Walking on potential energy surfaces

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An algorithm for locating stationary points corresponding to local minima and transition states on potential energy surfaces is developed and analyzed. This method, which represents a substantial extension of an earlier algorithm, utilizes local gradient and Hessian (i.e., first and second energy derivative) information to generate a series of "steps" that are followed to the desired stationary point. By designing the step sequence to move energetically downhill in all coordinates, local minima can be found. By stepping uphill along one local eigenmode of the Hessian while minimizing the energy along all other modes, one locates transition states. A key element of this development is a more efficient parametrization of the step vector in terms of quantities that permit the direction (i.e., uphill or downhill) and length of the step to be carefully controlled. This, in turn, allows "walks" that trace streambeds connecting local minima to transition states and to neighboring local minima more closely than has been found using the earlier methods. Such streambed walks provide information that can be used in subsequent reaction-path dynamics simulations.

I. INTRODUCTION

Locating stationary points on energy surfaces, given knowledge of the local gradients and curvatures, represents a challenging and important problem in computational chemistry.[1] Such points correspond to geometries at which all gradients (first derivatives with respect to coordinates) vanish. They include minima, where all eigenvalues of the second derivative or Hessian matrix are positive, and transition states, where the Hessian has one negative eigenvalue. There are, of course, stationary points at which more than one Hessian matrix eigenvalue is negative; they correspond to "mountain tops" and are usually not of as much importance in chemistry. An algorithm that efficiently locates the desired stationary points and allows one to trace out the "streambeds" that connect minima through transition states with other minima would be of great utility.

In earlier publications,[2] this research group[2] and others have described the development and implementation of two such algorithms. Based on substantial experience gained over the ensuing years, we are now in a position to describe substantial improvements in these tools.

In this paper, we develop a new procedure for locating minima and transition states and for walking in the streambeds connecting them. At each step, the method uses the local slope or gradient ($\mathbf{F}$) vector and curvature or Hessian matrix ($\mathbf{H}$) to compute a step vector ($\mathbf{x}$) which is added to the current atomic coordinates ($\mathbf{r}_0$) to obtain new coordinates ($\mathbf{r}$) at which new $\mathbf{F}$ and $\mathbf{H}$ matrices are computed so the process can be continued. Convergence to a desired stationary point is reached when the norm of $\mathbf{F}$ is less than some specified tolerance, the number of negative eigenvalues of $\mathbf{H}$ is correct (i.e., zero for a minimum and one for a transition state), and the energy change from step to step $E - E_0$ is within some tolerance.

We include in this class of problems walks that lead to fragmentation. For such events, a true transition state will not be reached because the potential energy surface only asymptotically approaches a point at which the forces vanish. Moreover, upon fragmentation, additional zero eigenvalues appear in the Hessian matrix[3] corresponding to the new translations and rotations that exist in the fragments, but were internal modes in the original molecule.

II. DEVELOPMENT OF THE METHOD

A. The local quadratic approximation

We begin by writing a local quadratic approximation to the potential energy surface in terms of the $3N$ Cartesian components of the gradient, Hessian, and step matrices

$$E = E_0 + \mathbf{xF} + 1/2\mathbf{xHx}. \tag{1}$$

By assumption, we know the energy surface only locally. Therefore, it is important to constrain our steps $\mathbf{x}$ to lie within a radius L for which the quadratic representation in Eq. (1) is valid. The determination of this "trust radius" L in terms of the ability of Eq. (1) to predict energy changes experienced for steps $\mathbf{x}$ within L is dealt with later in Sec. IV.

B. Partitioning into internal and external degrees of freedom

If the energy surface $E(\mathbf{x})$ pertains to a molecule in the gas phase for which translational and rotational motions have no restoring forces, five or six coordinates can be removed to yield $\mathbf{F}$, $\mathbf{H}$, and $\mathbf{x}$ in the $3N-5$ or $3N-6$ internal coordinates. In practice, our *ab initio* electronic structure codes yield $\mathbf{F}$ and $\mathbf{H}$ in terms of $3N$ Cartesian coordinates. We then partition these matrices into external and internal spaces by first constructing five or six orthonormal vectors that span the translational and (infinitesimal) rotational[2(d)] spaces together with $3N-5$ or $3N-6$ other orthonormal vectors that span the internal space. Projection of $\mathbf{F}$ and $\mathbf{H}$ onto these spaces then provides internal gradient and Hessian matrices. The components of $\mathbf{F}$ and $\mathbf{H}$ lying within the translational and rotational spaces can be ignored when dealing with an isolated species for which $E(\mathbf{x})$ is a function

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only of the internal coordinates. However, when treating a species imbedded in a solvent or other medium, translational and reorientational displacements may indeed be important to include. As described here, the walking algorithm can be applied separately to the internal and external degrees of freedom. For an isolated species, the external displacements can be removed and ignored and attention can be focused on the internal displacements only. If, in addition, there are degrees of freedom along which the force is zero by symmetry, it is possible to include these directions in the external displacement space. Doing so then permits symmetry-preserving walks to be realized. The remainder of the presentation is made in terms of the internal variables, whatever they may be.

C. Analysis in the Hessian eigenmode basis

Given **F** and **H**, the local quadratic energy expression can be rewritten in terms of the eigenmodes of **H**:

$$\mathbf{H}\mathbf{v}_i = h_i \mathbf{v}_i, \quad i = 1,2,...,3N-5 \text{ or } 3N-6, \tag{2}$$

where it takes on the form

$$E = E_0 + F_i x_i + 1/2 x_i^2 h_i. \tag{3}$$

Here the Einstein summation convention is used, h_i is the ith eigenvalue of the Hessian ($h_1 \leqslant h_2 \leqslant h_3 ...$), and x_i and F_i are the components of **x** and **F** along the ith eigenmode of **H**:

$$x_i = \langle \mathbf{x} | \mathbf{v}_i \rangle \tag{4a}$$

and

$$F_i = \langle \mathbf{F} | \mathbf{v}_i \rangle. \tag{4b}$$

D. Parametrization of the step vector

A primary element of the algorithm developed here is the introduction of steps $\{x_i\}$ characterized as follows:

$$x_i = \alpha F_i (\lambda - h_i)^{-1}. \tag{5}$$

When used in the above quadratic energy expression, this step gives the following first-order, second-order, and total energy changes

$$E - E_0 = \alpha F_i^2 (\lambda - h_i)^{-1} + 1/2 \alpha^2 h_i F_i^2 (\lambda - h_i)^{-2} \tag{6a}$$

$$= \alpha F_i^2 (\lambda - h_i)^{-2} \{\lambda - h_i (1 - \alpha/2)\}. \tag{6b}$$

In the step expression given above, α is to be viewed as a positive overall step scale factor ($\alpha < 1.0$) chosen to guarantee that a "well-behaved" streambed walk can be realized as detailed below. The parameter λ is introduced to permit the step along the ith mode to either be opposite in sign from the corresponding gradient (if $\lambda < h_i$) or directed along the gradient (if $\lambda > h_i$).

Moving along or opposed to F_i characterizes steps whose first-order energy changes $F x_i$ are increasing or decreasing, respectively. The sign of the second-order energy change $1/2\ h_i\ x_i^2$ is determined entirely by the sign of the Hessian eigenvalue h_i. In our method, we choose λ to produce steps that either have negative first-order and total energy changes along all modes, or along all but one mode along which the first-order and total energies increase. The former produce walks to minima; the latter walks to transition states.

E. Problems with "stitching"—short steps are better than long steps

In our earlier work,[2] emphasis was placed primarily on the total energy change along each mode. This point of view can lead to step lengths that "overshoot" the location of minima, or are too long in the sense that they give displacements beyond the region where the local quadratic approximation is accurate.

To clarify these points, consider the contribution to the local quadratic energy surface along a particular mode

$$\Delta E_j = F_j x_j + 1/2 x_j^2 h_j. \tag{7}$$

If h_j is positive, displacements x_j occur on an upward curved parabola; if h_j is negative, x_j is on a downward curved parabola. In either case, a specified desirable energy change (ΔE positive in the $h_j < 0$ case and ΔE negative in the $h_j > 0$ case) can be realized either by:

(i) taking a *small* step along which the linear energy change is of the desired sign, while the quadratic term is small and of opposite sign (n.b., the sign of the quadratic term is *always* opposite to what one wants; if $h_j > 0$, the quadratic term is positive and one is trying to minimize the energy; if $h_j < 0$, the quadratic term is negative, and one is trying to maximize the energy); or by

(ii) taking a *larger* step in the same direction [i.e., with x_j having the same sign as used above in (i)] along which the linear energy change is much larger yet still of the desired sign, while the quadratic contribution is large and of opposite sign.

We prefer to take the smaller steps characterized in (i) above. The longer steps of (ii) suffer two drawbacks:

(a) Being longer, they are more likely to move the coordinates outside the region where the local quadratic approximation used to generate the step is valid.

(b) They generate steps which "stitch"; i.e., steps that move back and forth across the streambed along which the walk proceeds. In contrast, the steps of (i) are found to undergo little stitching.

F. The form of the step elements

In our earlier work on this subject,[2] the form for the step elements shown in Eq. (5) was shown to arise from making the local quadratic energy functional of Eq. (1) stationary subject to the constraint (imposed by Lagrange multiplier $\lambda/2$) that the step be of a specified length. Here, we do not impose this constraint; instead, we take steps parametrized as in Eq. (5) and ask how λ and α can be determined to generate an optimal streambed walk, with λ chosen primarily to guide the *direction* of the step and α used to control the total length of the step.

III. WALKS TO MINIMA AND TO TRANSITION STATES

A. Minimization walks

As displayed in Eq. (6), steps for which both $\lambda < h_i$ and $\lambda < h_i(1 - \alpha/2)$ yield negative linear ($F_i x_i$) and negative total energy changes along the ith mode. This is, of course, a property that a walk to a minimum should possess. If the lowest Hessian eigenvalue h_1 is positive (this is characteris-

tic of regions near local minima), $\lambda < h_1(1-\alpha/2)$ is the more restrictive constraint; a λ that obeys this will also obey $\lambda < h_i(1-\alpha/2)$ for all other modes because the h_i are arranged in increasing order. If, on the other hand, h_1 is negative (this is characteristic of regions near transition states), $\lambda < h_1$ is the more restrictive constraint. Again, if λ obeys this condition, it will automatically also obey $\lambda < h_i$ and $\lambda < h_i(1-\alpha/2)$ for the other modes, independent of whether the other h_i are positive or negative.

Thus, for positive h_1, one wants $\lambda < h_1(1-\alpha/2)$ and for negative h_1 one needs $\lambda < h_1$. Although these statements limit λ, they do not determine the optimal value of λ. To do so, we examine the dependence of the quadratic energy functional on λ for values of λ that obey the above conditions. Differentiation of the quadratic energy functional to seek a value of λ for which it is stationary yields

$$dE/d\lambda = -\alpha F_i^2(\lambda - h_i)^{-3}\{\lambda - h_i(1-\alpha)\}$$

and

$$d^2E/d\lambda^2 = 2\alpha F_i^2(\lambda - h_i)^{-4}\{\lambda - h_i(1-3\alpha/2)\}.$$

The choice $\alpha = 1$ causes $\lambda = 0$ to be a stationary point corresponding to a minimum ($d^2E/d\lambda^2$ is positive) if h_1 is positive. This means that a Newton–Raphson step[2(a)] (i.e., the step with $\lambda = 0$ and $\alpha = 1$) is optimal as long as $h_1 > 0$ and as long as this unscaled step is within L.

If the Newton–Raphson step is too long (i.e., if it exceeds L), any choice of $h_1 > \lambda > 0$ will also generate too long a step $[x_i = F_i(\lambda - h_i)^{-1}]$ because $(\lambda - h_1)^{-1}$ will be larger than for $\lambda = 0$. Therefore, a value of $\lambda < 0$ must be chosen. In the range $\lambda < 0$ for $h_1 > 0$, $dE/d\lambda$ is negative; $d^2E/d\lambda^2$ is positive for $-h_1/2 < \lambda < 0$. Therefore, the most negative change in E will be realized for λ as large as possible. Choosing λ too close to zero generates an unscaled step length that is very large, as a result of which α must be chosen to reduce the step length, which then reduces the magnitude of $(E - E_0)$. In this case, the best choice of λ is the value that yields the maximum acceptable step length L. Therefore, we simply pick λ ($\lambda < 0$) by solving $F_1^2(\lambda - h_1)^{-2} = L^2$, after which α scaling is unnecessary. This gives $\lambda = h_1 - |F_1/L|$ and generates a step that is approximately L in length (the step formed using this λ value is actually scaled to be exactly of length L).

On the other hand, if h_1 is negative, the Newton–Raphson step $\lambda = 0$ is unacceptable because it violates the energy-lowering condition $\lambda < h_1$ determined earlier. In the range $\lambda < h_1$, $dE/d\lambda$ is negative and $d^2E/d\lambda^2$ is negative. Therefore, the most negative change in E will again be realized for λ as large as possible (i.e., as close to h_1 as possible). Once again, we pick λ by solving $F_1^2(\lambda - h_1)^{-2} = L^2$, after which α scaling is unnecessary.

In summary, to perform energy minimization walks, we choose λ and α as follows:

(i) If $h_1 > 0$, we take the Newton–Raphson step ($\lambda = 0$) if its length is within L, and we set α equal to 1.0.

(ii) If $h_1 > 0$, but the Newton–Raphson step length exceeds L, we determine λ ($\lambda < 0$) by requiring $F_1^2(\lambda - h_1)^{-2} = L^2$ to be obeyed. This yields $L = h_1 - |F_1/L|$. Again, we take $\alpha = 1.0$.

(iii) If $h_1 < 0$, we determine λ ($\lambda < h_1$) by requiring $F_1^2(\lambda - h_1)^{-2} = L^2$ to be obeyed ($\lambda = h_1 - |F_1/L|$) and α is once again set to 1.0.

In both (ii) and (iii), the step is formed with the specified value of λ, which yields a total step length near L and then rescaled to be exactly of length L.

B. Transition-state walks

1. Walks up the lowest eigenmode

Moving "uphill" along the lowest Hessian eigenmode while remaining at minima along the other eigenmodes generates a "streambed walk" along this lowest mode. As explained earlier, steps for which $\lambda < h_2$ and $\lambda < h_2(1-\alpha/2)$ produce linear and total energy lowering along all modes other than the first. To generate linear and total energy *increases* along the h_1 mode requires that $\lambda > h_1$ and $\lambda > h_1(1-\alpha/2)$.

If h_1 and h_2 are both positive (which is characteristic of geometries near local minima), these constraints reduce to $h_1 < \lambda < h_2(1-\alpha/2)$. If $h_2/2$ is less than h_1, the choice $\alpha = 1$ (which corresponds to an unscaled step) cannot be used because no value of λ obeys $h_1 < \lambda < h_2/2$. The largest value of α (i.e., the least scaling of the step) that gives rise to a nonzero range for choosing λ is $\alpha = 2(h_2 - h_1)/h_2$. This particular α gives $h_2(1-\alpha/2) = h_1$, as a result of which λ is bounded to $h_1 < \lambda < h_1$. The choice $\lambda = h_1$ generates a step lying entirely along the h_1 eigenmode; this step has no ability to incorporate movement along the other modes and is therefore unacceptable. To maintain a distinct range within which λ can be chosen, we choose to take an even smaller step and select $\alpha = (h_2 - h_1)/h_2$ as the scaling parameter. This then restricts λ to the range $h_1 < \lambda < (h_1 + h_2)/2$, within which we choose the midpoint $\lambda = (h_1 + (h_1 + h_2)/2)/2$. Using these values of α and λ, the step $x_i = \alpha F_i(\lambda - h_i)^{-1}$ is evaluated. If the length of this **x** is less than L, it is taken; if the step length exceeds L, x_i is further scaled back to yield a total step length equal to L.

If, in contrast to the above situation, $h_2/2$ exceeds h_1, the choice $\alpha = 1.0$ is acceptable, in which case we choose λ as the midpoint of the two bounds $\lambda = (h_1 + h_2/2)/2$. Again, if the step x_i obtained using this λ value and $\alpha = 1.0$ exceeds L, it is further scaled back to L.

If h_1 is negative, the appropriate constraints $h_1(1-\alpha/2) < \lambda < h_2(1-\alpha/2)$ can be met with $\alpha = 1$. In this case, we again choose λ as the midpoint of this range $[\lambda = (h_2 + h_1)/4]$ and we further scale back the x_i if the total step length obtained with this λ,α combination exceeds L.

In summary, to walk uphill along the streambed belonging to the lowest Hessian eigenvalue, we:

(i) take $\alpha = 1.0$ and $\lambda = (h_1 + h_2/2)/2$, if h_1 is positive and $h_2/2$ exceeds h_1;

(ii) take $\alpha = (h_2 - h_1)/h_2$ and $\lambda = (h_1 + (h_1 + h_2)/2)/2$, if h_1 is positive, but $h_2/2$ does not exceed h_1;

(iii) take $\alpha = 1.0$ and $\lambda = (h_2 + h_1)/4$, if h_1 is negative.

In all three cases, the step elements $x_i = \alpha F_i(\lambda - h_i)^{-1}$ are further scaled back if their total length exceeds L. As emphasized in Sec. II E, a step obtained by scaling back a step that has linear and total energy changes of the desired sign will also have linear and total energy changes of the

proper sign (because the quadratic energy change is always of the "wrong" sign and cutting x_j back reduces the magnitude of $1/2\, h_j\, x_j^2$ more than that of $F_j x_j$).

2. Walks up other eigenmodes

a. The extra difficulties for modes other than the lowest. To walk uphill along a streambed that connects with one of the other Hessian eigenmodes requires additional care. Choosing λ to obey $\lambda > h_2$ and $\lambda > h_2(1 - \alpha/2)$ will certainly generate a step that, within the local quadratic approximation, has positive linear and total energy changes along the h_2 mode. However, this choice will also cause the step to increase in energy along the h_1 mode. Such behavior is not characteristic of the desired streambed walk; the energy is supposed to be minimized for all modes except the one (h_2) along which uphill movement occurs.

Even if one had a technique for walking uphill along the h_2 mode while minimizing the energy for all other modes, another fact must be kept in mind. The Hessian eigenvalue (h_2 here) along whose eigenmode uphill movement is taking place will become smaller as the walk progresses (it will, of course, become negative if a transition state is approached) until it eventually becomes the lowest eigenvalue. Once this happens, the walking algorithm detailed above in Sec. III B 1 can be used without modification.

As the eigenvalue of the mode being followed moves downward through the other eigenvalues, one must be careful to follow the correct direction. We use an eigenvector tracking method in which the scalar product of the Hessian eigenvector ($\mathbf{v_k}$) corresponding to the "uphill" mode is computed from step to step. The quantity $\langle \mathbf{v_k}\ (\text{step } n) | \mathbf{v_k}\ (\text{step } n+1) \rangle$ should be approximately 1.0 at each step. This allows the desired eigenvector $\mathbf{v_k}$ (step $n+1$) to be properly identified even as its eigenvalue drops, in succession, past all other eigenvalues. This strategy must be used until the desired uphill direction (i.e., $\mathbf{v_k}$) lies along the lowest Hessian eigenmode, after which the conventional uphill walking strategy can be followed. With these qualifications in mind, let us explore how one can walk up streambeds that connect to higher eigenmodes until the mode being followed uphill becomes the lowest.

b. Two strategies. We have found two procedures that seem to overcome the above difficulties. In the first, we simply take an initial step along the eigenmode (h_2 here) that we plan to follow with no components along modes with smaller Hessian eigenvalues. This procedure is followed until the eigenvalue belonging to the mode being followed uphill becomes the lowest eigenvalue. To effect such a procedure, we simply set to zero the F_i values corresponding to all modes lying below the one being followed; this then yields zero step components $x_i = \alpha F_i (\lambda - h_i)^{-1}$ along these modes.

In our second approach, which is considerably more systematic, we express the step component along the mode (h_2 here, h_k in general) to be followed as

$$x_k = \beta y_k.$$

In terms of step components $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$, the local quadratic energy functional becomes

$$E = E_0 + F_i x_i + 1/2 h_i x_i^2 + (F_k\, \beta) y_k + 1/2 (h_k\, \beta^2) y_k^2,$$

where the sum over i runs over $1,2,\ldots,k-1,k+1,\ldots,3N-6$ or $3N-5$. When viewed as a function of the step components $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$, this local quadratic energy surface appears to have a Hessian eigenvalue of $\beta^2 h_k$, where the original surface had h_k, and to have a gradient βF_k, where the original surface had F_k.

By choosing β such that $\beta^2 h_k$ lies below h_1, one can then employ the transition-state walking strategy appropriate to the lowest eigenmode direction. In each such step, however, it is essential to keep in mind that one is generating step components $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$; the y_k component must then be multiplied by β to obtain x_k. Once the $\{x_1, x_2, \ldots, x_{k-1}, x_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ are in hand, transformation to Cartesian or to internal coordinate displacements can be performed.

When implementing the above coordinate-scaling method for walking up higher eigenmodes, it is important to understand that the maximum step length L appropriate for the walk in the $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ space is not necessarily the same as that for the $\{x_1, x_2, \ldots, x_{k-1}, x_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ space. This can be understood by considering the length of the $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ vector and of the resulting coordinate step vector. If $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ is constructed to be of length L', then $\{x_1, x_2, \ldots, x_{k-1}, x_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ will be of length L, where

$$(L)^2 = (L')^2 + (\beta^2 - 1) y_k^2.$$

Because the step $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ is constructed to have a significant or even dominant y_k component, y_k^2 will often be close to $(L')^2$, in which case $(L)^2$ will approach $\beta^2 (L')^2$. Therefore, to achieve a coordinate step $\{x_1, x_2, \ldots, x_{k-1}, x_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ within L, one should restrict the scaled step $\{x_1, x_2, \ldots, x_{k-1}, y_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ to lie within $L' = \beta^{-1} L > L$. In practice, we do not so expand the maximum step length simply to achieve a more "conservative" walk (as a result, our steps in $\{x_1, x_2, \ldots, x_{k-1}, x_k, \ldots, x_{3N-6}$ or $x_{3N-5}\}$ space are usually short).

This completes our description of the stepping algorithm. The procedure generates a step that may be taken to generate the next position about which a new local quadratic approximation to the energy surface will be formed. However, there are circumstances under which the step put forth for consideration must not be taken, but, rather, replaced by an alternative (shorter) step. It is this aspect of the algorithm to which we now turn attention.

IV. STEP LENGTH CONTROL

A. The maximum step size L

In the algorithm outlined in Sec. III, each step is constructed to have a total length less than or equal to a preassigned maximum length L. The choice of L is very much a matter of taste and of "common sense." We prefer to generate walks that smoothly trace out the locus of points characterizing their streambeds; therefore, we usually choose rather conservative L values (e.g., L less than a few tenths of an Å). Clearly, L must be less than the dynamic range over which the true potential energy surface changes its features

by amounts that are deemed important. For chemical bonds, changes of a few tenths of an Å usually correspond to appreciable energy changes.

Choosing L small requires many steps in the streambed walk, thereby increasing the computational expense. Choices of L that are large are less harmful than they might seem at first glance because of the step-size reduction strategy detailed below. In a nutshell, any step that is large enough that the true energy realized at the displaced geometry is in sharp disagreement with the local quadratic prediction of the energy undergoes further step-size reduction. Of course, this reduction process entails computational expense, so one would like to use an L value that would not often necessitate such action. In essence, L should be chosen with a good deal of common sense.

B. Step-size reduction

The procedure for generating step sequences described in Sec. III may produce a step that moves beyond the region where the local quadratic approximation to the true potential energy surface is valid. In such a case, the step must be further reduced until it lies within this range. Since we do not *a priori* know the true energy surface except at the point around which the local quadratic expansion is carried out (where the energy is E_0), we must allow the step generated by the algorithm detailed in Sec. III to be taken (on a trial basis) so that the true (E_T) energy at $\mathbf{r} = \mathbf{r}_0 + \mathbf{x}$ can be evaluated. If the quadratic prediction

$$E - E_0 = F_i x_i + 1/2 h_i x_i^2$$

accurately reproduces the true energy difference $E_T - E_0$, then one says that the step $\{x_i\}$ lies within the trust radius. On the other hand, if $F_i x_i + 1/2 h_i x_i^2$ does not agree well with $E_T - E_0$, then the step $\{x_i\}$ lies outside the trust radius and must be further scaled back.

It remains to state what it means for the two energies to agree well. In our implementation, we insist that the predicted energy difference $E - E_0 = F_i x_i + 1/2 h_i x_i^2$ and the energy difference $E_T - E_0$ observed once the step is taken (on a trial basis):

(i) be of the same sign—we do not want the predicted energy to direct the walk uphill only to find that the step actually moves downhill (this is indicative of a step for which the quadratic energy change, which is always undesirable in sign, has overcome the favorable linear term);

(ii) be equal within some range in the sense that $\min(|E - E_0|, |E_T - E_0|)/\max(|E - E_0|, |E_T - E_0|)$ be equal to unity within a specified tolerance.

In this most straightforward implementation of the trust radius concept, if agreement between $E_T - E_0$ and $E - E_0$ is not met, each of the step elements x_j is multiplied by a fraction; we usually cut the steps in half. The new step, which has the same direction as the original trial step becaue the elements were scaled in the same proportion, is then subjected to the same trial. This process is continued until the local quadratic approximation to the true surface is valid (in the sense described above) at which time the step is taken. It should be noted that generating such a series of step reductions does not require the evaluation of new gradient and Hessian matrices; the most time consuming element is the evaluation of E_T at each of the "trial steps."

Once a step to a new geometry is realized and new **F** and **H** matrices are computed, the stepping algorithm begins again. Each successive step is restricted by this algorithm to:

(i) have a total length less than some specified maximum step size L;

(ii) have its length further reduced to guarantee that the quadratic energy change accurately represents the true (observed) energy change for that step.

V. EXAMPLE APPLICATION

To illustrate the application of this walking algorithm, we consider the three-dimensional potential energy surface characteristic of the Be + H_2 system; this same case was treated in Ref. 2(b) where further details concerning the atomic orbital basis set are given. In the present calculations, the lowest energy orbital (i.e., the Be 1*s* orbital) is doubly occupied in all electronic configurations. The remaining four electrons are distributed among the nine other molecular orbitals in forming the 372 configurations of $^1A'$ symmetry in the C_s point group. In that earlier work, C_{2v} symmetry was imposed and finite-difference methods were used to obtain the Hessian matrix from the gradient because, at that time, we did not have computer codes to analytically evaluate the Hessian. The imposition of C_{2v} symmetry precluded consideration of the Be + $H_2 \Rightarrow$ BeH + H reaction; in the present work, such symmetry constraints are not imposed and full three-dimensional walks are carried out using analytical first and second derivative data.

The particular walks studied include a walk along the lowest energy $^1A_1$ reaction path from Be($1s^2 2s^2$) + $H_2(\sigma_g^2)$ to the transition state detailed in row 11 of Table I. Along this walk, which is not constrained to C_{2v} symmetry but still follows this symmetry, the nature of the lowest $^1A'$ (or $^1A_1$ in C_{2v} symmetry) state wave function changes from a dominant $1s^2 2s^2 \sigma_g^2 = 1a_1^2 2a_1^2 3a_1^2$ configuration to a strongly mixed state containing both $1a_1^2 2a_1^2 3a_1^2$ and $1s^2 \sigma_{a1}^2 \sigma_{b2}^2 = 1a_1^2 2a_1^2 1b_2^2$ configurations. The vibrational frequencies at the transition state are found to be 3085, 795, and 3770i cm^{-1}, with the imaginary frequency corresponding to the reaction path. The high-frequency mode is antisymmetric with respect to the plane bisecting the HBeH angle, and the 795 cm^{-1} mode is symmetric.

The second walk, detailed in Table II, begins near the linear HBeH geometry (at the linear minimum, the 1/2 H_2 distance is found to be 2.6107 bohr, the energy is $-$ 15.779 555 95 hartrees, and the vibrational frequencies are 757, 757, 1879, and 2123 cm^{-1}) and progresses to the transition state described above. We can not begin this or any walk exactly at the minimum-energy geometry because all forces vanish there; we therefore bend the molecule slightly as indicated in the first row of Table II to begin the walk. Along this walk (at the geometry given in row 7 of Table II), an electronic state of $^1B_2$ symmetry falls below the $^1A_1$ state that we are following. Also along this walk, at the step given in the ninth row, a step rejection takes place, the trust radius is decreased from 0.50 to 0.25 bohr, and the step given in the tenth row is taken. As described below, our algo-

TABLE I. Insertion walk from Be + H_2 to the $^1A_1$ transition state. Distances and energies in atomic units (0.529 Å and 27.21 eV).

	1/2 H_2	Be–H_2	Total energy	Gradient norm	Step norm
1	0.7000	3.5000	− 15.717 625 87	0.058 707 86	0.500 000 00
2	0.6944	2.8877	− 15.677 427 28	0.108 611 00	0.500 000 00
3	0.6818	2.2757	− 15.596 165 94	0.241 322 84	0.500 000 00
4	0.6933	1.6637	− 15.390 621 45	0.671 502 28	0.390 487 76
5	0.8733	2.0263	− 15.537 113 30	0.238 912 86	0.367 020 10
6	1.0286	2.3864	− 15.588 458 17	0.093 126 34	0.313 180 32
7	1.1873	2.6539	− 15.601 082 50	0.033 278 40	0.196 372 21
8	1.2947	2.8064	− 15.602 948 94	0.009 456 38	0.076 197 37
9	1.3383	2.8613	− 15.603 069 94	0.001 297 83	0.009 909 98
10	1.3442	2.8679	− 15.603 070 97	0.000 024 12	0.000 125 50
11	1.3442	2.8679	− 15.603 070 97	0.000 000 01	0.000 000 01

rithm continues to follow the $^1A_1$ state, ignoring the surface crossing, all the way to the transition state.

For both of these walks, an L value of 0.5 bohr was used and quadratic convergence is realized in the neighborhood of the transition state (see the final few rows of Tables I and II).

In realizing the walk described in Table II, which passed through the intersection with the $^1B_2$ surface and followed the $^1A_1$ surface, care had to be used in tracking the proper electronic wave function. In particular, to follow the $^1A_1$ surface dominated by the $1a_1^2 2a_1^2 3a_1^2$ and $1a_1^2 2a_1^2 1b_2^2$ configurations, we choose from among the roots of the configuration interaction problem arising in optimizing the multiconfiguration self-consistent field (MCSCF) wave function, the eigenvector that is dominated by these configurations. The eigenvalue corresponding to this eigenvector may or may not describe the lowest energy state. Such a walk, by the nature of the electronic wave function used, which determines the forces and curvatures, passes smoothly through the intersection with the $^1B_2$ surface.

On the other hand, if we allow the electronic structure code to converge to the lowest state of $^1A'$ symmetry (including those dominated by any of the $1a_1^2 2a_1^2 3a_1^2$, $1a_1^2 2a_1^2 1b_2^2$, or $1a_1^2 2a_1^2 3a_1 1b_2$ configurations), a different walk is generated. This walk proceeds from linear HBeH toward the transition state obtained in the earlier walk; along this path, the $^1B_2$ surface intersects and falls below the $^1A_1$ surface at which time the algorithm can direct the walk to move onto the lower energy $^1B_2$ surface.

As the $^1B_2$ surface is entered, strong gradients may exist along all directions because the geometry at which the "hop" occurred from the $^1A_1$ to the $^1B_2$ surface is by no means near a streambed of the $^1B_2$ surface. In particular, a large negative curvature along the asymmetric stretch vibration causes the molecule to distort from (nearly) C_{2v} to C_s symmetry. Once the walk moves to the $^1B_2$ surface, we choose to instruct the algorithm to move to a minimum on this surface, in which case it generates the BeH + H fragments.

This rather simple system illustrates much of the complexity that can arise in potential energy surface walking. Multiple electronic surfaces and multiconfiguration contributions to each surface cause the electronic structure aspect

TABLE II. Walk from linear BeH_2 to the $^1A_1$ transition state.

	1/2 H_2	Be–H_2	Total energy	Gradient norm	Step norm
1	2.5400	0.1000	− 15.778 694 17	0.014 704 76	0.337 837 67
2	2.6340	0.4804	− 15.775 181 72	0.023 671 32	0.500 000 00
3	2.5141	1.0565	− 15.759 972 08	0.046 907 49	0.500 000 00
4	2.2862	1.5245	− 15.737 967 74	0.063 682 88	0.500 000 00
5	2.0083	1.9032	− 15.709 102 36	0.079 318 19	0.500 000 00
6	1.7123	2.2380	− 15.670 529 03	0.098 490 08	0.500 000 00
7	1.4245	2.5938	− 15.620 103 42	0.105 806 79	0.500 000 00
8	1.6437	2.1133	− 15.672 149 87	0.092 988 32	0.500 000 00
9	1.3464	2.4447	− 15.620 780 97	0.108 151 11	0.499 999 99
10	1.3464	2.4447	− 15.620 780 97	0.108 151 11	0.249 999 99
11	1.2164	2.6522	− 15.601 278 15	0.017 753 36	0.164 702 22
12	1.2963	2.7990	− 15.602 903 89	0.005 211 66	0.075 074 40
13	1.3369	2.8583	− 15.603 068 00	0.000 967 32	0.012 743 43
14	1.3441	2.8677	− 15.603 070 97	0.000 029 97	0.000 302 65
15	1.3442	2.8679	− 15.603 070 97	0.000 000 02	0.000 000 15

of the problem to be complex. Finding several local minima and the transition states connecting them is also challenging. The algorithm presented here seems to robustly address all of these issues.

VI. SUMMARY

In this paper, we have presented an algorithm that permits the systematic location and characterization (via the nature of the Hessian eigenvalues) of local minima and transition states on potential energy surfaces. This method has the following characteristic features:

(i) it uses local gradient and Hessian information;

(ii) it generates steps that produce the desired behavior (i.e., uphill or downhill) in both the linear and total quadratic energy changes along each Hessian eigenmode;

(iii) it permits rotations and translations to be removed from consideration (e.g., for isolated species), or it allows translational and orientational motions to be treated independently of internal motions (e.g., for species imbedded in a surrounding medium);

(iv) through use of a maximum step size and a step-reduction strategy, it controls the step length to keep each step within a region where the local quadratic energy approximation is valid;

(v) it controls the step direction in a manner that is guaranteed to move either downhill in all Hessian eigenmode directions (when searching for minima) or uphill along one eigenmode and downhill along all others (when searching for transition states);

(vi) it permits streambeds along any eigenmode of the Hessian to be explored by introducing a coordinate scaling device.

The particular implementation of this walking algorithm is implemented and routinely used in the highly modular Utah MESSKIT (molecular electronic structure kit) electronic structure codes. Application of this walking algorithm to a three-dimensional problem (the Be + H_2 system) is illustrated. This particular problem involves motion on a $^1A_1$ surface whose electronic wave function contains two (or more) strongly mixed configurations; the relative mixing of these configurations varies strongly throughout the Be + $H_2 \Rightarrow$ HBeH reaction. This problem also involves a second electronic surface, which is of $^1B_2$ symmetry in the C_{2v} point group, but of $^1A'$ symmetry in the C_s point group. Walks that begin as Be + H_2 or as HBeH on the $^1A_1$ surface and "hop" to the $^1B_2$ surface can also be treated using our algorithm. These walks lead to formation of BeH + H products.

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[3] For example, in the $H_2CO \Rightarrow H_2$ + CO reaction, three modes are formed that have zero gradients and zero Hessian eigenvalues; these are the relative translational and relative rotational motions of the H_2 and CO moieties. In such cases, the walking algorithm must properly identify such degrees of freedom and not be "confused" by their presence (e.g., numerical precision limitations may cause the Hessian eigenvalues corresponding to these modes to be small and of arbitrary sign rather than identically zero). In particular, it is important that artifactual small negative Hessian eigenvalues not be confused with the physically relevant negative eigenvalue belonging to a transition state.