Proposed Exercise for the General Chemistry Section of the Teaching with Cache Workbook:

Calculating Bond Enthalpies of the Hydrides

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Overview

Periodic trends in atomic properties (such as ionization energy and electron affinity) are often discussed in general chemistry. Students are able to rationalize the trends based on a simple shell model for the electrons of the atoms. In this exercise, students will discover the trend in bond enthalpies for the hydrides (H to Na) and be able to explain it using graphical depictions of the electron density. These questions will be addressed:

- How stable is the diatomic molecule formed with hydrogen and these elements?
- What spin state exists for the molecule and the atoms which comprise it?
- How accurately can theory be used to reproduce experimental trends?

Introduction

Electronic structure theory can be used to predict thermochemical data for molecules. Computer programs such as CAChe and Gaussian have been developed to use various methods to evaluate the energy of a chemical system. A bond enthalpy is defined as the change in enthalpy (ΔH) for the reaction of forming a bond from its constituent atoms. To calculate the bond enthalpy of a diatomic molecule, one needs to evaluate the absolute enthalpy (H) of the molecule and also the absolute enthalpies of the atoms making up the molecule. The difference in enthalpy between the molecule and its atoms is the bond enthalpy:

$$\Delta H_{bond} = H_{AB} - H_A - H_B$$

Both CAChe and Gaussian could be thought of as enthalpy meters. You can provide a molecular structure and they will evaluate thermochemical properties such as energy, enthalpy, and free energy. Gaussian does so by solving Schrödinger’s equation within the framework of some approximate model. There are hundreds of different approximate models available and it takes a good working knowledge of these to be able to effectively apply the computer program in solving a real problem. CAChe has the capability of creating and running various Gaussian jobs that will then calculate the thermal enthalpy values.

In this exercise, we will evaluate several different approximate models. These all vary in terms of the accuracy and computational speed. Since we are dealing with only diatomic molecules, the speed of the calculation is of little concern to us. Here is a representative list of methods to use (your instructor may assign others):

- AM1
- HF/3-21G
- HF/6-311+G(2d,p)
- B3LYP/6-311+G(2d,p)
- G3

The details concerning these methods can be found in standard reference texts (1-3). For now, you only need to realize that these are automated procedures within CAChe and Gaussian which will produce a summary table showing the final enthalpy in the end. In performing this series of calculations, you will be able to discover the relationship between accuracy and choice of model. Here we are going from semiempirical theory (AM1) to ab initio small basis set (HF/3-21G) to ab initio large basis set (HF/6-311+G(2d,p)) to density functional theory large basis set (B3LYP/6-311+G(2d,p)) and finally to a compound method (G3) which combines results from several different theories in an additive fashion.

Procedure

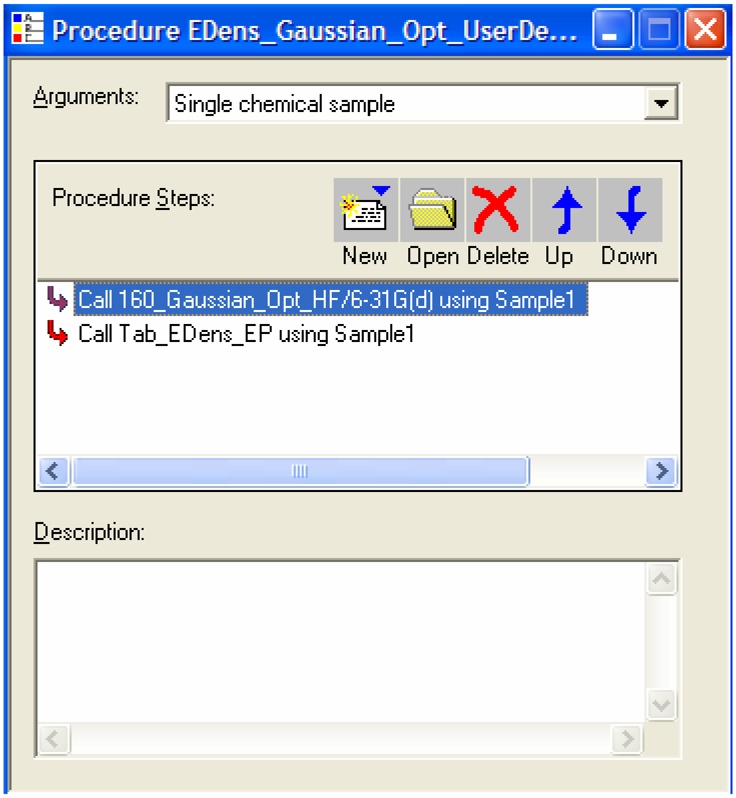
Each member of the class will choose a different theoretical model and perform the calculation of the bond enthalpies for the hydrides H through Na (H-H, H-Li, H-Be, H-B, H-C, H-N, H-O, H-F, and H-Na). For final analysis, you will need to share your results so that each student has data from all the theoretical models.

Follow the procedure outlined below for calculating the absolute enthalpies of each diatomic hydride and each atom. Pay particular attention to the spin multiplicity of the chemical species as you will need to enter this information before submitting the job. When all calculations have completed, you can organize the data using Project Leader (see instructions below). At that time you will want to add experimental numbers for comparison. A good source for these is found online (http://www.webelements.com/).

Calculating the Absolute Enthalpy for the Hydrides (Example: H-N)

Follow the instructions below for each hydride. Spin multiplicities will not be the same for all hydrides. In this example we will go through the steps need to calculate H-N.

1. Select the drawing pencil. Select Hydrogen from the periodic table. Click once in window. Select Nitrogen from the periodic table. Click on the Hydrogen and drag away to attach a bond to Nitrogen.
2. Click on the **Select** arrow. Click once in the window, but not on any atoms, to highlight the entire molecule.
3. Select **Beautify** > **Geometry**.
4. Select **Experiment** > **New**.
5. A window pops up telling you that you must save the chemical sample file in order to run an experiment on it. Select **Yes**. Enter an appropriate name and click **Save**. Make sure you note where the file is being saved because the output file will be needed to determine the enthalpy value.
6. Under experiment window select these options
    a. Property of: chemical sample
    b. Property: electrostatic potential on electron density
    c. Using: Gaussian User-Defined Model in the gas-phase (find this at the very bottom of the list).
7. Click **Edit**
    a. Double-click on the first step in the procedure, where it says "Call 160_Gaussian_Opt_HF/6-31G(d) using Sample1"


Procedure EDens_Gaussian_Opt_UserDe…

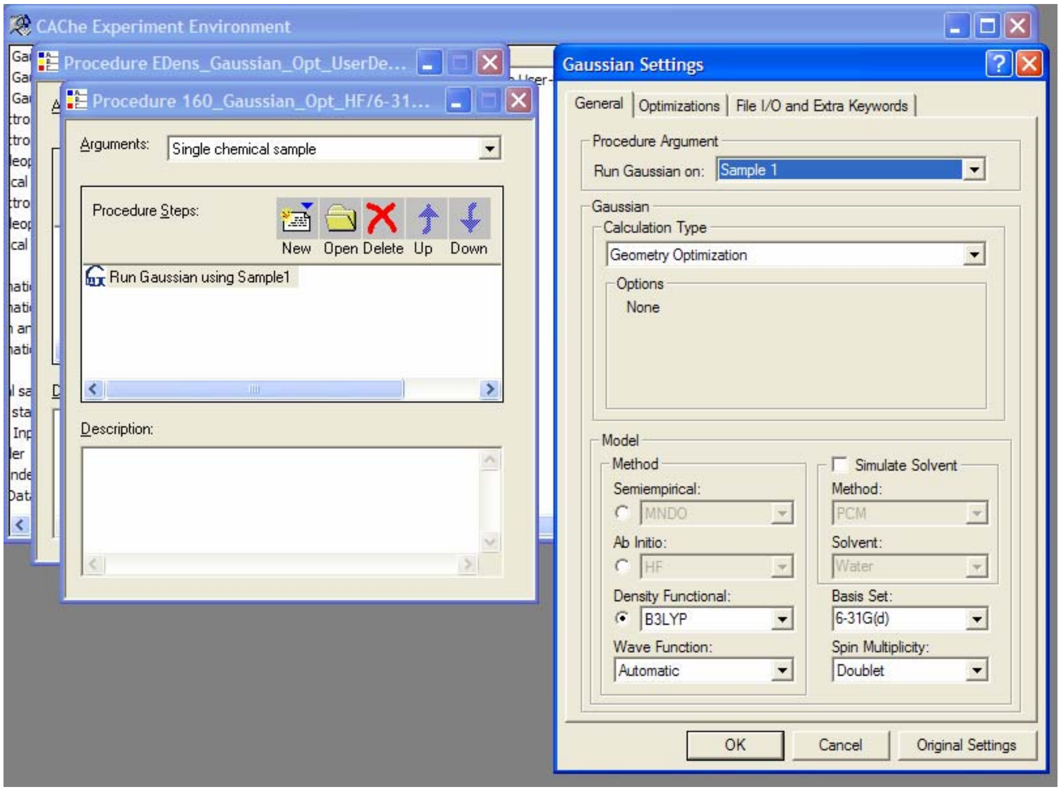
Arguments: Single chemical sample

Procedure Steps:

Call 160_Gaussian_Opt_HF/6-31G(d) using Sample1
Call Tab_EDens_EP using Sample1

Description:

b. Then click **EDIT**. Then double-click on “Run Gaussian using Sample1.” Then change the options according to what Gaussian model you would like to use.


CAChe Experiment Environment

Procedure EDens_Gaussian_Opt_UserDe…

Procedure 160_Gaussian_Opt_HF/6-31…

Arguments: Single chemical sample

Procedure Steps:

Run Gaussian using Sample1

Description:

Gaussian Settings

Procedure Argument
Run Gaussian on: Sample 1

Gaussian
Calculation Type: Geometry Optimization
Options: None

Model
Method
Semiempirical: ○ MNDO
Ab Initio: ○ HF
Density Functional: ● B3LYP
Wave Function: Automatic

☐ Simulate Solvent
Method: PCM
Solvent: Water
Basis Set: 6-31G(d)
Spin Multiplicity: Doublet

    c. For instance, to run B3LYP, choose that option under Density Functional.
    d. Also be sure to change to the correct multiplicity for this molecule. In this case, we want to specify triplet.
    e. Now go to the File I/O and Extra Keywords tab. Add the extra keyword "freq" to the extra keyword box. This will allow the computation of thermochemical information.
    f. After making the appropriate changes, close all windows associated with the procedure editor and click on yes when it asks whether you want to save changes.
8. Click **Start**.
9. An experiment status window appears. Wait until the State option reports Done. You will also see the words "Tabulation complete" in the center box of the window.
10. At this point you have optimized the molecular geometry and done an evaluation of the electrostatic potential. Examine the bond length of your molecule and record. This is done by clicking on one of the atoms, then shift-clicking on the second atom, then hitting F2 will give you a window with the distance at the top.
11. Select **Analyze > Show Surfaces**. Click on the label under displayed surfaces to make it active. Select **OK**. The electron density will appear as a translucent pattern. Click once in the window to make the electron density opaque.
12. Make some notes concerning the picture that you see. To understand the colors, select **Analyze > Surface Legend**. You may want to save the picture for quick reference later. In windows you can easily use the print screen key and then paste into Microsoft Paint.
13. Select **Analyze > Chemical Properties Spreadsheet**. Then select the **Thermodynamic Info** tab at the bottom of the window. The Enthalpy (energy_au) is found here. Record this value.

Procedure for Atomic Calculations (Example: H atom)

The procedure for calculating the absolute enthalpy of atoms is slightly different since CAChe assumes that you can not have frequencies for an atom and therefore does not allow thermochemical information to be displayed. It is true that one can take the electronic energy for an atom and then simply add 2.5RT to this value to get the atom enthalpy, but the procedure below shows how to get that information out of the Gaussian output file instead.

1. Select the drawing pencil. Select Hydrogen from the periodic table. Click once in window.
2. Click on the **Select** arrow. Click once in the window, but not on the atom, to highlight it.
3. Select **Experiment > New**.
4. A window pops up telling you that you must save the chemical sample file in order to run an experiment on it. Select **Yes**. Enter an appropriate name and click **Save**. (Make sure you note where the file is being saved because the output file will be needed to determine the enthalpy value).
5. Under experiment window select appropriate options
    a. Property of: chemical sample
    b. Property: IR transitions
    c. Using: Gaussian User-Defined Model in the gas-phase (find this at the very bottom of the list)
6. Now make the needed changes in the Gaussian User-Defined model as you did for the hydride calculation (step 7 above).

7. Click **Start**.
8. An experiment status window appears. Wait until the State option reports Done.
9. Now outside of CAChe, you will need to use a windows file browser to navigate to the folder where the experiment was saved. In there you will find a folder with the name you used followed by ".io" (for instance "hydrogen.io"). Open that folder.
10. Double click on the gaussian.out file.
11. Select **Edit** > **Find**. Type in thermochemistry. This brings to you to the section that contains the "Sum of electronic and thermal Enthalpies". Record this value. It is in atomic units.

Using ProjectLeader to Tabulate Results for This Experiment

One can use Project Leader to tabulate the results of this exercise. Alternatively you could record data in your notebook and enter into Excel. We will show the steps for using Project Leader:

1. Open the ProjectLeader application. When the program opens, there is an untitled table. The first column heading is labeled "Chemical Sample".
2. Double click in the first cell below the Chemical Sample heading. An Open dialog box containing a list of file locations appears. Find the location of your files saved as "experimentname.csf." Select the first diatomic hydride and click **Open**.
3. Repeat this operation in the next cell below for the remaining diatomic hydrides for the same procedure (e.g. B3LYP 6-311+G(2d,p)).
4. Double click in the top cell in the second column (Column B). An Enter Property dialog box opens. Click in the circle next to **Property of**. The circle fills in black. Click on the arrow in the Property of box to display the pull down menu. Select **labeled atom distance.**
5. Click **Next** >. The dialog box options change. In the **kind of property** box select **atom distance**.
6. Click **Next** >. In the **kind of procedure** box select **extract from sample component**.
7. Select **OK** to return to the table. Column B has the label "labeled atom distance" and Column C has the label "Atom Distance (angstrom)."
8. Double click in the top cell of Column D. Click in the circle next to **Property of**. Click on the arrow to display the pull down menu. Select **thermodynamic data**.
9. Click **Next** >. The dialog box options change. In the **Kind of** property box select **enthalpy**.
10. Click **Next** >. The options in the dialog box options change again. In the **kind of procedure** box, scroll down and select **extract from sample component**.
11. Click **OK** to return to the table. Column D has the label "Thermodynamic Data" and Column E has the label "Enthalpy (kcal/mole)."
12. Double click in the top cell of Column F. Click in the circle next to **Comment**. Select **Next** >. Type "Atom Enthaply (kcal/mole).
    a. This column will account for the atom involved in the diatomic that was not hydrogen.
    b. Be sure to convert the numbers obtained in Hartrees into kcal/mole.
    c. These calculated values will have to be entered manually by double clicking on the appropriate cell.
13. Repeat step 12 in the next column. Here, type "Hydrogen Enthalpy (kcal/mole)."

    a. This column will account for the hydrogen involved in the diatomic.

14. Double click in the top cell of Column H. Click in the circle next to **Analysis**. Select **Next** >. Select **Algebraic Equation**. Select **Next** >. In the **equation** box, enter "Bond Enthalpy (kcal/mol) =E-F-G."
15. Highlight all columns and right mouse click. Select **evaluate cell**.

Analysis Questions

1. Compare the pictures that you produce for each hydride. What graphical features can be associated with hydrides that have the most negative enthalpies? less negative enthalpies?
2. What can be said about the changes in these pictures in going across the second row of the periodic table? In analyzing the pictures, keep in mind that CAChe will produce the same density isosurface (0.01) and the same color map (see figure 1).
3. Prepare a plot of bond enthalpies for the series of molecules. The x-axis should have the molecules listed across. The y-axis should have the enthalpy values. How well does you model perform compared to the models used by other students in the class.

Instructor's Notes

In this exercise, students can gain familiarity with periodic trends in bond strength as computed by the bond enthalpy in Gaussian. In the series of hydrides we have representatives of the purely covalent species (H-H), strongly ionic species (H-Na), polar covalent species (H-F) as well as all gradations in between. The graphical pictures can be interpreted as showing the change in the charge on Hydrogen going from negative to positive as it is paired with elements that have greater and greater electronegativity. The most stable species (most negative bond enthalpies) are H-H and H-F. The pictures show why these are most stable: the two atoms allow nuclear fields where electron charge can be smoothly distributed from one end of the molecule to the other. In contrast, less stable species (such as H-B and H-Be) have positive charge in the bonding region between the two atoms. Species such as Na-H and Li-H are less stable because of charge separation.

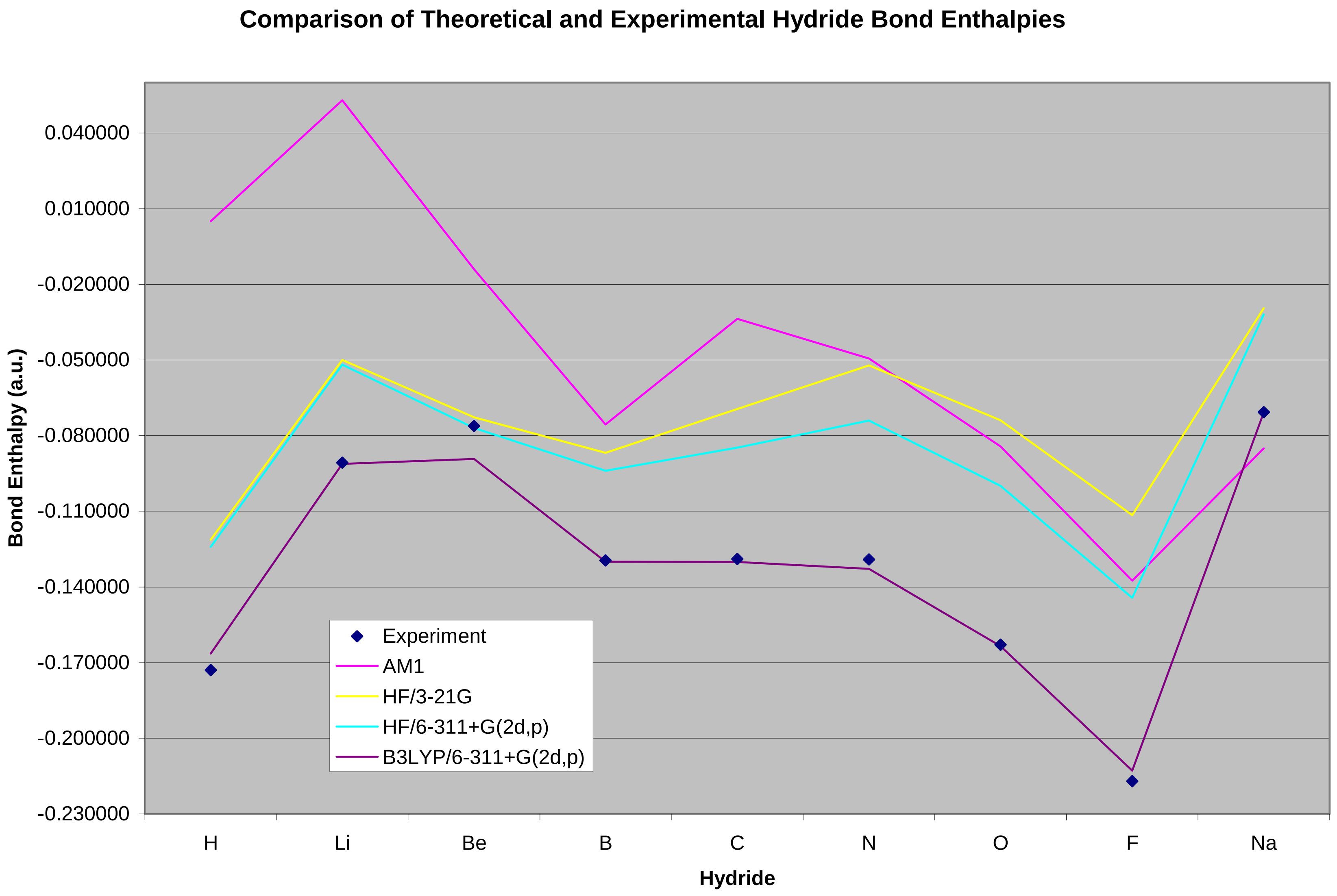
The other reality that is communicated to students performing this exercise is the accuracy of various theoretical models. The AM1 model gives a qualitatively correct trend for the series but severely overestimates most of the bond enthalpies. This error is also not consistent, with H-Na bond enthalpy being accidentally close to experiment. Hartree-Fock theory even with a small basis set more closely follows the experimental trend and is more consistently in error. There is little improvement in going to a large basis set. The real improvement comes in using a model such as B3LYP which includes the effects of electron correlation. This model along with the large basis set gives millihartree accuracy for most of these cases. The only exception is the pathological case, H-Be. Even this case, however, can be computed within a millihartree of experiment if one of the highly accurate thermochemical models available in Gaussian (such as G3) is used.

Absolute Enthalpies Calculated in Gaussian [a.u.]

	AM1	HF 3-21G	HF 6-311+G(2d,p)	B3LYP 6-311+G(2d,p)	G3
H-H	0.0049	-1.1090	-1.1187	-1.1662	-1.1641
H-Li	0.0529	-7.9233	-7.9794	-8.0798	-8.0525
H-Be	0.1106	-15.0512	-15.1438	-15.2576	-15.2316
H-B	0.1433	-24.9679	-25.1201	-25.2895	-25.2720
H-C	0.2407	-38.0420	-38.2696	-38.4853	-38.4550
H-N	0.1333	-54.6487	-54.9680	-55.2313	-55.1893
H-O	0.0125	-74.9587	-75.4033	-75.7514	-75.6916
H-F	-0.1049	-99.4477	-100.0405	-100.4705	-100.3978
H-Na	-0.0849	-161.3752	-162.3735	-162.8552	-162.6731
H	0.0000	-0.4938	-0.4974	-0.4998	-0.4986
Li	0.0000	-7.3792	-7.4297	-7.4890	-7.4628
Be	0.1250	-14.4845	-14.5696	-14.6690	-14.6574
B	0.2186	-24.3874	-24.5287	-24.6603	-24.6402
C	0.2747	-37.4787	-37.6878	-37.8551	-37.8254
N	0.1824	-54.1030	-54.3965	-54.5984	-54.5620
O	0.0973	-74.3913	-74.8057	-75.0877	-75.0286
F	0.0325	-98.8426	-99.3982	-99.7584	-99.6818
Na	0.0000	-160.8517	-161.8436	-162.2844	-162.1018

Hydride Bond Enthalpies [a.u.]

	AM1	HF 3-21G	HF 6-311+G(2d,p)	B3LYP 6-311+G(2d,p)	G3	Expt.
H	0.0049	-0.1214	-0.1238	-0.1666	-0.1668	-0.17292
Li	0.0529	-0.0503	-0.0522	-0.0911	-0.0911	-0.09067
Be	-0.0144	-0.0729	-0.0768	-0.0888	-0.0755	-0.0762
B	-0.0753	-0.0867	-0.0939	-0.1295	-0.1331	-0.13
C	-0.0340	-0.0695	-0.0843	-0.1304	-0.1310	-0.129
N	-0.0491	-0.0519	-0.0740	-0.1331	-0.1287	-0.129
O	-0.0847	-0.0736	-0.1002	-0.1639	-0.1643	-0.1629
F	-0.1374	-0.1112	-0.1448	-0.2123	-0.2173	-0.2171
Na	-0.0849	-0.0296	-0.0324	-0.0710	-0.0726	-0.0707


Comparison of Theoretical and Experimental Hydride Bond Enthalpies
Bond Enthalpy (a.u.)
0.040000
0.010000
-0.020000
-0.050000
-0.080000
-0.110000
-0.140000
-0.170000
-0.200000
-0.230000
H
Li
Be
B
C
N
O
F
Na
Hydride
Experiment
AM1
HF/3-21G
HF/6-311+G(2d,p)
B3LYP/6-311+G(2d,p)

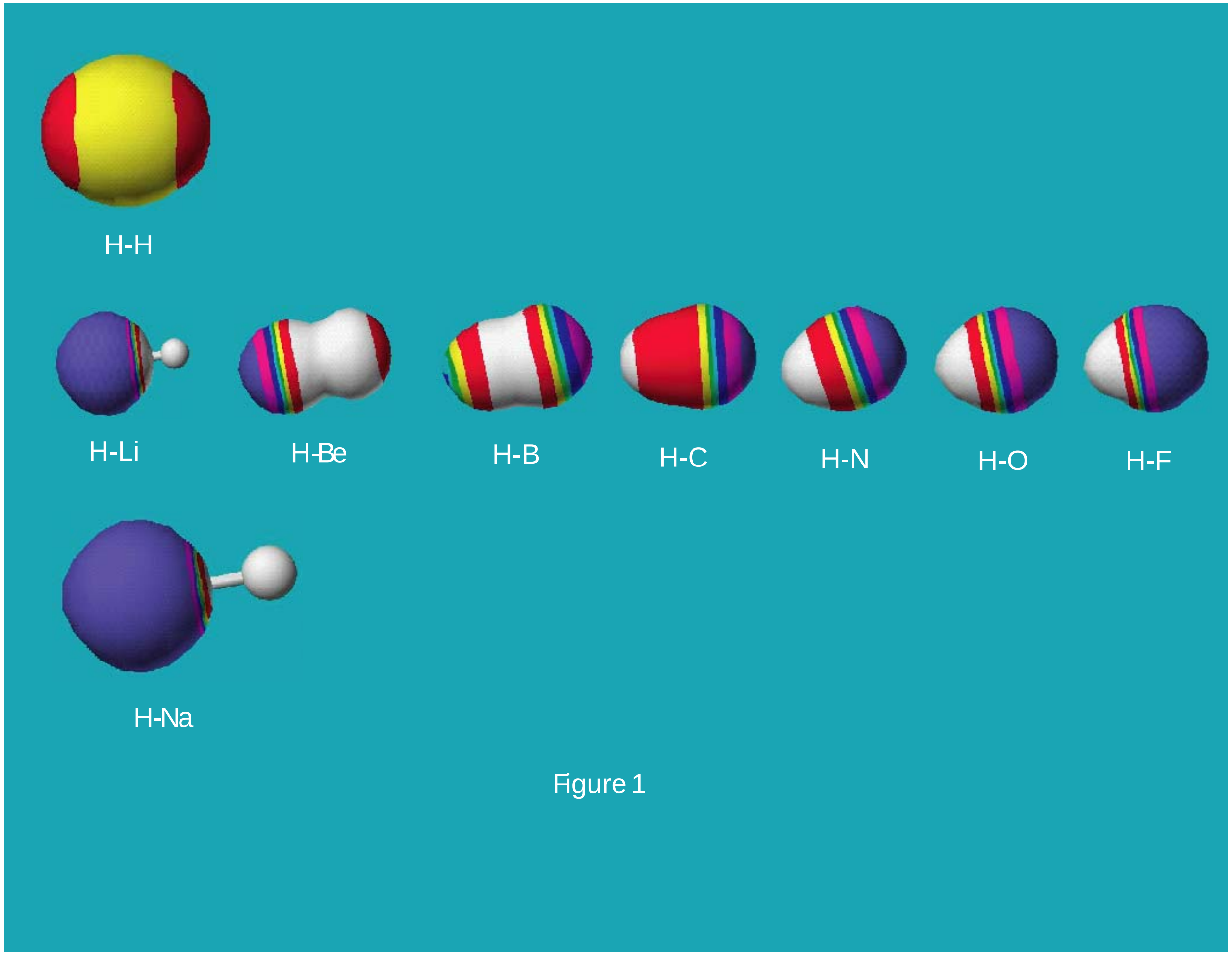
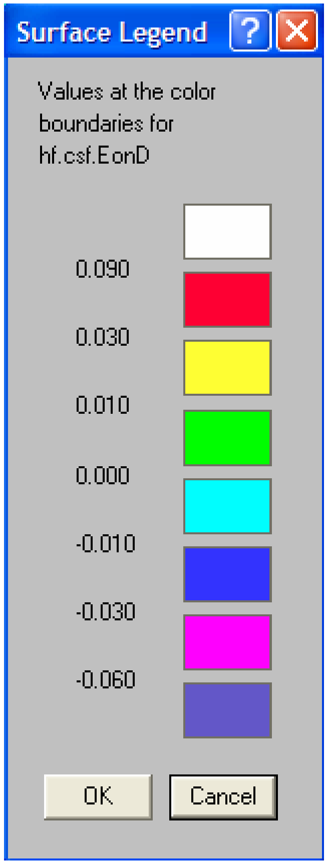


Figure 1



Values at the color boundaries for hf.csf.EonD

⬜
0.090
🟥
0.030
🟨
0.010
🟩
0.000
🟦
-0.010
🟦
-0.030
🟪
-0.060
🟪

References

(1) Foresman, J. B.; AE. Frisch, “Exploring Chemistry with Electronic Structure Methods,” 2nd edition, Gaussian, Inc., 1996.

(2) Jensen, F. “Introduction to Computational Chemistry,” Wiley, 1999.

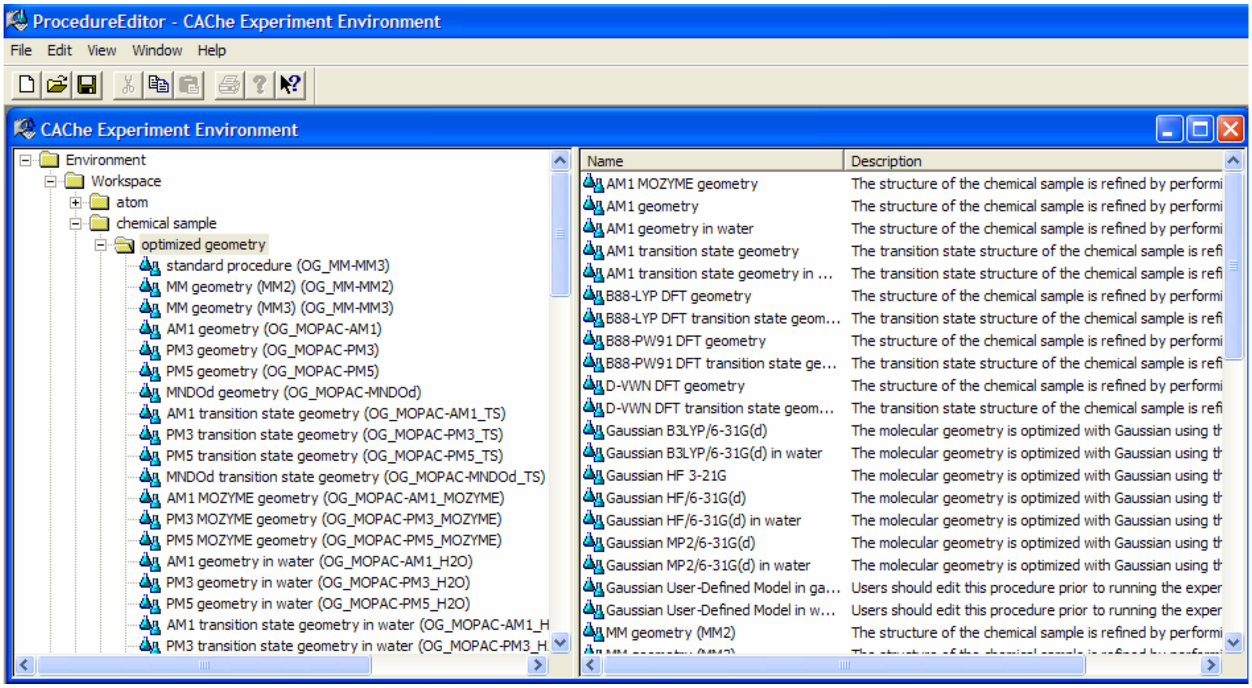
(3) Cramer, C. “Essentials of Computational Chemistry,” Wiley, 2002.

Appendix

It may be desirable for the instructor to create new CAChe procedures for the calculations done in this experiment. The students would then be able to perform them without needing to edit the User-Defined Gaussian models. Here are step-by-step procedures for this:

Creating a New Property Folder.

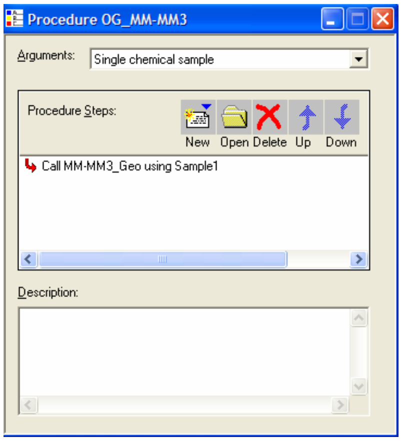
1. Open CAChe
2. Select **Experiment** > **New**.
3. Select options that are closest to what you need for your experiment
    a. Property of: chemical sample
    b. Property: Optimized Geometry
4. Click on **Edit**. The Procedure Editor application opens. In the Procedure Editor, a CAChe Experiment Environment window with two columns opens. In the left column is a tree view of the experiment environment.



- Environment
    - Workspace
        - atom
        - chemical sample
            - optimized geometry
                - standard procedure (OG_MM-MM3)
                - MM geometry (MM2) (OG_MM-MM2)
                - MM geometry (MM3) (OG_MM-MM3)
                - AM1 geometry (OG_MOPAC-AM1)
                - PM3 geometry (OG_MOPAC-PM3)
                - PM5 geometry (OG_MOPAC-PM5)
                - MNDOd geometry (OG_MOPAC-MNDOd)
                - AM1 transition state geometry (OG_MOPAC-AM1_TS)
                - PM3 transition state geometry (OG_MOPAC-PM3_TS)
                - PM5 transition state geometry (OG_MOPAC-PM5_TS)
                - MNDOd transition state geometry (OG_MOPAC-MNDOd_TS)
                - AM1 MOZYME geometry (OG_MOPAC-AM1_MOZYME)
                - PM3 MOZYME geometry (OG_MOPAC-PM3_MOZYME)
                - PM5 MOZYME geometry (OG_MOPAC-PM5_MOZYME)
                - AM1 geometry in water (OG_MOPAC-AM1_H2O)
                - PM3 geometry in water (OG_MOPAC-PM3_H2O)
                - PM5 geometry in water (OG_MOPAC-PM5_H2O)
                - AM1 transition state geometry in water (OG_MOPAC-AM1_H
                - PM3 transition state geometry in water (OG_MOPAC-PM3_H

Name	Description
AM1 MOZYME geometry	The structure of the chemical sample is refined by performi
AM1 geometry	The structure of the chemical sample is refined by performi
AM1 geometry in water	The structure of the chemical sample is refined by performi
AM1 transition state geometry	The transition state structure of the chemical sample is refi
AM1 transition state geometry in ...	The transition state structure of the chemical sample is refi
B88-LYP DFT geometry	The structure of the chemical sample is refined by performi
B88-LYP DFT transition state geom...	The transition state structure of the chemical sample is refi
B88-PW91 DFT geometry	The structure of the chemical sample is refined by performi
B88-PW91 DFT transition state ge...	The transition state structure of the chemical sample is refi
D-VWN DFT geometry	The structure of the chemical sample is refined by performi
D-VWN DFT transition state geom...	The transition state structure of the chemical sample is refi
Gaussian B3LYP/6-31G(d)	The molecular geometry is optimized with Gaussian using th
Gaussian B3LYP/6-31G(d) in water	The molecular geometry is optimized with Gaussian using th
Gaussian HF 3-21G	The molecular geometry is optimized with Gaussian using th
Gaussian HF/6-31G(d)	The molecular geometry is optimized with Gaussian using th
Gaussian HF/6-31G(d) in water	The molecular geometry is optimized with Gaussian using th
Gaussian MP2/6-31G(d)	The molecular geometry is optimized with Gaussian using th
Gaussian MP2/6-31G(d) in water	The molecular geometry is optimized with Gaussian using th
Gaussian User-Defined Model in ga...	Users should edit this procedure prior to running the exper
Gaussian User-Defined Model in w...	Users should edit this procedure prior to running the exper
MM geometry (MM2)	The structure of the chemical sample is refined by performi

5. The small Procedure window that opens up can be either closed or minimized.



Procedure OG_MM-MM3

Arguments: Single chemical sample

Procedure Steps:

Call MM-MM3_Geo using Sample1

Description:

6. On the left hand side of the larger window that opens, click once on the chemical sample folder. Right mouse click and select **New Property**.
7. Right mouse click on the new property folder and select **Rename**. Title the new property folder appropriately as Thermochemical Properties.

<u>Creating a new procedure using the Gaussian method AM1 (Geometry Optimization and Vibrational Frequency)</u>.

1. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named “AM1 geometry” (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as “AM1 Optimization”.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Geometry Optimization.
    b. Under Method, click on the Semiempirical drop-down list and select AM1.
    c. Set the Wave Function to automatic
    d. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

10. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
11. From the window on the right, select the experiment named "AM1 geometry" (click only once).
12. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "AM1 Frequency".
13. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
14. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
15. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
16. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Semiempirical drop-down list and select AM1.
    c. Set the Wave Function to automatic
    d. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
17. Select **OK**.
18. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method AM1 at current geometry.

1. Double click on the IR transitions folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "Gaussian HF/6-31G(d) at current geometry" (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Semiempirical drop-down list and select AM1.
    c. Set the Wave Function to automatic and Spin Multiplicity to correct multiplicity.
8. Select **OK.**
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method HF/3-21G (Geometry Optimization and Vibrational Frequency).

1. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "Gaussian HF/6-31G(d)" (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "HF 3-21G Optimization".
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Geometry Optimization.
    b. Under Method, click on the Ab Initio drop-down list and select HF.
    c. Click on the drop-down list for Basis Set and select 3-21G.
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

10. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
11. From the window on the right, select the experiment named "Gaussian HF/6-31G(d)" (click only once).
12. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "HF 3-21G Frequency".
13. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
14. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
15. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
16. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Ab Initio drop-down list and select HF.
    c. Click on the drop-down list for Basis Set and select 3-21G.
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.

17. Select **OK**.
18. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method HF/3-21G at current geometry.

1. Double click on the IR transitions folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named “Gaussian HF/6-31G(d) at current geometry” (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Ab Initio drop-down list and select HF.
    c. Click on the drop-down list for Basis Set and select 3-21G.
    d. Set the Wave Function to automatic and Spin Multiplicity to correct multiplicity.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method HF/6-311+G(2d,p) (Geometry Optimization and Vibrational Frequency).

1. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named “Gaussian HF/6-31G(d)” (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as “HF 6-311+G(2d,p) Optimization”.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Geometry Optimization.
    b. Under Method, click on the Ab Initio drop-down list and select HF.

    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

10. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
11. From the window on the right, select the experiment named "Gaussian HF/6-31G(d)" (click only once).
12. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "HF 6-311+G(2d,p) Frequency".
13. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
14. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
15. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
16. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Ab Initio drop-down list and select HF.
    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
17. Select **OK**.
18. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method HF/6-311+G(2d,p) at current geometry.

1. Double click on the IR transitions folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "Gaussian HF/6-31G(d) at current geometry" (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.

7. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Ab Initio drop-down list and select HF.
    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic and Spin Multiplicity to correct multiplicity.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method B3LYP/6-311+G(2d,p) (Geometry Optimization and Vibrational Frequency).

1. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "Gaussian B3LYP/6-31G(d)" (click only once).
3. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "B3LYP 6-311+G(2d,p) Optimization".
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Geometry Optimization.
    b. Under Method, click on the Density Functional drop-down list and select B3LYP.
    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

10. Double click on the optimized geometry folder. The contents of the folder should open in the folder tree and in the window on the right.
11. From the window on the right, select the experiment named "Gaussian B3LYP/6-31G(d)" (click only once).
12. Select **Edit** > **Copy**. Go to your new Thermochemical Properties folder and select **Edit** > **Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as "B3LYP 6-311+G(2d,p) Frequency".
13. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.

14. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
15. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
16. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Density Functional drop-down list and select B3LYP.
    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic
    e. Set the Spin Multiplicity to correct multiplicity for your assigned molecule.
17. Select **OK**.
18. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure using the Gaussian method B3LYP/6-311+G(2d,p) at current geometry.

1. Double click on the IR transitions folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "Gaussian B3LYP/6-31G(d) at current geometry" (click only once).
3. Select **Edit > Copy**. Go to your new Thermochemical Properties folder and select **Edit > Paste**. A copy of the selected experiment appears in your new folder.
4. Double click on the experiment copy. A Procedure dialog box opens. Highlight the call in the Procedure Steps list.
5. Select the **Delete** button in the Procedure window. The call disappears. If you were to edit the current procedure call, instead of deleting it, it changes the settings of other experiments that call the same procedure.
6. Click on the **New** button to create a new Gaussian. Click **OK** when the Procedure Editor window appears and says to select a new basis set.
7. Select all the appropriate options.
    a. Change the Calculation Type to Vibrational Spectrum.
    b. Under Method, click on the Density Functional drop-down list and select B3LYP.
    c. Click on the drop-down list for Basis Set and select 6-311+G(2d,p).
    d. Set the Wave Function to automatic and Spin Multiplicity to correct multiplicity.
8. Select **OK**.
9. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.

Creating a new procedure for electron density.

1. Double click on the electrostatic potential on electron density folder. The contents of the folder should open in the folder tree and in the window on the right.
2. From the window on the right, select the experiment named "standard procedure" (click only once).

3. Select **Edit > Copy**. Go to your new Thermochemical Properties folder and select **Edit > Paste**. A copy of the selected experiment appears in your new folder. Right mouse click and select **Rename**. Rename this file as “Electron Density”.
4. Close the procedure box. A box opens asking you to save changes. Select **YES**. The copied experiment is now altered; it appears as an experiment option in the Workspace.