

2.3. Valence Shell Electron Pair Repulsion (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 columbic repulsion between them.

3.1 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 occupy 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

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

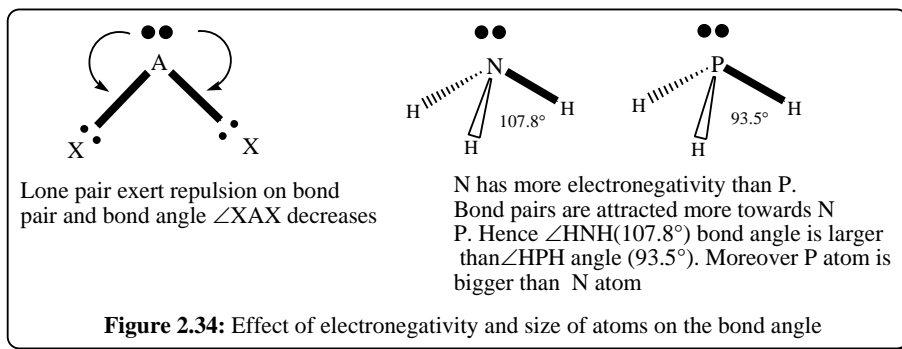
*Lone pairs are not involved in bond formation and are in attraction with only one nucleus. Hence they occupy more space. As a result, the lone pairs cause more repulsion. The order of repulsion between different types of electron pairs is as follows:
Lone pair - Lone pair > Lone Pair - Bond pair > Bond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

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 super 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.
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 repulsion
 - (c) The bonding pair-bonding pair repulsion.
7. The repulsion between electron pairs decreases in the following order:

- Lone pair – lone pair > Lone pair – bond pair > bond pair – bond pair
- When all the electron pairs are bonding in the valence shell of the central atom, linear, triangular planer, square planer/tetrahedral, trigonal bipyramidal/square pyramidal and octahedral shape molecules are formed for 2, 3, 4, 5 and 6 bond pairs of electrons respectively.
 - The lone pair – bond pair repulsions result in the distortion of regular molecular geometry.

Primary & Secondary effects of electronegativity and size of atoms on bond angle and shape:

- 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.
- 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.



- 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.
- 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 2.4.

Table 2.4: Shapes of molecules with different numbers of bonding and non-bonding electron pairs

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
2	 Linear				
3	 Trigonal Planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramidal	 Bent or angular		
5	 Trigonal bipyramidal	 Saw horse or seesaw	 T-Shape	 Linear	
6	 Octahedral	 Square pyramidal	 Square planar	 T-Shape	 Linear

3.2 Prediction of Shapes of Molecules using VSEPR Theory

To predict the shape of molecule using VSEPR Theory, Lewis dot structure of the molecule is written in the first step. In the second step the number of bond pairs and lone pairs in the valence shell of central atom are counted. While counting the number of bond pairs, treat multiple bonds as if they were single bonds. Thus electron pairs in multiple bonds are to be treated collectively as a single super pair. The table 2.3 is used to predict the shape of molecule based on steric number and the number of bond pairs and lone pairs. The molecules are divided into six types depending on the number of bond pairs and lone pairs. These types of molecules are given in table 2.5 with examples.

Table 2.5: Types of molecules with examples

Steric No.	Bond pairs	Lone pairs	Type	Shape	Examples
2	2	0	AX ₂ L ₀	Linear	BeX ₂ , CdX ₂ , CO ₂ , NO ₂ ⁺
3	3	0	AX ₃ L ₀	Trigonal planar	BX ₃ , HCHO, SO ₃
	2	1	AX ₂ L	V-Shaped	SnCl ₂ , SO ₂

4	4	0	AX ₄ L ₀	Tetrahedral	BF ₄ ⁻ , CF ₄ , NH ₄ ⁺ , SO ₄ ²⁻ , ClO ₄ ⁻
	3	1	AX ₃ L	Pyramidal	NH ₃ , PCl ₃ , PH ₃ , AsCl ₃ H ₂ O,
	2	2	AX ₂ L ₂	V-Shaped	H ₂ S
5	5	0	AX ₅ L ₀	Trigonal bipyramidal	PCl ₅ , SbCl ₅ , PF ₅
	4	1	AX ₄ L	Irregular tetrahedron	SF ₄ , TeCl ₄
	3	2	AX ₃ L ₂	T-Shaped	ClF ₃ , BrF ₃
	2	3	AX ₂ L ₃	Linear	XeF ₂ , I ₃ ⁻
6	6	0	AX ₆ L ₀	Octahedral	SF ₆ , MoF ₆ ⁻ , PCl ₆ ⁻
	5	1	AX ₅ L	Square pyramid	BrF ₅ , IF ₅
	4	2	AX ₄ L ₂	Square planar	Icl ₄ ⁻ , BrF ₄ ⁻
7	7	0	AX ₇ L ₀	Pentagonal bipyramidal	IF ₇
	6	1	AX ₆ L	Irregular Octahedron	[SbBr ₆] ³⁻

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

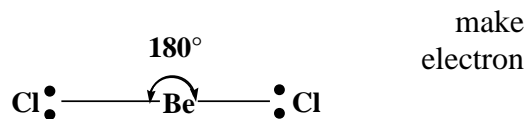
3.2.1 Shape of Molecule with Steric number 2 (Type AX₂)

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 available two equivalent orbitals for two bonding pairs.

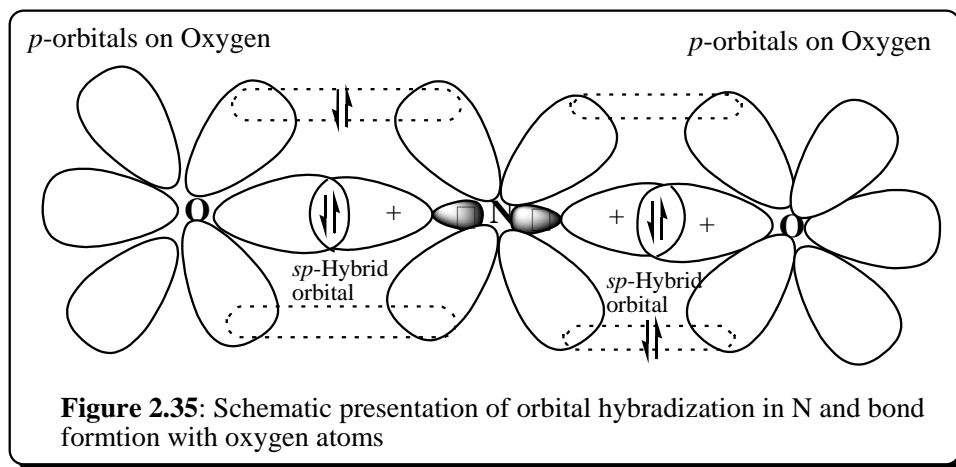


The Lewis structure of BeCl₂ shows that Be has two bonding electron pairs which arrange themselves as far apart as possible at an angle of 180° in order to have minimum repulsion between them. Thus BeCl₂ molecule will have linear structure. Similarly Hg, Zn and Cd having two electrons in their valence 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 AX₂ is NO₂⁺ ion.

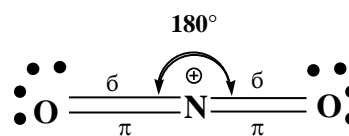
Ground state electronic configuration of N: [He] 2s²2p³

Excited state electronic configuration of N⁺: [He] 2s¹2p_x¹2p_y¹2p_z¹

N⁺ ion undergo sp hybridization and each sp hybrid orbital for sigma covalent bond with oxygen atoms. The each unhybridized p orbital of N atom overlaps with O atom to form π-bonds.



This means that NO_2^+ ion has two σ -bonding pairs and two π -bonding pairs of electrons. According to VSEPR theory, shapes of molecules containing multiple bonds depend on σ -bond pairs. NO_2^+ ion has 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.



3.2.2 Shape of Molecule with Steric number 3

Type AX_3

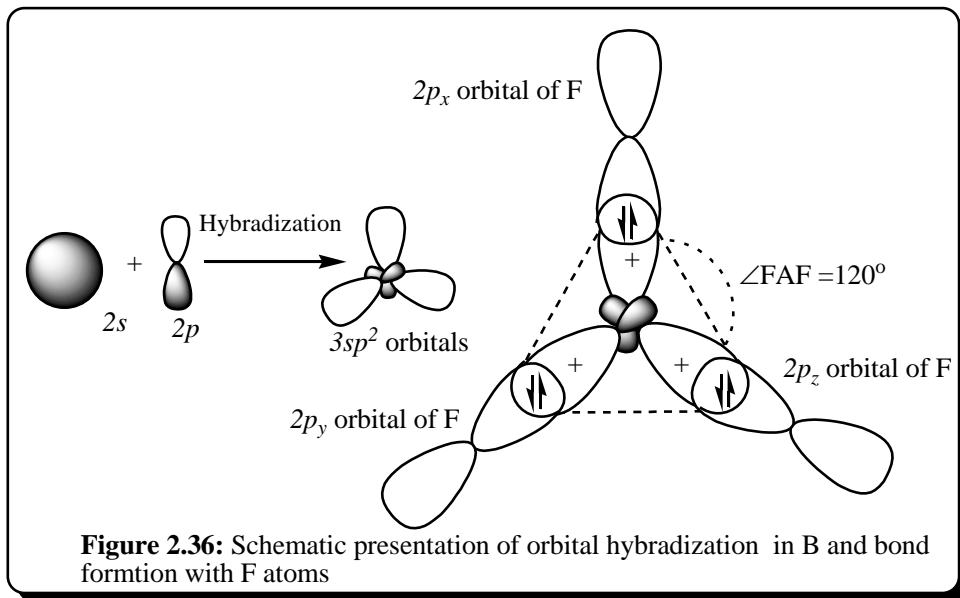
Three electron pairs surround the central in AX_3 types molecule. The Lewis structure shows three bond pairs which arrange themselves in trigonal planar shape and lie at 120° angle from each other to be at maximum distance in order to avoid electronic repulsion between them.

i) AX_3 Type, BF_3 : The common example of this type is BF_3 .

Ground state electronic configuration of B: $[\text{He}] 2s^2 2p^1$

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

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 (Fig.2.36). The Lewis structure of BF_3 , shown in figure 2.16, 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 $\text{F}-\text{B}-\text{F}$ bond angle of 120° . The sp^2 hybridization also predicts trigonal planar structure for BF_3 molecule.

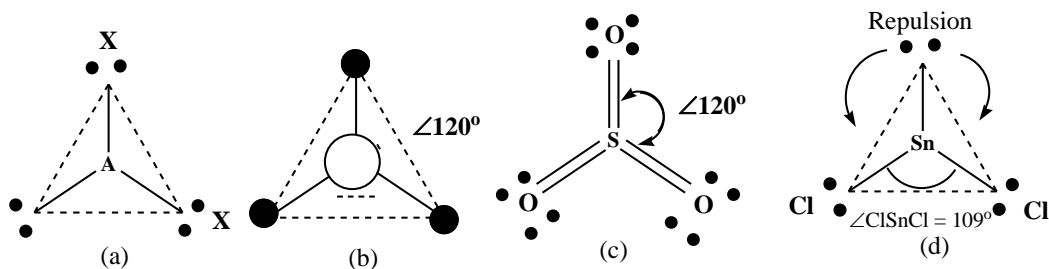
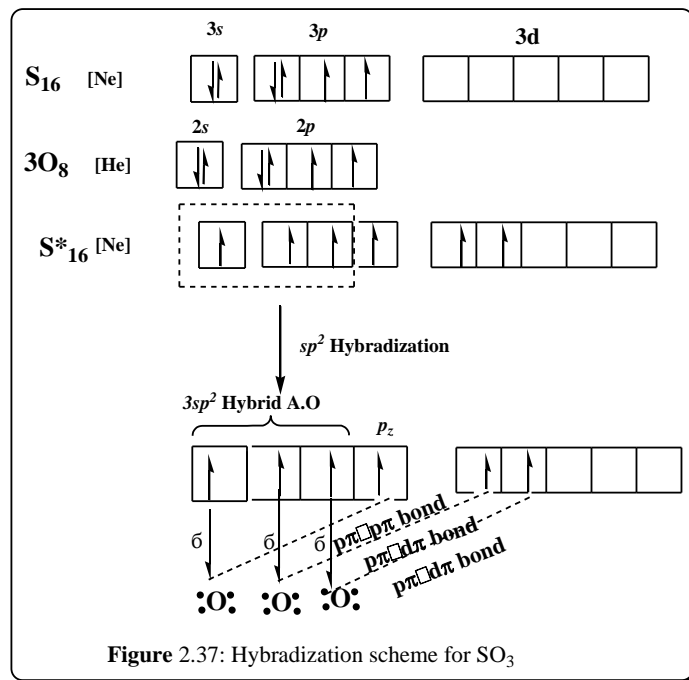


ii) SO_3 is an example of AX_3 type molecule involving multiple bonds. In SO_3 , S undergoes sp^2 hybridization forming trigonal planer structure. Hybridization scheme of S in SO_3 and formation of 3 σ and 3 π -bonds is shown in figure 2.37.

As shown in figure 2.37, 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 O – S – O bond angle of 120° .

AB₂L Type:

In this type, the central atom A have two bond pairs and one lone pair. The geometry of AB_2L type molecules is angular or V-shape. SnCl_2 represents the example of this type of molecule Lewis structure of SnCl_2 (Figure 2.17 d) shows that it has two σ – bonding electron pairs and one lone pair of electrons. 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 SnCl_2 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° .

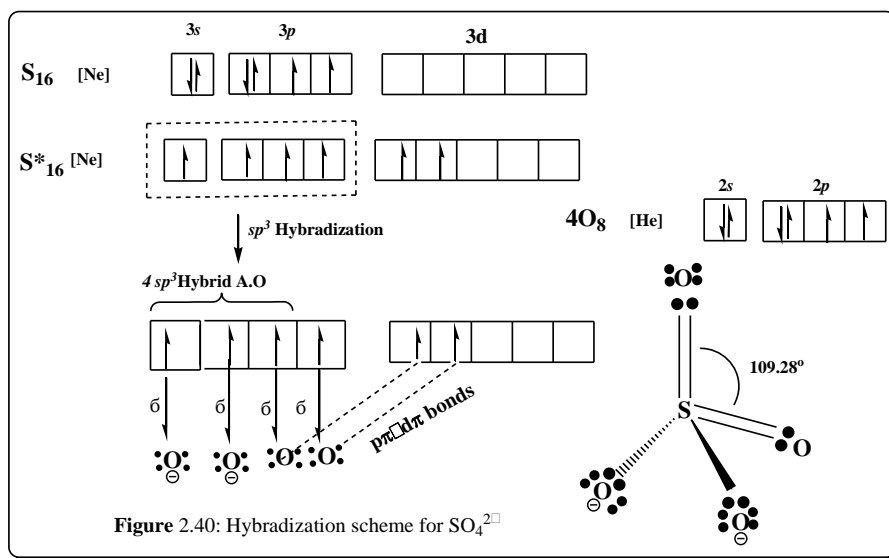
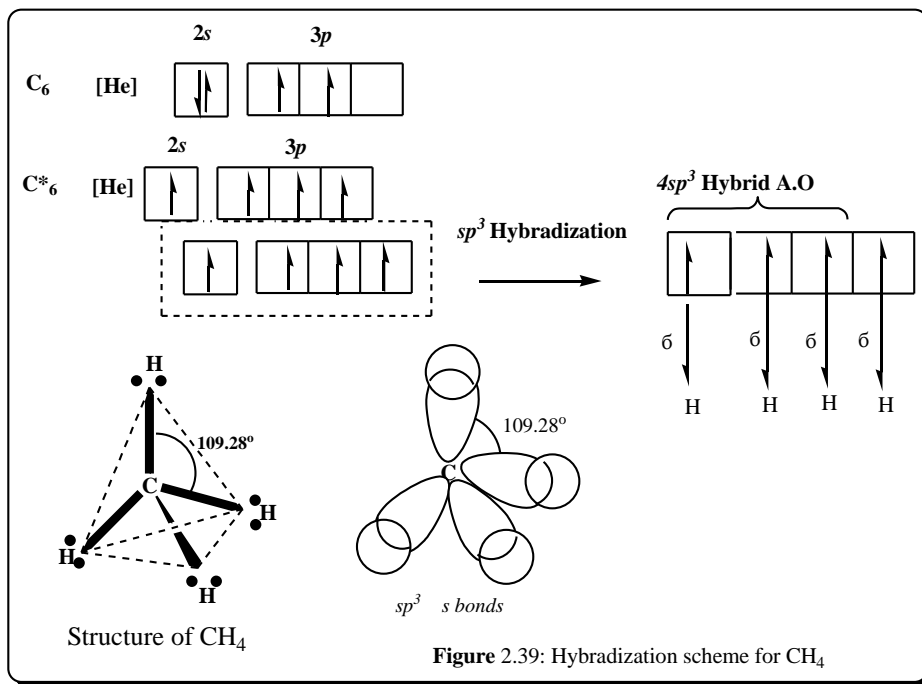


3.2.3 Shape of Molecule with Steric number 4

Type AX_4 : 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 CH_4 and TiCl_4 show that central atom, C in CH_4 and Ti in TiCl_4 have four bonding electron pairs. According to VSEPR theory, four bonding pairs in CH_4 will arrange themselves in a tetrahedral structure in order to have minimum repulsion between them. Thus VSEPR theory suggests a tetrahedral structure for CH_4 molecule with each $\text{H}-\text{C}-\text{H}$ bond angle of 109.28° .

SO_4^{2-} ion is AX_4 species involving multiple bonds. The Lewis structure of SO_4^{2-} 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 SO_4^{2-} , 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 SO_4^{2-} ion with each $\text{O}-\text{S}-\text{O}$ bond angle of 109.5° . The structures of BF_4^- , CF_4 , NH_4^+ and ClO_4^- can be explained on similar grounds.

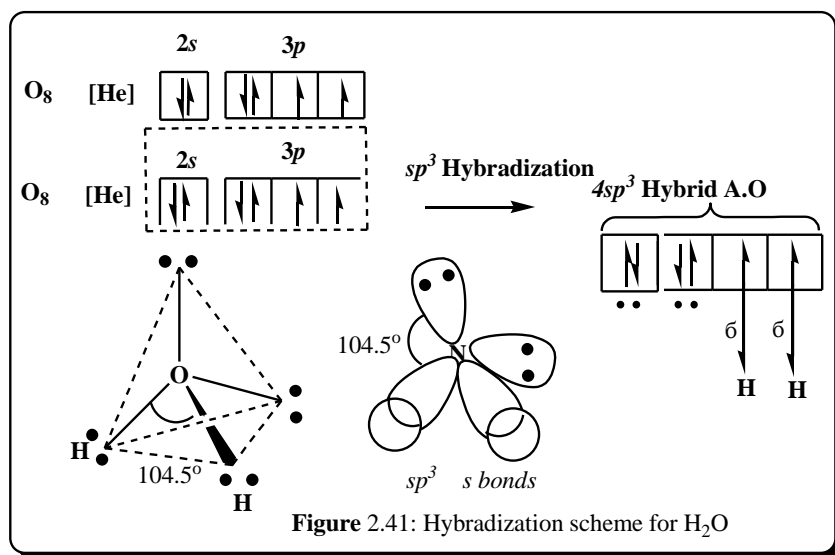
The S atom in SO_4^{2-} undergoes sp^3 hybridization and predicts the tetrahedral structure for SO_4^{2-} ions as given in figure 2.40. Two π -bonds are formed by overlapping of d orbitals of S and p orbitals of oxygen and are called $p\pi-d\pi$ bonds.



Type AX_3L : In this type of molecules, three σ -bond electron pairs and one lone pairs arrange themselves around the corners of a tetrahedron. The lone pair occupies more space than bond pairs and repels the bond pairs. Consequently $\text{X}-\text{A}-\text{X}$ bond angle decreases to 107.2° and tetrahedral shape becomes pyramidal. NH_3 , PCl_3 , PH_3 and AsCl_3 are examples of this type of molecules.

Lewis structure of NH_3 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 $\text{H} - \text{N} - \text{H}$ bond angle is of 107° in NH_3 rather than normal tetrahedral angle of 109° .

Type AX_2L_2 : 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 $\text{X}-\text{A}-\text{X}$ bond angle further decreases to 104.5° and tetrahedral shape becomes v–shape or angular. H_2O and H_2S are examples of this type of molecules. Lewis structure of H_2O 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 $\text{H} - \text{O} - \text{H}$ bond angle is of 104.5° in H_2O rather than normal tetrahedral angle of 109° as shown in figure 2.41.



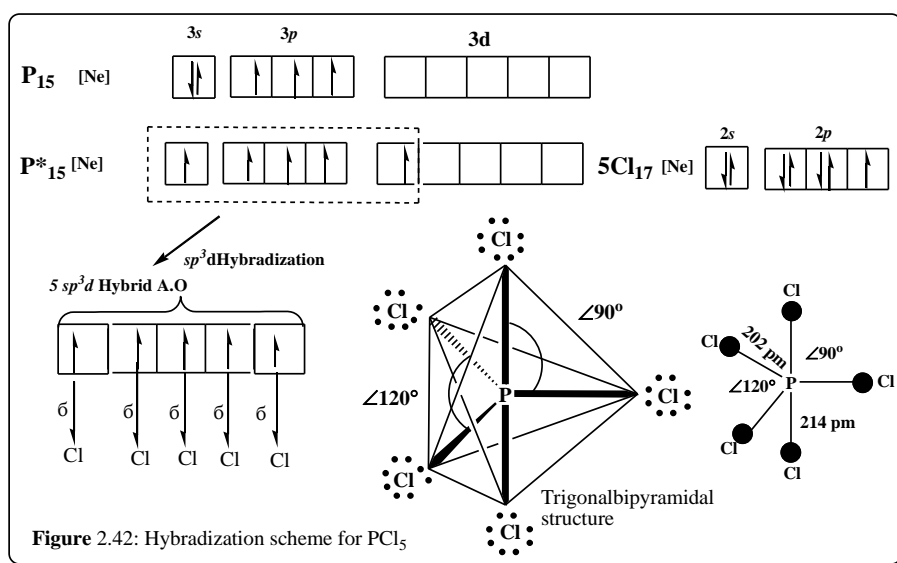
According to VSEPR theory shape of molecule is determined by two bonding pairs only. Thus VSEPR theory suggests a V– shaped structure for H_2O molecule.

3.2.4 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 shows 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 AX₅: PCl₅, PF₅ and SbCl₅ 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 2.42.

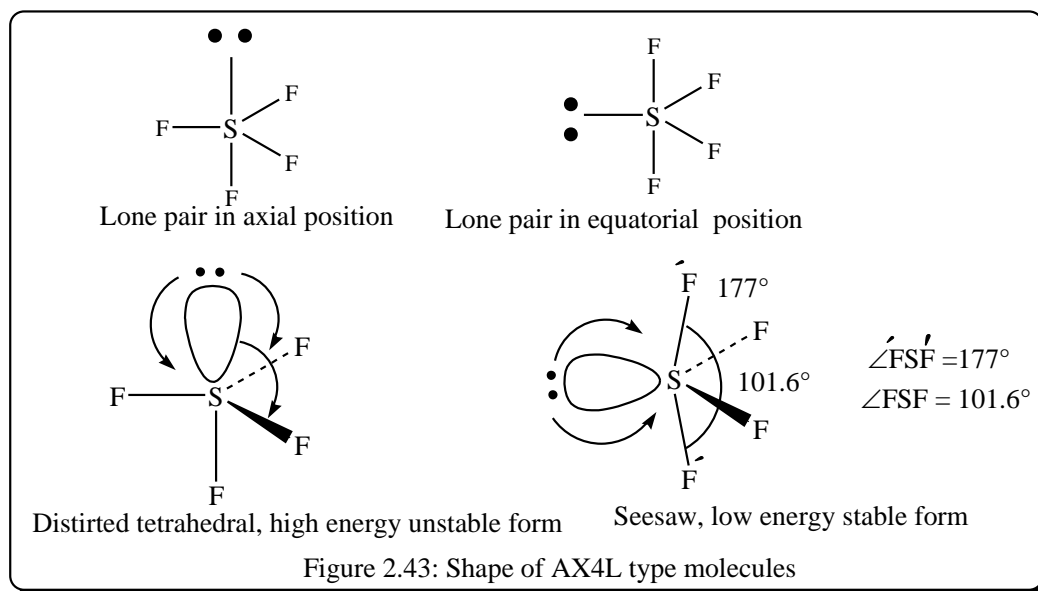
Type AX₄L: In this type of molecules, four σ -bond electron pairs and one lone pairs arrange themselves around the corners of a trigonal bipyramidal structure. The lone pair occupies more space than bond pairs and repels the bond pairs. Consequently X—A—X bond angle decreases and trigonal bipyramidal shape becomes seesaw shape. SF₄, SeF₄ and TeCl₄ are examples of this type of molecules. S atom in SF₄ is sp^3d hybridized resulting in the formation of the five coordinate bonds required for the decet. 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. 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 177°, the two equatorial S-F bonds, ideally at 120°, move much closer to an angle of 101.6°



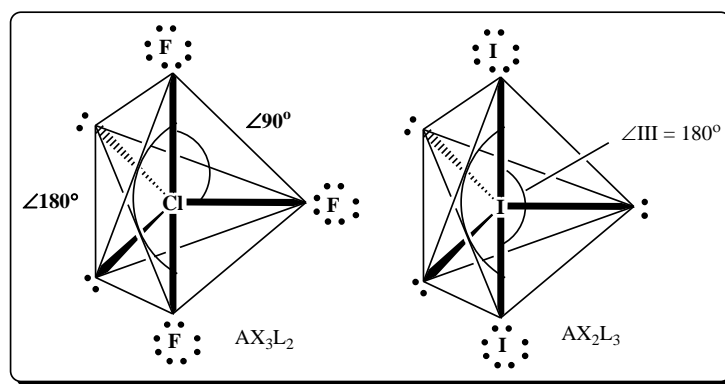
Lewis structure of SeF₄ shows that it has four σ - bonding pairs and one lone pair of electrons. These electron pairs will have trigonal bipyramidal geometry. According to VSEPR theory, lone pair occupies more space than bond pairs and, therefore, exerts greater repulsions on bond pairs. Thus F - S - 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 resulting 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 ClF_3 molecule with two lone pairs occupying the equatorial position. The bond angles are shown in the figure 2.43 . Another example of this type is BrF_3 .



Type AX_2L_3 : ClF_2 , XeF_2 and I_3^- 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 ClF_2 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 ClF_2 molecule with three lone pairs occupying the equatorial position. The bond angles are shown in the figure 2.44



3.2.5 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 central atom, S has six bonding electron pairs. According to VSEPR theory, six bonding pairs in

SF₆ will arrange themselves forming octahedral electronic geometry to have minimum repulsion between them.

Type AX₆: Sulfur hexafluoride (SF₆) is an example of AX₆ type molecules in which all six electron pairs are bonding pairs. Each electron pair 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 2.45. The Lewis structure of SF₆ shows that central atom, S, has six bonding electron pairs. According to VSEPR theory, six bonding pairs in SF₆ arrange themselves in an octahedral structure in order to have minimum repulsion between them. The VSEPR theory suggests an octahedral structure for SF₆ molecule. MoF₆⁻ and PCl₆⁻ are other examples of AX₆ molecules.

Type AX₅L: Iodine hexafluoride is an example of this class of molecules. The electronic geometry for IF₅ 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 IF₅ is square pyramidal. For the normal octahedral the bond angles are 90 and 180, but in IF₅ 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 IF₅ molecule. The bond angles are shown in figure. Same arguments can be extended to explain the shape of BrF₅.

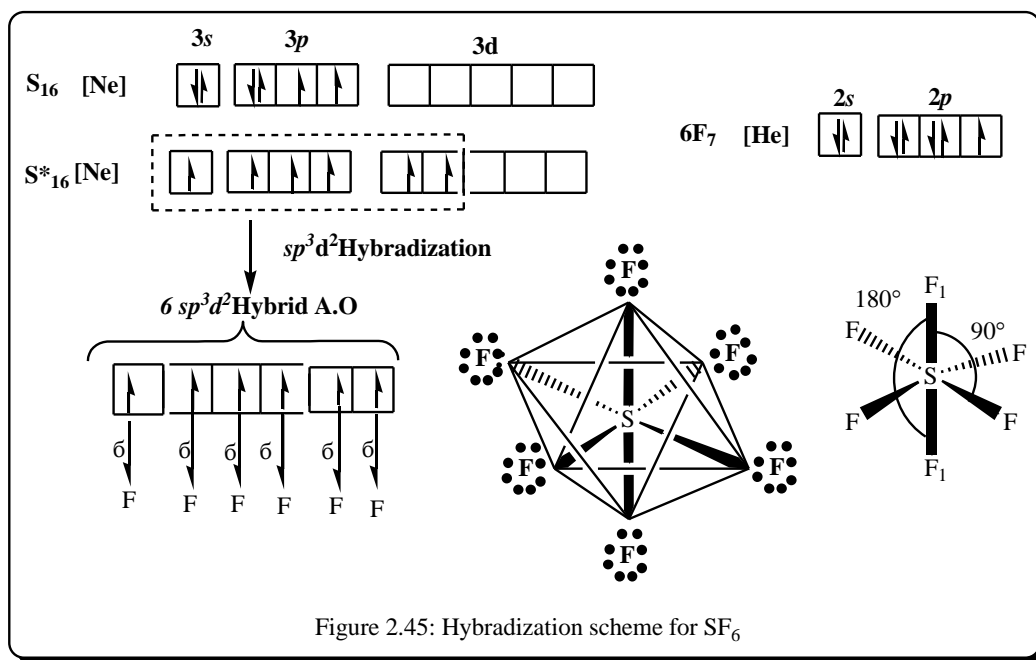
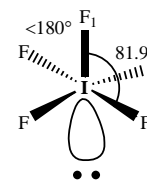
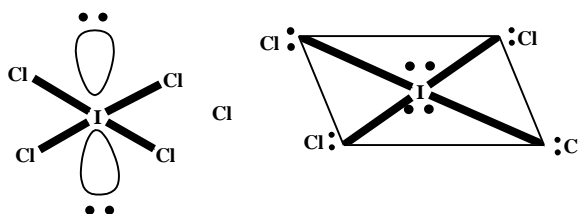


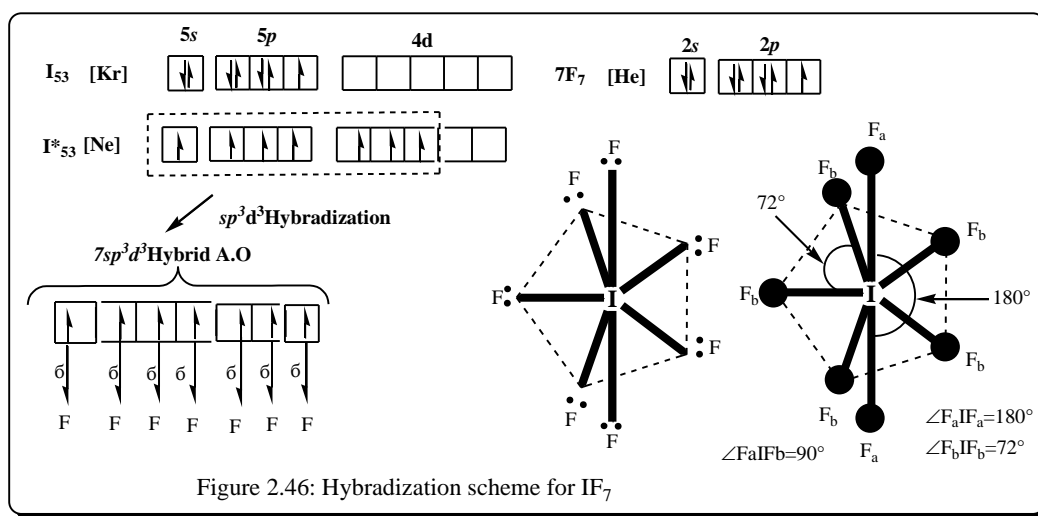
Figure 2.45: Hybridization scheme for SF₆



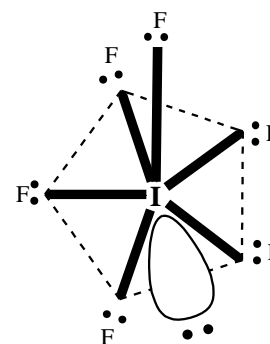
Type AX₄L₂: ICl₄⁻ and BrF₄⁻ are the examples of AX₄L₂ type molecule. There are six electron pairs in this type of molecules. These electron pairs will have octahedral geometry.

Lewis structure of ICl₄⁻ 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 ICl₄⁻ molecule.

3.2.6 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 IF₇ molecule



The Lewis structure of IF₇ shows that central atom, I, has seven bonding electron pairs. Each electron pair 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. I atom undergoes sp^3d^3 hybridization forming six hybrid orbitals which overlap with p orbitals of fluorine. The hybridization scheme and bond angles are shown in figure 2.23. IF₇ has five basal bonds (F_b—I bonds) in the plane of pentagon directed at angle of 72° while two axial bonds (F_a—I bonds) directed at right angle to the plane of pentagon. F_a—I—F_a bond angle is of 180°. Thus VSEPR theory suggests a pentagonal bipyramidal structure for IF₇ 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.