J Math Chem (2011) 49:1915–1927
DOI 10.1007/s10910-011-9864-x

ORIGINAL PAPER

Newton trajectories for finding stationary points on molecular potential energy surfaces

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Received: 27 April 2011 / Accepted: 4 June 2011 / Published online: 16 June 2011

Abstract We present a new algorithm for computing Newton trajectories based on the Quadratic String Method (QSM) and explain how this can be used to find key stationary points on the molecular potential energy surface (PES). This method starts by using the intersections of Newton trajectories to locate stationary points on the PES. These points could then be used to determine the minimum energy path. The new method, called QSM-NT, is shown to be efficient and reliable for both analytical potential energy surfaces and potential energy surfaces computed from quantum chemistry calculations. The advantages and pitfalls of this method for exploring PES are discussed. In particular, the problem of discontinuous Newton trajectories is elucidated.

Keywords Newton trajectory · Quadratic string method · Stationary points · Minimum energy path

1 Introduction

Finding a reaction path that connects the reactant to the product via transition states and key intermediates on the molecular potential energy surface (PES) is the key to obtaining both quantitative data and qualitative understanding of chemical reaction mechanisms. From the molecular structures along the path, the qualitative features (e.g., the sequence in which bonds fracture and form) of the chemical reaction are clear. From the energy of the transition state and the relative energies of the reactants

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and products, key quantitative information about chemical kinetics and equilibria may be computed. It is unsurprising, then, that computational chemists continue to devise novel algorithms for finding chemical reaction paths [1]. This paper is yet another contribution along these lines.

The distinguishing feature of this work is the focus on stationary points of the PES. Most of these methods focus on low-energy regions of the PES or directions on the PES with small force constants (large compliance). Chemically, however, the most important portions of PESs are the places where the gradient is zero: such stationary points are associated with reactants, products, intermediates, and transition states. Newton trajectories intersect at these locations, with the "density" of Newton trajectories being highest where the gradient of the potential energy is the smallest [2–4]. Using Newton trajectories to explore PESs, then, biases the search towards the most chemically relevant portions of the surface. This motivates the approach in this paper, where the quadratic string method [5] is used to compute Newton trajectories and the intersection of Newton trajectories is used to identify stationary points.

2 Background

2.1 Methods for finding the minimum energy path (MEP)

Most work on finding chemical reaction paths has focussed on the minimum energy path (MEP). The MEP is typically obtained by taking the union of the steepest-descent paths from the transition state structure(s) to the reactant and product (and intermediate) structures. With rare exceptions, the "intrinsic reaction coordinate" so defined is equal to the MEP [6].

There are generally two families of algorithms for finding the MEP: the surface-walking algorithms ("initial value" formulations; [7–15]) and the two-end algorithms ("boundary value" formulations; [5,16–30]). The two end methods require a good guess for the path linking the reactant and the product; otherwise a local MEP instead of the global MEP will be found. The surface-walking methods only need the reactant configuration, and then predict the products and the mechanism. Some surface-walking methods, like the fast marching method [8,9,12,31–35], guarantee that the global MEP will be found. Unfortunately, surface-walking algorithms usually are either very expensive or, if a heuristic is used to simplify the construction, they tend to be unreliable [24] for complicated systems. The two-end methods have great advantages in terms of computation costs and numerical stability.

The most efficient two-end methods include the string method (SM; [17,23]) and some improved string methods, such as the quadratic string method (QSM; [5]) and the growing string method (GSM; [24,36,37]). The string method divides the initial path into a certain number of nodes, then drives the nodes towards the MEP by a normal force along the corresponding hypersurface orthogonal to the path tangent at the node, reparameterizing the approximate path so that the nodes will be spaced evenly along the path. The quadratic string method uses the local quadratic approximation for the hypersurfaces to reduce the number of calculations on the potential and gradient, which makes it more efficient and affordable for larger systems. Conceptually, string methods can be imagined as what would occur if one draped a pearl necklace over the PES; the pearls (nodes) would slip towards lower potential energy, but remain evenly spaced between reactant and product.

2.2 The Newton trajectory (NT)

While the MEP is almost universally used to represent the reaction path, an alternative reaction path called the Newton trajectory (NT) has been proposed and explored by Quapp and coworkers [2–4,36–48]. They argue that the reaction path can be considered to be any curve that connects reactant to the product through the saddle point as long as the highest-energy point on the curve corresponds to the saddle point. The basic idea is that while the molecular structures of stationary points on the PES have chemical significance, intermediate structures are of superficial significance. (This contrasts somewhat with the common assertion that the MEP serves as a "leading line" about which reactive molecular dynamics trajectories are centered when the energy barrier is much higher than kT [49].)

A Newton trajectory is defined as a curve on which all gradients are pointing in the same (or opposite) direction. Each NT passes through all stationary points on the PES because when the magnitude of the gradient is zero, its direction is arbitrary. By the preceding argument, any NT that connects the reactant to the product through the transition state can be chosen as a reaction path. Notice that some NTs that can mimic these reaction paths, but have maxima that correspond to turning points in the trajectory, rather than stationary points on the PES [50]. The growing string method (GSM) is commonly used to find an appropriate NT [36,37,45]. Because only NTs without spurious turning points are acceptable reaction paths, it can be difficult to choose a gradient direction that defines an appropriate NT. Without prior knowledge of the PES, the fact that candidate NT-based reaction paths might have turning points means that each local maximum on a NT must be assessed to see if it is actually a saddle point.

In this paper we propose a new way to find the stationary points on the PES using NTs that avoids the "turning point problem" associated with the GSM-NT method. Specifically, since a complete NT passes all stationary points on the PES, the intersections of two NTs locate all the stationary points on a PES. We also provide a variant of QSM to find NTs; this reduces the computational cost of this approach significantly. To test our methods, we consider analytical PESs. With their validity established, we interfaced our approach to the *Gaussian* program and characterized an S_N2 reaction.

The primary advantage of this approach over more conventional approaches is that no prior knowledge of the PES is required and the computational effort is concentrated in regions of the PES where the NTs are close together—that is, the chemically important regions associated with stationary points. Unlike the fast marching method and most other "surface walking" approaches, all possible transition states, and therefore all possible reaction pathways, are found. This is particularly important where there are several competing reaction mechanisms.

3 Mathematical definitions and algorithms

3.1 Quadratic string method (QSM)

The Minimum Energy Path (MEP) is defined as the steepest-descent path (SDP) from the transition states (1st order saddle points) to their adjacent minima. The SDP, $\mathbf{x}(t)$, can be obtained by solving the following differential equation,

$$\frac{d\mathbf{x}(t)}{dt} = -\mathbf{g} = -\nabla V\left(\mathbf{x}(t)\right), \tag{1}$$

which indicates that the tangent of the SDP is always directed against the gradient of the potential $\mathbf{g} \equiv \nabla V\left(\mathbf{x}(t)\right)$.

To simplify the equations, we introduce the projection operators proposed by Quapp [40]. For a unit vector $\hat{\mathbf{u}}$, the dyadic product, $\mathbf{D}_{\hat{\mathbf{u}}} = \hat{\mathbf{u}}\hat{\mathbf{u}}^T$ projects a vector in the direction defined by $\hat{\mathbf{u}}$. The projection operator $\mathbf{P}_{\hat{\mathbf{u}}} = \mathbf{I} - \mathbf{D}_{\hat{\mathbf{u}}}$, projects a vector into the hyperplane perpendicular to $\hat{\mathbf{u}}$.

Parameterize the path $\mathbf{x}(t)$ by the arc length s. Then $d\mathbf{x}(t)/ds$ is the normalized tangent of the path. We denote the normalized tangent of the path as $\hat{\mathbf{o}}(\mathbf{x})$. Then, from Eq. (1),

$$\hat{\mathbf{o}}\left(\mathbf{x}\right) = -\frac{\mathbf{g}}{\|\mathbf{g}\|}. \tag{2}$$

For a point on the steepest descent path, the gradient and $\hat{\mathbf{o}}$ are both tangent to the SDP, so $\mathbf{P}_{\hat{\mathbf{o}}}\mathbf{g} = \mathbf{0}$. Away from the optimal path, however, there is an component of the gradient in the hyperplane orthogonal to the SDP,

$$\mathbf{g}_{\perp} = \mathbf{P}_{\hat{\mathbf{o}}}\mathbf{g}. \tag{3}$$

Minimizing $\|\mathbf{g}_{\perp}\|$ leads to the SDP; this transforms the differential equation in Eq. (1) into a minimization problem. String methods work by solving the minimization problem.

The basic string-method algorithm is:

1. An initial guess of the reaction path is given.
2. The initial path is discretized as several nodes.
3. The energies and gradients of all nodes are evaluated.
4. For each node, i, on the path,
   a. The tangent to the guessed reaction path, $\hat{\mathbf{o}}_i$ is calculated.
   b. The orthogonal projection is performed, giving $\mathbf{g}_{\perp,i} = \mathbf{P}_{\hat{\mathbf{o}}_i}\mathbf{g}_i$.
   c. Search in the direction $\mathbf{d}_i = -\mathbf{g}_{\perp,i}$ to minimize the value of $\left\|\mathbf{g}_{\perp,i}\right\|$ on the hyperplane orthogonal to the guessed path. This defines the updated position for node i.
5. If necessary, the nodes are redistributed so that they are relatively evenly spaced along the path.

6. If $\left\|\mathbf{g}_{\perp,i}\right\|$ is sufficiently small at each node, then a sufficiently accurate approximation to the SDP has been found. Otherwise, return to step 3.

The quadratic string method (QSM) uses the same algorithmic structure as the string method [5]. The primary difference is that instead of minimizing the projection of the gradient on the hyperplane perpendicular to the path (step 4c), the minimization occurs on a quadratic hypersurface that is tangent to the hyperplane,

$$\boldsymbol{d}_i(\mathbf{x}) = -\mathbf{P}_{\hat{\mathbf{o}}_i}(\mathbf{g}_i^0 + \mathbf{H}_i(\mathbf{x} - \mathbf{x}_i^0)) \tag{4}$$

The hypersurface is obtained using a quasi-Newton Hessian constructed from a variable step-size Runge-Kutta method. For further details, see ref. [5]. The QSM converges superlinearly and requires fewer energy/gradient calculations than simple string methods.

3.2 Newton trajectories (NTs)

A NT follows a curve on which the gradients point to the same (or opposite) direction. This direction is called the searching direction of the NT. For a given searching direction $\hat{\mathbf{u}}$, the corresponding NT can be formulated as a minimization problem: minimize $\|\mathbf{g}_\perp\|$, where

$$\mathbf{g}_\perp = \mathbf{P}_{\hat{\mathbf{u}}}\mathbf{g}. \tag{5}$$

This problem is mathematically similar to finding the SDP; the only change is that now we minimize on a hyperplane (or hypersurface) that is orthogonal to the searching direction $\hat{\mathbf{u}}$, rather than to the tangent vector of the guessed SDP, $\hat{\mathbf{u}}_i$. Notice that $\hat{\mathbf{u}}$ does not change along the reaction path; in this sense finding NTs is even simpler than finding the SDP.

It is easy to modify the QSM algorithm to find NTs; one merely fixes the searching direction, replacing $\mathbf{P}_{\hat{\mathbf{u}}_i}$ with $\mathbf{P}_{\hat{\mathbf{u}}}$ in step 4 and in Eq. (4). We call this algorithm QSM-NT. The resulting method has some similarities to the sequential quadratic programming method (SQPM; [30]), both mathematically and conceptually. At the conceptual level, both QSM-NT and SQPM are designed to concentrate points in the vicinity of the transition states. In addition, both methods are based on the idea that it is less important to have the full minimum energy path (as constructed by conventional QSM) and more important to quickly, accurately, and reliably locate the stationary points on the reaction pathway.

The NTs from all possible search directions intersect at each stationary point on the PES. The next step in the procedure is to choose two different search directions and then compute the associated NTs. These NTs intersect at stationary points (minima, maxima, and saddle points) on the PES. An NT is said to be complete if it passes through every stationary point on the PES. Unfortunately, not all NTs are complete; some NTs are discontinuous. Most path-finding methods, including QSM, only find part of the NT in the discontinuous case. In such cases, not every stationary point is found. As an initial guess for the path in QSM, we usually use the straight line linking the reactant and product. This setup does not guarantee the exploration of all stationary points, but it maximizes the possibility of finding all the stationary points in the "interesting" area of the PES that is positioned between the reactant and the product.

4 Applications

The QSM-NT method has been applied to the analytical PESs: the 4-well potential, the Müller–Brown potential; and a simple 1-step chemical reaction: the S_N2 reaction. For each PES, two NTs with different searching directions were found and plotted on the PES. We can clearly see that the intersections of the two NTs coincide with the reactive intermediate(s) and transition states (Figs. 1, 2, 3).

4.1 Müller–Brown PES

To apply the QSM-NT method, we need to use two searching directions. The first searching direction, shown as the black path in Figure 1, is the vector linking the two ends of the path: [−0.8, 1.0]. The gradient of the potential at each node in the QSM algorithm points either towards [−0.8, 1.0] or in the opposite direction [0.8, −1.0]. For the second searching direction, shown as the red path in Figure 1, we

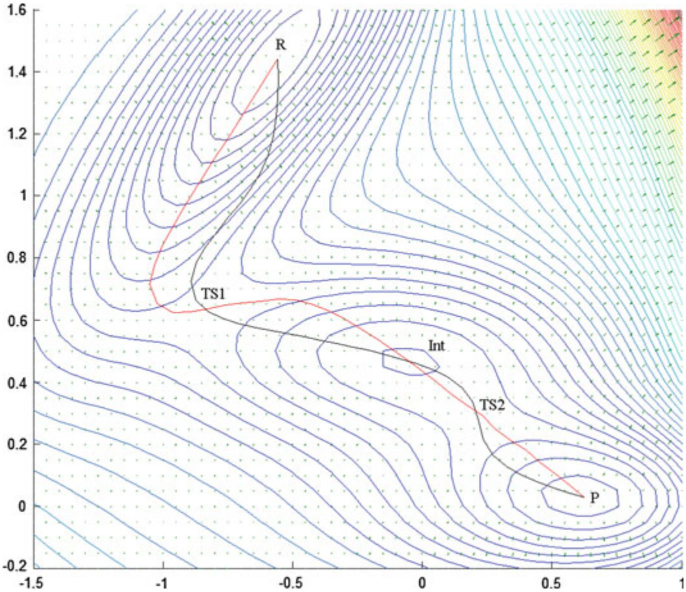


Fig. 1 Newton trajectories on the Müller–Brown potential. The gradient directions of the two Newton trajectories are: *black* [−0.8, 1.0] and *red* [−0.2, 1.0], respectively. The arrows represent the directions of the gradients on the grids of the PES, which are orthogonal to the contours. The intersections of these two NTs accurately show the stationary points (the intermediate and the transition states) linking the reactant and the product (Color figure online)

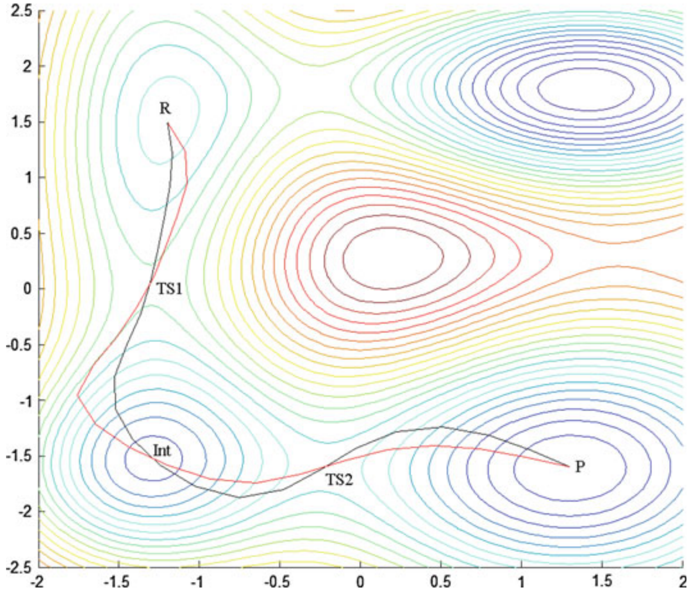


Fig. 2 Newton trajectories on the 4-well potential. The gradient directions of the two NTs are: *black*: [1.1, 1.0]; *red*: [1.9, 1.0]. The intersections of the two NTs clearly show the stationary points (transition states and intermediate) linking the reactant and the product structures (Color figure online)

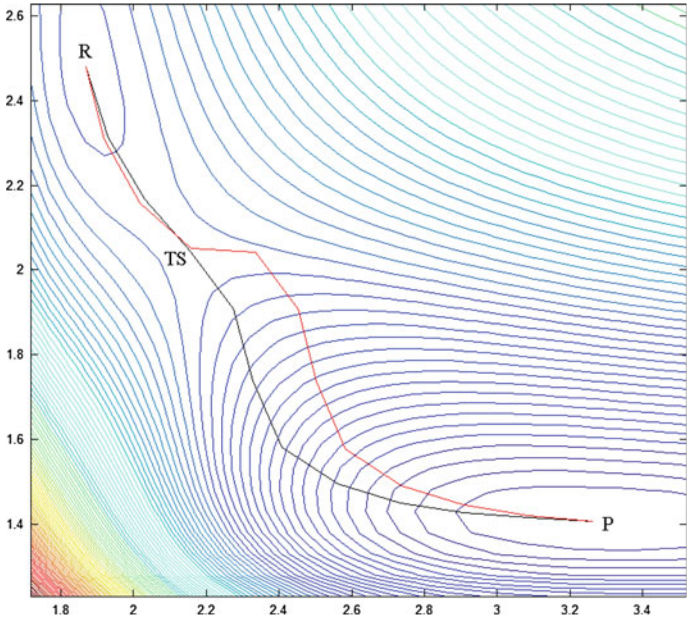


Fig. 3 Newton trajectories for the S_N2 reaction. The gradients of the two NTs are: *black*: [−1.3, 1.0]; *red*: [−0.4, 1.0]. The NTs cross at the transition state (TS) linking the reactant and the product (Color figure online)

chose [−0.2, 1.0]. These two NTs cross at 5 points: the reactant (R), transition state 1 (TS1), intermediate (Int), transition state 2 (TS2) and the product (P).

The form of the Müller-Brown PES is given in Appendix 1 [51].

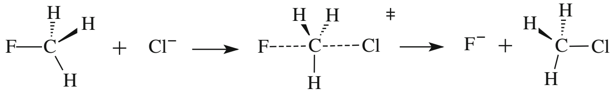
4.2 The 4-well PES

The 4-well PES is used to explore the case where there are two low-energy pathways between the reactant and the product structure; results are shown in Figure 2. The searching for the black path is the vector linking the two ends of the path: [1.1, 1.0]. The searching direction of the red path is [1.9, 1.0]. These two NTs cross at 5 points: the reactant (R), transition state 1 (TS1), intermediate (Int), transition state 2 (TS2) and the product (P).

The form of the 4-well PES is given in Appendix 2 [31].

4.3 The S_N2 reaction

Encouraged by the favourable results for the aforementioned analytical PES, we built an interface between the QSM-NT program and *Gaussian 03* [52]. We then tested the method on the following gas-phase S_N2 reaction,



(6)

All potential energy and derivative calculations are done using the BhandhLYP/6-311++G** level of theory [53,54]. For transition states, the larger amount of exact exchange in the Bhandh exchange functional, compared to the conventional hybrid functionals, is usually preferred.

We focused on the lengths of the C–F and C–Cl bonds that are formed/broken in the reaction. For each choice of these bond lengths, all of the other internal coordinates are minimized, so the only nonzero components of the gradient are in these directions. This corresponds to choosing searching directions of the form $[R_{\mathrm{C-F}}, R_{\mathrm{C-Cl}}, 0, 0, 0, \ldots 0]$. For simplicity, the zero-gradient directions will not be shown in what follows.

The searching direction of the first NT (the black path in Fig. 3) is [1.3, 1.0], the vector linking the reactant and the product. The searching direction of the red NT is [0.4, 1.0]. (The second direction was chosen to resemble the first one, because search directions that are less similar can lead problems with discontinuous trajectories.) As expected, the two NTs cross at the transition state (Fig. 3). Even without any previous knowledge about the PES of the S_N2 reaction, the transition state can still be located by finding the crossing point of two NTs.

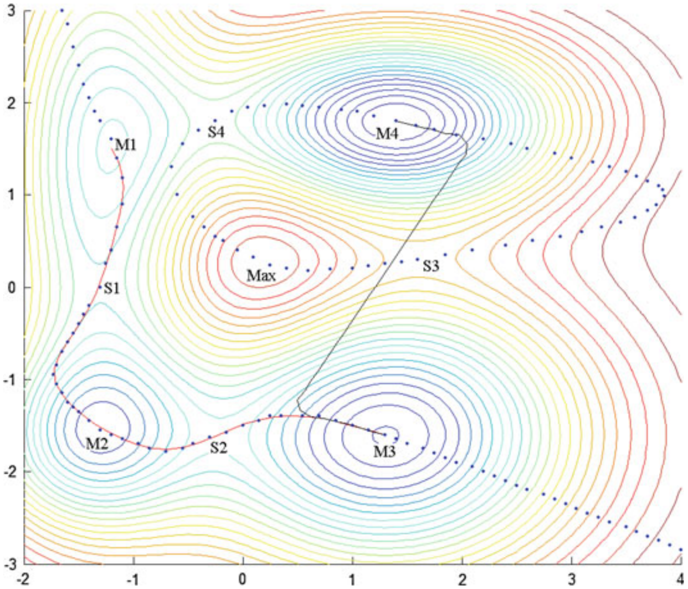


Fig. 4 The *dotted curves* denote the discontinuous Newton trajectory on the 4-well PES found using Matlab 7.0.1; the searching direction of this NT is [−1.75, 1.0]. The *solid curves* correspond to the same searching direction, but the NT was found using QSM, choosing the endpoints as either M1 and M3 (the *red curve*) or M3 and M4 (the *black curve*). Since the NT with this searching direction is discontinuous, the QSM-NT method does not converge in the latter case (Color figure online)

5 Difficulties

In favourable cases, the QSM-NT method converges to a NT that passes through all the stationary points of interest. The intersection points of two such NTs locates all the stationary points on the PES, and from that point more conventional tools for analyzing PES suffice. In some cases, however, the QSM-NT method fails.

5.1 Discontinuous trajectories

For some searching direction, the NT is composed of two or more branches; such NTs are said to be discontinuous. For example the NT in Fig. 4 (searching direction [−1.75, 1.0]) is composed of two branches: branch 1 crosses three minima (M1, M2, M3) and two saddle points (S1, S2); branch 2 is a closed curve that crosses one minimum (M4), the maximum (Max), and two saddle points (S3, S4).

A two-end path-finding method like QSM finds only branch 1 if M1 and M3 are fixed as the reactant and the product structures. If one attempts to explore both branches at the same time by setting the endpoints to M3 and M4, then the QSM calculation never converges because there is no continuous path that meets those boundary conditions. The result of the (nonconverging) QSM calculation is shown in Figure 4: it traces small portions of the lower branch of the NT and then jumps, as discontinuously as it can given the algorithmic constraints of the QSM method, to the upper branch of the NT. The stationary points for the 4-well potential could be located (cf. Figure 2) only by choosing the second searching direction to be close to the first one, so that the two NTs branched in a similar fashion. The alternative MEP, corresponding to the reaction mechanism M1-S4-M4-S3-M3, can be located, but requires looking for NTs with very different directions, like [2.0,1.0]. Such NTs intersect the NTs in Fig. 2 only at the reactant and product structures. If one wished to find a path from M2 to M4, then one would need to adjust the searching direction. Moreover, it is likely that only one of the two possible MEPs can be found: either M2-S1-M1-S4-M4 or M2-S2-M3-S3-M4.

A singular NT passes and branches on the valley ridge inflection point on the PES [55]. so a valley ridge inflection point might be confused with intersections of two NTs. But different branches of one NT and different NTs can be easily distinguished by examining the searching directions. Thus there is no danger of confusing valley ridge inflection points with stationary points on the PES. However, because of discontinuous trajectories, in order to find all the stationary points on a PES, one must vary not only the searching directions for the NTs, but consider several different choices for the path endpoints.

5.2 Multiple minima of $\|\mathbf{g}_{\perp}\|$ on the hypersurface

Recall, from section 3, that the NT is found by minimizing $\|\mathbf{g}_{\perp}\|$ on the hypersurface orthogonal to the searching direction. When the hypersurface is tangent to a contour line of the potential, the gradient $\mathbf{g}$ is orthogonal to the hypersurface and $\|\mathbf{g}_{\perp}\| = 0$.

In some cases, the hypersurface coincides with the tangent of potential contours from two potential wells. An example for the Müller-Brown potential is shown in Figure 5. When the searching direction is [0.0, 1.0] (vertical), the hypersurfaces are horizontal (the blue and yellow lines in Fig. 5). Hypersurfaces between the two yellow lines are tangent to contour-lines of the PES in two places, so there are two places where $\|\mathbf{g}_{\perp}\| = 0$ on these hypersurfaces. Two-end path finding method like QSM can only find the minimum closest to the initial path, which leads to an incorrect path (black solid line in Fig. 5).

While the problem of discontinuous NTs is inherent in the definition of the NT, the problems we encounter when $\|\mathbf{g}_{\perp}\|$ has multiple minima on the hypersurface orthogonal to the searching direction is a consequence of using a two-end algorithm to find the NT. Solving the differential equation directly avoids this problem. Using a growing string algorithm, with one free end, also solves this problem.

6 Conclusion

The QSM-NT method is a promising method for finding all stationary points on the PES, accordingly all alternative reaction paths linking the reactant and the product. Unlike two-end methods (which only find a single local minimum energy path) or the fast-marching method (which only finds the global minimum energy path), the basic approach pursued here can, in principle, find all possible reaction pathways. One of the most appealing features of this approach is that the density of the NTs is highest

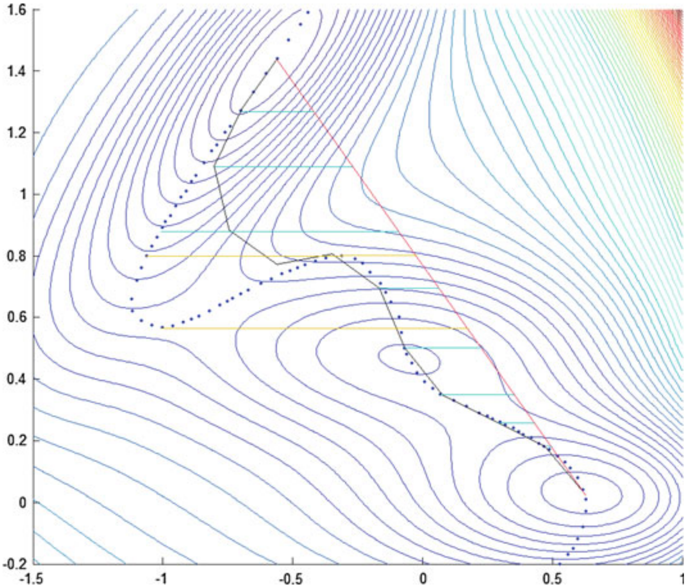


Fig. 5 A case where QSM-NT method fails to find the correct Newton trajectory. The searching direction is [0.0, 1.0]. The *dotted path* is the complete NT found by Matlab7.0.1. The *black solid line* is the trajectory found using the modified QSM program. The *red straight line* is the initial path. The *light blue lines* show the hypersurfaces orthogonal to the searching direction, which is also the moving direction of the nodes during minimization (Color figure online)

near the stationary points on the PES: the computational effort therefore concentrated in the most chemically interesting regions of the PES.

In our QSM-NT method, a modified version of the QSM program is used to find NTs for two different searching directions. The intersections between these NTs are stationary points on the PES. While the method does not always work (see Sect. 5), when it does work, it is computationally efficient. The main problem is that of discontinuous, or incomplete, Newton trajectories. Because not every NT is complete, finding all the stationary points on the PES requires, in general, not only considering several different searching directions, but also several different choices for the path endpoints.

The computational cost of the QSM-NT method is nearly twice of QSM, or more, if more than two NTs are required to locate all the stationary points than are needed to characterize a chemical process. Like other two-end methods, however, conventional QSM can find only the closest local MEP to the initial path, and cannot find the global MEP or other alternative paths. However, with proper setup and followed by further analysis, the QSM-NT method can find all stationary points on the PES, and therefore all reaction paths; this can reveal alternative reaction mechanisms.

Acknowledgments The authors thank the chemistry department of McMaster University, the Mutual Group and Sherman graduate scholarships of McMaster University, NSERC, SHARCNET, and the Canada Research Chairs for research support.

Appendix 1. The Müller-Brown Potential

The Müller–Brown PES is defined by the following function [51],

$$V(x,y)=\sum_{i=1}^{4} d(i)\cdot \exp\Big[a(i)(x-x_0(i))^2+b(i)(x-x_0(i))(y-y_0(i)) + c(i)(y-y_0(i))^2\Big] \tag{7}$$

i	1	2	3	4
$a(i)$(Å)	−1.0	−1.0	−6.5	0.7
$b(i)$(Å)	0.0	0.0	11.0	0.6
$c(i)$(Å)	−10.0	−10.0	−6.5	0.7
$x_0(i)$(Å)	1.0	0.0	−0.5	−1.0
$y_0(i)$	0.0	0.5	1.5	1.0
$d(i)$(kcal/mol)	−200.0	−100.0	−170.0	15.0

Appendix 2. The 4-well Potential

The 4-well PES is defined by the following function [31],

$$V(x,y)=V_0+\sum_{i=0}^{4} d(i)e^{-a(i)(x-x_0(i))^2-b(i)(y-y_0(i))^2} \tag{8}$$

i	0	1	2	3	4
V_0(kcal/mol)			5.0		
$d(i)$(kcal/mol)	0.6	3.0	1.5	3.2	2.0
$a(i)$(Å^{-2})	1.0	0.3	1.0	0.4	1.0
$b(i)$(Å^{-2})	1.0	0.4	1.0	1.0	0.1
$x_0(i)$(Å)	0.1	1.3	−1.5	1.4	−1.3
$y_0(i)$(Å)	0.1	−1.6	−1.7	1.8	1.23

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