UNIVERSITY OF ALASKA FAIRBANKS

Computational Chemistry Workshops
West Ridge Research Building-UAF Campus
9:00am-4:00pm, Room 009

Electronic Structure - July 19-21, 2016
Molecular Dynamics - July 26-28, 2016

Potential Energy Surfaces (PES)

For the reaction

$$\mathbf{A} \longrightarrow \mathbf{B}$$

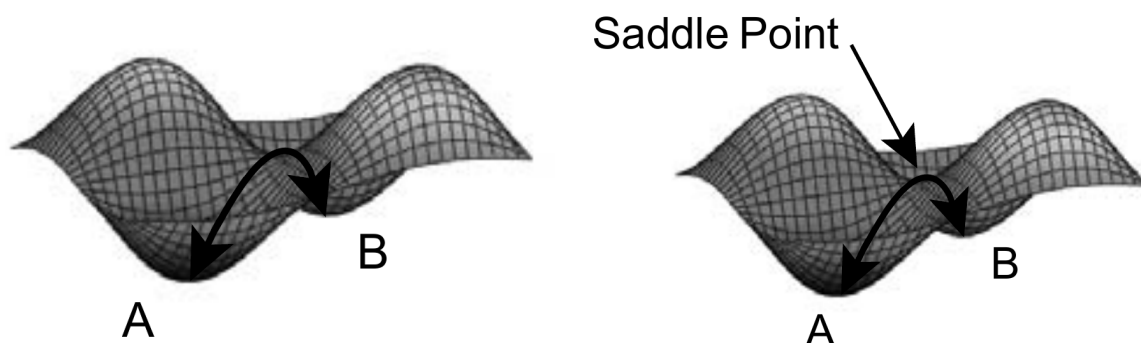a PES might look as shown in Figure 1

Figure 1: Transition State, Saddle Point, Reaction Pathway

- The minima are represented by **A** and **B**, which could be reactant and product, or two conformers.

- The ***reaction path*** is defined as the pathway between the two minima.

- The reactant passes through a maximum in energy the (***saddle point***) along the reaction pathway, connecting the two minima.

- There are minima in all other directions *perpendicular* to the saddle point on the reaction pathway.

- A ***transition state*** is defined as the geometry at the peak of the free energy (ΔG) profile, while a ***transition structure*** defines the geometry at the peak of the potential energy (ΔE) profile.

  A transition state is a first order saddle point on a potential energy surface (PES).

The Minima on a Potential Energy Surface

Following minimization, a molecule which is at a minimum on the PES is characterized by frequencies which are all **positive**, implying positive force constants. This means that the energy is a minimum in all directions. In order to verify if a stationary point is a minimum, a vibrational frequency calculation must be performed at the same computational level as for the geometry optimization to ensure that all vibrational frequencies are **positive**.

The Nature of Transition States

The vibrational spectrum of a transition state is characterized by one imaginary frequency, implying a negative force constant. This means that in one direction in nuclear-configuration space, the energy has a maximum, while in all other (orthogonal) directions, the energy is a minimum. In order to verify if a stationary point is a transition state, which connects reactants and products, a vibrational frequency calculation must be performed at the same computational level as for the geometry optimization. The normal mode corresponding to the imaginary frequency in the transition state usually reflects the change in geometry in going from reactants to products.

Locating transition states and estimating reaction barriers can be a rather difficult task. The first step is to obtain a reasonable guess for the structure of the transition state. In general, our intuition is not as well developed for transition states as it is for ground states. In addition, transition-state energies can be close to excited states, and this often implies that the usual MO-based computational methods may not be as accurate for transition states than they are for minima on a PES. A fairly high level of theory is often required to get a good quantitative estimate of a reaction barrier.

But, these exercises will be mainly focused on locating the transition state at lower levels of theory. Once a transition state is found at a lower level of theory, the calculation can be refined by re-optimizing the structure at a higher level of theory.

Intrinsic Reaction Coordinate

Another feature that can be very useful when examining transition states is the Intrinsic Reaction Coordinate (IRC) which is related to the minimum energy path (MEP) and is defined as the steepest descent path starting from the transition state, initially going in the direction of negative curvature in the Hessian. The path can be followed backwards (to reactants) and forward (to products). Following this path can indicate, if the transition state that connects the two minima of interest, has really been found.

The IRC is defined in terms of mass-weighted Cartesian coordinates in the Gaussian program, and it has a well-defined step length. Computationally, once a transition state is found, it is possible to restart from the checkpoint file and perform and IRC.

Exercises

Isomerization of H-C $\equiv$ N to C $\equiv$ N-H

As a first simple example of a transition state search, consider the process of hydrogen migration shown in Figure 2:

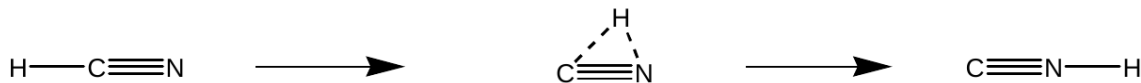Figure 2: Isomerization of H-C $\equiv$ N to C $\equiv$ N-H

1. In this case, the minima of H$-$C$\equiv$N and C$\equiv$N$-$H can be obtained in the usual fashion, and verified as minima by calculating vibrational frequencies.

2. Next, provide a reasonable estimate of the transition state geometry by changing the HCN angle from 180° to about 60°, but the H$-$C and N$-$H bond distances should be elongated as well.

   Then, perform a transition-state optimization using this initial geometry.

3. Optimizing to a transition state always requires the additional calculation of vibrational frequencies, because verification that there is precisely one imaginary frequency must be performed.

   After the calculation finishes in Step #2 finishes successfully, perform a frequency calculation, and view the vibrational frequencies using visualization software.

   One frequency should be imaginary, and the corresponding normal mode represents the hydrogen migration. Also, examine the other normal modes in the transition state.

4. Finally, locate the energy of reactants, products and transition state in the respective **log** files and construct a PES showing the reactant, transition state, and product. Calculate the activation energy, as well as the ΔG between reactant and product.

Inversion of Ammonia, NH_3

Another simple example involves the inversion of ammonia, which proceeds from an initial pyramidal C_{3v} equilibrium geometry through a planar D_{3h} transition state, and back to an inverted pyramidal C_{3v} equilibrium geometry as shown in Figure 3:
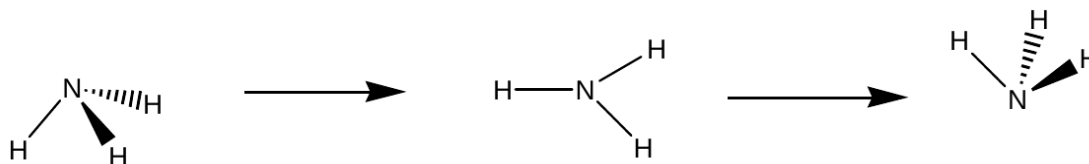

Figure 3: Inversion of Ammonia, NH_3

1. Optimize both the ground state and the transition state by imposing the proper symmetries.

2. Calculate vibrational frequencies for both the ground state and transition state.

3. Locate the single imaginary frequency and examine the corresponding normal mode. Verify that it corresponds to the inversion mode.

Butadiene

1. Optimize *cis*- and *trans*-butadiene.

2. Make a guess for the transition structure, by taking a dihedral angle of about 90 degrees.

   Locate the transition state, using the *Synchronous Transit-Guided Quasi-Newton (STQN) Method* in Gaussian which does not require a guess for the transition-state structure.

3. Perform a frequency calculation on the transition-state structure, inspect the frequencies, and determine if there is one negative frequency.

4. Perform an IRC calculation which shows the path connecting the **cis** and **trans** structures.

   Use an appropriate step size, and sufficient steps to unambiguously establish the reaction path.

Hydrogen Migration in Malonaldehyde

Some transition state structures have a higher symmetry than the ground state structure. These transition states are usually easy to locate, because the energy is a minimum, if the molecule is constrained to have the higher symmetry. If the optimization is started from a higher symmetry, it is maintained during the optimization.

An example for calculation of the reaction pathway for the enol form of malonaldehyde shown in Figure 4, includes the ground state (C_s symmetry), the transition state (C_{2v} symmetry), and hydrogen transfer.
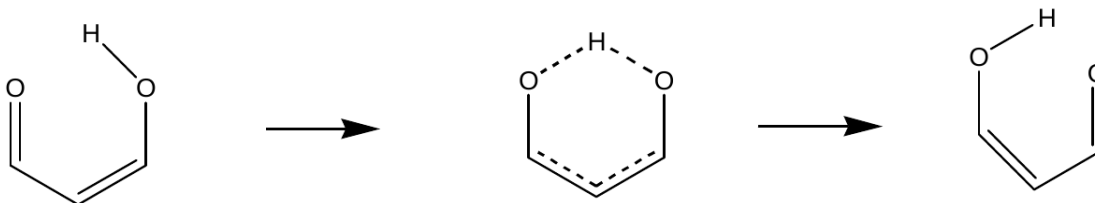
Figure 4: The Enol Forms of and Transition State of Malonaldehyde

The energy profile along the reaction pathway for proton transfer of the enol form of malonaldehyde is shown in Figure 5
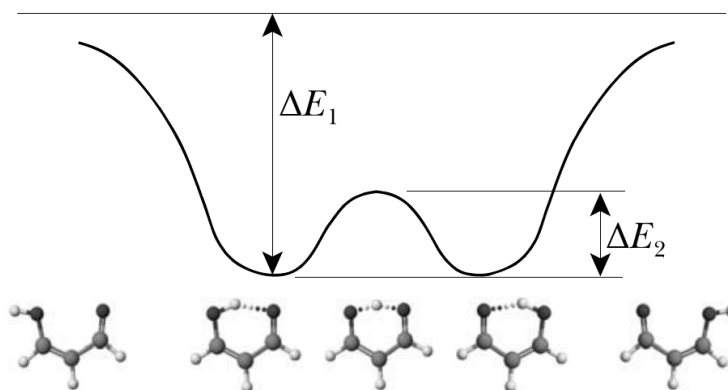
Figure 5: Energy Profile Along the Reaction Pathway for Proton Transfer in Malonaldehyde

The ground state has C_s symmetry, while the transition state has C_{2v} symmetry.

1. Optimize the ground state using C_s symmetry, and perform a vibrational analysis.
2. With C_{2v} symmetry specified, optimize the transition state to a minimum, and then calculate the frequencies.

   Verify through measurements that optimization of the minimum energy structure for the transition state worked. The transition state structure should indeed be symmetrical, and the negative (i.e. imaginary) frequency should correspond to hydrogen migration. The normal mode corresponding to the imaginary frequency at the transition state breaks the symmetry. Actually, any normal mode that is not a totally symmetric mode will reduce the symmetry.
3. Calculate the activation energy for hydrogen migration. Is the value obtained reasonable?

Walsh Diagrams

1. Perform calculations on the following molecules using the Hartree-Fock method and SVP basis set, and examine the variation of the total energy as a function of H-A-H angle by performing a rigid scan.

   - LiH_2^+ (Li-H = 1.7 Å)
   - BeH_2 (Be-H = 1.34 Å)
   - CH_2 (S=0; RKS calculation; C-H = 1.078 Å)
   - CH_2 (S=1; ROHF calculation; C-H = 1.078 Å)
   - H_2O (O-H = 0.956 Å)

2. A summary of the total energy as a function of angle will be printed at the bottom of the output file. Examine the orbitals and their energies at the bent geometry and the linear geometry, and visualize them.

   Discuss the variation of the orbital energies and the total energy as a function of bond angle. Are the Walsh Diagram results consistent with the *ab initio* results?

3. Plot the variation of the nuclear repulsion energy, the one-electron and two-electron energies, as well as the kinetic energy, of each molecule as a function of angle.

4. Also plot the sum of the occupied MO energies weighted by their occupancy as a function of bond angle. For each triatomic species, explain why the most stable geometry is either linear or bent.

H/D Kinetic Isotope Effect

Calculate the H/D effect on the reaction rate of the reaction

$$CH_4 + \cdot OH \rightarrow H_2O + \cdot CH_3$$
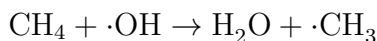
1. Build all molecules using Z-matrix format, then perform a geometry optimization on them, using B3LYP/SVP.

2. Determine the geometry and energy for the transition state structure:

$$H_3C \cdots H \cdots O - H$$

   In the transition state, one of the C-H bonds must be significantly stretched, i.e. $C \cdots H$, and the $H \cdots O$ bond should already be partially formed. Such a starting structure should be used.

   A rule of thumb is to stretch the bond to ~ 1.5 times its equilibrium value.

3. Calculate the activation enthalpy and entropy of the optimized transition state structure, using the zero-point corrected energies.

4. Then, calculate the reaction rates, and predict the resulting isotope effect.

5. Think of another possible transition state structure and try to guide the optimization to this transition state.

   Repeat questions #2 and #3 for this new transition state structure.

Symmetry Allowed and Forbidden Reactions

Photochemical Dissociation of Formaldehyde

1. Optimize the following structures employing the 6-311G* basis, and visualize the both the valence and lowest unoccupied orbitals for $H_2C=O$, H_2, and CO.
2. Investigate the orbital symmetry of the molecular orbitals with respect to the operations of the C_{2v} point group, and classify the valence and lowest unoccupied orbitals according to their irreducible representations using the following symmetry operations:

   - Identity (E)
   - two-fold rotation axis (C_2)
   - mirror plane (xz)
   - mirror plane (yz)

   Draw an MO correlation diagram, using C_{2v} symmetry, for $H_2C=O$ (left side) transforming to H_2+CO (right side).

   Connect those orbitals which belong to the same irreducible representation.
3. Repeat Step #2 for C_s symmetry with the symmetry elements Identity (E) and mirror plane (σ).

   There are two possibilities for the orientation of formaldehyde in this point group. What should attract your attention?
4. Determine whether C_{2v} or C_s symmetry, would yield an allowed photochemical decomposition of H_2CO to $H_2 + CO$ products.

   The axis used to show decomposition and the C_{2v} character table are shown in Figure 6 and Figure 7, respectively:
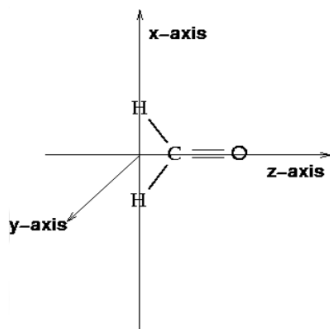

Figure 6: Coordinate System for $H_2C=O$·

C_{2v}	$\mathbf{E}$	$\mathbf{C_2}$	$\sigma_{\mathbf{xz}}$	$\sigma_{\mathbf{yz}}$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Figure 7: Character Table for the C_{2v} Point Group.

5. Another problem involves the transition state for H_2 dissociation in formaldehyde. Molecular hydrogen dissociation in formaldehyde presents a difficult case for determining an initial structure for the transition state.

   Make a reasonable guess for a transition-state geometry, and then perform a transition-state optimization for this initial transition-state geometry.

   Once a transition state is obtained, a calculation of vibrational frequencies for the proposed transition state structure should produce one imaginary frequency.

Comments

1. Make sure that there really is a transition state and not a reactive intermediate.

   If the transition state is a minimum, find the transition-state structure between reactant and product, and the transition state structure for dissociation.

2. Using whatever transition state you determine to be relevant, calculate the Kinetic Isotope Effect (**KIE**). It is possible to use a calculated $\Delta G^{\ddagger}$ to predict a unimolecular rate constant, k_i by using the equation

$$k_i = \frac{k_{\mathrm{B}}T}{h}e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

   where k_B is the Boltzmann constant, and $\Delta G^{\ddagger}$ is the free energy of activation.

   Rates of reaction are determined, in part, by the energy barrier for the reaction ($\Delta G^{\ddagger}$) which involves changes in both the potential energy surface and the zero point energy.

$$\Delta G^{\ddagger} \approx (\mathrm{PE}^{\ddagger} - \mathrm{PE}_{\mathrm{Reactant}}) + (\mathrm{ZPE}^{\ddagger} - \mathrm{ZPE}_{\mathrm{Reactant}})$$

   Calculated values of $\Delta \mathrm{H}^{\ddagger}$ and $\Delta \mathrm{S}^{\ddagger}$ can also be obtained.

   Since the zero point energy is isotope sensitive, the magnitude of the barrier may also be isotope dependent, and a kinetic isotope effect may be observed.

   The potential energy surface is the same for all isotopic derivatives, and the kinetic isotope effect for a reaction involving H-migration, including D-substitution, can be given as

$$\frac{k_H}{k_D} = e^{-\frac{(\Delta \mathrm{ZPE}_{\mathrm{H}} - \mathrm{ZPE}_{\mathrm{D}})}{RT}}$$

   It is possible to calculate the kinetic isotope effect, $\frac{k_H}{k_D}$ at different temperatures for a reaction, e.g. 00 K, 320 K, and 340 K, and then compare calculated values of **KIE** to the experimentally derived one.

3. Calculate the Intrinsic Reaction Coordinate (**IRC**) pathway from reactants to products.

   The **IRC** is related to the minimum energy path (**MEP**) which is defined as the steepest descent path starting from the TS and going in either the backward direction (i.e. to reactants) or forward direction (i.e. to products).

   Following this path can indicate if a TS was found that connects the two minima of interest.

4. Determine if the errors seem reasonable given the method and basis set used. Correct your electronic energies by performing single point calculations using B3LYP + a higher level basis set.

   Are things improved by comparison to experiment?

5. While it is always possible that deviations between theory and experiment represent inaccuracy in the modelling, what physical effects might be responsible for differences between theory and experiment?

Quick Reminders with Respect to Gaussian 09

- If you enter geometric or basis set data in a G09 input file, as opposed to reading it from the checkpoint file, end the input file with a blank line.

- To find transition states in the absence of a symmetry constraint, use **opt=(ts,calcfc)**.

  If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS structure breaks the symmetry, in which case, use neither **ts** nor **calcfc** as keywords. If you preserve symmetry, then use both key words.

  If you are looking for a TS, you may often find it helpful to use **opt=(ts,calcfc,noeigentest)**. The other keywords besides **ts** request calculation of analytic force constants on the first step (**calcfc**), and that the job not die if other than exactly one negative force constant is found at some step (**noeigentest**).

- You can save a lot of time by using useful information from previous calculations stored in the checkpoint file. Plan your calculations to try to save time. You can also save a lot of time by using symmetry when appropriate.

- The keywords **guess=read** and **geom=checkpoint** get the wave function and geometry, respectively, from the last completed calculation. So, if you have just performed an optimization, and want to follow-up with a frequency calculation, you will certainly want to use these keywords.

  If you know ahead of time that you will want frequencies after a given optimization, you can simply include the **freq** keyword in the same job as **opt**.

  Note: Frequencies must be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!

- If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include the keyword **opt=(readfc)**, or **opt=(ts,readfc)** for a second pass at a transition-state optimization. This causes G09 to start with the force constants from the previous calculation, which is efficient.

  It is usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.

- An example of the G09 keyword for IRC is **irc=(forward,maxpoints=20,stepsize=10)** which means to take 20 steps in the product (forward) direction from the TS.

- The **freqchk** utility of G09 may be used to rerun the thermochemical analysis from the frequency data stored in a Gaussian checkpoint file.