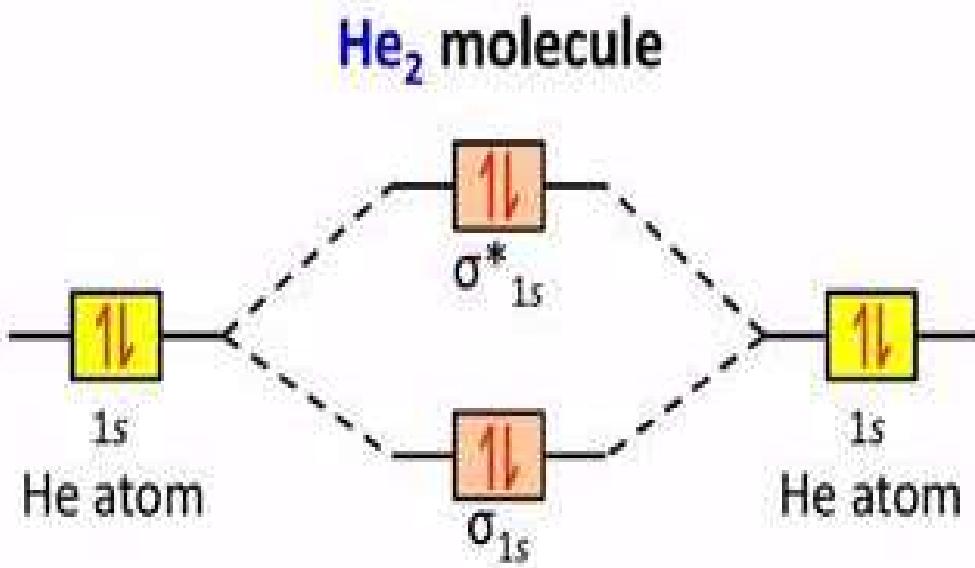
# Bonding in some Homonuclear di-atomic molecules

Molecular Orbital Diagram ( $H_2$ )



✓ Electronic configuration of H atom  $1s^1$   
✓ Electronic configuration of  $H_2$  molecule  $1s^2$   
✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{2-0}{2} = 1$   
✓ Molecule has no unpaired electron hence it is diamagnetic





*Unstable molecule*

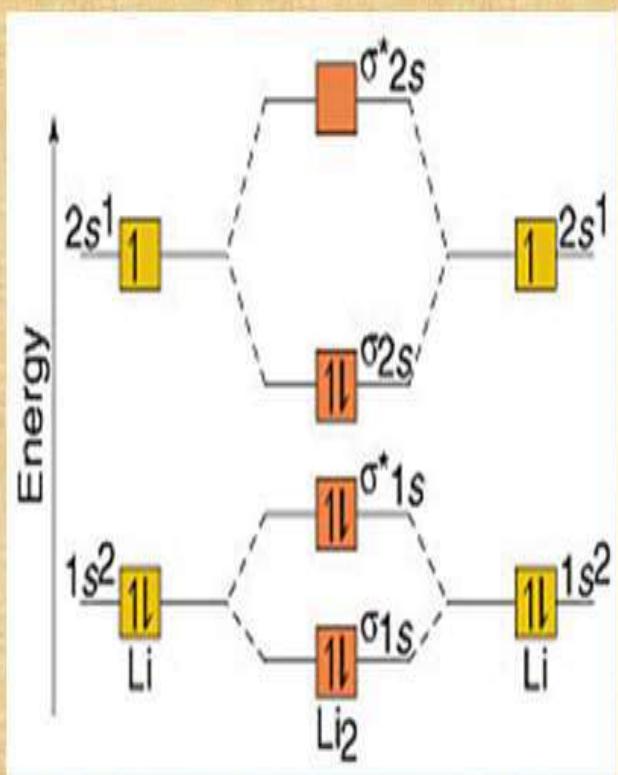
$$\text{Bond Order} = \frac{1}{2}(2 - 2) = 0$$

*Stable molecule*

$$\text{Bond Order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

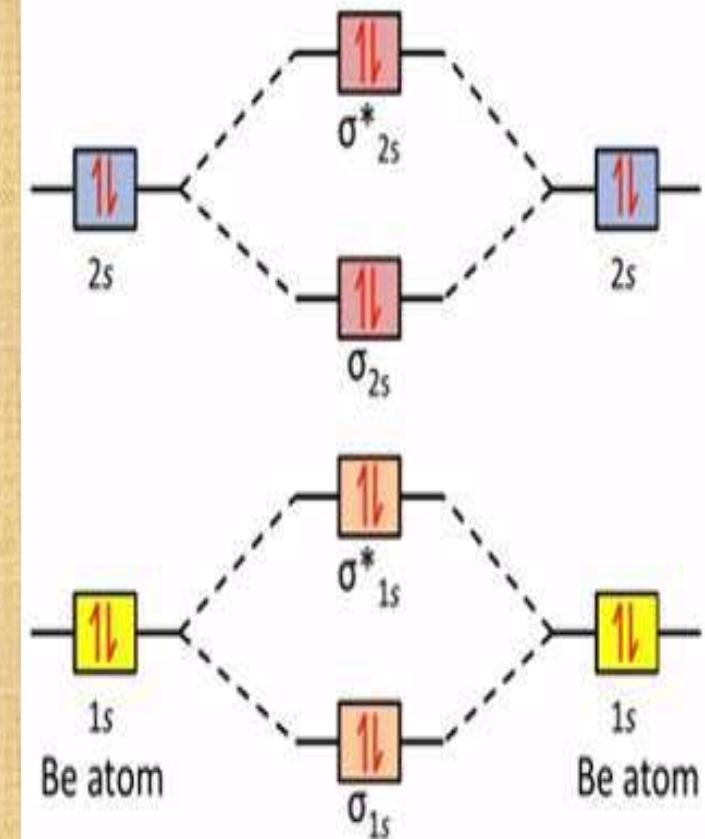
Molecular Orbital theory is powerful because it allows us to predict whether molecules should exist or not and it gives us a clear picture of the electronic structure of any hypothetical molecule that we can imagine.

## MO Diagram of $\text{Li}_2$ molecule

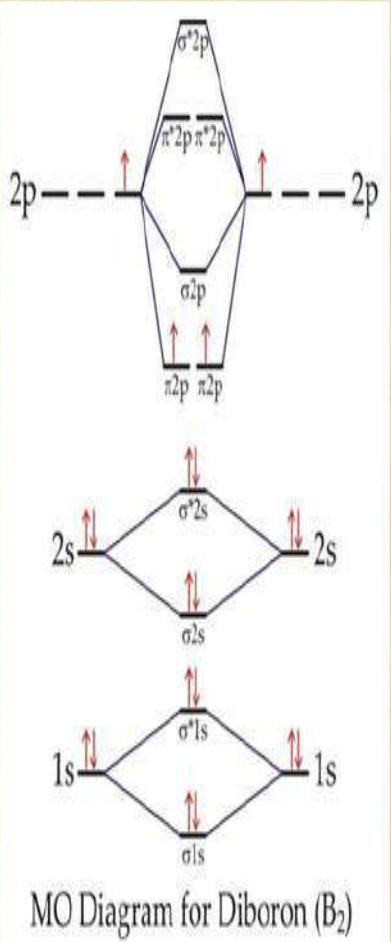


- ✓ Electronic configuration of Li atom  $1\text{s}^2 2\text{s}^1$
- ✓ Electronic configuration of  $\text{Li}_2$  molecule  $\sigma 1\text{s}^2 \sigma^* 1\text{s}^2 \sigma 2\text{s}^2$
- ✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{4 - 2}{2} = 1$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

## $\text{Be}_2$ molecule

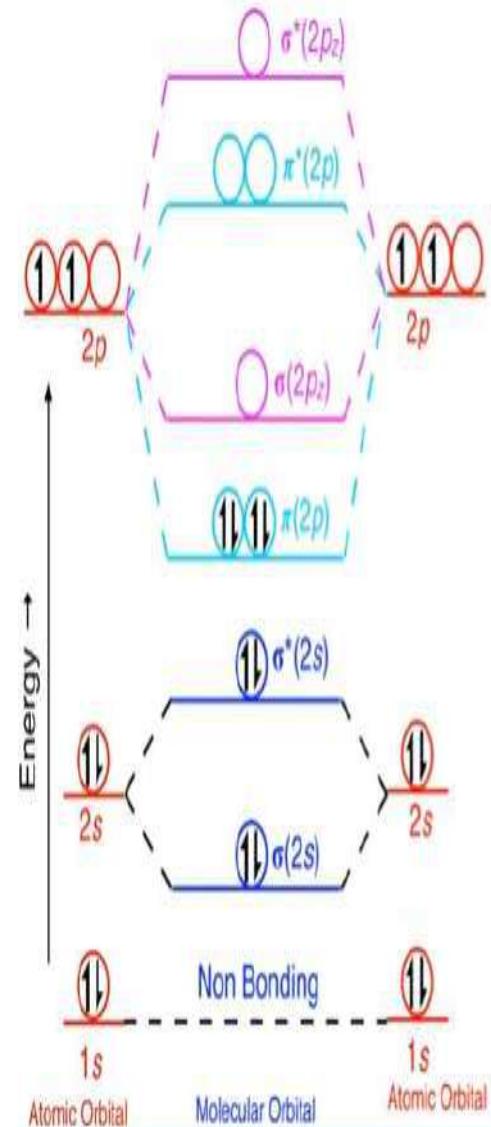


Unstable molecule

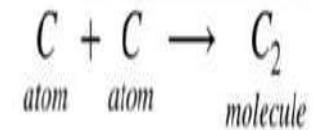


### MO Diagram of $B_2$ molecule

- ✓ Electronic configuration of B atom  $1s^2 2s^2 2p^1$
- ✓ Electronic configuration of  $B_2$  molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi^1 2p_x \pi^1 2p_y$
- ✓ Bond Order  $= \frac{Nb - Na}{2} = \frac{6-4}{2} = 1$
- ✓ Molecule has two unpaired electron hence it is paramagnetic



### Molecular Orbitals of $C_2$



As all electrons are paired,  $C_2$  molecule is **diamagnetic**.

$$\text{Bond order} = \frac{(N_{\text{bonding}} - N_{\text{antibonding}})}{2}$$

$$\text{Bond order} = \frac{(6 - 2)}{2} = 2$$

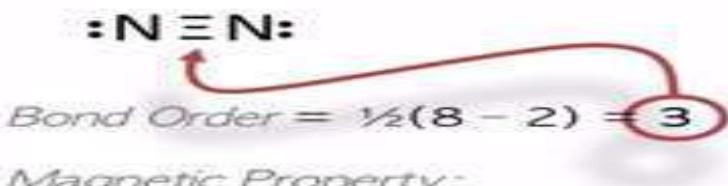
Therefore, two pi bonds are formed.

## MO DIAGRAM OF N<sub>2</sub> MOLECULE

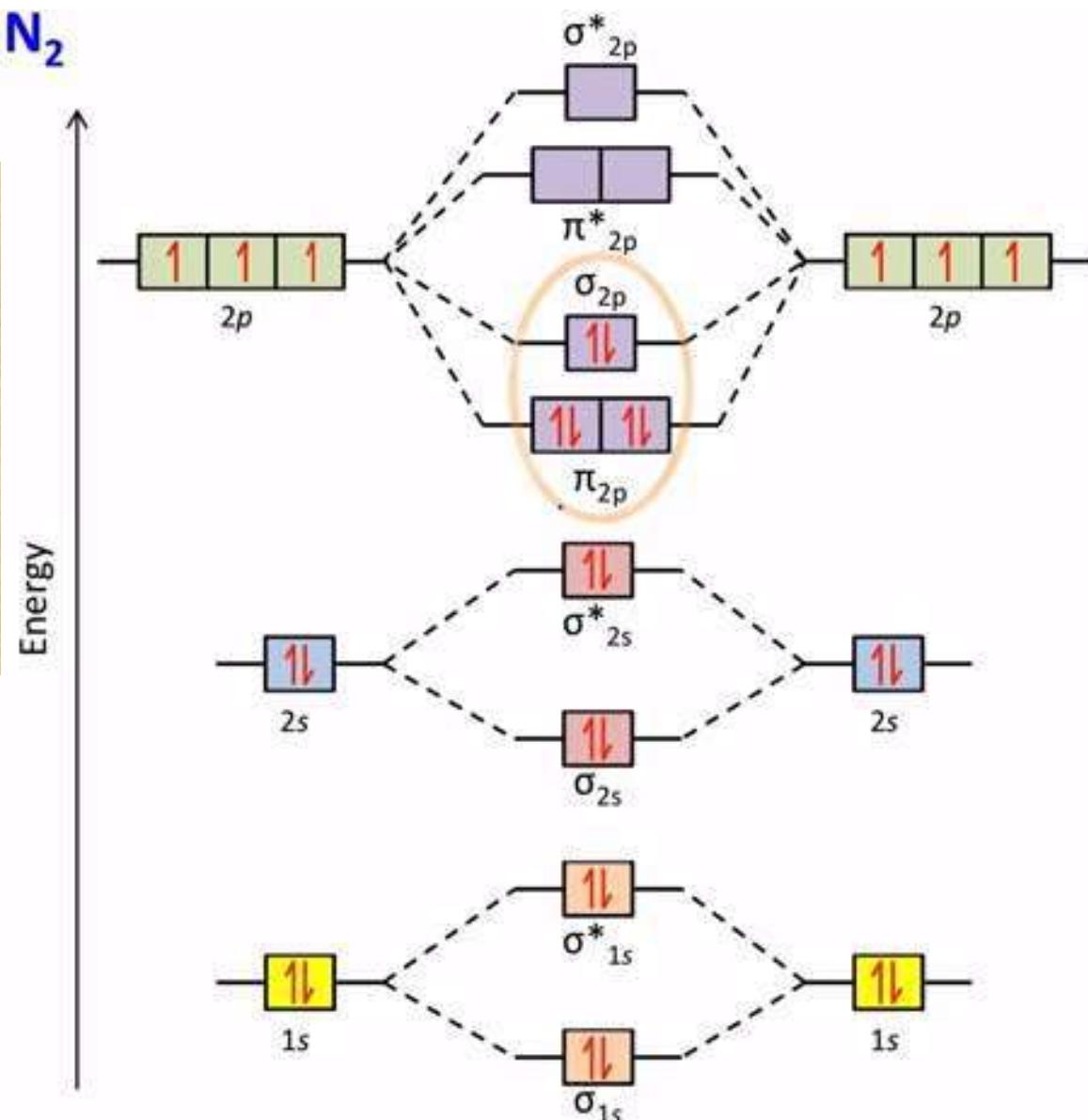
- ✓ Electronic configuration of N atom  $1s^2 2s^2 2p^3$
- ✓ Electronic configuration of N<sub>2</sub> molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi^2_{2px} \pi^2_{2py} \sigma^2_{2pz}$
- ✓ Bond Order =  $\frac{Nb - Na}{2} = \frac{10 - 4}{2} = 3$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

Nitrogen Atom Electron Configuration:  
N:  $1s^2 2s^2 2p^3$

Lewis Structure:

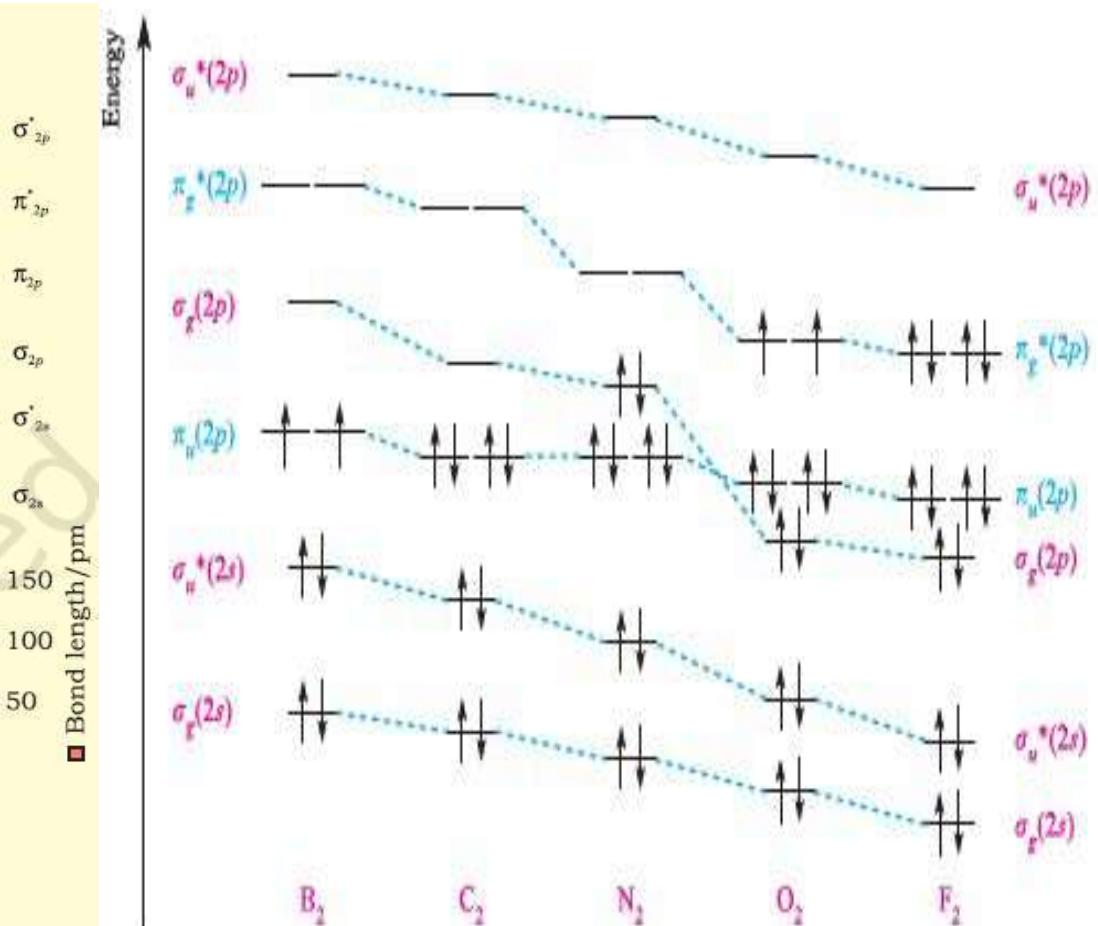


Magnetic Property:  
Diamagnetic



# MO OCCUPANCY AND MOLECULAR PROPERTIES

	With 2s-2p mixing			Without 2s-2p mixing		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
$\sigma^*_{2p}$	[1]	[1]	[1]	[1]	[1]	[↑↓]
$\pi^*_{2p}$	[2][1]	[2][1]	[2][1]	[↑↑]	[↑↓↑↓]	[↑↓↑↓]
$\sigma_{2p}$	[1]	[1]	[↑↓]	[↑↓↑↓]	[↑↓↑↓]	[↑↓↑↓]
$\pi_{2p}$	[↑↑]	[↑↓↑↓]	[↑↓↑↓]	[↑↓]	[↑↓]	[↑↓]
$\sigma^*_{2s}$	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]
$\sigma_{2s}$	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]	[↑↓]
Bond energy /kJmol <sup>-1</sup>	290	620	159	945	498	121
Bond order	1	2	3	2	1	0
Magnetic properties	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	-
Valence electron configuration	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\pi_{2p})^2$	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\pi_{2p})^4$	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\pi_{2p})^6 (\sigma_{2p})^2$	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\sigma_{2p})^2 (\pi_{2p})^4$ $(\pi^*_{2p})^2$	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\sigma_{2p})^2 (\pi_{2p})^4$ $(\pi^*_{2p})^4$	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$ $(\pi_{2p})^4 (\sigma_{2p})^2$



## MO DIAGRAM OF O<sub>2</sub> MOLECULE

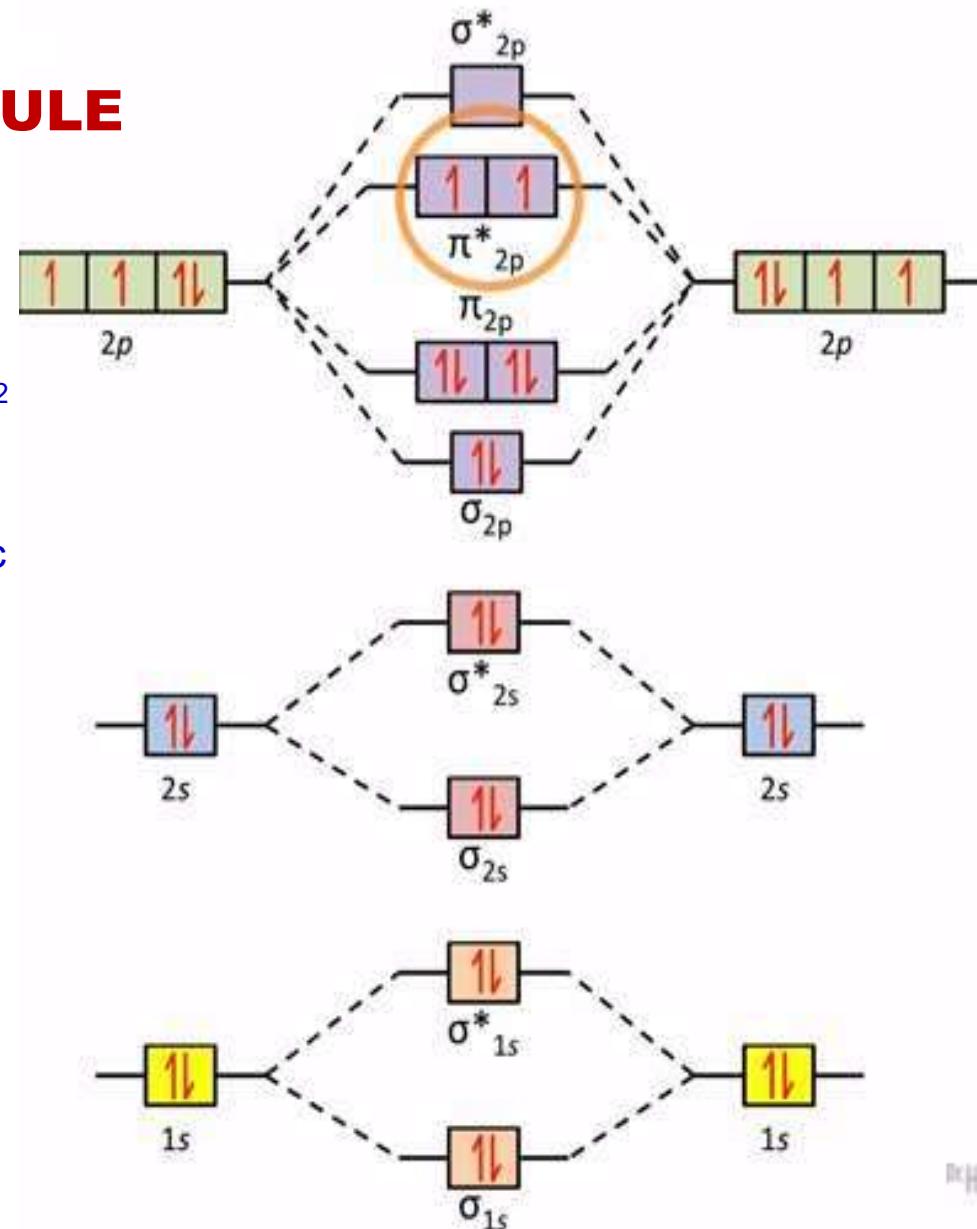
- ✓ Electronic configuration of O atom  $1s^2 2s^2 2p^4$
- ✓ Electronic configuration of O<sub>2</sub> molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$
- ✓ Molecule has two unpaired electron hence it is paramagnetic

Oxygen Atom Electron Configuration:  
<sub>8</sub>O:  $1s^2 2s^2 2p^4$

Lewis Structure:



Magnetic Property:  
 Paramagnetic



## Paramagnetism and Diamagnetism

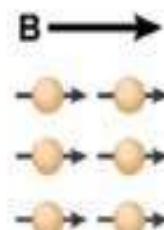
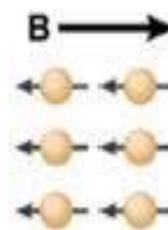
- Atoms with unpaired  $\uparrow$  electrons are called **paramagnetic**.
  - Paramagnetic atoms are attracted to a magnet.
- Atoms with paired  $\uparrow\downarrow$  electrons are called **diamagnetic**.
  - Diamagnetic atoms are repelled by a magnet.

### Types of magnetism

Diamagnetic	Paramagnetic
$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$ No unpaired electrons	$\uparrow\downarrow \uparrow\downarrow \uparrow$ At least one unpaired electron

#### Electron pairing

Spin alignment with magnetic field  $\mathbf{B}$



Anti-parallel

Parallel

#### Reaction to magnets

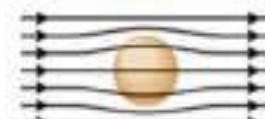


Very weakly repelled



Attracted

#### Effect on magnetic field lines



Field bends slightly away from the material



Field bends toward the material

## MO DIAGRAM OF F<sub>2</sub> MOLECULE

- ✓ Electronic configuration of F atom  $1s^2 2s^2 2p^5$
- ✓ Electronic configuration of F<sub>2</sub> molecule  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^2$
- ✓ Molecule has no unpaired electron hence it is diamagnetic

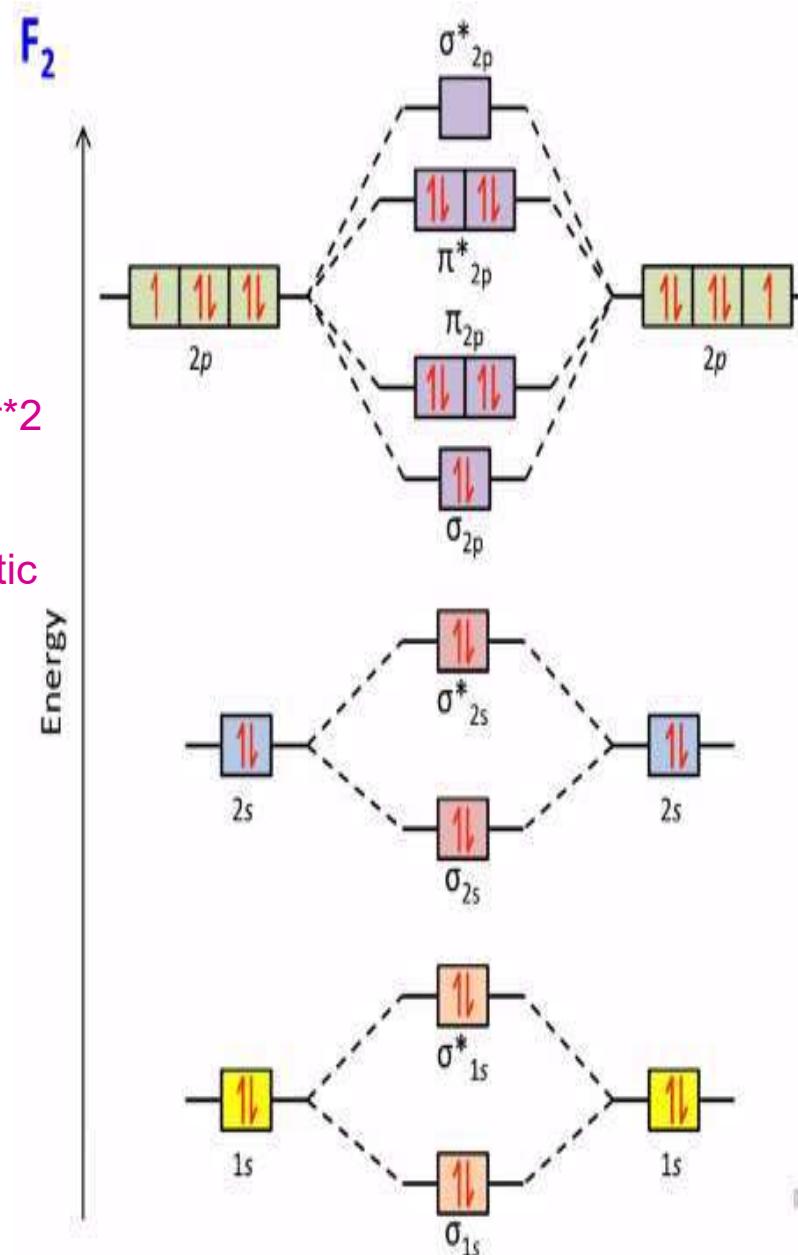
Lewis Structure:



$$\text{Bond Order} = \frac{1}{2}(8 - 6) = 1$$

Magnetic Property:

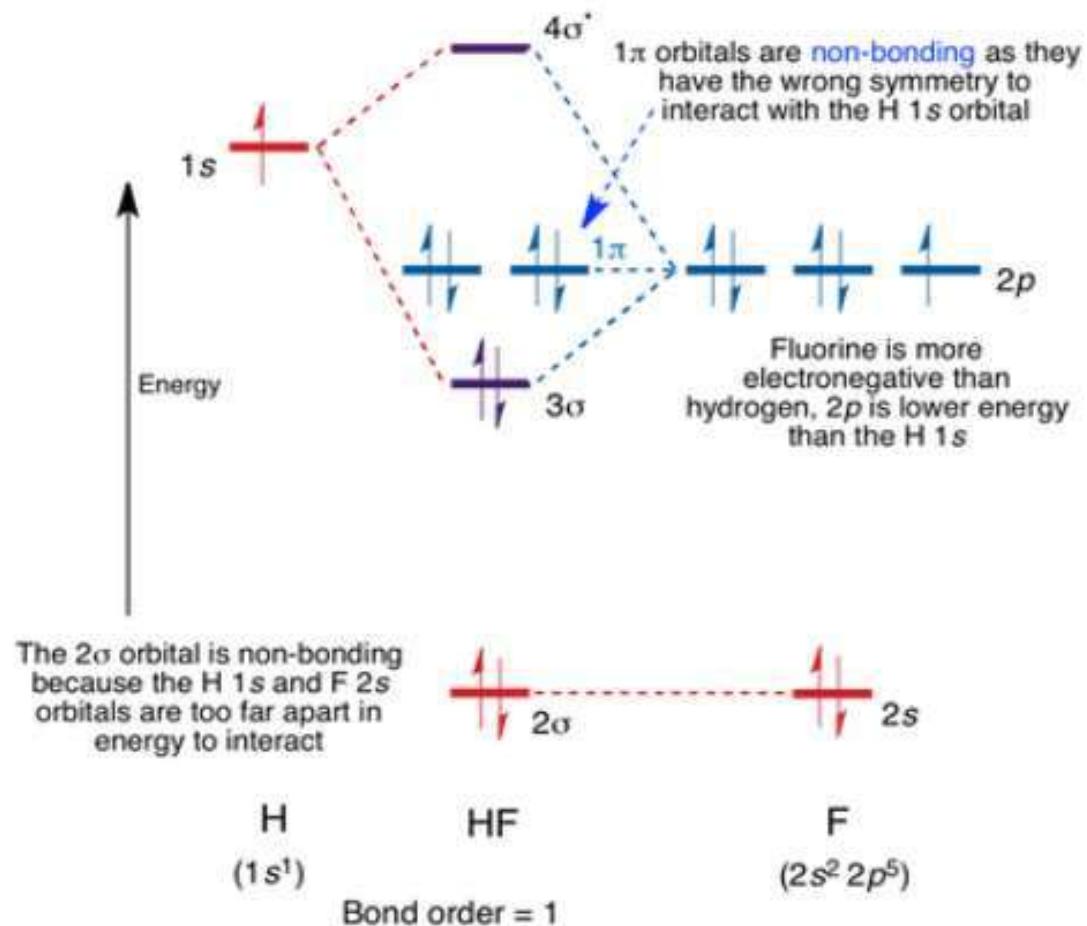
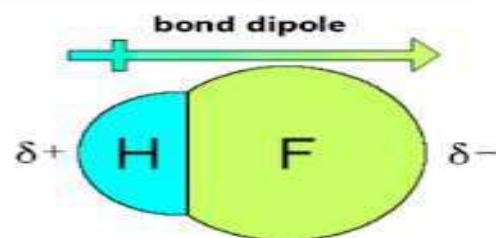
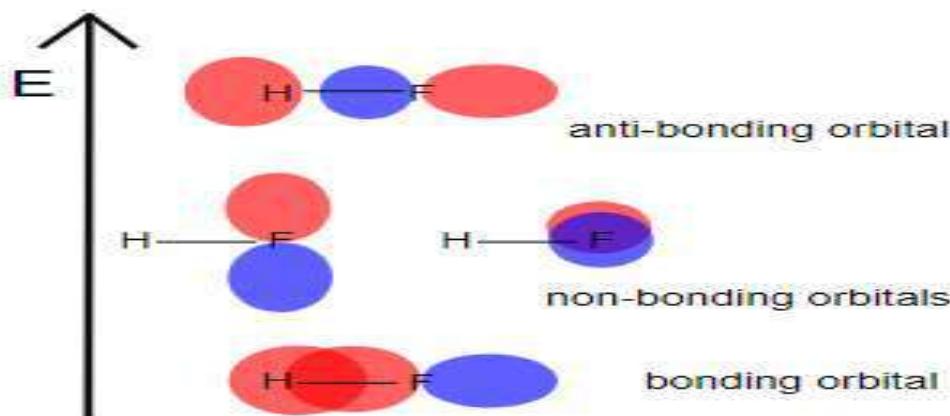
Diamagnetic



## MO BONDING IN HETERONUCLEAR DIATOMIC MOLECULES

### Let's Start Slowly: HF

- Valence electrons
  - H - 1s<sup>1</sup>
  - F - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>
- Focus on the valence interactions
- Accommodate for differences in electronegativity
- Allow mixing between symmetry-allowed states



HOMO = highest occupied molecular orbital.  
 LUMO = lowest unoccupied molecular orbital.  
 NBMO = Non-bonding molecular orbital.

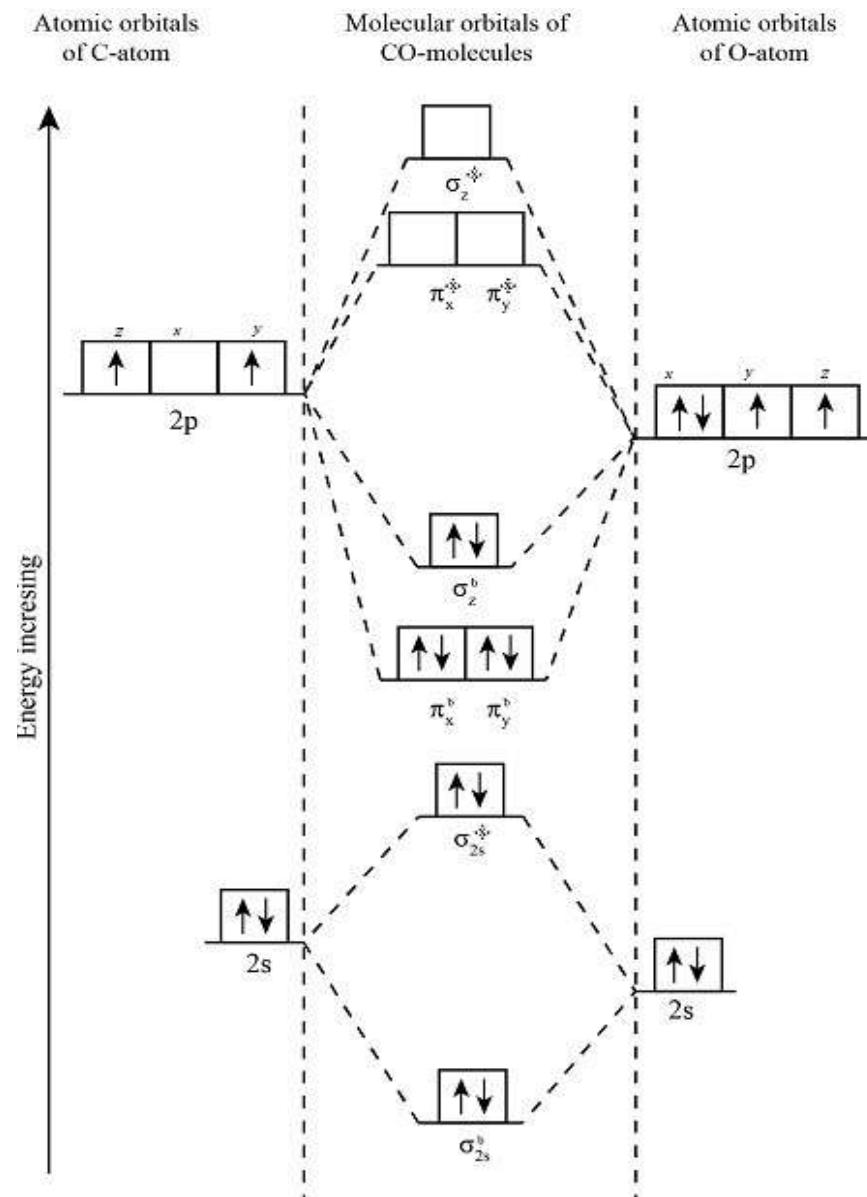
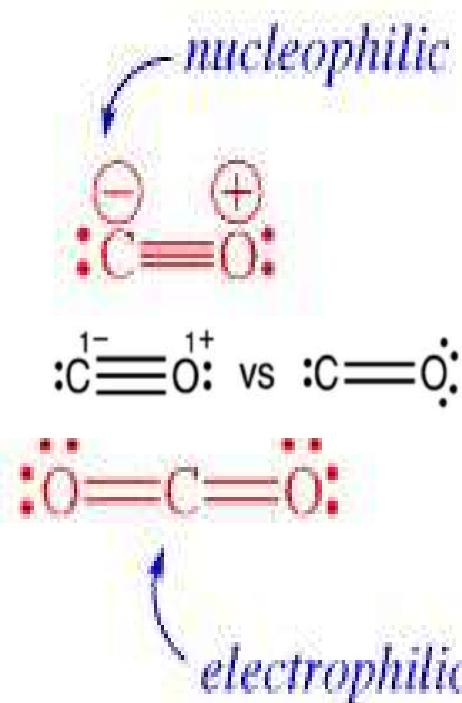
H  
(1s<sup>1</sup>)

HF

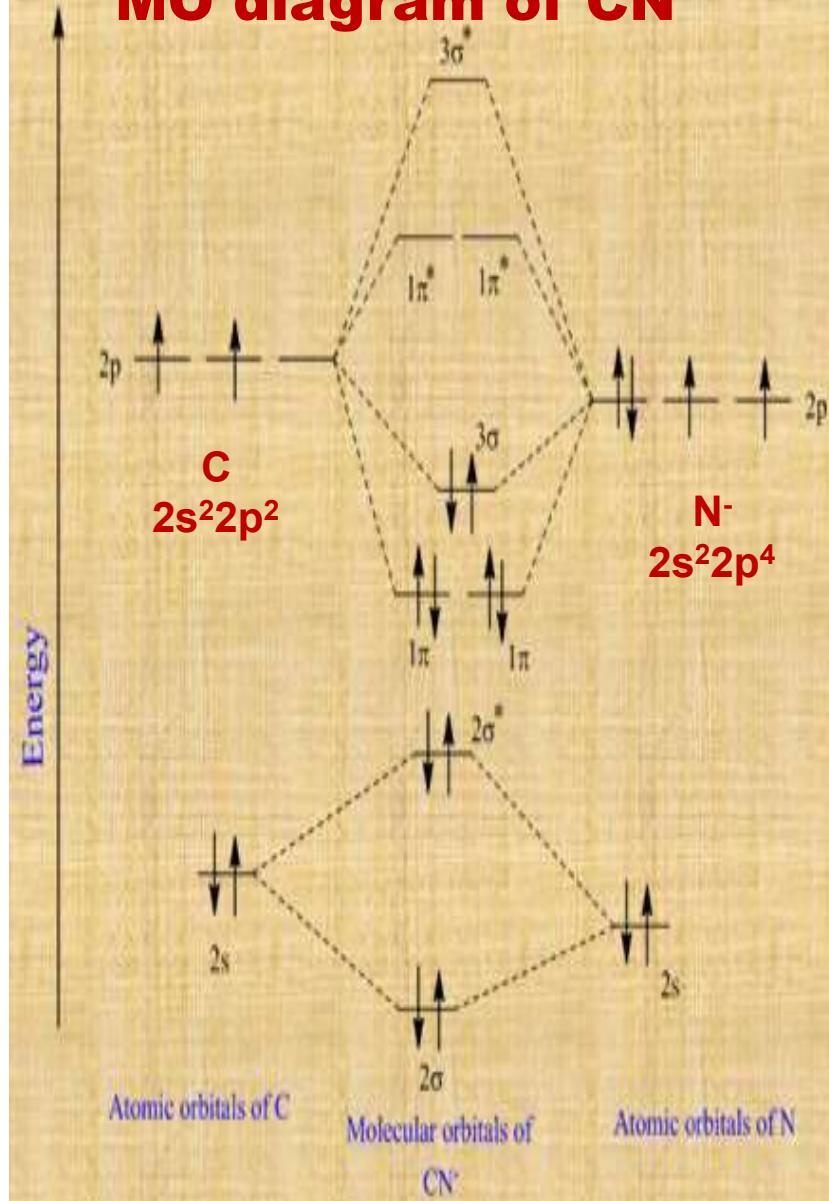
F  
(2s<sup>2</sup> 2p<sup>5</sup>)

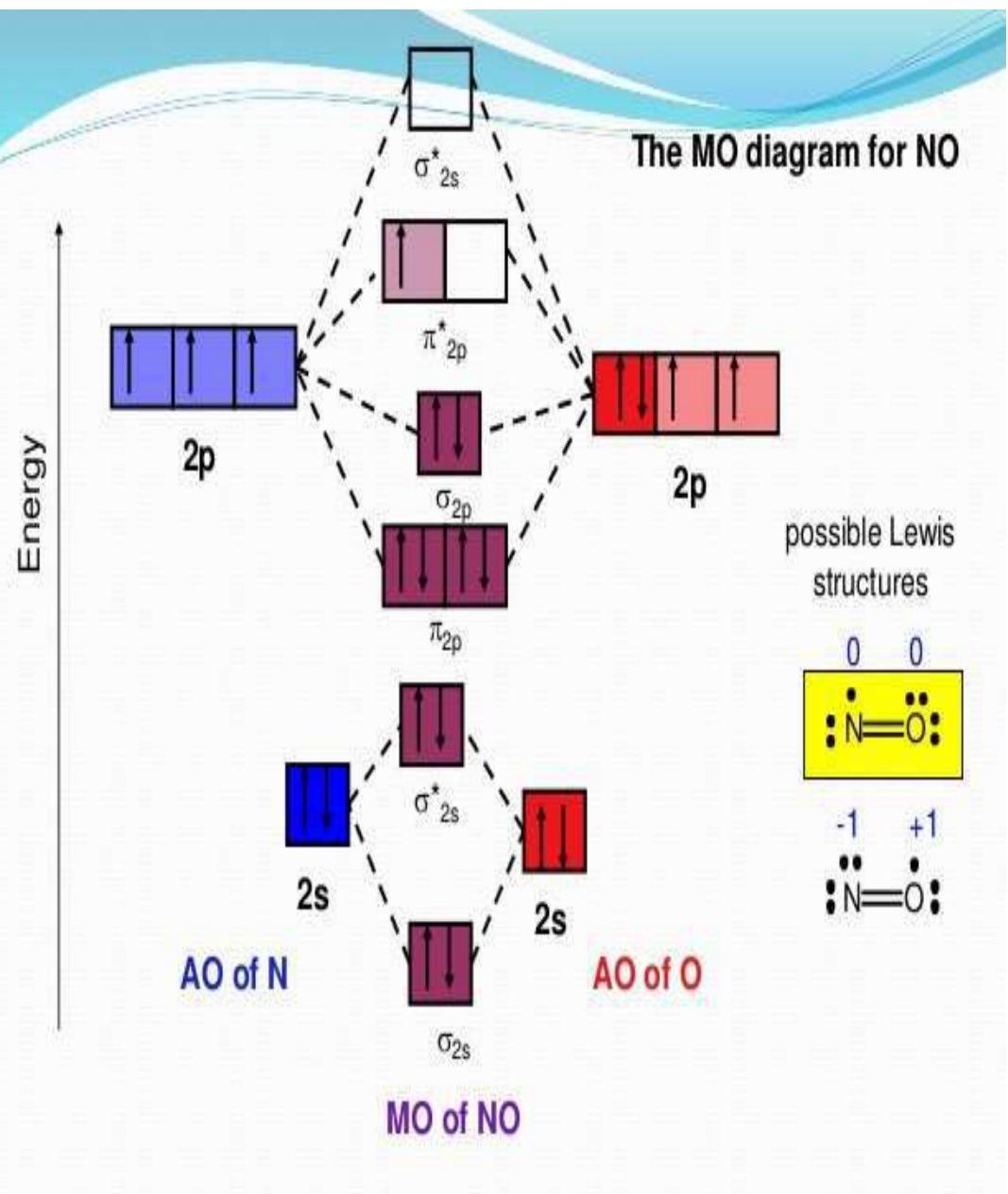
Bond order = 1

## MO DIAGRAM OF CO



## MO diagram of CN<sup>-</sup>





$$\text{N} = 1s^2 2s^2 2p^3$$

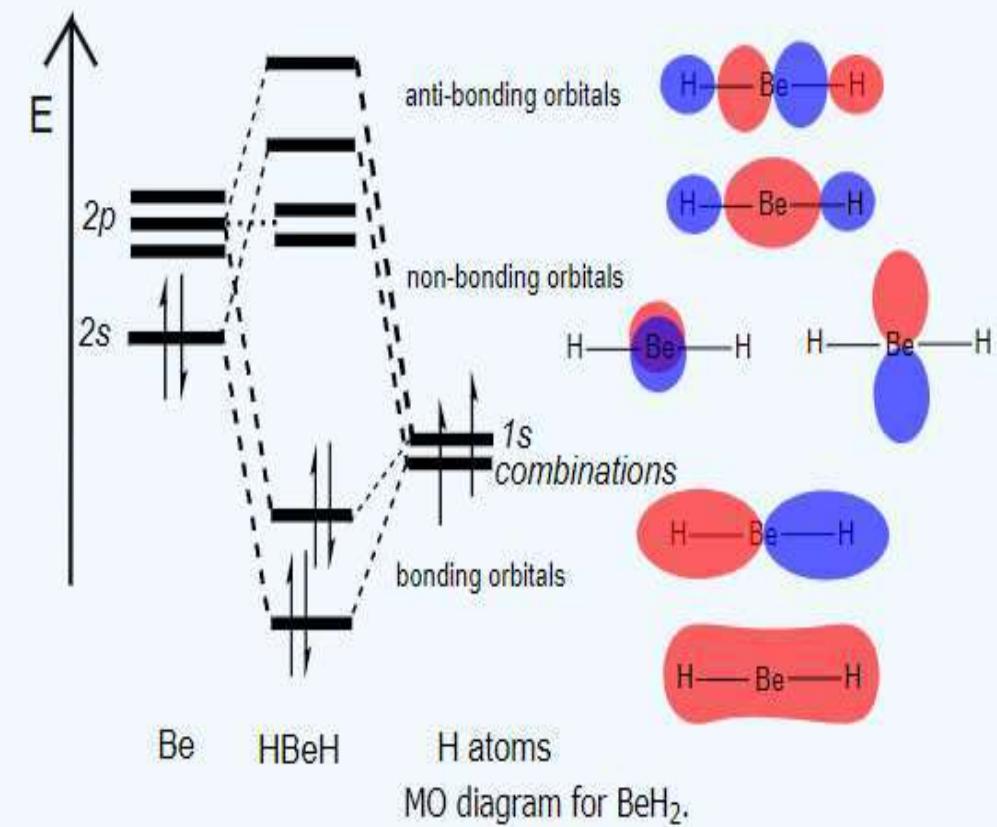
$$\text{O} = 1s^2 2s^2 2p^4$$

Bond Order=2.5

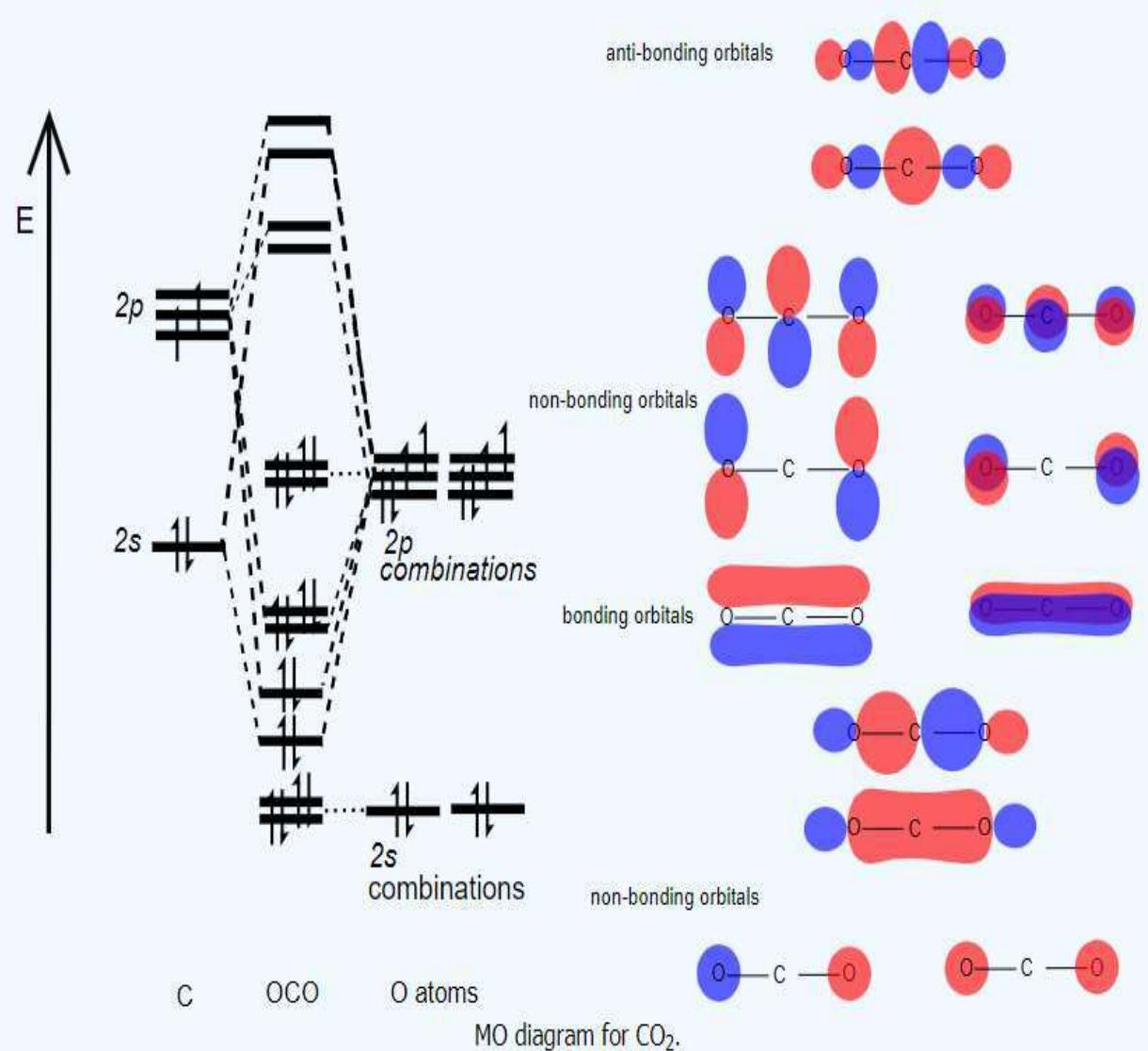
Bond Length=1.15A<sup>0</sup>

- ✓ Molecule has one unpaired electron  
hence it is paramagnetic

# MO DIAGRAM OF POLYATOMIC MOLECULE

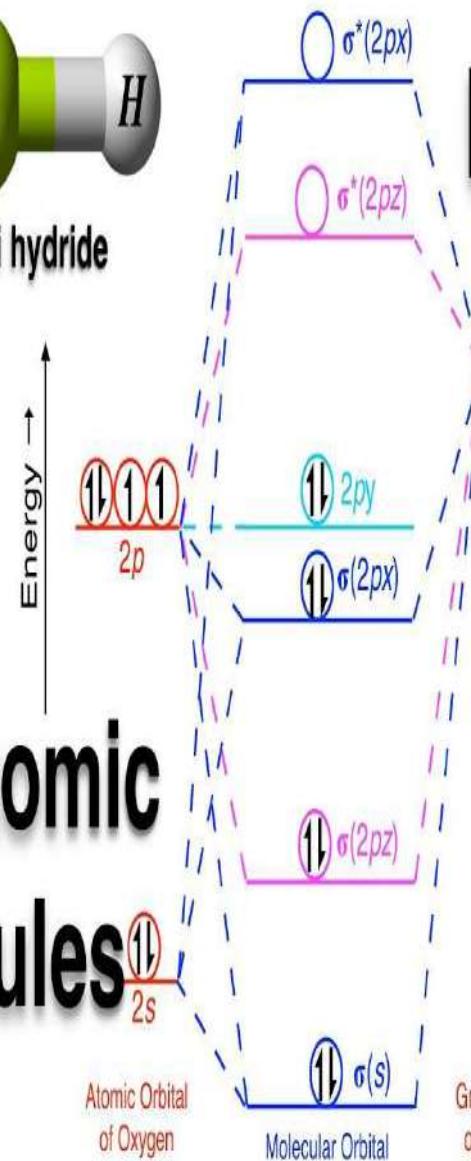


HOMO = highest occupied molecular orbital.  
 LUMO = lowest unoccupied molecular orbital.  
 NBMO = Non-bonding molecular orbital.

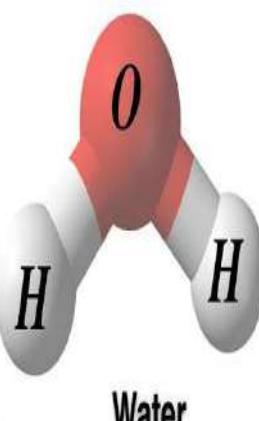




Beryllium Di hydride

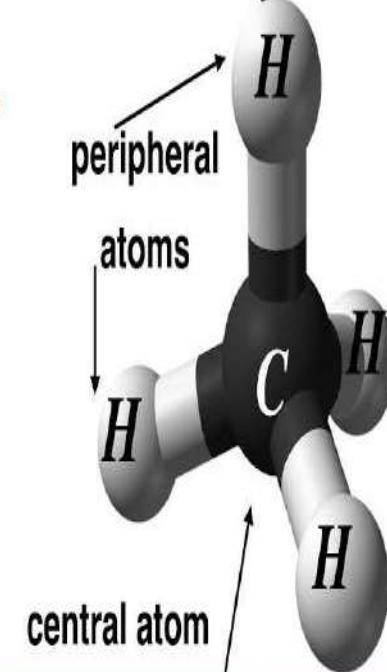
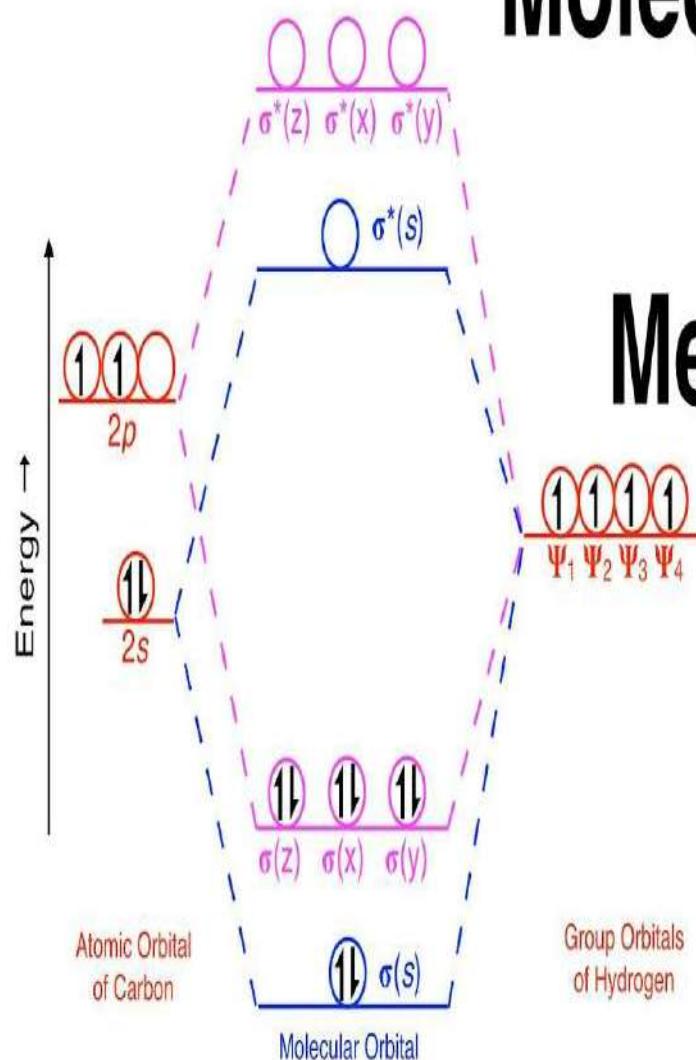


## Molecular Orbital Diagram



Group Orbitals of Hydrogen

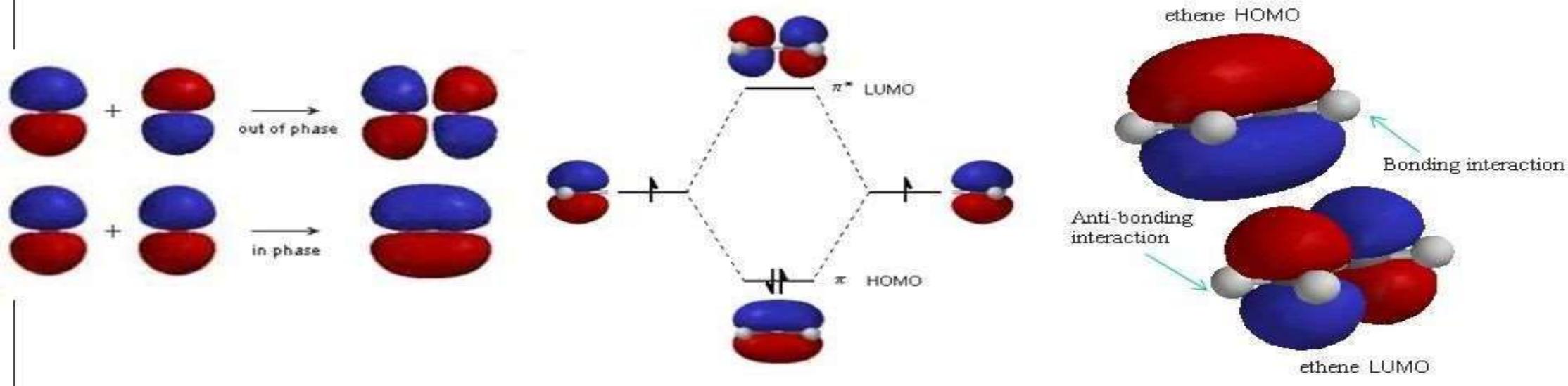
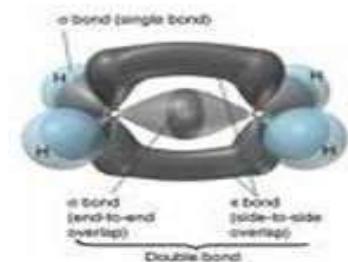
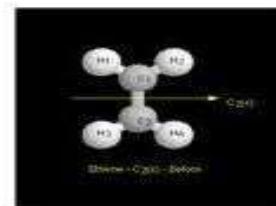
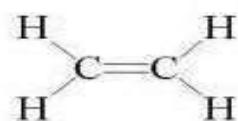
## Polyatomic Molecules



# Molecular Orbital Diagram Of Methane (CH<sub>4</sub>)

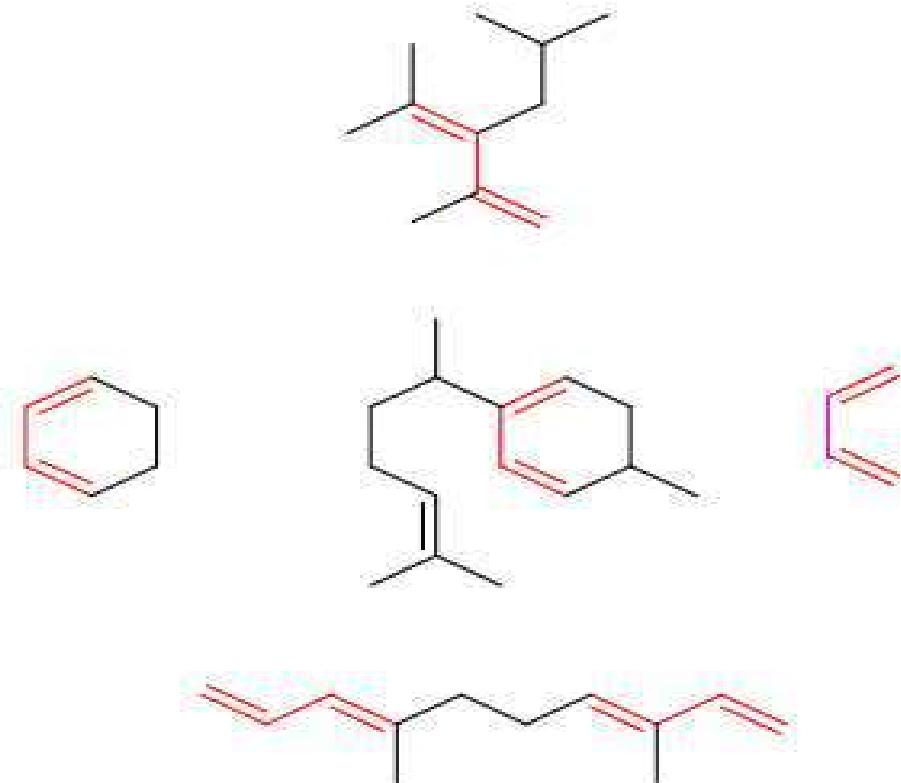
# Molecular Orbital (MO)

## $\pi$ Molecular Orbitals of Ethene



# What are Conjugated Dienes?

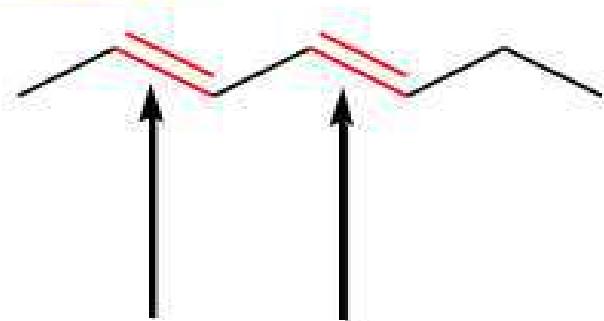
- **Conjugated Dienes** are carbon structures which maintain 2 double bond separated by a single bond.
- **Conjugated Dienes** can be found in many different molecules as shown.



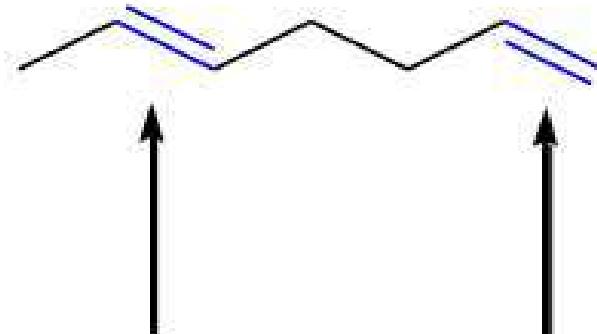
Examples of Conjugated Dienes

# Conjugated and Nonconjugated Dienes

- If Di = two and ene = double bond then Diene = two double bonds.
- If double bonds are separated by only **ONE** single bond, they are **conjugated** and their orbitals interact.
- The *conjugated diene* 2,4-heptadiene has properties that are very different from those of the *nonconjugated diene*, 1,5-heptadiene



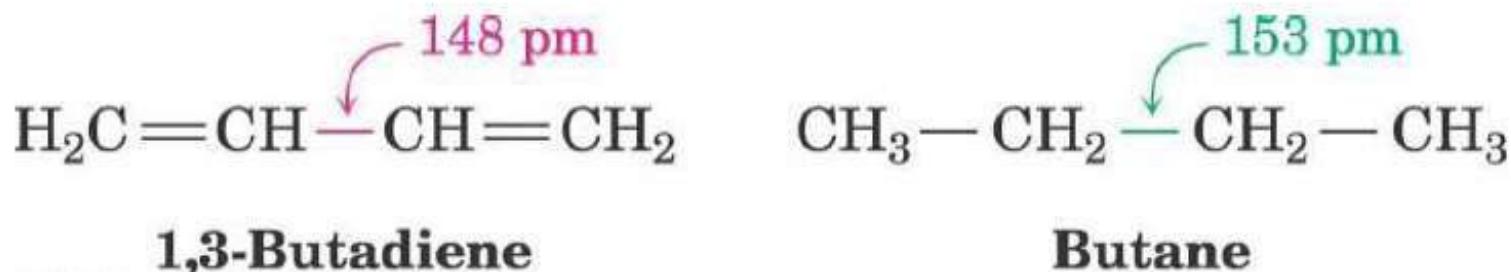
Conjugated Diene



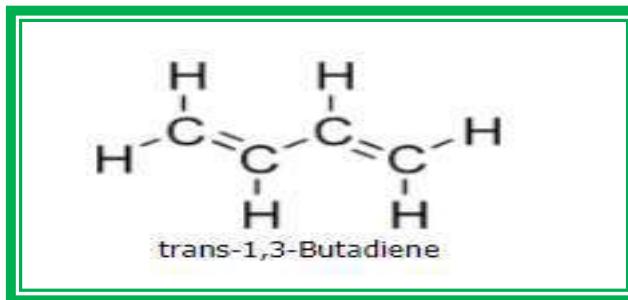
Non-Conjugated Diene

## 1,3-BUTADIENE

- The single bond between the conjugated double bonds is shorter and stronger than  $sp^3$

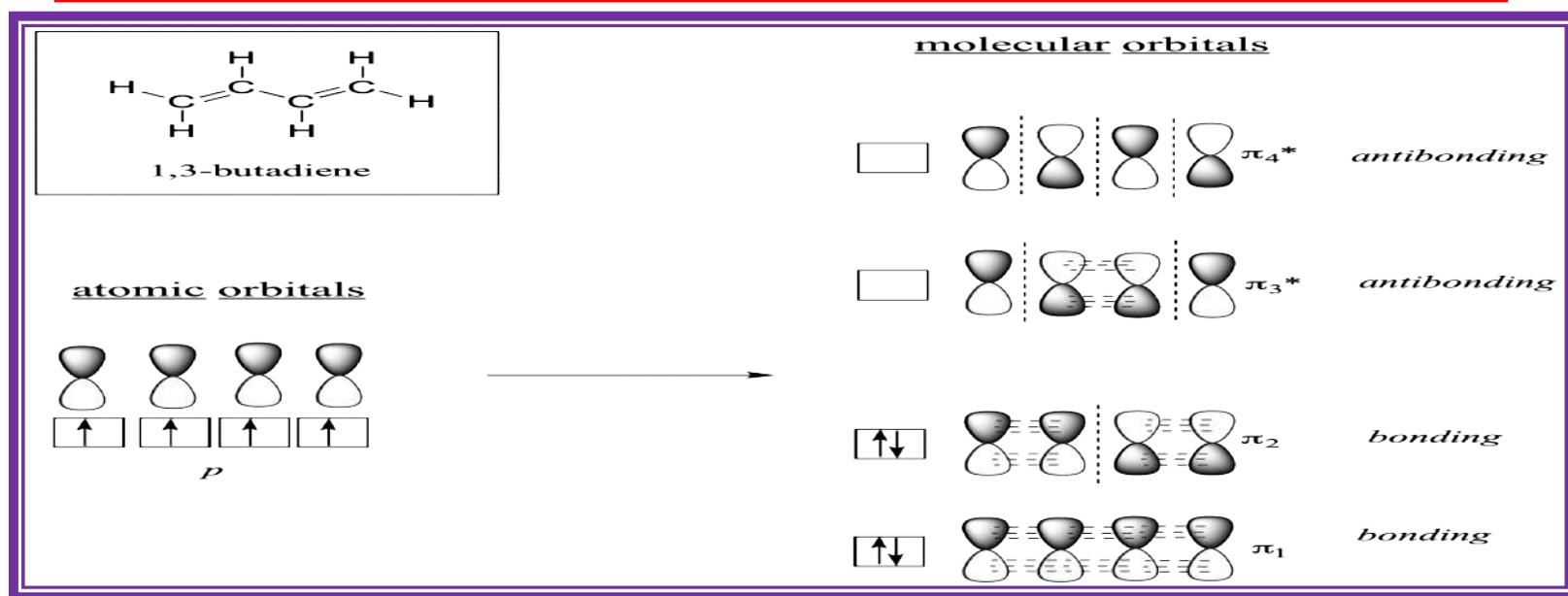
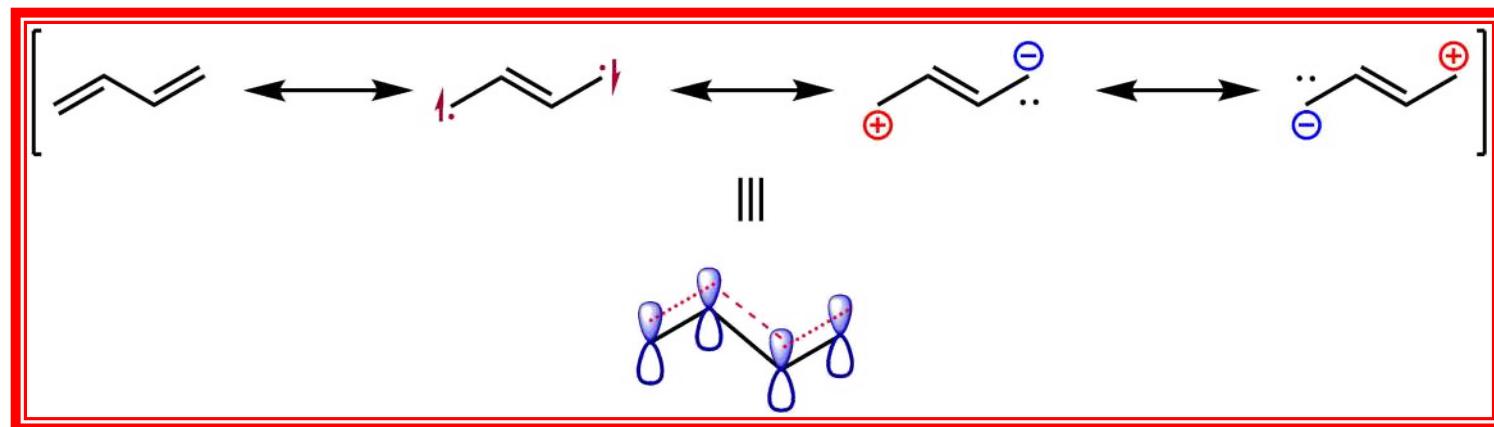


## **Π-MOLECULAR ORBITALS OF 1,3-BUTADIENE**

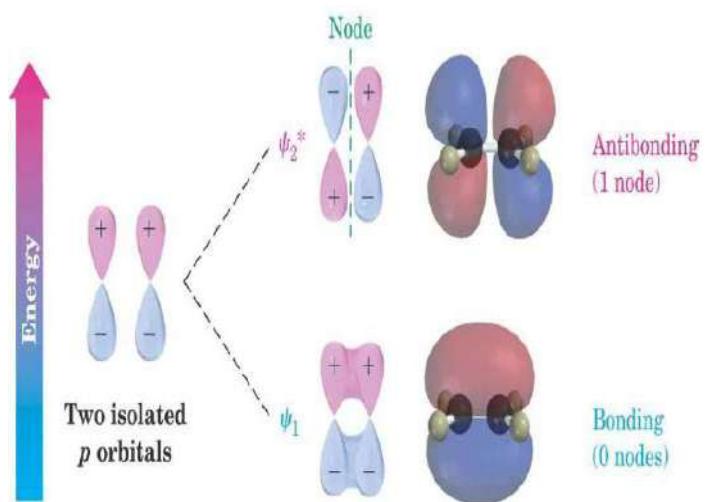


- ❖ Pi Molecular Orbitals of 1,3-Butadiene with a single sigma bond separating the pi bonds of 1,3-butadiene it is a conjugated system and some of the pi electron density will be delocalized between carbons 2 and 3 rather than just between 1 and 2 and 3 and 4.
- ❖ There are four adjacent carbon atoms involved in the pi system and the combination of a p orbital from each of these atoms will result in four pi molecular orbitals:  $\psi_1$ ,  $\psi_2$ ,  $\psi_3^*$ , and  $\psi_4^*$  (also referred to as  $\pi_1$ ,  $\pi_2$ ,  $\pi_3^*$ , and  $\pi_4^*$ ).

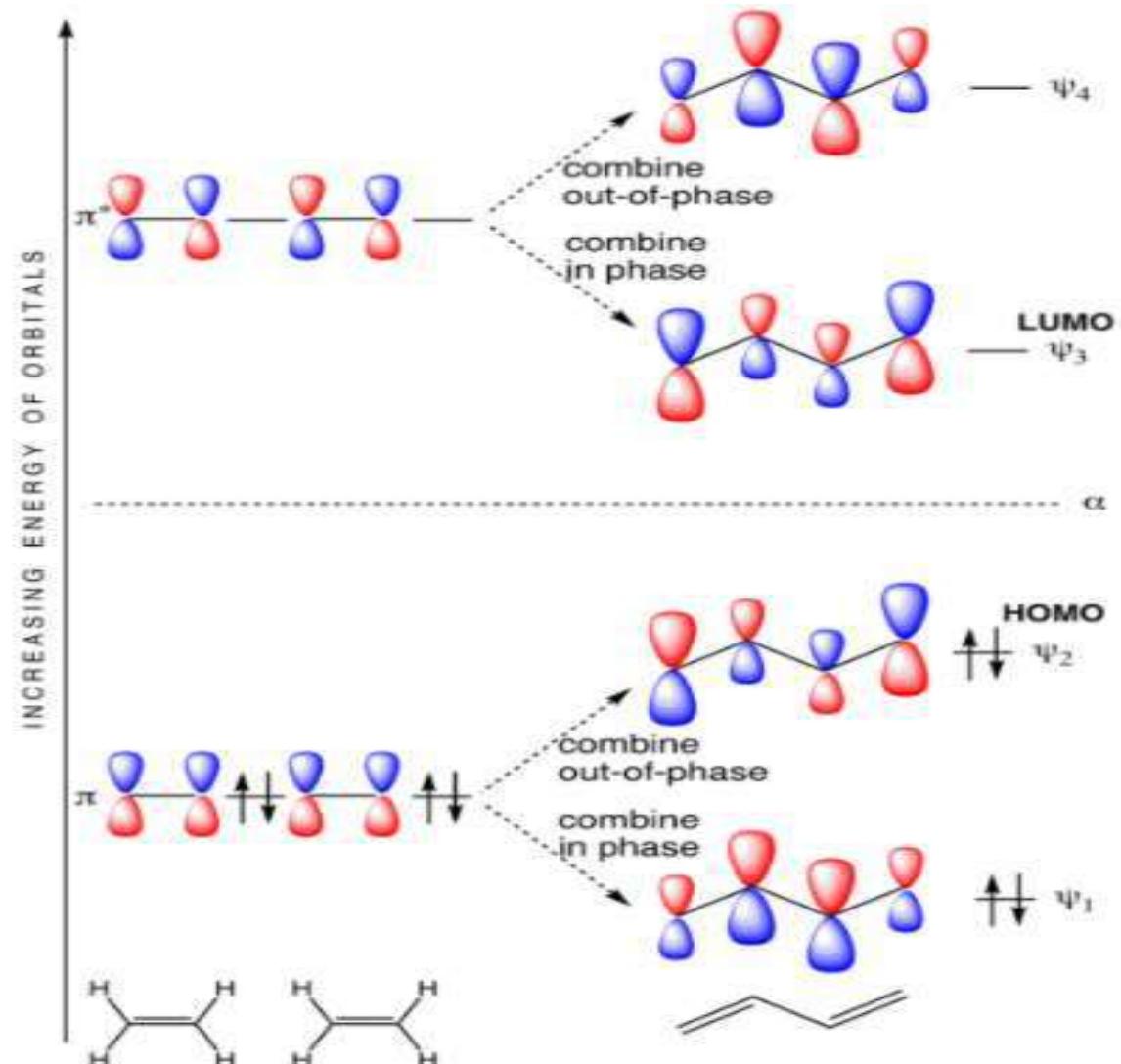
# RESONANCE FORM OF 1,3-BUTADIENE



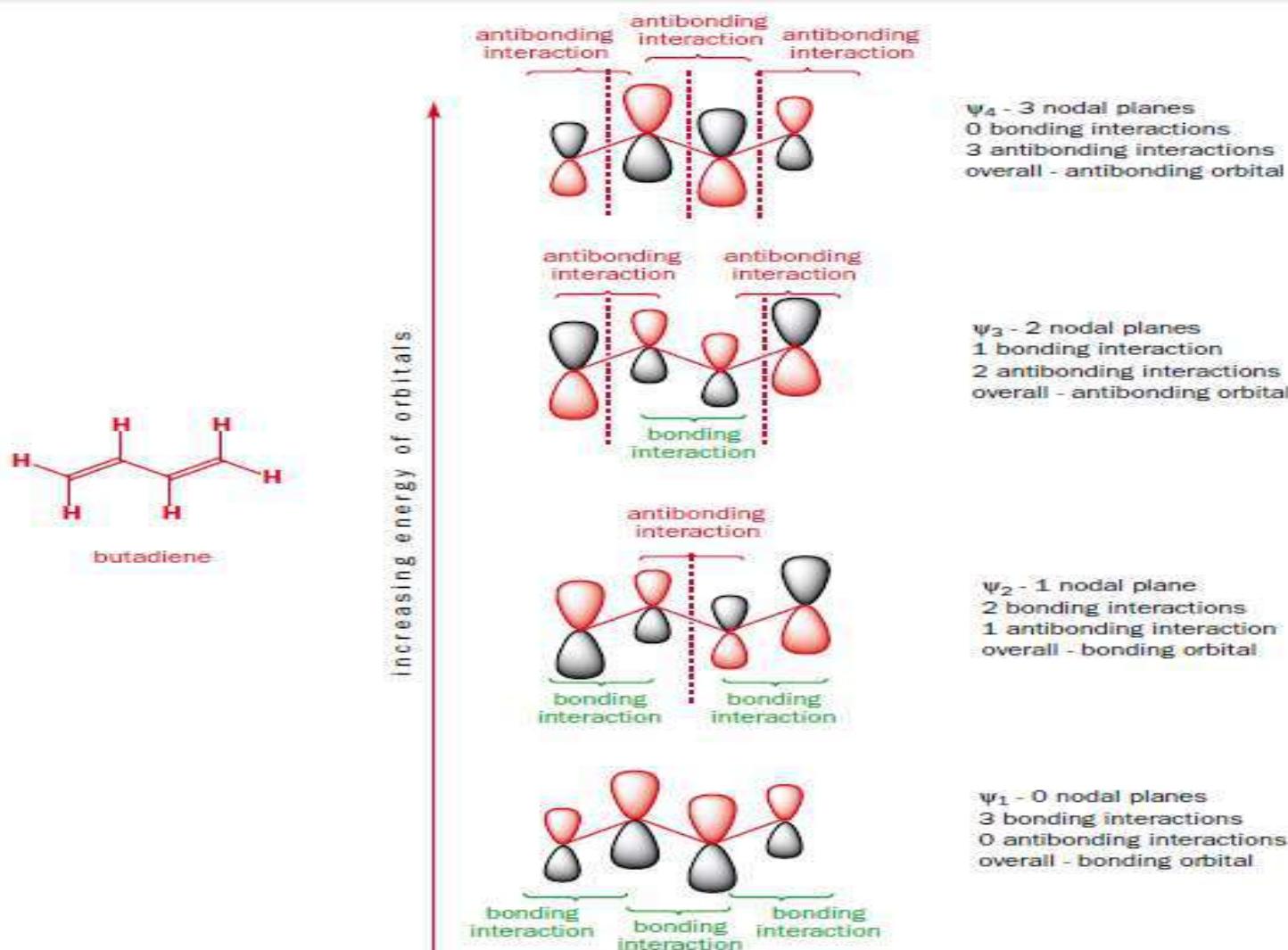
# MO DIAGRAM OF 1,3-BUTADIENE



The molecular orbital diagram for the  $\pi$ -molecular orbitals of butadiene as a result of combining the  $\pi$ -molecular orbitals of two ethene molecules. This shows the effect of conjugation.

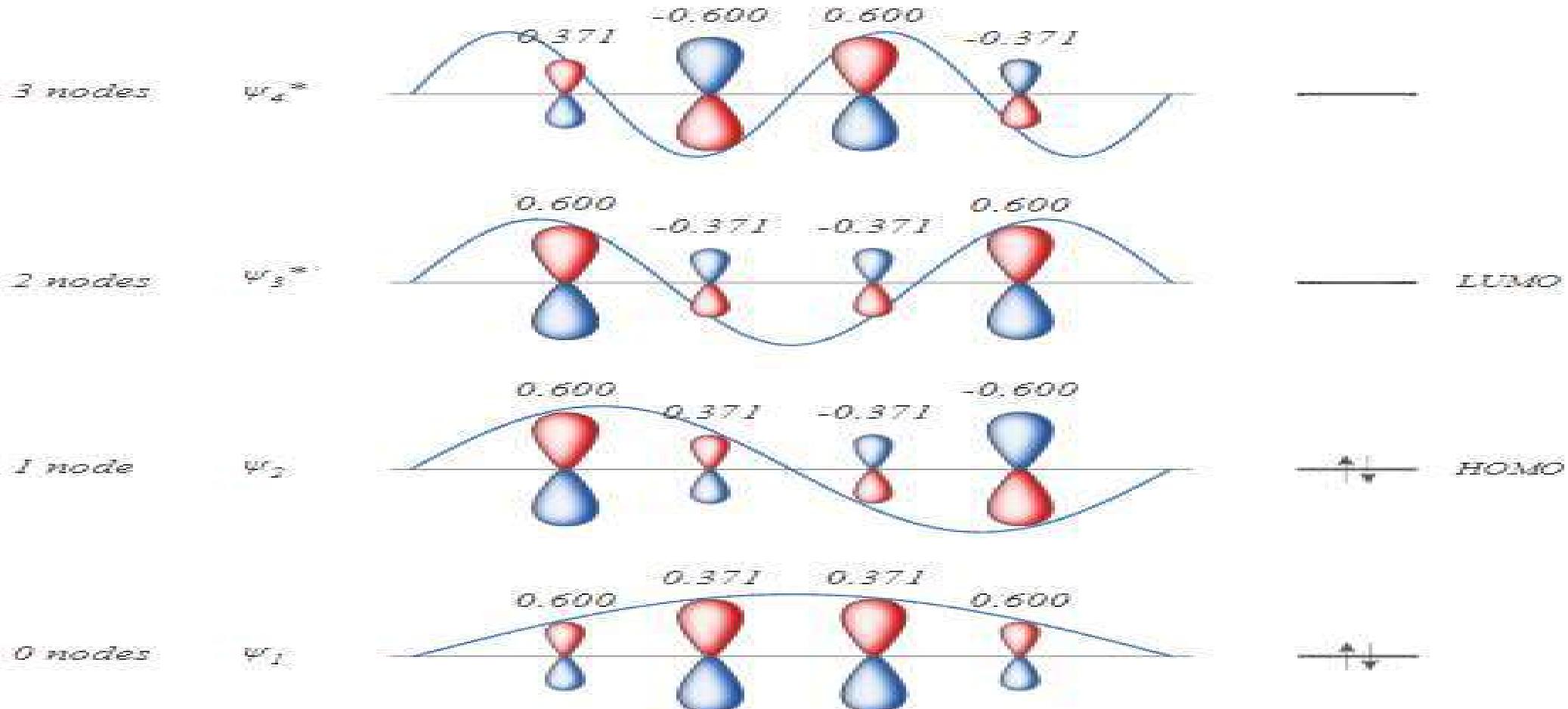


# MO DIAGRAM OF 1,3-BUTADIENE

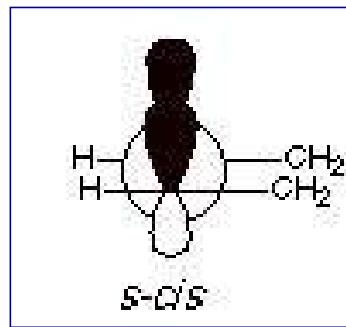
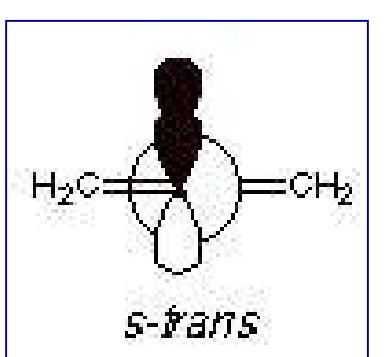
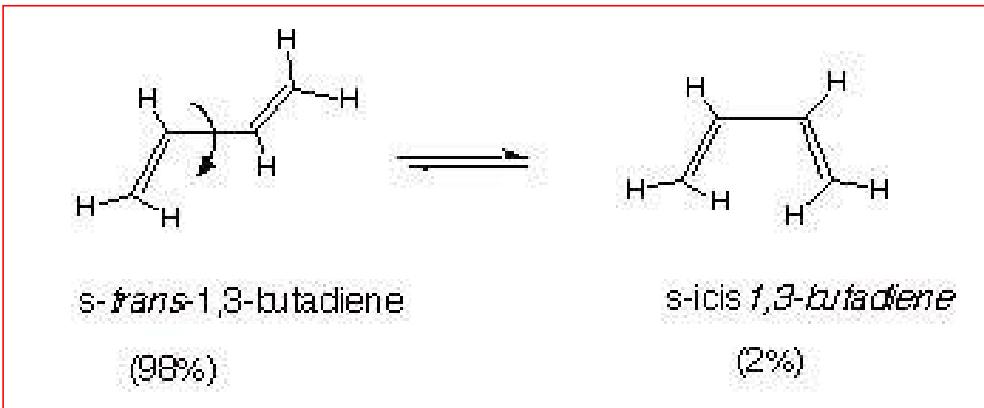


- ✓  $\psi_1$  and  $\psi_2$  are bonding molecular orbitals and are occupied in the ground state with  $\psi_2$  being the Highest Occupied Molecular Orbital (HOMO).
- ✓  $\psi_3^*$  and  $\psi_4^*$  are antibonding molecular orbitals and are unoccupied in the ground state with  $\psi_3^*$  being the Lowest Unoccupied Molecular Orbital (LUMO).
- ✓ The orbitals are arranged in the following table in order of increasing energy.
- ✓ It can also be seen that the number of vertical nodes in a molecular orbital increases as the energy increases.  $\psi_1$  has zero vertical nodes and they increase incrementally until  $\psi_4^*$  which has 3 vertical nodes.
- ✓ It should also be pointed out that these vertical nodes are always arranged symmetrically in the molecular orbital diagrams.

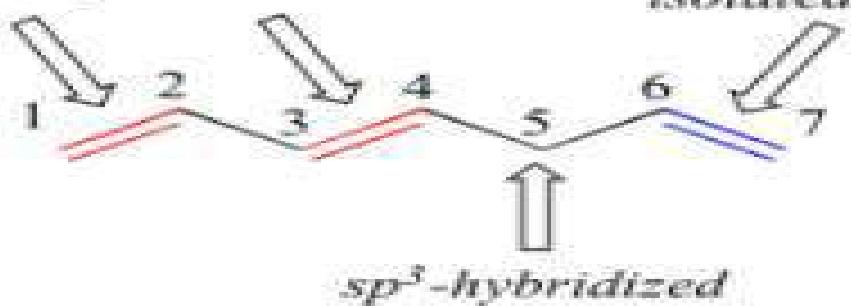
## NODAL PLANE OF 1,3-BUTADIENE



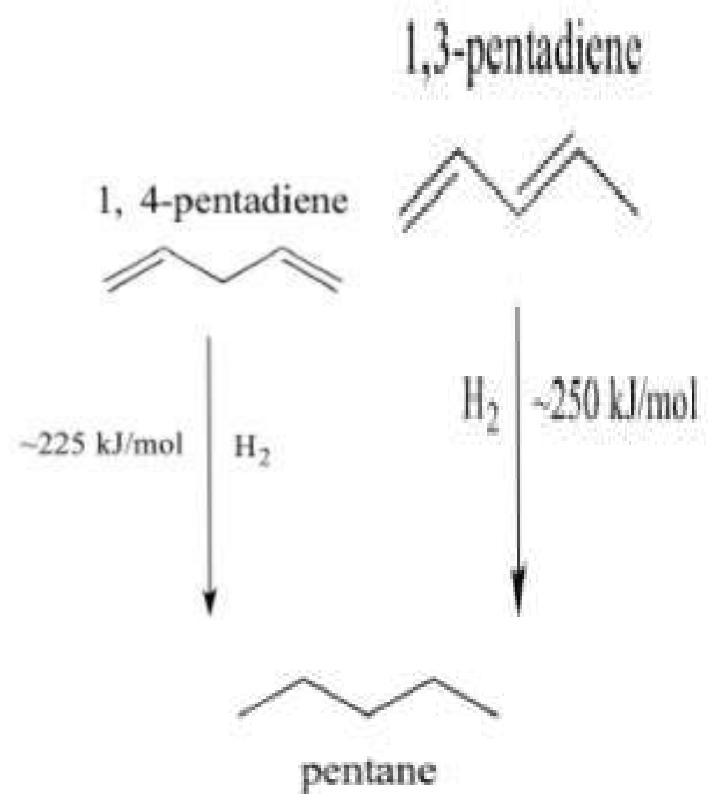
❖ Energy level diagram and decomposition of the  $\pi$  molecular orbitals of butadiene.



*conjugated π bonds*

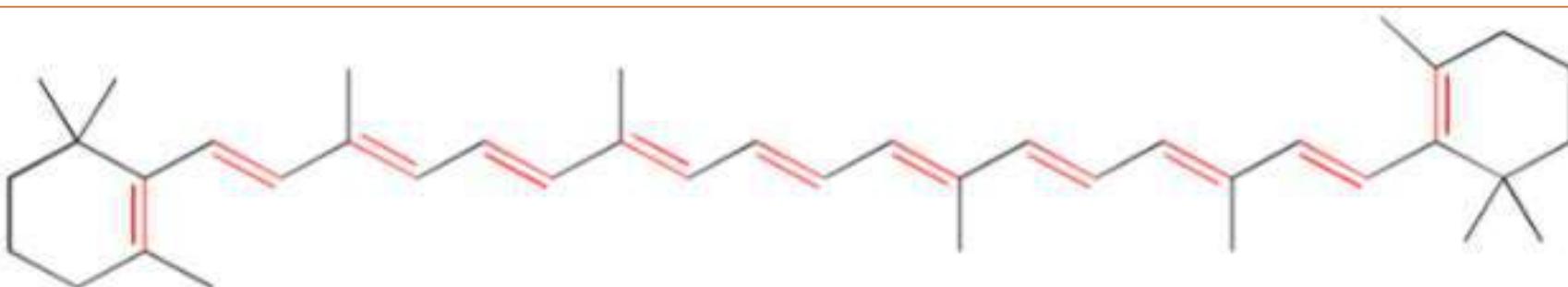


*isolated π bond*

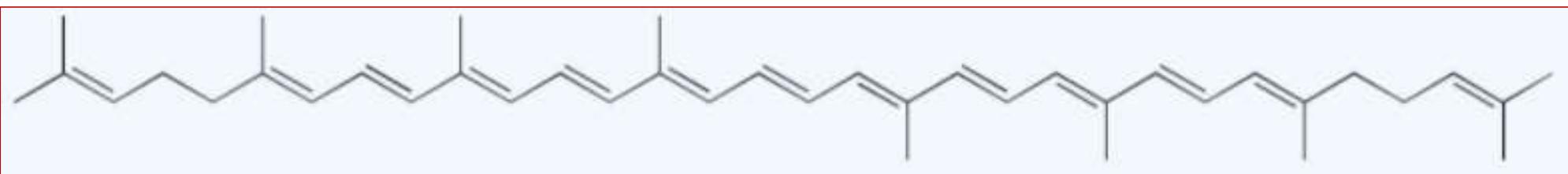


# Conjugation, Color and the Chemistry of Vision

- Visible region is about 400 to 800 nm
- Extended systems of conjugation absorb in visible region
- $\beta$ -Carotene, 11 double bonds in conjugation
  - $\lambda_{\text{max}} = 455 \text{ nm}$



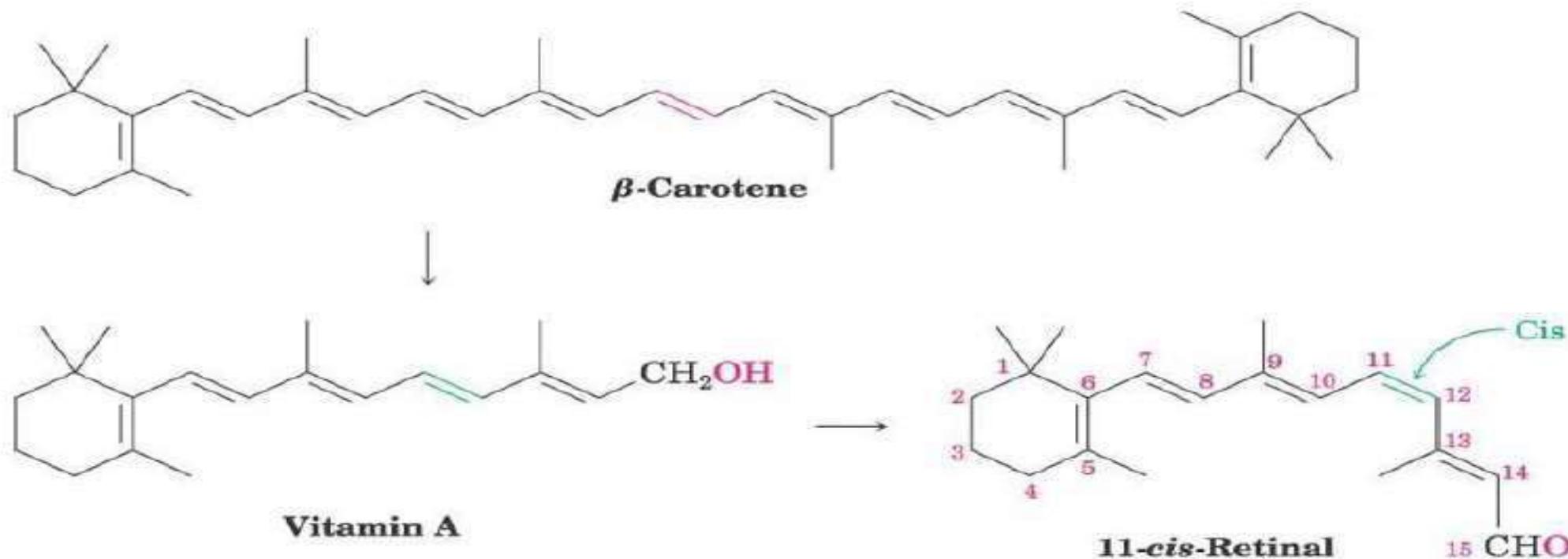
**beta-carotene**, orange colour of carrots



**Lycopene**, Red color in tomatoes

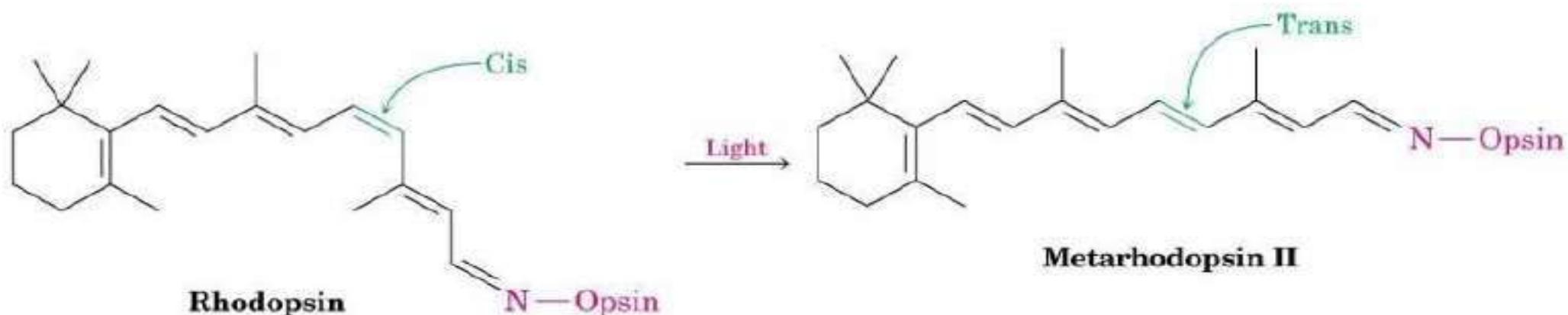
# Conjugation, Color and the Chemistry of Vision

- $\beta$ -Carotene is converted to Vitamin A, which is converted to 11-cis-retinal:

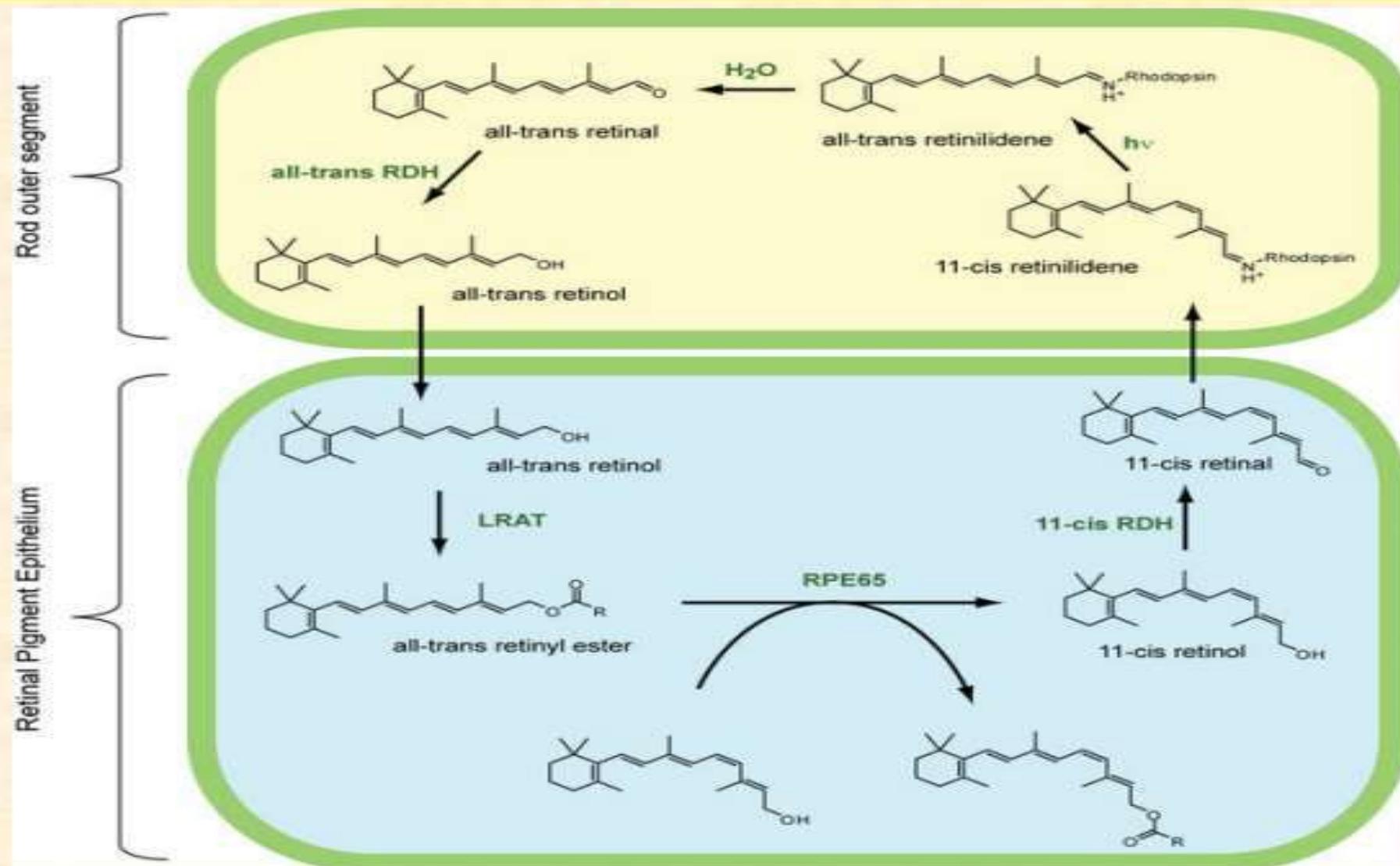


# Conjugation, Color and the Chemistry of Vision

- 11-cis-retinal is converted to rhodopsin in the rod cells of the retina.
- Visual pigments are responsible for absorbing light in eye and triggering nerves to send signal to brain



# Alkadienes and Polyunsaturated Hydrocarbons



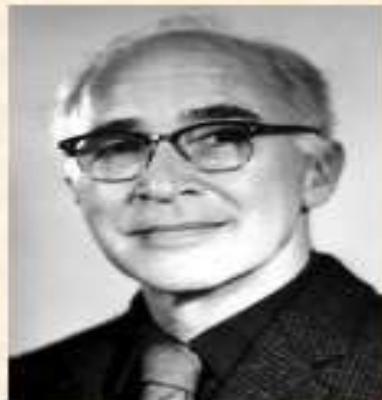
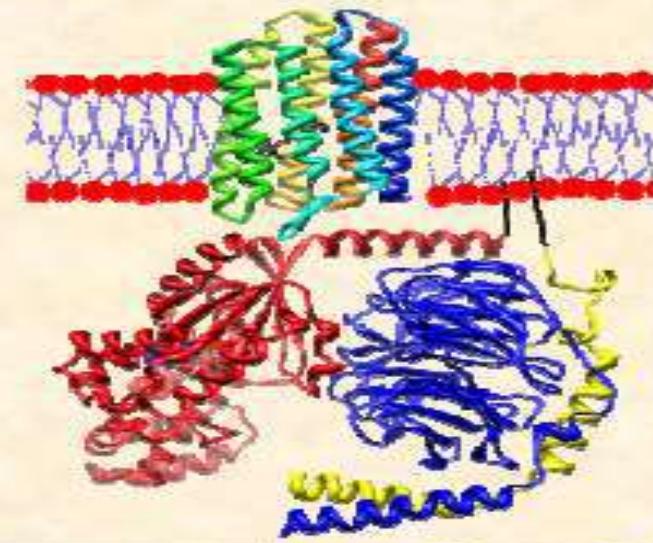
# Alkadienes and Polyunsaturated Hydrocarbons



Nobel Prize in Medicine

1967

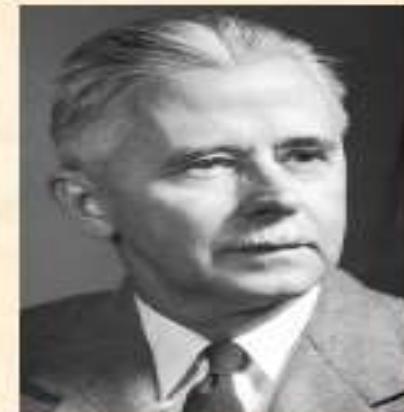
Type 2 rhodopsin



George Wald



Ragnar Granit



Haldan K. Hartline

# The Diels-Alder Reaction



Otto P. H. Diels



Kurt Alder



Nobel Prize in  
Chemistry  
1950



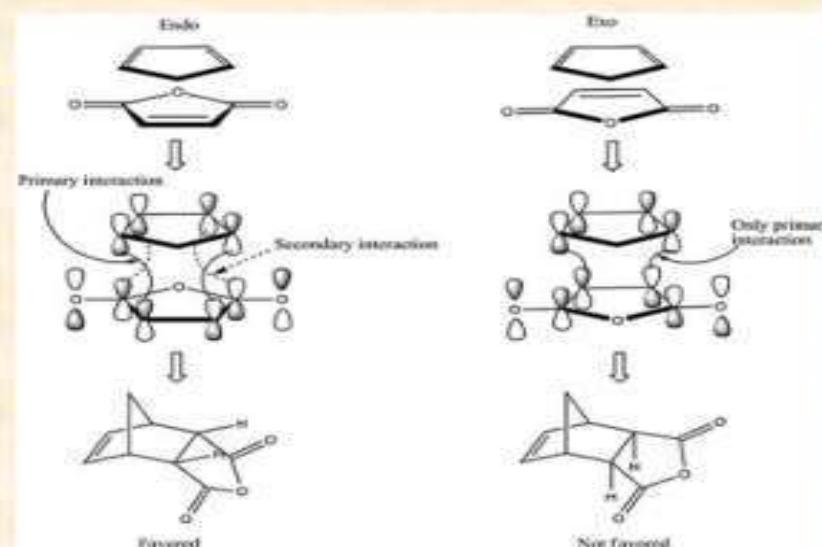
Nobel Prize in  
Chemistry  
1981



Roald Hoffmann

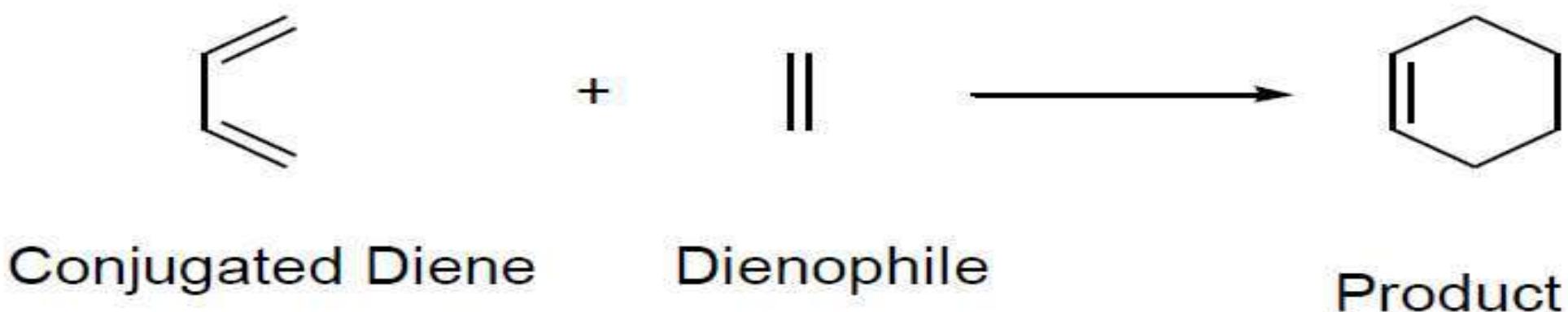


Kenichi Fukui



Robert B.  
Woodward

# What is the Diels-Alder Reaction?

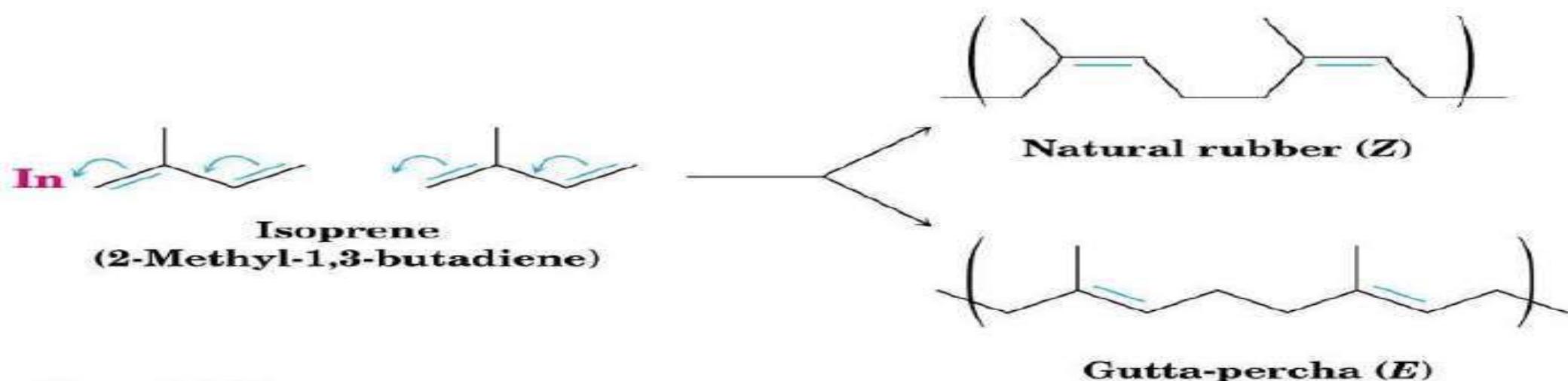


The **Diels-Alder reaction** uses a conjugated diene and a dienophile to produce cyclic and bicyclic carbon structures.

This is also called the **[4 + 2] cycloaddition reaction** for the reaction of 4 pi electrons (diene) and 2 pi electron (dienophile).

# Natural Rubber

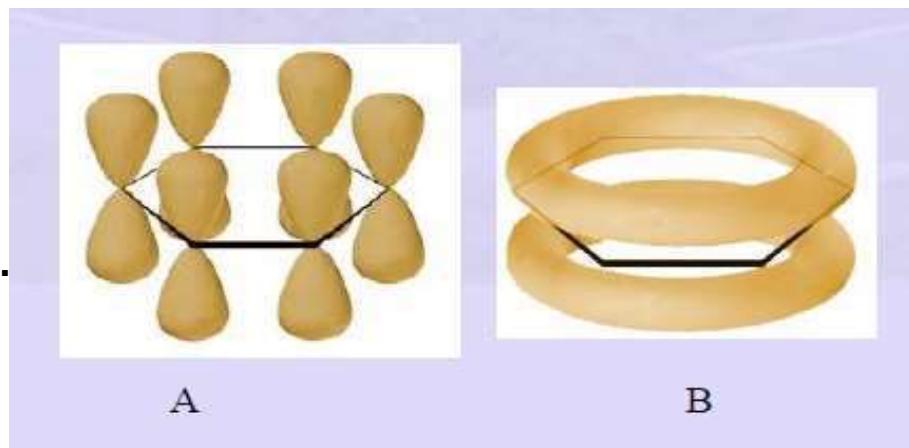
- A material from latex, in plant sap
- In rubber, the repeating unit has 5 carbons and **Z** stereochemistry of all C=C double bonds
- Gutta-Percha is natural material with **E** in all C=C
- They are head-to-tail polymers of isoprene (2-methyl-1,3-butadiene)



# AROMATICITY

The name ‘aromatic’ was originated from the characteristic odor or ‘aroma’ of benzene-like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not. Based on the analysis of a number of compounds with unusual resonance stabilization energies, the following characteristics have been accepted as criteria for aromaticity.

1. **The molecule must be cyclic, planar with uninterrupted cloud of  $\pi$ -electrons above and below the plane of the ring.**
2. **It should have  $4n+2$   $\pi$ -electrons.**



The German Chemist Erich Hückel was the first one to recognize that an aromatic compound must have an even number of pairs of electrons, which can mathematically be written as  $4n+2$  ( $n = 0, 1, 2, 3$  etc). Molecules which obey these rules are aromatic and those which follow these rules partially fall in the category of anti-aromatic and non aromatic compounds. The  $\pi$ -orbital array (A) and delocalization (B) in benzene can be pictorially represented.

# Cyclic

Atoms must be connected to form ring



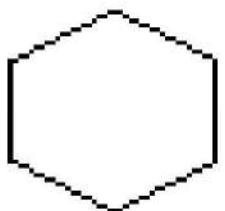
cyclopropane



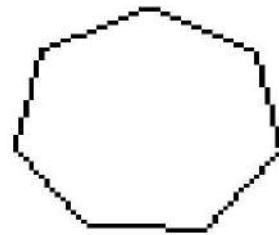
cyclobutane



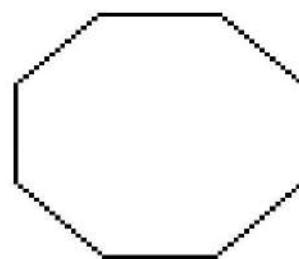
cyclopentane



cyclohexane



cycloheptane

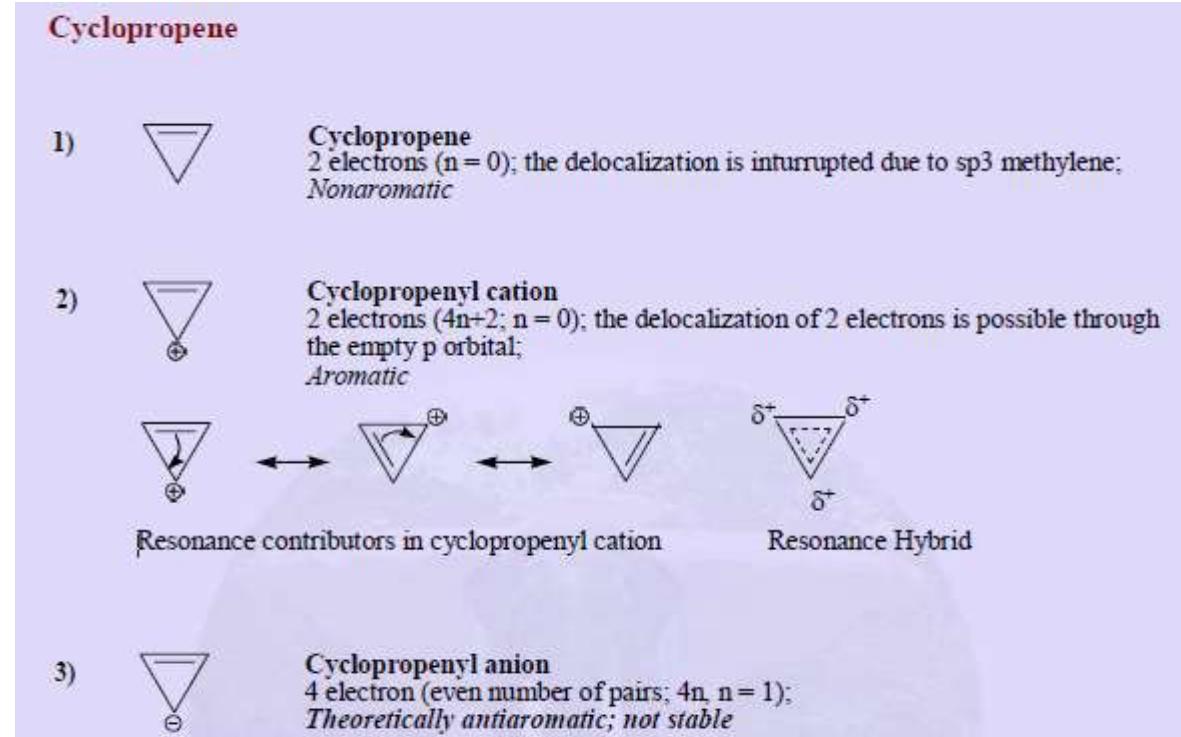


cyclooctane

# CYCLOPROPENE RING SYSTEMS AND THE PROPERTY OF AROMATICITY

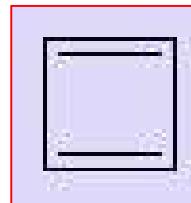
**Non aromatic compounds**, as the name implies, are not aromatic due to reasons such as lack of planarity or disruption of delocalization. They may contain  $4n$  or  $4n+2$   $\pi$ -electrons.

**Antiaromatic compounds** are planar, cyclic, conjugated systems with an even number of pairs of electrons. Such compounds satisfy the first three criteria for aromaticity. i.e. they are planar, cyclic with an uninterrupted ring of p orbital bearing atoms.

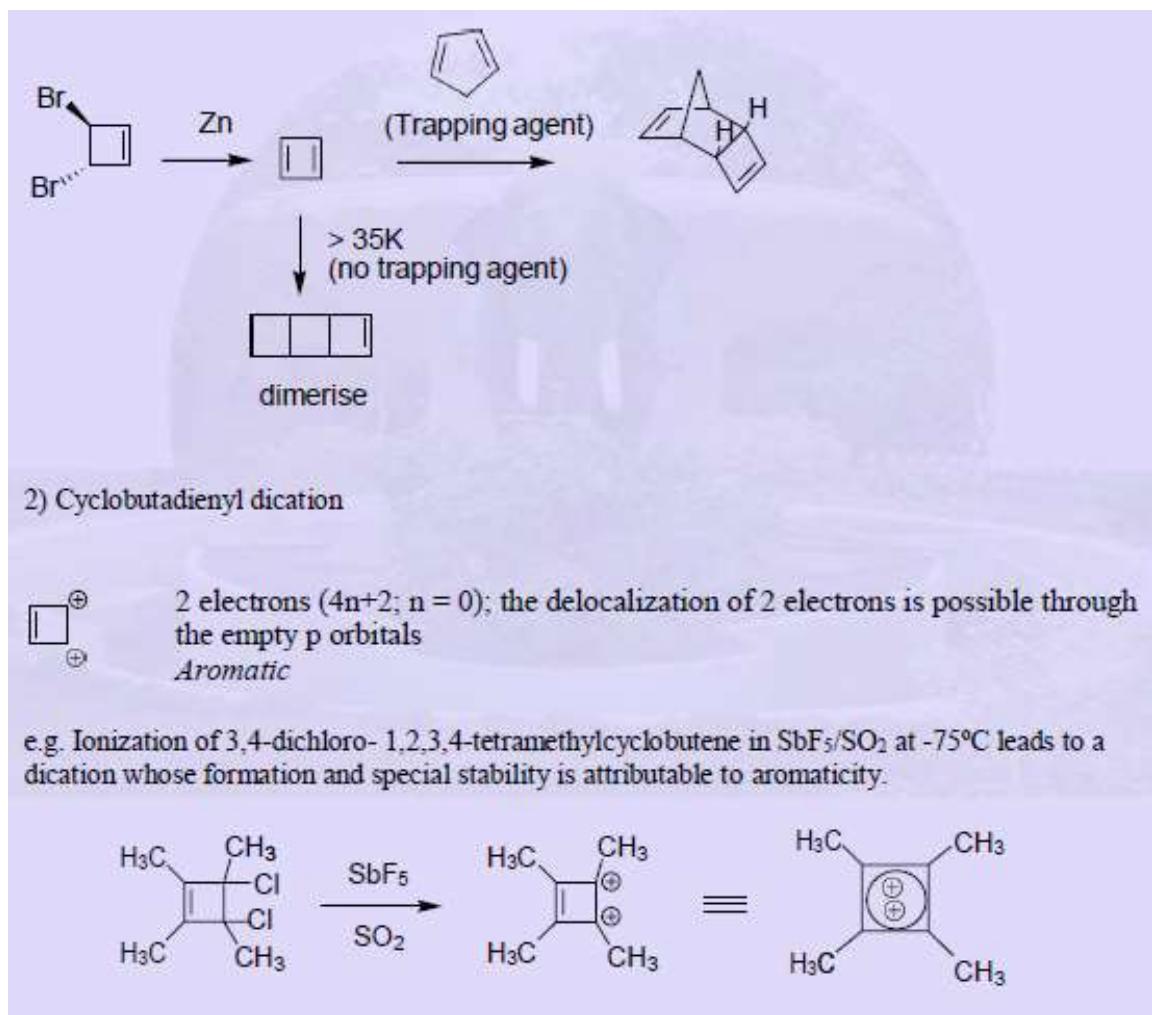
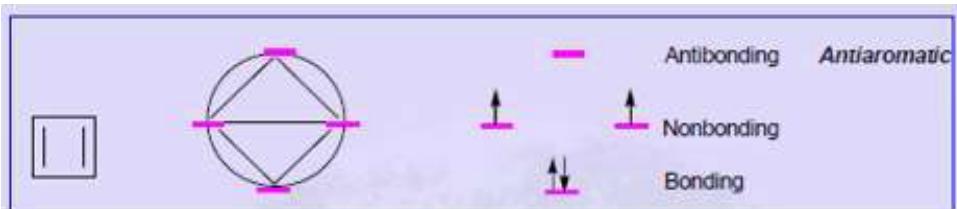


But they have an even number of pairs of  $\pi$ -electrons ( $4n$ ,  $n = 1, 2, 3$  etc). It should be noted that an aromatic compound is more stable compared to an analogous cyclic compound with localized electrons, whereas an antiaromatic compound is less stable compared to an analogous cyclic compound with localized electrons (in  $4n+2$  systems delocalization increases the stability where as in  $4n$  systems, delocalization decreases stability)

# CYCLOBUTADIENE OR [4]-ANNULENE

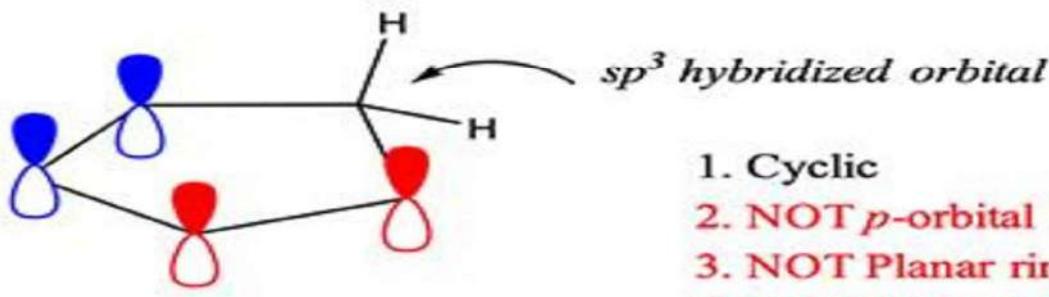


Monocyclic hydrocarbons with alternating single and double bonds are called annulenes. A prefix in brackets denotes the number of carbons in the ring. Being antiaromatic, cyclobutadiene is unstable. It can be isolated only under controlled conditions such as in Argon matrix or using trapping agents such as dienes. Studies show that it has a rectangular structure rather than a square, with C-C bond length of 1.567 Å and C=C bond length of 1.346 Å.



# Not contain SP<sup>3</sup> carbon atom

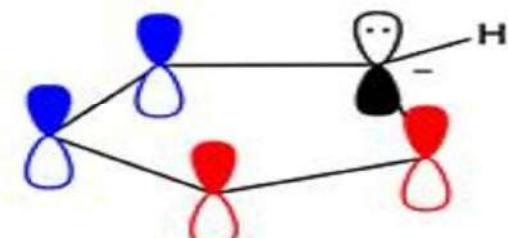
Compound contain SP<sup>3</sup> carbon atom are non



1. Cyclic
2. NOT *p*-orbital for each member of the ring
3. NOT Planar ring (sp<sup>2</sup> hybridized)
4. NOT Closed 4n+2 π-bond ring.

---

Not Aromatic



1. Cyclic
2. *p*-orbital for each member of the ring
3. Planar ring (sp<sup>2</sup> hybridized)
4. Closed 4n+2 π-bond ring.

---

Aromatic

# CYCLOPENTADIENE

1)



Cyclopentadiene

4 electron system (even number of pairs);

Does not have an uninterrupted ring of p orbital bearing atoms (conjugation);  
*Nonaromatic*.

2)



4 electron (even number of pairs;  $4n$ ,  $n = 1$ );

Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation);  
*antiaromatic*

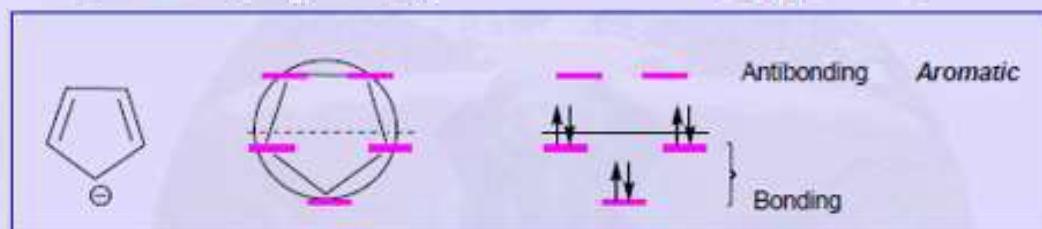
Cyclopentadienyl cation

3)



6 electron system ( $4n+2$ ,  $n = 1$ ), cyclic, planar with conjugation;  
*Aromatic*

Cyclopentadienyl anion



The  $pK_a$  of cyclopentadiene is 15, which is extraordinary for hydrogen bonded to a  $sp^3$  carbon.  
The reason for this low  $pK_a$  is its high tendency to become aromatic by releasing a proton.

## Benzene [6]-Annulene



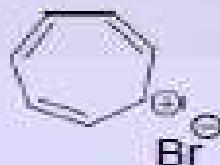
A perfect example of cyclic planar molecule with uninterrupted ring of p orbital bearing atoms; 6 electron system ( $4n+2$ ,  $n = 1$ )  
*Aromatic*

## 7-membered rings- Cycloheptatriene



Although a  $6\pi$  electron system, one of the atoms in the cyclic structure can not contribute a p orbital for conjugation.

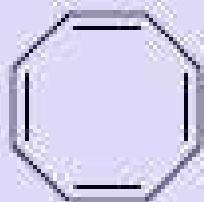
*Nonaromatic*



$6\pi$  electron system, Cyclic, conjugated, planar with  $4n+2$  p electrons  
*Aromatic*

Alkyl halides such as cyclopentyl chloride are nonpolar and dissolve in non-polar solvents and remain insoluble in water. Surprisingly, cycloheptatrienyl bromide is an exception. It is insoluble in nonpolar solvents, but dissolves in water! It turns out that cycloheptatrienyl bromide is an ionic compound, since its cation (known as tropylum cation) is aromatic. In the covalent form, there is no continuity in p orbital overlap as one of the carbon atoms is  $sp^3$  hybridized.

## 8 membered ring, Cyclooctatetraene or [8]-annulene



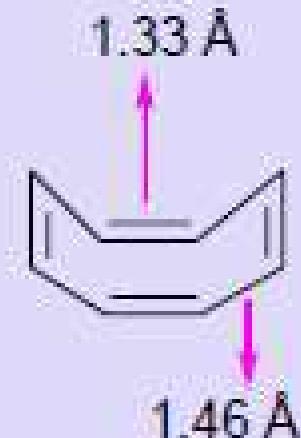
8  $\pi$  electron system;

If completely planar, this molecule will become **antiaromatic**

(bond angle for planar structure =  $135^\circ$  which can give considerable angle strain in a cyclic structure involving  $sp^2$  carbon atoms);

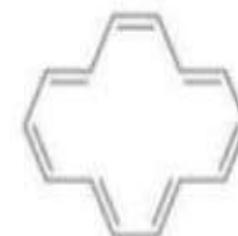
The molecule is actually boat shaped and **nonaromatic**.

(Nonaromatic form is more stable than an antiaromatic form)

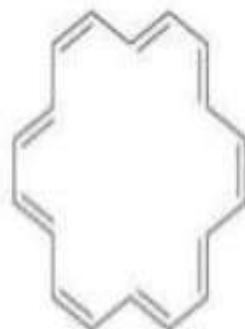


## Annulene

- Hydrocarbons containing a single ring with alternating double and single bonds are called annulenes.
- Completely conjugated rings larger than benzene are also aromatic if they are planar and have  $4n + 2 \pi$  electrons.
- To name an annulene, indicate the number of atoms in the ring in brackets and add the word annulene.



[14]-annulene  
 $4n + 2 = 4(3) + 2 =$   
14  $\pi$  electrons  
aromatic



[18]-annulene  
 $4n + 2 = 4(4) + 2 =$   
18  $\pi$  electrons  
aromatic

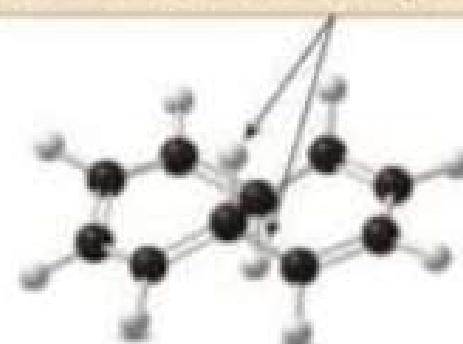
- [10]-Annulene has 10  $\pi$  electrons, which satisfies Hückel's rule, but a planar molecule would place the two H atoms inside the ring too close to each other. Thus, the ring puckers to relieve this strain.
- Since [10]-annulene is not planar, the 10  $\pi$  electrons can't delocalize over the entire ring and it is not aromatic.

[10]-Annulene fits Hückel's rule,  
but it's **not** planar.



[10]-annulene  
10  $\pi$  electrons  
not aromatic

The molecule puckers to keep  
these H's further away from each other.

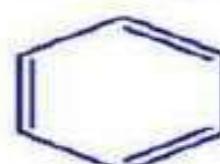


3-D representation

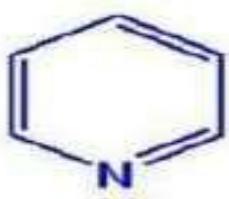
# Huckel's rule

The aromatic compounds must contain **(4n+2) π electrons**  
(n = integer number, 0, 1, 2, ....)

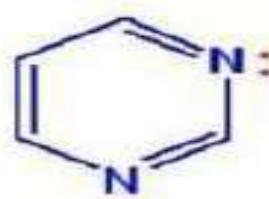
## Other Aromatic systems



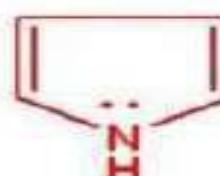
$$\pi \text{ electrons} = 6 = 4n + 2$$
$$n = 1 \text{ (integer number)}$$



Pyridine



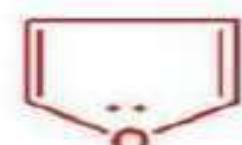
Pyrimidine



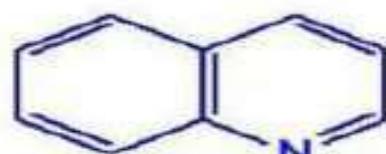
Pyrrole



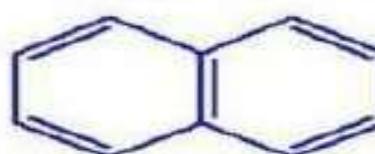
Thiophene



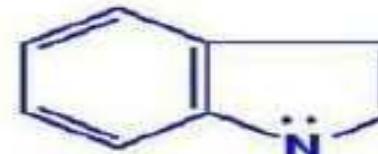
Furan



Quinoline



Naphthalene



Indole

6 π electrons

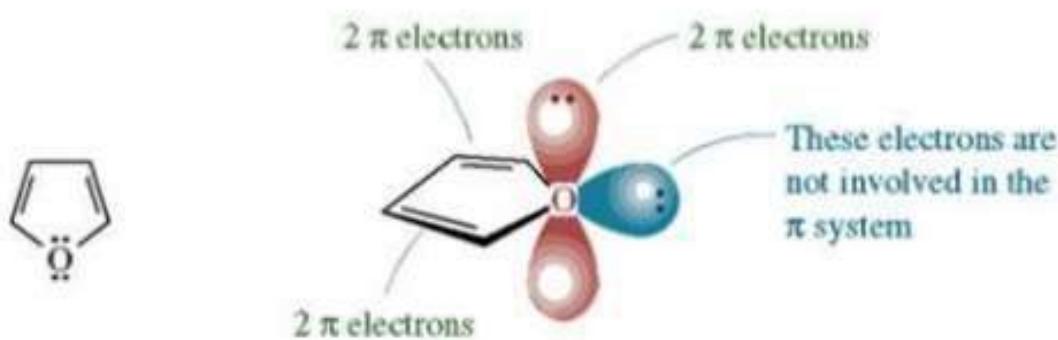
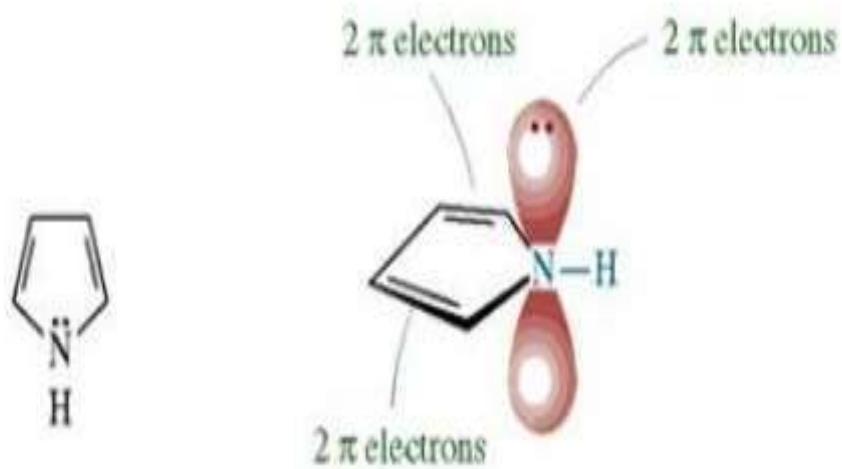
10 π electrons

## Pyrrole

A five-membered heterocycle with one nitrogen

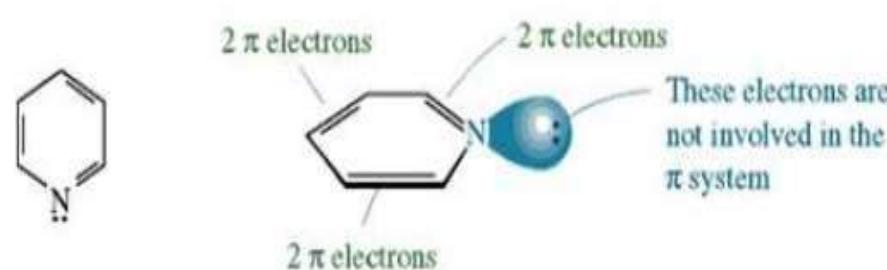
$\pi$  electron system similar to that of cyclopentadienyl anion

Nitrogen atom is  $sp^2$ -hybridized, and lone pair of electrons occupies a  $p$  orbital ( $6\pi$  electrons)

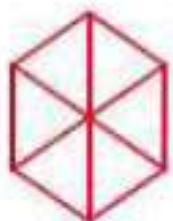


## Pyridine

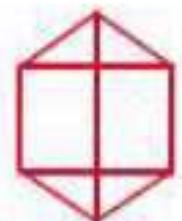
- A six-membered heterocycle with a nitrogen atom in its ring
- $\pi$  electron structure resembles benzene (6 electrons)
- The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)



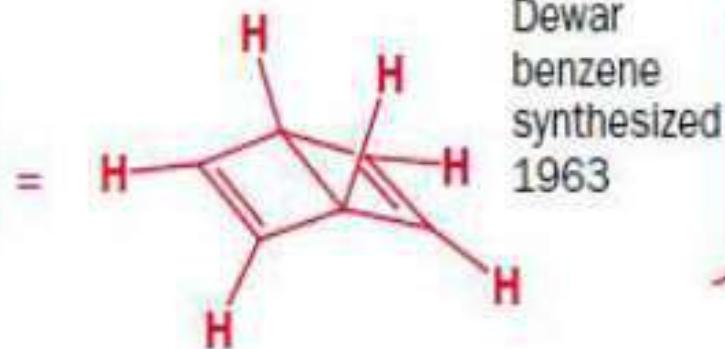
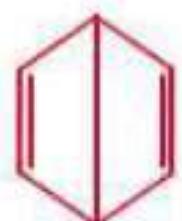
## PROPOSED STRUCTURES FOR BENZENE



these diagrams represent old structures for benzene. They do not represent compounds that could ever be made

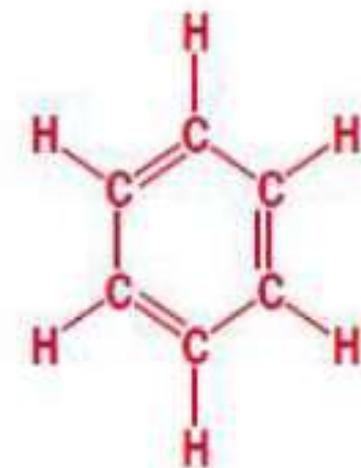


prismane  
synthesized  
1973



Dewar  
benzene  
synthesized  
1963

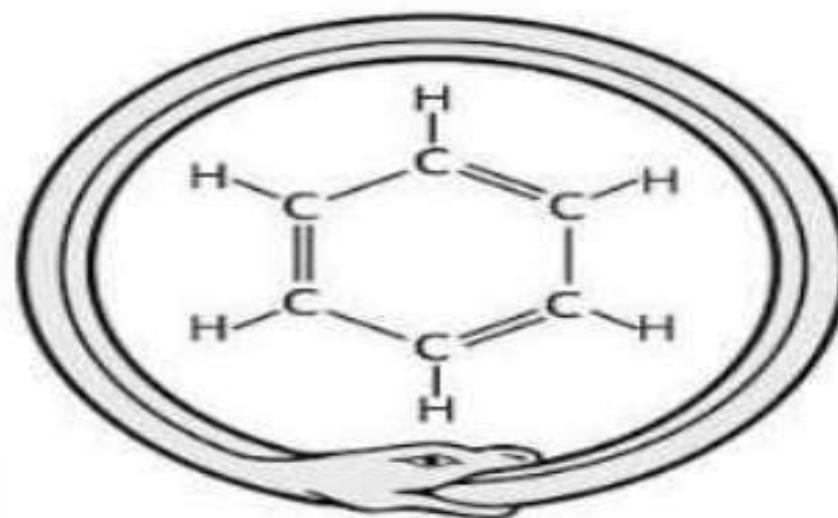
these early suggestions for the structure of benzene have now been made. they are certainly not benzene, but entirely different compounds



Kekulé's structure for benzene

## BENZENE

- ❖ KEKULE fall asleep while sitting in front of fire, dreamed about chains of atoms in form of twisting snakes. one of snake caught hold of its own tail , forming a whirling ring.
- ❖ KEKULE awoke , freshly inspired , spent remainder night working on his now-famous hypothesis.

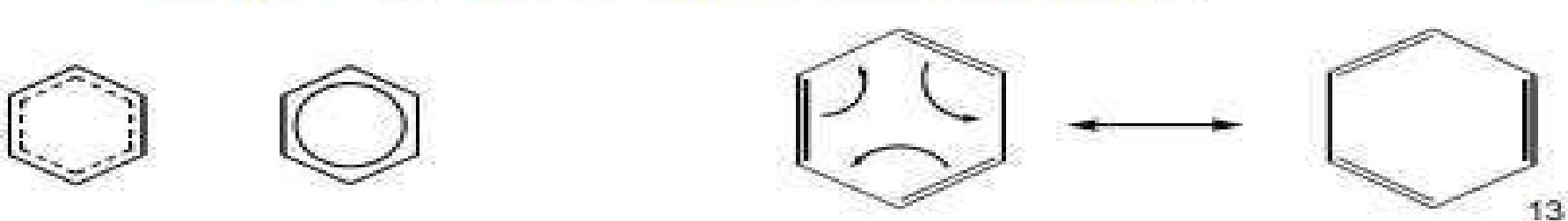


## Structure of Benzene:

Kekulé benzene: two forms are in rapid equilibrium



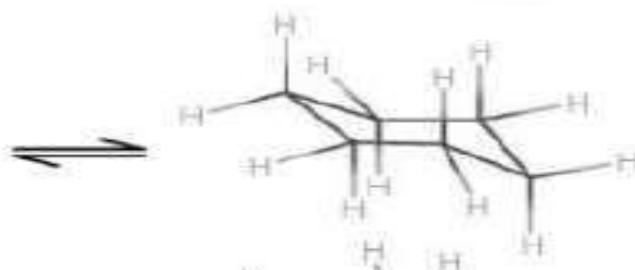
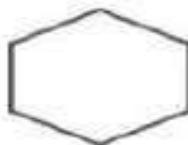
- All bonds are ~139 pm (intermediate between C-C and C=C)
- Electron density is distributed evenly between the six carbons
- Structure is planar, hexagonal
- C–C–C bond angles are 120°
- Each carbon is  $sp^2$  and has a  $p$  orbital perpendicular to the plane of the six-membered ring



# Planar with resonance bonds

Atoms must be connected to form ring

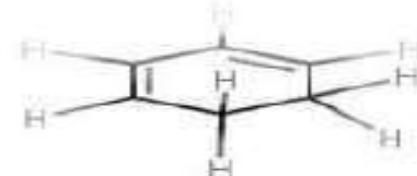
Chair conformation.  
NOT planar.



Half-chair conformation.  
NOT planar.



The **ring** is planar;  
The hydrogens are NOT.

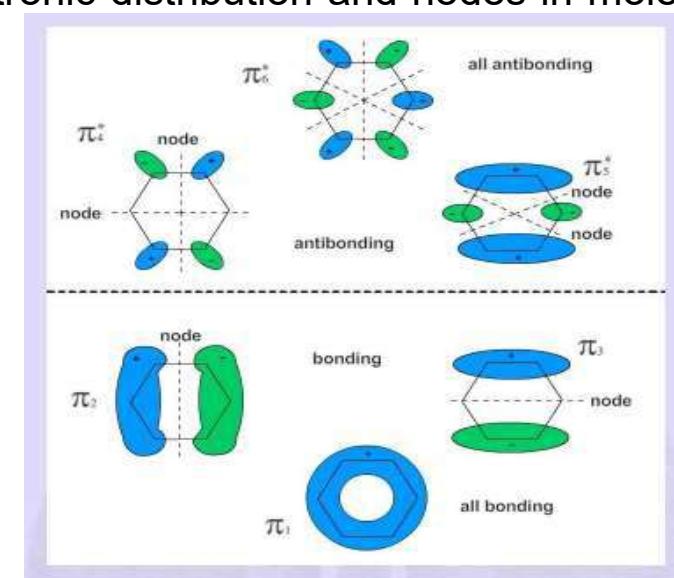
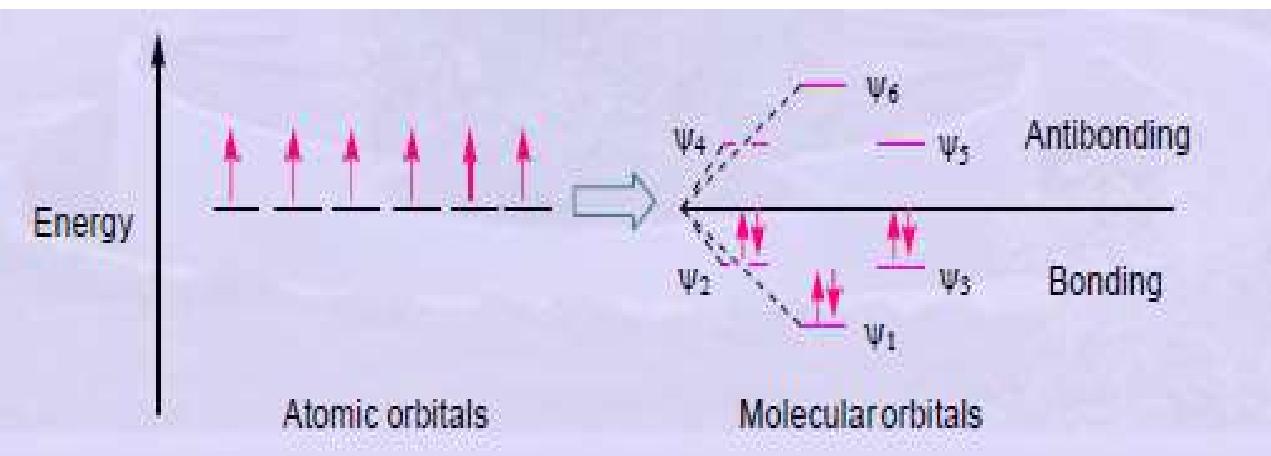


Planar

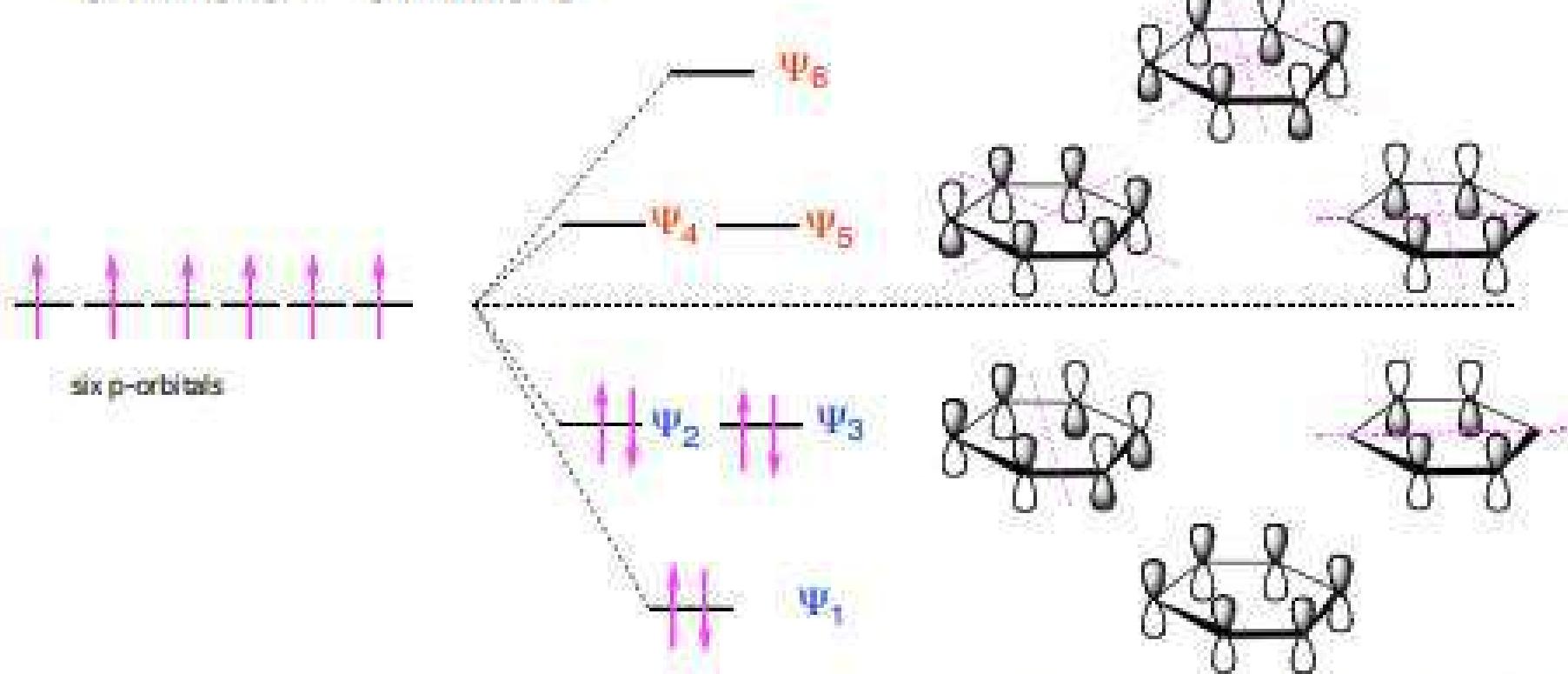


# MOT DESCRIPTION OF AROMATICITY

The structure of benzene is based on molecular orbital theory, all the six sp<sup>2</sup> carbon atoms are arranged in such a way that each uses two of its hybridized orbitals to bond to adjacent carbon atoms and the third one to bond to the 1s orbital of hydrogen. The un-hybridized p orbital associated with each carbon atom contain one electron and lie perpendicular to the plane of the ring. According to molecular orbital theory, these six p orbitals combine to form six molecular orbitals, three of which are bonding and three, anti-bonding. Six  $\pi$ -electrons occupy the bonding orbitals, which are lower in energy compared to the un-hybridized p orbitals (atomic orbitals). The relative energies of atomic orbitals and molecular orbitals and a more comprehensive picture of electronic distribution and nodes in molecular orbitals in benzene are shown below.



SIX AO's = SIX MO's



Degenerate orbitals: orbitals that have the same energy

$\Psi_1$ : zero nodes  
 $\Psi_2$  and  $\Psi_3$ : one node

$\Psi_4$  and  $\Psi_5$ : two nodes  
 $\Psi_6$ : three node

Bonding

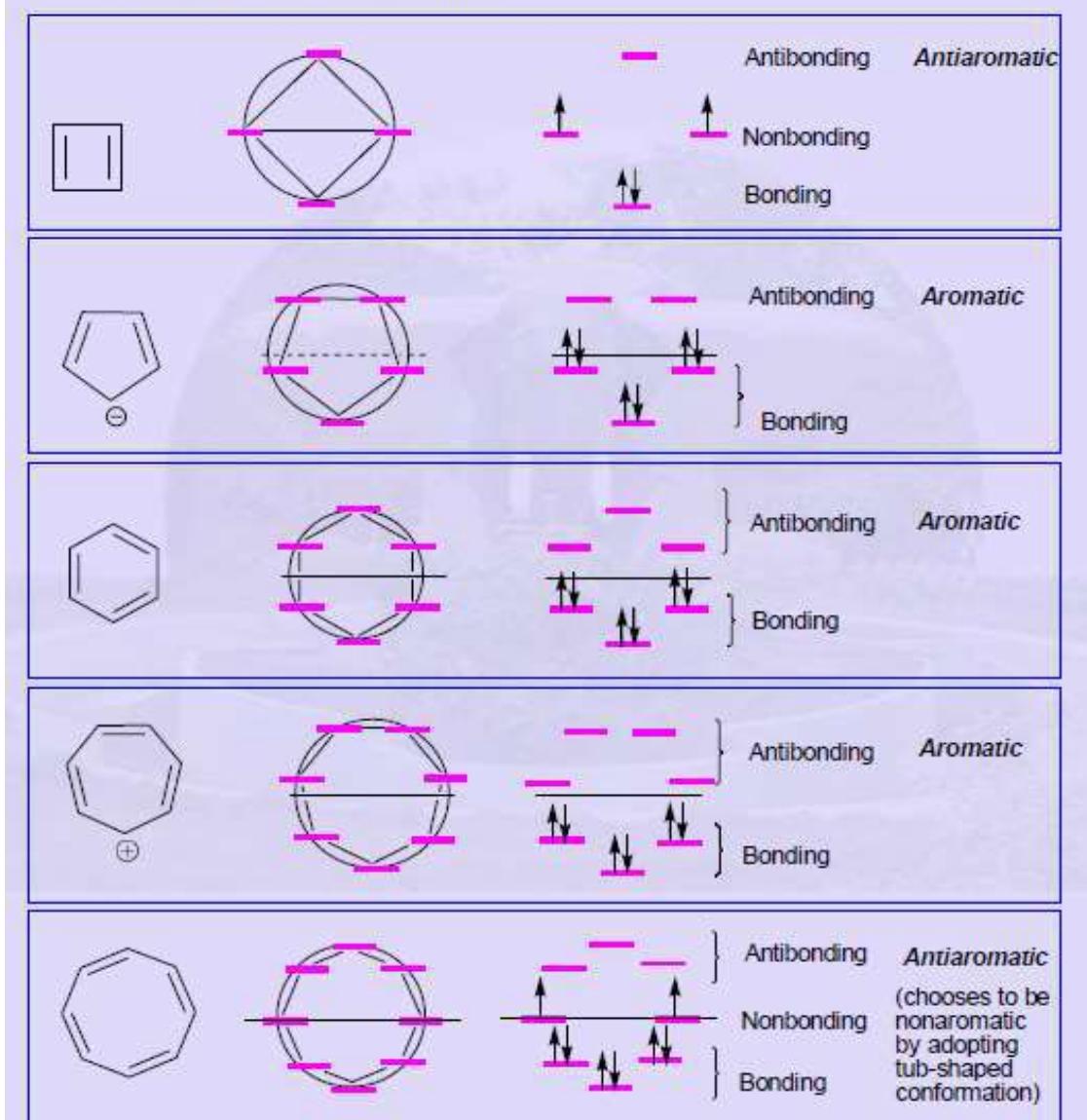
Anti-bonding

The relative energies of  $\pi$ -molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by A. A. frost in 1953. This involves the following steps:

- 1) Draw a circle
- 2) Place the ring (polygon representing the compound of interest) in the circle with one of its vertices pointing down. Each point where the polygon touches the circle represents an energy level.
- 3) Place the correct number of electrons in the orbitals, starting with the lowest energy orbital first, in accordance with Hund's rule.

If the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital. Energy levels below this line indicate bonding MOs and those above are anti-bonding.

Frost diagrams - Illustrative examples



## 15.9: Polycyclic aromatic hydrocarbons (PAH's):



benzene



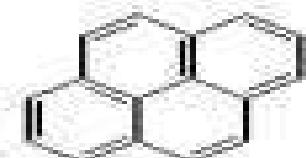
naphthalene



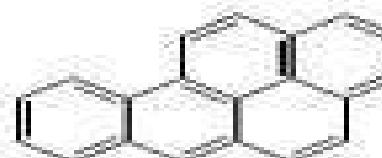
anthracene



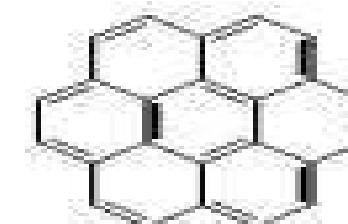
phenanthrene



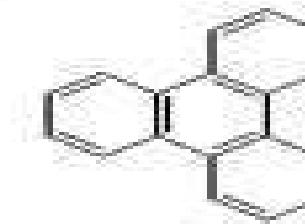
pyrene



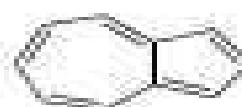
benzo[a]pyrene



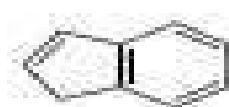
coronene



triphenylene



azulene



indene



flourene

## Polycyclic heterocycles



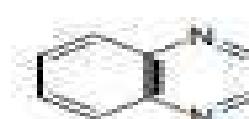
carbazole



indole



quinoline



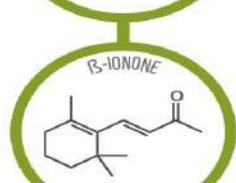
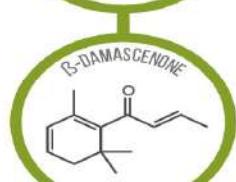
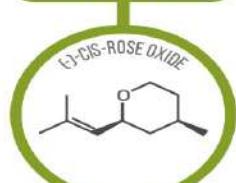
quinoxaline

# AROMA COMPOUNDS IN COMMON FLOWERS

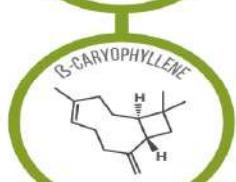
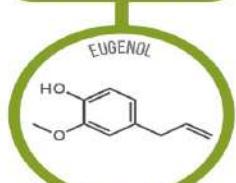
A wide range of compounds contribute to the scents of flowers. This graphic looks at a selection of major contributors for a number of common flowers. Note that volatile aroma compounds can vary significantly between species; this graphic represents a broad overview of common components, and is by no means definitive!



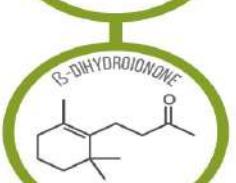
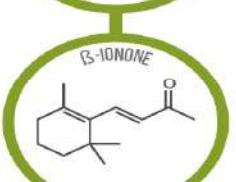
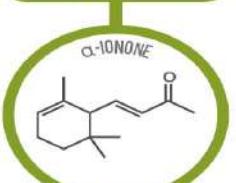
Roses



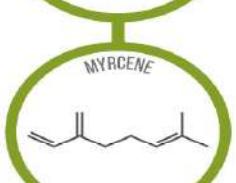
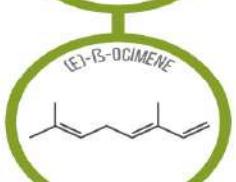
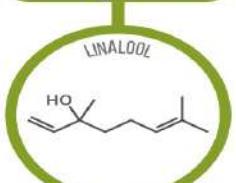
Carnations



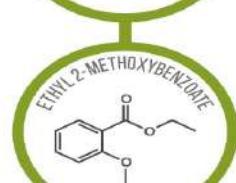
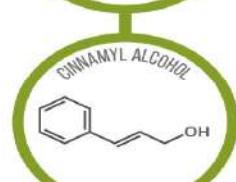
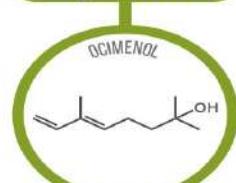
Violets



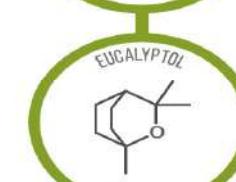
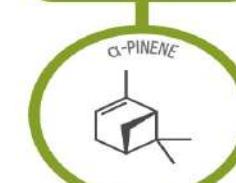
Lilies



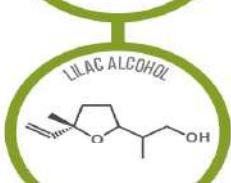
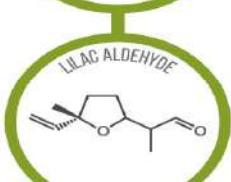
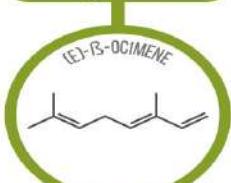
Hyacinth



Chrysanthemums



Lilacs

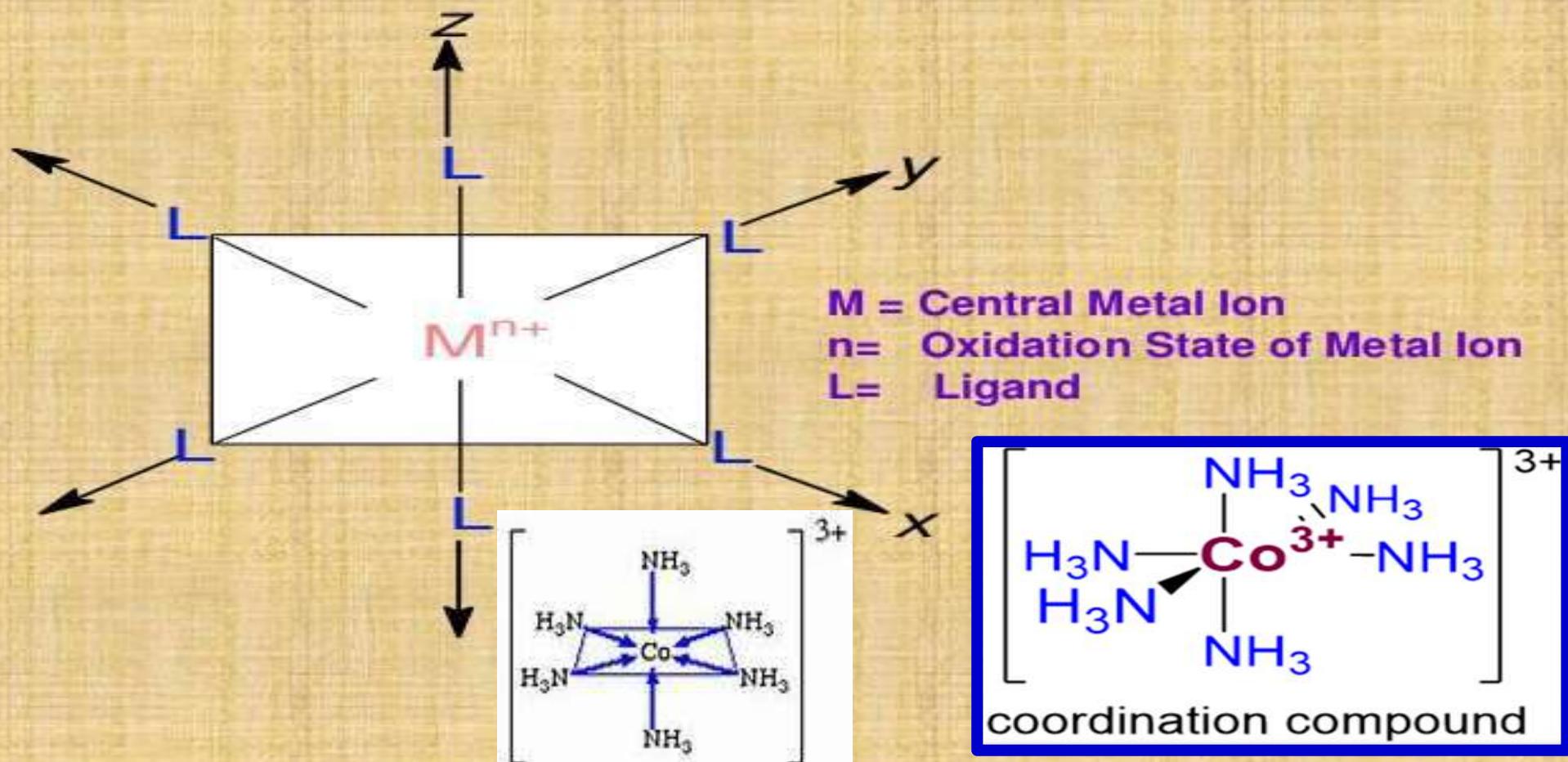


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# CRYSTAL FIELD THEORY

The Crystal Field Theory was developed by Bethe and Van Vleck in 1929 to explain bonding and properties of metal complexes and further modified by Orgel.



## Transition Metal Gems

Gemstone owe their color from trace transition-metal ions

Corundum mineral,  $\text{Al}_2\text{O}_3$ : Colorless

$\text{Cr} \rightarrow \text{Al}$  : Ruby

$\text{Mn} \rightarrow \text{Al}$ : Amethyst

$\text{Fe} \rightarrow \text{Al}$ : Topaz

$\text{Ti} \& \text{Co} \rightarrow \text{Al}$ : Sapphire

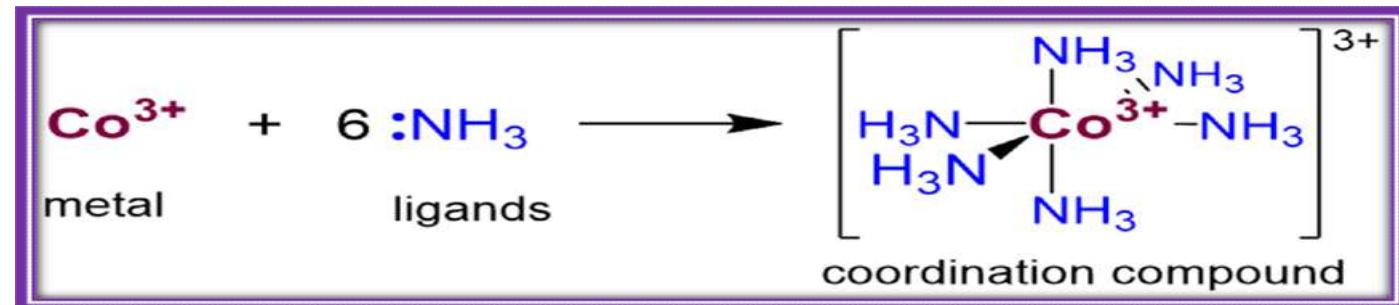
Beryl mineral,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ : Colorless

$\text{Cr} \rightarrow \text{Al}$  : Emerald

$\text{Fe} \rightarrow \text{Al}$ : Aquamarine



## ASSUMPTIONS



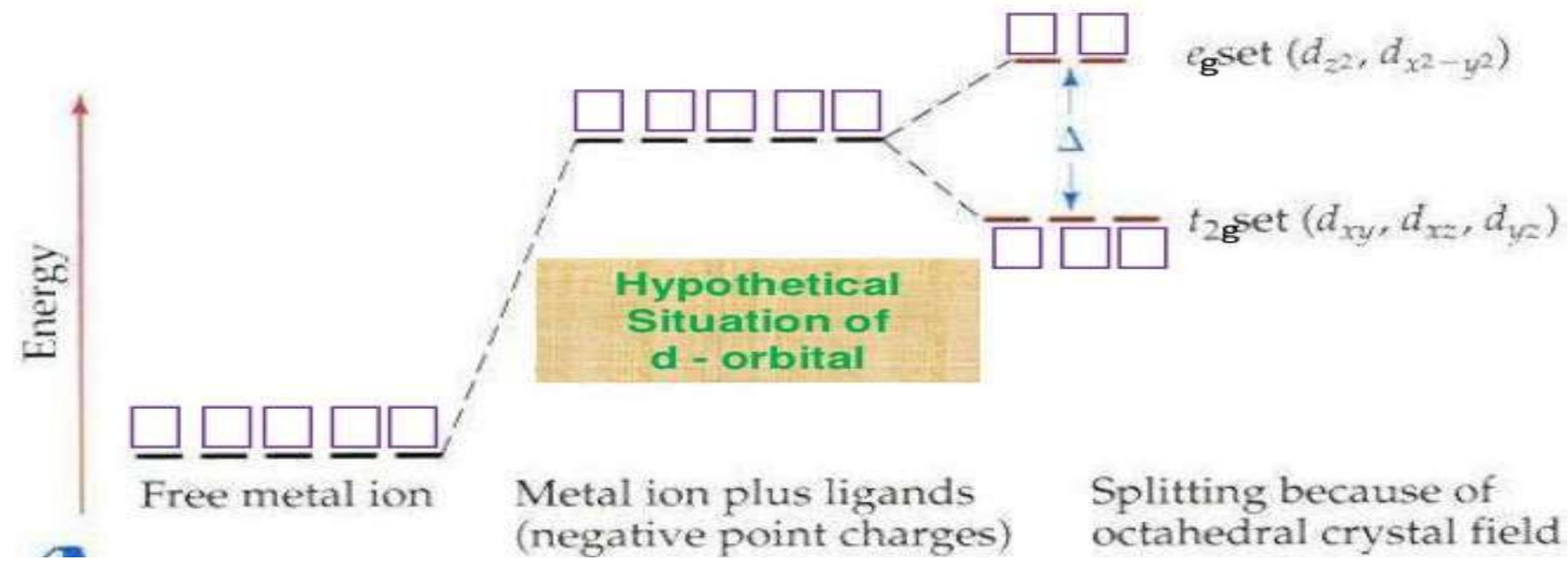
- The transition metal ions are placed in the centre and it is surrounded by ligand with lone pair of electrons.
- The ligand are either negative (e.g.  $\text{Cl}^-$ ,  $\text{CN}^-$ ) or neutral molecule (e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ) are considered as point charge. If ligand is neutral, then negative end of dipole (lone pair) is directed towards metal ion.
- There is no interaction between metal orbitals and ligand orbitals.
- The attraction between metal ion and ligand is purely electrostatic i.e. 100% ionic band.
- The degeneracy of d-orbital of free metal ion is removed by ligand when complex is formed.
- This theory has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colours).
- CFT successfully accounts for some magnetic properties, colours, hydration enthalpies, and spinel structures of transition metal complexes.
- CFT was subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

## CRYSTAL FIELD THEORY - ENERGY LEVEL DIAGRAM

- ❖ The nature of the metal ion means the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
- ❖ The coordination number of the metal means the arrangement of the ligands around the metal ion. (i.e. tetrahedral, square planar, octahedral)
- ❖ The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals ( $t_{2g}$ ) will be lower in energy than the  $d_{z^2}$  and  $d_{x^2-y^2}$  ( $e_g$ ).
- ❖ The most common type of complex is **octahedral**, in which **six ligands** form the vertices of an octahedron around the metal ion.
- ❖ In octahedral symmetry the d-orbitals split into **two sets** with an energy difference,  $\Delta_{\text{Oct}}$  (the crystal-field splitting parameter, also commonly denoted by  $10Dq$ ).
- ❖ These three lower-energy orbitals are collectively referred to as  $t_{2g}$ , and the two higher-energy orbitals as  $e_g$ .

The  $t_{2g}$  group is farther from the ligands than the  $e_g$  and therefore experiences less repulsion.

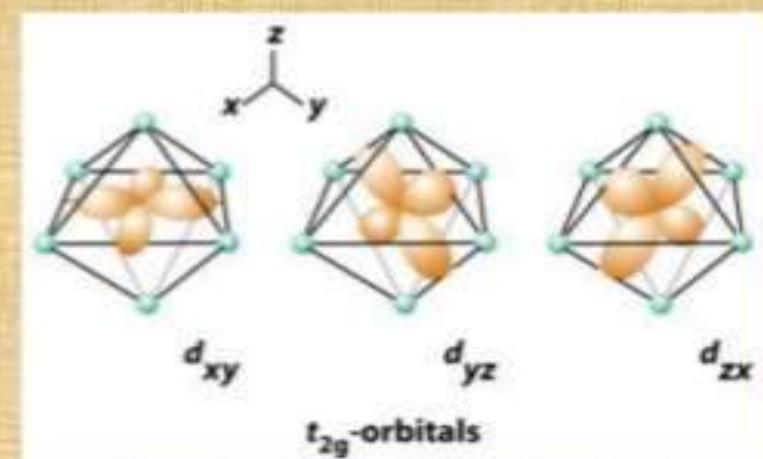
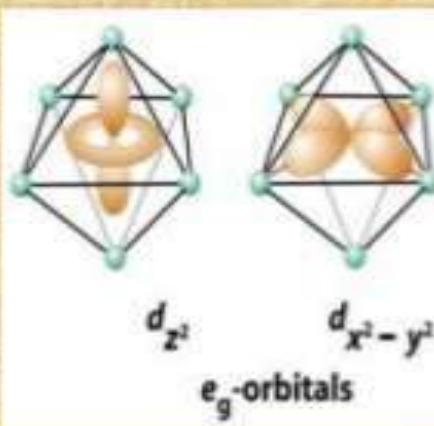
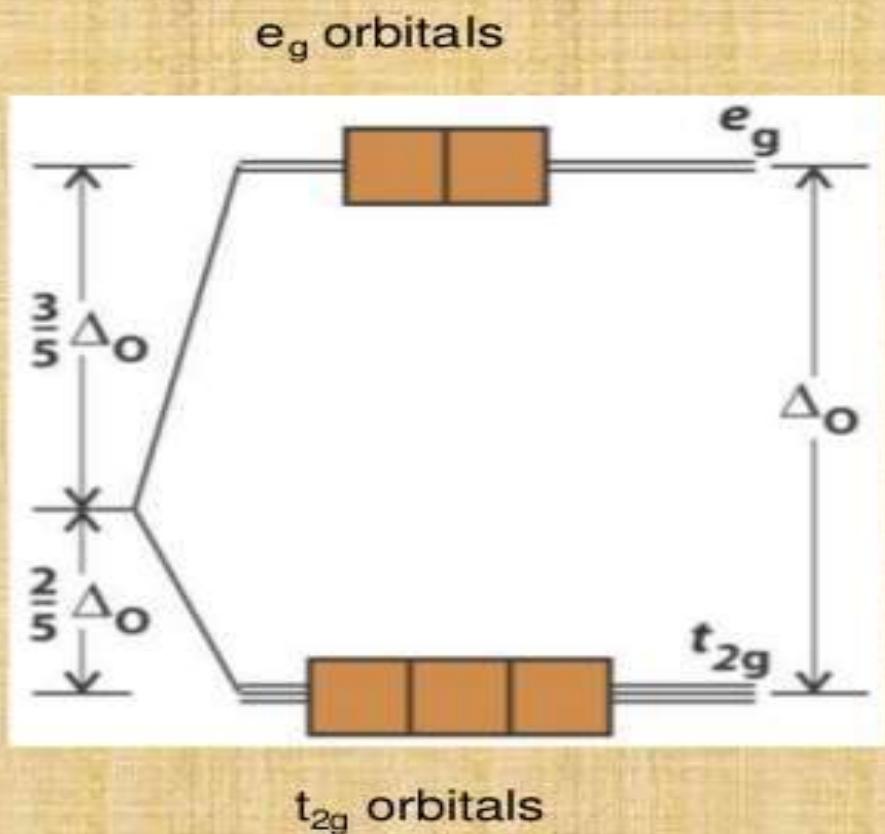
# DEGENERACY OF ORBITALS



## Crystal field splitting:-

The degeneracy of d-orbital is splits by ligand field or the energy of d-orbital becomes differentiated in presence of ligand. This effect is known as crystal field splitting. The gain in bonding energy achieved in this way is called crystal field stabilization energy (C.F.S.E.). **D and q are called Differential of quanta**

## Splitting of d – orbitals



## GROUP THEORETICAL SYMBOLS

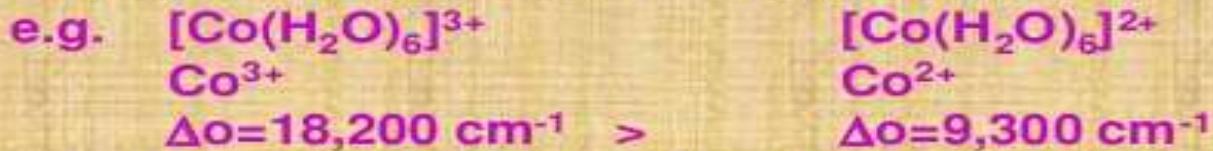
### Symbols and their meanings: -

- ❖ The 'a' means one degenerate orbitals.
- ❖ The 'e' means two degenerate orbitals.
- ❖ The 't' means three degenerate orbitals.
- ❖ The 'g' means gerade (in German - even) i.e. the orbitals are gerade, if it has same sign of wave function at same distance in opposite direction from center of symmetry.
- ❖ The 'u' – ungerade (in German - uneven) i.e. the orbitals are ungerade, if it change the sign of wave function at same distance in opposite direction from center of symmetry.
- ❖ Thus s and d orbitals are gerade (g), while P and f – orbitals are ungerade (u).
- ❖ The subscripts 1 means that the orbitals do not change sign on rotation about Cartesian axes.
- ❖ The 2 means orbital do not change sign on rotation about axes diagonal to Cartesian axes.
- ❖  $a_{1g} \rightarrow$  s orbital,  $e_g \rightarrow dx^2-y^2$  and  $dz^2$  orbitals.
- ❖  $t_{2g} \rightarrow dxy, dyz, dxz$  orbitals.  $t_{1u} \rightarrow Px, Py, Pz$  orbitals.

## Factors Affecting on CFSE

### 1) Nature of metal ion:

#### a) Same metal ion with different charge



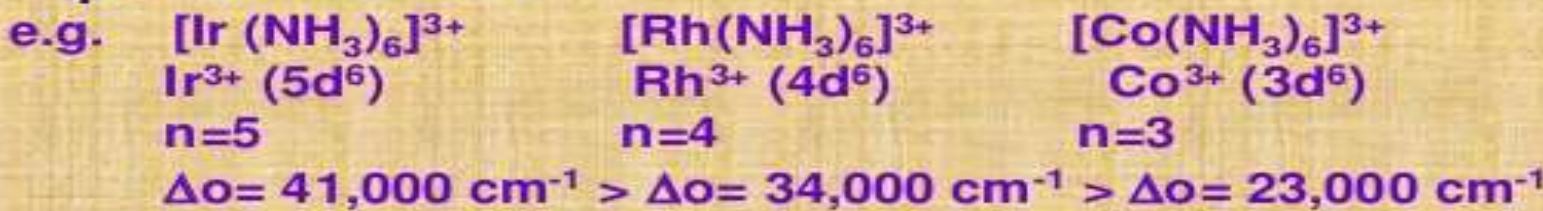
#### b) Different metal ion with same charge



#### c) Different metal ion with different charge but same number of d – electrons



#### d) Different metal ion with same charge but different principal quantum number.

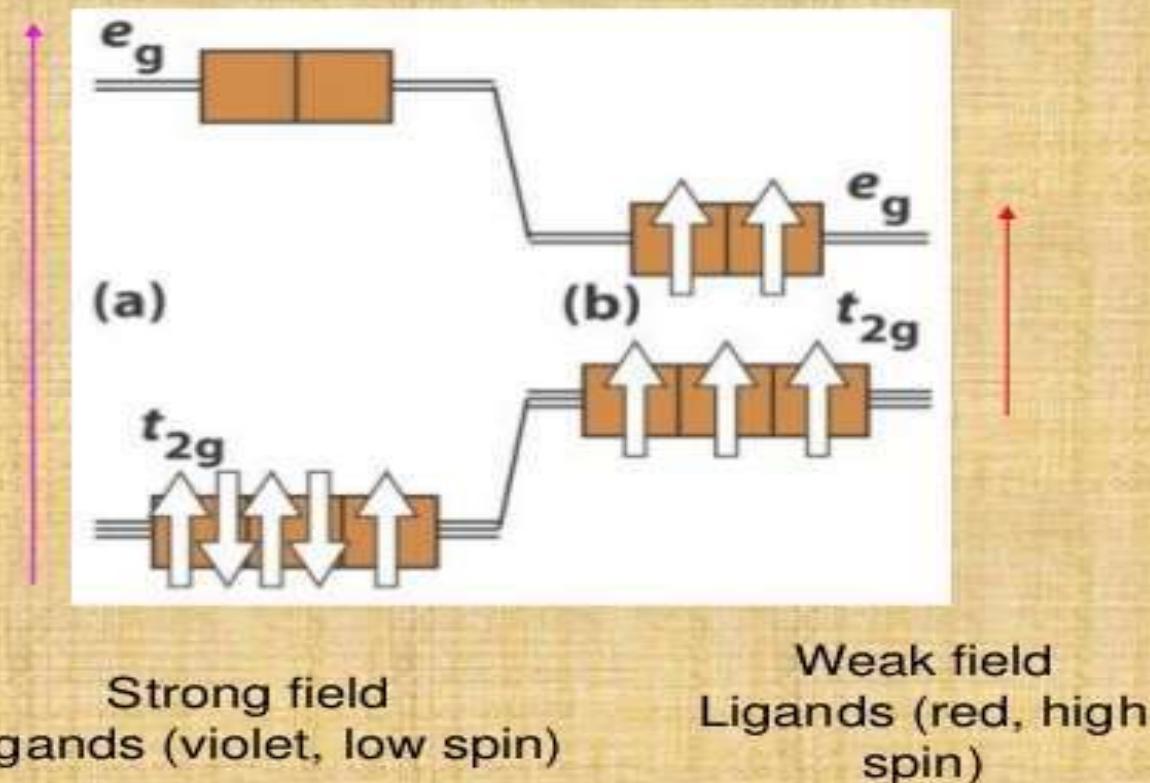


## Factors Affecting on CFSE

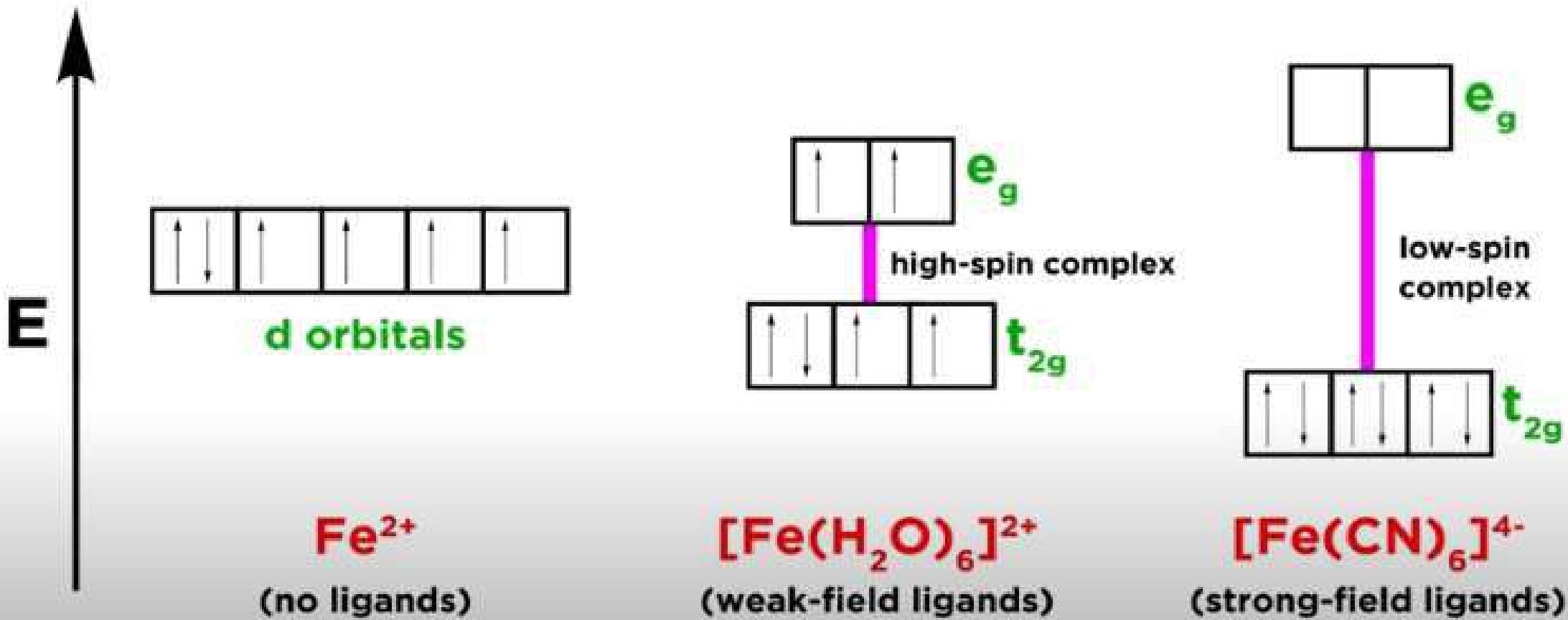
### 2) Nature of ligand

a) When the ligands are strong the energy gap between  $t_{2g}$  and  $e_g$  is more the distribution of electron does not takes place according to Hund's rule. These are Low spin Complexes .

b) When ligands are weak CFSE is relatively small hence five d- orbitals are suppose to be degenerate and therefore distribution of electrons takes place according to Hund's rule. These are High spin Complexes .



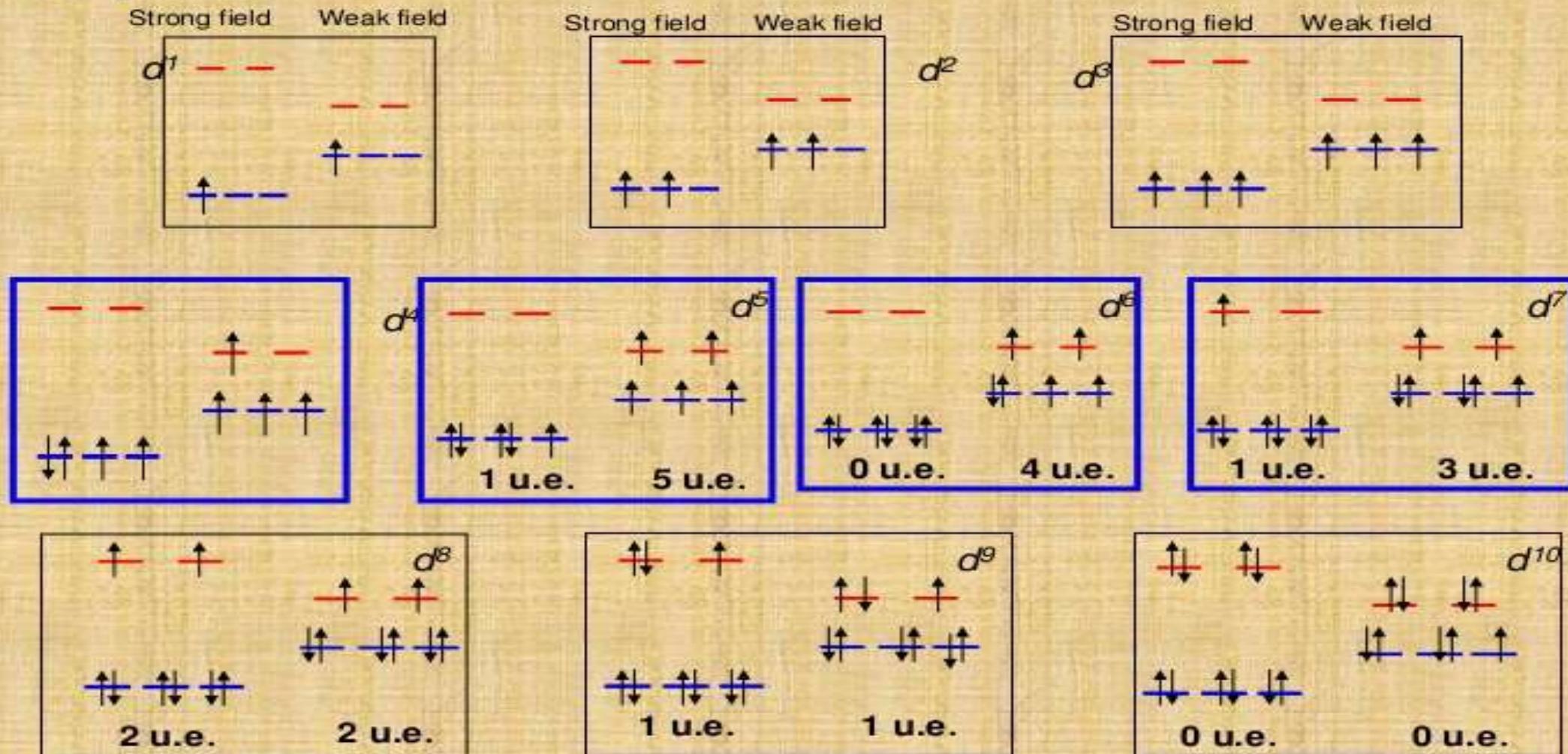
# CFT for Octahedral Complexes



electrons will fill the lower-energy orbitals first

## Factors Affecting on CFSE

2) Nature of ligand : c) Distribution of electron in High spin and Low spin Complexes

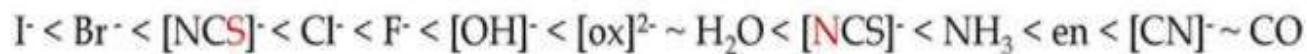


## Factors Affecting on CFSE

Weak – I<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>NC(O)NH<sub>2</sub>, OH<sup>-</sup>, ox<sup>2-</sup>, O<sup>2-</sup>, H<sub>2</sub>O, NCS<sup>-</sup>, py, NH<sub>3</sub>, en, bpy, phen, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>5</sub><sup>-</sup>, CN<sup>-</sup>, CO – Strong

### 2) Nature of ligand :

When the common ligand are arranged in the order of their increasing splitting power the series is obtained called **Spectrochemical series**.



- π donors

- σ donors

- π acceptors

Weak field ligands

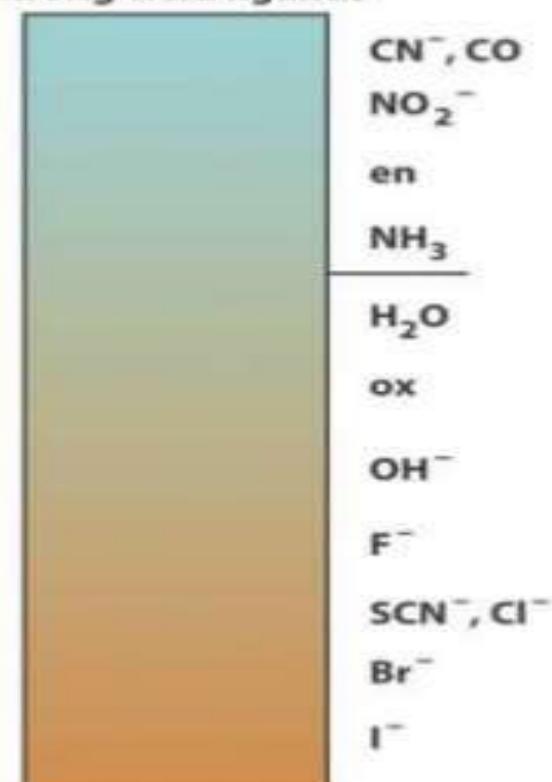
Ligands increasing  $\Delta_{\text{oct}}$

Strong field ligands

- Small Δ
- High spin
- π donors

- Large Δ
- Low spin
- π acceptors

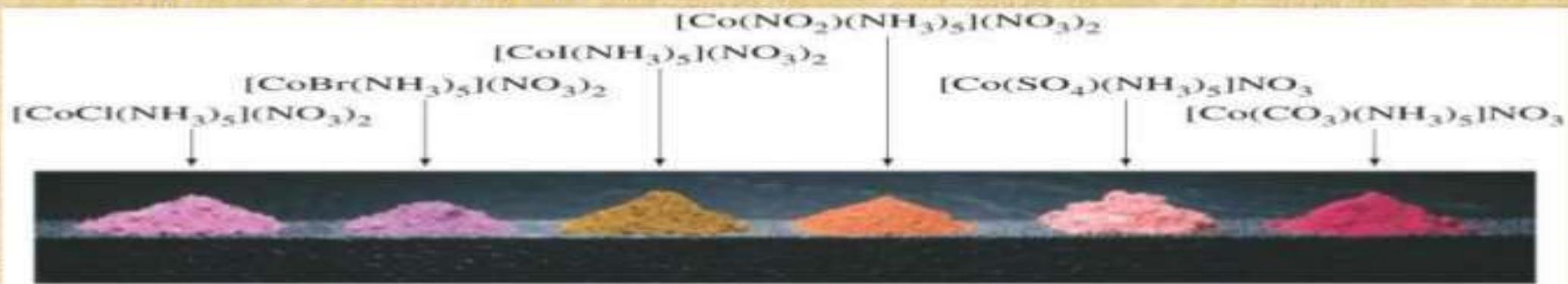
### Strong-field ligands



### Weak-field ligands

## Application of CFT

- 1) Colour of complexes : The transition metal complexes whose central metal ion contain partially filled d – orbitals are usually coloured in their solid and solution form.



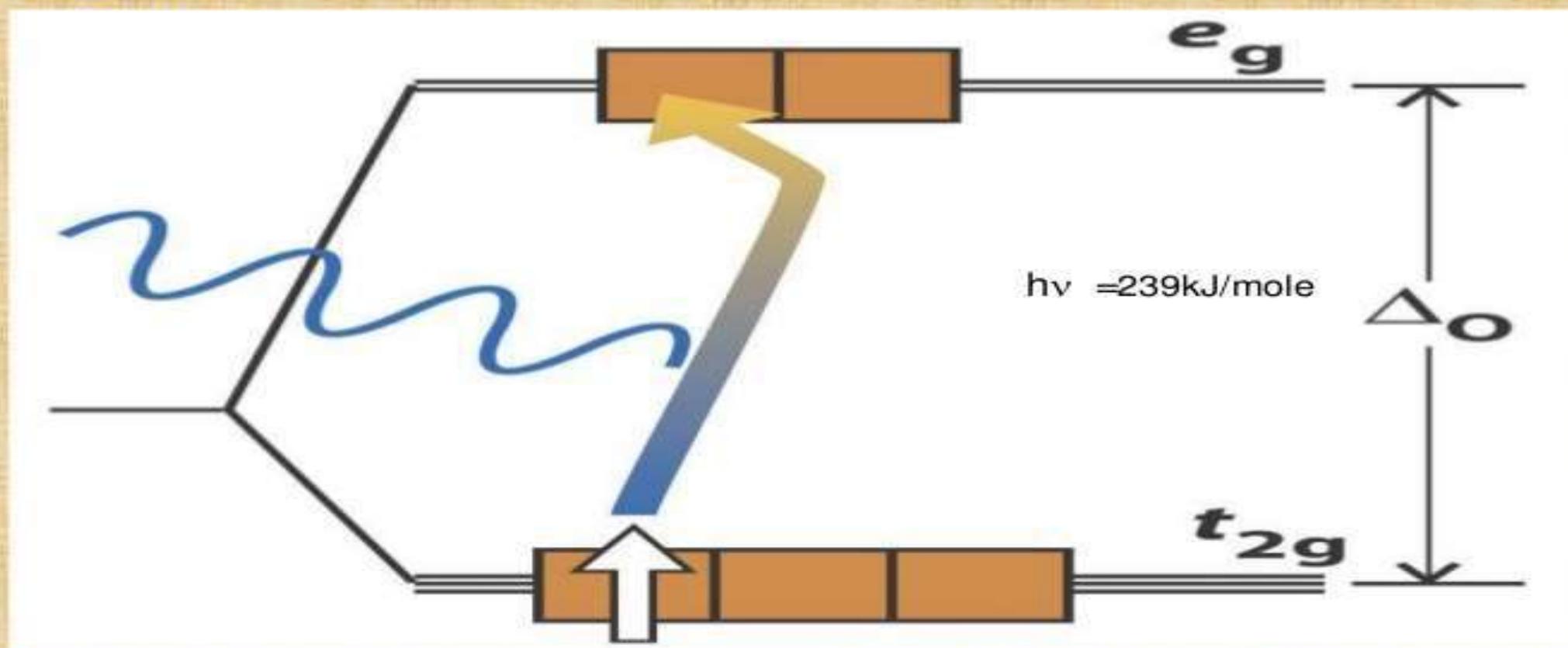
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## d – d transition of electron

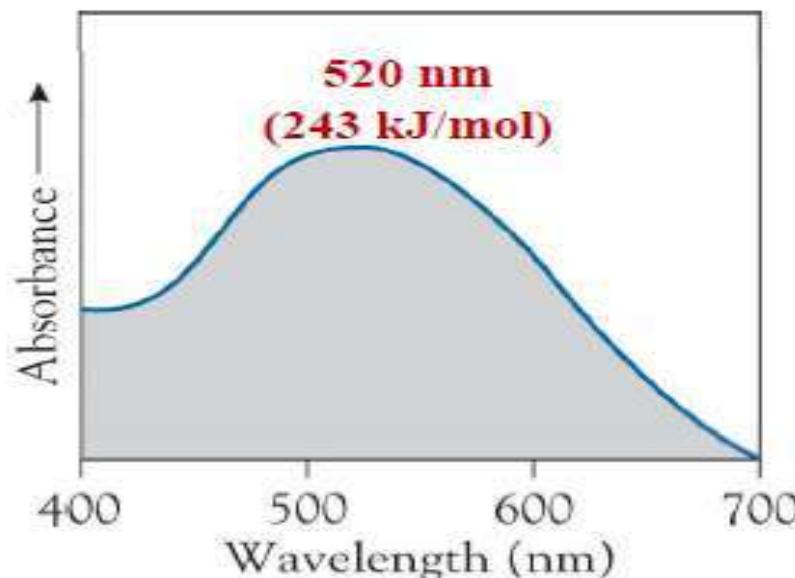
e.g.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  complex absorb green radiation at  $5000 \text{ \AA}^0$ . hence transmitted the radiation of purple colour due to d – d transition of electron



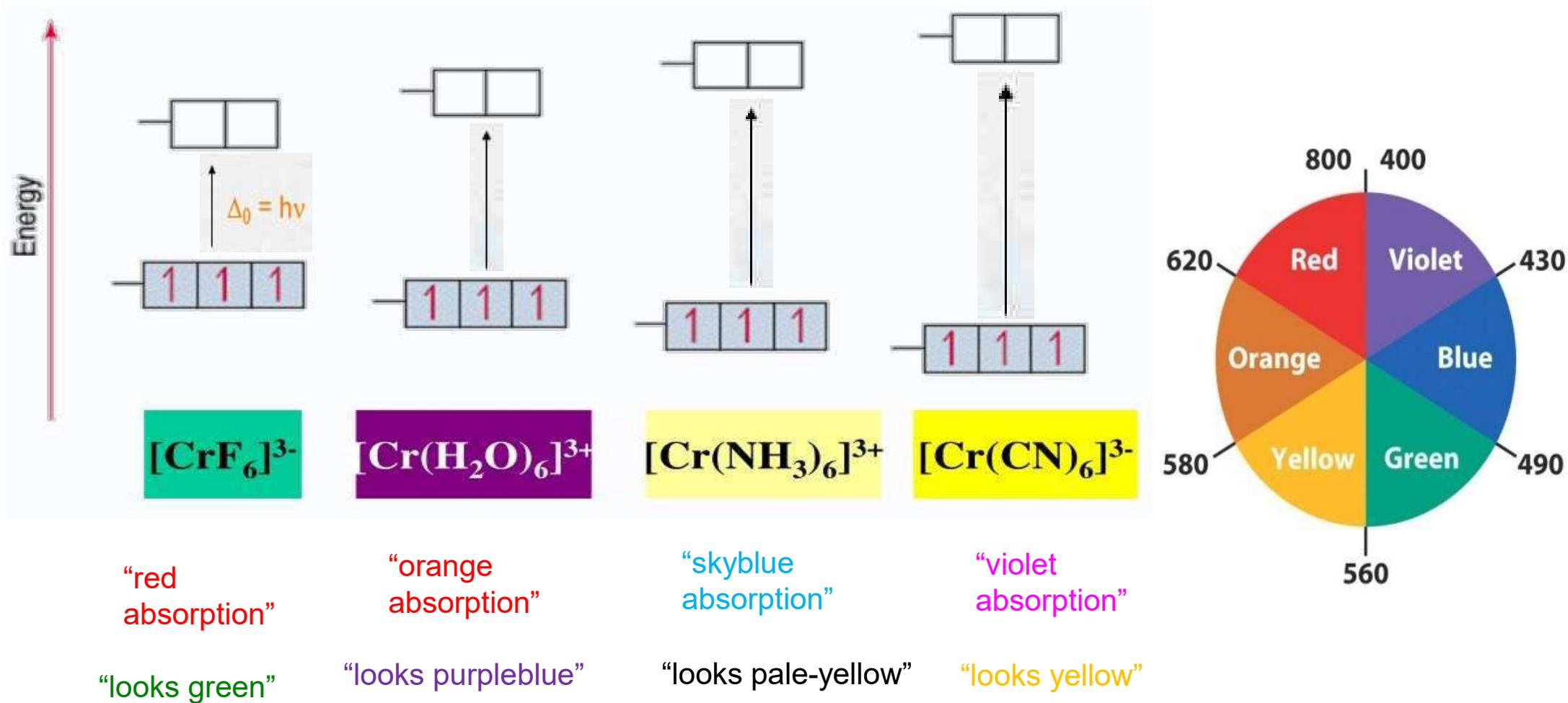
## $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ – a $d^1$ system



The single electron in the  $t_{2g}$  orbitals absorb energy in the form of light and gets excited to the  $e_g$  orbitals. In case of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , this corresponds to 520 nm ( $20,300 \text{ cm}^{-1}$ ).

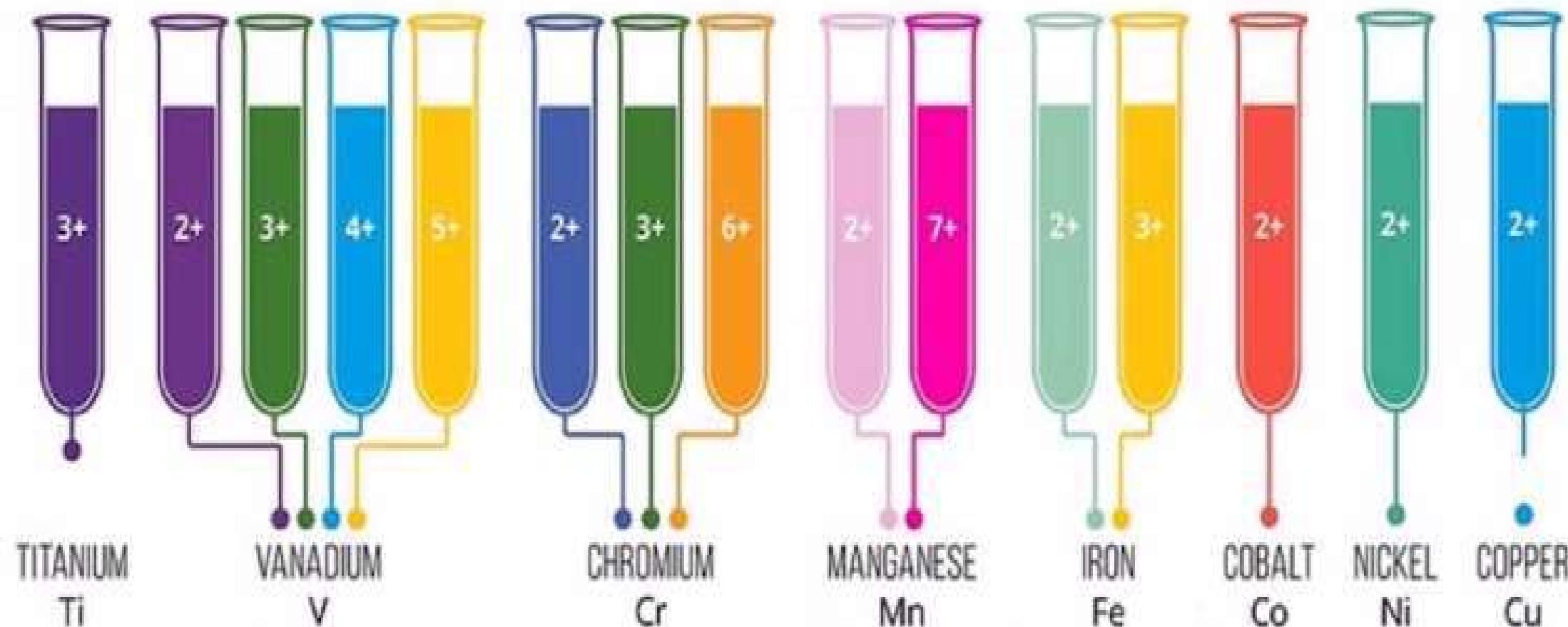


# COLOR OF Cr<sup>3+</sup> COMPLEXES WITH DIFFERENT LIGAND



As Cr<sup>3+</sup> goes from being attached to a weak field ligand to a strong field ligand,  $\Delta$  increases and the color of the complex changes from green to yellow.

# THE COLOURS OF AQUEOUS TRANSITION METAL IONS



# Classification of magnetic material

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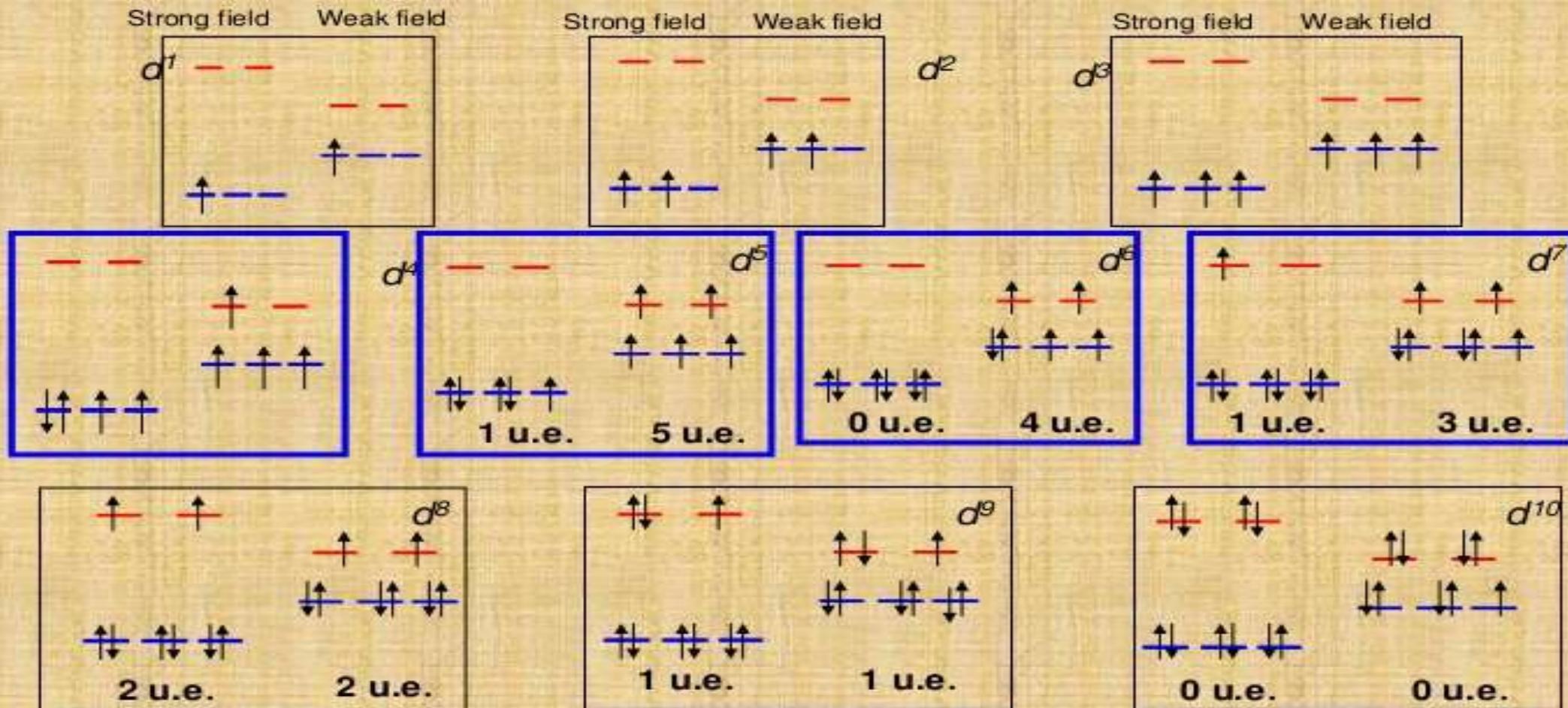
- Diamagnetic
- Paramagnetic
- Ferromagnetic
- Anti-ferromagnetic
- Ferrimagnetic
- Superconductors

## MAGNETIC PROPERTIES

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism*.
- **Diamagnetic substances** are repelled by the applied field while the **paramagnetic substances** are attracted.
- Substances which are attracted very strongly are said to be *ferromagnetic*.
- In fact, **ferromagnetism** is an **extreme form of paramagnetism**.

## 2) Magnetic Properties :

- a) in  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  complexes have same spin state and all are paramagnetic.
- b) The low spin  $d^6$  and  $d^{10}$  complexes are diamagnetic.
- c) In  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  the number of unpaired electron are different in high spin and low spin octahedral complexes .



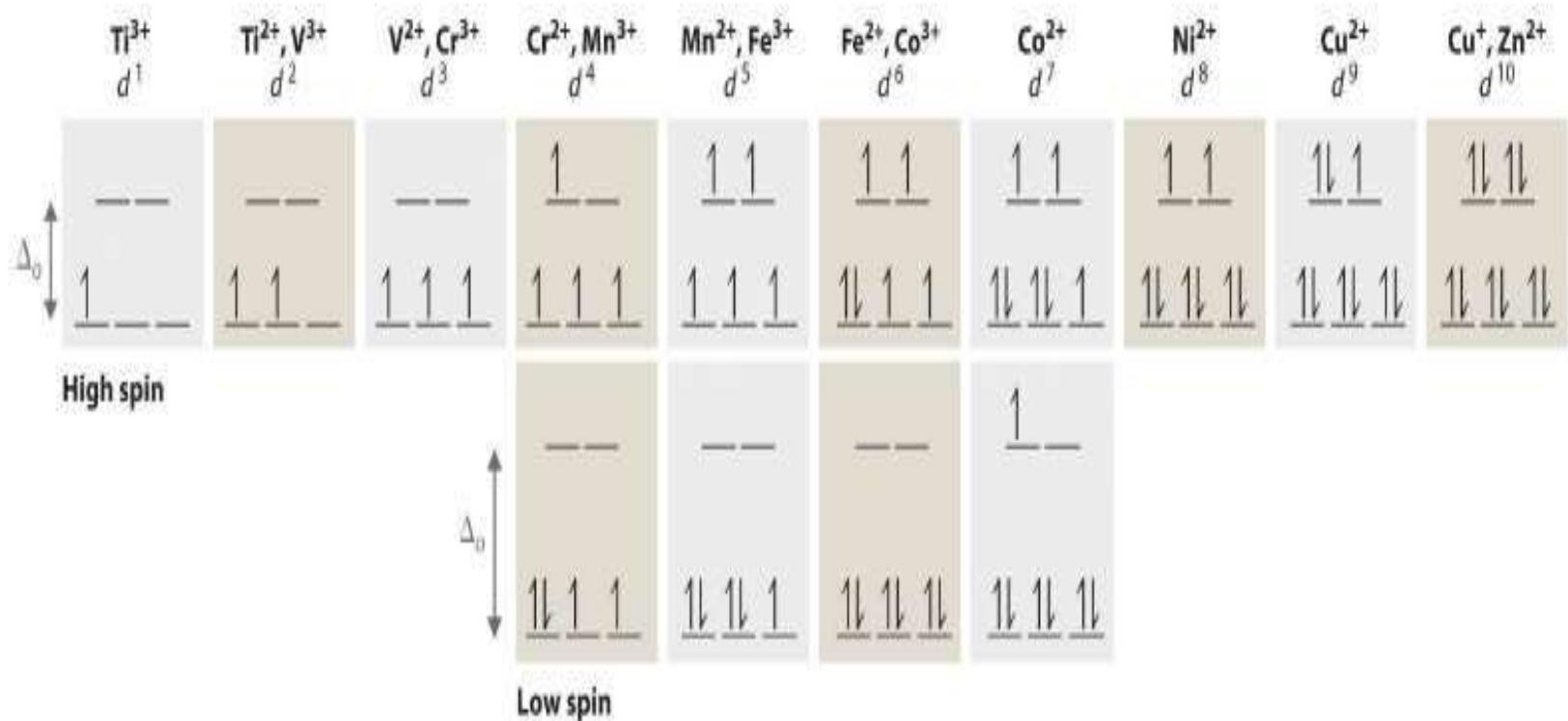


Figure 2.8.2: The Possible Electron Configurations for Octahedral  $d^n$  Transition-Metal Complexes ( $n = 1-10$ ). Two different configurations are possible for octahedral complexes of metals with  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations; the magnitude of  $\Delta_0$  determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

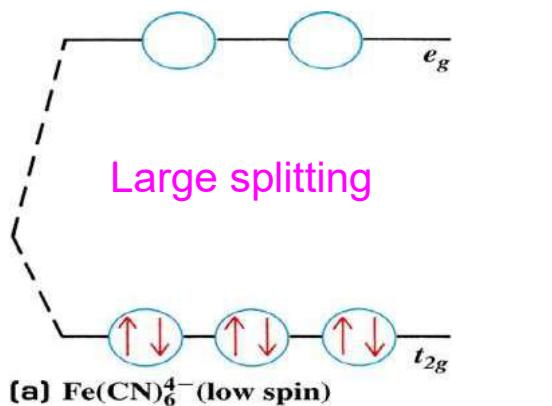
❖ Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

- ❖ If  $\Delta$  is less than  $P$ , then the lowest-energy arrangement has the fourth electron in one of the empty  $e_g$  orbitals.
- ❖ Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the  $[\text{Cr}(\text{HO})]$  ion, is called a high-spin complex.
- ❖ If  $\Delta$  is greater than  $P$ , then the lowest-energy arrangement has the fourth electron in one of the occupied  $t_{2g}$  orbitals.
- ❖ Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the  $[\text{Mn}(\text{CN})]$  ion, is called a low-spin complex.

# CRYSTAL FIELD SPLITTING OF D ORBITALS: HIGH SPIN AND LOW SPIN SITUATIONS FOR A D<sup>6</sup> METAL

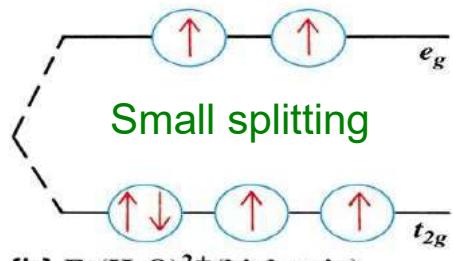
Ligand strength: (Weak) I<sup>-</sup> < F<sup>-</sup> < H<sub>2</sub>O < NH<sub>3</sub> < CN<sup>-</sup> (Strong)

Low spin  
Electrons spin pair



Net unpaired  
spins = 0:  
Diamagnetic

High spin  
Electrons do  
Not spin pair



Net unpaired  
spins = 4:  
Strongly paramagnetic

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How many unpaired spins in  $\text{Fe}(\text{CN})_6^{4-}$  and in  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ?

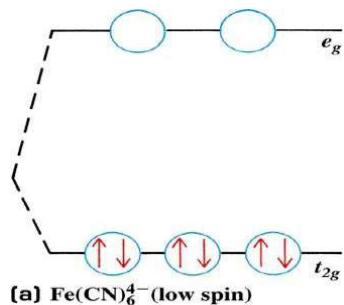
What is the charge of Fe in  $\text{Fe}(\text{CN})_6^{4-}$  and in  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ?

$\text{Fe}^{2+}$  in both cases

$\text{Fe} = [\text{Ar}]3\text{d}^64\text{s}^2$ ;  $\text{Fe}^{2+} = [\text{Ar}]3\text{d}^6$

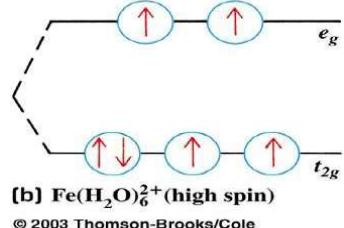
What kind of ligands are  $\text{CN}^-$  and  $\text{H}_2\text{O}$ ?  $\text{CN}^-$  is a strong field ligand and  $\text{H}_2\text{O}$  is a weak field ligand

Large splitting  
Low spin



Energy gap larger than advantage due to Hund's rule

Small splitting  
High spin



Energy gap small; Hund's rule applies

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- Most of the transition elements and their compounds show paramagnetism.
- Paramagnetism arises from the presence of unpaired electrons, each such electron have a magnetic moment.
- The magnetic moment of any transition element or its compound/ion is given by (assuming no contribution from the orbital magnetic moment).
  - $\mu_s = \sqrt{n(n+2)} BM$
  - Here n is the number of unpaired electrons

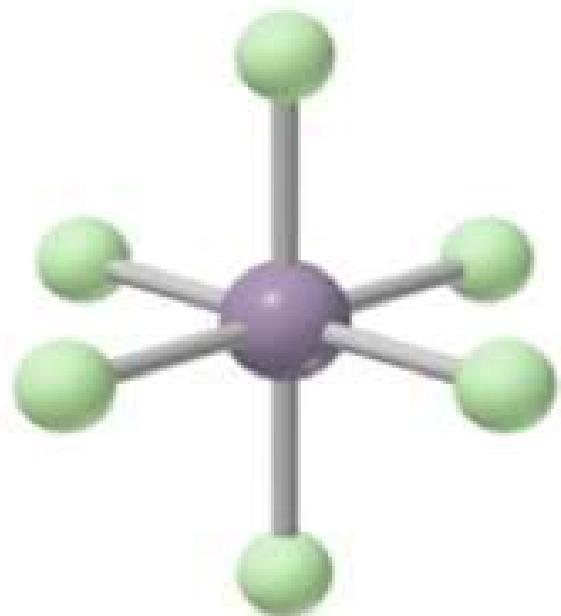
Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc <sup>3+</sup>	3d <sup>0</sup>	0	0	0
Ti <sup>3+</sup>	3d <sup>1</sup>	1	1.73	1.75
Ti <sup>2+</sup>	3d <sup>2</sup>	2	2.84	2.76
V <sup>2+</sup>	3d <sup>3</sup>	3	3.87	3.86
Cr <sup>2+</sup>	3d <sup>4</sup>	4	4.90	4.80
Mn <sup>2+</sup>	3d <sup>5</sup>	5	5.92	5.96
Fe <sup>2+</sup>	3d <sup>6</sup>	4	4.90	5.3 - 5.5
Co <sup>2+</sup>	3d <sup>7</sup>	3	3.87	4.4 - 5.2
Ni <sup>2+</sup>	3d <sup>8</sup>	2	2.84	2.9 - 3.4
Cu <sup>2+</sup>	3d <sup>9</sup>	1	1.73	1.8 - 2.2
Zn <sup>2+</sup>	3d <sup>10</sup>	0	0	

- The paramagnetism first increases in any transition element series, and then decreases. The maximum paramagnetism is seen around the middle of the series.

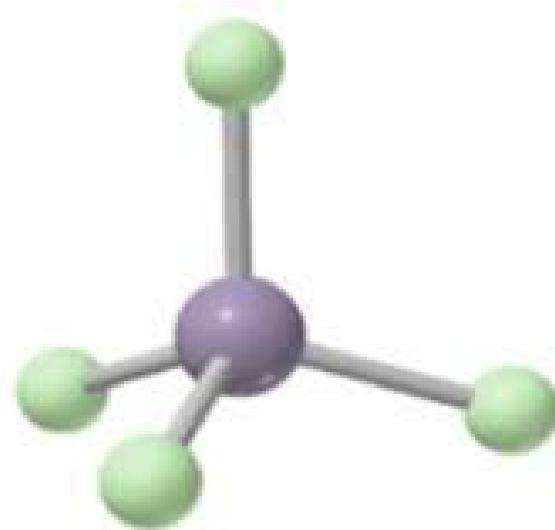
## QUESTIONS-

- Q. 1: Which ion has maximum magnetic moment
  - (a) V<sup>3+</sup>
  - (b) Mn<sup>3+</sup>
  - (c) Fe<sup>3+</sup>
  - (d) Cu<sup>2+</sup>
- Ans: c
- Q.2. What is the magnetic moment of Mn<sup>2+</sup> ion (Z=25) in aqueous solution ?
- Ans.- With atomic number 25, the divalent Mn<sup>2+</sup> ion in aqueous solution will have d<sup>5</sup> configuration (five unpaired electrons). Hence, The magnetic moment,  $\mu$  is
- $\mu = \sqrt{5(5 + 2)} = 5.92\text{BM}$

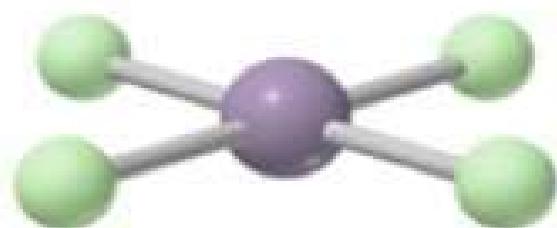
# Coordination Compounds



**octahedral**  
**(6)**



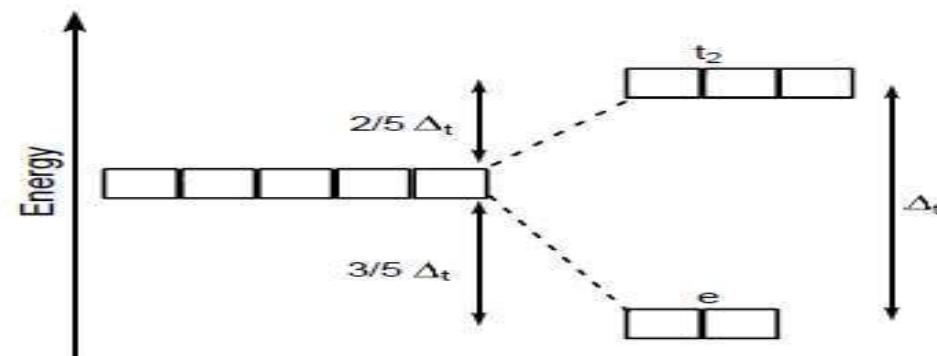
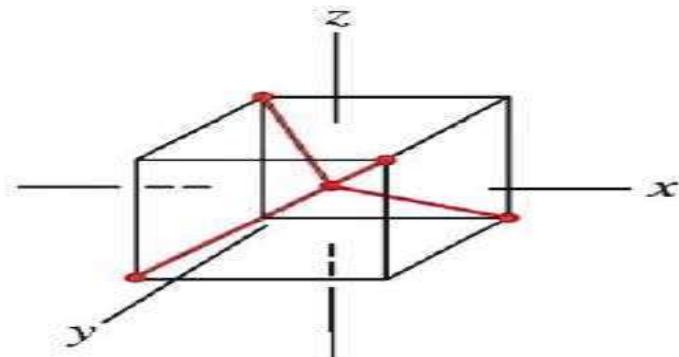
**tetrahedral**  
**(4)**



**square planar**  
**(4)**

- Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting, the *d*-orbitals again split into two groups, with an energy difference of  $\Delta_{\text{tet}}$ .
- The lower energy orbitals will be  $dz^2$  and  $dx^2-y^2$ , and the higher energy orbitals will be  $dxy$ ,  $dxz$  and  $dyz$  - opposite to the octahedral case.
- Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the *d*-orbitals, the energy splitting will be lower than in the octahedral case.
- Square planar and other complex geometries can also be described by CFT.

### Tetrahedral Field

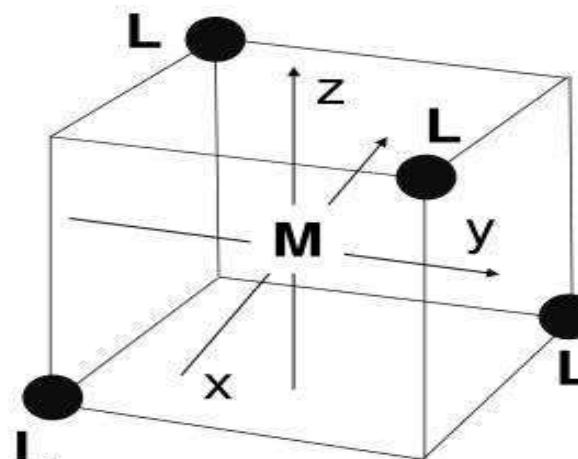


The higher energy set of orbitals ( $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ ) is labeled as  $t_2$  and the lower energy set ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) is labeled as  $e$ .

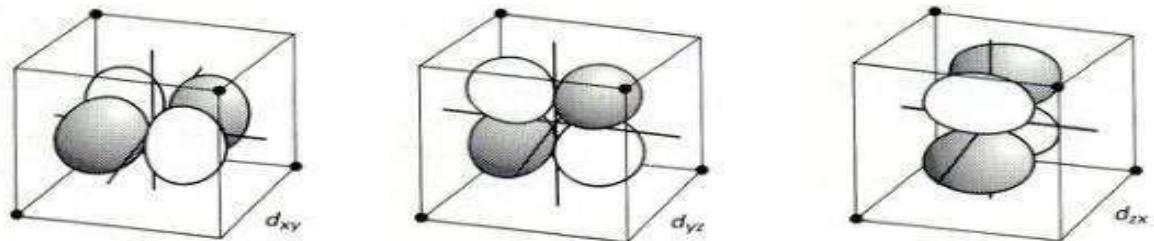
The crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For most purposes the relationship may be represented as  $\Delta_t = 4/9 \Delta_o$

# Tetrahedral Crystal Field Splitting

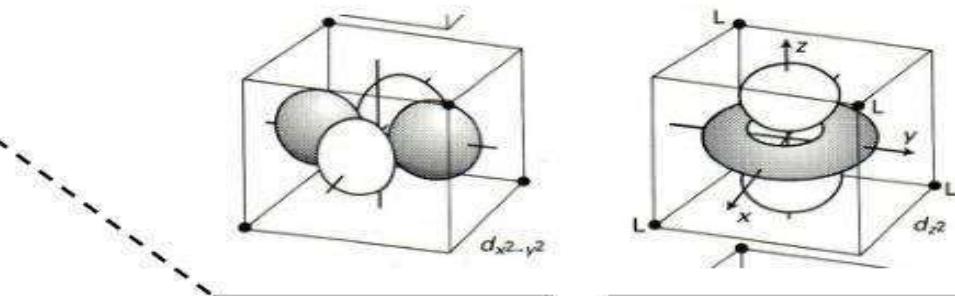
opposite splitting of octahedral field



barycenter  
(spherical field)



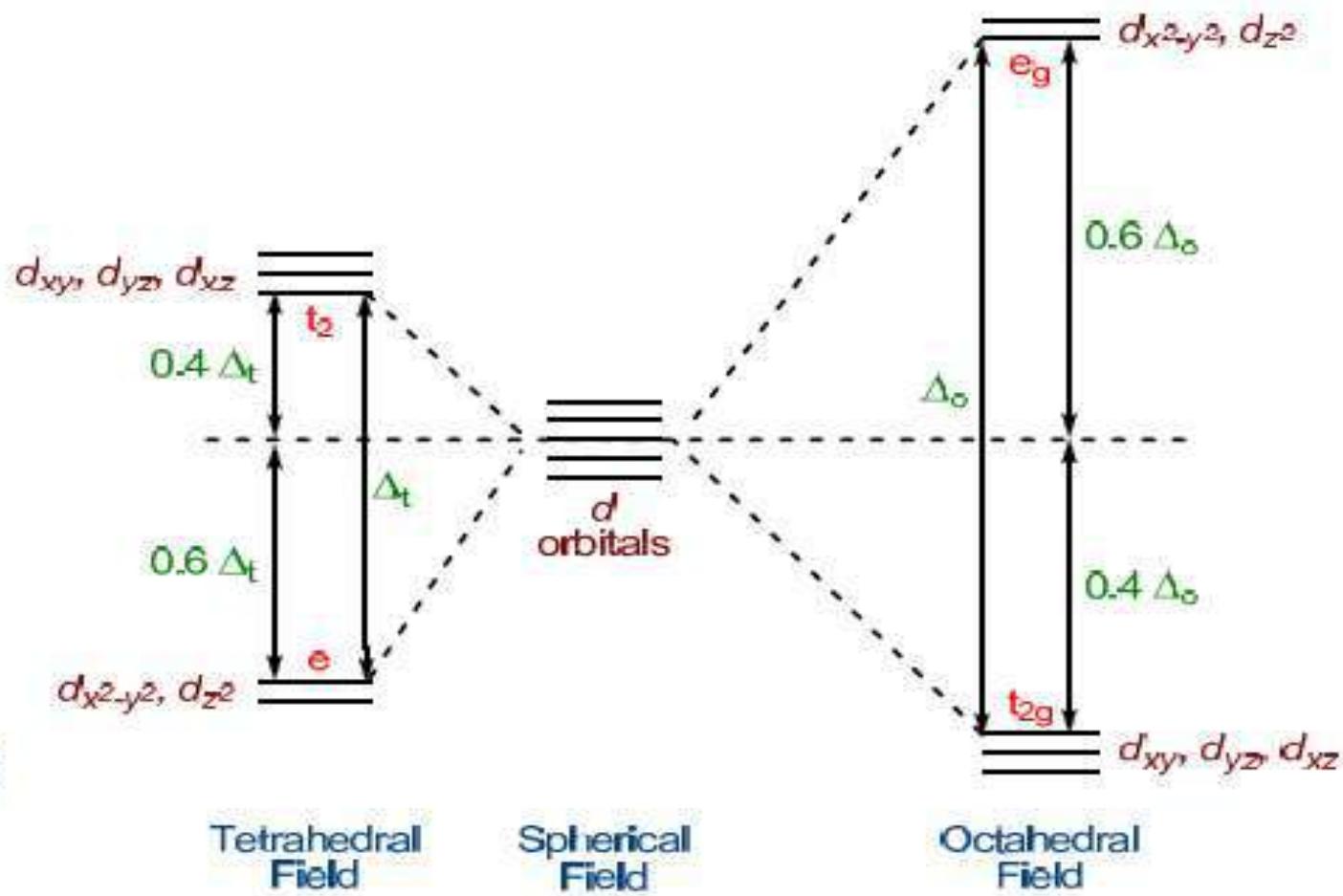
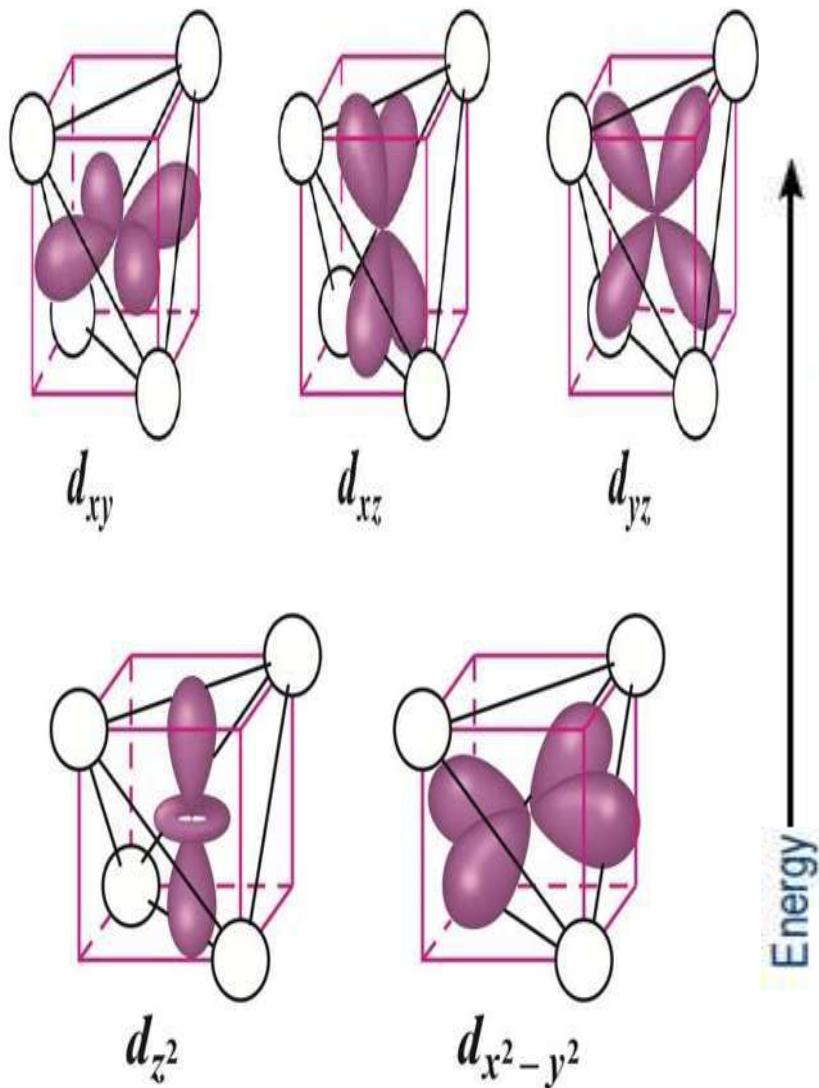
**t<sub>2</sub>** orbitals point more directly at ligands and are destabilized.



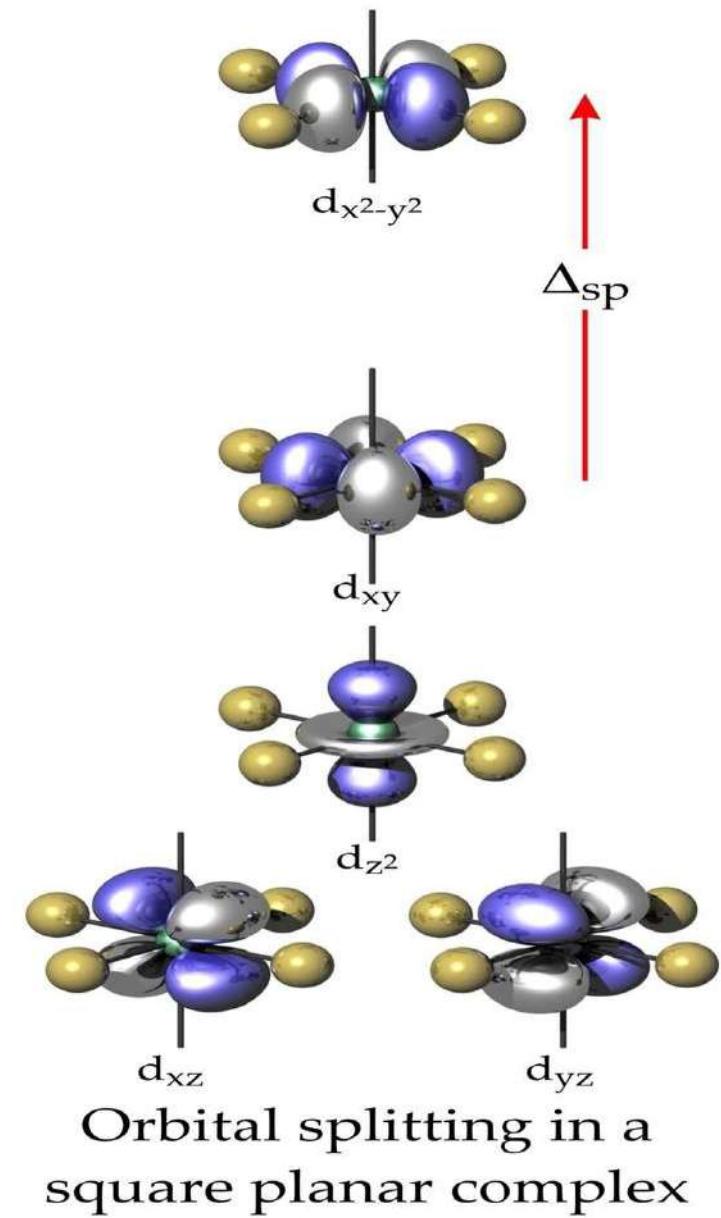
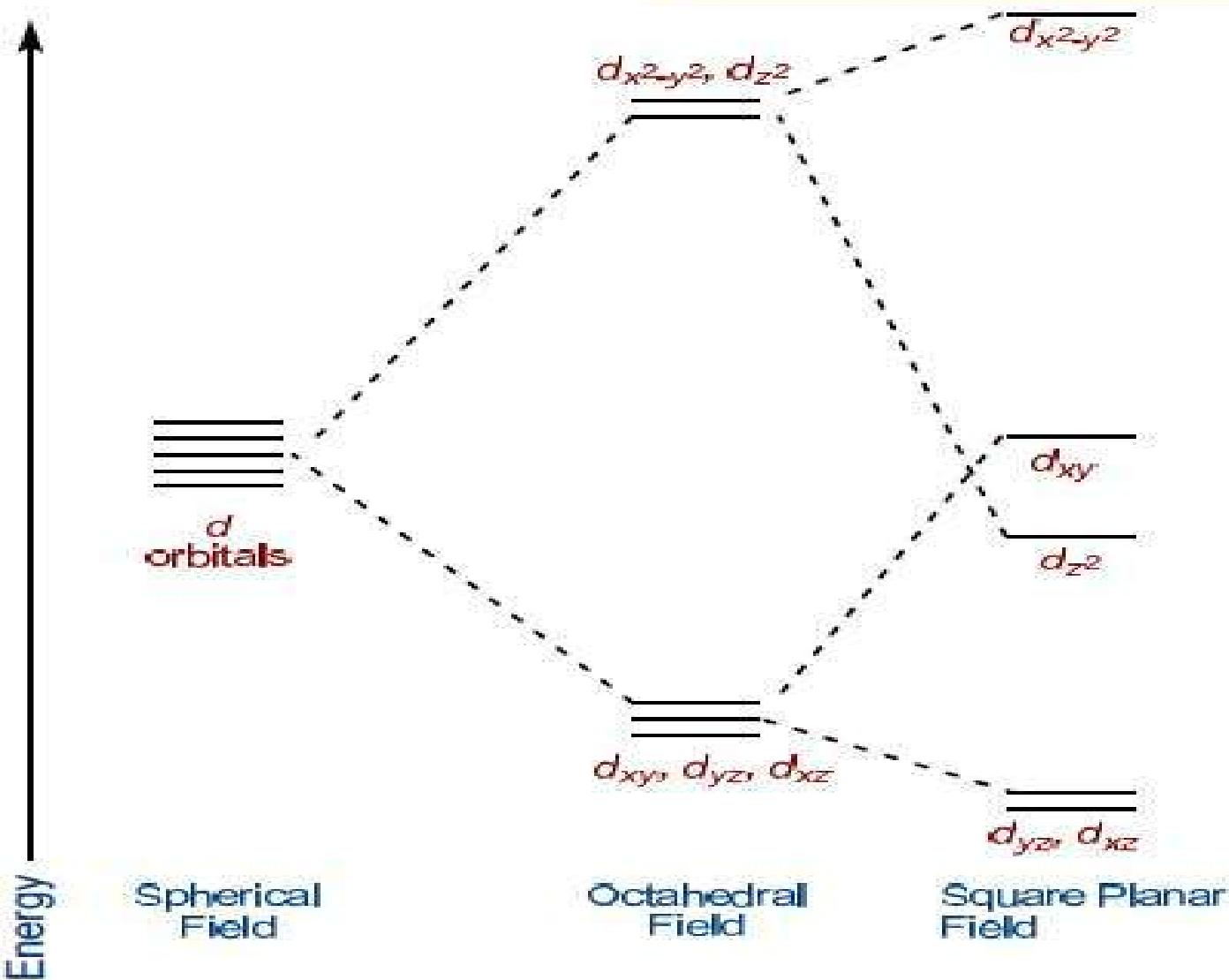
**e** orbitals point less directly at ligands and are stabilized.

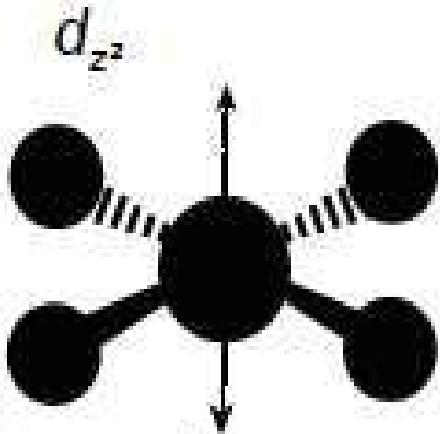
$\Delta_t < \Delta_o$  because only 4 ligands and d orbitals point between ligands

## Octahedral Vs Tetrahedral

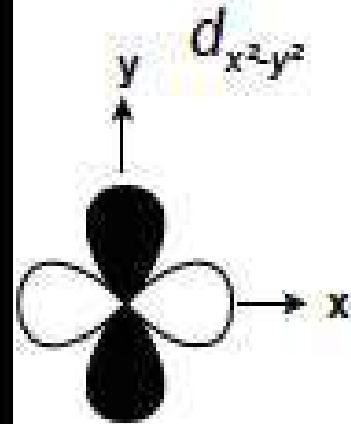


## Square Planar Field

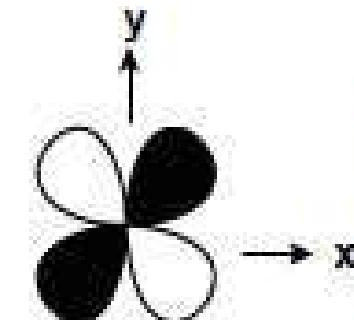




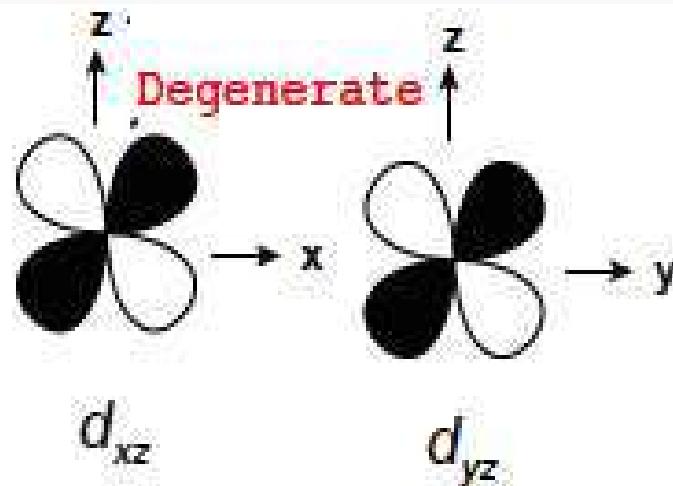
The ligands fuck off from here, so orbital is lower energy due to less repulsion



$Z_{eff}$  is higher due to ligand fucking off, so the ligands along the x and y axes are brought in towards the nucleus. Higher repulsion - higher energy.

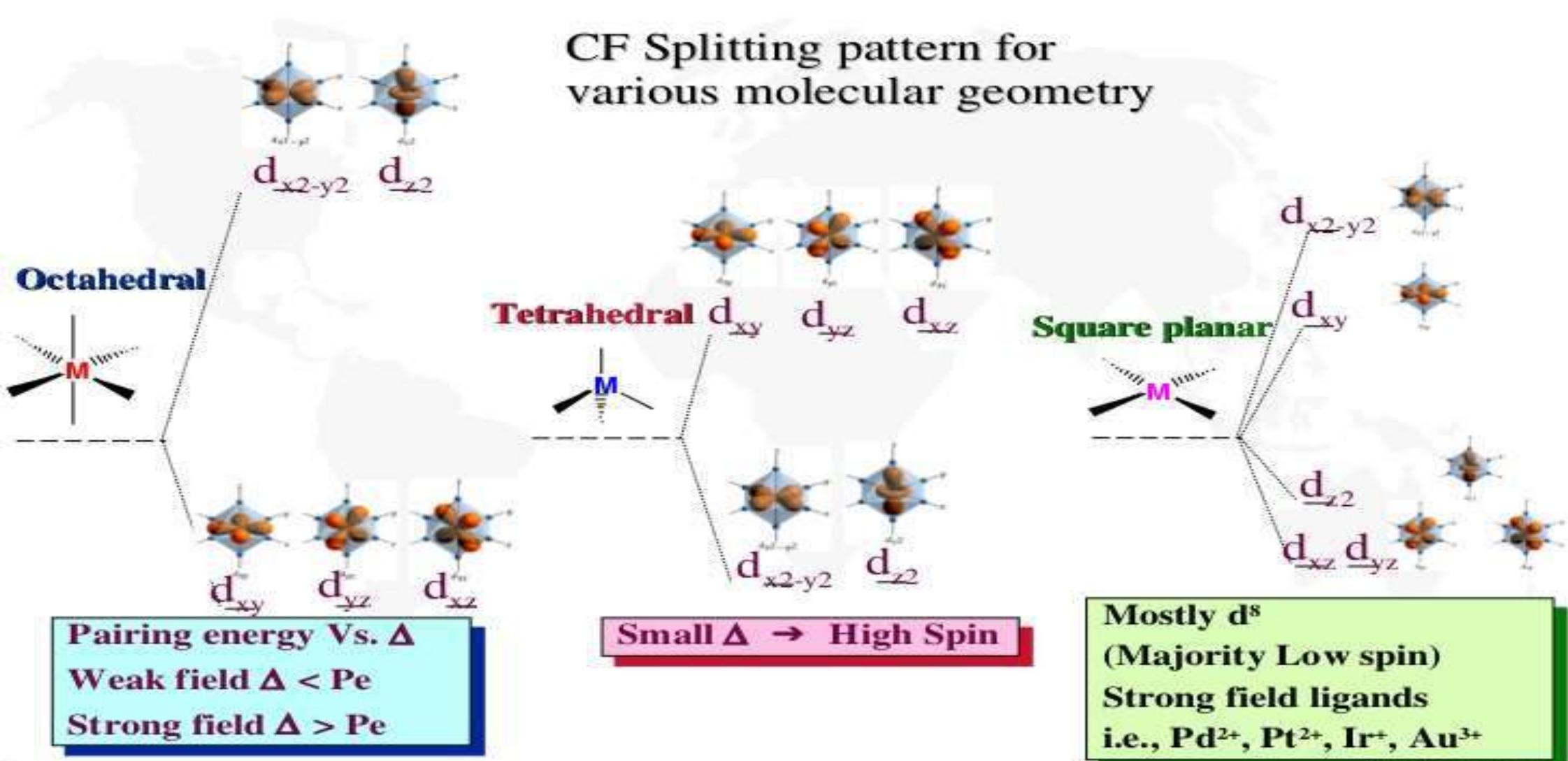


Affected by the ligands being closer, since they are in the xy plane  
Higher repulsion - higher energy.



Degenerate  
 $d_{xz}$                    $d_{yz}$   
No ligands in the zy and zx planes so lowest energy degenerate orbitals

# Octahedral, Tetrahedral & Square Planar



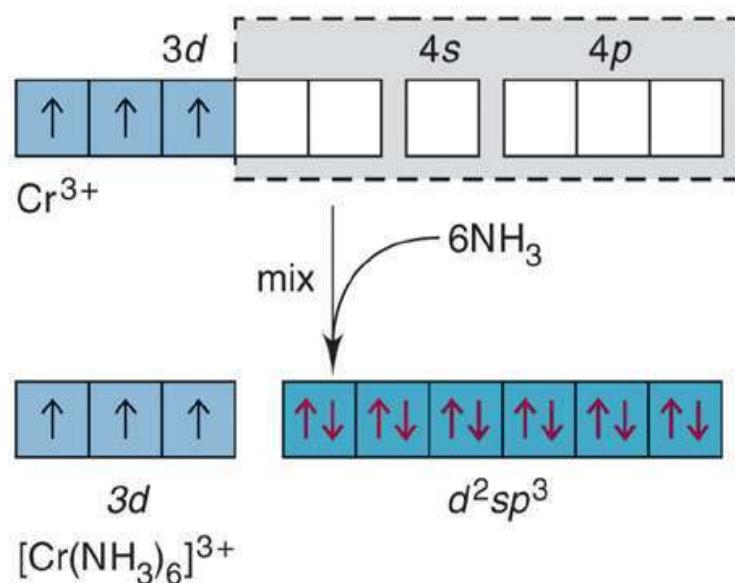
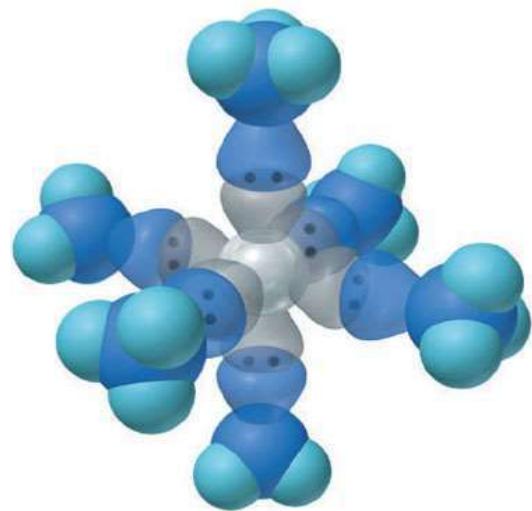
## Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape	Examples
2	Linear	$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{AuCl}_2]^-$
4	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{PdCl}_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral	$[\text{Cu}(\text{CN})_4]^{3-}$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , $[\text{CdCl}_4]^{2-}$ , $[\text{MnCl}_4]^{2-}$
6	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{CN})_6]^{4-}$ , $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ , $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{FeCl}_6]^{3-}$ , $[\text{Co}(\text{en})_3]^{3+}$

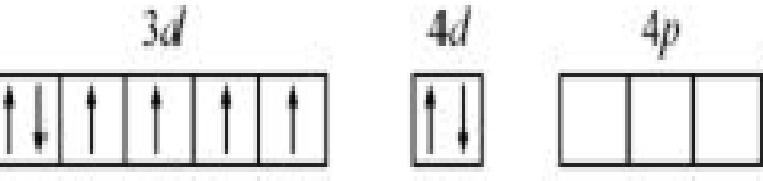
- The geometry of a given complex ion depends **both** on the coordination number and the metal ion.
- When a complex ion is formed, each ligand donates an electron pair to the metal ion.
- The ligand acts as a Lewis base, while the metal ion acts as a Lewis acid.
- This type of bond is called a **coordinate covalent bond** since both shared e<sup>-</sup> originate from one atom in the pair.
- In terms of valence bond theory, the **filled** orbital of the ligand overlaps with an **empty** orbital of the metal ion.
- The VB model proposes that the geometry of the complex ion depends on the hybridization of the metal ion.

# HYBRID ORBITALS AND BONDING IN THE OCTAHEDRAL

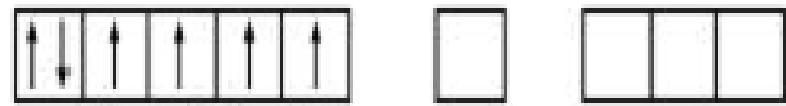
## $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ION & $[\text{Fe}(\text{CN})_6]^{4-}$



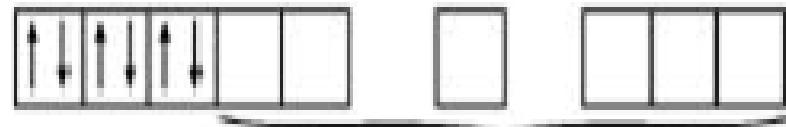
Fe atom (Z = 26)  
in ground state



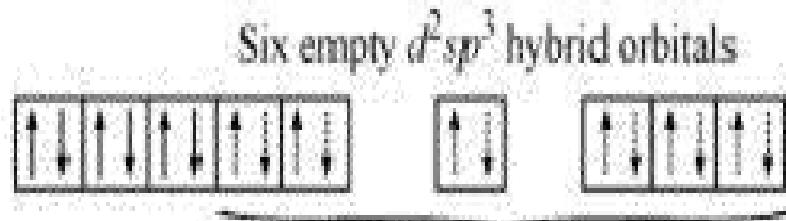
Fe<sup>2+</sup> ion



d<sup>2</sup>sp<sup>3</sup> hybridised  
orbitals of Fe<sup>2+</sup> ion



Formation of  $[\text{Fe}(\text{CN})_6]^{4-}$

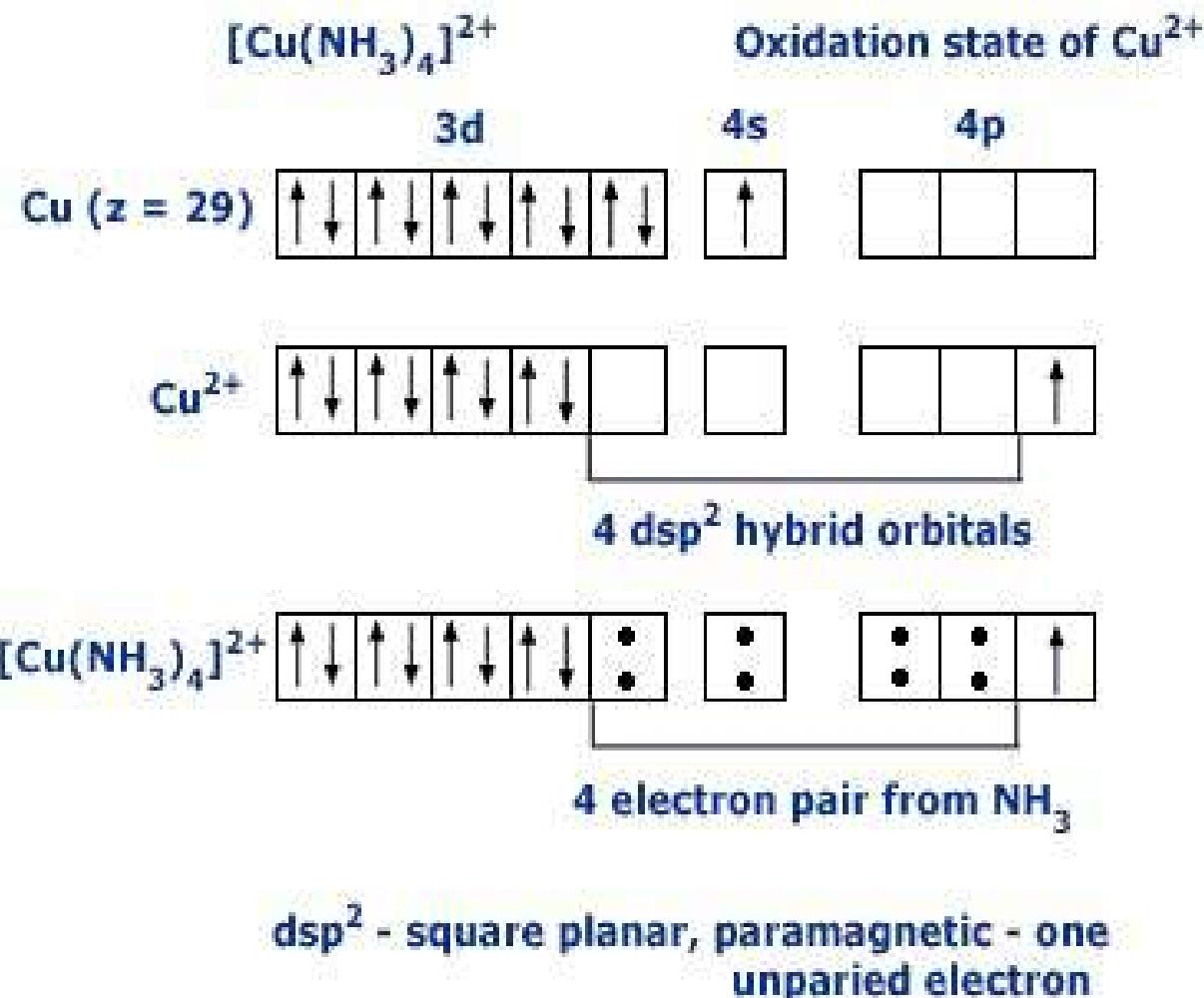
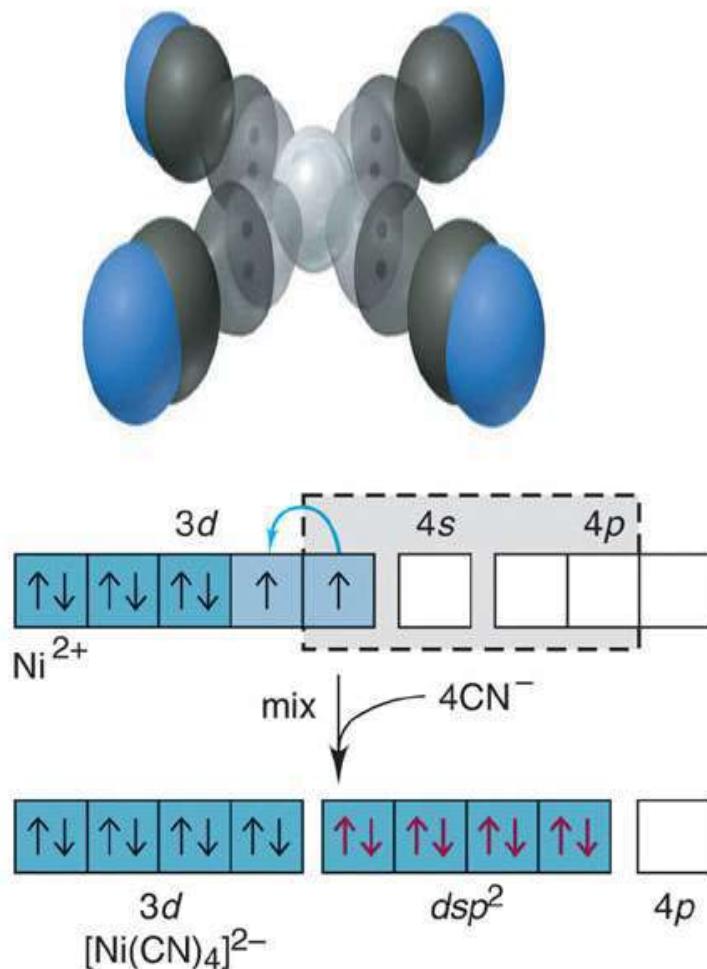


Six empty d<sup>2</sup>sp<sup>3</sup> hybrid orbitals

Six pairs of electrons from six CN<sup>-</sup> ions

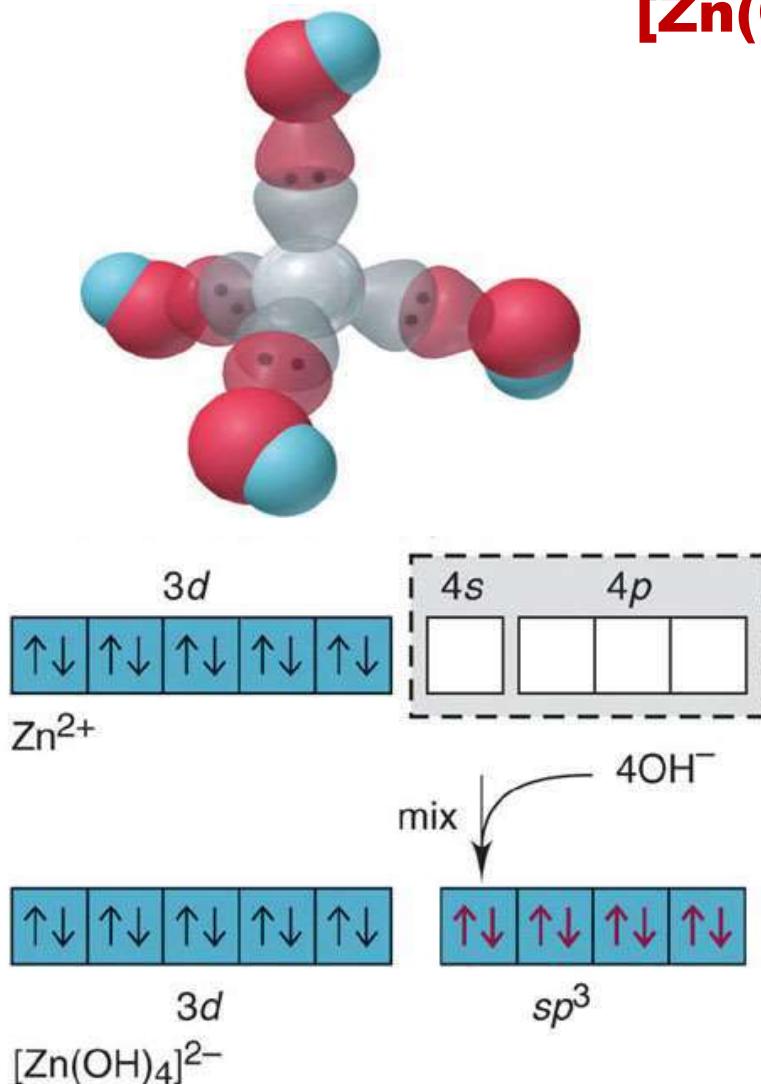
# HYBRID ORBITALS AND BONDING IN THE SQUARE PLANAR

## $[\text{Ni}(\text{CN})_4]^{2-}$ ION & $[\text{Cu}(\text{NH}_3)_4]^{2+}$



# HYBRID ORBITALS AND BONDING IN THE TETRAHEDRAL

## $[\text{Zn}(\text{OH})_4]^{2-}$ ION & $\text{Ni}(\text{CO})_4$



Electronic configuration of Ni atom in ground state

Ni	$1\downarrow 1\downarrow 1\downarrow 1\downarrow 1\downarrow$	$1\downarrow$	$\square \quad \square \quad \square$
	$3d^8$	$4s^2$	$4p^0$

Change in electronic configuration of Ni atom when CO ligands approach it

CO	$1\downarrow 1\downarrow 1\downarrow 1\downarrow 1\downarrow$	$\square$	$\square \quad \square \quad \square$
Ni	$3d^{10}$	$4s^0$	$4p^0$
OC OC	CO		

Electronic configuration of Ni atom in  $\text{Ni}(\text{CO})_4$

$\text{CO}$	$1\downarrow 1\downarrow 1\downarrow 1\downarrow 1\downarrow$	$\square$	$\square \quad \square \quad \square$
$\text{Ni}$	$3d^{10}$	$4s^2$	$4p^6$
$\text{OC}$ $\text{OC}$	CO		

$\text{Ni}(\text{CO})_4$

$\downarrow$

$\text{sp}^3$  hybridization

Tetrahedral & Diamagnetic

Prepared by: V. Aditya vardhan



# Spectrophotometry : Instruments & Applications



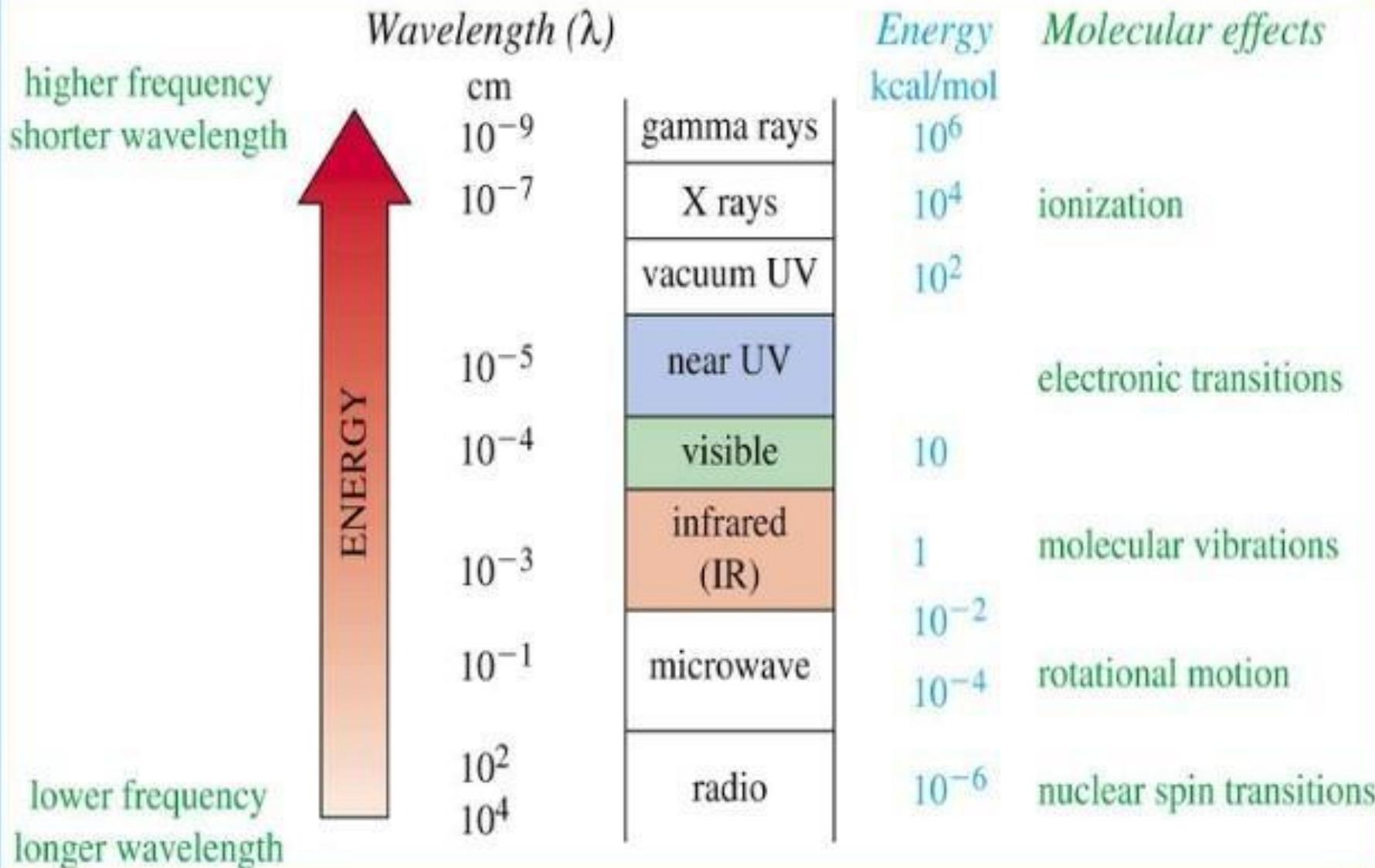
## SPECTROSCOPY

It is a branch of science that deals with interaction of matter with light or electromagnetic radiation.

- ❖ Spectroscopy is used as a tool for studying the structures of atoms and molecules. The large number of wavelengths emitted by these systems makes it possible to investigate their structures in detail, including the electron configurations of ground and various excited states.



## *Molecular effects:*



# Interaction of EMR with matter

- **Absorption** - Light is absorbed
- **Emission**-Light is emitted or released
- **Transmission**- light is allowed to pass through
- **Reflection**- light is reflected or bounced away
- **Diffraction**- shows wave nature
- **Refraction**- shows particle nature
- **Interference**- light is disturbed
- **Scattering**- light is dispersed
- **Polarization**- light vibration is restricted to one direction

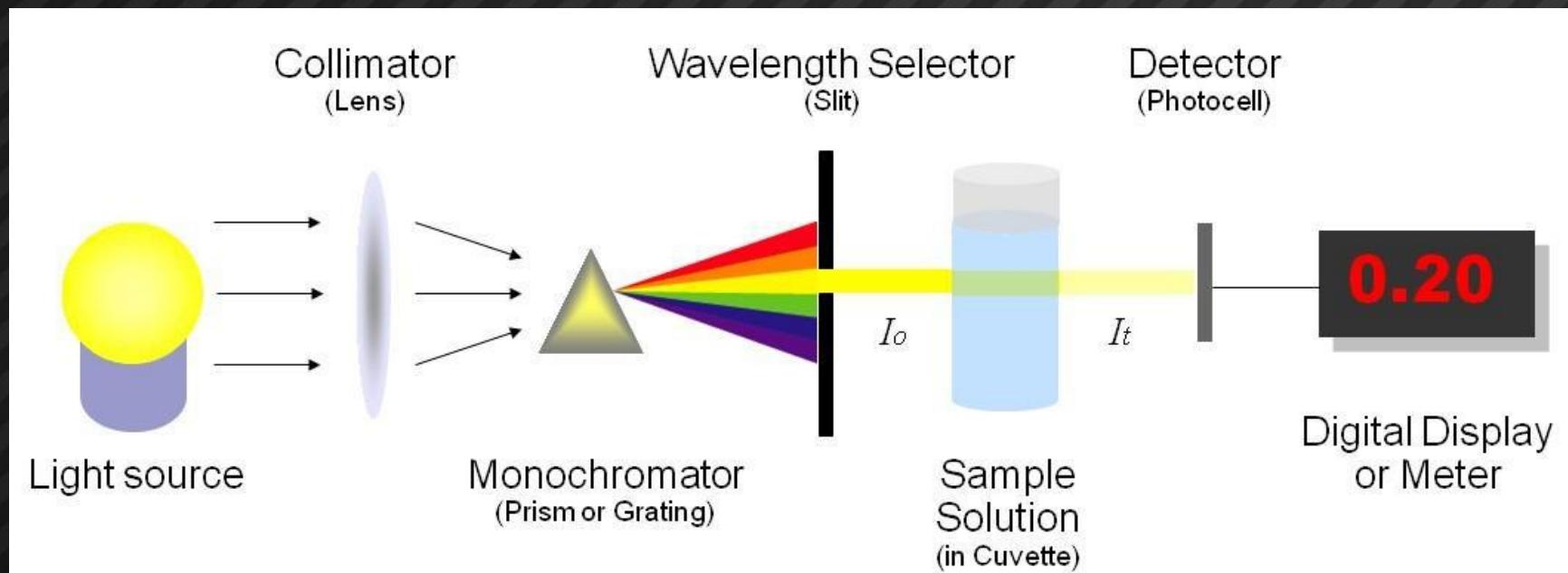


- ▶ Spectroscopy is the study of the interaction of electromagnetic radiation in all its forms with matter. The interaction might give rise to electronic excitations, (e.g. UV), molecular vibrations (e.g. IR) or nuclear spin orientations (e.g. NMR). Thus **Spectroscopy** is the science of the interaction of energy, in the form of electromagnetic radiation (EMR), acoustic waves, or particle beams, with matter.
- ▶ Analytical instruments exploit spectroscopy for both identification (qualitative analysis) and measurement (quantitative analysis) of atoms, ions and molecules.
- ▶ Can be used alone or in combination with chromatography to achieve both separation and measurement of multicomponent samples.
- ▶ The optical system that allows production and viewing of spectrum (VIBGYOR, and invisible to plain eyesight) is called spectroscope.
- ▶ **Spectrometry:** The measurement of the intensity ( $I$ ) of radiation, in the form of EMR or high energy particles (electrons, ions, etc.), with some form of electronic device.

# Introduction

- The spectrophotometer technique is to measures **light intensity** as a function of **wavelength**.
- It does this by:
  1. **diffracting** the light beam into a spectrum of **wavelengths**
  2. **direct** it to an object
  3. **receiving** the light reflected or returned from the object
  4. **detecting** the intensities with a charge-coupled device
  5. **displaying** the results as a graph on the detector and then the display device .[1],[2]

# Introduction



# Principles of absorption spectroscopy...

## Lamberts law:

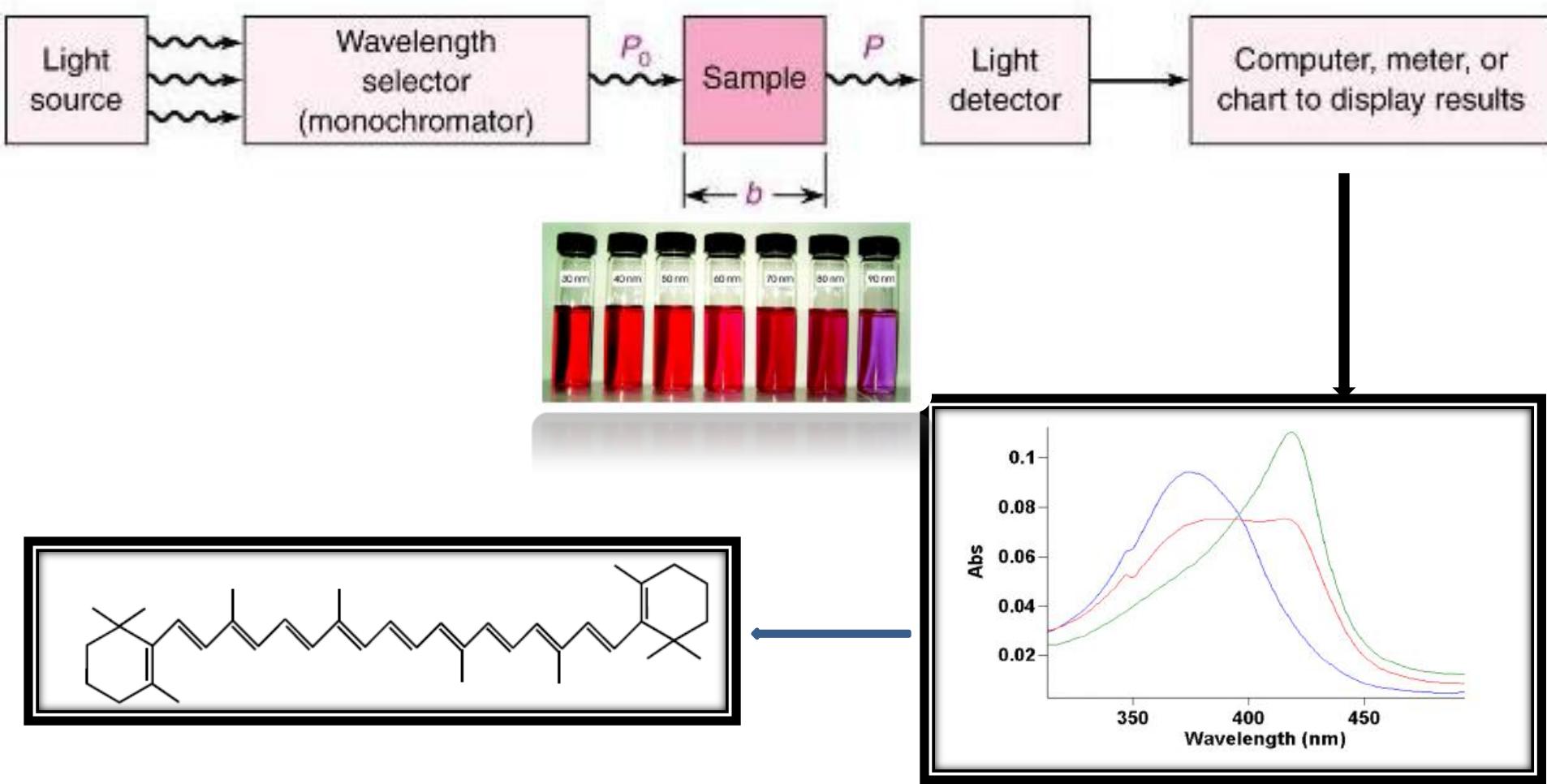
- It states that when monochromatic light passes through a transparent medium, the intensity of transmitted light decreases exponentially as the **thickness of absorbing material increases**

## Beer's law:

- It stats that the intensity of transmitted monochromatic light decreases exponentially as the **concentration of the absorbing substance increases**



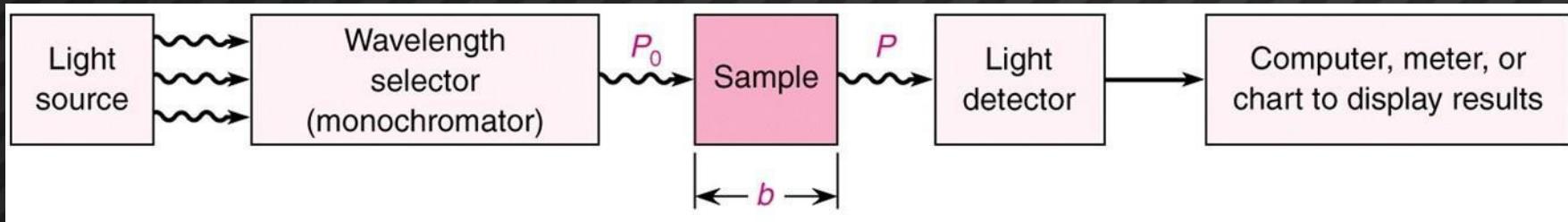
# Instrumentation



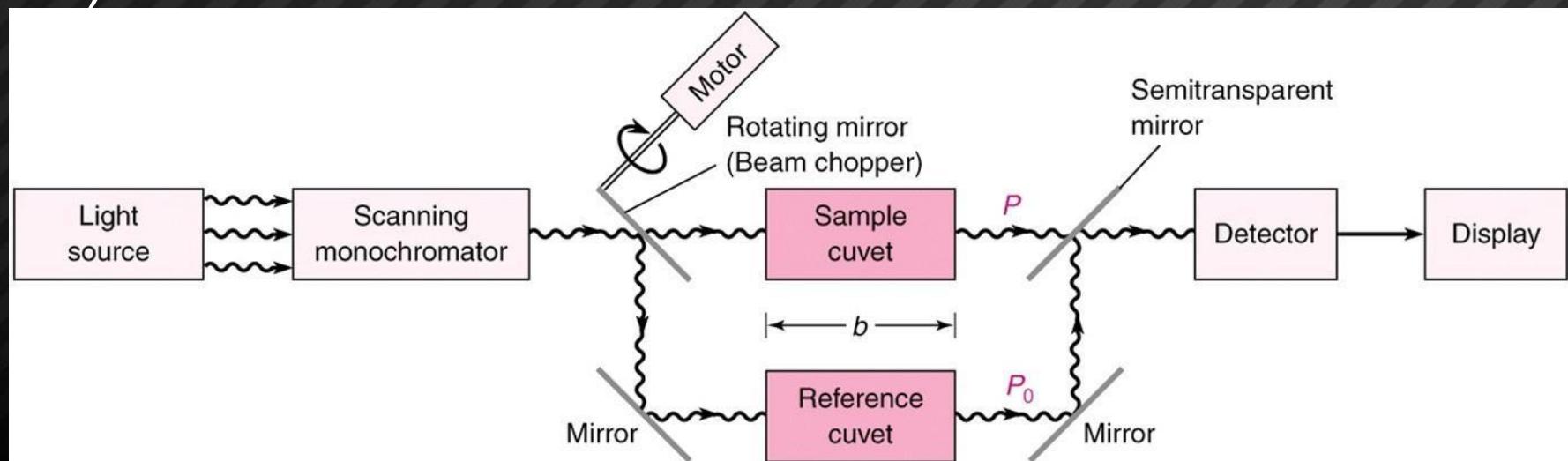
# Introduction

- Spectrophotometer:

a) Single-beam

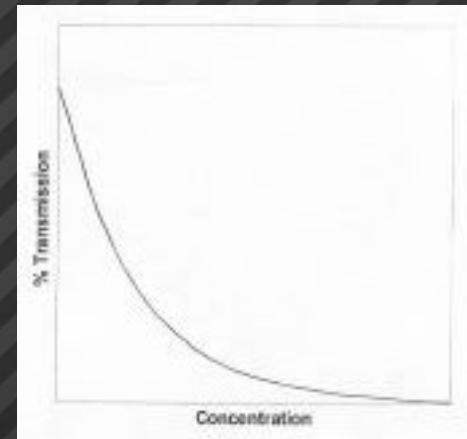
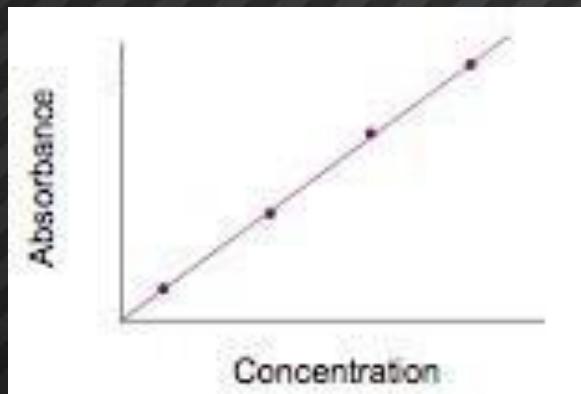


b) Double-beam



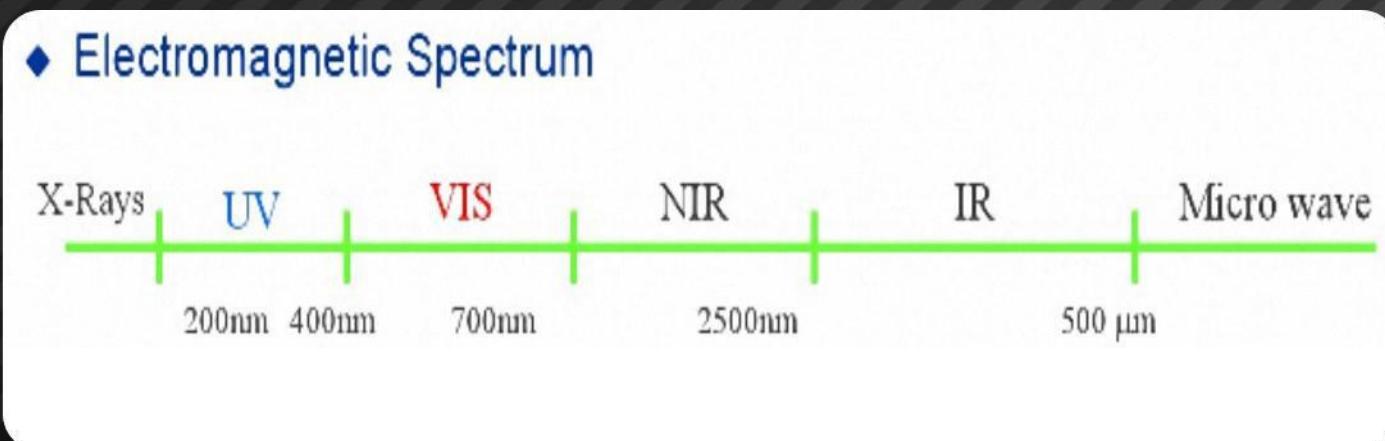
# Introduction

- compounds absorb light radiation of a **specific wavelength**.
- the amount of light radiation absorbed by a sample is measured.
- The **light absorption** is directly related to the **concentration** of the compound in the sample.
- As Concentration increases, light Absorption increases, **linearly**, As Concentration increases, light Transmission decreases, **exponentially**.[3]



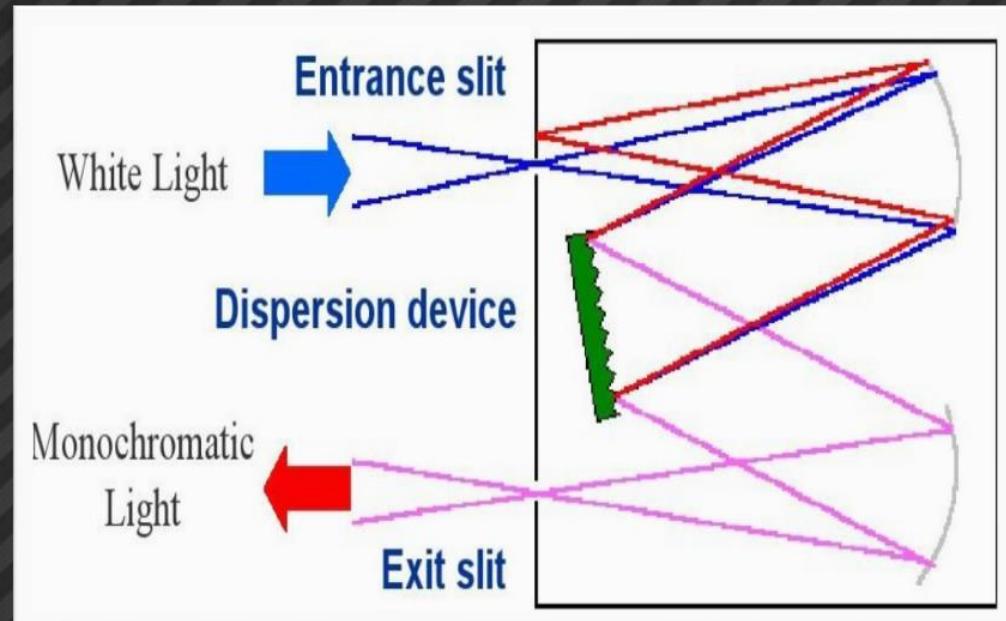
# Instruments

- **Light source:** provide a sufficient of light which is suitable for marking a measurement.
- The light source typically yields a high output of polychromatic light over a **wide range** of the spectrum.[4]



# Instruments

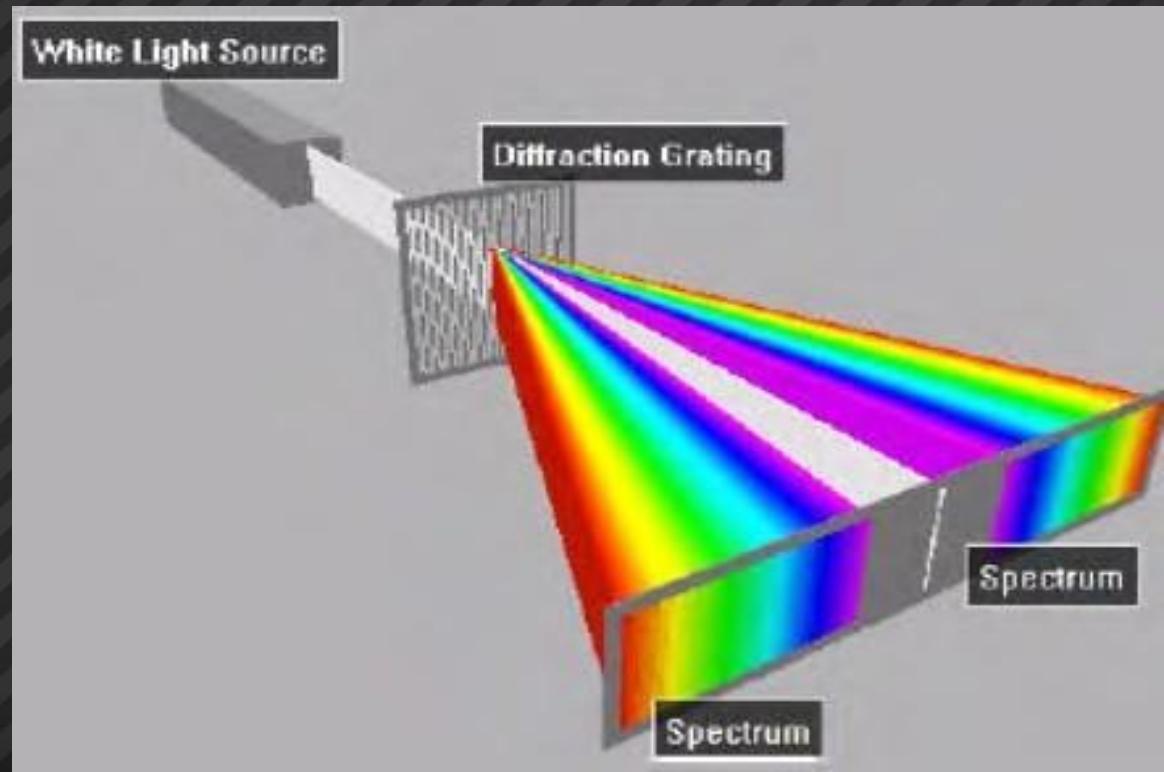
- **Monochromator** : Accepts **polychromatic** input light from a lamp and outputs **monochromatic** light.
- Monochromator consists of these parts:
  - I. Entrance slit
  - II. Collimating lens or mirror
  - III. Dispersion element
  - IV. Focusing lens or mirror
  - V. Exit slit [6]



# Instruments

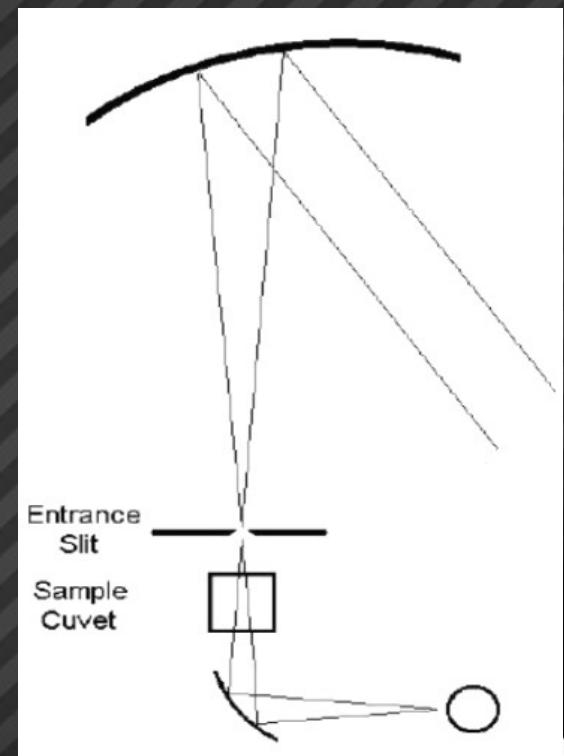
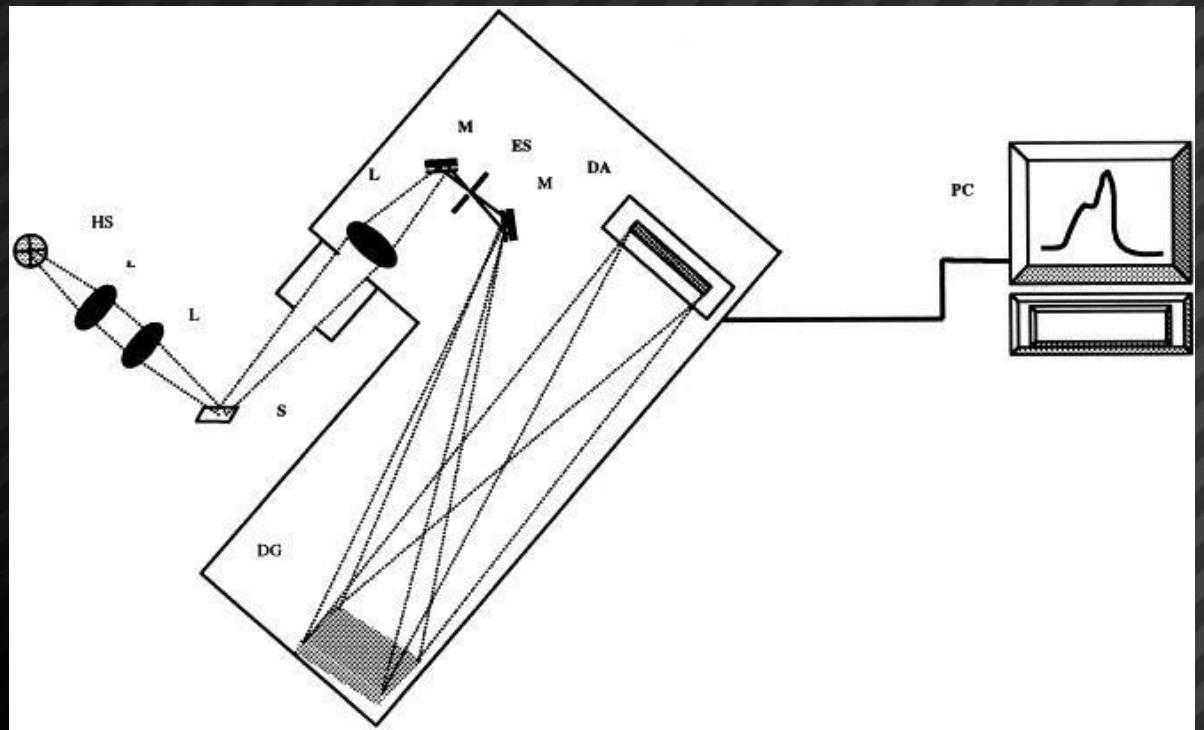
- **Dispersion devices:** A special plate with hundreds of **parallel grooved lines**.
- The grooved lines act to **separate** the white light into the visible light spectrum.

The more lines  
the smaller  
the wavelength  
resolution.[5]



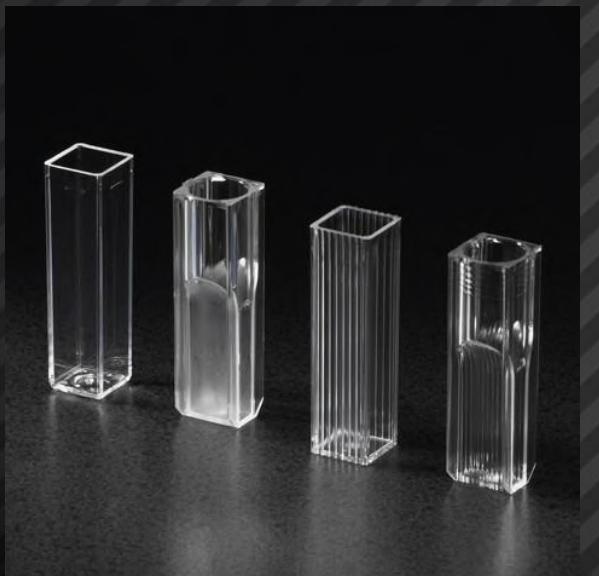
# Instruments

- **Focusing devices:** Combinations of lenses, slits, and mirrors.
- relay and focus light through the instrument.[2]



# Instruments

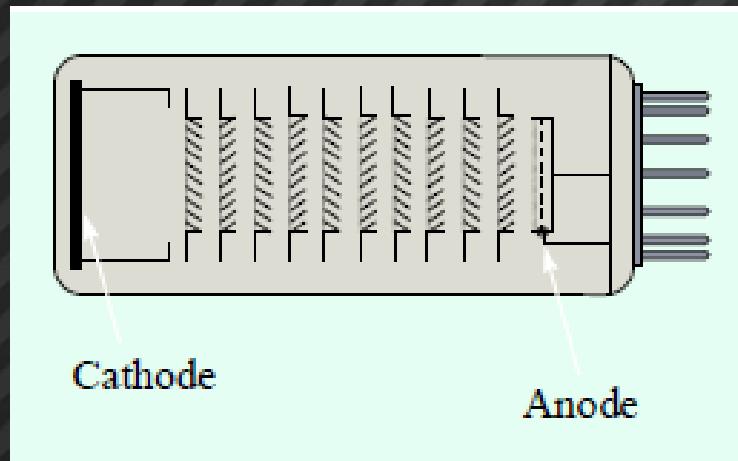
- **Cuvettes:** designed to hold samples for spectroscopic experiments. made of **Plastic**, glass or optical grade **quartz**
- should be as **clear** as possible, without impurities that might affect a spectroscopic reading.[2]



# Instruments

- **Detectors:** Convert radiant energy (photons) into an **electrical signal**.

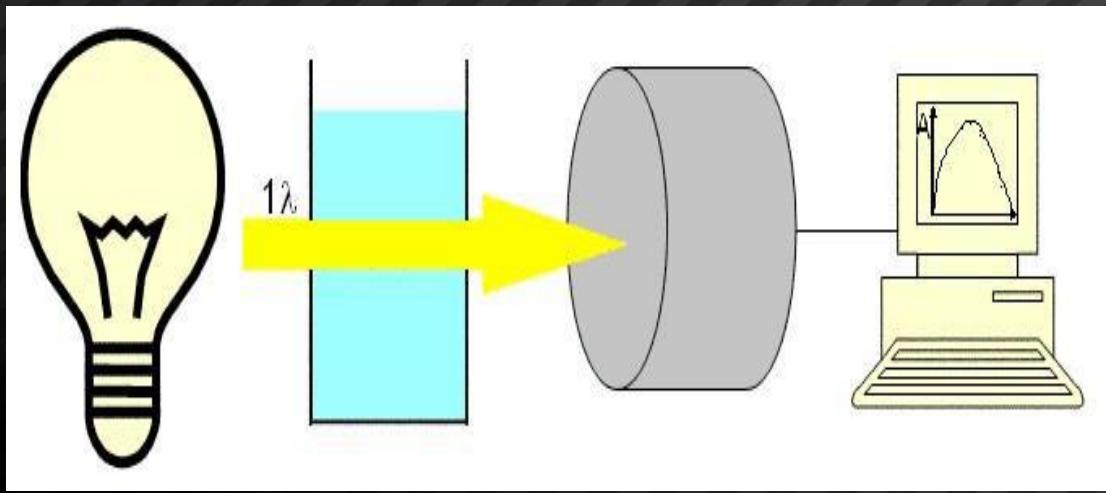
The **photocell** and **phototube** are the simplest photodetectors, producing current proportional to the intensity of the light striking them .[1],[2]



**The photomultiplier tube detector**

# Instruments

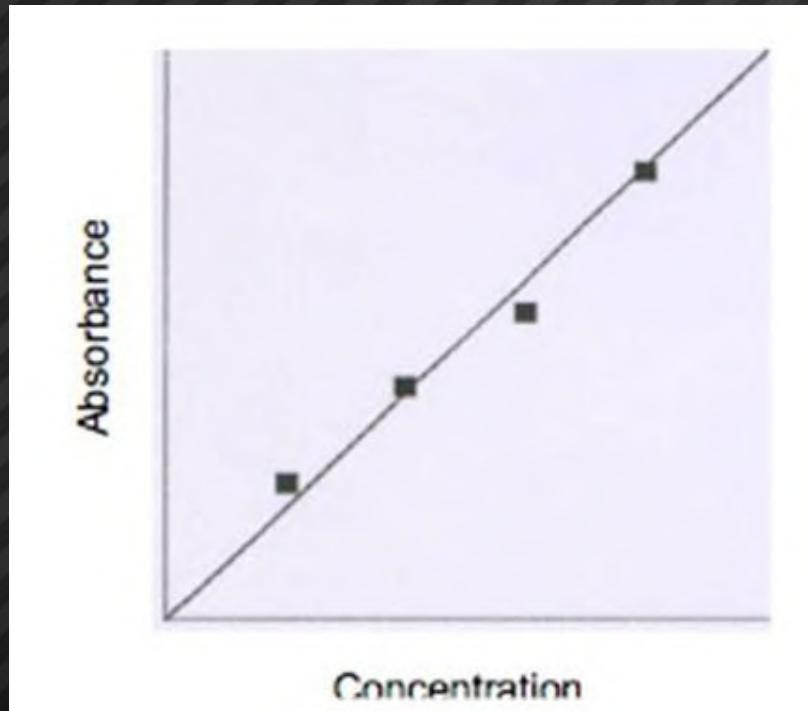
- **Display devices:** The data from a detector are displayed by a readout device, such as an **analog meter**, a light beam reflected on a scale, or a digital display , or **LCD** .
- The output can also be transmitted to a **computer** or **printer**. [3]



# Applications

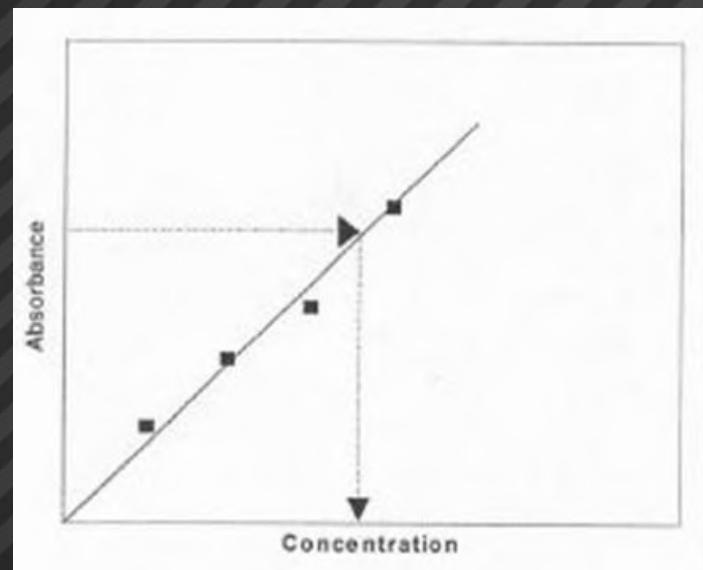
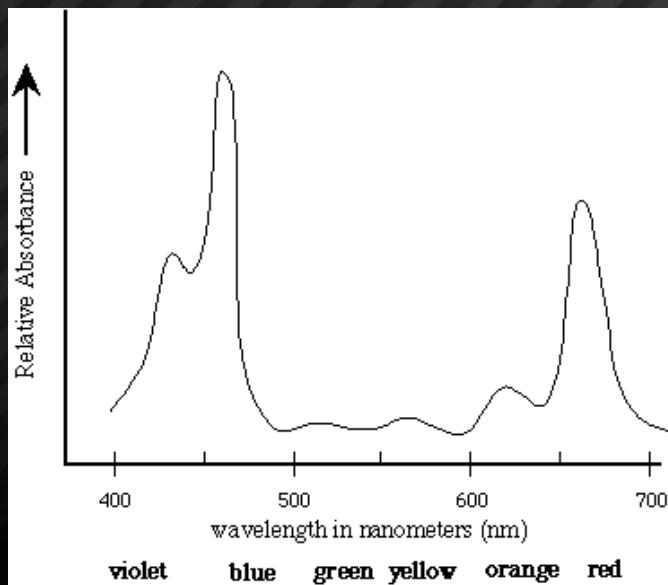
## 1. Concentration measurement

- Prepare samples
- Make series of standard solutions of known concentrations [4]



# Applications

- Set spectrophotometer to the  $\lambda$  of maximum light absorption
- Measure the absorption of the unknown, and from the standard plot, read the related concentration[4]

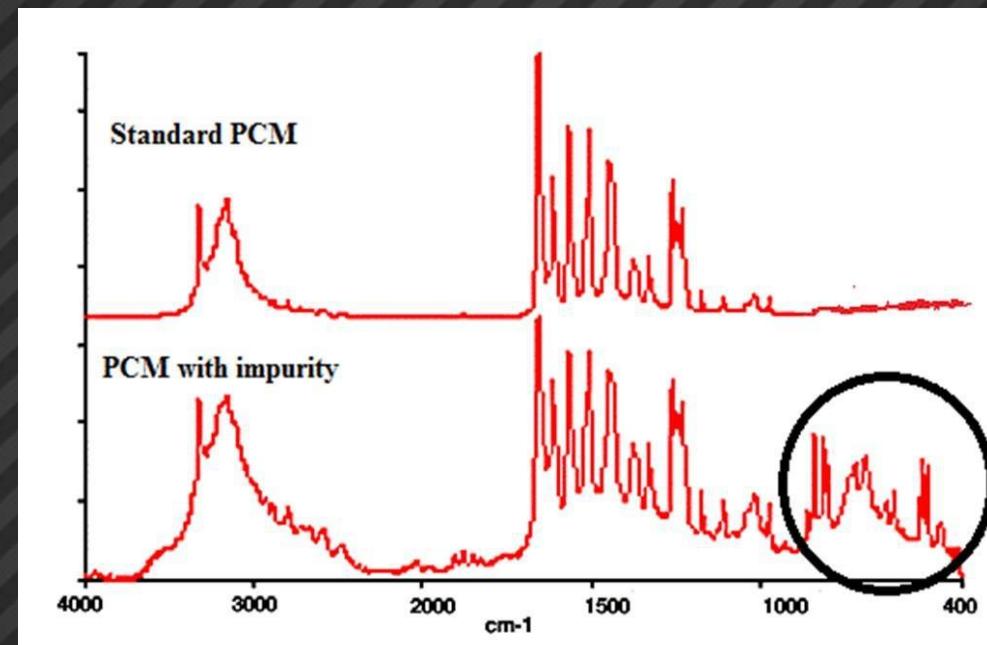


# Applications

## 2. Detection of Impurities

- UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules. [7]

Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.



# Applications

## 3. Structure elucidation of organic compounds.

- From the location of **peaks** and combination of peaks UV spectroscopy elucidate **structure** of organic molecules:
  - the presence or absence of **unsaturation**,
  - the presence of **hetero atoms**.[7]

# Applications

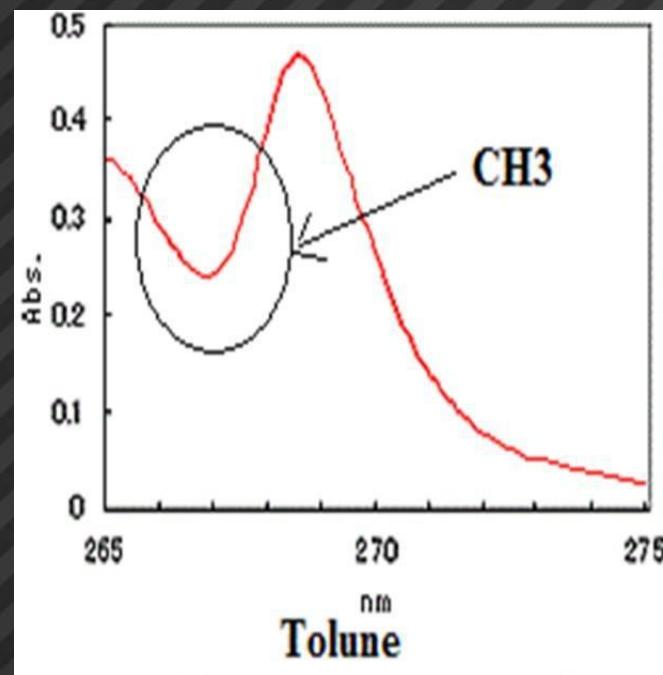
## 4. Chemical kinetics

- Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the **absorbance changes** can be observed.[7]

# Applications

## 5. Detection of Functional Groups

- Absence of a band at particular wavelength regarded as an evidence for absence of particular group [5]

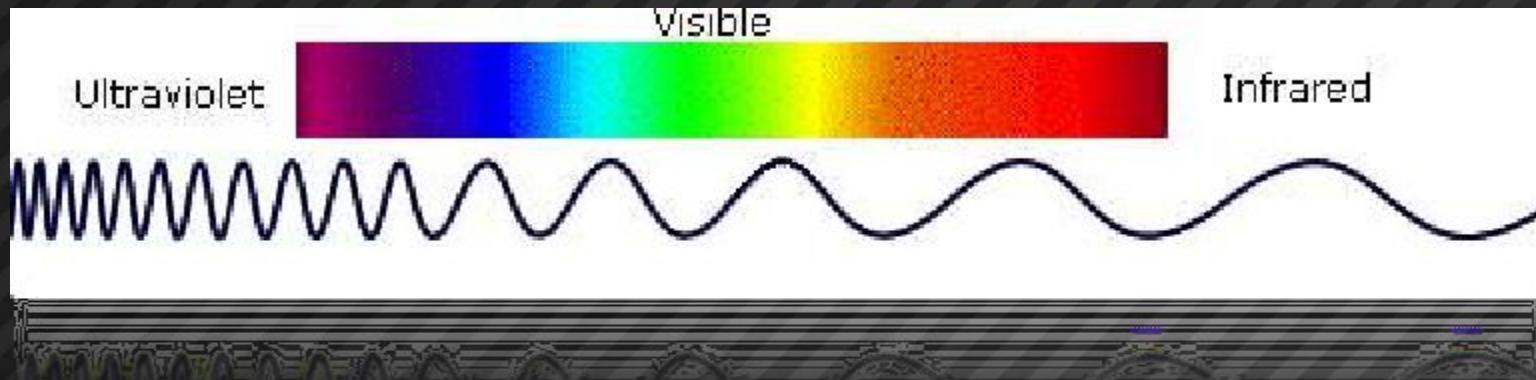


# Applications

## 6. Molecular weight determination

- Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable **derivatives** of these compounds.
- For example, if we want to determine the molecular weight of amine then it is converted in to **amine picrate**. [7]

# INFRARED REGIONS



INFRARED REGIONS	RANGE
<i>Near infrared region</i>	$0.8\text{-}2.5 \mu(12,500\text{-}4000 \text{ cm}^{-1})$
<i>Main infrared region</i>	$2.5\text{-}15 \mu(4000\text{-}667\text{cm}^{-1})$
<i>Far infrared region</i>	$15\text{-}200 m \mu(667\text{-}100 \text{ cm}^{-1})$

## **Definition:**

- It is the study of absorption of infrared radiation which results in vibrational transitions.
- IR spectrum is an important record which gives sufficient information about the structure of a compound and also determine the functional group.
- IR spectroscopy is an useful tool to identify functional groups in organic molecules.
- IR spectroscopy is a result of molecular vibrational transitions that occur when light interacts with matter. Molecules are always vibrating. For a molecule to be IR active, the vibrations should give rise to a net change in dipole moment. Infrared spectroscopy



- When energy in the form of infrared radiation is applied then it causes the vibration between the atoms of the molecules and when, Applied infrared frequency = Natural frequency of vibration
- Then, Absorption of IR radiation takes place and a peak is observed.
- Different functional groups absorb characteristic frequencies of IR radiation. Hence gives the characteristic peak value.
- Therefore, IR spectrum of a chemical substance is a finger print of a molecule for its identification.



# MOLECULAR VIBRATIONS

Stretching vibrations

Bending vibrations

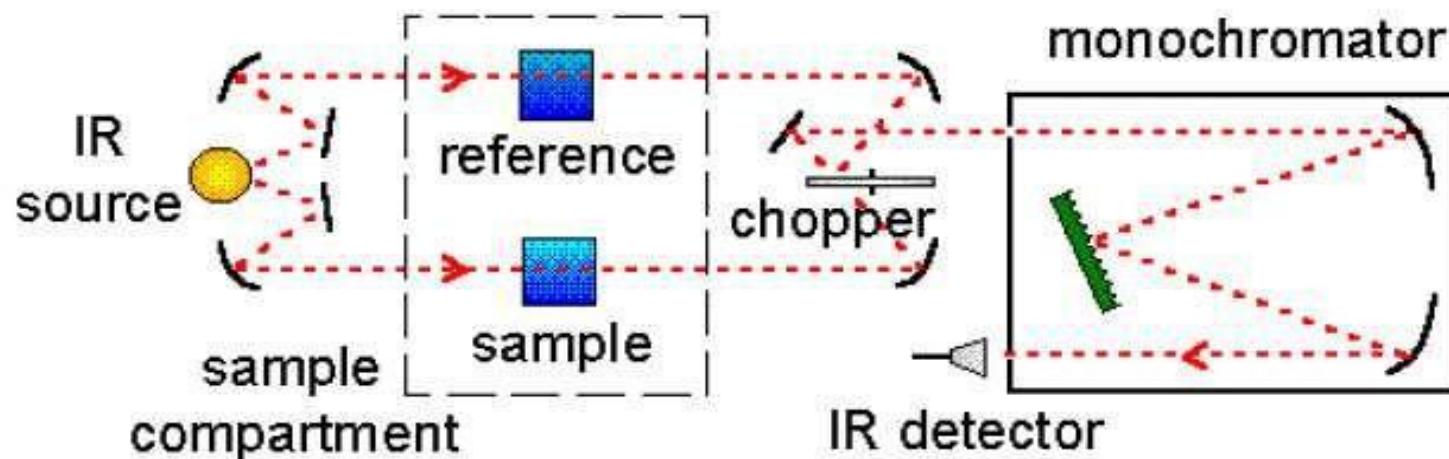
- Vibration or oscillation along the line of bond
- Change in bond length
- Occurs at higher energy:  
 $4000\text{-}1250\text{ cm}^{-1}$ 
  - a) Symmetrical stretching
  - b) Asymmetrical stretching
- Vibration not along the line of bond
- Bond angle is altered
- Occurs at low energy:  
 $1400\text{-}666\text{ cm}^{-1}$ 
  - a) In plane bending
  - b) Out plane bending

# Instrumentation

2 Types of IR spectrometer:

- Dispersive Grating Spectrophotometers
- Multiplex Instruments employing Fourier Transform (FTIR)

As infrared is an absorption technique, infrared radiation passes through the sample, and is detected. A **dispersive** spectrometer works as follows:



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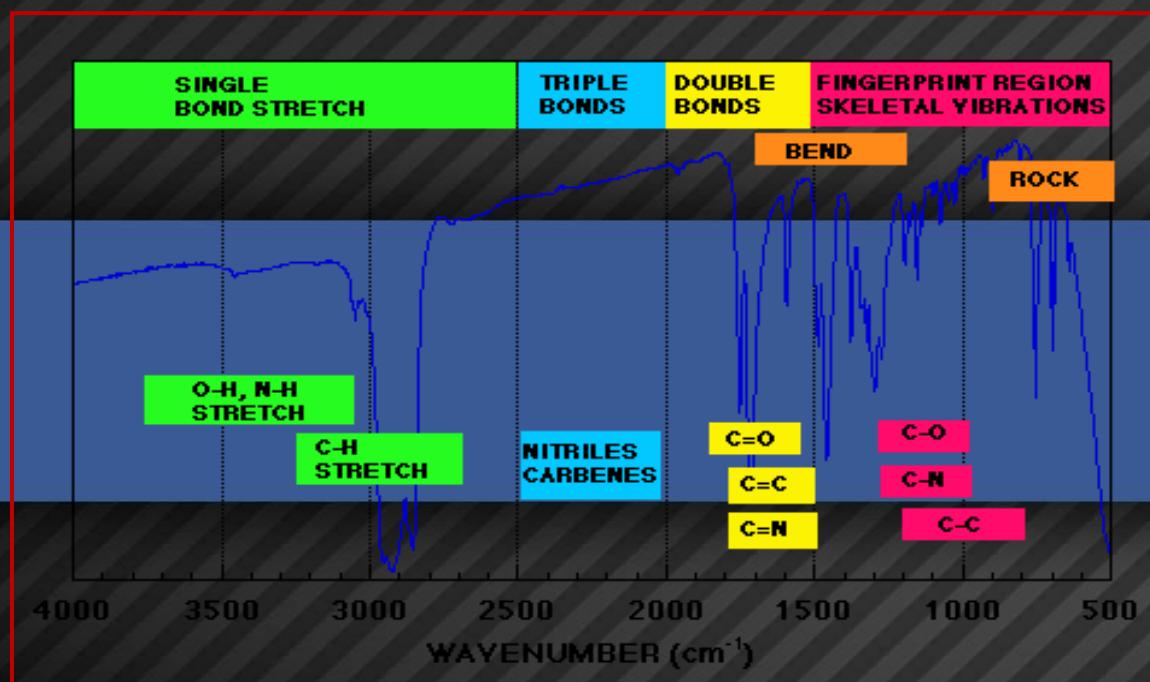
**NOTE:** It is the same configuration as a UV/Vis. absorption spectrometer except the light passes through the sample before reaching the monochromator.

## 1.) Qualitative Analysis (Compound Identification)

- main application
- Use of IR, with NMR and MS, in late 1950's revolutionized organic chemistry
  - decreased the time to confirm compound identification 10-1000 fold

### i.) General Scheme

- 1) examine what functional groups are present by looking at group frequency region -  $3600\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$

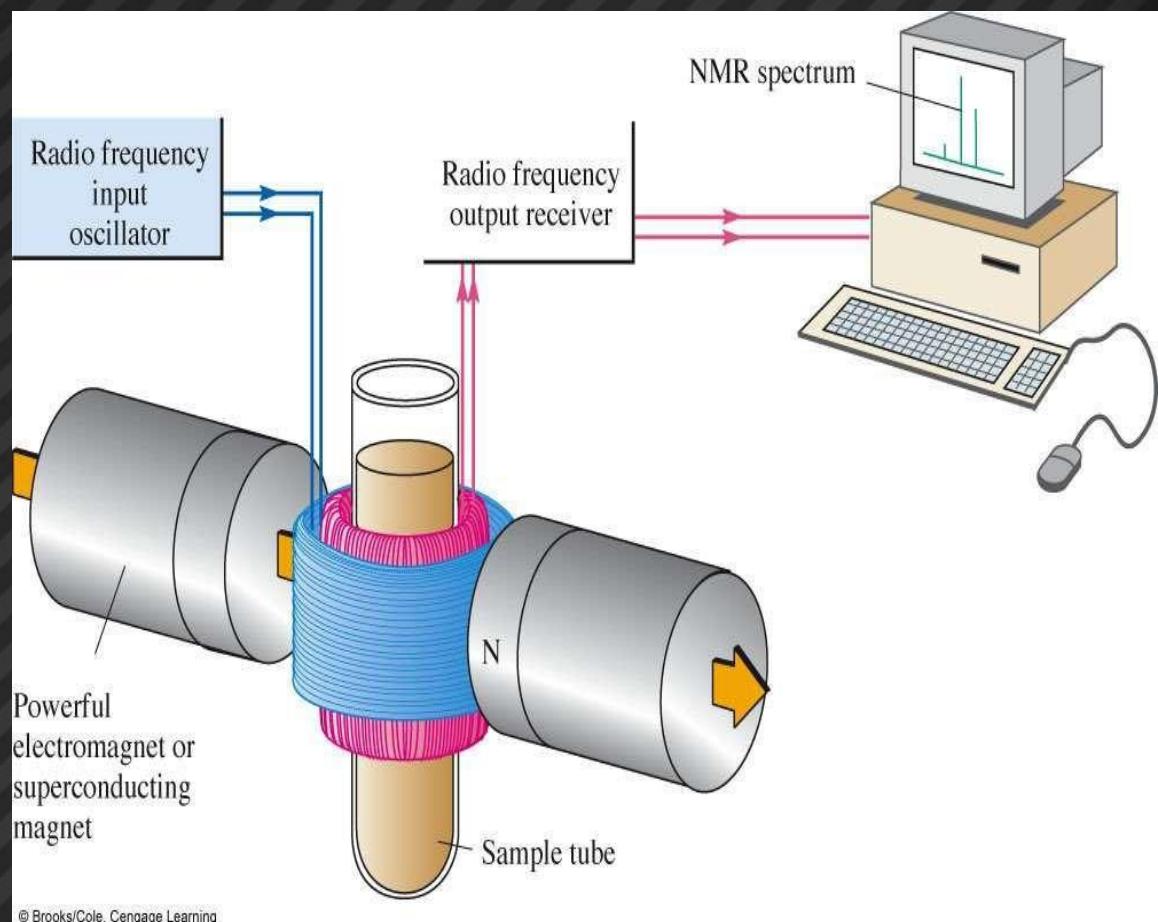


# Applications

- Analysis of urine and other biofluids (urea, creatinine, protein)
  - Quality control of pharmaceutical formulations
  - Determination of particle size
  - Determination of blend uniformity
  - Determination or identification of polymorphic drugs

# NMR INSTRUMENTATION

1. Sample tube/sample holder
2. Permanent magnet
3. Magnet coil
4. Sweep generator
5. Radio frequency transmitter
6. Radio frequency receiver
7. Readout system





## COMPONENTS OF THE SPECTROPHOTOMETER

**Basically NMR instrumentation involves the following units.**

**A magnet to separate the nuclear spin energy state.**

**Two RF channels, one for the field/frequency stabilization and one to supply RF irradiating energy.**

**A sample probe containing coils for coupling the sample with the RF field; it consists of Sample holder, RF oscillator, Sweep generator and RF receiver.**

**A detector to process the NMR signals.**

**A recorder to display the spectrum.**

- **Spectroscopy** is the study of interaction of EMR with matter, which may result in absorption, transmission, emission, reflection, rotation of EMR
- **Nuclear magnetic resonance spectroscopy**, most commonly known as **NMR spectroscopy**.

Nuclear Magnetic Resonance (NMR) is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the radio frequency region 4 to 900 MHz by nuclei of the atoms.

- Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.
- It is used to study a wide variety of nuclei:
  - $^1\text{H}$
  - $^{15}\text{N}$
  - $^{19}\text{F}$
  - $^{13}\text{C}$



**NMR spectroscopy is different from the interaction of electromagnetic radiation with matter.**

**In this spectroscopy the sample is subjected simultaneously with two magnetic field, One is a stationary and another is varying at same radio frequency.**

**The particular combination of these two field energy is absorbed by sample and signal is obtained when electromagnetic field is provided to the nucleus of sample. The nucleus start to spin around the nuclear axies and generate an another magnetic field. And particular combination of this two field the energy is absorbed by nucleus this technique is called as a NMR spectroscopy.**

- This transition of nucleus occurs in radio frequency region. The radio waves are considered for lowest energy and this energy is just sufficient to affect the nuclear spin of the atom in a molecule. Hence, this is a most fundamental part of NMR spectroscopy.
- In general, the study of radio frequency radiation by nuclei is called nuclear magnetic resonance.

The method of NMR was first developed by E.M. Purcell and Felix Bloch (1946).

