

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=32000000`), 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.**

5) You may find it useful to read up on the keyword `nmr` in the online G03 manual (link from class website).

6) Information on using `cubegen` and Chem-3D to visualize molecular orbitals:

To get a cube molecular orbital file for visualization in Chem-3D, you need to use the Gaussian utilities `formchk` and `cubegen`. 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 with `vi` or `more` if you like) named `myfile.fchk`. Now type `cubegen 0 mo=## myfile.fchk ##.cub 30 h`, where you are asking for a cube file of orbital `##` (an integer). So, if you want to look at the HOMO and this is orbital 22, you would use 22 for `##`. The utility will create file `##.cub`; once transferred to a PC/Mac (by `scp`) and opened as a Gaussian cube file in Chem-3D, you will have an orbital picture. Note that Chem-3D has a control window under View that is named Molecular Orbitals. The default isodensity surface of 0.01 a.u. is generally too diffuse to be useful, but you can change to a higher density surface (typically between 0.03 and 0.05 works well) using the control window.

So, how do you use `scp`? On a Mac, open the Terminal utility, and you will be in the Unix OS of the Macintosh (yup, it's a Unix machine). The command is, for example, `scp cm8021##@altix.msi.umn.edu:PS3/myfile.cub .` where `##` is your id number, and `PS3` is the subdirectory that your file `myfile.cub` is found in (if it is in the top directory, no more need be specified than `cm8021##@altix.msi.umn.edu:myfile.cub`). On a PC in the Microlab, Dan MacEwan instructs:

I just tested the FileZilla freeware FTP program in the microlab with an MSI account. It works well. We don't need to add or install any extra software for SCP support and your students are welcome to use FileZilla on their personal computers/laptops if they wish. Your instructions to use it would look something like this:

Go to Start, Programs, Internet Tools, and click on FileZilla. Open the Site Manager by either 1) clicking Ctrl-S 2) clicking the icon in the upper left corner under the 'file' menu 3) in the upper left corner, click 'file', 'site manager'

Enter your MSI host name in the 'Host' field at the top.
Enter your logon name in the 'User' field.
Click 'Connect' on the bottom or hit the 'Enter' key.

You will be prompted for your password. Enter your password and hit the <Ok> button or the 'Enter' key.

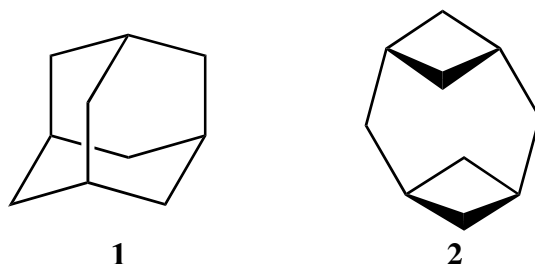
You MAY be asked if you want to cache the key to the server you are connecting to. Click Yes or No. It won't matter as the computer purges itself with each reboot.

On the right hand side you'll see your files. Navigate to/through the folders and files until you see the ones you want to transfer. On the left hand side, change the default destination from C:\ to 'desktop' for ease of use. You can transfer your files by 1) right clicking on the desired file in your MSI account and selecting 'download' 2) drag the desired file(s) from the right hand side of FileZilla to the desired folder on the left hand side.

Close the program when you're done.

Well, it's p. 3. Time to get to the actual problems!

1. Below are two isomeric geometries that we previously examined in Problem Sets 1 and 2 as both $C_{10}H_{16}$ and $Si_{10}H_{16}$. It is time to (i) see how DFT does and (ii) discover whether the high-symmetry structures with which we have been working are really minima! To that end, we will first reoptimize all geometries at the TPSS/6-31G(d) level and then compute the vibrational frequencies. We will take advantage of the cubic scaling of local (i.e., non-hybrid) DFT by using an auxiliary density fitting basis set that will speed the calculation considerably. In order to do this, the correct specification of the theoretical level in Gaussian 03 is `tpsstps/6-31g(d)/auto` (and, of course, you'll need to specify `opt` and `freq` to get the frequencies). Are all structures minima?



In addition, we should check the sensitivity to basis set by doing a single point calculation with a larger basis, in this case we will adjust the keywords to: `tpsstpss/6-311g(2df,p)/auto//tpsstpss/6-31g(d)/auto`
`scf=tight` and guess the prior structure and wave function. Finally, we should check sensitivity to functional with this larger basis by performing a `mpw1pw91/6-311g(2df,p)//tpsstpss/6-31g(d)/auto` single point calculation (note that we can't use `auto` in this calculation because we have a hybrid functional).

[Actually, you took this problem set home and began weeping in exhaustion, complaining bitterly about your sadistic professor, and fell into a catatonic sleep at the kitchen table overwhelmed by the horrors of `vi`, `unix`, `Gaussian`, etc.

Your secret house elf, secure in her invisibility, watched you throughout your philippic against all things computational and decided to take pity on you. House elves being born with intrinsic theoretical chemistry aptitude, she carried out all of the calculations requested above while you snored. You were surprised, but too happy to question providence, when you awoke to find the report on the next page next to your placemat-creased face.

Nevertheless, it is still incumbent on you to compare and contrast the DFT results for relative energies to prior results (found in the answer key to Problem Set 2). Comment as well on comparison of enthalpies and free energies from the TPSS/6-31G(d) level compared to simply electronic energies. If you had to make a best guess for the enthalpy differences, what would your guess be? What would your estimate of error in your guess be? How might you try to improve on your guess/error estimate with additional calculations? (You don't have to do them, just describe the plan.)

Oh, by the way, house elves are compassionate, but they are known to suffer from a form of dyslexia that causes them to interchange adjacent digits in numbers from time to time. If there are any odd inconsistencies in the data, you might want to see if interchanging a pair of adjacent digits would help. Of course, if you're really not sure, there's always the option of repeating the calculations...

And, leave out some milk and cookies next time, to say thank you to the elf.]

Level of Theory	$E(1)^a$	$E(2)^a$
<u>Carbon frame</u>		
TPSS/6-31G(d)/auto		
E	-390.802 62	-390.717 42
H_{298}	-390.552 15	-390.469 73
G_{298}	-390.858 60	-390.509 73
TPSS/6-131G(2df,p)/auto//	-390.900 48	-390.815 03
TPSS/6-31G(d)/auto		
mPW1PW91/6-311G(2df,p)//	-390.756 28	-390.663 06
TPSS/6-31G(d)/auto		
<u>Silicon frame</u>		
TPSS/6-31G(d)/auto		
E	-9204.722 79	-2904.679 87
H_{298}	-2904.558 48	-2904.515 94
G_{298}	-2904.621 41	-2904.528 77
TPSS/6-311G(2df,p)/auto//	-2904.974 66	-2940.931 68
TPSS/6-31G(d)/auto		
mPW1PW91/6-311G(2df,p)//	-2904.846 14	-2904.799 50
TPSS/6-31G(d)/auto		

^a Units are E_h .

2. Get a copy of Mochida, K.; Matsuhida, N.; Sato, R.; Nakadaira, Y. *Organometallics* **2006**, 25, 4231.
- Scheme 2 (page 4232) shows the reaction for the thermolysis of **1** to benzene and singlet dimethylgermylene, Ge(Me)₂, and suggests a possible transition state (**3**). Determine whether **3** is really a transition state or whether it is a reactive intermediate (i.e., a high-energy minimum). A good first step might be first to optimize structures for **1**, benzene, and Ge(Me)₂, and then use structural information from those structures to construct a guess geometry for **3** and see if it can be successfully minimized. Symmetry, possibly from employing a Z matrix, might prove useful in speeding up calculations. Ultimately use B3LYP/6-31G* for final calculations, but initial calculations at a lower level of theory could prove useful at your discretion. Is **3** a TS or minimum? If **3** is a minimum, find the transition state structure between **1** and **3**.
 - Using whatever transition state you find, compare your calculated ΔH^\ddagger to the experimental value given in the paper (assume the temperature difference between default 298 K in Gaussian and the experiment is negligible). Use ΔG^\ddagger to calculate the unimolecular rate constant, k , at 305.3 K. Include the equation that you used to get the rate constant. Do your errors seem reasonable given the method and basis set used?
 - In the paper, it is mentioned that the progress of the reaction was followed via proton NMR, but the shifts that were observed are not described. Perform NMR calculations on all minima for this reaction (as single-point calculations on the geometries already optimized). Remember that NMR calculations require a much larger basis set in order to ensure accuracy. An appropriate basis set might be 6-311G(2df,p). A calculation of the TMS standard is also required, of course, in order to compute chemical shifts relative to the TMS protons (recall that a TMS example in glorious T_d symmetry is already helpfully available in your `templates` subdirectory). What shifts might an experimentalist use to evaluate if the reaction were to be proceeding? If **3** were to be present in sufficient concentration to observe its NMR spectrum, what peaks might one use to distinguish between **1** and **3**?
 - Assume that **3** is a reactive intermediate that can be isolated. If **3** were to be reduced by one electron, would that tend to make easier formation of the reactant (**1**) or the products (benzene and Ge(Me)₂)? Explain your rationale based on inspection of a relevant molecular orbital of **3**; do not do expensive calculations on the radical anion.
3. Here continues a problem that will carry over to the final exam. We add to the data at:

pollux.chem.umn.edu/8021/C4H6S02/

Your present task is to update your structure on the potential energy surface (PES) with a calculation at the B3LYP/6-31G* level (since there is no double slash, this implies re-optimizing the geometry). The most efficient way to do this will be to read in the force constants and geometry from your RHF frequency calculation (i.e., `fopt=(readfc) geom=checkpoint, guess=read`) as keywords. Nota bene: if you were using `fopt=ts` you will need to continue to use `ts`, of course. Once you have a reoptimized structure, do a new frequency calculation at the B3LYP/6-31G* level and update your entry with the relevant thermochemical data requested by the DFT submission form.

Finally, compute the B3LYP/6-31G* aqueous solvation free energies for your DFT structures using the PCM model in Gaussian03 (as single-point calculations on the DFT optimized geometries). When the calculations complete, add the solvation free energies to the website data. Report only one position after the decimal place for the solvation free energies in units of kcal/mol (the solvation free energy is the difference between what G03 reports as the “total free energy in solution: with all non electrostatic terms” and the electronic energy (*not* the free energy) of the optimized molecule in the gas phase).