Reaction Pathways and Convexity of the Potential Energy Surface: Application of Newton Trajectories

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The reaction path is an important concept of theoretical chemistry. We employ the definitions of the intrinsic reaction coordinate (IRC), the gradient extremal (GE), and the Newton trajectory (NT).
The usual imagination in chemistry is that a minimum energy path is in a convex region of the potential energy surface.
We describe different schemes of convexity to handle the situation.
It comes out that NTs are the best ansatz for the problem:
NTs, which monotonically increase (or monotonically decrease), are automatically strictly pseudo-convex throughout, and they go throughout along a valley between minimum and saddle point.

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1. Introduction

• The minimum energy path (MEP) or reaction path of an adiabatic potential energy surface (PES) is roughly defined as a line in coordinate space, which connects two minima by passing the saddle point (SP), the transition structure of a PES [1]. The energy of the SP is assumed to be the highest value tracing along the reaction path.

• The MEP is a geometrically defined pathway. It means that only properties of the PES are taken into account, and that no dynamic behavior of the molecule is taken into consideration. We use here the driven coordinate method in the modern form of RGF [2-4], called Newton trajectory (NT) [5].

• Usually, in one's imagination the MEP is situated in a valley of the PES. All the different forms of a reaction path should connect minimum and SP of index one going through a valley. However, it contradicts the examples where the IRC does not fulfill the property: it is known that the IRC can go over a ridge of the PES.

• NTs can also go over a ridge of the PES, then they have a turning point [6]. Consequently, the classification of IRC and NTs belonging to MEPs or not, is of interest.

• We show that the IRC is an MEP if it does not cross the pseudo-convexity boundary of the PES, which is defined by a simple formula [7]. For NTs, the turning-point-case divides them into those which can serve as reaction paths, and others: if the NT does not contain a TP at the pathway from minimum up to the SP of index one, it can be used as a reaction path model [8].

• We show that NTs have a nice property: if they monotonically increase from minimum to SP then they automatically take a course throughout in a valley [7]. To our knowledge, NTs are the sole curves with this property.

2. Steepest Descent – IRC

• The steepest descent (SD) from the SP is a simple definition of a reaction path, which is well-known as the intrinsic reaction coordinate (IRC). Using the arc-length s for the curve parameter, an SD curve $\mathbf{x}(s)$ is defined by the system of vector equations

$$\frac{d\mathbf{x}(s)}{ds} = -\frac{\mathbf{G}(\mathbf{x}(s))}{|\mathbf{G}(\mathbf{x}(s))|} \tag{1}$$

where $\mathbf{G}(\mathbf{x})$ is the gradient vector of the PES.

• Starting at any $\mathbf{x}_0$ with $G(\mathbf{x}_0) \neq 0$, the solution of the differential equation leads monotonically decreasing to a minimum (or another deeper lying StP). The stationary points are the fixed points of the method – there the gradient is zero. In every non-stationary point the tangent of eq.(1) is defined and there cannot be a branching [9].

• SD curves can go down over a ridge. They do not always mirror the structure of valleys or ridges. The first derivatives of the PES are not sufficient to characterize the curvature of valleys, or ridges.

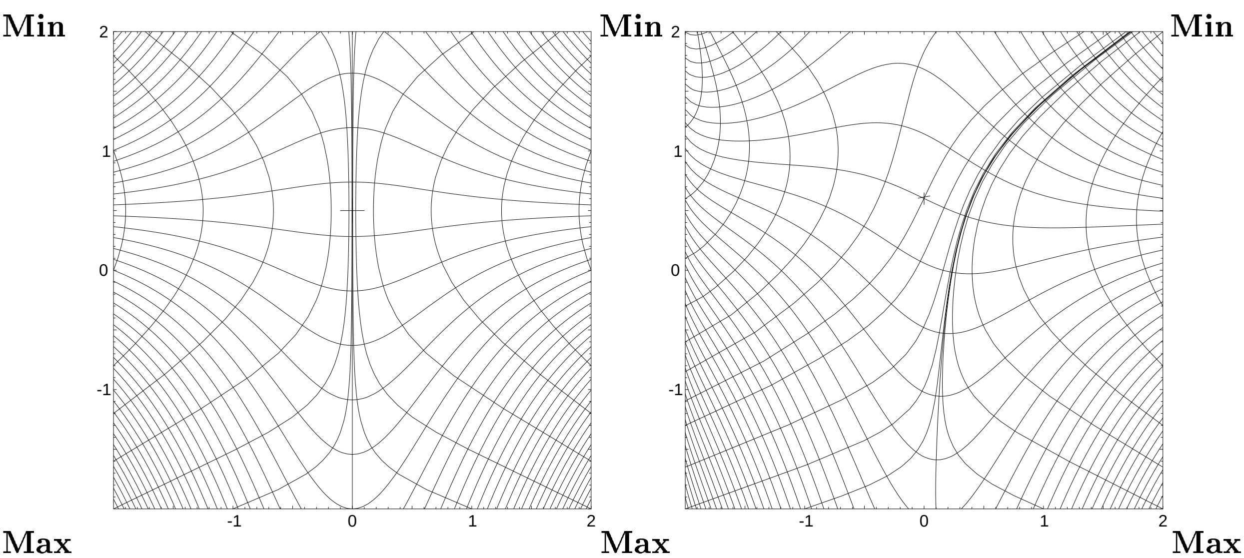

FIG. 1. Steepest descent over a ridge

On a ridge the SD does not go along a minimum. It goes down along a maximum seen across the pathway: this contradicts the definition of a MEP.

3. Turning point (TP)

Fig. 2 compares the distinguished coordinate method (right) with a Newton trajectory (left). If one starts at the global minimum A along the x direction, and minimizes orthogonally to x axis, then one follows the NT to $0°$ up to its first turning point. There the distinguished coordinate method (right) leaps, but the NT (left) continues. The x axis is the search direction, $r = (1, 0)$. The right hand side is a copy of Fig. 6 of K.Müller [10]. The pieces of the curves found there are from one and the same NT, see the left Figure.

Definition 1 ***A point is a turning point of a Newton trajectory if the tangent*** $\dot{\mathbf{x}}(t)$ ***is orthogonal to the search direction*** r ***which is parallel to*** $G(\mathbf{x}(t))$***.***

For the NT of Fig. 2, it is $(0, -1)$ the tangent at the TPs.

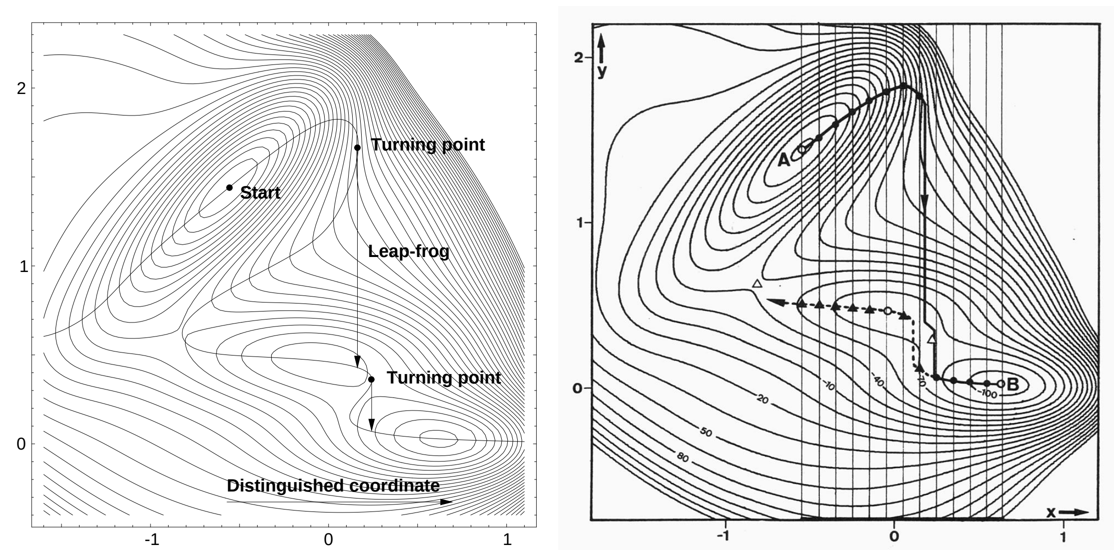

FIG. 2. Newton trajectory and distinguished coordinate method

4. Pseudo-convexity index

It is useful to have a criterion being simple and easy to calculate, if we follow curves through regions of valleys on a way from minimum upon saddle. Such a criterion is the index of pseudo-convexity. It is defined by the well known Rayleigh quotient with the adjoint A of the Hessian H .

Definition 2 *The pseudo-convexity index (*pcx *index) is the function*

$$\xi(\mathbf{x}) = \frac{G(\mathbf{x})^T A(\mathbf{x}) G(\mathbf{x})}{G(\mathbf{x})^T G(\mathbf{x})} \ . \tag{2}$$

Definition 3 *The set* $\Xi = \{\mathbf{x} : \xi(\mathbf{x}) = 0\}$ *is the **boundary of pseudo-convexity.***

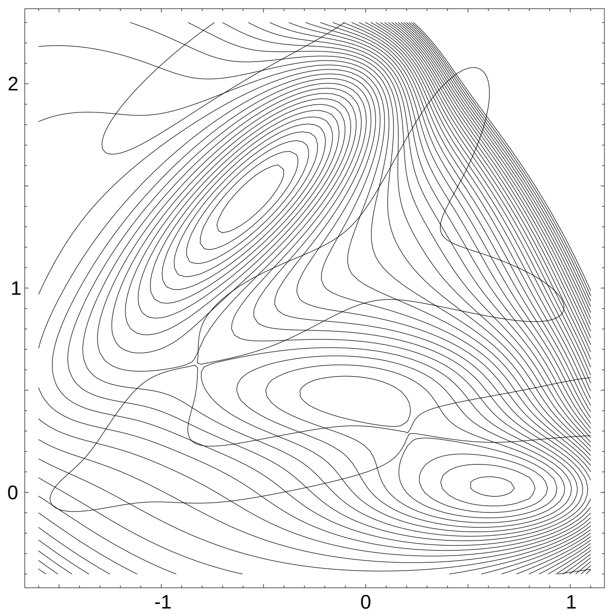

FIG. 3. Pseudo-convexity boundary Ξ on MB potential

Conclusion 1 *On a gradient extremal (GE) the relations of Table I hold for the signs of the eigenvalue* λ *belonging to the gradient, for the index of the curve point* x*, and for the* pcx *index* ξ*.*

Consequently, the pcx **index is positive in the neighborhood of an SP of index one in direction of the negative eigenvalue, but the** pcx **index is negative in direction of the positive eigenvalues.**

TABLE I. Relation between index, eigenvalue λ, and pcx index ξ

$\mathrm{ind}_2(\mathbf{x})$	0	0	1	1
λ	+	-	+	-
ξ	+	-	-	+

Conclusion 2 ***A gradient extremal crosses the boundary of pseudo-convexity*** Ξ ***in a VRI point.***

Proposition 3 ***The pseudo-convexity index*** ξ ***is zero at turning points and extraneous singularities of solutions of the Branin equation.***

In other words: the set Ξ is the set of all prospective TPs of NTs.

(Of course, not every NT has a TP.)

Definition 4 ***Two manifolds,*** M_1 ***and*** M_2***, are transversal in a common point*** $\mathbf{x}$***, if the tangential spaces of the manifolds in*** $\mathbf{x}$ ***span the whole*** $\mathbb{R}^n$***,***

i.e. $\mathbb{R}^n = T_{\mathbf{x}}M_1 + T_{\mathbf{x}}M_2$***.***

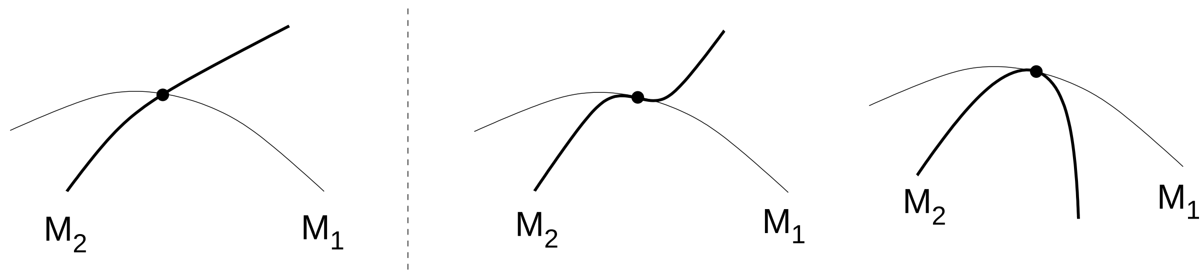

FIG. 4. Transversal (left) and tangential (right) curves

Let M be a compact, connected 1-codimensional differentiable manifold in $\mathbb{R}^n$, i.e. $\dim M = n-1$. Then $\mathbb{R}^n \setminus M$ consists of two open components, one of which is bounded. It is the interior of M. We use for M an equipotential surface.

We need definitions which connect the pcx index and convexity properties of the PES.

Definition 5 *[11] A set $\mathcal{K} \subset I\!R^n$ is named convex, if for all $x, y \in \mathcal{K}$ with $x \neq y$ the convex combination is lying in $\mathcal{K}$: $\lambda x + (1-\lambda) y \in \mathcal{K}$ for $\lambda \in (0,1)$.*

Let $\mathcal{K}$ be convex, $E : \mathcal{K} \to I\!R$. The set $\mathcal{L}_\alpha = \{\mathbf{x} \in \mathcal{K} \,|\, E(\mathbf{x}) \leq \alpha\}$ is named lower level set. Let $\lambda \in (0,1)$. A function E is named

- *pseudo-convex (pcx) if $(\mathbf{x}-\mathbf{y})^T \nabla E(\mathbf{y}) \geq 0 \Longrightarrow E(\mathbf{x}) \geq E(\mathbf{y})$,*
- *strictly pseudo-convex (s.pcx) if $(\mathbf{x}-\mathbf{y})^T \nabla E(\mathbf{y}) > 0 \Longrightarrow E(\mathbf{x}) > E(\mathbf{y})$.*

Definition 6 *M is named global boundary to vector field $\mathcal{N}_G$ of the tangents of Newton trajectories, if $\mathcal{N}_G$ is transversal to M.*

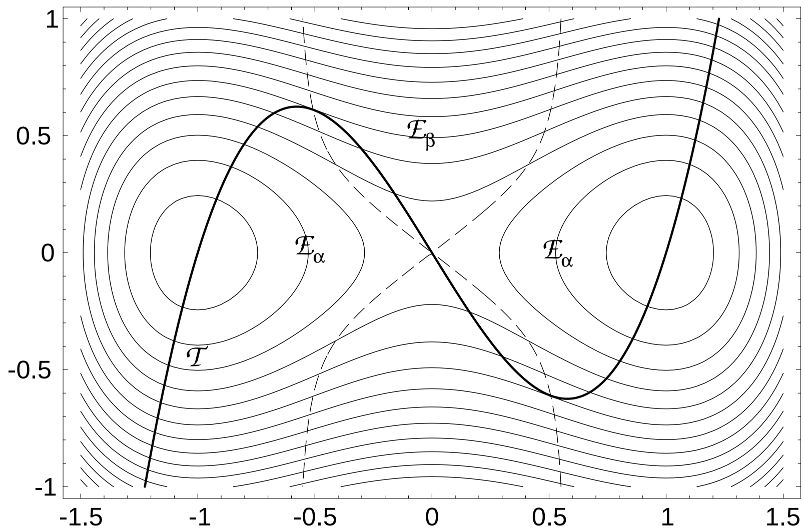

FIG. 5. Global boundary $\mathcal{E}_\alpha$ to Newton trajectory $\mathcal{T}$

In Fig. 5 the Newton trajectory $\mathcal{T}$ (bold) transversally crosses the equipotential surface $\mathcal{L}_\alpha$, and it tangentially touches $\mathcal{L}_\beta$. It holds $\xi(\mathbf{x}) = 0$ on the dashed line.

Conclusion 4 *A compact component of an equipotential surface $\mathcal{E}_\alpha$ is a global boundary of the vector field $\mathcal{N}_G$ to Newton trajectories if the* pcx *index is not zero on $\mathcal{E}_\alpha$.*

Proposition 5 *Be M a 1-codimensional, compact manifold in $I\!R^n$, and be the field of normals on M diffeomorph to S^{n-1}, then the interior of M is convex.*

Conclusion 6 *Let the* pcx *index not be zero on the boundary $\partial\mathcal{L}_\alpha = \mathcal{E}_\alpha$ of a compact component of a lower level set $\mathcal{L}_\alpha$, and let the boundary not contain stationary points, then the component is convex.*

Proposition 7 (Global boundary) *[12] Let $E : I\!R^n \longrightarrow I\!R$ and possible stationary points should not be degenerate. Additionally, let M be a global boundary to the Newton trajectories and M does not contain extraneous singularities of E. Then holds:*

- *The interior of M contains no periodic Newton trajectories.*
- *M is diffeomorph to S^{n-1},*
- *The interior of M contains only one stationary point.*

Figure 5 illustrates the proposition. Every component of the equipotential surface $\mathcal{E}_\alpha$ forms a global boundary to the field of tangent vectors to the NTs. Only on the line $\xi = 0$ the NTs have a TP. It means that compact components of equipotential surfaces which are not intersected by $\Xi = \{\mathrm{x} \in \mathcal{K} \,|\, \xi(\mathrm{x}) = 0\}$ form a global boundary to the tangent vector field belonging to Newton trajectories. These components enclose only one minimum. However, the other equipotential surfaces (i.e. $\mathcal{E}_\beta$) enclose both minima, and they do not form a global boundary to $\mathcal{N}_G$.

Theorem 1 *If the compact component of an equipotential surface $\mathcal{E}_\alpha$ does not contain stationary points, and if the pseudo-convexity index ξ is not zero on a corresponding lower level set $\mathcal{L}_\alpha \setminus \mathrm{Ess}(\mathcal{K})$ without stationary points, then the PES is strictly pseudo-convex (*s.pcx*) over this lower level set.*

The next step is to show that one can often continue the property of strictly pseudo-convexity uphill to an SP of index one.

Proposition 8 *Let $\mathcal{C}:(a,b)\rightarrow I\!R^n,\ \mathbf{x}(t)=\mathcal{C}(t)$ be a branch of a Newton trajectory connecting a minimum, $\mathcal{C}(a)$, and a saddle, $\mathcal{C}(b)$, then, the following items are equivalent:*

- *$\mathcal{C}$ is strictly pseudo-convex.*
- *The* pcx *index is larger than zero on $\mathcal{C}$.*
- *$\mathcal{C}$ increases strongly monotonically.*

Proposition 9 *Let $U_{\bar{\mathbf{x}}}$ be an open neighborhood of a regular point $\bar{\mathbf{x}}$, and let $U_{\bar{\mathbf{x}}}$ not contain stationary points. The* pcx *index for all $\mathbf{x}\in U_{\bar{\mathbf{x}}}$ is not equal to zero. Then for every $\alpha\in I\!R$ the restriction of the trajectory map on the intersection of $\mathcal{E}_\alpha$ and $U_{\bar{\mathbf{x}}}$ is a diffeomorphism on an open subset of S^{n-1}.*

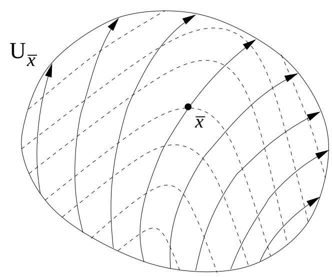

FIG. 6. Convex neighborhood of regular point $\bar{\mathbf{x}}$ with equipotential lines (dashed) and the field of Newton trajectories

In other words: if the pcx index is not zero over an open subset of the configuration space, and if the subset does not contain stationary points, then every NT crosses every equipotential surface once only in the subset. It means that the gradient never has the same direction on the intersection, and there do not exist NTs to every direction in the subset.

Now, the next aim is to transfer the content of Theorem 1 to the neighborhoods of proposition 9. It will be possible if the sets $\mathcal{E}_\alpha(U_{\bar{\mathbf{x}}})$ can be seen to be a part of a compact set being diffeomorph to S^{n-1} and convex.

Consequently, it is true if the $U_{\bar{\mathbf{x}}}$ is near a minimum, and the equipotential surfaces are curved positively in all directions.

For $\mathrm{ind}(\mathbf{x}) = 0$ the condition is fulfilled trivially.

For $\mathrm{ind}(\mathbf{x}) = 1$ the number of negative eigenvalues of the adjoint matrix A is $n-1$. From $\mathbf{u}_i^T H \mathbf{u}_i = \lambda \mathbf{u}_i^T \mathbf{u}_i < 0$ it follows $\mathbf{u}_i^T A \mathbf{u}_i = \mu \mathbf{u}_i^T \mathbf{u}_i > 0$, and vice versa. With Sylvester's law of inertia the number of positive and negative subspaces of a matrix is constant, respective of a linear operator, and it follows from $G^T A G = \xi ||G||^2 > 0$, $G^T H G < 0$, and so $\mathbf{v}^T H \mathbf{v} > 0$ for all $\mathbf{v}$ out of the tangential space to the equipotential surface staying orthogonally to G. So it holds:

Theorem 2 *Be $U_{\bar{\mathbf{x}}}$ an open and convex neighborhood of a regular point $\bar{\mathbf{x}}$, which does not contain stationary points. Be the* pcx *index larger than zero for all $\mathbf{x} \in U_{\bar{\mathbf{x}}}$, and $\mathrm{ind}(\mathbf{x}) \leq 1$. Then the PES is strictly pseudo-convex over $U_{\bar{\mathbf{x}}}$.*

5. Pseudo-convexity and structure of a valley

Around a minimum the pseudo-convexity boundary marks the end of pseudo-convexity, and in this sense the end of the valley character. The definitions of the pseudo-convexity index and the pseudo-convexity boundary are useful.

A sharpening of proposition 8 for a stricter convexity is not possible. A smooth curve connecting a minimum and an SP of index one always has at least one inflection point where the gradient has a local extremum. Such a curve cannot be convex. The pseudo-convexity makes that the curve increases strongly monotonically from minimum up to the SP. The change of the index at the inflection point is not important for answering the question of the character of the valley around the curve.

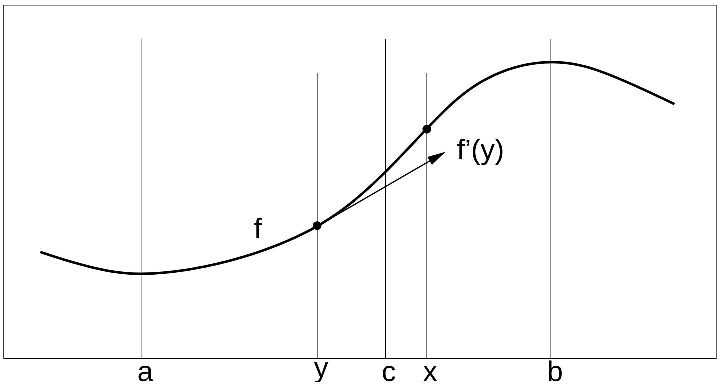

FIG. 7. Pseudo-convex curve between a and b. f is convex between a and c, but not between c and b

The pseudo-convexity of a curve is not a sufficient criterion for a valley. Every steepest descent curve is pseudo-convex, however, it can go over a ridge. On the other hand, also the condition that the pcx index is larger than zero over any smooth curve is not a sufficient criterion for the pseudo-convexity of the curve. A smooth curve $C : (a, b) \longrightarrow I\!R^n$, connecting a minimum, $C(a)$, and an SP of index one, $C(b)$, is strictly pseudo-convex if it increases strongly monotonically. On the basis of the Theorems 1 and 2 we find a general characterization for a valley with the help of the pseudo-convexity index.

Definition 7 ***Between a minimum, $\mathcal{C}(a)$, and a saddle, $\mathcal{C}(b)$, there is throughout a valley, if there is a smooth curve, a*** **valley curve**, ***connecting $\mathcal{C}(a)$ and $\mathcal{C}(b)$ and fulfilling throughout $\xi > 0$, and for which the energy increases strongly monotonically.***

From proposition 8 follows:

Theorem 3 ***The branch of a Newton trajectory may connect a minimum and a saddle point of index one. It is a valley curve if the*** pcx ***index over the branch is larger than zero.***

6. Discussion and Conclusion

• Up to now, there is no method which always finds a "valley path" between minimum and SP. The reason is that such a valley does not always exist. However, a valley curve can exist but not an NT which is a valley curve.

• We discuss the relation between the three curves of interest here, the IRC, the NT, and also the gradient extremal (GE), to describe a valley structure.

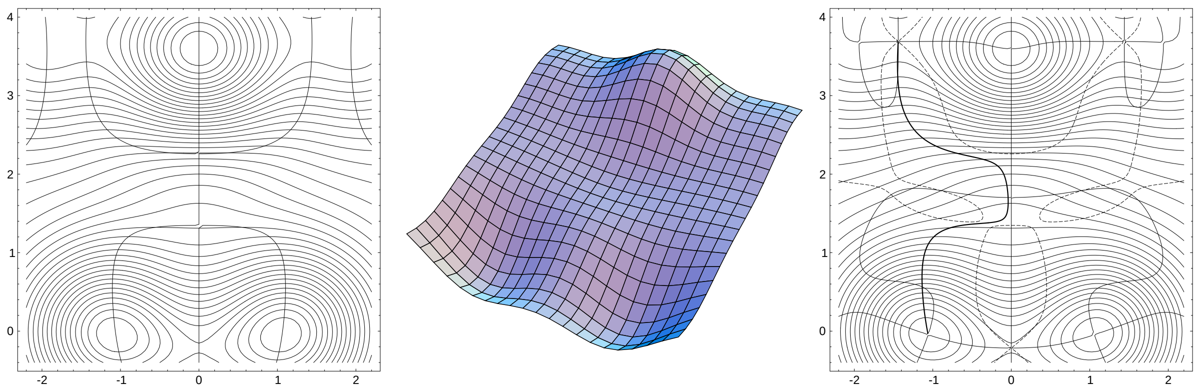

FIG. 8. Poseidon PES [7], left: the NT belonging to 90° has two consecutive VRI points and forms a double trident. Right: an NT being valley trajectory (bold), `pcx` boundary (dashed) and GEs (small)

The right part of Fig. 8 shows the "good" case for an NT being a valley trajectory from minimum to SP. Going through a valley region throughout means that along the increase of the reaction path we always have convex equipotential surfaces. NTs from the Branin method have special properties: a monotonically increasing NT automatically goes through a valley. Note that the GE does not connect the minimum and the SP of interest. (The IRC goes over a ridge.)

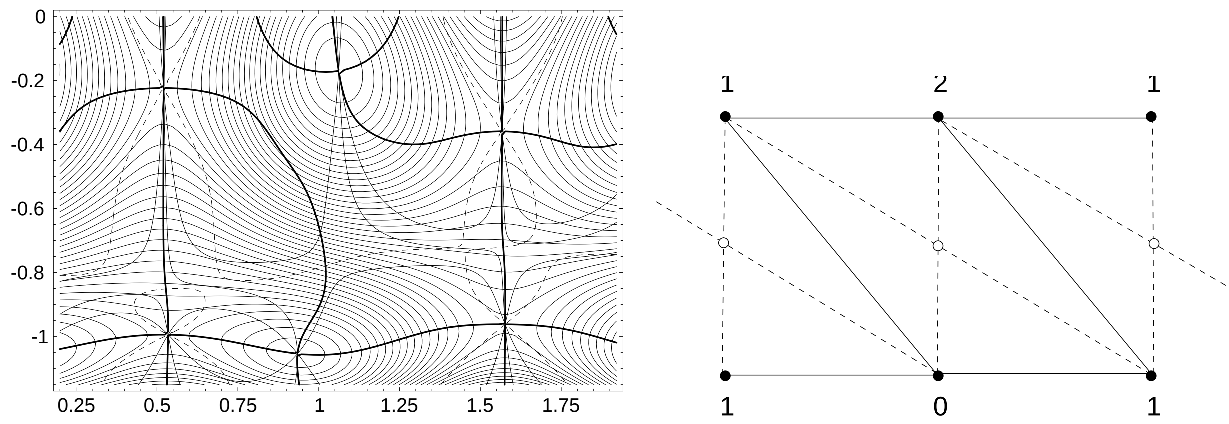

FIG. 9. PES of Smeyer et al. [19], modified [7,17], left: GEs (bold), `pcx` boundary (dashed) and three NTs (small); right: scheme of singular NTs (dashed) with VRI points (empty). Numbers are the index of the stationary points.

Fig. 9 shows the "bad" case, for an example where no NT connects the minimum, being below in the center, and the SP in the right upper corner. However, there is a valley curve.

From the minimum at $\approx (0.95, -1.05)$ **leads a small valley region around** $(1.45, -0.75)$ **to the saddle of index one at** $\approx (1.6, -0.3)$**. We may draw a valley curve "by hand" through that region like in a children's game.**

The scheme on the right hand side shows that there is no branch of an NT from the minimum to the SP of index one in the right upper corner. The situation for the other higher SP of the example seems to be quantitatively similar, however, it is qualitatively different.

There is a small "corridor" with valley character, here around $(0.65, -0.85)$**, being a bottle-neck, but the drawn NT exactly leads through the region of the corridor and connects minimum and the left upper SP with a valley trajectory.**

In Fig. 10 a NT wins the competition against the gradient extremal.

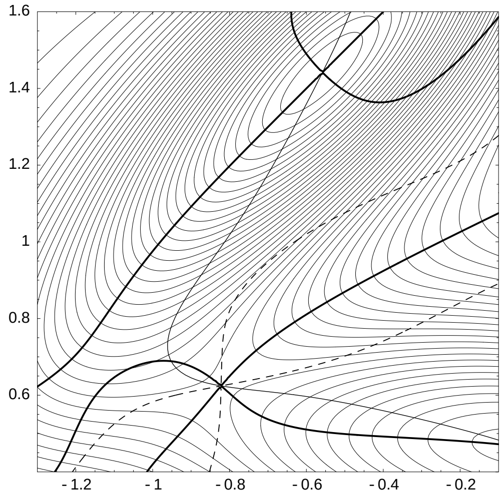

FIG. 10. Gradient extremals (bold), one Newton trajectory (thin) and `pcx` boundary (dashed) on MB potential

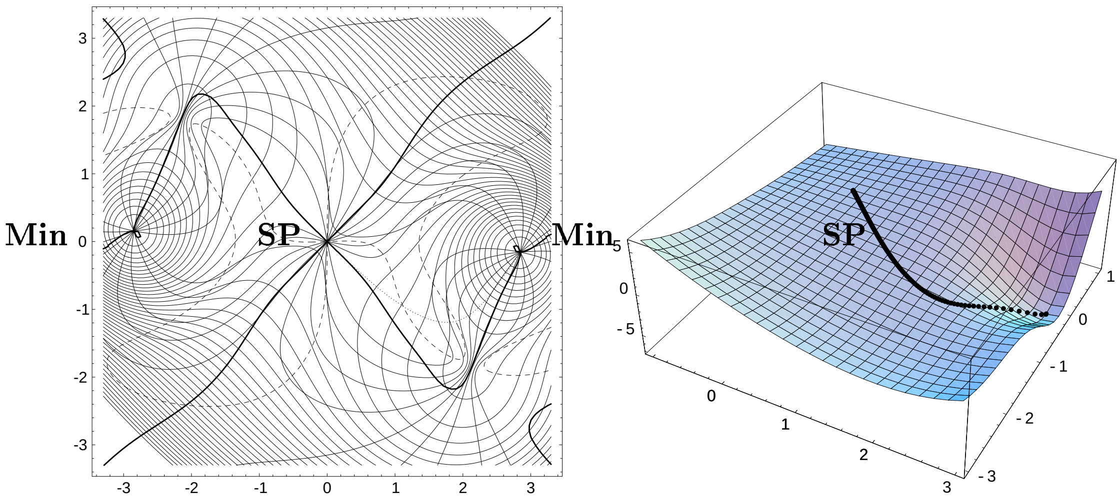

FIG. 11. PES [20], modified [7]. Dashed line is the `pcx` boundary between valley and ridge. Two minima at the sides are connected over SP at $(0, 0)$. The IRC (thin points) crosses the ridge. Right: IRC from SP.

A family of Newton trajectories is concentrated upon small gorges near $(\pm 2, \mp 2)$. However, none of them goes upon the SP throughout in the valley. They cross the other ridge near the SP, or diverge. None of the NTs are valley curves. There, the GE plays a lone hand: only the gradient extremal (bold) is a valley curve throughout.

• The aim of our visualizations is to support analysis and interpretation of reaction pathways. Chemists have a long tradition in inventing and applying models for the analysis of molecular transformations taking place in a reaction.

• The development of new ideas, definitions, and methods for modeling a reaction path critically depends on visualization as an effective way to gain an understanding of a problem.

• For a long time the IRC was the model of choice of theoretical chemistry. However, the IRC from SP downhill can enter a ridge. Then it loses the property to be an MEP.

• One may exclude this situation by employing the pcx index. If $\xi > 0$ on the whole IRC, it is a valley curve. The $\xi > 0$ condition gives one the possibility of a panoramic view over the reaction path of interest. The IRC is automatically decreasing throughout.

• If a Newton trajectory monotonically increases between minimum and saddle then it is automatically a valley curve. The $\xi > 0$ condition is fulfilled.

• Thus, the NTs are well adapted to the problem treated here: to enlighten the valley structure of the region around the reaction path.

7. References

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