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Analysis of the concept of minimum energy path on the potential energy surface of chemically reacting systems

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Some confusion regarding the properties of minimum energy paths is evident in the literature. We show that a way of steepest descent on a potential surface can be defined independently upon the choice of the coordinate systems. The result is applied to mass-weighted coordinates and their use is critically reviewed. Fukui's IRC appears to be a special case of the steepest descent path starting from a saddle point. The impossibility to define a general ascent path is illustrated and the relations of IRC to real trajectories are discussed.

Key words: Potential energy surface—role of coordinate system—path of steepest descent—curvilinear coordinates—mass weighted coordinates

1. Introduction and formulation of the problem

The concept of potential energy surfaces (PES) as a basis for the understanding of chemical reactions was successfully used in Transition State Theory [1]. Starting point for this concept is the adiabatic separation of the movement of the electrons from that of the nuclei in a given chemical system. The changes in the frame of the nuclei are controlled by a potential function $U(\boldsymbol{x})$ depending parametrically on the positions of nuclei x^i. Stable arrangements (reactants, products, intermediates) are minima in $U(\boldsymbol{x})$ characterized by $\boldsymbol{x}_{\min}$; transition states correspond to saddle points (sp) of first order [2] in $U(\boldsymbol{x})$ characterized by $\boldsymbol{x}_{\mathrm{sp}}$.

A suitable definition of a continuous line connecting reactants and products is still subject of extensive investigation and subject of some confusion as well. This line should be an important guide ("reaction path", "reaction coordinate", "minimum energy path" (MEP)) in finding all the transition states and intermediates between reactants and products. The first concept for reaching a saddle from the reactant minimum was the idea of following the way along the valley bottom ("valley path"). This is the direction of least curvature starting from the minimum. Mathematically it is defined by the direction given by the eigenvector of the smallest positive eigenvalue of the Hessian in $\boldsymbol{x}_{\min}$ (identical with the force constant matrix) and its corresponding continuation up to the saddle. This is what chemists in general consider as MEP. But it would be better to call it "path of least resistance" as proposed by Dunitz [3]. Pancíř [4] developed a procedure following this kind of path on the basis of an analysis of the normal vibrational modes (see also [5–7]). In a number of suitable examples this path successfully leads to a saddle point on the surface. Furthermore, reaction pathways on simple two-dimensional surfaces usually presented in chemical textbooks are of such "valley path" type. Unfortunately, a more general treatment requires consideration of the so-called blind valleys (cf. Fig. 1) which do not lead to the desired saddle along the valley path. The saddle point here exists "sideways" [8–11] from the path. That is why the valley path cannot serve as a basis for a general definition of the reaction path leading to the saddle points in question. The frequency of the occurrence of blind valley type potential surfaces in standard chemical reactions has still to be investigated.

Avoiding these problems already in 1970 Fukui [12] proposed to take the steepest descent from a saddle point to the minimum as reaction path introducing the "intrinsic reaction coordinate" (IRC). Such pathway is shown to include conservation of nuclear symmetry [13]. In a number of papers, Fukui et al. (for a review cf. [14]) demonstrated the high utility of this concept. Other authors also gave substantial contributions in the application of IRC [15–18].

We feel that the question how to reach generally saddle points from reactant or product minima will be solved only by treatments including the dynamics of the system (contrarily to opinions presented in [19, 20]). Fukui's IRC will not describe real dynamical behaviour of the N-particle system of atoms. Since the IRC presumes an annihilation of the kinetic energy after each infinitesimal step in the direction of steepest descent it cannot be overlooked that the interpretation of the curve of steepest descent on the surface $U(\boldsymbol{x})$ as the dynamical limit with $E_{\mathrm{kin}} \to 0$ (infinitely slow movement [21–24] without a moment of inertia for the moving masses [21]) produces difficulties in the physical modelling and understanding: To define an equation of motion for that case according to Newton, Lagrange or Hamilton remains problematic because any movement necessarily implicates the existence of kinetic energy in contradiction to the definition of that path.

Consequently, this path is nothing else but a mathematically defined curve going from a higher to a lower potential. Pechukas [13] formulated it as follows: "There is no dynamical significance to a path of steepest descent. It is a convenient mathematical device to get from high ground, around the transition state, to low ground where the stable molecules are".

Furthermore, some mathematical questions arise from the requirement of a coordinate invariant definition of the path of steepest descent. Tachibana and Fukui presented extensive studies to coordinate invariance of reaction paths and indicated how to use curvilinear coordinates [25–28]. The authors of the present paper observe difficulties and misunderstanding in the fundamental ideas of Tachibana and Fukui [25, 26] in the last years as pointed out in the next sections.

At present it seems of importance to explain the striking features of IRC mathematically without using the general differential–geometrical calculus.

2. What does the independence from coordinate systems mean?

The potential $U(\boldsymbol{x})$ is defined by the mutual positions of the atoms in a chemical system. A configuration A of the atoms corresponds uniquely to an energy U_A, any other to U_B. If we have $U_A > U_B$, so this relation holds in every system of coordinates chosen for the description of the positions of A and B. So we can speak from an "a priori potential surface". For its description one commonly uses the Cartesian system in $\boldsymbol{R}^{3N}$ $(x^i, i = 1, \dots, 3N)$ or in an internal curvilinear system q^k, $k = 1, \dots, n$ with $n = (3N-6)$. The description of stationary points (minima, saddle points) as well as the description of the path connecting minima over a first order saddle are given in that chosen coordinate system. A concrete arrangement of atoms in an equilibrium configuration has to be independent of the chosen coordinate system. The point $\boldsymbol{x}_{st}$ which corresponds to a stationary point on $U = U(x^1, \dots, x^{3N})$ satisfies $3N$ conditions

$$\left.\frac{\partial U(\boldsymbol{x})}{\partial x^i}\right|_{\boldsymbol{x}=\boldsymbol{x}_{st}} = 0, \qquad i = 1, \dots, 3N, \tag{1a}$$

or in vector notation

$$\nabla U(\boldsymbol{x})|_{\boldsymbol{x}=\boldsymbol{x}_{st}} = \boldsymbol{0}.$$

Analogously, the n conditions

$$\left.\frac{\partial V(\boldsymbol{q})}{\partial q^k}\right|_{\boldsymbol{q}=\boldsymbol{q}_{st}} = 0, \qquad k = 1, \dots, n \tag{1b}$$

hold in the $\boldsymbol{R}^n$ space. $U = U(\boldsymbol{x})$ and $V = V(\boldsymbol{q})$ are the expressions in the two different coordinate systems. Of course the concrete $\boldsymbol{x}_{st}$ and $\boldsymbol{q}_{st}$ respectively belonging to a stationary point depend strongly on the chosen coordinate system, already simply on its origin. On the other hand, the form of condition (1) is independent of any coordinate system. This is easy to understand, but how to show invariance of a path definition in the configuration space? This is a task for differential geometry including the theory of invariants (as tensors etc.). In the case of a gradient path for a function U over a coordinate space the situation is clear: At first we have to define the genuine configuration space of the potential U with physical reasoning. Textbooks of mathematics then show that in any transformed coordinate system the modified expression for the gradient vector represents the same direction of steepest descent. For our purpose follows: The gradient path from a saddle to a minimum describes exactly the same sequence of configurations in the Cartesian $\boldsymbol{R}^{3N}$ (with or without mass weighted coordinates) as the gradient path in the $\boldsymbol{R}^{n}$ space of internal curvilinear coordinates.

This elementary fact is in contradiction to the conclusions in other papers [15–18], where only mass-weighted coordinates are allowed, to the paper of Sana et al. [24] who derived the conclusion of a general dependence of a path of steepest descent upon coordinate systems, and to statements in a number of other papers [22, 30–33]. In the following section we give a more detailed analysis of the evident confusion.

3. The gradient equation for the path of steepest descent

We start in a $3N$-dimensional Cartesian system $x=(x^1,\dots,x^{3N})$ presuming this system to be a genuine configuration space for an N-atomic molecule (cf. [62, 63]). Let W be a point set of chemically important configurations and let us consider the potential function U over W ($\boldsymbol{R}$ is the real number axis):

$$U: W \rightarrow \boldsymbol{R} \quad \text{with } W \in \boldsymbol{R}^{3N}.$$

We assume that all second derivatives of U exist and are continuous.

Definition. A gradient system on the set W is a system of ordinary differential equations

$$\frac{dx^i}{dt} = -\frac{\partial U}{\partial x^i}(\boldsymbol{x}(t)), \qquad i=1,\dots,3N \tag{2}$$

for $3N$ functions of the coordinates $x^i = x^i(t)$ which describes the path of steepest descent on the potential function $U=U(\boldsymbol{x})$. Here t is a parameter of the curve length which should be not confused with a time parameter. The employment of a t or s curve length parameter is outlined in [26, 33], where the true curve length s is the canonical parametrization (cf. [34]). In this paper we use only t.

A point $\boldsymbol{x}_{st} \in W$ denotes a stationary (or singular) point if $\nabla U(\boldsymbol{x}_{st})$ is the zero vector (Eq. (1a)). All other configurations are regular points. Textbooks in mathematics (cf. [35]) show that exactly one solution of the system (2) goes through any regular point $\boldsymbol{x}$. For stationary points this statement is not valid.

Now $n=(3N-6)$ internal coordinates q^k are related to $3N$ Cartesian coordinates x^i by – in general – nonlinear transformations often containing trigonometric functions or roots

$$q^k = q^k(x^1,\dots,x^{3N}), \qquad k=1,\dots,n. \tag{3}$$

They may be rather complicated. The n functions (3) should be derivable; now we form the expression

$$g^{kl} = g^{kl}(\boldsymbol{x}) = \sum_{i=1}^{3N} \frac{\partial q^k}{\partial x^i} \frac{\partial q^l}{\partial x^i}, \qquad k, l = 1, \dots, n. \tag{4}$$

Fixing the molecule in the $\boldsymbol{x}$-system it is also described by (3) in the q-system. But the inverse transformation from the n coordinates q^k to $3N$ coordinates x^i will only be possible by adding still six (rather arbitrary) conditional equations to (3) in order to fix the molecule described rigidly in the internal coordinates also in the 3-dimensional ordinary space. Equations of the kind

$$0 = \sum_{l=0}^{N-1} x^{a+3l} \quad \text{with } a = 1, 2, 3, \tag{5a}$$

and the conditions [36, 37]

$$0 = \sum_{l=0}^{N-1} (x^{a+3l} x_{st}^{b+3l} - x^{b+3l} x_{st}^{a+3l}), \qquad b \neq a,\ a, b = 1, 2, 3 \text{ with cyclic changing} \tag{5b}$$

are often used for this purpose. Demanding the existence of the inverse transformation of the $3N$ Eqs. (3) and (5),

$$x^i = x^i(q^1, \dots, q^n), \qquad i = 1, \dots, 3N \tag{6}$$

and further assuming the existence of derivations to (6) with respect to all q^k, we obtain the following relations for the mutual derivations of these inverse transformations (using the chain rule)

$$\sum_{i=1}^{3N} \frac{\partial q^l}{\partial x^i} \frac{\partial x^i}{\partial q^k} = \delta_k^l, \qquad l, k = 1, \dots, n \tag{7}$$

if the q^k, $k = 1, \dots, n$ are, as commonly assumed, independent coordinates.

Theorem. *In curvilinear coordinates the gradient system* (2) *has for n functions* $q^k = q^k(t)$ *the form*

$$\frac{dq^k}{dt} = -\sum_{l=1}^{n} g^{kl}(\boldsymbol{x}) \frac{\partial V(q)}{\partial q^l}, \qquad k = 1, \dots, n \tag{8a}$$

and with the matrix $(g_{kl}) := (g^{kl})^{-1}$

$$\sum_{l=1}^{n} g_{kl} \frac{dq^l}{dt} = -\frac{\partial V}{\partial q^k}, \qquad k = 1, \dots, n. \tag{8b}$$

Proof. Using (6) for the solution $\boldsymbol{x}(t)$ of Eq. (2), we suppose

$$x^i(t) = x^i(q^1(t), \dots, q^n(t)), \qquad i = 1, \dots, 3N.$$

This means the solutions in the x-system $\boldsymbol{x}(t)$ and in the q-system $\boldsymbol{q}(t)$ describe the same path in the configuration space. Then the derivative of $x^i(t)$ is given by

$$\frac{dx^i}{dt}=\sum_{k=1}^{n}\frac{\partial x^i}{\partial q^k}\frac{dq^k}{dt}. \tag{9}$$

As we have to relate $U(\boldsymbol{x})$ to $V(\boldsymbol{q}(\boldsymbol{x}))$, it results

$$-\frac{\partial U}{\partial x^i}=-\sum_{k=1}^{n}\frac{\partial V}{\partial q^k}\frac{\partial q^k}{\partial x^i}, \qquad i=1,\ldots,3N. \tag{10}$$

Eq. (10) is well known as the Wilson $\boldsymbol{B}$-matrix formula [38] with

$$\boldsymbol{B}=\left(\frac{\partial q^k}{\partial x^i}\right)\Bigg|_{q_{st}}.$$

It has been used for linearized displacements dq^k and dx^i in Eq. (9) in the neighborhood of equilibrium points and, by Pulay [39], for a development up to quadratic terms. The $\boldsymbol{B}$-matrix represents a rectangular $3N\times n$-matrix, its inverse is not explained. One can use a pseudo-inverse which can be found by an arbitrary matrix $\boldsymbol{m}$. The free choice of this auxiliary matrix is related to the arbitrariness of the Eqs. (5) (cf. [40–43]). According to (2) both right hand sides in Eq. (9) and Eq. (10) are equal. For each $i=1,\ldots,3N$ we obtain one equation:

$$\sum_{k=1}^{n}\frac{\partial x^i}{\partial q^k}\frac{dq^k}{dt}=-\sum_{k=1}^{n}\frac{\partial V}{\partial q^k}\frac{\partial q^k}{\partial x^i}. \tag{11}$$

Multiplying the corresponding i-th Eq. in (11) with $\partial q^m/\partial x^i$ and summing up all the $3N$ equations we get

$$\sum_{k=1}^{n}\left(\sum_{i=1}^{3N}\frac{\partial q^m}{\partial x^i}\frac{\partial x^i}{\partial q^k}\right)\frac{dq^k}{dt}=\frac{dq^m}{dt}=-\sum_{k=1}^{n}g^{km}\frac{\partial V}{\partial q^k}, \qquad m=1,\ldots,n \tag{12}$$

because the sum of the mutual derivatives on the left hand side is δ_k^m considering (7). Eq. (12) is identical with Eq. (8a).

From (4) we conclude that the matrix (g^{kl}) is symmetric and positive definite. Thus its inverse does exist. Multiplying Eq. (12) with g_{ml} and summing up all n equations for $m=1,\ldots,n$ we obtain Eq. (8b).

It is noteworthy that in mathematics the r.h.s. of (12) is characterized as "gradient", but not the vector of the derivatives of the potential function V alone. The often used illustration of a potential function over orthogonal axes of internal coordinates leads to a distortion in nearly all directions. The interpretation of such diagrams has to consider that (see [61]).

3.1. Discussion of the theorem

(i) There is no dependence of the gradient path upon the choice of coordinates! Eq. (11) you can find in similar form in the paper of Sana and coworkers [24]. But these authors improperly deduce the condition $\boldsymbol{B}^T=\boldsymbol{B}^{-1}$ from (11). This condition leads to an improper restriction concerning the possible coordinate systems and also to the false statement concerning a dependence upon the choice of the coordinate system.

(ii) The curve $\boldsymbol{q}(t)$ satisfying (8) in the curvilinear system $\boldsymbol{q}$, is influenced by two factors. The metric tensor g^{kl} realizes the distortion due to internal coordinates, while $-\partial V/\partial q^k$ gives the direction of descent in the new coordinates. Setting up Eq. (8) all is involved what we need in differential geometry to trace the idealized reaction path defined within Fukui's IRC approach [12, 25]. The functions $g^{kl} = g^{kl}(\boldsymbol{x})$ are given a priori by the choice of the internal coordinates $\boldsymbol{q} = \boldsymbol{q}(\boldsymbol{x})$. Formulas for the establishment of $\boldsymbol{B}$-matrices are well known [38]. Having $\boldsymbol{B}$ we can sum up according to (4). In the papers [44–46] one can find advices concerning some problems of the transformation from Cartesian to internal coordinates and vice versa and other related questions.

The so called "analytical" point by point computation of the derivatives of the potential V in internal coordinates was pioneered by Pulay [39, 40] and is now a subroutine of most quantum chemical program systems for optimizing the geometry by Quasi-Newton-methods.

(iii) Some comment on the differential geometry calculus. The mutual transformation of the metric from different curvilinear systems $\boldsymbol{q}$ into $\boldsymbol{q}_+$, which is formally independent of an original $3N$-dimensional space, is given by

$$g_+^{rs} = \sum_{k,l=1}^{n} \frac{\partial q_+^r}{\partial q^k} \frac{\partial q_+^s}{\partial q^l} g^{kl}, \qquad r, s = 1, \ldots, n. \tag{13}$$

But because of $g^{kl} = g^{kl}(\boldsymbol{x})$ we have $g_+^{rs} = g_+^{rs}(\boldsymbol{x})$. Eq. (13) represents a generalization of Eq. (4) where $g^{kl} = \delta^{kl}$. In system (8b) covariant components g_{kl} of the metric tensor are necessary. They are well known as entities connected with the first fundamental form in the $\boldsymbol{q}$-system [34, 47]. From the derivatives of (6) we get the n $3N$-dimensional vectors

$$\boldsymbol{e}_k = \left(\frac{\partial x^1}{\partial q^k}, \ldots, \frac{\partial x^{3N}}{\partial q^k}\right), \qquad k = 1, \ldots, n. \tag{14}$$

They are in the $\boldsymbol{R}^{3N}$ a natural basis of the tangential plane on the n-dimensional subspace of $\boldsymbol{q}$-coordinates. With (14) we can define (cf. [25, 34])

$$g_{kl}(\boldsymbol{q}) = \boldsymbol{e}_k \cdot \boldsymbol{e}_l = \sum_{i=1}^{3N} \frac{\partial x^i}{\partial q^k} \frac{\partial x^i}{\partial q^l}, \qquad k, l = 1, \ldots, n. \tag{15}$$

Similar to (13) we have for the covariant g_{kl} the transformation [48]

$$g_{rs}^{+}(\boldsymbol{q}_+) = \sum_{k,l=1}^{n} \frac{\partial q^k}{\partial q_+^r} \frac{\partial q^l}{\partial q_+^s} g_{kl}(\boldsymbol{q}).$$

By means of (7) it is evident that for the co- and contravariant components of the metric tensor the following relation holds

$$\sum_{k=1}^{n} g^{lk} g_{ks} = \delta_s^l, \qquad l, s = 1, \ldots, n.$$

It is noteworthy that we do not need to construct the covariant terms for the system (8a). Only their assumed existence was used in (7). But there are in (8a) as well as in (8b) some specific "cliffs" for a numerical computation:

- —The g^{kl} in Eq. (8a) are only given as function of $\boldsymbol{x}$. Hence, from one step to the next it is additionally necessary to use transformation (6).
- —Using (8b) and (15) we have to solve a linear system of equations in each step. But the matrix of the coefficients $g_{kl}(\boldsymbol{q})$ has favorable properties: It is symmetric and positive definite.

The ordinary mathematical device to take over the metric from $\boldsymbol{R}^{3N}$ to $\boldsymbol{R}^n$ is given by Eqs. (6) and (15) using the dependence $g_{kl} = g_{kl}(\boldsymbol{q})$ to get the inverse $g^{kl} = g^{kl}(\boldsymbol{q})$ as function of $\boldsymbol{q}$ in Eq. (8a). Then in Eqs. (8a) and (13) we would have to deal with internal coordinates only. But experience shows the possible difficulty of the inversion process. It is hoped that our way of getting (8a) can serve as a good compromise.

(iv) What happens with the degrees of freedom for overall motions? The introduction of the gradient systems (8) involves a two-fold difficulty: Additional to the differential geometrical problems we have to reduce the $3N$ degrees of freedom to $n = (3N - 6)$. The crucial point are Eqs. (5) for the backtransformation (6). With $\boldsymbol{q} \to \boldsymbol{x}(q)$ we get from $\boldsymbol{R}^n$ in $\boldsymbol{R}^{3N}$ only a parametric representation of an n-dimensional submanifold, which is fixed by "initial values" (5) somewhere in the $\boldsymbol{R}^{3N}$. But we do not get the whole $\boldsymbol{R}^{3N}$ itself. In fact we lose a 6-dimensional manifold.

Nevertheless, the system (8) is correct because of the special structure of our problem. We explain this in view of system (5a): We choose n internal coordinates $q^1, \ldots, q^n$ and additional three coordinates for the geometrical center of the molecule with respect to the laboratory origin:

$$q^{n+a} := 1/N \sum_{l=0}^{N-1} x^{a+3l}, \qquad a = 1, 2, 3. \tag{16}$$

Thus contrarily to (5a) we do not constrain the q^{n+a} to 0. We get

$$\frac{\partial q^{n+a}}{\partial x^{b+3l}} = \begin{cases} 1/N & \text{for } a = b, \quad a, b = 1, 2, 3 \\ 0 & \text{for } a \neq b, \quad l = 0, \ldots, N-1. \end{cases} \tag{17}$$

We assume the potential to be independent of the locus in the ordinary 3-dimensional space. Let h be a displacement in any direction, e.g. in the x-direction:

$$U(x^1, \ldots, x^{3N}) = U(x^1 + h, x^2, x^3, x^4 + h, \ldots, x^{3N})$$

thus

$$\frac{\partial U}{\partial h} = 0 = \sum_{l=0}^{N-1} \frac{\partial U}{\partial x^{1+3l}}, \tag{18}$$

and consequently

$$\frac{\partial V}{\partial q^{n+a}}=0, \qquad a=1,2,3$$

if we take for example

$$q^{n+a}+h=1/N\sum_{l=0}^{N-1}(x^{a+3l}+h).$$

So the first n equations in the system (8a) have not to be changed. For the three new coordinates we get three additional equations

$$\frac{dq^{n+a}}{dt}=-\sum_{k=1}^{n}g^{(n+a)k}\frac{\partial V}{\partial q^{k}}, \qquad a=1,2,3. \tag{19}$$

With definition (4) and the particular property (17) the trivial factors $1/N$ or zero are obtained in the new $g^{(n+a)k}$ giving

$$g^{(n+a)k}=1/N\sum_{l=0}^{N-1}\frac{\partial q^k}{\partial x^{a+3l}}.$$

Now we expand:

$$\sum_{k=1}^{n}\frac{\partial V}{\partial q^k}\left(\frac{1}{N}\sum_{l=0}^{N-1}\frac{\partial q^k}{\partial x^{a+3l}}\right)=\frac{1}{N}\sum_{l=0}^{N-1}\sum_{k=1}^{n}\frac{\partial V}{\partial q^k}\frac{\partial q^k}{\partial x^{a+3l}}$$
$$=\frac{1}{N}\sum_{l=0}^{N-1}\cdot\frac{\partial U}{\partial x^{a+3l}}=0, \tag{20}$$

where we used the chain rule and Eq. (18). Hence we have in Eq. (19) always

$$\frac{dq^{n+a}}{dt}=0 \quad \text{for } a=1,2,3.$$

The geometrical centre of the chemical system does not move and we can really cancel the three Eqs. (19) in the system (8a), as we did above.

(v) The use of mass weighted coordinates. Our theorem additionally clarifies the question of using mass weighted coordinates for the path of steepest descent [15, 33, 49, 50]. In system (2) the trivial metric tensor is $g^{ij}=\delta^{ij}$, $i,j=1,\dots,3N$. Now we choose the centre of mass as origin. The transformations

$$Q^i=m_i^{1/2}x^i \quad \text{and} \quad V(Q^i)=U(Q^i/m_i^{1/2}) \tag{21}$$

give the mass weighted Cartesian system Q^i and the transformed potential (m_{a+3l}, $a=1,2,3$; $l=0,\dots,N-1$ labelling the $(l+1)$th atomic mass). According to (4) we have

$$g^{kj}=\sum_{i=1}^{3N}m_k^{1/2}\delta^{ki}m_j^{1/2}\delta^{ij}=(m_km_j)^{1/2}\delta^{kj}=\begin{cases}m_j & \text{for } k=j\\ 0 & \text{for } k\neq j.\end{cases} \tag{22}$$

Instead of (2) we get the following new gradient system

$$\frac{dQ^i}{dt} = -m_i \frac{\partial U}{\partial Q^i}(Q^1/m_1^{1/2}, \ldots, Q^{3N}/m_{3N}^{1/2}) = -m_i \frac{\partial V}{\partial Q^i}, \tag{23}$$

$i = 1, \ldots, 3N$, for the former path of steepest descent. It is easy to see that (23) is identical to (2) because the following relationship is valid

$$\frac{d(Q^i/m_i^{1/2})}{dt} = -\frac{\partial U(Q^i/m_i^{1/2})}{\partial (Q^i/m_i^{1/2})}.$$

Consequently, the curves solving both systems will be the same in the configuration space of the real molecule if we start from the same initial point.

Our descent path is only related to the potential energy and does not depend on atomic masses, because the genuine potential itself is independent from these masses and depends per definition only on the charges and the mutual distances of the atoms and electrons [62, 63].

Contrarily to (2) or (23), Fukui et al. [49, 50] use the following system of ordinary differential equations

$$m_i \frac{dx^i}{dt} = -\frac{\partial U}{\partial x^i} \quad \text{or} \quad \frac{dQ^i}{dt} = -\frac{\partial V}{\partial Q^i}, \qquad i = 1, \ldots, 3N \tag{24a, b}$$

for pure Cartesian or mass weighted Cartesian coordinates respectively (see also [15–18, 22, 30, 31, 33]. It results a curve crossing the equipotential lines of the genuine potential in general not rectangularly, but in a skew angle (cf. Fig. 5 in [51]). Nevertheless, the solution curve is a descent path, which explains the success in the treatment of chemical model reactions. The use of (24) was claimed to be necessary for fixing the centre of mass of the chemical system instead of the geometrical centre. That means to replace (5a) by the requirements

$$\sum_{l=0}^{N-1} m_{a+3l} \frac{dx^{a+3l}(t)}{dt} = 0, \qquad a = 1, 2, 3 \tag{25}$$

additionally to Eq. (24a) [49]. Eq. (5b) will be changed similarly. For a simultaneous displacement of all nuclei we have

$$\sum_{l=0}^{N-1} \frac{\partial U}{\partial x^{a+3l}} = 0 \quad \text{(see Eq. 18)}.$$

Thus we can satisfy Eq. (25) if we change the displacement of the steepest descent dx^i/dt of Eq. (2) by the mass-weighting of Eq. (24a). (Note that contrarily to the weighting in (24a) the so-called mass-weighted coordinates Q^i are only weighted by $m_i^{1/2}$. Eq. (24b) looks like a pure steepest descent path, if we take the mass-weighted potential for the genuine one by mistake. This is caused by the weighting of both the coordinates and the potential itself.)

The difference in the effect of Eqs. (2) and (24a) for the solution is evident in the simple case of two atoms. If r is greater than the equilibrium distance, $-\partial V/\partial r$

acts as a push on both nuclei to come closer. But there are different possibilities to displace two nuclei A and B: Firstly, the geometrical center can be held on $\frac{1}{2}(A+B)$, secondly, the center of masses can be conserved, or it is possible to fix any other particular "weighted" point between them. For example, A itself is fixed and only B moves towards A. We can realize this by cancelling three equations in (2) or in (23) for x^A, y^A, z^A. The same is available by the limes of a mass-weighting in (24) taking $m_A \to \infty$, $m_B = 1$ with the desired consequence $dx^A = dy^A = dz^A = 0$.

Now we can interpret our set of gradient equations as follows:

—Eqs. (2), (8), or (23) are the defining systems of ordinary differential equations for the invariant path of steepest descent on a genuine potential surface.

—Eq. (24) defines the ordinary differential equation for a *modified descent path* which preserves the centre of mass. It is in general not the path of steepest descent on the genuine potential. We can call it the mass weighted path.

Regarding the masses, the latter path is defined in a similar sense as it was done in trajectory calculations [33, 52] or in vibrational analysis [38, 54] but it cannot be interpreted as a trajectory (cf. also (vi)). The arbitrariness in this definition was already mentioned recently [55].

Omitting a sharp separation between the choice of coordinate systems and the question what the static descent path on a potential surface should mean physically, seems to be one source of misunderstanding in the literature. An example is given in Eq. (49) in [33]. This paper deals with mass-weighted coordinates, but in the equation pure Cartesians are used. The expression is similar to (24a). But there it is incorrectly remarked that this would be an opposite result in comparison to an equation of the (24b)-type.

(vi) A look to the dynamics. Mass-weighted coordinates are used for the calculation of vibrational frequencies [38, 54]. The crucial point is the assumption of a vibration across an equilibrium position. If we assume the vibrational equations to be approximately harmonic for small displacements, they are

$$m_i \ddot{x}^i + \sum_{j=1}^{3N} U_{ij} x^j = 0, \qquad i = 1, \ldots, 3N,$$

or

$$m_i^{1/2} \ddot{x}^i + \sum_{j=1}^{3N} \frac{U_{x^i x^j}}{(m_i m_j)^{1/2}} (m_j^{1/2} x^j) = 0,$$

hence

$$\ddot{Q}^i + \sum_{j=1}^{3N} V_{Q^i Q^j} Q^j = 0. \qquad (26)$$

The weighting of the coordinates transfers the different kinetic action of the different mass points into the distorted curvature of V. From the analysis of the Hessian $V_{Q^i Q^j}$ the vibrational frequencies of a molecule can be deduced [38, 54].

But in tracing a reaction path with large displacements from the original position the above mentioned approximation (26) fails. We should deal with purely geometric coordinates including the masses m_i in the kinetic term of the equations of motion

$$\ddot{q}^l + \Gamma^l_{kr}\dot{q}^k\dot{q}^r = G^{lr}\frac{\partial V}{\partial q^r}, \qquad l = 1, \ldots, n \tag{27}$$

(cf. [34, 52]). Here the masses m_i are given in form of linear terms in the so-called kinematic components of the metric tensor G_{kl} from which we derive the inverse G^{kl} and the Γ^l_{kr} expressions. Instead of (15) we have to consider here

$$G_{kl} = \sum_{i=1}^{3N} m_i \frac{\partial x^i}{\partial q^k}\frac{\partial x^i}{\partial q^l}. \tag{28}$$

This kinetic intrinsic mass weighting in the G_{kl} originates from the well-known representation of velocities and kinetic energy in internal coordinates

$$2T = \sum_{k,l=1}^{n} G_{kl}\dot{q}^k\dot{q}^l.$$

The weighting acts into the solution of the equations of motion for $q = q(t)$, (t: time). Since we have small vibrations around an equilibrium position, we can approximately linearize the curvilinear coordinates q^k and "forget" the distinction between q^k and its velocity $\dot{q}^k$ as it is done with great success in the ***FG*** matrix formulation of Wilson.

Schaefer et al. [22, 30, 31] proposed a method using an equation of the (24a)-type with respect to mass weighting. These authors obviously took the roundabout way over formula (28) by which they compute the contravariant G^{kl} for a system of ordinary differential equations of the kind as (8) (in [22] denoted as T^{-1}_{ab} with $a, b = R, r, \theta$). But remembering the fact that the masses m_i are included in the used kinematic elements G_{kl}, the resulting descent equations are again distorted as explained earlier.

(vii) Normal coordinates. On the basis of Eqs. (8) we formally have a further possibility: Along a solution curve we can transform the q^k-coordinates in new normal coordinates q'^k. Putting q'^n in the role of the reaction coordinate on the path of steepest descent, all other $q'^1, \ldots, q'^{n-1}$ remain zero on this path and should be orthogonal to q'^n [25, 26, 56]. The existence of such a transformation is settled in mathematics [35], but a practical realization is still unknown [57]. But at present it seems to be of theoretical interest only because we do not know a "simple" analytical expression for V or $\partial V/\partial q^k$. With the new $\boldsymbol{q}'$ we would lose the a priori character of the globally chosen curvilinear system $\boldsymbol{q}$ of the configuration space, contrarily we would have to include step by step in $\boldsymbol{q}'$ (numerically) the influence of the potential V. Difficulties of another kind arise if we restrict the $\boldsymbol{q}$-system by constraints to $n < (3N - 6)$ degrees of freedom, where these constraints are derived from an a priori-notion of the potential V itself (cf. [55]).

4. The IRC of Fukui, definition and conclusions

The gradient system (8) has for every point q with $\nabla V(\boldsymbol{q}) \neq \mathbf{0}$ exactly one solution going through $\boldsymbol{q}$. Now we are looking for curves connecting two singular points $\boldsymbol{q}_{\text{min}}$ being minima in V. The highest energy point $\boldsymbol{q}_{\text{sp}}$ on this continuous line is a further singular point, namely a saddle on V. Because $\nabla V = 0$ in these points, the r.h.s. in (8) is the zero vector and a solution $\boldsymbol{q}(t)$ does not move out of this point. Regardless of this problem we can include these singular points in a theory of descent paths by looking for possible entering or stepping out directions of a solution curve [13, 26]. In equilibrium positions the configuration space and the tangential hyperplane to the potential function V are parallel. Hence a computation of the eigenvalues of the Hessian matrix $(V_{q^k q^l})|_{\boldsymbol{q}=\boldsymbol{q}_{st}}$ yields the principal values of curvature in V and their directions as well. It is known [26, 58] that we can reach a minimum from all points of a suitable near neighborhood. All these curves are converging asymptotically to the directions of the eigenvectors, and most of them to the eigenvector direction of the smallest eigenvalue. In contrast to that a saddle can be reached exactly only from the subspace of eigenvectors belonging to the positive eigenvalues, and only be abandoned in the direction of the negative eigenvalue of the Hessian (cf. the definition of a saddle of first order). It is the so-called decomposition direction of the saddle.

Definition. A solution $\boldsymbol{q}(t)$ of the system (8) starting from a saddle point by an infinitesimally small displacement in the direction of the negative eigenvalue of the Hessian is called intrinsic reaction coordinate (IRC), see [12, 25].

Remarks. (i) The IRC is uniquely defined as the path connecting a saddle with a near minimum. On the other hand we do not know which of the infinitely many solutions entering asymptotically the direction of the smallest eigenvalue of the minimum will be that solution which crosses the saddle upwards on an ascent path [59]. Moreover, we do not know whether a direction of any other eigenvalue leads to the saddle. This uncertainty is – contrarily to recent results of Natanson [33] – independent of the clear numerical instability of an ascent following the gradient.

(ii) The potential function V has in a saddle $\boldsymbol{q}_{\text{sp}}$ in the direction of the transition vector the shape of a valley. This follows from the definition of a saddle. On the other hand it is known that the path of steepest descent enters the minimum along the direction of its smallest eigenvalue [26]. From this picture the idea was formed the IRC would describe that curve in the configuration space which represents the bottom of a valley. There are a lot of chemically relevant examples where this notion may be a more or less good approximation to the real situation, but there are also further examples with a significantly different characterization [8–11] (see also the detailed paper by Mezey [60]).

The point is the convexity or nonconvexity of equipotential surfaces. In Fig. 1 we show a two-dimensional picture of an IRC reaching the potential minima $\boldsymbol{x}_1$ or $\boldsymbol{x}_2$, respectively, not along the bottom of the valley (– – –), but along a path going down "sideways". If we assume a neighborhood of the minima as rigid

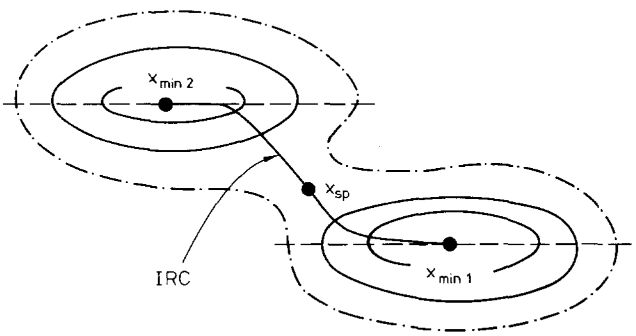

Fig. 1. The IRC on a two-dimensional model potential surface (--- valley paths and displacement lines, see text)

and change the potential surface by mutual displacements of the two rigid minima-hollows along the direction of the eigenvector of the smallest eigenvalue (that means we only change level lines upwards from the (–·–·–)-line) we will observe a change in the relative position of the saddle to those of the both minima. Hence, it results a change of the IRC also for the fixed part of the surface. The knowledge of the local curvatures of the potential in a minimum position does not generally allow a conclusion in which direction the lowest next saddle can be found.

It should be denoted that in Fig. 1 no branching of the (- - -)-valley exists. So we cannot follow one of the branches from the minimum to the saddle obtaining the IRC. Consequently, the idea of the optimal ascent path [6] fails here.

(iii) The solutions of the gradient equations (2, 8, or 23) cross the equipotential surfaces rectangular in every regular point [25, 26]. In a potential hollow the equipotential surfaces are convex, hence the potential has a minimal value on the tangential plane in any point x where this plane touches the potential function (see Fig. 2). The touching point be x_1. - This right insight nevertheless led to considerable trouble, because it suggested a valley-path character ("minimum energy path") of every solution curve $x(t)$. Of course, rectangular to the direction of the descent $-\nabla U$ we have an ascent to both sides. But besides the generally

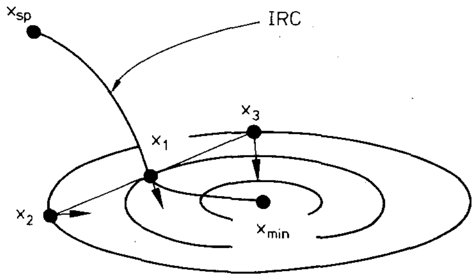

Fig. 2. IRC and its neighborhood (the arrows illustrate length and directions of $-\nabla U$)

strong anharmonic behavior of that section, the conclusions concerning back driving forces connected with this picture are in general wrong. If in a dynamical model by the action of the moment of inertia or, in the computation of the IRC itself by numerical effects we leave the IRC path, say to x_2 or x_3, then these points will be new starting points for other solutions of the gradient system and no "forces" bring back the system to the IRC. The come-back effect (such a curve is called "stable" by Mezey [60]) does only exist, if the IRC corresponds additionally to a valley path. Furthermore, only in this case it makes a sense to deal with vibrational states orthogonal to the path.

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