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.

A practical reminder: To run a job, your input file should be called **myfile.dat**. Simply issue the command **rung98 myfile.dat** and the script 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 load leveler queue on the sp, the command is **llq**; you may find **llq | egrep chem##** (where chem## is your userid) to be more convenient.

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 Gaussian94:

1) Always include the keyword: **scf=direct**.

2) Always specify **freq=noraman** for frequency calculations.

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, noraman)**. The other keywords request calculation of analytic force constants on the first step, that the job not die if you have more than one imaginary frequency (or have none), and that the force constant calculation be efficient, respectively.

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, 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!**

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)`. 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.   All alone one night in the lab, you pull a bottle of $C_{10}H_8$ off the shelf. It is oh-so-helpfully labeled "either naphthalene or difulvene" Unsatisfied with this uncertainty, you take an NMR spectrum and determine the ^{13}C chemical shifts to be 125.8, 127.8, and 133.1 ppm (relative to tetramethylsilane (TMS)). Note that the number and splitting pattern (not discussed here) of the peaks is *not* enough to distinguish between the hydrocarbon isomers.

naphthalene   difulvene
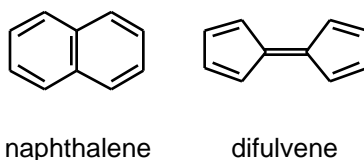
The network is down (no searching the Web) but your computer is working, so you decide to compute the NMR shifts for each possible compound and compare to your measurement. Since NMR calculations provide *absolute* isotropic chemical shifts, you will also need to do a calculation on TMS. To what point groups do TMS and each of the two hydrocarbons belong? *In order to complete this problem efficiently, you will absolutely need to ensure that you are providing the appropriate symmetry in your input geometries for all calculations!* Optimize all of the chemical structures at the HF/6-31G* level (as noted above, it may be more efficient to *start* with a smaller basis set, say STO-3G, to verify that you have the right symmetry and a decent starting geometry and force constants prior to doing the larger basis calculations). Now, compute the NMR shielding of ^{13}C in TMS at this level (the keyword required is simply **nmr**); what is the absolute isotropic shielding for this nucleus in ppm? Next, compute the isotropic shieldings of the unique ^{13}C nuclei in each of the two hydrocarbons at the same level (i.e., HF/6-31G* at the HF/6-31G* optimized geometries). Report these chemical shifts relative to TMS (which defines zero on the   ppm scale for both nuclei). Which hydrocarbon is in the bottle? Explain why you consider your choice to be correct.

Thermochemical data for difulvene are not available. However, experimental enthalpies of formation *are* available for benzene and fulvene (isomeric C_6H_6 analogs). What is the experimental difference in enthalpy between these two species at 298 K? What is the difference in energy between naphthalene and difulvene at the HF/6-31G* level (note: 1 E_h = 627.51 kcal/mol)? Is this consistent with the experimental difference for the smaller hydrocarbons? Why or why not? Compute the same energy difference for naphthalene and difulvene at the MP2/6-31G*//HF/6-31G* level. What do you conclude from comparing the HF difference to the MP2 difference?

2.   Find the UV spectrum of quinone on the NIST website. There are 3 absorptions. Assuming each is well described as a single excitation (i.e., $a \rightarrow b$ where a is the occupied orbital from which the electron comes and b is the virtual orbital to which it goes) sketch a and b for each of the 3 absorptions.
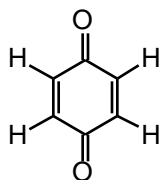
quinone

To do this, first optimize the structure of quinone at the RHF/6-31G* level (what point group should you take advantage of?). Then use the keyword line: `cis(n=4)/6-31G* guess=read geom=checkpoint pop=regular` in a new input file. This will give you the excited state absorptions and oscillator strengths (using the cis formalism) and the MO coefficients. The CIS output includes a vector that describes the nature of each excited state in terms of contributions of different $a \rightarrow b$ possibilities. You need only worry about the largest contribution for each of these vectors. Instructions for how to generate a sketch of the MO's appears as an appendix to this problem set. Remember that CIS always *overestimates* the energy required to reach the excited state. You may also assume that the first two transitions overlap in the experimental spectrum and cannot be separately identified.

Are the computed oscillator strengths consistent with the observed spectrum? Explain your answer.

Finally, use Koopmans' theorem to predict the ionization potential of quinone at the HF/6-31G* level. How does this compare with the experimental value?

3. Here begins a problem that will carry over to the third problem set and ultimately the final exam. Take a look at

> `http://pollux.chem.umn.edu/~kormos/8021/ProbSets-Exams/2000/C3H4N2O2/`

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

While there, select `View Surface`. You will see my contribution to mapping the $C_3H_4N_2O_2$ surface (click on `cramer.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). I found a [3+2] cycloaddition transition state for acetylene and *N*-nitrosomethylidene nitrone.

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.

Appendix

To sketch a molecular orbital, you need to adopt a convention for where you put the shading in s and p orbitals for positive coefficients (consistency is all that matters), and you need to add all of the basis set orbitals together according to their coefficients in that MO, and you need to make sure that you have the cartesian coordinates for the molecule so you know how the p orbitals relate to the atomic positions. [Modern programs will do all of this for you with glitzy graphics, but doing it by hand once or twice is good for the soul and provides more insight into what's going on.] We'll do water as a terrifically simple example.

Water molecule, minimum energy geometry:

1	O	0.00000	0.00000	0.00000
2	H	0.59492	0.75494	0.00000
3	H	0.59492	-0.75494	0.00000

so, the coordinate axes can be viewed as:

+ z direction
+ y direction
+ x direction

H2
O1
H3
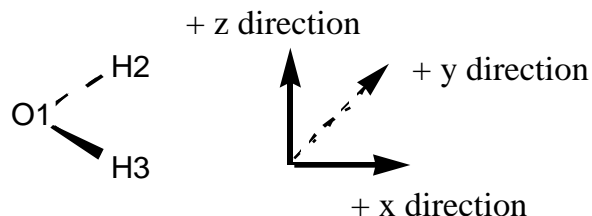
I'll use the convention that whenever I see a p orbital with a positive coefficient, that means the shaded lobe should point in the positive cartesian direction, and that a positive s is also shaded.

Here are the vectors for water's 4 occupied orbitals from an AM1 calculation. Since you are using a split valence basis set (6-31G*) just pretend that you can add the functions labeled 2 and 3 (s or p) in your output together. Also, don't go crazy with all the tiny coefficients! I just want *qualitative* MO sketches. Find the *bigger* coefficients and use them, but you can ignore the little ones.

ROOT NO.		1	2	3	4
		-36.10883	-17.92790	-14.55189	-12.01203
S 0	1	-0.89339	0.00000	-0.36499	0.00000
PX 0	1	-0.15803	0.00000	0.80115	0.00000
PY 0	1	0.00000	-0.77017	0.00000	0.00000
PZ 0	1	0.00000	0.00000	0.00000	-1.00000
S H	2	-0.29740	-0.45102	0.33536	0.00000
S H	3	-0.29740	0.45102	0.33536	0.00000

The first number is the energy of the orbital (in eV) — it gives a quite reasonable estimate of the ionization potential from this orbital (that results is called Koopmans' theorem). That energy is sometimes called the "eigenvalue" of the MO (which is itself an "eigenvector" of the secular matrix).
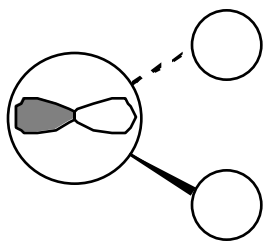
So, to sketch orbital one, I take a non-shaded s orbital (the coefficient is *negative*, and my convention is that *positive* is shaded) with a *big* weight. I add a little bit of a p_x orbital (small coefficient) and I put the shaded part pointing to the *negative* x direction (my convention is that if the coefficient is positive, I put the shaded part in the positive direction, but this coefficient is negative). I then add some non-shaded s orbitals on each H with moderate weight. The pieces are shown at right, the *sum* (which just involves adding the oxygen orbitals together) is:
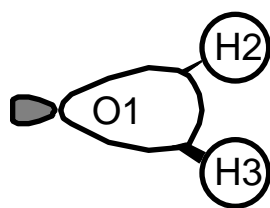
This is the lowest energy (valence) orbital for water, and properly has the same symmetry as the molecule (C_{2v}). The others can be similarly constructed. The resulting MO diagram after doing this for all the other orbitals too is shown below. Note, for instance, that water itself has two distinct lone pairs, one in plane, and one out of plane of higher energy. This is confirmed by photoelectron spectroscopy, and reflects one of the most annoying lies undergraduates are told (i.e., water has two identical sp^3 lone pairs).