11. MOLECULAR MODELING

Chemists frequently use models to better understand chemical phenomena. In this laboratory models are used to analyze chemical bonding and molecular structure. We will start with the Lewis electron dot (Localized Electron) model\(^1\) and use it to predict the electronic structure of some simple molecules. We will then use ball-and-stick models to construct three-dimensional models of those molecules. The three-dimensional models will be refined using Gillespie’s Valence Shell Electron Pair Repulsion (VSEPR) model\(^2\). Finally, we will use Spartan\(^3\), a computational chemistry program, to calculate the molecular geometry. The results from Spartan will then be compared with the VSEPR results.

Computational chemistry. In theory, all of chemistry can be understood as solutions of Schrödinger’s wave equation. In practice, solution of the Schrödinger equation is so complicated that chemically accurate calculations for molecules involving more than three electrons and three nuclei, e.g. \(\text{H}_3\), are beyond the reach of current computer hardware/algorithms. To model the properties of larger (and more interesting) molecules, chemists must use some form of approximate computational method.

The simplest, and thus fastest, computational method is called molecular mechanics. In molecular mechanics the bonds of a molecule are treated as springs and the force constants of the springs are determined from experimental measurements. The overall molecular energy is the sum of the energies of stretching, bending and torsion (the molecular force field) for all of the bonds in the molecule. Although molecular mechanics ignores electronic properties, it gives quite good structural results for large molecules such as proteins. Drug companies performed much of the pioneering work on molecular mechanics. Spartan uses a molecular mechanics program called MMFF (for Merck Molecular Force Field) developed by Merck Pharmaceuticals and one called SYBYL developed by Tripos, Inc., a St. Louis drug discovery company.

Semi-empirical molecular orbital methods are the next level of computational accuracy. Semi-empirical methods take advantage of the fact that some of the quantities that are hardest to calculate contribute very little to molecular energy. They can thus be ignored without a significant loss of accuracy. Other hard-to-calculate quantities can be replaced by experimental values. There is a veritable alphabet soup of semi-empirical methods. Spartan uses MNDO (Modified Neglect of Diatomic Overlap), AM1 (Austin Model 1) and PM3 (Parametric Model 3). All three were developed by M. J. S. Dewar’s research group at the University of Texas, Austin between 1975 and 1990. Each method has its own strengths and weaknesses. A lot of semi-empirical computational chemistry involves deciding which model works best for the problem you’re working on. In this laboratory, we will use AM1.

At a higher level of computational accuracy is the Hartree-Fock molecular orbital method. This was developed in the 1930s by Douglas Hartree, a British mathematician and Vladimir Fock, a Russian physicist, but was not widely used until digital computers became available in the 1960s. We will not be using the Hartree-Fock method, but when you get to the Calculations… screen in Spartan’s Setup menu, you will see Hartree-Fock listed as one of the choices.

To put this in perspective, for a molecule like \(\text{SF}_6\), a molecular mechanics calculation takes about one second, a semi-empirical calculation takes about five seconds and a Hartree-Fock calculation takes several minutes. Molecular mechanics does not give molecular energies but can do a reasonable job of predicting which molecular arrangement is most stable. Semi-empirical methods can calculate molecular energies to an accuracy of a few percent, while Hartree-Fock calculations give molecular energies accurate to a few tenths of a percent. The difficulty is that most chemical problems, such as predicting the path of a reaction, require accuracy of \(\sim 10^{-3}\) percent. Computational procedures that can work at this accuracy are available, but they are very complex and computationally intensive.

PROCEDURE - Your report will consist of the attached worksheet, which lists ten molecules that you will study. For each molecule:

1. Write the Lewis electron dot structure,
2. Using the “ball-and-stick” model kit, construct a 3-dimensional model,
3. Sketch the shape of the molecule, including lone pairs, and name the molecular shape.
4. Draw the molecule in Spartan (two examples are given below to illustrate the procedure) and measure the VSEPR model bond angles as discussed in the paragraph on the water molecule.
5. Log onto your server space (F: drive) and create a folder in which to save your molecular models. Set up and carry out the AM1 calculations in Spartan as follows to find the most stable structure and measure the theoretical bond angles, then compare them to the experimental bond angles listed on the work sheet. To carry out the calculations:

- When you are ready to calculate the structure, Select Calculations… from the Setup menu. In the Calculate: block, select Equilibrium Geometry with Semi-Empirical and AM1.
- In the Start from: block, select Initial geometry.
- In the Subject to: block, check Symmetry.
- The Total Charge should be Neutral unless the species has a net charge, in which case set it to the appropriate charge. The Multiplicity should be Singlet.
- In the Compute block, check Elect Charges.
- Check Global Calculations.
- Click on Submit. Spartan will prompt you to save your model. After saving the model, a window will open notifying you that Spartan has started. Click on OK to close that window. After 5 – 30 seconds, a window will open notifying you that Spartan has completed. Click on OK to close that window and you will see the calculated equilibrium geometry of the molecule.

After completing all of the molecules, answer the following questions on the back of the report form.
6. From your knowledge of electronic structure, explain any differences between the bond angles predicted by the VSEPR model and those predicted by Spartan.
7. For the molecules H₂O and H₂S, comment on the effect upon bond angles of changing the electronegativity of the central atom. Can this be explained using the idea of electron-pair repulsion?
8. In a similar manner, explain the trend in bond angles for the series PF₃, PCl₃, and PBr₃. Does atomic radius or electronegativity seem to play a role?

Your lab report (to be turned in at the end of lab) will consist of the completed worksheet and the answers to 6, 7, and 8 above.

Instructions for Spartan
Spartan runs on the campus network. Start Spartan by double clicking on the icon on your PC’s desktop (or look for Spartan ES on the start menu). When Spartan opens, maximize the screen so that you can read information at the bottom of the active window. Choose New from the File heading on the menu bar or click on the blank page icon. A partial periodic chart will appear to the right of the screen. Actually four tabs will appear there: Ent.; Exp.; Pep.; and Nuc. Choose the Exp. tab, which gives more choices than the Ent tab. A more complete periodic chart with several different choices for bonding arrangements for each atom will come up. These bonding arrangements correspond to the VSEPR theory geometries. You can now build any molecule atom-by-atom by choosing an atom and a configuration and clicking in the open space to the left. These instructions walk you through building two of the molecules on your list. Additionally, they tell you how to measure bond angles.

\[ \text{H}_2\text{O} \]
You should have already drawn the Lewis dot structure. Choose O from the periodic table and choose the tetrahedral bonding arrangement, since oxygen has four electron groups around it in the water molecule, as shown in your Lewis structure. (Careful: do not choose the square-planar arrangement.) Left-click on the big screen, the active window, to the left, and an O atom will appear with four empty bonding sites. You can rotate the atom by doing a click-and-drag operation with the mouse. Next, choose a H atom and the configuration with one bond from the periodic chart. Left-click on one of the open bonds of the O atom in the active window, and a H atom will appear bonded to O atom. Left-click
again on one of the other open bonds, and a second O-H bond will appear. You now need to get rid of the two remaining bonding sites on the O atom, or Spartan will automatically fill them with H atoms. To remove these bonding sites, choose the Delete tool, the red asterisk next to the Add Fragment icon, on the button bar. Left-click on the empty bonding sites one at a time and they will disappear. The complete H₂O molecule should now be displayed in the active window. You might try choosing the Space Filling model from the Model option on the button bar. This shows the actual size of the electron clouds associated with each atom. You will probably find it easier to build molecules using the Ball and Spoke model, but the Space Filling model will be instructive for viewing.

This structure serves as a starting point for the calculation to determine the lowest-energy geometry for the molecule. Measure the bond angle by choosing the ? angle icon on the button bar. Left-click on a H atom, the O atom, and the other H atom, in that order. You should see “Angle (H3,O1,H1) = 109.47°” in the bottom right-hand corner of the screen. You may instead see “Angle (H1,O1,H3) = 109.47°”, depending on which H atom you chose first. This display tells you that your initial guess for the bond angle is 109.47°, that predicted by VSEPR theory (this ignores distortions caused by lone pairs).

To have Spartan determine the lowest-energy (most stable) geometry, choose Setup from the button bar and choose Calculations. In the dialogue box, choose the options outlined earlier in the lab handout. After the calculations have completed, re-measure and record the bond angles as calculated by Spartan. After completing each molecule, be sure to clear the screen on the Edit menu and delete the molecule on the File menu. If you fail to do this, earlier molecules will be shown superimposed on the current molecule, which can make things very difficult to see and interpret.

SF₄
Clear your screen by choosing Edit from the button bar and selecting Clear. Make the SF₄ molecule by selecting the Add Fragment button, a bold plus sign, and choosing S from the periodic table to the right. Choose the trigonal bipyramidal configuration for S and click in the active window. (The Lewis dot structure shows 5 groups of electrons around the S atom, four bonding pairs and one lone pair.) Be careful that you do not choose the square pyramidal arrangement. Rotate the atom until you can see all the available bonding sites. Add F atoms (choose the single bond configuration) to 4 of the available bonding sites of the S atom; leave one of the equatorial sites vacant. (Why equatorial and not axial?) Select the Delete tool and remove the remaining bonding site, which is actually occupied by a lone pair of electrons on the S atom. Measure and record the VSEPR bond angles, then determine the lowest-energy geometry with AM1 as you did for H₂O above. Measure and record the bond angles. Are they different from what VSEPR theory predicts? Why?

References and Notes
3 Spartan '02 for Windows, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.

(Revised 04/26/07)
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| BrF₅           |                 |                | F_{eq}-Br-F_{eq} = 90  
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1. Using Austin Model 1 (AM1) semi-empirical method