

THE LOCAL DEFINITION OF THE OPTIMUM ASCENT PATH ON A MULTI-DIMENSIONAL POTENTIAL ENERGY SURFACE AND ITS PRACTICAL APPLICATION FOR THE LOCATION OF SADDLE POINTS

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An algorithm is suggested for searching transition states (TS) on multi-dimensional potential energy surfaces. A TS is reached by ascending along a curve linking the reactant and the TS configurations, for which a special term "the optimum ascent path" (OAP) is accepted. A local criterion is formulated allowing to distinguish the points located on OAP among other points in its vicinity. The curve constructed according to this definition does not generally coincide with the regular reaction path curve but it is identical with the curve constructed using the criterion previously suggested by Páncf. The invariance of the OAP configurations under coordinate transformations is proved. The OAPs for several simple reactions are investigated.

1. Introduction

The reaction path (RP) concept appeared when potential energy surfaces (PES) were introduced in chemical kinetics [1]. The RP on a PES is defined as a minimum energy curve, the gradient line that links the configurations representing reactants and products through a saddle point corresponding to a transition state. Since the gradient vanishes at stationary points, the RP direction is determined there by a vibrational mode, either a decay one with an imaginary frequency, at a saddle point, or a usual one, at regular minima points [2].

These statements have been formalized as a differential steepest descent equation, defining the curve of RP, by Fukui et al. [3, 4]. Internal coordinates of a chemical system spanning the space in which such a curve is defined are not at all the cartesian ones. It seems both natural and convenient to use tensor notations specially adapted for dealing with curvilinear coordinates. The tensor calculus methods have been applied to study the topography of PESs in recent papers [5, 6]. In the present paper we use some

notations and formulations introduced in ref. [5].

The RP equation in cartesian coordinates is

$$\begin{aligned} d|q\rangle/ds &= N^{-1/2}|u\rangle, \\ |u\rangle &= |\partial U/\partial q\rangle, \quad N = \langle u|u\rangle. \end{aligned} \quad (1)$$

Here s represents a scalar parameter, the arc length of the RP curve, U is the potential energy, $|q\rangle$ and $|u\rangle$ are the column-vectors of cartesian coordinates and of the gradient, respectively. The tensor reformulation of eq. (1) for general curvilinear coordinates takes the form

$$\begin{aligned} dq^i/ds &= N^{-1/2}g^{ij}U_{,j}, \\ U_{,i} &= \partial U/\partial q^i, \quad N = g^{ij}U_{,i}U_{,j}. \end{aligned} \quad (2)$$

Here g^{ij} is a contravariant metric tensor, that is to say, the kinetic energy matrix in the momentum representation. Summation over repeating indices is implied in (2).

Eqs. (1) or (2) should be solved with the initial conditions

$$|q\rangle = |q^{\#}\rangle, \quad q^i = q^{\#i}, \quad s = s^{\#}, \quad (3)$$

where the superscript “ \neq ” labels the values of the respective quantities at a saddle point.

Eq. (1), neglecting the coordinate metric, can also be considered for non-cartesian coordinates. The curve representing its solution defines a non-invariant RP, specific for a given coordinate system. It, however, still passes through the saddle point and the minima, because stationary configurations are independent of the choice of the coordinate set.

Definitions (1)–(3) can be utilized to calculate a RP if the saddle point is found beforehand. Such calculations have been reported [7, 8]. From a practical point of view the reverse problem is more interesting: to find the saddle point following the RP upwards along the valley, starting from the given reactant (or product) region. Definitions (1)–(3) are useless for that purpose. The reason is that a RP represents an asymptote of all gradient curves descending in the reaction valley from its side slopes [5]. When moving upwards in the tangent direction of a RP, as defined by eq. (1) or (2), the computational errors tend to accumulate and the curve is expected to arrive at a side ridge instead of the wanted saddle point. So there is a need of a criterion allowing to distinguish the bottom of a valley among a great number of adjacent points. Then mounting to the desired saddle point would be available by introducing a proper correction after every elementary step in the gradient direction. This criterion should be a local (differential) one, as opposed to the global (integral) criterion (1)–(3), which allows discerning the RP points (in the upwards sequence) only after the whole curve being calculated (in the downwards sequence).

Several authors [9–14] have suggested empirical, intuitive procedures for determination of RPs. Their thorough discussion may be found in a recent review [15]. As a rule, they need some iterative refinements inevitably invoking the global criterions (1)–(3). To our knowledge, the only attempt to present an explicit local definition of a RP was due to Panciř [16]. He assumed that at every RP point the gradient vector coincided with one of the eigenvectors of the second derivative (of the energy) matrix.

This definition, which later on will be referred to as the “Panciř criterion”, has been presented without any reasoning. Some tests on this criterion, reported by Müller [15], have demonstrated that it defines a curve, generally distinct from a RP as defined by eqs. (1)–(3).

The present work is devoted to the formulation of a method of constructing the smooth curve linking the reactant region with the saddle point. We call it “the mountaineer’s algorithm”, because it exactly imitates the strategy of a person climbing up to a saddle point along a valley. The Panciř criterion proves to define the same curve, and it can be deduced as a consequence of the mountaineer’s algorithm. This curve can coincide with a RP only if the latter represents a straight line. For the valleys characterized by curvilinear RPs the new curve is different from a RP, so we introduce a special term, “the optimum ascent path” (OAP), for it. The orthogonal energy sections are not minimal at the points located on an OAP. However, contrary to a RP, an OAP has the important property that there exists a local criterion for discerning its points. This criterion is invariant, being true for an arbitrary coordinate system.

On a technical level different realizations of the mountaineer’s algorithm may be considered. Two of them were tested in the present work. Their efficiency is illustrated in the second part of this paper by calculations of OAPs for several many-atomic reactions.

2. Construction of the optimum ascent path in cartesian coordinates

Consider first the local definition of an OAP in cartesian coordinates. A RP satisfies eq. (1) with initial conditions (3). In the case that non-cartesian internal coordinates are dealt with, this simplest OAP definition still allows locating saddle points by following non-invariant curves. In the next section we consider those complications necessary for the definition of an invariant OAP, which should be compared with an invariant RP satisfying eq. (2).

The mountaineer's algorithm. If a point is located on an OAP the gradient norm has a minimum at it as compared with adjacent points on the same constant energy surface. That is to say, in order to find the point on an OAP, one has to investigate the adjacent region of the constant energy surface, searching for a point where the ascent steepness passes through a minimum.

The mathematical formulation of this condition,

$$\delta\langle u|u\rangle = \langle\delta u|u\rangle + \langle u|\delta u\rangle = 0,$$

yields

$$\langle\delta u|u\rangle = 0 \quad (4)$$

(the variation δu being calculated on a constant energy surface).

The construction proceeds as follows. One starts from a point located exactly on the bottom of the reactant valley and makes the first step in the gradient direction. Then a correction based on the mountaineer's algorithm is performed. The next OAP point being located, the new step along the gradient is made, followed by a next correction, etc.

The curve, calculated using this strategy, certainly passes through a saddle point. [A singular situation resulting in an OAP ending up blindly (dissipating), without reaching the saddle point, is an important exclusion discussed in section 3.] Indeed, when mounting along an OAP, one reaches the constant energy level, whose energy is the same as that at a saddle point. By the definition, the OAP intersects that level surface at the point where the gradient norm $\langle u|u\rangle^{1/2} = N^{1/2}$ has a minimum. That should be just the saddle point where $N = 0$. The similar reasoning (neglecting again singular cases) ascertains that an OAP really either passes through a minimum corresponding to a reactant configuration (for monomolecular reactions), or flows together with the bottom of the valley in the asymptotic reactant region (for bimolecular reactions).

After a primary step from a point located on an OAP in the gradient direction we arrive at the point $|q\rangle$, where the gradient equals to $|u\rangle$. The subsequent displacement by a small vector

$|\delta q\rangle$ produces $|\delta u\rangle = F|\delta q\rangle$, where F is a second derivative matrix at $|q\rangle$. Now the condition (4) can be made more precise by writing

$$\langle\delta q F|u + F\delta q\rangle = 0, \quad (5a)$$

$$\langle\delta q|u\rangle = 0. \quad (5b)$$

Eq. (5b) represents the condition of variation on a constant energy surface.

The pair of equations (5a), (5b) is treated by the Lagrange method. We multiply the latter one by the indefinite factor $-\lambda$ and add it to the former one:

$$\langle\delta q|Fu + F^2\delta q - \lambda u\rangle = 0.$$

From this the displacement vector is extracted, satisfying condition (4) in the first smallness order:

$$|\delta q\rangle = (\lambda F^{-2} - F^{-1})|u\rangle. \quad (6)$$

Finally, the value of λ is obtained after applying the orthogonality condition (5b) for the vector (6):

$$\lambda = \langle u|F^{-1}|u\rangle / \langle u|F^{-2}|u\rangle. \quad (7)$$

For a point located on an OAP $|\delta q\rangle = 0$. Then the following relation arises from (6):

$$F|u\rangle = \lambda|u\rangle. \quad (8)$$

Thus we come out with the Panciř criterion [16]: The gradient vector is an eigenvector of the second derivative matrix (with the eigenvalue λ). Note, that this derivation and hence the Panciř criterion (as opposed to the original mountaineer's algorithm) both give an incomplete definition of an OAP, being unable to distinguish a true OAP from a curve representing a maximum of the gradient norm. It may also be shown that formulas (6) and (7) differ from the algorithm suggested by Panciř in higher order terms. Being more simple, they have the advantage of representing a regular Newton-Raphson procedure (with a constraint).

The above reasoning holds if F is a non-singular matrix. Otherwise, if at some point $\det F = 0$,

the proposed procedure becomes invalid. A more detailed knowledge of the shape of the

PES is required near that point. This situation is explicitly treated in the second part of this paper.

3. The distinction between the reaction path and the optimum ascent path

The formulation of the mountaineer's algorithm in an arbitrary coordinate system, producing an invariant OAP, starts from eq. (2) rather than (1). The gradient norm $N^{1/2}$ being a scalar, its usual and covariant variations are the same. It is convenient to treat δ as a covariant variation because then $\delta g^{ij} = 0$.

The condition

$$\delta(g^{ij}U_{,i}U_{,j}) = g^{ij}(\delta U_{,i}U_{,j} + U_{,i}\delta U_{,j}) = 0,$$

yields

$$g^{ij}U_{,i}\delta U_{,j} = 0 \quad (10)$$

(the covariant variation being calculated on a constant energy surface).

Next we introduce a tensor $U_{,jk}$ of covariant second derivatives (of the energy): $\delta U_{,j} = U_{,jk}\delta q^k$ and supplement (10) by the constant energy condition:

$$g^{ij}U_{,i}U_{,jk}\delta q^k = 0,$$

$$U_{,k}\delta q^k = 0.$$

The solution by the Lagrange method gives

$$g^{ij}U_{,jk}U_{,i} - \lambda U_{,k} = 0. \quad (11)$$

From that we conclude that the gradient $U_{,i}$ should be an eigenvector of the mixed tensor of covariant second derivatives:

$$U_{,k}^i = g^{ij}U_{,jk}.$$

An explicit comparison of the two curves, RP and OAP, is most conveniently performed in a special curvilinear coordinate system, the natural reaction coordinates (NRC) [17]. Originally introduced by Marcus for linear three-atomic reactions, they were then generalized for arbitrary many-atomic systems [5]. One of these coordinates, the translational coordinate s , is an arc length measured along the RP

curve from the saddle point. The transversal vibrational coordinates v^α are orthogonal to s and they all vanish on the RP. (For polyatomic systems the orthogonality holds only at the point $v^\alpha = 0$ on the RP.)

The following special form of the energy expansion in NRC is deduced from the fact that the RP is a gradient curve [eq. (2)] [5]:

$$U(s, v^\alpha) = V(s) + \sum_\alpha \frac{1}{2}\omega_\alpha^2(v^\alpha)^2 + (\text{terms of higher order in } v^\alpha). \quad (12)$$

The frequencies ω_α depend only on the translational coordinate.

Let us consider the simplest two-dimensional situation with a single vibrational coordinate v . The metric tensor is [17]:

$$\|g^{ij}\| = \begin{vmatrix} (1+Kv)^{-2} & 0 \\ 0 & 1 \end{vmatrix}. \quad (13)$$

Here K is the curvature of the RP; the first (i) and the second (j) indices correspond to s and v , respectively. Differentiation of the energy (12) on RP gives

$$\begin{aligned} \partial U/\partial s &= dV/ds; & \partial U/\partial v &= 0; \\ \partial^2 U/\partial s^2 &= d^2V/ds^2; & \partial^2 U/\partial v^2 &= \omega^2; \\ \partial^2 U/\partial s \partial v &= 0. \end{aligned} \quad (14)$$

Now we calculate the derivative of the gradient norm [see eq. (2)] with respect to v :

$$\begin{aligned} \partial N/\partial v &= \partial[(1+Kv)^{-2}U_{,s} + U_{,v}]/\partial v \\ &= -2(1+Kv)^{-3}K(dV/ds)^2 + 2v\omega^2. \end{aligned}$$

When $v = 0$ on the RP,

$$\partial N/\partial v = -2K(dV/ds)^2 = -2KN.$$

If the mountaineer's algorithm were valid on the RP then one could write $\partial N/\partial v = 0$ for $v = 0$. So we conclude that a RP and an OAP can be the same at some point only in two special cases:

- (a) Both curves represent a straight line at that point ($K = 0$). (15)
- (b) The point is a stationary one ($N = 0$).

Moreover, we can estimate the displacement of the OAP relative to the RP by equating to zero the above expression for $\partial N/\partial v$. It then becomes an equation defining the coordinate $v_{(\text{OAP})}$ of a proper OAP point, from which the following expansion is extracted:

$$v_{(\text{OAP})} = KN/\omega^2 - \dots$$

The quantities on the rhs are calculated on the RP ($v = 0$).

As follows from (14), the gradient on a RP coincides with an eigenvector of the second derivative matrix $U_{,ij} = \partial^2 U/\partial q^i \partial q^j$ associated with the NRC. (The latter comment is important, because the quantities $U_{,ij}$ do not form a tensor, so the respective eigenvector changes when passing from one coordinate system to another.) On the other hand, as shown above, the gradient on an OAP coincides with the eigenvector of the matrix of the mixed tensor $U_{,i}^j$. The covariant and the partial NRC derivatives are the same only when one of the conditions (15) is satisfied.

This formal reasoning can be illustrated by a straightforward evaluation of the covariant derivatives on the RP:

$$U_{,ij} = U_{,ij} - \Gamma_{ij}^a U_{,a}. \quad (16)$$

Calculating the Christofel symbols Γ_{ij}^a by a regular procedure [18] for the metric tensor (13) we obtain for $v = 0$;

$$\Gamma_{sv}^s = \Gamma_{vs}^s = K; \quad \Gamma_{ss}^v = -K.$$

All other Γ vanish. Then applying formula (16) we find for $v = 0$:

$$\begin{aligned} U_{,ss} &= U_{,ss} = d^2 V/ds^2, \\ U_{,sv} &= U_{,vs} = -K dV/ds, \\ U_{,vv} &= U_{,vv} = \omega^2. \end{aligned} \quad (17)$$

The mixed tensor $U_{,i}^j$ is recovered after multiplication of (17) by g^{ij} . Noting that $g^{ij} = \delta^{ij}$ for $v = 0$ verifies that $\|U_{,i}^j\| = \|U_{,ij}\|$. Again we observe that this tensor can be diagonal only under the conditions (15).

These results can be easily extended onto arbitrary many-atomic systems, if one combines the energy expansion (12) with the metric tensor of polyatomic NRC [5].

The main conclusion is that the properties of a RP are closely related to the properties of the second derivative matrix in NRC, whereas the properties of an OAP are similarly related to the covariant second derivative matrix. There exists a simple invariant local criterion (10) for finding points on a RP because the construction of NRC needed previously (actually, one should have calculated the curvature of a RP) can be performed only after having calculated the whole RP curve.

Another peculiarity of the OAP curves is the existence of singular points on them, namely, the branching and dissipation points. They are accompanied by branching or dissipation of a valley or a ridge of a PES. The above-mentioned vanishing of the determinant of the second derivative (or covariant second derivative) matrix usually presents itself in the vicinity of branching points. An explicit mathematical treatment of all these singularities is beyond the scope of the present study; it will be a subject of a future publication. We shall merely indicate their presence as an empirical observation, when they appear in the following calculations.

It should also be emphasized that there are no such points on RP curves. Consider, for instance, a situation, in which an OAP terminating at a saddle point originates from a point on a side slope of a PES. That is to say, it vanishes without reaching a minimum. (Such a situation is described in the calculations below.) An opposite case, in which an OAP originating from a minimum dissipates on a side slope without reaching a saddle point, is also possible. In both cases there exist continuous RP curves with no singularities connecting the respective minimum and saddle point. These gradient lines pass through a flat or even convex slope region of a PES, where an OAP (as well as the corresponding valley of a PES) does not exist.

This preliminary qualitative discussion shows that singular points may present certain specific difficulties when OAP curves are applied as a tool for searching saddle points. On the other hand, it becomes evident that there are just OAP curves which are closely related to intrinsic properties of a PES. The whole

discussion allows us to state that the OAP curves are more fundamental characteristics of a PES than the RP ones.

An advantage of a RP curve remains to be the fact that the transversal energy sections pass through minima on it. [That generates a special form (12) of the energy expansion.] However, the same can be achieved for an OAP curve if one sacrifices the property of orthogonality of transversal vibrational coordinates v^α to the translational coordinates s on that curve in the region of a non-zero curvature [then the first order in v^α terms would appear in (12)].

4. Practical realization of the mountaineer's algorithm

Suppose that a point $|q_{i-1}\rangle$ located on an OAP in a valley is known (fig. 1). A step of length α is made in the steepest ascent direction to the point $|q_i''\rangle$:

$$|q_i''\rangle = |q_{i-1}\rangle + \alpha N^{-1/2}(q_{i-1})|u(q_{i-1})\rangle. \quad (18a)$$

This point lies on the side slope of the valley. We calculate the gradient $|u(q_i'')\rangle$ and the matrix of second derivatives $F(q_i'')$ and, using formulas (6) and (7), find the displacement vector $|\delta q\rangle$ and the new point,

$$|q_i'\rangle = |q_i''\rangle + |\delta q\rangle. \quad (18b)$$

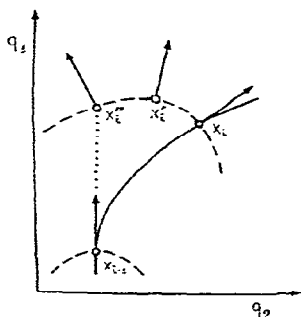


Fig. 1. Realization of the mountaineer's algorithm on a two-dimensional PES. The solid, broken and dotted lines indicate respectively the OAP, the constant energy curve and the step of length α made from the point $X_{i-1} = |q_{i-1}\rangle$ located on the bottom of the valley in the steepest ascent direction ($X_i'' = |q_i''\rangle$, $X_i' = |q_i'\rangle$, $X_i = |q_i\rangle$).

If all absolute values of the $|\delta q\rangle$ components are less than the beforehand specified number $\text{EPS} > 0$, then one accepts $|q_i'\rangle = |q_i\rangle$, makes a new step (18a), calculates a new displacement vector, etc. The climbing along the value is continued until one eigenvalue of matrix F becomes negative after passing an inflexion point of OAP. Then we supplement the $|\delta q\rangle$ calculation by the calculation of the step of the Newton-Raphson method,

$$|\delta q^N\rangle = -F^{-1}(q'')|u(q'')\rangle. \quad (19)$$

If at least one component of $|\delta q^N\rangle$ exceeds in absolute value some beforehand specified number $\text{SLIM} > 0$, then the climbing according to the mountaineer's algorithm is continued. Otherwise, we change $|\delta q^N\rangle$ for $|\delta q\rangle$ in (18b) and find the transition state (TS) by the Newton-Raphson method.

As mentioned above, this procedure fails to be valid at the points where $\det F = 0$. Such a situation occurs at least once on the way to a TS. One of the frequencies vanishes, namely, that operating the translation along the bottom of the valley and parallel to the gradient vector at that point. (This is the abovementioned inflexion point of the OAP.) This causes not serious complications: the chance of getting exactly at that point is quite small while moving with a fixed step α . In the case that the eigenvalue corresponding to the translational motion becomes smaller than a fixed number $\text{EVLIM} > 0$, an extra step (18a) is made instead of evaluating the correction $|\delta q\rangle$. Then mounting is continued in a standard manner.

The case that another frequency vanishes, namely, that corresponding to a transversal vibrational motion, is more complicated. Provided all other eigenvalues of F remain positive, this branching situation corresponds to a transformation of a valley into a ridge with a pair of new valleys arising asides. The following prescription is recommended to treat such a point. Consider the region situated before that point, in its vicinity. The displacement vector $|\delta q\rangle$, as calculated by (6) and (7), becomes practically parallel to the eigenvector of F corresponding

to its minimal eigenvalue. As a rule, its length greatly exceeds SLIM [it becomes infinite if (9) holds exactly]. Therefore the correction procedure (18b) is changed for the minimization of the square of the gradient norm N (1) along the $|\delta q\rangle$ direction by the DSC-Powell method [19]. The point found after the next step (18a) is expected to be sited on the ridge. Applying the mountaineer's algorithm would now generate the OAP along the ridge. Generally it would end up at the hill top (a pair of negative eigenvalues of F), however, a situation with the blind termination (dissipation of the OAP) cannot be excluded.

The valleys arising at the triple branching point where $\det F = 0$ are, however, more interesting. The descent to one of them from the ridge can be performed by the energy minimization along the decay eigenvector of F . Then formulas (18) can be applied again.

An alternative realization of the mountaineer's algorithm does without calculations of the second derivatives of the energy. It substitutes the stage (18) by an iterative procedure performing a straightforward minimization of the square of the gradient norm N on a constant energy surface according to the local OAP definition. A modification of the Powell method has been applied (see Himmelblau [19, ch. 4]). The restricted minimization proceeded as follows: the first column in the matrix of search directions in the Powell algorithm was substituted by the $|u(q_i')\rangle$ and then the linearly independent vector set determining the direction of the one-dimensional search was constructed by the Gramm-Schmidt orthogonalization with respect to $|u(q_i')\rangle$. (This procedure does not change the vector $|u(q_i')\rangle$ itself.) Next one iteration of the Powell method was performed in order to minimize N in the subspace of dimension $n-1$ (n is the dimension of the whole space of arguments). That yielded the point $|q_i'\rangle$ located on the same energy level surface which was closer than $|q_i'\rangle$ to the point $|q_i\rangle$, the bottom of the valley. Then the first column of the matrix of search directions was substituted by $|u(q_i')\rangle$ and the process was repeated beginning from the orthogonalization step until

the point $|q_i\rangle$ was located within a given precision (fig. 1).

The subsequent points $|q_{i+1}\rangle$, $|q_{i+2}\rangle$, etc. were located similarly until the relation $N(q_k) < N(q_{k-1})$ became true at some point $|q_k\rangle$. Then the saddle point was located by the unrestricted Powell minimization of N .

It might occur that the so located minimum of N does not represent an energy extremum ($N \neq 0$). In this case a new step (18a) was made and the construction of the OAP was continued.

From now on we shall refer to the alternative realizations of the mountaineer's algorithm, those with second derivatives and those without them, as versions A and B, respectively. Version B yields a practically continuous OAP curve. The minimization on the energy level proceeds more accurately than in version A. However, the calculation of matrix F gives useful extra information that allows distinguishing between OAPs following either valleys or ridges as well as the identification of the character of a stationary point finally located. Moreover, the main disadvantage of the version B is that it needs computer time consumption 3-6 times as large as needed by version A. This estimation is based on our calculations reported in the next section. The relative efficiency of version A will increase with the increase of the number of variables involved in the optimization. So version B is recommended only to treat the complicated situations, such as a triple branching point with $\det F = 0$.

5. Application of the mountaineer's algorithm for the search of TSS

The routine realizing the method described in the preceding section (versions A and B) was tested by calculations on the analytical two-dimensional PES by Müller and Brown [13], having three minima (A, B, C) and two saddle points (1, 2). The results presented below were obtained by version A. The following algorithm parameters were used (for their definition see section 4): $\alpha = 0.1$, $\text{EPS} = 0.001$, $\text{SLIM} = 0.1$,

EVLIM ≈ 0.1 . The original ascent directions from the minima were so chosen to coincide with the proper normal modes. The OAPs between the points $C \rightarrow 1$, $C \rightarrow 2$ were successfully constructed.

The results summarized in table 1 allow making a comparison of the relative efficiency of the two methods, the mountaineer's algorithm and the restricted simplex optimization [13], by considering an equivalent number of energy calculations. The computational time consumption was rather similar but the precision of the geometry localization in our calculations was higher by one order of magnitude. Our procedure naturally failed to find the OAP for the $A \rightarrow 1$ transition. This can be explained by the absence of a valley directed to the saddle point 1 (antisymmetrical mode) in the vicinity of the minimum *A*. We verified that by drawing a steepest descent path from 1 to *A* and beginning the search by our method from different points located on it. In any case, even when the starting point was in the middle between 1 and *A*, the algorithm led to another valley corresponding to a symmetrical mode. The peculiarity of the given PES was that there was no saddle point on that way (see fig. 16 of ref. [15]). So we can conclude that the valley originating from the saddle point 1 and directed to the minimum

A dissipates somewhere on the side slope as mentioned in the above discussion.

Version B of our algorithm gave practically the same OAPs but the computational efforts increased significantly.

We also tested the mountaineer's algorithm by calculating several simple reactions. All calculations were performed by the MINDO/3 procedure [20]. The derivatives, both first and second, were numerically evaluated using the central difference approximation [21]. Scaling of geometrical variables was accepted (1 Å and 100° being the length and the angle units respectively).

5.1. Isomerization $\text{HCN} \rightarrow \text{HNC}$ (I)

This reaction, calculated previously both by *ab initio* [22, 23] and semi-empirical [13] methods, presents a usual test for new algorithms destined for searching TSs. The three independent variables are: the HC and CN bond lengths, and the HCN valence angle. In our MINDO/3 calculation the structure of the TS and its relative energy were close to the results of the *ab initio* CI treatment [23] that used the two-exponential basis set (DZ P/CI). The results of the latter calculation are given in parentheses below.

Table 1
The statistics of the OAP calculations on the model PES by Müller and Brown [13]

OAP	Number of points on the OAP	Number of iterations ^{a)}	Number of calculations of the function ^{b)}	Equivalent number of the energy calculations		α
				this work ^{c)}	Müller and Brown	
$B \rightarrow 2$	10	25	35	180	74	0.05
$C \rightarrow 2$	6	16	22	114	73	
$C \rightarrow 1$	16	24	40	192	113	
$B \rightarrow 2$	6	20	26	138	74	0.10
$C \rightarrow 2$	4	12	16	84	73	
$C \rightarrow 1$	9	16	25	123	113	

^{a)} The iterations (18a)–(18b) of the mountaineer's algorithm. Their number is equal to the number of calculations of the matrix of second derivatives *F*.

^{b)} Equal to the number of gradient calculations.

^{c)} The time needed for the calculations of one gradient and of one second derivative (one element of the *F* matrix) was accepted to be the same.

The saddle point characteristics were: HCN angle: 79.9° (78.8°); the CN and HC bond lengths: 1.196 (1.181) and 1.149 (1.171) Å, respectively. The TS energy relative to the HCN configuration was 53.0 (49.5) kcal/mole. The only drawback of the MINDO/3 treatment was the prediction that HNC configuration, that has not been observed experimentally, was by 15.3 kcal/mole more stable than HCN. The ab initio calculation correctly predicted the inverse stability order, with an energy difference of 14.6 kcal/mole [23].

We tested both versions of the algorithm in studying this reaction. The time consumptions of the calculations by versions A and B were in the ratio 1:4.

5.2. The hydrogen abstraction radical reaction $\text{CH}_3 + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3$

We calculated this reaction only by version B using unrestricted HF modification of MINDO/3. The TS was located previous to the OAP calculation by optimizing the collinear structure $\text{C}(1)\text{H}_3\text{--H}(1)\text{--C}(2)\text{H}_3$ in the framework of S_6 symmetry [3 independent variables being the bond lengths $\text{C}(1)\text{--H}(1)$, $\text{C}(1)\text{--H}$, and the angle $\text{H}(1)\text{C}(1)\text{H}$]. The OAP search started from the collinear C_3 configuration at the $\text{C}(1)\text{--H}(1)$ distance equal to 2.2 Å (all other degrees of freedom being optimized). The ascent (version B of the algorithm, $\alpha = 0.3$) proceeded until the bond length $\text{C}(1)\text{--H}(1)$ became 1.3 Å. At that point the square of the gradient norm N proved to be smaller than at the preceding point. Then unrestricted minimization of N gave the structure identical with the TS within a given precision EPS. The bond lengths $\text{C}(1)\text{--H}(1)$ and $\text{C}(1)\text{--H}$ were, 1.256 and 1.101 Å, respectively, the $\text{H}(1)\text{C}(1)\text{H}$ angle was 108°. The calculated activation energy was 6.9 kcal/mole (the experimental value is 14.7 kcal/mole [24]).

5.3. Electrocyclic reaction cyclobutene \rightarrow butadiene (II)

A lot of calculations on this reaction have been reported [9, 25–27]. Contrary to the rear-

angement (1), where the TS is easily localized by using a traditional "reaction coordinate" method, this reaction cannot be successfully treated by that approach. As was shown [9, 27], when taking the $\text{C}(5)\text{--C}(6)$ bond length (see fig. 2) as a natural reaction coordinate, the so calculated "reaction path" displayed a rupture at a value of this coordinate of ≈ 2.2 Å. We have calculated a complete OAP from the cyclobutene structure to the desired TS. The direction for the initial step was chosen to coincide with the normal mode involving the maximum contribution from the $\text{C}(5)\text{--C}(6)$ stretching motion. The existence of a triple branching point, near where a valley was transformed into a ridge, was a remarkable peculiarity of this reaction. The $\text{C}(5)\text{--C}(6)$ distance was ≈ 1.7 Å at that point. The above specified prescription of how to treat such a situation has been elaborated just on this particular system.

The calculated structure of the TS is presented in table 2 together with the reactant and product structures. The calculated activation energy (48.9 kcal/mole) was close to the MINDO/2 result (49.5 kcal/mole [27]) and far from the experimental estimation (33 kcal/mole [28, 29]). The exothermicity of the reaction was underestimated (0.8 kcal/mole instead of the experimental value of 8.9 kcal/mole [27]).

An experiment was also performed in order to investigate how the mountaineer's algorithm behaves being switched on at an arbitrary point. We began from the configuration obtained by optimizing 12 internal coordinates in the

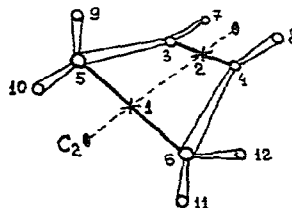


Fig. 2. Specification of the atomic indices in the C_4H_6 system. The broken line is the symmetry C_2 axis; the crosses indicate the "false atoms", i.e. the extra points used for the convenience of geometry presentation in a symmetrical system.

Table 2

The characteristics of the stationary points of the PES for the electrocyclic reaction cyclobutene \rightarrow butadiene (MINDO/3 calculation)

	Configuration		
	cyclobutene ^{a1}	saddle point ^{b1}	butadiene ^{c1}
R(1, 2) ^d	1.505	1.335	0.833
R(3, 4)	1.348	1.418	1.447
R(3, 5)	1.507	1.388	1.327
R(5, 6)	1.537	2.059	3.403
R(3, 7)	1.098	1.101	1.113
R(5, 9)	1.114	1.104	1.099
R(5, 10)	1.114	1.110	1.100
$\angle(2, 3, 7)$	135.8	128.3	110.9
$\angle(3, 5, 9)$	116.6	124.4	125.3
$\angle(3, 5, 10)$	116.6	124.0	124.2
$\angle(3, 2, 1, 5)$	0.0	14.0	17.3
$\angle(1, 2, 3, 7)$	180.0	151.3	150.3
$\angle(2, 3, 5, 9)$	-118.0	-60.4	-1.1
$\angle(2, 3, 5, 10)$	118.0	148.2	178.4

^{a1} C_{2v} symmetry, heat of formation 33.0 kcal/mole.

^{b1} C₂ symmetry, heat of formation 81.2 kcal/mole.

^{c1} C₂ symmetry, heat of formation 32.2 kcal/mole.

^{d1} For the numeration of atoms see fig. 2. Bond lengths (R) in Å; angles (\angle) in degrees.

framework of a given C₂ symmetry at a C(5)C(6) distance fixed at 2.2 Å. This point, corresponding to a breakdown of the "reaction coordinate" method, proved to be far from the bottom of the valley. On the other hand, the calculation revealed a negative eigenvalue of *F* (and a nonzero gradient) which indicated that the saddle point region had been already reached. However, that starting point was still too remote from the saddle point to be treated by the Newton-Raphson method. The Newton-Raphson step greatly exceeded the SLIM value (the parameters of the algorithm being $\alpha = 0.1$, EPS = 0.001, SLIM = 0.125, EVLIM = 1). Therefore the algorithm A was applied. It needed three steps (18b) to locate an OAP point lying on a ridge (not in the valley). Hence, some descending to the saddle point was needed. The condition to change for the Newton-Raphson procedure was satisfied there. Next two Newton-Raphson steps downwards localized the saddle point.

This kind of behaviour can be explained as follows. The transition to a ridge would be impossible if the condition of moving on a constant energy level were exactly obeyed. That condition has been violated since the linearized eq. (6), based on the quadratic approximation for a PES, was inadequate to exactly treat the situation far from an OAP. (The version B of the algorithm, being free from this defect, is fit for the accurate treatment of that case.) Nevertheless the algorithm was able to find an OAP, and after that it behaved in a regular manner. This example manifests the necessity of having a criterion to distinguish between a valley and a ridge in the vicinity of a transition state. This situation was treated as follows. We observed that the angle between the directions of the gradient and the Newton-Raphson step was close to 0 in a valley and to π on a ridge. In the latter case the change of α for $-\alpha$ ensured descending along the ridge to the saddle point.

6. Estimation of the efficiency of the algorithm

A number of methods have been proposed for the purpose of searching the TSs [9–16, 27, 30]. Unfortunately, the lack of detailed information on the testifying calculations gives no opportunity to conclude on their power. The simplex-optimization procedure [13] presents a nice exclusion, so we have to confine ourselves to a comparison of our method with this one.

The reaction (I) was common for both calculations. In our work 5 steps (18a) and 9 iterations (18b) of the mountaineer's algorithm were needed altogether in order to reach the saddle point. The energy and the gradient were calculated 14 times and the matrix of force constants (the lower triangle) 9 times. This is equivalent to 38 energy calculations (the time needed for a calculation of a gradient component constituted less than 100% of the time consumption in a single energy calculation). We multiply this figure by the factor 3 noting that the numerical evaluation of the second derivatives poses very high requirements on the precision of a self-consistency procedure. So we estimate our computational effort as 114 standard energy calculations. Our geometry calculations were more precise than those reported by Müller and Brown, so we reduce that number down to 90 in order to make a consistent comparison. This should be compared with 207 energy calculations by the restricted simplex-optimization method [13]. So the mountaineer's algorithm is a more economical procedure and its advantage will increase with the increase of the number of variables involved in the optimization.

The attempt of discussion of the synchronous-transit method [9] is more complicated. In the reported calculations on reaction (II) the number of optimized geometrical variables was less than in our calculation. So a direct comparison was impossible. We were able only to conclude from the reported data that the computer time consumption by the two procedures is of comparable magnitude.

It should be noted that the information on the properties of a PES supplied by the moun-

taineer's algorithm is considerable greater than that given by other methods. Not only stationary points are located by our procedure but also the whole reaction path and the invariant points of the valley branching. More detailed calculations on the PES topography using this algorithm will be reported later.

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