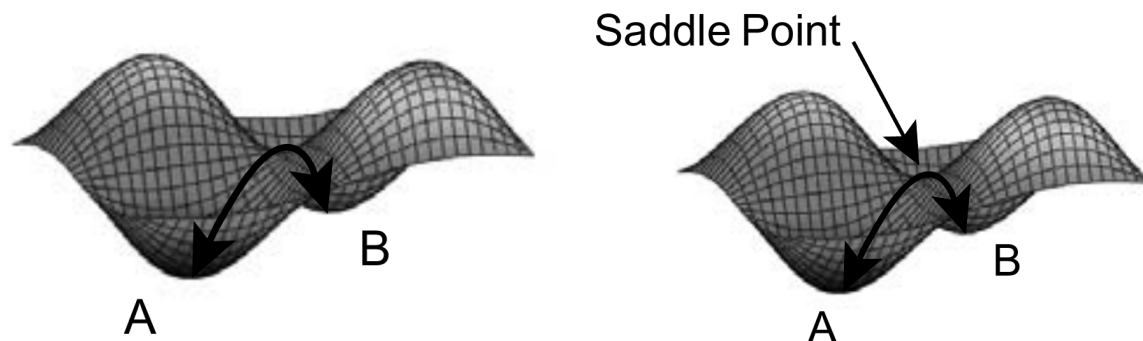


Potential Energy Surface (PES), Transition State, Saddle Point, Reaction Pathway

For the reaction



a PES might look like the following:



- 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.
- There is one imaginary frequency at the saddle point.
- A **transition state** is defined as the geometry at the peak of the free energy (G) profile while a **transition structure** defines the geometry at the peak of the potential energy (E) profile.

Rate Constants

Transition State Theory

According to Transition State Theory, the rate constant, k , is given by the following equation:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

where $\Delta G^\ddagger = G(\text{transition state}) - G(\text{reactant})$, and $\frac{k_B T}{h}$ is the Transmission Coefficient which has values between 0.5 - 2. There is also the possibility of re-crossings (reflecting back over the transition state) as well as quantum-mechanical tunneling.

Arrhenius Theory

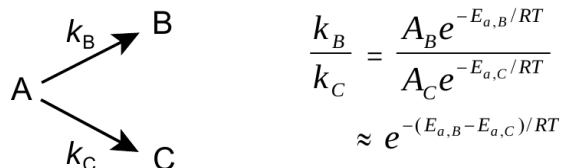
The rate constant, k is given by:

$$k = A e^{-\frac{E_a}{RT}}$$

where $E_a = E(\text{transition state}) - E(\text{reactant})$, and A is obtained from hard-sphere collision theory.

Relative Reaction Rates

As an example, consider the relative rates of reaction for ortho/para in electrophilic aromatic substitution reactions. The following calculations can be performed:



If $E_{a,B} - E_{a,C} \sim 2$ kcal/mol, then at 25 C°, $\frac{k_B}{k_C} = \frac{1}{29}$.

Transition States

A transition state is a first order saddle point on a potential energy surface (PES). 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, a vibrational frequency calculation must be performed at the same computational level as for the geometry optimization.

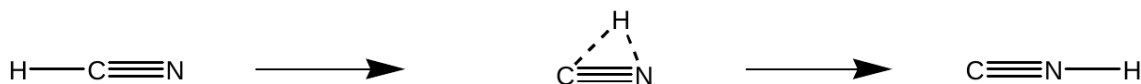
The normal mode corresponding to the imaginary frequency in the transition state usually reflects the change in geometry in going from reactants to products. There are more advanced techniques to verify if the transition state connects reactants and products which will be discussed later.

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, this exercise 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.

Isomerization of $\text{H}-\text{C}\equiv\text{N}$ to $\text{C}\equiv\text{N}-\text{H}$

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



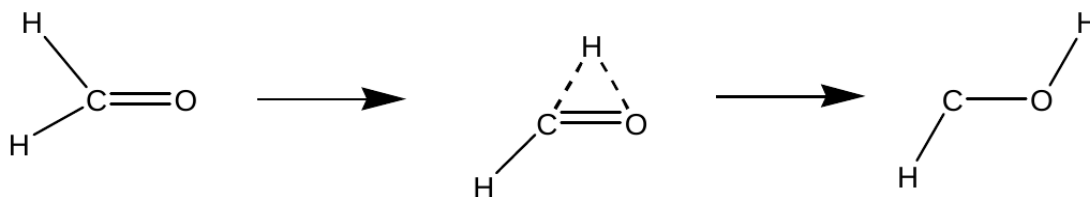
In this case, the minima of $\text{H}-\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{N}-\text{H}$ can be obtained in the usual fashion and verified as minima by calculating vibrational frequencies. Next, provide a reasonable estimate of the transition state geometry by changing the HCN angle from 180° to about 60°, but the H-C and N-H bond distances should be elongated as well.

To calculate a transition state, the OPT=TS and FREQ options should be selected. Calculating a transition state always the calculation of vibrational frequencies, because one has to verify that there is precisely one imaginary frequency. After the calculation finishes successfully, the vibrational frequencies can be viewed, One frequency

should be imaginary, and the corresponding normal mode represents the hydrogen migration. Also, examine the other normal modes in the transition state. Finally, locate the energy of reactants, products and transition state in the respective *.log files.

Hydrogen Migration in Formaldehyde

Another example involves the transition state for hydrogen migration in formaldehyde



First optimize the reactants and products. Then, guess a transition-state geometry. It is required that the force constant matrix have one negative eigenvalue at your initially specified geometry for the transition state. If this is not the case the program stops. If a message such as *Wrong number of Negative eigenvalues: Desired = 1 Actual = 2* appears, which indicates the initial geometry is too far from the transition state. One might modify the initial geometry guess, or use the option `OPT=(TS,NoEigenTest)`. This is often counterproductive, as it avoids the test that indicates an initial guess is not good enough. But, it might allow the ability to find a better guess for the transition state. If you have succeeded in calculating a transition state, a calculation of vibrational frequencies for the transition state structure should produce one imaginary frequency.

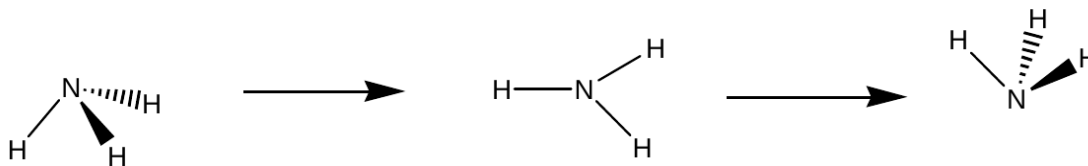
Intrinsic Reaction Coordinate

One more feature that can be very useful when examining transition states, the Internal Reaction Coordinate (IRC) is related to the minimum energy path (MEP), which 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 you really found the transition state that connects the two minima of interest. The IRC is defined in terms of mass-weighted Cartesian coordinates and it has a well defined step length. Computationally, once a transition state is found, it is possible to restart from the checkpoint file (name.chk) and perform an IRC.

By default, six small steps are taken in either direction. Specify more steps, or increase the step size (default=10 steps in units of $0.01 \text{ amu}^{1/2}\text{-Bohr}$). by employing on the command: `IRC=(StepSize=30)`.

Inversion of Ammonia, NH_3

As a very simple example, consider the inversion of ammonia, which proceeds through a planar D_{3h} transition state.

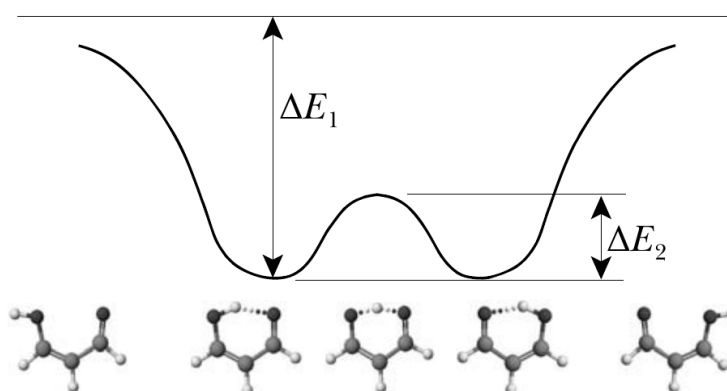
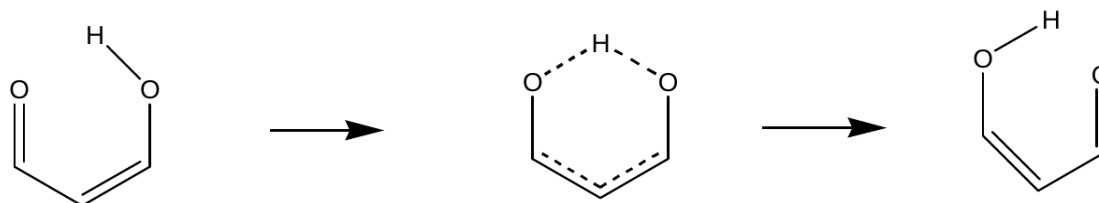


Optimize both the ground state and the transition state using simple optimization (imposing the proper symmetry) and calculate vibrational frequencies. Locate the single imaginary frequency and examine the corresponding normal mode. Verify that it corresponds to the inversion mode.

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.

As another example of the use of symmetry in transition state searches calculate the ground state and transition state for hydrogen transfer in the enol form of malonaldehyde

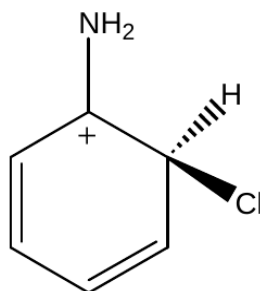


PES for proton transfer in malonaldehyde enol which is similar to that for malonaldehyde above.

The ground state has C_s symmetry while the transition state has C_{2v} symmetry. Please note that the normal mode corresponding to the transition state breaks the symmetry (any non- A_1 normal mode will reduce the symmetry). Searching for the minimum will work, if the structure is initially specified as C_{2v} geometry. With $C_{C_{2v}}$ symmetry specified, one can simply optimize to a minimum, and immediately calculate frequencies. Verify through measurements that the structure is indeed symmetrical, and that the negative (i.e. imaginary) frequency corresponds to hydrogen migration.

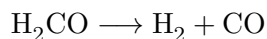
Additional Examples of Transition States

1. It is interesting to explore electrophilic aromatic substitution. The following structure is an intermediate (i.e., a minimum) for the ortho-addition of Cl^+ to aniline



First, optimize this structure, which is a minimum on the PES and, therefore, has no imaginary frequencies. There is a transition state in which Cl^+ approaches aniline, and bridges between carbon atoms 2 and 3 (the $\text{C}-\text{NH}_2$ is numbered carbon 1). Another transition state develops when H^+ leaves the chlorine substituted species, and locates on top, and in between, carbons 2 and 3. The transition state is similar to connecting the chlorine and hydrogen shift reaction products. Locate both transition states, using whatever tools necessary.

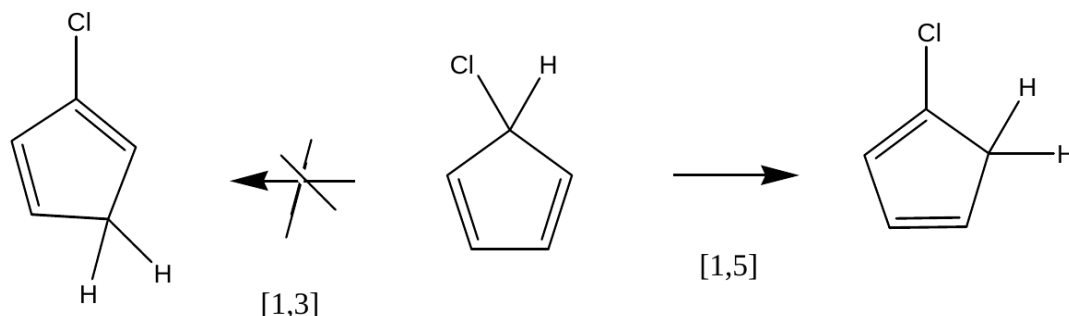
2. Optimize *cis*- and *trans*-butadiene, and make a guess for the transition structure, by taking a dihedral angle of about 90 degrees. Locate the transition state, using the OPT=QST3 option, calculate vibrational frequencies, and then perform an IRC calculation which shows the path connecting the *cis* and *trans* structures. Use a StepSize of 30 and sufficient steps to unambiguously establish the reaction path.
3. Find the transition state for the reaction



by making a guess for the transition state. Also, calculate the energies of reactants and products. Compare this transition state with previous results for the transformation $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ and its transition state. Make an energy profile, listing all minima and the transition states that connect them. Perform an IRC calculation for both reactions, and verify that the proper transition states are obtained.. List the relevant geometrical features and total energies in a table.

To make this a more meaningful calculation, it is necessary to include zero point energy effects.

4. Consider both [1,5] and [1,3] sigmatropic shifts in cyclopentadiene. level of theory.



Find the transition state for the [1,5] sigmatropic shift. Also plot the orbitals that are involved in the hydrogen transfer reaction at all stages in the reaction (reactants, products and transition state). You will see that the [1,5] shift is suprafacial. The [1,3] shift would require an antarafacial hydrogen migration and this can be clearly seen by examining the orbitals for the reactant. Try to find a transition state for the [1,3] shift and locate the transition state. Explain what happened during your search. Obtaining The [1,3] transition-state structure is a difficult problem.