3-D Geometry / VSEPR Theory

In our discussion of Lewis structures, it was emphasized that they are 2-D representations of 3-D objects. Real ions and molecules bear little resemblance to the structure depicted by Lewis structures. How can the real 3-D structures be determined? The only "real" way to determines a substances 3-D appearance is through some kind of diffraction technique (x-ray and electron diffractions are the commonest). The instruments are quite expensive ($100K+) and thus out of the realm of possibility for our use! Fortunately, there is a way to "predict" the 3-D structure from our previously drawn Lewis structures. These "predictions" are quite accurate (~99%). The method has the acronym of VSEPR theory. This stands for **V**alence **S**hell **E**lectron **P**air **R**epulsion theory.

Although there are literally billions and billions of compounds known, diffraction studies show that the 3-D structures represented inside of these compounds constitute a mere handful geometric shapes. Clearly, geometries are repeated in nature even though the atoms that comprise those geometries may change. How many geometries are there and how can we tell which geometry will be adopted by a particular set of atoms? These are the questions that must be addressed by our VSEPR theory.

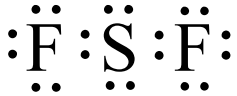
Before we plunge into the VSEPR theory itself, we will introduce a **very, very** useful simplification. This simplification is not of the theory, as it doesn't alter the outcomes (the predicted geometry) at all. Instead, the simplification helps the beginning student (YOU) to focus on the important factors and decrease the number of distractions which could lead to errors in your predictions.

The simplification involves replacing the actual atomic symbols of the various elements with a "generic" set of symbols. The idea being that IF the "generic" formula changes THEN the geometry changes but if the "generic" formula is the same for a set of Lewis structures then all of the Lewis structures will have the same 3-D geometry.

Generic Formulas

Begin by looking at the Lewis structure (say, HOCl which we drew previously). 

We replace the "central atom" (in this case the "O") with the generic symbol, A. Next, we replace **each** "terminal atom" (in this case the H and Cl) with the generic symbol, X. Finally, we replace **each** unbonded electron pair (lone pairs) **on the central atom only** with the generic symbol, E. In this way, the structure of HOCl is replaced with the formula, AX_2E_2.

Lets take another example, 

We replace the "central atom" (in this case the "S") with the generic symbol, A. Next, we replace **each** "terminal atom" (in this case both F's) with the generic symbol, X. Finally, we replace **each** unbonded electron pair (lone pairs) on "S" with the generic symbol, E. In this way, the structure of SF_2 becomes the formula, AX_2E_2.

This simplification points out that even though the atoms are different in HOCl and SF_2, these two molecules will have that same geometry as both are represented as AX_2E_2. VSEPR will tell us that what that geometry looks like!

VSEPR Theory

As with any theory, VSEPR theory starts with basic postulates. Postulates in a theory are the "IF" statements in the logical development of an explanation. IF these postulates are accepted, THEN the theory will logically explain a set of facts (in this case the observed 3D geometries of molecules and ions).

Basic Postulates of VSEPR:

1) **Electron pairs are sites of negative charge and as such they repel one another. Thus, the electron pairs in covalent bonds and lone pairs will migrate to positions as far from each other in 3-D space as possible.** (This is merely, a statement of Coulomb's Law applied to the electron pairs.

   Coulomb's Law: $\mathbf{F} \propto \frac{q_1 \times q_2}{r^2}$

   where q_1 and q_2 are the electrical charges on two different particles, in this case, the charges on the electron pairs. The quantity, r^2 , is the square of distance between the electron pairs. This shows that as the distance, r, increases, the force of repulsion **decreases**. Thus, it is favorable for the electron pairs to be farther apart!).

2) **The magnitude of the repulsion between electron pairs increase as follows:**

   bonding pair - bonding pair < bonding pair - lone pair < lone pair - lone pair

   This trend is easily rationalized. Electron pairs that are involved in bonding between two atoms, A and B, are **farther** from the center of atom, A, than lone pairs of electrons on atom, A.

   I.e., **: A : B** Atom B is attracting the electron pair in the bond to itself and thus "pulling" it farther away from atom A.

   Thus, lone pairs are closer to the center of atom A and thus closer to each other which increases the repulsion between them. Bonding pairs are farther from the center of atom A and thus farther from each other which lowers the repulsion between them. Clearly, the distance between a lone pair and a bonding pair would be shorter than the distance between two bonding pairs but longer than the distance between two lone pairs. Therefore, Coulomb's Law demands that the above pattern of repulsion exist.

3) **Single, double, and triple bonds are treated alike.**

   In order for electrons to be shared between two atoms they must **remain** between the two atoms and **NOT** migrate apart! Thus, single, double, and triple bonds must be treated as a single entity.

3-D Geometries

How can we logically move from these three postulates to predictions of 3-D geometries?

We begin with our generic formulas.

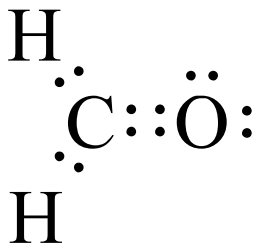
1) **Lewis structures with the generic formulas; AX, AXE, AXE_2...AXE_n** As two points define a line in math, we don't need <u>any</u> theory to determine that an ion or molecule that contains only 2 atomic centers, A and X, must have a linear geometry regardless of whether or not there are lone pairs of electrons around atom A. Thus, the formulas: AX, AXE, AXE_2, ...AXE_n must all be linear as there are only two atoms.

2) **Lewis structures with the generic formula AX_2** (3 atoms, one central atom A and 2 terminal atoms X). The first postulate says that the sets electron pairs bonding the X's to the central atom A will repel and migrate to positions as far apart in 3-D space as possible. Thus the two X's must be spread out 180° apart. For example, HCN and CO2, both have linear geometries.

(X----A----X) (X----A----X)

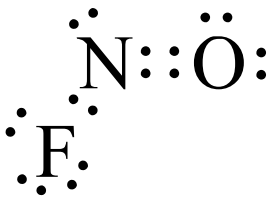
Recall, the third postulate treats single, double, and triple bonds alike (as a single direction). As 180° defines a line, all AX_2 structures are said to be "linear".

3) **Lewis structures with the generic formula AX_3** (4 atoms, one central atom A and 3 terminal atoms X). Again. the first postulate demands that the sets electron pairs bonding the X's to the central atom A repel and migrate to positions as far apart in 3-D space as possible. Thus the three X's must migrate to positions 120° apart. For example, CH_2O looks like



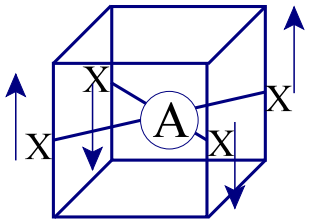
In CH_2O, the terminal atoms (2 H's and O) form an equilateral triangle with the central atom in same plane as the triangle. This geometry is called "trigonal planar".

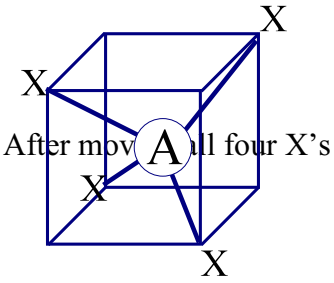
4) **Lewis structures with the generic formula AX_2E** (3 atoms, one central atom A plus 2 terminal X atoms and a lone pair of electron on A). Again. the first postulate demands that the electron pair E on the central atom A plus the sets electron pairs bonding the X's to the central atom A will all repel one another and migrate to positions as far apart in 3-D space as possible. Thus the two X's and the lone pair E must migrate to positions 120° apart. An example of this the molecule FNO.



In FNO, the terminal atoms (F and O) plus the lone pair E form an equilateral triangle with the central atom in same plane as the triangle. Looking at the atoms only, the three atoms are not on a straight line but are only 120° apart. Structures of this shape are said to be "bent" or "angular.

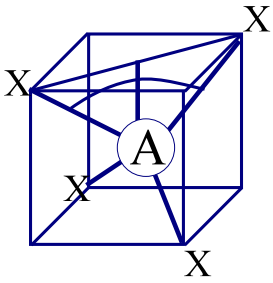
5) **Lewis structures with the generic formula AX_4** (5 atoms, one central atom A and 4 terminal atoms X). Repulsions between the sets electron pairs bonding the X's to the central atom A cause these atoms to migrate to positions as far apart in 3-D space as possible. In 2-D space the X atoms would move to positions 90° apart (I.e., at the corners of a square). In 3-D space, the atoms can move to positions even farther apart. This can be seen by taking 2 of the X's that are 180° apart and moving them above the plane of the square and taking the remaining 2 X's and moving them below the plane of the square.

I.e., 

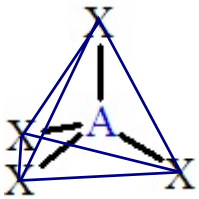


After mov ll four X's

The angles between the X's can now be determined through geometry. The length of the diagonal of any square is equal to the $\sqrt{2}$ times the length of the edge of the square. If the midpoint of the diagonal is connected to the center of the cube (atom A) , the angle between the X's will bisected. This will produce two right-triangles, each with one leg of a length of one-half the edge and the other leg of length equal to one-half the diagonal length or $\sqrt{2}$ / 2 times the edge.

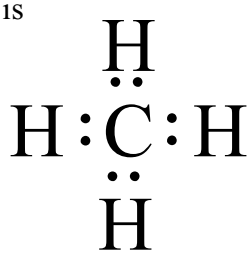


Now the angle which includes atom A can be determined. The tangent of this angle is the length of the opposite leg divided by the length of the adjacent leg or $\sqrt{2}$ 2 edge divide by 1/2 edge. This reduces to $\tan\theta = \sqrt{2}$. Thus, $\theta = \tan^{-1}(\sqrt{2}) = 54.73561...°$ and finally the entire angle between any two X's will be twice this value or about 109.5 °.

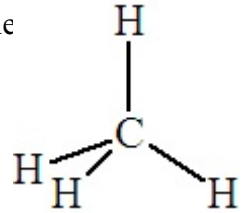


When the X's are connected, a 3-D shape known as a tetrahedron is generated and all molecules with the generic formula of AX_4 are said to be "tetrahedral"

An example is CH_4 (methane). The Lewis structure of CH_4 is

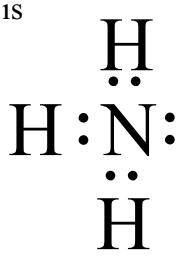


In 3-D, the VSEPR geome

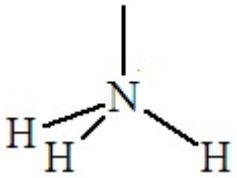


6) **Lewis structures with the generic formula AX_3E** (4 atoms, one central atom A and 3 terminal atoms X plus a lone pair of electron on A). Repulsions between the 4 sets electron pairs cause them to migrate to positions as far apart in 3-D space as possible. As with the AX_4, these pairs will move to positions 109.5° apart. An example of this is NH_3.

An example is NH_3 (ammonia). The Lewis structure of NH_3 is



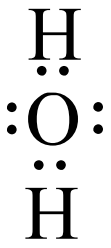
In 3-D, the VSEPR geometr



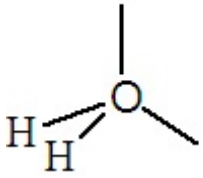
When the 3 X's are connected they form a triangle with the A above the triangle. Structure that are high in the center are called pyramids. Thus, the AX_3E structure is called "trigonal pyramidal".

7) **Lewis structures with the generic formula AX_2E_2** (3 atoms, one central atom A and 2 terminal atoms X plus 2 lone pairs of electron on A). Repulsions between the 4 sets electron pairs cause them to migrate to positions as far apart in 3-D space as possible. As with the AX_4, these pairs will move to positions 109.5° apart. An example of this is H_2O.

An example is H_2O (water). The Lewis structure of H_2O is



In 3-D, the VSEPR geometr



When the 2 X's are connected they form a line with the A not on the straight line connecting the X's. To include the A, the line is required to be bent. Thus, the AX_2E_2 structure is called "bent" or "angular".