A deterministic method for finding first order saddle points starting from a minimum

Katrín Blöndal

May 30, 2017

Faculty of Physical Sciences, University of Iceland, 107 Reykjavík, Iceland

This paper describes a deterministic method for finding first order saddle points on potential energy surfaces. The method consists of analyzing a quantity obtained from the gradient of the energy and Hessian matrix around each point along a search path from a given local minimum. A suggestion of an algorithm is presented here, along with implementations on four two-dimensional test surfaces. The results show that the method works as long as appropriate input parameters are used. Possible further improvements for the method are discussed, as well as how it can be generalized for systems with more degrees of freedom.

Keywords: saddle point, potential energy surface.

1 Introduction

Locating first order saddle points on potential energy surfaces (PES) is an important task as it appears in chemical reactions, diffusion and molecular rearrangements that are an effect of thermal activation [1]. In those cases, saddle points are found on a PES that describes the variation of the energy of the system as a function of atomic coordinates [1]. One example is the identification and estimation of the rate of atomic scale transitions in the condensed phase within harmonic transition state theory (HTST) [2].

A first order saddle point is a maximum in the direction of one of the eigenvectors of the Hessian and a minimum in the direction of all other eigenvectors. Therefore, methods for finding saddle points invariably involve some kind of maximization of one degree of freedom and minimization in orthogonal degrees of freedom. Many powerful methods have been developed for climbing up a PES from minima to saddle points. It is not sufficient to just follow the direction of slowest ascent, as can be seen on the potential energy surfaces presented later in this paper. Several methods have been developed where information from second derivatives is built in to guide the climb, such as the method using Lagrange multipliers presented by Cerjan and Miller [3] and the local surface approximation method presented by Simons et al. [4]. These methods have become widely used in studies of small molecules and clusters. Their disadvantage is that they require the second derivatives of the energy with respect to all the atomic coordinates, i.e. the full Hessian matrix. Analytical second derivatives are sometimes not readily available, for example in plane wave based density functional theory (DFT) calculations.

The minimum mode following (MMF) method is used for finding first order saddle points on a PES using information about only the lowest eigenvector of the Hessian estimated from just a few function evaluations [1]. Using only the minimum mode of the Hessian, and not having to construct the whole Hessian matrix, is what makes the MMF method more computationally feasible [1]. The minimum mode is found by minimizing the energy of a dimer (two replicas of the system) or using an iterative method such as the Davidson algorithm [2]. It is used to transform the force in such a way that optimization leads to convergence to a saddle point. A disadvantage of using this method is that there is a possibility of reconverging onto a previously found saddle point in searches starting from different points on the surface.
Another limitation of the MMF method can be seen from the basins of attraction on the PES, see Fig. 1 [5]. The limitation is apparent in Fig. 1b; a search starting from the initial state region on the left hand side will not be able to locate the saddle point labeled ‘S4’, since its basin of attraction does not connect to the region around the minimum where all eigenvalues are positive [2]. However, the method presented in this paper can be used to locate S4 and the other saddle points in a systematic way as shown in Fig. 1c.

![Figure 1](a) The potential energy contour plot and contour lines of a PES. (b) The regions of attraction around each saddle point on the PES. The colors indicate to which saddle point the MMF method will converge. Both eigenvalues of the Hessian are positive in the white areas. (c) The method presented in this paper applied to the same PES. It successfully locates S4, unlike the MMF method.

Another way to locate saddle points on a PES is the nudged elastic band (NEB) method [6,7]. It is used to find minimum energy paths (MEP) of atomic rearrangements for given initial and final states [8]. In NEB calculations, some initial path is constructed between two local minima on the energy surface. The path is represented by a discrete set of system replicas connected by springs [8]. The replicas are then optimized simultaneously to bring the elastic band to the MEP by minimizing the magnitude of the force acting on the images in the direction perpendicular to the path [6]. Saddle points can be found using NEB as they are the maxima of MEPs [9]. This paper however, addresses more challenging problems, in the sense that only one local minimum of a PES is used to start each search.

The purpose of this paper is to suggest an algorithm for finding first order saddle points on a PES in a deterministic way. This method consists of using the squared cosine of the angle between the energy gradient and the lowest mode of the Hessian at each point along a search path from a local minimum.

The paper is organized as follows: a general description of the methodology is given in section two. In section three, we discuss the results of applying the method to three different two-dimensional test problems, excluding the one in Fig. 1. Concluding remarks are given in section four, and acknowledgements are given in section five.
2 Methodology

The task is to find as many first order saddle points as possible on two-dimensional surfaces given the local minima. The quantity used is the projection of the normalized energy gradient onto the eigenvector that corresponds to the lowest eigenvalue of the Hessian matrix, squared. In other words, the cosine of the angle between the normalized gradient and the lowest Hessian mode is used:

$$\omega(x) = \frac{\omega \cdot \nabla V(x)}{||\nabla V(x)||}, \quad (1)$$

where

$$H(x)\omega = \lambda \omega. \quad (2)$$

$H(x)$ is the Hessian matrix, $\lambda$ is the lowest eigenvalue of the Hessian, $\omega$ is the corresponding normalized eigenvector, $\nabla V(x)$ is the gradient of the energy, and $\omega(x)$ is the projection value, or the cosine of surface coordinate $x$.

Instead of taking the absolute value to get a positive result, this value is squared (since the cosine could be positive or negative depending on the direction of the eigenvector). Taking the absolute value would result in a discontinuity in the derivative. The maxima of $(\omega(x))^2$, which will for the rest of this paper be referred to as $\cos^2$ or “squared cosine”, around points on the path of the surface are therefore used to construct search paths. The circles that $\cos^2$ are maximized along have a predetermined radius depending on which test case is used. Each circle consists of 200 surface coordinates in this implementation.

In some cases, both the energy and the gradient of the surface are given. Finite difference is used to construct the Hessian at each point of the search, and also the gradient in cases where it is not given.

At points close enough to a saddle point, a Newton-Raphson step is most efficient [3]:

$$\Delta x = -H^{-1}\nabla V(x), \quad (3)$$

where $\Delta x$ is the step length from the current step to the saddle point. Newton-Raphson is used in this method as described in the algorithm below.

An algorithm for a deterministic saddle point search

**Input:** the surface coordinate boundaries, energy (and gradient if available), step size, radius around minima, and the upper energy boundary of the search, all depending on the PES used.

**Output:** an image that shows the $\cos^2$ surface and saddle point searches starting at the local minima.

See Fig. 2 for the basic construction of the algorithm. Detailed information, supplemental to Fig. 2 is listed here:

1. If there are more than two maxima on the circle, or if there are two maxima where one of them is not too close to the step before (“too close to” here and in Fig. 2 means “within a distance of a third of the predetermined step radius from”), this indicates a potential branching. In that case, the maximum that corresponds to the second highest vector projection value is chosen as the potential start of a branch. However, if there are more than three maxima on the circle or hypersphere, the maximum with the third highest vector projection value is also examined. It is chosen instead as the branch starting point only if the coordinate is not too close to the step before and if either of the following conditions apply:
   A. It has a higher $\cos^2$ value than the original branch starting point (exception when the $\cos^2$ value of the original point is above 0.999, at that point the difference is considered negligible),

\[3\]
B. the coordinate of the original branch starting point is too close to the next step.

2. The conditions that need to apply to the steps for the paths to continue are as follows:
   I. The step is not in an area with more than one negative eigenvalue,
   II. it is within the predetermined coordinate boundaries of the surface,
   III. the energy is below the upper energy limit,
   IV. the step is not on a parallel ridge to the one that the previous step is on*,
   V. there is a saddle point in between the steps. Calculate the gradient of the energy
      in the next step and find the projection on to the current step gradient. If the
      projection is negative, it indicates that a saddle point is in between the steps. In
      this case, a Newton-Raphson step is taken to the saddle point instead of the original
      step.
   VI. The step is not too close to any other point of previous paths on the surface.

*A possible way to find out whether branch or nextstep is on a parallel ridge: find the minimum
value of $cos^2$ along the vector from branch to the current step and compute $cos^2$ on the minima on
each side of branch on the circle, $L_1$ and $L_2$. If the minimum value along the vector is lower than
either $L_1$ or $L_2$, branch is on a parallel ridge. An exception is made when the $cos^2$ value of $L_1$
or $L_2$ is higher than 0.985, since that could mean that there is a sharp turn on the ridge.
Maximize $\cos^2$ on a circle a predetermined radius around a local minimum. Store the coordinates of the maxima as starting points.

Set one of the starting points as the current step.

Find the extrema coordinates of $\cos^2$ on a circle around the current step.

Find the vector that goes from the coordinate of each maximum to the current step.

Save the value of the projection of each vector onto the vector that goes from the current step to the previous one.

The maximum that corresponds to the highest projection value is chosen as the next step.

If there are more than two maxima on the circle, determine the coordinate of a first branching point based on paragraph 1 in the supplemental info.

Do conditions I. - V. apply to the next step?

Is the potential start of a branch too close to the other step (the corresponding "next step")?

Delete point

Do conditions I. - V. apply to the branching step?

The point is stored as a starting point for later

Set the next step as the current step.

Stop when all branch starting points have been covered

If all starting points from local minima have been covered, set a branch starting point as the current step

Does condition VI. apply to the current step?

Delete the step and go to next starting point, or the next local minimum.

Does condition VI. apply to the next step?

Delete the step and go to next branch starting point

Start

Figure 2: A flowchart for the suggested algorithm. A more detailed discussion about the conditions is given above.
3 Applications

The method is tested on three two-dimensional test problems: The Müller-Brown potential, a built-in Matlab function called Peaks, and a LEPS potential surface with an added harmonic oscillator [10] and two Gaussian peaks. In the following figures, white points represent local minima, black points are the steps of the search paths, green points represent the first steps of new branches and red points are saddle points. The squared cosine is maximized along the white circles around the local minima and the grey circles around the stepping points. Areas on the surfaces where both eigenvalues of the Hessian are negative are marked as white.

A contour plot of the Müller-Brown potential is shown in Fig. 3a and a contour plot of $\cos^2$ on the Müller-Brown potential with saddle point searches starting from the local minima is shown in Fig. 3b.

![Figure 3a: A potential energy contour plot of the Müller-Brown surface.](image1)

![Figure 3b: A contour plot of $\cos^2$ on the Müller-Brown potential with energy contour lines. Saddle point searches starting from local minima are illustrated. The black points on the white circles are the first points of each saddle point search. Single white points are the local minima, black points represent the steps of the search paths, green points are the first steps of new branches and red points are saddle points. Areas on the surfaces where both eigenvalues of the Hessian are negative are marked as white.](image2)

It is apparent in Fig. 3b that $\cos^2$ forms ridges that connect the minima and saddle points on the surface. These ridges are followed by the search paths, sometimes leading to saddle points and occasionally ending without converging to saddle points, if the ridges suddenly end or lead to stationary points that are not saddle points. This is also clearly illustrated on the built-in Matlab function Peaks, see Fig. 4.
Figure 4: (a) A function value contour plot of the *Peaks* surface. (b) A contour plot of $\cos^2$ on the *Peaks* function with function value contour lines. Saddle point searches starting from local minima are shown.

Furthermore, the *Peaks* surface reveals a limitation in the implementation of our method. The circle radius around the steps in Fig. 4b could not be any smaller. Using shorter radii and simultaneously smaller steps, the search from the bottom minimum would not be able to converge to the saddle point, because a bifurcation signal due to the wide side ridge would not be detected. This limitation can make the method challenging to generalize for higher dimensional systems.

The test problem in Figs. 1 and 5 are formulated by coupling the LEPS potential - a model that mimics a reaction involving three atoms confined to motion along a line with an extra degree of freedom that represents a harmonic oscillator condensed phase environment (see supporting information of ref. [10]). Two Gaussian functions, see Eq. 4, are added to both test problems using the parameters in Table 1. The Gaussian parameters for Fig. 1 are taken from a correction document made for ref. [2], except that the central Gaussian peak is turned into a local minimum by changing the sign of $A_1$ [5].

$$G_i(x, y) = A_i e^{-(x-x_{0i})^2/2\sigma_{xi}^2} e^{-(y-y_{0i})^2/2\sigma_{yi}^2}, \quad (4)$$

Table 1: The Gaussian function parameters for Figs. 1 and 5.

<table>
<thead>
<tr>
<th>$i$</th>
<th>Fig. 1</th>
<th>Fig. 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>-1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>$x_{0i}$</td>
<td>2.02083</td>
<td>2.02083</td>
</tr>
<tr>
<td>$y_{0i}$</td>
<td>-0.172881</td>
<td>-0.172881</td>
</tr>
<tr>
<td>$\sigma_{xi}$</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$\sigma_{yi}$</td>
<td>0.35</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Figure 5: (a) A potential energy contour plot of a LEPS+HO+2Gauss potential, where the Gaussian in the middle is positive. (b) A contour plot of $\cos^2$ on a LEPS+HO+2Gauss potential with energy contour lines, where the second Gaussian (the one in the middle) is positive. Saddle point searches starting from local minima are shown.

In both Figs. 1c and 5b, there is a large ridge on the $\cos^2$ surface that connects the left hand side minimum and the saddle point at the top, labeled 'S4' in Fig. 1b. As illustrated in sec. 1, MMF is unable to locate this saddle point if the search is started from the left hand side minimum [2]. This indicates that the method presented here has an advantage over MMF for finding saddle points that cannot be located using MMF, starting in the same initial area.

4 Discussion

The method presented in this paper locates first order saddle points in a deterministic way. The results show that it works as long as the radius is chosen to be long enough so that signals of wide, bifurcating surface ridges are not missed. The method only requires the lowest mode of the Hessian matrix as in MMF, but it is systematic, which is an advantage over MMF.

There are numerous possible ways to improve the implementation of this method. For example, it would be advantageous to find only the lowest mode of the Hessian in the same manner as in MMF, since the full Hessian is not required. The white circles around the local minima should also be removed. Instead, the search would start at a predetermined distance away from the minima in both directions of the lowest Hessian mode. This would reduce computer function calls.
The method has currently only been implemented for two-dimensional test problems, but the objective is to generalize it for systems with many degrees of freedom. Maximizing \( \cos^2 \) on relatively large circles around the minima will translate poorly onto higher dimensions. This can be attributed to the notable increase in function calls required to compute the squared cosine on large hyperspheres. Therefore, further developments are in need before the method can be convincingly applied to larger test cases. In further developments of this method, the gradient of the squared cosine value will also be important in order to perform maximizations and minimizations on multidimensional energy landscapes.

To make this method even more efficient, machine learning could be used to significantly reduce computational effort by constructing an approximate representation of the energy surface \([8, 11]\). Then the method would be used to conduct saddle point searches on this approximate energy surface.

5 Acknowledgements

I would like to thank my advisor Dr. Hannes Jónsson of the Faculty of Physical Sciences and Science Institute at the University of Iceland. He always kept his door open for me to discuss my research and steer me in the right direction when needed. I would also like to express my gratitude to Vilhjálmur Ásgeirsson, a PhD student in Prof. Jónsson’s group at the University of Iceland, for extremely helpful discussions and help with the construction of the algorithm.

References