7.4: Molecules with Lone Pairs

The VSEPR theory is able to explain and predict the shapes of molecules which contain lone pairs. In such a case the lone pairs as well as the bonding pairs are considered to repel and avoid each other. For example, since there are two bonds in the $SnCl_2$ molecule, one might expect it to be linear like $BeCl_2$. If we draw the Lewis diagram, though, we find a *lone pair* as well as two bonding pairs in the valence shell of the Sn atom:

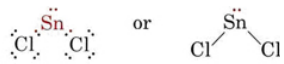
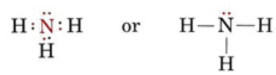


Figure 7.4.1.

Lewis diagram of S n C l 2 shows that are one lone pair on the valence of S n. Two pairs are shared with 2 C l.

A lone pair also affects the structure of ammonia, NH_3. Since this molecule obeys the octet rule, the N atom is surrounded by *four* electron pairs:



Lewis diagram of N H 3 shows that are one lone pair on the valence of N. Three pairs are shared with three H.

If these pairs were all equivalent, we would expect the angle between them to be the regular tetrahedral angle of 109.5°. Experimentally, the angle is found to be somewhat less, namely, 107°. Again this is because the lone pair is “fatter” than the bonding pairs and able to squeeze them closer together.

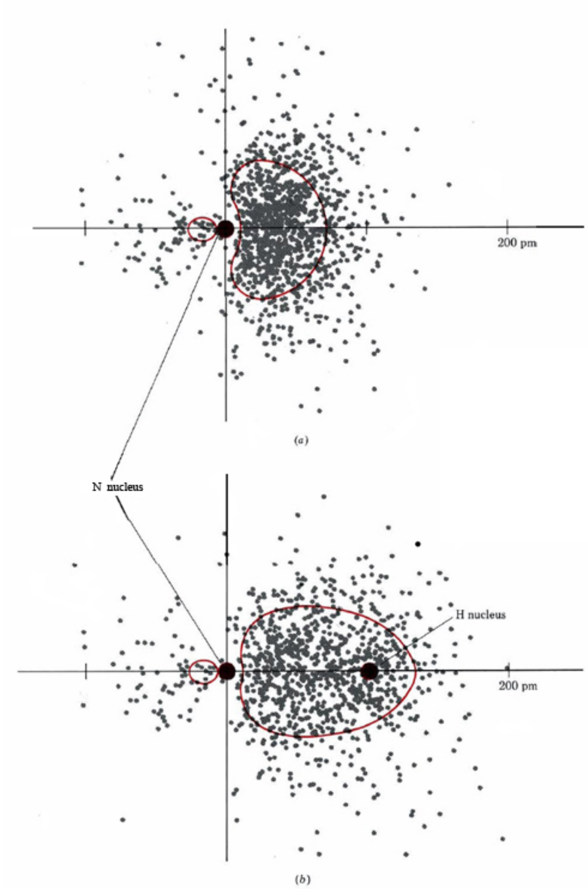


Figure 7.4.2: Comparison of the electron clouds of a lone pair and a bonding pair. (a) The lone pair of electrons on the nitrogen in an ammonia molecule. (b) One of the three bonding pairs of electrons in the ammonia molecule. Boundary lines that enclose equal percentages of each electron cloud have been drawn. Note that the lone pair (a) takes up more space (is "fatter") near the nitrogen nucleus than the bonding pair (b).

A. A nitrogen nucleus is shown as a small black circle in the center of a vertical and horizontal axis. A relatively large region to the right of the nucleus is tightly packed with black dots. Diagram B shows a similar nitrogen nucleus in the center. Another black circle representing a hydrogen nucleus is found to the right of the nitrogen nucleus. Between the two nucleus is a region of highly concentrated black dots. This region is more spread out relative to the region in diagram A.

The electronic structure of the H_2O molecule is similar to that of NH_3 except that one bonding pair has been replaced by a lone pair:

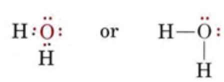


Figure 7.4.3. Again, because of their frequent occurrence, it is wise to commit these to memory. Note in particular that the shape of a molecule is described in terms of the geometry of the *nuclei* and not of the electron clouds. For example, the shape of the NH_3 molecule is described as a *trigonal pyramid* since the N nucleus forms the apex of a pyramid, slightly above an equilateral triangle of H nuclei. Although the electron-pair clouds are arranged in an approximate tetrahedron around the N nucleus, it is incorrect to describe the molecular shape as tetrahedral. The atomic *nuclei* are not at the corners of a tetrahedron.

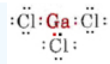
Lewis diagram of H 2 O shows that there are two lone pairs on the valence of O. Two pairs are shared with two H.

✔ Example 7.4.1 : Molecular Geometry

Sketch and describe the geometry of the following molecules: (a) $GaCl_3$, (b) $AsCl_3$, and (c) $AsOCl_3$.

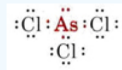
Solution

a) Since the element gallium belongs to group III, it has three valence electrons. The Lewis diagram for $GaCl_3$ is thus



Since there are three bonding pairs and no lone pairs around the Ga atom, we conclude that the three Cl atoms are arranged *trigonally* and that all four atoms are in the same plane.

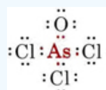
b) Arsenic belongs to group V and therefore has five valence electrons. The Lewis structure for $AsCl_3$ is thus



Central "A" "s" atom sharing three pairs of electrons with three chlorine atoms. There is a lone pair of electrons remaining on the "A" "s".

Since a lone pair is present, the shape of this molecule is a trigonal pyramid, with the As nucleus a little above an equilateral triangle of Cl nuclei.

c) The Lewis diagram for $AsOCl_3$ is similar to that of $AsCl_3$.



Central "A" "s" atom shares three pairs of electrons with three "C" "L" atoms. It also shares one pair of electron with an "O" atom.

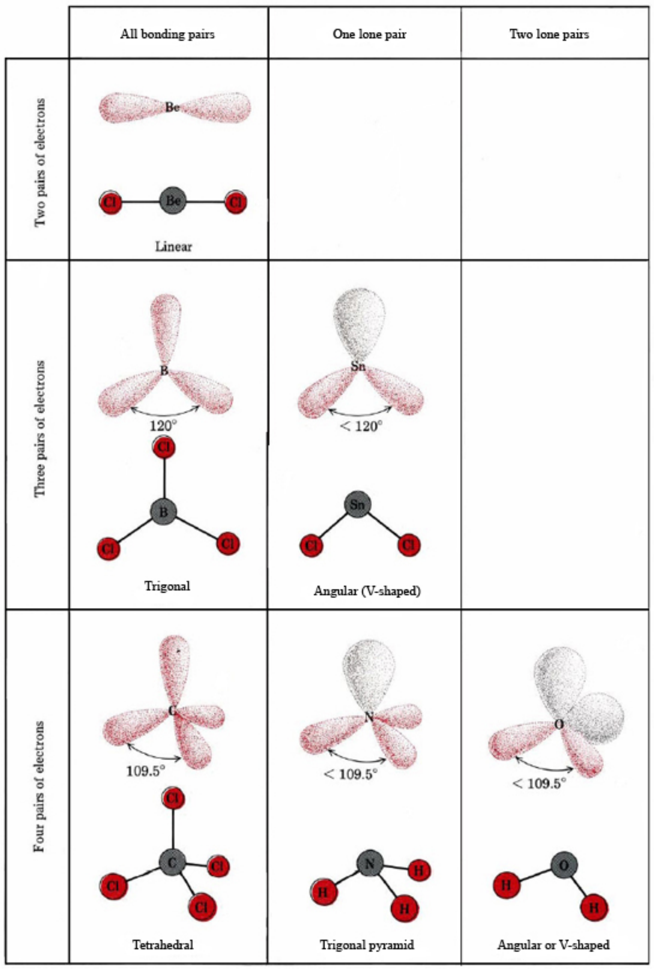
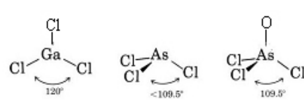


Figure 7.4.4 : The arrangement of electron pairs and the shapes of molecules which contain lone pairs. Bonding pairs are indicated in color and have purposely been made very thin for diagrammatic effect. Lone pairs are indicated in gray. Note that the geometry of these molecules is described in terms of the nuclei and not of the electron pairs; it is described in terms of the ball-and-stick diagrams shown in the figure.

Table shows geometry of a molecule based on the number of pairs of electrons and the number of lone pairs. Two pairs of electrons with all bonding pairs creates a linear geometry. Three pairs of electrons with all bonding pairs has a trigonal shape. Three pairs of electrons with one lone pair is angular or "V" shaped. Four pairs of electrons with all bonding pairs, one lone pair, and two lone pairs has shapes of tetrahedral, trigonal pyramid, and "V" shaped respectively.

Since there are four bonding pairs, the molecule is tetrahedral. Sketches of each of these molecules are



Sketches shows that the geometry of "G" "a" "c" "l" 3, "A" "s" "c" "l" 3, and "A" "s" "O" "C" "L" 3, are trigonal, trigonal pyramid, and tetrahedral respectively.

The VSEPR theory can also be applied to molecules which contain five and six pairs of valence electrons, some of which are lone pairs. We have not included such species here because the majority of compounds fall into the categories we have described.