

TOPOGRAPHY OF POTENTIAL ENERGY SURFACES

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Abstract - The curves on a multi-dimensional potential energy surface (PES) linking the reactant and the transition state configurations are constructed. They are generally distinct from usual reaction path curves and a special term "optimum ascent path" (OAP) is accepted for them. A local criterion is formulated allowing to distinguish the points located on an OAP among other points in its vicinity. A mathematical analysis of singular points of a PES, where its valleys or ridges emerge, dissipate or bifurcate, is presented. These points are specified as different branching points of OAPs.

INTRODUCTION

Potential energy surface (PES) is a basic concept of the modern theory of chemical reactions. Since heavy molecular fragments are usually transferred in organic reactions so their motion can be treated as classical one with the high degree of accuracy. If a potential barrier is sufficiently large and temperature is not too high then the majority of classical trajectories follow from the reactant to the product region close to the minimum energy path through the saddle point region. Under these circumstances the elementary geometrical elements of a PES, such as stationary points (the minimum and saddleones), energetical valleys and ridges, reaction coordinates etc, become of fundamental importance for chemistry. The topographic interpretation of these concepts is obvious for a PES depending on two geometrical variables. It can be also extended onto multi-dimensional PESs.

SEVERAL DEFINITIONS

Let potential energy U depend on internal coordinates q_i , $U = U(q_i)$. Then stationary points obey the relation

$$\partial U / \partial q_i = 0 \quad (1)$$

Energetical valley is determined by the condition that all cross-sections orthogonal to its local direction pass through minima at the points of its bottom. At least one of the transversal cross-sections has a maximum at the top line of an energetical ridge.

The reaction path (RP) curve is usually defined (1) as a minimum energy path, a gradient steepest descent line starting from a saddle point. If coordinates q_i can be treated as cartesian the following differential equation determines a RP curve

$$\partial q_i / \partial s = N^{-1/2} \partial U / \partial q_i \quad (2)$$

$$N = \sum_i (\partial U / \partial q_i)^2 \quad (3)$$

Here scalar parameter s represents an arc length of the RP curve and N is the square of the gradient norm.

Internal variables q_i are not uniquely chosen, moreover, they are usually noncartesian. Stationary points, as defined by equation (1), are, nevertheless, invariant. That is to say, they represent the same geometrical configuration of a chemical system for any choice of q_i . That is not the case when a collection of points lying on a RP is considered because equations (2) and (3) are not invariant and generate a noninvariant RP specific for a given particular coordinate system. However, these noninvariant curves connect invariant minimum and saddle points. This property is sufficient for many chemical applications as well as for a general discussion. Therefore we don't consider below the mathematically refined equations generating an invariant RP (2,3) or related invariant curves.

LOCATION OF SADDLE POINTS ON A MULTI-DIMENSIONAL PES

Definitions (2) and (3) can be utilized to calculate a RP if the saddle point of interest is found beforehand. The necessary initial condition is

$$q_i = q_i^{\neq} \quad \text{for} \quad s = s^{\neq} \quad (4)$$

where q_i^{\neq} and s^{\neq} denote the values of respective quantities at the saddle point. From practical point of view an inverse problem is more interesting: to find the saddle point following the RP upwards along the valley, starting from the reactant (or product) region. Unfortunately, a straightforward application of relations (2)-(4) appears to be inefficient for that purpose because the respective computational procedure is unstable and diverges (3). So there is a need of a correctional criterion allowing to distinguish the bottom of a valley among the adjacent points. It should be a local (differential) one, as opposed to the global (integral) criterion as given by (2)-(4), which allows discerning the RP points (in the upwards sequence) only after the entire curve being calculated (in the downwards sequence).

The empirical intuitive methods realizing the RP calculation are thoroughly discussed in the recent review (4). They represent different iterative procedures inevitably invoking the conventional criterion (2)-(4) at some stage.

THE MOUNTAINEER'S ALGORITHM

An alternative approach is to formulate a local criterion for constructing the smooth curve linking a reactant (or product) region with a saddle point. It exactly imitates the strategy of a person climbing a saddle point along a valley. We call it "the mountaineer's algorithm" (5). It generates a curve which is generally distinct from the RP curve. So we accept a special term "the optimum ascent path" (OAP) for it.

The local criterion reads as follows: If a point is located on an OAP then the gradient norm has a minimum at it as compared with the adjacent points on the same constant energy surface. That is, in order to find a point on an OAP one has to investigate the adjacent sector of the constant energy surface searching for a locus where the ascent steepness passes through a minimum.

It is expedient to check whether this minimum condition can be fulfilled for the points belonging to a RP. In the simplest two-dimensional case we obtain the relation

$$\partial N / \partial v = -2KN = 0 \quad (5)$$

where K is the curvature of a RP curve and v is the transversal vibrational coordinate orthogonal to the RP. It follows that the RP and OAP curves coincide in the two special cases: either if both of them are straight lines ($K=0$) or at stationary points ($N=0$). If $\partial N / \partial v \neq 0$ at the points of a RP then RP and OAP are quite different curves.

The criterion so formulated is mathematically equivalent (5) to another criterion reported earlier by Pantič (6). The latter one defines a curve at any point of which the gradient direction is simultaneously the direction

of one of eigenvectors of the second derivative matrix of U .

The mountaineer's algorithm proved to be an efficient tool for a practical search of saddle points (5). Its merits become more visible with the increase of number of internal variables.

It should be noted that the curve passing along the top of an energetical ridge can be detected using the same mountaineer's algorithm.

THE SINGULAR POINTS

An important peculiarity of OAP curves is the existence of singular points on them where they emerge, dissipate or bifurcate. They are also the points of emergence, dissipation or bifurcation of valleys and ridges of a multi-dimensional PES. For instance, the dissipation of a valley takes place on the PES of disrotatory decyclization



forbidden by the orbital symmetry rules. As originally demonstrated by Dewar and Kirshner (7), the valley originating from the saddle point which corresponded to the transition state of this reaction was quite poorly displayed and was not revealed at the bottom of the main reactant valley. The above reasoning allows us to claim that it has dissipated prior to reaching the main valley. It is likely that such structure of a PES is generally characteristic of symmetry forbidden reactions.

The situation of valley branching has been studied (5) for the symmetry allowed conrotatory reaction (6). This system has a pair of chemically equivalent saddle points corresponding to rotations in opposite directions of the two terminal methylene groups, as shown in Fig.1.

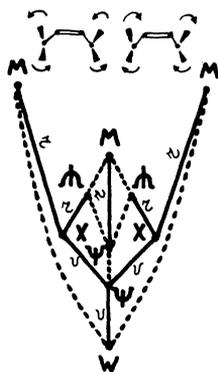


Fig. 1

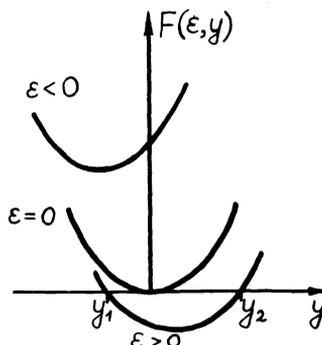


Fig. 2

Fig. 1. The scheme of the PES of conrotatory electrocyclic reaction (6). The outlook from the side of reactants, the valleys and ridges leading to the product region are not seen. The points of a PES are denoted by capital letters: W, M and X are minimum, maximum and saddle points respectively; Ψ and ψ are triple branching points. The full lines with indices v and r represent valley and ridges respectively. The broken lines represent rocks (see below).

Fig.2. The emergence of double points. Different parabolas represent function $F(\epsilon, y)$ for different ϵ values. The roots of equation (7) are y_1 and y_2 .

The two valleys are directed towards two saddle points (X points). At the place of branching (combination of two Ψ points in Fig.1) the three OAP curves, namely, a pair of valleys and the ridge between them, arise from a single curve, the valley coming from the reactant minimum.

There are no such singularities on RP curves. The gradient lines can evidently pass through flat regions of a PES ramp displaying neither valleys nor ridges.

The presence of singular points encumbers utilization of OAPs as a means of searching transition states. More specifically, there is a necessity of careful extra calculations in the vicinity of points of valley branching whereas the mountaineer's algorithm fails at all to be valid at dissipation

points. It is evident, from the other hand, that there are just OAP curves that are closely related to intrinsic properties of a PES, so that their special study would supply us with a valuable information on the PES structure.

THE ANALYSIS OF SINGULAR POINTS (8)

The above mentioned singularities can be classified either as branching points of a certain order ($\nu = 2, 3, \dots$) of the equation determining an OAP curve or as combinations of such elementary branching points. Consider, for instance, the simplest two-dimensional situation with geometrical variables x, y . The equation of a constant energy contour, $U(x, y) = \epsilon$, allows one to express x in terms of y and ϵ leading to a resultant OAP equation in the form $F(\epsilon, y) = 0$. We can set $x = y = \epsilon = 0$ at the branching point investigated. Then in the vicinity of a second order point ($\nu = 2$) function $F(\epsilon, y)$ can be substituted by its Taylor expansion, the parabola

$$F(\epsilon, y) = a_1 \epsilon + (b_0 + b_1 \epsilon) y + c_0 y^2 = 0 \quad (7)$$

If $b_0 = 0$ then parabola $F(\epsilon, y)$ is tangent to the absciss axis at the coordinate origin (Fig. 2) when $\epsilon = 0$. Equation (7) determines the OAP curve $y = y(\epsilon)$, $x = x(\epsilon)$ and it is seen that a pair of solutions, corresponding to a pair of real roots of (7), emerge or dissipate at $\epsilon = 0$. The similar treatment of triple points ($\nu = 3$) needs the consideration of a cubic parabola.

The coefficients of the expansion in (7) can be expressed in terms of partial derivatives U_x, U_y, U_{xx}, U_{xy} etc ($U_x \equiv \partial U / \partial x$ etc) calculated at the branching point. So the basic branching condition $b_0 = 0$ reduces to

$$\frac{U_{xyy} - U_{yy} U_{xx}}{U_{yy} - U_{xx}} + \frac{U_{yy}}{U_x} = 0; \quad (U_y = U_{xy} = 0) \quad (8)$$

This equation defines a dissipation double point on a PES as well as equation (1) defines a stationary point.

In a multi-dimensional situation with coordinates x, y_j ($j = 1, 2, \dots, n$) a set of equations $F_i(\epsilon, y_1, \dots, y_n) = 0$ ($i = 1, 2, \dots, n$) should be dealt with. The generalization of the basic branching condition is

$$\det B = 0; \quad B_{ij} = \partial F_i / \partial y_j \quad (9)$$

where matrix B is constructed of partial derivatives $\partial F_i / \partial y_j$ at the branching point. It can be shown that in the vicinity of a branching point the multi-dimensional situation actually reduces to a two-dimensional one. One of the pair of the finally selected coordinates, denoted as x , should be measured along the gradient direction. The other one, denoted as y , is associated with the direction of the eigenvector of matrix corresponding to its zero eigenvalue.

An important comment is in order. One of the two solutions emerging or dissipating at second order branching points always correspond to a maximum of the square of the gradient norm N rather than to a minimum. Since the ascent steepness exhibits a maximum rather than a minimum along such curves, so we accept the term "rocks" in order to distinguish them from OAPs. The second solution is evidently an OAP (see Fig. 3 for an illustration).

The different double and triple points can be further detailed: the double V and Λ points, the triple Ψ and \mathcal{H} points as explained in Figs. 3 and 4. Different topographical situations are described as combinations of elementary singular points. So, the emergence of a pair valley + ridge is displayed as a combination of V and Ψ points whereas the valley branching emerges from a combination of two Ψ points of different character. This symbolism is used in Fig. 1 for schematically drawing the PES of reaction (6).

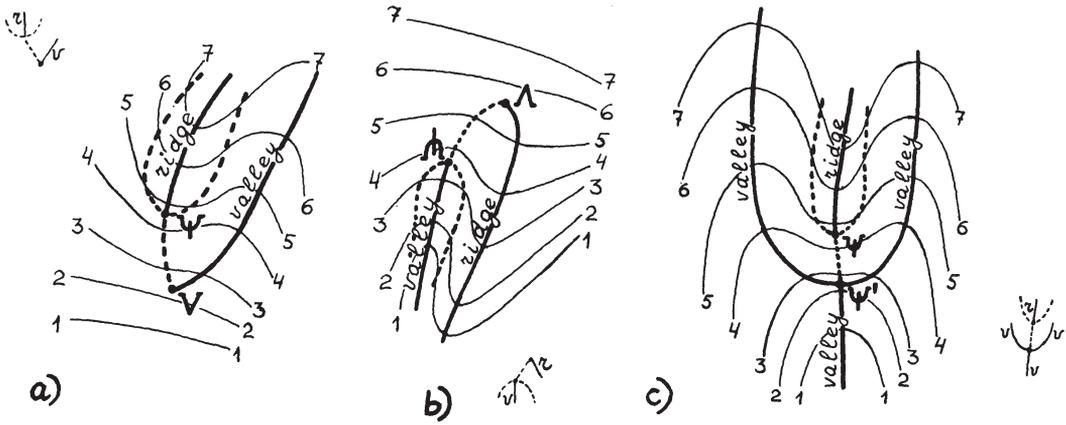


Fig.3. The illustration how branching points emerge. The full and broken lines represent OAPs and rocks (see the text). Thin lines represent constant energy contours, the numbers are energy values in conditional units. a,b) The situations of valley emergence and dissipation. c) The situation of valley branching. Ψ , Ψ' and Ψ'' are different types of triple points; ∇ and Λ are the double points.



← The main valley

Fig. 4. The side ramp of the Mt. Suffetku (the Darvaz mountain range, Pamirs). The three characteristic situations of Fig. 3 can be seen. The lower part of this Fig. represents the same situation of the valley dissipation as that observed for disrotatory reaction (6).

HOW DISSIPATION POINTS CAN BE OBSERVABLE

The polymer chains that are formed in the course of solid-phase polymerization are expected to move inside the parent monomeric molecular crystal during their growth (9). The respective motion can be imitated (10) by a system of point masses connected by massless strings moving in a sinusoidal external field (Fig. 5). The motion is performed by an external force operating the point $Z=0$, the head of the chain. The respective coordinate x_0 represents the overall translational motion of the chain.

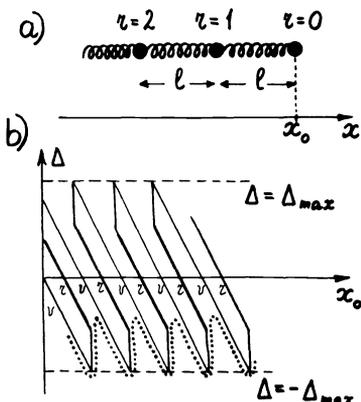


Fig. 5. a) The model of polymer chain. The chain period is $l = l_0 - \Delta$ where l_0 represents the period when the external crystalline field is absent (the free chain). x is the translational coordinate.

b) The dependence of the regular chain deformation Δ on the translational coordinate x_0 . The scales for Δ and x_0 are quite different. The sloped lines are the projections of energetical valleys (index z) and ridges (index v) respectively. The dots show how the chain moves.

If the chain period is not an integer (or even not approximately integer) of the period of the crystalline potential then, under certain circumstances, the translation is accompanied by stretching of the chain so that the period changes by the negative value of Δ depending on x_0 . The dependence shown in the lower part of Fig. 5 represents a piecewisely linear multi-valued function bounded by the upper and lower values $\Delta = \pm \Delta_{max}$ ($\Delta_{max} > 0$).

We can now consider the adiabatic potential energy of the chain (the sum of the deformation energy and the potentials of its fragments in the sinusoidal external field) as a function of two parameters: $U = U(\Delta, x_0)$. Then the sloped lines in Fig. 5b correspond to the valleys and ridges of such a PES. In the vicinity of critical values $\Delta = \pm \Delta_{max}$ the neighbouring valley and ridge dissipate so that for $|\Delta| > \Delta_{max}$ the equilibrium adiabatic solutions $\Delta(x_0)$ do not exist at all. While moving adiabatically along a valley the chain is stretched and its energy increases. That proceeds continuously until the dissipation point is reached. After its passing the system finds itself on a side slope of a PES and spontaneously slides down to the nearest valley. On reaching the next dissipation point this situation is repeated and so on. The overall motion becomes periodically discontinuous. This is a nontrivial mechanism of eliminating the overstrain of the chain during its motion.

So we have described still a single example demonstrating a physical importance of singular points of a PES. It seems plausible, however, that a similar behaviour may be intrinsic for large complicated systems, the biological ones for instance. Such a reasoning agrees with the ideology of the catastrophe theory (11).

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