Unit 1 3rd sem

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VBT (valance bond theory)
(Pauling)

2) Molecular Orbital theory (MOT):
Given by Hund & Mulliken.

- This theory is proposed by Hund and Mulliken
- In 1966. the main point of this theory are -
1. All atomic orbitals (filled or unfilled) of bonding atom take part in overlapping (Bond formation).
2. When two atomic orbitals overlaps with each other, two new molecular orbitals are formed which are known as bonding molecular orbitals & antibonding m.ob.,
Bonding atomic orbital have lower energy and greater stability.
while antibonding m.o has higher energy and low stability.
3. By overlapping of all atomic orbitals of two Bonding atoms, same no. of new m.o are formed, Half of them will be Bonding M.O and remaning half will be antibonding m.o. these new m.o have different energies.

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(Some of them may have equal energy).

4. each M.O have max. two electrons with opposite spin.

5. All e^-s of Bonding Atoms are filled in New M.O in increasing Order of their energies. In case of M.O of equal energy, hund's Rule is followed

6. The bond Order (no of bond is given by

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

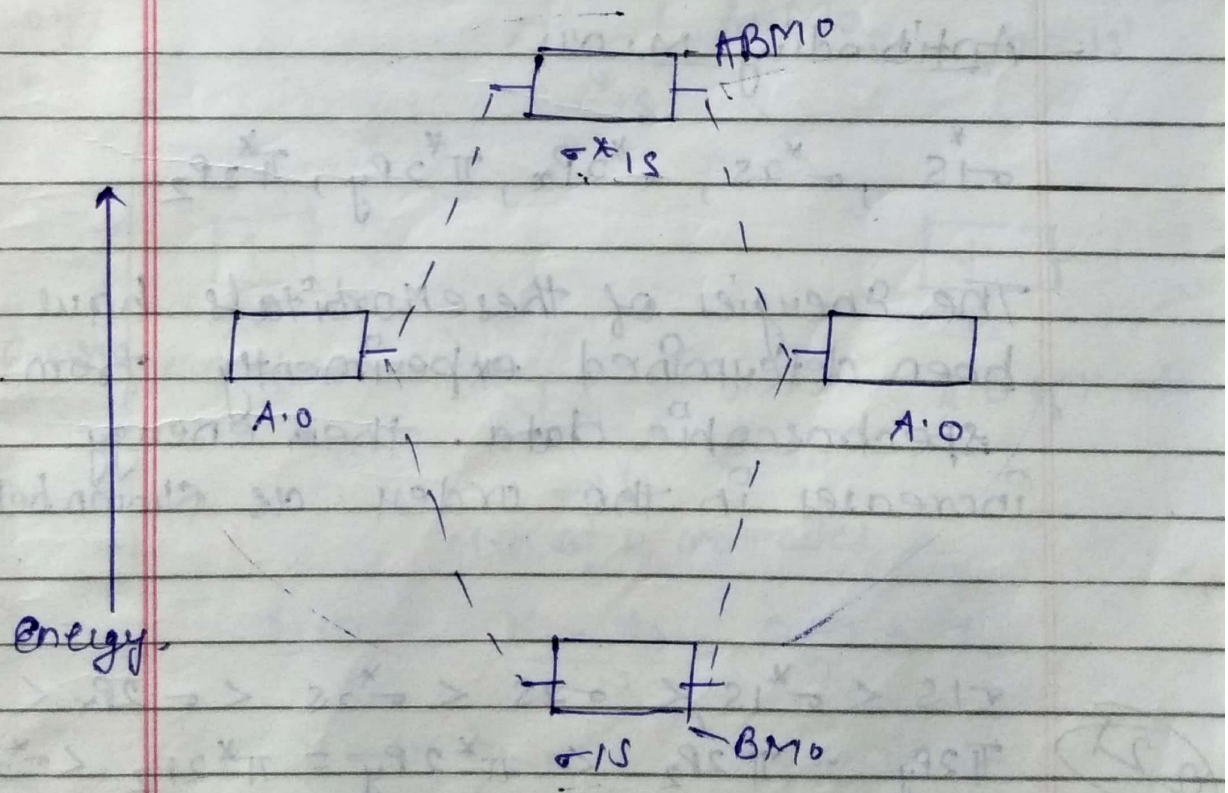
Here N_b is no. of $\bar{e}$'s in bonding M.O
N_a is " " " " antibonding "

7. The bond Order and the bond Strength are directly related with each other. therefore, Higher the bond order greater will be the Bond strength and greater will be the stability of molecules.

Bond order ∝ Bond strength ∝ Stability

According to MO theory when two atomic Orbitals come closer together, attraction and

repulsion forces act together. this theory proposes that two M·O are formed by overlapping of two atomic orbitals. one new M·O is due to attractive forces and other New M·O is due to repulsion forces. and they will be named as Bonding M·O and Antibonding M·O respectively. Bonding M·O has lower energy and greater stability while antibonding M·O has higher Energy and lesser stability. It may be shown as



5 marks

complete

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① Write a short note on followings

1- Bonding M.O.
2. Anti Bonding M.O
3. Non-Bonding M.O.

② Differenciate b/w VBT and MOT.
③ Diff. b/w antibonding M.O and Bonding M.O.

* Energy levels of M.O

- Bonding Molecular atoms :

$\sigma 1s, \sigma 2s, \sigma 2p_x, \pi 2p_y, \pi 2p_z$.

- Antibonding M.O's :

$\sigma^* 1s, \sigma^* 2s, \sigma^* 2p_x, \pi^* 2p_y, \pi^* 2p_z$.

The Energies of these M.orbitals have been determined experimently from spectroscopic data. then energy increases in the order as shown below:

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$

(12.21)

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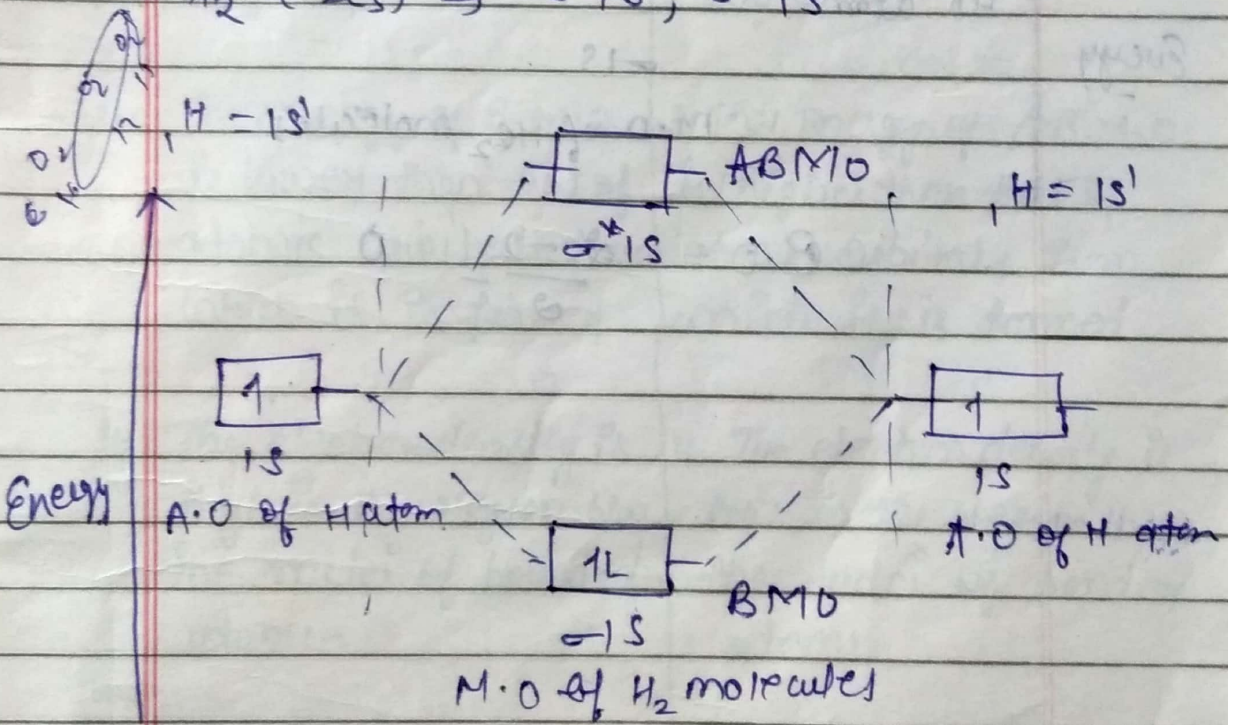
Note: In case of B_2, C_2, N_2 the order of energy of M.O's will be different as

2|2|1

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_y = \pi 2p_z < \sigma 2p_x < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$$

* Draw the M.O's Diagram of H_2 molecules

H_2 (2e⁻s) ⇒ $\sigma 1s^2, \sigma^* 1s^0$



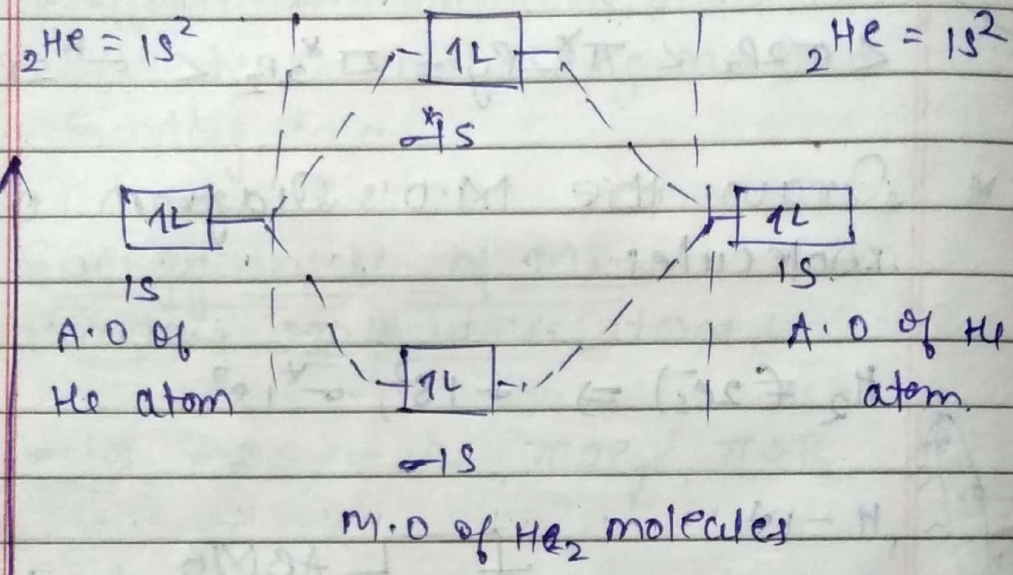
$$B.O = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

H – H ⇒ H_2

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Draw the MO of diagram of Helium molecule.

He_2 (4 e^-s) = $\sigma 1s^2$, $\sigma^* 1s^2$



$$B.O = \frac{2-2}{2} = 0$$

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* difference b/w Bonding M.O and Antibonding M.O.

Bonding M.O	Antibonding M.O
1. It is formed by aditive overlap of atomic orbitals.	1. It is formed by subtr. overlap of Atomic orbital.
2. Its formation takes place when lobes of atomic orbitals have same signs	2. Its formation takes place when lobes of atomic orbitals have different signs.
3. The energy of B.M.O. is lower than that of atomic orbitals from which it is formed	3. The energy of A.B.M.O is higher then that of atomic orbitals from which it is formed.
4. The electron density is high in the region b/w the nuclei of bounded atoms.	4. The electron density is low in the region b/w the nuclei of bonded atoms.
5. Every $e^{\ominus}$ in B.M.O contributes toward stability of the molecules	5. Every electron in A.B.M.O contributes toward unstability of the molecules.

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* Difference b/w VBT and MOT

VBT:

1. A molecule is considered to be made up of atoms.
2. Electrons in atom occupy atomic orbitals.
3. Orbitals may or may not be hybridized
4. If they are hybridized, atomic orbitals from the same atom combine to produce hybrid orbitals which can overlap more effectively with orbitals from other atom, thus producing stronger bonds.
5. The atomic orbitals (or the hybrid orbitals) are thought to remain even when the atom is chemically bonded in a molecules.

* MOT (molecular orbital theory):

1. The valence es are considered to be associated with all the nuclei in the molecules. Thus the atomic orbitals from different atoms must be combined to produce molecular orbitals.

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2. e^- may be considered either as particle or waves. An electron in an atom may therefore be described as occupying an atomic orbitals, or by a wave function Ψ (which is a solution to the Schrodinger wave eq^n). Electrons in a molecules are said to occupy molecular orbitals

3. The wave function describing a m.o may be obtained by linear combination of atomic orbitals.

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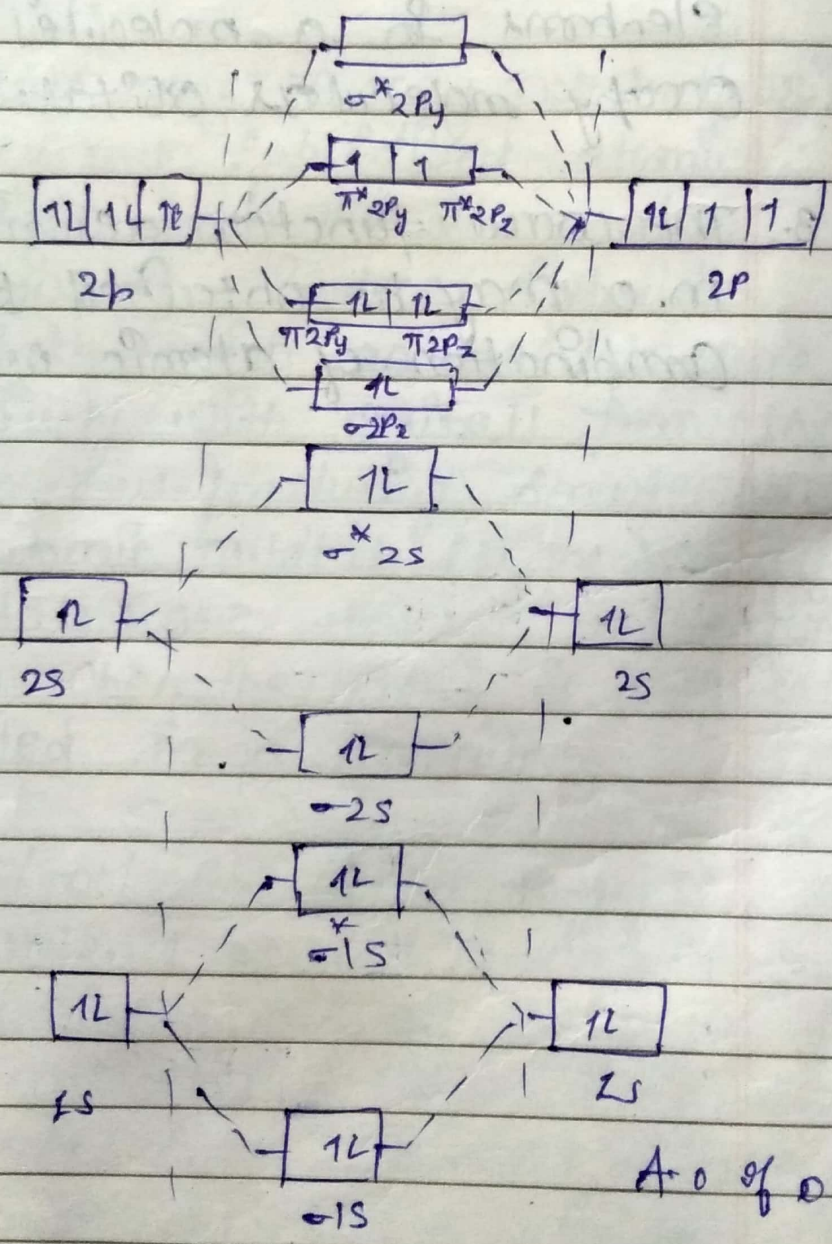
Q Draw the molecular diagram of O_2 molecule.

$O_2 \Rightarrow (16\ e^-s)$

$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s_2, \sigma^* 2s_2, \sigma 2p_x^2,$

$\pi 2p_y^2 = \pi 2p_z^2, \pi^* 2p_y^1 = \pi^* 2p_z^1$

$_8O \Rightarrow 1s^2, 2s^2, 2p^4$ $_8O \Rightarrow 1s^2, 2s^2, 2p^4$.



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$$B.O = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2,$$

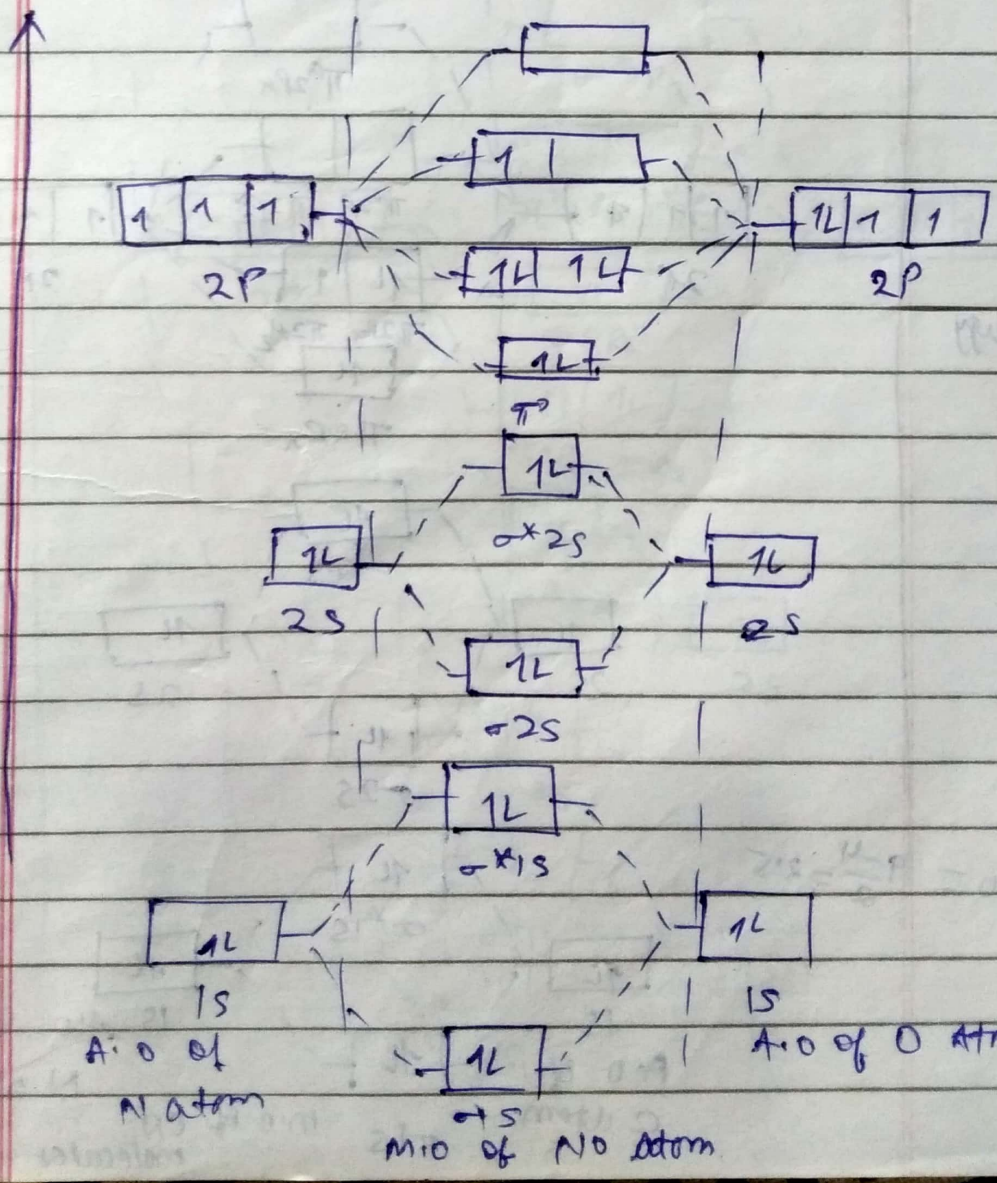
It will be paramagnetic in nature due to unpaired $e^{\ominus}$ in m.o orbitall.

Q. Draw the m.o diagram of NO molecule

$NO = 15e^{\ominus} =$

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

$_7N = 1s^2, 2s^2, 2p^3$ $\qquad$ $_8O = 1s^2, 2s^2, 2p^4$



Imp= MOT

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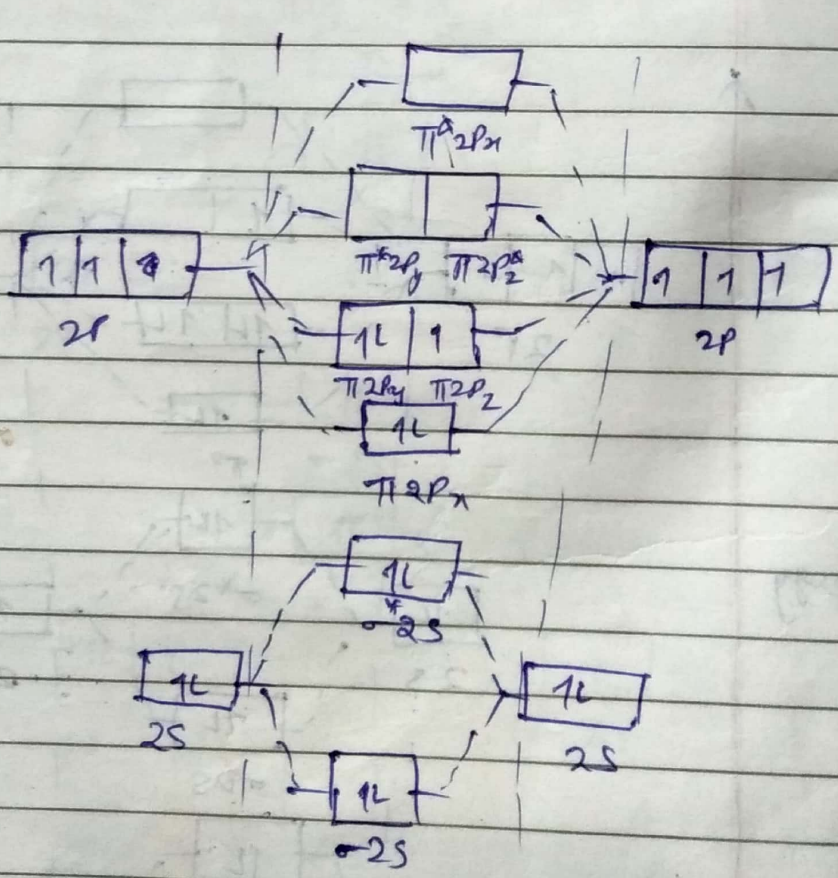
It will be Paramagnetic nature due to unpaired e

Q Draw the m.o diagram of CN molecule.

$CN = (Be_{13})$

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

$_6C = 1s^2, 2s^2, 2p^2$ $\quad$ $_7N = 1s^2, 2s^2, 2p^3$



B.O = $\frac{9-4}{2} = 2.5$

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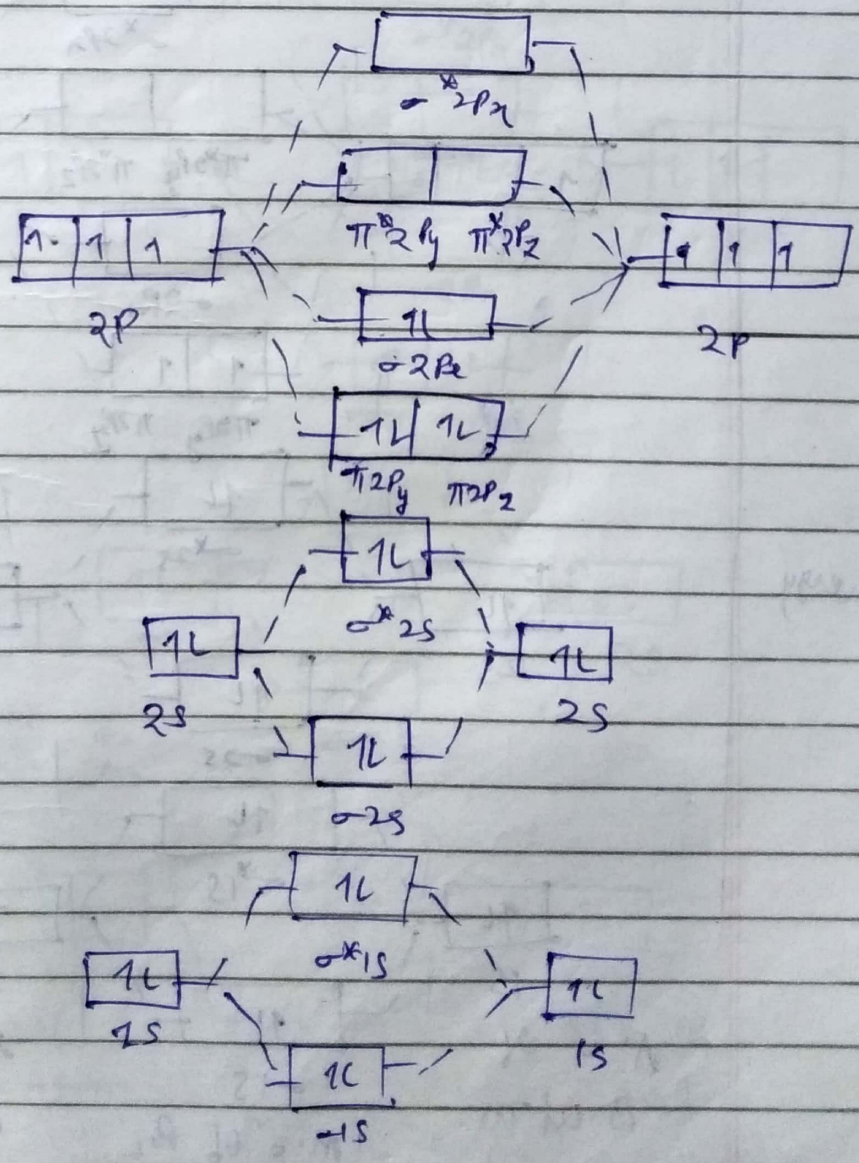
It will be Paramagnetic

Q. Draw the M.O diagram of N_2 molecules

N_2 = 14 e's =

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

$_7N = 1s^2, 2s^2, 2p^3$ $\quad$ $_7N = 1s^2, 2s^2, 2p^3$



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

= 3

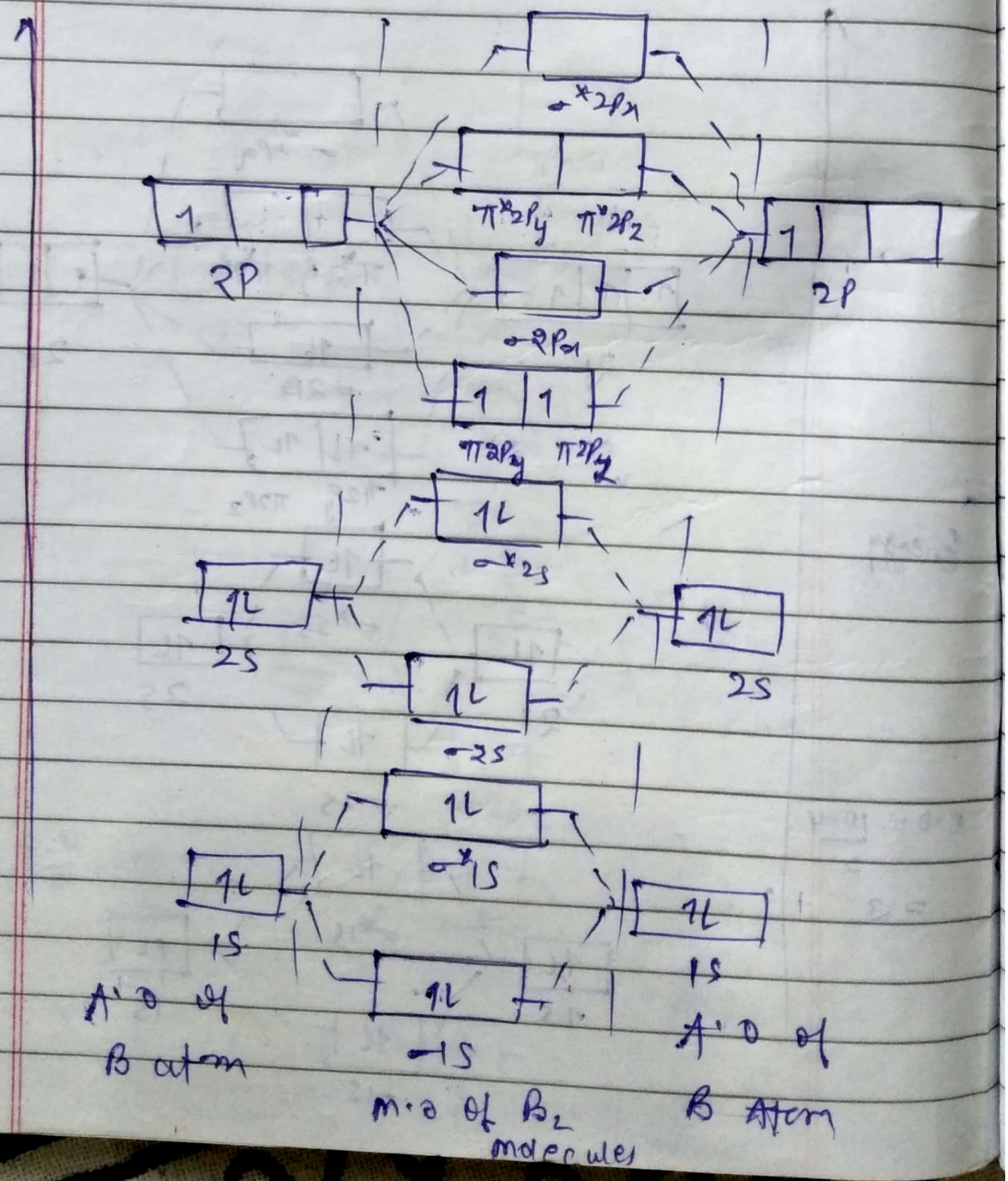
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It will be diamagnetic due to paired $e^{\ominus}$s

4 Draw the M.O diagram of B_2 molecule

$B_2 = (10e^{\ominus}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y = \pi 2p_z$

$_5B = 1s^2, 2s^2, 2p^1$ $\quad$ $_5B = 1s^2, 2s^2, 2p^1$



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$$B.O = \frac{6-4}{2} = \frac{2}{2} = 1$$

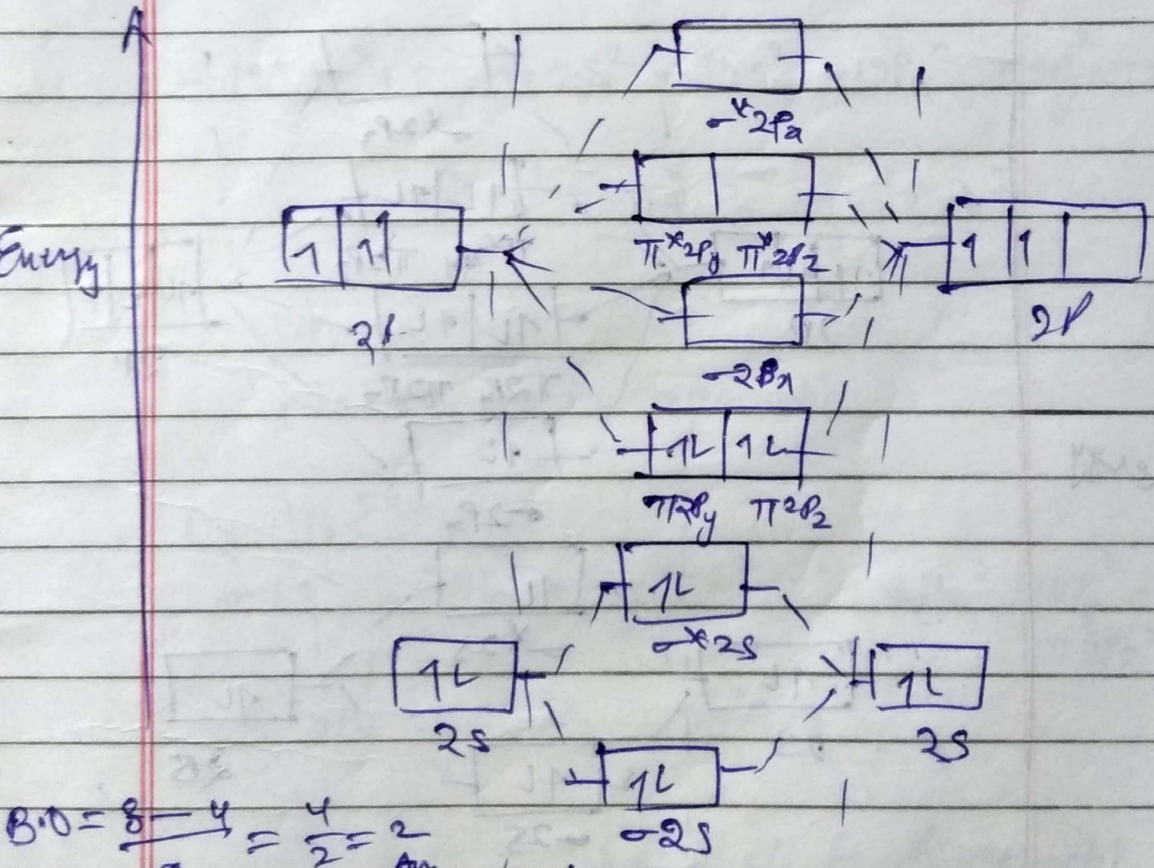
Paramagnetic Nature

Q Draw the M.O of C_2 molecules.

$C_2 = (12\ e^{\ominus}) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

$\pi 2p_y^2 = \pi 2p_z^2, \sigma 2p_x, \pi^* 2p_y = \pi^* 2p_z$

$_6C = 1s^2, 2s^2, 2p^2$ $\quad$ $_6C \Rightarrow 1s^2, 2s^2, 2p^2$



$B.O = \frac{8-4}{2} = \frac{4}{2} = 2$ Ans

diamagnetic.

A.O of C atom

M.O of C_2 atm

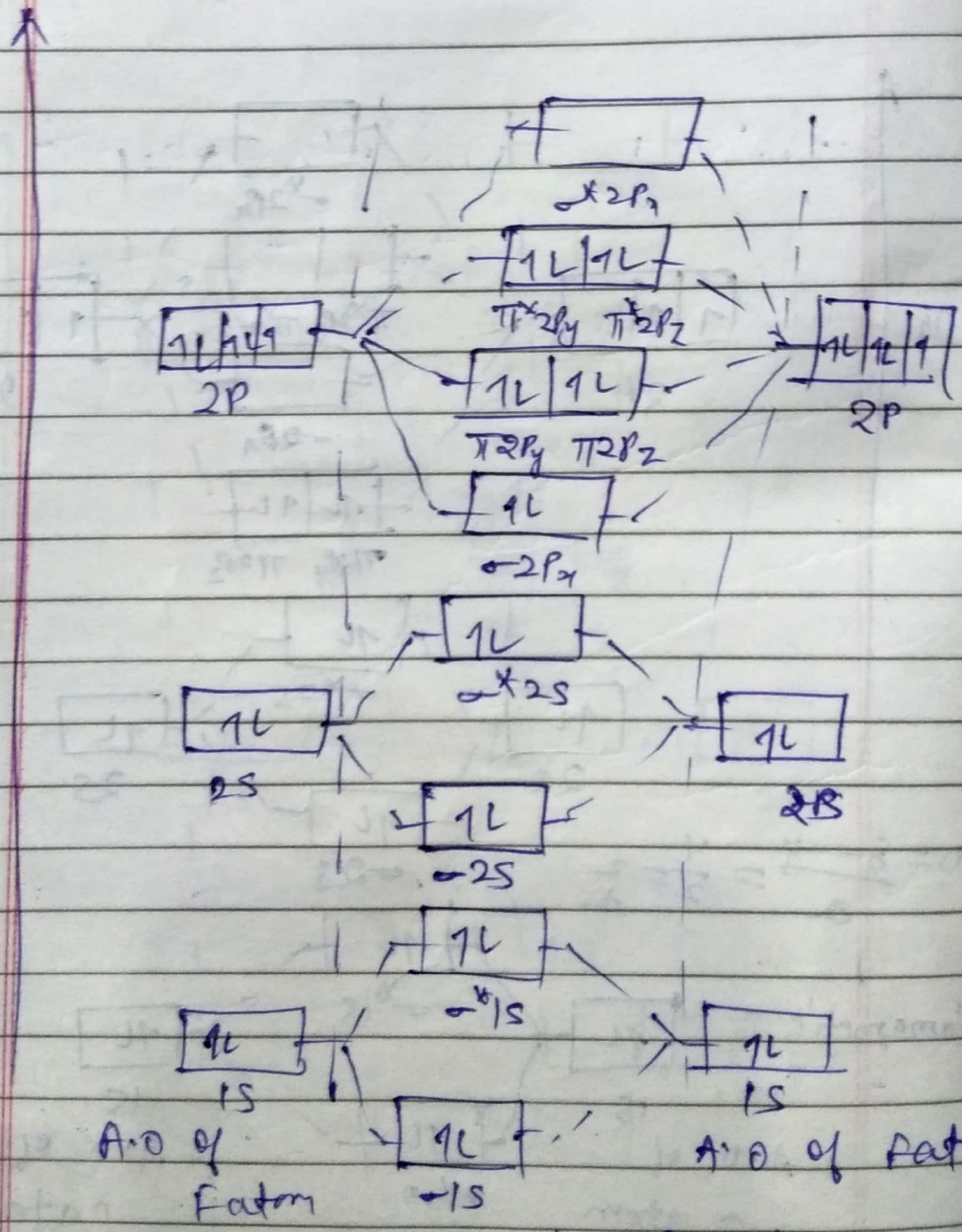
A.O of C atom

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Q Draw the M.O diagram of F_2 molecule

$F_2 = (18e^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2 = \pi 2p_z^2, \pi^* 2p_y^2 = \pi^* 2p_z^2, \sigma^* 2p_x^0$

$_9F = 1s^2, 2s^2, 2p^5$ $\quad$ $_9F = 1s^2, 2s^2, 2p^5$



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

Diamagnetic in nature

Prob. Q

Calculate B.O in following
i) O_2^+, O_2, O_2^-, O_2^{2-} also mention there magnetic nature and arrange them in increasing order of stability

- $O_2^+ (15e^\ominus)$

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

$\pi^* 2p_y^1 = \pi^* 2p_z^0, \sigma^* 2p_x^2$

$B.O = \frac{10-5}{2} = 2.5$

Nature $\Rightarrow$ Paramagnetic

- $O_2 (16e^\ominus)$

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

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

$B.O = 2$, It will be paramagnetic in nature

- $O_2^\ominus (17e^\ominus)$

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2 \sigma 2p_x^2,$

$\pi 2p_y^2 = \pi 2p_z^1, \pi^* 2p_y^2 = \pi^* 2p_z^1$

expection
nf, ro,

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B.O = 1.5
Paramagnetic natu

O_2^{2-} = (18 e⊖)

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

B.O = 1,
d/a :

The stability will be in following order

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

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

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* Linear Combination of Atomic Orbitals : (LCAO):

(i) The atomic orbital must be of the same type this is when consider overlapping b/w two different type of atoms

(ii) In order to produce bonding orbitals and antibonding orbitals the symmetry of the two atomic orbitals must remain unchanged (bonding is formed) and if changed (antibonding is formed).

Ex: Formation of ~~Symplest~~ Simplest Hydrogen molecules (H_2)

1. $H_2 \rightarrow H_A + H_B$

from wave machanics we know that atomic orbitals are represented by a wave function ψ.

2. Let ψ_A is Atomic Orbital of 1st H atom.
and ψ_B is A.O of 2nd H atom.

to the linear combination of the two wave function we can write as follows.

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$$\psi_{AB} = c_1 \psi_A + c_2 \psi_B \quad \text{--- i)}$$

where c_1 and c_2 are known as Normalization factor.

For hydrogen molecules (H_2) $\Rightarrow c_1 = c_2 = 1$

then from eq^n (1)
we can conclude that

$$\psi_{AB} = \psi_A \pm \psi_B \quad \text{--- (2)}$$

According to fundamental rules of M'O theory there are two atomic orbital participating therefore the molecular orbital is bonding Atomic orbital and other is antibonding.

For Addition, there is a formation of Bonding orbital, Now eq^n (2) becomes

$$\psi_{bonding} = \psi_A + \psi_B \quad \text{--- (3)}$$

Similarly, when two atomic orbitals are subtracted, the eq^n (2) become

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Since we know that ψ^2 term represent the probability of finding electrons. therefore on doing square of eq^n ③, we get

$$(\psi_{bonding})^2 = (\psi_A + \psi_B)^2$$

$$\psi^2_{bonding} = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

the $\ominus$ density is greater in bonding state, it can be shown by the following relation.

$$\psi^2_{bonding} > \psi_A^2 + \psi_B^2 \text{ by } 2\psi_A\psi_B \text{ times} \quad -(5)$$

thus, we conclude that bonding state is rich in $\ominus$ density more stable form

on doing square of eq^n ④ we get

$$\psi^2_{antibonding} = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

the $\ominus$ density is less in antibonding state it can be shown by the following relation

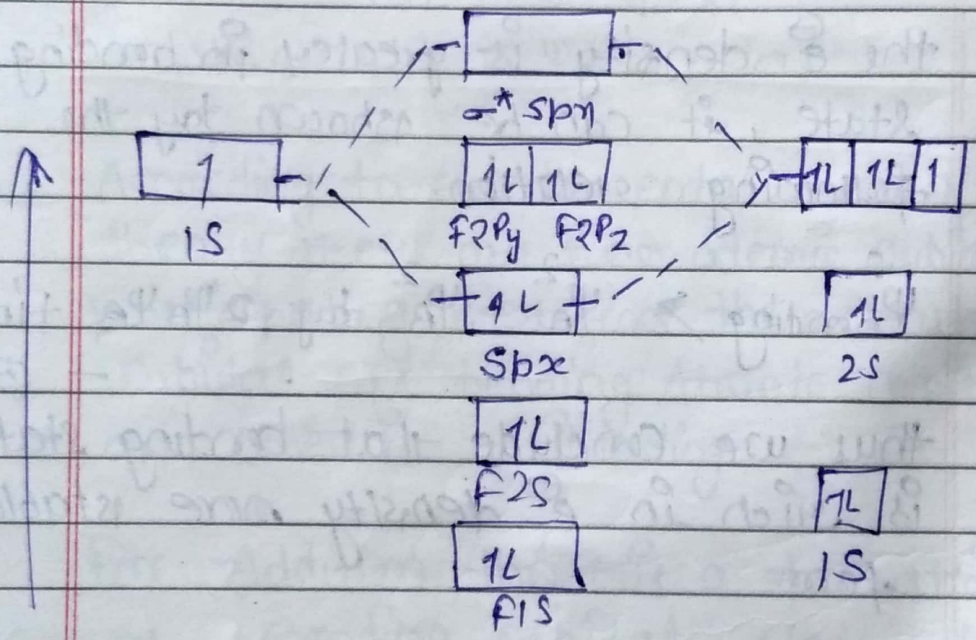
$$\psi^2_{antibonding} < \psi_A^2 + \psi_B^2 \text{ by } 2\psi_A\psi_B \text{ times}$$

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Now, we conclude that antibonding is deficient in $\bar{e}$ density. therefore it is less stable

Ans: Q Draw the M.O diagram of HF molecule
HF $\Rightarrow (10e^{\ominus})$

H = $1s^1$ qf = $1s^2, 2s^2, 2p^5$



$B.O = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$ Ans

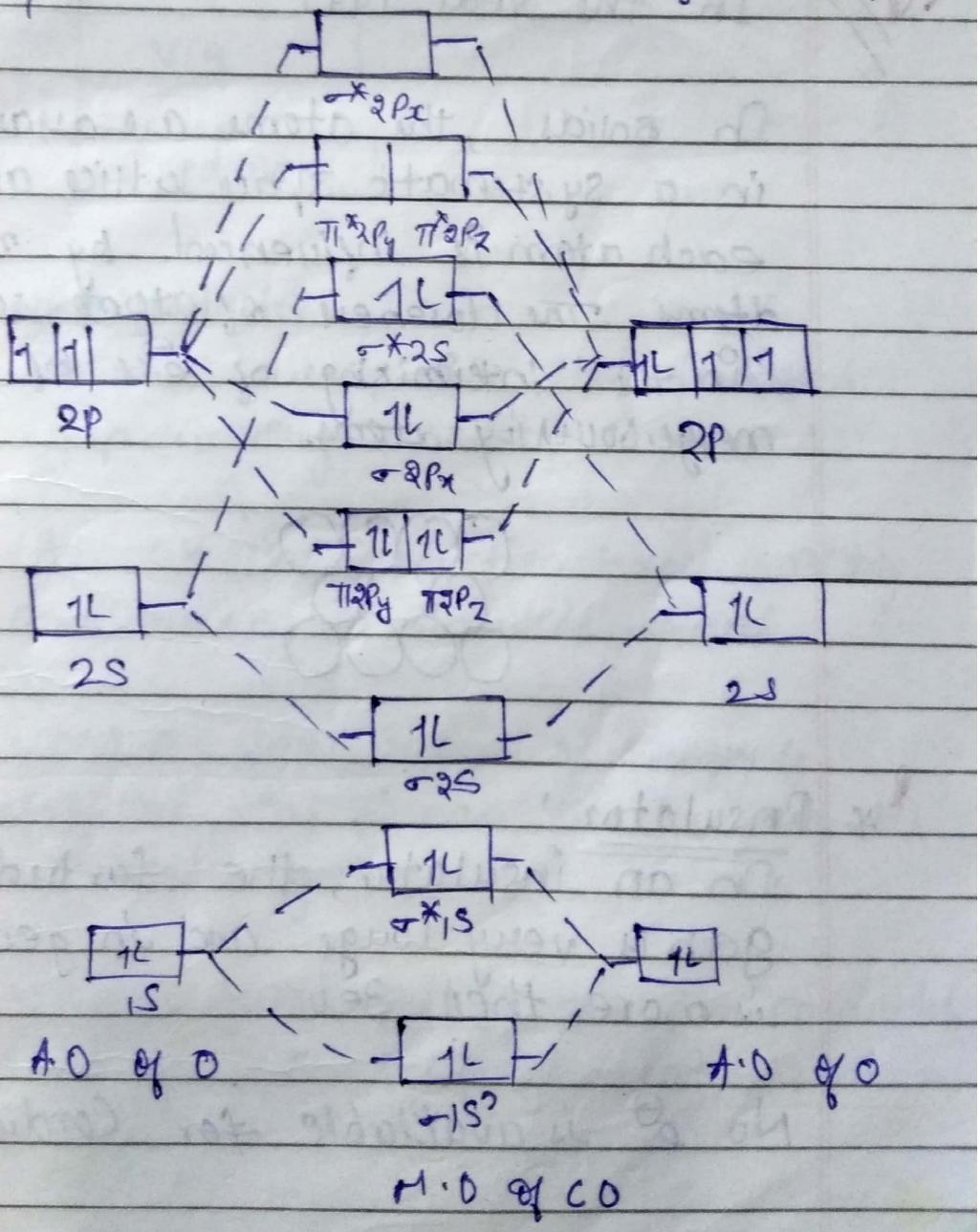
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(2.) Draw the M.O diagram of Co molecule, Co^+ molecule ion is more stable than Co molecule. Explain why.

$CO(14e^\ominus) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \pi 2p_y^2 = \pi^2 p_z^2, \sigma 2p_x^2, \sigma^* 2s^2$

$_6C = 1s^2, 2s^2, 2p^6$ $\quad$ $_8O = 1s^2, 2s^2, 2p^4$



B.O = 3

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the B.O of CO^+ = 2.5

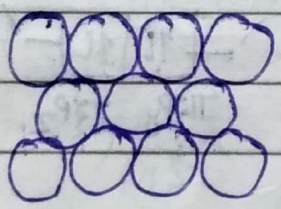
" " " CO = 3

so, CO^+ is more stable than CO

* Band theory :

In the year 1947.

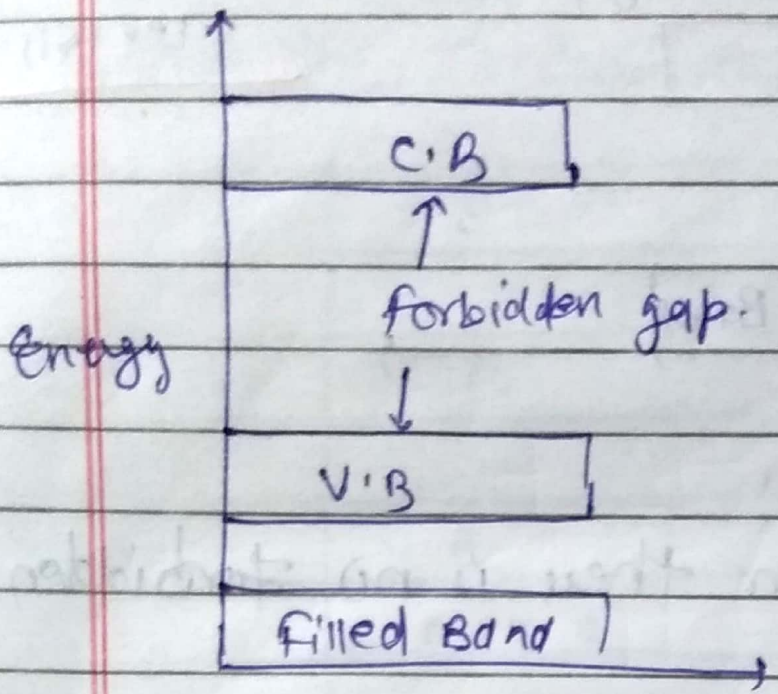
In solids, the atoms are arranged in a systematic space lattice and each atom is influenced by neighbouring atoms. The closeness of atoms result in the intermixing of $e^\ominus$'s of neighbouring atoms.



* Insulator :

In an insulator, the forbidden gap is very large and in general is more than 3ev.

No $e^\ominus$ is available for conduction



* Semiconductor:

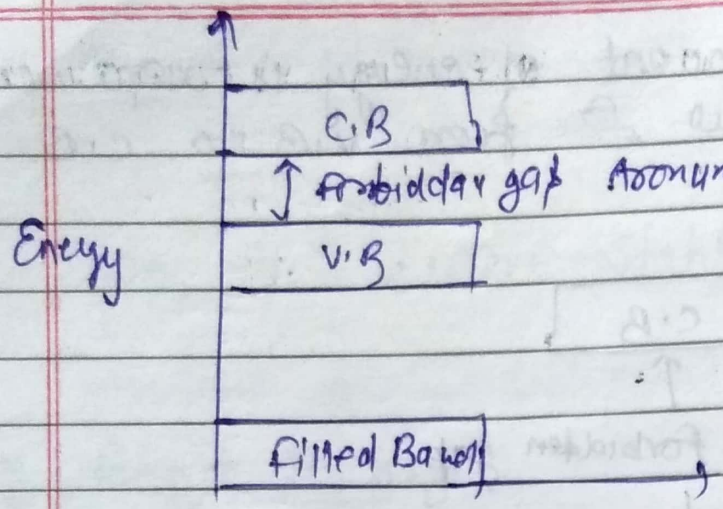
In the case of Si/c the forbidden gap is very small

At 0K the Conduction band is empty and the VB is completely filled

When a small amount of energy is supplied, the $e^{\ominus}$ can easily jump the forbidden gap

The conductivity of a semiconductor is of the orde of 10^2 mhom^{-1}

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Around 0.7ev (Ge) and 1.1ev (Si)

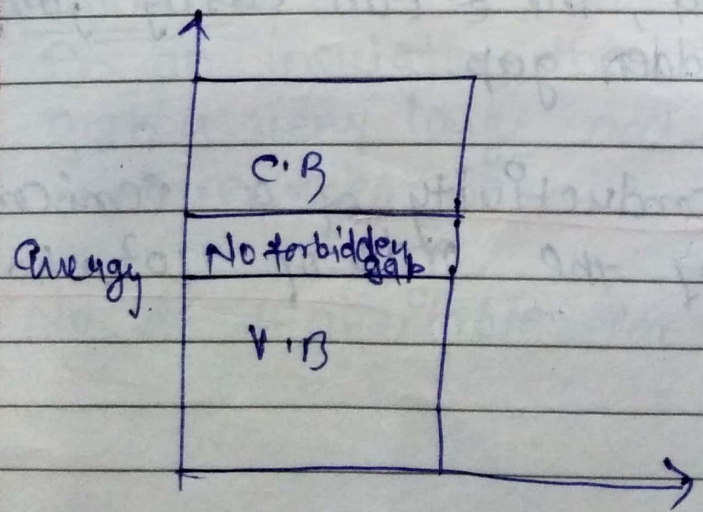
* Conductor:

In conductor there is no forbidden gap

the V.B and the C.B overlap

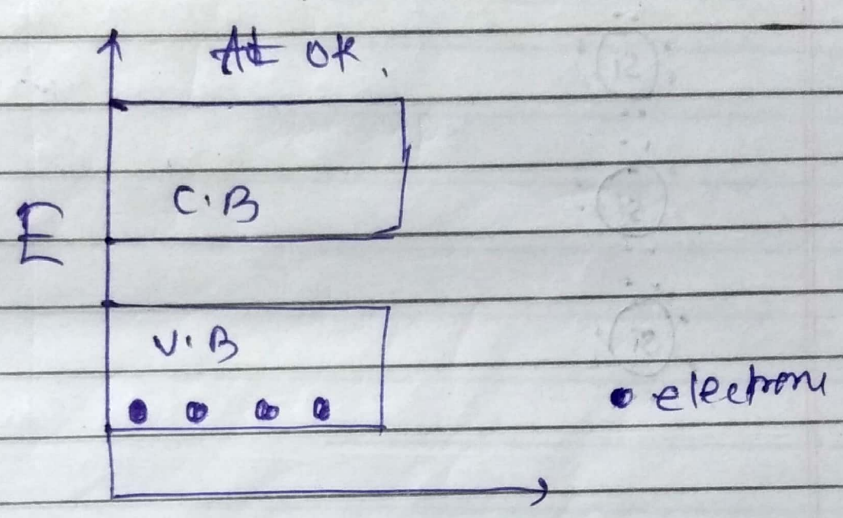
The $e^{\ominus}$ from V.B freely enter into the C.B due to overlapping of bands

Therefore very low potential difference can cause continuous flow of current

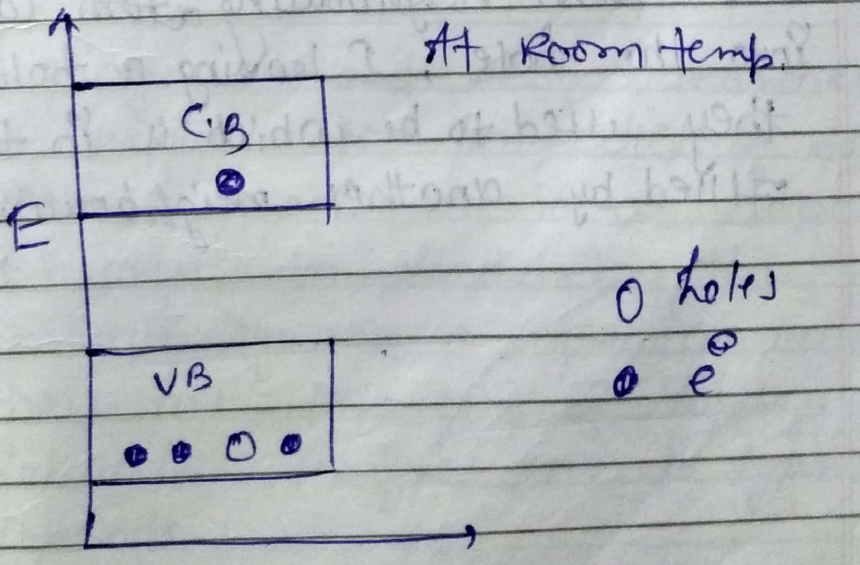


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* Electrons and holes in semiconductor:
At absolute 0 temp. in a pure s/c the V.B is completely filled and the conduction band is vacant.



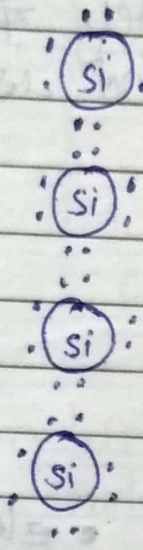
At room temp. some of the $e^{\ominus}$ get energy to break the covalent bond bond and moves in to the conduction band



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add Pentavalent impurity

* formation of N type s/c :

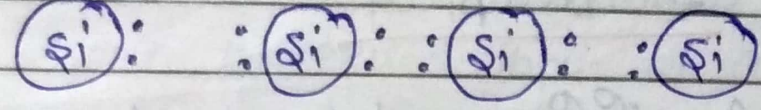


Group 5 atom have one less $e^{\ominus}$ than si so when they are introduced into the crystal, there is a hole where one extra electron should be.

$e^{\ominus}$'s from neighbouring atom can move into the hole, leaving a hole where they used to be which is in turn filled by another neighbouring $e^{\ominus}$.

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* formation of P- type material



* Role of doping in Band structure:

1. ~~IC's~~ are doped to generate either a surplus or a deficiency in ~~the~~ valence e

2. doping allowed ~~us~~ researcher to exploit the properties of sets of elements, refered to as dopands, in order to modulate the conductivity of a semiconductor. there are two type of dopings dopands n type and p type dopands

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n type dopants act as $e^{\ominus}$ donors and p type dopands act as $e^{\ominus}$ acceptors.

3. Combining n type and p-type SICs creates system which have useful application in modern electronics.

* Aromaticity:

Concept of Aromatic character (Aromaticity):

Benzene and other organic compound which resemble benzene in certain characteristic properties are called aromatic compound. These characteristic properties constitute which is commonly known as aromatic character and aromaticity. Such imp. property are summerised below;

1. Unusally stability
2. Substitution later than addition Rxn
3. resistant to oxidation (loss of $e^{\ominus}$)
4. Cyclic flat molecules

Sure ⇒ MOT

Friday test.

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* Theoritical criteria for Aromaticity :-

Ans. On the basic of molecular orbital twice of various aromatic compounds, it has been observed that an aromatic compound must full fill the following theortical requirments

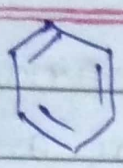
1. It must have Cyclic cloud of delocalised π electrons above and below the plane of the molecules.

2. The π clouds must contain a total of $(4n+2)\pi$ electrons, where n is an integer. i.e its value may be 0, 1, 2, 3, 4 ---. this rule is known as (4n+2) rule or Huckel rule. Therefore acc. to Huckel rule the no. of $\pi e^{\ominus}$'s in an aromatic compound may be 2 (n=0), 6 (n=1), 10 (n=2), 14 (n=3), 18 (n=4) etc.

In benzene it is $6 e^{\ominus}$ (n=1), Huckel rule is based on quantum mechanics.

6/10/17, 18

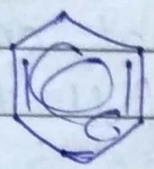
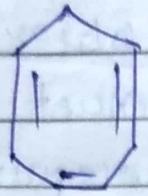
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Ex 1. 

$4n+2 = 6$

$n = 1$

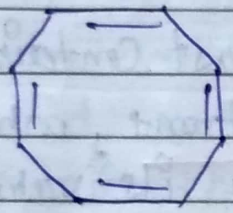
Aromatic

2.   cycloheptatriene

$4n+2 = 6$

$n = 1$

Non-Aromatic

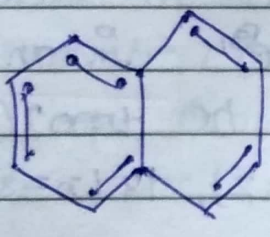
3. 

$4n+2 = 8$

$n = \frac{6}{4} = 1.5$

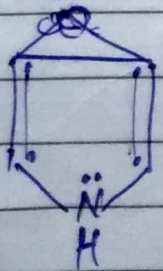
non-Aromatic

Cyclooctatetraecene

4. 

$4n+2 = 10$ $n = 2$

Aromatic in nature

5. 

Pyrrol

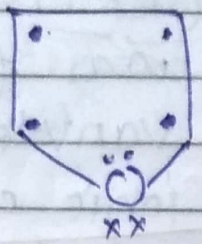
$4n+2 = 6$

$n = 1$

Aromatic

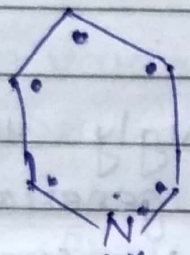
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6.



furan.

7.

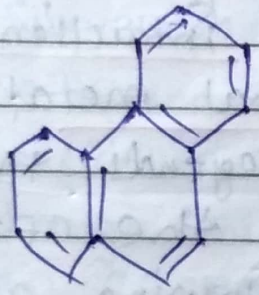


Pyridine.

$4n+2=6$

$n=1$

8.



$4n+2=14$

$n=3$

Aromatic in nature

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* Crystal field theory (CFT):

CFT : This theory was first introduced by bethe and vanvleck and applied mainly to ionic crystals, and is therefore called crystal field theory (CFT).

later orgel was largly responsible for developing its general chemical aspect. the CFT is mainly concened with the interaction of d-orbitals of central metal with the surrounding legends that produce crystal effect. the CFT is based on the following assumptions

1. The metal ion and legend act as point charges and the interaction b/w them is purely electrostatic. i.e metal legand bond are 100% ionic

2. There is no interaction b/w metal orbital and legand orbital.

3. The d-orbital on the metal which were all of the same energy, i.e d generate in a free atom,

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have there d-generacy destroid by the legands when the complex is formed

Salient features of Crystal field theory (CF

- The various postulates are summerised below:

1. A complex is considered to be a combination of central metal ion surrounded by various legands.
2. the legands in the compleres to be considered are either negatively charge ions for ex: F^-, $CN^\ominus$ or neutral molecules for ex: H_2O and NH_3 which have a dipole such that the negative ion is clogest to the central ion.

2. The attraction between central atom and legand in a complex is regarded as purily electrostatic.
The intraction between the elements electrons of the cation and those of the legands is purily repulsive. It is these repulsive forces that are responsible for causing the splitting of d-orbital of the metal cations into two groups t_{2g} and e_g

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The splitting depends on whether the legend are arranged in octa-hedral, tetrahedral or square planner way around the central ion. This effect is known as Crystal field splitting.

3. The electrons of the metal ion are repaired by the negative field of the legands and therefore the metal electrons will occupy those d-orbitals which have their lobes farthest way from the direction of the legend.

4. In this theory the covalent character of the bond between metal and legands is not taking into account.

5. This theory does not permits the e^- to enter the metal orbitals. It means that it does not consider any orbital overlap

6. The no. of legands and their arrangement around the central ion will determine the crystal field.

weak ' ... Strong ...

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splitting
↑
- Crystal field of d-orbitals:

In an isolated gaseous metal ion, all the five d-orbitals are degenerate i.e have the same energy. The electrons which occupy such orbitals, do so acc. to Hunds rule of maximum multiplicity

Crystal field theory is basically concerned with the effect of different arrangement of surrounding ligands on the energy of d orbitals, and the subdivision of the orbitals into two groups t2g and eg.

On the approach of the ligand the e⁻'s in the d-orbital of the central ion are repelled by the lonepair of the ligands. This repulsion will raise the energy level of atomic orbitals All the ligand is approaching the Eucary of d-orbitals will increase the same amount.
They will remain d-degenerate. although they will have now higher energy then before.

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But actually the d-orbitals differ in their orientation. Therefore the energy of the orbitals lying in the direction of the legands is raised to a larger extent and then that of the orbitals lying in b/w the legends.
It means that the five degenerate d orbitals of the metal ion will split into two sets of orbital having different energies. This spleting of five degen degenerate d orbitals of the metal ion under the influence of approaching legends, into two sets of orbital having different energies is called Crystal field spleting or Energy level splitting

The legand field spleting depends on whether the legends are arranged in octahedral, tetrahedral or square planar way around the central ion.

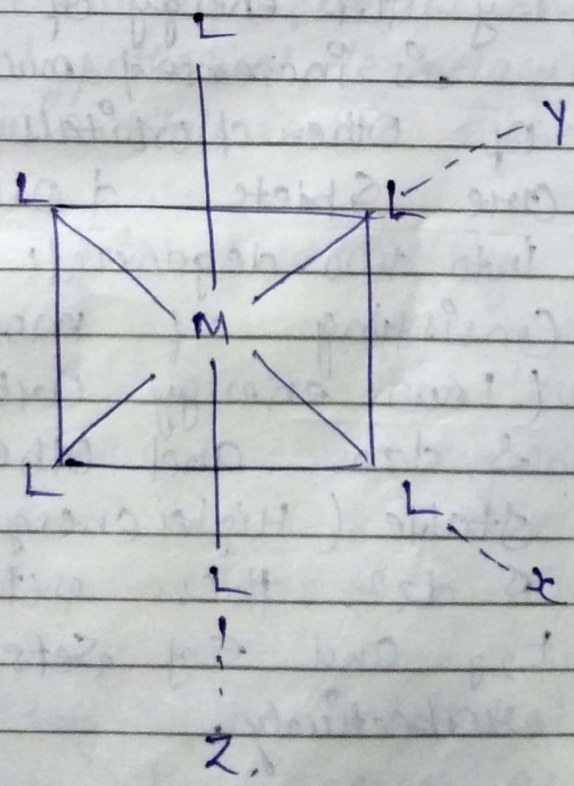
The magnitude of the crystal field spleting of the d orbitals energies may be represented by the symbol Δ

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It is used to denote energy difference (the total energy diff. may be regarded as made up of the energy lost or released in the lower tables together with the energy gained in the upper layers.)

The cf spleting Energy, Δ, is frequently measured in terms of a parameter D_q. The magnitude of spleting is arbitrarily set at $10 D_q$. i-e $2 D_q$ for each unpaired electrons.

* Crystal field spleting in Octahedral Complexes:-



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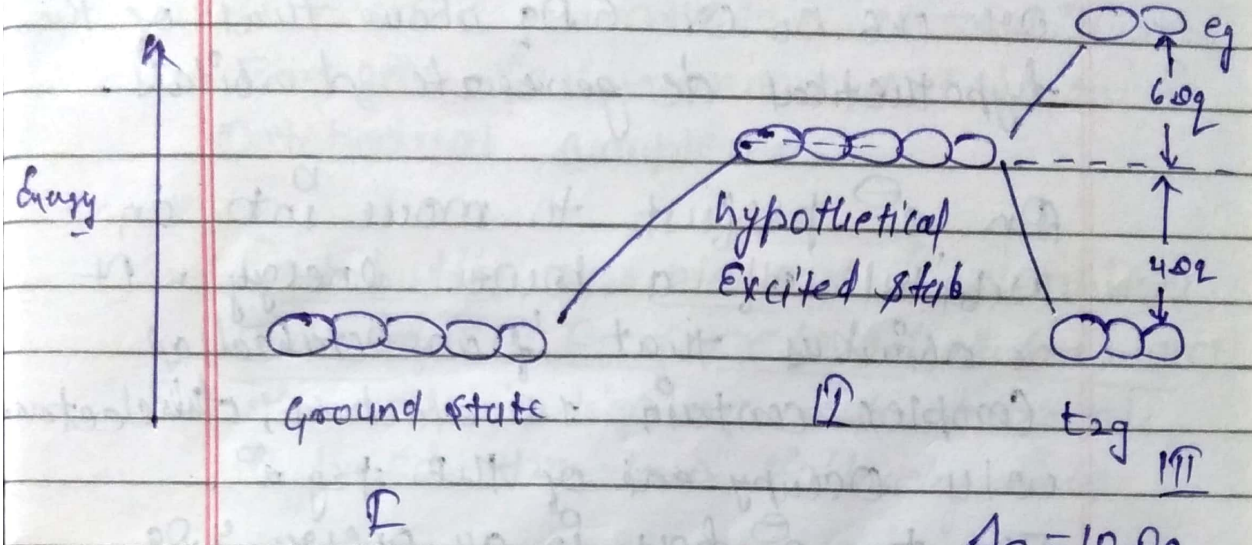
* In the octahedral complexes, six legends are arranged octahedrely around the central metal ion as above

In such an arrangement, $d_{x^2-y^2}$ & d_{z^2} orbitals lie along the axis and there fore point directly towards the legends and they experienced much more repulsion than dxy, dyz and dzx orbitals. which are between the axis.

By this energy of dx^2-y^2 and dz^2 is increased much more in comparision of other d orbitals. Thus, d orbitals are Splete. d orbitals are Spleated into two degenerate sets, one consisting of more stable (low energy orbitals) dxy, dyz & dzx and other set of less stable (Higher energy orbitals) dx^2-y^2, & dz^2. these sets are known as t_{2g} and e_g sets of orbitals respectively.

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The spleting of d-orbitals under the influence of Octahedral legemd field may be so as shown as;



Step-1 Represent d-orbital of metal ions.

Step-2 Represent hypothetical degeneracy of all the five orbitals at a higher energy level

Step-3 Represent Crystal field spleting.

The crystal field spleting is thus the energy difference b/w t_{2g} and e_g Orbitals. It is denoted by the Symbol Δ_o or $10Dq$

The geometry of an octahedral system shows that the energy of the t_{2g} orbital is $\frac{2}{5}\Delta_o$ or $0.4\Delta_o$ or

$4Dq$. less than that of the hypothetical degenerated d-orbital.

eg

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t2g

d-orbital

the energy of eg orbitals is $\frac{3}{5}\Delta_o$

or 0.6 Δ_o or 6 Dq above that of the hypothetical de generate d-orbitals.

An $e^{\ominus}$ prefers to move into an orbital of a lower energy. It is obvious that if an octahedral complex contain 1 electron, that electron will occupy one of the t_{2g} $e^{\ominus}$.

The t_{2g} $e^{\ominus}$ has in an energy 4 Dq less than that of the degenerate orbitals. therefore the complex will be 4 Dq more stable than predicted by the purely electrostatic theory which does not recognize any splitting of energy levels. This value 4 Dq is called the crystal field stabilizing energy (CFSE) of the complex.

If for each $e^{\ominus}$ entering into a t_{2g} orbital, the crystal field stabilizing is 4 Dq then for each electron entering in an eg orbital, the stabilizing energy is 6 Dq.

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In other words the stabilization energy or CFSE for an electron in eg orbital is $-6Dq$. working on the basic of, it is possible to calculate CFSE stabilization Energies for various metal ions in Octahedral compleres.

* Distribution of electrons in d-orbitals and CFSE of octahedral complexes

The distribution of $e^{\ominus}$ in d-orbitals is based upon following Rules

1. $e^{\ominus}$ prefer to occupy the orbitals of lowest energy

2. $e^{\ominus}$ obey Hunds Rule i.e electron pairing will not take place all the available orbitals of the given sets contain one $e^{\ominus}$ each

3. if the energy to place an $e^{\ominus}$ in the upper easy level is greater then the energy to pair electrons (Pairing Energy = P) in the lower t_{2g} level ($10Dq > P$), then the electrons will pair a in t_{2g} orbitals.

π orbital of Benzene
Butadiene
Schrödinger eq^n.

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4. If the energy to place an electron in upper e_g level is less than the pairing energy in the lower t_{2g} orbitals. ($10Dq < P$) then the $e^\ominus$ will occupy e_g orbitals

Energy difference in

* Weak and strong ligand fields:
Ligands which cause only a small degree of spleting of d orbitals, i.e weak field are called weak field ligand and those which cause an large i.e strong field, are called strong field ligands. the magnitude of $10Dq$ and hence the distribution of $d\ e^\ominus$ in d orbitals are very much influenced by the strength of ligand field. The CF splitting ~~abi~~ ability of the ligands decreases in the following order

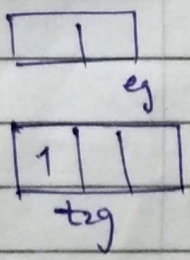
$CO > CN > NO_2^- > en > NH_3 > H_2O >$
strong field ligand
$> F^\ominus > OH^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$
weak field ligand

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In a weak field, $10Dq$ is generally less than pairing Energy. i.e $10Dq < P$.
It means that $e^{\ominus}$s obey hunds rule and remain unpaired. But of In case of a strong field $10Dq > P$,

It follows that $e^{\ominus}$ pair up in the lower energy orbitals. we shall Now consider the distribution of the electron in in octahedral complexes in the presence of weak field and strong field, In octahedral Complexes with with d^1 to d^7 configuration The $e^{\ominus}$ will occupy the lower energy Orbital.

For Ex: d^1



$(1 \times -4Dq)$
$= -4Dq$

*

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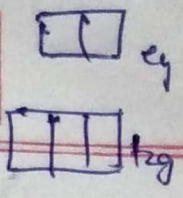
* Distribution of d^n $e^\ominus$ in octahedral complexes and corresponding crystal field stabilization energies

weak ligand
~~fitted~~ fielded

d^n	Distribution of $e^\ominus$ t_{2g}	e_g	No of unpaired $e^\ominus$	CFSE
d^1	↑		1	$-4Dq$
d^2	↑↑		2	$-8Dq$
d^3	↑↑↑		3	$-12Dq$
d^4	↑↑↑	↑	4	$-6Dq$
d^5	↑↑↑	↑↑	5	0
d^6	↑↑↑	↑↑	4	$-4Dq + P$
d^7	↑↑↑	↑↑	3	$-8Dq + 2P$
d^8	↑↑↑	↑↑		$-12Dq + 3P$
d^9				$-16Dq + 4P$
d^{10}				$-20Dq + 5P$

-16+12

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Strong ligand field

Distribution of $e^{\ominus}$ t2g eg	no. of unpaired $e^{\ominus}$s	CFSE
↑	1	$-4Dq$
↑↑	2	$-8Dq$
↑↑↑	3	$-12Dq$
↑↑↑↑	2	$-16Dq + P$
↑↑ ↑↑ ↑	1	$-20Dq + 2P$
↑↑ ↑↑ ↑↑	~~2~~	$-24Dq + 3P$
↑↑ ↑↑ ↑↑ ↑	1	$-18Dq + 3P$
		$-12Dq + 3P$
		$-16Dq + 4P$
		$-20Dq + 5P$

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Q Calculate the CFSE for following molecules

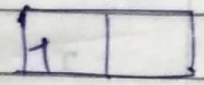
i) $[Cu(NH_3)_6]^{2+}$

ii) $[Cu(H_2O)_6]^{2+}$ $[Cu(Cl)_4]^{2-}$

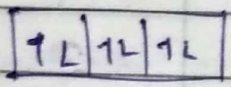
iii) $[Cu(NH_3)_4]^{2+}$

$Cu^{+2} = d^7$

Strong ve field ligand



eg



t_{2g}

$= 6 \times (-4Dq) + 6(1)Dq + 2P$

$= -24Dq + 6Dq + 2P$

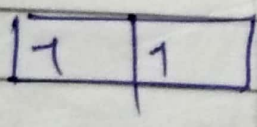
$= -18Dq + 3P$

$n-6 = \frac{n}{2}$

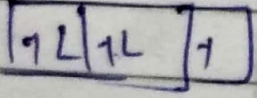
(ii) $[Cu(Cl)_6]^{2(+4)}$

$Cu^{+2} = d^7$

weak field ligand



eg



t_{2g}

$-20Dq + 12Dq + 2P$

$-8Dq + 2P$

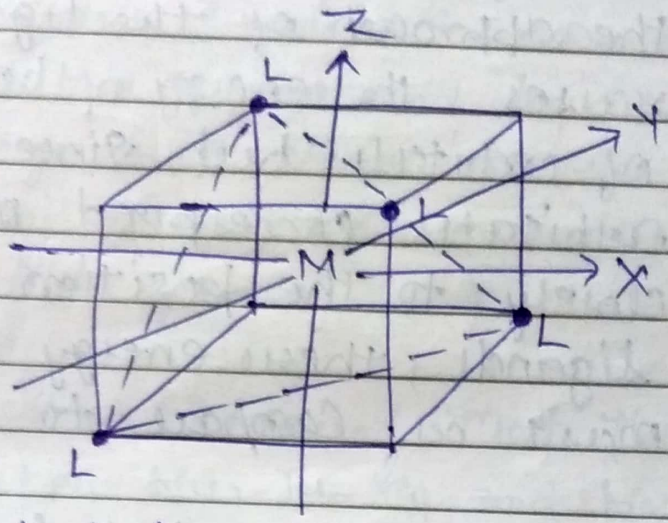
$-\log Q(P) + \log(Q)$

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CFSE for tetrahedral complexes

- CFT for tetrahedral complex:

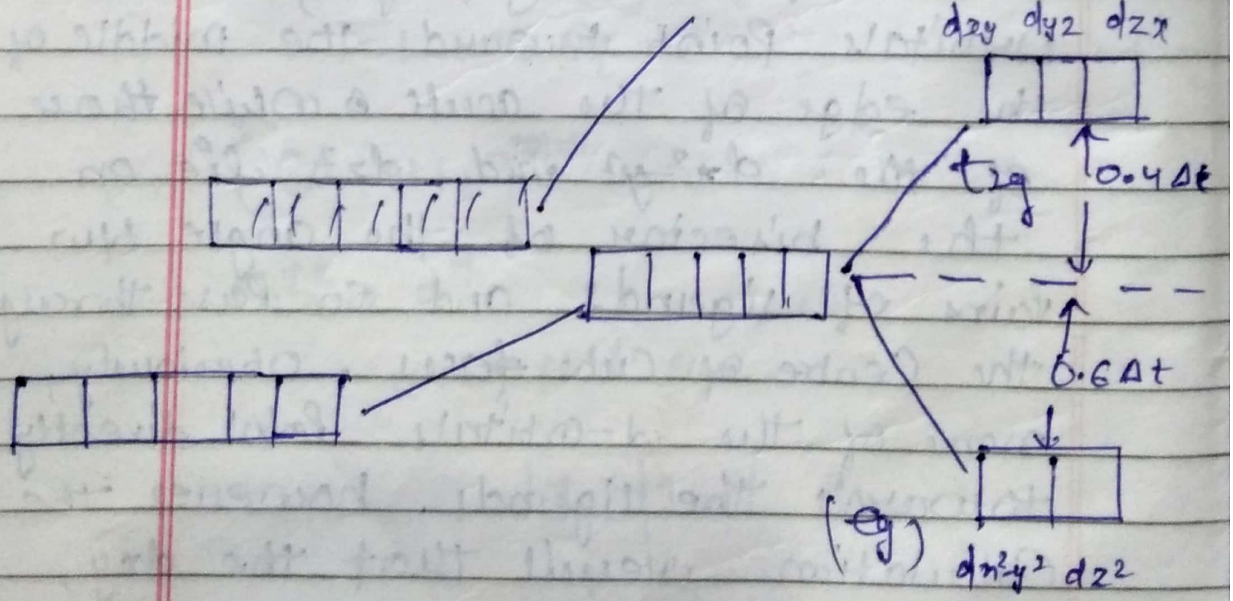


In tetrahedral complexes, the four ligands occupy the alternate corners of acute, in the centre of which is placed the metal cation. The lobes of the dxy, dyz, and dzx orbitals point towards the middle of the edge of the acute while those of the dx^2-y^2 and dz^2 lie on the bisector of the angle b/w pairs of ligands and so pass through the centre of cube faces. Obviously, none of the d-orbitals point directly towards the ligands. however the Calculation reveal that the dxy, dyz and dzx (termed t_{2g}) are closer to the ligands. then dx^2-y^2 and dz^2 (e_g).

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On the formation of a regular tetrahedral structure in a complex, the approach of the ligands raises the energy of both sets of orbitals but since the t_{2g} orbitals correspond more closely to the position of the ligands, there energy increases most as compare to eg.

Therefore, eg orbitals (Lower energy) are filled first, this is opposite to an octahedral complexes.



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It has been
for maintaining the average cent. t_{2g} orbitals are raised to $4Dq$ while e_g orbitals are lowered by $6Dq$ therefore the energy level scheme for the tetrahedral symetry is exactly reverse of that for octahedral symmetry.

It has been observed that the energy seperation b/w the e_g and t_{2g} levels Δ_t, in tetrahedral symmetry is small than in octahedral symmetry Δ_o ($10Dq$).

This observation is as expected as because the d orbitals are not directly affected by the ligands and more over the no. of ligands are smaller.

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

where the -ve sign mean of the reversal of the orbital levels.

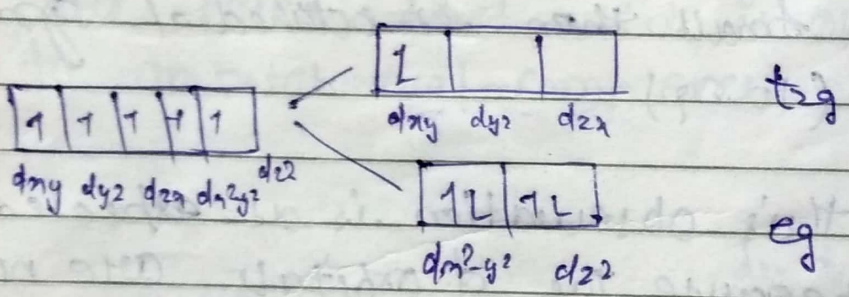
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Q. Calculate the

Q what are the main Postulate of CFT. discuss Crystal field Splitting in $[Co(NH_3)_6]^{2+}$

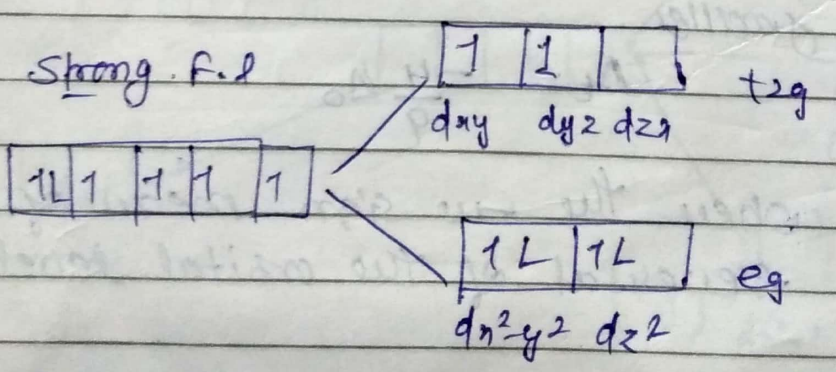
Q. what are the main Postulate of CFT. (
Discuss CF Splitting in $[Co(NH_3)_4]^{2+}$

$Co^{2+} = (5)\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

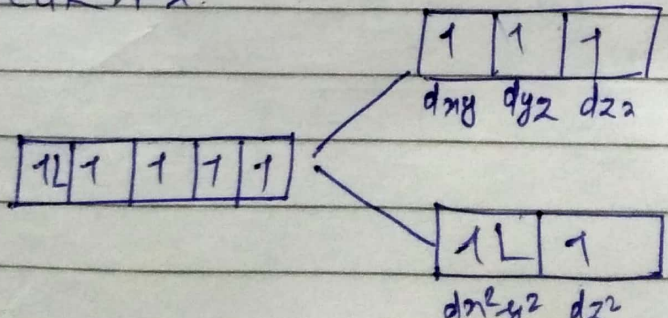


CFSE = $(4 \times (-6Dq) + 1(4Dq)) + 2P$

d^6 = Strong f.l



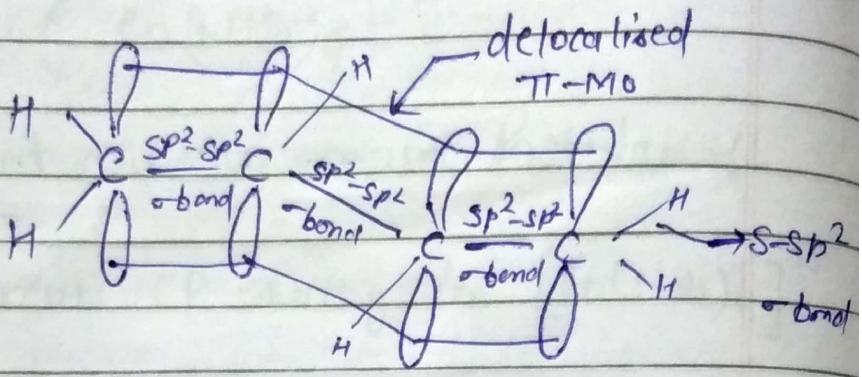
Weak f.l



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* π molicular orbital of butadiene :

$CH_2 = CH - CH = CH_2$



All four carbon atom in 1-3 butadiene are sp^2 Hybridised. The sp^2 hybrid orbitals overlap with each other and with s orbitals of the hydrogen atoms to form C-C and C-H σ bonds. Since bonds result from overlap of trigonal sp^2 hybrid orbitals, All carbon and H atom lie in one plane. All bond angles are 120°.

Also each carbon atom has an unhybrised p orbital standing to perpendicular to the plane of σ bonds. The p orbitals on C_2 can overlap with p orbital of C_1 and C_3

Schrodinger wave equation

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Spectroscopy

The P orbital of C_3 can overlap with P orbital of C_2 and C_4. In other words, all four P orbitals overlap with each other two form a large π molecular orbital. each pair of π electron is thus attracted, not by two, but all four carbons.

The overlap of P orbitals of C_2 and C_3 in both directions, which allows the P-electrons to be spread over a large Area, is known as <u>delocalization</u>.

This delocalization of π electrons is responsible for greater stability of 1,3 butadiene.

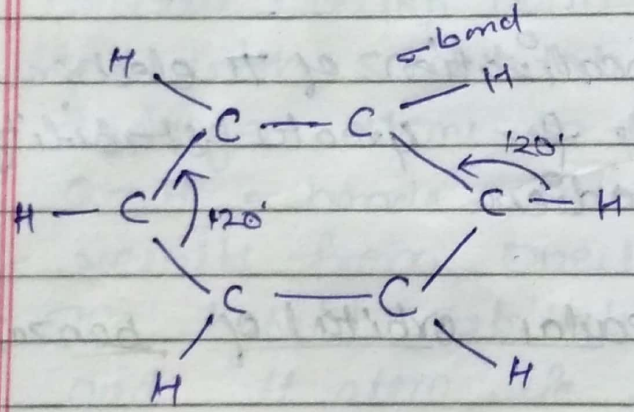
* <u>π molecular orbital of benzene</u> <u>orbital</u>

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Molecular Orbital structure of benzene:

1. all six carbon atom in benzene are sp^2 hybridised. the sp^2 hybridised orbital overlap with each other and also with s orbital of six H atoms forming C-C and C-H σ bond

2. Since the bonds result from overlap of planner sp^2 orbitals, all C and H atoms in benzene lie in the same plane. all bond angles are 120°

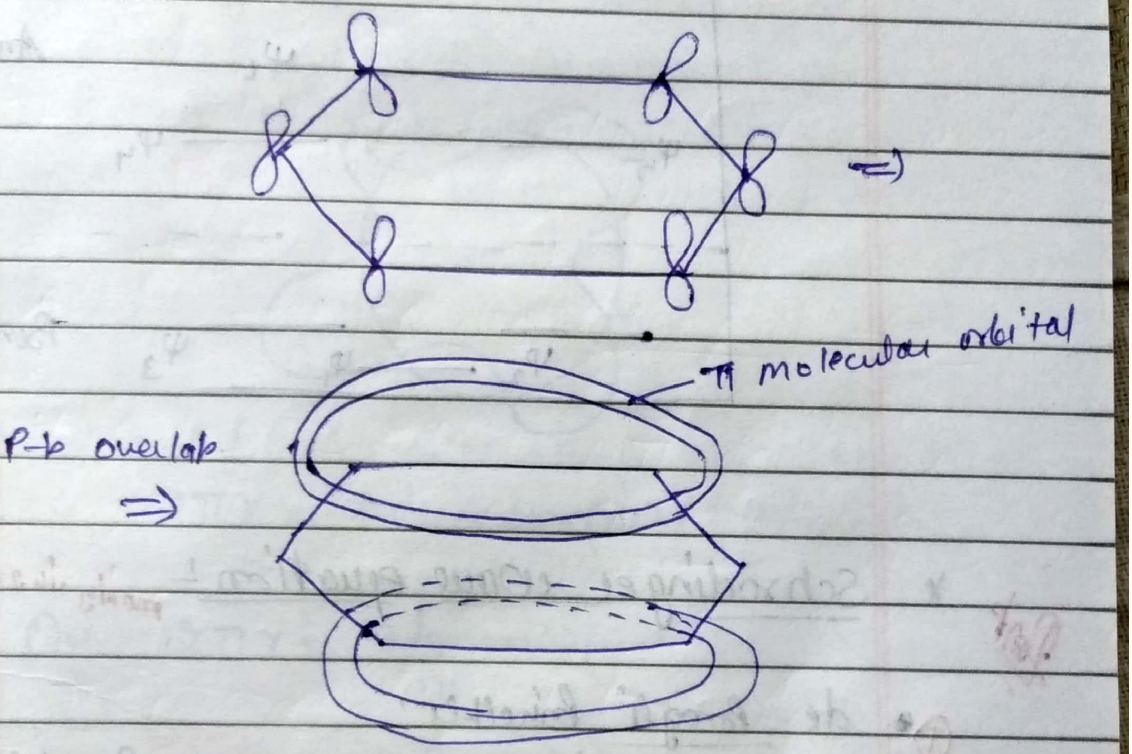


- all six C-C σ bond and six C-H σ bond lie in the same plane
- all bond angles are 120°

3. Also each carbon atom in benzene an unhybridised P orbital containing one electron. These P orbitals are perpendicular to the plane of σ bond.

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The lateral overlap of these p orbital produces a π molecular orbital containing six electrons. one half of this π molecular orbitals lies above and other half lies below the plane of the σ bonds.

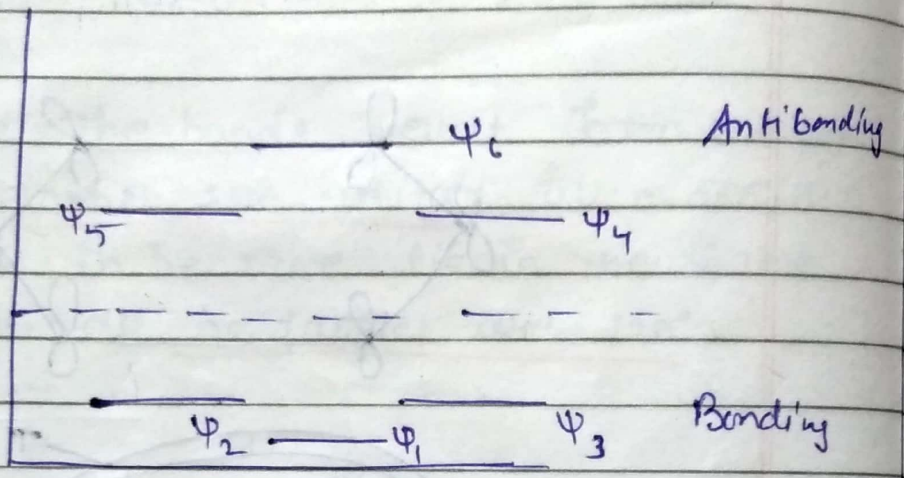


4. The six electrons of P orbital cover all the six C atoms and are said to be delocalised. due to delocalization, strange π bond is formed and makes molecules more stable

5 Thermochemical data shows that stabilization energy of delocalised π m.o in benzene is 36 kg calori

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6. Linear Combination of six atomic orbitals to form six M.O according to MOT Give the energy and Nature of M.O on the basis of mathematical Calculation.



* Schrodinger wave equation :- modify in 2D

1. de-Broglie Principle :

Acc. to de-Broglie every Particle (including $e^{\ominus}$ and photon) is associated with a wave and wavelength λ of the wave is given by

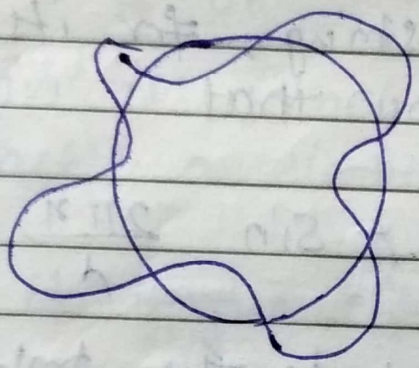
$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad -(1)$$

where mv is momentum

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Here h is Plancks Constant
v = velocity, m = mass

When an $e^{\ominus}$ move in a circular orbit around the nucleus the circumfrance of the circle must be integral (n) no. of wavelength λ.



(2) $$2\pi r = n\lambda \quad \text{---(ii)}$$

Or $$2\pi r = \frac{nh}{mv}$$

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

where mvr is the angular momentum i.e the angular momentum is the Integral no. of $\frac{h}{2\pi}$ units.

acc. to Schrodinger the Probability of the Presence of the electron near the nucleus is greatest;

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as the dist. from the nucleus increases the Probability decreases

a general wave eqⁿ for a small particle, for its wave motion was given by schrodinger.

3. Consider a system such as a streak string, for its vibration we know that

$$\Psi = A \sin \frac{2\pi x}{\lambda} \quad \text{---(iii)}$$

where A is the Amplitude of wave
Ψ = wave function
λ = wave length
x = displacement.

differentiating eqⁿ (iii)

$$\frac{d\Psi}{dx} = A \cos\left(\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$\frac{d\Psi}{dx} = A \frac{2\pi}{\lambda} \cos\left(\frac{2\pi x}{\lambda}\right)$$

again differentiate.

$$\frac{d^2\Psi}{dx^2} = A \cdot \frac{2\pi}{\lambda} \cdot \frac{2\pi}{\lambda}\left(-\sin\frac{2\pi x}{\lambda}\right)$$

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$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda} \cdot A \sin\left(\frac{2\pi x}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = -4\frac{\pi^2}{\lambda^2}\psi \quad \text{— (iv)}$$

$$\lambda^2 = -\frac{4\pi^2\psi}{\frac{d^2\psi}{dx^2}} \quad \text{— (v)}$$

eq^4 (iv) is applicable to all particle as electron, photons etc

acc. to de-Broglie eq^4

4. $$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda^2 = \frac{h^2}{(mv)^2}$$

$$m^2v^2 = \frac{h^2}{\lambda^2}$$

$$v^2 = \frac{h^2}{m^2\lambda^2}$$

we know that the kinetic energy

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

$$= \frac{1}{2} \times m \times \frac{h^2}{m^2\lambda^2}$$

$$K.E = \frac{h^2}{2m\lambda^2} \quad \text{— (vi)}$$

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from eq^{n} (vii) and (v) we get

$$K.E = \frac{1}{2} \frac{h^2}{m x} - 4\pi^2 \psi \frac{d^2\psi}{dx^2}$$

$$= -\frac{1}{2} \frac{h^2}{m x 4\pi^2 \psi} \times \frac{d^2\psi}{dx^2}$$

$$= -\frac{1}{8} \frac{h^2}{m \pi^2 \psi} \times \frac{d^2\psi}{dx^2}$$

the total energy of a particle is the sum of the K.E and Potential energy

$$E = K.E + P.E$$

$$K.E = E - P.E$$

$$-\frac{h^2}{8m\pi^2\psi} \times d^2\psi/dx^2 = E - P.E$$

$$\frac{d^2\psi}{dx^2} = -\frac{(E - P.E) \times 8\pi^2 m\psi}{h^2}$$

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

This is Schrodinger wave eq^n in one dimension system, this may extended in 3 dimensions. (x, y, z) as

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

This is known as Schrodinger wave eq^n or wave eq^n of single particle.

Here ψ is written for $\psi(x, y, z)$

But Laplacian operator (∇^2) is given for

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - PE) \times \psi = 0$$

Or

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

The above eq^n is know as Schrodinger wave eq^n

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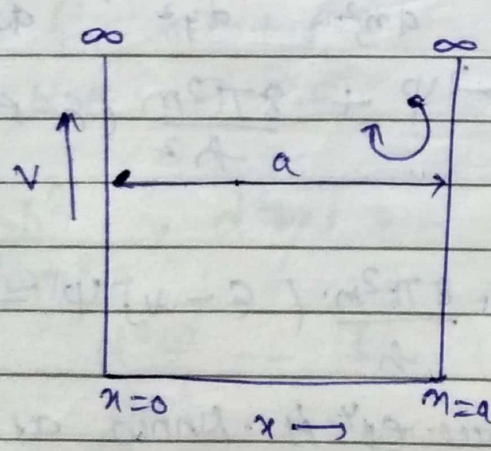
* ψ^2 :

The value of ψ^2 is the schrodinger wave eq^n for an $e^\ominus$ indicates the probability of finding the $e^\ominus$ at that point.

The values of all the four quantum no.s can be easily determine by solving the schrodinger eq^n.

The average dist. of an $e^\ominus$ from nucleus, and average speed of $e^\ominus$ in an atom are also known from this eq^n.

* Particle in one Dim. Box :



The calculation of ψ wave formation $e^\ominus$ move in a
of length a in the dirn x involves the use of Schrodinger wave eq^n.

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The Potential energy (V) is taking 0 with in this box of length a, it is infinite at $x = 0$ and at $x = a$

This is a solution of, as if an $e^{\ominus}$ enclosed in box with its potential energy infinite at walls. since the particle cannot have infinite energy, it can not remain outside the box. therefore wave function ψ vanishes for x

$x \leq 0$ $\quad x \geq a$

with in the box the schrodinger eq^{n} for the particle becomes $V = PE = 0$

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

or $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$

there are two possible solutions

$$\psi = A \sin \sqrt{\frac{8\pi^2 m E}{h^2}} \cdot x \quad - (A)$$

$$\psi = B \cos \sqrt{\frac{8\pi^2 m E}{h^2}} \cdot x \quad - (B)$$

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when $x = 0$ then $\psi = 0$
but this is not satisfy by eq^n (B), eq^n (A) satisfied this condition so eq^n (A) is solution of the eq^n (i)

the eq^n (A) must also satisfy that when $x = a$ then

$$\psi = 0$$

$$\psi = A \sin \sqrt{\frac{8\pi^2 m E}{h^2}} \cdot x$$

$$\psi = A \sin \sqrt{\frac{8\pi^2 m E}{h^2}} \times a = 0$$

Or

$$0 = \sin \sqrt{\frac{8\pi^2 m E}{h^2}} \times a$$

this is possible when

$$\sqrt{\frac{8\pi^2 m E}{h^2}} \times a = n\pi \quad \text{— (2)}$$

when when $n = 1, 2, 3 \ldots$ energy levels

Squaring eq^n (2)

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$$\frac{8\pi^2 mE}{h^2} \times a^2 = n^2\pi^2$$

$$\frac{8mE}{h^2} \times a^2 = n^2$$

$$E_n = \frac{n^2 h^2}{8ma^2} \quad \text{— (3)}$$

where E_n indicates the Energy in the n^{th} level of the Particle since, the n (Principle quantum no.) can have integral values.

So the Particle will have the certain definate values of E.,
E can not zero because n can not zero.
then

$$\psi_n = A \sin \frac{n\cdot\pi x}{a} \quad \text{— (4)}$$

Since the Probability of finding the Particle is 1 in the box is 1.
Hence

$$1 = \int_0^a |\psi_n^2| \, dx$$

Or

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

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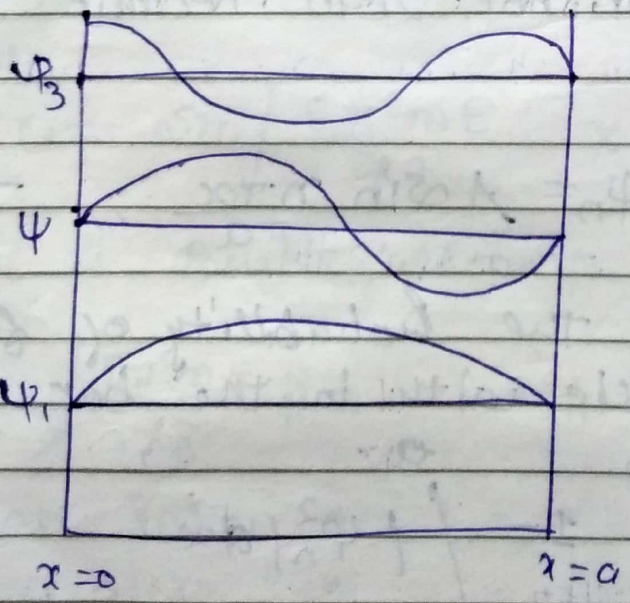
$$1 = \frac{A^2}{2} \cdot a \qquad \text{— (5)}$$

$$A = \frac{\sqrt{2}}{\sqrt{a}} \qquad \text{— (6)}$$

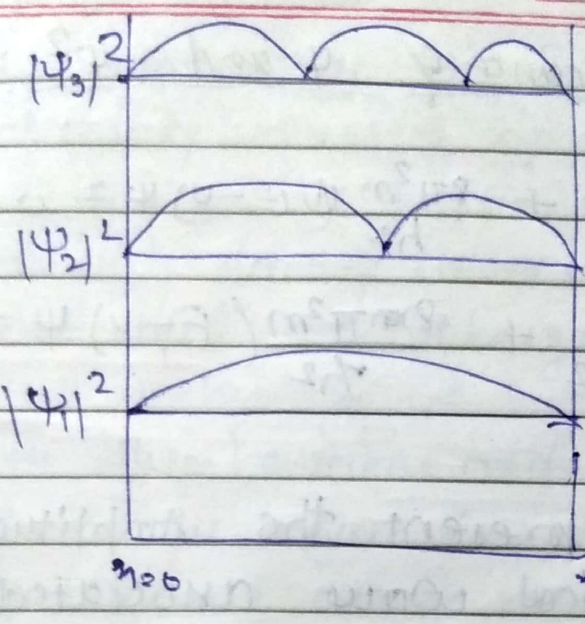
eq^{n} (4) the normalised wave fn ψ_n of the particle given by

$$\boxed{\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}} \qquad \text{— (7)}$$

In fig (ii) a ploat ψ_n and ψ_n^2 against x



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It is clear that ψ_n may be negative or positive by ψ^2_n is always is positive i.e the probability of finding an $e^\ominus$ at any point is always positive

* Laplacian Operator (∇^2):
Laplacian is one of most common operator in
and it is represented by ∇^2 and it is equal to

$$= \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} = \nabla^2$$

Schrodinger wave eq^n may be represented in the form of laplacian -

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

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Ans

* Significance of ψ and ψ^2 :-

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

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

ψ represent the Amplitude of spherical wave associated with the motion of electron around the nucleus. The value of ψ depends upon the value of potential and K.E of electron.

The value of ψ changes with the change in position of electron in an atom.

acc. to theory of propagation of light and sound waves, the square of Amplitude (ψ^2) proportional to the intensity of light.
The similar concept have been developed in the interpretation of wave fn (ψ). the square of ψ gives the probability of finding the e in small value

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In same ways ψ^2 gives the probability density of $e^{\ominus}$.

Probability density means the density of cloud of the -ve charge. The density of " " " " " changes with the position and distance from the nucleus. It means that cloud of -ve charge denser at some point and lighter at other points

* Difference b/w ψ and ψ^2 :-

ψ	ψ^2
- ψ represent the amplitude of spherical wave associated with the motion of $e^{\ominus}$ around the nucleus	- ψ^2 represent the prob. the finding the $e^{\ominus}$ in a small volume around the nucleus.
- ψ should have +ve and -ve value.	- ψ^2 has only +ve value