

*This problem set will take longer than the last one in the sense that you may need to submit some jobs, leave, and check your results later. **Get started early.***

Some mechanical reminders: To run an AMSOL or G03 job, your input file should be named `myfile.dat`. Issue the commands `qamsol myfile.dat` or `qg03 myfile.dat`, respectively, and the scripts will take care of the rest. If you want to look at an output deck while a job is running, you can either `vi myfile.out` or `more myfile.out`. To examine the queue on the SP, the command is `llq`; you may find that `llq | egrep chem##` (where `chem##` is your userid) to be more convenient. A link to `vi` commands is provided on the class webpage.

A nomenclature reminder: the notation `x/y//w/z` means level of theory `x` using basis set `y` at a geometry optimized at level of theory `w` with basis set `z`. E.g., `MP4/6-311G(d,p)//HF/6-31G(d)` means the geometry was optimized at the `HF/6-31G(d)` level but the energy (and/or other properties) are being calculated at the `MP4/6-311G(d,p)` level.

Some quick notes/reminders with respect to Gaussian03:

- 1) Template files have been provided in the directory `~chem01/G03_templates` — feel free to study them carefully to ensure you have proper file formats, memory requests (`%mem=32000000`), and checkpoint naming conventions (`%chk=myfile.chk`). (Template files for AMSOL jobs are also available in `~chem01/amsol_templates`.)
- 2) If you are entering geometric data (as opposed to reading it from the checkpoint file) you *must* end the input file with a blank line.
- 3) To find transition states *in the absence of a symmetry constraint*, use `fopt=(ts)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS *breaks* the symmetry (in which case, don't use `ts` as a keyword) or *preserves* it (in which case continue to use it). If you are looking for a TS, you may often find it helpful to do `fopt=(ts, calcfc, noeigentest)`. The other keywords request calculation of analytic force constants on the first step, and that the job not die if you have other than exactly one imaginary frequency.

4) You can save a *lot* of time by using useful information from previous calculations stored in the checkpoint file. *Plan* your calculations to try to save time.

a) Keywords `guess=read` and `geom=checkpoint` get the wave function and the geometry, respectively, from the last completed calculation. So, if you have just done an optimization, and want to follow-up with a frequency calculation, for instance, you will certainly want to use these keywords. **Note: Frequencies *must* be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!** (Note that if you know ahead of time you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `fopt`).

b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `fopt=( )` keyword, e.g., `fopt=(ts,readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants from the previous calculation, which is efficient. **It's usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.**

1. Get a copy of Armstrong, A.; Chivers, T.; Parvez, M.; Boeré, R. T. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 502.

a. Construct a Z-matrix for compound **2a** in that article, but with all THF ligands removed and all methyl groups replaced by H atoms. Write the Z-matrix in such a way that the structure has  $C_3$  symmetry (your Z-matrix may be in either Gaussian or AMSOL format) and in such a way that the various bond lengths reported in Figure 1 of the *Angewandte* article agree with your Z-matrix structure to within 0.2 Å. E-mail your Z-matrix to Casey as clear text when you are satisfied that you have successfully completed this portion of the problem (so that he can verify it has the proper symmetry and meets the geometry constraints).

b. Optimize structure **3'** at the MNDO level of theory including two tetrahydrofuran ligands on the Li atom (see Scheme 1 and in-text drawing). Note that **3'** is a radical anion, so use the keywords UHF and CHARGE=-1 in your calculation. Once you are satisfied that you have a reasonable structure (you are welcome to ask Casey or me for our opinion on that front) compute ESR hyperfine coupling constants to compare to those reported on p. 503 of the article for this putative structure in solution. Carry out this calculation for your MNDO-optimized structure but at the B3LYP level using the MIDI! basis set for all atoms

but Li and using the 3-21G basis set for Li (a template file is provided to show how to set up this mixed-basis set calculation).

c. Are your computed splittings consistent with the experimental data (keep in mind that solution experiments measure the absolute value of an isotropic hyperfine coupling constant and thus *cannot distinguish* negative and positive values)? If your results are not perfectly consistent with experiment, thoughtfully discuss what other computational approaches you might take in order, in principle, to improve agreement with experiment (if you think that possible—if you think the structure is just totally wrong, you may attempt to support that position, too). In that discussion, address any practical issues that might arise in doing any calculations you suggest.

2. Get a copy of Saraf, S. R.; Rogers, W. J.; Mannan, M. S.; Hall, M. B.; Thomson, L. M. *J. Phys. Chem. A*, **2003**, *107*, 1077.

a. Verify the reported G2, G2MP2, G3, G3B3, and CBS-Q numbers reported in Table 3 for rxns 1 and 2. Show how you carry out at least one such verification of a number in the table and report enthalpies for all necessary species.

b. Compute the 298 K enthalpy of formation for hydroxylamine using its atomization energy at the 5 indicated levels and the table at the end of this problem set (which corrects errors in Table 10.2 of the textbook). Again, show the equations/values you used to accomplish this calculation.

c. How do your answers from part a compare to those from part b? If there is a difference, which number(s) do you trust more? Explain your reasoning.

3. Here begins a problem that will carry over to the third problem set and ultimately the final exam. Take a look at

[pollux.chem.umn.edu/8021/C4H6N2O2-PES/](http://pollux.chem.umn.edu/8021/C4H6N2O2-PES/)

When prompted, your username is chem## (your SP account ID) and your password is that part of your e-mail address preceding “@umn.edu”. If you have any problems, see Casey.

While there, select **View Surface**. You will see my contribution to mapping the  $C_4H_6N_2O_2$  surface (click on [chem01.html](#) to see it in 3D -- if working from home, you will need to get the Chime Plug-in if you don't already have it -- if you don't have the plug in, or can't seem to get it to work, you'll see text cartesian coordinates, which you can always visualize in Chem-3D after pasting them into a text file, adding a new first line with the total number of atoms (14), and opening it as cartesian coordinates from Chem-3D). My point on the surface is a transition-state structure for the retro-Diels-Alder cycloreversion of 3,6-dihydroxy-3,6-dihydropyrazine to make *s-cis E,E*-1,4-dihydroxy-1,3-butadiene and molecular nitrogen.

Your task is to find a point of your own on the potential energy surface (PES)—either a minimum or a transition state—*that is not already in the table* (easy if you're the first to finish, harder and harder the longer you wait...) To complete an entry, you will need a frequency calculation at the HF/6-31G(d) level (and thus, of course, you will first have to have optimized the structure at this level of theory). When you have the data, click on **Submission Form** and paste in the number of imaginary frequencies (0 or 1), the HF energy, enthalpy, and free energy, and finally the optimized cartesian coordinates (you can cut and paste right from the output file of the frequency calculation). If you make any mistakes, you can delete an entry and start again.

Each new submission will be visible to all students, so you can see if the structure you're working on has already been taken. Full credit for this problem simply consists of entering sensible data. In future exercises, we will make comparisons of different levels of theory and different isomers to learn more about the chemistry of the surface.

**Table 10.2.** Experimental  $\Delta H_{f,0}^{\circ}$ ,  $\Delta H_{f,298}^{\circ}$ ,  $\Delta G_{f,298}^{\circ}$  values and spin-orbit corrections (kcal mol<sup>-1</sup>) for the atoms.

Atom	$\Delta H_{f,0}^{\circ}$ <sup>a</sup>	$\Delta H_{f,298}^{\circ}$ <sup>a</sup>	$\Delta G_{f,298}^{\circ}$ <sup>a</sup>	Spin-orbit <sup>b</sup>
H (2S)	51.63 ± 0.001	52.103	43.93	
Li (2S)	37.69 ± 0.20	38.074	28.19	
Be (1S)	76.48 ± 1.20	77.438	67.73	
	75.8 ± 0.8 <sup>c</sup>	76.75 ± 0.8 <sup>c</sup>	66.04 ± 1.2 <sup>c</sup>	
B (2P)	136.2 ± 0.2	133.84	122.91 ± 0.2	-0.03
C (3P)	169.98 ± 0.10	171.29	160.03	-0.09
N (4S)	112.53 ± 0.02	112.97	102.05 ± 0.02	
O (3P)	58.99 ± 0.02	59.553	48.08	-0.23
F (2P)	18.47 ± 0.07	18.97	7.66	-0.38
Na (2S)	25.69 ± 0.17	25.645	14.70	
Mg (1S)	34.87 ± 0.20	35.158	24.57	
Al (2P)	78.23 ± 1.00	78.800	67.08	-0.21
Si (3P)	106.6 ± 1.9	107.55	95.59	-0.43
	108.1 ± 0.5 <sup>c</sup>	109.0 ± 0.5 <sup>c</sup>	97.1 ± 0.5 <sup>c</sup>	
P (4S)	75.42 ± 0.20	75.619	64.00	
S (3P)	65.66 ± 0.06	66.200	54.25	-0.56
Cl (2P)	28.59 ± 0.001	28.991	17.23	-0.84

<sup>a</sup> All data, unless otherwise noted, are from the JANAF tables, see Chase, M. W., Jr. (1998) *J. Phys. Chem. Ref. Data, Monograph 9*, 1 for most recent versions. <sup>b</sup> Amount by which lower energy spin-orbit state lies below unsplit term, see Moore, C. Natl. Bur. Stand. (US) Circ 467, 1952. <sup>c</sup> Estimates considered to improve on experimental values, see Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.