

*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 G98 job, your input file should be named `myfile.dat`. Issue the commands `qamsol myfile.dat` or `qsubg98 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 Origin, the command is `qstat -a`; you may find that `qstat -a | egrep chem##` (where `chem##` is your userid) to be more convenient. To get a cube molecular orbital file for visualization in Chem-3D, you need to use the scripts `formchk` and `cmo`. In step 1, type `formchk myfile.chk`, where `myfile.chk` is the checkpoint file for the molecule in whose MOs you are interested. This will create a formatted checkpoint file (you can look at it if you like) named `myfile.fchk`. Now type `cmo myfile.fchk n1 n2`, where you are asking for cube files of all orbitals between numbers `n1` and `n2`. So, if you want to look at the HOMO and LUMO, and they are orbitals 22 and 23 of your molecule, you would use 22 and 23 for `n1` and `n2`. The script will create files `n1.cub` through `n2.cub`; once transferred to a PC/Mac and opened as Gaussian cube files in Chem-3D, they will visualize the orbitals.

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**//HF/6-31G*` means the geometry was optimized at the `HF/6-31G*` level but the energy (and/or other properties) are being calculated at the `MP4/6-311G**` level.

Some quick notes/reminders with respect to Gaussian98:

- 1) Template files have been provided in the directory `~inst8021/G98_templates` — feel free to study them carefully to ensure you have proper file formats, memory requests (`%mem=8000000`), parallel requests (`%nproc=2`), and checkpoint naming conventions (`%chk=myfile.chk`). (Template files for AMSOL jobs are also available in `~inst8021/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, that the job not die if you have other than 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`).

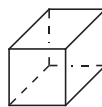
b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `fopt=( )` keyword, e.g., `fopt=(ts, readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants 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.**

### The Problems:

1. Cyclooctatetraene (COT) and cubane are two isomers of  $C_8H_8$ . To what point group does each molecule belong? What is the difference in their heats of formation predicted at the PM3 level (you do not need to impose symmetry in the PM3 calculations)? Is the sign of the difference (i.e., the prediction of which one is more stable) what you expected? Why or why not?



COT



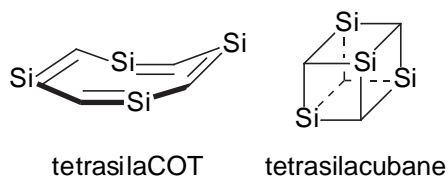
cubane

Now construct cartesian coordinate sets for the two molecules that *do* have the correct symmetry (hint: think about these molecules placed symmetrically around the origin in a 3-dimensional cartesian space. For every atom at a position  $(x,y,z)$ , what other cartesian positions must be occupied by equivalent atoms?) You'll probably want to visualize your cartesians in Chem-3D to verify reasonable structures. Compute  $\Delta E$  for COT and cubane

at the HF/6-31G\*, MP2/6-31G\*//HF/6-31G\*, and B3LYP/6-31G\* levels. Comment on the values compared to one another and to PM3.

What is the experimental difference in the 298 K heats of formation for COT and cubane? How do the different levels of theory compare to experiment? Explain any particularly good or bad agreement. Although they are too expensive to have each student perform, the instructor has carried out G3 calculations on the two isomers, and you may find them in ~inst8021/PS2\_data. How does the 298 K enthalpy difference at the G3 level compare to experiment? A possible criticism of our earlier analysis would be that we were using  $\Delta E$  values from some levels of theory to compare to  $\Delta H$  from experiment. Based on the data in the G3 output files, is this a significant criticism?

Now, consider the tetrasilic analogs of COT and cubane below.



Repeat all of the calculations done above for these sila analogs (except that no G3 data need to be considered). Compare and contrast the two sets of systems: which features are similar and which are different? To what point groups do the optimized sila structures belong? Is there any disagreement on this point between different levels of theory? To better understand the structure of tetrasilaCOT, visualize its HOMO and LUMO. Explain how these orbitals differ from the HOMO and LUMO of COT (you may visualize these too, or simply look in any standard textbook) and why this affects the geometry.

2. In the attached communication from *Angewandte Chemie, International Edition in English*, Lambert et al. report the isolation and X-ray crystal structure of the pentamethylcyclopentadienyl (Cp\*) cation. Note that Cp\*<sup>+</sup> is formally antiaromatic, so its been an attractive synthetic target for many years.

Lambert et al. report structural data and <sup>13</sup>C NMR data. Optimize the structure of the Cp\* cation at the HF/6-31G\* level (don't worry about trying to impose symmetry). How do your structural data compare to the reported data? Now compute the isotropic <sup>13</sup>C NMR chemical shifts for all carbons at the B3LYP/6-31G\*//HF/6-31G\* level (simply include the keyword `nmr` in a single-point calculation). Since NMR calculations provide *absolute* shieldings, you will also need to know the computed shieldings for tetramethylsilane (TMS, which is the standard for  $\delta = 0$  on the <sup>13</sup>C chemical shift scale). I have done this calculation for you, and it may be found in the file ~inst8021/PS2\_data/tmsnmr.out (note the lovely  $T_d$  symmetry!). A *deshielding* <sup>13</sup>C shift  $\delta$  is then determined as shielding for

TMS minus shielding for carbon of interest. How do your data compare to those reported by Lambert et al.? (Use a picture to report your structural and NMR data).

Now consider the pentamethylcyclopentenyl cation (i.e., not *dienyl*, but just *monoenyl*; add the two H atoms trans to one another on adjacent carbon atoms). Compute structural and  $^{13}\text{C}$  chemical shifts for this structure at the same levels of theory as already done for  $\text{Cp}^{*+}$ . How do your data compare to those reported by Lambert et al.?

Which of these two molecules do you think was actually made?

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/~kinsinge/8021/8021.2003/ProbSets-Exams/2003/C3H7NO/](http://pollux.chem.umn.edu/~kinsinge/8021/8021.2003/ProbSets-Exams/2003/C3H7NO/)

When prompted, your username and password are identical to those for the origin. If you have any problems, see Chris.

While there, select **View Surface**. You will see my contribution to mapping the  $\text{C}_3\text{H}_7\text{NO}$  surface (click on [inst8021.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 and opening it as cartesian coordinates from Chem-3D). My point on the surface is a transition-state structure for a 1,2-hydride shift converting cyclopropylamine *N*-oxide to *N*-cyclopropylhydroxylamine.

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\* 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.