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.

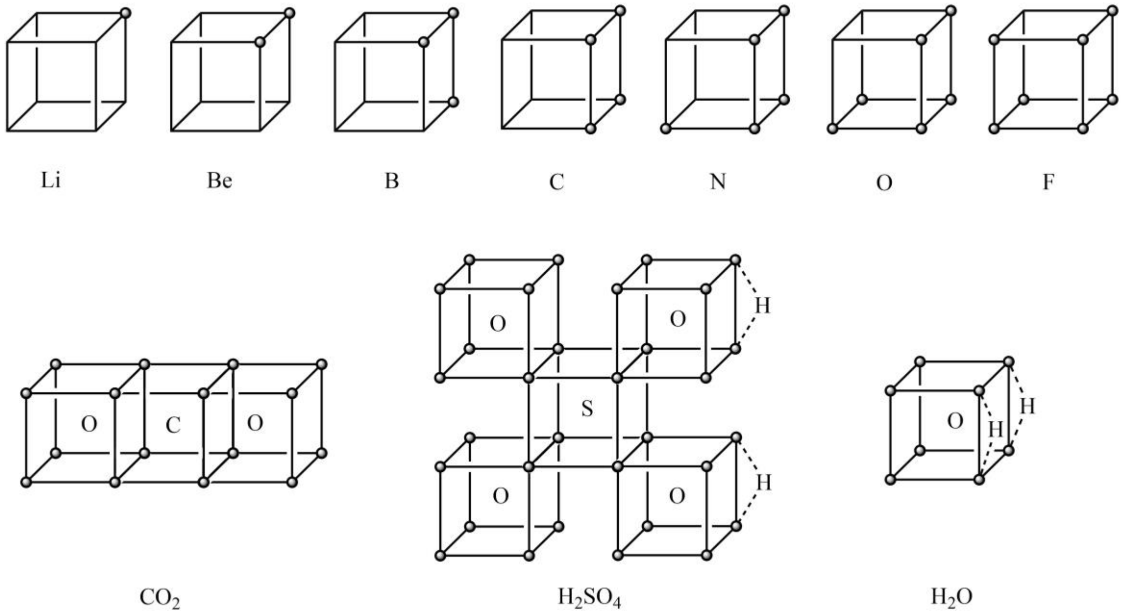


Figure 1. The Lewis concept of electron-pair sharing between cubical atoms.

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.

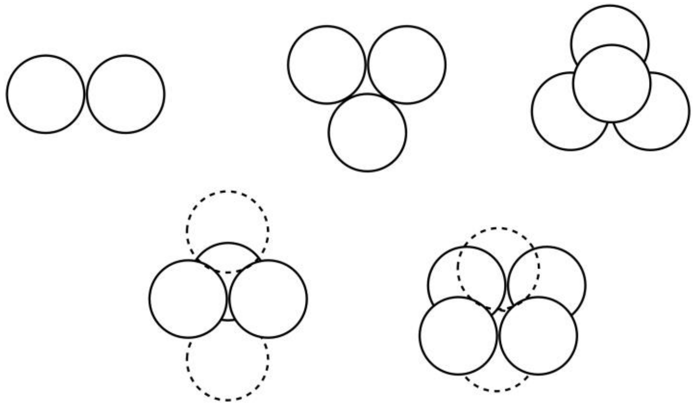


Figure 3. The spherical electron-pair domain model of molecular geometries.

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.

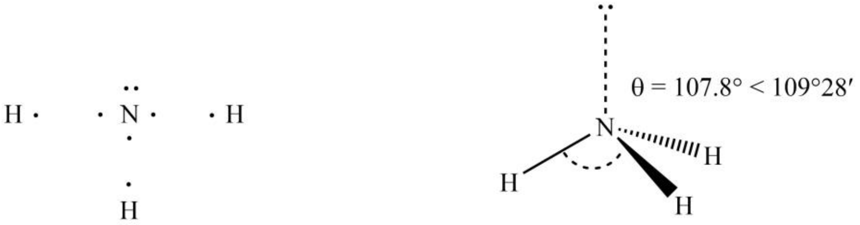


Figure 8. Structure of NH_3 molecule from the VSEPR model.

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.

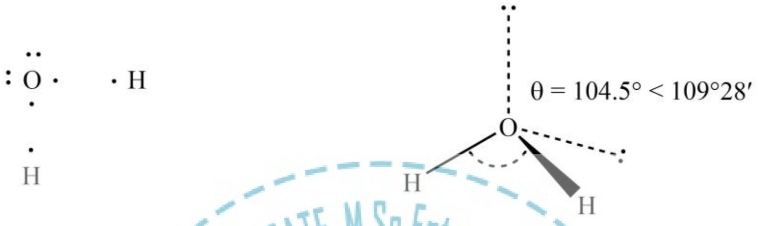


Figure 9. Structure of H_2O molecule from the VSEPR model.

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°.

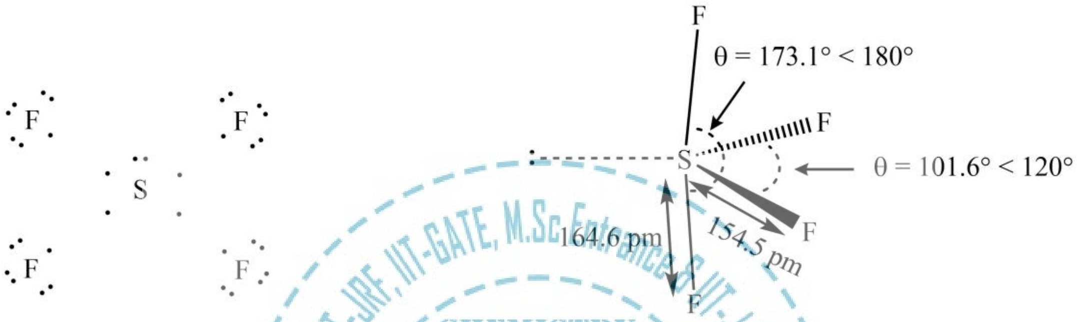


Figure 11. Structure of SF_4 molecule from the VSEPR model.

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°.

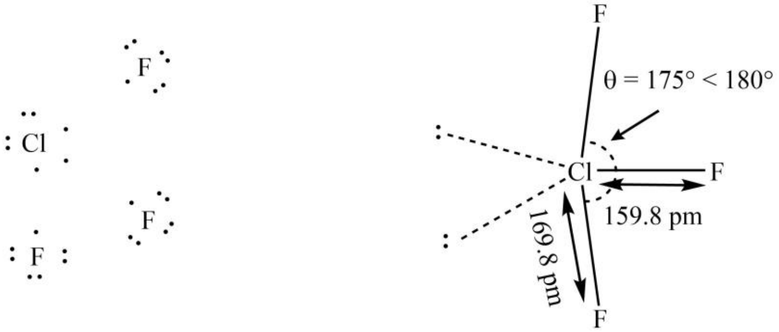


Figure 12. Structure of ClF_3 molecule from the VSEPR model.

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°.

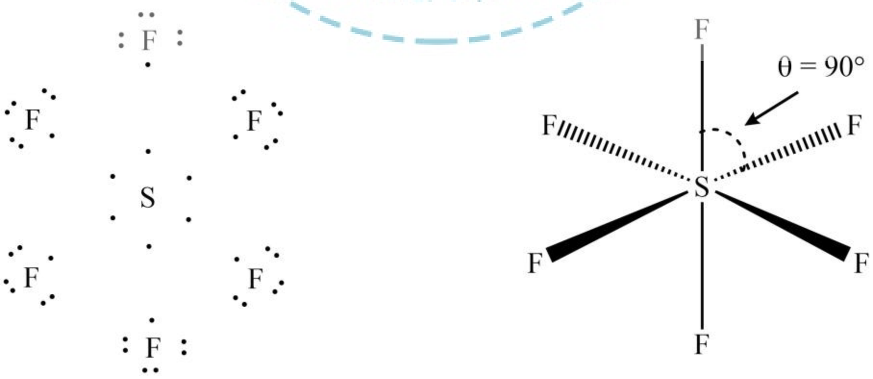


Figure 14. Structure of SF_6 molecule from the VSEPR model.

ii) BrF₅: 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.

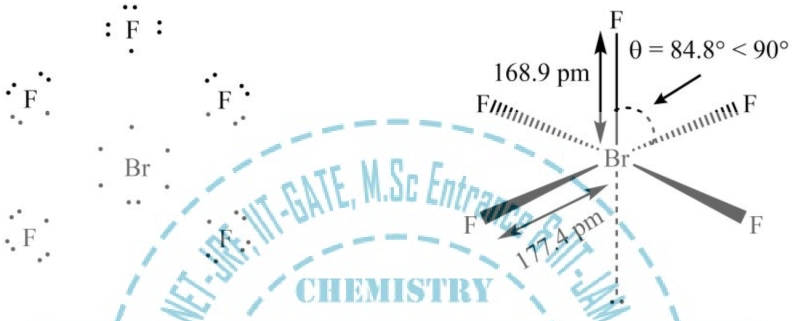


Figure 15. Structure of BrF_5 molecule from the VSEPR model.

iii) XeF₄: 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.

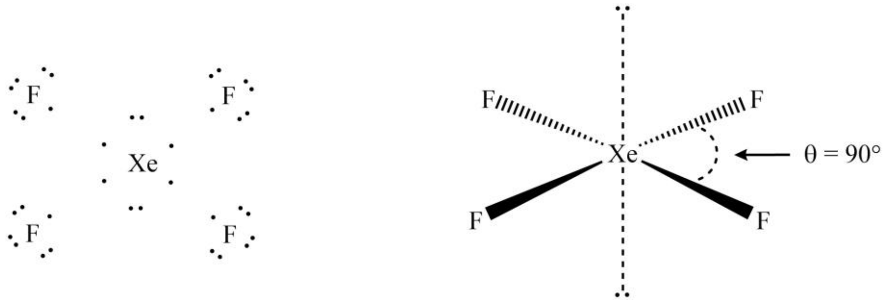


Figure 16. Structure of XeF_4 molecule from the VSEPR model.

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.

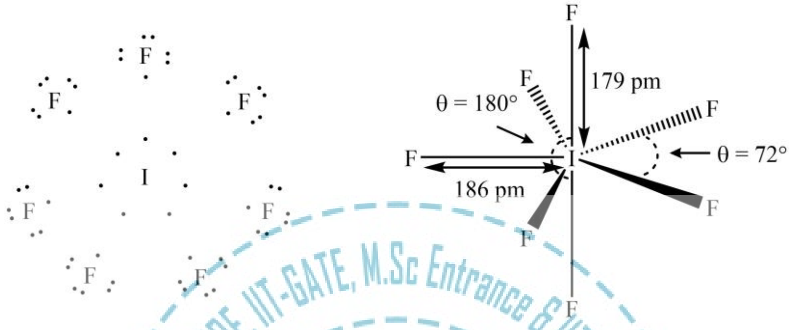


Figure 17. Structure of IF_7 molecule from the VSEPR model.

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°.

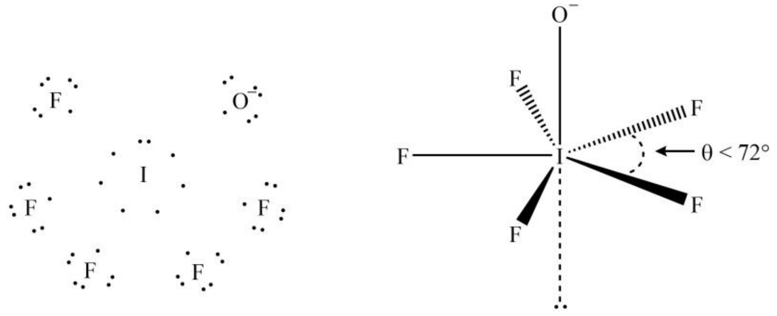


Figure 18. Structure of $XeOF_5^-$ molecule from VSEPR model.

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.

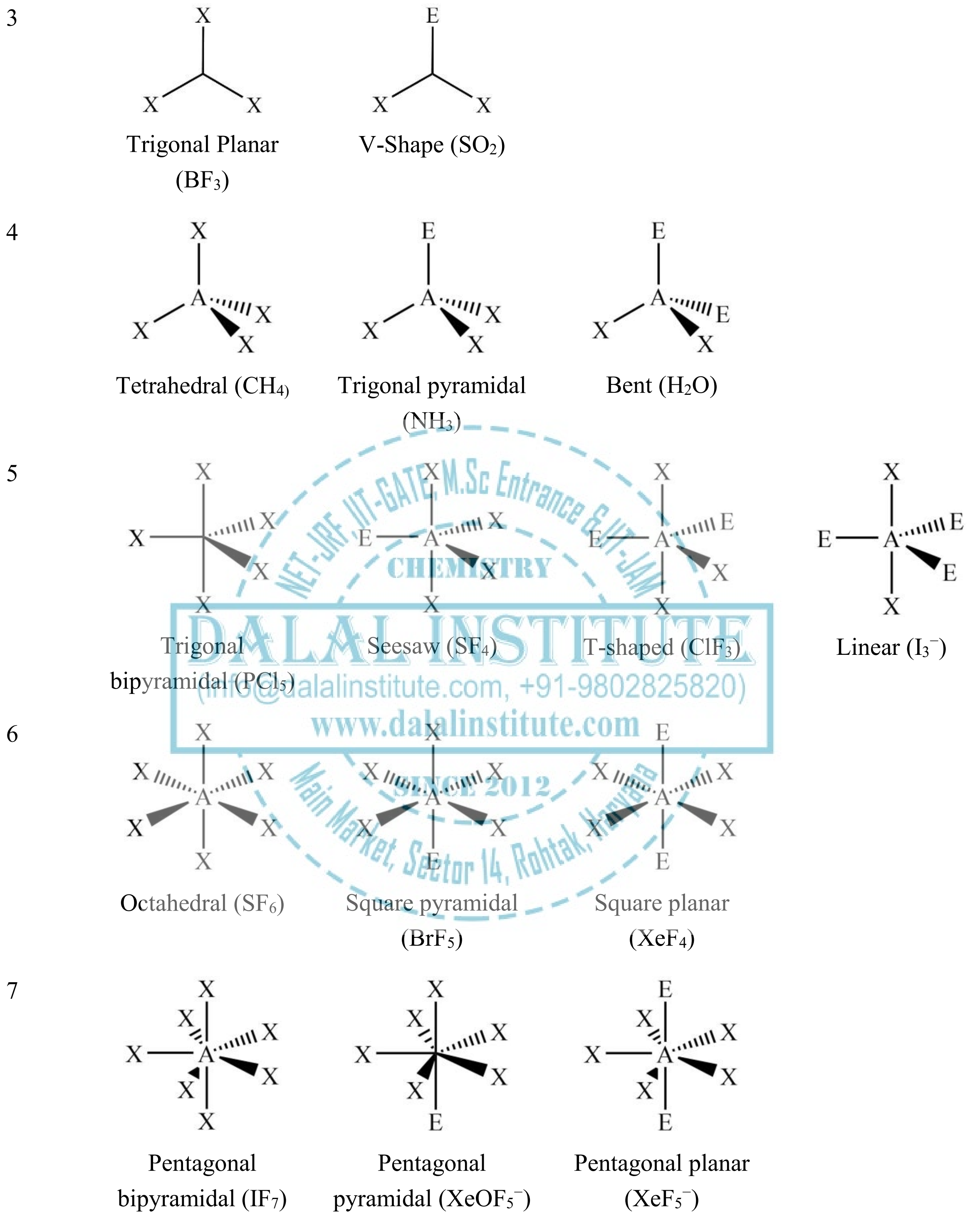
Figure 19. Structure of XeF_5^- molecule from the VSEPR model.

- ***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…



Trigonal Planar (BF_3)
V-Shape (SO_2)
Tetrahedral (CH_4)
Trigonal pyramidal (NH_3)
Bent (H_2O)
Trigonal bipyramidal (PCl_5)
Seesaw (SF_4)
T-shaped (ClF_3)
Linear (I_3^-)
Octahedral (SF_6)
Square pyramidal (BrF_5)
Square planar (XeF_4)
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.

❖ *dπ–pπ* Bonds

This is a special type of bonding found in the molecular species having a central atom with *d* or *p* valence shell and surrounding groups with empty, partially or completely filled *p* or *d* orbitals. In addition to direct overlap resulting in the σ-bonding, *dπ–pπ* bonds are formed by the sidewise overlap. The exact nature of the orbitals from central atom participating in the formation of *dπ–pπ* bond can be obtained by resolving the irreducible components of the reducible representation based upon the vectors-set perpendicular to the σ-bonds for a particular geometry.

➢ *Molecules with Central Atom Having d-Valence Shell for Sidewise Overlap*

Some of the most well-documented cases in main-group chemistry are AB_4 type molecules like SiO_4^{4-}, SO_4^{2-}, PO_4^{3-}, ClO_4^{-}, SiF_4; which are found to have A–O bond lengths too short for the single bond confirming a *dπ–pπ* overlap responsible for this anomaly.

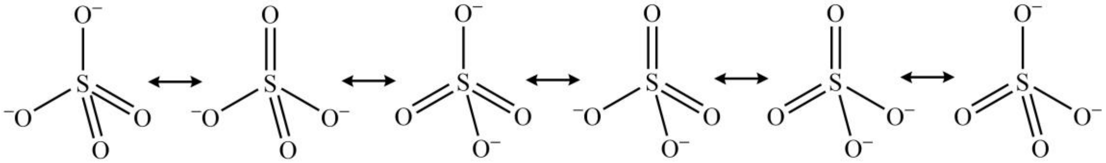


Figure 21. The *dπ–pπ* bonding in SO_4^{2-} ion.

The character table for T_d point group is given below.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2+y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

The reducible representation based upon the *s*, *p* and *d* orbitals of the central atom in tetrahedral geometry is:

Table 1. Reducible representation based on *s*, *p* and *d* orbitals.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_π	9	0	1	−1	3

Resolving the reducible into irreducible components, the symmetry designations of different orbitals of the central atom taking part in tetrahedral overlap are given below:

s — a_1

p_x, p_y, p_z — t_2

d_{xy}, d_{xz}, d_{yz} — t_2

$d_{z^2}, d_{x^2-y^2}$ — e

The symmetry adapted linear combinations of atomic orbitals (SALCs) of surrounding groups for sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of σ overlap.

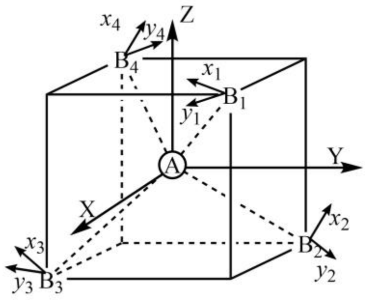


Figure 22. The π-basis set for ligand orbitals in tetrahedral molecules.

The symmetry adapted linear combinations of these fall into two triply and one doubly degenerate irreducible representations labeled as e, t_1 and t_2. The symmetry designations of different ligand orbitals taking part in sidewise overlap in tetrahedral molecules can be given as:

Table 2. Reducible representation based on perpendicular vectors in a tetrahedral geometry.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Irreducible components
Γ_π	8	–1	0	0	0	$e + t_1 + t_2$

Two of these aforementioned sets are of e and t_2 symmetry. The $d_{x^2-y^2}$ and d_{z^2} orbitals set on the metal also have e-symmetry, and therefore the π-overlap between a central atom and four ligands is possible as far as the generation of molecular orbitals with e-symmetry is concerned. Moreover, p_x, p_y, p_z and d_{xy}, d_{yz}, d_{zx} set are of t_2 symmetry, and therefore, can take part in sidewise overlap. However, the p-subshell largely engaged in σ-bonding and therefore has little or no contribution. While the transition metals show a tendency to use their d_{xy}, d_{yz} and d_{zx} orbitals for $d\pi$–$p\pi$ interactions in octahedral complexes, the main group elements primarily use $d_{x^2-y^2}$ and d_{z^2} as they generally form tetrahedral complexes. The primary reason for this selective behavior is that these two orbitals yield $\sqrt{3}$ times higher $d\pi$–$p\pi$ overlap than that of d_{xy}, d_{yz} and d_{zx} The general scheme for $d\pi$–$p\pi$ overlap for main group compounds with tetrahedral geometry is shown in 'Figure 23'.

$d_{x^2-y^2}$ overlap with p-Orbitals

d_{z^2} overlap with p-Orbitals

Figure 23. The overlap mechanism for the $d\pi$–$p\pi$ interactions when the central atom has valence d-orbitals.

Apart from the tetrahedral molecules, some less symmetrical main group compounds are also found to have $d\pi$–$p\pi$ interactions. Although the exact nature of these interactions is quite difficult to analyze as the lowering of symmetry makes the d-subshell of central atom susceptible to the surrounding groups to a different extent yet the inverse variation of bond length with bond order may be used to approximate the extent of $d\pi$–$p\pi$ overlap. Quantum mechanical calculations have also shown that significant $d\pi$–$p\pi$ interaction is present in molecules like SO_2F_2, PF_3O, ClO_3F, ClO_2^-, ClO_3^-.

➢ *Molecules with Central Atom Having p-Valence Shell for Sidewise Overlap*

Sometimes, the existence of *dπ–pπ* bonding can be viewed in terms of the molecular geometry. For example, Si_3N and Ge_3N skeleton is planar in $(H_3Si)_3N$, $(H_3Ge)_3N$ and Si/Ge–N bond length is somewhat shorter that what is expected for a single bond. This can be explained by assuming that the electron density from N($2p_z$) is overlapping with the 3*d* orbitals of surrounding Si and Ge.

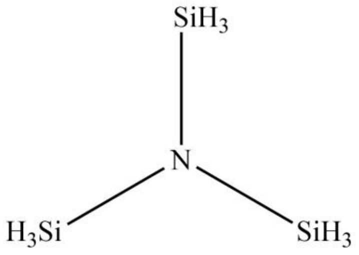


Figure 24. The *dπ–pπ* bonding in $N(SiH_3)_3$ molecule.

The character table for the D_{3h} point group is given below.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

The reducible representation based on the *s*, *p* and *d* orbitals of the central atom in trigonal planar geometry is:

Table 3. Reducible representation based on *s*, *p* and *d* orbitals.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_π	9	0	1	3	0	3

Resolving the reducible into irreducible components, the symmetry designations of different orbitals of the central atom taking part in trigonal planar overlap are:

s – a_1'

p_z – a_2''

p_x, p_y	–	e'
d_{z^2}	–	a_1'
d_{xy}, $d_{x^2-y^2}$	–	e'
d_{xz}, d_{yz}	–	e''

The symmetry adapted linear combinations of atomic orbitals (SALCs) of surrounding groups for sidewise overlap can be obtained just by resolving the reducible representation based on the displacement vectors perpendicular to the axis of σ-overlap.

Figure 25. The π-basis set for ligand orbitals in trigonal planar molecules.

The symmetry adapted linear combinations of these fall into two singly and two doubly degenerate irreducible representations labeled as a_2', e', a_2'' and e''. The symmetry designations of different ligand orbitals taking part in sidewise overlap in trigonal planar molecules are:

Table 4. Reducible representation based on perpendicular vectors in trigonal planar geometry.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Irreducible components
Γ_π	6	0	−2	0	0	0	$a_2' + e' + a_2'' + e''$

Three of these aforementioned sets are of a_2'', e' and e'' symmetry. The $d_{x^2-y^2}$ and d_{xy} orbitals set on the central atom also have e'-symmetry, while the d_{xz} and d_{yz} has e''-symmetry; therefore, the π-overlap between a central atom and the ligands is possible as far as the generation of molecular orbitals with e'- and e''-symmetry is concerned. Moreover, p_z orbital of the central atom is of a_2''-symmetry, and therefore, can also take part in sidewise overlap. Now though the symmetry allows the central atom to use $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz} *and* p_z; the overlap extent and energy criteria permits largely the p_z to do sidewise overlap.

However, the presence of partially filled p_z orbital of the central atom is prone to overlap with the empty d-subshell of surrounding groups yet it does not assure the sufficient $d\pi{-}p\pi$ bonding leading to a planar structure in all cases. The Si–A–Si bond angles in $P(SiH_3)_3$ and $As(SiH_3)_3$ are 96.5° and 93.8° respectively and both of these compounds exist as pyramidal geometry like $P(GeH_3)_3$ does. This is due to the fact that $3p_z$ orbitals of P and As do not overlap with d-orbitals as efficiently as in the case of $2p_z$ orbital of N atom. Furthermore, $S(SiH_3)_2$ is bent with a Si–A–Si bond angle of 98° resembling its tri-coordinated pyramidal analogs in terms of $d\pi{-}p\pi$ overlap. However, $(H_3Si)_2O$ is also bent in geometry with a bond angle of 144° but shows a small extant of $d\pi{-}p\pi$ overlap which is also confirmed by the shortening of the Si–O bond length. The extant of $d\pi{-}p\pi$ overlap is much larger in flat and linear geometries than that of bent ones.

p_z overlap with d-Orbitals in linear molecules p_z overlap with d-Orbitals in bent molecules

Figure 26. The overlap mechanism for $d\pi{-}p\pi$ interactions when the central atom has valence p-orbitals.

❖ Bent’s Rule and Energetic of Hybridization

The success of the valence-shell-electron-pair-repulsion (VSEPR) theory in rationalizing various molecular geometries is quite remarkable as far as simplicity is concerned. However, the failure of VSEPR theory in the case of transition metal complexes or some other serious limitations like inert-pair effect in some main group compounds are also undeniable facts that need to be addressed in a more sophisticated way. The limited applicability of VSEPR theory is actually rooted in the fact that it does not consider any wave-mechanical picture of atomic structure; in other words, as the VSEPR theory does not talk in terms of atomic orbitals, it is quite bound in terms of flexibility required to model the chemical bonds. However, as we know that the Lewis ideas of electron sharing inspired not the Sidgwick and Powell only, but some other physicists like Walter Heitler and Fritz London also. Whilst on the one side the Sidgwick and Powell were working on the VSEPR theory, which was completely immune to the concept of orbitals; Heitler and London were treating the chemical bond in a hundred percent wave-mechanical framework. In 1926, Walter Heitler found out how to use Schrödinger's wave equation to show that the single electron wave-functions of two hydrogen atoms interact with each other to form a covalent bond. Soon after that, he and his associate Fritz London worked on some more theoretical details of the theory and labeled it as valence bond theory (VBT). Thought the VBT was quite effective in the calculation of bonding properties of the H_2 molecule, it was still unable to rationalize complex molecules. Later, an American chemist, Linus Pauling modified the Heitler-London theory by incorporating two key concepts, resonance (1928) and orbital hybridization (1930).

The initial development of the concept of orbital hybridization was to explain the structure of simple molecular geometries like CH_4, BF_3 or $BeCl_2$. The methane molecule had actually been the test case for all bonding theories at that time. Before 1874, the CH_4 molecule was thought to be of square planar geometry with a carbon atom in the center.

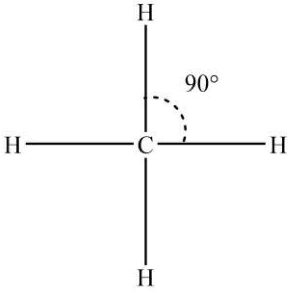
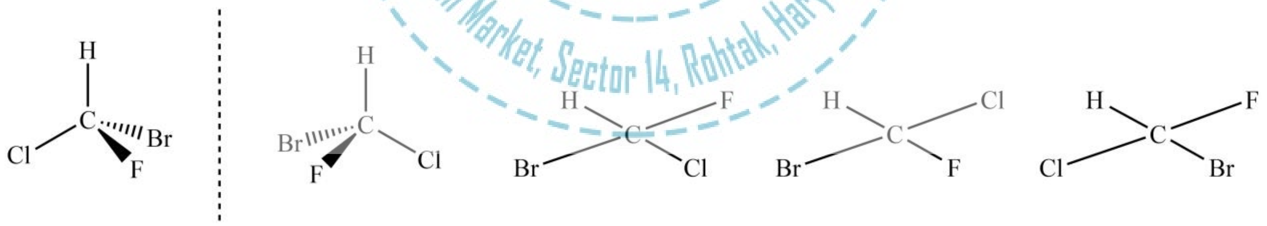


Figure 27. The visualization of the structure of methane before 1874.

Now today it might seem very funny but at that time this structure was quite reasonable because it could explain the observed magnetic moment which is zero for methane. The square planar structure has four C−H bonds of equal length and all adjacent bonds at 90°; the cancellation of two opposite dipole moments from two trans bonds would also give a zero dipole moment. However, if we attach four different groups to the carbon, the resulting molecule is actually optically active i.e. it would rotate the plane of polarized light in left or right; and therefore, it must exist as two isomers (enantiomeric pair). It is possible only if the arrangement of groups around central carbon is tetrahedral rather square planar; because the later one would exist as three isomers, all optically inactive.



Two optical isomers of asymmetric carbon

Three geometrical isomers of asymmetric C in square-planar structure
All are optically inactive

Figure 28. Isomers for asymmetric carbon in tetrahedral and square-planar geometry.

A Dutch physical chemist, Jacobus Henricus van't Hoff, was the first to formulate the three-dimensional carbon. In 1874, he showed that a tetrahedral arrangement of four different groups around a carbon atom is the only way to give rise to two optical isomers. Using the same theory, he also explained the three isomers of tartaric acid, one enantiomeric pair, and one meso form. The tetrahedral coordination around carbon was also proved in 1913 when X-ray diffraction studies of diamond showed a bond and angle of 109°28′.

Now although the VSEPR theory, a successor of Lewis idea (1913), explained the tetrahedral coordination in CH_4 molecule by minimum repulsion of four bond pairs; it did not help us to understand the nature of the orbitals involved in the bonding. Linus Pauling in 1931 Pauling pointed out that, in the frame of simple "valence bond theory", a carbon atom can form four bonds by using one s and three p orbitals by promoting its one $2s$ electron to empty $2p_z$ orbital and thus creating four half-filled orbitals. However, it might would mean that a C atom creates three bonds at right angles (from use of p subshell) and a fourth bond (weaker one) using the s wave-function in some arbitrary direction (this fourth C−H bond would be maximum away from the other three bonds if it is put at 135°) as shown below.

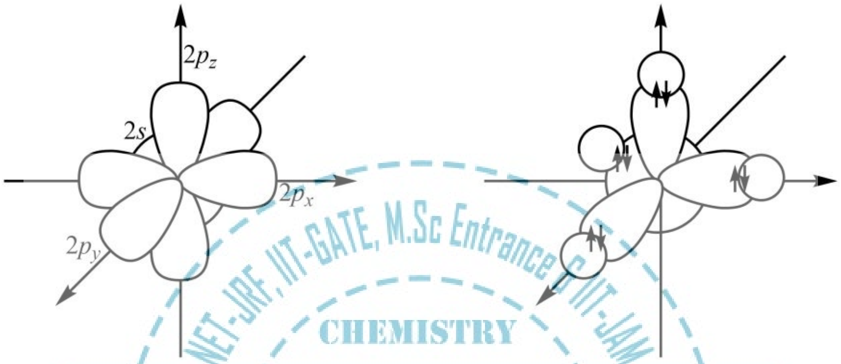


Figure 29. The possible bonding mode in CH_4 molecule from valence bond theory without considering orbital hybridization (one lobe of p-orbitals in the right image are omitted for clarity.

The experimental results like four equal bonds separated by a bond angle of 109.5° or the zero dipole moment cannot be explained by the structure given above. Hence, the aforementioned geometry was a wrong proposal for sure because, besides the bond angle anomaly, it would give rise to small dipole due to the difference in electronegativity between C (2.5) and H (2.2). Moreover, according to simple valence bond theory, as the bonding of hydrogen is happening with one s and three p orbitals of carbon, we should expect one s–s bond to be shorter than three s–p bonds.

To explain this situation, Pauling thought that what would happen if instead of using pure one s and three p wave functions, we use a linear combination of these four. Now though there can be an infinite number of linear combinations of these four single-electron-wave-functions, one should not forget that every single electron-electron-wave-functions must be normalized and orthogonal to others. Linus Pauling found that out of infinite linear combinations, there are only four expressions that are normalized as well as orthogonal to each other. When he plotted these four linearly combined functions in space round carbon nucleus, they were of the same shape, same energy and were oriented at 109°28′. Linus Pauling created the tetrahedral frame of half-filled orbitals, ready for overlap with approaching hydrogens. This was a revolutionary step, he called these functions as hybrid orbitals.

Hybridization is the intermixing of atomic orbitals of different energies and shapes so as to produce new orbitals with the same energy and equivalent shape.

➢ *Characteristic Features of Hybridization*

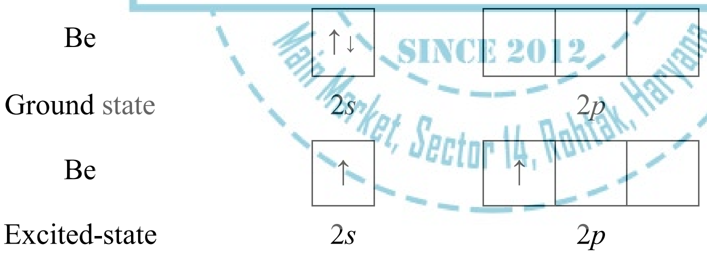
The orbital hybridization in the main group or the transition metal compounds has the following characteristic features:

1. The number of hybrid orbitals is the same as the number of atomic orbitals intermixed.
2. Hybrid orbitals are equivalent in shape and have the same energies.
3. Hybrid orbitals form stronger bonds than their pure atomic counterparts.
4. Hybrid orbitals are directed in specific directions and therefore control the geometry of the molecule.
5. Only valence shell orbitals take part in hybridization.
6. There should be only a small energy difference in the orbitals undergoing hybridization.
7. Electron promotion is not a necessary condition to be followed.
8. In addition to the half-filled orbitals, fully filled and empty orbitals can also undergo hybridization.

➢ *Types of Hybridisation*

Hybrid orbitals are assumed to be the mixtures of atomic orbitals, superimposed on each other in various proportions. For example, in the CH_4 molecule, the hybrid orbital of C, which forms a carbon-hydrogen bond consists of 25% *s*-character and 75% *p*-character and is thus labeled as sp^3 hybridized. The main types of hybridization are as follows.

1. *sp*-hybridization: One *s* and one *p*-orbitals intermix to form two hybrid orbitals oriented at 180° from each other and form the basis for the linear geometry of $BeCl_2$, BeH_2, BeF_2 like molecules.



Which gives

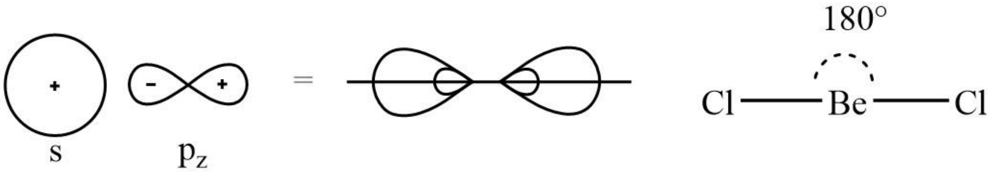


Figure 30. Pictorial representation of *sp*-hybrid orbitals e.g. $BeCl_2$ molecule.

2. *sp*^{2}-hybridization: One *s* and two *p*-orbitals intermix to form three hybrid orbitals oriented at 120° from each other and form the basis for the trigonal geometry of BF_3 type molecules.

B	↑↓	↑		
Ground state	2*s*	2*p*		
B	↑	↑	↑	
Excited-state	2*s*	2*p*		

Which gives

Figure 31. Pictorial representation of sp^2 hybrid orbitals e.g. BF_3 molecule.

3. *sp*^{3}-hybridization: One *s* and three *p*-orbitals intermix to form four hybrid orbitals oriented at 109°28' from each other and form the basis for the tetrahedral geometry of BF_3 type molecules.

C	↑↓	↑	↑	
Ground state	2*s*	2*p*		
C	↑	↑	↑	↑
Excited-state	2*s*	2*p*		

Which gives

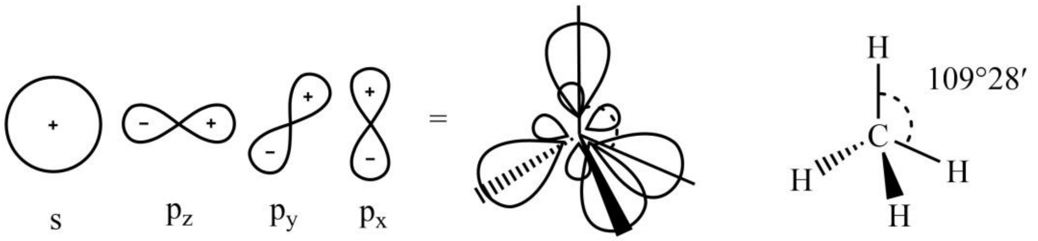


Figure 32. Pictorial representation of sp^3 hybrid orbitals e.g. CH_4 molecule.

4. *sp*^{3}*d*-hybridization: One *s,* three *p* and one *d*-orbitals intermix to form five hybrid orbitals where three hybrid orbitals are oriented at 120° and at 90° from two axial bonds to form the basis for the trigonal bipyramidal geometry of PF_5 type molecules.

	3*s*	3*p*			3*d*				
P Ground state	↑↓	↑	↑	↑					
P Excited-state	↑	↑	↑	↑	↑				

Which gives

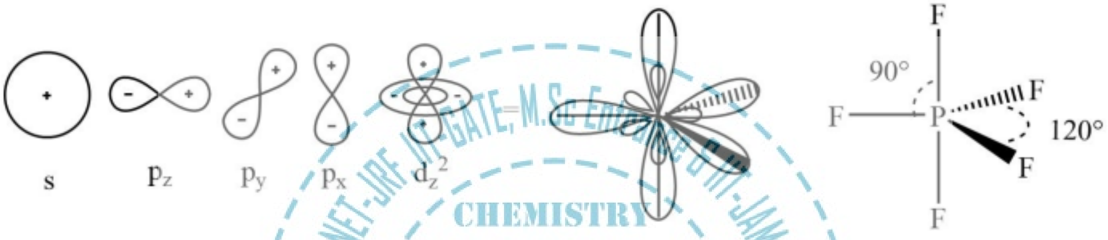


Figure 33. Pictorial representation of *sp*^{3}*d* hybrid orbitals e.g. PF_5 molecule.

5. *sp*^{3}*d*^{2}-hybridization: One *s,* three *p* and two *d*-orbitals intermix to form six hybrid orbitals where each orbital is at 90° from 4 and at 180° from one to form the basis for the octahedral geometry of SF_6.

	3*s*	3*p*			3*d*				
S Ground state	↑↓	↑↓	↑	↑					
S Excited-state	↑	↑	↑	↑	↑	↑			

Which gives

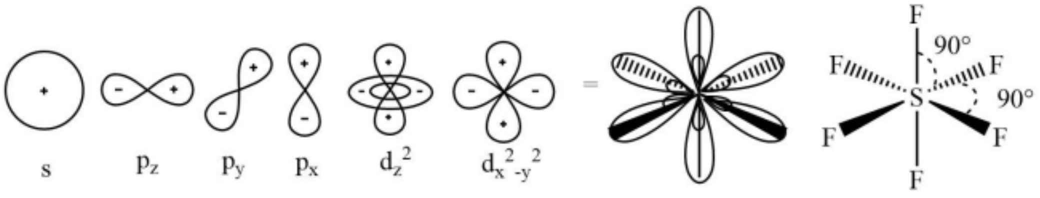


Figure 34. Pictorial representation of *sp*^{3}*d*^{2} hybrid orbitals e.g. SF_6 molecule.

6. *sp^3d^3*-hybridization: One *s,* three *p* and three *d*-orbitals intermix to form seven hybrid orbitals where five equatorial hybrid orbitals are oriented at 72° from each other and at 90° from two axial hybrid orbitals to form the basis for the pentagonal bipyramidal geometry of IF_7 type molecules.

	5*s*	5*p*			5*d*				
I Ground state	↑↓	↑↓	↑↓	↑					
I Excited-state	↑	↑	↑	↑	↑	↑	↑		

Which gives

Figure 35. Pictorial representation of sp^3d^3 hybrid orbitals e.g. IF_7 molecule.

➢ ***Some Other Less Common Hybridization Schemes***

Besides the simple and hyper-valent molecules like IF_7, there are also some less common hybridization schemes as given below.

1. *dsp^2*-hybridization: One *d,* two *p* and one *s*-orbitals intermix to form four hybrid orbitals which are oriented at 90° to each other and form the basis for the square planar geometry of tetra-coordinated molecules.

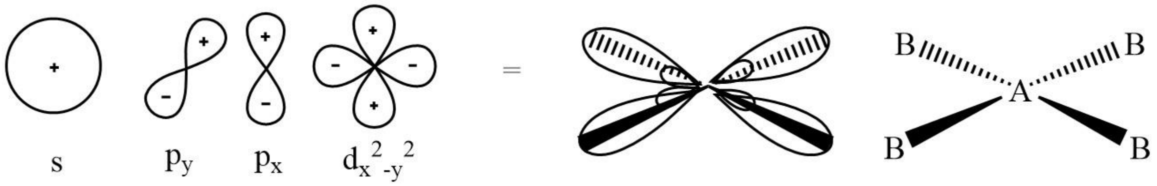


Figure 36. The pictorial representation of dsp^2 orbitals hybridization scheme forming the basis for square planar geometry.

2. *sp^3d*-hybridization: One *s*, three *p* and one *d*-orbitals intermix to form five hybrid orbitals which are oriented at 90° to each other and form the basis for square pyramidal geometry of penta-coordinated molecules.

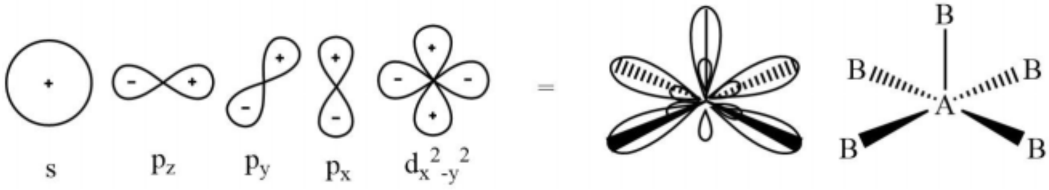


Figure 37. The pictorial representation of sp^3d hybrid orbitals forming the basis for square pyramidal geometry.

3. *sp^3d^2*-hybridization: One *s*, three *p* and two *d*-orbitals intermix to form six hybrid orbitals which are oriented towards the corners of a trigonal prismatic geometry in hexa-coordinated molecules.

Figure 38. The pictorial representation of sp^3d^2 orbitals hybridization scheme forming the basis for trigonal prismatic geometry.

4. *sp^3d^3*-hybridization: One *s*, three *p* and three *d*-orbitals intermix to form seven hybrid orbitals which are oriented towards the corners of a mono-capped trigonal-prismatic geometry in hepta-coordinated molecules.

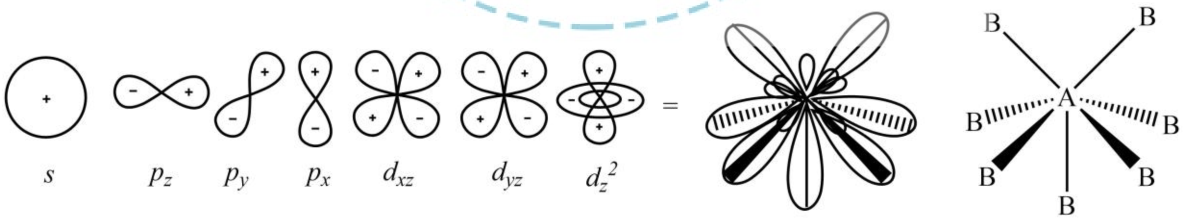


Figure 39. The pictorial representation of sp^3d^3 orbital hybridization scheme for the formation of mono-capped trigonal-prismatic geometry.

However, main group Compounds rarely show these hybridizations like dsp^2-square planar or sp^3d-square pyramidal geometry due to stability issues which makes them more predictable structure than transition metal complexes.

➢ *Bent's Rule*

The introduction of the concept of hybridization by Linus Pauling was a huge success in the rationalization of the chemical bond, especially in the organic compounds. However, in the 1940s it became apparent that a lot of molecular geometries, including even the simple ones, show slight deviations from the predictions of orbital hybridization concept of valence bond theory. For instance, consider the case of H_2O molecule; where the H−O−H bond angle is 104.5°, which far less than the normal tetrahedral angle of 109.5°. Besides the isovalent species like H_2O or NH_3, the conventional hybridization theory was also unable to explain why the Cl−C−Cl and Me−C−Me bond angles in sp^3-hybridized CCl_2Me_2 are 108.5° and 113°, respectively.

Figure 40. The comparison of the bond angle of methane and water though both have of sp^3 hybridization.

In 1947, a British chemist, A. D. Walsh tried to explain such inconsistencies by describing a correlation between the electronegativity of ligand attached to carbon and the hybridization scheme involved. it was suggested that hybridization may yield orbitals with different magnitude of *s* and *p* character. In 1961, Henry A. Bent published a more sophisticated treatment of the problem that correlated the molecular structure, hybridization scheme of the central atom, and the electronegativity strengths of the attached groups. The work is generally labeled as Bent's rule and is based upon the perturbation theory which suggests that isovalent hybridization should transfer more *s*-character towards more electropositive substituents to maximize the bonding energy. This can be explained in terms of electron density available for bonding. The more electropositive groups would be able to withdraw more electron density from *p*-orbital than *s*-orbital.

In the compounds containing mixed substituents and hybridized orbitals, a trend has been observed according to which atomic s-character tends to concentrate in the orbitals that are directed towards electropositive groups and atomic p-character tends to concentrate in the orbitals that are directed towards electronegative groups.

Valence orbitals for main group elements consist of *s* and *p* orbitals with s-orbital having lower energy, which means that the bonding orbital is lower in energy and shape more like *s*-orbital rather than *p*-orbital. However, in the case where the central atom or ion has a lone pair, it will be having large s-character because *s*-orbital are closer to the nucleus, allowing greater stabilization for the lone pair. The deviation of molecular geometries from their perfectly tetrahedral, octahedral or other symmetrical counterparts can be explained and predicted by examining the substituent groups and lone pair of electrons.

➢ *Applications of Bent's Rule*

The Bent's rule can be used to rationalize many aspects of structure, bonding, spectra and the physical and chemical properties of a wide range of compounds. Some of the important applications of Bent's rule which are quite popular in the field of chemical science are given below.

1. Bond angles: *i)* In $A(Cl)_2(Me)_2$ molecules, where A is C, Si, Ge, Sn or Pb; the Cl–A–Cl bond angle is smaller than that of Me–A–Me bond angle. With high electronegativity halogen substituent Cl, more *p*-character is concentrated in A–Cl bond than A–Me bonds. Subsequently, bonds with greater *p*-character have smaller bond angles than those with *s*-character because *s*-orbitals are closer to the nucleus and hence exert larger inter-electronic repulsion producing higher bond angles.

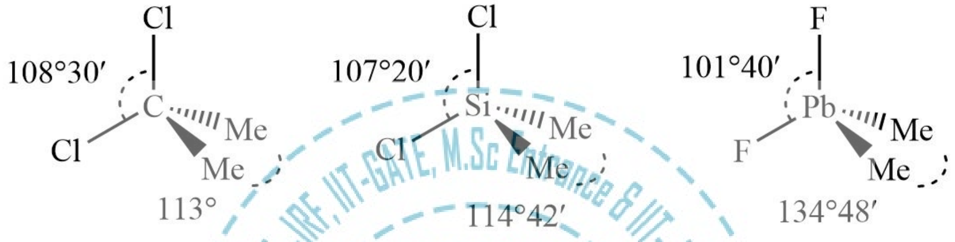


Figure 41. Increasing p-character in A–X bond, decreasing halogen–A–halogen bond angle.

ii) In SF_4, the bond angle of axial F–S–F bond is 173° (ideally 180°) and the equatorial F–S–F bond angle is 101° (ideally 120°). The axial, as well as equatorial bond angles, are decreased slightly due to increased s-character of the lone pair and more *p*-character in bond pairs. Furthermore, thionyl tetrafluoride shows the same trend but the slightly higher bond angle between equatorial fluorines than that of sulfur tetrafluoride. This anomaly can be explained in terms of comparatively larger *s*-character in equatorial fluorines as the lone pair has been replaced by a more electronegative oxygen atom.

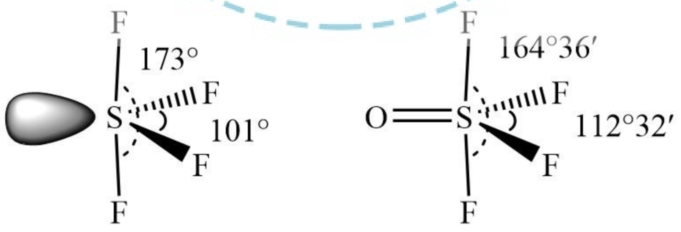


Figure 42. SF_4 molecule and SOF_4 molecules.

iii) As one moves left to right in the figure given, the substituents become more electronegative and the bond angle between them decreases. According to Bent's rule, as the electronegativity strength of substituents increase, orbitals rich in *p*-nature will be oriented towards those substituents. From the abovementioned argument, it will reduce the bond angle; which is in good agreement with the experimental data. If we compare this justification with VSEPR theory, the VSEPR model cannot explain why the angle in dimethyl ether is larger than the normal tetrahedral angle of 109.5°. In the prediction of the bond angle in H_2O molecule, Bent's rule proposes that the hybrid orbitals which are rich in *s*-character should be oriented towards more electropositive lone pairs, whilst the orbitals of more *p*-nature should point towards the hydrogens. This enhanced *p*-character in orbitals decreases the corresponding bond angle to less than the normal tetrahedral of 109.5°. The same reason can be applied to NH_3 molecule, the other canonical cases of this kind.

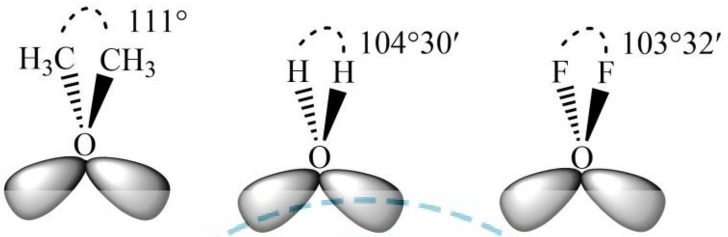


Figure 43. The decreasing trend of the B–A–B bond angle between substituents with increasing electronegativity.

2. Bond lengths: *i)* The bond lengths can also be changed by changing the hybridization or by adding electronegative groups to the central atoms. If a molecule geometry has X–A–Y component, replacement of the group X by a more electronegative substituent would manipulate the hybridization of the central atom and reduces the neighboring A–Y bond length. Now owing to the higher electronegativity of fluorine than hydrogen, the carbon of fluoromethane will direct its hybrid orbitals with the higher *s*-character towards the three H groups rather than the fluorine. In the case of difluoromethane, only two hydrogens are present, so the *s*-character in total is pointed towards them is less and more is pointed towards the two fluorine groups. This reduces the carbon–fluorine bond lengths relative to the fluoromethane molecule.

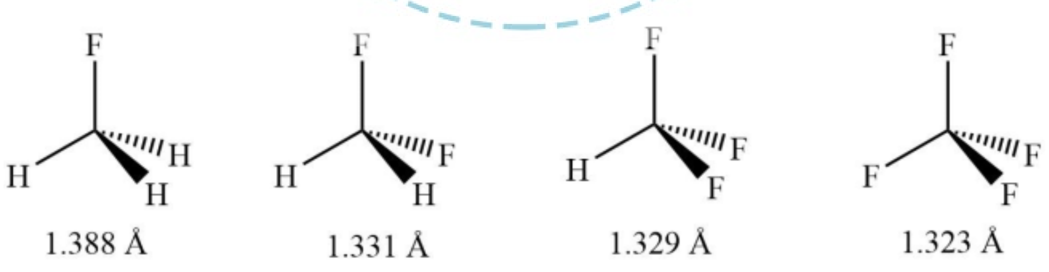


Figure 44. The decreasing trend of average carbon–fluorine bond lengths as we move from CH_3F to CF_4 molecular geometries.

This pattern continues to the CF_4 whose carbon–fluorine bonds have the largest *s*-character (25%) and the shortest bonds in the whole series.

ii) The same pattern also continues for the chlorinated equivalents of CH_4, though the effect is less efficient because the chlorine is of lower electronegativity strength than the fluorine.

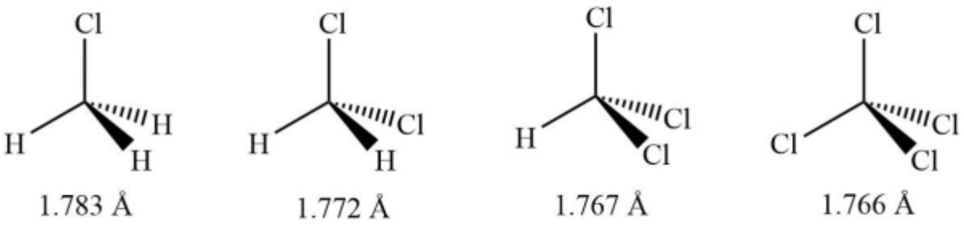


Figure 45. Average carbon–chlorine bond length.

The abovementioned cases seem to prove that the atomic radius of chlorine is less significant than its electronegativity strength because the prediction based on steric factors alone would yield the opposite pattern due to greater setting-apart tendency of larger chlorine groups. As the steric clarification is in contradiction with the experimental results, Bent's rule plays a significant role in structure elucidation.

iii) A similar trend is observed for single, double and triple carbon–carbon bonds, as the change of hybridization scheme from *sp*^{3} to *sp*-type would lead to more *s*-character and therefore shorter bond.

Figure 46. Average carbon–carbon bond length with changing hybridization.

3. J_{CH} coupling constants: Bent's rule is very much effective in explaining the variation of carbon-hydrogen coupling constant with increasing electronegativity strength of the attached substituents. The ^{1}H-^{13}C coupling constants (J_{CH}) measured from nuclear magnetic resonance (NMR) spectra is one of the most direct scales that can be used to estimate the magnitude of *s* character in a bonding overlap between carbon and hydrogen.

Now as we know from the quantum theory that the J_{CH} values will be much greater in bonds with more *s* character than the one with the less. Therefore, as the electronegative character of the attached group increases, the magnitude of *p*-character oriented towards the corresponding group increases as well. This induces more *s* character in the bonds directed towards the methyl protons; which in turn, increases the J_{CH} coupling constants.

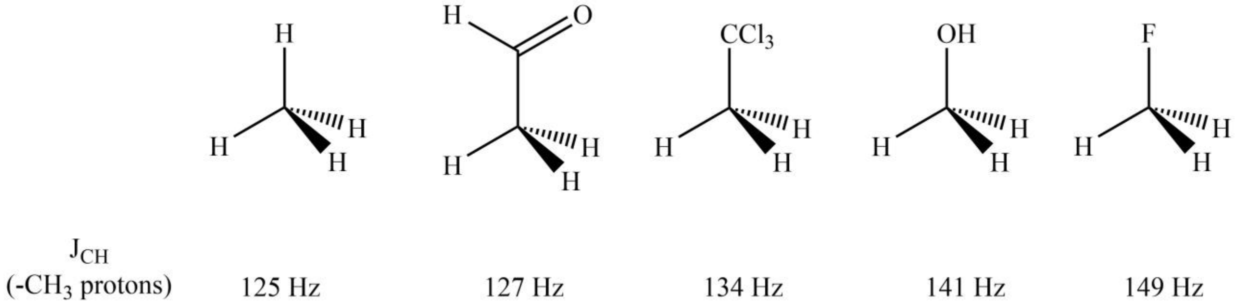


Figure 47. The variation of carbon-hydrogen coupling constants (J_{CH}) with increasing electronegative strength of the attached group.

4. Inductive effect: One of the most important phenomena in the field of organic chemistry, the inductive effect, can also be rationalized with the help of Bent's rule. The phenomenon of inductive effect is actually the passing of charge via the covalent bonds and Bent's rule offers a reasonable mechanism for such observations by exploiting the differences in the hybridization scheme involved. It has been observed that with the increase in the electronegativity strength of the groups attached to the central carbon, the electron-withdrawing power of the central carbon also increases and can be measured by the polar-substituent-constant values. According to the Bent's rule, the increase in the electronegativity of the groups attached would attract more *p* character towards them; consequently, leaving higher *s* character for the C−R bond. Now because the s orbitals have higher electron-density near the nuclei than their *p* counterparts, a shift of electron density towards the carbon in the C−R bond is expected; which in turn would make the central carbon atom more electron-withdrawing to the ligand attached i.e. R.

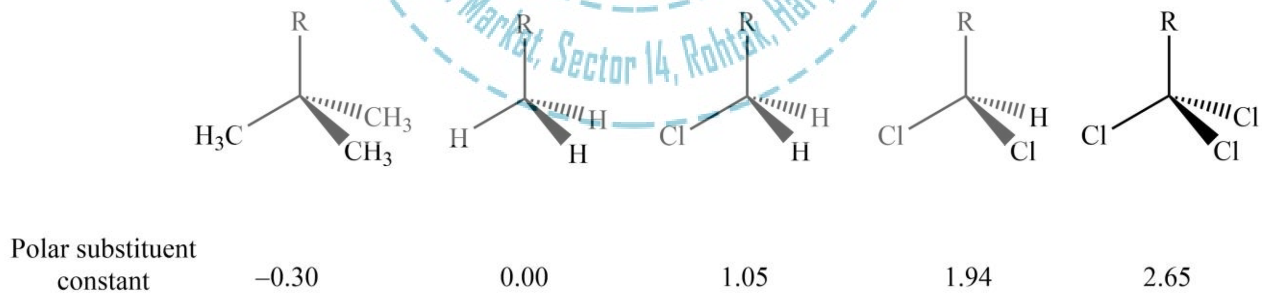


Figure 48. The variation polar-substituent-constants with increasing electronegative strength of the attached group.

In words, we can say that the electron-withdrawing capability of the substituents-attached is transferred to the neighboring carbon atoms in the carbon chain under consideration. This is exactly the same conclusion what the inductive effect states.

➢ *Exceptions of Bent's Rule*

The general statement of Bent's rule, atomic *s*-character concentrates in orbitals directed towards electropositive substituents, is true only for main group compounds. However, transition metal complexes show quite strange behavior. It has been observed that the group four transition metals Ti–Hf do not rigorously follow Bent's rule. With these complexes, the more electronegative substituents have larger bond angles indicating greater s-character. This can be explained by the fact that the *d*-orbitals in transition metals are generally lower in energy than *s*-orbital. Thus, more electronegative substituents will be attracted to the high lying *s*-orbitals. Transition metal orbitals are sd^3 hybridized with very little contribution from *p*-orbitals.

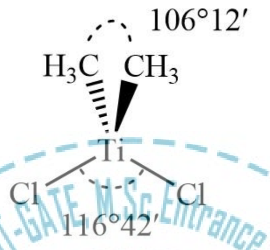


Figure 49. Distorted structure of $TiMe_2Cl_2$.

The broad form of Bent's rule can be stated as follows, "The energetically low-lying valence orbital concentrates in bonds directed towards electropositive substituents". This satisfies both the main group and transition metal complexes.

❖ Problems

Q 1. Write down the basic postulates of the valence-shell-electron-pair-repulsion (VSEPR) theory.

Q 2. How would you use the VSEPR theory to explain the molecular geometry of seven electron-pair-domains?

Q 3. Draw and discuss the structure of ClF_3 molecule on the basis of the VSEPR model.

Q 4. The axial bond lengths than the equatorial one in trigonal bipyramidal geometries, while shorter in pentagonal bipyramidal structure. Why?

Q 5. Write down the five main limitations of the VSEPR theory.

Q 6. How would you explain the nature of the orbitals used by main-group elements for $d\pi$–$p\pi$ bonding in tetrahedral molecules?

Q 7. What are the characteristic features of orbital hybridization?

Q 8. Draw and explain the orbital hybridization in hypervalent molecules using suitable examples.

Q 9. Discuss the orbital hybridization of NH_3 and H_2O molecules in a comparative framework.

Q 10. Discuss the stereochemistry of the following: (i) $SnCl_2$ (ii) ClF_3.

Q 11. Define the Bent's rule and explain Why the bond angle of PH_3 is less than that of PF_3?

❖ Bibliography

[1] R. J. Gillespie, *Electron Densities and the VSEPR Model of Molecular Geometry*, E. Can. J. Chem., 70, 1992, 742.

[2] I. Hargittai and B. Chamberland, *The VSEPR Model of Molecular Geometry*, Comp. & Maths. with Appls., 12B, 1986, 1021.

[3] R. J. Gillespie and R. S. Nyholm, *Inorganic Stereochemistry*, Q. Rev. Chem. Soc., 11, 1957, 339.

[4] J. D. Lee, *Concise Inorganic Chemistry*, Chapman & Hall, New York, USA, 1994.

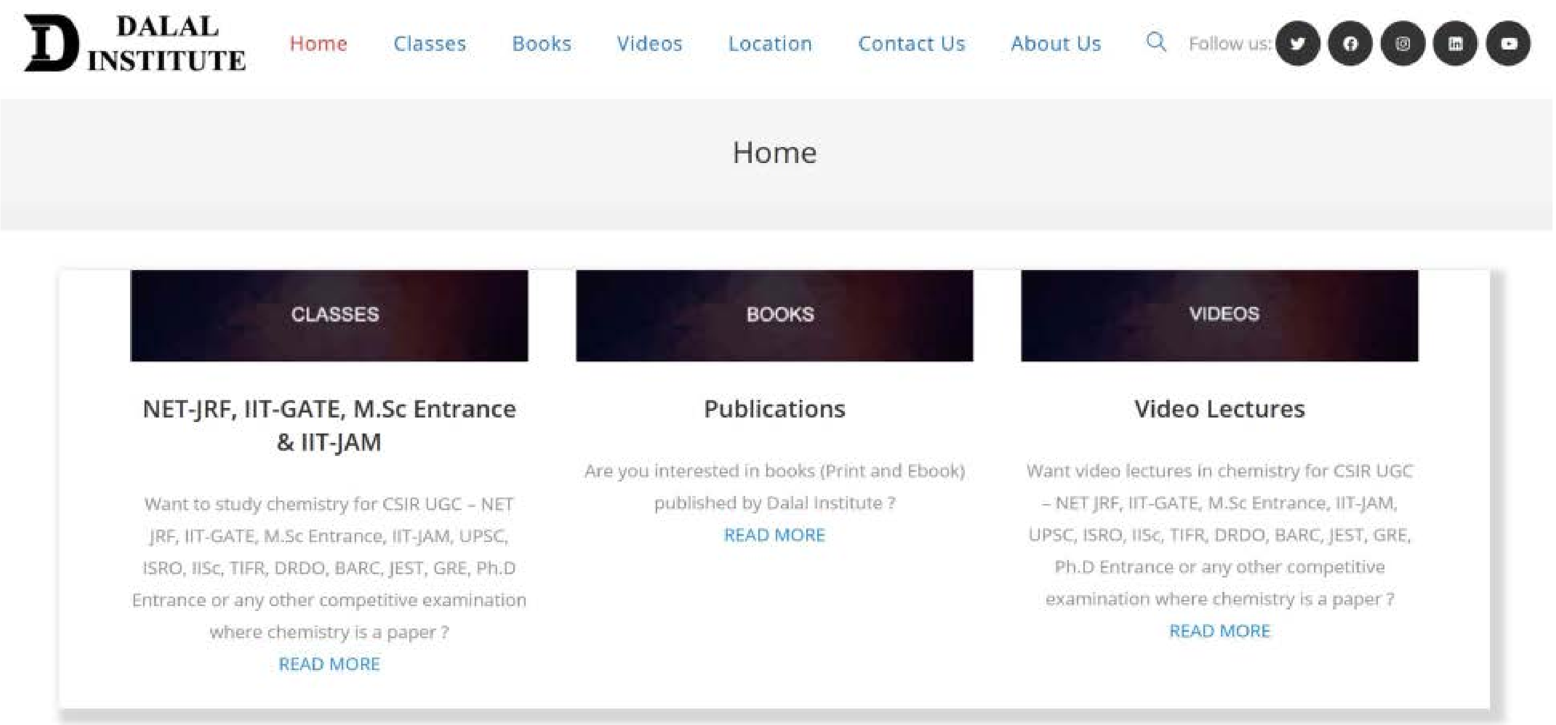
[5] B. R. Puri, L. R. Sharma, K. C. Kalia, *Principals of Inorganic Chemistry*, Milestone Publishers, Delhi, India, 2012.

[6] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principals of Structure and Reactivity*, HarperCollins College Publishers, New York, USA, 1993.

[7] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, UK, 1975.

[8] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, New Jersey, USA, 1999.

[9] W. U. Malik, G. D. Tuli, R. D. Madan, *Selected Topics in Inorganic Chemistry*, S. Chand Publishers, New Delhi, India, 2014.



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