Comment: Catch-slip bonding, Pathway switching, and Singularities [Phys. Rev. Research 5, 023161 (2023)]

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I. COMMENT

This remark concerns articles [1, 2] by Barkan and Bruinsma (BB). They use parts of the theory of Newton trajectories (NT) [3, 4] as a tool to rationalize the biochemical phenomena of slip- and catch-bonds.

BB study the mechanochemical potential

$$V_f(\mathbf{x}) = V(\mathbf{x}) - f \, \hat{l} \cdot \mathbf{x} \qquad (1)$$

where $V(.)$ is the potential energy surface (PES), or the free energy surface, of a molecule, $\hat{l}$ is the direction of an external force vector acting on the molecule, and f is the magnitude of the force. Note that ansatz (1) is the simplest possible, with a linear external force.

The stationary points of the PES move under the action of the force. For the movement of any critical point, $\mathbf{x_c}$, BB create a misleading differential equation, their Eq.(2), by

$$\frac{d\mathbf{x}_c}{df} = H^{-1}(\mathbf{x}_c)\,\hat{l} \qquad (2)$$

where H^{-1} is the inverse of the Hessian matrix of the original PES.

We wonder about this equation. The determinant of H is positive in minima and negative in saddle points of index one (SP$_1$) of the PES. So there is always a point on the way from a minimum to an SP$_1$ where the determinant of H is zero and where Eq.(2) becomes singular.

This problem was solved long ago by Branin [5], cf. also text book [6], using the so-called adjunct Hessian.

$$A = Det(H)\; H^{-1}\;. \qquad (3)$$

The better equation with A is given in ref. 34 of BB citing one of our articles [3]

$$\frac{d\mathbf{x}_c}{dt} = Det(H)\; H^{-1}(\mathbf{x}_c)\,grad(\mathbf{x}_c)\;, \qquad (4)$$

So the right one desingularized equation is made worse into an equation with a singularity. Of course you need

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more effort to deal with it, with the situation of singular points on every possible reaction pathway. This is then a part of the annotated paper, compare Eq.(3) of ref.[1].

A second change in the clumsy differential Eq.(2) is the direct use of direction $\hat{l}$, in contrast to the gradient of the PES in Eq. (4). This does not change a correct NT to direction $\hat{l}$. However, if one starts anywhere in the configuration space then it causes false solution curves, see below the Section: "The field of NT".

The singularities of Eq.(2) are artificial, so to speak. And they do not generally generate a force-induces switch, like it is claimed in paper [1]. Every solution of Eq. (4) to different directions $\hat{l}$ connecting a minimum with an SP$_1$ has to cross the curve of points where $Det(H) = 0$ applies, so also right regular and 'direct' solutions. The force in direction $\hat{l}$ with the special magnitude, f, to reach the $Det(H) = 0$ curve forces a coalescence of former minimum and former saddle SP$_1$ for the effective PES. These points now form a shoulder on the effective PES (1). This event is named bond breaking point (BBP) [7, 8]. Each local point on the $Det(H) = 0$ curve determines one solution curve of Eq.(4), through its corresponding gradient direction there. The reason is that along each solution curve of Eq.(4) the gradient direction is fixed because it is equal to $\hat{l}$. It means that one cannot start on different points on the $Det(H) = 0$ curve with the same direction $\hat{l}$.

We have to identify a further weakness in Eq.(2) of ref.[1], the use of the force f for a curve length parameter. The Branin equation uses here an 'extra' curve length parameter, t, because f has to have on the way from minimum to SP a maximal value in between, at the corresponding BBP, compare many illustrations in ref. [3]. Thus f is not the curve length parameter of the NT. However, f decreases to zero again to reach the SP.

II. THE FIELD OF NT

A remark to the 'flow' images in Figs. 1(e) and 1(f), and in the SM of ref. [1]. These pictures are misleading for the imagination of NTs. Every NT starts in a stationary point of the original PES, $V(x)$, and a family of NTs

leads to the next stationary point with an index difference of one [13]. Each NT follows exactly one direction, $\hat{l}$. There is not such an arrow field like the named Figures offer. No, there is always a one-to-one relationship of the external directions and the NTs. The field which the NTs follow is the field of constant gradient directions of the original PES.

This remark also touches on the claimed 'ellipticity' near an $\hat{l}$ switching point. The word implicates a circular behavior of NTs which is not true. (For an exceptional case see in ref. [15] the dent by a thumb on the ridge of the PES where a compact NT exits.)

The incorrect field of NT curves through the $Det(H) = 0$-curve around the $\hat{l}$-switch point of ref. [1] may be the result of the awkward use of Eq. (2) for the Branin equation for a mechanochemical ansatz.

III. DISCUSSION

We propose to lead back Eq.(2) to the desingularized form, the Branin equation (4) and use it consistently. Note that for Eq.(3) of ref.[1] the essential $Det(H)$-factor is used, compare Eq.(SM18). We propose to use Eq.(4) because we think that paper [1] examines an important topic in mechano-bio-chemistry, namely the switching behavior of reaction pathways under external force. It is an important point.

We state that the theory of Newton trajectories (NT), this is the name of solution curves of differential equation (4), which is correctly named only in the SM of paper [1], already offers many tools for the investigating of reaction path models. Because the solutions of Eq.(4) can just serve by itself for reaction pathway models, apart from the well known steepest descent model of the IRC [9, 10] or gradient extremals [11–14].

A remark to the $\hat{n}$ points of ref. [1]: they are the known and often discussed valley-ridge inflection points (VRI) [3, 4, 16–22] of the PES. They are characterized by a special kind of NTs, so called singular NTs which bifurcate at the VRI point. The singular NT through the bifurcation then has four branches. From minimum one to the VRI point, from there it has two branches to the two next SP_1, and one branch normally continues uphill to an SP_2, a saddle of index two. The bifurcation explains the observed 'hyperbolicity' of NTs nearby a VRI in ref.[1].

IV. CONCLUSION

A consequent application of the theory of NTs would make paper [1] easier to understand. We demand the use of the Branin equation (4) for the treatment of mechanochemical problems.

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