

Chem 442: Homework for lecture L30

(only turn in **BOLD** assignment first lecture next week of classes; do all assignments)

1. For two electrons in the ground state $\frac{1}{\sqrt{2}}|\sigma\rangle_1|\sigma\rangle_2\{|\alpha_1\rangle|\beta_2\rangle - |\alpha_2\rangle|\beta_1\rangle\}$ or 1st excited state $(\frac{1}{\sqrt{2}}\{|\sigma\rangle_1|\sigma^*\rangle_2 - |\sigma^*\rangle_1|\sigma\rangle_2\})|\alpha_1\rangle|\alpha_2\rangle$, show again that $\langle\psi_0|\hat{H}|\psi_1\rangle = 0$.

2. **Turn in:** In this problem, we investigate the normal vibrational modes of ammonia using IQmol and Hartree-Fock Self-Consistent-Field (HF SCF) calculations:

- Open IQmol and construct a structure for ammonia. The easiest way would be to select “N” using the “Periodic table” button, drop a nitrogen atom in the structure window, and then add hydrogens to it by using the “Add hydrogens” button. By clicking the “Hand” button, you can rotate the ammonia molecule
- Perform a preliminary energy minimization (the “E-down arrow” button next to the “Add hydrogens” button).
- Open the Q-Chem setup in the “Calculation” menu.
- We’re going to perform two jobs with this input. First, an equilibrium geometry/energy optimization and then calculation of frequencies. Select “Geometries” from the “Calculate” drag-down menu, then hit the green “+” to add the second job, and select “Frequencies” from the “Calculate” menu. Your Q-Chem input file should show both jobs and look something like this:

The screenshot shows the IQmol software interface with the Q-Chem setup window open. The window is divided into two main sections: 'Setup' and 'Advanced'. The 'Setup' section contains fields for Job Section (Job 2), Calculate (Frequencies), Method (HF), Basis (6-31G), Exchange (HF), Charge (0), Multiplicity (1), ECP (None), and Correlation (None). The 'Advanced' section contains SCF Control options: Algorithm (DIIS), Convergence (8), Guess (SAD), Max Cycles (50), Second Basis (None), Guess Mix (0%), and checkboxes for Dual Basis Energy and Unrestricted. Below these are Wavefunction Analysis options, with 'Frequencies' selected. On the right, the 'Generated Input File' window shows the Q-Chem input file for two jobs: a geometry optimization job and a frequency calculation job. The input file includes coordinates for ammonia, basis set (6-31G), and job-specific parameters.

```
Generated Input File:

$molecule
0 1
N -1.0119043 0.6560698 0.0000000
H 0.0080957 0.6560698 0.0000000
H -1.3519006 1.1306838 0.8363875
H -1.3519053 -0.3055684 -0.0071654
$end

$rem
BASIS = 6-31G
GUI = 2
JOB_TYPE = Optimization
METHOD = HF
SCF_CONVERGENCE = 8
$end

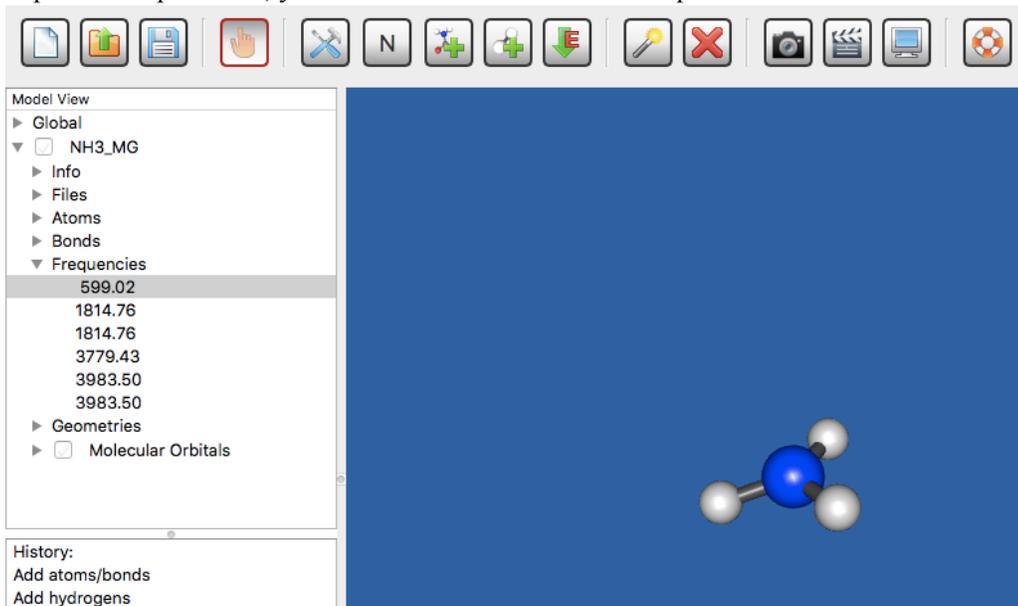
===

$molecule
read
$end

$rem
BASIS = 6-31G
GUI = 2
JOB_TYPE = Frequency
METHOD = HF
SCF_CONVERGENCE = 8
$end
```

- “Submit” the job and wait patiently! The server should return an output file within a few minutes.

- Create a new folder and save the results there as “NH3_PES”. Now you should see the name of your output file “NH3_PES” in the IQmol sidebar, and if you expand it and expand “Frequencies”, you should see the vibrational frequencies in cm^{-1} :



(If not, you can open the output file NH3_PES.out that you saved in the new folder).

- Choosing individual frequencies (single-click) will display vectors describing the motion of the normal modes. Double-clicking on each frequency will animate the vibrational motion in the structure window.
- How many** normal modes do you obtain for NH₃? Is this the number of normal modes you would have expected before applying the calculation, and what is the formula you would use to calculate how many normal modes there are? Where does the “-6” in that formula come from?
 - Describe** what type of normal mode each frequency is: stretch or bend? Which bending frequency corresponds to the ammonia molecule flipping over like an umbrella, the “quantum tunneling” we discussed in lecture 24?
 - Two pairs of modes are degenerate. **What are** their frequencies? Just like some of the electronic orbitals of benzene are degenerate (corresponding to clockwise and counter-clockwise rotation of electrons around the ring), vibrational energy levels also can be degenerate.
 - Three out of the four distinct calculated frequencies are too high, one is too low (experiment: 932, 1626, 336 and 3343 cm^{-1}). **In one sentence each**, what could be two reasons for this?