Finding Saddle Points using Stability Boundaries

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ABSTRACT

The task of finding saddle points on potential energy surfaces plays a crucial role in understanding the dynamics of a micro-molecule as well as in studying the folding pathways of macro-molecules like proteins. This paper primarily focusses on computing saddle points on potential energy surfaces. A stability boundary based approach that explores the dynamic and geometric characteristics of stability boundaries of a nonlinear dynamical system has been used to compute saddle points. A novel *ray-adjustment procedure* is used to trace the stability boundary. A simpler version of the algorithm has also been used to find the saddle points of symmetric systems. Our approach was also successful in finding saddle points on higher dimensional energy surfaces.

Keywords

Bioinformatics, potential energy surfaces, saddle points, stability regions, stability boundaries

1. INTRODUCTION

Understanding the process of protein folding not only involves predicting the folded structures of foldable sequences but also requires finding the folding pathways in which the proteins attain their native structure. Usually, proteins have multiple stable macrostates and the conformations associated with each macrostate will have a specific biological function. To understand kinetics of folding process we need the structures that correspond to the transition state between these macrostates. These transition state conformations are *saddle points*. Saddle points are the points on the potential energy surface where the gradient is zero and the Hessian matrix of the second derivatives of the potential energy has only one negative eigenvalue. The problem of finding the saddle points is more challenging than the problem of finding local minima on a potential energy surface. The primary focus of this paper is to find the saddle points on different potential energy surfaces.

SAC'05 March 13-17, 2005, Santa Fe, New Mexico, USA

2. BACKGROUND

Several methods have been proposed in the literature that are based on the idea of diagonalization of the Hessian matrix. Eventhough these methods appear to find saddle points accurately, they are not practical for higher dimensional problems because the computational cost increases tremendously as the number of dimensions increase. Some other methods have been developed that work by computing only the first derivatives. A detailed description of these methods along with their advantages and disadvantages is given in a review paper [2]. This paper discusses a novel *stability boundary* based approach to compute the saddle points between two given local minima. Our method crops from the fundamental results on stability regions of nonlinear dynamical systems [1, 3]. Our method is easily scalable to higher dimensional systems because it requires only first derivatives.

We transform the problem of finding the saddle point on the energy surface into the problem of computing the decomposition point of the nonlinear dynamical system. Consider the following nonlinear dynamical system:

$$\dot{x}(t) = f(x(t)) \tag{1}$$

where the state vector x belongs to the Euclidean space $\Re^n$, and the vector field $f : \Re^n \rightarrow \Re^n$ satisfies the sufficient condition for the existence and uniqueness of the solutions. The solution curve of Equation (1) starting from x at time $t = 0$ is called a *trajectory* and it is denoted by $\Phi(x, \cdot) : \Re \rightarrow \Re^n$. A state vector x is called an *equilibrium point* x_s of Eq. (1) if $f(x)$=0. An equilibrium point is called a (asymptotically)*stable* equilibrium point if all the eigenvalues of its corresponding Jacobian have nonpositive real part.

Definition 1. *The stability region (also called region of attraction) of a stable equilibrium point x_s of a nonlinear dynamical system (1) is denoted by $A(X_s)$ and is*

$$A(x_s) = \{x \in \Re^n \ : \ \lim_{t \rightarrow \infty} \Phi(x, t) = x_s\} \tag{2}$$

Definition 2. *The boundary of stability region is called the stability boundary of x_s and is denoted by $\partial A(x_s)$.*

If the Jacobian of the equilibrium point has exactly k eigen values with positive real parts, then it is called a type-k equilibrium point. A type-1 equilibrium point (k=1) on the stability boundary of a stable equilibrium point x_s is called a *decomposition point.*

3. ALGORITHM

The method described in this section finds the decomposition point when the two neighborhood minima are given. The two local minima are A and B and the decomposition point is D (see Fig. 3).

Step 1: *Locating the exit point (X_{ex})* : Along the direction AB, starting from A, the function value is evaluated at different step intervals. The energy value will monotonically increase and then starts to decrease. The point where the value attains its peak is called the *exit point*.

Step 2: *Tracing the stability boundary* : The exit point (X_{ex}) is integrated for a predefined number of times. Let m_1' be the new point obtained after integration of the exit point. The energy value between m_1' and one of the local minima (say B) is evaluated. A new boundary point is obtained along the vector $m_1'B$ where the value attains the peak (m_2). This process is repeated and the value of the gradient is noted at each of the boundary points.

Step 3: *Finding the Decomposition point* : This process of moving along the boundary is terminated when the minimum vector-field point is reached. Let the point m_n be the point on the boundary corresponding to the minimum vector-field point. The MVP(m_n) will be present in the neighborhood of the decomposition point. The decomposition point is obtained by applying a local minimizer with m_n as initial guess.

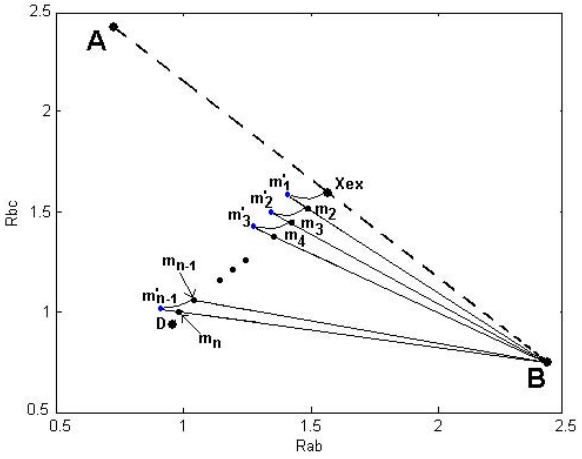

Figure 1: Illustration of our method to find the decomposition point between two local minima. A and B are the two local minima and D is the decomposition point.

4. RESULTS AND DISCUSSION

The algorithm has been tested on the two-dimensional Muller-Brown surface which forms a standard example of a potential energy function in theoretical chemistry [4]. Equation (3) gives the Muller-Brown energy function.

$$C(x,y) = \sum_{i=1}^{4} A_i \; exp\Big[a_i(x-x_i^o)^2 + b_i(x-x_i^o)(y-y_i^o) + c_i(y-y_i^o)^2\Big]. \quad (3)$$

A = (-200, -100, -170, -15)	a = (-1, -1, -6.5, -0.7)
x^o = (1, 0, -0.5, -1)	b = (0, 0, 11, 0.6)
y^o = (0, 0.5, 1.5, 1)	c = (-10, -10, -6.5, 0.7)

The Muller-Brown energy surface contains three local minima (LM) and two decomposition points (DP). A =(-0.558, 1.442), B=(-0.05, 0.467) and C=(0.623, 0.028) are the three local minima and DP1=(-0.822, 0.624) and DP2=(0.212, 0.293) are the two decomposition points. DP1 is present between A and B and it is more challenging to find it when compared to the DP2 which is present between B and C. Our algorithm found both the decomposition points on this energy surface.

A simplified version of the algorithm has also been used to find saddle points on the energy surface corresponding to three-atom Lennard Jones clusters. This energy surface is symmetric and hence one can compute the exit point analytically (not numerically). Because the exit point is not an approximate value, one can eventually reach the decomposition point by integrating the exit point without any need of the ray adjustment procedure. We have also tested our algorithm on a heptamer island over the surface of an Face-centered cubic (FCC) crystal. This system has been used as a benchmark to evaluate different saddle point finding algorithms in [2]. This is an example of 525 dimensional search problem and our algorithm found the saddle points successfully.

5. CONCLUSIONS

This paper focusses on finding saddle points on potential energy surfaces. A new stability boundary based method that explores some fundamental results of nonlinear dynamical systems is presented. A novel *ray adjustment procedure* has been used to move along the stability boundary. Our method was successful in finding the saddle points on different potential energy surfaces of varying dimensions. A simplified version of our algorithm has been developed to estimate the saddle points on symmetric energy surfaces. The algorithm was also successful in finding saddle points on higher dimensional energy surfaces.

6. REFERENCES

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