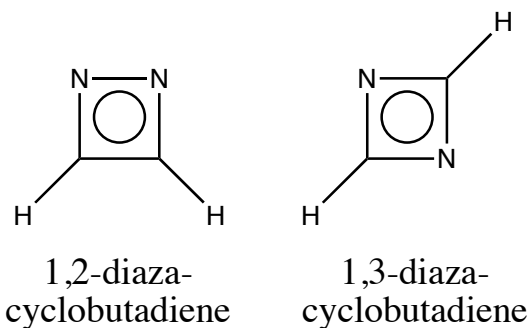1.   In class, we went through Hückel theory as applied to the allyl cation in considerable detail (following the textbook). Consider now 1,2- and 1,3-diazacyclobutadiene, where we have gone to a 4-membered ring system, and we have replaced two C–H fragments with isoelectronic N atoms: (each having an 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.

      Including an N atom in Hückel theory requires us to do several things. First, we must decide what basis function to put on the N atoms; a $2p_z$ orbital seems obvious (just like for a C atom). Next, we need to define overlap matrix elements involving this orbital with others; using the same **S** = **1** approximation as with all-C Hückel theory seems sensible. Finally, we need to know H_{ii} and H_{ij} for all combinations of N and C atoms as atoms i and j. By analogy to the all-C theory, we should make the H_{ii} value equal to the negative of the ionization potential (IP) of the corresponding mono-N species, which in this case is the amidogen radical, $NH_2 \cdot$. Since the −IP of the methyl radical defines α, the data above suggest that we should use roughly 1.1α for H_{ii} when i refers to an N atom.

As for nearest neighbor interactions, since data suggest that the rotational barrier about $H_2C=NH$ is equal to that for $H_2C=CH_2$, we can evidently continue to use β for both H_{CC} and H_{CN} values; we can call the N–N interaction (that occurs in the 1,2-isomer) δ, but we aren't given any experimental information about its possible value.

With all these definitions, for 1,3-diazacyclobutadiene the secular equation $|\mathbf{H} - E\mathbf{S}| = 0$ becomes

$$\begin{vmatrix} 1.1\alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & 1.1\alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad (1)$$

Expanding this determinant requires the use of minors, leading to

$$(1.1\alpha - E) \bullet \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & 1.1\alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} - \beta \bullet \begin{vmatrix} \beta & \beta & 0 \\ 0 & 1.1\alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} + 0 - \beta \bullet \begin{vmatrix} \beta & \alpha - E & \beta \\ 0 & \beta & 1.1\alpha - E \\ \beta & 0 & \beta \end{vmatrix} = 0 \quad (2)$$

Continuing, using Cramer's rule

$$\begin{aligned} &(1.1\alpha - E)\left[(\alpha - E)^2(1.1\alpha - E) + 0 + 0 - 0 - \beta^2(\alpha - E) - \beta^2(\alpha - E) \right] \\ &\quad - \beta \bullet \left[\beta(\alpha - E)(1.1\alpha - E) + \beta^3 + 0 - 0 - \beta^3 - 0 \right] \\ &\quad + 0 \\ &\quad - \beta \bullet \left[\beta^3 + \beta(\alpha - E)(1.1\alpha - E) + 0 - \beta^3 - 0 - 0 \right] = 0 \end{aligned} \qquad (3)$$

Now expanding and collecting terms

$$(\alpha - E)^2(1.1\alpha - E)^2 - 4\beta^2(\alpha - E)(1.1\alpha - E) = 0 \qquad (4)$$

Two roots for this equation are clearly $E = \alpha$ and $E = 1.1\alpha$. Factoring these out from eq. 4, we have

$$(\alpha - E)(1.1\alpha - E) - 4\beta^2 = 0 \qquad (5)$$

This is a quadratic in E, which may be more easily solved by expanding to

$$E^2 - 2.1\alpha E + 1.1\alpha^2 - 4\beta^2 = 0 \tag{6}$$

which has solutions

$$
\begin{aligned}
E &= \frac{2.1\alpha \pm \sqrt{4.41\alpha^2 - 4(1.1\alpha^2 - 4\beta^2)}}{2} \\
&= \frac{2.1\alpha \pm \sqrt{16\beta^2 + 0.01\alpha^2}}{2} \\
&\approx 1.05\alpha \pm 2\beta
\end{aligned}
\tag{7}
$$

The final simplification is adequate for qualitative purposes (the term involving α in the square root changes the value of the square root by about 2%). If we really wanted quantitative accuracy, we could always plug back in the true energy values for α and β, but I'll focus here more on the qualitative aspects. Thus, the 4 roots, from lowest to highest (remember that α and β are negative quantities) are $1.05\alpha + 2\beta$, $1.1\,\alpha$, α, and $1.05\alpha - 2\beta$.

Now, with those 4 values of E as roots for the secular equation, we can determine molecular orbital coefficients. Let's do the lowest-energy case first. The relevant system of linear equations is

$$
\begin{aligned}
a_1[1.1\alpha - (1.05\alpha + 2\beta) \bullet 1] + a_2[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_3[0 - (1.05\alpha + 2\beta) \bullet 0] + a_4[\beta - (1.05\alpha + 2\beta) \bullet 0] &= 0 \\
a_1[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_2[\alpha - (1.05\alpha + 2\beta) \bullet 1] + a_3[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_4[0 - (1.05\alpha + 2\beta) \bullet 0] &= 0 \\
a_1[0 - (1.05\alpha + 2\beta) \bullet 0] + a_2[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_3[1.1\alpha - (1.05\alpha + 2\beta) \bullet 1] + a_4[\beta - (1.05\alpha + 2\beta) \bullet 0] &= 0 \\
a_1[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_2[0 - (1.05\alpha + 2\beta) \bullet 0] + a_3[\beta - (1.05\alpha + 2\beta) \bullet 0] + a_4[\alpha - (1.05\alpha + 2\beta) \bullet 1] &= 0
\end{aligned}
\tag{8}
$$

A *little* ugly. Let's simplify.

$$
\begin{aligned}
a_1(0.05\alpha - 2\beta) + a_2\beta + a_4\beta &= 0 \\
a_1\beta + a_2(-0.05\alpha - 2\beta) + a_3\beta &= 0 \\
a_2\beta + a_3(0.05\alpha - 2\beta) + a_4\beta &= 0 \\
a_1\beta + a_3\beta + a_4(-0.05\alpha - 2\beta) &= 0
\end{aligned}
\tag{9}
$$

Subtraction of the 4th equation from the 2nd gives

(10)

$$a_2\left(-0.05\alpha - 2\beta\right) - a_4\left(-0.05\alpha - 2\beta\right) = 0$$

which establishes that $a_2 = a_4$. A similar subtraction of the 3rd equation from the 1st establishes that $a_1 = a_3$. Knowing that, one can then write the 1st equation as

$$a_1\left(0.05\alpha - 2\beta\right) + 2a_2\beta = 0$$

(11)

In which case we know the ratio of a_1 and a_2 as

$$\frac{a_1}{a_2} = -\frac{2\beta}{\left(0.05\alpha - 2\beta\right)} = \frac{2\beta}{\left(2\beta - 0.05\alpha\right)}$$

(12)

Since α is a negative number, the denominator in eq. 12 is larger than the numerator, which means that a_1 is a bit less than a_2; plugging in values (β = 30 kcal/mol and α = 228.3 kcal/mol), we obtain $a_1 = 1.23\, a_2$ (and so $a_3 = 1.23\, a_4$). Now, applying the normalization constraint

$$\sum_{i=1}^{4} a_i^2 = 1 \quad \Rightarrow \quad a_1^2 + (1.23)^2 a_1^2 + a_1^2 + (1.23)^2 a_1^2 = 1$$

$$\Rightarrow \quad a_1 = 0.45, a_2 = 0.55, a_3 = 0.45, a_4 = 0.55$$

(13)

Thus, the amplitude at the N atoms is *increased* in the lowest energy orbital compared to the C atoms. This result is as we would expect noting that the N is more electronegative than C (that's why its –IP parameter is 10% larger than C).

Now for the *second* orbital, with energy determined above as E = 1.1α. The system of linear equations becomes

$$a_1\left[1.1\alpha - 1.1\alpha \bullet 1\right] + a_2\left[\beta - 1.1\alpha \bullet 0\right] + a_3\left[0 - 1.1\alpha \bullet 0\right] + a_4\left[\beta - 1.1\alpha \bullet 0\right] = 0$$

$$a_1\left[\beta - 1.1\alpha \bullet 0\right] + a_2\left[\alpha - 1.1\alpha \bullet 1\right] + a_3\left[\beta - 1.1\alpha \bullet 0\right] + a_4\left[0 - 1.1\alpha \bullet 0\right] = 0$$

$$a_1\left[0 - 1.1\alpha \bullet 0\right] + a_2\left[\beta - 1.1\alpha \bullet 0\right] + a_3\left[1.1\alpha - 1.1\alpha \bullet 1\right] + a_4\left[\beta - 1.1\alpha \bullet 0\right] = 0$$

$$a_1\left[\beta - 1.1\alpha \bullet 0\right] + a_2\left[0 - 1.1\alpha \bullet 0\right] + a_3\left[\beta - 1.1\alpha \bullet 0\right] + a_4\left[\alpha - 1.1\alpha \bullet 1\right] = 0$$

(14)

which simplifies nicely to

$$a_2\beta + a_4\beta = 0$$
$$a_1\beta + a_2(-0.1\alpha) + a_3\beta = 0 \tag{15}$$
$$a_2\beta + a_4\beta = 0$$
$$a_1\beta + a_3\beta + a_4(-0.1\alpha) = 0$$

Note that the 1st and 3rd equations imply $a_2 = -a_4$. But, subtraction of the 4th equation from the 2nd equation implies $a_2 = a_4$. These two equations can be satisfied only if $a_2 = a_4 = 0$. In that case, the 2nd and 4th equations require that $a_1 = -a_3$. Normalization requires that $a_1 = 0.71$ and $a_3 = -0.71$.

While the algebra is not shown here, solving for the 3rd MO will go much like the first, except that positions are reversed for the orbital. Thus, $a_1 = a_3 = 0$ and $a_2 = 0.71$ and $a_4 = -0.71$. The highest energy MO will lead to a relationship just like that in eq. 12 but with a "+" 0.05α in the denominator instead of minus. Thus, the coefficients end up reversed compared to MO1: the contribution of N to π_4 orbital is diminished (which is necessary, actually, to balance for its *enhanced* contribution to π_1). Looking at the AM1 orbitals for this system in GaussView, one sees:

π_3 π_4

π_1 π_2
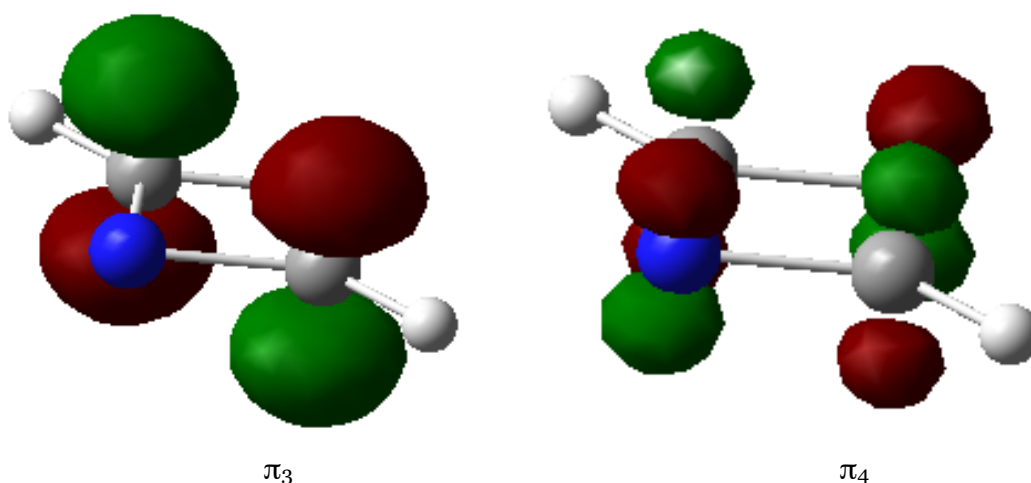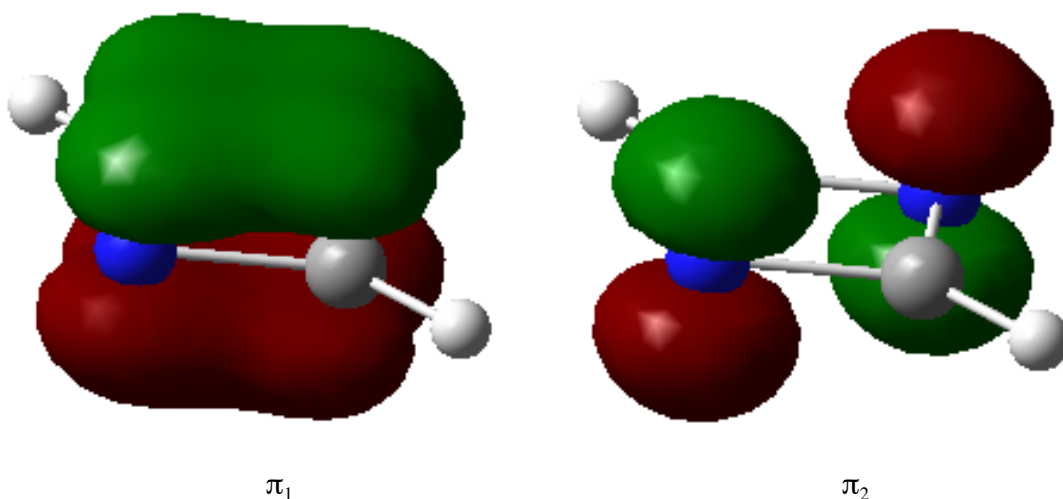
which agrees perfectly with Hückel theory for orbitals 2 and 3, and it's difficult to say for orbitals 1 and 4, since the amplitudes differ by small margins, but things mostly seem OK (inspection of MO coefficients in the AM1 output shows that they are 0.51 and 0.49 where with Hückel theory we predicted 0.55 and 0.45— pretty close). The AM1 HOMO-LUMO gap is about 0.27 a.u. Hückel theory says the gap should be 0.1α, or about 1 eV, which is about 0.04 a.u. So, why is the gap so small with Hückel theory compared to the calculation? The issue is that in HF theory the virtual orbital energy is an estimate of the electron affinity — i.e., the energy of the orbital if another electron were to be added to make an anion. That's quite different than the energies for MOs with the same number of electrons. The energy between the S_0 ground state and the S_1 excited state might be much closer to the Hückel theory difference, since that involves moving an electron from π_2 to π_3 and costs the energy difference between the two orbitals; sure enough, the $S_1 - S_0$ difference is computed to be 0.0918 eV (very close to 0.1 eV) at the CIS level, but we haven't discussed the CIS level yet, so that will not be included in grading.

Now, let's turn to 1,2-diazacyclobutadiene. With all the above definitions, the secular equation $|\ \mathbf{H} - E\mathbf{S}\ | = 0$ is

$$\begin{vmatrix} 1.1\alpha - E & \delta & 0 & \beta \\ \delta & 1.1\alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{16}$$

Expanding this determinant requires the use of minors, leading to

$$(1.1\alpha - E) \bullet \begin{vmatrix} 1.1\alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} - \delta \bullet \begin{vmatrix} \delta & \beta & 0 \\ 0 & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} + 0 - \beta \bullet \begin{vmatrix} \delta & 1.1\alpha - E & \beta \\ 0 & \beta & \alpha - E \\ \beta & 0 & \beta \end{vmatrix} = 0 \quad (17)$$
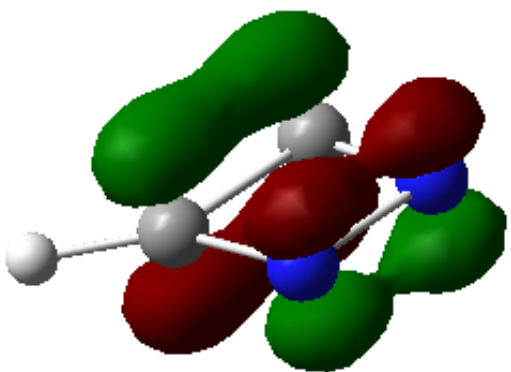
Continuing, using Cramer's rule

$$
\begin{aligned}
& (1.1\alpha - E)\left[(1.1\alpha - E)(\alpha - E)^2 + 0 + 0 - 0 - \beta^2(1.1\alpha - E) - \beta^2(\alpha - E)\right] \\
& - \delta \bullet \left[\delta(\alpha - E)^2 + \beta^3 + 0 - 0 - \beta^2\delta - 0\right] \\
& + 0 \\
& - \beta \bullet \left[\beta^2\delta + \beta(\alpha - E)(1.1\alpha - E) + 0 - \beta^3 - 0 - 0\right] = 0
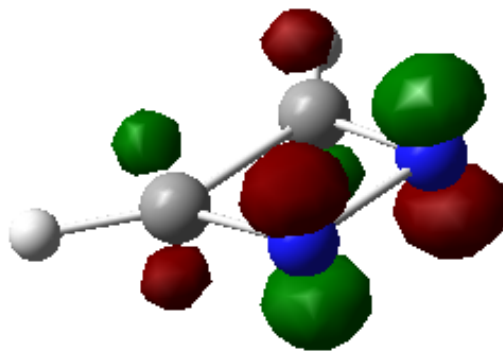\end{aligned}
\quad (18)
$$

Now expanding and collecting terms

$$
\begin{aligned}
& (\alpha - E)^2(1.1\alpha - E)^2 - \beta^2(1.1\alpha - E)^2 - 2\beta^2(\alpha - E)(1.1\alpha - E) \\
& - \delta^2(\alpha - E)^2 - 2\delta\beta^3 + \delta^2\beta^2 + \beta^4 = 0
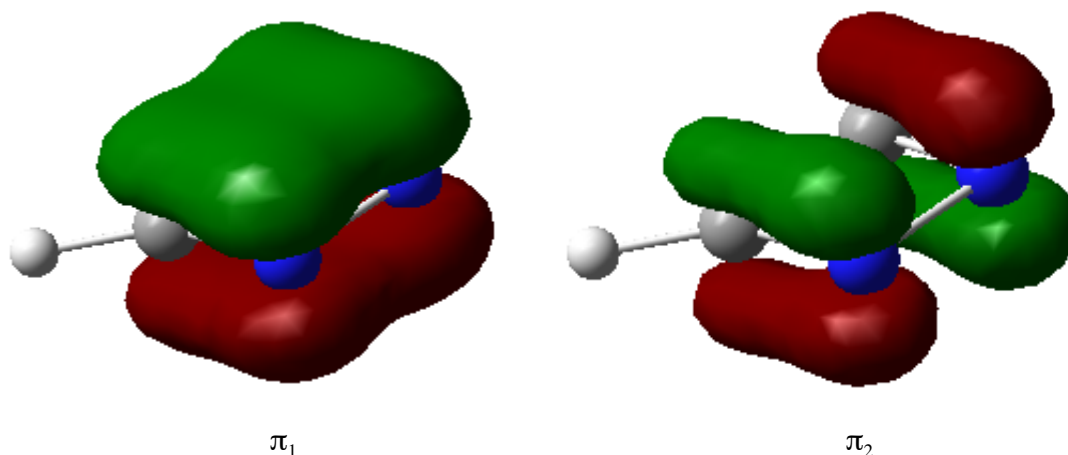\end{aligned}
\quad (19)
$$

Yuck!! Glad we get to punt and do the calculation with AM1. The orbitals are

π_3 π_4

$$\pi_1 \qquad\qquad\qquad\qquad \pi_2$$

Based on the computed orbitals, it appears that 2 C=N bonds are stronger than 1 C=C and 1 N=N bonds (as π_2 is lower in energy than π_3). The HOMO-LUMO gap here is predicted to be 0.35 a.u.—larger than for the 1,3-isomer. Without plugging in a lot of numbers into eq. 19 and solving a complex quartic equation, it's hard to evaluate this quantity using Hückely theory for this system.

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 unexpectedly deviated enormously from the MM3 reference structures.

The following table has results computed at various levels of electronic structure theory. Because the semiempirical levels are quite bad at maintaining the rough

structures predicted by MM3, I started the AM1, PM3, PM6, and HF calculations from the MM3 structures. For the MP2 optimization, I began from the HF structures.

Table 1. Electronic or thermal energies (a.u.) computed for *Z*-cyclooctene isomers.

	Conformer 1	Conformer 2	Conformer 3	Conformer 4
AM1	-0.029 10	-0.024 29	-0.025 87	-0.025 33
PM3	-0.015 90	-0.012 40	-0.012 99	-0.011 34
PM6	-0.015 99	-0.012 63	-0.013 35	-0.012 67
HF/6-31G(d)	-311.074 69	-311.071 43	-311.069 55	-311.064 13
ΔH_{298}	0.227 36	0.227 61	0.227 52	0.227 46
ΔG_{298}	0.188 17	0.188 13	0.187 74	0.186 92
MP2/6-31G(d)// HF/6-31G(d)	-312.111 89	-312.108 30	-312.105 12	-312.100 41
CCSD(T)/6-31G(d)// HF/6-31G(d)	-312.234 82	-312.231 55	-312.228 72	-312.224 14
MP2/6-311G(2df,2p)// HF/6-31G(d)	-312.506 19	-312.502 86	-312.499 60	-312.494 68
MP2/6-31G(d)	-312.113 98	-312.110 33	-312.107 11	-312.102 58
Composite H_{298}	-312.403 84	-312.400 55	-312.397 67	-312.393 11
Composite G_{298}	-312.443 03	-312.440 02	-312.437 45	-312.433 65

where, the composite values are computed as

$$
\begin{aligned}
X_{comp} = &\ \text{CCSD(T)/6-31G(d)//HF/6-31G(d)} \\
&+ \left[\text{MP2/6-311G(2df,2p)//HF/6-31G(d)} - \text{MP2/6-31G(d)//HF/6-31G(d)}\right] \quad \text{basis set incompleteness} \quad (20)\\
&+ \left[\text{MP2/6-31G(d)} - \text{MP2/6-31G(d)//HF/6-31G(d)}\right] \quad \text{geometry optimization} \\
&+ \Delta X \quad X \text{ is } H \text{ or } G
\end{aligned}
$$

and, now, in terms of relative energy

Table 2. Energies (kcal/mol) computed for *Z*-cyclooctene isomers relative to conformer 1.

	Conformer 1	Conformer 2	Conformer 3	Conformer 4
AM1	0.0	3.0	2.0	2.4
PM3	0.0	2.2	1.8	2.9
PM6	0.0	2.1	1.7	2.1

HF/6-31G(d)	0.0	2.0	3.2	6.6
ΔH	0.0	0.2	0.1	0.1
ΔG	0.0	0.0	-0.3	-0.8
MP2/6-31G(d)// HF/6-31G(d)	0.0	2.3	4.3	7.2
CCSD(T)/6-31G(d)// HF/6-31G(d)	0.0	2.1	3.8	6.7
MP2/6-311G(2df,2p)// HF/6-31G(d)	0.0	2.1	4.1	7.2
MP2/6-31G(d)	0.0	2.3	4.3	7.2
Composite H	0.0	2.1	3.9	6.7
Composite G	0.0	1.9	3.5	5.9
MM3	0.0	1.6	3.5	7.0

Without going into enormous detail, the semiempirical levels are obviously howlingly bad for this conformational analysis, and if anything PM6 is worse than PM3 (disappointing). Perhaps surprisingly, HF/6-31G(d) is as accurate as any of the more complete models, although composite H_{298} is arguably the most physical approach, and thus would be viewed with much more confidence in the absence of knowing the right answer. Note, of course, that MM3 costs pretty much zero and works wonderfully.

The thermal contributions to enthalpy don't vary much over the different conformers, but there is a significant entropy (and thus free energy) gain predicted for conformer 4. This conformer has its two lowest frequency normal modes (torsions) at lower energy than the other conformers, and this increases its partition function accordingly.

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/

    Full credit for this problem simply consists of entering sensible data.