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 altix, the command is `qstat -a`; you may find that `qstat -a | egrep cm8021##` (where cm8021## is your userid) to be more 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)//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 ~cm8021/templates — feel free to study them carefully to ensure you have proper file formats, memory requests (`%mem=64000000`), and checkpoint naming conventions (`%chk=myfile.chk`). (Template files for AMSOL jobs are also available in the same directory.)

2) If you are entering geometric data in a G03 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 `fopt=(ts,calcfc)`. 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. Below are two isomeric geometries that we previously examined in Problem Set 1 as both $C_{10}H_{16}$ and $Si_{10}H_{16}$. To what symmetry point group does each structure belong? Compute energies for all 4 cases for geometries optimized at the AM1, PM3, HF/MIDI!, and HF/6-31G(d). For the final set of geometries, compute single point energies at the MP2/6-311G(2df,p)//HF/6-31G(d) level (*do not optimize at this level*). Report the relative energies of the two isomeric forms at all levels of theory for the two elemental compositions. How have things changed compared to PCModel's predictions and how do your numbers influence your assessment of what may be the "right" answer?
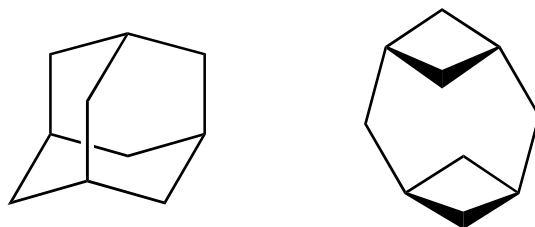
Note that if you enter z-matrices or cartesian coordinates that correctly reflect the molecular symmetry, you will have a vastly easier time as the calculations will run much, much more quickly at the ab initio and mp2 levels of theory. For the AM1 and PM3 calculations, this is not a serious issue.

2.
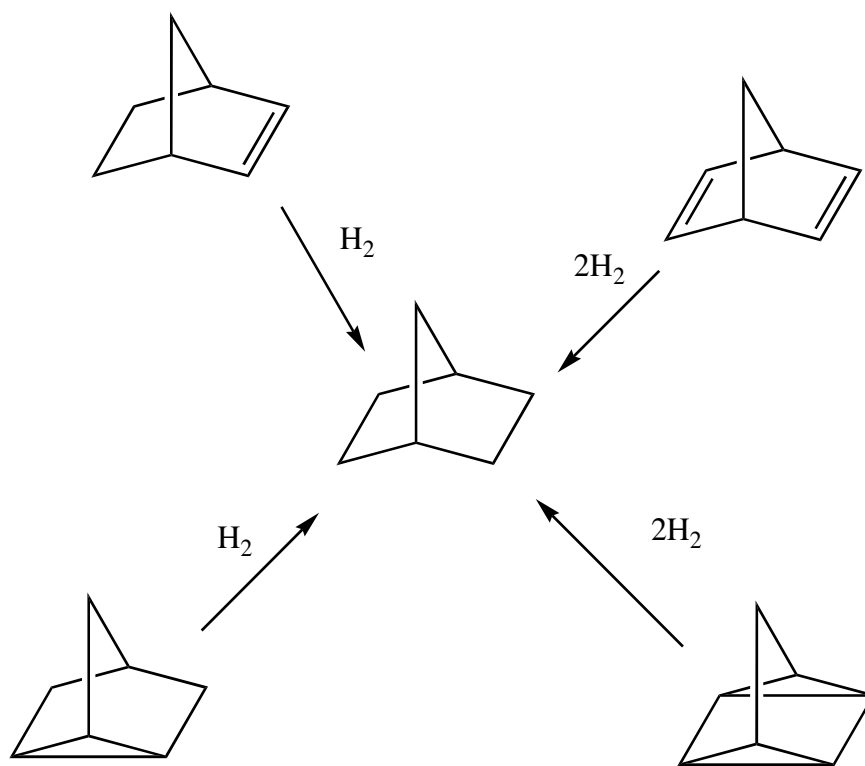
Enthalpies of Formation of the Norbornadiene Cycle

Compound	MMX	MNDO	AM1	PM3	Expt.
Norbornadiene	55.5	62.7	67.7	58.8	57.4
Norbornene	19.5	25.3	26.0	22.0	21.4
Norbornane	-12.8	-10.4	-14.4	-13.7	-12.4
Nortricyclane	19.5	27.1	33.8	26.0	20.2
Quadricyclane	79.4	79.1	104.4	86.3	79.5

*units are in kcal/mol
Rogers, D.W. et al., 1992, *Structural Chemistry*, **3(1), 53.

Looking at the above table of heats of formation, does the accuracy of any of the methods surprise you? Is it possible to rationalize the difference in accuracy of the molecular mechanics method and the semi-empirical methods?

Now construct a Z-matrix for norbornadiene (of the windshield wiper mechanism fame) and include it in your answer. Make sure to check the structure in Chem3D to see if it is reasonable.

Compute the $\Delta H_{f,298}$ for norbornadiene (using its atomization energy and Table 10.2 in the text) at the B3LYP, HF, and MP2 levels with both the 6-31G and 6-311G(2df,p) basis sets. Also compute $\Delta H_{f,298}$ using the G3 method (there is a G3 keyword in Gaussian 03). For any one of the methods, demonstrate how you did one of the calculations of the heat of formation.

Which of the higher level methods does best compared to experiment? Which does the worst? How sensitive are the methods to basis set incompleteness? How does the G3 composite method perform compared to the single level methods? Why do the single level methods do so poorly compared to molecular mechanics and the semi-empirical methods (which are vastly cheaper), and G3 (the composite method)?

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/C4H6SO2/

    While there, select View Surface. You will see my contributions to mapping the $C_4H_6SO_2$ surface (click on either 00.html or 900.html to see them in 3D — you'll need a browser with Java capabilities — you'll also 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 (13), and opening it as cartesian coordinates from Chem-3D). My points on the surface are 2H-thiophene-1,1-dioxide and a transition-state structure for the [2,3] sigmatropic shift converting S-formyl allylsulfenate to allyl formyl sulfoxide.

    Your task is to find two points of your own on the potential energy surface (PES)—both a minimum and a transition-state structure—*that are not already in the table* (easy if you're the first to finish, harder and harder the longer you wait...) To complete each 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 and fail to realize until after submission, contact me with the details and I will fix the website.

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.