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Research paper

An improved reaction path optimization method using a chain of conformations

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ABSTRACT

The efficient fast path optimization (FPO) method is proposed to optimize the reaction paths on energy surfaces by using chains of conformations. No artificial spring force is used in the FPO method to ensure the equal spacing of adjacent conformations. The FPO method is applied to optimize the reaction path on two model potential surfaces. The use of this method enabled the optimization of the reaction paths with a drastically reduced number of optimization cycles for both potentials. It was also successfully utilized to define the MEP of the isomerization of the glycine molecule in water by FPO method.

1. Introduction

Theoretical investigations of chemical reactions occurring in the condensed phase are important in understanding reaction mechanisms and environmental effects. Although forces can be easily obtained for small and even large molecules by *ab initio* molecular orbital calculations or quantum mechanical/molecular mechanical [1–5] approximation, to find the minimum energy path (MEP) from the reactant to the product is not always trivial problem and many different approaches have been formulated particularly to find reaction paths in the condensed phase. For instance, the nudged elastic band (NEB) [6–8] and string methods [9] are popular approaches in searching for MEPs by using chains of conformations named "images." The beginning of all these technologies was the study by Ulitsky et al [10]. These are conventional approaches that proceed by finding some intermediate structures and transition states along the MEPs via a single optimization. In the NEB method, the force on each image is projected onto the perpendicular component of the tangent vector of the reaction path. Artificial spring forces are then applied to cause the images to be equally separated along the reaction path during optimization cycles. In the string method, after images have been displaced to lower energies following their forces, they are replaced via the spline interpolation method to align all images on a smooth reaction pathway.

Neither the NEB nor the string method require time-consuming Hessian calculations for MEP optimization; they only require forces. Although optimization can be easily performed in reduced computational time, both methods require the implementation of many successive cycles as a consequence of the fluctuations of the image coordinates until a converged MEP is obtained. In the NEB method, these fluctuations often evoke so-called "kinks instability problems" [11–13], whereby the existence of large bent angles in the reaction path causes convergence instability.

In this investigation, an efficient approach named fast path optimization (FPO) is proposed to reduce the number of optimization cycles needed to achieve MEP convergence. To examine the efficiency of the method, FPO was applied on two simple model potentials, and the results were compared with those obtained by the NEB and string methods. It was confirmed that for both potentials, the application of the FPO method could help reach convergence to the reaction paths with drastically reduced optimization cycles compared with the other two methods.

2. Methods

2.1. Model potentials

Two model potential surfaces were considered to demonstrate MEP optimizations. One is the Müller–Brown (MB) potential [14], which is represented by the following:

$$f(x,y) = f_1(x,y) + f_2(x,y) + f_3(x,y) + f_4(x,y) \quad (1)$$

$$f_i(x,y) = A_i \cdot exp\left\{a_i (x-x_i)^2 + b_i (x-x_i)(y-y_i) + c_i (y-y_i)^2\right\} \quad (2)$$

where, $A_i = (-200/-100/-170/15)$, $a_i = (-1/-1/-6.5/0.7)$, $b_i = (0/0/11/0.6)$, $c_i = (-10/-10/-6.5/0.7)$, $x_i = (1/0/-0.5/-1)$, and $y_i = (0/0.5/1.5/1)$.

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The second model potential is the original s-shaped potential:

$$f(x,y) = \cos(\pi(x + \sin(y))) - \cos\left(\frac{\pi y}{2}\right) \quad (3)$$

This potential has a characteristic feature: the simple eigenvector following algorithm from the reactant or the product cannot smoothly reach the transition state (TS) on the MEP. These potential energy surfaces are illustrated in Fig. 1.

2.2. The first path optimization method

In a similar fashion to the NEB and string methods, the FPO method requires the use of images, which are the conformations that define the reaction path on the energy surface in chain. Prior to MEP optimization, the energy minima for the reactant and the product should be fully optimized as terminal images of the MEP. These terminal images are then fixed during the subsequent MEP optimization procedure. Therefore, if the reaction path consists of N images, the 1st and Nth images are fixed, and the remaining N-2 images are optimized through FPO. Since the number of images N may vary depending on the shape of the potentials, 16 and 21 images were used in this study for the MB and s-shaped potentials, respectively, unless otherwise stated.

A diagram illustrating the FPO method is given in Scheme 1. The perpendicular component of the force on the ith image, $\mathbf{F}_i^{\perp}$ $(2 \le i \le N-1)$, is derived as follows:

$$\mathbf{F}_i^{\perp} = \mathbf{F}_i - (\mathbf{F}_i \cdot \hat{\boldsymbol{\tau}}_i)\,\hat{\boldsymbol{\tau}}_i \quad (4)$$

where $\mathbf{F}_i$ is the force on the ith image, and $\hat{\boldsymbol{\tau}}_i$ is the unit vector of the tangent vector $\boldsymbol{\tau}_i$. Henkelman et al. [11] proposed to define $\boldsymbol{\tau}_i$ as the improved tangent, which is denoted as $\boldsymbol{\tau}_i^{\mathrm{IT}}$. By using the potential energy height V_i of the ith image, $\boldsymbol{\tau}_i^{\mathrm{IT}}$ is defined as follows:

$$\boldsymbol{\tau}_i^{\mathrm{IT}} = \begin{cases} \boldsymbol{\tau}_i^{+} & \text{if} \quad V_{i+1} > V_i > V_{i-1} \\ \boldsymbol{\tau}_i^{-} & \text{if} \quad V_{i+1} < V_i < V_{i-1} \end{cases}$$

where

$$\boldsymbol{\tau}_i^{+} = \mathbf{r}_{i+1} - \mathbf{r}_i, \quad \text{and} \quad \boldsymbol{\tau}_i^{-} = \mathbf{r}_i - \mathbf{r}_{i-1} \quad (6)$$

$\mathbf{r}_i$ represents the coordinates of the ith image (see Fig. 2). If both potential energies $V_{i\pm1}$ are lower or higher than V_i, then

$$\boldsymbol{\tau}_i^{\mathrm{IT}} = \begin{cases} \boldsymbol{\tau}_i^{+}\Delta V_i^{\max} + \boldsymbol{\tau}_i^{-}\Delta V_i^{\min} & \text{if} \quad V_{i+1} > V_{i-1} \\ \boldsymbol{\tau}_i^{+}\Delta V_i^{\min} + \boldsymbol{\tau}_i^{-}\Delta V_i^{\max} & \text{if} \quad V_{i+1} < V_{i-1} \end{cases}$$

where

$$\Delta V_i^{\max} = \max\left(\,|V_{i+1} - V_i|,\ |V_{i-1} - V_i|\,\right) \quad (8)$$

$$\Delta V_i^{\min} = \min\left(\,|V_{i+1} - V_i|,\ |V_{i-1} - V_i|\,\right) \quad (9)$$

Furthermore, Henkelman et al. [11] also propose the bisection tangent $\boldsymbol{\tau}_i^{\mathrm{BT}}$ aside from $\boldsymbol{\tau}_i^{\mathrm{IT}}$:

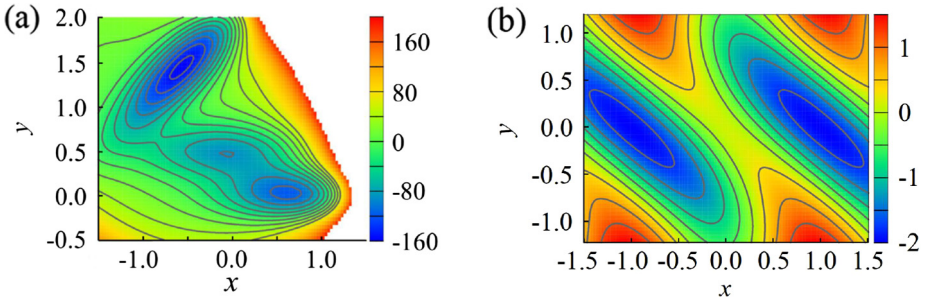
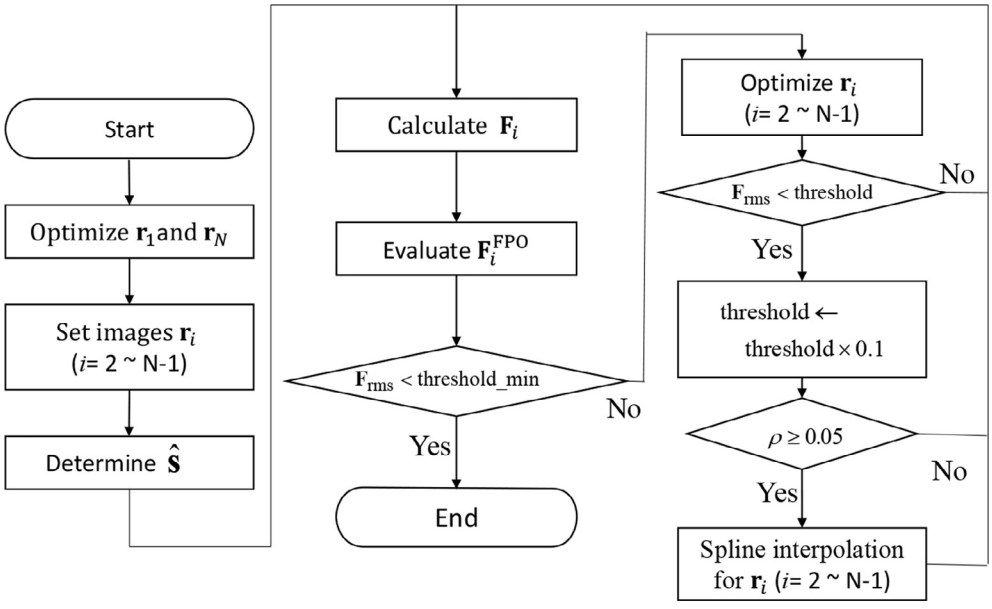


Fig. 1. Model potential surfaces. (a) Müller-Brown potential and (b) s-shaped potential.



Scheme 1. Schematic diagram of the FPO method. The threshold_min is a minimum threshold to terminate the optimization.