CHAPTER # 3

THEORY OF COVALENT BONDING AND SHAPES OF MOLECULES

QI. Briefly give the introduction of

VSEPR theory

i. valence bond theory (VBT)

ii. Molecular orbital theory (MOT)

Ans: i. **VSEPR Theory:**

VSEPR (valence shall, electron pair repulsion) model, which allows us to connect two dimensional Lewis structures into three dimensional shapes.

ii. Valence bond theory (VBT}:

Valence bond theory explains how the observed shape arises from the interactions of atomic orbitals.

iii. Molecular orbital theory {MOT):

Molecular orbital theory proposes the existence of orbit 3s that extend over the whole molecule.

Q2. Briefly describe the limitations of Lewis concept for the formation of covalent bond.

Ans: Limitations of Lewis Concept:

The Lewis concept of covalent bond as a shared pair of electrons between two atoms do not provide much help in determining the shapes and geometry of molecules. Similarly, many other properties such as bond energy, relative strengths of bonds, and Para magnetism cannot be explained on the basis of his concept.

Q3.list the different theories of Covalent Bonding.

Ans: Covalent bonding:

The modern theories which are used to understand the nature of Covalent bonding also help to determine the shapes of the molecules are.

(i) The valence shell electron pair repulsion **(VSEPR)** pronounced as "Vesper" theory

Q4. Highlight: The Valence Shell Electron Pair Repulsion Theory.

Ans: The Valence Shell Electron Pair Repulsion Theory:

This theory was suggested by Sedgewick and Powell (1910). According to VSEPR theory, the shapes or geometry of a molecule or ion depend on the number of shared pairs as well as the lone pairs of electrons around the central atom of the molecule or ion.

Gillespie and Nyholm in 1957 proposed that the arrangement of atoms in a molecule is mainly determined by the repulsive interactions among all electron pairs in the valence shell of central atom. They named this theory Valence Shell Electron pair Repulsion Theory (VSEPR).

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". The arrangement of electron pairs in the manner gives minimum energy and maximum stability to the molecules or ion.

Before, we discuss the shapes and geometry of the molecules with the help of VSEPR theory.

Q5. Define and explain central atom and how can we predict central atom?

Ans: Central Atom:

"An atom in a molecule to which all other atoms are attached is called a central atom".

Finding the central atom in a molecule or ion:

Keep in view the following points for finding the central atom in a molecule or ion.

i. Electronegativity:

Generally, the atom with the lowest electronegativity is the central atom in a a central atom when attached with O atom or more electronegative halogens. 0 atoms are not at the center unless it is combined with two other atoms as in H_2O or OF_2 or H-O-Cl

iii. Binary covalent compounds:

For binary (two elements) covalent compounds and polyatomic ions. the central atom is the one that appears only once in the formula.

it should be remembered that the bending within all polyatomic ions is covalent

Formula	central atom	formula	Central atom	formula	Central atom
i.$BeCl_2$	Be	i. SO_3	S	i. PO_4^3	P
ii.CS_2	C	ii. NH_3	N	ii.NH_4	N
iii. SO_2	S	iii. PCl_3	P	iii. SO_4^2	S
iv. H_2S	S	iv. SiH_4	Si	iv. CrO_4^2	Cr

iv. Oxy acids

for oxy acids the atom other than H or O is the central atom

Formula	central atom	Formula	central atom
i. $HClO_2$	Cl	i. H_2SO_3	S
ii. $HClO_3$	Cl	ii. H_2SO_4	S
iii. HNO_3	N	iii. $HClO_4$	Cl
iv. H_3BO_3	B	iv. H_3PO_4	P

v. Carbon containing compounds:

Carbon is the central atom in any Carbon containing compounds e.g. in CO_2, CH_4, CCl_4. the C atom is the central atom.

Q6. Define bond angle and explain causes of deviation in **bond angle.**

Ans: Bond Angle:

"The angle between adjacent chemical bonds is called bond angle"

Causes of Change in Bond Angle:

which in turn, changes the regular molecular geometry. The greater the number of Lone electron pairs on the central atom, the greater is the decrease in bond angles in the regular molecular geometry. This is because Lone pair will exert more repulsion on any adjacent electron pair then a bond pair on the same electron pair. The order of decrease in repulsion between electron pairs is,

Lone pair - **Lone pair** >**Lone pair** - **Bond pair** > Bond pair - Bond pair.

ii. Multiple bonds: (bond angle increases)

Bond angles involving multiple bonds are generally larger than those involving only single bonds. This is because the bended pairs of multiple bonds occupy more space than the one electron pair of a single bond. However, the multiple bonds do not affect molecular geometry.

iii. More electronegative atom present at neighbor (bond angle decreases):

If all the atoms bonded to the central atom are not identical, then the bond angles deviate to 3ame extent from the c in the regular geometry, because of the difference in size and electronegativity of atoms that are not identical. The bond angle decreases with the increase in the electronegativity of atom bonded with the central atom.

Q7. Explain electron pair geometry.

Ans: Electron pair Geometry:

The relative arrangement of electron pairs around a central atom in a \ molecule is called electron pair geometry. According to VSEF'R theory·

(i) If the central atom is surrounded by two electron pairs the geometry electron pairs will be linear and the angle between each electron will be180

(ii) If the central atom is surrounded by three electron pairs the geometry of the electron pairs will be triangular planer and the angle between each 81ectron pair i120°.

(iii) If the central atom is surrounded by four electron pairs, the geometry of the

Q8. Explain molecular geometry and in which conditions it can be different from electronic geometry?

Ans: Molecular Geometry:

"The relative arrangement of the bonded atoms: round a central tom in a molecule is called molecular geometry"

the molecular geometry depends upon the number of bonds and not on the number of electron pairs the molecular geometry may or may not be the same as the electron pair geometry. Keep in g point while determining the geometry of molecule

Conditions:

i. If there are no lone electron pairs on the central atom, then the electron pair geometry and molecular geometry are identical

ii. If all the electron around the central, atom are shared (bond pairs) then there is only one particular regular geometry.

"A structure of molecule in which the shared pairs around a central atom occupy identical positions in space is called a regular geometry".

iii. If there are lone pair of electrons around the central atom then only the arrangement of bonded atoms is considered in determining the molecular geometry. In this case, the molecular geometry will be distorted or irregular geometry.

iv. The multiple bonds do not affect molecular geometry, both pairs of electrons in a double bond behave like a group of two electrons in single bond or bond pair.

Q9. Define Geometry and molecular shape of a molecule.

Ans: Geometry or Shape of a Molecule:

A structure that minimizes the repulsion between the pairs of electrons around a central atom determines the geometry of a molecule.

Molecular Shape:

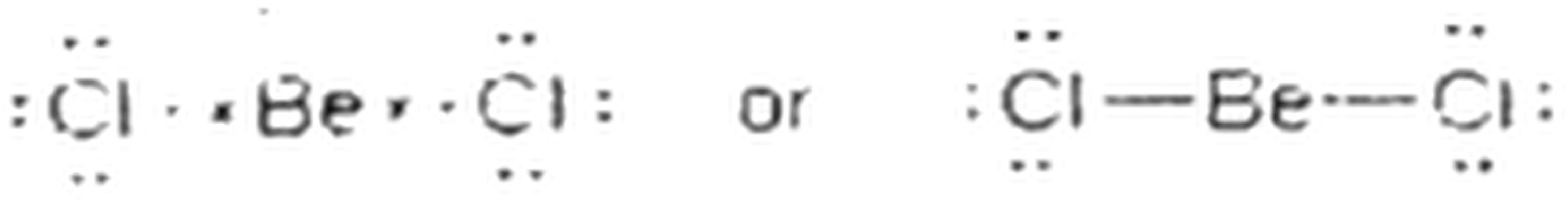
angles.

Q10. Use VSEFR theory to describe Shapes of molecules containing two election pairs around a central atom.

Ans: Shapes of molecules containing two electron pairs around a central atom

AB_2 type molecule:

A molecule having two bond pairs of electrons but no Lone pairs around a central atom always has a linear geometry, because such as arrangement of atoms keeps the two pairs as. For as possible Bond angle will be 180.



Bond angle 180°

Electronic geometry =linear

Molecular geometry =linear

Q11. Use VSEPR theory to describe Shapes- of molecules containing the-N electron pairs around a central atom AB1.

Ans: Shapes of molecules containing three electron -pairs around a central atom. AB_3:

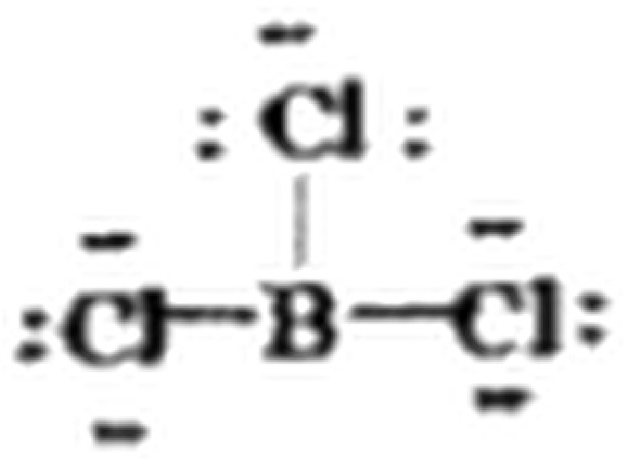
AB_3 type with no lone pair:

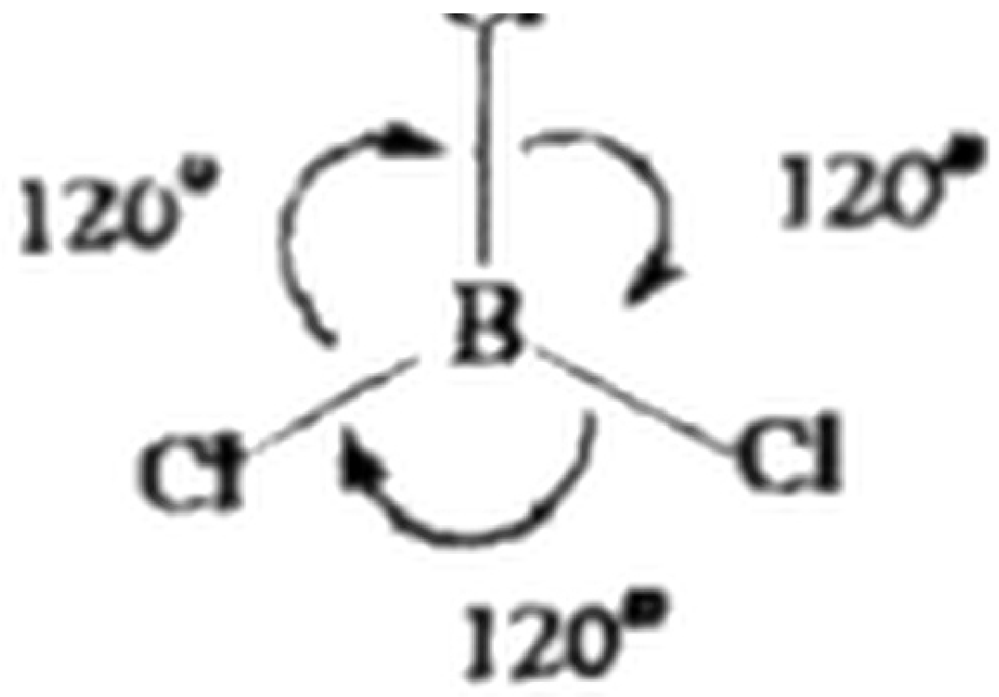
A molecule having three bond pairs of electrons but no tone pairs around a Central atom always has a planar triangular geometry, because such an arrangement of atoms keeps the three pairs of electrons as far apart as possible.

The bond angle will be 120°.

Example: (BCl_3):

Boron trichloride BCl_3) is a typical example of molecules. which contains three bond pairs of electrons.





Bond angle = 120°.

Electronic geometry= triangular planer

Molecular geometry = triangular planer

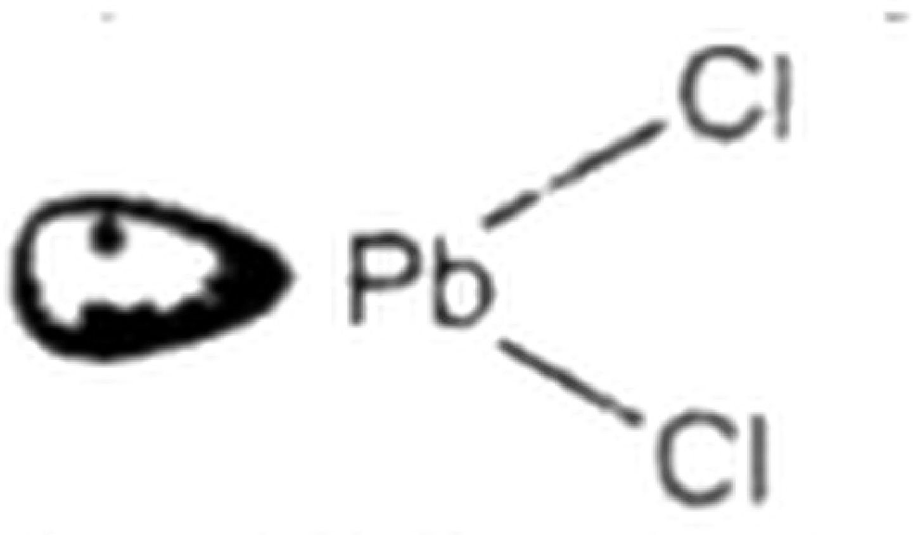
Other examples: AlH_3, $AlCl_3$. GaH_3, InH_3

Q12. Use VSIPR theory to describe AB2E- type with one Lone pair and Two bond pairs.

Ans: AB2E- type with one Lone pair and two bond pairs:

Examples: $PbCl_2$ molecule, $SnCl_2$ molecule

In case of $PbCl_2$ and $SnCl_2$ molecules, there are three electron pairs around the central atoms one lone pair and two bond pair. According to VSEPR concept. The Lone pair (non-lending of electron occupies more room and exerts a greater repels, on the bond pairs resulting in the shortening of Cl-Pb-Cl angle.

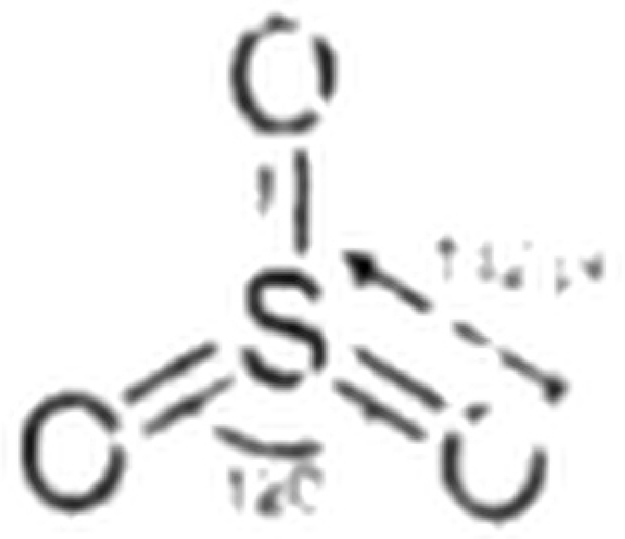


V. shaped $PbCl_2$ molecule

Thus, the shape of $PbCl_2$ molecule is distorted and becomes V-shape with Cl-Pb-Cl.

Bond angle = less than 120°. Electronic geometry = triangular planer

Molecular geometry = bent, angular, V-shape in SO_3 all the three regions each occupied by S-O bonds. No lone pair hence the shape will be



Bond angle= 120°.

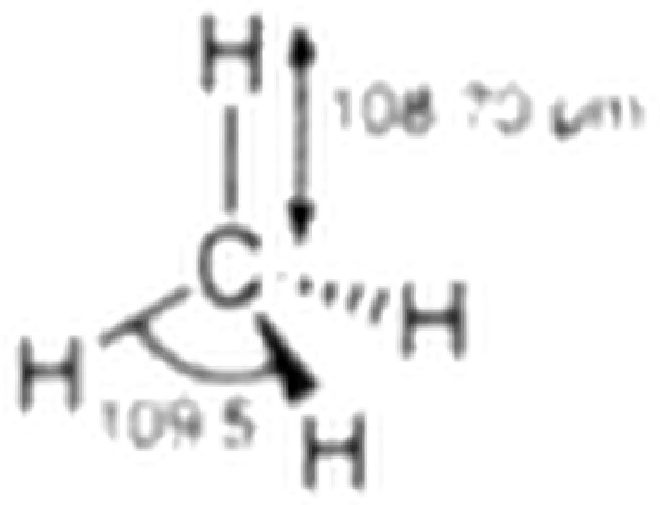
Electronic geometry = triangular planer

Molecular geometry = triangular plane

Q14. Use VSEPR theory to describe AB_4 type.

Ans: AB4 type:

A molecule having four bond pairs of electrons but no lone pairs around a central atom always has regular tetrahedron geometry, because such an arrangement of atoms keeps the four pairs of electrons as far apart as possible.



Bond angle=109.5°.

electronic geometry= tetrahedral

Molecular geometry=tetrahedral

Examples:CH4(Methane), CCl4 SiF_4, $SnCl_4$ etc.

Methane is a typical example of this type.

QI5. Use VSEPR theory to describe AB_3E type with one lone pair and three bond pair.

Ans: AB_3E type with one lone pair and three bond pair:

A molecule having three bond pairs and a lone pair around the central atom has

Bond angle= 107.8°.

Electronic geometry = tetrahedral Molecular geometry = triangular pyramidal

Example: NH_3 is a typical example.

Other Examples: PH_3, AsH_3, SbH_3, etc.

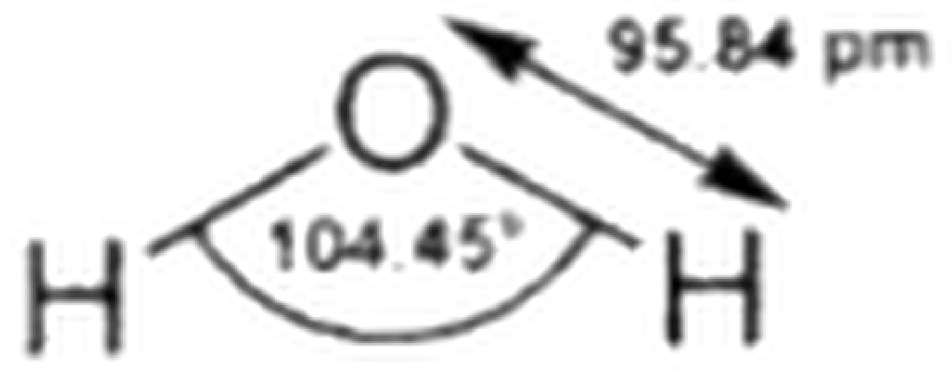
Q16. Use VSEPR theory to describe AB_2E2 type with two Lone pairs and two bond pairs.

Ans: AB_2E2 type with two Lone pairs and two bond pairs:

In this case, presence of two Lone pairs, introduces three type of repulsion i.e. lone pair-lone pair, lone pair-Bond pair and bond pair - bond pair repulsion.

Example: H_2O.H_2S etc.

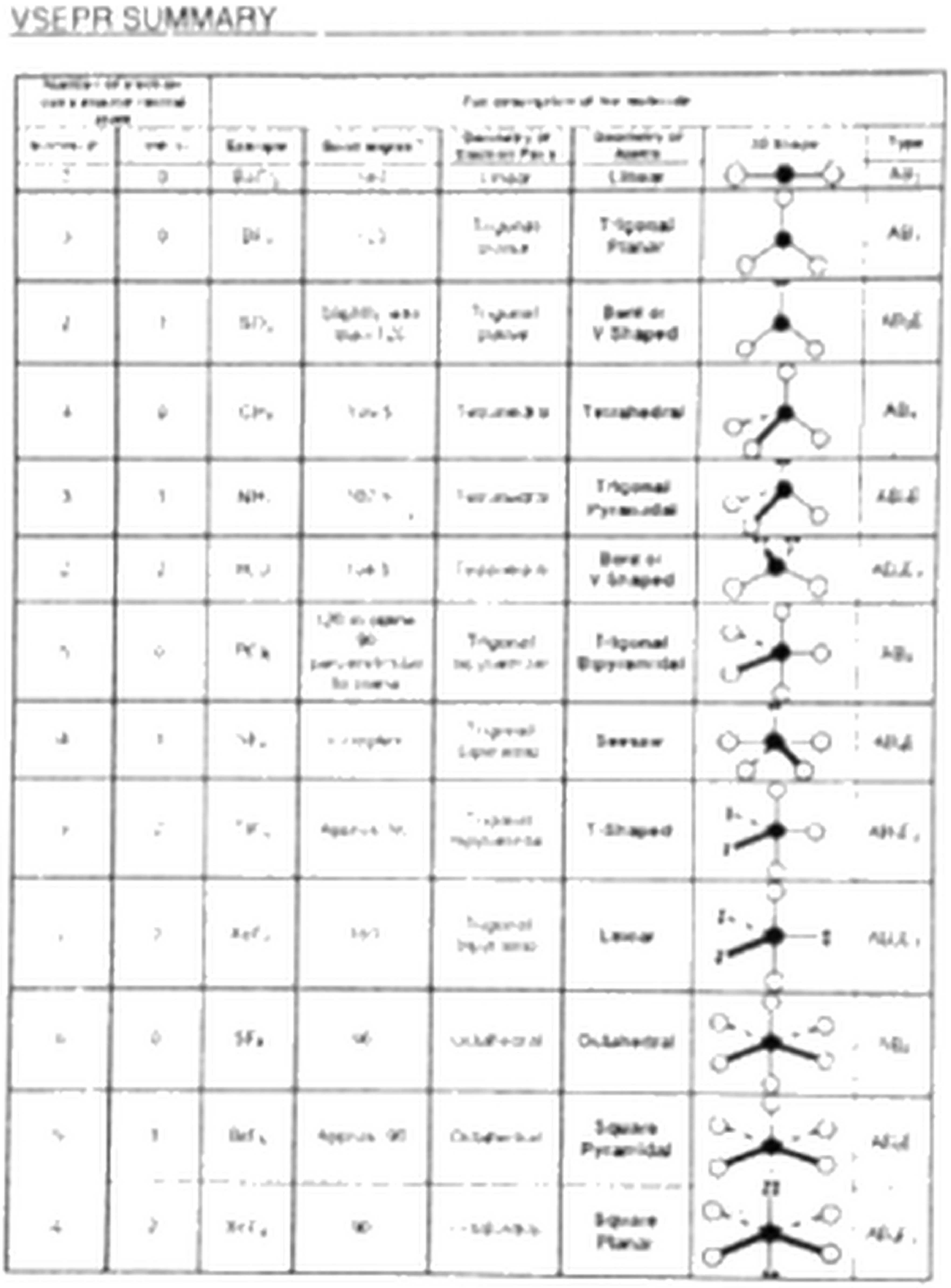
VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pair in addition to bond pairs in determining overall geometry of water molecule. Two of the comers of a tetrahedron are occupied by each of the two lone pairs and remaining by and pairs. But due to spatial arrangement of lone pairs and their repulsion among themselves and with the bond pairs, the bond angle is further reduced to 104.5° and V shaped.



Bond angle= 104.5°

Electronic geometry = tetrahedral

Molecular. Geometry = V shape, Bent, Angular



VSEPR SUMMARY

Number of electron pairs around central atom		Full description of the molecule					
bonding	lone	Example	Bond angles°	Geometry of Electron Pairs	Geometry of Atoms	3D Shape	Type
2	0	$BeCl_2$	180	Linear	**Linear**		AB_2
3	0	BF_3	120	Trigonal planar	**Trigonal Planar**		AB_3
2	1	SO_2	Slightly less than 120	Trigonal planar	**Bent or V Shaped**		AB_2E
4	0	CH_4	109.5	Tetrahedral	**Tetrahedral**		AB_4
3	1	NH_3	107.5	Tetrahedral	**Trigonal Pyramidal**		AB_3E
2	2	H_2O	104.5	Tetrahedral	**Bent or V Shaped**		AB_2E_2
5	0	PCl_5	120 in plane 90 perpendicular to plane	Trigonal bipyramidal	**Trigonal Bipyramidal**		AB_5
4	1	SF_4	complex	Trigonal bipyramidal	**Seesaw**		AB_4E
3	2	ClF_3	Approx. 90	Trigonal bipyramidal	**T-Shaped**		AB_3E_2
2	3	XeF_2	180	Trigonal bipyramidal	**Linear**		AB_2E_3
6	0	SF_6	90	Octahedral	**Octahedral**		AB_6
5	1	BrF_5	Approx. 90	Octahedral	**Square Pyramidal**		AB_5E
4	2	XeF_4	90	Octahedral	**Square Planar**		AB_4E_2

Q17.Use VSEPR theory to describe Molecules containing five electron pairs AB_5-type

Ans: Molecules containing five electron pairs AB_5 type:

With the increasing number of electron pairs, it becomes increasingly difficult to visualize the true shapes of the molecules. Thus, a central atom containing five electron pairs presents a more complicated system. A trigonal bipyramidal arrangement - represents a structure in which five electron pairs can have minimum repulsion in PCl_5, there are five electron pairs in the valency shell of phosphorus atom. All of them are bonding pairs and thus, PCl_5 molecule adopts trigonal bipyramidal structure,

Electronic geometry= trigonal bipyramidal

Molecular geometry =trigonal bipyramidal

Examples: $AsCl_5$, $SbCl_5$

Q18. Use VSEPR theory to describe Molecules containing six electrons pairs (AB-type).

Ans: Molecules containing six electron pairs (AB-type):

Molecules, in which the central atom has six electron pairs, adopt Octahedral geometry. The examples of such molecules or ions are SF_6, SeF_6, TeF_6

Q19. Describe the various steps which are generally required to predict geometrical shape by VSEPR method.

Ans: The following steps are generally required to predict geometrical shape by VSEPR-method.

i. Draw dot diagram for the molecule.

ii. Determine the number of valence electrons surrounding the central atom.

iii. Determine the number of bond pairs and lone pairs of electrons.

iv. Determine the geometrical distribution of electron pairs so that they areas far apart as possible

Example: Predict the shape of H_2S.

Solution.

Valence electrons of S-atom=6

Electrons contributed by H-atoms =2

Total no. of electrons around S-atom=a

Electron pairs =4

Bond pair=2

Lone pairs =2

Thus, H_2S is ... type molecule. it will possess V-Shaped geometry

Q20. Explain the limitations of VSEPR theory.

Ans: Limitations of VSEPR theory.

i. It could not explain the formation of covalent bonds

ii. H could not exptalr the bond energies.

iii. It does not give any paramagnetic and diamagnetic behavior of molecules

Q21. Give the bask assumptions of Valence Bond Theory (VBT) of Covalent Bend.

Ans: Valence Bond Theory (VBT) of covalent Bond:

This theory was proposed by Heftier and London (1927) and later on developed by Pauling. This concept is based on wave - mechanical treatment of molecules and has been successful in explaining the bond energies, bond lengths and shapes of covalent molecules

According to valence bond theory, a covalent bond between two atoms is formed when the atoms come so close that a partially filled atomic orbital of one atom overlaps with a partially filled atomic orbital of the other. The two overlapping atomic orbitals retain their identities B) the term overlap means that the two orbitals share same common space.

Q22. Give the postulates of Valence Bond Theory (VBT) of Covalent Bond.

Ans: Main principle:

A covalent bond is formed by the overlapping of two half-filled orbitals of combining atoms.

Postulates of VBT:

- **i.** A bond between two atoms is formed by the overlap of half-filled orbitals of two atoms. The two overlapping atomic orbitals retain their identities.
- **ii.** The two overlapping orbitals must have electrons of opposite spin.
- **iii.** The number of bonds formed by an atom is equal to the number of unpaired electrons present in the valence shell of the atom.
- **iv.** If only two orbitals overlap a single bond is formed. If additional orbitals of atoms overlap then multiple bonds are formed.
- **v.** In order to form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis. "A line Joining the nuclei of two bonded atoms is called bond axis"
- **vi.** In overlapping of orbitals energy is released. The greater the overlap between the orbitals, the greater is the energy released and the stronger will be the bond formed.

Q23. Give different applications of Valence Bond Theory.

Ans: Application of Valence Bond Theory:

The valence bond approach describes bonds in terms of the pairing of electrons and may be considered an extension of the Lewis concept of covalent bond formation.

The valence bond theory pictures the bond as forming from the coupling or pairing of electrons having opposite spin (from each of the combining atoms).

It should be noted that atoms involved in bond formation should have unpaired electrons in them.

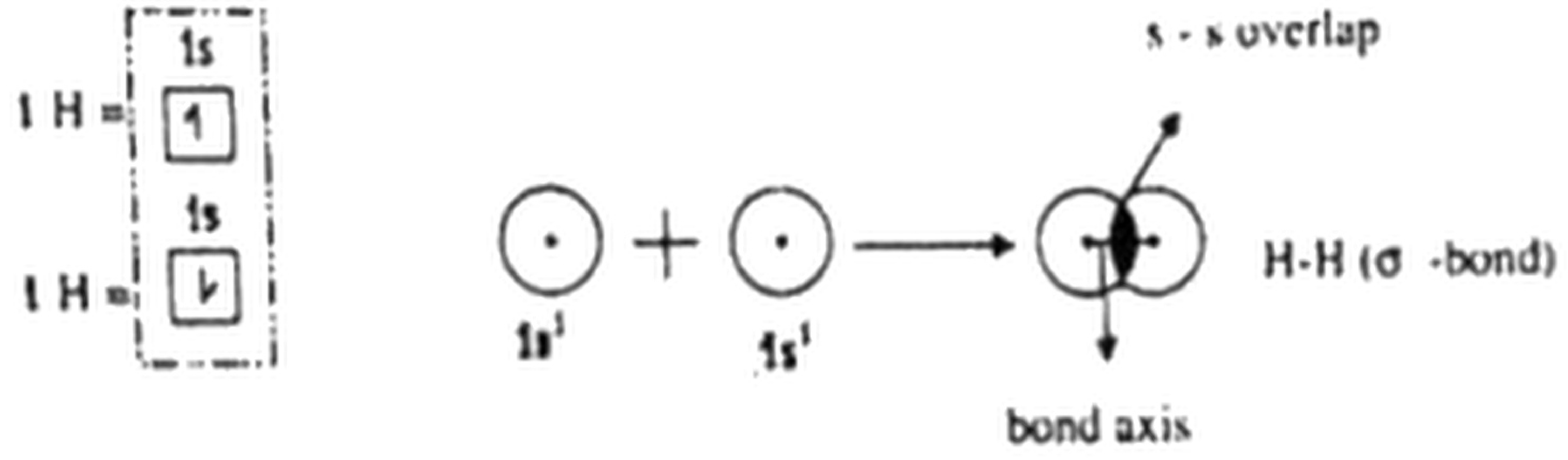
The number of unpaired electrons gives rise to equal number of bonds which may be formed by any given atom.

The isolated numbers of pair of electrons are considered to be the lone pairs in the approach.

Q24. Explain formation of H_2 molecule on the basis of Valence Bond Theory.

Ans: Formation of H_2 molecule:

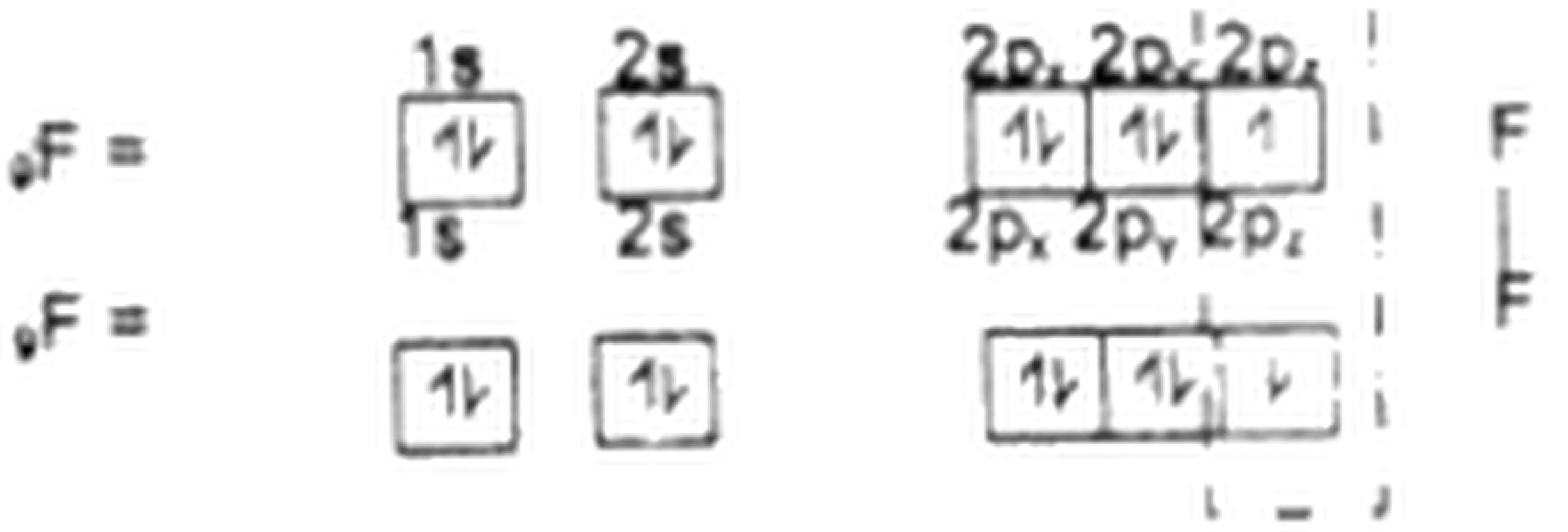
Each H atom has the electron configuration $1s^1$. As two hydrogen atoms approach each other, their half-filled 1s orbitals overlap, giving H-H bond the overlap of orbitals provides a means for sharing electrons, thereby allowing each 1s to complete its valence shell. The electron density is concentrated in the ion along the line joining the two nuclei. The bond formed **is a** sigma (σ) bond.

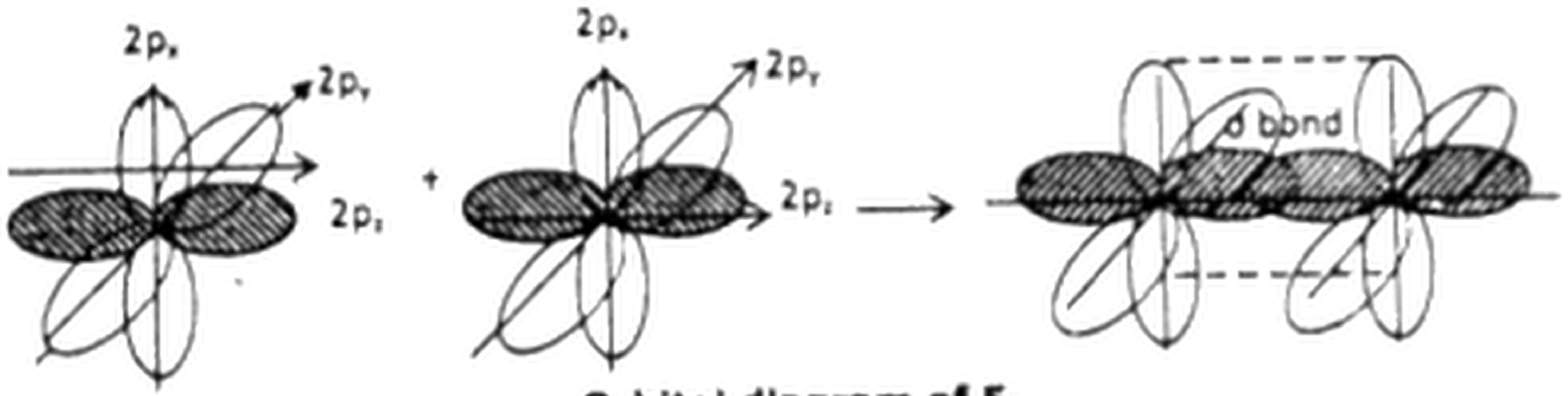


Q25. Explain bond formation of F2 molecule on the basis of Valence Bond Theory.

Ans: Formation of F2 molecule

The electronic configuration of fluorine atom is:





Orbital diagram of F_2

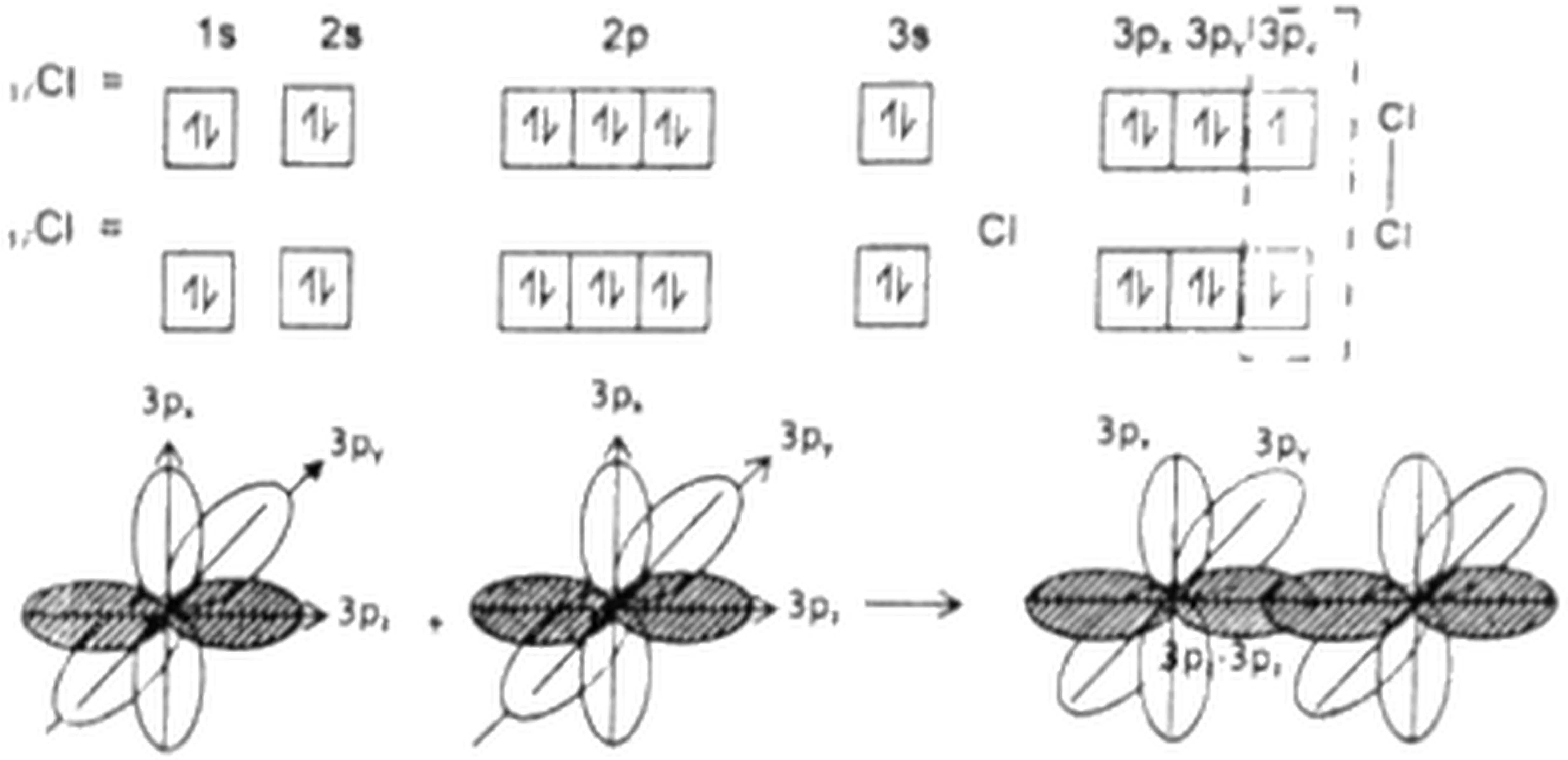
Each F atom has one half filled 2p orbital. On the **basis** of VBT one covalent Bond is formed between the two F stoma their 2pz orbitals overlap by end to end. The bond formed is a sigma (σ) bond.

Q26. Explain formation of Cl_2 molecule on the basis of Valence Bond

Theory.

Ans:

The electronic configuration of Cl_2 atom is:

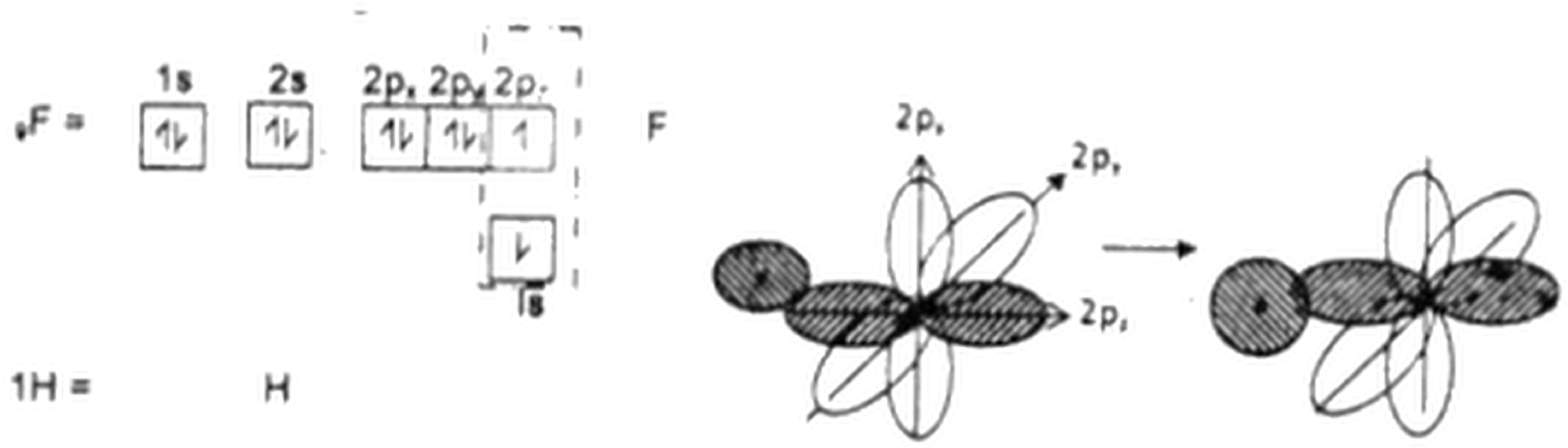


Orbital diagram of Cl_2

Q27. Explain formation of HF molecule on the basis of Valence Bond Theory.

Ans:

The electronic configuration of F and H atom are:



Orbital diagram of HF

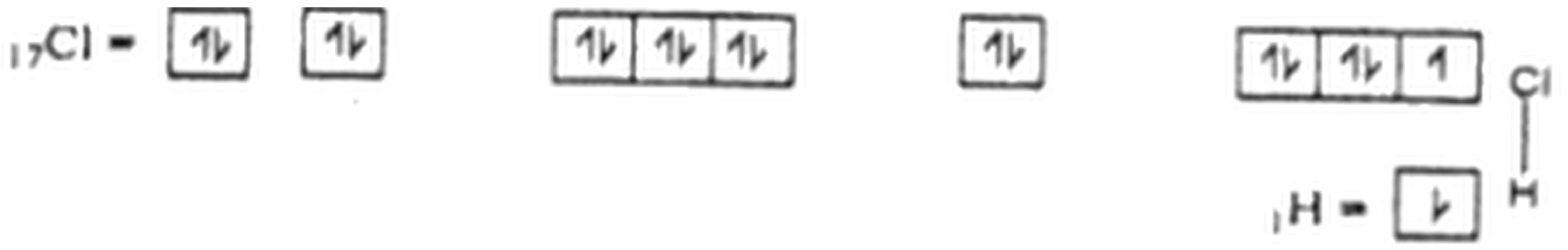
Each F atom has one half filled 1s orbital. their 2pz orbitals overlap by end to end.

The bond formed is a sigma (σ) bond.

Q28. Explain formation of HCl molecule on the basis of Valence Bond Theory.

Ans:

The electronic configuration of Cl and H atom are:

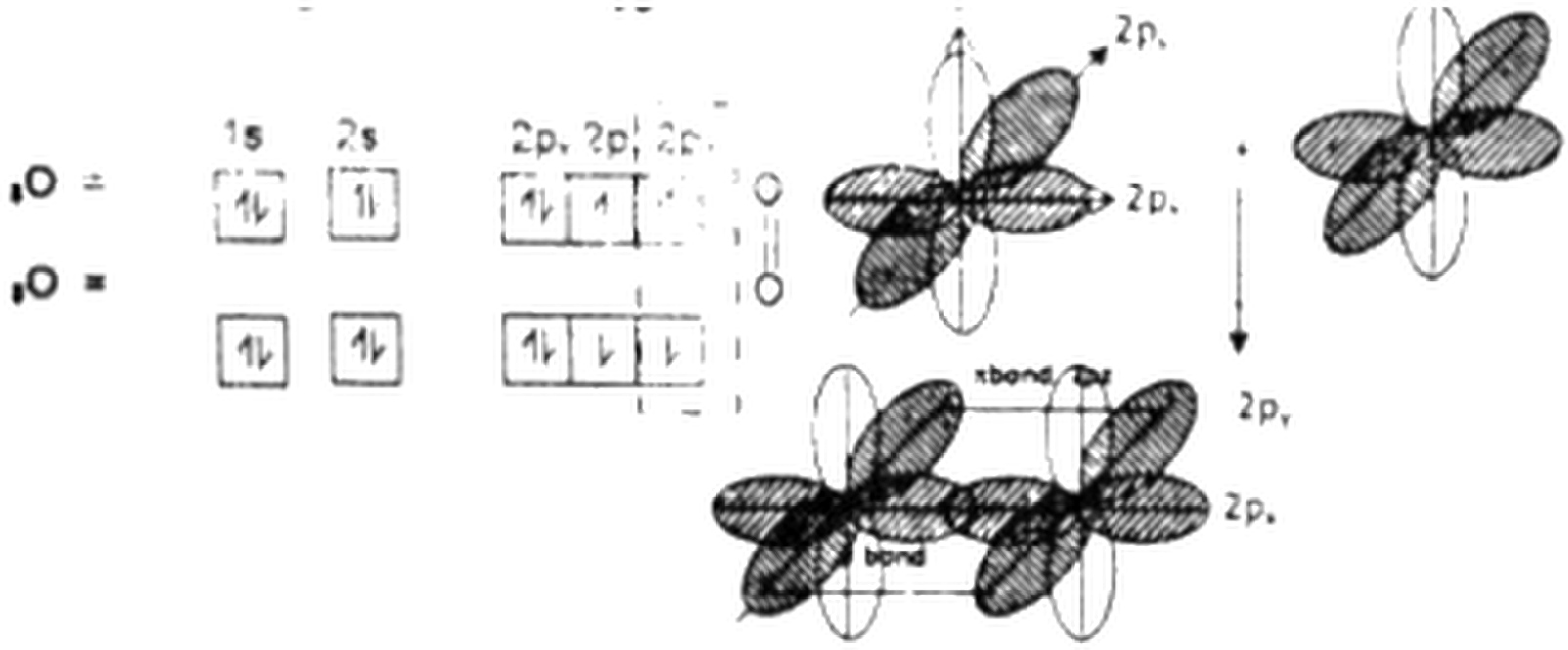


Q29. Explain O_2 molecule on the basis of Valence Bond Theory.

Ans:Formation of O_2 molecule:

Oxygen molecule O_2 is obtained by the combination of two oxygen atoms:

Electronic configuration of an oxygen atom is:



Orbital diagram of O_2

Each oxygen atom has two half-filled 2p orbital in the valence shell. On the basis of VBT two covalent bonds can be formed between two O atoms. One bond is formed by the end-to-end overlap of half-tilled 2P orbitals on each oxygen atom. This gives a σ bond. This bond is formed by the side-to-side overlap of half- filled 2pz orbitals on each oxygen atom. This gives a π bond thus a double bond is formed between two oxygen atoms. One is a bond while the other is bond.

Remember:

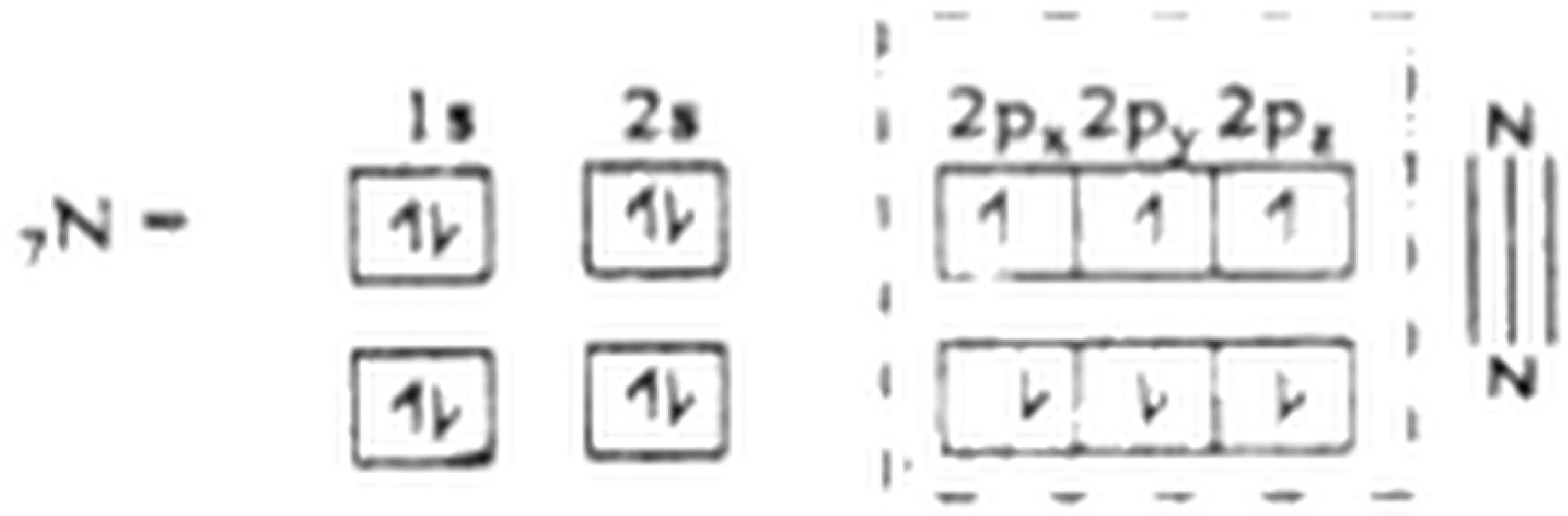
In multiple bond formation firstly the σ bond is formed and secondly the n bond is formed.

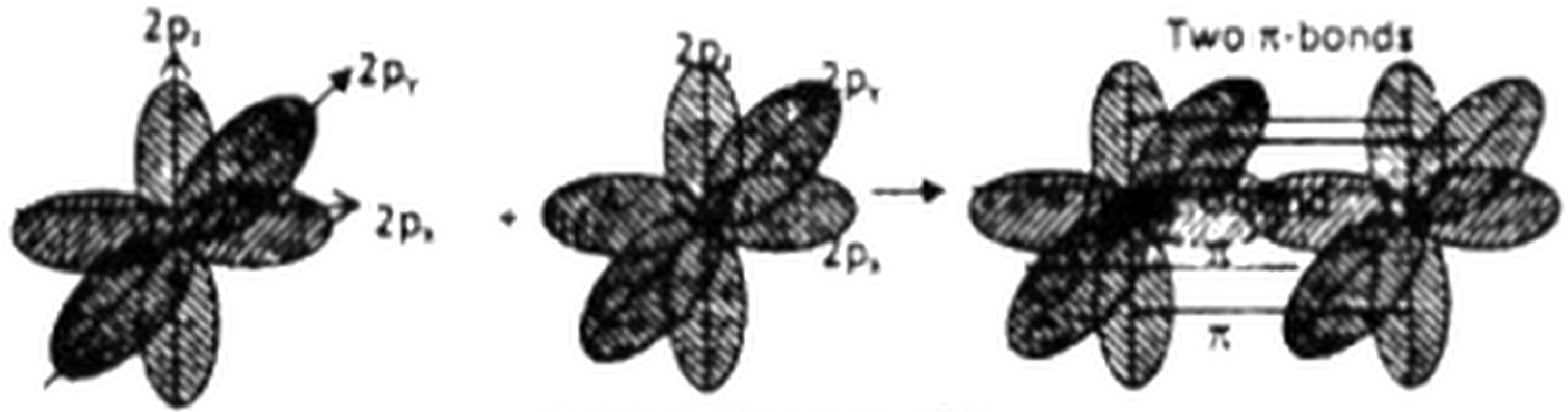
Q30. Explain formation of N2 molecule on the basil of Valence Bond Theory.

Ans: Formation of N2 molecule:

Nitrogen molecule, N_2 is formed by the combination of two N atoms. The

Electronic configuration of N atom is:





Orbital diagram of N_2

Each N atom has three half-filled p orbitals on the basis of VBT. three covalent bonds can be formed between two nitrogen atoms. When the two nitrogen atoms approach each other, their 2Px orbitals undergo end-to-end overlap, giving a triple bond.

The end-to-end overlapping brings the two nitrogen atoms so close together that their parallel 2p orbitals undergo side-to-side overlap to produce two pi bonds. Note that each pi bond is in two separate regions surrounding a σ bond. There are five distinct regions of electron charge density in the nitrogen molecules.

i. The σ electrons between the nuclei form σ bond.

ii. The pi-electrons above and below the σ electrons form pi-bond.

iii. The pi-electrons in front of and behind the σ electrons form another σ bond.

Note: Thus, a triple bond is formed between two nitrogen atoms; one is cj bond while the other two are 1t bonds.

Q31. Give the drawback of Valence Bond- Theory (VBT) of Covalent Bond.

Ans: Drawbacks of Valence Bond Theory:

It fails to explain:

i) The formation of coordinate covalent bond.

ii) The formation of odd electron molecules or ions

iii) The paramagnetic behavior of oxygen molecule.
iv) It could not explain the tetra valency of carbon
v) It could not explain the bonding in $BeCl_2$

Q32. Explain the concept of Hybridization of Atomic Orbitals.

Ans: Hybridization:

Hybridization is defined. a process of mixing atomic orbitals of different energy and shape to form set of new orbitals of the same energy and same shape is called hybridization and the orbitals so obtained are called "hybrid orbitals".

Explanation:

According to this concept atomic orbitals differing slightly in energy intermix to form new orbitals called hybrid atomic orbitals which differ from the parent atomic orbitals in shape energy and possess specific geometry. It also gives a satisfactory explanation for the valence of the elements. In this process, the electron belonging to the ground state structure is promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

The atomic orbitals, undergo hybridization. The energy required for the excitation is compensated by the energy released during the process of bond formation with other atoms. Depending upon the nature of orbitals involved there are many types of hybridization.

For example, sp^3 sp^2 sp hybridization

Q33. Define sp^3 Hybridization.

Ans: sp^3 Hybridization:

"The process of mixing one s orbital and three p orbitals to form four new equivalents to sp^3 hybrid orbitals is called sp^3 hybridization".

Q34. Discuss the Structure of Methane (CH_4) with the reference to sp^3 Hybridization.

Ans: Structure of Methane:

${}_6C$ (Ground state) = $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$
${}_6C$ (Excited state) = $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$
${}_6C$ (Hybrid state) = $1s^2\ (2sp^3)^1\ (2sp^3)^1\ (2sp^3)^1\ (2sp^3)^1$

When carbon atom in a molecule is attached to four other atoms, then sp) hybridization occurs.

Each sp^3hybrid orbital consists of two lobes, one larger and the other smaller. The energies of hybrid orbitals are lower than unhybridized orbitals. Further, the ratio of s and p character in each sp^3 hybrid orbitals is 1:3. The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon at the center and are oriented in space in such a manner that the angle between them is109.5°.

Structure of Methane (CH_4)

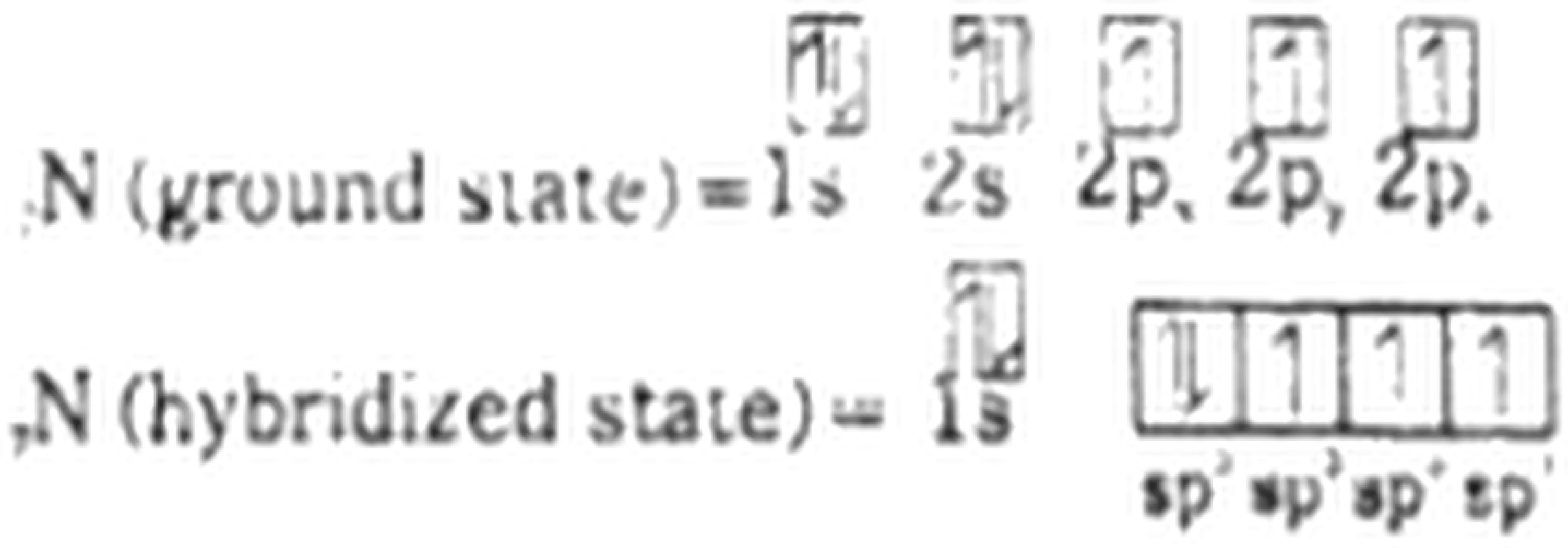
Methane molecule is formed by the overlap of sp^3hybrid orbitals of carbon with 1**s** orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule of methane. Thus, formed possesses a tetrahedral geometry. The C-H bonds which result from sp^3. s overlaps are directed towards the corners of a regular tetrahedron. Each H-C-H bond angle is 109.5°. The tetrahedral structure of CH_4 molecule has four faces and four corners.

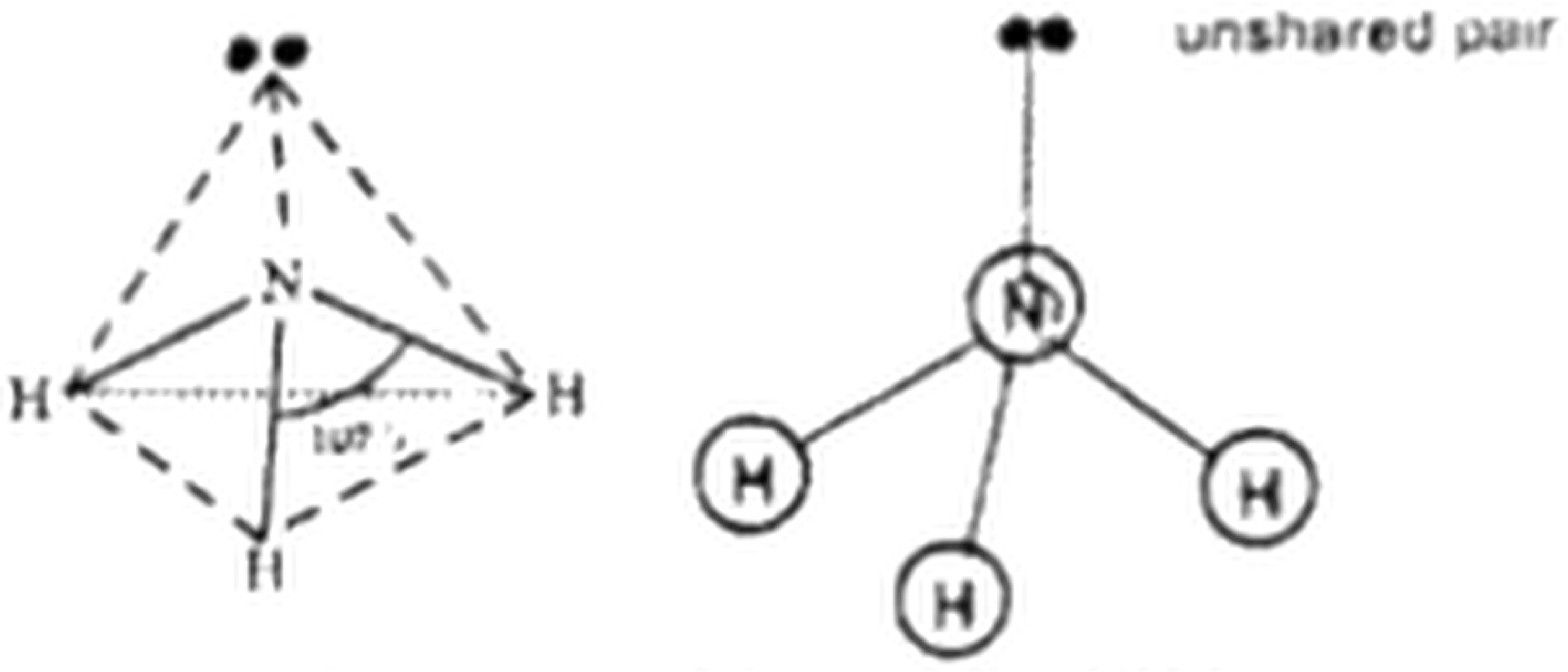
Q35.Discuss the Structure of Ammonia (NH_3) with the reference to sp^1 Hybridization.

Ans: Structure of Ammonia (NH_3):

In NH_3 molecule. the central atom is nitrogen. It contains five electrons in its valence shell. Hence, one s and three p orbitals of nitrogen atom hybridize to form four sp^3hybrid atomic orbitals. They are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled by a lone pair of electrons and the remaining three orbitals are half filled.

The sp hybridized orbitals of nitrogen overlap with three 1s-orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners, whereas the electrons lone pair is at the fourth corner of the tetrahedron. This results in a pyramidal molecule, in which three hydrogen atoms, form the base and the lone pair





Structure of Ammonia (NH_3)

The experimentally determined value of H-N-H bond angle in NH3 molecule is 107.5° which is less than the normal tetrahedral value of 109.5° The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pair and bond pairs. The lone pair bond pair repulsion is greater than bond pair-bond pair repulsion. As a result, the bond pairs move away from the lone pair and come closer to each other. Hence, the angle between bond pairs decreases.

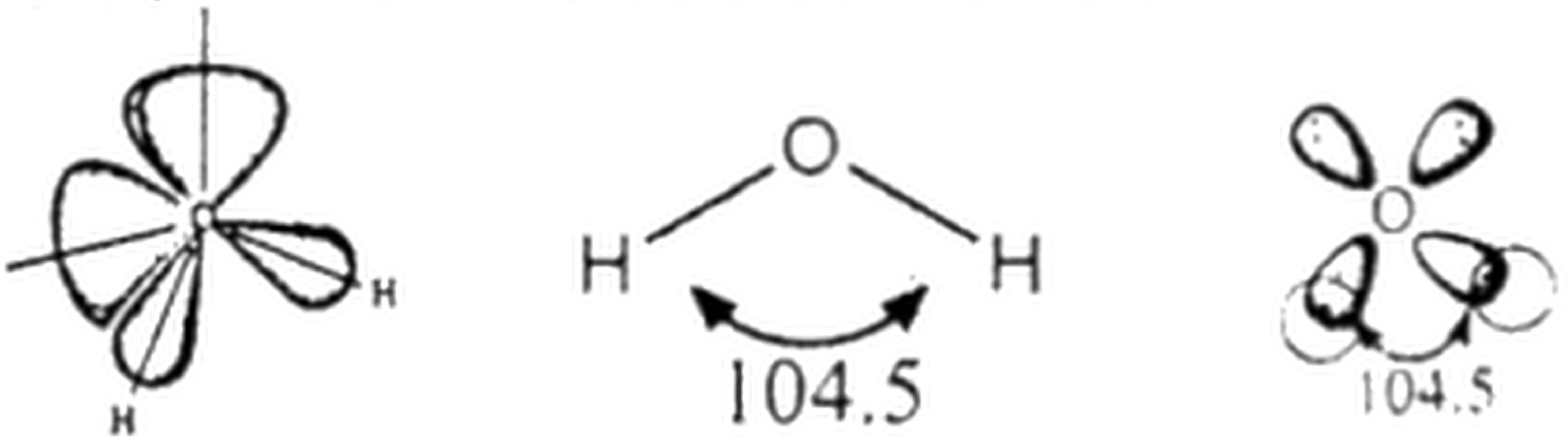
Q36. Discuss the Structure of Water (H_2O) with the reference tosp^{3}Hybridization.

Ans: Structure of Water:

In H_2O molecule, the central atom is oxygen. It contains six electrons in the valence shell. Its electronic configuration is as follows,

$_8O$(Ground state)$=1s^2\ 2s^2\ 2px^2\ 2py^1\ 2pz^1$

$_8O$ (Hybrid state) = $1s^2, (2sp^3)^2, (2sp^3)^2, (2sp^3)^1, (2\ sp^3)^1$



Structure of Water (H_2O)

One 2s and three 2p orbitals of O-atom intermix to produce four sp^3 hybrid orbitals. The four sp^3hybrid orbitals are directed towards the four corners of ii regular tetrahedron with oxygen atom at the center. Two of the sp^3 hybrid orbitals contain two electron& each are completely filled. The remaining two sp^3 hybrid orbitals contain one electron each and are partially filled. Thus, the two partially filled sp^3 hybrid orbitals now overlap with the two 1s orbitals of two hydrogen atoms to form two sigma bonds. Each sigma bond i1 formed by sp^3-s overlap. The two hydrogen atoms are located at two corners of a tetrahedron, whereas the two lone pairs at the remaining two corners of the tetrahedron. The result is a V-shaped molecule.

The experimentally determined value of H-O-H bond angle in H_2O molecule is 104.5°, which is lesser than the normal tetrahedral value (109.5°). The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pairs and bond pairs. The repulsion of lone pair-lone pair > lone-pair-bona pair > bond pair-bond-pair. a result the bond pairs move away from the lone pairs and come closer to each other. Hence the angle between bond pairs decreases up to 104°

Q37. Define sp^2 Hybridization.

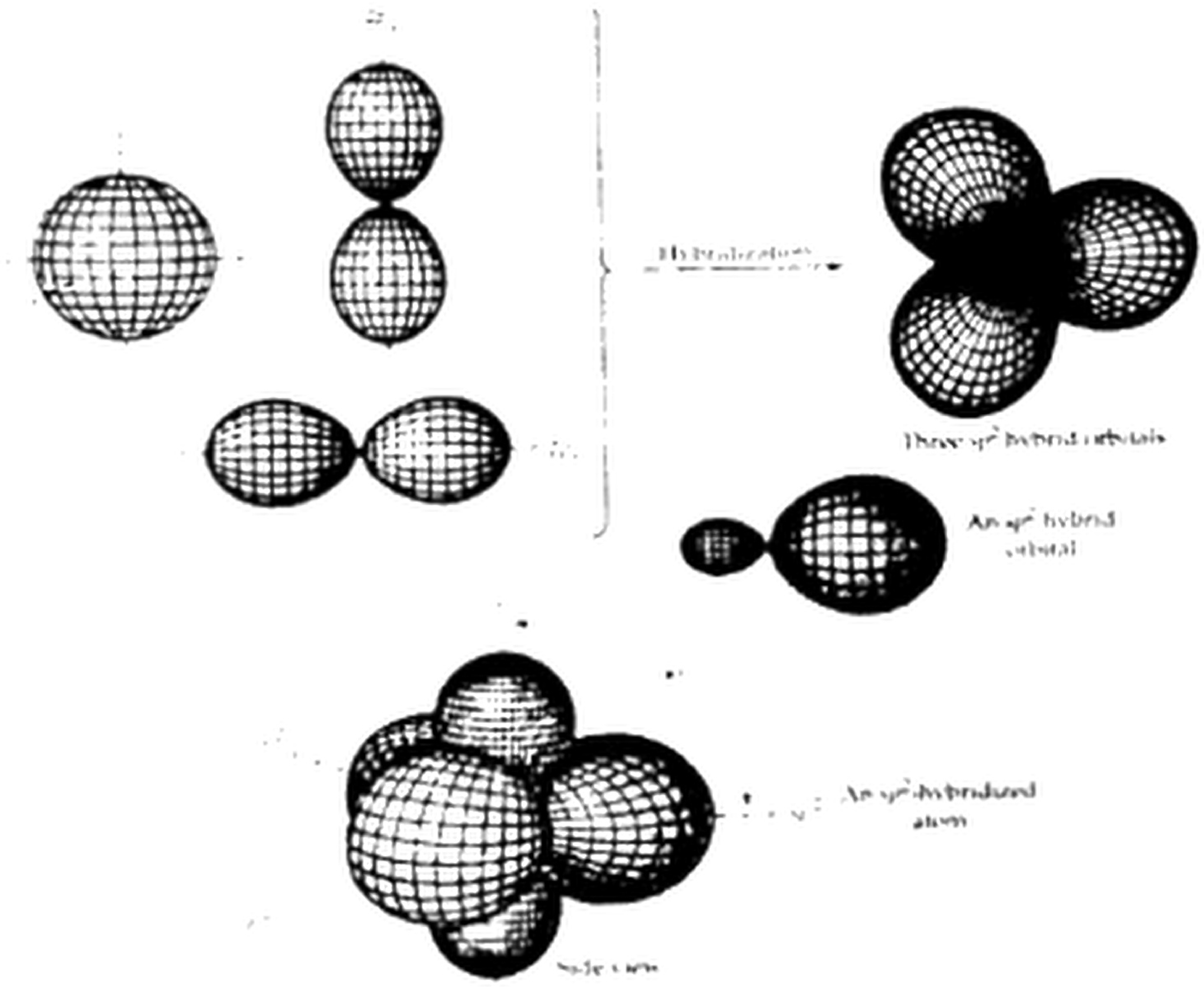
Ans: sp^2 Hybridization:

"The mixing of one s and two p orbitals of the same atom to form three identical sp^2 hybrid orbitals is called sp^2 -hybridization.

The hybrid orbitals are directed towards the three corners of an equilateral triangle. the angle between any two hybrid orbitals 120 degrees. Each sp^2 hybrid orbital has

33.31% s-character and 66.7% p-character. The sp^2 hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals

Examples: Boron Trifluoride and Ethene



Structure of Hybridization (sp^2)

Q38. Discuss the Structure of Born trifluoride, BF_3withthe reference tosp^2 Hybridization.

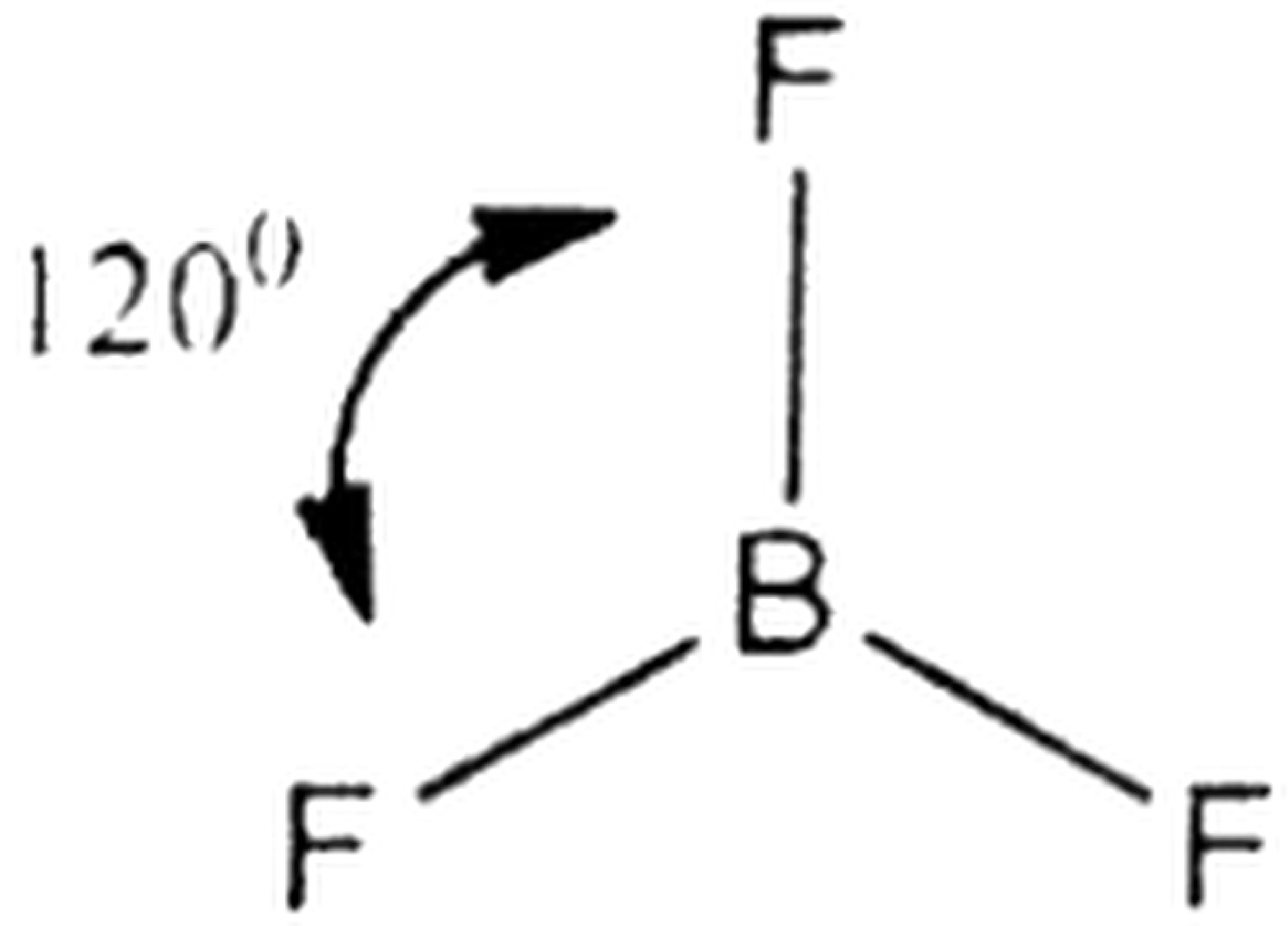
Ans: Structure of Born trifluoride, BF_3:

In BF_3 molecule, the central atom is boron. It contains three electrons in its valence shell. The electronic configuration of the valence shell of 8-atom in the ground and excited states are as follow,

B=5=$1s^2$,$2s^2$,$2Px^1$,$2py^1$2pz (ground state electronic configuration)

B = 5 =$1s^2$, $2s^1$. $2px^1$,$2py^1$. 2pz (excited state electronic configuration)

One 2s and two 2p orbitals of boron atom intermix to give three sp^2 hybridized orbitals. The three sp^2 hybrid orbitals lie in the same plane and are directed towards the corners of an equilateral triangle with boron atom at the center



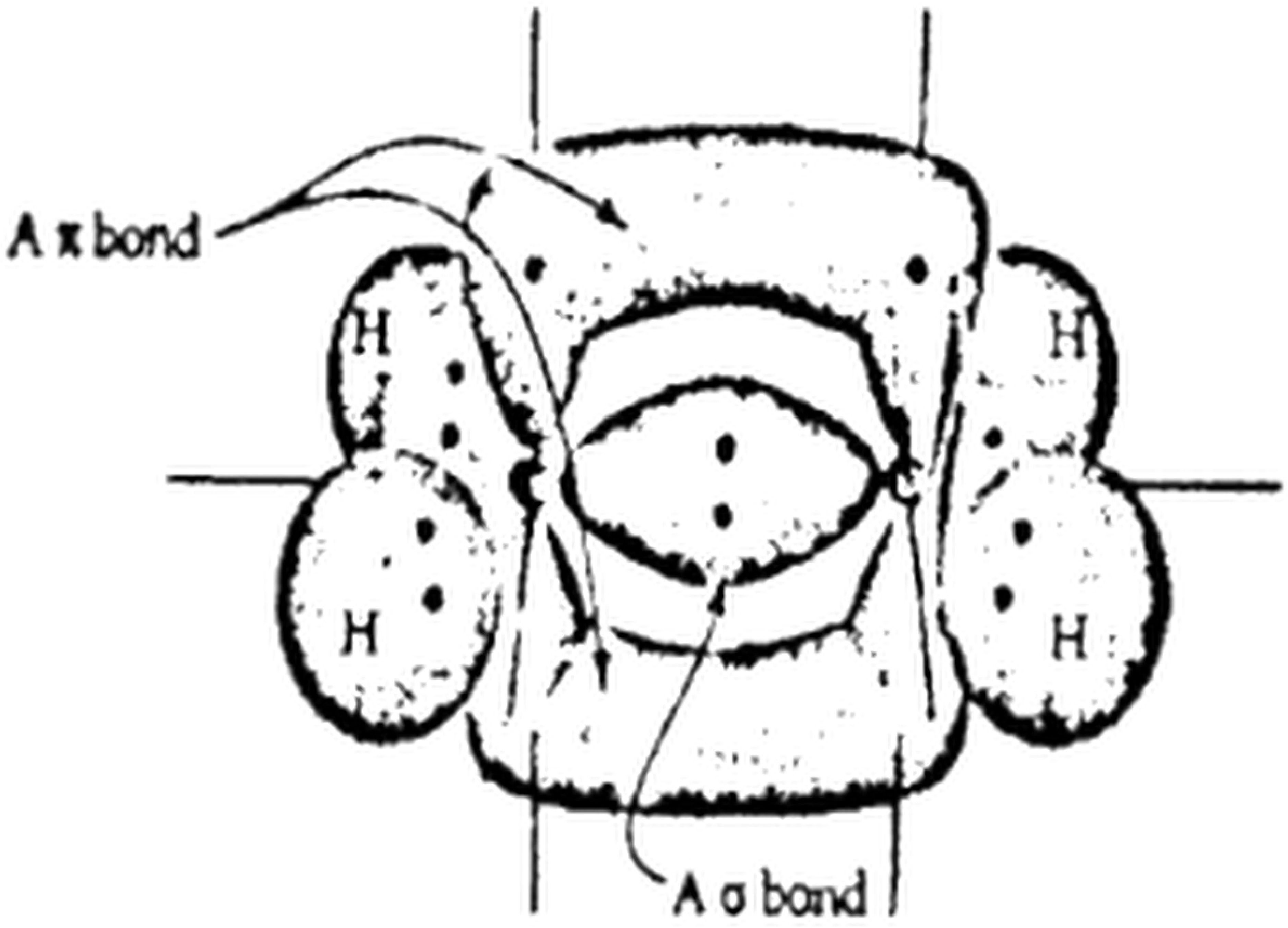
Thus, the angle between any two sp^2 orbitals is 120°. The three sp^2orbitals contain one electron in each and are thus partially filled. The partially filled 2p orbitals of three fluorine atoms overlap with each sp ^{2} hybrid orbitals of boron atom to form three sp^2- p sigma bonds. As a result. BF_3molecule has triangular planar structure

Q39.Discuss the Structure of Ethene, CH2=CH2 with the reference to sp^2 Hybridization.

Ans: Structure of Ethane, CH_2= CH_2

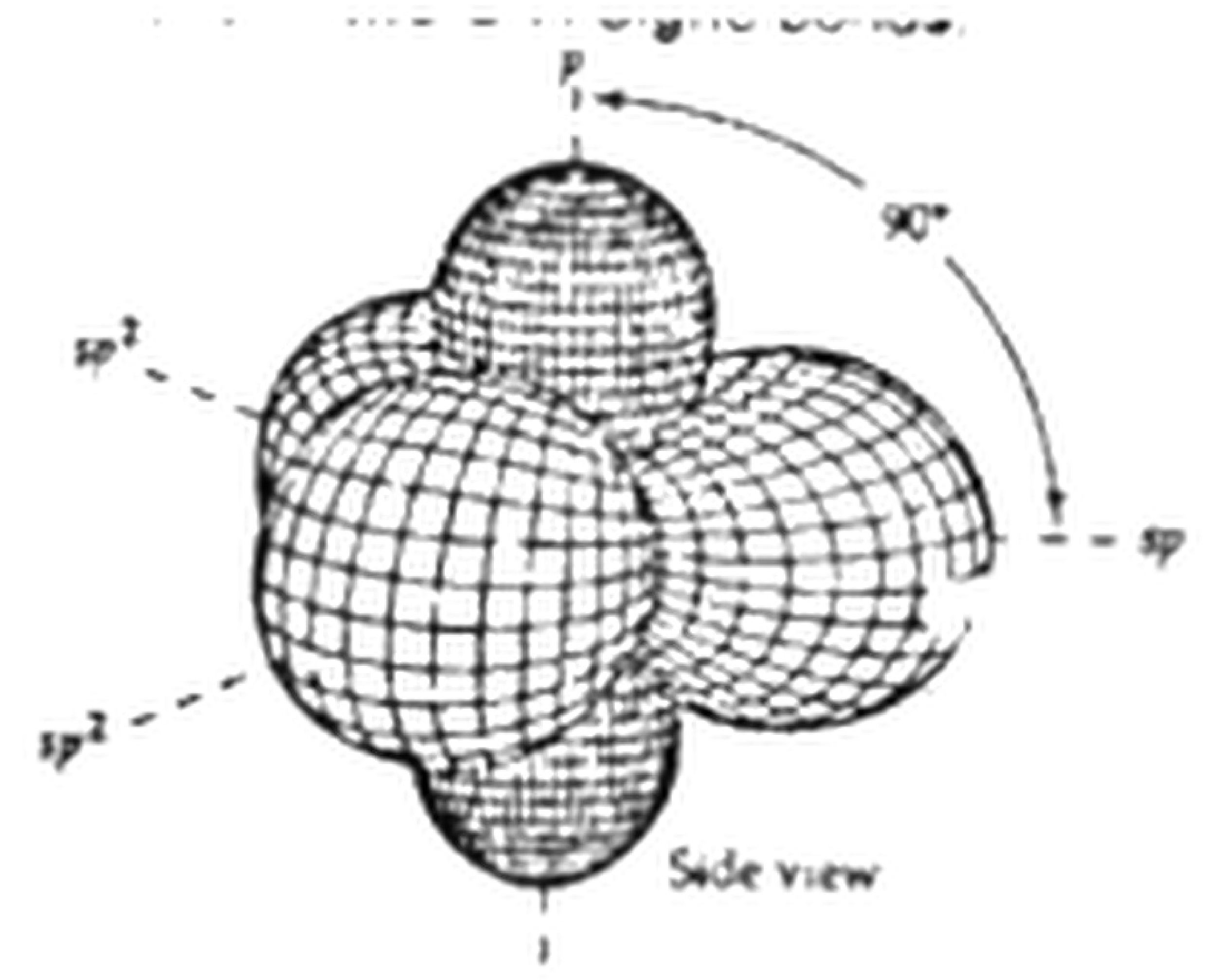
In CH_2= CH_2 molecule. there are two central carbon atoms.

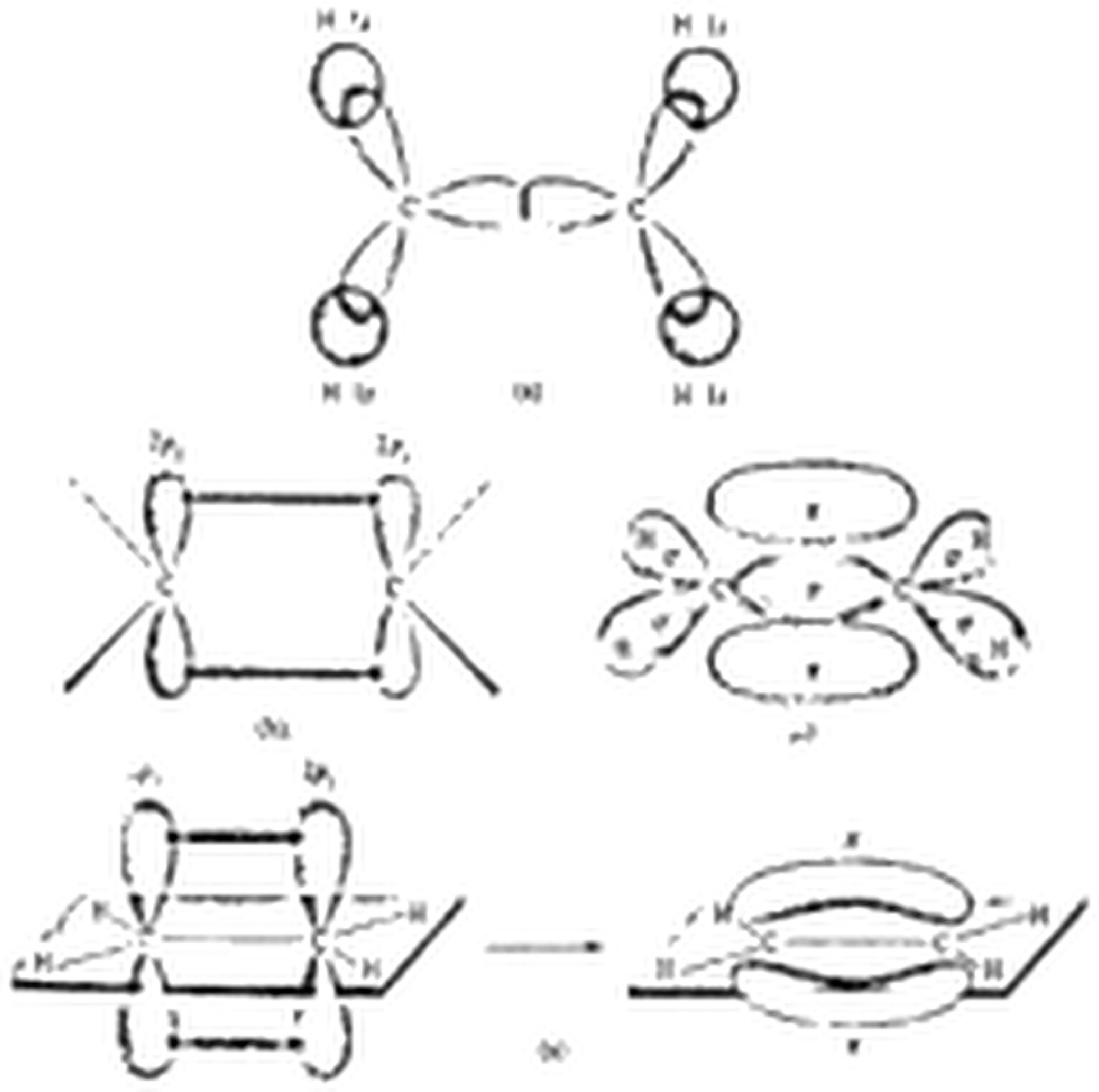
One s and two p orbitals of each C-atom intermix to form three hybrid sp^2 orbitals. The geometry of molecules depends upon. the orientation of hybrid orbitals. Hybrid orbitals are triangular planar and oriented at the angle of 120° to each.



Structure of Ethene (CH_2 = CH_2)

Each atom is left with one half filled p-orbital perpendiculars to the planar sp^2 hybrid orbitals. One sp orbital of each C-atom overlaps linearly to form one C-C sigma bond. Remaining two Sp^2 orbitals of each C-atom overlap linearly with 1s atomic orbital of H-atom to form two C-H Signe bonds.





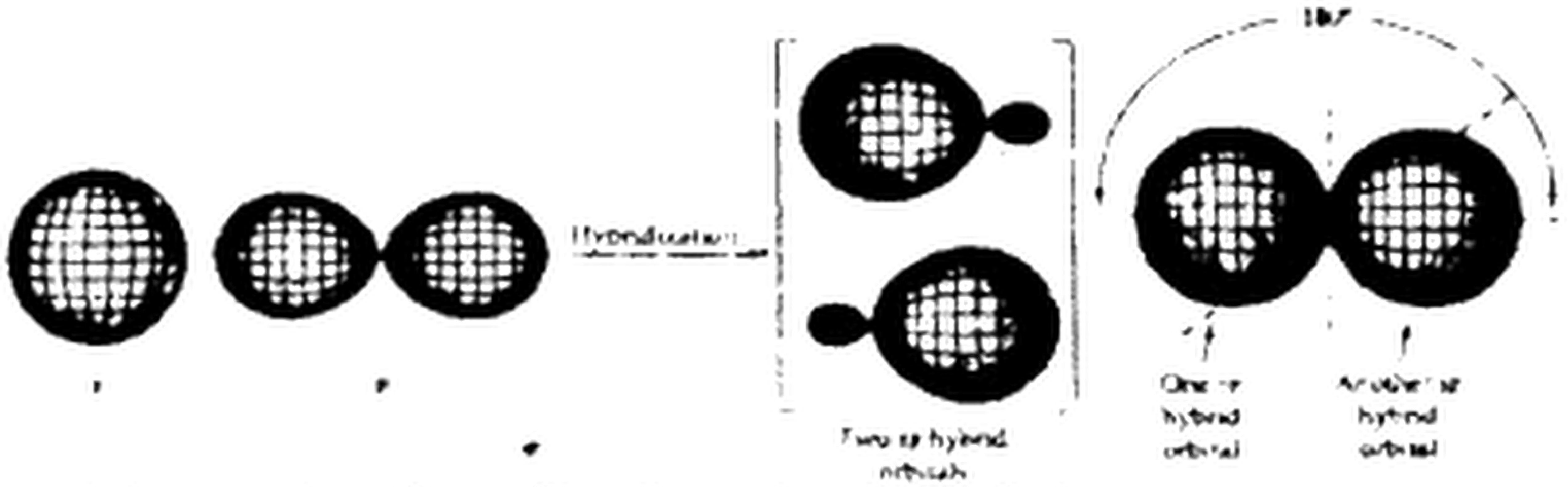
Structure of Ethene

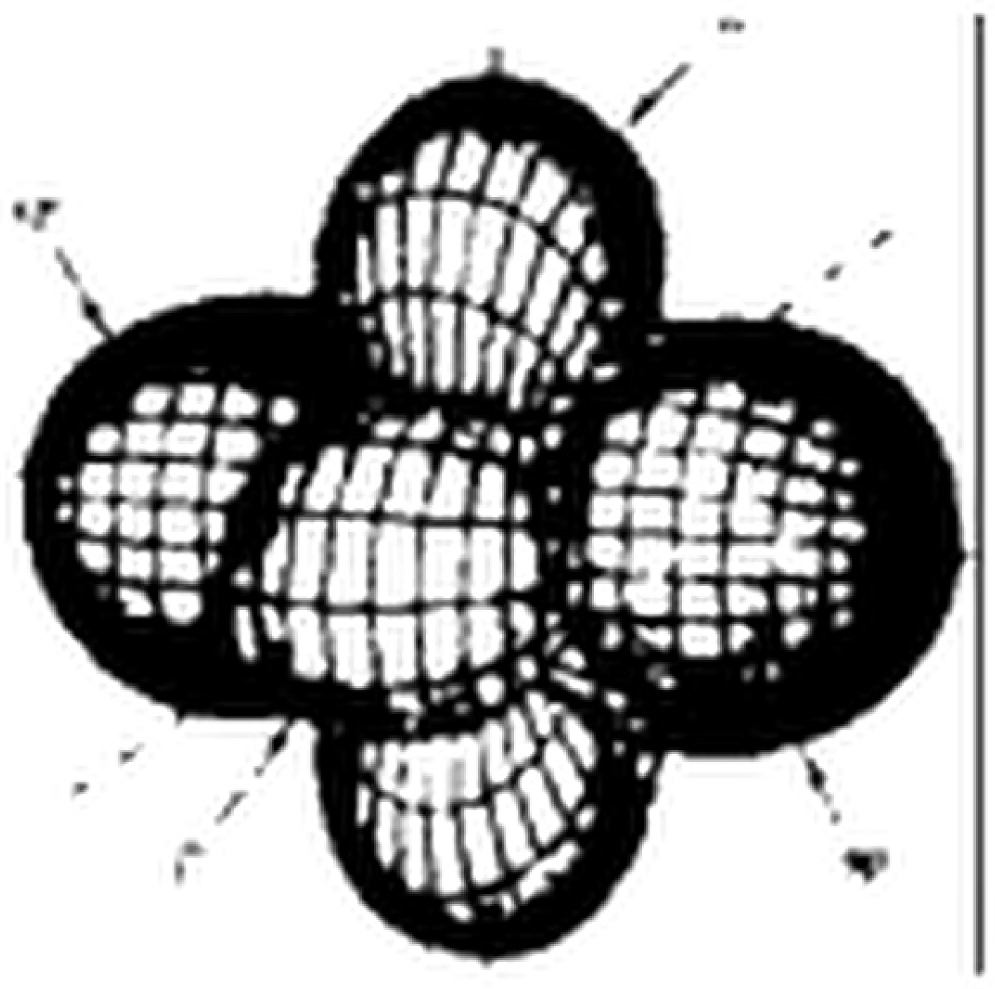
The partially filled p-orbitals undergo overlap sideways to form a pi-bond So, a pi-bond is formed by the sideways overlap of two half-filled co-planar p-orbitals in such a way that the pi probability of finding the electron is maximum perpendicular to the line joining the two nuclei.

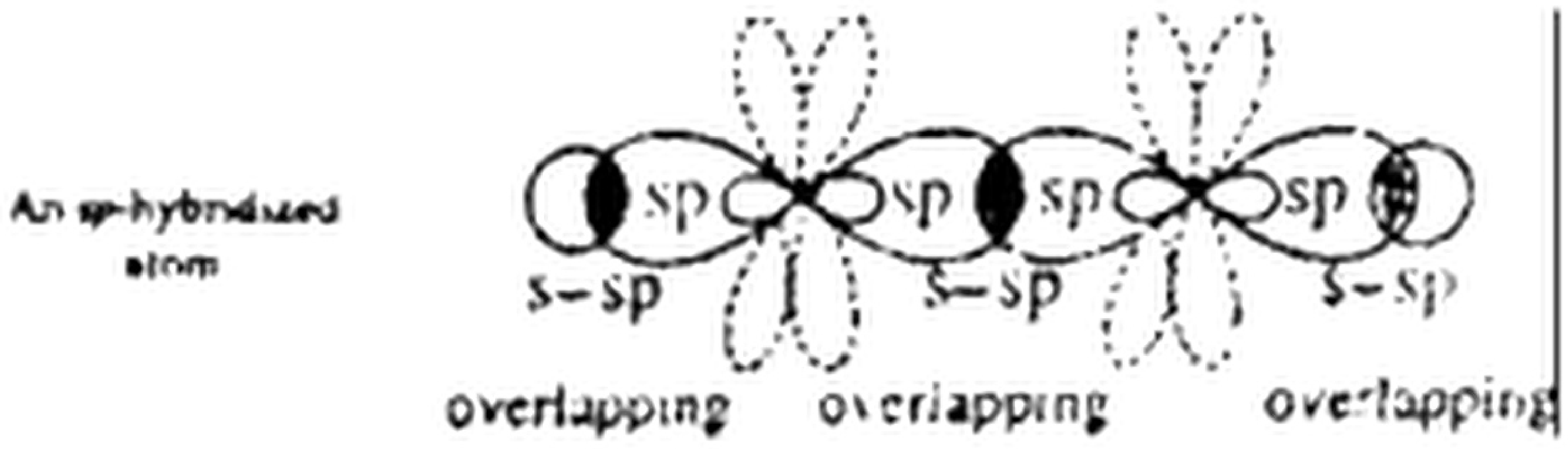
Q40. Briefly explain sp -Hybridization.

"The mixing of one s-orbital and one p-orbital of an atom to form two equal energy hybrid orbitals is called sp hybridization"

The two so hybrid orbitals are linear and angle between them is 180°. Each sp-hybrid orbital has 50% s-character and 50% p-character. The sp- hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.







Structure of sp Hybridized orbitals

Examples: $BeCl_2$, C_2H_2

Q41.Discuss the Structure of $BeCl_2$ (Beryllium Chloride) with the reference to sp^2 Hybridization.

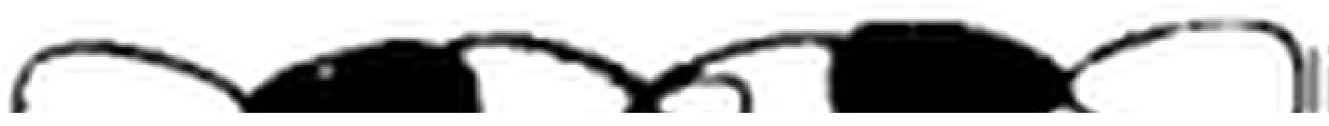
Ans: Structure of $BeCl_2$ (Beryllium Chloride):

In $BeCl_2$ molecule. the central atom is beryllium atom. Beryllium atom contains two electrons. in its valence shell. The electronic configuration of valence shell of beryllium atom in the ground state and excited state is as follow:

Be=2=$1s^2$, $2s^2$,2Px,2Py2Pz (ground state electronic configuration

Be =$1s^2$, $2s^1$,$2Px^1$,2Py2Pz (excited state)

One 2s and one 2p orbitals of beryllium atom intermix to form two sp hybrid orbitals. Each sp hybrid orbital contains one electron. The two sp hybrid orbital lie in a straight line



with beryllium atom at the center One sp orbital of Be overlaps linearly with sp-orbital of other Be to form Be-Be sigma bond remaining sp hybrid of Be overlaps linearly with 3Pz orbital of Cl to form sigma bond Thus $BeCl_2$ molecule is linear. The Cl-Be-Cl bond angle is 180°

Cl-Be-Cl

Q42. Discuss the Structure of Ethyne, CH≡CH with the reference to sp^2 Hybridization.

Ans: Structure of Ethyne CH≡CH

is as follow:

$_6$**C(Ground state)**=$1s^2, 2s^2 2px^1 2py^1 2pz^1$

$_6$**C (Excited state)**==$1s^2, 2s^1 2px^1, 2py^1, 2pz^1$

$_6$C (Hybrid **state)**= $1s^2, (2sp)^1 (2sp)^1, 2py^1, 2Pz^1$

Formation of σ bonds

formation of π bonds

space filling model

H-C≡C-H

Structure of Ethyne (CH =CH)

One 2s and one 2p orbitals of carbon atom intermix to give two sp hybrid orbitals. The 2py and 2pz orbitals remain unhybridized. Each sp hybrid orbitals contains one electron. The two sp hybrid orbitals are directed along a straight line at an angle of 180° between them. The two unhybridized p orbitals which are perpendicular to each other are also perpendicular to the plane of the two sp hybrid orbitals. Thus, each carbon atom possesses two sp hybrid orbitals and two pure p atomic orbitals. Each C-atom undergoes sp-s overlap with one H-atoms and sp-sp overlap with other carbon atom to form two a-bonds.

The two half-filled P orbitals of two carbon atoms overlap sideways to form two a-bonds. Thus, ethyne molecule contains one a-bond and two 11-bonds between two carbon atoms and two carbon-hydrogen a-bonds. The electronic clouds of two n-bonds merge into each other to form cylindrical shaped 1t-electron cloud.

Q43. Explain the Molecular Orbital Theory.

Ans: Molecular Orbital Theory:

The method of molecular orbital theory was developed in 1927-1928 by Hybrid and Mullikan and in 1929 by Lennard-Jones.

It is assumed that linear combination of atomic orbitals forms new orbitals called molecular orbitals which are characteristics of the whole molecule. The molecular orbital surrounds two or more nuclei of the bonded atoms. Two atomic orbitals after combining linearly form two molecular orbital which differ in energy.

Bonding Molecular Orbital (BMO):

Orbitals having lower energy, is called bonding molecular orbital (BMO).

Anti-bonding Molecular Orbital (ABMO):

Orbitals having high energy is called anti-bonding molecular orbital (ABMO).

The bonding molecular Orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital, while the anti-bonding molecular orbital is called σ *.

The filling of electrons into the molecular orbitals takes place according to:

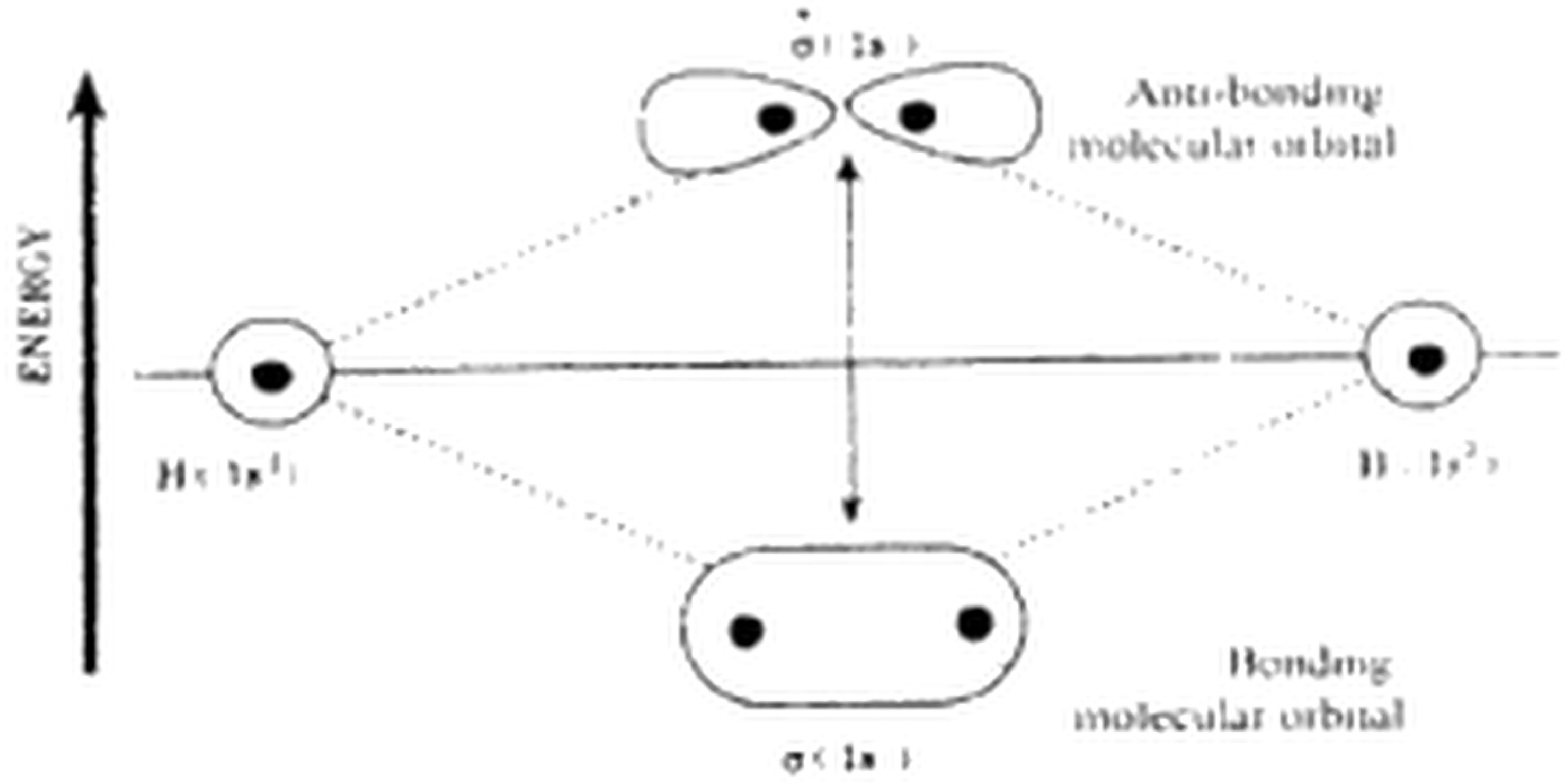
i. Aufbau principle

ii. Pauli's exclusion principle

iii. Hund's Rule

The two electrons from each atom fill the low energy σ orbital or π orbital while the high energy σ orbital or π orbital may have electrons or remain empty.

The following diagram illustrates the formation of the molecular orbitals (lower energy and higher energy) and also the processing of filling of electrons according the rules mentioned above



In this type of diagram, the combining atomic orbitals are shown on two extremes and the resulting molecular orbitals (MO) are represented 1n the middle column. Atomic orbitals of same energy are shown at the same level. The difference between the energies of atomic orbitals and the bonding MO's depend upon the extent of overlap of atomic orbitals. A large overlap results in greater lowering of the energy of bonding MO (and a corresponding large rise in energy in the anti-bonding MO). Larger the overlap, stronger will be the resulting bond. According to the above diagram the sequence of energy levels in which they are filled up is:

$\sigma\ 1s, < \sigma^*\ 1s < \sigma\ 2s, < \sigma^*\ 2s, < \sigma\ 2px < \pi\ 2py = \pi\ 2pz < \pi^* 2py = \pi^* 2pz < \sigma^*\ 2px$

Q44. Explain the types of overlapping in molecular orbital theory.

Ans: Types of overlapping in molecular orbital theory:

There are two types of overlapping in molecular orbital theory

i. Head on approach (linear overlapping) or linear combination.

ii. Sideways approach (parallel overlapping).

1. Head on approach (linear overlapping):

Head on approach can take place between s-s, s-p and p-p atomic orbitals. When twos atomic orbital overlap, they form two molecular orbitals. Molecular orbital of low energy than atomic orbital is called as. Molecular orbital which has high energy then atomic orbital is called as orbital.

2. Sideways approach or parallel overlapping:

When the axes of two-p orbitals (i.e. Py or Pz orbitals) are parallel to each other, They interact to form molecular orbitals. The bonding molecular orbital π(2Py) or π (2pz) has zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below then odal plane. On the other hand, π_y(2Py) or π_z (2Py) anti- bonding molecular orbital has the least electron density in the inter-nuclear region. Since the 2p.; and 2pz atomic orbitals are degenerate orbitals (having the same energy) the πmolecular orbitals i.e. π y (2Py are also degenerate. Similarly, the π_y(2Py) and πz(2Pz) molecular orbitals are also degenerate.

Two sets of 2-p atomic orbitals form six molecular orbitals (three bonding and three anti-bonding). The bond formed as a result of linear overlapping is a bond while that formed as a result of sideways overlap is called a π (pi) bond. Thus, p orbital overlaps can lead to the formation of three bonds. One sigma and two pi bonds.

Q45. Explain Bond order.

Ans: Bond order (number of bonds):

The number of bonds formed between two atoms after the atomic orbitals overlap is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No .of electrons in BMO- No.of electrons.in ABMOs}}{2}$$

The number of bonds formed in hydrogen molecule may be calculated as follows.

No. of electrons in the bonding orbital = 2

No. of electrons in the anti-bonding orbitals =0

Bond order=2-0 /2 =1

It is common practice that only MOs formed from valence orbital are considered in bond order calculations. It should be noted that a bond between two atoms can be formed only, when the number of electrons in the bonding orbital must be greater than the number of electrons in the anti-bonding molecular orbitals.

Q46.ExplainRelativeEnergiesoftheMolecularOrbitalswithreasons.

Ans: Relative Energies of the Molecular Orbitals:

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals are determined by spectroscopic measurements.

a. The molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions can be in the following increasing order of energy.

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2pi) < \pi(2py) = (\pi 2Pz) < \pi(2Py) = \pi^*(2Pz) < \sigma^*(2Px)$

b. The diatomic molecule such as $H2$, He_2, B_2, C_2, and N_2 (lighter molecules) show slightly different energy order.

$\Sigma\ 1s < \sigma^*\ 1s < \sigma\ (2s) < \sigma^*(2s) < \pi\ (2py) = \pi\ (2Pz) < \sigma\ (2Px) < \pi^*\ (2Pv) = \pi\ (2pz) < \sigma^*\ (2Px)$

Q47.Why lighter molecules are higher in energy than π2Py=π2Py molecular orbitals.

Ans: Reasons:

We have seen in the energy order of lighter molecules like B_2, C_2,N_2,σ_2Pxis higher in energy than π2py = π2pz, molecular orbitals. This reversal is due to mixing of 2s and 2px atomic orbitals.

Explanation:

Actually the energy difference of 2s and 2p atomic orbitals is small there is a possibility of mixing of these orbitals (hybridization of A.O.). As a result, σ2s and σ^*2s MO do not retain pure-character.

Similarly, σ2px and σ2Px MOs do not have pure p-character. All the tow MOs acquire sp-character Due to this, mixing, their energies change in such a way that MOs σ2s and σ^*2s become more stable and are lowered in energy MOs as σ2Px.andσ^*2Px become less stable and are raised in energy. Since, π2py=π2Pz remains unchanged. σ2Px is raised to such an extent that it becomes higher in energy than π-bonds.

Examples:

But, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 KJ/mol and 2078 KJ/mole for O, and F_2 respectively. The values are 554 KJ/mol for Boron, 846 KJ/mol for carbon ,and 1195 KJ/mol for nitrogen and these energy differences have been calculated by spectroscopic techniques

Q48. Explain the structure of Hydrogen Molecule H2 on the basis of molecular orbital theory.

Ans: Hydrogen Molecule H_2:

H = 1s

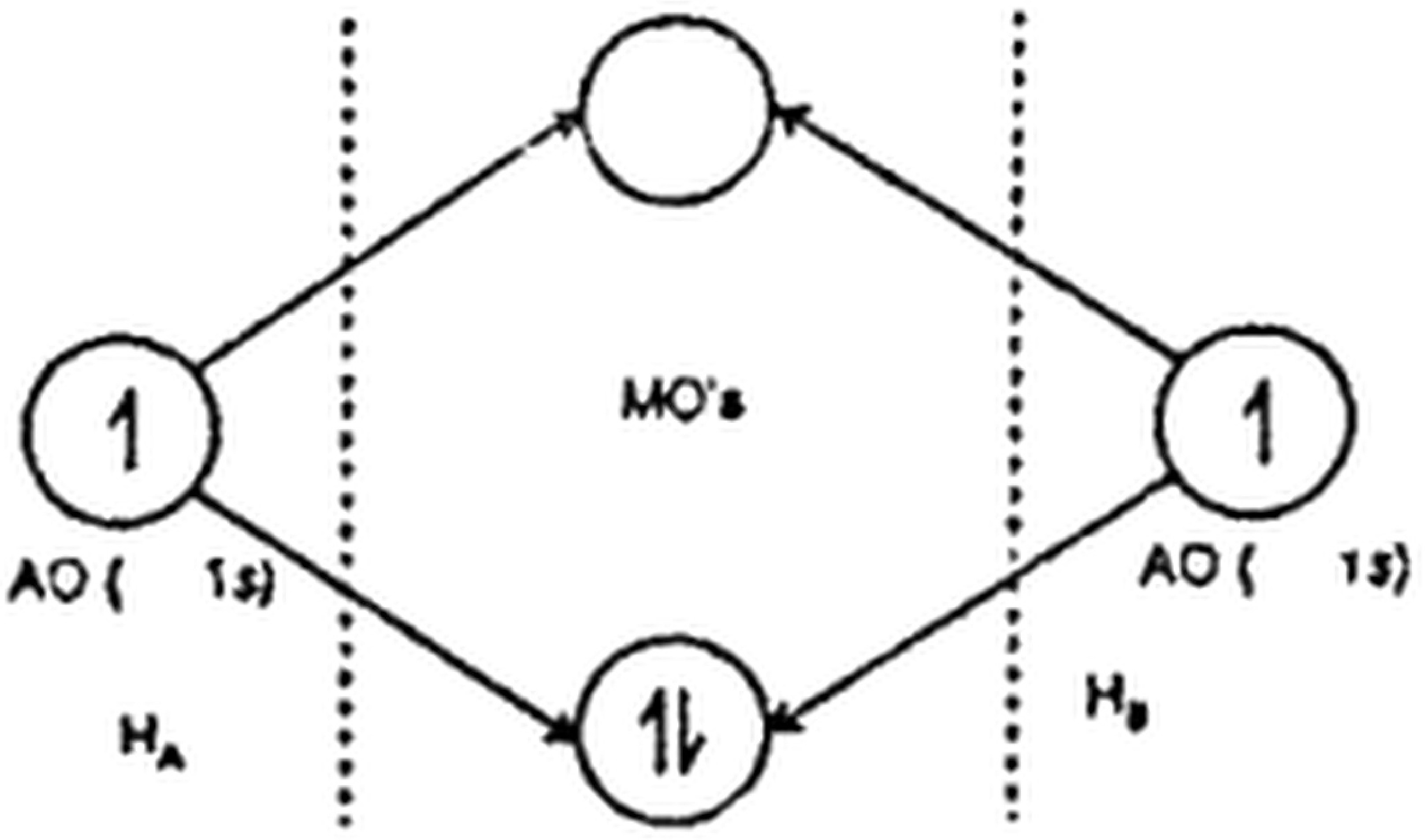
Hydrogen molecule is formed from the overlap of 1s atomic orbital_s of two hydrogen atoms. They give rise to two molecular orbitals σ 1s and σ^* 1 s. The molecule has two electrons which occupy the lower energy σ1s orbital as shown in the diagram. The electronic configuration of the molecule is represented by the equation

$2H\ (1s^1) \rightarrow H_2\ [(\sigma\ 1s)^2]$

Bond order= 2-0 /2 = 1

Thus, the two hydrogen atoms are bonded through only one bond in the molecule. We conclude that the H_2 molecule is stable, which indeed is. It has bond dissociation energy of 435 $KJmol^{-1}$ and is diamagnetic in nature i.e. (atoms, ions or molecules in which electrons are all paired in their molecular electronic configuration are diamagnetic). They are repelled by both poles of magnet

σ (Antibonding)



σ (Bonding)

Molecular orbitals energy level diagram of H_2

Q49.Discussthe structure of Helium Molecule He_2on the basis of molecular orbital theory.

Ans: Helium Molecule (Hypothetical) He_2:

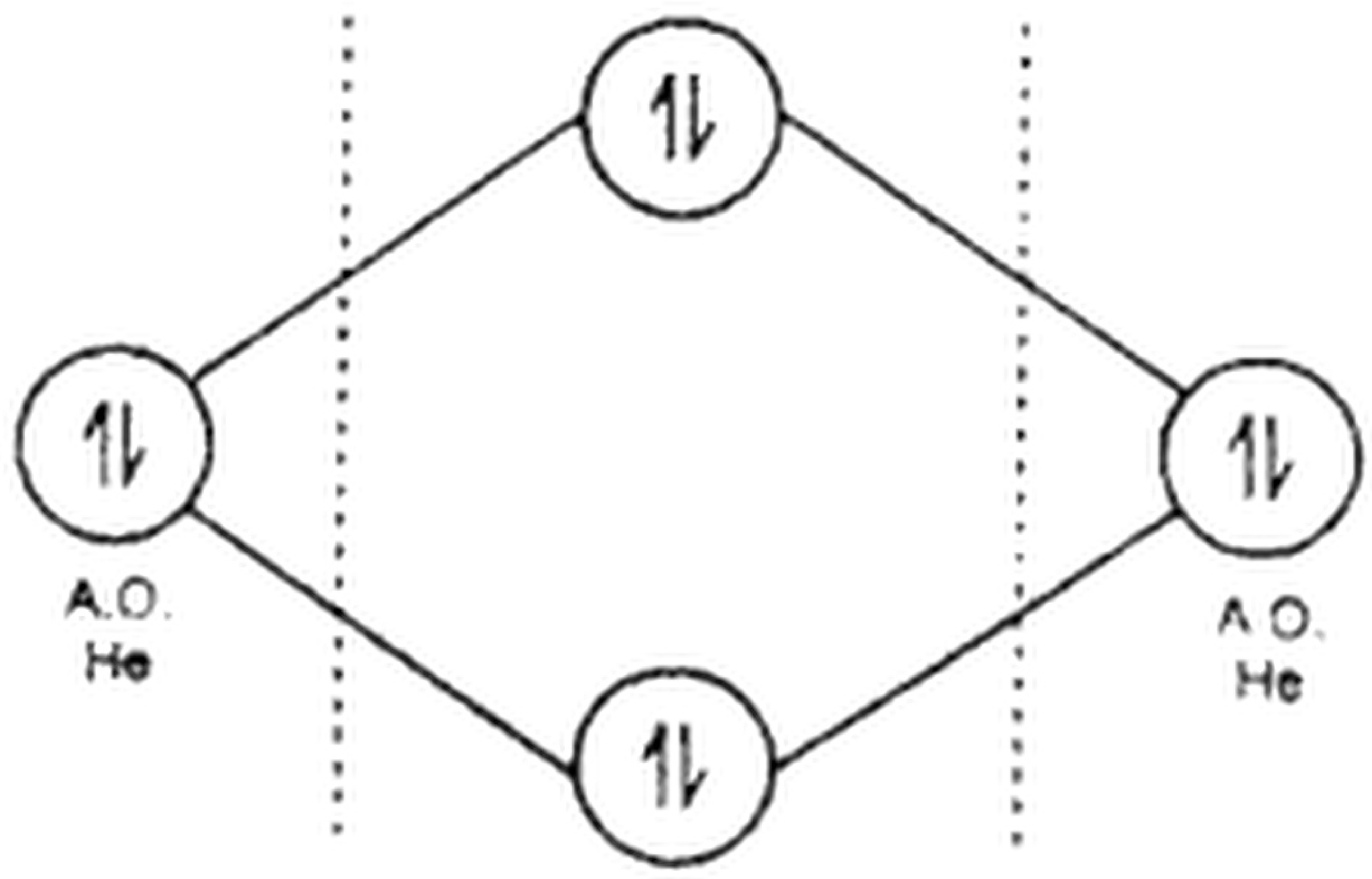
He= $1s^2$

The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons which occupy the anti-bonding o- · s orbital shown in the diagram.

Bond order=0

Thus, its bond order is zero and we conclude-that the molecule is not stable. Infect, He2 is not known, helium exists only as mono-atomic molecules.

(Anti-Bonding)



(Bonding)

M.O.

Molecular orbitals energy level diagram of He_2

Q50.Explain structure of Lithium Molecule Li on the basis of molecular orbital theory.

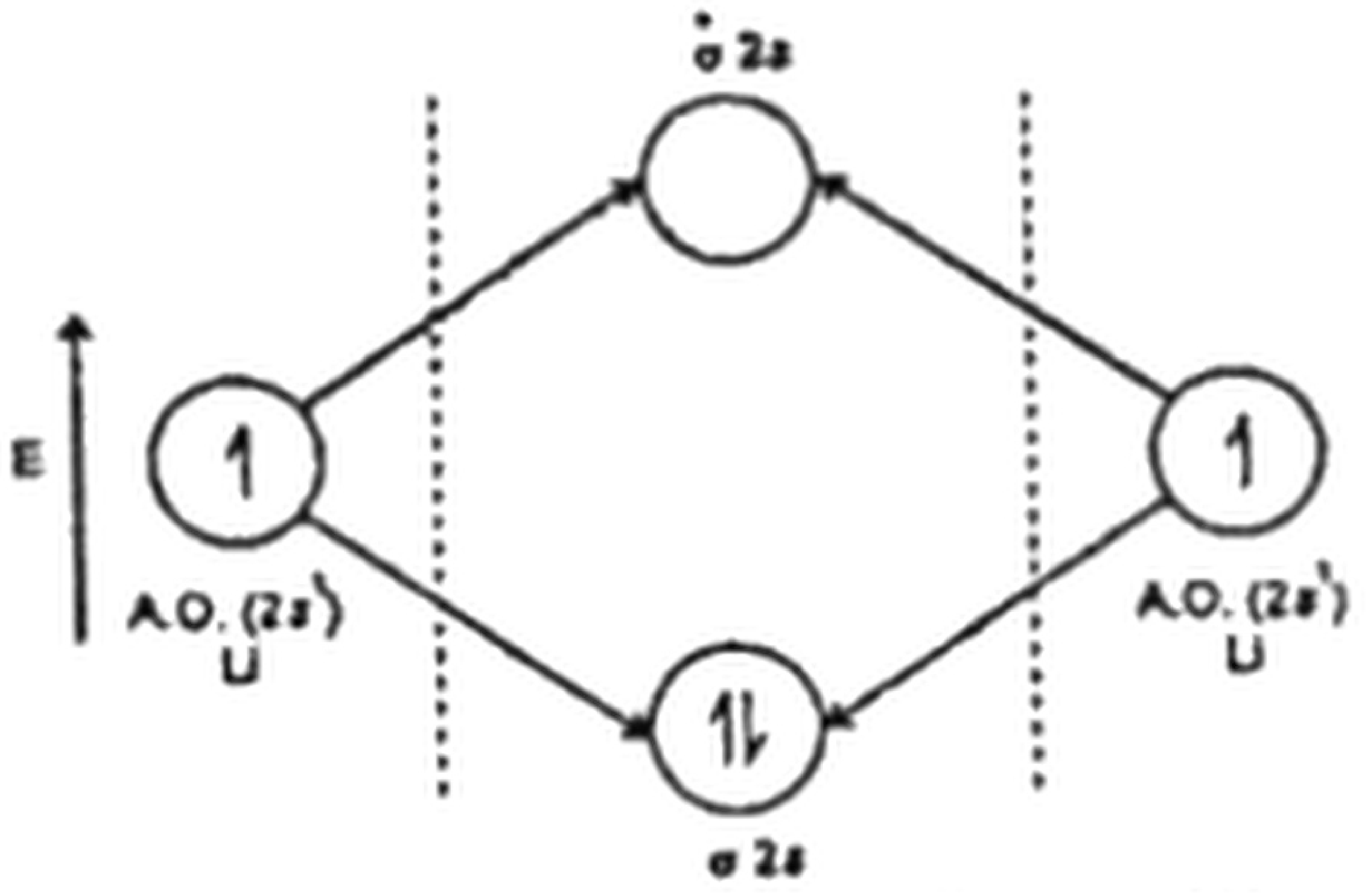
Ans: Lithium Molecule Li_2:

Li= $1s^2\ 2s^1$

The electronic configuration for Li_2has a total of six electrons, two each in o 1s, 0·1s and o2s molecular orbitals. In short hand notation this can be represented as o $1s^2$, o'$1s^2$ and o $2s^2$. There are two more electrons in the bonding orbitals than in anti-bonding orbitals and the bond order is one. We conclude that the molecule is stable and diamagnet c it is indeed to exist in the vapor phase. It possesses bond energy of 110 KJ mor^1 which is less than H_2 molecule.

$2Li\ (1s^2) \longrightarrow Lt_2[KK\ (\sigma 2s)^2]$

Bond order = 1



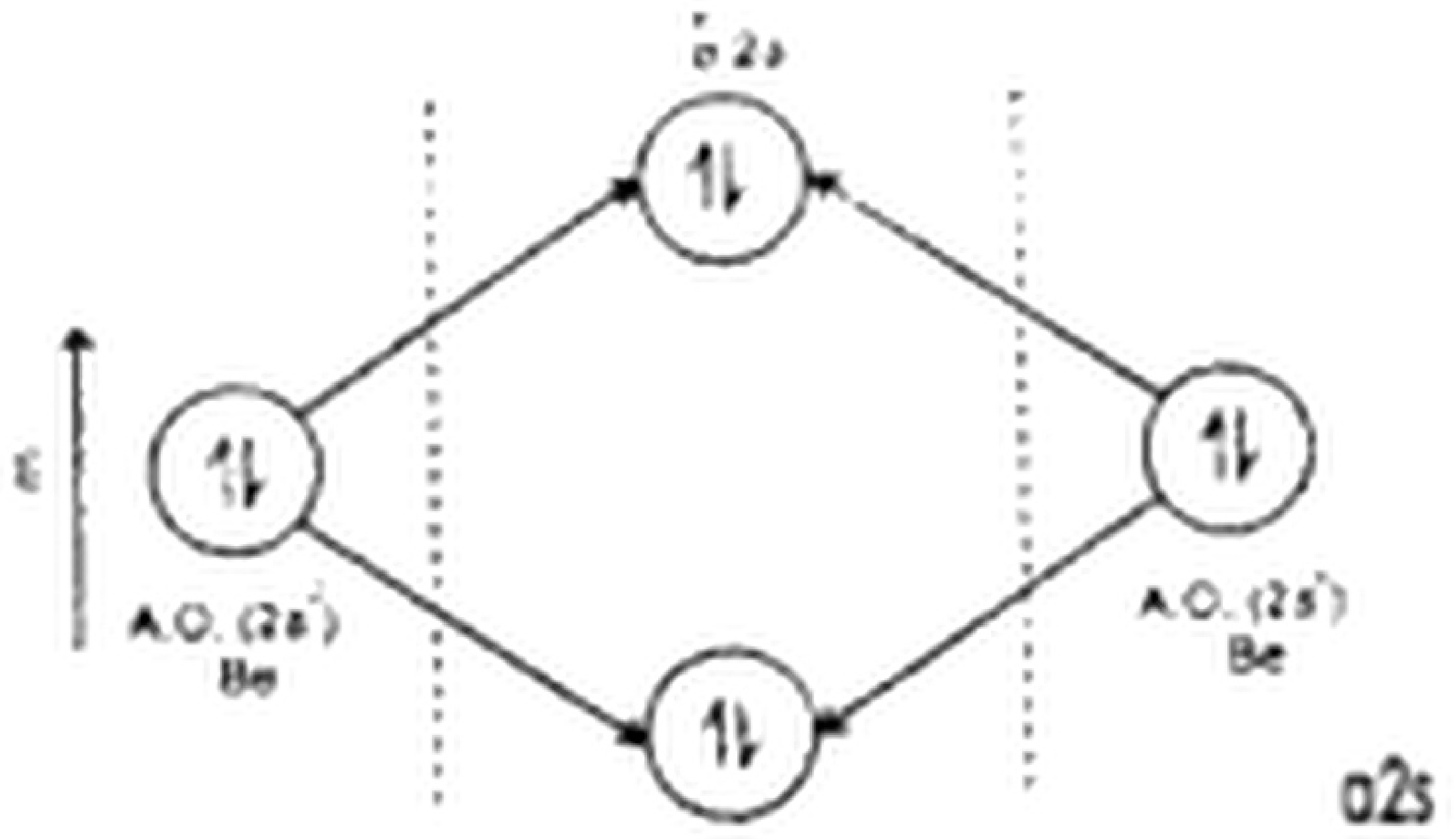
Molecular orbitals energy level diagram of Li_2

Q51. Explain the structure of Beryllium Molecule Be2 on the basis of molecular orbital theory

Ans: Beryllium Molecule, Be_2:

The situation for the Be_2 molecule is similar to that for He. Bonding and anti- bonding orbitals are equally populated and the bond order is zero. The electronic configuration is 6 $1s^2$, 5·$1s^{2,}$ 6 $2s^2$ 5·$2s^2$. The Be2 molecule is known but is very unstable.

Bond order = 2-2 / 2 = 0



Molecular orbitals energy level diagram of Be_2

Q52. Explain the structure of Boron Molecule, B_2 on the basis of Molecular orbital theory.

Ans: Boron Molecule B_2:

B =5 $1s^2 2s^2 2p^1$

The boron atom has the configuration of $1s^2$ $2s^2$, $2p^1$ and is the first element with P electrons to participate in bonding.

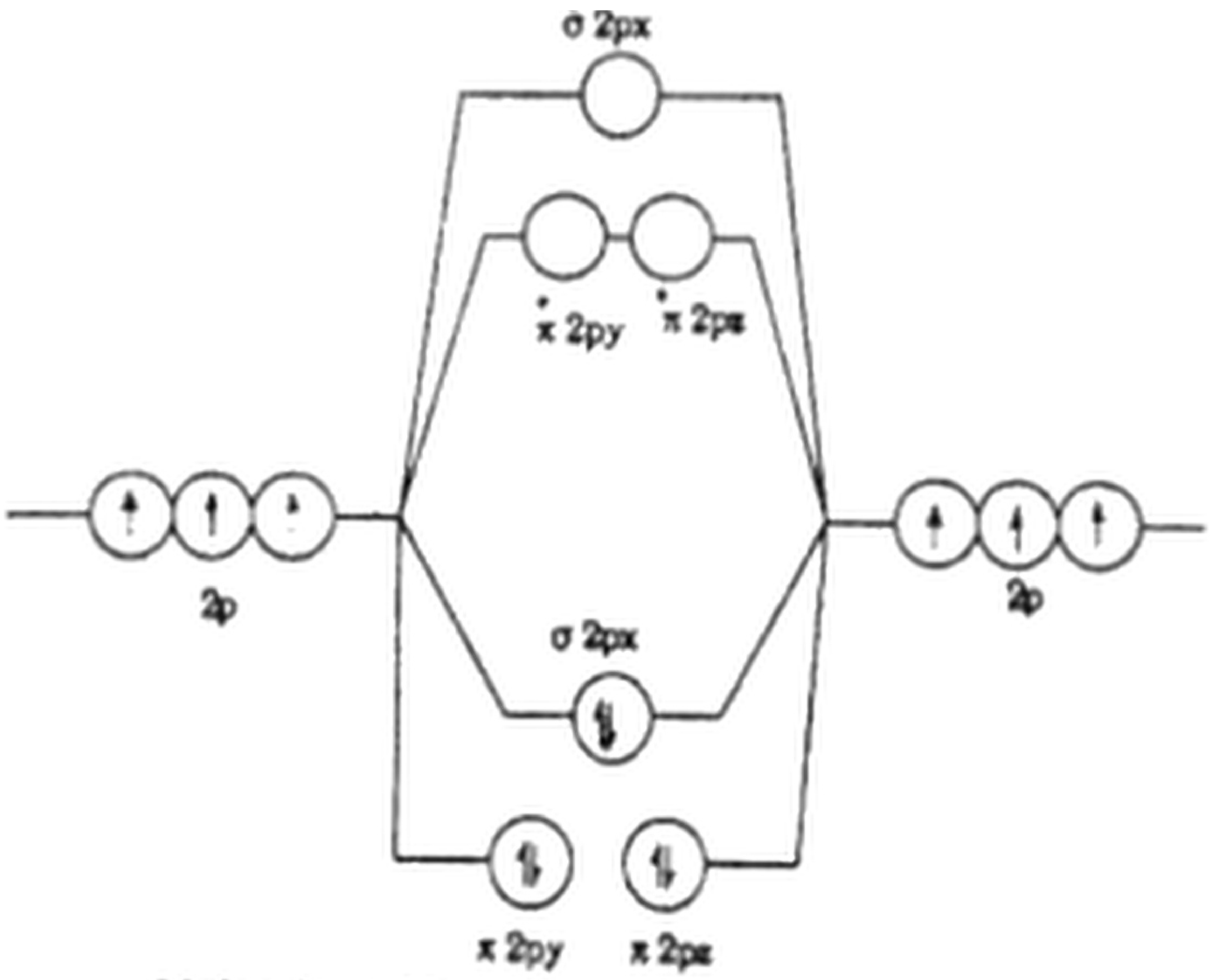
Thus, the two B - atoms are bonded through only one bond in the molecule.

The experiments verify not only that the molecule exists in vapor phase but that it is paramagnetic (atoms, ions or molecules) with two unpaired electrons. The bond energy is 270 KJ mor ^{1} which have one or more unpaired electrons in their molecular electronic configuration is paramagnetic. They are attracted to a magnetic field.

Q53. Explain the structure of Nitrogen Molecule N_2 on the basis of molecular orbital theory.

Ans: Nitrogen Molecule N_2:

Looking at. the electronic configuration, only 2s and three 2p electrons from each N atom are to be considered in the bond formation



Molecular orbitals energy level diagram of N_2

Thus, the electronic configuration of N

Bond order= 6 - 0 / 2= 3

It is obvious that the two N-atoms are bonded through triple bond. Ni molecule is very stable molecule and has a very high energy 946 KJ mol^{-1} which is with MOT. It is diamagnetic in nature and possesses a very short bond length.

Q54.Explainthe structure of Oxygen Molecule O_2 on the basis of molecular orbital theory.

Ans: Oxygen Molecule O_2:

$0 = 8 = 1s^2\ 2s^2\ 2Px^2\ 2Py^1\ 2Pz^1$

The valence bond theory predicts that 0_2 would be diamagnetic. However, experiments show that it is paramagnetic having two unpaired electrons. A structure consistent with this observation is predicted by MOT. Spectroscopic evidence indicates that for 0_2, the o2p orbital is lower in energy than 7t2p orbitals.

The electronic configuration of 0_2 molecule is:

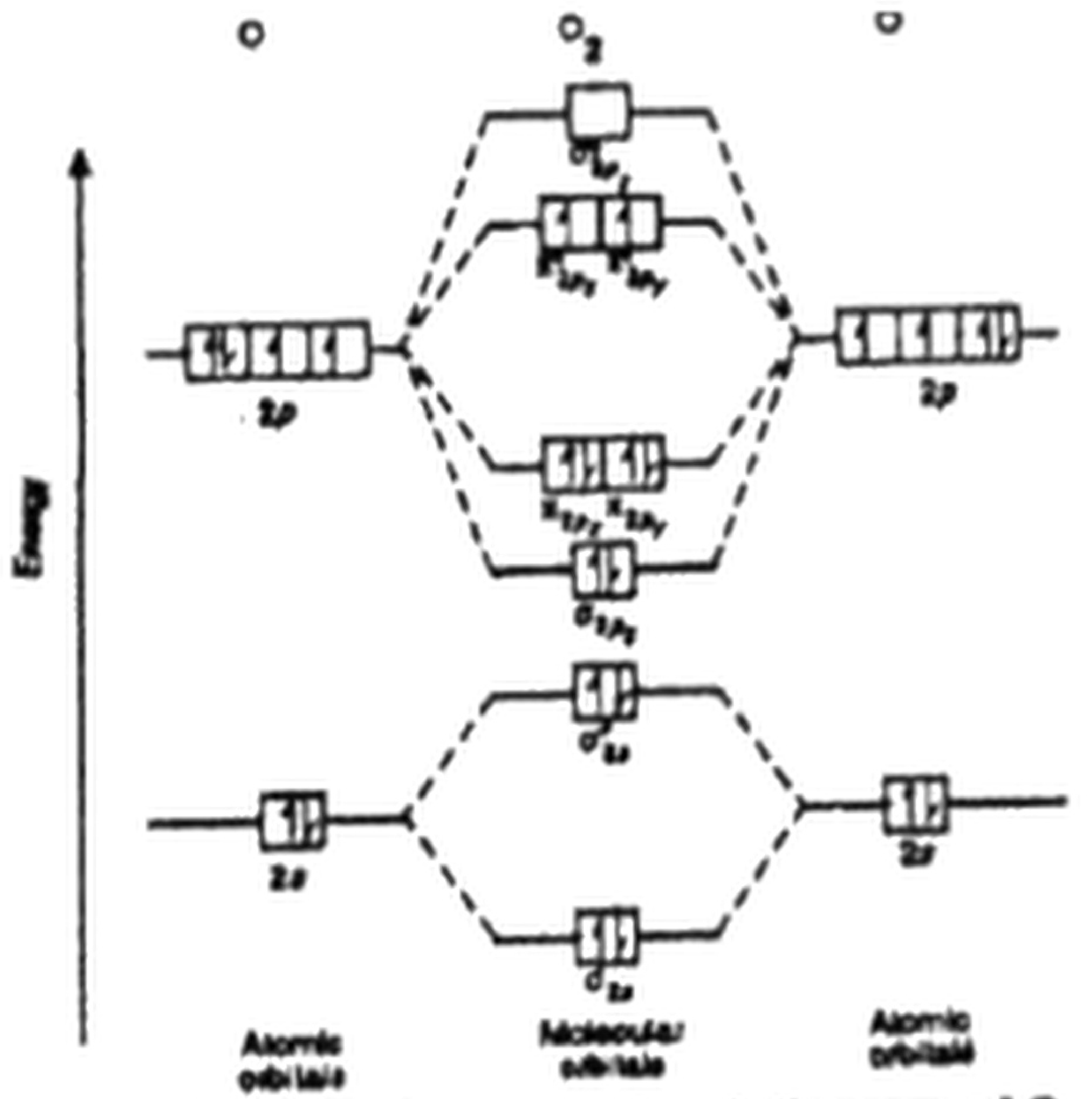
$2O(1s^2 2s^2 2px^2 2py^1 2pz^1)$

$O_2[KK(\sigma 2s)^2(\sigma^*2s)^2\ (\sigma 2pz)^2\ (\pi 2py)^2\ (\pi 2px)^2\ (\pi^*2py)^1\ (\pi 2px)^1$

Bond Order=6-2/2=2

It is obvious that the two O atoms are bonded through a double bond. The

Two unpaired electrons, reside in the degenerate anti-bonding orbitals π $2p_y$ and π $2p_z$ hence, it is paramagnetic in nature. So, we conclude that the molecule should be very stable as it is. It possesses bond energy of 498 KJ mol^{-1} with bond length 1.21 °A.



Molecular orbitals energy level diagram of O_2

Q55.Explain the structure of Fluorine Molecule F2 on the basis of molecular orbital theory.

Ans: Fluorine Molecule F2:

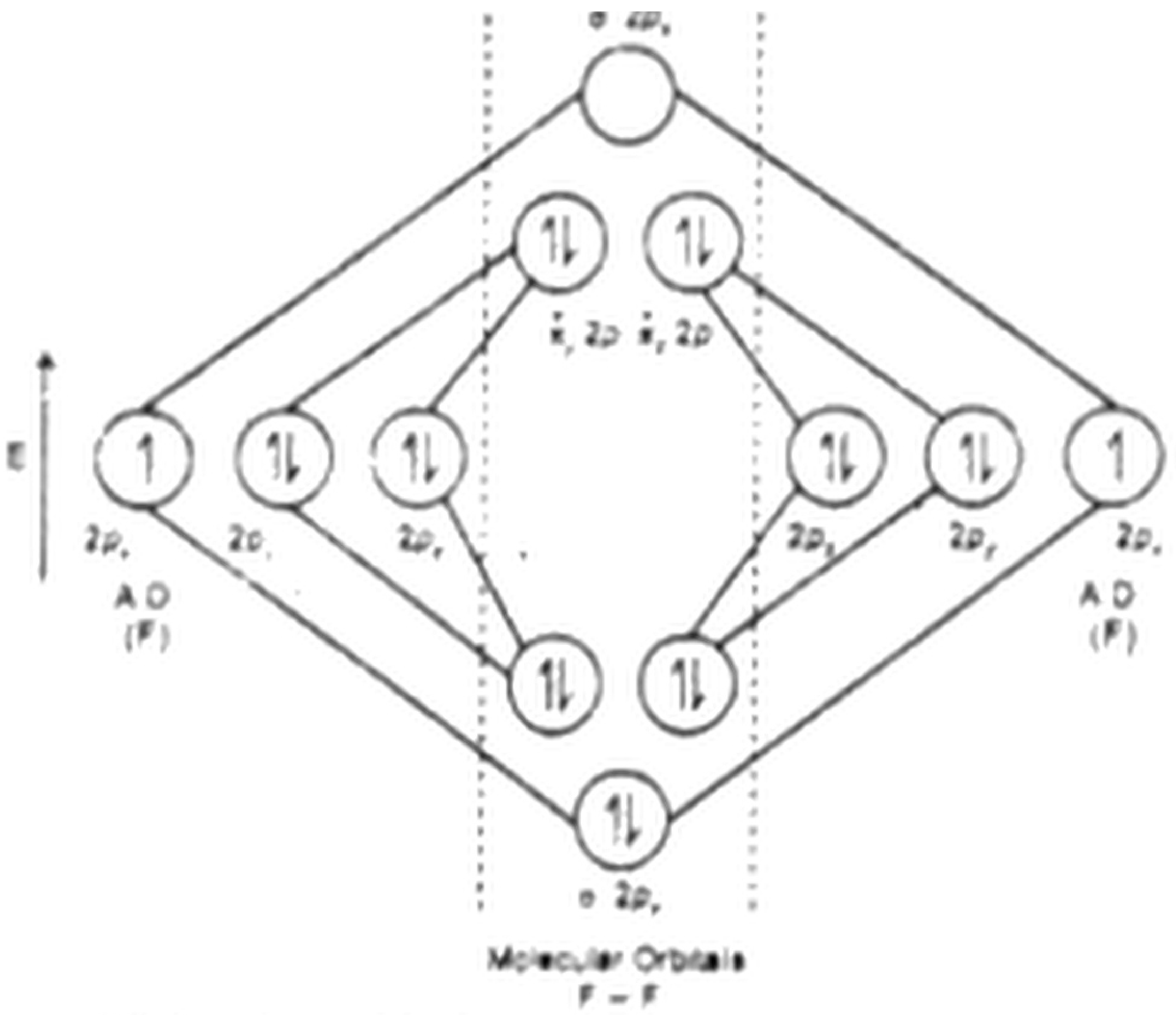
$F = 9 = 1s^2\ 2s^2\ 2p^5$

Each F-atom has the $1s^2\ 2s^2\ 2p^5$ configuration. The two participation oF-atoms contribute a total of F molecule is:

$F=KK(\sigma 2s)^2(\sigma^* 2s)^2\ (\sigma\ 2p_z)^2(\pi\ 2p_y)^2(\pi 2p_x)^2(\pi^* 2p_y)^2(\pi^*\ 2px)^2$

Bond Order= 6-4/2 =1

It is obvious that two F-atoms are bonded through a single bond. The F-F bond distance is longer (1.43°A) than the bond distance for O_2 (1.21°A) and N_2 (1.09°A) molecules. The bond energy of F_2 molecule is quite low(159KJ/mol) diamagnetic in nature



Molecular orbitals energy level diagram of F_2

Q56. Give common features of Valence Bond and Molecular Orbital Theories.

Ans: Common features of Valence Bond and Molecular Orbital Theories:

Similarities:

The common features of the two theories are:

i. Both the theories explain the formation of covalent bond.

ii. In both the theories, a covalent bond is formed by the overlapping of atomic orbitals have appropriate symmetry about the molecular axis.

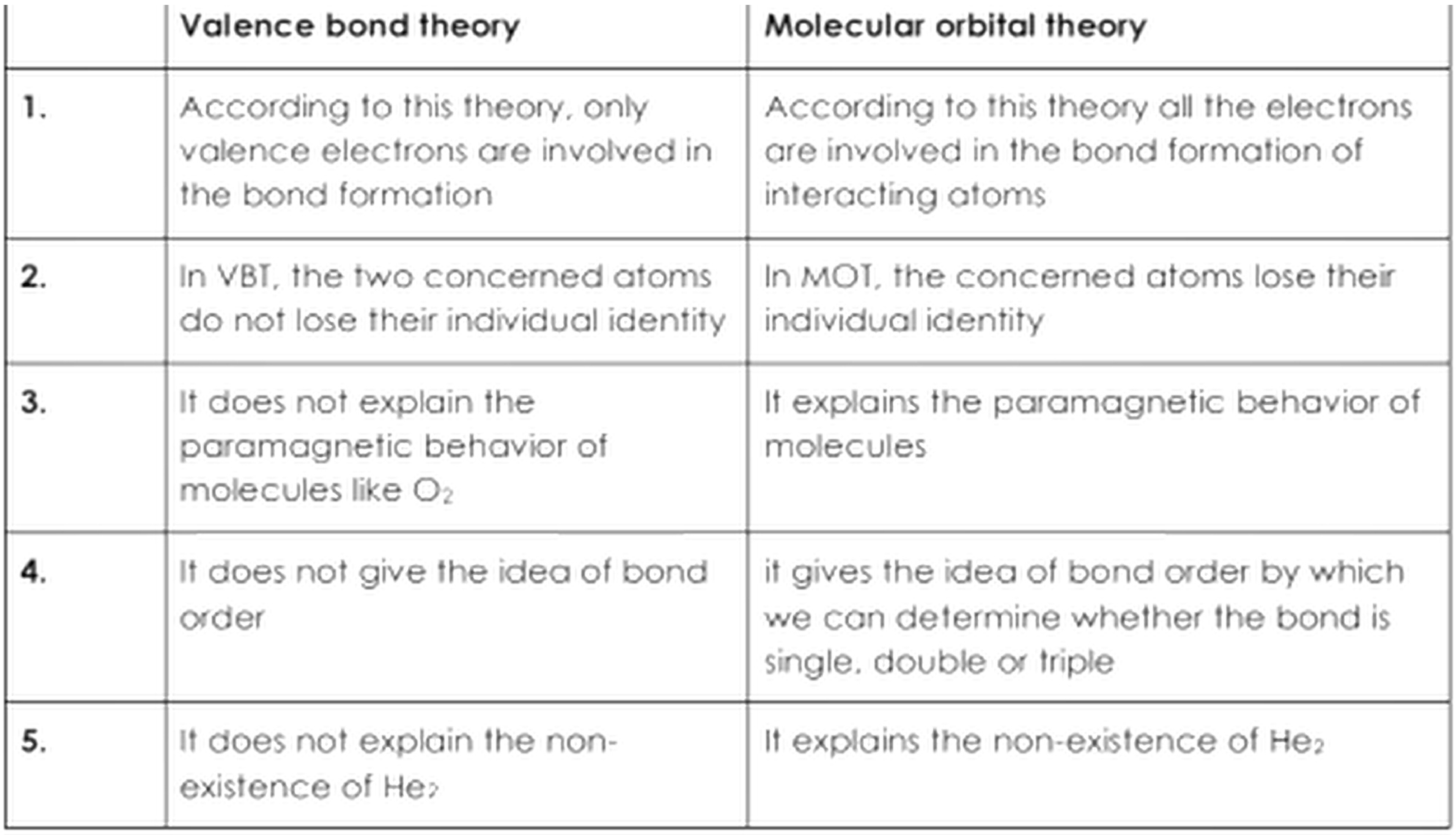
iii. According to both, the electronic charge resides in the region between the atomic nuclei.

iv. Both the methods lead to the formation of two types of bonds o and n bonds.

v. In both the methods, the atomic and molecular orbitals are filled up according to the same principles.

Q57. Differentiate between Valence Bond and Molecular Orbital Theories.

Ans: Difference



	Valence bond theory	Molecular orbital theory
1.	According to this theory, only valence electrons are involved in the bond formation	According to this theory all the electrons are involved in the bond formation of interacting atoms
2.	In VBT, the two concerned atoms do not lose their individual identity	In MOT, the concerned atoms lose their individual identity
3.	It does not explain the paramagnetic behavior of molecules like O_2	It explains the paramagnetic behavior of molecules
4.	It does not give the idea of bond order	it gives the idea of bond order by which we can determine whether the bond is single, double or triple
5.	It does not explain the non-existence of He_2	It explains the non-existence of He_2

Q58. What do you understand by Bond Energy or Bond Enthalpy? Explain various factors parameters which determine the strength of bond energy.

Ans: Bond Energy (Bond Enthalpy):

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

Strength of a bond:

The strength of a bond is measured by its bond energy. The higher the bond energy, the stronger is the bond. It is determined experimentally by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is measure of enthalpy change at 298K.

Enthalpy of atomization:

The enthalpy changes in splitting a molecule into its component atoms is called enthalpy of atomization.

Units:

It is expressed in kilojoules per mole (KJmor^{1}

Bond energy is the energy required to break up an Avogadro number (6.02×10^{23}) of bonds i.e. one mole of bond.

It is found that energies of multiple bonds are greater than those of single bonds. But a double bond is not twice as a strong as a single bond or a triple bond is not thrice as strong as a single bond. It means that a σ bond is stronger than a π bond. Also, a polar covalent bond is stronger than a non-polar covalent bond.

Examples:

i. The bond energy of H-H in H_2 molecule at 25°C 298K is 435KJ/mole. The bond energy of Cl. Cl bond in Cl_2 molecule at 25°C is243KJ/mole.

ii. The bond energy of H-Cl bond in HCl molecule at 25°C is 431KJ/mole

Q59.Explain Ionic character and Bond energy with the help of examples and factors on which they depend in detail.

Ans: Ionic character and Bond energy:

Bond energy is a measure of bond strength. Higher the bond energy, the stronger is the bond. The strength of a bond depends upon the following factors.

i. Electronegativity

ii. Size of the bonded atoms

iii. Bond length

iv. Bond order (number of bonds)

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

Bond type H-X	**H-F**	**H-Cl**	**H-Br**	**H-I**
Bond energy ($KJmol^{-1}$)	567	431	366	299
ΔEN	1.9	0.9	0.7	0.4

From the above data it is observed that HF molecule has higher bond energy (567 $KJmol^{-1}$) due to greater electronegativity difference i.e. 1.9.

The smaller the size of the bonded atoms, the greater is the bond energy and stronger is the bond. The bond energy of H-H bond is 435KJmor^{1} and that Cl-Cl is 243KJmor^{1}. It is due to the shorter bond length in H_2 molecule and greater bond length in Cl_2 molecule (larger size of Cl atom than H atom).

Multiple bonds also affect the bond energy, greater the no. of bonds greater will be the bond energy.

Average Bond energies (KJmol^{-1}) of single bonds.

Bond	Bond Energy (KJmol^{-1})	Bond	Bond Energy (KJmol^{-1})	Bond	Bond Energy (KJmol^{-1})	Bond	Bond Energy (KJmol^{-1})	Bond	Bond Energy (KJmol^{-1})
C-H	413	Si-H	323	H-H	436	S-H	339	Cl-F	253
C-C	348	Si-Si	226	H-F	567	S-F	327	Cl-Cl	242
C-N	293	Si-C	301	H-Cl	431	S-Cl	253	Br-F	237
C-O	358	Si-O	368	H-Br	366	S-Br	218	Br-Cl	218
C-F	485	N-N	163	H-I	299	S-S	266	Br-Br	193
C-Cl	328	N-O	201	H-O	463	O-O	146	I-Cl	208
C-Br	476	N-F	272	H-F	155	O-F	190	I-Br	175
C-I	240	N-Cl	200	H-N	391	O-Cl	203	I-I	151
C-S	259	N-Br	243			O-I	234		

Average Bond energies of multiple bonds (KJmol^{-1})

Bond	Bond Energy (KJmol^{-1})	Bond	Bond Energy (KJmol^{-1})
C = C	614	N = N	418
C ≡ C	839	N ≡ N	941
C ≡ N	891	O = O	495
C = O	799	S = O	523
C ≡ O	1072	S = S	418

Q60.Why experimentally determined value of H-Cl bond energy is greater than theoretically calculated bond energy of H-Cl bond?

Ans: Relationship between the Bond Energy and Polarity or Strength of Bond and Its Ionic Character:

polar bonds are stronger than non-polar bonds and greater amount of energy is required break these bonds. Due to the ionic characters, the strength of bond increases. Increase in strength of H-Cl bond or ionic character in H-Cl bond can be observed from the experimentally determined values of H-H, Cl-Cl and H-Cl bond and theoretically calculated bond energy value of H-Cl bond. It involves the following steps:

Step (i) Calculation of bond energy contribution of one H atom.

Bond energy of I mole of H-H bonds = 436 KJ

or Bond energy of 6.02×10^{23} H-H bonds = 436KJ

or Bond energy of one H-H bonds = $\frac{436}{6.02 \times 10^{23}}$ KJ

= 72.42×10^{-23}KJ

Bond energy contribution of one H atom: $\frac{7.42 \times 10^{-23}}{2}$

= 36.21×10^{-23} KJ

Step (ii) Calculation of bond energy contribution of one Cl atom.

Bond- energy of I mole of Cl-Cl bonds = 242KJ

or Bond energy of 6.02×10^{23}Cl-Clbond = 242 KJ

= 40.19×10^{-23} KJ

Bond energy contribution of one Cl atom =40.19×10^{-23} /2

= 20.09×10^{-23} KJ

Step (iii) Calculation of bond energy of I mole of H-Cl bonds.

Hence calculation is based on the assumption that H-Cl bond is non polar.

Bond energy of one H-cl bond = Bond energy of H-atom + Bond energy of Cl atom.

= (36.21×10^{-23} + 20.09×10^{-23}) KJ

= 56.3×10^{-23} KJ

Bond energy of 8.02x1 H-Cl bonds= $56.3 \times 10^{-23} \times 6.02 \times 10^{23}$

= 338.93KJ

Bond energy of one mole of H-Cl bond = 338.93KJ/mole

The relation between bond energy and electronegativity can been seen from theoretically calculated and experimentally determined values of HCl bond.

Theoretically calculated bond energy of H-Cl bond = 338.93KJmol^{-1}.

Experimentally determined energy of H-Cl bond = 436KJmor^{1}.

The experimentally determined bond energy is significantly greater than the calculated values, which means a more stable H-Cl bond. This stability is due to the ionic character present in the bond. The amount of additional bond energy depends on the electronegativity of the two bonded atoms. Greater the difference of electronegativity between bonded atoms, stronger is the bond.

Comparison of experimental and theoretical bond energies

Bond	**Bond energy KJmol^{-1}**			
	X=F	**X=Cl**	**X=Br**	**X=I**
X-X	155	242	193	151
H-X (calculated)	293	338	311	291
H-X (observed)	567	431	366	299
Difference	274	95	55	08

This data clearly indicates the part played by electronegativity in the strength of a bond. Electrons are not equally shared between hydrogen and halogen atoms in HX. Since halogen atom is more electronegative, the bonded electron pair is more attracted towards halogen atom. This develops polarity in H-X molecules which produces an additional attractive binding force.

Q61.Define Bond Length. Describe different methods to measure bond length experimentally.

Ans: Bond Length:

Bond length may be defined as the distance between the nuclei of atoms joined by covalent bond. This distance between the bonded atoms is not constant, because the bonded atoms are always vibrating with respect to each other. Therefore, average inter nuclear distance is considered as bond length or bond distance. Bond length may be may also be defined as inter nuclear distance when the maximum possible overlap of concerned atomic orbitals occurs.

Measurements of Bond Length:

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

Measuring units:

It is measured in A or picometer:1pm=10^{-12}m,100pm=1A =10^{-10}m.

It is observed that its measurements may vary in accuracy but still similar bonds have fairly constant lengths in different molecules, variation generally being less than 1%. In most of the compounds, the C-C single bond length is very close to 1.54A.

For example, in ethane molecule the C-C bond length is 1.54 A and in ethyl chloride (C2H5Cl) the C-Cl bond length is1.55A.

Covalent Radius:

One half of the bond length between nuclei of two similar atoms join by single covalent bond is called the covalent radius of that atom.

For example, the covalent radius of Carbon is 0.77 A i.e. half of the C-C bond length which is 1.54 A. The covalent-radii of other atoms are given in the following table:

Covalent-radii of various atoms

Atom	Covalent-radius	Atom	Covalent-radius
H	0.28	F	0.72
C	0.77	Cl	0.99
N	0.75	Br	1.14
0	0.74	I	1.33

Covalent-radii can be used to calculate the bond length:

The covalent-radii can be used to calculate the bond length between two unlike atoms, which in some cases, is equal to the sum of the covalent radii of the two bonded atoms. For example, the C-Cl bond length in CH_3Cl is 1.76A, which is exactly the sum of the covalent radio carbon (0.77A) and chlorine (0.99A).

However, in most cases, the length of a bond between two unlike atoms is markedly shorter than the sum of the two covalent radii. For example, the covalent radii of C and N add up to 1.52 A whereas the observed C-N bond length in methylamine (CH3NH$_2$) is 1.47 A. Similarly, the observed C-O bond length is ethanol (C_2H_5OH) is 1.42A, although the sum of the covalent radii of carbon and oxygen is 1.51 A. In general, the shrinkage in bond length becomes more and more marked as the difference in electronegativity of the two bonded atoms increases. Average single bond lengths of some of the important covalent bonds are given in the following table:

Bond Lengths of some Covalent Bonds

Covalent	Bond Length	Covalent	Bond Length
C-H	1.07	C-Br	1.93
C-C	1.54	C-I	2.14
C-O	1.42	C-Cl	1.76
C-N	1.47	O-H	0.96
C-F	1.38	N-H	1.01

Q62. Discuss the different factors affecting the bond length.

Ans: Factors affecting the bond length:

Nature of hybridization:

Bond length is also affected by the nature of hybridization of the bonded atoms.

Effect of Hybridization on the Bond Length

Hybridization of Carbon	Bond length		
	C-H	C-O	C-N
sp^3	1.11 methane	1.41 (ethanol)	1.47 (methylamine)
sp^2	1.10 (ethylene)	1.34 (formic acid)	1.36 (formamide)
sp	1.08 (acetylene)		

Increase in s character:

It can be noticed that the bonds are short end by increasing character.

This is because the hybrid orbital with increased s character is held more tightly by the nucleus.

A double bond between two atoms is shorter than a single bond between the same

two atoms and a triple bond is shorter than the double bond as shown in table:

Bonded Atoms	Bond Length A˚		
	Single Bond	Double Bond	Triple Bond
C, C	1.54	1.38	1.19
C, N	1.47	1.28	1.16
C, O	1.42	1.20	…

Shrinkage of the multiple bonds:

The shrinkage of the multiple bonds is due to the presence of extra electrons (two in the case of a double bond and four in the case of triple bond) between the two nuclei, which exert additional attraction on both the nuclei bringing them closer to each other.

Q63. Define Dipole Moment. Write Its units.

Ans: Dipole Moment (Determination of degree of polarity of molecules):

The degree of polarity of a molecule can be expressed in terms of dipole moment.

It is the product of the magnitude of the charge (positive or negative) and the distance between them.

If q is the charge at each end of dipole and r is the distance between the positive and negative centers, then dipole moment represented as μ is given by

$$\mu = q \times r$$

In SI units, Coulombs meter (cm) but most common units used is Debye (D).

1 Debye (D) = 3.336×10^{-3} Cm

Q64. Write the applications of Dipole moment and also explain CIs and Trans.

Ans: Application of dipole moment:

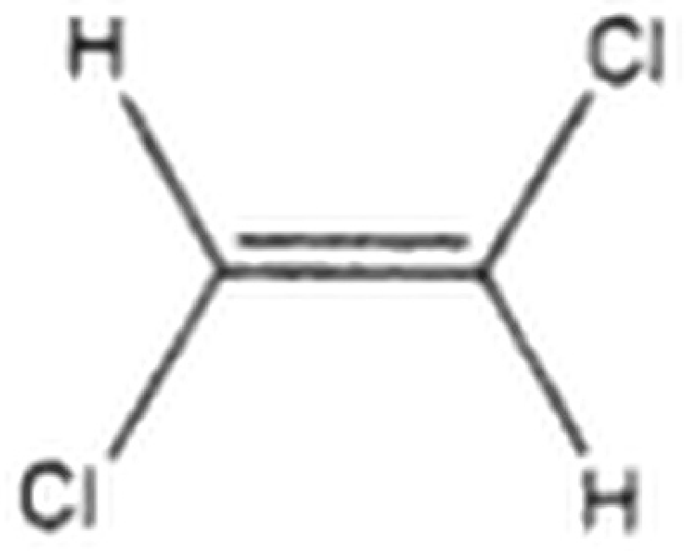
i. Determination of polarity of molecule:

Molecules which have zero dipole moment are non-polar, whereas molecules which have dipole moment are polar.

For example, benzene has zero dipole moment, so it is non-polar. But Chlorobenzene has dipole moment a: 12D, so it is polar.

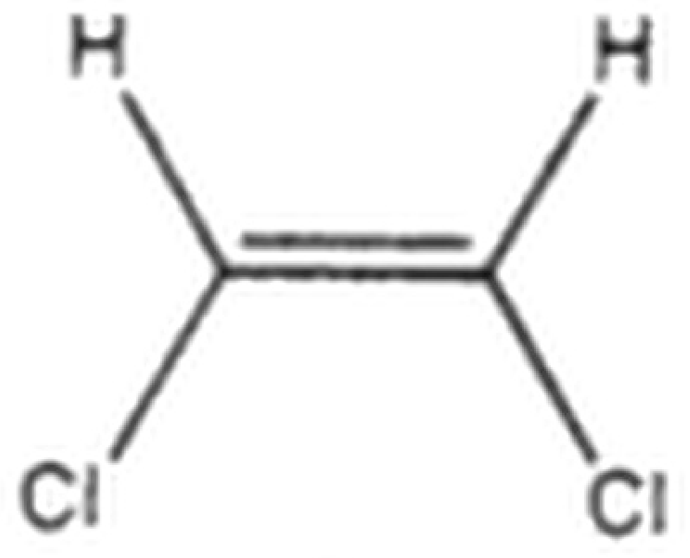
ii. Applications in **Stereo chemistry:**

The study of dipole moment also finds applications in. stereochemistry. For example, dipole moments of isomer 1, 2-dichloroethene have been calculated are given below:



Trans

$\mu = 0 D$



Cis

$\mu = 1.89D$

Thus, knowing the dipole moment of the given sample of 1, 2-dichloroethene, one can predict whether it is Cis or the trans isomer.

(iii) Calculation of %age ionic character in a bond.

The dipole moment helps to calculate the percentage ionic character in a bond.

Q65. The observed dipole moment of HF is 1.90D. Find the percentage ionic character in HF bond. The distance between the charges is 0.917×10^{-10}m. (Unit positive change = 1.6022×10^{-19}c)

Ans: Solution:

Let us suppose that an HF molecule is 100% ionic. It means that H has full positive charge and F has full negative charge. To calculate their dipole moments, Multiply the bond length with full charges of electron or proton

i.e. 1.6022×10^{-19}cm

This dipole moment is called μ_{ionic}. So, μionic =

Since D =3.336×10^{-30}cm

q x r

$(1.6022 \times 10^{-19} C)(0.917 \times 10^{-10} m)$

1.489×10^{-29} cm

The actual dipole moment as it is observed.

$\mu_{Observed}$=1.90D

%ionic character 1.90*100/4.4D = 43.2%

Hence 43% HF bond is ionic in nature and 57% covalent. The bond is predominantly covalent

Q66. Give detailed account of Solubility of Ionic Compounds.

Ans: Solubility of Ionic Compounds:

Most ionic compounds are soluble in water but insoluble in non-aqueous solvents.

Reason:

When a crystal of ionic compound is placed in water, the polar water molecules detach the cation and anion from the crystal lattice by their electrostatic attraction. The ions are freed from the crystal lattice by hydration. This happens when the hydration energy is equal to or greater than the lattice energy. The energy released in hydration is used to overcome the lattice energy. Thus, the Iona are freed from their positions in the crystal.

Reason:

Many ionic compounds do not dissolve in water because the attraction of water molecules cannot overcome the attraction between the Iona. Their lattice energy dominates over their hydration energy. For the same reasons, the non-polar solvent, benzene and hexane do not dissolve ionic compounds.

Q67. Give a detailed account of Solubility of Covalent-Compounds.

Ans: Solubility of Covalent-Compounds:

Covalent compounds dissolve in non-polar organic solvents such as benzene, ether. Most covalent compounds are insoluble in water. However, some of them dissolve in water.

Reason:

The attractive forces of solvent molecules in non-polar solvents are enough for overcoming the intermolecular forces of attraction in covalent compounds. Hence covalent compounds dissolve easily in non-polar organic solvents.

The solubility of covalent compounds in water depend on their ability to form hydrogen bonds with water molecules. Many organic compounds containing oxygen or nitrogen like carbohydrates, alcohols and amines are soluble in water due to hydrogen bonding.

Q68. Justify the Non-directional nature of Ionic compounds.

Ans: Non-directional nature of Ionic compounds:

Ionic bonds are non-directional and rigid in nature. They do not show the phenomenon of isomerism.

Q69. Justify the directional Nature of covalent compounds.

Ans: Directional Nature of covalent compounds:

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

Reason:

Due to non-rigid and directional nature of the covalent bond, covalent compounds have different orientation of atoms in space. Hence many covalent compounds show the phenomenon of isomerism. For example, C2HeO show structural isomerism.

CH3-O-CH3 and CH3 - CH2 -OH

Dimethyl ether Ethyl alcohol

Q70. Why the speed of reaction is higher in ionic compounds?

Ans: Speed of reaction of Ionic compounds:

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occurs rapidly. There action is so rapid because no bond is to be broken, only a new bond is formed. The ionic bonds have already been broken during the formation of solution.

For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously.

The oppositely charged ions combine at once to give the product. This is because no force is required to break the bonds of enacting compounds.

Q71. Why the speed of reaction is slow in covalent compounds?

Ans: Speed of reaction of covalent compounds:

Since there is no strong electrical force to speed up a chemical reaction, like in ionic reaction the covalent bonds are generally much slower to react a, they involve both breaking and making of bonds. The molecules undergo a chemical change as a whole. It is because high energy Is required to break the covalent bonds. Covalent compound reacts in a variety of ways. The reactivity of covalent compounds depends upon the way a reaction proceeds and the kind of product obtained at the end of a reaction.

Q72. Why Ionic crystals have high density?

Ans: Density:

The electrostatic force of attraction existing between the cations and anion, in an ionic crystal brings these ions very close to one another. This decrease the volume of the crystal and consequently, the ionic crystals have high density.

Q73. Briefly describe metallic solids and molecular network.

Ans: Metallic solids and molecular network:

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

Type of solids: Four types of solids exist namely.

(a) Molecular Solid:

Consists of atoms or molecules held together by inter-molecular forces. Solid water (ice) and solid CO_2 (dry ice) are common examples.

(b) Metallic Solids:

Consist of solids held together by metallic bonding.

Examples: silver, copper, and gold

(c) Ionic solids:

Consist of cations and anions held together by virtue of electrical attraction of the opposite charges. Examples are NaCl and CaCl2

(d) Covalent Network Solids:

Consist of atoms held together in large network or chains by covalent bonds. Diamond and Graphite are typical examples

Q74. Differentiate between metallic solids and molecular network solids.

Ans: Difference between metallic solids and molecular network solids (network crystal solids)

Metallic Solids:

Metallic solids consist of infinite arrays of bonded atoms; each cation in a metal has a high co-ordination number sometimes four or six, but more often eight or twelve, they are good conductors of electricity.

Network Molecular Solids or Non-metallic Network Solids:

They consist of infinite arrays of bonded atoms; no individual molecules can be distinguished. Thus any given piece of network solids may be considered as giant covalently bonded molecule. Network solids are generally poor conductor of heat and electricity. Strong covalent bonds among neibouring atoms thought out the structure give these solids strength and high melting temperature. Some of the hardest substances known are non-metallic network solids.

Structure of Diamond:

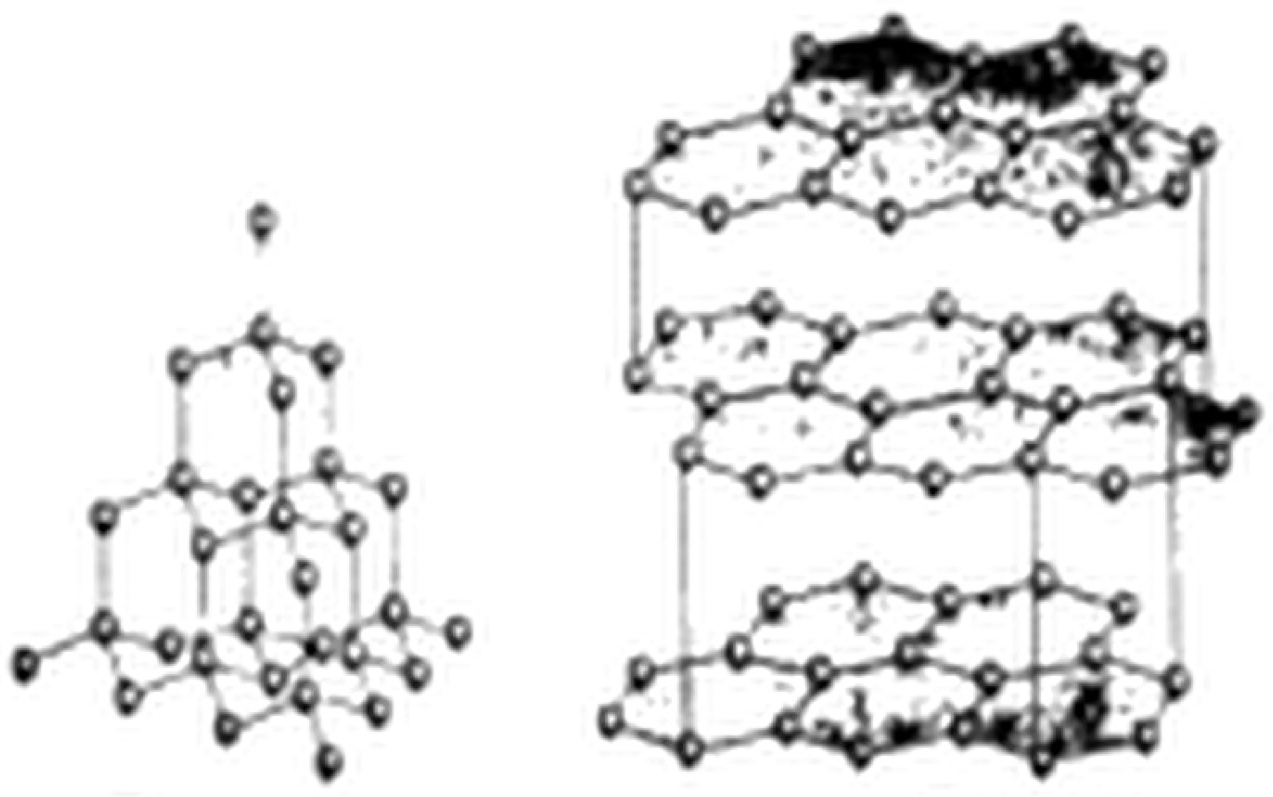
Diamond the hardest allotrope of carbon, has the network structure shown in the diagram. Diamond sublimes (volatilizes directly to ash rather than melts at 3500oC and above.

Structure of graphite:

Graphite, a softer allotrope of carbon has three layered structure shown in the diagram. One feature that distinguishes network solids from metals is the lower co-ordination number in network structures.

Example:

Co-ordination number of C in Diamond is four, Silicon (Si) and that of oxygen in quartz is two



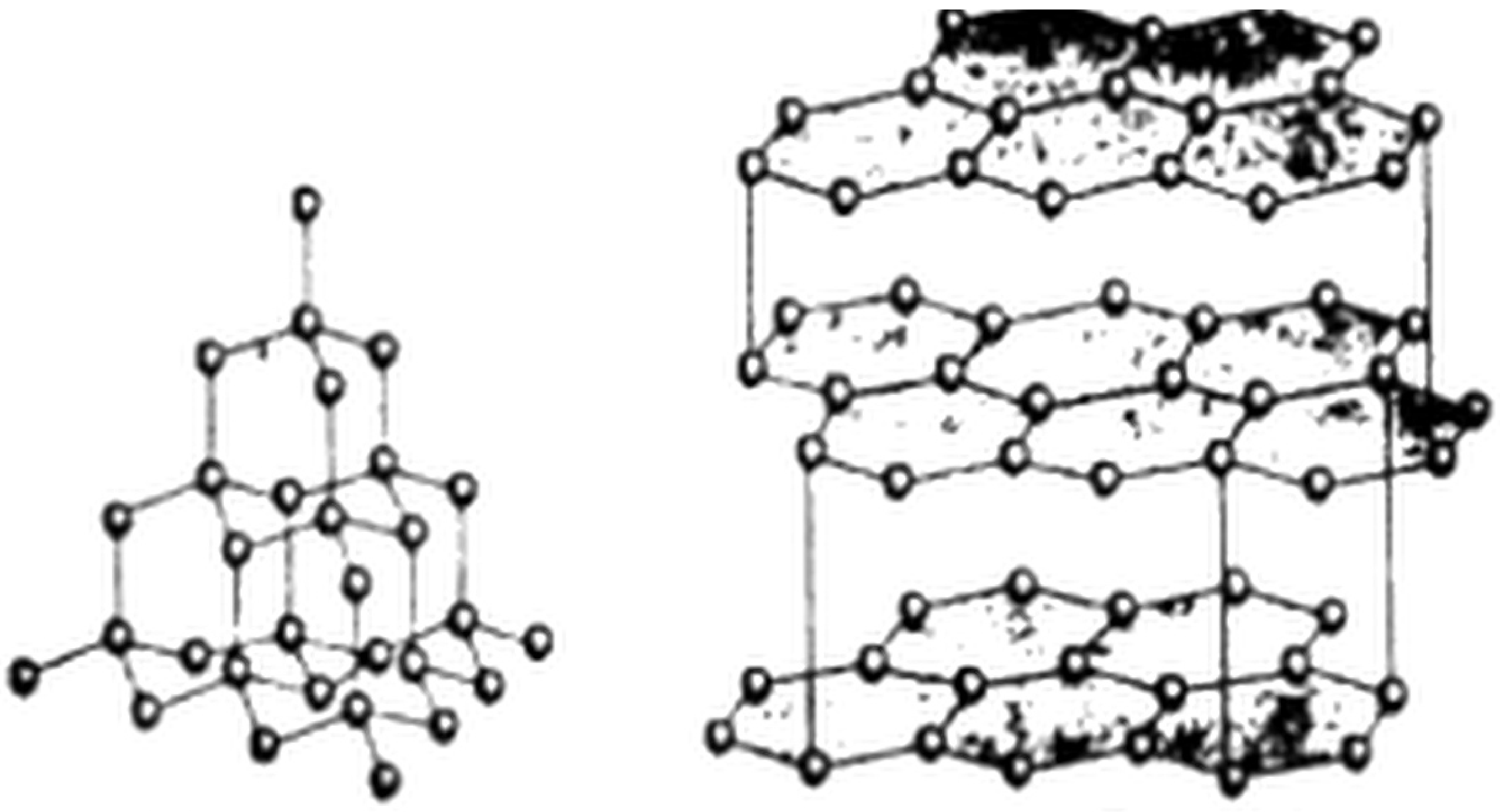
Diamond Graphite

Allotropic forms of carbon

Activity for students

Students have to make models of diamond and graphite as home work

Diamond and Graphite



Diamond Graphite

Allotropic forms of carbon