

Chem 442: Homework for lecture L33

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

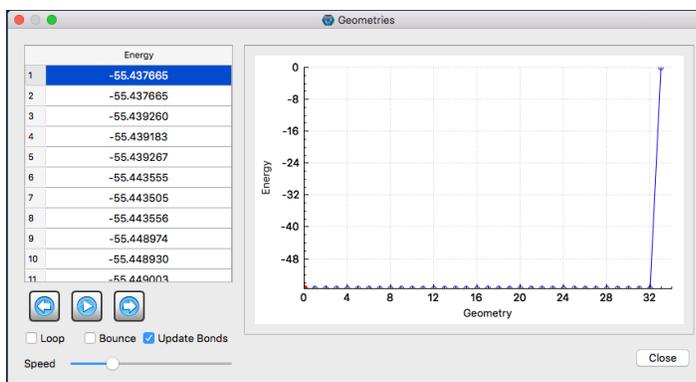
1. Write down the electron configuration (= full product wavefunction) for the excited $^3\Pi$ state of hydrogen fluoride with $M_S=+1$ and $M_L=-1$. Draw the corresponding orbital energy diagram, labeling each orbital with the one-electron basis function (e.g. 1σ , $2\pi_+$, etc) and fill in the correct number of electrons.
2. If one ionizes the HF molecule in the $^3\Pi$ state from problem 3 by removing the highest energy electron to get HF^+ , what is its term symbol then? ($^3\Pi$, $^1\Sigma$ etc are “term symbols”).

3. Turn in: In this problem, we apply Hartree-Fock (HF-SCF) theory to the inversion reaction (tunneling) of ammonia. Review the lecture Gruebele gave on tunneling and ammonia as a “Schrödinger’s cat” molecule. Places where you need to put an answer in your solution are in bold, **A.** through **F.**

- Go to <http://robinson.chem.nottingham.ac.uk/files/iqmol/> and download the file nh3.xyz into by double-clicking. This file is an IQmol text file to specify the (x, y, z) coordinate of NH_3 . Put it and everything else later into a folder “Ammonia”.
- This geometry of ammonia is close to the transition state of the inversion reaction. Let’s use HF theory to find the actual transition state:
 - o Open nh3.xyz by dropping it onto IQmol or using “open” in IQmol. NH_3 should appear in the IQmol window, and “nh3” should appear in the Model View panel.
 - o Go to Calculation → Q-Chem Setup.
 - o In the Calculate cell, select Transition State.
 - o For Method, choose HF. For Basis, choose STO-3G. Everything else stays default.
 - o Submit. Provide a job name “nh3_TS”.
 - o Copy the results into the folder “Ammonia”. In the “Model View” panel, click on the little arrow next to “nh3_TS” and then on the little arrow next to Geometries. Find the highest energy (least negative) energy (-55.4... in hartrees). That is the transition state.

- **A. What is the geometry of the transition state? Is it sp^3 or sp^2 hybridized?**

- Now let’s calculate the reaction pathway for this reaction
 - o Go to Calculation → Q-Chem Setup.
 - o Create Job 2 by clicking on the  button.
 - o Select Job 1 in the Job Section drop-down menu, and in the Calculate cell select Frequencies.
 - o For Method, choose HF. For Basis, use STO-3G.
 - o Select Job 2 in the Job Section drop-down menu, and in the Calculate cell, select Reaction Path. Notice that the text file on the right has been updated to include two jobs. Job 1 calculates vibrational frequencies, then job 2 calculates a reaction path. This text file is what gets sent to the IQmol server. Calculations are done at the server and returned in an output file that IQmol can plot.
 - o Submit. Provide a job name “nh3_path”. Save results in folder “Ammonia”. Click on the arrow next to “nh3_path” in the Model View panel.
 - o Double-click the Geometries tab (not the arrow next to it) and you should see this:



○ Click on **Loop**. Slide **Speed** to roughly half the scroll bar. Make sure you are not blocking the molecule view window with the Geometries panel, and click the **Play** arrow above the **Bounce** checkbox to animate the reaction path search. Watch the NH₃ molecule.

- **B. What do you see?** Is the ammonia molecule tunneling back and forth through the planar sp² geometry?

- **Now make a quantitative plot of the reaction path energy.** Go into the folder “Ammonia” where you saved all your calculations, and find the file “nh3_path.out”. Obviously, if we double-click this file, it leads us to IQmol. We’d like to see the output information in this file, so we don’t want to do that.

○ Make a copy of this file called “nh3_path.txt”. This allows us to open the file in MS Word. Now open it with MS Word.

○ The top of the file should look like this:

```
Running Job 1 of 2 input
qchem input_30090.0 /scratch/qchem30090/ 1
iqmol 127.0_0

Welcome to Q-Chem
A Quantum Leap Into The Future Of Chemistry

Q-Chem 4.3, Q-Chem, Inc., Pleasanton, CA (2015)

Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit,
J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh,
M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin,
T. Kus, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard,
M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock III,
P. M. Zimmerman, D. Zuev, R. Albrecht, E. Alguire, R. Austin,
```

○ Use Ctrl-F (Windows) or Cmd-F (Mac) to find the following phrase: “Reaction path following”. Skip the first result that belongs to job 1, which is the frequency calculation.

(Continued on next page)

- o What you should see is a table as indicated below:

```

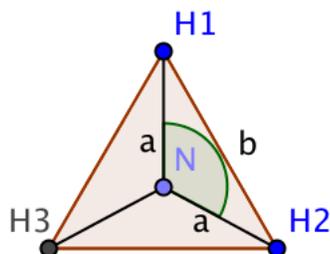
gradient time: CPU 0.02 s wall 0.02 s
IRC --- Status = 4. Checking bisection search.
IRC --- Bisection search finished successfully.
-----
Reaction path following. The coordinates are cartesian
Step 6 E= -55.455416 |G|= 0.001244 S Lin= 0.7231 S_tot= 0.7389
-----
IRC -- convergence criterion reached.
-----
Standard Nuclear Orientation (Angstroms)
I Atom X Y Z
-----
1 N 0.0000000000 0.0000000000 0.0000880200
2 H 1.0054272000 0.0000000000 -0.0002053800
3 H -0.5027136000 0.8707255000 -0.0002053800
4 H -0.5027136000 -0.8707255000 -0.0002053800
-----
Molecular Point Group C3v NOD = 6
Largest Abelian Subgroup Cs NOD = 2
Nuclear Repulsion Energy = 11.9643498278 hartrees
There are 5 alpha and 5 beta electrons
In calcReactionPath2: starting direction = -1
-----
Distance Matrix (Angstroms)
N ( 1) H ( 2) H ( 3)
H ( 2) 1.005427
H ( 3) 1.005427 1.741451
H ( 4) 1.005427 1.741451 1.741451
-----
Applying Cartesian multipole field
Component Value
-----
(2,0,0) 1.00000E-10
(0,2,0) 2.00000E-10
(0,0,2) -3.00000E-10
Nucleus-field energy = 0.0000000016 hartrees
Requested basis set is STO-3G
There are 5 shells and 8 basis functions
A cutoff of 1.0D-11 yielded 15 shell pairs
There are 42 function pairs
Smallest overlap matrix eigenvalue = 2.77E-01
Guess from superposition of atomic densities
Warning: Energy on first SCF cycle will be non-variational
A restricted Hartree-Fock SCF calculation will be
performed using Pulay DIIS extrapolation
SCF converges when DIIS error is below 1.0E-08
-----
Cycle Energy DIIS Error
-----
1 -55.1350750314 3.85E-01
2 -55.4216985148 4.06E-02
3 -55.4375177688 4.03E-03
4 -55.4376651871 9.83E-05
5 -55.4376653047 1.81E-05
6 -55.4376653092 1.63E-07
7 -55.4376653092 6.41E-08
8 -55.4376653092 5.88E-12 Convergence criterion met
-----
SCF time: CPU 0.01 s wall 0.01 s
SCF energy in the final basis set = -55.4376653092
Total energy in the final basis set = -55.4376653092
Analysis of SCF Wavefunction
-----
Orbital Energies (a.u.) and Symmetries
-----

```

- o In the file you will find about 32 sets of these tables. These are the 32 points IQmol plotted in **B**, to visualize the tunneling reaction path. Each set in the file consists of a “Standard nuclear orientation” matrix, a “Distance matrix”, and a “Total energy in the final basis set,” all circled in red above. You will now use these three items (they repeat about 32 times in the file) to make a plot of the reaction path. Here we use Microsoft Excel as an example, but you can use Matlab or your favorite plotting program to make the plot.
- o The distance matrix tells you the distances from N to H and from H to H.
- o In Excel or your plotting software, paste in the following four values for all 33 reaction path steps:
 - Column A: N–H distance from the “Distance Matrix”.
 - Column B: H–H distance from the “Distance Matrix”.
 - Column C: Energy in hartrees (numbers should be roughly -55).
 - Column D: +1 if Z for the nitrogen atom (N) in the “Standard Nuclear Orientation Matrix” is positive, -1 if it is negative.
 - Your spreadsheet should look like this (without column E, which you calculate next):

E2						
x ✓ fx =-D2*(360-6*ASIN(B2/(2*A2))*180/3.14159265)						
	A	B	C	D	E	F
1	N-H distance	H-H distance	Energy	z sign	Out of plane angle	
2	1.0054270000	1.7414510000	-55.4376653026	1	0.0001210057	
3	1.0096070000	1.7414240000	-55.4392595523	1	-2.4590959866	
4	1.0030040000	1.7302320000	-55.4391831311	1	-2.3923188574	
5	1.0080980000	1.7388660000	-55.4392669778	1	-2.4440033765	

- Look at the geometry below for the N-H distance “a” in Column A, H-H distance “b” in Column B, and the HNH angle θ (in green). Only when the molecule is planar does 3θ equal 360° (2π radians). If the molecule is bent out-of-plane, $3\theta < 360^\circ$.



- Thus the out-of-plane angle ϕ can be found by subtracting $360^\circ - 3\theta$, then multiplying by the ± 1 sign in column D so $\phi > 0$ when nitrogen has $z > 0$, and $\phi < 0$ when nitrogen has $z < 0$.
- C. Find a formula for θ and show that the expression for the out-of-plane angle ϕ in radians is:**

$$\phi = [2\pi - 6 \sin^{-1}\left(\frac{b}{2a}\right)] * sign$$

- Now use Excel, Matlab, or your calculator to evaluate the 32 or so out-of-plane angles. In Excel, you could use the formula

$$= -D2 * (360 - 6 * ASIN(B2/(2 * A2)) * 180/3.14159265)$$

and save it in column E. The $180/\pi$ is there to convert from radians to degrees units.

D. Plot Energy vs. Out-of-plane angle. This is your reaction path. It should have a barrier at roughly -55.44 hartrees between two minima in the energy at roughly -55.46 hartrees.

Other questions:

- E.** The transition state is defined to have the highest energy along the path of a reaction. **What is the absolute energy** of the transition state to 4 figures after the decimal point? **The energy** of product and reactant? **Are the energies** of the reactant and product different? **Should they be different? Why?**
- F.** **What is the geometry** of the stable product/reactant? Intuitively, **why do you think** this geometry is lower in energy than the transition state?
- G.** The difference between the energy of the transition state and the stable reactant (lowest energy) is the reaction barrier. Use the conversion factor: $1 \text{ hartree} = 2625.50 \text{ kJ/mol}$ to **calculate the barrier to this reaction in kJ/mol**. The experimental value is 24.2 kJ/mol . **What does this tell you about the accuracy of your HF calculation with a small basis set**