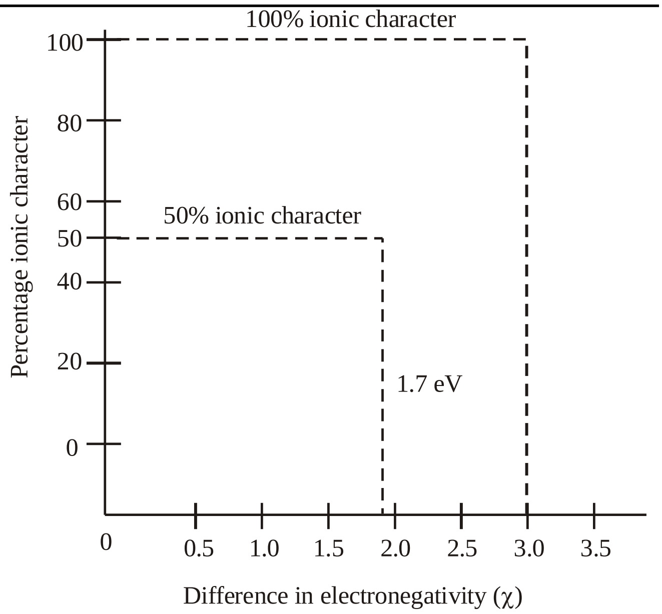
e.g. $\xrightarrow[\text{Percentage ionic character increases because difference in electronegativity increases}]{\text{Cl—Cl} \quad \text{H—Cl} \quad \text{NaCl}}$



* If electronegativity difference between atom is 1.7 eV. Then ionic character in covalent bond will be 50%.

Several emperical formulas have been proposed to calculate the amount of ionic character in polar covalent bond.

(i) **Electronegativity difference method:**

(a) Pauling's equation: Amount of ionic character in A–B bond $= \left[18\left(\chi_A - \chi_B\right)^{1.4}\right]\%$

$\boxed{\chi_A > \chi_B}$ χ = Electronegativity of atom

Problem: On the basis of Pauling equation calculate the percentage of ionic character in HF molecule, given that $\chi_F = 4.0$ $\chi_H = 2.2$

Soln. $\chi_F - \chi_H = 4 - 2.2 = 1.8$

Ionic character in HF molecule $= 18 \times (1.8)^{1.4} = 44.12\%$

(b) Hanny and Smith equation:

Percentage ionic character in A–B bond $= \left[16\left(\chi_A - \chi_B\right) + 3.5\left(\chi_A - \chi_B\right)^2\right]\%$

Problem: On the basis of Hanny and Smith equation, calculate the percentage of ionic character in gaseous HF, HCl, HBr and HI molecules, given that

$$\chi_F = 4.0, \chi_{Cl} = 3.2, \chi_{Br} = 3, \chi_I = 2.7 \ \& \ \chi_H = 2.2$$

Soln. $\chi_F - \chi_H = 4.0 - 2.2 = 1.8$

So, ionic character in H—F bond $= \left[16 \times 1.8 - 3.5 \times (1.8)^2\right] = 40.14\%$

HCl = 19.5 %
HBr = 15.04 %
HI = 8.875 %

(ii) Dipole-moment method:

$$\text{Percentage ionic character of bond A–B} = \frac{\mu_{\text{exp}}}{(\mu_{\text{cal}})\text{ionic}} \times 100\% = \frac{\mu_{\text{exp}}}{d_{A-B} \times \text{electronic charge } (e)} \times 100\%$$

where, μ_{exp} = experimental value of dipole moment.

μ_{cal} = calculated (theoritical) value of dipole-moment of molecule when molecule is assumed to be completely ionic.

$$\begin{array}{c} \overset{\delta-}{A} — \overset{\delta+}{B} \\ \leftarrow d \rightarrow \end{array}$$

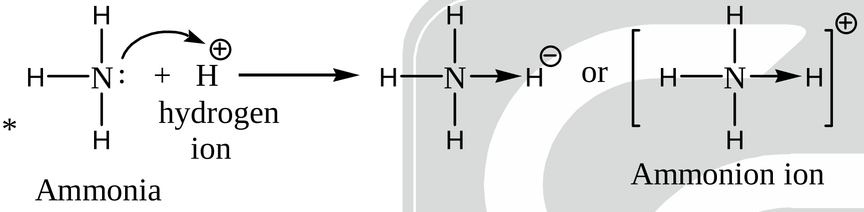
$$\mu_{\text{cal}} = d \times \text{electronic charge } (e)$$

$$\boxed{\mu_{\text{cal}} = d \times e}$$

1.5 **Coordinate bond:** A covalent bond in which both the electrons of the shared pair come from one of the two atoms (or ions), called coordinate bond.

e.g. NH_4^+, BF_4^-, H_3O^+ $H_3N \rightarrow BCl_3$, $CH_3NO_2, SO_2, SO_3, Al_2Cl_6, SO_4^{--}, O_3, CO, Ni(CO)_4$ etc.

*



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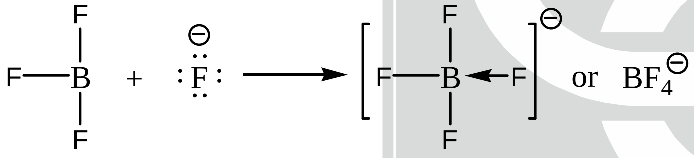

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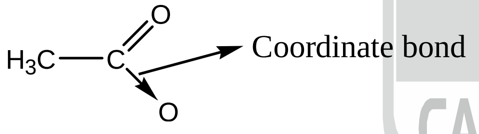
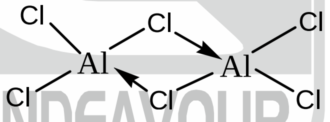


* Al_2Cl_6:



2.6 Valence shell electron pair repulsion (VSEPR) Theory:

In order to predict the geometry of molecules, Nyholm and Gillespie developed a qualitative model konwn as **Valence Shell Electron Pair Repulsion Theory (VSEPR)**. The basic assumptions of this theory are summarized below.

1. The electron pairs (both lone pairs and bond pairs) in the valence shell around the central atom of a molecule repel each other and tend to orient in space so as to minimize the repulsions and maximize the distance between them.
2. There are two types of valence shell electron pairs viz
   (i) Bond pairs and (ii) Lone pairs

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.

3. In VSEPR theory, the multiple bonds are treated as if they were single bonds. The electron pairs in multiple bonds are treated collectively as a single super pair.
4. The shape of a molecule can be predicted from the number and type of valence shell electron pairs (bond pairs and lone pairs) around the central atom.

   When the valence shell of central atom contains only bond pairs, the molecule assumes symmetrical geometry due to even repulsions between them.
   However the symmetry is distorted when there are also lone pairs along with bond pairs due to uneven repulsion forces.
5. The magnitude of repulsion between bonding pairs of electrons depends on the electrnegativity difference between the central atom and other atoms.
   Double bond causes more repulsion than single bonds and triple bonds cause more repulsion than a double bond.
   Double bond and triple bond causes more repulsion than single bonds–but does not effect the structure. Bond angles involving multiple bonds generally larger than those involving only single bond.
   Keeping the central atom (having lone pair) same, if the electronegativity of the surrounding atom increases, the bond angle will decrease no other factors like size and back bonding play and role.
   Keeping the surrounding atoms same, if the electronegativity of the central atom (having the lone pair) increases, the bond angle increases. Some times the lone pair may be transferred from filled shell of an atom to unfilled shell of the adjacent bonded atom. This phenomenon of transferring electron is known as “back bonding”.

Effect of Lone Pairs

Molecules with four electron pairs in their outer shell are based on a tetrahedron. In CH_4 there are four bonding pairs of electrons in the outer shell of the C atom, and the structure is a regular tetrahedron with bond angles H—C—H of 109°28'. In NH_3 the N atom has four electron pairs in the outer shell, made up of three bond pairs and one lone pair. because of the lone pair, the bond angle H—N—H is reduced from the theoretical tetrahedral angle of 109°28' to 107°48'. In H_2O the O atom has four electron pairs in the outer shell. The shape of the H_2O molecule is based on a tetrahedron with two corners occupied by bond pairs and the other two corners occupied by lone pairs. The presence of two lone pairs reduces the bond angle further to 104°27'.

In a similar way SF_6 has six bond pairs in the outer shell and is a regular octahedron with bond angles of exactly 90°. In BrF_5 the Br also has six outer pairs of electrons, made up of five bond pairs and one lone pair. The lone pair reduces the bond angles to 84°30'. Whilst it might be expected that two lone pairs would distort the bond angles in an octahedron still further, in XeF_4 the angles are 90°. This is because the lone pairs are trans to each other in the octahedron, and hence the atoms have a regular square planar arrangement.

Molecules with five pairs of electrons are all based on a trigonal bipyramid. Lone pairs distort the structures as before. The lone pairs always occupy the equatorial positions (in the triangle), rather than the apical positions (up and down). Thus in the I_3^- ion the central I atom has five electron pairs in the outer shell, made of two bond pairs and three lone pairs. The lone pairs occupy all three equatorial positions and the three atoms occupy the top, middle, and bottom positions in the trigonal bipyramid, thus giving a linear arrangement with a bond angle of exactly 180°.

Effect of Electronegativity: The effect of electronegativity can be explained by considering the following cases.

(A) When the central atom having lone pair is the same with different surrounding atoms:

NF_3 and NH_3 both have structures based on a tetrahedron with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in NH_3. Thus repulsion between bond pairs is less in NF_3 than in NH_3. Hence the lone pair in NF_3 causes a greater distortion from tetrahedral and give a F—N—F bond angle of 102°30', compared with 107°48' in NH_3. The same effect is found in H_2O (bond angle 104°27') and F_2O (bond angle 102°), H_2O (bond angle 104°27') and H_2S (bond angle 92°2').

The following examples highlight the significance of having lone pair on the central atom. In absence of lone pair, the effect of electronegativity is not observed.

CH_4 and CF_4	SiH_4 and SiF_4	BH_4^- and BF_4^-
109°28′ and 109°28′	109°28′ and 109°28′	109°28′ and 109°28′

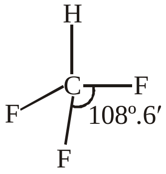
In the following case bond angles are distorted but, the decrease in bond angle is due to decrease in steric crowding.

PI_3	PBr_3	PCl_3	PF_3
102°	101°	100.3°	97.8°

Bent's rule is also consistent with Gillespie's VSEPR model. So it is restated as : more electronegative atom not only prefers to stay in the orbital having more P character but also can increase the P character in its attached orbital from the central atom depending on the circumstance.

- **Application on the bond angle.** The different bond angles in CHF_3 and CH_2F_2 can be explained on the basis of the following figure.

  But it is not applicable for $CHCl_3$ and CH_2Cl_2 where the corresponding bond angles increase due to larger size of Cl atoms.



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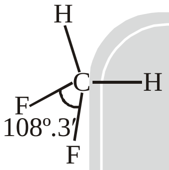

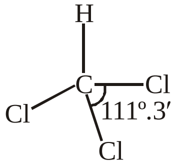

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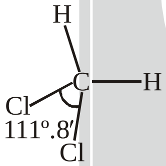


- **Application on bond length with increase in p character** in an orbital, bond length will increase while with increase in S character in an orbital, bond length will decrease.

Ex. d_{C-Cl} in CH_3Cl (1.78Å) > d_{C-Cl} in CF_3Cl (1.75Å)

d_{N-N} in N_2H_4 > d_{N-N} in N_2F_4

d_{C-C} in C_2H_6 > d_{C-C} in C_2F_6

d_{O-O} in O_2H_2 > d_{O-O} in O_2F_2

(B) When the surrounding atom is same with different central atom having lone pair:

The effect of electronegativity as postulated in VSEPR theory explains the order of the angle for the following molecules.

NH_3	PH_3	AsH_3	SbH_3
107°	93°	91.8°	91.3°
H_2O	H_2S	H_2Se	H_2Te
104.5°	92°	91°	89.5°

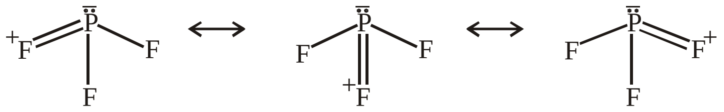
(C) The complexing ability of NH_3 is much higher as compared to that of PH_3.

Back bonding: The phenomenon of back bonding involves transfer of lone pair from filled shell of an atom to the unfilled shell of the adjacent bonded atom.

It is a kind of coordinate π-bonding which may be partial or full, depending of the relative donating and accepting ability of the donor and acceptor atoms. Generally, the donor atoms are the second period elements carrying lone pairs, such as F, O, N, C, some times Cl, Br, I, P, S can also act as donor atoms depending on circumstance.

(A) Back bonding with F as donor atom:

- As the considering of electronegativity of the surrounding atoms, the expected bond angle order for PH_3 and PF_3 is $PH_3 > PF_3$. But in reality, it is $PH_3 < PF_3$. This is due to lack bonding in PF_3.



So, due to back bonding the partial double bond character develops in a bond causing a decrease in the bond length; bond angle may or may not increase, but it never decreases.

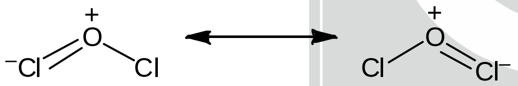
Ex.

PH_3	93.8º
PF_3	97.8º
AsH_3	91.8º
AsF_3	96.2º

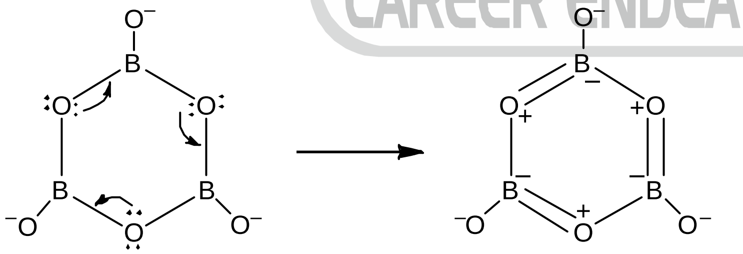
In BF_3, the extent of back bonding is more than that observed in PF_3 because of the $2p\pi - 2p\pi$ overlap in case of BF_3, while that in P–F bond is $3d\pi - 2p\pi$. However, there is no change in the bond angle due to absence of the lone pair on the central atom.

(B) Back bonding with O as donor atom:

- The expected bond angle order for H_2O, Cl_2O and F_2O is $H_2O > Cl_2O > F_2O$ according to the electronegativities of the surrounding atoms. But in reality, the order is $Cl_2O > H_2O > F_2O$. This is also explained on the basis of back bonding in Cl_2O, which is not possible in H_2O and F_2O.

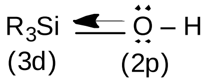


- The d_{B-O} in $B(OH)_3 < d_{B-O}$ in $[B(OH)_4]^-$. Because, of the back bonding possible in $B(OH)_3$ from O atom to vacant P-orbital of B-atom, which is not available in case of $[B(OH)_4]^-$.
- Boroxine (B_3O_6) ring is planar due to back bonding and it is aromatic in nature.



Similarly $B_3N_3H_6$ (Borazine) is also planar and aromatic due to back bonding.

- $R_3Si - OH$ is more acidic than $R_3C - OH$. Because, of the back bonding from O atom to Si atom which increases the polarity of O–H bond and stabilize the conjugate base $R_3Si - O^-$.



(C) Back bonding with N as donor atom:

- Bond angle order is $NCl_3 > NH_3 > NF_3$

Because, the very slight back bonding in NCl_3 from 2p orbital of N to 3d orbital of Cl the extent of which is very less.

- $(CH_3)_3N$ is pyramidal which $(H_3Si)_3N$ is planar and similarly $(SiH_3)_3P$ is pyramidal and $(GeH_3)_3N$ is planar. In case of $(CH_3)_3N$, there is no back bonding, however, $2p\pi - 3d\pi$ and $2p\pi - 4d\pi$ back bonding in $(SiH_3)_3N$ and $(GeH_3)_3N$ respectively makes them planar and 1X atom is forced to adopt sp^2 hybridization. It is also observed that $(CH_3)_3N$ is more basic as compared to $(SiH_3)_3N$ due to the same reason and they behave differently towards HCl.

$$(CH_3)_3N + HCl \rightarrow (CH_3)_3NH^+Cl^-$$

$$(SiH_3)_3N + 4HCl \rightarrow NH_4Cl + 3SiH_3Cl$$

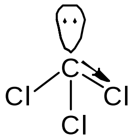
- The bond length order of B–N bond in the following compound is

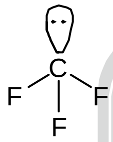
$$B(NR_2)_3 > HB(NR_2)_3 > H_2B - NR_2$$

and the order of energy required for the rotation of B–N bond is just reverse.

(D) Back bonding with C as donor atom:

$CHCl_3$ is more acidic than CHF_3





$$CHCl_3 \rightleftharpoons H^+ + {}^-CCl_3$$

$$CHF_3 \rightleftharpoons H^+ + {}^-CF_3$$

The lone pair on C-atom get delocalized through $2p\pi - 3d\pi$ bonding in Cl_3C^-, which is not possible in case of F_3C^-.

- R_3C^- is pyramidal while $(CN)_3C^-$ is planar.

(E) Back bonding with halogens (Cl, Br, I) as donor atom:

- The Lewis acidity order is $BF_3 < BCl_3 < BBr_3 < BI_3$. Because, the back donation ability order for halogens towards B atom is F >> Cl > Br > I.
- The relative stability order for the diradicals is

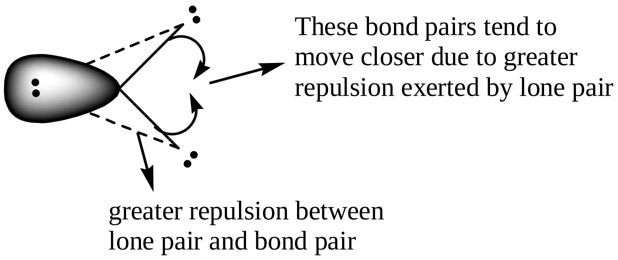
$$:CH_2 < :CCl_2 < :CF_2$$

Isoelectronic Principle:

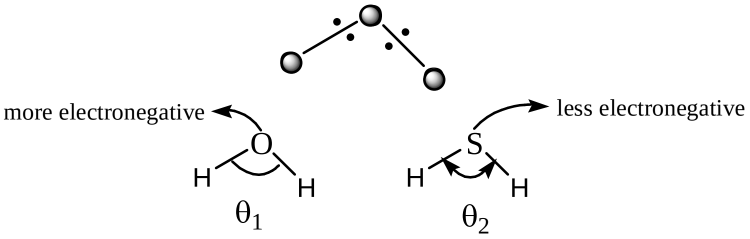
Isoelectronic species usually have the same structure. This may be extended to species with the same number of valence electrons. Thus BF_4^-, CH_4 and NH_4^+ are all tetrahedral, CO_3^{2-}, NO_3^- and SO_3 are all planar triangles, and CO2, N_3^- and NO_2^+ are all linear.

Primary and secondary effects on bond angle and shape:

(i) The bond angle decreases due to the presence of lone pairs, which cause more repulsion on the bond pairs and as a result the bond pairs tend to come closer.

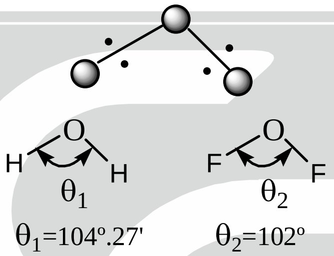


(ii) The repulsion between electron pair increases with increase in electronegativity of central atom and hence the bond angle decreases. The bond pairs are closer and thus by shortening the distance between them, which in turn increases the repulsion. Hence the bonds tend to move away from each other.
e.g. H_2O, H_2S



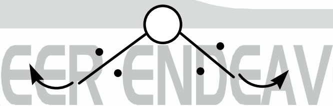
$\boxed{\theta_1 > \theta_2}$

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 resulting in the decrease in bond angle.
e.g. H_2O, F_2O

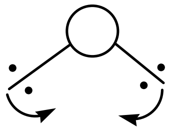


$\boxed{\theta_1 > \theta_2}$

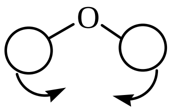
(iii) The bond angle decreases with increase in the size of central atom. On smaller central atoms the bond pairs are closer and hence tend to move away from each other so as to minimize repulsion. Hence bond angle will be more.



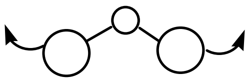
On bigger central atoms, the bond pairs are more distant from each other and hence there is less repulsion. Hence they tend to move closer and thus by decreasing the bond angle.

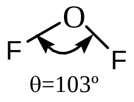


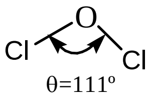
However the bond angle increases with increase in the size of ligand atoms, which surround the central atom. There is less repulsion between smaller ligand atoms they can move closer to each other and thus decrease the bond angle.



These is more repulsion between bigger ligand atoms and hence they tend to move away from each other. Thus bond angle increases.
e.g. F_2O, Cl_2O, Br_2O







(iv) The bond angles are also changed when multiple bonds are present. It is due to uneven repulsions. When there are two or more resonance structures, the VSEPR theory is applicable to any of such contributing structure.

Relation between number and type of valence electron pairs with the shape of molecule.

- The shape of molecule and also the approximate bond angles can be predicted from the number and the type of electron pairs in the valence shell of central atom as tabulated below.

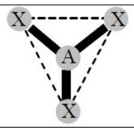
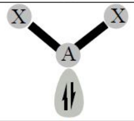
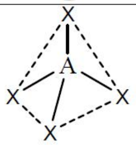
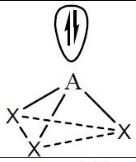
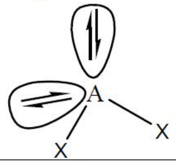
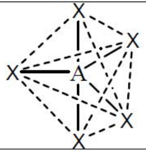
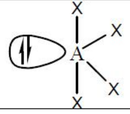
In the following table the molecule is represented by "AXE" notation, where

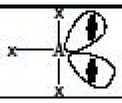
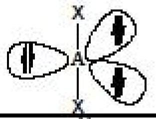
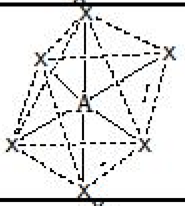
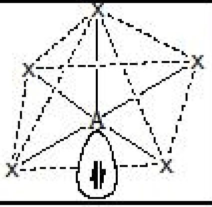
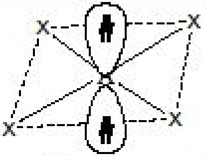
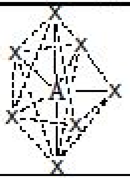
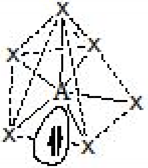
A = Central atom

X = Ligand atom, indicating a bond pair.

E = Lone pair.

Note: The sum of number of ligand atoms (X) and number of lone pairs (E) is also known as steric number

Steric No.	**Number of Bond pairs**	**Number of lone pairs**	**Formula**	**Shape of molecule**		**Approximate Bond angles**	**Examples**
1	1	0	AX	Linear		–	ClF, BrF, BrCl, HF, O_2
2	2	0	AX_2	Linear		180°	$BeCl_2$, $HgCl_2$, CO_2
3	3	0	AX_3	Trigonal planar		120°	BF_3, CO_3^{2-}, NO_3^-, SO_3
	2	1	AX_2E	Angular		<120°	SO_2, $SnCl_2$, O_3, NSF, NO_2^-
4	4	0	AX_4	Tetrahedral		109°28′	CH_4, $SiCl_4$, NH_4^+, PO_4^{3-}, SO_4^{2-}, ClO_4^-
	3	1	AX_3E	Trigonal pyramidal		Around <109°28′	NH_3, PCl_3, XeO_3
	2	2	AX_2E_2	Angular		<109°28′	H_2O, SCl_2, Cl_2O, OF_2
5	5	0	AX_5	Trigonalbipyramidal		120° and 90°	PCl_5, SOF_4
	4	1	AX_4E	See saw or distorted tetrahedral			SF_4, $TeCl_4$
	3	2	AX_3F_2	T-shape		<90°	ClF_3, BrF_3, $BrCl_3$

5							$BrCl_3$
	2	3	AX_2F_3	Linear		180°	XeF_2, I_3^-
6	6	0	AX_6	Octahedral		90°	SF_6
	5	1	AX_5E	Square pyramidal		90°	ClF_5, BrF_5, ICl_5
	4	2	AX_4E_2	Square planar		90°	XeF_4
7	7	0	AX_7	Pentagonal bipyramidal		72° and 90°	IF_7
	6	1	AX_6E	Pentagonal pyramidal		Around 72° and 90°	$XeOF_5^-$, IOF_5^{2-}

Steps involved in predicting the shapes of molecules using VSEPR theory:

The first step: Find out the hybridization of molecules by using formula of hybridization.

$$\boxed{H = S + \frac{1}{2}(E - V \pm C)} \text{ or } \boxed{\text{H = lone pair of electrons + number of surrounding atoms.}}$$

H = hybridization, S = No. of atoms bonded with central atom, E = Valence electrons of central atom, V = Valency of central atom (equal to number of monovalent atoms bonded with central atom.

e.g. OH, Cl, F, H etc. and double of number of divalent atoms, e.g. O, S etc). C = Electrical charge on molecule, if molecule is ionic (+C for anion and –C for cation).

The second step: Then find out the number of bond pairs and lone pairs in the valence shell of central atom.

$$\text{Lone pairs (unshared pair) of central atom (L)} = \frac{1}{2}(\text{E} - \text{valency of central atom } \pm \text{C}) \text{ or}$$

$$= \frac{1}{2}(\text{E} - \text{no. of bonds around central atom } \pm \text{C}) \text{ or}$$

$$= \frac{1}{2}(\text{E} - \text{no. of bond pair of electrons around central } \pm \text{C})$$