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 $x=(x^1,\ldots,x^{3N})$ 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):

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

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

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

for $3N$ functions of the coordinates $x^i = x^i(t)$ which describes the path of steepest descent on the potential function $U=U(x)$. 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 $x_{st} \in W$ denotes a stationary (or singular) point if $\nabla U(x_{st})$ 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 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

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

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

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

Fixing the molecule in the 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),

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

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)

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

if the q^k, $k=1,\ldots,n$ 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*

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

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

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

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

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

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