REGULAR ARTICLE

Chemical reaction paths and calculus of variations

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Abstract The reaction path is an important concept of theoretical chemistry. We analyze different forms of reaction pathways in the light of the abstract theory of calculus of variations such as steepest descent from saddle point, the intrinsic reaction coordinate (IRC), Newton trajectory, variationally optimized reaction paths and others. The paper is both a mathematical review and a pointer to future research. Besides the theoretical definitions, we shortly discuss hints at the numerical effect of the definitions.

1 Introduction

The concept of the minimum energy path (MEP) is the static model of a reaction path (RP) of an adiabatic potential energy surface (PES). It is the usual approach to the theoretical kinetics of larger chemical systems [1–5], see also [6–10]. It is roughly defined as a line in the coordinate space, which connects two minimizers by passing the saddle point (SP), the transition structure (TS) or a "mountain pass" of an adiabatic PES following the valley. It is also able to describe pathways of conformational rearrangements. The energy of the SP is assumed to be the highest value tracing along the RP. It is the minimal energy a reaction needs to take place. Reaction theories are based either implicitly (transition state theory [1]) or explicitly (variational transition state theory [5,6]) on

the knowledge of the RP. These theories require only local information about the PES along the RP. They circumvent the dimension problem: it is impossible to fully calculate the PES which remains to be *a terra incognita*. The SP and the minimums form stationary points of the PES. Roughly speaking, it is only of secondary interest, how a reaction path ascends to the SP. This looseness makes a variety of RP definitions possible.

The fundamental problem in handling an n-dimensional hypersurface is the dimension. Molecules with more than $N = 4$ atoms would cause an overwhelming number of net points for the PES. The RP concept is a promising way out because it reduces the problem of finding an algorithm for one-dimensional curves, without any knowledge of the whole PES. A parameterization t of the RP $\mathbf{x}(t) = (x^1(t), \ldots, x^n(t))^{\mathrm{T}}$ is called *reaction coordinate*. Any algorithm which allows to determine this pathway in a suitable approximation should be tested. The search for valley pathways especially is an important part of the PES analysis; up to date it still offers no satisfying concept for all aspects of the problem.

Nowadays, the use of variational treatments reaches a renovation [11–15]. In this paper, we will explore the different definitions by the calculus of variations [16], like

- IRC, or steepest descent (SD) from SP [11–15,17,18],
- distinguished or driven coordinate method [19,20], or in modern form Newton trajectories (NT) [8,9,21–23],
- the variational path method [24–27],
- gradient extremal (GE) [28–33].

The definitions lead to different curves which may well reflect different aspects of the idea of a static MEP. These differences are the reason for treating other methods than SD once for all. (So, the search for an appropriate MEP is not equivalent to the finding of the SD pathway from the SP [7,34–36].)

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The curve which follows a driven coordinate, or the NT can also be used in certain cases for the minimum path [8,9]. The GE [4,28–33] appeared to represent a suitable ansatz for a minimum path, however, with its many additional solution curves and turning points [32,37,38] this concept in its general form is not suited to be used as a routine program for the calculation of such paths.

The valley structure may be of interest by itself as it is the case in spectroscopy or for the selective choice of a reactive channel in chemistry. There, it is assumed that a molecular vibration takes place along the valley of the PES, and if such a vibration is further excited, it may lead to a chemical reaction. All the detailed activities for a simple calculation of RPs are prerequisites for a number of dynamical theories to come into operation, including the famous reaction path Hamiltonian [2]. Further, the methods of direct dynamics [5,6,39,40] need an exact and physical sensible description of the reaction path [41]. This way, the MEP is the leading line characterizing the reaction channel in which the reaction trajectories should move.

The mathematical simplest RP definition is the steepest descent from an SP, resulting in the well-known intrinsic reaction coordinate (IRC) of Fukui [7,34–36,42,43]. Its usual use is in mass-weighted Cartesians, cf. [7]. This pathway is defined by an autonomous system of differential equations for a tangent vector along the curve searched for. Its solution is unique. Therefore, no bifurcation can occur before reaching the next stationary point. Hence, no branching of PES valleys will be truly described by following the IRC, see the discussion in [44,45]. The unique character will also emerge in a variational approach [11], which we will explain again in Sect. 4.

An NT is a curve where the selected gradient direction comes out equally at every curve point. There are curves, which pass all stationary points in most cases. Thus, NTs are an interesting procedure to determine by way of trial all types of stationary points [8], as well as some kinds of valley-ridge inflection points [9,10]. Pieces of NTs can also be defined by a variational integral. This is developed in this paper for the first time, to our best knowledge. However, a whole family of NTs connects minimum and TS of index one. Thus, there is no unique NT between a minimum and a TS.

Gradient extremals (GE) form another approach for RP following [4,28–33,37,38]. They are more complicated than the IRC, but better fitted to solve the valley branching problem by the determination of a GE bifurcation [33]. However, other problems arise due to the occurrence of pairs of turning points (TP) instead of a branching point (BP) of the curve. Such turning points may interrupt the pathway between minimum and SP. The GE curves often show some kind of avoided crossing [4,30,31,44,45]. In the light of the variational ansatz, GEs do not fit to this idea, in contrast to their name.

The paper is organized as follows. Section 2 repeats fundamentals of the theory of variations. That will be applied to the IRC and other RP definitions in Sect. 3. Section 4 discusses conjugate points and the exceptional role of the IRC in this respect. In Sect. 5 we apply transformations of the curve parameter. We finally add a conclusion.

2 Variational methods [16]

2.1 The variational integral

Before we give the go-ahead, some basics. Let be $F(x_1, \ldots, x_n, z_1, \ldots, z_n)$ a function with continuous first and second partial derivatives with respect to all its arguments. We search an extremum of a functional of the form

$$I(a,b) = \int_a^b F(x_1(t), \ldots, x_n(t), x_1'(t), \ldots, x_n'(t)) \mathrm{d}t \qquad (1)$$

which depends on n continuously differentiable functions $\mathbf{x}(t) = (x_1(t), \ldots, x_n(t))^\mathrm{T}$ being the components of an RP, $\mathbf{x}(t)$, in an n-dimensional configuration space. We regard all vectors as column vectors. The prime is derivation to t. Note that I is a one-dimensional integral. The boundary conditions of the RP are $(x_1(a), \ldots, x_n(a))^\mathrm{T} = \mathbf{A}$, and $(x_1(b), \ldots, x_n(b))^\mathrm{T} = \mathbf{B}$. These are usually the coordinates of minimum and transition state, or of two adjacent minimums, and $t \in [a,b]$ is the curve parameter. With $\mathbf{A}$ and $\mathbf{B}$ given, the task is named the *simple fixed endpoint problem in the calculus of variations*.

2.2 Necessary condition for extremals

The necessary condition for a curve $x_i = x_i(t)$, $i = 1, \ldots, n$, to be an extremal of the functional (1) is the system of Euler equations where we use subscripts to denote differentiation

$$F_{x_i} - \frac{\mathrm{d}}{\mathrm{d}t} F_{x_i'} = 0, \quad i = 1, \ldots, n. \qquad (2)$$

The integral curves of Euler equations are called *extremals* in mathematics in the field of variational calculus.

Example 1 The arc-length functional is

$$L(a,b) = \int_a^b \sqrt{\mathbf{x}'(t)^\mathrm{T} \mathbf{x}'(t)} \, \mathrm{d}t, \qquad (3)$$

with $F(x_k, x_k') = \sqrt{\sum_{k=1}^n x_k'^2}$, which does not explicitly depend from the x_k. Thus, with

$$l(\mathbf{x}'(t)) = \sqrt{\mathbf{x}'(t)^\mathrm{T} \mathbf{x}'(t)} = \sqrt{\sum_{k=1}^n x_k'(t)^2} \qquad (4)$$

the Euler equations (2) become

$$\frac{d}{dt}\, l_{x_i'} = 0, \tag{5}$$

and it follows $l_{x_i'} = C_i$, where C_i is a constant. Thus we have

$$\frac{x_i'}{\sqrt{\mathbf{x}'^{\mathrm{T}}\mathbf{x}'}} = C_i, \tag{6}$$

but not all C_i are independent; it is

$$(x_i')^2 = C_i^2 \sum_{k=1}^{n} (x_k')^2, \quad i = 1, \ldots, n. \tag{7}$$

Summation over i leads to the condition $\sum_{i=1}^{n} C_i^2 = 1$. We get the general solution of the arc-length extremal

$$x_i(t) = \alpha_i t + \beta_i \quad \text{and} \quad C_i = \alpha_i / \sqrt{\sum_k \alpha_k^2}. \tag{8}$$

2.3 A nonlocal variational integral

The development of the Euler equations (2) in [16] employs arguments essentially local in nature. They apply to every local point of the extremal $\mathbf{x}(t)$. Sometimes one treats the *nonlocal functional*

$$I_{\mathrm{nl}}(a, b) = \frac{1}{L(a, b)} \int_a^b E(\mathbf{x}(t)) l(\mathbf{x}'(t)) dt. \tag{9}$$

The Euler equations for the extremals of I_{nl} become somehow more complicated, cf. [46]. We use with Eq. (3) the $L(\mathbf{x}') = L(a, b)$ for a subsidiary condition in an isoperimetric problem, and we form a Lagrange ansatz [16] with the functionals of nominator and denominator of (9), where the denominator is the arc-length (3)

$$E(\mathbf{x}(t)) l(\mathbf{x}'(t)) + \lambda\, l(\mathbf{x}'(t)) = (E(\mathbf{x}) + \lambda)\, l(\mathbf{x}'). \tag{10}$$

λ is the Lagrange multiplier. The first variation has to be

$$\mathbf{0} = \mathbf{g}\, l - \frac{d}{dt}\left((E(\mathbf{x}) + \lambda)\frac{\mathbf{x}'}{l}\right) \tag{11}$$

$$= \mathbf{g}\, l - (\mathbf{g}^{\mathrm{T}}\mathbf{x}')\frac{\mathbf{x}'}{l} - (E + \lambda)\frac{d}{dt}\left(\frac{\mathbf{x}'}{l}\right),$$

where $\mathbf{g}$ is the gradient of E.

2.4 Sufficient conditions for a minimal extremal

An important kind of points in the variational theory is the following definition [16]:

If a curve is an extremal of Eq. (1), starting at any point $\mathbf{A}$, and a second "neighboring" extremal of Eq. (1), also starting at $\mathbf{A}$, intersects the first curve in a next point, say point $\mathbf{B}$, then the intersection point is called *conjugate point* (CP).

Example 2 On a sphere the meridians through the poles are the great circles with the shortest arclength (in one hemisphere) but the poles are CPs because the extremals intersect there.

Besides the condition of the Euler equations, there are two further conditions for a minimum:

1. One of the sufficient conditions of a curve $\mathbf{x}(t)$ to be an extremal is the Jacobi condition that the curve has not to contain CPs.
2. The second sufficient condition is the positive definiteness of the second variation, of the matrix $F_{x'x'}$.

3 Variational analysis of RPs

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 atomic kernels and the Schrödinger equation of the electrons, $\mathscr{H}\Psi = E\Psi$. The explicit calculation of the energy E is not of interest here. We assume that the PES is given by a scalar function of the coordinates of the molecule at every point of interest.

Let K be a subset of $\mathbf{R}^n$. K is the *configuration space* of the PES. Let $\mathbf{x} = (x_1, \ldots, x_n)^{\mathrm{T}} \in K$. The function $E(\mathbf{x}): K \to \mathbf{R}$ is an $n-$dimensional *potential energy surface* (PES). The set $E_c = \{\mathbf{x} \in K, E(\mathbf{x}) = c\}$ is named *equipotential hypersurface*. The configuration space of a molecule is restricted. We assume at least a twofold differentiability of the PES for practical reasons. The vector of first derivatives $\mathbf{g} : K \to \mathbf{R}^n$ with

$$\mathbf{g}(\mathbf{x}) = \left(\frac{\partial E}{\partial x_1}(\mathbf{x}), \ldots, \frac{\partial E}{\partial x_n}(\mathbf{x})\right)^{\mathrm{T}} \tag{12}$$

is the *gradient*.

The next definition is the functional $\sigma(\mathbf{x})$, the norm of the gradient

$$\sigma(\mathbf{g}(\mathbf{x})) = \sqrt{\mathbf{g}^{\mathrm{T}}(\mathbf{x})\,\mathbf{g}(\mathbf{x})} = \sqrt{\sum_{k=1}^{n} g_k^2(\mathbf{x})}. \tag{13}$$

σ^2 is the scalar product of the gradient with itself.

The second derivatives of E form the *Hessian* matrix $\mathbf{H}(\mathbf{x}) \in \mathbf{R}^{n \times n}$

$$\mathbf{H}(\mathbf{x}) = \left(\frac{\partial^2 E}{\partial x_i \partial x_j}(\mathbf{x})\right)_{i,j=1}^{n}. \tag{14}$$

The Hessian is symmetric.

The *adjoint matrix* $\mathbf{A}$ of the Hessian matrix $\mathbf{H}$ is defined as $((-1)^{i+j} m_{ij})^{\mathrm{T}}$ where m_{ij} is the minor of $\mathbf{H}$ obtained by

deletion of the ith row and the jth column from $\mathbf{H}$, and taking the determinant.

The adjoint matrix satisfies the relation

$$\mathbf{H}\,\mathbf{A} = \det(\mathbf{H})\,\mathbf{I}_n, \tag{15}$$

$\det(\mathbf{H})$ is the determinant of $\mathbf{H}$, and $\mathbf{I}_n$ is the unit matrix.

3.1 Steepest descent: IRC

A pathway of wide interest is the IRC [42,43], cf. also [7].

The steepest descent from the SP in (usually mass-weighted) Cartesian coordinates [47] is a simple definition of a reaction path, which is well known as the intrinsic reaction coordinate (IRC), but its definition may go back to Euler. Using t for the curve parameter, a general *steepest descent* curve $\mathbf{x}(t)$ is defined by the system of vector equations in n dimensions

$$\mathbf{x}'(t) = -\,\mathbf{g}(\mathbf{x}(t)). \tag{16}$$

The SD system is a system of autonomous differential equations of the first order allowing an integration constant. Thus, its solution can start at an arbitrary initial point (where the gradient is not zero). The path (16) is given by the negative gradient of the PES for the tangent vector of the curve. But the potential force is the zero vector at stationary points. With the exception of the stationary points the solution of the differential equation of the IRC is unique.

Taking the IRC as a model, in some cases, we may understand the definition of the RP by a system of "simple", autonomous differential equations

$$\mathbf{x}'(t) = \mathbf{f}(\mathbf{x}(t)), \tag{17}$$

for example, even if $\mathbf{f}(\mathbf{x}(t)) = -\mathbf{g}(\mathbf{x}(t))$, it is the SD. If the Jacobian matrix of $\mathbf{f}(\mathbf{x})$ is symmetric, then there is a simple possibility to transform such an RP definition from a differential equation into the variational form of Eq. (1). If $\mathbf{x}(t)$ is an RP with definition (17), and $l(\mathbf{x}'(t))$ is given by (4), then its variational formulation works with

$$F(\mathbf{x}, \mathbf{x}') = \sqrt{\mathbf{f}^{\mathrm{T}}(\mathbf{x}(t))\,\mathbf{f}(\mathbf{x}(t))}\; l(\mathbf{x}'(t)), \tag{18}$$

because this F immediately fulfills the Euler equations.

It is

$$F_{x_i} = \frac{1}{\sqrt{\mathbf{f}^{\mathrm{T}}\,\mathbf{f}}} \sum_k f_k\,\frac{\partial f_k}{\partial x_i}\, l = \sum_k f_k\,\frac{\partial f_k}{\partial x_i}, \tag{19}$$

because here is $l = \sqrt{\mathbf{f}^{\mathrm{T}}\,\mathbf{f}}$ using (4) and (17), and

$$-\frac{\mathrm{d}}{\mathrm{d}t}\,F_{x_i'} = -\frac{\mathrm{d}}{\mathrm{d}t}\left(\sqrt{\mathbf{f}^{\mathrm{T}}\,\mathbf{f}}\;\frac{x_i'}{\sqrt{\mathbf{x}'^{\mathrm{T}}\,\mathbf{x}'}}\right). \tag{20}$$

If one uses Eq. (17) then the two roots again cancel each other out. We obtain

$$-\frac{\mathrm{d}}{\mathrm{d}t}(f_i) = -\sum_k \frac{\partial f_i}{\partial x_k}\, x_k' = -\sum_k \frac{\partial f_i}{\partial x_k}\, f_k. \tag{21}$$

If the derivation is symmetric: $\dfrac{\partial f_i}{\partial x_k} = \dfrac{\partial f_k}{\partial x_i}$, the Euler condition is fulfilled. With $\mathbf{f}(\mathbf{x}(t)) = -\mathbf{g}(\mathbf{x}(t))$ the symmetry holds. One has the variational formula for the steepest descent [11–15,17,18]

$$I_{\mathrm{SD}} = \int_a^b \sqrt{\mathbf{g}^{\mathrm{T}}(\mathbf{x}(t))\,\mathbf{g}(\mathbf{x}(t))}\;\sqrt{\mathbf{x}'^{\mathrm{T}}\,\mathbf{x}'}\,\mathrm{d}t. \tag{22}$$

The extremal of $I_{\mathrm{SD}} = \min!$, for $A = \min$ and $B = TS$, is the IRC. For integrants like Eq. (18), the matrix $F_{x_i'\,x_i'}$ has a zero determinant. The matrix is not positive definite. The second sufficient condition of Sect. 2.4 for a minimum is not fulfilled. However, because the integrant of the task (22) has a positive first part, the extremal is a minimal curve [48].

3.2 Newton trajectory (NT) or reduced gradient [49]

A quarter of a century ago it was proposed to chose a driving coordinate along the valley of the minimum, to go a step in this direction, and to perform an energy optimization of the residual coordinates [20]. A combination of the distinguished coordinate method starting at the SP and steepest descent was also used [50]. Recently, the method was transformed into a new mathematical form [8]. The chemically most important features of the PES are the reactant and the product minimum and the SP lain in between. These stationary points of the PES are characterized by the condition $\mathbf{g}(\mathbf{x}) = \mathbf{0}$. It is valid at extremizers of the PES, but single components of the gradient can also vanish in other regions of the PES. Using this property, a curve of points $\mathbf{x}$ can be followed which fulfills the $n-1$ equations

$$g_i = 0, \quad i = 1, \ldots, k-1,\, k+1, \ldots, n \tag{23}$$

omitting the kth equation [8,19]. This produces the $(n-1)$-dimensional zero vector of the *reduced gradient*; the method was subsequently called reduced gradient following. Equation (23) means that the gradient points into the direction of the pure x^k coordinate. The concept may be generalized by the challenge that any selected gradient direction is fixed

$$\mathbf{g}(\mathbf{x})/|\mathbf{g}(\mathbf{x})| = \mathbf{r}, \tag{24}$$

where $\mathbf{r}$ is the selected unit vector of the search direction; and the corresponding curve is named *Newton trajectory*. The search direction may correspond to the start direction of a chemical reaction. The "reduction" of Eq. (24) is realized by a projection of the gradient onto the $(n-1)$-dimensional subspace which is orthogonal to the one-dimensional subspace

spanned by the search direction $\mathbf{r}$. A curve belongs to the search direction $\mathbf{r}$, if the gradient of the PES always remains parallel to the direction of $\mathbf{r}$ at every point along the curve $\mathbf{x}(t)$

$$\mathbf{P_r}\, \mathbf{g}(\mathbf{x}(t)) = \mathbf{0} \tag{25}$$

where $\mathbf{P_r}$ projects with the search direction $\mathbf{r}$. This means that $\mathbf{P_r}\, \mathbf{r} = \mathbf{0}$. Employing such a projector, instead of Eq. (24), one refrains from the use of the very uncomfortable differentiation of the absolute value in the denominator. A possibility to define $\mathbf{P_r}$ is [9,51]

$$\mathbf{P_r} = \mathbf{I}_n - \mathbf{r}\,\mathbf{r}^{\mathrm{T}}, \tag{26}$$

where $\mathbf{I}_n$ is the unit matrix. This $\mathbf{P_r}$ is an $n \times n$ matrix of rank $n - 1$, because $\mathbf{r}$ is a column vector, $\mathbf{r}^{\mathrm{T}}$ is a row vector, and their dyadic product is a matrix of rank 1.

NTs have also a definition by a differential equation. The adjoint matrix $\mathbf{A}$ has to be used [52–56] to define an autonomous system of differential equations, similar to Eq. (17), for an NT curve $\mathbf{x}(t)$, where t is again the curve parameter

$$\mathbf{x}'(t) = \pm \mathbf{A}(\mathbf{x}(t))\, \mathbf{g}(\mathbf{x}(t)), \tag{27}$$

see also [57,58]. With the symmetric Hessian, the adjoint matrix $\mathbf{A}$ is also symmetric. However, the Jacobian matrix of (27) is non-symmetric, in the general case. If the additional symmetry holds:

$$\frac{\partial A_{ik}}{\partial x_l} = \frac{\partial A_{lk}}{\partial x_i} \tag{28}$$

we have, with one line of system (27)

$$x_i' = \pm \sum_k A_{ik}\, g_k := f_i \tag{29}$$

the derivation of f_i

$$\begin{aligned}
\frac{\partial f_i}{\partial x_l} &= \pm \sum_k \left(\frac{\partial A_{ik}}{\partial x_l}\, g_k + A_{ik}\, \frac{\partial g_k}{\partial x_l} \right) \\
&= \pm \sum_k \left(\frac{\partial A_{lk}}{\partial x_i}\, g_k + A_{ik}\, H_{kl} \right) \\
&= \pm \sum_k \left(\frac{\partial A_{lk}}{\partial x_i}\, g_k + A_{lk}\, H_{ki} \right) = \frac{\partial f_l}{\partial x_i}.
\end{aligned} \tag{30}$$

The last line holds because of Eq. (15), we have for $i \neq l$ that $\sum_k A_{ik} H_{kl} = 0 = \sum_k A_{lk} H_{ki}$. Thus, an NT with definition (27) and symmetry (28) fulfills the necessary extremal condition of the variational integral

$$\begin{aligned}
I_{\mathrm{NT}} &= \int_a^b \sqrt{(\mathbf{Ag})^{\mathrm{T}}\,(\mathbf{Ag})}\; l(t)\, \mathrm{d}t \\
&= \int_a^b \sqrt{\mathbf{g}^{\mathrm{T}}\, \mathbf{A}^2\, \mathbf{g}}\; \sqrt{\mathbf{x}'^{\mathrm{T}}\, \mathbf{x}'}\,\mathrm{d}t.
\end{aligned} \tag{31}$$

A special case where the condition (28) holds is the PES in an exact quadratic form, see [33],

$$E(\mathbf{x}) = E_0 + (\mathbf{x} - \mathbf{x}_0)^{\mathrm{T}}\, \mathbf{H}\, (\mathbf{x} - \mathbf{x}_0)/2.$$

$\mathbf{x}_0$ is the critical point, $\mathbf{H}$ is a constant matrix and the gradient is $\mathbf{H}\, (\mathbf{x} - \mathbf{x}_0)$. Then the mixed derivatives (28) are all zero. In the general case, where the symmetry relation (28) is not fulfilled, the ansatz (31) is unlikely for an NT calculation. One may use a different variational functional by the general ansatz (see [15] for SD)

$$F(\mathbf{x}, \mathbf{x}') = \left(\mathbf{x}' \mp A(\mathbf{x})\, \mathbf{g}(\mathbf{x}) \right)^{\mathrm{T}} \left(\mathbf{x}' \mp A(\mathbf{x})\, \mathbf{g}(\mathbf{x}) \right). \tag{32}$$

Of course, it is the differential equation (27) put into a variational functional. If the minimum of a variational integral with this integrant exists, it should be zero.

3.3 Variationally optimized reaction path

It is remarked (not fully correctly) that the RP of an SD, Eq. (16), fulfills the extremal task

$$I_{RP} = \int_a^b E(\mathbf{x}(t))\, l(\mathbf{x}'(t))\mathrm{d}t = \min! \tag{33}$$

where a and b are the parameters of reactant and product of a reaction, respectively [59]. We will see that the extremals of this variational integral are not exactly SD pathways. It is $F(\mathbf{x}, \mathbf{x}') = E(\mathbf{x})\, l(\mathbf{x}')$. With the parts

$$F_{x_i} = g_i l, \quad i = 1, \ldots, n \tag{34}$$

and

$$\begin{aligned}
-\frac{\mathrm{d}}{\mathrm{d}t} F_{x_i'} &= -\frac{\mathrm{d}}{\mathrm{d}t} \left(E\, \frac{x_i'}{\sqrt{\mathbf{x}'^{\mathrm{T}}\mathbf{x}'}} \right) \\
&= -\sum_k \frac{E_{x_k}\, x_k'\, x_i'}{l} + E\, \frac{\sum_k (x_i''\, x_k'\, x_k' - x_i'\, x_k'\, x_k'')}{l^3} \\
&= -\frac{1}{l}\, (\mathbf{g}^{\mathrm{T}}\, \mathbf{x}')\, x_i' - \frac{E}{l^3}\, (x_i''\, l^2 - x_i'(\mathbf{x}''^{\mathrm{T}}\mathbf{x}')),
\end{aligned} \tag{35}$$

the vectorial Euler equations are the following expression

$$\mathbf{0} = \mathbf{g}\, l - \frac{1}{l}(\mathbf{g}^{\mathrm{T}}\mathbf{x}')\, \mathbf{x}' - \frac{E}{l^3}(\mathbf{x}''\, l^2 - \mathbf{x}'(\mathbf{x}''^{\mathrm{T}}\mathbf{x}')\,). \tag{36}$$

It is a complicate system of differential equations of second order for the RP which is not fulfilled by the steepest descent (in the usual curvilinear case), because with $\mathbf{x}' = \mp \mathbf{g}$, and

$\mathbf{g}^T \mathbf{g} = l^2$, only the first two terms cancel each other out, and we get with $\mathbf{x}'' = \mp \mathbf{H} \mathbf{x}' = \mathbf{H} \mathbf{g}$

$$0 \overset{?}{=} \frac{E}{l^3}(\mathbf{H} \mathbf{g}\, l^2 - \mathbf{g}(\mathbf{g}^T \mathbf{H} \mathbf{g})\,). \tag{37}$$

$\mathbf{g}^T \mathbf{H} \mathbf{g}/l^2$ is a scalar, the Rayleigh-quotient [60], and usually the vectors $\mathbf{H} \mathbf{g}$ and $\mathbf{g}$ point into different directions, thus the Euler equations are not fulfilled for an SD curve. Only if $\mathbf{g}$ is an eigenvector of the Hessian matrix itself, the last two terms also nullify as well. In the case, the steepest descent additionally has to be a gradient extremal, see below, and this is the case if the SD is a straight line only [33]. The second derivatives $\mathbf{x}''$ in Eq. (36) describe the curvature of the RP. If $\mathbf{x}(t)$ is SD and GE, they are zero. Thus, the ansatz (33) is an interesting proposal for an MEP, but it does not produce the IRC of Fukui (if A = minimum, and B = TS) [46].

Pratt [27] and Elber and Karplus [20,24,26] proposed to solve the nonlocal extremal integral along a set of curve points $\mathbf{x}(t)$ again seen as the reaction path approximation:

$$I_{\text{ORP}} = \frac{1}{L(a,b)} \int\limits_a^b E(\mathbf{x}(t))\, l(\mathbf{x}'(t)) \mathrm{d}t \tag{38}$$

like Eq. (9), where a and b may again be the parameters of reactant and product of a reaction, respectively. The path length L additionally emerges in the denominator. It was assumed that the solution is an MEP, a reasonable approximation of the IRC. The derivation of the first variation is similar to the above mentioned. Additionally, we have to use the Lagrange multiplier λ. We get the Euler equations (11) for a non-local variational task [46]. The difference to Eq. (36) is only the factor: for E we have $(E + \lambda)$. If one tests the SD path, then again the first two summands nullify, but the third term is only zero for linear pathways, like above. Thus, in the general case, the task (38) will not be solved by SD curves. If the SD, coming from a strong side slope, reaches the valley floor with a "sharp" curvature then the corresponding Elber–Karplus path cuts the corner [61]. Note that in the former reference, the functional $\mathbf{I}_{\text{RP}}$, Eq. (33), is replaced by [62]

$$I_{\text{HS}} = \int\limits_a^b \mathrm{Exp}(\beta E(\mathbf{x}(t)))\, l(\mathbf{x}'(t)) \mathrm{d}t. \tag{39}$$

However, arguments concerning Eq. (37) still hold further. Here, $\beta = 1/k_B T$ with k_B is the Boltzmann constant, and T is the temperature. The variational task (39) sends the temperature in a factor of the curvature term of the Euler equations. The corresponding pathways become dependent from T, if there is a curvature, although, they be further quasi "static" RPs.

The ansatz (38) is an interesting proposal for an MEP under a simple numerical approximation by discrete differences, see also [63]. Applications are given in [61,64], and in references therein. The extremal task (38) has triggered a long row of interesting works to MEPs and TS searches called nudged elastic band method, cf. [65–67] and references therein.

3.4 Gradient extremal (GE)

Pancíř [68] and Basilevsky/Shamov [28,29] formulated local criteria for describing a valley floor line. Pancíř determined two conditions which he assumed to be obviously given:

1. The energy must increase along all directions perpendicularly to the direction of the valley floor line.
2. The curvature of the energy surface along the direction of the valley must be less than the curvature along any other direction.

Pancíř came to the conclusion that a path satisfying (1) and (2) should be a sequence of points where the gradient, $\mathbf{g}$, is an eigenvector of the Hessian, $\mathbf{H}$.

If the norm of the gradient forms a minimum along points of an equi-hypersurface, $E_c(\mathbf{x})$, i.e. along all directions perpendicular to the gradient [28–32,69,70], a point of gentlest ascent of a valley is found. The measure for the ascent of the function $E(\mathbf{x})$ is the norm of the gradient vector, the functional σ^2. The implicit condition $E(\mathbf{x}) = c$ may be fulfilled by the sub-hypersurface $\mathbf{x}(\mathbf{u}, c)$, where $\mathbf{u}$ may be an $(n-1)$-dimensional parameter. One treats the parametric optimization problem with the objective function

$$\sigma(\mathbf{x})^2 \rightarrow \underset{\mathbf{x}(\cdot, c)}{\mathrm{Min}}\ ! \tag{40}$$

where the nonlinear constraint is $E(\mathbf{x}) = c$. Thus, objective function and constraint are developed from the function E itself. We are interested in following a path of local minimums as the parameter increases (if we do an ascent to the surface) or decreases (if we go downhill). For almost all values of c one generally might expect that a local minimum $\mathbf{x}(c)$ of problem (40) depends differentially on c. Using the normalized gradient

$$\mathbf{w}(\mathbf{u}, c) := \mathbf{g}(\mathbf{x}(\mathbf{u}, c))/|\mathbf{g}(\mathbf{x}(\mathbf{u}, c))| \tag{41}$$

and

$$\mathbf{P}_{\mathbf{w}(\mathbf{u},c)} := \mathbf{I}_n - \mathbf{w}(\mathbf{u}, c)\, \mathbf{w}(\mathbf{u}, c)^T, \tag{42}$$

the requirement for an extremal value of σ is expressed by

$$\mathbf{P}_{\mathbf{w}(\mathbf{u},c)} \nabla\, (\sigma^2(\mathbf{x}(\mathbf{u}, c))) = 0, \tag{43}$$

where c is constant. Because of $\nabla(\sigma(\mathbf{x})^2) = 2\mathbf{H}(\mathbf{x})\, \mathbf{g}(\mathbf{x})$, and setting $\lambda = \mathbf{w}^T \mathbf{H} \mathbf{w}$, it results in the basic eigenvector relation

$$\mathbf{H}(\mathbf{x})\, \mathbf{g}(\mathbf{x}) = \lambda(\mathbf{x}) \mathbf{g}(\mathbf{x}). \tag{44}$$

The proportional factor $\lambda(\mathbf{x})$ is an eigenvalue of the Hessian matrix, and the gradient is its eigenvector. The GE equation (44) selects points of the configuration space having an extreme value of $\sigma(\mathbf{x})$ with respect to variations on equi-hypersurfaces. So, if $\sigma(\mathbf{x})$ has a minimum the PES may have a valley-floor GE. (Note: the extrema of $\sigma(\mathbf{x})$ can also be maxima or degenerate stationary points [4,32,33].) The development gives rise to the formulation of the streambed description of the valley ground GE, which follows the smallest eigenvalue: If we are on this gradient extremal, then from the left as well as from the right hand side the SD lines confluent to this valley line [33]. The GE forms an isolated curve in the configuration space. It does not form a family of curves as the SD lines do. But if the lines of two different families of SD curves confluent into the GE, from the right as well as from the left, it may serve as a model of the valley floor.

Curves $\mathbf{x}(c)$ defined by Eq. (44) consisting of such points on consecutive equi-hypersurfaces for different sections of increasing or decreasing c are termed *gradient extremals* [30]. This kind of curves do not build a field of curves spreading over the PES, however, they are "single" solutions.

Although a GE can be seen to be a curve with an induced tangent by the derivation of $\mathbf{P_g}\,\mathbf{H}\,\mathbf{g} = \mathbf{0}$, see [71], where $\mathbf{P_g}$ is the projector in direction of $\mathbf{g}$, as well as NTs which allow an analogous definition, for GEs we do not know a definition like Eq. (17). And because GEs are not a field of curves, an integral extremal condition with boundaries a and b should not be possible, indeed. So, it seems that this RP curve which is named an extremal, even the GE, does not have a variational extremal definition.

4 Conjugate points of extremals

4.1 IRC

To see the deeper meaning of the CPs, we treat the catchment region of a minimum of the PES [3]. Catchment regions generate a partition of the n-dimensional configuration space K. Using the concept of SD curves, a catchment region $K_{\mathbf{A}}$ of the PES in K is defined as the collection of all those nuclear configurations $\mathbf{B}$ from where an infinitely slow, vibrationless relaxation path, as expressed by the SD, leads to a given critical point $\mathbf{A}$. The index $\mathbf{A}$ is connected with the index of the critical point (the number of negative eigenvalues of the local Hessian matrix of the PES) at $\mathbf{A}$. The concept of catchment regions is closely related to ridges of the PES. Usually, an $(n-1)$-dimensional ridge system separates the catchment regions of two adjacent minimums, and every ridge ends below at an SP, cf. the 3D example of HCN in [72], and [73]. An SP of index one is the TS which connects the two adjacent minimums by the IRC.

The catchment regions have their origins in the inspired works of Cayley and Maxwell, cf. [74], who used some of the mathematical properties of catchment regions for the description of geographical terrains, expressing the relations between hills, valleys, dales, and watersheds. However note that here in chemical applications, the dividing surface between two catchment regions is an $(n-1)$-dimensional hypersurface.

A basic point in the theory of variational extremals [11] is the possibility of embedding the extremal curve under consideration in a family of neighboring curves which is fit to a field of directions. If the endpoint $\mathbf{B}$ of the extremal curve is in the catchment region of start point $\mathbf{A}$, then the original extremal can be embedded in a field. A field of curves is defined by the set of extremal curves cutting the hypersurfaces E_c transversally [11]. But still more explicitly, the cutting of SD curves to E_c is orthogonal.

The set of extremal curves emerging from a central point $\mathbf{A}$ will constitute a field up to its conjugate points to the central point. In the present problem of SD curves flowing together into the point $\mathbf{A}$, which is a minimum, other SD curves may intersect this SD for the first time at the stationary points of the PES of a character saddle point, or maximum. These types of stationary points are the possible CPs with respect to central point $\mathbf{A}$ because there the gradient becomes zero again. Other points are not possible, because in other points the vector equations (16) for SD curves are unique. Thus, a CP can be a stationary point of a character saddle point of any index, or maximum on the PES. However, for saddle points with one negative eigenvalue, saddle points of index one, only one SD curve emerging form the central point $\mathbf{A}$ arrives at this type of stationary points. As a consequence, the first-order saddle points are not conjugate points with respect to the central point. This result is proved from a rigorous mathematical point of view in [11], using the Jacobi equation associated with the variational problem under consideration.

For the IRC no CP can exist. We illustrate it by the simple, schematic Fig. 1. Different SD curves can only cross or confluent at saddle points. At maximums, as well as minimums, the field of SD curves starts, or confluents, at all [33,75]. For a saddle of index 1 there is the IRC trough the SP, and the $(n-1)$ corresponding ridge lines along the orthogonal directions do cross the curve. However, those ridge lines can never start at the minimum. All neighboring curves do circumvent the SP in a hyperbolic kind. This is the reason that a variational minimization of the IRC path works, if we fix the two startpoints to two minimums. From another point of view, seeing the SD curves from the two minimums, there are infinitely many SD curves which confluent there. However, only the IRC comes from the SP, and it is the single curve which connects the two minimums. So to say, the IRC is a singular SD curve.
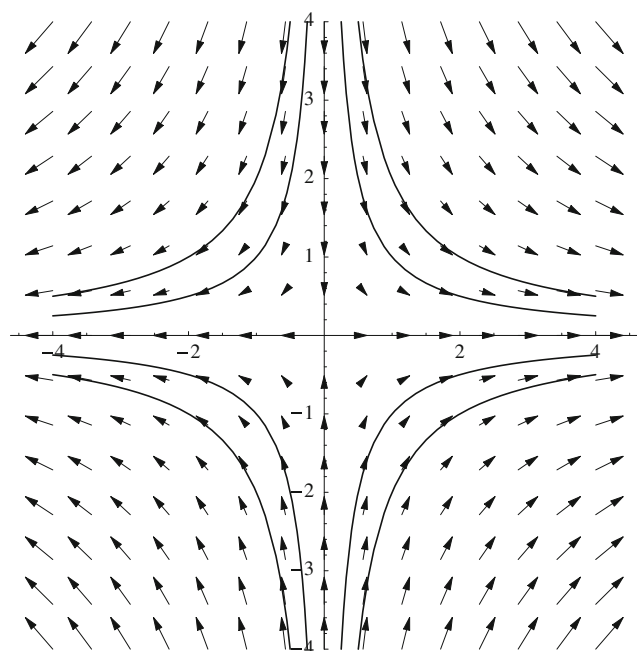
Fig. 1 Pedagogical example of a gradient field around an SP at zero, and some SD curves

Fig. 2 Five NTs (*dashed curves*) of the family of NTs between minimum at (1, 0) and SP at (0, 0). Vector field $\mathbf{A}\,\mathbf{g}$. Level lines (*thin*) E_c

In Fig. 1 we show the schematic situation at SPs of index one in a two-dimensional example. The surface $y^2 - x^2$ is used. The zero is the SP, and the x-axis may be the IRC. At the SP a second SD crosses; however, it comes from above.

If an IRC is a "broken" extremal, like an IRC between two SPs of index one and a minimum, where the IRC runs down first between the two adjacent SPs, and then turns to the final minimum, the discussed relations are in order, see [13]. The case concerns ramified reaction valleys. Of course, an IRC connection between two SPs is only possible in special, symmetric cases of the PES [72].

SPs of an index higher than 1, on the other side, are CPs of an adjacent minimum. It starts with SPs of index 2, cf. [76, 77], which often are of chemical interest, too. Consequently, an SD between an SP of index two and a minimum is not unique.

4.2 NTs

For NTs Eq. (27) is also unique, in nonstationary points, if additionally Det($\mathbf{A}$) of the adjoint matrix is not zero. But if Det($\mathbf{A}$) = 0, we have a bifurcation point (BP) of an NT. The NT divides different families of NTs which connect different stationary points [57]. However, for NTs the structure of the CP relation is quite more complicate than for SD curves. The reason is that adjacent stationary points like minimum and TS are conjugate points of NTs. Any NT without a BP connects stationary points with an index difference of one. Figure 2 shows a family of NTs between minimum and SP.
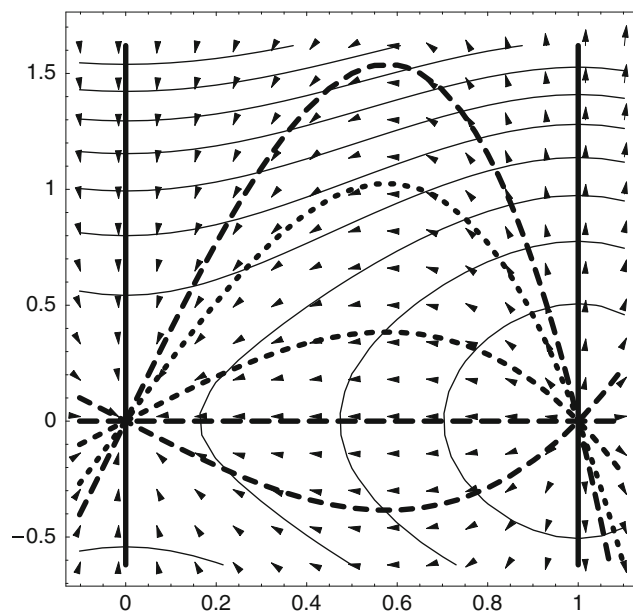
The surface $x^2(x^2 - 2) + y^2$ with a double minimum at $(\pm 1, 0)$ is used, being the ideal case: it is found to occur in many systems. Additionally, the field of directions of the NT, Eq. (27), of $\mathbf{A}\,\mathbf{g}$ is shown. It is to observe that the minimum is a repulsive stationary point, but the SP of index one is an attractive stationary point. The NTs fit the directions of $\mathbf{A}\,\mathbf{g}$. Figure 2 shows that a minimization of a variational functional with integrant Eq. (32) between a minimum $\mathbf{A} = (1, 0)$ and a TS $\mathbf{B} = (0, 0)$ is not useful, because the solution is not unique. Of course, that NT with the shortest pathlength, $L(a, b)$, can be used for an MEP [78]. It is here the line between 0 and 1 on the x-axis, the IRC.

Only points $\mathbf{B}$ in the "NT-catchment region" of $\mathbf{A}$ being no stationary points are possible to uniquely calculate (at least theoretically) by the ansatz (32).

In contrast to the determination of stationary points, NTs open the possibility for a new method to calculate all kinds of valley-ridge inflection (VRI) points. (The symmetric case is already discussed [9,10,72].) The pattern of NTs around a VRI is the same like the pattern of SD curves around an SP, see Fig. 1 above, and Figs. 2–4 in [72]. The analogy is like the IRC is spanned over the SP of index one which is not a CP because the IRC is the single curve which is going through the SP, a singular NT is going through a VRI which is not a CP either. A VRI point is the location which is crossed by the one, single NT which connects a minimum and an SP of index two, or which connects two SPs of index one. The branch of the single NT separates families of hyperbolic NTs which connect different stationary points. So to say, the branch of a single NT is the border of catchment regions

of different TSs. The corresponding regions of the PES are also named "reaction channels" to TSs [57]. A method to calculate the VRI-NT by a variational ansatz will be reported in a forthcoming paper.

5 Transformation of the parameter

In the extremal task of Eq. (1), we will change the used parameter, t. We have a first possibility with $L(a, t)$ in Eq. (3) with $a \leq t \leq b$

$$L(a, t) = s(t) = \int_a^t \sqrt{\mathbf{x}'(\tau)^{\mathrm{T}} \mathbf{x}'(\tau)} \, \mathrm{d}\tau = \int_0^L \mathrm{d}s. \tag{45}$$

$s(t)$ is a new parameter instead of t, and the pathway now will be $\mathbf{x}(s)$. The boundary for $t = a$ is $s = 0$, and for $t = b$ it is even $s = L(a, b)$. Note that $L(a, b) \neq 1$, in the general case. The tangent to the curve $\mathbf{x}(s(t))$ is

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}s} \frac{\mathrm{d}s}{\mathrm{d}t},$$

thus with the derivation of Eq. (45)

$$\mathbf{x}^{\cdot} = \frac{\mathrm{d}\mathbf{x}(s)}{\mathrm{d}s} = \frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t} \bigg/ \left| \frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t} \right|. \tag{46}$$

It has unit length. The $\cdot$ is the derivation to path length s. In Eq. (16) we get the path length, s, for the parameterization, if we normalize the gradient by its length to unit vector

$$\frac{\mathrm{d}\mathbf{x}(s)}{\mathrm{d}s} = -\frac{\mathbf{g}(\mathbf{x}(s))}{|\mathbf{g}(\mathbf{x}(s))|}. \tag{47}$$

It is the well-known equation for the SD with IRC-parameter, s. Using the right hand side for the vector function $\mathbf{f}(s)$ in ansatz (18), we may obtain the variational integral

$$I_{SDs} = \int_0^L \frac{\sqrt{\mathbf{g}^{\mathrm{T}}(\mathbf{x}(s)) \, \mathbf{g}(\mathbf{x}(s))}}{\sqrt{|\mathbf{g}|^2}} \sqrt{\mathbf{x}^{\cdot \mathrm{T}}(s) \, \mathbf{x}^{\cdot}(s)} \, \mathrm{d}s. \tag{48}$$

The two square roots with the gradients cancel each other out in the integral, and the tangent vectors have unit length, see above, so it remains the task $\int_0^L \mathrm{d}s = \min!$, which is useless because nothing is to variate.

Another transformation of the curve parameter may also be interesting [11,13]. We start with a new variational integral and look for the Euler equations.

$$\int_\alpha^\beta (\mathbf{g}^{\mathrm{T}}(\mathbf{x}(\tau)) \, \mathbf{g}(\mathbf{x}(\tau))) \, (\mathbf{x}^{\cdot \mathrm{T}}(\tau) \, \mathbf{x}^{\cdot}(\tau)) \mathrm{d}\tau \tag{49}$$

where "·" is the differentiation to the parameter τ. The Euler equations are

$$(\mathbf{H} \, \mathbf{g}) \, (\mathbf{x}^{\cdot \mathrm{T}} \mathbf{x}^{\cdot}) - \frac{\mathrm{d}}{\mathrm{d}\tau} (\mathbf{g}^{\mathrm{T}} \, \mathbf{g} \, \mathbf{x}^{\cdot}) = 0. \tag{50}$$

If one put

$$\mathbf{x}^{\cdot} = \frac{-\mathbf{g}}{\mathbf{g}^{\mathrm{T}} \mathbf{g}} \tag{51}$$

and if one uses

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \mathbf{g} = \mathbf{H} \, \mathbf{x}^{\cdot} = -\mathbf{H} \, \mathbf{g}/(\mathbf{g}^{\mathrm{T}} \, \mathbf{g}) \tag{52}$$

then the Euler equations are fulfilled. Of course, the differential equations (51) describe a field of SD curves. The new normalization leads to a special parameterization. We treat an SD curve $\mathbf{x}(\tau)$ starting at TS in the direction of the mountain pass. We know that it is orthogonal to the hypersurfaces E_c. We study a region around $E(\mathbf{x}(\tau)) = c$. If τ goes on, we get a function $c(\tau)$. We can do the derivation

$$\frac{\mathrm{d}c}{\mathrm{d}\tau} = \mathbf{E}_x^{\mathrm{T}} \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}\tau} = \mathbf{g}^{\mathrm{T}} \mathbf{x}^{\cdot}. \tag{53}$$

If we insert Eq. (51) we get $\mathrm{d}c/\mathrm{d}\tau = -1$. The parameter c is the value of the PES itself, it is the inverted τ. The parameterization of the SD curves in differential equations (51) goes on with the energy as the curve parameter. Of course, it only works in monotone regions of E. This is also obtained directly: in regions where $\mathbf{g} \neq 0$ and $\mathbf{x}^{\cdot} \neq 0$ one can define the inverse derivation

$$\frac{\mathrm{d}\tau}{\mathrm{d}c} = \frac{1}{\mathbf{g}^{\mathrm{T}} \mathbf{x}^{\cdot}}. \tag{54}$$

If we use now c for the new parameter, $c = -\tau$, we obtain

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}c} = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}\tau} \frac{\mathrm{d}\tau}{\mathrm{d}c} = \frac{\mathbf{x}^{\cdot}}{\mathbf{g}^{\mathrm{T}} \mathbf{x}^{\cdot}} = \frac{\mathbf{g}}{\mathbf{g}^{\mathrm{T}} \mathbf{g}} > 0 \tag{55}$$

where $\cdot$ is still the derivation to τ. The parameterization of bf x by c of the SD curves goes on with an analogous direction as E itself, because it is E.

In general, starting with a variational ansatz by integrant (18) in the functional (1), we can do any regular parameter transformation, $t = t(\theta)$. We put $\mathbf{x}(t(\theta)) = \tilde{\mathbf{x}}(\theta)$ and use the dot for derivation to θ. With $t^{\cdot}(\theta) > 0$ we get

$$\tilde{\mathbf{x}}^{\cdot} = \frac{\mathrm{d}\tilde{\mathbf{x}}(\theta)}{\mathrm{d}\theta} = \frac{\mathrm{d}\mathbf{x}(t(\theta))}{\mathrm{d}t} \frac{\mathrm{d}t}{\mathrm{d}\theta} = \mathbf{x}' t^{\cdot}. \tag{56}$$

Because $l(\mathbf{x}'(t))$ is homogenous with degree one, we get the variational integral

$$\int_\alpha^\beta \sqrt{\mathbf{f}^{\mathrm{T}}(\tilde{\mathbf{x}}(\theta)) \, \mathbf{f}(\tilde{\mathbf{x}}(\theta))} \sqrt{\frac{\tilde{\mathbf{x}}^{\cdot \mathrm{T}}(\theta)}{t^{\cdot}} \frac{\tilde{\mathbf{x}}^{\cdot}(\theta)}{t^{\cdot}}} \, t^{\cdot} \, \mathrm{d}\theta \tag{57}$$

The transformation cancels each other out in the integral. The integral is of the same kind as the starting form. However, in the corresponding differential equation, the transformation will have an effect, at least by a different normalization. The conclusion is: the variational integral to a given curve definition by a differential equation is not unique. The possibility to transform the parameter in the variational integral

opens a very practical way. The parameters in Eqs.(16) and (51) are not truly comfortable: In Eq. (16) the range for t is $(-\infty, \infty)$ for the SD between TS and minimum, but in Eq. (51) the length of the tangent vector diverges to infinity for the approximation of a stationary point. The transformation to pathlength parameter s opens the possibility to use equidistant, or nearly equidistant, steps for a discrete approximation of the integral, because integral (57) becomes the trivial form

$$\int_0^L \sqrt{\mathbf{f}^T(\tilde{\mathbf{x}}(s))\,\mathbf{f}(\tilde{\mathbf{x}}(s))}\,ds. \tag{58}$$

In Eq. (16) any change in the scaling of the right-hand side does not change the direction of the tangent along the path, the left-hand side. The scaling only changes the curve parameter but not the curve points $\mathbf{x}$ itself in K. So to say, the curve parameter, t, comes out to be only a "dummy" integration parameter [17].

6 Conclusions

We review the findings of [11–15,17,18] at a general mathematical level that the IRC can be defined by a variational integral. The IRC is frequently used as a synonym for the MEP. The result is that the IRC is a unique extremal. But we obtain that a corresponding definition of the integral is not unique. Besides the IRC, there are other "static" RP models. We use here the term minimum energy path (MEP) for the whole category of these pathways. The ansatz (18) for a general variational integral is also applicable for other RP definitions like NTs in special cases. However, using NTs for an RP, the adjacent stationary points for an RP, minimum and TS, are conjugate points. That disturbs one of the sufficient conditions for a unique minimal extremal, the Jacobi condition.

Other extremal definitions, like the one for the variationally optimized RP, result also in an MEP. They are proven not to be solved by steepest descent curves, because the necessary Euler equations are not fulfilled. Thus, they have to give different MEP solutions than the IRC. The possibility to do a parameter transformation in the variational integrant (18) has opened the definition for a wide use by approximate formulas.

Not discussed here are the differences of a path which minimizes a certain integral, and the (possibly other) RP which maximizes the rate of transitions at the SP, between reactant and product, see [15,61,62,79–81]. So, with IRC, NTs, ORPs in their different kinds, GEs or still other pathways, we find unsolved the ultimate question [49,71]:

"What is the 'true' MEP?"

Because the careful identification of a "good" reaction coordinate is crucial for the calculation of reaction rates.

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