

MOLECULAR GEOMETRY AND ELECTRON DOMAIN THEORY

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Abstract

Molecular Geometry and Electron Domain Theory

1 Foundation

We begin by assuming a **Lewis structure model** for chemical bonding based on valence shell electron pair sharing and the octet rule. We thus assume the nuclear structure of the atom, and we further assume the existence of a valence shell of electrons in each atom which dominates the chemical behavior of that atom. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. A number of atoms, including C, N, O, P, and S, can form double or triple bonds as needed to complete an octet. We know that double bonds are generally stronger and have shorter lengths than single bonds, and triple bonds are stronger and shorter than double bonds.

2 Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. The relationship between bonding, structure, and properties is comparatively simple in **diatomic** molecules, which contain two atoms only, *e.g.* HCl or O_2 . A **polyatomic** molecule contains more than two atoms. An example of the complexities which arise with polyatomic molecules is molecular geometry: how are the atoms in the molecule arranged with respect to one another? In a diatomic molecule, only a single molecular geometry is possible since the two atoms must lie on a line. However, with a triatomic molecule (three atoms), there are two possible geometries: the atoms may lie on a line, producing a linear molecule, or not, producing a bent molecule. In molecules with more than three atoms, there are many more possible geometries. What geometries are actually observed? What determines which geometry will be observed in a particular molecule? We seek a model which allows us to understand the observed geometries of molecules and thus to predict these geometries.

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Once we have developed an understanding of the relationship between molecular structure and chemical bonding, we can attempt an understanding of the relationship of the structure and bonding in a polyatomic molecule to the physical and chemical properties we observe for those molecules.

3 Observation 1: Geometries of molecules

The geometry of a molecule includes a description of the arrangements of the atoms in the molecule. At a simple level, the molecular structure tells us which atoms are bonded to which. At a more detailed level, the geometry includes the lengths of all of these bonds, that is, the distances between the atoms which are bonded together, and the angles between pairs of bonds. For example, we find that in water, H_2O , the two hydrogens are bonded to the oxygen and each O-H bond length is 95.72pm (where $1\text{pm} = 10^{-12}\text{m}$). Furthermore, H_2O is a bent molecule, with the H-O-H angle equal to 104.5° . (The measurement of these geometric properties is difficult, involving the measurement of the frequencies at which the molecule rotates in the gas phase. In molecules in crystalline form, the geometry of the molecule is revealed by irradiating the crystal with x-rays and analyzing the patterns formed as the x-rays diffract off of the crystal.)

Not all triatomic molecules are bent, however. As a common example, CO_2 is a linear molecule. Larger polyatomics can have a variety of shapes, as illustrated in Figure 1. Ammonia, NH_3 , is a pyramid-shaped molecule, with the hydrogens in an equilateral triangle, the nitrogen above the plane of this triangle, and a H-N-H angle equal to 107° . The geometry of CH_4 is that of a tetrahedron, with all H-C-H angles equal to 109.5° . (See also Subfigure 2(a).) Ethane, C_2H_6 , has a geometry related to that of methane. The two carbons are bonded together, and each is bonded to three hydrogens. Each H-C-H angle is 109.5° and each H-C-C angle is 109.5° . By contrast, in ethene, C_2H_4 , each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° . All six atoms of ethene lie in the same plane. Thus, ethene and ethane have very different geometries, despite the similarities in their molecular formulae.

We begin our analysis of these geometries by noting that, in the molecules listed above which do *not* contain double or triple bonds (H_2O , NH_3 , CH_4 and C_2H_6), the bond angles are very similar, each equal to or very close to the tetrahedral angle 109.5° . To account for the observed angle, we begin with our valence shell electron pair sharing model, and we note that, in the Lewis structures of these molecules, the central atom in each bond angle of these molecules contains four pairs of valence shell electrons. For methane and ethane, these four electron pairs are all shared with adjacent bonded atoms, whereas in

ammonia or water, one or two (respectively) of the electron pairs are not shared with any other atom. These unshared electron pairs are called **lone pairs**. Notice that, in the two molecules with no lone pairs, all bond angles are *exactly* equal to the tetrahedral angle, whereas the bond angles are only close in the molecules with lone pairs

One way to understand this result is based on the mutual repulsion of the negative charges on the valence shell electrons. Although the two electrons in each bonding pair must remain relatively close together in order to form the bond, different pairs of electrons should arrange themselves in such a way that the distances between the pairs are as large as possible. Focusing for the moment on methane, the four pairs of electrons must be equivalent to one another, since the four C-H bonds are equivalent, so we can assume that the electron pairs are all the same distance from the central carbon atom. How can we position four electron pairs at a fixed distance from the central atom but as far apart from one another as possible? A little reflection reveals that this question is equivalent to asking how to place four points on the surface of a sphere spread out from each other as far apart as possible. A bit of experimentation reveals that these four points must sit at the corners of a tetrahedron,

Molecular Structures

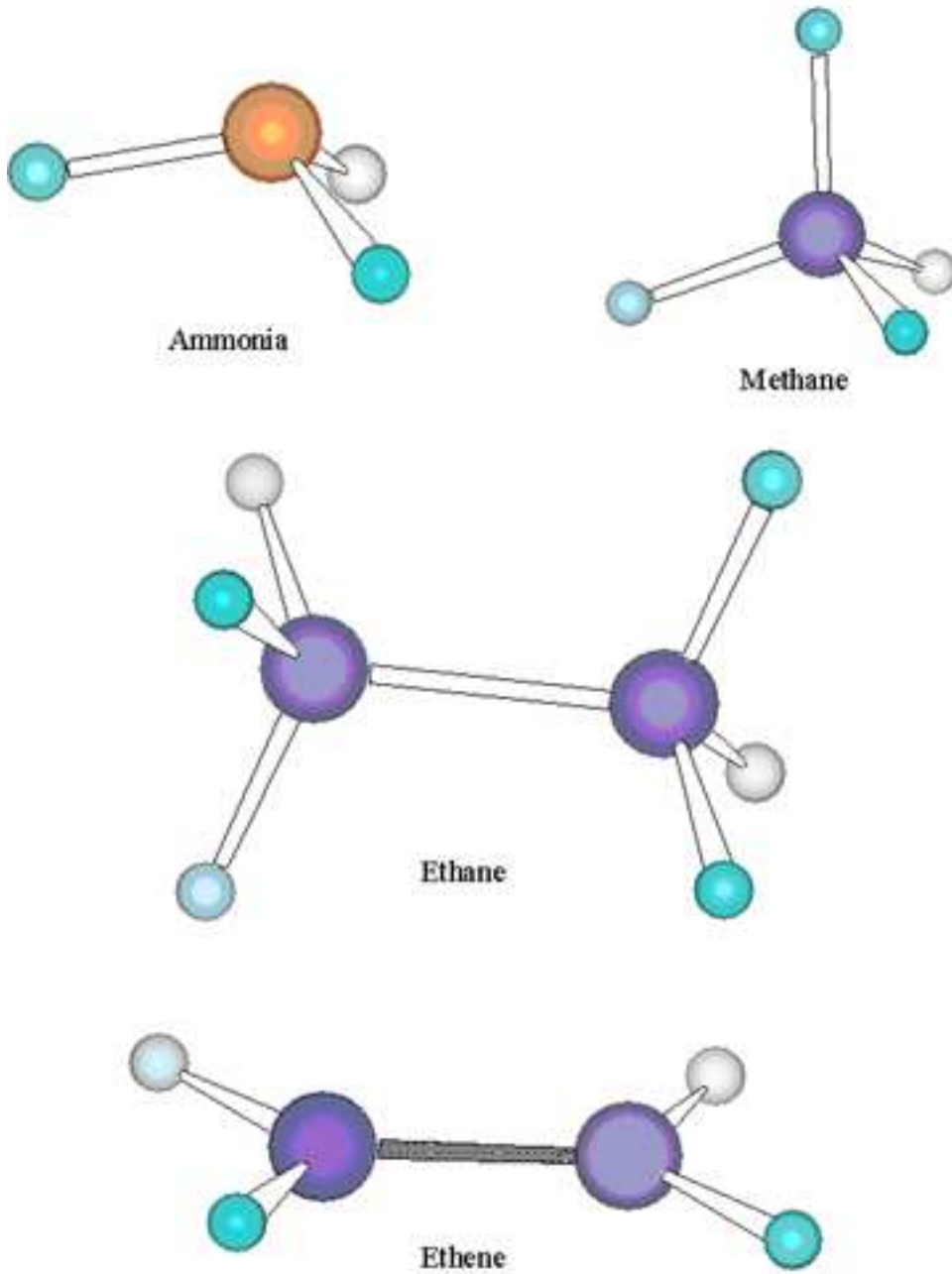


Figure 1

an equilateral triangular pyramid, as may be seen in Subfigure 2(b) . If the carbon atom is at the center of this tetrahedron and the four electron pairs are placed at the corners, then the hydrogen atoms also form a tetrahedron about the carbon. This is, as illustrated in Subfigure 2(a) , the correct geometry of a methane molecule. The angle formed by any two corners of a tetrahedron and the central atom is 109.5° , exactly in agreement with the observed angle in methane. This model also works well in predicting the bond angles in ethane.

We conclude that molecular geometry is determined by minimizing the mutual repulsion of the valence shell electron pairs. As such, this model of molecular geometry is often referred to as the **valence shell electron pair repulsion (VSEPR) theory** . For reasons that will become clear, extension of this model implies that a better name is the **Electron Domain (ED) Theory** .

This model also accounts, at least approximately, for the bond angles of H_2O and NH_3 . These molecules are clearly not tetrahedral, like CH_4 , since neither contains the requisite five atoms to form the tetrahedron. However, each molecule does contain a central atom surrounded by four pairs of valence shell electrons. We expect from our Electron Domain model that those four pairs should be arrayed in a tetrahedron, without regard to whether they are bonding or lone-pair electrons. Then attaching the hydrogens (two for oxygen, three for nitrogen) produces a prediction of bond angles of 109.5° , very close indeed to the observed angles of 104.5° in H_2O and 107° in NH_3 .

Note, however, that we do not describe the geometries of H_2O and NH_3 as "tetrahedral," since the *atoms* of the molecules do not form tetrahedrons, even if the valence shell electron pairs do. (It is worth noting that these angles are not exactly equal to 109.5° , as in methane. These deviations will be discussed later (Section 5).)

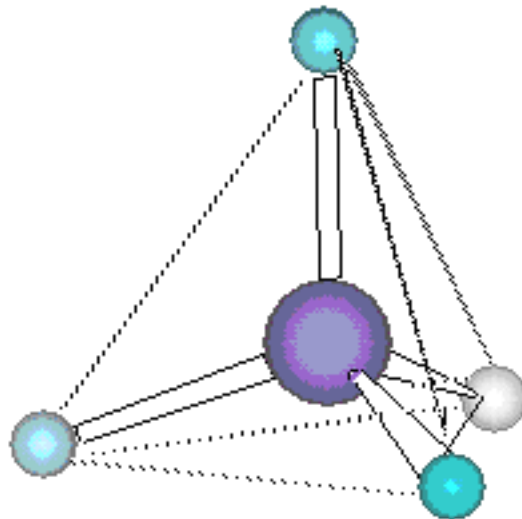
We have developed the Electron Domain model to this point only for geometries of molecules with four pairs of valence shell electrons. However, there are a great variety of molecules in which atoms from Period 3 and beyond can have more than an octet of valence electrons. We consider two such molecules illustrated in Figure 3.

First, PCl_5 is a stable gaseous compound in which the five chlorine atoms are each bonded to the phosphorous atom. Experiments reveal that the geometry of PCl_5 is that of a **trigonal bipyramid** : three of the chlorine atoms form an equilateral triangle with the P atom in the center, and the other two chlorine atoms are on top of and below the P atom. Thus there must be 10 valence shell electrons around the phosphorous atom. Hence, phosphorous exhibits what is called an **expanded valence** in PCl_5 . Applying our Electron Domain model, we expect the five valence shell electron pairs to spread out optimally to minimize their repulsions. The required geometry can again be found by trying to place five points on the surface of a sphere with maximum distances amongst these points. A little experimentation reveals that this can be achieved by placing the five points to form a trigonal bipyramid. Hence, Electron Domain theory accounts for the geometry of PCl_5 .

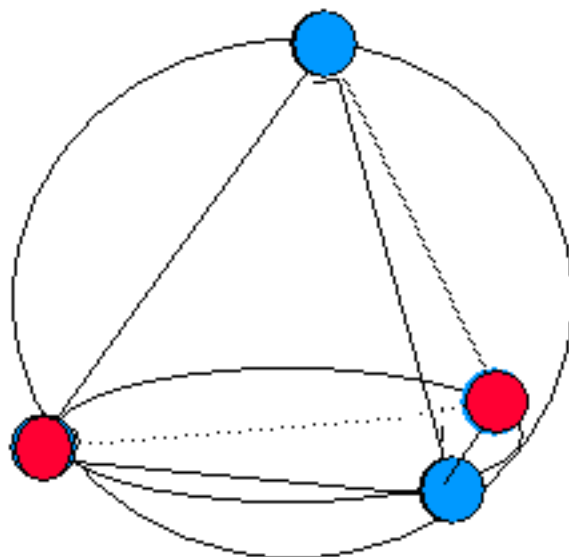
Second, SF_6 is a fairly unreactive gaseous compound in which all six fluorine atoms are bonded to the central sulfur atom. Again, it is clear that the octet rule is violated by the sulfur atom, which must therefore have an expanded valence. The observed geometry of SF_6 , as shown in Figure 3, is highly symmetric: all bond lengths are identical and all bond angles are 90° . The F atoms form an **octahedron** about the central S atom: four of the F atoms form a square with the S atom at the center, and the other two F atoms are above and below the S atom. To apply our Electron Domain model to understand this geometry, we must place six points, representing the six electron pairs about the central S atom, on the surface of a sphere with maximum distances between the points. The requisite geometry is found, in fact, to be that of an octahedron, in agreement with the observed geometry.

As an example of a molecule with an atom with less than an octet of valence shell electrons, we consider boron trichloride, BCl_3 . The geometry of BCl_3 is also given in

Tetrahedral Structure of Methane



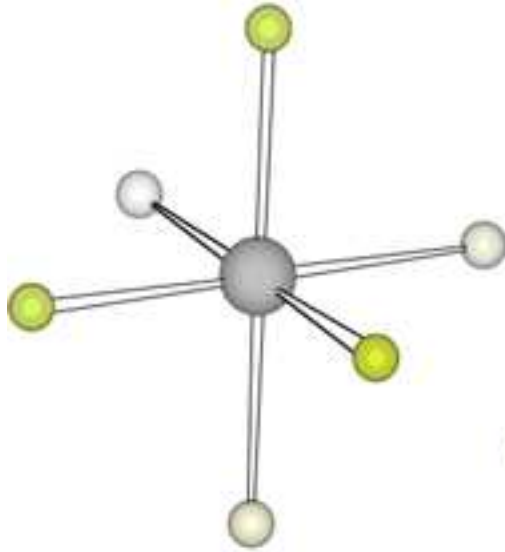
(a)



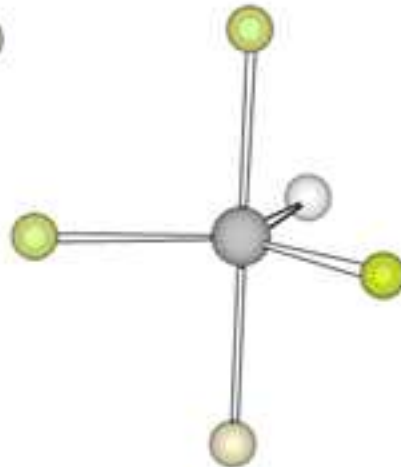
(b)

Figure 2: (a) The dotted lines illustrate that the hydrogens form a tetrahedron about the carbon atom. (b) The same tetrahedron is formed by placing four points on a sphere as far apart from one another as possible.

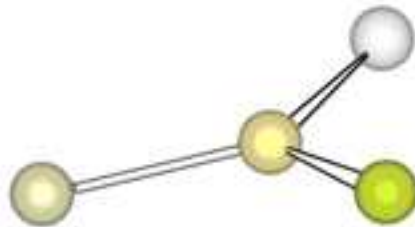
More Molecular Structures



Sulfur Hexafluoride



Phosphorous Pentachloride



Boron Trichloride

Figure 3

Figure 3: it is **trigonal planar**, with all four atoms lying in the same plane, and all Cl-B-Cl bond angles equal to 120° . The three Cl atoms form an equilateral triangle. The Boron atom has only three pairs of valence shell electrons in $B\text{Cl}_3$. In applying Electron Domain theory to understand this geometry, we must place three points on the surface of a sphere with maximum distance between points. We find that the three points form an equilateral triangle in a plane with the center of the sphere, so Electron Domain is again in accord with the observed geometry.

We conclude from these predictions and observations that the Electron Domain model is a reasonably accurate way to understand molecular geometries, even in molecules which violate the octet rule.

4 Observation 2: Molecules with Double or Triple Bonds

In each of the molecules considered up to this point, the electron pairs are either in single bonds or in lone pairs. In current form, the Electron Domain model does *not* account for the observed geometry of C_2H_4 , in which each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° and all six atoms lie in the same plane. Each carbon atom in this molecule is surrounded by four pairs of electrons, all of which are involved in bonding, *i.e.* there are no lone pairs. However, the arrangement of these electron pairs, and thus the bonded atoms, about each carbon is not even approximately tetrahedral. Rather, the H-C-H and H-C-C bond angles are much closer to 120° , the angle which would be expected if *three* electron pairs were separated in the optimal arrangement, as just discussed for $B\text{Cl}_3$.

This observed geometry can be understood by re-examining the Lewis structure. Recall that, although there are four electron pairs about each carbon atom, two of these pairs form a double bond between the carbon atoms. It is tempting to assume that these four electron pairs are forced apart to form a tetrahedron as in previous molecules. However, if this were this case, the two pairs involved in the double bond would be separated by an angle of 109.5° which would make it impossible for both pairs to be localized between the carbon atoms. To preserve the double bond, we must assume that the two electron pairs in the double bond remain in the same vicinity. Given this assumption, separating the three *independent* groups of electron pairs about a carbon atom produces an expectation that all three pairs should lie in the same plane as the carbon atom, separated by 120° angles. This agrees very closely with the observed bond angles. We conclude that the our model can be extended to understanding the geometries of molecules with double (or triple) bonds by treating the multiple bond as two electron pairs confined to a single **domain**. It is for this reason that we refer to the model as Electron Domain theory.

Applied in this form, Electron Domain theory can help us understand the linear geometry of CO_2 . Again, there are four electron pairs in the valence shell of the carbon atom, but these are grouped into only two domains of two electron pairs each, corresponding to the two C=O double bonds. Minimizing the repulsion between these two domains forces the oxygen atoms to directly opposite sides of the carbon, producing a linear molecule. Similar reasoning using Electron Domain theory as applied to triple bonds correctly predicts that acetylene, HCCH , is a linear molecule. If the electron pairs in the triple bond are treated as a single domain, then each carbon atom has only two domains each. Forcing these domains to opposite sides from one another accurately predicts 180° H-C-C bond angles.

5 Observation 3: Distortions from Expected Geometries

It is interesting to note that some molecular geometries (CH_4 , CO_2 , HCCH) are exactly predicted by the Electron Domain model, whereas in other molecules, the model predictions are only approximately correct. For examples, the observed angles in ammonia and water

each differ slightly from the tetrahedral angle. Here again, there are four pairs of valence shell electrons about the central atoms. As such, it is reasonable to conclude that the bond angles are determined by the mutual repulsion of these electron pairs, and are thus expected to be 109.5° , which is close but not exact.

One clue as to a possible reason for the discrepancy is that the bond angles in ammonia and water are both *less* than 109.5° . Another is that both ammonia and water molecules have lone pair electrons, whereas there are no lone pairs in a methane molecule, for which the Electron Domain prediction is exact. Moreover, the bond angle in water, with two lone pairs, is less than the bond angles in ammonia, with a single lone pair. We can straightforwardly conclude from these observations that the lone pairs of electrons must produce a greater repulsive effect than do the bonded pairs. Thus, in ammonia, the three bonded pairs of electrons are forced together slightly compared to those in methane, due to the greater repulsive effect of the lone pair. Likewise, in water, the two bonded pairs of electrons are even further forced together by the two lone pairs of electrons.

This model accounts for the comparative bond angles observed experimentally in these molecules. The valence shell electron pairs repel one another, establishing the geometry in which the energy of their interaction is minimized. Lone pair electrons apparently generate a greater repulsion, thus slightly reducing the angles between the bonded pairs of electrons. Although this model accounts for the observed geometries, why should lone pair electrons generate a greater repulsive effect? We must guess at a qualitative answer to this question, since we have no description at this point for where the valence shell electron pairs actually are or what it means to share an electron pair. We can assume, however, that a pair of electrons shared by two atoms must be located somewhere between the two nuclei, otherwise our concept of "sharing" is quite meaningless. Therefore, the powerful tendency of the two electrons in the pair to repel one another must be significantly offset by the localization of these electrons between the two nuclei which share them. By contrast, a lone pair of electrons need not be so localized, since there is no second nucleus to draw them into the same vicinity. Thus more free to move about the central atom, these lone pair electrons must have a more significant repulsive effect on the other pairs of electrons.

These ideas can be extended by more closely examining the geometry of ethene, C_2H_4 . Recall that each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° , whereas the Electron Domain theory prediction is for bond angles exactly equal to 120° . We can understand why the H-C-H bond angle is slightly less than 120° by assuming that the two pairs of electrons in the C=C double bond produce a greater repulsive effect than do either of the single pairs of electrons in the C-H single bonds. The result of this greater repulsion is a slight "pinching" of the H-C-H bond angle to less than 120° .

The concept that lone pair electrons produce a greater repulsive effect than do bonded pairs can be used to understand other interesting molecular geometries. Sulfur tetrafluoride, SF_4 , is a particularly interesting example, shown in Figure 4.

Note that two of the fluorines form close to a straight line with the central sulfur atom, but the other two are approximately perpendicular to the first two and at an angle of 101.5° to each other. Viewed sideways, this structure looks something like a seesaw.

To account for this structure, we first prepare a Lewis structure. We find that each fluorine atom is singly bonded to the sulfur atom, and that there is a lone pair of electrons on the sulfur. Thus, with five electron pairs around the central atom, we expect the electrons to arrange themselves in a trigonal bipyramid, similar to the arrangement in PCl_5 in Figure 3. In this case, however, the fluorine atoms and the lone pair could be arranged in two different ways with two different resultant molecular structures. The lone pair can either go on the axis of the trigonal bipyramid (*i.e.* "above" the sulfur) or on the equator of the bipyramid (*i.e.* "beside" the sulfur).

The actual molecular structure in Figure 4 shows clearly that the lone pair goes on

Molecular Structure of SF₄

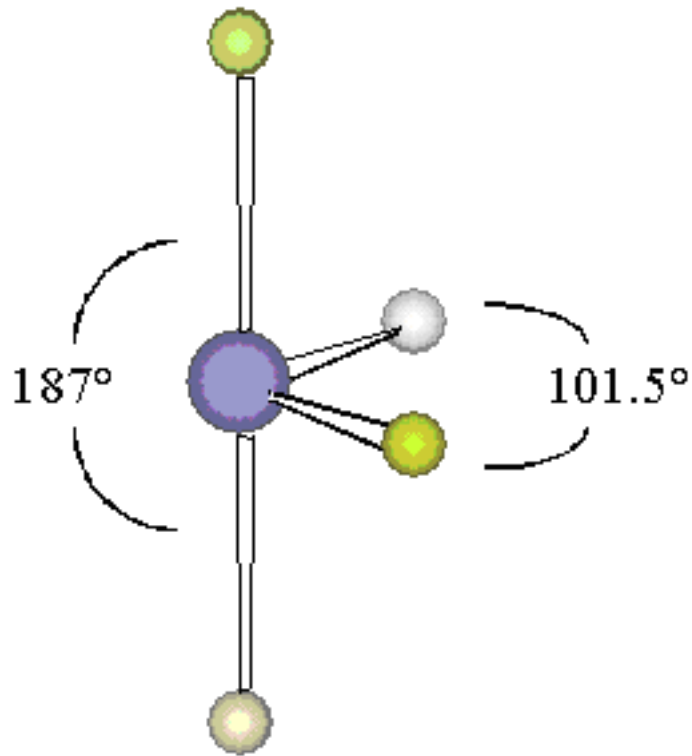


Figure 4

the equatorial position. This can be understood if we assume that the lone pair produces a greater repulsive effect than do the bonded pairs. With this assumption, we can deduce that the lone pair should be placed in the trigonal bipyramidal arrangement as far as possible from the bonded pairs. The equatorial position does a better job of this, since only two bonding pairs of electrons are at approximately 90° angles from the lone pair in this position. By contrast, a lone pair in the axial position is approximately 90° away from three bonding pairs. Therefore, our Electron Domain model assumptions are consistent with the observed geometry of SF_4 . Note that these assumptions also correctly predict the observed distortions away from the 180° and 120° angles which would be predicted by a trigonal bipyramidal arrangement of the five electron pairs.

6 Review and Discussion Questions

Exercise 1:

Using a styrofoam or rubber ball, prove to yourself that a tetrahedral arrangement provides the maximum separation of four points on the surface of the ball. Repeat this argument to find the expected arrangements for two, three, five, and six points on the surface of the ball.

Exercise 2:

Explain why arranging points on the surface of a sphere can be considered equivalent to arranging electron pairs about a central atom.

Exercise 3:

The valence shell electron pairs about the central atom in each of the molecules H_2O , NH_3 , and CH_4 are arranged approximately in a tetrahedron. However, only CH_4 is considered a tetrahedral molecule. Explain why these statements are not inconsistent.

Exercise 4:

Explain how a comparison of the geometries of H_2O and CH_4 leads to a conclusion that lone pair electrons produce a greater repulsive effect than do bonded pairs of electrons. Give a physical reason why this might be expected.

Exercise 5:

Explain why the octet of electrons about each carbon atom in ethene, C_2H_4 , are not arranged even approximately in a tetrahedron.

Exercise 6:

Assess the accuracy of the following reasoning and conclusions:

A trigonal bipyramid forms when there are five electron domains. If one ED is a lone pair, then the lone pair takes an equatorial position and the molecule has a seesaw geometry. If two EDs are lone pairs, we have to decide among the following options: both axial, both equatorial, or one axial and one equatorial. By placing both lone pairs in the axial positions, the lone pairs are as far apart as possible, so the trigonal planar structure is favored.



Figure 5

Exercise 7:

Assess the accuracy of the following reasoning and conclusions:

The Cl-X-Cl bond angles in the two molecules (Figure 5) are identical, because the bond angle is determined by the repulsion of the two Cl atoms, which is identical in the two molecules.