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.a02` 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 -s lustre myfile.com` and the script will submit a 5 hour job to the batch queue to run on one 8-processor node using the lustre filesystem 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 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,noeigentest)`. 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 (`noeigentest`).

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. This will be especially true for Problem #3.

   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.

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

1.   In class, we went through Hückel theory as applied to the allyl cation in considerable detail (following the textbook). Consider now 1,2- and 1,3-diazacyclobutadiene, where we have

gone to a 4-membered ring system, and we have replaced two C–H fragments with isoelectronic N atoms: (each having an in-plane lone pair).

1,2-diaza-
cyclobutadiene

1,3-diaza-
cyclobutadiene
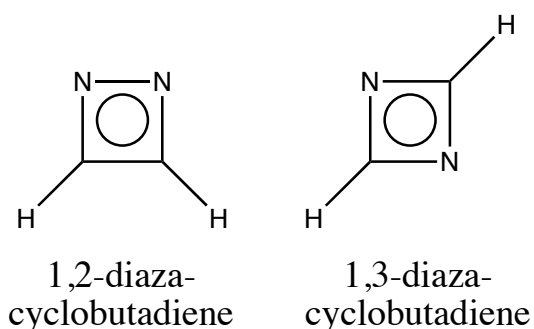
Here are a few experimental facts that you may find useful: (i) the ionization potential of the methyl radical is 9.9 eV, (ii) the ionization potential of the amidogen radical is 10.8 eV, (iii) the rotational barrier of ethylene is 60 kcal/mol, (iv) the rotational barrier of formaldimine is 60 kcal/mol. Now, some tasks/questions: Solve for the orbital energies and coefficients in the 1,3-diazabutadiene system. What qualitative difference is there compared to the all-carbon cyclobutadiene system? Carry out AM1 calculations for the 1,3-diazabutadiene system and visualize the π orbitals. Are they consistent with your Hückel theory predictions? How does the AM1 HOMO-LUMO separation compare to that predicted by Hückel theory? Rationalize any significant difference. Finally, what is the secular equation for 1,2-diazabutadiene? What makes it intractable? Forget about Hückel theory and look at the AM1 computed π orbitals; rationalize differences with the 1,3-diazabutadiene case.

2.   In Problem Set 1, we computed MM3 energies for four conformations of Z-cyclooctene. We will now compare the force field predictions to various levels of molecular orbital theory. Thus, for each of the four conformations, compute relative energies at the following levels and summarize your results: AM1, PM3, PM6, HF/6-31G(d), HF/6-31G(d), CCSD(T)/6-31G(d)//HF/6-31G(d), MP2/6-311G(2df,2p)//HF/6-31G(d), and finally MP2/6-31G(d) (no double slash…) Comment on variations between the models and any interesting price/performance issues. At the HF/6-31G(d) level, compute frequencies and thermal contributions to enthalpy and free energy therefrom. By how much do these thermal contributions cause ΔH and ΔG to differ from ΔE? Given your various data, how might you define an optimal *composite* estimate of computed enthalpy (hint: the CCSD(T) output includes some intermediate results that may be useful)? How do the most expensive models compare with the (really, really fast) force field?

Note that while it is usually a good idea to use information from a lower level of theory to make more efficient a subsequent calculation, this is *not* true if the lower level of theory is ill suited to the problem. Thus, if you plan to read geometries or wave functions from

checkpoint files for this exercise, you should first visualize the structures to ensure that they have not deviated enormously from the MM3 reference structures.

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/PES/

While there, select View Surface. You will see my contributions to detailing the energetics of select stationary points on various potential energy surfaces (click on ##.html, where ## refers to the list at the end of this problem set, to see them in 3D—you'll also see text cartesian coordinates, which you can also visualize by pasting the coordinates into a Gaussian 09 input file and using GaussView). My stationary points are for a variety of minima and transition-state structures, and include more data than you will generate in *this* problem set, but you ultimately will create entries equivalent to my own.

Your task is to find two stationary points of your own—both a minimum and a transition-state structure—taken from the table starting on the next page. *You will receive by email the numbers of your two structures, which will be assigned randomly.* To complete each entry, you will need a frequency calculation at the HF 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* following the instructions on the form; here, for example, is a correctly formatted copy ready to be pasted:

1	24	0	−0.064962	−0.034883	−0.096630
2	6	0	−1.141129	1.696746	−0.284156
3	6	0	−1.704425	−1.219553	−0.075460
4	6	0	−0.309697	−0.105930	−2.000636
5	6	0	2.247794	1.302449	0.456239
6	6	0	2.107300	1.423400	−0.863351
7	1	0	2.879366	0.545440	0.886439
8	1	0	1.845197	2.033939	1.133979
9	1	0	1.572343	2.243740	−1.303743
10	1	0	2.593114	0.756824	−1.548461
11	6	0	−0.078791	0.023111	2.023115
12	8	0	−0.120268	0.001756	3.135913
13	8	0	−2.637648	−1.824964	−0.203096
14	8	0	−1.744877	2.600319	−0.549794
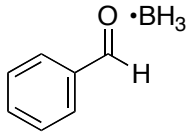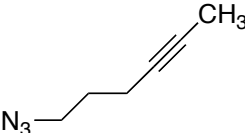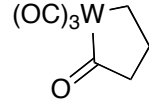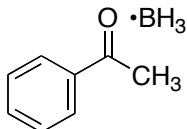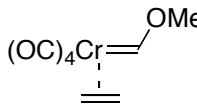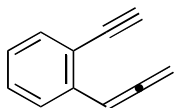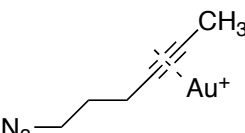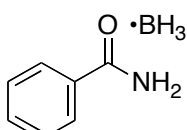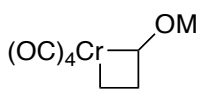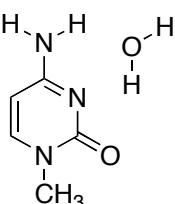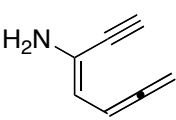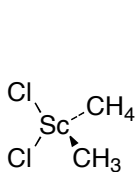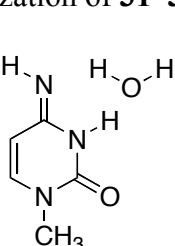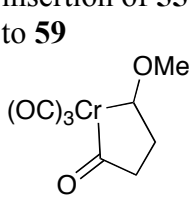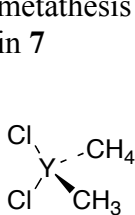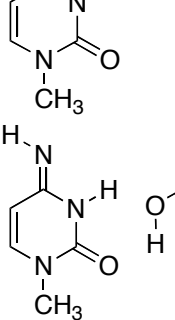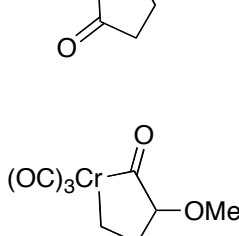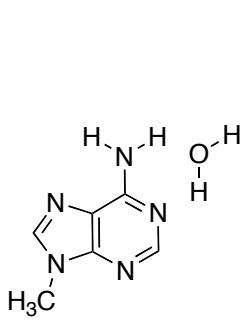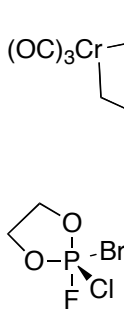
15	6	0	1.211517	−1.645996	−0.290967
16	8	0	1.949469	−2.443506	−0.553117
17	1	0	−0.611209	−0.985150	−2.572495
18	1	0	−0.288539	0.728182	−2.704543
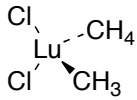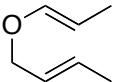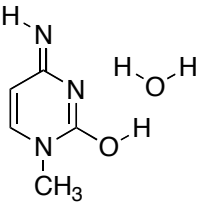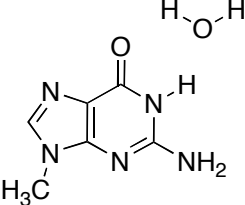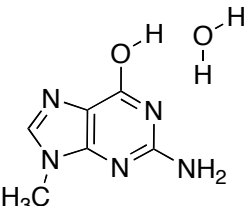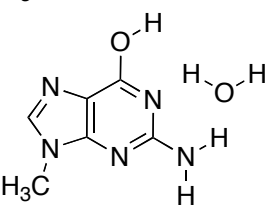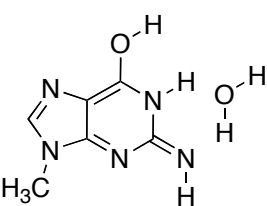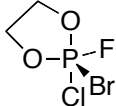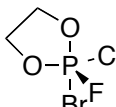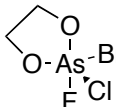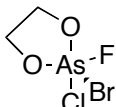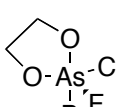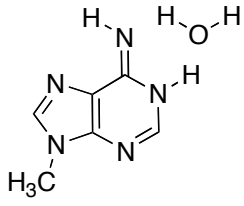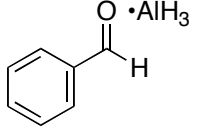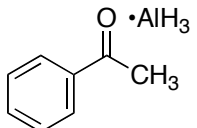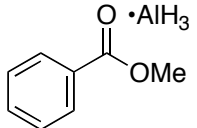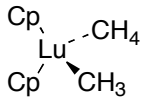
of course, you'll need to vi or more the output file (the *end* of the output file) to copy the optimized coordinates). **Please note that your copy/paste *must* include the spaces preceding the "1" in the first line, or else the first line comes in corrupted.** If you make any mistakes and fail to realize until after submission, contact me with the details and I will fix the website.

With respect to basis set, we will use the 6-31G(d) basis set for all atoms for which it is defined (H–Kr). If you have a molecule with an atom that is *not* defined in the 6-31G(d) basis (e.g., lutetium), then you should use the SDD basis set and associated pseudopotentials for those atoms, and 6-31G(d) for all the rest (see the *Gaussian 09* documentation for use of the gen basis set keyword). Note that you may find it more efficient to *start* looking for stationary points with a smaller basis set, and then finish with the larger one, but that is up to you.

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 congeners to learn more about the chemistry of the surfaces.

Class molecules:

01		**26**	Click [3+2] TS for **25**	**51**	TS for carbonyl insertion of **50**	**76**	Myers-Saito TS for **75**
02	TS for addn of BH₃ to C=O of **1**	**27**		**52**		**77**	Schmittel TS for **75**
03		**28**	Click [3+2] TS for **27**	**53**		**78**	
04	TS for addn of BH₃ to C=O of **3**	**29**		**54**	TS for [2+2] of **53**	**79**	Myers-Saito TS for **78**
05		**30**	Click [3+2] TS for **29**	**55**		**80**	Schmittel TS for **78**
06	TS for addn of BH₃ to C=O of **5**	**31**		**56**	TS for carbonyl insertion of **55** to **58**	**81**	
07		**32**	TS for tautomer-ization of **31**–**33**	**57**	TS for carbonyl insertion of **55** to **59**	**82**	Myers-Saito TS for **81**
08	TS for symmetric CH bond metathesis in **7**	**33**		**58**		**83**	Schmittel TS for **81**
09		**34**		**59**		**84**	
10	TS for symmetric CH bond metathesis in **9**	**35**	TS for tautomer-ization of **34**–**36**	**60**		**85**	TS for tautomer-ization of **84**–**86**

11

12 TS for symmetric CH bond metathesis in **11**

13

14 [3,3] sigmatropic shift chair TS of **13**

15 [3,3] sigmatropic shift boat TS of **13**

16

17 [3,3] sigmatropic shift chair TS of **16**

18 [3,3] sigmatropic shift boat TS of **16**

19

20 [3,3] sigmatropic shift chair TS of **19**

21 [3,3] sigmatropic shift boat TS of

36

37

38 TS for tautomerization of **37–39**

39

40

41 TS for tautomerization of **40–42**

42

43 $(OC)_4Cr=$

44 TS for [2+2] of **43**

45 $(OC)_4Cr$

46 TS for carbonyl insertion of **45**

61 pseudorotation TS **60→62**

62

63 pseudorotation TS **62→64**

64

65 pseudorotation TS **64→60**

66

67 pseudorotation TS **66→68**

68

69 pseudorotation TS **68→70**

70

71 pseudorotation TS **70→66**

86

87

88 TS for addn of AlH_3 to C=O of **87**

89

90 TS for addn of AlH_3 to C=O of **89**

91

92 TS for addn of AlH_3 to C=O of **91**

93

94 TS for symmetric CH bond metathesis in **93**

19

22	OMe structure	**47**	(OC)$_3$Cr structure	**72**	structure
23	[3,3] sigmatropic shift chair TS of **22**	**48**	(OC)$_4$W= structure	**73**	Myers-Saito TS for **72**
24	[3,3] sigmatropic shift boat TS of **22**	**49**	TS for [2+2] of **48**	**74**	Schmittel TS for **72**
25	N$_3$ structure with H	**50**	(OC)$_4$W structure	**75**	structure