
Calculations of reaction mechanism and rate

This lab session involves calculations of the minimum energy path (MEP) for two chemical reactions. The displacement along the MEP is often chosen as the reaction coordinate. The point of highest energy along the MEP gives an estimate of the activation energy of the transition within the harmonic approximation to transition state theory. It corresponds to a first order saddle point on the energy surface characterizing the system. The most challenging part of a calculation of a reaction rate is finding the relevant saddle point. The matrix of second derivatives of the energy, the Hessian matrix, has one and only one negative eigenvalue at a first order saddle point. The eigenvector corresponding to the negative eigenvalue shows how the atoms move along the MEP at the transition state, the bottleneck for the transition. The vibrational frequencies are proportional to the square root of the eigenvalues of the Hessian, so the vibrational frequency associated with the negative eigenvalue is an imaginary number. The ORCA output, however, reports it as a negative number with the tag `***imaginary mode***`. We will thus refer to it as negative frequency here. The corresponding eigenvector is often referred to as the unstable mode since in this direction the energy is at a maximum at the saddle point, while it is at minimum along all the other vibrational modes.

The mechanism and the reaction rate of two reactions will be calculated: the isomerisation of HCN and pyrolysis of ethyl formate. The MEP is found using the nudged elastic band (NEB) method as implemented in ORCA. Given the local energy minima corresponding to the reactant and product states, an initial path connecting the two is generated in some way and represented by a set of replicas of the system ($\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_N$ where \mathbf{R}_i is a 3-N dimensional array containing the coordinates of the system). The replicas provide a discrete representation of the path and are often referred to as *images* of the system. The NEB method then provides a way to adjust the location of the images so as to bring them to the nearest MEP. The distribution of images along the path is controlled by adding fictitious spring forces that act only in the direction of the path.

Q1: Write an expression for the effective NEB force acting on an image and explain it is important to have an estimate of the tangent to the path.

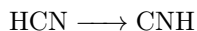
Q2: If two MEPs exist connecting a given pair of reactant and product energy minima, to which one will the NEB converge?

Q3: Often, saddle points are referred to as transition states. Why is that strictly not correct?

The energy of each image and force acting on the atoms can be calculated using any electronic structure method that provides the energy and gradient of the energy. The calculations can be done in parallel since the evaluation of the energy and gradient of each images is independent. However, the calculations will be carried out in serial here using a recently developed tight-binding model, the GFN-XTB (Keyword in ORCA: XTB) because of technical difficulties with the implementation of ORCA on Jotunn. XTB is a semi-empirical method based on the PBE exchange-correlation functional. Note that you need to use numerical frequencies for the calculations of vibrational frequencies at all stationary points throughout this exercise, keyword in ORCA: 'NUMFREQ', since analytical second derivatives are not available for this method.

A. Isomerisation of HCN

The isomerization reaction of hydrogen cyanide to isocyanide is



Before starting the NEB calculations, find the local energy minima corresponding to the reactant and product states. Take the reactant to be HCN and the product to be CNH. Optimize the two structures by minimizing the energy using the electronic structure method GFN-XTB (Keyword: 'XTB'). After the calculation of the reactant and product energy minima has completed, the NEB calculation can be prepared. Remember that the optimized configuration of the atoms after an energy minimization are placed in a file called 'orca.xyz'.

Before starting a NEB calculation it is important to **make sure that the ordering of the atoms in the two configuration files is the same**, i.e. there is a one-to-one mapping of atom indices between the reactant and product energy atom configurations. That is, atom 1 in the reactant configuration will move to the position of atom 1 in the product configuration, etc.

Two different ways of constructing the initial path will be used to illustrate how it can affect the efficiency of the NEB calculation and possibly even the MEP that is obtained, namely

- linear interpolation in Cartesian coordinates between the reactant and product configurations,
- image-dependent pair potential (IDPP) interpolation, which is a closer to the MEP.

The simple-input-line keyword for NEB calculations in ORCA is 'NEB'. Furthermore, there is an additional 'neb' block where you can control several aspects of the NEB calculation. It contains various parameters that allow the user to customize the calculation. Only some of the more important parameters are discussed below.

The keyword 'nimages' specifies the number of intermediate images in the path (in addition to the two end points) and the keyword 'interpolation' specifies which interpolation method is used to generate the initial path. The keyword 'neb_end_xyzfile' specifies the configuration file for the product state. The reactant configuration should be placed within the geometry block. Make sure that the reactant and product configurations are in fact local energy minima computed at the same level of theory as is specified for the NEB calculation.

Create two individual ORCA input files for the two NEB calculations using linear interpolation and IDPP. Both calculations should use 5 intermediate images, as shown in the following example:

```
!XTB NEB

%nep
nimages = 5
interpolation = linear
neb_end_xyzfile = "your_product_file.xyz"
end

*xyz 0 1
...
*
```

Copy and use the jobscript: 'jobscriptneb.sh' from '/home/via9/jobscriptneb.sh' to your working directory and submit the calculation to the queue. After the two NEB calculations have finished, inspect the minimum energy paths, the progress of the optimization and the convergence of the calculations, as described below. A python script has been prepared and stored at /home/via9/neb_path.py for this purpose. When you execute this script in your working directory, a sub-directory named 'neb_frames' will be generated containing two graphs ('.png') that show how (i) how the calculation progressed and (ii) the minimum energy path (relative energy as a function of displacement). The script requires the 'orca.interp' file as an input argument. You can execute the script, using the following command; »> python neb_path.py". Notice how the potential energy barrier and the atomic forces decrease as the calculation progresses.

It is important to run each NEB calculation in a separate directory. Otherwise, important files may be overwritten. Also, remember that the results of the calculation are written to temporary directories. Therefore, the files will not be visible until the calculation is complete and the files are copied back to the 'login/main' node.

Q4: *How large is the energy barrier for the isomerisation reaction of hydrogen cyanide? How does the barrier height compare to the thermal energy available at room temperature?*

Q5: *How do the two NEB calculations started from the two initial paths compare in computational efficiency, i.e. in number of optimization steps and the number of times the energy and gradient of energy need to be evaluated? Explain the difference.*

Q6: *Make a graph of the minimum energy path (show the relative energy as a function of displacement along the MEP)*

The NEB optimization algorithm will bring the images to the minimum energy path. But, the highest energy image will not necessarily be at the saddle point, the most important point along the path. With a slight modification of the NEB algorithm, the highest energy image can be made to converge rigorously on the saddle point by forcing it to climb up in energy along the path. This is the so-called climbing image and the algorithm is referred to as CI-NEB method.

Now perform a CI-NEB calculation for the $\text{HCN} \rightarrow \text{CNH}$ reaction. Change the 'NEB' keyword in the simple-input-line to 'NEB-CI'. Since the convergence of the climbing image to the saddle point is more important than the convergence of the other images to other points on the MEP, it is reasonable to save computational effort by setting a tight convergence only on the climbing image. This can be done by using the keyword 'convtype' and set it to 'cionly'.

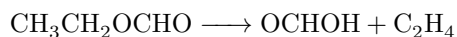
To check whether a first order saddle point has indeed been found, calculate the vibrational frequencies at the saddle point configuration. A saddle point of order n has n negative eigenvalues. A negative eigenvalue corresponds to an imaginary frequency and an unstable mode, i.e. one where the force pushes the atoms away from the configuration. If more than one imaginary frequency is in the list of frequencies, then the optimization has not converged well enough to the saddle point and the calculation needs to be carried out with a tighter tolerance on the atomic forces. Chemcraft can be used to animate the vibrational modes. The unstable mode at a first order saddle point corresponds to the reaction coordinate at the transition state.

Q7: *How does the energy barrier obtained from the CI-NEB calculation compare with the one obtained from the regular NEB? Include a picture of the CI-NEB saddle point geometry in your report (stored in the file `orca_NEB-CI_converged.xyz`).*

Q8: *Describe the reaction coordinate at the transition state, i.e. the atomic motion involved in traversing the saddle point along the unstable mode.*

B. Pyrolysis of ethyl formate

Pyrolysis of ethyl formate is represented by the chemical equation



The task is to find the saddle point and estimate the reaction rate using harmonic transition state theory (HTST).

To generate the reactant configuration, build the ethyl formate molecule using Chemcraft. Optimize the structure using the semi-empirical GFN-XTB method. Make sure the calculation has converged to within the given tolerance. If not, carry out another optimization calculation starting from the previous output configuration. Remember to compute the vibrational frequencies and verify that a minimum has been found by inspecting the vibrational frequencies and the atomic forces. All reported vibrational frequencies should be positive, corresponding to positive eigenvalues of the Hessian.

To generate the product configuration (i.e., the two separated product molecules OCHOH and C_2H_4) use Chemcraft to modify the optimized reactant configuration. Move one of the methyl H atoms to the neighboring oxygen atom. Break the bonds and move the ethylene fragment slightly away from the formic acid. Optimize the geometry of the system with the same methodology as before. After the optimization has finished, make sure the calculation converged to a minimum, i.e. that the atomic forces are small enough

and the vibrational frequencies are positive.

To identify the saddle point, use the NEB-TS method. In NEB-TS, the CI-NEB method is first used to partially converge towards the minimum energy path and the climbing image moves close to the saddle point. This approximate saddle point is then used to initiate a subsequent eigenvector-following calculation to converge rigorously on the saddle point. Note that eigenvector-following methods require less computational effort than path-optimization methods (such as NEB), since only one configuration of the atoms is optimized and converged to the saddle point. However, eigenvector-following methods tend to require an initial configuration that is already close to the desired saddle point. Therefore, it is efficient to combine the two classes of methods, where CI-NEB is first used to obtain information about the shape of the MEP (possibly identifying intermediate minima and more than one saddle point) while a tight convergence on the most relevant saddle point is obtained using eigenvector-following method.

Create an ORCA input file for a NEB-TS calculation using the simple-input-line keyword 'NEB-TS' and submit. An example input file is:

```
!XTB NEB-TS

%nneb
neb_end_xyzfile = "prod.xyz"
nimages = 5
end

*xyz 0 1
...
```

Monitor the progress of the calculation. As usual, make sure convergence is reached and re-submit the optimization as necessary. Remember to compute the vibrational frequencies at the end. If a stationary point has been reached (i.e. zero atomic force) and only one negative frequency is obtained, you have located first order saddle point!

Q9: Describe the reaction coordinate at the transition state, i.e. which atoms are moving mostly and how.

Q10: Make a graph of the energy along the MEP. Show the atomic configurations at reactant, product and saddle point as insets in the figure.

Q11: Briefly discuss/explain transition state theory (TST). What are the four basic assumptions of TST? What are some of the challenges of applying TST to molecular reactions?

Q12: What is the harmonic approximation to TST (HTST)? When is it a good approximation?

Q13: Calculate the rate constant of the pyrolysis reaction using HTST assuming (a) room temperature and (b) a temperature of 1000 K.

Appendix: relevant output files

Information regarding the output files from a converged and/or partially converged NEB (and CI-NEB) calculations:

- File: 'orca.HEI-NEB_converged.xyz'. The highest energy image configuration along the MEP in a converged NEB calculation.
- File: 'orca.CI-NEB_converged.xyz'. The climbing image configuration in a converged CI-NEB/NEB-TS calculation.
- File: 'orca.NEB-TS_converged.xyz'. The TS configuration in a converged NEB-TS calculation.
- File: 'orca.allxyz'. File that is used to restart NEB calculations and includes the configurations of the images.
- File: 'orca_MEP_ALL_trj.xyz'. Includes the configurations of each image, for each step along the optimization.
- File: 'orca_initial_path.trj'. Configurations of the initial path generation.
- File: 'orca_MEP.trj'. MEP configurations in a converged NEB calculation.
- File: 'orca.interp'. Includes the energy profile for each step along the optimization.
- File: 'orca.log'. Important information about each step of the optimization is printed into the log file. This includes e.g. energy, forces, step size and angles between images.