

Section 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.

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. 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 shows clearly that the lone pair goes on 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 SF₄
- . 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.

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