

# Problem Set 4

CHEM 26800/36800 and MENG 25510/35510

Due May 09, 2024

## 1 Exploration of Single Reference and Electron Correlation

1. (5 points) Lets start with a simple geometry optimization of neutral methanol. What should the spin multiplicity be for ground-state methanol? Given the following starting structure (in xyz form), optimize methanol at the RHF/3-21G level of theory. Perform a frequency calculation for the optimized structure and report the vibrational frequencies and IR spectrum. Do your calculations confirm that the structure is at a minimum of the PES? If not, redo the optimization with a slightly altered initial guess structure.

C	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.070000
H	1.008806	0.000000	-0.356667
H	-0.672537	0.000000	-0.832222
O	-0.143593	1.360959	-0.177687
H	-1.017125	1.624439	0.086925

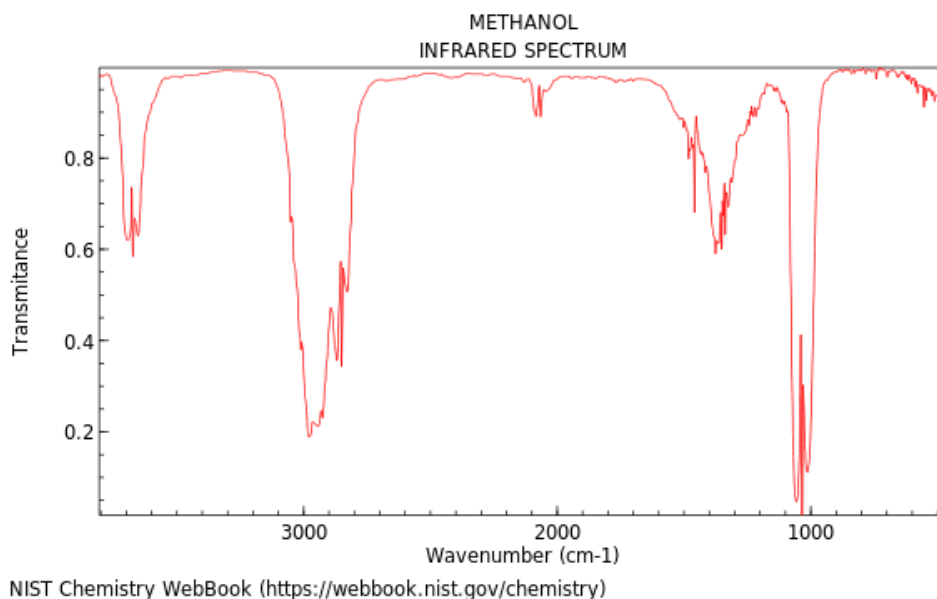
In your report, please include the following:

- The optimized structure of methanol at the RHF/3-21G level of theory.
- Confirmation that the optimized structure is at a minimum of the PES.
- The theoretical IR spectrum.

Additionally, please respond to the following question: the experimental IR spectrum for methanol is given in fig. 1. Compare and contrast your theoretical and experimental IR spectra. How could we improve our theoretical IR spectrum to match the experimental one? Label the peaks in the experimental IR spectrum with the various vibrational modes you see in your theoretical calculation.

2. (5 points) Using your optimized methanol structure, lets consider how our energy changes with different basis sets. Compute the ground state energy for methanol (at your optimized geometry from 1) using RHF and the STO-3G, 3-21G, 6-31G\*, and 6-311++G\*\* basis sets. Construct a table or graph reporting the energies for each basis set. Describe any trends you observe and relate it to topics discussed in class.
3. (5 points) Now we can explore electron correlation and how that affects our results. Using the def2-TZVP basis set, and starting from the **unoptimized** methanol geometry in 1, optimize the structure using RHF, MP2, KS-DFT with the B3-LYP functional, KS-DFT with the PBE functional, and KS-DFT with the TPSSh functional. Report the final electronic energies and CPU time for each method. Given the balance between speed and accuracy, discuss which method you would choose for geometry optimizations of small organic molecules going forward and why.

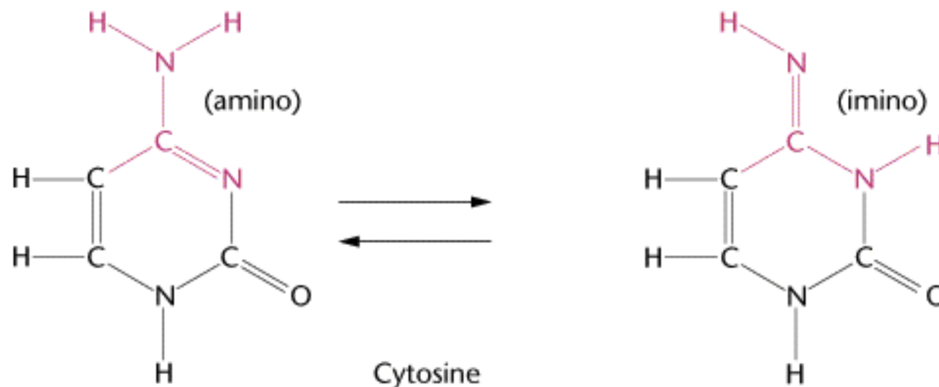
Figure 1: Experimental IR spectrum of methanol.



## 2 Local and Global Minima

(5 points) The nucleobase cytosine is known to exist in either the imino or amino form shown in fig. 2. Using the following initial guesses for the amino and imino structures, perform a geometry optimization at the B3-LYP/6-31G\* level of theory. Confirm your structures at a minimum of the PES (include in your report how you know this!). In your report, please include the electronic energy, zero-point correction, and free energy for each structure. Calculate the  $\Delta G$  (in kcal/mol) between the two structures and identify which is the global minimum structure.

Figure 2: Amino-imino tautomerism of cytosine.



Amino:

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.345071
C	1.206227	0.000000	2.124548
C	2.382067	-0.000701	1.434438
N	2.372781	-0.001172	0.073637
C	1.180897	-0.000470	-0.682143
N	-1.197828	0.002514	1.965567
O	1.260673	-0.000629	-1.927588
H	1.188763	-0.000081	3.212038
H	3.360268	-0.001552	1.913294
H	-1.867946	-0.745438	1.826923
H	-1.297179	-0.440037	2.874136
H	3.249642	-0.001696	-0.444896
Imino:			
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.436164
C	1.217807	0.000000	2.049190
N	2.355696	0.000185	1.302816
C	2.343578	0.000879	-0.108440
N	1.129723	0.000660	-0.730029
O	3.432918	0.001349	-0.717401
N	-1.171273	0.001840	-0.669276
H	-0.922855	-0.000616	2.011731
H	1.346537	-0.000777	3.130674
H	1.076082	0.011513	-1.744043
H	-2.060071	-0.011018	-0.181847
H	3.267125	0.000186	1.757853