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A gradient extremal walking algorithm

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Gradient extremals define stream beds connecting stationary points on molecular potential energy surfaces. Using this concept we have developed an algorithm to determine transition states. We initiate walks at equilibrium geometries and follow the gradient extremals until a stationary point is reached. As an illustration we have investigated the mechanism for exchange of protons on carbon in methylenimine ($H_2C{=}NH$) using a multi-reference self-consistent-field wave function.

Key words: Potential energy surfaces — Gradient extremals — Reaction paths

1. Introduction

An important task of quantum chemistry is to systematically search Born-Oppenheimer potential energy surfaces for equilibrium and transition-state structures. The methods presently favored for determining equilibrium structures calculate the molecular gradient explicitly at each point in the search and use update techniques to approximate the molecular Hessian [1-8].

Transition states are stationary points on the Born-Oppenheimer potential energy surface with Hessian index one (one negative eigenvalue). The determination of transition-state structures is more difficult than the determination of equilibrium structures, partly because minima are intrinsically easier to locate and also because usually no *a priori* knowledge is available about transition-state structures. For

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smaller molecular systems with few degrees of freedom, transition states have been determined by searching the whole potential energy surface or that part of it that is believed to be of interest [5, 6]. These searches are usually carried out having available at each point the molecular gradient and updates of the molecular Hessian [1–8]. With more degrees of freedom it becomes increasingly more difficult to use such an approach. Also the risk to miss a transition state becomes large, even with few degrees of freedom.

Algorithms which determine the transition states by tracing the valley floors (stream beds) leaving equilibrium structures, have previously been described [9–13]. These walks are defined in terms of an uphill movement in the walk direction and a downhill movement (in some cases minimization) in the orthogonal directions. No rigorous definition is given of the moving direction in these algorithms. Recently, stream beds have been given a rigorous definition by Hoffman et al. [14] as the locus of points in the contour subspace where the gradient is extremal. (Work along this line has also been carried out by Pancíř [15] and by Basilevsky and Shamov [16]). With this definition well-defined searches for transition states can be performed by tracing the gradient extremals. The gradient extremals connect stationary points on the potential energy surface, and are locally characterized by the requirement that the molecular gradient is an eigenvector of the (mass-scaled) molecular Hessian at each point on the line. At an equilibrium structure gradient extremals leave in all normal coordinate directions (positive and negative), and a systematic search for transition states therefore requires a search along all these gradient extremals. Gradient extremals may also bifurcate, a fact that has to be considered in a systematic search for transition states. In an appropriately mass-scaled coordinate system gradient extremals may be used as reaction path models in a simple description of the dynamics of a molecular reaction.

In this paper we develop a simple and efficient algorithm to walk along gradient extremals. The algorithm uses the concept of having a trust region where the second-order Taylor expansion of the potential energy approximates well the exact potential energy surface [17]. Steps are determined inside the trust region from the second-order expansion. If the expansion has a stationary point inside the trust region with the desired index of the Hessian, then the Newton step is used to converge quadratically to this stationary point. If no stationary point with the desired Hessian structure exists inside the trust region, then the gradient-extremal point for the second-order expansion is determined on the boundary of the trust region and used as the next iteration point. The exact energy function has cubic and higher-order terms and the point that is obtained from a second-order expansion therefore gives only an approximate location of the true gradient-extremal point. However, by appropriately adjusting the size of the trust region an accurate estimate of the gradient extremal point of the exact potential energy surface can be determined to desired accuracy and a safe walk can therefore be carried out to the stationary point. We give in this paper numerical examples of walks along gradient extremals and demonstrate how the algorithm is capable of closely following gradient extremals.

2. The gradient-extremal walking algorithm

2.1. Definition of the gradient extremal

Following Hoffman et al. [14] we define gradient extremals as lines on the mass-scaled potential energy surface $E(\boldsymbol{x})$ having the property that at each point $\boldsymbol{x}_0$ the molecular gradient $\boldsymbol{g}(\boldsymbol{x}_0)$ is a minimum (an extremum) with respect to variations within the contour subspace

$$E(\boldsymbol{x}) = k = \text{constant} \tag{1}$$

passing through $\boldsymbol{x}_0$. Introducing the Lagrangian multiplier λ this condition may be expressed as

$$\partial[\boldsymbol{g}^T\boldsymbol{g} - 2\lambda(E-k)]/\partial\boldsymbol{x} = \boldsymbol{0}. \tag{2}$$

Carrying out the differentiation we obtain

$$\boldsymbol{H}(\boldsymbol{x})\boldsymbol{g}(\boldsymbol{x}) = \lambda(\boldsymbol{x})\boldsymbol{g}(\boldsymbol{x}) \tag{3}$$

where we have introduced the Hessian matrix $\boldsymbol{H}(\boldsymbol{x})$. As will become apparent later, Eq. (3) provides an extremely useful local characterization of gradient extremals. Also Eq. (3) may be given the following simple interpretation: The gradient of $|\boldsymbol{g}|^2$ (i.e. $2\boldsymbol{Hg}$) is proportional to the gradient $\boldsymbol{g}$ at $\boldsymbol{x}$. Since $\boldsymbol{g}$ is orthogonal to the contour subspace, Eq. (3) states that the gradient of $|\boldsymbol{g}|^2$ is orthogonal to the contour subspace at gradient extremals. For a more detailed discussion of the properties of gradient extremals, see Ref. [14].

The usefulness of gradient extremals is related to the fact that they are unique lines connecting stationary points on potential energy surfaces. This, coupled with the fact that they are locally characterized, makes gradient extremals potentially more useful than steepest descent directions (which are only globally characterized) for exploring potential energy surfaces and molecular dynamics.

2.2. Step size control

We will describe an algorithm that may be used to walk along a gradient extremal from one stationary point to another. The gradient extremal may bifurcate during such a walk. We defer the discussion of such cases to a later publication.

We assume that the potential energy as well as its gradient and Hessian are calculated at each iteration. Before describing how steps are determined in the algorithm, we discuss the sizes of the steps that can be taken with confidence when the gradient and Hessian are calculated explicitly.

Let us denote the geometry of the kth iteration $\boldsymbol{x}_k$, and assume that we have determined a step $\boldsymbol{\Delta x}_k$

$$\boldsymbol{x}_{k+1} = \boldsymbol{x}_k + \boldsymbol{\Delta x}_k. \tag{4}$$

The second-order Taylor expansion predicts a total energy at geometry point $\boldsymbol{x}_{k+1}$

$$E^{(2)}(\boldsymbol{x}_{k+1}) = E(\boldsymbol{x}_k) + \boldsymbol{g}^T(\boldsymbol{x}_k)\boldsymbol{\Delta x}_k + (1/2)\boldsymbol{\Delta x}_k{}^T\boldsymbol{H}(\boldsymbol{x}_k)\boldsymbol{\Delta x}_k \tag{5}$$

and the actual energy at this point is

$$E(\boldsymbol{x}_{k+1}) = E^{(2)}(\boldsymbol{x}_{k+1}) + RM, \tag{6}$$

where RM contains terms of third and higher orders in $\boldsymbol{\Delta x}_k$. As steps are determined using gradient and Hessian information, they can only be taken with confidence if $E^{(2)}(\boldsymbol{x}_{k+1})$ approximates $E(\boldsymbol{x}_{k+1})$ well. A quantitative measure of the agreement between $E^{(2)}(\boldsymbol{x}_{k+1})$ and $E(\boldsymbol{x}_{k+1})$ may be obtained from the ratio r, which compares the actual energy change $E(\boldsymbol{x}_{k+1}) - E(\boldsymbol{x}_k)$ with the energy change predicted by the second-order expansion

$$\begin{aligned} r &= [E(\boldsymbol{x}_{k+1}) - E(\boldsymbol{x}_k)]/[E^{(2)}(\boldsymbol{x}_{k+1}) - E(\boldsymbol{x}_k)] \\ &= 1 + RM/[E^{(2)}(\boldsymbol{x}_{k+1}) - E(\boldsymbol{x}_k)]. \end{aligned} \tag{7}$$

If this ratio is close to one, third-order terms are unimportant and the second-order expansion approximates the exact potential surface well. The size of the steps that can be taken in each iteration thus depends on how close r is to one. We introduce in each iteration a trust region with radius h where the second-order expansion approximates well the exact potential surface and we update in each iteration the trust radius according to the size of r. Algorithms for updating the trust radius have been described in [10, 17].

2.3. *Direction of the step*

We now describe how the step $\boldsymbol{\Delta x}_k$ in Eq. (4) is determined. Inside the trust region the gradient extremal of the second-order surface will describe accurately the gradient extremal of the exact surface. We use the gradient extremal of the second-order surface to determine the steps in the walk. We first describe how the gradient extremal is determined for a second-order surface.

On the second-order surface the following simplifications occur in the gradient-extremal Eq. (3):

$$\begin{aligned} &\boldsymbol{H}(\boldsymbol{x}) = \boldsymbol{H} \quad \text{(constant)} \\ &\lambda(\boldsymbol{x}) = \lambda \quad \text{(constant)} \\ &\boldsymbol{g}(\boldsymbol{x}) = \boldsymbol{g} + \boldsymbol{Hx} \end{aligned} \tag{8}$$

assuming that the origin is the center of expansion. Substituting Eqs. (8) in (3) we obtain

$$(\boldsymbol{H} - \lambda\boldsymbol{1})\boldsymbol{Hx} = -(\boldsymbol{H} - \lambda\boldsymbol{1})\boldsymbol{g}. \tag{9}$$

Let $\boldsymbol{v}$ be the eigenvector of $\boldsymbol{H}$ belonging to λ (i.e. the eigenvector along the reaction path):

$$(\boldsymbol{H} - \lambda\boldsymbol{1})\boldsymbol{v} = \boldsymbol{0}. \tag{10}$$

If λ is non-degenerate, then $(\boldsymbol{H}-\lambda \boldsymbol{1})$ is non-singular on the orthogonal complement to $\boldsymbol{v}$. Hence, introducing the projector

$$\boldsymbol{P}=\boldsymbol{1}-\boldsymbol{v}\boldsymbol{v}^T, \tag{11}$$

Eq. (9) may be written as

$$\boldsymbol{PHx}=-\boldsymbol{Pg}. \tag{12}$$

Since $\boldsymbol{P}$ and $\boldsymbol{H}$ commute, we obtain

$$\boldsymbol{Px}=-\boldsymbol{PH}^{-1}\boldsymbol{g} \tag{13}$$

assuming $\boldsymbol{H}$ is non-singular. The general solution of this equation is

$$\boldsymbol{x}(\alpha)=-\boldsymbol{PH}^{-1}\boldsymbol{g}+\alpha\boldsymbol{v}, \tag{14}$$

where α is an arbitrary real parameter. $\boldsymbol{x}(\alpha)$, the gradient extremal for the second-order surface, defines a straight line which is parallel to the eigenvector $\boldsymbol{v}$ and which passes through the solution of the projected Newton equation $-\boldsymbol{PH}^{-1}\boldsymbol{g}$.

We return to the problem of determining the step $\boldsymbol{\Delta x}_k$ in the gradient-extremal walking algorithm. We recall that the step must either be inside or on the boundary of the trust region and that it also must be on the gradient extremal given by Eq. (14). To decide which point to choose we first examine if the stationary point of the second-order expansion is inside the trust region and if the Hessian has the desired number of negative eigenvalues. If this is the case then the stationary point of the second-order surface (the Newton step) is used as the next iteration point x_{k+1}. If the stationary point of the second-order surface is outside the trust region or if the Hessian does not have the desired index, then the gradient-extremal point on the boundary becomes the next iteration point. The gradient-extremal point on the boundary is determined by varying α in Eq. (14) to obtain a step length equal to the current trust radius h.

It may happen that the gradient extremal of the second-order surface does not pass through the trust region. To move back toward the gradient extremal we then take a step of length h in the orthogonal complement direction of the gradient extremal using the first term in Eq. (14). A better solution may be to reject the step that resulted in the iteration point far from the gradient extremal, go back to the previous iteration point, and calculate a new step using a reduced trust radius h.

To clarify how a walk is carried out we describe a typical walk which begins at an equilibrium geometry and follows the gradient extremal leaving the stationary point in eigendirection $\boldsymbol{v}$. As the gradient is zero at the equilibrium geometry the first step is of length h_1 (default value) in the $\boldsymbol{v}$ direction. At iteration point 2 the trust radius is updated, the Hessian is diagonalized, and the eigenvector of the Hessian that has the largest projection onto $\boldsymbol{v}$ (close to one) is identified and used to define the gradient extremal for the second-order Taylor expansion. The gradient-extremal point on the boundary of the trust region is then determined and the iterative procedure is continued. At some stage of the walk the stationary point of the second-order expansion will be inside the trust region and this point can then be used as the next iteration point. In the following iterations a sequence of Newton steps is taken to converge quadratically to the stationary point. The walk may also be abandoned if the gradient extremal leads to a potential energy above a preset energy threshold so that the stationary point will have too high energy to be of interest.

3. Numerical results

To illustrate the described algorithm we have investigated the mechanism for exchange of protons on carbon in methylenimine ($H_2C{=}NH$) in order to establish whether this occurs by rotation around the C=N bond or by planar inversion at the nitrogen atom.

From previous theoretical studies it is known that the equilibrium structure for methylenimine is planar. The proton exchange mechanism has been studied by Lehn and Munsch [18] and Pople et al. [19] at the Hartree-Fock level. (Pople et al. have also carried out Møller-Plesset calculations, but only at stationary points obtained from Hartree-Fock calculations.) These authors have concluded that the isomerization occurs by inversion rather than rotation, and that the transition state has C_{2v} symmetry.

We have previously found that closed-shell Hartree-Fock gives a qualitatively wrong description of the cis-trans isomerization mechanism in diazene (HN=NH) [20]. Using a complete-active-space self-consistent-field (CASSCF) wave function we established that the diazene isomerization proceeds both by planar inversion at nitrogen and by rotation around the N=N bond. Conversely, at the closed-shell SCF level only the planar transition state exists. We therefore concluded that it is necessary to investigate the isomerization mechanism of methylenimine using a multi-reference rather than a closed-shell SCF wave function.

The wave function was constructed by distributing four electrons among four orbitals (the σ and π bonding and antibonding CN orbitals). We used Tatewaki's (421/21) basis set on carbon and nitrogen augmented with a set of d functions (exponents 0.600 and 0.864, respectively) [21]. On hydrogen we used Dunning's $2s$ contraction [22] of Huzinaga's $4s$ basis [23] with a set of p functions added (exponent 1.000). The calculations were performed using the SIRIUS/ABACUS program system [24-26]. During the walks the translational and rotational coordinates were projected out of the molecular Hessian as described in [13].

The optimized equilibrium geometry is depicted in Fig. 1. The calculated energy and dipole moment are −93.943384 Hartree and 1.95 Debye, respectively. There is no experimentally determined structure for methylenimine, but our results are in reasonable agreement with the empirical geometry suggested by Botschwina [27]. The largest difference is the NH bond length, which is 0.016 Å shorter than that of Botschwina.

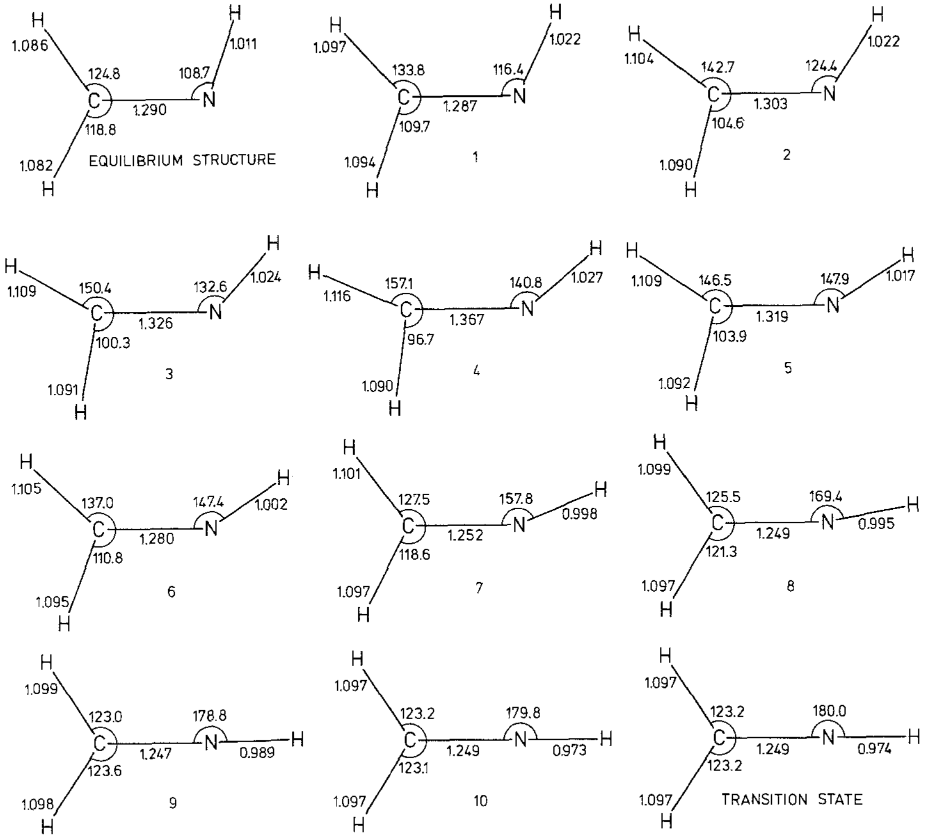

Fig. 1. Geometries of methylenimine in walk from equilibrium to transition state

Table 1. Calculated harmonic vibrational frequencies (cm^{-1}) and double-harmonic infrared intensities (km/mol) for methylenimine

Equilibrium (C_s)				Transition state (C_{2v})		
Sym.	Freq.	Intens.	Mode	Sym.	Freq.	Mode
A'	3648	7.8	NH str	A_1	4188	NH str
	3301	43	asym CH_2 str		3066	sym CH_2 str
	3204	36	sym CH_2 str		1760	CN str+sym CH_2 def
	1701	4.5	CN str+sym CH_2 def		1648	sym CH_2 def+CN str
	1511	0.3	sym CH_2 def+CN str	B_2	3099	asym CH_2 str
	1493	59	CNH bend+CH_2 rock		1292	CH_2 rock
	1122	28	CH_2 rock+CNH bend		1472 *i*	in-plane CNH bend
A''	1235	42	torsion	B_1	1133	CH_2 wag
	1091	16	CH_2 wag		638	out-of-plane CNH bend

The calculated harmonic frequencies are reported in Table 1. Our NH stretching frequency (3648 cm^{-1}) is significantly higher than that determined by Botschwina [27] (3386 cm^{-1}). The frequencies of Botschwina are in fair agreement with experiment. A better NH stretching frequency and bond length would be obtained by explicitly correlating the NH bond.

The planar transition state was investigated by walking along the lowest eigenmode of A' symmetry (1122 cm^{-1} at equilibrium). Using mass-weighted Cartesian coordinates, the transition state was reached after eleven iterations (see Fig. 1 and Table 2). The transition-state energy is −93.880729 Hartree. The CN and NH bonds are both significantly shorter at the transition state, while the NH stretching frequency is significantly higher. The torsional frequency at equilibrium (1235 cm^{-1}) correlates with the NH out-of-plane linear bend at the transition state (638 cm^{-1}), while the NH in-plane linear bend (1472i cm^{-1}) corresponds to the reaction coordinate.

The predicted energy barrier for the isomerization is 155.6 kJ/mol (vibrational zero-point harmonic correction included), which is considerably higher than the barriers obtained by Lehn and Munsch [18] (116.7 kJ/mol) and Pople et al. [19] (127.6 kJ/mol).

From Table 2 we see that the walk traces the valley closely except in iterations 4 and 5, and in the last three iterations where Newton steps are taken on the gradient extremal. In the region of iterations 4 and 5 the reaction mode changes character: whereas in the first four iterations stretching of the CN bond and rocking of the CH_2 group occur, in the remaining iterations the CN bond shrinks and the CH_2 group returns to a symmetrical configuration (see Fig. 1).

It is clear that in iterations 4 and 5 the walk passes through a difficult region. In particular, the step determined in iteration 3 appears too large, so that the CN bond becomes too extended and the energy too high (in fact, higher than the transition-state energy). The algorithm may be modified to handle such situations more efficiently. The present implementation is designed to backstep only when the ratio between the predicted and actual energies is unacceptable. A more flexible algorithm may backstep and adjust the trust region based on additional criteria. Firstly, the overlap between the Hessian reaction eigenvectors of the previous and current iterations should always be larger than some preset value (for example 0.90) to ensure that the reaction mode is correctly identified. Secondly, the energy increase from one iteration to another may possibly also be required to be less than some preset value (perhaps based on the expected energy change in the reaction). Finally, in each iteration the ratio between the orthogonal and parallel components of the gradient should always be less than some preset value (for example 0.25) to ensure that the walk traces the valley closely.

To investigate the presence of an out-of-plane transition state we carried out walks along each of the two A'' eigenmodes. Both walks resulted in a stretching of the CN bond and the appearance of one negative eigenvalue associated with this stretching, indicating that the molecule dissociates. We therefore conclude

Table 2. Hessian, gradient, energy, and step size for each iteration in walk from equilibrium to transition-state configuration of methylenimine[a]

	Equil.	1	2	3	4[b]	5[b]	6	7	8	9[c]	10[c]	Transition state
Hessian eigenvalues	0.045	0.047	0.045	0.044	0.037	0.017	0.007	−0.025	−0.055	−0.072	−0.083	− 0.082
	0.048	0.048	0.046	0.044	0.039	0.041	0.040	0.034	0.028	0.023	0.015	0.015
	0.058	0.061	0.059	0.053	0.040	0.049	0.050	0.050	0.049	0.049	0.049	0.049
	0.084	0.078	0.067	0.056	0.052	0.049	0.057	0.062	0.063	0.063	0.063	0.063
	0.086	0.090	0.087	0.080	0.068	0.080	0.094	0.101	0.102	0.103	0.103	0.103
	0.110	0.109	0.108	0.109	0.111	0.109	0.110	0.117	0.117	0.118	0.117	0.117
	0.389	0.365	0.357	0.347	0.335	0.343	0.348	0.350	0.353	0.353	0.356	0.356
	0.412	0.384	0.383	0.377	0.377	0.374	0.370	0.364	0.362	0.360	0.363	0.363
	0.504	0.468	0.468	0.462	0.452	0.484	0.539	0.560	0.577	0.605	0.666	0.664
Gradient[d]	0.000	0.000	0.041	0.058	0.037	0.042	0.045	0.040	0.023	0.003	0.000	0.000
	0.000	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.063	0.047	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.001	0.000	0.000	0.001	0.021	0.002	0.002	0.000	0.000	0.000
	0.000	0.006	0.005	0.007	0.017	0.001	0.002	0.001	0.001	0.000	0.000	0.000
	0.000	0.002	0.002	0.003	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.010	0.009	0.008	0.008	0.006	0.007	0.004	0.001	0.001	0.000	0.000
	0.000	0.002	0.002	0.003	0.004	0.002	0.002	0.001	0.000	0.000	0.000	0.000
	0.000	0.011	0.012	0.013	0.014	0.016	0.008	0.016	0.021	0.017	0.001	0.000
Energy[e]	0.0	15.8	52.8	109.2	184.9	146.4	105.3	127.3	156.0	165.0	164.5	164.5
Step size[f]	0.50	0.46	0.44	0.45	0.48	0.43	0.46	0.34	0.34	0.05	0.00	—
	0.00	0.08	0.07	0.10	0.48	0.43	0.37	0.05	0.05	—	—	—

[a] Hessian, gradient, and step size in mass-weighted atomic units. Energy in kJ/mol

[b] Step orthogonal to gradient extremal

[c] Newton step

[d] Absolute values of components of gradient in diagonal representation

[e] Energy relative to equilibrium configuration

[f] First row: total step. Second row: component of step orthogonal to gradient extremal

that the CN σ bond is not sufficiently strong to keep methylenimine from dissociating when the π orbital is broken. Thus methylenimine behaves differently from diazene, which does not dissociate when the N=N bond is twisted.

For comparison we carried out the same calculations at the closed-shell SCF level. These calculations gave similar equilibrium and transition-state geometries (the main difference being a significantly shorter CN bond length at the SCF level). However, the SCF potential surface is qualitatively incorrect for non-planar geometries since the CN bond does not dissociate when twisted. Instead, there exists a non-planar saddle point of C_{2v} symmetry with two directions of negative curvature (rotation around the CN bond and CNH bending). A walk initiated along the rotational eigenmode of the equilibrium geometry passed through this region after ten iterations and then proceeded along the CNH bending mode until it finally arrived at the planar transition state described above.

4. Discussion

The stream beds connecting equilibrium geometries and transition states have recently been rigorously defined by Hoffman et al. [14] as the locus of points in the contour subspace where the gradient is extremal. As an implication the stream beds or gradient extremals become locally characterized by the requirement that the molecular gradient is an eigenvector of the (mass-scaled) molecular Hessian at each point on the gradient extremal. This local characterization of stream beds has been used to develop a walking algorithm which follows the gradient extremals from equilibrium structures to transition states. We assume that the molecular gradient and Hessian are calculated at each iteration point, and we define at each iteration a trust region inside which the second-order expansion of the potential energy is a good approximation to the exact surface. Steps may only be taken inside or on the boundary of the trust region. The actual direction and size of the steps are determined by locating the gradient extremal for the second-order Taylor expansion. If the gradient extremal for this expansion contains a stationary point with the desired Hessian index inside the trust region, then the Newton step is taken to converge to this point. If no stationary point with the desired Hessian index exists inside the trust region, then the crossing between the gradient extremal of the second-order expansion and the boundary of the trust region is used to determine the step of the walking algorithm. By appropriately adjusting the size of the trust region we can trace the gradient extremal of the exact potential surface to desired accuracy. Our numerical experience has shown that the algorithm determines transition states efficiently if the gradient extremal does not bifurcate. The complications which occur when bifurcations occur will be discussed in a future publication.

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