

# Crystal field theory

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• d Crystal field theory (CFT) is a model for d bonding interaction b/w transition metals & ligand. It describes d effect of d attraction b/w d +ve charge of d metal cation & -ve charge on d non-bonding e<sup>-</sup>s of d ligand.

- CFT was developed by physicist Hans Bethe & John Hasbrouck van Vleck in 1930s.
- Metal & ligand formed complex. The d orbital splitting shown in CFT can't explain splitting of only d-orbitals does not comment on s & p orbital.
- CFT always give d exact value of magnetic moment.
- It doesn't give information about hybridization.
- Shape of orientation of 3d-orbitals in metal ions.

① d<sub>xy</sub>

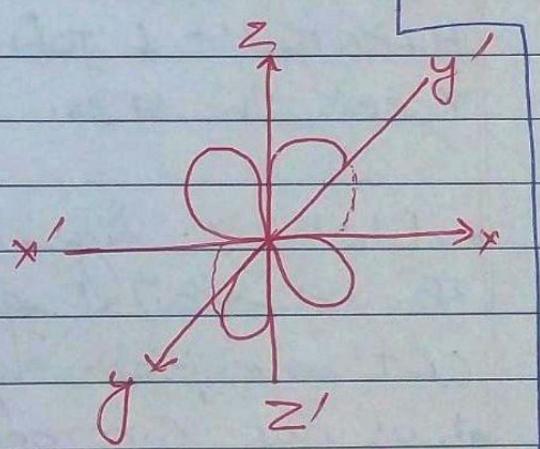
② d<sub>yz</sub>

③ d<sub>zx</sub>

④ d<sub>xyz</sub>

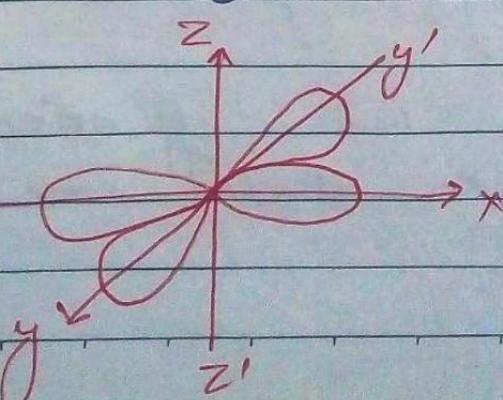
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Lobes by axis

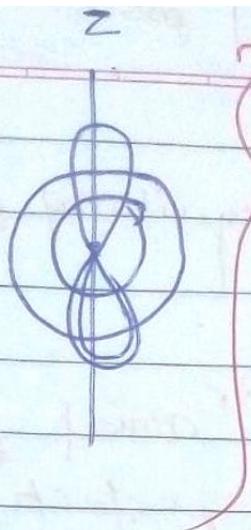


- CFT is bonding model that explains many important properties of Transition metal complexes including their color, magnetic prop., stability & reactivity.

llobes  
on a  
axis



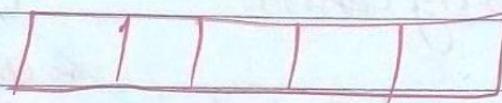
⑤  $d_{2^2}$



lobes on d axis

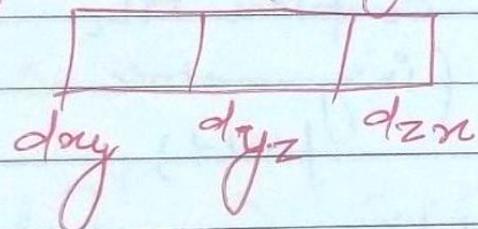
### Basic terms

①

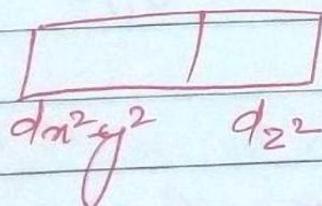


degenerated orbitals  
means orbitals of  
equal energy.

②  $t_{2g}$  set (triply degenerated)



③  $eg$  set (doubly degenerated)

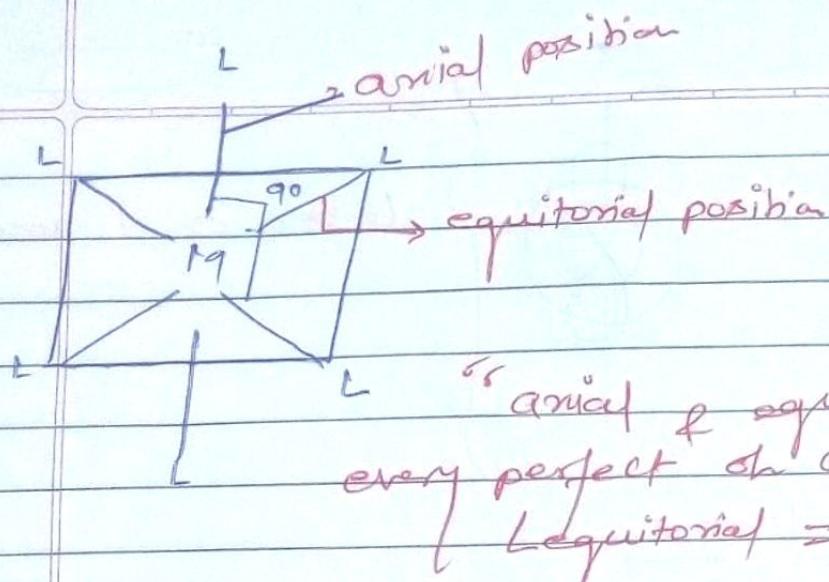


~~Crystal field splitting~~

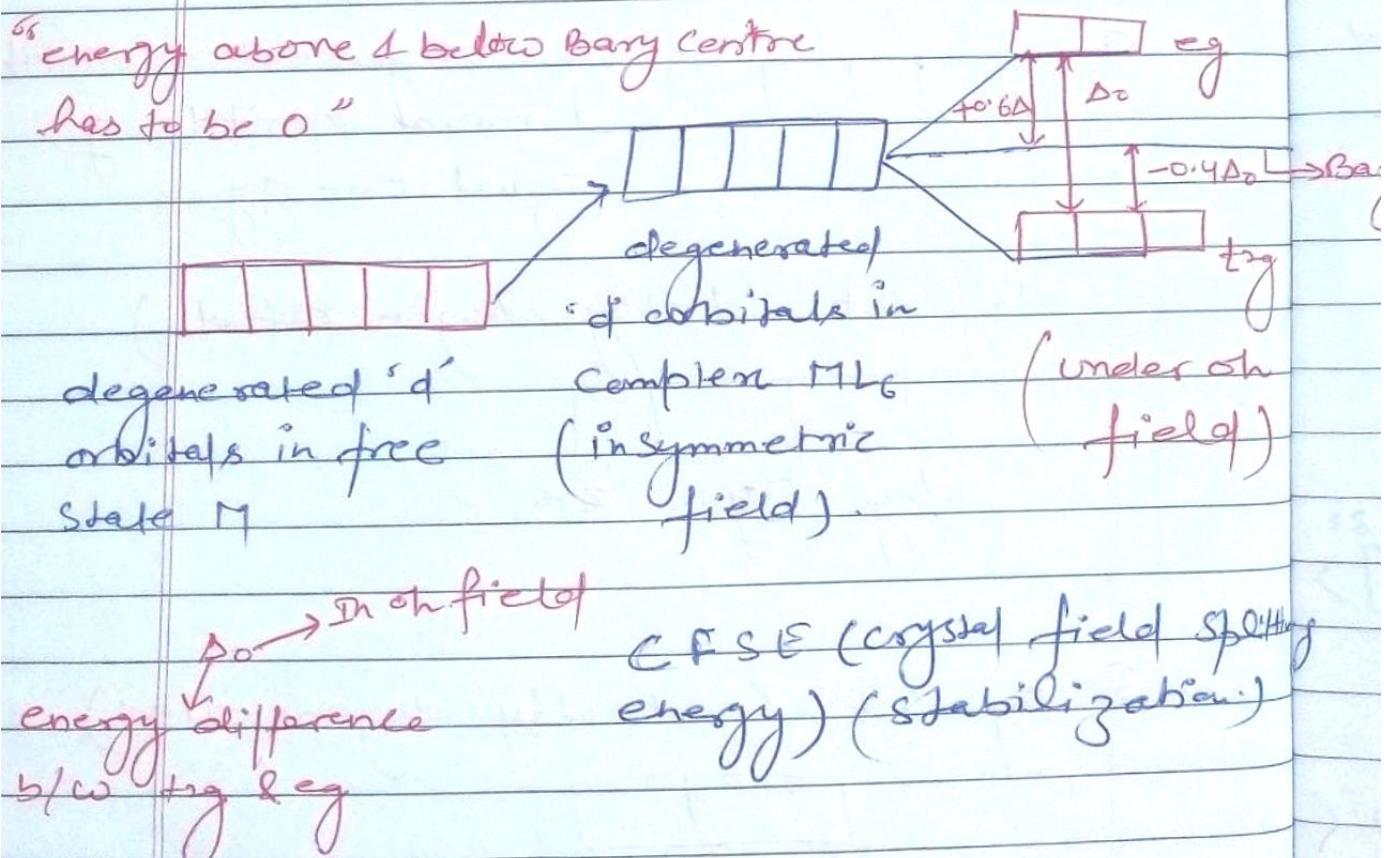
① oh case:-

{  $e^-e^-$  repulsion more in case of lone pair on anis  
 electrostatic attraction in case of lobes by d.o.m.

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"energy above & below Bary centre  
has to be 0"

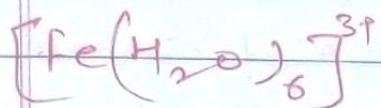
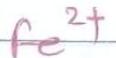
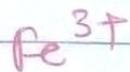
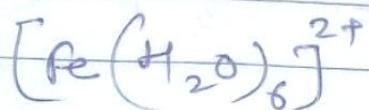
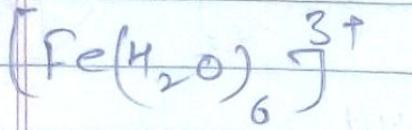


factor affecting (CFSE):-

- ① oxidation no. of central metal : - Generally higher oxi<sup>n</sup> no. of metal d greater o CFSE crystal field splitting.

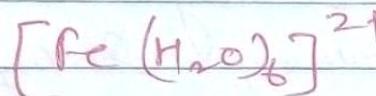
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CFSE  $\propto$  oxi no. of Central metal.



$$\Rightarrow n + (6 \times 0) = +3$$

$$n = +3$$



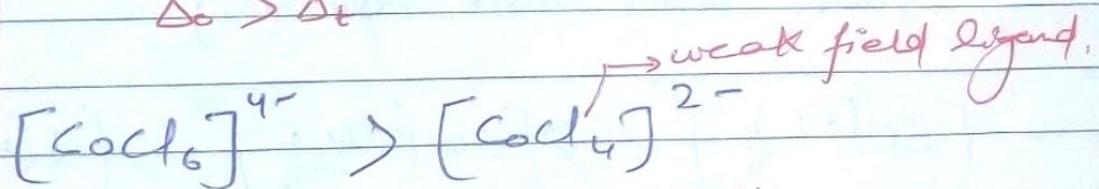
$$\Rightarrow n + (6 \times 0) = +2$$

Barycentre

$$n = +2$$

## ② Geometry:-

$$\Delta_o > \Delta_t$$



Coordination no. = 6

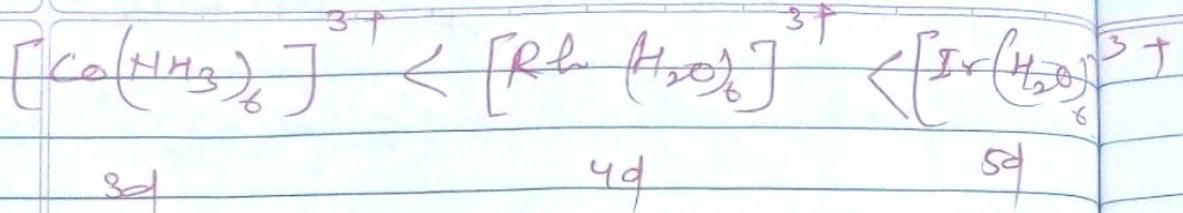
Coordination no. = 4

oh

td

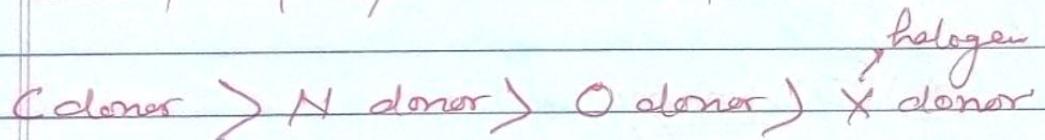
③ d-series) - d crystal field splitting  
 oh  $\leftarrow$   $\Delta_o$  is about 50% greater than  $\Delta_t$  for  
 II<sup>nd</sup> transition series compared to I<sup>st</sup>  
 whereas d 3rd series is about 25%  
 greater than d II<sup>nd</sup>.

$$3d < 4d < 5d$$

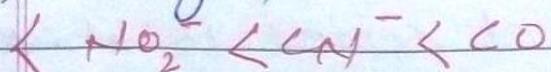
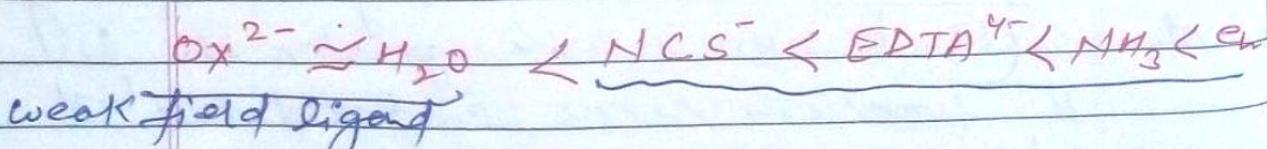
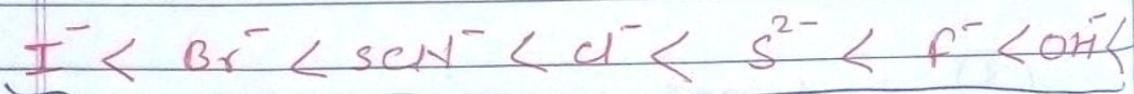
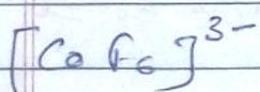
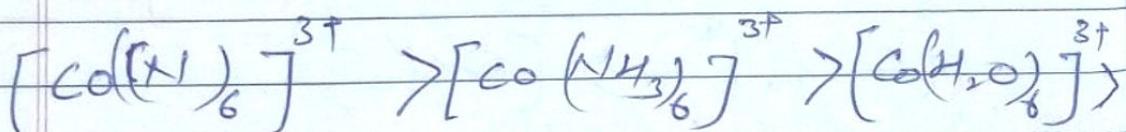


(<sup>z</sup> Greater size more repulsion)

④ Nature of Ligand: " of Common ligands can be ordered on the basis of d effect at dy lone and CFSE splitting. This increasing listing is called d Spectrochemical series.



(more donor more repulsion)



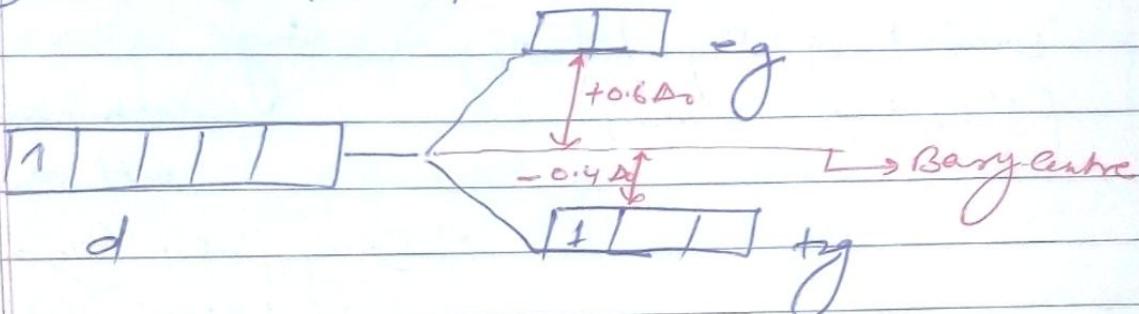
Strong field ligand

## Calculation of CFSE

(1) In d<sub>4</sub> Case (Co-ordination No. = 6)

$$CFSE = (+0.6 \Delta_0) \times eg + (-0.4 \Delta_0) \times tg$$

(2) Case i.e. d<sup>1</sup>



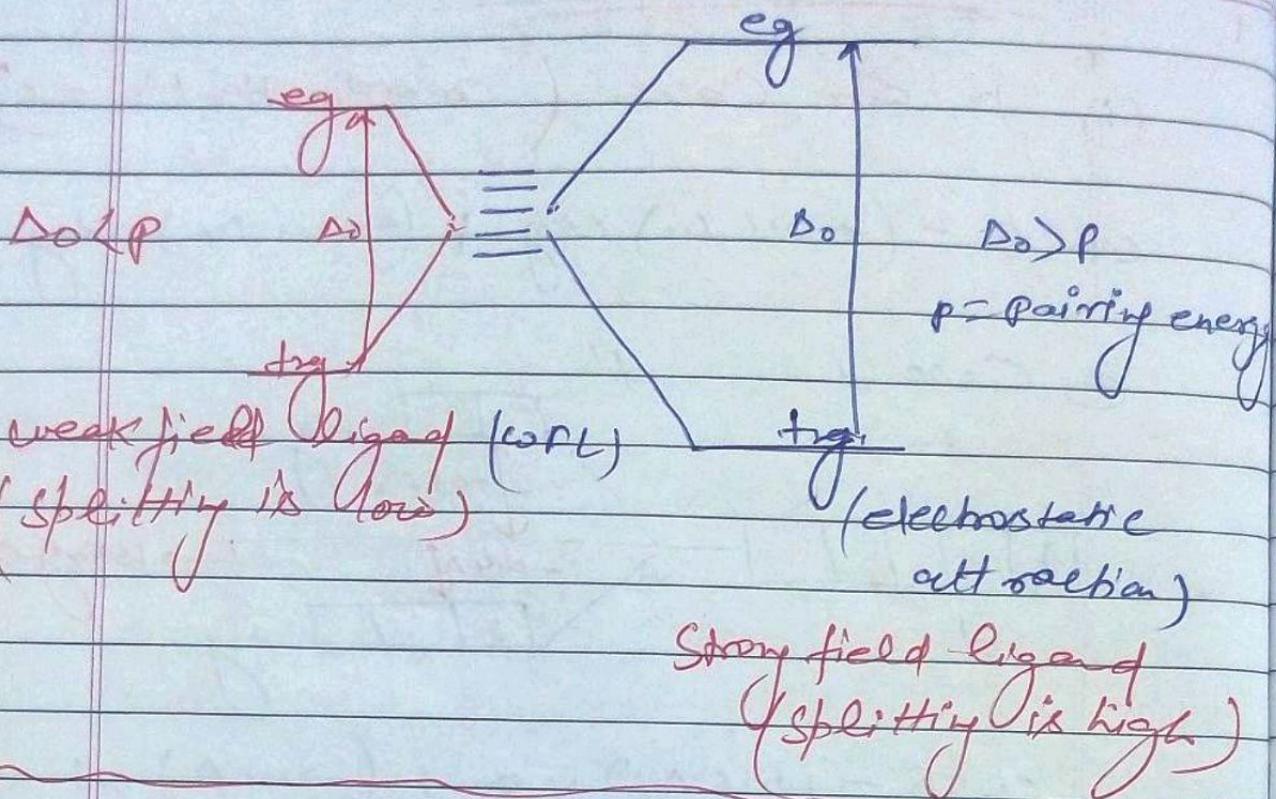
$$CFSE = (+0.6 \Delta_0) \times 0 + (-0.4 \Delta_0) \times 1$$

$$= -0.4 \Delta_0$$

same as d<sup>2</sup> d<sup>3</sup> d<sup>4</sup> d<sup>5</sup> d<sup>6</sup> d<sup>7</sup> d<sup>8</sup>  
d<sup>9</sup> & d<sup>10</sup>.

NOTE :- d more Strong field ligand you take more electrostatic repulsion thus more splitting of d-orbitals. ~~so d splitting of d-orbitals will depend on d ligand field.~~

- Higher oxidation state of metal hence higher electrostatic attractions  $\rightarrow$  higher  $e^- - e^-$  repulsion  $\rightarrow$  higher splitting of orbitals



$\text{Cr}^{3+}$  (d<sub>3</sub>) (C<sub>2h</sub>) (High spin complex)  $\rightarrow$  follows Hund's rule

## Key points:-

pairing energy need to be taken into account only for pairing at is additional to d pairing at occurs in spherical field.

Configuration	$t_{2g}$	$e_g$	$n$	$M.M.$ (u)	Spin(s) ( $2s+1$ )	spin multiplicity ( $2s+1$ )	Nature
d <sub>1</sub>	1 - -	- -	1	$\sqrt{3}$	1/2	2	paramagnetic
d <sub>2</sub>	1 1 1	- -	2	$\sqrt{8}$	1	3	4
d <sub>3</sub>	1 1 1	- -	3	$\sqrt{15}$	3/2	4	4
d <sub>4</sub>	1 1 1	1 -	4	$\sqrt{24}$	2	5	4
d <sub>5</sub>	1 1 1	1 1	5	$\sqrt{35}$	5/2	6	4
d <sub>6</sub>	1 1 1 1	1 1	4	$\sqrt{24}$	2	5	4

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$$\begin{aligned}
 \underline{\underline{d^6}} &\Rightarrow (0.6\Delta_0) \times 2 + (-0.4\Delta_0) \times 4 \\
 &= 1.2\Delta_0 - 1.6\Delta_0 \\
 &= -0.4\Delta_0
 \end{aligned}$$

same as  $d^7$   $d^8$   $d^9$  &  $d^{10}$ .

CFSE ( $\Delta_h$ ) (SFL) ( $\Delta_o \rightarrow P$ ) (Low spin Coflen)  $\rightarrow$

does not follow Hund's rule

Configur + g eg n m.m. spins (2S+1) Nature CFSE

$d^1$	$1_{--}$	$--$	$1_{-}$	$\sqrt{3}$	$1/2$	$2$	para.	$-0.4\Delta_0$
$d^4$	$1_{\bar{b}} 1_{\bar{b}} 1_{\bar{b}}$	$--$	$2_{\bar{b}}$	$\sqrt{12}$	$1$	$3$	$4$	$-1.6\Delta_0$
$d^7$	$1_{\bar{b}} 1_{\bar{b}} 1_{\bar{b}}$	$1_{\bar{b}}$	$1_{\bar{b}}$	$\sqrt{3}$	$1/2$	$2$	$4$	$-1.8\Delta_0$
$d^9$	$1_{\bar{b}} 1_{\bar{b}} 1_{\bar{b}}$	$1_{\bar{b}} 1_{\bar{b}}$	$1_{\bar{b}}$	$\sqrt{3}$	$1/2$	$2$	$4$	$-0.6\Delta_0$
$d^{10}$	$1_{\bar{b}} 1_{\bar{b}} 1_{\bar{b}}$	$1_{\bar{b}} 1_{\bar{b}}$	$0$	$0$	$0$	$0$	diaagnetic	$0$

### Magnetic properties

specific

CFSE

① biamagnetic - repel in magnetic field  
     • No unpaired e<sup>s</sup>

② paramagnetic, attracted in magnetic field

• unpaired e<sup>s</sup> present

$-0.8\Delta_0$

$-0.2\Delta_0$

$-0.6\Delta_0$

$-0.0\Delta_0$

$-0.4\Delta_0$

- Greater d no of unpaired e<sup>-</sup>, greater will be paramagnetism & magnetic moment.

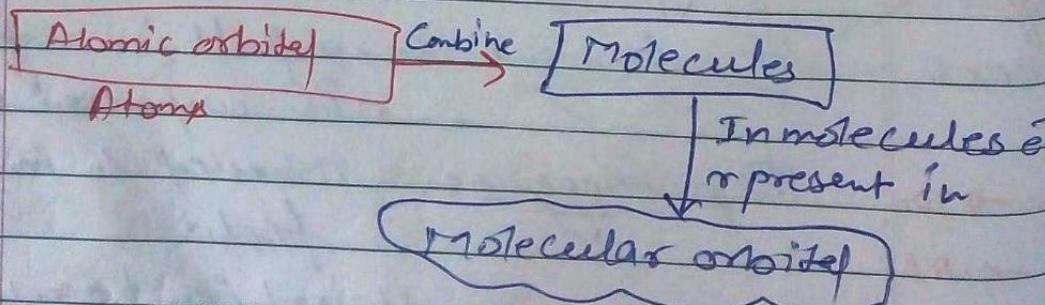
- For ferromagnetic magnetic moment is given by contribution of spin angular momentum & orbital angular momentum

$$\mu_{(S+L)} = \sqrt{4s(s+1) + L(L+1)} \text{ B.M.}$$

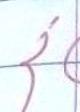
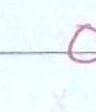
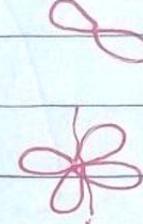
## MOT (Molecular orbital theory)

introduced by F. Hund & R.S. Mulliken

VBT Consider O<sub>2</sub> as diamagnetic. Experimentally O<sub>2</sub> was found to be paramagnetic. Magnetic behavior of the molecule was explained by the theory.

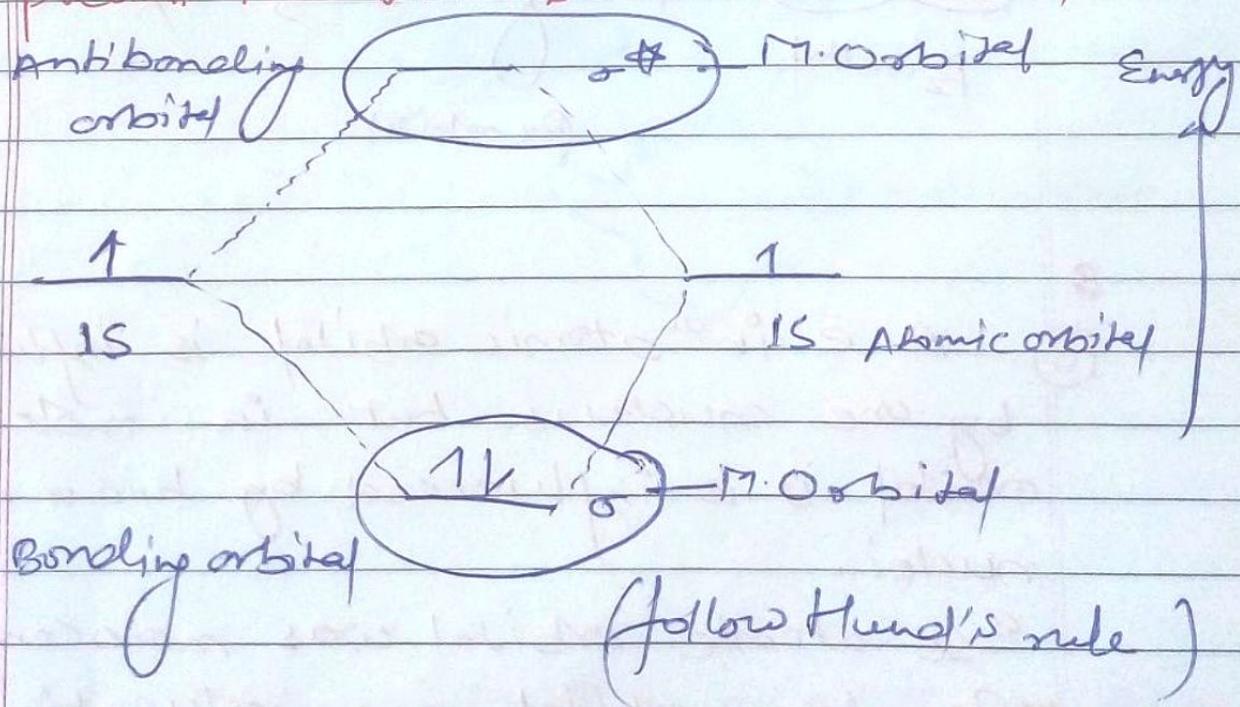


what & type of atomic orbital (A.O.)

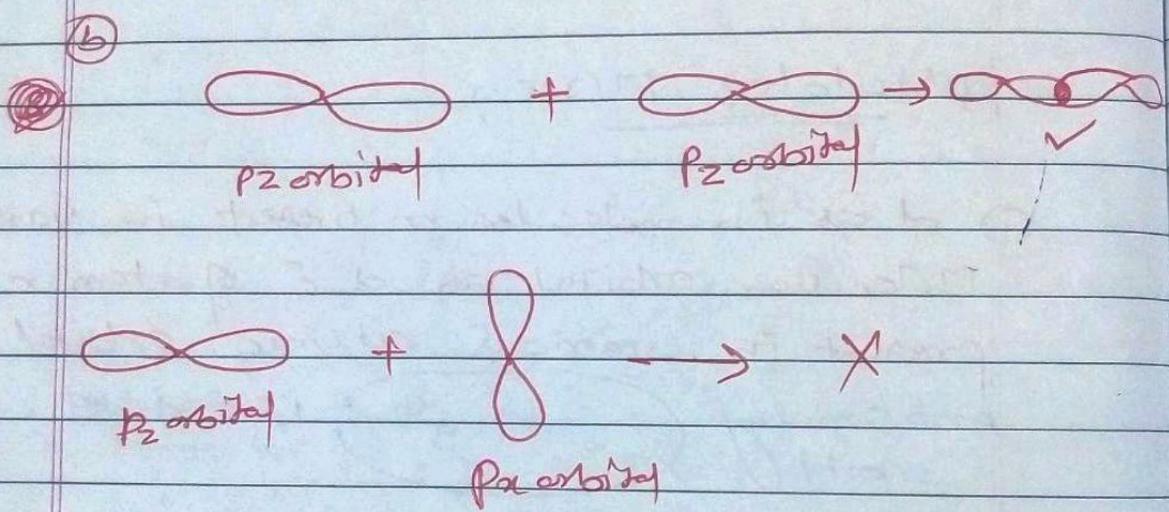
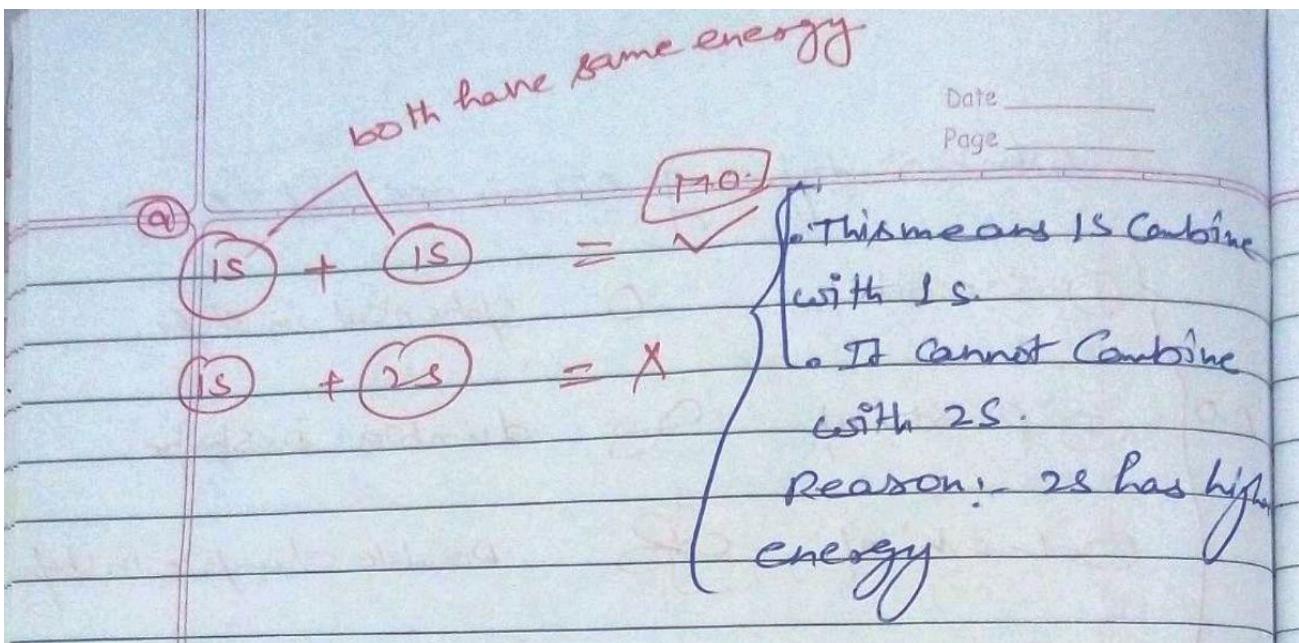
- |  |  |  |
|--|--|--|
| <br>① s orbital | <br>② p orbital | <br>③ d orbital |
|  |  | spherical in shape.  |
|  |  | dumbbell in shape.   |
|  |  | Double dumbbell in shape.  |

### Postulates MOT :-

- ① d es in molecules & present in various molecular orbital as d e of atom & present in various atomic orbitals.



- ② d atomic orbitals of comparable energies & proper symmetry to form molecular orbitals.



③ A  $\text{e}^-$  in an atomic orbital is influenced by one nucleus but in molecular orbital it is influenced by two or more nuclei.

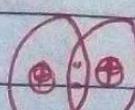
"So atomic orbital was mono centric but molecular orbitals are poly centric"

$\rightarrow \text{H}$

nucleus ①



$\text{H}_2$



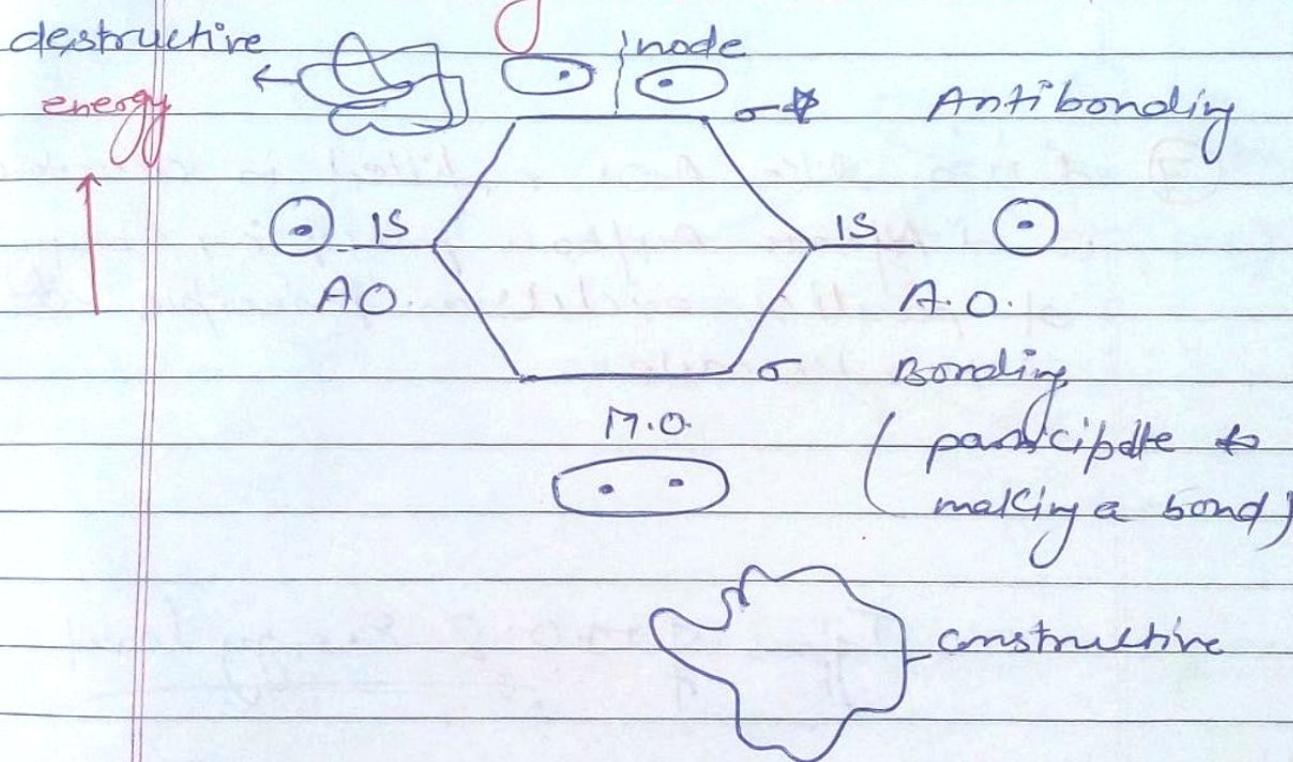
poly nucleus

{more energy less stable}  
 {less energy more stable}

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N.Dub  
④

d no. of M.O. formed is equal to d no. of combining A.Os. when two A.Os combine, two molecular orbitals are formed. one is known as bonding M.O. while the other is called anti-bonding molecular orbital.



⑤ d bonding molecular orbital has lower energy & hence greater stability than d corresponding antibonding molecular orbital.

{  
 orbital - e<sup>-</sup> found  
 A.O. - e<sup>-</sup> found in atom  
 M.O. - e<sup>-</sup> found in molecule

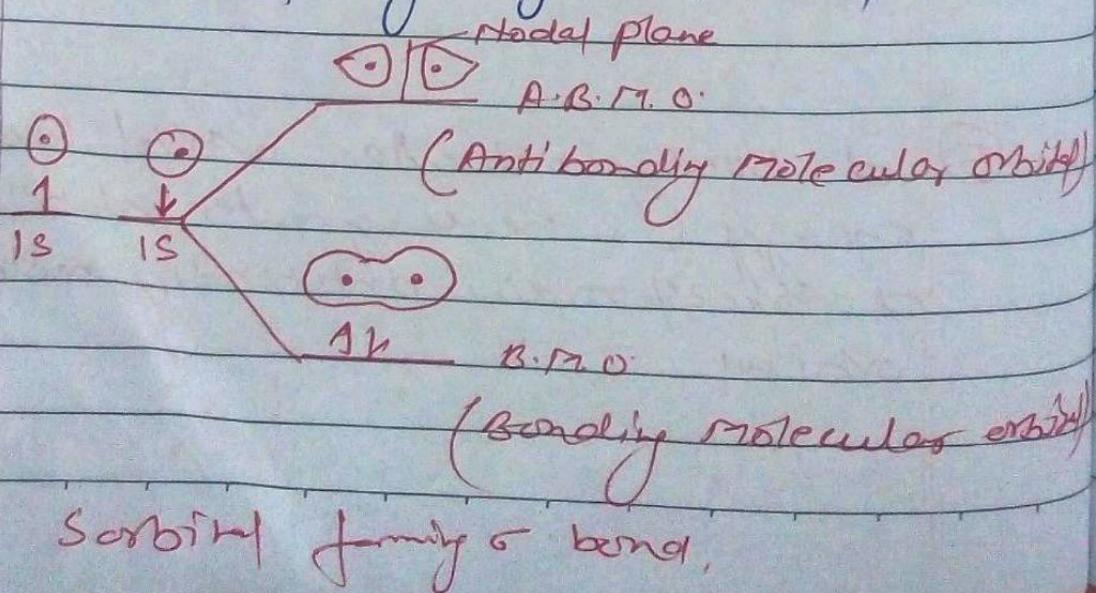
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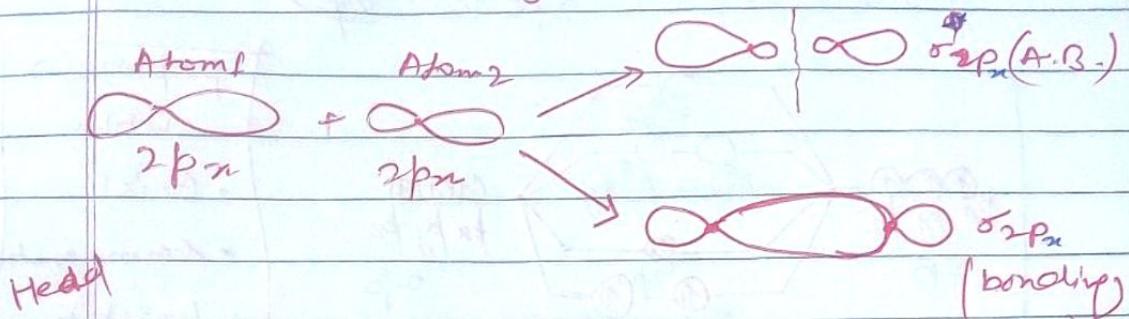
- just as d e<sup>-</sup> probability distribution around a nucleus in an atom is given by A.O., d e<sup>-</sup> probability distribution around a group of nuclei in molecule is given by a molecular orbital.
- ⑦ d M.O. like A.O.s r filled in accordance w/ d ~~Aufbau~~ Aufbau principle, obeying d pauli's exclusion principle & d Hund's rule.

### Types of M.O. & Energy level

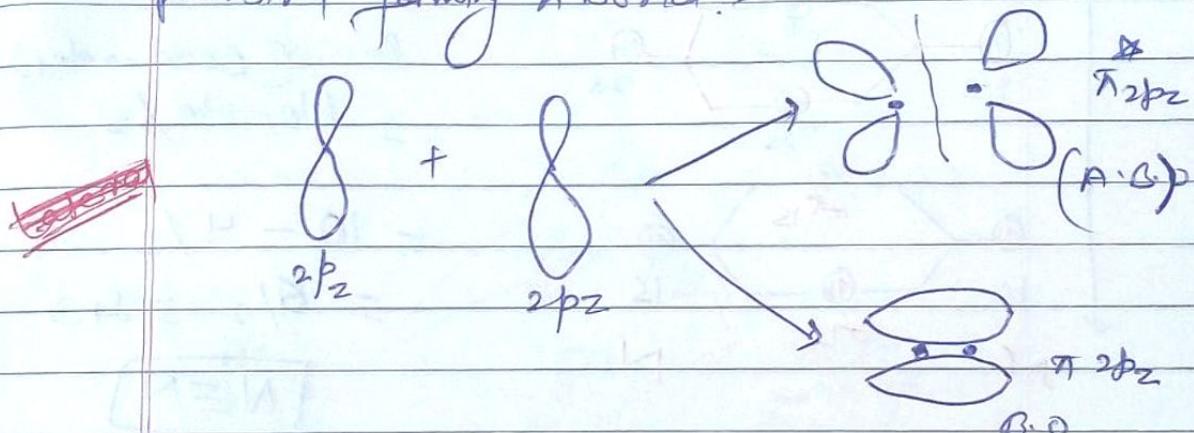
NoTE:- S orbitals forming sigma bond & p orbitals forming sigma & pi bond.



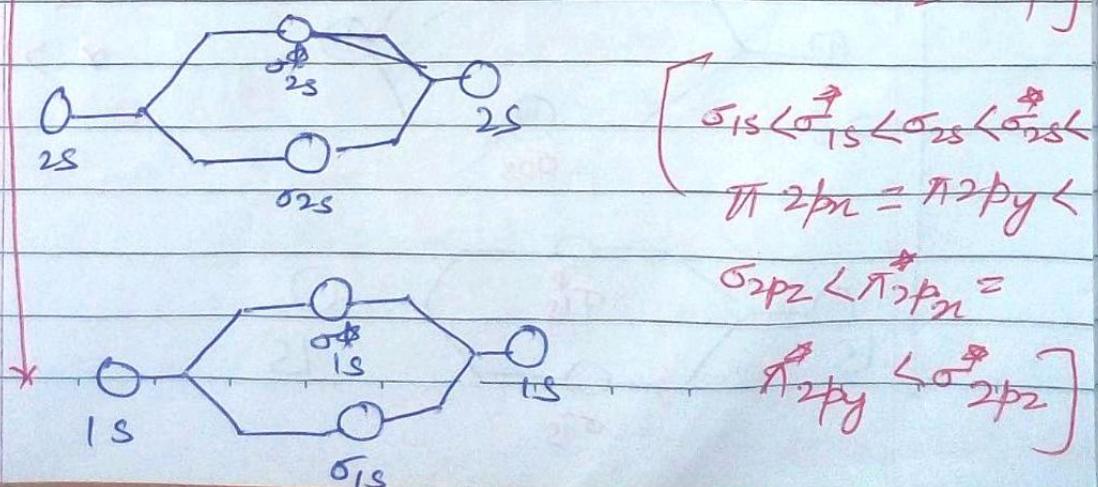
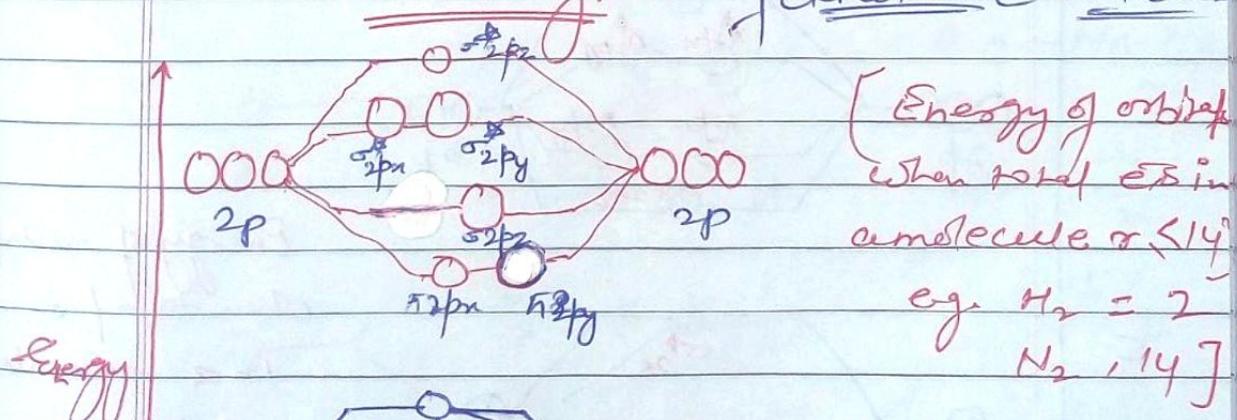
p-orbital forming sigma bond:-



p-orbital forming pi bond:-

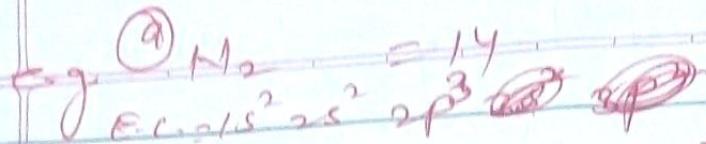


M.O. Diagram of diatomic molecule

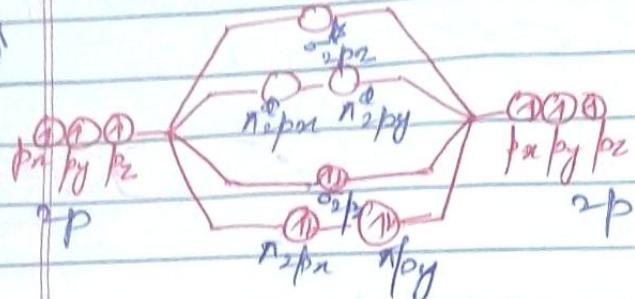


$\sigma$  bond is more stronger than  $\pi$  bond.

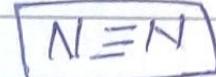
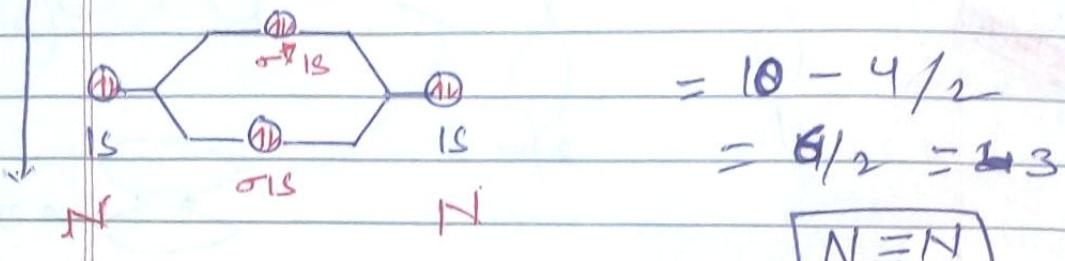
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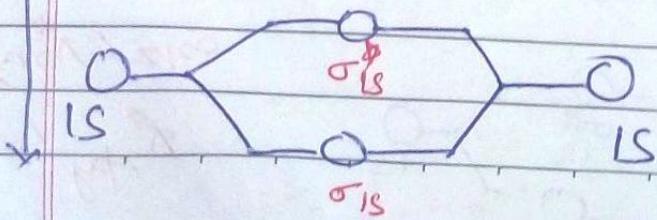
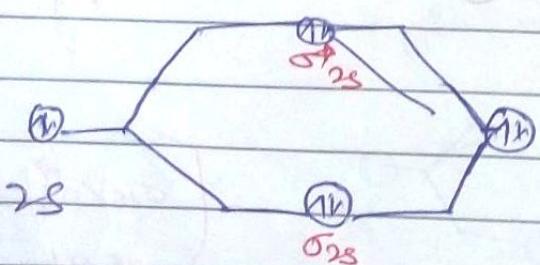
properties →  
 - stable  
 - Exist  
 - diamagnetic  
 - low spin colorless

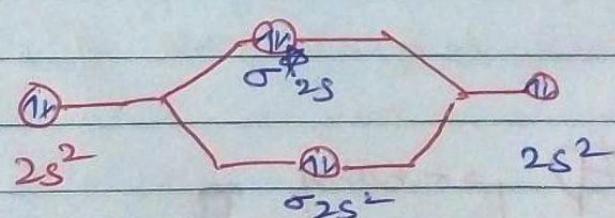
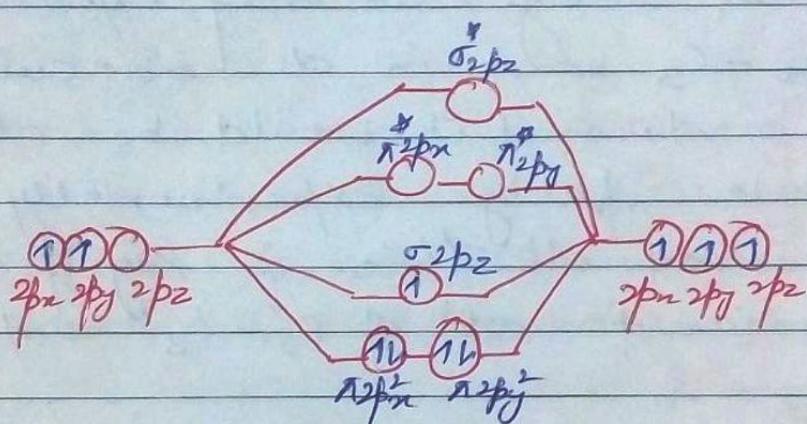
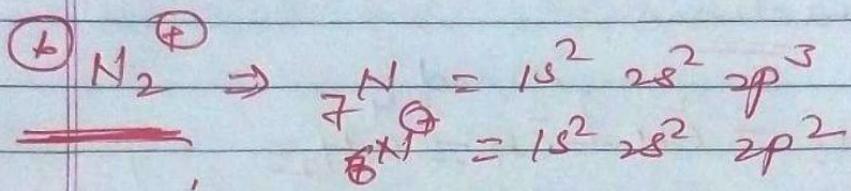
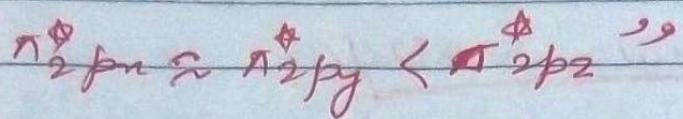
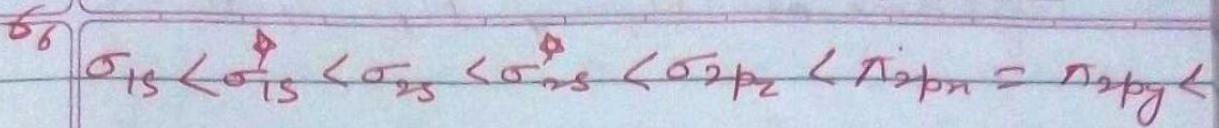


B.O. (Bond order)  
 $= \frac{16 - 4}{2} = 6$



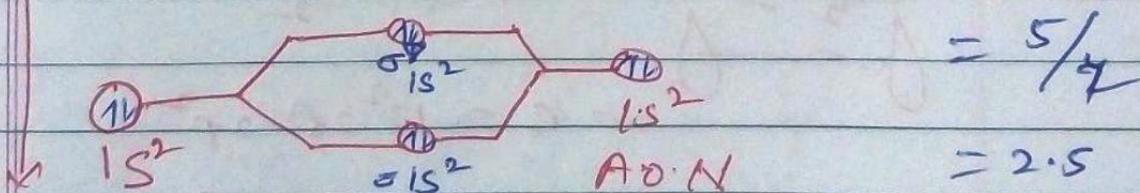
Energy of orbitals  
 when total  $E_{\text{C}}$   
 in a molecule  
 $> 14$





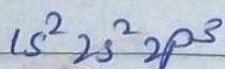
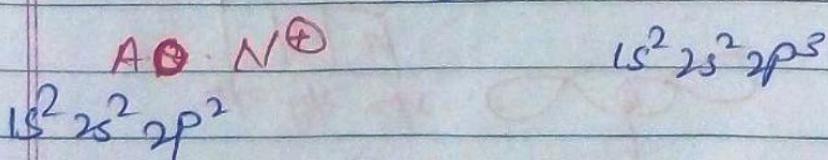
$$\text{B.O.} = \frac{N_B - N_A}{2}$$

$$= \frac{9 - 4}{2}$$



$$= \frac{5}{2}$$

$$= 2.5$$



Properties -

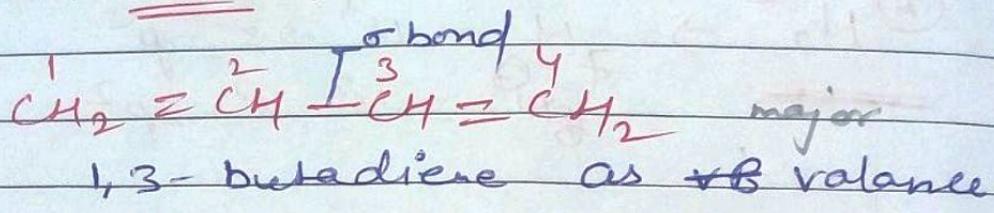
- Stable
- Exist
- paramagnetic
- High spin - coloured

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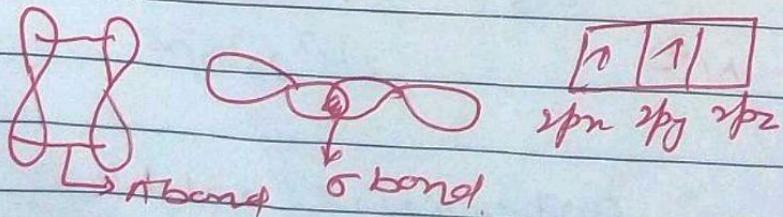
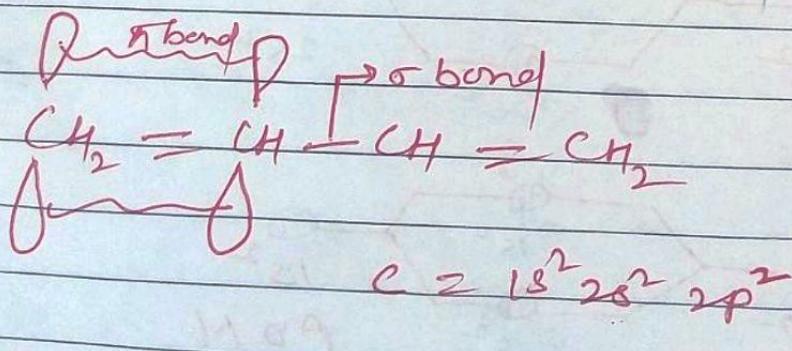
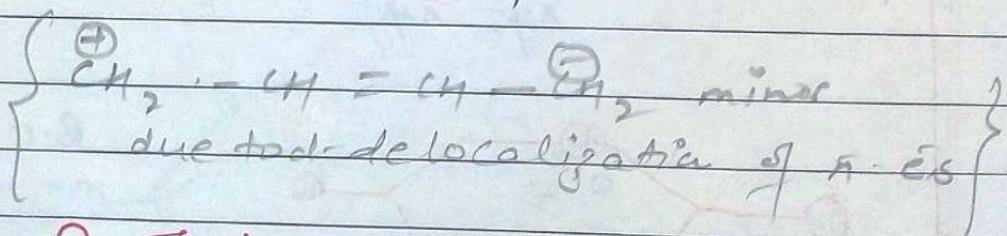
Same as  $H_2^{2+}$ ,  $N_2^-$ ,  $O_2$

### $\pi$ -molecular orbitals :-

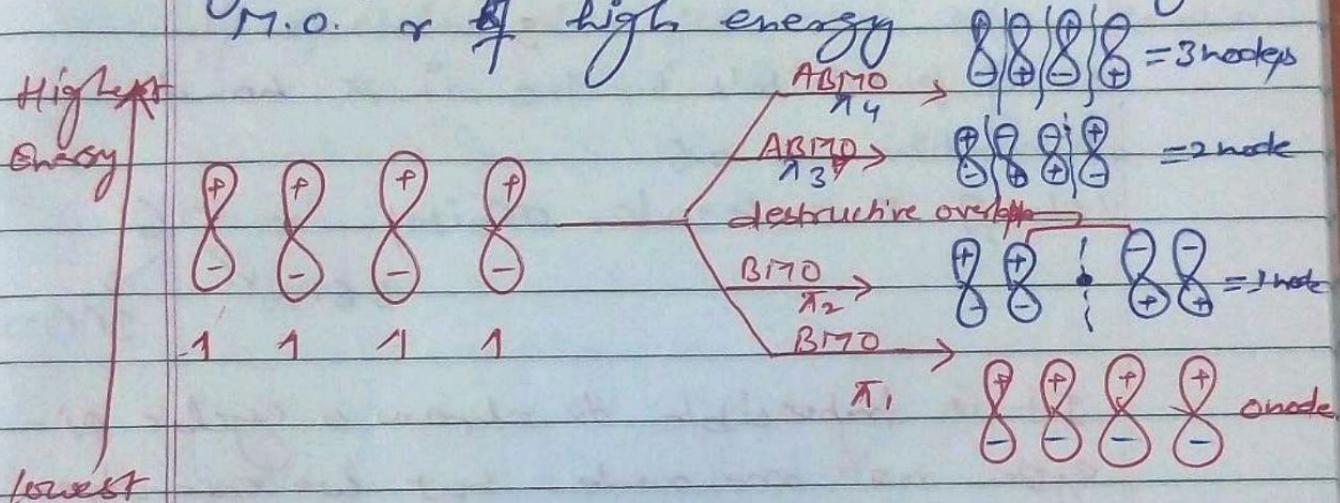
#### (i) Butadiene:-



orbital theory, we may expect all  $C_2 - C_3$  bond in the molecule to be  $\sigma$  bond, and it would be able to rotate freely. Experimentally it is observed that there is significant barrier to rotation of  $C_2 - C_3$  bond.



↓ four 2p orbitals combine mathematically to form 4  $\pi$  molecular orbitals of increasing energy. Two of these are bonding MOs & having low energy than d p-orbitals (atomic orbital from which they are formed), while two antibonding  $\pi^*$  MOs are at high energy.



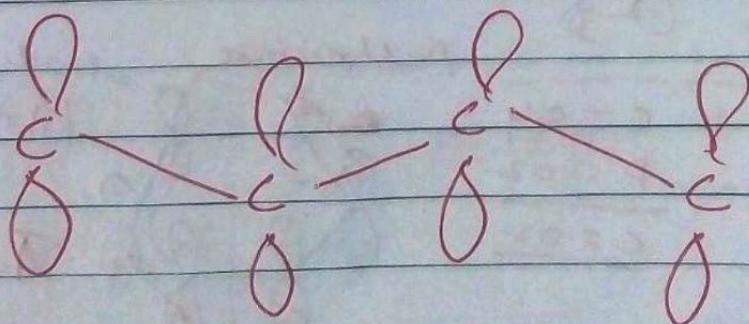
node → where probability of finding an  $e^-$  is minimum, where phase change.

level =  $(n-1)$  node

$\pi_1 = (1-1) \text{ } 0 \text{ node}$

$\pi_2 = (2-1) \text{ } 1 \text{ node}$

$\pi_3^* =$

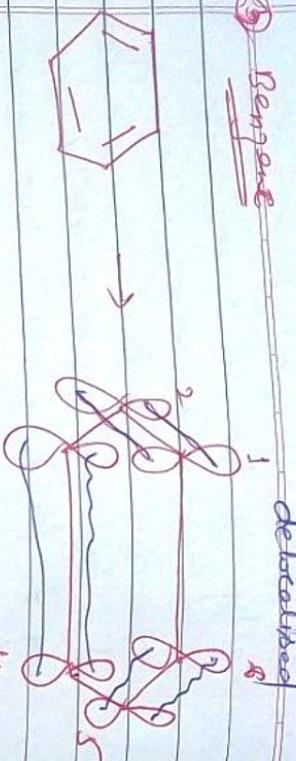


Bengene

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- Planar, hexagonal, cyclic structure
- Each carbon has sp<sup>2</sup> hybridizing
- All C-C bonds are equal in length due to delocalization of electrons
- Stable compound
- one hybridized p orbital is present perpendicular at each carbon.



No. of  $\sigma$ -bonds involve in  $\pi$  bond formation = 06  
No. of  $\pi$  molecular orbitals = 06

It is impossible to draw a cyclic  $\pi$ -system with one node, but we can draw a system in one nested plane.

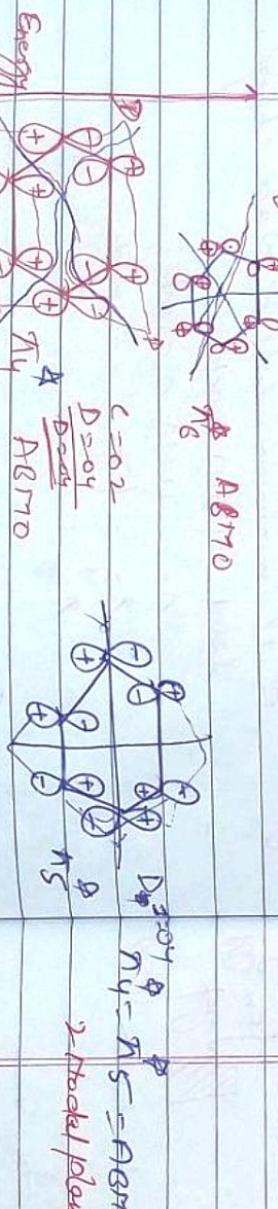


Diagram illustrating the atomic structure of Boron (B) in its ground state.

- Outermost shell:** Contains three 2p atomic orbitals (AOs), each containing one electron ( $+/-$ ). These are labeled  $\pi_1$ ,  $\pi_2$ , and  $\pi_3$ .
- Second shell:** Contains two 2p AOs, each with one electron ( $+/-$ ).
- Third shell:** Contains one 2p AO with one electron ( $+/-$ ).
- Inner shells:** Two 1s AOs, each with two electrons ( $++$  and  $--$ ).

The total number of electrons is 5.

Annotations:

- Nodes:** Nodes are shown as dashed circles. The 1s shell has no nodes; the 2s shell has one node; the 2p shell has three nodes; and the 3s shell has one node.
- Energy:** The energy levels are indicated by horizontal lines. The 1s level is the highest, followed by the 2s, then the 2p, and finally the 3s.
- Degeneracy:** The 2s,  $\pi_1$ , and  $\pi_2$  levels are labeled as "degenerate orbits".
- Pauli Principle:** The label "No two electrons can have the same set of quantum numbers" is present.

~~Diagrammatic representation of the construction of a bridge~~