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Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theory called Valence Shell Electron Pair Repulsion or in short VSEPR theory was given by Sidgwick and Powell in 1940 to explain the shapes of molecules. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

POSTULATE I

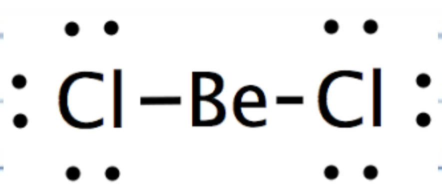
The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in a molecule will be energetically most stable when they are as far apart from each other as possible. For example:

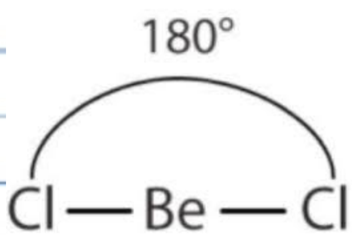
1. $BeCl_2$

Electronic configuration: Beryllium (Be) $1s^2\ 2s^2$

Chlorine (Cl) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180o which gives the molecule a linear shape.



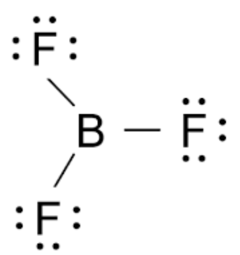


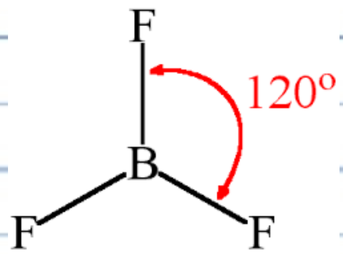
2. BF_3 (Boron trifluoride)

Electronic configuration: Boron (B) $1s^2\ 2s^2\ 2p^1$

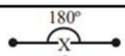
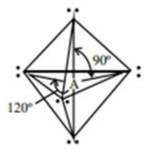
Fluorine (F) $1s^2\ 2s^2\ 2p^5$

In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.





Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 1

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX_2	2	Linear		$HgCl_2$, BeH_2
AX_3	3	Planer trigonal		BF_3, BCl_3
AX_4	4	Tetrahedral		CCl_4, CH_4, $SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs The order of repulsive force between different possibilities is as under. **lone pair - lone pair > lone pair - bond pair > bond pair - bond pair**

The shapes of the molecules given in Table (previous page) correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom.

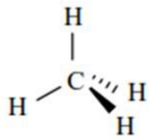
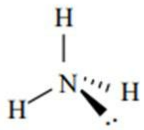
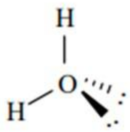
In methane molecule (CH_4) the central carbon atom (C) has 4 valence electrons and it shares 4 electrons with four H atoms. So there are a total of 4 bond pairs and it should have a tetrahedral shape.

In case of ammonia (NH_3) also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair.

Similarly, in case of water (H_2O) again there are four pairs of electrons ; two are bond pairs while two are lone pairs.

Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 2.

Table 2 Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107
H_2O	2	2	angular or bent		104.5

Although VSEPR theory provides a good idea of the shapes of the molecules. But according this theory, the elctrons are represented as localized particles. This is in contradiction with the probabilistic (orbital) representation of the electrons . Thus we nedd to explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

Homework:

1. What are the basic postulates of VSEPR theory?

2. Predict the shape of CH_4, BCl_3, PF_5, SF_6, and NH_3 on the basis of VSEPR theory.