

# 4 Chemical Bonding & Molecular Structure

\* Chemical bond Defined as a force that acts between two or more atoms to hold them together as a stable molecule.

\* Modes of Chemical Combination This occurs in two ways

1) By complete transference of one or more electrons from one atom to another. This process is called electrovalent or ionic bond

2) By sharing electrons.

a) When the shared electrons are contributed by the two combining atoms equally, the bond formed is called covalent bond

b) When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a coordinate bond, also called dative bond.

\* Kossel-Lewis Approach to Chemical Bonding (1916)

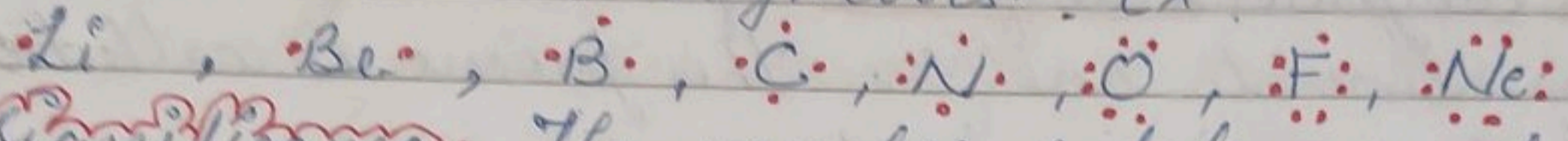
Both succeeded independently in giving a satisfactory explanation. Theory was based on Electronic theory of valency. Kossel's field was largely limited to inorganic compounds, Lewis focused his attention mainly to organic compounds.

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. This led to the following conclusion, called Octet rule.

1. The atoms of different elements <sup>combine</sup> with each other in order to complete their respective octets (i.e., 8 electrons in their outermost shell) or duplet (i.e. outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

### \* Lewis Symbols of Elements:

Gr. No. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or electron-dot symbols. Ex.



Significance: The number of dots around the symbol gives the number of electrons present in the outermost shell and helps to calculate the common valency.

### \* Electronic theory of Valency:

Kosel and Lewis formulated a comprehensive statement which was completed by Langmuir and called electronic theory of valency. Main points

- i) Valency depends on valence electrons.
- ii) Electronic config. of noble gases is stable.
- iii) Atoms having less than 8 electrons in the outermost orbit are chemically active.
- iv) Two ways by which atom can acquire noble gas config. are
  - a) by losing or gaining electrons.
  - b) by sharing electrons.

\*\* The union of two or more atoms involving redistribution of electrons in their outer shells in such a way so that all the atoms acquire the stable noble gas configuration of minimum energy is known as electronic theory of valency.

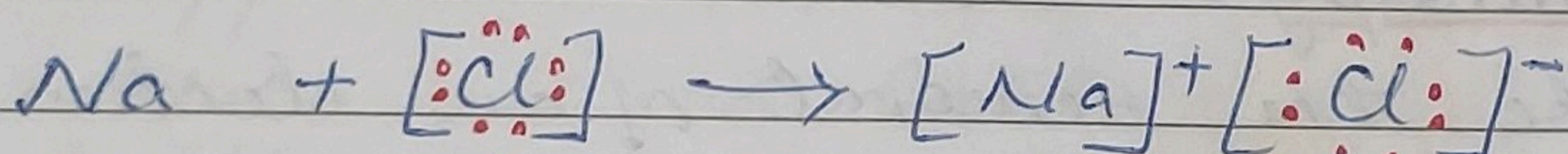
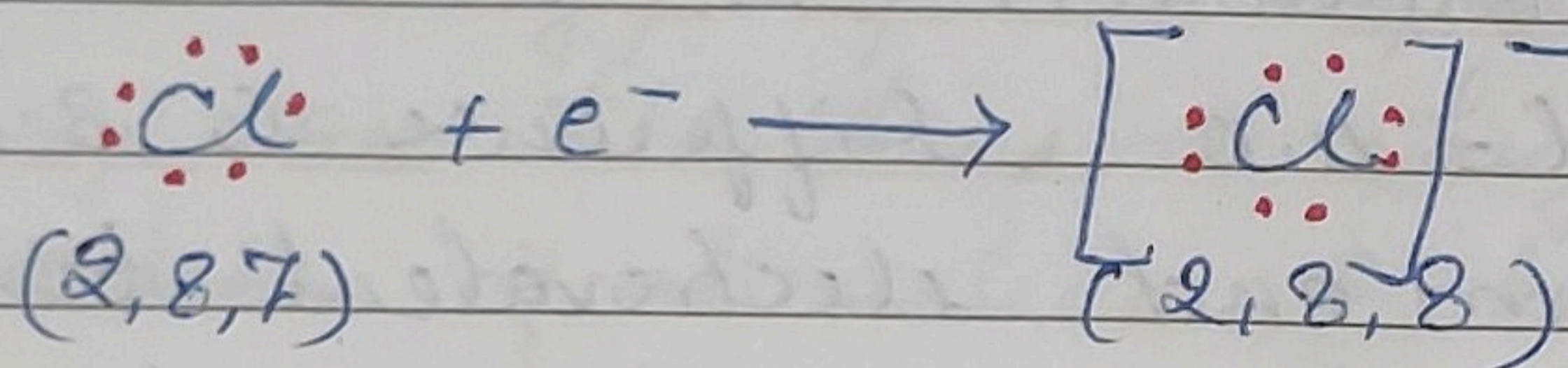
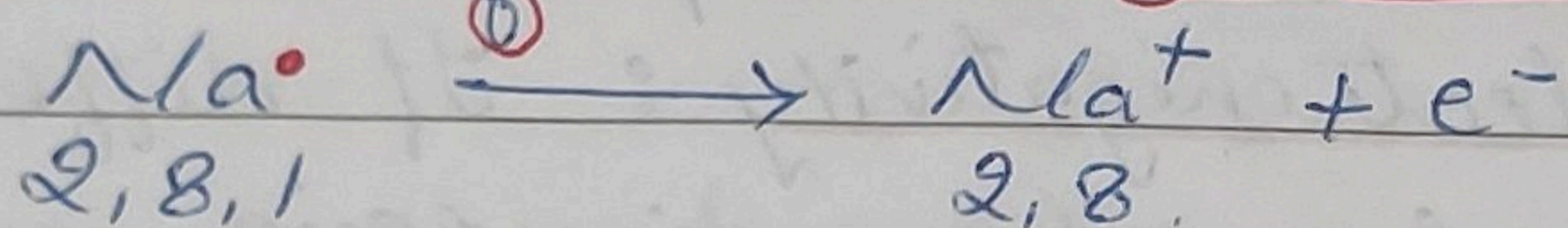
## \* Electrovalent or Ionic bond.

The chemical bond formed between two or more atoms as a result of the transfer of one or more electrons from a electropositive atom is called electrovalent bond or ionic or polar bond.

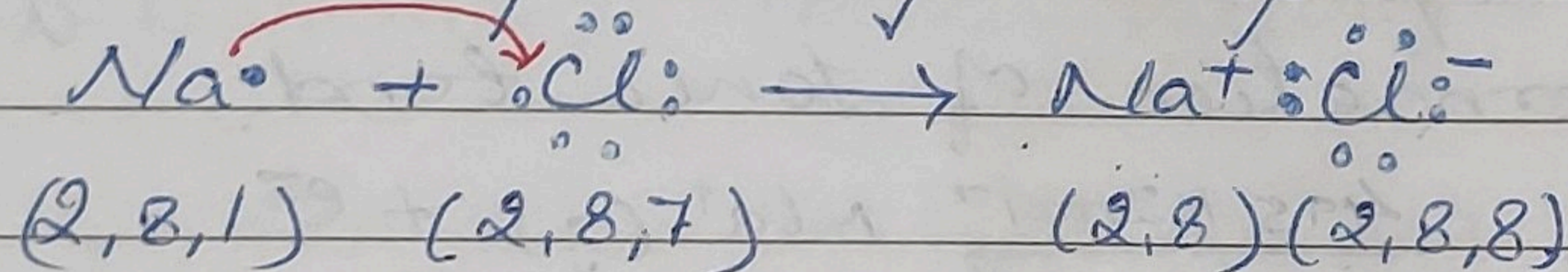
This bond formation is possible between the atoms having electropositive and electronegative nature.

Examples:

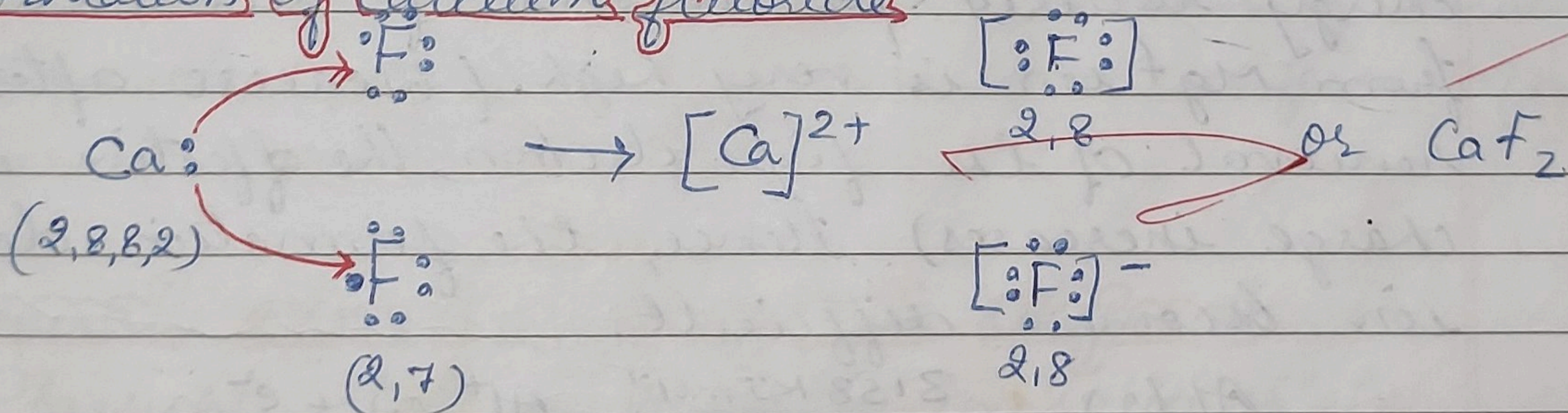
### a) Formation of Sodium Chloride



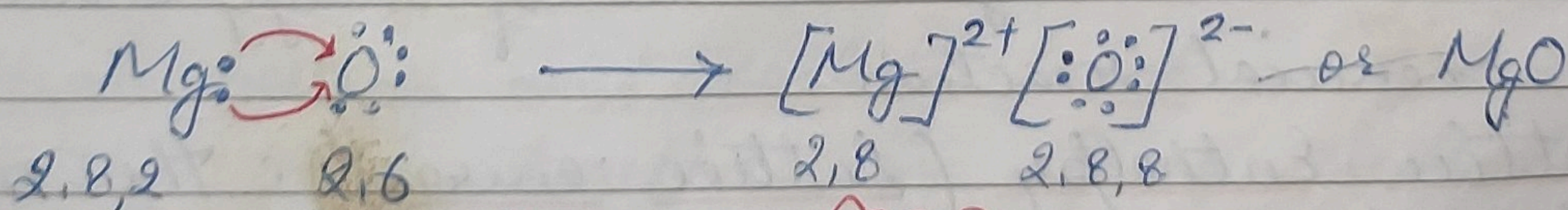
The above steps may be represented directly as follows:



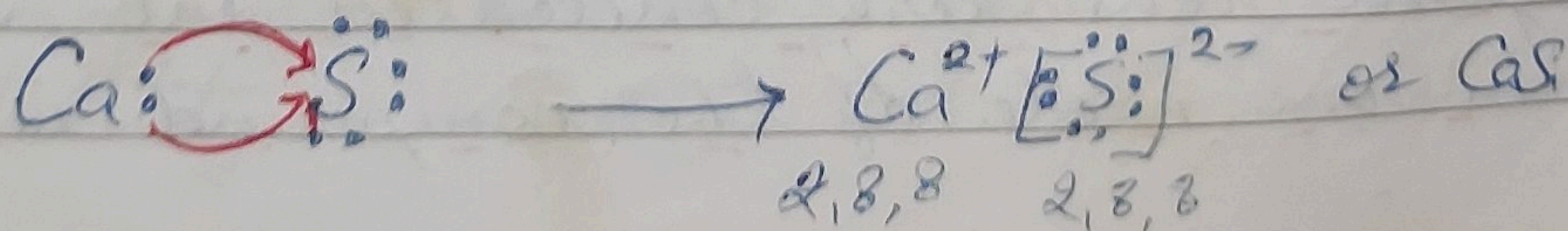
### b) Formation of Calcium fluoride:



### c) Formation of Magnesium oxide.

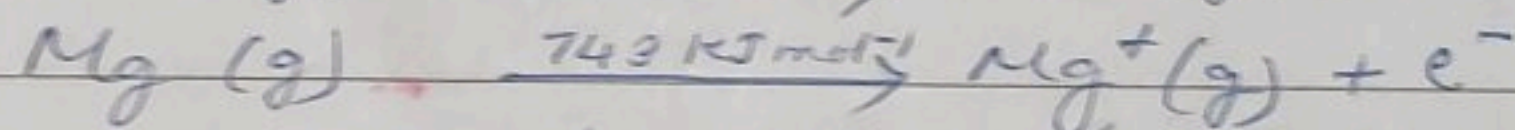
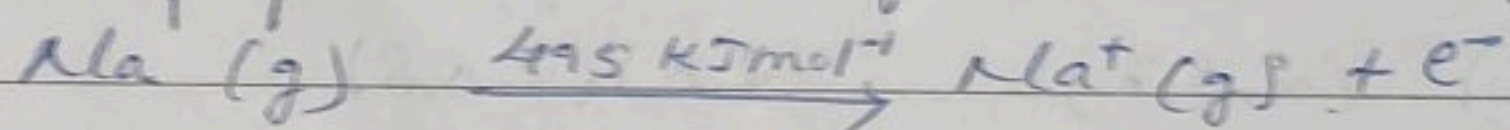


### d) Formation of Calcium sulphide.

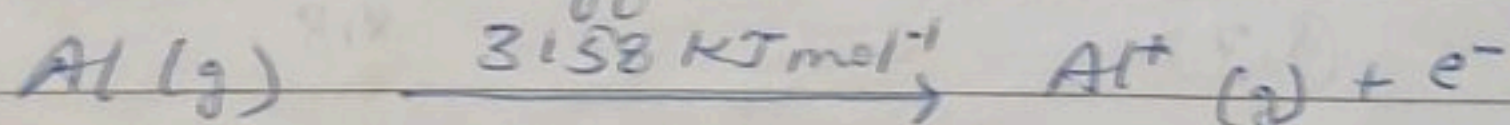


## Factors Governing the formation of Ionic bond

- i) Number of valency electron: One atom should possess 1, 2 or 3 valency electrons while the other atom should have 5, 6 or 7 valency electrons and changes into cations and anions. The atoms of transition metals can lose electron or electrons and converted into cations, can form electrovalent bonds but do not acquire inert gas configuration.
- ii) Difference in electronegativity: If difference is more, the bond formation is easier.  
Ex. Na = 0.9 and Cl = 4.0. Difference is 3.1, both with readily form an electrovalent bond.
- iii) Ionisation Enthalpy: Lesser the ionisation enthalpy, easier will be the removal of an electron, i.e. formation of a positive ion and hence greater the chances of formation of ionic bond.



Energy required for removal of second electron from  $\text{Mg}^+$  ion is very high. (because after the removal of the first electron, the effective nuclear charge increases). Hence, the formation of divalent ion becomes difficult.



This is not generally possible to form this ion since such a huge amount of energy is not available in chemical reaction.

- iv) Lattice Enthalpy (Lattice energy): The energy released when the requisite number of positive and negative ions are condensed into crystal to form one mole of the compound is called

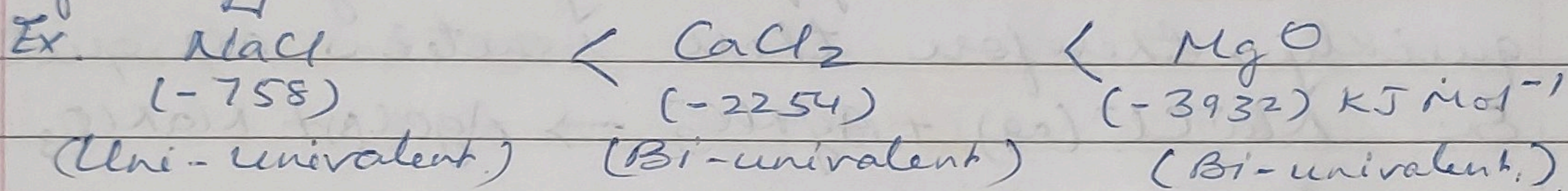
lattice energy. Higher the lattice energy, greater will be the ease of forming an ionic compound.

Higher the value of lattice energy, of the resulting ionic compound, the greater will be the stability of the compound, and hence greater will be the ease of its formation.

$$\text{Force of attraction} \propto \frac{q_1 \times q_2}{d^2} \quad \left( \text{where, } \begin{array}{l} q_1, q_2 = \text{magnitude} \\ \text{of charges.} \\ d = \text{distance.} \end{array} \right)$$

Lattice energy depends upon:

a) Charge on the ions  $\rightarrow$  Higher the charge, greater the force of attraction & hence larger is the amount of energy released.



b) Size of the ions  $\rightarrow$  If the size of the ions is large, internuclear distance will be more and force of attraction will be less while in case of small ions, internuclear distance is less and so force of attraction is greater.

### General characteristics of Ionic Compound:

- 1) Physical state  $\rightarrow$  usually in solid state
- 2) Crystal structure  $\rightarrow$  Ions are arranged in a regular pattern in three dimensional structure.
- 3) High melting and boiling point  $\rightarrow$  because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice.
- 4) Solubility  $\rightarrow$  Mostly soluble in solvents like water.

which are polar in nature and have high dielectric constant. It is due to the reasons that the polar solvents interact with the ions of the crystals and further the high dielectric constant of the solvent (i.e., capacity of the solvent to weaken the forces of attraction) cut off the force of attraction between these ions.

5.) Electrical conductivity → Good conductor. In sol<sup>n</sup> or molten state, these ions are free to move. Being charged, ions are attracted towards electrodes and thus act as carriers of electric current.

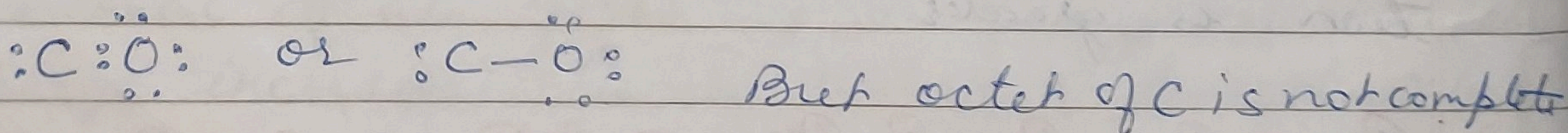
6.) Ionic reaction → oppositely charged ions combine quickly, therefore these reactions are quite fast.  
 Ex:  $\text{Na}^+\text{Cl}^-(\text{aq}) + \text{Ag}^+\text{NO}_3^- \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

### Lewis structure:

1) CO molecule

$$\text{C} = 4 + 6 \quad [6\text{C} = 2, 4, \quad 8\text{O} = 2, 6]$$

$$= 10$$



2)  $\text{NO}_2^-$

$\text{N} = 2, 5$

$\text{O} = 2, 6$

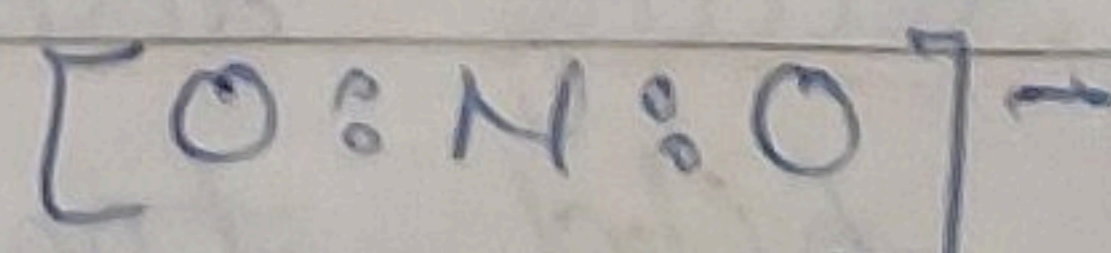
-ve charge = 1

Total valence electrons

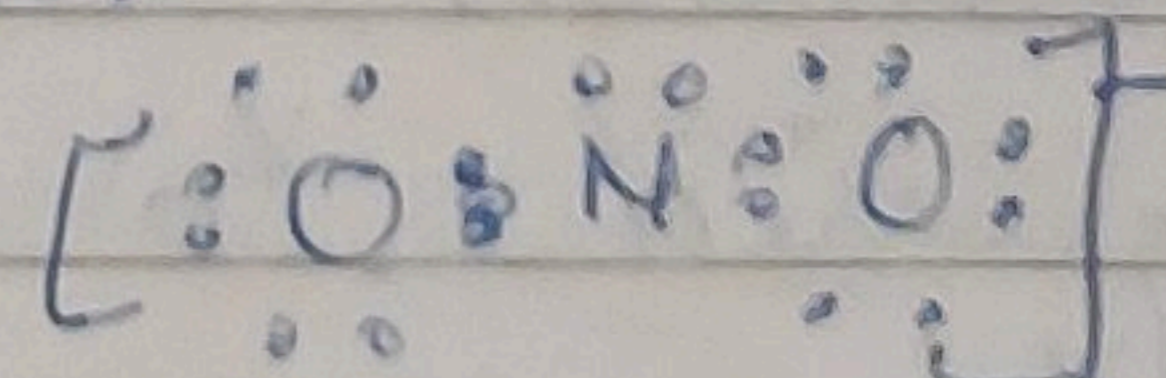
$$\text{NO}_2^- = 5 + 2 \times 6 + 1 = 18$$

$$= 9 \text{ pairs.}$$

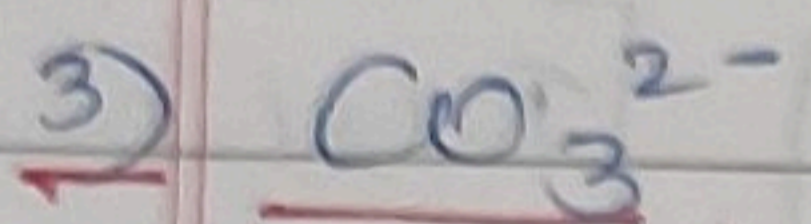
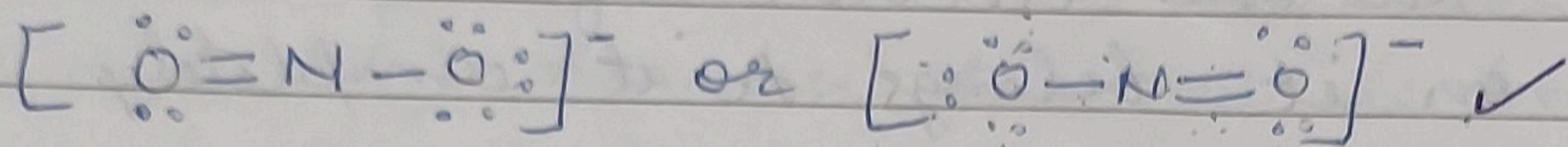
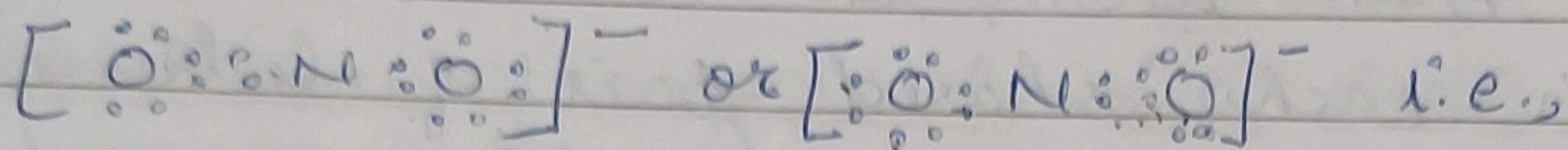
1) By putting one pair of electrons



2) By putting 7 pairs of electrons as lone pair



As octet of N is not complete, multiple bond is required. By shifting O, as shared pair between O and N or N and O, i.e., a double bond should exist.



$$\text{C} = 2, 4$$

$$\text{O} = 2, 6$$

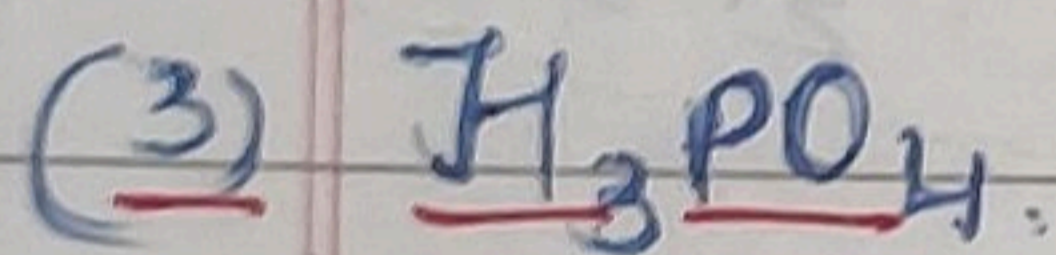
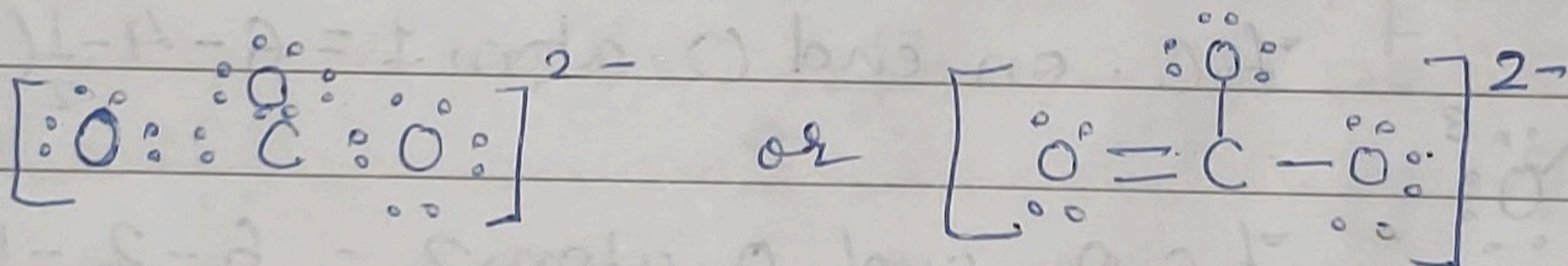
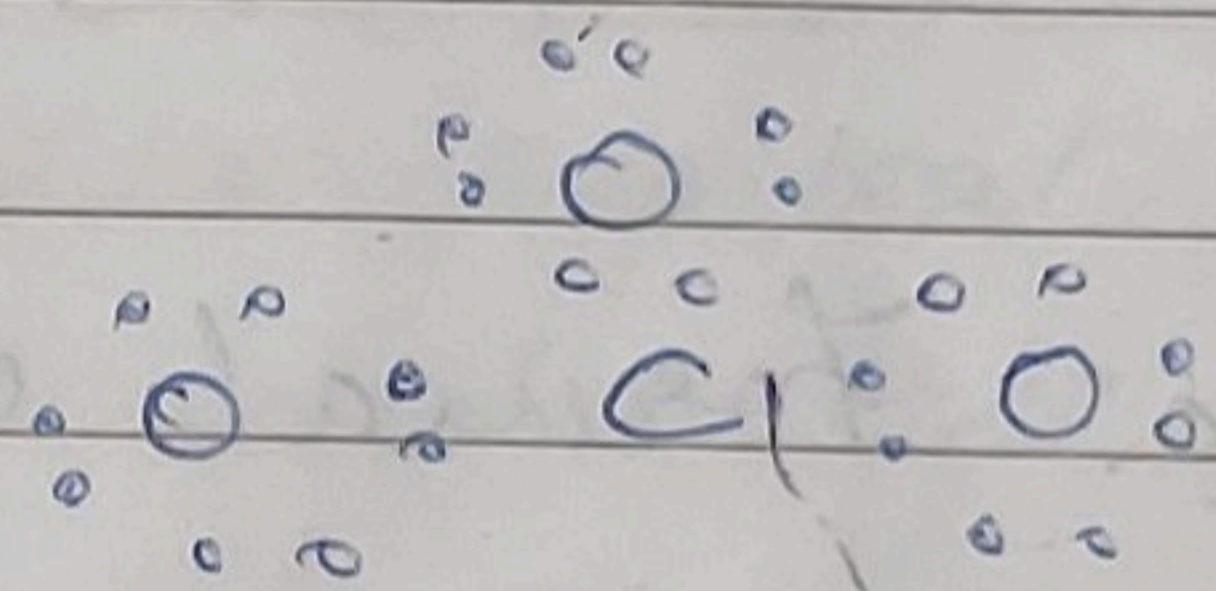
$$\text{CO}_3 = 4 + 3 \times 6$$

$$= 22$$

$$\text{CO}_3^{2-} = 22 + 2$$

$$= 24$$

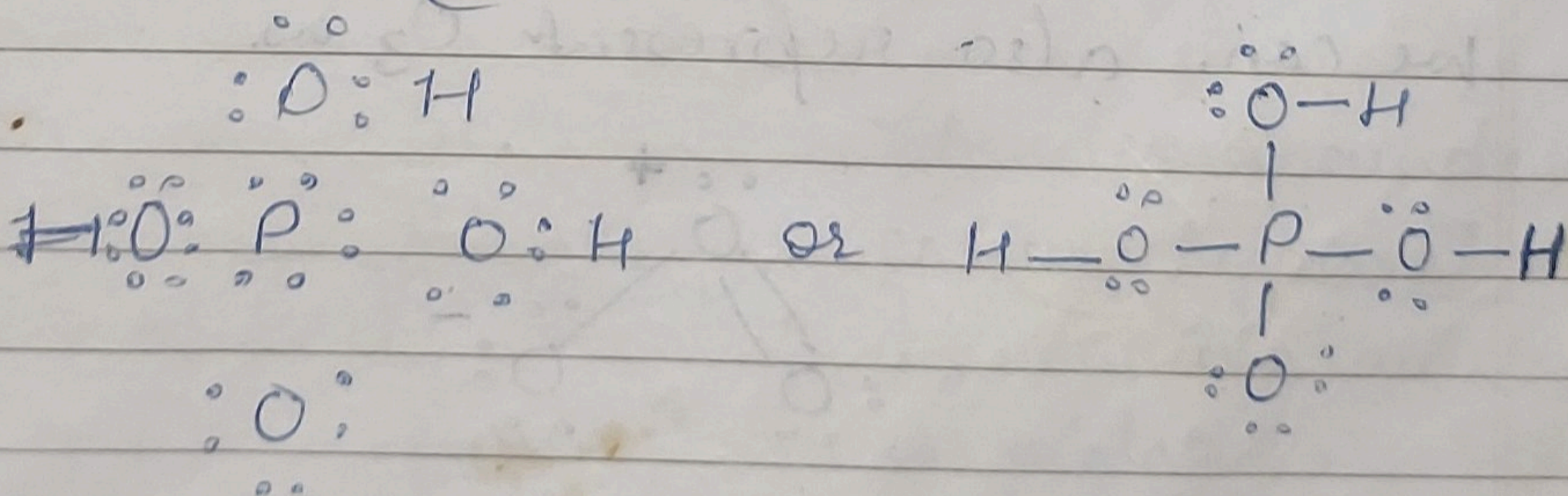
Skeletal structure of CO<sub>3</sub>



$$= 1 \times 3 * 5 * 6 \times 4$$

$$= 3 + 5 + 24$$

$$= 32 \text{ (pairs = 16.)}$$



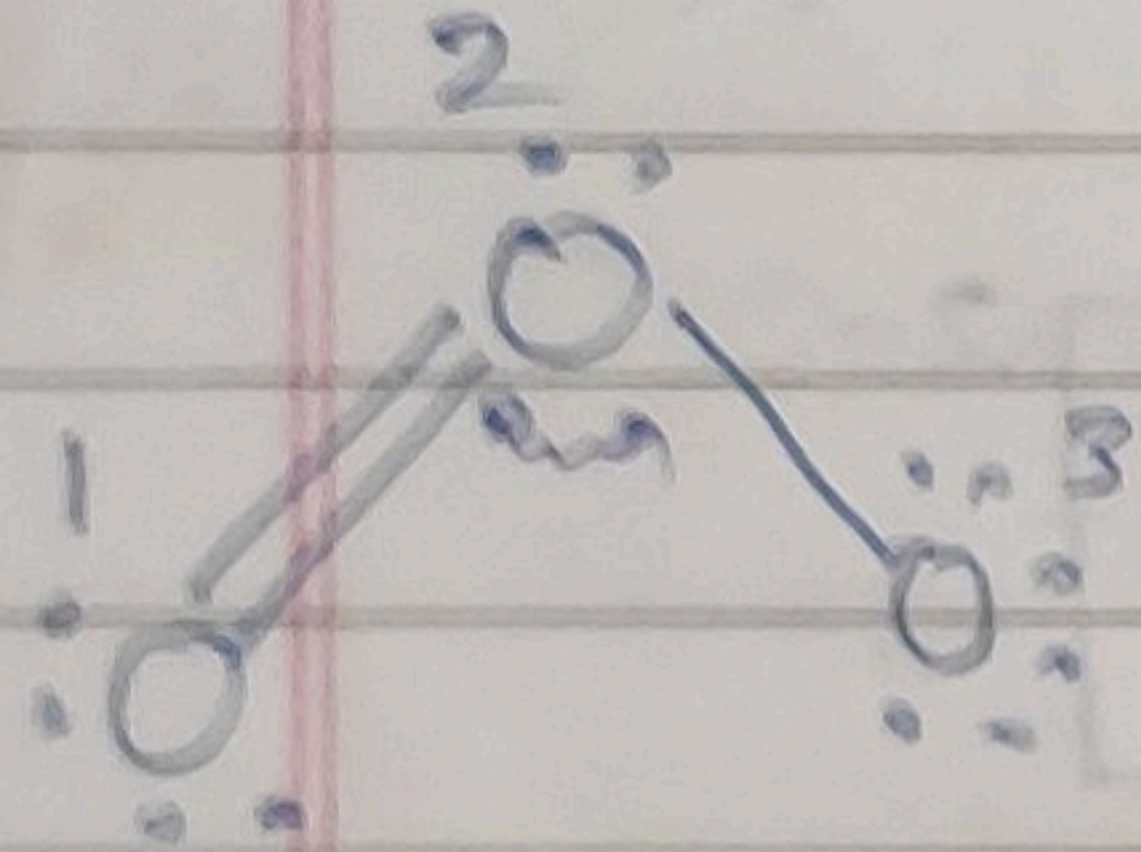
## Formal charge:

Defined as the difference between the number of valence electrons of that atom in the free state and number of electrons assigned to that atom in Lewis structure, assuming that in each shared pair of electrons, the atom has one electron of its own and the lone pair on it belongs to it completely.

$$\left[ \text{Formal charge (F.C.) on an atom in a molecule/ion} \right] = \left[ \text{Total no. of valence electrons in the free atom} \right] - \left[ \text{Total no. of electrons of lone pairs (non bonding electrons)} \right] - \frac{1}{2} \left[ \text{Total no. of shared electrons (bonding electrons)} \right]$$

$$\text{i.e. F.C.} = v - L - \frac{1}{2} S.$$

Ex. Formal charge on each O-atom of  $O_3$ .

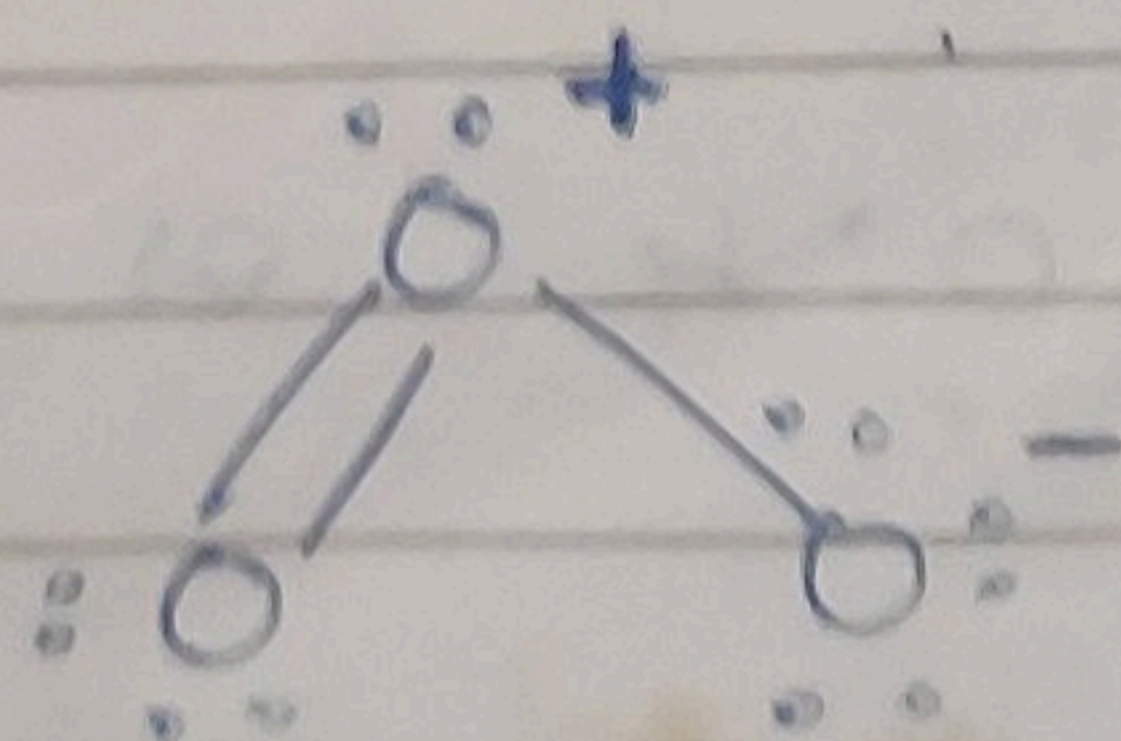


$$\text{F.C. on end O-atom 1} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{F.C. on end O-atom 2} = 6 - 2 - \frac{1}{2}(6) = +1$$

$$\text{F.C. on end O-atom 3} = 6 - 6 - \frac{1}{2}(2) = -1.$$

We can also represent  $O_3$  as.

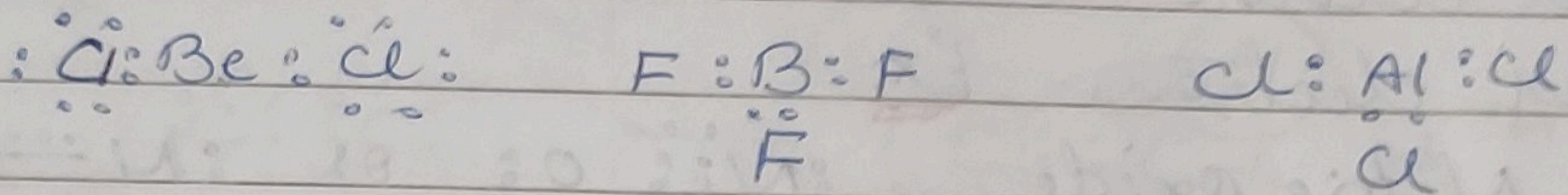




Limitations of the Octet Rule, There are some exceptions to this rule.

(i) Formation of compounds involving Hydrogen: Hydrogen needs one electron to complete its duplet and not octet.

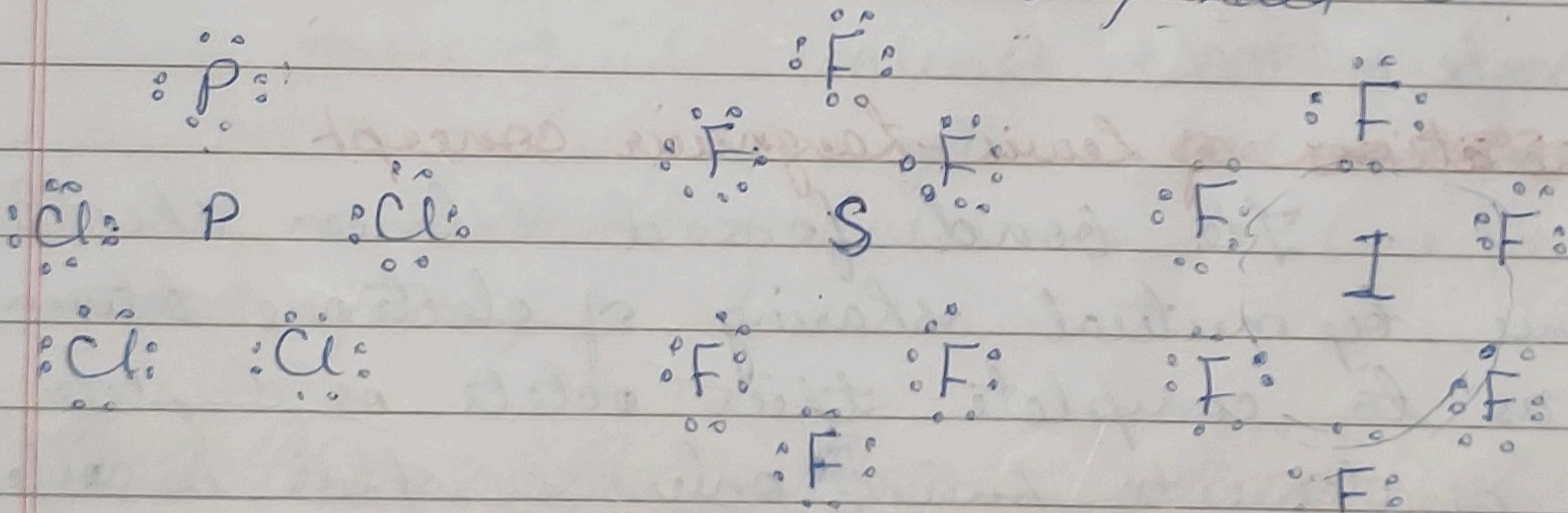
(ii) Formation of compounds like  $\text{BeCl}_2$ ,  $\text{BF}_3$ ,  $\text{AlCl}_3$ , etc. In each of these molecules, the central atom (Be, B or Al) has less than 8 electrons, i.e. they are electron deficient compounds.



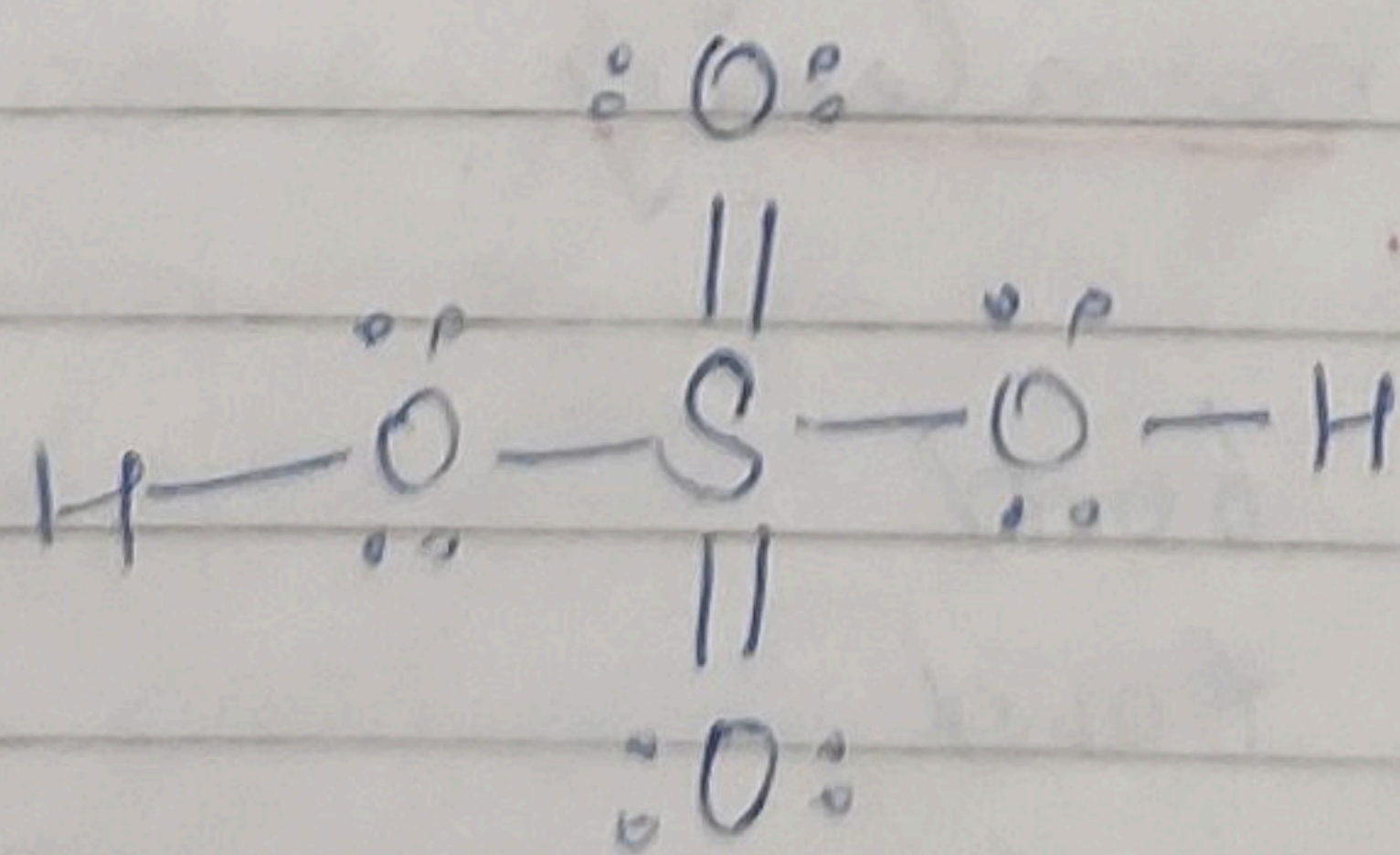
(Be has 4 electrons) (B, Al have 6 electrons) around it around them.

Thus, octet rule is violated.

(iii) Formation of compounds like  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ ,  $\text{H}_2\text{SO}_4$ , etc. In each of these molecules, the central atom has more than 8 electrons (expanded octets).



(10  $e^-$  around P) (12  $e^-$  around S) (14  $e^-$  around I)

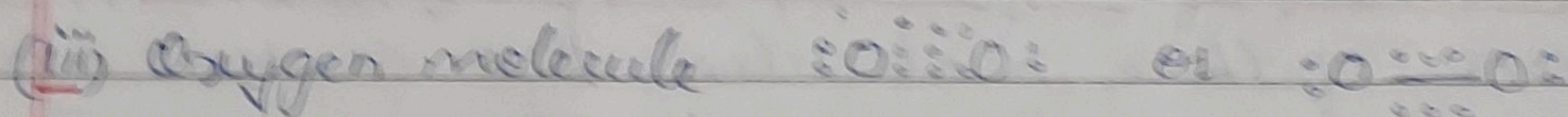
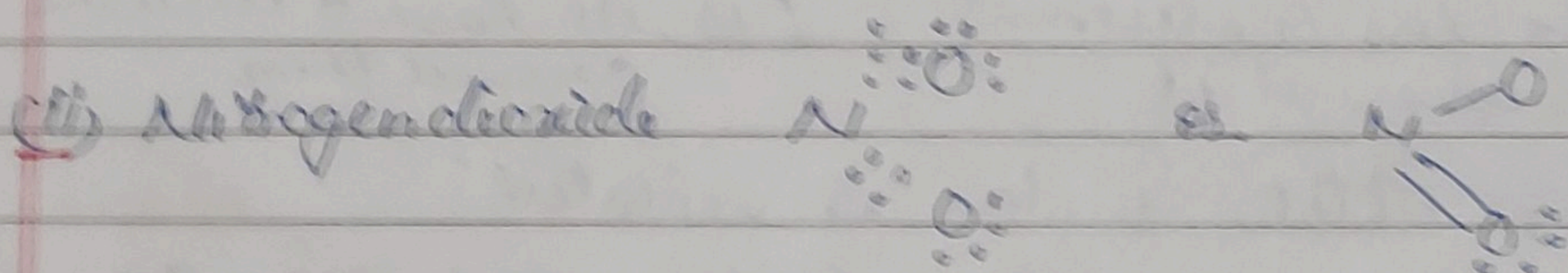


(12  $e^-$  around S).

These compounds are called hypervalent compounds. Again, the octet rule is violated in these molecules.

(iv) Formation of compounds of noble gases: Noble gases which have already complete octets should not form compounds. However their compounds like  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{KrF}_2$  etc. have been actually prepared.

(v) Odd electron bonds / odd electron molecules: Some molecules and ions in which the bonded atoms contain odd number of electrons usually 3) between them. The bond thus formed are called odd electron bonds and the molecules are called odd electrons. Ex.



Covalent bond:

### Definition of Lewis-Langmuir concept

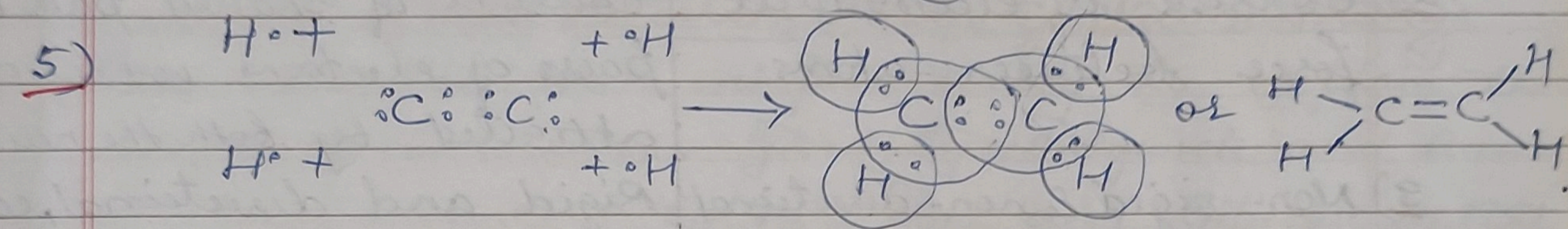
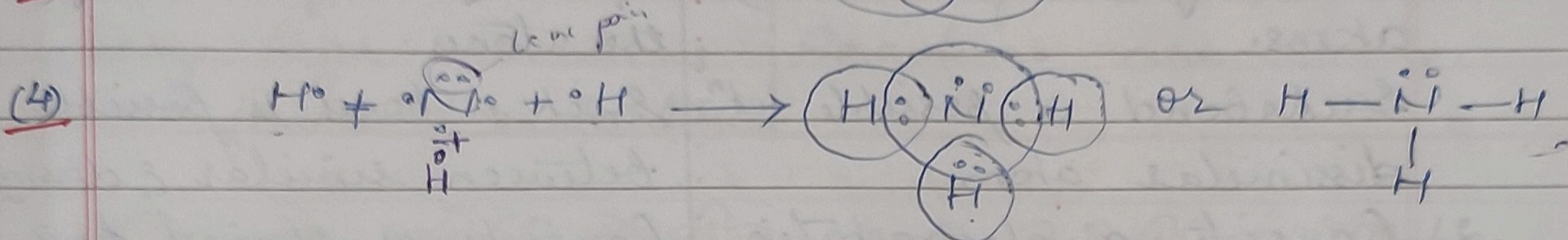
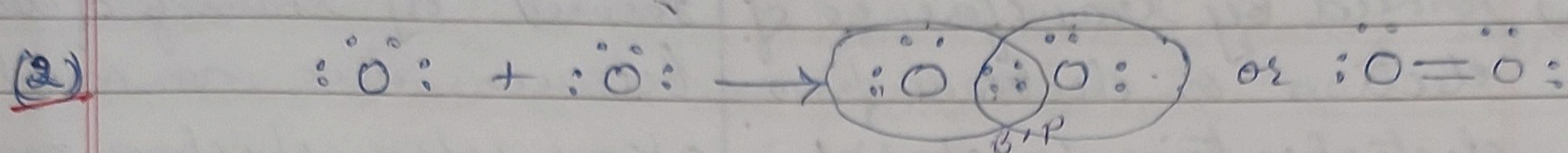
The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called covalent bond or covalent linkage.

The number of electrons contributed by each atom is known as covalency.

Types

- 1) Single covalent bond
- 2) Double covalent bond
- 3) Triple covalent bond.

## Examples:



Bond pairs  $\rightarrow$  The shared pairs of electrons present between the atoms are called bond pairs because they are responsible for the bonding between the atoms.

Lone pairs  $\rightarrow$  The valence electrons not involved in bonding (i.e. sharing) are shown as such are called non-bonding electrons or lone pairs or unshared pairs.

## Limitations of Lewis Langmuir's concept of covalent bond

- 1) It could not explain the shapes of molecules containing covalent bonds.
- 2) It could not explain the release of energy during the formation of a covalent bond.
- 3) It could not explain how the atoms are held together in molecules like  $H_2$ ,  $Cl_2$ , etc. where there is no electrostatic force of attraction. i.e., it could not explain the formation of a covalent bond.

## Comparison:

### Ionic bond

### Covalent bond

- |   |  |
|---|--|
| 1) Formed by transference of electron or electrons from electropositive (metal) to electronegative (non-metal) atoms.               | Formed by sharing of electrons between two non metal atoms when electrons are equally contributed by both the atoms. |
| Such a bond is possible bet <sup>n</sup> dissimilar atoms.  | Such a bond is possible between similar & dissimilar atoms.  |
| 2) Consists of electrostatic force between atoms.   | Consists of shared pair or pairs of electrons which are attracted by both the nuclei.                                |
| 3) Non-rigid & non-directional does not cause isomerism.  | Rigid and directional, cause space and structural isomerism.   |
| 4) It is a <sup>strong</sup> <del>weak</del> bond, since the electrostatic force bet <sup>n</sup> the ions cannot be broken easily. | It is <sup>weak</sup> <del>strong</del> bond, since the paired electrons can be separated easily.                    |
| 5) It is polar in nature.   | It is non-polar if the electronegativity difference is zero or small.  |

### Ionic compound

### Covalent Compound

- |   |  |
|---|--|
| 1) Crystalline solids at room temp.   | Gases, liquids or soft solids under ordinary conditions.                         |
| 2) High M.P & B.P.  | Low m.p, b.p, exception of giant molecules.                                      |
| 3) Hard & brittle.  | Soft and waxy with the giant molecules.  |
| 4) Freely soluble in water and in polar solvents. Insoluble in non-polar solvent. | usually insoluble in water and in polar solvents. Soluble in non-polar solvents. |

5) In solid state bad cond. of Electricity. Good cond. in molten state & in sol?	Bad cond. of electricity with few exceptions having layer lattice structure
6) Undergo ionic reactions. Rates of reactions are very high. Reactions are fast and instantaneous.	Undergo molecular reactions. Rates of reactions are low. Reactions are slow.

## Valence Shell Electron Pair Repulsion Theory

This was the first simple theory to explain the shapes of molecules. Given by Sidgwick and Powell in 1940, improved by Nyholm and Gillespie in 1957.

### Basic concept:

"The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability."

The central atom is linked to other atoms by covalent bonds which are formed by sharing of electrons. Thus, the central atom is surrounded by bond pairs and lone pairs. The stability of the molecule demands that it should have minimum energy. If the electron pairs surrounding the central atom are nearer, they will repel each other, thereby increasing the energy of the molecule. But if the electron pairs are far apart, the repulsions between them will be less and so the energy of the molecule will be low.

After repulsions between them, the electron pairs take up definite positions around the central atom, hence the molecule has a definite shape or geometry.

## Basic assumptions of the VSEPR theory

- 1) The shape of a molecule containing only two atoms is always linear.
- 2) For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.
- 3) If the central atom is linked to similar atoms and is surrounded by bond pairs, the repulsion between them are similar. As a result, the shape of the molecule is symmetrical and have regular geometry.
- 4) If central atom is linked to different atoms or is surrounded by bond pairs as well as lone pairs the repulsion between them are different. As a result, the molecule has an irregular or distorted geometry. The order of repulsion between electron pair is as follows:-

$$lp-lp > lp-bp > bp-bp.$$

- 5) The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

## Calculation of total number of electron pairs, bond pairs and predicting the shapes of the molecules & ions

(i) Total no. of electron pairs around the central atom =  $\frac{1}{2}$  (No. of valence electrons of central atom + No. of atoms linked to central atom by single bonds)

(ii) No. of bond pairs = No. of atoms linked to central atom by single bonds.

(iii) No. of lone pairs = Total no. of electron pairs - No. of shared pairs

## Shapes of following compounds. (On the basis of VSEPR theory.)

1)  $\text{ClF}_3$

No. of valence electrons of Central Cl atom = 7.

No. of atoms linked to Cl by single bonds = 3.

$\therefore$  Total no. of electron pairs around Cl =  $\frac{7+3}{2} = 5$ .

No. of bond pairs = No. of atoms linked to Cl = 3.

$\therefore$  No. of lone pairs =  $5-3 = 2$ .

Thus, the molecule is of the type  $\text{AB}_3\text{L}_2$  (T-shaped).

2)  $\text{BrF}_5$

No. of valence electrons of Central Br atom = 7.

Atoms linked to Br = 5.

$\therefore$  Total no. of electron pairs around Br =  $\frac{7+5}{2} = 6$ .

No. of bond pairs = No. of atoms linked to Br = 5.

$\therefore$  No. of lone pairs =  $6-5 = 1$ .

The type of molecule is of  $\text{AB}_5\text{L}$  (square pyramidal shape).

3)  $\text{NH}_2^-$

No. of valence electrons of central N atom =  $5+1$  (due to  $-$  charge) = 6.

No. of atoms linked to it = 2.

Total no. of electron pairs =  $\frac{6+2}{2} = 4$ .

No. of bond pairs = 2.

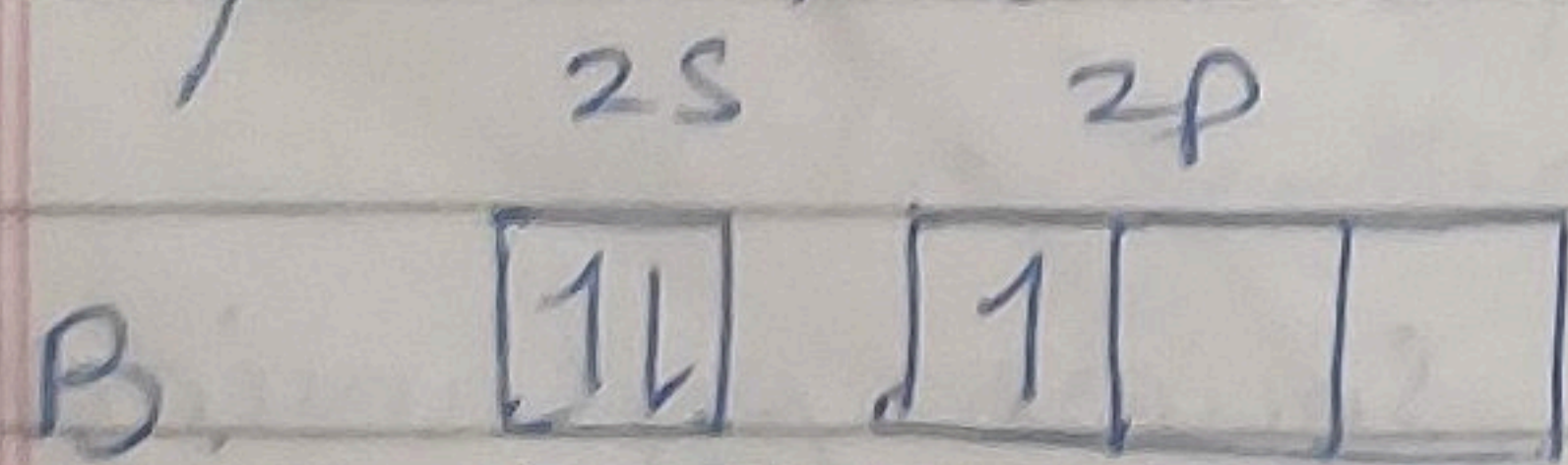
$\therefore$  No. of lone pairs =  $4-2 = 2$ .

The type of ion is  $\text{AB}_2\text{L}_2$  (square pyramidal shape).

# Valence Bond Theory:

This theory was presented by Heitler and London, in 1927, to explain how a covalent bond is formed. This theory was extended by Pauling and Slater, in 1931. The main points of the theory are:-

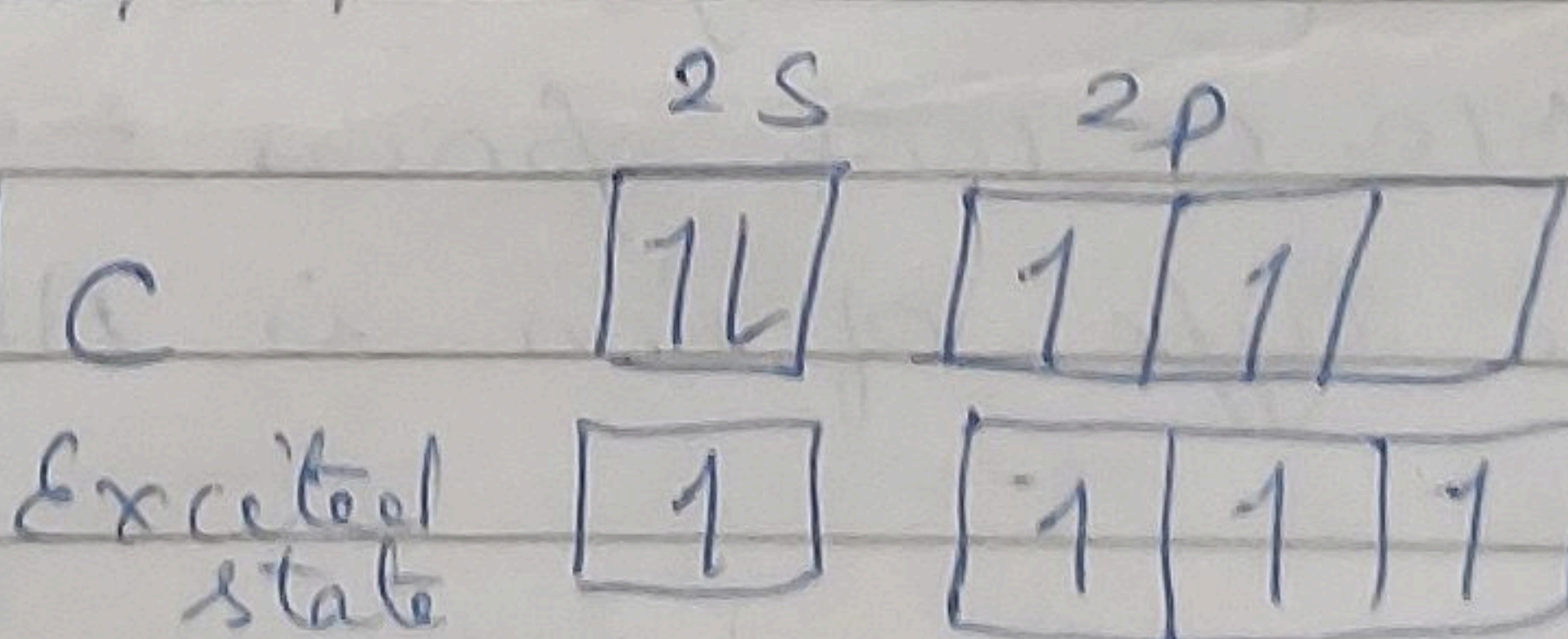
- i) A covalent bond is formed by overlapping of atomic orbitals of valency shell of the two atoms.
- ii) Only half filled atomic orbitals can enter into overlapping process. The resulting bond acquires a pair of electrons with opposite spins.
- iii) The atoms with half filled orbitals must come closer to one another with their axes in proper directions for overlapping.
- iv) As a result of overlapping, there is maximum electron density somewhere between the two atoms.
- v) Greater the overlapping, higher is the strength of chemical bond. The energy released per mole during overlapping is termed bond energy. This energy stabilizes the system.
- vi) Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell (valency shell). This point explain the valency of B, C, P.



Excited state 

1	1	1	
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 one electron is shifted to p-orbital

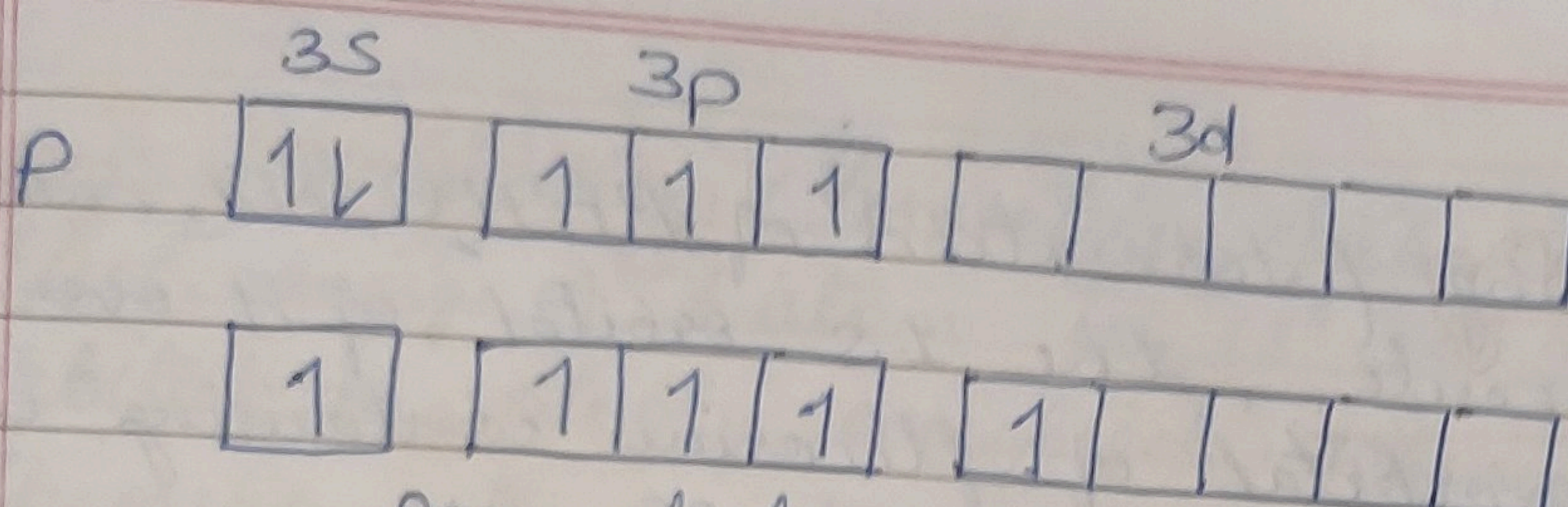


Excited state 

1	1	1	1
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 one electron is shifted to p-orbital





One electron is shifted to d-orbital.

vii) Between two orbitals of the same stability (i.e. having same energy) one more directionally concentrated would form a stronger bond. Dumbbell shaped p-orbitals will form stronger bond as compared to spherically symmetrical s-orbital. It is formed by head on or axial overlap.

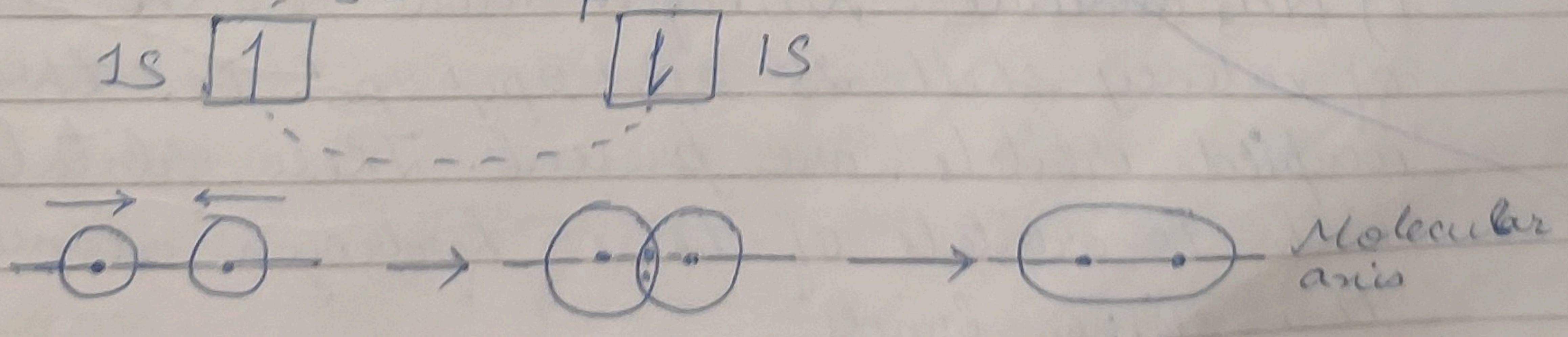
viii) Two types of bonds are formed on account of overlapping. These are (a) Sigma ( $\sigma$ ) and (b) Pi ( $\pi$ ) bonds.

(a) Sigma ( $\sigma$ ) bond: A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma ( $\sigma$ ) bond.

"Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond."

Sigma bonds are formed by three types of overlapping.

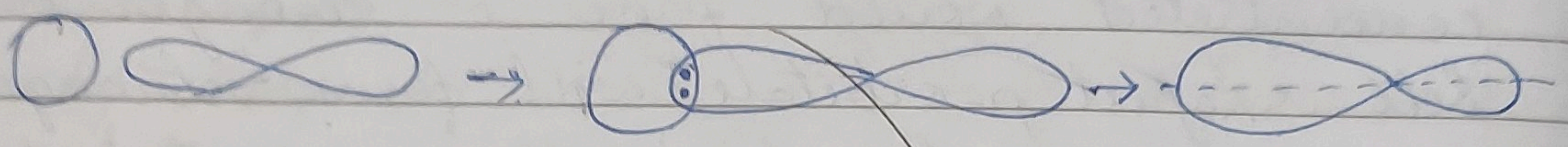
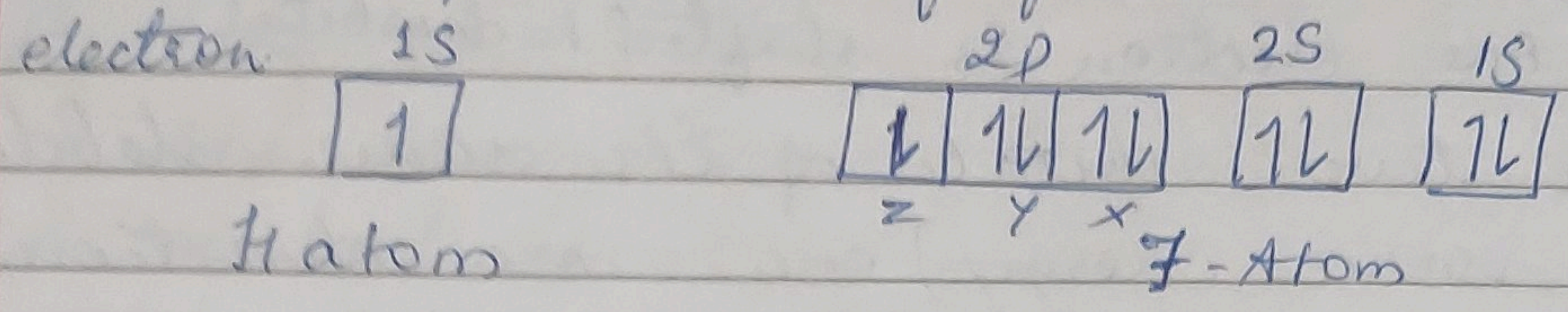
(i) s-s overlapping (Formation of H<sub>2</sub> molecule)



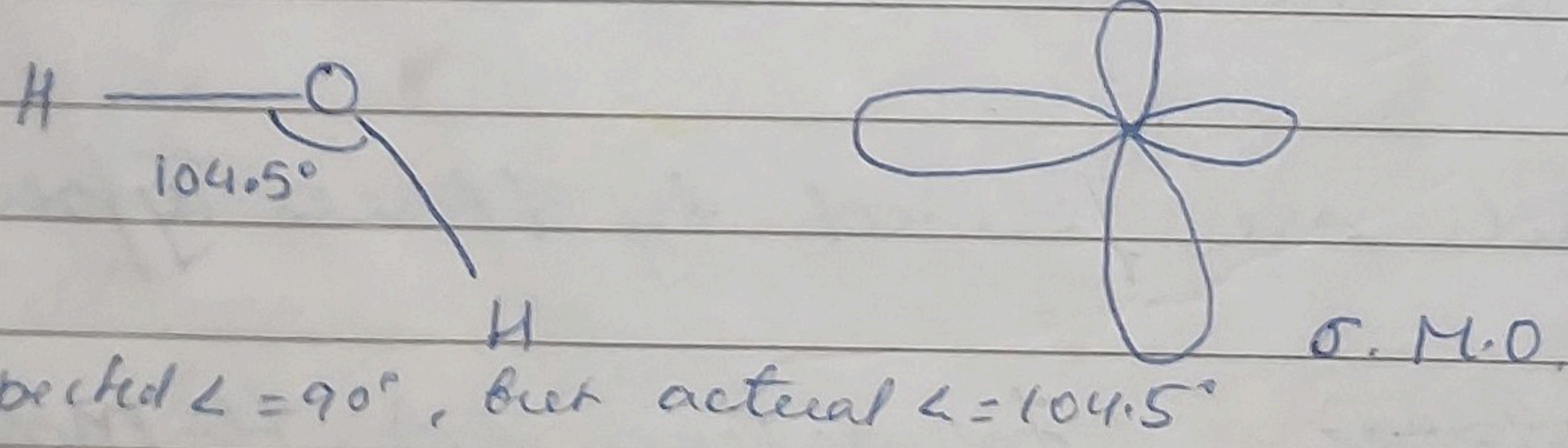
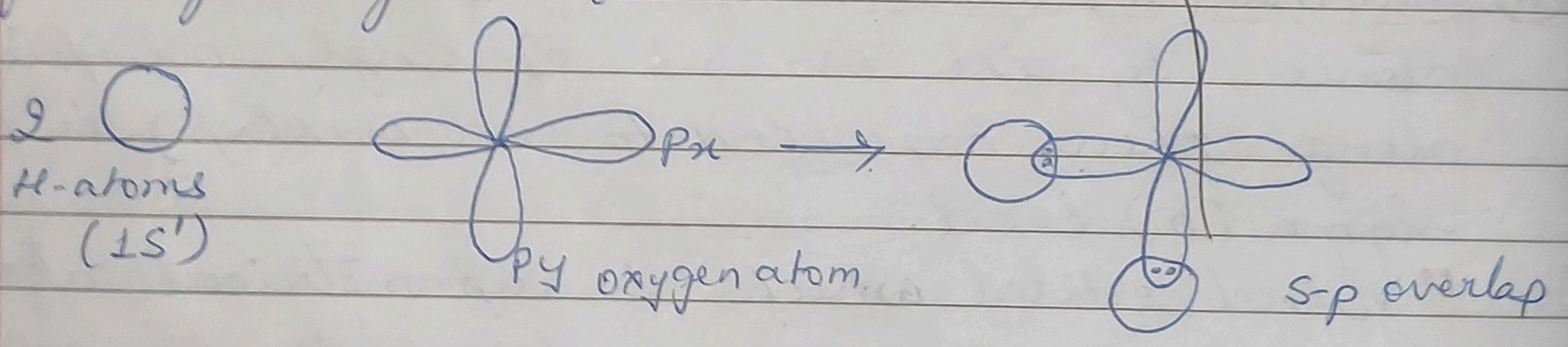
The bond has two electrons which have opposite spins. The probability of finding these electrons is max. in the region between the two nuclei on the molecular axis.

ii) S-p overlapping (Formation of HF, H<sub>2</sub>O, NH<sub>3</sub> molecules)

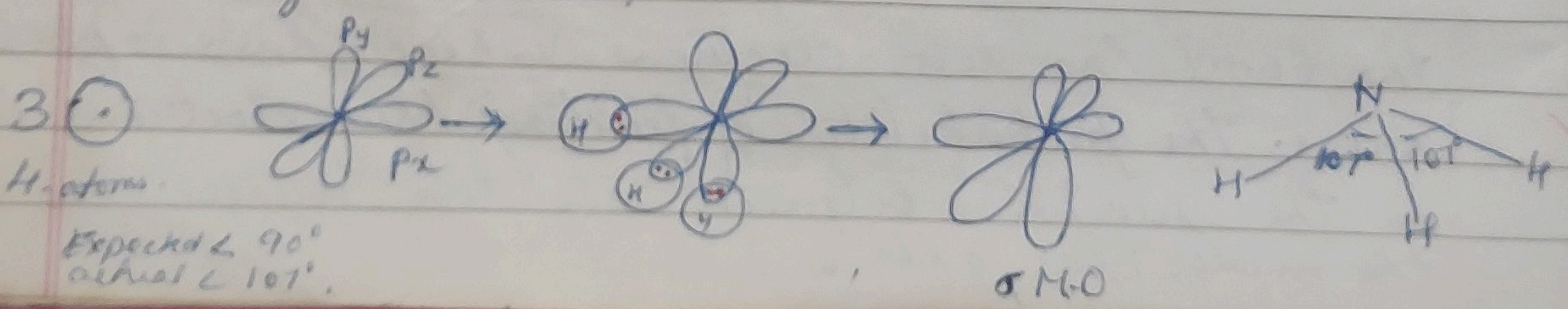
a) HF molecule, the 1s orbital of H overlaps with the p-orbital of fluorine containing unpaired electron



b) Water (H<sub>2</sub>O) molecule: Oxygen atom has the configuration of valency shell 1s<sup>2</sup> 2p<sub>z</sub><sup>2</sup> 2p<sub>y</sub><sup>1</sup> 2p<sub>x</sub><sup>1</sup> i.e. it has two orbitals singly occupied. These two orbitals overlap with 1s-orbital of two H-atoms forming sigma-bonds.

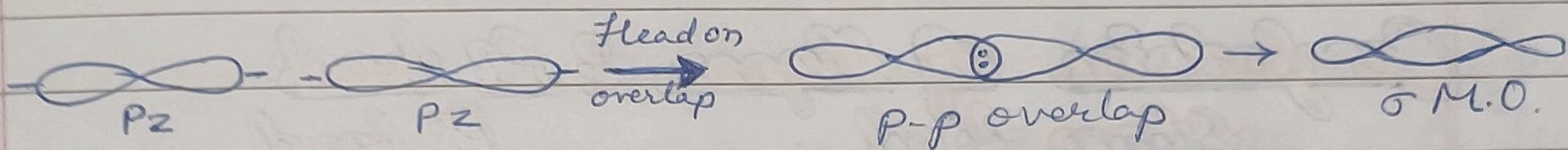
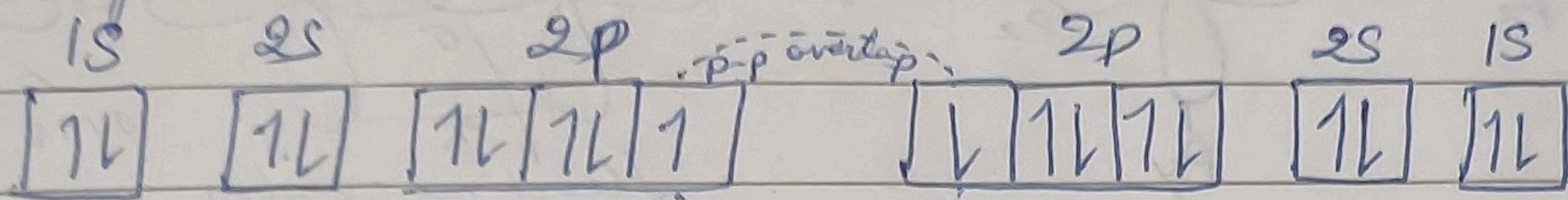


c) NH<sub>3</sub> molecule: Nitrogen atom has the configuration of valency shell 2s<sup>2</sup> 2p<sub>x</sub><sup>1</sup> 2p<sub>y</sub><sup>1</sup> 2p<sub>z</sub><sup>1</sup>. i.e. three singly occupied orbitals are present. These orbitals overlap with 1s-orbitals of three hydrogen atoms forming three sigma bonds.

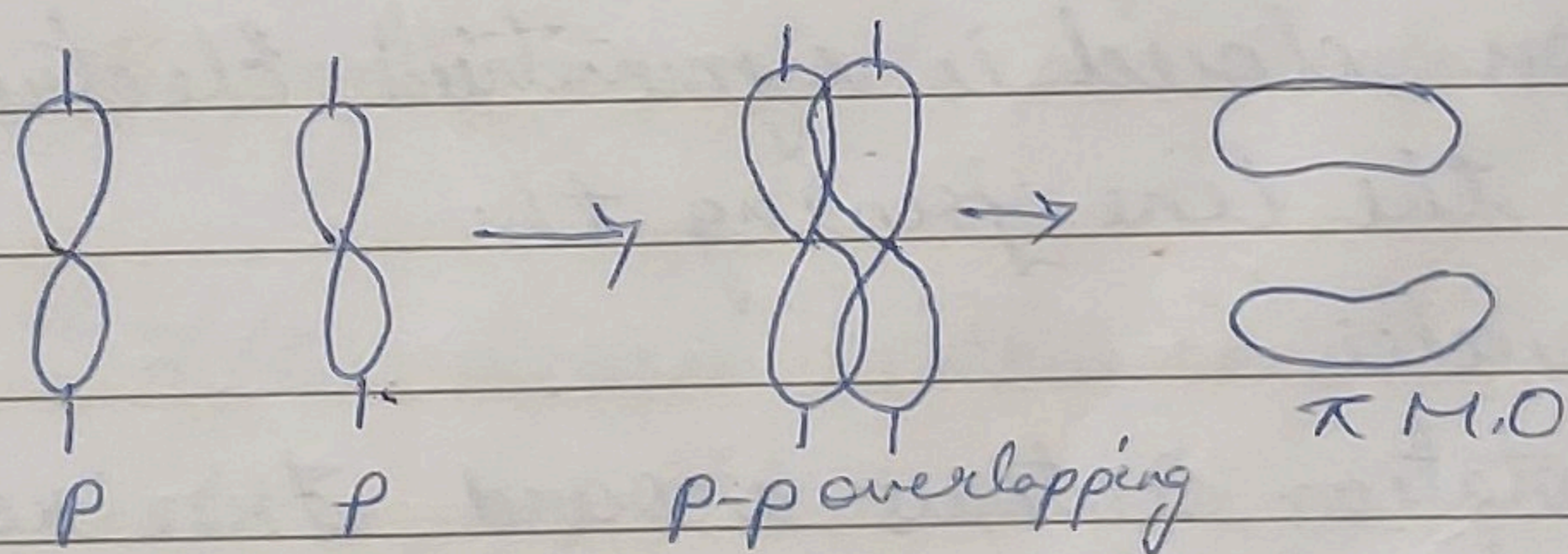


iii) p-p overlapping (Formation of Fluorine molecule)

Elect. config of F-atom is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ . i.e. one orbital is singly occupied. When p-orbitals of two fluorine atoms approach each other with their heads directly towards one another, they overlap and form a sigma bond.

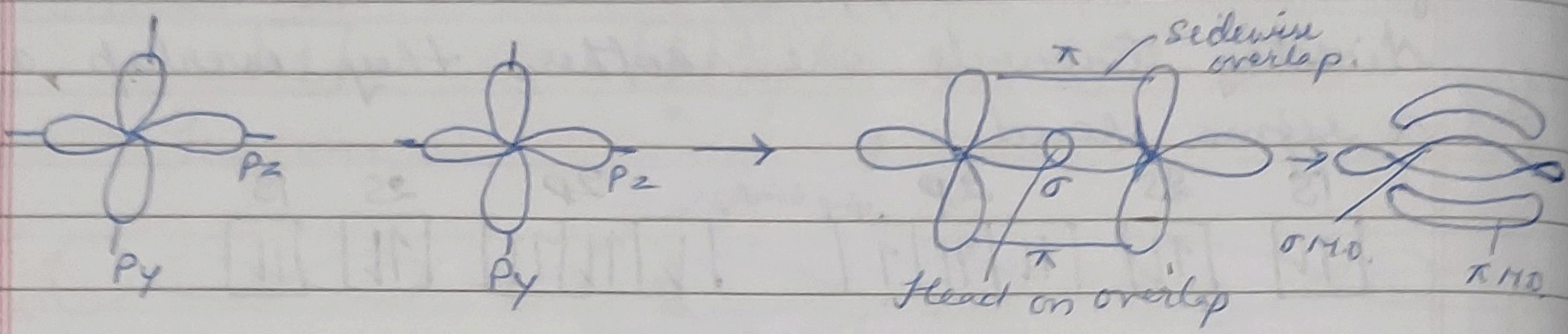
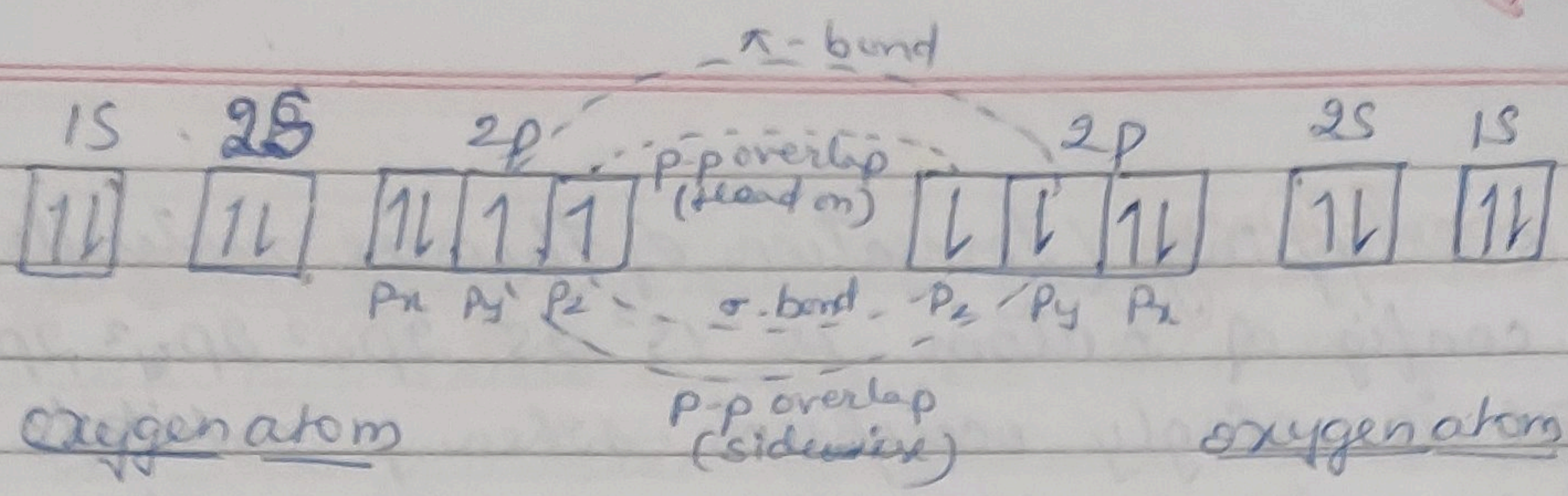


(b) Pi ( $\pi$ ) bond:  $\pi$  bonds are formed by the sideways or lateral overlapping of p-orbitals. The overlapping takes place at the side of two lobes and hence, the extent of overlapping is relative smaller. Thus,  $\pi$  bond is a weaker bond in comparison to sigma bond.



Formation of  $\pi$ -bond.

Formation of Oxygen molecule: Oxygen atom has two p-orbitals singly occupied in the valency shell. When two oxygen atoms approach each other, one set of p-orbitals experiences head on overlap forming a sigma bond while other set of p-orbitals overlap sideways wise to form a  $\pi$ -bond. Thus, oxygen molecule has one  $\sigma$ - and one  $\pi$  bond.



## Comparison of sigma & pi bond.

<u>Sigma bond</u>	<u>pi bond</u>
-------------------	----------------

- |  |  |
|--|--|
| <p>1) The bond is formed by the overlap of orbitals along their axes (end to end overlap). It includes s-s, s-p and p-p overlapping.</p> <p>2) It is a strong bond.</p> <p>3) Electron cloud is symmetrical about the line joining the two nuclei.</p> <p>4) Free rotation of atoms around this bond.</p> <p>5) These are less reactive.</p> <p>6) The shape of the molecule is determined by these bonds.</p> <p>7) <math>\sigma</math>-electrons are referred as localized.</p> <p>8) <math>\sigma</math>-bond can have independent existence.</p> | <p>The bond is formed by sidewise overlapping of orbitals (lateral overlapping). It includes p-p overlapping.</p> <p>It is a weak bond.</p> <p>Electron cloud is unsymmetrical.</p> <p>Free rotation is not possible around this bond.</p> <p>These are more reactive.</p> <p>These bonds do not affect the shape of the molecule.</p> <p><math>\pi</math>-electrons are referred as mobile electrons.</p> <p><math>\pi</math>-bond always exists along with a <math>\sigma</math>-bond.</p> |
|--|--|

All single bonds are sigma bonds.  
 All double bonds have one sigma & one pi bond.  
 All triple bond have one sigma & two  $\pi$  bonds.

## Hybridisation:

Pauling and Slater introduced an hypothetical concept. According to this concept, any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals.

[The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy]

### Rules of Hybridization:

- 1) Only orbitals (atomic) of nearly same energy belonging to same atom or ion can take part.
- 2) No. of atomic hybrid orbitals formed is always equal to number of atomic orbitals which have taken part in the process of hybridization.
- 3) Hybrid orbitals are similar but they are not necessarily identical in shape. They may differ in orientation in space.
- 4) Actually the orbitals which undergo hybridization and not the electrons.
- 5) Hybrid orbitals form only sigma bond.

No. of atomic orbitals involved in hybridization	Type of hybridization	No. of hybrid orbitals	Shape of molecules	Bond angles	Example
2	$sp$	2	Linear	$180^\circ$	$BeCl_2, BeF_2$
3	$sp^2$	3	Plane triangular	$120^\circ$	$BF_3, BCl_3$
4	$sp^3$	4	Tetrahedral	$109^\circ 28'$	$CH_4, CCl_4$
4	$dsp^2$	4	Square planar	$90^\circ$	$[Ni(CN)_4]$

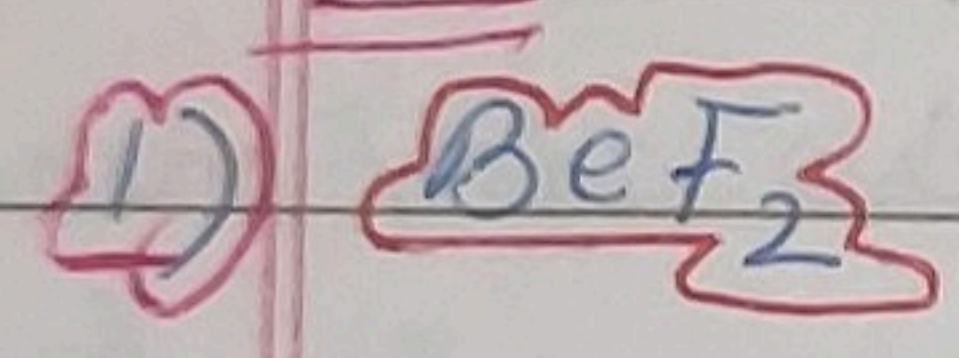
5	$dsp^3$ or $sp^3d$	5	Trigonal bipyramidal	$120^\circ$ & $90^\circ$	$PCl_5$
6	$d^2sp^3$ or $sp^3d^2$	6	Octahedral	$90^\circ$	$SF_6$
7	$d^3sp^3$ or $sp^3d^3$	7	Pentagonal bipyramid	$72^\circ$ & $90^\circ$	$IF_7$

## Types of Hybridisation

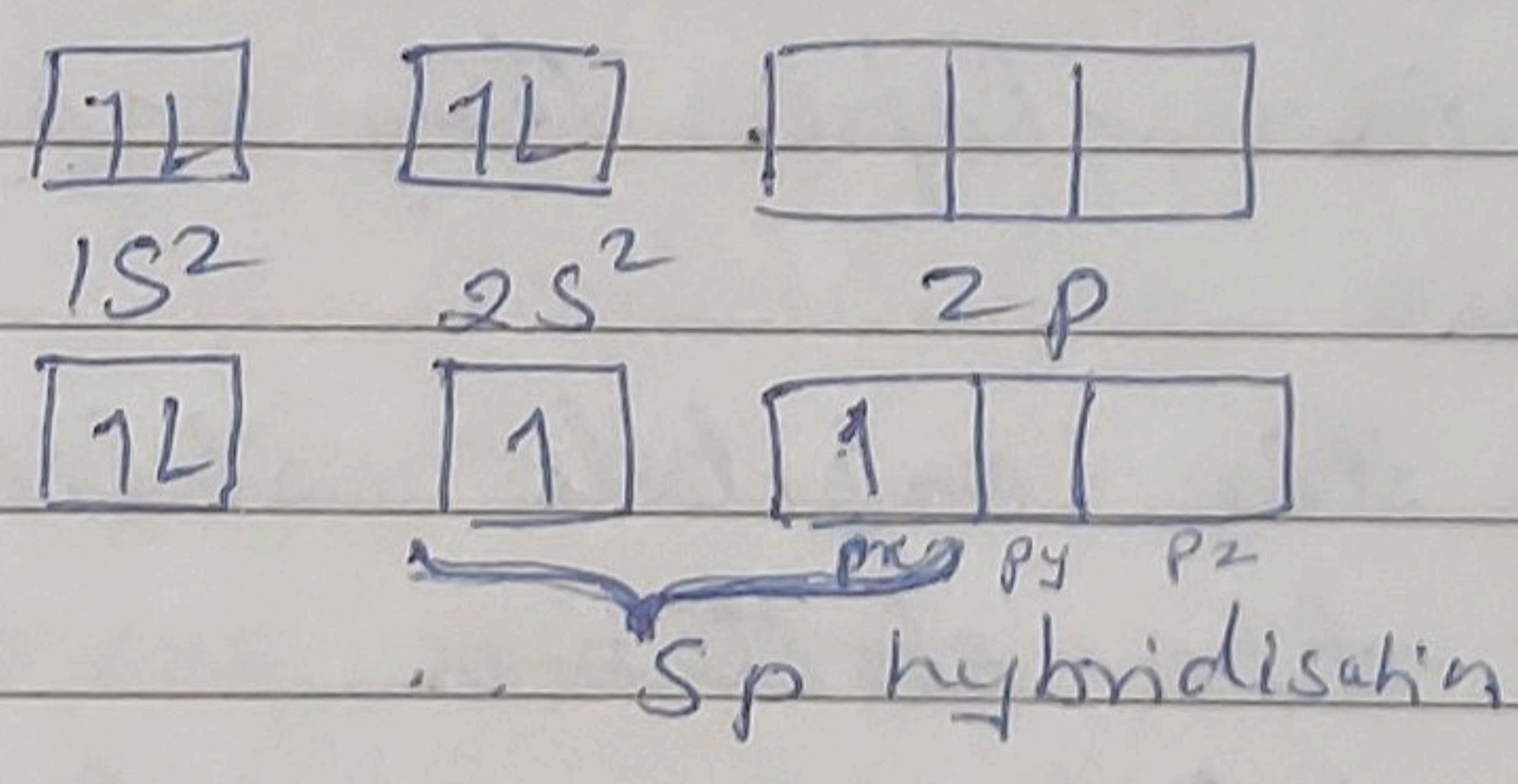
Various types involving s, p and d orbitals.

- 1)  $sp$  hybridisation = 50% s and 50% p character
- 2)  $sp^2$  hybridisation =
- 3)  $sp^3$  hybridisation

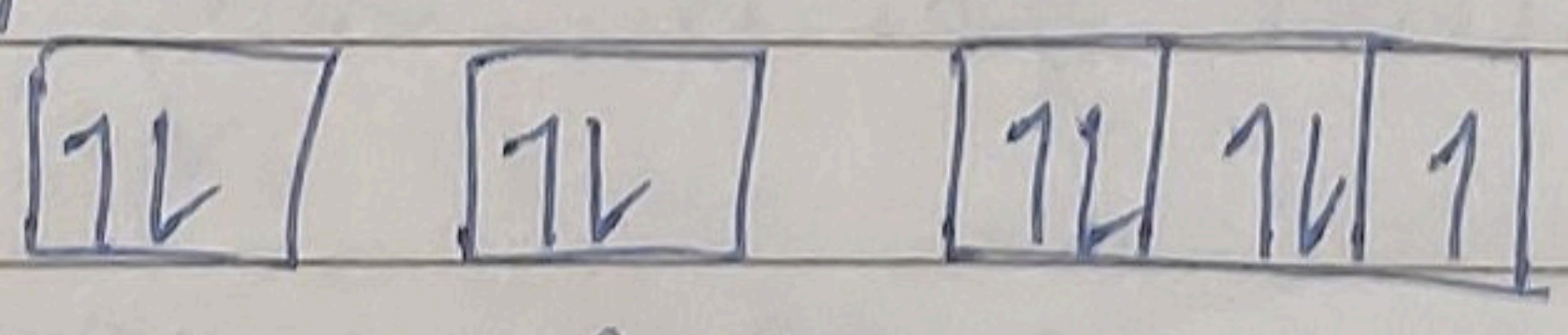
Ex:



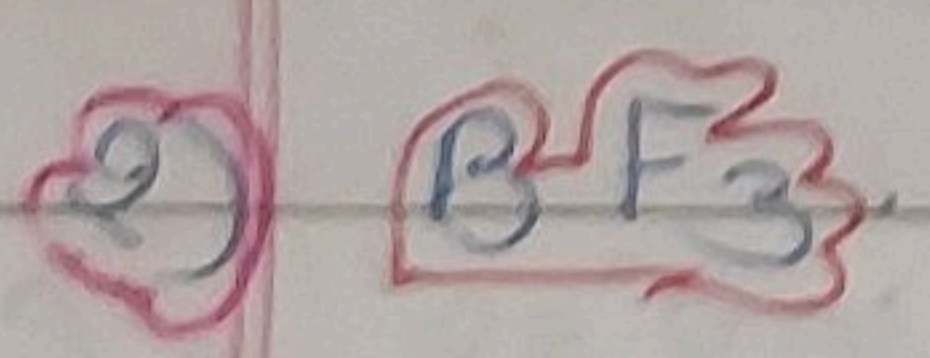
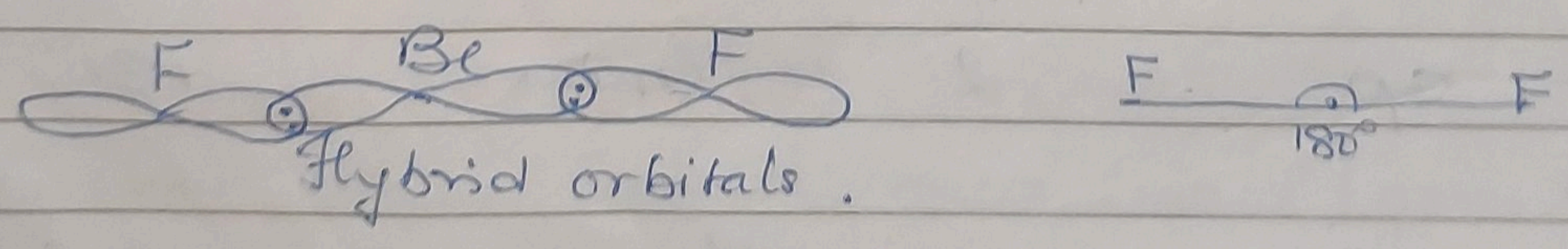
$Be = 4$



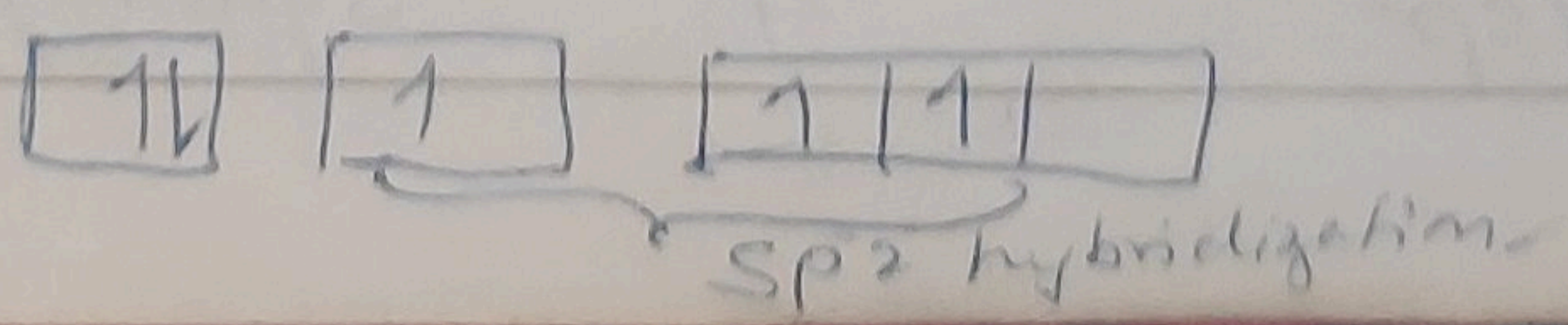
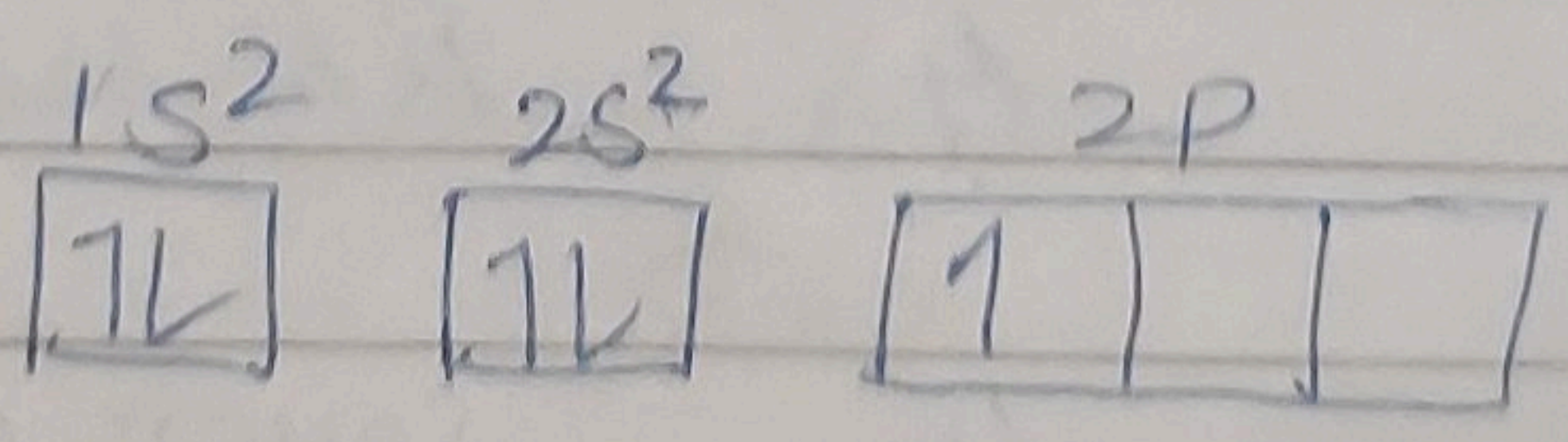
$Be = 9$

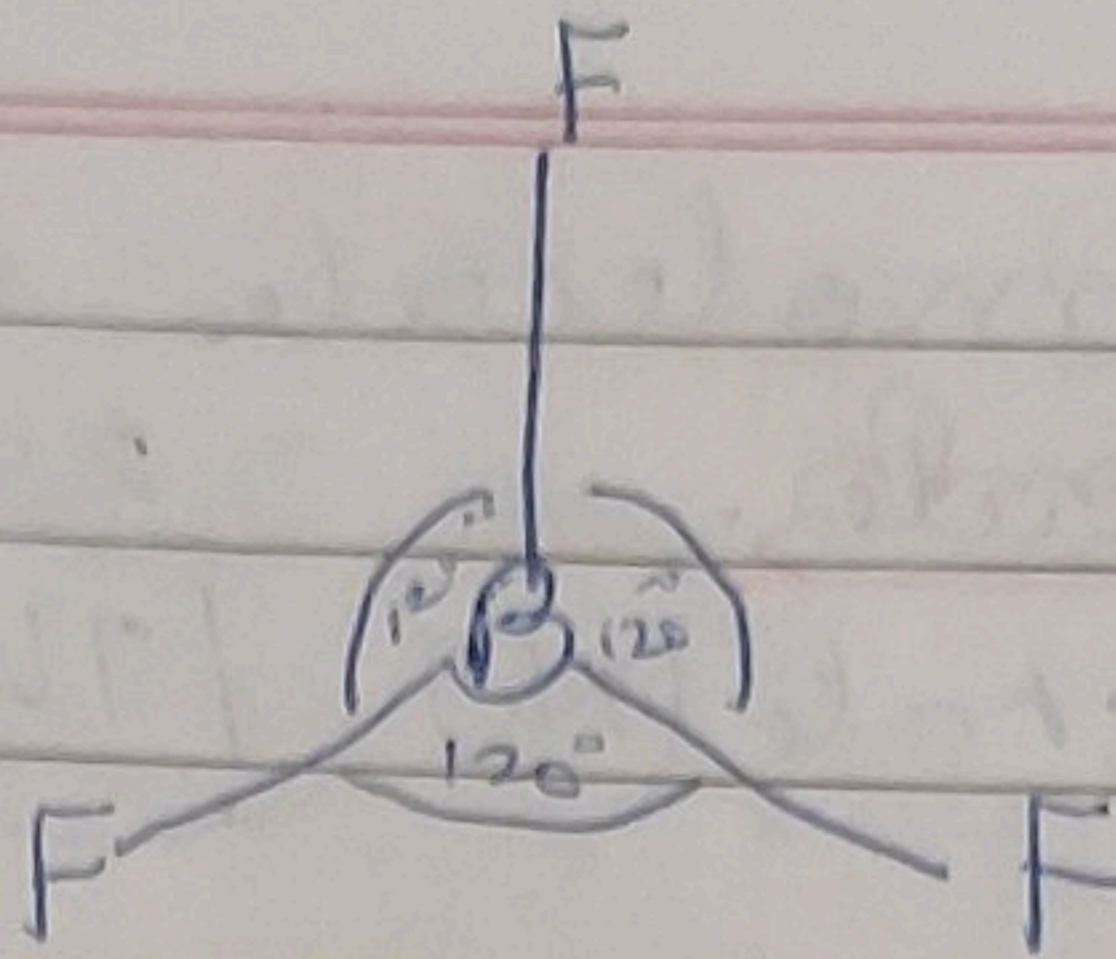
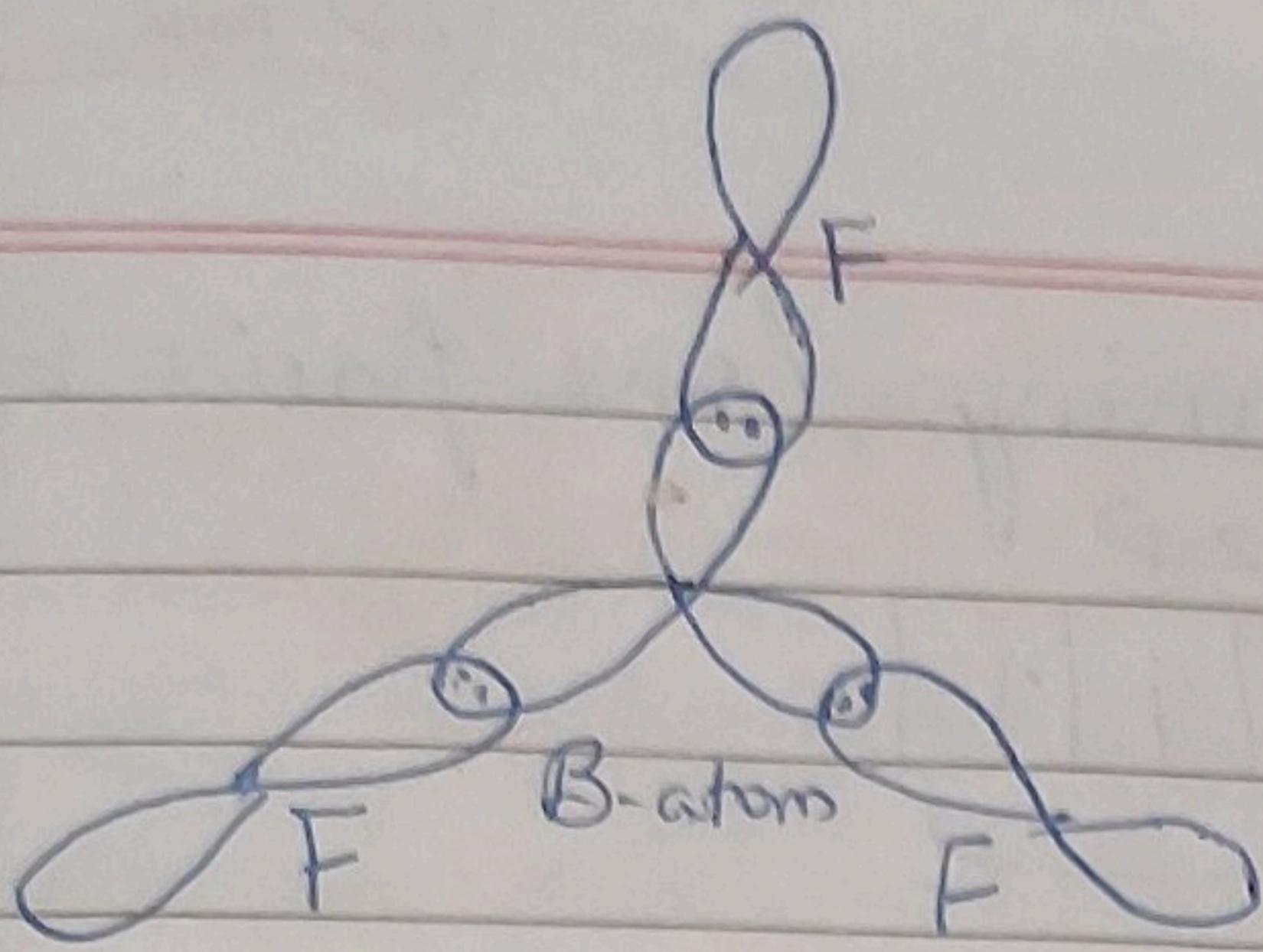


In  $Be$ , hybridization between s and p takes place. They overlap with two F atoms.



$B = 5$





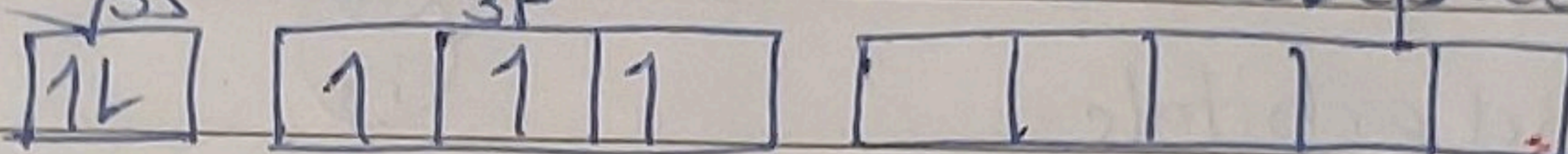
3) PCl<sub>5</sub> molecule:

$$P = 1s^2, 2s^2, 2p^6, 3s^2 3p^3$$

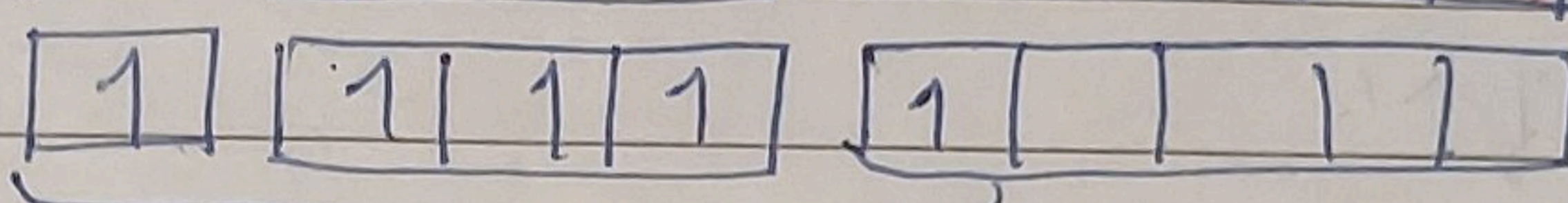
$$= 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$$

To get pentavalency, 3s-orbital is unpaired

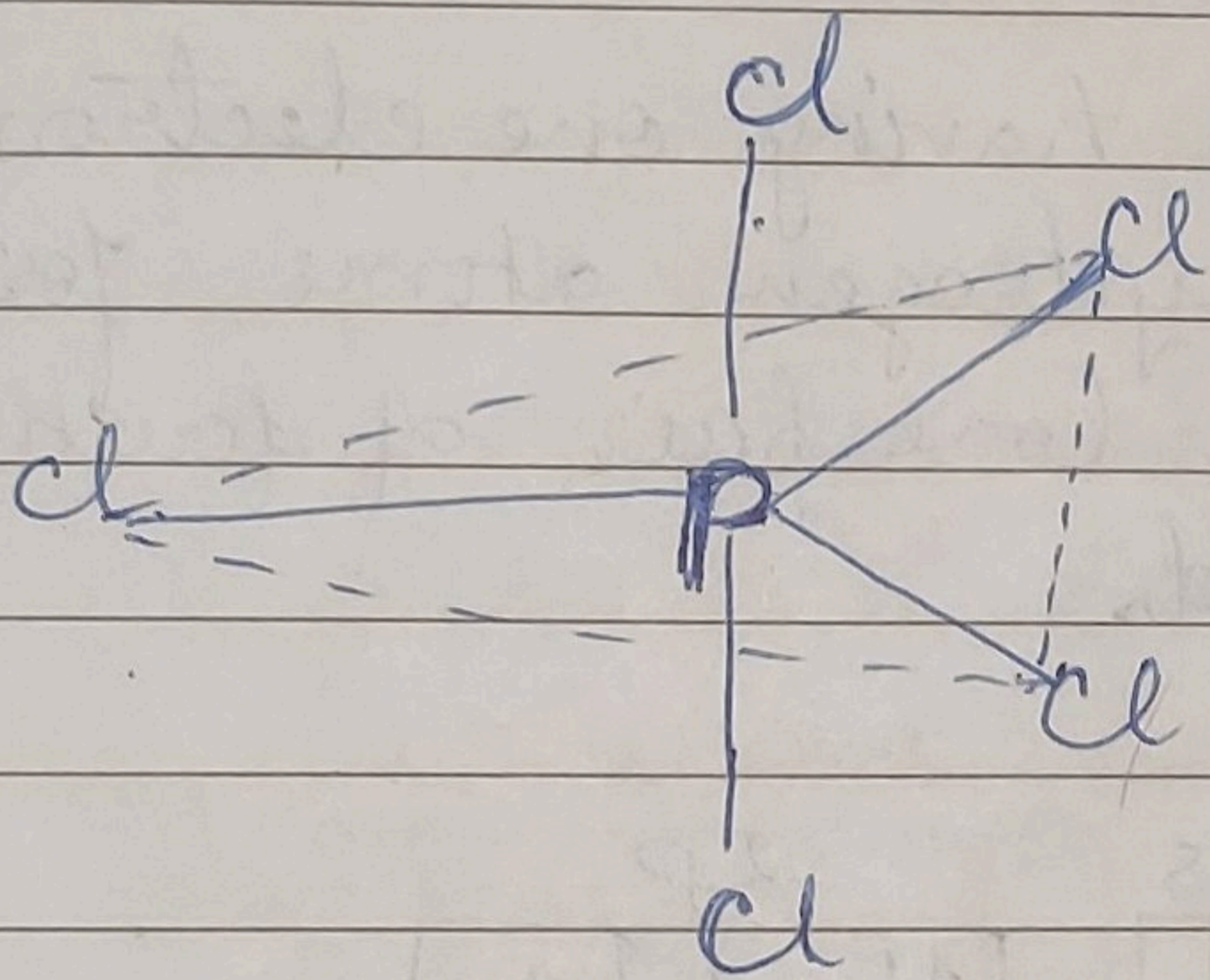
Ground state



Excited state



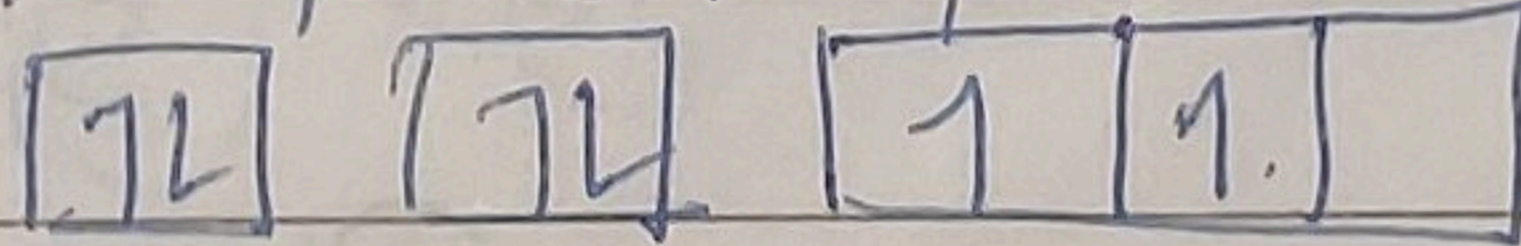
sp<sup>3</sup>d hybridization



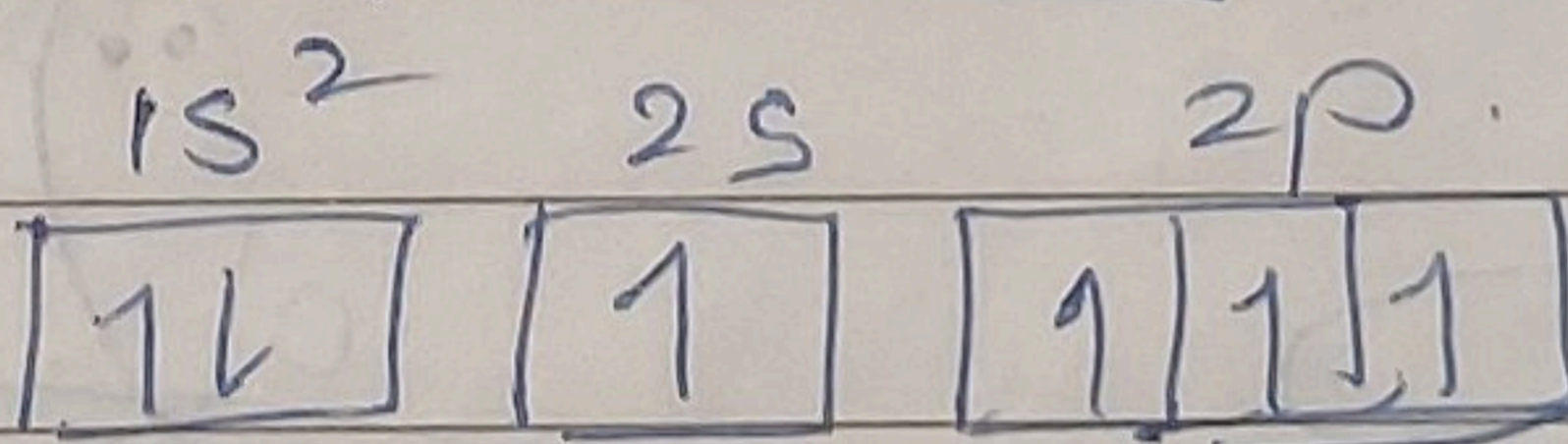
Trigonal bipyramidal

4) CH<sub>4</sub>

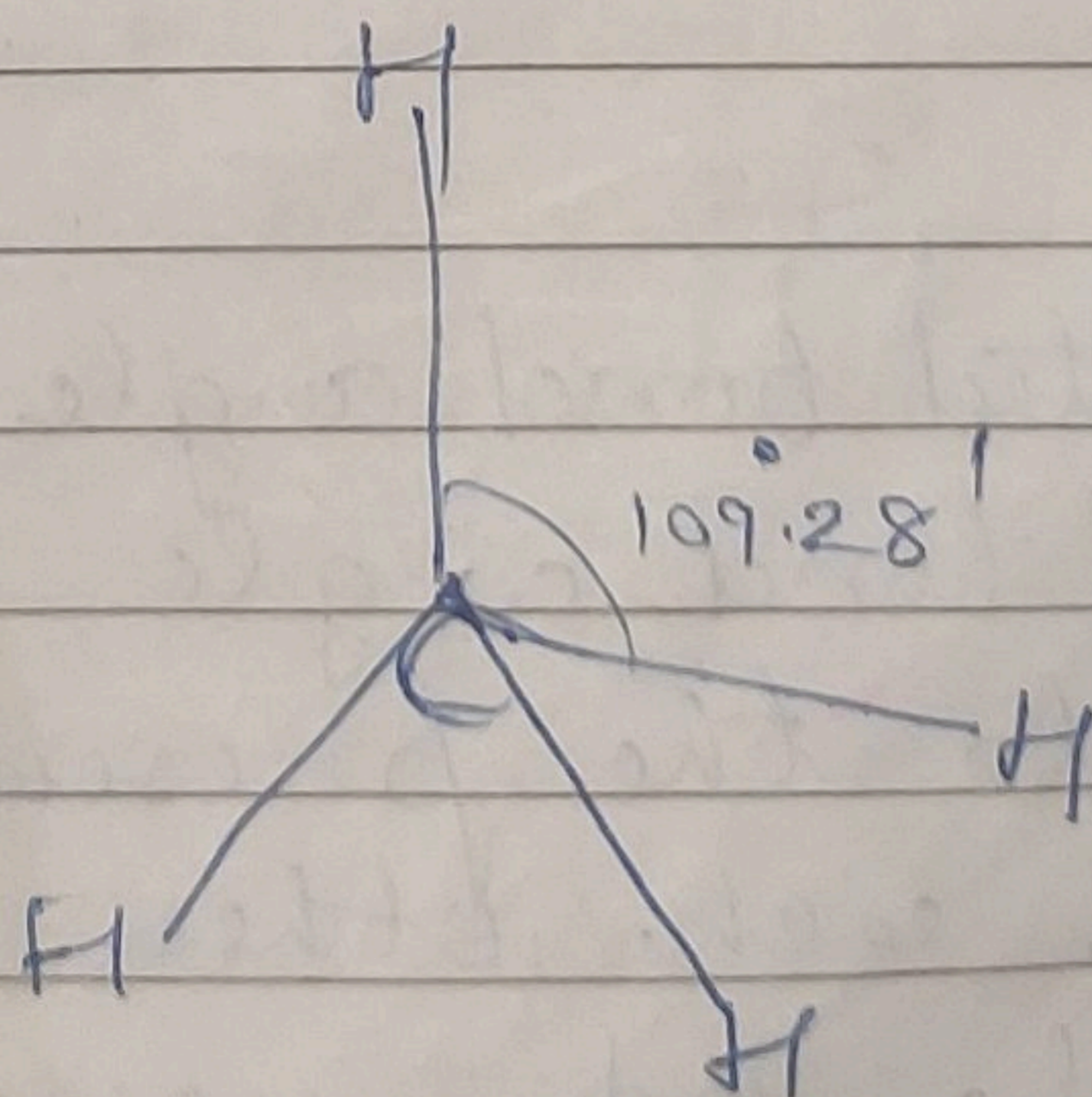
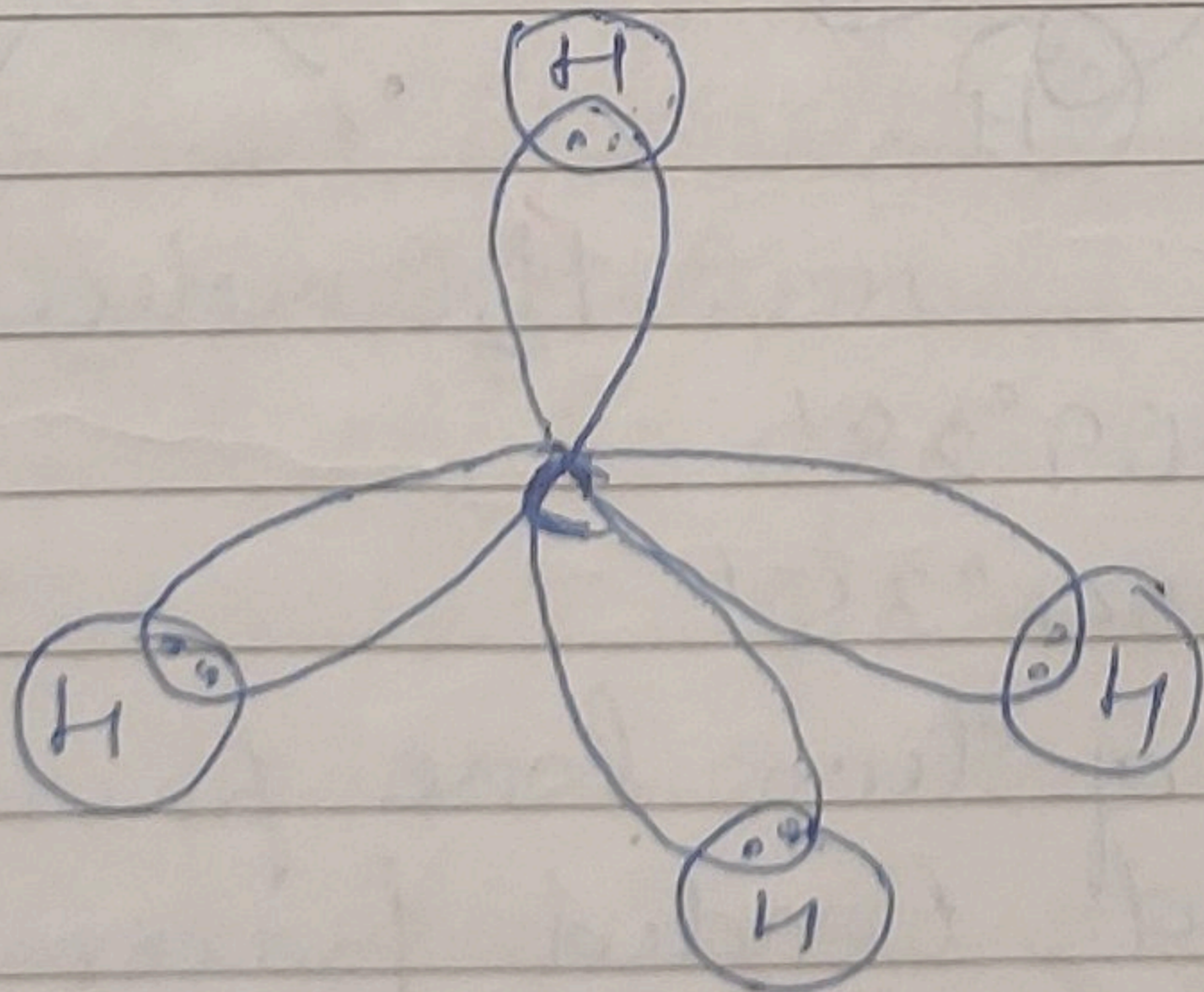
$$C = 1s^2, 2s^2, 2p^2$$



To get tetravalency



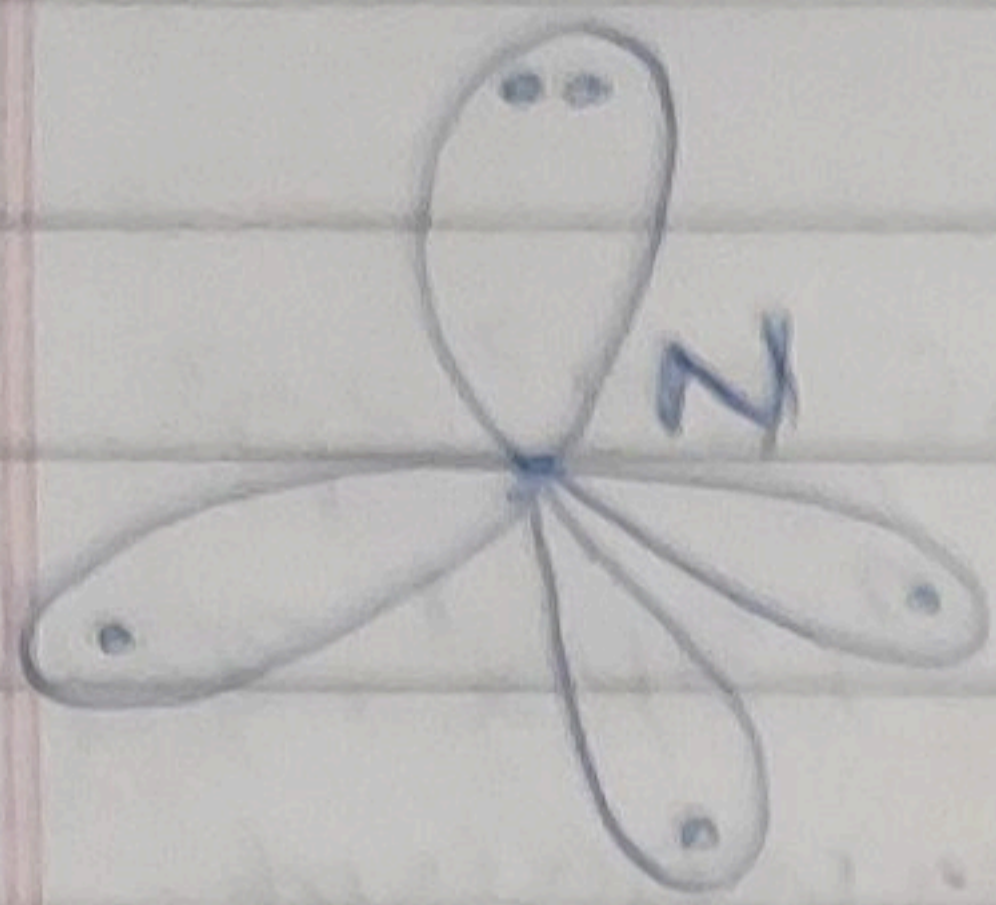
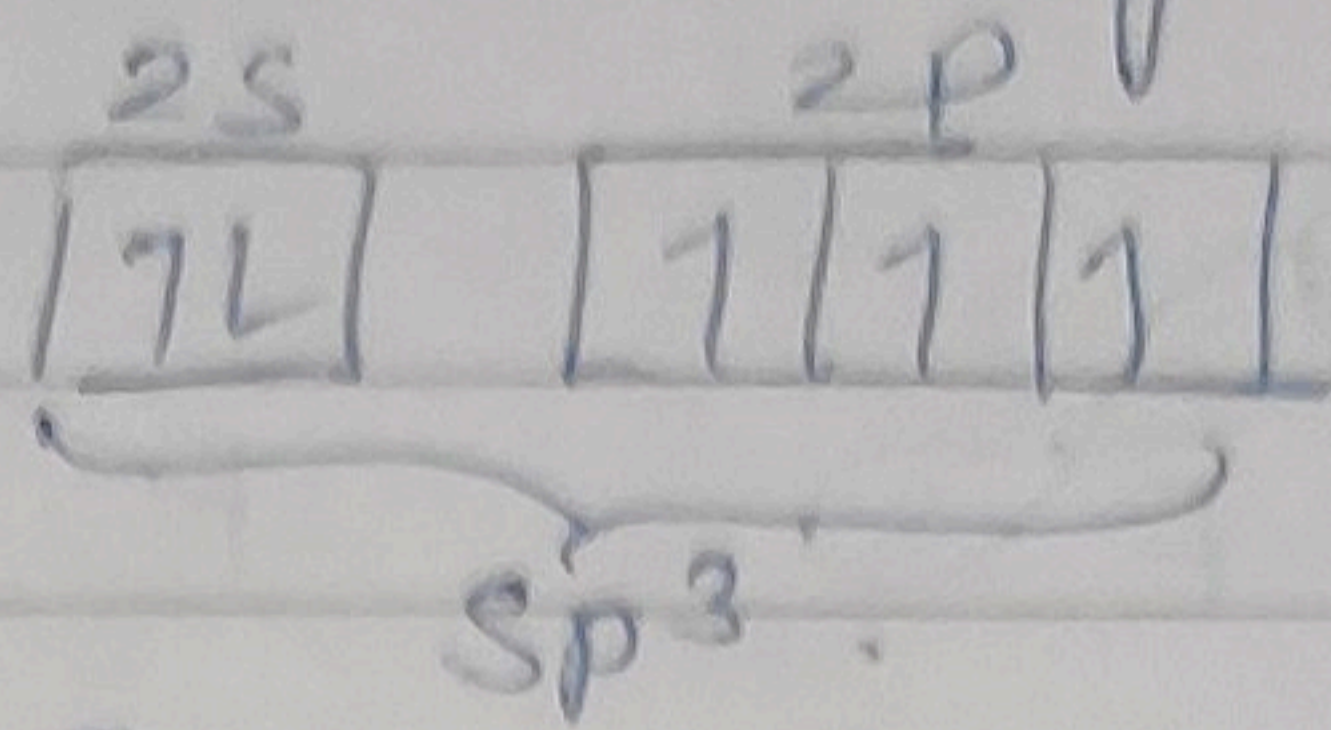
sp<sup>3</sup> hybridization



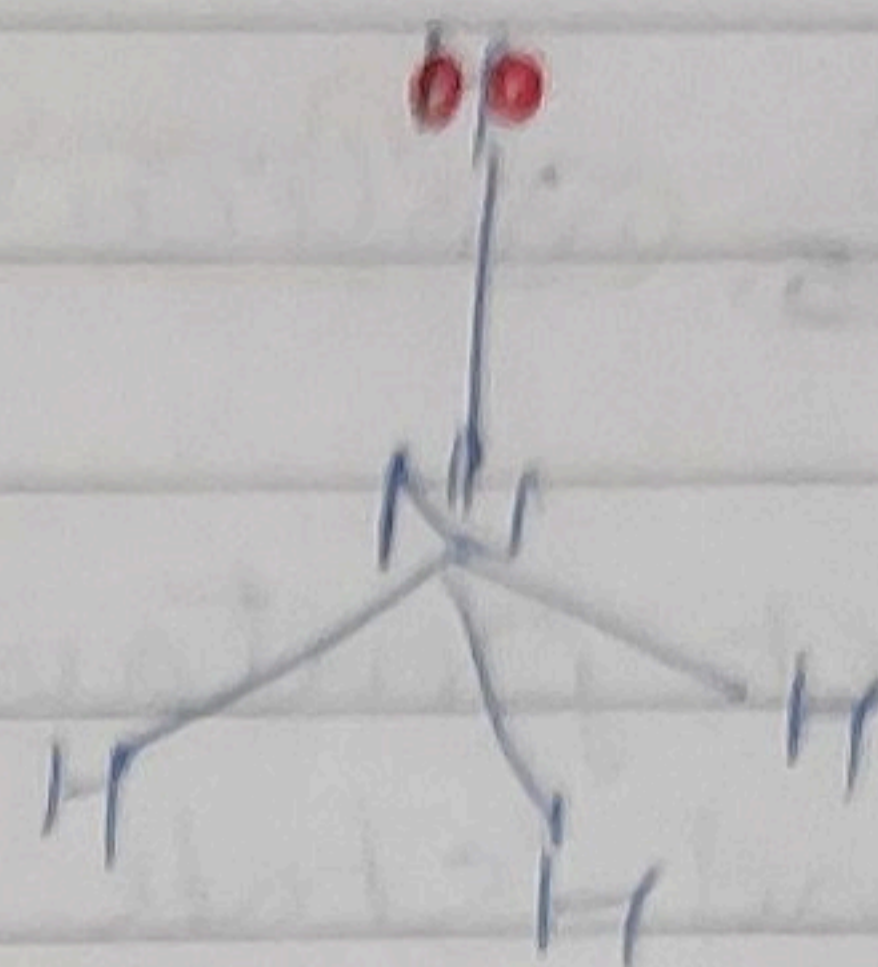
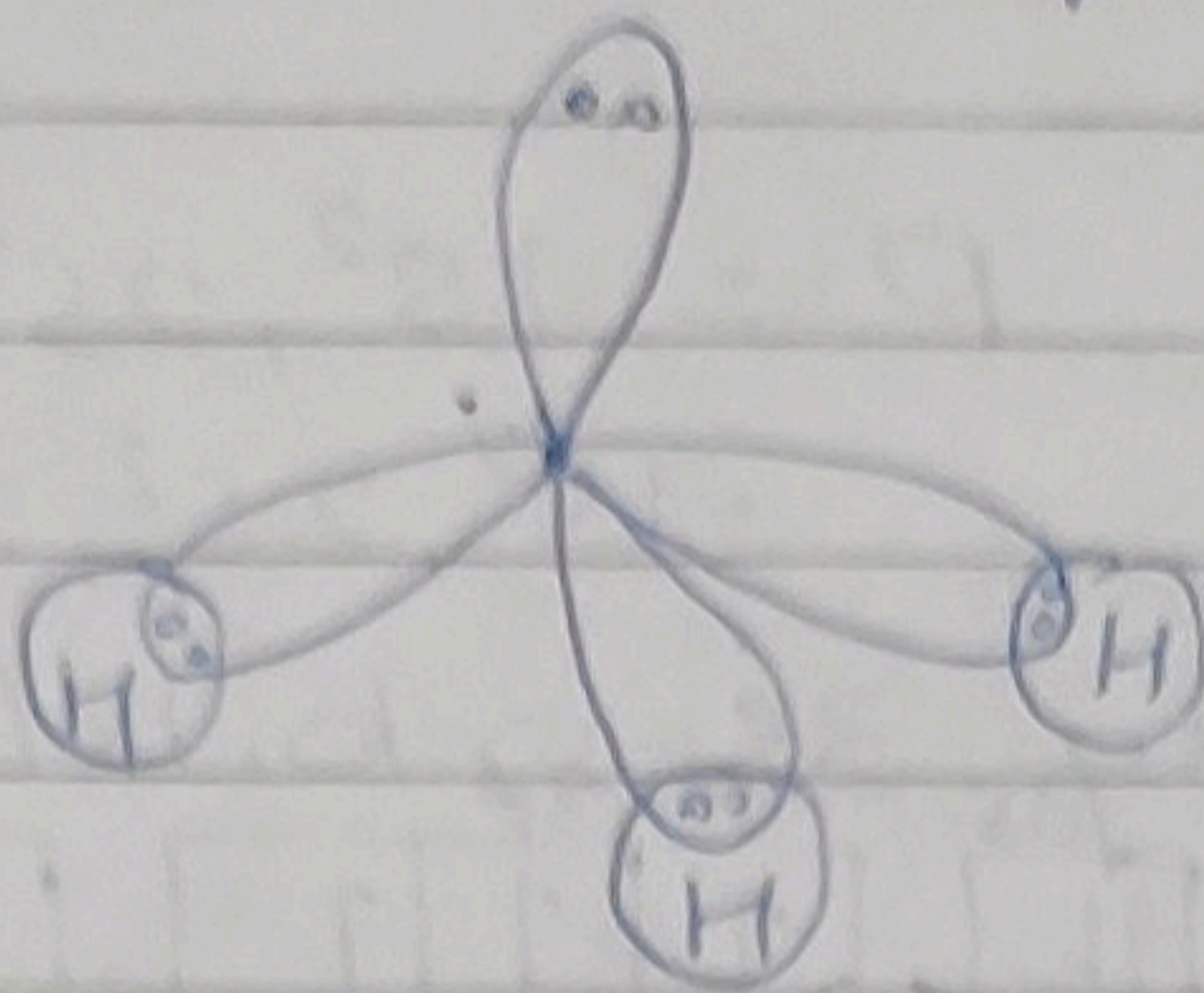
Geometry of molecules containing lone pairs of electrons

(1)  $\text{NH}_3$  molecule.

Ground state (N)



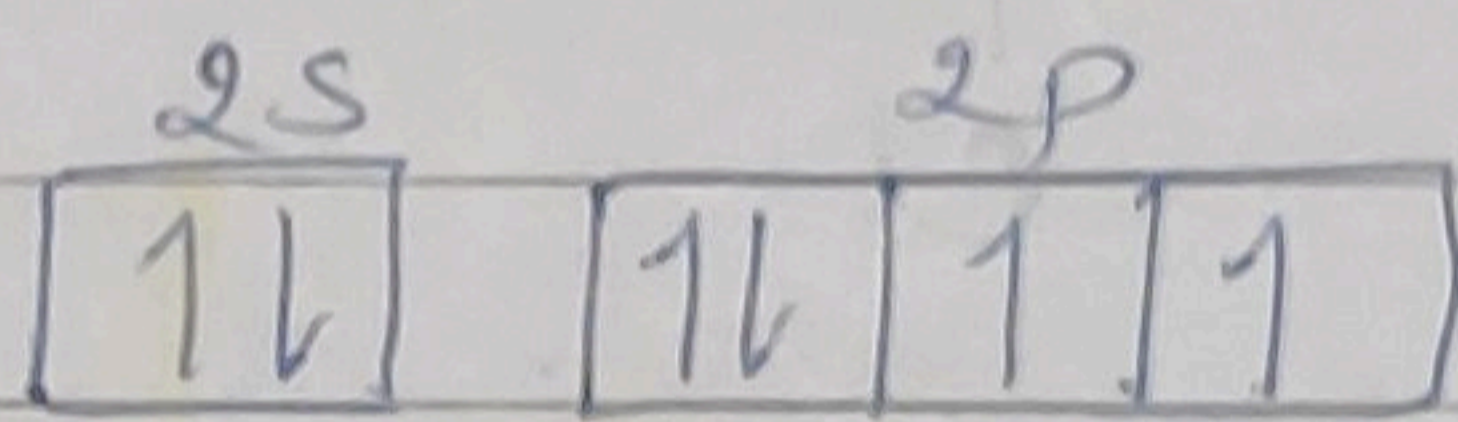
Hybrid orbitals of N.



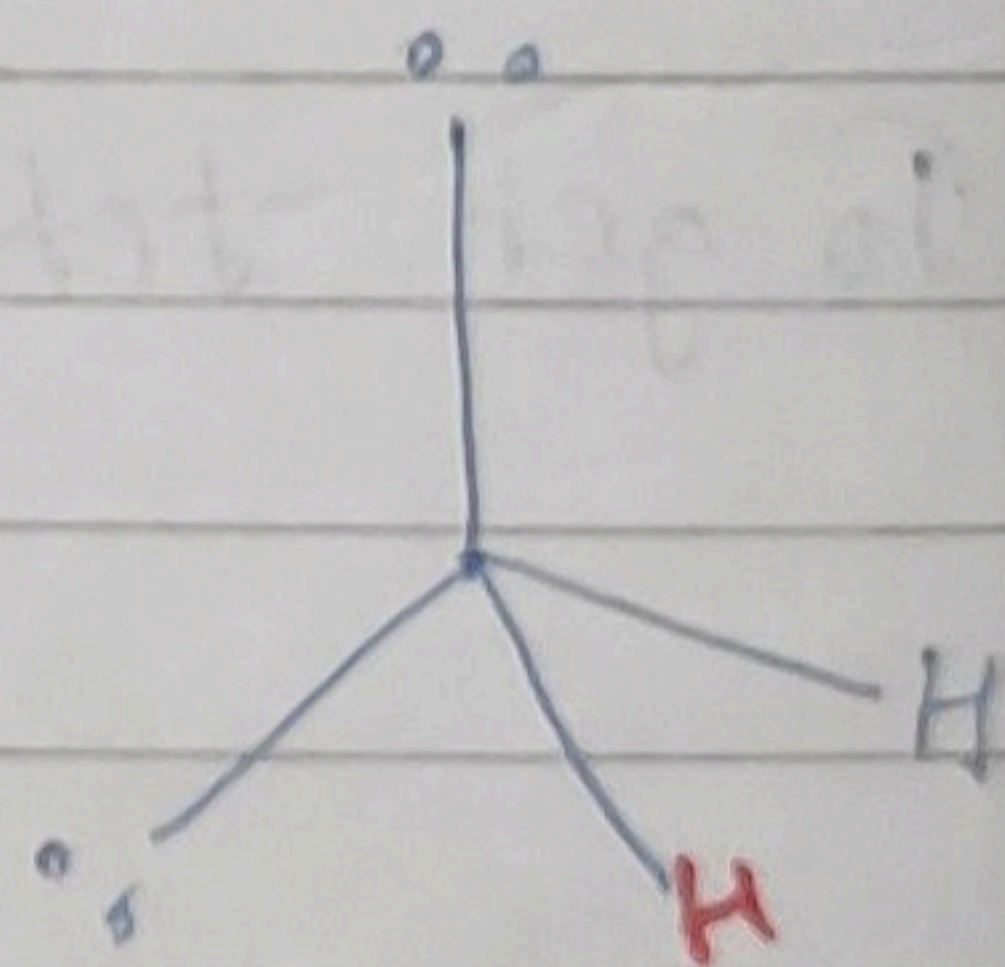
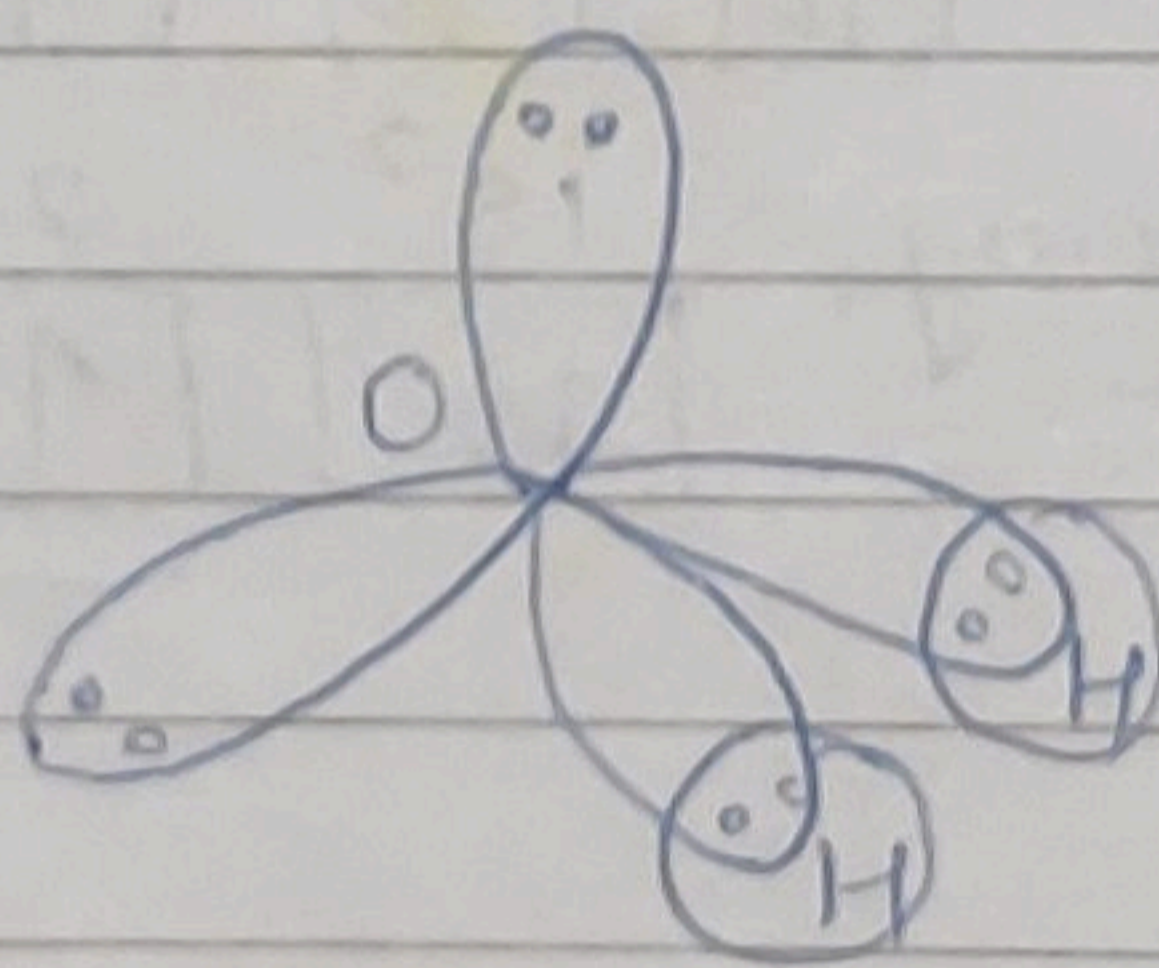
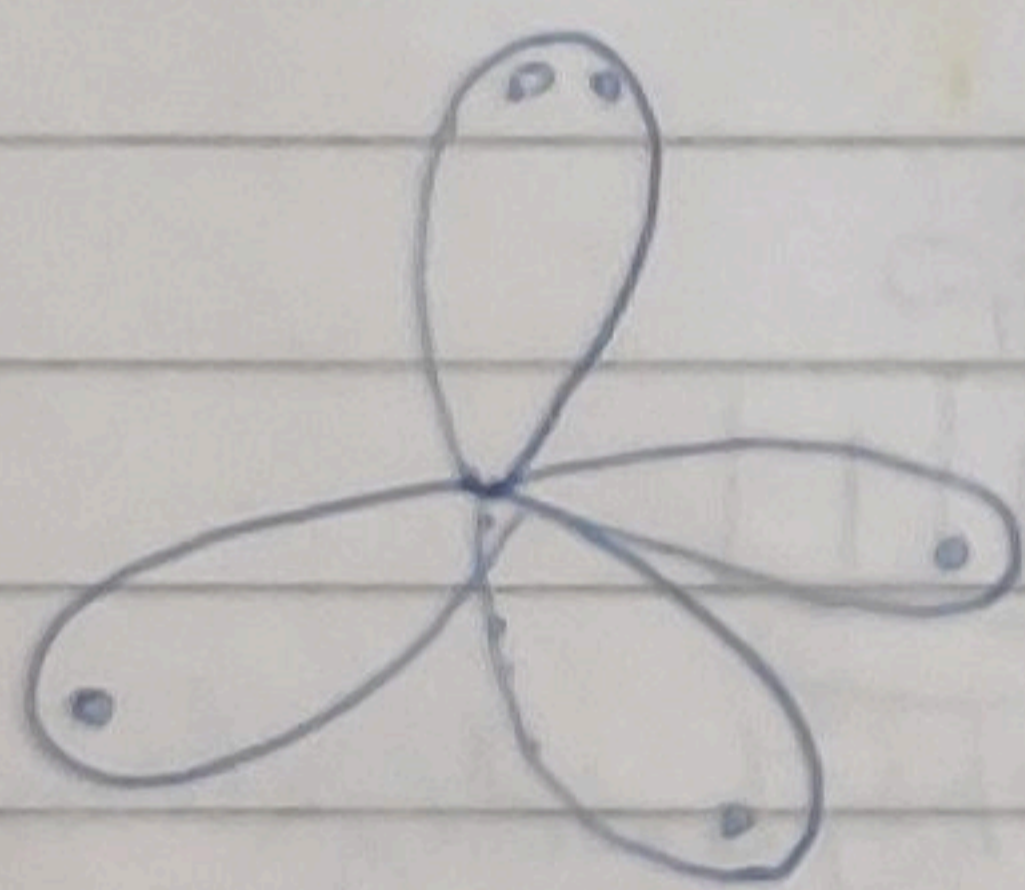
(2) Three hybrid orbitals having one electron each overlap with three hydrogen atoms forming three sigma bonds while the lone pair of fourth hybrid orbital remains unused.

(2) Water molecule.

O ground state



$sp^3$  hybridization



$\text{H}_2\text{O}$  molecule (V-shaped)

Expected bond angle =  $109^\circ 28'$

actual bond angle =  $104^\circ 35'$

due to the presence of two lone pairs which repel each other and bonded pairs more strongly and cause them to come closer and thereby reducing the bond angle from  $109^\circ 28'$  to  $104^\circ 35'$ . "Higher the number of lone pairs present on a central atom, the greater is the contraction caused in the bond angle."

Other examples

- $\text{PCl}_3, \text{NF}_3,$
- $\text{H}_2\text{S}, \text{PH}_3,$
- etc.



# Molecular Orbital Theory :

(By Hund and Mulliken in 1932.)

Molecular orbital is defined as the region in space comprising the nuclei of the combining atoms around where there is maximum probability of finding the electron density.

## Salient features :

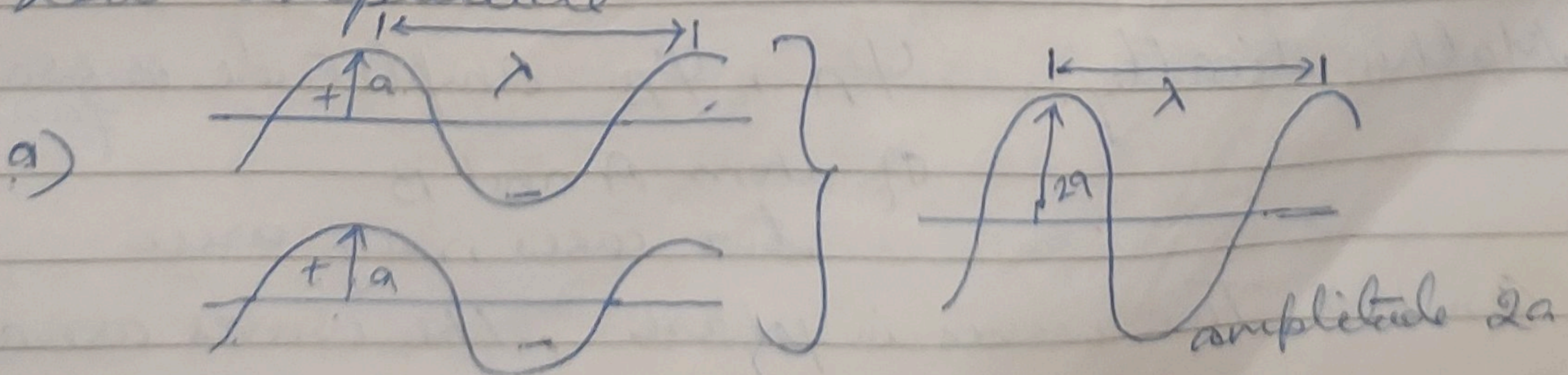
- 1) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- 2) The atomic orbitals of comparable energies & proper symmetry combine to form molecular orbitals.
- 3) Atomic orbital is monocentric while a molecular orbital is polycentric.
- 4) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding.

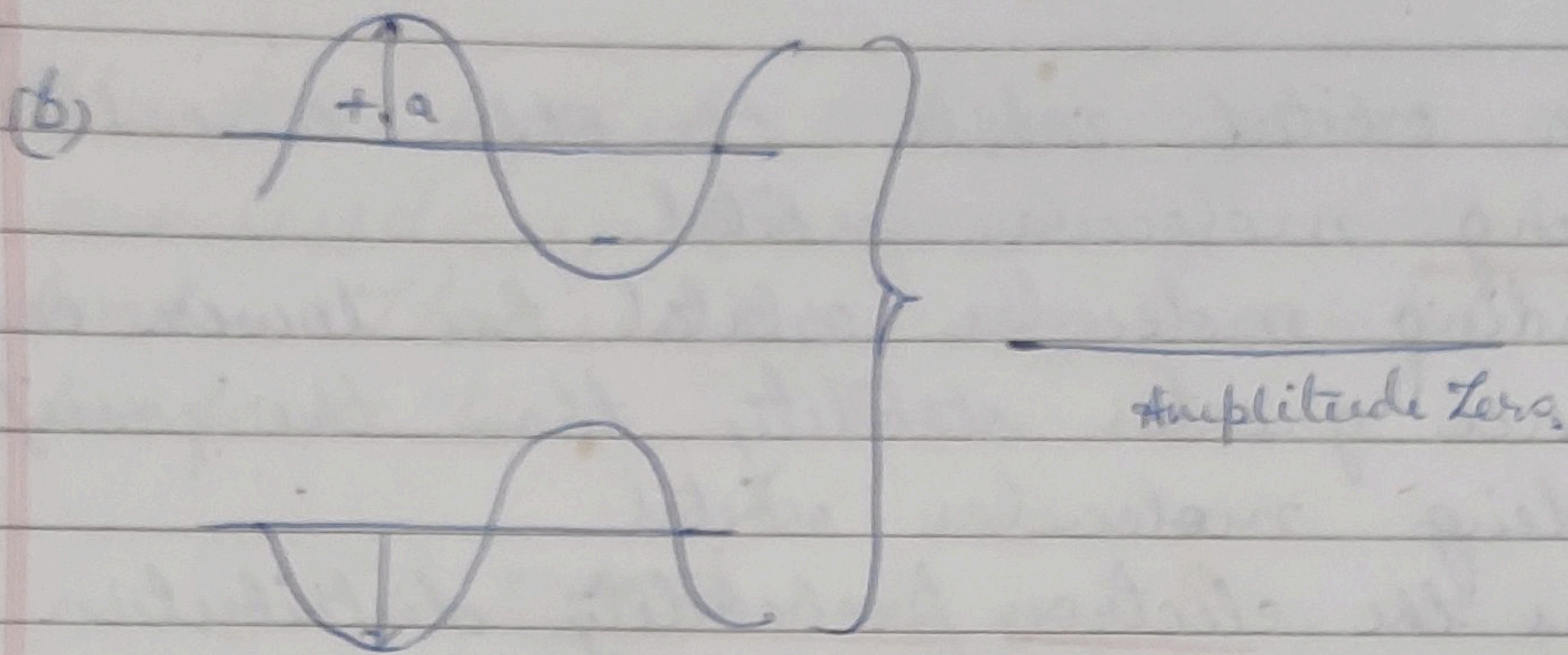
molecular orbital while the other is called antibonding molecular orbital.

- 5) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- 6) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- 7) The molecular orbitals like atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

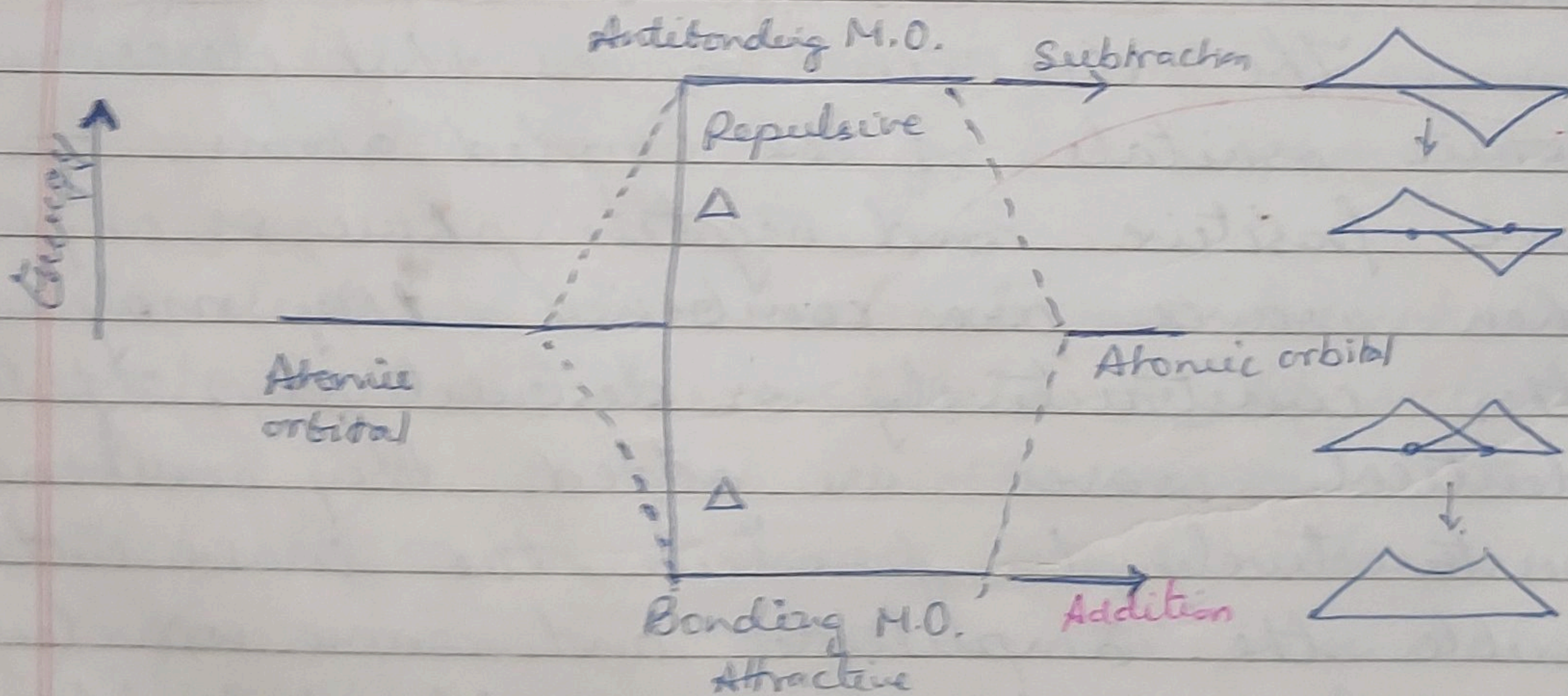
### Linear combination of Atomic orbital (LCAO)

The electron waves that describes the atomic orbitals of the bonded atoms. ~~The~~ electrons have positive and negative phase or amplitude. When waves are combined, they may interact either constructively or destructively. If two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wavelength. Conversely, if they are subtracted, they combine destructively to produce the wave with zero amplitude.





When two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase (constructive interaction) between two nuclei and a bonding orbital is produced. When they overlap out of phase (destructive interference) reduces the probability of finding an electron in the region between the nuclei & antibonding orbital is produced.



## Energy level diagrams for molecular orbitals

1) The energies of the atomic orbitals involved in the formation of molecular orbitals

$$1s < 2s < 2p.$$

within the same pair bonding molecular orbital has lower energy than the antibonding M.O.

2) The extent of overlapping between the atomic orbitals.  $\Rightarrow$

greater the overlap, more the bonding orbital is lowered and antibonding orbital is raised in energy relative to atomic orbital.

$2p$  orbitals form six molecular orbitals bet<sup>n</sup> two atoms  
Bonding orbitals  $\Rightarrow \sigma_{2p_z}, \pi_{2p_x}, \pi_{2p_y}$

Antibonding orbitals  $\Rightarrow \sigma^*_{2p_z}, \pi^*_{2p_x}, \pi^*_{2p_y}$

The energy levels of these MO's have been determined experimentally by spectroscopic methods.

The energy levels of M.O have been determined experimentally by spectroscopic methods.

$\pi 2p_x$  and  $\pi 2p_y$  have equal energy

$\pi^* 2p_x$  and  $\pi^* 2p_y$  have equal energy

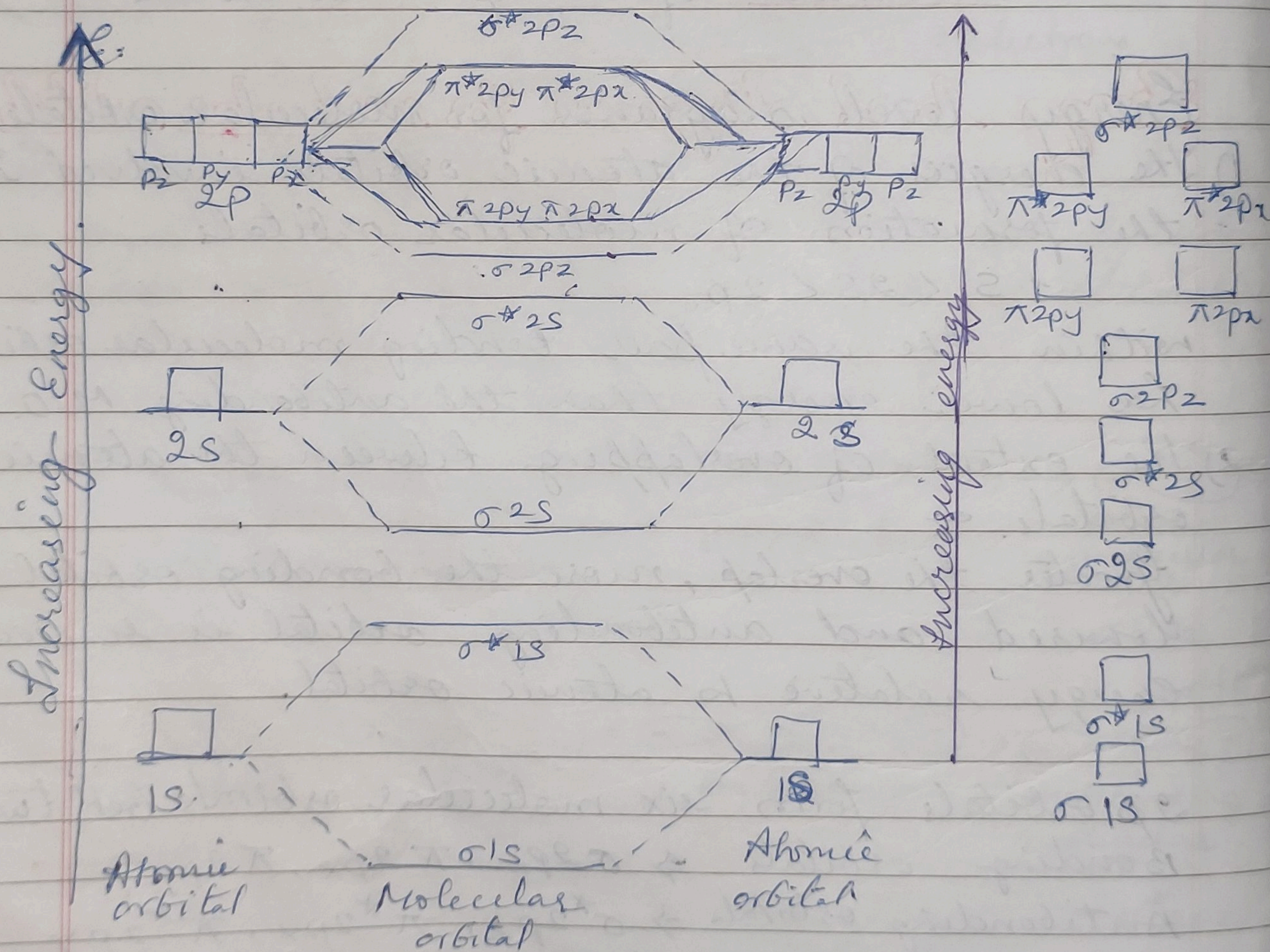
$\sigma^* 2p_z$  has maximum energy among the six 2p molecular orbitals

$\sigma 2p_z$  energy is not definite.

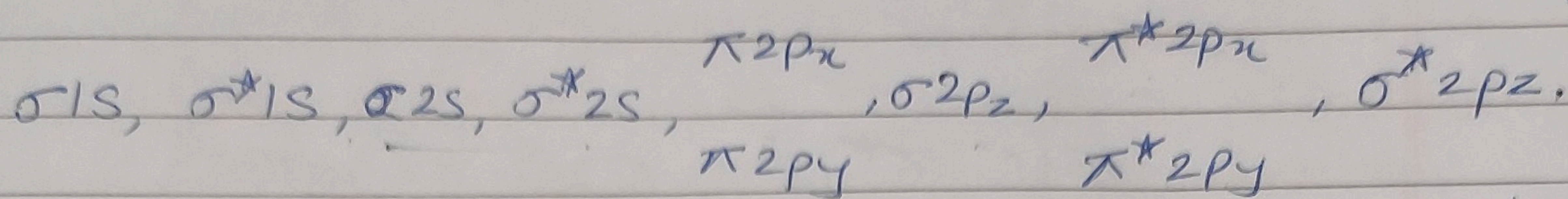
For diatomic molecules  $Li_2, Be_2, B_2, C_2, N_2$ .

energy  $\sigma 2p_z$  is higher than  $\pi 2p_x$  or  $\pi 2p_y$ ,

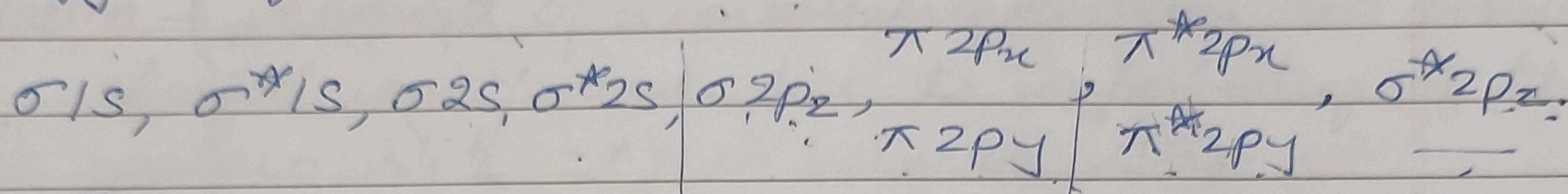
while for  $O_2, F_2, Ne_2$  energy of  $\sigma 2p_z$  is lower than  $\pi 2p_x$  or  $\pi 2p_y$ .



Energy diagrams for first ten MO's for diatomic homonuclear molecules such as  $\text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2$



Energy diagram for  $\text{O}_2, \text{F}_2, \text{Ne}_2$ ,



Rules for filling MO's with electrons Accord. to

- i) Aufbau principle
- ii) Pauli's exclusion principle
- iii) Hund's rule.

Bond order: Defined as one half of the difference between the number of electrons present in the bonding and the antibonding orbitals, i.e.

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

Stability of molecules: A molecule is formed only when the total energy of the system decreases. This is only possible when bonding electrons are more than antibonding electrons.

Magnetic nature: If electrons are paired, then nature is diamagnetic, if electron is unpaired, then it is paramagnetic.