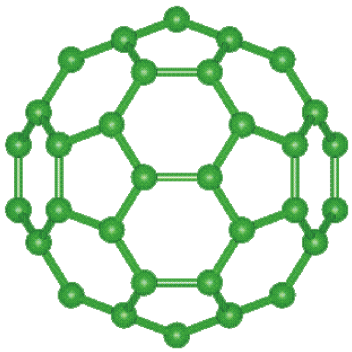
CHEMISTRY 185

Foundations of Chemistry I- Honors

Fall 2010

Molecular Geometry



Department of Chemistry

University of Kansas

Molecular Geometry

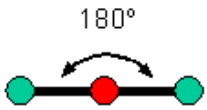
Introduction

In this lab, you will explore how the geometry and structure of molecules are influenced by the number of bonding electron pairs and lone pairs of electrons around different atoms. You will be asked to build models of a number of different molecules that will allow you to predict and explain the observed geometries of the different molecules. The lab will consist of several parts in which you will build balloon models of different structures, use model kits to build models of a series of molecules, and use Chem3D to explore the geometries and molecular orbitals of these molecules computationally.

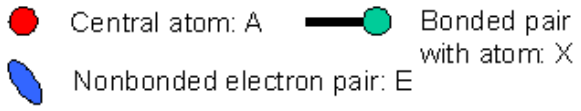
The shapes of the molecules are important for a variety of reasons. The melting points, boiling points, density and reactivity are all influenced by the shape of the molecule. There are a number of ways to determine the shape of molecules. Spectroscopy and crystallography are experimental methods that allow the determination of structure of the molecule (you should have seen one influence of structure on spectroscopy in the Particle in a Box laboratory). Computationally you can calculate the geometry of the molecule and the bond lengths and bond angles of the minimum energy structure by solving the Schrodinger equation. You will calculate the minimum energy structures for a number of molecules in this exercise using Chem3D. However, there are also simple tools available that allow one to quickly predict the rough geometry of the molecules once an appropriate Lewis structure has been determined. Using the valence electrons (the outer shell electrons) one can determine a Lewis structure for the molecule. This Lewis structure can be used to determine the number of bonds and lone pairs of electrons that each atom has. A theory generally known as VPSEPR theory (Valence Shell Electron-Pair Repulsion theory) can be used to predict the arrangement of these lone pairs of electrons and bonding electrons around an atom. The model of the molecule that comes out of this idea is called the VSEPR model for the molecule. The idea behind this theory is that the electron pairs and lone pairs within a molecule repel each other and therefore would prefer to be as far apart as possible in order to minimize this repulsive interaction. In order to determine the structure of the molecule using VSEPR theory, you need to know how many electron pairs need to be arranged around a central atom and then arrange those so that they are as far apart as they can be. This requires the geometry to be the one that maximizes the distance between the different electron pairs. The diagram below shows the geometries that maximize the distance between each of the electron pairs.

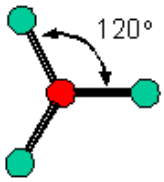
The inclusion of nonbonding lone pairs of electrons has dramatic consequences for the structure of the molecules. These electron pairs must be included in the number of electron pairs to be arranged around the atom. In addition, it turns out that the nonbonding pairs of electrons actually also change the observed bond angles from the one which puts all of the lone pairs and bonding pairs as far apart as possible. You will explore the effect of these lone pairs within this exercise.

Electron Density and Molecular Geometry

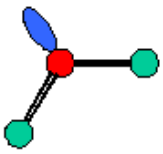


AX_2
linear
BeF_2

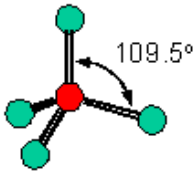




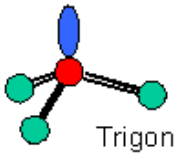
AX_3
triangular planar
BeF_3



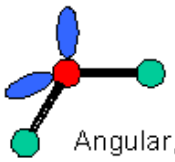
bent
AX_2E
SO_2



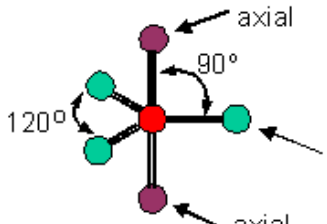
AX_4
tetrahedral
CH_4



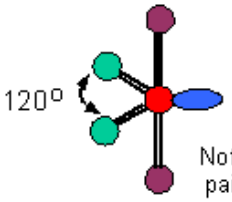
Trigonal pyramidal
AX_3E
NH_3



Angular, Bent
AX_2E_2
H_2O

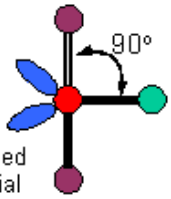


AX_5
triangular bipyramidal
PCl_5

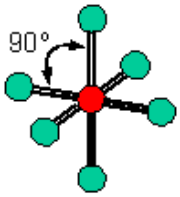


Seesaw
AX_4E
SF_4

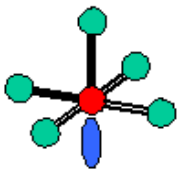
Notice: nonbonded pairs in equatorial plane



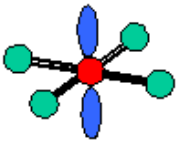
T-shape
AX_3E_2
ClF_3



AX_6
octahedral
SF_6



Square pyramidal
AX_5E
IF_5



Square planar
AX_4E_2
XeF_4

A case study in molecular geometery: Fullerenes

In September of 1985 Jim Heath, a graduate student working at Rice University, was puzzled by the results of an experiment that he and his professors were doing. The group was vaporizing carbon with a laser and looking at the size of carbon clusters that resulted. For an unknown reason, they kept seeing a large number of clusters with 60 carbon atoms. The abundance of 60-carbon clusters was 50 times greater than that of any other cluster.

That evening Jim decided he would try to figure out what was special about 60-carbon clusters, so on his way home he purchased a sack of Gummi Bears and a box of toothpicks. At home he began to make models using the Gummi Bears as carbon atoms and the toothpicks as bonds. He knew that each carbon would have four bonds, and that somehow the structure of the cluster with 60 carbons would be more stable than one with 61, 62, or any other number.

The other members of the group also tried different ways of building models, and within the next few days they had determined a possible structure that they called buckminsterfullerene ("buckyball," for short), after the architect R. Buckminster Fuller. The structure that they proposed was made up of groups of six-carbon rings joined together with rings of five carbons. The final structure looked exactly like a soccer ball (or a football, to the visiting English professor who was part of the group).

Prior to this discovery there were two known allotropes (different molecular forms of the same element) of carbon: diamond and graphite. With this discovery they developed a new class of molecules called fullerenes, and began a new field of study that led to nanotubes and other molecular structures. The field became more exciting in 1990 when scientists discovered methods of producing buckyballs by the pound instead of the small amounts previously made.

In 1996, Robert Curl, Harold Kroto, and Richard Smalley were awarded the Nobel Prize in Chemistry for the discovery of fullerenes. Jim Heath was not included because he had been a graduate student on the project.

For more information about this discovery read *The Most Beautiful Molecule: The Discovery of the Buckyball*, by Hugh Aldersey-Williams.

The use of the rules above is consistent with this geometry, but obviously this is a much more complicated structure than the ones you will investigate in the laboratory for this experiment. It does however, illustrate the power of these simple predictive tools for understanding molecular structure.

Pre-lab

This laboratory is designed to help you think about molecular geometries and what factors influence the shapes of molecules. Based on the information from the lecture and from your textbook, draw an appropriate Lewis structure for the following molecules and attempt to predict their shape.

H_2S CH_4 XeF_4

Once you have drawn the appropriate Lewis structures for these molecules choose another molecule and write the appropriate Lewis structure for that molecule.

You can build reasonable models of molecules using household items, as described above in the introduction. Locate suitable "bonds" and "atoms" and use those to build models of the four compounds above. Suitable bonds might include paper clips or tooth picks and suitable atoms might include things like gummi bears or marshmallows. Be creative and use whatever materials you have available. If you have molecular model kits, feel free to use those and please bring them with you to the lab.

Safety: Goggles *must* be worn at all times. You will be working with ordinary balloons during this lab period. Balloons have a limited capacity. Over-inflation may result in small pieces of rubber littering the bench top and floor. You may also experience ringing in your ears. This tinnitus should be temporary. Balloons should be kept away from young children because of a danger of choking and suffocation. Do not ask your TA to blow up the balloons! Do not bring your food models from your prelab into class with you. There is no food allowed in the laboratory.

Pre-lab Assignment: Please answer the following questions in your lab notebook. This assignment is due at the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and submitted to your TA.

1.) What are the objectives of the experiment?

2.) How do lone pairs of electrons influence the structure of molecules?

3.) What does VSEPR stand for? In VSEPR theory, what determines the shape of the molecule?

4.) Describe what is meant by HOMO and LUMO orbitals. What shape would you predict for the HOMO for hydrogen.

5.) Draw the appropriate Lewis structures for the three molecules above and predict the geometry for each of those molecules in addition to one molecule of your own choosing.

6.) Create the appropriate tables in your lab notebooks to record your observations for the three different parts of the experiment.

Procedure

Part 1 – VSEPR geometries of molecules using balloons

Ronald J. Gillespie and Ronald S. Nyholm are famous for having devised a method for predicting the three-dimensional structures of molecules (VSEPR theory as discussed above). For the lab, we will explore some of their assumptions and examine different structures that molecules form. This VSEPR theory says that the repulsive interactions between lone pairs of electrons and bonding electron pairs causes them to be arranged in such a geometry that they are as far apart as possible.

Obtain several white balloons and use each balloon to represent one pair of electrons on a central atom. As you work through Part 1, remember that the white balloons represent *bonds between atoms,* not the atoms themselves. Make sure that these balloons are inflated to roughly equal size. Tie two white balloons together to symbolize the arrangement of electron pairs around an atom bonded to two surrounding atoms. Draw a picture of the electron pair arrangement in a table in your notebook similar to Table I below. (This really is equivalent to drawing a picture of the two balloons tied together).

Tie additional balloons to this assembly in a stepwise manner to symbolize three, four, five, and six electron pairs surrounding a central atom. Add your drawing to Table I. (Everyone but the artist in your group will soon bemoan the challenge of representing three-dimensional geometries on a flat piece of paper. It's an issue that chemists—especially textbook authors—face often! It does not have to be pretty, just try to demonstrate what you observe as well as you can.)

Determine the chemical formulas for the molecules listed below. Now place each compound on the list below into the appropriate box in the last column of Table I.

Compound	Chemical Formula
Beryllium Chloride	_____
Phosphorus Pentabromide	_____
Methane	_____
Aluminum Chloride	_____
Dichloromethane	_____
Boron Trifluoride	_____
Tungsten Hexachloride	_____

Table I. Arrangement of Bonding Electron Pairs around a Central Atom with no Lone Pairs

# of Atoms Connected to Central Atom	Sketch of Electron Pair Arrangement around Central Atom	Name of Electron Pair Arrangement	Example Compounds
2			
3			
4			
5			
6			

The above exercise should have illustrated the arrangement of bonding electron pairs around a central atom. Gillespie and Nyholm's theory incorporates one other idea that helps predict the three-dimensional structure of water and many other molecules. Electrons in the valence shell that are not involved in bonding "pair up," and these pairs of electrons (called non-bonding pairs or "lone pairs") repel other pairs of electrons just as bonding pairs do. Black balloons are available to represent lone pairs. For each molecule in Table II below, build a balloon model that includes all of the electron pairs (i.e., bonding electron pairs as well as lone pairs). Draw and label the picture of each balloon model such that any lone pairs are distinguished from bonding electron pairs. *Hint:* To determine whether one or more lone pairs are present on the central atom of a molecule, it may be helpful to draw its Lewis structure, being careful to account for *all* of the valence-shell electron pairs. If you need assistance with drawing Lewis structures, try the tutorial at http://cost.georgiasouthern.edu/chemistry/general/molecule/lewis.htm. Detailed information about drawing Lewis structures is also available in Chapter 3 of your textbook.

In the appropriate column of Table II, draw the shape of the molecule itself. Single bonds connecting atoms can be represented either by a solid line between the atoms, or

with two dots (electrons) between the atoms. Include two dots for each lone pair in your structure to emphasize the impact that lone pairs have on molecular geometry.

Table II. Geometry of Simple Molecules

	ELECTRON PAIR ARRANGEMENT		MOLECULAR SHAPE	
Molecule	Sketch of Electron Pair Arrangement around Central Atom	Name of Electron Pair Arrangement	Sketch of Predicted Molecular Shape	Name of Molecular Shape
PF_3				
SF_2				
XeF_4				
H_2O				
BrF_5				

Part 2 – Molecular Modeling Kits for Structures of Molecules

Obtain components of a molecular modeling kit from your TA. Differently colored spheres represent different atoms. Carbon (black), hydrogen (white), oxygen (red), chlorine/fluorine (green), nitrogen (blue), sulfur (yellow) and generic atom types are available. Each grey connector represents a pair of bonding electrons, analogous to each white balloon in Part 1. Begin with two white spheres and a grey connector to build the simplest known molecule, elemental hydrogen. Build each molecule indicated in the table below and draw the corresponding three-dimensional structure. Some of these same molecules will be modeled computationally in Part 3. Note any lone pairs present on the molecules and try to determine what effect they have on the structure. What are the bond angles for each of these molecules?

Compound	Sketch of Molecular Shape
H_2	
Cl_2	
H_2O	
SO_2	
NH_3	
MoF_6	
C_2H_6	
C_2H_4	
C_2H_2	

Part 3 – Using ChemDraw to explore the geometries and orbitals for simple molecules

In this part of the experiment, you will use a subset of the molecules used in Part II in order to draw these molecules in ChemDraw and Chem3D. Your results from the computational exercise can be compared with the geometries you observed for the models in Part II. In this exercise, you will minimize the energy for each of the molecules and determine the lowest energy structure for the optimized geometry. You will also be able to look at the shapes of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for these molecules. Explore the shapes of these molecules and orbitals as described below. Note the shapes of the HOMO and LUMO orbitals, paying particular attention to the places where the color of the orbital changes, as this indicates a change in sign of the wavefunction, and therefore a node.

Begin with H_2 as a staring molecule. Once you have done the calculations and recorded the shapes of the orbitals for this molecule, move on to H_20, NH_3, C_2H_6, C_2H_4, and C_2H_2.

Instructions for using ChemDraw and Chem3D are available through the help programs of this software. Molecules can often be drawn in ChemDraw and copied into Chem3D, although Chem3D doesn't recognize metals very well. Also, some planar structures lose their planarity when copying into Chem3D. In order to minimize energy, choose the Calculations tab, then Minimize Energy. This will perform a series of calculations to locate the minimum energy structure of the selected molecule. After this is done, under the Surfaces tab, select Choose Surfaces and then Molecular Orbital (Huckel Calculation). This will bring up the HOMO on the molecule. You can change to the LUMO by going to the Surfaces tab and highlighting Select Molecular Orbital. The number in brackets is the approximated energy of the orbital.

Save pictures of both the HOMO and LUMO orbitals for each of the molecules studied. In addition, save a picture of the molecule. It might be helpful to switch the background color to white before saving these pictures, so that they are more easily inserted into your report. Determine the bond lengths and bond angles in these molecules. This can be done by going under the Structure tab and clicking on Measurements. A table can be generated here with all of the bond lengths and bond angles. In addition, if you highlight a particular bond in the molecule, the bond length will be displayed.

Why do the molecular orbitals look the way they do? Would the LUMO orbital for the H_2 molecule be a bonding orbital? Why or Why not? What is the H-O-H bond angle in the H_2O molecule? Why is this bond angle different from the tetrahedral bond angle? Compare the bond lengths and bond angles in the C_2H_4 and C_2H_6 molecules and discuss the differences in these structures.

Report

Your lab report should be a formal, individual report that addresses all the questions posed in this write-up. It should be prepared according to the "Guidelines for Laboratory Reports" you have been given. The experimental section in this report should be very brief. Tables of your observations should be reported in the results section. The discussion should include the answers to the questions posed in the writeup. A discussion of the role of bonding electron pairs and nonbonding pairs of electrons in determining the geometry of the molecules should be included.

References

Below are three web sites where you can view information about Fullerenes.

The following link shows several different fullerene structures:
http://www.chem.sunysb.edu/msl/fullerene.html

The following contains background on R. Buckminster Fuller from the PBS special about him: http://www.thirteen.org/cgi-bin/bucky-bin/bucky.cgi

For information about VSEPR theory and molecular geometry:

B. B. Laird, *University Chemistry*, McGraw Hill, Boston MA (2009). (Chapter 3 and 4)

\