

Molecular Orbital Theory...

- According to molecular orbital theory all atomic orbital of the atom participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule. These are called molecular orbitals.

- The molecular orbital formed by the addition of atomic orbitals is called the bonding molecular orbital. [Energy ↓ Stability ↑]
- The molecular orbital σ^* formed by the subtraction of atomic orbitals is called the antibonding molecular orbital. [Energy ↑ Stability ↓]

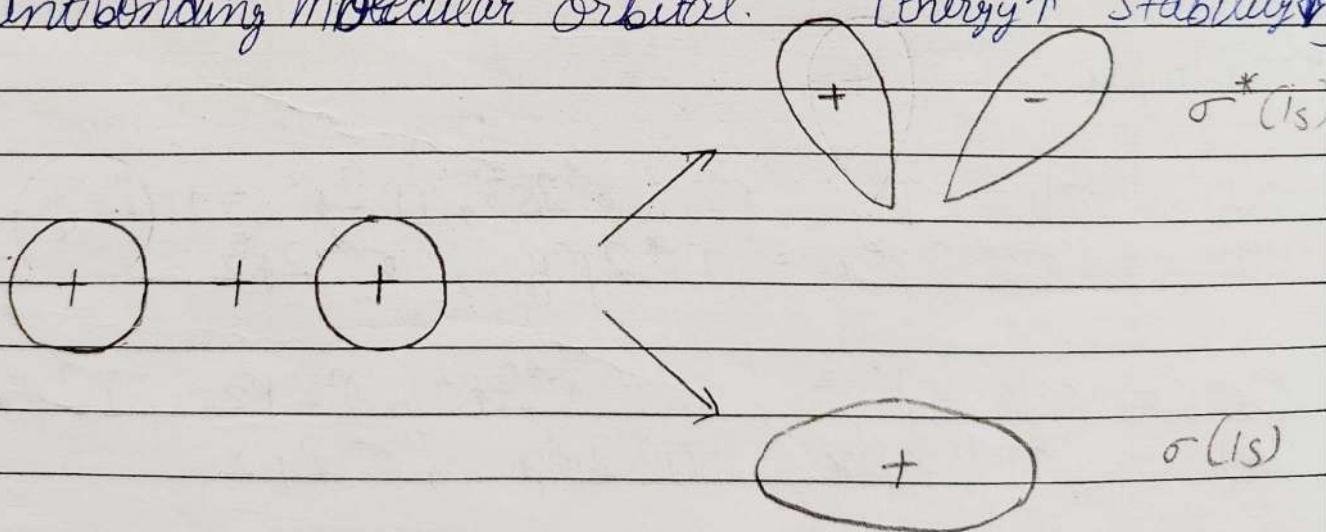


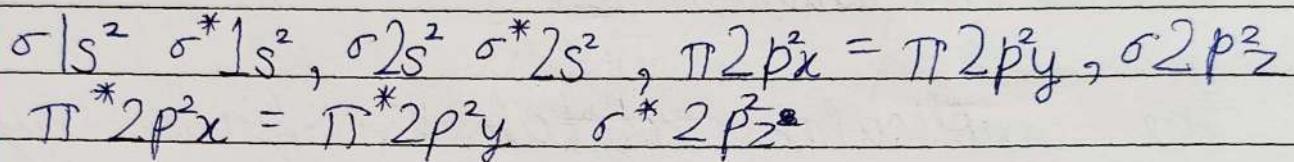
Fig- Formation of M.O. from two 1s orbital of hydrogen atoms.

* Node → A node is a region or point in an atom where the probability of finding an electron is zero.

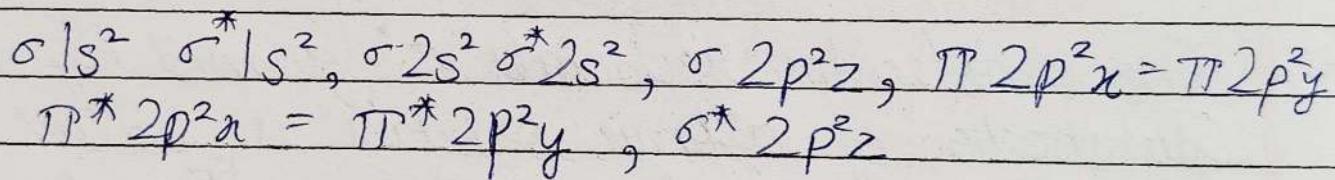
* Electronic Configuration of diatomic molecule -

- For . Be, B , C , N₂

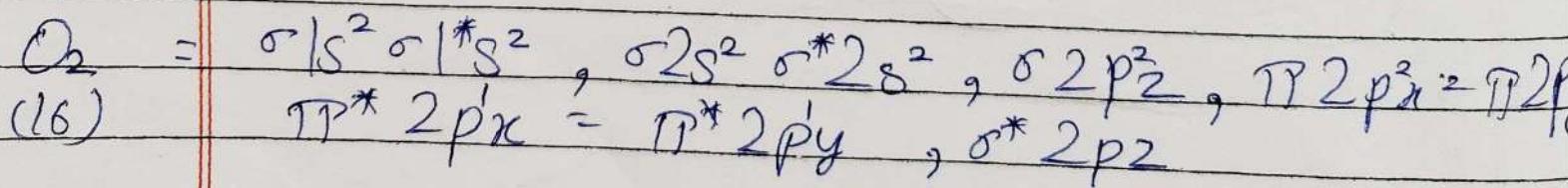
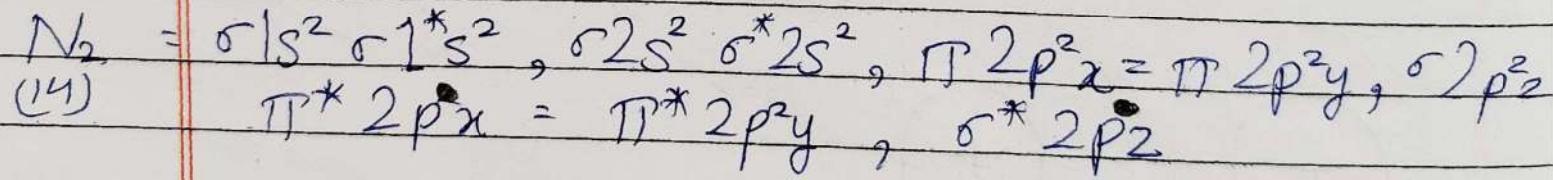
Molecular Atomic Conf. →



- For O₂ & F₂



- Example

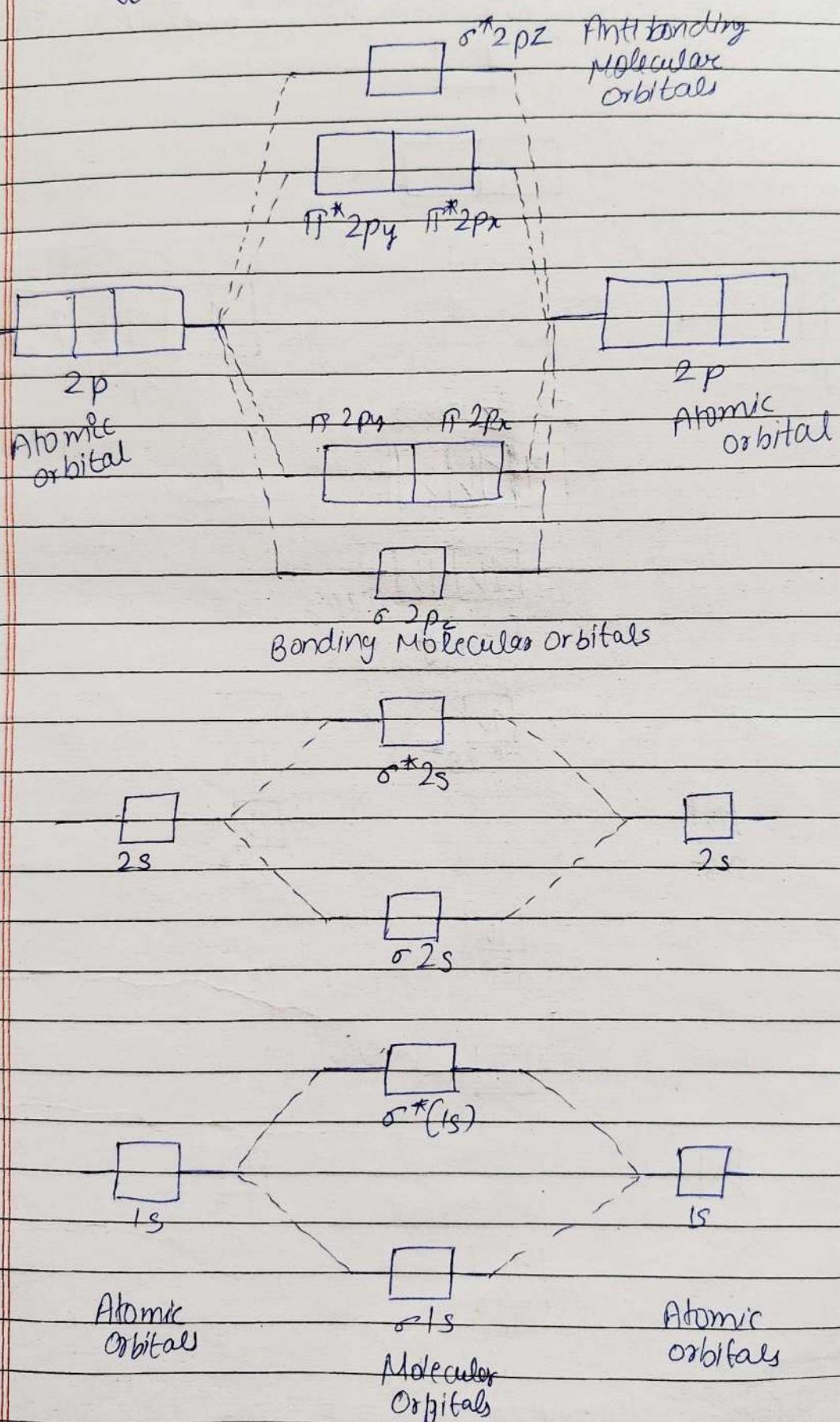


CASE-1 no of e⁻ in a molecule > 14

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* Energy level diagram for diatomic molecule



Energy order = σ1s < σ^{*}1s < σ2s < σ^{*}2s < σ2p < π2p_x = π^{*}2p_x < π^{*}2p_y < σ^{*}2p_z

$$N = 1s^2 2s^2 2p^3$$

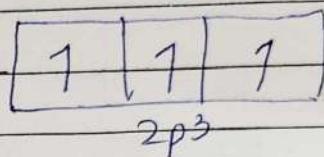
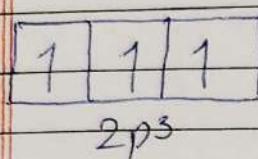
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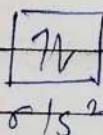
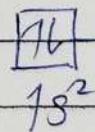
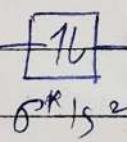
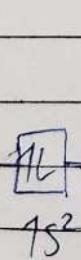
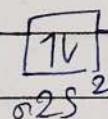
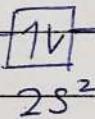
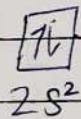
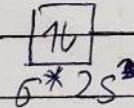
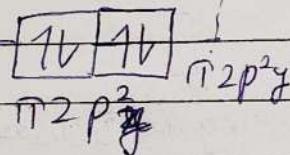
~~3mp~~

$$N_2 = 14e^- \leq 14e^-$$

$$= \sigma 1s^2, \sigma^* 1s^2, \pi 2s^2 \sigma^* 2s^2, \pi 2p_z^3, \pi 2p_y^2, \sigma 2p_z$$



~~σ2p_z σ2p_y~~



$$B.O. = \frac{10-4}{2} = \frac{6}{2} = 3$$

$$B.O. = 3$$

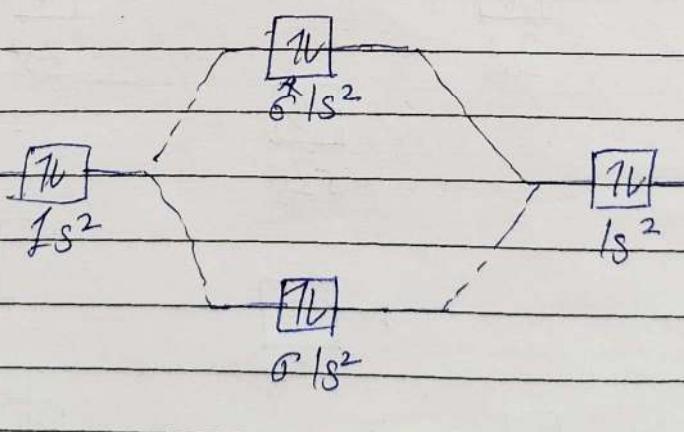
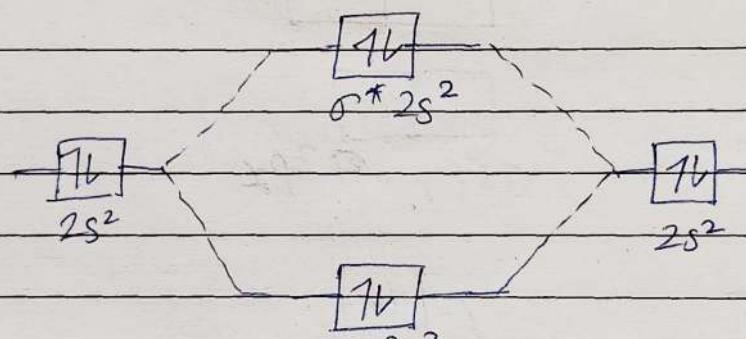
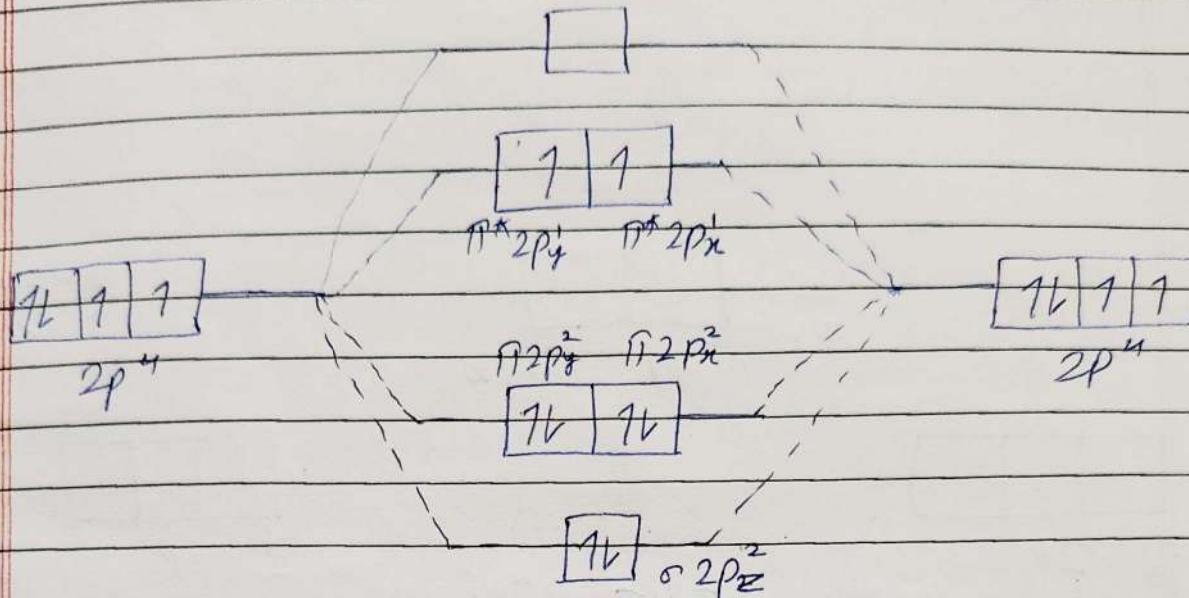
O = $1s^2 2s^2 2p^4$

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Imp
2.

$O_2 = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$
 $16e^- > 14e^-$



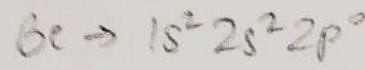
O

O_2

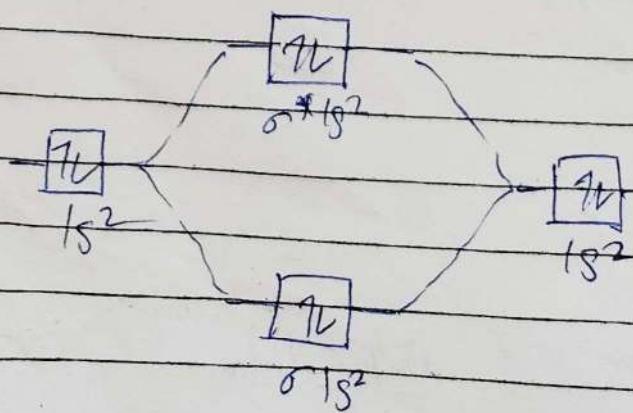
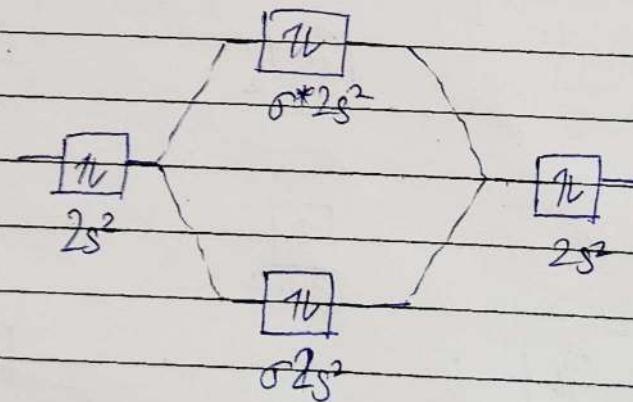
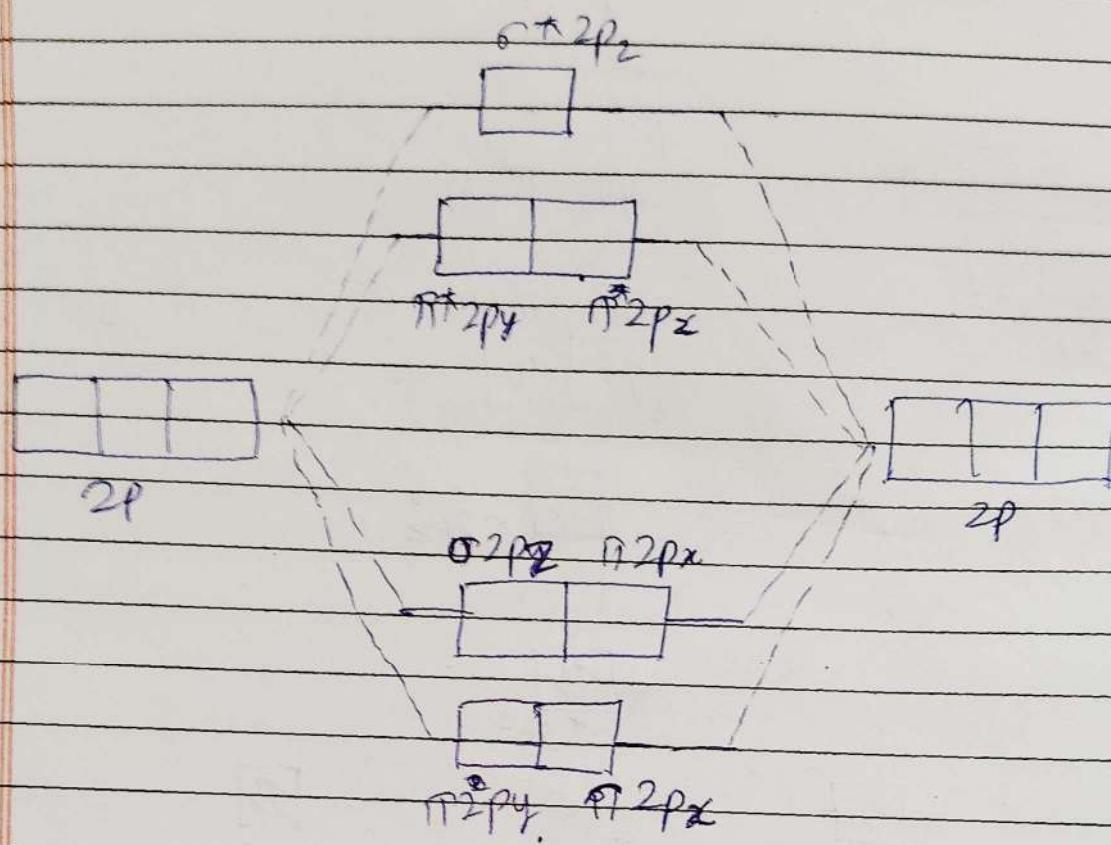
O

$$\text{Bond Order (BO)} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

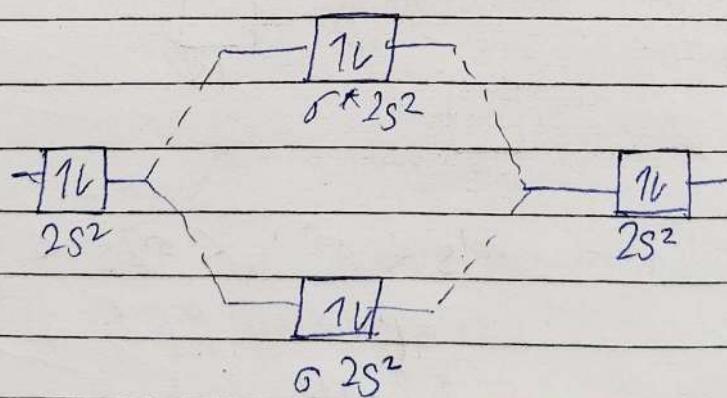
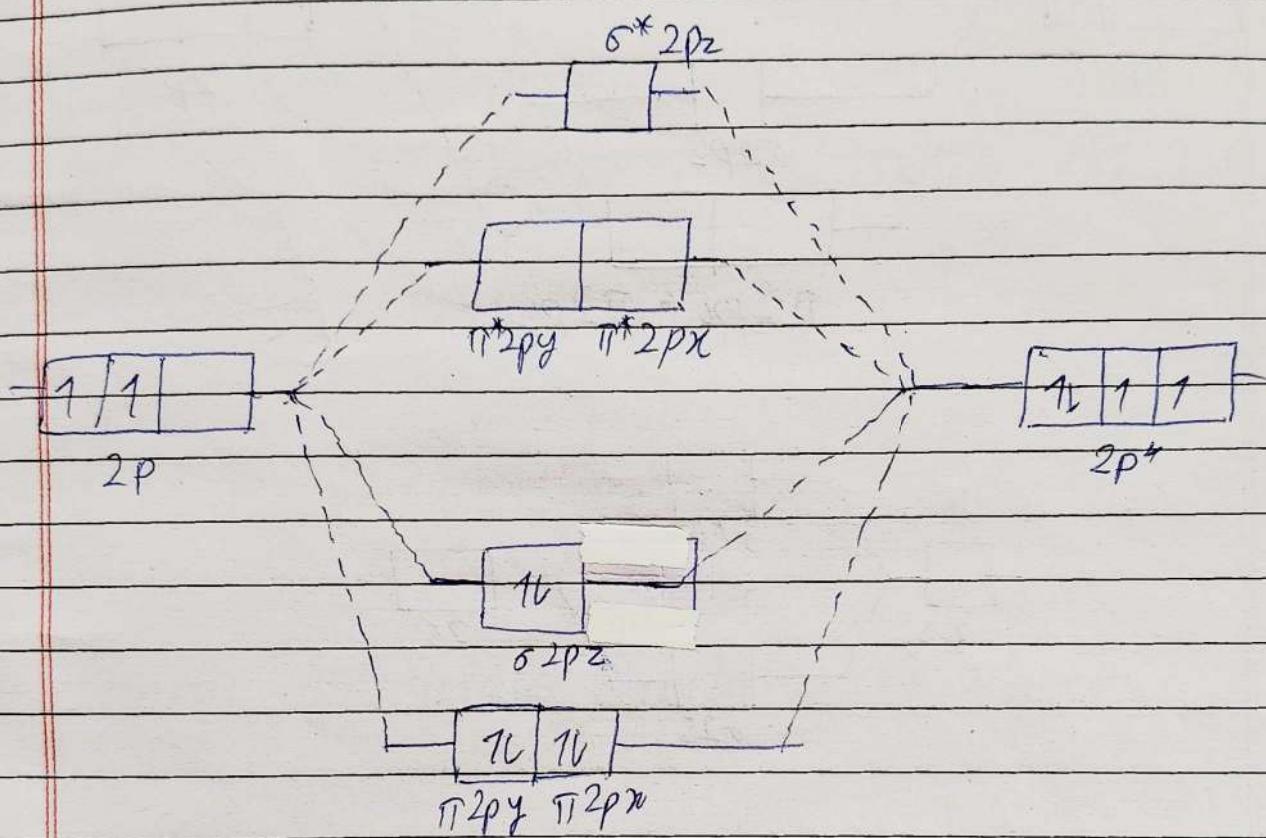
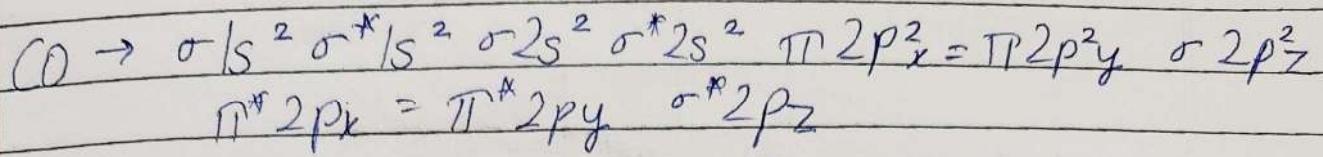
It signify the multiplicity of the bond. For example if bond order is 1 - single bond
2 = double bond
3 = triple bond



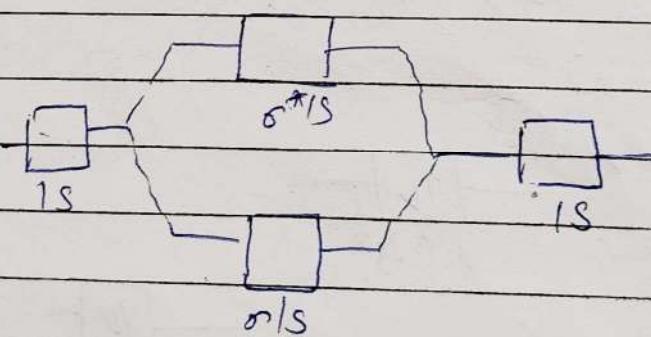
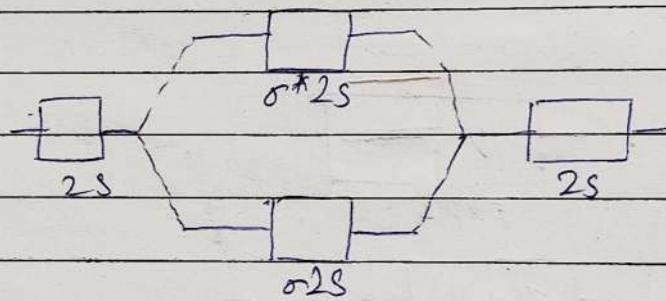
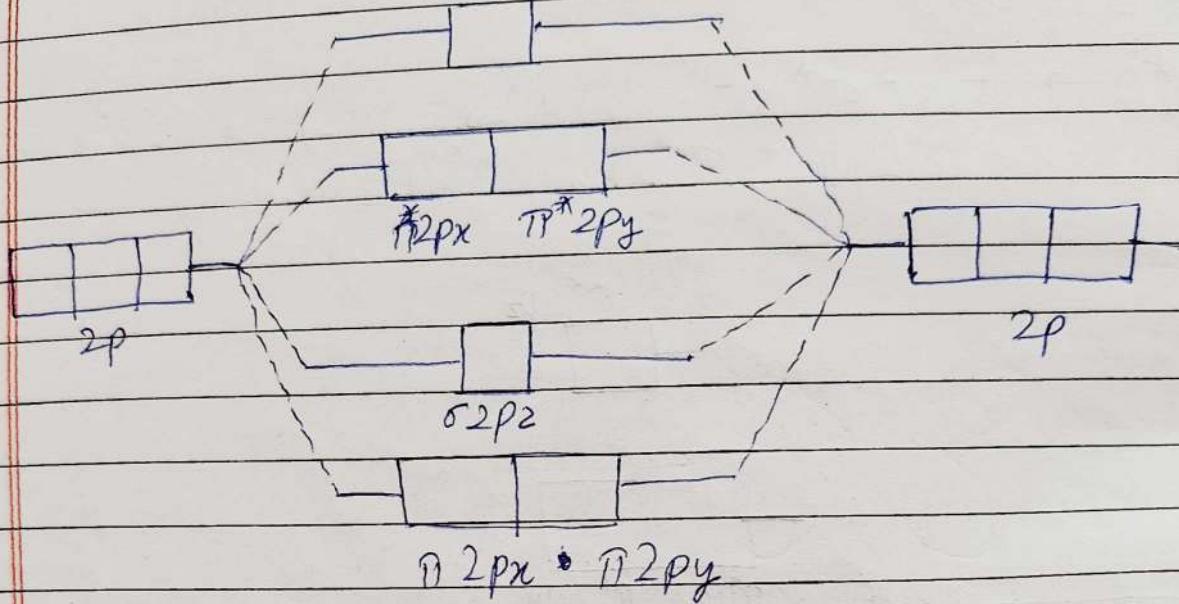
3. $\text{Be}_2 = (8) \quad 8e^- \leq 14e^-$



~~Ans~~ 4. Energy level diagram for CO $(6+8) = 14e^- \leq 14e^-$
Carbon Monoxide



CASE 2 No of e⁻ in a molecule = 14



Energy Order = $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \sigma 2p_y < \sigma^* 2p_x < \sigma^* 2p_y <$

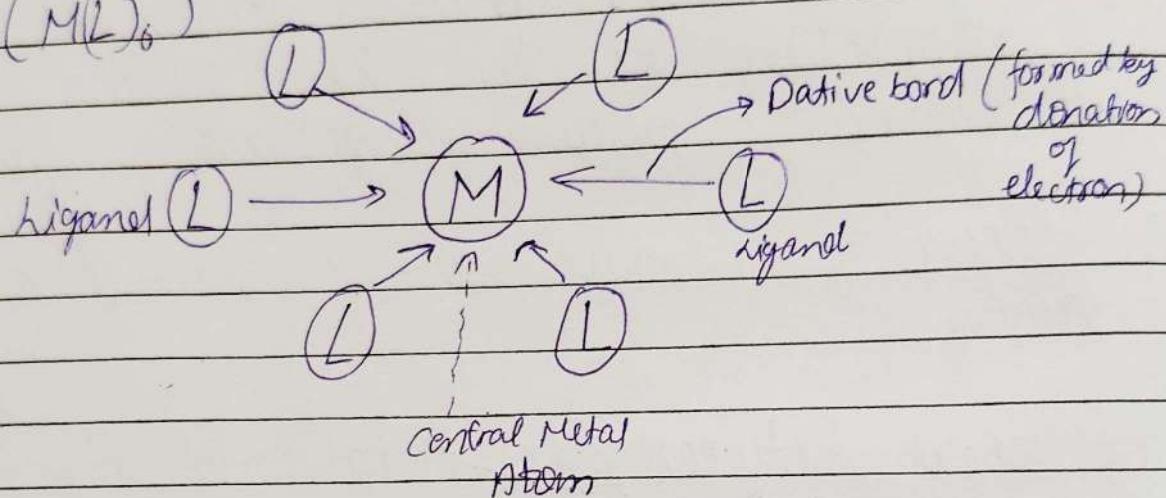
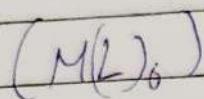
6) Crystal field theory (CFI) →

• Basic Assumptions →

- (i) The transition metal is surrounded by the ligand with lone pair of electron. Hence, the interaction between the metal and the ligand is purely electrostatic in nature.
- (ii) All type of ligands are considered as point charges.
- (iii) The bond between the metal and the ligand is 100% ionic (electrostatic).
- (iv) The ligand surrounding the central metal ion generates the electric field that influence the energy of the d-orbital of central metal ion.

Note
(for general
purpose
only)

Co-ordination compounds are the compound in which central metal atom is linked to a number of ion (ligands) by dative bond (co-ordinate bond).



Ligand (e⁻-donor, Lewis base)

Central Metal Atom (e⁻-acceptor, Lewis Acid)

Denticity → no of co-ordinating or ligating

- Terdentate - (dien) { sites present in a ligand.
- Tetradentate - (trien) { unidentate → H₂O, NH₃, CO, CN
- Polydentate - (EDTA) { Bidentate → (en, Gly, ox)

C.N = No of ligands × dentricity

C.N Hybridisation Orbital involve

Geometry

2

(S+P) SP (S+P) sp

Linear

4

SP³

(S+3P)

Tetrahedral

4

dsp²

(d_{xz}, d_{yz}, ts + 2p)

Squareplanar

C.N. Hyperdissociation

Orbital involve

Geometry

5

 dsp^3 $(dz^2) 1s + 3p$

Trigonal bipyramidal

6

 d^2sp^3 $(2d + s + 3p)$

Octahedral (inner)

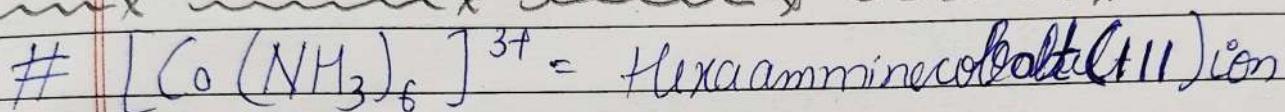
7

 sp^3d^2 $(s + 3p + 3d)$

Octahedral (outer)

 sp^3d^3

Pentaagonal bipyramidal



Electronic configuration $\rightarrow (Z) = 27 = [Ar] 3d^7 4s^2 4p^0 4d^0$

Configuration

$$\text{Oxidation state} \Rightarrow n + 6(0) = +3$$

$$\boxed{n = +3}$$

$Co^{+3} = [Ar] 3d^6 4s^0 4p^0 4d^0$

•	6	<table border="1"> <tr><td>1L</td><td>1L</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1L</td><td>1</td><td>1</td></tr> </table>	1L	1L	1	1	1	1	1L	1	1
1L	1L	1	1	1	1	1L	1	1			
(Ground state)											

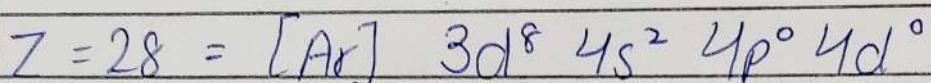
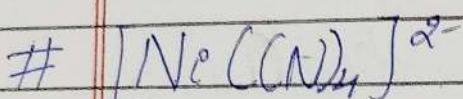
•	Co^{+3}	<table border="1"> <tr><td>1L</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr> </table>	1L	1	1	1	1	1	1	1	1
1L	1	1	1	1	1	1	1	1			

NH_3 is a strong field ligand, so pair up e^- in $3d$ orbital

$[Co(NH_3)_6]^{3+}$	<table border="1"> <tr><td>1L</td><td>1L</td><td>1L</td><td>x x</td><td>x x</td><td>3d</td><td>4s</td><td>4p</td></tr> </table>	1L	1L	1L	x x	x x	3d	4s	4p
1L	1L	1L	x x	x x	3d	4s	4p		
	<table border="1"> <tr><td>1L</td><td>1L</td><td>1L</td><td>x x</td><td>x x</td><td>3d</td><td>4s</td><td>4p</td></tr> </table> <p>$\underbrace{[d^2 sp^3]}$</p>	1L	1L	1L	x x	x x	3d	4s	4p
1L	1L	1L	x x	x x	3d	4s	4p		

• Characteristics

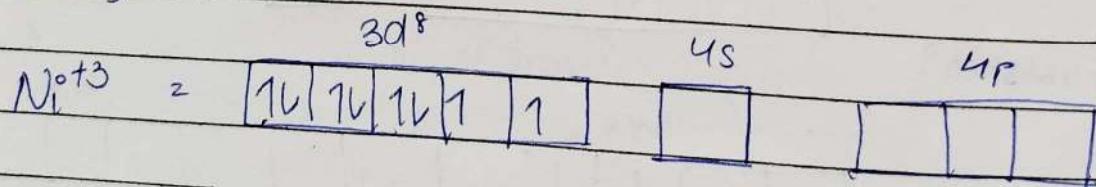
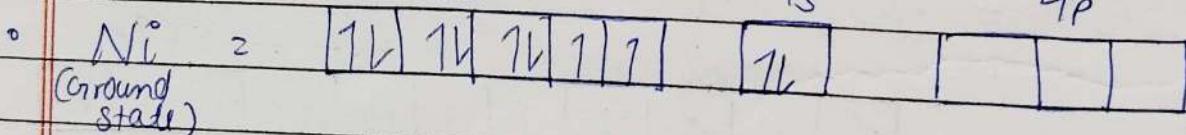
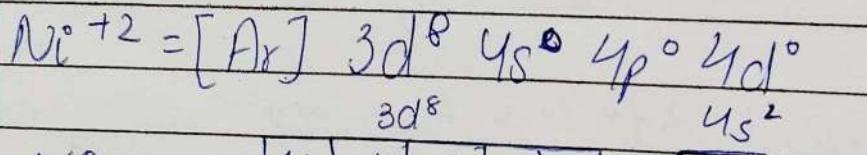
- (i) State of hybridisation $\rightarrow d^2sp^3$
 - (ii) Nature of complex \rightarrow inner orbital complex
 - (iii) Geometry \rightarrow Octahedral
 - (iv) Magnetic Nature \rightarrow ~~Paramagnetic~~ Diamagnetic



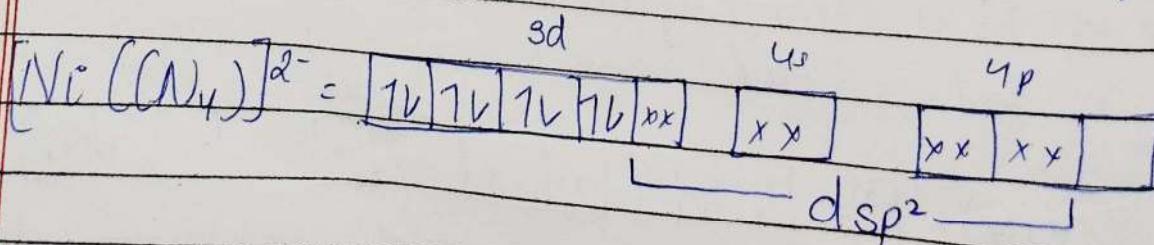
$$\text{Oxidation state} = x + 4(-1) = -2$$

$$n = -2 + 4 = +2$$

$$n = 12$$



CN is a strong field ligand so pairs up electrons in 3d orbital

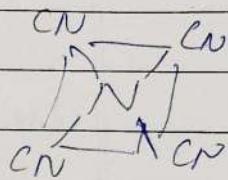


- Characteristics

(i) State of hybridisation = dsp^2

(ii) Geometry = Square planar

(iii) Magnetic behaviour = Diamagnetic



$[Ni(CO)_4]$

$Z = 28 = [Ar] 3d^8 4s^2 4p^0 4d^0$

Oxidation state = $x + 4(O) = 0$
 $n = 0$

$Ni^{+0} = [Ar] 3d^8 4s^2 4p^0$

• Ni^0 = $\begin{array}{|c|c|c|c|c|c|} \hline 1L & 1L & 1L & 1 & 1 & 1L \\ \hline \text{(Ground state)} & & & & & \end{array} \quad \begin{array}{|c|} \hline 1L \\ \hline \end{array} \quad \begin{array}{|c|c|c|} \hline & & \\ \hline \end{array}$

• Ni^{+0} = $\begin{array}{|c|c|c|c|c|} \hline 1L & 1L & 1L & 1\bullet & 1\bullet \\ \hline \end{array} \quad \begin{array}{|c|} \hline 1L \\ \hline \end{array} \quad \begin{array}{|c|c|c|} \hline & & \\ \hline \end{array}$

CO is a strong field ligand so pair up electron.

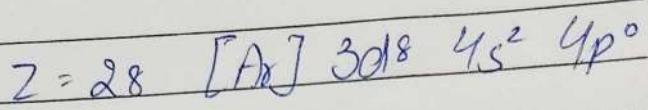
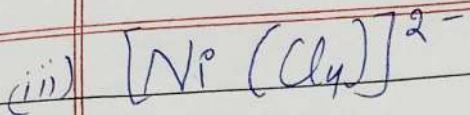
$[Ni(CO)_4] = \begin{array}{|c|c|c|c|c|c|} \hline 1L & 1L & 1L & 1L & 1L & \begin{array}{|c|c|} \hline xx \\ \hline \end{array} \quad \begin{array}{|c|c|c|} \hline xx & xx & xx \\ \hline \end{array} \\ \hline \end{array} \quad \underbrace{\quad}_{SP^3}$

- Characteristics

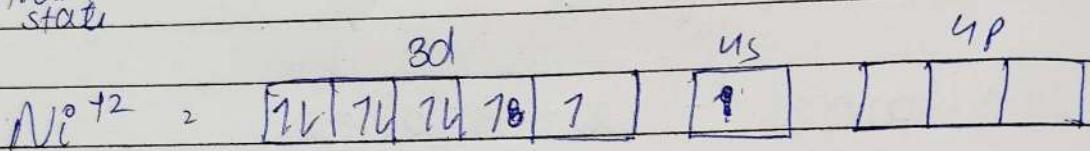
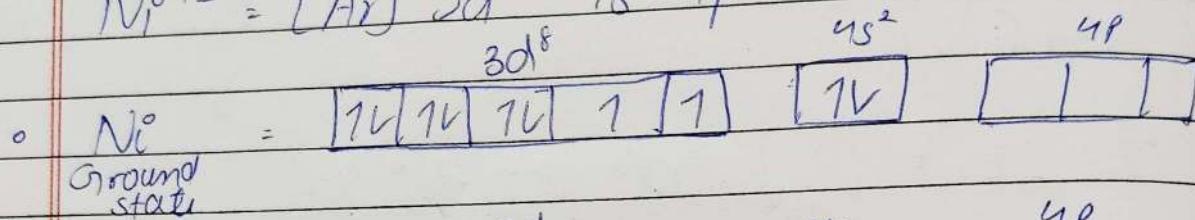
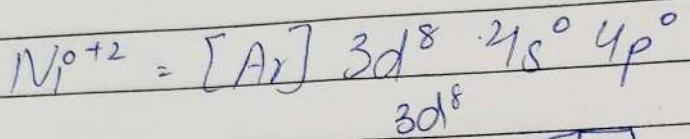
(i) State of hybridisation - SP^3 Tetrahedral

(ii) Geometry - Trigonal bipyramidal

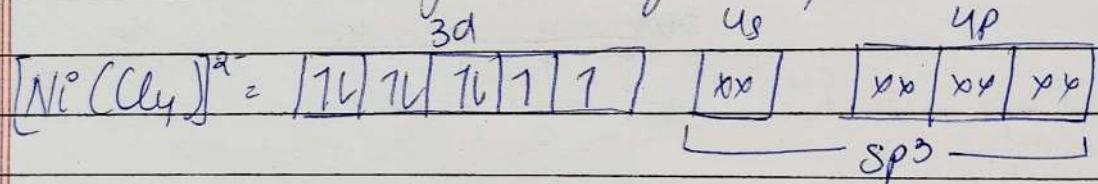
(iii) Magnetic behaviour - Diamagnetic



$$\text{Oxidation state} \Rightarrow x + 4(-1) = -2 \\ x = -2 + 4 = +2$$



Cl is a weak field ligand, so electron does not pair.



Characteristics

(i) State of hybridisation = sp^3

(ii) Geometry = Tetrahedral

(iii) Magnetic behaviour = Paramagnetic



Strong ligand
Cause pairing

Inner Orbital Complex
 $(n+1)d$

Diamagnetic

$\text{CO}_{\text{SL}} > \text{CN}_{\text{SL}} > \text{Cl}_{\text{ax}}$

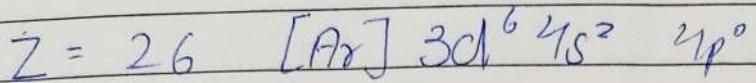
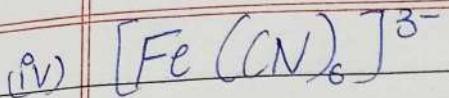
Weak ligand

Do not cause pairing

Outer Orbital Complex
 (nd)

Paramagnetic

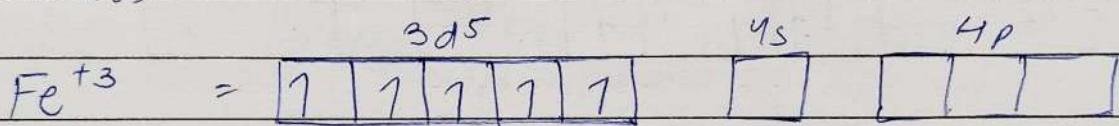
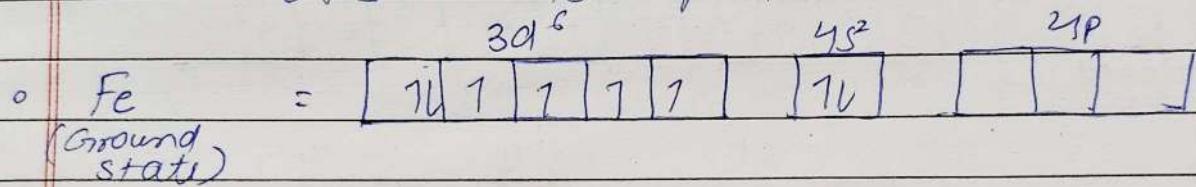
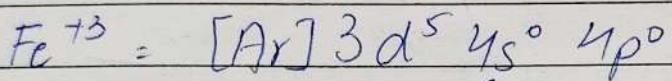
$\text{CN}_{\text{SL}} > \text{H}_2\text{O}_{\text{ax}}$



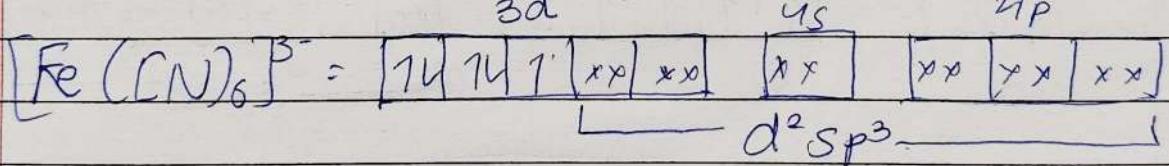
$$\text{Oxidation state} \Rightarrow n + 6(-1) = -3$$

$$n - 6 = -3$$

$$n = 3$$

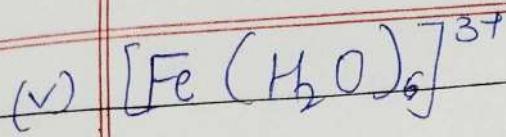


CN is a strong field ligand, so pair up electrons



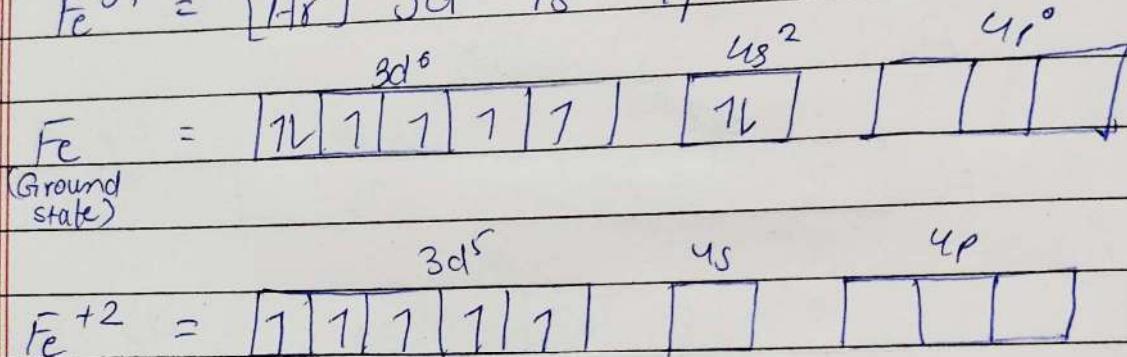
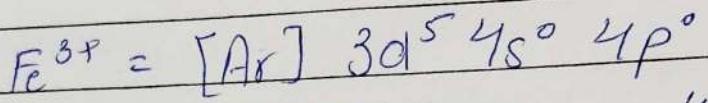
Characteristics

- (i) State of Hybridisation - $d^2\text{sp}^3$
- (ii) Geometry - Octahedral
- (iii) Magnetic behaviour - Weak paramagnetic
- (iv) Nature of Complex - Inner orbital complex.

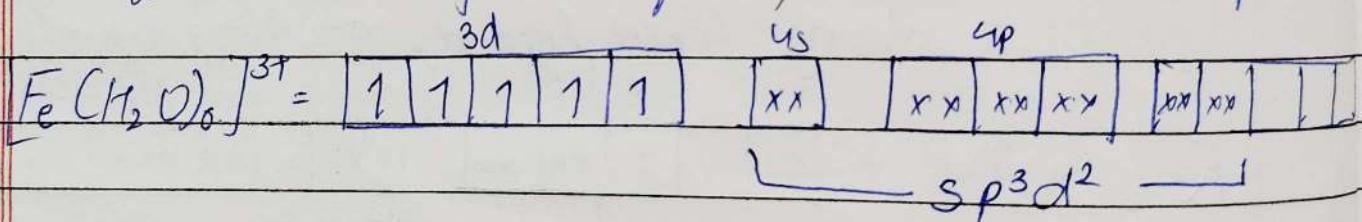


$$Z = 26 \quad [\text{Ar}] \quad 3d^6 \quad 4s^2 \quad 4p^0 \quad 4d^0$$

oxidation state $\Rightarrow x + 6(\text{O}) = +3$
 $x = +3$



H_2O is weak field ligand, so e^- does not pair



* Characteristics

- (i) State of Hybridisation - sp^3d^2
- (ii) Geometry - Octahedral
- (iii) Magnetic behaviour - Paramagnetic
- (iv) Nature of Complex - Outer orbital Complex

* $[\text{Fe}(\text{CO})_5]$

$Z = 26$ [Ar] $3d^6 4s^2 4p^0 4d^0$

Oxidation state $x + 5(0) = 0$
 $x = -3$

$\text{Fe}^{+3} = [\text{Ar}] 3d^5 4s^2 4p^0$

Fe Ground state = $[1\downarrow | 1\uparrow | 1\downarrow | 1\uparrow | 1\downarrow | 1\downarrow | \quad | \quad | \quad | \quad |]$

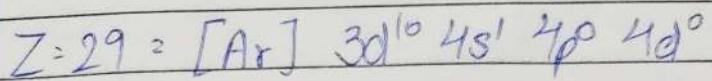
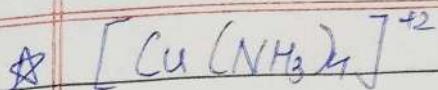
CO is strong field ligand, so e⁻ will pair up.

$[\text{Fe}(\text{CO})_5] = [1\downarrow | 1\downarrow | 1\downarrow | 1\downarrow | \underbrace{\text{xy} | \text{xy} | \text{xx} | \text{xx}}_{\text{d } \text{s } \text{p}^3} | 1\uparrow]$

* Characteristics

- i) State of hybridisation = $\text{d } \text{s } \text{p}^3$
- ii) Geometry = trigonal bipyramidal
- iii) Magnetic behaviour = Diamagnetic.

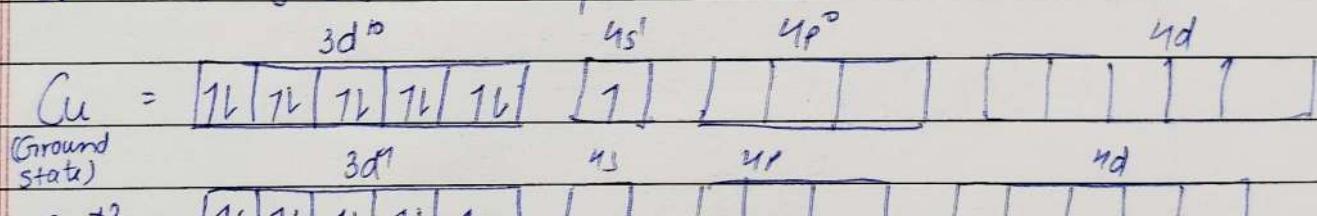
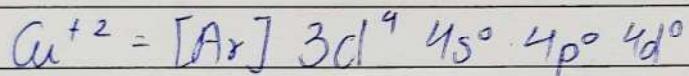
✓ Correct



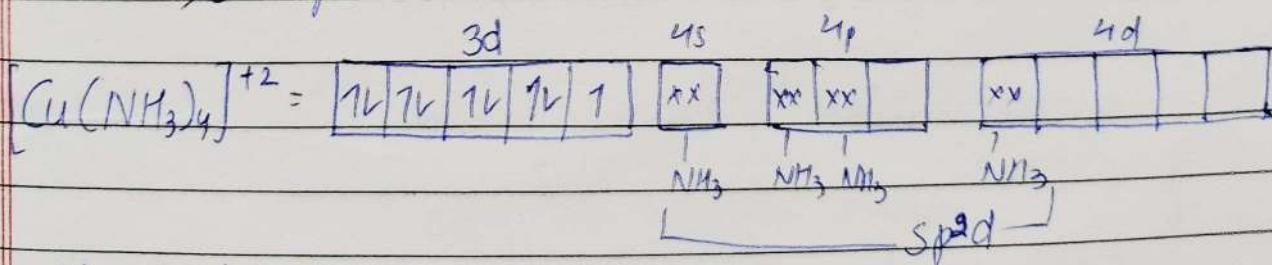
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	21	22	23	24	25	26	27	28	29	30
	$3d^1 4s^2$	$3d^2 4s^2$		$3d^5 4s^2$						
	$3d^1 4s^2$	$3d^5 4s^1$		$3d^6$						

Bc^2 half filled and fully filled d-orbitals are exceptional.

- Oxidation state = $\text{P} + \text{A} + \text{B} + x + (4)\text{O} = 2 \Rightarrow x = 2$



Here, NH₃ is a weak field ligand; so pairing will not take place.



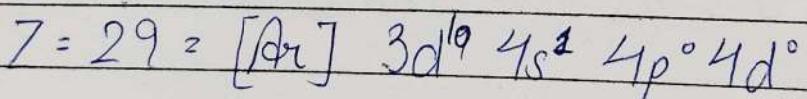
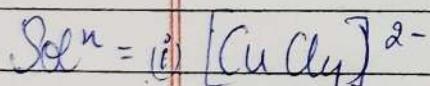
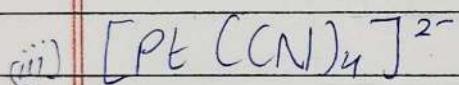
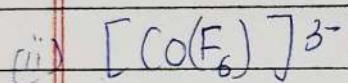
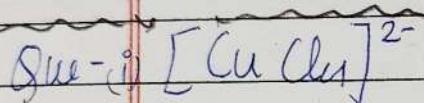
* Characteristics

- (ii) State of hybridisation - sp^2d
 - (iii) Geometry - Weak paramagnetic
 - (iv) Magnetic Behaviour - Square planar

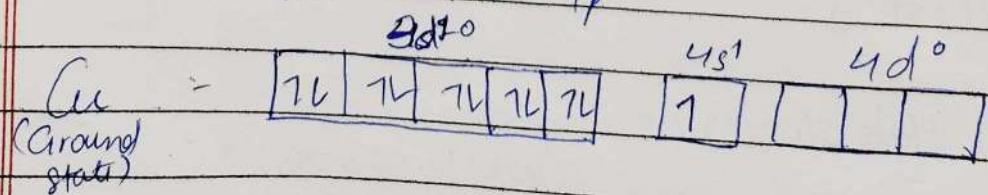
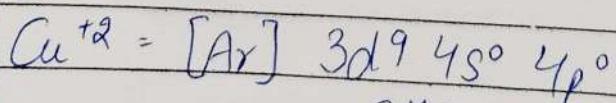
Ques~ Why fully filled and half filled e⁻ configuration are extra stable

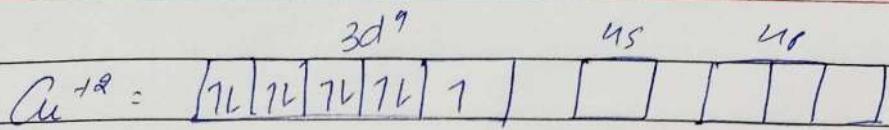
Ans → This is due to 2 reasons

- (i) Symmetry
- (ii) Exchange Energy

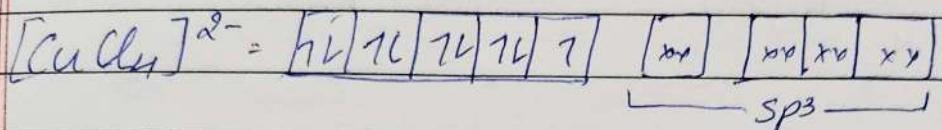


Oxidation state = $x + 4(-1) = -2$
n = +2



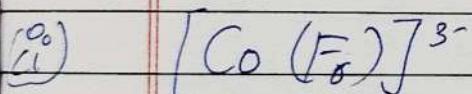


Since, Cl is a weak field ligand, so it does not cause pairing of electrons.



* Characteristics

- (i) State of hybridisation - sp^3
- (ii) Geometry - Weak paramagnetic
- (iii) Magnetic Behaviour - tetrahedral.

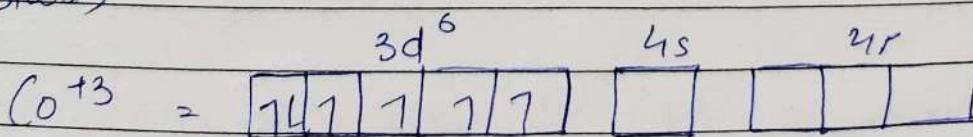
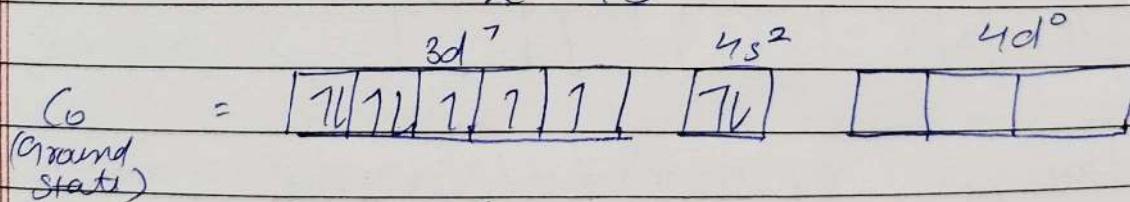


$$Z = 27 = [\text{Ar}] 3d^7 4s^2 4p^0 4d^0$$

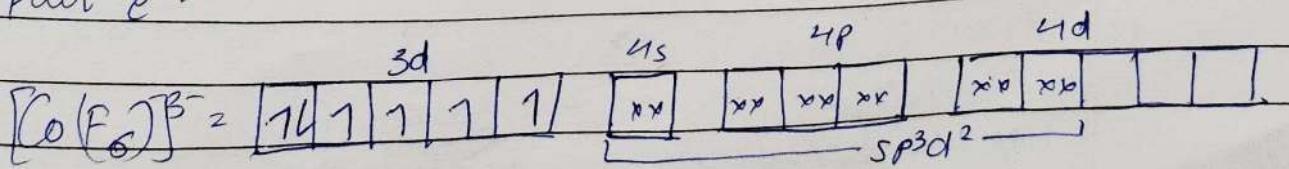
$$\text{Co}^{+3} = [\text{Ar}] 3d^6 4s^0 4p^0 4d^0$$

$$\text{Oxidation state} = \kappa - 6 = -3$$

$$\kappa = +3$$

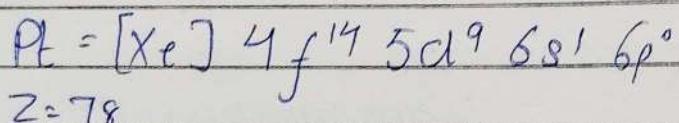
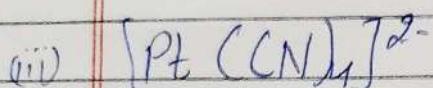


Since, F is a weak field ligand, so it does not pair e^- .



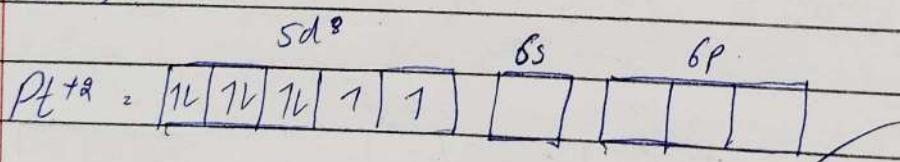
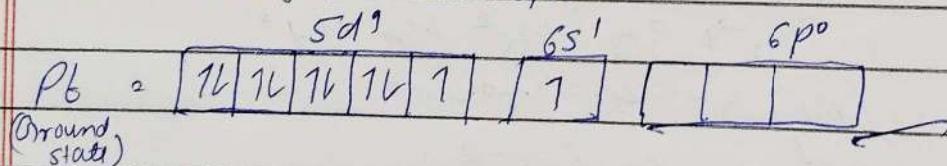
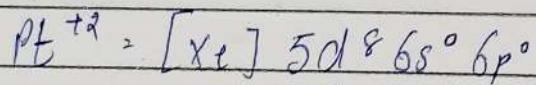
* characteristics

- | | | | |
|-------|------------------------|---|-----------------------|
| (i) | State of Hybridisation | - | sp^3d^2 |
| (ii) | Geometry | - | Octahedral |
| (iii) | Magnetic Behaviour | - | Paramagnetic. |
| (iv) | Nature of Complex | - | Outer orbital complex |

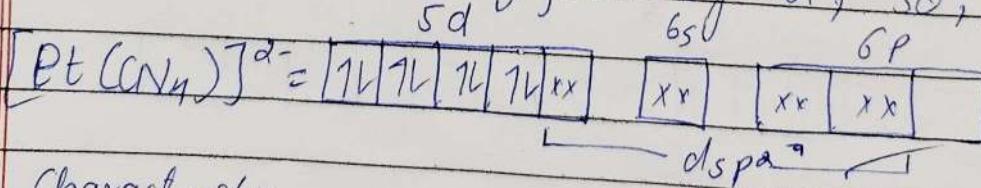


$$\text{Oxidation state} = x + 4(-1) = -2$$

n = +2



Here, CN is the strong field ligand, so, pair up:



* Characteristic

- (i) State of hybridisation - dsp^2
 (ii) Geometry - Square planar
 (iii) Magnetic Behaviour - Diamagnetic

~~Imp~~ [Pt Cl₂(NH₃)₂]

$Pt = [Xe] 4f^{14} 5d^9 6s^1 6p^0$
 $Z=78$

$$\text{Oxidation state} = x + 0 + 2(-1) = 0$$

$$x = +2$$

$$\text{Pt}^{+2} = [\text{Xe}] \ 5\text{d}^8 \ 6\text{s}^0 \ 6\text{p}^6$$

5d⁹ 6s¹ 6p⁰

~~Ground~~

Pt ⁺²	=	1u	2u	1v	1	1		

Here, raising takes place

$$[PtCl_2(NH_3)_2] = \begin{array}{|c|c|c|c|c|c|c|} \hline & & & 5d & & 6s & GP \\ \hline 1L & 1V & 1V & Pt & xx & xx & xx \\ \hline \end{array}$$

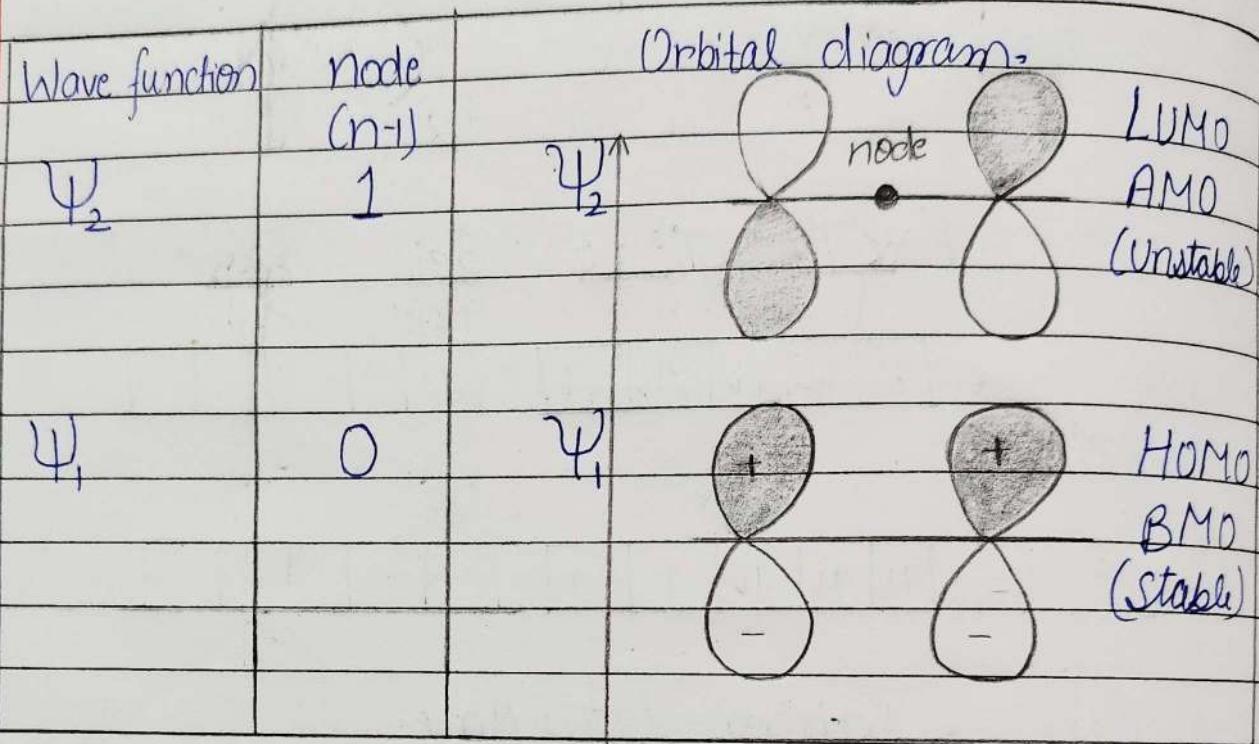
dsp^2

* Characteristics

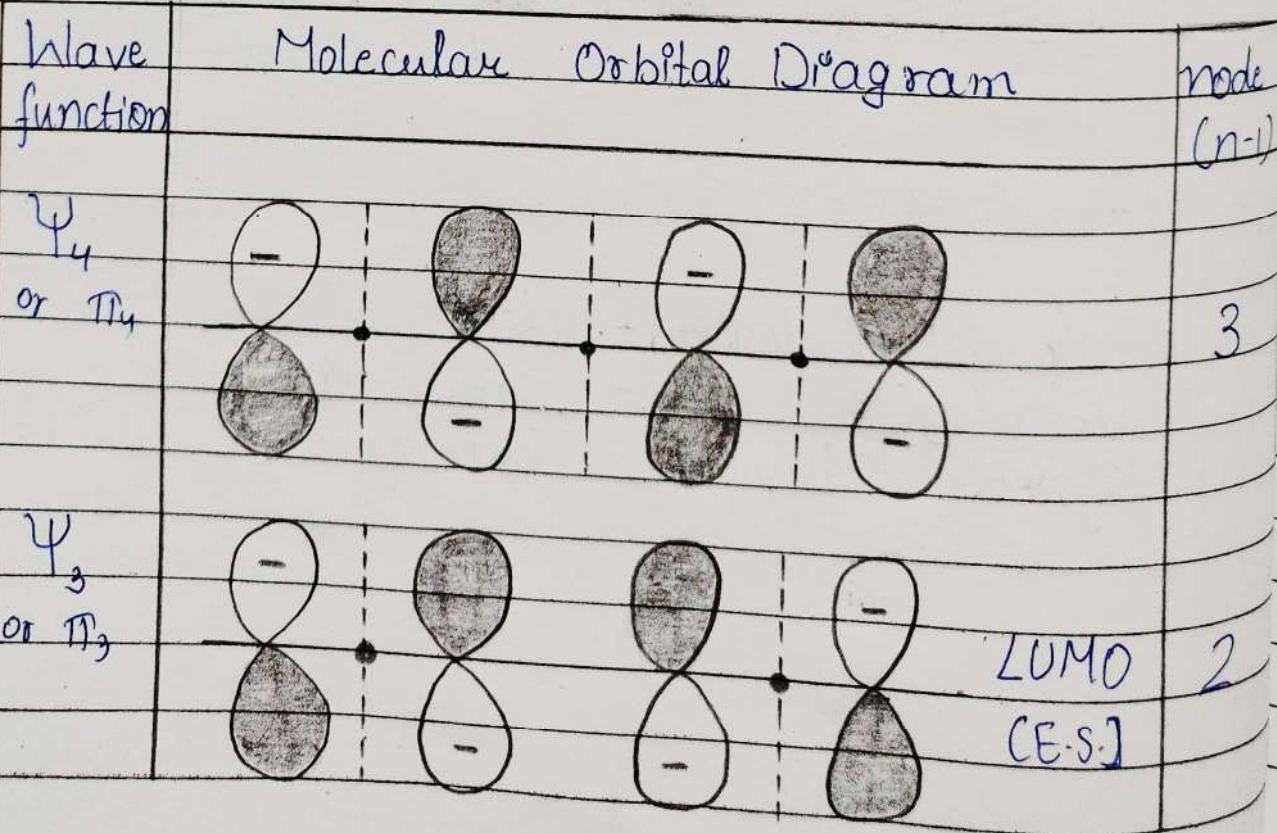
- (ii) State of Hybridisation - dsp^2
 - (ii) Geometry - Square Planar
 - (ii) Magnetic Behaviour - Diamagnetic

π -molecular orbital of butadiene system
 $(H_2C=CH-CH=CH_2)$

(a) Ethene ($CH_2=CH_2$)



^{imp}
(b) Butadiene

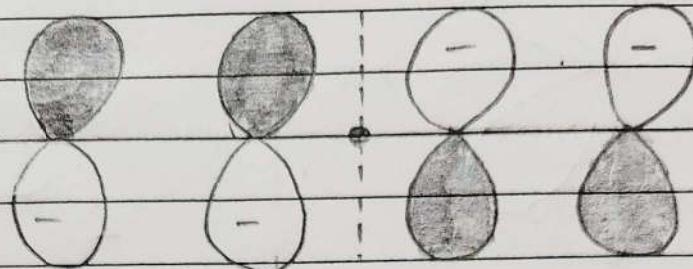


Wave
function

Molecular Orbital Diagram

node
($n-1$)

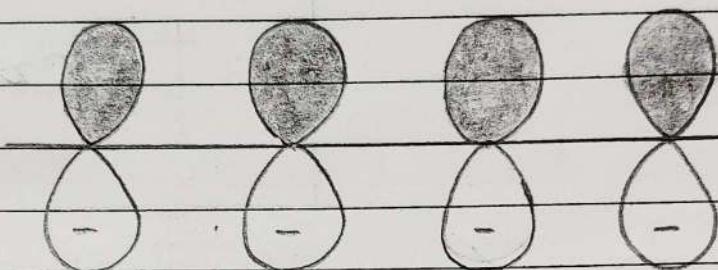
Ψ_2
or Π_2



HOMO
(G-S)

1

Ψ_1
or Π_1

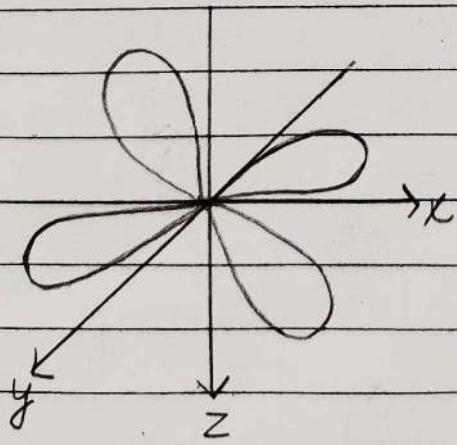


0

Shapes of d-orbital

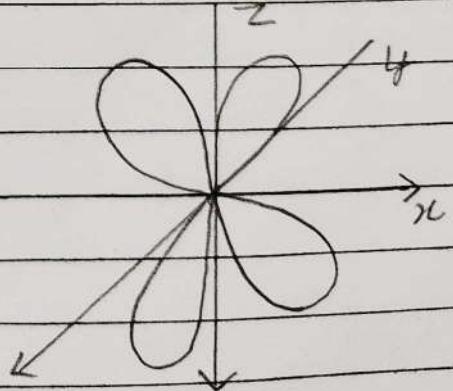
$\Rightarrow d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$

(i)



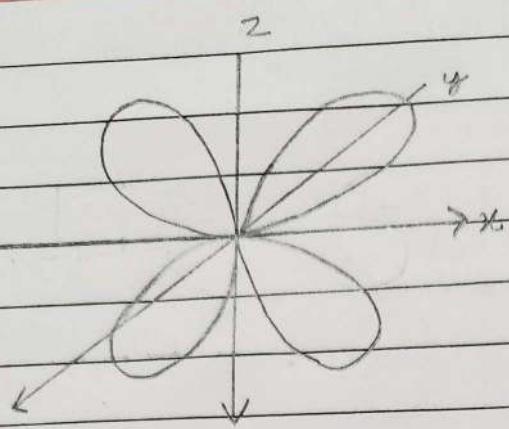
d_{xy}

(ii)



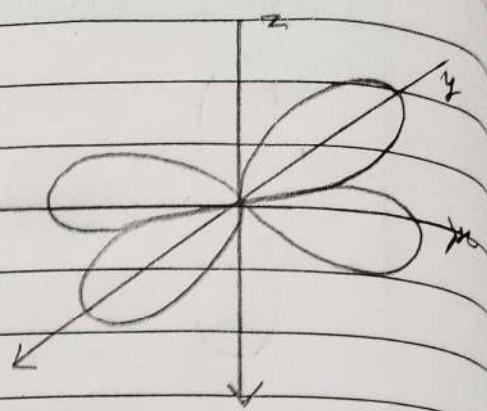
d_{yz}

(iii)



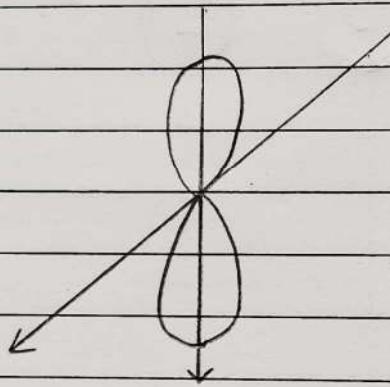
$$dx^2 - y^2$$

(ii)



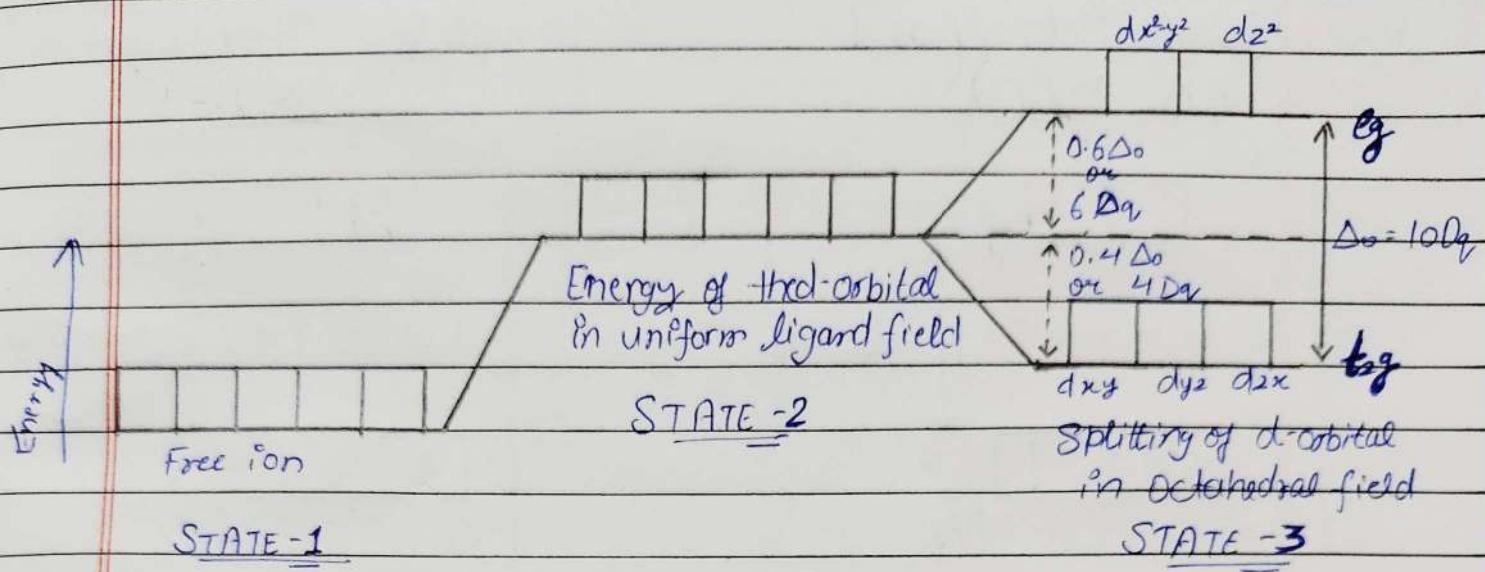
$$dx^2 - y^2$$

(iv)

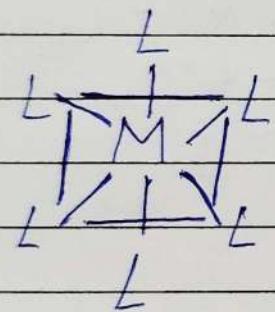


$$dz^2$$

Crystal field splitting in Octahedral Complexes.



★



Octahedral Complex
 d^2sp^3 / sp^3d^2

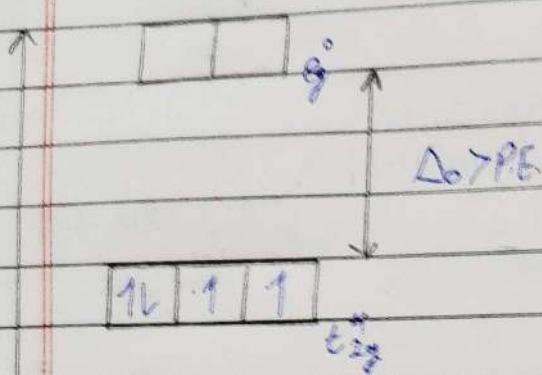
- (i) Inner orbital Complex $(n-1)d$
- (ii) Outer orbital Complex (nd)

★ For, $d^1 = t_{2g} e_g$; C.F.S.E = $-1(4) + 0(6) = -4 D_q$
 $d^2 = t_{2g}^2 e_g$; C.F.S.E = $-2(4) + 0(6) = -8 D_q$
 $d^3 = t_{2g}^3 e_g$; C.F.S.E = $-3(4) + 0(6) = -12 D_q$

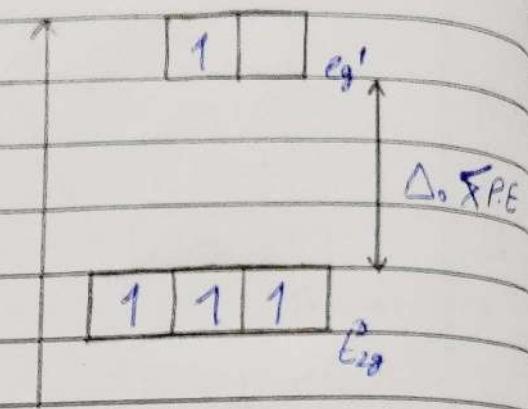
★ d^4 system

d^4 system

Strong field ligand
($\Delta_o > P.E.$)



Weak field Ligand
($\Delta_o < P.E.$)



- C.F.S.E

$$= -4(4) + 0(6) D_q$$

$$= -16 D_q + P.E$$

- C.F.S.E

$$= -3(4) + 1(6) D_q$$

$$= -6 D_q$$

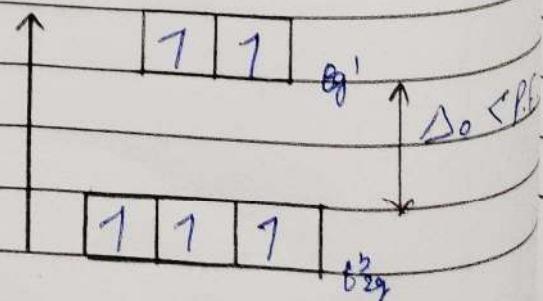
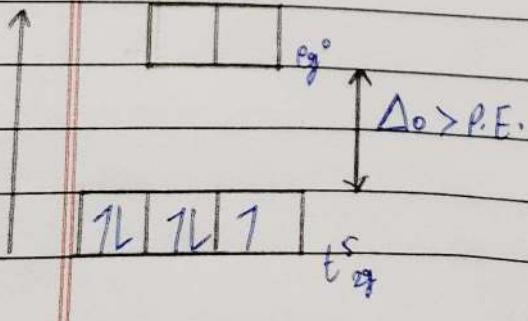
d^5 system

- For Strong Field Ligand ($\Delta_o > P.E.$) - Low Spin (L.S.)

$$\Rightarrow C.F.S.E = -5(4) + 0(6) D_q = -20 D_q + 2P.E.$$

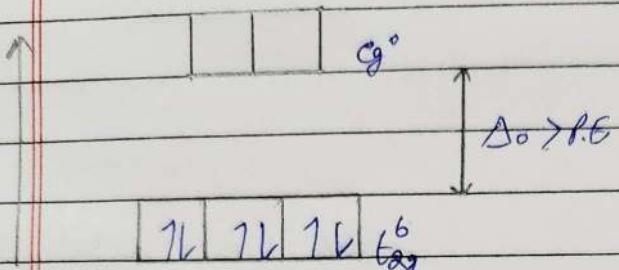
- For Weak field Ligand ($\Delta_o > P.E.$) - High Spin (H.S.)

$$\Rightarrow C.F.S.E = -3(4) + 2(6) = -12 + 12 = 0 D_q$$

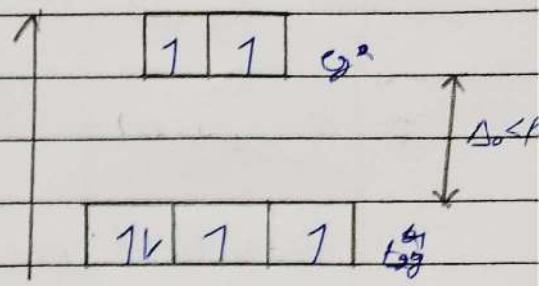


* d^6 system

Strong Field Ligand



Weak Field Ligand



◦ C.F.S.E

$$= -6(4) + 0(6) Dq$$

$$\rightarrow \boxed{-24 Dq + 3 P.E}$$

◦ C.F.S.E

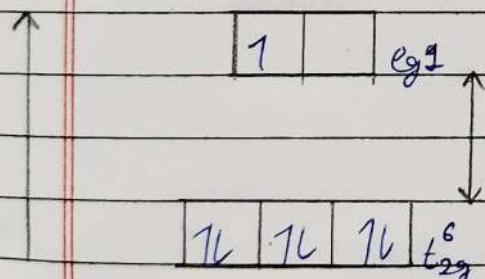
$$= -4(4) + 2(6) Dq$$

$$= -16 Dq + 12 Dq + 1 P.E$$

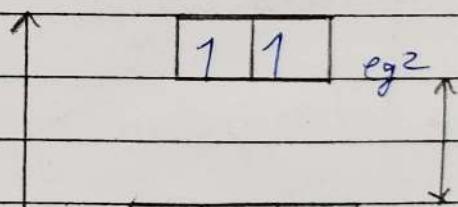
$$= \boxed{-4 Dq + P.E.}$$

* d^7 system

Strong Field Ligand



Weak Field Ligand



◦ C.F.S.E

$$= -6(4) + 1(6) Dq$$

$$= -24 + 6 Dq + 3 P.E$$

$$= \boxed{-18 Dq + 3 P.E}$$

◦ C.F.S.E

$$= -5(4) + 2(6) Dq$$

$$= -20 + 12 Dq + 2 P.E$$

$$= \boxed{-8 Dq + 2 P.E}$$

* d^8 system \rightarrow

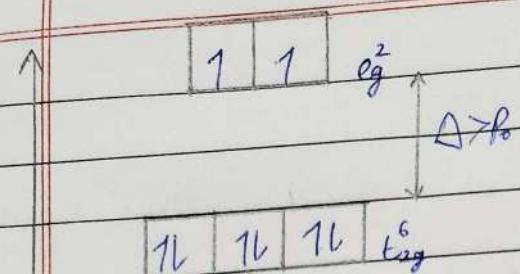
Strong F.L. \Rightarrow C.S.F.E

$$= -6(4) + 2(6) Dq$$

$$= \boxed{-12 Dq + 3 P.E}$$

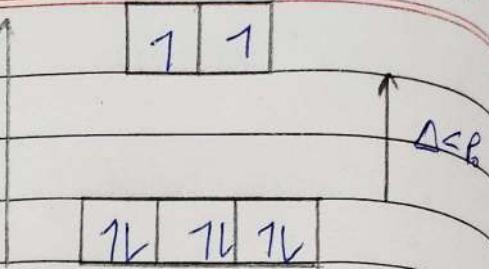
$$W.F.L \geq -6(4) + 2(6) Dq$$

$$= \boxed{-12 Dq + 3 P.E}$$

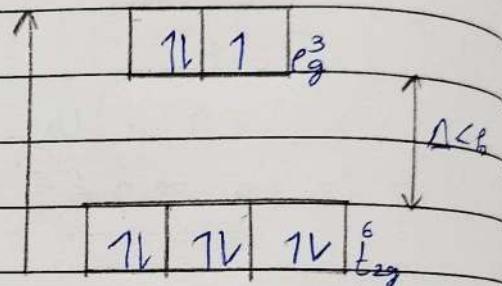
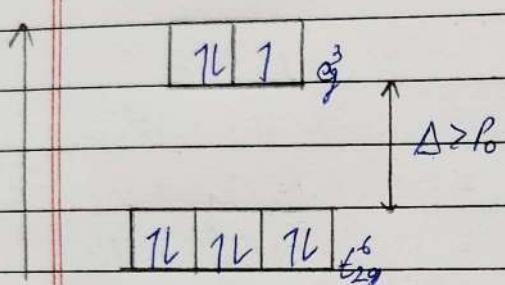


* d^9 system -

Strong Field Ligand



Weak Field Ligand



◦ CFSE

$$\Rightarrow -6(4) + 3(6) D_q$$

$$\Rightarrow -24 + 18 D_q$$

$$\Rightarrow -6 D_q + 4 \text{B.E.}$$

◦ CFSE

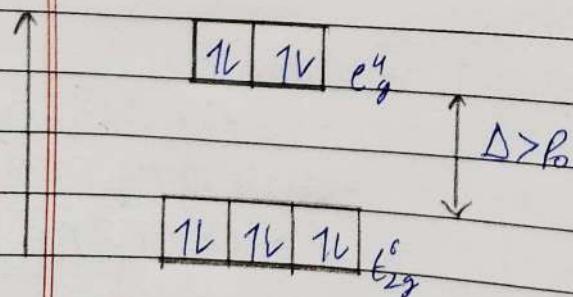
$$\Rightarrow -6(4) + 3(6) D_q$$

$$\Rightarrow -24 + 18 D_q$$

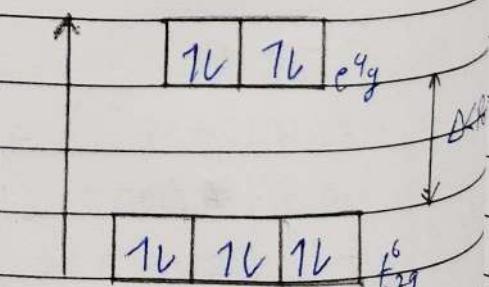
$$\Rightarrow -6 D_q + 4 \text{B.E.}$$

* d^{10} system -

Strong Field Ligand



Weak Field Ligand



◦ CFSE

$$\Rightarrow -6(4) + 4(6) D_q$$

$$\Rightarrow 0 D_q + 5 \text{B.E.}$$

◦ CFSE

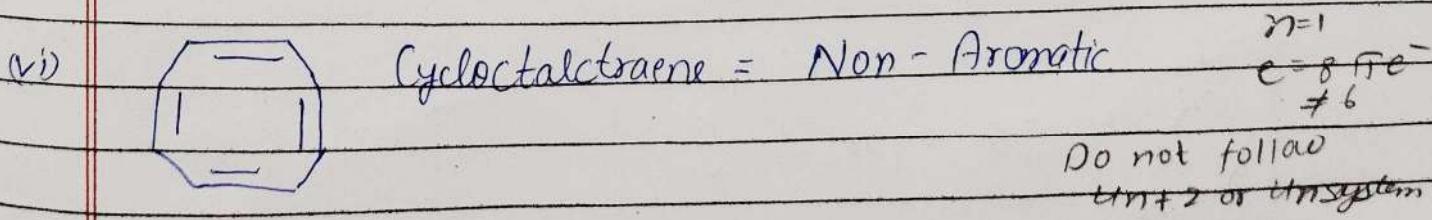
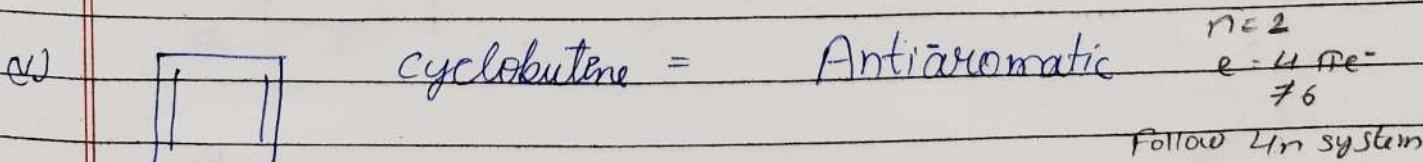
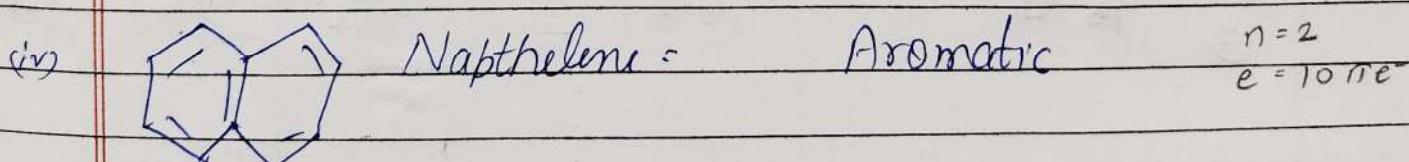
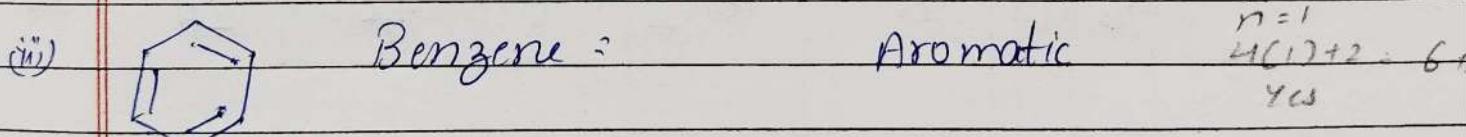
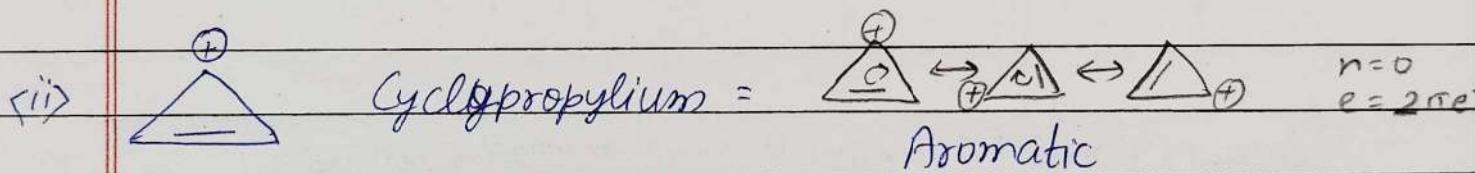
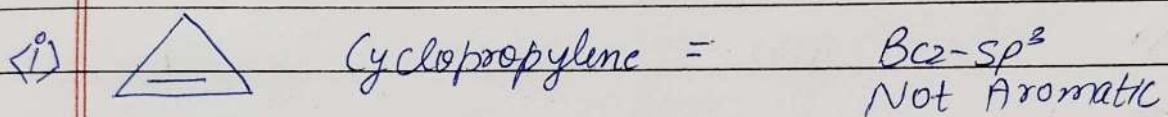
$$\Rightarrow -6(4) + 4(6) D_q$$

$$\Rightarrow 0 D_q + 5 \text{B.E.}$$

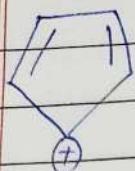
AROMATICITY (Hückel rule)

	Cyclic Planer C=C SP ²	(4n+2) π System n = no. of ring	π electron
①	Conjugation C-C=C-C=C	0	2 πe ⁻
②	(4n+2) π electron	1	6 πe ⁻
③		2	10 πe ⁻
④		3	14 πe ⁻
⑤		4	18 πe ⁻

* Ques



(vii)



= Anti-Aromatic

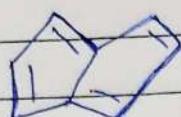
$n = 1$

$e = 4\pi e^-$

$+ 6\pi e^-$

but follows $4n$ system

(viii)



= Anti-Aromatic

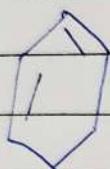
$n = 2$

$e = 8\pi e^-$

$+ 10\pi e^-$

but follows $4n$ system

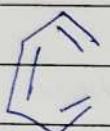
(ix)



= Non-Aromatic

Bcz Conjugation
not take place

(x)



= Non-Aromatic

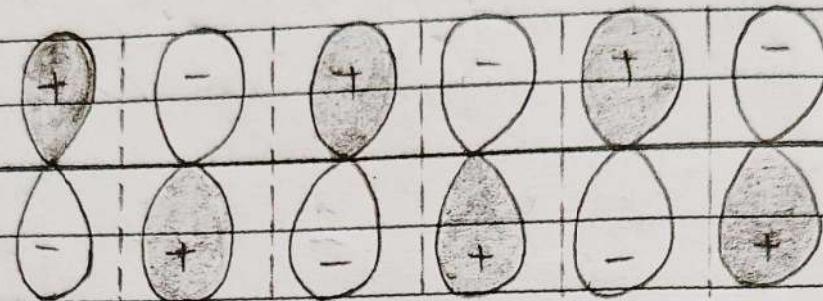
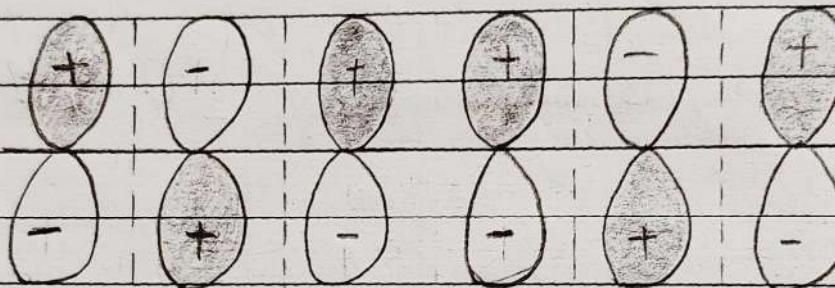
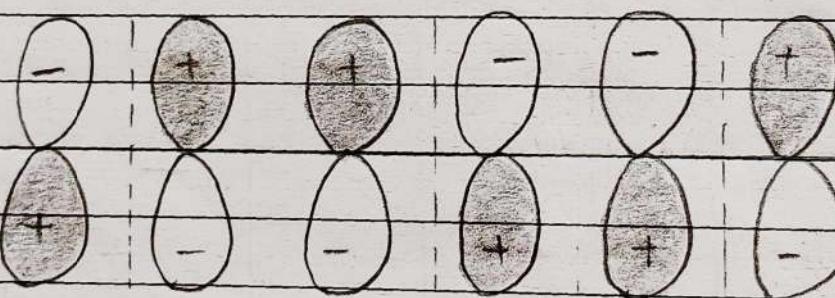
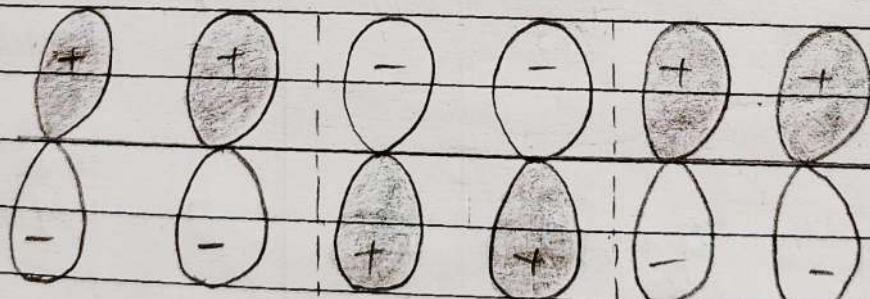
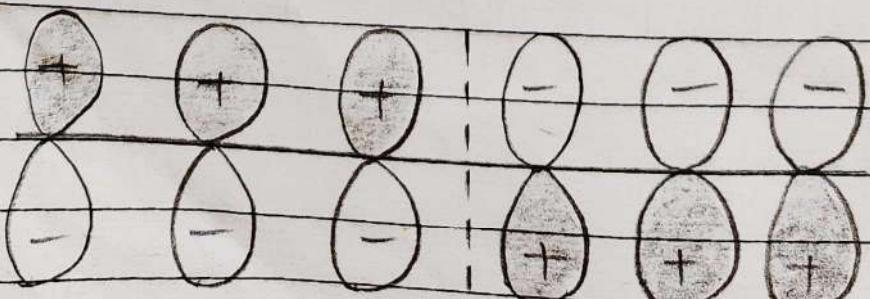
Bcz non-cyclic

	Cyclic/ Planar	Conjugation	Pi-bond	lon pairs e^-	Total πe^-	$(4n+2)$	Aromatic
①		Yes	Yes	Yes \rightarrow 1	0	$2\pi e^-$ $n=0$	Yes
②		No	Yes	Yes \rightarrow 2	1	$4\pi e^-$ $n=0$	$2 \neq 4$ No
③		Yes	Yes	Yes \rightarrow 3	1	$6\pi e^-$ $n=1$	Yes
④		Yes	Yes	Yes \rightarrow 2	0	$4\pi e^-$ $n=1$	$6 \neq 4$ No follows unsystem
⑤		Yes	No Benz SP ²	Yes	3		No

π° -Molecular Orbital of benzene

Wave
function

Molecular Orbital Diagram

 Ψ_6 or Π_6  Ψ_5 or Π_5  Ψ_4 or Π_4  Ψ_3 or Π_3  Ψ_2 or Π_2 No.
Co.

5

4

3

2

1

Π^0 - Molecular Orbital of benzene

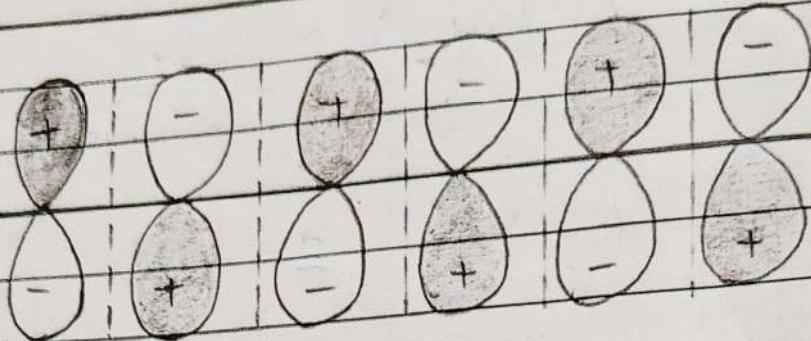
Wave
function

Molecular Orbital Diagram

Node
(n-1)

Ψ_6

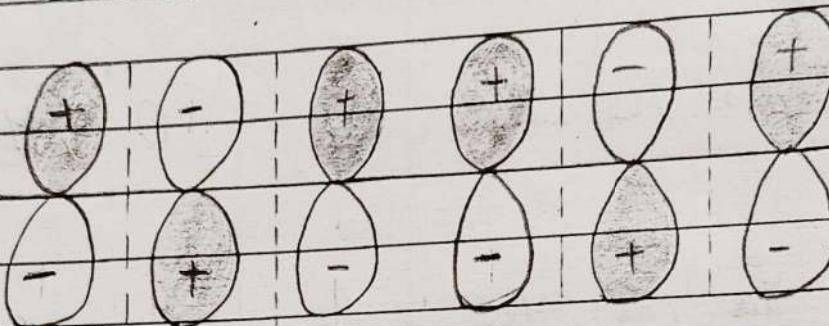
or Π_G



5

Ψ_5

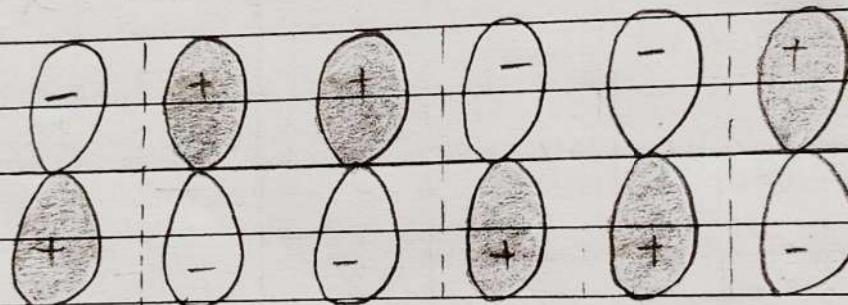
or Π_S



4

Ψ_4

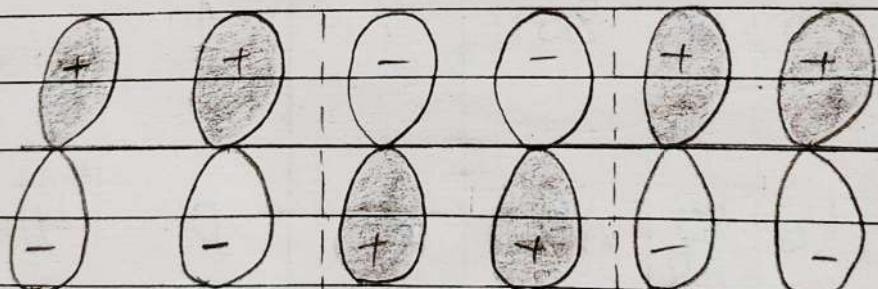
or Π_4



3

Ψ_3

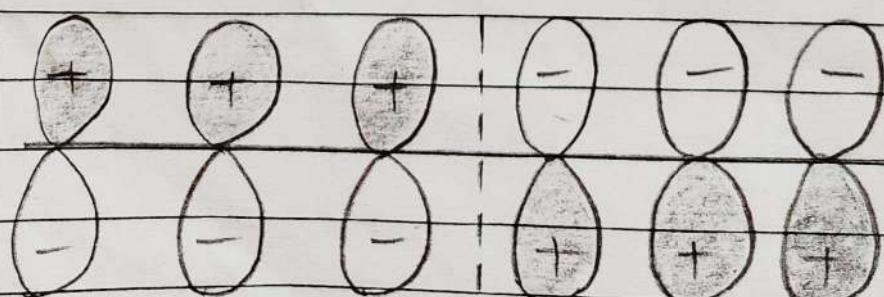
or Π_3



2

Ψ_2

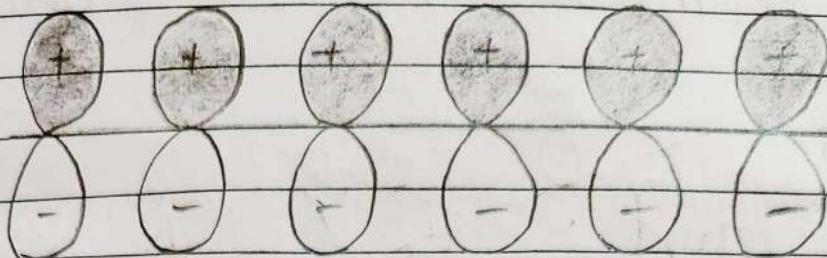
or Π_2



1

Ψ_1
or π_1

Ψ_1
or π_1



O

Wave Function node ($n-1$)

Ψ_6 5

—

} AMO (Antibonding Molecular Orbital)

Ψ_5 4

—

} LUMO (lowest occupied Molecular orbital)

Ψ_4 3

—

} HOMO (Highest occupied Molecular orbital)

Ψ_3 2

1L

Ψ_2 1

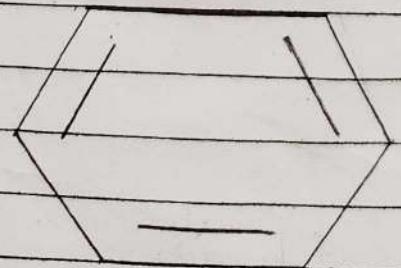
1L

Ψ_1 0

1L

} BMO (Bonding Molecular Orbital)

amp
Benzene

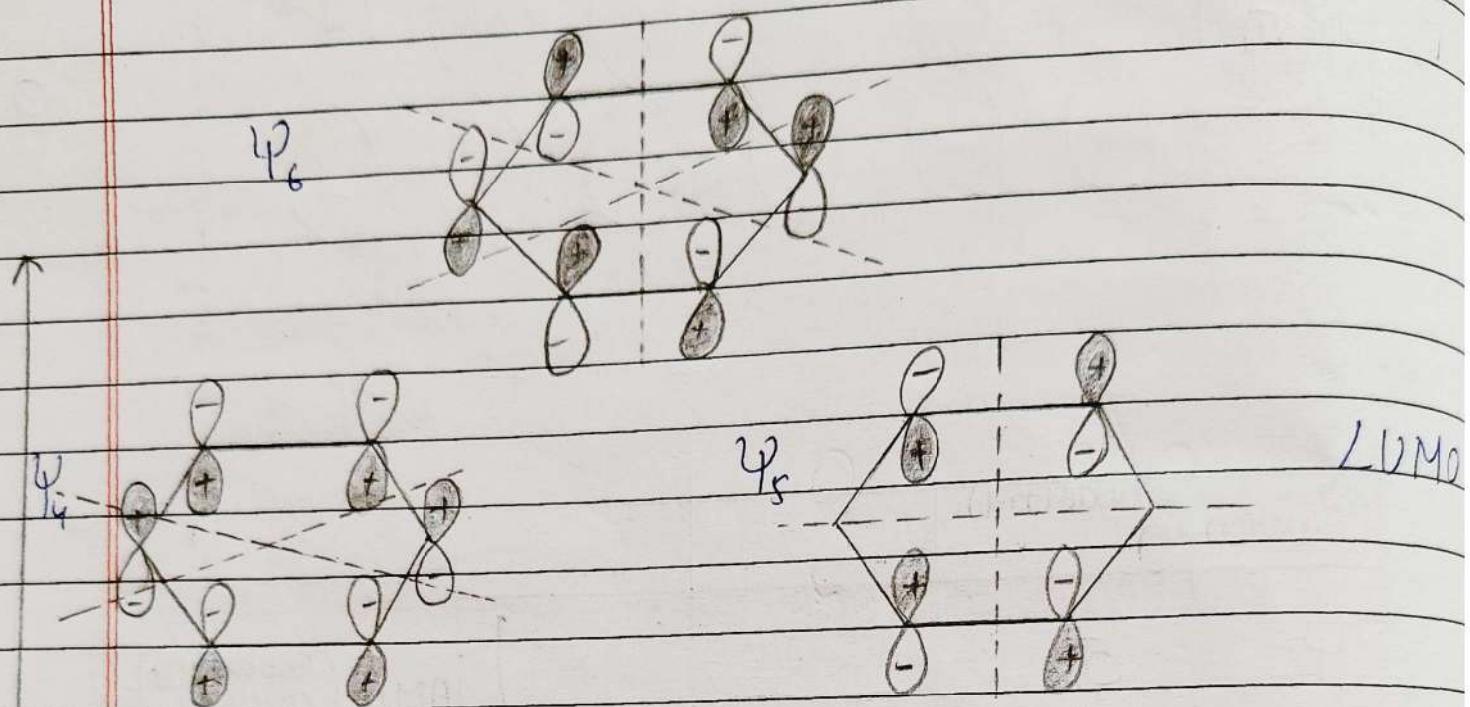


$\Rightarrow C_6H_6$

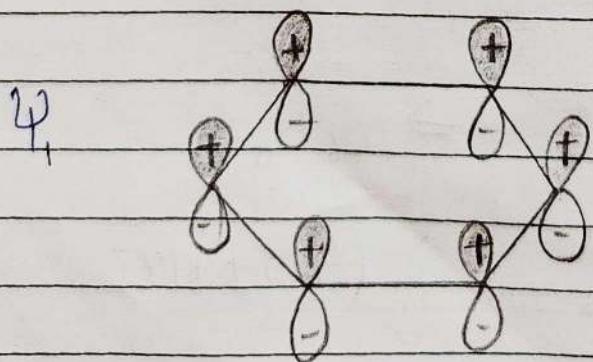
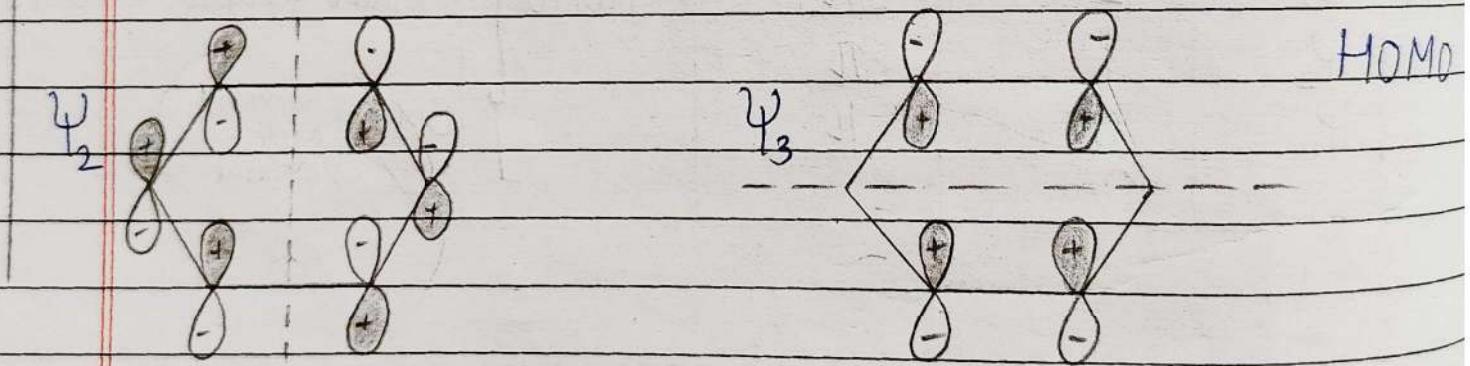
$\Rightarrow (4n+2)\pi e^-$

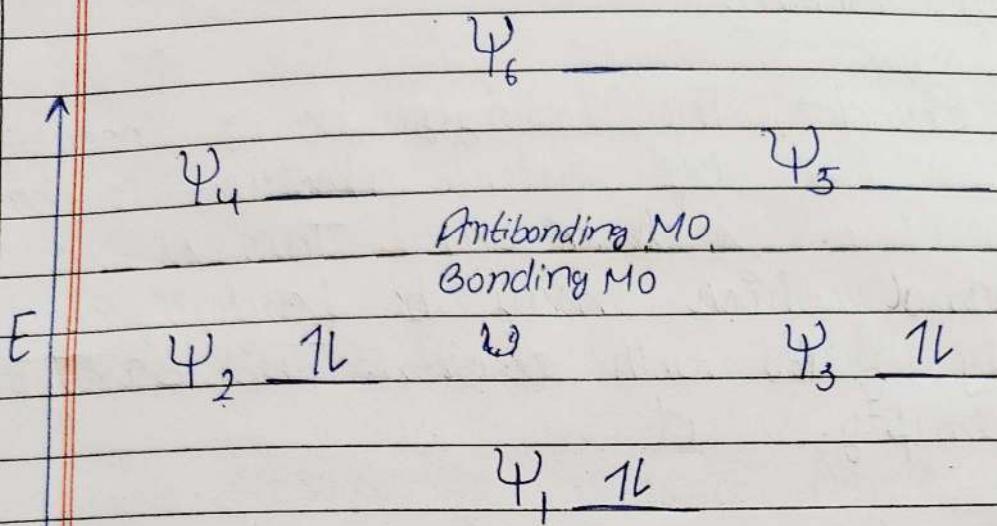
$\Rightarrow 4(1) + 2 = 6\pi e^-$

o The π molecular orbitals of Benzene



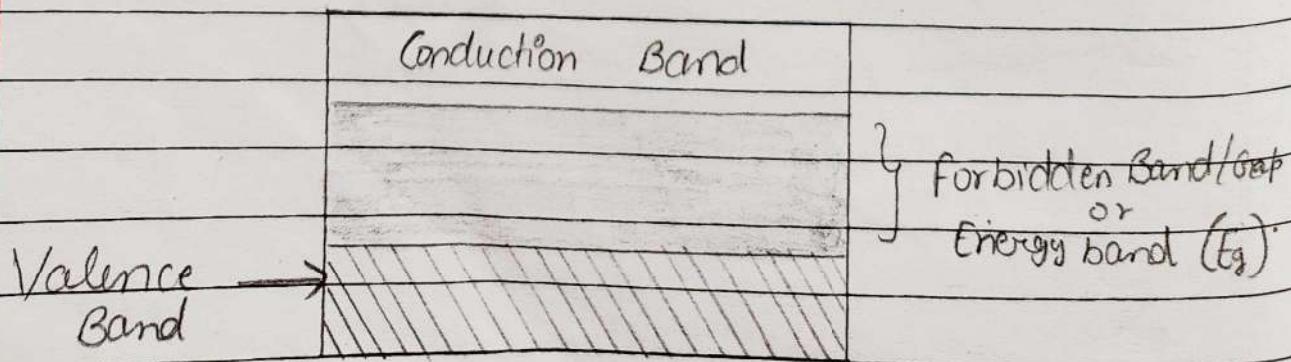
Antibonding Molecular Orbitals
Bonding Molecular Orbitals





• TYPES OF BANDS

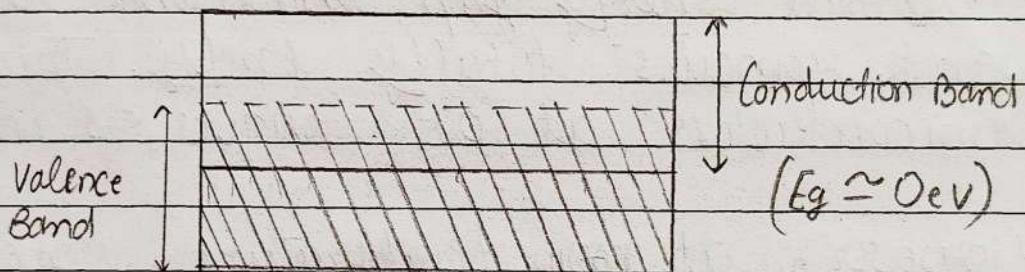
- (i) Valence Band → The energy band occupied by valence electron is called valence band. This is a lower band which may be partially or completely filled with electrons. This band is never empty.
- (ii) Conduction Band → The energy band of higher energy level which is either empty or partially filled at room temperatures, present above the valence band is called conduction band. (Electrons are not present at 0K)
- (iii) Energy band gap / forbidden Band →
 - It is the separation between highest energy level of valence band and lowest energy level in conduction band.
 - or • The valence band and conduction band are separated by a gap which is known as forbidden gap/band.



Defining Conductors, Insulators and Semiconductors on the basis of band theory.

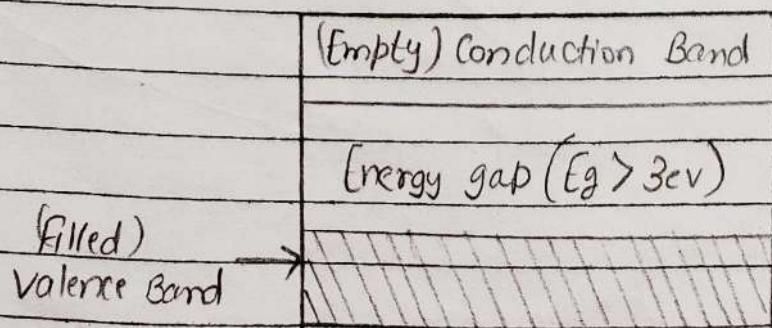
(i) Conductors :- The solids in which valence band and conduction band partially overlap each other and there is no forbidden energy gap in between.

- The electrons of valence band can easily jump to conduction band and vice-versa.



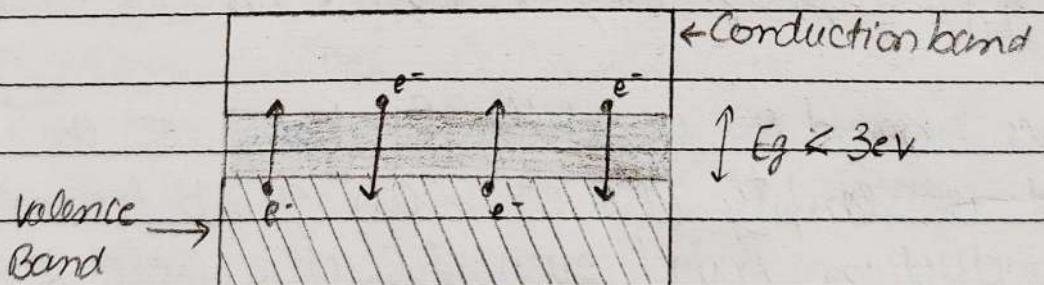
(ii) Insulators :- Insulators are the solids in which valence band and the conduction band are separated by an energy gap of ($E_g > 3 \text{ eV}$). For ex = Diamond ($E_g = 6 \text{ eV}$)

- Valence band is completely filled with e^- and conduction band is empty. (No e^- can jump from valence band to conduction band even if electric field is applied)



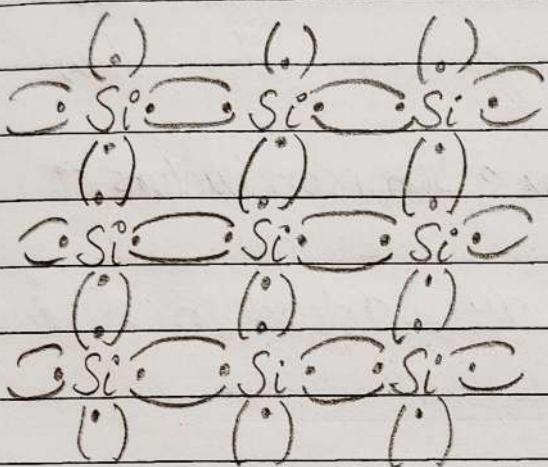
(iii) Semiconductors :- The solids in which valence band and conduction band are separated by an energy gap of less than 3 e.v. (E_g is small)

- In semiconductors, valence band and conduction band are partially filled.
- At 0°K temp., e^- are not able to cross even the small energy gap and hence the conduction band remains totally empty. Therefore, Semiconductors at 0°K behaves as insulators.
- However, at room temperature, some e^- in valence band acquire thermal energy greater than 3eV & jump over to the conduction band. So, Semiconductors acquire small conductivity at room temperature.



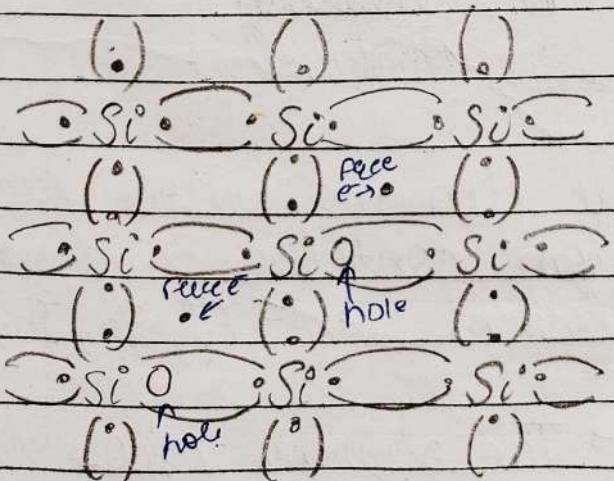
(i) Intrinsic Semiconductors :-

- A pure semiconductor is called intrinsic semiconductors.
- Current carriers are produced by temperature
- Ex → Silicon (Si), Germanium (Ge)



• Each Si has 4 valence electron

- At low temperature → act as insulator
- At high temperature from temperature → covalent bond breaks → e⁻ becomes free
- The valency so created is called hole.
- The hole is of +ve charge



- The hole can be filled by e^- when other covalent bond breaks. The same pattern is followed by holes and e^- again & again and ~~and~~ electric current will flow.
 - Intrinsic Concentration $\rightarrow n_i = \frac{N_e}{\text{no of } e^-} = \frac{N_h}{\text{no of holes}}$

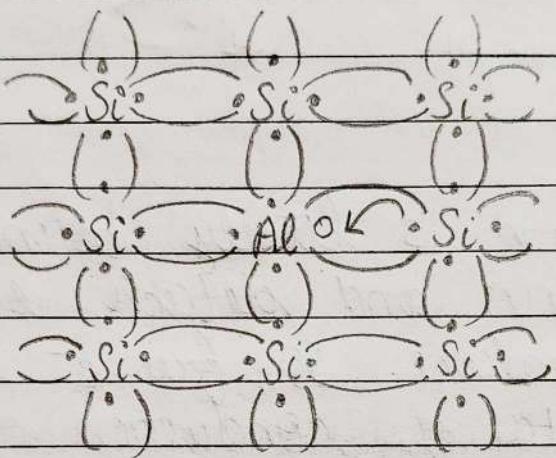
* Extrinsic Concentration \Rightarrow Semiconductors \rightarrow

- Suitable impurities are added in extrinsic semiconductors.
 - Doping → The process of adding impurities in the intrinsic or pure semiconductor is called doping.
 - Dopant → The impurities so added are called dopant

- Trivalent impurity \rightarrow The elements whose each (Acceptor impurities) atom contains 3 valence electrons, ex \rightarrow Al, Ga, In, Th
 - Pentavalent impurity \rightarrow The elements whose each (Donor impurities) atom contains 5 valence electrons \rightarrow P, As, Sb, Bi

Types of Extrinsic Semiconductor

(i) P-type semiconductor :- When a trivalent impurity is added to pure $^{(Si)}$ crystal, a p-type extrinsic semiconductor is formed. ex (Al)

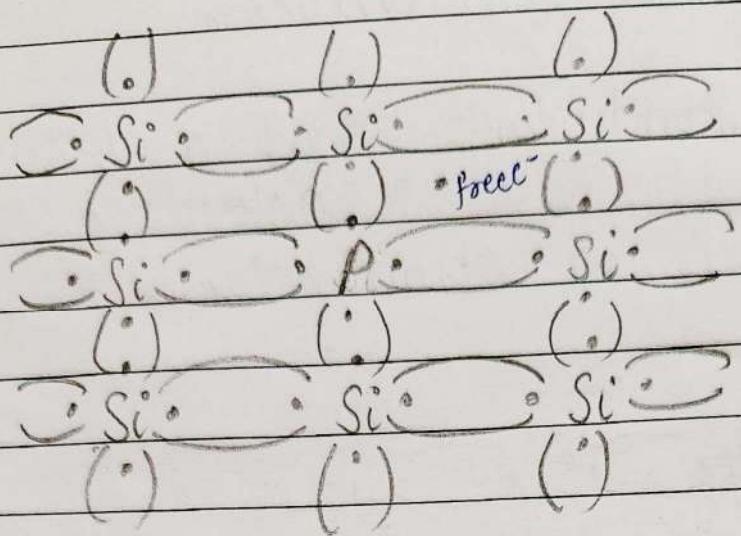


- The Al forms 3 covalent bonds with neighbouring 3 Si atoms. The 4th bond remain unaccommodate which was deficient of one electron (This deficiency is called hole). This hole attract e^- to fill itself.

$$\text{Concentration} \rightarrow N_A > N_e$$

(ii) n-type semiconductor \rightarrow When a pentavalent impurity is added to the pure silicon crystal, n-type semiconductor is formed.

- Trivalent impurity has 5 valence e^- , i.e. are free to move.

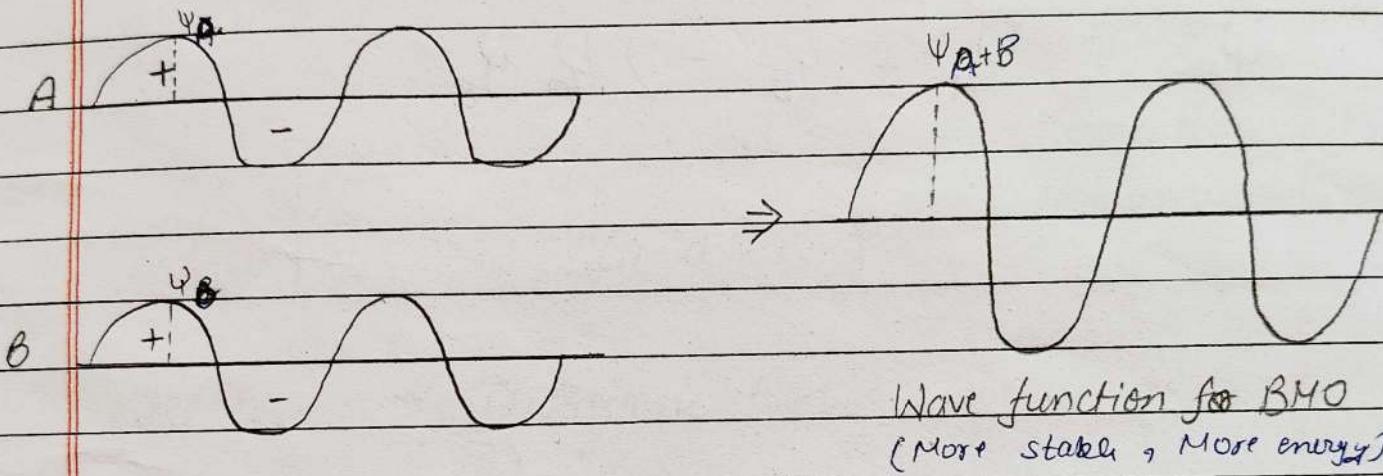
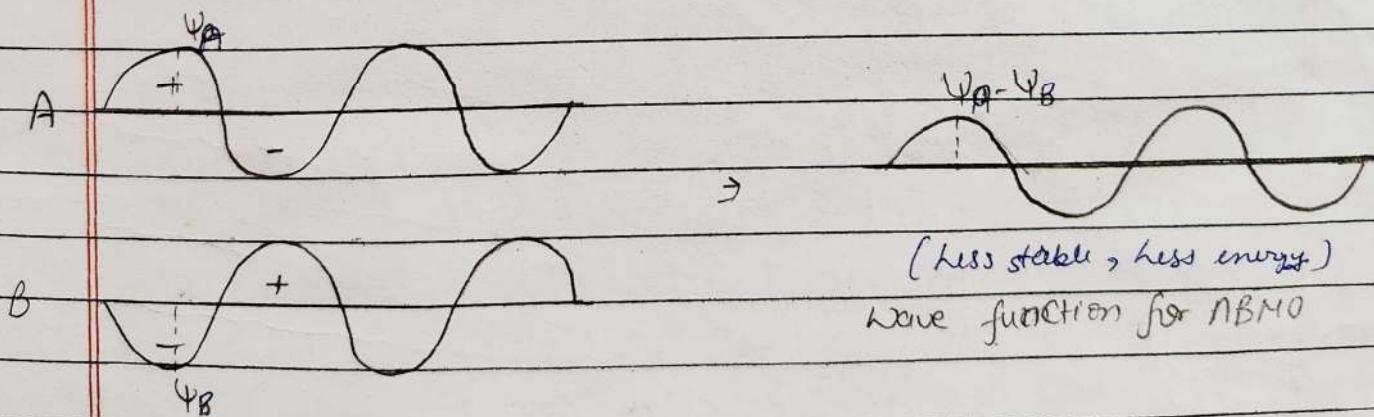


- The 5th electron is loosely bounded to its parent nucleus and detach easily at room temperature. So, free e^- are available in the crystal for conduction of current.
- Concentration $\rightarrow n_e \gg n_h$

Equation of atomic and molecular orbital (LCAO)

① Addition \rightarrow (in phase bonding)

- When the two waves are in phase so they add up and the amplitude of the wave is $\Psi_A + \Psi_B$

② Subtraction \rightarrow (out phase bonding)

- When the two waves are out of phase, the waves are subtracted from each other so that amplitude of new wave is $\Psi_A - \Psi_B$

$$\psi_b = \psi_A + \psi_B$$

-(1)

$$\psi_a = \psi_A - \psi_B$$

-(2)

Wave function for BMO

$$\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\psi_a^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$