

# Comment on: "Analyses of bifurcation of reaction pathways on a global reaction route map: A case study of gold cluster Au<sub>5</sub>" [J.Chem.Phys.143, 014301 (2015)]

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We demonstrate by an example that the search for valley-ridge transition (VRT) points used in the commented paper does not always indicate a bifurcation of a reaction path. This was claimed.

Given an  $N$ -dimensional potential energy surface (PES) over an  $N$ -dimensional configuration space of a molecular reaction. Level lines, or level hypersurfaces in higher dimensions, are convex if we are in the minimum bowl. Usually they keep this character on the pathway from the minimum to the SP along the so called 'minimum-energy path'.<sup>1,2</sup> However, if a valley then bifurcates, a ridge emerges between the two branches, and uphill the ridge we find concave levels. The bifurcation point is named valley-ridge inflection (VRI) point.<sup>3</sup> The change from the convex to the concave character is indicated by a zero of the eigenvalue of the Hessian matrix belonging to an eigenvector which is orthogonal to the gradient of the PES.<sup>4-7</sup> A proper method to determine valley-ridge inflection points is the search of singular Newton trajectories<sup>8,9</sup> which bifurcate in such points. Newton trajectories (NT) are curves where the gradient direction of the PES does not change. The bifurcation point of a singular NT is mathematically characterized by the condition

$$\mathbf{A} \mathbf{g} = 0 . \quad (1)$$

The matrix  $\mathbf{A}$  is the adjoint of the Hessian, its desingularized inverse<sup>4,10</sup> and  $\mathbf{g}$  is the gradient of the PES. Matrix  $\mathbf{A}$  is defined as  $((-1)^{i+j} m_{ij})^T$  where  $m_{ij}$  is the minor of the Hessian  $\mathbf{H}$  obtained by deletion of the  $i^{\text{th}}$  row and the  $j^{\text{th}}$  column from  $\mathbf{H}$ , and taking the determinant. The superscript  $T$  denotes the transposition.

In contrast to the bifurcation of a valley, there are many more points on the PES where the levels change the character. The border between convex and concave regions is characterized by the condition<sup>10</sup>

$$\mathbf{g}^T \mathbf{A} \mathbf{g} = 0 \quad (2)$$

where  $\mathbf{g}^T$  means transposition of the vector  $\mathbf{g}$ . We name it the Hirsch condition that the Rayleigh coefficient (2) vanishes. All points fulfilling such a condition are called valley-ridge transition (VRT) points. Note that a VRI is on a VRT region, however, there are much more VRT points than VRI points.

Given a curve which describes the steepest descent (SD) from the SP of index one. It finishes in a minimum.

Thus, the inversely thought SD is a model for a reaction pathway up to the SP.

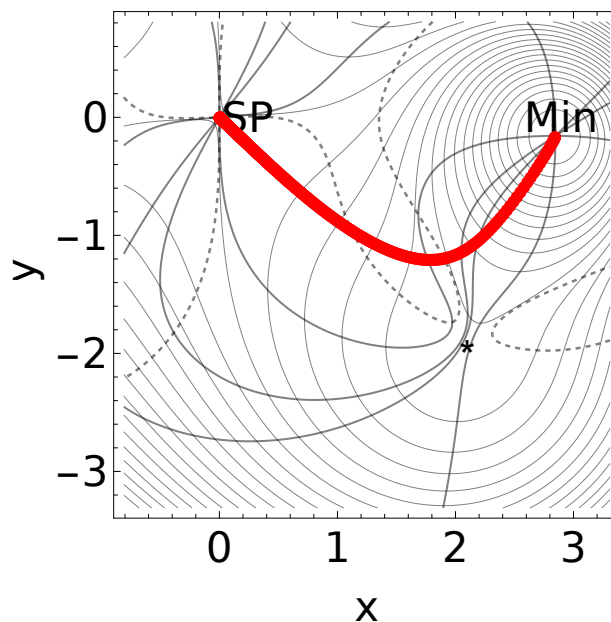


FIG. 1. Two-dimensional toy potential (3). Thin lines are the levels of constant energy. The border between valleys and ridges is the dashed curve. The SD from the SP (thick red) crosses the border line. The  $\star$  marks a quasi-shoulder or a quasi-SP. Many NTs (black curves) concentrate near this point  $\star$ , however, there does neither exist any singular NT nor a VRI point in the region of observation.

In paper 11 it is assumed that if this SD crosses the valley-ridge border, Eq.(2), on the PES then it indicates a VRI event. We show by a simple 2-dimensional toy surface that this assumption is not always true. The example surface is a modified NFK case,<sup>12,13</sup> see Figs. 1 and 2,

$$V(x, y) = C(x^2 + y^2)^2 + xy \quad (3)$$

$$-9\exp(-(x-3)^2 - y^2) - 9\exp(-(x+3)^2 - y^2) .$$

The constant is  $C = 0.03$ , where it was used  $C = 0.06$  for the original surface.<sup>12</sup> There is one minimum and one

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SP. The steepest descent from the SP goes across the promontory between the SP and the minimum. It crosses a ridge, and it crosses the border line of the ridge twice, however there does not exist any VRI point. (An enlarged version of Fig. 1 is figure 23 in reference 10.)

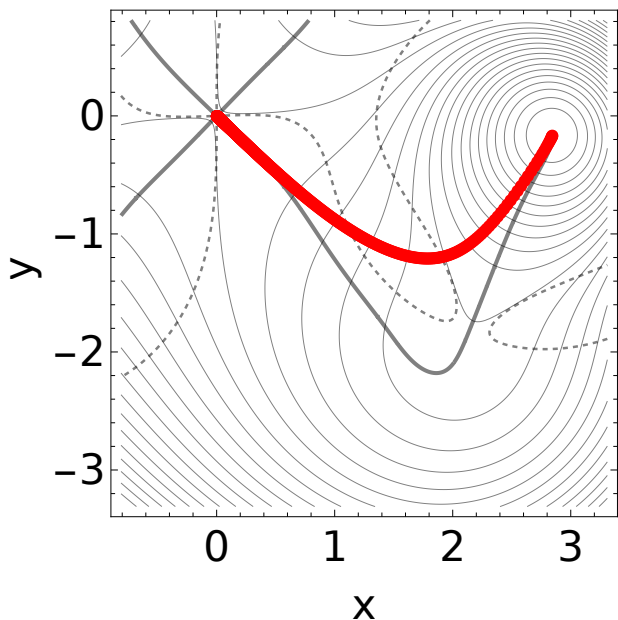


FIG. 2. Same surface. The gradient extremal (black curve) paves the reaction path along the valley floor. The SD (thick red) goes aside over the nose downhill. The SD is not the 'minimum-energy path'.

For comparison in Fig.2 we show the gradient extremal<sup>13-17</sup> which completes here the minimum-energy path. There is a unique reaction pathway from the minimum to the SP. It does not suffer under any bifurcation; the example surface only demonstrates a

reaction pathway with a sharp kink.

We know that the crossing of a valley-ridge border by a steepest descent line can indicate a VRI point, compare Fig. 1 of reference 7. However, as a conclusion of example (3), we cannot assume from such a crossing that the VRI is nearby, or that the VRI exists, at all. And contrary, there can exist a VRI point although the SD from the SP does not cross a VRI point, compare figures 3 and 4 in reference 5. The SD from the SP may be a help tool for the guess of VRI points, however it is not the method of choice. We propose the search of singular NTs for the detection of VRI points.<sup>8,9</sup>

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