...ory) is essential.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

This approach to predict the shapes of covalent molecules was developed by **Gillespie** and **Nyholm** (1957).

The theory is mainly based upon the fact that in a polyatomic molecule the direction of bonds around he central atom depends upon the total number of electron pairs (bonding as well as non-bonding) in its valence shell. These electron pairs place themselves as far apart as possible in space to have minimum repulsive interactions between them. The minimum repulsions correspond to the state of minimum energy and maximum stability of the molecule. The main points of VSEPR Theory are as follows :

(i) The unpaired electrons in the valence shell of central atom form bond pairs with the unpaired electrons of surrounding atoms while paired electrons remain as lone pairs.

(ii) The electron pair surrounding the central atom repel one another. As a result, they remain as far apart as possible in space to attain maximum stability.

(iii) The geometry and shape of molecule depend upon the number of electron pairs (bonded as well as non-bonded) surrounding the central atom.

(iv) Repulsion between the lone pair and lone pair of electrons is different than that between the bond pairs or one lone pair and one bond pair. The repulsive interactions decrease in the order : **Lone pair—Lone pair > Lone pair—Bond pair >Bond pair—Bond pair.** The presence of lone pairs in addition to bond pairs will result in certain distortions in the regular geometry of molecules.

Regular and irregular geometric arrangement. The molecules in which the central atom is surrounded by ~~similar shared pair of electrons or bonded electron pairs~~ will have regular geometries. For example, CH_4, CCl_4, SiF_4, $SiCl_4$, BF_3, SF_6, etc. On the other hand, the molecules in which the central atom is surrounded by bond pairs as well as lone pairs will have *irregular geometries*.

Geometry of Molecules on the basis of VSEPR Theory or Predicting the Geometry of Molecules on the basis of VSEPR Theory

According to the VSEPR theory, the geometry of a molecule is determined by the number of electron-pairs around the central atom. So, to use this theory for predicting the shapes of molecules count the number of electron pairs (both, shared and lone pairs).

The use of this theory in predicting the shapes of molecules is explained below by taking a typical molecule of the type AB_n, where A is the central atom, B atoms are bonded to A by single electron pair bonds (single covalent bonds), and n is the number of B atoms bonded to one atom of A.

For the sake of easier understanding, molecules have been divided into various categories.

Applications of VSEPR Theory

1. AB_2 Type or Shape of Molecules containing two electron pairs around central atom. In case there are two electron pairs around the central atom in a molecule, the only way to keep them as far apart as possible is to arrange them at an angle of 180° to each other. In these cases the molecule will acquire linear geometry. For example, in case of BeF_2, beryllium (Z = 4, $1s^2\ 2s^2$) atom has two electrons in the valence shell, in the formation of BeF_2, each of these valence electrons is shared by two F atoms. Thus, Be atom is surrounded by two bond pairs and its geometry is linear and the bond angle is 180°.

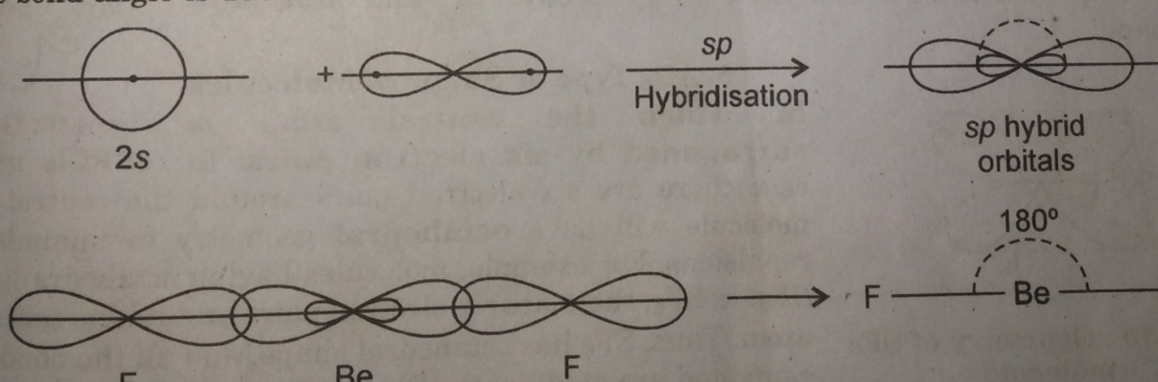

Fig. 4.6

Other examples $BeCl_2$, $ZnCl_2$, $HgCl_2$ have same shape.

2. AB_3 Type or Shape of Molecules in which central atom is surrounded by three electron pairs. In the molecules of the type AB_3 the central atom is surrounded by three shared pairs of electrons and the three atoms bonded to the central atom are similar. In such a case the most suitable arrangement involving minimum possible energy is the **triangular planar** geometry in which the three atoms bonded to the central atom are placed at the corners of an equilateral triangle while the central atom is at the centre of the triangle as shown in the molecule of BCl_3. Each Cl—B—Cl bond angle is 120° (Fig. 4.7).

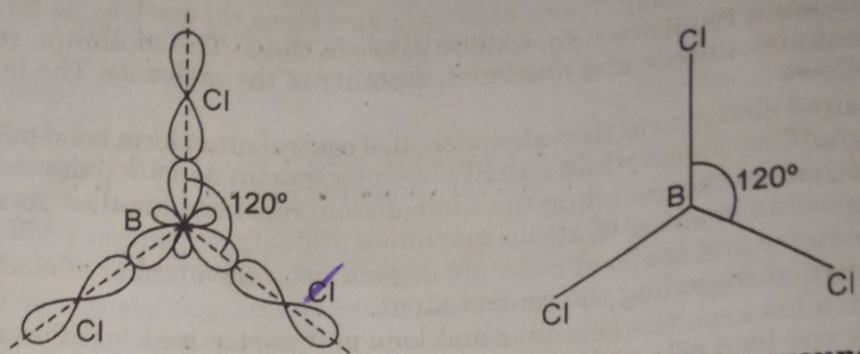

Fig. 4.7 : Shape of BCl_3 molecule having three electrons pairs around Be atom

Central B atom (Z = 5, $1s^2\ 2s^2\ 2p^1$) has three valence electrons, each of these is shared by three Cl atoms. Thus central B atom is surrounded by three bond pairs.

Other molecules having trigonal planar geometry are BH_3, BF_3, $AlCl_3$, etc.

3. AB_4 Type or Shape of Molecules in which central atom is surrounded by four electron pairs. In case there are four electron pairs around the central atom, the molecule acquires **tetrahedral** geometry. For example, in methane molecule the central carbon atom has four valence electrons. These electrons are shared mutually with four hydrogen atoms to form four C—H bonds (bond pairs).

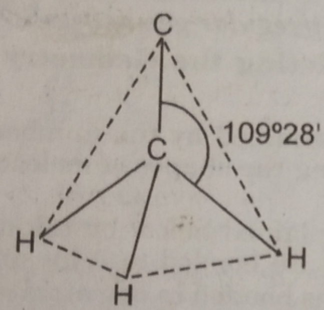

Fig. 4.8 : Shape of CH_4 molecule having four electron pairs around C-atom

The four bond pairs acquire tetrahedral geometry as shown in Fig. 4.8. In this geometry all the H – C – H bond angles are 109°28′.

SiF_4, CCl_4, NH_4^+ and BF_4^- also have four electron pairs around the central atom and thus, have tetrahedral geometry.

4. AB_5 Type or Shape of Molecules in which central atom is surrounded by five electron pairs. In case there are five electron pairs around the central atom, the molecule has **trigonal bipyramidal** shape. For example, in PCl_5, there are five electron pairs around the central phosphorus atom and so it has trigonal bipyramidal shape as shown in Fig. 4.9. In this type, all the bond angles are unequal. Three electron pairs are in the same plane at an angle of 120°, while other two are perpendicular to the plane. Thus, in this arrangement, three bond angles are of 120° each and two are of 90° each and this makes PCl_5 very reactive. PF_5 and $SbCl_5$ have same shape.

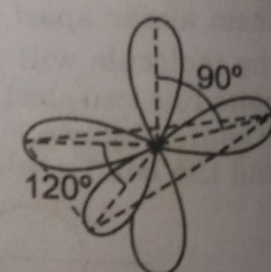

Fig. 4.9 : Geometry of PCl_5 molecule

5. AB_6 Type or Shape of Molecules in which the central atom is surrounded by six electron pairs. In case there are six electron pairs around the central atom, the molecule will have **octahedral** geometry to minimise electron repulsions. For example, molecules having octahedral geometry is SF_6. In SF_6, there are six electron pairs around the central sulphur atom. Thus, SF_6 has octahedral shape, and all the bond angles are same and are of 90° each (Fig. 4.10).

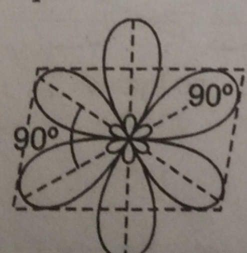

Fig. 4.10 : Geometry of SF_6 molecule

Geometry and Shapes of Molecules containing Lone Pairs and Bond Pairs

Shape of ammonia molecule. In ammonia molecule the central nitrogen atom has five electrons in the valence shell ($1s^2\ 2s^2\ 2p^3$). Three of these electrons are mutually shared with three hydrogen atoms to form three N—H bonds as shown in Fig. 4.11.

Thus, there are four electron pairs (3 bond pairs and one lone pair) around nitrogen atom. The arrangement of these electron pairs is tetrahedral. The presence of lone pair in the geometry of the molecule. The lone pair exerts greater repulsive interaction and therefore, the three N—H bonds move slightly closer thereby decreasing the H—N—H angle from normal 109.5° to 107°.

The shape of ammonia molecules is considered to be pyramidal with three H-atoms occupying the triangular base of the pyramid and N-atom lying at the apex, as shown in Fig. 4.11

Other examples having pyramidal shape are PH_3, PCl_3, NF_3, H_3O^+, etc. However, the bond angles are different as compared to the bond angle of ammonia.

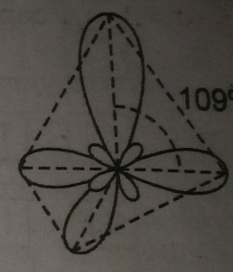

Fig. 4.11 : Shape of ammonia molecule

Shape of water molecule. In H_2O, the central atom oxygen (Z = 8) has the configuration $1s^2\,2s^2\,2p^4$ in the ground state having six valence electrons. While forming water molecule two of these electrons are mutually shared with two hydrogen atoms to form two O—H bonds as shown in Fig. 4.12.

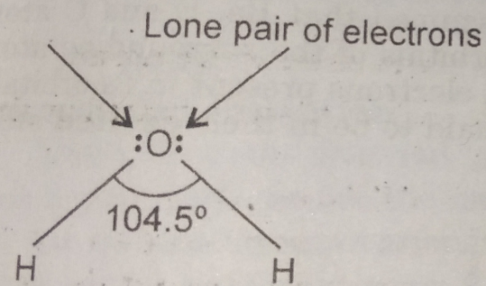

Fig. 4.12 : Shape of water

Hence, there are four electron pairs, two lone pairs and two bond pairs around oxygen atom. These four electron pairs acquire tetrahedral arrangement. The presence of two lone pairs causes distortion in the geometry of the molecule. The lone pairs repel the bond pairs which brings about the decrease of H—O—H bond angle from 109.5° to 104.5°. Water molecule has a **bent or V-shape** as shown in the Fig. 4.12.

Other examples of compounds having bent geometry are H_2S, H_2Se and H_2Te. However, the bond angles are different as compared to the bond angles in case of water.

11.4 LIMITATIONS OF VSEPR THEORY

VSEPR Theory has been well used because of its high degree of accuracy, but this theory has some limitations as follows :

(*i*) This theory can not be applied to complex covalent molecules.

(*ii*) It cannot be used for ionic compounds.

(*iii*) VSEPR theory cannot predict the shapes of transition metal complexes.

(*iv*) This theory treats all electrons of the valence shell alike even if they belong to *s,p,d* or *f* subshell which does not seem to be a correct assumption.