

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

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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.

submitted: October 13, 2025 revised: January 9, 2026

Keywords: chemical reaction, computing, education, mathematics, modeling, molecular, nonlinear effects

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 to 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 to S16 of ref.[3].

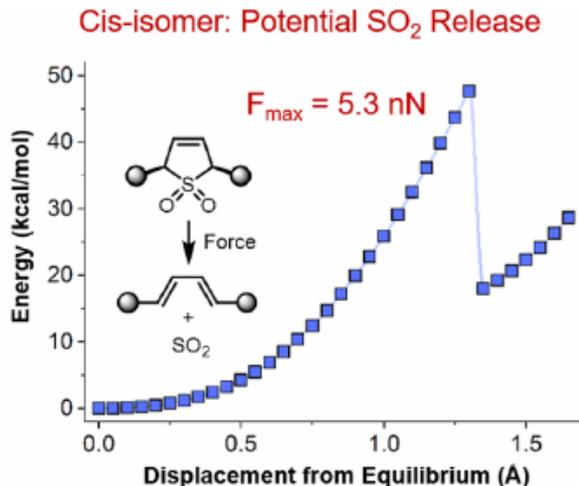


Fig. 1 Fig.2(a) of ref.[1] shows a discontinuous jump on the PES, which has no physical meaning.

We note that the CoGEF method used, which employs a fixed direction, is very outdated [4, 5].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. Therefore, 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The DCM method has since been replaced by the reduced gradient, which was later named the Newton Trajectory (NT) method [7–14].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}

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

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]

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

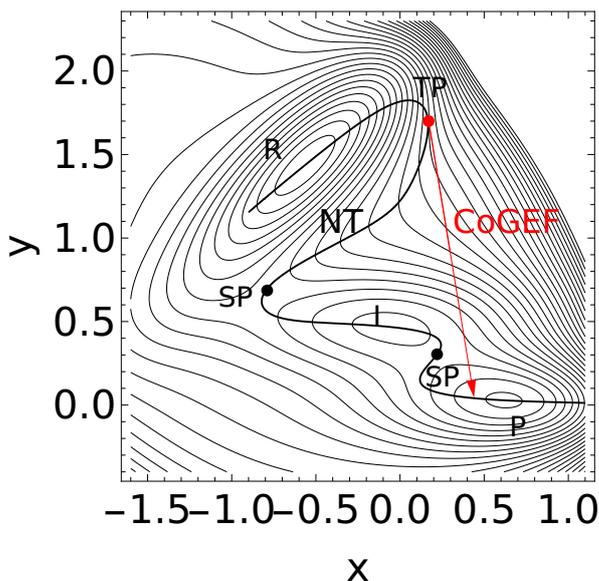


Fig. 2 Müller-Brown PES with NT to direction (1,0) from reactant, R, over an SP to intermediate, I, via another SP to product, P. A TP is marked in red. There the CoGEF method shows a discontinuous jump on the PES, which is a mathematical artefact.

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 paraphrases are incorrect. The original paper by M. K. Beyer [39] investigated the one-dimensional case and is therefore correct.

Acknowledgements

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.

Conflict of Interest

There is no conflict of competing interests.

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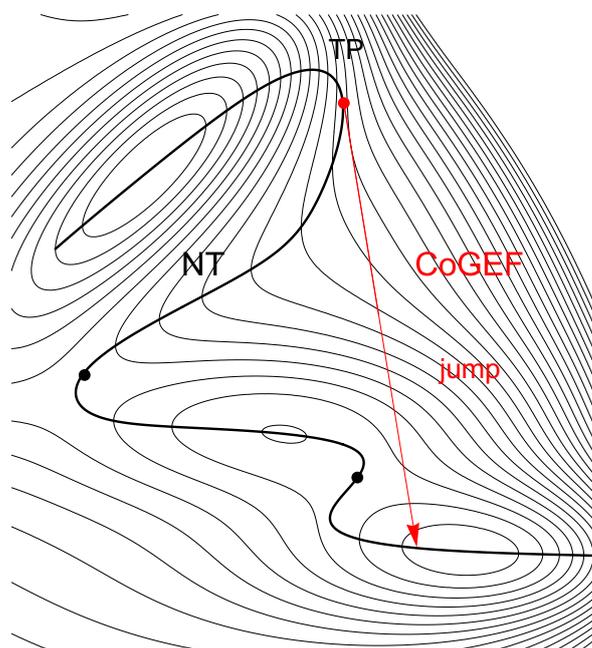
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TOC



Newton trajectory (black) and CoGEF (red)