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A CONCURRENT SEARCH ALGORITHM FOR MULTIPLE PHASE TRANSITION PATHWAYS

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ABSTRACT

The challenge of accurately predicting a phase transition in computer-aided nano-design is estimating the true value of transition rate, which is determined by the saddle point with the minimum energy barrier between stable states on the potential energy surface (PES). In this paper, a new algorithm for searching the minimum energy path (MEP) is presented. Unlike existing pathway search methods, the new algorithm is able to locate both the saddle points and local minima simultaneously. Therefore no prior knowledge of the precise positions for the reactant and product on the PES is required. In addition, the algorithm is able to search multiple transition paths on the PES simultaneously. In this method, a Bézier curve is used to represent each transition path. Starting from a single Bézier curve, multiple curves with ends connected can be generated during the search process. For each Bézier curve, the reactant and product states are located by minimizing the two end control points of the curve, while the transition pathway is refined by moving the intermediate control points of the curve in the conjugate directions. A curve subdivision scheme is developed so that multiple transition paths can be located. The algorithm is demonstrated by examples.

1. INTRODUCTION

An important problem in computer-aided nano-design is to simulate phase transition processes, which is one of the most important design issues for functional materials. From the material's microstructure point of view, a phase transition is a geometric and topological transformation process of materials from one phase to another, each of which has a unique and homogeneous physical property. Simulation that allows engineers to predict the transition process efficiently and accurately under desirable conditions is critical in designing phase change materials.

The general process to simulate the phase transition process is as follows. First, a potential energy surface (PES), which represents the potentials of a group of atoms as a function of internal coordinates, is generated. It characterizes the energy levels for various possible configurations of the materials system. PES can be regarded as a hyper surface in a high-dimensional configuration space. It has values of minimum and maximum energy values, where the minima correspond to the stable or metastable states. Then a minimum energy path (MEP) [1, 2], which is the lowest energy path for re-organization of the atoms from one stable configuration to another, is located. The maximum energy potential along the MEP is the saddle point which determines the activation energy barrier. The MEP can be interpreted as the steepest descent path on the PES from saddle point(s) connecting the reactant and the product, also respectively known as the initial and final stable configurations with local minimum energy level on the PES. Finally the activation energy is obtained by finding the saddle point energy along the MEP and the transition rate is calculated using the transition state theory [3]. The challenge of accurately predicting a phase transition is the knowledge of the true value of transition rate, which is determined by the energy barrier that exists between the initial and final stable configurations. That is, some activation energy is required to enable the transition from the initial structure to the final one. Mathematically it is the saddle point on the PES with the global minimum energy barrier that determines the transition rate.

A number of methods [4, 5] already exist to search the transition path and saddle points on a PES. All of the current methods need the prior knowledge of either the reactant or product, or both, in order to search a MEP. And they can search only one MEP or saddle point at a time with one initial guess of the transition path. In this paper we develop an algorithm which can locate both the minimum energy positions and MEP

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simultaneously on a PES. Therefore the precise knowledge of the stable configuration is not required in advance to the MEP search. In addition, the algorithm is able to search multiple local minimums and transition paths on the PES simultaneously, which can provide a more comprehensive view of the energy landscape than searching individual ones.

In our algorithm the Bézier curve is used to represent the transition path. A Bézier curve is a parametric curve defined by control points which can be used to manipulate the shape of the curve. During the searching process, reactant and product states are located by minimizing the two end control points of the Bézier curve, while the shape of the transition path is refined by moving the intermediate control points of the curve in the conjugate directions. In each iteration, the two end points will be minimized respectively by using the conjugate gradient method. Each end point will be minimized along a set of n (for n dimensional functions) successive conjugate directions with the starting minimization direction defined as the negative gradient at the starting point. For each intermediate control point, several minimization steps are applied along its associated conjugate directions with positive eigenvalues. By doing so, the Bézier curve will gradually converge to MEP. Since there could be more than one saddle point with extra local minimums between two stable states, one curve could be broken into two curves to represent two stages of transition. In this paper, we propose a scheme to check whether there is more than one saddle point with an extra local minimum between the two stable states or not. If there is, we break this curve into two curves. The two newly created curves are regarded as the initial guess of the transition path for the two stages of transitions. Then those two curves are optimized by the same procedure as we did to the original initial guess of the path. The algorithm will continue this check-and-break process until each of the curves crosses only two adjacent basins of local minimums.

In the remainder of the paper, Section 2 gives a background introduction of current transition path and saddle point search methods. Section 3 presents the method of searching local minimums and saddle point for a single transition path. Section 4 extends the single transition pathway search method to search multiple paths on the PES. Section 5 demonstrates the algorithm using two examples, and section 6 summarizes the paper.

2. BACKGROUND

2.1 Transition Pathway Search

Transition pathway search methods are classified either as chain-of-states methods, including nudged elastic band (NEB) and string methods, or as one of the other methods. Chain-of-states methods rely on a collection of images that represent intermediate states of the atomic structure as it transforms from initial to final configurations along the transition path. These discrete states are chained to each other after the search converges, and the transition path and saddle point are obtained. The most common one among these methods is the NEB [2], which relies on a series of images connected by springs. To increase the resolution at the region of interest (ROI) and the accuracy of saddle point energy estimates, the NEB method omits the perpendicular component of the spring force, as well as the parallel component of the true force due to the gradient of the potential energy. In some cases, this method produces paths with unwanted kinks, or may not have any images that are directly on the saddle point. The improved tangent NEB [6] and doubly nudged elastic band [7] methods reduce the appearance of kinks by generating a better estimate of the tangent direction of the path and re-introducing a perpendicular spring force component, respectively. The free-end NEB method [8] only requires knowledge of either the initial or final state, rather than both, and the climbing image NEB [9] allows the image with the highest energy to climb in order to locate the saddle point. Eigenvector following optimization can be applied to the result of NEB to locate actual saddle points, and the resolution of ROI can be increased by using adaptive spring constants [10].

String methods [11, 12] represent the transition path continuously as Splines that evolve and converge to the MEP. As opposed to NEB, the number of points used in the String method can be modified dynamically. The Growing String method [13] takes advantage of this by starting with points at the reactant and product, and then adding points which meet at the saddle point. The quadratic String method [14] is a variation that uses a multi-objective optimization approach.

Methods that are not classified as chain-of-states include the accelerated Langevin dynamics method [15] and the conjugate peak refinement method [16], which finds saddle points and the MEP by searching the maximum of one direction and the minima of all other conjugate directions iteratively. The Hamilton-Jacobi method [17] relies on the solution of a Hamilton-Jacobi type equation to generate the MEP.

2.2 Saddle Point Search

Instead of searching the complete MEP, saddle point search methods only locate the saddle point on the MEP. They are categorized into local and global search methods. One of the original local methods is the automated surface walking algorithm [18, 19]. It is based on eigenvectors of the Hessian matrix with local quadratic approximations of the PES. The more recent ridge method [20] and dimer method [21] use a pair of images to search for the saddle point. Reduced Gradient Following [22] and Reduced Potential Energy Surface Model [23] methods use intersections of zero-gradient curves and surfaces, with saddle point search occurring within the subspace of these curves or surfaces. Finally, the Synchronous Transit method [24] estimates the transition state and refines the saddle point estimate through conjugate gradient optimization.

Local search methods may locate the saddle point which does not have the maximum energy on the MEP if there are multiple saddle points. Global search methods have the advantage that the saddle point with the maximum energy is located if the search converges. The Dewar-Healy-Stewart method [25] searches for the saddle point by iteratively

reducing the distance between reactant and product images. The Activation-Relaxation technique [26] can travel between many saddle points using a two-step process; an image first jumps from a local minimum to a saddle point, and then back down to another minimum. The Step and Slide method [27] uses an image from the initial and final state. Energy levels of each are increased gradually, and the distance between them is minimized while remaining on the same isoenergy surface. The interval Newton's method [28] is capable of finding all stationary points by solving the equation of vanishing gradient.

The proposed algorithm in this paper is to locate multiple local minimums as well as their corresponding transition paths. The initial guess of the path in this algorithm is represented by a fourth order Bézier curve. The algorithm includes three stages. The first stage involves the optimization of a single transition path, during which two local minimums and one transition path that is close to the MEP is located. The second stage is searching multiple transition paths starting from one single transition path obtained from the first stage. One curve is divided into two curves representing two stages of transition, which will be optimized in the same way as in the first stage. This stage will output several transition paths that approximate the true MEPs with those end points located at local minimums. Then at the third stage, we let the control point with the maximum energy within each of those transition paths climb up in order to locate the actual saddle points.

3. A SINGLE TRANSITION PATHWAY SEARCH

For the initial guess of a transition path which is represented by a single Bézier curve, the searching process for the stable configurations and the MEP is carried out in a sequential manner within a given iteration. A total of five control points are used for the initial curve. The more control points the curve has, the more accurate the search results will be, but with higher computational costs. The general process for a single transition pathway search is as follows. First, the two end control points of the curve are minimized by using the conjugate gradient method. Then, a set of conjugate directions for each intermediate control point is determined based on the new positions of the two end control points. Several minimization steps are applied to each intermediate control points along their associated conjugate directions. After several iterations, the two end control points of the curve will gradually converge to the minimum energy positions and the curve will approach to the MEP. Table 1 lists the pseudo-code of the algorithm for a single transition pathway search. The details are described in the following subsections.

3.1 Searching the Stable Configuration

As shown in Tab. 1, the local minimums are located by minimizing the two end control points of the curve iteratively. By definition the minimum energy location $\mathbf{x}^*$ on the PES satisfies

Table 1: PSEUDO-CODE OF THE ALGORITHM FOR A SINGLE TRANSITION PATH SEARCH WITH FIVE CONTROL POINTS

INPUT: Initial guess of a curve with control points of $\mathbf{p}_0, \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4$.
OUTPUT: A curve with two end points located at two local minimums and the curve itself approaches to the MEP.
TOL=threshold for the percentage of change in potential energy value;
$V(\mathbf{p}_*^{(\#)})$ =potential energy value at points $\mathbf{p}_*^{(\#)}$;
$\mathbf{D}_0^{(i)}, \mathbf{D}_4^{(i)}$ =search direction for $\mathbf{p}_0$ and $\mathbf{p}_4$ respectively;
$\alpha_0^{(i)}, \alpha_4^{(i)}$ =step size for minimizing $\mathbf{p}_0$ and $\mathbf{p}_4$ respectively;
WHILE The end control points did not converge to the minimums

IF $\left\|(V(\mathbf{p}_0^{(i)}) - V(\mathbf{p}_0^{(i-1)}))/V(\mathbf{p}_0^{(i-1)})\right\| > TOL$ and
$\left\|(V(\mathbf{p}_4^{(i)}) - V(\mathbf{p}_4^{(i-1)}))/V(\mathbf{p}_4^{(i-1)})\right\| > TOL$
$\mathbf{p}_0^{(i)} = \mathbf{p}_0^{(i-1)} + \alpha_0^{(i)}\mathbf{D}_0^{(i)}$; $\mathbf{p}_4^{(i)} = \mathbf{p}_4^{(i-1)} + \alpha_4^{(i)}\mathbf{D}_4^{(i)}$;
Minimize $\mathbf{p}_1^{(i)}, \mathbf{p}_2^{(i)}, \mathbf{p}_3^{(i)}$ in their associated conjugate directions (see Section 3.2).
IF There is zigzag along the curve
Do degree elevation or reduction locally (see Section 3.3 and 3.4).
END IF
ELSEIF $\left\|(V(\mathbf{p}_0^{(i)}) - V(\mathbf{p}_0^{(i-1)}))/V(\mathbf{p}_0^{(i-1)})\right\| < TOL$ and
$\left\|(V(\mathbf{p}_4^{(i)}) - V(\mathbf{p}_4^{(i-1)}))/V(\mathbf{p}_4^{(i-1)})\right\| > TOL$
$\mathbf{p}_4^{(i)} = \mathbf{p}_4^{(i-1)} + \alpha_4^{(i)}\mathbf{D}_4^{(i)}$;
Minimize $\mathbf{p}_1^{(i)}, \mathbf{p}_2^{(i)}, \mathbf{p}_3^{(i)}$ in their associated conjugate directions.
IF There is zigzag along the curve
Do degree elevation or reduction locally.
END IF
ELSEIF $\left\|(V(\mathbf{p}_0^{(i)}) - V(\mathbf{p}_0^{(i-1)}))/V(\mathbf{p}_0^{(i-1)})\right\| < TOL$ and
$\left\|(V(\mathbf{p}_4^{(i)}) - V(\mathbf{p}_4^{(i-1)}))/V(\mathbf{p}_4^{(i-1)})\right\| > TOL$
$\mathbf{p}_0^{(i)} = \mathbf{p}_0^{(i-1)} + \alpha_0^{(i)}\mathbf{D}_0^{(i)}$;
Minimize $\mathbf{p}_1^{(i)}, \mathbf{p}_2^{(i)}, \mathbf{p}_3^{(i)}$ in their associated conjugate directions.
IF There is zigzag along the curve
Do degree elevation or reduction locally.
END IF
END IF
ELSE The end control points converged to the minimums
END WHILE
IF Two end points converge to the same local minimum
Re-input the initial guess of the curve.
END IF

$$\nabla V\left(\mathbf{x}^*\right) = [\mathbf{g}_1, \ldots, \mathbf{g}_n]^T = 0 \qquad (0)$$

where $V(\mathbf{x}^*)$ is the potential energy function with respect to the position $\mathbf{x}^*$ in an n-dimensional configuration space. The iterative location update during the minimization is given by

$$\mathbf{x}^{(i)} = \mathbf{x}^{(i-1)} + \alpha^{(i)}\mathbf{d}^{(i)} \tag{0}$$

where $\alpha^{(i)}$ is the step length and $\mathbf{d}^{(i)}$ is the search direction for the i^{th} iteration. The minimization process for the end points is carried out using the conjugate gradient method [29]. The conjugate searching direction $\mathbf{d}^{(i)}$ in the i^{th} iteration is defined as a linear combination of $-\mathbf{g}^{(i)}$ and $\mathbf{d}^{(i-1)}$ [29],

$$\mathbf{d}^{(i)} = \begin{cases} -\mathbf{g}^{(i)} & \text{for } i = 1 \\ -\mathbf{g}^{(i)} + \dfrac{\left\|\mathbf{g}^{(i)}\right\|^2}{\left\|\mathbf{g}^{(i-1)}\right\|^2}\mathbf{d}^{(i-1)} & \text{for } i \geq 2 \end{cases} \tag{1}$$

The step size $\alpha^{(i)}$ is determined by using the inexact line search along the corresponding conjugate directions. Namely, along each conjugate direction, several mini steps are applied to the end points in order to locate the minimums along that direction. The minimum position in one conjugate gradient direction is the starting point for the following conjugate search direction. In Table 1, in an n-dimensional search space, the search direction $\mathbf{D}^{(i)}$ in i^{th} iteration can be represented as

$$\alpha^{(i)}\mathbf{D}^{(i)} = \alpha_1^{(i)}\mathbf{d}_1^{(i)} + \cdots + \alpha_n^{(i)}\mathbf{d}_n^{(i)} \tag{1}$$

For a quadratic potential function with n-dimensional inputs, the local minimum can be determined in at most n steps. For a non-quadratic function, local quadratic approximation is involved during the minimization process. For a non-quadratic function with n-dimensional inputs, it requires more than n steps to locate a minimum. For those functions, the conjugate search directions determined by Eqn. (1) will gradually lose conjugacy when searching process continues, which could lead to divergence. In our algorithm, we recalculate the conjugate directions from one iteration to another, namely after n steps of conjugate search in order to avoid the divergence.

3.2 Search the MEP

Mathematically, for an n-dimensional PES, the Hessian matrix $\mathbf{H}$ at a first-order saddle point has one negative eigenvalue and $n-1$ positive ones. The eigenvectors $\mathbf{s}_i$ form a conjugate basis (i.e. $\mathbf{s}_i^T\mathbf{H}\mathbf{s}_j = 0, \forall i \neq j$) with respect to the Hessian matrix. For a set of conjugate directions $\mathbf{s}_i$'s in the vicinity of a first-order saddle point, there is one direction $\mathbf{s}_0$ along which the potential energy has a local maximum. For each of the other $n-1$ directions, the potential energy has a local minimum. The method presented here constructs a set of conjugate directions by making use of Eqn. (2) developed by Beal [30] which starts with a given arbitrary direction $\mathbf{s}_0$. The rest conjugate directions are defined as

$$\begin{aligned} \mathbf{s}_1 &= -\mathbf{g}_1 + \frac{\mathbf{g}_1^T(\mathbf{g}_1 - \mathbf{g}_0)}{\mathbf{s}_0^T(\mathbf{g}_1 - \mathbf{g}_0)}\mathbf{s}_0 \\ \mathbf{s}_{i+1} &= -\mathbf{g}_{i+1} + \frac{\mathbf{g}_{i+1}^T(\mathbf{g}_1 - \mathbf{g}_0)}{\mathbf{s}_0^T(\mathbf{g}_1 - \mathbf{g}_0)}\mathbf{s}_0 + \frac{\mathbf{g}_{i+1}^T\mathbf{g}_{i+1}}{\mathbf{g}_i^T\mathbf{g}_i}\mathbf{s}_i, \quad i \geq 1 \end{aligned} \tag{2}$$

In this algorithm, for each intermediate control points, a set of corresponding conjugate directions are constructed by setting $\mathbf{s}_0$ as the tangent direction approximated by the backward finite difference for the first half of the intermediate control points and by the forward finite difference for the second half respectively. For example, for the k^{th} control point $\mathbf{p}_k$,

$$\mathbf{s}_0 = \begin{cases} \mathbf{p}_k - \mathbf{p}_{k-1} & \text{if } k \leq \left\lceil \dfrac{N}{2} \right\rceil \\ \mathbf{p}_k - \mathbf{p}_{k+1} & \text{if } k > \left\lceil \dfrac{N}{2} \right\rceil \end{cases} \tag{3}$$

where N is the total number of control points and $\lceil\ \rceil$ rounds up to an integer. In order to calculate $\mathbf{s}_1$ in Eqn. (2), we first need to determine $\mathbf{g}_0$ and $\mathbf{g}_1$. Here for the k^{th} control point $\mathbf{p}_k$, $\mathbf{g}_0$ is defined as the gradient at the middle point of the line segment connecting $\mathbf{p}_k$ and its neighbor, namely,

$$\mathbf{g}_0 = \begin{cases} \nabla V\left(\dfrac{\mathbf{p}_{k-1} + \mathbf{p}_k}{2}\right) & \text{if } k < \left\lceil \dfrac{N}{2} \right\rceil \\ \nabla V\left(\dfrac{\mathbf{p}_k + \mathbf{p}_{k+1}}{2}\right) & \text{if } k > \left\lceil \dfrac{N}{2} \right\rceil \end{cases} \tag{4}$$

$\mathbf{g}_1$ is defined as the gradient at the position with maximum energy $\mathbf{p}_{\max}$ along the direction $\mathbf{s}_0$. Several steps of line maximization are applied to the point $\mathbf{p}_k$ along $\mathbf{s}_0$ in order to locate $\mathbf{p}_{\max}$. Then several steps of line minimization along the conjugate direction $\mathbf{s}_1$ are applied to $\mathbf{p}_k$. The rest of the conjugate basis set are then built recursively using Eqn.(2). Simultaneously, each time when a new conjugate direction is determined, several steps of line minimization along this direction are applied to the associated new positions of $\mathbf{p}_k$.

3.3 Constrained Degree Elevation and Reduction

After the evolution of the intermediate control points along the conjugate directions, those points may become too close to each other. As a result, the control points only capture part of the information along the transition path. The resolution around the saddle region may be too low. This could lead to an underestimation of the energy barrier. Similar to the re-parameterization process in the string method [31], a redistribution process of the control points after each evolution

step is introduced in order to ensure that these intermediate control points are relatively well distributed. The degree elevation and reduction scheme for the Bézier curve are employed to redistribute the intermediate control points in our algorithm.

Degree elevation increases the flexibility of a curve by introducing more degrees of freedom for control. By adding an extra control point to the definition of a Bézier curve, its degree is raised by one. The advantage of using the degree elevation technique is that we can increase the degree of a Bézier curve without changing its shape. The degree elevation of an n^{th} order Bézier curve produces an $(n+1)^{th}$ order curve with a new set of vertices $\mathbf{q}_k$ defined by [32]

$$\begin{cases} \mathbf{q}_k = \mathbf{p}_k, & k = 0 \\ \mathbf{q}_k = \dfrac{k}{n+1}\mathbf{p}_{k-1} + \left(1 - \dfrac{k}{n+1}\right)\mathbf{p}_k, & k = 1,...,n \\ \mathbf{q}_k = \mathbf{p}_{k-1}, & k = n+1 \end{cases} \tag{4}$$

where $\mathbf{p}_k$'s are the original vertices of the n^{th} order Bézier curve. The Bézier curve can be elevated more than one degree by applying Eqn. (4) multiple times. In our algorithm, the curve is elevated only once within each iteration in order to make control points well distributed.

The purpose of degree elevation in our algorithm is to redistribute the intermediate control points. In other words, we are concerned more about how well the procedure makes the control points distributed than about how small the error between the elevated curve and the original curve may have, as long as the introduced error is within a tolerance range. Based on those two considerations, a constraint is added to the original degree elevation scheme in order to better serve our purpose. When two control points become too close to each other after the degree elevation by Eqn. (4), we manually set the new control point to be the arithmetic average of the two adjacent control points in the original curve. In other words, for each newly created control points of the elevated curve, we calculate the Euclidean distance between this point and the middle point of its corresponding adjacent points of the original curve. For the k^{th} control points $\mathbf{q}_k$ of the elevated curve, if it satisfies the condition

$$\left\| \mathbf{q}_k - \frac{\mathbf{p}_{k-1} + \mathbf{p}_k}{2} \right\| > c \left\| \mathbf{p}_k - \mathbf{p}_{k-1} \right\| \tag{4}$$

where c $(0 < c < 1)$ is a predefined constant, then $\mathbf{q}_k$ is set as the middle point of the straight line $\overline{p_{k-1}p_k}$. Since it is too computationally expensive to keep elevating the curve recursively, degree reduction is introduced to keep a balance with degree elevation and maintain a reasonable computational cost.

Degree reduction approximates an n^{th} order Bézier curve with an m^{th} $(m < n)$ order curve. Different from degree elevation, no exact degree reduction is possible in practice. So approximation is inevitable. Here we treat the degree reduction as an inverse process of the degree elevation. Eqn. (4) shows that the control points of an elevated Bézier curve can be exactly determined by the control points of the original curve through linear interpolation of the two adjacent points. For the degree reduction, we need to solve the over-determined system in Eqn. (4) for the unknowns $\{\mathbf{p}_k\}_{k=0}^{n}$ as a linear combination of $\{\mathbf{q}_k\}_{k=0}^{n+1}$.

We developed a reduction scheme similar to Eck's [33] but with a modified forward and backward procedure. In order to determine the new control points for the reduced curve, we make use of the information of three adjacent points instead of one as in Eck's scheme from the original curve. The three-step procedure is described as follows. In the forward step, three sets of points are calculated by using

$$\mathbf{p}_{k,1}^{I} = \frac{1}{n+1-k}\left((n+1)\mathbf{q}_k - k\mathbf{p}^{I}{}_{k-1}\right) \tag{5}$$

$$\mathbf{p}_{k,2}^{I} = \frac{1}{n+1-k}\left((n+1)\mathbf{q}_{k+1} - k\mathbf{q}_k\right) \tag{6}$$

and

$$\mathbf{p}_{k,3}^{I} = \frac{1}{n+1-k}\left((n+1)\mathbf{q}_{k+2} - k\mathbf{q}_{k+1}\right) \tag{6}$$

where $k = 1,\ldots,n-1$. Then an average of them

$$\mathbf{p}_k{}^{I} = \frac{\mathbf{p}_{k,1}{}^{I} + \mathbf{p}_{k,2}{}^{I} + \mathbf{p}_{k,3}{}^{I}}{3} \tag{7}$$

forms a new set of points $\left\{\mathbf{p}^{I}{}_k\right\}_{k=1}^{n-1}$. Similarly, in the backward step, a new set of points $\left\{\mathbf{p}^{II}{}_k\right\}_{k=1}^{n-1}$ can be obtained by using Eqns. (8), (9) , (9) and (10).

$$\mathbf{p}_{k-1,1}^{II} = \frac{1}{k}\left((n+1)\mathbf{q}_k - (n+1-k)\mathbf{p}^{II}{}_k\right) \tag{8}$$

$$\mathbf{p}_{k-1,2}^{II} = \frac{1}{k}\left((n+1)\mathbf{q}_{k-1} - (n+1-k)\mathbf{q}_k\right) \tag{9}$$

$$\mathbf{p}_{k-1,3}^{II} = \frac{1}{k}\left((n+1)\mathbf{q}_{k-2} - (n+1-k)\mathbf{q}_{k-1}\right) \tag{9}$$

$$\mathbf{p}_{k-1}{}^{II} = \frac{\mathbf{p}_{k-1,1}{}^{II} + \mathbf{p}_{k-1,2}{}^{II} + \mathbf{p}_{k-1,3}{}^{II}}{3} \tag{10}$$

Finally, the control points $\{\mathbf{p}_k\}_{k=0}^{n}$ of the reduced curve are calculated as a linear combination of the points in $\{\mathbf{p}^I{}_k\}_{k=1}^{n-1}$ and $\{\mathbf{p}^{II}{}_k\}_{k=1}^{n-1}$ as

$$\begin{cases} \mathbf{p}_k = \mathbf{q}_k & k = 0 \\ \mathbf{p}_k = (1-\lambda_k)\mathbf{p}_k^I + \lambda_k \mathbf{p}_k^{II} & k = 1,\ldots,n-1 \\ \mathbf{p}_k = \mathbf{q}_k & k = n \end{cases} \tag{10}$$

where λ_k is the weights for $\mathbf{p}_k^{II}$.

The degree reduction problem is then converted to the one of determining the weights of the corresponding control points. In Eck's method, λ_k's are determined by minimizing the least square distance between the original curve and the reduced one, which is too costly for our purpose. Since the degree reduction in our algorithm is to redistribute the control points instead of transforming geometric information of curves which requires the error between the reduced curve and the original one should be as small as possible. In order to reduce the computational cost, here the weights λ_k are defined as

$$\lambda_k = \frac{k}{n} \quad (k = 1,\cdots,n-1) \tag{11}$$

In addition, Eck's method may introduce loops, which should be avoided in our searching algorithm.

3.4 Local Degree Elevation and Reduction

The degree elevation and reduction of a Bézier curve changes the shape of the curve globally, which will gradually smooth out the curve. Consequently, this prevents the curve from converging to a curved MEP. The remedy for this issue is to introduce a local degree elevation and reduction scheme. Within each iteration, we check whether there is zigzag along the curve. For example, for the k^{th} control point $\mathbf{p}_k$ ($k = 1,...,n-1$), if it satisfies the condition

$$\arccos\left(\frac{\overrightarrow{p_{k-1}p_k} \cdot \overrightarrow{p_k p_{k+1}}}{\left\|\overrightarrow{p_{k-1}p_k}\right\| \left\|\overrightarrow{p_k p_{k+1}}\right\|} \right) > \beta \tag{11}$$

where $\beta\,(0 < \beta < \pi)$ is a predefined constant, then it indicates that there is a zigzag at the control point $\mathbf{p}_k$. If there is no zigzag along the curve, degree elevation or reduction is not needed; otherwise, degree elevation or reduction is done locally. If the zigzag only exists within the first half of control points, degree elevation or reduction is only performed to the first half of control points. Similarly, it is performed only to the second half of control points if the zigzag only exists within the second half. If the zigzag exists in both, we do degree elevation or reduction globally.

4. MULTIPLE TRANSITION PATHWAY SEARCH

Here, how to search multiple transition paths on the PES is presented. Our algorithm starts with the initial guess of a single transition path. Once the local minimums are found as described in Section 3.1, this single path will be divided into two curves if an extra basin is located along the path. Both subdivided curves will then be treated individually and the algorithm will be applied to them. This subdivision process continues recursively until there is only one possible saddle point between any pair of local minimums. As a result, multiple local minimums and transition paths can be found within a target search area. Therefore, the initial guess of this single path should be set up such that the search area of interest can be covered.

During the multiple transition path search stage, a curve with two end control points located at the two local minimums obtained from the single transition path search will be examined by using the curve subdivision scheme. It determines whether the curve crosses an extra basin with another local minimum. If yes, the curve is divided into two new curves at the intermediate control point that is located in the extra basin. Since the number of control points for those two newly created curves may be less than five, the degree elevation is applied to the two curves recursively until the number of control points for each curve reaches five. Those two elevated curves now represent the initial guesses for the two new transition paths. The elevated curves are optimized using the procedure listed in Table 1. After their respective local minimums are identified, the curve subdivision scheme is applied to them again. The check-and-break procedure continues until all of the curves are unbreakable with their end control points located at local minimums. By now, those curves are still the approximations of the individual MEPs. In order to find the actual energy barrier for each curve, the algorithm selects the control point with the maximum energy and makes it climb up to locate the saddle point. During the climbing process, a set of conjugate directions corresponding to the identified control point with the maximum energy are constructed. Different from the procedure in the single transition path search, the point with the maximum energy will be first maximized along $\mathbf{s}_0$ direction, and then minimized along other directions $\mathbf{s}_i$'s ($i \geq 1$). The same procedure in the single transition path search, i.e. minimization along directions with positive eigenvalues, is applied to the rest of intermediate control points during the climbing process. This further makes the curve converge to the MEP. Table 2 lists the pseudo-code of the algorithm for multiple transition path search.

The major step during the multiple transition path search is to determine some criteria of whether a curve is breakable and which intermediate control point we should select to break the

curve. Here the subdivision scheme for the fourth-order (with five control points) and fifth-order (with six control points) curves are used to demonstrate. If we use a curve with a degree lower than four, the limited number of control points may miss the detailed curvature information of the actual path on the PES. As a result, some of the local minimums will be missed. The subdivision scheme can be similarly extended to higher-order curves.

Table 2: PSEUDO-CODE OF THE ALGORITHM FOR MULTIPLE TRANSITION PATH SEARCH

INPUT: A curve $\varphi(\mathbf{x})$ with two end control points located at two local minimums.
OUTPUT: Multiple curves with their end points connected together locating at multiple local minimums. Besides, each curve has one point locating at the saddle point position.
N_i =number of newly produced curve for i^{th} iteration (N_0 is set to be 1).
$i = 0$
WHILE There exists newly produced curves in i^{th} iteration
$i = i + 1$;
N_i =0;
FOR $j = 1, 2..., N_{i-1}$
IF $\varphi_j(\mathbf{x})$ is breakable (using the scheme in Section 4.1)
Break the curve $\varphi_j(\mathbf{x})$ into two curves $\varphi_j^{\,1}(\mathbf{x})$ and $\varphi_j^{\,2}(\mathbf{x})$.
$N_i = N_i + 2$;
END IF
IF The number of control points for $\varphi_j^{\,1}(\mathbf{x})$ or $\varphi_j^{\,2}(\mathbf{x})$ is less than five
Do degree elevation to the curve $\varphi_j^{\,1}(\mathbf{x})$ or $\varphi_j^{\,2}(\mathbf{x})$.
END IF
Optimize $\varphi_j^{\,1}(\mathbf{x})$ and $\varphi_j^{\,2}(\mathbf{x})$ after degree elevation to get two optimized curve $\varphi_k(\mathbf{x})$ and $\varphi_{k+1}(\mathbf{x})$ ($k = N_i - 1$).
END FOR
END WHILE
FOR $j = 1, 2...,$ (total number of non-breakable curves produced during the WHILE loop)
Select the maxi-energy control point of $\varphi_j(\mathbf{x})$ to climb up in order to locate the saddle point.
END FOR

4.1 Scheme for Selecting Breakpoint

In this section, the curve subdivision scheme to determine whether a curve can be divided and which control point to be selected as the breakpoint. This curve subdivision scheme is based on an assumption that the control points are relatively evenly distributed in a sequential manner. In other words, the curve itself has no loop or large curvature. We make use of the information of the gradient and potential energy value at each of the intermediate control points as well as their relative positions. Figure. 1 shows a Bézier control polygon on the PES with two end control points located at the minimums of two separate basins of local minimums. $\mathbf{p}_0, \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ and $\mathbf{p}_4$ are control points. $-\nabla V(\mathbf{p}_1)$, $-\nabla V(\mathbf{p}_2)$, and $-\nabla V(\mathbf{p}_3)$ illustrate the negative gradient directions at the position $\mathbf{p}_1, \mathbf{p}_2$, and $\mathbf{p}_3$ respectively. θ_1, θ_2, and θ_3 are the angles between the negative gradients and the control polygon. By examining the three angles as well as the potential energy values at those intermediate control points, it is able to determine whether the curve crosses a third basin of local minimums. There are a total of eight combinations with the angle distributions. The process of this scheme includes three steps. The first step is to check the combination of θ_1 and θ_3. If no conclusion can be reached, a second step is to check θ_2. If we still cannot decide by the second step, the energy values at the intermediate points will be considered as the third step. The details about the scheme to determine a breakpoint for a fourth-order curve is described in the remainder of this section.

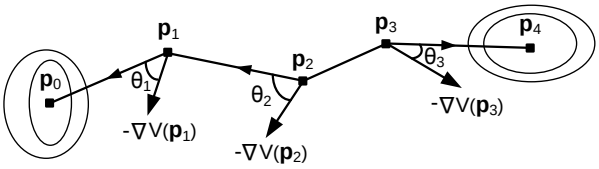


Figure. 1: ILLUSTRATION FOR MULTIPLE PATHWAY SEARCH (FIVE CONTROL POINTS)

Table 3 summarizes the curve subdivision scheme for a fourth order curve. "Y" indicates that the curve is breakable, and "U" means that it is unable to determine whether the curve is breakable or not only based on the combination of the angles. In those cases, potential energy value at all of the intermediate control points should be considered.

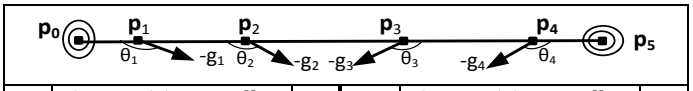
The first step of the process is to check the angles θ_1 and θ_3. If both θ_1 and θ_3 are larger than $\pi/2$ (i.e. Case 2 and Case 3 in Table 3), not only $\mathbf{p}_0$ and $\mathbf{p}_1$ are in different basins of local minimums but also $\mathbf{p}_3$ and $\mathbf{p}_4$, which indicates that the curve crosses at least a third basin of local minimum. Any of the three intermediate control points could be a breakpoint. In our algorithm, we choose $\mathbf{p}_2$ as the breakpoint. If either θ_1 or θ_3 is less than $\pi/2$ (i.e. Case 1, 4, 5, 6, 7, and 8 in Table 3), it is not guaranteed that the curve would go through a third basin of local minimum by checking θ_1 and θ_3 only. For example, when θ_1 is larger than $\pi/2$ and θ_3 is less than $\pi/2$, there are two sets of possible positions for the control points, i.e. Case 1 and 4. Since θ_3 is less than $\pi/2$, $\mathbf{p}_3$ and $\mathbf{p}_4$ could be located in the same basin. If $\mathbf{p}_2$ is located in a different basin from $\mathbf{p}_3$,

the curve crosses the third basin. Otherwise, $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$, and $\mathbf{p}_4$ could be in the same basin and the curve crosses only two adjacent basins. Therefore, we are unable to decide whether the curve is breakable or not with the only information that θ_1 is larger than $\pi/2$ and θ_3 is less than $\pi/2$. More information is required.

Table 3: CURVE SUBDIVISION SCHEME (FIVE CONTROL POINTS)

Case No	Greater (>) or smaller (<) than $\pi/2$			Breakable?	Case No	Greater (>) or smaller (<) than $\pi/2$			Breakable?
	θ_1	θ_2	θ_3			θ_1	θ_2	θ_3	
1	>	<	<	Y	**5**	<	<	>	U
2	>	<	>	Y	**6**	<	<	<	U
3	>	>	>	Y	**7**	<	>	<	U
4	>	>	<	U	**8**	<	>	>	Y

Table 4: CURVE SUBDIVISION SCHEME (SIX CONTROL POINTS)



Case No	Greater (>) or smaller (<) than $\pi/2$				Breakable?	Case No	Greater (>) or smaller (<) than $\pi/2$				Breakable?
	θ_1	θ_2	θ_3	θ_4			θ_1	θ_2	θ_3	θ_4	
1	>	<	<	>	Y	**9**	<	>	<	>	Y
2	>	<	>	>	Y	**10**	<	>	>	>	Y
3	>	>	>	>	Y	**11**	<	<	<	>	Y
4	>	>	<	>	Y	**12**	<	<	>	>	U
5	>	<	<	<	Y	**13**	<	<	<	<	U
6	>	<	>	<	Y	**14**	<	<	>	<	U
7	>	>	>	<	Y	**15**	<	>	>	<	Y
8	>	>	<	<	U	**16**	<	>	<	<	U

As a second step, we take $\mathbf{p}_2$ into consideration by checking θ_2. Here we use Cases 1 and 4 to illustrate. When θ_2 is less than $\pi/2$ (Case 1), it indicates that $\mathbf{p}_2$ cannot be located in the same basin as $\mathbf{p}_3$ and $\mathbf{p}_4$. Also as discussed in the first step, $\mathbf{p}_0$ and $\mathbf{p}_1$ are located in two different basins as in Case 1. Thus the curve should cross at least a third basin. Either $\mathbf{p}_1$ or $\mathbf{p}_2$ could be a breakpoint. Here, we select $\mathbf{p}_2$ to break. When θ_2 is larger than $\pi/2$ (Case 4), the negative gradients at the position $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$ are in the similar directions. $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$, and $\mathbf{p}_4$ could be in the same basin which means that the curve crosses only two adjacent basins of local minimums. Thus we need further information to determine if the curve is breakable.

In the third step, the potential energy values at $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$ are considered. If the potential energy values at positions $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$ have the monotonic relationship $V(\mathbf{p}_1) > V(\mathbf{p}_2) > V(\mathbf{p}_3)$, $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$ are considered as in the same basin, although there is still a slight chance that they are not. The curve is defined as unbreakable under this condition; otherwise, we break up the curve at the point $\mathbf{p}_1$.

The above three-step procedure for Cases 1 and 4 can be extended to Cases 5, 6, 7, and 8. For Cases 5 and 8, θ_1 is less than $\pi/2$ and θ_3 is larger than $\pi/2$. When θ_2 is larger than $\pi/2$ (Case 8), the curve is breakable at the points $\mathbf{p}_2$ and $\mathbf{p}_3$. Here we select $\mathbf{p}_2$ as the break point. When θ_2 is less than $\pi/2$ (Case 8), and $V(\mathbf{p}_3) > V(\mathbf{p}_2) > V(\mathbf{p}_1)$, the curve is unbreakable; otherwise, we break it at $\mathbf{p}_3$. When both θ_1 and θ_3 are less than $\pi/2$ (Cases 6 and 7), the additional information of θ_2 does not help to determine. Hence we use the potential energy value directly. When a curve crosses two adjacent basins and the control points are relatively evenly distributed, the energy level at the middle point should be the largest. Based on this fact, when $V(\mathbf{p}_2) > V(\mathbf{p}_1)$ and $V(\mathbf{p}_2) > V(\mathbf{p}_3)$, the curve is defined as unbreakable in the algorithm; otherwise, at the break point is chosen as $\mathbf{p}_2$.

The above procedure for breaking a fourth order curve can be extended to higher order curves. As an example, Table 4 summarizes the curve subdivision scheme for a fifth order curve.

5. DEMONSTRATION

Here the Rastrigin and Schwefel function defined in Tab. 5 are used to demonstrate the algorithm developed in this paper. The Rasrigin function is a non-convex function which is frequently used to test the optimization algorithm. The function has a global minimum at $\mathbf{x} = (0, \cdots, 0)$ and uniformly distributed local minimums as shown by a contour plot in Fig. 2. As discussed in Section 4, the initial guess for the transition path should be a curve with control points which are relatively evenly distributed. Here, we choose a curve $\varphi(\mathbf{x})$ with five control points located at (−2.81, 0.50), (−1.43, 2.90), (0.23, −2.47), (1.57, 2.67), and (2.91, −0.11), as indicated in Fig. 3 as 'Initial path of position 1'. First, the optimization procedure listed in Tab. 1 is applied to $\varphi(\mathbf{x})$, which produces a curve $\varphi'(\mathbf{x})$ with two end control points located at two local minimums. Then the multi-transition pathway search algorithm listed in Tab. 2 is applied to $\varphi'(\mathbf{x})$. A total of eleven local minimums and ten saddle points are located by this algorithm.

The result of a second set of initial positions, (−2.81, −1.50), (−1.43, −1.50), (0.23, −1.50), (1.57, −1.50), and (2.91, −1.50), is also shown in Fig. 2. For the second set of initial positions, a total of nine local minimums and eight saddle points are located. It is seen the curve subdivision scheme performs well and successfully locates all saddle points and local minimums along the paths.

A second example to test our algorithm is the Schwefel function which has a relatively non-uniform potential energy surface, as shown in Fig. 3. The first set of initial positions are (−100.3, 25), (−40.5, 40), (17.8, −10), (69.8, 70.6), and (130.2, 98.7). A total of six local minimums and five corresponding saddle points are located. The second set of initial positions are (−100.3, −70), (−40.5, −70), (17.8, −70), (69.8, −70), and (130.2, −70). A total of five local minimums and four corresponding saddle points are located.

Table 5: TEST FUNCTION

Function	Definition
Rastrigin	$f(\mathbf{x}) = 10n + \sum_{i=1}^{n}[x_i^2 - 10\cos(2\pi x_i)]$
Schwefel	$f(\mathbf{x}) = 418.9829n - \sum_{i=1}^{n} x_i \sin\sqrt{\lvert x_i \rvert}$

6. CONCLUSION

In this paper, we proposed a concurrent transition path search algorithm to search for multiple local minimums as well as saddle points simultaneously. Different from existing transition path search and saddle point search methods, no prior knowledge of the reactant and product is required for our algorithm. In addition, the algorithm can search multiple transition paths starting from one initial curve, which provides a better view of the PES than the methods that only search one transition path.

The search algorithm includes three stages. The first stage involves the optimization of a single transition path, during which two local minimums and one transition path that is close to the MEP will be located. The conjugate gradient method is employed to minimize the two end control points. The intermediate control points are evolved along their associated conjugate directions. A modified degree elevation and reduction scheme is used to redistribute the control points. The second stage is searching multiple transition paths starting from one single transition path obtained from the first stage. One curve is divided into two curves if a third minimum along the path is possible. A curve subdivision scheme is developed. Recursively, the check-break-optimize procedure is applied to each of the new curve. This stage will output several transition paths that approximate the true MEPs with those end points located at local minimums. Then at the third stage, the control point with the maximum energy within each of those transition paths climbs up in order to locate the actual saddle points.

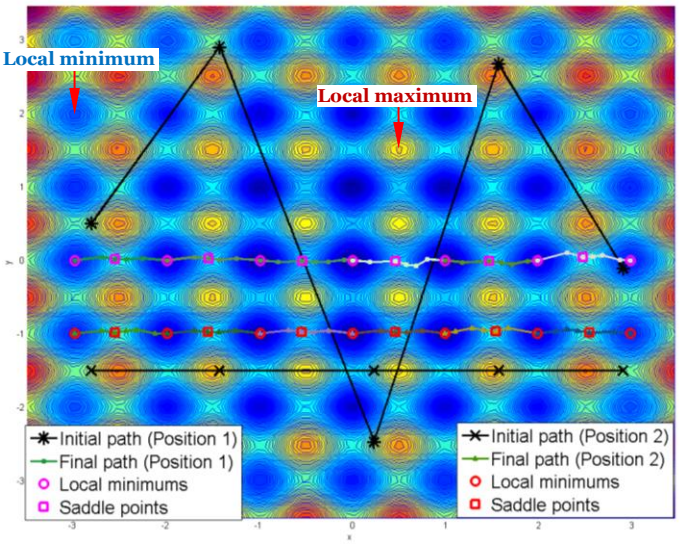


Figure. 2: TEST RESULT FOR RASTRIGIN FUNCTION WITH TWO SETS OF INITIAL POSITIONS. INITIAL POSITION_1 ARE LOCATED AT (-2.81, 0.50), (-1.43, 2.90), (0.23, -2.47), (1.57, 2.67), AND (2.91, -0.11). INITIAL POSITION_2 ARE LOCATED AT (-2.81, -1.50), (-1.43, -1.50), (0.23, -1.50), (1.57, -1.50), AND (2.91, -1.50).

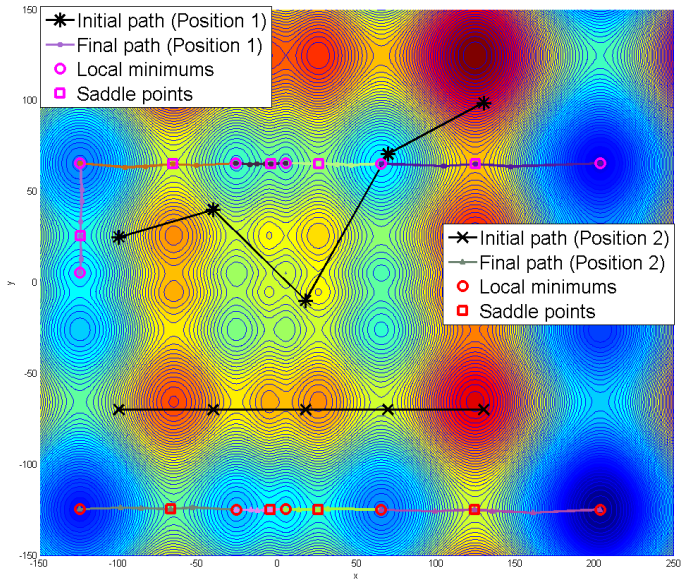


Figure. 3: TEST RESULT FOR SCHWEFEL FUNCTION WITH TWO SETS OF INITIAL POSITIONS. INITIAL POSITION_1 ARE LOCATED AT (-100.3, 25), (-40.5, 40), (17.8, -10), (69.8, 70.6), AND (130.2, 98.7). INITIAL POSITION_2 ARE LOCATED AT (-100.3, -70), (-40.5, -70), (17.8, -70), (69.8, -70), AND (130.2, -70).

It should be noted that the proposed curve subdivision scheme for selecting the breakpoint is not perfect. It could treat some breakable curves as unbreakable ones. For example, for a curve with five control points, when $\theta_1 > \pi/2$, $\theta_3 < \pi/2$ and $V(\mathbf{p}_1) > V(\mathbf{p}_2) > V(\mathbf{p}_3)$, we define the curve as unbreakable. It is true if the curve only passes through two adjacent basins of local minimum. But if the curve covers a long range with several extra local minimums, there is still a small chance that the control points are positioned in the manner which satisfies the unbreakable conditions. The scheme will treat both of the two curves as unbreakable curve. A remedy for missing breakable curves is adding an extra step to double check each unbreakable curve for one more time. If a curve is identified as unbreakable curve for the first time, the control points of the curve will be redistributed by using degree elevation or degree reduction. Then this elevated or reduced curve will be checked again to see whether it is breakable. This extra step will increase the accuracy of subdivision but also with extra computational cost.

ACKNOWLEDGMENTS

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