

BSc 1st year

Inorganic Chemistry

- ~~1. Atomic Structure and Periodic Properties~~ → Pg - 1
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- ~~3. Ionic Solids~~ → 96
- ~~4. s-Block, p-block, Noble Gases~~
- ~~5. Chemistry of Compounds~~

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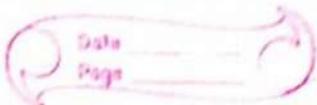
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Atomic Structure And Periodic Properties

ATOMIC STR.



Unit - I Idea of De-Broglie Matter Waves

Acc to de-Broglie e^- and particle of matter has dual character i.e. wave character as well as particle character.

And wave associate with these particle as well as particle character is known as matter wave and wave length associate with these is called as de Broglie wavelength.

$$\text{E} = h\nu \quad \text{--- ① Planck's quantum theory}$$
$$\text{E} = mc^2 \quad \text{--- ② Einstein energy mass.}$$

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

$$\lambda = \frac{c}{\nu}$$

$$\frac{h}{\lambda} = m \cdot c$$

$$\lambda = \frac{h}{m \cdot c}$$

c = velocity of light

h = Planck's constant

m = mass of e^-

$$h = 6.62 \times 10^{-34} \text{ J.s}$$

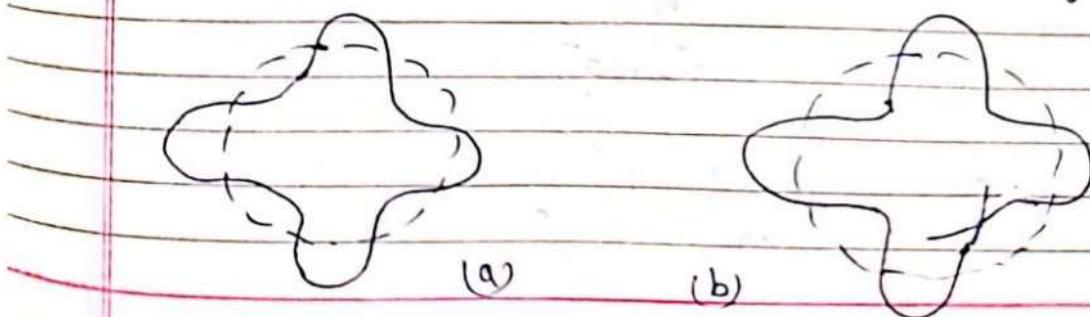
Difference b/w Electromagnetic waves and Matter waves

- ① Matter waves have less velocity compare to Electro mag. waves.
- ② Matter waves cannot be radiate.
- ③ Matter waves not immetate by particle. But simply it associate with its motion.
- ④ Matter waves have very small I compare to EM Waves.

20) De Broglie Equation Application

According to Bohr theory e^- can revolve only those orbits in which angular momentum is multiple integral of $\frac{h}{2\pi}$. But Bohr can't explain it

Consider an e^- moving in circular orbit around a nucleus as following



(a) wave continuously in phase

(b) wave out of phase

$$2\pi r = nd \quad \text{Bohr's postulate}$$

$$\frac{2\pi r}{mv} = \frac{nh}{mv} \quad \left\{ mvr = nh \right\}$$

if wave is continuously in phase
 the circumference of the circle
 must be multiple integral of
 wave length

²⁰¹¹
 Experimental verification of de-Broglie
 eqn :-

if a charge particle have charge
 q is accelerated by V volt
 then its K.E will be

$$\frac{1}{2}mv^2 = qV$$

$$v = \sqrt{\frac{2qV}{m}}$$

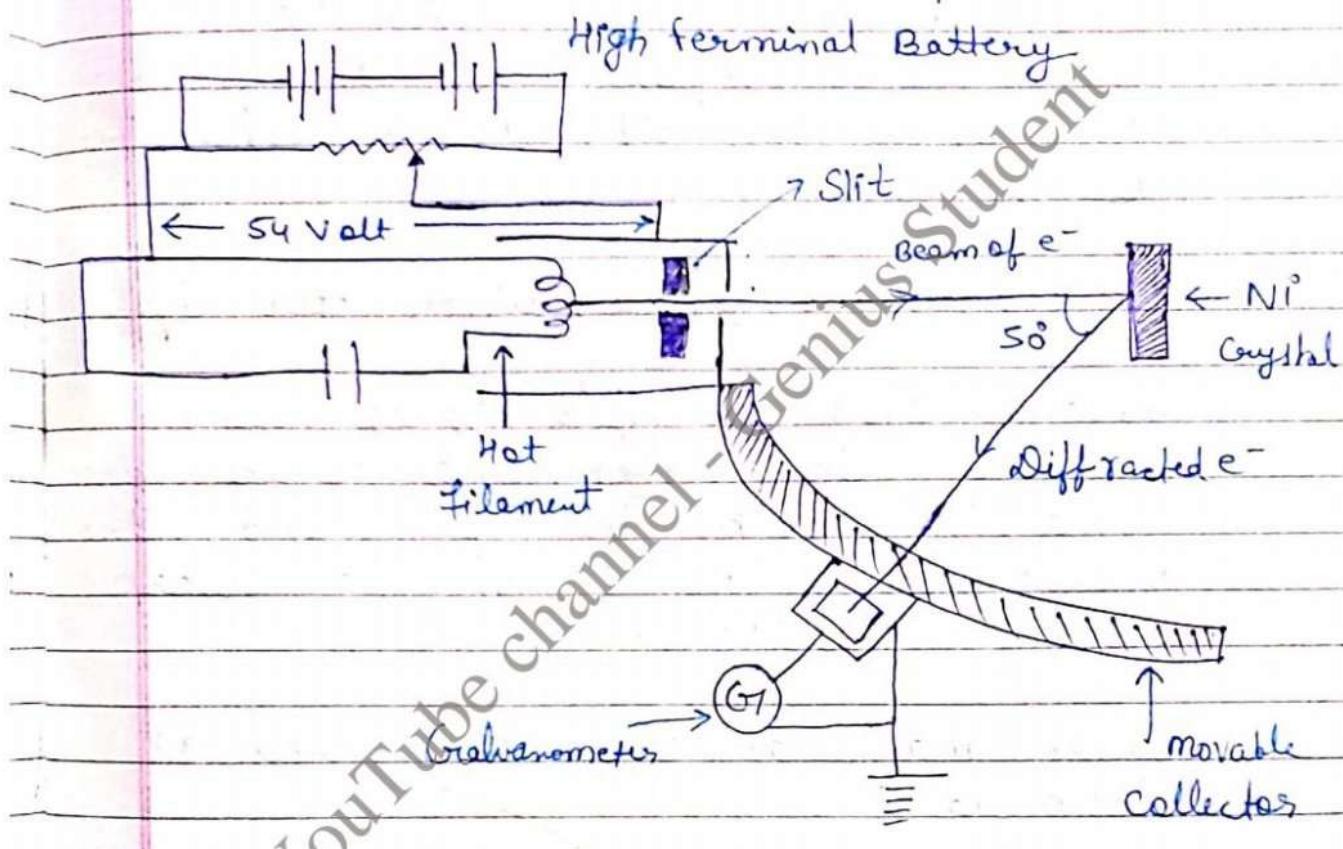
$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mqV}}$$

$$\left\{ \lambda = \frac{1.26}{\sqrt{V}} \text{ Å} \right\} \text{ for e-}$$

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if potentials are vary b/w $10 \rightarrow 1000$
 then it should vary b/w $3.877 \text{ Å} \rightarrow$
 0.1226 Å and these values are in orders of
 wavelength of X ray

Davison & Germer Experiment



In this experiment e^- work emitted from a hot filament and were accelerated by a potential varying b/w 40 to 68 volt before striking a Ni crystal. It was found that reflection was most intense and took place at an angle of 50° when e^- s were accelerated through 54 volt.

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And wavelength comes out to be 2.66 Å . This wavelength also lies in the X-ray range.

Since X-ray have wave character, the e⁻'s must also have wave character associate with them. Thus this experiment give direct evidence for the wave character of electron.

Heisenberg's uncertainty principle

Acc to this principle it is not possible to determine precisely exactly both the position and the momentum of a moving microscopic particle.

It is mathmatically expressed as following :-

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

Where Δx = uncertainty in position
 Δp = uncertainty in momentum
= $m \Delta v$

Δv = uncertainty in velocity

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

Ques An e^- has a speed of 300 m/sec which accurate upto 0.001 %. What is the uncertainty in its pos'n?

Solve $m_e = 9.1 \times 10^{-31} \text{ gm}$

$$\Delta x = \frac{6.21 \times 10^{-27} \text{ gm cm sec}^{-1}}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ gm} \times \Delta v}$$

$$\Delta v = \frac{0.001}{100 \times 10^3} \times 300 = 3 \times 10^{-3} \text{ m/s}$$

$$\Delta x = 1.93 \times 10^{-2} \text{ m}$$

Schrodinger wave equation

for a standing wave of wavelength λ , the amplitude of the wave at any point along x axis may be described by a func' $f(x)$ is such that

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x) \quad \textcircled{1}$$

for e^- which considered a wave which move only one direc'

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$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{d^2} \psi$$

In all 3 direcⁿ it can be written
as :-

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{d^2} \psi$$

$$\nabla^2 \psi = -\frac{4\pi^2}{d^2} \psi \quad \textcircled{2}$$

$$\begin{aligned} \nabla^2 &= \text{Laplacean operator} \\ &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \end{aligned}$$

$$d = \frac{\hbar}{mv}$$

$$\nabla^2 \psi = -\frac{4\pi^2 m^2 v^2 \psi}{\hbar^2} \quad \textcircled{3}$$

$$\begin{aligned} T \cdot \varepsilon &= K \cdot \varepsilon + P \cdot \varepsilon \\ E &= K + V \end{aligned}$$

$$K = \varepsilon - V$$

$$\frac{1}{2} mv^2 = E - V$$

$$v^2 = \frac{2}{m} (\varepsilon - V) \quad \text{Div.} \quad \textcircled{4}$$

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put value of ④ in ③

$$\nabla^2 \psi = -\frac{8\pi^2 m}{\hbar^2} (\epsilon - V) \psi$$

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

$$\left\{ \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + \frac{8\pi^2 m}{\hbar^2} (\epsilon - V) \psi = 0 \right\}$$

This is Schrö. wave eq.

$$\nabla^2 \psi = -\left(\frac{2\pi}{\hbar}\right)^2 2m(\epsilon - V) \psi$$

$$-\nabla^2 \psi = \frac{1}{\hbar^2} 2m(\epsilon - V) \psi \quad \left\{ \hbar = \frac{\hbar}{2\pi} \right\}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = (\epsilon - V) \psi$$

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

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

$$H \psi = E \psi$$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V = H \right\} = \text{Hamiltonian operator}$$

~~Topic~~ Significance of ψ and probability density :-

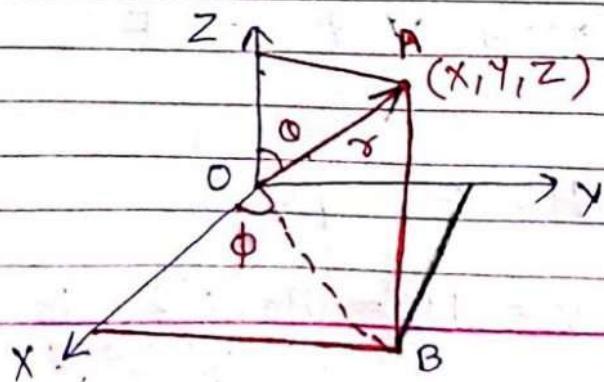
ψ represents the amplitude of wave which have no significance but its square (ψ^2) has significance and denotes the probability of finding of e^- at any point all over the space and also known as probability density.

Exact explanation of ψ^2 is given in terms of volume element $d\tau$

$$\int_{-\infty}^{+\infty} \psi^2 d\tau = 1$$

$\psi^2 d\tau$ is probability of finding of e^- in small volume element $d\tau$.

Radial and angular function



This graph is the relation b/w cartesian coordinate and polar coordinate.

$$\left. \begin{array}{l} X = r \cos \theta \cos \phi \\ Y = r \sin \theta \sin \phi \\ Z = r \cos \theta \end{array} \right\}$$

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2}$$

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right)$$

Solution of this Equation

$$[\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)]^*$$

(i) $R(r)$ is the funcⁿ of r , which depend on n, l and known as radial wave funcⁿ.

(ii) $\Theta(\theta)$ is the funcⁿ of θ , which depend on l, m

(iii) $\Phi(\phi)$ is the funcⁿ of ϕ , which depend on m

(iv) and (v) are known as angular wave function.

Quantum Numbers

The numbers which provides complete information about e^- i.e. Shell, Subshell, orientation of orbitals, distance of e^- from nucleus, energy of an electron and spin of electrons etc. are known as quantum no.

There are four :-

1. Principal quantum number

- It is denoted by n .
- It tells about shell i.e. size of atom.
- Its values are lying 1 to ∞ .

$n=1$ K shell $\rightarrow 2e^-$

$n=2$ L shell $\rightarrow 8e^-$

$n=3$ M shell $\rightarrow 18e^-$

$n=4$ N shell $\rightarrow 32e^-$

$$\left. \begin{array}{l} \text{Max. no} \\ \text{of } e^- \\ = 2n^2 \end{array} \right\}$$

- Radius of atom and energy of e^- also depend on principal quantum no.

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$$r = 0.529 \frac{n^2}{z} \text{ Å}^{\circ}$$

$$E = -13.6 \times \frac{z^2}{n^2} \text{ eV/atom}$$

2. Azimuthal quantum number,

- It is denoted by l .
- Values are lying from 0 to $(n-1)$.
- This quantum no. denotes shape of subshell.
- Max^m no of e^- in any subshell given by $2(2l+1)$
- Orbital angular momentum can be calculated $= \sqrt{l(l+1)} \frac{\hbar}{2\pi} = \sqrt{l(l+1)} \frac{\hbar}{2\pi}$

$l=0$ (s subshell)	Max ^m no of e^-
$= 1$ (p subshell)	2
$= 2$ (d subshell)	6
$= 3$ (f ")	10
$= 4$ (g ")	14
	18

s = sharp

f = fundamental

p = principle

d = diffuse

shape

orbital ang momen.

S Spherical symm.

p dumb-bell

d double dumb-bell

f complex

g complex

o

$\sqrt{2} \frac{\hbar}{2\pi}$

$\sqrt{6} \frac{\hbar}{2\pi}$

$\sqrt{3} \frac{\hbar}{\pi}$

$\sqrt{5} \frac{\hbar}{\pi}$

3. Magnetic quantum number

→ This quantum no. denotes orientation of orbitals.

→ Total values of m_l are $(2l+1)$

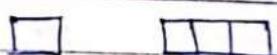
→ Possible values are $[-l, +l]$ each value represent 1 orbital.

l 0 1 2 3.

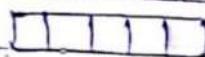
Subshell	s	p	d	f
Total value of m_l	1	3	5	7

$-l$ to l 0 $[-1, 1]$ $[-2, 2]$ $[-3, 3]$

Orbital

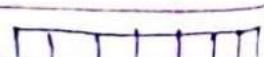


s



dx^2, dy^2, dz^2

d_{3z^2}

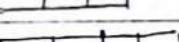


f orbital

4. Spin quantum number

- It is denoted by m_s .
- This quantum no tells the direcⁿ of spin of an e^- on its axis.
- m_s can have 2 values $+\frac{1}{2}, -\frac{1}{2}$

Shell	Subshell	Orbitals	No of e^-
-------	----------	----------	-------------

$n=1$	K shell	1S		$2e^-$
$n=2$	L shell	2S		$2e^-$
		2P		$6e^-$
$n=3$	M shell	3S		$2e^-$
		3P		$6e^-$
		3d		$10e^-$
$n=4$	N shell	4S		$2e^-$
		4P		$6e^-$
		4D		$10e^-$
		4F		$14e^-$

Degenerate orbitals

Orbitals belonging to the same subshell having equal energy are known as degenerate orbitals.

For eg → P subshell have 3 degenerate orbitals namely p_x, p_y, p_z

d subshell have 5 degenerate orbital
 $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$

Aufbau's principle.

This principle states that in the ground state of an atom, the orbital with a lower energy is filled up first before the filling of the orbital with a higher energy.

In other words the e⁻ enter the various subshell in the order of increasing energy.

Aufbau principle have following 3 rules:-

* ① (n+l) rule \rightarrow

That subshell have lowest energy which have lowest value of (n+l)

$$\begin{array}{lll} n+l \\ \text{1S} & 1+0 & = 1 \\ \text{2S} & 2+0 & = 2 \\ \text{2P} & 2+1 & = 3 \end{array}$$

Order of Energy $1S < 2S < 2P$

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★② Pauli's Exclusion Rule →

Acc to Pauli it is impossible for any 2 e^- in the same atom to have all the four quantum no. identical.

Ae^-	$\boxed{1\downarrow}$	Be^-	$\leftarrow 2P_z$
$n=2$		$n=2$	
$l=1$		$l=1$	
$m_l=0$		$m_l=0$	
$m_s=+\frac{1}{2}$		$m_s=-\frac{1}{2}$	

Acc to pauli's exclusion rule n^{th} orbital can accomodate max^m e^- but their spin must be opposite to each other.

★③ Hund's Maximum multiplicity rule →

Acc to Hund's rule that electron config'n is more stable which have max^m no. of unpaired e^- with parallel spin i.e. max^m multiplicity.

$$p^3 \quad \boxed{1\downarrow 1\downarrow 1\uparrow} \quad S = \text{total spin} \\ = 3 \times \frac{1}{2} = \pm \frac{3}{2}$$

$$\text{Spin multiplicity} = 2 \times \frac{3}{2} + 1$$

$$= 4 \quad (\text{more stable})$$

P³

↑	↓	↑	.
---	---	---	---

$$S = \pm \frac{1}{2}$$

$$\begin{aligned} \text{spin multiplicity} &= 2|S| + 1 \\ &= 2 \times \frac{1}{2} + 1 = 2 \\ &= 2 \text{ (less stable)} \end{aligned}$$

When e⁻ are filled in degenerate orbit then pairing of e⁻ can't take place until each orbital has got 1 e⁻.

Reason for extra stability of half filled and full filled electronic configuration :-

① Symmetrical distribution of electron:-

It is well known fact that symmetry leads to stability. That's why d⁵, d¹⁰, f⁷ and f¹⁴ electronic configⁿ are extra stable rather than other elec configⁿ.

② Exchange Energy :-

The e⁻s which have parallel spin tends to exchange their posⁿ and during these exchanges some amount of energy is released which is known as exchange energy.

More the exchange energy system will be more stable.

It is calculated by the following formula :-

$$E_K = -\frac{n(n-1)}{2} K$$

n = no of e^- with parallel spin

E_K = exchange energy

K = constant

③ Pairing Energy :-

The energy which is required for pairing of e^- is known as pairing energy.

It makes system unstable.

eg. $d^4 \rightarrow \boxed{111111}$

$$E_K = -\frac{4(4-1)}{2} K = -6K$$

eg. $d^5 \rightarrow \boxed{111111}$

$$E_K = -\frac{5(5-1)}{2} K = -10K$$

$$\cancel{E_K = -\frac{1(i-1)K}{2} = 0K}$$

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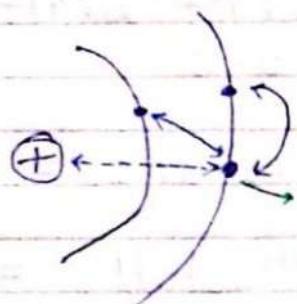
Total exchange energy

$$= -10K + 0K + \Pi$$

$$= -10K + \Pi \leftarrow \text{pairing energy}$$

It is obvious that exchange energy for d^5 electronic configuration is greater than d^4 and d^6 electronic configuration.

Effective nucleus charge and shielding effect



$$\begin{array}{c} \longleftrightarrow \\ A \cdot F \\ \longleftrightarrow \\ R \cdot F \end{array}$$

$$Z_{\text{eff}} = Z - \sigma$$

Z_{eff} = effective nucleus charge

σ = Shielding / screening effect constant

SHIELDING EFFECT

The repulsion of inner shell e^- or valence shell electron on a particular electron is called as screening or shielding effect.

Magnitude of this repulsive force is called shielding constant.

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Periodic Properties

But important for other competitions

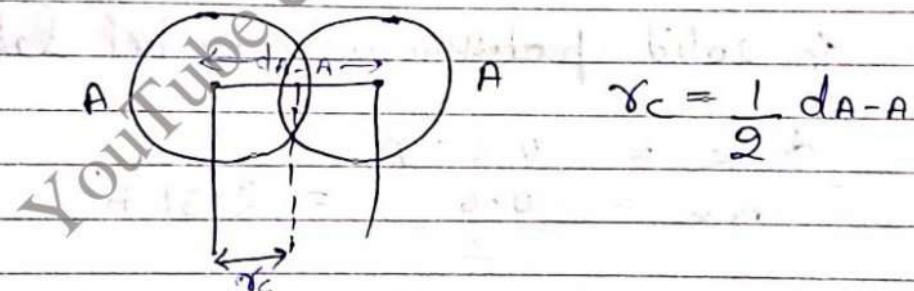
1. Atomic Radii

The distance b/w the centre of the nucleus and outer most shell where e⁻'s are present is called atomic radii.

Type of Radii

a) Covalent Radius

The half of the distance b/w nuclei of 2 light atoms bonded together by a single covalent bond.



d_{A-A} = internuclear distance / Bond length

Eg. i) H₂ molecule $d_{H-H} = 0.74 \text{ \AA}$

$$r_H = \frac{0.74}{2} \text{ \AA} = 0.37 \text{ \AA}$$

ii) Cl₂ molecule: $d_{Cl-Cl} = 1.98 \text{ \AA}$

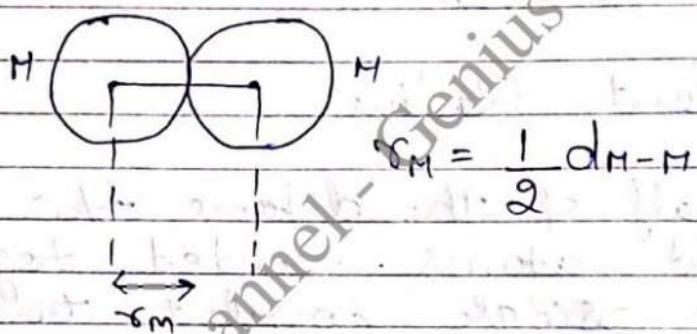
$$r_{Cl} = \frac{1.98}{2} \text{ \AA} = 0.99 \text{ \AA}$$

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(iii) in diamond $d_{C-C} = 1.54 \text{ \AA}$
 $r_C = \frac{1.54}{2} \text{ \AA}$

b) Metallic Radius / Crystal radius

It is defined as the half of the distance b/w the nuclei of 2 adjacent metal atom in the metallic close packed crystal lattice.



Eg → in solid potassium crystal lattice

$$d_{K-K} = 4.62 \text{ \AA}$$

$$r_K = \frac{4.62}{2} = 2.31 \text{ \AA}$$

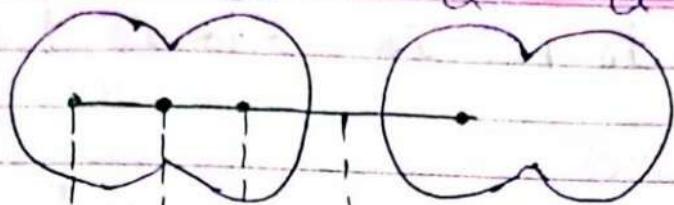
c) Vanderwall radius

It is the half of the distance b/w the nuclei of 2 non-bonded neighbouring atoms of two adjacent molecule in solid state.

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Cl Cl

Cl Cl



$$r_{\text{Cl}} = 1.99 \text{ Å} \\ = 99 \text{ pm}$$

(Covalent radius)

$$r_{\text{Cl}} = 1.8 \text{ Å} = 180 \text{ pm} \\ (\text{Vanderwall radius})$$

Order of Radii

Vanderwall > Metallic > Covalent

Factors affecting atomic radii :-

① Effective nuclear charge

$$Z_{\text{eff}} \propto \frac{1}{r}$$

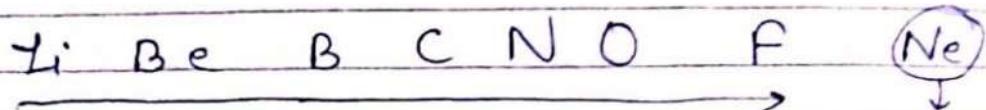
② Shielding effect $S.E. \propto \gamma$

③ No of shells $n \propto r$



Periodic trend in Atomic Radii

① In period:



$z_{eff} \uparrow, r \downarrow$

Vanderwall
Radius
(Highest r_1)

② In group:

H

Li

Na

K

Rb

Cs

$z_{eff} = \text{constant}$

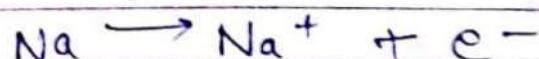
No of shell \uparrow

radius \uparrow

Q. Ionic Radius

It is defined as the distance b/w the nucleus and outer most shell of an ion.

(a) Cationic Radii



2, 8, 1 2, 8

K L M P=11

$$e^- = 10 \quad P/e = 1.1$$

$$P = 11$$

$$e^- = 11 \quad P/e = 1$$

$Z_{\text{eff}} \uparrow, r \downarrow$

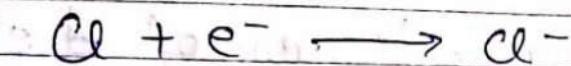
$Z_{\text{eff}} \propto P/e$

$Z_{\text{eff}} \propto V_Z$

$\{\gamma_{\text{Na}} > \gamma_{\text{Na}^+}\} *$

Cation always smaller than its parent atom.

(b) Anionic Radii



$$P = 17$$

$$P = 17$$

$Z_{\text{eff}} \downarrow r \uparrow$

$$e^- = 17$$

$$e^- = 18$$

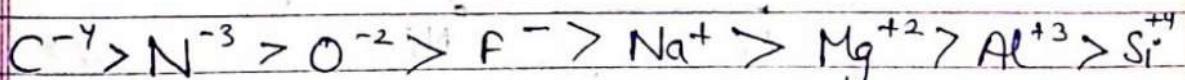
$$P/e^- = 1$$

$$P/e^- < 1$$

$\{\gamma_{\text{Cl}^-} > \gamma_{\text{Cl}}\} *$

Anion is always greater than its parent atom.

Radius of iso-electronic species :-



P	6	7	8	9	10	11	12	13	14
---	---	---	---	---	----	----	----	----	----

e ⁻	10	10	10	10	10	10	10	10	10
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$Z_{\text{eff}} \uparrow, r \downarrow$

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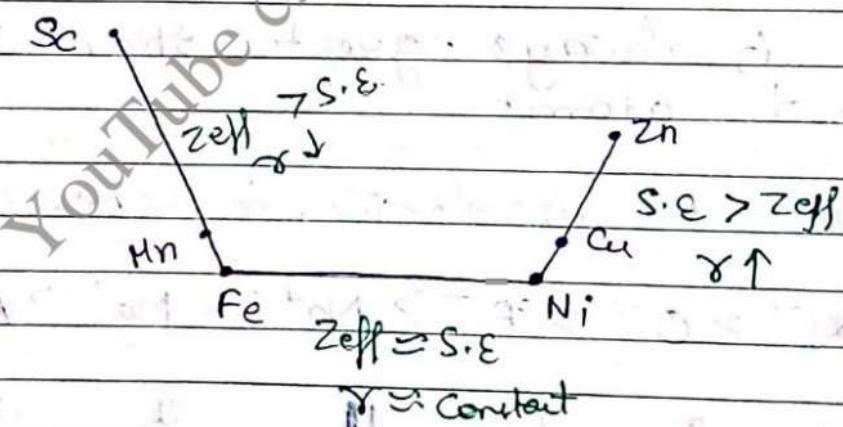
Radius of Transition element :-

In initial element of transition series Z_{eff} is dominated over shielding effect. Hence radius increases.

In middle elements both factors counter balance to each other. Hence radius remains constant.

But in last elements no. of d^- 's increase so shielding effect is dominated over Z_{eff} . Hence radius decreases.

But in a transition series overall radius increases from left to right



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Radius of inner transition element:-

In inner transition element e^- enter in f subshell due to poor shielding effect of f electron effective nuclear charge is increased on outer valence shell e^- . Hence radius decreases.

This effect is known as Lanthanid contraction.

When we move across in a f series radius continuously decreases from left to right.

Method of determination of atomic radius :-

The exact measurement of atomic radius is not easy due to following reasons :-

- ① Atom does not have well defined boundary.
- ② The probability of finding the e^- is never zero even at large distance from nucleus.

- ② It is not possible to get an isolated atom

An estimate of the size of the atom can be made by knowing the distance b/w the atoms in the combined state.

Homo nucleus system :-

To calculate atomic radii of oxygen we used H_2O_2 compound

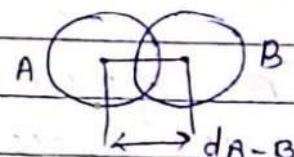
To calculate atomic radii of nitrogen atom we used $\text{NH}_2 - \text{NH}_2$ compound.

Heteronucleus system

for Heteronuclear System internuclear distance is calculated by the help of Stevenson-Schoonmaker formula

$$d_{A-B} = r_A + r_B - 0.09 (\Delta EN)$$

$$r_{A-B} = d_{A-B}/2$$



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Method of determining of ionic radii

① Pauling's Method

Acc to pauli ionic radii of mono valent ion is inversely proportional to their Z_{eff} .

$$\frac{r_+ \alpha}{Z_{eff \text{ of cation}}} = \frac{c}{Z_{eff \text{ of cation}}}$$

$$\frac{r_- \alpha}{Z_{eff \text{ of Anion}}} = \frac{c}{Z_{eff \text{ of anion}}}$$

$$\left\{ \begin{array}{l} \frac{r_+}{r_-} = \frac{Z_{eff \text{ of anion}}}{Z_{eff \text{ of cation}}} \\ \end{array} \right\} \quad c = \text{constant}$$

Ques Calculate the ionic radii of K^+ and Cl^- in KCl by pauling's method.

Given Shielding constant for $Ar = 11.6$ and interionic distance 6.60

K^+ and Cl^- is 3.14 \AA .

$$\text{Solve } d_{K^+Cl^-} = r_{K^+} + r_{Cl^-}$$

$$3.14 = \frac{c}{19 - 11.6} + \frac{c}{17 - 11.6}$$

$$K^+ = Ar$$

$$Z_{eff} = Z - \sigma$$

$$c = 9.8$$

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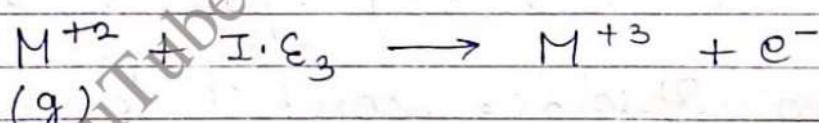
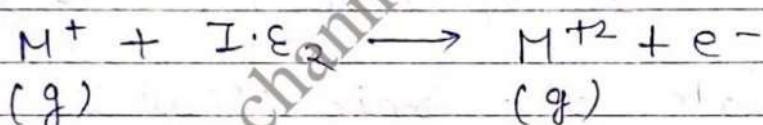
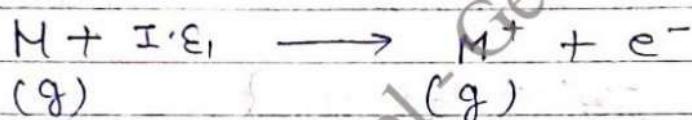
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$$\gamma_{K^+} = \frac{9.8}{7.4} = 1.32 \text{ A}^\circ$$

$$\gamma_{ce^-} = \frac{9.8}{5.4} = 1.81 \text{ } \textcircled{A}$$

Ionisation Energy

The min^m amount of energy which is require to remove an electron from isolated gaseous atom is known as ionisation energy.



$$I \cdot \varepsilon_1 < I \cdot \varepsilon_2 < I \cdot \varepsilon_3 < \dots < I \cdot \varepsilon_n$$

The value of successive $I.E_p$ becomes
less after removal of e^-
electrostatic force of attraction
increases b/w nucleus and remaining
electrons i.e. effective nuclear
charge increases.

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$$1 \text{ ev/atom} = 93.06 \text{ kcal/mole}$$
$$= 96.49 \text{ kJ/mole}$$

$$1 \text{ cal} = 4.2 \text{ Joule}$$

Factors affecting ionisation energy

① Effective nucleus charge

$$I.E \propto Z_{\text{eff}}$$

② Shielding effect

$$I.E \propto \frac{1}{S.E}$$

③ Size

$$I.E \propto \frac{1}{\text{Size}}$$

④ penetration power

Closeness to the nucleus is \propto P.P.

order of p.p.

s > p > d > f Shell must be same

$$\text{eg} \rightarrow 4s > 4p > 4d > 4f$$

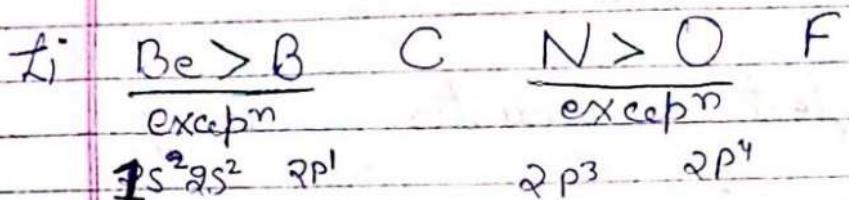
⑤ Special electronic configuration

Half-filled and full-filled e.c are extra stable. Hence more amount of energy is required to

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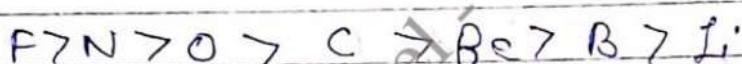
remove e^- from these enic config.

Periodicity in I.P / I.E.

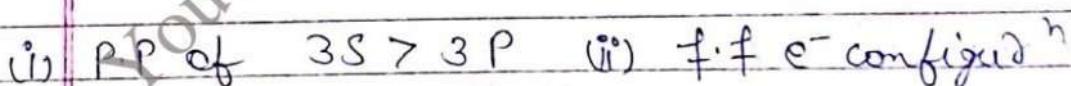
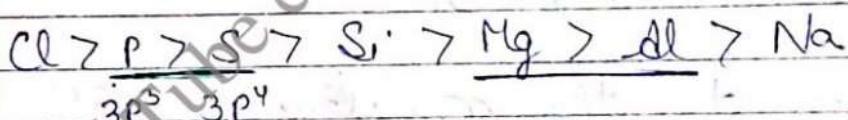


- (i) P.P of $2s > 2p$ P.P = pench'a power
 (ii) F.F e^- Configⁿ f.f = full filled

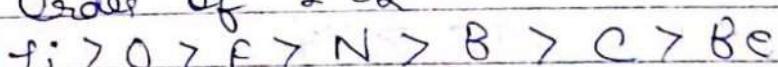
* Order of I.E,
(2nd period)



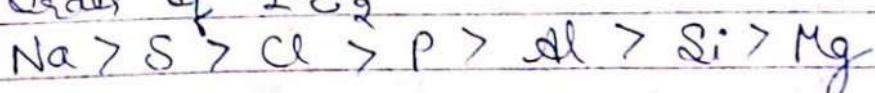
* Order of I.E₂ (3rd period)



* Order of I.E₃



* Order of I.E₄



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H		B	
Li	F	Al	Size ↑
Na	Cl	Cr	I.E. ↓
K	Br	In	
Rb	I	Tl	
Cs			

$Z_{eff} \approx \text{const}$

Size ↑

I.E. ↓

I.E. of Cr > I.E. of Al

due to poor S.E. of 3d e^-

$Z_{eff} \uparrow$, I.E. ↑

I.E. of Tl > I.E. of In

due to poor S.E. of 4f e^-

(Lanthanoid contraction)

$Z_{eff} \uparrow$, I.E. ↑

Method of determining "n" of I.E.

(v) Theoretical Calculation

$$I.E. = E_\infty - E_1 \quad E_\infty = 0,$$

$$I.E. = -E_1$$

$$E_n = -13.6 \times \frac{z^2}{n^2} \text{ ev/atom}$$

$$= -1312 \times \frac{z^2}{n^2} \text{ kJ/mole}$$

for H atom $I.E = -(-1312 \text{ kJ/mole})$
 $= 1312 \text{ kJ/mole}$

for He atom $I.E = -(-1312 \times 4 \text{ kJ/mole})$
 $= 5248 \text{ kJ/mole}$

$I.E$ and explanation of its chemical behaviour

① Nature of bond in a molecule

$I.P \uparrow$, tendency to lose e⁻, C.C \uparrow in Bond \rightarrow

$I.P \downarrow$, I.C in Bond

tendency to lose e⁻ \uparrow

C.C = covalent character

T.C = Ionic character

② Metallic and non Metallic character

$I.P \uparrow$, Non-Metallic character \uparrow \rightarrow

$I.P \downarrow$

Metallic character \uparrow

Metallic character $\propto 1/I.P$

Non Metallic character $\propto I.P$

Teacher's Signature.....

Reducing property or tendency to lose -
 $\alpha \pm$

I.P

G_i is the Best R.A in gaseous state
But Li is the best R.A in aqueous state

③ Relative Stability of O.S

Rule 1 → if difference b/w two conjugative I.E_g is equal or greater than 1500 kJ/mole for an element then lower O.S will be stable.

For e.g. → difference b/w I.E₁ & I.E₂ for sodium metal is 4000 kJ/mole

Hence Na^+ is more stable than Na^{+2}

Rule 2 → If an element have difference b/w two successive I.E_g less than 1050 kJ/mole then O.S will be stable.

For e.g. → Mg have difference of 700 kJ/mole b/w 1st and 2nd I.E.

Hence Mg^{+2} is more stable.

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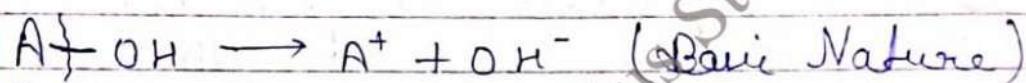
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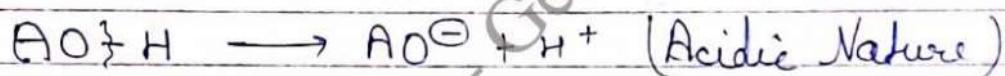
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NOTE → Difference b/w 1st and 2nd I.E. for Al is 1240 kJ / mole. Hence Al^+ must be quite stable but comp'd of Al^+ are unstable. Only in gas phase in solid state due to lattice energy Al^+ disproportionate in Al^{+3} & Al^- .

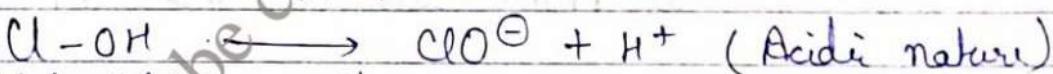
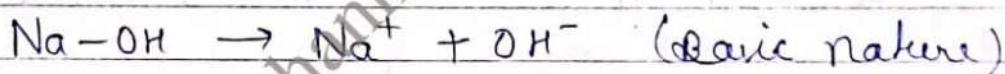
(4) Acidic or Basic Nature of Hydroxide



Low I.P.



High I.P.



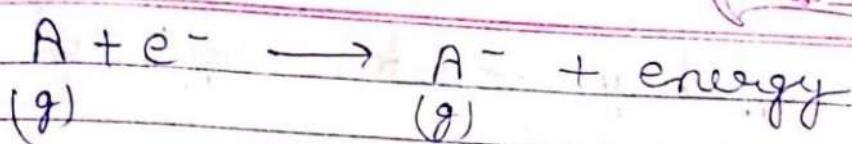
Hypochlorous acid

High I.P.

- Electron gain Enthalpy / electron affinity

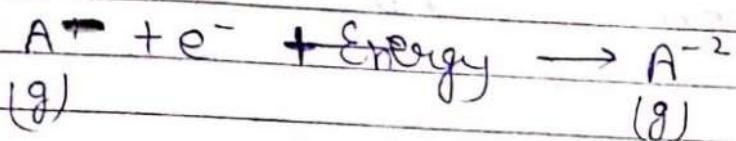
The amount of energy which is released when e^- is added in isolated gaseous atom is known as e^- affinity / e^- gain enthalpy.

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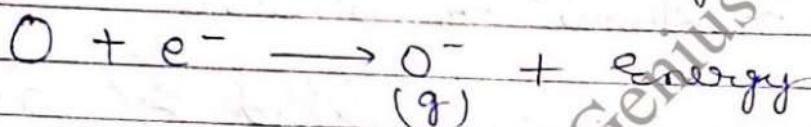
$$\Delta H_{\text{eg},1} = -\text{ve} \text{ (exothermic process)}$$

$E \cdot A_1 = +\text{ve}$ (Attracⁿ force)

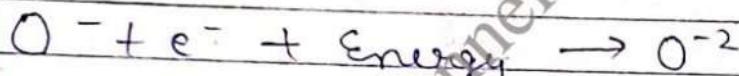


$$\Delta H_{\text{eg},2} = +\text{ve} \text{ (endothermic process)}$$

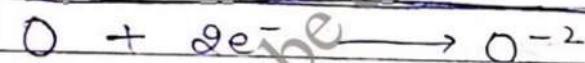
$E \cdot A_2 = \text{zero}$ (Repulsⁿ force)



$$\Delta H_{\text{eg},1} = -141 \text{ kJ/mole}$$



$$\Delta H_{\text{eg},2} = +04 \text{ kJ/mole}$$



$$(g) \Delta H_{\text{eg}} = +563 \text{ kJ/mole}$$

It is obvious from the above eqn that we require 563 kJ/mole energy for oxide (O^{-2}) formⁿ. That is oxide formation is unfavourable but salt of O^{-2} & S^{2-} are quite stable bcoz during crystal formⁿ more amount of lattice energy is released & overall process becomes exothermic.

Factors affecting Electron Affinity

① $Z_{\text{eff}} :- \quad E.A \propto Z_{\text{eff}}$

② Shielding effect:- $E.A \propto \frac{1}{S.E}$

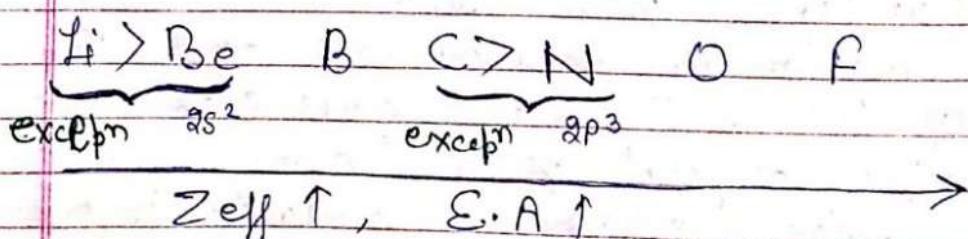
③ Size :- $E.A \propto \frac{1}{\text{Size}}$

④ Special electronic configuration :-

Half filled and full filled E.C are quite stable. Hence they have very less/no tendency to gain electron. That's why e^- affinity of grp 2nd element (nS^2), grp 15 element ($ns^2 np^3$) and inert gases ($ng^2 np^6$) have almost zero E.A.

Periodicity :-

→ In period



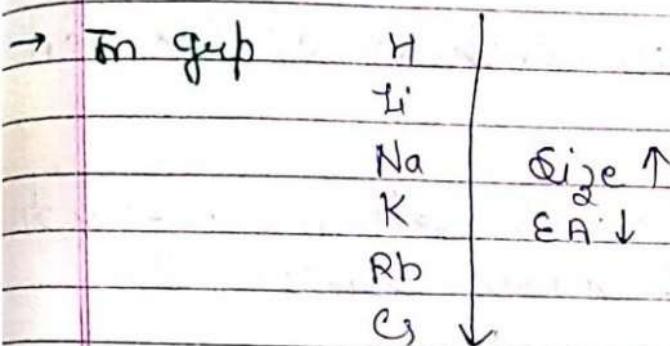
E.A order

$F > O > C > B > Li > N > Be$

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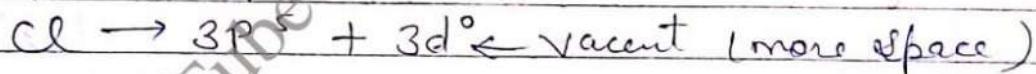
$\text{Na} > \text{Mg} : \text{Al} \quad \text{Si} > \text{P} \quad \text{S} \quad \text{Cl}$

$Z_{\text{eff}} \uparrow, \epsilon\cdot A \uparrow$



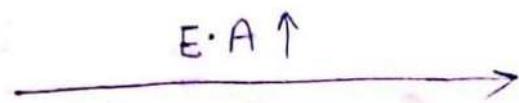
* Exceptions

- ① 2nd-period element have low $\epsilon\cdot A$ compare to 3rd-period element or Cl have higher $\epsilon\cdot A$ compare to fluorine

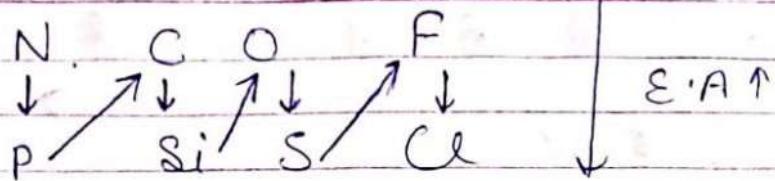


Due to small size of fluorine atom electron density is greater and incoming e^- feels more interelectronic repulsion that's why $\epsilon\cdot A$ is less.

Due to large size of chlorine atom e^- density is small and incoming e^- feels less electronic repulsion that's why Cl has highest $\epsilon\cdot A$ in periodic table.

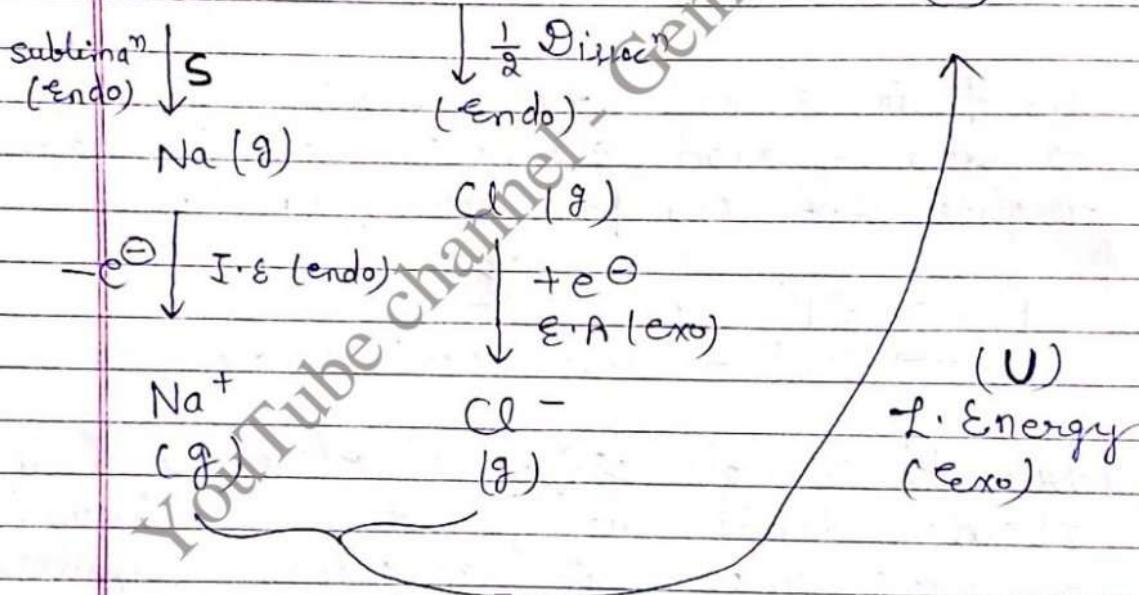
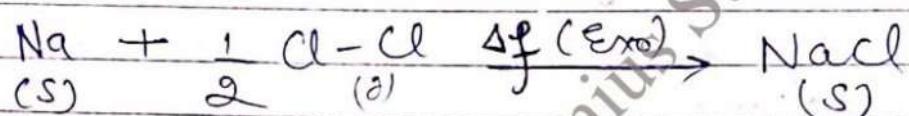


Date _____
Page _____



Method of determination of electron affinity :-

Electron affinity is determined by the help of Born - Haber cycle.



Acc to Hess law

$$\Delta f = S + I \cdot E + \frac{1}{2} D + E \cdot A + U$$

$$-\Delta f = S + I \cdot E + \frac{1}{2} D - E \cdot A - U$$

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Δf = Heat of formation

S = Sublimⁿ energy

D = Dissociⁿ energy

$E.A$ = Electron affinity

U = Lattice energy

Ques Calculate $E.A$ of I_2 with the help
of following data.
All energies are given in kcal/mole.

$$\Delta f(\text{NaI}) = -68.8$$

$$S(\text{Na}) = 25.9$$

$$D/2(I_2) = 25.5$$

$$I.P(\text{Na}) = 118.4$$

$$U(\text{NaI}) = 165.4$$

Solve $-68.8 = 25.9 + 118.4 + \underline{25.5} - E.A - 165.4$

$$E.A = 73.2 \text{ kJ/mol}$$

Electro Negativity

Tendency to attract shared electron towards itself by an atom in a molecule is known as Electronegativity.

It has no unit.

Factors affecting Electro negativity

$$① z_{\text{eff}} \quad \epsilon \cdot N \propto z_{\text{eff}}$$

$$② S.E \quad S.E \propto \frac{1}{\epsilon N}$$

$$③ \text{Size} \quad \epsilon \cdot N \propto \frac{1}{\text{Size}}$$

$$④ \% \text{ S character} \quad \epsilon \cdot N \propto \% \text{ S}$$

⑤ the oxidn state

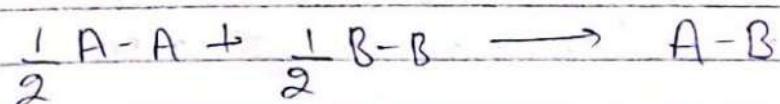
$$\begin{array}{c} C_{sp} > C_{sp^2} > C_{sp^3} \\ 2.5 > 2.75 > 3.25 \end{array}$$

Periodicity



Method of determination of ϵ^- negativity

① Pauling Scale



The Bond dissoc'n energy of A-B molecule
is higher than the mean of the
bond dissociation Energy of A-A

and B-B bond.

$$\Delta = E_{n-\sigma} - \frac{E_{A-A} + E_{B-B}}{2}$$

$E_{A-B} = B.E$ of A-B molecule in kcal
per mol

Δ = Resonance energy of A-B molecule

Pauling gives the following relation
b/w resonance energy and electro
negativity of p and B atom.

$$0.208 \sqrt{\Delta} = \chi_A - \chi_B$$

$$\Delta = 23.06 (\chi_A - \chi_B)^2$$

$$(\chi_A - \chi_B)^2 = 0.043 \Delta$$

E.N of some element on pauling scale

H
2.1

Li	Be	B	C	N	O	F
1	1.5	2	2.5	3	3.5	4
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3
K					Ba	
0.8					2.8	
Rb					I	
0.8					2.5	

C₆ 0.7

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② Mullikan scale

Acc to Mullikan solution the m

$$\rightarrow X_M = \frac{I \cdot P + E \cdot A}{2} \text{ (ev/atom)}$$

Electronegativity

relation b/w mullikan and pauling scale

$$X_P = \frac{X_M}{2.8}$$

$$X_P = \frac{I \cdot P + E \cdot A}{5.6} \text{ (ev/atom)}$$

$$X_P = \frac{I \cdot P + E \cdot A}{5.6 \times 23.06} \text{ (Kcal/mole)}$$

$$= \frac{I \cdot P + E \cdot A}{56 \times 96.49} \text{ (KJ/mole)}$$

$$= \frac{I \cdot P + E \cdot A}{540} \text{ (KJ/mole)}$$

③ Allred and Roschow scale

$$X_{AR} = 0.359 \frac{Z_{eff}}{r_c^2} + 0.744$$

r_c = covalent radius

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Application of Electronegativity

① Nature of Bond

- a) if $X_A - X_B = 0$ Bond is purely covalent and Non polar.

e.g. $\rightarrow H_2, Cl_2, F_2, N_2, O_2$

- b) if $X_A - X_B = \text{small}$

Bond is purely covalent e.g. $\rightarrow HCl$

- c) if $X_A - X_B = \text{very large}$

Bond is ionic e.g. $\rightarrow CsF$

② To calculate % ionic character in a bond

% ionic character is calculated by Henry Smith formula

$$\% IC = 16(\Delta EN) + 3.5 (\Delta EN)^2$$

- a) if $\Delta EN > 1.9$ $\% IC > \% CC$

- b) if $\Delta EN = 1.9$ $\% IC = \% CC = 50\%$

- c) if $\Delta EN < 1.9$ $\% IC < \% CC$

Author's Signature

③ // Nature of Oxides

$X_o = E \cdot N$ of oxygen Atom

$X_e = E \cdot N$ of any element

ⓐ $X_o - X_e > 2.3$ (Nature of oxide will be Basic)

ⓑ $X_o - X_e \approx 2.3$ (Amphoteric nature)

ⓒ $X_o - X_e < 2.3$ (Nature of oxide will be Acidic)

Amphoteric					
Ti_2O	BeO	B_2O_3	CO_2	N_2O_5	Acidic
Basic					
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl_2O_7
		Amphoteric			

$X_o - X_e \downarrow$, Acidic Nature \uparrow 

* Difference b/w orbit and orbital

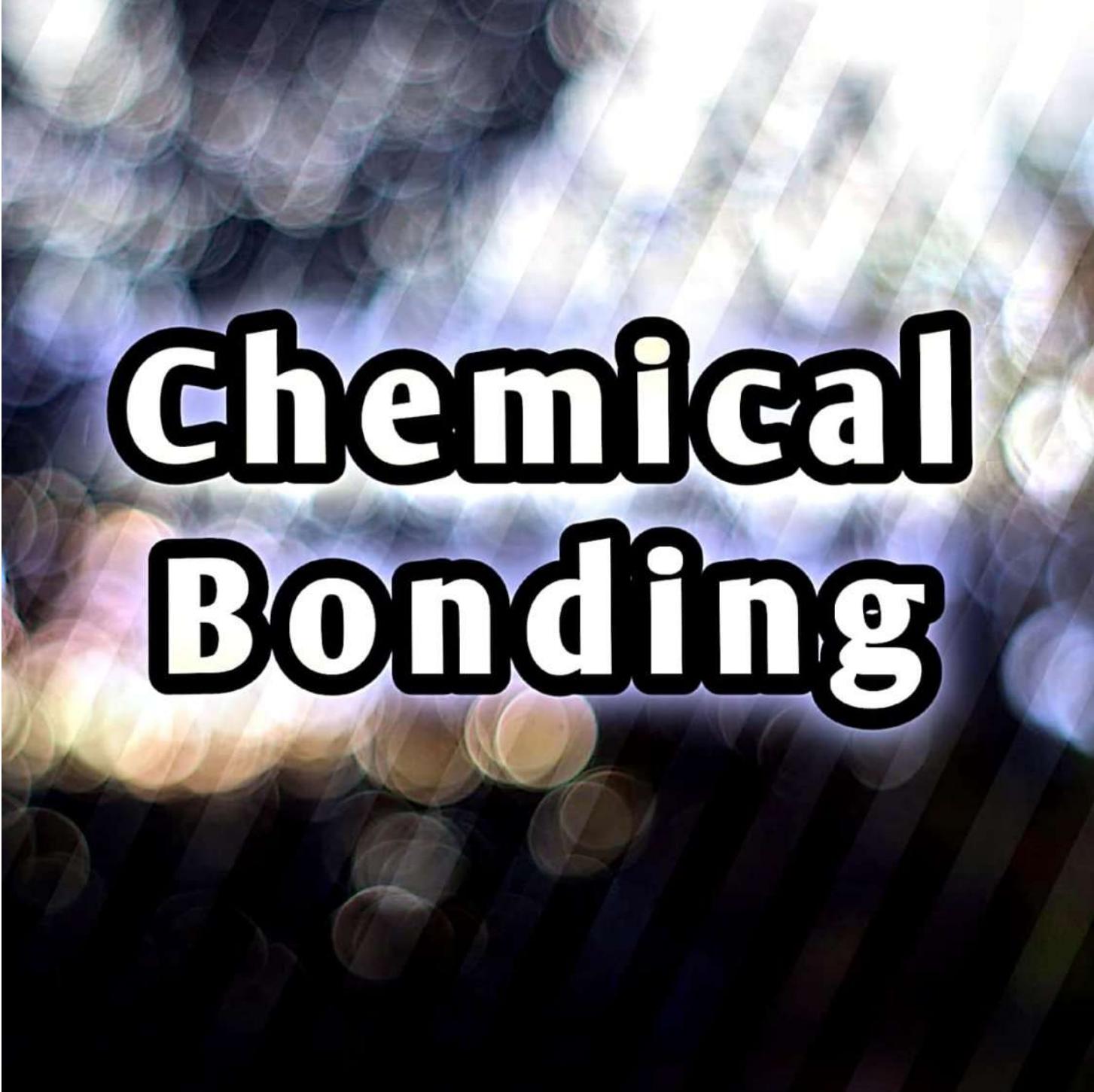
ORBIT

Orbit is well defined circular path around the nucleus in which an e^- revolves

ORBITAL

Orbital is a region in the space around the nucleus where probability of finding an e^- is maximum

Teacher's Signature



Chemical Bonding

CHEMICAL BONDING

Hybridisation → Defⁿ from organic

Rules of Hybridisation

- ① Orbitals of same atom participate in hybridisation.
- ② In hybridisation only those orbital participate which have very small difference of energy.
- ③ In hybridisation vacant, half filled and full filled orbital can participate.
- ④ No of hybrid orbital always equals to atomic orbitals, which participate in hybridisation.
- ⑤ Hybrid orbital forms a bond.
- ⑥ Hybrid orbital have definite geometry.
- * ⑦ Hybrid orbital are always directional in nature. Hence form stronger bond.

Orbitals which participate in hybrids"

Steric No.	Hyb.	Orbital	Geometry	B · A
2	SP	S + P _z	linear	180°
3	SP ²	S + P _x + P _y	trigonal planar	120°
4	SP ³	S + P _x + P _y + P _z	tetrahedral	109°28'
	d ³ S	d _{xy} + d _{yz} + d _{xz} + S	"	"
	dSP ²	d _{xz} ² y ² + S + P _x + P _y	Square planar	90°, 180°
5	SP ³ d	S + P _x + P _y + P _z + d _z ²	TBP	120°, 90°, 180°
	dSP ³	d _{xz} ² y ² + S + P _x + P _y + P _z	Square pyramidal	90°
6	SP ³ d ²	S + P _x + P _y + P _z + d _z ² + d _{xz} ² y ²	Octahedral	90°, 180°
	d ² SP ³	"	/ SP	"
7	SP ³ d ³	S + P _x + P _y + P _z + d _{xz} ² y ² + d _{xy} + d _z ²	Pentagonal BP	72°, 90°, 180°
	d ³ SP ³	"	"	"

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no l.p. \rightarrow Geometry,
with l.p. \rightarrow shape

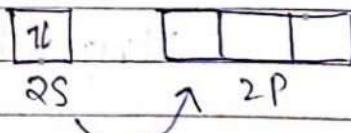
Data
Page

Steric No	Hyb.	B.P	L.P	Geometry / Shape
2	SP	2	0	linear
3	SP ²	3	0	Trigonal planar
		2	1	Vshape / Bent / angular
4	SP ³	4	0	Tetrahedral
		3	1	Pyramidal
		2	2	Vshape / " / "
5	SP ^{3d}	5	0	TBP sec-sew/
		4	1	Distorted Tetrahedral
		3	2	T shaped
		2	3	Linear
6	SP ^{3d} ²	6	0	Square BP / Octahedral
		5	1	Square pyramidal
		4	2	Square planar
7	SP ^{3d} ³	7	0	Pentagonal BP
		6	1	Distorted / Capped Octahed.
		5	2	Pentagonal planar

① SP Hybridization

Eg., H-C≡CH, BeCl₂

(G.s) Be



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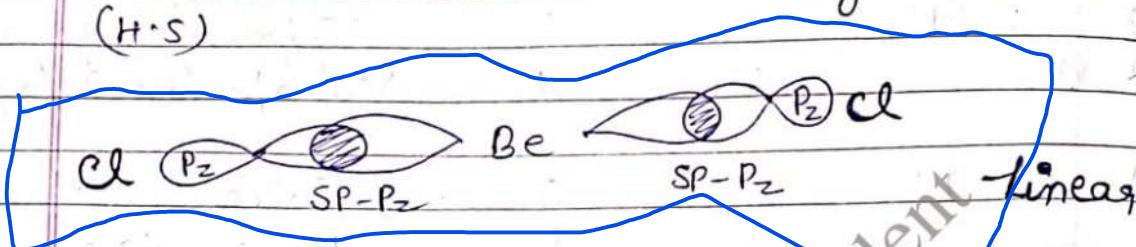
Be
(E.S)

[7]	[1]	[1]	[1]
-----	-----	-----	-----

Be
(H.S)

[1]	[1]
-----	-----

2 SP Hybrid orbital



② SP^2 Hybridization

Eg - $CH_2=CH_2$, BF_3

B
(G.S)

[7L]

2S

[1]	[1]	[1]
-----	-----	-----

2P

B
(E.S)

[1]

2S

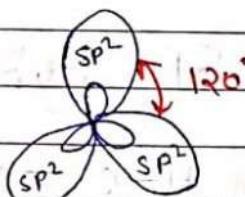
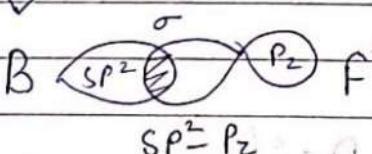
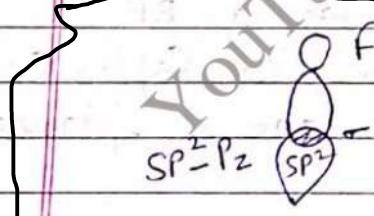
[1]	[1]	[1]
-----	-----	-----

2P

B (H.S)

[1]	[1]	[1]	[1]
-----	-----	-----	-----

3 SP^2 Hybrid orbital



Trigonal planar

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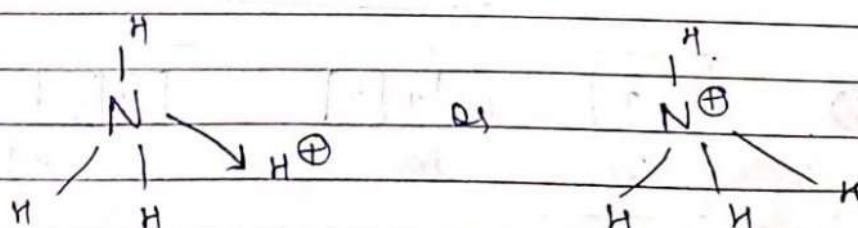
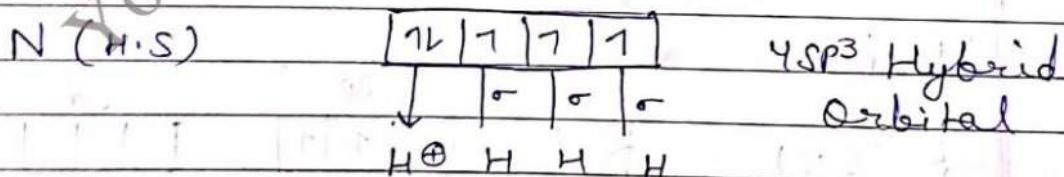
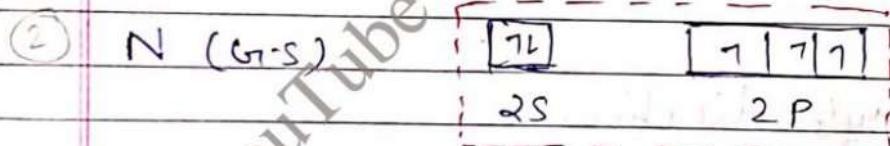
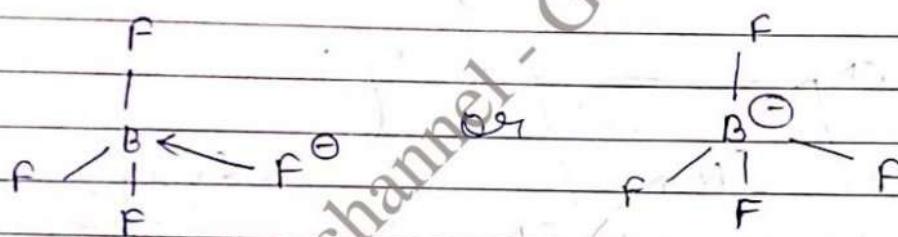
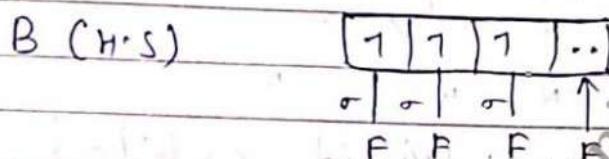
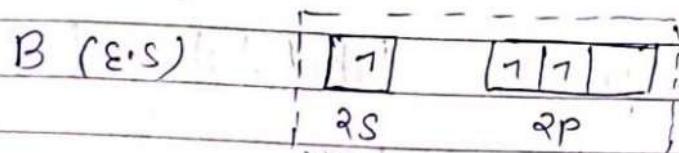
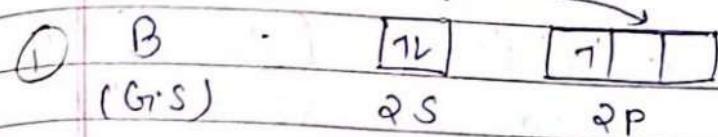
Scanned with CamScanner

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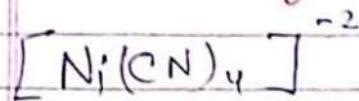
③ SP^3 Hybridisation

e.g. CH_4 , BF_4^- , NH_4^+

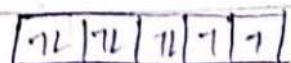


Teacher's Signature.....

④ dsp^2 Hybridisation



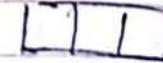
$^{28}Ni^{+2}$
(face state)



3d

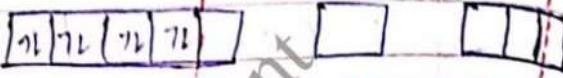


4s

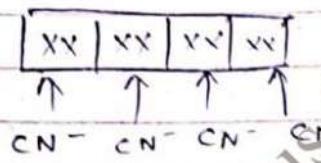


4p

Ni^{+2} (in complex)

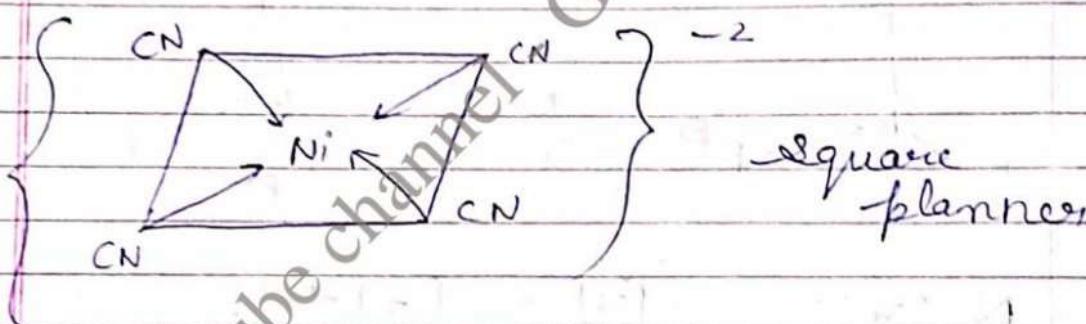


Ni^{+2}
(In H.S.)

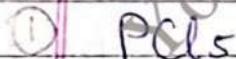


↑ ↑ ↑ ↑
CN - CN - CN - EN

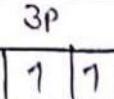
$4d\,sp^2$ hybrid orbital



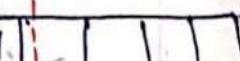
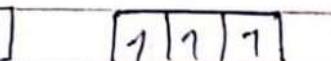
③ SP^3d Hybridisation



P (G.S.)



P (E.S.)



3s

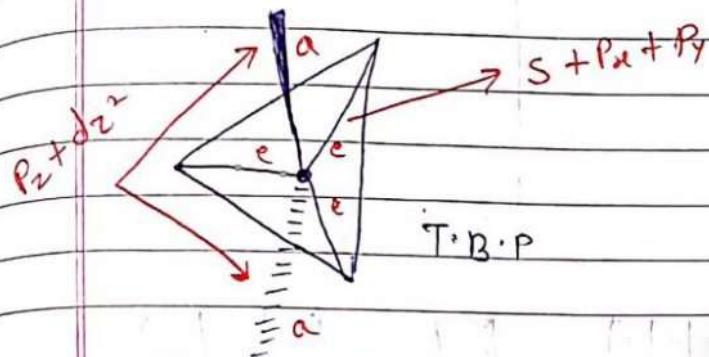
3p

3d

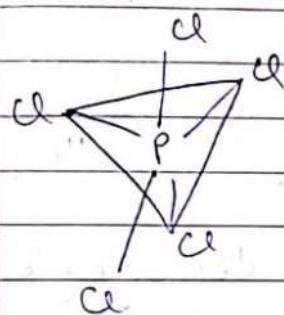
Teacher's Signature.....

P
(H.S)

1	1	1	1	1
---	---	---	---	---

5 sp^3d Hybrid orbital

B.A	No.
e-e	120°
a-e	90°
a-a	180°



axial P-Cl B.L > eq. P-Cl B.L
weaker bond strong bond

when we heat PCl_5
 $PCl_5 \rightarrow PCl_3 + Cl_2$

This Cl_2 is axial bond of PCl_5 .

(2) $[Fe(CO)_5]$ $^{26}Fe^0$

(in free state)

1L	1	1	1	1
----	---	---	---	---

1L

1	1
---	---

 $^{26}Fe^0$

(in complex)

1L	1L	1L	1L
----	----	----	----

1S

1P

 Fe^0

(in H.S)

xx	xx	xx	xx	xx
Co	Co	Co	Co	Co

5 dsp^3 hybrid orbital

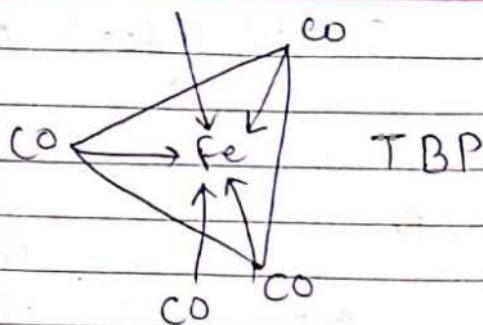
Teacher's Signature.....

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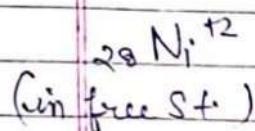
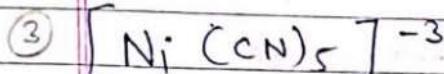
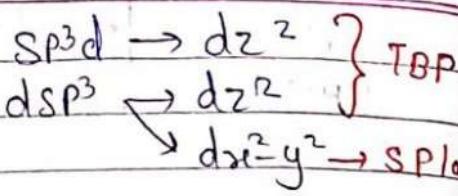
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CO



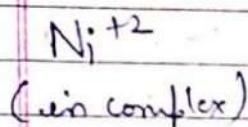
**



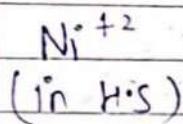
11	11	11	11
----	----	----	----

1	1	1
---	---	---

1	1	1
---	---	---



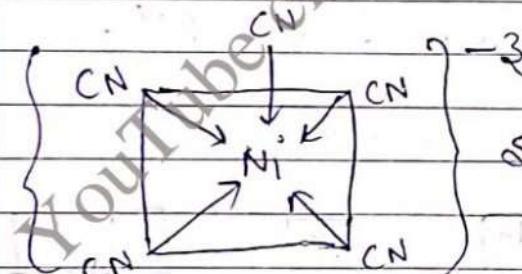
11	11	11	11	1	1	1	1
----	----	----	----	---	---	---	---



xx	xx	xx	xx	xx
----	----	----	----	----

s dSP^3 -hybrid orbital

CN⁻ CN⁻ CN⁻ CN⁻ CN⁻



Square pyramidal

⑥ SP^3d^2 hybridization



(G.S.)

S

11	11	11	11	11	11
----	----	----	----	----	----

3S

3P

3D

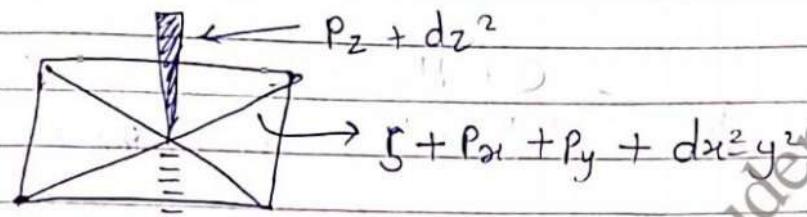
Teacher's Signature.....

S
(E.S)

1	1	1	1	1	1	1
---	---	---	---	---	---	---

SCH'S

1	1	1	1	1	1
---	---	---	---	---	---

6 SP^3d^2 Hybrid orbital

Square bipyramidal / octahedral

⑦ SP^3d^3 HybridizationIF₇

	5s	5p	5d
I (G.S)	1	1 1 1	1 1 1 1 1

I (E.S)

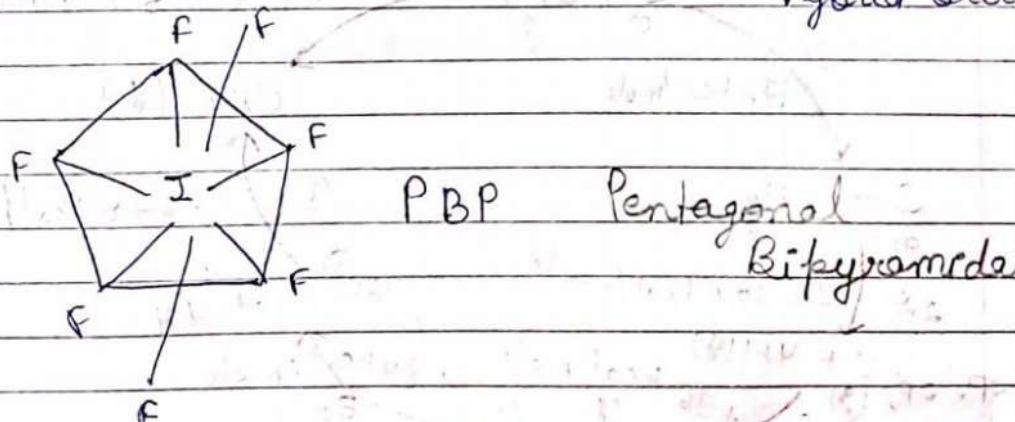
1	1 1 1	1 1 1 1	1
3s	3p	3d	

I (H.S)

1	1	1	1	1	1	1
---	---	---	---	---	---	---

7 SP^3d^3

Hybrid orbital



Teacher's Signature

Energy change cycle for CH_4 formⁿ (b)

It is obvious that due to directional overlapping of hybrid orbitals more amount of energy is liberated. Hence CH_4 is more stable than CH_2 .

**Valence shell e-pair repulsion Theory
VSEPR Theory**

Given by Gillespie and Nyholm.

This Theory is based on the fact that in a poly atomic molecule the direction of bond around the central atom depends upon the total no of e-pairs in its valence shell.

These e-pairs placed themselves in such a order that repulsion b/w them will be minⁿ. So that stability of molecule will be maxⁿ.

The main postulate of VSEPR theory are as follow:-

- ① The shape of a molecule depends upon no of bond pairs and lone pairs on central atom.

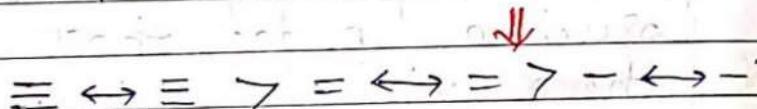


② if central atom have only bond pair then geometry of molecule will be regular.

Steric No.	No. of B.P	Hyb.	Geometry
2	2	SP	Linear
3	3	SP ²	Trigonal planar
4	4	SP ³	Tetrahedral
5	5	SP ³ d	TBP
6	6	SP ³ d ²	SBP
7	7	SP ³ d ³	PBP

if central atom have d.p as well as B.P
 ③ then due to repulsion geometry becomes irregular.

Order of repulsion will be following



90° > 120° > 180° repulsion angle
 max^m x-A

④ When d.p are present then B.A are small than predicted.

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B.P I.P B.A

Shape

CH_4

4

O

$109^\circ 5'$

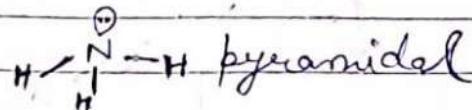
Tetrahedral

NH_3

3

I

107°

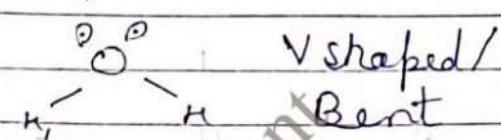


H_2O

2

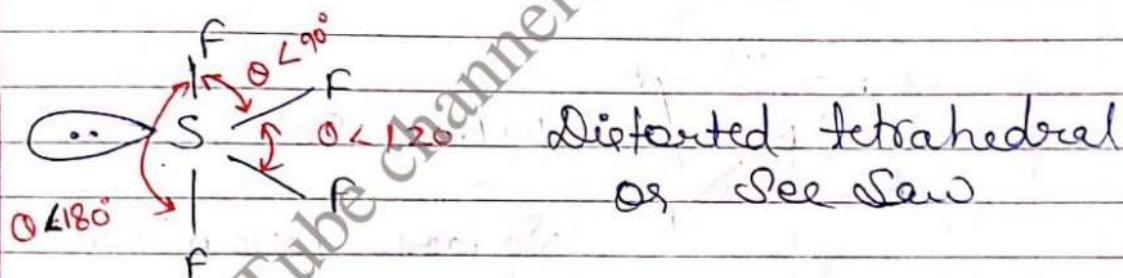
2

105°

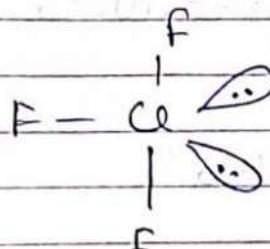


(5) I.P and double bond occupy more space than single bond. i.e. equatorial posn in trigonal bipyramidal shape.

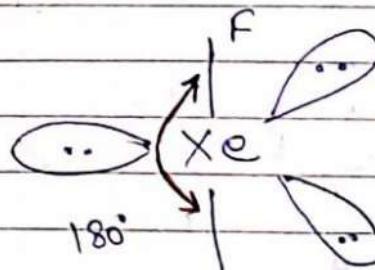
(a) :SF₄ 4 B.P + 1 l.p

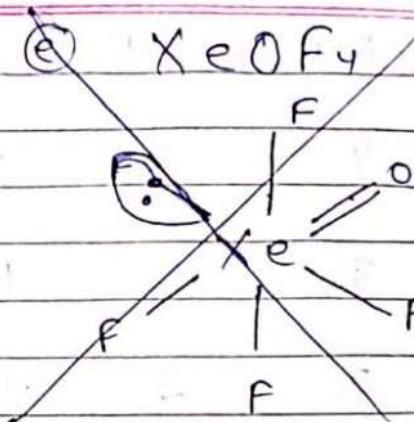
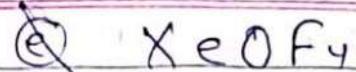
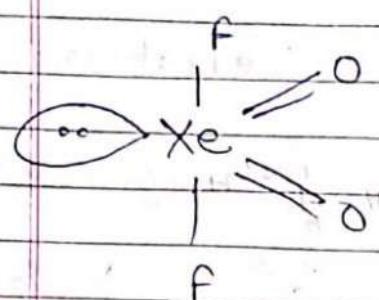
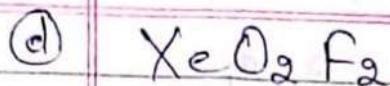


(b) :ClF₃

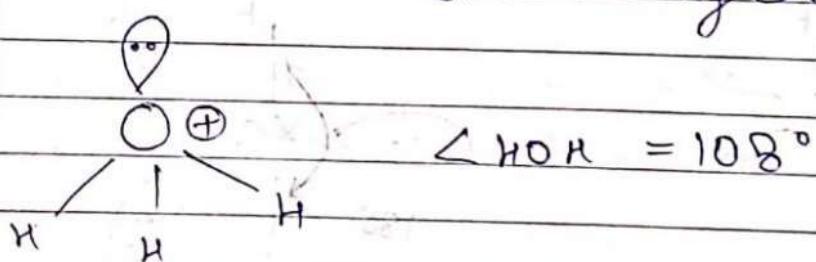
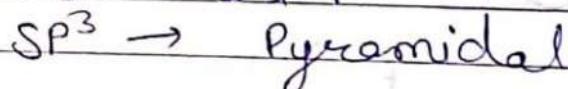
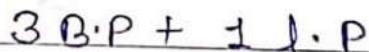
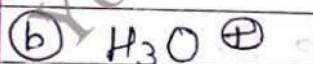
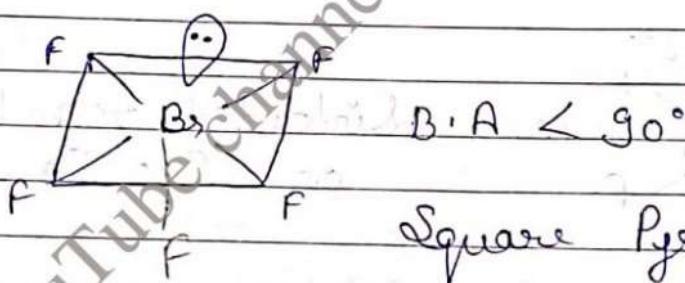
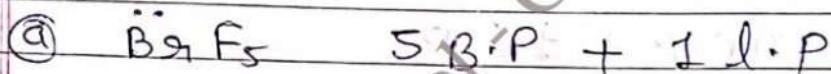


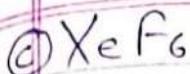
(c) :XeF₄





(f) if all sides are equal then one l.p can be placed anywhere
but if 2 l.p are present then they must be transed (180°) to each other.

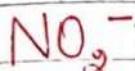
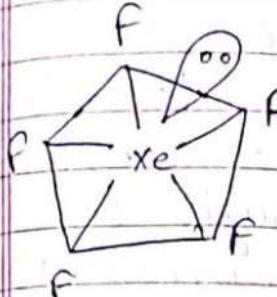




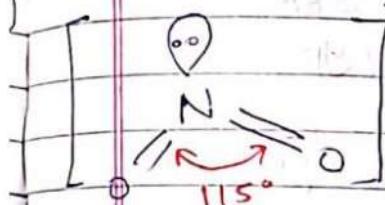
G.B.P + 2.l.p.

SP^3d^3

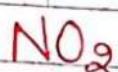
\rightarrow Capped / distorted
Octahedral



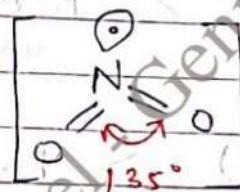
SP^2



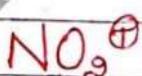
V shaped



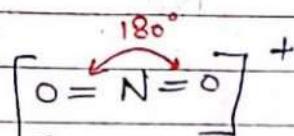
SP^2



bent

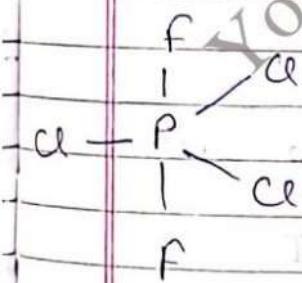


SP



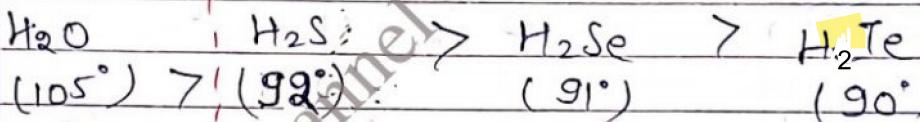
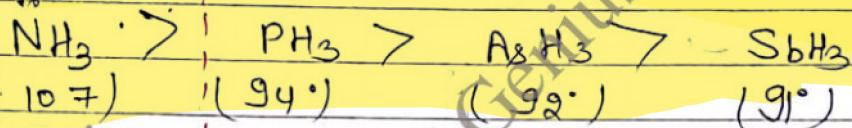
linear

Ques Draw the str of PCl_3F_2 on the basis of VSEPR Theory?



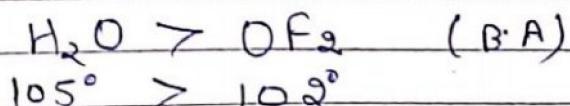
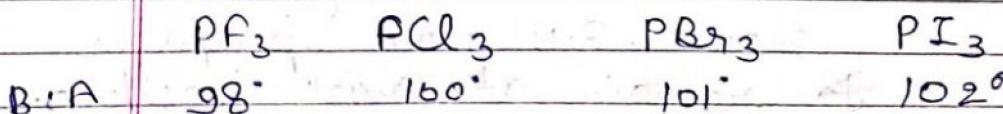
Acc to VSEPR theory more e.N atom prefers to remain where less space is available i.e. in SP^3d^3 hybridization
more e.N atom prefer to remain at axial position.

★ if central atom belongs to 3rd period or below in the periodic table then lone pair will remain in stereochemically inactive s orbital and bonding will take place through p orbital and B.A becomes approx. 90° if the E.N of substituent is less than or equal to 2.5.



In these compound hybrid. does not take place bond made by pure s & p orbital acc to Bent's rule.

$B \cdot A \propto$ E.N. of surrounding atom



Teacher's Signature _____

Molecular Orbital Theory

proposed by → Hund and Mulliken

This theory is based on the fact that e⁻ behave equally in atom as well as in molecule.

In atom e⁻ is attracted by one nucleus of that atom but in molecule e⁻ attracted by more than one nucleus of atoms.

Acc to this theory atomic orbital combine to form new molecular orbital.

Linear combination of Atomic orbital Method

When atomic orbital combine with each other their resulting wave function may be equal to addⁿ or subⁿ corresponding of atomic orbital.

Atom A → have wave funcⁿ Ψ_A

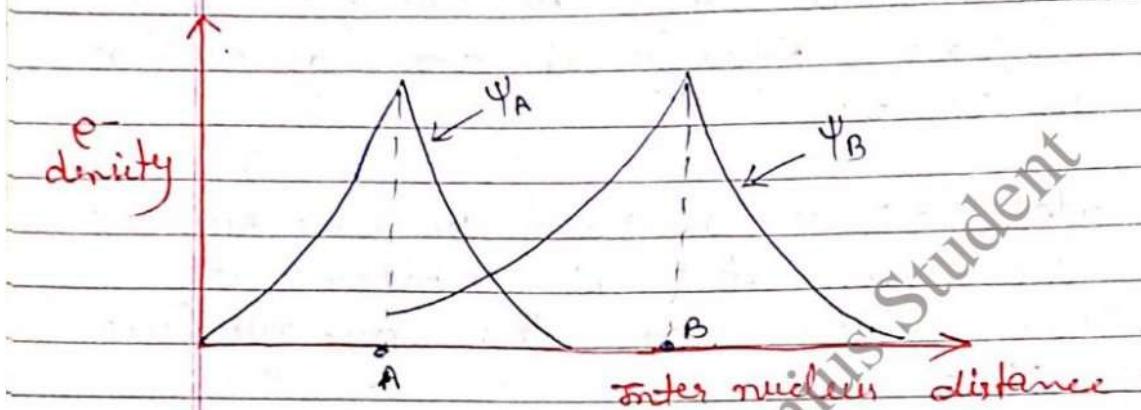
Atom B → have wave funcⁿ Ψ_B

Case I → when both wave funcⁿ have same sign; e overlap in same phase

In this situation e⁻ density b/w nuclei of both atoms increase due to attract.

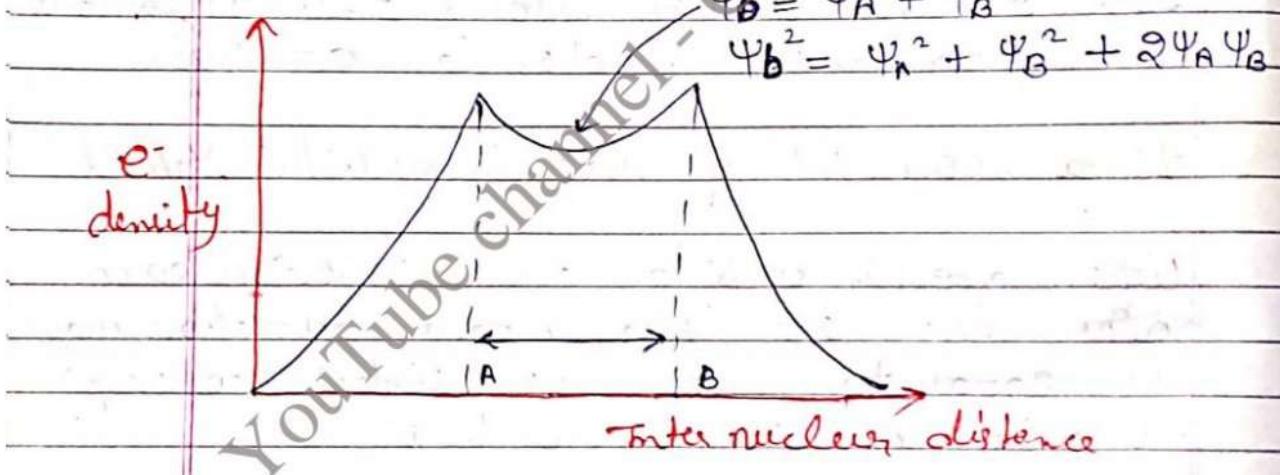
Teacher's Signature

Due to attrⁿ energy of resulting wave funⁿ decreases and system gets stability.
 Due to this type of O.P bonding molecular orbital formed. over-lapping



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

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

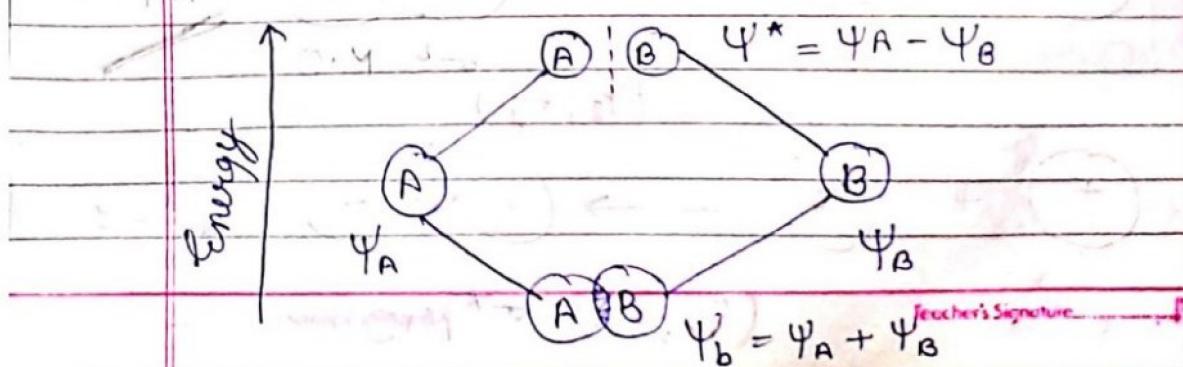
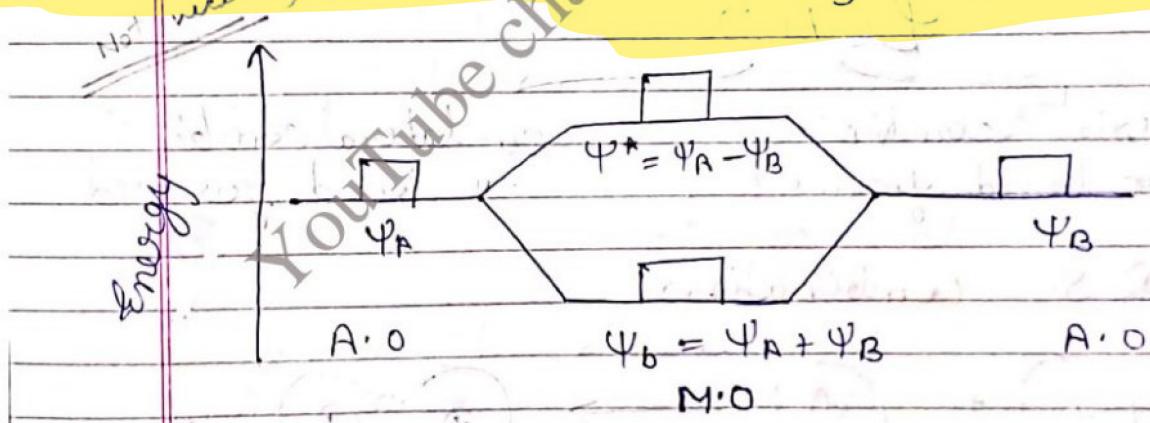
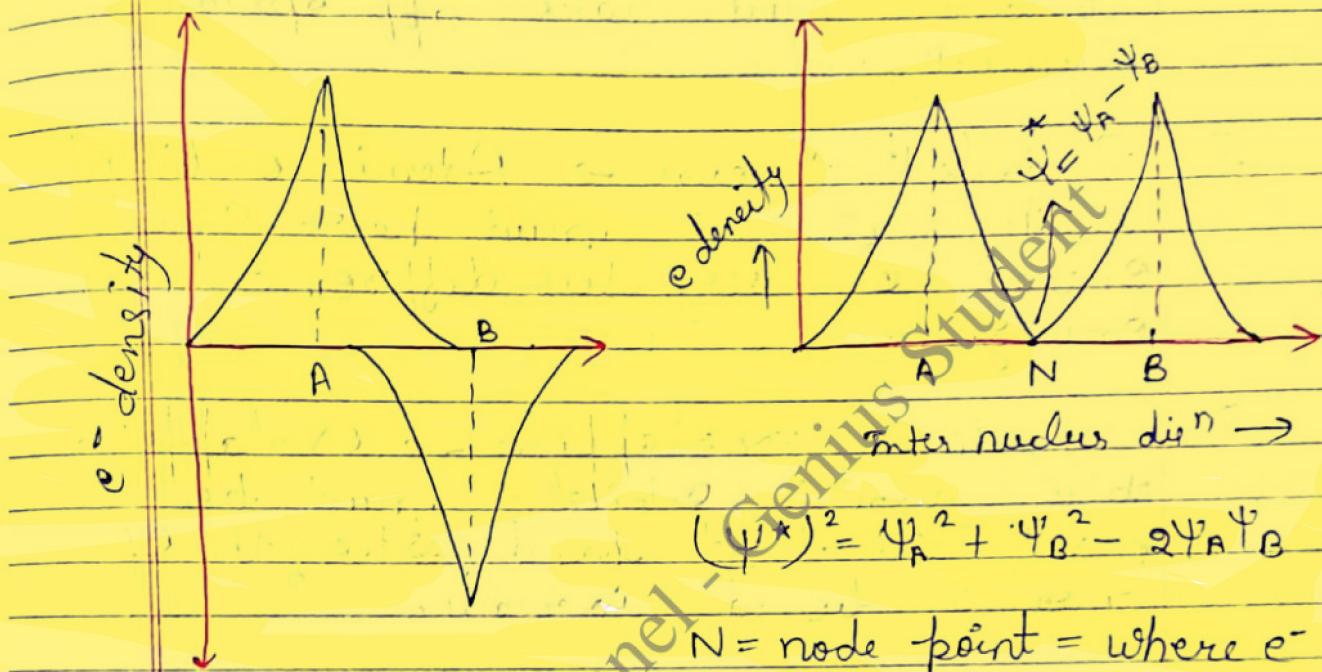


Case 2 → when both wave funⁿ have opp. sign i.e. overlap in opp. phase.

In this situation e- density b/w nuclei of both atom less due to repulⁿ. Due to repulⁿ, energy of resulting wave funⁿ increases and system

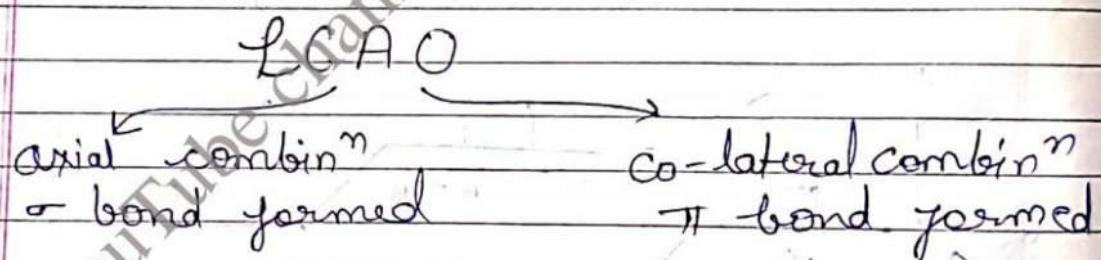
Teacher's Signature _____

un
gets ~~destabilized~~ stabilized. Due to this type of overlapping Anti bonding molecular orbital formed.

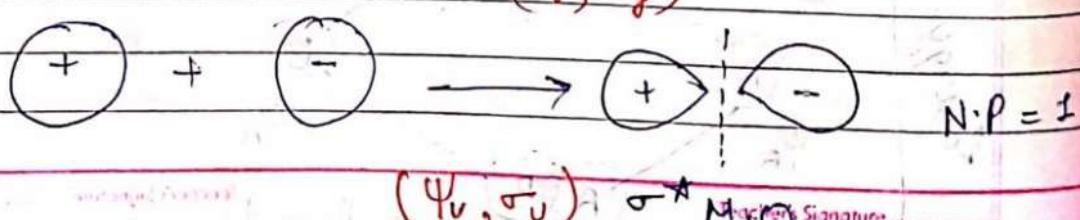
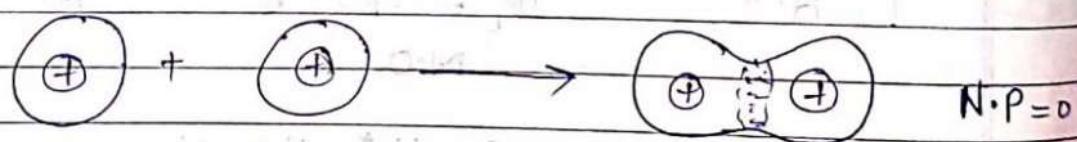


Rules for overlapping / Combination

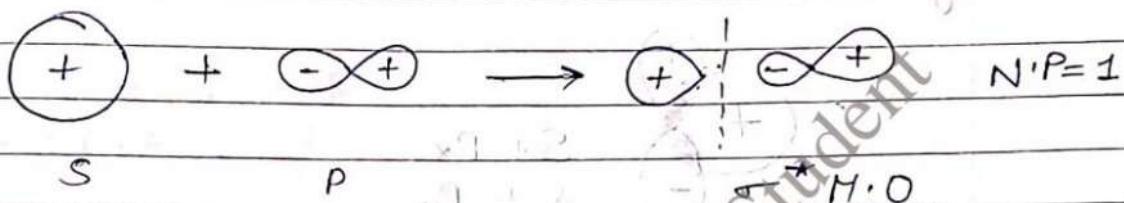
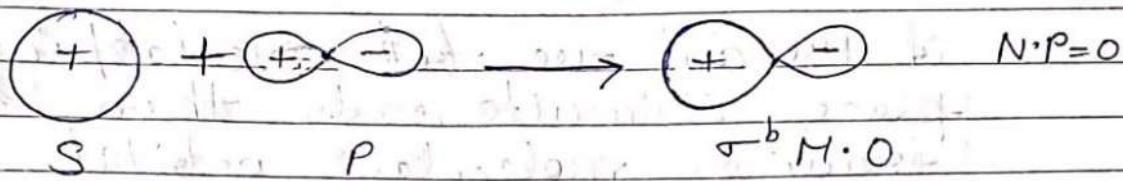
- ① Same Symmetry \rightarrow Atomic orbital which combine must have appropriate symmetry.
- ② Equivalent Energy \rightarrow Atomic orbital which combine must have equal energy or very less difference b/w energies.
- ③ Maximum overlapping \rightarrow overlapping b/w atomic orbital must be max^m so that bond strength of covalent bond increases.



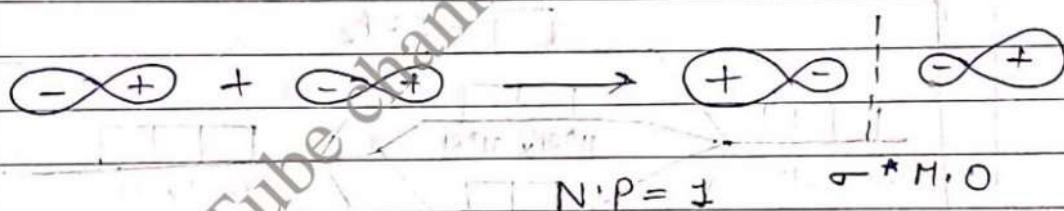
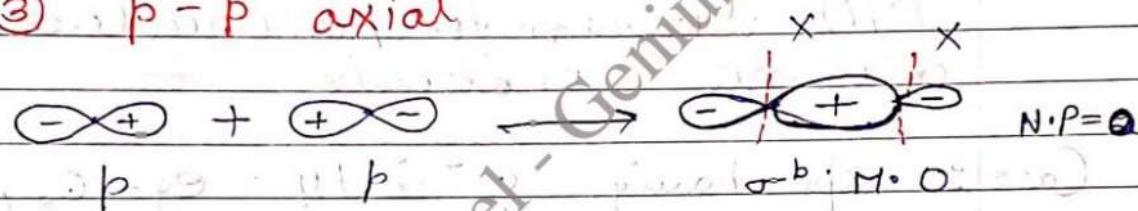
① S-S combination



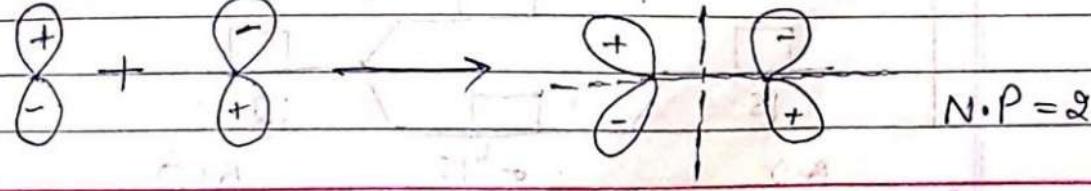
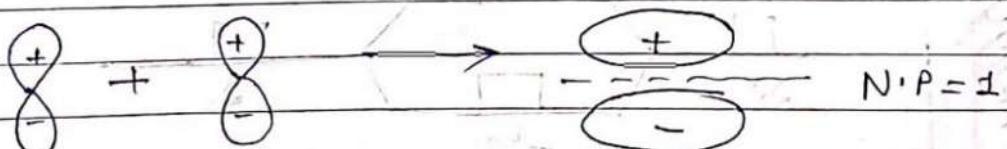
② S-P combination



③ p-p axial



④ p-p collateral overlapping



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$\pi M.O.$

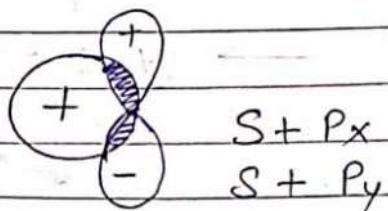
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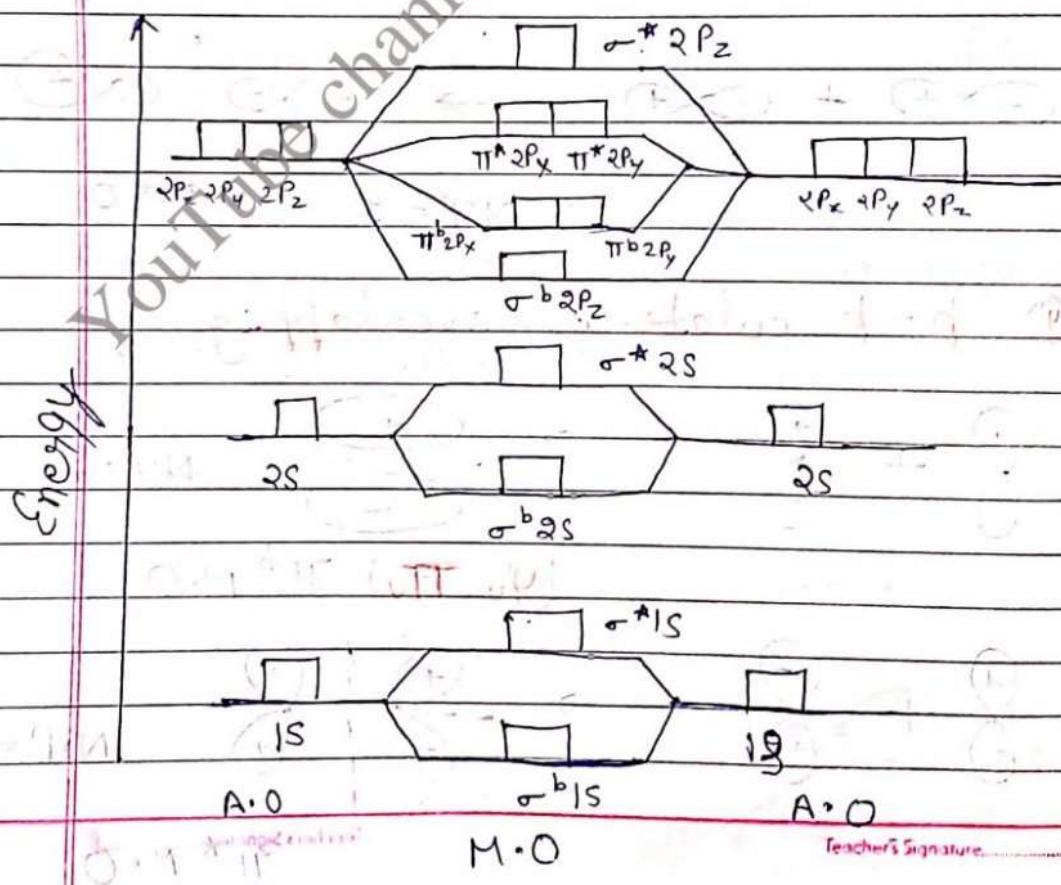
Non Bonding Molecular Orbital

If two and -ve both overlapping take place simultaneously then non-bonding molecular orbital is formed.



MO Diagram for Homonuclear diatomic molecule

Case 1 s_{1s} having c = 7.14 eg → O₂, F₂, N₂



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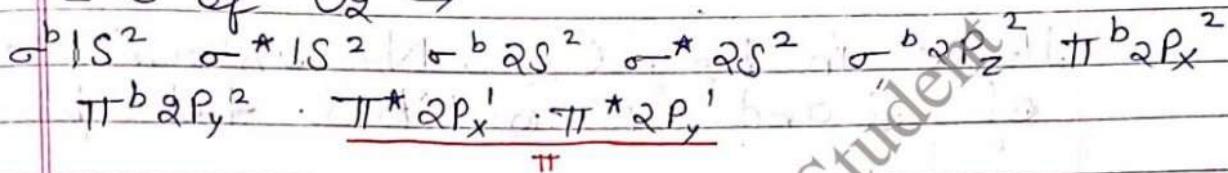
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$$B.O = \frac{1}{2} (N_B - N_A)$$

N_B = No. of e⁻'s in B.M.O's.

N_A = No. of e⁻'s in A.B.M.O's

E.C of O₂ →



$$B.O = \frac{1}{2} (6 - 2) = 2$$

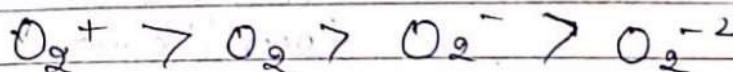
$\textcircled{O} \equiv \textcircled{O}$ paramagnetic

All e⁻'s are paired in M.O's then
s.p.s. will be Diamagnetic.

If all e⁻'s are unpaired in M.O's
then s.p.s. will be paramagnetic

B.O	O ₂	→ 2
	O ₂ ⁻	→ 1.5
	O ₂ ⁺	→ 2.5
	O ₂ ⁻²	→ 1

Stability Order



B.O ∝ B.S

∝ B.E

∝ Stability

B.O ∝ 1

B.L

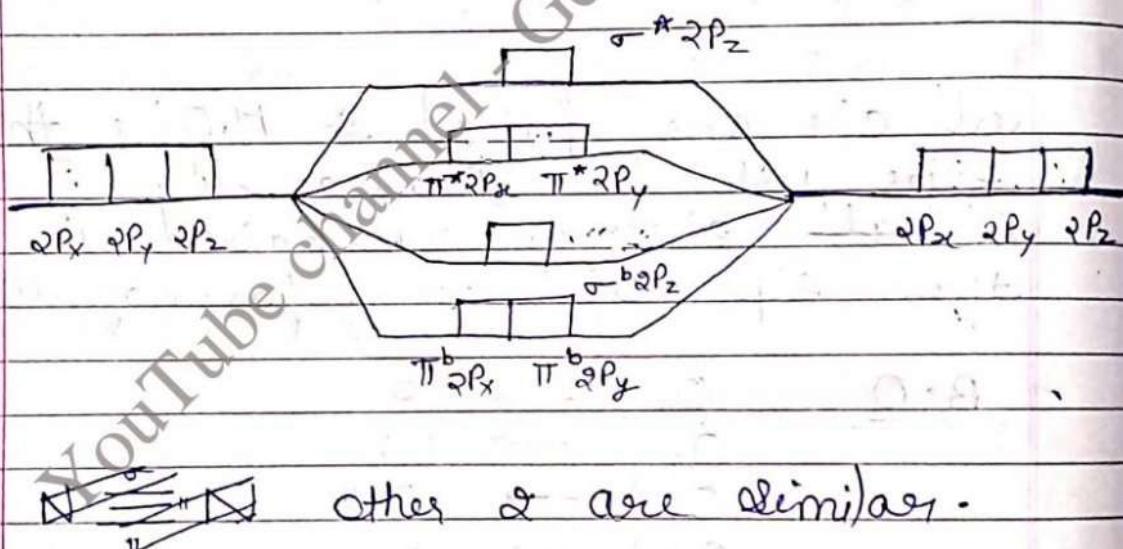
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Case 2 atoms having $e^- \leq 14$ e.g. $\text{B}_2, \text{C}_2, \text{N}_2$

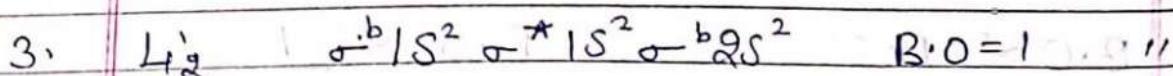
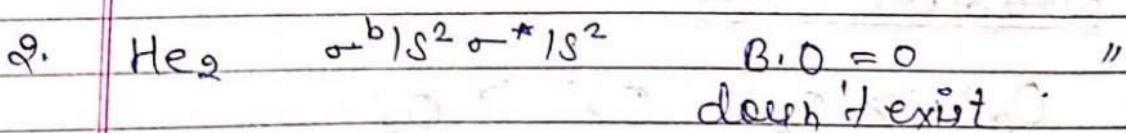
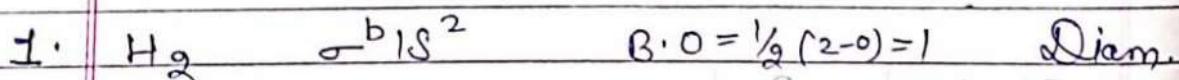
In 2nd row element upto Nitrogen
There is very less energy difference b/w $2s$ and $2p$ orbital.

Hence in $\text{B}_2, \text{C}_2, \text{N}_2$ intermixing of s and p orbital take place.

Due to which energy of π^b & σ^b & $\sigma^b 2p$.



other 2 are similar.



4. Be_2 $\sigma^b 1s^2 \sigma^* 1s^2 \sigma^b 2s^2 \sigma^* 2s^2$ B-O=0 not exist
5. B_2 Be_2 $\pi^b 2p_x^1 \pi^b 2p_y^1$ B-O=1 Para $\text{B} \equiv \text{B}$
6. C_2 Be_2 $\pi^b 2p_x^2 \pi^b 2p_y^2$ B-O=2 Dia
(In vapour phase) $\text{C} \equiv \text{C}$
7. N_2 C_2 $\sigma^b 2p_z^2$ B-O=3 Dia $\text{N} \equiv \text{N}$
8. O_2 $\text{O} \equiv \text{O}$ B-O=2 Para

Gerade orbital :-

The molecular orbital which have even no nodal plane are called Gerade molecular orbitals.

Ungerade Molecular Orbital :-

The molecular orbitals which have odd no. of nodal plane.

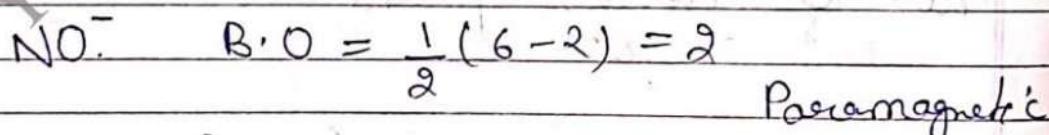
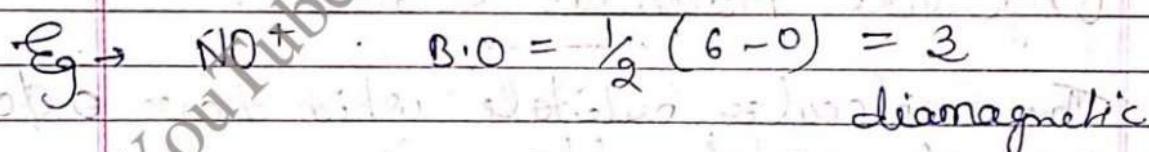
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MO Diagram of Hetero-nuclear diatomic molecule

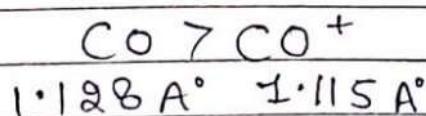
In Hetero nucleus diatomic molecule atomic orbitals of both atoms have different energy of atomic orbitals.

Atomic orbitals of more e⁻ve element have lower energy due to more Z_{eff}.

In MO Diagram BMO are closer to the atomic orbital of more e⁻ve element while anti-bonding molecular orbitals are closer to atomic orbital of less e⁻ve element.



* C.O B.F Order



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$\sigma^* 2P_2$

$\begin{array}{|c|c|c|} \hline 1 & 1 & 1 \\ \hline \end{array}$
 $\sigma P_x \sigma P_y \sigma P_z$

$\begin{array}{|c|} \hline 1 \\ \hline \end{array}$
 $\pi^* 2P_x \pi^* 2P_y$

$\begin{array}{|c|c|} \hline 1 & 1 \\ \hline \end{array}$
 $\pi^b 2P_x \pi^b 2P_y$

$\begin{array}{|c|c|c|} \hline 1 & 1 & 1 \\ \hline \end{array}$
 $2P_x \sigma P_y 2P_z$

Energy

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
2S

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
 $\sigma^* 2S$

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
 $\sigma b 2S$

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
2S

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
1S

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
 $\sigma^* 1S$

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
1S

N

$\begin{array}{|c|} \hline 1L \\ \hline \end{array}$
 $\sigma b 1S$

O

M.O. Diagram of NO

$$B.O = \frac{1}{2} (6 - 1) = 2.5$$

paramagnetic in nature.

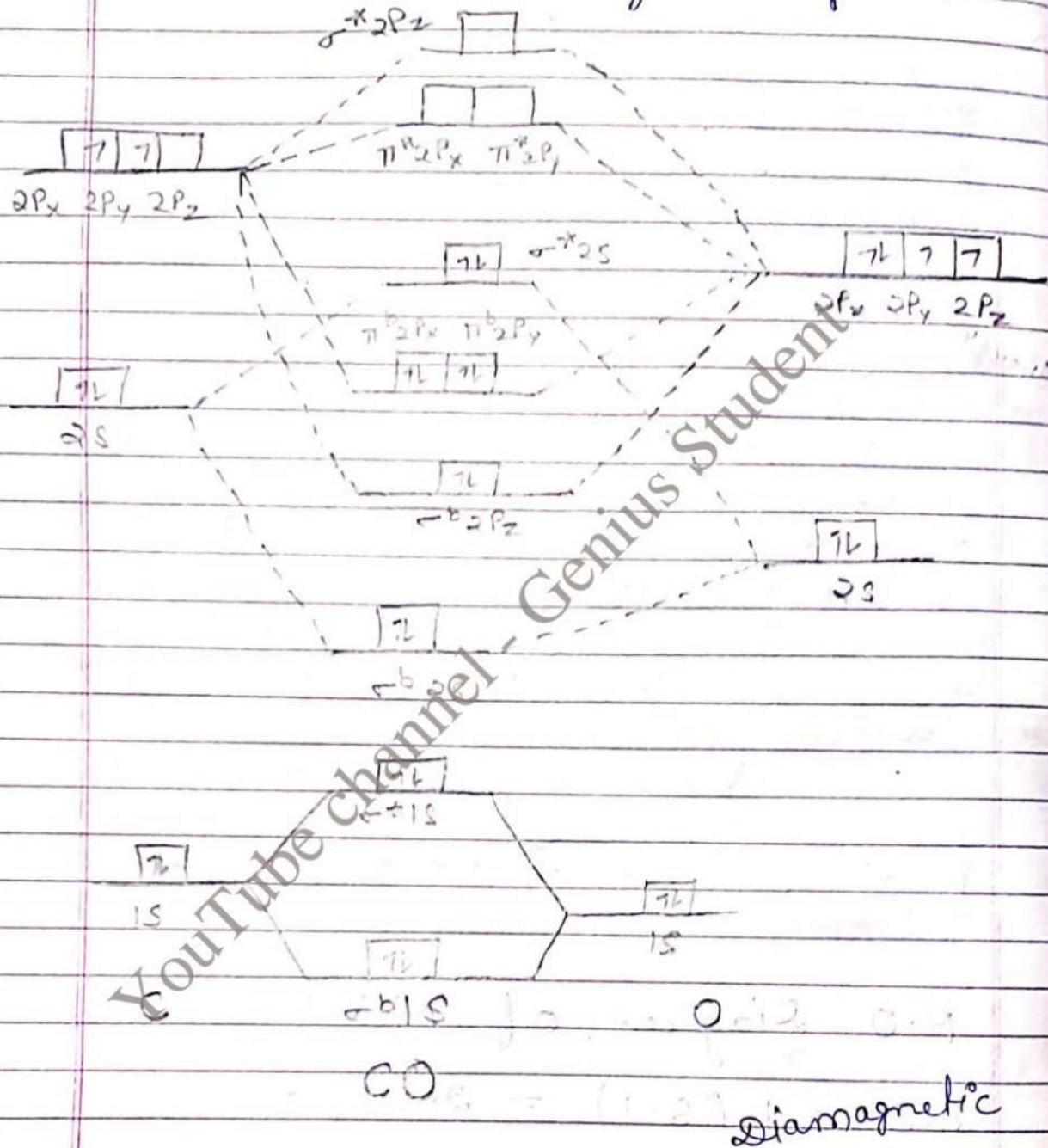
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Molecular Orbital diagrams of CO



$$CO \rightarrow B.O = \frac{1}{2}(8-2) = 3 \quad C \equiv \overset{\pi}{\text{O}}$$

$$CO^+ \rightarrow B.O = \frac{1}{2}(8-1) = 3.5$$

Paramagnetic

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Dipole Moment

It is defined as the product of magnitude of charge present on any atom and internuclear distance of atoms.

$$\mu = q \times d \quad \text{unit} \rightarrow \text{Debye}$$

$$1 \text{ D} = 10^{-18} \text{ esu} \cdot \text{cm}$$

$$1 \text{ D} = 3 \times 10^{-30} \text{ C} \cdot \text{m} \quad \text{S.I}$$

Dipole moment is a vector quantity which have direction from less electro-negative to more e- -ve or central atom to lone pair.

Calculation of Dipole Moment

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

$$\theta = 0^\circ \quad \cos 0^\circ = +1$$

$$|\mu_R| = \mu_1 + \mu_2 (\text{max})$$

$$\theta = 180^\circ \quad \mu_R = \mu_1 - \mu_2 \quad (\text{min})$$

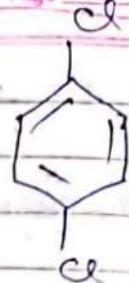
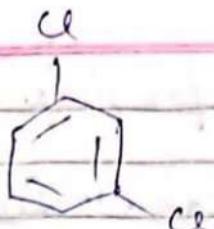
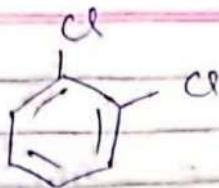
$$\theta \uparrow, \mu_R \downarrow$$

$$\text{if } \mu_1 = \mu_2$$

$$\mu_R = \sqrt{2\mu^2 + 2\mu^2 \cos\theta}$$

$$= 2\mu \cos \theta / 2$$

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$$\theta = 60^\circ$$

$$\theta = 120^\circ$$

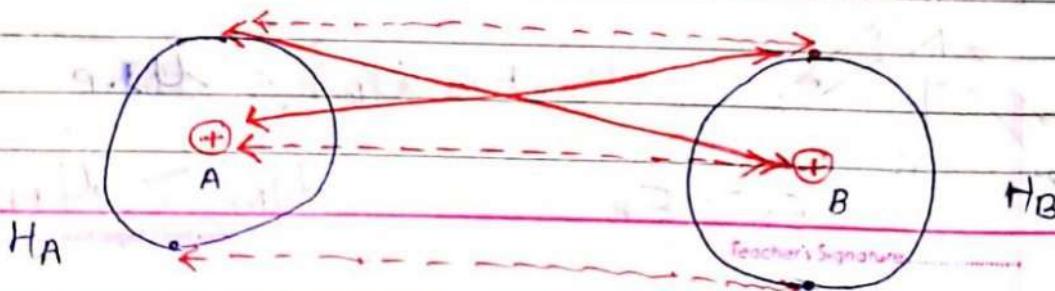
$$\theta = 180^\circ$$

$$M_R = 0$$

$$\theta > M > P$$

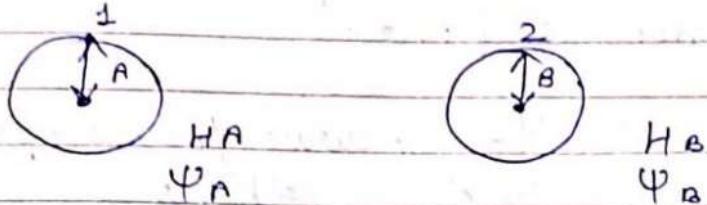
Ques Explain Valence bond Theory on the basis of bond formation b/w two hydrogen atoms.

Solve According to VBT bond form" take place b/w 2 atoms due to pairing of unpaired electron of opposite spins and this electron pair remains localised b/w these 2 atoms and does not participate in bond formation with another atoms when 2 hydrogen atoms are present at infinite distance then this electron is attracted only by their nucleus but when they comes close to each other electron of one atom is attracted by the nucleus of other atom.



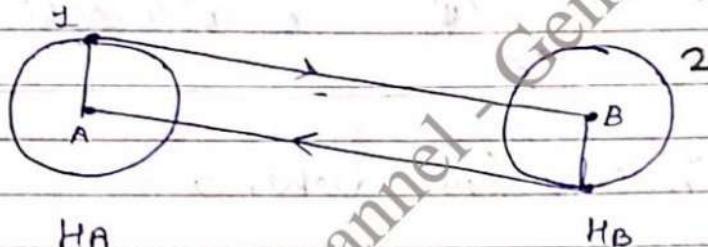
\longleftrightarrow Repulsive force
 \longleftrightarrow Attractive force

- When H atoms are at infinite distance



$$\Psi_I = \Psi_A(1) \Psi_B(2)$$

- When H atoms are at finite distance



$$\Psi_{II} = \Psi_A(2) \Psi_B(1)$$

Now atomic orbitals of both H atom combines and formed two new orbitals and there wave func" given by following equations.

$$\Psi_+ = c_1 \Psi_I + c_2 \Psi_{II} \quad \uparrow \quad \uparrow$$

$$\Psi_- = c_1 \Psi_I - c_2 \Psi_{II} \quad \uparrow \quad \downarrow$$

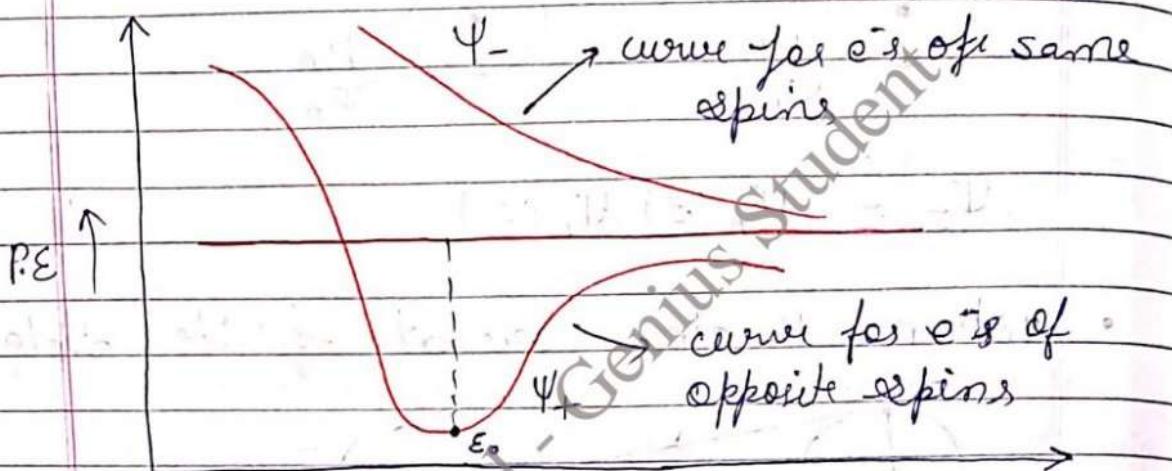
$$\Psi_+ = c_1 \Psi_A(1) \Psi_B(2) + c_2 \Psi_A(2) \Psi_B(1)$$

$$\Psi_- = c_1 \Psi_A(1) \Psi_B(2) - c_2 \Psi_A(2) \Psi_B(1)$$

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here Ψ_+ shows Attrac' b/w e's of opposite spins

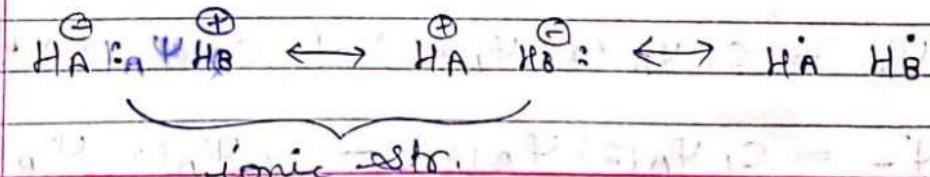
here Ψ_- shows repulsion b/w e's of same spins.



Intermolecular distance \rightarrow

Thus bond energy and bond length calculated by the help of Ψ_+ for H_2 molecule are 302 KJ/mole and 0.80 \AA respectiv. which are not matched with theoretical values.

Pauling explain the concept of resonance. acc to him any instant deln electrons can be present at a single atom.



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Now by including S.E and other effect of B.E and B.L for H_2 molecule are 430 KJ/mole and 0.74 \AA which are comparable to real values.

Directional character of covalent bond

Covalent bond is directional in nature. Pauling and Slater give some sugg's for covalent bond formation.

- ① Covalent bond is formed by overlapping of atomic orbitals.

Extent of overlapping \propto strength of C.B
(covalent bond)

- ② Orbitals approach to each other from the direction in which max^m overlapping can take place.
- ③ Dirⁿ of overlapping will be dirⁿ of covalent bond.

Types of Overlapping

Overlapping

Axial

\leftrightarrow take place at INA
 σ bond form

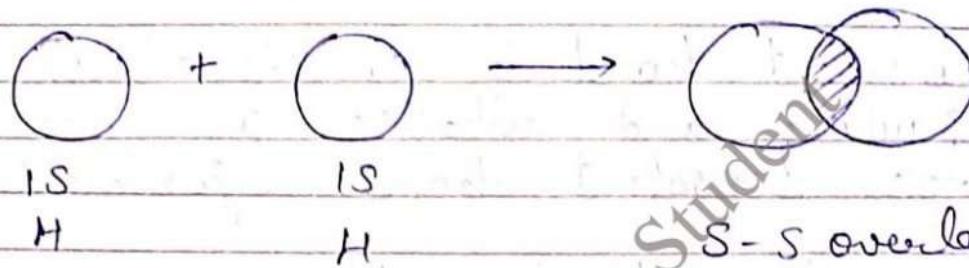
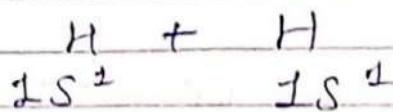
C_{lateral}

it take \perp to INA
 π bond form

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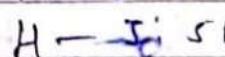
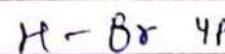
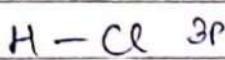
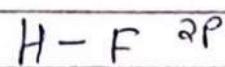
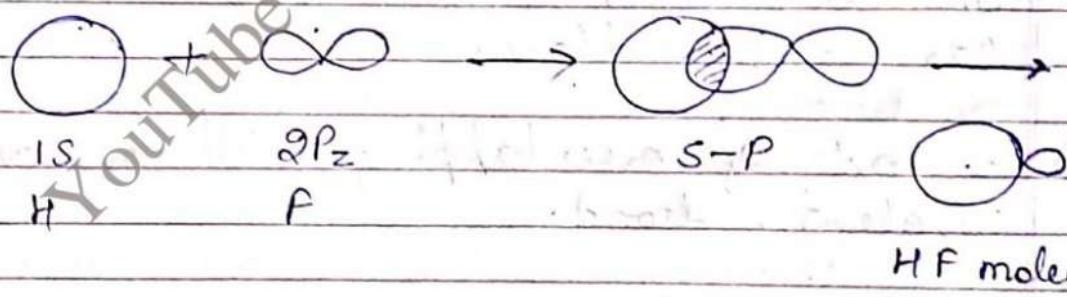
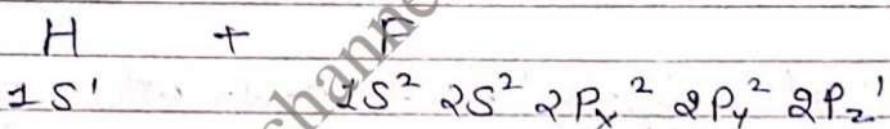
1. S-S overlapping :-

formⁿ of H₂ molecule



2. S-P overlapping

formⁿ of HX molecule



Size ↑

Extent of overlapping ↓

B.S ↓

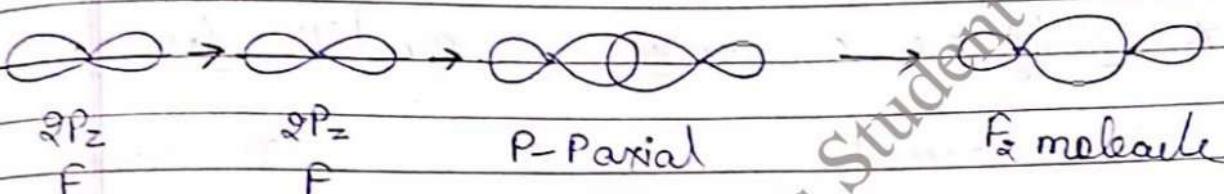
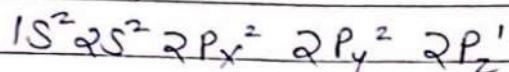
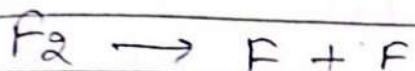
B.E ↓

B.L ↑

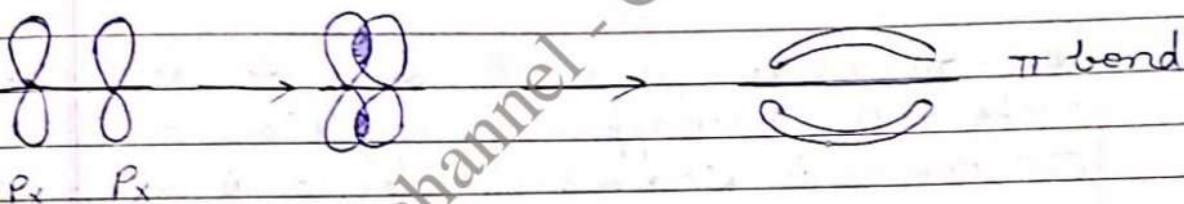
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3. P-P axial overlapping :-

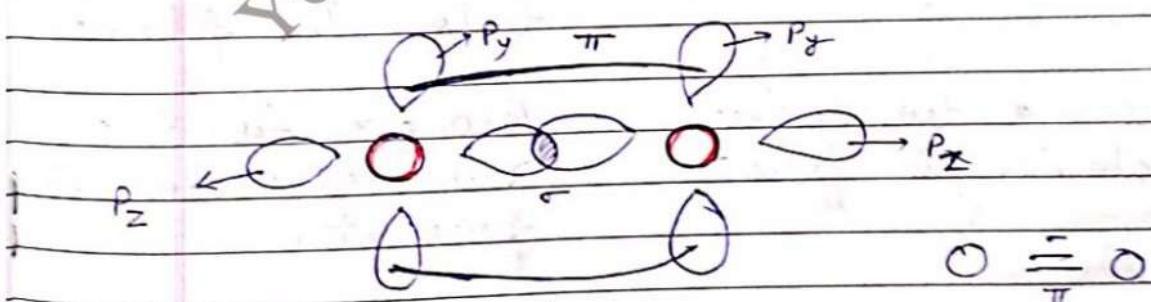
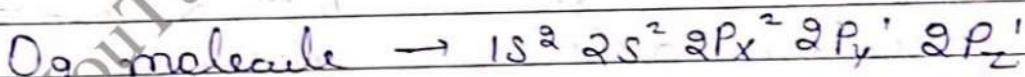
formⁿ of X₂ Molecule.



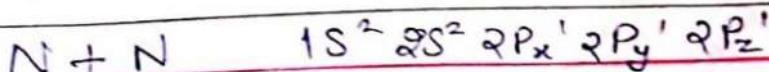
4. P-P lateral overlapping :-



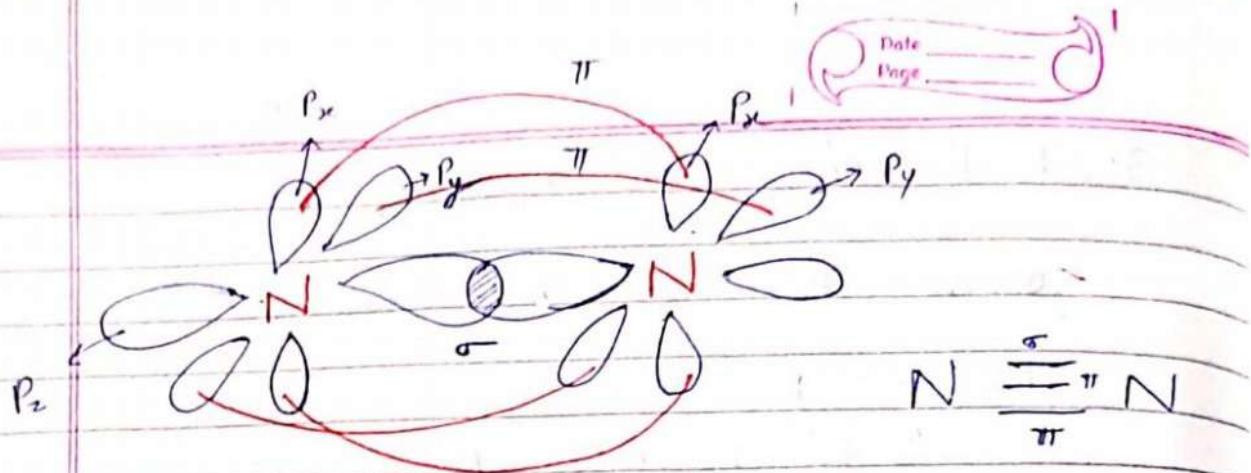
(a) formⁿ of O₂ molecule



(b) formⁿ of N₂ molecule



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* Difference b/w σ and π bond

σ bond

It is formed due to axial overlapping

Due to more extent of overlapping
 σ bond is stronger.

Whole e⁻ cloud is present at inter nucleic axis.

Along σ bond free rotation is present.

π bond

It is formed due to co-lateral over.

Due to less extent of overlapping π bond is weaker.

e⁻ cloud is divide into 2 parts. 1 is above and 2nd is below the plane.

Along π bond restricted rotatⁿ is present.

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2015

Comparison of valence bond and Molecular orbital theories

Similarities →

- Most of the result such as $B\cdot O$, $B\cdot L$, $B\cdot E$ for diatomic molecule obtained from both the theories are similar.
- Acc to both the theories, overlapping of atomic orbital having same symmetry is necessary for the "form" of a bond.
- Acc to both the theories, electron density is more b/w the nuclei of the atom forming a bond.

Dissimilarities →

- Acc to VBT e^- must be paired for the form of a bond. However in MOT unpaired e^- also can contribute in bond form.
- Acc to VBT the ionic character in both bond in heteronuclear molecule is due to difference in electronegativities of the atoms but acc to MOT, ionic character in a bond is due to difference in energy of overlapping atomic orbital.

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Superiority of the MOT →

- (a) MOT itself is able to explain polarity and electronic delocalisation, whereas in VBT we have to use the concept of resonance to explain the two facts.
- (b) To explain paramagnetism of Oxygen, 2 unpaired electron are obtain in MOT diagram itself, whereas in VBT we have to depend on new type of 3 electron bond.
- (c) The VBT concludes that an e⁻ pair is completely localised b/w 2 bonded nuclei such assumption is unrealistic. On the other hand, in MOT each e⁻ is supposed to be delocalised over whole molecule.

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