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 $x_{\min}$ (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]. Pančíř [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 $U(x)$ as the dynamical limit with $E_{\text{kin}} \to 0$ (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 $U(x)$ 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, $i = 1, \ldots, 3N$) or in an internal curvilinear system q^k, $k = 1, \ldots, n$ 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 $U = U(x^1, \ldots, x^{3N})$ satisfies $3N$ conditions

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

or in vector notation

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

Analogously, the n conditions

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

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