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Comment on "Reaction Coordinates and Pathways of Mechanochemical Transformations"

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The adiabatic potential energy surface (PES) is a basic concept of many theoretical chemistry models. Over the past several years, the phenomena of the action of a mechanical stress over a molecular system have motivated experimental and theoretical research. In a recent article, Avdoshenko and Makarov[1] describe how the concepts of an effective PES and of a reaction path (RP), or a reaction coordinate, can be used for mechanochemistry.

The RP is a one-dimensional description of a pathway on the PES in an N-dimensional configuration space. We use $N = 3n-6$ nonredundant internal coordinates, and n is the number of the atoms of the molecule. An early used curve is the distinguished coordinate,[2] which was later generalized as a distinguished coordinate path (DCP)[3] and finally refined as a Newton trajectory (NT).[4−6] This type of RP holds the following property: the gradient of the PES points to the same direction at every point of the curve. It is the reason that NTs should be taken into account for mechanochemical problems.

Basically, the mechanochemistry model[1] consists of a first order perturbation on the associated PES of the unperturbed molecular system due to a stress or pulling force, $\mathbf{f}$

$$V_{\mathrm{f}}(\mathbf{r}) = V(\mathbf{r}) - \mathbf{f}^T\mathbf{R} \tag{1}$$

$\mathbf{R}$ is the distance between the two pulling points of the molecule.[7] It will be associated with one of the coordinates,[7] or a linear combination of them. So we can assume that $\mathrm{d}R \approx \mathrm{d}r$ for a coordinate change in the direction of $\mathbf{R}$. The potential $V_{\mathrm{f}}(\mathbf{r})$ with a fixed $\mathbf{f}$ can be seen as an effective PES where "normal" chemistry takes place. Due to the external force, the stationary points of $V_{\mathrm{f}}(\mathbf{r})$ are located at different positions,[8] with respect to the unperturbed potential. The new minimum holds with eq 1

$$\nabla_{\mathbf{r}} V_f(\mathbf{r}) = \mathbf{0} = \mathbf{g} - \mathbf{f} \tag{2}$$

thus one searches a point where the gradient, $\mathbf{g}$, of the zero-force PES has to be equal to the mechanochemical force. If the mechanical stress in a defined direction is $\mathbf{f} = F\mathbf{l}$ with a fixed unit vector, $\mathbf{l}$, then it is $\mathbf{l} = \mathbf{g}/|\mathbf{g}|$ and $F = |\mathbf{g}|$. Another form of eq 2 is the projector equation which was applied many years ago[5,9]

$$(\mathbf{U} - \mathbf{l}\mathbf{l}^T)\mathbf{g} = \mathbf{0} \tag{3}$$

where $\mathbf{U}$ is the unit matrix. Solution curves of both eqs 2 and 3 are equal, and they are also equal[5] to the solutions of the differential equation of Branin[10]

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \pm\mathbf{A}(\mathbf{r})\mathbf{g}(\mathbf{r}) \tag{4}$$

t is a curve parameter, and matrix $\mathbf{A}$ is constructed by a multiplication of the inverse Hessian with the determinant of the Hessian, $\mathbf{A} = \det(\mathbf{H})\mathbf{H}^{-1}$. Curves $\mathbf{r}(t)$ satisfying eq 4 are called Newton trajectories (NTs). The name is also used for the equivalent solution curves of eqs 2 and 3.

For different, point-to-point changing forces, F, one should get a curve of the reaction path following force displaced stationary points (FDSPs)[1,7,11]

$$\delta\mathbf{r} = \mathbf{H}^{-1}(\mathbf{r})\mathbf{f}(\mathbf{r}) = \mathbf{H}^{-1}(\mathbf{r})\mathbf{g}(\mathbf{r}) \tag{5}$$

where $\delta\mathbf{r}$ is the distance from the minimum of $V(\mathbf{r})$ to the minimum of $V_{\mathrm{f}}(\mathbf{r})$. Note that the inverse Hessian $\mathbf{H}^{-1}$ will be singular on the pathway from the minimum to the saddle point of the original PES, and eq 5 loses its meaning. However, such points are the important catastrophe points in ref 1.

There is another way to make the FDSPs without the singularity: the Branin equation, eq 4. It is the result of a different parametrization of the curve parameter, t, by the multiplication of the right-hand side of eq 5 by the determinant of the Hessian. The determinant is a number. It does not change the direction of the vector of the right-hand side of eq 5. However, it removes the singularity of $\mathbf{H}^{-1}$ on the way to the SP. Matrix $\mathbf{A}$ is named the desingularized inverse Hessian, or the adjoint to $\mathbf{H}$.

The solution curve of the Branin equation to a given initial direction is a regular curve (if no valley-ridge inflection point is crossed,[5,12] but this is another, seldom property). The Branin equation is a well-known model for RPs.[5] However, the model is used here for the FDSPs. The stationary points of the different effective potentials with fixed $\mathbf{l}$ move with increasing F on the original PES along an NT. The behavior of NTs is well-known.[13]

We will still discuss an example:[1] the ring opening of *trans*-1,2-dimethylcyclobutane. There is chosen a DCP for the curve of FDSPs. However, the DCP jumps over the PES. The DCP method has been criticized during its first years for such jumps.[3] Avdoshenko and Makarov[1] circumvent the problem by calculating two different curves, one DCP from the minimum,

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and one direct FDSPs by eq 5 from the SP, and both curves meet at the jump point. The reason is, both curves are parts of a Newton trajectory (NT) with a turning point, compare Figure 1 and Figure 2 of ref 1.

A general solution of the DCP jump problems was given in 1998 by Quapp et al.[4,5] using eqs 3 and 4. NTs can have turning points (TPs) where the energy profile over the curve changes its direction. These TPs are the breakdown points of the DCP method. Important points are also the valley-ridge inflection points (VRI) of the PES[5,12] where singular NTs bifurcate. VRIs discriminate different families of NTs which lead to different SPs around the initial minimum. An NT which leads to a not desired SP represents an incorrect pulling scenario. On the PES of Figure 1, a VRI is at ≈ (3,0). We show an NT (thick and dashed) which does not find the SP.

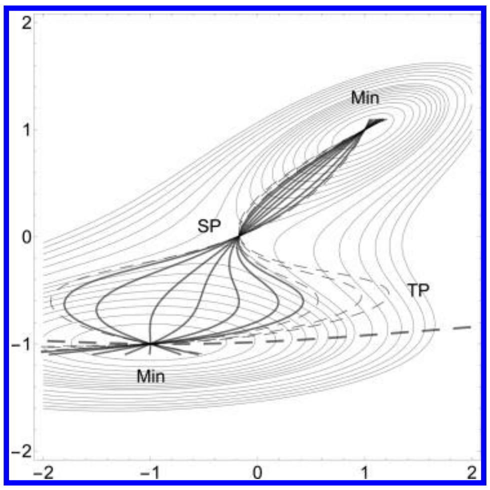

Figure 1. NTs on a PES which is similar to Figure 2 in ref 1. The thicker NTs are direct curves from the lower minimum to the SP. The thin dashed curves are NTs with a turning point (TP) in the lower bowl with higher energy than the SP. They may be questionable pulling scenarios. The thick dashed NT goes wrong. It represents a pulling force which does not enforce the desired reaction.

It should be noted that an additional mathematical method gives curves in the coordinate space which are equivalent to NTs, the Newton homotopy method.[14−16] It can extend the arsenal of methods to get the FDSPs curve.

We conclude that Newton trajectories can be used for the reaction path following force displaced stationary points (FDSPs). This kind of curve forms an important model for the treatment of mechanochemistry. The theory of NTs is well-prepared. We hope that it can accomplish deeper insights into the understanding of mechanochemistry.

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Notes

The authors declare no competing financial interest.

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