



Comment “On the Quadratic Reaction Path Evaluated in a Reduced Potential Energy Surface Model and the Problem to Locate Transition States”

[by J. M. Anglada, E. Besalú, J. M. Bofill, and R. Crehuet, *J Comput Chem* 2001, 22, 4, 387–406]

WOLFGANG QUAPP

Mathematisches Institut, Universität Leipzig, Augustus-Platz D-04109 Leipzig, Germany

Received 30 August 2000; accepted 11 October 2000

ABSTRACT: The difference is explained between steepest ascent and following a reduced gradient (distinguished coordinate method) for the location of saddle points. © 2001 John Wiley & Sons, Inc. *J Comput Chem* 22: 537–540, 2001

Keywords: potential energy surface; path following; saddle point; turning point; reduced gradient

Introduction

The pivot equation of the paper of J. M. Anglada et al.¹ seems to be “the equation for a path”

$$\frac{d\mathbf{q}(s)}{ds} = \frac{\mathbf{g}(\mathbf{q}(s))}{|\mathbf{g}(\mathbf{q}(s))|} = \mathbf{t}, \quad (1)$$

where $\mathbf{q}(s)$ are the coordinates of the path with arclength s , $\mathbf{g}(\mathbf{q})$ is the gradient of the potential energy surface (PES), and \mathbf{t} is the tangent to the path. \mathbf{g} , \mathbf{q} ,

Correspondence to: W. Quapp; e-mail: quapp@server1.rz.uni-leipzig.de

and \mathbf{t} are N -dimensional vectors. The authors maintain in the second paragraph of the introduction that the integration of eq. (1) is the task of the reaction path following. Starting in the headline and throughout the article, the authors use the conception “reaction path” for their solution. The reader is undoubtedly led to the assumption that

$$\begin{aligned} \text{reaction path} &= \text{minimum energy path (MEP)} \\ &= \text{steepest ascent of eq. (1)} \\ &= \text{solution of the article.}^1 \end{aligned}$$

This is not true, and cannot be accepted without comment.

Steepest Ascent

Any direct practical use of eq. (1) in the uphill form given above is nonsense, if we deal with a reaction path in more than one dimension. The reason is the funnel character of steepest descent lines, see Figure 2 of ref. 2. Only the descent to the minimum works numerically (usually badly³), but never the ascent.

Reaction Paths and Other Pathways

Figures 1 to 9 of ref. 1 show in all cases that the energy at some points of the calculated pathways does not increase monotonously along the path. The pathways show some points higher in energy than the saddle point, and the path finds the final SP after a decrease in energy! Thus, the solutions of ref. 1 cannot be the solutions of eq. (1), which would mean steepest ascent throughout. Note, the saddle point (the transition state) is defined as that point at the reaction path from reactant to product where the energy is maximal. A reaction path, on the other hand, is a path that has to go through the saddle point. But indeed: the authors speak about the “minimum energy reaction path” in example IV.C. All solutions, which are shown in Figures 1 to 9, are in contradiction to the reaction path assumption. The underlying deep problem seems to be a more principal one; it concerns many workers in the field: they assume (mostly implicitly) that there is only *one* MEP, and they further assume that all of the different methods are methods to calculate *this one* MEP. This is not true. We have to discriminate between different pathways: (a) steepest descent from saddle point:³ eq. (1) with minus sign, and (b) gradient extremals^{2,7-10} are direct approaches to the MEP. (c) The distinguished coordinate,⁴ or in renewed form following a reduced gradient (RGF),^{5,6} may be considered as a model for the reaction path only in selected cases, namely, if not a turning point occurs. The curves show different drawbacks and advantages. To search for saddle points, (c) seems to be an appropriate method.

The method of ref. 1 belongs to group (c) of the procedures. It is a bad combination of eq. (1) and (c), as will be discussed in the following. The result of (c) is usually not a reaction path. This becomes clear in analyzing Figure 9 of ref. 1, which shows an analogous solution as it is given in Figure 3 of ref. 5. But the solution of Figure 9 is not a solution of eq. (1), neither uphill nor downhill.

If we go into the formulae, we can compare the eq. (1) for steepest ascent with eq. (6) for the definition of the reduced PES, with eq. (10) for the relation of \mathbf{q}_p to the \mathbf{q}_r coordinates using (6), and with eq. (23) for the tangent of the solution. The definition of the distinguished coordinate requirements in eq. (6) is $(\mathbf{g}_p)_i = 0$ for $i = 1, \dots, m$ coordinates. If we directly include these $(\mathbf{g}_p)_i$ into eq. (1), we would obtain $dp_i/ds = 0$, thus, every movement is forbidden in every p_i direction. This is in contradiction to eq. (23b), where the \mathbf{t}_p are not zero. Because eq. (23) is the key idea of the article¹ [together with eqs. (6) and (10)], the contradiction to eq. (1) in full dimensionality can only be solved if we conclude that eqs. (6), (10), and (23) form a different ansatz in comparison to eq. (1). However, the authors explicitly claim (at the beginning of section II.B), that they “study the general mathematical form of the differential eq. (1) ...” By way of intimation, the authors say [after formula (25)], “... that the differential equation (23) is the equivalent analogous to equation (1) ...” I claim: no, eq. (1) does not play the main role here! Figure 9 suggests that the article by J. M. Anglada et al.¹ indeed gives a version of the RGF method (c),^{5,6} and that there is no solution of eq. (1). As already remarked,⁵ RGF may follow a valley, but usually it does not follow the MEP. It is clear from the solution shown in Figure 9 that this curve is also not a typical reaction path.

RGF Lines

It makes sense to think a little closer about the difference of eq. (1) and eq. (23) of ref. 1. The solutions of eq. (1) are well known; there are, for example, extensive illustrations.^{9,11} Steepest ascent lines only flow into each other at a summit of the potential being a saddle point of index N , where N is the full dimension of the problem. (As well as steepest descent lines only flow into each other at a minimum being a “saddle point of index zero.”) Saddle points of an index lower than N dissipate steepest ascent lines. Saddle points of lower index, especially saddle points of an index one, which are of chemical interest, are only met by accident with one lonely steepest ascent line. Numerically, it is almost impossible to follow uphill this lonely line; but there are proposals to do this.^{10,12}

We find a very different situation for the generalized distinguished coordinate method, the RGF.^{5,6} This method searches a line that has at every point the same gradient direction. The behavior of such lines at stationary points of every index is quite better for numerical usage: they flow into each other at

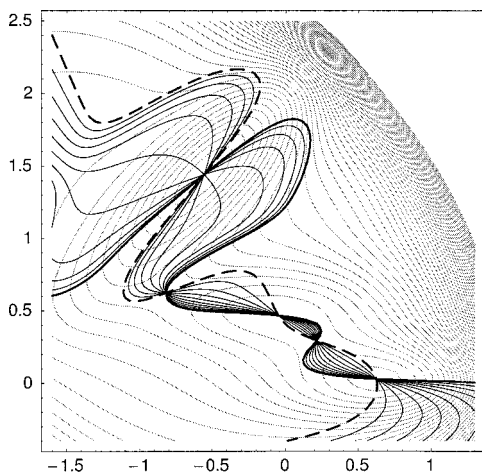


FIGURE 1. A family of RGF lines on the Müller-Brown model potential,¹³ see text. Level lines are gray. RGF lines are the black lines. The two bold lines are the corresponding RGF solutions to the coordinate directions x (bold), and y (bold dashed). RGF lines flow into each other at the stationary points. The drawing is made by Mathematica.¹⁴

every stationary point, at least in a certain region of attraction. Figures 1 and 2 show this behavior with the help of the Müller-Brown surface.¹³ The two fat lines are the original lines of distinguished coordinates x or y (where the y line is dashed). The other RGF lines are solutions where a linear combination of the gradient components is zero [see eq. (11) of ref. 5]

$$g(q_1)(\pm r_2) - g(q_2)r_1 = 0, \quad (2)$$

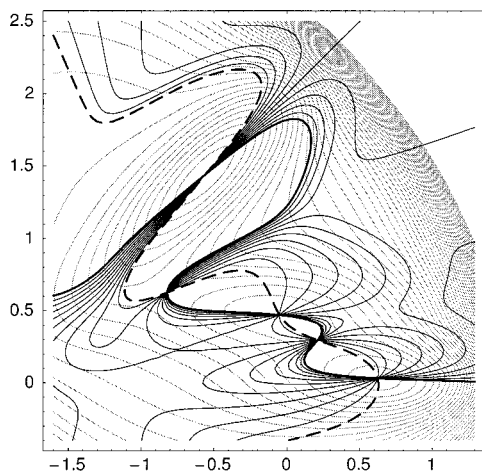


FIGURE 2. Another family of RGF lines on the Müller-Brown model potential.¹³ See caption of Figure 1.

where $(q_1, q_2) = (x, y)$ are coordinates, and $\mathbf{r} = (r_1, \pm r_2)$ are search directions that are at every curve point parallel to the gradient, \mathbf{g} , of the surface. The $(-)$ sign is used in Figure 1, but the $(+)$ sign is used in Figure 2. The curves drawn form a family of curves with a parameter c , which is used in $(r_1, \pm r_2) = (1 - c * 0.1, \pm c * 0.1)$ with $c = 1, \dots, 9$.

Equation (23a)¹ act as steepest ascent in the \mathbf{r} -subspace. The combination with (23b) causes that the method does not follow the steepest ascent in the full N -space. The tangent to this line will diverge from the search direction in the full N -space, because of (23b). The tangent has also a component in the m -dimensional remainder of the N -dimensional space. While ansatz (5) looks like a definition of an n -dimensional submanifold for the reduced PES, the solution of (23) “only” is a curve that we can follow numerically. Translated into the search direction \mathbf{r} of ref. 6 it means that (23a) may be compared with $\mathbf{r} = ((\mathbf{g}_r)_i, (\mathbf{0})_j)$, $i = 1, \dots, n$, $j = 1, \dots, m$, $n + m = N$, to use after an additional normalization. So, while ref. 5 treats a single distinguished coordinate, the article¹ attempts to handle a “distinguished coordinate” in n dimensions of the full N -space, but ref. 6 deals with a general “distinguished coordinate” in the N -dimensional space that is searched for. Because all such lines of RGF pave the configuration space, and because they are attracted by a next stationary point in a certain region, it is not so important to follow a selected line numerically exactly to find the saddle point. For example, in Figure 1 all lines of RGF between the bold faced x and y lines flow into each other at the saddle points, as well as at the minima. This makes the difference to eq. (1) in the full N -space, and it opens the possibility to easily find the saddle point. And this is the reason for the numerical stability of RGF, which is manifest in the examples of the article.¹ As conclusion from this section, we see that the authors of ref. 1 use the clever strategy of following one member of a family of curves, where all of them lead to the saddle point; unfortunately, they compare the curves in terms of the steepest ascent eq. (1). To follow steepest ascent is no concept to find saddle points.

Turning Points

The methodology of the distinguished coordinate method (c) to locate saddle points has been criticized for 20 years,^{4,15} for the problem of turning points. The definition of a turning point is that the orientation of the curve direction changes in comparison to the search direction, the gradient $\mathbf{g}(\mathbf{q}_r)$ in

the r -subspace,¹ \mathbf{q}_r . Thus, the scalar product with the tangent, $\mathbf{g}(\mathbf{q}_r) \cdot \mathbf{t}$, is zero at the turning point. At turning points, the paths of the old method can jump uncontrollably to another region of the PES. The task to overcome the turning points by a continuous procedure has been solved by RGF.⁵ There, the minimization of eq. (5) is not treated,¹ however, the system (6) is solved using a Newton step.⁵

The turning point is wrongly explained in the description of Figure 9 in ref. 1, cf. Figure 3 of ref. 5. The turning point of the x -line of the Müller–Brown surface¹³ is crossed if the step in direction x is zero (where x is the search direction). The TP is at (0.169, 1.670). The tangent \mathbf{t} of the solution in Figure 9 is orthogonal to the gradient vector of the PES, at the turning point. Thus, the solution of the article¹ cannot be a solution of (1). Namely, eq. (1) is solved by curves where the tangent points into the direction of the gradient. But nevertheless, in the article,¹ saddle points are found by path following, whatever the path is defined. It is described in the text of Figure 9 that turning points occur. It becomes manifest by Figures 1 to 9 that the method of ref. 1 handles the crossing of a turning point along a pathway. Note, in refs. 5 and 6 the numerical stability of RGF at a turning point was as well as at any other point, because there the solution of the system (6) is used, and it is independent of the character of the RGF line to be a valley line, or to be a ridge line.

After the turning point, the solution in Figure 9 of ref. 1 goes downhill a ridge. This is again in contradiction to the authors statement [after formula (41)] that their curve is a steep-ascent line. A further important problem is the following: the minimization of eq. (5) in the y direction, thus, orthogonal minimization to x , would not find the solution. That was the problem of the old distinguished coordinate method.¹⁵ This problem is solved in ref. 1 by using the image quadratic function,¹⁶ which turns the ridge into a valley. The use of the image quadratic function is necessary for the modification of the old

distinguished coordinate method in ref. 1 to overcome the turning point problem. Thus, ref. 1 uses another modification of the distinguished coordinate method in comparison to the RGF method.^{5,6}

Acknowledgment

I am very grateful to Prof. D. Heidrich for critically reading the manuscript.

References

1. Anglada, J. M.; Besalú, E.; Bofill, J. M.; Crehut, R. *J Comput Chem* 2001, 22, 387–406.
2. Quapp, W.; Imig, O.; Heidrich, D. In *The Reaction Path in Chemistry: Current Approaches and Perspectives*; Heidrich, D., Ed.; Kluwer: Dordrecht, 1995, p. 137.
3. Fukui, K. *Acc Chem Res* 1981, 14, 363; Quapp, W.; Heidrich, D. *Theoret Chim Acta* 1984, 66, 245; Garrett, B. C.; Redmon, M. J.; Steckler, R.; Truhlar, D. G.; Baldrige, K. K.; Bartol, D.; Schmidt, M. W.; Gordon, M. S. *J Phys Chem* 1988, 92, 1476.
4. Williams, I. H.; Maggiora, G. M. *J Mol Struct (Theochem)* 1982, 89, 365.
5. Quapp, W.; Hirsch, M.; Imig, O.; Heidrich, D. *J Comput Chem* 1998, 19, 1087.
6. Quapp, W.; Hirsch, M.; Heidrich, D. *Theoret Chem Acc* 1998, 100, 285.
7. Hoffman, D. K.; Nord, R. S.; Ruedenberg, K. *Theoret Chim Acta* 1986, 69, 265.
8. Quapp, W. *Theoret Chim Acta* 1989, 75, 447.
9. Sun, J.-Q.; Ruedenberg, K. *J Chem Phys* 1993, 98, 9707.
10. Quapp, W.; Hirsch, M.; Heidrich, D. *Theoret Chem Acc* 2000, DOI 10.1007/s00214990000192; Quapp, W. *Comput Math Appl* 2001, 41(3–4).
11. Ruedenberg, K.; Sun, J.-Q. *J Chem Phys* 1994, 100, 5836.
12. Quapp, W. *Chem Phys Lett* 1996, 253, 286.
13. Müller, K.; Brown, L. D. *Theoret Chim Acta* 1979, 53, 75.
14. Wolfram, S. *Mathematica 3.0*; Wolfram Research Inc.: Champaign, IL, 1997.
15. Müller, K. *Angew Chemie* 1980, 92, 1.
16. Smith, C. M. *Theor Chim Acta* 1988, 74, 85.