



# The reaction pathway of a potential energy surface as curve with induced tangent

Michael Hirsch, Wolfgang Quapp \*

*Mathematical Institute, University of Leipzig, Augustus-Platz, D-04109 Leipzig, Germany*

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## Abstract

The reaction path is an important concept of theoretical chemistry. We employ the definitions of the Newton trajectory (NT) and of the gradient extremal (GE). An NT follows a curve where the gradient is always a pointer to a fixed direction. A GE is a curve where the gradient of the potential energy surfaces (PES) is eigenvector of the Hessian. Examples are given with the Müller–Brown potential and further model PESs. An induced tangent opens the possibility to follow the curve by a predictor–corrector method. We show that the two kinds of curves can be treated as curves with induced tangent, however, the gradient descent, or intrinsic reaction coordinate not.

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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 [1,2]. It is a 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 [2]. These theories require local information about the PES along the RP only. They circumvent the dimensionality dilemma for medium-sized or large molecules: it is impossible to fully calculate their PES. The starting point is a geometrically defined pathway which may serve as an RP. Geometrically defined means that only properties of the PES

are taken into account, and that no dynamic behavior of the molecule is taken into consideration. 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 RP definition. We use here the distinguished coordinate method [3] in the modern form of RGF [4,5], also called Newton trajectory (NT), and the gradient extremal [6].

To be able to numerically follow a curve point by point using a predictor–corrector method, it is important that the curve can be defined by an induced tangent [7,8]. In this Letter we prove in Section 3 that NTs and gradient extremals (GEs) fulfill that important property [8].

## 2. Potential energy surface

The adiabatic PES of the molecular system of observation is the basis of our treatment. Using the Born–Oppenheimer approximation, the PES is the sum of the Coulomb-repulsion of the atom kernels and the Schrödinger equation of the electrons  $\mathcal{H}\Psi = E\Psi$ .

\* Corresponding author. Fax: 49 341 97 32199.

E-mail address: [quapp@rz.uni-leipzig.de](mailto:quapp@rz.uni-leipzig.de) (W. Quapp).

URL: <http://www.mathematik.uni-leipzig.de/MI/quapp>

Another way of computation is the molecular mechanics. The explicit calculation of the energy  $E$  is not of interest, here. We assume the PES is given by a scalar function of the coordinates of the molecule at every point of interest:

**Definition 1.** Let  $\mathcal{K}$  be an open subset of  $\mathbb{R}^n$ .  $\mathcal{K}$  is the *configuration space* of the PES. Let  $\mathbf{x} = (x_1, \dots, x_n) \in \mathcal{K}$ . The function  $E(\mathbf{x}) : \mathcal{K} \rightarrow \mathbb{R}$  is an  $n$ -dimensional *potential energy surface* (PES). The derivative  $G : \mathcal{K} \rightarrow \mathbb{R}^n$  with

$$G(\mathbf{x}) = \left( \frac{\partial E}{\partial x_1}(\mathbf{x}), \dots, \frac{\partial E}{\partial x_n}(\mathbf{x}) \right)^T$$

is the *gradient* and the *Hessian* matrix  $H(\mathbf{x}) \in \mathbb{R}^{n \times n}$  is

$$H(\mathbf{x}) = \left( \frac{\partial^2 E}{\partial x_i \partial x_j}(\mathbf{x}) \right)_{i,j=1}^n.$$

The configuration space of a molecule is restricted. We assume at least a twofold differentiability of the PES for practical reasons – for the use of the diverse applications. The Hessian is symmetric and has the partition into eigenvalues and eigenvectors:

$$H = UAU^T, \quad (1)$$

with  $U = (\mathbf{u}_1, \dots, \mathbf{u}_n)$  and  $A = \text{Diag}(\lambda_1, \dots, \lambda_n)$ , with  $H\mathbf{u}_i = \lambda_i\mathbf{u}_i$ ,  $i = 1 \dots n$ .

**Definition 2.** A point  $\mathbf{x} \in \mathcal{K}$  is *nondegenerate* if  $\det H(\mathbf{x}) \neq 0$ . The *index* of a nondegenerate point  $\mathbf{x} \in \mathcal{K}$  is the number of negative eigenvalues of  $H(\mathbf{x})$ . We write  $\text{ind}(\mathbf{x})$ . A point  $\mathbf{x}_0 \in \mathcal{K}$  with  $G(\mathbf{x}_0) = \mathbf{0}$  is named *stationary point* (StP). A nondegenerate stationary point,  $\mathbf{x}_0$ , is *minimum* if  $\text{ind}(\mathbf{x}_0) = 0$ , or *maximum* if  $\text{ind}(\mathbf{x}_0) = n$ , or *saddle point of index  $i$*  if  $\text{ind}(\mathbf{x}_0) = i$ ,  $0 < i < n$ .

We assume that no StP is degenerate, i.e., that for all  $\mathbf{x} \in \mathcal{K}$  it holds the regularity condition  $\|G(\mathbf{x})\| + |\det H(\mathbf{x})| > 0$ . Nondegenerate StPs are isolated [9].

### 2.1. Valley-ridge-inflection point

A special subset of degenerate points can be conjunctured to be the branching points of RPs. A valley-ridge-inflection point (VRI) is located where the gradient is orthogonal to a zero eigenvector of the Hessian [10]. At a VRI, the gradient does not lie in the kernel of the Hessian, and an augmented Hessian with gradient does not lift the defect of the rank:

$$\{\text{VRI points}\} = \{\mathbf{x} \in \mathcal{K} \mid \text{rank}[H(\mathbf{x}), G(\mathbf{x})] < n\}. \quad (2)$$

The bracket means matrix augmentation:  $[H(\mathbf{x}), G(\mathbf{x})] \in \mathbb{R}^{n \times (n+1)}$ . A VRI point need not be ‘symmetric’ [11]. VRI points are independent on any curve definition.

### 2.2. Reaction pathways

A central definition in *activated-complex theory* [12] is the reaction coordinate. It is the unfolded  $x$  axis for the energy profile of the reaction in Fig. 1. The reaction coordinate is the Interval  $(a, c)$  of a curve parameter of a reaction path  $\mathcal{C} : (a, c) \rightarrow \mathcal{K}$  on the PES connecting the reactant and the product over a transition state. (Since a reaction results in more products than the RP branches.) The shape of the energy profile depends on the pathway chosen. But the height of the barrier does not depend on the way. It is the energy of the SP. The reaction profile takes its global maximum there. If a chemical system has an energy at least like the SP, the activated state, the system transforms to the product. We treat a piece of the RP  $\mathcal{C}$ , a curve which connects two StPs, say minimum,  $\mathbf{x}$ , and SP of index 1,  $\mathbf{y}$ . In the following, we use that  $\mathcal{C}$  is defined over the open interval  $(a, b)$ , thus,  $\mathcal{C} : (a, b) \rightarrow \mathbb{R}^n$ ,  $C(t) = \mathbf{x}(t)$ . Let  $C$  be smooth and injective, and we assume that no StP is contained. Let the limit of the lower interval point  $\mathcal{C}(a)$  be the minimum  $\mathcal{C}(a) := \mathbf{x} = \lim_{t \rightarrow a} \mathcal{C}(t)$ , and let the SP be the limit of the upper interval point  $\mathcal{C}(b) := \mathbf{y} = \lim_{t \rightarrow b} \mathcal{C}(t)$ . The tangent  $\dot{\mathbf{x}}(t)$  of such a curve  $\mathcal{C}$  on  $(a, b)$  is unique and not zero  $\dot{\mathbf{x}}(t) \neq \mathbf{0}$ . But the limit  $\lim_{t \rightarrow a} \dot{\mathbf{x}}(t)$  will be zero (as well as the limit  $t \rightarrow b$ ).

The assumption of the reaction coordinate to be a curve parameter is also a possibility to use curvilinear coordinate systems [13].

### 3. Induced tangent

For special curves, the tangent can be given by an  $(n-1) \times n$ -matrix. An important property of such a definition is the possibility to locally decide whether a point belongs to the curve, or not. (For example, the intrinsic

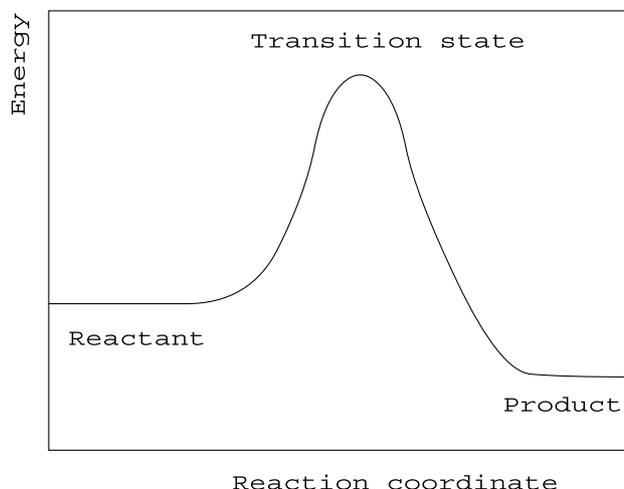


Fig. 1. Schematic reaction coordinate unfolded on  $x$  axis.

reaction coordinate (IRC) does not possess the property, see below.)

**Definition 3.** Let  $M = M(\mathbf{x})$  be an  $(n-1) \times n$  matrix of rank  $n-1$ . We define a unique vector  $\mathbf{t}(\mathbf{x}) \in \mathbb{R}^n$  by three conditions:

$$\begin{aligned} M\mathbf{t} &= \mathbf{0}; && \text{subspace,} \\ \|\mathbf{t}\| &= 1; && \text{length,} \\ \det \begin{pmatrix} M \\ \mathbf{t}^\top \end{pmatrix} &> 0; && \text{orientation.} \end{aligned}$$

We will call  $\mathbf{t}(\mathbf{x}) \in \mathbb{R}^n$  the *tangent induced by M* [7].

There is a singularity of the definition in points  $\mathbf{x} \in \mathcal{X}$  where rank  $M(\mathbf{x})$  is smaller than  $n-1$ . The curve branches there. The map  $M \rightarrow \mathbf{t}$  is smooth for the set of all  $(n-1) \times n$ -matrices with maximal rank [7].

### 3.1. Projection operator

It is  $S^{n-1} = \{x \in \mathbb{R}^n \mid \|\mathbf{x}\| = 1\}$  the unit sphere in  $\mathbb{R}^n$ . We choose a column vector  $\mathbf{r} \in S^{n-1}$  for a projection. We define a matrix  $\mathcal{P}_r \in \mathbb{R}^{(n-1) \times n}$  by  $(n-1)$  row vectors of  $\mathbb{R}^n$  being with  $r$  an orthonormal basis of  $\mathbb{R}^n$ . Thus  $\text{Ker}(\mathcal{P}_r) = \text{lin}\{r\}$  and  $\text{Im}(\mathcal{P}_r) = \text{lin}\{r\}^\perp$ .  $\mathcal{P}_r$  projects a vector  $\mathbf{v}$  in direction  $\text{lin}\{r\}$  and on  $\text{lin}\{r\}^\perp$ . The construction of  $\mathcal{P}_r$  can be done by a Gram–Schmidt method [14].

### 3.2. Newton trajectories

An NT is a first example of a curve with induced tangent. The NT concept [4,5,15–18] is that a selected gradient direction is fixed along the curve  $\mathbf{x}(t)$

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

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

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

$\mathcal{P}_r$  is a constant  $(n-1) \times n$  matrix of rank  $n-1$ . The map  $\mathcal{R} : \mathbb{R}^n \times S^{n-1} \rightarrow \mathbb{R}^{n-1}$ , 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

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

is for any 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) [5] traces a curve (4) along its tangential vector by the derivative to obtain the tangent  $\mathbf{x}'$

$$\begin{aligned} \mathbf{0} &= \frac{d}{dt} [\mathcal{P}_r G(\mathbf{x}(t))] = \mathcal{P}_r \frac{dG(\mathbf{x}(t))}{dt} \\ &= \mathcal{P}_r \mathbf{H}(\mathbf{x}(t)) \mathbf{x}'(t). \end{aligned} \tag{6}$$

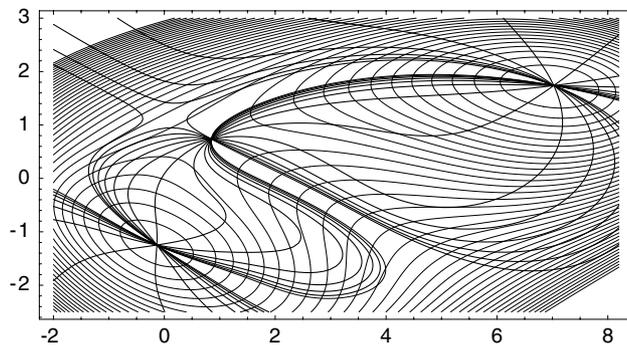


Fig. 2. A family of Newton trajectories on a test surface [8], see Appendix A.

Eq. (6) defines the induced tangent by the matrix  $M = \mathcal{P}_r \mathbf{H}(\mathbf{x}(t))$ . The RGF is a simple but effective procedure in order to determine all types of StPs [4]. In the general good-natured case, each RGF curve passes each StP. A whole family of RGF curves connects the extrema if we vary the search direction  $\mathbf{r}$  [19], see Fig. 2. We will use the names *Newton trajectory* and **RGF curve** as synonyms.

### 3.3. Gradient extremal

GEs are the next example for a curve with induced tangent. At every point of a GE the gradient is eigenvector of the Hessian [6,20–22]

$$H(\mathbf{x})G(\mathbf{x}) = \lambda G(\mathbf{x}). \tag{7}$$

GEs are curves where the norm of the gradient has a local extremum on equipotential surfaces,  $\mathcal{E}_x$ . For the norm of the gradient one uses the functional

$$\sigma : \mathbb{R}^n \rightarrow \mathbb{R} \text{ with } \sigma(\mathbf{x}) = \frac{1}{2} G(\mathbf{x})^\top G(\mathbf{x}).$$

The gradient extremal is given by

$$(\mathcal{P}_G d\sigma)(\mathbf{x}) = \mathcal{P}_{G(\mathbf{x})} H(\mathbf{x}) G(\mathbf{x}) = \mathbf{0}, \tag{8}$$

where it is  $\mathcal{P}_G d\sigma : \mathbb{R}^n \rightarrow \mathbb{R}^{n-1}$  and the projector  $\mathcal{P}_G$  acts in direction  $G$ .  $\text{lin}\{G(\mathbf{x})\}$  is the kernel of  $\mathcal{P}_G$  at point  $\mathbf{x}$ . To grasp the tangent, one has to differentiate the equation to the curve parameter  $t$  [22]. It follows  $d(\mathcal{P}_G d\sigma)|_{\mathbf{x}} \dot{\mathbf{x}} = \mathbf{0}$ . It has the structure of an induced tangent with  $M(\mathbf{x}) = d(\mathcal{P}_G d\sigma)|_{\mathbf{x}} \in \mathbb{R}^{(n-1) \times n}$ . To decide that a point  $\mathbf{x} \in \mathcal{X}$  is on the GE, it is sufficient to use the criterion (8) without a further derivation.

The importance of the GE is its geometrical interpretation as a valley floor line. If a point  $\mathbf{x} \in \mathcal{X}$  is on the gradient extremal then the norm of the gradient has an extremum on the corresponding equipotential surface  $\mathcal{E}_{E(\mathbf{x})}$ . It means the restriction of  $\|G\|$  on  $\mathcal{E}_{E(\mathbf{x})}$  has a critical point at  $\mathbf{x}$ . One problem of using GEs is that ridges are also indicated by GEs. Another problem is that not in all cases the valley floor leads from minimum to the

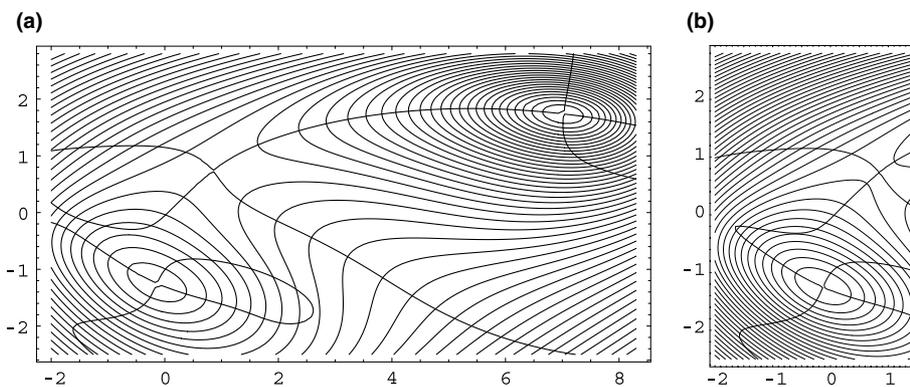


Fig. 3. Gradient extremals on a 2D test surface[8].

next SP. It may happen that the valley ends at the slope. Fig. 3(a) shows GEs on a 2D model surface. A valley pathway very well connects the minimum at North-East and the SP. But the other valley at South-West lies quasi orthogonally. There the worst case can be observed: the second minimum has no GE connection to the SP. There is ‘no’ valley floor between SP and minimum. The smaller picture Fig. 3(b) shows a situation which is not totally bad: the two GE lines going to North-West meet, and they are connected by a turning point.

#### 3.4. Comparison of newton trajectory and gradient extremal

Both, the following of a GE, as well as the following of an NT, can be seen to be a method with induced tangent, see Table 1. The ansatz in a predictor–corrector method gives the criterion to jump between a predictor step or a corrector step. The proof of the ansatz does not need the derivation of the tangent. Both, predictor and corrector, need the induced tangent: the predictor step goes along the tangent, and the corrector step goes orthogonally to the tangent. The matrix which induces the tangent to the corresponding curve is the Jacobi matrix. It is the matrix of the partial derivatives of a vector function. The Hessian is the Jacobi matrix of the gradient. Here we have to use the maps  $\mathcal{G}$  and  $\mathcal{R}$ , see Table 1. The curve has a singularity if the rank of the Jacobi ma-

trix decreases. The singularities of the NTs are the VRIs [5]. The Jacobi matrix of the GE needs third derivatives of the PES [22]. The requirement is one of the practical breakdowns of the direct GE ansatz, however, see an alternate approximation in [11,23] by NTs.

#### 3.5. Steepest descent, intrinsic reaction coordinate

Now we show that the IRC is not a curve with induced tangent. The steepest descent (SD) from the SP in mass-weighted Cartesian coordinates is a simple definition of a reaction path, which is well-known as the IRC [24]. Using the arc-length  $s$  for the curve parameter, a steepest descent curve  $\mathbf{x}(s)$  is defined by the system of vector equations in  $n$  dimensions

$$\frac{d\mathbf{x}(s)}{ds} = -\frac{\mathbf{G}(\mathbf{x}(s))}{\|\mathbf{G}(\mathbf{x}(s))\|} = -\mathbf{w}(s), \quad (9)$$

where  $\mathbf{G}(\mathbf{x})$  is the gradient vector of the PES and  $\mathbf{w}(s)$  is the gradient with unit length. Numerically, the SD of the IRC is started by curve following at an SP of index one, by a step in the direction of the decomposition vector. It is the eigenvector of the Hessian matrix with negative eigenvalue.

Because the SD follows the gradient of the PES, its tangent is parallel to the gradient and orthogonal to the equipotential hypersurface. Trivially, every SD fulfills a projector equation where the tangent  $\mathbf{w}(s)$  of the curve is used for the construction of the projector. If  $\mathbf{x}(s)$  is the SD curve, then  $\mathbf{t}(s) = \mathbf{w}(s)$  of Eq. (9) is the tangent vector for use in a projector. Additionally to Eq. (9), we have a second definition of the SD by a projector equation. There is also an old second method to find the IRC by this ansatz. Liotard and Penot [25] have chosen a smooth curve which connects two minima. If it is outside the IRC then the equation

$$\mathcal{P}_{\mathbf{t}(s)}(\mathbf{G}(\mathbf{x}(s))) = \mathbf{0} \quad (10)$$

is not fulfilled at least in some points. Because, there is one and only one curve which goes through the SP

Table 1  
Comparison of gradient extremal and Newton trajectory

	Gradient extremal	Reduced gradient
Ansatz	$\mathcal{P}_G d\sigma = 0$	$\mathcal{P}_r G = 0$
Map	$\mathcal{G} : \mathbb{R}^n \rightarrow \mathbb{R}^{n-1}$ $\mathbf{x} \rightarrow \mathcal{P}_G d\sigma(\mathbf{x})$	$\mathcal{R}(\cdot, r) : \mathbb{R}^n \rightarrow \mathbb{R}^{n-1}$ $\mathbf{x} \rightarrow \mathcal{P}_r G(\mathbf{x})$
Jacobi matrix	$\mathcal{G}_x = d(\mathcal{P}_G d\sigma)$ $= d\mathcal{P}_G d\sigma + \mathcal{P}_G d^2\sigma$	$\mathcal{R}_x = d\mathcal{P}_r G$ $= \mathcal{P}_r H$
Singularity	$\text{rank } \mathcal{G}_x < n - 1$	$\text{rank } \mathcal{R}_x < n - 1$

and is SD. We have a resulting vector  $\mathbf{p}$  after the projection with the tangent of the curve, cf. [25,26]

$$\mathcal{P}_{\mathbf{t}(s)}(-\mathbf{G}(\mathbf{x}(s))) = \mathbf{p}(s). \quad (11)$$

The orthogonal part to  $\mathbf{t}$  of  $-\mathbf{G}$  (downhill) is used for a numeric approximation of a better curve. The chain of points is varied along the  $\mathbf{p}$  vectors under some iterations. Usually, if successful, the iteration loops find the IRC without pre-knowledge of the SP. The Eqs. (10) and (11) need a global chain of points which connect the basins of two minima over the SP. The way to locally follow the IRC from a minimum uphill, or downhill from SP, is not possible by predictor–corrector steps using Eq. (10)! If we search for the tangent of the curve by derivative to the curve parameter of the projector equation  $\mathcal{P}_{\mathbf{w}}\mathbf{g} = \mathbf{0}$ , we do not get an equation for the tangent of the curve. By contrast, only a zero operator results throughout. We prove the impossibility to use the steepest gradient projector for the induced tangent in a predictor step. We employ an alternate form of the projector, Eq. (10), using the normalized gradient  $\mathbf{w}$ . The transposed vector  $\mathbf{w}^T$  is a row vector. The dimension of  $\mathbf{w}$  is  $(n \times 1)$  where that of  $\mathbf{w}^T$  is  $(1 \times n)$ . We form the dyadic product  $\mathbf{D}_{\mathbf{w}} = \mathbf{w} \cdot \mathbf{w}^T$  which is an  $(n \times n)$  matrix of rank 1.  $\mathbf{D}_{\mathbf{w}}$  projects with  $\mathbf{w}$ :

$$\mathbf{D}_{\mathbf{w}}\mathbf{w} = (\mathbf{w} \cdot \mathbf{w}^T) \cdot \mathbf{w} = \mathbf{w}(\mathbf{w}^T \cdot \mathbf{w}) = \mathbf{w}, \quad (12)$$

where we use the unit length of  $\mathbf{w}$  in the scalar product. The projector which projects orthogonally to  $\mathbf{w}$  is with the unit matrix  $\mathbf{I}$

$$\mathbf{P}_{\mathbf{w}} = \mathbf{I} - \mathbf{D}_{\mathbf{w}}. \quad (13)$$

With the normalized gradient  $\mathbf{w}$  of Eq. (9) and the projector of Eq. (13), we start again with the trivial relation (10) which holds for all curves of steepest descent. We have

$$\mathbf{P}_{\mathbf{w}(s)}\mathbf{G}(\mathbf{x}(s)) = \mathbf{0} \quad (14)$$

because, the tangent to the steepest descent is the gradient itself. The map by the matrix for the induced tangent of Eq. (10),  $\mathbf{M} = \mathcal{P}_{\mathbf{w}}$ , being an  $(n-1) \times n$  matrix, and the map of Eq. (14) being an  $n \times n$  matrix, is equal: both have rank  $(n-1)$ . If one formally searches for the tangent to such a curve by the derivative to the curve parameter, one gets

$$\frac{d\mathbf{P}_{\mathbf{w}(s)}\mathbf{G}(\mathbf{x}(s))}{ds} = \sum_{i=1}^n \frac{\partial \mathbf{P}_{\mathbf{w}(s)}\mathbf{G}(\mathbf{x}(s))}{\partial x_i} \frac{dx_i}{ds}, \quad (15)$$

but every partial derivative of the sum is zero

$$\frac{\partial \mathbf{P}_{\mathbf{w}(s)}\mathbf{G}(\mathbf{x}(s))}{\partial x_i} = \mathbf{P}_{\mathbf{w}} \frac{\partial \mathbf{G}}{\partial x_i} - \frac{\partial \mathbf{w}}{\partial x_i} \mathbf{w}^T \mathbf{G} - \mathbf{w} \frac{\partial \mathbf{w}^T}{\partial x_i} \mathbf{G} = \mathbf{0} \quad (16)$$

using the relation [22]

$$\mathbf{P}_{\mathbf{w}}d\mathbf{G} = \|\mathbf{G}\|d\mathbf{w}, \quad (17)$$

as well as

$$\mathbf{P}_{\mathbf{w}}^T = \mathbf{P}_{\mathbf{w}} \quad \text{and} \quad d(\mathbf{G}^T)\mathbf{P}_{\mathbf{w}} = \|\mathbf{G}\|d(\mathbf{w}^T). \quad (18)$$

Thus, the derivative to the curve parameter  $s$  in Eq. (14) becomes singular at every regular point of the configuration space. The predictor step along the tangent becomes undefined. The corrector step orthogonal to the tangent becomes singular. Every direction of a ‘tangent’-predictor goes to a next point which fulfills the Eq. (14). The IRC cannot be defined locally. An equation like (6) does not exist for it.

The result contradicts some older proposals which try to correct locally the IRC to an MEP. For example, the effort to minimize the energy under the constraint of a

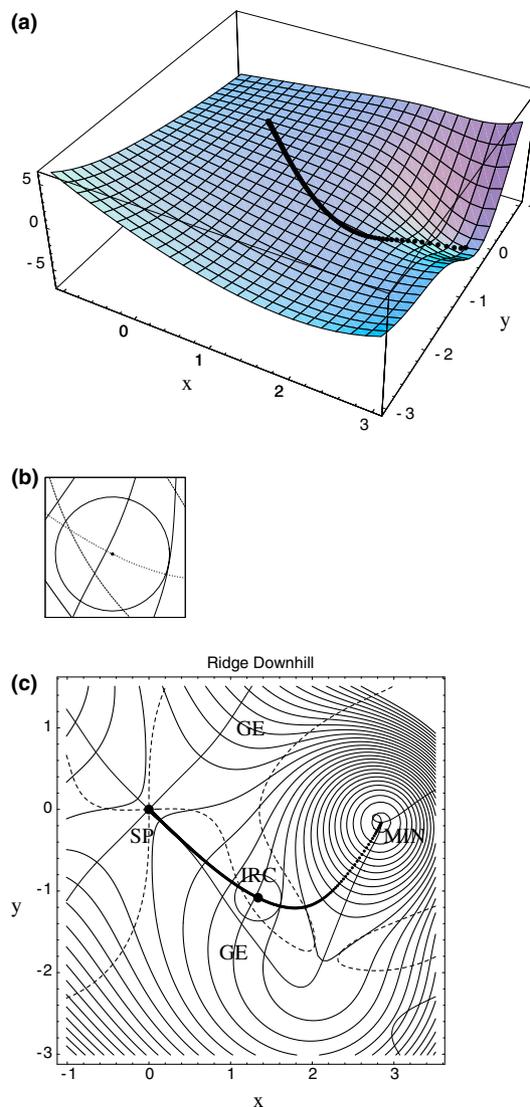


Fig. 4. IRC and Gradient extremals on a modified NFK surface [8,28]. Bullets, IRC. Fat curves, GEs. Light solid curves, level lines. Thin dashes, border: between convex and concave regions [8]. A circle at the point (1.34, -1.08) on the IRC in the ridge region gives a counterexample against the ‘minimum property’ of the IRC, see also the enlargement of the circle. The circle is tangentially touched by the lowest energy level line at a point being not the intersection of the IRC and the circle.

constant step length (for references see the review [27]) does not lead to the IRC, in every case. Fig. 4 shows the modified NFK surface [8,28] being originally devoted to an alanine dipeptide rearrangement. There is an SP, a minimum, and a valley leading from minimum to SP, or vice versa. However, the IRC cuts the corner of the valley which itself is well described by the GE. The border between valley and ridge regions of the PES [8] is also included in Fig. 4(c). Note that a mild ‘hanging ridge’ is situated between SP and the minimum. That ridge is crossed by the IRC. In the ridge region, we draw a circle around any point on the IRC. The minimal energy on that circle is given by the lowest level line which touches the circle. This line is drawn, see also the enlargement (b) in Fig. 4(c). Curves of the enlargement are exactly the same curves like in Fig. 4. Bold bullets are the IRC points; and it is clearly to be seen that the IRC does not cross the circle at the lowest energy point.

As long as the IRC leads over the ridge, it is not an MEP in the original sense of Fukui [24]. Fukui demanded that:

‘Since the reaction coordinate is orthogonal to the tangential plane of the equipotential surface, the potential energy value on this tangential plane has always an extremum at the point crossing the reaction coordinate. For this path to have a definite physical meaning of reaction coordinate, this extremum should be an absolute minimum.’

- On a ridge, the corresponding extremum is a maximum.

### 3.6. Discussion of SD curves

Usually, we are interested in the stationary points of the PES, especially, minima and SPs of index 1. To find a minimum is possible by steepest descent [24]

$$\dot{\mathbf{x}}(t) = -G(\mathbf{x}(t)), \mathbf{x}(0) = \mathbf{x}_0. \quad (19)$$

The solution strongly monotonically decreasing leads to a minimum. Also any neighbouring steepest descent with an  $\mathbf{x}(0) = \mathbf{x}_0 + \epsilon$  converges to the minimum. If searching for the minimum region only, one may jump from the steepest descent curve to a neighbouring curve at every step of a calculation.

The SPs are fixed points, there the tangent disappears. In all other points of  $\mathcal{H}$  the tangent is unique. No singularity or branching can appear. The steepest descent can go over a ridge. Thus, SD alone does not mirror the structure of valleys or ridges of the PES. The first derivative of the energy is not sufficient to characterize the curvature of the PES [29].

The IRC is frequently used as a synonym for the MEP of the PES. But it has a serious imperfection: in one’s imagination Eq. (19) permits to ascend from the

minimum to the SP by changing  $-G(t)$  by  $+G(t)$ , however, it is not possible for practical use due to the funnel character of SD near the minimum [30] leading to the instability of an Eq. (19) ‘uphill’ [19], cf. [31], too.

## 4. Conclusion

The reaction path is a tool of theoretical chemistry without direct physical meaning [2]. The task of a geometrical treatment of the PES is to search for pathways with a given property: to connect minimum and SP by an ascending curve, or to connect SP and minimum by a descending curve. We have studied the three definitions: Newton trajectories, gradient extremals, and the intrinsic reaction coordinate. To numerically follow a curve by predictor–corrector methods, it is important that the curve can be defined by an induced tangent. We can define the first two curves by the induced tangent using the corresponding projector operators. The IRC cannot be followed by this treatment. For the IRC, Euler polygon steps or quadratic or higher approximations of a discretized Eq. (19) can be done [27,32], giving approximations of the special curve from saddle with gradient descent. However, no local corrector to the ‘true’ IRC is possible.

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## Appendix A. Model surfaces

In Figs. 2 and 3 the 2D model potential is used

$$\begin{aligned} E(x, y) = & 0.3(y^2 - 2x + y + 0.3x^2)^2 - 0.3x^2y \\ & - 6\delta\left(\begin{pmatrix} 0.5x \\ y \end{pmatrix}, \begin{pmatrix} 0.1 \\ -1.5 \end{pmatrix}\right) \\ & - 5\delta\left(\begin{pmatrix} 0.5x \\ y \end{pmatrix}, \begin{pmatrix} -0.85 \\ -0.75 \end{pmatrix}\right) \\ & - C\delta\left(\begin{pmatrix} 0.5x \\ y \end{pmatrix}, \begin{pmatrix} -1.8 \\ 0 \end{pmatrix}\right). \end{aligned}$$

For Fig. 2 and the left surface of Fig. 3(a) is  $C = 5$ , and for the piece of the right surface (b) holds  $C = 7$ . The function  $\delta$  makes a depression around  $(x_0, y_0)$ :

$$\begin{aligned} \delta(\mathbf{x}, \mathbf{x}_0) := & \exp(-(\mathbf{x} - \mathbf{x}_0)^\top (\mathbf{x} - \mathbf{x}_0)) \\ & \text{with } \mathbf{x} = (x, y)^\top \text{ and } \mathbf{x}_0 = (x_0, y_0)^\top. \end{aligned}$$

For Fig. 4 the surface is

$$E(x, y) = C(x^2 + y^2)^2 + xy - 9 \exp(-(x - 3)^2 - y^2) - 9 \exp(-(x + 3)^2 - y^2),$$

with  $C = 0.03$ , where in the original surface [28] the constant  $C = 0.06$  is used. The PES is a 2D model of the 66-dimensional  $C_{7eq}$  to  $C_{7ax}$  transition in alanine dipeptide.

## References

- [1] P.G. Mezey, Potential Energy Hypersurfaces, Elsevier, Amsterdam, 1987.
- [2] D. Heidrich (Ed.), The Reaction Path in Chemistry: Current Approaches and Perspectives, Kluwer, Dordrecht, 1995.
- [3] I.H. Williams, G.M. Maggiora, J. Mol. Struct. (Theochem.) 89 (1982) 365.
- [4] W. Quapp, M. Hirsch, O. Imig, D. Heidrich, J. Comput. Chem. 19 (1998) 1087.
- [5] W. Quapp, M. Hirsch, D. Heidrich, Theor. Chem. Acc. 100 (1998) 285.
- [6] D.K. Hoffman, R.S. Nord, K. Ruedenberg, Theor. Chim. Acta 69 (1986) 265.
- [7] E.L. Allgower, K. Georg, Numerical Continuation Methods – An Introduction, Springer, Berlin, 1990.
- [8] M. Hirsch, Zum Reaktionswegcharakter von Newtontrajektorien, Dissertation, Fakultät für Chemie and Mineralogie, Universität Leipzig, Dezember, 2003.
- [9] J. Milnor, Morse Theory, fifth edn., Princeton University Press, 1973.
- [10] J. Baker, P.M.W. Gill, J. Comput. Chem. 9 (1988) 465.
- [11] W. Quapp, M. Hirsch, D. Heidrich, Theor. Chem. Acc. 112 (2004) 40.
- [12] K. Laidler, Theory of Reaction Rates, McGraw-Hill, New York, 1969.
- [13] W. Quapp, J. Theor. Comp. Chem. 2 (2003) 385.
- [14] A. Kiełbasiński, H. Schwetlick, Numerische Lineare Algebra, Deutscher Verl. Wiss., Berlin, 1988.
- [15] J.M. Anglada, E. Besalú, J.M. Bofill, R. Crehuet, J. Comput. Chem. 22 (2001) 387.
- [16] J.M. Bofill, J.M. Anglada, Theor. Chem. Acc. 105 (2001) 463.
- [17] R. Crehuet, J.M. Bofill, J.M. Anglada, Theor. Chem. Acc. 107 (2002) 130.
- [18] M. Hirsch, W. Quapp, J. Comput. Chem. 23 (2002) 887.
- [19] W. Quapp, J. Comput. Chem. 22 (2001) 537.
- [20] S. Pantič, Collect. Czech. Chem. Commun. 40 (1975) 1112.
- [21] M.V. Basilevsky, A.G. Shamov, Chem. Phys. 60 (1981) 347.
- [22] J.-Q. Sun, K. Ruedenberg, J. Chem. Phys. 98 (1993) 9707.
- [23] W. Quapp, M. Hirsch, D. Heidrich, Theor. Chem. Acc. 105 (2000) 145.
- [24] K. Fukui, J. Phys. Chem. 74 (1970) 4161.
- [25] D.A. Liotard, J.P. Penot, in: J. DellaDora, J. Demongeot, B. Lacolle (Eds.), Study of Critical Phenomena, Springer, Berlin, 1981, p. 213.
- [26] W. Quapp, J. Comput. Chem. 25 (2004) 1277.
- [27] H.B. Schlegel, in: P.v.R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Collman, H.F. SchaeferIII, P.R. Schreiner (Eds.), Encyclopedia of Computational Chemistry, John Wiley, Chichester, 1998, p. 2432.
- [28] E. Neria, S. Fischer, M. Karplus, J. Chem. Phys. 105 (1996) 1902.
- [29] M. Hirsch, W. Quapp, J. Math. Chem., accepted.
- [30] J.H. Hubbard, B.H. West, Differential Equations, A Dynamical System Approach, Part I, Springer, New York, 1991.
- [31] W. Quapp, Chem. Phys. Lett. 253 (1996) 286.
- [32] J.-Q. Sun, K. Ruedenberg, J. Chem. Phys. 99 (1993) 5269.