Pearson

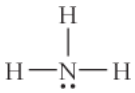
5.8: VSEPR Theory: The Effect of Lone Pairs

Key Concept Video **VSEPR Theory: The Effect of Lone Pairs**

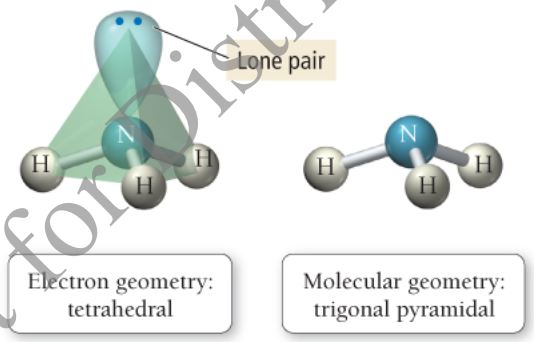
Each of the examples we looked at in Section 5.7 had only bonding electron groups around the central atom. What happens in molecules that have lone pairs around the central atom as well? The lone pairs also repel other electron groups, as we see in the examples that follow.

Four Electron Groups with Lone Pairs

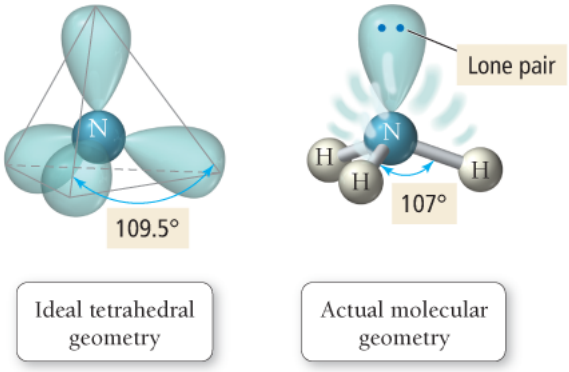
Consider the Lewis structure of ammonia:



The central nitrogen atom has four electron groups (one lone pair and three bonding pairs) that repel each other. If we do not distinguish between bonding electron groups and lone pairs, we find that the **electron geometry**—the geometrical arrangement of the *electron groups*—is still tetrahedral, as we expect for four electron groups. However, the **molecular geometry**—the geometrical arrangement of the atoms—is **trigonal pyramidal**, as shown here:



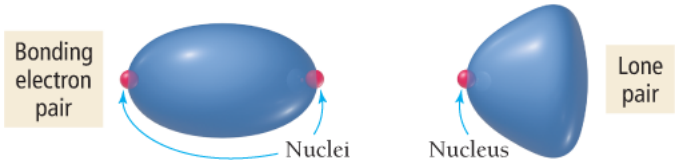
Notice that although the electron geometry and the molecular geometry are different, *the electron geometry is relevant to the molecular geometry*. The lone pair exerts its influence on the bonding pairs.



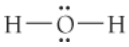
As we noted previously, different kinds of electron groups generally result in different amounts of repulsion. Lone pair electrons generally exert slightly greater repulsions than bonding electrons. If all four electron groups in NH_3 exerted equal repulsions on one another, the bond angles in the molecule would all be the ideal tetrahedral angle, 109.5°. However, the actual angle between N–H bonds in ammonia is slightly smaller, 107°. A lone electron pair is more spread out in space than a bonding electron pair because a lone pair is attracted to only one nucleus while a bonding pair is attracted to two (Figure 5.9). The lone pair occupies more of the angular space around a nucleus, exerting a greater repulsive force on neighboring electrons and compressing the N–H bond angles.

Figure 5.9 Nonbonding versus Bonding Electron Pairs

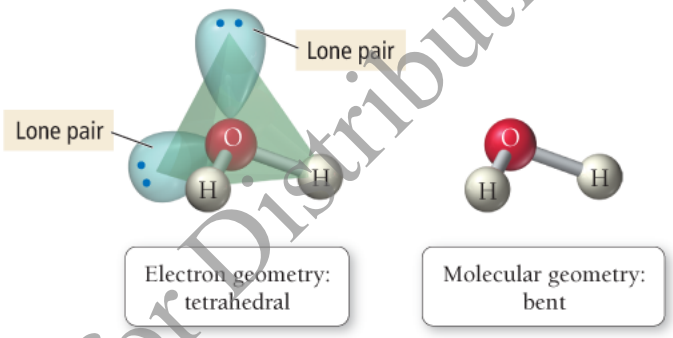
A lone electron pair occupies more angular space than a bonding pair.



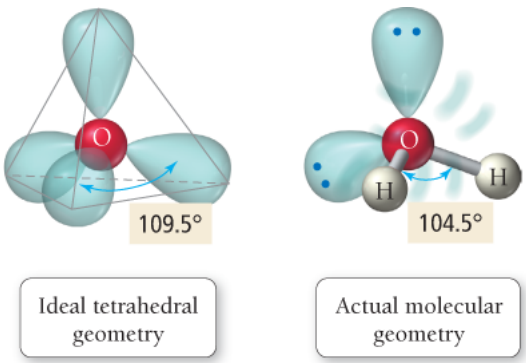
We see a similar effect in water. The Lewis structure of water has two bonding pairs and two lone pairs:



Since it has four electron groups, water's *electron geometry* is tetrahedral (like that of ammonia), but its *molecular geometry* is **bent**.



As in NH_3, the bond angles in H_2O are smaller (104.5°) than the ideal tetrahedral bond angles because of the greater repulsion exerted by the lone pair electrons. The bond angle in H_2O is even smaller than that in NH_3 because H_2O has *two* lone pairs of electrons on the central oxygen atom. These lone pairs compress the H_2O bond angle to a greater extent than in NH_3:



In general, electron group repulsions vary as follows:

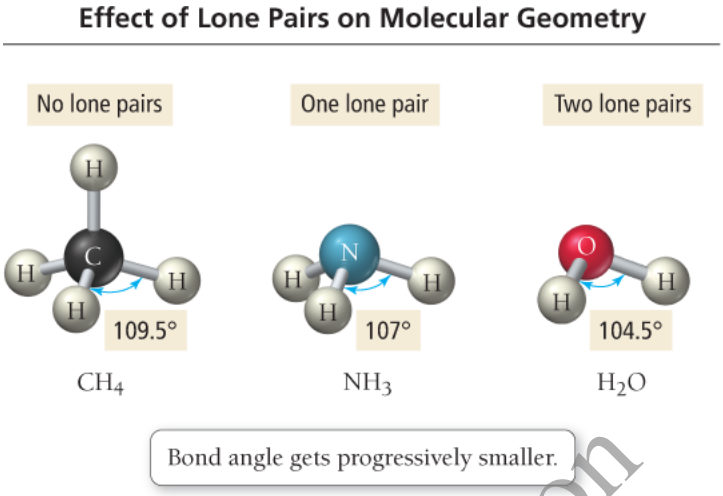
Lone pair – lone pair > Lone pair – bonding pair > Bonding pair – bonding pair

Lone pair—lone pair > Lone pair—bonding pair > Bonding pair—bonding pair
Most repulsive Least repulsive

We see the effects of this ordering in the progressively smaller bond angles of CH_4, NH_3, and H_2O, as shown in Figure 5.10. The relative ordering of repulsions also helps to determine the geometry of molecules with five and six electron groups when one or more of those groups are lone pairs.

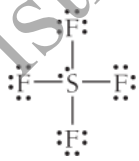
Figure 5.10 The Effect of Lone Pairs on Molecular Geometry

The bond angles get progressively smaller as the number of lone pairs on the central atom increases from zero in CH_4 to one in NH_3 to two in H_2O.

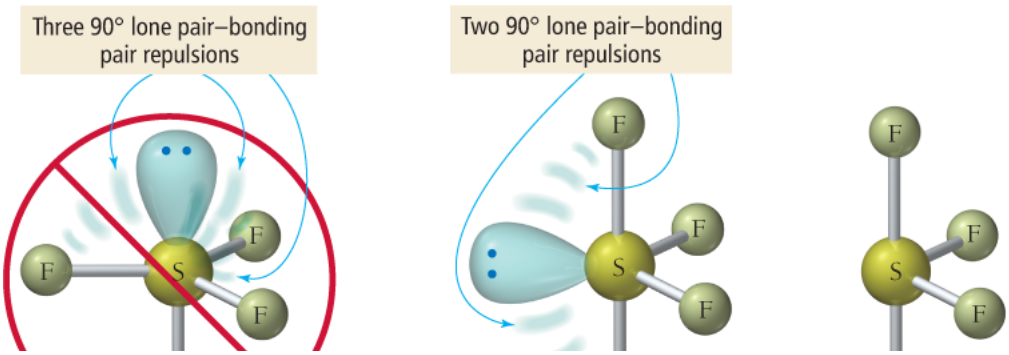


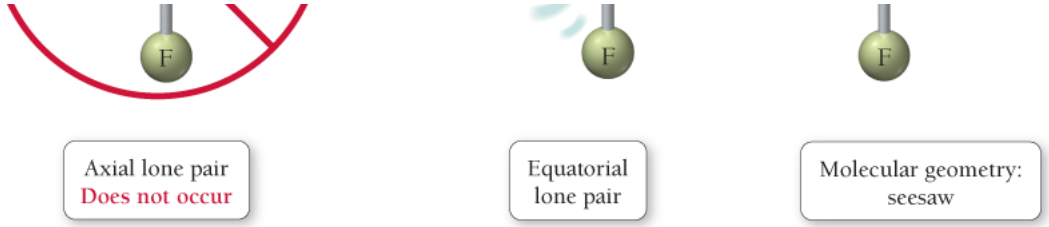
Five Electron Groups with Lone Pairs

Consider the Lewis structure of SF_4:



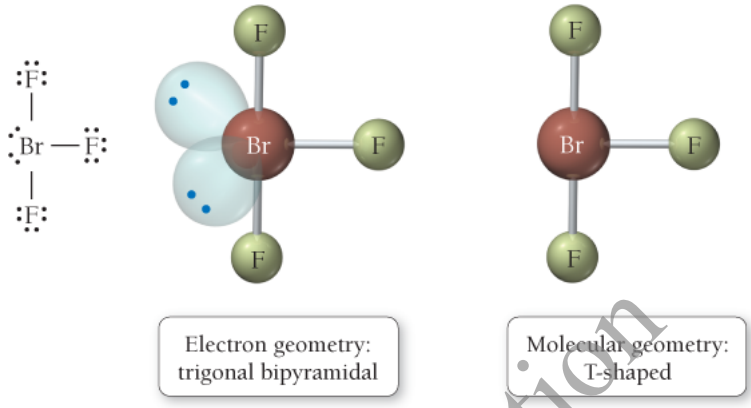
The central sulfur atom has five electron groups (one lone pair and four bonding pairs). The *electron geometry*, due to the five electron groups, is trigonal bipyramidal. In determining the molecular geometry, notice that the lone pair could occupy either an equatorial position or an axial position within the trigonal bipyramidal electron geometry. Which position is more favorable? To answer this question, we must consider that, as we have just seen, lone pair–bonding pair repulsions are greater than bonding pair–bonding pair repulsions. Therefore, the lone pair occupies the position that minimizes its interaction with the bonding pairs. If the lone pair were in an axial position, it would have three 90° interactions with bonding pairs. In an equatorial position, however, the lone pair has only two 90° interactions. Consequently, the lone pair occupies an equatorial position. The resulting molecular geometry is called **seesaw** because it resembles a seesaw (or teeter-totter).



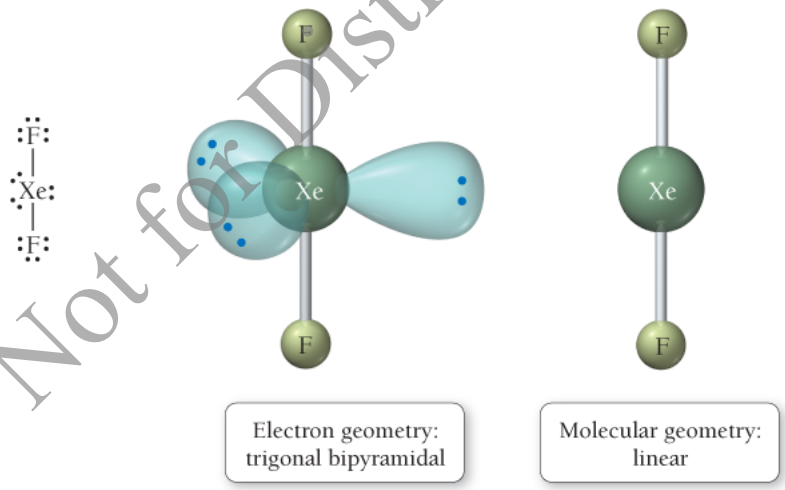


The seesaw molecular geometry is sometimes called an *irregular tetrahedron*.

When two of the five electron groups around the central atom are lone pairs, as in BrF_3, the lone pairs occupy two of the three equatorial positions—again minimizing 90° interactions with bonding pairs and also avoiding a lone pair–lone pair 90° repulsion. The resulting molecular geometry is **T-shaped**.

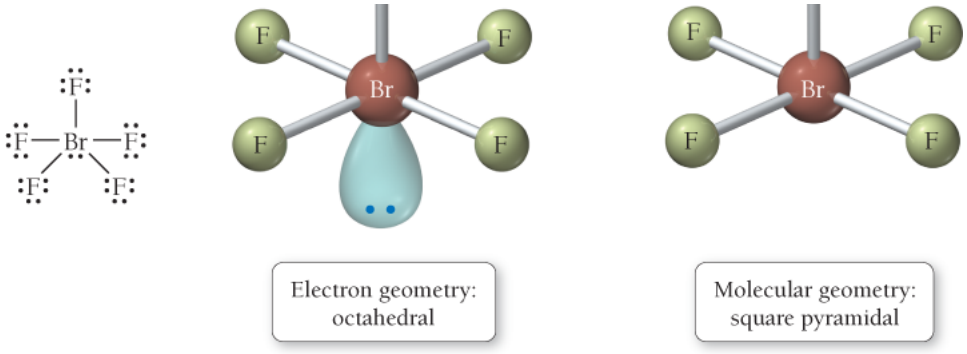


When three of the five electron groups around the central atom are lone pairs, as in XeF_2, the lone pairs occupy all three of the equatorial positions and the resulting molecular geometry is linear.

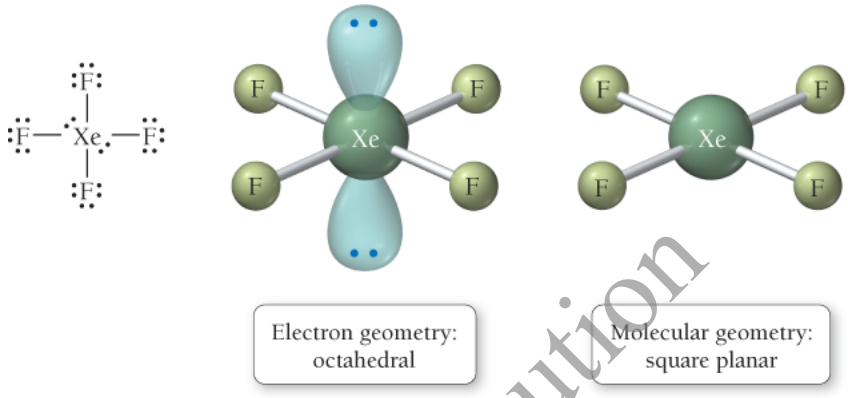


Six Electron Groups with Lone Pairs

The Lewis structure of BrF_5 is shown here. The central bromine atom has six electron groups (one lone pair and five bonding pairs). The electron geometry, due to the six electron groups, is octahedral. Since all six positions in the octahedral geometry are equivalent, the lone pair can be situated in any one of these positions. The resulting molecular geometry is **square pyramidal**.



When two of the six electron groups around the central atom are lone pairs, as in XeF_4, the lone pairs occupy positions across from one another (to minimize lone pair–lone pair repulsions). The resulting molecular geometry is **square planar**.



Conceptual Connection 5.7 Lone Pair Electrons and Molecular Geometry

Summarizing VSEPR Theory:

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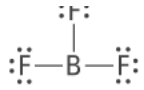
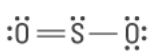
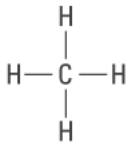
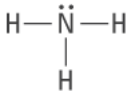
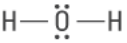
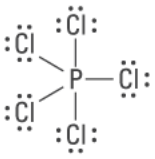
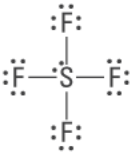
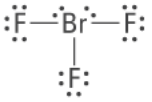
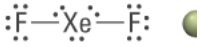
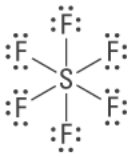
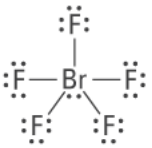
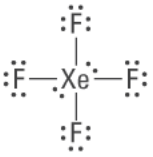
- The geometry of a molecule is determined by the number of electron groups on the central atom (or on each interior atom, if there is more than one).
- The number of electron groups is determined from the Lewis structure of the molecule. If the Lewis structure contains resonance structures, we can use any one of the resonance structures to determine the number of electron groups.
- Each of the following counts as a single electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron.
- The geometry of the electron groups is determined by their repulsions as summarized in Table 5.5. In general, electron group repulsions vary in relative ordering of repulsions as follows:

Lone pair—lone pair > Lone pair—bonding pair > Bonding pair—bonding pair

- Bond angles can vary from the idealized angles because double and triple bonds occupy more space than single bonds (they are bulkier even though they are shorter), and lone pairs occupy more space than bonding groups. The presence of lone pairs usually makes bond angles smaller than the ideal angle for the particular geometry.

Table 5.5 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	Exam
2	2	0	Linear	Linear	180°	:Ö=C=Ö:

3	3	0	Trigonal planar	Trigonal planar	120°	
3	2	1	Trigonal planar	Bent	<120°	
4	4	0	Tetrahedral	Tetrahedral	109.5°	
4	3	1	Tetrahedral	Trigonal pyramidal	<109.5°	
4	2	2	Tetrahedral	Bent	<109.5°	
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal	120° (equatorial) 90° (axial)	
5	4	1	Trigonal bipyramidal	Seesaw	<120° (equatorial) <90° (axial)	
5	3	2	Trigonal bipyramidal	T-shaped	<90°	
5	2	3	Trigonal bipyramidal	Linear	180°	
6	6	0	Octahedral	Octahedral	90°	
6	5	1	Octahedral	Square pyramidal	<90°	
6	4	2	Octahedral	Square planar	90°	

*Count only electron groups around the central atom. Each of the following is considered one electron group: a lone pair, a single b
a triple bond, or a single electron.

Conceptual Connection 5.8 **Molecular Geometry and Electron Group Repulsions**

Interactive