

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

Some mechanical reminders: To run a G09 job, you must have the `gaussian` module loaded. After login, type `module list`—if you don't see `gaussian/g09.d01` listed, type `module load gaussian`, and then `module list` again, and now you should see it. Next, remember that your input files should be named, for example `myfile.com`. Issue the command `qg09 myfile.com` and the script will submit a 5 hour job to the batch queue to run on one 8-processor node using local scratch space. You can look at the output from `qg09 -h` if you want to include flags that will send you an email on completion, ask for more (or less) time, ask for more nodes, etc. (note that asking for more than 8 nodes (64 processors) will not generally be helpful). 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 itasca, the command is `qstat -a`; you may find that `qstat -a | egrep cm8021##` (where `cm8021##` is your userid (or the analogous `cm4021##`)) is also convenient. [Links to vi commands and a unix primer are 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)//MP2/6-31G(d)` means that the geometry was optimized at the `MP2/6-31G(d)` level but the energy (and/or other properties) are being calculated at the `MP4/6-311G(d,p)` level. The notation x/y in the absence of a trailing $//w/z$ implies optimization and energy evaluation were performed with the same level of theory.

Some quick notes/reminders with respect to *Gaussian 09*:

- 1) Some files have been provided in my directory `~cm8021pr/templates` — feel free to study them carefully to ensure that you have proper file formats, e.g., checkpoint naming conventions (`%chk=myfile.chk`).
- 2) If you are entering geometric or basis set data in a G09 input deck (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 `opt=(ts,calcfc)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS structure *breaks* the symmetry (in which case, use neither `ts` nor `calcfc` as keywords, because

the symmetry will hold you at the TS structure) or preserves it (in which case use both keywords). If you are looking for a TS, you may often find it helpful to do `opt=(ts,calcfc,noigentest)`. The other keywords besides `ts` request calculation of analytic force constants on the first step (`calcfc`), and that the job not die if other than exactly one negative force constant is found at some step (`noigentest`). In addition, note that there is a very useful subkeyword to `opt`, namely, `modredundant`, that allows one to freeze certain degrees of freedom so that other degrees of freedom can be relaxed first, and then the frozen coordinates can be unfrozen to permit, say, a TS optimization to start with most of the molecule relaxed but certain bonds stretched (for example...)

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. You can also save a lot of time by using *symmetry* when appropriate.

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 that you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `opt`).

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 `opt=()` keyword, e.g., `opt=(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.**

5) Serving GaussView across the local network can be slow owing to the massive amounts of graphics data being transferred. It will often be more convenient to transfer readable files to a local machine (e.g., a computer in Chemistry's Computer Lab) and run GaussView locally. In particular, output files (which are text) can be transferred easily. For inspection of molecular orbitals, it is convenient to transport a formatted checkpoint file. To generate such a file, the command is `formchk myfile.chk`, where `myfile.chk` is the name of the (binary) checkpoint file. A text formatted checkpoint file `myfile.fchk` will be created and can be moved in the same fashion as an output file. GaussView accepts `.fchk` as an option for file types to be opened.

6) PC Model can save structures as Gaussian input files (it's one of the options in the Save dialog box). You may find it convenient to generate structures that way if you doubt your ability to draw in *GaussView*, or simply want to do an MM optimization first.

***** THE PROBLEMS *****

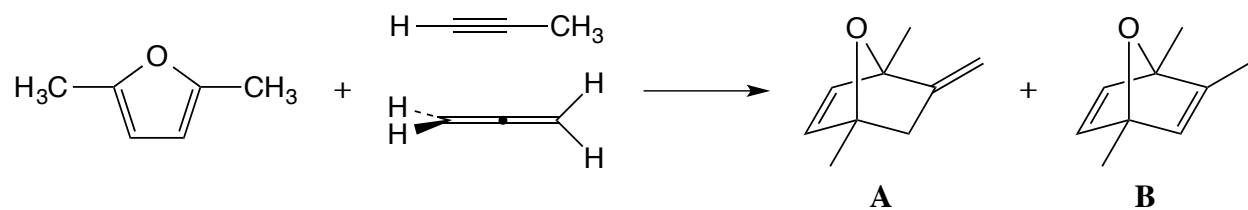
1. What is your best estimate of the 298.15 K gas-phase heat of formation for *O*-methyl formaldoxime? To answer this question, do at least AM1 and PM6 calculations and some other quantum chemical model beyond semiempirical molecular orbital theory. Explain your reasoning in coming up with your best estimate. Incidentally, you may be interested to know that the equivalent heat of formation for acetaldoxime is known.

2. Let us revisit the pyrazine dimer from problem set 1. Using the pi-stacked geometry that was common to all 3 force fields in Problem Set 1 as a starting guess, minimize the geometry using B3LYP with the def2-svp basis set. Now, do single point energy calculations at the HF, MP2, M06-2X, and B3LYP + D3BJ (Grimme dispersion correction) levels of theory with the same basis set. How do the interaction energies from these 5 levels of theory compare for this geometry? Now, repeat the geometry optimization at the B3LYP + D3BJ/def2-svp level, and repeat the single-point calculations (substituting B3LYP without dispersion for the fifth calculation). Again, how do the interaction energies compare, and how do they vary compared to the other geometry? At the MP2 level, how does the interaction energy for the second geometry change if you switch the basis set from def2-svp to def2-tzvp? What about at the M06-2X level? How might you rationalize any trends as a function of basis set?

3. For the following problem, carry out all calculations at the M06-2X level of density functional theory (gas phase, for now). Use the 6-31G(d) basis set for all non-metal atoms; use the SDD basis set for gold.

Let's set the stage. You have an extremely unlucky synthetic organic colleague. She is cursed with glassware that seems always to have an acidic surface. Thus, whether she uses a tank of pure propyne, or a tank of pure allene, she always ends up with an equilibrated mixture of the two when she wants to use one in a reaction. At 298.15 K, what is the ratio of the two that she would find in her reaction flasks after equilibration?

Now, it turns out that she wants to make compound **B**, and *not* compound **A**, and they're a pain to separate if they are present as a mixture.



She's pretty certain that the free energy of activation for the acid-catalyzed process that is interconverting allene and propyne on the flask walls is about 10 kcal/mol. So, here are some questions for you to answer — do *not* include any acid catalysis in your analyses of the Diels-Alder cycloadditions:

- Is it possible to obtain a single isomer (**A** or **B**) from the illustrated reaction of the allene/propyne mixture with 1,4-dimethylfuran? Explain your answer through invocation of the Curtin-Hammett principle.
- What 298.15 K ratio of products will your colleague actually obtain? Will she be happy?
- Your colleague asks you whether you think running the reaction in the presence of AuCl will be helpful. A great skill to a theoretician is being able to rationalize *any* result. Offer a rationale for why AuCl might lead to *more* product **B** and then another rationale for why it might lead to *less*.
- Now, compute the effect of added AuCl on the reaction and the product distribution. Will your colleague's mood improve?
- If AuCl is not the perfect solution to the problem of making **B**, based on what you've learned thus far, what *might* you suggest as an alternative reagent to your colleague? You don't have to do calculations to bolster your suggestion (although you're welcome to), but do explain your reasoning.