Walking on Potential Energy Surfaces

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By combining a local quadratic approximation to the potential energy surface with the concept of a trust radius within which this quadratic approximation is accurate, and a scaling of one active coordinate, we have developed an automated surface walking algorithm. This algorithm allows one to walk from geometries characteristic of equilibrium molecular structures, uphill along stream beds, through transition-state geometries, and onward to product-molecule equilibrium geometries. The method has been applied to model and ab initio test cases with encouraging results. The success of using the algorithm in connection with approximate Hessian matrices formed via so-called update techniques, which require only local force information, is especially encouraging in light of the high cost of ab initio analytical evaluation of the Hessian.

Introduction

State-of-the-art methods in molecular quantum chemistry[1] promise to soon permit the efficient determination of potential energy surfaces and their associated local slopes (gradients) and curvatures (Hessians) for Born–Oppenheimer electronic surfaces. The ability to *systematically* move on such a surface from one stable molecular geometry (i.e., local minimum) through one or more transition states and, subsequently, on to a product-state equilibrium geometry is essential for obtaining both static structural data and information relevant to dynamical studies. To attempt such a "walking" process using a simple grid of geometrical steps in each of the molecule's internal degrees of freedom is not efficient. For example, even a molecule as small as H_2CO has six internal geometrical degrees of freedom upon which the electronic energy depends. In trying to use a geometry-grid approach to find transition states on say an excited singlet surface for either the $H_2CO \rightarrow H + HCO$ or $H_2CO \rightarrow H_2 + CO$ reactions, one would require that the molecule's energy be computed at of the order of m^6 geometries where m is the number of grid steps along each of the six coordinates. The number of such grid steps could be quite large since one has little information about how large a grid step size to take along each degree of freedom. If one makes use of gradient and Hessian information, more reliable and step-length controlled walks may be carried out. For example, a recently developed surface walking algorithm,[2] which makes use of local force and curvature information, located the transition state for $H_2CO \rightarrow H_2 + CO$ in a total of 11 molecular deformation steps! Clearly, the larger the number of "active" internal degrees of freedom (i.e., those upon which the energy depends substantially) a molecule has, the more important it is to employ such automated surface walking algorithms. Because the cost involved in analytically computing the Hessian via ab initio quantum chemical methods can be quite high, it is also important to explore methods which utilize only local gradient data in an efficient manner.

It is the purpose of this paper to describe a walking algorithm that uses both gradient and Hessian information. It is shown how this algorithm may be modified such as to require only gradient information. This is done by using approximate Hessian matrices determined by so-called Hessian update techniques. The success of the stable walking algorithm that makes use of only gradient information is highly encouraging for future applications.

The essence of the walking algorithm described here is to use the gradient and Hessian matrices to construct a second-order Taylor series polynomial in the step vector **X** and to then define a trust region for this second-order polynomial. The trust region is the region within which the second-order Taylor polynomial approximates reasonably well the true energy surface. The trust region is updated in each iteration to ensure that maximum step lengths are taken. The update of the trust region is carried out by measuring the agreement between the energy change predicted by the second-order Taylor series and the actual energy change obtained when the predicted step is taken. The steps are restricted by the algorithm to remain inside the trust region. The direction of the steps depends on the characteristics of the stationary point toward which one is walking. In searching for a potential energy minimum the energy is minimized in all directions on the energy surface. In uphill walks from one minimum-energy geometry to a transition state, the energy is maximized in one direction and minimized in all orthogonal directions thereby forcing the walk to be in a stream bed. In the present paper, stable walking algorithms are defined for walking away from one local minimum along directions which might not correspond to the lowest-energy distortion direction, to a transition state, and onward to product equilibrium geometries. Consideration is also given to cases where, in the early stages of the walk, molecular symmetry artificially restricts the steps along certain directions to vanish because the forces along these directions vanish.

The algorithm described here follows an outline similar to that used by Cerjan and Miller[2] for determining the directions of all the steps. However, substantial differences appear in the conclusions that are reached about what step directions are optimal. The energy minimization aspect of the algorithm used here has been discussed by Fletcher[3] in numerical analysis where it has been shown that the iterative process is guaranteed to converge to a local minimum.[3] An algorithm containing many of the same characteristics as the one employed here has successfully been used to optimize both ground and excited electronic state wave functions within multiconfiguration self-consistent field theory.[4] None of the above described al-

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gorithms, however, thoroughly discussed how transition states (saddle points) may be determined by carrying out systematic walks from one stable local minimum geometry along several possible distortion directions.

A common feature of the above walking algorithms is their use of the information content of the local gradient and (perhaps) Hessian. A walking procedure which utilizes a somewhat different approach has been suggested by Crippen and Scheraga.[5] The idea of the Crippen–Scheraga walking algorithm is to take a step in one energy distortion direction and to subsequently minimize the energy (e.g., by line search techniques) in all directions orthogonal to this direction. The energy minimization in all the orthogonal directions must be carried out in each step of the iterative algorithm. The fact that such minimizations tend to be rather time consuming lends support to our attempt to explore walking algorithms that only use the information available in the local gradient (and Hessian) and which do not require finding minima at each iteration.

In the next section of this paper we develop the theory of the walking algorithm. In section III the algorithm is applied to the model potential of Cerjan and Miller,[2] to a model and an ab initio potential for the ground[6] and excited C^1A' state of HCN,[7] respectively, as well as to a model potential studied by Crippen and Scheraga.[5] The last section contains our concluding remarks.

In addition to the Cerjan–Miller and Crippen–Scheraga methods, to which we make further comparison later, a number of other techniques have been developed for searching for local minima and transition states. References 12–17 include some of the techniques which are relevant to chemical potential energy surface investigations.

II. Definition of the Method

A. The Local Quadratic Surface. Let us assume that one has the ability to generate, at any molecular geometry $X_{0,i}$ ($i = 1, 2, ..., n$), the potential energy (electronic energy) E_0, the gradient $F_{0,i}$ ($i = 1, 2, ..., n$) of this energy along any of the n internal degrees of freedom being considered, and the second derivatives $H_{0,ij}$ of the energy along each of these n directions. For a molecule containing N atoms, n can be as large as $3N - 6$ ($3N - 5$ for a linear molecule); n can be smaller if one has decided to hold fixed certain internal geometrical degrees of freedom. The information contained in E_0, the forces or gradients $F_{0,i}$, and the curvatures or Hessian matrix elements $H_{0,ij}$ allows one to write a *local* second-order approximation $\tilde{E}$ to the true potential energy surface $E(\mathbf{X})$ in the neighborhood of the point $\mathbf{X}_0 = \{X_{0,i};\ i = 1, 2, ..., n\}$:

$$\tilde{E}(\mathbf{X}) = E_0 + \mathbf{F}_0\mathbf{X} + \tfrac{1}{2}\mathbf{X}\mathbf{H}_0\mathbf{X} \quad (1)$$

where the vector $\mathbf{X}$ has components equal to the displacements away from the geometry $\mathbf{X}_0$ where E_0, $\mathbf{F}_0$, and $\mathbf{H}_0$ were evaluated.

If one knew that $\tilde{E}(\mathbf{X})$ represented the true surface $E(\mathbf{X})$ to within a reasonable tolerance within some region of trust (h_0), then it would be possible to "walk" on the $\tilde{E}(\mathbf{X})$ surface to some new geometry $\mathbf{X}_1$ at which a new gradient and Hessian could be evaluated. At the new point a new $\tilde{E}(\mathbf{X})$ could be formed, and if a new trust radius (h_1) could be evaluated, a step on the $\tilde{E}(\mathbf{X})$ surface could again be safely used to move to a new geometry $\mathbf{X}_2$. Such a step-by-step surface walking procedure is exactly what this paper offers.

B. The Fletcher Algorithm. An algorithm for computing the trust radius (h) based on comparing the approximate energy function $\tilde{E}(\mathbf{X})$ to the true $E(\mathbf{X})$ has been given by Fletcher.[3] Within the Fletcher algorithm the trust radius h_k appropriate to the kth step in the surface walk is defined in terms of the radius h_{k-1} used in the preceding step and the ratio (r) of the actual energy change $E(\mathbf{X}_k) - E(\mathbf{X}_{k-1})$ and the energy change $\tilde{E}(\mathbf{X}_k) - E(\mathbf{X}_{k-1})$, which the quadratic function $\tilde{E}$ predicted for the kth step: $\mathbf{X}_{k-1} \rightarrow \mathbf{X}_k$:

$$r = \frac{E(\mathbf{X}_k) - E(\mathbf{X}_{k-1})}{\tilde{E}(\mathbf{X}_k) - E(\mathbf{X}_{k-1})} \quad (2)$$

The closer r is to unity the more quadratic is the true energy surface. When carrying out an energy minimization walk (e.g., to find a local minimum) Fletcher suggested[3] the following algorithm for updating the trust region h: (1) if $r < 0.25$ then $h_k = h_{k-1}/4$, (2) if $0.25 < r < 0.75$ then $h_k = h_{k-1}$, (3) if $r > 0.75$ then $h_k = 2h_{k-1}$, (4) if r is smaller than zero the step is rejected and a new step is evaluated whose trust radius is the new shorter trust radius $h_{k-1}/4$.

In transition-state saddle point applications, positive and negative energy contributions arising from the linear and quadratic terms in eq 1 cancel and fortuitously good r values may be obtained. For this reason and for others as will be discussed below, a slightly more conservative update of the trust region has been used in such saddle point cases. The algorithm being put forth can be described as follows: (1) If $r_{min} \leq r \leq r_{good}$ or $2 - r_{good} < r < 2 - r_{min}$ the step $\mathbf{X}_{k-1} \rightarrow \mathbf{X}_k$ is allowed to occur and the trust radius (h_k) in the next step is taken to be the same as h_{k-1}. (2) If $r_{good} \leq r \leq 2 - r_{good}$ the step $\mathbf{X}_{k-1} \rightarrow \mathbf{X}_k$ is taken and the trust radius h_{k-1} is increased, $h_k = \alpha h_{k-1}$. (3) If $r < r_{min}$ or $r > 2 - r_{min}$, the step $\mathbf{X}_{k-1} \rightarrow \mathbf{X}_k$ is not allowed to occur. Instead the trust radius is decreased ($h_k = (1/\alpha)h_{k-1}$) and a *new* step (whose maximum length is equal to the new shorter trust radius) is evaluated. For this new step $\mathbf{X}_{k-1} \rightarrow \mathbf{X}_k$ a new r value is computed and the above process is then continued. In the first case described above, the goal is to carry out a downhill walk to a local minimum. Steps are only rejected when they are in the wrong direction (i.e., uphill). Even r values much greater than one can be accepted because they indicate only that the true energy function has a nonquadratic character; the fact that r is positive means that the walk is still progressing downhill as desired. In transition-state applications, the energy function is being maximized in one direction and minimized in all other directions. Because the energy changes in the various directions are opposite in sign, large step sizes cannot be accepted except when justified through a high degree of quadratic character (i.e., a good r value). For this reason, tight constraints have been applied in transition-state applications when r is both smaller than and greater than unity.

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This Fletcher algorithm thus allows one to update the maximum step length during the step-by-step walking procedure. Clearly the algorithm contains parameters (r_{min}, r_{good}, α) whose values will determine the number of steps needed to walk from the starting geometry to some desired final geometry (e.g., local minimum or transition state). The algorithm is, however, shown below to be rather insensitive to their actual choice.

C. Surface Walking Strategies. Although the Fletcher procedure gives valuable information about the maximum step *length* which can safely (within r) be taken on the approximate surface $\tilde{E}(\mathbf{X})$, more information is needed for determining the *direction* in which the step should be taken. The best direction to walk depends upon whether one is seeking a local minimum (i.e., stable molecular geometry) or a saddle point (i.e., transition state). In the former case, one wants to find a region of the potential energy surface in which the Hessian matrix has all positive eigenvalues ($0 < b_1 < b_2 < b_3 < ... < b_n$). Within that region, one attempts to find the particular geometry $\mathbf{X}_{min}$ where all gradients $F_{0,i}$ vanish $\mathbf{F}_0 = \mathbf{O}$; at this geometry, one has a stable molecular geometry. In seeking transition states, one attempts to walk into regions of the surface where the Hessian matrix has one negative and $n - 1$ positive eigenvalues ($b_1 < 0 < b_2 < b_3 < ... < b_n$).

The step-by-step walking process therefore can be divided into two phases. In the first phase, one is faced with moving *away* from a starting region in which the structure of the Hessian (i.e., the number of negative eigenvalues) may not be what is desired. In the second phase of the walk process, one has entered a region of geometry space in which the Hessian has the proper structure. From this step on, the goal is to walk *toward* the stationary point (minimum or transition state) which lies in a neighborhood close to the present location.

In sections II.D and II.E it is shown how to implement a surface walking algorithm which achieves these goals. In summary, it should be kept in mind that, at *each* step of the walk, one is faced with the following problems:

(1) One must characterize, via the signs of the Hessian eigenvalues at the present location, the *local* surface structure and decide whether the structure is consistent with that of the region of the desired stationary point (i.e., local minimum or transition state).

(2) One must decide, based upon the above Hessian analysis, whether to walk *toward* the stationary point lying near to the present location (if the local Hessian structure is consistent with the desired structure) or *away from* the stationary point lying near the present location.

(3) One must decide which *direction* to take if one plans to walk away from the nearby stationary point. If there seems to be more than one promising direction (e.g., more than one "valley" leading away from a nearby minimum), each such direction must be explored.

(4) One must attempt to remain on the "valley floor" which leads along the walking direction. This is done by minimizing $\tilde{E}$ along directions perpendicular to the walk direction.

The following section provides the tools needed to implement such surface walks within the Fletcher-driven algorithm utilized here.

D. The Optimal Walk Direction. Suppose, as is typical, that the Hessian does not have the proper structure (number of negative eigenvalues) at the starting point $\mathbf{X}_k$. This means that nowhere *within* the current trust radius (h_k) ($|X| < h_k$) does the approximate surface $\tilde{E}(\mathbf{X})$, which adequately represents $E(\mathbf{X})$, possess a stationary point ($\mathbf{F}_k = \mathbf{O}$) which has the desired Hessian structure. Given that the sought after point does not lie *within* h_k, one is directed to examine stationary points which might exist on the *boundary* $|X| = h_k$. For example, if all Hessian eigenvalues are positive and one is seeking a transition state, it is inappropriate to move to the local minimum of $\tilde{E}$ within h_k. Rather one should move "uphill" along some one direction defining a "valley floor" away from the local minimum. This can be achieved by trying to maximize $\tilde{E}$ along the one "valley floor" direction while minimizing $\tilde{E}$ along the $n - 1$ other directions, thereby staying in the "stream bed" which runs along the direction of uphill movement. A search on the boundary $|X| = h_k$ for a stationary point satisfying the above requirements can be accomplished by looking for stationary points of the Lagrangian function[3]

$$L(\mathbf{X}) \equiv \tilde{E}(\mathbf{X}) - \frac{\lambda}{2}(\mathbf{XX} - h_k^2) \tag{3}$$

where λ is a Lagrange multiplier whose value will eventually be chosen to guarantee that one is on the boundary $|\mathbf{X}| = h_k$ and walking uphill in the chosen direction while remaining, to as high a degree as possible, in the "stream bed". Setting $d\mathbf{L}/d\mathbf{X} = \mathbf{O}$ determines the stationary points of the energy function on the boundary and yields a set of equations which can be solved for the step length

$$\mathbf{X} = (\lambda\mathbf{1} - \mathbf{H})^{-1}\mathbf{F} \tag{4}$$

In terms of the eigenvectors $\mathbf{v}_i$ and eigenvalues b_i of the Hessian matrix $\mathbf{H}$, this result can be expressed as follows:

$$\mathbf{X} = \sum_i (\lambda - b_i)^{-1}(\mathbf{v}_i\boldsymbol{F})\mathbf{v}_i = \sum_i X_i\mathbf{v}_i \tag{5}$$

The value of λ will be chosen to make the length of the step equal to h_k while keeping the direction of the walk within a "stream bed".

To better understand how to choose λ to fulfill these criteria, it helps if one examines both the step-length function

$$h_k^2(\lambda) = \mathbf{XX} = \sum_i (\lambda - b_i)^{-2}\,\bar{F}_i^2 \tag{6}$$

and the quadratic energy change $\tilde{E}$

$$\tilde{E}(\lambda) = \sum_i (\lambda - b_i)^{-2}\,\bar{F}_i^2(\lambda - \tfrac{1}{2}b_i) \tag{7}$$

which result when a step given by eq 5 is taken. For convenience, the component of the force vector $\mathbf{F}$ along the local eigendirection $\mathbf{v}_i$ has been denoted $\bar{F}_i = (\mathbf{v}_i\boldsymbol{F})$. Note that the energy contributions from each eigendirection are then uncoupled. Assume now, for example, that one has decided to walk uphill along the stream bed characterized by the $\mathbf{v}_1$ direction corresponding to the "softest" local Hessian eigenvalue. Uphill walks along other directions and downhill walks in all directions will be discussed later. As such a soft-mode uphill walk progresses, the forces $\bar{F}_i$ ($i \geq 2$) should be kept small (i.e., one should stay near the "stream bed") while the force F_1 along the walking direction can become large.

Before stating the criteria for choosing a value or range of λ values which characterize the above described "stream bed" walk, it is helpful to consider the direction and quadratic energy changes which result from taking a straightforward Newton–Raphson (NR) step (i.e., setting $\lambda = 0$). Clearly, the NR step (see eq 5 with $\lambda = 0$) is directed along the forces whose Hessian eigenvalues are negative and in opposite to those forces whose Hessian eigenvalues are positive. From eq 7 (with $\lambda = 0$) it is seen that the NR step leads to decreases in $\tilde{E}$ along directions having positive Hessian eigenvalues and increases in $\tilde{E}$ for directions with negative eigenvalues. That is, the NR step tries to minimize the energy along directions with positive

b_i (also opposing the forces along these directions) and to maximize $\tilde{E}$ along directions with negative b_i (also moving along these $\bar{F}_i$). Steps which either oppose or move along the force $\bar{F}_i$ assure that the *linear* term of $\tilde{E}$ in eq 1 (F_iX_i) becomes positive or negative, respectively.

With this insight derived from analyzing the NR step, it is now possible to make definite statements about how to choose λ in the step-vector expression of eq 5. For example, to walk uphill along $\mathbf{v}_1$ (corresponding to the softest eigenmode having eigenvalue b_1) and remain in the "stream bed", λ should be chosen such that following applies:

(1) $(\lambda - b_1)^{-1}$ is positive. This guarantees that the walk is along the force in this direction and assures that the linear term $\tilde{E}$ in the $\mathbf{v}_1$ direction is positive. Hence $\lambda > b_1$ is required.

(2) The $(\lambda - b_i)^{-1}$ ($i \geq 2$) are negative. This means that the steps along other directions oppose the forces F_i and therefore should give positive linear contributions in $\tilde{E}$. Hence $\lambda < b_2 < b_3 < \ldots$.

(3) $(\lambda - {}^1/_2 b_1)$ must be positive so that $\tilde{E}$ will increase in the $\mathbf{v}_1$ direction: $\lambda > {}^1/_2 b_1$.

(4) The $(\lambda - {}^1/_2 b_j)$ ($j \geq 2$) must be negative so that $\tilde{E}$ decreases along the $\mathbf{v}_j$ ($j \geq 2$) directions.

Condition (4) combined with that in (2) permit the walk to, within the approximation that $\tilde{E}$ adequately represents the true $E(\mathbf{X})$, find the "stream bed". Conditions (1) and (3) dictate that the walk should be energetically uphill along $\mathbf{v}_1$. Based on the above analysis, it is clear that one should choose λ in the range $b_1 < \lambda < {}^1/_2 b_2 < \ldots$ if one desires to walk up the valley along the soft-mode $\mathbf{v}_1$ direction. Modification of this algorithm to permit walks up the stiffer-mode $\mathbf{v}_2$, $\mathbf{v}_3$, etc. valleys will be discussed later.

There is one problem which, however, needs to be dealt with now in relation to the soft-mode walk discussed above. It is possible that the local Hessian eigenvalues b_1 and b_2 may not obey $b_1 < {}^1/_2 b_2$, as a result of which the range

$$b_1 < \lambda < {}^1/_2 b_2 \tag{8}$$

in which λ needs to be chosen may not exist. A simple transformation (scaling) of the coordinate along which the walk is to occur

$$X_1 = nX_1' \tag{9}$$

may, however, be carried out to assure that the condition in eq 8 can be met by the Hessian eigenvalues in the new transformed (scaled) coordinate system. The stationary (critical) points of the true energy function are invariant with respect to such a coordinate scaling while the numerical values (not signs) of the Hessian eigenvalues change as such a coordinate transformation is carried out. Introducing the transformation in eq 9 into the local quadratic energy function in eq 1 gives

$$\tilde{E} = nF_1X_1' + {}^1/_2 n^2 b_1 (X_1')^2 + \sum_{i \geq 2} (F_iX_i + {}^1/_2 b_i X_i^2) \tag{10}$$

In terms of the variables X_1', X_2, X_3, ..., this quadratic energy expression can be viewed as having a modified force $F_1' = nF_1$ and Hessian eigenvalue $b_1' = n^2 b_1$ in the $\mathbf{v}_1$ direction. By choosing the scale factor n properly, it is thus possible to make $b_1' < {}^1/_2 b_2$. In practice, it is found (see later) that choosing n such that $b_1' = {}^1/_4 b_2$ works quite well. Hence, if one simply scales the active (X_1) coordinate by scaling its force and Hessian eigenvalue, one can perform the kind of uphill stream bed walk outlined in the X_1', X_2, X_3, ... coordinate system by taking λ in the interval $b_1' < \lambda < {}^1/_2 b_2$. Equation 5 (with b_1' and F_1' substituted for b_1 and F_1) then gives X_1', X_2, X_3, ... after which the *real* step in the $\mathbf{v}_1$ direction $X_1 = nX_1'$ can be evaluated.

The above coordinate scaling device is thus useful in the soft-mode type walk discussed earlier. It can also be used to develop an algorithm for walking up one of the "stiffer" modes (e.g., to walk along $\mathbf{v}_2$ keeping the energy along $\mathbf{v}_1$, $\mathbf{v}_3$, ... minimized). By scaling the active mode (i.e., the mode along which the walk is to occur) $X_2 = nX_2'$ one can guarantee that the scaled Hessian $n^2 b_2 = b_2'$ obeys $b_2' < {}^1/_2 b_1 < b_1 < b_2 < \ldots$. Hence, in the scaled coordinate system, the $\mathbf{v}_2$ direction is the "soft mode" and the proper range for choosing λ is $b_2' < \lambda < {}^1/_2 b_1$, in this walk along $\mathbf{v}_2$. After choosing λ in this range and using eq 5 (with b_2 and F_2 replaced by $n^2 b_2$ and nF_2) to generate X_1, X_2', X_3, ... (and $X_2 = nX_2'$), one is able to walk up this ($\mathbf{v}_2$) stiff-mode valley. In carrying out such a stiff-mode iterative procedure the eigenvector $\mathbf{v}_2$ has to be smoothly followed during the iterative procedure. This may be done by projecting the eigenvectors of the Hessian matrix in one iteration onto the eigenvector $\mathbf{v}_2$ of the previous iteration, selecting the eigenvector whose overlap is closest to unity as the new $\mathbf{v}_2$ direction. As the iterative procedure progresses, the eigenvalue b_2 corresponding to the new $\mathbf{v}_2$ crosses the eigenvalue b_1. From this point on, the iterative walking procedure may be continued as a normal soft-mode walk, since the direction along which one is walking now is the softest mode. At or close to the crossing (i.e., when b_1 is very close to b_2) the eigenvectors of the Hessian matrix contain little directional information (i.e., the eigenvectors of a degenerate root can be arbitrarily rotated). Directional information has then to be transferred either from the previous iteration; alternatively the iterative procedure can be forced to jump this region of near degeneracy by taking a larger step. Since this region where b_1 is very close to b_2 is very small, no serious problem would result by simply "jumping" this region via a larger step.

In summary, the criteria (1)–(4) given above allow one to determine a range of λ values appropriate for the kind of uphill valley walk described early in this section. The coordinate scaling device allows one both to guarantee that the desirable λ range exists and to achieve stiff as well as soft-mode walks. There still remains a problem as to exactly what value of λ in the desirable region (e.g., $b_1 < \lambda < {}^1/_2 b_2$ or $b_1' < \lambda < {}^1/_2 b_2$ or $b_2' < \lambda < {}^1/_2 b_1$) should be employed. Considering, for example, the most straightforward case (i.e., that of an uphill walk along $\mathbf{v}_1$ in which the region $b_1 < \lambda < {}^1/_2 b_2$ exists), it is clear that neither $\lambda = b_1$ nor $\lambda = {}^1/_2 b_2$ are desirable. The former ($\lambda = b_1$) gives rise to a step (eq 5) which is entirely along the $\mathbf{v}_1$ direction; no adjustments along $\mathbf{v}_2$, $\mathbf{v}_3$, etc. would be allowed. The latter choice ($\lambda = {}^1/_2 b_2$) gives rise to no predicted energy change along $\mathbf{v}_2$ since $\bar{F}_2(\lambda \vee b_2)^{-2}(\lambda - {}^1/_2 b_2)$ vanishes at $\lambda = {}^1/_2 b_2$. This is clearly not an optimal step unless $\bar{F}_2$ were equal to zero.

If there exists a value of λ within the desirable range (e.g., $b_1 < \lambda < {}^1/_2 b_2$) for which the present radius (h_k) equals the total step length given in eq 6, it is appropriate to choose this value of λ (λ_- of Figure 1a). In Figure 1 is depicted graphs of $h_k^2(\lambda)$ from eq 6 vs. λ for various values of the b_i and $\bar{F}_i$. It can clearly be seen that, in certain circumstances (e.g., graph a and c of Figure 1), there exists a choice of λ in $b_1 < \lambda < {}^1/_2 b_2$ which obeys $h_k^2 = h_k^2(\lambda)$. In such cases, this is the optimal choice of λ since it generates a step direction and length which are consistent with the stated goals of the walk. However, there are other cases (e.g., graphs b and d of Figure 1) for which no solution of $h_k^2 = h_k^2(\lambda)$ occurs in the proper interval. In such situations, it is probably best to choose λ within $b_1 < \lambda < {}^1/_2 b_2$ (e.g., at the midpoint $\lambda = {}^1/_2(b_1 + {}^1/_2 b_2)$) so as to guarantee

that the *direction* of the step is correct (i.e., uphill along $\mathbf{v}_1$, downhill along other modes) and to then rescale the magnitudes of *all* step lengths X_i to make the step lie on the current step-length perimeter: $\sum_i X_i^2 = h_k^2$.

Before closing this discussion of how to deal with "uphill" stream-bed walks of either the soft- or stiff-mode variety it is worth noting that there is one more case in which a unique choice of λ can be made. If b_1 is negative and b_2 is positive (such will always be the case as the walk approaches the transition state), the range $b_1 < \lambda < {}^1/_2 b_2$ certainly exists. Moreover, if the current trust radius h_k is greater than the h_k ($\lambda = 0$) of eq 6 evaluated at $\lambda = 0$ (the NR value), then $\lambda = 0$ is an optimal choice. It is optimal because it lies in $b_1 < \lambda < {}^1/_2 b_2$ and because the predicted energy changes along all modes $\mathbf{v}_2$, $\mathbf{v}_3$, ... are minimized at $\lambda = 0$:

$$0 = \frac{\mathrm{d}}{\mathrm{d}\lambda} \frac{F_i^2(\lambda - {}^1/_2 b_i)}{(\lambda - b_i)^2} \rightarrow \lambda = 0 \qquad (11)$$

Therefore, once $\lambda = 0$ it is in the acceptable range and h_k^2 ($\lambda = 0$) $\leq h_k^2$, the NR step direction should be taken. However, when the NR step is larger than the trust radius ($h_k^2 \leq h_k^2$ ($\lambda = 0$)) but within the acceptable λ interval we have chosen to scale the NR step length such as to remain on the current step length perimeter.

Keep in mind that the above strategy has been developed based upon the assumption that one desires to walk *uphill* along some stream bed. This is, of course, the case when one is walking away from a local minimum (i.e., stable molecular geometry) in search of a transition state (where one Hessian eigenvalue is negative). The strategy appropriate to walking toward a local minimum is more straightforward. The λ parameter should be chosen so that all of the individual steps $X_i = \bar{F}_i/(\lambda - b_i)$ oppose their forces (i.e., $\lambda < b_i$ (i = 1, 2, 3, ...)) and so that all of the predicted energy changes $(\lambda - b_i)^{-2} F_i^2 (\lambda - {}^1/_2 b_i)$ are negative (i.e., $\lambda < {}^1/_2 b_i$). Choosing $\lambda < {}^1/_2 b_i$ and $\lambda < b_i$ means either taking λ from the left most intersection (λ_1) of $h_k^2 = h_k^2(\lambda)$ (see graph b in Figure 1) if the NR step length is too long ($h_k^2(0) > h_k^2$) or taking $\lambda = 0$ (the NR step) if $h_k^2(0) \leq h_k^2$ (see graph a of Figure 1). The NR step is optimal in the latter case because, as was shown above, all of the individual quadratic energy changes $(\lambda - b_i)^{-2} F_i^2 (\lambda - {}^1/_2 b_i)$ have minima at $\lambda = 0$. Hence, in a walk toward a minimum, the NR step is appropriate whenever it is acceptable (i.e., when $h_k^2(0) < h_k^2$ and $\lambda = 0$ is contained in the interval $\lambda < {}^1/_2 b_1$ and $\lambda < b_1$) to cover the case of a downhill walk from a transition state.

The walk strategies described above form the basis of the algorithms utilized here to walk from local minima, uphill along various (soft- or stiff-mode) stream beds, to transition states, and onward toward product-state local minima. There is one final point which needs to be addressed before this section can be closed.

Given that one begins at a local-minimum geometry where all forces $\bar{F}_i$ vanish, it is not possible to form the $h_k^2(\lambda)$ function shown in the graphs of Figure 1. Hence it is difficult to know how to *start* the surface walking algorithm. To search for the lowest-energy transition state, it is most logical to *begin* the walking process by taking a step of length h_0 along or opposite the $\mathbf{v}_1$ direction. Both directions have to be explored when systematically searching for transition states. Other transition states could be explored by taking the initial step to be of length h_0 and along or opposite $\mathbf{v}_2$, $\mathbf{v}_3$, $\mathbf{v}_4$, etc. After such an initial step, the $h_k^2(\lambda)$ graph as depicted in graphs a–d of Figure 1 will obtain *except* if the force $\bar{F}_2$ (or $\bar{F}_1$) remains zero (for example, due to molecular symmetry). In such a case, the graph will have the structure shown in graph e of Figure 1 with an actual crossing at the b_2 (or b_1) asymptote. If the force in the b_2 direction were infinitesimally small the step length function of eq 6 would have the structure indicated with the dashed lines paralleling closely the b_2 asymptote in graph e of Figure 1. Now it is appropriate to choose the step of total length h_0 to have components along $\mathbf{v}_1$ of δ and along the residual directions of magnitudes $(h_0^2 - \delta^2)^{1/2}$, respectively. The residual step length δ is small and is introduced to ensure that the step has a $\mathbf{v}_2$ component even though symmetry, for example, would keep the force in this direction equal to zero. If no $\mathbf{v}_2$ component were introduced in such a case, the search for stationary points could seriously be restricted and the desired stationary point may be out of reach. An example of such a behavior is given in the transition state walk in the model potential of Cerjan and Miller in Figure 2.

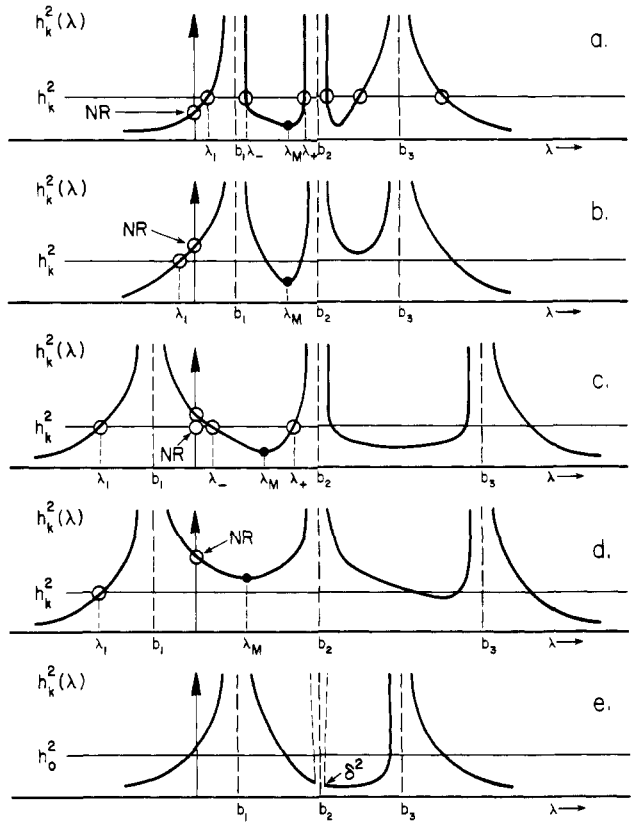

Figure 1. Plot of the square of the λ-dependent step length (eq 6) as a function of λ for several possible values of the Hessian eigenvalues and forces.

E. Updating the Hessian. The treatment outlined above required from the start that the force $\mathbf{F}$ and Hessian $\boldsymbol{H}$ could be readily evaluated at any geometry ($\mathbf{X}_k$). The state-of-the-art in quantum chemical methodology does permit efficient calculation of $\mathbf{F}$, but analytical formulas for $\boldsymbol{H}$ have only recently begun to appear in the literature. Even when the optimal expressions for $\boldsymbol{H}$ for a multiconfigurational wave function are known and programmed for use, it is likely that the cost involved in evaluating $\boldsymbol{H}$ will be high. Therefore, it is natural to explore the possibility that the Hessian $\boldsymbol{H}$ might be adequately approximated by using one of the so-called Hessian update methods which appear in the numerical analysis literature.[3] These techniques are designed to determine an approximate Hessian at $\mathbf{X}_{k+1}$ in terms of the Hessian or approximate Hessian $\boldsymbol{H}_k$ at $\mathbf{X}_k$, the force difference $\mathbf{F}_k - \mathbf{F}_{k+1}$, and the previous step vector $\mathbf{X}_{k+1} - \mathbf{X}_k$. Expanding $\mathbf{F}_k$ around $\mathbf{F}_{k+1}$ gives

$$\mathbf{F}_k - \mathbf{F}_{k+1} = \boldsymbol{H}_{k+1}(\mathbf{X}_k - \mathbf{X}_{k+1}) + 0(\mathbf{X}_k - \mathbf{X}_{k+1})^2 \qquad (12)$$

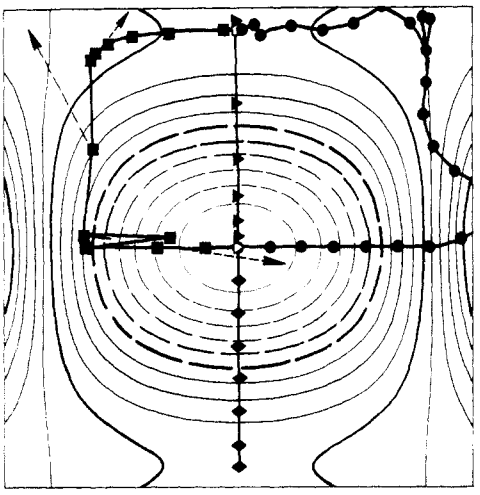

Figure 2. Walks on the CM potential surfaces: ■, soft-mode walk using the analytical Hessian matrix (the pure Newton–Raphson step is shown at three of the points by an arrow); ●, soft-mode walk using an updated Hessian; ▲, stiff-mode walk using the analytical Hessian; ♦, stiff mode walk using the updated Hessian.

which shows that the gradient difference $\mathbf{F}_k - \mathbf{F}_{k+1}$ contains a component of the finite-difference approximation to the exact Hessian $\boldsymbol{H}_{k+1}$ along the direction $\mathbf{X}_k - \mathbf{X}_{k+1}$. This finite-difference Hessian information, together with structural characteristics of the exact Hessian are used to form the Hessian updates described below.

The so-called BFGS update approach[3] is considered in the numerical analysis literature to be the most efficient update approach to use in finding local minima. For that reason it was decided to use the BFGS update in all walks whose goal was to find local minima. The BFGS update formula reads[3]

$$H_{k+1} = H_k + \frac{\mathbf{P}_k\mathbf{P}_k{}^T}{\mathbf{P}_k{}^T\mathbf{K}_k} - \frac{\boldsymbol{H}_k\mathbf{K}_k\mathbf{K}_k{}^T\boldsymbol{H}_k}{\mathbf{K}_k{}^T\boldsymbol{H}_k\mathbf{K}_k} \tag{13}$$

where

$$\mathbf{P}_k = \mathbf{F}_{k+1} - \mathbf{F}_k \tag{14}$$

$$\mathbf{K}_k = \mathbf{X}_{k+1} - \mathbf{X}_k \tag{15}$$

One important characteristic of the BFGS update is that if $\boldsymbol{H}_k$ is positive definite then $\boldsymbol{H}_{k+1}$ will also be positive definite. Such a characteristic is, of course, undesirable when one is carrying out a walk toward a transition state since the Hessian must be allowed to change structure (i.e., number of negative eigenvalues) as the walk progresses. For this reason, the updating algorithm given below (the so called Powell update[9]) has been chosen for use in transition-state walks. The Powell update[9] procedure does not force $\boldsymbol{H}_{k+1}$ to have the same structure as $\boldsymbol{H}_k$ yet it preserves the Hermitian character of $\boldsymbol{H}$ while assuming that the updated Hessian satisfy eq 12. The Powell update expression is

$$\boldsymbol{H}_{k+1} = \mathbf{H}_k + \left[\mathbf{T}_k\mathbf{K}_k{}^T + \mathbf{K}_k\mathbf{T}_k{}^T - \mathbf{K}_k\frac{(\mathbf{T}_k{}^T\mathbf{K}_k)}{(\mathbf{K}_k{}^T\mathbf{K}_k)}\mathbf{K}_k{}^T\right](\mathbf{K}^T\mathbf{K})^{-1} \tag{16}$$

where $\mathbf{K}_k \equiv \mathbf{X}_{k+1} - \mathbf{X}_k$ and $T_k \equiv \mathbf{F}_{k+1} - \mathbf{F}_k - \mathbf{H}_k(\mathbf{X}_{k+1} - \mathbf{X}_k)$. Notice that construction of the updated Hessian in both eq 13 and 16 involves simple matrix and vector multiplications of the force and step vectors which are presumed to be readily available.

It should be clear that the Hessian update process has to be given some starting Hessian $\boldsymbol{H}_0$ with which to begin its recursive updating. In many numerical analysis applications it is common to begin with $\mathbf{H}_0 = \mathit{1}$, the identity matrix. In the surface walking studies treated here, a reasonable starting Hessian to use in moving away from a local minimum toward a transition state is that Hessian determined in locating the equilibrium geometry ($\mathbf{X}_{eq}$) via an update walk. In this update walk $\mathbf{X}_{eq}$ one can utilize the unit matrix as the initial approximation to $\boldsymbol{H}$. The BFGS update method together with the Fletcher walking algorithm can then be used to move from the initial geometry to $\boldsymbol{X}_{eq}$. The Hessian matrix which exists upon reaching $\boldsymbol{X}_{eq}$ can then be used to start the transition-state walk. Alternatively, if the force constants characteristic of the local minimum energy geometry are known from experimental data, they can be used to generate a starting Hessian matrix. In walking down from transition states toward product-state minima the updated Hessian at the stationary point can be used as an initial Hessian for the downhill walk.

The requirements for the Hessian update approaches to be successful in the surface walking algorithm are different at the initial and final stages of the iterative procedure. In the initial part of the surface walk where even the exact local Hessian is structurally incorrect, it is important that the Hessian update is of sufficient quality to correctly locate the lowest few Hessian eigenvalues (and eigenvectors) thereby assuring that steps will be taken in approximately the desired directions. As our numerical examples demonstrate the Hessian update procedures used here are able to locate the lowest Hessian eigenvalues relatively accurately. As the walk progresses into the region where the local Hessian has the proper structure, it becomes important that the Hessian update procedure also be able to locate accurately the stationary point in reasonably few iterations. The Hessian update procedures employed here certainly are able to do so because they have superlinear convergence characteristics.[10]

III. Application to Model and Ab Initio Surfaces

The above-outlined Fletcher-based surface walking algorithm has been tested on four potential energy surfaces: a model potential used previously by Cerjan and Miller[2] to test their own surface walking method, a surface for the C^1A' state of HCN computed by ab initio quantum chemical methods,[7] a ground-state HCN surface developed by Murrell et al.,[6] and a model potential utilized by Crippen and Scherage[5] in their polypeptide conformation studies. For each of these surfaces, the goal of this work was to explore the performance of the walking method by using both analytical and updated Hessian matrices and to compare with the results of others and of the Newton–Raphson method. The primary emphasis of the applications has been directed toward walking from local minima to transition states and subsequently onward to product local minima.

A. The Cerjan–Miller Model Potential. A simple two-dimensional (x,y) model potential energy function

$$V_{CM}(x,y) = (a - by^2)x^2e^{-x^2} + \frac{c}{2}y^2 \tag{17}$$

was used in Cerjan and Miller's innovative work on finding transition states. A contour representation of $V_{CM}(x,y)$ is given in Figure 2 for $a = 1$, $b = 1.2$, and $c = 1.0$. Although this surface may appear to be especially straightforward to handle, it has at least two difficulties. First, near the local minimum at $x = y = 0$ the lowest Hessian eigenvalue corresponds to motion along the y axis. Hence, the surface walking routine employed here, when taking its initial step along the soft-mode y axis, does not make a very "wise" first step. As a result, it must evolve an efficient path

which allows for motion in the x direction to increase while that along y is reduced. The second pathology of the V_{CM} surface has to do with its left–right and top–bottom symmetry. Even following the above-discussed initial step along the y axis, the force along the x axis remains zero. Hence, the device presented in section II.E for allowing both the $\mathbf{v}_2$ and $\mathbf{v}_1$ directions to contribute in this symmetry-restricted situation must be employed.

The quality of the resultant walk path (WP) was not found to be very sensitive to the choices made for r_{min} and r_{good} parameters used in the step-length update process for $0.50 < r_{min} < 0.90$ and $0.75 < r_{good} < 0.95$. Therefore, to be somewhat conservative, values of $r_{good} = 0.85$ and $r_{min} = 0.70$ were used for all other transition-state surface walks reported in this paper. The amount (α) by which the step length h_k is increased or decreased as described in section II.B was taken to be $\alpha = 1.50$. This choice was made after trying several values of α in the range $1.25 < \alpha < 3.00$ and finding little sensitivity of the walking path to the value of α in this range.

In Figure 2 are shown two types of walking paths starting from the local minimum at $x = y = 0$. The first starts out by moving along the soft mode (the y direction) whereas the second involves initial movement along the x axis. Handling the latter case requires the coordinate scaling algorithm introduced in section II.E. Also included in Figure 2, for comparison, are soft- and stiff-mode walks in which updated Hessians are used. The initial Hessian $\boldsymbol{H}_0$ used in these update walks was obtained by first performing a minimum-energy geometry walk in the region of (0,0).

On the basis of the qualitative aspects of the paths followed by the various walks mentioned above, it seems reasonable to conclude the following:

(1) The soft-mode Fletcher-type walk in which the analytical Hessian is used is of very good quality, although it seems to take an unexpected fourth step. However, a detailed analysis shows that the third step leads to a crossing of the eigenvalues b_1 and b_2. Once the third step is taken, the (new) local soft-model eigendirection is predominantly of x-motion character; the y direction is now essentially the stiff mode. The algorithm therefore moves uphill along the new soft mode and attempts to minimize $\tilde{E}$ along the new stiff mode (the y axis). Due to the very small size of the force in the x direction, the major part of the fourth step is in the current stiff-mode direction thereby generating the unusual, but correct, fourth step. The size of this "jerky" fourth step would, of course, have been much smaller if shorter step sizes had been used. However, when the directions along which the maximization is to occur change, a discontinuity has to show up in the walking path.

(2) The soft-mode walk in which an updated Hessian is employed is also of good quality when a moderately small (0.15) and fixed step length is used. It was found that the step-length updating algorithm described in section II.B could not be used with an updated Hessian. The updated Hessian is simply not accurate enough to use in predicting the quadratic energy change $\tilde{E}(\mathbf{X}_k) - E(\mathbf{X}_{k-1})$ which enters into eq 2 where r is computed. For this reason, it is felt that fixed step lengths of modest magnitude should be used in updated Hessian walks even though this may result in these Hessian update walks requiring more total steps.

(3) The NR step direction and length (indicated with arrows in Figure 2) cannot be trusted until the walk process reaches a region close to the desired transition state where the surface is quite quadratic. In the early stages of the walk, the NR step is trying to return to the local minimum. Once the structure of the Hessian changes, the NR step moves away from the local minimum but not in a controlled manner; its step lengths tend to be too long and also its directions are often not toward the stationary point.

(4) Both the stiff-mode exact- and updated-Hessian walks progress rapidly to the transition state. The analytical Hessian version, which allows the step length to be updated ($\alpha = 1.5$), takes fewer than the fixed-step length (0.15) updated-Hessian version, but both follow the stiff-mode stream bed very well.

(5) The updated-Hessian walks seem to require approximately twice as many steps as the analytical-Hessian walks. As an implication for implementation of Hessian update methods in ab initio quantum chemistry computer codes, this is encouraging since the cost of evaluating the analytical Hessian is far more than twice the cost of computing the gradient.[1]

(6) As can be seen from Table I, the eigenvalues of the transition-state Hessian obtained from the updated and analytical Hessians agree remarkably well. The Hessian obtained in the stiff-mode-update walk is not quite in agreement with the others. This is probably a result of the fact that this stiff-mode walk did not "experience" much of the potential energy surface in the direction perpendicular to the x axis as a result of which the Hessian update formula could not develop data in this direction.

Cerjan and Miller have previously carried out a soft-mode walk on the potential of eq 17 to test their walking algorithm. In their procedure the value of the Lagrange parameter λ is chosen to be the one for which $h_k(\lambda)$ is minimum in the interval $b_1 < \lambda < b_2$ (i.e., λ_M of Figure 1). Step sizes are also normalized to be of "reasonable" magnitude in the Cerjan–Miller algorithm. The λ_M value often falls outside what we consider to be the acceptable interval as a result of which the walking path obtained by Cerjan and Miller is much less smooth than the walking path reported in Figure 2.

B. The Crippen–Scheraga Potential. To illustrate our walking algorithm's ability to follow a very curved stream bed, it has been applied to the model potential

$$V_{CS}(x,y) = 100(y - x^2)^2 + (1 - x)^2 \qquad (18)$$

whose stream bed lies along $y = x^2$ and whose only minimum lies at $x = y = 1$. The potential in eq 18 has previously been used by Crippen and Scheraga to test their own walking algorithm. The result of the Crippen–Scheraga walk is given in Figure 3 along with the path generated by using the soft-mode walking algorithm described in this paper with a fixed step length of 0.10 units. The walk in which variable step lengths are employed deviates very little from the fixed step length walk path (except that it takes steps of 0.100–0.375 units) until the region near $x = y = 0$. Entering the $x = y = 0$ region, the variable step length walk takes too long a step (0.375 units) and thereby moves out of the stream bed by about 0.12 units (to $x = 0$, $y = -0.12$). It then rejects several steps, reduces its step length trust radius appropriately, and moves back to the stream bed in an orderly manner (near $x \sim -0.12$, $y \sim 0.0$). From this point on, the variable-step length walk proceeds up the $y = x^2$ stream bed increasing its trust radius as it moves to more negative x values and more positive y values. A fixed-step updated Hessian walk with a step length of 0.1 was found to be identical with the one reported in eq 6 using the analytical Hessians.

The CS walk was generated not by the method outlined in our paper but by taking steps along one direction (usually the direction of smallest curvature) and then minimizing the energy along the directions (one direction

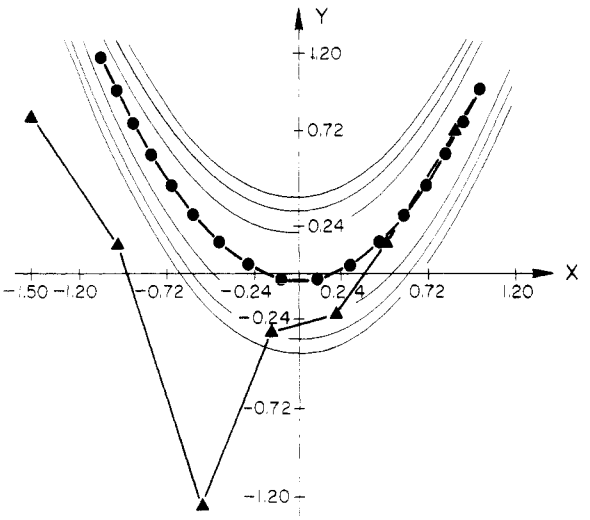

Figure 3. Walks on the Crippen–Scherage surface: ●, analytical Hessian walk; ▲, Crippen–Scheraga walk (see text).

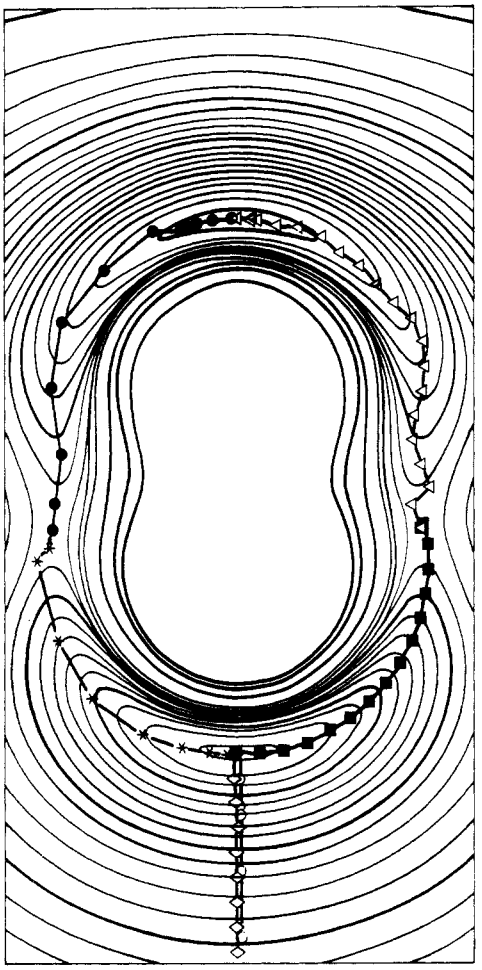

Figure 4. Walks on the ground-state HCN surface: O, stiff-mode analytical Hessian walk; ◇, stiff-mode updated Hessian walk; *, soft-mode analytical Hessian walk; ■, soft-mode updated Hessian walk; ●, downhill analytical Hessian walk; △, downhill updated Hessian walk.

for this two-dimensional example) orthogonal to the first direction. As is clear from Figure 3, this procedure results in a less satisfactory walking path and is likely to be more difficult to employ than our approach in higher dimensional surfaces.

C. Ground and Excited (C^1A') States of HCN. In Figures 4–6 several walk paths are presented for walks on both the linear $X^1\Sigma$ ground state and the bent C^1A' excited

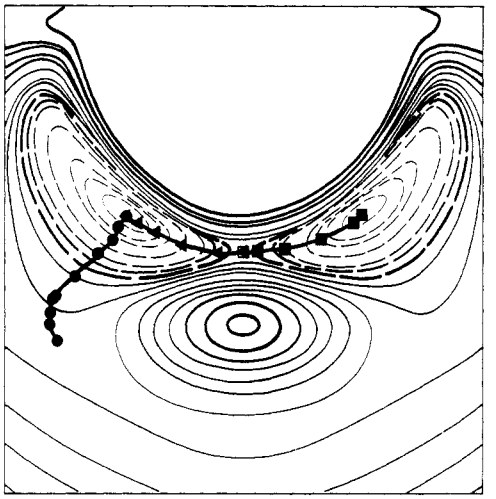

Figure 5. Walks on the Chuljian-Simons ab initio C-state HCN surface: ▲, soft-mode walk with analytical Hessian; ■, downhill walk using analytical Hessian; ●, stiff-mode walk using analytical Hessian.

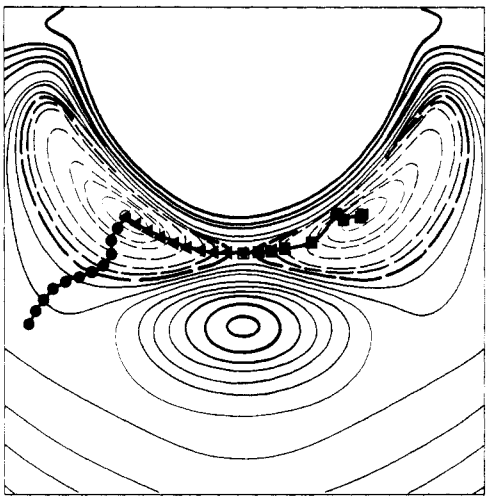

Figure 6. Walks on the Chuljian–Simons ab initio C-state HCN surface: ▲, soft-mode walk with updated Hessian; ■, downhill walk using updated Hessian but with variable-step length; ●, stiff-mode walk using updated Hessian.

state of HCN. The former potential energy surface is given, as a function of the distances between the three atoms by Murrell et al.[6] In constructing Figure 4 the CN bond length has been held fixed at 1.159 Å; the surface depicted is thus dependent only on the CH bond length and the HCN bond angle as is the excited-state surface shown in Figures 5 and 6. This latter surface was generated by fitting an analytical function to the energies resulting from more that 150 ab initio configuration interaction calculations. The explicit form of this analytical fit is given in ref 7.

Based upon the data presented in Figures 4–6 we conclude the following:

(1) The soft-mode analytical Hessian walks and updated Hessian walks are both very reliable. The updated Hessian walks in which fixed step lengths are used seem to be approximately as efficient as the walks which employ analytical Hessians. In downhill walks to an energy minimum (see Figure 6) it may be safe to update the trust region also in a Hessian-update walk. The observation that Hessian update walks work so well paints an optimistic picture for using Hessian update techniques in ab initio quantum calculations.

(2) Both analytical and updated Hessian walks from the transition states to product-state local minima are reliable

TABLE I: Analytical and Updated Hessian Eigenvalues

surface	eigenvalues	
	analytical	updated
CM	−1.4635[a]	−1.4485[a]
	0.11709[a]	0.1171[a]
	−1.4636[b]	−1.3046[b]
	0.11709[b]	0.1225[b]
HCN C state	−0.0486[c]	−0.0562[c]
	0.2704[c]	0.2383[c]
	0.0329[d]	0.0318[d]
	0.2284[d]	0.2261[d]
HCN ground state	−3.9300[e]	−3.9154[e]
	19.4262[e]	19.5437[e]
3-D HCN ground state	−3.9305[e]	−3.2171[e]
	17.4763[e]	19.1557[e]
	77.4965[e]	101.2579[e]

[a] Obtained via soft-mode walk to the transition state. [b] Obtained via stiff-mode walk to the transition state. [c] Obtained via soft-mode walk to the transition state. [d] Product Hessian eigenvalues obtained by walking from the transition state to the product geometry. [e] Obtained via soft-mode walk to the transition state.

and efficient, again supporting the use of an updated Hessian procedure.

(3) Both analytical and updated Hessian stiff-mode walks lead to correct dissociation, although they differ more than do the respective soft-mode walks.

(4) As Table I shows, the transition-state and product-state Hessian eigenvalues obtained via the update method are again in good agreement with the analytical values.

The two-dimensional walks described above have been extended to three dimensions in the ground-state HCN case. The Murrell surface[6] is given in terms of all three internal degrees of freedom of HCN, so it permits a full geometry optimization.

As can be seen from Table I, the three Hessian eigenvalues obtained via the analytical- and updated-Hessian walks are in relatively good agreement although the highest mode eigenvalue (corresponding approximately to CN stretching) is less consistent. The two lower-energy eigenvalues in each case match reasonably well those found in the two-dimensional walk (with the CN bond-length frozen). The actual walk path taken, for example, in the variable-step length analytical-Hessian walk appears, as far as movement of the H atom relative to the C atom is concerned, to be very close to the corresponding path shown in Figure 4. The CN bond length changed (monotonically) throughout this same walk from 1.153 to 1.181 Å, its value at the transition state. The fact that the CN bond length changed so little and the observation that the walking path of the H atom in the two- and three-dimensional walks are nearly identical indicate that the CN degree of freedom is relatively weakly coupled to the H-atom stretching and bending motion.

IV. Concluding Remarks

The results presented in this paper illustrate the utility of the algorithm being proposed for use in chemical reaction path walks. By combining Fletcher trust-radius updating, active coordinate scaling, and the concept of stream bed walking, it has been possible to develop this practical and highly efficient algorithm. The outlook for other ab initio applications of the procedure is further brightened by the success of the Hessian update walks. The high cost, in terms of computer time and storage space needs, involved in the analytical evaluation of the Hessian matrix via ab initio quantum chemical methods[1] makes the implementation of efficient Hessian-update methods important if not essential.

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