

1 Aug/23

## Chapter-4

### Chemical Bonding and Molecular formula

**Chemical Bond:-** The attractive force which holds various constituents (atoms, ions) together in different chemical species is called chemical force and the association of species with chemical force is called chemical bond.

**Octet Rule** (Kassel & Lewis approach for a chemical bond)

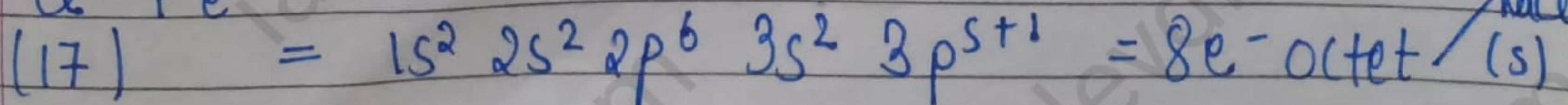
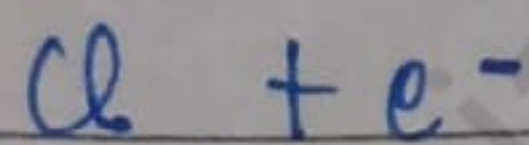
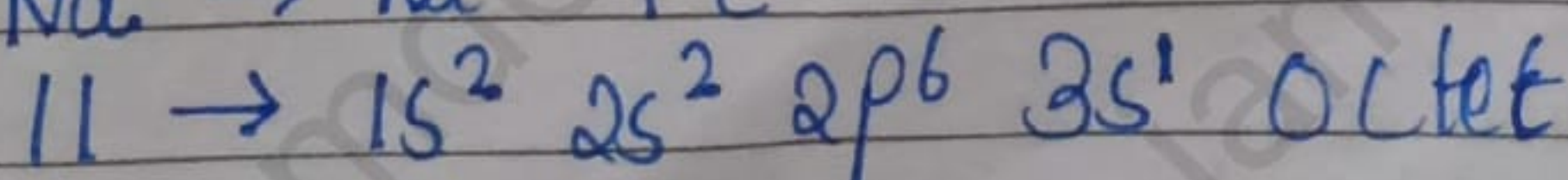
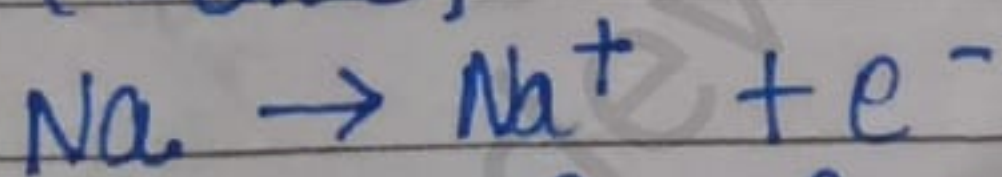
1. Kassel and Lewis in 1916 developed an important theory which is called electronic theory of chemical bond.
2. According to this atoms combine either by transfer of electrons or by sharing in order to complete their octet which contains 8 electrons in their outermost shell. This is called octet theory.

### Types of bonding

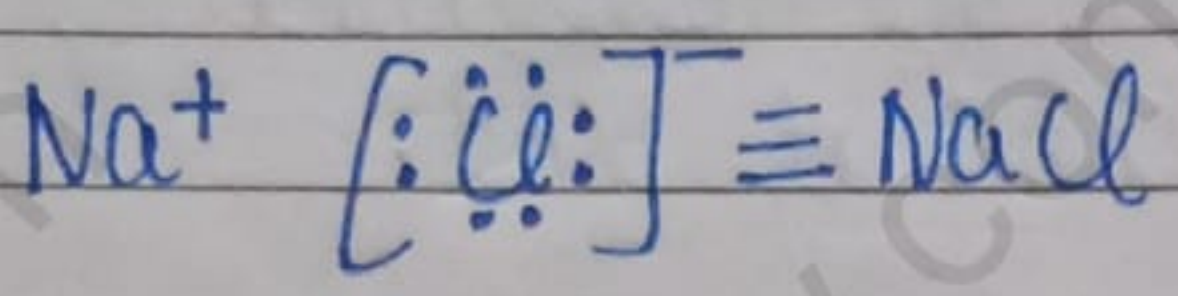
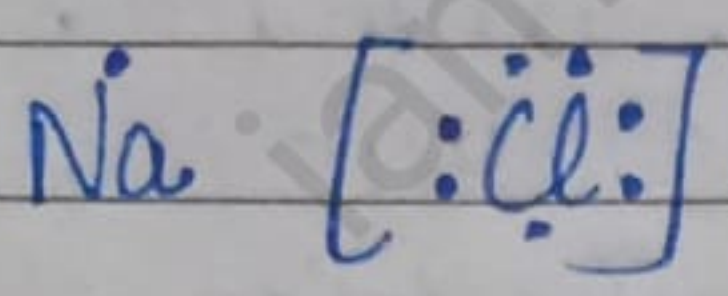
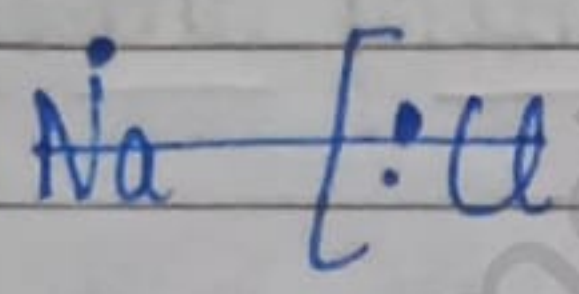
1. Ionic bond
2. Covalent bond

1. Ionic bonds are formed by the transfer of electrons from one species to another which takes place according to the following mechanism

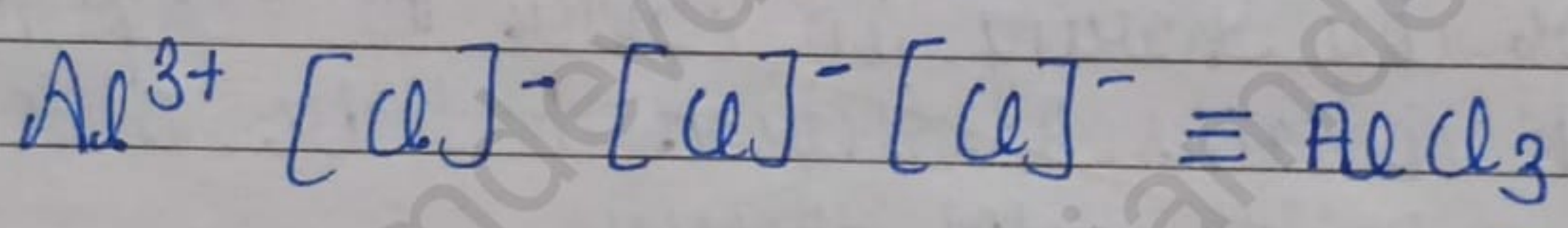
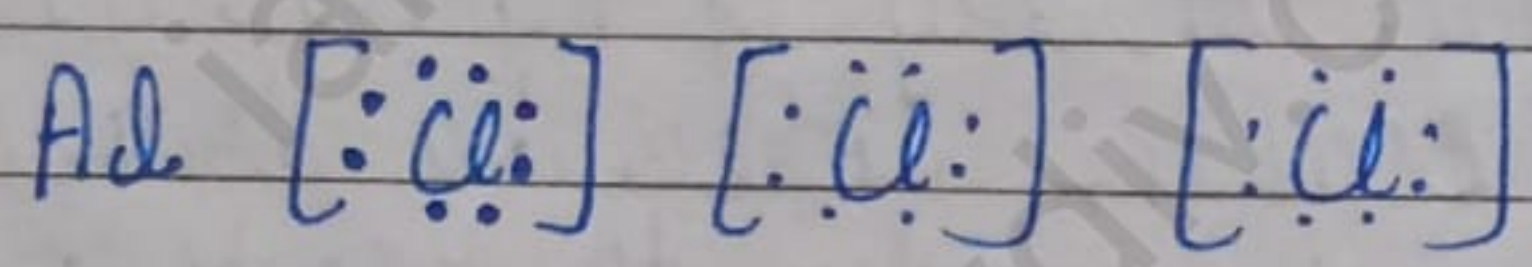
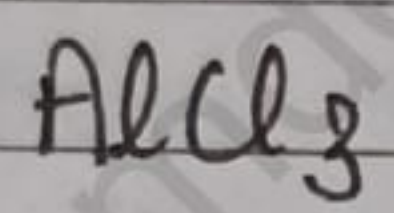
Ex:- NaCl (Ionic)



## Lewis dot structure



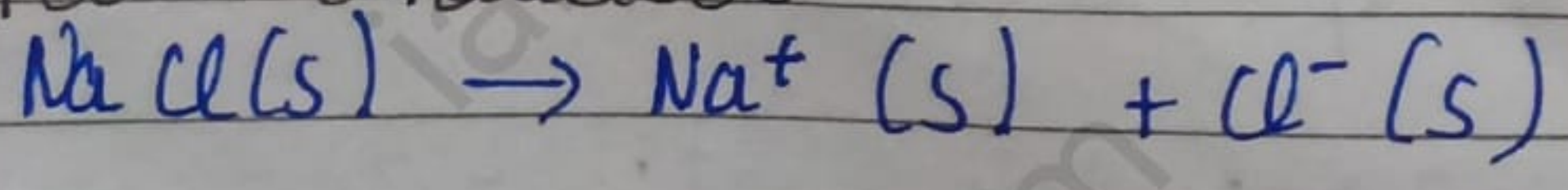
## Formation of Aluminium chloride



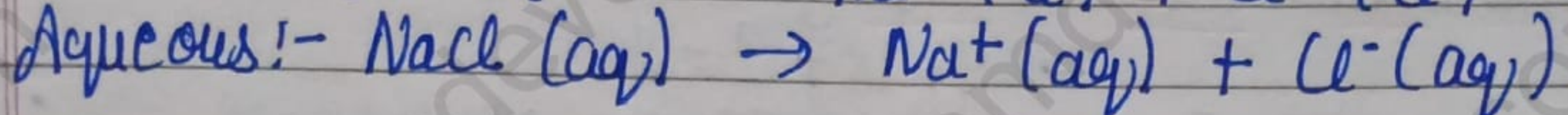
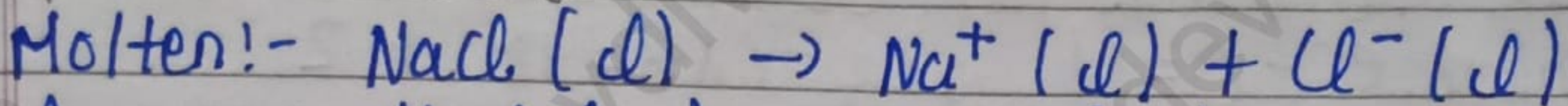
## Properties of ionic compound

- They have high melting and boiling point.
- They have greater solubility in polar solvent like water but do not dissolve in organic solvents.
- Ionic compounds exist as crystalline solid in which oppositely charged ions are closely packed in space.
- Electrical conductivity - due to the movement of free ions. They are poor conductors in solid and good conductors in molten as well as aqueous state.

Poor conductor



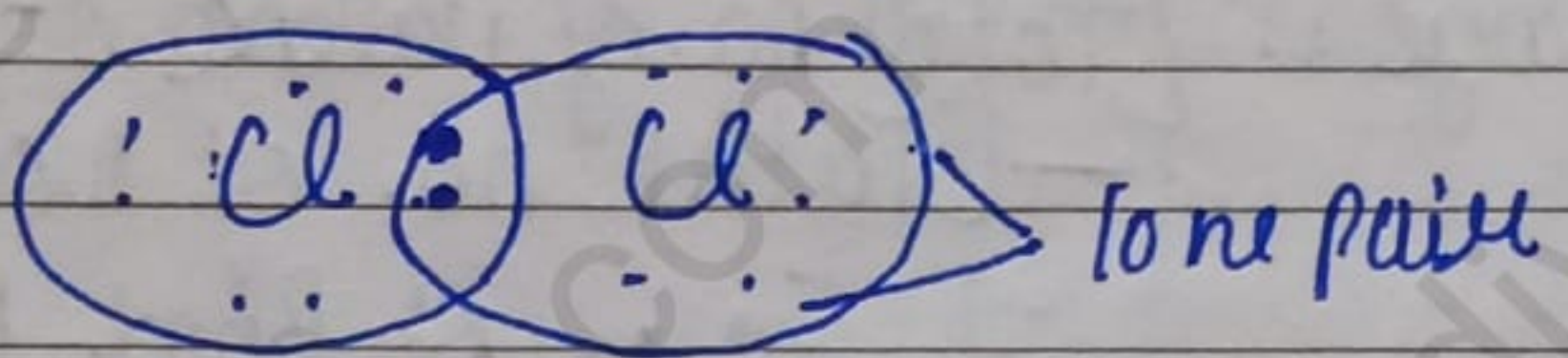
Good conductor



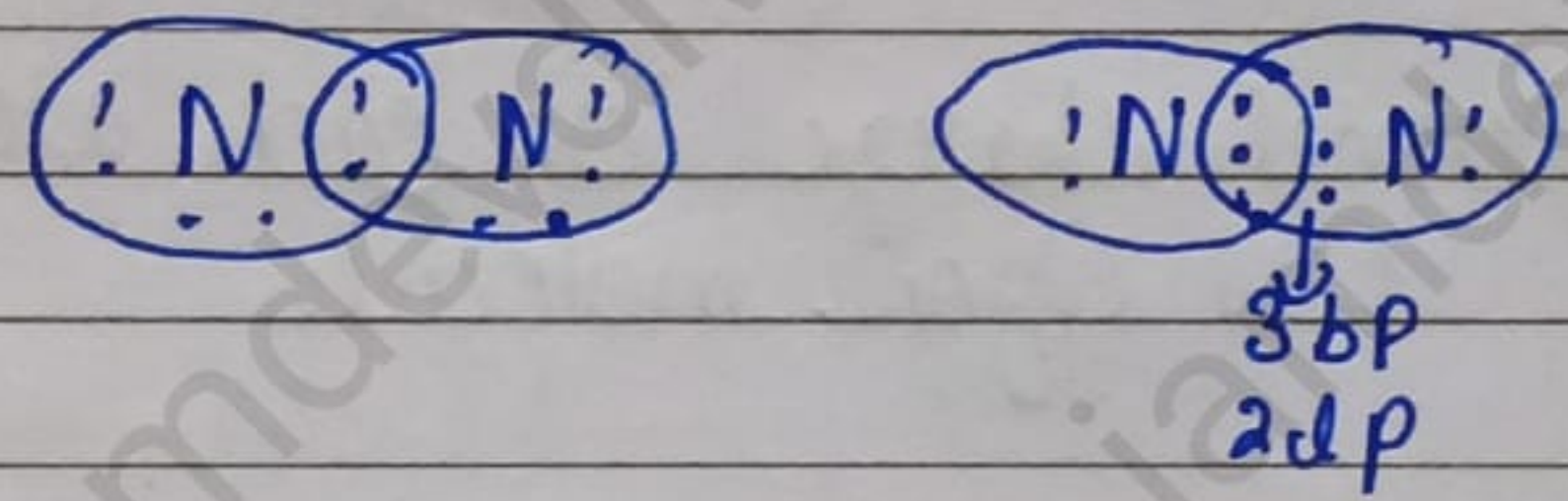
★ Solubility Covalent Bond  
Ion

• These are formed by sharing of electrons between two species  
Eg:- The covalent bonding may be achieved in two ways:

- (i) Polar Covalent  $\text{HCl}$  due to E.N. diff.
- (ii) Non-Polar Covalent  $\text{H}_2$   $\text{Cl}_2$



$\text{N}_2$



Lewis Dot Structure

Step 1:- Calculate the no. of electron in valence shell

Step 2:- Calculate the total no. of electrons to complete their octet

Step 3:- Now find out shared electrons

$$\text{Shared } e^- = [\text{octet } e^- - \text{Valence } e^-]$$

Step 4:- Now calculate the unshared electrons

$$\text{Unshared } e^- = [\text{Valence } e^- - \text{Shared } e^-]$$

Ques - write the Lewis dot structure of  $\text{CN}^-$

Valence = C=4, N=5, +1  $4+5+1=10$

Octet = 16

Shared =  $16 - 10 = 6$



Lone pair =  $10 - 6 \Rightarrow 4e^-$

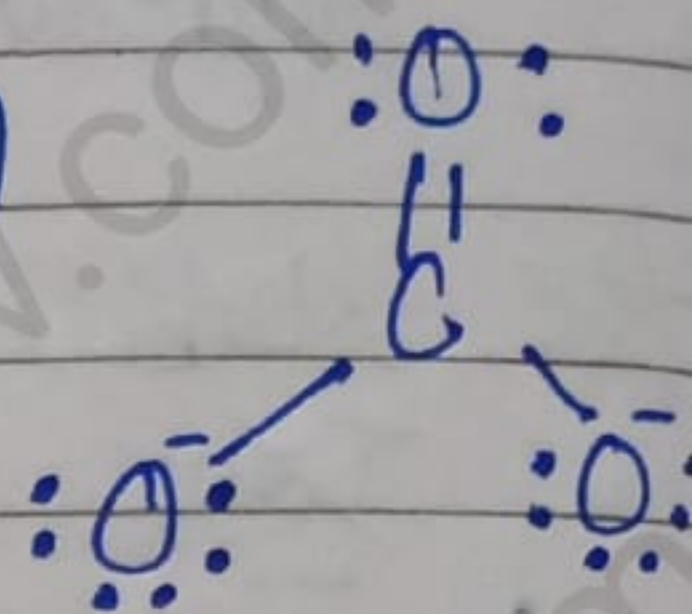
Ques write the Lewis dot Structure of  $\text{CO}_3^{2-}$

$$\text{Valence } e^- = \text{C} = 4, \text{O}_3 = 6 \times 3 = 18 + 2$$

$$= 4 + 18 + 2 = 24$$

$$\text{Octet} = 32e^- \quad \text{Shared} = 32 - 24 \Rightarrow 8 \text{ (4 bond)}$$

$$\text{Unshared} = 24 - 8 = 16$$

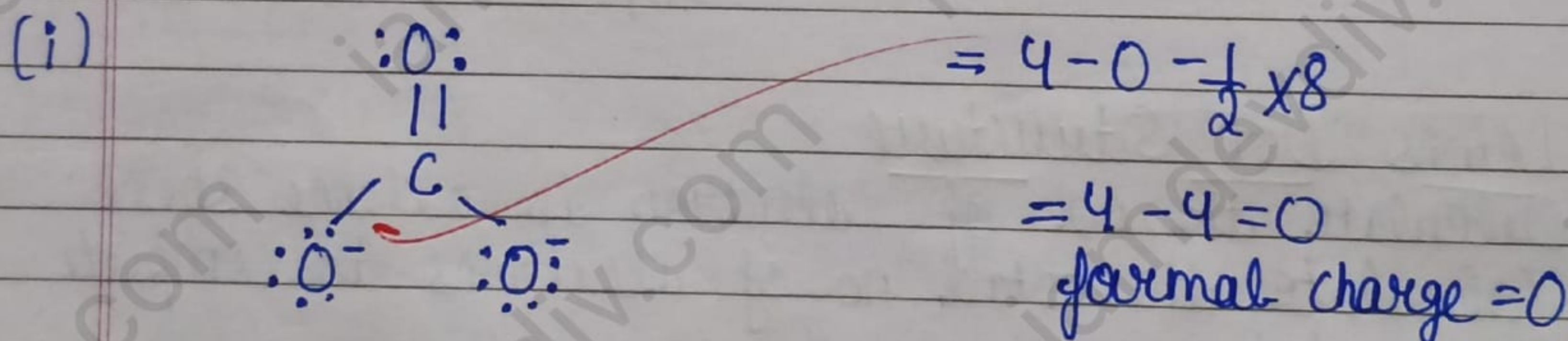


### ★ FORMAL CHARGE

It is the difference between no. of valence electrons in its free state and its combined state

$$\text{Formal charge} = \left[ \text{Total no. of valence } e^- \text{ in free atom} \right] - \left[ \text{Total no. of Non bonding } e^- \right] - \frac{1}{2} \left[ \text{No. of Bond Pairs } e^- \right]$$

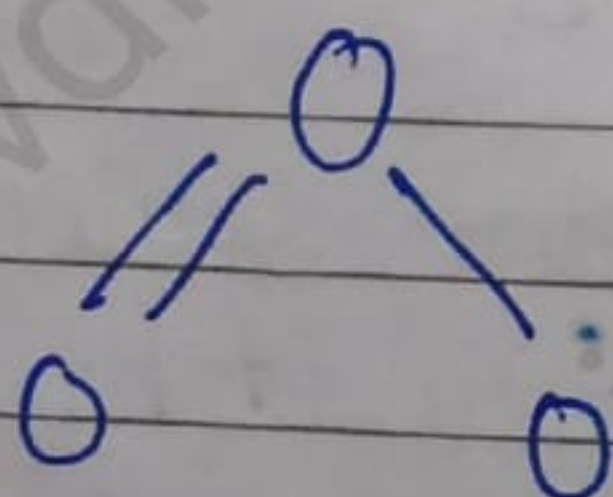
Ques Calculate the formal charge on each atom of  
(i) carbonate ion (ii) Ozone molecule



$$\text{Formal } O^- = 6 - 6 - \frac{1}{2} \times 2$$

$$= 6 - 6 - 1 = -1$$

(ii) Form  $\text{O}_3$



## Fajan's Rule

It states that no ionic bond is 100% ionic and no covalent bond is 100% covalent there is some opposite character present in the nature of the bond.

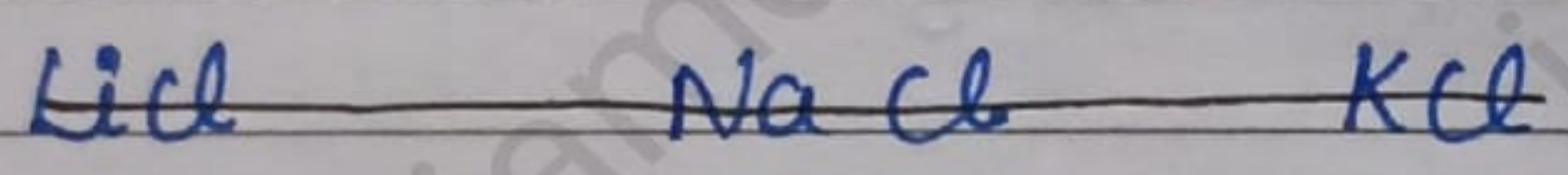
For a molecule to be covalent there are some condition with respect to cation and anion

### Cation

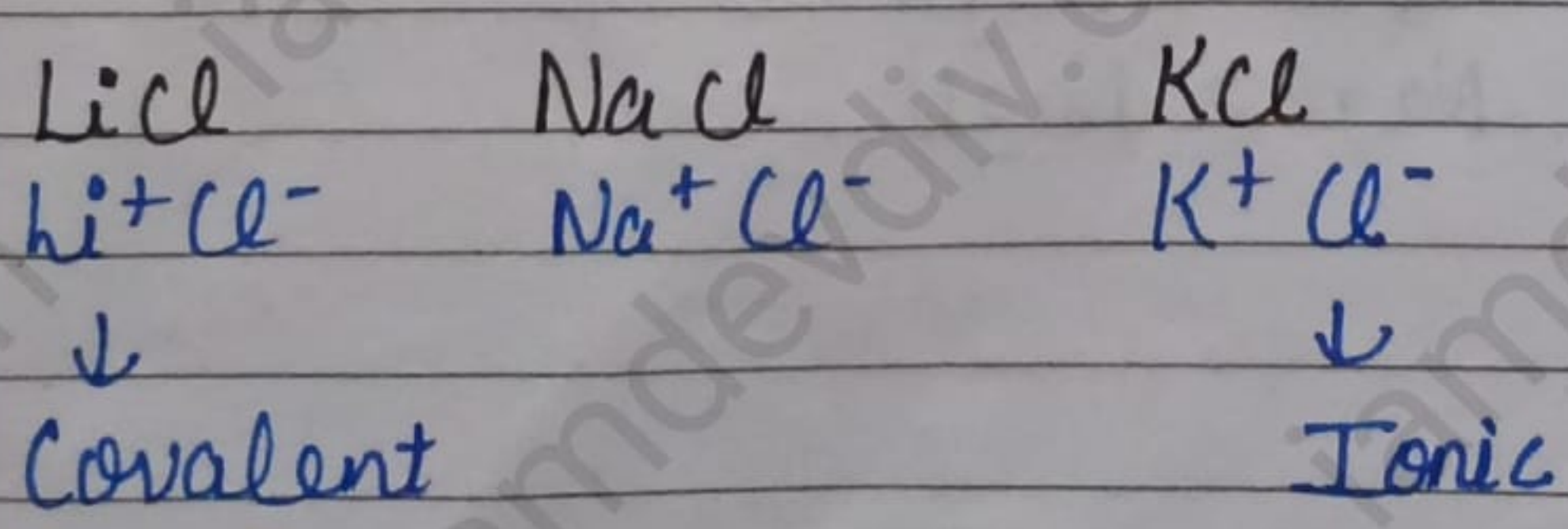
- 1. Small size
- 2. high charge
- 3. d-block involved

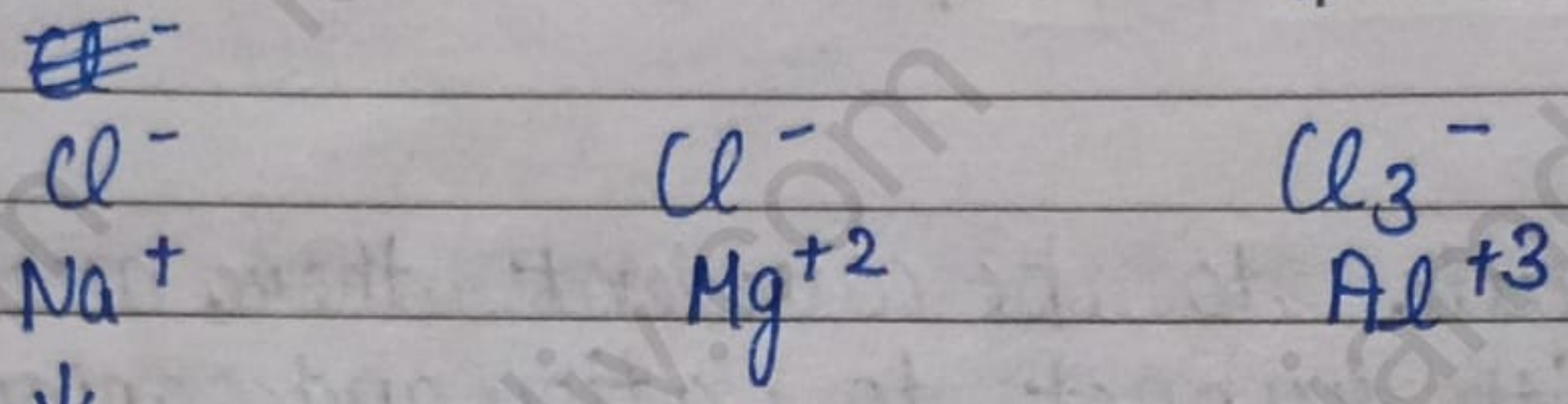
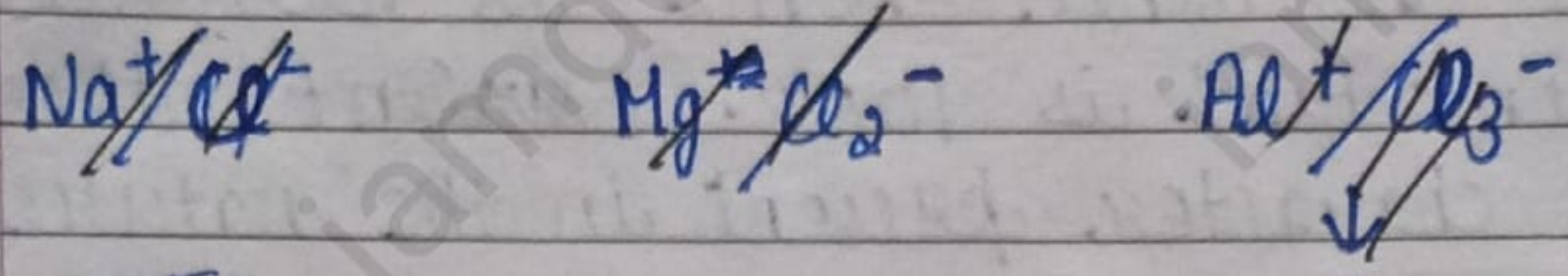
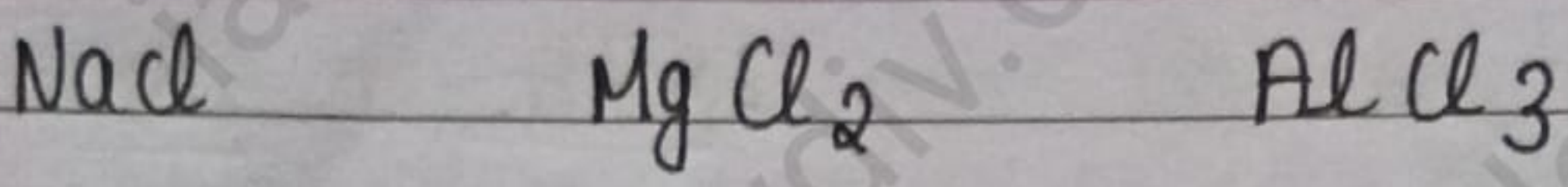
### Anion

- 1. Atomic size bigger
- 2. higher charge



Ques Which of the following is supposed to be more covalent in nature

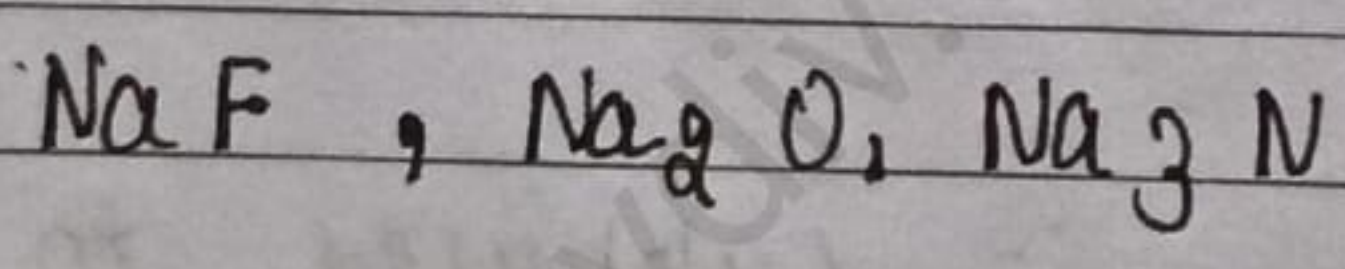




↓  
 Ionic

- ★ Ionic      NaCl > MgCl<sub>2</sub> > AlCl<sub>3</sub>  
 Stability    NaCl > MgCl<sub>2</sub> > AlCl<sub>3</sub>  
 M.P.        NaCl > MgCl<sub>2</sub> > AlCl<sub>3</sub>  
 Covalent    NaCl < MgCl<sub>2</sub> < AlCl<sub>3</sub>

Ques Arrange the following into decreasing order of their melting point. Covalent character, stability



- Covalent - Na<sub>3</sub>N > Na<sub>2</sub>O > NaF  
 M.P. - NaF > Na<sub>2</sub>O > Na<sub>3</sub>N  
 Stability - NaF > Na<sub>2</sub>O > Na<sub>3</sub>N

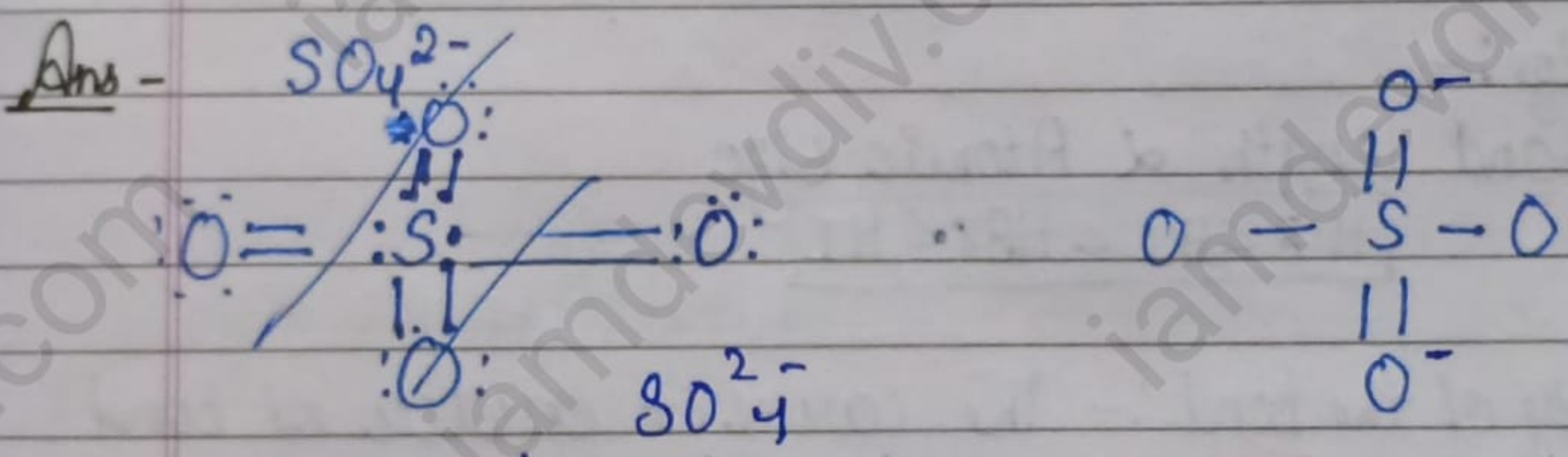
Ans

Ques - Which of the following is found to be more stable

- 1.  $\text{NaCl}$   $\text{CuCl}$

Stability -  $\text{NaCl}$  is more stable

Ques - Draw the structure and calculate formal charge of each atom of sulphate ion



$e^-$  in valence shell =  $6 (s) +$

## \* Bond Parameters

1. Bond length
2. Bond enthalpy
3. Bond order
4. Bond Angle

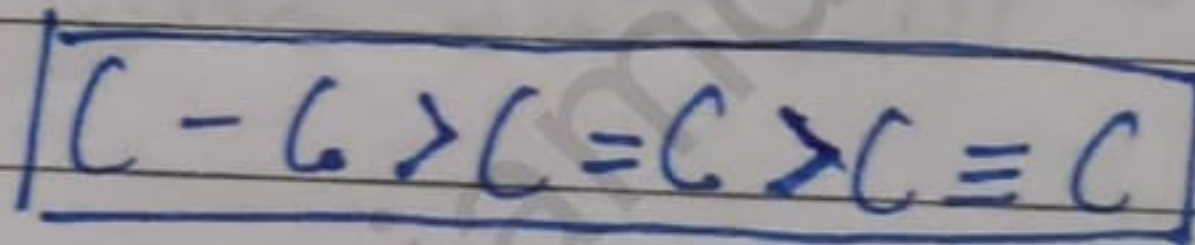
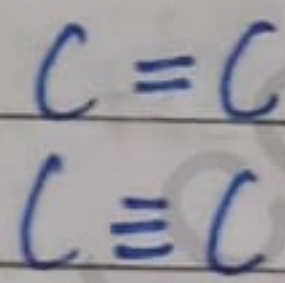
1. Bond Length: - It is defined as the internuclear distance between two atoms when bonded to each other.

Factors affecting bond length:-

1. Atomic size:-

Bond length  $\propto$  Atomic size  
 $\boxed{HF < HCl < HBr < HI}$

2. Multiplicity of the bond:- The correct order of bond length is



3. Bond enthalpy:- Bond enthalpy of chemical bond can be defined as total amount of energy required to break 1 mole of that chemical bond.

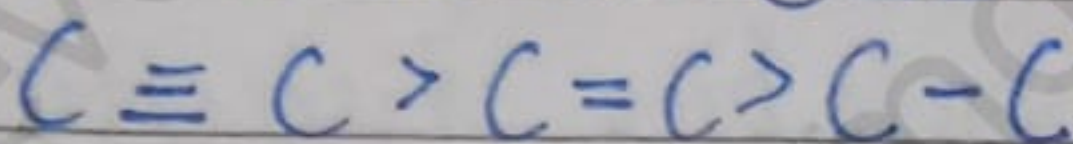
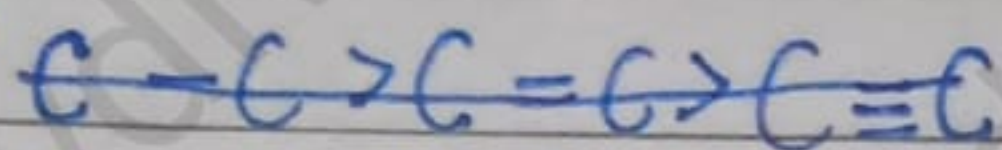
Factors affecting Bond Enthalpy:-

1. Atomic size:-

Atomic size is inversely proportional to atomic size. The correct order of bond enthalpy  $\boxed{HF > HCl > HBr > HI}$



2. Bond Multiplicity:-



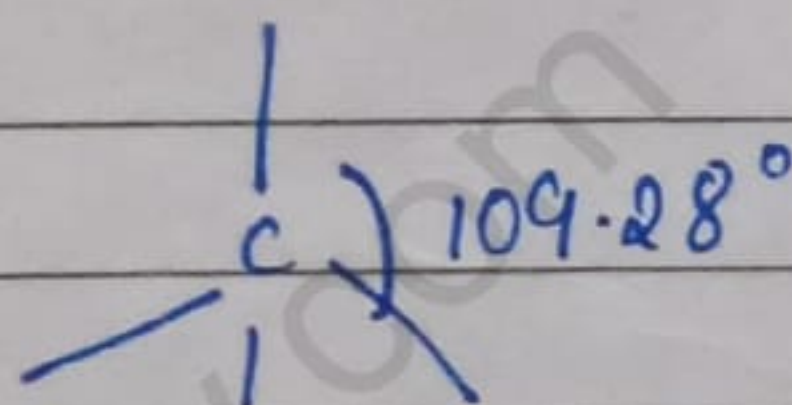
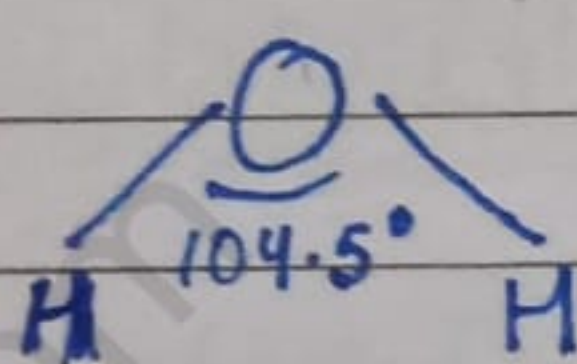
3. Bond order:- Bond order is the measurement of no. of electrons involved in bond formation between two atoms in a molecule

(ii) Bond order is used to indicate the stability of the bond

(iii) Bond order is directly proportional to Bond enthalpy

(iv) Bond order is directly proportional to Bond strength

→ Angle between the orbitals containing bonding electron pairs around the central atom in a molecule or in a complex



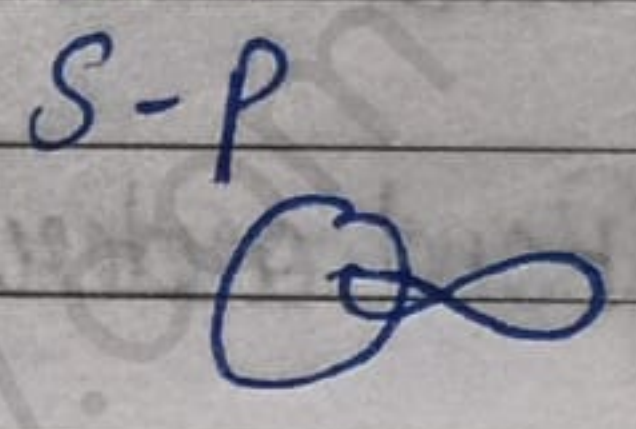
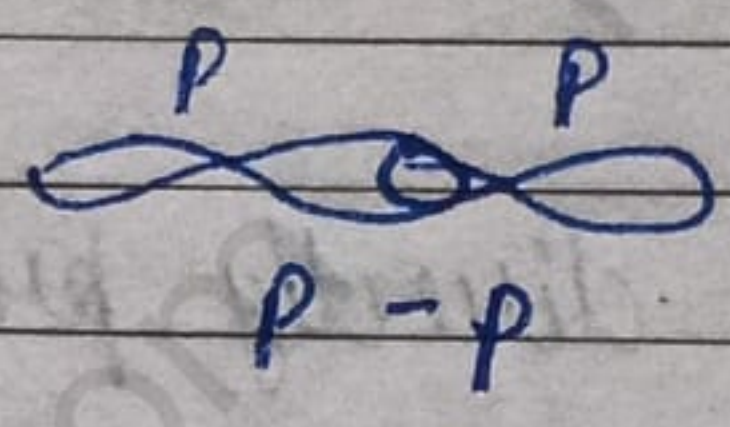
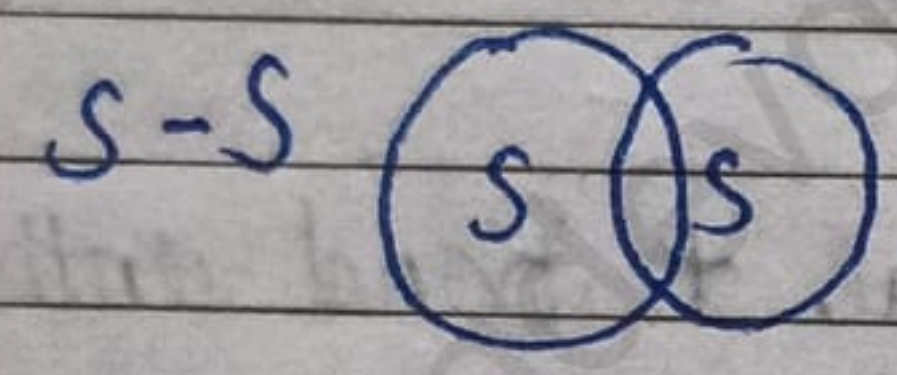
★ Valence bond theory (VBT)  
Postulates:-

- Valence bond theory was given by Heitler & London in 1927 and was modified later by Pauling
- For the formation of <sup>covalent bond</sup> atomic orbitals must overlap.
- Only half filled orbital with opposite spin overlap

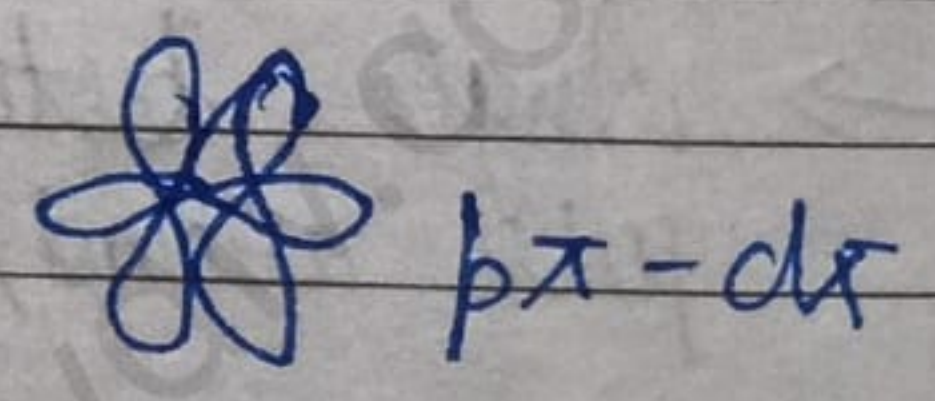
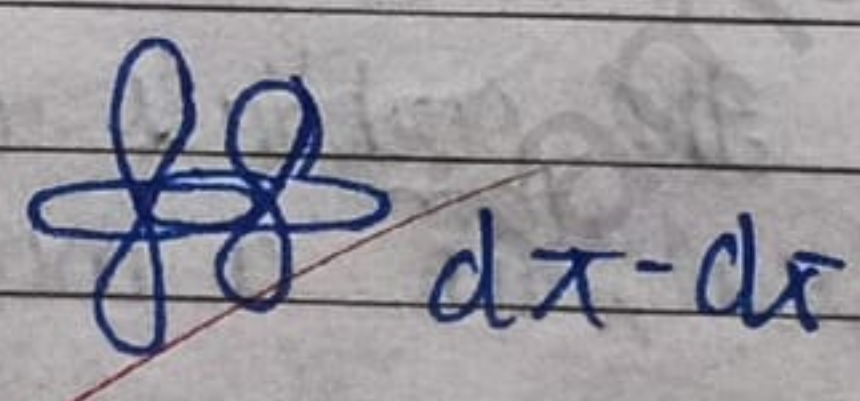
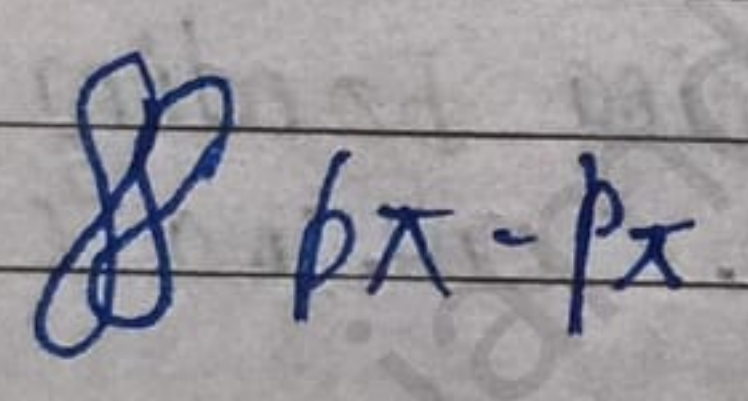
- The overlapping should be less than 50%.
- The extent of overlapping directly proportional to bond strength

### Types of overlapping

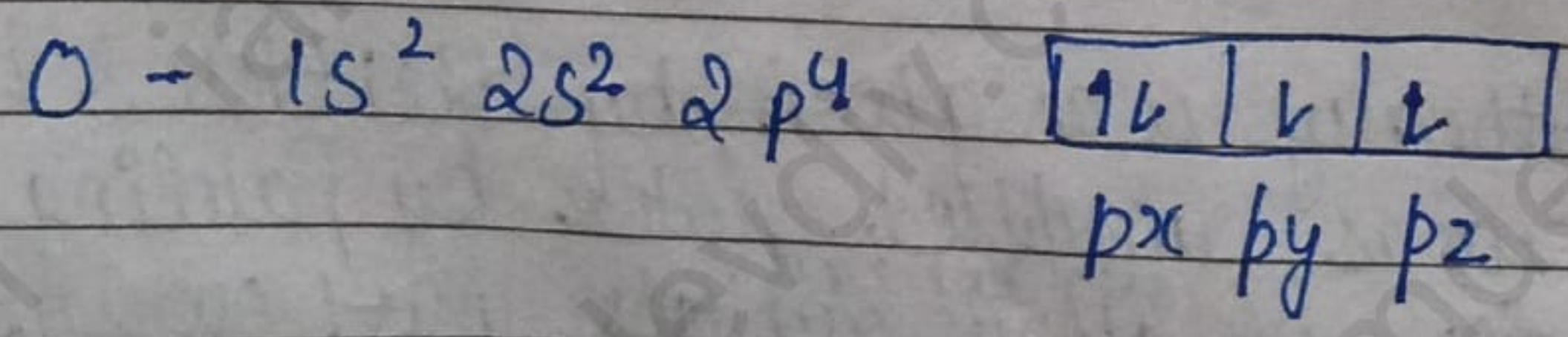
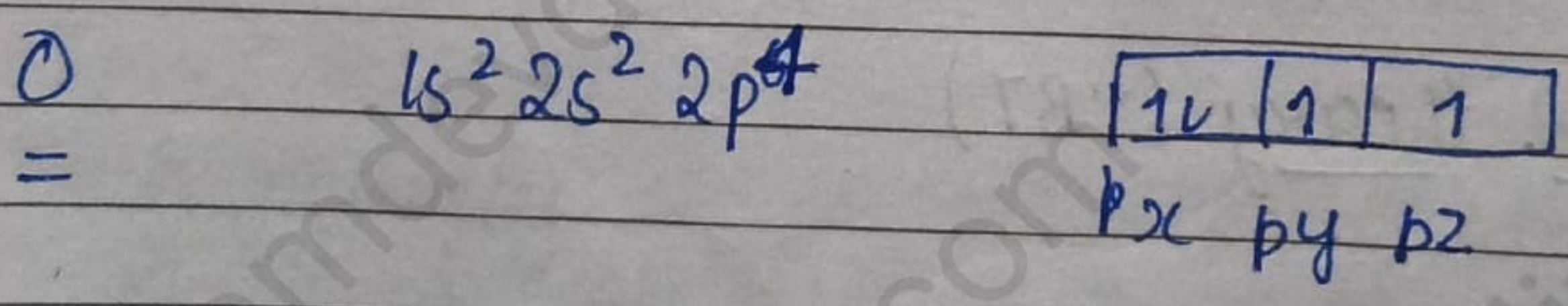
→ Sigma bond formation (Head to head overlap)



→ Pi Bond formation (side to side)



Q

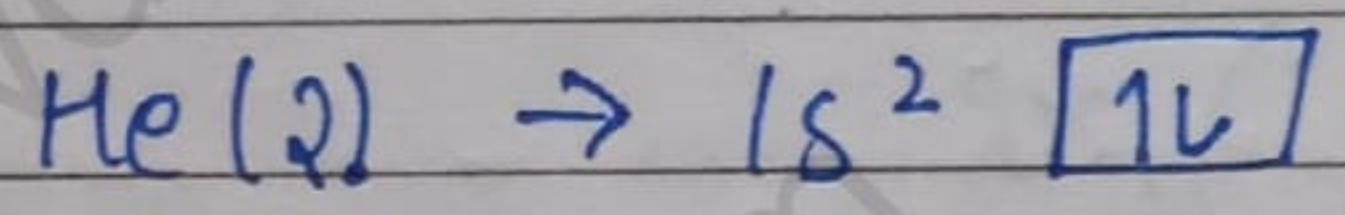
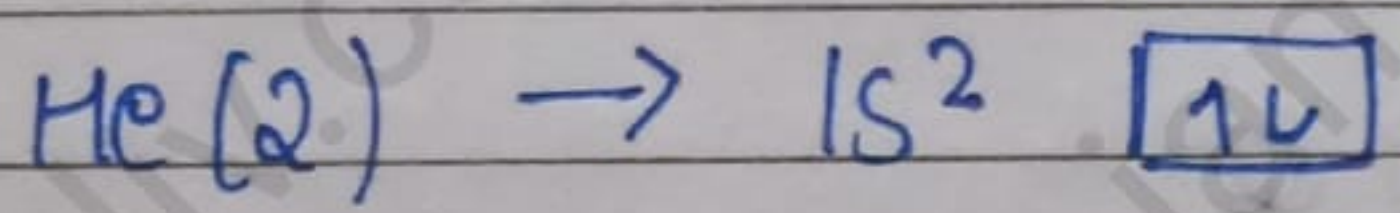


A

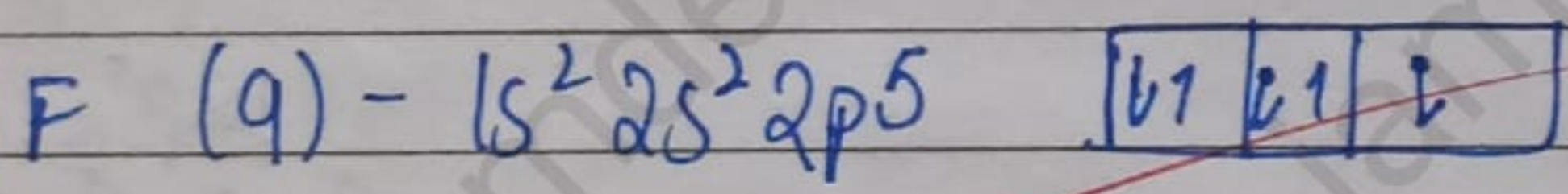
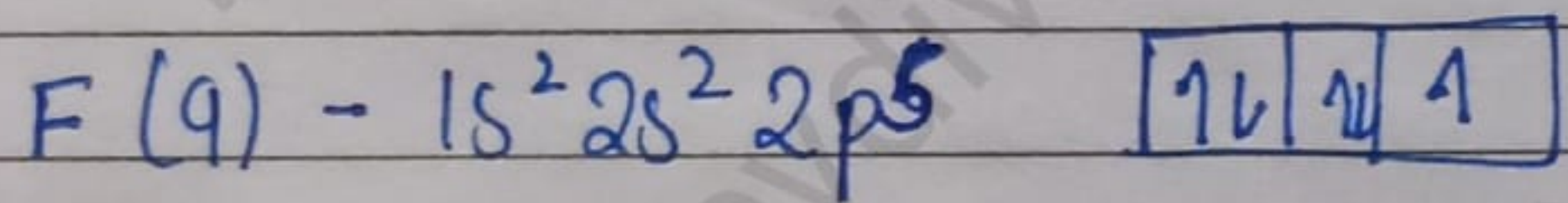
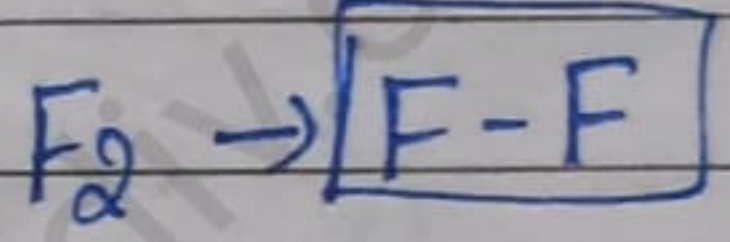
Ques - Why  $He_2$  doesn't exist explain with the help of Valence bond theory?

$He_2$

duplet =  $4e^-$  → According to Octet Rule  
 Valence =  $4e^-$   
 $\underline{\quad 0e^-}$



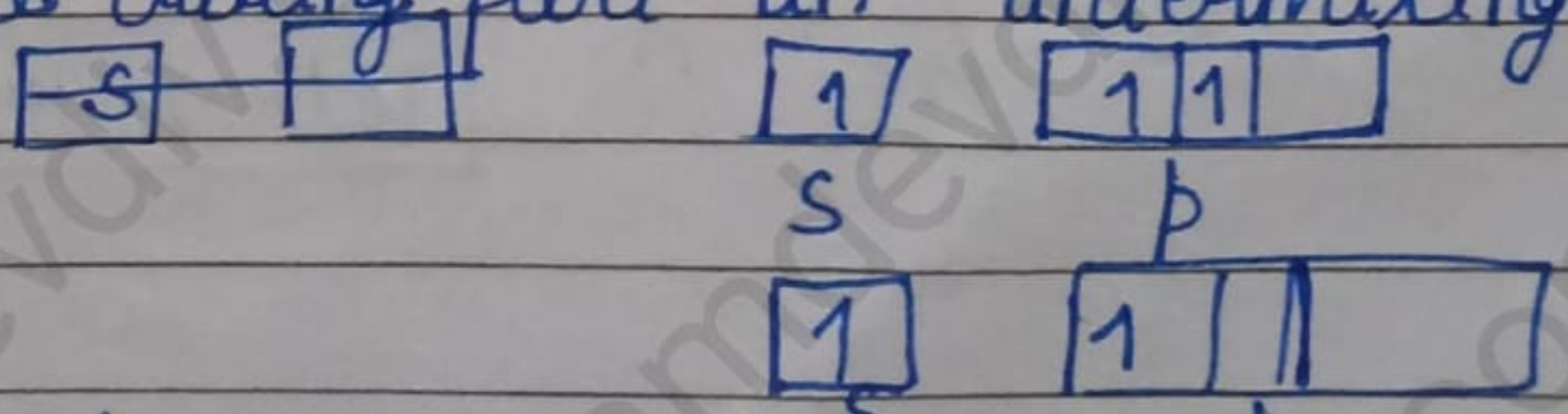
Ques - Formation of  $F_2$  molecule



Hybridisation

- Intermixing of same or nearly same energy orbitals to give new hybrid orbitals is called hybridisation.

- The no. of hybrid orbitals are just equal to the no. of which are taking part in intermixing

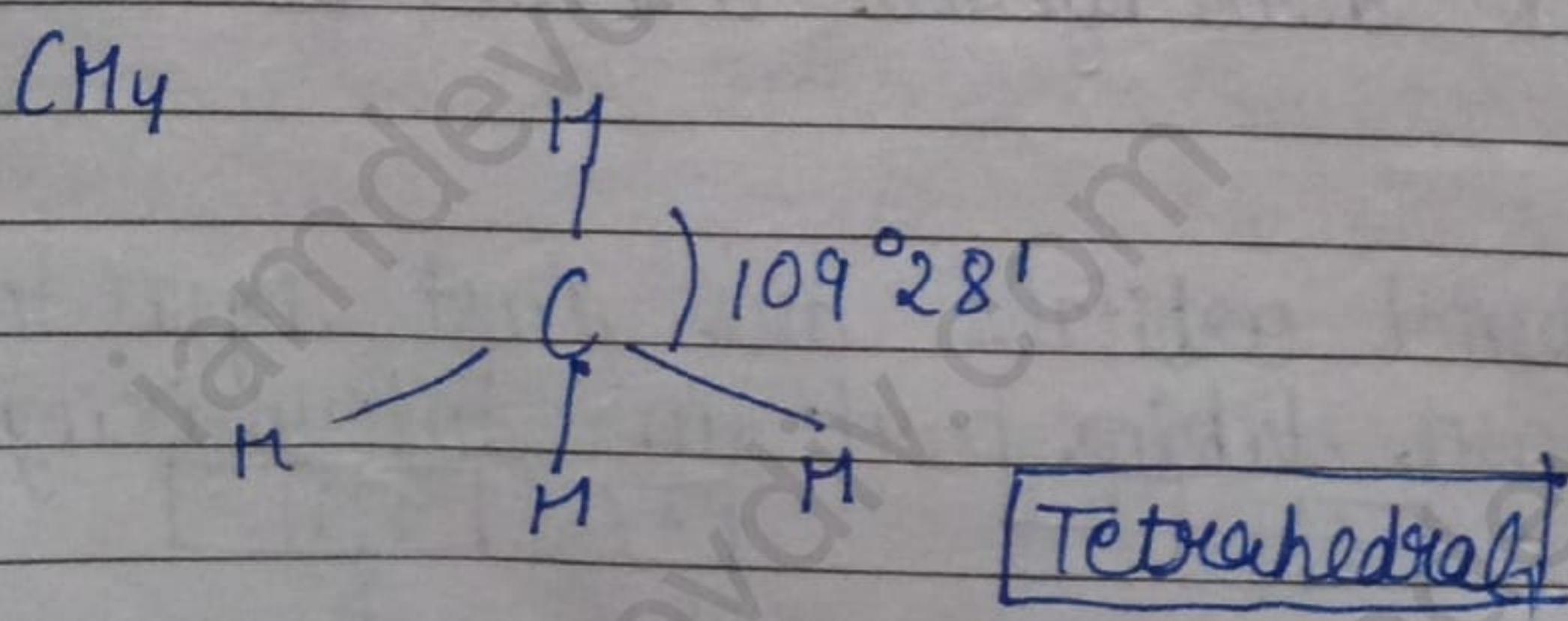
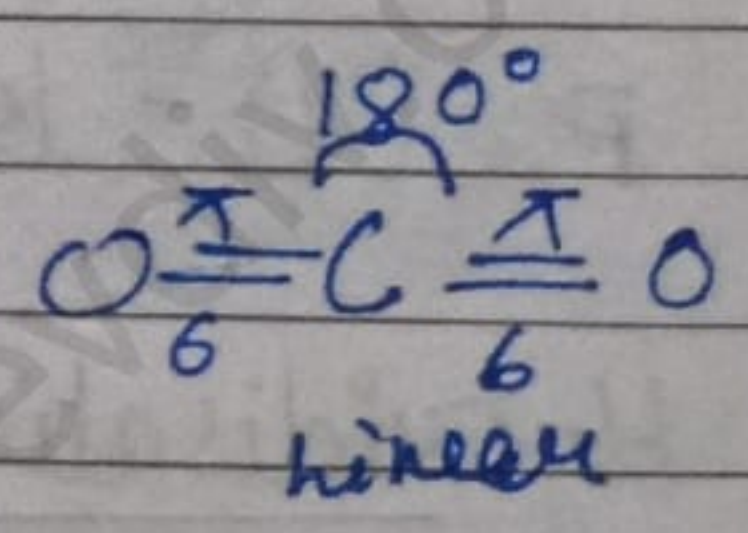
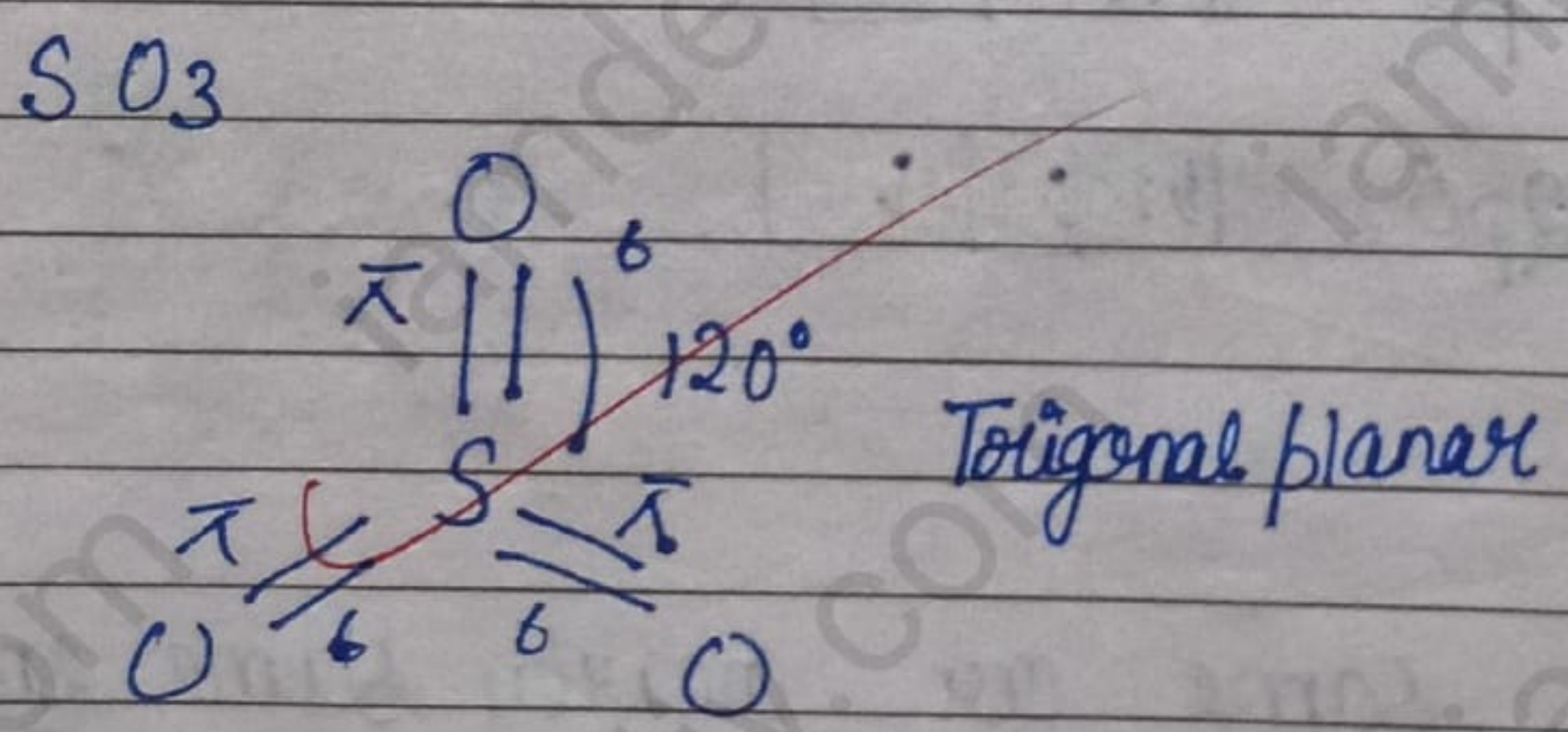
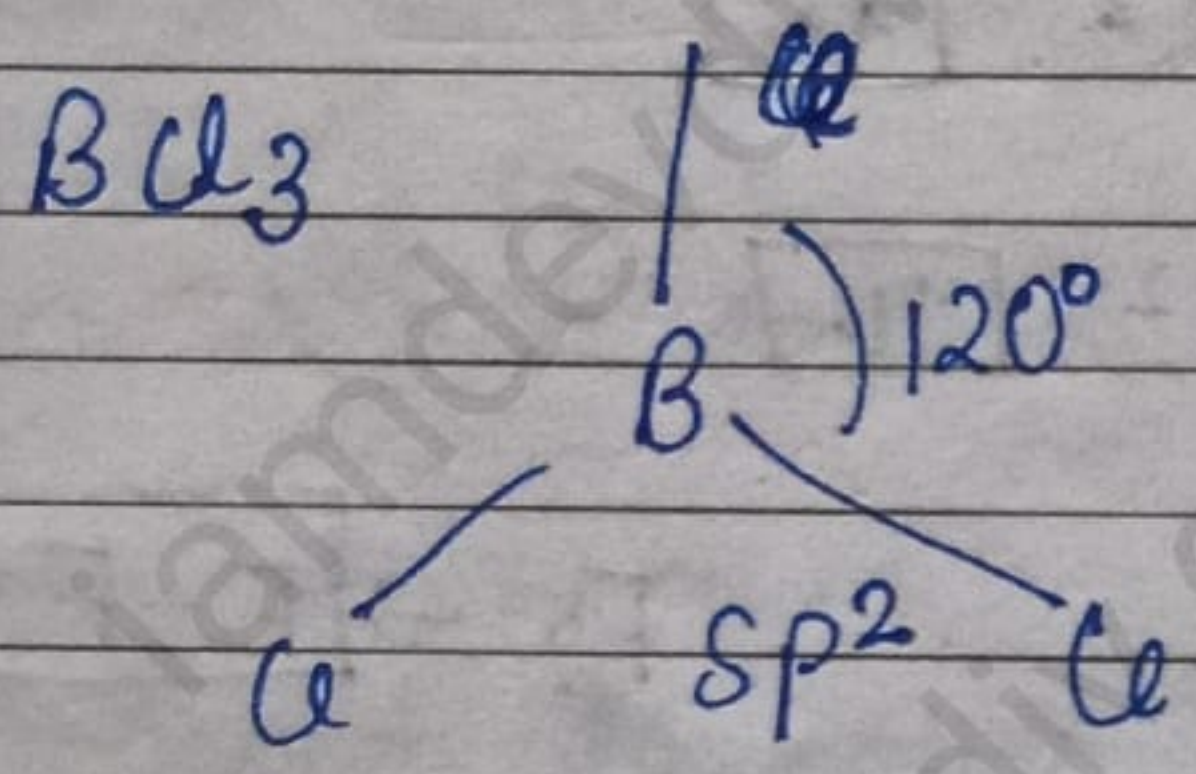
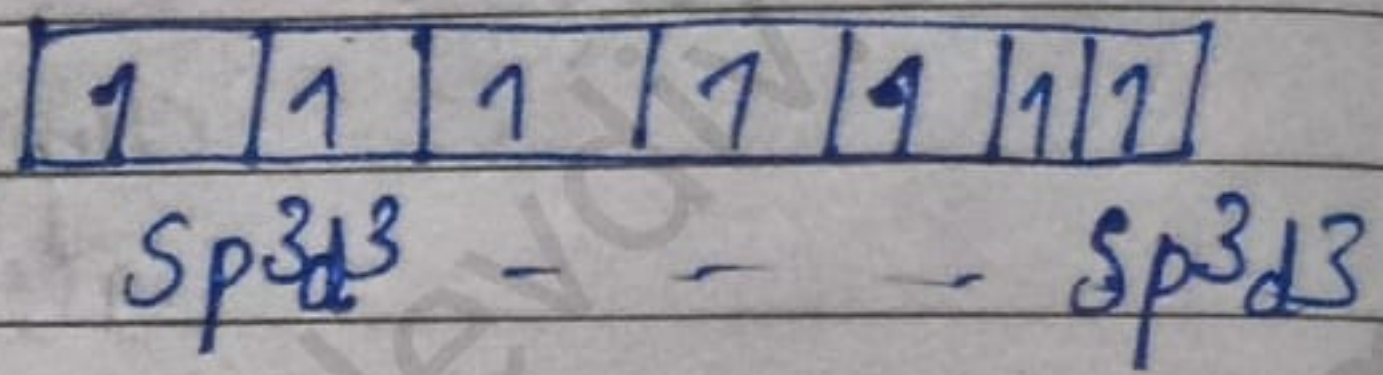
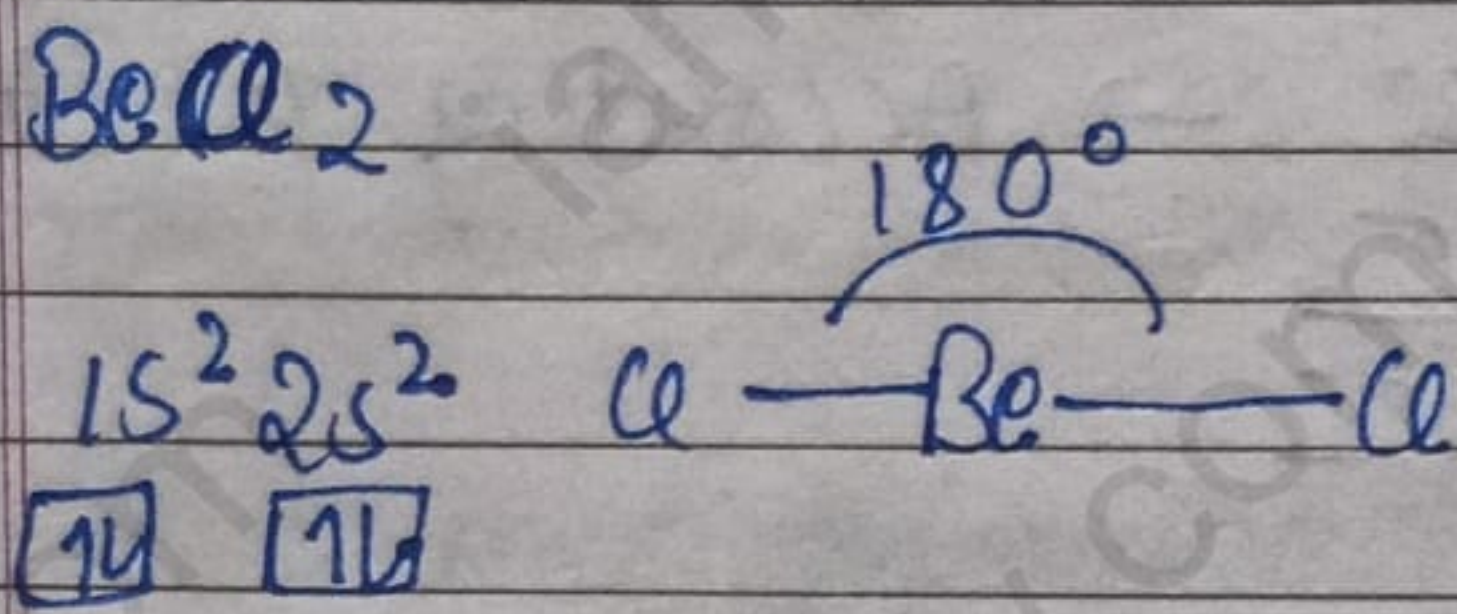


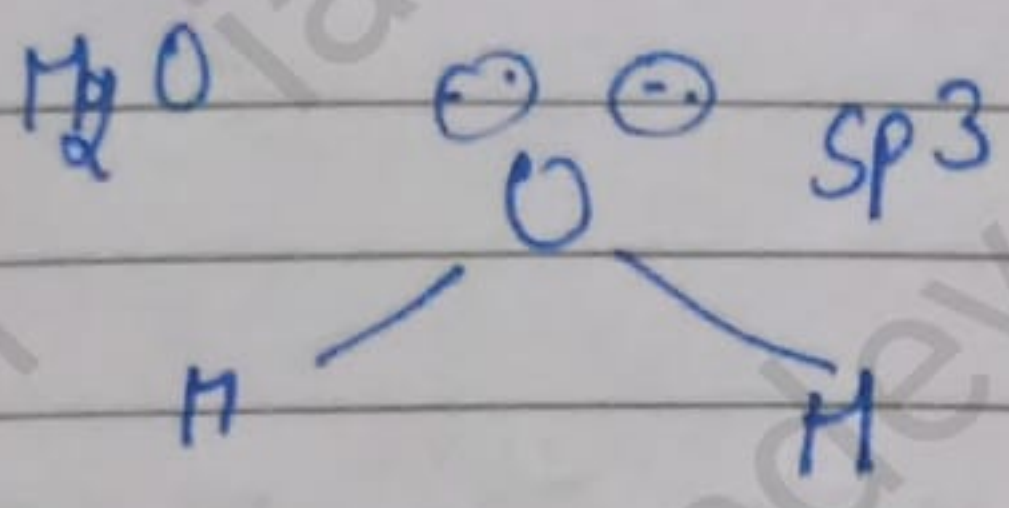
Only

- Only Sigma bond and non pairs are involved in this concept no pi bond is taken

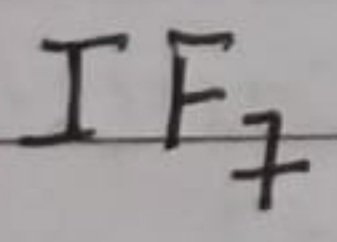
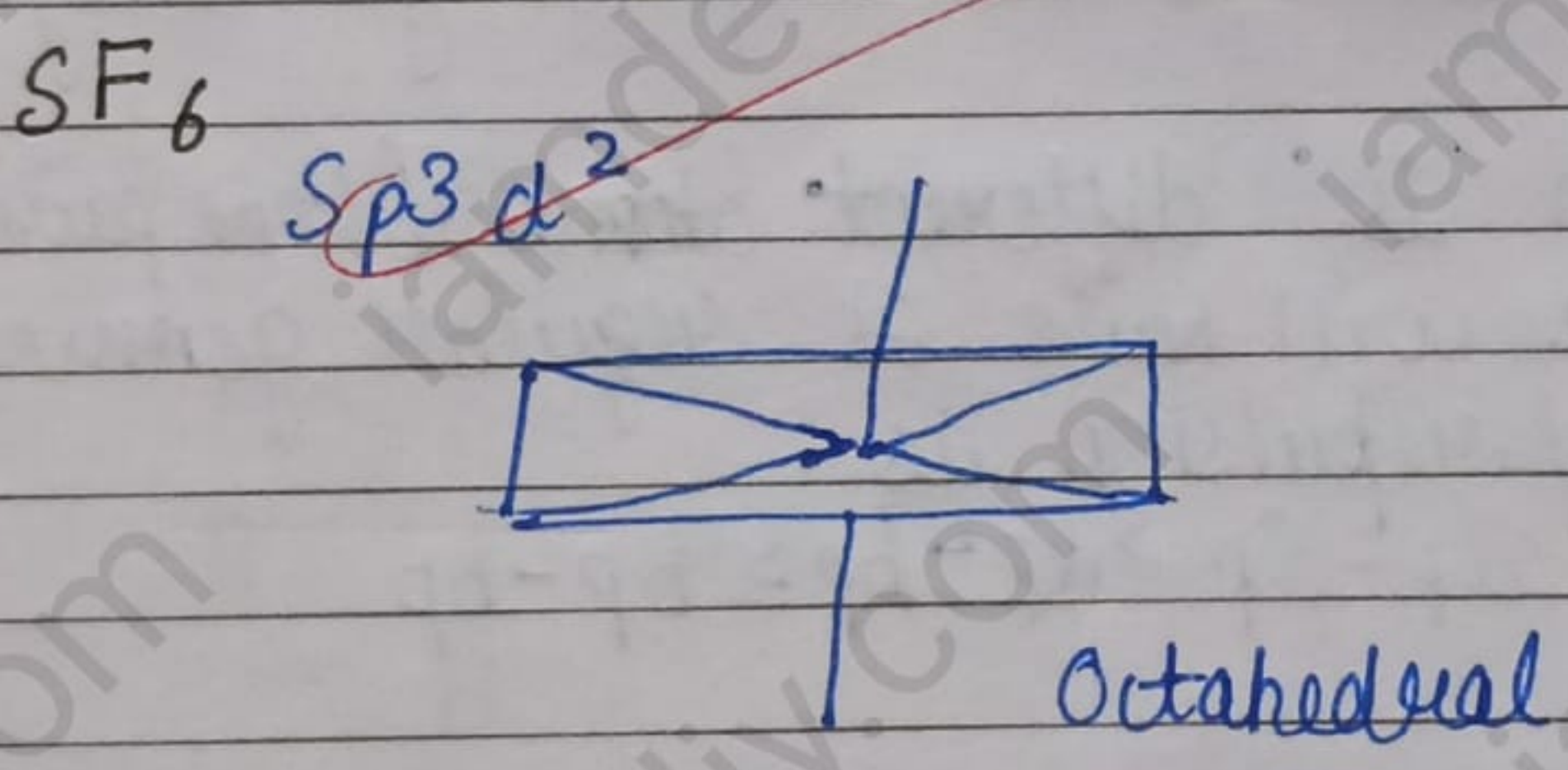
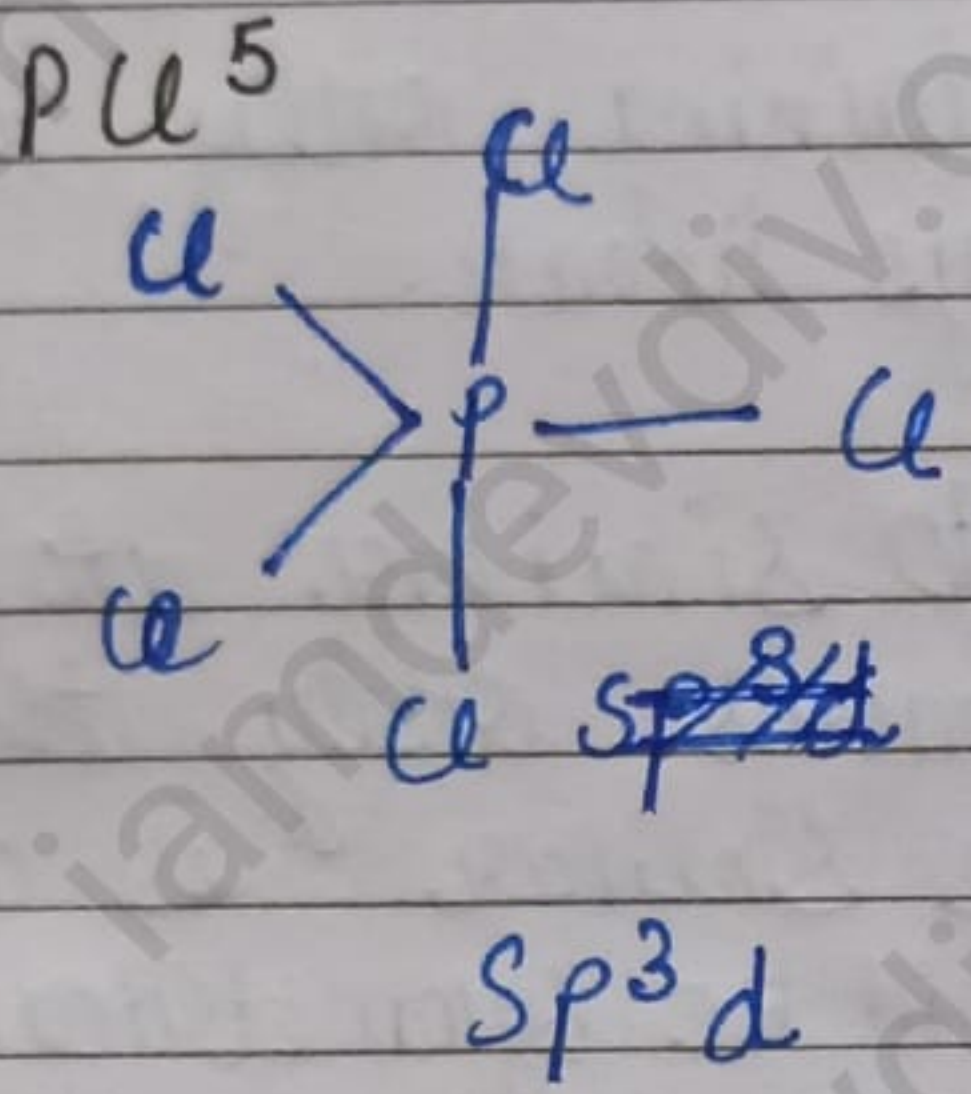
Hybrid orbitals are named after the parent orbitals

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

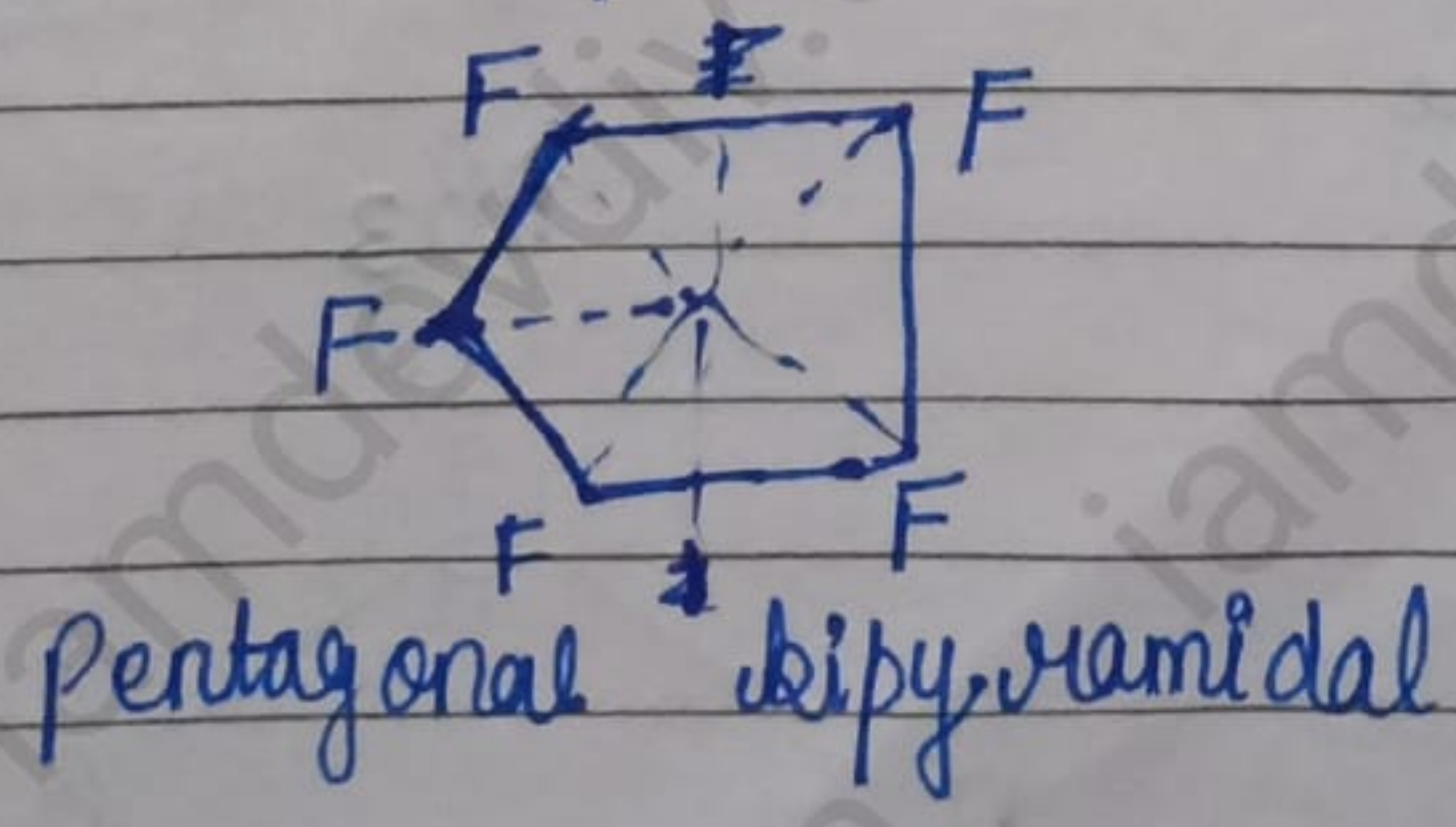




Geometry



Hybridisation -  $sp^3d^3$



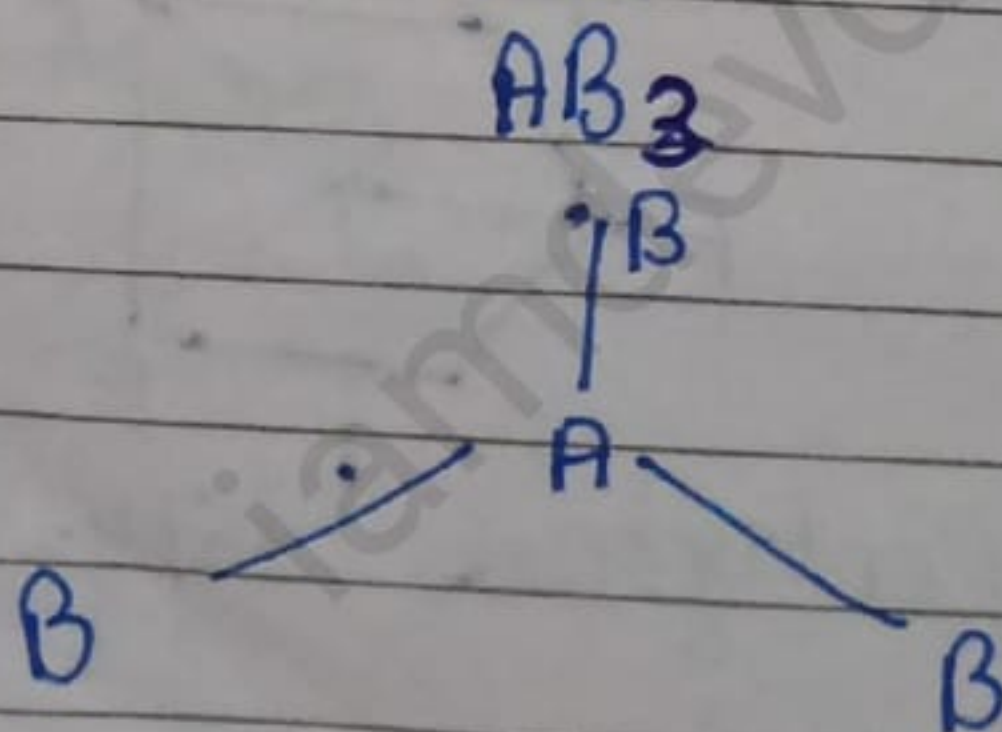
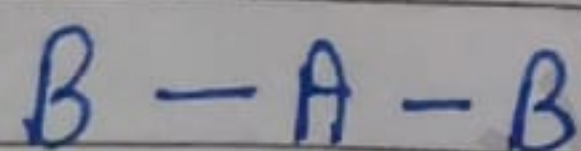
## Valence shell electron pair Repulsion theory (VSEPR)

The shape of a molecule depends upon the no. of valence shell electron pairs (Bond pairs and lone pairs) around the central atom.

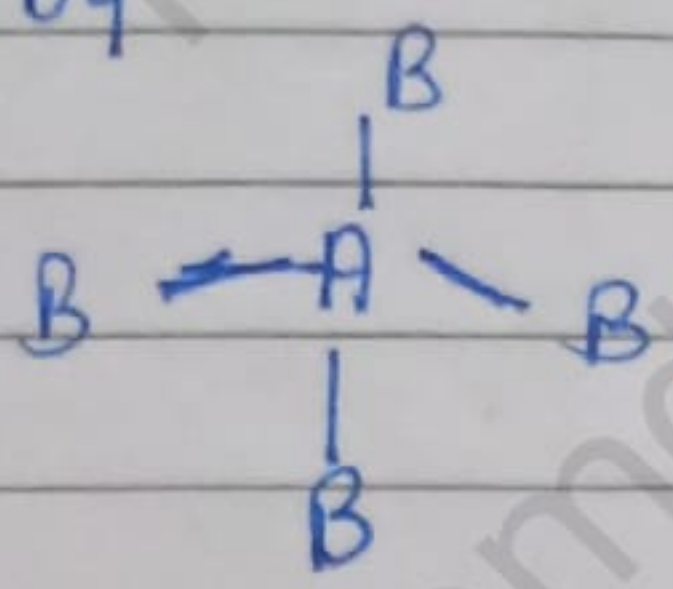
- The shape of a molecule containing only two atoms with no ~~none~~ lone pair is always linear.
- If a central atom is linked to similar atoms and is surrounded by bond pairs only the repulsion between them are similar as a result the shape of the molecule will be symmetrical and the molecule is said to have regular geometry.
- If the central atom is different atoms (lone pair and bond pairs) molecule will have its regular geometry and the order of repulsion is  

$$lp-lp > lp-bp > bp-bp$$
- During VSEPR on the concentration of geometry only sigma bond pairs and lone pairs are considered. (no  $\pi$  bond will be considered)

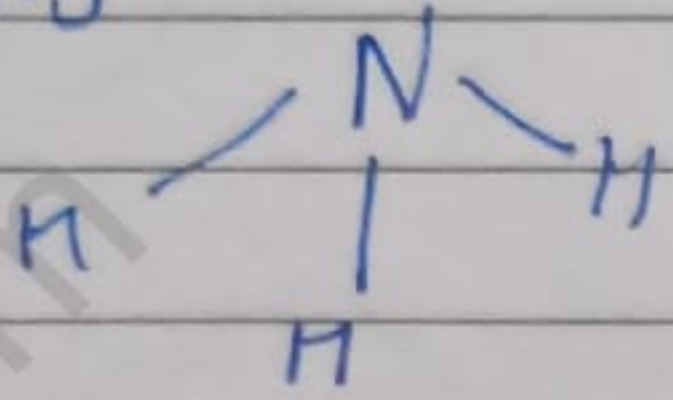
Ex:-  $AB_2$  type



AB<sub>4</sub>

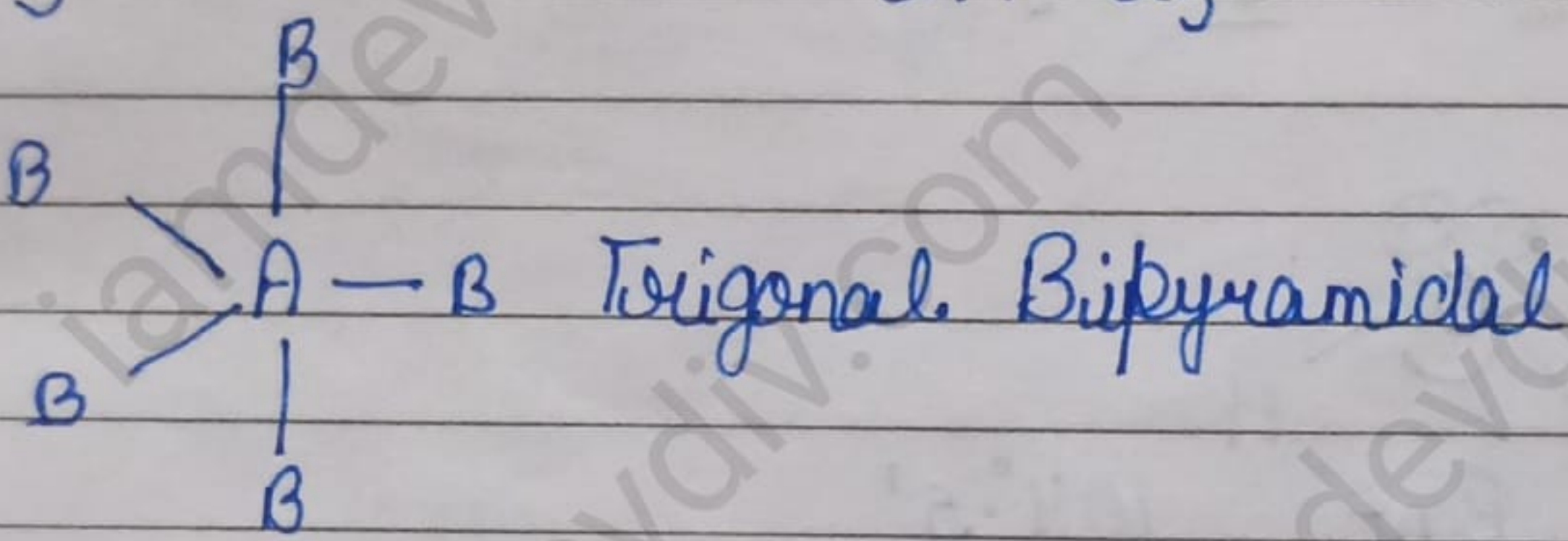


NH<sub>3</sub>



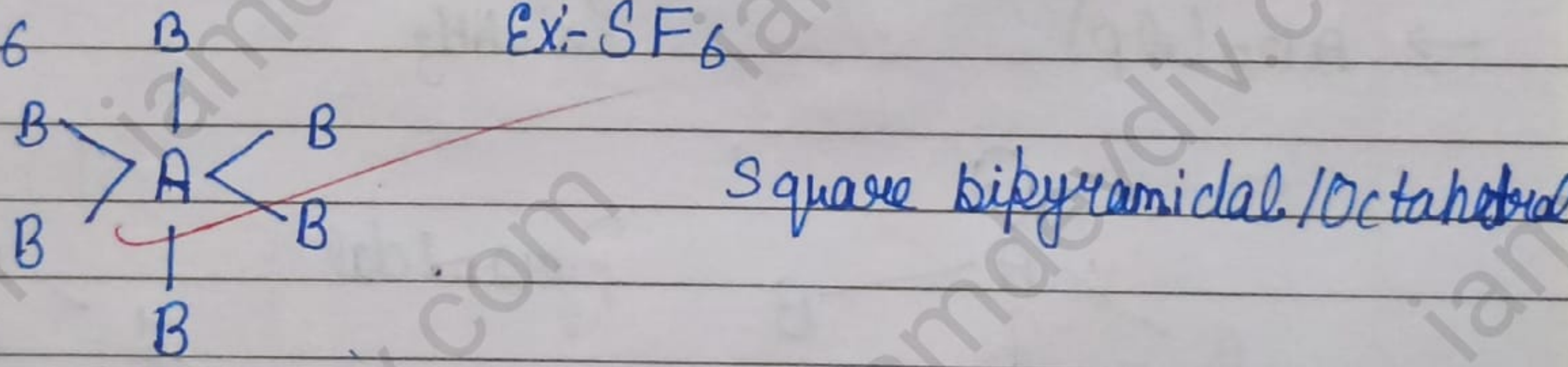
AB<sub>5</sub>

Ex: - PCl<sub>5</sub>



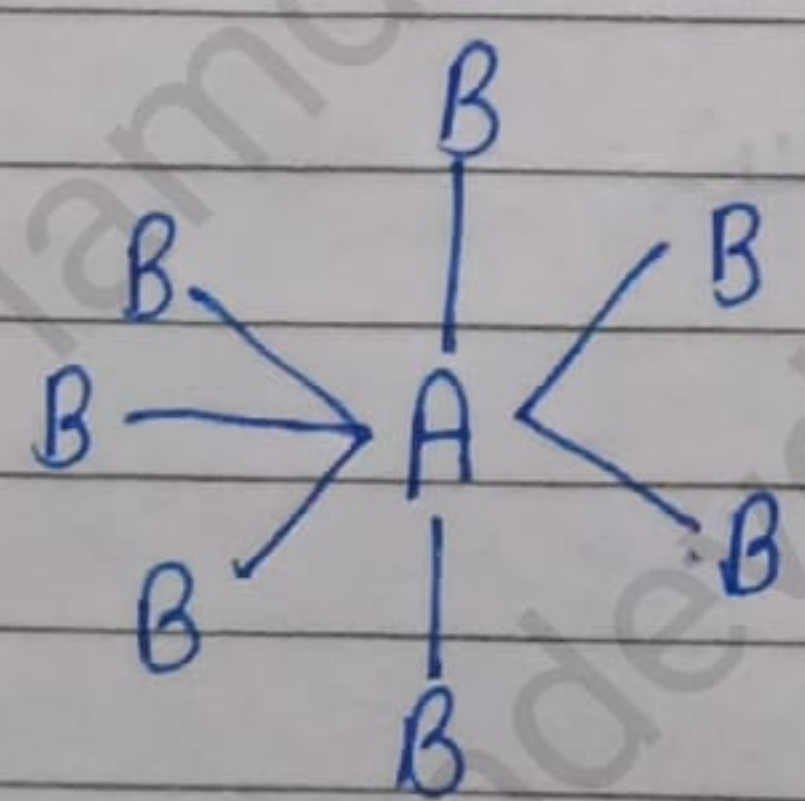
AB<sub>6</sub>

Ex: - SF<sub>6</sub>



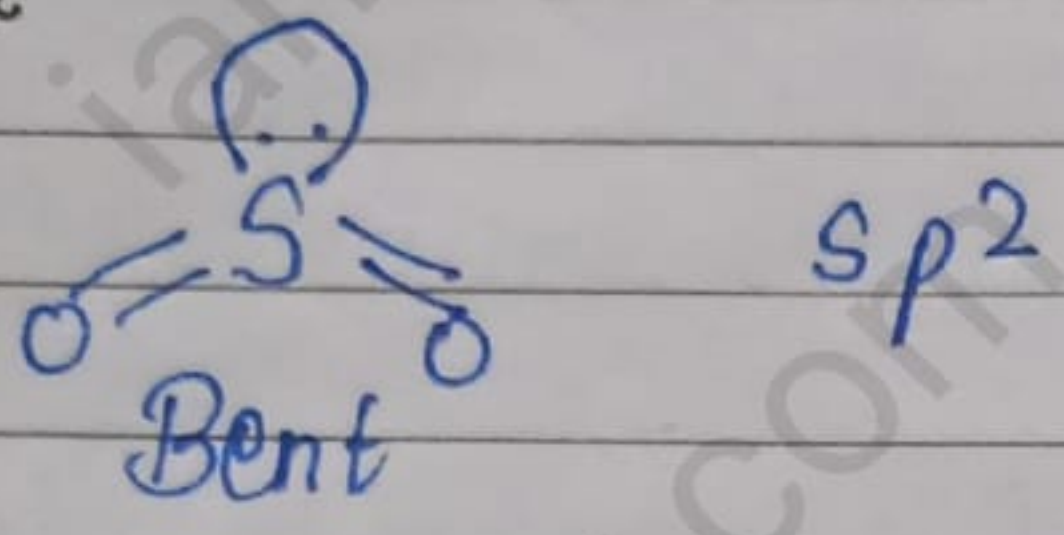
AB<sub>7</sub>

Ex: - I<sub>7</sub>

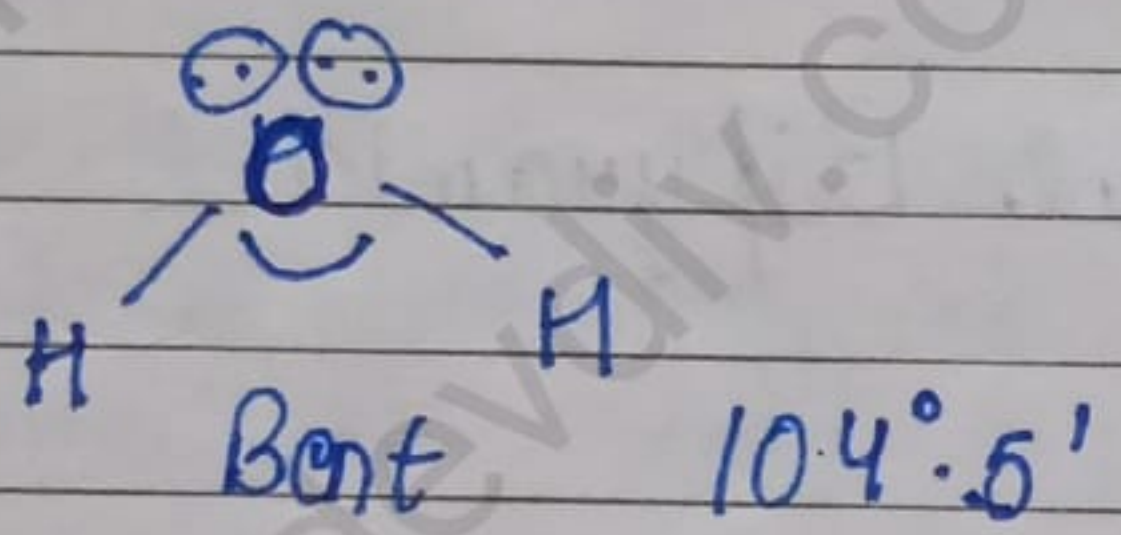


# Irregular geometry

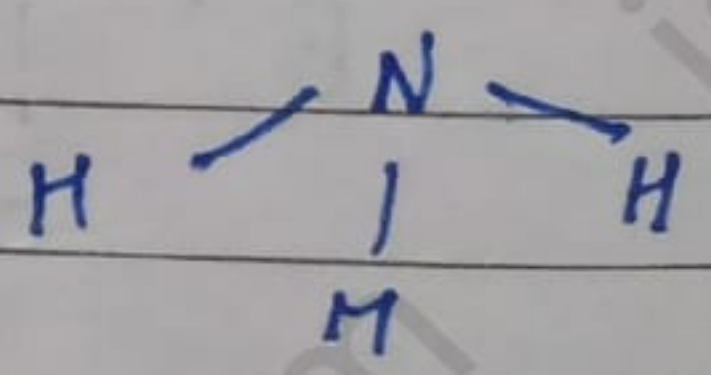
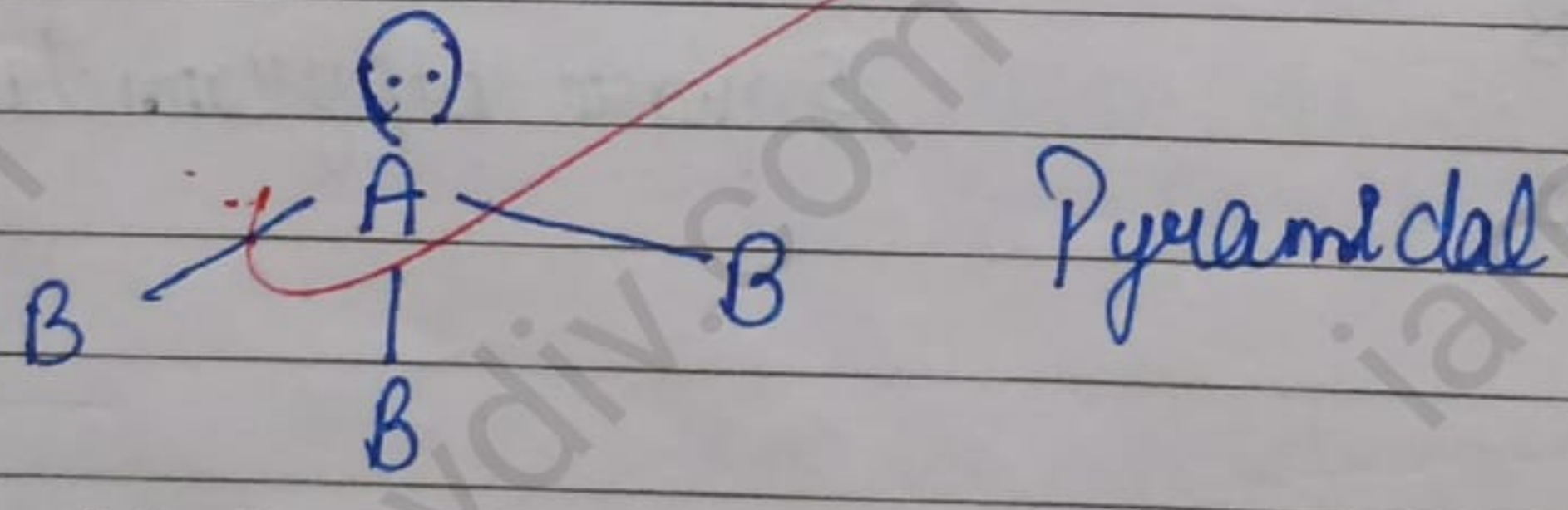
→  $AB_2$  (lp),  
Ex:-  $SO_2$

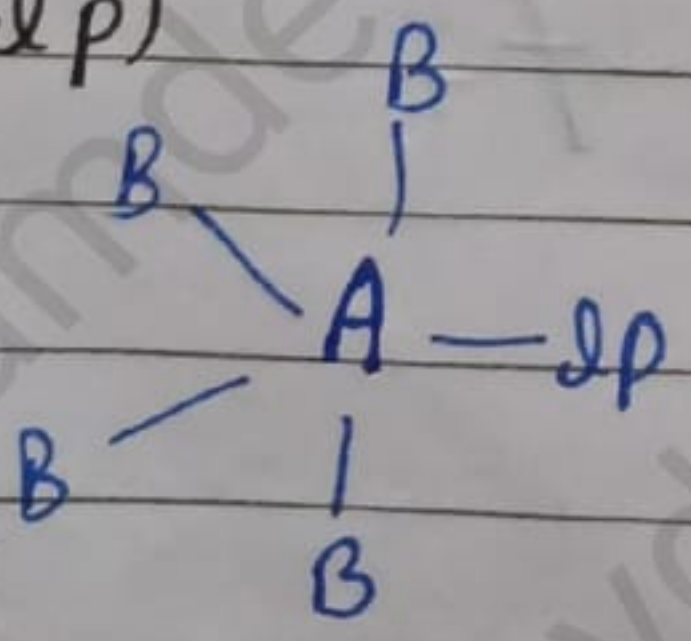


→  $AB_2$  (lp)<sub>2</sub> Ex:-  $H_2O$



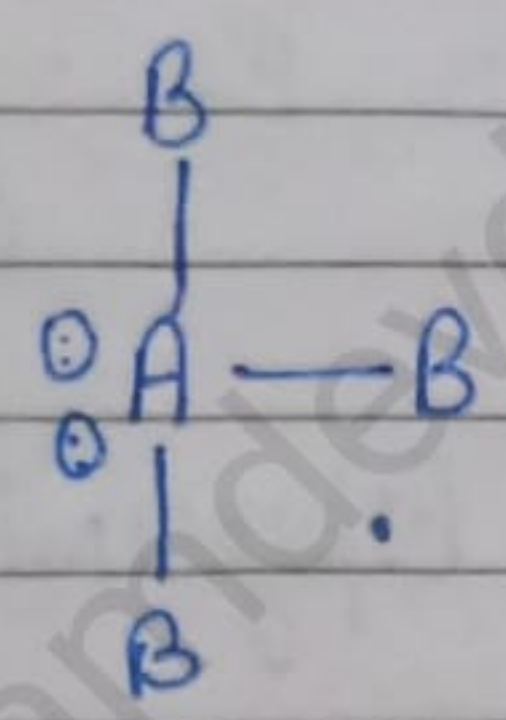
→  $AB_3$  (lp) Ex:-  $NH_3$



→  $AB_4$  (lp)   $See - Saw$



→  $AB_3 (lp)_2$

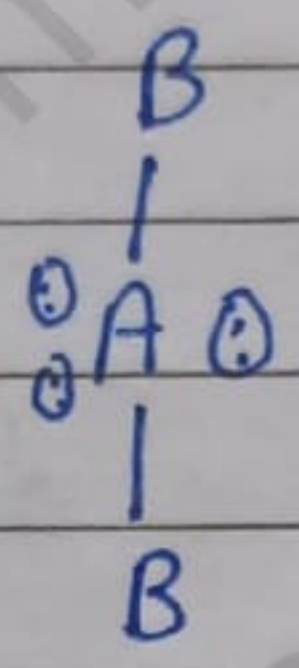
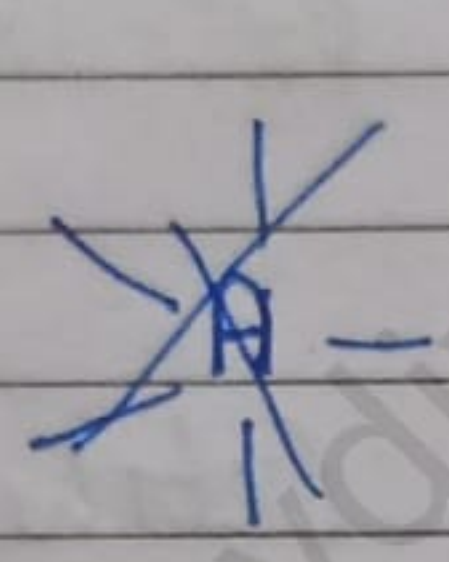


T-shape

Ex: -  $IF_3 / ICl_3$

→  ~~$AB_2 (lp)_3$~~

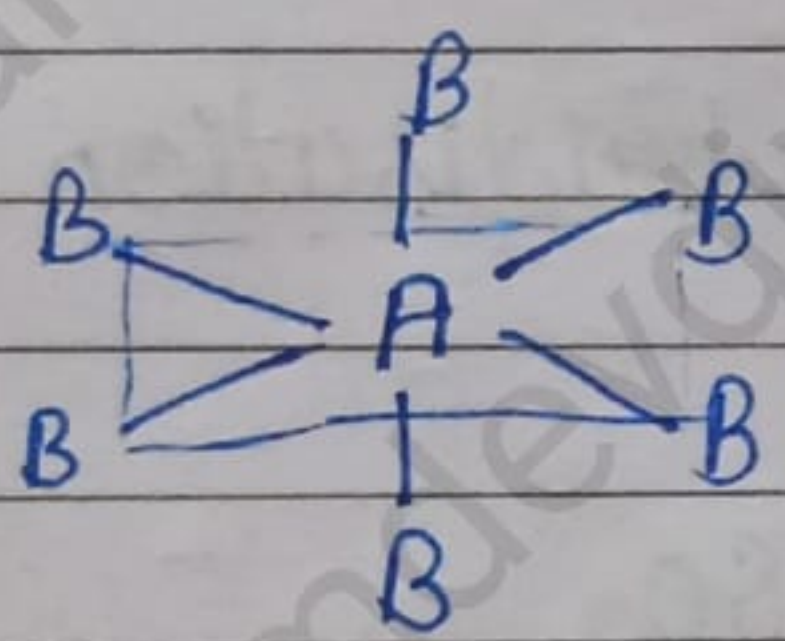
Ex: -  $XeF_2$



Linear

→  $AB_6$

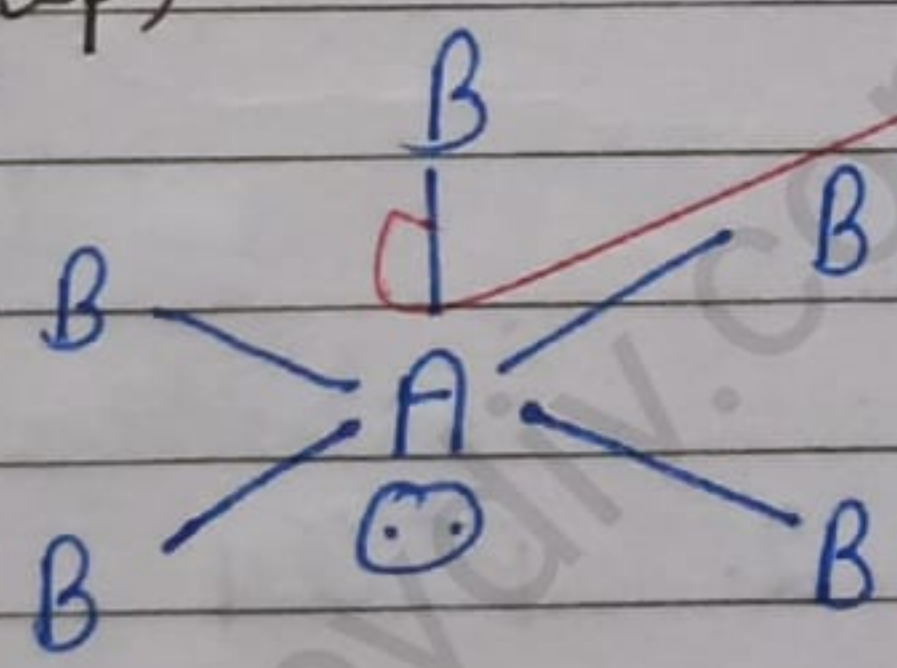
Ex: -  $SF_6$



Square bipyramidal

→  $AB_5 (lp)$

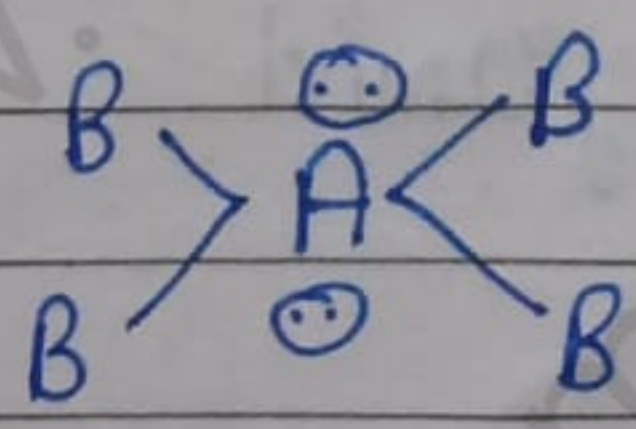
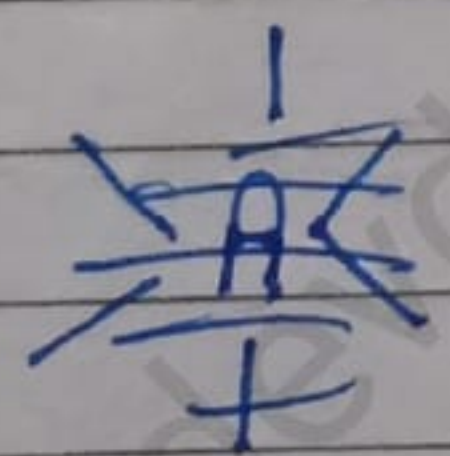
Ex: -  $ICl_5$



Square pyramidal

→  $AB_4 (lp)_2$

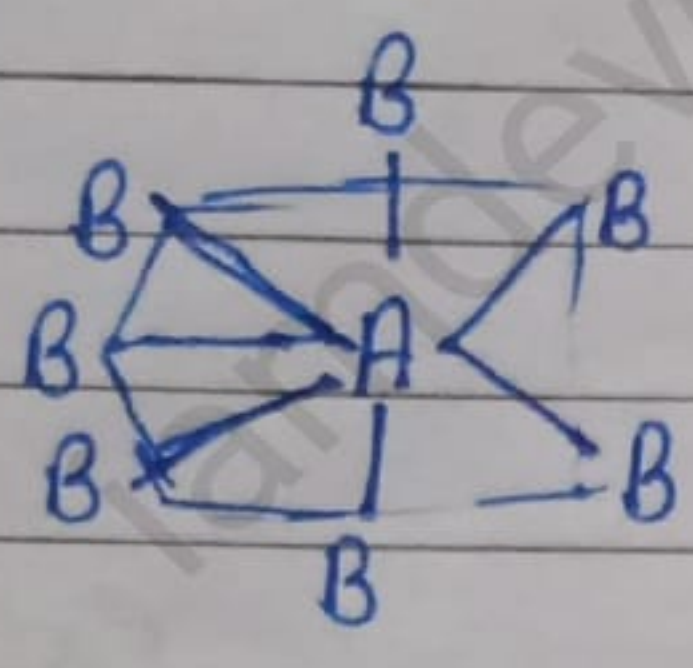
Ex: -  $XeF_4$



Square planar

→  $AB_7$

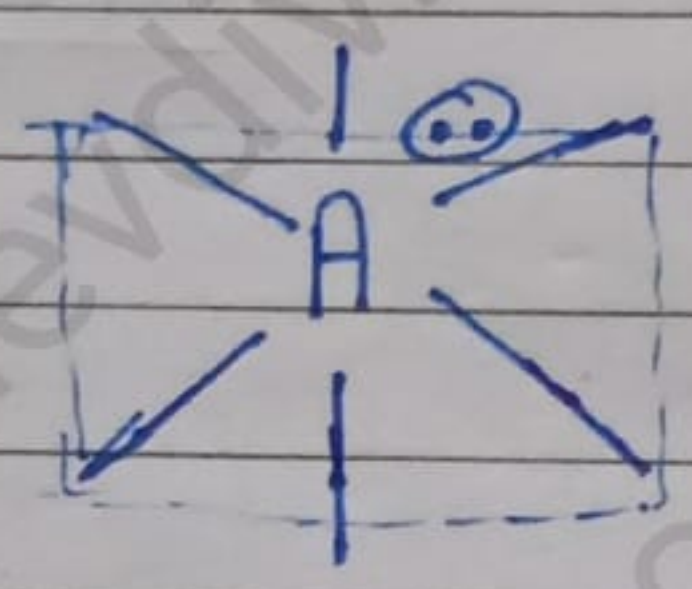
Ex: -  $IF_7$   
 $ClF_7$



Pentagonal Bipyramidal

→  $AB_6 (lp)$

Ex: -  $XeF_6$

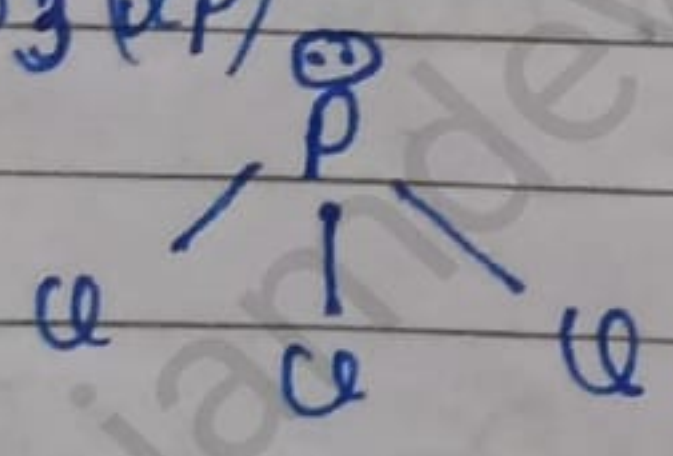


distorted Octahedral

Ques - Predict the geometry and hybridisation of the following molecules

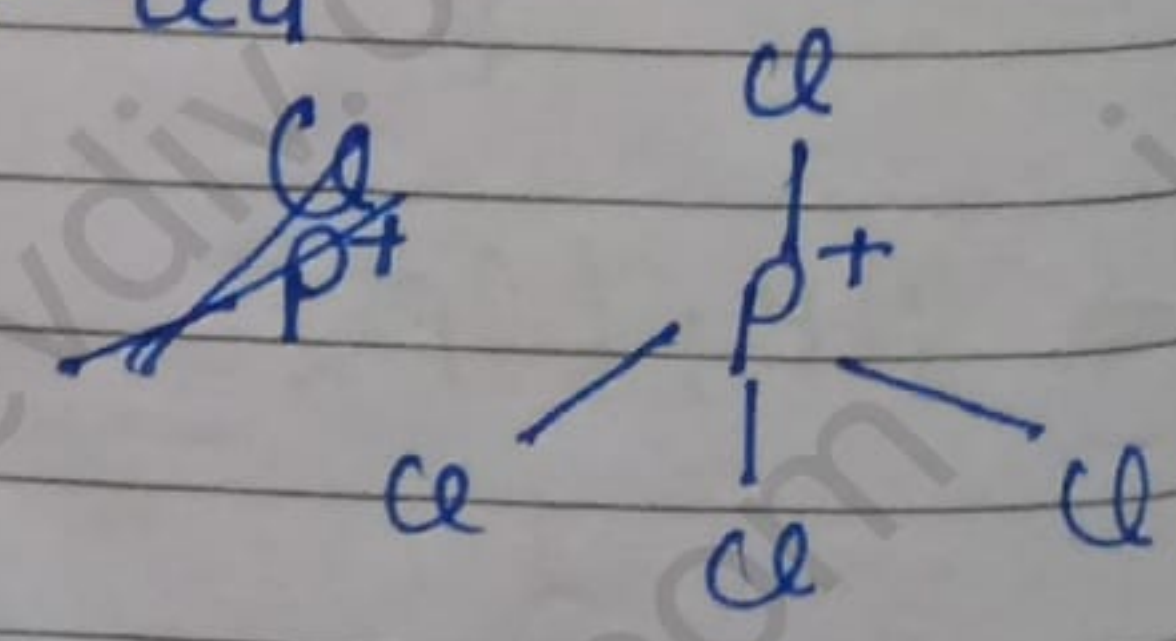
- |              |             |                |
|--------------|-------------|----------------|
| 1. $PCl_3$   | 3. $H_3O^+$ | 5. $SO_2$      |
| 2. $PCl_4^+$ | 4. $XeF_2$  | 6. $CO_3^{2-}$ |

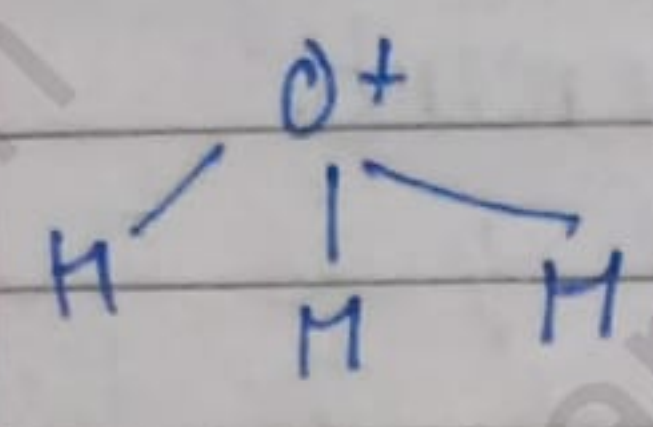
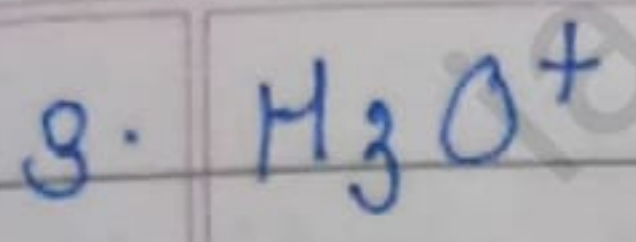
1.  $AB_3 (lp)$



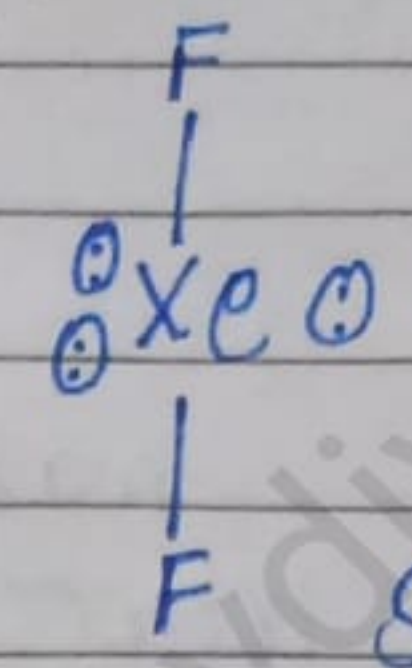
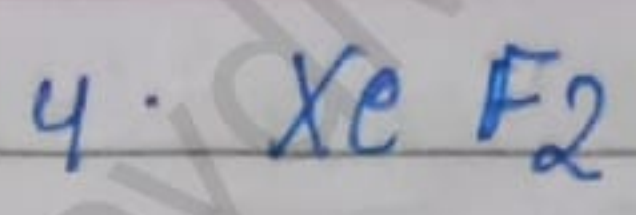
Hybridisation =  $sp^3$   
 Shape - Trigonal pyramidal

2.  $PtCl_4$

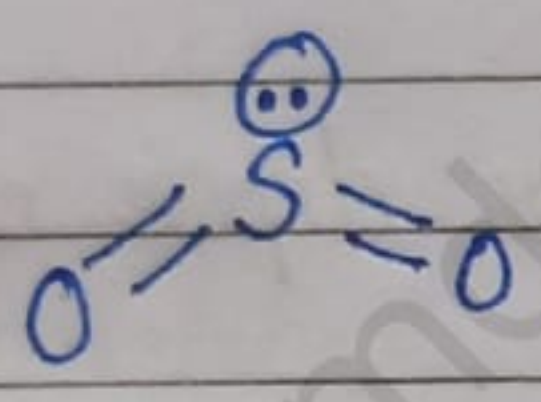
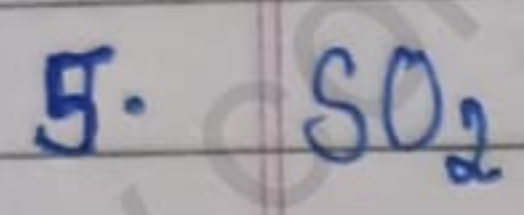




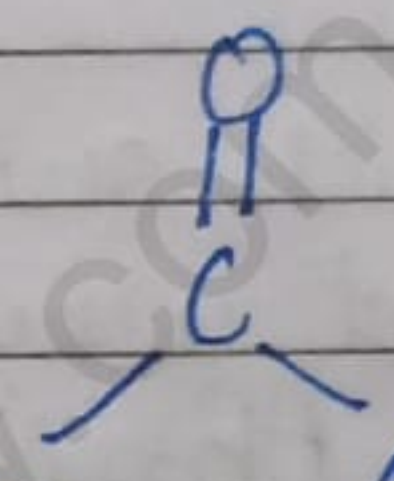
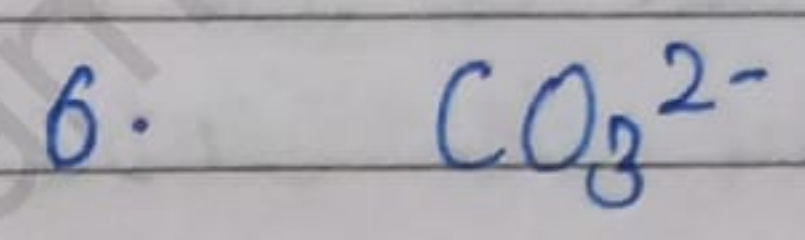
Trigonal pyramidal



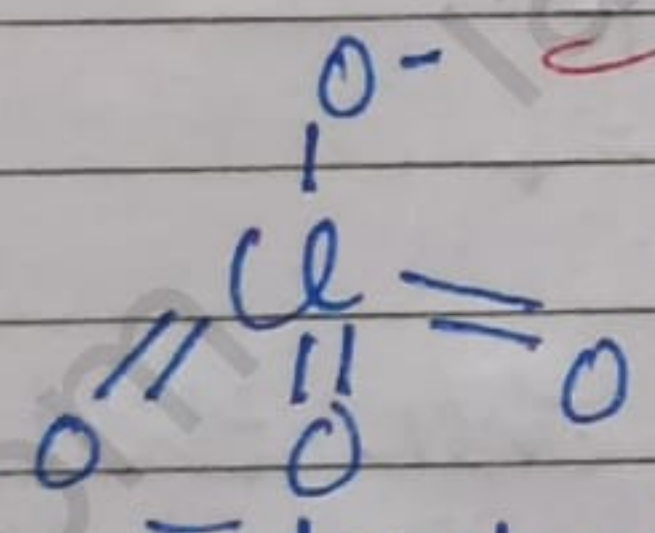
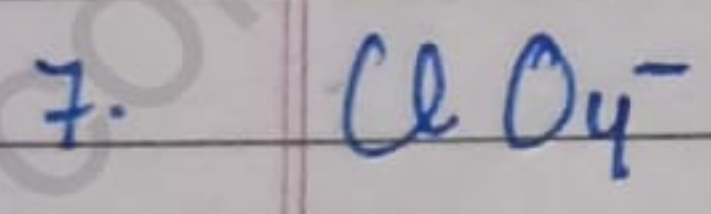
Shape - Linear  
Hybridisation -  $sp^2$



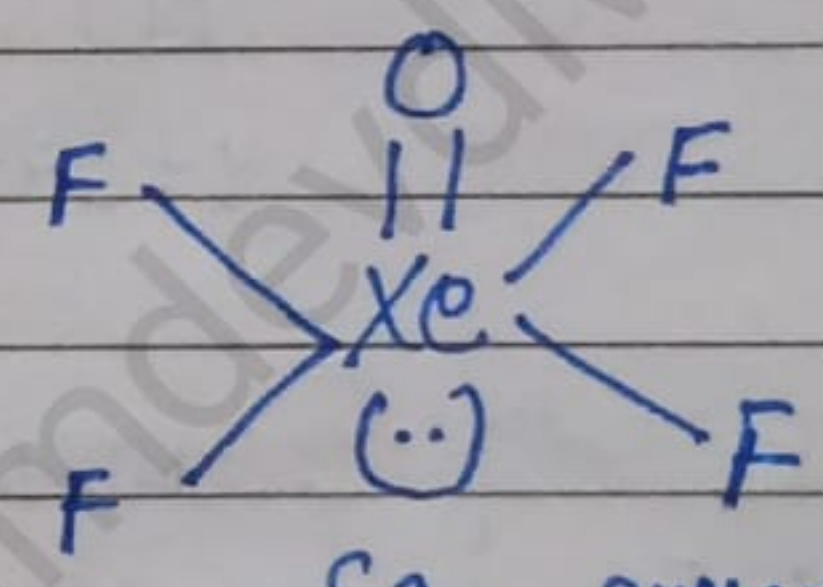
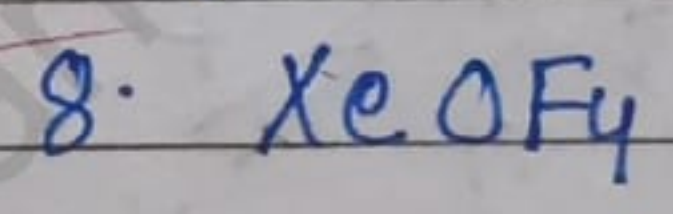
Shape - bent  
Hybridisation -  $sp^2$



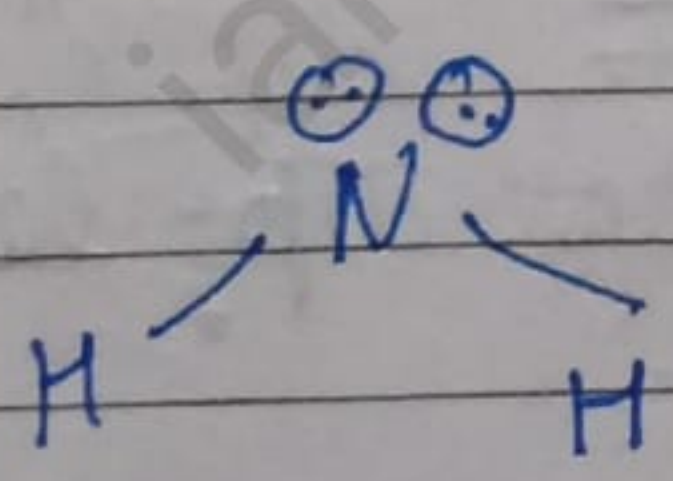
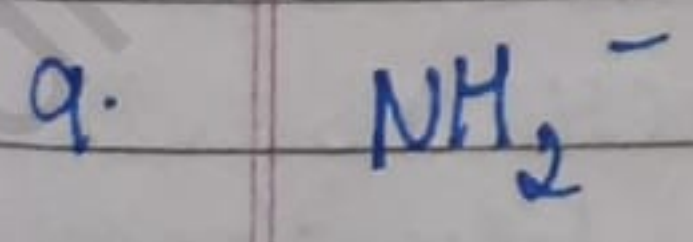
Shape - Trigonal Planar  
Hybridisation -  $sp^2$



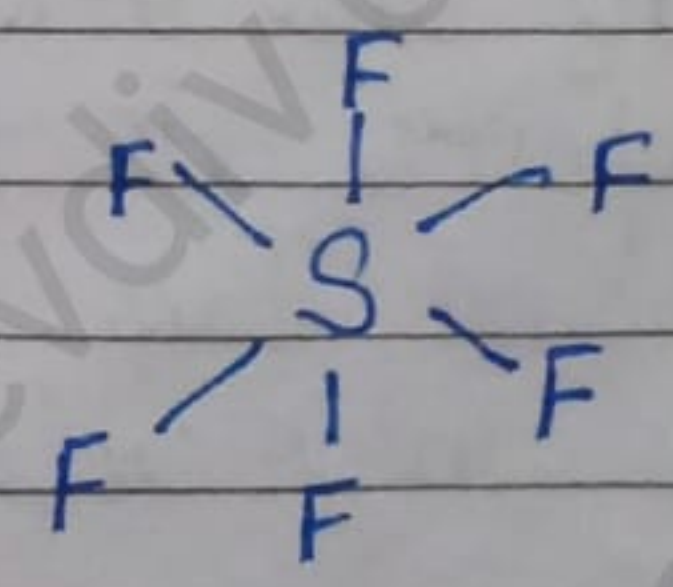
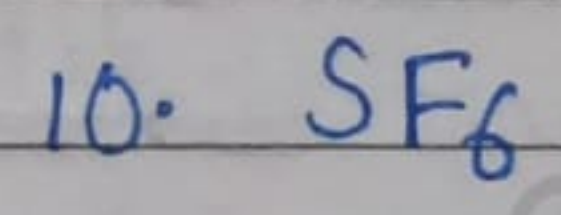
Tetrahedral



Sq. pyramidal

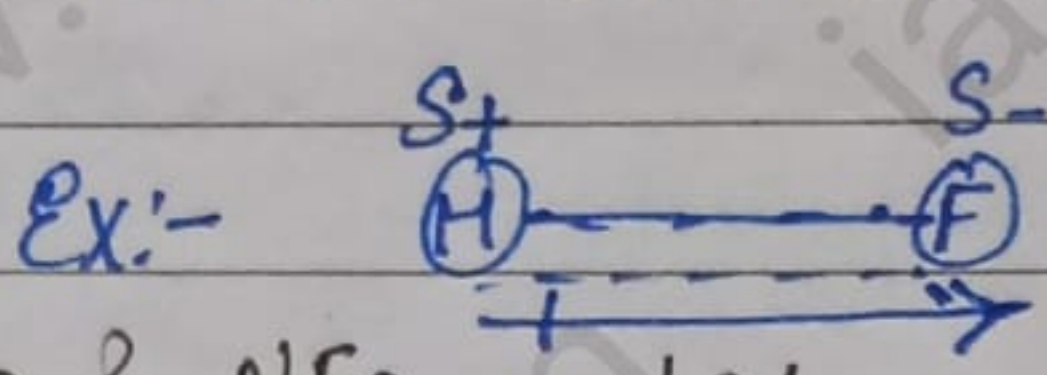


Bent



Square bipyramidal

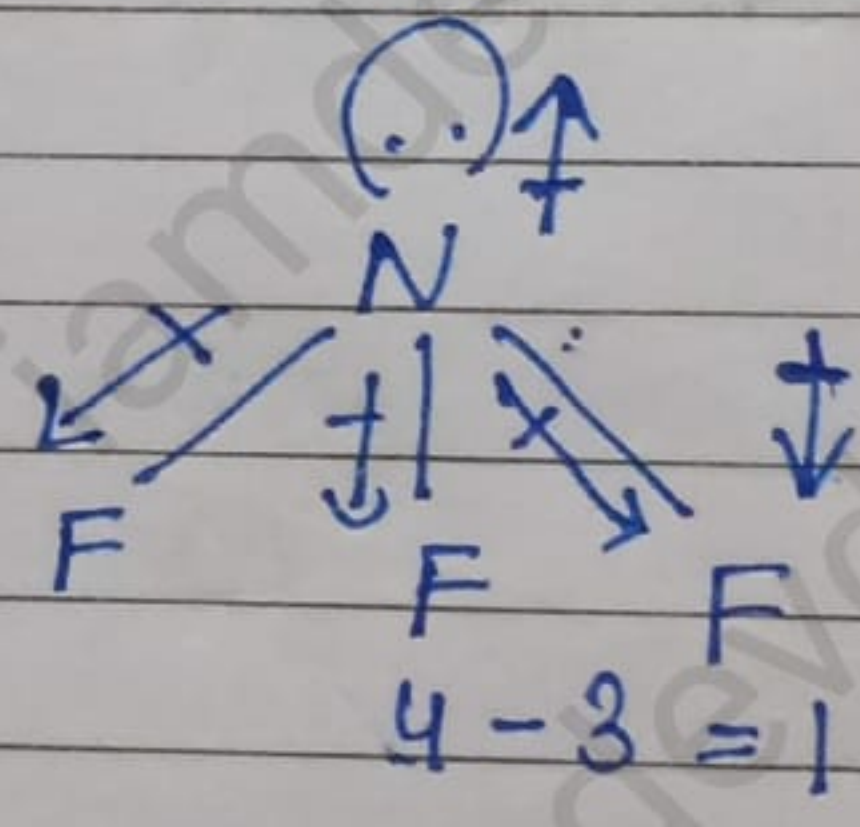
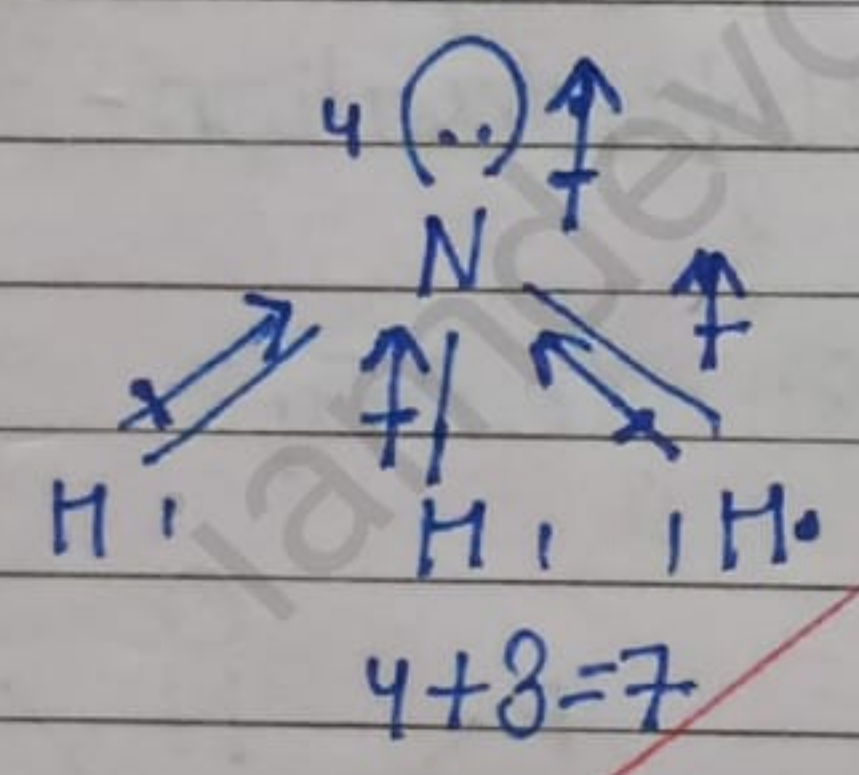
Dipole Moment:- It is a vector quantity  
 • It is the vector sum of all the individual bond movements  
 • Formula =  $q \times d$  where  $q$  is the magnitude of partial charges  $d$  is the distance between opposite charges  
 • It is depicted by a small arrow with tail on the +ve centre and the head pointing towards the -ve centre



Q- Which out of  $\text{NH}_3$  &  $\text{NF}_3$  has higher dipole moment and why?

$\text{AB}_3(\text{lp}) \text{NH}_3$

$\text{NF}_3$

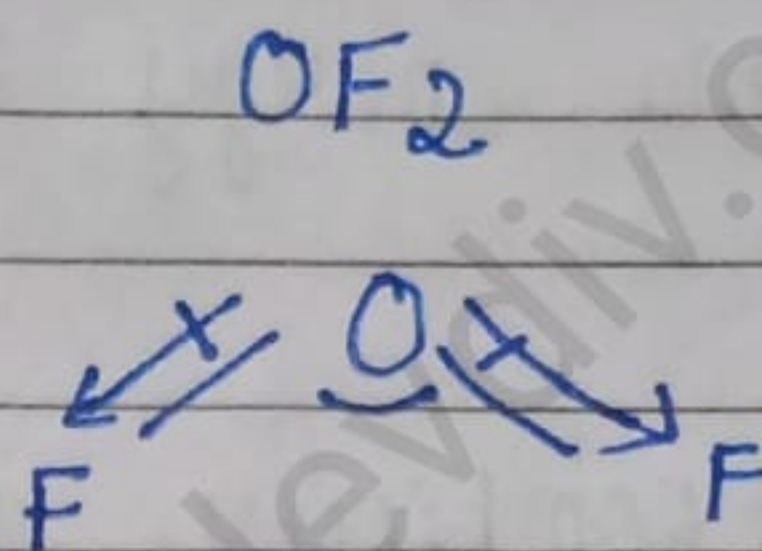
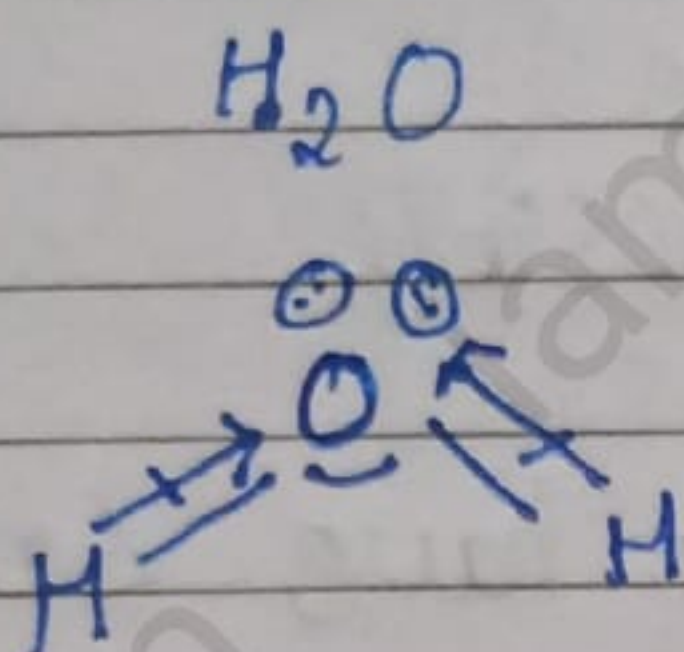


The dipole moment of  $\text{NH}_3$  is higher than that of  $\text{NF}_3$  because in case of ammonia, the orbital dipole due to lone pair is in the same direction as the resultant ~~diagonal~~ <sup>dipole</sup> moment of N-H Bonds. whereas in  $\text{NF}_3$  the orbital ~~diagonal~~ <sup>dipole</sup> is in the direction of opposite to the resultant ~~diagonal~~ <sup>dipole</sup> moment of N-F bond this decreases the resultant ~~dipole~~ <sup>dipole</sup> of the molecule.

*(Handwritten signature)*

14/08/23

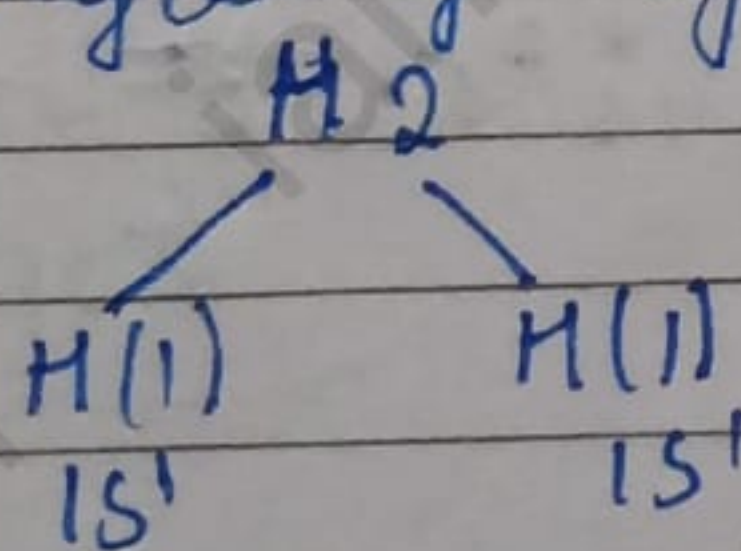
⇒ Out of the two  $H_2O$  &  $OF_2$  which has greater dipole moment. Explain with reason  $H_2O$



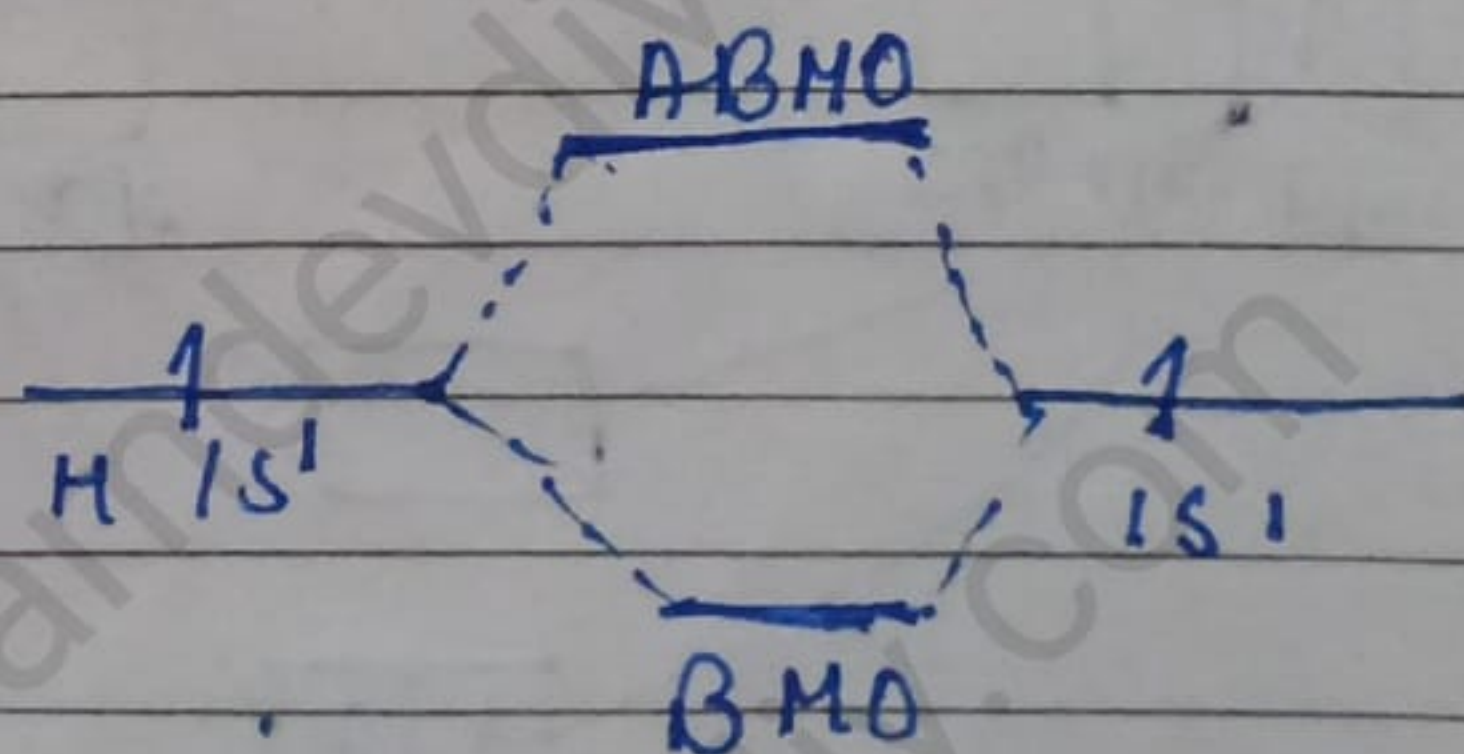
The dipole moment of  $H_2O$  is higher than  $OF_2$  because in case of  $OF_2$  the orbital

### # Molecular Orbital Theory

- ⇒ Postulates:-
- 1.) The electrons in a molecule are present in the various molecular orbitals.
  2. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbital.
  3. The no. of molecular orbitals formed is equal to the no. of combining orbitals when 2 atomic orbitals combine, 2 molecular orbitals are formed:-
    - (a) Bonding M.O.
    - (b) Anti Bonding M.O.
  4. The BMO has lower energy & thus greater stability as compared to ABMO.
  5. Molecular orbitals are filled acc to Aufbau's principle, Hund's Rule, Pauli's exclusion principle. Ex:- Molecular diagram of Hydrogen molecule.



Increasing Energy

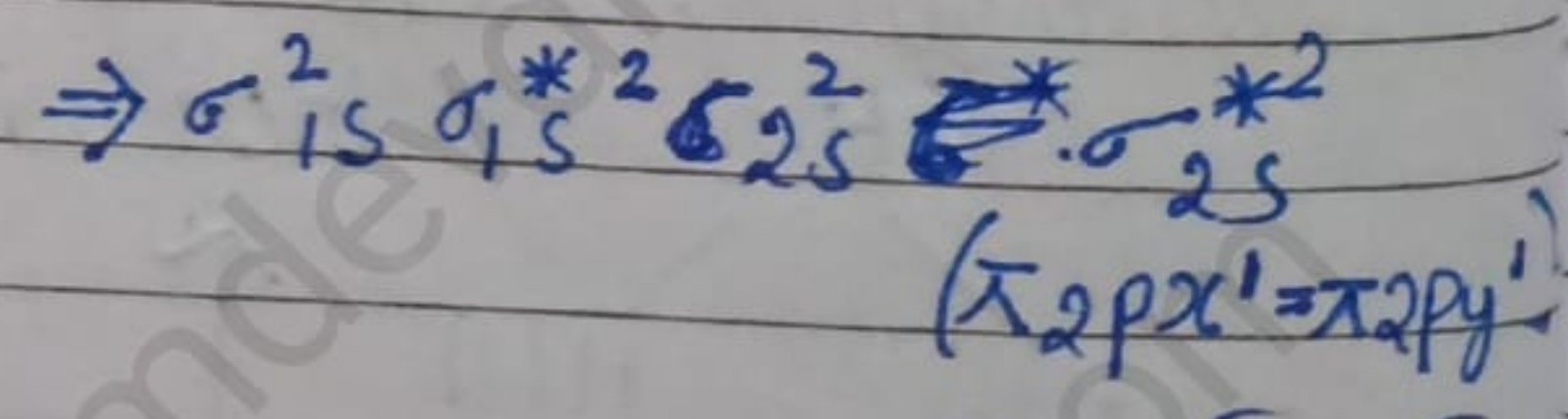
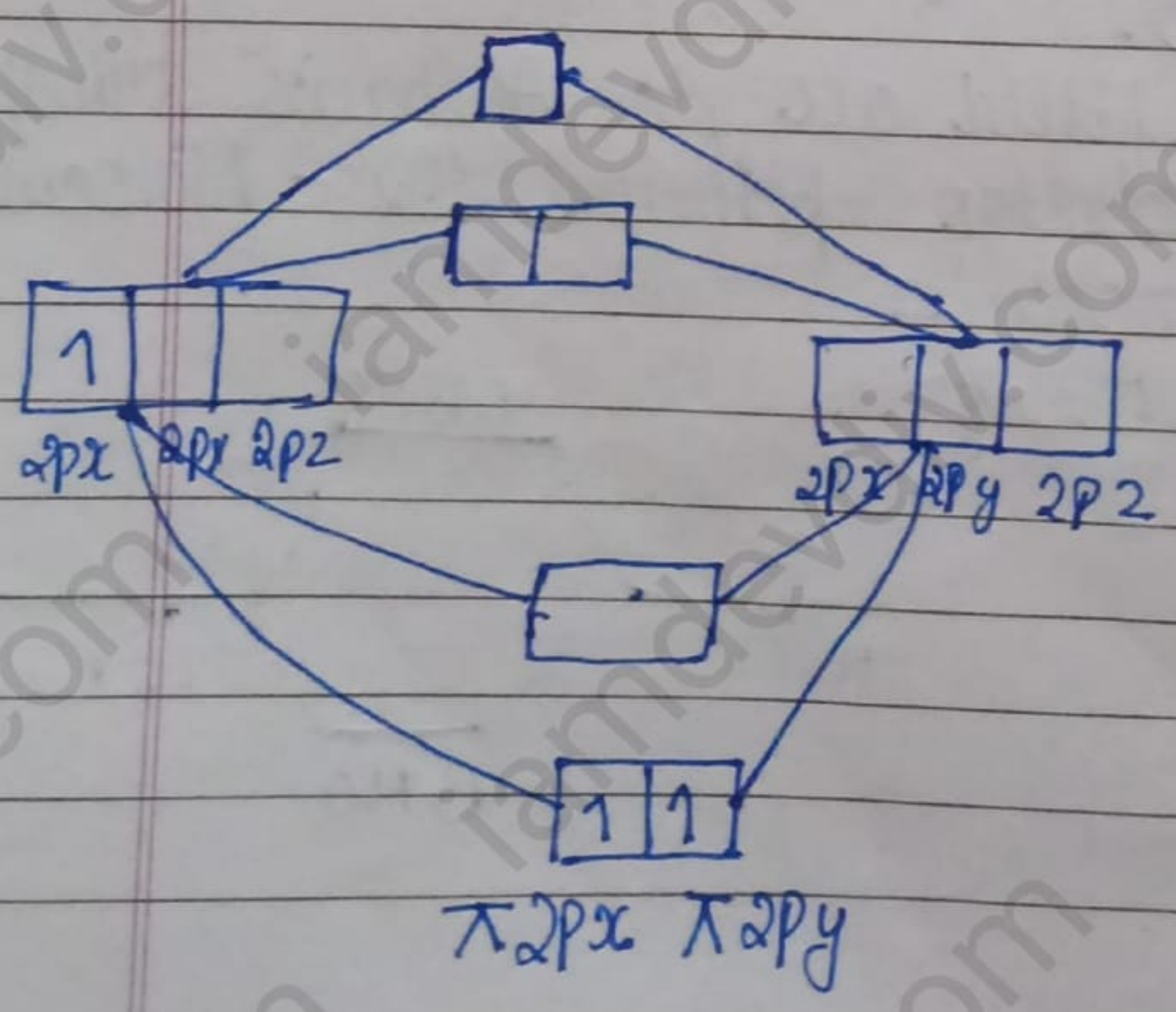
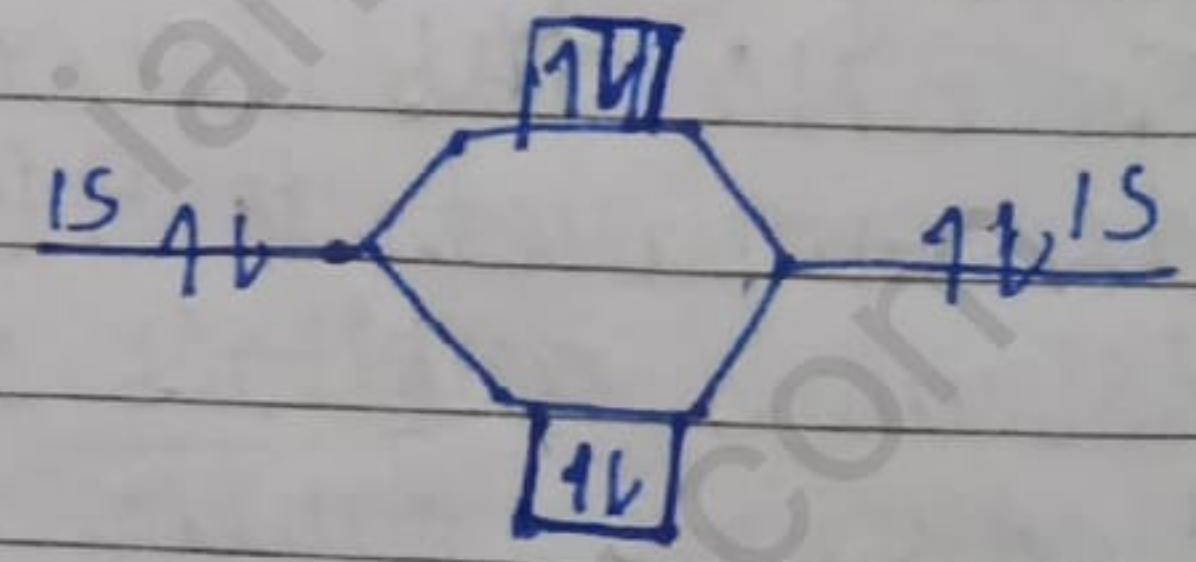
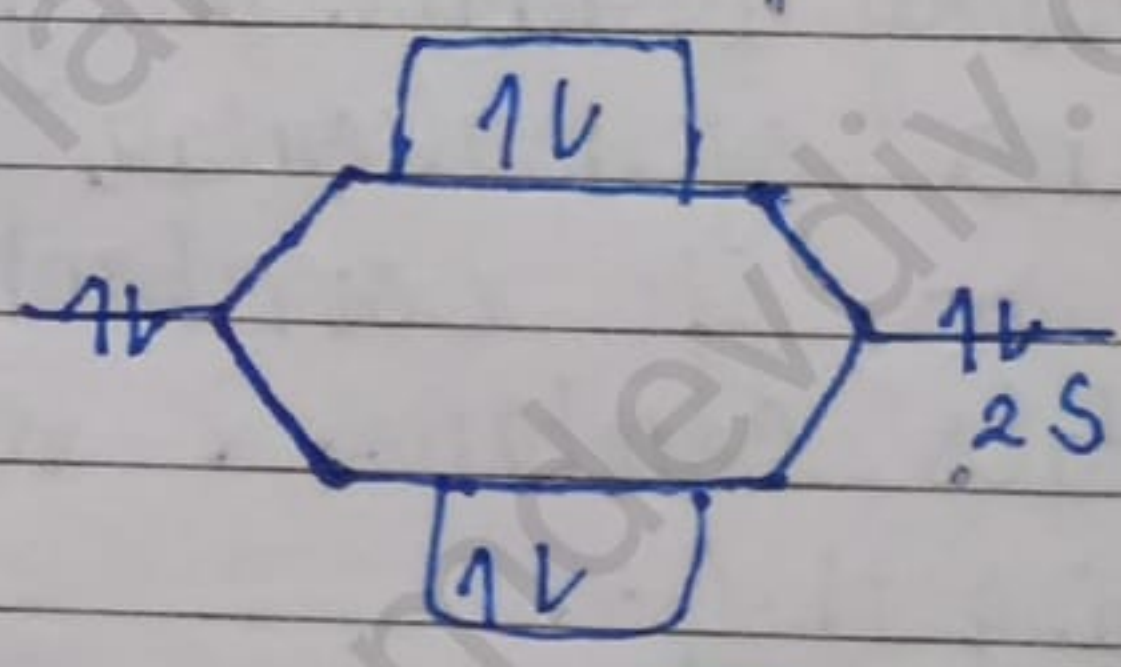
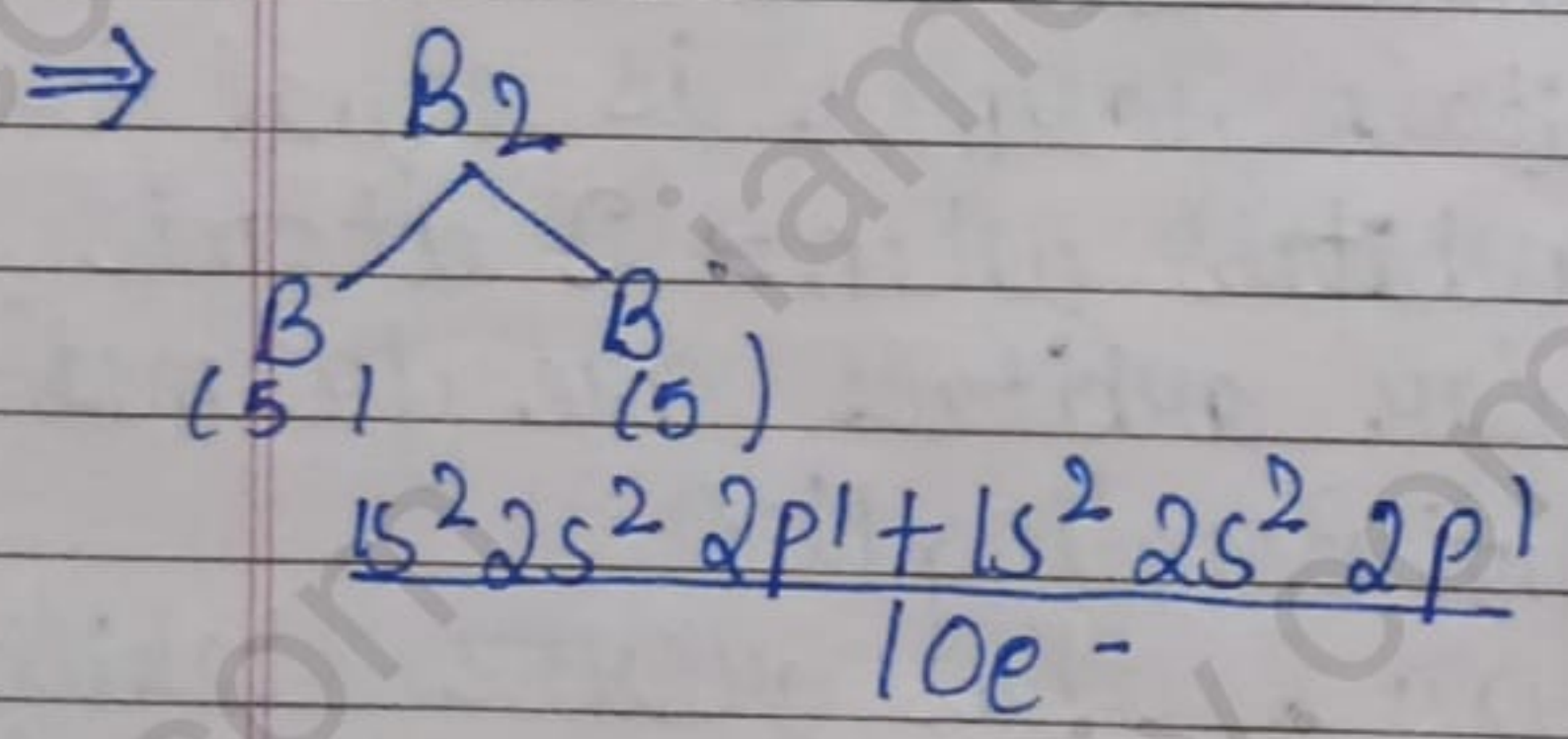
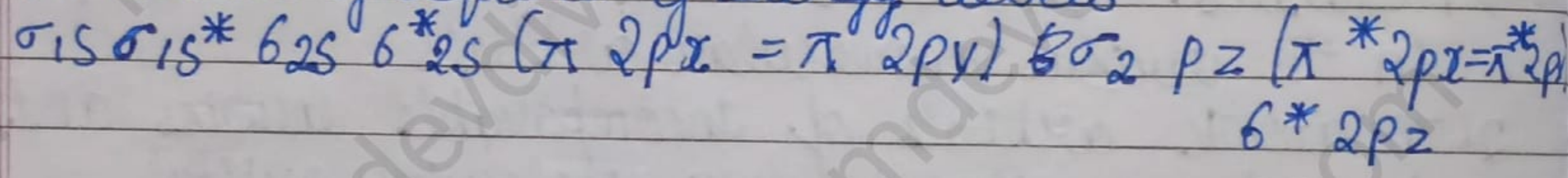


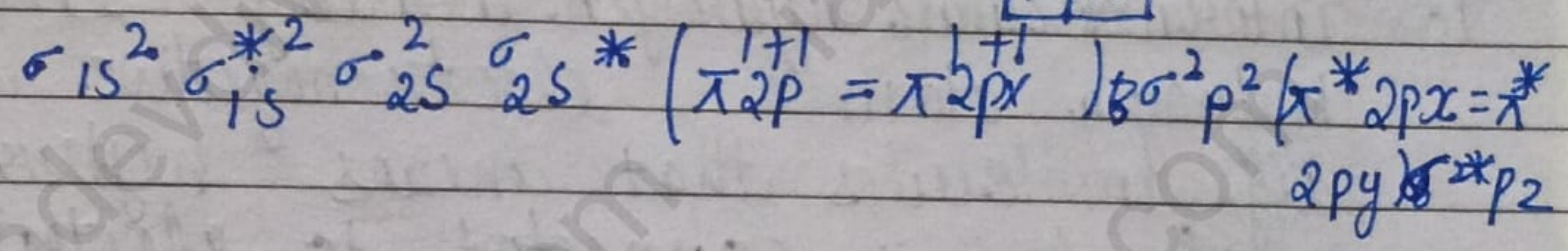
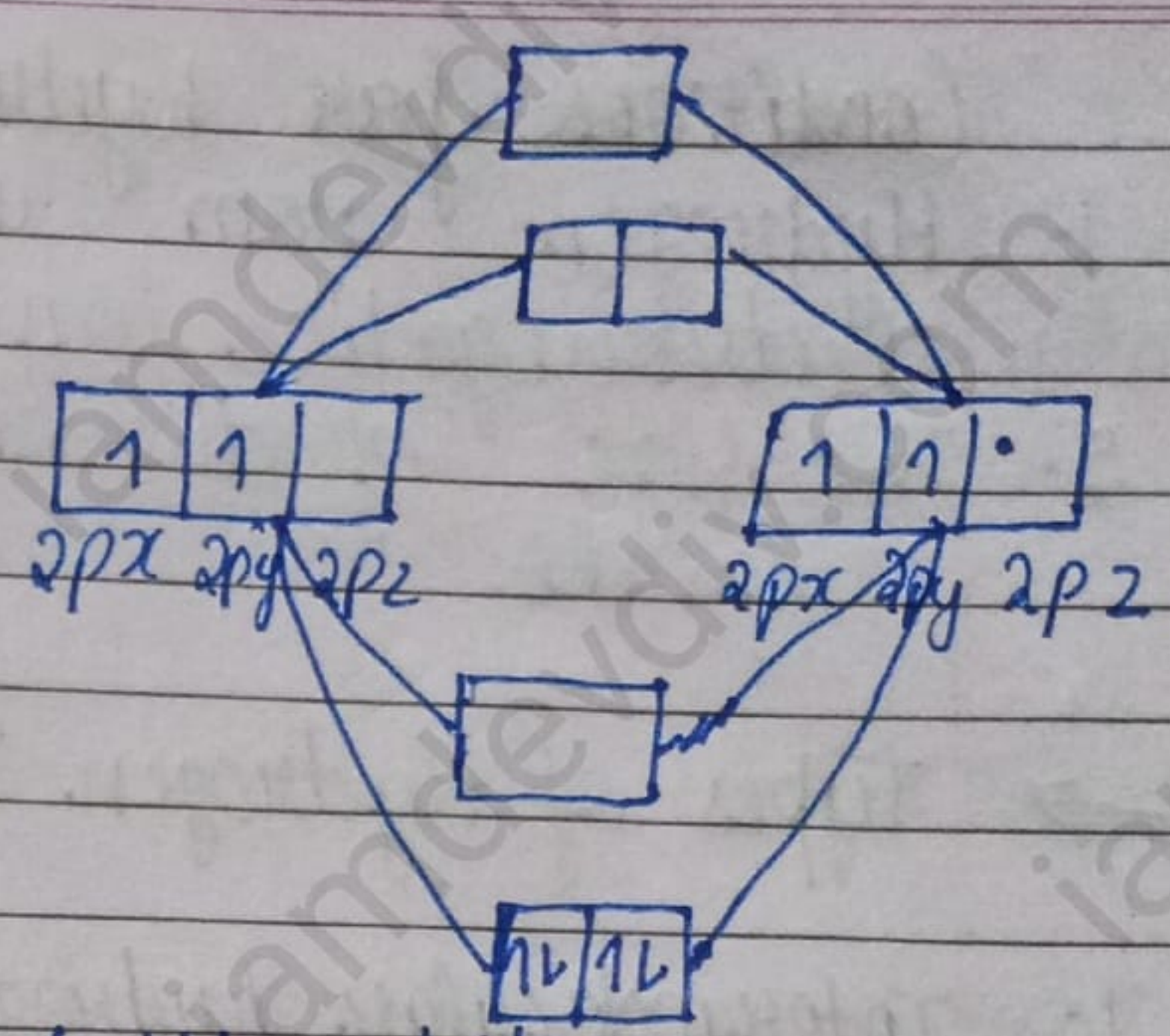
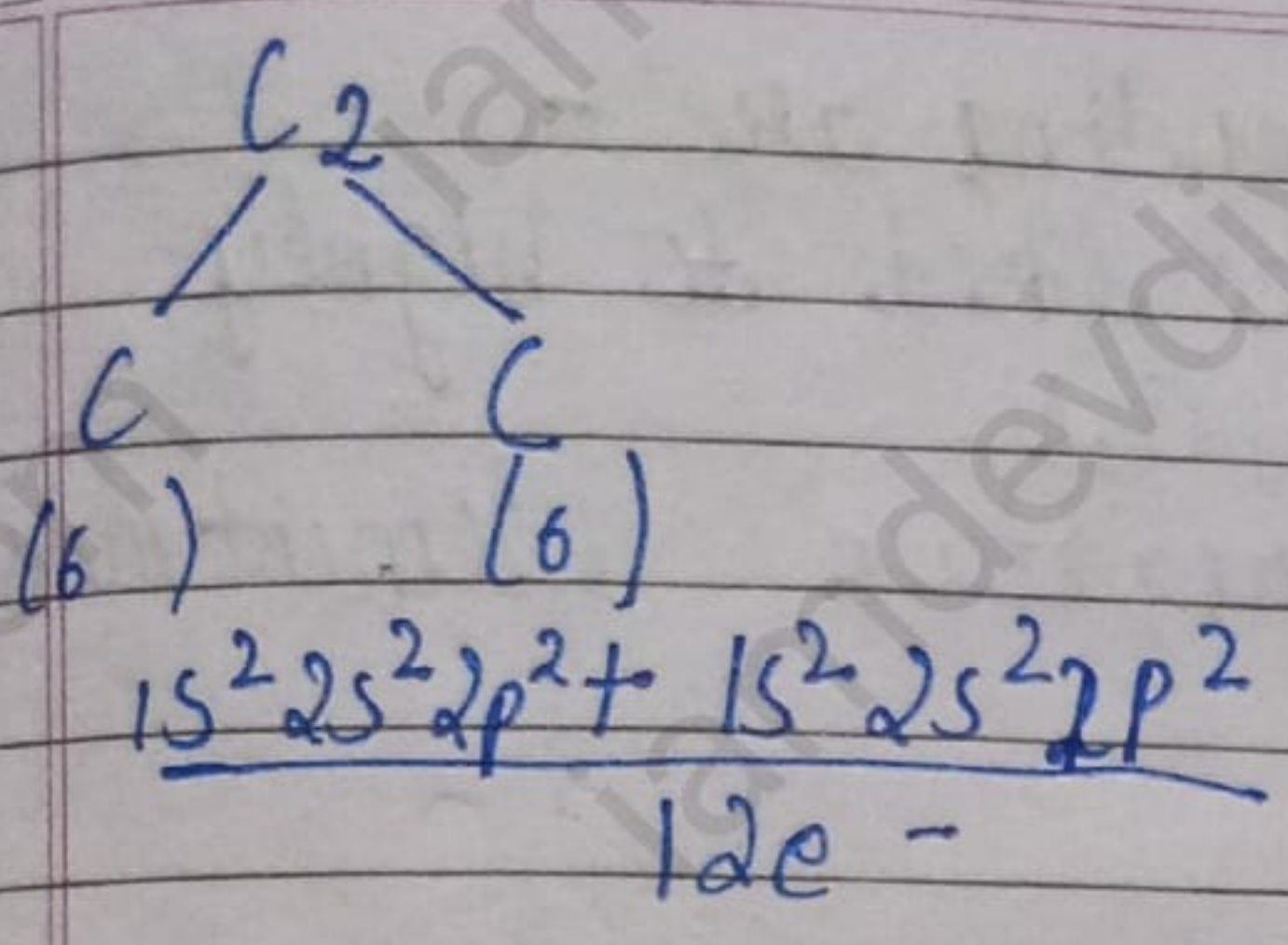
# # Conditions for Combination of atomic orbitals

1. The atomic orbitals must have same or nearly same energy. Eg:-  $1s - 1s'$  possible  
 $1s - 2s$  Not possible
2. The combining atomic orbitals must have same symmetry.
3. The combining atomic orbitals must overlap to the maximum extent.

# # Molecular

The order of sequence of energy levels





# Bond order =  $\frac{1}{2} \times [N_b - N_a]$

bonding
Anti-bonding

$$= \frac{1}{2} [8 - 4] = \frac{1}{2} \times 4 = 2$$

Imp.  
 # Hydrogen bonding

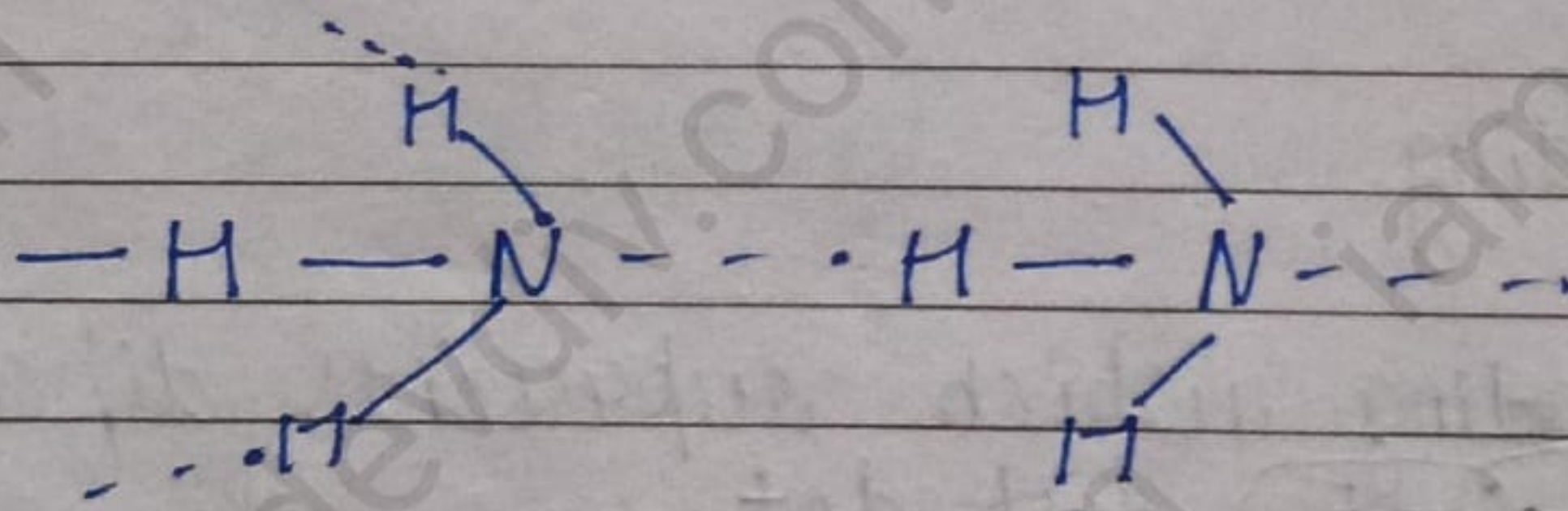
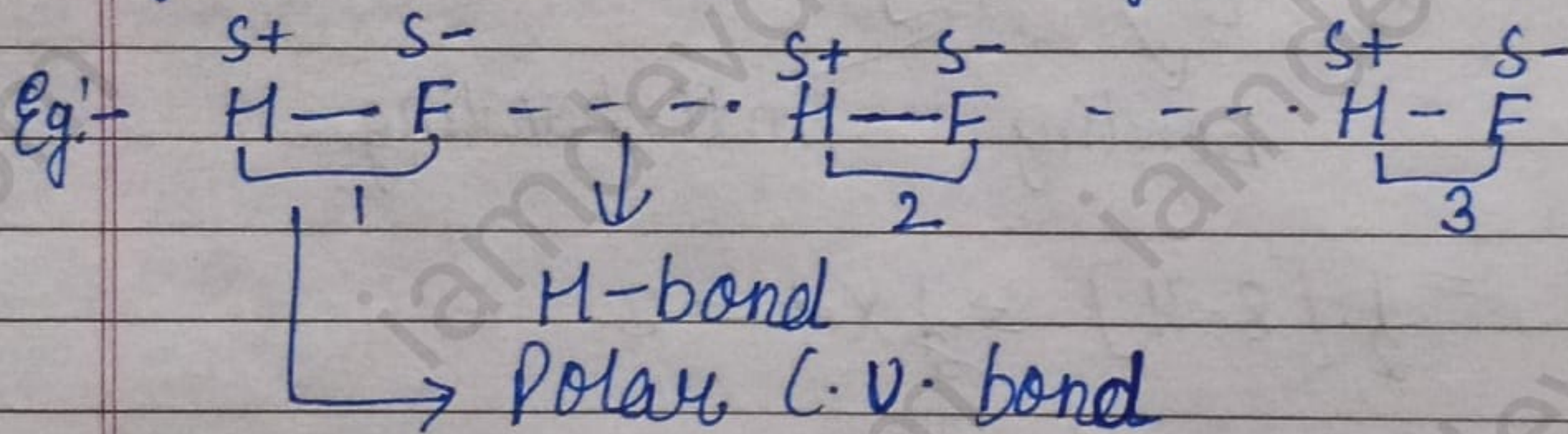
1. It is the bonding which represents dipole attraction shown by:  $(H - \overset{\cdot\cdot}{O} - F)$  dash, dot.
2. When electronegative atoms like F, O, N are connected to hydrogen they show hydrogen bonding due to difference in electronegativity.

Conditions for hydrogen bonding are:-

1. Hydrogen atom must be linked to highly electronegative element F, O, N.
2. The size of the electronegative element must be small.

### → Types of Hydrogen Bonding

1. Intermolecular hydrogen bonding:- In this case, the hydrogen atom & electronegative atom are of diff. molecules that means hydrogen of 1 molecule is connected to electronegative atom of another molecule through H-bonding.

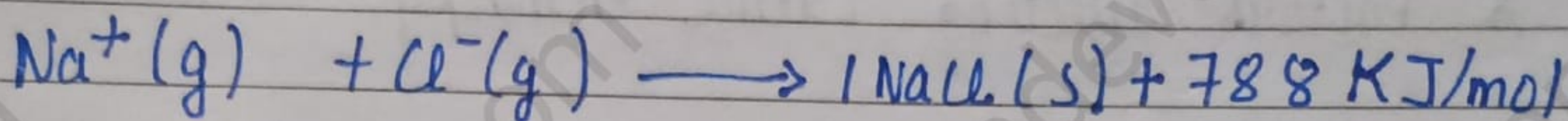


2. Intra molecular hydrogen bonding:- In this type of H-bonding the hydrogen atom & electronegative atoms are present in the bond belonging to the same molecule.

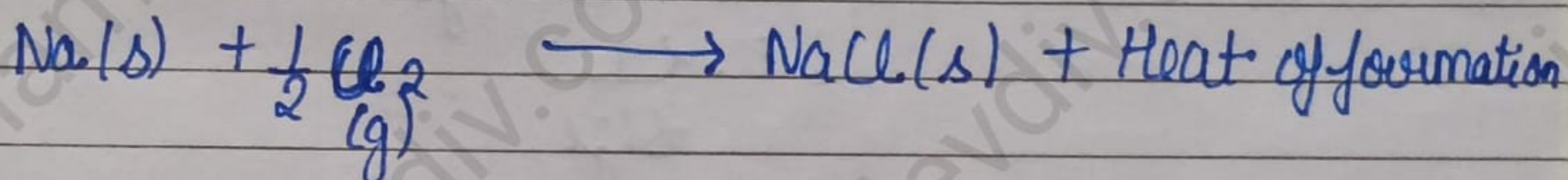


## Lattice Enthalpy

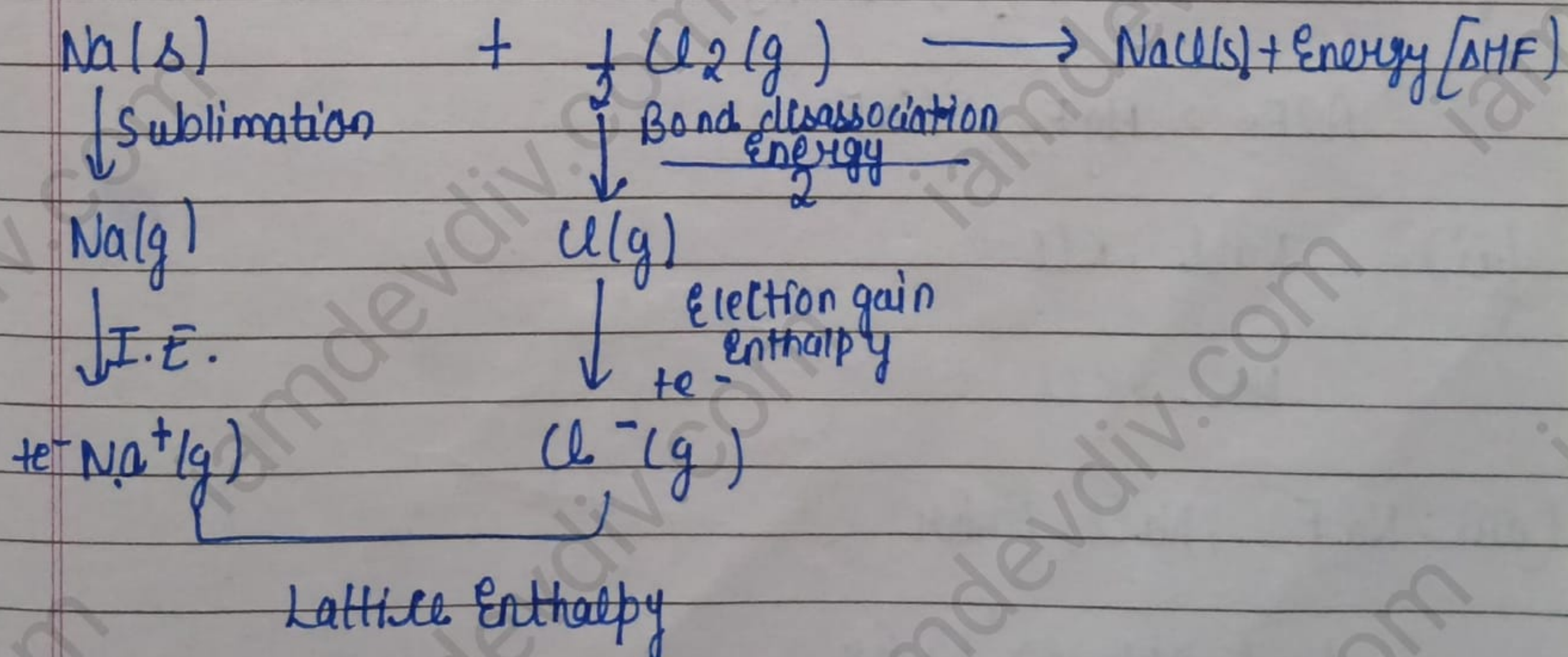
Lattice Enthalpy is the amount of energy released when crystal lattice of one mole solid ionic compound is formed from their gaseous constituent ions.



Heat of Formation:- The amount of energy released when 1 mol ionic compound is formed from its constituent elements in their pure & natural state.



- Lattice Enthalpy cannot be calculated directly but it is calculated from by Born-Haber cycle where there is a series of different values of enthalpies



$$\Delta H_f = \Delta H_{sub} + \Delta I.E.H + \Delta H_{diss} + \Delta e_{g.H} + L.E.$$

$$\Rightarrow \Delta H_{sub} + \Delta H_{I.E.} + \Delta H_{diss} - \Delta e_{g.H} - LE$$

\* Factors affecting Lattice Enthalpy

1. Size of ion

$$F = \frac{q_1 q_2}{r^2}$$

2. Charge present on ion

$$L.E. \propto \text{Charge}$$

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

Ques Compare the following & arrange them in increasing order of their L.E.

(i) NaF, Mg<sup>+2</sup>F<sub>2</sub>, Al<sup>+3</sup>F<sub>3</sub>

$$AlF_3 > MgF_2 > NaF$$

(ii) NaCl, KCl

$$NaCl > KCl$$

(iii) NaF, NaCl, NaBr

$$NaF > NaCl > NaBr$$