Valence Shell Electron Pair Repulsion (VSEPR) Theory

This is a very useful theory to predict the geometry or shape of a number of polyatomic molecules or ions of non-transition elements.

This theory was proposed for the first time by Sidgwick and Powell in 1940 and developed by **Gillespie and Nyholm** in 1957. This theory says that the shape -of a given species (molecule -or ion) depends on the number and nature of electron pairs surrounding the central atom / ion of the species.

This theory makes the following assumptions:

Assumptions of VSEPR Theory

1.Spatial arrangement of electron pairs round the central atom/ion of a given molecule/ion.

The electrons already present in the valence-shell of the central atom/ion of a given species (= a) plus the electrons acquired by the central atom/ion as a result of bonding with other atoms (= b) are called its valence-shell electrons. Half of (a + b), i.e. (a + b)/2, gives the number of electron pairs present in the valence-shell of the central atom/ion. This theory assumes that these electron pairs occupy localised orbitals which arrange themselves in space in such a way that they _keep apart from one another as far as possible so that they may experience minimum electrostatic repulsion between them and hence may give minimum energy and maximum stability to the species.

According to this assumption:

(a) If the central atom/ion is surrounded by two electron pairs, i.e. if the sum of bonding electron pairs (bps) and non-bonding electron pairs, also called lone pairs of electrons Ups) is two, then in order to keep them farthest apart these are directed in opposite directions along the same axis, i.e. their spatial arrangement is linear (diagonal) and the angle between them (i.e. bond angle) is 180°

(b) If the central atom/ion is surrounded by three electron pairs (i.e. bps + lps = 3), then in order to keep them farthest apart they are directed towards the corners of a triangle, i.e. their spatial arrangement is triangular or trigonal and if all the three electron pairs are bonding electron pairs, the -angle between. Each electron-pair is 120^o.

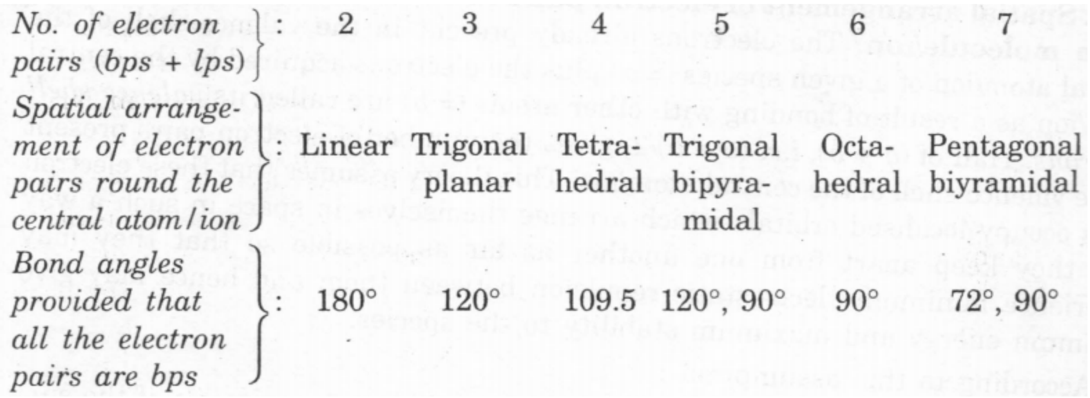
(c) If the central atom/ion is surrounded by four electron pairs (i.e. bps' + lps = 4), then these electron pairs are directed towards the corners of a regular tetrahedron i.e. their spatial arrangement is tetrahedral and if all the four electron pairs are bps, the bond angle is 109.5°.

(d) If the central atom/ion is surrounded by five electron pairs (i.e. bps + lps = 5), then these electron pairs are directed towards the corners of a trigonal bipyramid, i.e. their spatial arrangement is trigonal bipyramidal and if all the five electron pairs are bonding pairs, the bond angle between the two equatorial (i.e. basal) electron pairs is 120° while that between axial and equatorial electron pairs is 9.0°.The angle between the two axial electron pairs is 180°.

(e) If the central atom/ion is surrounded by six electron pairs (i.e. bps +lps = 6), then these electron pairs are directed towards the corners of a octahedron, i.e., their spatial arrangement is octahedral and the bond angle between the two adjacent (cis) electron pairs is 90° while the angle between the axial (trans) electron pairs is 180°.

(f) If the central atom/ion is surrounded, by seven electron pairs ii.e. bps +lps = 7), then these electron pairs are directed towards the corners of a pentragonal bipyramid and hence their spatial arrangement is pentagonal bipyramidal. The angle between the two equatorial electron pairs is 72° while that between the equatorial and axial electron pairs is 90°. The angle between the two axial electron pairs is 180°.

Relationship between the number of electron pairs (i.e. bps + lps) round the central atom/ion of a given species, the spatial arrangement of the electron pairs and the bond angle (provided that all the electron pairs are bonding electron pairs. i.e. there are no lone pairs of electrons) is shown as follows:



No. of electron pairs (bps + lps)	2	3	4	5	6	7
Spatial arrangement of electron pairs round the central atom/ion	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral	Pentagonal biyramidal
Bond angles provided that all the electron pairs are bps	180°	120°	109.5	120°, 90°	90°	72°, 90°

2. Regular and irregular geometry of the molecule/Ion

The electron pairs surrounding the central atom/ion are either bps or some of them are bps and the remaining are lps. The central atom/ion is surrounded only by the bps, then the species has a regular geometry, i.e. there is no distortion in the shape of the species. If, however, the central atom/ion is surrounded by the bps as well as by lps, the bond angle gets altered from the value expected for a particular geometry of the molecule or ion. Now since the magnitude of bond angle gives an idea of the geometry of the .molecule or ion, the change in the magnitude of the bond angle also changes the geometry of the molecule or ion, i.e. with the change of the magnitude of the bond angle, the shape of the molecule or ion gets distorted.

In short we can say that the presence of one or more 'lone pairs of electrons on the central atom changes the magnitude of bond angle which, in turn, changes the geometry of the molecule or ion i.e. the presence of one or more lone pairs of electrons in the valence shell of the central atom or ion gives irregular or distorted geometry to the molecule or ion.

Cause of change in bond angle

The change in the magnitude of bond angle is due to the fact that (lp - lp) repulsion is greater than (lp-bp) repulsion which, in turn, is greater than (bp-bp) repulsion, i.e.

(lp-lp) repulsion.> (lp-bp) repulsion > (bp-bp) repulsion

Here lp and bp have been used to represent the lone pairs and bonding pairs of electrons surrounding the central atom. Since a bp experiences less repulsion from another bp than from a lp, it (i.e. bp) becomes closer to the bp and a contraction in the bond angle (i.e., the angle between the two bps)" occurs.

More the number of lps on a central atom, the greater is the contraction caused in the angle between the bps. This fact is clear when we compare the bond angles in CH_4, NH_3 and H_2O, molecules.

Molecules	CH_4	NH_3	H_2O
No. of lps on the central atom	0	1	2
Bond angle (Angle between two bps)	109.5°	107.5°	105.5°
Contraction in bond angle relative to that of CH_4	0	109.5°—107.5° = 2°	109.5° –105.5° = 4°

The comparison of bond angles of NH_3 and H_2O with that of CH_4 shows that each of H-O-H bond angles in H20 is decreased from a tetrahedral angle (= 109.5°) to a greater extent than each of H-N-.H bond angles in NH_3. The greater decrease in case of H_2O is explained as follows :

The valence-shell of O-atom in H_2O molecule has four electron pairs as N-atom in NH_3 molecule has. Two of these electron pairs are bps each of which is attracted by two nuclei (of H and O atoms) while the remaining electron pairs are lps each of which is attracted only by one nucleus (of O-atom), since these lps originate from O-atom only. Thus we see that O-atom in H_2O molecule has two lps while N-atom in NH_3 molecule has only one lp on it.

Consequently in H_2O molecule there are three types of electron pair-electron pair repulsions which are;

(i) (lp = lp) repulsion

(ii) (lp-bp) repulsion and

(iii) (bp - bp) repulsion

In the NH_3 molecule there are only two types of repulsions which are

(i) lp - bp repulsion and
(ii) bp - bp repulsion (See Fig. 1)

The magnitude of these repulsions, as shows above, is the following order;

(lp-lp) repulsion > (lp-bp) repulsion > (bp-bp) repulsion

The net effect of this difference in electron pair-electron pair repulsions is that the two lps on O-atom force the two (O-H) bps to come more closer to each .other than one lp on N-atom in NH_3 molecule forces three (N - H) bps to come closer to each other. Thus each of H-O-H bond angles in H_2O is decreased from a tetrahedral angle to a greater extent than each of H-N-H bond angles in NH_3 (H-N-H bond angle in NH_3 = 107.5°, H-O-H bond angle in H_2O = 105.5°). Due to the decrease in the expected tetrahedral angle, shape of H_2O molecule gets distorted and hence H_2O molecule assumes planar V-shape (angular or bent shape).

Shape of Molecules on the basis of VSEPR Theory

1. Shape of molecules/ions whose central atom/ion has two electron pairs.

Such molecules may be of AB_2 (e.g. BeF_2) type. These have two σ-bonding electron pairs and no lone pair. (bps = 2, lp = 0) These have linear shape. Here A is the central atom/ion and B are the atoms bonded to atom A by a-bonds only. π-bonds are not present.

2. Shape of molecules/ions whose central atom/ion has three electron pairs

Such species may be of AB_3 (bps = 3, lp = 0) and AB_2 (lp) (bps = 2, lp = 1) type. The species of AB_3 (e.g. BF_3, $GaCl_3$) and AB_2 (lp) [e.g. $SnCl_2$ (gaseous), $PbCl_2$] type have trigonal planar and angular or V-shape respectively. Here lp represents the lone pair of electrons in the valence-shell of the central atom/ion, A.

3. Shape of molecules/ions whose central' atom/ion has four electron pairs.

Such species may be of AB_4 (bps = 4, lp = 0), AB_3 (lp) (bps = 3, lp = 1), $AB_2(lp)_2$ (bps = 2, lps = 2) and AB $(lp)_3$ (bp = 1, lps = 3) type. The species of AB_4 (e.g. CH_4, PCl_4^+, $SiCl_4$, BH^{4-}, NH_4^+), AB_3 (lp) (e.g. NH_3, PH_3), AB_2 $(lp)_2$ (H_2O, ICl_2^+, SCl_2) and AB $(lP)_3$ (e.g. ICl) type have regular tetrahedral, trigonal pyramidal, angular or V-shape and linear shape respectively.

4. Shape of molecules/ions whose central atom/ion has five electron pairs.

Such species may be of AB5 (bps = 5, lp = 0), ABilp) (bps = 4, lp = 1). $AB_3(lp)_2$ (bps = 3, lps =) and AB_2 $(lp)_3$ (bps = 2, lps = 3) type. The species of AB_5 (e.g. PF_5, PCl_5 (g), AB_4(lp) (e.g. SF_4, IF_4^+), AB_3 $(lp)_2$ (e.g. ClF_3, BrF_3), AB_2 $(lp)_3$ (e.g. XeF_2,I_3^-, ICl_2^-) type have trigonal bipyramidal, distorted trigonal bipyramidal, T-shape and linear structures respectively. The lone pairs occupy the equatorial positions.

5. Shape of molecules/ions whose central atom/ion has six electrons pairs.

Such species may be of AB$_6$ (bp = 6, lp = 0), AB$_5$ (lp) (bps = 5, lp = 1) and AB$_4$ (lp)$_2$ (bps = 4, lps = 2) type. The species of AB$_6$ (e.g. SF$_6$, PCl$_6^-$), AB$_5$(lp) (e.g. SbX$_5^{-2}$, BrF$_5$, IF$_5$) and AB (lp)$_2$ (e.g. XeF$_4$, ICl$_4^-$) type have regular octahedral, square pyramidal and square planar shapes respectively. The lone pairs occupy the axial positions.

6. Shape of molecules/ions whose central atom/ion has seven electron pairs

Such species may be of AB$_7$ (bps = 7, lp = 0) and AB$_6$ (lp) (bps = 6, lp = 1). The species of AB$_7$ (e.g. IF$_7$) and AB$_6$ (lp) (e.g. XeF$_6$) type have trigonal bipyramidal and distorted octahedral shapes respectively.

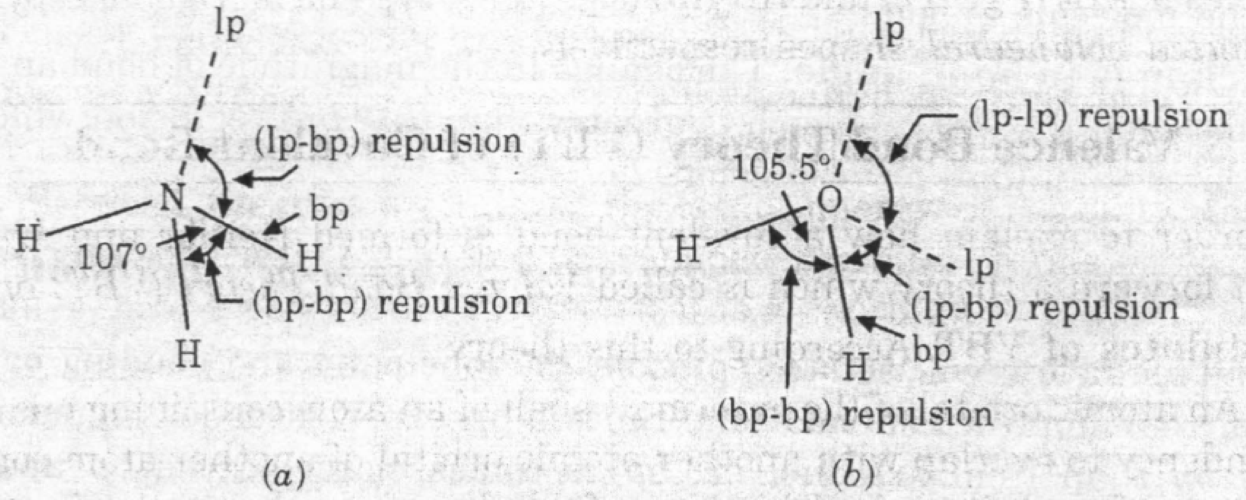


Fig. 8.6. Different types of electron pair—electron pair repulsions in (*a*) NH$_3$ and (*b*) H$_2$O molecules.