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

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