

Molecular Modeling 2: Computational Chemistry

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Introduction

Computational chemists use the principles of quantum mechanics, classical physics and thermodynamics to answer questions about chemical processes. Since its birth in the 1960's, the growth of computational chemistry has generally followed advances in computer technology and it has become an essential tool in chemical research. It is used both as a guide to new avenues of research and as a way to understand fundamental chemical processes. Computational chemistry is used in areas as diverse as materials science to pharmaceutical research where most companies have a computational chemistry division that helps guide the development of new drugs.

Of all the areas in computational chemistry, calculations that solve Schrödinger's equation are the most prevalent. Almost any property associated with where electrons are in the molecule, and how those electrons behave can be calculated. For example, molecular geometries, the polarity of a bond, the molecular orbitals, or the visible spectrum of a molecule can all be calculated using quantum calculations.

Schrödinger's equation is written succinctly as

$$\hat{H}\Psi = E\Psi \quad (1)$$

where \hat{H} is the Hamiltonian operator, ψ is the wavefunction, and E , the energy, is the eigenvalue of \hat{H} . [If you have a function e^{5x} and the operator is to take the derivative, $\frac{d}{dx}$, then our eigenvalue equation would be $\frac{d}{dx}(e^{5x}) = 5 e^{5x}$ where 5 is the eigenvalue since you apply the operator to the function and get back the function multiplied by a value which we call the eigenvalue.]

In quantum chemistry methods, Schrödinger's equation is solved to give the electron density and the allowed electronic energies in a molecule (among other things). Solving Schrödinger's equation is dependent upon two primary considerations: 1) the form of the Hamiltonian and 2) the space electrons are allowed to occupy.

The *level of theory* describes the type of Hamiltonian and the *basis set* describes the space electrons are allowed to occupy. In general, the Hamiltonian for a molecule must include terms that take into account the kinetic energy of the electrons, the kinetic energy of the nuclei, electronic-nuclear attraction, electron-electron repulsion and nuclear repulsion. The full Hamiltonian is impossible to solve exactly for systems with more than one electron. Therefore we must make some approximations in order to solve the Schrödinger equation, and we must take an iterative approach which is

facilitated by computers. In this exercise we will use three different levels of theory (essentially different approximations) to solve Schrödinger's equation: Austin Model 1 (AM1), Hartree-Föck (HF) and Density Functional Theory (DFT).

The AM1 level of theory is based upon a *semi-empirical* theory where certain portions of the molecule's energy are approximated *empirically* (determined experimentally). In semi-empirical methods, only valence electrons are considered explicitly, while paired core electrons are approximated. In addition, the space the electrons are allowed to occupy is restricted to the bare minimum (H –1 set of s orbitals; C, O, N – 1 set of s, 3 sets of p orbitals).

HF is what is termed an *ab initio* (Latin: from the beginning) method because the Hamiltonian is based upon fundamental principles. The Hartree Hamiltonian is written so that the last term is a single potential that describes an average electron-electron repulsion energy or an interaction potential of electron *i* with all other electrons *j*. A general term for electron-electron repulsion and neglect of electron-electron correlation is needed to make the calculation more feasible. Methods that account for electron-electron correlation are available but computationally expensive and are usually restricted to molecules with unpaired electrons.

DFT is similar to HF in that all electrons are considered. However, in DFT the electron density ($|\psi|^2$) rather than the explicit ψ is solved for. In addition, electron-electron correlation is empirically parameterized based upon the density. DFT levels of theory are named to give specific information about them, but since these can be long, they are abbreviated (e. g., B3LYP, BPW91, mPWPW91) and often look like a bowl of alphabet soup.

In this exercise you will be using WebMO,¹ which is a web-based, user-friendly interface to the program Gaussian,² to calculate orbital energies and other properties of a series of molecules.

Experimental

General Instructions

Open a web browser such as Safari or Mozilla Firefox or Internet Explorer and go to the Truman WebMO website <http://pyrite2.truman.edu/~webmo/cgi-bin/webmo/login.cgi> (Google Chrome no longer supports Java applets.) If you are reading this on-line, click on the link to go there, or copy and paste the link into the address bar. The *Login screen* shown in Figure 1 will be displayed. If one web browser does not work for you, try a different one. Also make sure that you have the most recent version of Java.

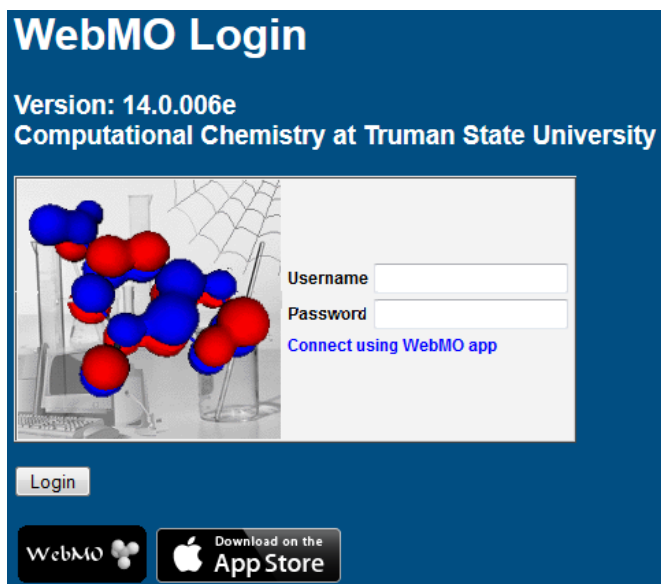


Figure 1. WebMO *Login* screen.

Enter your username and password which will be given to you by your instructor. Click the "Login" button (or just hit enter) and the *Job Manager* screen (Figure 2) will be displayed. You are now ready to set up your first calculation. If more than one person is logged on to an account at the same time, WebMO will behave erratically.

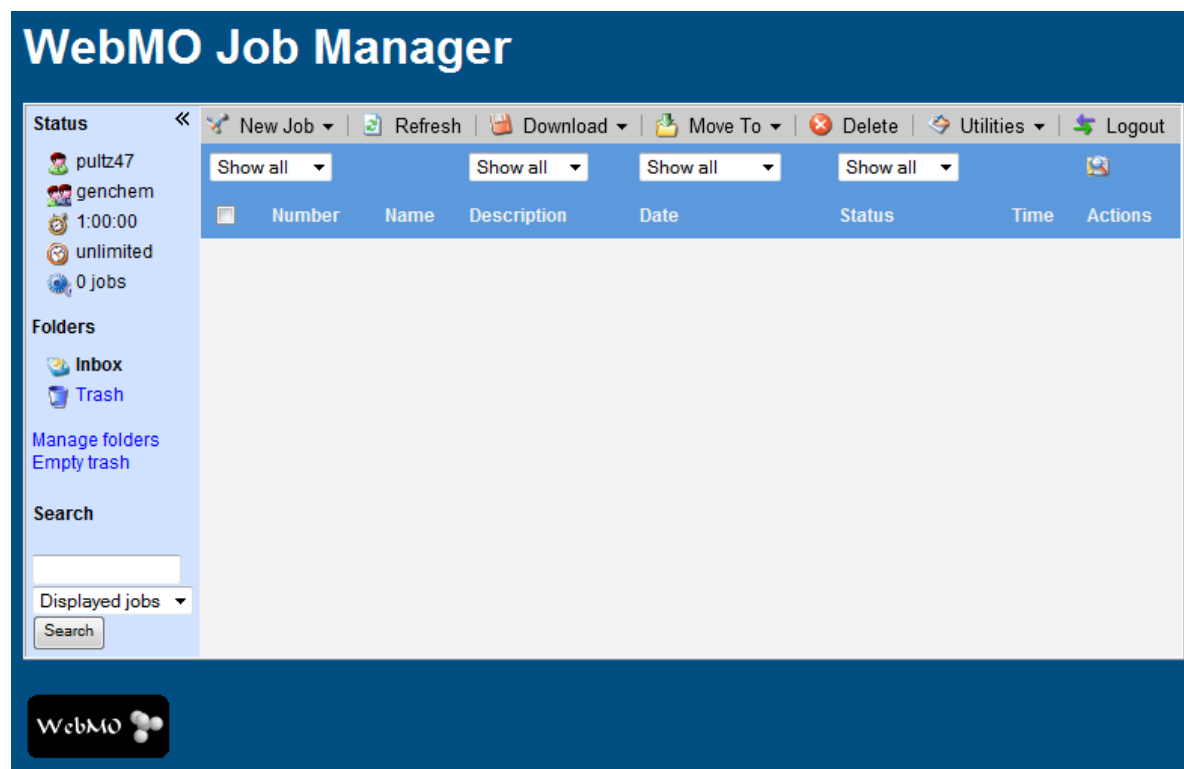


Figure 2. WebMO *Job Manager* screen.

Before performing any calculations you will need to input information about the molecule, what calculations to do and what level of theory that you want the program to use. The steps are 1) building the molecular framework, 2) selecting the calculation to do (geometry optimization, energy level calculation, etc.), 3) selecting the level of theory, 4) choosing a basis set, and 5) specifying the charge and number of unpaired electrons (multiplicity) on the molecule. With WebMO you are guided through the configuration process; start it by going to "New Job" and clicking on "Create New Job". This will take you to the *Build Molecule* screen shown in Figure 3.

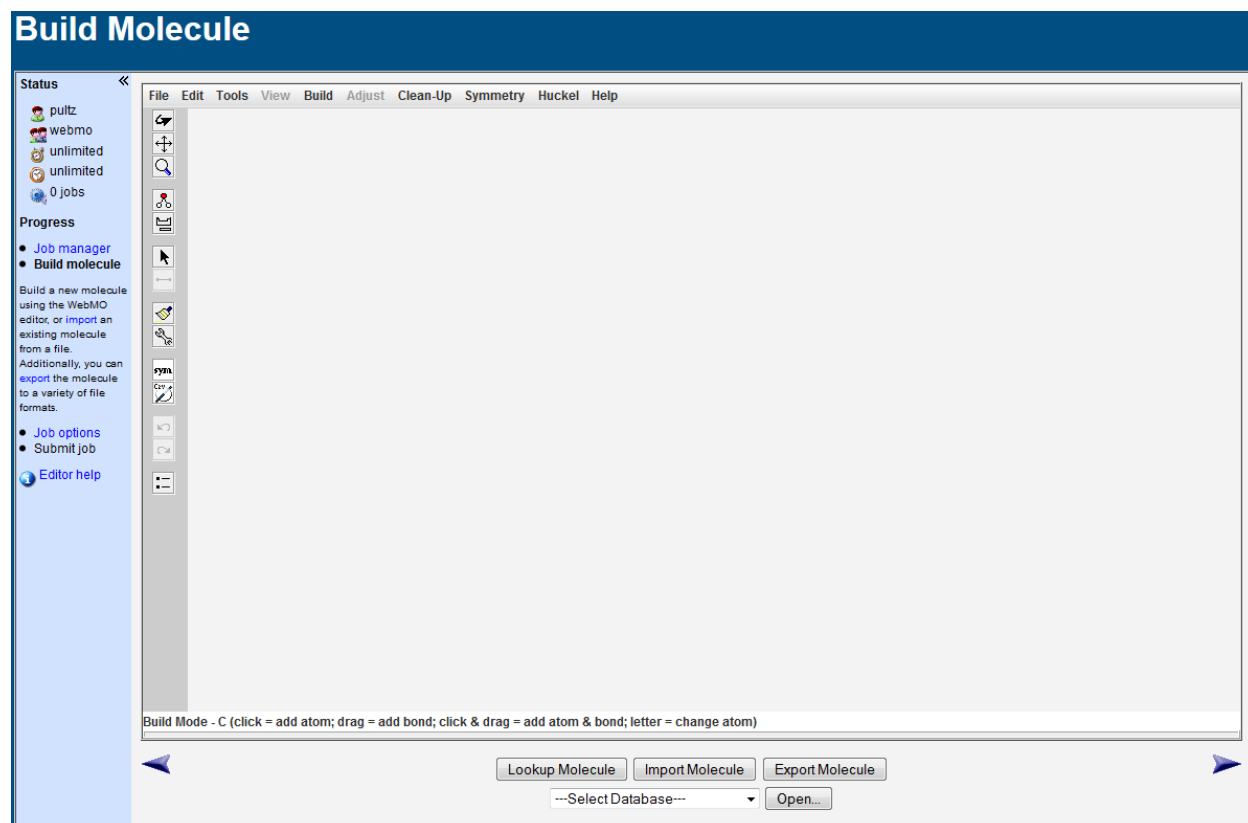



Figure 3. WebMO *Build Molecule* screen.

WebMO assumes that you want to create a new molecule when you create a new job, so "New Job: Create New Job" takes you straight to the editor. Click on the "Periodic Table" button, , to display a pop-up periodic table and click on the element you want to add. Then click in the gray space to add that atom. If you want additional atoms of the same element, click to place them in appropriate spots, being guided by VSEPR as best you can. For a new element, go back to the "Periodic Table" button and repeat the process until all the atoms you need for your molecule have been added. To draw bonds between atoms, click and drag the mouse from one atom to another. It is not usually necessary to specify any bond over a single bond because the program will determine the number of bonds that are needed.














| WebMO Editor | | |
|---|--------------------------|--|
| Button | Name | Function |
|  | Rotate | Allows you to rotate your molecule by clicking and holding the left mouse button and then dragging. |
|  | Translate | Click and hold left mouse button and then drag to move your molecule within the display window. |
|  | Zoom | Zooms in on or out of your molecule. |
|  | Build | Places atoms in the display window. |
|  | Periodic Table | Allows selection of atom to be placed when build button is active. |
|  | Adjust/Select | When selected you can click on any atom or bond in your molecule and change its properties. In the View Job screen this button allows you to select atoms to determine bond lengths and bond angles. |
|  | Help | Mouse over this button gives you more information on what the last button pressed does. |
|  | Clean Up | Performs a comprehensive clean up of the drawn molecule. Program takes its best guess as to what you really meant to draw. You can choose to clean up only certain parts of the molecule from the menu bar (<i>Clean-Up</i>) |
|  | Clean Up using Mechanics | Same as the comprehensive clean up button except the program uses molecular mechanics to determine the best angles and bond lengths. |
|  | Undo | Undoes the last action. |
|  | Redo | Repeats the last action. |
|  | Preferences | Allows you to edit some of the Editor's settings. |

Figure 4. WebMO Editor Buttons.

Comprehensive Cleanup adds hydrogen atoms to bonded atoms you have already drawn so that the octet rule is usually followed or zero formal charges are achieved. If you do perform a *Comprehensive Cleanup* on a molecule after you have drawn it, make sure the number of atoms agrees with the molecular formula and your starting geometry is still what you want. Unless otherwise directed to do so, do **not** perform a *Comprehensive Cleanup*.

If nothing is happening, look at the bottom of your screen and see if the icon  is present. If so, click on it and click the Allow button. Always run any application associated with WebMO.

When you are done drawing the molecule, click on the blue right arrow in the lower right corner. This will take you to the *Configure Job Options Screen* shown in Figure 5.

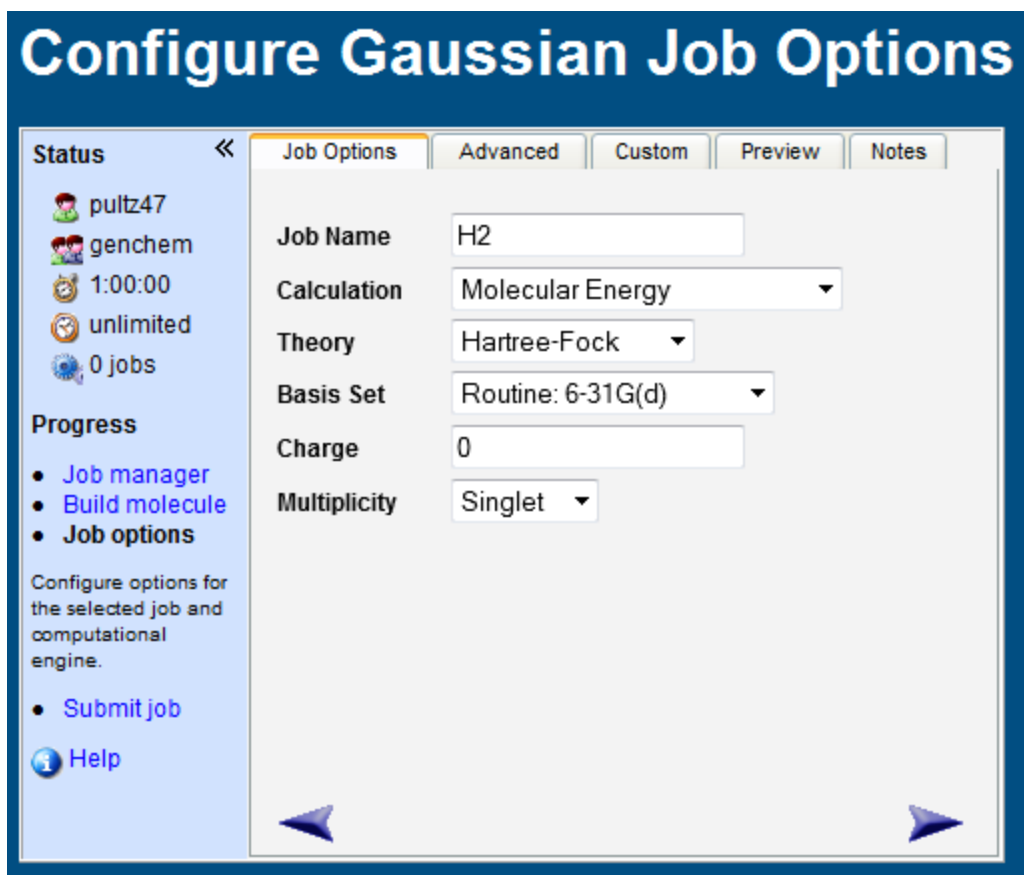


Figure 5. WebMO *Configure Job Options* Screen.

The program will give your job a name based on the molecule that you drew. Be sure that your job has a unique name (it helps if the name is somewhat descriptive of what the calculation was about, like "H2 Hartree-Fock 3-21G"). Choose the type of calculation to do from the *Calculation Pulldown* menu; **your initial calculation will never be the default** in this exercise. Choose a theory from the *Theory Pulldown* menu and then select a basis set from the *Basis Set Pulldown* menu. If you are performing a calculation on an ion, enter its charge. For molecules the charge is 0. Leave the multiplicity as a singlet (this means that there are no unpaired electrons). Verify what you have entered and then start the calculation by clicking the right hand blue arrow head or "Submit job."

WebMO returns to the *Job Manager* screen. The *Job Manager* lists all the jobs you have submitted to be calculated along with pertinent information about them (from left to right this is job number, job name, type of job, the date you submitted it, job status, the length of the job). In the far right column ("Actions") there will be displayed one of several icons ("View", "Kill", "Restart") that you can use to control how the computer handles your job. If you made a mistake, one of two things usually happens; the program terminates your job and your results file contains nothing (or gibberish) or the program runs for a long time. If you want to stop a job for any reason, click the "Kill" icon (✖). You can restart a stopped job by clicking on the "Restart" icon (🔄) which is

displayed whenever a job is terminated abnormally. When your job is finished, its status will be *Complete* and the "View job" icon (🔍) will be displayed to the right of the job. After you have submitted a job it is a good idea to occasionally click on the "Refresh" button on the WebMO Job Manager screen to get the most up to date information about your jobs; this is not the web page refresh button.

Important: If a calculation fails, click on the "View job" icon under Actions for the job. If you see the message "Optimization not converged (too many iterations)" and if the molecule looks okay (the molecule may be rotated from how you initially drew it), click on the button New Job Using This Geometry. The next screen is Build Molecule. Click on the right hand blue arrow head to go to the "Configure Gaussian Job Options" screen. You probably should modify your job name to distinguish it from the previous failed job. Verify that the entries for Calculation, Theory, Basis Set, Charge, and Multiplicity are the same as specified in this exercise, and if they are not, correct them. Click on the right hand blue arrow head to submit your job again.

When you click on the "View job" icon, the results of your calculation will be displayed on the *View Job* screen like the one shown in Figure 6. At the top of the screen will be displayed the job number, the name you gave the job and what calculations were performed. Below this will be the *Viewer*, which is similar to that on the *Build Molecule* screen, but with some new buttons and actions that are listed in Table 1.

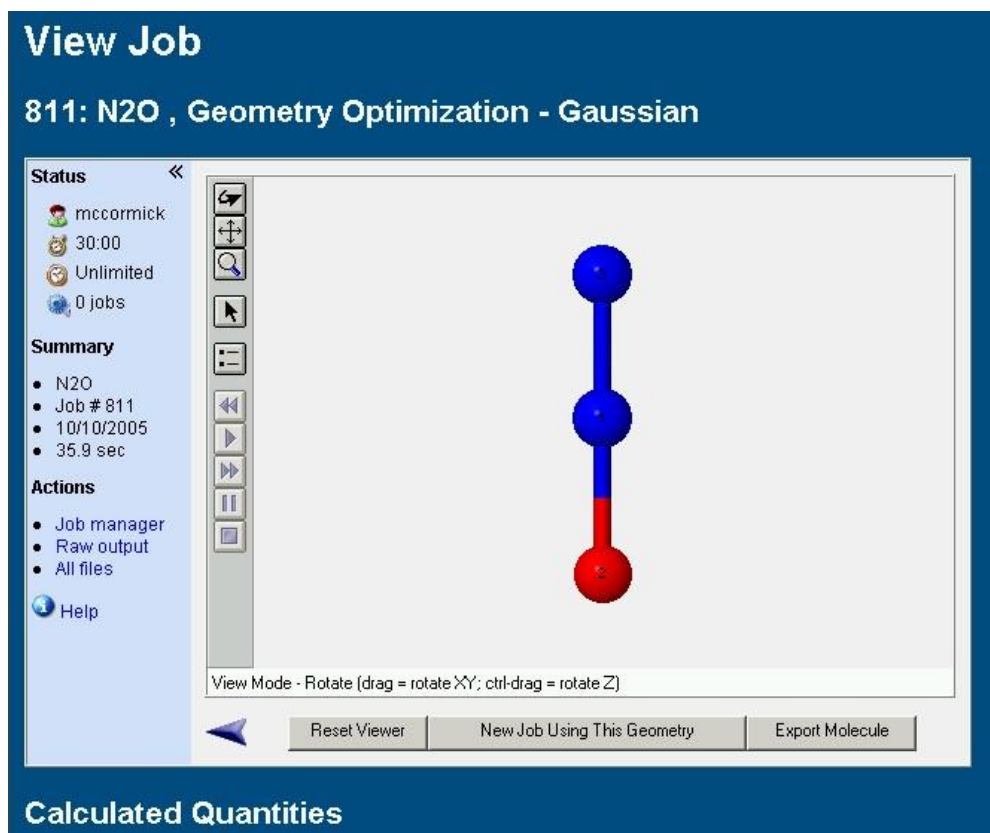


Figure 6. A portion of the View Results screen.

| Button/Actions | Function |
|------------------------------------|--|
| <i>Job Manager</i> | Returns to the <i>Job Manager</i> screen. |
| <i>Raw Output</i> | Shows the program's main output file. |
| <i>All files</i> | Lets user view all the output files and change whether they are text or binary (if you select binary the program will download the file to your computer, so don't do it). |
| <i>Reset Viewer</i> | Returns the Viewer to how it was when you entered the <i>View Results</i> screen. |
| <i>New Job Using This Geometry</i> | Starts a new job using the results of this job as a starting point (very useful). |
| <i>Export Molecule</i> | Allows user to take structures that you have created and pass them to other programs for viewing or additional calculations. |

Table 1. Buttons on the WebMO *Viewer* that are active in the *View Results Screen*.

Below this will be a listing of the calculated quantities, which vary depending on what you told the computer to calculate. Be sure to scroll all the way to the bottom of this screen.

H₂ Geometry Optimization and Molecular Orbital Calculations

In the *Job Manager* screen go to the "New Job" tab and click on "Create New Job" to open the *Build Molecule* screen. Specify the element H by using either the Periodic Table button on the left side of the screen or the Build tab at the top. Put two H atoms in the window. Click on one H atom and drag the mouse to the second to create a bond between them. Continue to the next screen by clicking on the right hand blue arrow head. WebMO defaults to "Job Options" which is where you want to be for this exercise. Perform a "Geometry Optimization" calculation (not the default option) using "Hartree-Fock" theory and the "3-21G" basis set. Leave the charge as "0" and the multiplicity as "Singlet." Give your job a name. What you have told the computer to do is to repeatedly solve Schrödinger's equation each time adjusting bond angles and lengths (in this case, only the bond length) until it finds the lowest energy structure. Verify that you will do a geometry optimization and use the specified basis set. After the job is complete, click on the "View job" button in the *Job Manager* screen to look at the output.

Open a new Word document to record your molecule. Format the "2" as a subscript in H₂. Copy and paste the Route line (found under "Calculated Quantities") to have a succinct record of the theory, basis set, and type of calculation, and the route line is useful in determining why you may have obtained unexpected results. Record the RHF energy, including sign and units, and again it may be easiest to copy and paste. Compare your value to the value calculated by classmates. You should converge to almost the same value; if there are significant differences, discover the reason and fix the problem.

If you get a warning "The application's digital signature cannot be verified" and the name is "MOViewer Applet," click Run. If MOViewer fails to show your MO, press Ctrl/Alt/Delete, click on Task Manager, then Processes, close Java.exe, and try again.

Once the H₂ geometry is set, we can perform a molecular orbital calculation on H₂. In a molecular orbital calculation, you will specifically ask the program to render the shapes of the molecular orbitals from what is known about the wavefunction. From the *View Job* screen, click on "New Job Using This Geometry". You should now be in the *Build Molecule* screen. Click on

the blue right hand arrow head or "Job Options". For this new job the *Calculation* is "Molecular Orbitals," *Theory* remains "Hartree-Fock," the *Basis Set* is "3-21G," the *Charge* is "0" and the *Multiplicity* is "Singlet." Give the job a name. Click either the right hand blue arrow head or "Submit Job." When the job is complete, click on the *View Job* button and scroll down to the section called "Molecular Orbitals". To view a molecular orbital, click the "View" button to the right of the molecular orbital. For H₂, the two lowest-energy molecular orbitals are labeled "1" and "2". These are the σ (bonding) and σ^* (antibonding) molecular orbitals, respectively. A screen may appear asking you what to do. Click "Open" to open the MOViewer file (*.mo). One issue that you might encounter when viewing the molecular orbitals is that the program may clip the pictures (the MOs will look like sections were shaved off). To fix this, left click on the molecular orbital and use the center mouse wheel to adjust the size. If you do not have a mouse, right click in the display window and select preferences in the pop-up menu. (Or click on View to access Preferences.) Set *Iso. Value (MO)* to 0.08 and click Okay.

The default view for molecular orbitals often does not allow you to see where the nuclei are located. Put the cursor on the molecular orbital picture and drag to rotate it so that you can see both nuclei. There may be holes or windows in the solid surface so that you can see inside to the nuclei. You can also modify the display by right clicking in the display window, point to the *Opacity* option and then select *Transparent* or *Mesh* from the sub-menu that appears.


In the "View Job" screen, click on the molecular orbital, then Ctrl-C to copy, go to your Word document, and press Ctrl-V to paste. (Alternatively, you could click File and Save Image, then import the file into your Word document.) Label the MO and record its energy. **Do not close MOViewer when you are finished with this orbital since you will use it several more times.** Also copy MO # 2, label it, and record the energy. Note that in the "View Job" screen there will now be a second tab labeled "job####_mo2" where the job number replaces ####, and you can switch between the MOs. Everything you record for H₂ should fit on one page.

N₂ Molecular Orbital Calculation

Build N₂ and perform a "Geometry Optimization" using Hartree-Fock theory and the 3-21G basis set (remember that N₂ is a singlet and has no charge). When the job is complete, record N₂ in your Word document and paste the Route line and RHF Energy, again including the sign and unit. On the optimized structure, perform a "Molecular Orbitals" calculation. View molecular orbitals 3 through 7. They are σ_{2s} , σ_{2s}^* , the two π_{2p} orbitals, and σ_{2p} , respectively. In your Word document make a table with headings **Molecular Orbital Number**, **Unrotated**, and **Rotated**. Copy the five molecular orbitals (without rotation). How do the π molecular orbitals differ? Then rotate each of the five molecular orbitals to see both nuclei, and copy the rotated molecular orbitals. Also record the energy and occupancy for the first ten molecular orbitals.

Structure of N₂O

There are two potential isomers of N₂O: one with a N-N-O framework and another with a N-O-N framework. Build both frameworks for N₂O (an uncharged singlet) in the *Build Molecule* screen, each as a separate job, using only single bonds. It is important that the N-O-N calculation start with a linear geometry. (The N-N-O framework can also be set to start with a linear geometry, but it usually turns out to be very close to linear as the result of the calculation. If your NNO calculation fails or your energy is significantly different from classmates, try building NNO again


and impose a linear geometry.) To start with an exactly linear geometry, click on the "Select" button, , and then click on one of the end atoms in the structure. While depressing the shift key, click on the central atom (the bond length will be displayed in the lower left corner of the window) and then the third atom (the bond angle, which should be around 180°, will be displayed). From the menu bar at the top of the *Build Molecule* screen, select *Adjust* and then *Bond Angle*. Enter 180 in the pop-up window and then select *OK*.

Perform a geometry optimization on each structure (be sure to give each a different name) using Hartree-Fock theory and the 6-31G(d) basis set. When each job is complete, click on the *View job* button. In your Word document, type your structure, either NON or NNO, and paste the Route line and RHF Energy, including unit, from the WebMO screen. Copy just the value, starting just before the negative sign and ending just before the unit, into Excel. Repeat the recording in Word and Excel for the other structure. In Excel calculate the magnitude of the energy difference in Hartree and record the result to four significant figures in Word, including the unit. Typical bond energies are given in kJ/mol, so convert the energy difference from Hartree to kJ/mol using Excel. Go to <http://physics.nist.gov/cuu/Constants/index.html> and search for Hartree. Choose hartree-joule relationship and copy the value into Excel. Delete the spaces in the value and replace " x 10" by "e" to get the format that Excel recognizes. Click your browser back button twice and search for Avogadro constant. Copy this value into another Excel cell and convert to the format expected by Excel. Multiplying the two cells gives 1 Hartree equals some number of J/mol. Convert from J to kJ so that you have 1 Hartree equals some number of kJ/mol. Multiplying your energy difference by this number should give you the energy difference in kJ/mol between the lowest energy structure (i. e., the one that actually exists) and the highest energy structure. Report the difference to four significant figures. Compare your RHF energies and energy difference to those of your classmates.

Now scroll down to the section called "Partial Charges." The partial charge on each atom is listed by atom number and element. Click on the "View" button (magnifying glass in Partial Charges section) to graphically display the partial charges on each atom in the viewer at the top of the page. The values should be in close agreement with values calculated by other students. Copy the three atoms of each N₂O structure in your Word document and show the calculated partial charges on each atom. (To copy in Windows, press the PrtScn button, press Ctrl-C to copy, open Paint and press Ctrl-V to paste. In Paint, click on Select, then Rectangular Selection, and use the mouse to put a rectangle around the molecule. Press Ctrl-C and then paste into your Word file.)

Bond Orders of N₂O

Return to the results for the lower energy structure. Below the picture of the molecule click on "New Job Using This Geometry" to return to the *Build Molecule* screen. Select "Job Options" (or click the right hand blue arrow head) and set up a "Bond Order" calculation using Hartree-Fock theory and the 6-31G(d) basis set. The charge is again 0 and the multiplicity is singlet. Name the job and submit it. **Note:** you do not need to run the higher energy structure, but you may if you are interested and time permits.

When the job is complete, view the results. In the *Viewer*, click on the "Select" button, . Then click on the central N (atom will be highlighted) and then while depressing the shift key, click on the other N. The N-N bond length will be displayed in the *Viewer's* status window; record this number (the units of bond length used here are Ångstroms, symbol Å, 1 Å = 1x10⁻¹⁰ m).

Unselect the terminal N by holding the shift key and clicking on it. Now select the O and record the N-O bond length. Determine the N-N-O bond angle by highlighting all three atoms, starting at an end atom; the angle should be 180°.

Note the number on the central N and scroll down to the section called "Bond Order". The numbers with four digits after the decimal indicate the bond order between the atom listed in the row heading (on the left) and the column heading (on the top). The bond order of an atom with itself is zero. Record the calculated N-N and N-O bond orders between adjacent atoms.

You may wish to include a picture.

Structure of ClF₃

Draw the Lewis electron dot structure for ClF₃ and predict its molecular shape with VSEPR theory. Use this as the starting point to build ClF₃ in WebMO. Perform a "Geometry Optimization" on ClF₃ using the semi-empirical theory AM1. The *Basis Set Pulldown*, will no longer be active because an AM1 calculation does not require a basis set (do not be concerned that there is an entry in the pulldown, the program will ignore it). **Note:** this calculation may fail because it exceeds the default maximum number of iterations. If this happens, simply restart the job, although you may have to select the "Other ()" option in the *Basis Set Pulldown*.

While this calculation is running, set up another geometry optimization calculation for ClF₃ using the VSEPR geometry as the starting point. This time use the theory B3LYP and the basis set 6-31G(d).

Copy the structures predicted by each calculation. Be sure to include the starting geometry and which theory was used. Determine the Cl-F bond lengths (there are three of them) and the F-Cl-F angles (there may be several) and include these on your sketches.

Now perform a "Geometry Optimization" on the ClF₃ structure predicted by AM1 theory, but using the theory B3LYP and the 6-31G(d) basis set. Record the results of this calculation in your report, again specifying the starting geometry and theory.

Bond Polarity

Create separate jobs for the following molecules: CH₄, CH₃BH₂, CH₃NH₂, CH₃OH and CH₃F. After you draw each molecule in the *Build Molecule* screen, do a *Comprehensive Cleanup* to get better results. (For CH₄ you only need to put in a C atom and the *Comprehensive Cleanup* will enter the four H atoms in a tetrahedral arrangement. For the other four molecules, enter atoms other than hydrogen and connect them with a bond. *Comprehensive Cleanup* will then add the hydrogen atoms.) Perform a geometry optimization on each using HF theory and the basis set 6-31G(d). All of these molecules are singlets and have no charge.

When the jobs are complete, go to the *View Job* screen for each molecule. Scroll down to the section called "Dipole Moment" and record the dipole moment value (the unit of dipole moment is the Debye). Click on the "View" icon and scroll back to the top to see the direction of the dipole (i. e., which direction are the electrons pulled in the bond). You may need to rotate the molecule to see the arrow. Put a picture of each molecule with the dipole moment in your report.

Results and Analysis

H_2 and N_2

Make a molecular orbital energy-level diagram for H_2 which is to scale; an Excel scatter chart may be the easiest approach. The program assumes the atomic H 1s orbitals are at 0.000 Hartree. You may wish to include in your MO diagram the pictures of the σ and σ^* molecular orbitals.

Make a molecular orbital energy-level diagram for N_2 which shows the ten lowest-energy MOs (use occupancies to help place the electrons). You may wish to make two diagrams, one which emphasizes the difference between the MOs formed from $n=1$ atomic orbitals and $n=2$ atomic orbitals. The second diagram could then zoom in on the MOs formed from the valence atomic orbitals. Both of these diagrams must be to scale, not the caricatures shown in textbooks.

In the Lewis dot structure of N_2 we would predict three bonds and two lone pairs arising from the valence electrons. Is this consistent with the MO picture? How does MO theory describe the bonds and lone pairs in N_2 ?

According to Valence Bond theory, what hybridization would you expect each N atom to have? How does this compare to the MO description? (Hint: think about the following: how are the bonds described? how are the lone pairs described? do the valence bond orbitals look like the molecular orbitals?).

N_2O

Draw the two best resonance structures for NNO and calculate the formal charges on each atom in both cases. Draw the best Lewis dot structure for NON and calculate the formal charges on each atom. Based on formal charges and electronegativity, which connectivity is predicted to be more stable? Does this prediction match the structure which you calculated to have the lowest energy? Based upon your MO calculation, which resonance structure for NNO is slightly dominant? Why is this resonance structure dominant?

The N-N bond length in N_2O has been measured to be 1.128 Å and the N-O bond length has been measured to be 1.184 Å.³ Given the average bond lengths shown in Table 2, are the measured bond lengths and the calculated bond lengths consistent with the bond orders? How well did the calculation do in obtaining the true values of the bond lengths?

| Bond | Bond Length (Å) |
|-----------------------------|-----------------|
| N-N single bond | 1.45 |
| N-N double bond | 1.25 |
| N-N triple bond (in N_2) | 1.10 |
| N-O single bond | 1.40 |
| N-O double bond | 1.21 |
| N-O triple bond | 1.08 |

Table 2. Average bond lengths for different N-N and N-O bonds.⁴

ClF_3

On your VSEPR-predicted structure of ClF_3 indicate the predicted distortions from the ideal angles caused by the repulsion of the bonding pairs by the lone pairs. Do your predictions (using different levels of theory) match that predicted by VSEPR? Which theory can give a better match to the VSEPR model? Why?

The structure of ClF_3 has been determined at $-120\text{ }^\circ\text{C}$ using X-ray crystallography,⁵ and is shown in Fig. 7. Also shown in Fig. 7 are the measured bond angles and bond lengths. Which of the models considered (VSEPR, AM1 or B3LYP) always gives a better qualitative agreement to the actual structure of ClF_3 ? Which can give a better quantitative agreement to the actual structure?

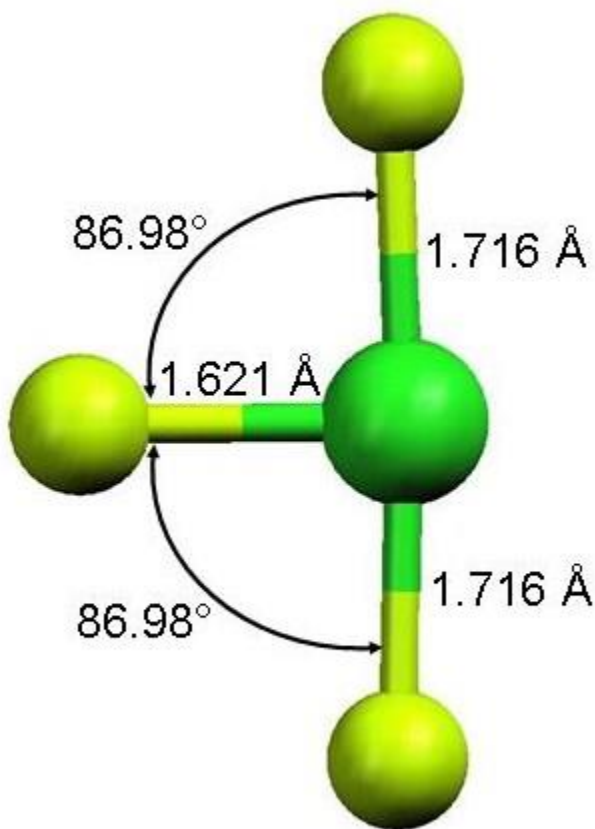


Figure 7. Structure of ClF_3 as determined by X-ray crystallography at $-120\text{ }^\circ\text{C}$ showing the relevant bond angles and bond distances.⁵ Here the fluorines are represented by yellow-green balls and the chlorine by a darker green ball.

With ClF_3 you should have found that the AM1 calculation gave the wrong answer and that when you start from a structure that is not close to the "true" structure, you are not guaranteed that you can arrive at the "true" answer. These illustrate two important considerations in computational chemistry (and anywhere where we use computer models): the appropriateness of the model and the problem of "local" versus "global" minima. The AM1 result is an example of the first consideration because AM1 theory ignores important aspects of bonding, which are included in the B3LYP model, that lead to an incorrect predicted structure. The trigonal planar structure predicted by AM1 theory is a local minimum (it is a structure that has a low energy, but

not the lowest energy) from which the program cannot escape even using a better model. Although computers are very good at performing calculations, they have no chemical intuition, which is why the human element is an essential component of computational chemistry.

Bond Polarity

The experimentally determined dipole moments for compounds considered here are given in Table 3.⁶ Note that there is no entry for CH₃BH₂. Qualitatively rationalize the calculated dipole moment's direction and magnitude with what you know about electronegativity. How do the calculated dipole moments quantitatively compare with the actual values? If we were able to measure the dipole moment of CH₃BH₂, predict how it would compare to the calculated value.

| Substance | Dipole Moment (D) |
|---------------------------------|-------------------|
| CH ₄ | 0.00 |
| CH ₃ BH ₂ | ----- |
| CH ₃ NH ₂ | 1.31 |
| CH ₃ OH | 1.70 |
| CH ₃ F | 1.85 |

Table 3. Experimental dipole moments measured in the gas phase.⁶

Conclusions

Report any typos or inaccuracies in this version of the exercise. If things could be explained better, suggest new prose. Remember to answer the questions in the Results and Analysis section above.

References

1. Polik, W. F and Schmidt, J. R. *WebMO Enterprise 14.0.006e*; WebMO LLC: Holland, MI, 2011; <http://www.webmo.net/> accessed 21 June 2014.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford CT, 2010.
3. Pyykko, P. and Zhao, Y. *J. Phys. Chem.* **1990**, *94*, 7753-7759, and references therein.
4. Huheey, J. E. *Inorganic Chemistry*, 3rd Ed.; Harper and Row, NY, 1983, p. A-32ff.
5. Burbank, R. D. and Bensey, F. N. *J. Chem. Phys.* **1953**, *21*, 602-8.
6. *Handbook of Chemistry and Physics*, 64th Ed., Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983.