

Computational Chemistry
Problem Set 2
Due Monday, February 9, 2009 (at the start of class)
Total Possible Points: 67

Basic Technical Notes: (1) For security reasons, you are allowed to log into the Hope College computers only from a computer connected to the Macalester network. (2) On Macintosh computers, the WebMO software works with the Safari browser, but not with the (Macalester-endorsed!) Mozilla Firefox browser. On Windows computers, both Firefox and Internet Explorer should work.

Material We Will Work on Together in Class

Getting started:

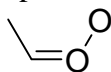
- Open the Safari web browser
- Go to mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi
- Login—do you remember your Username and Password?

Setting up a geometry optimization of hydrogen peroxide (HOOH)

- Use the WebMO Editor to build hydrogen peroxide (HOOH). Draw in the hydrogens explicitly, instead of using the Clean-Up:Add Hydrogens feature.
- Let's think about what the conformation of HOOH should be....adjust the H-O-O-H dihedral angle to an appropriate value (WUG pp. 18-19).
- Click on Job options and choose Calculation: Geometry Optimization. Keep the default option of Theory: Hartree-Fock, but change the Basis Set to Basic: 3-21G.
- Click on the Preview tab and the Generate button. You are seeing the .com (short for command) file that tells *Gaussian 03* what to do. Let me explain what we are seeing....

Performing geometry optimizations of *syn* and *anti* acetaldehyde oxides

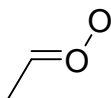
- Clear HOOH off the screen, and then use the WebMO Editor to build *syn* acetaldehyde oxide (where “*syn*” implies that dihedral angle is $0^\circ \pm 30^\circ$):



- Notes: (1) Do not use the Clean-Up:Comprehensive feature. (2) When using the Clean-Up:Add Hydrogens feature, you will probably end up with a hydrogen on the terminal oxygen. Please delete that H. (3) When using the Clean-Up:Geometry feature, the program may swing the C-C and O-O bonds away from each other, as they are in the *anti* conformation below. In any case, adjust the O-O-C-C dihedral

angle to 30° . Click on the terminal O atom first; it will be that atom which moves when you change the dihedral angle. (4) The WebMO rendering of the structure should ultimately show the formal charges we would predict from General Chemistry rules.

- Click on Job options and choose Calculation: Geometry Optimization, Theory: B3LYP, and Basis Set: Routine: 6-31G(d). Make sure that the Charge is 0 and that the Multiplicity is Singlet (change them if they're not.).
 - Click on Submit Job.
 - Let's work through the Calculated Output....and look at some of the **raw output**...
- Repeat the above process for *anti* acetaldehyde oxide (where “*anti*” implies a dihedral angle of $180^\circ \pm 30^\circ$):

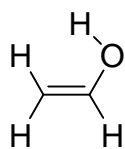


This time, accept the assumed O-O-C-C dihedral angle of 180° . Everything else about this calculation will be the same as for the *syn* acetaldehyde oxide. Again, we'll go over some of the output together.

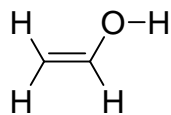
- Why do we care: atmospheric chemistry!

Your homework for the week:

1. (14 points total) Let us start with some basic conformational analysis:
 - (a) Build *n*-butane, C_4H_{10} , setting its C-C-C-C dihedral angle to 30° . Do a Geometry Optimization Hartree-Fock 3-21G calculation. Edit the Job Name to remind yourself that you started with a 30° dihedral angle. Write down the optimized dihedral angle (to the nearest 0.1°) and the energy (in Hartrees, to the fifth decimal place.)
 - (b) Repeat the calculation in part (a), except that you should set the initial dihedral angle to 150° .
 - (c) Briefly explain why the optimizations in (a) and (b) lead to different final structures. Which structure is the global minimum?
 - (d) Report the relative energy of the two conformers in kcal/mol (to the nearest 0.01 kcal/mol).
2. (12 points total) WebMO can (sort of) automate the process of comparing the energies of different molecules.
 - (a) Build the following four isomers/conformers of the molecule C_2H_4O :

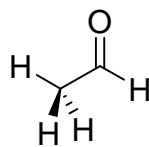


vinyl alcohol-0

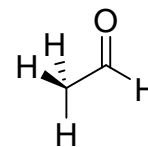


vinyl alcohol-180

(0 and 180 refer to the
H-O-C=C dihedral angle)



acetaldehyde-0



acetaldehyde-60

(0 and 60 refer to the smallest O=C-C-H
dihedral angle in the conformer)

Perform a Geometry Optimization Hartree-Fock 3-21G calculation on each structure. Be sure to provide descriptive Job Names to each of the calculations.

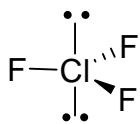
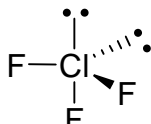
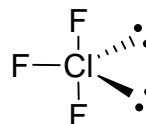
(b) In the WebMO Job Manager, select (by clicking on the boxes at the left) these four calculations and then choose Download: Spreadsheet.

- On a Mac, you will want to use File: Save As to save the results summary. Then run Excel and use File: Open. Enable All Documents and open the file you have just saved.
- On a Windows machine, you will probably be prompted to Open or Save an Excel file. Choose to save it. Then run Excel and open Files of type: Text Files to open the file you have just saved.

The Excel file summarizes all sorts of data for each of the four calculations. The only results we care about are the "RHF Energy" values. Use Excel to compute the relative energy of the four molecules in both Hartree and kcal/mol. As always, set the energy of the global minimum (the structure with the lowest energy) to zero.

(c) Delete all the irrelevant columns and print out your spreadsheet to turn in.

3. (21 points total) Build each of the three possible conformers of ClF_3 (shown below), each of which has a trigonal bipyramidal electron-pair geometry (that is, a steric number of 5). Perform a B3LYP 6-31G(d) Geometry Optimization on each of these conformers. In the Job Name, tell yourself which conformer you are optimizing.

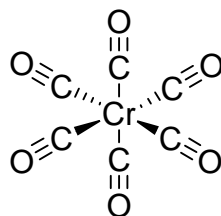
trigonal
planartrigonal
pyramidal

T-shaped

Building hints: (1) Start by drawing ClF_5 without worrying about getting the right geometry. Then using the Adjust Tool, CTRL-click (Mac) or right-click (Windows) the Cl to change its hybridization to dsp^3 . Then use Clean-Up: Geometry (not Clean-Up: Comprehensive!). Make sure this results in the

ideal trigonal bipyramidal geometry. (2) Delete two of the F's to produce the desired conformer. Note that in quantum mechanical calculations (unlike in the "stereochemical formulas" shown above), one never draws in electron pairs. It is the "job" of quantum mechanics to predict where the electron pairs should go.

- (a) If any calculation fails, make a note of this. A failed geometry optimization usually means that the starting geometry you provided was too different from the optimized geometry. In the Job Manager, click on the icon near the end of the failed calculation line that says "Restart job." The structure that loads shows the geometry that the calculation was headed towards when the program gave up. What conformer does this look like?
 - (b) Write down the absolute energy of each conformer (in hartree, to five decimal places), and the relative energy of each conformer in both hartree and in kcal/mol (to two decimal places). Set the relative energy of the most stable conformer to be zero.
 - (c) Discuss if the results in parts (b) and (c) are consistent with the predictions of VSEPR theory.
 - (d) Measure and write down the bond angle(s) (to one decimal place) for all successfully optimized geometries. Note any deviations from ideal bond angles, and briefly explain the deviations using VSEPR theory.
4. (8 points total) Build the important organometallic molecule chromium hexacarbonyl:



- (i) Start by drawing $\text{Cr}(\text{CO})_6$ without worrying about getting the right geometry. Then using the Adjust Tool, CTRL-click (Mac) or right-click (Windows) the Cr to change its hybridization to d^2sp^3 , and do the same thing to change the hybridization of each C atom to sp. Then use Clean-Up: Geometry (not Clean-Up: Comprehensive!). Make sure this results in the ideal octahedral geometry, and that all Cr-C-O bond angles are 180° .
- (ii) In Job Options, set up a Geometry Optimization B3LYP calculation. For Basis Set, select Other and type in LANL2DZ. (This is a special basis set designed for transition metal compounds.)

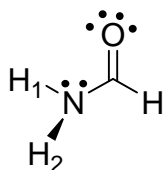
- (iii) Click on the Advanced tab and click on the box next to Cartesian Coordinates. (This is the same thing you did with the 2-butyne calculation last week. The reason is that *Gaussian 03*'s geometry optimization program can't deal with 180° bond angles. We get around this by defining the geometry in the .com file with Cartesian coordinates instead of the Z-matrix we discussed in class.)
- (iv) Go ahead and submit the job.

When the job is Complete, write down the predicted Cr-C and C-O bond lengths (in Å, to three decimal places). Calculate the relative error in these bond lengths, using the experimental data on p. 53 of the Foresman and Frisch book.

By the way, Prof. Fischer **loves** assigning hybridizations to transition metal atoms. You should e-mail him about it sometime....

5. (12 points) When necessary, one can optimize geometries quite precisely with *Gaussian 03*.

- (a) Build formamide, H₂NCHO:



Before you click on Job options, use the adjust tool to measure the H₁-N-C=O and H₂-N-C=O dihedral angles. Write them down to one decimal place. If formamide were completely planar (that is, all of its atoms lay in one plane), what would the H₁-N-C=O and H₂-N-C=O dihedral angles be?

- (b) Perform a Hartree-Fock 6-311+G(d,p) geometry optimization on formamide. When the calculation is Complete, measure and write down the optimized H₁-N-C=O and H₂-N-C=O dihedral angles to one decimal place. If the calculation went well, the molecule should be very close to planar! But doesn't this contradict the *sp*³ hybridization of the N, as shown in the Lewis structure above? Rationalize this (apparent) contradiction.
- (c) Indeed, experiment tells us that formamide is a completely planar molecule. So, what's wrong with our Hartree-Fock 6-311+G(d,p) geometry optimization? Remember that the default precision for predicted angles is ±0.1°. We can do better. In the View Job window, click on the New Job Using This Geometry button, then on Job options. Set up a Hartree-Fock 6-311+G(d,p) geometry optimization calculation as before. Then click on the Preview tab and the Generate button. Add `=(tight,calcall)` to the "keyword" OPT. Submit the job.

[Problem 5 continues on the back of this page.]

- (d) When the calculation is Complete, click on the Raw output link. This opens the actual output file created by *Gaussian 03*. In the web browser window that opens, search for the word Stationary. This should take you to the satisfying statement in the output file “Stationary point found.” (That is, the geometry optimization has completed successfully.) Write down the Maximum Displacement threshold (which, for angles, is in units of radians), and convert it to degrees. (Remember that π radians = 180° .) This is an estimate of the precision to which angles in the optimized geometry are known. Then measure and write down the optimized H₁-N-C=O and H₂-N-C=O dihedral angles (in degrees) to any many decimal places as is justified by the Maximum Displacement threshold.