Commentary

Comment on “Exploring potential energy surfaces to reach saddle points above convex regions” [J. Chem. Phys. 160, 232501 (2024)] by M.Gunde et al.

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We comment on the work on convex regions of the potential energy surface (PES) of a molecule by M. Gunde; A. Jay; M. Poberžnik; N. Salles; N. Richard; G. Landa; N. Mousseau; L. Martin-Samos and A. Hemeryck[1]. In contrast to the activation-relaxation technique nouveau (ARTn), in the present work we apply the theory of Newton trajectories (NTs) to the 2D PES. NTs have no problem traversing convex or concave regions of the PES. The ARTn is compared with NTs.

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I. Introduction

This letter concerns a mathematical detour which discusses the use of the activation-relaxation technique nouveau (ARTn) for a potential energy surface (PES), $V(\mathbf{x})$, with various convex regions[1]. In contrast, we use a curve $\mathbf{x}(t)$ where at each point the gradient of the PES is parallel to a given direction, $\mathbf{f}$

$$\mathbf{grad}(\mathbf{x}(t)) \quad || \quad \mathbf{f}, \tag{1}$$

t is a curve length parameter. Curves that solve Eq.(1) are of particular interest in mechanochemistry, where the direction $\mathbf{f}$ can be the direction of an external force[2][3][4]. It changes the PES in the simplest, linear case by the equation

$$V_{eff}(\mathbf{x}) = V(\mathbf{x}) - F\mathbf{fx}. \tag{2}$$

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where $\mathbf{f}$ is the normalized force direction, F is the force magnitude, and $\mathbf{f}$ and x form a scalar product.

The problem of Eq.(1) was formulated by Branin in a differential equation[5][6]

$$\frac{d\mathbf{x}(t)}{dt} = Det(H(\mathbf{x}(t)))H^{-1}(\mathbf{x}(t))\mathbf{grad}(\mathbf{x}(t)), \tag{3}$$

H is the Hessian of the second derivatives of the PES. It is important that the matrix

$$A = Det(H)H^{-1} \tag{4}$$

is desingularized when the Hessian becomes singular. The matrix A is called the adjoint matrix for H. The full Hessian matrix can be computationally expensive at each step of the positions $\mathbf{x}(t)$. However, it can be updated[7][8][9][10][11]. A first numerical step from a stationary point goes in direction $\mathbf{f}$. The following steps then secure that the gradient maintains this direction[6]. The solution curves are called Newton trajectories (NT).

NTs have the nice property that they connect stationary points with an index difference of one[6][12], compare the example in Section II. If we start at a minimum, we obtain a next saddle point (SP) with index one. A special case is a singular NT that crosses a valley ridge inflection (VRI) point[6]. Normally it connects a minimum with a saddle of index two and two SPs of index one via the VRI. A VRI represents the branching of a valley. With these properties, we can fully investigate the toy PES in Ref.[1] as well as any high-dimensional PES. We can follow a one-dimensional curve by Eq. (3) in any dimension. Note that the number of steps to reach an SP depends mainly on the step length used, and of course on the length of the path from the minimum to this SP. So we do not need 'drastically different numbers of steps' [1] for different SPs.

The following of an NT is included in the COLUMBUS program system [13] (under the name reduced gradient following, RGF). There are some links to different programs [14][15][16]. The Newton trajectory method has been established in chemistry since 1998, see refs.[4][17][18][19][20][21][22][23] and the references therein. We report that NTs are calculated for the PES of Frenkel-Kontorova chains with up to 500 atoms [24] and for medium molecules with up to 150 atoms [25]. Generalizations of the method for nonlinear forces are proposed instead of Eq. (2) [26].

In Section II we demonstrate the application of the theory of NTs for a 2D test PES. The conclusions are given in Section III.

A few notes in advance: To calculate the stationary points of the PES of a molecule, only $3N_{at}$-6 internal degrees of freedom (DoF) are needed.

A second gap is the wayward definition of a ridge on page 3 in Ref.[1]. For example, at an SP of index one we have one negative eigenvalue of the Hessian but N-1 positive eigenvalues (if N is the dimension). If we go uphill from the SP perpendicular to the valley direction, we have positive curvature. This it is a (hyper)-ridge of dimension N-1. In Fig. 2 below, in the region around the maximum, the region with two negative eigenvalues is inside the green line around the maximum.

A third gap in the annotated paper is the lack of knowledge about the well known streambed methods such as gradient extremal following, see for example Refs.[27][28].

A fourth gap in the commented work is the lack of knowledge about the Gentlest Ascent Dynamics (GAD) method, where the gradient of the PES is projected into a certain direction and also perpendicular to it, see for example Ref.[29]. ARTn is, so to speak, a special case of the GAD technique.

A further gap is the distinction between 'valley branching' and VRI points. This is not correct. Singular NTs unambiguously define the branching[6][30][31][32]. There is an illustrative introduction to the higher dimensional case[33]. For a PES with more than two (toy) dimensions manifolds of VRI points arise[34]. If the PES is symmetric, the VRI manifold often forms a symmetry hypersurface. However, asymmetric VRI manifolds can also be computed[15][34][35]. Recently, the role of VRI points in dynamical processes has been discussed[36].

II. Find the SP of an Example PES

The PES of Ref.[1] is

$$V(x,y) = \frac{1}{2}cos(\frac{xy}{5})cos(\frac{3x}{5})cos(\frac{y}{2}) + cos(x)cos(\frac{3y}{2}) + exp(-[(x-17)^2 + (y-17)^2]/125) \quad (5)$$

for $x \in [13, 18]$ and $y \in [14.7, 18.6]$, as shown in Fig.1.

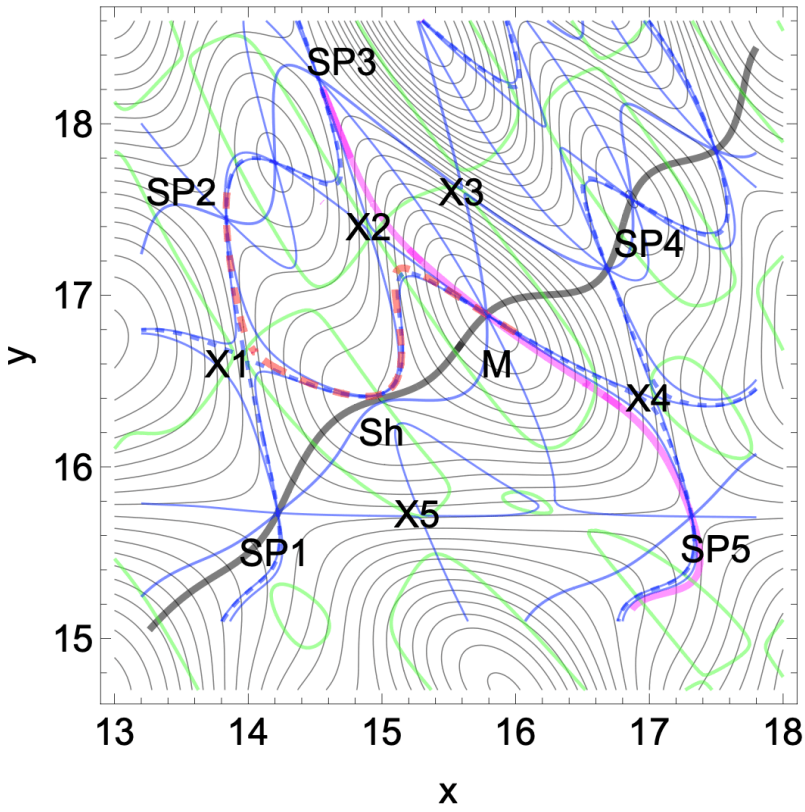

Figure 1. Level lines (thin black) of the PES (5). M is the central minimum, SPi are the 5 closest transition states, but Xi are the 5 VRI points between the SPs. A special region is the shoulder, Sh. See the text for the meaning of each colored line.

There is a central minimum, M, which is surrounded by five SPs. Five VRI points are shown between the SPs through Xi, where i is a consecutive number. The boundaries of the convex-concave regions are enclosed by green lines. They are given by the condition $det(H) = 0$. These lines also cross the VRI points. Normally they are curvilinear, so that the points of a molecule on a higher dimensional PES with $det(H) = 0$ form curved hypersurfaces (not 'hyperplanes' as claimed in[1]).

Each VRI is intersected by its own singular NT, all of which are represented by thin blue lines. For example, the dashed blue curve is the singular NT through the VRI point X1. Singular NTs are the boundaries of families of NTs that connect the minimum, M, with different SPs. Two singular NTs each form a corridor for all NTs connecting the minimum, M, with the same SPi[37].

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To find all SPs, you have to choose an appropriate direction in the corresponding corridor. For example, a branch of the thick black NT (direction $\mathbf{f}=\frac{1}{\sqrt{2}}(1,1)$) connects SP1 to M via Sh, which leads to SP4. A branch of the magenta NT ($\mathbf{f}$=(1,0)) connects SP3 with M and goes to SP5. Incidentally, it is not necessary to follow the specified NT exactly within a corridor, since a neighboring NT also leads to the same next stationary point.

The special region of this PES here is the shoulder, Sh, where some NTs come close to each other, but do not intersect[38]. The steepest descent from SP2 leads to the shoulder. To connect SP2 with the minimum, M, we have to find a direction between the blue singular NTs through VRI points $X1$ and $X2$. For example, this is fulfilled by the dashed red NT to direction $(0.987, 0.163)$. Before M, the red NT moves together with the magenta NT to SP5. This means that the corridors before M and after M are different.

Note that there is no bifurcation of the valley of M at the shoulder, Sh. The corresponding bifurcation points are $X1$ and $X5$, which are the boundary points for the corridor of the thick black NT from the minimum M to $SP1$.

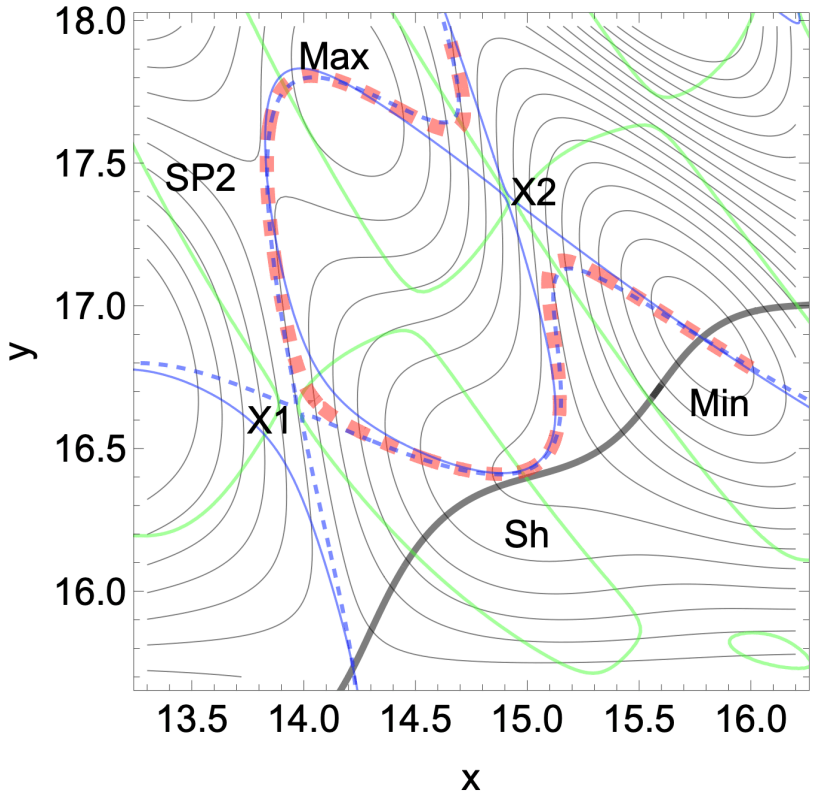

Figure 2. Extended range of Fig. 1 to include the minimum, the shoulder, the VRI points X1 and X2, the SP2 and a maximum.

The dashed red NT is also shown in an extended region of the PES in Fig. 2. The corridor for this NT is quite small. A boundary is the dashed blue singular NT through VRI point X1 on the left, but the other boundary is the blue singular NT through VRI point X2. It connects the minimum, Min, directly to X2 and the maximum, Max. Its other branch leads from X2 to the desired SP2, but in a large arc. The dashed red NT lies above and to the right of the dashed blue boundary, and below and to the left of the solid blue NT. Near the shoulder, Sh, all NTs come close to each other but do not cross, compare also Fig. 1 of ref. [39] where a similar situation is described.

One can observe in Fig. 2 the different convex or concave regions of the PES through which the dashed red NT passes, crossing the green lines. Around M the region is convex, near $X2$ up to Sh it is concave, between Sh and $X1$ it is convex again and then up to $SP2$ it is finally concave. This NT goes uphill through a valley from M to $SP2$.

Similarly, other singular NTs form other corridors to SPs numbered 1, 3, 4, or 5.

On this PES, the dashed red NT does not find the next minimum after SP2, but continues uphill to the maximum, an SP of index two, with two negative eigenvalues of the Hessian matrix. This is allowed by the property of regular NTs. They connect stationary points with an index difference of one[6][12]. Here the NT moves from index one of SP2 to index two of the maximum. Note that saddles of index two have been discussed in chemistry since 1986[40][41]. Currently they play a role in the discussion about roaming atoms[42].

III. Conclusion

We propose to applied Newton trajectories that can immediately find all SPs of a given minimum basin, see Fig. (1a) of Ref.[1]. The special curvature of the PES does not matter[43]. The starting point does not need to be changed. All NTs to the five SPs around M start at M.

Statements and Declarations

Conflict of Interest: We declare that we have no affiliation with or involvement in any organization that has financial interest in the subject matter or materials discussed herein.

Author Contributions: WQ and JMB contributed equally.

Methods: We have used Mathematica 13.3.1.0 for Linux x86(64-bit) in the calculations and in the representation of the figure.

Data Access Statement: All relevant data are included in the paper. Further data can be obtained from WQ.

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Declarations

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