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Potential energy surface exploration with equilibrial paths. Part I: Theory

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The equilibrial path concept is further developed. Special attention is spent the symmetry conservation along equilibrial paths and symmetry-breaking. Symmetry-breaking can occur only at singular points. The simple singular points of an equilibrial path are valley–ridge inflection points. In contrast to the intrinsic reaction paths and the gradient extremal paths, the equilibrial paths enable to describe the branching of reaction channels.

1. Introduction

Within the classical transition state theory [1] the transition structure of a chemical reaction is determined by a first order saddle point of the energy function. Educt and product are associated with a minimizer. Thus each theoretical investigation of a molecular system starts with the computation of the stationary points. Minimizers can simply be determined by well-working descent procedures. But the computation of saddle points is remained a hard task till today; see, e.g., [2,3]. Since only poor guesses are available in general, saddle point searches call for *non-local* numerical procedures.

Besides the stationary points the valley–ridge inflection points are of particular interest for the theoretical description of chemical reactions because they indicate the branching of a reaction channel on the potential energy surface [4]. They are no distinguished points of the energy function or the energy derivatives. Therefore valley–ridge inflection points can be detected only by *non-local* search procedures; cf. [5] and the literature cited therein. In general the educt and the product of a chemical reaction are connected with some transition structure by two intrinsic reaction paths [6,7] which start at the saddle point and lead to the educt and product minimizer.

The valley–ridge inflection points are no distinguished points of the intrinsic reaction paths. Therefore they can only be detected by monitoring the eigenvalues of the Hessian matrix along the path [8]. This procedure is, however, very expensive.

Very recently the concept of equilibrial paths has been proposed by the author [9]. Equilibrial paths enable to locate both minimizers and saddle points. At the same time

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they connect an educt with the transition structure or a transition structure with the product. The valley–ridge inflection points are distinguished points at equilibrial paths. The most important properties are the following:

(i) Equilibrial paths can start at a minimizer as well as a saddle point. An equilibrial path that originates at a minimizer ends at a saddle point (or a plateau of the potential energy surface). An equilibrial path that starts at a saddle of order μ leads to a stationary point of the order $(\mu - 1)$ in general.

(ii) The initial search direction can be prescribed such that several saddle points surrounding a given minimizer can be found.

(iii) The simple singular points of an equilibrial path are valley–ridge inflection points. The additional numerical effort necessary to detect these points is next to nothing.

Thus equilibrial paths are well suited for the exploration of large parts of potential energy surfaces. They enable to gain an insight into the reaction topography.

In the present paper the concept of equilibrial paths is further developed. The equilibrial path definition given in section 3 differs in some points from that in [9] because it considers the observation that bifurcation points are not a rare, but a frequent occurance. The common idea of a branching reaction channel (cf., e.g., [4]) is met for a certainty only at the symmetry-breaking simple bifurcation points. In other words, valley–ridge inflection points may also found in more general bifurcation situations.

Special attention is spent the conservation of symmetry and symmetry-breaking. In section 4 it is proven that (under certain assumptions) along a regular equilibrial path the symmetry of a nuclear system is conserved. Symmetry-breaking can occur only at singular points. In the vicinity of a symmetry-breaking simple bifurcation point the changes in the potential energy are greater along the symmetric branch than along the nonsymmetric branches. In other words, in the stage of activation the increase in the potential energy is less if some symmetry is broken. In the stage of relaxation the decrease in the potential energy is greater if the symmetry is preserved or some symmetry is gathered. Thus in a stage of activation a nuclear system will follow a nonsymmetric branch at a valley-ridge inflection point whereas in a stage of relaxation it will follow the symmetric branch.

In the second part the results of a potential energy surface exploration with equilibrial paths are presented.

2. Background material

The position vectors $\mathsf{p}_i = (p_{ix}, p_{iy}, p_{iz})^\top \in \mathbb{R}^3$, $i = 1(1)n$, of the n nuclei of a molecular system are collected in a vector $\boldsymbol{p} = (\mathsf{p}_1, \ldots, \mathsf{p}_n)^\top$. Thus each nuclear configuration of a molecular system is described by a vector of the configuration space

$$\mathbb{P} := \left\{ \boldsymbol{p} \;\middle|\; \boldsymbol{p} = (\mathsf{p}_1, \ldots, \mathsf{p}_n)^\top,\ \mathsf{p}_i \in \mathbb{R}^3,\ i = 1(1)n \right\}.$$

The vector space $\mathbb{P}$ is endowed with the inner product $\langle \cdot | \cdot \rangle$,

$$\langle \boldsymbol{p} \mid \boldsymbol{q} \rangle := \sum_{i=1}^{n} \langle \mathsf{p}_i \mid \mathsf{q}_i \rangle, \qquad \boldsymbol{p}, \boldsymbol{q} \in \mathbb{P},$$

where $\langle\cdot|\cdot\rangle$ denotes the inner product on $\mathbb{R}^3$. A norm $\|\cdot\|$ is defined on $\mathbb{P}$ by

$$\|\boldsymbol{p}\| := \sqrt{\langle \boldsymbol{p} \mid \boldsymbol{p}\rangle}, \quad \boldsymbol{p} \in \mathbb{P}.$$

Since $\mathbb{P}$ is the Cartesian product of $\mathbb{R}^3$-copies, a cross-product can be defined on $\mathbb{P}$ by

$$\boldsymbol{d} \times \boldsymbol{p} := (\mathsf{d}_1 \times \mathsf{p}_1, \ldots, \mathsf{d}_n \times \mathsf{p}_n)^\top, \quad \boldsymbol{d}, \boldsymbol{p} \in \mathbb{P}.$$

Recall that on $\mathbb{R}^3$ the cross-product can be written as

$$\mathsf{d} \times \mathsf{p} = \mathsf{C}(\mathsf{d})\mathsf{p}$$

with the matrix

$$\mathsf{C}(\mathsf{d}) := \begin{pmatrix} 0 & -d_3 & d_2 \\ d_3 & 0 & -d_1 \\ -d_2 & d_1 & 0 \end{pmatrix}, \quad \mathsf{d} = (d_1, d_2, d_3)^\top.$$

Thus

$$\boldsymbol{d} \times \boldsymbol{p} = \boldsymbol{C}(\boldsymbol{d})\boldsymbol{p},$$

where $\boldsymbol{C}(\boldsymbol{d})$ is the blocked diagonal matrix built up by the $(3,3)$-matrices $\mathsf{C}(\mathsf{d}_i)$, $i = 1(1)n$, i.e.,

$$\boldsymbol{C}(\boldsymbol{d}) := \operatorname{diag}\big(\mathsf{C}(\mathsf{d}_1), \ldots, \mathsf{C}(\mathsf{d}_n)\big).$$

Since a nuclear ensemble can always be arranged in $\mathbb{R}^3$ so that the barycenter of the nuclei coincides with the origin, the nuclear configurations of a molecular system are just described by the vectors of the subspace

$$\mathbb{P}_0 := \left\{ \boldsymbol{p} \in \mathbb{P} \;\middle|\; \sum_{i=1}^{n} \mathsf{p}_i = 0 \right\}$$

of $\mathbb{P}$. Below nuclear configurations are always described by a vector of $\mathbb{P}_0$. The vectors of the subspace

$$\mathbb{L}_0(\mathsf{d}) := \{\boldsymbol{p} \in \mathbb{P}_0 \mid \mathsf{p}_i = \alpha_i \mathsf{d}\}, \quad 0 \neq \mathsf{d} \in \mathbb{R}^3,$$

of $\mathbb{P}_0$ represent the collinear configurations while the vectors of the direct sum

$$\mathbb{L}_0(\mathsf{d}_1, \mathsf{d}_2) := \mathbb{L}_0(\mathsf{d}_1) \oplus \mathbb{L}_0(\mathsf{d}_2), \quad \mathsf{d}_1 \times \mathsf{d}_2 \neq 0,$$

represent the planar configurations. If the vectors d_i, $i = 1(1)3$, form a base in $\mathbb{R}^3$, then

$$\mathbb{P}_0 = \mathbb{L}_0(\mathsf{d}_1) \oplus \mathbb{L}_0(\mathsf{d}_2) \oplus \mathbb{L}_0(\mathsf{d}_3).$$

The vectors of the three-dimensional subspace

$$\mathbb{T} := \big\{\boldsymbol{d} \in \mathbb{P} \mid \boldsymbol{d} = (\mathsf{d}_1, \ldots, \mathsf{d}_n)^\top,\ \mathsf{d}_i = \mathsf{d} \in \mathbb{R}^3,\ i = 1(1)n\big\}$$

of $\mathbb{P}$ describe the overall translations of a nuclear ensemble in $\mathbb{R}^3$. Since for any $\boldsymbol{p} \in \mathbb{P}_0$ and any $\boldsymbol{d} \in \mathbb{T}$ the inner product $\langle \boldsymbol{p} \mid \boldsymbol{d} \rangle$ vanishes, the vector space $\mathbb{P}$ is the direct sum of its subspaces $\mathbb{P}_0$ and $\mathbb{T}$, i.e.,

$$\mathbb{P} = \mathbb{P}_0 \oplus \mathbb{T}.$$

The vectors of the subspace

$$\mathbb{S}(\boldsymbol{p}) := \{\boldsymbol{q} \in \mathbb{P} \mid \boldsymbol{q} = \boldsymbol{d} \times \boldsymbol{p},\ \boldsymbol{d} \in \mathbb{T}\}, \quad \boldsymbol{p} \in \mathbb{P},$$

of $\mathbb{P}$ describe the infinitesimal rotations of the configuration $\boldsymbol{p}$ about an axis d. If $\boldsymbol{p} \in \mathbb{P}_0$ then $\mathbb{S}(\boldsymbol{p}) \subset \mathbb{P}_0$ and $\dim \mathbb{S}(\boldsymbol{p}) = 3$ for all non-collinear configurations $\boldsymbol{p}$ [9].

In the present paper the energy function $\mathrm{E} : \mathbb{P} \mapsto \mathbb{R}$ is assumed to be thrice continuously differentiable. The gradient and the Hessian matrix of E at a point $\boldsymbol{p} \in \mathbb{P}$ are denoted by $\mathbf{g}(\boldsymbol{p})$ and $\boldsymbol{H}(\boldsymbol{p})$, respectively. Some important properties are summarized in the next theorems.

Theorem 1 [9]. For any $\boldsymbol{p} \in \mathbb{P}$ the following relations are valid:

(a) $\mathbf{g}(\boldsymbol{p}) \in \mathbb{P}_0$,

(b) $\mathbf{g}(\boldsymbol{p}) \times \boldsymbol{p} \in \mathbb{P}_0$,

(c) $\boldsymbol{H}(\boldsymbol{p})\boldsymbol{d} = \mathbf{0}\ \forall \boldsymbol{d} \in \mathbb{T}$,

(d) $\boldsymbol{H}(\boldsymbol{p})(\boldsymbol{d} \times \boldsymbol{p}) = \boldsymbol{d} \times \mathbf{g}(\boldsymbol{p})\ \forall \boldsymbol{d} \in \mathbb{T}$.

Notice that statement (c) implies $\boldsymbol{H}(\boldsymbol{p})\mathbb{P} \subseteq \mathbb{P}_0$.

Theorem 2 [9]. For any $\boldsymbol{p} \in \mathbb{P}_0$ the following inclusions are valid:

(a) $\ker \boldsymbol{H}(\boldsymbol{p}) \cap \mathbb{P}_0 \subseteq (\mathbb{T} \oplus \mathbb{S}(\mathbf{g}(\boldsymbol{p})))^{\perp}$,

(b) $\boldsymbol{H}(\boldsymbol{p})(\mathbb{T} \oplus \mathbb{S}(\mathbf{g}(\boldsymbol{p})))^{\perp} \subseteq (\mathbb{T} \oplus \mathbb{S}(\boldsymbol{p}))^{\perp}$.

Recall that $^{\perp}$ indicates the orthogonal complement of a subspace in $\mathbb{P}$.

A point $\boldsymbol{p}_0 \in \mathbb{P}$ which satisfies the condition $\mathbf{g}(\boldsymbol{p}_0) = \mathbf{0}$ is a *stationary point* of the energy function E. The set of all stationary points of E is denoted by $\mathbf{g}^{-1}(\mathbf{0})$. By virtue of theorem 1(c), (d)

$$\mathbb{T} + \mathbb{S}(\boldsymbol{p}) \subseteq \ker \boldsymbol{H}(\boldsymbol{p}) \quad \forall \boldsymbol{p} \in \mathbf{g}^{-1}(\mathbf{0}).$$

The kernel of a Hessian matrix $\boldsymbol{H}(\boldsymbol{p})$, which is denoted by $\ker \boldsymbol{H}(\boldsymbol{p})$, coincides with the eigenspace that belongs to the zero eigenvalue of $\boldsymbol{H}(\boldsymbol{p})$. A point $\boldsymbol{p} \in \mathbf{g}^{-1}(\mathbf{0})$ is called *pseudo-regular* if $\ker \boldsymbol{H}(\boldsymbol{p}) = \mathbb{T} + \mathbb{S}(\boldsymbol{p})$.

A stationary point $\boldsymbol{p}_0$ is a *saddle point of order* k, $k \geqslant 1$, if the Hessian matrix $\boldsymbol{H}(\boldsymbol{p}_0)$ possesses k negative eigenvalues. A stationary point $\boldsymbol{p}_0$ is a *minimizer* if there is a neighborhood $\mathcal{U}_\delta$ of $\boldsymbol{p}_0$ such that $\mathrm{E}(\boldsymbol{p}_0) \leqslant \mathrm{E}(\boldsymbol{p})$ for all $\boldsymbol{p} \in \mathcal{U}_\delta$. At a minimizer all eigenvalues of the Hessian matrix are non-negative.

3. Concept of equilibrial paths

The equilibrial path concept, which is explained in detail in [9], requires the subdivision of a reactive process into two stages: a stage of activation and a stage of relaxation. The latter may consist of several substages. A *stage of activation* is characterized by the educt $\boldsymbol{m}$ and an excitation vector $\boldsymbol{e} \in (\mathbb{T} \oplus \mathbb{S}(\boldsymbol{m}))^{\perp}$ which is associated with some vibrational modes of the educt. A (*sub*)*stage of relaxation is* characterized by a saddle point structure $\boldsymbol{s}$ and a transition vector $\boldsymbol{t} \in (\mathbb{T} \oplus \mathbb{S}(\boldsymbol{s}))^{\perp}$. Here the term transition vector is used in a more general sense as is the convention. It is also defined for saddle points of higher than first order. Thus transition vector means a linear combination of eigenvectors or projected normal mode vectors that belong to a negative eigenvalue or a imaginary frequency, respectively. Excitation and transition vectors are always normalized.

Within a stage of activation or a (sub)stage of relaxation the motion of a nuclear ensemble is described by the equation [9]

$$\boldsymbol{M}\ddot{\boldsymbol{p}} = -\mathbf{g}(\boldsymbol{p}) + \frac{\varrho(\boldsymbol{p})}{\|\dot{\boldsymbol{p}}\|}\left(\boldsymbol{r} - \frac{\langle \dot{\boldsymbol{p}} \mid \boldsymbol{r} \rangle}{\|\dot{\boldsymbol{p}}\|^2}\dot{\boldsymbol{p}}\right), \quad \|\dot{\boldsymbol{p}}\| \neq 0. \tag{1}$$

The vector $\boldsymbol{r}$ stands for an excitation vector if the equation is associated with a stage of activation while it stands for a transition vector if equation (1) is associated with a (sub)stage of relaxation. It is called a *reaction vector* in the following. The *activation function* ϱ, which is not specified here, is a non-negative, differentiable function which is invariant with respect to the overall translations/rotations of a nuclear ensemble. Furthermore it is required that $\varrho(\boldsymbol{p}) = 0$ for all stationary points $\boldsymbol{p}$ of E. The activation function provides some activation power. $\boldsymbol{M}$ denotes the mass hypermatrix.

The idea behind equation (1) is that within the semiclassical framework

(i) each nuclear configuration $\boldsymbol{p}$ is associated with some activation power $\varrho(\boldsymbol{p})$ and

(ii) the deformations of a nuclear skeleton are caused by two contrary acting forces, namely an *activation force* and a *relaxation force.*

The activation force which is defined by the rightmost term in equation (1) gives rise to bond fissions whereas the relaxation force which is given by the negative gradient of the potential energy works towards bond preservation and bond formation.

3.1. Definition of equilibrial paths

The equilibrial paths are strict connected with the quasi-stationary solutions of equation (1). Each point $(\boldsymbol{p}_*, \rho_*)$, $\rho_* \neq 0$, of the set

$$\mathcal{E}_1 := \left\{(\boldsymbol{p}, \rho) \in \mathbb{P}_0 \times [0, \infty) \mid \mathbf{g}(\boldsymbol{p}) - \rho\boldsymbol{r} = \mathbf{0}\right\}$$

is associated with a family

$$\boldsymbol{p}(t) = \boldsymbol{p}_* + t\boldsymbol{d}, \quad \boldsymbol{d} \in \mathbb{T},\ \|\boldsymbol{d}\| = \varrho(\boldsymbol{p}_*)/\rho_*,$$

of quasi-stationary solutions of equation (1). Along a quasi-stationary solution the relaxation force and the activation force are balanced. Each point $(\boldsymbol{p}_*, 0)$ of the subset

$$\mathcal{E}_0 := \big\{(\boldsymbol{p}, \rho) \in \mathcal{E}_1 \mid \rho = 0\big\}$$

of $\mathcal{E}_1$ is associated with a family

$$\boldsymbol{p}(t) = \boldsymbol{p}_* + t\boldsymbol{d}, \quad \boldsymbol{d} \in \mathbb{T}\backslash\{\mathbf{0}\},$$

of stationary solutions of equation (1). Along a stationary solution the relaxation and activation force vanish. The set $\mathcal{E}_0$ is the set of the boundary points of $\mathcal{E}_1$. It is closely related to the stationary points of the energy function E:

$$\boldsymbol{p} \in \mathbf{g}^{-1}(\mathbf{0}) \cap \mathbb{P}_0 \Longleftrightarrow (\boldsymbol{p}, 0) \in \mathcal{E}_0.$$

The set $\mathcal{E}_1$ is a subset of the zero set of *any* function $\mathbf{h}_1(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$,

$$\mathbf{h}_1(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) := \mathbf{g}(\boldsymbol{p}) - \rho\boldsymbol{r} + \sum_{i=1}^{3} \langle \boldsymbol{p} \mid \boldsymbol{b}_i \rangle \boldsymbol{b}_i, \quad z = (\boldsymbol{p}, \rho),$$

where the vectors $\boldsymbol{b}_i$, $i = 1(1)3$, are linearly independent vectors of $\mathbb{T}$.

Lemma 1 [9]. For any base $\{\boldsymbol{b}_i\}_{i=1}^3$ of $\mathbb{T}$

$$\mathcal{E}_1 = \mathbf{h}_1^{-1}(\mathbf{0}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) \cap \big(\mathbb{P}_0 \times [0, \infty)\big).$$

Definition. A point $z \in \mathbb{P}\times\mathbb{R}$ is a *regular* point of a continuously differentiable function $\mathbf{h} : \mathbb{P} \times \mathbb{R} \mapsto \mathbb{P}$ if the Jacobian matrix $\mathbf{h}'(z) = \mathrm{d}\mathbf{h}(z)/\mathrm{d}z$ has maximal rank. A point is called *singular* if it is not regular. The set of all regular points of $\mathbf{h}$ is denoted by $\mathcal{R}(\mathbf{h})$.

Proposition 1. A point $z = (\boldsymbol{p}, \rho) \in \mathbb{P} \times \mathbb{R}$ is a regular point of the function $\mathbf{h}_1(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ if one of both conditions is fulfilled:

(i) $\ker \boldsymbol{H}(\boldsymbol{p}) \cap \mathbb{P}_0 = \{\mathbf{0}\}$,

(ii) there is a vector $\boldsymbol{v}_0 \in \mathbb{P}_0$, $\boldsymbol{v}_0 \neq \mathbf{0}$, such that $\ker \boldsymbol{H}(\boldsymbol{p}) \cap \mathbb{P}_0 = \mathrm{span}\{\boldsymbol{v}_0\}$ and $\langle \boldsymbol{v}_0 \mid \boldsymbol{r} \rangle \neq 0$.

Proposition 1 results from the equation

$$\mathbf{h}_1'(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \left(\boldsymbol{H}(\boldsymbol{p}) + \sum_{i=1}^{3} \boldsymbol{b}_i \boldsymbol{b}_i^\top \quad -\boldsymbol{r} \right)$$

in conjunction with theorem 1(c).

By virtue of proposition 1 a point $z \in \mathbb{P}\times\mathbb{R}$ is either a regular or a singular point of *all* functions $\mathbf{h}_1(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$. The points of the set $\mathcal{E}_0$ are always singular points because $\mathbb{S}(\boldsymbol{p}) \subset \ker \boldsymbol{H}(\boldsymbol{p}) \cap \mathbb{P}_0$ for all $\boldsymbol{p} \in \mathbf{g}^{-1}(\mathbf{0}) \cap \mathbb{P}_0$.

Lemma 2. The set $\mathcal{M} := \mathcal{E}_1 \cap \mathcal{R}(\mathbf{h}_1)$ is a one-dimensional manifold, i.e., the components of $\mathcal{M}$ are diffeomorphic to either the unit circle or the open interval $(0, 1)$.

Lemma 2 is a consequence of the Global Rank Theorem; cf. [10, p. 176].

For any $(\boldsymbol{p}, \rho) \in \mathcal{E}_1 \backslash \mathcal{E}_0$ and any $\boldsymbol{d} \in \mathbb{T}$

$$\langle \boldsymbol{p} \mid \boldsymbol{d} \times \boldsymbol{r} \rangle = \rho^{-1} \big\langle \boldsymbol{p} \mid \boldsymbol{d} \times \mathbf{g}(\boldsymbol{p}) \big\rangle = -\rho^{-1} \big\langle \boldsymbol{d} \mid \boldsymbol{p} \times \mathbf{g}(\boldsymbol{p}) \big\rangle = 0$$

by theorem 1(b). Hence $\mathcal{E}_1 \backslash \mathcal{E}_0 \subset (\mathbb{S}(\boldsymbol{r}) \oplus \mathbb{T})^{\perp} \times (0, \infty)$. The vector space

$$\mathbb{P}_r := \big(\mathbb{S}(\boldsymbol{r}) \oplus \mathbb{T}\big)^{\perp}$$

is a $(3n - 6)$-dimensional subspace of $\mathbb{P}_0$ if

(R) *the reaction vector* $\boldsymbol{r}$ *includes two subvectors* r_i *and* r_j, $1 \leqslant i, j \leqslant n$, *such that* $\mathsf{r}_i \times \mathsf{r}_j \neq 0$.

If condition (R) is not fulfilled, i.e., all subvectors of the reaction vector are parallel, then $\dim \mathbb{P}_r = 3n - 5$; cf. [9].

The equilibrial path concept is based on the set

$$\mathcal{E}_2 := \mathcal{E}_1 \cap \big(\mathbb{P}_r \times [0, \infty)\big)$$

which includes the one-dimensional manifold $\mathcal{M}$ and some limit points of $\mathcal{M}$.

Definition. Each continuous curve $z(\tau) = (\boldsymbol{p}(\tau), \rho(\tau))$, $\tau \geqslant 0$, in the set $\mathcal{E}_2$ is called an *equilibrial path.* If $\boldsymbol{p}(0)$ is a minimizer (saddle point) then $z(\tau)$ is an *activation path* (a *relaxation path*).

Equilibrial paths are no paths on potential energy surfaces. Along an equilibrial path the relation $\rho(\tau) = \|\mathbf{g}(\boldsymbol{p}(\tau))\|$ holds. Thus equilibrial paths are paths on surfaces generated by the function $\sigma(\boldsymbol{p}) = \|\mathbf{g}(\boldsymbol{p})\|$.

The set $\mathcal{E}_2$ is contained in the zero set of the function

$$\mathbf{h}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) := \mathbf{h}_1(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) + \sum_{i=1}^{3} \langle \boldsymbol{p} \mid \boldsymbol{b}_i \times \boldsymbol{r} \rangle (\boldsymbol{b}_i \times \boldsymbol{p}), \quad z = (\boldsymbol{p}, \rho).$$

The vectors $\boldsymbol{b}_i \times \boldsymbol{p}$, $i = 1(1)3$, are linearly independent if $\boldsymbol{p}$ represents a non-collinear configuration. The term added to the function $\mathbf{h}_1$ excludes all points of the set $\mathcal{E}_0$ which do not belong to the vector space $\mathbb{P}_r \times \mathbb{R}$, from the set $\mathcal{E}_1$. This way the continuous curves in the set $\mathcal{E}_1 \backslash \mathcal{E}_0$ which approach the boundary set $\mathcal{E}_0$ are continued into the set $\mathcal{E}_0$ in a unique manner. The unique continuability is of particular importance for the numerical path tracing.

Lemma 3. For any base $\{\boldsymbol{b}_i\}_{i=1}^3$ of $\mathbb{T}$

$$\mathbf{h}_2^{-1}(\mathbf{0}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) \cap \big(\mathbb{P} \times [0, \infty)\big) = \mathcal{E}_2.$$

The proof is omitted here because it follows the proof of [9, lemma 4.4].

Now the question is whether a regular point of a function $\mathbf{h}_2(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ remains a regular point if the base $\{\boldsymbol{b}_i\}_{i=1}^3$ of $\mathbb{T}$ is changed. To answer this question some information about the Jacobian matrices of the functions $\mathbf{h}_2(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ is needed.

For any $z = (\boldsymbol{p}, \rho) \in \mathbb{P}_r \times \mathbb{R}$ the Jacobian matrix $\mathbf{h}_2'(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ has the form

$$\mathbf{h}_2'(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \big(\boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) \quad -\boldsymbol{r}\big), \tag{2}$$

where

$$\boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \boldsymbol{H}(\boldsymbol{p}) + \sum_{i=1}^{3} \boldsymbol{b}_i \boldsymbol{b}_i^\top + \sum_{i=1}^{3} (\boldsymbol{b}_i \times \boldsymbol{p})(\boldsymbol{b}_i \times \boldsymbol{r})^\top. \tag{3}$$

This observation proves

Proposition 2. A point $z = (\boldsymbol{p}, \rho) \in \mathbb{P}_r \times \mathbb{R}$ is a regular point of the function $\mathbf{h}_2(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ if one of both conditions is satisfied:

(i) $\boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ is a regular matrix,

(ii) $\dim\ker \boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = 1$ and $\boldsymbol{r} \notin \text{range } \boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$.

Considering theorem 1(d)

$$\begin{aligned}(\boldsymbol{b}_i \times \boldsymbol{p})(\boldsymbol{b}_i \times \boldsymbol{r})^\top &= \rho^{-1}(\boldsymbol{b}_i \times \boldsymbol{p})\big(\boldsymbol{b}_i \times \mathbf{g}(\boldsymbol{p})\big)^\top \\ &= \rho^{-1}(\boldsymbol{b}_i \times \boldsymbol{p})\big(\boldsymbol{H}(p)(\boldsymbol{b}_i \times \boldsymbol{p})\big)^\top \\ &= \rho^{-1}(\boldsymbol{b}_i \times \boldsymbol{p})(\boldsymbol{b}_i \times \boldsymbol{p})^\top \boldsymbol{H}(\boldsymbol{p}),\end{aligned}$$

for all $(\boldsymbol{p}, \rho) \in \mathcal{E}_2 \backslash \mathcal{E}_0$. Thus equation (3) results in

$$\boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \sum_{i=1}^{3} \boldsymbol{b}_i \boldsymbol{b}_i^\top + \boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{H}(\boldsymbol{p}) \tag{4}$$

for $z = (\boldsymbol{p}, \rho) \in \mathcal{E}_2 \backslash \mathcal{E}_0$, where

$$\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) := \boldsymbol{I} + \rho^{-1} \sum_{i=1}^{3} (\boldsymbol{b}_i \times \boldsymbol{p})(\boldsymbol{b}_i \times \boldsymbol{p})^\top.$$

$\boldsymbol{I}$ denotes the identity matrix. Observe that the matrix $\boldsymbol{H}_2(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ is symmetric for all $z \in \mathcal{E}_2 \backslash \mathcal{E}_0$.

Proposition 3. For $\rho > 0$

(a) $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ is a regular matrix,

(b) $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\, \mathbb{P}_0 \subseteq \mathbb{P}_0$,

(c) $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{r} = \boldsymbol{r} \quad \forall \boldsymbol{p} \in \mathbb{P}_r$.

Proof. (a) Each vector $\boldsymbol{v} \in \mathbb{P}$ can be written as a sum of a vector $\boldsymbol{v}_1 \in \mathbb{S}(\boldsymbol{p})^{\perp}$ and a vector $\boldsymbol{v}_2 \in \mathbb{S}(\boldsymbol{p})$. Thus

$$\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{v} = \boldsymbol{v}_1 + \boldsymbol{v}_2 + \rho^{-1} \sum_{i=1}^{3} \langle \boldsymbol{b}_i \times \boldsymbol{p} | \boldsymbol{v}_2 \rangle (\boldsymbol{b}_i \times \boldsymbol{p}).$$

Hence $\boldsymbol{v}$ belongs to the kernel of the matrix $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ if and only if $\boldsymbol{v}_1 = \boldsymbol{0}$ and $\boldsymbol{v}_2 + \rho^{-1} \sum_{i=1}^{3} \langle \boldsymbol{b}_i \times \boldsymbol{p} | \boldsymbol{v}_2 \rangle (\boldsymbol{b}_i \times \boldsymbol{p}) = 0$. The last equation implies the condition

$$\rho = -\|\boldsymbol{v}_2\|^{-2} \sum_{i=1}^{3} \langle \boldsymbol{b}_i \times \boldsymbol{p} | \boldsymbol{v}_2 \rangle^2 < 0$$

which is a contradiction to the assumption $\rho > 0$. Thus $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ is a regular matrix for all $\rho > 0$.

(b) If $\boldsymbol{v} \in \mathbb{P}_0$ then $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{v} \in \mathbb{P}_0$ because $\boldsymbol{b}_i \times \boldsymbol{p} \in \mathbb{P}_0$, $i = 1(1)3$, for $\boldsymbol{p} \in \mathbb{P}_0$.

(c) If $\boldsymbol{p} \in \mathbb{P}_r$ then $\langle \boldsymbol{b}_i \times \boldsymbol{p} \mid \boldsymbol{r} \rangle = -\langle \boldsymbol{b}_i \times \boldsymbol{r} \mid \boldsymbol{p} \rangle = 0$, $i = 1(1)3$. Therefore $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{r} = \boldsymbol{r}$. □

The next lemma answers above question.

Lemma 4. If $\boldsymbol{z} = (\boldsymbol{p}, \rho) \in \mathcal{E}_2$ then for any base $\{\boldsymbol{b}_i\}_{i=1}^3$ of $\mathbb{T}$

$$\ker \mathbf{h}_2'(\boldsymbol{z}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \big\{(\boldsymbol{v}, \mu) \in \mathbb{P}_r \times \mathbb{R} \mid \boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} = \mu \boldsymbol{r}\big\}.$$

Proof. The kernel of the Jacobian matrix $\mathbf{h}_2'(\boldsymbol{z}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ consists of all vectors $\boldsymbol{y} = (\boldsymbol{v}, \mu) \in \mathbb{P} \times \mathbb{R}$ which fulfil the equation

$$\mathbf{h}_2'(\boldsymbol{z}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{y} = \boldsymbol{0}. \tag{5}$$

(i) $\boldsymbol{z} \in \mathcal{E}_2 \cap \mathcal{E}_0$. Considering equation (2) the equation

$$\boldsymbol{0} = \big(\boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} - \mu \boldsymbol{r}\big) + \sum_{i=1}^{3} \langle \boldsymbol{b}_i \mid \boldsymbol{v} \rangle \boldsymbol{b}_i + \sum_{i=1}^{3} \langle \boldsymbol{b}_i \times \boldsymbol{r} \mid \boldsymbol{v} \rangle (\boldsymbol{b}_i \times \boldsymbol{p}) \tag{6}$$

results from equation (5). Because $\boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} \in (\mathbb{T} \oplus \mathbb{S}(\boldsymbol{p}))^{\perp}$ for any $\boldsymbol{v} \in \mathbb{P}$ by theorem 1(c), (d), the right hand side of equation (6) vanishes if and only if the three terms vanish simultaneously. In other words, $(\boldsymbol{v}, \mu)$ belongs to $\ker \mathbf{h}_2'(\boldsymbol{z}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ if and only if $\boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} - \mu \boldsymbol{r} = \boldsymbol{0}$ and $\boldsymbol{v} \in \mathbb{P}_r$.

(ii) $\boldsymbol{z} = (\boldsymbol{p}, \rho) \in \mathcal{E}_2 \backslash \mathcal{E}_0$.

Considering equation (4) and proposition 3(c) the equation

$$\boldsymbol{0} = \sum_{i=1}^{3} \langle \boldsymbol{b}_i \mid \boldsymbol{v} \rangle \boldsymbol{b}_i + \boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\big(\boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} - \mu \boldsymbol{r}\big)$$

is obtained from equation (5). Because of proposition 3(b) both right hand terms vanish. By virtue of proposition 3(a) the matrices $\boldsymbol{B}_\rho(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$ are regular, such that the equivalence relation

$$(\boldsymbol{v}, \mu) \in \ker \mathbf{h}_2'(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) \iff (\boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} - \mu \boldsymbol{r} = \mathbf{0}) \wedge \boldsymbol{v} \in \mathbb{P}_0$$

is valid. If $\mu \neq 0$ then by theorem 1(b), (d)

$$\begin{aligned} 0 &= \langle \boldsymbol{r} \times \boldsymbol{p} \mid \boldsymbol{d} \rangle = \mu^{-1} \langle \boldsymbol{d} \times \boldsymbol{p} \mid \boldsymbol{H}(\boldsymbol{p})\boldsymbol{v} \rangle = \mu^{-1} \langle \boldsymbol{d} \times \mathbf{g}(\boldsymbol{p}) \mid \boldsymbol{v} \rangle \\ &= \rho \mu^{-1} \langle \boldsymbol{d} \times \boldsymbol{r} \mid \boldsymbol{v} \rangle \end{aligned}$$

for any $\boldsymbol{d} \in \mathbb{T}$. Hence $\boldsymbol{v} \in \mathbb{P}_r$. If $\mu = 0$ then $\boldsymbol{v} \in \mathbb{P}_r$ by theorem 2(a). This observation completes the proof. □

A consequence of lemma 4 is that a point $z \in \mathcal{E}_2$ is either a regular or a singular point of *all* functions $\mathbf{h}_2(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$. Thus the set

$$\mathcal{E}_{\text{reg}} := \{ z \in \mathcal{E}_2 \mid z \in \mathcal{R}(\mathbf{h}_2(\cdot; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)) \}$$

is well defined. An equilibrial path is called *regular* if it is contained in the set $\mathcal{E}_{\text{reg}}$.

The next lemma supplies information about the dimension of the set of singular points. It is a consequence of Sard's lemma; cf. [10, p. 186].

Lemma 5. The set $\mathcal{E}_2 \backslash \mathcal{E}_{\text{reg}}$ has the Lebesgue measure zero.

Unless otherwise said, below the base $\boldsymbol{u}_i = (\mathsf{u}_i, \ldots, \mathsf{u}_i)^\top$, $i = 1(1)3$, is chosen for the subspace $\mathbb{T}$, where

$$\mathsf{u}_1 = (1, 0, 0)^\top, \qquad \mathsf{u}_2 = (0, 1, 0)^\top, \qquad u_3 = (0, 0, 1)^\top.$$

For simplicity we write $\mathbf{h}_2$ instead of $\mathbf{h}_2(\cdot; \boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3)$, $\boldsymbol{H}_2(z)$ instead of $\boldsymbol{H}_2(z; \boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3)$, etc. in the following.

3.2. Some properties of equilibrial paths

In the present subsection some basic properties of the equilibrial paths are proven. Particularly it is shown that the regular equilibrial paths coincide with certain trajectories of an ordinary differential equation.

Definition. If z is a regular point of the function $\mathbf{h}_2$ then the unique solution of the system of equations

$$\mathbf{h}_2'(z)\boldsymbol{t} = \mathbf{0}, \tag{7}$$

$$\|\boldsymbol{t}\| = 1, \tag{8}$$

$$\operatorname{sign} \det \begin{pmatrix} \mathbf{h}_2'(z) \\ \boldsymbol{t}^\top \end{pmatrix} = \nu = \text{const} \tag{9}$$

is called the *tangent vector* induced by the matrix $\mathbf{h}_2'(z)$. It is denoted by $\boldsymbol{t}_\nu(\mathbf{h}_2'(z))$.

The solution $\boldsymbol{c}(s) = (\boldsymbol{p}(s), \rho(s))$ of the initial value problem

$$\dot{z} = \boldsymbol{t}_\nu\big(\mathbf{h}_2'(z)\big), \qquad \nu = \text{const}, \tag{10}$$

$$z(0) = z_0, \qquad z_0 \in \mathcal{E}_{\text{reg}}, \tag{11}$$

is a curve of regular points in the zero set $\mathbf{h}_2^{-1}(\mathbf{0})$; cf. [11]. If $\nu = 1$, the trajectory follows the positive direction. It follows the negative direction if $\nu = -1$. By virtue of condition (8) the solution curves $\boldsymbol{c}(s)$ are parametrized with respect to the arclength s. The following theorem results from [12, lemma 2.1.12].

Theorem 3. Each regular equilibrial path is a segment of a solution curve of the initial value problem (10)–(11).

Thus the set $\mathcal{E}_{\text{reg}}$ consists of regular equilibrial paths and single regular points $z_* \in \mathcal{E}_0$ which are a turning point of a curve contained in the set $\mathbf{h}_2^{-1}(\mathbf{0}) \cap (\mathbb{P}_0 \times (-\infty, 0])$; see figure 1.

If $z_0 \in \mathcal{E}_0 \cap \mathcal{E}_{\text{reg}}$, the solution curve of the initial value problem (10)–(11) includes an equilibrial path if $\dot{\rho}(0) > 0$, i.e., if the initial tangent belongs to the set $\mathbb{P}_r \times (0, \infty)$. If $\dot{\rho}(0) = 0$, the solution curve need not include an equilibrial path. In figure 1 the point $z_* \in \mathcal{E}_0 \cap \mathcal{E}_{\text{reg}}$ with $\dot{z}_* = (\dot{\boldsymbol{p}}_*, 0)$ determines a trajectory which is completely contained in the set $\mathbb{P}_r \times (-\infty, 0]$. The equation [11]

$$\dot{\rho} \det \begin{pmatrix} \mathbf{h}_2'(z) \\ \boldsymbol{t}_\nu(\mathbf{h}_2'(z))^\top \end{pmatrix} = \det \boldsymbol{H}_2(\boldsymbol{p}), \quad z = (\boldsymbol{p}, \rho), \tag{12}$$

shows in conjunction with condition (9) that

$$\dot{\rho}(0) > 0 \quad \text{if } \nu = \operatorname{sign} \det \boldsymbol{H}_2(\boldsymbol{p}_0) \neq 0.$$

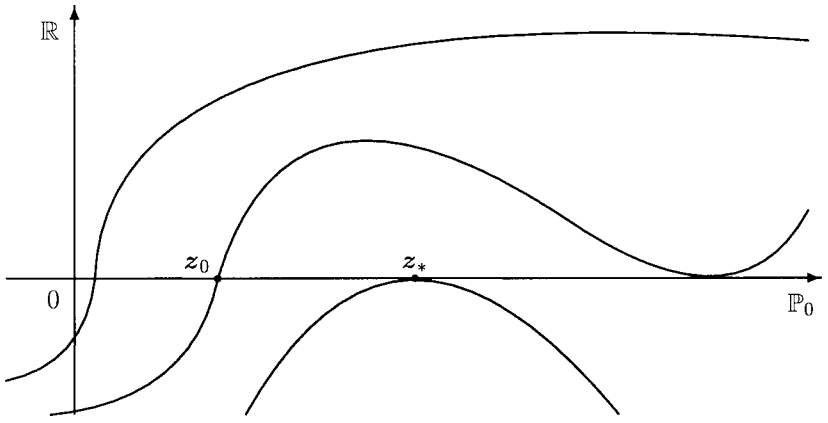

Figure 1. Zero set of a function $\mathbf{h}_2$.

Therefore $\nu = \operatorname{sign}\det \boldsymbol{H}_2(\boldsymbol{p}_0)$ is chosen from now on. The lower index ν of the tangent vectors is omitted below. The next lemma provides a condition which guarantees that a matrix $\boldsymbol{H}_2(z_0)$, $z_0 \in \mathcal{E}_0$, is regular.

Lemma 6. Suppose $z_0 = (\boldsymbol{p}_0, 0) \in \mathcal{E}_0$. Then the matrix $\boldsymbol{H}_2(z_0)$ is regular if both conditions are satisfied:

(i) The Hessian matrix $\boldsymbol{H}(\boldsymbol{p}_0)$ is pseudo-regular.

(ii) The matrix

$$\mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r}) := \begin{pmatrix} \langle \boldsymbol{u}_1 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_1 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_1 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_2 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_1 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_3 \times \boldsymbol{r}\rangle \\ \langle \boldsymbol{u}_2 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_1 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_2 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_2 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_2 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_3 \times \boldsymbol{r}\rangle \\ \langle \boldsymbol{u}_3 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_1 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_3 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_2 \times \boldsymbol{r}\rangle & \langle \boldsymbol{u}_3 \times \boldsymbol{p}_0 \mid \boldsymbol{u}_3 \times \boldsymbol{r}\rangle \end{pmatrix}$$

is regular.

If the matrix $\mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r})$ is singular then the matrix $\boldsymbol{H}_2(z_0)$ is also singular.

Proof. For each vector $\boldsymbol{v} \in \mathbb{P}$ there are a vector $\boldsymbol{v}_1 \in \mathbb{S}(\boldsymbol{p}_0)^\perp$ and a vector $\boldsymbol{v}_2 = (\boldsymbol{d} \times \boldsymbol{p}_0) \in \mathbb{S}(\boldsymbol{p}_0)$ such that $\boldsymbol{v} = \boldsymbol{v}_1 + \boldsymbol{v}_2$ and

$$\boldsymbol{H}_2(z_0)\boldsymbol{v} = \left(\boldsymbol{H}(\boldsymbol{p}_0) + \sum_{i=1}^{3} \boldsymbol{u}_i \boldsymbol{u}_i^\top\right)\boldsymbol{v}_1 + \sum_{i=1}^{3} \langle \boldsymbol{u}_i \times \boldsymbol{r} \mid \boldsymbol{v}\rangle (\boldsymbol{u}_i \times \boldsymbol{p}_0). \tag{13}$$

The first term of the right hand side is a vector of $\mathbb{S}(\boldsymbol{p}_0)^\perp$ while the rightmost term is a vector of $\mathbb{S}(\boldsymbol{p}_0)$. If $\boldsymbol{v}_1 \neq \boldsymbol{0}$ then $\boldsymbol{H}_2(\boldsymbol{p}_0)\boldsymbol{v} \neq \boldsymbol{0}$ because of condition (i). If $\boldsymbol{v}_1 = \boldsymbol{0}$ then $\boldsymbol{H}_2(\boldsymbol{p}_0)\boldsymbol{v} \neq \boldsymbol{0}$ for $\boldsymbol{v} \neq \boldsymbol{0}$ if and only if

(C) *for each vector* $\boldsymbol{d} \in \mathbb{T}$, $\boldsymbol{d} \neq \boldsymbol{0}$, *there is an index* i_*, $1 \leqslant i_* \leqslant 3$, *such that* $\langle \boldsymbol{u}_{i_*} \times \boldsymbol{r} \mid \boldsymbol{d} \times \boldsymbol{p}_0\rangle \neq 0$.

Since for $\boldsymbol{d} = \sum_{j=1}^{3} \gamma_j \boldsymbol{u}_j$

$$\langle \boldsymbol{u}_i \times \boldsymbol{r} \mid \boldsymbol{d} \times \boldsymbol{p}_0\rangle = \sum_{j=1}^{3} \gamma_j \langle \boldsymbol{u}_i \times \boldsymbol{r} \mid \boldsymbol{u}_j \times \boldsymbol{p}_0\rangle,$$

condition (C) is fulfilled if and only if the right hand side of the equation

$$\mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r})(\gamma_1, \gamma_2, \gamma_3)^\top = (\alpha_1, \alpha_2, \alpha_3)^\top, \quad \alpha_i = \langle \boldsymbol{u}_i \times \boldsymbol{r} \mid \boldsymbol{d} \times \boldsymbol{p}_0\rangle,$$

differs from zero for all non-vanishing vectors $(\gamma_1, \gamma_2, \gamma_3)^\top \in \mathbb{R}^3$. In other words, condition (C) is fulfilled if and only if the matrix $\mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r})$ is regular.

If the matrix $\mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r})$ is singular, then there is a vector $\mathsf{d}_* \in \ker \mathsf{U}(\boldsymbol{p}_0, \boldsymbol{r})$, $\mathsf{d}_* \neq 0$, for which $\boldsymbol{d}_* \times \boldsymbol{p}_0 \in \ker \boldsymbol{H}_2(z_0)$, $\boldsymbol{d}_* = (\mathsf{d}_*, \ldots, \mathsf{d}_*)^\top$. □

If the initial configuration $\boldsymbol{p}_0$ is collinear or planar, then the matrix $\boldsymbol{H}_2(z_0)$ is always singular if the reaction vector is chosen in a special manner.

Proposition 4. Suppose $z_0 = (\boldsymbol{p}_0, 0) \in \mathcal{E}_0$ and $\langle \boldsymbol{r} \mid \boldsymbol{p}_0\rangle = 0$.

(a) If $\boldsymbol{r} \in \mathbb{L}_0(\mathsf{u}_1, \mathsf{u}_2)$, then the cross-product $\boldsymbol{u}_3 \times \boldsymbol{p}_0$ belongs to the kernel of the matrix $\boldsymbol{H}_2(z_0)$, i.e., $\boldsymbol{H}_2(z_0)$ is singular.

(b) If $\boldsymbol{r} \in \mathbb{L}_0(\mathsf{u}_3)$, then $\boldsymbol{u}_j \times \boldsymbol{p}_0 \in \ker \boldsymbol{H}_2(z_0)$ for $j = 1, 2$.

Proof. By virtue of equation (13) a vector $\boldsymbol{u}_j \times \boldsymbol{p}_0$ belongs to the kernel of the matrix $\boldsymbol{H}_2(z_0)$ if and only if $\langle \boldsymbol{u}_j \times \boldsymbol{p}_0 \mid \boldsymbol{u}_i \times \boldsymbol{r} \rangle = 0$ for $i = 1(1)3$. Considering Lagrange's identity [13]

$$\langle \boldsymbol{u}_j \times \boldsymbol{p}_0 \mid \boldsymbol{u}_i \times \boldsymbol{r} \rangle = \langle \mathsf{u}_j \mid \mathsf{u}_i \rangle \langle \boldsymbol{p}_0 \mid \boldsymbol{r} \rangle - \sum_{k=1}^{n} \langle \mathsf{p}_{0k} \mid \mathsf{u}_i \rangle \langle \mathsf{r}_k \mid \mathsf{u}_j \rangle.$$

If $\boldsymbol{r} \in \mathbb{L}_0(\mathsf{u}_1, \mathsf{u}_2)$, then $\langle \mathsf{r}_k \mid \mathsf{u}_3 \rangle = 0$ for all subvectors r_k. On the other hand, if $\boldsymbol{r} \in \mathbb{L}_0(\mathsf{u}_3)$, then $\langle \mathsf{r}_k \mid \mathsf{u}_j \rangle = 0$ for $k = 1(1)n$ and $j = 1, 2$. □

Each planar configuration possesses $n - 3$ vibrational modes that act perpendicular to the plane in which the nuclei are lying [9]. By virtue of proposition 4 the accompanying normal mode vectors are an unsuitable choice for the reaction vector.

Theorem 4. A regular, non-closed equilibrial path of finite length either ends at a point of the boundary set $\mathcal{E}_0$ or converges to a singular point of the function $\mathbf{h}_2$.

Proof. Suppose the equilibrial path $\boldsymbol{z}(s)$ is a segment of the solution curve $\boldsymbol{c}(s)$ of the initial value problem (10), (11). Let (a, b), $a < 0 < b$, be the maximal interval of existence of the solution curve $\boldsymbol{c}(s)$. If $b < \infty$ then the curve $\boldsymbol{c}(s)$ converges to a limit point z_* as $s \to b$, $s < b$ which is a singular point of the function $\mathbf{h}_2$ [11]. The maximal interval of existence of the equilibrial path $\boldsymbol{z}(s)$ is contained in the interval (a, b).

Case 1: The solution curve $\boldsymbol{c}(s)$ does not leave the set $\mathbb{P}_r \times [0, \infty)$ for $s \geqslant 0$, i.e., $\boldsymbol{z}(s) \in \mathbb{P}_r \times (0, \infty)$ for all $s > 0$. Since $\boldsymbol{z}(s)$ is of finite length by assumption, $\boldsymbol{z}(s)$ is a closed curve or it converges to a singular point of the function $\mathbf{h}_2$. But closed curves are excluded by assumption.

Case 2: The solution curve $\boldsymbol{c}(s)$ leaves the set $\mathbb{P}_r \times [0, \infty)$ (for the first time) at the point $\boldsymbol{c}(s_*) \in \mathcal{E}_0$. Then the equilibrial path $\boldsymbol{z}(s)$ is of finite length and ends at the point $\boldsymbol{c}(s_*)$. □

Equilibrial paths of infinite length occur when the path $\boldsymbol{p}(s)$ runs into a domain where the energy surface is almost flat (plateau of an energy mountain).

Definition. An equilibrial path $z(s)$ that joins two points z_0 and z_1 of the set $\mathcal{E}_0$ is called *proper* if

(i) $z(s)$ is a regular equilibrial path,

(ii) the points z_0 and z_1 are the only curve points that belong to $\mathcal{E}_0$,

(iii) $\det \boldsymbol{H}_2(z_i) \neq 0$, $i = 0, 1$.

Theorem 5 [9]. Suppose $z(s) = (\boldsymbol{p}(s), \rho(s))$ is a proper equilibrial path that starts at the point $z_0 = (\boldsymbol{p}_0, 0)$ and ends at the point $z_1 = (\boldsymbol{p}_1, 0)$.

(a) If $\boldsymbol{p}_0$ is a minimizer then $\boldsymbol{p}_1$ is a saddle point or a maximizer.

(b) If $\boldsymbol{p}_0$ is a saddle point then $\boldsymbol{p}_1$ is also a saddle point or a minimizer.

A proper equilibrial path that originates at a minimizer need not end at a saddle point of first order.

Along a regular equilibrial path $\boldsymbol{z}(s) = (\boldsymbol{p}(s), \rho(s))$ the relation

$$\begin{aligned}\frac{\mathrm{dE}(\boldsymbol{p}(s))}{\mathrm{d}s} &= \big\langle \mathbf{g}\big(\boldsymbol{p}(s)\big) \mid \dot{\boldsymbol{p}}(s)\big\rangle = \rho(s)\big\langle \boldsymbol{r} \mid \dot{\boldsymbol{p}}(s)\big\rangle \\ &= \rho(s)\cos\varphi(s)\sqrt{1-\dot{\rho}^2(s)} \end{aligned} \tag{14}$$

holds, where $\varphi(s)$ denotes the angle between the reaction vector $\boldsymbol{r}$ and the tangent $\dot{\boldsymbol{p}}(s)$. Thus the potential energy is a monotonically increasing (decreasing) function along the path $\boldsymbol{p}(s)$ as long as the condition $\cos\varphi(s) > 0$ ($\cos\varphi(s) < 0$) is fulfilled. A curve point $\boldsymbol{p}(s_*)$ at which the inner product $\langle \boldsymbol{r} \mid \dot{\boldsymbol{p}}(s_*)\rangle$ vanishes is a minimizer, a maximizer, or an inflection point of the function $\mathrm{E}(\boldsymbol{p}(s))$.

Theorem 6 [9].Suppose $z(s) = (\boldsymbol{p}(s), \rho(s))$ is a regular equilibrial path along which $\cos\varphi(s) \neq 0$ for all s.

(a) If the initial point $\boldsymbol{p}(0)$ is a minimizer then the potential energy is monotonically increasing along $\boldsymbol{p}(s)$.

(b) If the initial point $\boldsymbol{p}(0)$ is a saddle point then the potential energy is monotonically decreasing along $\boldsymbol{p}(s)$.

3.3. Distinguished points at equilibrial paths

Distinguished points at a regular, non-closed equilibrial path of finite length are the initial point, the turning point(s) and the final point. By theorem 4 the final point is either a singular point (which is not a point of the path but only a limit point) or a regular point of the boundary set $\mathcal{E}_0$. The first turning point encountered along a regular activation path indicates the entry into the reactive domain [9]. A regular relaxation path that ends at a minimizer enters the product valley at the turning point encountered at last. The singular points are of particular interest because they are connected with the branching of reaction channels.

Definition. A point $z_* = z(s_*)$ of a regular equilibrial path $z(s) = (\boldsymbol{p}(s), \rho(s))$ is a *turning point* if the derivative $\dot{\rho}(s)$ changes its sign at s_*.

By virtue of equation (12) the matrix $\boldsymbol{H}_2(\boldsymbol{p})$ becomes singular at a turning point. Because turning points are regular points of the function $\mathbf{h}_2$, case (b) of proposition 2 is met at a turning point.

Theorem 7 [9]. Each regular equilibrial path that joins two points of the boundary set $\mathcal{E}_0$ possesses at least one turning point $z_{tp} = (\boldsymbol{p}_{tp}, \rho_{tp})$. At z_{tp} one and only one eigenvalue of the Hessian matrix $\boldsymbol{H}(\boldsymbol{p}_{tp})$ changes its sign.

Definition. A singular point $z_* \in \mathbb{P}_r \times \mathbb{R}$ of the function $\mathbf{h}_2$ is called *simple* if $\dim\ker \boldsymbol{H}_2(z_*) = 1$. The point z_* is a *double* singular point if $\dim\ker \boldsymbol{H}_2(z_*) = 2$.

If z_* is a simple singular point then the vector that spans the kernel of the matrix $\boldsymbol{H}_2(z_*)$ is perpendicular to the reaction vector by proposition 2. The simple singular points of the function $\mathbf{h}_2$ are closely related to the valley–ridge inflection points.

Definition [4]. A non-stationary point $\boldsymbol{p}_*$ is a *valley–ridge inflection point* if

$$\dim\bigl(\ker \boldsymbol{H}(\boldsymbol{p}_*) \cap \mathbb{P}_0\bigr) = 1 \quad \text{and} \quad \mathbf{g}(\boldsymbol{p}_*) \in \bigl(\ker \boldsymbol{H}(\boldsymbol{p}_*)\bigr)^{\perp}.$$

Lemma 7. If the point $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2 \backslash \mathcal{E}_0$ is a simple singular point of the function $\mathbf{h}_2$ then $\boldsymbol{p}_*$ is a valley–ridge inflection point.

Proof. The relation

$$\ker \boldsymbol{H}_2(z) = \ker \boldsymbol{H}(\boldsymbol{p}) \cap \mathbb{P}_0, \quad z = (\boldsymbol{p}, \rho),$$

results from equation (4) in conjunction with proposition 3(b). Thus

$$\dim\bigl(\ker \boldsymbol{H}(\boldsymbol{p}_*) \cap \mathbb{P}_0\bigr) = \dim\ker \boldsymbol{H}_2(z_*) = 1.$$

Since $z_* \in \mathcal{E}_2$, the gradient $\mathbf{g}(\boldsymbol{p}_*) = \rho_* \boldsymbol{r}$ belongs to $(\ker \boldsymbol{H}(\boldsymbol{p}_*))^{\perp}$. □

4. Symmetry

The symmetry of a nuclear ensemble is described by a regular blocked matrix

$$\boldsymbol{S} = \begin{pmatrix} \mathsf{S}_{11} & \dots & \mathsf{S}_{1n} \\ \vdots & \ddots & \vdots \\ \mathsf{S}_{n1} & \dots & \mathsf{S}_{nn} \end{pmatrix}, \quad \mathsf{S}_{ij} \in \mathcal{O}(3),$$

which satisfies the following assumption:

(S) *For any index* i, $1 \leqslant i \leqslant n$, *there is an index* j_*, $1 \leqslant j_* \leqslant n$, *such that* $\mathsf{S}_{ij_*} = \mathsf{S} \in \mathcal{O}(3)$ *and* $\mathsf{S}_{ij} = \mathsf{O}$ *for all* $j \neq j_*$.

$\mathcal{O}(3)$ is the group of the orthogonal $(3, 3)$-matrices. The set of all $(3n, 3n)$-matrices which satisfy assumption (S) is denoted by $\mathcal{S}$.

By differentiating the equation

$$\mathrm{E}(\boldsymbol{p}) = \mathrm{E}(\boldsymbol{S}\boldsymbol{p})$$

the following identities are obtained:

$$\mathbf{g}(\boldsymbol{S}\boldsymbol{p}) = \boldsymbol{S}\mathbf{g}(\boldsymbol{p}), \qquad \boldsymbol{H}(\boldsymbol{S}\boldsymbol{p}) = \boldsymbol{S}\boldsymbol{H}(\boldsymbol{p})\boldsymbol{S}^{\top}.$$

Definition. A vector $\boldsymbol{p} \in \mathbb{P}$ is called *symmetric* with respect to a matrix $\boldsymbol{S} \in \mathcal{S}$ if $\boldsymbol{S}\boldsymbol{p} = \boldsymbol{p}$.

The symmetric matrices of $\mathcal{S}$ are collected in the subset

$$\mathcal{S}_0 := \left\{\boldsymbol{S} \in \mathcal{S} \mid \boldsymbol{S}^2 = \boldsymbol{I}\right\}$$

of $\mathcal{S}$. Since the eigenvalues of a matrix $\boldsymbol{S} \in \mathcal{S}_0$ equal either 1 or -1, for each matrix $\boldsymbol{S} \in \mathcal{S}_0$ there exist two eigenspaces, namely the subspaces

$$\mathbb{P}_s := \{\boldsymbol{p} \in \mathbb{P} \mid \boldsymbol{S}\boldsymbol{p} = \boldsymbol{p}\} \quad \text{and} \quad \mathbb{P}_a := \{\boldsymbol{p} \in \mathbb{P} \mid \boldsymbol{S}\boldsymbol{p} = -\boldsymbol{p}\}$$

of $\mathbb{P}$. The vectors of $\mathbb{P}_a$ are called *antisymmetric* with respect to the matrix $\boldsymbol{S}$. Since any two non-vanishing vectors $\boldsymbol{p} \in \mathbb{P}_s$ and $\boldsymbol{q} \in \mathbb{P}_a$ are orthogonal, $\mathbb{P}$ is the direct sum of the subspaces $\mathbb{P}_s$ and $\mathbb{P}_a$,

$$\mathbb{P} = \mathbb{P}_s \oplus \mathbb{P}_a.$$

Proposition 5. For any two vectors $\mathsf{d}, \mathsf{p} \in \mathbb{R}^3$ the following relation is valid:

$$\mathsf{S}(\mathsf{d} \times \mathsf{p}) = \det \mathsf{S}(\mathsf{S}\mathsf{d} \times \mathsf{S}\mathsf{p}), \quad \mathsf{S} \in \mathcal{O}(3).$$

Proof. Since $\mathsf{S}(\mathsf{d} \times \mathsf{p}) = [\mathsf{S}\mathsf{C}(\mathsf{d})\mathsf{S}^{\top}]\mathsf{S}\mathsf{p}$ and $\mathsf{S}\mathsf{d} \times \mathsf{S}\mathsf{p} = \mathsf{C}(\mathsf{S}\mathsf{d})\mathsf{S}\mathsf{p}$, it suffices to prove that

$$\mathsf{C}(\mathsf{S}\mathsf{d}) = (\det \mathsf{S})\mathsf{S}\mathsf{C}(\mathsf{d})\mathsf{S}^{\top}. \tag{15}$$

Let s_i be the ith row of the matrix S. Then the following straightforward calculation proves equation (15):

$$\begin{aligned}\mathsf{S}\mathsf{C}(\mathsf{d})\mathsf{S}^{\top} &= \mathsf{S}(\mathsf{d} \times \mathsf{s}_1\ \mathsf{d} \times \mathsf{s}_2\ \mathsf{d} \times \mathsf{s}_3) \\ &= \begin{pmatrix} \langle \mathsf{s}_1 \mid \mathsf{d} \times \mathsf{s}_1\rangle & \langle \mathsf{s}_1 \mid \mathsf{d} \times \mathsf{s}_2\rangle & \langle \mathsf{s}_1 \mid \mathsf{d} \times \mathsf{s}_3\rangle \\ \langle \mathsf{s}_2 \mid \mathsf{d} \times \mathsf{s}_1\rangle & \langle \mathsf{s}_2 \mid \mathsf{d} \times \mathsf{s}_2\rangle & \langle \mathsf{s}_2 \mid \mathsf{d} \times \mathsf{s}_3\rangle \\ \langle \mathsf{s}_3 \mid \mathsf{d} \times \mathsf{s}_1\rangle & \langle \mathsf{s}_3 \mid \mathsf{d} \times \mathsf{s}_2\rangle & \langle \mathsf{s}_3 \mid \mathsf{d} \times \mathsf{s}_3\rangle \end{pmatrix} = \mathsf{C}(\tilde{\mathsf{d}}),\end{aligned}$$

where

$$\tilde{\mathsf{d}} = \begin{pmatrix} (\mathsf{s}_2 \times \mathsf{s}_3)^{\top} \\ (\mathsf{s}_3 \times \mathsf{s}_1)^{\top} \\ (\mathsf{s}_1 \times \mathsf{s}_2)^{\top} \end{pmatrix} \mathsf{d} = \begin{pmatrix} (\mathsf{s}_2 \times \mathsf{s}_3)^{\top} \\ (\mathsf{s}_3 \times \mathsf{s}_1)^{\top} \\ (\mathsf{s}_1 \times \mathsf{s}_2)^{\top} \end{pmatrix} \mathsf{S}^{\top}\mathsf{S}\mathsf{d} = (\det \mathsf{S})\mathsf{S}\mathsf{d}.$$

Recall that $\langle \mathsf{s}_1 \mid \mathsf{s}_2 \times \mathsf{s}_3\rangle = \det \mathsf{S}$; cf., e.g., [13]. □

Proposition 5 proves the identity

$$\boldsymbol{S}(\boldsymbol{d} \times \boldsymbol{p}) = \det \mathsf{S}(\boldsymbol{S}\boldsymbol{d} \times \boldsymbol{S}\boldsymbol{p}), \quad \boldsymbol{S} \in \mathcal{S}_0. \tag{16}$$

Proposition 6. Suppose $\boldsymbol{p}_0 \in \mathbb{P}_0$ is a stationary point with C_s-symmetry. If the reaction vector $\boldsymbol{r}$ is C_s-antisymmetric, then $\boldsymbol{u}_j \times \boldsymbol{p}_0 \in \ker \boldsymbol{H}_2(z_0)$, $j = 1, 2$, where $z_0 = (\boldsymbol{p}_0, 0)$.

Proof. Without loss of generality we may assume that the plane of reflection is spanned by the vectors u_1 and u_2 such that $\mathsf{S} = \operatorname{diag}(1, 1, -1)$. By virtue of equation (16) the vectors $\boldsymbol{u}_i \times \boldsymbol{p}_0$, $i = 1, 2$, are antisymmetric whereas the vector $\boldsymbol{u}_3 \times \boldsymbol{p}_0$ is symmetric. On the other hand the vectors $\boldsymbol{u}_i \times \boldsymbol{r}$, $i = 1, 2$, are symmetric while the vector $\boldsymbol{u}_3 \times \boldsymbol{r}$ is antisymmetric. Thus

$$\boldsymbol{H}_2(z_0)(\boldsymbol{u}_j \times \boldsymbol{p}_0) = \langle \boldsymbol{u}_3 \times \boldsymbol{r} \mid \boldsymbol{u}_j \times \boldsymbol{p}_0 \rangle (\boldsymbol{u}_3 \times \boldsymbol{p}_0), \quad j = 1, 2;$$

cf. equation (13). It is easy to verify that

$$\langle \boldsymbol{u}_3 \times \boldsymbol{r} \mid \boldsymbol{u}_j \times \boldsymbol{p}_0 \rangle = -\sum_{k=1}^{n} \langle \mathsf{p}_{0k} \mid \mathsf{u}_3 \rangle \langle \mathsf{r}_k \mid \mathsf{u}_j \rangle, \quad j = 1, 2.$$

If $\langle \mathsf{p}_{0k} \mid \mathsf{u}_3 \rangle \neq 0$ then there is an index l such that $\langle \mathsf{p}_{0l} \mid \mathsf{u}_3 \rangle = -\langle \mathsf{p}_{0k} \mid \mathsf{u}_3 \rangle$ because of the C_s-symmetry. On the other hand $\langle \mathsf{r}_k \mid \mathsf{u}_j \rangle = \langle \mathsf{r}_l \mid \mathsf{u}_j \rangle$ for $j = 1, 2$, since $\boldsymbol{r}$ is antisymmetric. Thus $\langle \boldsymbol{u}_3 \times \boldsymbol{r} \mid \boldsymbol{u}_j \times \boldsymbol{p}_0 \rangle = 0$ for $j = 1, 2$. □

4.1. Symmetry conservation

In the present subsection it is proven that along a regular equilibrial path the symmetry is conserved if the reaction vector is symmetric. For the proof the following proposition is needed:

Proposition 7. If the reaction vector $\boldsymbol{r}$ is symmetric with respect to the matrix $\boldsymbol{S} \in \mathcal{S}$, then

$$\boldsymbol{S}\mathbf{h}_2(\boldsymbol{p}, \rho; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \mathbf{h}_2(\boldsymbol{S}\boldsymbol{p}, \rho; \boldsymbol{S}\boldsymbol{b}_1, \boldsymbol{S}\boldsymbol{b}_2, \boldsymbol{S}\boldsymbol{b}_3). \tag{17}$$

The proof is straightforward. Therefore it is omitted.

Theorem 8. Suppose $z(s) = (\boldsymbol{p}(s), \rho(s))$ is a regular equilibrial path that starts at the point $z(0) = (\boldsymbol{p}_0, 0) \in \mathcal{E}_0 \cap \mathcal{E}_{\text{reg}}$. If $\boldsymbol{p}_0$ is symmetric and the reaction vector $\boldsymbol{r}$ has the same symmetry as $\boldsymbol{p}_0$, then the symmetry is conserved along the curve $\boldsymbol{p}(s)$.

Proof. The curve $\boldsymbol{p}(s)$ of an equilibrial path $z(s) = (\boldsymbol{p}(s), \rho(s))$ is the limit of a sequence of Euler polygons $\boldsymbol{p}_\tau(s)$, $\tau \in (0, \delta)$, $\delta \ll 1$; cf. [14]. Thus the symmetry is conserved along $\boldsymbol{p}(s)$ if this property holds for all Euler polygons $\boldsymbol{p}_\tau(s)$. Along an Euler polygon the symmetry is conserved if all nodes

$$\boldsymbol{p}_{k+1} = \boldsymbol{p}_k + \tau \dot{\boldsymbol{p}}_k, \quad k = 0, 1, \ldots,$$

are symmetric. Thus it remains for us to prove that a tangent $\dot{\boldsymbol{p}}_k$ is symmetric if the configuration $\boldsymbol{p}_k$ is symmetric.

Along an equilibrial path the tangent vectors $\boldsymbol{t}(\mathbf{h}_2'(z; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)) = (\dot{\boldsymbol{p}}, \dot{\rho})^\top$ satisfy the equation

$$\mathbf{h}_2'(\boldsymbol{p}, \rho; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\begin{pmatrix}\dot{\boldsymbol{p}}\\ \dot{\rho}\end{pmatrix} = \mathbf{0}. \tag{18}$$

By differentiating equation (17) the equation

$$\mathbf{h}_2'(\boldsymbol{p}, \rho; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3) = \boldsymbol{S}^\top \mathbf{h}_2'(\boldsymbol{S}\boldsymbol{p}, \rho; \boldsymbol{S}\boldsymbol{b}_1, \boldsymbol{S}\boldsymbol{b}_2, \boldsymbol{S}\boldsymbol{b}_3)\begin{pmatrix}\boldsymbol{S} & \mathbf{0}\\ \mathbf{0}^\top & 1\end{pmatrix}$$

is obtained and equation (18) can be rewritten as follows:

$$\boldsymbol{S}^\top \mathbf{h}_2'(\boldsymbol{S}\boldsymbol{p}, \rho; \boldsymbol{S}\boldsymbol{b}_1, \boldsymbol{S}\boldsymbol{b}_2, \boldsymbol{S}\boldsymbol{b}_3)\begin{pmatrix}\boldsymbol{S} & \mathbf{0}\\ \mathbf{0}^\top & 1\end{pmatrix}\begin{pmatrix}\dot{\boldsymbol{p}}\\ \dot{\rho}\end{pmatrix} = \mathbf{0}.$$

If $\boldsymbol{p}$ is symmetric, then

$$\begin{pmatrix}\boldsymbol{S} & \mathbf{0}\\ \mathbf{0}^\top & 1\end{pmatrix}\begin{pmatrix}\dot{\boldsymbol{p}}\\ \dot{\rho}\end{pmatrix} = \mu\begin{pmatrix}\dot{\boldsymbol{p}}\\ \dot{\rho}\end{pmatrix}, \quad \mu \in \mathbb{R}\backslash\{0\},$$

by lemma 4. Hence $\boldsymbol{S}\dot{\boldsymbol{p}} = \mu\dot{\boldsymbol{p}}$ and $\dot{\rho} = \mu\dot{\rho}$. The proof is complete if we have shown that $\mu = 1$.

If $\dot{\rho} \neq 0$ then μ equals 1. If $\dot{\rho} = 0$ then $z = (\boldsymbol{p}, \rho)$ is a turning point of the equilibrial path and case (b) of proposition 2, which implies $\langle \boldsymbol{r} \mid \dot{\boldsymbol{p}} \rangle \neq 0$, is met. Since $\|\dot{\boldsymbol{p}}\| = 1$ by equation (8), the relation

$$0 \neq \mu\langle \boldsymbol{r} \mid \dot{\boldsymbol{p}} \rangle = \langle \boldsymbol{r} \mid \boldsymbol{S}\dot{\boldsymbol{p}} \rangle = \langle \boldsymbol{S}^\top \boldsymbol{r} \mid \dot{\boldsymbol{p}} \rangle = \langle \boldsymbol{r} \mid \dot{\boldsymbol{p}} \rangle$$

shows that $\mu = 1$. □

4.2. Symmetry-breaking

Only symmetries that are described by a matrix $\boldsymbol{S} \in \mathcal{S}_0$ are considered in the present section. The reaction vector $\boldsymbol{r}$ is assumed to be symmetric. Because $\boldsymbol{S}\mathbb{T} \subseteq \mathbb{T}$, the vectors $\boldsymbol{b}_i$, which form the base of $\mathbb{T}$, can always be chosen so that $\boldsymbol{S}\boldsymbol{b}_i = \pm\boldsymbol{b}_i$, $i = 1(1)3$.

Lemma 8. Suppose the reaction vector $\boldsymbol{r}$ and the position vector $\boldsymbol{p}$ are symmetric with respect to the matrix $\boldsymbol{S} \in \mathcal{S}_0$. If λ is a single eigenvalue of the matrix $\boldsymbol{H}_2(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)$, $\boldsymbol{S}\boldsymbol{b}_i = \pm\boldsymbol{b}_i$, then the eigenvector belonging to λ is either symmetric or antisymmetric.

Proof. A straightforward calculation shows that

$$\boldsymbol{S}\boldsymbol{H}_2(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{S} = \boldsymbol{H}_2(\boldsymbol{S}\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3).$$

If $\boldsymbol{v}$ is the eigenvector that belongs to the eigenvalue λ then

$$\lambda\boldsymbol{v} = \boldsymbol{H}_2(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{v} \quad \text{and} \quad \lambda\boldsymbol{S}\boldsymbol{v} = \boldsymbol{H}_2(\boldsymbol{p}; \boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3)\boldsymbol{S}\boldsymbol{v}$$

such that $\boldsymbol{S}\boldsymbol{v} = \mu\boldsymbol{v}$. Because the matrix $\boldsymbol{S}$ has only the eigenvalues 1 and -1, the eigenvector $\boldsymbol{v}$ is either symmetric or antisymmetric. □

At a simple singular point $z_* = (\boldsymbol{p}_*, \rho_*)$ of the function $\mathbf{h}_2$ the kernel of the matrix $\boldsymbol{H}_2(z_*)$ is spanned by a non-vanishing vector $\phi_0 \in \mathbb{P}$ which is called a *kernel vector*. A kernel vector is always perpendicular to the reaction vector by proposition 2. By virtue of lemma 8 ϕ_0 is either symmetric or antisymmetric. Furthermore there is a (uniquely determined) vector $\boldsymbol{v}_0 \in \mathbb{P}_s$ which satisfies the equation

$$\boldsymbol{H}_2(z_*)\boldsymbol{v}_0 = \boldsymbol{r}. \tag{19}$$

Definition. A simple singular point $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$ with symmetric $\boldsymbol{p}_*$ is called *symmetry-breaking* if $\ker \boldsymbol{H}_2(\boldsymbol{p}_*) \subset \mathbb{P}_a$.

At a symmetry-breaking simple singular point $z_* = (\boldsymbol{p}_*, \rho_*)$ the set $\mathcal{E}_2$ consists locally of two smooth transversally intersecting branches, $\mathcal{C}_s \subset \mathbb{P}_s \times [0, \infty)$ and $\mathcal{C}_a \subset \mathbb{P}_a \times [0, \infty)$, with the following representation [15]:

$$\mathcal{C}_s = \big\{(\boldsymbol{p}, \rho) \in \mathcal{E}_2 \mid \boldsymbol{p} = \boldsymbol{p}_* + \xi\boldsymbol{v}_0 + \boldsymbol{w}_1(\xi),\ \rho = \rho_* + \xi,\ |\xi| < \delta\big\},$$
$$\mathcal{C}_a = \big\{(\boldsymbol{p}, \rho) \in \mathcal{E}_2 \mid \boldsymbol{p} = \boldsymbol{p}_* + \xi\phi_0 + \boldsymbol{w}_2(\xi),\ \rho = \rho_* + \mathrm{O}(\xi^2),\ |\xi| < \delta\big\},$$

where $\|\boldsymbol{w}_i(\xi)\| = \mathrm{O}(\xi^2)$, $i = 1, 2$.

Theorem 9. In the vicinity of a simple symmetry-breaking singular point $z_* \in \mathcal{E}_2$ the changes in the potential energy are greater along the symmetric path $\mathcal{C}_s$ than along the antisymmetric path $\mathcal{C}_a$.

Proof. At the point $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$ the Taylor expansion of the energy function E provides the relations

$$\mathrm{E}(\boldsymbol{p}) - \mathrm{E}(\boldsymbol{p}_*) = \rho_*\big(\xi\langle\boldsymbol{r} \mid \boldsymbol{v}_0\rangle + \big\langle\boldsymbol{r} \mid \boldsymbol{w}_1(\xi)\big\rangle\big) + \mathrm{O}\big(\xi^2\big) = \mathrm{O}(\xi), \quad (\boldsymbol{p}, \rho) \in \mathcal{C}_s,$$
$$\mathrm{E}(\boldsymbol{p}) - \mathrm{E}(\boldsymbol{p}_*) = \rho_*\big\langle\boldsymbol{r} \mid \boldsymbol{w}_2(\xi)\big\rangle + \mathrm{O}\big(\xi^2\big) = \mathrm{O}\big(\xi^2\big), \quad (\boldsymbol{p}, \rho) \in \mathcal{C}_a,$$

which prove the theorem. □

Under the hypothesis that in the stage of activation a nuclear system follows the path of gentlest increase on a potential energy surface, at a symmetry-breaking simple singular point a molecular system will prefer the branch that is associated with the loss of symmetry. In the stage of relaxation it will prefer the branch that is associated with the preservation of symmetry or the gain of some symmetry.

Definition. A simple singular point $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$ is called a *pitchfork bifurcation point* if the kernel vector ϕ_0 satisfies the following conditions:

(i) $\langle\phi_0 \mid \boldsymbol{r}\rangle = 0$, $\phi_0\mathbf{h}_{2pp}(\boldsymbol{p}_*, \rho_*)\phi_0\phi_0 = 0$,

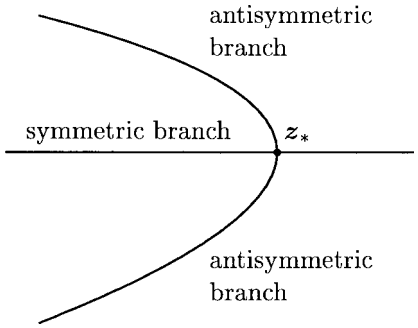

Figure 2. Symmetry-breaking pitchfork bifurcation.

(ii) $\phi_0 \mathbf{h}_{2pp}(\boldsymbol{p}_*, \rho_*)\phi_0 \boldsymbol{v}_0 \neq 0$, where $\boldsymbol{v}_0$ satisfies equation (19).

$\mathbf{h}_{2pp}(\boldsymbol{p}, \rho)$ is the second partial derivative of the function $\mathbf{h}_2$ with respect to the position vector $\boldsymbol{p}$.

Lemma 9 [16]. A symmetry-breaking simple singular point $(\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$ of the function $\mathbf{h}_2$ is a pitchfork bifurcation point if and only if there is a vector $\phi_* \in \mathbb{P}_a$, $\phi_* \neq \mathbf{0}$, such that $(\boldsymbol{p}_*, \rho_*, \phi_*)$ is an isolated zero of the function $\boldsymbol{b} : \mathbb{P}_s \times \mathbb{R} \times \mathbb{P}_a \mapsto \mathbb{P}_0$,

$$\boldsymbol{b}(\boldsymbol{p}, \rho, \phi) = \begin{pmatrix} \langle \phi \mid \phi \rangle - 1 \\ \mathbf{h}_2(\boldsymbol{p}, \rho) \\ \boldsymbol{H}_2(\boldsymbol{p})\phi \end{pmatrix}. \tag{20}$$

The pattern that the set $\mathcal{E}_2$ shows in the vicinity of a symmetry-breaking simple singular point z_* is depicted in figure 2. The consequences of proposition 2 and the preceding lemma are summarized in

Theorem 10. Suppose $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$ and $\ker \boldsymbol{H}_2(z_*) = \operatorname{span}\{\phi_0\}$, $\phi_0 \neq \mathbf{0}$. If the position vector $\boldsymbol{p}_*$ and the reaction vector $\boldsymbol{r}$ are symmetric with respect to $\boldsymbol{S} \in \mathcal{S}_0$ then

(a) z_* is a turning point if and only if $\phi_0 \in \mathbb{P}_s$ and $\langle \phi_0 \mid \boldsymbol{r} \rangle \neq 0$,

(b) z_* is a pitchfork bifurcation point if and only if z_* is an isolated singular point and $\phi_0 \in \mathbb{P}_a$.

By virtue of lemma 8 the kernel vector ϕ_0 is either symmetric or antisymmetric such that always $\langle \phi_0 \mid \boldsymbol{r} \rangle = 0$ if $\phi_0 \in \mathbb{P}_a$.

Definition. A double singular point $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$, $\boldsymbol{p}_* \in \mathbb{P}_s$, is a *symmetry-breaking double turning point* if

(i) $\ker \boldsymbol{H}_2(z_*) = \operatorname{span}\{\phi_0, \phi_1\}$, $\phi_0 \in \mathbb{P}_a$, $\phi_1 \in \mathbb{P}_s$,

(ii) $\langle \boldsymbol{r} \mid \phi_1 \rangle \neq 0$ and

(iii) $\phi_0 \mathbf{h}_{2\,pp}(\boldsymbol{p}_*, \rho_*)\phi_0\phi_1 \neq 0$.

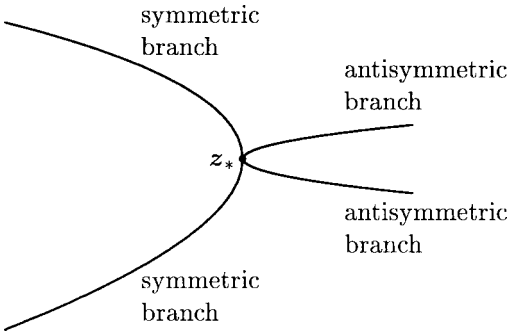

Figure 3. Symmetry-breaking double turning point.

Through a symmetry-breaking double turning point z_* there is a symmetric branch having a turning point at z_* and there is a nonsymmetric branch $\mathcal{C}_a \subset \mathbb{P}_a \times [0, \infty)$ having a bifurcation point at z_*; see figure 3.

Lemma 10 [16]. Let $z_* = (\boldsymbol{p}_*, \rho_*) \in \mathcal{E}_2$, $\boldsymbol{p}_* \in \mathbb{P}_s$, be a double singular point of the function $\mathbf{h}_2$ with $\ker \boldsymbol{H}_2(z_*) = \operatorname{span}\{\phi_0, \phi_1\}$, $\phi_0 \in \mathbb{P}_a$, $\phi_1 \in \mathbb{P}_s$. Then $(\boldsymbol{p}_0, \rho_0, \phi_0)$ is an isolated solution of equation (20) if and only if z_0 is a symmetry-breaking double turning point.

5. Summary

In the present paper the equilibrial path concept introduced in [9] has further been developed. Special attention is spent the symmetry conservation along equilibrial paths and symmetry-breaking. Along regular equilibrial paths the symmetry is always conserved if the reaction vector is symmetric. Symmetry-breaking can occur only at singular points. At a simple symmetry-breaking bifurcation point a nuclear system follows a nonsymmetric branch in the stage of activation because the increase in the potential energy is less along the nonsymmetric branches than along the symmetric branch. In the stage of relaxation it follows the symmetric branch because the energy decrease is greater along the symmetric branch than along a nonsymmetric branch. The simple bifurcation points are associated with valley–ridge inflection points.

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