Assignment A01: Geometry Definition: Cartesian and Internal Coordinates

In Assignment A00 you studied a donor-acceptor substituted (hetero)arene to familiarize yourself with *GaussView* and *G09W* and to learn basics about input (GJF) and output files (LOG, CHK). In Assignment A01, we are considering various ways to define the initial structure in the GJF input file and we learn how to locate minima and simple transition state structures. We will consider the systems YH_3^{n-} (n = 0, X = N, P; n = -1, Y = C, Si). Pick one system (Y, n) and perform all computations for that system. It is the goal of this exercise to determine the minimum structure of YH_3^{n-} in C_{3v}-symmetry, to determine the transition state structure of YH_3^{n-} in D_{3h}-symmetry, and to compute a step-by-step scan of the potential energy surface (PES) along the inversion coordinate.

The specific tasks include (a) the creation of GJF files for YH_3^{n-} with *GaussView* in different symmetries (pyramidal, planar), (b) the setup of entry-level Hartree-Fock computations of this molecule in both symmetries, the optimization of each structure to a minimum, and the computation of vibrational frequencies using *G09W*, (c) the setup of an entry-level Hartree-Fock computations of the inversion transition state structure of YH_3^{n-} starting from a near-planar structure, the optimization of the structure to the inversion transition state structure, and the computation of vibrational frequencies using *G09W*, and (d) the computation of a scan the potential energy surface (PES) along the inversion coordinate while maintaining C_{3v} symmetry.

(a) Building YH_3^{n-} in C_{3v}- and D_{3h}-Symmetry. Consider ammonia as an example. Select "N" and "pyramidal" in the "Element Fragment" window and build ammonia in the **active View window**. Use "Save" in the "File" menu and save the ammonia structure in a GJF file with internal coordinates and then again in a second GJF file with Cartesian coordinates (see examples below). Do these GJF file contain precise C_{3v} symmetry? Why, or why not?

In the "Edit" menu, select "Point Group", mark "Enable Point Group Symmetry", and constrain the subgroup to "C3v". Use "Save" in the "File" menu and save the ammonia structure in a GJF

file with internal coordinates and then again in a second GJF file with Cartesian coordinates (see examples below). Do these GJF file contain precise C_{3v} symmetry? Why, or why not?

How many degrees of freedom are there in C_{3v} symmetric YH_3^{n-}? From scratch, setup a GJF file with a Z-matrix for C_{3v}-symmetric YH_3^{n-} that has as many variables as there are degrees of freedom. (Hint: You need to place a dummy atom "X" to define the C_3 symmetry axis.)

How many degrees of freedom are there in D_{3h} symmetric YH_3^{n-}? From scratch, setup a GJF file with a Z-matrix for D_{3h}-symmetric YH_3^{n-} that has as many variables as there are degrees of freedom. (Hint: No dummy atoms are required. But you may place a dummy atom X to define the C_3 symmetry axis; i.e., setup the D_{3h} symmetric structure as a special case of the C_{3v} symmetric structure.)

(b) Optimizations and Frequency Computation at RHF/6-31G* Level in Perfect C_{3v} or D_{3h} Symmetry. You setup GJF files for YH_3^{n-} with Z-matrices with C_{3v}-symmetry and D_{3h}-symmetry. For each do this: Open the GJF file in *GaussView*; your initial structure will be displayed in the **active View window**. Select menu "Calculate"; the "Gaussian Calculation Setup" window opens. Under "Job Type", select "Opt+Freq". Under "Method", select the 6-31G* basis set. Under "Title", add a job title. Under "Link 0", select memory limit 256 MW and specify "2" shared processors. Click "submit". The *G09W* window opens while each job runs (a few minutes). When *G09W* is done, close the *G09W* window. You now have sets of GJF, LOG and CHK output files for YH_3^{n-} with C_{3v}-symmetry and D_{3h}-symmetry. Explore the LOG files. Explore the frequencies and note the imaginary mode of the D_{3h}-symmetric structure. Compare the energies, compute the relative energy.

(c) Transition-State Optimizations and Frequency Computation at RHF/6-31G* Level Without Symmetry Constraints. Open an new molecule window in *GaussView*, build your YH_3^{n-} system, and use the tools in the Builder menu to deform the structure to your best initial guess of the inversion transition state structure. This initial structure will usually not be exactly planar and an optimization with just "opt" in the command line will lead to the pyramidal

minimum structure. Instead, use "opt=TS" as the command to have *G09W* locate the stationary structure with one imaginary eigenvalue. It is usually best to start a TS search with accurate forces and you should use "opt=(TS,calcfc)". Select these options in the "Calculate" menu in the section "Job Type". Continue with the setup as usual and run the job.

You will now have a third set of GJF, LOG and CHK output files for YH_3^{n-}. Explore the LOG file. Did you locate the desired inversion TS? Is the structure *de facto* D_{3h}-symmetric? Explore the frequencies, note the imaginary mode, and explore the transition vector. Compare the energies, compute the relative energy.

(d) Step-by-Step Scan of the Inversion Path of YH_3^{n-} in C_{3v}-Symmetry. The inversion coordinate is the angle between the C_3 symmetry axis and any one of the H-atoms. Compute a series of structures along the inversion path of YH_3^{n-}. A sample input file follows.

```
%nprocshared=1
%mem=128MW
%chk=C:\Users\glaserr\Desktop\partd_80.chk
# opt=z-matrix hf/6-31G*

Ammonia with a1 angle 80 degrees

0 1
 N
 X    1         1.0
 H    1          b1    2         a1
 H    1          b1    2         a1     3  120.0     0
 H    1          b1    2         a1     3 -120.0     0

b1=1.          Variable will be optimized

a1=80.         Variable after the extra line with NOT be optimized
```

Setup a number of files with different a1 values using a text editor. The points along the path shall not differ by more than 5 degrees. Run these jobs directly with *G09W*. Launch *G09W*. Drop the GJF file into the *G09W* window. Under "Process", click "Begin Processing".

(e) Write-Up. Submit one Excel file "A01_'your_last_name(s)'.xlsx" containing computed data for all of the structures along the inversion scan (including all stationary structures) on sheet #1

(sheet label "Inversion Scan Data") and with a plot of the inversion scan on a separate sheet (sheet label "Inversion Plot"). Write author name(s) clearly visible on sheet #1 (because we will need the author name(s) on the hardcopies). The data sheet should contain five columns: the (X-Y-H) angle in degrees (to 2 digits), the *d*(Y-H) bond length in Angstroms (to 3 digits), the total energy in atomic units (to 6 digits), the relative energy in kcal/mol (relative to energy of minimum, to 2 digits), and the dipole moment in Debye (to 3 digits). The plot should be a "marked scatter" plot. Use different marks for points that correspond to stationary structures. Use appropriate major and minor tick marks. Show units in axis titles.

Enthusiastic students may search the literature for the experimentally measured inversion barrier of their YH_3^{n-} systems.

Submission & Deadlines: Submit "A01_'your_last_name(s)'.xlsx" as attachment to email on Tuesday, 09/06/16 by midnight. Bring one (stapled) hardcopy to class on Wednesday, 09/07/16, for evaluation by peer review.

Global: The subject line of any submission by email should contain the assignment number, i.e., "A01 submission".
Global: If you work together with another student, there should be one submission for the pair and the collaborator must be copied.

Draw NH_3 in Active Window without using Point Group

Save as internal coordinates from "File" menu

```
%chk=C:\Users\glaserr\Desktop\ammonia.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1            B1
 H                  1            B2    2            A1
 H                  1            B3    3            A2    2            D1    0

   B1             1.00000000
   B2             1.00000000
   B3             1.00000000
   A1           109.47120255
   A2           109.47125080
   D1          -119.99998525

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")

```
%chk=C:\Users\glaserr\Desktop\ammonia_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    1.00000000
 H                  0.94280915    0.00000000   -0.33333304
 H                 -0.47140478   -0.81649655   -0.33333304

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

Draw NH_3 in Active Window with using Point Group and C3v

Save as internal coordinates from "File" menu

```
%chk=C:\Users\glaserr\Desktop\ammonia_C3v.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N
 H                  1    0.99999994
 H                  1    0.99999994    2  109.47122406
 H                  1    0.99999994    2  109.47122406    3 -120.00000838    0

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```

Save as Cartesian coordinates from "File" menu (mark "Write Cartesians")

```
%chk=C:\Users\glaserr\Desktop\ammonia_C3v_coord.chk
# hf/6-31G* geom=connectivity

Title Card Required

0 1
 N                  0.00000000    0.00000000    0.00000000
 H                  0.00000000    0.00000000    0.99999994
 H                  0.94280897    0.00000000   -0.33333337
 H                 -0.47140460    0.81649645   -0.33333337

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
```