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 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 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 $\boldsymbol{q}_{\min}$ being minima in V. The highest energy point $\boldsymbol{q}_{sp}$ 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 $(V_{q^kq^l})|_{\boldsymbol{q}=\boldsymbol{q}_{st}}$ 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 $\boldsymbol{q}_{sp}$ 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 x_1 or 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