

**Computational Chemistry****Problem Set 6****Due Thursday, March 26, 2009 (by 4:00 p.m.)**

(this is the day I'll be back in town from the American Chemical Society meeting)

Total Possible Points = 70

Basic Technical Notes: (1) 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. (2) For security reasons, you are allowed to log into the Hope College computers only from a computer connected to the Macalester network.

**Material We Will Work on Together in Class**

- Open the Safari web browser
- Go to [mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi](http://mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi)
- Login—Do you remember your Macalester Username and Password?

**Highly Accurate Calculations and Visualization of Molecular Orbitals**

Use one of my favorite composite methods, CBS-QB3, to compute 298 K enthalpy changes ( $\Delta_{\text{rxn}}H^\circ$ ) for the following bond dissociation reactions:



These  $\Delta_{\text{rxn}}H^\circ$  values are by definition C-H bond dissociation enthalpies. Note that CBS-QB3 is not a default method in WebMO. So to specify this, you will need to click on the Preview tab and Generate button, and then edit the command line to read

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#N CBS-QB3
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Use WebMO's Spreadsheet feature to download the results of all five CBS-QB3 calculations (that is, on  $\text{CH}_4$ ,  $\cdot\text{CH}_3$ ,  $\cdot\text{H}$ ,  $\text{CH}_3\text{F}$ , and  $\cdot\text{CH}_2\text{F}$ ) and calculate the  $\Delta_{\text{rxn}}H$  values in kcal/mol. We will admire the accuracy of these calculations as compared to experiment.

Next, click on New Job Using This Geometry for  $\cdot\text{CH}_2\text{F}$ . Do a Molecular Orbitals HF/STO-3G calculation. We will work through the results together in class also.

Two chemical comments on the Molecular Orbitals calculation:

- Calculations on species with unpaired electrons are referred to as unrestricted. This means that the orbitals holding spin-up (or  $\alpha$ ) and spin-down (or  $\beta$ ) electrons are optimized separately and can therefore take on different shapes. WebMO lists all  $\alpha$  orbitals first (both occupied and unoccupied), and then all  $\beta$  orbitals (again, both occupied and unoccupied).
- By convention, the single unpaired electron in a monoradical like  $\cdot\text{CH}_2\text{F}$  is spin-up. We will therefore focus on the  $\alpha$  MO's together in class.

Three technical comments on Molecular Orbitals calculation:

- When the calculation is complete, you can examine a particular molecular orbital by clicking on the magnifying glass at the end of its line in the Molecular Orbitals table.
- Java3D needs to be loaded on your computer. ITS guru Adam Nave has done this for the computers in Olin-Rice 341, but you may need to do this on your own computer.
- The first time you click on a magnifying glass, it will take several minutes for your computer to load the MOViewer. What's more, the MO you clicked on may not show up. If this is the case, just click on the magnifying glass again.

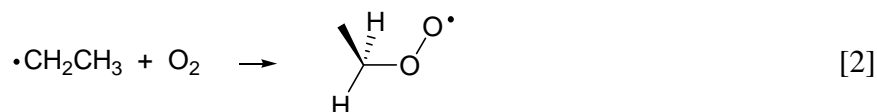
### **Your Homework for the Week:**

1. (18 points) Continue the work we started together in class:
  - (a) Do CBS-QB3 calculations to predict the C-H bond dissociation enthalpy (BDE) (in kcal/mol to two decimal places) in methanol (CH<sub>3</sub>OH) and in methylamine (CH<sub>3</sub>NH<sub>2</sub>). Be sure you have located the ground state conformers.
  - (b) The experimental BDE for CH<sub>3</sub>OH is  $96.0 \pm 0.4$  kcal/mol, and for CH<sub>3</sub>NH<sub>2</sub> is  $93 \pm 2$  kcal/mol. (*CRC Handbook of Chemistry and Physics*, 85th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2004.) Do your CBS-QB3 predictions lie within these experimental confidence intervals?
  - (c) Do a Molecular Orbitals HF/STO-3G calculation on either ·CH<sub>2</sub>OH or ·CH<sub>2</sub>NH<sub>2</sub>. Sketch (or copy and paste from WebMO) and label (*e.g.* as MO 6) the  $\alpha$  molecular orbitals responsible for the stabilization of the radical product.
  - (d) What is the trend in the C-H BDE for the series CH<sub>3</sub>F, CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>? Rationalize this trend.
2. (12 points) Experiments indicate that hydrogen fluoride has a bond length of 0.917 Å, a dipole moment of 1.91 D, and a vibrational frequency of 4139 cm<sup>-1</sup>. Using a rather high level of theory, let's see how varying basis set size affects the accuracy of our predictions for HF:

Do Optimize + Vib Freq calculations with Moller Plesset 4 (MP4) theory and the following basis sets: STO-3G, 3-21G, 6-31G(d), 6-311++G(d,p), and 6-311++G(2df,2p). Note that the last two basis sets are not "pre-defined" in WebMO, so you will have to enter them manually.

- (a) Construct a spreadsheet with columns for basis set, bond length (to three decimal places), dipole moment (to two decimal places), and vibrational frequency (to the nearest cm<sup>-1</sup>).
- (b) In the spreadsheet, calculate the relative error (in %, to the correct number of significant figures) in each of the predicted bond lengths, dipole moments, and vibrational frequencies.
- (c) Overall, which basis set gives the most accurate predictions?

3. (20 points) Let us consider how varying the level of theory affects the accuracy of geometry optimizations. Consider the molecule *N,N*-dimethylformamide (see p. 105 of the textbook for the structure and selected experimental bond lengths). Do Geometry Optimization calculations with Hartree Fock, B3LYP, and Moller Plesset 2 (MP2) theory. In all cases use the (not pre-defined) 6-31+G(d,p) basis set.
- Construct a spreadsheet with columns for level of theory, each of the five bond lengths (in Å, to three decimal places) tabulated on p. 105, and cpu time.
  - In the spreadsheet, calculate the relative error (in %, to the correct number of significant figures) in each of the predicted bond lengths.
  - Overall, which level of theory gives the highest accuracy for the least amount of cpu time?
4. (20 points) Part of my research at Macalester has involved characterizing the thermochemistry of peroxy radicals. This has included calculating enthalpy changes ( $\Delta_{\text{rxn}}H^\circ$ ) for the formation of methylperoxy radical (Reaction 1) and the formation of ethylperoxy radical (Reaction 2):



My students and I reported B3LYP/6-31G(d), G2 (“G2 High Accuracy Energy”), and CBS-QB3  $\Delta_{\text{rxn}}H^\circ$  values for these reactions in the *Journal of Physical Chemistry A*.

Please note the following:

- WebMO does not correctly extract information from G2 output files! You must click on the Raw output link and scroll down towards the very bottom. Paste into your spreadsheet the value (in hartree) next to G2 Enthalpy=**
  - The methylperoxy radical has synclinal C-H and O-O bonds.
  - The ground state conformer of the ethylperoxy radical has synclinal C-C and O-O bonds.
  - Use the ground electronic state of  $\text{O}_2$  (*i.e.* the triplet state).
- Compute  $\Delta_{\text{rxn}}H^\circ$  for both Reaction 1 and Reaction 2 using the B3LYP/6-31G(d), G2 (“G2 High Accuracy Energy”), and CBS-QB3 model chemistries. Report your results in kcal/mol to two decimal places.
  - Look up and write down the experimental  $\Delta_{\text{rxn}}H^\circ$  values (and their uncertainties) in this paper by Knyazev and Slagle: *Journal of Physical Chemistry A* **1998**, 102, 1770. Which of your predictions fall within the experimental confidence intervals?
  - Overall, which level of theory gives the highest accuracy for the least amount of cpu time?