

CHM 115 Laboratory 6

Lewis Diagrams, Molecular Geometry, Formal Charge, and Bonding Theories

We understand bonding through the application of abstract models to explain phenomenological evidence related to how atoms form into molecules with specific structural and electronic properties. While studying chemistry, you will be exposed to many different bonding theories. The theories themselves range in complexity from simple Lewis diagrams, to LCAO-MO theory, to very time consuming all electron multireference configuration interaction methods. As a scientist you need to appreciate the strengths and weaknesses in these methods as accurate application of the theories help us make correct predictions. In this lab you will draw on your knowledge of simple bonding theory and extend it to using computational methods.

1. For the water molecule,
 - a) Draw the Lewis diagrams, fill in the formal charges, and predict the shape.
 - b) Based on your Lewis diagram, do you expect the O-H bond lengths to be the same?
 - c) Predict if the molecule has a permanent dipole moment.
 - d) Using the model kits, make a model for water. Is the model kit representation consistent with your Lewis diagram? Take a picture of your model.
 - e) Open the *WebMO* web page.
<http://theochem.mercer.edu/~webmo/cgi-bin/webmo/login.cgi>
Log in with the name `chm115` and the pw `MercerBears`.
 - i. In the Job Builder click on “New Job” in the upper left part of the window. This should open a viewer for you to build a molecule. Click “Build” and select “O”, then click on the builder canvas. You should see a red dot appear. This represents an oxygen atom. Click on “Build” again. This time select H. Move down to the build canvas. Left click on oxygen atom and while holding down the left mouse button drag the mouse away from the oxygen atom and then release the left mouse button. A bond should now be seen with a hydrogen atom at the end of the bond. Repeat this procedure on the other side of the molecule so that you have two hydrogens attached to the oxygen.
 - ii. On the top menu click “Clean-Up” and select the option “Comprehensive-Idealized”. You should now have a water molecule on the screen with an approximately correct geometry.
 - iii. Click the right pointing chevron (arrow) in the lower right part of the screen. This will move you to the screen to choose your computational engine. For the first calculation we will use Mopac. Select this and then hit the right facing chevron below the select server option.
 - iv. The job name should already be filled in with H2O. Append your last name to this (e.g. - H2O_Pounds). This will help you identify your calculations from those done by your classmates. For the calculation type select “Geometry Optimization”. Move to the “Advanced Pane” and on the Additional Parameters line add the command “GEO-OK” (no spaces and the dash is required). Leave everything else at its default value.
 - v. Click the lower right chevron again and your calculation should start. You will be returned to the Job Builder and should see your job either running or queued at the top of the screen. Once it completes hit the magnifying glass under the “Actions” column.
 - vi. Your calculation results should open with your molecule in the middle of the canvas. Click the arrow pointing up and to the left on the left pane of the window. This will allow you to select individual components of your molecule. Click on the oxygen. In the bottom part of the screen you should see the hybridization of the oxygen atom. Now,

- holding down the shift key, select one of the hydrogens. The bond length should appear at the bottom of the screen. Now, holding down the shift key, select all three atoms in the order H, O, H. You should now see the bond angle at the bottom of the screen.
- vii. Move to the lower section of the webpage where it says "Calculated Quantities". Record the PM3 Heat of Formation and the Dipole moment. Be sure to record the units.
 - viii. Look at the partial charges, how do these compare to your formal charges?
 - ix. Move back up to the molecule viewer pane. Using the button at the bottom, start a new job using this geometry. Once the Build Molecule window opens, go ahead and click the chevron in the lower right corner.
 - x. Select Gamess as the computational engine. When the configuration page opens once again fix the name of the job by appending your last name. Change the calculation type to "Geometry Optimization." Leave all the other parameters at their default values and hit the lower right chevron to start the calculation.
 - xi. As before, check the bond lengths and bond angles. Are they different than those from Mopac?
 - xii. Move down to the calculated Quantities section and record the RHF Energy and the dipole moment. Be sure to record the units.
 - xiii. Look at the partial charges. Are they different than Mopac?
2. For the molecules $\text{O}\equiv\text{C}-\text{O}$ and $\text{O}=\text{C}=\text{O}$:
 - a) Complete the Lewis diagrams and add formal charges.
 - b) Build models of each and photograph them
 - c) Predict if the molecule has a dipole moment
 - d) Using Mopac and Gamess, try to determine which of the two structures is preferred? You will not be able to build double and triple bonds. Just connect the atoms and then examine the bond length and charge properties after you optimize the structure to help you determine which structure is preferred.
 3. Repeat what you did in step 2 for the molecule $\text{N}\equiv\text{N}-\text{O}$ and $\text{N}=\text{O}=\text{N}$. Note that when you have two conformers generally the lower energy conformer is the preferred structure. Based on the Mopac and Gamess results, which conformer is preferred? Please note, for structures that may be linear or may become linear, you will have to select the "Cartesian Coordinates" option on the "Advanced" pane in the computational engine setup procedure.
 4. For the ozone molecule, O_3 ,
 - a) Draw the Lewis diagram
 - b) Build a model and photograph it
 - c) Predict if the molecule has a dipole moment
 - d) Complete Mopac and Gamess calculations and try and explain any inconsistencies between the calculated optimal bond lengths, partial charges, and your Lewis diagram with formal charges. Please note, after you "Clean-Up" the structure you will have to remove the extra hydrogen atoms added by the builder. To do this click on "Tools" and then select "Adjust". Left click on a hydrogen, then right click. A dropdown menu should appear that allows you to delete the atom. Repeat for the other hydrogen.
 5. For the molecule PF_5
 - a) Draw the Lewis diagram and predict the VSEPR shape of the molecule.
 - b) Can you build a model with the model kit? If so, photograph it.
 - c) Using Mopac and Gamess, do you get the same shape you predicted with VSEPR theory

- when you do a geometry optimization? Please note, you will need to use the “Clean-up” option to force the program to produce a 3D structure prior to optimizing the molecule.
- d) Comparing Gamess and Mopac, do the methods distinguish between axial and equatorial bonding sites? How?
6. For the molecule SF₆
- Draw the Lewis diagram and predict the VSEPR shape of the molecule.
 - Can you build a model with the model kit? If so, photograph it.
 - Using Mopac and Gamess, do you get the same shape you predicted with VSEPR theory when you do a geometry optimization? As with PF₅, you will have to “Clean-Up” the structure before optimization.
 - Comparing Gamess and Mopac, do the methods distinguish between axial and equatorial bonding sites? How?
7. For the molecule IF₅
- Draw the Lewis diagram and predict the VSEPR shape of the molecule.
 - Can you build a model with the model kit? If so, photograph it.
 - Using Mopac do you get the same shape you predicted with VSEPR theory when you do a geometry optimization? Be sure to “Clean-Up” the molecule prior to optimization.
 - Do the same type of optimization calculation we have been doing before with Gamess (RHF/6-31G(d)). If the calculation fails, look at the bottom of the RAW output file to try and determine what went wrong. Record the error reported by the program. Try to change options to the computational engine to get it to run to completion (Hint: 3-21G is a good thing here). Are your results consistent with your predicted geometry? Describe any discrepancies.

Writeup: This lab will be submitted to me electronically. You may use any word processing program you like, but the final report will be submitted to me as a PDF file. For each molecule include:

- Your Lewis diagram (in a worst case scenario you could draw it on a sheet of paper and include a picture of your drawing taken with your camera, in a best case scenario you could use some software to draw the Lewis diagram).
- A picture of the model you made (where applicable)
- A chart with columns for predictions from your Lewis diagram and/or VSEPR shape (e.g. - shape of molecule, dipole moment, equal bond lengths) and relevant information from the computational chemistry programs (method used, parameters, basis sets, molecular energy, bond lengths, bond angles, failed calculation, etc)
- A picture of the optimized structure from each of the computational engines (you can save these images in WebMO)
- A paragraph describing any discrepancies between your predicted results for the particular molecule and the those results produced by the molecular model kits and the computational chemistry engines. For instance, where you were asked to predict the best structure, describe your reasoning for the choice and explain any reasons why your results may differ from those of the computational chemistry programs. If your results do agree, then state that. If you could not build the model of the molecule with the model kit then is that a problem with the molecule

or the model kit? How would you fix it? If you could not run a certain calculation with a program because of basis set limitations, is that a problem with the molecule or the computational program? How would you fix it?

Send your PDF file as an attachment to pounds_aj@mercer.edu with the subject LAB 6 REPORT.