CHAPTER 1

Stereochemistry and Bonding in Main Group Compounds:

❖ VSEPR Theory

One of the most important discoveries of the 20th century was Lewis's description of the chemical bond as a shared pair of electrons. This remarkably brilliant idea connected some of the most important inventions in chemistry from the 19th century; like the Mendeleev's periodic table of elements and the van 't Hoff's formulation of the tetrahedral carbon. Lewis's idea also laid down the foundation of some advanced theoretical models for chemical bonding used today. The cubical atoms and the concept of shared electron pairs proposed by Lewis in 1919 can be illustrated as shown below.

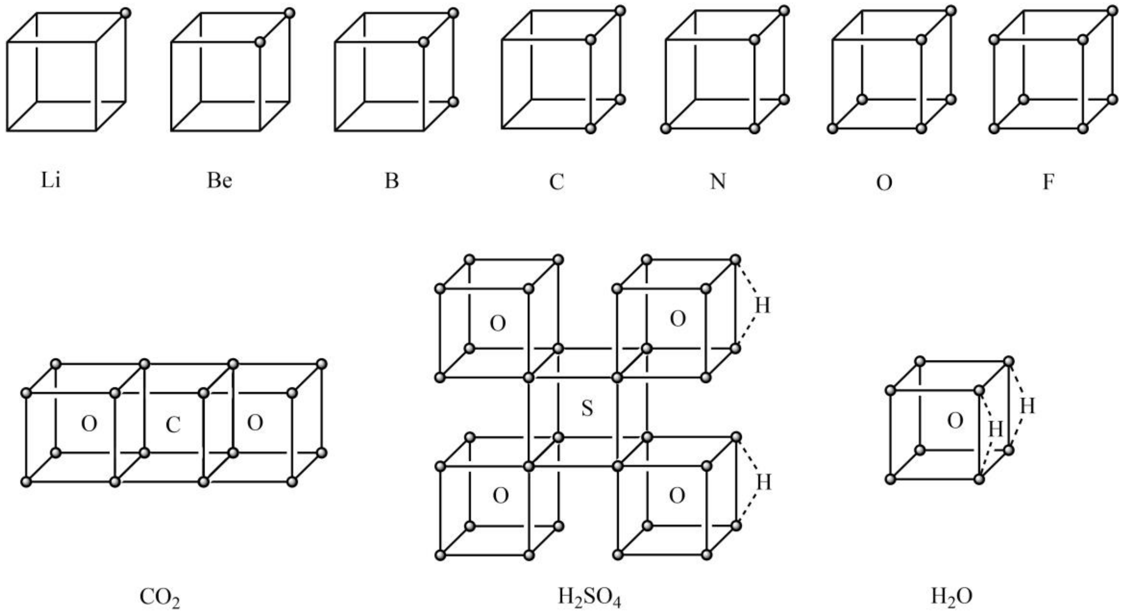


Figure 1. The Lewis concept of electron-pair sharing between cubical atoms.

The valence-shell-electron-pair-repulsion (VSEPR) theory is actually the successor of Lewis's idea which also says that the covalent bond can be portrayed as a shared electron-pair. Now, although Lewis's model explained the correlation between valence and bonding in an extremely beautiful manner, it had no theoretical basis at that time. Later in 1924, Wolfgang Pauli rationalized the electron pairing by proposing the Pauli exclusion principle. Now being an extension of the Lewis idea, the VSEPR theory also finds its roots in the Pauli exclusion principle. The initial formulation of the VSEPR model was actually carried out by two British chemists, Nevil Sidgwick and Herbert Powell, who correlated the number of valence shell electron pairs of the central atom in a molecule to the bonding profile around.

The basic proposal of Sidgwick and Powell was that all the electron-clouds in the outermost shell of an atom (valence shell) must be taken into consideration before any geometry profiling is carried out. In other words, all electron pairs of the valence shell, whether they participate in bonding or not (lone pair as well as bond pairs), have their space requirement; and therefore govern the bonding profile around the central atom. The initial version of the VESPR model also postulated that electron pairs in a Lewis description of a molecule can be represented by points which are arranged on the surface of a hypothetical sphere as far apart as possible. However, later it was thought that the more realistic representation of valence shell electron-pair is a negatively charged cloud which is comprised of two opposite-spin electrons; and this cloud is trying to occupy as much space as possible while eliminating its other counterparts from this space. Therefore, in addition to the "points on the sphere" model; an alternative model can also be given which is based on the different numbers of circles of equal radii arranged in such a way that they occupy maximum possible surface of a sphere without any mutual overlap; though both of these models lead to the same geometrical profile.

Figure 2. The points-on-the-sphere model of molecular geometries.

A third version, the tangent-sphere model, was also developed by Kimball and Bent that considers all electron-pairs as the spherical entities of the same size. These spherical domains are expected to get packed around the central atom as efficiently as possible. Sidgwick and Powell, in 1940, proposed these most primitive coordination profiles of two to six electron pair domains which are actually fundamental to the VSEPR model and they set the stage for the prediction of the molecular geometries. Now although these predictions explained a wide range of molecular geometries, the distortion from these ideal structures was still a challenge to solve. The most decisive step towards the development of modern VSEPR theory was made Gillespie and Nyholm in 1957 when they published their revolutionary paper entitled "Inorganic Stereochemistry". They treated bond pair and lone pair distinctly and incorporated the necessary allowances. They not only coined the term "VSPER theory", but also worked a lot to popularize the same.

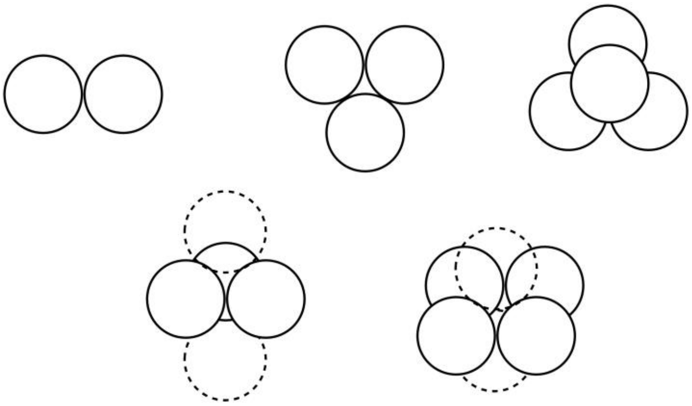


Figure 3. The spherical electron-pair domain model of molecular geometries.

The valence-shell-electron-pair-repulsion or simply the VSEPR theory is a theoretical model that is used to predict the geometry of individual molecules or complexes from the number of electron pairs surrounding their central atoms or ions.

It is also worthy to mention that the VSEPR theory is based purely upon observable electron-density rather than single electron wave functions or orbitals, and therefore is not related to the hybridization in any sense.

- ***Basic Postulates of VSEPR Theory***

The modern valence-shell-electron-pair-repulsion or the VSEPR theory is founded upon five basic postulates as given below.

1. All of the electron pairs of the valence shell, whether they participate in bonding or not i.e. lone pairs as well as bond pairs, have space requirements; and therefore govern the bonding profile around the central atom.

2. These valence electron pairs domains, surrounding an atom, tend to repel each other, and will thus prefer to adopt an arrangement that minimizes this repulsion, thus determining the molecule's geometry.

3. Lone pairs of electrons (nonbonding domains) are bigger in size than their single-bond counterparts; which in turn implies that they require more space in the valence shell comparatively. This is simply because the non-bonding electron-pair domain is influenced by only one positive core while the bonding one is held by two positively charged centers. This rationalization, therefore, predicts the following order of domain repulsion:

$$\text{Lone pair} - \text{Lone pair} > \text{Lone Pair} - \text{Bond Pair} > \text{Bond Pair} - \text{Bond Pair}$$

4. The size of the valence shell electron pair domain participating in a single bond decreases with rising electronegativity strength of the attached group.

5. The double and triple bonds should be considered as two- and three-electron-pair-domains, respectively; in which the individual electron pairs are not distinguished. Owing to the greater electron density, electron-pair-domain size increases as we move from a single to the triply bonded system.

➢ *Application of the VSEPR Theory to Predict Molecular Geometries*

The VSEPR theory can successfully be used to explain the qualitative geometrical profile of molecular species with coordination numbers ranging from two to seven. Some of the most common illustrative examples are given below.

1. Two electron-pair domains: *i) $BeCl_2$:* The central atom in $BeCl_2$ molecule is Be which has two valence electrons (2, 2). Now because each chlorine atom needs one electron to complete its octet (2, 8, 7), the Be atom uses its both valence electrons to create two bond pair domains only. Hence the geometry for minimum repulsion will be linear and the normal bond angle will be 180°.

Figure 4. Structure of $BeCl_2$ molecule from the VSEPR model.

2. Three electron-pair domains: *i) BF_3:* The central atom in BF_3 molecule is B which has three valence electrons (2, 3). Now because each fluorine atom needs one electron to complete its octet (2, 7), the B atom uses its three valence electrons to create three bond pair domains only. Hence the geometry for minimum repulsion will be trigonal and the normal bond angle will be 120°.

Figure 5. Structure of BF_3 molecule from the VSEPR model.

ii) SO_2: The central atom in the SO_2 molecule is S which has six valence electrons (2, 8, 6). Now because each oxygen atom needs two electrons to complete its octet (2, 6), the S atom uses its four valence electrons to create two bonding two-electron-pair domains, while two electrons are left as a lone pair domain. Now though the geometry for three electron pair domains is trigonal planar with 120°, in this case, the non-bonding one-electron-pair domain would require more space than the bonding domains. This, in turn, would result in a greater lone-pair–bond-pair repulsion yielding a V-shapes geometry with an actual bond angle slightly less than the normal 120° of a perfectly trigonal planar system. However, the actual O−S−O bond angle is 119.3° which is still not very much less than ideal 120° as we expected it to be; this can be attributed to the larger electron density from the two-electron-pair nature of each bond pair domains.

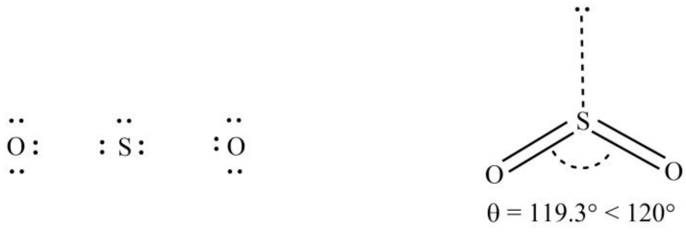


Figure 6. Structure of SO_2 molecule from the VSEPR model.

3. Four electron-pair domains: *i) CH_4:* The central atom in CH_4 molecule is C which has four valence electrons (2, 4). Now because each hydrogen atom needs one electron to complete its duplet (1), the C atom uses its all four valence electrons in sharing to create four bonding one-electron-pair domains only. Hence the geometry for minimum repulsion will be perfect tetrahedral and the normal bond angle will be 109°28′.

Figure 7. Structure of CH_4 molecule from the VSEPR model.

ii) NH_3: The central atom in NH_3 molecule is N which has five valence electrons (2, 5). Now because each hydrogen atom needs one electron to complete its duplet (1), the N atom uses its three valence electrons to create three bonding one-electron-pair domains, while two electrons are left as lone pair domain. Now though the geometry for four electron-pair domains is tetrahedral with 109°28′, in this case, the non-bonding domain would require more space than the bonding domains. This, in turn, would result in greater lone-pair–bond-pair repulsion yielding a pyramidal-shaped geometry with H−N−H bond angle (107.8°) slightly less than the normal 109°28′ of a perfectly tetrahedral system.

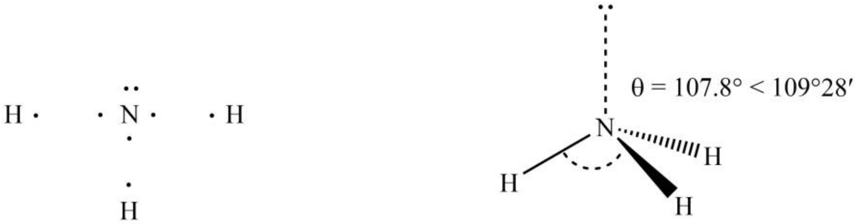


Figure 8. Structure of NH_3 molecule from the VSEPR model.

iii) H_2O: The central atom in H_2O molecule is O which has six valence electrons (2, 6). Now because each hydrogen atom needs one electron to complete its duplet (1), the O atom uses its two valence electrons to create two bond pair domains, while four electrons are left as two lone pair domains. Now though the geometry for four electron-pair domains is tetrahedral with 109°28′, in this case, the two non-bonding domains would require more space than the bonding domains. This, in turn, would result in a greater lone-pair–lone-pair repulsion yielding a V-shaped geometry with H−O−H bond angle (104.5°) less than the normal 109°28′ of a perfectly tetrahedral system. It is also worthy to note that the bond angle in water is also less than NH_3 which is obviously due to the presence of one extra lone pair in H_2O.

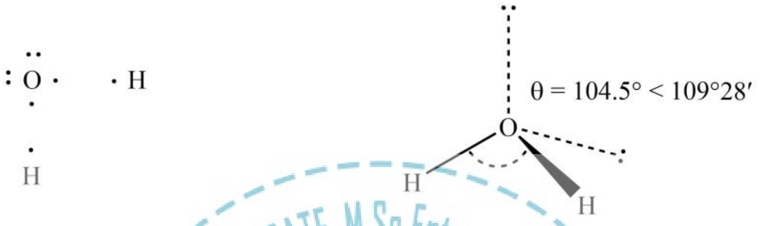


Figure 9. Structure of H_2O molecule from the VSEPR model.

4. Five electron-pair domains: *i) PF_5:* The central atom in PF_5 molecule is P which has five valence electrons (2, 8, 5). Now because each fluorine atom needs one electron to complete its octet (2, 7), the P atom uses its all five valence electrons in sharing to create five bond pair domains only. Hence the geometry for minimum repulsion will be perfect trigonal bipyramidal and the normal bond angle between equatorial groups should be 120°, while the normal bond angle between axial fluorine should be 180°. Now because each axial position has three neighbors at 90° while every equatorial position has only two 90° neighbors, we can conclude that the more crowding at the axial position would lead to longer axial bonds comparatively.

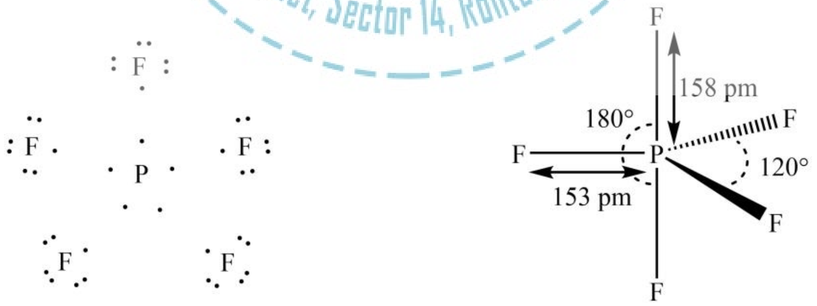


Figure 10. Structure of PF_5 molecule from the VSEPR model.

ii) SF_4: The central atom in SF_4 molecule is S which has six valence electrons (2, 8, 6). Now because each fluorine atom needs one electron to complete its octet (2, 7), the S atom uses its four valence electrons to create four bond pair domains, while two electrons are left as lone pair domain. Now, although the geometry for five electron-pair domains is trigonal bipyramidal with equatorial and axial bond angles of 120° and 180°, respectively; in this case, the non-bonding domain would require more space than the bonding domains. Now the question arises here is what position this non-bonding electron-pair domain should occupy in a trigonal-bipyramidal frame. After seeing that each axial position has three neighbors at 90° while every equatorial position has only two 90° neighbors, we can conclude that the equatorial position is more suitable for the placement of lone pair. This, in turn, would result in a greater lone-pair–bond-pair repulsion yielding the distortion of a perfect seesaw-shaped derivative with axial and equatorial bond angles slightly less than their normal of 180° and 120°.

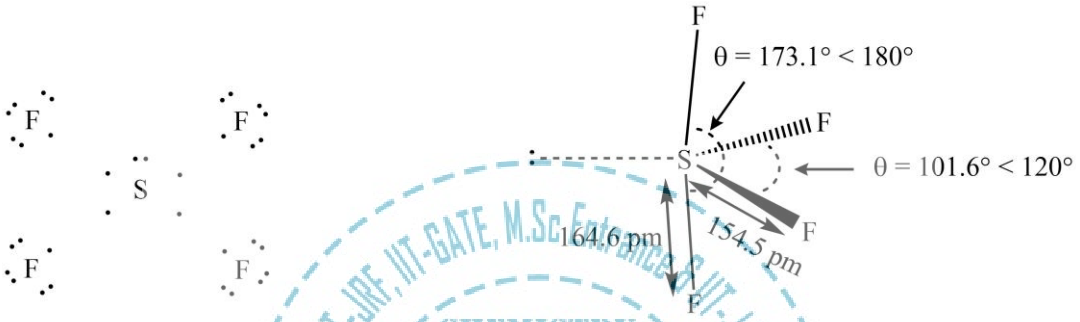


Figure 11. Structure of SF_4 molecule from the VSEPR model.

iii) ClF_3: The central atom in ClF_3 molecule is Cl which has seven valence electrons (2, 8, 7). Now because each fluorine atom needs one electron to complete its octet (2, 7), the Cl atom uses its three valence electrons to create three bond pair domains, while four electrons are left as two lone pair domain. Now though the geometry for five electron pair domains is trigonal bipyramidal equatorial and axial bond angles of 120° and 180°, respectively; but in this case, the non-bonding domain would require more space than the bonding domains, and therefore need to be placed on the equatorial position. This, in turn, would result in greater lone-pair–lone-pair repulsion yielding the distortion of perfect T-shaped derivative with axial equatorial bond angles less than their normal of 180°.

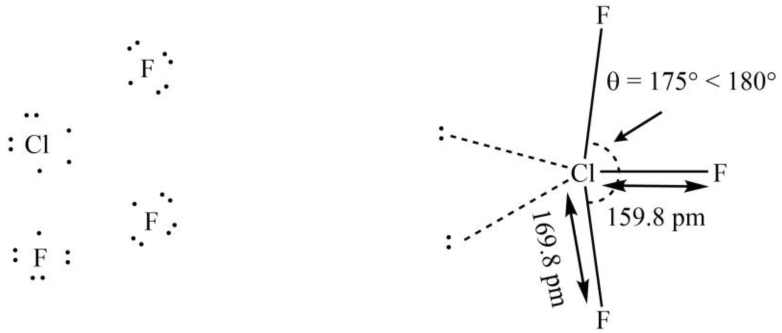


Figure 12. Structure of ClF_3 molecule from the VSEPR model.

iv) I_3^-: The central atom in I_3^- ion is I which has seven valence electrons (2, 8, 18, 18, 7). Now because one iodine atom needs one electron to complete its octet (2, 8, 18, 18, 7) while the iodide ion needs zero electrons (2, 8, 18, 18, 8), the I atom uses its one valence electrons to create two bond pair domains, while six electrons are left as three lone pair domains. Now though the geometry for five electron pair domains is trigonal bipyramidal with equatorial and axial bond angles of 120° and 180°, respectively; but in this case, the non-bonding domain would require more space than the bonding domains, and therefore need to be placed on the equatorial position. This, in turn, would result in a perfectly linear geometry with a normal bond angle of 180°.

Figure 13. Structure of I_3^- from the VSEPR model.

5. Six electron-pair domains: *i) SF_6:* The central atom in SF_6 molecule is S which has six valence electrons (2, 8, 6). Now because each fluorine atom needs one electron to complete its octet (2, 7), the S atom uses its all six valence electrons in sharing to create six bond pair domains only. Hence the geometry for minimum repulsion will be perfect octahedral and the normal angle between two any adjacent bonds will be 90°.

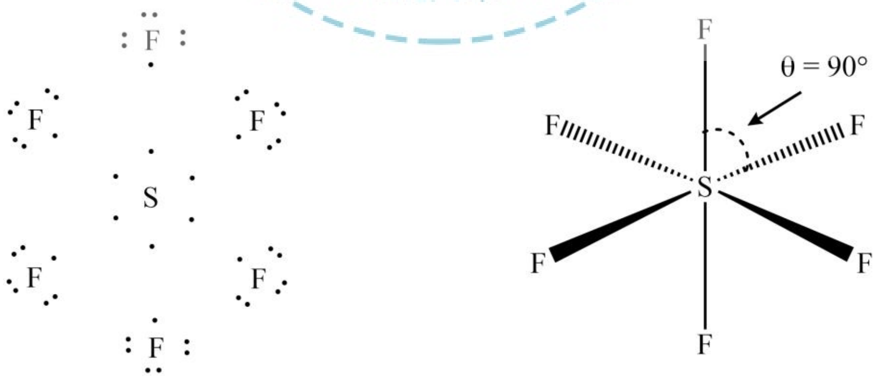


Figure 14. Structure of SF_6 molecule from the VSEPR model.

ii) BrF_5: The central atom in BrF_5 molecule is Br which has seven valence electrons (2, 8, 18, 7). Now because each fluorine atom needs one electron to complete its octet (2, 7), the Br atom uses its five valence electrons to create five bond pair domains, while two electrons are left as a lone pair domain. Now though the geometry for six electron pair domains is perfectly octahedral; but in this case, the non-bonding domain would require more space than the bonding domains. The question arises here is what position this non-bonding electron pair domain should occupy in an octahedral frame. Now owing to the fact that all positions in an octahedral frame are equivalent, we can conclude that the lone pair can be placed at any of the six site. This, in turn, would result in greater lone-pair–bond-pair repulsion yielding the distortion of perfect octahedral geometry to a square-pyramidal one.

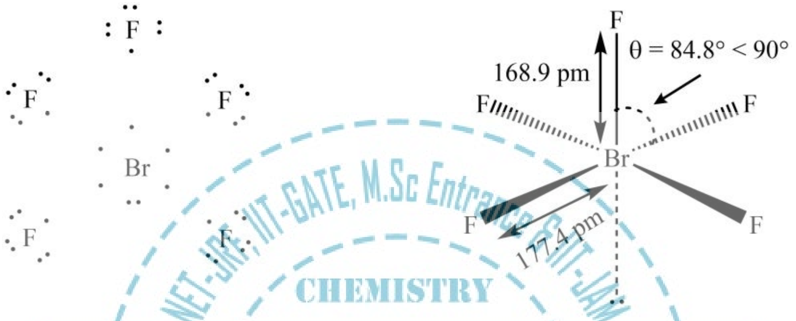


Figure 15. Structure of BrF_5 molecule from the VSEPR model.

iii) XeF_4: The central atom in XeF_4 molecule is Xe which has eight valence electrons (2, 8, 18, 18, 8). Now because each fluorine atom needs one electron to complete its octet (2, 7), the Xe atom uses its four valence electrons to create four bond pair domains, while the four electrons are left as two lone pair domains. Now though the geometry for six electron pair domains is perfectly octahedral; but in this case, the non-bonding domain would require more space than the bonding domains. The question arises here is what position this non-bonding electron pair domain should occupy in an octahedral frame. Now owing to the fact that lone-pair–lone-pair repulsion is highest, both non-bonding domains should be placed trans to each other in an octahedral frame to give a perfect square-planar geometry.

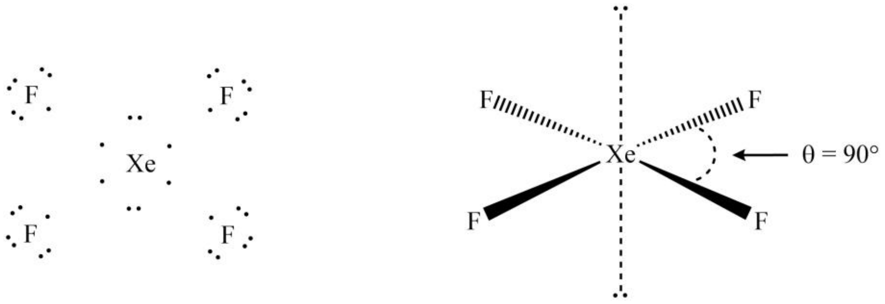


Figure 16. Structure of XeF_4 molecule from the VSEPR model.

6. Seven electron-pair domains: *i) IF_7:* The central atom in IF_7 molecule is I which has seven valence electrons (2, 8, 18, 18, 7). Now because each fluorine atom needs one electron to complete its octet (2, 7), the I atom uses its all seven valence electrons in sharing to create seven bond pair domains only. Hence the geometry for minimum repulsion will be pentagonal bipyramidal; and the normal bond angle between equatorial groups will be 72°, while the normal bond angle between axial fluorine will be 180°. Now because each axial position has nearest neighbors at 90° while every equatorial position has nearest neighbors at 72°, we can conclude that the less crowding at the axial position would lead to shorter axial bonds comparatively.

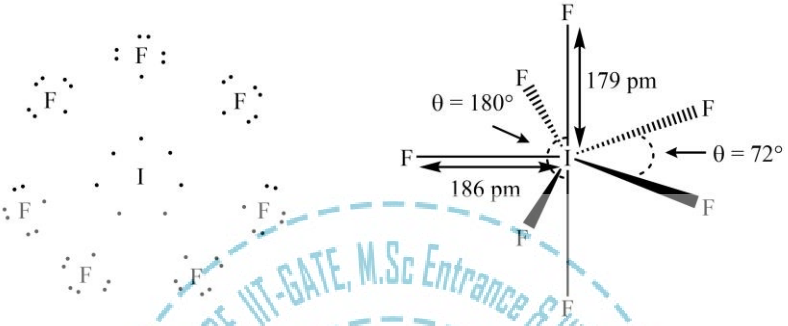


Figure 17. Structure of IF_7 molecule from the VSEPR model.

ii) $XeOF_5^-$: The central atom in $XeOF_5^-$ molecule is Xe which has eight valence electrons (2, 8, 18, 18, 8). Now because each fluorine atom, as well as O^-, needs one electron to complete its octet (2, 7), the Xe atom uses its six valence electrons to create six bond pair domains, while two electrons are left as a lone pair domain. Now though the geometry for seven electron pair domains is pentagonal bipyramidal; but in this case, a non-bonding domain is present which would require more space than the bonding domains. Now because each axial position has the nearest neighbors at 90° while every equatorial position has nearest neighbors at 72°, we can conclude that the axial position is more suitable for the placement of lone pair. This, in turn, would result in greater lone-pair–bond-pair repulsion yielding the distortion of perfect pentagonal pyramidal-shaped geometry with equatorial bond angles slightly less than their normal of 72°.

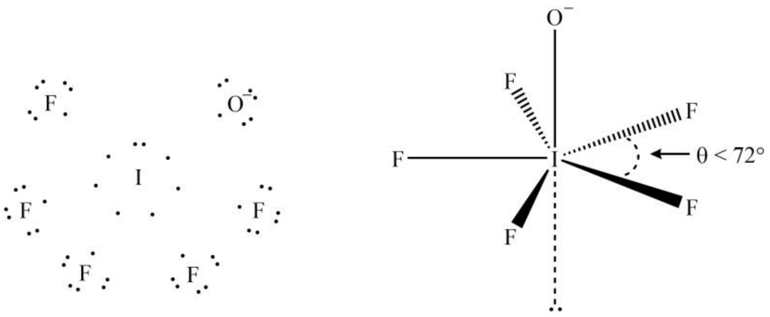


Figure 18. Structure of $XeOF_5^-$ molecule from VSEPR model.

iii) XeF_5^-: The central atom in the XeF_5^- molecule is Xe which has eight valence electrons (2, 8, 18, 18, 8). Now because four fluorine atom needs one electron to complete its octet (2, 7) while the fifth group F^- needs zero electrons, the Xe atom uses its four valence electrons to create five bond-pair-domains, while the four electrons are left as two lone pair domains. Now though the geometry for seven electron pair domains is perfectly pentagonal bipyramidal; but in this case, the non-bonding domain would require more space than the bonding domains. The question arises here is what position these non-bonding electron pair domains should occupy in a pentagonal bipyramidal frame. Out of the axial and equatorial sites, the axial site is more suitable for the placement of lone pair as explained earlier. Now owing to the fact that lone-pair–lone-pair repulsion is highest, the second non-bonding domains should be placed trans to the first one in a pentagonal bipyramidal frame to give a perfect pentagonal-planar geometry.

Figure 19. Structure of XeF_5^- molecule from the VSEPR model.

- ***The AXE Method***

The commonly used electron counting scheme when applying the VSEPR theory is generally called as the "AXE method". The A represents the central atom while the X represents each of the ligands attached. The latter E symbolizes the number of lone electron pair domains around the central atom. The value of X and E is collectively labeled as the steric number. The VSEPR uses this steric number to predict the molecular geometries according to the atomic positions only. For instance, the AX_2E_1 infers a bent molecule that has three atoms AX_2 which are not in one straight line because of the presence of a lone pair. The deviations from idealized geometries can be rationalized from the lone pairs, multi-electron-electron-pair domains and the presence of electronegative groups.

Steric Number	Molecular geometry 0 lone pairs	Molecular geometry 1 lone pair	Molecular geometry 2 lone pairs	Molecular geometry 3 lone pairs
2	X—A—X Linear (CO_2)			

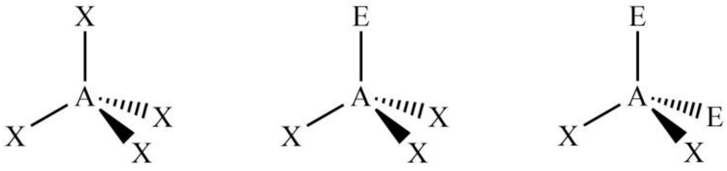
Figure 20. Continued on the next page…

3

Trigonal Planar (BF_3)

V-Shape (SO_2)

4



Tetrahedral (CH_4)

Trigonal pyramidal (NH_3)

Bent (H_2O)

5

Trigonal bipyramidal (PCl_5)

Seesaw (SF_4)

T-shaped (ClF_3)

Linear (I_3^-)

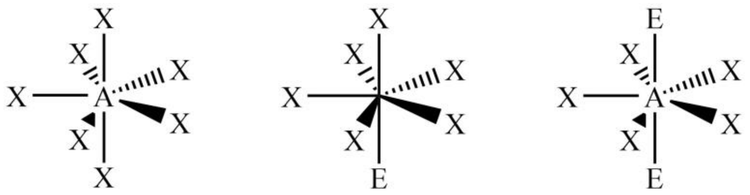
6

Octahedral (SF_6)

Square pyramidal (BrF_5)

Square planar (XeF_4)

7



Pentagonal bipyramidal (IF_7)

Pentagonal pyramidal ($XeOF_5^-$)

Pentagonal planar (XeF_5^-)

Figure 20. The overall geometry of the compound is predicted by the total number of lone pairs and bond pairs of the electrons i.e. the steric number of the system.

➢ ***Limitations of VSEPR Theory***

The VSEPR theory is pretty much successful in explaining a wide range of geometries in main group chemistry but there are some serious limitations also for which it offers no rational solution. Some of the most common limitations of the VSEPR theory are given below.

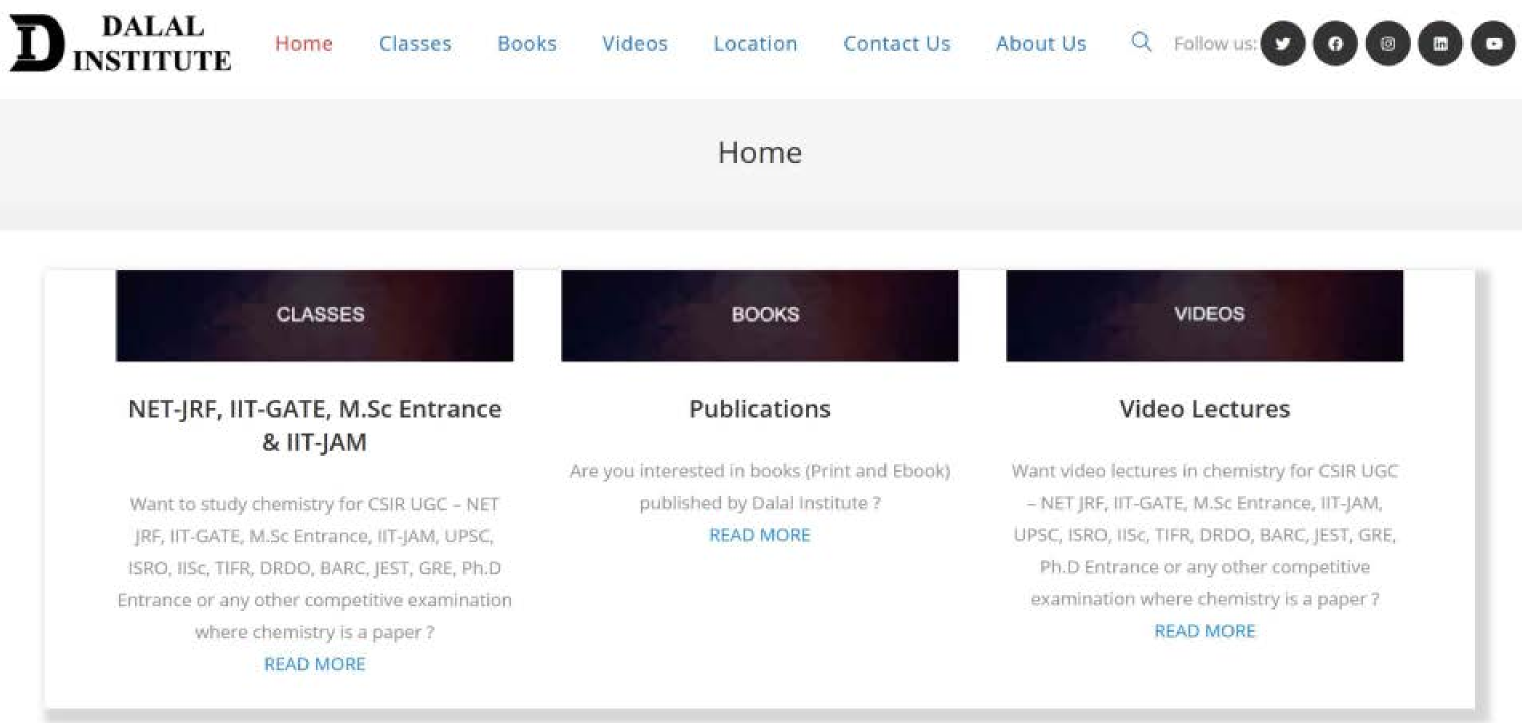
1. The valence-shell-electron-pair-repulsion theory has no sound explanation for molecular geometries having very polar bonds; like Li_2O is linear whereas its counterpart H_2O is bent is nature.

2. The VSEPR theory offers no solution for molecular geometries with a high magnitude of π-cloud delocalization.

3. It does not consider the "inert pair effect", and thus fails to rationalize the bonding characteristic in molecular geometries possessing the same. For example, $[SeCl_6]^{2-}$, $[TeCl_6]^{2-}$and $[BrF_6]^{-}$ are expected to adopt a pentagonal bipyramidal structure due to seven electron pair domains but are found to be octahedral systems.

4. It fails to predict the structure of transition metal complexes. For example, many bivalent complexes of nickel are square-planar and not tetrahedral.

5. The VSEPR theory does not consider the wave function treatment of chemical bonds and therefore fails to explain many bond length and bond angle variations. For example, the bond C−Cl bond length decreases as we move from CH_3Cl to CCl_4, which is unexpected because of the larger size of Cl in comparison to H.



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