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Search for Saddle Points of Energy Hypersurfaces Using a Multi-Dimensional Space of "Guiding" Coordinates*

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For the determination of saddle points (SPs) of adiabatic potential surfaces a novel method defining a "pseudo reaction path" (PRP) is presented. The PRP consists of two components, the one is being the function of some selected "guiding" coordinates and the other is depending on the remaining ones. The tangent components of the PRP are parallel and antiparallel to the normals of the tangential planes of the equipotential surfaces defined by the two groups of coordinates. PRPs starting from points in an appropriately chosen domain of the configurational space arrive at the SP.

Key words: Saddle point – Adiabatic potential energy surface – Multi-dimensional space of guiding coordinates – Pseudo reaction path.

1. Introduction

For the theoretical study of chemical reactions the best way is so far based upon the investigation of adiabatic potential energy hypersurfaces constructed as functions of nuclear coordinates using the Born–Oppenheimer approximation. The various domains, critical points and surface curves of the adiabatic energy function are of different importances from the viewpoint of the reaction system. The surface can – on the basis of its local curvature properties – be partitioned into domains of different reactivities [1], "catchment regions" [2] determining the direction of the reaction, critical points whose classification is possible by

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the examination of the harmonic force constant matrix [3, 4, 16], and surface curves along which the reaction takes place [5–21]. These characteristics – with the exception of extrema – are generally not invariant under coordinate transformations in Euclidean coordinate spaces thus their determinations give no unambiguous solutions. Efforts have therefore been made to define these properties in a coordinate-free form [5–17, 20–22]. Beside several well-known methods for localization of minima/maxima [23–32] there are useful procedures also for determining SPs [3, 4, 20, 33–44].

In this paper a searching procedure, characterized by gradient controlled step-directions, converging to the SP of the adiabatic potential energy surface is presented. In Chap. 2 some essential characteristics of potential surfaces in Riemannian space will be described and – by referring mostly to Fukui's results [5–17, 21] – some fundamental relations to be employed in latter considerations will be introduced. In Sec. 3.1 the differential equation/equation system defining the PRP in a normal/critical point of the coordinate space will be presented for the ideal case, and in Sec. 3.2 the approximation of the SP occurring in practice will be discussed.

2. General Theory

The adiabatic potential energy of a molecular system as a function of nuclear coordinates is described mainly either in the system of mass-weighted Cartesian coordinates of nuclei [45] or – for many cases more practically – in the system of independent "internal coordinates" relevant from the physical point of view [2, 5–17].

To investigate the changes of coordinates independently, we are going to study the course of searching in the Riemannian configuration space of internal coordinates, by using the general notation convention of tensor algebra [46].

An elementary displacement belonging to the dq^i coordinate differential of contravariant character[1] is represented in the Cartesian coordinate system by a displacement vector

$$d\boldsymbol{x} = \sum_{t=1}^{3N} \frac{\partial x_t}{\partial q^i} dq^i. \tag{1}$$

Both the $3N$-dimensional (N is the number of nuclei) Euclidean coordinate space and the $n = 3N\text{-}6(5)$-dimensional Riemannian coordinate space can be completed by an additional coordinate, the "function value" U:

$$U(x_1, x_2, \ldots, x_{3N}) = U(q^1, q^2, \ldots, q^n) = x_{3N+1} \tag{2}$$

[1] For indexing coordinates, the convention [46] is used that the superscripts refer to contravariant and the subscripts to covariant transformation properties.

which is invariant under the allowed coordinate transformations. The square of the arc length is naturally identical in both spaces:

$$ds^2 = dx_1^2 + dx_2^2 + \cdots + dx_{3N+1}^2 = a_{ij} dq^i dq^j + dx_{3N+1}^2$$

where

$$a_{ij} = \sum_{t=1}^{3N} \frac{\partial x_t}{\partial q^i} \frac{\partial x_t}{\partial q^j} = \boldsymbol{e}_i \boldsymbol{e}_j \tag{3}$$

are the covariant components of the metric tensor and $\boldsymbol{e}_i$ are local basis vectors. A possible geometrical structure of the adiabatic potential energy function $U(q^1, q^2, \ldots, q^n)$ is determined by the extrema [5]. It is known that Fukui's meta-IRC [5, 7–9] is a curve whose tangent is, in every point, the element of the gradient field and on proceeding toward the stable position the displacement vector is directed antiparallel to the gradient. According to the "stable limit theorem" [7] such a motion should converge to the eigenvector of the least absolute value of the hessian belonging to the extremum, i.e. to the weakest normal vibrational mode at the stable equilibrium configuration.

Now we wish to study the conditions and the progression of a combined motion starting from the point P ∈ Cell (C) [7, 9] toward the SP along a pseudo-RP (PRP)[2] to be defined later (here Cell (C) denotes the set of points starting from where the minimum C can be reached along the meta-IRC). We presume that in most cases chemical experiences and/or "intuition" provide sufficient information to judging right the position of P relative to SP, with respect to only a few but relevant coordinates. The coordinates whose changes result – in the course of approaching the SP – in an increase of the potential, should be ranged into group *A* (group of "guiding" coordinates), and – in an ideal case – all the remaining coordinates, i.e. those lowering the potential, into group *B*. As we can never be sure in the proper classification of coordinates, we only presume that the coordinates have properly been ranged[3] into the group *A*, however, we don't know whether all the coordinates increasing the potential by approaching the SP are actually included in this group. This means that our model allows – between certain limits – the misclassification of some potential increasing coordinates into the group *B*. It is now evident that the point P ∈ Cell (C) satisfies also the relation P ∈ Cell ($SP_{1,2}$) where Cell ($SP_{1,2}$) means the interval of the configuration space from which – regarding a given classification of the coordinates into groups *A* and *B*, i.e. by an actual definition of the PRP – the SP associated with the minima 1, 2 can be reached along the PRP.

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[2] PRP has the meaning that no real system moves along this curve under natural circumstances though such a motion could in principle be realized e.g. by continuously tuned selective laser excitations.

[3] Convergence of the procedure will verify the right ranging into groups (see latter discussion).

The curves assigned to the changes of group A and group B coordinates[4] are defined by differential equations similarly as in [5]:

$$\frac{dq_1}{\partial U/\partial q^1}=\frac{dq_2}{\partial U/\partial q^2}=\cdots=\frac{dq_k}{\partial U/\partial q^k} \tag{4}$$

and

$$\frac{dq_{k+1}}{-(\partial U/\partial q^{k+1})}=\frac{dq_{k+2}}{-(\partial U/\partial q^{k+2})}=\cdots=\frac{dq_n}{-(\partial U/\partial q^n)}. \tag{5}$$

The solutions of Eqs. (4) and (5) depending upon $(k-1)$ and $(n-k-1)$ parameters are the curves given by Eq. (4, 7) in [5]. Exactly in the same way as in [5] new local coordinates $\tilde{q}^i$ can be defined by the tangents of the curves satisfying the differential Eqs. (4) and (5). The kth and nth coordinates – one in each group – fulfilling the conditions (4, 12) in [5] can arbitrarily be chosen. With respect to the new $\tilde{q}^i$ coordinates, only (the last) one of the gradient components in each group will not vanish:

$$\frac{\partial U}{\partial \tilde{q}^1}=\frac{\partial U}{\partial \tilde{q}^2}=\cdots=\frac{\partial U}{\partial \tilde{q}^{k-1}}=0, \qquad \frac{\partial U}{\partial \tilde{q}^k}\neq 0 \tag{6}$$

and

$$\frac{\partial U}{\partial \tilde{q}^{k+1}}=\frac{\partial U}{\partial \tilde{q}^{k+2}}=\cdots=\frac{\partial U}{\partial \tilde{q}^{n-1}}=0, \qquad \frac{\partial U}{\partial \tilde{q}^n}\neq 0. \tag{7}$$

Consequently, the coordinates $q^1, q^2, \ldots, q^{k-1}$ and $q^{k+1}, q^{k+2}, \ldots, q^{n-1}$, i.e. the curves (4, 7) in [5] – being the functions of group A and group B coordinates – are in the equipotential surfaces described by the functions

$$U(q^1, q^2, \ldots, q^k, Q^{k+1}, Q^{k+2}, \ldots, Q^n)=W, \tag{8}$$

$$U(Q^1, Q^2, \ldots, Q^n, q^{k+1}, q^{k+2}, \ldots, q^n)=W \tag{9}$$

where $Q^1, Q^2, \ldots, Q^n$ are constant values of coordinates and W is the function value of U in the given point. The parametric equations of the curves satisfying the differential Eqs. (4) and (5) are given by

$$\frac{dq_{i'}}{ds_A}=\frac{\partial U}{\partial q^{i'}}\Big/\left|\frac{dU}{ds_A}\right| \tag{10}$$

and

$$\frac{dq_{i''}}{ds_B}=-\frac{\partial U}{\partial q^{i''}}\Big/\left|\frac{dU}{ds_B}\right|. \tag{11}$$

[4] For the two groups of coordinates, instead of $i=1, 2, \ldots, n$, the indices $i'=1, 2, \ldots, k$ and $i''=k+1, k+2, \ldots, n$ will also be used. Through the allowed permutations of indices it can be realized that the coordinate group A should be indexed by i' and the group B by i''.

The Eqs. (10) and (11) can be derived from the equations

$$\frac{dU}{ds_A} = \frac{\partial U}{\partial q^{i'}} \frac{dq^{i'}}{ds_A} \tag{12}$$

and

$$\frac{dU}{ds_B} = \frac{\partial U}{\partial q^{i''}} \frac{dq^{i''}}{ds_B} \tag{13}$$

(or from their covariant counterparts) and from the differential properties of inverse functions. In these equations the meanings of ds_A and ds_B are as follows:

$$ds_A = \sqrt{a_{i'j'}\, dq^{i'}\, dq^{j'}}, \tag{14}$$

$$ds_B = \sqrt{a_{i''j''}\, dq^{i''}\, dq^{j''}}. \tag{15}$$

For the sake of latter discussion it is important to note that the union $\{\boldsymbol{e}_{i'}\} \cup \{\boldsymbol{e}_{i''}\}$ of the local bases belonging to the groups of coordinates A and B are identical to the local basis systems of the complete (n-dimensional) coordinate space but their dual bases $\{\bar{\boldsymbol{e}}^{i'}\}$; $\{\bar{\boldsymbol{e}}^{i''}\}$ are not the same as the corresponding elements ($\boldsymbol{e}^{i'}$; $\boldsymbol{e}^{i''}$) of the dual basis system $\{\boldsymbol{e}^{i}\}$ belonging to $\{\boldsymbol{e}_i\}$. The contravariant metric tensors $\bar{a}^{i'j'}$; $\bar{a}^{i''j''}$ are chosen to be the inverts of only the blocks of the metric tensor belonging to the indices (i', i'')[5] to keep the dual basis vectors in the space of $\{\boldsymbol{e}_{i'}\}$ and $\{\boldsymbol{e}_{i''}\}$, therefore for group A coordinates the following relations are valid[6]:

$$dq_i(j') = a_{ij}\, dq^{j'},$$

$$dq_{i'} = a_{i'j'}\, dq^{j'},$$

$$dq_{i'} = dq_i(j'),$$

$$dq^{i'} = a^{ij}\, dq_{j'},$$

$$dq^{i'} = a^{i'j'}\, dq_{j'}.$$

Owing to the covariant representation of curves given by (10) and (11), it can be assured that the displacement is parallel or antiparallel to the vectors of the gradient field belonging to the groups A and B coordinates at any differentiable point of the $U(q^i)$ surface and they are therefore orthogonal to the equipotential surfaces (8) and (9).

3. The Method

3.1. Approximation of the SP in the Ideal Case

Let us now return to our original aim, to examine the behaviour of a curve – parametrically defined in covariant representation – crossing the point P∈

[5] The fact that these metric tensors depend either on group A or on group B coordinates is reflected by barred notations $\bar{a}^{i'}$, $\bar{a}^{i'j'}$ and $\bar{a}^{i''}$, $\bar{a}^{i''j''}$.

[6] For group B coordinates quite similar expressions (with double primes) hold.

Cell (C) and $P \in \text{Cell}(SP_{1,2})$. In this section momentarily – in contrast to our former assumptions – we suppose that ranging of coordinates into groups A and B has been properly performed, and then we present the differential equations of PRP in normal and critical points of the coordinate space.

The components are given by Eqs (10) and (11). First we renorm the components, introducing in place of ds_A and ds_B the arc $d\bar{s}$:

$$d\bar{s} = a_{ij}(dq^{i'} - dq^{i''})(dq^{j'} - dq^{j''}), \tag{16}$$

$$\frac{dq_{i'}}{ds_A}\frac{ds_A}{d\bar{s}} = \left[\frac{\partial U}{\partial q^{i'}} \Big/ \left|\frac{dU}{ds_A}\right|\right]\frac{ds_A}{d\bar{s}} = \frac{dq_{i'}}{d\bar{s}}, \tag{17}$$

$$-\frac{dq_{i''}}{ds_B}\frac{ds_B}{d\bar{s}} = \left[\frac{\partial U}{\partial q^{i''}} \Big/ \left|\frac{dU}{ds_B}\right|\right]\frac{ds_B}{d\bar{s}} = \frac{dq_{i''}}{d\bar{s}}. \tag{18}$$

The PRP is now defined by the equation

$$\frac{dq_i}{d\bar{s}} = \frac{dq_{i'}}{d\bar{s}} - \frac{dq_{i''}}{d\bar{s}} = \frac{\partial U/\partial q^{i'}}{|dU/ds_A|}\frac{ds_A}{d\bar{s}} - \frac{\partial U/\partial q^{i''}}{|dU/ds_B|}\frac{ds_B}{d\bar{s}}. \tag{19}$$

The (local) inclination of the curve (19) to the meta-IRC (Eq. (3.10) in [7]) at a given point can be got with help of the scalar product of the tangents.

The inclination angles of Eqs. (10), (11) and (19) to the meta-IRC are:

$$\cos\varphi_A = \frac{a_{jp}\left(-a^{pk}\frac{dq_k}{ds}\right)\left(\bar{a}^{i'l'}\frac{dq_{l'}}{d\bar{s}}\right)}{\sqrt{\left(a^{ij}\frac{dq_i}{ds}\frac{dq_j}{ds}\right)\left(\bar{a}^{i'j'}\frac{dq_{i'}}{d\bar{s}}\frac{dq_{j'}}{d\bar{s}}\right)}} = -\frac{ds_A}{ds}$$

$$= -\frac{dU/ds_A}{dU/ds}, \tag{20}$$

$$\cos\varphi_B = \frac{ds_B}{ds} = \frac{dU/ds_B}{dU/ds}, \tag{21}$$

$$\cos\varphi_{PRP} = \frac{a_{jp}\left(-a^{pk}\frac{dq_k}{ds}\right)\left(\bar{a}^{i'l'}\frac{dq_{l'}}{d\bar{s}} - \bar{a}^{i''r''}\frac{dq_{r''}}{d\bar{s}}\right)}{\sqrt{a^{ij}\frac{dq_i}{ds}\frac{dq_j}{ds}}\sqrt{a_{ij}\left(\frac{dq^{i'}}{d\bar{s}} - \frac{dq^{i''}}{d\bar{s}}\right)\left(\frac{dq^{j'}}{d\bar{s}} - \frac{dq^{j''}}{d\bar{s}}\right)}}$$

$$= -\frac{ds_A^2 + ds_B^2}{ds\,d\bar{s}} = (-\cos^2\varphi_A + \cos^2\varphi_B)\frac{ds}{d\bar{s}}. \tag{22}$$

Using these results, Eq. (19) can be transcribed into

$$\frac{dq_i}{d\bar{s}} = -\frac{\partial U/\partial q^{i'}}{|dU/ds_A|}\cos\varphi_A\frac{ds}{d\bar{s}} - \frac{\partial U/\partial q^{i''}}{|dU/ds_B|}\cos\varphi_B\frac{ds}{d\bar{s}}. \tag{23}$$

The directions of the tangents of the two components of the curve described by Eq. (23) either are parallel or one of them (or both) are antiparallel to the directions of the components of the meta-IRC (in our case only the one component has opposite direction to the corresponding component of the meta-IRC). At the critical points, owing to the equalities

$$\frac{\partial U}{\partial q^i} = \frac{dU}{ds} = 0,$$

the PRP is defined by a second order differential equation system derived from Eq. (23) by virtue of L'Hôpitals theorem:

$$\frac{dq^i}{d\bar{s}} = -\frac{\dfrac{\partial^2 U}{\partial q^{i'} \partial q^j} \dfrac{dq^j}{d\bar{s}} \cos\varphi_A \dfrac{ds}{d\bar{s}}}{\dfrac{d^2 U}{ds_A^2} \dfrac{ds_A}{d\bar{s}}} - \frac{\dfrac{\partial^2 U}{\partial q^{i''} \partial q^j} \dfrac{dq^j}{d\bar{s}} \cos\varphi_B \dfrac{ds}{d\bar{s}}}{\dfrac{d^2 U}{ds_B^2} \dfrac{ds_B}{d\bar{s}}}. \tag{24}$$

Regarding that the components $dq_{i'}/d\bar{s}$ and $dq_{i''}/d\bar{s}$ are independent, and using the expressions (20) and (21), (24) can be separated to two equations:

$$-\frac{\partial^2 U}{\partial q^{i'} \partial q^j} \frac{dq^j}{d\bar{s}} \cos\varphi_A \frac{ds}{d\bar{s}} + \frac{d^2 U}{ds_A^2} \cos\varphi_A \frac{ds}{d\bar{s}} a_{i'j} \frac{dq^j}{d\bar{s}}$$
$$= \left(\frac{\partial^2 U}{\partial q^{i'} \partial q^j} - \frac{d^2 U}{ds_A^2} a_{i'j} \right) \frac{dq^j}{d\bar{s}} = 0 \tag{24a}$$

and

$$-\frac{\partial^2 U}{\partial q^{i''} \partial q^j} \frac{dq^j}{ds_B} \cos\varphi_B \frac{ds}{d\bar{s}} - \frac{d^2 U}{ds_B^2} \cos\varphi_B \frac{ds}{d\bar{s}} a_{i''j} \frac{dq^j}{d\bar{s}}$$
$$= \left(-\frac{\partial^2 U}{\partial q^{i''} \partial_q^j} - \frac{d^2 U}{ds_B^2} a_{i''j} \right) \frac{dq^j}{d\bar{s}} = 0. \tag{24b}$$

By combining (24a) and (24b) we obtain

$$\left(\frac{\partial^2 U}{\partial q^i \partial q^j} - \frac{d^2 U}{ds_A^2} a_{i'j} + \frac{d^2 U}{ds_B^2} a_{i''j} \right) \frac{dq^j}{d\bar{s}} = 0. \tag{25}$$

The curve (23) satisfying the equation system (25) apparently does not converge to any eigenvectors of the hessian but to a curve whose tangent is transformed by the hessian (belonging to the critical point) in such a way that one of its components turns into its multiple by $K_A (= d^2U/ds_A^2)$ and the other into its multiple by $-K_B (= d^2U/ds_B^2)$.

The asymptote approximated by the PRP at the SP and the parameters of the equation system (25), i.e. the second derivatives of U, can be obtained by the following considerations. Starting from any x_0 point, the changes of the gradient and the gradient components in the eigenvector system of the hessian are

described by the formulas:

$$\boldsymbol{\alpha}^0 = \boldsymbol{g}_A^0 \equiv \boldsymbol{g}_A(x_0) = \left(\boldsymbol{V} \frac{\partial U}{\partial q^i} = \right) \boldsymbol{V}\mathscr{P}_A \frac{\partial U}{\partial q^i}, \tag{26}$$

$$\boldsymbol{\beta}^0 = \boldsymbol{g}_B^0 \equiv \boldsymbol{g}_B(x_0) = \boldsymbol{V}\mathscr{P}_B \frac{\partial U}{\partial q^i}, \tag{27}$$

$$\boldsymbol{\alpha}^1 = \boldsymbol{g}_A^1 \equiv \boldsymbol{g}_A(x_1) = \boldsymbol{V}\mathscr{P}_A\{\boldsymbol{I} + \boldsymbol{V}^T\boldsymbol{\Lambda}\boldsymbol{V}[c_A\mathscr{P}_A(\cdot) - c_B\mathscr{P}_B(\cdot)]\} \frac{\partial U}{\partial q^i}(x_0), \tag{28}$$

$$\boldsymbol{\beta}^1 = \boldsymbol{g}_B^1 \equiv \boldsymbol{g}_B(x_1) = \boldsymbol{V}\mathscr{P}_B\{\boldsymbol{I} + \boldsymbol{V}^T\boldsymbol{\Lambda}\boldsymbol{V}[c_A\mathscr{P}_A(\cdot) - c_B\mathscr{P}_B(\cdot)]\} \frac{\partial U}{\partial q^i}(x_0), \tag{29}$$

$$\boldsymbol{g}^1 = \boldsymbol{V}\{\boldsymbol{I} + \boldsymbol{V}^T\boldsymbol{\Lambda}\boldsymbol{V}[c_A\mathscr{P}_A(\cdot) - c_B\mathscr{P}_B(\cdot)]\} \frac{\partial U}{\partial q^i}(x_0). \tag{30}$$

Beside the notations already introduced $\boldsymbol{V}$ denotes the matrix consisting of eigenvector columns defined in the space of the coordinates q^i, $\mathscr{P}_A$ and $\mathscr{P}_B$ are operators which perform projections in the coordinate spaces A and B, Λ is the diagonal matrix of the eigenvalues of the hessian, $\boldsymbol{I}$ is the unit matrix, the superscript T refers to the transpose and

$$c_A = \left(\frac{d^2U}{ds_A^2} - \left| \frac{d^2U}{ds_B^2} \right| \right)^{-1}, \tag{31}$$

$$c_B = \left(\frac{d^2U}{ds_B^2} + \left| \frac{d^2U}{ds_A^2} \right| \right)^{-1}. \tag{32}$$

The coefficients c_A and c_B are obtained from the following considerations. By a suitable classification of the coordinates, the displacement along both components of the curve described by Eq. (23) takes place in the direction of gradient decrease. By the displacement taken in the direction of potential increase, the second derivative K_A satisfies the relation

$$\frac{d^2U}{ds_A^2} - \left| \frac{d^2U}{ds_B^2} \right| < \lambda^-. \tag{33}$$

By the displacement taken in the direction of potential decrease, similar condition is to be fulfilled for K_B:

$$\frac{d^2U}{ds_B^2} + \left| \frac{d^2U}{ds_A^2} \right| < k_b\lambda_b^+ \cdot (b = 1, \ldots, n-1) \tag{34}$$

λ^- and λ_b^+ denote the negative and $(n-1)$ positive eigenvalues of the hessian and k_b are the coordinates of the displacement vector in the space of eigenvectors belonging to the positive eigenvalues.

Now, for simplifying the Eqs. (28)–(30), it is practical to introduce the operator

$$\tilde{\mathscr{M}} := \{\boldsymbol{I} + \boldsymbol{V}^T\boldsymbol{\Lambda}\boldsymbol{V}[c_A\mathscr{P}_A(\cdot) - c_B\mathscr{P}_B(\cdot)]\}. \tag{35}$$

The repeated displacements along the PRP, for successive gradient components, yield the following general formulas[7]

$$\boldsymbol{\alpha}^m = \boldsymbol{V}\mathscr{P}_A\left[\tilde{\mathscr{M}}^m \frac{\partial U}{\partial q^i}(x_0)\right], \tag{36}$$

$$\boldsymbol{\beta}^m = \boldsymbol{V}\mathscr{P}_B\left[\tilde{\mathscr{M}}^m \frac{\partial U}{\partial q^i}(x_0)\right], \tag{37}$$

$$\boldsymbol{g}^m = \boldsymbol{V}\tilde{\mathscr{M}}^m \frac{\partial U}{\partial q^i}(x_0). \tag{38}$$

In the points of the curve, the cosines of the angles included by the components (in the groups A and B) of the direction vector and the gradient at the point x_0 can be represented by

$$\cos\varphi_A^0 = \frac{(-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0)\cdot\boldsymbol{\alpha}^0}{|-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0||\boldsymbol{\alpha}^0|} = \frac{(-\boldsymbol{g}^0)\cdot(\boldsymbol{V}\tilde{\mathscr{P}}_A\boldsymbol{g}^0)}{|-\boldsymbol{g}^0||\boldsymbol{V}\tilde{P}_A\boldsymbol{g}^0|}, \tag{39}$$

$$\cos\varphi_B^0 = \frac{(-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0)\cdot\boldsymbol{\beta}^0}{|-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0||\boldsymbol{\beta}^0|}\ \frac{(-\boldsymbol{g}^0)\cdot(V(-\tilde{\mathscr{P}}_B\boldsymbol{g}^0))}{|-\boldsymbol{g}^0||\boldsymbol{V}\tilde{\mathscr{P}}_B\boldsymbol{g}^0|}, \tag{40}$$

$$\cos\varphi_{\mathrm{PRP}}^0 = \frac{(-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0)\cdot(\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0)}{|-\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0||\boldsymbol{\alpha}^0-\boldsymbol{\beta}^0|} = \frac{(-\boldsymbol{g}^0)\cdot\boldsymbol{V}[\tilde{\mathscr{P}}_A(\cdot)-\tilde{\mathscr{P}}_B(\cdot)]\boldsymbol{g}^0}{|-\boldsymbol{g}^0||\boldsymbol{V}[\tilde{\mathscr{P}}_A(\cdot)-\tilde{\mathscr{P}}_B(\cdot)]\boldsymbol{g}^0|} \tag{41}$$

where

$$\tilde{\mathscr{P}}_A = \mathscr{P}_A(\cdot)\boldsymbol{V}^T \quad \text{and} \quad \tilde{\mathscr{P}}_B = \mathscr{P}_B(\cdot)\boldsymbol{V}^T.$$

By employing the relations (36)–(38), the inclination angles associated with the point x_m are

$$\cos\varphi_A^m = \frac{(-\boldsymbol{g}^m)\cdot(\boldsymbol{V}\tilde{\mathscr{P}}_A\boldsymbol{g}^m)}{|-\boldsymbol{g}^m||\boldsymbol{V}\tilde{\mathscr{P}}_A\boldsymbol{g}^m|}, \tag{42}$$

$$\cos\varphi_B^m = \frac{(-\boldsymbol{g}^m)\cdot(\boldsymbol{V}(-\tilde{P}_B\boldsymbol{g}^m))}{|-\boldsymbol{g}^m||\boldsymbol{V}\tilde{\mathscr{P}}_B\boldsymbol{g}^m|}, \tag{43}$$

$$\cos\varphi_{\mathrm{PRP}}^m = \frac{(-\boldsymbol{g}^m)\cdot\boldsymbol{V}[\tilde{\mathscr{P}}_A(\cdot)-\tilde{\mathscr{P}}_B(\cdot)]\boldsymbol{g}^m}{|-\boldsymbol{g}^m||\boldsymbol{V}[\tilde{\mathscr{P}}_A(\cdot)-\tilde{\mathscr{P}}_B(\cdot)]\boldsymbol{g}^m|}. \tag{44}$$

If the operator $\tilde{\mathscr{M}}$ is a contraction operator (see below), i.e. if

$$\lim_{m\to\infty}|\boldsymbol{g}^m| \to 0 \tag{45}$$

then

$$\cos\varphi_{\mathrm{PRP}}^m \underset{m\to\infty}{\to} 0$$

[7] The powers of the operator $\tilde{\mathscr{M}}$ are defined by successive applications (the zeroth power by the unit operator).

also holds. Thus for the limits of the cosines of the inclination angles in the critical points, we obtain that

$$\cos \varphi_{\mathrm{PRP}}^{m} = 0 \tag{46}$$

and

$$\cos \varphi_{A}^{m} = \cos \varphi_{B}^{m}. \tag{47}$$

From the form of the operator (35) the statements of the "stable limit theorem" [7] also follow. Let us decompose the displacement vector so that its one component $\boldsymbol{d}^{-}$ belongs to the one-dimensional sub-space of the eigenvector associated with the negative eigenvalue and its other component $\boldsymbol{d}^{+}$ belongs to the $(n-1)$-dimensional subspace of the eigenvectors associated with the positive eigenvalues and thus

$$\boldsymbol{d} = \boldsymbol{d}^{-} + \boldsymbol{d}^{+} = \boldsymbol{V}[c_A \mathscr{P}_A(\cdot) - c_B \mathscr{P}_B(\cdot)] \frac{\partial U}{\partial q^i}(x_0). \tag{48}$$

As follows from the form of Eq. (38), the components of the gradient, at the mth point in the eigenvector space belonging to the positive eigenvalue least in absolute sense and to the negative eigenvalue, will vanish in the last place. Therefore, in the subspace spanned by these two eigenvectors, the PRP will converge to an asymptote along which the inclination angles of the derivative and of the derivative components belonging to the groups A and B satisfy the relations (46) and (47). When the PRP and the meta-IRC coincide (and therefore $ds = d\bar{s}$) the Eq. (25), because of the equalities

$$\frac{d^2U}{ds_A^2} = \frac{d^2U}{ds_B^2} = \frac{d^2U}{ds^2}, \tag{49}$$

will turn into the equation system (5.2) in Ref. [7]. Consequently, by using the equality (46), the direction vector of the asymptote at the critical point in the subspace of eigenvectors belonging to the negative eigenvalue λ^{-} and to the least positive eigenvalue $\lambda_{\min}^{+}$ is given by the coordinates of the minimum of the function

$$\phi(\xi_f) = (\lambda^{-}\xi_1 + \lambda_{\min}^{+}\xi_2) \cdot (\boldsymbol{V}[\tilde{\mathscr{P}}_A(\cdot) - \tilde{\mathscr{P}}_B(\cdot)](\lambda^{-}\xi_1 + \lambda_{\min}^{+}\xi_2)); \tag{50}$$
$$(f = 1, 2)$$

where ξ_f are the coordinates of the tangent of the asymptote in terms of the two eigenvectors. This means that the parameters K_A and K_B are, as a matter of fact, the negative and the least positive eigenvalue, respectively.

It is also concluded from the above considerations that Eq. (23) is converging to an SP and not to any other extrema (nevertheless this SP is not necessarily the first order SP interesting from the chemical point of view and therefore the determination of the eigenvalues of the hessian is inevitable). The equality (25) can not be fulfilled unless the hessian has both positive and negative eigenvalues.

3.2. Approximation of the SP in Real Cases

In the course of our discussion we have so far adhered to the presumption that the classification of coordinates into groups A and B has been properly done. Next we examine cases in which the classification of coordinates is improper.

Returning now to our original assumption: we will only state here that there are coordinates which can be ranged properly into the group A and all the remaining ones into the group B. Thus group A will at most be incomplete and group B will contain also elements improperly ranged. Now we ask whether the curve defined by Eq. (23) could reach a critical point under such circumstances (it has already been stated that the limit can only be an SP). If the operator $\tilde{\mathcal{M}}$ defined over a set of vectors, i.e. over a subdomain of the total configuration space of the reacting system, is a contraction operator, i.e. the relation

$$\rho(\tilde{\mathcal{M}}\mathbf{g}, 0) \leq \kappa\rho(\mathbf{g}, 0); \; (\kappa < 1) \tag{51}$$

is satisfied

$$\left(\text{here } \rho = \sqrt{\boldsymbol{V}\frac{\partial U}{\partial q^i} \cdot \boldsymbol{V}\frac{\partial U}{\partial q^j}} = \sqrt{a^{ij}\frac{\partial U}{\partial q^i}\frac{\partial U}{\partial q^j}}\right)$$

then this condition is satisfactory to get the series of points converging to a critical point:

$$\rho^1 = \rho(\tilde{\mathcal{M}}\mathbf{g}^0, 0) \leq \kappa\rho(\mathbf{g}^0, 0) = \kappa\rho^0, \tag{52}$$

$$\rho^{m+1} = \rho(\tilde{\mathcal{M}}\mathbf{g}^m, 0) = \rho(\tilde{\mathcal{M}}^{m+1}\mathbf{g}^0, 0) \leq \kappa\rho(\mathbf{g}^m, 0) = \kappa^m\rho(\mathbf{g}^0, 0)$$
$$= \kappa^m\rho^0. \tag{53}$$

Owing to the condition $\kappa < 1$, for large values of m, $\rho^m \to 0$. In such cases also $\rho(\mathbf{g}^{m+1}, \mathbf{g}^m)$ (quite naturally) will converge to zero because of the triangular inequality:

$$\rho(\rho^m, \rho^{m+1}) \leq \rho(\mathbf{g}^m, 0) + \rho(\mathbf{g}^{m+1}, 0)$$
$$= \rho(\mathbf{g}^m, 0) + \kappa(\mathbf{g}^m, 0) = \kappa^m(\mathbf{g}^0, 0) + \kappa^{m+1}(\mathbf{g}^0, 0)$$
$$= \kappa^m(1+\kappa)\rho(\mathbf{g}^0, 0). \tag{54}$$

The norm of gradient increments form a geometrical series of ratio κ:

$$\frac{\rho^{m+1,m+2}}{\rho^{m,m+1}} = \frac{\rho(\mathbf{g}^{m+1}, \mathbf{g}^{m+2})}{\rho(\mathbf{g}^m, g^{m+1})} = \frac{\kappa^{m+1}(1+\kappa)}{\kappa^m(1+\kappa)} = \kappa \tag{55}$$

and its sum S^m will converge to $|\mathbf{g}^0|$:

$$S^m = |\mathbf{g}^0 - \mathbf{g}^1|\frac{1-\kappa^{m+1}}{1-\kappa} = |\mathbf{g}^0|(1-\kappa)\frac{1-\kappa^{m+1}}{1-\kappa} = |\mathbf{g}^0|. \tag{56}^8$$

[8] S^m denotes partial sums.

Now we can answer the question whether – when having classified the coordinates improperly – the SP could be reached at all. We can state that if the operator $\tilde{\mathcal{M}}$ is a contracting one then the PRP will cross the SP. The effect of improper classification is manifested only in smaller contractions (larger κ values), i.e. in a longer path. However, in the close neighbourhood of the SP the improper classification of the coordinates can be corrected by defining an operator $\tilde{\mathcal{M}}'$ which provides the maximum of the functional $\bar{\omega}$, assigning to each point the length of the vector

$$\boldsymbol{g}^{m+1} - \boldsymbol{g}^m = \tilde{\mathcal{M}}'\boldsymbol{g}^m - \boldsymbol{g}^m = (\tilde{\mathcal{M}}' - \boldsymbol{I})\boldsymbol{g}^m \tag{57}$$

as

$$\bar{\omega}\left(\frac{\partial U}{\partial q^i}(x)\right) := \rho\left(\tilde{\mathcal{M}}' \frac{\partial U}{\partial q^i}(x^m), \frac{\partial U}{\partial q^i}(x^m)\right). \tag{58}$$

By the consecutive reclassification of the B group coordinates into the group A, the functional $\bar{\omega}$ will have maximum and the operator $\tilde{\mathcal{M}}'$ – which has been constructed by taking into account the classification of coordinates at the maximum of the functional – will be optimal over the set of vectors $\partial U/\partial q^i(x)$ in the close neighbourhood of the SP.

By using approximately proper classification of coordinates the present procedure is comparable in convergence speed with most known function minimizing procedures [23–31].

4. Example

For sake of simplicity, the procedure is demonstrated on a surface represented by a quadratic function of two variables $U(\eta_1, \eta_2)$[9]. Let be the eigenvalues of the hessian of this function $\lambda_1 = -1$ and $\lambda_2 = 5$, the transformation matrix relating the spaces of the orthogonal basis vectors $\{\boldsymbol{e}_1, \boldsymbol{e}_2\}$ or $\{\boldsymbol{e}_1', \boldsymbol{e}_2'\}$ and the eigenvectors $\{\boldsymbol{v}_i\}$ of the hessian:

$$\boldsymbol{Tr} = \begin{pmatrix} -0.7071 & 0.7071 \\ 0.7071 & 0.7071 \end{pmatrix}$$

or

$$\boldsymbol{Tr}' = \begin{pmatrix} -0.8944 & 0.4472 \\ 0.4472 & 0.8944 \end{pmatrix}$$

and the coordinates of the SP in the space of $\{\boldsymbol{e}_i^{(I)}\}$ SP: (1; 1). The coordinates $e_1^{(I)}$ and $e_2^{(I)}$ belong to the group A and B respectively. The points of the PRPs starting from various x_0 points have been generated by using the formulas (35) and (38) and the curves so obtained are displayed on Fig. 1.

[9] The variables of the function U are coordinates represented in the space of basis vectors $\{\boldsymbol{e}_i^{(I)}\}$.

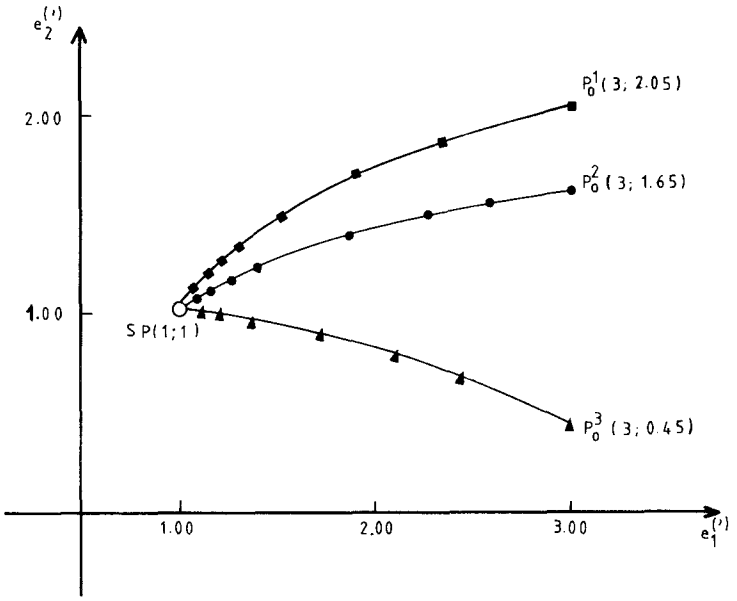

Fig. 1. Pseudo reaction paths (PRPs) approximating the saddle point (SP). For the PRP starting from P_0^1 the reference system of basis vectors $\{e_1, e_2\}$ and for the PRPs starting from P_2^0 and P_3^0 the reference system $\{e_1', e_2'\}$ were used

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