Lab 4

Transition states and reaction paths

Theoretical background

Transition states

A transition structure is the most energetic molecular configuration along the path between reactants and products. In a system with a single degree of freedom this point is a maximum of the potential energy function. The difference between this maximum energy and the minimum energy associated with the stable reactant configuration is the activation energy of the reaction, which is the most significant parameter affecting reaction rate.

The geometry of a transition structure is an important piece of information in describing the reaction mechanism. To understand it we need to generalize the one-degree-of-freedom picture above to many degrees-of-freedom. The transition structure is mathematically defined as a saddle point on this multidimensional molecular potential surface. At such a point the first derivative of the potential with respect to any nuclear coordinate is zero, and the second derivative is positive for all but one coordinate. Thus, such a point looks like a minimum on the potential energy surface in every direction except one. Along this particular direction (that actually defines the reaction coordinate at the transition state) this point is a maximum of the potential.

Unfortunately, there are many saddle point structures, such as an eclipsed conformation or the intermediate point in a ring flip or any structure with a higher symmetry than the ground state of the compound, that are not the transition structures for a given reaction. Our task is to find the correct transition point and calculate its properties.

Predicting what a transition structure will look like (without the aid of a computer) is difficult. We can use our physical intuition aided by our assumed knowledge of the reaction mechanism to predict the structure. One source of difficulty stems from the fact that the potential energy surface around the transition structure is often much flatter than the surface around a stable geometry. Thus, there may be large differences

in the transition structure geometry between two reactions that look similar and with very small differences in energy. Computer aided determination transitions state geometries and energies is the subject of this laboratory.

Optimizing to a transition state or higher-order saddle point

Transition State Optimizations Using Synchronous Transit-Guided Quasi-Newton (STQN) Methods. *Gaussian* includes the STQN method for locating transition structures. This method, implemented by H. B. Schlegel and coworkers[1], uses a quadratic synchronous transit approach to get closer to the quadratic region of the transition state and then uses a quasi-Newton or eigenvector-following algorithm to complete the optimization. **QST2** requires two molecule specifications, for the reactants and products, as its input, while **QST3** requires three molecule specifications: the reactants, the products, and an initial structure for the transition state, in that order. *The order of the atoms must be identical within all molecule specifications*.

The following are some Gaussian keywords for calculating a transition state:

Opt=TS
Requests optimization to a transition state rather than a local minimum using the Berny optimization method.

Opt=QST2
Search for a transition structure using the STQN method. This option requires the reactant and product structures as input, specified in two consecutive groups of title and molecule specification sections. Note that the atoms must be specified in the same order in the two structures. **Opt=QST2** generates a guess for the transition structure that is midway between the reactants and products, then it goes on to optimize that starting structure to a first-order saddle point automatically. **TS** should *not* be specified with **QST2**.

[1]   C. Peng and H. B. Schlegel, *Israel J. Chem* . **33**, 449 (1994).
     . Peng, P. Y. Ayala, H. B. Schlegel, and M. J. Frisch, *J. Comp. Chem.* **17**, 49 (1996).

Opt=QST3

Search for a transition structure using the STQN method. This option requires the reactant, product, and initial TS structures as input, specified in three consecutive groups of title and molecule specification sections. Note that the atoms must be specified in the same order within the three structures.

CalcFC

Specifies that the force constants be computed at the first point using the current method (available for the HF, MP2, CASSCF, DFT, and semi-empirical methods only).

Reaction path

A transition structure is of course a maximum on the reaction pathway. One well-defined reaction path is the least energy or intrinsic reaction path (IRC). Quasi-Newton methods oscillate around the IRC path from one iteration to another and several groups have proposed methods for obtaining the IRC path from the quasi-Newton optimization.

Likewise, a transition structure can be obtained by following the reaction path from the equilibrium geometry to the transition structure. This technique is known as eigenvalue-following because the user specifies which vibrational mode should lead to a reaction given sufficient kinetic energy. This is not the best way to obtain an IRC, nor is it the fastest or most reliable way to find a transition structure. However, it has the advantage of not making assumptions about concerted motions of atoms or what the transition structure will look like.

Another technique is to use a pseudo reaction coordinate. This can be quite a bit of work for the user and requires more computer time than most of the other techniques mentioned. However, it has the advantage of being very reliable and thus will work when all other techniques have failed. A pseudo reaction coordinate is calculated by first choosing a geometric parameter intimately involved in the reaction (such as the bond length for a bond that is being formed or broken). A series of calculations then run in which this parameter is held fixed at various values between this associated with the reactants and that which characterizes the products – while all other geometric parameters are optimized. This does not give a true reaction coordinate but

an approximation that matches it only at the equilibrium geometries and transition structure. Typically, the highest energy calculation from this set is used as the starting geometry for a quasi-Newton optimization. In a few rare cases involving very flat potential surfaces the quasi-Newton optimization may still fail. In this case, the transition structure can be calculated to any desired accuracy (within the theoretical model) by finding the energy maximum by varying the chosen geometric parameter in successively smaller increments.

The IRC method keyword requests that a reaction path be followed[2]. The initial geometry (given in the molecule specification section) is that of the transition state, and the path can be followed in one or both directions from that point. By default, the *forward* direction is defined as the motion direction along the transition vector corresponds to an increase in the specified internal coordinate, designated by up to four atom numbers. If two atom numbers are given, the coordinate is a bond stretch between the two atoms; three atom numbers specify an angle bend, and four atoms define a dihedral angle.

The geometry is optimized at each point along the reaction path such that the segment of the reaction path between any two adjacent points is described by an arc of a circle and the gradients at the end points of the arc are tangent to the path. By default, an IRC calculation uses 6 points in the forward direction and 6 points in the reverse direction, in steps of 0.1 $\text{amu}^{1/2}$ bohr along the path.

The force constants of the IRC calculation can be provided in the input stream (**IRC=FCCards**) and computed at the beginning of the IRC calculation (**IRC=CalcFC**).

MaxPoints=N

Number of points along the reaction path to examine (in each direction if both are being considered). The default is 6.

CalcFC

Specifies that the force constants be computed at the first point.

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[2]   C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* **90**, 2154 (1989).
         C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.* **94**, 5523 (1990).

CalcAll

Specifies that the force constants be computed at every point.

In this lab, we will use the Gaussian program in order to calculate transition state structures and energies, activation energy and reaction path of the following chemical reactions:

1. $SiH_2 + H_2 \rightleftarrows SiH_4$

2. $HCN \rightleftarrows HNC$
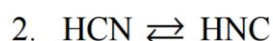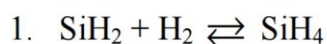
For all Gaussian calculations, use the RHF method the 6-31G(d) basis set and the SCF=Tight option, unless requested otherwise.

Part 1 - Silane

$$SiH_2 + H_2 \rightleftharpoons SiH_4$$
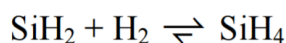
1. Calculate the transition state of the above reaction with QST2.

   Steps of calculation:

   - Use the GaussView program to perform geometry optimization calculations of SiH_2, H_2 and SiH_4 molecules (perform three separate calculations, one for each molecule). Record the structure and the energy of each optimized molecule.

   To perform the calculation using GaussView, one should create an input file that contains two sheets. The first sheet should include the reactants with a reasonable distance between them (in this case about three angstroms). The second sheet should include the products. To create the first sheet, you should:

   - Open the optimized structure of SiH_2 in GaussView Press the Edit button and select Copy.

   - Press the File button, open a new file and press the Edit button and select Paste and Append Molecule.

- Save the new file with the name QST2-calc.

- Open the optimized structure of H_2 in GaussView, Press the Edit button, and select Copy.

- Open the QST2-calc file, press the Edit button, select Paste and Append molecule.

- Verify the distance between the SiH_2 and the hydrogen atoms (use the Modify Bond button).

- Set the distance between the SiH_2 and the hydrogen atoms to three angstroms.

- Open the optimized structure of SiH_4 in GaussView ,Press the Edit button, and select Copy.

- Open the QST2-calc file, press the Edit button, select Paste, and Add to molecule group.

Now, make sure that the order of the atoms in the reactants and product sheets are similar.

- Highlight the first sheet, press the Atom List Editor button. Document the atoms order.

- Highlight the second sheet (use the arrow button to get from one sheet to another), press the Atom List Editor button. Document the atoms order.
  The order of the atoms in each sheet should be the same. For example, if the silicon atom is the first in the first sheet and third in the second sheet, go the second and change the number near the silicon atom from 3 to 1 and press enter. Continue this procedure until the atoms in both sheets appear in the same order.

Performing the QST2 calculation:

- Highlight the QST2-calc file, press the Calculate and select Gaussian.

- In the Job type dialog box, select optimization and TS (QST2), calculate force constants – never.

- In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.

- In the general dialog box select Ignore Symmetry.

- Select 'None' in the Solvation dialog box.

- Insert SCF=Tight in the Additional Keywords.

- Submit the calculation. If you encounter convergence problems, try changing the parameters of reactants, such as the angle between the molecules in the input file, and resubmit the calculation.
- Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was achieved.
- Open the output file in GaussView to observe the transition state of the reaction.

2. Does the transition state look reasonable? tabulate the energy and the structure of the transition state as calculated with QST2 method. What are the activation energy and the energy difference between the product and reactants?

3. Use the TS (Berny) method to calculate the transition state of the above reaction. In the case of a transition state calculation with Berny algorithm, one needs to give an initial guess of the transition state.
   Use the calculated transition state (with QST2) to perform the TS calculation:
   - In the Job type dialog box, select optimization and TS (Berny), calculate force constants – once.
   - In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.
   - In the general dialog box select Ignore Symmetry.
   - Select 'None' in the Solvation dialog box.
   - Insert SCF=Tight in the Additional Keywords.
   - Submit the calculation.
   - Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was achieved.
   - Open the output file in GaussView to observe the transition state of the reaction. Document the energy and the structure of the transition state as calculated with Berny method. Report the activation energy and the energy difference between the product and reactants.

4. Compare the activation energy and structure of the transition states that were calculated using both methods. What are your conclusions from the results?

5. Which transition state will you use to perform a reaction path calculation? Explain.

6. Calculate reaction path of the above reaction:

- Open the calculated transition state in GaussView.

- In the Job type dialog box, select IRC Follow IRC – both directions, Calculate Force Constants – Once, select compute more points, N=42.

- In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.

- In the general dialog box select Ignore Symmetry.

- Select 'None' in the Solvation dialog box.

- Insert SCF=Tight in the Additional Keywords.

- Submit the calculation.

- Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was achieved.

- Open the output file in GaussView, press the green button to watch a "movie" of the reaction path.

7. Use the GaussView program to print the total energy and the RMS gradient as a function of the IRC reaction coordinate: press the Results button and select IRC, use the arrow to make the window larger to observe both graphs. What can you say about the total energy and the gradient of the transition state?

8. Compare the energy and the structure of the reactants and product with the first and last steps of your calculated IRC, explain your result.

Part 2 – Hydrogen Cyanide

$$HCN \rightleftarrows HNC$$
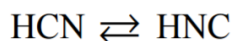
1. Use the GaussView program to perform an energy optimization calculation of HCN and HNC molecules. Report the energy and the structure of the optimized molecules.

2. What would you expect the atomic charges of each atom in the two molecules to be? (negative or positive partial charges), explain your prediction. Compare with the calculated atomic charges of the optimized molecules[3].

3. Perform a transition state calculation using the QST2 method:

   - Open the optimized structure of HCN in GaussView, Press the Edit button, and select Copy.

   - Press the File button, select New and create MolGroup.

   - Press the Edit button, select Paste and Append Molecule.

   - Open the optimized structure of HNC in GaussView Press the Edit button and select Copy.

   - Highlight the window titled "New", press the Edit button, select Paste and Add to molecule group.

   - Make sure that the order of the atoms in the reactants and product sheets are similar.

   - Performing the QST2 calculation: In the Job type dialog box, select optimization and TS (QST2), calculate force constants – never.

   - In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.

   - In the general dialog box select Ignore Symmetry.

   - Select 'None' in the Solvation dialog box.

   - Insert SCF=Tight in the Additional Keywords.

   - Submit the calculation.

   - Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was achieved.

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[3]   Open the optimized structure of each molecule in GaussView, press the Results button and charges.

- Open the output file in GaussView to observe the transition state of the reaction.

4. Tabulate the energy and the structure of the transition state as calculated with QST2 method. What are the activation energy and the energy difference between the product and reactant?

   If you had no problems with QST2, perform a TS (Berny) calculation, using the calculated transition state structures (output) of QST2.

   - In the Job type dialog box, select optimization and TS (Berny), calculate force constants – once.
   - In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.
   - In the general dialog box select Ignore Symmetry.
   - Select 'None' in the Solvation dialog box.
   - Insert SCF=Tight in the Additional Keywords.
   - Submit the calculation.
   - Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was achieved.
   - Open the output file in GaussView to observe the transition state of the reaction. Document the energy and the structure of the transition state as calculated with the Berny method. Report the activation energy and the energy difference between the product and reactant.

5. If you encounter problems with QST2 or Berny, then perform a QST3 calculation. To do so, you need to create an input file that contains three sheets: reactant, product, and an initial guess of transition state.

   - Open the optimized structure of HCN in GaussView, Press the Edit button, and select Copy.
   - Press the File button, select New, and create MolGroup.
   - Press the Edit button, select Paste, Append Molecule.
   - Save the new file.
   - Open the optimized structure of HNC in GaussView, Press the Edit button, and select Copy.
   - Open the saved file, press the File button, select Paste and Add to MolGroup.

- Highlight the saved file, press the File button, select New and Add to MolGroup. In this third file you should build your own reasonable guess of transition state.

- Make sure that the order of the atoms in the reactants and product sheets are similar.

- Performing the QST3 calculation: In the Job type dialog box, select optimization and TS (QST3), calculate force constants – never.

- In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.

- In the general dialog box select Ignore Symmetry.

- Select 'None' in the Solvation dialog box.

- Insert SCF=Tight in the Additional Keywords.

- Submit the calculation.

- Open the output file in Notepad, verify that the calculation had terminated successfully, and that convergence was chieved.

- Open the output file in GaussView to observe the transition state of the reaction.

6. Report the energy and the structure of the transition state as calculated with QST3 method. What are the activation energy and the energy difference between the product and reactant?

7. Compare the H-C, C-N and N-H bond lengths of your guess and of the QST3 calculation.

8. Use this guess and three other guesses to calculate a transition state. Compare the calculated geometries and energies of these transition states. What is the calculated transition state energy variance?

> **Note:** In this section, initial guesses that are too symmetric might lead to convergence problems. If you observe convergence problems, try changing the Hydrogen's position, for instance move it closer to the carbon atom.

9. Use the calculated transition state structures (output) of the above four calculations and perform a TS (Berny) calculation, as described above.

- Compare the four obtained results. What is the calculated transition state energy variance?

10. What are the activation energy and energy difference between the product and the reactant of the reaction? Which output (method) did you use to answer this question and why?

11. Based on the two parts, what are some advantages and the disadvantages of TS (Berny), QST2 and QST3 methods?

12. Calculate the reaction path of the above reaction:

    - Open the calculated transition state in GaussView.

    - In the Job type dialog box, select IRC Follow IRC – both directions, Calculate Force Constants – Once, select compute more points, N=42.

    - In the method dialog box, selected ground state, Restricted Hartree-Fock, 6-31G(d) basis set, Charge – 0, Spin multiplicity – Singlet.

    - In the general dialog box select Ignore Symmetry.

    - Select 'None' in the Solvation dialog box.

    - Insert SCF=Tight in the Additional Keywords.

    - Submit the calculation.

    - Open the output file in Notepad, verify that the calculation terminated successfully, and that convergence was achieved.

    - Open the output file in GaussView, press the green button to watch a "movie" of the reaction path.

Note: The movie appears "reversed", from reactants to products, and the log file is "reversed" with respect to the movie. That's a known behavior of Gaussian03, and it is fine.

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13. Use the GaussView program to print the total energy and the RMS gradient as a function of the IRC reaction coordinate. If you've got a large gradient at the first or last point, try to increase the number of points in the job dialog box. What can you say about the total energy and the gradient of the transition state?

14. Compare the energy and the structure of the reactant and product with the first and last steps of your calculated IRC, explain your result.