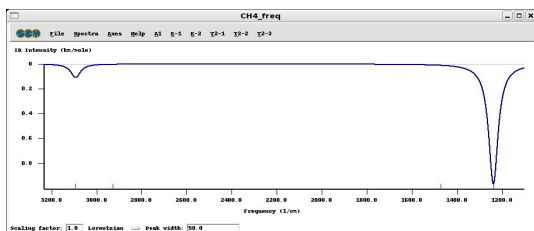


Lab 6

The Second Derivative of the Energy



6.1 Overview

In this lab we will examine the use of the second derivative of the energy with respect to nuclear displacements in computational chemistry. Second derivatives have a number of uses including identification of a stationary point as a minimum, a transition state or something else, the evaluation of the entropy contribution to Gibbs free energy and the calculation of vibrational spectra.

6.2 The Second Derivative

In the previous two labs we have studied calculations where the first derivative of the energy with respect to geometry were of primary importance. In a geometry optimization we look for a minimum in the energy. At a minimum the first derivative of the energy with respect to any change in the geometry is zero and the energy will go up with any change in geometry. At a transition state the first derivative of the energy with respect to any change in the geometry is again zero and the energy will go up with any change in geometry except in one direction where the energy will go down (the MEP).

The first derivative is the slope of the PES at a certain point. The second derivative is the curvature of the PES at a certain point. As we shall see, the second derivative contains useful information. It also takes longer to calculate than the first derivative.

6.3 Infrared Spectroscopy

In infrared spectroscopy the observed signals are usually associated with molecular vibrations. From your physical chemistry classes you may recall that the energy required (in cm^{-1}) to cause a vibrational mode of a diatomic molecule to increase in quantum number by one is

$$E(\nu \rightarrow \nu + 1) = \frac{h}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (6.1)$$

where h is Planck's constant c is the speed of light, k is the force constant associated with the vibration and μ is the reduced mass. h and c are physical constants, 2 and π are numbers

and μ depends on the masses of the two atoms that make up the diatomic. The final variable is the force constant k . k is simply the second derivative of the energy at the minimum in the potential energy curve. Thus, if we know the second derivative of the energy of a diatomic molecule at this minimum and the masses of the atoms in the molecule then we can evaluate the energy of the vibration of the molecule.

The process is somewhat more complicated for a polyatomic molecule because the form of the vibrations (the normal modes) must also be determined but this can be done.

You may also recall that the intensity of a band in an infrared spectrum depends on the change in dipole moment of the molecule as the vibration takes place or, in an equation

$$I_i \propto \frac{\partial \mu}{\partial Q_i} \quad (6.2)$$

where Q_i is the normal mode of the i th vibration. Once the second derivatives of the energy have been calculated the $\partial \mu / \partial Q_i$ can also be calculated quite easily.

With the energies and intensities of the vibrational excitations available it is possible to predict what the IR spectrum of the molecule will look like.

Further Information For more theoretical background on infrared spectroscopy look at <http://orgchem.colarado.edu/hndbksupprt/irtutor/IRtheory.pdf> or <http://sis.bris.ac.uk/~sd9319/spec/IR.htm>. A detailed theoretical description is given in the book *Molecular Vibrations* by E.B. Wilson Jr, J.C. Decius and P.C. Cross, Dover, New York, 1980. A nice description of theory required to calculate infrared spectra using quantum mechanics is given in the article by J. Neugebauer, M. Reiher, C. Kind and B.A. Hess in *J. Comput. Chem.* vol. 23 pg 895-910 2002.

6.3.1 ADF and IR Spectra

We choose to calculate the second derivatives of the energy by selecting the *Frequencies* option from the *Preset* menu on the *Main Options* window (Figure 6.1). As usual, some option of the frequencies calculations can be modified through the *Task:Frequencies* option of the *Details* menu but usually the default parameters will work well.

Once the second derivatives have been calculated the predicted IR spectrum can be analyzed using the *SPECTRA* program from the *SCM* menu. If a *Frequencies* calculation has been run we can run *SPECTRA* and a simulated spectrum should appear (figure 6.2). If the mouse is moved over a peak the energy and intensity of that peak will appear. It is also possible to visualize what a given vibration looks like using the *SPECTRA* program. If the left mouse button is pressed while the arrow is over a particular peak then a window (or windows for degenerate vibrations) will appear showing a movie of the vibration.

Some peaks may be difficult to find because their intensity is low. Other peaks will have zero intensity by symmetry. The energies and intensities of these peaks can be accessed through menus. Each symmetry irreducible representation that has a mode has its own menu. Clicking on this menu will list all vibrations of that symmetry and their energies and intensities. Choosing a vibration from the list will create a red dot on your simulated spectrum. Chicking on this red dot will produce a movie of the vibration.

Of the other options of *SPECTRA*, those along the bottom of the window control the shape and width of the peaks, the options in the *axes* menu control the units and overall

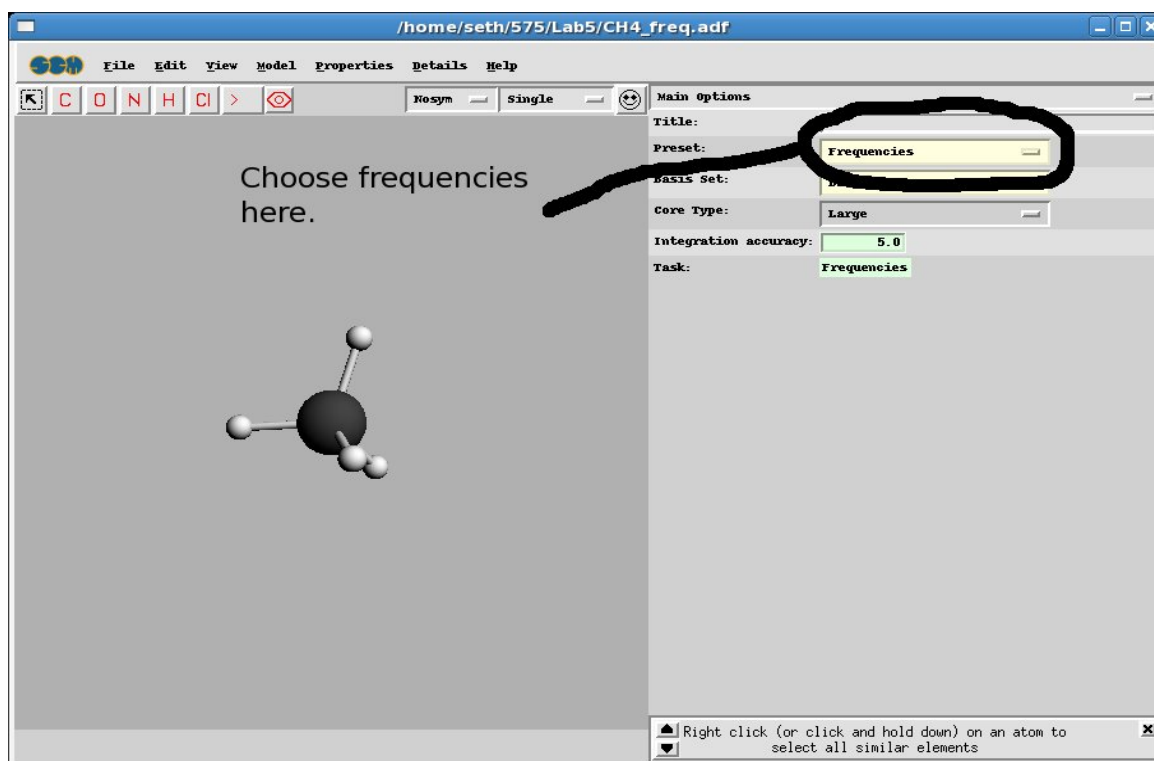


Figure 6.1: Choosing a frequencies calculation.

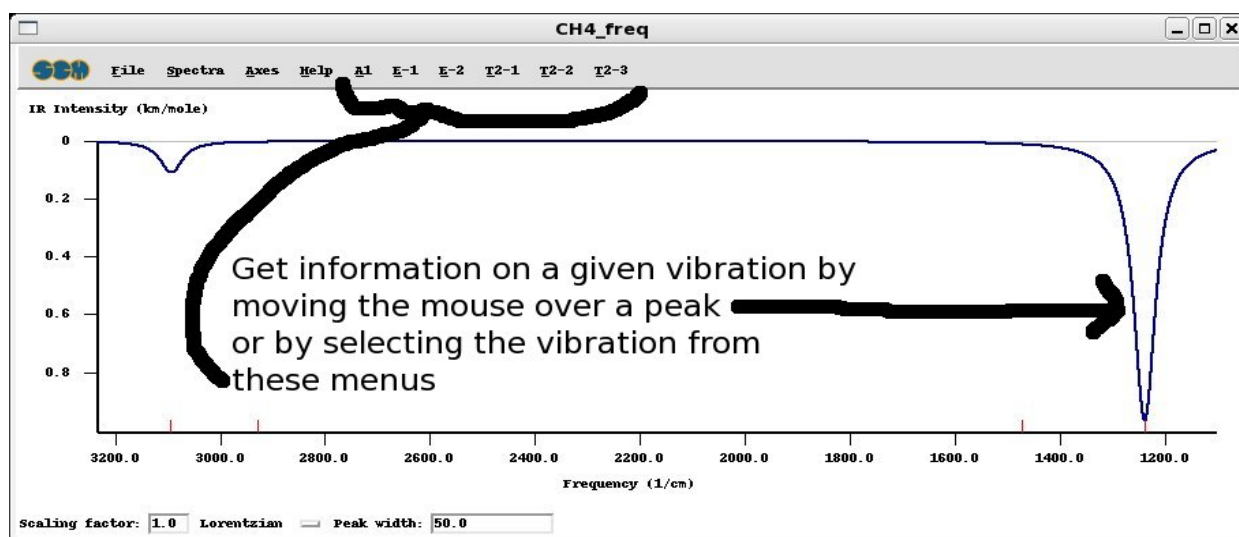


Figure 6.2: A SPECTRA window after a frequencies calculation.

form of the spectrum and those in the *file* menu allow the spectrum to be saved (as a picture or as pointwise data).

Exercise 6.1 Use a *DZP* basis set and the LDA functional for this exercise. Optimize the geometry of ammonia, NH_3 . Evaluate the second derivatives of the energy at the optimized geometry. Compare the length of time that it took to optimize the geometry of the molecule with the length of time that it took to calculate the second derivatives. Simulate the infrared spectrum of NH_3 with *SPECTRA*. What is the general formula for the number of vibrations of a nonlinear polyatomic molecule with N atoms? Do you get this number of peaks in your simulated spectrum? Why or why not? Save a picture of your spectrum in the transmission form with units cm^{-1} and peak width 100. Save a second picture of your spectrum in the absorption form with units eV and peak width 0.003. Which peak corresponds to a scissoring motion of the H atoms? Which peak corresponds to the symmetric stretching of the N-H bonds?

6.4 Characterization of Minima and Transition States

As was mentioned in section 6.2, a minimum and a transition state are similar in that the first derivatives with respect to all changes in geometry are zero for both. Other situations exist where the first derivatives are zero but we don't have a minimum or a transition state. It is possible to ask for a transition state and find a minimum because, in terms of first derivatives at least, they both look the same. If a geometry optimization or a transition state search finished successfully it is possible to say that the first derivatives are zero but not for sure whether what has been found is a minimum or a transition state or something else.

Second derivatives can be used to confirm that what has been found is a minimum, a transition state or something else. You may recall from calculus that if a one-dimensional function is minimized the second derivative of that function will be positive. If the second derivative is negative then the function is maximized. (If you don't recall this, take a look at <http://www.ugrad.math.ubc.ca/coursedoc/math100/notes/apps/second-deriv.html>, http://en.wikipedia.org/wiki/Maxima_and_minima or http://www.karlscalculus.org/calc5_0.html)

Similar ideas hold for functions of more than one dimension like a PES. Here we have many dimensions. If the gradient of the energy is zero in all dimensions then the energy is a maximum *or* a minimum in each direction. Each direction has a second derivative and if that second derivative is positive then the energy is minimized in that direction while if the second derivative is negative then the energy is maximized in that direction. Therefore, at a local minimum the second derivative is positive for all directions and at a transition state the second derivative is positive in all directions except one.

Evaluating the second derivatives is clearly a good test to see if the stationary point (place where all first derivatives are zero) that has been found is a minimum (all second derivatives > 0) a transition state (exactly one second derivative < 0) or something else (> 1 second derivative < 0).

In the *SPECTRA* program vibrations with second derivative < 0 are easy to see because they have energy and intensity < 0 . The movie of the negative vibration is particularly

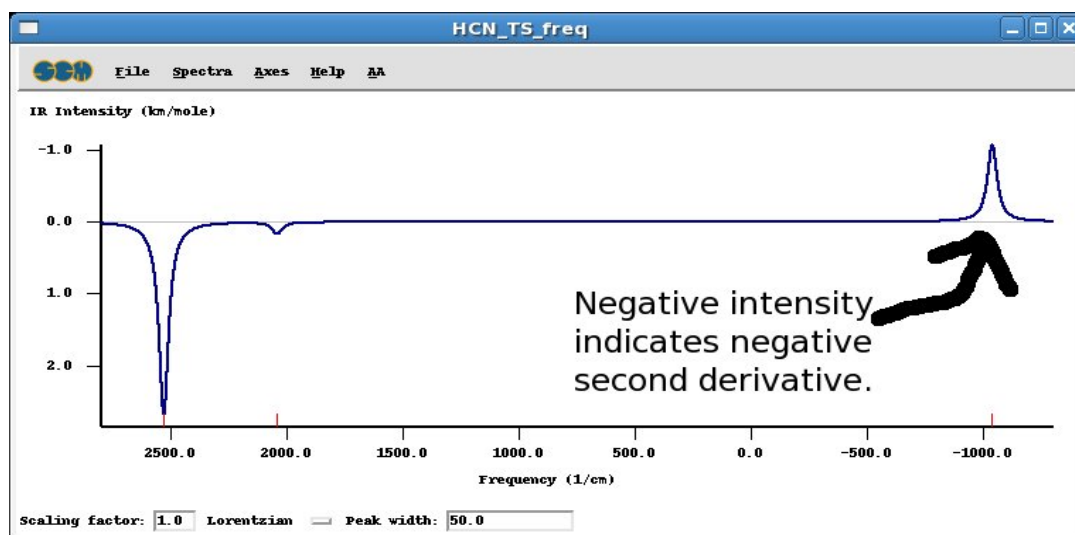


Figure 6.3: The SPECTRA window of a transition state. Note the one negative intensity frequency.

informative because it shows how the geometry of the molecule changes as it crosses the TS state of the reaction.

Note that in reality the frequency of a vibration that has a negative second derivative is actually imaginary because $E(\nu \rightarrow \nu + 1) \propto \sqrt{k}$. Imaginary numbers are hard to plot however so negative works better.

Exercise 6.2 In the last lab we considered the reaction $\text{HCN} \rightarrow \text{CNH}$. We calculated the reactants, the products and the transition state. Take your optimized geometries of the reactants, products and TS and run a frequencies calculations for each to confirm that the first two are indeed minima and the third is indeed a transition state. List the vibrational frequencies of the reactant, product and TS. Briefly describe the geometry change occurring at the transition state of this reaction.

6.5 Enthalpy, Entropy and Gibbs Free Energies

Many of the equations of this section come from the theory of statistical mechanics. We will not go over any of the details of how the equations come about. If you are interested in the details of this theory see your physical chemistry text books.

6.5.1 Enthalpy

In the previous lab we calculated the energies of reactants, products and transition states of reactions and used these results to approximate reaction enthalpies and enthalpy barriers. Enthalpies and free energies are macroscopic quantities that can be directly measured. We calculate the properties of a single molecule. Using statistical mechanics the properties of

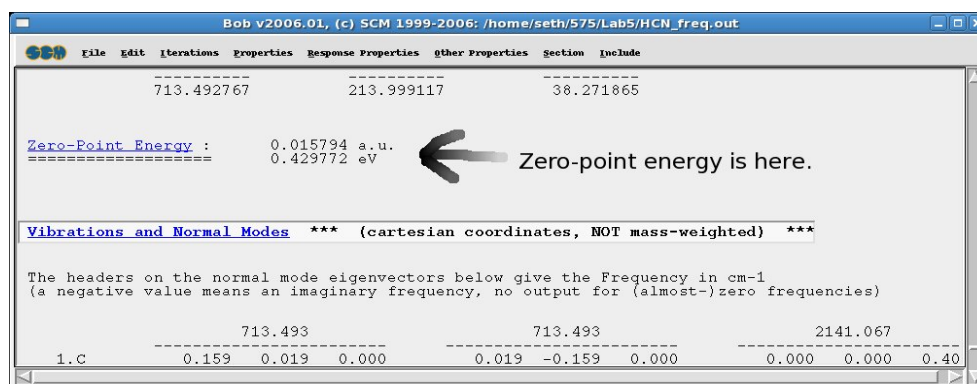


Figure 6.4: Zero-point energy contributions.

one molecule can be extrapolated to the macroscopic frame. Now that we have the energy second derivatives we have all the information required to calculate enthalpies.

What we have been calculating so far is the electronic contribution to the enthalpy. The enthalpy can be written as

$$H = E_{elec} + E_{ZPE} + E_{int} + nRT \quad (6.3)$$

where E_{elec} is the electronic contribution that we already have, E_{ZPE} is the vibration zero-point energy, E_{int} is the internal energy and nRT is the energy of the system at constant pressure as is required for the enthalpy.

E_{ZPE} depends on the vibrational frequencies of the molecule. Once we have calculated the second derivatives we have these frequencies and so can evaluate E_{ZPE} .

ADF calculates E_{ZPE} whenever a frequencies run is performed. It can be found in the detailed output. If the *OUTPUT* program is run the zero-point energy can be found through the *Other Properties:Zero-point Energy* menu item (see figure 6.4).

E_{int} is made up of thermal energy divided into contributions from translational, rotational, vibrational and electronic motion. We will always assume that the electronic thermal energy is zero. The evaluation of the translational thermal energy requires that we know the mass of the molecule. The rotational thermal energy can be evaluated if we know the masses of the atoms in the molecule and the geometry of the molecule. The vibrational thermal energy can be calculated if we know the masses of the atoms in the molecule and the energies of all its vibrations. All of this information is available once a frequencies calculation has been completed. It can be found in the detailed output by selecting the *Other Properties:Statistical Thermal Analysis* menu option of the *OUTPUT* program. The translational, rotational and vibrational internal energies are listed in kCal/mol. It is important to note that the E_{ZPE} is included in the vibrational internal energy.

The thermal contributions to the internal energy are obviously temperature dependent. By default the temperature is chosen to be 298.15 K. You can choose a different temperature or a range of temperatures through the *Properties:Thermodynamics* option of the *ADFIN-PUT* program.

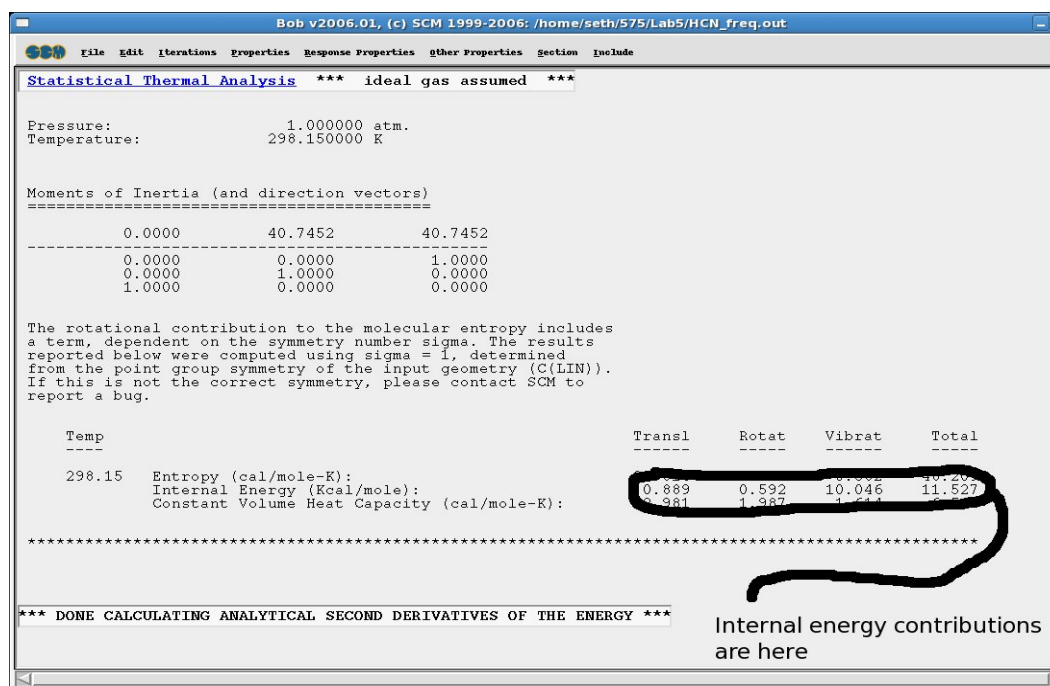


Figure 6.5: Internal energy contributions.

Exercise 6.3 Make up a table of the thermodynamic data of the reactants, products and transition state of the $\text{HCN} \rightarrow \text{CNH}$ reaction at 298.15 K. Your table should include a row for E_{elec} , E_{ZPE} , E_{int} , nRT and the enthalpy H . Don't forget that ADF includes E_{ZPE} in the vibrational part of E_{int} so you should ensure that you do not count it twice. From the data in your table, evaluate ΔH the enthalpy of the reaction and ΔH^\ddagger the enthalpy barrier of the reaction. Compare your ΔH values with the approximate energies you evaluated last lab using just E_{elec} . You can use any units for your analysis but give your final ΔH values in kJ/mol.

6.5.2 Entropy and the Gibbs Free Energy

The enthalpies of a reaction are important but more important still are the Gibbs free energy and free energy barrier of the reaction, ΔG and ΔG^\ddagger . With these quantities in hand it is possible to evaluate the important chemical quantities the equilibrium constant and the rate constant since

$$K_{eq} \propto e^{-\frac{\Delta G}{kT}} \quad (6.4)$$

$$k_{rate} \propto e^{-\frac{\Delta G^\ddagger}{kT}} \quad (6.5)$$

This equation for the rate constant is more correct than the one given in the previous lab.

We know from thermodynamics that

$$G = H - TS \quad (6.6)$$

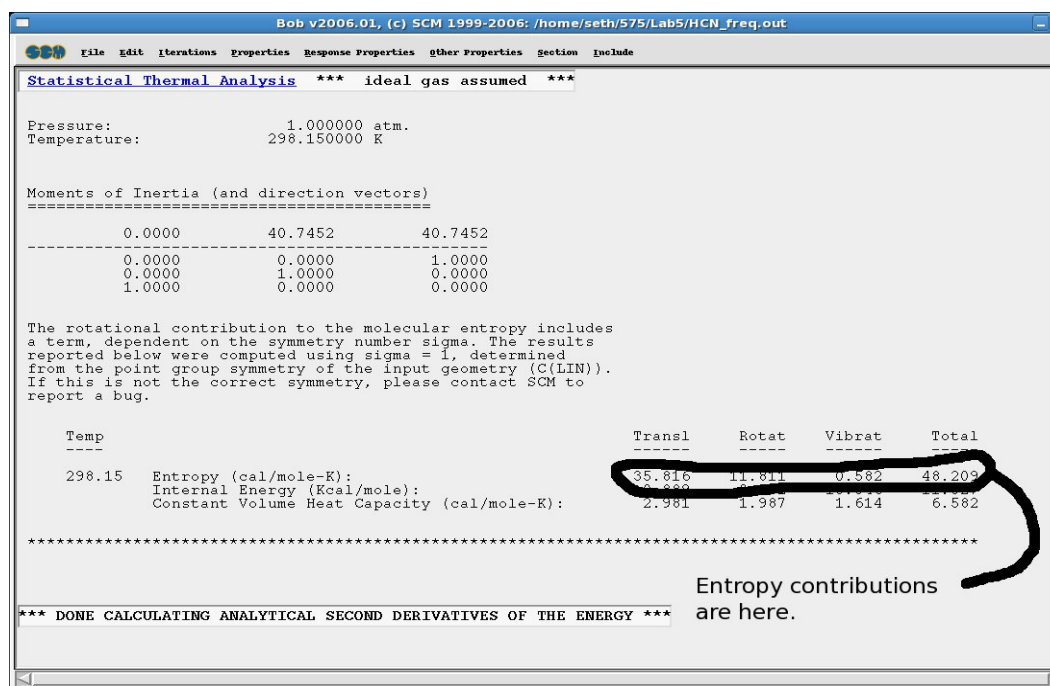


Figure 6.6: Entropy contributions.

We have already gone through how to calculate H . S is similar to the internal energy in that it has contributions from translation, rotation and vibration. The information required to calculate these entropy contributions is the same as that required to obtain the internal energy contributions. Thus, it is not surprising that the contributions to the entropy of the molecule (in cal/mol K) are listed in the detailed output in the same place as the contributions to the internal energy. (The *Other Properties:Statistical Thermal Analysis* menu option of the *OUTPUT* program(see figure 6.6.)

Exercise 6.4 Make another table where you list the entropies of the reactants, products and transitions state of the reaction $\text{HCN} \rightarrow \text{CNH}$. Add to your table the Gibbs free energy of each species. Evaluate ΔG and ΔG^\ddagger of the reaction. Compare ΔG and ΔG^\ddagger with the values you obtained for ΔE and ΔE^\ddagger in the last lab. Could you have predicted ahead of time the qualitative result of this comparison? Why?

6.6 Project

Evaluate ΔE_{elec} , ΔH and ΔG for the reaction $\text{H}_2\text{O} + \text{BH}_3 \rightarrow \text{H}_2\text{O-BH}_3$. Note that we are only interested in the overall reaction energy. We are not interested in the barrier or transition state. Use the PBE functional and a TZP basis. The calculations involving $\text{BH}_3\text{-H}_2\text{O}$ might take a little while (10 to 20 minutes) so it is a good idea to run them on 2 processors or 4 if you are running outside of normal lab time. How do ΔE_{elec} , ΔH and ΔG compare with each other? Why the change from the HCN case?