

Computational Chemistry – Gauss View and Gaussian Chemistry 105

Prelab

Please complete and turn in the worksheet on the last page of this document.

This experiment introduces you to Gaussian (through its graphic user interface Gauss View). Gaussian is the most widely used program in the computation chemistry research community for performing quantum mechanical calculations on molecules, and is capable of far more than we will have time to explore here.

I. What is Computational Chemistry?

Computational chemistry (also known as molecular modeling) is the application of computer-based models to the simulation of chemical processes and the computation of chemical properties. It accounts for roughly a third of the supercomputer usage worldwide. However, improved desktop computers mean that these methods are also becoming more available to scientists who are not purely computationalists. According to a recent textbook, "Today, the situation has been reached where, in many cases, the computational chemist can substitute the computing machine for the test tube,"

Computational chemistry is a valuable tool for experimental chemists to bypass tedious, time consuming, costly, and sometimes dangerous experiments. In the drug industry, computer design of molecules with specified properties is now becoming more common. Furthermore, computational chemistry allows one to investigate molecules that are too unstable to be studied experimentally, analyze quantities (such as atomic charges) that are not experimentally observable, and rectify incorrect experimental assignments (For example, based on spectroscopic experimental results, Gerhard Herzberg, a Nobel prize winning scientist, concluded that the methylene radical (:CH₂) with two unpaired electrons had a linear geometry. Sophisticated calculations by Bender and Schaefer, however, demonstrated that methylene was bent with a bond angle of 135.1°. Further experiments of methylene confirmed the latter assignment. The measured bond angle was 137.7°). Also, computational chemistry allows one to both calculate certain quantities (such as heats of formation) with more accuracy than can be determined experimentally (special cases only) and improve one's general understanding of chemical phenomena.

Paraphrasing Mike Colvin of Sandia National Laboratory: It is now generally possible to obtain molecular structures (with ~1% accuracy), reaction enthalpies (~1 kcal/mol), dipole moments and infrared intensities, vibrational frequencies (~5%), reaction free energies (~2 kcal/mol), relative acid constants (~2 pK_a units), and reaction rates (for certain types of reactions) without doing any laboratory experiments, i.e. at reduced cost. There is also increased safety and faster turnaround when toxic or explosive compounds are involved. There is the prospect of an improved understanding especially when we have both an experimental and theoretical perspective on a problem. There is a caveat, however. "Computational Chemistry is far from a black box - Care must be taken in choice of method and interpretation of results."

The following is a brief introduction to four major methods of computational chemistry:

a) *Ab Initio*:

Ab Initio means based on first principles. These methods are based on quantum mechanics (solving the Schrödinger equation) and use no experimental parameters in their calculations. Despite the fact that they employ some mathematical approximations, the major disadvantage of *Ab Initio* quantum chemistry is the heavy demands on computer power because the computational time scales as the fourth power of the basis set size. Hartree-Fock (HF) and Quantum Monte Carlo (QMC) are two common wave-function-based ab initio calculations. Density Functional Theory is another type of ab initio calculation that is much less expensive (in terms of CPU time, memory, and disk space) than HF and QMC because it is based on total electron density rather than wave functions. It is now generally agreed that density functional theory provides the most promising approach to accurate quantum chemical calculations for large systems. *Ab initio* calculations are qualitatively good, and for very small molecules give excellent quantitative results.

b) Semi-empirical:

Semi-empirical methods are quantum mechanical methods that have been applied to relatively large chemical systems for over three decades. They are much faster than ab initio methods because they involve a series of approximations, restrictions, and incorporation of experimental data. One of the largest simplifications is that empirical data is used for core electrons, and only the valence electrons are considered explicitly. Different semi-empirical methods have been optimized for different purposes. The MNDO, AM1 and PM3 methods were designed to reproduce heats of formation and structures of a large number of organic molecules. Other semi-empirical methods are specifically optimized for spectroscopy. For example, ZINDO/S is quite good at prediction of electronic transitions in the UV/VIS spectral region. One rule of thumb is that semi-empirical methods are often very good for determining structures, or for calculating relative energies for molecules that are similar to molecules in the data base used. However, the results can be very erratic for other molecules, and calculations of absolute energies can be problematic.

c) Molecular Mechanics (MM):

In molecular mechanics methods, Newtonian mechanics (classical physics) is used to predict the structures and properties of molecules. Since the theory is not based on quantum mechanics, electrons are not treated explicitly in molecular mechanics. The method treats molecules as spheres (nuclei) connected by springs (bonds). Actually, molecules are treated as though they are a collection of charged balls connected by springs. Molecular mechanics methods can be used to model very large systems such as DNA or proteins. Although these molecules are too large for semi-empirical calculations, they are manageable in MM because the approximations markedly simplify calculations. Molecular mechanics methods cannot be used to address bond making or breaking because electrons are not treated explicitly in these methods. As with semi-empirical calculations, the quality of MM calculations can be very high for systems similar to those used to parameterize the method.

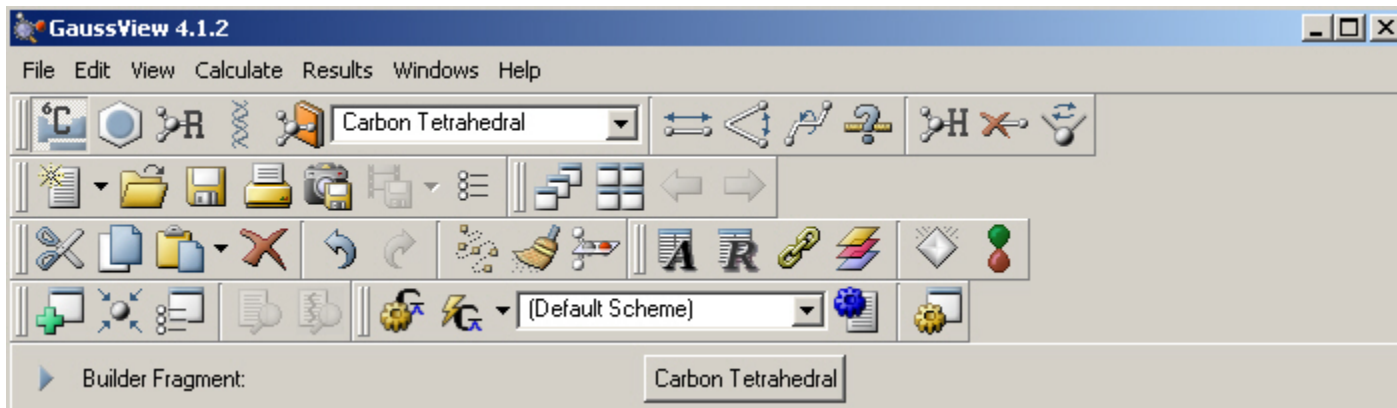
d) Molecular Dynamics (MD)

MD calculations are used to simulate the time-dependent behavior (also known as motion, dynamics, vibrations, or trajectory) of molecules. Any one of the three techniques listed above can be used to calculate molecular trajectories, however MM is most common. MD makes it possible to study the dynamic behavior of a collection of thousands of separate molecules, for example diffusion of a solute molecule through a liquid. MD can even be used for calculations involving large bio-molecules in solution.

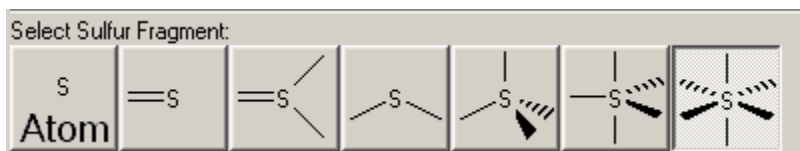
II. Using Gauss View



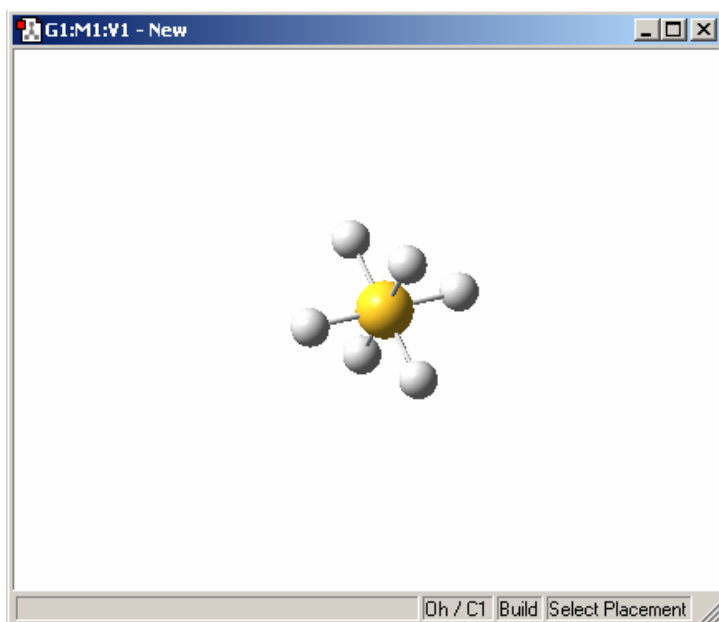
Open Gauss View by clicking on its icon. You will see two windows, the Gauss View control panel, which will look something like this



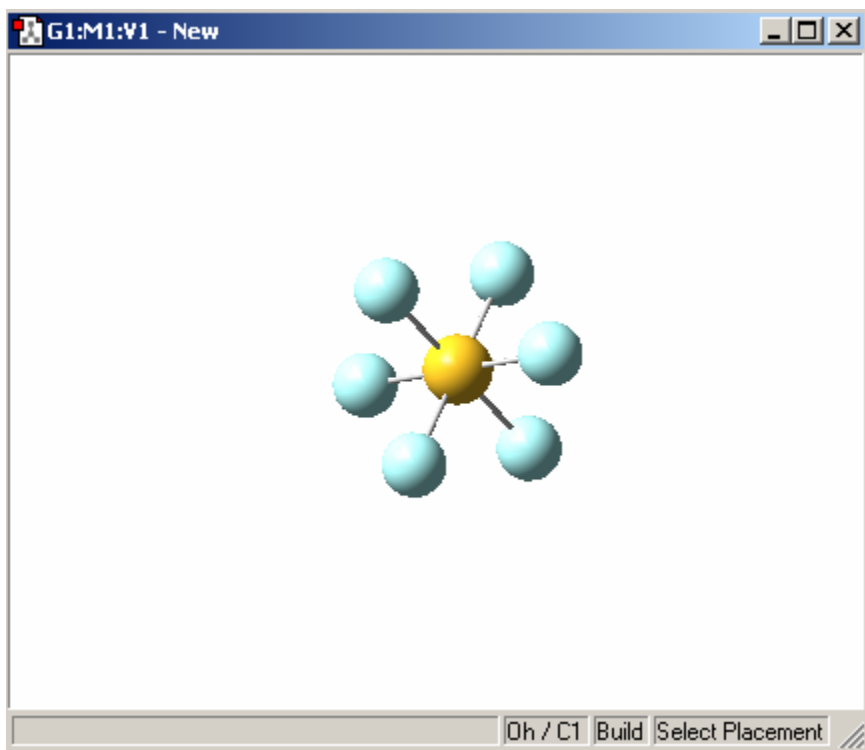
and a blank window where you will build molecules. Molecules are drawn using elements from the first four icons on the left side of the control panel. Note that the default fragment is a tetrahedral carbon atom. Click on the button labeled Carbon Tetrahedral and a periodic table will open. Pick an element, let's use S, and you will see many choices of the kind of S you wish.



So, to draw SF₆, you would choose the octahedral S on the right. If you click on that button, and then click on the blank window, you should see the following:






The white spheres represent hydrogen atoms that you can then replace with what the atoms you wish. Now go back to the periodic table, select F, and choose either the F atom or the F with a single bond. Clicking on each H atom should give you an SF₆.



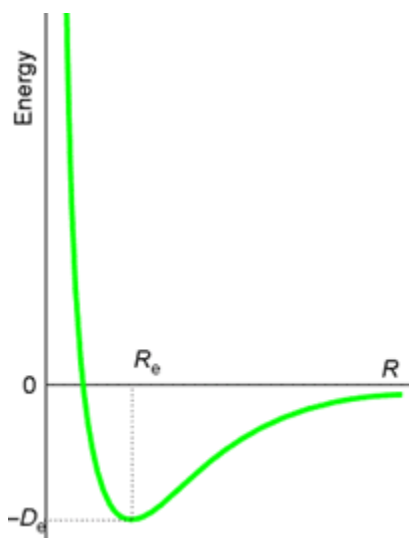
As soon as you have built the molecule, click on the question mark on the control panel. This is the Inquire button that we will use to measure bond lengths, bond and torsion angles, identify atoms, etc., but more importantly, it stops you from adding other atoms to your workspace.

Using the inquire button, measure the lengths of the S-F bonds, and the various FSF bond angles, and record the values. To do this, click on 2 or 3 neighboring atoms (for bond length and angle measurements, respectively). Move your cursor away from the molecule, and a measurement will appear in the lower left corner of your window.

Now run your mouse over the top row of icons on the control panel and read the popup text to see what they do. We will use the icons on the left over to  (delete atom) as well as  (cleanup and symmetrize – two separate buttons)) and  (orbitals) from the second row.

III. Geometry Optimization

The process of finding the arrangement of nuclei for which the potential energy is a minimum is known as geometry optimization. The potential energy as a function of internuclear distance for a diatomic molecule is shown in the diagram below. Note that it takes a lot of energy to get atoms very close to each other there is a distance with minimum energy R_0 , and it takes energy to pull the atoms apart farther than R_0 . Why does the energy approach zero as the intermolecular distance gets very large? The lowest-energy is at R_0 (equilibrium bond length), where the derivative of the potential energy curve is zero. The geometry optimization procedure involves making an initial guess for the geometry and then calculating the derivative (gradient) of the potential energy with respect to each of the nuclear coordinates. The gradient represents the force acting upon each atom. These energy gradients are then used to obtain a new geometry that is likely to be closer to the equilibrium geometry. This process is repeated until the energy gradients (forces) approach zero, indicating that an equilibrium geometry has been found.



To prepare for doing calculations, add a new folder to your desktop and give it a name that you can remember (and spell). That is where you will store all of the results of your calculations. Let's begin by doing a calculation on water.

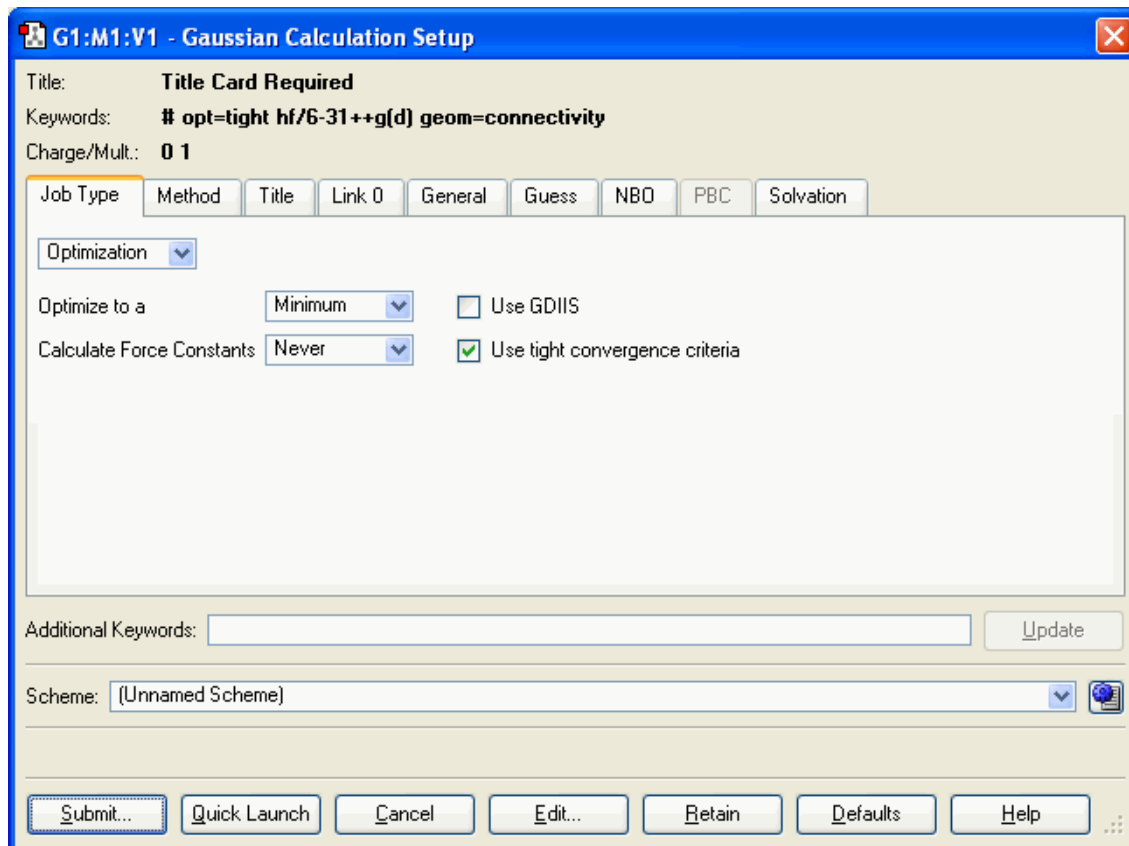
Start with a blank workspace – close the one you were playing with and then go File → New → Create MolGroup.

Now make a water molecule in this workspace.

Press the broom icon and the symmetrize icon.

Using the Inquire tool, measure and record the pre-optimization bond lengths and bond angle.

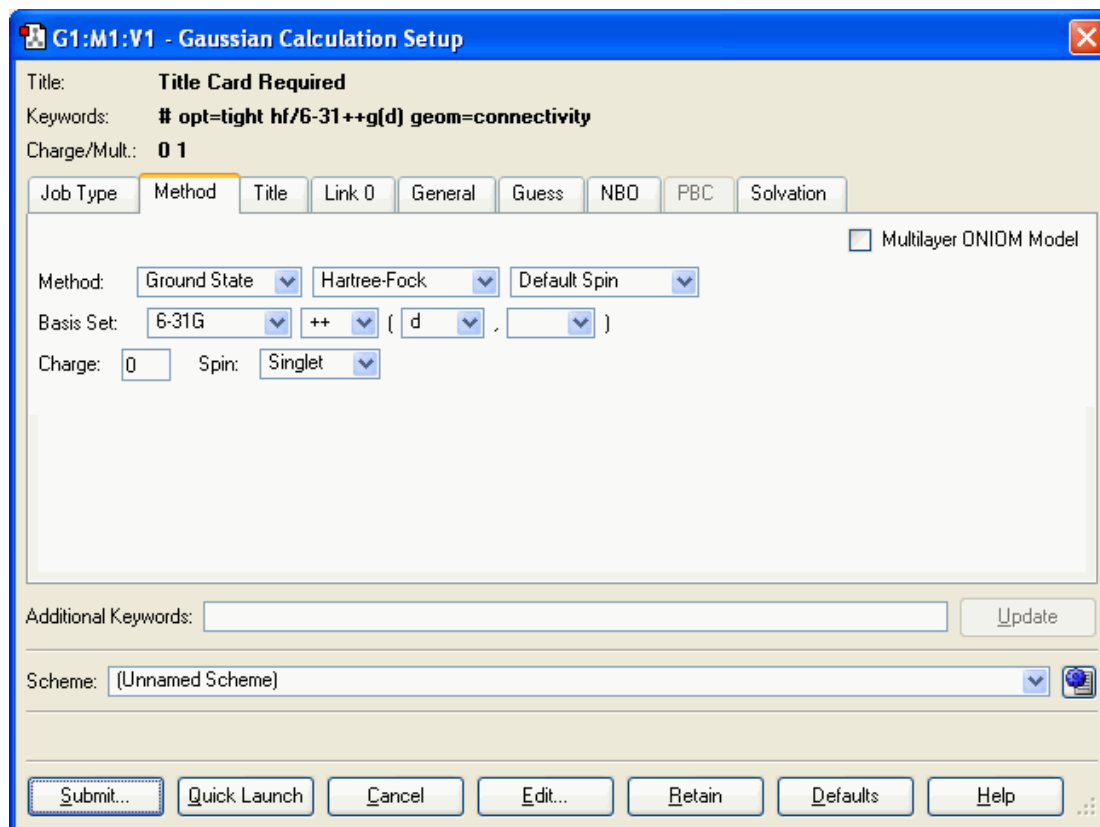
On the control panel menu select Calculate → Gaussian Calculation Setup and this menu comes up:



There are many options on this menu, and there is also the ability to write additional keywords in the space where I have written pop=full. There are several hundred of these keywords that tell Gaussian to do tasks beyond what is possible in the Calculate menu.

Under Job Type, look at the various calculation options – we will focus on optimization, frequency, scan and energy calculations today. Choose Optimization to calculate the optimum geometry.

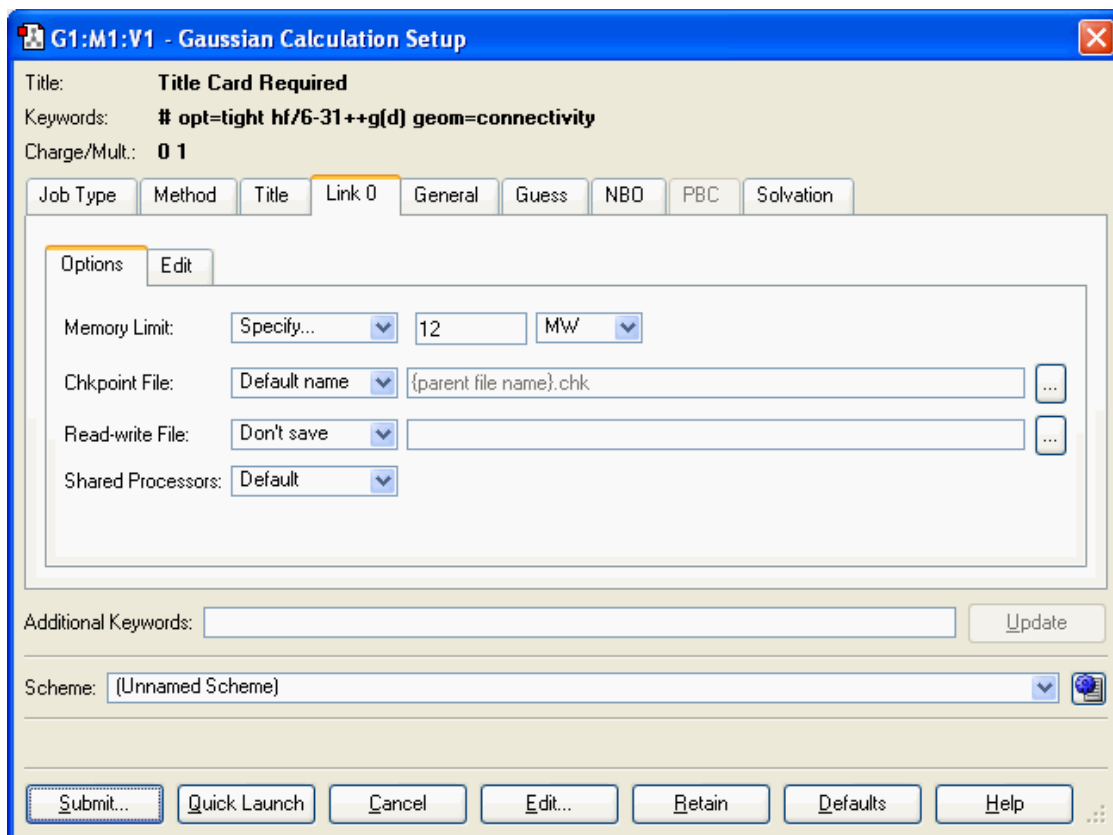
Now you need to choose a computational method. Gaussian provides you with a range of choices under the Method menu:



In this case we are doing a calculation on the ground state, using an *ab initio* Hartree-Fock model. All electrons are paired so we have a singlet and we will leave the spin at Default Spin. There is no charge. The basis set choice is one of the most important one when choosing to model chemistry. In this case I have chosen what has become the standard basis set for such calculations, 6-31G+d (also called 6-31G*) and added to it (the ++) diffuse functions on both the O and the Hs (the O is the first + and the Hs are always the second +). This should produce very good results in a reasonable time.

If you wish to title your job, open the Title tab and give it an appropriate title.

Now go to the Link0 tab. This is where you tell Gaussian where to put your files and how much memory to use. Unless you are told otherwise, set the memory at 12 MW (mega-words). Interestingly enough, you can set aside too much memory and it will slow Gaussian down, not speed it up. You need to specify a filename and location in the Chkpoint File item.



Now press submit to send the calculation from Gauss View to Gaussian. You will be asked for another file name. Since it has a different extension (.gjf rather than .chk) than the one you just did, I would give it the same name as your chkpoint file. Say yes when asked if you really want to do this, and the calculation begins. You will be able to watch the progress of the calculation in the new window that pops up.

When the calculation is complete, read the quote and then close the Gaussian file and open your chk file. Click on the Results tab on the control panel and look at the summary.

Repeat this process for ammonia and methane, following all of the same steps, and record the data in your Prelab on the next page. Submit only the following page as your prelab.

Fill in the following table using data calculated by GaussView:

| | Angle - VSEPR predicted (i.e. 109.5°, <109.5°) | Angle after “cleanup” | Angle after <i>ab initio</i> optimization | Angle - experimental | Bond length after “cleanup” (Å) | Bond length after <i>ab initio</i> optimization (Å) |
|------------------|--|--------------------------|---|-------------------------|--|--|
| H ₂ O | | | | 104.5° | | |
| NH ₃ | | | | 107.3° | | |
| CH ₄ | | | | 109.5° | | |

Do you see a trend for water, ammonia, and methane bond angles? Explain in terms of their VSEPR structures.

Which was closest to experimental bond angle: “cleanup” or *ab initio* optimization?

Give an example of a type of experiment that would be better performed computationally rather than in the laboratory (see beginning paragraphs of prelab)?