Lecture 12:  
Path Optimization Calculations

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Reaction Paths

▸ Calculations for **minimum energy paths** are widely used in chemistry, physics and materials science

▸ Typical examples are migration paths for defects in a solid or on a surface and chemical reactions

▸ When the minimum energy path is known, the rate of occurrence for the related events can be easily calculated from the energy by the Arrhenius equation:

\[
\Gamma = \nu_0 \exp\left[-\frac{E}{k_B T}\right]
\]  

(1)

where \( \nu \) is an attempt frequency, such as a typical frequency for lattice vibrations in the case of defect migration (see [Landauer & Swanson, Phys. Rev. 121, 1668–1674 (1961)] for a theoretical analysis on \( \nu \)) and \( E \) is the activation energy
In a two-dimensional case, the most simple example is given by two energy minima with a saddle point in the middle.

In principle, such processes can be studied with the MD method, as will be explained below.

However, if the barrier is too high, the processes are so slow that they won’t be observed during MD time scales at reasonable temperatures.

Therefore, we need a method which allows calculating these energy barriers without carrying out a dynamical simulation.

**Transition State Theory**

In the case of rare events, one can use the **transition state theory** (TST) to study reaction rates.

According to TST, the reaction rate is

$$
\Gamma = \left( \prod_{j=1}^{N} \nu_j \right) \left( \prod_{j=1}^{N-1} \nu'_j \right)^{-1} e^{-E/k_B T}
$$

(2)

where $\nu_j$ and $\nu'_j$ are the vibrational frequencies at the initial potential minimum and at the saddle point, respectively.
The saddle point is associated with one less frequency, because there is one direction in which the system is driven away from the saddle point rather than towards it.

It is typical, at least in solid state physics calculations for defect migration to simply assume that the frequencies can be described by just one material-dependent vibrational frequency $\nu_0$.

Values are often in the range of $\nu_0 \approx 10^{12} \text{ s}^{-1}$.

Now, if we can follow the system over a period of time and observe the reaction rate, we can calculate the reaction path energy barrier $E$.

On the other hand, if we know the barrier, we can calculate the reaction rate without carrying out the (maybe impossibly long) dynamical simulation.

The barrier energy is defined as the potential energy difference between the saddle point and the initial energy minimum.

Schematic presentation of the energy barrier
Locating the minimum energy reaction path (MEP)

- There are several methods for finding the minimum energy path and calculating thus the energy barrier

- These methods include at least the following [Wikipedia]

  - **Synchronous Transit** The linear synchronous transit (LST) method generates an estimate of the transition state by finding the highest point along shortest line connecting two minima. A quadratic synchronous transit method (QST) extends LST to subsequently search for a minimum along a line perpendicular to the previous one. The path connecting minima and the found point may then be searched for a saddle point (a maximum).

  - **Nudged elastic band** NEB works by guessing the MEP which connects the two stable structures. A discrete number of structures (images) are placed along the guessed path. These images are moved according to: (A) the force acting on them perpendicular to the path and (B) an artificial spring force keeping the images spaced along the path. The highest energy image gives a good estimate of the transition state.

  and:

  - **String method** The string method is similar to the NEB. It also involves a series of images along a guess of the MEP, but in this case the images are moved in two steps. Firstly, the images are moved according to the force acting on them perpendicular to the path. Using an interpolated path, the images are moved short distances along the MEP to make sure they are evenly spaced.

  - **Dimer method** The dimer method can be used to find possible transition states without knowledge of the final structure or to refine a good guess of a transition structure. Thus, it is fundamentally different from the above methods. The “dimer” is formed by two images very close to each other on the potential energy surface. The method works by moving the dimer uphill from the starting position whilst rotating the dimer to find the direction of lowest curvature (ultimately negative).

- Of these, only NEB will be discussed during this lecture due to its popularity
As mentioned above, NEB starts by a guessed MEP which is generated as a set of images along the path.


Simplest way of generating the guessed MEP is, obviously, direct interpolation between the two configurations.

For the true MEP, all the forces acting on the atoms are along the MEP.

The reaction coordinate is the relative distance along the MEP.
- MEP often has one or more local minima in addition to the saddle point maximum and the minima of the end points
- These correspond to stable intermediate structures
- For estimating the actual reaction rate $\Gamma$, it is critical that the real maximum is found along the MEP instead of one or more possible lower maxima
- Spring interaction between the images along the MEP ensure continuity of the path
- Hence, the system resembles an elastic rubber band

- Optimizing this band, involving minimizing the force, brings the band to the MEP
- What distinguishes NEB from string method and other elastic band methods is a force projection which ensures that the spring forces do not interfere with the convergence of the elastic band to the MEP
- This also ensures that the true force does not affect the distribution of images along the MEP
- By estimating the tangent of the path at each image, the force can be separated into two components: perpendicular and parallel to the MEP
The force components which are included in the calculation are:
- Perpendicular component of the true force
- Parallel component of the spring force

This separation of the forces is called “nudging”

As a result of the nudging, the spring components only control the spacing of the images along the band

The only adjustable parameter in the method is the spring constant

In the original work, the authors mention that it can be varied by several orders of magnitude without affecting the MEP

**NEB Algorithm**

- The elastic band with $N + 1$ images can be denoted by

$$[R_0, R_1, R_2, \ldots, R_N] \tag{3}$$

- End points $R_0$ and $R_N$ are fixed and given by the energy minima corresponding to the initial and final stages

- The $N - 1$ middle images are adjusted by the optimization algorithm

- As mentioned before, the force acting on the images is

$$F_i = F^S_i \| - \nabla \mathcal{U}(R_i) \| \tag{4}$$

- The true force is given by

$$\nabla \mathcal{U}(R_i) \| = \nabla \mathcal{U}(R_i) - \nabla \mathcal{U}(R_i) \cdot \hat{r}_i \tag{5}$$
The $E$ is the energy of the system as a function of all coordinates, and $\hat{\tau}_i$ is the normalized local tangent at image $i$.

The spring force is

$$F_{S,i} = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \cdot \hat{\tau}_i \quad (6)$$

where $k$ is the spring constant.

An optimization algorithm is used to move the images according to the force $F_i$.

In principle, any optimization algorithm can be used, e.g., conjugent gradient method.

In the original work, the authors used velocity Verlet algorithm.

The spacing between the images is determined by $k$, and is thus a constant along the band if $k$ is not varied.

Therefore, it should come as no surprise that none of the images typically occur at the saddle point.

Thus, the saddle point energy has to be interpolated from the results.

Even if carried out with care, the interpolation can result in large errors in the results.

Luckily this problem can be solved by a rather small modification to the NEB algorithm.
Within the climbing-image NEB, the path of the MEP is not changed, but a rigorous convergence to the saddle point is also obtained.

Also, it doesn’t add a significant computational effort.

In CI-NEB, after a few iterations of NEB, the image with the maximum energy is determined: will go to the saddle point.

The force on this image is given by

\[ F_{i_{\text{max}}} = -\nabla U(R_{i_{\text{max}}}) + 2\nabla U(R_{i_{\text{max}}}) \cdot \hat{t}_{i_{\text{max}}}, \hat{t}_{i_{\text{max}}} \]

This is the full force due to the potential with the component along the elastic band inverted.

The maximum energy image is not affected by the spring forces at all.

So, the climbing image moves up the potential energy surface along the elastic band and down the potential surface perpendicular to the band.

Other images define the one degree of freedom for which the energy maximization is carried out.

Obviously, this method is much better than the standard NEB where one can never be sure about finding the actual saddle point.

FIG. 1. Density functional theory calculations of the minimum energy path for CH₃ dissociative adsorption on a Ir(111) surface. The dissociated H and CH₂ fragments sitting on adjacent on-top sites correspond to reaction coordinate of 0.0. The CH₃ molecule 4 Å away from the surface corresponds to 1.0. A regular NEB calculation and a climbing image NEB calculation are compared, both involving 8 movable images. The regular NEB results in a low resolution of the barrier, and the interpolation gives an underestimate of the activation energy. The climbing image NEB brings one of the images right to the saddle point and gives the activation energy precisely with insignificant additional computational effort.
Because the climbing image is not affected by the spring forces, the spacing between the images becomes non-uniform.

Since the saddle point is the most important point along the MEP, it would be better if the area around this point would be especially well sampled.

If the images get closer, the approximation of the tangent becomes better which leads to more accurate estimate for the saddle point.

The uneven sampling (tighter around the saddle point) can be achieved by using a variable spring constant.

One way to do this, used by the authors, has been to make the spring constant linearly dependent on the potential energy.

This will automatically lead to a better sampling of the important part of the MEP.

One possible choice for the variable spring constant is

\[ k'_i = \begin{cases} 
  k_{\text{max}} - \Delta k \left( \frac{u_{\text{max}} - u_i}{u_{\text{max}} - u_{\text{ref}}} \right) & \text{if } u_i > u_{\text{ref}} \\
  k_{\text{max}} - \Delta k & \text{else} 
\end{cases} \]

\( u_i = \max\{u_i, u_{i-1}\} \) is the higher energy of the two images connected by spring \( i \), \( u_{\text{max}} \) is the maximum value of \( u_i \) for the band, and \( u_{\text{ref}} \) is a reference value for the energy, e.g., the energy of the higher energy endpoint of the MEP.

Therefore, \( k \) is linearly scaled from a maximum value for highest energy images to a minimum value for images with energy of \( u_{\text{ref}} \) or lower.
Combining the methods

- Methods presented have different strengths and weaknesses
  - For example, climbing-image NEB is very efficient in finding the saddle point, but at the expense of poor resolution for the rest of the path, if the number of images (computational cost) is small
  - Thus, it can be useful to combine the methods, for example:
    1. Use a minimal (5-image) climbing-image NEB to find the saddle point
    2. Then use a cheap optimizer (e.g. stepwise descent, steepest descent) to calculate the MEP down towards the minima.

- Recent test shows this is superior in efficiency compared to NEB in the simple test system:


- How well the method works, depends on the complexity of the potential surface
Implementing the NEB method into an existing MD code is straightforward

The following steps are involved in the process:

1. Input the coordinates for all atoms in all images of the band, and construct a neighbor list without including atom pairs which belong to different images
2. Calculate the tangent $\hat{\tau}_i$
3. Add the calculation of the spring force
4. Modify the force routine to calculate only the perpendicular component of the force
5. Choose a force constant $k$

Run MD until the minimum force is reached

SUMMARY

Many processes require an activation energy for overcoming a barrier, e.g., defect migration and chemical processes

According to transition state theory, rate of occurrence for such rare events can be calculated if the characteristic vibrational frequencies and the energy barrier are known

MD can be used to evaluate the energy barriers if the simulation time is long enough for obtaining the rate, but this is often not possible

For such cases, methods for finding the minimum energy path (MEP) have been developed, e.g., the climbing image nudged elastic band method

In this method, a series of images created along a guessed MEP, joined by springs, and allowed to relax into the actual MEP by including only forces along direction perpendicular to the MEP tangent
Exam

- Tue 11.12.2012 at 10.00-14.00 (note the different time and place than lectures and exercises): Hall E207, Physicum

- Exam will include questions that can be
  1. Explanation of concepts
  2. Broader essay questions, e.g. for a given problem, what kind of tools could be used to solve it
  3. Simple calculations

- You do not need to remember the exact mathematical forms of different potentials or models. However, the basic forms and the theoretical basis of different models should be known

- No ‘real’ code writing will be asked in the exam.

- Preparation material: Lecture notes.