Comment to:"Exploring the potential energy landscape of the Thomson problem via Newton homotopies" by D.Mehta et al., JCP 142, 194113(2015)

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We report that the Newton homotopy used in the paper [D. Mehta et al. J. Chem. Phys. 142, 194113 (2015)] is equivalent to the method of Newton trajectories. We use this method to clear the picture of the Griewank and Osborne function used as an example in the paper by Mehta et al.. They describe the state of affairs of numerical experiments, while we can derive an explicit formula for the Newton trajectories of this function. With such a formula we can explain the findings of the commented paper.

In paper 1, the Newton homotopy (NH) is applied for a potential energy surface (PES) $V(\mathbf{x})$ over an N-dimensional configuration space with the extra homotopy parameter, t

$$\nabla_{\mathbf{x}} V(\mathbf{x}(t)) - (1-t)\nabla V(\mathbf{a}) = 0 . \qquad (1)$$

$\mathbf{x}(t)$ is a smooth curve in the $(\mathbf{x}, t)$ space. The initial values $t=0$ and $\mathbf{x}=\mathbf{a}$ fulfill Eq.(1). The NH method is to follow the curve to a stationary point of V at $t=1$. However, it is long known that the Newton homotopy and the Newton trajectory (NT) are equivalent.[2,3] So to say, an NT can be interpreted to be the projection of the NH backwards into the initial configuration space in the $\mathbf{R}^N$, without the t-dimension. Because NTs are a family of unique curves which cover the configuration space, this projection is also unique. It seems unquestionable that the NTs are the 'simpler' ansatz, in comparison to the NH. But in any case the two curves, NH and NT, can be directly compared over their parametrization.[4]

Paper 1 does not only ignore all the references to NTs,[2,5–27] as well as of applications of NTs in Chemistry,[28–35] but also an application of homotopy methods in Chemistry including the NH.[3] We have to establish that it does not apply that the theory of the NH is a 'previously known but rather underutilized method' as the authors write.[1] Here holds the old hint: 'nomen atque omen'[36] that the theory of NTs is also a key for applications to NH curves.

A special case of the potential function of Griewank and Osborn[37] is the used example[1]

$$V_{GO}(x, y) = \frac{29}{64}x^4 - x^2 y + \frac{y^2}{2} . \qquad (2)$$

It is a polynomial surface were the highest exponents are even while the coefficients are positive: PES sections along the axes should have a minimum. But decreasing side valleys exist there, see Fig. 1. Since there is only one solution of $\nabla^T V_{GO} = (0,0)$, in the (x,y)-plane, the point $(0,0)$ is the stationary point: it is a flat saddle point. In Fig. 1(a) we show the contour lines, and the two standard

NTs with gradient directions along the axes. It is clear that the SP is also a valley ridge inflection (VRI) point. There the valley downhill to the SP along the negative y-axis bifurcates into the two side valleys going further downhill, and the ridge on the positive y-axis going uphill. Singular NTs bifurcate at VRI points. Because we have an SP, all NTs go through this singular point. Because SP and VRI point coincide, there also holds the bifurcational condition that one eigenvalue of the Hessian at the point is zero. Thus, the point $V_{GO}(0,0)$ is degenerate. We guess that such a coincidence of stationary points and bifurcation points of NTs (VRIs) happens not very often in Chemistry, neither for SPs like in Fig. 1, nor for other degenerate SPs like monkey saddles.[38,39]

There is a fundamental property for NTs: the existence of the bifurcation point divides the plane into different regions: the border is the singular NT, the fat curve in Fig. 1(a). This border also governs the pathways of numerical NTs. Which NTs can meet the searched SP? We can start with a simple definition of an NT that the gradient of the PES along the curve always points into a given direction:[7] $\mathbf{g}(\mathbf{x}(t)) \,\|\, \mathbf{r}$. The V_{GO} problem is

$$\mathbf{r} = \begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{D}\begin{pmatrix} g_x \\ g_y \end{pmatrix} = \frac{1}{D}\begin{pmatrix} \alpha x^3 - 2xy \\ y - x^2 \end{pmatrix} \qquad (3)$$

where a and b are two real numbers such that $a^2 + b^2 = 1$, $D = \sqrt{(\alpha x^3 - 2xy)^2 + (y - x^2)^2}$, and $\alpha = 29/16$. An explicit expression is possible for the NT for the simple V_{GO} potential for every $a \neq \pm 1$

$$y(x) = \left(\frac{\alpha x + a/b}{2x + a/b}\right) x^2 . \qquad (4)$$

The formula holds for the full x-axis except for $2x=-a/b$. The exceptional point is a pole of the NT. One easily inspects that Eq. (3) is fulfilled. The NT solution holds for every possible pair a and b: every NT meets the SP. But by the pole, shown in Fig. 1(b) for a special example, we see that nearly all NTs fall apart to two pieces. So it is correct that not every start point can serve as an initial point of a numerical curve tracing for the SP.[1] In Fig. 1(b) we show the regular NT to direction $y=-x$ with $a=-b=\pm 1/\sqrt{2}$. The right part does not cross the singular point $(0,0)$. The limit behavior of formula (4) for an NT
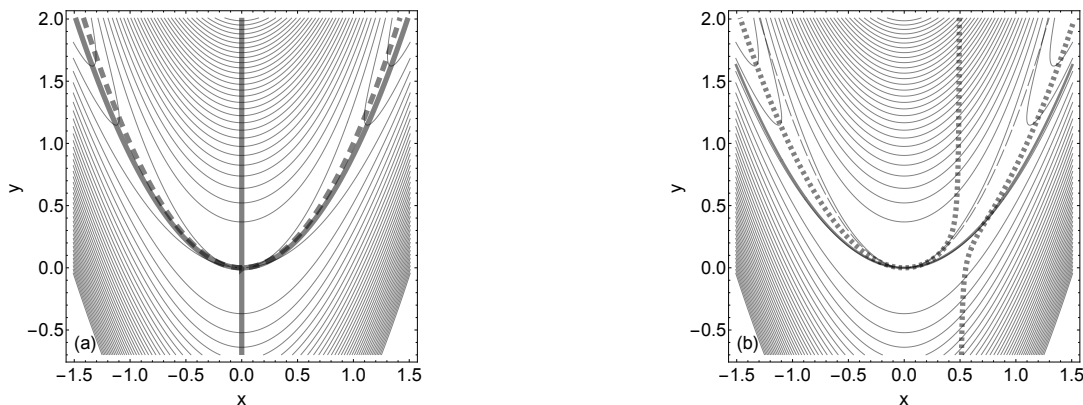
FIG. 1. GO surface with flat saddle at (0,0). **(a)** The fat curve is the NT were the x-component of the gradient is zero, it bifurcates at the VRI point. The fat-dashed curve is the NT were the y-component of the gradient is zero. **(b)** The NT to direction $y=-x$ (fat squares) falls apart to two pieces. If one starts anywhere on the right piece one avoids the singular point. The full parabola is a set of points with zero eigenvalues of V_{GO}. The thin dashed parabola is the border between the ridge and the valleys.

is the Fig. 1(a): for the limit $a \to 0, b \to 1$ we get the parabola $y = 29/32\, x^2$, the fat bifurcating curve, and for the limit $a \to 1, b \to 0$ we get the dashed parabola $y = x^2$. In the first case, the pole wanders into the bifurcation; in the second case, the pole wanders to infinity.

A further peculiarity of the GO surface is the following: on the curve $y = 23/32\, x^2$ throughout an eigenvalue of the Hessian is zero. It is the full line in Fig. 1(b). This parabola describes a last remainder of a ridge: only points with curvature zero emerge, however, no transition from convex to concave regions takes place. A further curve in Fig. 1(b) is the set of the true valley-ridge transition points, which fulfill the Hirsch condition[16] that the Rayleigh coefficient vanishes: $\mathbf{g}^T \mathbf{A} \mathbf{g} = 0$. The matrix $\mathbf{A}$ is the adjoint of the Hessian $\mathbf{H}$, its desingularized inverse.[16] The full region in Fig. 1(b) under the thin dashed curve is valley-region.

Note that for more than two dimensions of the PES, manifolds of VRI points exist (thus infinitely many points) which cannot coincide with finitely many stationary points.[8,40]

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