CHEMISTRY NOTES

CHAPTER #3

"THEORIES OF COVALENT BONDING"

⇒ SHAPES OF MOLECULES AN THEORIES OF COVALENT BONDING:

The Lewis Concept of covalent bonds does not ~~share~~explain shape of molecules.
The modern theories of covalent bonding explain shape of molecules as well as many other properties such as:

1- Bond energy
2- Relative strength of bonds
3- Paramagne-tism

THEORIES OF COVALENT BONDING:

There are three modern theories which are used to understand nature of covalent bond and also determine shape of molecules:

1- Valence shell electron pair repulsion theory (Abbreviated as VESPER and pronounced as "Vesper" theory)
2- The Valence bond theory (Abbreviated as VBT)
3- The Molecular orbital theory (Abbreviated as: MOT)

1- VSEPR THEORY

DISCOVERY:

This theory was suggested by "Sidgewick" and "Powell" in "1940"

According to "VSEPR theory".

"The shape or geometry of a molecule or ion depends on the number of shared pair as well as lone pairs of electrons around central atom of molecule or ion."

MODIFICATIONS:

"Gillespie" and "Nyholm" in "1957" modified the VSEPR theory.

They proposed:

"The arrangement of atoms in a molecule is mainly determined by repulsive interaction among all electron pair in valence shell of central atom."

BASIC ASSUMPTION OF VSEPR THEORY:

"The electron pairs around the central atom are arranged in space in such a way that they keep as far apart as possible so that there is minimum repulsion between them."

SEQUENCE:

1- Central atom
2- Repulsion Order
3- Nuclear attraction
4- No. of electron pair
5- Final geometry of molecule
6- Bond -formation

The arrangement of electron pair in this manner gives minimum energy and maximum stability to molecule or ion.

CENTRAL ATOM:

"An atom in a molecule or ion to which all other atoms are attacted is Central atom."

POSTULATES OF VSEPR THEORY.

ARRANGMENT OF ELECTRONS:

The electron pair present around central polyvalent atom try to keep themselves as far apart as possible.

NUCLEAR ATTRACTION:

A non bonding pair or lone pair occupies more space than bonding pair.

GEOMETRY OF MOLECULE:

Both lone pair as well as bond pair determine geometry of molecule.

MAGNITUDE OF REPULSION:

The magnitude of repulsion between electron pair decreases as follow:

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond par.

No. OF BONDS:

The two electron pair of a double and

and three electron pair of a triple bond contain a higher electron density. Therefore they occupy more space than one electron pair of a single bond. However they behave like single electron pair.

APPLICATIONS OF VSEPR THEORY:

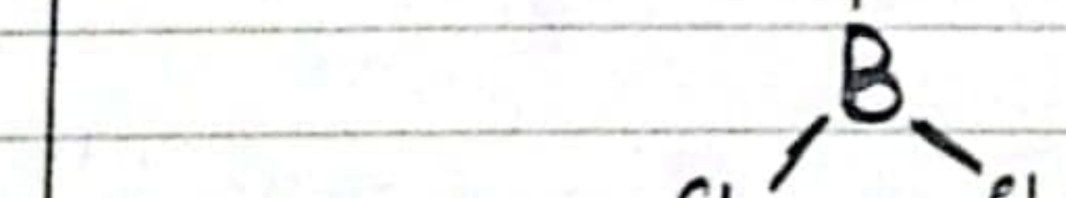
a) **AB_2 TYPE:**

No. of bond pair = 2

No. of lone pair = 0

Molecular geometry = linear

Bond angle = 180°



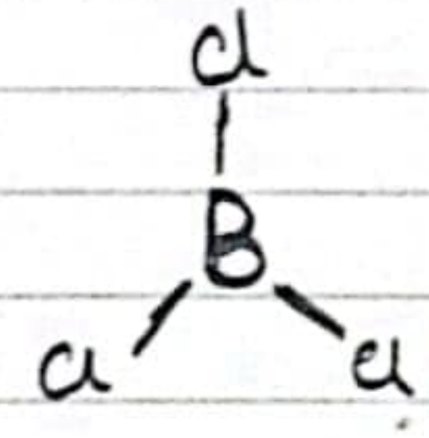
bi) **AB_3 TYPE:**

No. of bond pair = 3

No. of lone pair = 0

Molecular geometry = Planar triangular

Bond angle = 120°



ii) **AB_2E TYPE:**

No. of bond pair = 2

No. of lone pair = 1

Molecular geometry = V-shape

Bond Angle = less than 120°

c) **AB_4 TYPE:**

No. of bond pair = 4

No. of lone pair = 0

Molecular geometry= Tetrahedral geometry
Bond angle = 109.5°

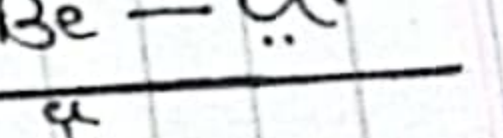
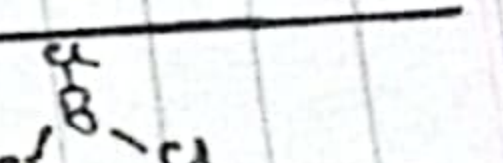
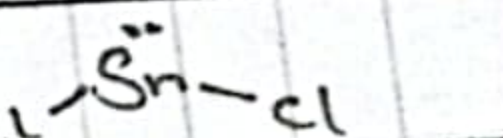
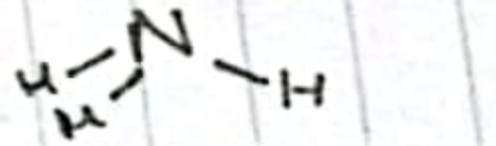
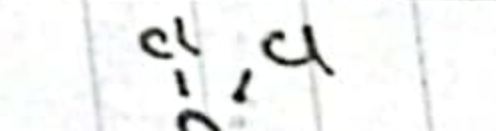
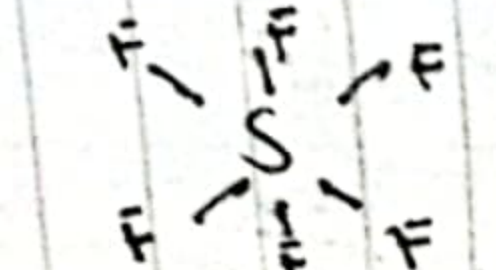
ii) AB_3E TYPE=
No. of bond pair= 3
No. of lone pair = 1
Molecular geometry = triangular pyramidal geometry
Bond angle = less than 109.5°

iii) AB_2E_2 TYPE
No. of bond pair = 2
No. of lone pair = 2
Molecular geometry = Bent
Bond angle = $\angle 109.5^\circ$

d) AB_5 TYPE
No. of bond pair= 5
No. of lone pair= 0
Molecular geometry = trigonal bipyramidal
Bond angle = 90°, 180°, 120°

e) AB_6 TYPE
No. of bond pair = 6
No. of lone pair= 0
Molecular geometry = Tetragonal bipyramidal
Bond angle = 90°, 180°

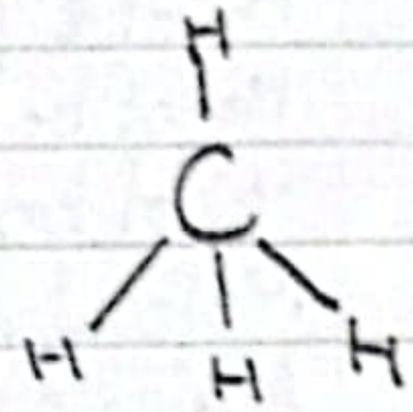
TABLE FOR VSEPR THEORY
IS ON NEXT PAGE:-

TYPE	No. of e^- Pair	Bond Pair	Lone Pair	Arrangement of e^- pairs	Geometry	Angle	Example
AB_2	2	2	0	Linear	Linear	180°	
AB_3	3	3	0	Trigonal Planar	Trigonal Planar	120°	
AB_2E	3	2	1	Trigonal planar	Bent, V-shaped	$\angle 120°$	
AB_4	4	4	0	Tetrahedral	Tetrahedral	109.5°	
AB_3E	4	3	1	Tetrahedral	Trigonal Pyrimidal	$\angle 109.5°$	
AB_2E_2	4	2	2	Tetrahedral	Bent, V-shaped	$\angle 109.5°$	
AB_5	5	5	0	Trigonal bipyrimidal	Trigonal bipyrimidal	90°, 120°, 180°	
AB_6	6	6	0	Octahedral	Octahedral	90°, 180°	

Explain the following structures on basis of VSEPR Theory.

CH_4, CCl_4, SO_4^{-3}, NH_3, H_2O, NF_3, H_2S, BF_3, SO_2, $SnCl_2$, $BeCl_2$, $HgCl_2$, HNO_3, PF_5, SF_6

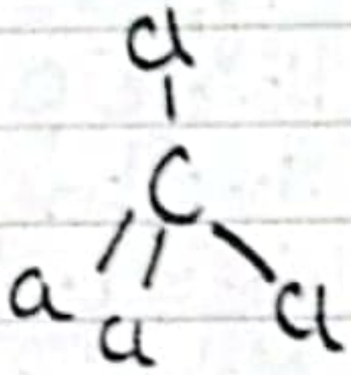
1⇒ CH_4



Type = AB_4
No. of e^- pairs = 4
No. of bond pairs = 4
No. of lone pairs = 0
Molecular geometry = Tetra hedral
Angle = 109.5°

2. CCl_4

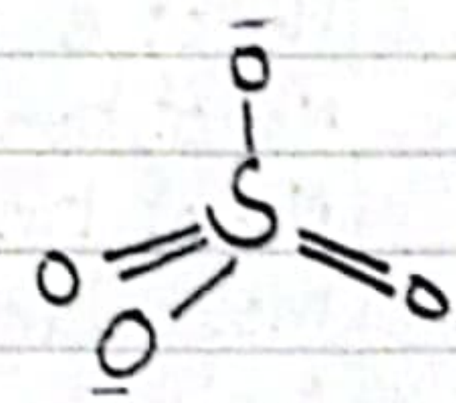
Structure:-



Type = AB_4
No. of e^- pairs = 4
No. of bond pairs = 4
No. of lone pairs = 0
Molecular geometry = Tetrahedral
Angle = 109.5°

3. SO_4^{-2}

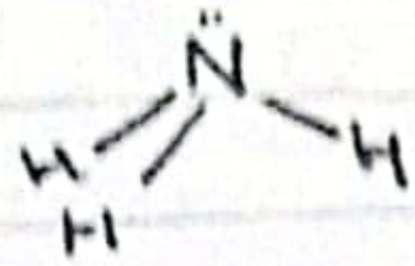
Structure:-



Type = AB_4
No. of e^- pairs = 4
No. of bond pairs = 4
No. of lone pairs = 0
Molecular geometry = Tetrahedral
Angle = 109.5°

4- NH_3

Structure:-



Type= AB_3E

No. of e^- pairs= 4

No. of bond pairs= 3

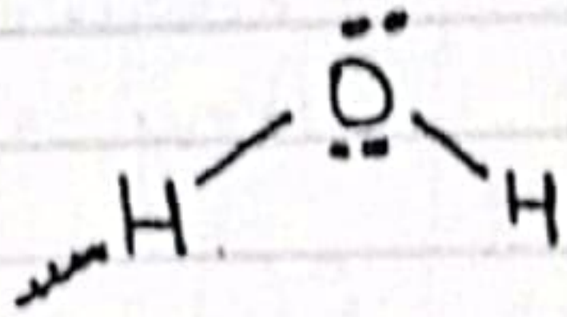
No. of lone pairs= 1

Molecular geometry= Trigonal pyrimidal

Angle= $\angle 109.5^\circ$

5- H_2O

Structure:-



Type= AB_2E_2

No. of e^- pairs= 4

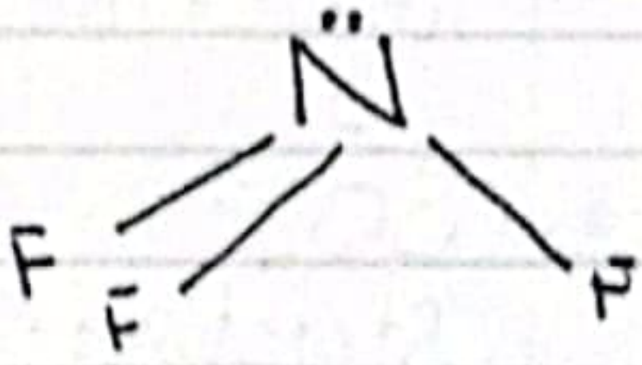
No. of lone pairs= 2

No. of bond pairs= 2

Molecular geometry= Bent

Angle= $\angle 109.5^\circ$

6- NF_3



Type= AB_3E

No. of e^- pairs= 4

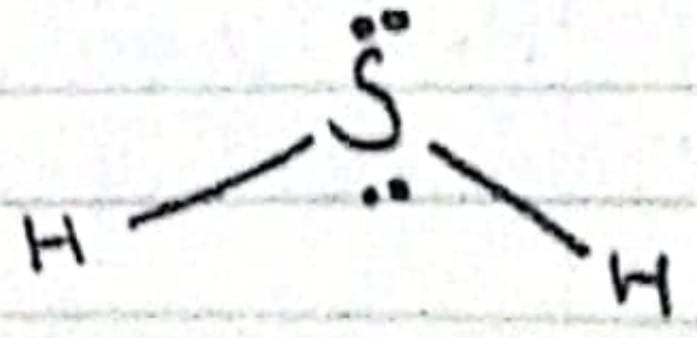
No. of bond pairs= 3

No. of lone pairs= 1

Molecular geometry= Trigonal pyrimidal

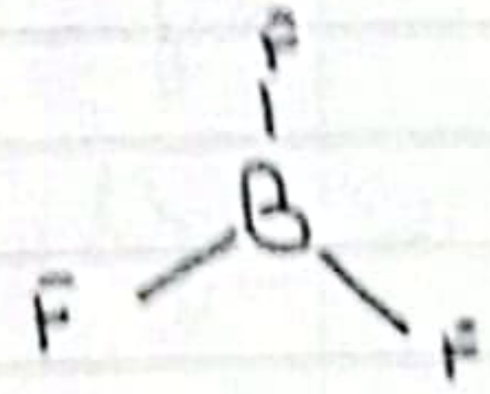
Angle= $\angle 109.5^\circ$

7- H_2S



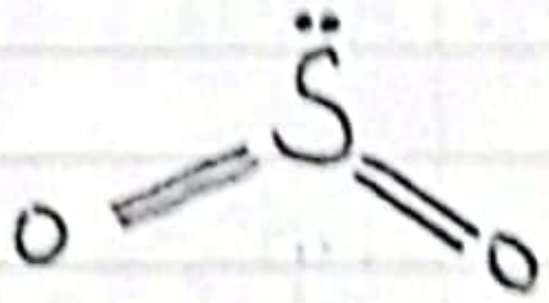
Type = AB_2F_2
No. of e^- pair = 4
No. of bond pair = 2
No. of lone pair = 2
Molecular geometry: Bent
Angle = $\angle 109.5°$

8. BF_3



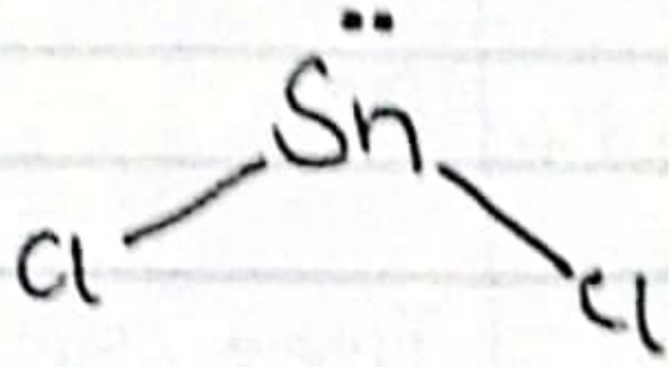
Type = AB_3
No. of e^- pair = 3
No. of bond pair = 3
No. of lone pair = 0
Molecular geometry = Trigonal planar
Angle: 120°

9. SO_2



Type = AB_2E
No. of e^- pair = 3
No. of bond pair = 2
No. of lone pair = 1
Molecular geometry = Bent
Angle = $\angle 120°$

10. $SnCl_2$



Type = AB_2E
No. of e^- pair = 3
No. of bond pair = 2
No. of lone pair = 1
Molecular geometry = Bent
Angle = $\angle 120°$

11- $BeCl_2$

Type = AB_2
No. of e^- pair = 2
No. of bond pair = 2
No. of lone pair = 0
Molecular geometry = Linear
Angle = 180°

Cl — Be — Cl

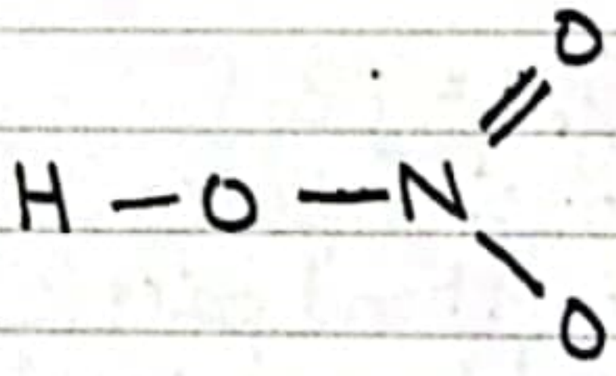
12 $HgCl_2$

Type = AB_2
No. of e^- pairs = 2
No of bond pairs = 2
No. of lone pair = 0
Mdecular geometry = linear
Angle = 180°

Cl — Hg — Cl

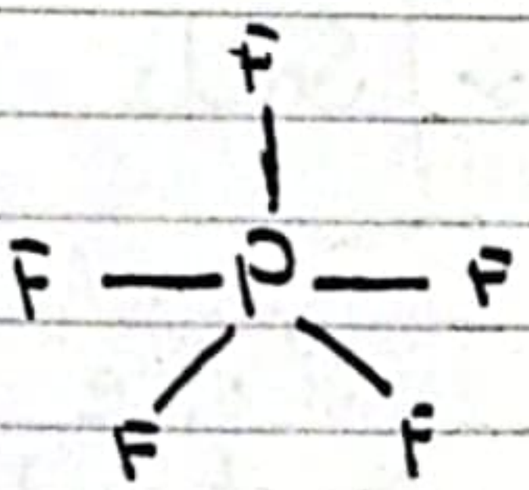
13- HNO_3

Type = AB_3
No. of e^- pair = 3
No. of bond pair = 3
No. of lone pair = 0
Molecular geometry = Trigonal planar
Angle = 120°



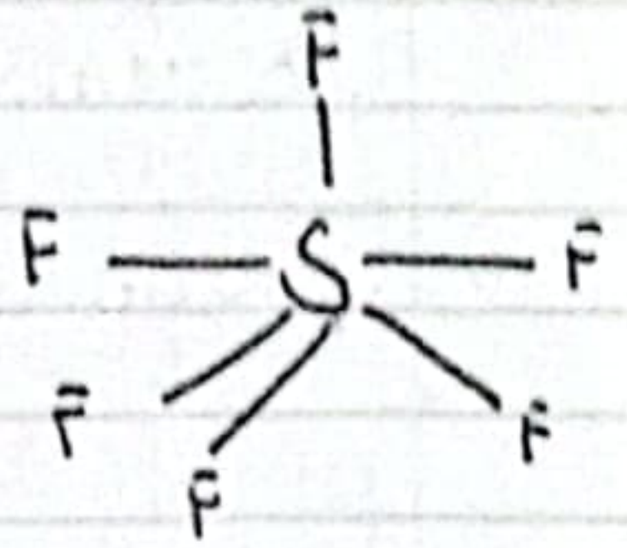
14. PF_5

Type = AB_5
No. of e^- pair = 5
No. of bond pair = 5
No. of lone pair = 0
Molecular geometry = Trigonal bipyrimidal



Angle = 90°, 180°, 120°

15- SF_6



Type = AB_6
No. of e^- pair = 6
No. of bond pair = 6
No. of lone pair = 0
Molecular geometry = Octahedral
Angle = 90°, 180°

VALENCE BOND THEORY (VBT)

DISCOVERY:

This theory was proposed by Heitler and London in 1927

BASIC CONCEPT:

This concept is based on wave-mechanical treatment of molecules. This theory explains bond energies, bond length and shape of molecules.

STATEMENT:

According to VBT:

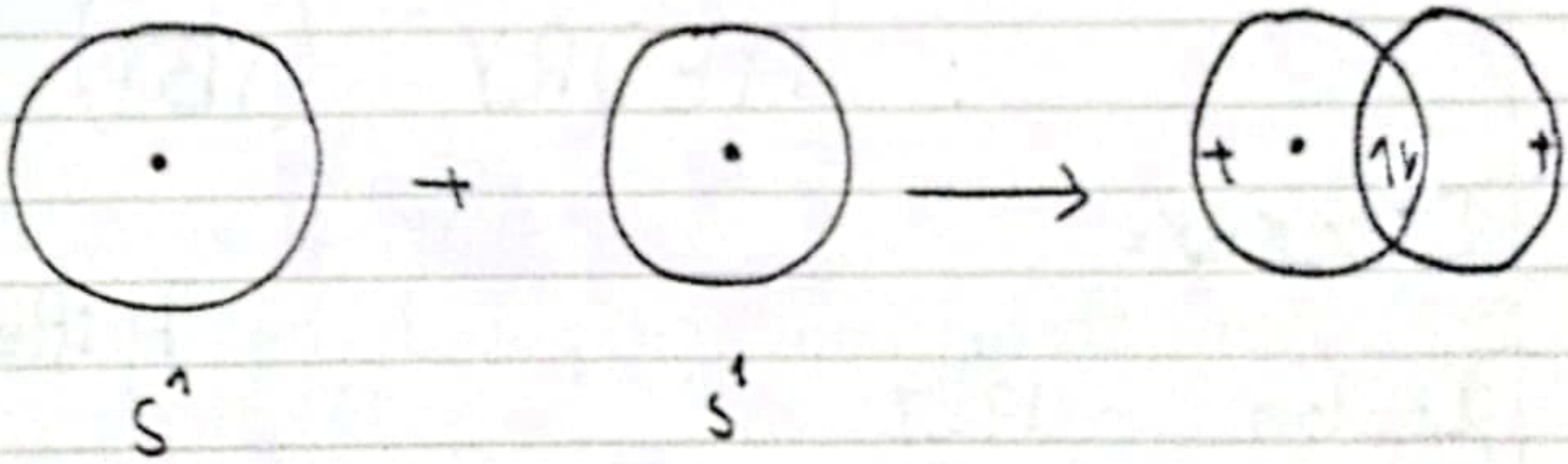
"A covalent bond between two atoms is formed when the atoms come so close that partially filled atomic orbital of one atom overlaps with other."

KEY POINTS OF VBT:

→ **FORMATION OF COVALENT BOND:**
A covalent is formed by overlapping of partially filled atomic orbitals

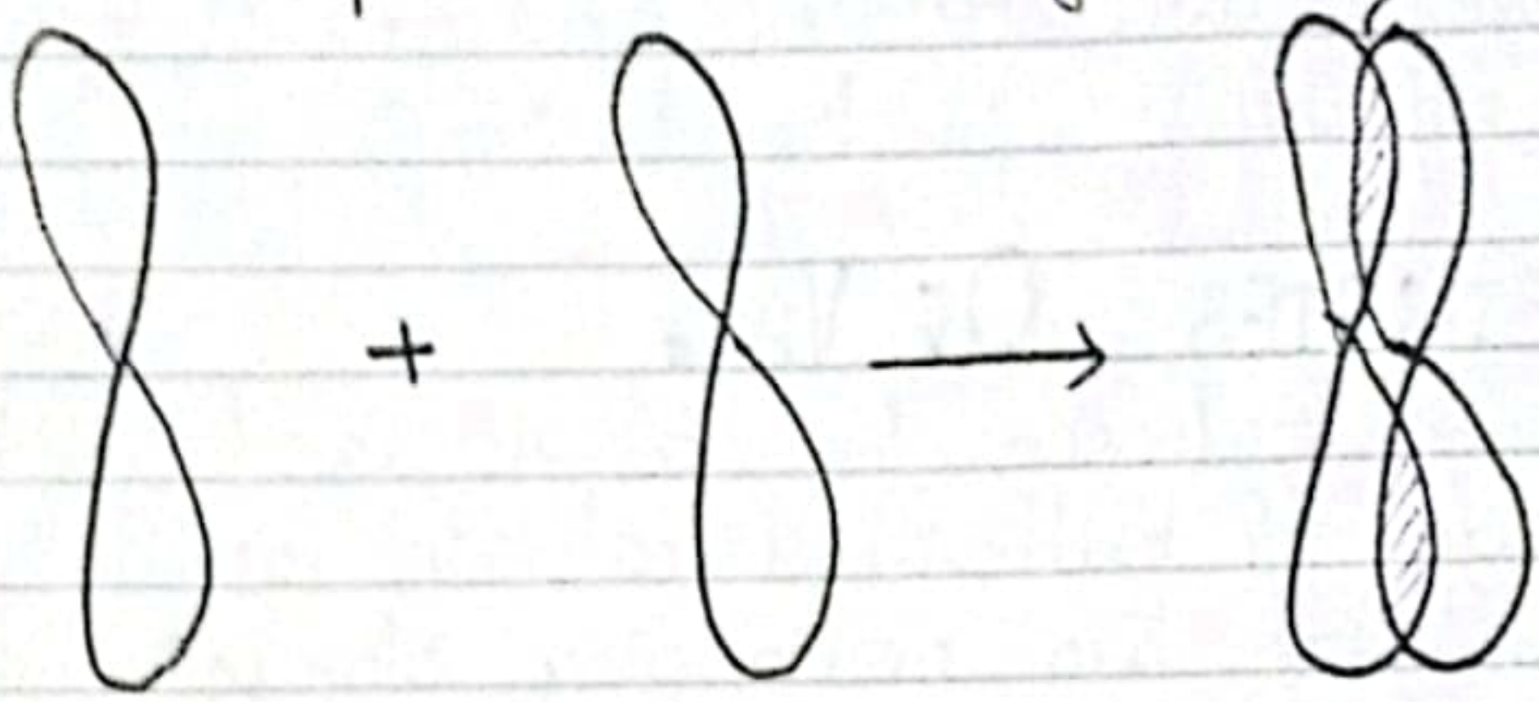
→ **OVERLAPPING**
There are two types of overlapping:
a) Linear overlapping or head to head overlapping.
b) Parallel overlapping or sideways overlapping.

→ **FORMATION OF SIGMA BOND:**
Sigma bond is formed by linear overlapping.
Its formation doesnot depend upon pi bond.



N) FORMATION OF pi- Bond.

Parallel overlapping form pi · bond · Its formation depends upon sigma bond.



→ SINGLE BOND=

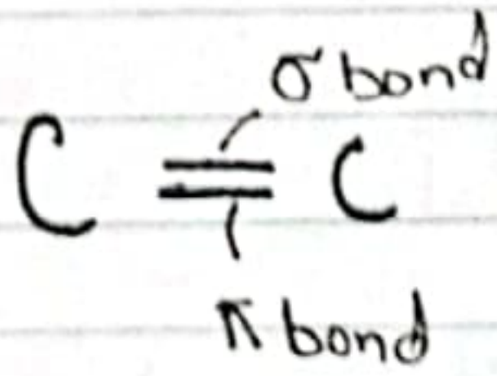
Single bond consist of sigma bond or σ.

→ DOUBLE BOND:

Double bond consists of one sigma bond and one pi bond.

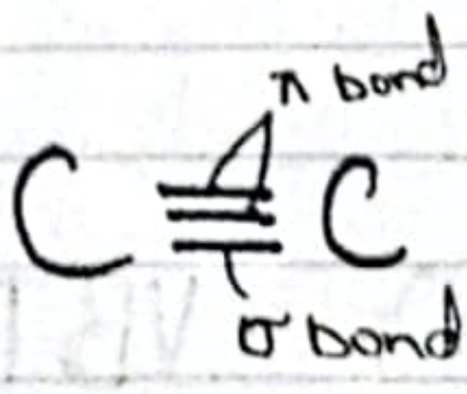
EXAMPLE

→



→ TRIB TRIPLE BOND=

Triple bond ~~forms~~ ~~both~~ consist of one σ bond and two pi bonds.



EXTENT OF OVERLAPPING=

Extent of overlapping is strong in

sigma bond and weak in pi-bond.

ELECTRIC DENSITY=

In sigma bond electric density exists between two nuclei and exist away from two nuclei in pi bond.

POSTULATES OF VBT=

1- A bond between two atoms is formed by the overlap of half-filled atomic orbitals of two atoms. The two overlapping atomic orbitals retain their identity.

2- Electrons have opposite spin in the overlapping orbitals.

3- A single bond is formed by overlapping of two orbitals.

4- A multiple bond is formed by overlapping of more than two orbitals.

5- The number of bonds of an atom is equal To number of unpaired electron in outer (valence) shell of an atom.

6- The overlapping orbitals of same symmetry can form a bond.

7- Overlapping of orbitals releases energy. The greater energy is released stronger is bond formed.

⇒ **BOND AXIS=**

A line joining the nuclei of two bonded atoms is called bond axis.

DRAW BACKS OF VBT=

⇔ It does not explain=

1- Formation of coordinate covalent bonds.
2- The paramagnetic behaviour of Oxygen molecule.
3- Formation of odd electrons molecules or ions.

Explain the structures of following by VBT=
$H_2, F_2, Cl_2, HF, O_2, N_2, NH_3, H_2O$.

1- H_2

ELECTRONIC CONFIGURATION =

$_1H = \boxed{1s^1}$
$_1H = \boxed{1s^1}$

Structure =

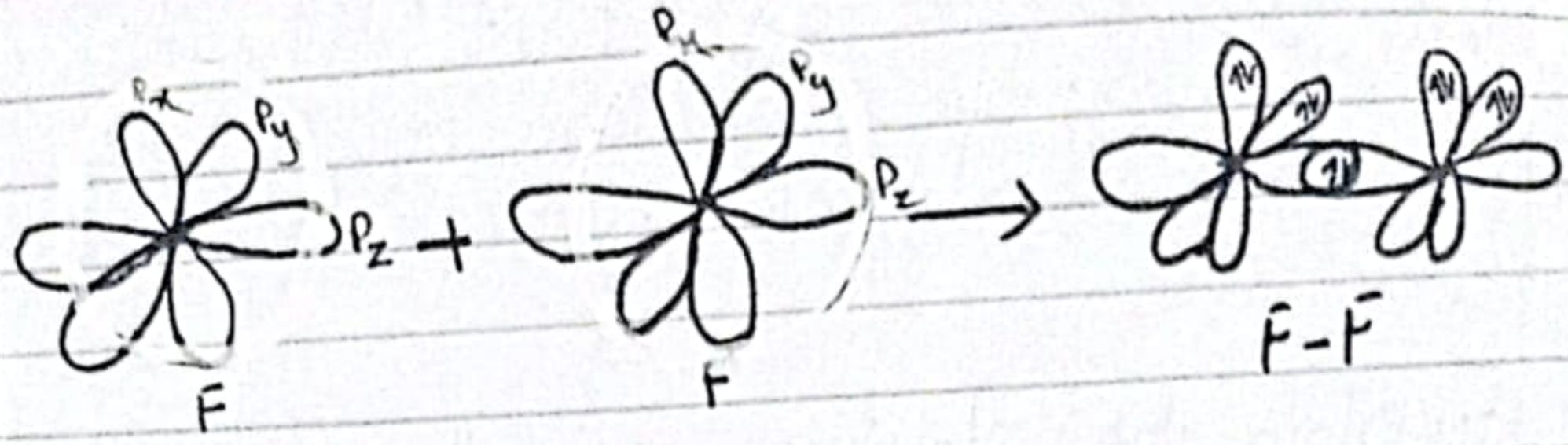
2- Flourine (F_2) =

ELECTRONIC CONFIGURATION=

$_9F = 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{\uparrow\downarrow}\ 2p_y^{\uparrow\downarrow}\ \boxed{2p_z^{\uparrow}}$ F
$_9F = 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{\uparrow\downarrow}\ 2p_y^{\uparrow\downarrow}\ \boxed{2p_z^{\uparrow}}$ F

Structure=

→

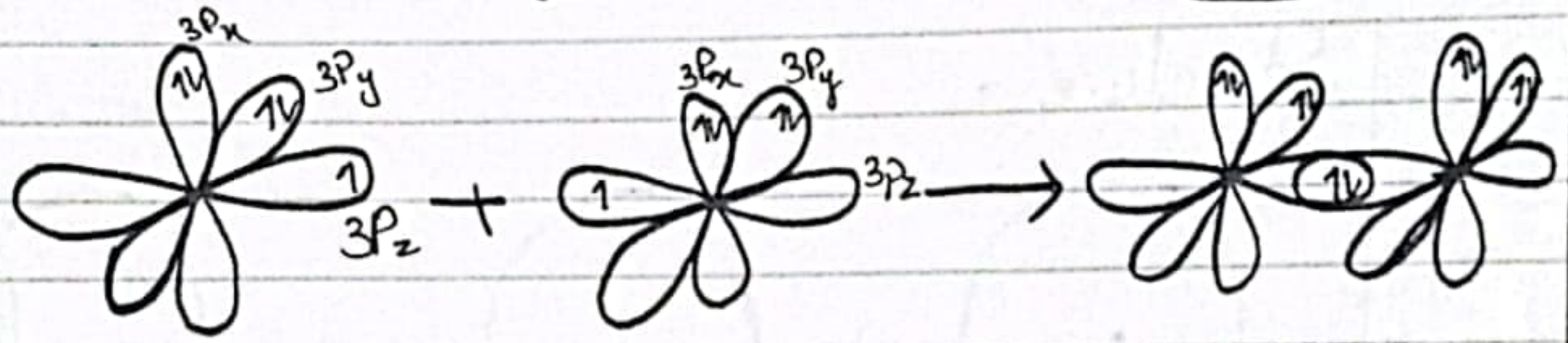


3- Chlorine (Cl_2) molecule:

Electronic Configuration =

$_{17}Cl = 1s^{2} 2s^{2} 2p_x^{2} 2p_y^{2} 2p_z^{2} 3s^{2} 3p_x^{2} 3p_y^{2} \boxed{3p_z^{1}}$ Cl

$_{17}Cl = 1s^{2} 2s^{2} 2p_x^{2} 2p_y^{2} 2p_z^{2} 3s^{2} 3p_x^{2} 3p_y^{2} \boxed{3p_z^{1}}$ Cl

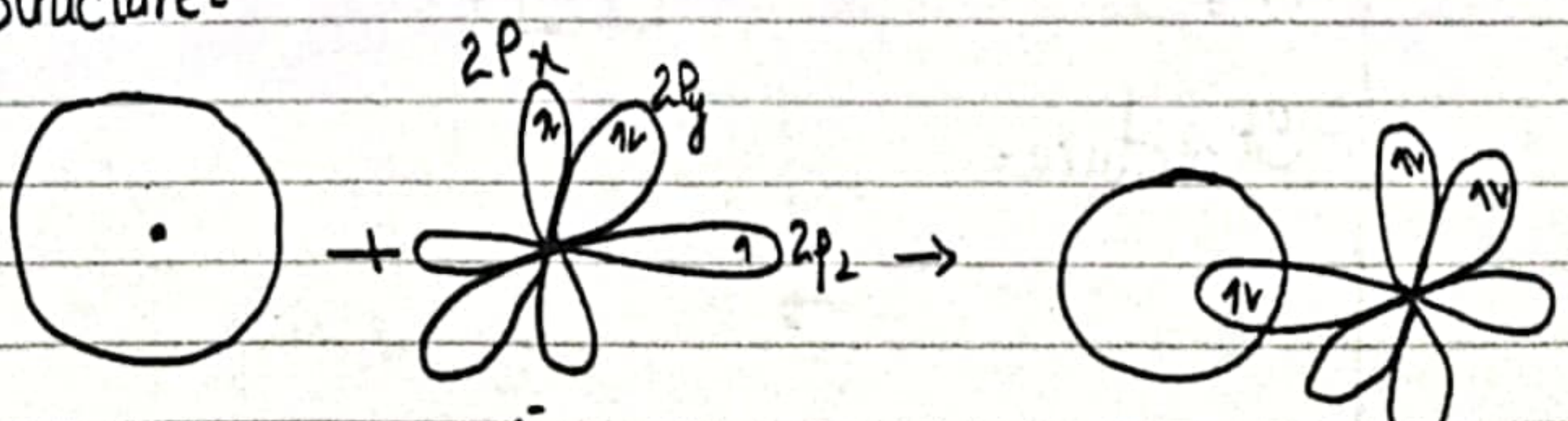


4- Hydrogen flouride (HF) molecule=

Electronic Configuration=

$_{1}H =$ ′

$_{9}F = 1s^{2} 2s^{2} 2p_x^{2} 2p_y^{2} \boxed{2p_z^{1}}$ F



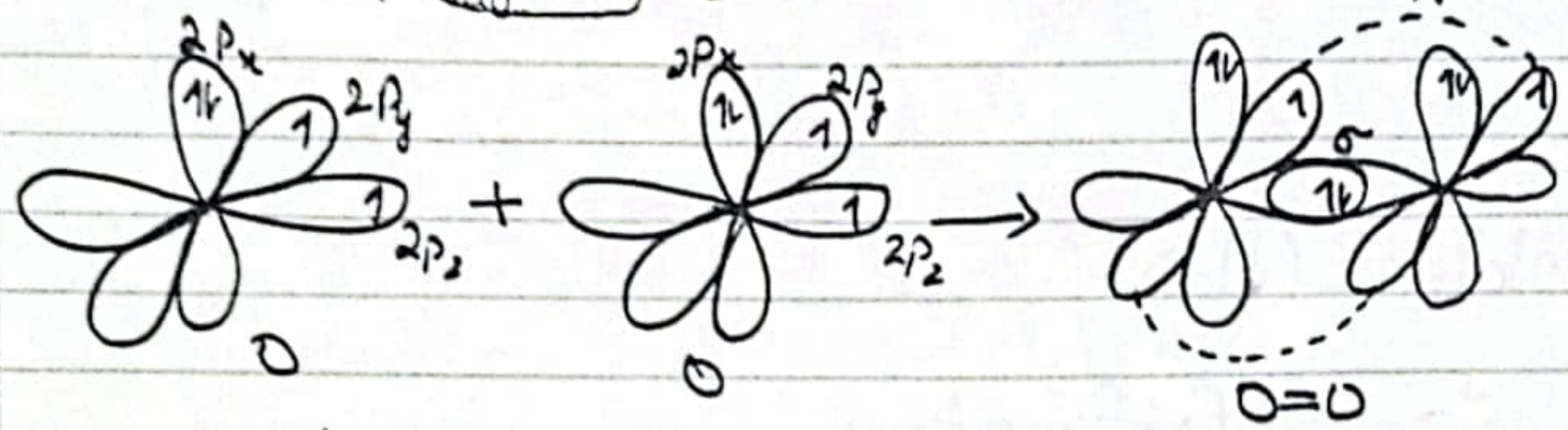
5- Oxygen (O_2)

Electronic Configuration:

$_8O = 1s^{2} \; 2s^{2} \; 2p_x^{2} \; 2p_y^{1} \; 2p_z^{1}$

$_8O = 1s^{2} \; 2s^{2} \; 2p_x^{2} \; 2p_y^{1} \; 2p_z^{1}$

O
||
O



6 Nitrogen (N_2)

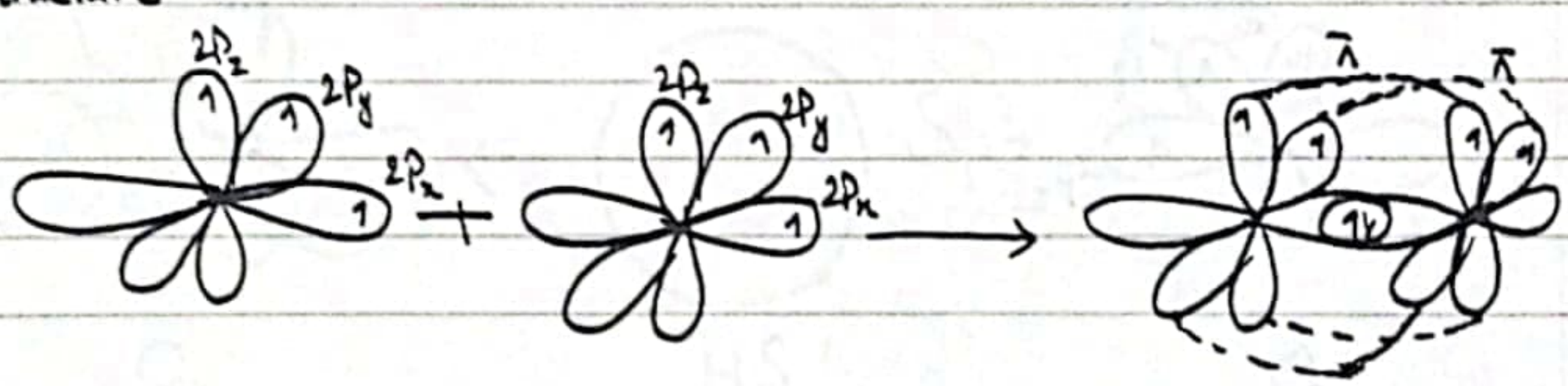
Electronic Configuration

$_7N = 1s^{2} \; 2s^{2} \; 2p_x^{1} \; 2p_y^{1} \; 2p_z^{1}$

$_7N = 1s^{2} \; 2s^{2} \; 2p_x^{1} \; 2p_y^{1} \; 2p_z^{1}$

N
|||
N

Structure =



7- Ammonia (NH_3)

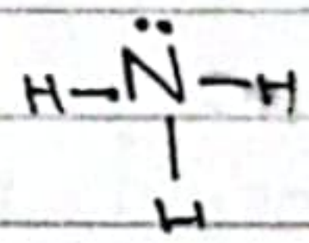
Electronic Configurations:

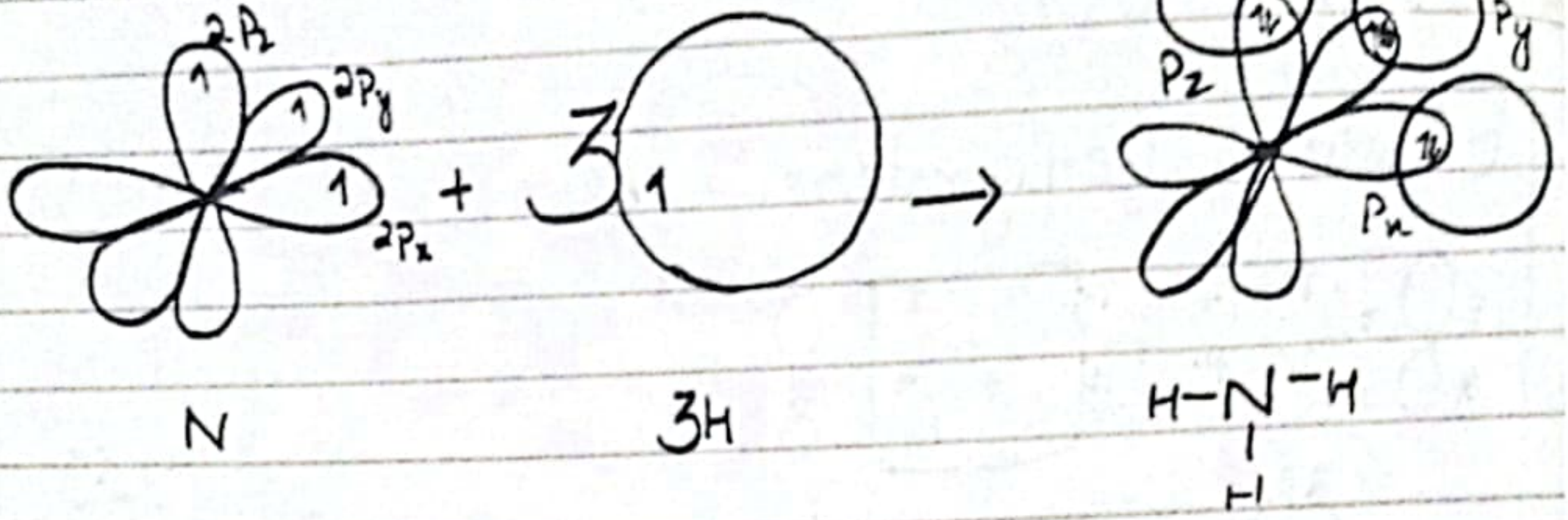
$_1H = 1s^{1}$

$_1H = 1s^{1}$

$_1H = 1s^{1}$

$_7N = 1s^{2} \; 2s^{2} \; 2p_x^{1} \; 2p_y^{1} \; 2p_z^{1}$





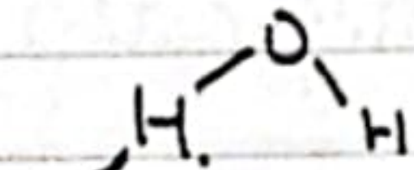
8- Water (H_2O)

Electronic Configuration:

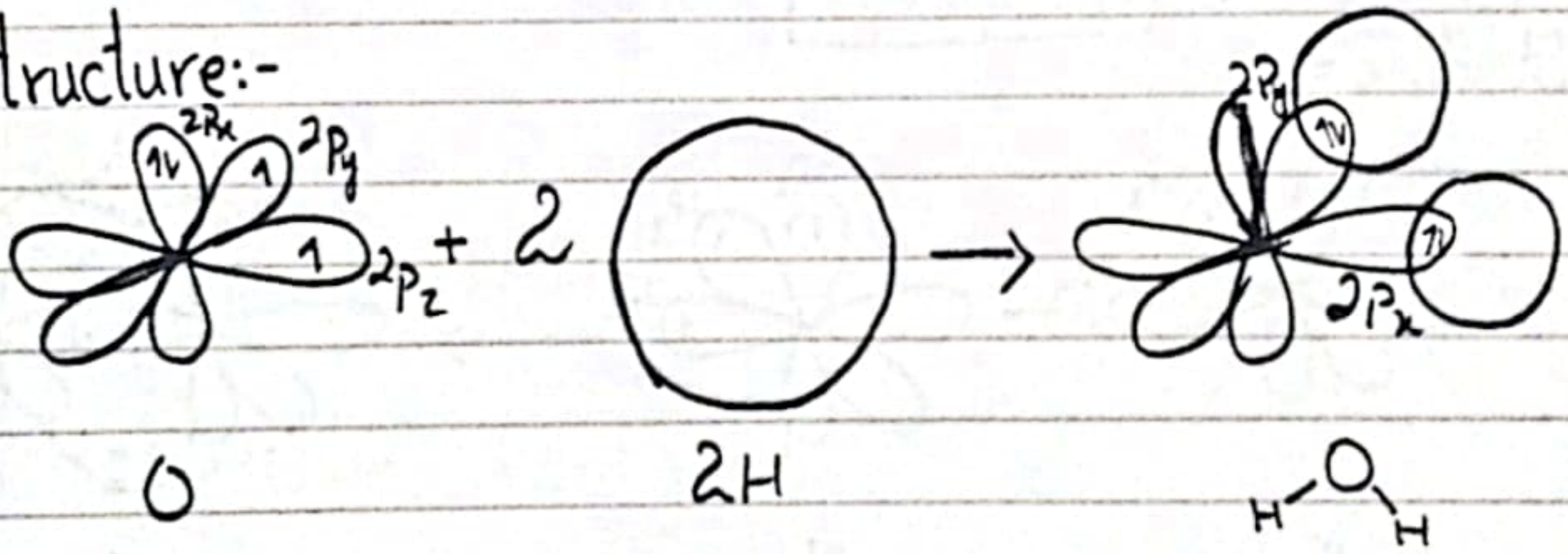
$_1H$ =

$_1H$ =

$_8O = 1s^{2} 2s^{2} 2p_x^{2} \boxed{2p_y^{1} 2p_z^{1}}$ (1s¹ 1s¹)



Structure:-



9- Carbon tetrachloride (CCl_4)

$_6C$ — "HYBRIDIZATION"

DISCOVERY:

The concept of hybridization was introduced by Pauling and Slater.

It is defined as:-

"The process in which orbital of different **energy** and **shape** mix into each other to form new orbitals i.e. **hybrid orbitals** of **equal energy** and **same shape** is called hybridization."

TYPES:-

The various types of this process are:-

1- sp^3- hybridization
2- sp^2- hybridization
3- sp- hybridization
4- dsp^3- hybridization
5- d^3sp^3- hybridization
6- d^3sp^3- hybridization

RULE:-

No. of sigma bond + lone pair = Ans

= 2 = sp
= 3 = sp^2
= 4 = sp^3 or dsp^2
= 5 = dsp^3
= 6 = d^2sp^3
= 7 = d^3sp^3

1- sp^3- HYBRIDIZATION:-

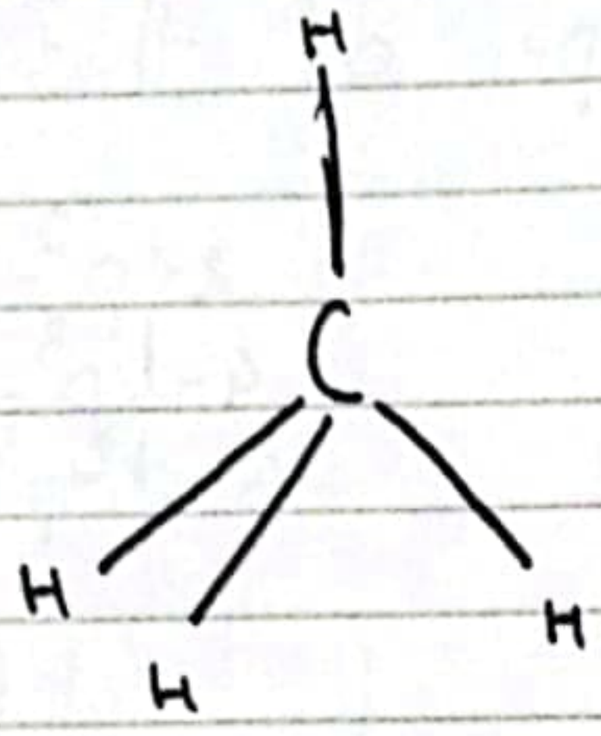
It is defined as:

"The mixing of one s and three p's p_x, p_y and p_z forming four new orbitals of equal energy and same shape."

COMPOSITION:
It contains 25% s-character and 75% p-character.

EXAMPLES:

Structure of Methane (CH_4)

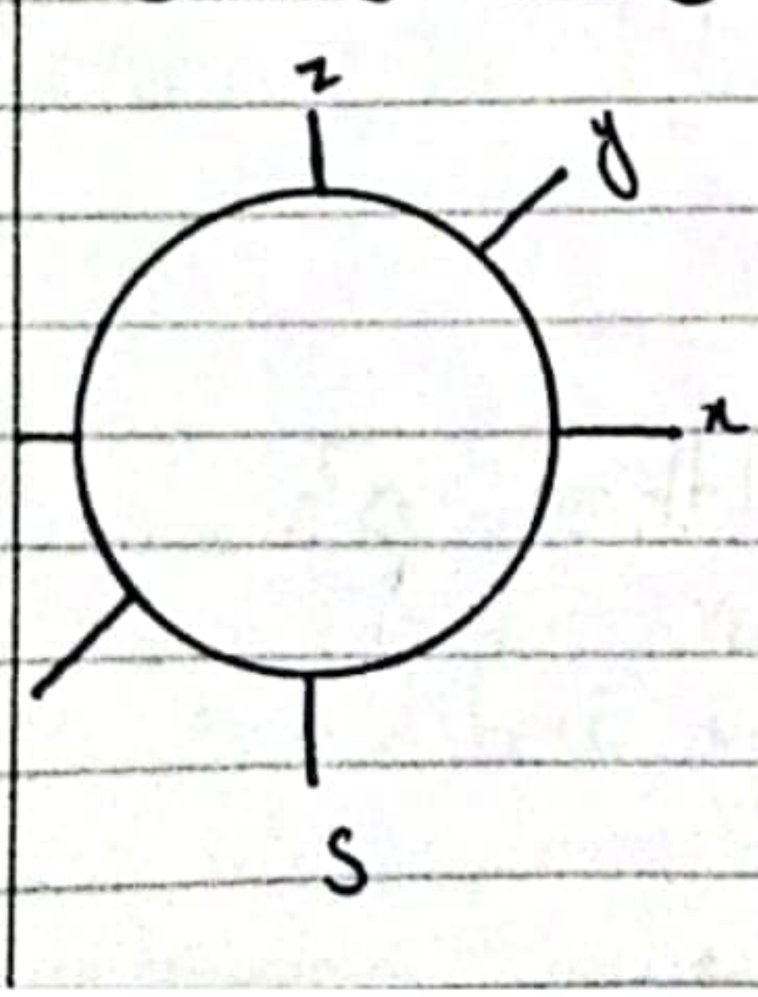


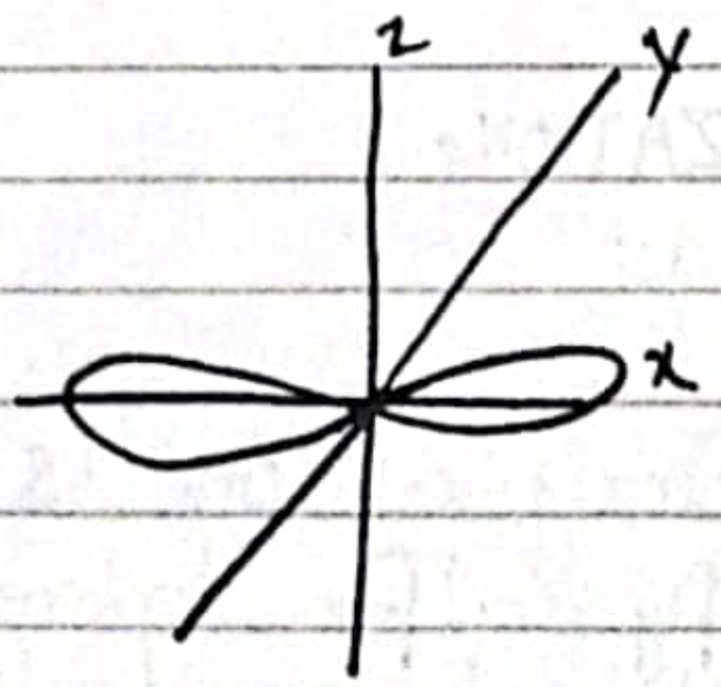
Electronic Configuration:

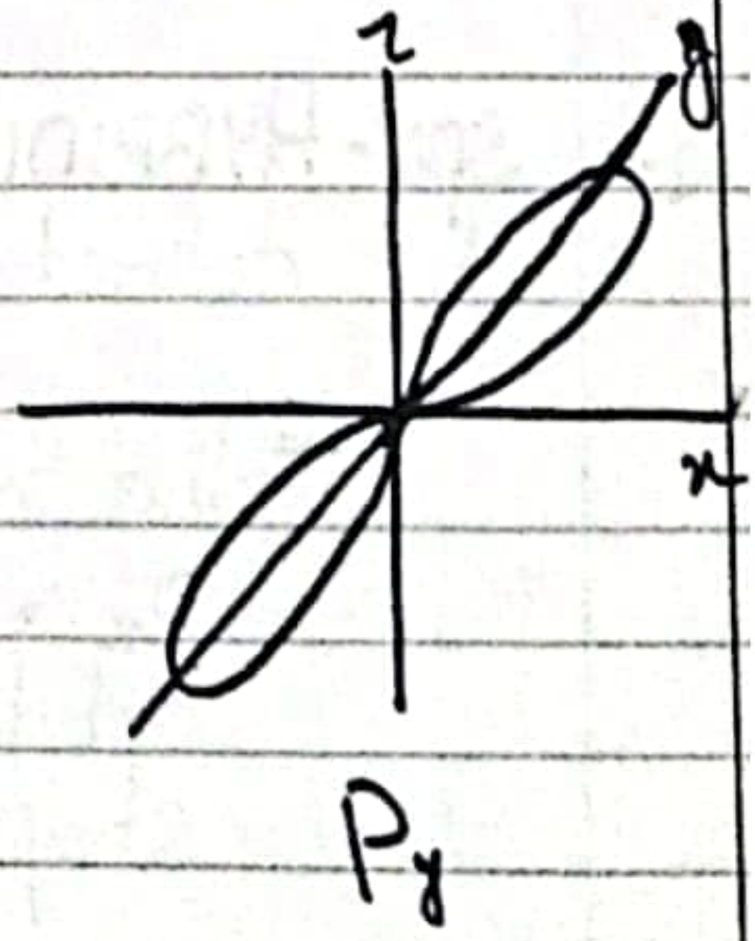
$_6C = 1s^{1v} 2s^{1v} 2p_x^1 2p_y^1 2p_z^0$ (ground state)
$_6C = 1s^{1v} 2s^1 2p_x^1 2p_y^1 2p_z^1$ (excited state)

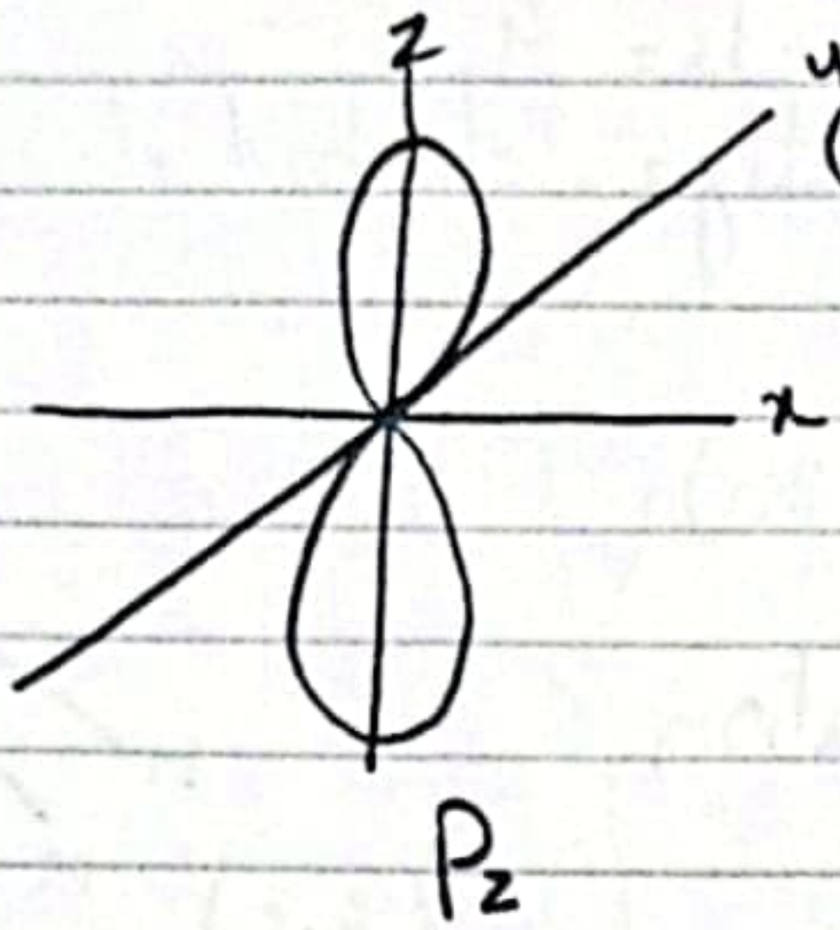
$_6C = 1s^{1v}$ | 1 | 1 | 1 | 1 | (hybrid state)
sp^3 sp^3 sp^3 sp^3

UNHYBRID ORBITATS



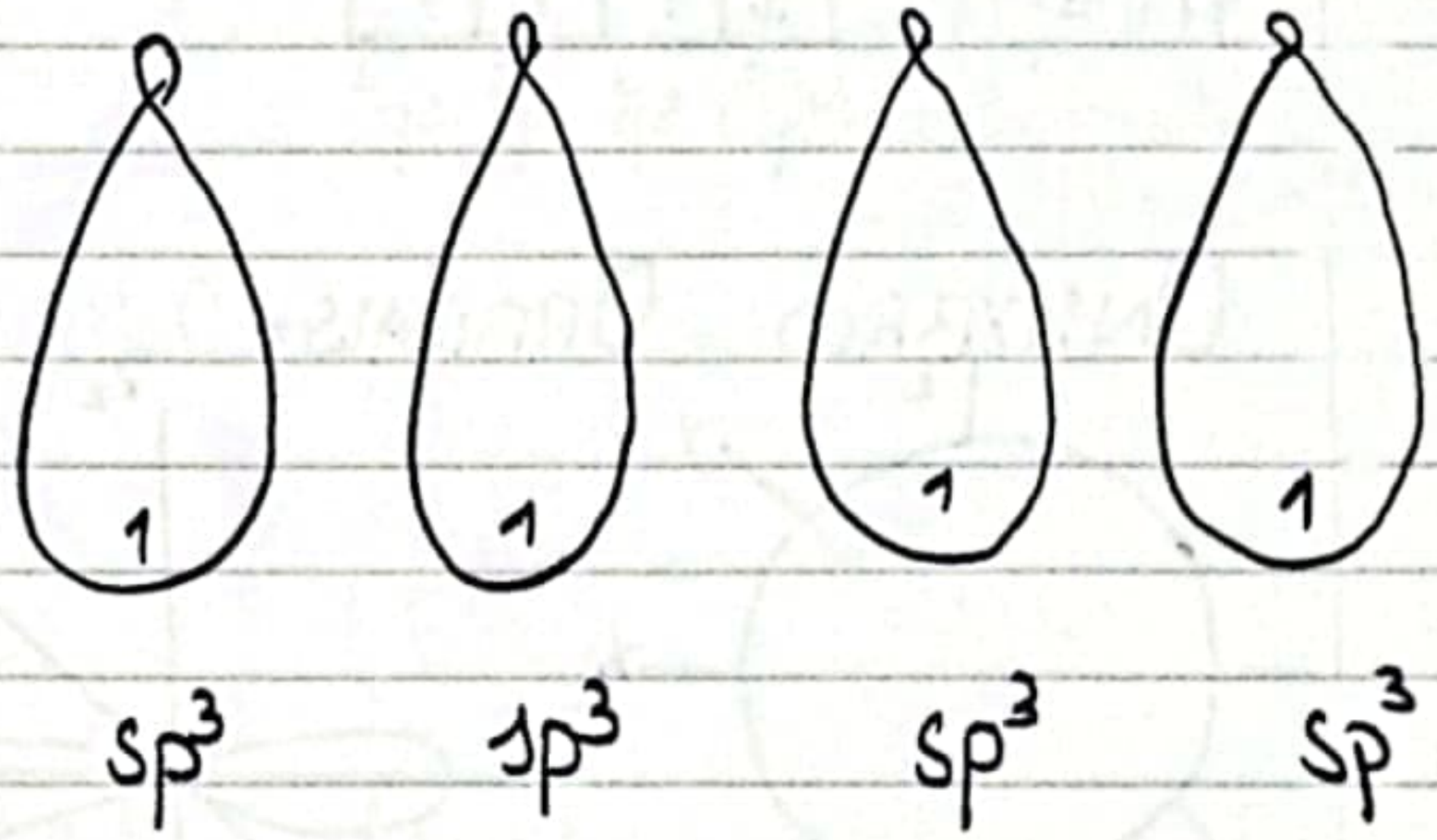






P_z

HYBRID ORBITALS =

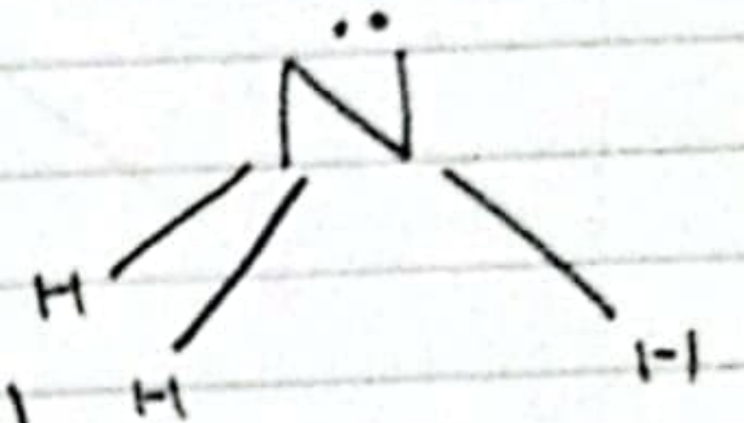


HYBRIDIZED STRUCTURE OF CH_4

CH_4

No. of Sigma bonds = 4
Molecular geometry: Tetrahedral
Angle: 109.5°

2. Structure of Ammonia (NH_3)



(E.S)

Electronic Configuration

$_7N = 1s^{2} 2s^{2} 2p_x^{1} 2p_y^{1} 2p_z^{1}$

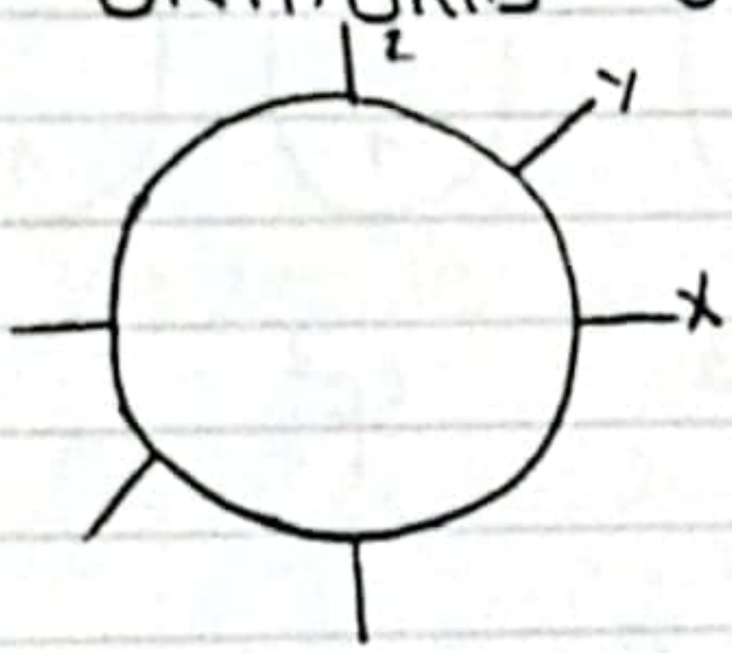
$_7N = 1s^{2}$ | 2 | 1 | 1 | 1 |

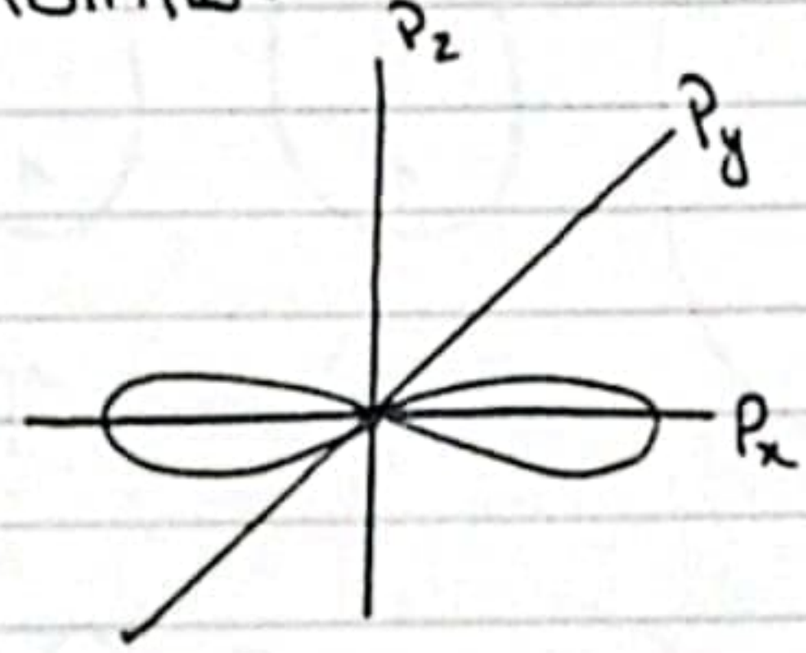
sp^3 sp^3 sp^3 sp^1

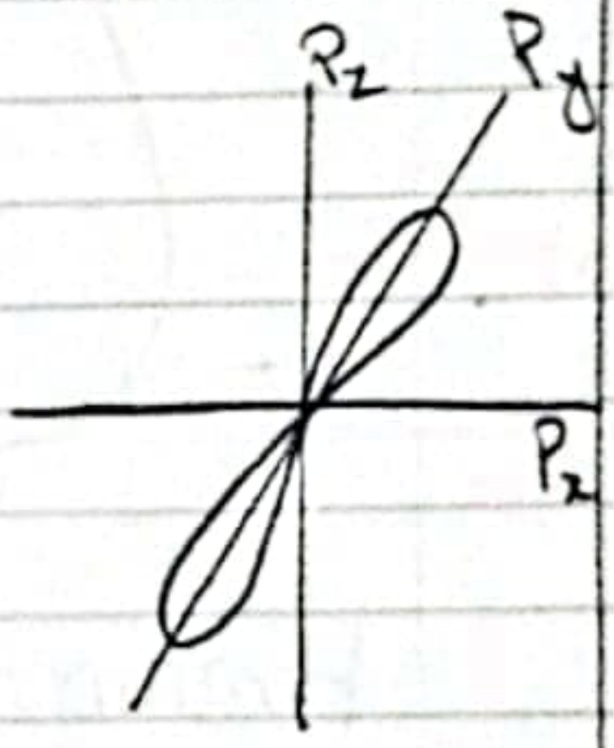
(H.S)

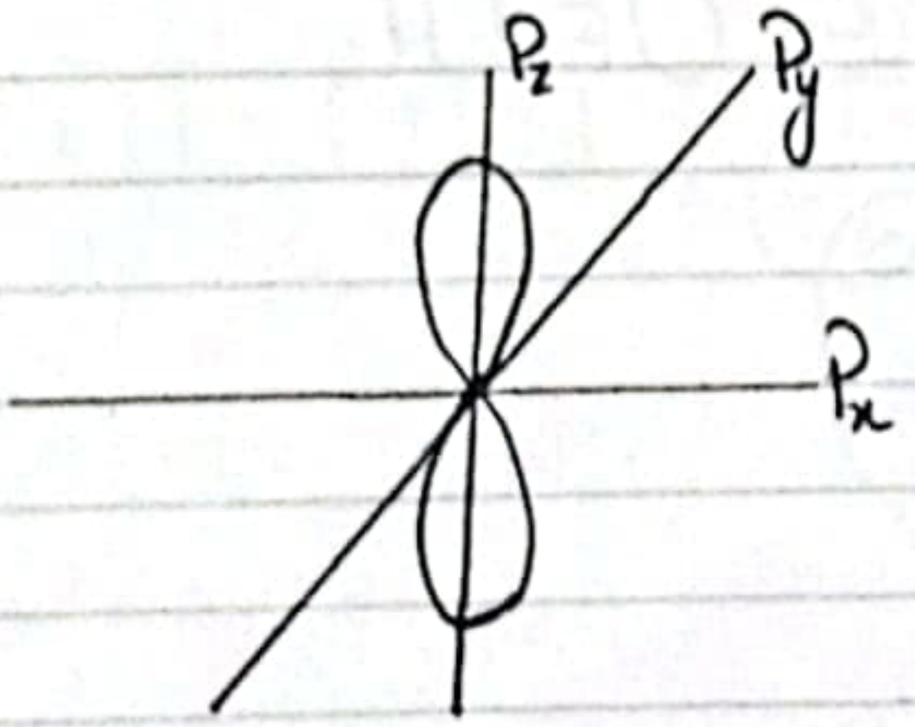
$_1H = 1s^1$

UNHYBRID ORBITALS:

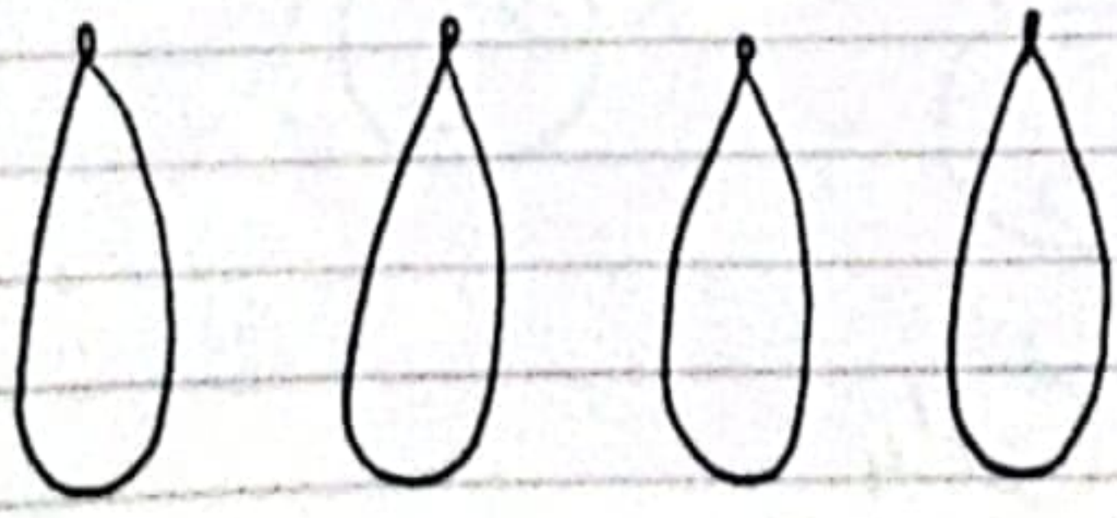




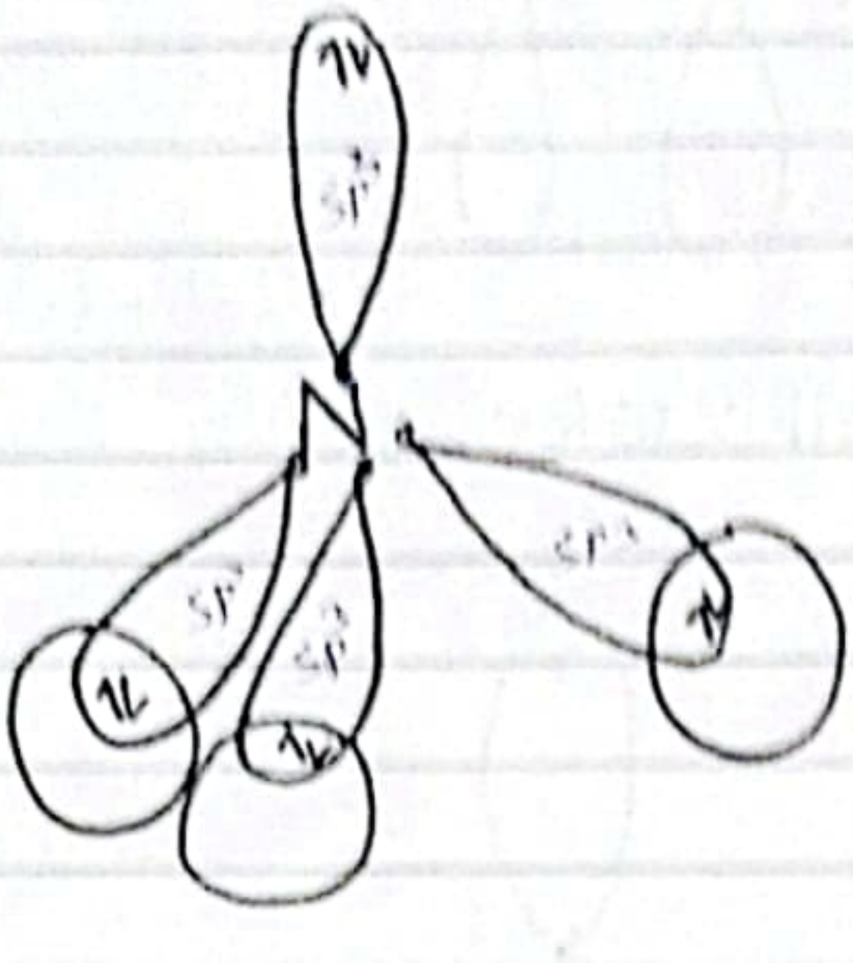




HYBRID ORBITALS:



Hybridized Structure

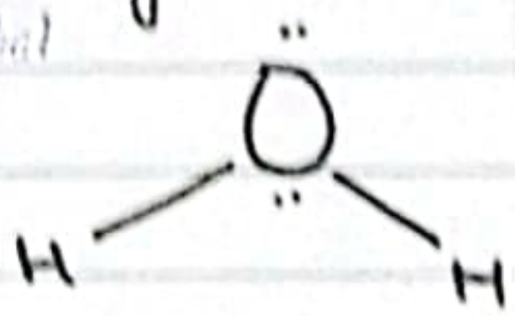


Sigma bonds = 3
Lone pair = 1
Molecular geometry = Trigonal
Angle = 107.5°

3- Structure of Water (H_2O):-

Electronic Configuration

$_8O = 1s^{\uparrow\downarrow}\ 2s^{\uparrow\downarrow}\ 2p_x^{\uparrow\downarrow}\ 2p_y^{1}\ 2p_z^{1}$ (E.S)

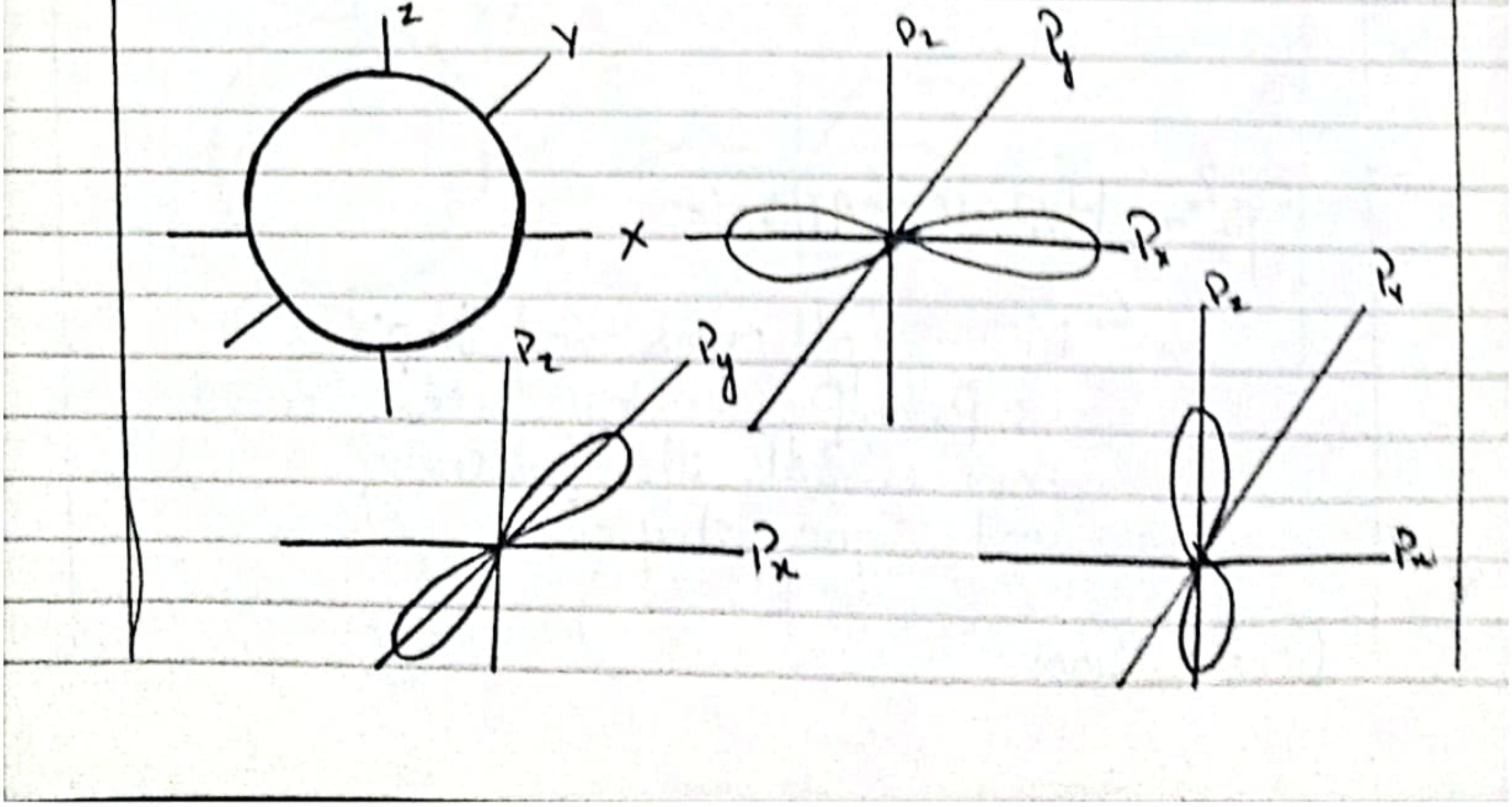


$_8O =$ $1s^{\uparrow\downarrow}$ | $\uparrow\downarrow$ | $\uparrow\downarrow$ | 1 | 1 (H.S)

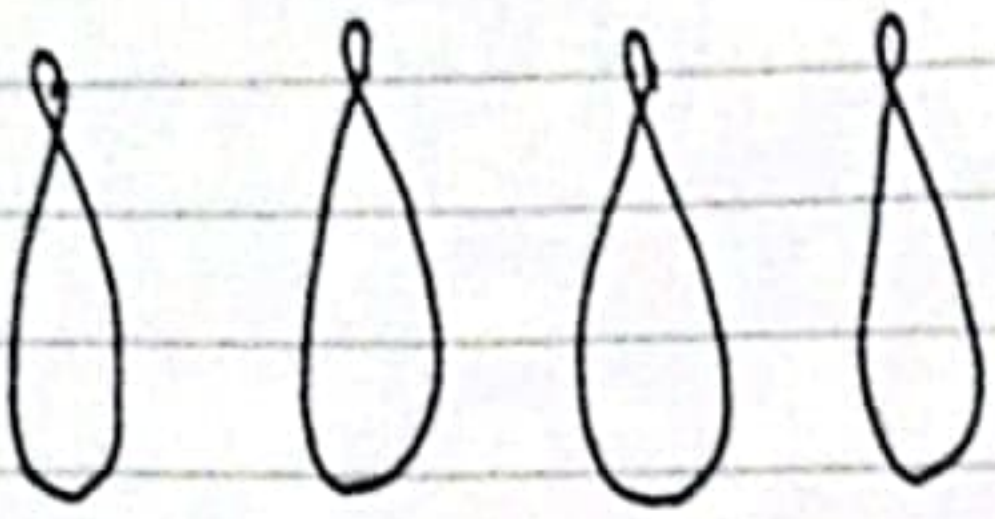
sp^3 sp^3 sp^3 sp^3

$H = 1s^1$

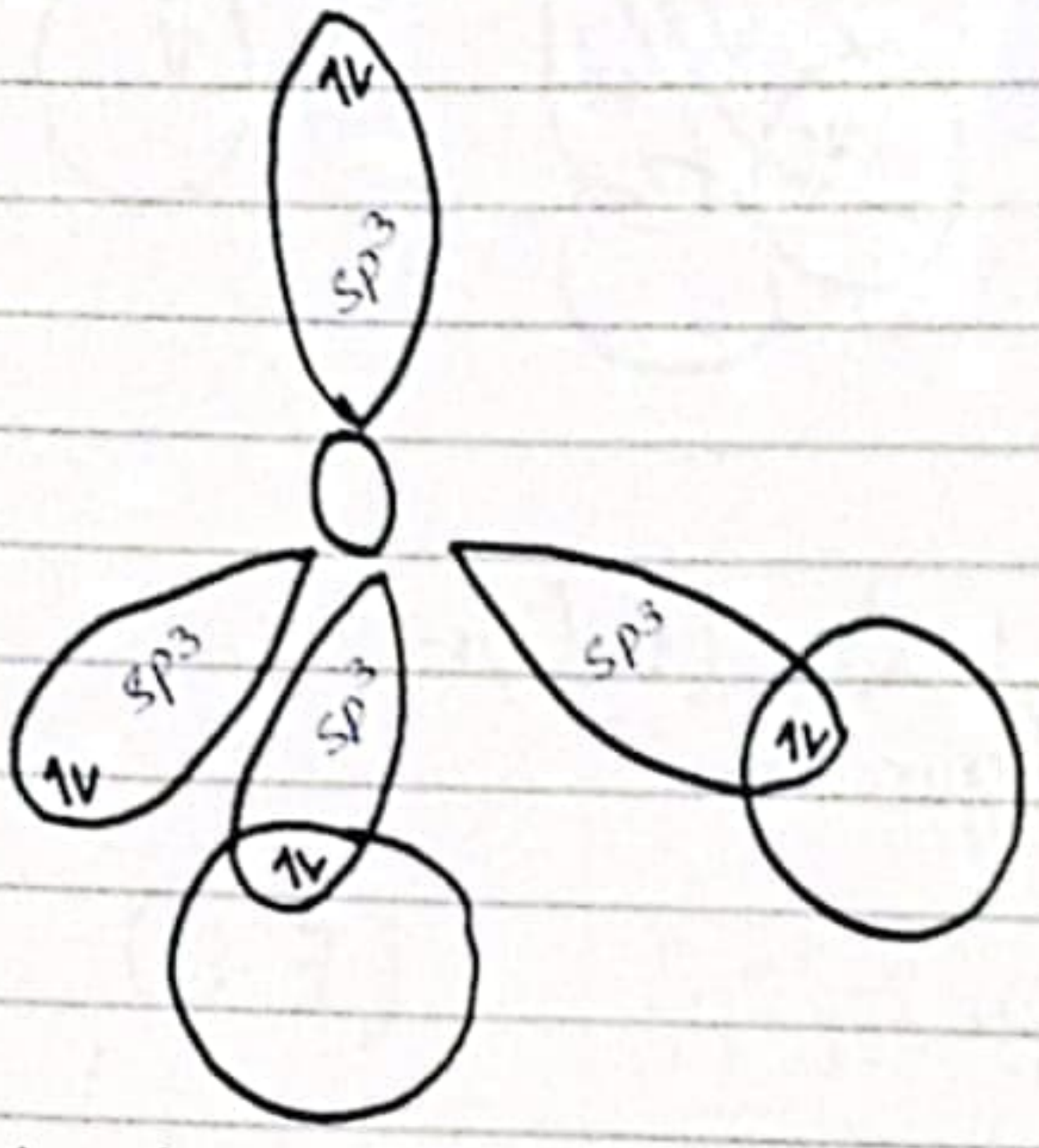
Unhybrid Orbitals



HYBRID ORBITALS =



HYBRIDIZED STRUCTURE



No. of sigma bonds = 2
No. of lone pairs = 2
Molecular geometry = bent
Angle = 104.5°

Sp^2- HYBRIDIZATION =

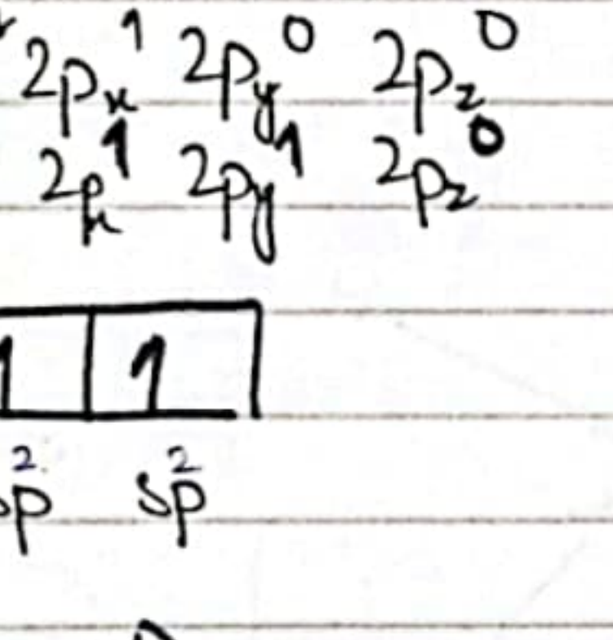
"Mixing of ones and twop's i.e. P_x and P_y forming three new orbitals of equal energy and same shape."

COMPOSITION

It is composed of 33.3% S and 66.7% P's.

EXAMPLE=

⇒ Boron triflouride BF_3



$_9F_2$ $1s^{2}2s^{2}2p_x^{2}2p_y^{2}2p_z^{1}$

Electronic Configuration

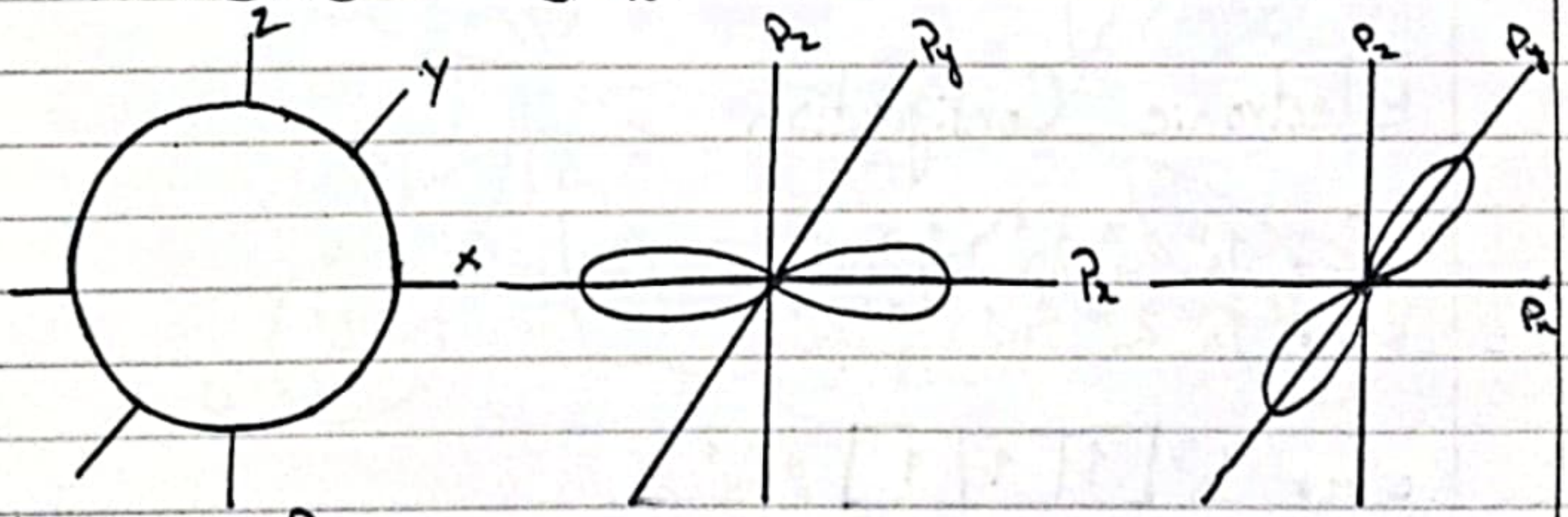
$_5B = 1s^{2}\ 2s^{2}\ 2p_x^{1}\ 2p_y^{0}\ 2p_z^{0}$ (G.S)

$_5B = 1s^{2}\ 2s^{1}\ 2p_x^{1}\ 2p_y^{1}\ 2p_z^{0}$ (E.S)

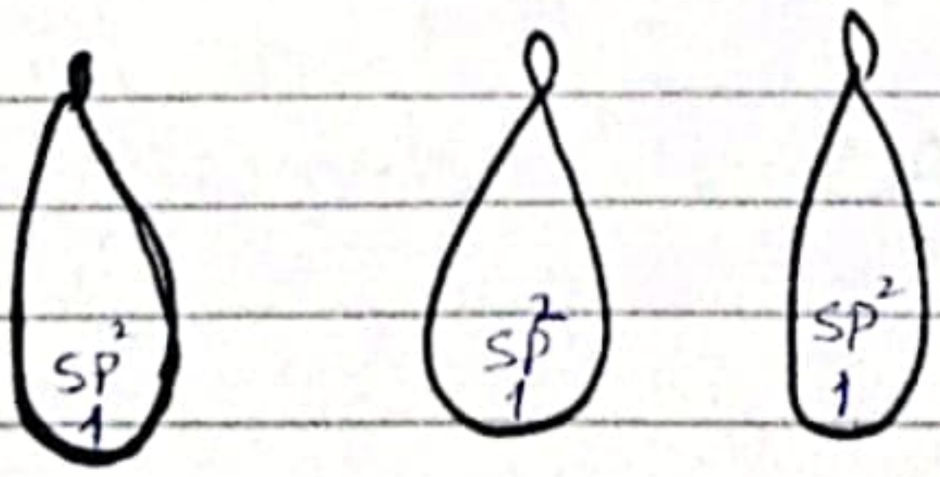
$_5B = 1s^{2}$ | 1 | 1 | 1 | (H.S)

sp^2 sp^2 sp^2

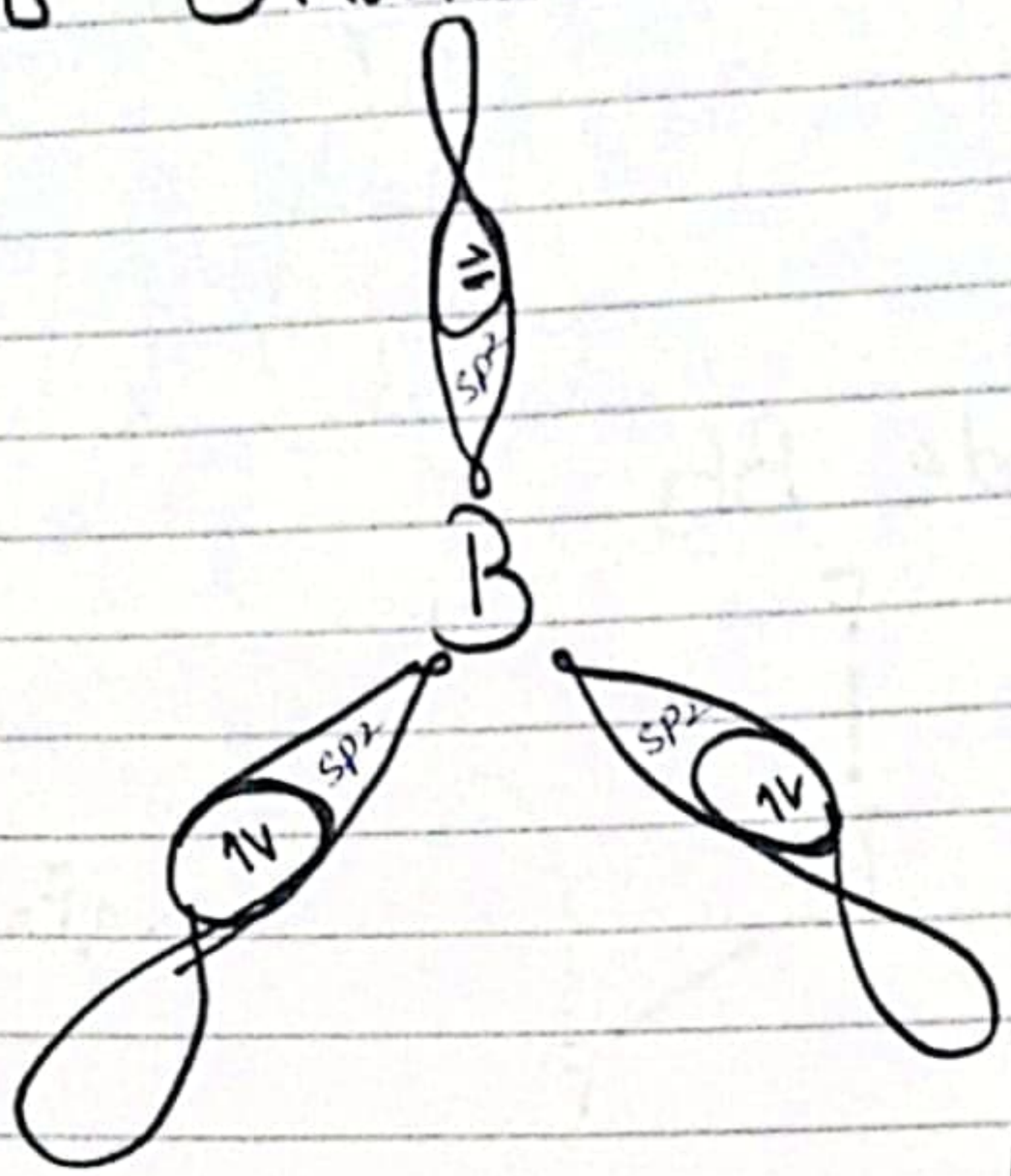
UNHYBRID ORBITALS=



HYBRID ORBITALS

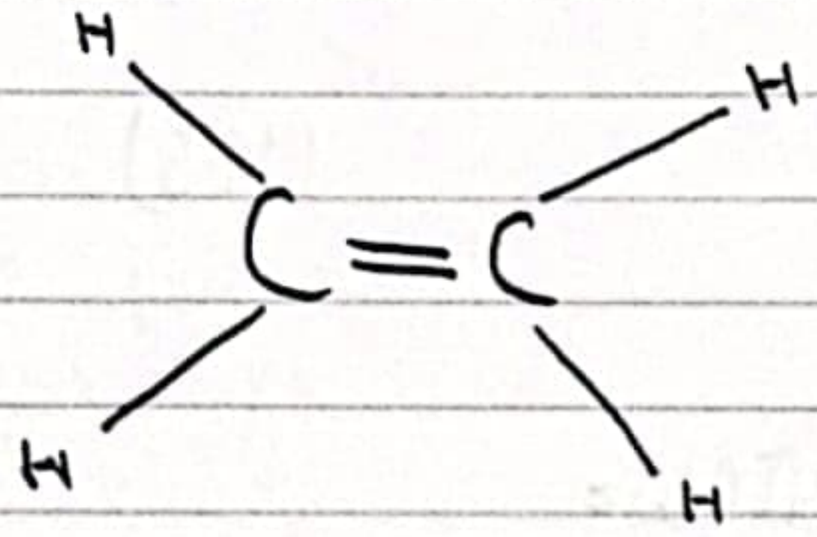


HYBRIDIZED STRUCTURE



Sigma bonds = 03
pi- bonds = 0
Molecular = Triangular
geometry planar
Angle = 120°

⇒ Ethene (C_2H_4):



$_1H = 1s^1$

Electronic Configuration

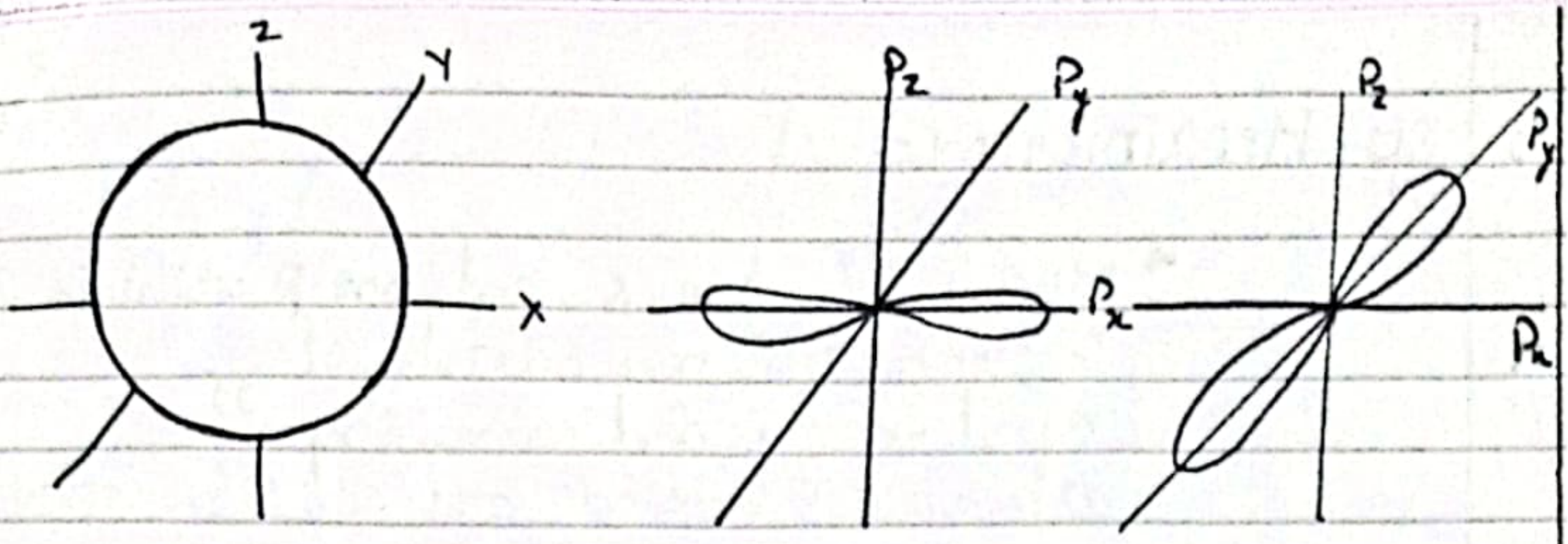
$_6C = 1s^{1V}\ 2s^{1V}\ 2p_x^1\ 2p_y^1\ 2p_z^0$

$_6C : 1s^{1V}\ 2s^{1V}\ 2p_x^1\ 2p_y^1\ 2p_z^1$

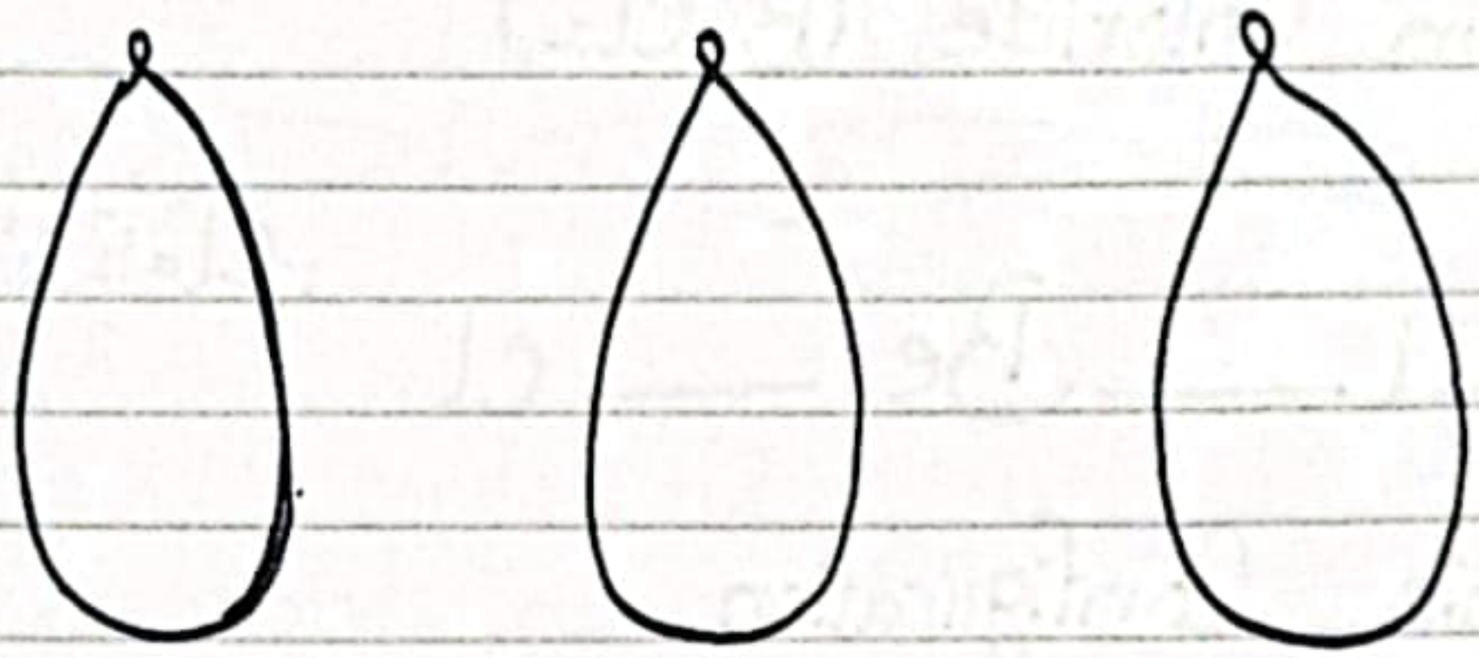
$_6C : 1s^{1V}$ | 1 | 1 | 1 | $2p_z^1$

$sp^2\ sp^2\ sp^2$

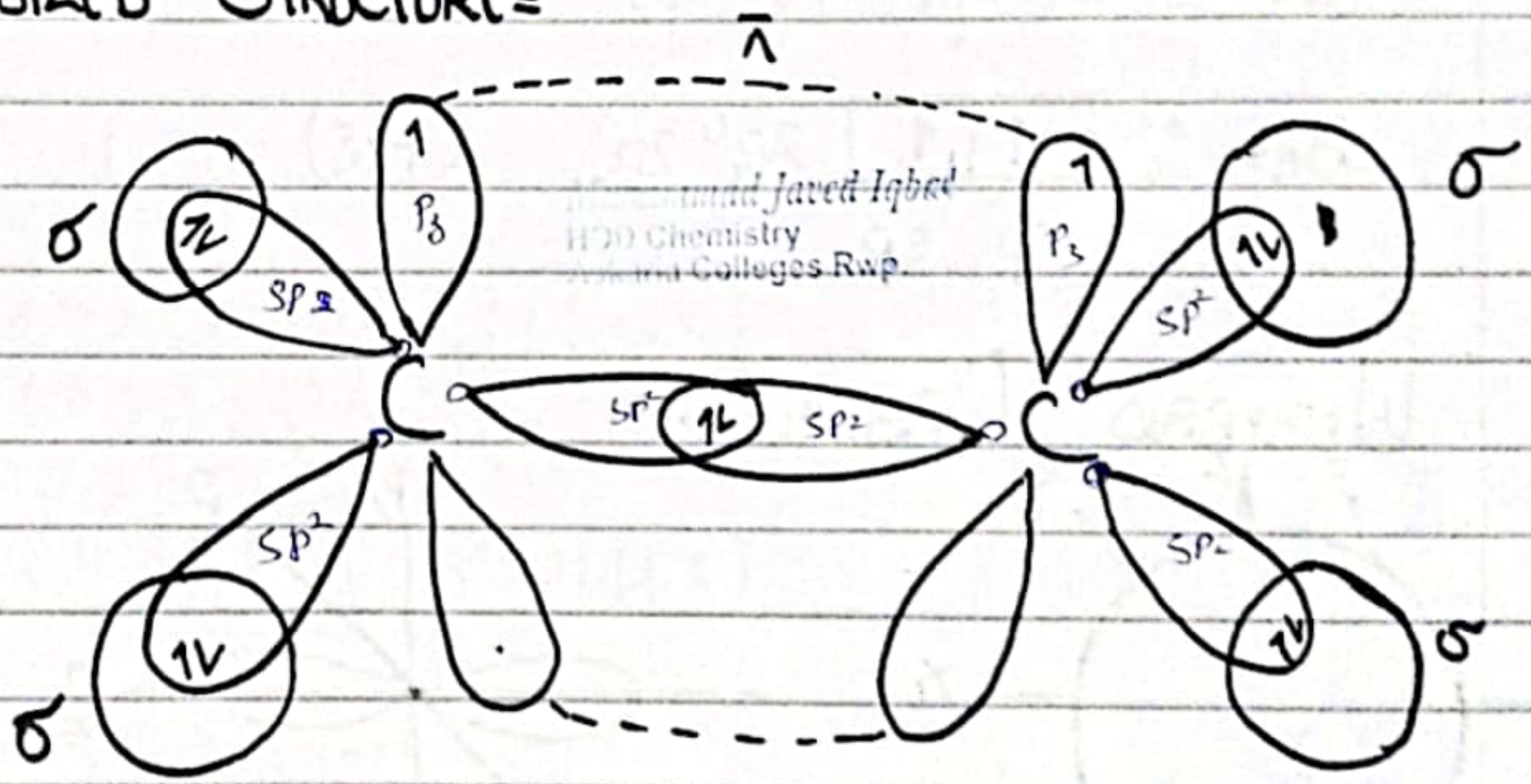
UNHYBRID ORBITALS



HYBRID ORBITALS =



HYBRIDIZED STRUCTURE =



No. of sigma bonds =
No. of pi - bonds = 01
Molecular geometry = triangular planar
Angle = 120°

3- SP- HYBRIDIZATION:

"Mixing of one s and one p orbital i.e p_x to form two new orbitals of equal energy and same shape."

It contain 50% s character and 50% p character

EXAMPLES:

Beryllium Chloride ($BeCl_2$)

Cl — Be — Cl

$_{17}Cl = 1s^{2\downarrow} 2s^{2\downarrow} 2p_x^{2\downarrow} 2p_y^{2\downarrow} 2p_z^{2\downarrow}$
$3s^{2\downarrow} 3p_x^{2\downarrow} 3p_y^{2\downarrow} 3p_z^{1}$

Electronic Configuration

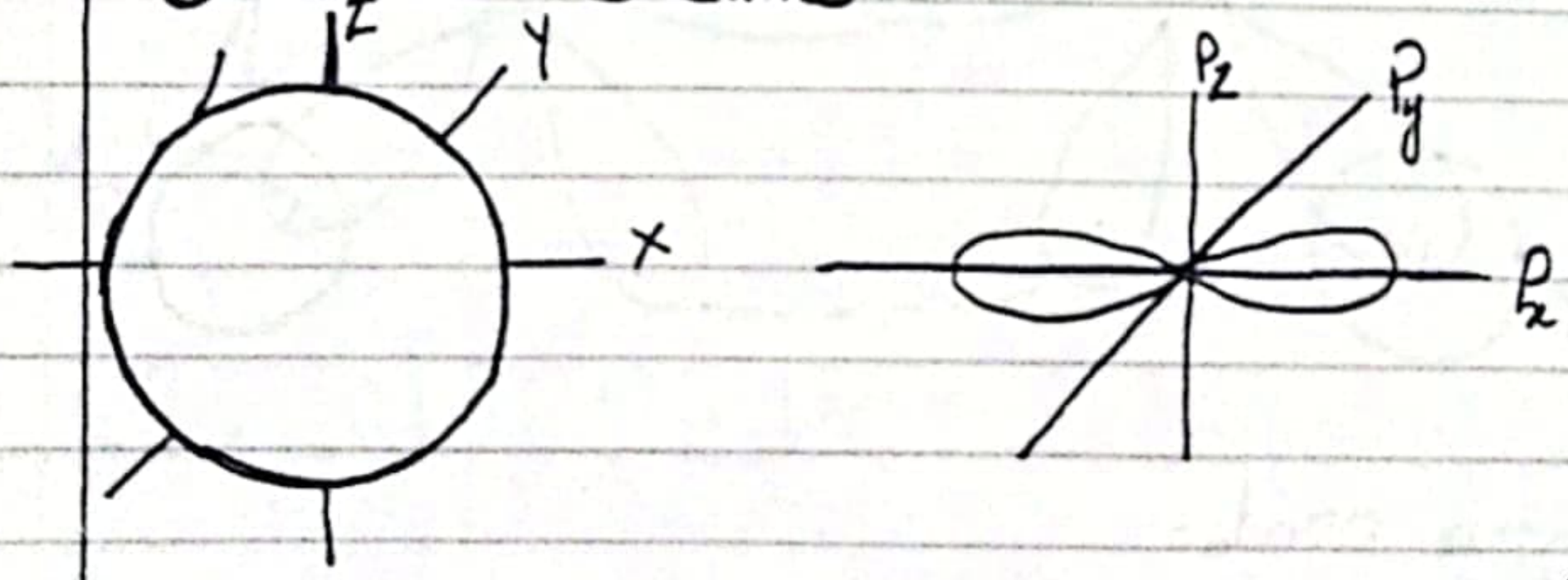
$_4Be = 1s^{2\downarrow} 2s^{2\downarrow} 2p_x^{0} 2p_y^{0} 2p_z^{0}$ (G.S)

$_4Be = 1s^{2\downarrow} 2s^{1} 2p_x^{1} 2p_y^{0} 2p_z^{0}$ (E.S)

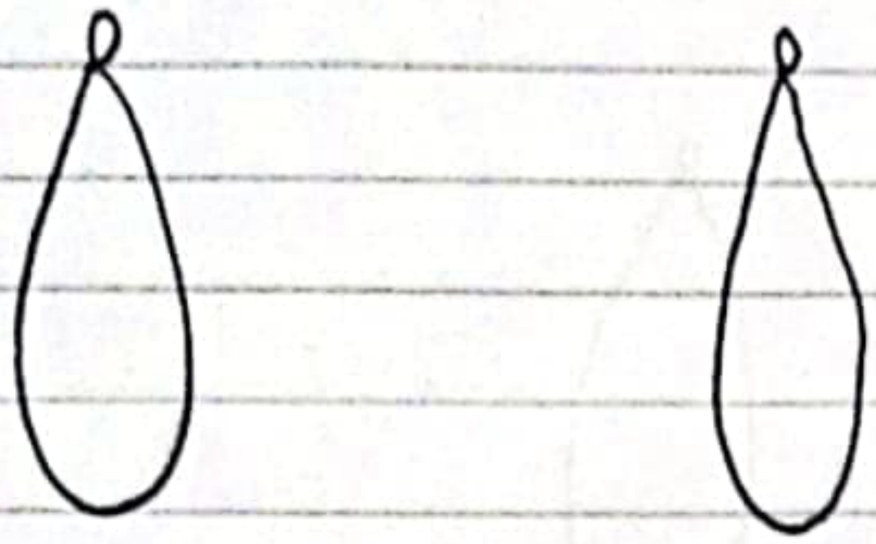
$_4Be = 1s^{2\downarrow}$ | 1 | 1 | $2p_y^{0} 2p_z^{0}$ (H.S)

sp sp

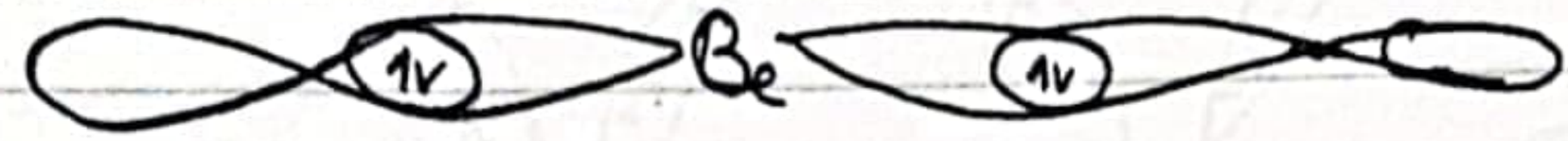
UNHYBRID ORBITALS:



HYBRID ORBITALS



HYBRIDIZED STRUCTURE



No. of sigma bonds = 02
No. of pi-bonds = 0
Molecular geometry = Linear
Angle = 180°

⇒ Ethyne ($CH \equiv CH$)

$_6C = 1s^{1V} 2s^{1V} 2p_x^1 2p_y^1 2p_z^0$ (G.S)

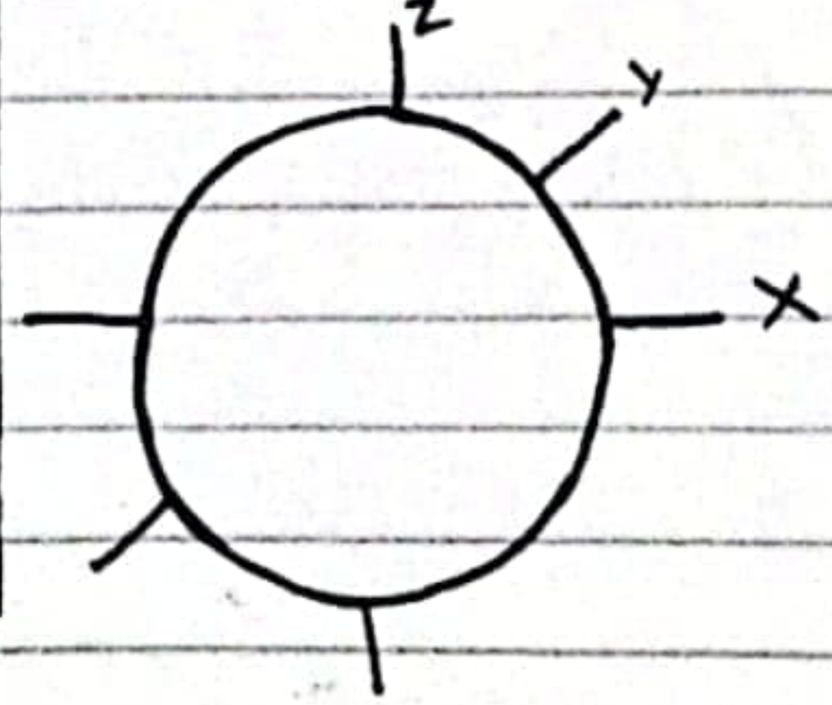
$_6C = 1s^{1V} 2s^1 2p_x^1 2p_y^1 2p_z^1$ (E.S)

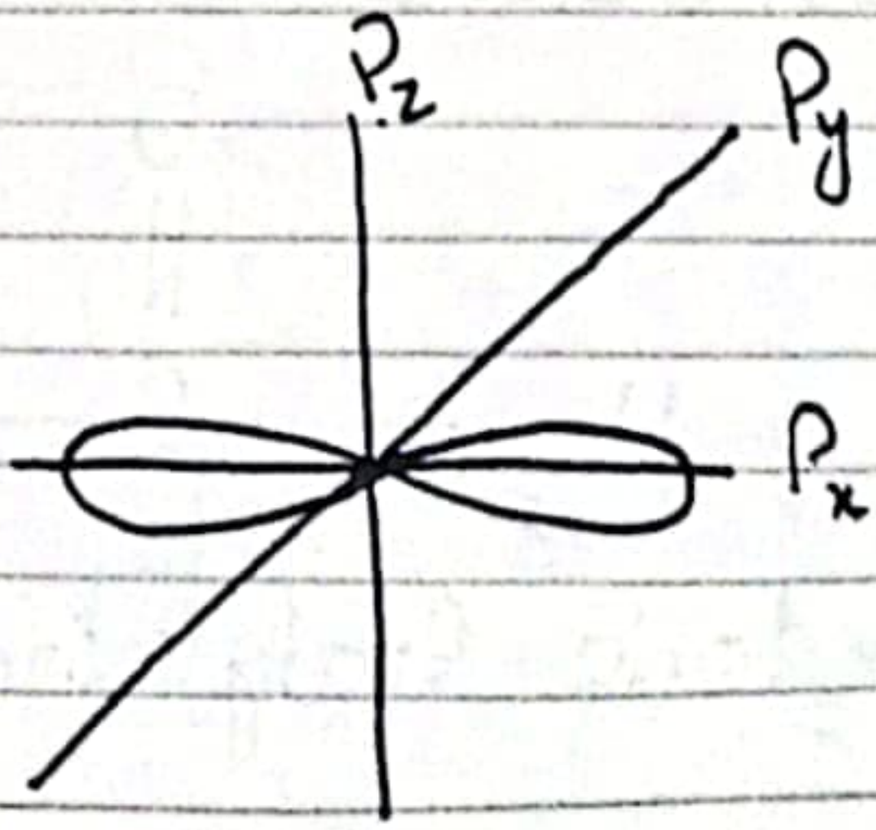
$_1H = 1s^1$

$_6C = 1s^{1V}$ [1] [1] $2p_y^1 2p_z^1$ (H.S)

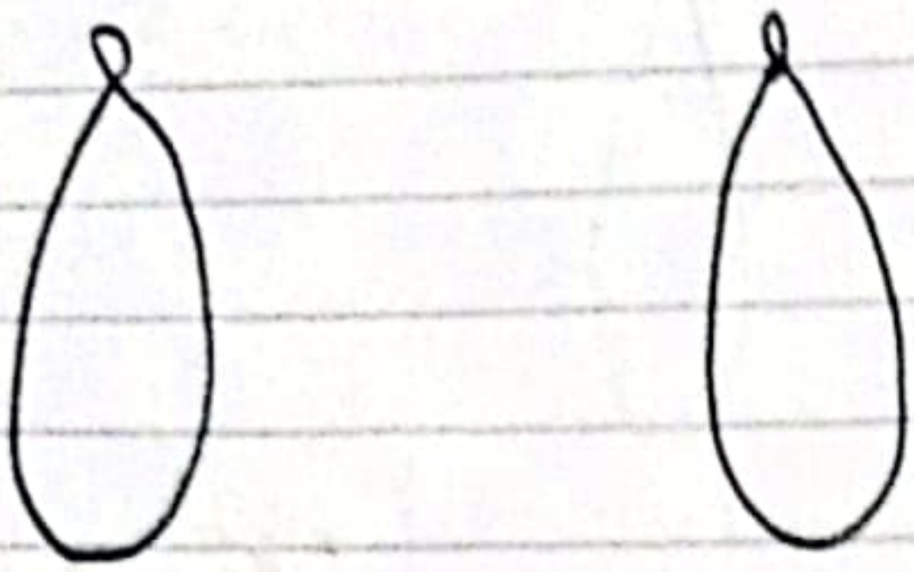
SP SP ORBITALS

UNHYBRID

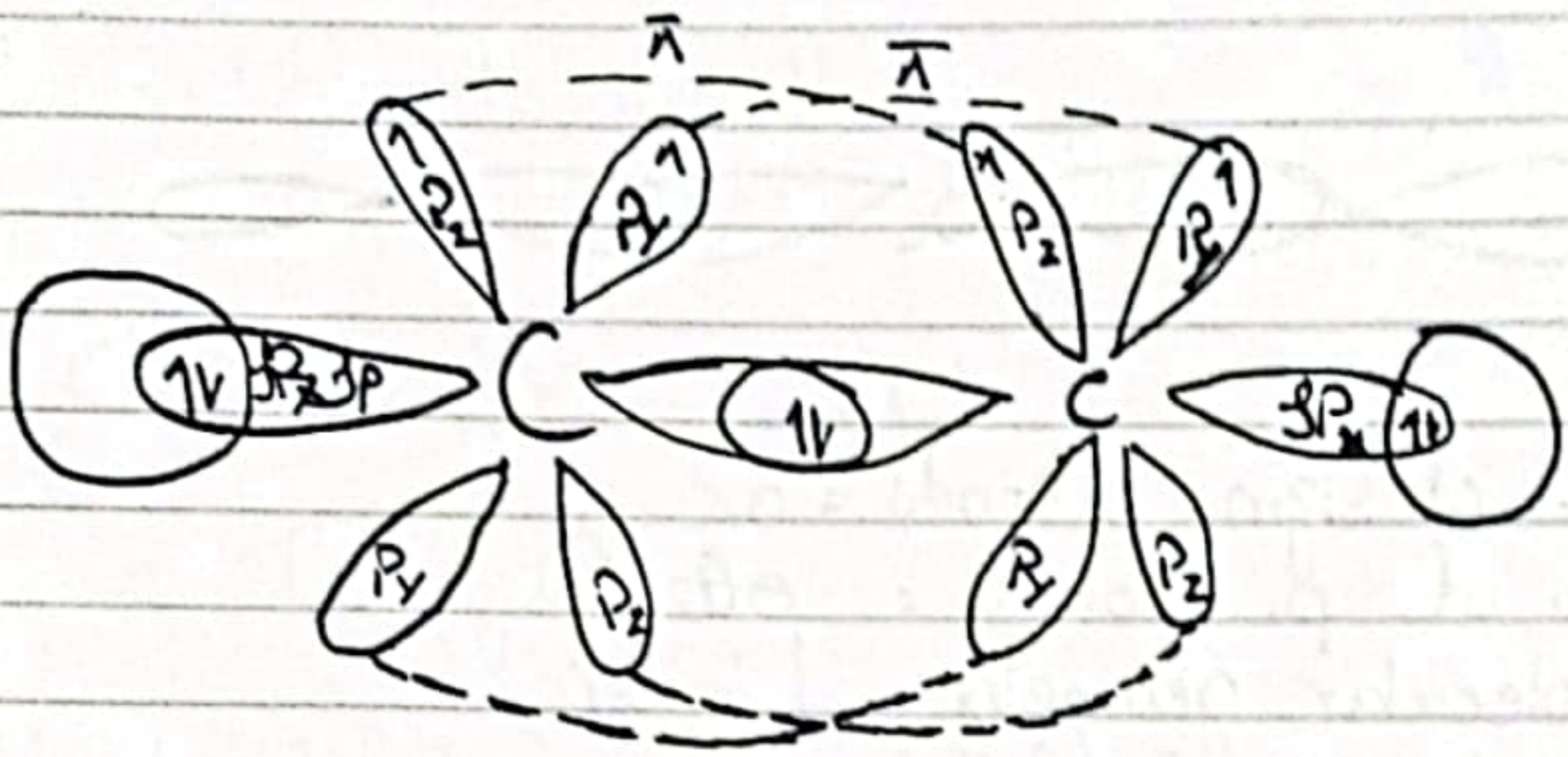




HYBRID ORBITALS=



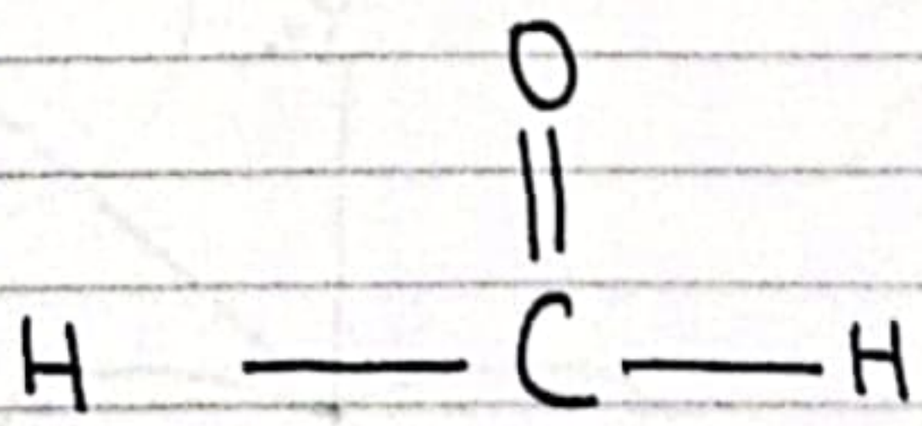
HYBRIDIZED STRUCTURE=



No. of Sigma bond = 02
No. of π bond = 02
Molecular geometry = Linear
Angle = 180°

Q Draw the structure of CH_2O by hybridization?

→ STRUCTURE OF FORMALDEHYDE (CH_2O)



Electronic Configuration

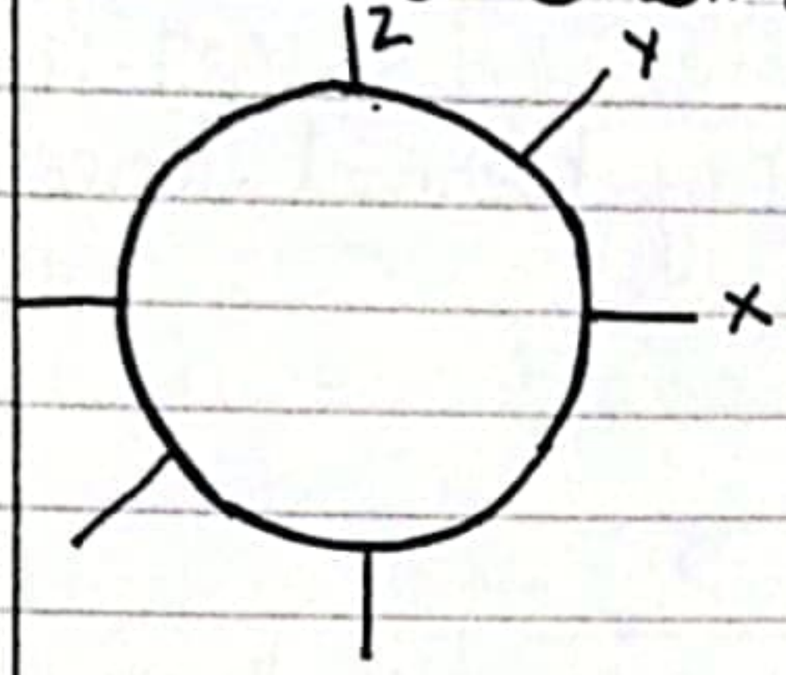
$_6C = 1s^{2} 2s^{2} 2p_x^{1} 2p_y^{1} 2p_z^{0}$

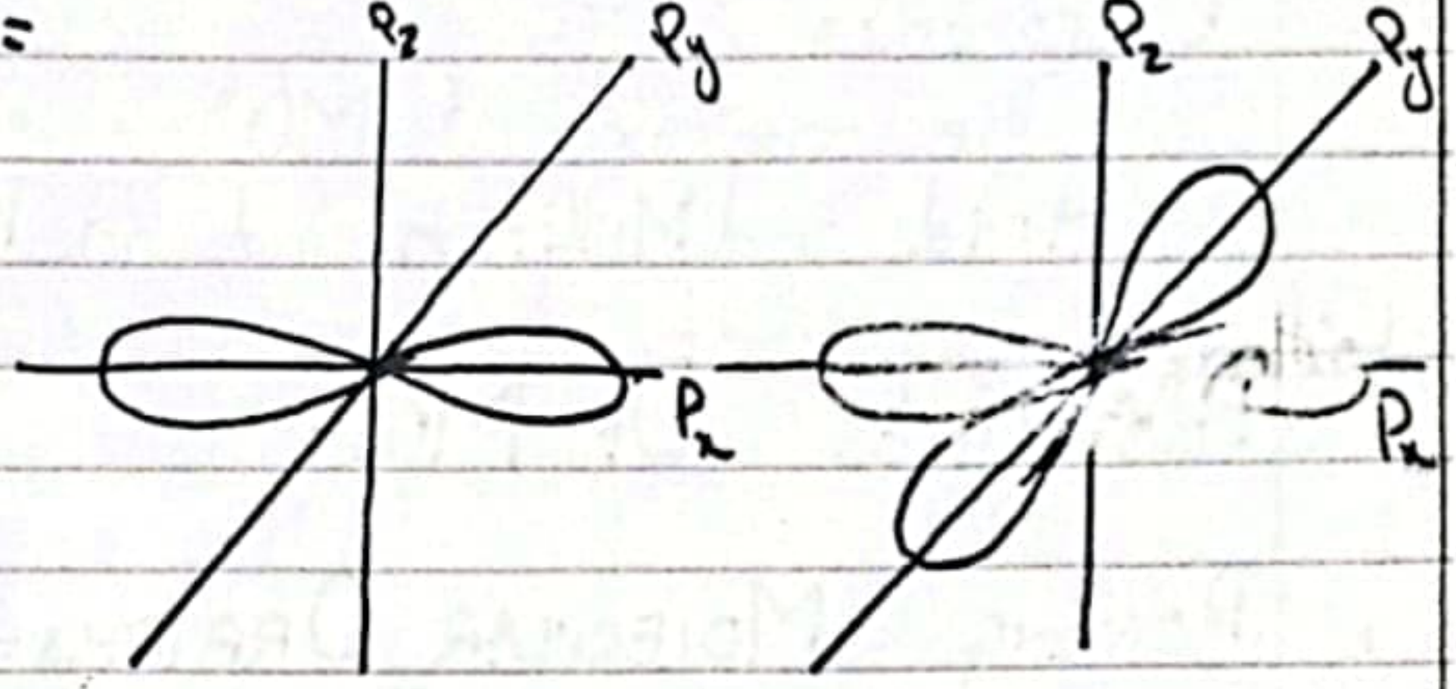
$_6C = 1s^{2} 2s^{1} 2p_x^{1} 2p_y^{1} 2p_z^{1}$

$_6C = 1s^{2}$ [1] [1] [1] $2p_z^{1}$

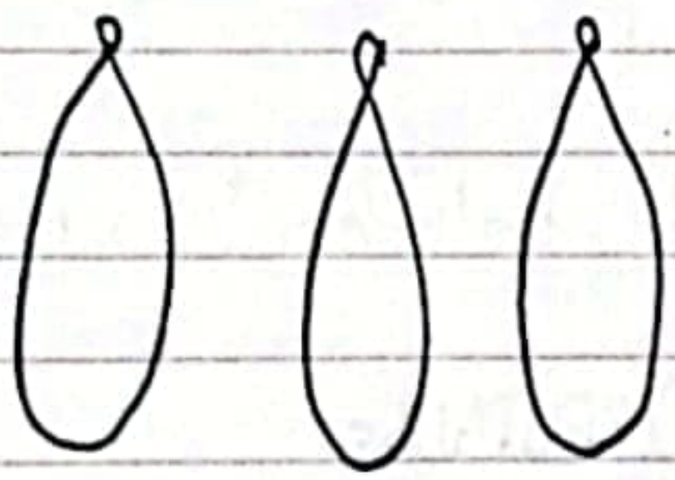
sp^2 sp^2 sp^2

UNHYBRID ORBITALS =

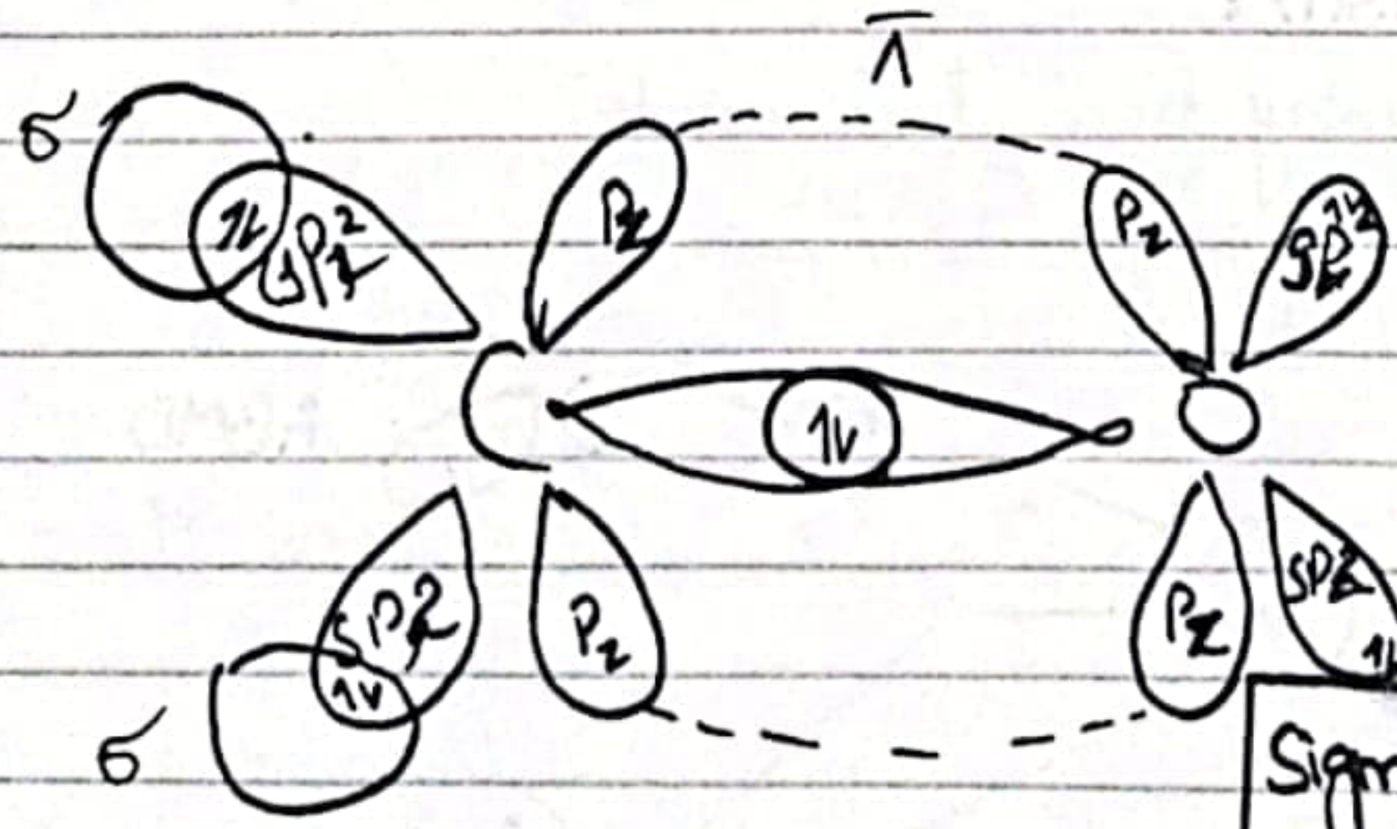




HYBRID ORBITALS =



HYBRIDIZED STRUCTURE=



CH_2O

Sigma bond = 02
pi- bond = 01
Molecular geometry Trigonal planar
Angle = 120°

MOLECULAR ORBITAL THEORY (MOT):

DISCOVERY:

The method of MOT was developed in 1927-1928 by Hurid and Mullikan and in 1929 by Lennard Jones.

POSTULATES OF MOT:

1- **BONDING MOLECULAR ORBITALS:**

Molecular orbitals having energy less than atomic orbitals.

ELECTRON DENSITY:

Es. density exist between two nuclei.

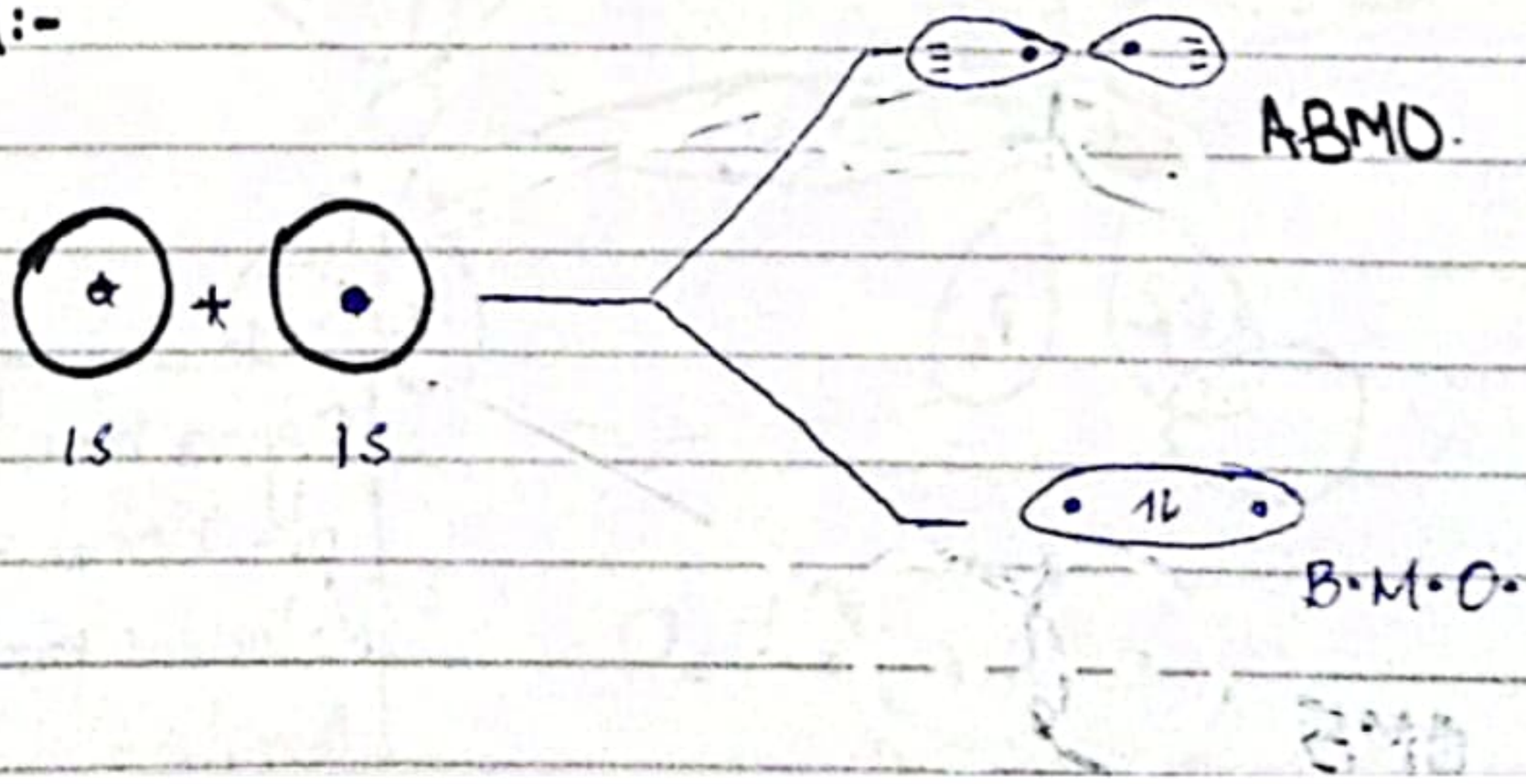
ANTI-BONDING MOLECULAR ORBITALS:

Molecular orbitals having energy greater than atomic orbitals.

ELECTRON DENSITY:

Es. density exist away from two nuclei

DIAGRAM:-



2- **BOND ORDER:**

Bond order can be found by:-

$$\text{Bond order} = \frac{\text{No. of } \bar{e}\text{s in BMO} - \text{No. of } \bar{e}\text{s in ABMO}}{2}$$

3- **PARAMAGNETIC SUBSTANCES:**

"Substances which are attracted in magnetic field due to presence of unpaired electrons."

e.g: O_2

DIAMAGNETIC SUBSTANCES:

"Substance which are weakly repelled in magnetic field due to presence of pair of electron."

e.g: N_2

4- **ENERGY LEVEL FOR F_2, O_2 AND THEIR IONS**

Their energy level is as follow:-

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

REACTIVITY:

They are very reactive.

ENERGY LEVEL FOR N_2, B_2, C_2, He, Be AND OTHER

Their energy level is as follow:

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

REACTIVITY:

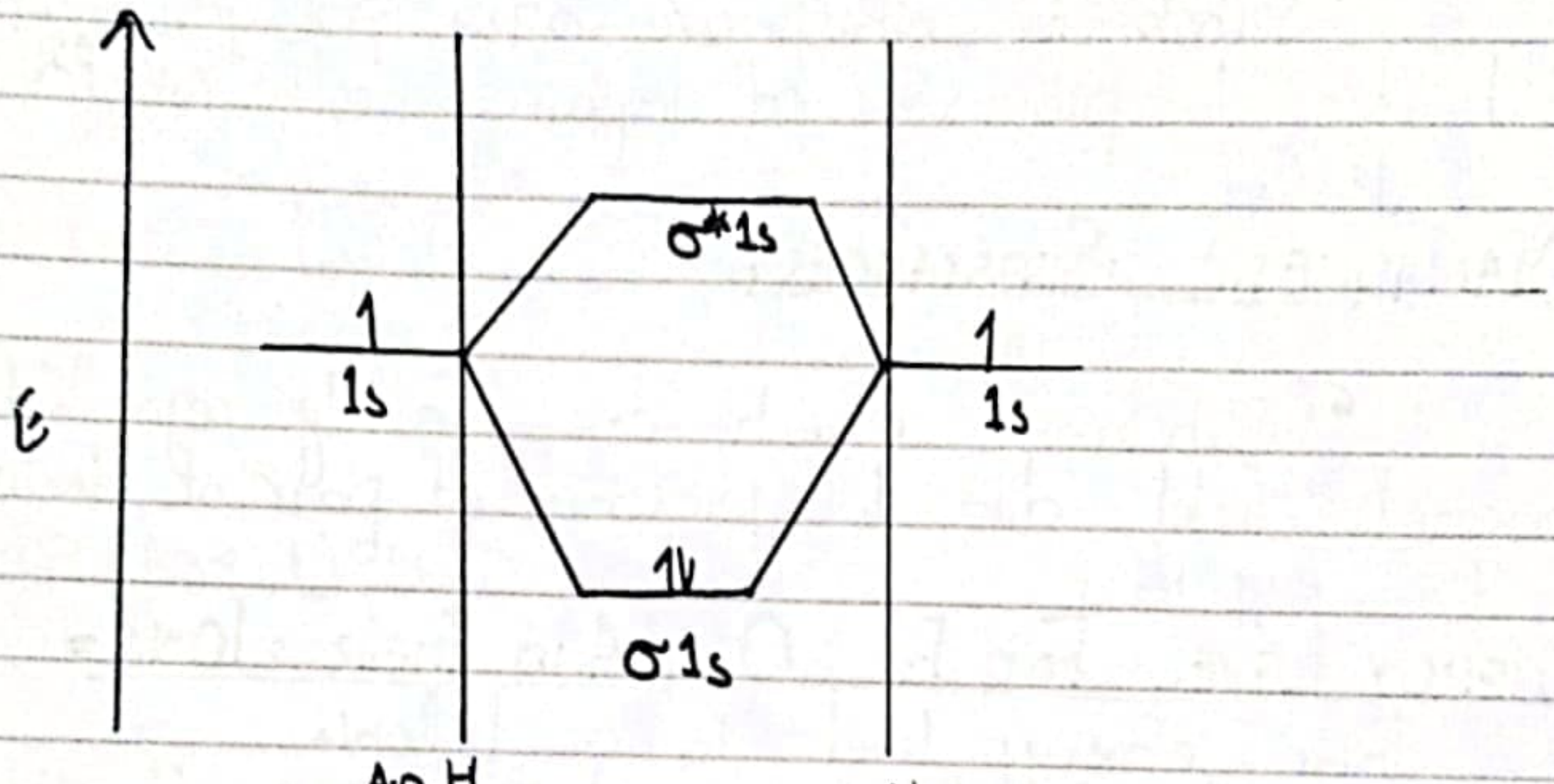
Diamagnetic are less reactive than paramagnetic substances.

APPLICATIONS FOR MOT:-

Explain the following on the basis of MOT
$H_2, He_2, Li_2, Be_2, , O_2, N_2, F_2, O_2^{+2}, N_2^{-2}$.

HYDROGEN (H_2)

1. $H = 1s^1$



Bond order = $\frac{2-0}{2} = 1$

H – H

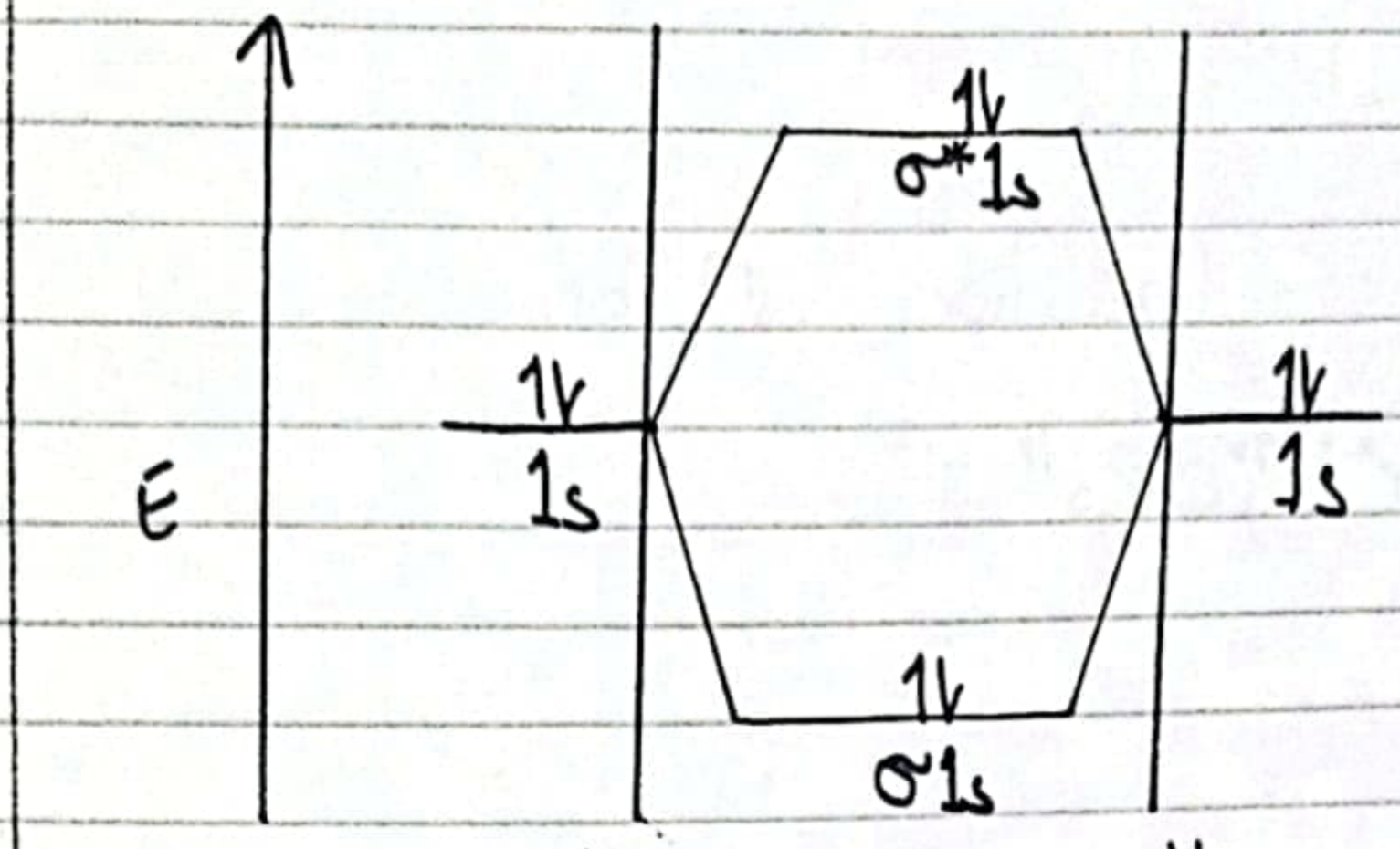
H_2 is diamagnetic

Electronic configuration of H_2

$H_2 = \sigma 1s^{1\downarrow}$

2. Helium (He_2)

$He = 1s^{1\downarrow}$

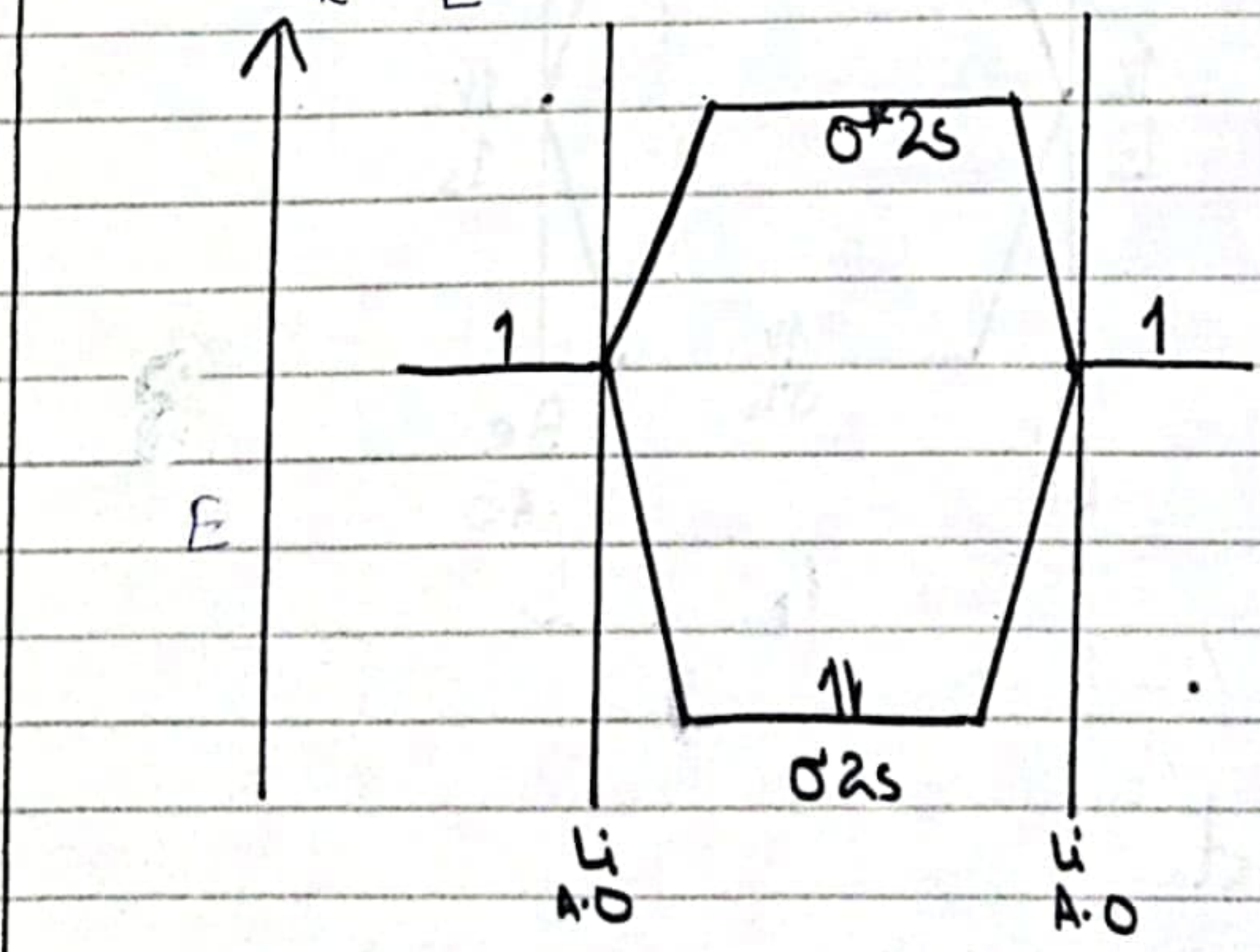


Bond Order = $\frac{2-2}{2} = 0$

He_2 doesnot exist.

3- Lithium (Li_2)

$_3Li = \underbrace{1s^{1v}}_{K}\ \underbrace{2s^{1}}_{L}$



Bond order = $\frac{2-0}{2} = 1$

Li – Li

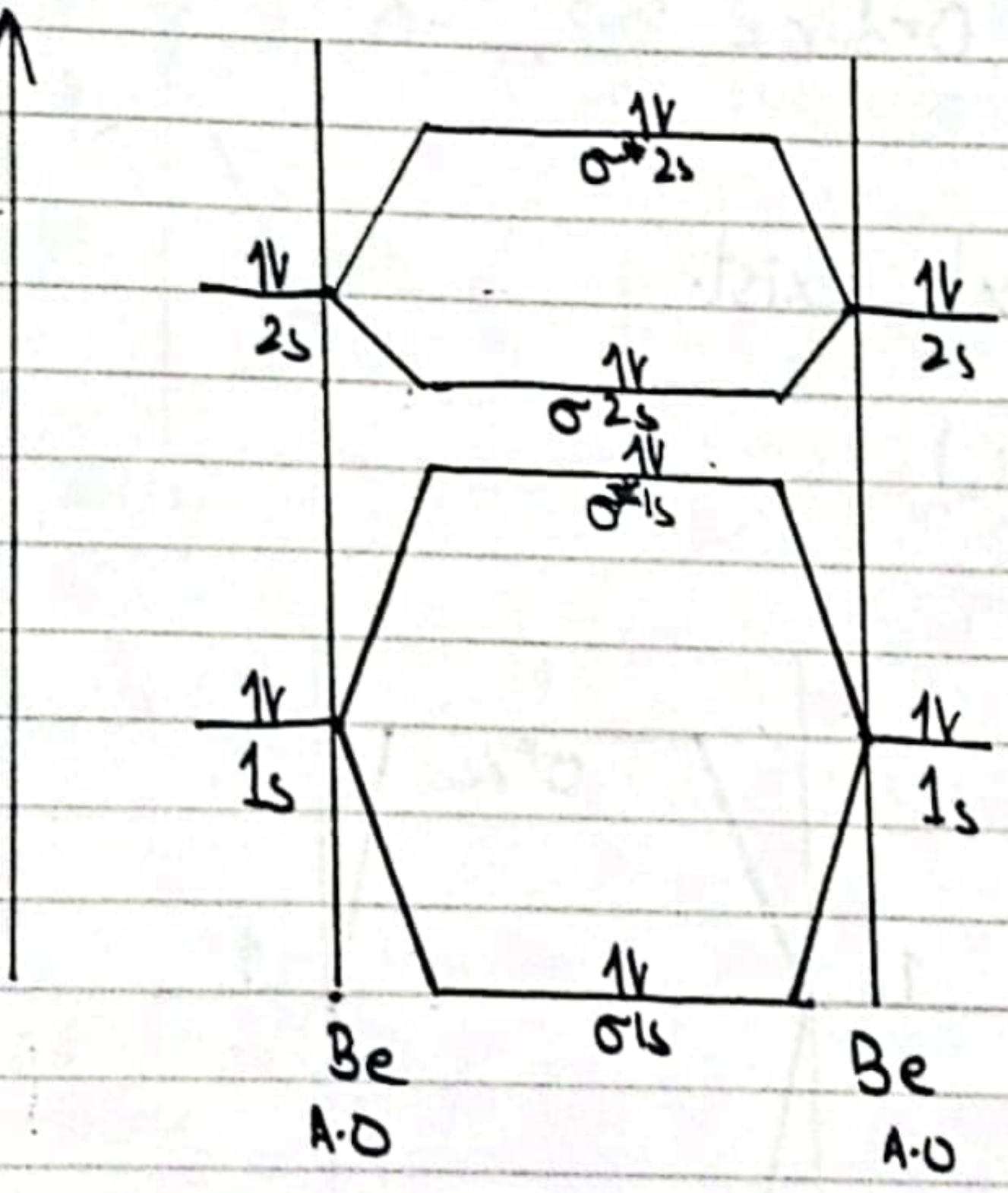
Li is diamagnetic.

It's electronic configuration will be.

$Li_2 = \sigma 1s^{1v}, \sigma^* 1s^{1v}, \sigma 2s^{1v}$

4- Beryllium Be_2

$_4Be = \underbrace{1s^{1v}}_{K}\ \underbrace{2s^{1v}}_{L}$

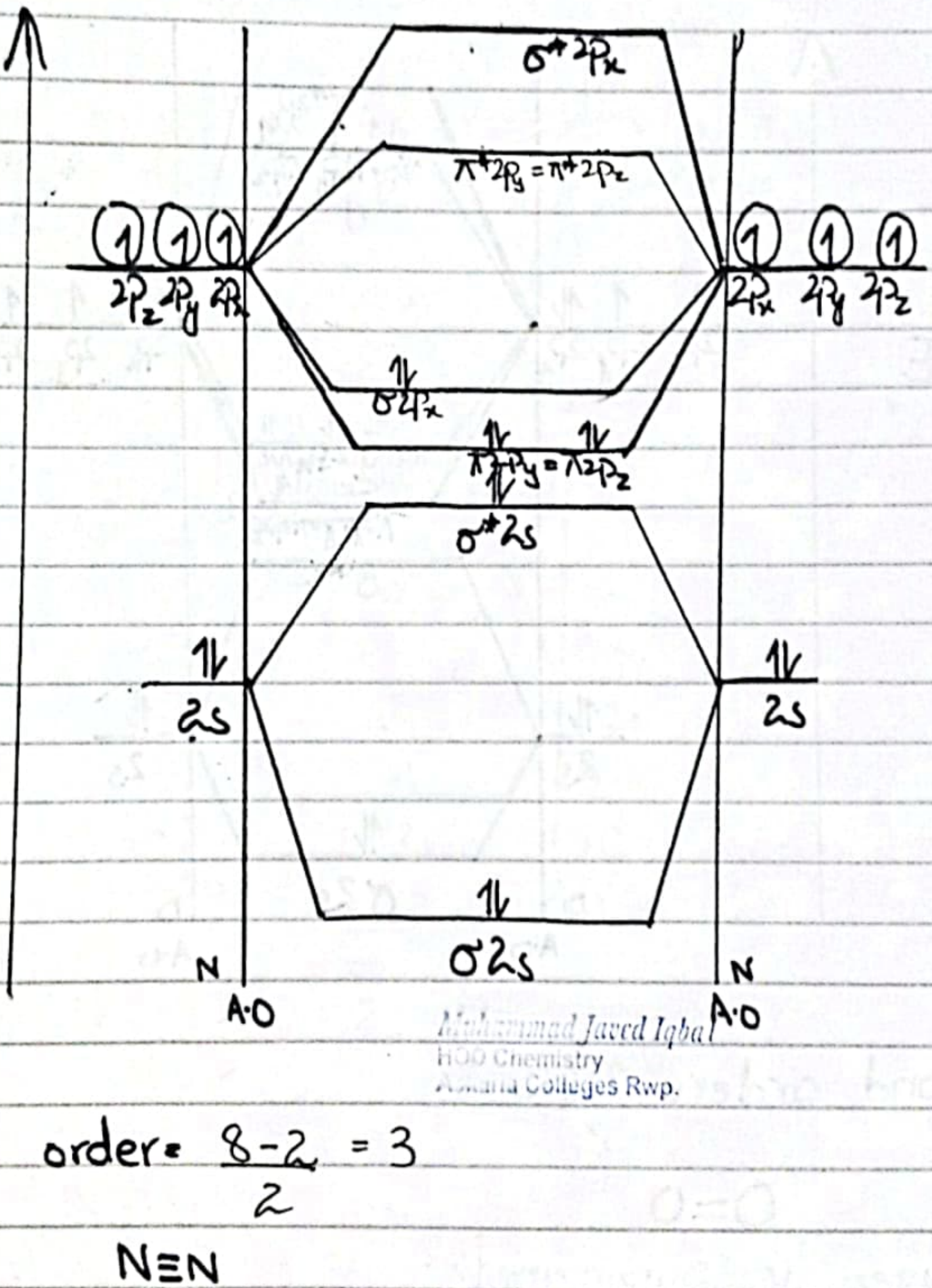


Bond order = $\frac{4-4}{2} = 0$

Be_2 does not exist

5- Nitrogen (N_2)

$_7N = 1s^{2}\,2s^{2}\,2p_x^{1}\,2p_y^{1}\,2p_z^{1}$



Bond order = $\frac{8-2}{2} = 3$

N≡N

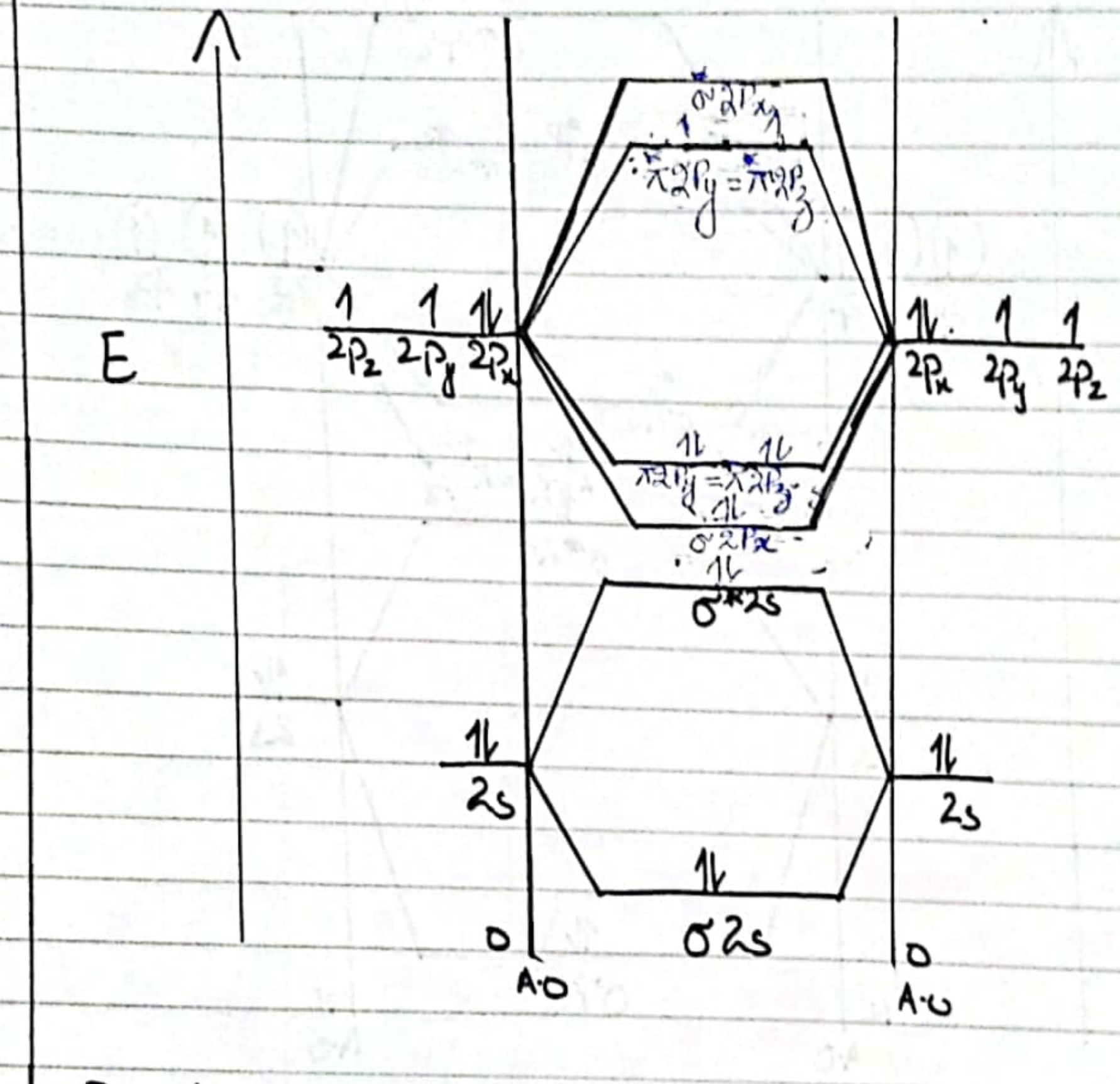
Nitrogen is diamagnetic.

The electronic configuration is =

$N_2 = K.K, \sigma 2s^{2}, \sigma^{*} 2s^{2}, \pi 2p_y^{2} = \pi 2p_z^{2}, \sigma 2p_x^{2}$

7- Oxygen (O_2)

$_8O = 1s^{\uparrow\downarrow} 2s^{\uparrow\downarrow} 2p_x^{\uparrow\downarrow} 2p_y^{\uparrow} 2p_z^{\uparrow}$



Bond order = $\frac{8-4}{2} = 2$

O=O

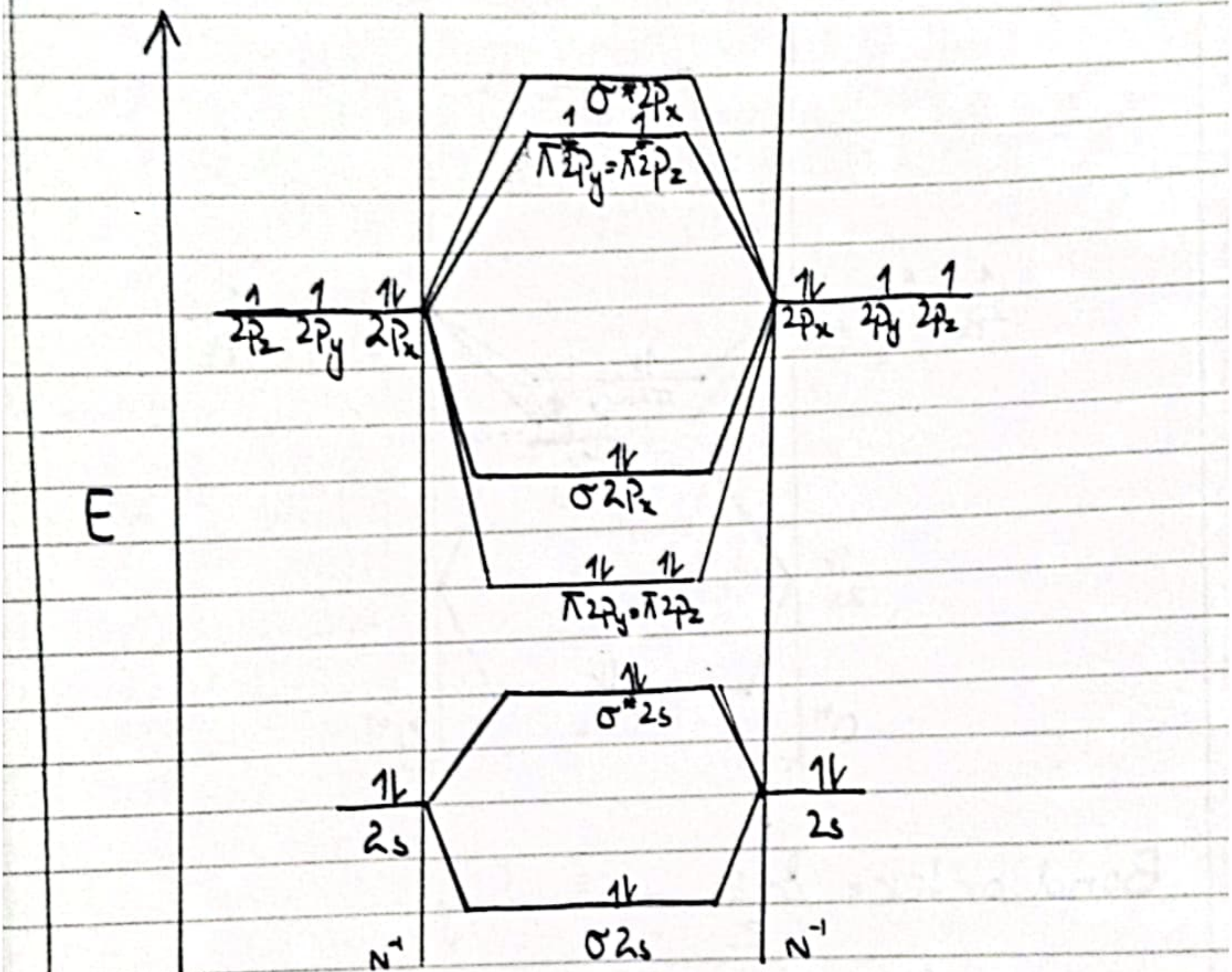
Oxygen is paramagnetic.

The electronic configuration is as follow

$O_2 = K, K\ \sigma 2s^{\uparrow\downarrow}\ \sigma^*2s^{\uparrow\downarrow}\ \sigma 2p_x^{\uparrow\downarrow}\ \pi 2p_y^{\uparrow\downarrow} = 2p_z^{\uparrow\downarrow}\ \pi^*2p_y^{1} = \pi^*2p_z^{1}$

8- N_2^{-2} :-

$_7N^{-1} = 1s^{\uparrow\downarrow} 2s^{\uparrow\downarrow} 2p_x^{\uparrow\downarrow} 2p_y^{1} 2p_z^{1}$



Bond order = $\frac{8-4}{2} = 2$

$N^{-1} \equiv N^{-1}$

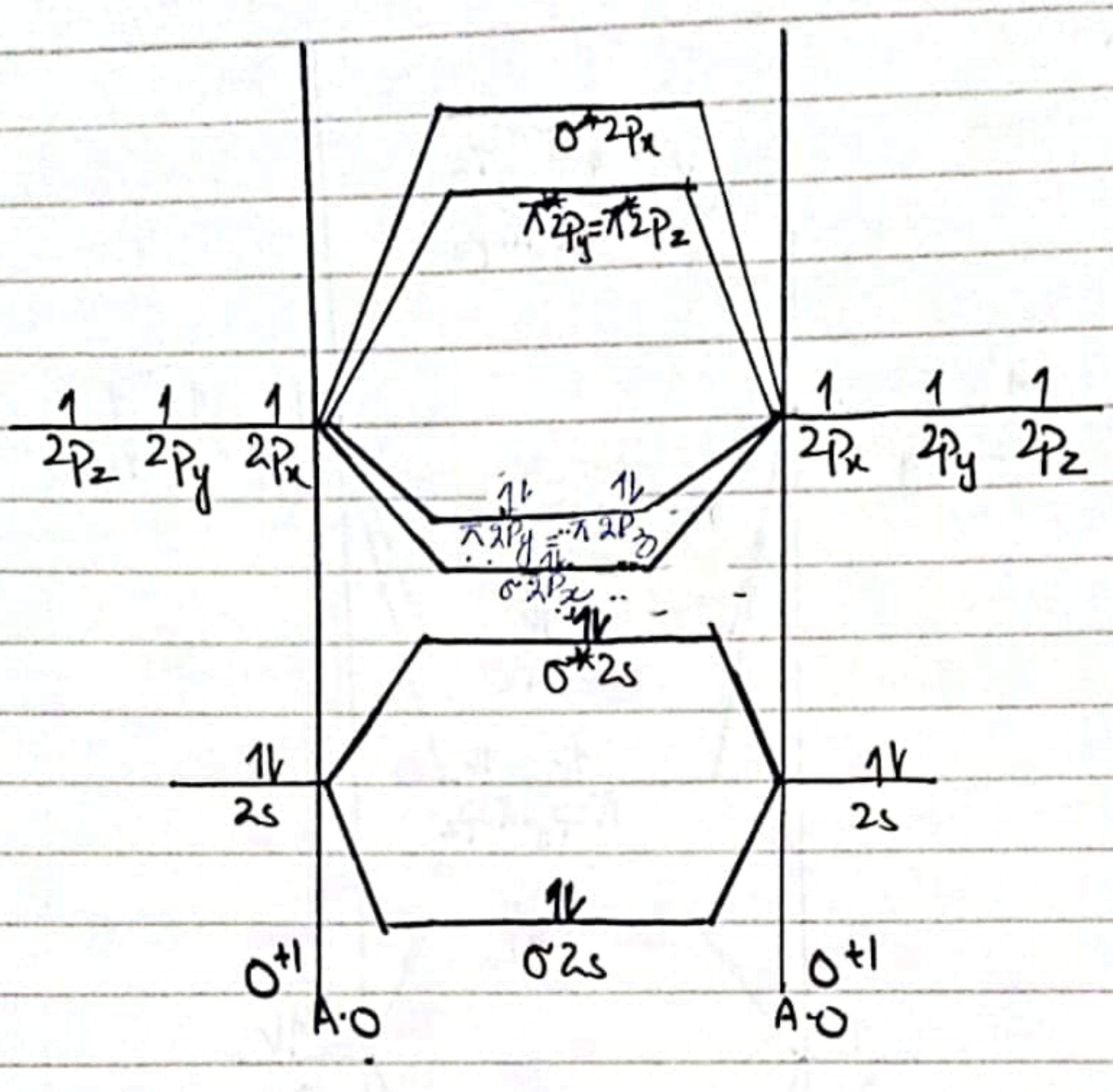
N_2^{-2} is paramagnetic substance.

Thus, it's electronic configuration is given by:-

$N_2^{-2} = k,k,\sigma 2s^{\uparrow\downarrow}\ \sigma^* 2s^{\uparrow\downarrow}\ \pi 2p_y^{\uparrow\downarrow} = \pi 2p_z^{\uparrow\downarrow},\ \sigma 2p_x^{\uparrow\downarrow},\ \pi^* 2p_y^{1} = \pi^* 2p_z^{1}$

9- O_2^{+2}

$_8O^{+1} = 1s^{2}\,2s^{2}\,2p_x^{1}\,2p_y^{1}\,2p_z^{1}$



Bond order = $\frac{8-2}{2} = 3$

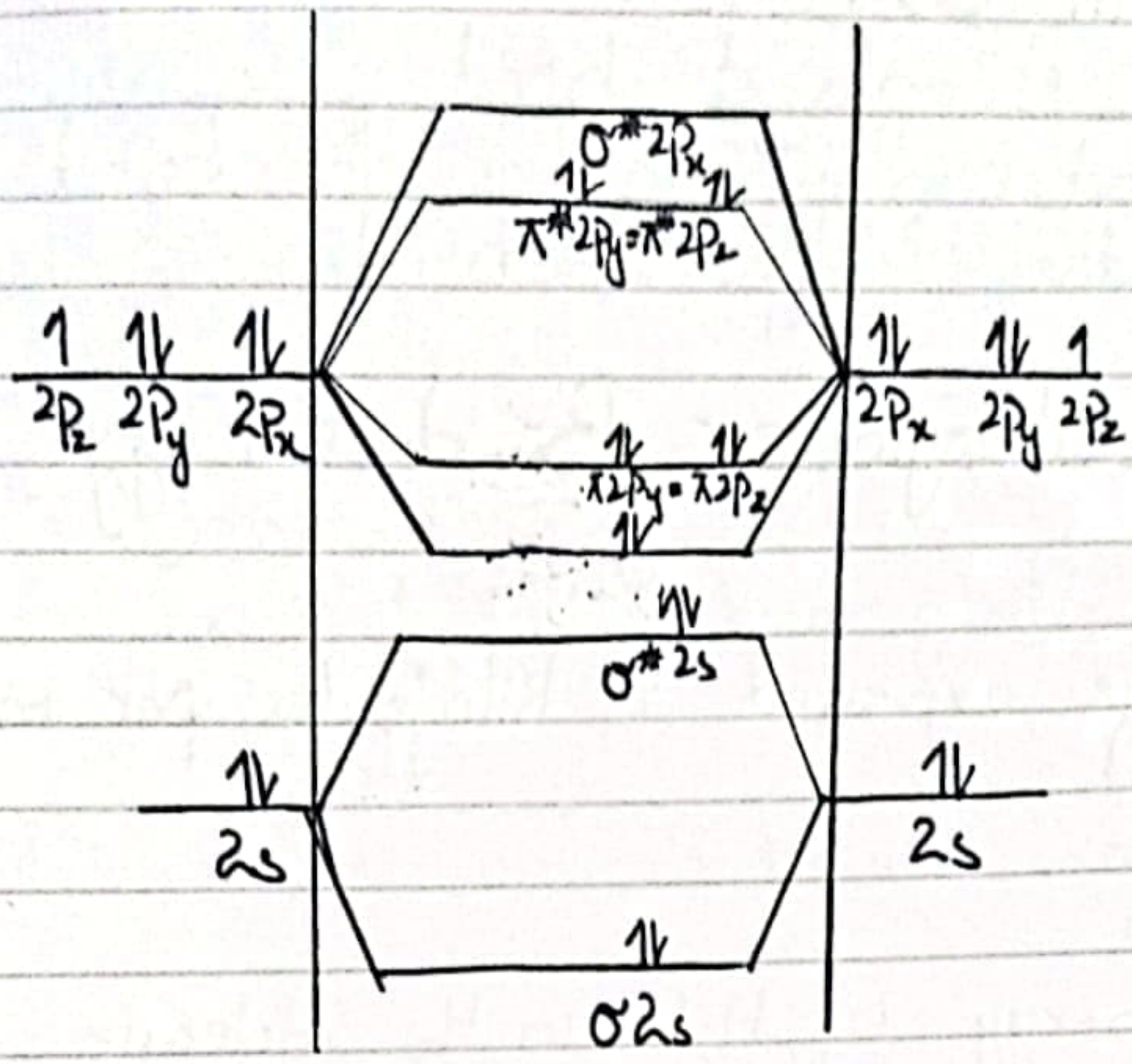
Oxygen is diamagnetic.

The electronic configuration will be as follow:-

$O_2^{+1} = \text{ØK,K, } \sigma 2s^{2}\,\sigma^{*}2s^{2}\,\sigma 2p_x^{2},\ \pi 2p_y^{2} = \pi 2p_z^{2},$

10- Flourine (F_2)

$_9F = 1s^{2}\,2s^{2}\,2p_x^{2}\,2p_y^{2}\,2p_z^{1}$



Bond order = $\frac{8-6}{2} = 1$

F - F

Flourine is diamagnetic

The electronic configuration is:-

$F_2 = KK\ \sigma 2s^{\uparrow\downarrow}\ \sigma^* 2s^{\uparrow\downarrow}\ \sigma 2p_x^{\uparrow\downarrow}\ \pi 2p_y^{\uparrow\downarrow} = \pi 2p_z^{\uparrow\downarrow}\ ;\ \pi^* 2p_y^{\uparrow\downarrow} = \pi^* 2p_z^{\uparrow}$

"BOND ENERGY"

BOND ENERGY:

"Bond energy is the amount of energy required to break all bonds of particular type in one mole of a substance."

STRENGTH OF BOND:

The strength of bond is measured by its bond energy. The higher the bond energy the stronger is bond.

Bond Strength $\propto$ Bond energy

UNITS:

It is expressed in kilojoules per mole ($KJ\ mol^{-1}$)

EXAMPLE:

1- Bond energy of H-H in H_2 molecule at 25°C, 298K is ~~43k~~ k 435 KJ/mol. Bond energy of Cl-Cl in Cl_2 molecule at 25°C is 242KJ/mol

FACTORS AFFECTING BOND STRENGTH

It depends upon following factors:

1) Electronegativity
2) Size of bonded atom
3) Bond length
4) Bond order

Electronegativity:

"Greater the difference in electronegativity between bonded atoms, greater is bond energy and stronger is bond."

Bond energy $\propto$ Electronegtivity difference.

SIZE OF BONDED ATOM:

"The smaller the size of bonded atom greater is bond energy and stronger is the bond."

BOND LENGTH:

"Shorter is the bond length greater is bond energy and stronger is the bond."

BOND ORDER:

"Greater is the no. of bonds greater will be bond energy"or

Multiple bonds also affect bond energy.

BOND LENGTH

BOND LENGTH:

"Distance between nuclei of atom joined by covalent bond is called bond lenght."

It is not constant because bonded atoms are always vibrating with respect to each other.

UNITS:

It is measured in Å or picometer

$1 pm = 10^{-12} m$

$100 pm = 1 Å = 10^{-10} m$

MEASURING TECHNIQUES:

It is measured by techniques such as X-ray diffraction, neutron diffraction and microspectroscopy.

DIPOLE MOMENT

DIPOLE MOMENT:

"The product of magnitude of charge and distance between them is called dipole moment."

It is given by:

$$M = q \times r$$

UNITS:

Its SI unit is Coloumb-metre but commonly we use Debye.

$$1\ Debye(D) = 3.36 \times 10^{-30}\ C.m$$

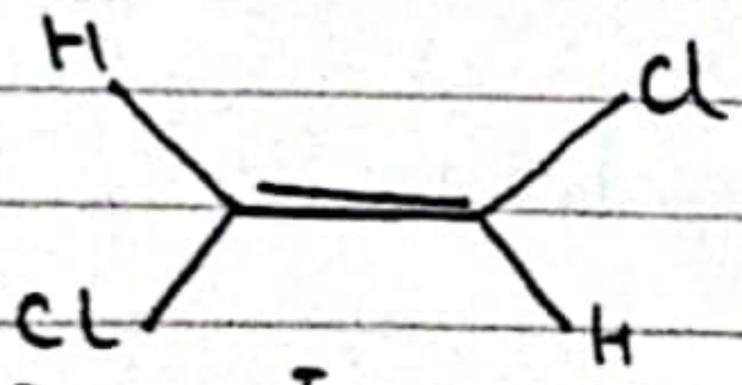
APPLICATIONS:

Determination of polarity:

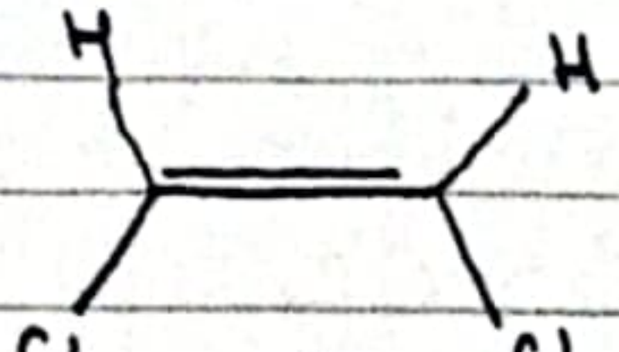
Molecules with zero dipole moment are non-polar. Those which has dipole moment are polar.

Study of dipole moment also find application is in stoichoimetry.

EXAMPLE



M=0D Trans



Cis M=1.89D

% IONIC CHARACTER IN BOND:-

It helps to calculate % ionic character in bond.

$$\% \text{ ionic character} = \frac{\mu obs}{\mu ionic} \times 100$$

EFFECT OF BONDING ON PROPERTIES OF COMPOUND.

Propeties of compound.

SOLUBILITY=

IONIC COMPOUNDS=

Most of them are soluble in water but some are non-aqueous solvents.

REASON=

As ionic compound ~~dissolve~~ are placed in water. As they have ~~been~~ hydration energy equal to or greater than lattice energy the compound dissolve and if hydration energy is less than lattice energy compound does not dissolve.

COVALENT COMPOUNDS=

Covalent compounds are usually non polar in nature. Chemistry says:

"Like dissolves like"

Hence covalent compounds are not soluble in water but soluble in non-polar solvents such as benzene, ether etc.

REASON:

The attractive forces of non-polar solvents is enough to overcome the attractive forces of covalent compounds. Hence the compound dissolve in solvent.

Most covalent compounds if they are soluble in water is due to hydrogen bonding.

c) Non-directional nature of ionic compound

Ionic compounds are rigid and nondirectional in naturae. They do not show isomerism.

d) Directional nature of covalent compound:

They are directional and non-rigid and show the phenomenon of isomerism.

Reason:

They show isomerism and occur in large no.

REACTION KINETICS:

IONIC COMPOUNDS:

Ionic compounds exist in form of ion in solution. So the reaction occurs rapidly. This is because no bond is broken.

COVALENT COMPOUNDS:

In covalent compounds reaction is slow. This is because energy is involved

in both breaking and forming bonds.

DENSITY:

The electrostatic force of attraction brings ions very close to each other. So density of ionic compounds is greater.

TYPES OF SOLIDS:

A solid is a structural unit of atoms, molecules or ions which are held together to give rigid structure.

MOLECULAR SOLIDS:

Consists of atoms or molecules held together by inter-molecular forces.

e.g.

Solid CO_2 and solid water.

METALLIC SOLIDS:

Consists of atoms held together by metallic bonding.

e.g.

Silver, copper, gold.

IONIC SOLIDS:

Consist of ~~anion~~ anions and cations held together by electrostatic force of attraction

e.g.

NaCl and $CaCl_2$

COVALENT NETWORK SOLIDS:

Consist of network held together by covalent bonds.

Difference b/w metallic solid and covalent network solid.

	METALLIC SOLIDS	COVALENT NETWORK SOLIDS
1-	Consist of infinite arrays of bonded atoms	Consist of finite arrays of bonded atoms.
2-	They are poor conductor of heat and electricity	They are good conductor of heat and electricity
3-	They have high co-ordination number.	They have low co-ordination number
4-	Examples Sodium, potassium	Examples: Diamond, graphite

EXERCISE

MCQ's

i) b
ii) b
iii) c
iv) a, b, c
v) a
vi) c
vii) c
viii) b
ix) a
x) b

EXERCISE

Short Questions

a) Give reason for difference in calculated and observed value?

The experimentally determined bond energy is greater than calculated value which means a more stable bond. This stability is due to presence of ionic character in the bond. The amount of additional bond energy depends on electronegativity of two bonded atoms. "Greater the difference between two bonded atoms greater is ionic character and stronger is bond."

b) Effect of high bond energy on bond length with ~~values~~ reason?

Ans **BOND LENGTH:**

"The distance between the atoms bonded by single covalent bond is called Bond length."

EFFECT OF HIGH BOND ENERGY:

"Smaller will be the bond length higher will be the bond energy and stronger will be the bond and vice versa.

REASON:

Bond energy decreases with increase in bond length because this cause increase

in the distance between nuclei of atoms joined by covalent bonding which decreases electrostatic force of attraction. This weaken the bond and causes decrease in bond energy.

c) Ionic character on basis of bond energies with reason:

IONIC CHARACTER:

"Electronegativity difference between two atoms is called ionic character."

EFFECT OF BOND ENERGY:

"Greater is the electronegativity difference greater is bond energy and stronger is the bond."

REASON:

This stability is due to ionic character present in bond. The amount of additional energy depend on electronegativity of bonded atom.

Q3

a) Draw energy diagram for nitrogen N_2 molecule.

DIAGRAM HAS ALREADY BEEN Drawn. Please see pg#37.

b) Give reason why $\sigma 2p_x$ energy is greater than $\pi 2p_y$.

$\sigma 2p_x$ and $\sigma^* 2p_x$ MOs donot have pure p-p-character. Due to mixing of sp-character their energy change in such a way that MOs of $\sigma 2p_x$ become less stable and are raised in energy. Whereas $\pi 2p_y = \pi 2p_z$ remain Unchanged. So $\sigma 2p_x$ energy is greater than $\pi 2p_y = \pi 2p_z$.

Q4

a) Explain formation of ethyne molecule on basis of hybridization.

Please See Pg# 29 for

"FORMATION OF ETHYNE MOLECULE ON BASIS OF HYBRIDIZATION"

b) Draw a diagram of ethyne molecule

$H-C\equiv C-H$

structure of ethyne

Q5 MOT can explain paramagnetic character of O_2, O_2^{+2} and O_2^{-2} species. Evaluate it?

~~VBT~~ pred

Valence bond theory predicts that O_2 would be diamagnetic. However experiments proved O_2, O_2^{+2} and O_2^{-2} be paramagnetic. These structures were explained and predicted by "Molecular Orbital theory". The spectroscopic evidence indicates that for these structures (O_2, O_2^{+2}, O_2^{-2}) σ 2p orbital is lower in energy that π 2p orbitals.

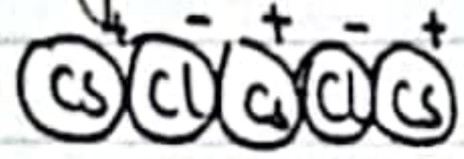
Q6 Melting points, boiling point, heat of vaporization and heat of sublimation of electrovalent-compound are higher as compared with those of coralent compounds. Argue.

Ionic compounds involve complete transfer of electrons whereas in coralent compounds there is mutual sharing of electrons. The electrostatic force of attraction of ionic compounds is greater than intermolecular forces that held in coralent compound. So, ionic compound form lattice energy which requires much more energy to break bonds however intermdecular forces of coralent compounds have less energy and it is easier to break bonds.

EXAMPLE =

In CsCl each Cs^+ is surrounded by

eight Cl^- atom and each Cl^- atom is surrounded by eight Cs^+ atoms. So there exist strong ionic bond.



In wax, there is a disordered structure as there are intermolecular forces which are easy to break

CONCLUSION:

Hence, the difference in force of attraction accounts for difference in melting point, boiling points, heat of vaporization and heat of sublimation.

Q7 Dipole moment of HCl is 1.03D and the distance b/w atoms is 127pm. Calculate ionic character of HCl bond.

Data

$\mu_{obs.} = 1.03D$

$r = 127pm$

$= 127 \times 10^{-12} m$

$q = 1.6022 \times 10^{-19} C.$

% ionic character = ?

$\mu_{ionic} = q \times r$

$= 1.6022 \times 10^{-19} \times 127 \times 10^{-12}$

$= 2.035 \times 10^{-29} C.m$

$= \frac{2.035 \times 10^{-29}}{3.336 \times 10^{-30}}$

$\mu_{ionic} = 6.100D$

% ionic character $= \frac{1.03}{6.1} \times 100$

% ionic character = 16.9%

Q8 Distingwisb b/w σ and π bond

	SIGMA BOND	Pi BOND
1-	Sigma bond is formed by linear overlapping of partially filled atomic orbitals	Pi bond is formed by parallel overlapping of atomic orbitals
2-	It is represented by "σ"	It is represented by "π"
3	Stronger than pi-bond.	Weaker than sigma bond.
4-	Atoms form sigma bond first	Pi bond proceed by sigma bond formation.
5-	Sigma bonds are usually inert.	Pi bonds are comparitively reactive.
6-	Electron density exist between two nuclei.	Electron desdensity exist above and below the nuclei.
7-	Charged density is less diffused due to stronger nuclear atraction	Charged density is more diffused due to weak bonds.
8-	S-S, S-P, ~~S-p~~, P_x-P_x overlapping are sigma in nature.	P_y-P_y, P_z-P_z overlapping are pi in nature
	EXAMPLE:-	EXAMPLE:-

i) A + B → A B (S + S → S-S)

ii) A + B → (S + P → S-P)

iii) A + B → (P_x-P_x)

i) P_y + P_y → P_y-P_x

ii) P_z + P_z → P_z-P_z

Arrange the following in order of increasing stability

Li_2 , Li_2^+ , Li_2^-

Justify your choice with MOT?

In order of increasing stability it is given as:

$Li_2^- < Li_2^+ < Li_2$

EXPLAINATION:

"Greater is the no. of bonds (bond energy) stronger is the bond."

Since the bondienergy of Li_2 is 1, and that of Li_2^- and Li_2^+ is 0.05. That is why, Li_2 is much stable then Li_2^- and Li_2^+. The reason that Li_2^+ is more stable than Li_2^- is that energy level in B.M.O (bonding molecular orbital) is higher in Li_2^+ than in Li_2^-.

Q A double bond is stronger than single bond and triple bond is stronger than double bond?

Ans As

"Shorter is bond length greater will be bond energy and stronger will be bond"

EXPLAINATION:

Since the bond length of a double bond is shorter and bond length of a single bond is greater. That is why

double bond has greater bond energy and is stronger than single bond.

Similarly, the bond length of a triple bond is much shorter than double bond. So a triple bond is stronger than a double bond.

Q Write down similarities between VBT and MOT?

SIMILARITIES:

a) Both theories explain the formation of covalent bond.
b) Both theories involve formation of two types of bonds .i.e. σ and π bonds.
c) Atomic and molecular orbital are filled by same principle.
d) In both methods, overlapping of all atomic and molecular orbitals of same symmetry forms bonds.
e) According to both theories electronic charge resides between the atomic nuclei.

Q Write down difference between VBT and MOT?

	VALENCE BOND THEORY	MOLECULAR ORBITAL THEORY
1-	According to VBT, Valence ~~bond~~ es are involved in bond formation.	According to MOT, electrons of interacting atoms are involved in bond formation.
2-	It does not give idea of bond order.	It gives idea about bond order.
3-	It does not explain paramagnetic behaviour of substances like O_2.	It explains paramagnetic behaviour of substances.
4-	It does not explain non-existence of He_2.	It explains non-existence of He_2.
5-	Atomic orbitals do not lose individual identity	Atomic orbitals loose individual identity.