

## 10: Modeling Molecular Structure, Part II—CH141L

November 17, 2014

This week, we'll use Gaussian to explore electronic structure and bonding. Work from this document during lab. At the end of the lab period, hand in the completed *Electronic Structure Report Sheet*.

### Running Gaussian on WebMO

Gaussian is a program that uses approximate methods to solve the Schrodinger equation for molecules and other chemical systems. We'll use the program WebMO to run Gaussian. WebMO a web-based Java applet that writes and reads Gaussian files.



Access Colby's WebMO applet by opening this page <http://schupflab.colby.edu/> on Firefox (Use Firefox instead of Safari. WebMO works better on Firefox). Click the link to "WebMO start page" near the top of the screen. Enter your lab group's username and password. Hit login.

WebMO's main screen is the "Job Manager". There you'll see a list of past, completed jobs you can open, options to manage the past jobs, and a button for a "New Job" at the top left corner of the list. Click that button. This is where you will start each part of today's lab.

**Important:** Due to security problems with Java applets, MacOS and Firefox will *frequently* ask for permission to run WebMO. We trust WebMO, so we can ignore these warnings, and by clicking "Don't show again" in the warning, this should stop happening.

### Part 1: Atomic orbitals of hydrogen

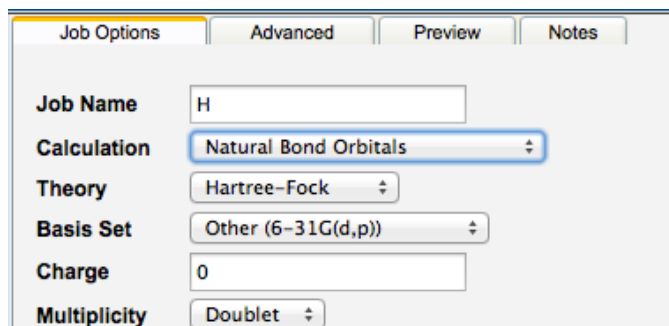
We'll calculate the densities and energies of the hydrogen atom and compare them to the atomic orbitals we saw in lecture.

On the Job Manager page, start a New Job. A viewer window will open. Click on the periodic table tool () and click on the hydrogen atom. Click anywhere on the main screen, and a little white atom representing hydrogen should appear. Click the forward arrow in the bottom right corner ()

In the next screen, we'll tell WebMO to use Gaussian to do a calculation. Use the settings as in the screen below. These should be the default settings. Click the forward arrow.

Engine	Description
<input checked="" type="radio"/> Gaussian	Ab initio and semi-empirical calculations
<input type="radio"/> Mopac	Semi-empirical calculations
Select Server	<input type="text" value="schupflab.colby.edu"/>

In the next screen, you will set up your calculation. You need to change several things: 1) For "Calculation", select "Natural Bond Orbitals". 2) Under "Basis Set" select "other" and write 6-31G(d,p). The screen should look like this:



Job Options	Advanced	Preview	Notes
Job Name	<input type="text" value="H"/>		
Calculation	Natural Bond Orbitals		
Theory	Hartree-Fock		
Basis Set	Other (6-31G(d,p))		
Charge	<input type="text" value="0"/>		
Multiplicity	Doublet		


**Explanation:** “Hartree-Fock” is a method to approximate solutions to the Schrodinger equation. In part, the wavefunctions are approximated as linear combinations of functions in the “Basis Set”. By setting our basis set to 6-31G(d,p), we include p-type orbitals on the hydrogen atom. The “Multiplicity” is “Doublet” because there is one unpaired electron. A singlet has no unpaired electrons, a triplet has two unpaired electrons.

Click the forward arrow to start the calculation.

### Analyzing the results

Your job should appear at the top of the “Job Manager” screen. Once it is complete, click on the job title to open the “Job View” window.

Scroll down to the “Natural Atomic Orbitals” to view a list of orbitals and energies. **Complete Part 1a on the report sheet.**

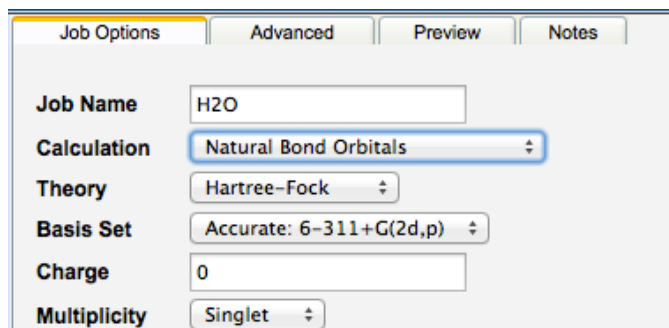
Click on one of the magnifying glass () next to one of the orbitals in the “Natural Atomic Orbitals” list. This will open the “Orbital Viewer”. Click on the viewer and use the mouse’s scroll bar to zoom in and out. You can also click and move the mouse to rotate the image. Under the “View” option, select “transparent” under “opacity” and “Axes” under “Display”. You’ll see the hydrogen atom under the orbital and the axes. Pick an orbital that should have a node, select the view options, and you’ll see the coloring scheme for positive and negative amplitude. **Complete the rest of Part 1 on the report sheet.**

### Part 2: Molecular orbitals of water

We’ll look at the calculated bond orbitals of water, and compare them to the Lewis structure.

Start a new job. First, make the backbone for a water molecule by clicking on the viewer screen to make one atom. Click on that atom and drag to add another atom bonded to the first, and repeat to make the third. If you make a mistake, you can right click on an atom to delete it. Once you have the backbone, hit the letter “H” on the keyboard and click the outer atoms to make them hydrogens. Similarly, make the central atom an oxygen. Click the forward arrow. If a dialog appears asking about symmetry, click ok.

Prepare a Gaussian calculation with parameters as follows:



Job Options	Advanced	Preview	Notes
Job Name	H2O		
Calculation	Natural Bond Orbitals		
Theory	Hartree-Fock		
Basis Set	Accurate: 6-311+G(2d,p)		
Charge	0		
Multiplicity	Singlet		


Go to the “Preview” tab, and click “Generate”. This displays the text of the Gaussian input file.


In the first line of the input file, change “SP” to “OPT” to change from a single-point calculation on the geometry you just made to an optimization calculation, where the minimum-energy geometry will be found. The first line should read #N HF/6-311+G(2d,p) OPT GFINPUT POP=(FULL,NBORed) Geom=Connectivity.

Click the forward arrow, and click “OK” on the dialog box.

This calculation can take about 20 seconds. If the completed calculation doesn’t appear hit “Refresh” in the Job Manager window.

### Analyzing the results

Open the completed job. If the molecule doesn’t appear in the viewer window, click “Reset Viewer”. You can select two atoms by using the atom selector tool () and holding shift. The bond length will appear. If you select 3 atoms, you can see the bond angle.

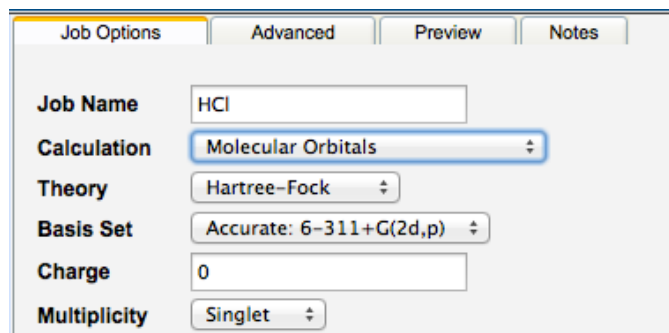
You can watch the optimization steps by clicking the film strip on under “Geometry Sequence” () , and graph the change in energy by clicking the magnifying glass. **Complete Part 2a on the report sheet.**

Observe the “Natural Bond Orbitals” using the orbital viewer. Remember to turn on transparency and the axes. **Complete the rest of Part 2 on the report sheet.**

### Part 3: Bond polarization in diatomic molecules with hydrogen

We’ll determine the bond length and dipole moment in a series of hydrogen-containing molecules.

Start a new job, make a HCl molecule, and prepare a Gaussian calculation with parameters as follows:



Job Options	Advanced	Preview	Notes
Job Name	HCl		
Calculation	Molecular Orbitals		
Theory	Hartree-Fock		
Basis Set	Accurate: 6-311+G(2d,p)		
Charge	0		
Multiplicity	Singlet		

Go to the “Preview” tab, and click “Generate”. Again change “SP” to “OPT” to run a geometry optimization calculation. Submit the job.

While the HCl job is running. Prepare and submit similar jobs for H<sub>2</sub> and LiH.

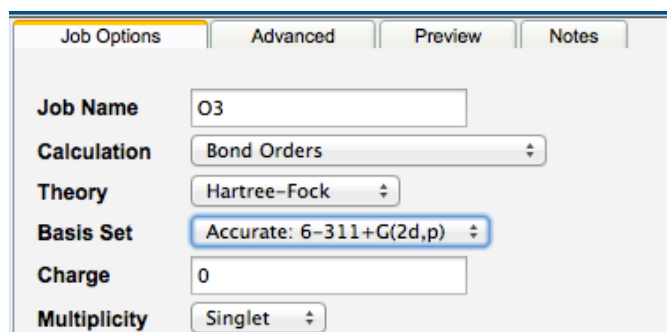
### Analyzing the results

Open one of the three jobs. Visualize the dipole by clicking on the magnifying glass under “Dipole Moment”. Visualize the electron density by clicking on the magnifying glass next to one of the “Molecular Orbitals”, and clicking “Electron density” in the orbital viewer. Don’t forget to make the surface transparent. **Complete Part 3 on the report sheet.**

### Part 4: Bond orders and energies in ozone: Is it cyclic?

We’ll build two models of ozone to determine the preferred bonding configuration.

Build a O<sub>3</sub> molecule following the Lewis structure for the bent geometry. Before you click forward, go to “Clean-Up” and pick “Mechanics Optimize”. This does a simple optimization based on the bent shape and the two bonds. Run a Gaussian calculation with the following parameters:



Job Options	Advanced	Preview	Notes
Job Name	O3		
Calculation	Bond Orders		
Theory	Hartree-Fock		
Basis Set	Accurate: 6-311+G(2d,p)		
Charge	0		
Multiplicity	Singlet		

Again, go to the “Preview” tab, and change the file to run a geometry optimization calculation. Submit the job.

While this job is running, prepare another job with cyclic ozone. Repeat the previous steps, but add an additional bond between the two outer oxygens. Run a geometry optimization calculation on this molecule.

### Analyzing the results

For each of the ozone molecules, measure bond lengths and angles, look at the final, optimized energy and the “Bond Order” table. The order of a bond between two atoms is reported in the table. Atom numbering corresponds to the structure in the viewer. **Complete Part 4 on the report sheet.**

### Part 5: Choose your own experiment

Pick another molecule from last week’s lab. Prepare a geometry optimization calculation that determines the molecular orbitals, the bonding orbitals, or bond orders. **Report your results in Part 5 on the report sheet.**