

Laboratory 2

HyperChem, Practical Guide

Lesson	Information covered	Time to complete
Single point calculation with different methods	Single point calculation for H_2O and NH_3 molecules	10 minutes
Geometry Optimization of H_2O and NH_3 molecules; Vibrations of Ammonia and Water	Geometry optimization and vibrational analysis with and without molecular mechanical restraints in terms of ab initio methods. Transition state searching.	70 minutes
Molecular Dynamics	Simulating Alanine Zwitterion in water.	60 minutes

Creating Ammonia

L-click on Explicit Hydrogens of the Build menu until it is not selected. Select Default Element of the Build menu to bring up the periodic table dialog box. Double-click on N (Nitrogen) to select this element and simultaneously dismiss the periodic table dialog box. L-click on the Drawing tool to select it. L-click once in the workspace to create a single Nitrogen atom. Select Add H & Model Build of the Build menu to create NH₃ at the standard model builder geometry (or load the molecule from previous lesson).

Choosing a Basis Set

In this lesson you will use a 3-21G double zeta basis set augmented with *d* orbitals on the nitrogen atom.

To choose a basis set:

Select Labels from the Display menu. Choose an atom label of Basis Set and then choose OK to close the Labels dialog box. Labels on each atom should now be the basis set for that atom. At this point the labels should read, „None”. Select *Ab Initio* from the **Setup** menu. Select Small (3-21G) as the basis set and then L-click on Apply Basis Set. Then L-click on either OK or Close. You should now see labels on each atom that read, „3-21G”. 5. Select the nitrogen atom of ammonia by L-clicking on the Selection tool and then L-clicking on the nitrogen atom. Only the nitrogen atom should be selected, as indicated by a small circle around it. To select individual atoms like this, Atoms of the Select menu must be checked and be the smallest unit of selection rather than Residues or Molecules. Select *Ab Initio* from the Setup menu again. Push the Advanced Options button and be sure Six is chosen as the number of d orbitals before clicking on OK and returning to the *Ab Initio* Method dialog box. Push the Extra Basis Function button and choose a D shell type with an Exponent of 1.0 in the Extra Basis Function dialog box. Click on OK twice to dismiss the Extra Basis Function dialog box and the *Ab Initio* Method dialog box. You have now added an extra shell of 6 primitive d-type orbitals, each with an orbital exponent of 1.0, to the nitrogen atom. The basis function label for the nitrogen should indicate this. R-click in empty space to de-select the nitrogen atom. You are now ready to perform *ab initio* calculations on ammonia with this basis set.

Vibrational Analysis on Pyramidal Ammonia

To perform a vibrational analysis:

Select Geometry Optimization from the Compute menu and perform a Polak-Ribiere optimization to a RMS gradient of 0.001. Do The resultant structure (H-N-H angle = 106.5° and N-H bond length = 1.01 Å) turns out to be very close to experimental results. This is a „balanced” basis set. Go to Setup Menu, select *ab initio* than Options. Mark MP2 correction Energy. Click OK.

Select Single Point from the Compute menu to calculate the total energy including the MP2 correlation energy. The total energy at the SCF level is -35086.49 kcal/mol and the total energy including the MP2 correlation energy is -35191.11 kcal/mol.

Prepare the table with all the data you have - bond length, angle, energy.

Select Vibrations from the Compute menu to perform a vibrational analysis at the optimized geometry. This calculation requires the numerical calculation of all second derivatives with respect to Cartesian displacements of the atoms and requires a few minutes. Size the HyperChem window to approximately one third of the screen and place it on the right-hand-side of the screen. Select Vibrational Spectrum from the Compute menu to display the vibrational spectrum.

Put spectral data to the table. Name fundamental modes of NH₃ molecule (stretching, bending etc.) Compare your results with the one from experiment (find it in Internet).

Do similar calculation in medium basis set 6-31G*.(optimize structure, do vibrational analysis...) Put all data from this calculation to the table. Compare results from STO-3G and 6-31G*. Next step do for the 6-31G* basis set.

Important: It is always important to perform a geometry optimization before a vibrational analysis calculation since the basic vibrational procedure assumes all first derivatives of the energy are zero, i.e., the molecule is at an energy extremum.

Optimizing Planar Ammonia

You will now create an optimum planar structure for ammonia. To create this particular structure you will use restraints. Restraints are extra molecular mechanics terms added to the potential to restrain bond lengths, bond angles, and bond torsions. You will use an „improper torsion” to restrain ammonia to a planar form.

Eliminate any labels. Be sure that Multiple Selections of the Select menu has been selected and that you are selecting Atoms rather than Residues or Molecules. Select in turn, the nitrogen atom, one of the hydrogen atoms, and then the other hydrogen atoms until all four atoms are selected. Select Name Selection from the Select menu, choose Other, and then type in an arbitrary name for the selection such as „imptor”. Close the Name Selection dialog box by choosing OK. The named selection „imptor” now refers to an improper torsion angle in ammonia. You can now restrain this improper torsion to a specific angle ($180^\circ = \text{planar}$) by adding a restraining force for deviations from this angle. This will keep ammonia planar, provided the force is large enough. R-click in empty space to de-select all atoms. Select Restraints from the Setup menu. Select 4-imptor (a 4-atom selection named imptor) and push Add to add this named selection to the list of restraints. Choose Other for Restrained Value and type in a value of 180 for the torsion angle. Choose Other for the Force Constant and type in a reasonably large value, 500, to ensure that ammonia is kept planar. Choose OK to dismiss the Restraints dialog box. Select Geometry Optimization from the Compute menu for an optimization to the best planar structure of ammonia. Choose Polak-Ribiere as the method and 0.001 for an RMS gradient, as before. Click on OK to initiate the optimization. The optimized structure you obtain should be planar with a bond length of 0.99 Å. Select Single Point from the Compute menu to calculate the energy of the planar structure including the MP2 correlation energy. The total energy at the SCF level is -35079.16 kcal/mol and the total energy including the MP2 correlation energy is -35183.80 kcal/mol. The difference between this energy and the energy of optimized pyramidal ammonia is the inversion barrier of ammonia. The SCF value for this is 7.33 kcal/mol. The effect of correlation energy on this barrier is predicted to be negligible at .05 kcal/mol.

Vibrational Analysis on Planar Ammonia

Select Restraints from the Setup menu. Select the 4-imptor restraint and push Remove to move this improper torsion from the list. Click on OK to dismiss the dialog box and remove the restraint. If you do not remove the restraint, a vibrational analysis will include second derivative components from the molecular mechanics restraining force as well as those from the straightforward quantum mechanical ab initio calculation on the planar structure of ammonia. Select Vibrations from the Compute menu to perform a vibrational analysis at the optimized planar geometry. This calculation requires the numerical calculation of all second derivatives with respect to Cartesian displacements of the atoms.

Note that the lowest energy vibration has a negative frequency. Actually, the solution of the equations for the normal modes gives eigenvalues that are the square of the vibrational frequencies. When one of these squares of the vibrational frequency is negative, HyperChem plots it as the negative of the square root of the magnitude rather than as an imaginary number. Thus this negative value $-\nu$, actually means there is an imaginary vibrational frequency. A single imaginary frequency with all the remaining frequencies being positive implies that this planar structure is a transition state, not a minimum energy structure, as the pyramidal

structure is. Click on the negative frequency transition and animate it.

Put some conclusion to your report.

Finding a Transition State by Eigenvector Following

Read the optimized pyramidal ammonia structure. Select method and basis set (ab initio 6-31G*). Select Transition State... on the Compute menu. In the dialog box, specify Eigenvector following, then click on OK. The status bar shows that HyperChem is performing a vibrational calculation. When this has been completed, the Transition State Search dialog box opens. Click on the lowest energy eigenvector at the right-hand side of the spectrum. As before, this corresponds to the lowest-frequency breathing mode of ammonia, which moves the atoms in directions that lead to the inversion of the pyramid. The lowest-energy vibration is often the mode which is most appropriate for a transition state search.

HyperChem finds a planar transition state.

Water

Optimize geometry of H_2O with different method semi-empirical (PM3 and AM1), ab initio (6-31G* and 6-31G**) and DFT (6-31G* and 6-31G**). Compare obtained results (bond angles, vibrational spectrum). Make assignment of a bands - compare with experiment.

CO_2

Do geometry optimization for CO_2 and vibrational analysis in 6-31G* basis set using DFT method. Write few words about „Fermi resonance” in CO_2 in your report.

Molecular Dynamics

Creating the Isolated Alanine Zwitterion.

If necessary, reopen HyperChem. Double-click on the Drawing tool to open the Default Element dialog box. Turn on Allow Arbitrary Valence and Explicit hydrogens. Choose carbon and then close the dialog box. Turn Show Hydrogens on. Set the label option to label atoms by symbol. L-click on the Drawing tool to get into drawing mode. Draw the alanine zwitterion.

In this exercise, you make a simple approximation of a formal charge of +1.0 on the nitrogen atom and charges of -0.5 on the oxygens. This results in nonzero values for these three atoms.

To assign atomic charges get into selection mode and set the select level to atoms. Make sure Multiple Selections is turned on. Select the nitrogen atom. Choose Set Charge on the Build menu and assign a charge of 1.0. R-click in an empty area to clear the selection. Select both oxygen atoms and assign a charge of -0.5. This sets a charge of -0.5 for each of the oxygen atoms. R-click in an empty area to deselect the atoms.

Select Molecular Mechanics on the Setup menu. The Molecular Mechanics Force Field dialog box opens. Select AMBER, then L-click on Options. Use such a options: Dielectric distant dependent; scale factor 1, electrostatic 0.5, van der Waals 0.5, cutoffs: none

Now, double-click on the Selection tool to invoke the Model Builder. Open the Labels dialog box from the Display menu and choose Chirality for atoms. If the central carbon is labelled R rather than S, then switch to the drawing tool, hold down the **Shift** key and click on the central carbon. Change the atom labels back to Symbol.

Measure structural properties(example: C-O bond length, O-C-O angle, N-C-C-O torsion angle). Put it to a raport.

Perform a single point calculation. Write down the energy and gradient (Compute - Properties). Optimize geometry - RMS gradient 0.0001; 900 cycles. Write down the energy and gradient. Measure structural properties(example: C-O bond length, O-C-O angle, N-C-C-O torsion angle).

Select N-C-C-O angle and with the angle still selected, choose Name Selection on the Select menu. Select Other, enter ncco, then choose OK. R-click in an empty area to deselect the angle.

Save structure as ala.hin!!!!!!!!!!

Solvating the Structure

Remove labels. Choose Periodic Box on the Setup menu to open the Periodic Box Options dialog box. Specify a box size of 12.0 by 10.0 by 12.0 Å. Minimum distance between solvent and solute atoms is equal 2.3 Å.

Choose Rendering on the Display menu. Turn on Perspective in the Rendering/Sticks dialog box, and then choose OK. Set the select level to Molecules. When you use periodic boundary conditions, you need to check the options for cutoffs and dielectric in the Force Field Options dialog box. Choose Molecular Mechanics on the Setup menu. Choose Options to open the Force Field Options dialog box. Look at the Cutoffs options at the right of the dialog box. When you choose the Periodic box menu option, HyperChem automatically changes the options for cutoffs to Inner and Outer options, which are more appropriate for the solvated system with the nearest-image periodic boundary conditions (Cutoffs - switched). The Outer cutoff is set to one-half of the smallest box dimension (5 Å), and the Inner cutoff is set to 4 Åless (1 Å) to ensure that there are no discontinuities in the potential surface. When you use explicit solvent, you should use a **constant dielectric** (scale factor = 1, electrostatic = 0.5, van der Waals = 0.5). Choose OK to close the Molecular Mechanics Force Field dialog box.

Optimizing the Solvated Molecule

Get into selection mode and R-click in an empty area to deselect the alanine. When there is an active selection, an optimization is performed on the selection only. Therefore if you started the optimization with alanine selected, only the position of the alanine atoms is allowed to change and the water molecules are constrained. To optimize the complete system and allow reorganization of the solvent structure in the presence of alanine, you must clear the selection. Choose Geometry Optimization on the Compute menu. Choose OK to start the optimization (gradient = 0.001).

The optimized structure for the solvated system might only be a local minimum. In a system with many degrees of freedom, such as this one, there might be many minima and it can be very difficult to locate the global minimum.

Save the structure as ala-liq.hin!!!!!!

Superposition

The system currently displayed is a minimized structure for the alanine zwitterion in water. It is instructive to compare the structure with the corresponding isolated optimized structure. Instead of comparing the molecules by measuring individual structural properties, you use HyperChem's superposition feature to visually compare the two structures by superimposing.

Delete the water molecules - get into selection mode and set the select level to Molecules. L-click on the alanine. Choose Complement Selection. Choose Clear on the Edit menu. Choose Show Periodic box so that it is not set and only the alanine molecule is shown.

Save the file as ala-sol.hin!!!!!!

Select the alanine. Choose Name Selection on the Select menu and save the selection as solvated. This makes it convenient for you to display this selection later if you want to recover it. Choose Merge on the File menu and open ala.hin. Both the isolated and the solvated structures should now be on screen. The solvated structure should still be selected. Color the selected solvated structure yellow and label the molecule by symbol. Choose Complement Selection on the Select menu. The solvated system is deselected and the isolated alanine is selected. Color the selected isolated alanine violet and label it by symbol. R-click in an empty area to deselect the isolated alanine.

To perform the superposition:

Get into selection mode, set the select level to atoms, and turn Multiple Selections on. L-drag the N-C-C' bond angle of each molecule. You might have to rotate the structures to do this. Choose Overlay on the Display menu. R-click in an empty area to clear the selection. Press the space bar to center the superposed structures in the workspace. Choose Save As on the File menu and save the superposed molecules as ala-sup.hin.

Simulated Annealing

Open the file ala-liq.hin. If necessary, turn on Show Periodic Box to display the periodic box you defined earlier. If necessary, remove labels from the display. Choose Molecular Dynamics on the Compute menu. Set options:

Heat time = 0.1ps, run time = 0.5ps, cool time = 0ps, step size = 0.0005ps, periodic boundary conditions on, starting temperature = 100K, simulation temperature = 300K, temperature step = 30K. Set the Data Collection period to 4.

A dynamics run has three optional phases: heat, run, and cool. The first phase occurs over a simulation period of heat time, using the starting temperature to set initial velocities with rescaling of velocities at temperature increments to reach the simulation temperature. In the middle phase, velocities are rescaled only if constant temperature is selected. The final phase occurs over a simulation period of cool time, with rescaling of velocities at temperature increments to reach the final temperature.

Choose Snapshots at the bottom of the Molecular Dynamics Options dialog box. Enter ala-run as the filename. HyperChem generates two files with the prefix ala-run. One file, ala-run.hin, is a HIN file that contains a snapshot entry. Another file, ala-run.snp, is a binary file containing atomic coordinates and velocities. Use a Snapshot period of 1 data step. Choose OK to return to the Molecular Dynamics Options dialog box. Choose Averages to open the Molecular Dynamics Averages dialog box. L-click on EKIN, EPOT, ETOT, and ncco in the Selection box, then L-click on Add to move them to the Average only box. L-click on EKIN, EPOT, ETOT, and ncco in the Average only box, then L-click on Add to move them to the Avg. & graph box. This specifies a plot of total energy, potential energy, kinetic energy, and the N-C-C'-O torsion angle you saved as a named selection earlier. HyperChem generates a file named ala-run.csv (or chem.csv if playback dynamics is not set up), which records the quantities being averaged in a format that can be easily read by plotting or spreadsheet programs for analysis.

Finally, DYNAMICS

Choose OK to return to the Molecular Dynamics Options dialog box, then choose Proceed to start dynamics. Move the graph so that you can watch the simulation. As the

simulation continues, choose Rescale to rescale the values being plotted. Once the heating phase is finished, (when energy is being added) the total energy remains constant, and the kinetic energy mirrors the potential energy. **Caution:** You cannot recover the plot if you L-click on Done. To recover the plot, you must use replay dynamics.

Now that the dynamics run is finished, you can optimize the structure to determine a new local minimum. Choose Geometry Optimization on the Compute menu. Choose OK to perform a molecular mechanics optimization using the options from the previous calculation. After the optimization finishes, the status line shows a structure that has lower energy than the solvated local minimum found earlier.

What demonstrate results from molecular dynamics? Put all results and conclusions in your report.