

CHEM – 653 Advanced Inorganic Chemistry (Cr.03)

A: Stereochemistry Periodicity

Concepts of Stereochemistry and Periodicity (Periodic Properties)

Introduction, First and Second row anomalies, the use of d-orbitals by non-metals, Reactivity and d-orbital participation, The use of p-orbitals in pi-bonding, Periodic anomalies of non-metals and post transition metals.

B: Nuclear Chemistry

Introduction, classification of Nuclides, Radioactivity and radioactive series, Artificial radioactivity, units of radioactivity, Determination of Half-life, Nuclear Fission and Fusion reactions, Applications of radio Isotopes as tracers.

C: Structure of Inorganic Solids

Introduction, The close packing of spheres, the structure of ionic solids, Ionic radii, Crystals structures and defect solid state.

D: Thermal Methods of analysis

Introduction, instrumentation, applications

Recommended Books

1. Huheey, J. E., Keiter, E. A. and Keiter, R. L., "Inorganic Chemistry: Principles of Structure and Reactivity", 4th Ed., Harper and Row, New York, (2001).
2. Cotton, F. A., Wilkinson, G. and Gaus, P. L., "Basic Inorganic Chemistry", 3rd Ed., Wiley, New York, (1995).

Concepts of Stereochemistry

Stereochemistry, a sub-discipline of chemistry, involves the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation. Stereochemistry spans the entire spectrum of organic, inorganic, biological, physical and especially supra-molecular chemistry.

Stereochemistry of the main Group Elements

VSEPR Theory

Stereochemistry of the main Group Elements: VSEPR Theory

The theory is also called Gillespie–Nyholm theory. Sidwick, Powell (1940) Gillespie and Nyholm (1957) are the main developers of this theory. This theory predicts the shapes of covalent molecules. VSEPR theory is based on the idea that the geometry of a molecule or polyatomic ion is determined primarily by repulsion among the pairs of electrons associated with a central atom occupying the valence shell. The pairs of electrons may be bonding or nonbonding (also called lone pairs). These electrons are said to occupy localized orbitals. These orbitals arrange themselves in space in manner so that there are maximum distances between them and minimum coulombic repulsion between them.

Basic Assumptions of VSEPR Theory

Main postulates of this theory are summarized here.

1. The electron pairs in the valence shell of a central atom repel each other. These pairs of electrons tend to occupy positions in space that minimize repulsions and maximize the distance of separation between them. The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its steric number.
2. The valence shell is taken as a sphere with electron pairs localizing on the spherical surface at maximum distance from one another.
3. A non-bonding electron pair occupies more space than bonding pair because the non-bonding electron pair is under the influence of one nucleus whereas bonding pair is attracted by two nuclei. The influence of bonding pair diminishes with the increasing value of electronegativity forming a molecule
4. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single electron pair. However double electron pairs of a double bond or three electron pairs of a triple bond occupy more space than one electron pair of a single bond.

Bond pairs are shared by two atoms and are attracted by two nuclei. Hence they occupy less space and cause less repulsion.

*Lone pairs are not involved in bond formation and are in attraction with only one nucleus. Hence they occupy more space. As a result, the lone pairs cause more repulsion. The order of repulsion between different types of electron pairs is as follows:
Lone pair - Lone pair > Lone Pair - Bond pair > Bond pair - Bond pair*

5. Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.
6. Three types of repulsion take place between the electrons of a molecule:
 - (a) The lone pair-lone pair repulsions
 - (b) The lone pair-bonding pair repulsions
 - (c) The bonding pair-bonding pair repulsions.
7. The repulsions between electron pairs decrease in the following order:
Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
8. When all the electron pairs are bonding in the valence shell of the central atom, linear, triangular planar, square planar/tetrahedral, trigonal bipyramidal/square pyramidal and octahedral shape molecules are formed for 2, 3, 4, 5 and 6 bond pairs of electrons respectively.
9. The lone pair – bond pair repulsions result in the distortion of regular molecular geometry.

10. *Primary & Secondary effects of electronegativity and size of atoms on bond angle and shape*

- (a) The bond angle decreases due to the presence of lone pairs, which cause more repulsion on the bond pairs and bond pairs are pushed closer.
- (b) If the central atom is more electronegative than the surrounding atoms, the electron pairs are more attracted toward the central atom, the repulsion between electron pairs increases with increase in electronegativity of central atom and the bond angle increases. However the bond angle decreases when the electronegativities of ligand atoms are more than that of central atom. There is increase in the distance between bond pairs since they are now closer to ligand atoms. Due to this, they tend to move closer which cause the decrease in bond angle as shown in Figure 2.40.
- (c) The bond angle decreases with increase in the size of central atom. However the bond angle increases with increase in the size of ligand atoms, which surround the central atom.
- (d) The bond angles are also changed when multiple bonds are present. It is due to uneven repulsions.

The shapes of molecules with different numbers of bonding and non-bonding electron pairs are given in table 2.5.

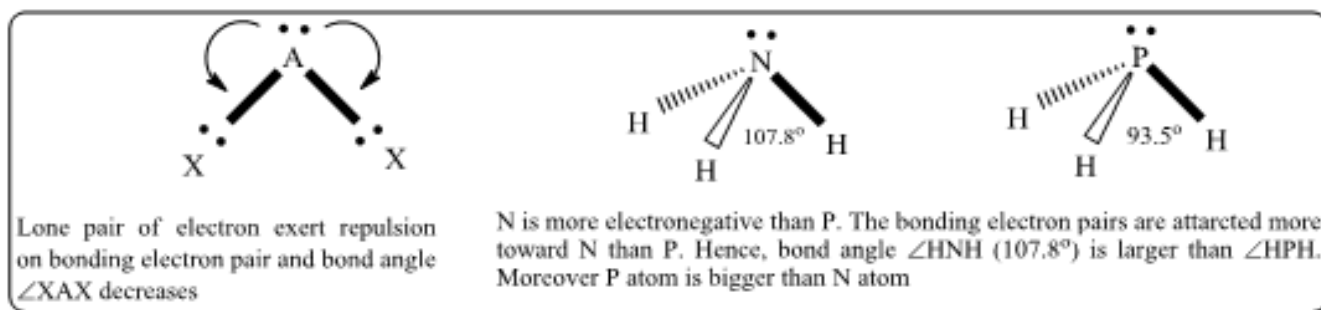


Figure 2.40: Effect of electronegativity and size of atoms on bond angle

Steric Number	Basic Geometry without lone pair	Geometry with 1 lone pair	Geometry with 2 lone pairs	Geometry with 3 lone pairs	Geometry with 4 lone pairs
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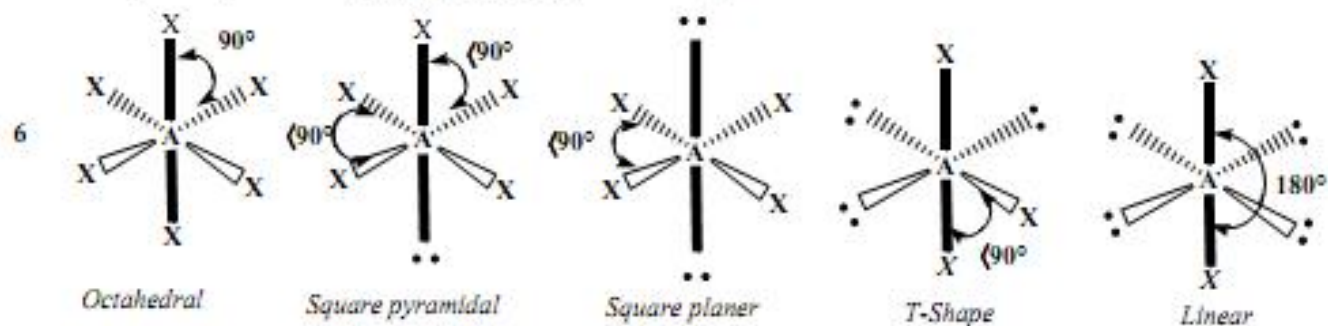
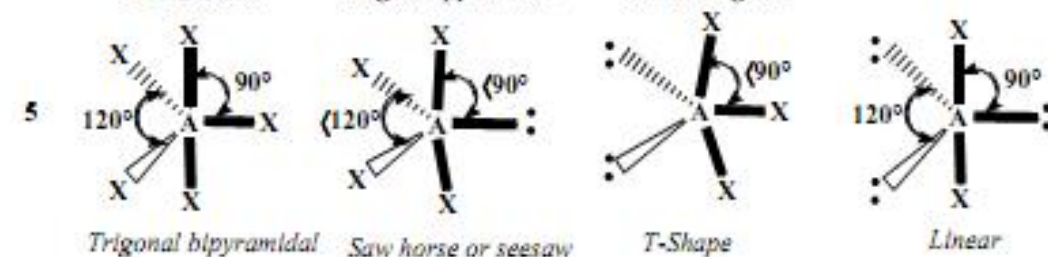
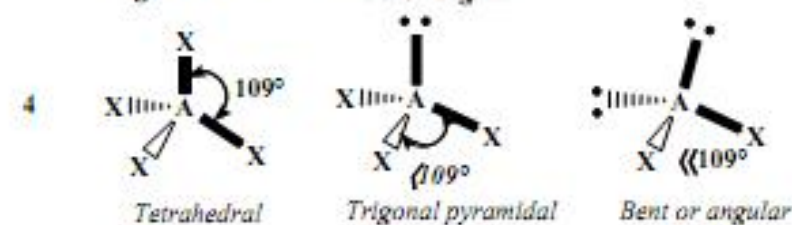
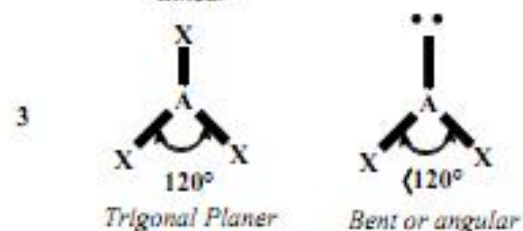
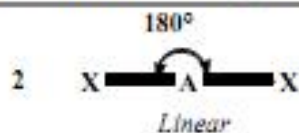


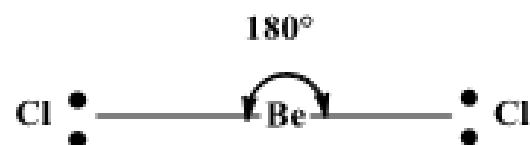
Table 2.6: Types of molecules with examples

Steric No.	Bond pairs	Lone pairs	Type	Shape	Examples
2	2	0	AX_2L_0	Linear	BeX_2 , CdX_2 , CO_2 , NO_2^+
3	3	0	AX_3L_0	Trigonal planar	BX_3 , HCHO, SO_3
	2	1	AX_2L	V-Shaped	$SnCl_2$, SO_2
4	4	0	AX_4L_0	Tetrahedral	BF_4^- , CF_4 , NH_4^+ , SO_4^{2-} , ClO_4^-
	3	1	AX_3L	Pyramidal	NH_3 , PCl_3 , PH_3 , $AsCl_3$, H_2O ,
	2	2	AX_2L_2	V-Shaped	H_2S
5	5	0	AX_5L_0	Trigonal bipyramidal	PCl_5 , $SbCl_5$, PF_5
	4	1	AX_4L	Irregular tetrahedron	SF_4 , $TeCl_4$
	3	2	AX_3L_2	T-Shaped	ClF_3 , BrF_3
	2	3	AX_2L_3	Linear	XeF_2 , I_3^-
6	6	0	AX_6L_0	Octahedral	SF_6 , MoF_6^- , PCl_6^-
	5	1	AX_5L	Square pyramidal	BrF_5 , IF_5
	4	2	AX_4L_2	Square planar	Icl_4^- , BrF_4^-
7	7	0	AX_7L_0	Pentagonal bipyramidal	IF_7
	6	1	AX_6L	Irregular Octahedron	$[SbBr_6]^{3-}$

N.B: A = Central atom, X = surrounding atoms, L = lone pair

(a) Shape of Molecules with Steric Number 2

Type AX₂: According to VSEPR model, AX₂ molecules have two bonding electron pairs and adopt linear shape as explained below. BeCl₂ is an example of this type.



Ground state electronic configuration of Be: [He] 2s²

Excited state electronic configuration of Be : [He] 2s¹2p¹

One 2s¹ and 2p¹ orbitals undergo *sp* hybridization to make available two equivalent orbitals for two bonding electron pairs.

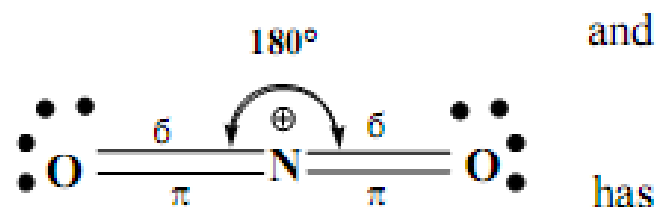
The Lewis structure of BeCl_2 shows that Be has two bonding electron pairs which arrange themselves as far apart as possible at an angle of 180° in order to have minimum repulsion between them. Thus BeCl_2 molecule will have linear structure. Similarly Hg, Zn and Cd having two electrons in their valence shell form linear structures. These atoms (Hg, Zn and Cd) undergo sp hybridization which also predicts linear structure of the type X—A—X type. Another example of AX_2 is NO_2^+ ion.

Ground state electronic configuration of N: $[\text{He}] 2s^2 2p^3$

Excited state electronic configuration of N^+ : $[\text{He}] 2s^1 2p_x^1 2p_y^1 2p_z^1$

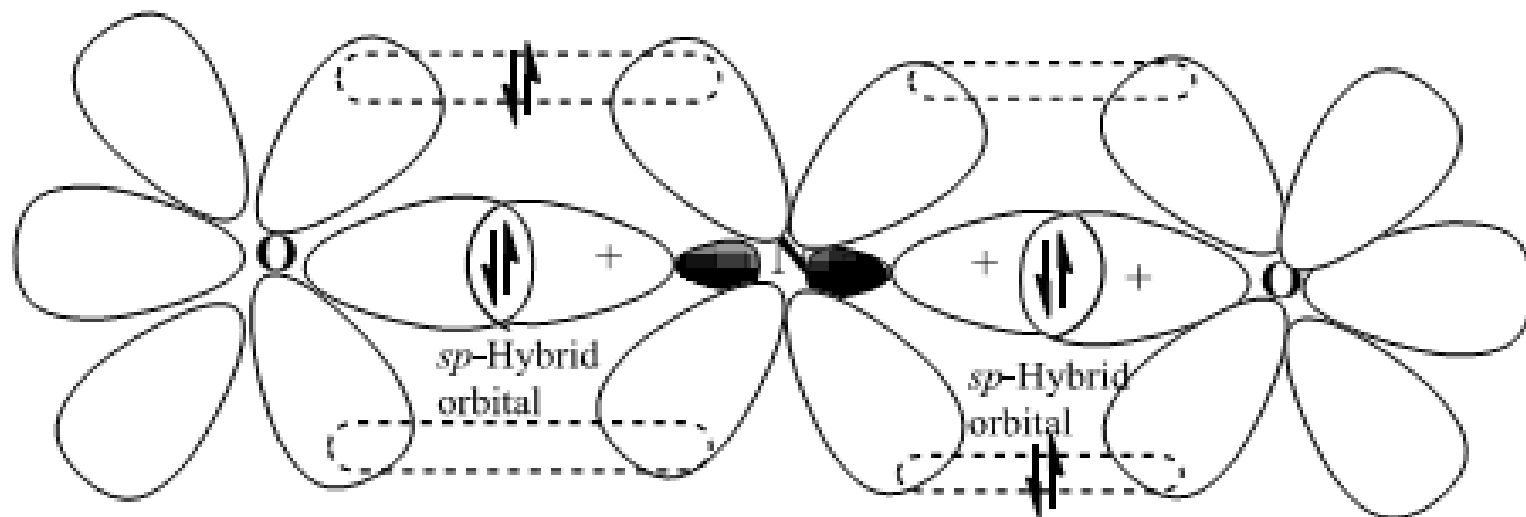
N^+ ion undergo sp hybridization and each sp hybrid orbital forms sigma covalent bond with oxygen atoms. The each unhybridized p orbital of N atom overlaps with O atom to form π -bonds as shown in Figure 2.41

This means that NO_2^+ ion has two σ - bonding pairs two π - bonding pairs of electrons. According to VSEPR theory, shapes of molecules containing multiple bonds depend on σ - bond pairs. NO_2^+ ion only two σ - bond pairs which arrange themselves 180° apart in order to have minimum repulsion between them and shape of ion is linear according to VSEPR theory. .



p -orbitals on Oxygen

p -orbitals on Oxygen



(b) Shape of Molecule with Steric Number 3

Type AX₃: Three electron pairs surround the central atom in AX₃ types molecule. The Lewis structure shows three bond pairs which arrange themselves in trigonal planar shape and lie at 120° angle from each other to be at maximum distance in order to avoid electronic repulsion between them. The common example of this type is BF₃ whose structure is explained here.

Ground state electronic configuration of B: [He] 2s²2p¹

Excited state electronic configuration of B: [He] 2s¹2p_x¹2p_y¹2p_z

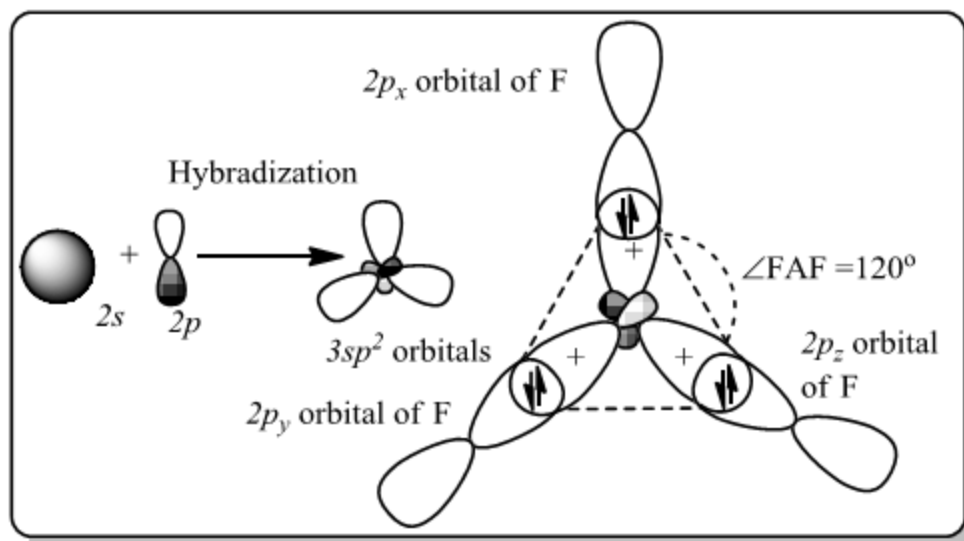


Figure 2.42: Schematic presentation of orbital hybridization in B and bond formation with F atoms

Atomic orbital, $2s^1$, $2p_x^1$, and $2p_y^1$ undergo sp^2 hybridization to produce $3sp^2$ hybrid orbitals. Each sp^2 hybrid orbital form sigma covalent bond with F atoms by overlapping with p_x orbital of F atom(Fig.2.42). The Lewis structure of BF_3 , (Figure 2.42) shows that central atom has three bond electron pairs and these pairs arrange themselves as far apart as possible in a trigonal planar structure in order to have minimum repulsion between them. Hence the VSEPR theory suggests a trigonal planar structure for BF_3 molecule with each $F - B - F$ bond angle of 120° . The sp^2 hybridization also predicts trigonal planar structure for BF_3 molecule.

SO_3 is also an example of AX_3 type molecule involving multiple bonds. In SO_3 , S undergoes sp^2 hybridization forming trigonal planar structure. Hybridization scheme of S in SO_3 and formation of 3 σ and 3 π -bonds is shown in Figure 2.43.

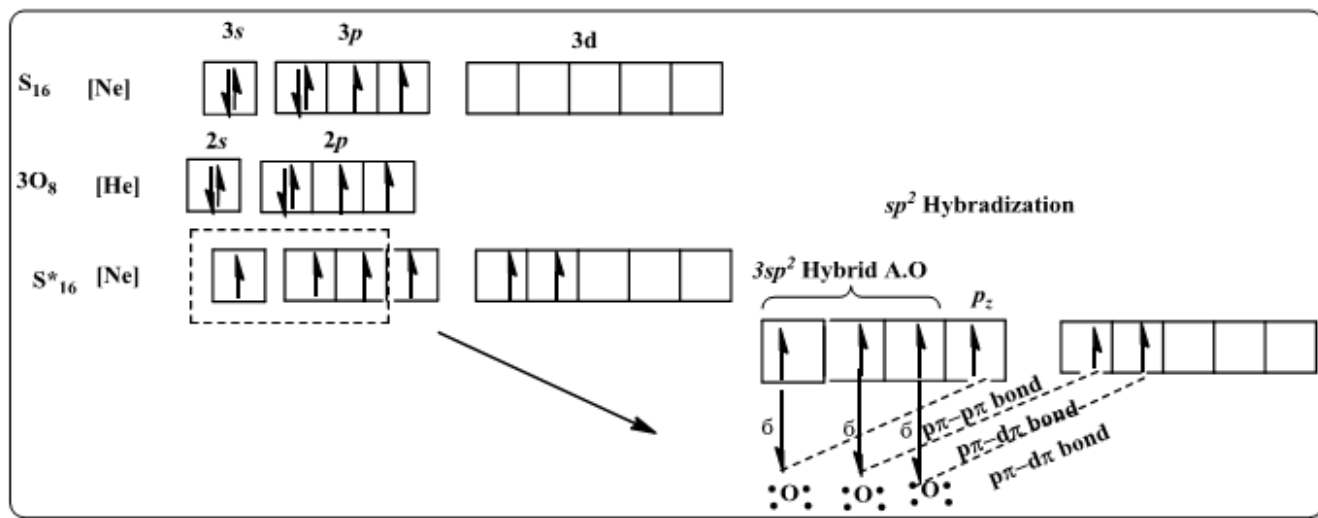


Figure 2.43: Hybridization scheme for SO_3

As shown in Figure 2.43, SO_3 has three σ -bonding pairs and three π -bonding electron pairs. According to VSEPR theory, shapes of molecules containing multiple bonds depend on σ -bonding pairs only. The three σ -bonding pairs will arrange themselves in a trigonal planar structure in order to have minimum repulsions between them. Thus VSEPR theory suggests a trigonal planar structure for SO_3 molecule with each $\text{O}-\text{S}-\text{O}$ bond angle of 120° .

AB₂L Type: In this type, the central atom A has two bond pairs and one lone pair. The geometry of AB₂L type molecules is angular or V-shape. SnCl₂ represents the example of this type of molecule. Lewis structure of SnCl₂ (Figure 2.44 d) shows that it has two σ – bonding electron pairs and one lone pair of electrons.

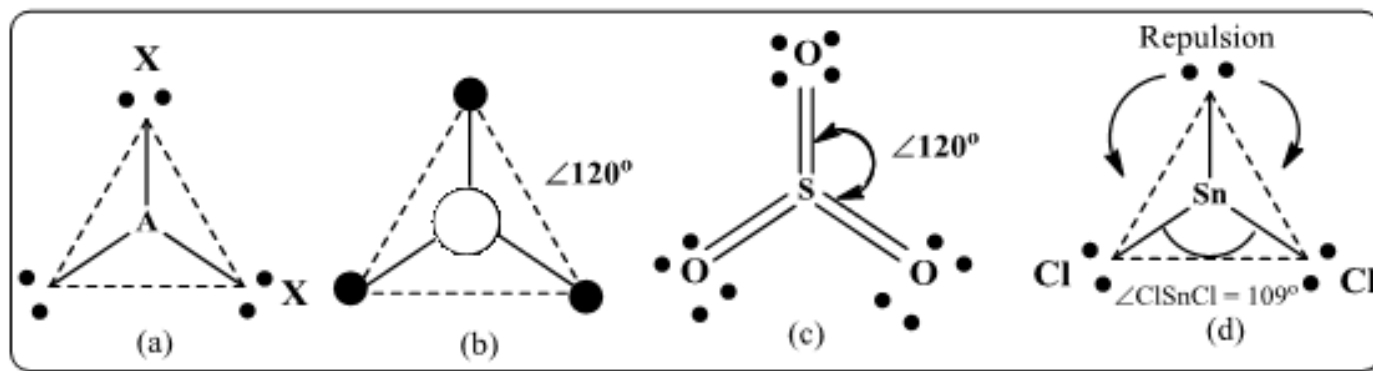


Figure 2.44: Geometries of AX₃ type molecules

These electron pairs will have trigonal planar geometry. According to VSEPR theory, the shape of molecule is determined by bonding pairs. Thus VSEPR suggests a V-shaped structure for SnCl₂ molecule due to presence of lone pair of electron which cause repulsion on bond pairs and bond angle, Cl—Sn—Cl reduces to 109° from 120°.

(c) Shape of Molecule with Steric Number 4

Type AX₄: The minimum repulsion between four electron pairs is possible only when each electron pair occupies the corner of a tetrahedron. For example the Lewis structures of CH₄ and TiCl₄ show that central atom, C in CH₄ and Ti in TiCl₄ have four bonding electron pairs. According to VSEPR theory, four bonding pairs in CH₄ will arrange themselves in a tetrahedral structure in order to have minimum repulsion between them. Thus VSEPR theory suggests a tetrahedral structure for CH₄ molecule with each H – C – H bond angle of 109.28° (Figure 2.45).

SO₄²⁻ ion is AX₄ species involving multiple bonds. The Lewis structure of SO₄²⁻ ion exhibits four σ-bonding electron pairs and two π-bonding electron pairs. According to VSEPR theory, σ-bonding electron pairs determine shapes of molecules containing multiple bonds. In SO₄²⁻, there are only four σ-bonding pairs which will arrange themselves in a tetrahedral structure in order to have minimum repulsion between them. Therefore, VSEPR theory suggests a tetrahedral structure for SO₄²⁻ ion with each O – S – O bond angle of 109°5'. The structures of BF₄⁻, CF₄, NH₄⁺ and ClO₄⁻ can be explained on similar grounds.

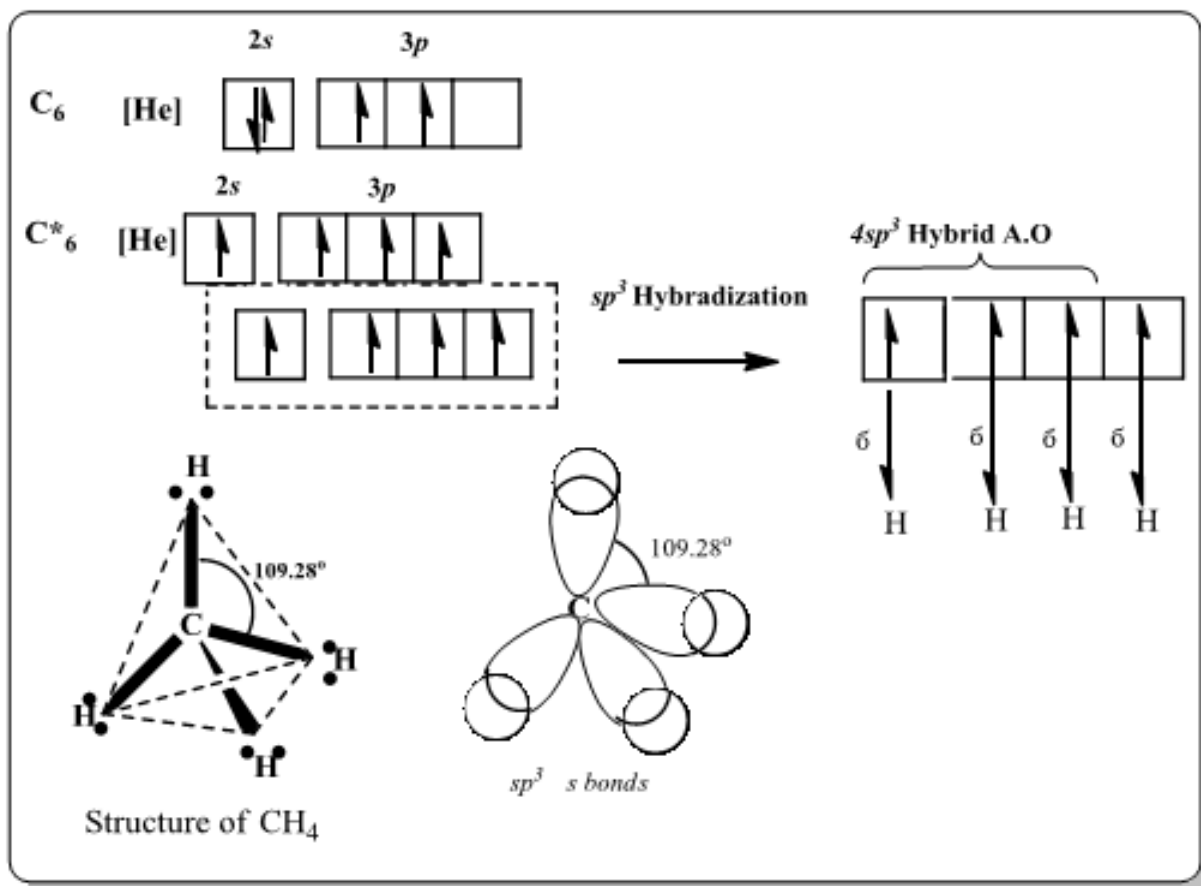


Figure 2.45: Hybridization scheme for CH_4

The S atom in SO_4^{2-} undergoes sp^3 hybridization and predicts the tetrahedral structure for SO_4^{2-} ions as given in Figure 2.46. Two π -bonds are formed by overlapping of d orbitals of S and p orbitals of oxygen and are called $p\pi$ - $d\pi$ bonds.

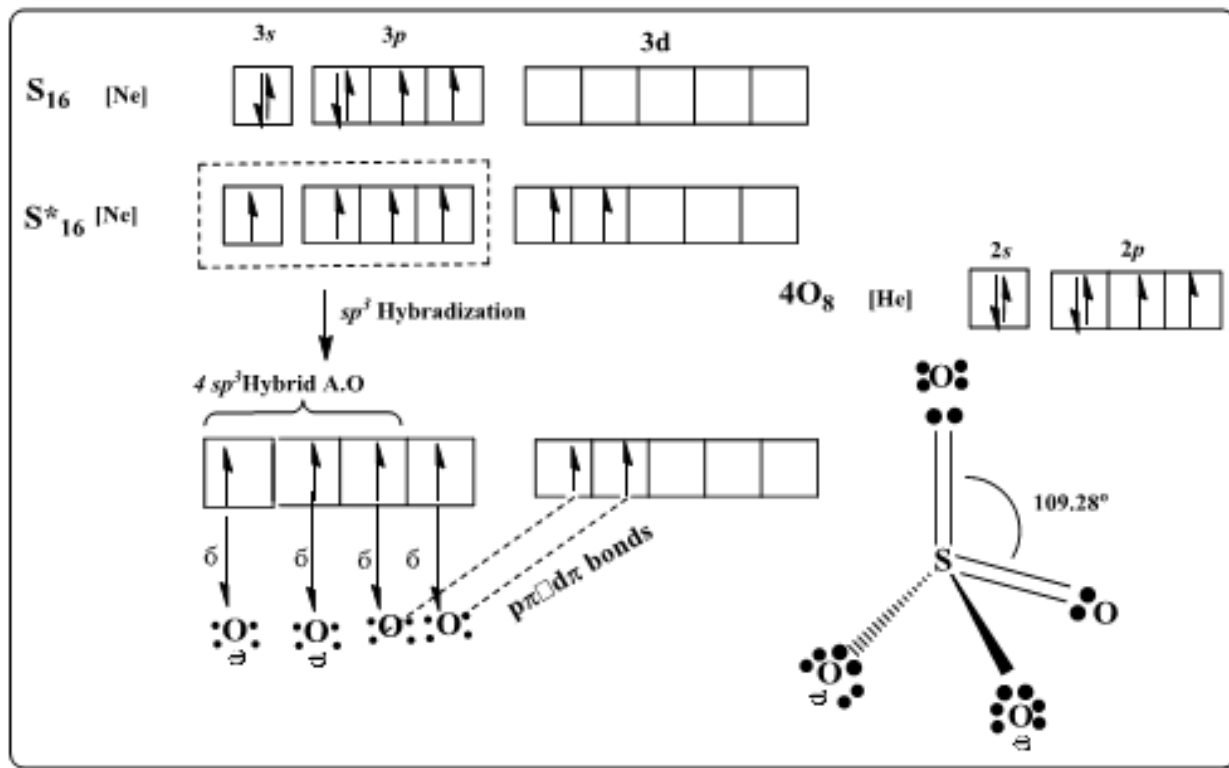


Figure 2.46: Hybridization scheme for SO_4^{2-}

Type AX₃L: In this type of molecules, three σ -bond electron pairs and one lone pair arrange themselves around the corners of a tetrahedron. The lone pair occupies more space than bond pairs and repels the bond pairs. Consequently X—A—X bond angle decreases to 107.2° and tetrahedral shape becomes pyramidal. NH₃, PCl₃, PH₃ and AsCl₃ are examples of this type of molecules.

Lewis structure of NH₃ shows that it has three σ – bonding pairs and one lone pair of electrons. These electron pairs will have tetrahedral geometry. According to VSEPR theory, lone pair occupies more space than bond pairs and, therefore, exerts greater repulsions on bond pairs. Thus H – N – H bond angle is of 107° in NH₃ rather than normal tetrahedral angle of 109° .

Type AX₂L₂: In this type of molecules, two σ -bond electron pairs and two lone pairs arrange themselves around the corners of a tetrahedron. The lone pairs occupy more space than bond pairs and repel the bond pairs. Consequently, the X—A—X bond angle further decreases to 104.5° and tetrahedral shape becomes v-shape or angular. H₂O and H₂S are examples of this type of molecules. Lewis structure of H₂O shows that it has two σ – bonding pairs and two lone pairs of electrons. These electron pairs will have tetrahedral geometry. According to VSEPR theory, lone pairs exert greater repulsions on bond pairs. Thus H – O – H bond angle is of 104.5° in H₂O rather than normal tetrahedral angle of 109° as shown in Figure 2.47.

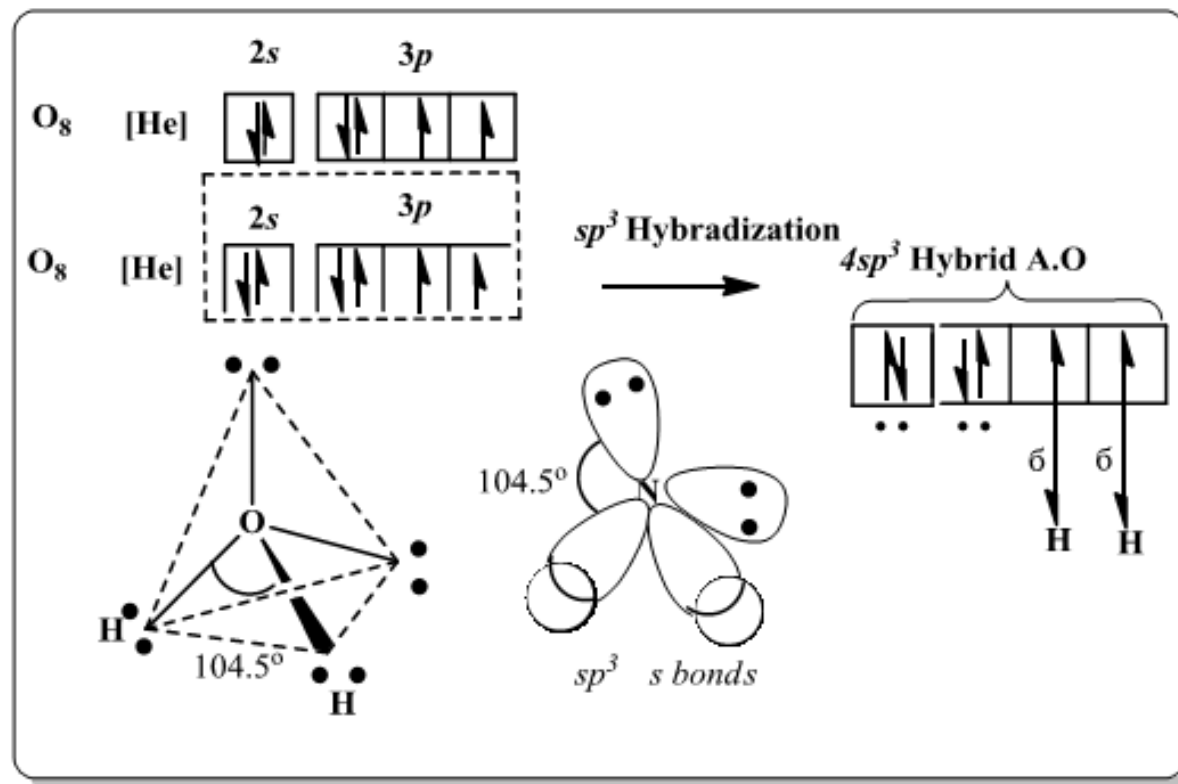


Figure 2.47: Hybridization scheme for H₂O

According to VSEPR theory shape of molecule is determined by two bonding pairs only. Thus VSEPR theory suggests a V-shaped structure for H₂O molecule.

(d) Shape of Molecule with Steric Number 5

The minimum repulsion between five electron pairs is possible only when each electron pair occupies the corner of a trigonal pyramidal structure. For example the Lewis structures of PCl_5 show that central atom, P in PCl_5 has five bonding electron pairs. According to VSEPR theory, five bonding pairs in PCl_5 will arrange themselves in a trigonal pyramidal structure in order to have minimum repulsion between them.

Type AX_5 : PCl_5 , PF_5 and SbCl_5 fall in this type of molecule in which central atom (P and Sb) is surrounded by five bonding electron pairs which are arranged along the corners of trigonal pyramidal structure in order to have maximum distances and minimum repulsions among them as shown in Figure 2.48.

Type AX_4L : In this type of molecules, four σ -bond electron pairs and one lone pairs arrange themselves around the corners of a trigonal bipyramidal structure. The lone pair occupies more space than bond pairs and repels the bond pairs. Consequently X—A—X bond angle decreases and trigonal bipyramidal shape becomes seesaw shape. SF_4 , SeF_4 and TeCl_4 are examples of this type of molecules.

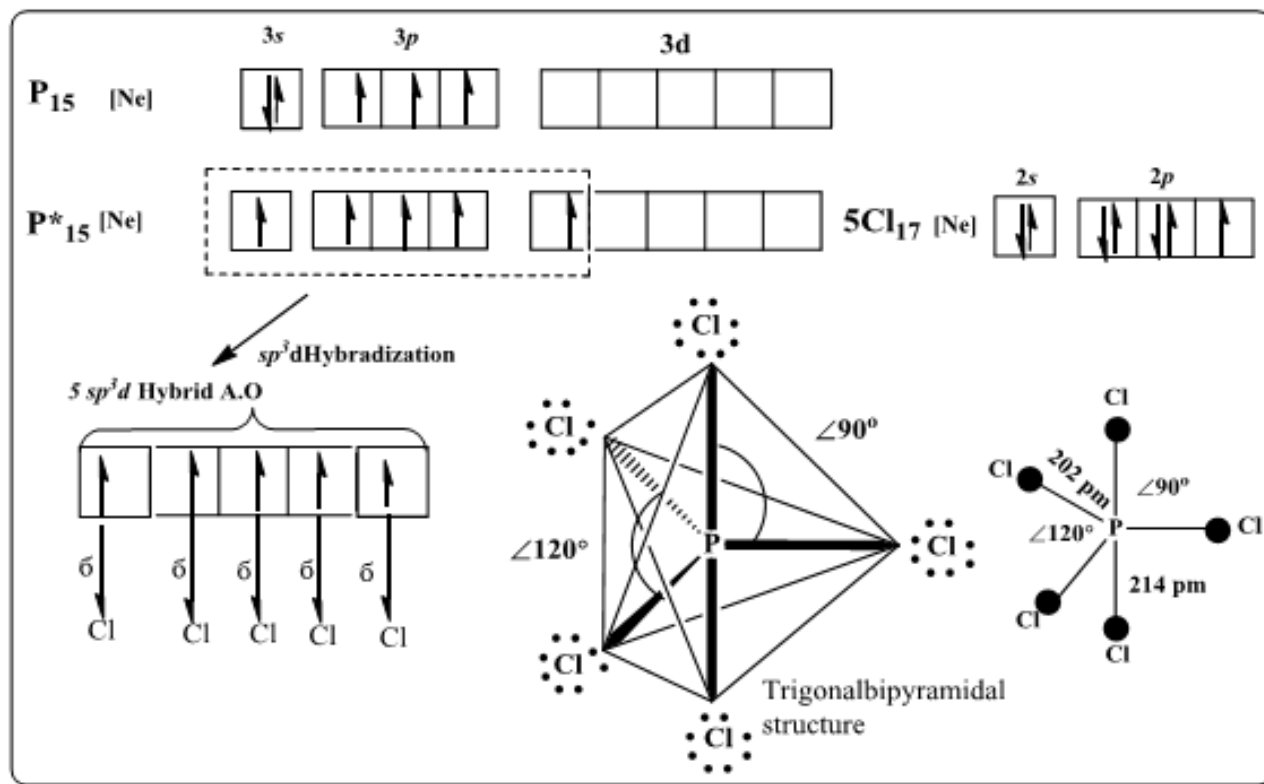


Figure 2.48: Hybridization scheme for PCl_5

The S atom in SF_4 is sp^3d hybridized resulting in the formation of the five coordinate bonds required for the decet (10 electron). The lone pair can occupy axial or equatorial position in trigonal bipyramidal structure. When the lone pair is in axial position, then there will be three lone pair - bond pair repulsion but when lone pair is in equatorial position, then there will be two Lone pair - Bond pair repulsion.

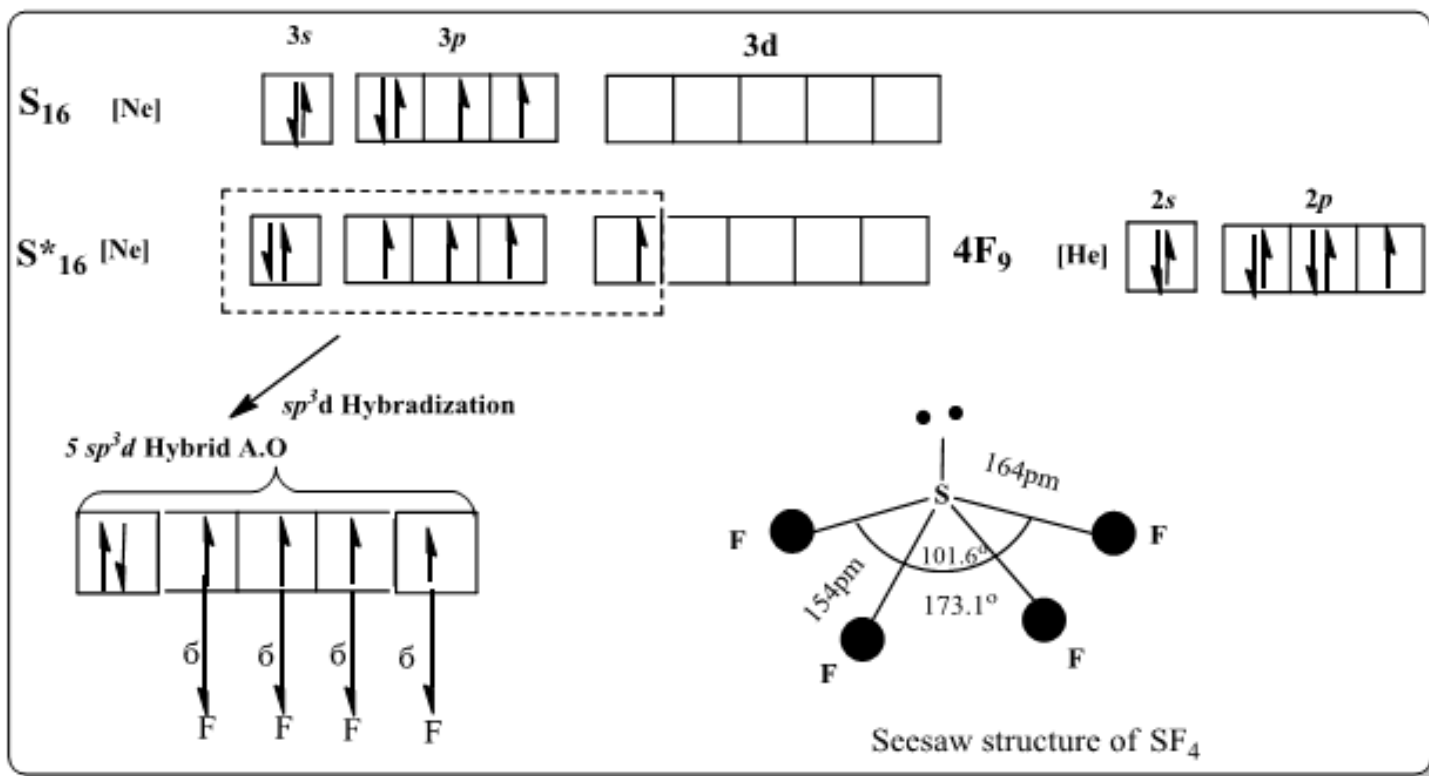


Figure 2.49: Hybridization scheme for SF₄

The lone pair - bond pair repulsion in the seesaw molecules SF₄ causes distortion of the axial; S-F bonds away from the lone pair to an angle of 173.1°, the two equatorial S-F bonds, ideally at 120°, move much closer to an angle of 101.6° (Figure 2.49).

Lewis structure of SeF₄ shows that it has four σ – bonding pairs and one lone pair of electrons. These electron pairs will have trigonal bipyramidal geometry. According to VSEPR theory, lone pair occupies more space than bond pairs and, therefore, exerts greater repulsions on bond pairs. Thus F – S – F bond angle is decreased 101.6°.

Type AX₃L₂: This type of molecules have three bonding electron pairs and two lone pairs of electrons. Two lone pairs of electrons occupy equatorial positions of trigonal bipyramidal structure to have minimum repulsion from bond pairs yielding a T-Shaped structure.

For example Lewis structure of ClF₃ shows that it has three σ - bonding pairs and two lone pair of electrons. These electron pairs will have trigonal bipyramidal geometry. According to VSEPR theory shape of molecule is determined by three bonding pairs only. Thus VSEPR suggests a T-Shaped structure for ClF₃ molecule with two lone pairs occupying the equatorial position. The bond angles are shown in the Figure 2.50 . Another example of this type is BrF₃.

Type AX₂L₃: ClF₂, XeF₂ and I₃⁻ species are example of this class of molecules in which there are two bonding σ - electron pairs and three lone pairs which give rise to trigonal bipyramidal electronic geometry. Lewis structure of ClF₂ shows that it has two σ - bonding pairs and three lone pair of electrons. These electron pairs have trigonal bipyramidal geometry. The VSEPR suggests a linear structure for ClF₂ molecule with three lone pairs occupying the equatorial position. The bond angles are shown in the Figure 2.50.

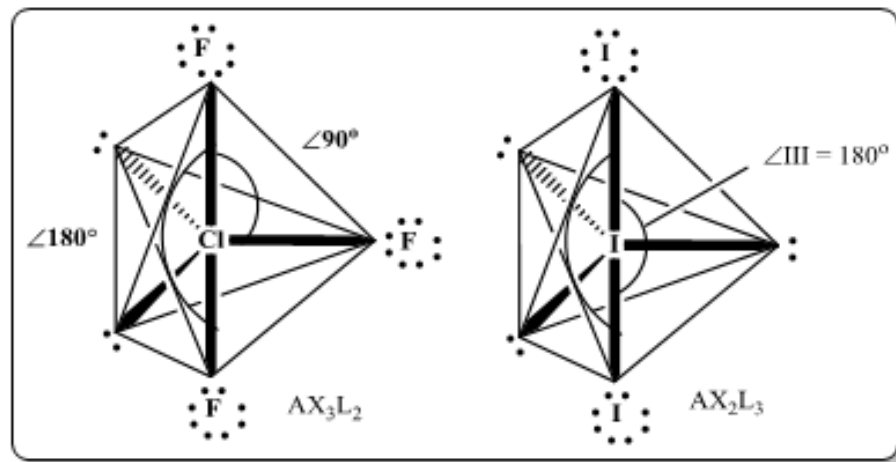


Figure 2.50: Structure of AX_3L_2 and AX_2L_3

(e) Shape of Molecule with Steric Number 6

The minimum repulsion between six electron pairs is possible only when each electron pair occupies the corner of an octahedron. For example, the Lewis structure of SF_6 shows that the central atom, S, has six bonding electron pairs. According to VSEPR theory, six bonding pairs in SF_6 will arrange themselves forming octahedral electronic geometry to have minimum repulsion between them.

Type AX_6 : Sulfur hexafluoride (SF_6) is an example of AX_6 type molecules in which all six electron pairs are bonding pairs.

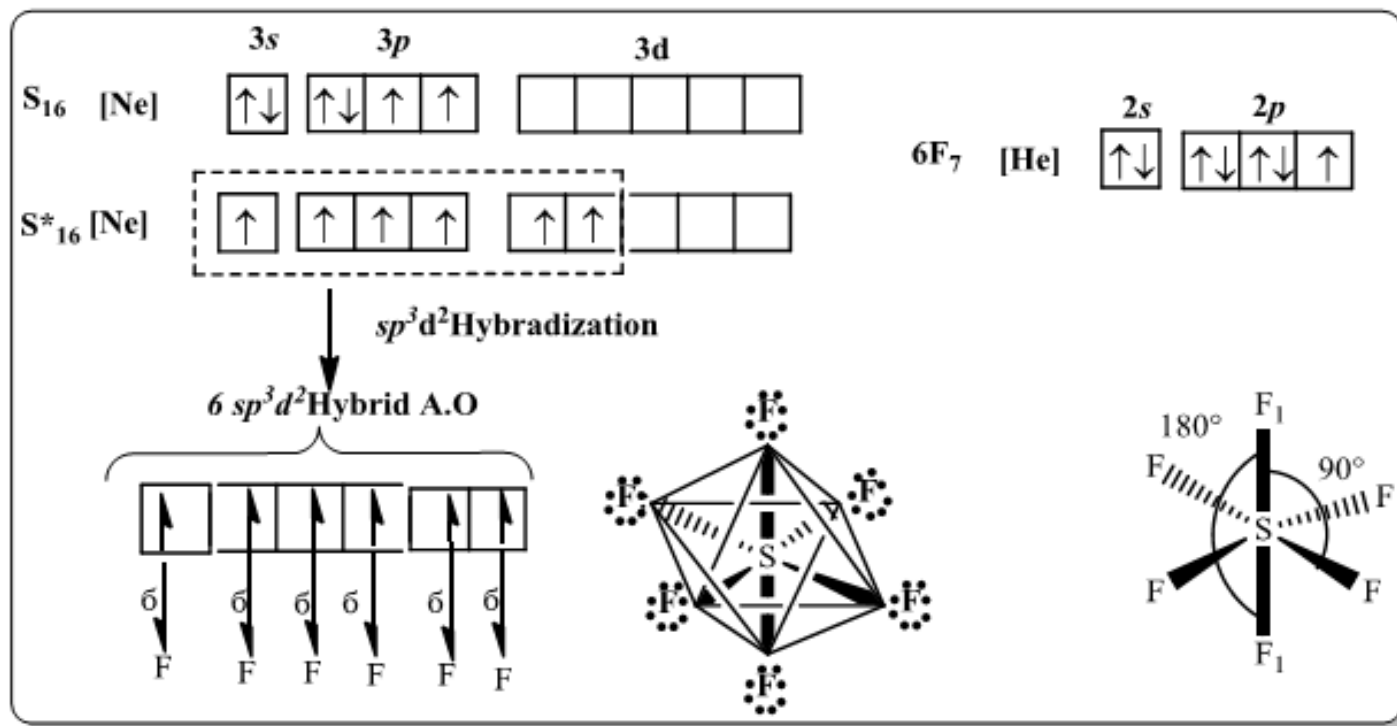


Figure 2.51: Hybridization scheme for SF₆

Each electron pairs occupies the corner of an octahedron and octahedral shape molecule is formed with sulfur atom in the center. Sulfur atom undergoes *sp*³*d*² hybridization forming six hybrid orbitals which overlap with p orbitals of fluorine. The hybridization scheme and bond angles are shown in Figure 2.51.

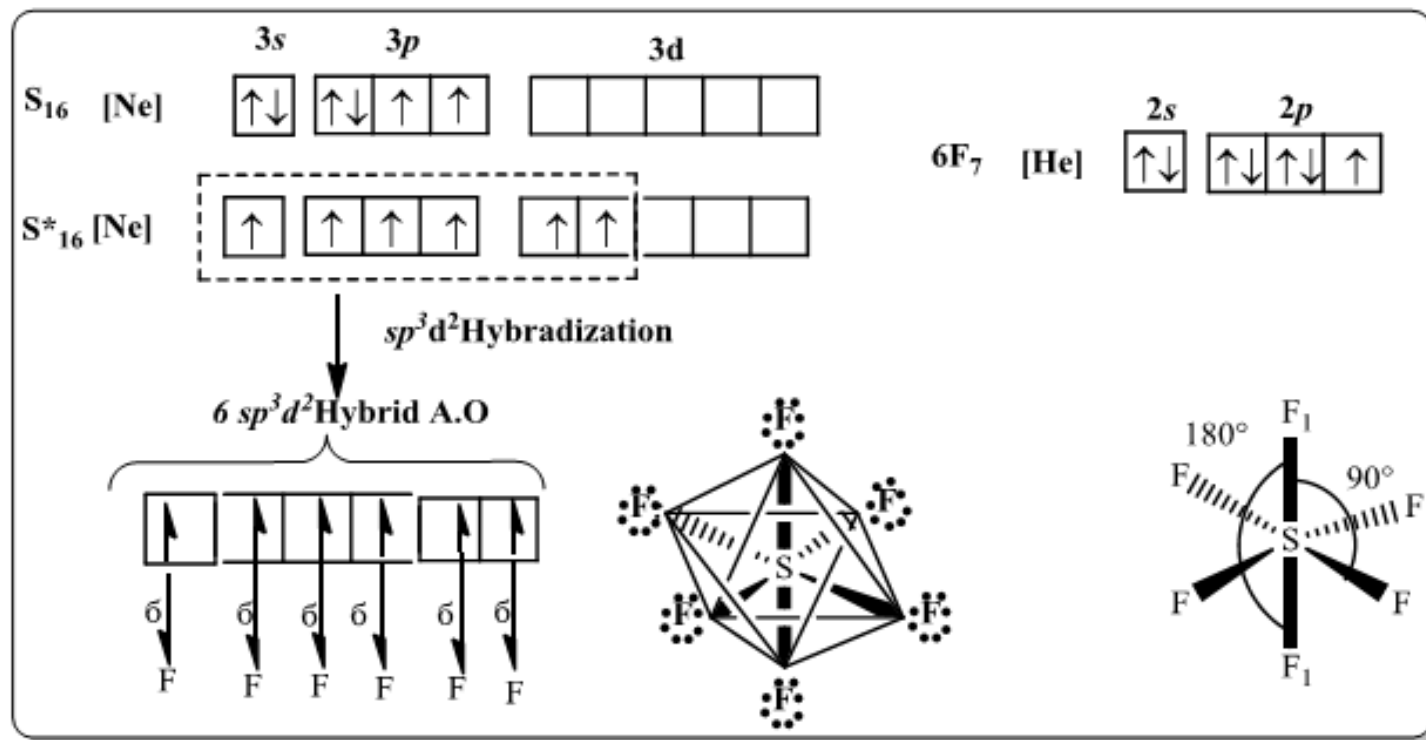
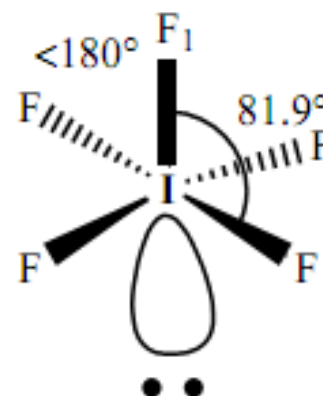


Figure 2.51: Hybridization scheme for SF₆

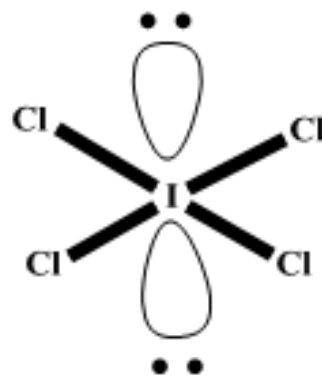
Each electron pairs occupies the corner of an octahedron and octahedral shape molecule is formed with sulfur atom in the center. Sulfur atom undergoes sp^3d^2 hybridization forming six hybrid orbitals which overlap with p orbitals of fluorine. The hybridization scheme and bond angles are shown in Figure 2.51.

The Lewis structure of SF_6 shows that central atom, S, has six bonding electron pairs. According to VSEPR theory, six bonding pairs in SF_6 arrange themselves in an octahedral structure in order to have minimum repulsion between them. The VSEPR theory suggests a octahedral structure for SF_6 molecule. MoF_6^- and PCl_6^- are other examples of AX_6 molecules.

Type AX_5L : Iodine pentafluoride is an example of this class of molecules. The electronic geometry for IF_5 is octahedral, because the central atom, iodine undergoes sp^3d^2 hybridization. In the iodine atom, there are 5 bonding and 1 lone pair so the molecular geometry for IF_5 is square pyramidal. For the normal octahedral, the bond angles are 90 and 180, but in IF_5 there is one lone pair thus the bond angles are less than 90 and 180, Because of repulsions between the lone-pair electrons and the I—F bonding pairs, the plane of the four F atoms at the base is raised slightly above the I atom. Thus VSEPR theory suggests a square pyramidal structure for IF_5 molecule. The bond angles are shown in Figure. Same arguments can be extended to explain the shape of BrF_5 .



Type AX_4L_2 : ICl_4^- and BrF_4^- are the examples of AX_4L_2 type molecule. There are six electron pairs in this type of



molecules. These electron pairs will have octahedral geometry. Lewis structure of ICl_4^- shows that it has four σ - bonding pairs and two lone pairs of electrons. The shape of molecule is determined by four bonding pairs only. Thus VSEPR suggests a square planar structure for ICl_4^- molecule.

(f) Shape of Molecule with Steric Number 7

These types of molecules have 7 electron pairs surrounding the central atom and are arranged in pentagonal bipyramidal shape in order to have minimum repulsion between them. An example is IF_7 molecule. The Lewis structure of IF_7 shows that central atom, I, has seven bonding electron pairs. Each electron pairs occupies the corner of a pentagonal bipyramidal shape and pentagonal bipyramidal shape molecule is formed with I atom in the center. In this arrangement there is minimum repulsion between bond pairs. Iodine atom undergoes sp^3d^2 hybridization forming six hybrid orbitals which overlap with p orbitals of fluorine. The hybridization scheme and bond angles are shown in Figure 2.52. IF_7 has five basal bonds ($F_b\text{—I}$ bonds) in the plane of pentagon directed at angle of 72° while two axial bonds ($F_a\text{—I}$ bonds) directed at right angle to the plane of pentagon. $F_a\text{—I—}F_a$ bond angel is of 180° . Thus VSEPR theory suggests a pentagonal bipyramidal structure for IF_7 molecule.

Type AX₆L: An example of this type of molecule is [SbBr₆]³⁻ in which Sb undergoes sp^3d^3 hybridization forming seven hybrid orbitals. Six hybrid orbitals form σ -bonds with 6 Br atoms while seventh hybrid orbital has lone pair of electron. These electron pairs will have octahedral geometry. According to VSEPR theory shape of molecule is determined by six bonding pairs only. Thus VSEPR theory suggests an irregular octahedron structure for [SbBr₆]²⁻ molecule.

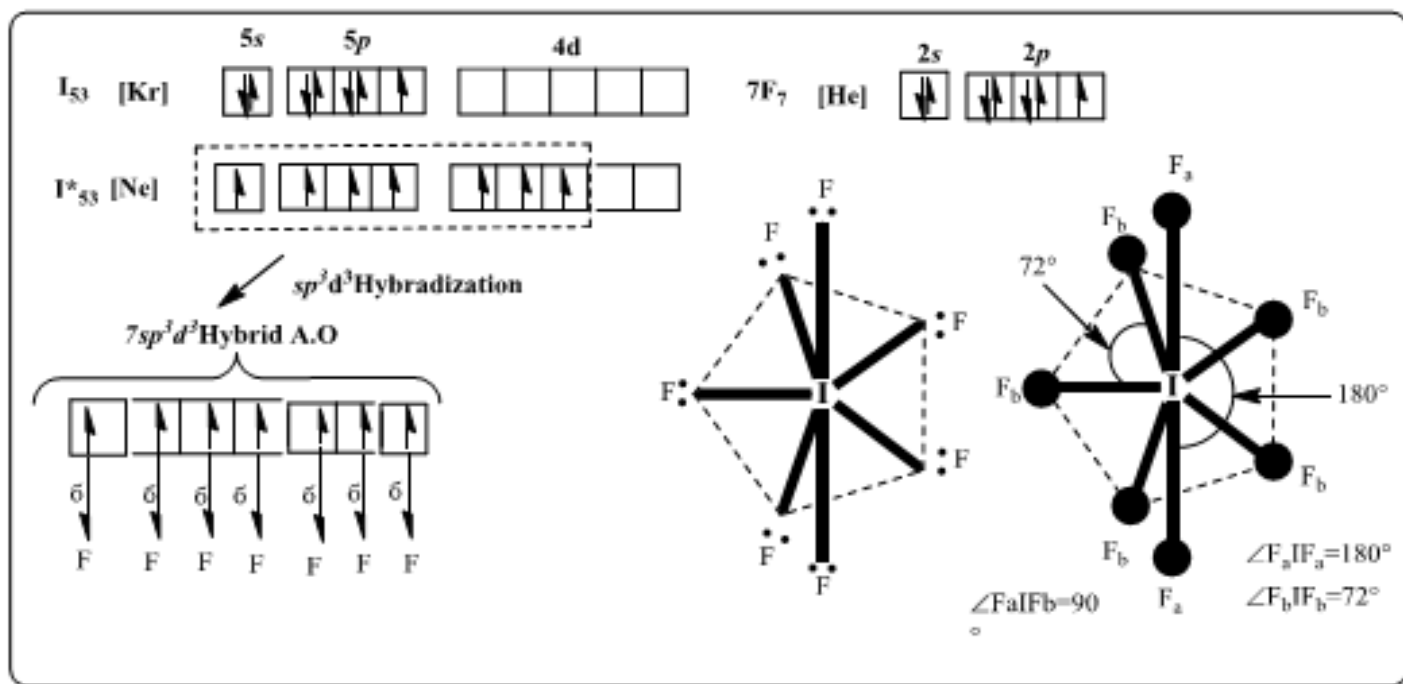
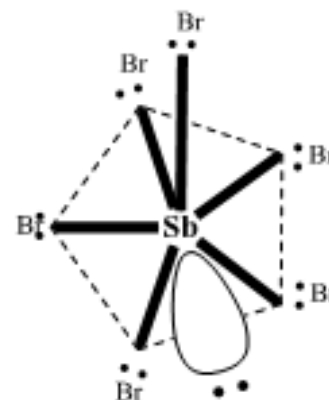


Figure 2.52: Hybridization scheme for IF₇