MRS Communications
© The Author(s), 2026
https://doi.org/10.1557/s43579-026-00924-z

MRS Communications
Commentary

Commentary on “A systematic workflow for mechanophore design” in MRS Communications

Wolfgang Quapp, Mathematisches Institut, Universität Leipzig, PF 100920, 04009 Leipzig, Germany
Josep Maria Bofill, Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain; Institut de Química Teòrica i Computacional, (IQTCUB), Universitat de Barcelona, Barcelona, Spain

Address all correspondence to Wolfgang Quapp at **quapp@math.uni-leipzig.de**

(Received 14 October 2025; accepted 19 January 2026)

Abstract

We reject the usage of a very old, questionable method, the CoGEF (Constrained Geometries simulated External Force) method. It was named originally distinguished coordinate method. It is meanwhile replaced by the Newton trajectory method.

Comment

In a recent contribution to this Journal[1] Moore and co-workers reported a computational study on polymer mechanochemistry. Our comment is directed against the used method Constrained Geometries simulated External Force (CoGEF) for reaction path calculations, which can generate uncontrollable jumps over the potential energy surface (PES), compare the copy in Fig. 1. An analogous discontinuous energy profile is shown in Fig. 1 of Ref. 2. Even more strange is that in some Figs. S9–S16 of Ref. 3 two jumps can be found in the profile. We suspect that the profiles ascent in the PES mountains and then jump to another valley, without, however, crossing the corresponding saddle point between the valleys. This is not the pattern of a reaction pathway. In contrast, it seems to be a random generator for valley hopping. It must also apply at least to the two jumps in the cases of Figs. S9–S16 of Ref. 3.

We note that the CoGEF method used, which employs a fixed direction, is very outdated.[4,5] It was already obsolete and questionable by 1979. It was originally called distinguished coordinate method (DCM). The two-dimensional counter example by Müller and Brown[4,6] is a widely cited example of a toy PES in chemistry. Therefor, it should be well known. In Fig. 2, we reproduce the central image of Ref. 4.

The DCM method has since been replaced by the reduced gradient, which was later named the Newton Trajectory (NT) method.[7–14] This method starts with analogue solution curves like the DCM, however it avoids the uncontrollable jumps on the PES. It is well-established in mechanochemistry.[15–18]

The central idea of an NT is that there is a curve where, at every point, the gradient of the PES points in the same normalized direction $\mathbf{f}$

$$\mathbf{g}(\mathbf{x}) = F\,\mathbf{f}\,, \tag{1}$$

where $\mathbf{g}$ is the gradient of the PES. The value F changes as a non-linear parameter along the solution curve. At every point $\mathbf{x}$, the parameter value F matches with the square root of the gradient norm. One can use a differential equation along the curve[19]

$$\frac{d\mathbf{x}}{dt} = Det(\mathbf{H})\mathbf{H}^{-1}(\mathbf{x})\,\mathbf{g}(\mathbf{x}) \tag{2}$$

here, $\mathbf{H}^{-1}$ is the inverse of the Hessian matrix of the original PES, and $Det(\mathbf{H})$ is its determinant. Variable t is the curve length parameter. Solutions to Eqs. (1) and (2) are now called Newton trajectories (NTs). Eq. (2) was formulated by Branin.[20]

General solutions of Eqs. (1) and (2) in different directions, $\mathbf{f}$, connect a minimum with a saddle point (SP) of index one. In chemistry, this is called a transition state (TS).

However, not all NTs lead directly to the next TS; there can be NTs with a so-called turning point (TP) that has a higher energy than the TS, compare Fig. 2. Such NTs ascent through a convex region, but at the TP they turn downhill again and, via a concave ridge, to reach the TS following an orthogonal ridge direction to the SP. The solutions of the DCM or of the CoGEF method do not exhibit this behavior. The search for a minimum orthogonal to the search direction in $N-1$ dimensions does not find a solution on a ridge. Therefore, the method jumps to a next valley on the PES, usually in an uncontrollable kind. Note that the jumping is not a technical problem of the step size of the CoGEF method, but rather an intrinsic geometrical property. The method must jump after a TP.

We are concerned that the usage of the CoGEF method has become widespread in computational chemistry, despite a warning[21] and in SI of Ref. 22. This is the reason for this comment. We add a list of further works with jumpy (therefor erroneous) trajectories for reaction paths,[23–38] to list a few. Mostly, the discontinuities were described by rupture forces in these papers, in contrast to cleavage of chemical bonds within the polymer backbone by Ref. 1. However, both paraphases are incorrect. The original paper

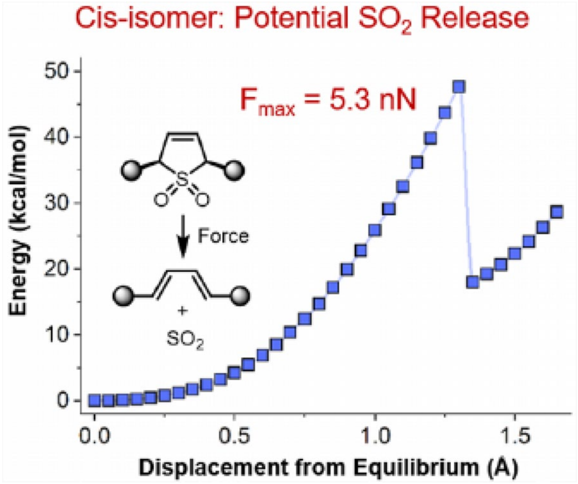

Figure 1. Fig. 2(a) of Ref. 1 shows a discontinuous jump on the PES, which has no physical meaning.

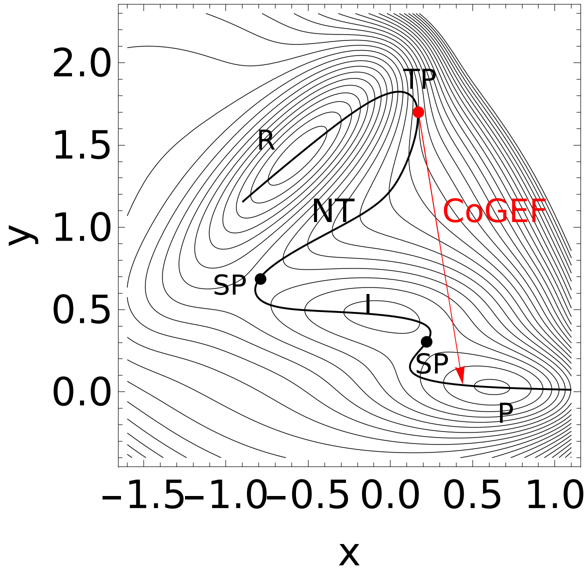

Figure 2. Müller–Brown PES with NT to direction (1,0) from reactant, R, over an SP to intermediate, I, via another SP to product, P. A TP is marked in red. There the CoGEF method shows a discontinuous jump on the PES, which is a mathematical artifact.

by Beyer[39] investigated the one-dimensional case and is therefore correct.

Acknowledgments

We acknowledge the financial support from the Spanish Structures of Excellence Mariá de Maeztu program, Grant MDM-2017-0767 and Generalitat de Catalunya, Project 2017 SGR 348. We acknowledge the help of the reviewers.

Funding

Open Access funding enabled and organized by Projekt DEAL.

Data availability

The data is available via W. Quapp upon request.

Declarations

Conflict of interest

There is no conflict of interest.

Open Access

References

1. F. Xie, Y. Sun, J.S. Moore, A systematic workflow for mechanophore design. MRS Commun. **15**, 1030–1039 (2025)
2. H. Qian, N.S. Purwanto, D.G. Ivanoff, A.J. Halmes, N.R. Sottos, J.S. Moore, Fast, reversible mechanochromism of regioisomeric oxazine mechanophores: developing in situ responsive force probes for polymeric materials. Chem **7**, 1080–1091 (2021)
3. Y. Liu, S. Holm, J. Meisner, Y. Jia, Q. Wu, T.J. Woods, T.J. Martinez, J.S. Moore, Flyby reaction trajectories: chemical dynamics under extrinsic force. Science **373**(6551), 208–212 (2021)
4. K. Müller, L.D. Brown, Location of saddle points and minimum energy paths by a constrained simplex optimisation procedure. Theor. Chim. Acta **53**, 75–93 (1979)
5. I.H. Williams, G.M. Maggiora, Use and abuse of the distinguished-coordinate method for transition-state structure seraching. J. Mol. Struct. (THEOCHEM) **89**, 365–378 (1982)
6. W. Quapp, J.M. Bofill, Mechanochemistry on the Müller-Brown surface by Newton trajectories. Int. J. Quant. Chem. **118**, 25522 (2018)
7. W. Quapp, M. Hirsch, O. Imig, D. Heidrich, Searching for saddle points of potential energy surfaces by following a reduced gradient. J. Comput. Chem. **19**, 1087–1100 (1998)
8. W. Quapp, M. Hirsch, D. Heidrich, Bifurcation of reaction pathways: the set of valley ridge inflection points of a simple three-dimensional potential energy surface. Theor. Chem. Acc. **100**(5/6), 285–299 (1998)
9. J.M. Bofill, J.M. Anglada, Finding transition states using reduced potential-energy surfaces. Theor. Chem. Acc. **105**, 463–472 (2001)
10. R. Crehuet, J.M. Bofill, J.M. Anglada, A new look at the reduced-gradient-following path. Theor. Chem. Acc. **107**, 130–139 (2002)
11. W. Quapp, Reduced gradient methods an their relation to reaction paths. J. Theor. Comput. Chem. **2**, 385–418 (2003)

12. M. Hirsch, W. Quapp, Reaction channels of the potential energy surface: application of newton trajectories. J. Mol. Struct. (THEOCHEM) **683**(1–3), 1–13 (2004)
13. J.M. Bofill, W. Quapp, Variational nature, integration, and properties of the Newton reaction path. J. Chem. Phys. **134**, 074101 (2011)
14. J.M. Bofill, Comment on "exploring the potential energy landscape of the Thomson problem via Newton homotopies" [J. Chem. Phys. 142, 194113 (2015)]. J. Chem. Phys. **143**, 247101 (2015)
15. W. Quapp, J.M. Bofill, Pathways of most mechanochemical transformations are Newton trajectories. J. Phys. Chem. B **120**, 2644–2645 (2016)
16. W. Quapp, J.M. Bofill, A contribution to a theory of mechanochemical pathways by means of Newton trajectories. Theor. Chem. Acc. **135**(4), 113 (2016)
17. W. Quapp, J.M. Bofill, J. Ribas-Ariño, Towards a theory of mechanochemistry, simple models from the very beginnings. Int. J. Quant. Chem. **118**, 25775 (2018)
18. W. Quapp, J.M. Bofill, Newton trajectories for the Frenkel-Kontorova model. Mol. Phys. **117**, 1541–1558 (2019)
19. W. Quapp, J.M. Bofill, Reaction rates in a theory of mechanochemical pathways. J. Comput. Chem. **37**, 2467–2478 (2016)
20. F.H. Branin, Widely convergent methods for finding multiple solutions of simultaneous nonlinear equations. IBM J. Res. Dev. **16**, 504–522 (1972)
21. I.M. Klein, C.C. Husic, D.P. Kovacs, N.J. Choquette, M.J. Robb, Validation of the CoGEF method as a predictive tool for polymer mechanochemistry. J. Am. Chem. Soc. **142**, 16364–16381 (2020)
22. Y. Sun, I. Kevlishvili, T.B. Kouznetsova, Z.P. Burke, S.L. Craig, H.J. Kulik, J.S. Moore, The tension-activated carbon–carbon bond. Chem **10**, 3055–3066 (2024)
23. O. Brügner, M. Walter, Temperature and loading rate dependent rupture forces from universal paths in mechanochemistry. Phys. Rev. Mater. **2**, 113603 (2018). https://doi.org/10.1103/PhysRevMaterials.2.113603
24. T. Bettens, M. Alonso, P. Geerlings, F.D. Proft, Implementing the mechanical force into the conceptual DFT framework: understanding and predicting molecular mechanochemical properties. Phys. Chem. Chem. Phys. **21**, 7378–7388 (2019)
25. C.R. Wick, E. Topraksal, D.M. Smith, A.-S. Smith, Evaluating the predictive character of the method of constrained geometries simulate external force with density functional theory. Forces Mech. **9**, 100143 (2022)
26. L.C. Wu, G.D. Bo, Stereoelectronic effects in force-accelerated retro-Diels-Alder reactions. Synlett **33**, 890–892 (2022)
27. A. Das, A. Datta, Designing site specificity in the mechanochemical cargo release of small molecules. J. Am. Chem. Soc. **145**, 13484–13490 (2023)
28. S.M. Luo, R.W. Barber, A.C. Overholts, M.J. Robb, Competitive activation experiments reveal significantly different mechanochemical reactivity of furan-maleimide and anthracene-maleimide mechanophores. ACS Polym. Au **8**(3), 202–208 (2023)
29. R. Küng, A. Germann, M. Krüsmann, L.P. Niggemann, J. Meisner, M. Karg, R. Göstl, B.M. Schmidt, Mechanoresponsive metal-organic cage-crosslinked polymer hydrogels. Chem. Eur. J. **29**, 202300079 (2023)
30. W. He, Y. Yuan, M. Wu, X. Li, Y. Shen, Z. Qu, Y. Chen, Multicolor chromism from a single chromophore through synergistic coupling of mechanochromic and photochromic subunits. Angew. Chem. Int. Ed. **62**, 202218785 (2023)
31. S. Aydonat, A.H. Hergesell, C.L. Seitzinger, R. Lennarz, G. Chang, C. Sievers, J. Meisner, I. Vollmer, R. Göstl, Leveraging mechanochemistry for sustainable polymer degradation. Polym. J. **56**, 249–268 (2024). https://doi.org/10.1038/s41428-023-00863-9
32. M. Zhang, R. Nixon, F. Schaufelberger, L. Pirvu, G. De Bo, D.A. Leigh, Mechanical scission of a knotted polymer. Nat. Chem. **16**, 1366–1372 (2024)
33. A. Bhusal, K. Adhikari, Q. Sun, A hybrid density functional study on the mechanochemistry of silicon carbide nanotubes. RSC Mechanochem. **1**, 413–421 (2024). https://doi.org/10.1039/D4MR00043A
34. C. Wang, C. Yang, J. Wu, Z. Wang, K. Yang, How external forces affect the degradation properties of perfluorooctanoic acid in mechanochemical degradation: a DFT study. RSC Mechanochem. **2**, 692–705 (2025). https://doi.org/10.1039/D5MR00048C
35. S.G. Patra, A. Poddar, R. Jha, S.S. Kadam, C. Paul, P.K. Chattaraj, Mechanochemical Diels-Alder reactions: conceptual density functional theory and information-theoretic analyses. ChemPhysChem **26**, 202500019224103 (2025). https://doi.org/10.1002/cphc.202500019
36. S. Mittal, R.E. Wang, R. Ros, A.E. Ondrus, A. Singharoy, Molecular dynamics model of mechanophore sensors for biological force measurement. Heliyon **11**, 41178 (2025)
37. D. Xu, W. Liu, S. Tian, H. Qian, Versatile mechanochemical reactions via tailored force transmission in mechanophores. Angew. Chem. Int. Ed. **64**, 202415353413–421 (2025)
38. A. Das, C. Hajra, A. Datta, Force governs product diversity in the mechanochemical reactivity of triprismane. RSC Mechanochem. (2025). https://doi.org/10.1039/d5mr00050e
39. M.K. Beyer, The mechanical strength of a covalent bond calculated by density functional theory. J. Chem. Phys. **112**, 7307 (2000)