

Computational Chemistry I

Text book for the first part: Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 1. Total Energy (Cramer: chapters 1 and 2)

Introduction

This course will focus on computational chemistry. The first part of the course is related to Quantum Chemistry and the second part to Empirical Molecular Modelling. The Quantum Chemistry (QC) will focus mostly on the **electrons wave function** and **total energy** of the system. Most of the properties of a single molecule can be computed using QC but a group of molecules at finite temperature need some kind of dynamical simulations which can take the **entropy** into account. The dynamical simulations will use either Molecular Dynamics or Monte-Carlo simulations. These methods are mostly discussed in the second part of the course. The basics of electrons wave function and total energy have been discussed in course CHEM-E4100, Quantum Mechanics and Spectroscopy, which is a prerequisite for this course.

Total energy

Before going to the wave functions and Schrödinger equation we can first look what can be learned from the **atomic total energy**. We assume that the electrons are at their **ground state** so the total energy depend only on the atomic coordinates.

$$E_{tot}^{el}(R_1, \dots, R_N)$$

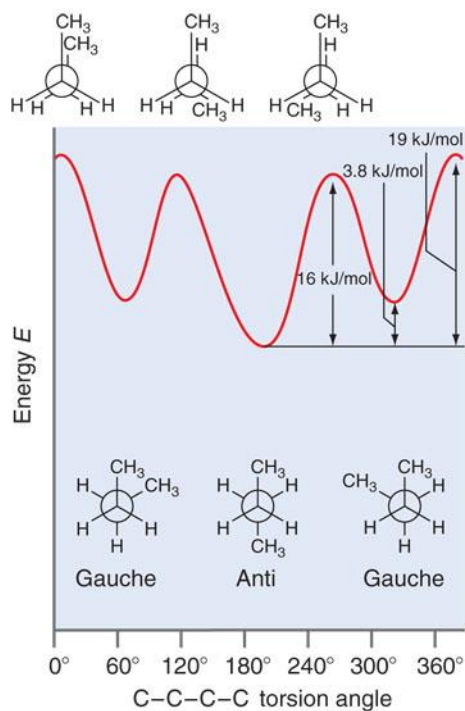
Here we have used the **Born-Oppenheimer approximation** in which we have assumed that the atoms are point-like from the point of

view of the electrons. Here we do not take into account the atomic wave functions. This is a very good approximation at room temperature and for all atoms except hydrogen. The atomistic quantum effects can be later taken into account using harmonic approximation near the minima of the total energy (This will be discussed later.) or using the Path-Integral Methods (not discussed in this course).

We can always compute the forces acting on each atom

$$F_I = -\frac{\partial E_{tot}^{el}}{\partial R_I} \quad \text{or} \quad F_I = -\frac{\Delta E_{tot}^{el}}{\Delta R_I} = -\frac{E_{tot}^{el}(R_I) - E_{tot}^{el}(R_I + \Delta)}{\Delta}$$

The first equation means direct derivative and the second a numerical derivative.



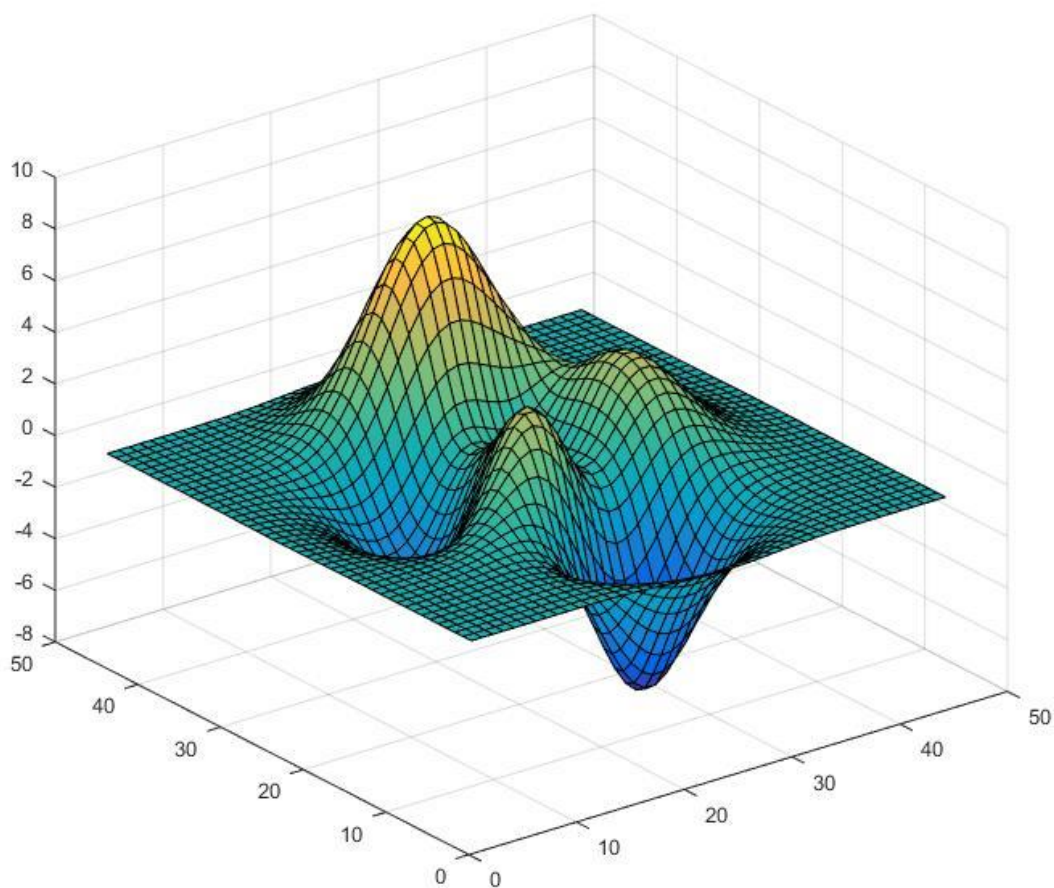
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Several minimization algorithms can be used to minimize the molecules geometry. We can easily find the nearest minima from the starting geometry. Often the molecule will have several **local minima**. In simple molecules we can find the minima rather easily but unfortunately the number of minima will increase rapidly when the size of the molecule increases. There is an estimation that a cluster of 55 atoms interacting with simple Lennart-Jones potential would have 10^{21} minima! (Of course most of them are not relevant but there is still a huge amount of relevant ones. Relevant means that a minimum has a low energy.) Note that the problem has **3N-6 dimensions**.

(In the case of non-linear molecule.

The -6 comes from the fact that we can fix the molecules center of mass, 3 coordinates, and its orientation, also 3 coordinates.) There is no general method to estimate the number of minima of a relatively large molecule but it is very high. For this reason, any computational research of large molecules like proteins is difficult or impossible if we do not have a good guess of the structure. To some extent, this is true for

solid materials too but still for most molecules we are interested in chemistry this is not a (big) problem.



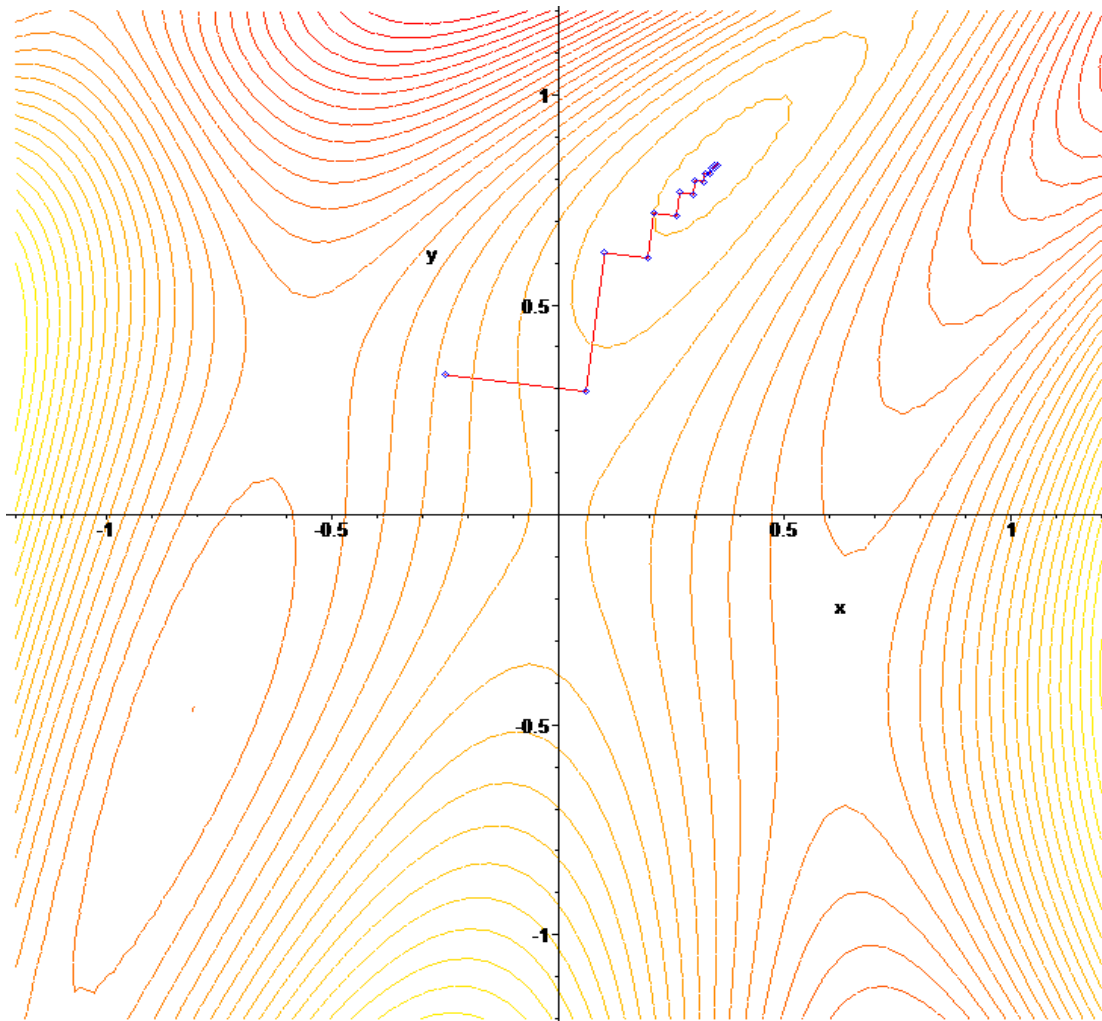
Minimization

The minimization is not actually a topic of this lecture but a very good book of it (and many other numerical methods) is W.H. Press et al. *Numerical Recipes*. In multidimensional minimization it is important to find good **minimization directions** in the multidimensional space. In given minimization direction a simple **1-D minimization is performed**. In 1-D minimization we need few energy (and force) calculations to locate a minimum. Most of the

algorithms are based on the assumption that near a minimum the energy is of form:

$$E(x) \approx c + \frac{1}{2} x \cdot A \cdot x$$

The simplest method is the Steepest Descent. In this method one starts from point x_0 and the minimization direction is taken from $-\nabla E(x_0)$. This will lead to a very inefficient method. Typically, there will be a large amount of minimization directions.



A better method is the Conjugate Gradient method where orthogonal optimization directions are constructed. (See the details from Numerical Recipes, or web.) Another type of methods are so called **quasi-Newton methods** where an iterative approximation of the inverse of matrix A is build, $\lim_{n \rightarrow \infty} H_n = A^{-1}$. A popular version of a quasi-Newton method is the BFGS method. (Broyden-Fletcher-Goldfarb-Shannon, see details from Numerical Recipes). At the moment the BFGS is one of the most used method. Note that the matrix A can be very big. It contain ca. $(3N-6)^2/2$ elements (it is symmetric). So for 200 atom molecule there is ca. 180 000 values so direct computation of A is very time consuming.

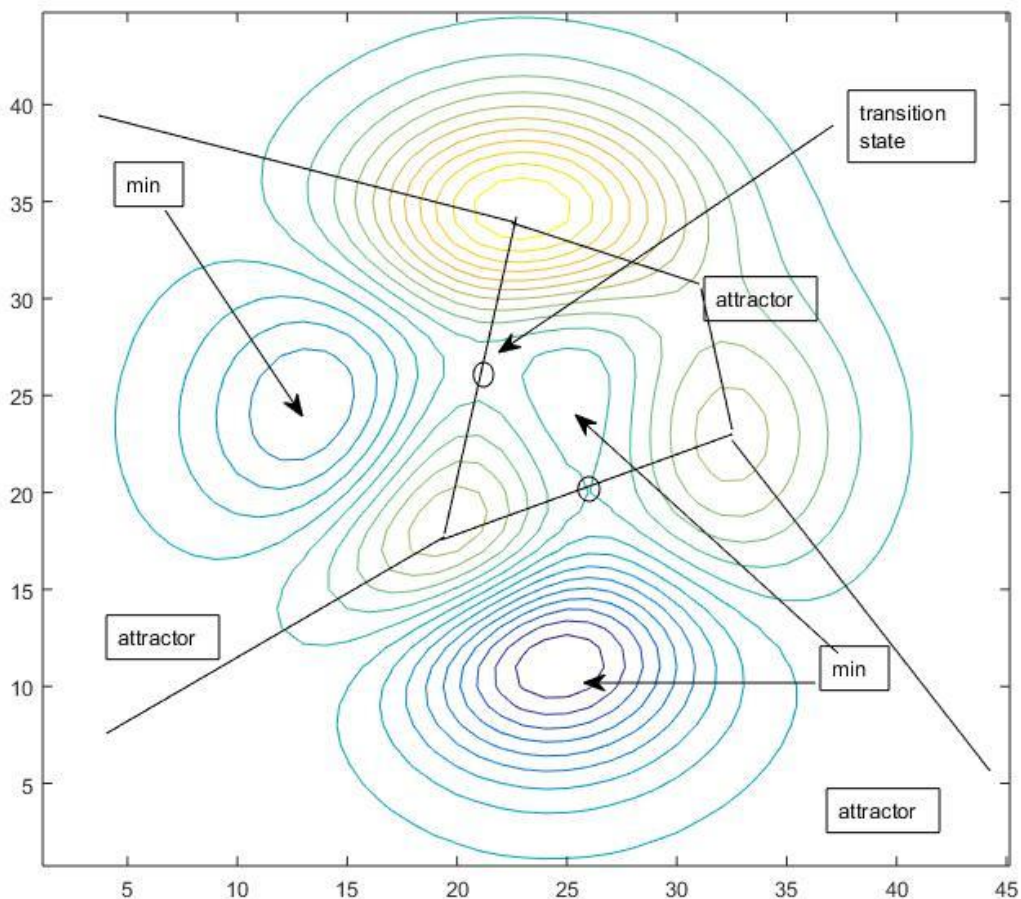


Figure: 2D map of a potential

The search of global minimum is very difficult. In general, the parameter space can be divided to volumes (in N-dimensions) which each corresponds to one minimum (see a figure above). From any point in this volume minimization will converge to minimum $\{R_n\}$. This volume is called an attractor of minimum $\{R_n\}$. In global optimization we try to find the best minimum. Usually there are so many minima that any direct search method is not possible. All effective global minimization algorithm use some **randomness**.

Genetic algorithm will present the system with binary "DNA" and it will make a new position by combining different position of old systems by choosing each new gene from either of the "parents". There is also some randomness of the new genes, "mutations". The choice of the parent gene is random and the new offspring is accepted if it has lower energy than the parents have. The details of the algorithm are rather complex.

https://en.wikipedia.org/wiki/Genetic_algorithm

The genetic algorithm is ideal for discrete problems but molecules have continuous variables. Usually the global optimization methods are accompanied with local optimization.

Another method is Simulated Annealing where Monte Carlo (or Molecular Dynamics) simulation is done and the temperature of the systems is slowly reduced. This is not very efficient method.

In chemistry we usually know the general structure of the molecule of interest.

Problem: how many molecules can be made from 6 C and 6 H's. (I do not know the correct answer.) Most of them are strange. What is very likely the lowest one?

Frequencies

In addition, the vibrational frequencies can be computed from the atomic total energy. The vibrations are computed as the **second derivative** of the total energy

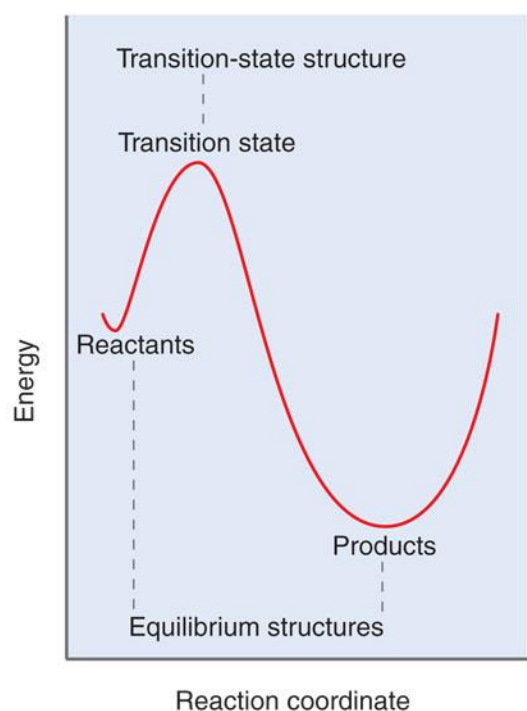
$$A_{IJ} = \frac{\partial^2 E_{tot}^{el}}{\partial R_I \partial R_J}$$

or using the finite difference method. From this matrix we can find the vibrational normal coordinates and the **vibrational eigenvalues**. The computations are rather easy, essentially we need to find the eigenvalues and vectors of matrix A. (We will come back to them later). The most demanding part is the calculation of the second derivative since the matrix A can be rather large.

The second derivatives are also useful for 1) determining that a found minimum is a true minimum (then all the frequencies are positive) and 2) computing the vibrational entropy of the system.

Transition states

In fact any property related to molecules structure can be



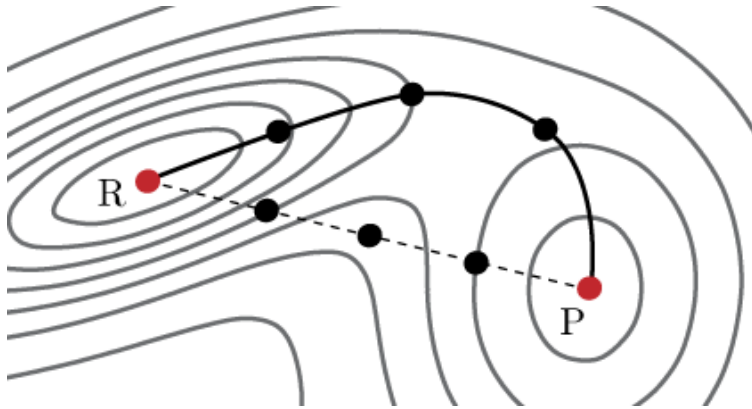
computed from the atomic total energy. One very interesting property is the chemical reactivity. Reactions equilibrium constant and reaction rate can be computed (but they are not very accurate). The reactants will have a certain lowest energy geometry, the transition state will have an other geometry and the products will again have some geometry. These geometries can be found and then the Reactant, Transition state and Product energies can be computed. The picture in left is very simple. In general case the problem has many dimensions, namely $3N-6$ (for non-linear molecules), but there is always one transition state between

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two near by minima. If the minimas are "far appart" there can be several transition states between them. See also Figure 2D Map. This illustrates the situation in 2D. The real situation is multidimensional and not drawable.

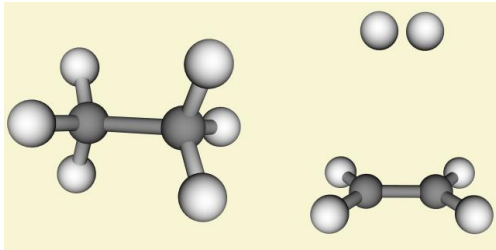
Unfortunately the relevant energy in chemical reactions is not the total energy but the **Free energy**, $F = H - TS$, so we need to estimate the **entropy**. For gas phase molecules and on surfaces this is easy (we need the molecular vibrations) but it is not easy in liquids.

The transition state search algorithms are more complex than minimization algorithms. There are several methods and here we consentrate to the NEB (Nudged Elastic Band) method. It is important to remember that points in these pictures always correspond to some real geometry of the atoms. In the NEB method a reaction path can be drawn as follows. In all practical calculations the energy is the electrons total energy, NOT the Free energy.



From: <http://www.quantumwise.com/documents/manuals/ATK-2008.10/chap.relax.html>

We can look a simple reaction like: $C_2H_6 \rightarrow C_2H_4 + H_2$

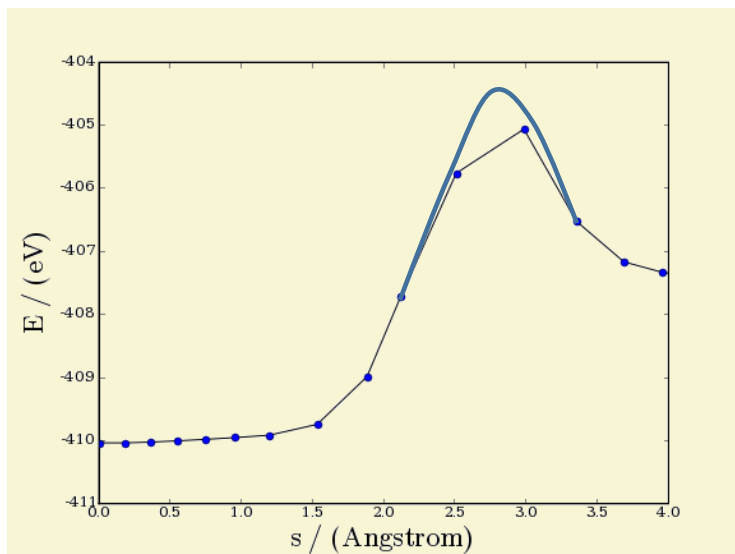
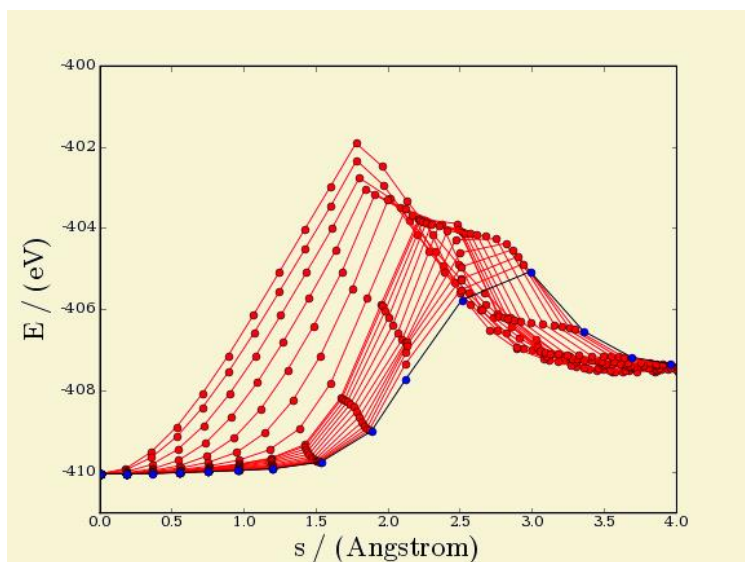


We can now construct the initial reaction path as linear interpolation of the reactant and product coordinates:

$$R_I(i) = [(N_{Neb}-i) * R_I(react) + i * R_I(prod)] / N_{Neb}$$

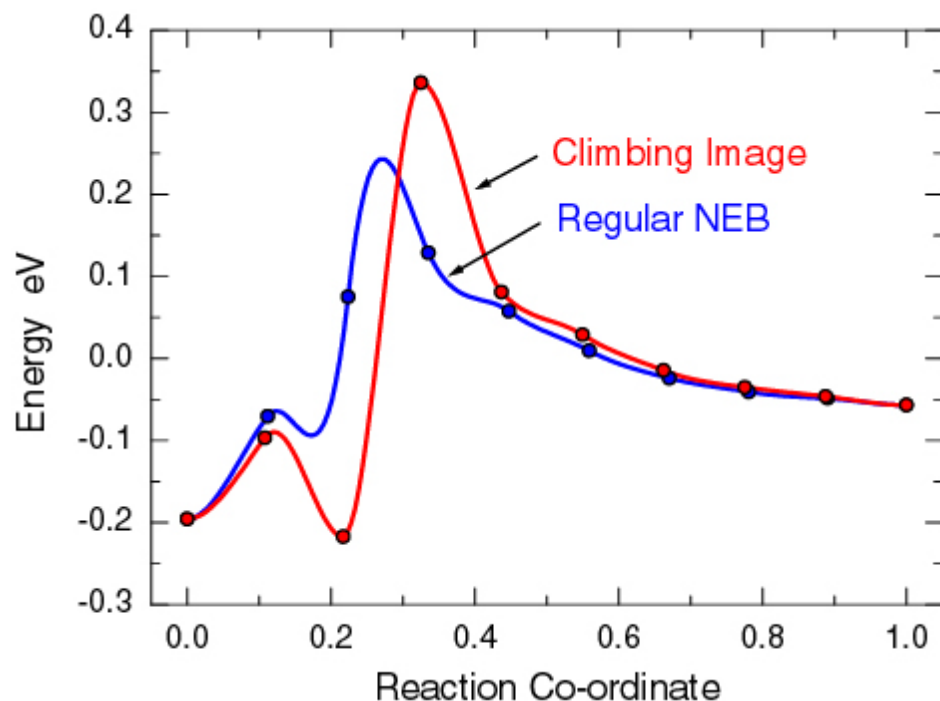
(The straight dotted line in the figure above). N_{Neb} is typically around 10. In the NEB methods there is a spring between the points R_I : $k(R_I - R_{I+1})^2$. Now we need to minimize the energy of the whole path (the end-points are fixed). In ideal case the original path slide to the correct path (solid line in the picture above). For a stable algorithm only the perpendicular force of the energy and the parallel force of the spring are used. (The perpendicular and parallel forces are with respect of the NEB path.) See the added NEB document. (http://www.openmx-square.org/tech_notes/NEB.pdf)

The NEB method do not find directly a good estimation of the transition state but a simple polynomial interpolation gives reasonable results. NEB has also a tendency to pack the points to either ends of the system. This will minimize the NEB path energy.



There are also several improved versions of NEB, like Climbing-Image-NEB. Also NEB can be restarted from any points near the maximum.

In general, it is not easy to find the transition state. Note also that the NEB will find the maxima of the atomic total energy, not the free energy, so the entropy need to be estimated separately. The NEB calculation are time consuming since every point in the path is a quantum mechanical calculation.



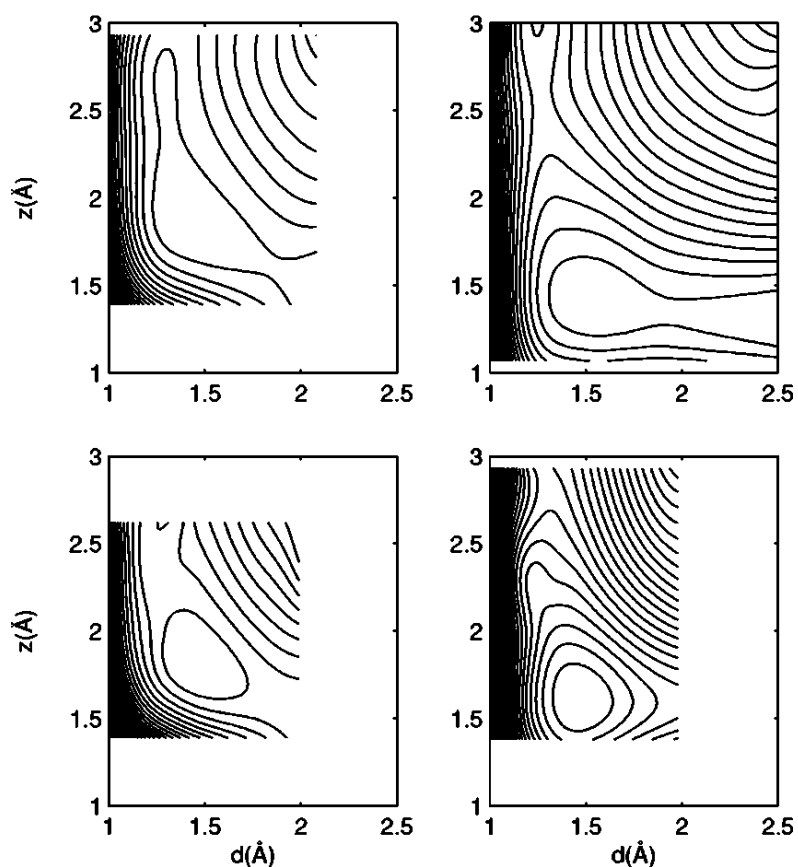
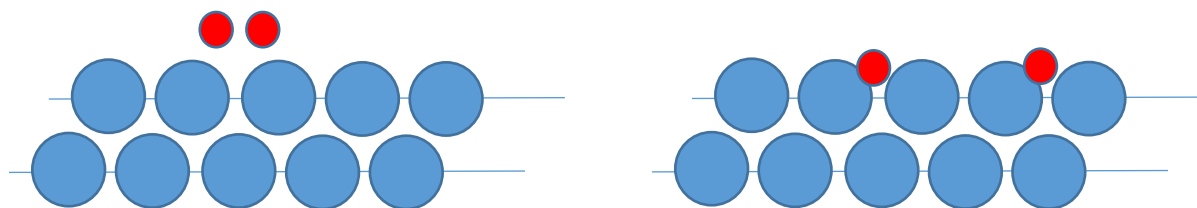
Source: <http://theochem.org/CompChem11f/NEBandQuantumHTST.pdf>

The NEB is one of the most popular TS search algorithm but not the only one. It is not easy to use and it is limited to energy (not free energy).

Potential energy surface

The most general approach to the atomic total energy is the potential energy surface (PES). In most general case it is the same as the atomic total energy. Because the total energy is so high dimensional this approach is impractical. Even in very simple case of reactions of two diatomic molecules (or a diatomic molecule approaching to rigid surface) the coordinate space is 6 dimensional. If one uses 10 points in each dimension

it takes 10^6 calculations to map this surface. This is just doable but not for larger systems. The full PES is almost never used but some parts of it can be useful. A rather common approach is so called elbow plot, where a diatomic molecule is approaching a surface horizontally (it can also tilt and rotate if liked). In the elbow plot the height and atom distance are plotted in 2-D. Several elbow plots can be made on different location on the surface.



Above one see that the EB plot are rather different. In general a well-chosen 2-D plot of the PES are very useful tool to

understand the molecular interactions or reactions. (Even we would have a high dimensional PES we have difficulties to visualize it beyond 3-D.

To summarize: the atomic total energy is a very useful quantity. From it, many chemical properties, like molecules structure, vibrational modes and energies, estimation of reaction barriers, etc., can be computed. Its main limitation is that often we would need the free energy instead of total energy. Even the free energy can be computed within the harmonic approximation.