Reaction Channels 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 definition of the Newton trajectory (NT). An NT follows a curve where the gradient is always a pointer to a fixed direction. Usually, a whole family of NTs connects two adjacent stationary points of an index difference of one. We will name such a family a reaction channel. The border between two reaction channels is formed by singular NTs which cross valley-ridge inflection (VRI) points. Examples are given with the Müller-Brown potential, and the potential energy surfaces of formaldehyde.

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1. Introduction

• The concept of the minimum energy path (MEP) or reaction path (RP) of an adiabatic potential energy surface (PES) is the usual approach to the theoretical kinetics of larger chemical systems [1].

• It is defined as any line in coordinate space, which connects two minima by passing the saddle point (SP), the transition structure of a PES. The energy of the SP is assumed to be the highest value tracing along the RP.

• Reaction theories are based either implicitly (transition state theory), or explicitly (variational transition state theory) on the knowledge of the RP [1]. These theories require local information about the PES along the RP only. They circumvent the dimension problem for medium-sized or large molecules: it is impossible to fully calculate their PES.

• The starting point is a geometrically defined pathway. It means that only properties of the PES are taken into account, no dynamic behavior of the molecule is taken into consideration.
Any parameterization s of the RP $\mathbf{x}(s)=(x^1(s),\ldots,x^n(s))^T$ is called reaction coordinate. We use here the distinguished or driven coordinate method in the modern form of RGF [2,3], also called Newton trajectory (NT) [6].

• Usually, in one's imagination the MEP is situated in a valley of the PES. But how the RP ascends to the SP is an uncertainty of the general definition of a reaction path. That opens the possibility to use a family of similar trajectories to define a reaction channel: it may be formed by "all" lines of a special character which connect, for example, the reactant minimum with one SP of interest.

• We propose the definition of Newton trajectories (NT) [2,3] to define reaction channels [4]. The older definition of an RP by gradient descent, the intrinsic reaction coordinate (IRC) of Fukui, or the steepest descent (SD), opens the possibility to divide the configuration space into basins of attraction, or catchment basins. They are defined as the set of points that will flow to it through gradient descent. The reaction channels of the NTs are another classification scheme for the configuration space. Thus, NTs are curves with an alternate property, in comparison to SD curves.

• Since there are different SPs around a minimum, different reaction channels have to exist. The question emerges, what are the borders between the channels? The answer is: every border is formed by NTs leading to valley-ridge inflection (VRI) points, so-called singular NTs.

2. Projection Operator

It is $S^{n-1} = \{\mathbf{x} \in I\!R^n \mid \|\mathbf{x}\| = 1\}$ the unit sphere in $I\!R^n$. Elements from S^1 - the unit circle - are given as angles with point $(1,0) \in S^1$ to be $0°$.
We choose a column vector $\mathbf{r} \in S^{n-1}$ for a projection. It is a unit vector. The transposed vector $\mathbf{r}^T$ is a row vector. The dimension of r is $(n \times 1)$ where that of $\mathbf{r}^T$ is $(1 \times n)$. We form the dyadic product $\mathcal{D}_r = \mathbf{r} \cdot \mathbf{r}^T$ which is an $(n \times n)$ matrix. $\mathcal{D}_r$ projects with r:

$$\mathcal{D}_r \ \mathbf{r} = (\mathbf{r} \cdot \mathbf{r}^T) \cdot \mathbf{r} = \mathbf{r} \ (\mathbf{r}^T \cdot \mathbf{r}) = \mathbf{r} \ . \tag{1}$$

The projector which projects orthogonally to r is with the unit matrix I

$$\mathcal{P}_r = \mathbf{I} - \mathcal{D}_r \ . \tag{2}$$

3. RGF, Newton trajectories

The concept is that a selected gradient direction is fixed along the curve $\mathbf{x}(s)$

$$G(\mathbf{x}(s))/\|G(\mathbf{x}(s))\| = \mathbf{r}, \tag{3}$$

where r is the unit vector of the search direction. The property (3) is realizable by a projection of the gradient employing $\mathcal{P}_r$ of (2). We pose

$$\mathcal{P}_r\, G(\mathbf{x}(s)) = \mathbf{0}\ . \tag{4}$$

$\mathcal{P}_r$ is a constant matrix of rank $n-1$.

Definition 1 *The map* $\mathcal{R} : I\!R^n \times S^{n-1} \longrightarrow I\!R^{n-1}$, *with* $\mathcal{R}(\mathbf{x}, \mathbf{r}) = \mathcal{P}_r G(\mathbf{x})$ *will be called the* reduced gradient, *and* $\mathbf{r} \in S^{n-1}$ *will be called* search direction. *The equation*

$$\mathcal{R}(\mathbf{x}, \bar{r}) = \mathbf{0} \tag{5}$$

is for a fixed $\bar{\mathbf{r}} \in S^{n-1}$ *the* reduced gradient equation *to the search direction* $\bar{\mathbf{r}}$.

Based on the explicit definition, the predictor-corrector method of the reduced gradient following (RGF) [3] traces a curve (4) along its tangential vector by the derivative to obtain the tangent $\mathbf{x}'$

$$\mathbf{0} \ = \ \frac{d}{d\,s}[\mathcal{P}_r\ G(\mathbf{x}(s))] = \mathcal{P}_r\ \frac{d\,G(\mathbf{x}(s))}{d\,s} = \mathcal{P}_r\ \mathbf{H}(\mathbf{x}(s))\ \mathbf{x}'(s)\ . \tag{6}$$

The RGF is a simple but effective procedure to walk along the PES in order to determine all types of StPs [2]. A family of RGF curves connects the extrema if we vary the search direction r [6,7].

Definition 2 *Let* $r \in S^{n-1}$. *We will name* Newton trajectory (NT) *in* $\mathcal{K}$ *to the direction* r *the set:*

$$\{\mathbf{x} \in \mathcal{K} \,|\, G(\mathbf{x}) = r\|G(\mathbf{x})\|\}\ . \tag{7}$$

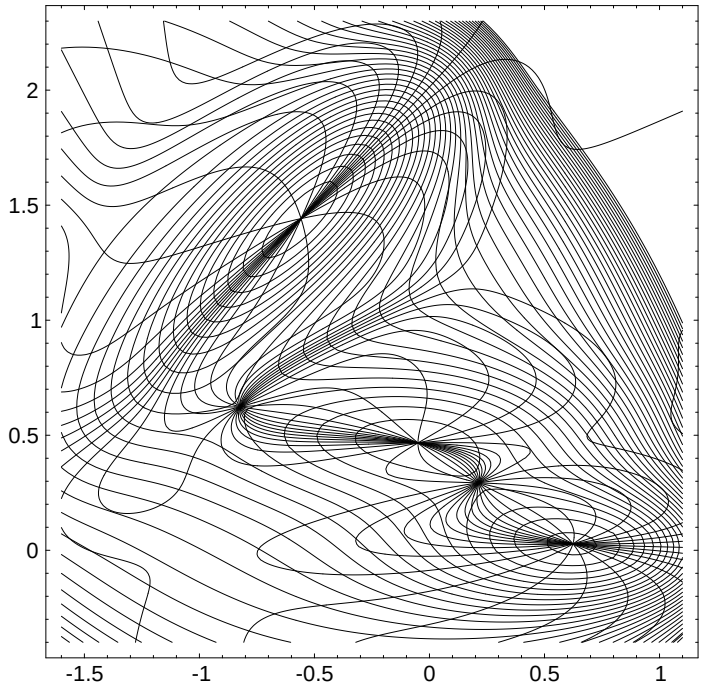

FIG. 1. A family of Newton trajectories on Müller-Brown (MB) PES

4. Branin's method

The reduced gradient approach shows an analogy to the mathematical theory of Branin [8], the global Newton method. It utilizes the adjoint matrix A of the Hessian matrix H. The adjoint matrix satisfies the relation

$$H\,A = \det(H)\,I\ , \tag{8}$$

where $\det(H)$ is the determinant of H, and I is the unit matrix. The adjoint matrix A is used to define an autonomous system of differential equations for the curve $\mathbf{x}(s)$, where s is a curve parameter

$$\frac{d\mathbf{x}(s)}{ds} = A(\mathbf{x}(s))\ G(\mathbf{x}(s))\ . \tag{9}$$

Proposition 1 ***Solutions of Branin (9) are branches of Newton trajectories.***

5. Extraneous singularities

A special subset of degenerate points can be interpreted to be the branching points of reaction paths.

Definition 3 *A* valley-ridge-inflection point (VRI) *is located where the gradient is orthogonal to a zero eigenvector of the Hessian.*
The subset of such points is $\mathrm{Ext}(\mathcal{K})$.

We use results of Diener [9]. On a 2D PES the VRI points are single, isolated points. They form a "zero-dimensional manifold". For an $n-$dimensional PES the VRI points can be a manifold of a dimension up to $n-2$.
Such manifolds are found for the PES of water by Hirsch et al. [10], for formaldehyde by Quapp and Melnikov [11], for $C_2H_5^+$ by Quapp and Heidrich [12].

• It is a fundamental property that the VRIs are not isolated points in higher dimensions. In theoretical chemistry it is practice to report single VRI points. However, for molecules, these points are part of the high-dimensional manifold of VRI points of the PES.
A VRI point in two dimensions is characterized by a 1-dimensional kernel of the reduced Hessian $\mathcal{P}_r H(\mathbf{x})$. Thus, there are two tangents to the NT at x.

Proposition 2 *(*Index theorem *[9]) Let* $\mathbf{x}_1$ *and* $\mathbf{x}_2$ *be stationary points connected by a regular branch of a Newton trajectory. Then it holds*

$$\mathrm{ind}_2(\mathbf{x}_1) \neq \mathrm{ind}_2(\mathbf{x}_2) \ . \tag{10}$$

A regular branch of a Newton trajectory connects an StP of an odd index and an StP of an even index. The index theorem has direct practical use: if one numerically follows the branch of an NT, and one connects StPs of a "false" index by the procedure then one has a tool to detect the error.

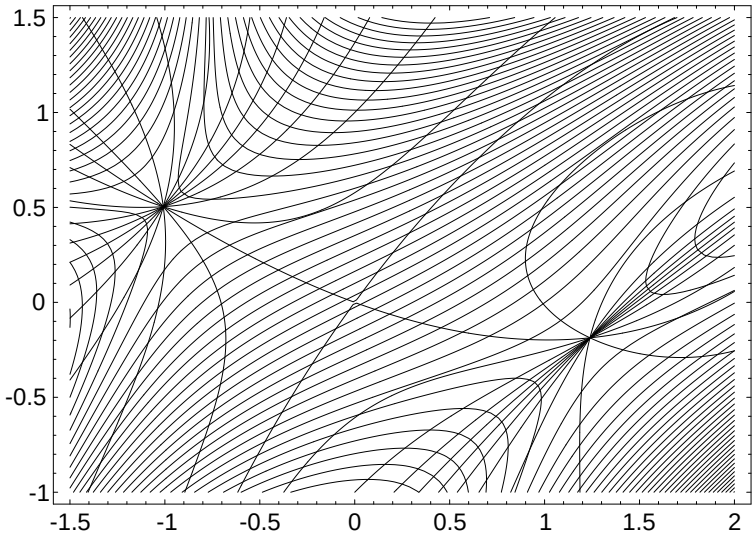

FIG. 2. Index theorem. The surface shows two adjacent SPs of index one. There is no regular branch of an NT connecting the SPs. Between the SPs a VRI point has to exist. The singular NT is shown which leads to the VRI point and branches there.

At least one change of the index of a regular NT is given by an inflection point of the energy profile. Every continuous connection of two StPs has at least one such inflection point. The extraneous singularity breaks the index along an NT by an additional odd number (by ± 1), see Fig. 3: the change of the index happens at the VRI point. We find the index transformations 0-2 and 1-1′. Around the VRI point there are regular branches of neighboring NTs which connect 0-1′ and 1-2, or 0-1 and 1′-2, correspondingly. The word creation "valley-ridge inflection" point is coined by the 2D imagination of a valley branching. Such a singularity has a phase portrait of saddle type, see Figs. 4 and 5.

The imagination in the $n-$dimensional case is difficult. For 3D there are three different types: center type and saddle type, and for the transition between both the cusp type.

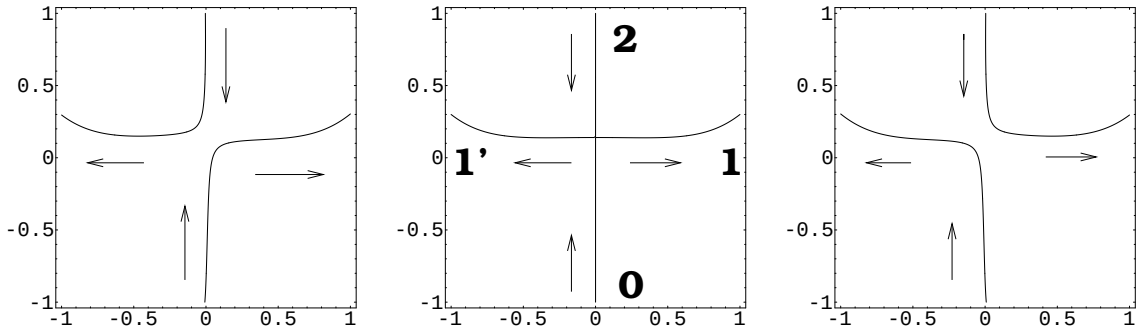

FIG. 3. Index theorem. Typical scheme for the relation of StPs with different index surrounding the VRI point of an NT (center). Side parts: neighboring regular NTs.

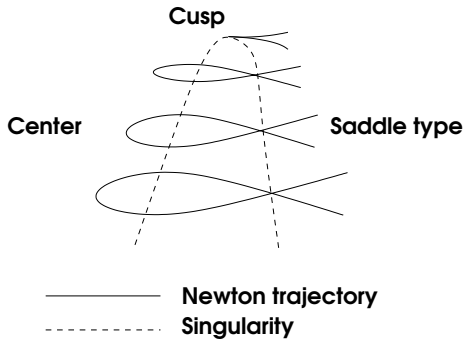

FIG. 4. Phase portraits of Newton trajectories

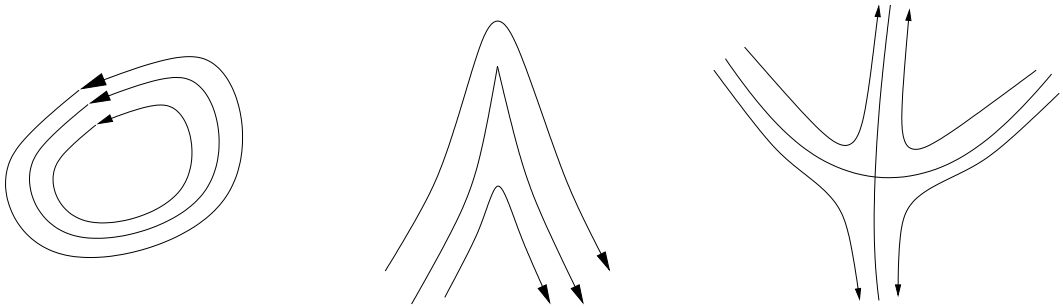

FIG. 5. Phase portraits of NTs around extraneous singularities. From left to right: center type, cusp type and saddle type

6. Example: VRI points along an NT on the PES of formaldehyde

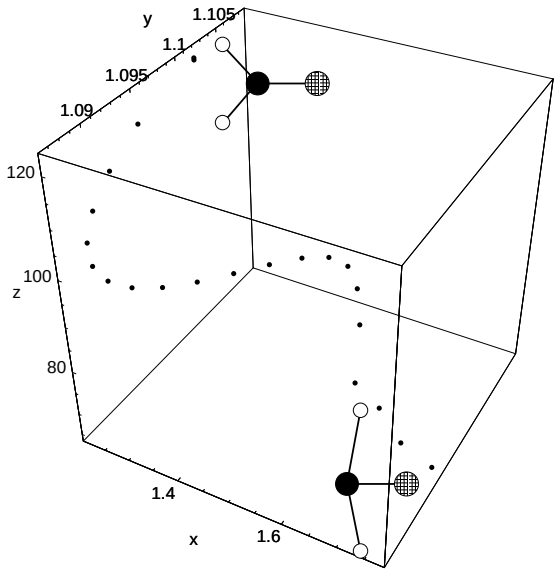

FIG. 6. Newton trajectory on PES of H_2CO. The path is given in reduced configuration space with x=r_{CO}, y=r_{HC}, z=$\angle$HCO in C_{2v} symmetry. The NT goes from global minimum (top) to an SP of index 3 (bottom).

The formaldehyde is calculated with the restricted Hartree-Fock method (RHF) and STO-3G basis set. There are many StPs up to SPs of index 3. The example NT starts with the global minimum and follows the search direction of the symmetric bending. Along the curve the energy strongly monotonously increases from the global minimum left-above to the SP of index 3 right-below.
Along the NT there are two VRI points.
The Figures 7, 8 are 2D sections of the 6-dimensional PES passing the two VRI points.

TABLE 1. Two stationary points on PES of H_2CO connected by an NT [2].

Index	Energy (a.u.)	Symmetry	r_{CO} (Å)	r_{CH} (Å)	α_{HCO} (deg.)
0	-112.3544	C_{2v}	1.217	1.101	122.74
3	-112.0122	C_{2v}	1.770	1.095	65.44

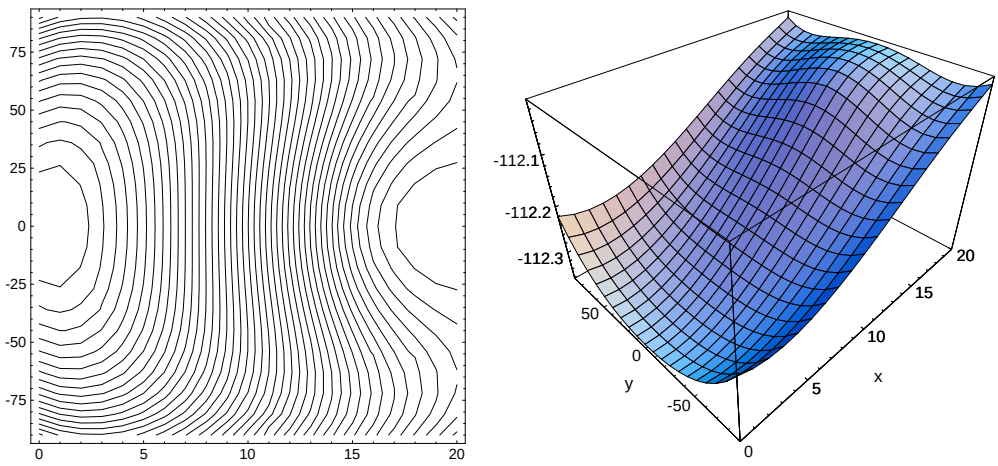

FIG. 7. PES section of H_2CO with VRI1. y axis: dihedral angle, x axis: change of r_{CO} and the symmetric α_{HCO}. At VRI point the valley branches uphill and breaks the C_{2v} symmetry to C_S symmetry.

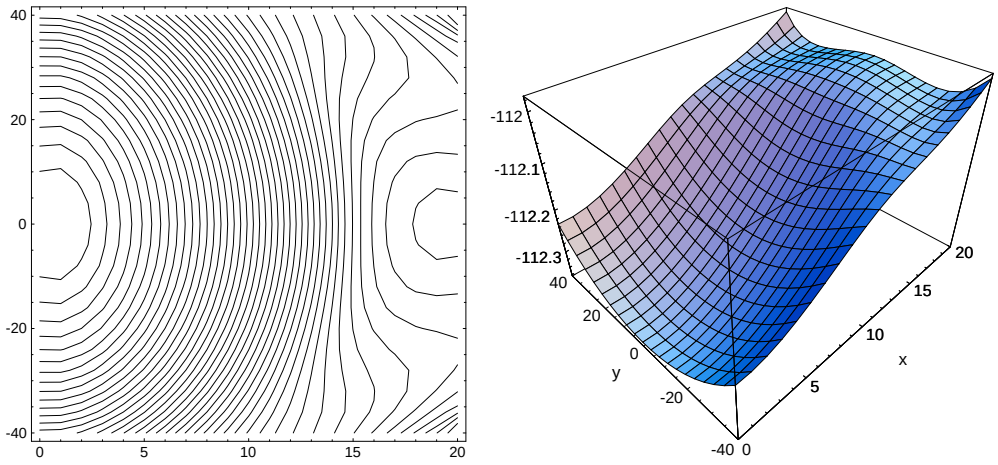

FIG. 8. PES section of H_2CO with VRI. y axis: deviation of the symmetry of the angles α_{HCO}, x axis: parameter with r_{CO} and α_{HCO}. At VRI point the valley branches and breaks the C_{2v} symmetry to C_2 symmetry.

7. Newton channels

Every StP is on all NTs.

Definition 4 Two stationary points are adjacent ***if they are connected by a regular branch of a Newton trajectory.***

Now, we look for all branches which start at a fixed StP, A. Which part of that family connects A with other StPs? To any branch beginning at A belongs a direction $r \in S^{n-1}$. Thus, since we fix A, we can turn the point of view to S^{n-1}, if we identify the directions r with their corresponding branches by the help of the trajectory map $\underline{r} = G/\|G\|$. We put A for the initial point of all branches, and identify the search directions of all these NTs with all points of S^{n-1}. Every branch has three possible final points:

(i) an StP with an index difference of 1 to A, or

(ii) a VRI point, or

(iii) a point of the border of the configuration space.

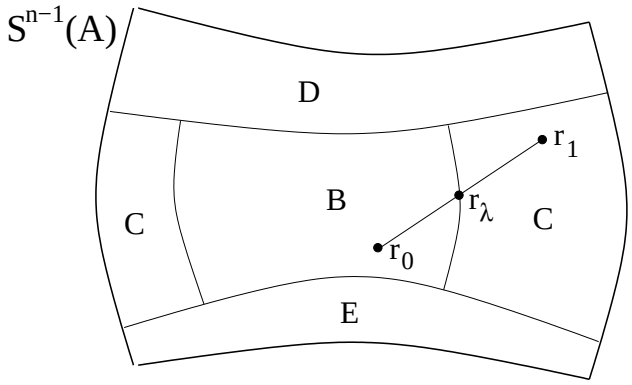

FIG. 9. Scheme of S^2 for the Newton channels starting at A. The representation is opened like a map of the world in Mercator projection. Points B to E depict the sets of different search directions belonging to the Newton channel, respectively. Every Newton channel leads to one StP (B, C, D or E). If A is minimum then the points B to E will be SPs of index one.

The VRI points can form pieces a manifold of a dimension up to $(n-2)$. Branches which meet the VRI points are singular branches. They form a $1-$codimensional submanifold on S^{n-1}. It divides the S^{n-1} into a disjunct system of open sets. The border of the sets of S^{n-1} is formed only from singular directions.

Definition 5 *Regular branches of different Newton trajectories will be named* equivalent *if they can be transformed from one to the other without meeting a singular branch, where the transformation is a continuous variation of the search direction. The corresponding equivalence class is the* Newton channel.

- The Newton channels starting in one StP are divided by walls formed by singular branches. The walls are "thin" because they have a lower dimension. The walls are a separatrix and there is a disconnection of the sets formed by the regular NTs. An NT starting at a point that is strictly on a wall will never leave the border (by definition).
- The StP, to which a channel leads, has to belong to the wall of the channel as well, thus, to the component of connection of the singular NTs forming the wall. Singular NTs usually lead to at least three StPs because they bifurcate at a VRI point.
- We interpret the Newton channels as approximations of reaction channels. Fig. 9 is a model of the region around reactant A for reactions $\mathrm{A} \longrightarrow \mathrm{P}_1$ over the transition structure B and $\mathrm{A} \longrightarrow \mathrm{P}_2$ over the transition structure C, taking place from the same reactant A to the product systems P_1 and P_2, and so on. To every reaction belongs one reaction channel, and the channels are divided by thin walls. Pathways going on in the walls meet a bifurcation from which branches lead aside to the two transition structures. Thus, the singular NTs of the wall between B and C belong to both SPs.

• To every point of the PES belongs an NT. Thus, it is possible to divide the PES into Newton channels, totally. All channels are partitioned by thin walls of singular branches of NTs.

Theoretically, there can be channels without StPs.

Theoretically, the system of channels needs not be simply connected.

• It emerges that we can connect the StPs of a PES by Newton channels in form of a graph.

Conclusion 3 *A PES can be represented as a* Newton graph*: vertices are the StPs, edges are the Newton channels. With the index theorem it follows that a Newton graph cannot contain circles with an odd number of edges. Further, Newton graphs do not have loops (edges connecting one vertex with itself).*

• To any Newton channel belongs the volume of the induced tangents. We can assign to every edge a weight by the volume of the Newton channel. It is the measure of the set of directions of S^{n-1}, the NTs of which have branches in this Newton channel.

• In this kind we can assign many NTs, or few NTs to a region of the PES !

It is not trivial because to every point of the PES belongs one NT.

The "density" of NTs differs from region to region.

• Conclusion: we can define an RP as the region of the PES where the density of NTs is high and the PES forms a valley. The devise will be useful at least in the cases where the SP is on the top of the valley, and where the RP does not bifurcate [15]. In these cases the imagination of a reaction channel is well adapted to reality.

8. Example Müller-Brown potential

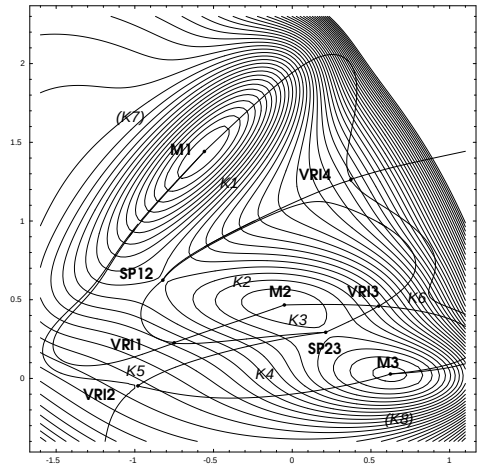

FIG. 10. Singular branches of Newton trajectories on Müller-Brown potential dividing the configuration space in channels

It is possible to fully study the 2D PES with NTs. We follow an NT along its branches. We begin at the global minimum M_1 in all directions ($r \in [0°, 360°)$). In Fig. 1 the distance of the search directions from one trajectory to the next is always equal. It can be observed that the trajectories concentrate in valleys, or on ridges. It can be seen that the more NTs lead through a region the more the equipotential surfaces are curved. This effect will grow dramatically in higher dimensions.

Now we treat the Newton trajectories to all search directions in the interval $[0, 180°)$, $\mathcal{K} = (-1.6, 1.1) \times (-0.4, 2.3)$. Four NTs meet singular points, see Fig. 10. The other NTs belong to 4 sets of the topological equivalence classes of regular NTs in Fig. 11. The singular branches of MB potential are the "walls" (here lines) of the Newton channels. The classes of regular branches, which connect two stationary points, respectively, are shown summarily in Figs. 11 and 12. Newton channels are depicted by K1 to K8, where the channels K7 and K8 lead from a minimum to the border of $\mathcal{K}$.

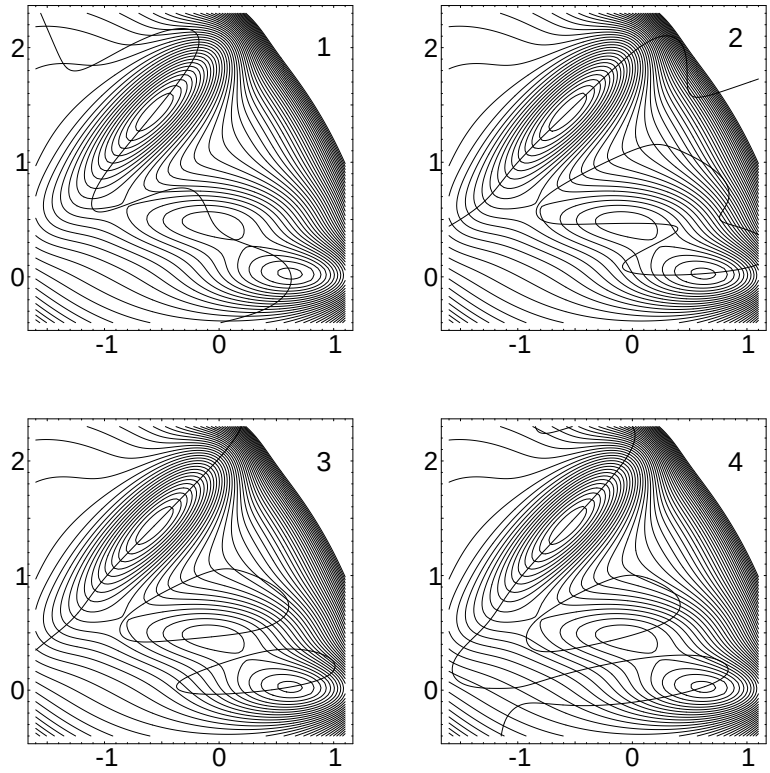

FIG. 11. Representatives of the 4 classes of regular NTs.

In Fig. 11 four representatives are shown, respectively. Class 1 is best suited for the search of StPs. It connects all StPs with one line, one connected component. Class 1 has a measure of 143.6° from 180°.

Figs. 10 and 12 show, that the Müller-Brown potential is separated into an internal and an outer region of NTs, correspondingly. The outer region itself is again separated into two parts. It is covered with regular trajectories only from the minima M1 and M3. Starting at minimum M2, two Newton channels lead only to the SPs S12 and S23. Starting at the minima M1 and M3 a main channel leads to direction of M2 (K1 with 39,9% of all branches, or K4 with 56,8% of all branches). Side channels (K5 with 1.3%, or K6 with 2%) "jump over" the central minimum M2.

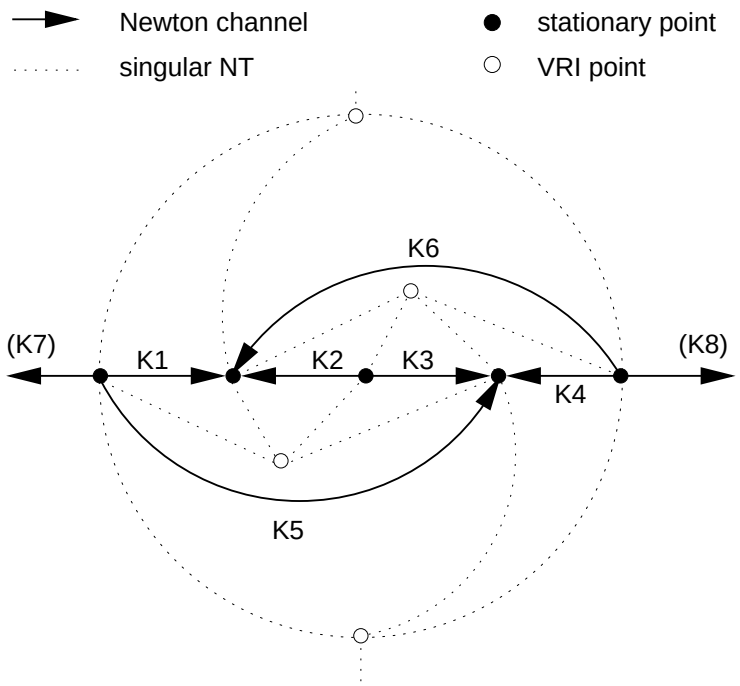

FIG. 12. Graph of Newton channels (arcs are pointer to SPs), and singular Newton trajectories on Müller-Brown potential. Vertices are minima and SPs.

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