CHAPTER-1 ATOMIC & MOLECULAR STRUCTURE

Classical Mechanics – (Newtonian Mechanics)

→ Contains 3 laws of motion

- First-law - Law of Inertia
- 2nd Law ⇒ $F \propto \frac{dP}{dt}$
- 3rd Law ⇒ Equal and opposite Reaction.

} only followed by MACROSCOPIC OBJECTS ↓ Have Particle Nature

* Classical Mechanics failed to Explain motion of MICROSCOPIC Objects.

* Microscopic object like electron posses DUAL Nature (Wave + Particle)

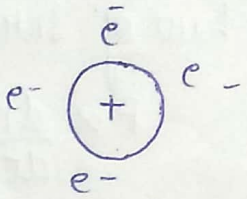
Failure of classical Mechanics gave Birth to Quantum Mechanics

Particle Nature	Wave Nature
→ Localised in space	Delocalised in space
→ Two Particles cannot occupy same space	→ can occupy same space (co-exist) in same Region (Interference)
ex. Cricket ball.	ex. Sound wave

Both Macroscopic and Microscopic Particles have Dual Nature (Particle + Wave) But wave attached to Macroscopic object has small wavelength which is not significant (very small)

Models of ATOM

(i) J. J. THOMSON



→ PLUM PUDDING MODEL OR RAISIN PUDDING MODEL

→ Explained Neutrality of atom but cannot explained Rutherford scattering experiment.

James Chadwick - Neutron
↓
B bombarded by α particles
↓
neu particles emitted
↓
No charge

(ii) RUTHERFORD MODEL

He Bombarded thin foil of metal like Au, Ag or Pt with beam of fast moving α - Particles.

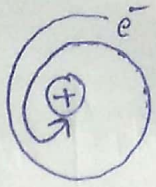
ATOM consist of Two Parts

(i) Nucleus
↓
(a) +ve charge
(b) Entire mass of atom Concentrated

(ii) Extra Nuclear Part
↓
Space around Nucleus

wbak of Rutherford

PART Unable to explain stability of atom



- (maxwell electromagnetic) - i.e charge Particle goes under accleration due to change in direction even if speed Remains constant & start loosing energy in form of EM Radiations.

→ Unable to explain distribution and energies of e-

→ " " line spectra of elements

BOHR MODEL OF ATOM

Quanta ← Rad. energy emitted

↑

* Based on PLANCK Quantum Theory $E \propto \nu$ or $E = \frac{hc}{\lambda}$

$h = 6.626 * 10^{-34}$ J sec

$\boxed{E = Nh\nu}$

Postulates

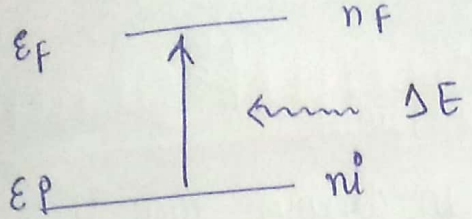
→ atom consist of small, heavy, +vley charg Nucleus & e- revolve around Nucleus

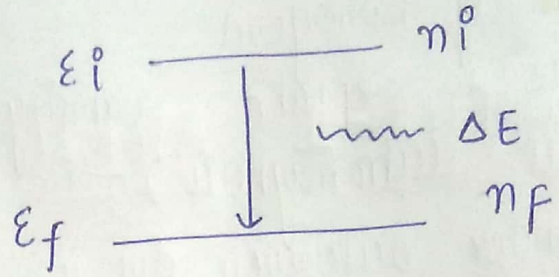
→ Circular Path are called orbit or allowed energy levels or stationary states. (K, L, M, N)

→ Quantisation of Energy

[Quantisation → quantity cannot change continious to have arbitary value but can change only discountinously to have specific value

→ Also e- Donot Radiate energy if stayed in one orbit and hence do not slow down.





Angular Momentum also Quantised

$$mvr = \frac{nh}{2\pi}$$

m = mass of e⁻
n = any integer
v = velocity of e⁻

Success of BOHR MODEL

* Explained Concept of Orbits Stationary state $n = 1, 2, 3,$ principal Quantum No.
* Explained Stability of Atom
* BOHR Radii of Orbit $r = \frac{0.529\, n^2}{Z}$ A^0
* BOHR Energy of e⁻ $E_n = -\left(\frac{13.6}{n^2}\right) Z^2$ ev/atom

$$1 ev = 1.6022 * 10^{-19} J$$

$E_1 = -2.18 * 10^{-18}$, $E_2 = -0.545 * 10^{-8} J$, $E_\infty = 0$

→ This shows @ ∞ distance No force of attraction is There on e⁻ by Nucleus

* Bohr velocity of e⁻ = $V_n = V_0 * \frac{Z}{n}$ $V_0 = 2.18 * 10^8 cm\, s^{-1}$
* Quantative explanation of Line Spectrum (H like atoms He^+, Li^{2+} & Be^{3+})

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

1 J = 10^7 erg

Absorption	Emission
$n_f > n_i$	$n_F < n_i$
+ve	-ve

n_i = 1	L – Ultraviolet
2	B = Visible
3	P = Infrared
4	B = Infr
5	P → Far Infrared

$R_H = 1.0937 * 10^7 m^{-1}$

Limitation

* Spectra of Multielectron ~~Atoms~~.
* Finer Details of H atom
* Splitting of spectral lines in presence of MF & EF (Zeeman effect ↑, Stark effect ↑)
* Bohr ⇒ 1D model but actually it is 3D

SOMMERFELD THEORY OR BOHR SOMMERFELD THEORY

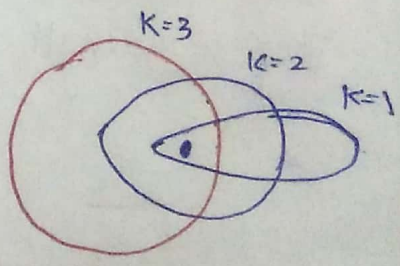
Explaination of splitting of fine spectral lines into very fine spectral lines

→ Stationary orbit around the Nucleus in atom are not circular but elliptical in shape

$$\frac{\text{major axis}}{\text{minor axis}} = \frac{n}{k}$$ when = k = n

k → azimuthal or Subsidiary Quantum No.

n = 3



n = 3 , k = 0 to n-1

(a) Energy of stationary orbit does Not depend upon n but K to some extent as well

So when transition occur from Higher to lower level It would be different because of more than one value of K

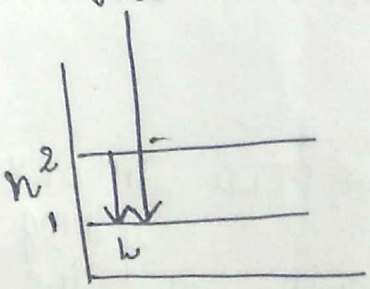
(b) Zeeman effect explained ⇒ magnetic Quantum Number

elliptical orbitals takes upon certain orientations

$m = (2l+1)$ $\quad -l$ to $+l$

Q.- Calculate Short and long wave length limit of Lyman Series

$$\nu = \frac{1}{\lambda} = R_H \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$



Short wave lengt $n_i = 1$, $n_f = \infty$

$$\frac{1}{\lambda} = 1.09691 * 10^7 m^{-1} * \left[\frac{1}{1} - \frac{1}{\infty} \right]$$

$$= \boxed{\lambda_S = 91.16 \text{ nm}}$$

Long wavelength = $\frac{1}{\lambda} = 1.09691 * 10^7 m^{-1} \left[\frac{1}{1} - \frac{1}{2^2} \right]$

$$= \frac{1}{\lambda} \quad \boxed{\lambda = 0.1215 \text{ nm}}$$

Reason For Failure of BOHR MODEL

(i) BOHR model contradict Heisenbergs Uncertainity Principle

(ii) BOHR model ignore De-broglie dual Nature of matter.

(i) De-Broglie

In 1905, Einstien suggested Light or Radiation Has dual Nature as wave and as Particle.

Louis-Victor de Broglie 1924 proposed that Matter also Has Dual Character : as wave and as Particle.

Wave associated with material Particle is called matter or Debroglie waves

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

*Using Mass Energy Relationship $E = mc^2$

$E = h\nu$

$$h\frac{c}{\lambda} = mc^2$$

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

$\lambda \propto \frac{1}{p}$

D.B. equation Relates Particle character with wave character of material Particles.

Replacing c with velocity of $e^\ominus$

$$\lambda = \frac{h}{mv} \text{ or } \frac{h}{p}$$

Electromagnetic waves	Matter waves
→ Electrically charged Particles moves under acceleration, alternating electric and magnetic field are produced which are ⊥ to each other & Transmitted as EM waves	Not associated with electric & Magnetic field.
→ Can pass through vacuum	Cannot Pass through vacuum (Requires medium)
→ Travel with speed of light	→ cannot travel through speed of light
→ $\lambda = \frac{c}{\nu}$	$\lambda = \frac{h}{m\nu}$
→ Emitted from Particular source in form of Radiation	→ attached to moving Particle not emitted from source.

Derivation of BOHR POSTULATE OF ANGULAR MOMENTUM

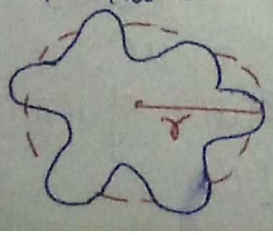
→ Duality to BOHR THEORY.

→ e^- moving in circular orbit of radius r around a nucleus evidently if wave is to Remain Continuously in phase

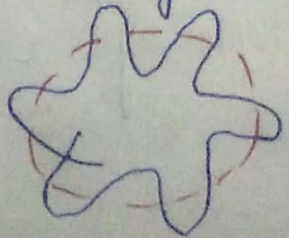
(circumference) $2\pi r = n\lambda$ (integral multiple of waves)

$$2\pi r = \frac{n\lambda}{m\nu}$$

in Phase



out of Phase



Angular momentum

$$mvr = \frac{nh}{2\pi}$$

$m_e = 9.1 * 10^{-28} g$, $e = 4.8 * 10^{-10}$ esu

1 J = Kg m2 s-2

* mass of $e^- = 9.1 * 10^{-31}$ Kg & K.E = $5 * 10^{-25}$ J

Calculate de-Broglie wavelength

$$K.E = \frac{1}{2} m v^2 \quad \text{or}$$

$$5 * 10^{-25} \text{ Kg m2 s-2} = \frac{1}{2} * 9.1 * 10^{-31} \text{ Kg} *$$

$$= \boxed{V = 1.048 * 10^{3}} \text{ ms-2}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 * 10^{-34} \text{ Kg m2 s-1}}{9.1 * 10^{-31} \text{ Kg} * 1.048 * 10^{3} \text{ m s-1}}$$

$$\boxed{\lambda = 6.94 * 10^{7} \text{ m}}$$

$$\lambda = \frac{h}{\sqrt{2meV}} \quad \text{or} \quad \lambda = \frac{12.25}{\sqrt{V}} \qquad \boxed{\lambda \propto \frac{1}{\sqrt{V}}}$$

$m_e = 9.1 * 10^{-28} g$, $e = 4.8 * 10^{-10}$ esu

1 J = Kg m2 s-2

* mass of $e^- = 9.1 * 10^{-31}$ Kg & K.E = $5 * 10^{-25}$ J

Calculate de-Broglie wavelength

$$K.E = \frac{1}{2} m v^2 \quad \text{or}$$

$$5 * 10^{-25} \text{ Kg m2 s-2} = \frac{1}{2} * 9.1 * 10^{-31} \text{ Kg} * V^2$$

$$= \boxed{V = 1.048 * 10^{3}} \text{ ms-2}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 * 10^{-34} \text{ Kg m2 s-1}}{9.1 * 10^{-31} \text{ Kg} * 1.048 * 10^{3} \text{ ms-1}}$$

$$\boxed{\lambda = 6.94 * 10^{-7} \text{ m}}$$

$1eV = 1.602 * 10^{-19} J$ $1ev = 1.6 * 10$ what

$1eV = 1.602 * 10^{-12}$

$1erg = 10^{-7}$ Joule

Ques - An e^- beam is accelerated by potential difference of 10,000 eV. Find λ ?

$K.E = 10{,}000 * 1.6 * 10^{-19}$ Joules $\quad \lambda = \frac{h}{P}$

$K.E = \frac{1}{2} mv2 * \frac{m}{m} = \frac{1}{2} \frac{m2\,v2}{m}$

$E = \frac{P2}{2m}$

$P = (2mE)^{1/2}$

or

$v = \sqrt{\frac{2 * 1.6 * 10^{-15} J}{9.11 * 10^{-31}}} = 5.9 * 10^7 ms^{-1}$

$\lambda = \frac{h}{mv} = \frac{6.626 * 10^{-34} kg\ m2s^{-1}}{9.11 * 10^{-31} kg * 5.9 * 10^7 ms^{-1}}$

$\lambda = 0.123\ A^0$ or $.123 * 10^{-10}$.

Alternatively = $\lambda = \frac{12.25\ A^0}{\sqrt{V}}$

Ques- Calculate mass of photon which a wave is associated with λ 2.5 A^0 $\quad V = 3 * 10^8 m/s$

$\lambda = \frac{h}{m * v}$

$m = \frac{h}{\lambda v}$

$\boxed{m = 0.88 * 10^{-32} kg}$

(Q-) Calculate D.B.W of e^- moving with velocity = $1.20 * 10^5 ms^{-1}$

$$\lambda = \frac{h}{m * V} = \frac{6.626 * 10^{-34}\ kg\ m^2 s^{-2}\ s}{9.1 * 10^{-31}\ kg * 1.20 * 10^5\ ms^{-1}}$$

$$\boxed{\lambda = 6.068 * 10^{-9}\ m}$$

Q → Calculate de broglie 1kg with $2000\ ms^{-1}$

$$\lambda = \frac{h}{m * V} = \frac{6.626 * 10^{-34}\ kg\ m^2 s^{-2}\ s}{1\ kg\ \ 2000\ ms^{-1}}$$

$$\boxed{\lambda = 3.313 * 10^{-37}\ m}$$

Postulates of Quantum Mechanics

Heisenberg Uncertainty Principle

German Physicist → Nobel prize in 1932.

* It states that it is NOT possible to determine precisely both position and momentum (velocity) of small moving particle like $e^{\ominus}$.

If photon of light incident on Particle The e⁻ will suffer a change in velocity & Path due to impact of single photon of light used to observe it.

e⁻ moving in x direction

$$(\Delta x)(\Delta p_x) \geq \frac{h}{4\pi}$$

Δx = Uncertainity in position

Δp_x = " " momentum

Ques- A microscope using suitable photon is employed to locate an e^- in atom within a distance of 0.1 A°.

$\Delta p_x = ?$, mass of $e^- = 9.1 * 10^{-31}$ kg

$$\Delta x * \Delta p_x \geq \frac{h}{4\pi}$$

$$\Delta x * m * \Delta u_x \geq \frac{h}{4\pi}$$

$$\Delta U_x = \frac{6.626 * 10^{-34} \text{ Js}}{4\pi * 9.1 * 10^{-31} \text{ kg} * 0.1 * 10^{-10} \text{ m}}$$

$$\Delta U_x = \frac{6.626 * 10^{-34} \text{ kg m}^2 \text{s}^{-2} * \text{s}}{4\pi * 9.1 * 10^{-31} \text{ kg} * 0.1 * 10^{-10} \text{ m}}$$

$$\boxed{\Delta U_x = 0.579 * 10^7 \text{ ms}^{-1}}$$

Q- Wicket ball 100g to be located with 0.1 A° what is Δv_x? comment

$$\Delta U_x = \frac{6.626 * 10^{-34} \text{ kg m}^2 \text{s}^{-2} \text{ s}}{4\pi * 0.1 \text{ kg} * 0.1 * 10^{-10}}$$

$$\boxed{\Delta U_x = 0.527 * 10^{-22} \text{ ms}^{-1}}$$

We can disregard the uncertainity principle for motion of Macroscopic bodies

Postulates of Quantum Mechanics

1st Postulate

Physical state of system at time t is described by wavefunction $\psi(x,t)$

2nd Postulate

$\psi(x,t)$, 1st derivative $\frac{\partial \psi}{\partial x}$ and $\frac{\partial^2 \psi}{\partial x^2}$ are continuous, finite and single valued for all value of x . Also wavefunction is Normalised

$$\int_{-\infty}^{+\infty} \psi^*(x,t)\, \psi(x,t)\, dx = 1$$

3rd Postulate

Physically observable Quantity can be Represented by Hermitian operator .

$$\int \psi_i^* \hat{A} \psi_j \, dx = \int \psi_j (\hat{A}\psi_i)^* dx$$

4th Postulate

allowed value of observable A are eigen values a_i, in operator equation

$$\boxed{\hat{A}\psi_i = a_i \psi_i}$$ eigen value equation

ψ_i : eigen fn ; a_i : eigen value

1926

DERIVATION OF TIME INDEPENDENT SCHRODINGER WAVE Eqn

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

♡ of QM

→ In schrodinger wave equation The discrete energy levels or orbits proposed by BOHR are Replaced mathematically by $f^n \psi$. which are Related to probability of finding an electron.

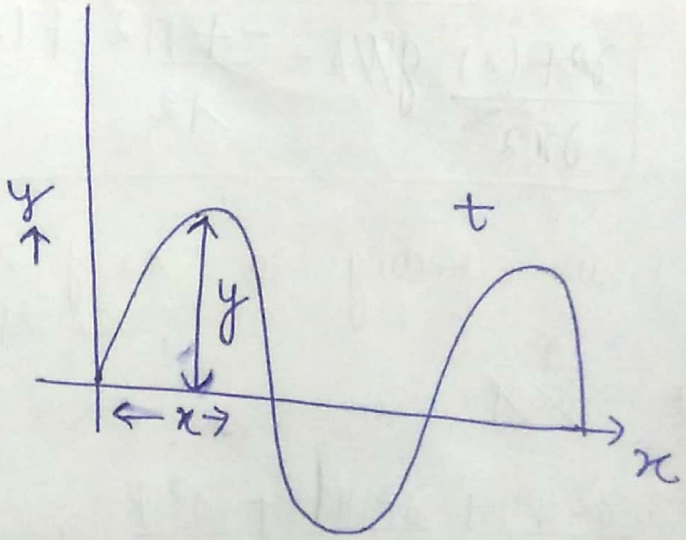
→ He considered that Nucleus is surrounded by vibrating e- wave which may be compared mathematically with stationary or standing wave

Differential equation

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} * \frac{\partial^2 y}{\partial t^2} \quad -(1)$$

v = velocity of wave

amplitude y depends upon t & x



$$y = F(x)\, g(t) \quad -(2)$$

For stationary waves $g(t) = A \sin(2\pi\nu t) \quad -(3)$

ν = vibrational frequency and A = constant = Maximum amplitude

$$y = F(x)\, A \sin(2\pi\nu t) \quad -(4)$$

Hence $\frac{\partial y}{\partial t} = f(x) A \cos(2\pi\nu t) * 2\pi\nu$

$\frac{\partial^2 y}{\partial t^2} = -f(x) 4\pi^2\nu^2 \sin(2\pi\nu t) = -4\pi^2\nu^2 f(x) g(t)$ — (5)

Similarly from (3)

$\frac{\partial^2 y}{\partial x^2} = \frac{\partial^2 F(x)}{\partial x^2} g(t)$ — (6)

Putting value of 5, 6 in 1

$\frac{\partial^2 F(x)}{\partial x^2} g(t) = \frac{1}{V^2} (-4\pi^2\nu^2) f(x) g(t)$ — (7)

Now $V = \nu\lambda$

$$\boxed{\frac{\partial^2 F(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} F(x)}$$ only for 1-D — (8)

Now extending to x, y and z direction

$f(x) = \psi(x, y, z)$

$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi$ — (9)

Schrodinger applied above to material waves $\lambda = \frac{h}{mv}$

$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2 m^2 v^2}{h^2} \psi$ — (10)

m = mass, v = velocity of Particle

ENER

Total Ener = KE + V

$(E-V) = \frac{1}{2} m v^2$

$m v^2 = 2(E-V)$ — (11)

Put (11) in (10)

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

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

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

∇^2 = Laplacian operator

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

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

Dividing Throughout by $\frac{8\pi^2 m}{h^2}$

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

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

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right]\psi = E\psi \text{ or}$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi$$

$\hat{H} = \frac{-K2}{2m}\nabla 2 + V$ or $\left[\frac{-h2}{8\pi 2m}\nabla 2 + V\right]$ = Hamiltonian operator

$$\boxed{\hat{H}\psi = E\psi}$$

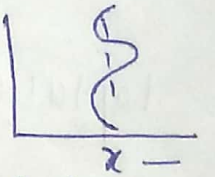
$$\hat{H} = \hat{T} + \hat{V}$$

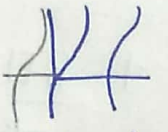
$$\boxed{\hat{T} + \hat{V} = E\psi}$$

it should be continious first Derivative, be single valued

[finite, single valued & continious].

WELL BEHAVED FUNCTION

(1) ψ must be single valued (s) 

(2) ψ must be ~~continuous~~ continuous 

Sin & Cos plots, Tan plot are Non continuous.

(3) ψ must finite value $(i = \sqrt{-1})$ Not acceptable

(4) ψ must be bounded in space.

(5) ψ must be Normalized

Probability of finding particle inside bounded space is 1

$$\int_{-\infty}^{+\infty} \psi^* \psi d\tau = 1$$

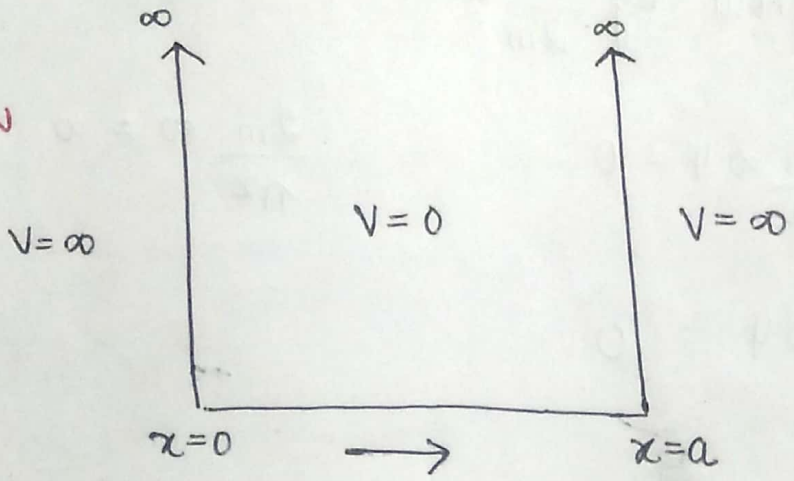
PARTICLE IN ONE DIMENSIONAL BOX: QUANTISATION OF TRANSLATION ENERGY

* Simplest application of Schrodinger WEq. To Translational motion of a Particle in space

→ Energies are Quantized i.e discrete values NOT continuously.

* It is a Hypothetical case, we assume that a single particle of mass m restricted to move in a Imaginary 1-D Box of length 'a' with ∞ high walles

PARTICLE IN POTENTIAL WELL



High Potential diff. Particle cannot Jump Outside box.

Soln of SWE

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x,y,z)$$

Only x direction To be considered

$$\hat{H}\psi = E\psi$$

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi = E\psi \quad - (1)$$

(i) Schrodinger WE when Particle is outside Box ($V = \infty$) (ii)

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \infty\psi = E\psi$$

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

Since ($E <<< \infty$) Neglecting E

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - \infty\psi = 0$$

Dividing throughout by $\frac{\hbar^2}{2m}$

$$\frac{\partial^2\psi}{\partial x^2} - \frac{2m}{\hbar^2}\infty\psi = 0 \qquad \frac{2m}{\hbar^2}\infty = \infty$$

$$\frac{\partial^2\psi}{\partial x^2} - \infty\psi = 0$$

$$\frac{\partial^2\psi}{\partial x^2} = \infty\psi$$

$$\psi = \frac{1}{\infty}\frac{\partial^2\psi}{\partial x^2}$$

$$\boxed{\psi = 0}$$

Only possible soln when Particle outside box is $\psi = 0$

Significance => Particle Do not exist outside Box

*(ii) SWE when Particle is Inside Box (V=0)

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

$$\Rightarrow \quad \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

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

Dividing Throughout by $\frac{\hbar^2}{2m}$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0$$

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

where K^2 is constant

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + K^2\psi = 0}$$

2nd Order Differential equation

General soln has to be found out

Let the General soln

$$\boxed{\psi = A\sin Kx + B\cos Kx}$$

$$K = \sqrt{\frac{2mE}{\hbar^2}}$$

A & B are arbitary constant

All soln Not acceptable only that soln acceptable which satisfy boundary conditions.

Boundary conditions on wall $x=0, \psi=0$ }
$x=a \quad \psi=0$ }

Imposing boundary condition on general soln of ψ

When $x=0, \psi=0$

$\psi = A\sin kx + B\cos kx \Rightarrow 0 = A\sin 0 + B\cos 0$

$\Rightarrow 0 = A(0) + B(1)$

$\boxed{B=0}$

$\Rightarrow \boxed{\psi = A\sin kx}$

When $x=a, \psi=0$

$\psi = A\sin kx + B\cos kx$

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

$\boxed{A\sin ka = 0}$

Here $A \neq 0$ because if A & $B = 0$, ψ becomes zero at all values of x

Value of $n \neq 0$ because $a=0$ or $\psi(x)=0$ every where within box

$\sin ka = 0$

$\sin ka = \sin n\pi$

$ka = n\pi$

$k = a(n\pi)/a$

$$\boxed{\psi = A\sin\left(\frac{n\pi x}{a}\right)}$$

****

Normalisation of wavefunction ⇒

why ⇒ because equation consist undetermined constant A

Born Interpretation $\int_{-\infty}^{+\infty} \psi^* \psi \, d\tau = 1$ $\psi = \psi^* = A \sin\left(\frac{n\pi x}{a}\right)$

$$\int_0^a \left[A \sin\left(\frac{n\pi x}{a}\right) A \sin\left(\frac{n\pi x}{a}\right)\right] dx = 1$$

$$A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1$$

$\frac{n\pi x}{a} = y$

$\frac{n\pi}{a} dx = dy$

$dx = dy \frac{a}{n\pi}$

$$\begin{cases} x = 0, & y = 0 \\ x = a, & y = n\pi \end{cases}$$

$$A^2 \int_0^{n\pi} \sin^2 y \cdot \frac{a}{n\pi} dy = 1 \qquad \sin^2 y = \frac{1 - \cos 2y}{2}$$

$$\frac{A^2 \cdot a}{n\pi} * \frac{1}{2} \int_0^{n\pi} (1 - \cos 2y) dy = 1$$

$$\frac{A^2 \cdot a}{2n\pi} \left[\int_0^{n\pi} dy - \int_0^{n\pi} \cos 2y \, dy\right] = 1$$

$$\frac{A^2 \cdot a}{2n\pi} \left[y - \frac{\sin 2y}{2}\right]_0^{n\pi} = 1$$

$$\frac{A^2 \cdot a}{2n\pi} \left(n\pi - \frac{\sin 2n\pi}{2}\right) - \left(0 - \frac{\sin 0}{2}\right) = 1$$

$$\frac{A^2 a \, n\pi}{2n\pi}$$

$A^2 = 2/a \quad A = \sqrt{2/a}$

$A = \sqrt{2/a}$

$\psi = \sqrt{2/a} \sin\left(\frac{n\pi x}{a}\right)$ Unit = $cm^{-1/2}$

$K2 = \frac{2mE}{\hbar 2}$ $K = \frac{n\pi}{a}$ and $\hbar = \frac{h}{2\pi}$

$E = \frac{K2\,\hbar 2}{2m}$

$E = \left(\frac{n\pi}{a}\right)^2 * \frac{h^2}{4\pi^2} * \frac{1}{2m}$

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

$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ are solution of SWE

Quantisation of Energy $E = \frac{n^2 h^2}{8ma^2}$

n Value = 1, 2, 3, 4, 5 .... etc $(n \neq 0)$

Whenever Particle is confined energy will be Quantised

(b) xx- Zero Point Energy & Violation HUP.

$E = \frac{n^2 h^2}{8ma^2}$ when $n=1$ $E = \frac{h^2}{8ma^2}$ (Z.P.E)

* This shows that Particle is not at Rest even at absolute zero or 0 Kelvin. (i.e Position & momentum cannot be predicted)

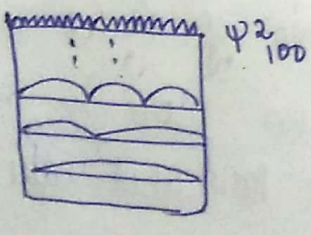
when $n=0$

* $E=0$, $\psi = 0$ [exact Position defined violation of HUP) $(\psi \neq 0)$

(c) BOHR correspondence Principle

→ Quantum Mechanics merges with Classical Mechanics at very high Quantum No. This called BCP.

→ There is more or less equal probability of finding Particle inside box at every point as concluded by class. mechanics



(d) Relation of n with λ K.E = $E = \frac{n^2 h^2}{8ma^2}$ i.e $K.E \propto n$

$K.E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$ $K.E \propto p$

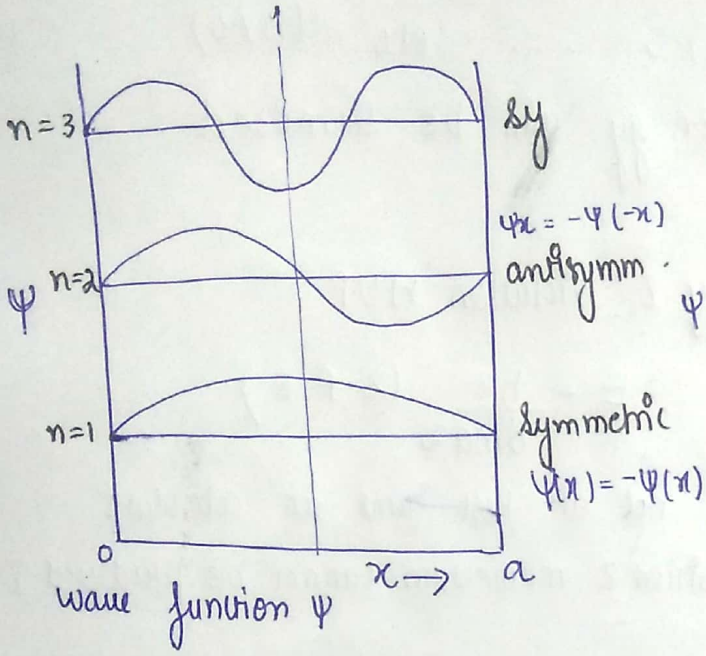
$\lambda = \frac{h}{p}$ $\lambda \propto \frac{1}{p}$

$n \propto 1/\lambda$ with ↑ in n wavelength ↓es

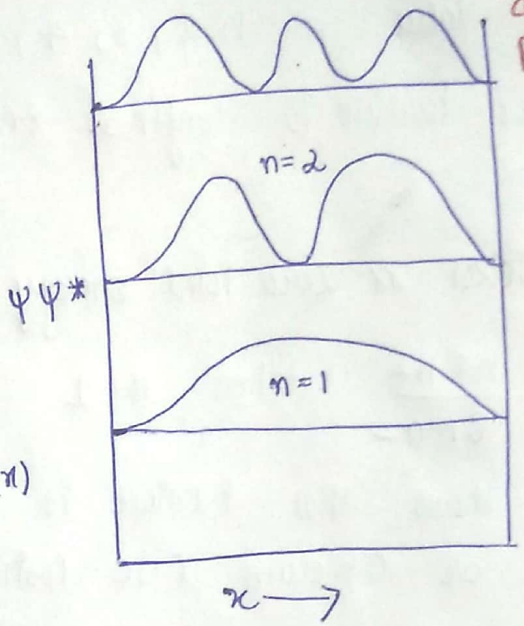
C

THEORIES PUTED FORWARD FOR BONDING IN COORDINATION COMPLEXS

Forms of wave function



Probability of finding a Particle at any Point is always Positive.



Probability density fn

$\psi_1 = \sqrt{2/a} \sin\left(\frac{n\pi x}{a}\right)$

$\psi_2 = \sqrt{2/a} \sin\left(\frac{2\pi x}{a}\right)$

$\psi_3 = \sqrt{2/a} \sin\left(\frac{3\pi x}{a}\right)$

No other wave fn possible in b/w These

Such Discrete wave fn are called Eigen wave fn or well behaved fn

Node = Point at which probability of finding Particle is zero.

(Nodes = n - 1)

Energy level (n)	nodes
1	0
2	1
3	2

Greater the No. of Nodes in wavefunction more is the curvature in Particular wave.

as No. of Nodes ↑) curvature ↑es

↑↓ (distance b/w 2 nodes) & K.E ↑es

EORIES PUTED FORWARD FOR BONDING

MPLEXS

Application of Particle in 1-D Box

→ It provides satisfactory interpretation of electronic spectra (UV or visible) of CONJUGATED ORGANIC molecules like linear CONJUGATED POLYENE molecule.

→ A linear conjugated Polyene molecule may be Regarded as 1D Box and π electrons of molecule as Particle.

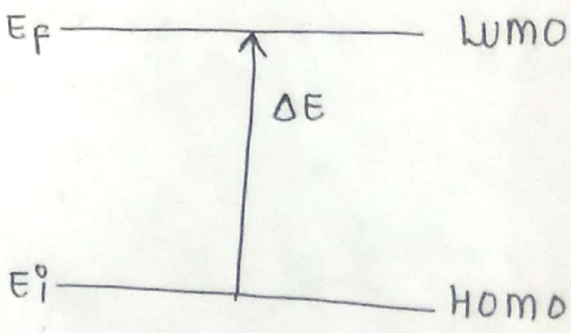
→ If chain less → mass less Then energy gap = Large {U.V}

→ If chain more → mass more Then energy gap = Small {visible}

$\Delta E = E_f - E_i$

$\Delta E = E_{n+1} - E_n$

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



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

$h\nu = \frac{(2n+1)h^2}{8ma^2}$ $\qquad \nu = \frac{(2n+1)h}{8ma^2}$

$\frac{c}{\lambda} = \frac{(2n+1)h}{8ma^2}$

$\tilde{\nu} = \frac{(2n+1)h}{8ma^2c}$

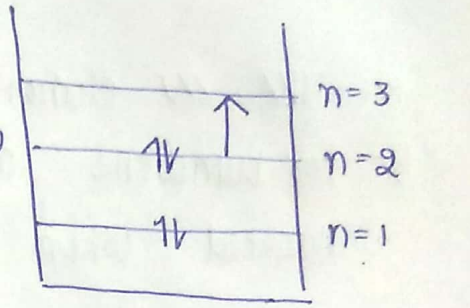
Taking example of Butadiene $R_{C-C} = 154\,pm$, $R_{C=C} = 135$

Length $a = R_{C-C} + R_{C=C} + 2 * \frac{R_{C-C}}{2}$ → End effect length

$= 154 + 2(135) + 154 = 578 * 10^{-12} = 5.78 * 10^{-19}\,m$

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

$$\Delta E = \frac{[2*2+1](6.6*10^{-34}\,J.s)^2}{8*\,9.11*10^{-31}\,Kg*(5.78*10^{-10})^2}$$



$$\boxed{\Delta E = 8.945 * 10^{-19}\ Joules}$$

$$\bar{\upsilon} = \frac{(2n+1)\,h}{8ma^2c}$$

$$\bar{\upsilon} = \frac{[2*2+1]*(6.6*10^{-34})}{8*\,9.11*10^{-31}\,Kg*(5.78*10^{-10})^2*(3*10^8)}$$

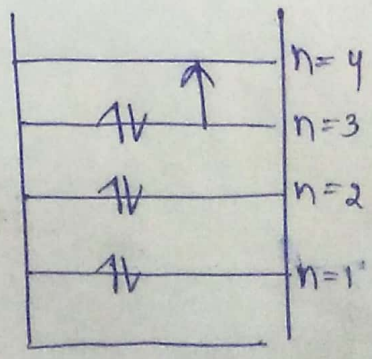
$$\boxed{\bar{\upsilon} = 4.52 * 10^6\ m^{-1}}$$

* Calculate the wavelength in nm corresponding to Transition from HOMO to LUMO in 1,3,5-Hexatriene molecule The C-C and C=C bond length are 154 & 135 pm

$n = 3$ $\qquad H_2C = CH - CH = CH - CH = CH_2$

$a = 2*154 + 3*135 + 154$

$a = 867\,pm = 867 * 10^{-12}\,m$



$$\lambda = \frac{8ma^2c}{(2n+1)h}$$

$= 8$

C

THEORIES PUTED FORWARD FOR BONDING AND [illegible]ON

$$= \frac{8 * (9.11 * 10^{-31})kg * (867 * 10^{-12})2 * (3 * 10^{8})\ ms^{-1}}{[2(3)+1] * 6.6 * 10^{-34}}$$

$$\boxed{\lambda = 3.55 * 10^{-7} m = 3.55 * 10^{-2} nm}$$

* The π electron

Q- For butadiene $a = 7.0 A^{\circ}$, Estimate the λ of light absorbed when π e^- is excited from HOMO to LUMO.

$a = 7.0 * 10^{-10} m$

$n = 3$

~~π~~ $n = 2$

~~π~~ $n = 1$

$$\lambda = \frac{8ma^2c}{(2n+1)h}$$

$$\lambda = \frac{8 * 9.11 * 10^{-31} kg * (7 * 10^{-10})^2 m^2 * (3 * 10^{8}) m s^{-1}}{(2(2)+1) * 6.6 * 10^{-34} - kg\ m^2\ s^{-1}}$$

$$\boxed{\lambda = 324.6 nm}$$

Quantized wave fn are orthogonal to each other

$$\psi_n \psi_m = \sqrt{2/a} \sin\left(\frac{l\pi x}{a}\right) \sqrt{2/a} \sin\left(\frac{m\pi x}{a}\right)$$

C

In nanomaterial the valence e_s^- which are almost free in finite volume leads to Quantification of their energy Band gap Decreases when Particle size is decreased and energy gap gradually converts into discrete ~~energy~~ molecular electronic level.

If Particle size is less than wavelength of e^-, the charge carries may Be Treated as "Particle in a Box"

Spatial confinement of e^- within crystallite boundary is reffered to as Quantum confinement

Properties of Bulk material change completely as their dimension are Reduced to Nanoscale (<100nm).

* If 1 Dimension changed to Nano range - Quantum wells are obtained.
* If Two Dimension are reduced the Resulting Structure = Quantum wire
* When all three dimension are Reduced = Quantum dots are obtained = Zero Dimensional Semiconducting Spheres.

Nanostructure material can be classified on the no. of dimensions that are not confined to nanoscale Range <100nm

(i) Zero Dimensional ⇒ Each Dimension in NANO Scale (Quantum Dots)

(ii) 1D ⇒ Two Dimension is in NANOscale while Third one not. Example ⇒ nano wires.

(iii) 2D ⇒ One Dimension in nanoscale
Example ⇒ nanofilms & nanocoating.

(iv) 3D ⇒ Not Nanoscale in any of Dimensions
Consist of Multiple arrangement of nanosize Particles or Crystal, bundles of nanosize wires, Strand or Tubes.

MOLECULAR ORBITAL THEORY

Covalent Bond formation the e^- are shared b/w atoms and localised in Nuclei.

→ Heisenberg Uncertainity principle

→ Repulsion b/w similar charges of e-

Quantum Theory of Covalent Bonding & further development of wave mechanics gave birth to 2 New Theories.

(I) Valence Bond Theory (VB)

(II) Molecular Orbital Theory (Hund & mulliken 1932)

In Valence B Theory atom were considered to Retain their identity except valence shell ~~which~~ atomic orbital which overlap.

In MOT atomic orbital of Bonded atom loose their identity and get mix up to form as molecular Orbitals

Salient features of MOT

1. Molecule differ from constituent atom.
2. formed through combination of atomic Orbital of comparable energies.
3. No. of molecular orbitals = No. of atomic Orbitals.
4. Bonding molecular Orbital have lower Energy (More stable) while AntiBonding MO have higher Energy (less stable)
5. Molecular Orbitals arranged in Increasing Order of Energy.

An e⁻ in molecule said to occupy molecular orbitals. wave function ψ describing MO are done by Two procedures.

(i) Linear Combination of Atomic Orbitals (LCAO)

(ii) United Atom Method.

*** LCAO - Linear Combination of Atomic Method

imp

Atomic orbital can be expressed in terms of ψ (wave fn)

→ ψ is obtained through solution of Schrodinger wave equation

→ complexity is there for multielectron & multinuclear sys. It is very difficult to solve SW function

LCAO is approximate method to determine the wave fn of molecular orbitals.

→ Consider Two atoms A & B which have atomic orbitals described by wave function $\psi_{(A)}$ & $\psi_{(B)}$

→ ~~Now when~~ e⁻ cloud of these atoms overlap when atom approach each other Then the wave fn (ψ_{AB}) of MO can be obtained by Linear combination of atomic orbital ψ_A & ψ_B

$$\psi_{AB} = N(C_1\psi_A + C_2\psi_B)$$

N = Normalising constant
↓
e⁻ probability = 1

C_1 and C_2 are constant to give minimum energy for ψ_{AB}.

The probability of finding e^- in volume of space dv is $\psi^2 dV$

∴ Probability density for combination is Related to wave fn Square

For bonding MO

$$\psi_{AB} = N(C_1\psi_{(A)} + C_2\cdot\psi_{(B)})$$

$$\boxed{\psi^2_{AB} = C_1^2\psi_A^2 + C_2^2\psi^2_{(B)} + 2C_1C_2\psi_A\psi_B}$$

$C_1^2\psi_A^2$ = P of finding e^- in atom A if A is isolated

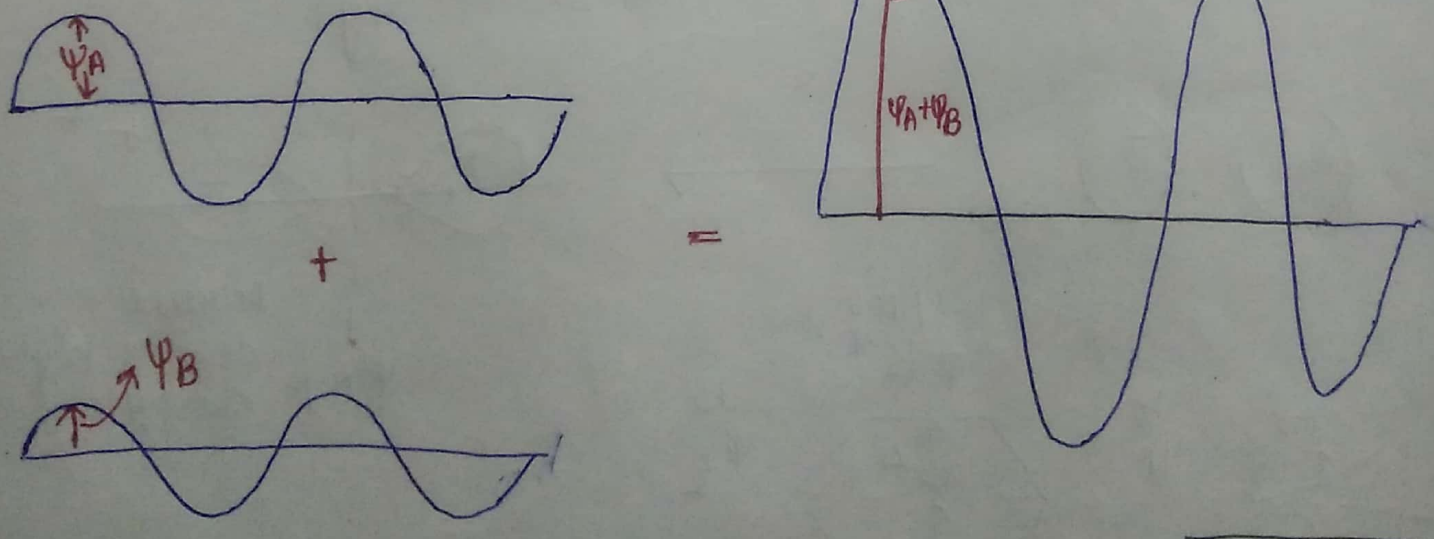
$C_2\psi^2_B$ = Probability of finding e^- in atom B if B is isolated

$2C_1C_2\psi_A\psi_B$ = overlap Integral (More the overlap stronger is Bond

Since $\psi^2_{AB} > (C_1^2\psi_A^2 + C_2^2\psi_B^2)$

So There is High Probability of finding e^- in MO than isolated atomic orbital.

$\psi = \boxed{\psi_{MO}} = \psi_A + \psi_B$

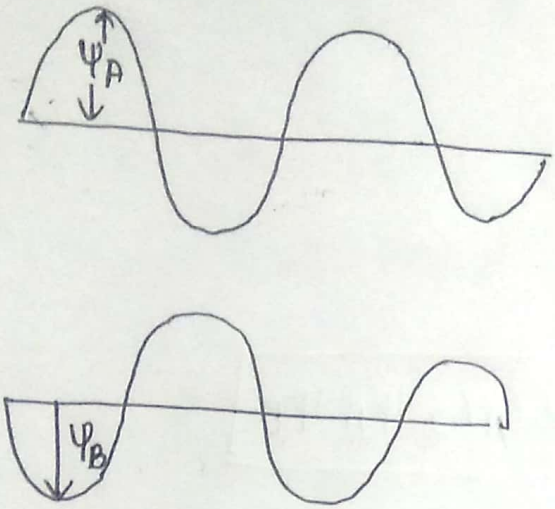


Waves in Same Phase adds & New amplitude $\boxed{\psi = \psi_A + \psi_B}$

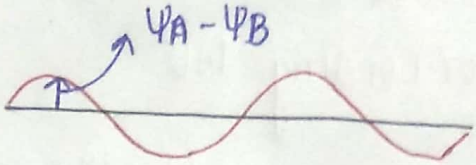
(Constructive Interference

THEORIES PUTED FORWARD FOR BONDING IN COORDINATION

FOR ANTIBONDING MO : Represented y $\sigma^*, \pi^*, \delta^*$



=



$\psi^*_{MO} = \psi_A - \psi_B$

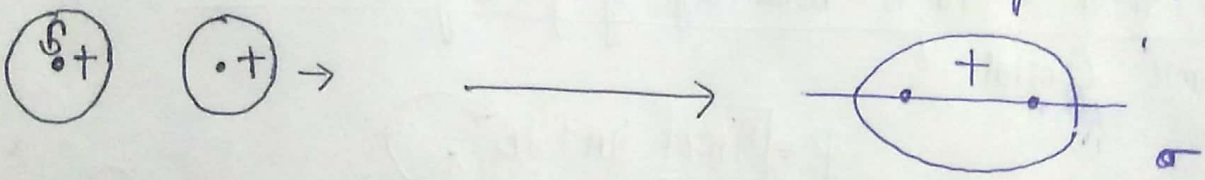
(Destructive Interference)

Both waves are out of phase they cancel out effect of each other and New amplitude $\boxed{\psi^* = \psi_A - \psi_B}$

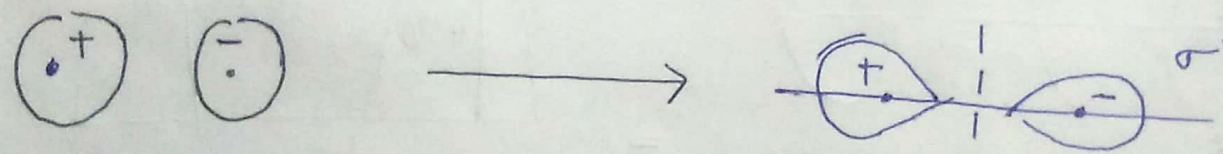
(i) S-S combination of orbitals

(a) when sign are same

Increased e⁻ density
Bonding orbital

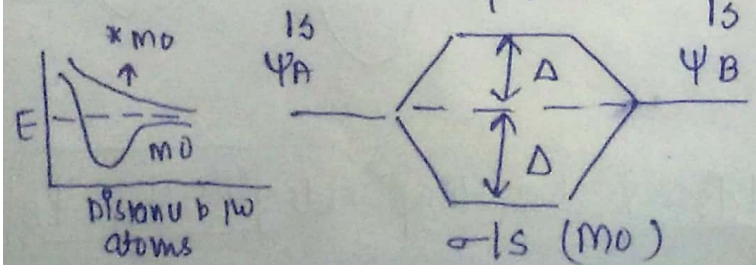


$\psi_{(g)}$

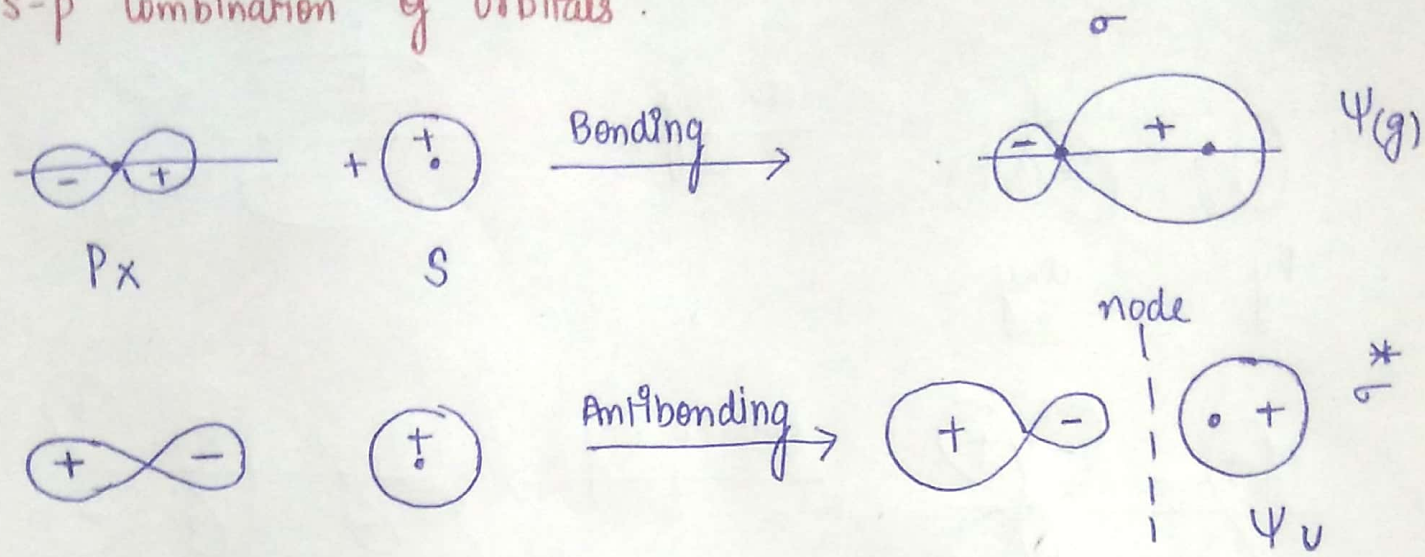


$\psi_{(u)}$ Decrease e⁻ density higher energy

(AMO)
ψ 1s*

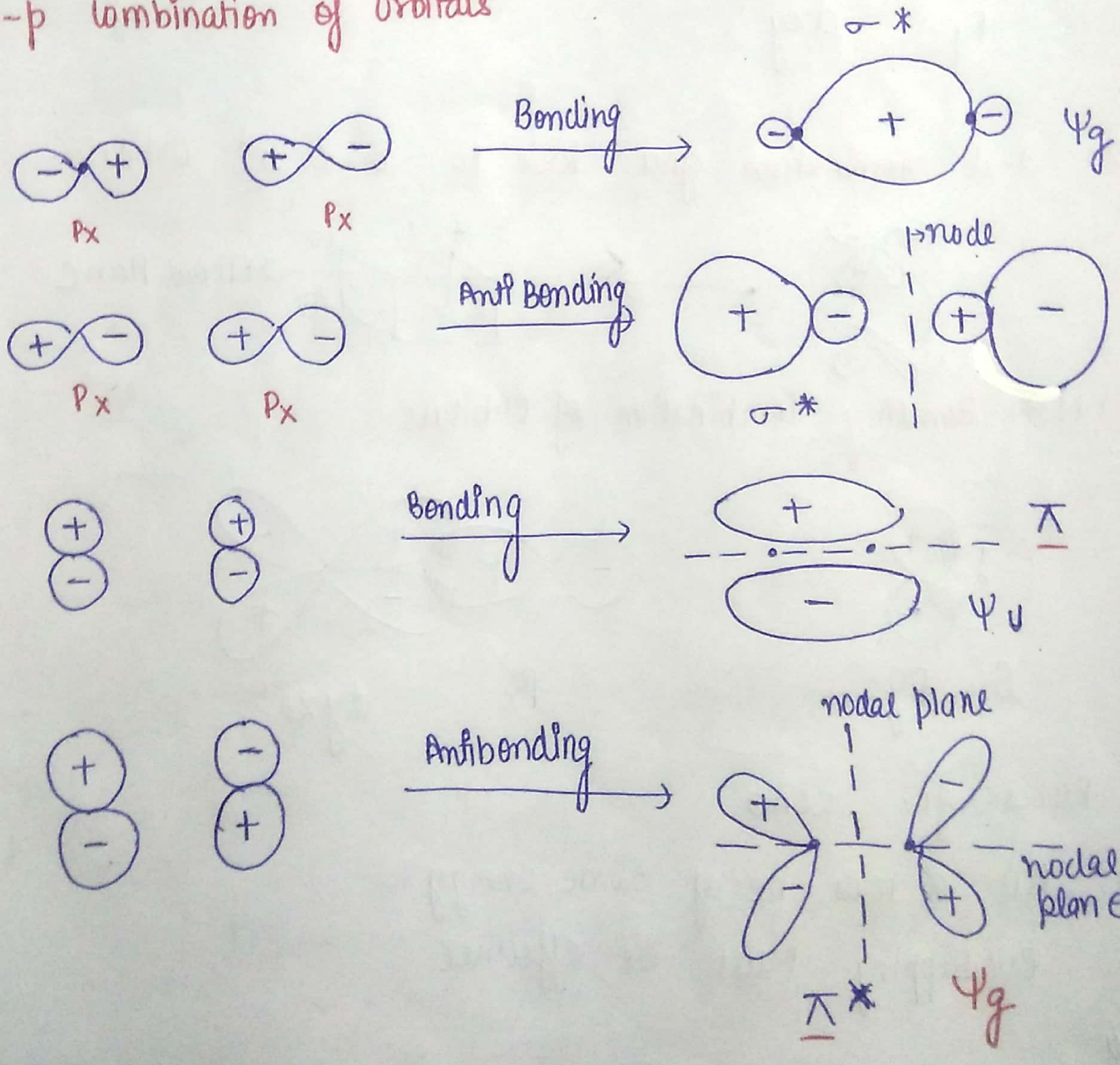


(ii) S-p combination of Orbitals.

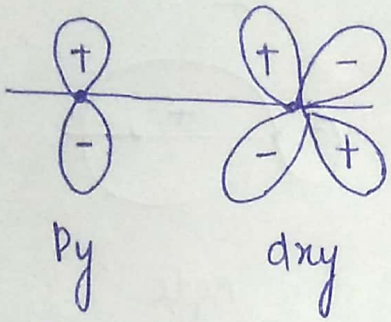


(iii)

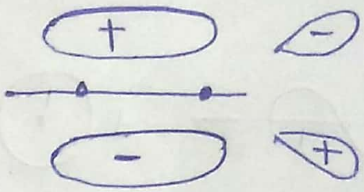
p-p combination of Orbitals

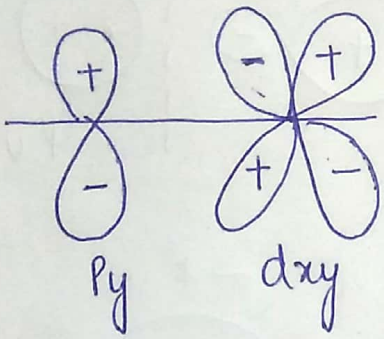


(iv) P-d Combination of Orbitals.

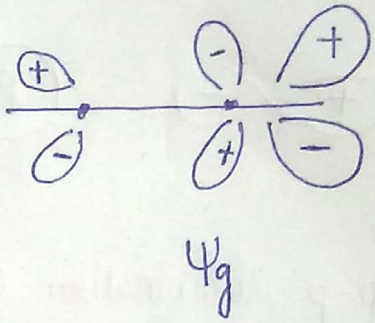


Bonding →

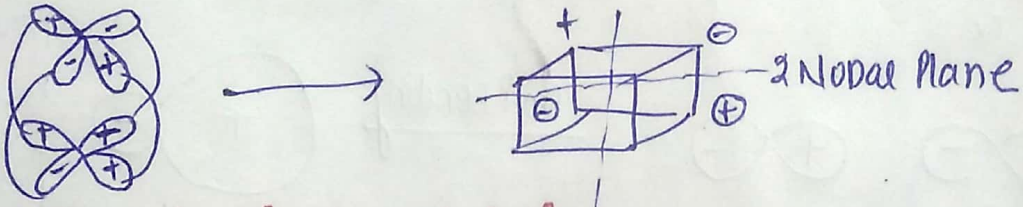




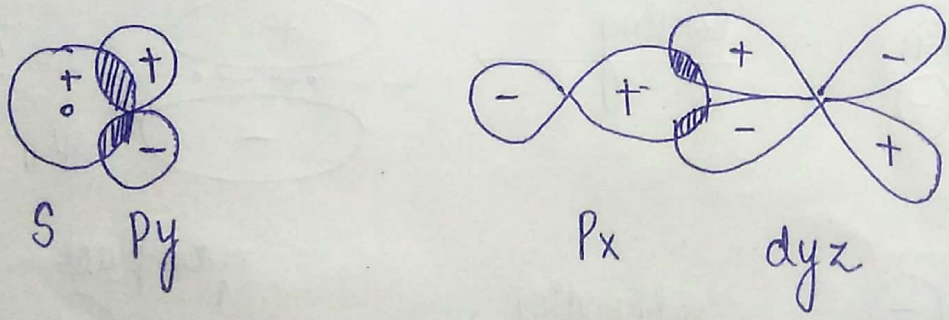
Anti-Bonding →



(v) d-d Combination give Rise to δ & δ* Orbitals.



(vi) NON Bonding Combination of Orbitals



Rules for LCAO

(1) AO must be of same energy.

2. Overlapping Must be effective

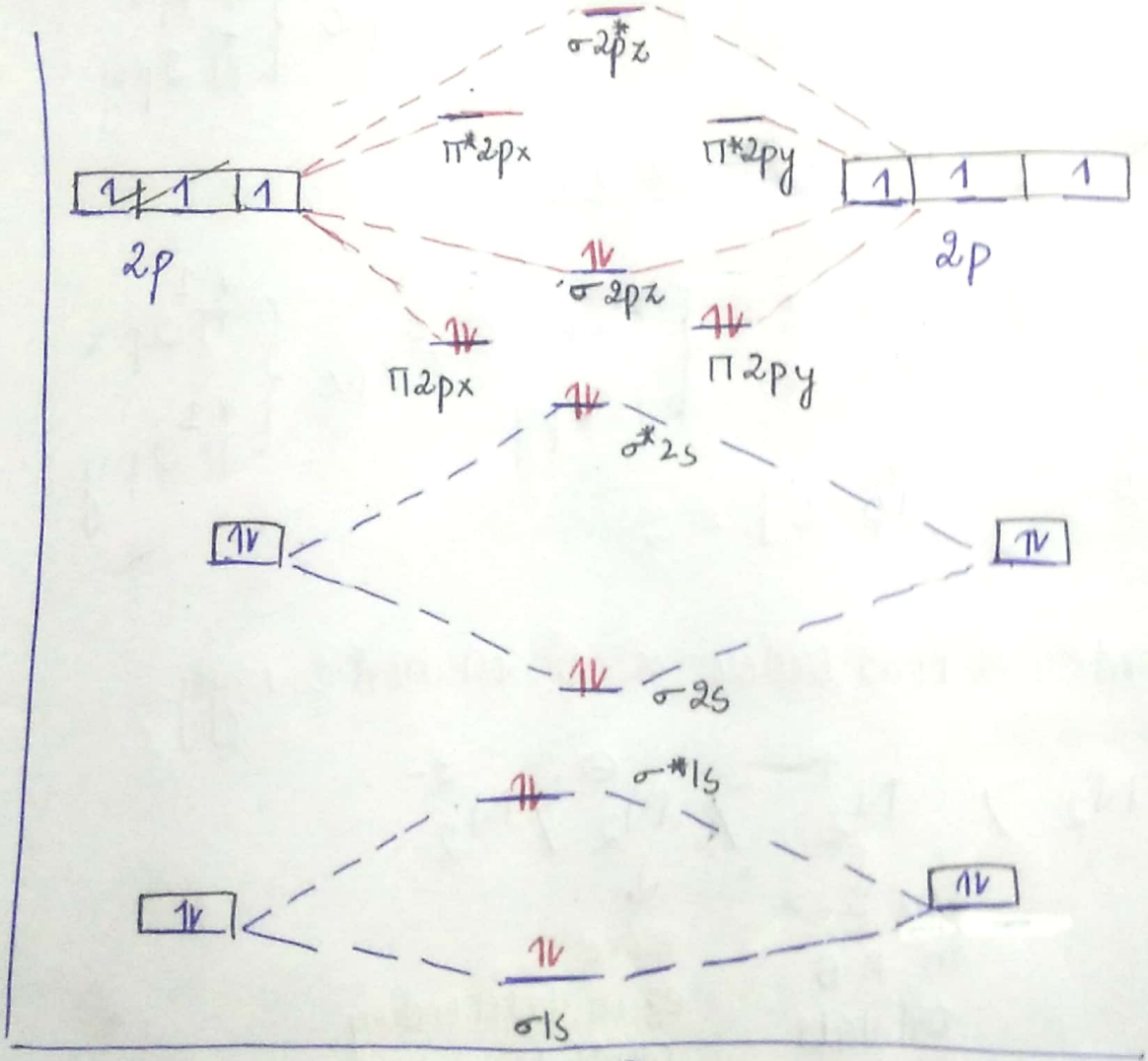
THEORY

Molecular Diagram for Diatomic molecules

H_2, C_2, N_2, N_2^+, N_2^-, N_2^{2-}, B_2, Be_2, Li_2

Diagram will be same as shown below only No. electronic arrangement will be different

MOT for N_2



σ_{1s}^2 σ_{1s}^{*2} σ_{2s}^2 σ_{2s}^{*2} { π_{2px}^2 π_{2py}^2 σ_{2pz}^2

B.O = $\frac{1}{2}$ [Bonding e⁻ − Anti Bonding] = $\frac{1}{2}$ [10 − 4] = 3

Diamagnetic – all e⁻ are paired

N_2^+ = Dinitrogenyl ion = 13 electrons

$\sigma_{1s}^2 \; \sigma^*_{1s}{}^2 \; \sigma_{2s}^2 \; \sigma^*_{2s}{}^2 \; \begin{cases} \Pi^2_{2px} \\ \Pi^2_{2py} \end{cases} \; \sigma^1_{2pz}$

$B.O = \frac{1}{2}[9-4] = \frac{1}{2} * 5 = \boxed{2.5}$

N_2^- = $\sigma_{1s}^2 \; \sigma^*_{1s}{}^2 \; \sigma_{2s}^2 \; \sigma^*_{2s}{}^2 \; \begin{cases} \Pi^2_{2px} \\ \Pi^2_{2py} \end{cases} \; \sigma^2_{2pz} \; \begin{cases} \Pi^{1*}_{2px} \\ \Pi^{*}_{2py} \end{cases}$

$B.O = \frac{1}{2}[10-5] = \boxed{2.5}$

N_2^{2-} $\sigma_{1s}^2 \; \sigma^*_{1s}{}^2 \; \sigma_{2s}^2 \; \sigma^*_{2s}{}^2 \; \begin{cases} \Pi^2_{2px} \\ \Pi^2_{2py} \end{cases} \; \sigma^2_{2pz} \; \begin{cases} \Pi^{*1}_{2px} \\ \Pi^{*1}_{2py} \end{cases}$

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

Stability order $\propto$ Bond order $\propto$ Dissociation energy

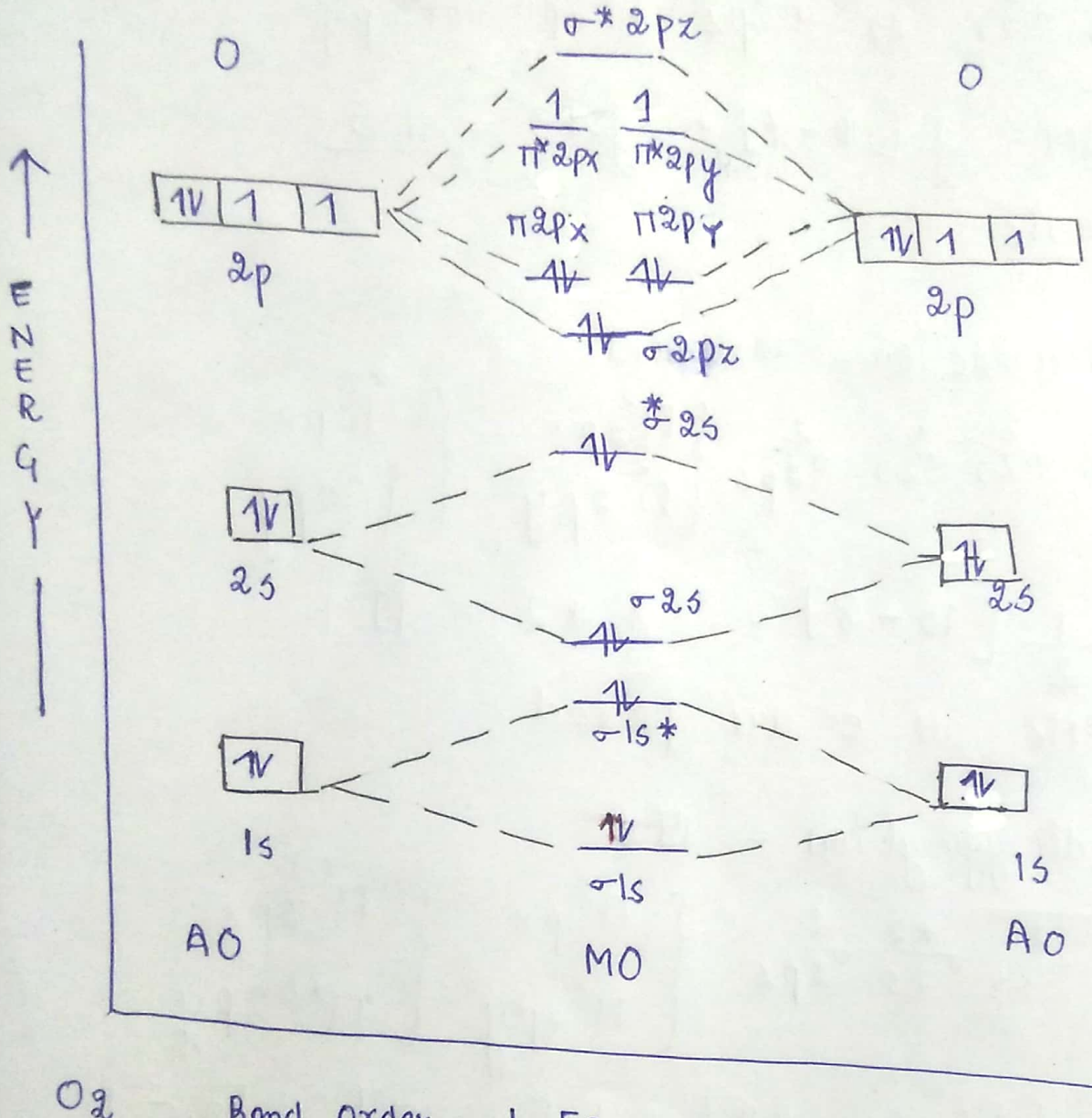
Highest B.O $\leftarrow$ $N_2 > N_2^+ > N_2^{\ominus} > N_2^{2-}$

N_2^+: Less e^- in A.B Orbitals

$N_2^{\ominus}$: more e^-s in antibonding orbitals

MOT Diagram for O_2 or Energy Level Diagram for O_2

No. of electron = $8 * 2 = 16\ e^-$



O_2 Bond order = $\frac{1}{2}[B.O_{e^-} - A.O_{e^-}]$

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

Electronic configuration $O_2 = \sigma_{1s}^2\ \sigma^*_{1s}{}^2\ \sigma_{2s}^2\ \sigma^{*2}_{2s}\ \sigma_{2pz}^2 \begin{cases} \Pi^2 2px \\ \Pi^2 2py \end{cases} \begin{cases} \pi^{*1} 2px \\ \pi^{*1} 2py \end{cases}$

Dia Paramagnetic Due to Presence of unpaired electrons.

O_2^- = Superoxide ion = 17 electrons

$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2pz}^2\ \pi_{2px}^2\ \pi_{2py}^2\ \pi_{2px}^{*2}\ \pi_{2py}^{*1}\ \sigma_{2pz}^{*}$

Bond Order = $\frac{1}{2}[10-7] = \frac{1}{2} * 3 = 1.5$

Paramagnetic

O_2^{2-} ion = Peroxide ion = 18 electrons

KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2pz}^2$ { π_{2px}^2, π_{2py}^2 } { π_{2px}^{*2}, π_{2py}^{*2} }

B.O = $\frac{1}{2}[10-8] = \frac{1}{2} * 2 = \boxed{1}$

Diamagnetic all e⁻ are paired.

O_2^+ ion = dioxygenyl ion = 15 e⁻

KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2pz}^2$ { π_{2px}^2, $\pi^2 2py$ } { π^{*1}_{2px}, $\pi^{*0} 2py$ }

B.O = $\frac{1}{2}$[Bonding e⁻ − AB e⁻] = $\frac{1}{2}[10-5] = \boxed{2.5}$

Stability ∝ Bond order ∝ Bond dissociation energy

$O_2^+ > O_2 > O_2^- > O_2^{2-}$

F_2 = 18 electrons

B.O = $\frac{1}{2}[10-8] = 1$

Diamagnetic

Ne_2 = 20 e⁻

Not exist because Bond order = 0

MOT for Heteronuclear Diatomic molecule

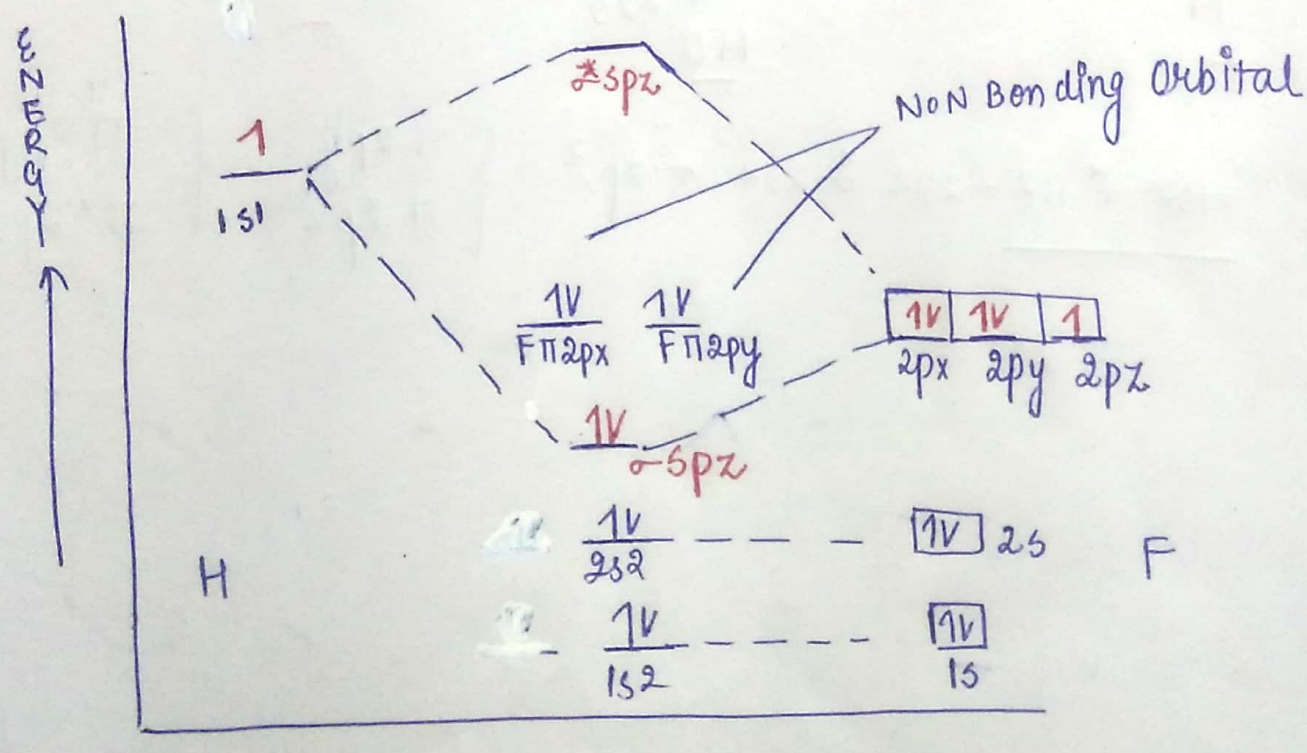
* Energies of Atomic Orbital are different due to difference in electronegativities.
* Bonding MO will lie closer to atom having higher electronegativity and e⁻ in antibonding MO will lie closer to less electronegative atom

HF molecule

H = 1s1

F = 1s2 2s2 2p5

2pz orbital combine with 1s orbital

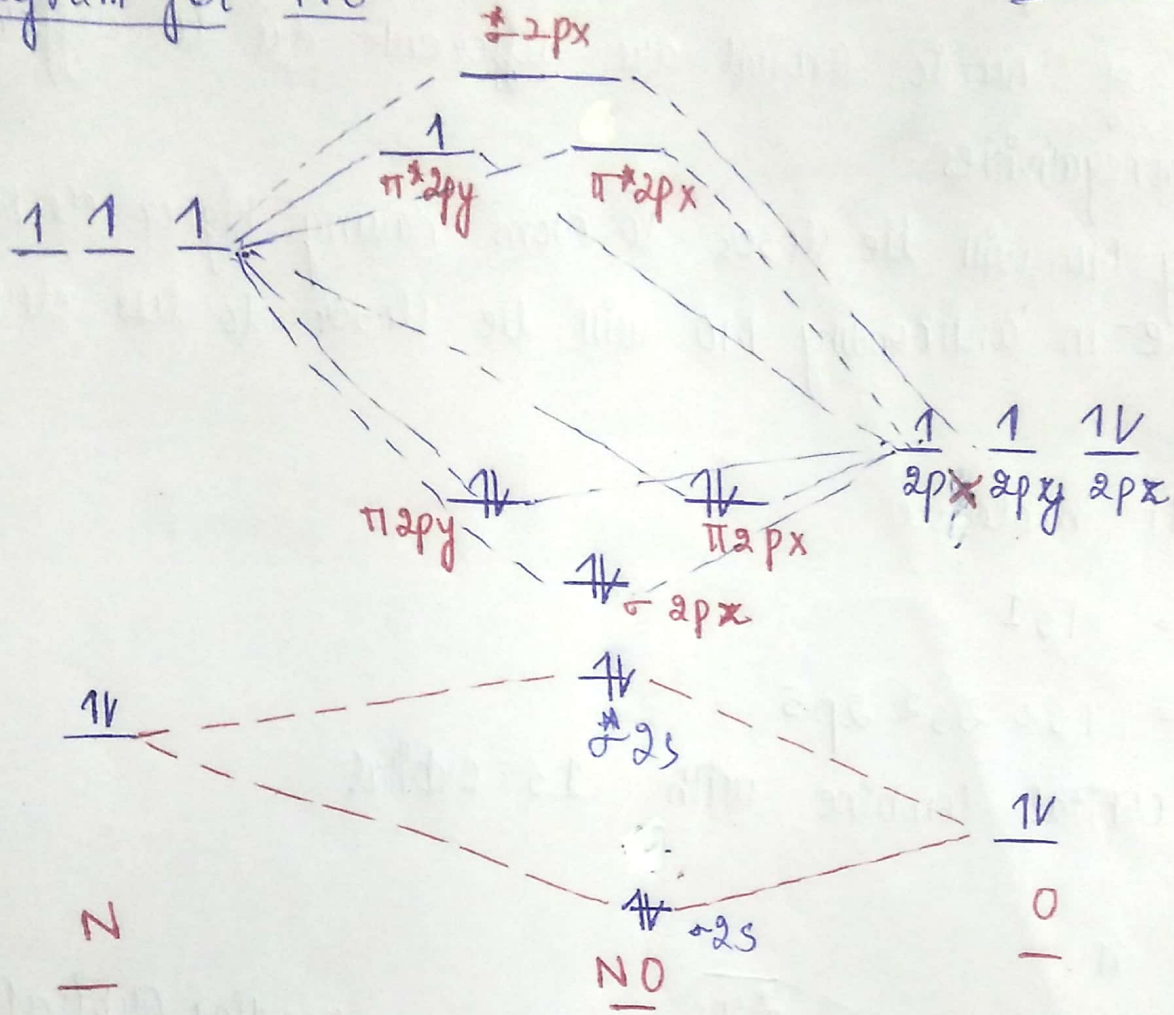


Bond Order = $\frac{1}{2}[2-0] = 1$

HF = KK $(2s)^2 (\sigma spz)^2 (2px)^2 (2y)^2$

= Total No. of e^- = 7 + 8 = 15 electrons

Diagram for NO



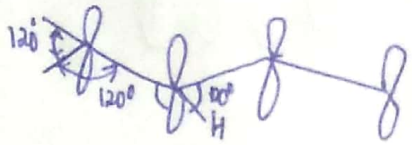
$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2$ { $\pi 2p_y^2$, $\pi 2p_z^2$ } { $\pi^* 2p_y^1$, $\pi^* 2p_z^0$ }

Difference between Bonding MO & Antibonding MO

BONDING MO	ANTIBONDING MO
→ Formed by addition overlap of atomic orbital	Subtraction overlap of AO.
$\psi_{MO} = \psi_A + \psi_B$	$\psi^*_{MO} = \psi_A - \psi_B$
→ e^- density b/w Nuclei is quite large	e^- b/w Nuclei is very less
→ More stable / less energy	Less stable More energy
→ designated by σ, π, δ etc	σ^*, π^*, δ^* etc.

Pi molecular Orbitals of Buta-diene (C_4H_6)

$H_2C=CH-CH=CH_2$



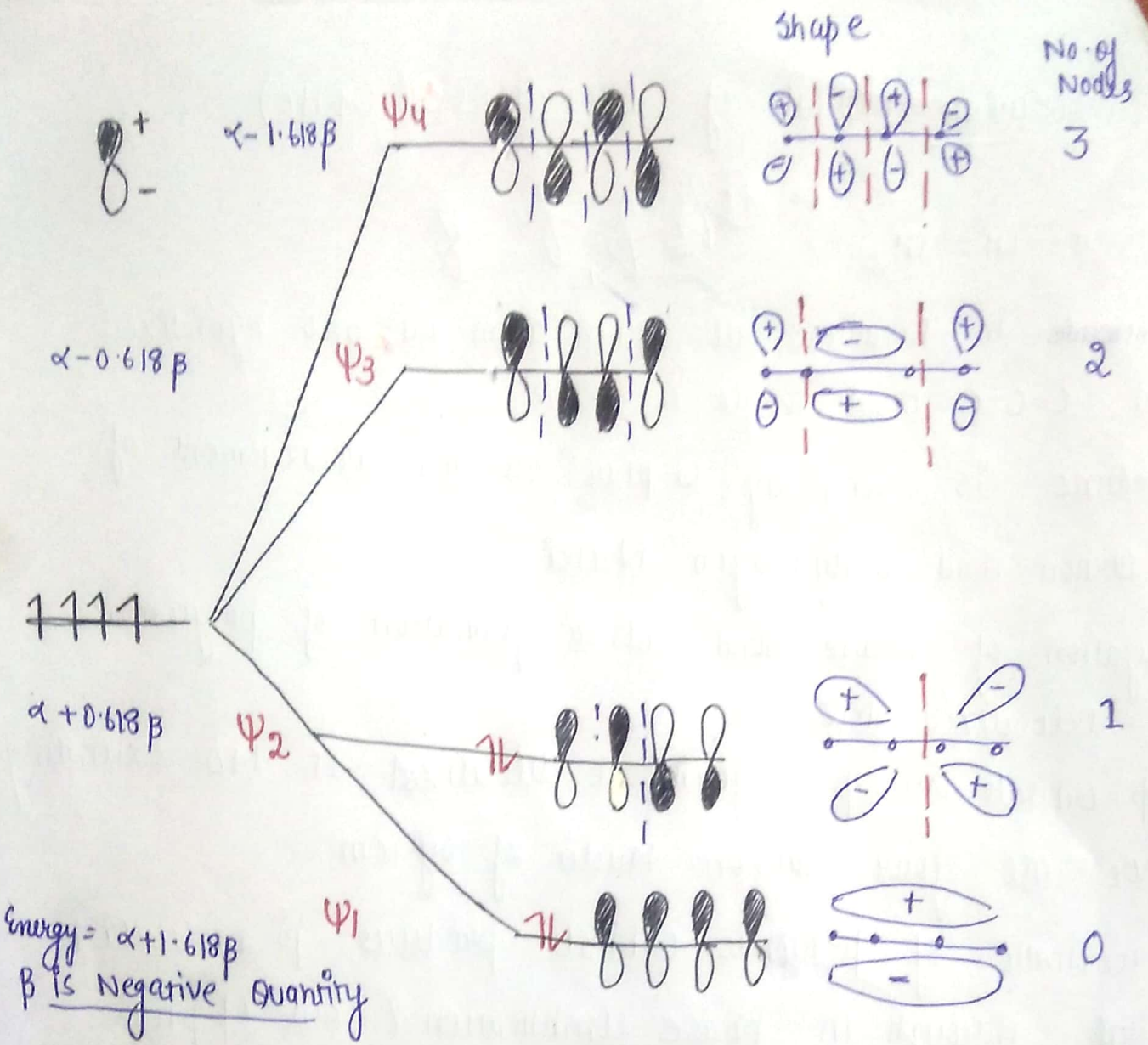
In Butadiene all carbon atom are sp^2 hybridized and C-C-C bond angle is 120°.

Butadiene is completely co-plar skeleton arrangement of 4 carbon and 6 Hydrogen Nuclei.

* Conjugation of Double Bond leads to formation of polycentric or Delocalized MO.
* 4 p orbitals overlap to form a delocalized π MO extending over all four carbon Nuclei of system.

The combination of p-atomic orbitals produces pi molecular orbital through in phase combination & out of phase combination.

Each p orbital contributes one electron Resulting in arrangement of four electrons from p orbitals which combine in 4 different ways to form four molecular Orbitals designated as ψ_1, ψ_2, ψ_3 & ψ_4



ψ_1 has 3 Bonding Interactions & 0

ψ_2 has 2 Bonding Interactions

ψ_3 has 1 Bonding Interaction

ψ_4 has 0 " "

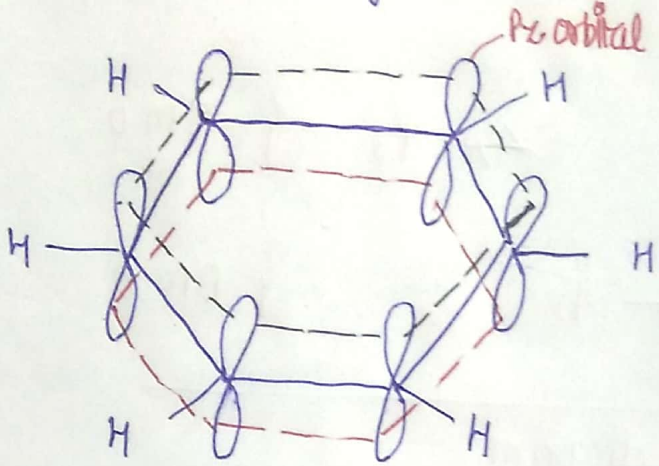
ψ_1 and ψ_2 are Bonding MO

ψ_3 & ψ_4 are AntiBonding MO

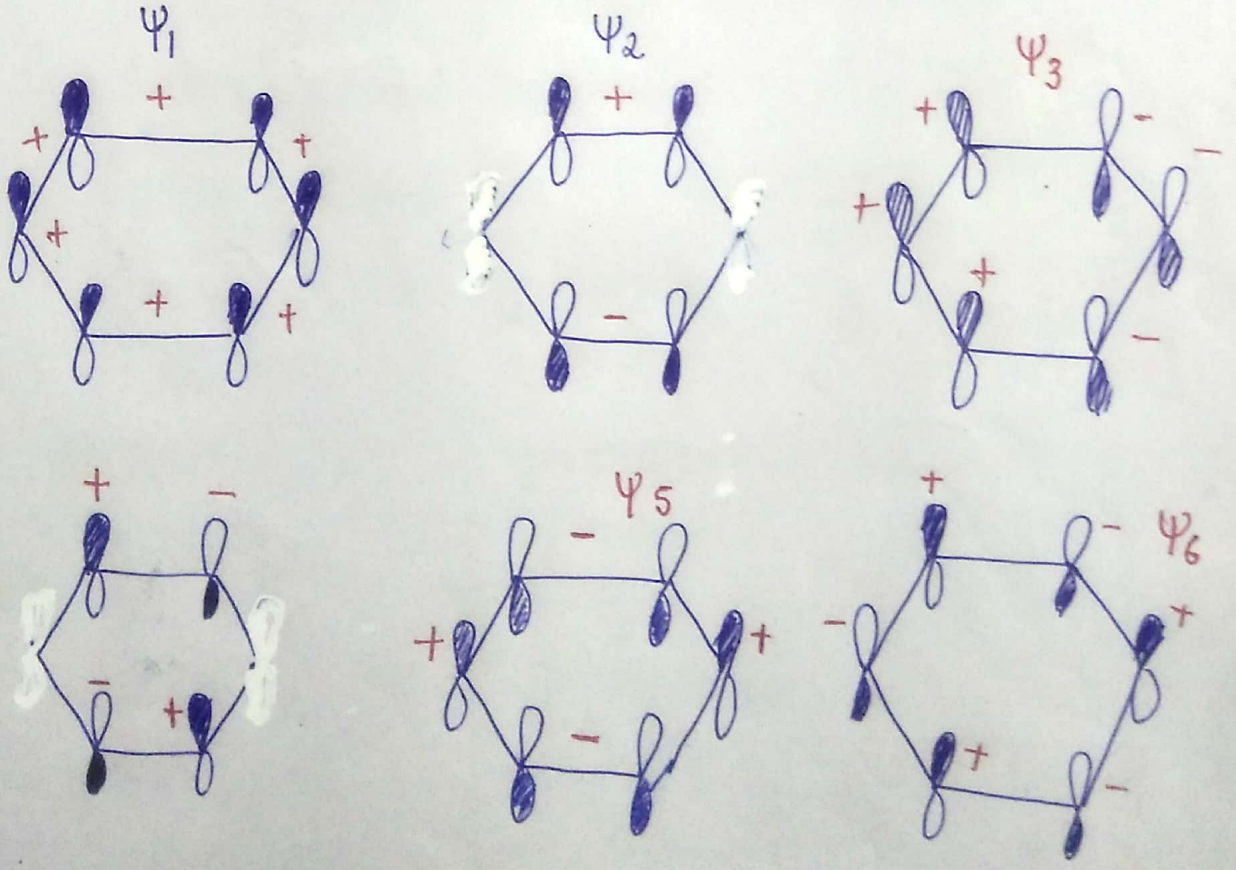
as No. of Nodes Increases the energy of MO Rises.

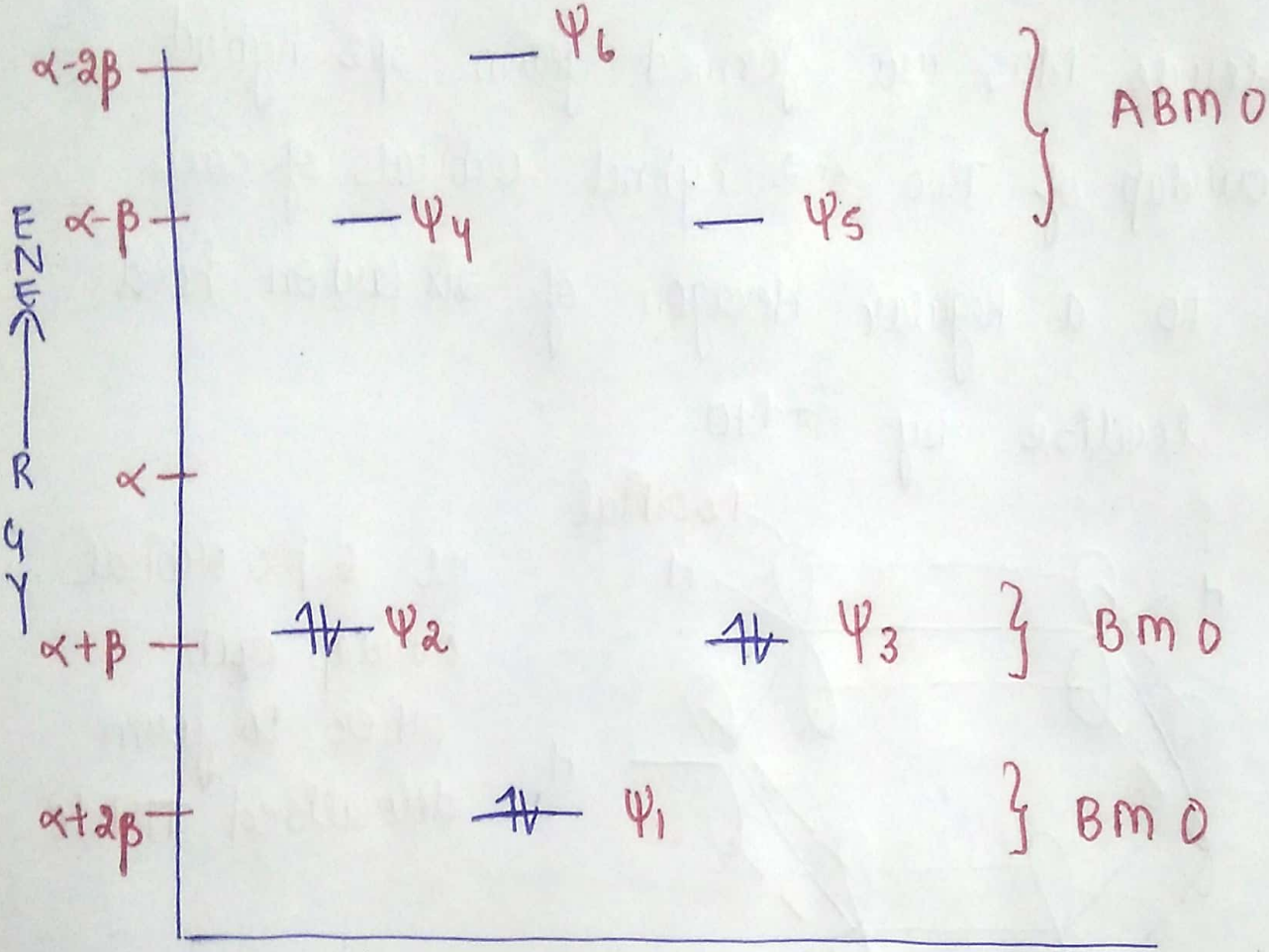
Pi- molecular Orbitals of Benzene

In benzene molecule MOs are formed from sp^2 hybrid orbitals. The overlap of two sp^2 hybrid orbitals of each carbon leads to a Regular Hexagon of six carbon held in a plane localise by σ-MO.



all 6 pz orbital overlap each other to form delocalised π MO





HMO diagram of Benzene

AROMATICITY

Benzene and all those compounds which Resemble Benzene in chemical Behaviour are called aromatic compounds.

Properties of Aromatic Compound

→ Cyclic Compound
→ Unusual Stability
→ Resonance Stabilization
→ Planar
→ Although Unsaturated do no go addition rather substitution Reaction

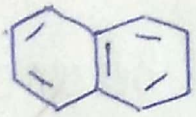
These characteristic properties are Termed as Aromaticity and class of compound possesing such characteristic are called aromatic compound.

Huckel Rules for Aromatic compound

1. System should be cyclic
2. System should be Planar and conjugated
3. follow $(4n+2)\pi e^-$ Rule where $n=0,1,2,3,$ etc.

AROMATIC	ANTI AROMATIC	NON AROMATIC
usally stable	Highly Unstable	Unstable
→ cyclic	→ cyclic	these compound fails in any one criteria
→ conjugated	→ conjugated	
→ $(4n+2)\pi e^-$	→ $(4n)\pi e^-$	
→ Planar	→ Planar	
Benzene	cyclobutadiene	COT

Napthalene



$n=2$

$(4(2)+2)\pi e^-$

$10\pi e^-$

Planar, conjugated

AROMATIC

Anthracene

$n=3$

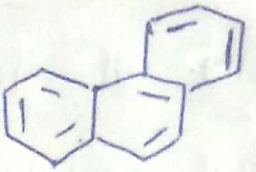
$(4(3)+2)\pi e$

$14e^-$

Planar

Conjugated

Phenanthrene



$n=3$

$(4(3)+2)\pi e^-$

$= 14\pi e^-$

Planar, conjugated

AROMATIC

→ Heterocyclic compounds

Furan

Thiopene

Pyrrole

Pyridine

AROMATIC

→ follow $(4(1)+2)\pi e^- = 6\pi e^-$

→ Planar

→ conjugated

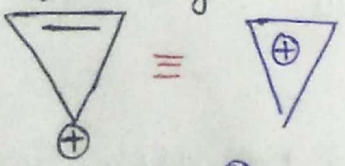
$(4(1)+2)\pi e^-$

Planar

conjugated

→ Aromatic Ions

cyclopropenyl cation

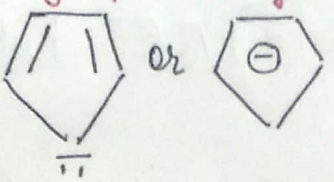


$2\pi e^{\ominus}$

$(4(0)+2)\pi e^-$

Planar & conjugated

cyclopentadienyl anion

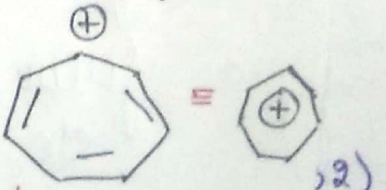


$(4n+2)\pi e$

$(4(1)+2)\pi e^-$

$6\pi e^-$

Tropylium ion



$(4n+2)\pi e^-$

$n=1$

Planar, conjuga

cycloheptatrienyl cati

→ NON AROMATIC

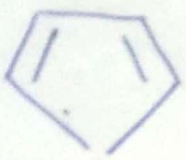
cyclopropene

→ Planar

→ NOT conjugated

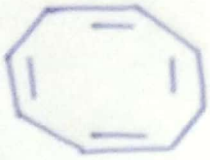
of

cyclopenta diene

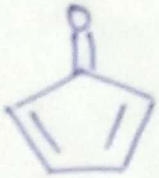


→ Planar
→ NOT Conjugated
or
Delocalisation absent

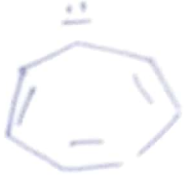
Doesn't follow Hückel Rule
$(4n+2)\pi e^-$



→ NOT Planar (Tub like structure)
→ Does Not follow Hückel Rule
→ NON aromatic.



(NON aromatic)

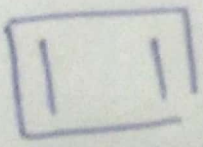


NON aromatic

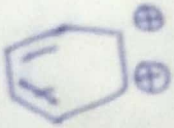
ANTI-AROMATIC COMPOUND

cyclopropenyl anion
4n Pi electron

cyclopentadiene cation



cyclobutadiene



C

THEORIES PUTED FORWARD FOR BONDING IN COORDINATION COMPLEXS

1. Valence Bond Theory
2. Crystal field Theory
3. Ligand field Theory
4. Molecular orbital Theory
5. Sidgwick Electronic concept

Limitations of VBT

→ Does Not explained color of metal complexes & electronic spectra.

→ No explanation of Magnetic data & Variation with Temp.

→ Does Not distinguish b/w Strong & weak field ligand.

→ No explanation for Thermodynamic & Kinetic stability.

CRYSTAL FIELD THEORY

Developed by Hans Bethe 1929 & John Van Vleck (1932)

Postulates or Assumptions Taken

1) Attraction b/w Central Metal and ligand is Purley electrostatic.

2.) Central Metal atom is Regarded as positive ions of

charge equal to its oxidation state in crystal.

③ Ligands are Treated as positive charge

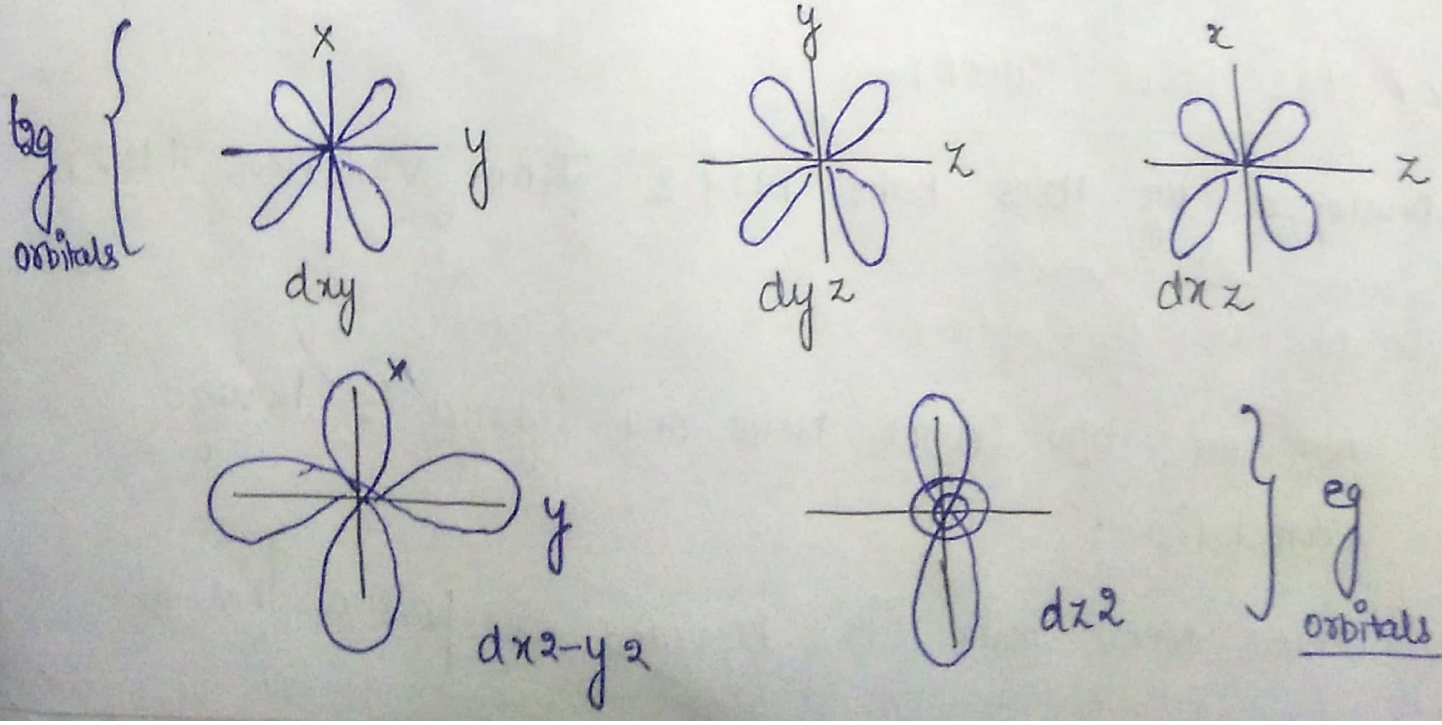
④ No interaction b/w metal orbital & ligand orbital

⑤ d orbital in free metal are degenerate however when complex are formed ligand destroy degeneracy of orbitals splitting them in eg and t_{2g} orbitals.

⑥. In spherically symmetrical field of Negative charges surrounds the metal ion the d orbital remain degenerate.

⑦ field produced by ligand in Octahedral & Tetrahedral complex is not spherically symmetrical.

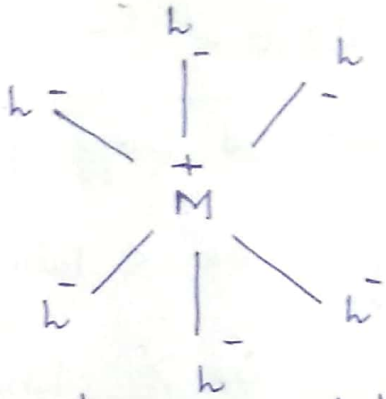
Shapes of d Orbitals



OCTAHEDRAL SPLITTING

* lobes of eg orbitals ($d_{x^2-y^2}$ & d_{z^2}) point along x, y, z axis

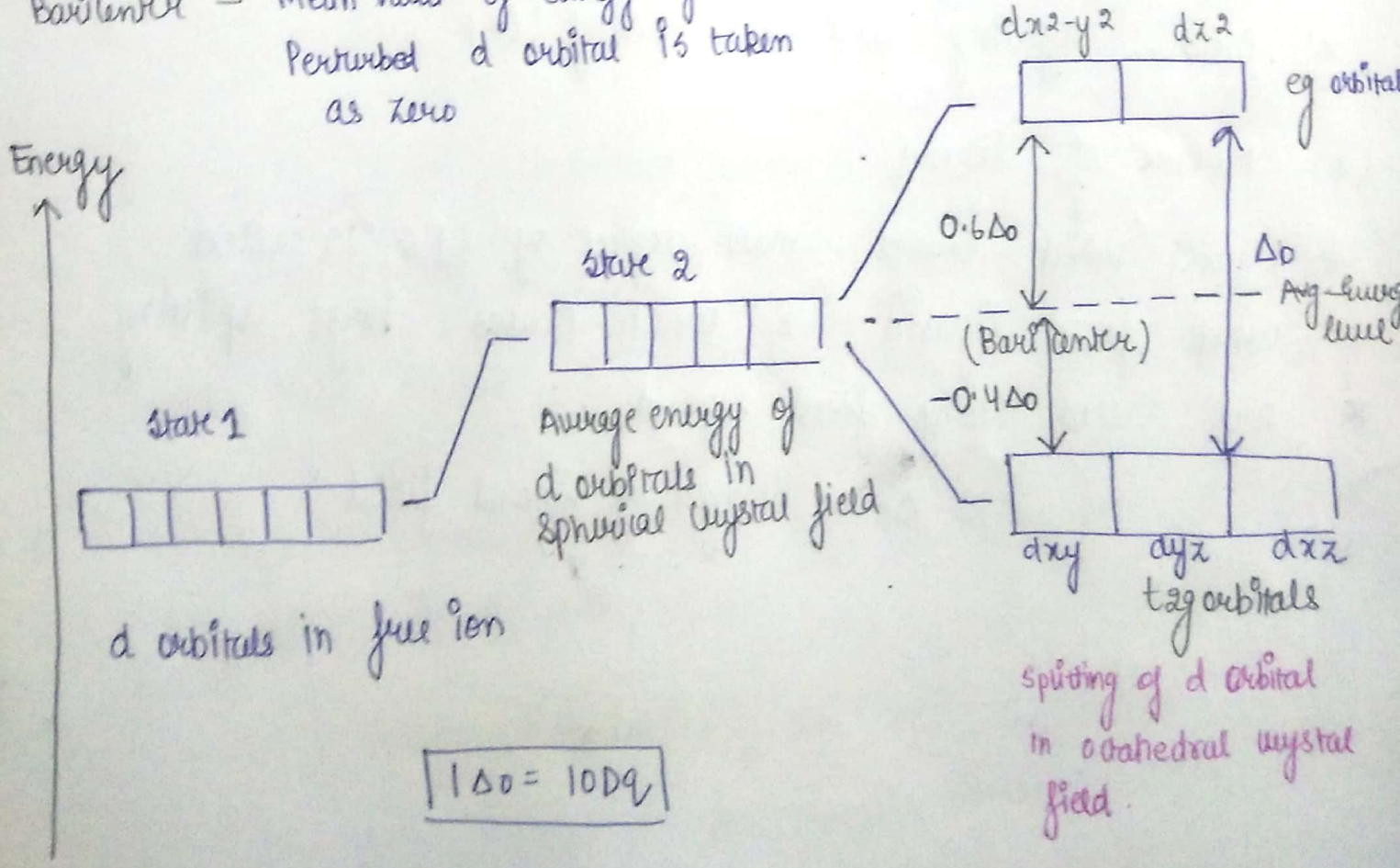
* lobes of t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) point in between x, y & z axis



* Approach of six ligand along x, y, z and -x, -y & -z direction will increase the energy of $d_{x^2-y^2}$ and d_{z^2} much more increase than d_{xy}, d_{yz} and d_{zx}

Thus Octahedral splitting takes place

Barycenter – Mean value of energy of three perturbed d orbital is taken as zero



$10Dq = 1\Delta_o$

$$\boxed{CFSE = [-0.4\ t_{2g}(e^-_s) + 0.6\ e_g(e^-_s)]\Delta_o}$$

difference b/w energy of two sets of d orbital is called CFS energy

If $\Delta_o <$ Pairing energy (High spin complex)

$\Delta_o >$ Pairing energy (Low spin complex)

If $\Delta_o \simeq$ Pairing energy H.S.C $\rightleftharpoons$ L.S.C

* Factors Affecting Octahedral Splitting (Δ_o)

(a) Nature of ligand

* Ligand which causes small degree of CFS is called weak field ligand & which causes large splitting are called strong field ligand.

$\Delta_o \propto$ Strength of ligand field

Weak field ligand

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O$

$< NCS^- < NH_3 < en < NO_2^- < CN^- < CO$

(Strong field ligand)

Above arrangement of ligands in increasing value of CFSE or Δ_o is called <u>Spectrochemical series</u>.

(b) Oxidation state of metal ion

$\Delta_o(+3) > \Delta_o(+2)$ by 25%.

$\Delta_o = 28600 cm^{-1}$ $\quad$ $\Delta_o = ?$

$[Ru(H_2O)_6]^{3+}$?

(c) Size of metal ion or Position in Transition series

Δ_o for $5d > 4d > 3d$

$(Pt) > (Pd) > (Ni)$

<u>Conclusion</u> : For Octahedral complexes

* Strong field ligands $\longrightarrow$ High Δ_o value $\longrightarrow$ Low spin complexes
* Weak field ligand $\longrightarrow$ Low Δ_o value $\longrightarrow$ High spin complexes
* No difference for High spin & Low spin for d^1, d^2 d^3, d^8 & d^9 & d^{10} system.
* d^4, d^5, d^6 & d^7 system Has differences in High spin & Low spin complexes.

High spin complex

$d5 = t_{2g}^3 e_g^2 = 0.0$

$d6 = t_{2g}^4 e_g^2 = -0.4$

$d7 = t_{2g}^5 e_g^2 = -0.8$

$d8 = t_{2g}^6 e_g^2 = -1.2$

Low spin complex

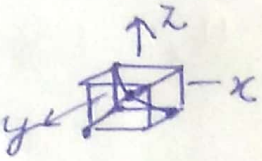
$d5 = t_{2g}^5 e_g^0 = -2.0$

$d6 = t_{2g}^6 e_g^0 = -2.4$

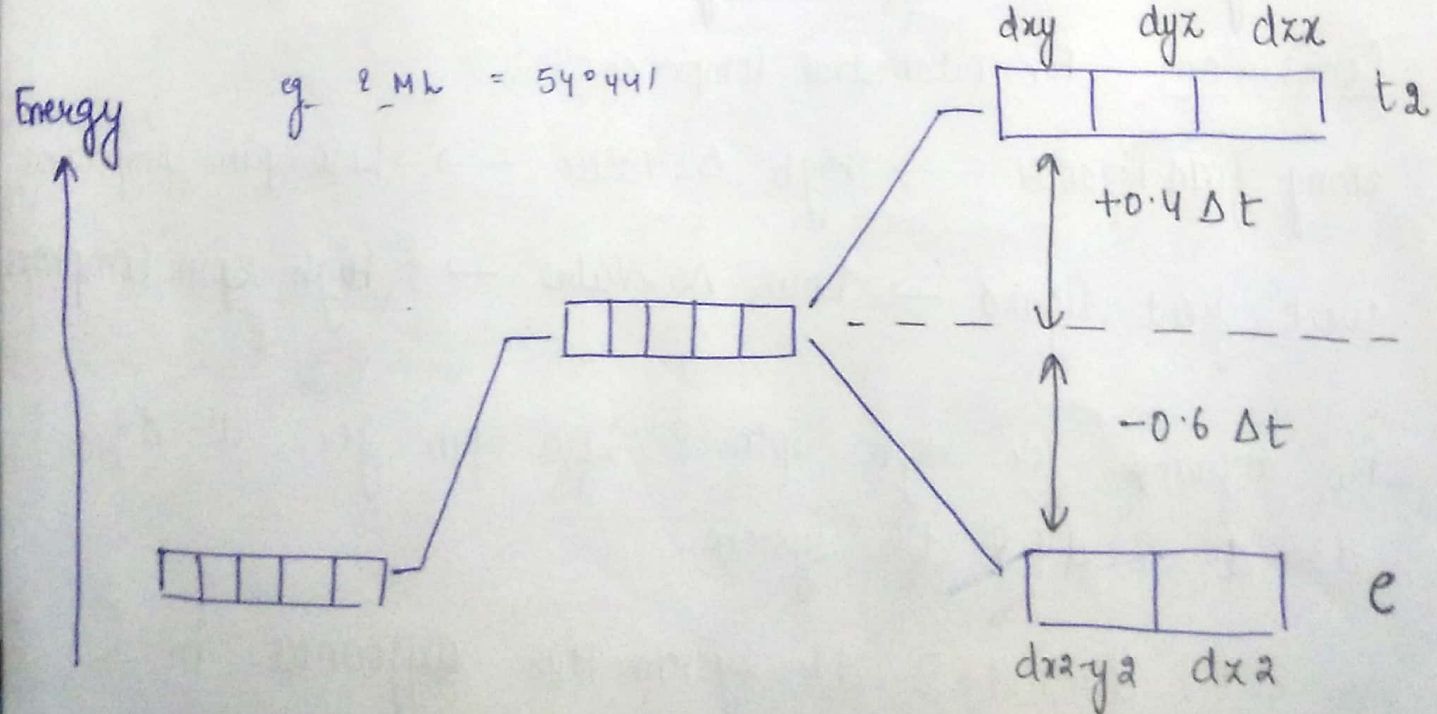
$d7 = t_{2g}^6 e_g^1 = -1.8$

$d8 = t_{2g}^6 e_g^2 = -1.2$

Tetrahedral Splitting



* eg orbital point along x, y, z axis (center of faces)
* t_{2g} orbital point in b/w x, y, z (towards center of edges of cube)
* Direction of approach of ligand does not coincide with t_{2g} or eg orbital
* t_{2g} orbital are nearer to direction of ligand than eg orbitals thus approach of ligand raises energy of t_{2g} orbitals.



* eg Not coincide with approach of ligand
* t_{2g} Orbital have more value at center of edges of cube than

CFSE = $(-0.6\ n_{eg} + 0.4\ n_{t2g})\ \Delta t$

$\Delta t = 4/9\ \Delta o$

Why Magnitude of CFSE is less than octahedral field

* Only 4 Ligand instead of 6 ligand [2/3]
* Direction of orbital does not coincide with direction of ligands ∴ Reduces Splitting by 2/3

$\Delta t = 2/3 * 2/3 = 4/9\ \Delta o$

* Octahedral complex more stable than Tetrahedral complexes (CFSE is large in OC)

* High spin complex are formed in Tetra. complexes

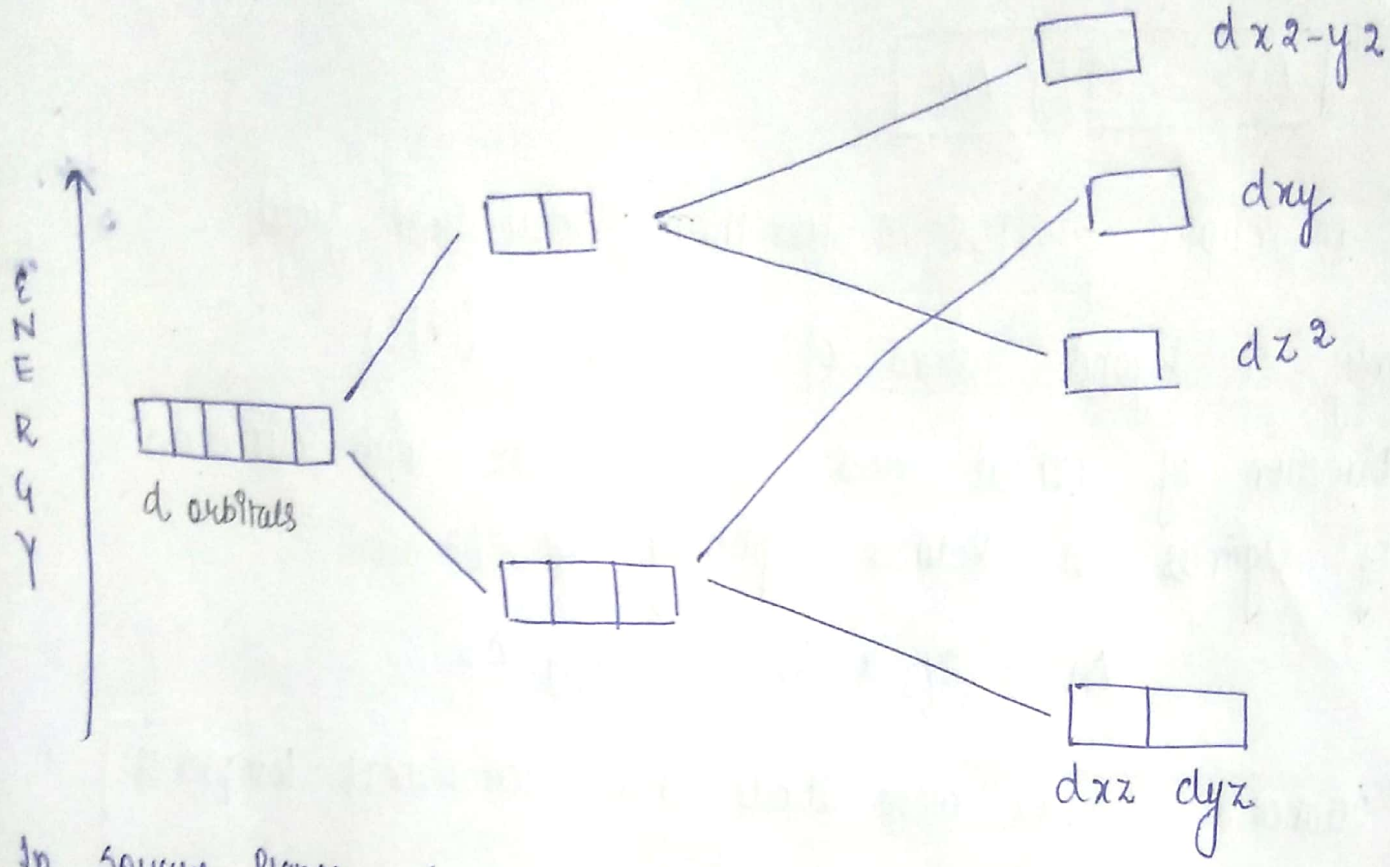
$d6 = eg^3\ t2g^3 = -0.6$

$d7 = eg^4\ t2g^3 = -1.2$

$d8 = eg^4\ t2g^4 = -0.8$

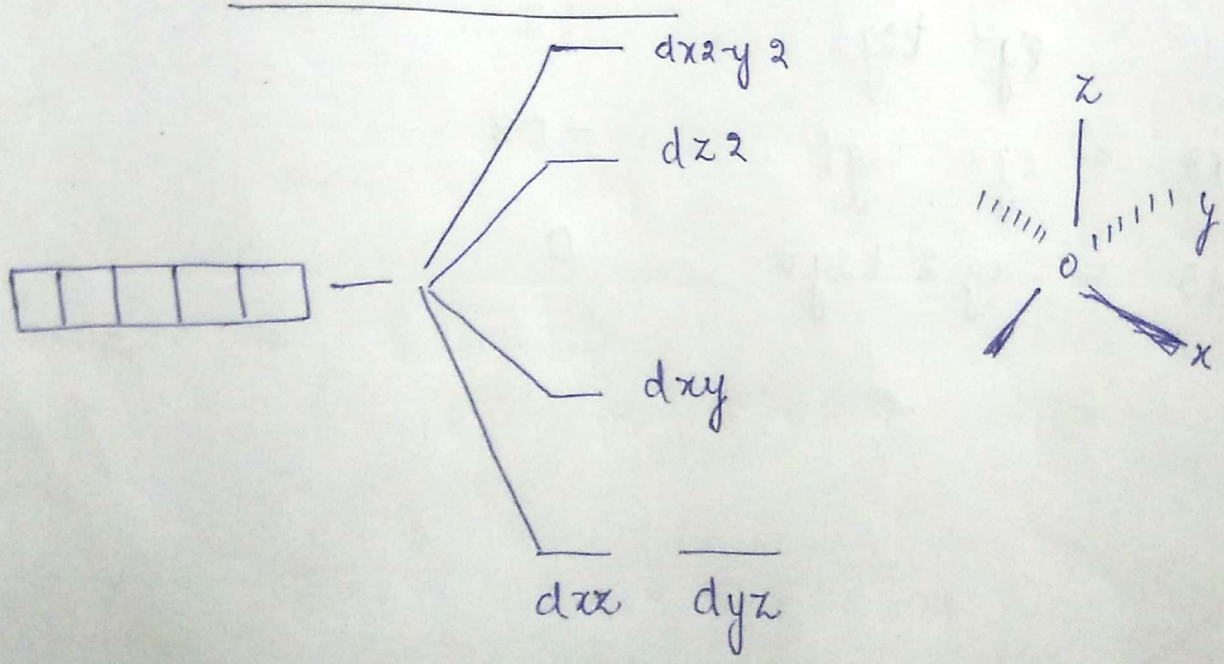
$d5 = eg^2\ t2g^3 = 0$

SPLITTING IN SQUARE PLANAR SYSTEM

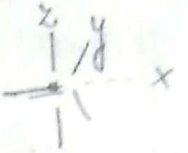


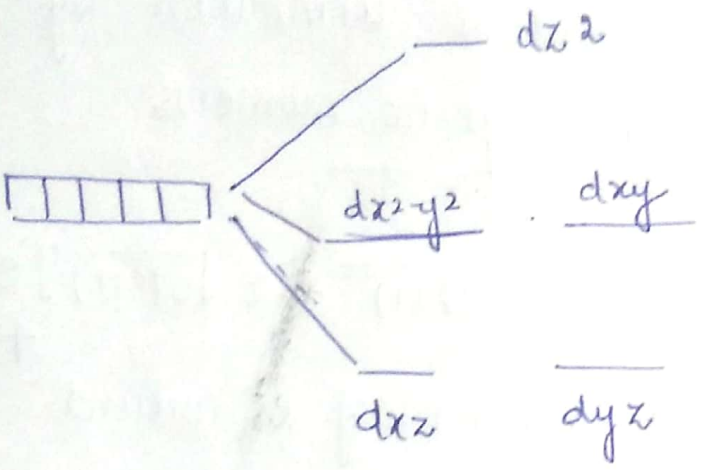
In Square Planar $d_{x^2-y^2}$ orbital alone directly faces four ligand along x and y axes. So Most destabilized.

SPLITTING IN SQUARE PYRAMIDAL

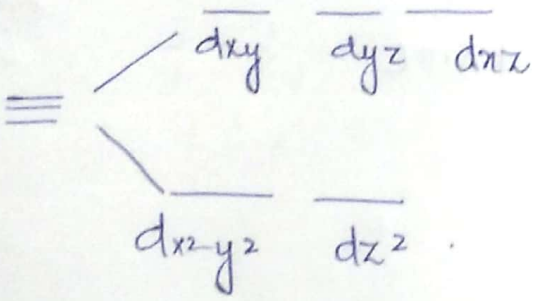


SPLITTING IN TRIGONAL Bipyramidal





SPLITTING IN CUBIC SYSTEM



$$\Delta_c = \frac{8}{9}\Delta_o$$

Magnetic Property

Diamagnetism

* Substances not attracted by Magnetic field are called diamagnetic substance
* It is due to Paired electrons

Paramagnetism

* Substances are attracted by Magnetic field are called Paramagnetic substance
* It is due to unpaired electrons

→ More the no. of unpaired electrons in substance More is Paramagnetism.

Resultant Magnetic moment arises due to contribution by both spin and Orbital angular magnetic moments.

$$\mu_{Total} = \mu_{orbital} + \mu_{spin} = \left[\sqrt{l(l+1)} + 2\sqrt{S(S+1)}\right]\frac{eh}{4\pi mc}$$

In 3d metals Ligand Restrict movement of e^- around Nucleus in orbitals.
The Orbital contribution therefore Quenched & Negligible

$$\mu_{eff} = \mu_{spin} = 2\sqrt{S(S+1)}\ \frac{eh}{4\pi mc}$$

$1\,BM = 9.27 * 10^{-21}$ erg/g

$$= 2\sqrt{S(S+1)}\ BM$$

$$= 2\sqrt{\frac{n}{2}\left(n/2+1\right)}$$

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

where n = no. of Unpaired electrons

$Ni^{2+} = 3d^8 =$ ↑↓ ↑↓ ↑↓ ↑ ↑

$= \sqrt{2(2+2)} = \sqrt{8} = 2.84$ B.M

$Co^{2+} = 3d^7 =$ ↑↓ ↑↓ ↑ ↑ ↑

$= \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M

Limitations of CFT

* Ligands are considered as point charges and hence anionic ligand should exert greater splitting effect but actually the anionic ligand are found at low end of Spectrochemical series.

* Purely ionic character is taken in account in b/w Metal-ligand and covalent character are ignored.