A Simplified Eigenvector-Following Technique for Locating Transition Points in an Energy Landscape

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We derive an eigenvector-following technique for locating transition points in an *N*-dimensional energy landscape. A separate Lagrange multiplier is used for each eigendirection to provide maximum flexibility in determining step sizes. In contrast to previous techniques based on a similar approach, we provide a simple algorithm for choosing specific values of these Lagrange multipliers. We demonstrate the robustness of the algorithm using two-dimensional Cerjan−Miller and Adams landscapes. The technique has also been applied to the S_{12} molecular cluster.

1. Introduction

The investigation of energy landscapes is of critical importance to many of the most challenging problems in chemical physics, including the study of molecular clusters,[1−4] biomolecules,[4] supercooled liquids,[5−10] and structural glasses.[4,11−13] An energy landscape itself consists of many peaks and valleys in a multidimensional configuration space. Energy minima correspond to mechanically stable configurations of the system and are often termed inherent structures.[9] Transitions between minima govern such important properties as reaction kinetics, protein folding dynamics, and glass transition range behavior.[4−9] Although it is straightforward to locate energy minima using geometry optimization,[14,15] the search for transition points has proved much more challenging.[4,15]

A transition point is formally defined as a stationary point where precisely one of the eigenvalues of the Hessian matrix is negative.[4] Thus, a transition point corresponds to an energy maximum in one eigendirection and an energy minimum in all other eigendirections. Many methods for finding transition states have been proposed on the basis of an eigenvector-following technique, in which the second derivatives of the energy function are used to construct a Hessian matrix.[1,4,15−21] The eigenvector-following technique is useful for finding likely transitions from a particular minimum to adjacent minima without having *a priori* knowledge of these neighboring minima. This technique is particularly relevant in kinetic Monte Carlo[22] and other types of dynamic simulations involving energy landscapes.

Previous eigenvector-following methods have employed a Lagrange formalism to constrain the walk from an energy minimum to a transition point. Though initial techniques employed just a single Lagrange multiplier,[16−21] a significant improvement by Wales[1] made use of a separate Lagrange multiplier for each eigendirection.

In this paper, we present an extension of the Wales eigenvector-following technique using a simplified choice of Lagrange multipliers based on rigorous geometrical arguments. We also provide a clear derivation of the eigenvector-following technique in the Lagrange formalism. We then outline an algorithm for implementing our simplified eigenvector-following method and show applications with the two-dimensional Cerjan−Miller[16] and Adams[21] landscapes, where the technique is shown to be remarkably robust, even with large step sizes. Finally, we use the algorithm to find transition states in an S_{12} cluster.

2. Derivation

Consider an *N*-dimensional energy landscape,

$$E = E(x_1,x_2,...,x_N) \tag{1}$$

with the generalized position coordinates x_1, x_2, ..., x_N. Equation 1 may denote a potential energy, free energy, enthalpy, or other type of landscape. In a particle-based system such as in molecular mechanics simulations, the number of dimensions *N* is typically three times the number of particles, minus any constraints.

If the energy of the system at an initial position x_i^0, where $i = 1, 2, ..., N$, is given by $E(x_i^0)$, then we may approximate the energy at a new position $x_i = x_i^0 + h_i$ using the Taylor series expansion,

$$E(x_i) \approx E(x_i^0) + \sum_{j=1}^{N} \frac{\partial E}{\partial x_j}\bigg|_{x_{ij}=x_{ij}^0} h_j + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} h_i \frac{\partial^2 E}{\partial x_i \partial x_j}\bigg|_{x_{ij}=x_{ij}^0} h_j \tag{2}$$

This can be written in matrix notation as

$$E(\mathbf{x}) \approx E(\mathbf{x}^0) + \mathbf{g}^T\mathbf{h} + \frac{1}{2}\mathbf{h}^T\mathbf{H}\mathbf{h} \tag{3}$$

where the position $\mathbf{x}$ and displacement $\mathbf{h} = \mathbf{x} - \mathbf{x}^0$ vectors are given by

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$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix} \qquad \mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \\ \vdots \\ h_N \end{pmatrix} \tag{4}$$

respectively. The gradient vector $\mathbf{g}$ and $N \times N$ Hessian matrix $\mathbf{H}$, evaluated at $\mathbf{x} = \mathbf{x}^0$, are given by

$$\mathbf{g} = \begin{pmatrix} \frac{\partial E}{\partial x_1} \\ \frac{\partial E}{\partial x_2} \\ \vdots \\ \frac{\partial E}{\partial x_N} \end{pmatrix}_{\mathbf{x}=\mathbf{x}^0} \tag{5}$$

and

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_N} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_N} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_N \partial x_1} & \frac{\partial^2 E}{\partial x_N \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_N^2} \end{pmatrix}_{\mathbf{x}=\mathbf{x}^0} \tag{6}$$

respectively. The Hessian matrix is symmetric by construction.

2.1. Newton−Raphson Method. In an unconstrained system, the Newton−Raphson method can be used to locate a stationary point in the energy landscape.[14] On the basis of eq 2, a stationary point must satisfy

$$\frac{\partial E}{\partial h_k} = 0 = \sum_{j=1}^{N} \left.\frac{\partial E}{\partial x_j}\right|_{x_j=x_j^0} \delta_{jk} + \sum_{i=1}^{N}\sum_{j=1}^{N} \delta_{ik} \left.\frac{\partial^2 E}{\partial x_i \partial x_j}\right|_{x_{ij}=x_{ij}^0} h_j \tag{7}$$

or, more compactly,

$$\mathbf{0} = g_k + \sum_{j=1}^{N} H_{kj} h_j \tag{8}$$

In matrix notation, we have

$$\mathbf{0} = \mathbf{g} + \mathbf{H}\mathbf{h} \tag{9}$$

so that the Newton−Raphson step is given by

$$\mathbf{h} = -\mathbf{H}^{-1}\mathbf{g} \tag{10}$$

We now define b_k and $\mathbf{V}_k$ as the eigenvalues and associated eigenvectors of the symmetric Hessian matrix,

$$\mathbf{H}\mathbf{V}_k = b_k \mathbf{V}_k \tag{11}$$

where the eigenvectors are normalized and satisfy $\mathbf{V}_j^{\mathrm{T}}\mathbf{V}_k = \delta_{jk}$. Because the eigenvectors $\mathbf{V}_k$ form a complete set, we can express the gradient vector as

$$\mathbf{g} = \sum_{k=1}^{N} F_k \mathbf{V}_k \tag{12}$$

Substituting this expression into eq 10, we obtain

$$\mathbf{h} = -\sum_{k=1}^{N} \frac{F_k}{b_k} \mathbf{V}_k \tag{13}$$

The change in energy after taking the Newton−Raphson step is

$$E(\mathbf{x}) - E(\mathbf{x}^0) = \Delta E = \mathbf{g}^{\mathrm{T}}\mathbf{h} + \frac{1}{2}\mathbf{h}^{\mathrm{T}}\mathbf{H}\mathbf{h} \tag{14}$$

Substituting in eqs 12 and 13, we obtain

$$\Delta E = -\sum_{j=1}^{N} \frac{F_j^2}{2b_j} \tag{15}$$

Hence, a positive eigenvalue $b_j > 0$ leads to a decrease in energy along the associated $\mathbf{V}_j$ eigendirection, and a negative eigenvalue $b_j < 0$ leads to an increase in energy along its associated eigendirection.

2.1.1. Newton−Raphson in One Dimension. To understand the implications of the Newton−Raphson method, let us consider the simple one-dimensional landscapes in Figure 1. In one dimension, the Newton−Raphson step in eq 13 simplifies to

$$h = -\frac{F}{b} = -\frac{\left.\frac{\partial E}{\partial x}\right|_{x=x^0}}{\left.\frac{\partial^2 E}{\partial x^2}\right|_{x=x^0}} \tag{16}$$

and the change in energy in eq 15 becomes

$$\Delta E = -\frac{F^2}{2b} = -\frac{\left(\left.\frac{\partial E}{\partial x}\right|_{x=x^0}\right)^2}{2\left.\frac{\partial^2 E}{\partial x^2}\right|_{x=x^0}} \tag{17}$$

Consider point A in Figure 1, where the gradient $\partial E/\partial x$ is negative and the curvature $\partial^2 E/\partial x^2$ is positive. On the basis of eq 16, this leads to a positive Newton−Raphson step, $h > 0$, driving the system to the right of A and toward the minimum in energy. Appropriately, the change in energy associated with the Newton−Raphson step, given by eq 17, is negative. If we take a Newton−Raphson step starting from point B, we see that $\partial E/\partial x > 0$ and $\partial^2 E/\partial x^2 > 0$. Hence the Newton−Raphson step from point B is leftward, again driving the system toward the minimum in energy. Hence, the sign of ΔE depends only on the sign of the curvature, $\partial^2 E/\partial x^2$: a positive curvature leads to a decrease in the energy of the system, and a negative curvature leads to an increase in energy.

Performing a similar analysis for points C and D in Figure 1, we see the Newton−Raphson step again drives that system toward a stationary point, but in this case it is a maximum rather than a minimum in energy. This is in agreement with eq 17, which predicts an increase in energy when starting from a point of negative curvature. Finally, if we consider a step from point E or F, we see that the Newton−Raphson method drives the system toward any type of stationary point—it need not be an absolute minimum or maximum in energy.

2.2. Lagrange Approach. A transition point is a stationary point where exactly one eigenvalue of the Hessian matrix $\mathbf{H}$ is negative. In other words, a transition point corresponds to an energy maximum in one direction and an energy minimum in all other directions. Whereas the Newton−Raphson method

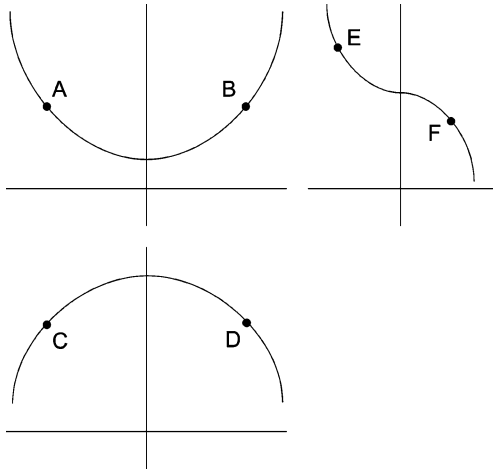

Figure 1. Model one-dimensional landscapes. The Newton−Raphson method always drives the system toward a stationary point.

finds any type of stationary point, we wish to constrain ourselves to just these first-order transition points. Following the approach of Wales,[1] we define the Lagrange function

$$L = -E(\mathbf{x}) + \frac{1}{2}\sum_{i=1}^{N}\lambda_i(h_i^2 - c_i^2) \tag{18}$$

where c_i are the desired step sizes in the various directions and λ_i are Lagrange multipliers. Substituting eq 2 into the above expression and taking the derivative of L with respect to an arbitrary step h_k yield

$$0 = -g_k - \sum_{j=1}^{N}H_{kj}h_j + \lambda_k h_k \tag{19}$$

In matrix notation, we have

$$\mathbf{0} = -\mathbf{g} - \mathbf{H}\mathbf{h} + \boldsymbol{\lambda}\mathbf{h} \tag{20}$$

where $\boldsymbol{\lambda}$ is a diagonal matrix given by

$$\boldsymbol{\lambda} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_N \end{pmatrix} \tag{21}$$

Solving for $\mathbf{h}$ in eq 20 and substituting eq 12 for the gradient, we obtain

$$\mathbf{h} = \sum_{k=1}^{N}\frac{F_k}{\lambda_k - b_k}\mathbf{V}_k \tag{22}$$

The associated change in energy is

$$\Delta E = \sum_{j=1}^{N}\frac{F_j^2\left(\lambda_j - \frac{b_j}{2}\right)}{(\lambda_j - b_j)^2} \tag{23}$$

Hence, the sign of the energy change in a particular eigendirection $\mathbf{V}_j$ depends on both the eigenvalue b_j and the choice of Lagrange multiplier λ_j.

2.2.1. Lagrange Approach in One Dimension. Let us again consider the simple one-dimensional landscapes in Figure 1 to understand the role of the Lagrange multipliers in eqs 22 and 23. In one dimension, these equations reduce to

$$h = \frac{F}{\lambda - b} = \frac{\left.\frac{\partial E}{\partial x}\right|_{x=x^0}}{\lambda - \left.\frac{\partial^2 E}{\partial x^2}\right|_{x=x^0}} \tag{24}$$

and

$$\Delta E = \frac{F^2\left(\lambda - \frac{b}{2}\right)}{(\lambda - b)^2} = \frac{F^2\left(\lambda - \frac{1}{2}\left.\frac{\partial^2 E}{\partial x^2}\right|_{x=x^0}\right)}{\left(\lambda - \left.\frac{\partial^2 E}{\partial x^2}\right|_{x=x^0}\right)^2} \tag{25}$$

If we want to minimize the energy, then $\lambda - b/2 < 0$, or $\lambda < b/2$. Starting from point A, we wish to have $h > 0$ to move in the appropriate direction. Because the gradient is negative at this point, eq 24 leads to the condition $\lambda - b < 0$, or $\lambda < b$. Because $b > 0$ at point A, we must therefore choose $\lambda < b/2$ to satisfy both conditions.

Let us now suppose that we wish to minimize the energy starting from point B. The same condition, $\lambda < b/2$, holds from eq 25. From eq 24, we have the condition $\lambda < b$ because $F > 0$ and we wish to have $h < 0$ from this point. Because we are still in the regime of $b > 0$, we must again choose $\lambda < b/2$ to both decrease energy and move in the leftward direction. Hence, the condition $\lambda < b/2$ for energy minimization is the same for both points A and B.

Suppose now that we wish to maximize the energy starting from point A. From eq 24, we have $\lambda - b/2 > 0$, or $\lambda > b/2$. From eq 24, we have $\lambda - b > 0$, or $\lambda > b$. Because $b > 0$, we must have the condition $\lambda > b$. A similar analysis starting from point B gives the same result.

Now let us consider points C and D, where $b < 0$. For energy minimization we obtain the condition $\lambda < b$, and for energy maximization we have $\lambda > b/2$. Thus, for any arbitrary value of b, we may walk downhill on the energy landscape with $\lambda < -|b|$ and uphill with $\lambda > |b|$.

2.2.2. A Simplified Choice of Lagrange Multipliers. Let us now return to our N-dimensional energy landscape. We may rewrite eq 23 as a summation of energy changes in the various eigendirections:

$$\Delta E = \sum_{j=1}^{N}\Delta E_j \tag{26}$$

where

$$\Delta E_j = \frac{F_j^2\left(\lambda_j - \frac{b_j}{2}\right)}{(\lambda_j - b_j)^2} \tag{27}$$

Suppose we wish to find a transition point by maximizing energy in a particular $\mathbf{V}_i$ direction while minimizing energy in all of the orthogonal $\mathbf{V}_{j\neq i}$ directions. It follows from our analysis in section 2.2.1 that a choice of $\lambda_i > |b_i|$ and $\lambda_j < -|b_j|$ would guarantee a step in the correct direction. However, it specifies neither the particular values of $\lambda_{i,j}$ nor the magnitude of the step.

We may simplify our analysis by assuming that a transition point search always starts from a local minimum in the energy landscape. This is also the most practical case to consider from an applications point of view, because we are typically interested in finding the transition energy between two stable configura-

tions, e.g., reactant and product in chemical kinetics or two inherent structures using Stillinger's terminology.[9] A minimum in the potential energy landscape has the property $b_k > 0$ for all $k = 1, 2, ..., N$. As we walk on the potential energy landscape from the minimum to a transition point, we are essentially walking uphill along a valley or streambed. If the direction of our walk up the streambed is $\mathbf{V}_i$ and the step size is sufficiently small, we should have $b_j > 0$ for all $j \neq i$ and be near the energy minima in the $\mathbf{V}_{j\neq i}$ directions along the entire walk. In the case of an infinitesimal step size, we would exactly follow the streambed; however, due to finite step sizes, we may have slight deviations from the streambed. These deviations may be corrected by an appropriate choice of $\lambda_{j\neq i}$, which is accomplished by finding the nearest stationary point in the $\Delta E_{j\neq i}$ contribution:

$$\frac{\partial \Delta E_{j\neq i}}{\partial \lambda_{j\neq i}} = 0 \tag{28}$$

leading to $\lambda_{j\neq i} = 0$.

The choice of $\lambda_{j\neq i} = 0$ reduces our Lagrange approach to exactly the Newton−Raphson method in all $\mathbf{V}_{j\neq i}$ eigendirections, and it is in agreement with our previous condition of $\lambda_{j\neq i} < b_{j\neq i}/2$ for energy minimization with $b_{j\neq i} > 0$. Note that if we accidentally step outside of the regime where $b_{j\neq i} > 0$, a negative $\lambda_{j\neq i} < b_{j\neq i}$ should be chosen. (This also indicates that the chosen step size in the $\mathbf{V}_i$ eigendirection is too large—so large that we have effectively stepped out of the streambed and started climbing hills in an orthogonal direction.)

The magnitude of the step size along the $\mathbf{V}_i$ eigendirection is given by

$$h_i^2 = c_i^2 = \frac{F_i^2}{(\lambda_i - b_i)^2} \tag{29}$$

This leads to the condition

$$\lambda_i = b_i \pm \left|\frac{F_i}{c_i}\right| \tag{30}$$

Because $\lambda_i > b_i$ is required for energy maximization with $b_i > 0$, we choose

$$\lambda_i = b_i + \left|\frac{F_i}{c_i}\right| \tag{31}$$

for this case. This is also the appropriate choice of λ_i for $b_i = 0$. The step sizes $c_{j\neq i}$ in the other directions are fixed by $c_{j\neq i} = |F_j/b_j|$. The total step size is thus

$$\mathbf{h}^T\mathbf{h} = \frac{F_i^2}{(\lambda_i - b_i)^2} + \sum_{j=1,j\neq i}^{N} \frac{F_j^2}{b_j^2} \tag{32}$$

If we are close to the energy minima in the $\mathbf{V}_{j\neq i}$ eigendirections, then $F_{j\neq i} \approx 0$ such that

$$\mathbf{h}^T\mathbf{h} \approx \frac{F_i^2}{(\lambda_i - b_i)^2} = c_i^2 \tag{33}$$

Any deviation from $\mathbf{h}^T\mathbf{h} = c_i^2$ is a result of having finite values of $F_{i\neq j}^2$.

As we progress up the streambed, eventually we will pass through an inflection point where b_i becomes negative. The condition for energy maximization with $b_i < 0$ is $\lambda_i > b_i/2$. Because in this case the nearest stationary point is the transition point of interest with exactly one negative eigenvalue b_i, the most efficient choice of Lagrange multiplier is $\lambda_i = 0$, corresponding again to the Newton−Raphson step of eq 13. Thus in the case of $b_i < 0$, the step size c_i is determined by the Newton−Raphson method.

Finally, we note that the first step from the initial minimum point must follow a different scheme than that given by eq 29 because $F_i = 0$. In this case, we choose a simple step of magnitude c_i in the $\mathbf{V}_i$ eigendirection. There should be no components of $\mathbf{h}$ in the other $\mathbf{V}_{j\neq i}$ eigendirections because we also have $F_{j\neq i} = 0$ and wish to remain in the streambed.

3. Algorithm

We now provide an algorithm for implementing the above Lagrange approach for finding transition states.

1. Starting at a minimum point in the energy landscape, compute the Hessian matrix and determine its eigenvalues and normalized eigenvectors. Choose the eigenvector $\mathbf{V}_i$ corresponding to the direction of interest, typically that of the "softest mode," i.e., that corresponding to the smallest eigenvalue. (Higher-order modes can be chosen to locate other transition states adjacent to the current energy minimum. These transition points are likely to be of higher energy than that corresponding to the softest mode. In techniques such as kinetic Monte Carlo, it is desirable to obtain a thorough list of transition states available from a given minimum.)

2. Step in the direction of the eigenvector $\mathbf{V}_i$ of interest using a desired magnitude c_i. This initial step $\mathbf{h}$ should have no components from the other $\mathbf{V}_{j\neq i}$ eigendirections. When a complete list of transition points is mapped out, a second search should be initiated in the opposite $-\mathbf{V}_i$ direction.

3. Compute the gradient $\mathbf{g}$ and Hessian $\mathbf{H}$ at the new point, and determine the eigenvalues and normalized eigenvectors of the new Hessian matrix. Choose the eigenvalue b_i of interest, typically the smallest, and its corresponding eigenvector $\mathbf{V}_i$. The eigenvectors form the columns of an $N \times N$ unitary matrix:

$$\mathbf{U} = (\mathbf{V}_1 \quad \mathbf{V}_2 \quad \cdots \quad \mathbf{V}_N) \tag{34}$$

4. Compute the vector $\mathbf{F} = \mathbf{U}^T\mathbf{g}$. Note that this is just eq 12 where F_k are the components of $\mathbf{F}$.

5. Choose the Lagrange multipliers $\lambda_{j\neq i} = 0$ corresponding to the Newton−Raphson step for all directions orthogonal to $\mathbf{V}_i$. If $b_i \geq 0$, choose $\lambda_i = b_i + |F_i/c_i|$, where c_i is the desired step size in the $\mathbf{V}_i$ direction. If $b_i < 0$, choose $\lambda_i = 0$. (Note that the choice of $\lambda_{j\neq i} = 0$ assumes that we are sufficiently close to the streambed such that $b_{j\neq i} > 0$. If $b_{j\neq i} \leq 0$, the desired step size c_i is probably too large. This can be corrected by either choosing a smaller value of c_i or by choosing $\lambda_{j\neq i} < b_{j\neq i}$.)

6. Compute the step

$$\mathbf{h} = \sum_{k=1}^{N} \frac{F_k}{\lambda_k - b_k} V_k \tag{35}$$

and update the system coordinates $\mathbf{x}$ appropriately.

7. Repeat steps 3−6 until converged at a transition point. The criterion for convergence is $|F_i| < \epsilon$, where ϵ is chosen to reflect the desired level of precision.

We note that some previous techniques have incorporated a dynamically variable maximum step size, which may be combined with a trust radius.[4] In our algorithm, the step size in the $b_i \geq 0$ regime is controlled by the c_i parameter, which is user-definable. However, in the $b_i < 0$ regime the step size is

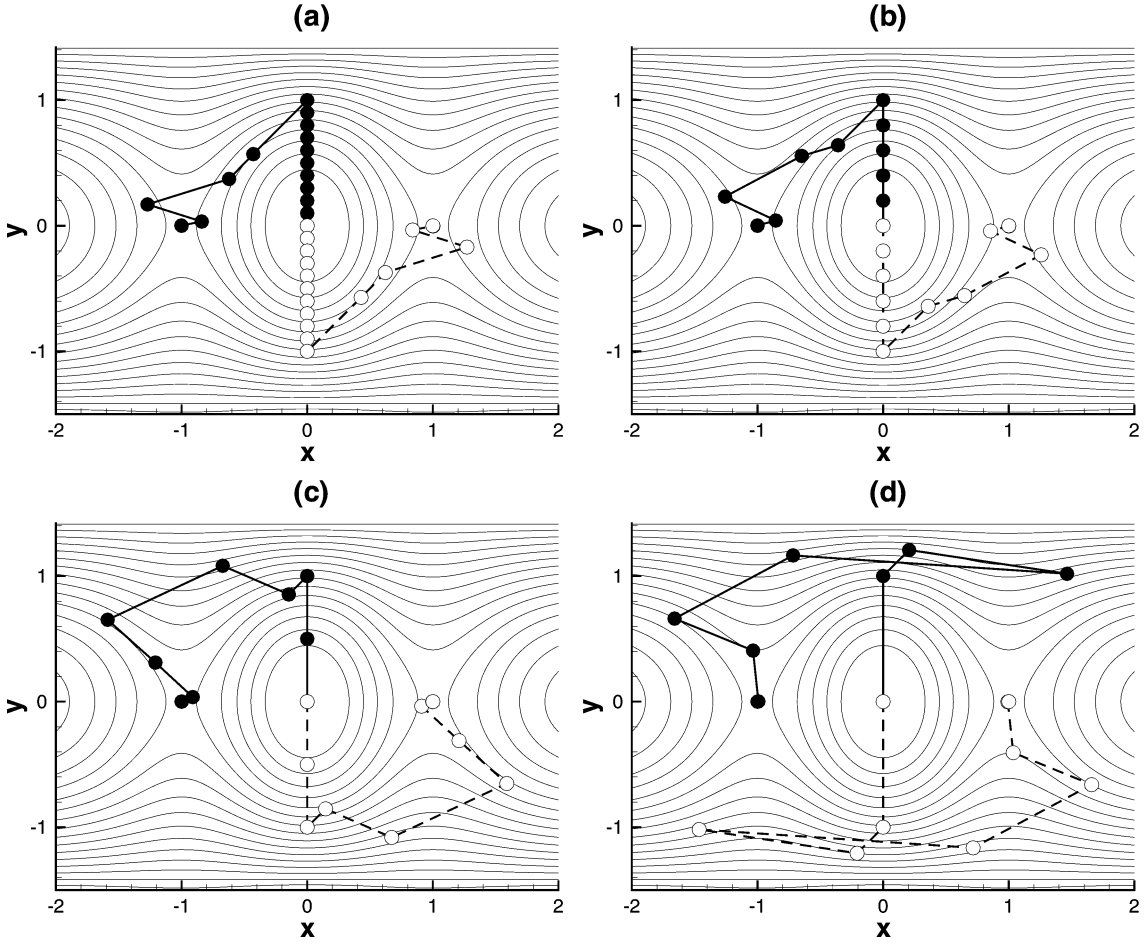

Figure 2. Contour plot of the two-dimensional Cerjan−Miller function of eq 36, using $a = 1$, $b = {}^1/_2$, and $c = 1$. Starting from the minimum at $(x, y) = (0, 0)$, we find the transition points at $(\pm 1, 0)$ using a step size of (a) 0.1, (b) 0.2, (c) 0.5, and (d) 1.0. Solid lines indicate an initial step in the $+y$ direction, and dashed lines indicate an initial step in the $-y$ direction.

governed entirely by the values of F_i and b_i to choose an optimum step toward the transition point. We also note that for large atomistic systems, it may be undesirable to compute or diagonalize the Hessian matrix. In this case, hybrid techniques exist for estimating the smallest Hessian eigenvalues and corresponding eigenvectors.[4]

One final consideration for atomistic systems is that translation or rotation of the entire simulation cell leads to zero Hessian eigenvalues, making inversion of the Hessian matrix impossible. However, this problem may be avoided by either changing to a minimal set of internal coordinates[4] or using an eigenvalue−eigenvector solver that does not rely on explicit matrix inversion, such as the excellent Template Numerical Toolkit.[23]

4. Examples

As a first example of the above algorithm, let us consider the two-dimensional Cerjan−Miller energy function,[16]

$$E_{\mathrm{CM}}(x,y) = (a - by^2)x^2 \mathrm{e}^{-x^2} + \frac{c}{2}y^2 \tag{36}$$

The minimum energy is located at the origin, and the two transition points are located symmetrically at $(x, y) = (\pm 1, 0)$. To provide a difficult test for our algorithm, we choose $a = 1$, $b = {}^1/_2$, and $c = 1$, which gives the softest mode in the y direction. Figure 2 shows a contour plot of the Cerjan−Miller function with transition point searches shown for four different step sizes: 0.1, 0.2, 0.5, and 1.0. Choosing an initial step in the $+y$ direction, all four cases converge upon the left transition point at $(-1, 0)$. If the opposite $-y$ direction is chosen for the initial step, then the algorithm converges symmetrically to the right transition point at (1, 0). Figure 2 shows that a shorter step size leads to a more direct path to the transition point, but it can be less efficient because a greater number of steps are required. The fact that even the relatively large step size of 1.0 leads to convergence illustrates the robustness of the algorithm, even when the initial step is chosen in what is essentially the wrong direction. Note that in all four cases shown in Figure 2, the step size is determined solely by the Newton−Raphson method after leaving the regime where $b_i \geq 0$.

For a second example, we consider the Adams function,[21]

$$E_{\mathrm{A}}(x,y) = 2x^2(4 - x) + y^2(4 + y) - xy[6 - 17\mathrm{e}^{-(1/4)(x^2 + y^2)}] \tag{37}$$

Starting from the minimum at the origin, we locate the two transition points at (2.4104, 0.4419) and (−0.1985, −2.2793). Results are shown in Figure 3 using an initial step size of 2.0. The two transition points are found by starting in opposite directions along the softest mode. The first transition point at (2.4104, 0.4419) is found in seven steps, and the second transition point at (−0.1985, −2.2793) is found in only four steps, a vast improvement over prior eigenvector-following techniques.[21]

As a final example, let us consider the more complicated case of an S_{12} molecular cluster. We employ the ab initio potentials of Mauro and Varshneya[24] for sulfur, which include two-, three-, and effective four-body terms. A portion of the potential energy

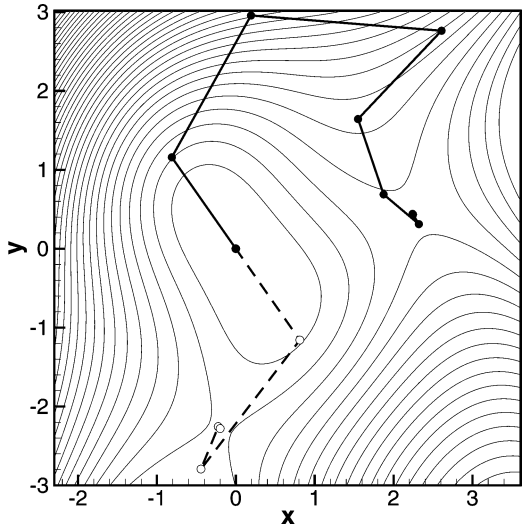

Figure 3. Contour plot of the two-dimensional Adams function of eq 37. Starting from the minimum at $(x, y) = (0, 0)$, we find the two transition points at (2.4104, 0.4419) and (−0.1985, −2.2793). The initial step size is chosen to be 2.0, and the initial step is taken in opposite directions along the softest mode.

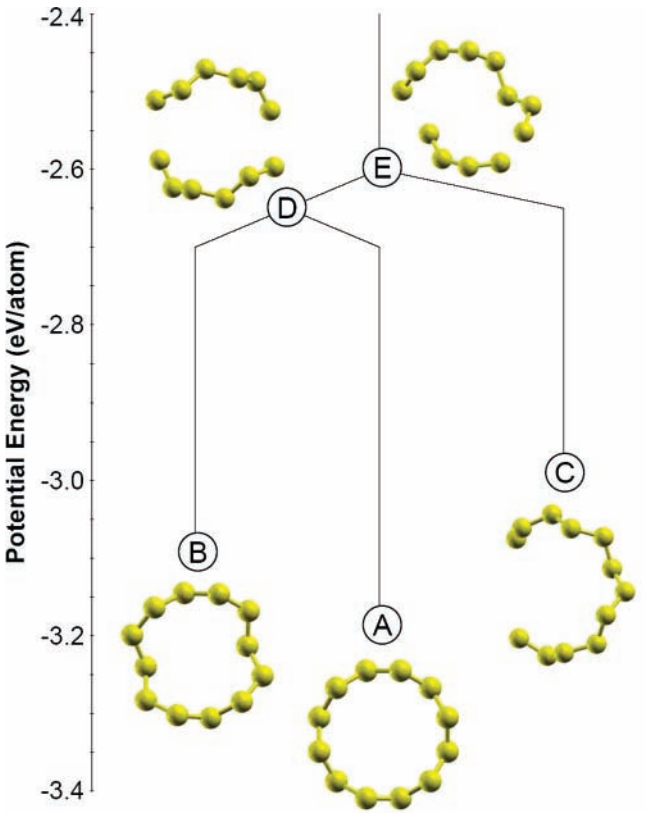

Figure 4. A portion of the potential energy landscape of S_{12}, including three inherent structures (A, B, and C) and two transition states (D and E).

landscape, including three inherent structures (A, B, and C) and two transition points (D and E), is shown in Figure 4. Inherent structures A and B correspond to the two well-known ring conformations for S_{12}.[25] The S_{12} cluster may transition between these configurations through transition point D. A third inherent structure with higher energy is the chain configuration of point C in Figure 4. To transition between ring and chain structures, the S_{12} cluster can pass through transition state E. In our simulations, the simplified eigenvector-following technique is able to locate transition points D and E with about 50% fewer iterations than previous techniques that use the same number of Lagrange multipliers.[4] We have also used our simplified eigenvector-following technique to give complete mappings of the potential energy landscapes of other elemental and heterogeneous chalcogen clusters,[26] including Se_3-Se_8, $(S,Se,Te)_8$, and $Se_n(S,Te)_{8-n}$. From our experience, the simplified choice of Lagrange multipliers provides for a more optimum step vector **h** than previous techniques[4] and consequently leads to convergence in roughly 40−50% fewer iterations.

5. Conclusions

We have derived an eigenvector-following technique for locating transition points in an energy landscape. Our method is based on maximizing energy in one eigendirection of interest while simultaneously minimizing energy in all orthogonal directions. We have outlined an algorithm for implementation of this technique and demonstrated its robustness using the two-dimensional Cerjan−Miller and Adams landscapes. The technique has also been successfully applied to realistic molecular clusters, including S_{12}. This method for locating transition points should be useful in computing reaction kinetics and transition probabilities in a wide range of fields, including the study of molecular clusters, biomolecules, and structural glasses.

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References and Notes

(1) Wales, D. J. *J. Chem. Phys.* **1994**, *101*, 3750−3762.
(2) Miller, M. A.; Doye, J. P. K.; Wales, D. J. *J. Chem. Phys.* **1999**, *110*, 328−334.
(3) Murrell, J. N.; Laidler, K. J. *J. Chem. Soc., Faraday Trans. 2* **1968**, *64*, 371−377.
(4) Wales, D. J. *Energy Landscapes*; Cambridge University: Cambridge, U.K., 2003.
(5) Debenedetti, P. G. *Metastable Liquids*; Princeton University: Princeton, NJ, 1996.
(6) Goldstein, M. *J. Chem. Phys.* **1969**, *51*, 3728−3739.
(7) Stillinger, F. H. *J. Chem. Phys.* **1988**, *88*, 7818−7825.
(8) Debenedetti, P. G.; Stillinger, F. H.; Truskett, T. M.; Roberts, C. J. *J. Phys. Chem. B* **1999**, *103*, 7390−7397.
(9) Debenedetti, P. G.; Stillinger, F. H. *Nature* **2001**, *410*, 259−267.
(10) Stillinger, F. H.; Debenedetti, P. G. *J. Chem. Phys.* **2002**, *116*, 3353−3361.
(11) Middleton, T. F.; Wales, D. J. *Phys. Rev. B* **2001**, *64*, 024205.
(12) Middleton, T. F.; Wales, D. J. *J. Chem. Phys.* **2003**, *118*, 4583−4593.
(13) Hernández-Rojas, J.; Wales, D. J. *J. Non-Cryst. Solids* **2004**, *336*, 218−222.
(14) Fletcher, R. *Practical Methods of Optimization*: John Wiley & Sons: 1980; Vol. 1.
(15) Schlegel, H. B. *Adv. Chem. Phys.* **1987**, *67*, 249−286.
(16) Cerjan, C. J.; Miller, W. H. *J. Chem. Phys.* **1981**, *75*, 2800−2806.
(17) Simons, J.; Jørgensen, P.; Taylor, H.; Ozment, J. *J. Phys. Chem.* **1983**, *87*, 2745−2753.
(18) O'Neal, D.; Taylor, H.; Simons, J. *J. Phys. Chem.* **1984**, *88*, 1510−1513.
(19) Bell, S.; Crighton, J. S. *J. Chem. Phys.* **1984**, *80*, 2464−2475.
(20) Nichols, J.; Taylor, H.; Schmidt, P.; Simons, J. *J. Chem. Phys.* **1990**, *92*, 340−346.
(21) Banerjee, A.; Adams, N.; Simons, J.; Shepard, R. *J. Phys. Chem.* **1985**, *89*, 52−57.
(22) Fichthorn, K. A.; Weinberg, W. H. *J. Chem. Phys.* **1991**, *95*, 1090−1096.
(23) Pozo, R. *Template Numerical Toolkit*, http://math.nist.gov/tnt/, 2004.
(24) Mauro, J. C.; Varshneya, A. K. *6th Pacific Rim Conference on Ceramic and Glass Technology*; American Ceramic Society: Kapalua, HI, 2005.
(25) Hohl, D.; Jones, R. O.; Car R.; Parrinello M. *J. Chem. Phys.* **1988**, *89*, 6823−6835.
(26) Mauro, J. C.; Loucks, R. J.; Balakrishnan, J.; Varshneya, A. K. *Phys. Rev. A* **2005**, submitted.