This problem set provides you with only very general instructions for certain tasks. You are not merely encouraged but expected *to ask for advice/help as you need it. Of course, first you should* think *about things, but after that, talk to me, Casey, or a confident classmate.*

Some general reminders: To run a G03 job, your input file should be named `myfile.dat`. Issue the command `qg03 myfile.dat`, and the script will take care of the rest. If you absolutely cannot get a job to make progress with a 30-minute limit (I've tested almost all of them, and as long as you take advantage of symmetry they should finish easily in 30 minutes), you may submit jobs using `qg03 -t 2:00:00 myfile.dat` which will ask for 2 hours.

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.

Some quick notes/reminders with respect to Gaussian03:

1) 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.

2) 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.

3) Getting symmetry right will really help you on problem 1.

4) You may find it useful to read up on the keywords `nmr` and `td` in the online G03 manual (link from class website).

Information on using `cmo` and Chem-3D to visualize molecular orbitals:

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 with `vi` or `more` if you like) named `myfile.fchk`. Now type `~/chem01/bin/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* (if you just want one orbital you must list its number for both *n1* and *n2*). The script will create files *n1*.cub through *n2*.cub; once transferred to a PC/Mac (by ftp) and opened as Gaussian cube files in Chem-3D, you will have orbital pictures. 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.

1. Mixing $AgCN_2$ and $Ni(CO)_4$ in chloroform under a CO atmosphere, you isolate a solid precipitate that microanalysis and mass spectroscopy indicate to be $NiC_4N_2O_2$. A ^{13}C NMR spectrum of the precipitate in chloroform with $Ni(CO)_4$ added as an internal standard shows a strong peak 6.6 ppm upfield from $Ni(CO)_4$ and a much smaller peak 8.4 ppm upfield from $Ni(CO)_4$. There is also a very strong peak 84 ppm upfield from $Ni(CO)_4$. An IR spectrum of the precipitate in a KBr pellet shows a strong absorption at 2154 cm^{-1} and very weak absorptions/shoulders at 2143, 2170, and 2188 cm^{-1}.

    After three recrystallizations from diisopropyl ether, your solid is composed of beautifully twinned light orange crystals. NMR and IR spectra of the recrystallized solid show only the strong peaks noted above, and none of the weak ones.

An ultraviolet spectrum of the recrystallized solid in freon (who knew it would be soluble?) shows absorptions at 310 and 333 nm.

Here are the questions:

a. What is the structure of the molecules in the recrystallized solid? In a narrative fashion, describe in some detail how you came to your conclusion. Note that achieving 100% confidence can be very much more expensive than 99% confidence. It is perfectly OK to be satisfied with 99%.

b. To what electronic transitions do the two peaks in the UV spectrum correspond (show pictures of the orbitals)? Based on the nature of these transitions, how might you expect the geometries of the first and second excited states to differ from the ground state (don't do an excited-state geometry optimization, just infer from the orbitals).

2.   Here continues a problem that will carry over to the final exam. We add to the data at:

    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.

    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 that data.

    Finally, compute the B3LYP/6-31G* aqueous solvation free energy for your DFT structure using the CPCM model in Gaussian03 (as a single-point calculation on the DFT optimized geometry). When the calculation completes, add the solvation free energy to the website data. Report only one position after the decimal place for the solvation free energy in units of kcal/mol (the solvation free energy is the difference between the total energy in solution and in the gas phase).