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The structural stability principle and branching points on multidimensional potential energy surfaces

M. V. Basilevsky

Karpov Institute of Physical Chemistry, 107120 Moscow B-120, USSR

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The chemically interesting potential energy surfaces (PES) are considered on which the conditions underlying application of structural stability principle and Morse inequalities are violated. The possibility of treatment of singular branching points on a PES slope in terms of intrinsic reaction curves (IRC) is discussed.

Key words: Potential energy surfaces — Branching points

Recently, the problems of structure of multidimensional potential energy surfaces (PES),

$$U = U(q^i); \qquad i = 0, 1, \ldots, N-1 \tag{1}$$

(q^i are cartesian coordinates[1]) are discussed using terminology and concepts of differential geometry and topology. In particular, the structural stability principle was used [6-8] to formulate the rule stating that, in the case $N = 2$, the gradient curve linking a pair of saddle points (having the signature of Hessian matrix $\sigma = 0$) should necessarily pass through a stationary point, either a maximum ($\sigma = -2$) or a minimum ($\sigma = 2$). The idea of utilizing the Morse inequalities,

[1] The whole number of variables is $N+6$. We consider only internal coordinates for brevity. They can be approximately selected to be cartesian ones which means that the metric is assumed to be euclidean in the vicinity of the curves under investigation [1], either intrinsic reaction curves [2] or optimum ascent path [3, 4] ones. This is the condition allowing to construct the reaction path hamiltonian [1, 5] along these curves. Thereby interactions between q^i and overall rotations are neglected

restricting available combinations of critical points with different signatures was also announced [6, 9–11].

There exists a set of necessary conditions [12, 13] which restrict the manifold of functions displaying the aforementioned topological properties. Any of them being violated in a real chemical system discards the application of purely topological reasoning. In the present note only one, probably the most remarkable of these limitations, is considered. It implies nonsingularity of Hessian matrix at all the critical points:

$$\det \left\| \frac{\partial^2 U}{\partial q^i\, \partial q^j} \right\| \neq 0; \qquad \frac{\partial U}{\partial q^i} = 0. \tag{2}$$

We demonstrate a PES illustrating that condition (2) can be violated in the cases of chemical interest. The respective topographical scheme is shown in Fig. 1a. The valley descending from saddle point X_1 bifurcates at point O. A pair of arising at this point new valleys further descend to minima W_1 and W_2. The latter two are connected via saddle point X_2.

The branch point O is an umbilic point [14] where

$$\det \left\| \frac{\partial^2 U}{\partial q^i\, \partial q^j} \right\| = 0; \qquad \frac{\partial U}{\partial q^i} = 0. \tag{3}$$

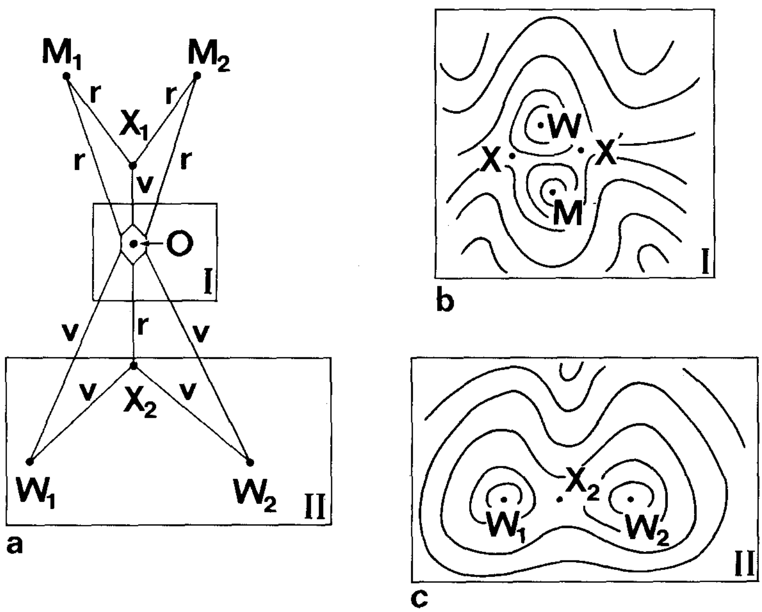

Fig. 1. a The scheme of a PES with an umbilic point (shown as a hexagon). Symbols M, X and W denote maxima, saddles and minima, respectively; v and r denote valleys and ridges. **b** Splitting of an umbilic point by a small perturbation. Shown are level lines of region I indicated in **a**. **c** Level lines of region II indicated in **a**

So the energy profile along the pathway X_1OX_2 decreases steadily and has a zero slope at inflection point O. Thus the above mentioned prohibition rule [6–8], forbidding the topographical situations with "adjacent" saddle points, definitely fails to be valid in this case.

Such a topographical situation as represented by Fig. 1a takes place in Diels-Alder reaction [15]. It was also registered in calculations of several intramolecular rearrangements [16].

It is worth to comment that the exactly degenerate case (3) can be met only in highly symmetrical systems. Symmetry perturbations will split the umbilic point into four regular critical points, namely, minimum W, maximum M, pair of saddles X and X', as shown in Fig. 1b. By that the conditions allowing application of structural stability principle and Morse inequalities formally regenerate. However, the so arising new critical points are vague, chemically uninteresting and their appearance cannot be anticipated. Such an obscurely displayed topographic situation in practive behaves as an umbilic.

Our other comment concerns the methodics of drawing one-dimensional topographical PES schemes. Originally, the curves of optimum ascent path (OAP) were used for this purpose [15]. The PES schemes were alternatively formulated in terms of gradient lines, namely, intrinsic reaction curves (IRC) and separatrices [6–8, 17]. Both approaches coincide in the vicinity of critical points ($\partial U/\partial q^i = 0$) where the IRC and OAP curves coincide. However, basing on OAPs, one can extend the schematical one-dimensional description of critical point regions onto the branching (or bifurcation) points of PES valleys and ridges which, being not critical ($\partial U/\partial q^i \neq 0$), still constitute important elements of PES structure. The question arises whether it is possible to repeat similar extention with IRCs.

This problem has been considered recently [18] for a special case of triple branching points with C_s symmetry. We present below a qualitative discussion of a general case. From the differential equation defining IRC as a gradient line it follows that its noncritical singularity should be located at a point where

$$\det\left\|\frac{\partial^2 U}{\partial q^i\,\partial q^j}\right\| = 0; \qquad \frac{\partial U}{\partial q^i} \neq 0, \qquad i, j = 0, 1, \ldots, N-1. \tag{4}$$

On the other hand, an elementary topographical reasoning indicates that a zero frequency mode in the reaction path Hamiltonian [1, 5] must appear at points where IRC bifurcate. Therefore

$$\det\left\|\frac{\partial^2 U}{\partial q^\alpha\,\partial q^\beta}\right\| = 0, \qquad \alpha, \beta = 1, \ldots, N-1. \tag{5}$$

Here coordinates q^α, q^β are orthogonal to IRC whereas the q^0 direction is tangent to IRC. Let us choose q^α in such a manner to diagonalize matrix (5) and assume that q^{α_1} corresponds to its zero eigenvalue. We suppose also that matrix (4) has a single zero eigenvalue. Then from the requirement of consistency of (4) and

(5) we conclude

$$\frac{\partial^2 U}{\partial q^0 \partial q^{\alpha_1}} = 0. \tag{6}$$

We restrict the following consideration by the case $N = 2$. Let a cartesian coordinate frame be centered at our branching point with x and y axes tangent to the gradient and constant level curves, respectively. Introducing the notation $\partial U/\partial x = U_x$, $\partial U/\partial y = U_y$, $\partial^2 U/\partial x\, \partial y = U_{xy}$ etc. we can present the IRC branching conditions (5), (6) at several point T in the form

$$U_{yy} = 0; \qquad U_{xy} = 0 \quad (\text{at point } T). \tag{7}$$

In terms of OAPs the situation of triple valley branching is described by a combination of triple points ψ' and ψ [15]. At a ψ' point a valley OAP converts into a pair of valley OAPs and a "rock curve" between them, on which the gradient norm goes through a maximum when following along a constant energy level. At a ψ point this rock curve bifurcates into a pair of rocks and a ridge OAP between them. The condition that an OAP curve bifurcates at point ψ or ψ' is

$$U_{yy}(U_{yy} - U_{xx}) + U_x U_{xyy} = 0; \qquad U_{xy} = 0 \ (\text{at points } \psi, \psi'). \tag{8}$$

Here the first relation is the main condition of OAP branching [15] while the second one [3] states that points ψ, ψ' lie on a gradient extremal, either an OAP, or a rock curve.

Because generally $U_{xyy} \neq 0$, the points T and ψ or ψ' do not coincide. Since $U_{yy} > 0$ at ψ' and $U_{yy} < 0$ at ψ so we conclude that the triple IRC point T with $U_{yy} = 0$ is located between them as shown in Fig. 2. However, as the second relations of (7) and (8) are the same, we conclude that T lies on the IRC and on a gradient extremal simultaneously. It follows then [4] that the curvature of both curves vanish at T and they both have the x axis as a common tangent direction. On the other hand, if we consider ψ and ψ', then again both IRC and a gradient extremal pass through them and have a common tangent direction, as a consequence of a condition [15] that $U_{xxy} = 0$ at a triple point. In a special

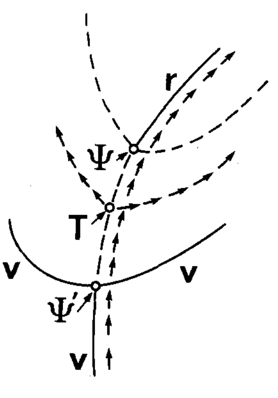

Fig. 2. The scheme of valley branching at triple points ψ', T, ψ. *Solid* and *broken lines* represent OAPs and rocks respectively. *Arrow lines* represent IRCs

case of C_s symmetry [18] the curvature of the central line in Fig. 2 exactly vanishes by the symmetry argument. So this line can be equally well considered either as an IRC or as a gradient extremal. In a general case it is still so at three branching points ψ, ψ', T. Therefore between these points the curvature is expected to be small and local C_s symmetry is approximately obeyed.

The analysis proves to be different if we consider more usual double branching points, where PES valleys or ridges arise or dissipate. The IRCs, contrary to OAPs, cannot arise or dissipate on a PES slope ($\partial U/\partial q^i \neq 0$). So they seem to be inefficient as a tool of treatment of double points. The disadvantage of IRCs in studying bifurcations is due to the fact that their local properties are not well defined.

Finally, the conditions (7) and (8) do not necessarily mean that an IRC or an OAP bifurcate. They are, for instance, true for a continuum of gradient curves covering a plane slope of a PES. In this highly degenerate case indeed $U_{xyy}=0$ so that conditions (7) and (8) become the same. Hence this family of IRC curves may be equally well considered as a family of OAP curves, so a concept of a single isolated IRC or OAP curve makes no sense.

The similar comparison of branching conditions for IRC and gradient extremal curves for $N>2$, being more complicated, is not considered here.

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