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Catchment Region Partitioning of Energy Hypersurfaces, I

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The space of internal coordinates of a molecular system is partitioned into catchment regions of various critical points of the energy hypersurface. The partitioning is based on an ordering of steepest descent paths into equivalence classes. The properties of these catchment regions and their boundaries are analyzed and the concepts of chemical structure, reaction path and reaction mechanism are discussed within the framework of the Born–Oppenheimer and energy hypersurface approximations. Relations between catchment regions and the chemically important reactive domains of energy hypersurfaces, as well as models for "branching" of reaction mechanisms, caused by instability domains D_μ, $\mu \geq 1$, are investigated.

Key words: Catchment regions – Potential energy surfaces – Reaction paths – Chemical structure.

1. Introduction

Quantum chemical calculations of conformational changes and chemical reactions of polyatomic molecules are of considerable importance, since such calculations may provide information that is unavailable at present by experimental means. The detailed calculation of even small portions of potential energy hypersurfaces of many dimensions, however, is a very complicated, if not formidable task, and it is important to explore the possibilities of simplifying the associated mathematical and computational problems. If one is able to locate the chemically important regions of a multidimensional energy hypersurface, then the analysis may be restricted to these regions and the computational effort may be reduced considerably. Alternatively, if it is possible to identify those regions of the hypersurface from which conversion into a given product is likely, the details of

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the interior of such regions, far away from the energy minimum, become of secondary importance.

In an earlier study a scheme has been proposed for the identification and classification of the chemically most important "reactive domains" of potential energy hypersurfaces [1]. The proposed scheme is based on the partitioning of the space of the internal coordinates of the molecule into various domains that are distinguished according to the curvature properties of the hypersurface. These curvature properties are well defined in regions of the hypersurface where no surface crossing occurs and neighbourhoods of singularities or chemically unrealistic points are explicitly excluded. The energy hypersurface is assumed to be twice continuously differentiable at every "chemically realistic" point and the partitioning scheme is directly applicable only to single-surface chemical processes. Since the analysis is applicable only to the energy hypersurface model, relations between properties of the model are investigated, and terms like "equilibrium geometry" or "transition state geometry" are interpreted as points of the model, rather than real chemical structures. The partitioning leads to a hierarchy of domains $\{D_\mu^{(i)}\}$, $\mu = 0, 1, \ldots, 3N-7$, with D_0 domains being the chemically most important, since all energy minima and transition states fall into such D_0 domains. In spite of the fact that the classification of these domains utilizes only the *local* curvature properties of energy hypersurfaces, some general characteristics of reaction paths, i.e. intrinsically *non-local* features on the hypersurface, may be related to the index μ of domain D_μ, if the path or a part of it lies within D_μ.

The *local* properties of energy hypersurfaces and reaction paths at a point may characterize a given nuclear configuration in the absolute sense. The gradient and curvature properties of the hypersurface at the given point may be used to describe the direction of the most likely change of this configuration. For infinitely slow nuclear motion, this direction is that of the ideal "vibrationless" steepest descent path. In order to characterize a nuclear configuration in a relative sense, with respect to an *equilibrium* geometrical arrangement of the nuclei, some non-local features of the energy hypersurface must also be considered. One may ask the question, how similar is the actual configuration to an equilibrium arrangement, or, more importantly, how likely is the eventual conversion of the actual configuration into a given equilibrium one? To answer this question generally one needs some information on the global features of the energy hypersurface. Qualitatively speaking, all those nuclear configurations which are most likely to become converted into a given equilibrium configuration are expected to show some similarities. The points on the energy hypersurface corresponding to these configurations are likely to fall into a neighbourhood of the local minimum point $\boldsymbol{m}$ describing the equilibrium configuration. The collection of all these points may be visualized as a "catchment region" for the given minimum point $\boldsymbol{m}$. Most experimental information on the stereochemistry of molecules and reacting systems refer to equilibrium or near-equilibrium nuclear arrangements, and it is of some interest to study, what are these catchment regions of energy hypersurfaces, surrounding various local minima. D_μ domains of *small* μ index contain the most likely reaction paths describing chemical processes confined to a *single* energy hypersurface of a given electronic state. By contrast, chemical processes involving transitions between various hypersurfaces, such as photochemical reactions, are more likely to pass through points in D_μ domains with *large* index μ, even if the process eventually leads to a minimum in a D_0 domain. For the prediction of the ultimate outcome of such processes it appears essential to determine the location and boundaries of catchment regions belonging to various minima.

The concept of catchment regions about points of minimum energy nuclear configurations is related to the internal motions of the molecular system, and it is convenient to describe these regions in a $3N-6$ dimensional frame of internal coordinates. Whereas most of our examples will be given in an orthogonal coordinate system, specified below, for the derivation of general relations a Riemannian tensor formalism will be used; thus the results will not be affected by the choice of the internal coordinates.

The most commonly used model for the analysis of conformational changes and chemical reactions of polyatomic molecules ($N \gg 2$) is based on the Born–Oppenheimer approximation [2]. In this approximation the total energy of the molecular system of a given electronic state may be written as a function of the nuclear positions. By excluding translational motion of the molecule as a whole a cartesian coordinate system may be defined with origin fixed to the molecule; for vibrational analysis the origin is usually defined at the centre of mass. Furthermore, if only internal motions and no rotations of the molecule as a whole are considered, then it is always possible to attach the cartesian axes to the molecule. This leads to the reduction of $3N$ cartesian coordinates to $n = 3N-6$ coordinates. For the analysis of large amplitude vibrational motions with respect to a given nuclear configuration the mass-weighted cartesian displacement coordinates are transformed to normal coordinates with the Eckart conditions [3] being used to specify the molecular axis system. Although extensive domains of potential energy surfaces, including all essential features of a complete reaction path (reactant and product minima and transition state) may be treated by using the large amplitude formalism [4], this technique is not ideally suited for studying more general nuclear rearrangements. In routine MO calculations the conformational motion or reaction is usually approximated by assigning essentially rigid molecular models to each point of the reaction path. In computational practice the transformations between internal and cartesian coordinates are usually defined with respect to such rigid models, e.g. by using the Z matrix technique [5]. Although for some choices of internal coordinates the kinetic energy expressions become much too complicated to be of practical use in dynamical studies, it is possible to define a metric for a non-redundant set of bond-length, bond angle internal coordinates[1]. It is often convenient to describe the energy hypersurface as a Riemannian relief map $E(\boldsymbol{r})$ over the n-dimensional

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[1] We exclude here the possibility of identical positions for two nuclei that would correspond to a nuclear reaction. We shall not consider points that belong to the closure $\bar{D}_{\mathrm{excl}}$ of a set D_{excl}, containing neighbourhoods of such "chemically unrealistic" nuclear configurations [1].

Riemannian space R of a set of generalized internal coordinates[2]. Contravariant components r^i of position vector $\boldsymbol{r} \in R$ may be augmented by component $r^{n+1} = E(\boldsymbol{r})$; the resulting $n+1$ dimensional vector ${}^{n+1}\boldsymbol{r}$ is an element of a space ${}^{n+1}\boldsymbol{R}$, embedding the energy hypersurface. At each chemically realistic point $\boldsymbol{r} \in R$, $\boldsymbol{r} \notin D_{\text{excl}}$ an $n-1$ dimensional subspace, ${}^{n-1}\boldsymbol{R}(\boldsymbol{r})$ may be defined, over which the relief map $E(\boldsymbol{r})$ is locally horizontal [1]. The curvature properties of $E(\boldsymbol{r})$ over this ${}^{n-1}\boldsymbol{R}(\boldsymbol{r})$ subspace characterize a hierarchy of reactive domains $\{D_\mu\}$ of the hypersurface, where index μ is related to the Hessian matrix ${}^{n-1}\boldsymbol{H}(\boldsymbol{r})$, defined over ${}^{n-1}\boldsymbol{R}(\boldsymbol{r})$. For critical points $\boldsymbol{r}_C$ and ${}^{n-1}\boldsymbol{r}$ of R and ${}^{n-1}\boldsymbol{R}(\boldsymbol{r})$, respectively, indices $\lambda(\boldsymbol{r}_C)$ and $\mu({}^{n-1}\boldsymbol{r})$, are the number of negative eigenvalues of Hessian matrices $\boldsymbol{H}(\boldsymbol{r}_C)$ and ${}^{n-1}\boldsymbol{H}({}^{n-1}\boldsymbol{r})$, respectively. Since to each ordinary point $\boldsymbol{r} \in R$ a unique ${}^{n-1}\boldsymbol{R}(\boldsymbol{r})$ space may be assigned, at each such point $\boldsymbol{r}$ the $\boldsymbol{r} \to {}^{n-1}\boldsymbol{r}$ assignment is also unique. Consequently, ${}^{n-1}\boldsymbol{H}$ and μ may be referred to as ${}^{n-1}\boldsymbol{H}(\boldsymbol{r})$ and $\mu(\boldsymbol{r})$, respectively [1, 6]. Index μ is zero at all minima and first order saddle points of $E(\boldsymbol{r})$, consequently D_0 domains are particularly important, since they contain all points $\boldsymbol{r}$ that correspond to equilibrium nuclear configurations and to transition states [1]. Furthermore, minimum energy reaction paths are stable only within such D_0 domains.

2. Local and Global Properties

In the present study we shall consider a straightforward generalization of the conventional geographical concept of catchment regions of three dimensional relief maps to higher dimensional energy hypersurfaces[3]. These regions may be associated with basins of attractors of a vector field, using the terminology of Thom's catastrophe theory [7]. Minima of the hypersurface take the role of the attractors. A rigorous definition of catchment regions, based on the properties of steepest descent relief paths ${}^{n+1}P$ in ${}^{n+1}R$ [1] and their projections ${}^{n}P$ into ${}^{n}R$ (orthogonal trajectories [8–10]), will be given in terms of equivalence classes, defined for the ${}^{n}P$ paths. Since these regions are related to the global features of the hypersurfaces, it is important to determine, how the more readily calculable local properties may be utilized in their analysis. Relations between D_μ domains and various catchment regions are expected to simplify the analysis of multidimensional reaction paths of polyatomic molecules.

Points where the $E(\boldsymbol{r})$ function is non-differentiable (such points may occur at intersections of energy hypersurfaces [11]) require special treatment. In the strict sense, for ideal single-surface chemical processes the problem of surface intersections is irrelevant [1]. However, when considering multiple-surface problems of polyatomic molecules with intersecting surfaces the definition of domain D_{excl}

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[2] We shall use the same notations as in Ref. [1]. Left superscript specifies the dimension of the space and it is omitted if the dimension is n. Distances and angles are defined in terms of the Riemannian metric ${}^{m}g_{ij}$ of the actual space ${}^{m}R$.

[3] One may note the formal analogy between watersheds around lake basins and the proposed concept of catchment regions of potential energy hypersurfaces.

[1] must include neighbourhoods of such intersection points:

$$D_{\text{excl}} = \bigcup_{\gamma} G(\boldsymbol{r}_{\gamma}, \rho). \tag{1}$$

Here $\boldsymbol{r}_{\gamma}$ is either a point where the coordinates of two or more of the nuclei become identical or any point where $E(\boldsymbol{r})$ is not twice continuously differentiable. The ρ radius of the $G(\boldsymbol{r}_{\gamma}, \rho)$ open balls is a suitably chosen small positive value.

We shall assume that the collection of all non-degenerate $\boldsymbol{m}^{(i)} \notin \bar{D}_{\text{excl}}$ minimum points of the energy hypersurface form a countable set, $M' = \{\boldsymbol{m}^{(i)}\}$ and that this set is ordered, by the relation

$$E(\boldsymbol{m}^{(i)}) \leq E(\boldsymbol{m}^{(i+1)}). \tag{2}$$

An ordering is possible even for such periodic hypersurfaces, where a finite set of symmetrically non-equivalent minima is repeated infinitely, since for such periodic surfaces one may always choose, without loss of chemical information, a representative subdomain within which no periodicity occurs.

To any non-critical point $\boldsymbol{r} \in R$, $(\boldsymbol{r} \notin \bar{D}_{\text{excl}})$ i.e. where the gradient $\boldsymbol{g}(\boldsymbol{r})$ is non-zero, $\boldsymbol{g}(\boldsymbol{r}) \neq \boldsymbol{0}$, one may assign a steepest descent path P_r. This path P_r starts at point $\boldsymbol{r}$, $\boldsymbol{r} \in P_r$ and it follows the direction of the negative gradient, $-\boldsymbol{g}(\boldsymbol{r})$. That is, at any non-critical point of the path, $\boldsymbol{r}_A \in P_r$

$$\lim_{\boldsymbol{r}_B \to \boldsymbol{r}_A} \frac{\boldsymbol{r}_B - \boldsymbol{r}_A}{|\boldsymbol{r}_B - \boldsymbol{r}_A|} = -\boldsymbol{a}(\boldsymbol{r}_A) = -\frac{\boldsymbol{g}(\boldsymbol{r}_A)}{|\boldsymbol{g}(\boldsymbol{r}_A)|} \tag{3}$$

where

$$\boldsymbol{r}_B \in P_r \tag{3a}$$

and

$$E(\boldsymbol{r}_B) < E(\boldsymbol{r}_A). \tag{3b}$$

Here vector $\boldsymbol{a}$, i.e. the normalized gradient vector is also referred to as the *path vector* [1]. Since for any finite molecular system the energy hypersurface is bounded from below, every steepest descent path P_r must terminate at a point $\boldsymbol{r}_E$. Points $\boldsymbol{r}$ and $\boldsymbol{r}_E$ are called the *origin* and *extremity*, respectively, of path P_r. If P_r does not enter the closure $\bar{D}_{\text{excl}}$ of excluded domain D_{excl}

$$P_r \cap \bar{D}_{\text{excl}} = \emptyset \tag{4a}$$

then the extremity must be a critical point, $\boldsymbol{r}_C$,

$$\boldsymbol{r}_E = \boldsymbol{r}_C \tag{4b}$$

e.g. a minimum, $\boldsymbol{r}_C = \boldsymbol{m}$ or a saddle point $\boldsymbol{r}_C = \boldsymbol{s}$ of some index λ, $\lambda \geq 1$ [1]. We shall always assume that this $\boldsymbol{r}_C$ critical point also belongs to P_r

$$\boldsymbol{r}_C \in P_r. \tag{4c}$$

The concept of path vector $\boldsymbol{a}$ may be extended to critical points by assuming continuous dependence of $\boldsymbol{a}(\boldsymbol{r}')$ on $\boldsymbol{r}' \in P_r$ along the path P_r [1].

Steepest descent paths $P'_r, P'_r \cap \bar{D}_{\text{excl}} \neq \varnothing$, with their extremities in $\bar{D}_{\text{excl}}$, $\boldsymbol{r}_E \in \bar{D}_{\text{excl}}$, will deserve special attention. Also, if a steepest descent path P'_r enters $\bar{D}_{\text{excl}}$ but after entering also leaves $\bar{D}_{\text{excl}}$, i.e. it does not reach its extremity $\boldsymbol{r}_E$ in $\bar{D}_{\text{excl}}$, we still shall regard it terminated at the boundary point of $\bar{D}_{\text{excl}}$. That portion of the original P'_r that remains after leaving $\bar{D}_{\text{excl}}$ will be regarded a different path with its extremity in the complementer of $\bar{D}_{\text{excl}}$.

Several steepest descent paths may have the same extremity $\boldsymbol{r}_C$. A trivial example is the case where $\boldsymbol{r}' \in P_r$, clearly then $P_{r'} \subset P_r$ i.e. the two paths are identical between $\boldsymbol{r}'$ and the extremity. More important are those cases where $P_{r'} \cap P_r = \boldsymbol{r}_C$ i.e. only the extremity is common. In general, if $\lambda(\boldsymbol{r}_C) \leq n-2$, e.g. if $\boldsymbol{r}_C$ is a minimum along at least two coordinates, then there are infinitely many different paths with $\boldsymbol{r}_C$ as their only common point. An example for such a critical point is the optimum planar structure of NH_3, here $\lambda(\boldsymbol{r}_C) = 1$ and $n = 6$. There are infinitely many steepest descent paths with the common extremity $\boldsymbol{r}_C$, all of these paths representing in-plane rearrangements of the NH_3 molecule. If for two such paths, P_r and $P_{r'}$, the path vectors at the common extremity $\boldsymbol{r}_C$ are the negatives of each other, $\boldsymbol{a}(\boldsymbol{r}_C) = -\boldsymbol{a}'(\boldsymbol{r}_C)$, then $P_{r'}$ is called the *continuation* of P_r. Such continuations of steepest descent paths beyond their extremities are necessary for the description of vibrational problems, and $P_r \cup P_{r'}$ may be regarded a single path, passing through $\boldsymbol{r}_C$. If $\lambda(\boldsymbol{r}_C) \leq n-2$, then infinitely many such paths may pass through $\boldsymbol{r}_C$.

Whereas a steepest descent path $P_r, P_r \cap \bar{D}_{\text{excl}} = \varnothing$, contains exactly one critical point, by contrast, a minimum energy path P always contains a saddle point $\boldsymbol{s}$ of index $\lambda(\boldsymbol{s}) = 1$, and from $\boldsymbol{s}$, P follows the steepest descent directions on both sides of $\boldsymbol{s}$ toward two minima. That is, a minimum energy path P contains exactly three critical points, two of which are minima and one is a saddle point:

$$\boldsymbol{m}^{(1)} \in P, \qquad \lambda(\boldsymbol{m}^{(1)}) = 0, \qquad \mu(\boldsymbol{m}^{(1)}) = 0 \tag{5a}$$

$$\boldsymbol{s} \in P, \qquad \lambda(\boldsymbol{s}) = 1, \qquad \mu(\boldsymbol{s}) = 0 \tag{5b}$$

$$\boldsymbol{m}^{(2)} \in P, \qquad \lambda(\boldsymbol{m}^{(2)}) = 0, \qquad \mu(\boldsymbol{m}^{(2)}) = 0. \tag{5c}$$

3. Catchment Regions

The set of all steepest descent paths $\{P_r\}$, $\boldsymbol{r} \notin \bar{D}_{\text{excl}}$, $\boldsymbol{g}(\boldsymbol{r}) \neq \boldsymbol{0}$, may be ordered into equivalence classes according to their extremities, $\{\boldsymbol{r}_E\}$:

$$P^{(\boldsymbol{r}_C)} = \{P_r \colon \boldsymbol{r}_C \in P_r\} \tag{6}$$

or, if P_r enters $\bar{D}_{\text{excl}}$, $P_r \cap \bar{D}_{\text{excl}} \neq \varnothing$, then all these paths are regarded as belonging to a single class:

$$P^{(\bar{D}_{\text{excl}})} = \{P_r \colon P_r \cap \bar{D}_{\text{excl}} \neq \varnothing\}. \tag{6a}$$

If the $\boldsymbol{r}_C$ critical point is a minimum, then equivalence class $P^{(\boldsymbol{r}_C)}$ reflects the chemical property that all steepest descent paths $P_r \in P^{(\boldsymbol{r}_C)}$ are equivalent in the sense that they all lead to the same product, represented by point $\boldsymbol{r}_C$, $\lambda(\boldsymbol{r}_C) = 0$.

Steepest descent paths may, however, lead to a saddle point, $\lambda(\boldsymbol{r}_C) > 0$, that may be a transition state if $\lambda(\boldsymbol{r}_C) = 1$. It is clear from the definition of steepest descent paths that equivalence classes for critical points $\boldsymbol{r}_C$ with index $\lambda(\boldsymbol{r}_C) = n$ are empty; however, equivalence classes $P^{(\boldsymbol{r}_C)}$, $\lambda(\boldsymbol{r}_C) < n$, are in general non-empty. That is, if $\boldsymbol{r}_C$ is a non-degenerate critical point, and $\boldsymbol{r}_C \notin \bar{D}_{\mathrm{excl}}$, then

$$P^{(\boldsymbol{r}_C)} = \varnothing \quad \text{iff } \lambda(\boldsymbol{r}_C) = n. \tag{6b}$$

Particularly important are those equivalence classes $P^{(\boldsymbol{r}_C)}$ for which $\lambda(\boldsymbol{r}_C) = 0$, $\boldsymbol{r}_C = \boldsymbol{m}$, a minimum, since they lead to a convenient definition of catchment regions. A definition[4] of *catchment region* $C^{(i)}$ for *minimum* point $\boldsymbol{m}^{(i)} \in M'$ of the energy hypersurface $E(\boldsymbol{r})$ may be given as the set of origin points $\{\boldsymbol{r}\}$ of all paths $P_{\boldsymbol{r}} \in P^{(\boldsymbol{m}^{(i)})}$, i.e. the collection of all those points $\boldsymbol{r}(\boldsymbol{r} \notin \bar{D}_{\mathrm{excl}})$ from which the steepest descent path $P_{\boldsymbol{r}}$ terminates at minimum $\boldsymbol{m}^{(i)}$:

$$C^{(i)} = \{\boldsymbol{m}^{(i)}, \boldsymbol{r} \colon \boldsymbol{m}^{(i)} \in P_{\boldsymbol{r}}\}. \tag{7}$$

Minimum $\boldsymbol{m}^{(i)}$ is assumed to belong to its own catchment region.

Since all steepest descent paths are ordered into equivalence classes, and all $\boldsymbol{m}^{(i)}$ minima are different, these catchment regions are disjoint,

$$C^{(i)} \cap C^{(i')} = \varnothing, \qquad \text{if } i \neq i'. \tag{8}$$

The definition of $C^{(i)}$ is consistent with the geographical concept of catchment regions, since one can assign a steepest descent path $P_{\boldsymbol{r}}$ to each non-critical point $\boldsymbol{r}$ ($\boldsymbol{r} \notin \bar{D}_{\mathrm{excl}}$). On the other hand, if no steepest descent path passes through point $\boldsymbol{r}$, then the gradient must vanish there, $\boldsymbol{g}(\boldsymbol{r}) = \boldsymbol{0}$, i.e. $\boldsymbol{r}$ is a critical point of the energy hypersurface. It is clear then, that critical points other than non-degenerate minima, $\boldsymbol{m} \in M'$, do not belong to any of these catchment regions $C^{(i)}$.

Definition (7), however, may be extended to degenerate minima as well. In this context, we shall distinguish between two types of degenerate critical points of index $\lambda = 0$. A critical point $\boldsymbol{r}_C$ with a positive semidefinite Hessian [1]

$$\lambda(\boldsymbol{r}_C) = 0, \tag{9}$$

$$\det|\boldsymbol{H}(\boldsymbol{r}_C)| = 0 \tag{10}$$

will be referred to as a *degenerate minimum*, if there exists an open ball $G(\boldsymbol{r}_C, \rho)$, such that

$$E(\boldsymbol{r}_C) \leq E(\boldsymbol{r}) \tag{11a}$$

if

$$\boldsymbol{r} \in G(\boldsymbol{r}_C, \rho) \tag{11b}$$

for a small enough ρ, $\rho > 0$.

If no such open ball $G(\boldsymbol{r}_C, \rho)$ can be found for any ρ, $\rho > 0$, then degenerate critical point $\boldsymbol{r}_C$ will be referred to as a *shoulder*. If degenerate minimum $\boldsymbol{r}_C$ is separated

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[4] For catchment region of $\boldsymbol{m}^{(i)}$ the $C^{(i)}$ notation will be used, unless we wish to emphasize that this is a catchment region of a minimum, when $C^{(\boldsymbol{m}^{(i)})}$ will be written instead.

from other such minima, then condition (11a) may be replaced by the stronger condition:

$$E(\boldsymbol{r}_C) < E(\boldsymbol{r}), \qquad \boldsymbol{r} \neq \boldsymbol{r}_C. \tag{12}$$

In this case the order of the first non-vanishing derivative along each coordinate must be an even number and all of these derivatives must be positive. Relation (12) is also valid for non-degenerate minima. Furthermore, separated degenerate minima and non-degenerate minima have the common property that there exists $\rho', \rho' > 0$ such, that the condition

$$P_{\boldsymbol{r}} \in P^{(\boldsymbol{r}_C)} \tag{13a}$$

if

$$\boldsymbol{r} \in G(\boldsymbol{r}_C, \rho') \tag{13b}$$

holds for steepest descent paths[5]. Truly degenerate minima, and in general, critical points with a positive semi-definite Hessian matrix $\boldsymbol{H}(\boldsymbol{r}_C)$ rarely occur on chemical energy hypersurfaces although *ab initio* calculations for molecules, containing second row elements frequently indicate extremely flat and possibly degenerate potential minima [12]. As long as these degenerate minimum points are separated, each may be added to set M', with a distinct index i, and definition (7) may then be applied for the $C^{(i)}$ catchment region of degenerate minimum $\boldsymbol{m}^{(i)}$ as well. However, if degenerate minima form a connected point set, such as a horizontal line segment or a horizontal domain at the bottom of a valley, no index i may be assigned to the individual minimum points. Nevertheless, to the entire connected point set a common index i may be assigned and one may define a catchment region $C^{(i)}$ by allowing any one of these degenerate minima to take the role of $\boldsymbol{m}^{(i)}$ in definition (7). Taking this generalized interpretation of index i, set M of all minimum points may be partially ordered, using relation (2). In the following a similar ordering will be assumed for all critical points of each index λ. The fact that the ordering is partial, i.e. it does not distinguish between elements of a set of connected degenerate minima, will not affect our analysis.

For a general polyatomic molecule ($N \gg 2$), with the exception of highly symmetric species, the energy cannot be constant along the entire domain of an internal coordinate, $E(\boldsymbol{r}^{(0)} + \alpha \boldsymbol{a}) \neq \text{const.}$ (for every $\alpha, -\infty < \alpha \leq \infty$)[6]. Consequently, if the actual energy hypersurface $E(\boldsymbol{r})$ is an analytic function of $\boldsymbol{r}$ then all minima must be isolated and the above problem does not arise. However, both

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[5] In general, only those Q connected sets of critical points are problematic, for which $E(\boldsymbol{r})$ is not twice continuously differentiable at the boundary points of Q, since then the boundary of $\bar{D}_{\text{excl}}$ may contain critical points from set Q.

[6] In principle, if a group of atoms in a molecule have a local C_∞ symmetry element, e.g. the —C≡C—H group in methylacetylene, then at least one of the $n = 3N-6$ coordinates may be chosen as a rotational angle along which the energy is constant. In this case a connected set of degenerate minima exists along the entire range of this coordinate. However, in such cases this coordinate may be omitted and the dimension of R reduced, $n < 3N-6$.

restricted and unrestricted Hartree–Fock (RHF and UHF, resp.) potential energy surfaces may show non-analyticities [13] or erratic behaviour [14], furthermore, if the $E(\boldsymbol{r})$ functional is generated by spline fitting, the result is often non-analytic. Consequently, the occurrence of non-isolated critical points cannot be excluded. Similar problems may arise at intersections of potential energy hypersurfaces [11] where the energy functional $E(\boldsymbol{r})$ is not differentiable along some of the nuclear coordinates.

4. Boundaries of Catchment Regions

The maximum points $\boldsymbol{z}$ of $E(\boldsymbol{r})$ form a set denoted by Z:

$$Z = \{\boldsymbol{z}: \boldsymbol{g}(\boldsymbol{z}) = \boldsymbol{0}, \lambda(\boldsymbol{z}) = n, \boldsymbol{z} \notin \bar{\boldsymbol{D}}_{\text{excl}}\}. \tag{14}$$

The collection of all saddle points $\boldsymbol{s}$, i.e. all critical points with index $1 \leq \lambda(\boldsymbol{s}) < n$ will be denoted by S:

$$S = \{\boldsymbol{s}: \boldsymbol{g}(\boldsymbol{s}) = \boldsymbol{0}, 1 \leq \lambda(\boldsymbol{s}) < n, \boldsymbol{s} \notin \bar{\boldsymbol{D}}_{\text{excl}}\}. \tag{15}$$

Set S' is defined as

$$S' = S \cup \{\boldsymbol{r}_C: \boldsymbol{g}(\boldsymbol{r}_C) = \boldsymbol{0}, \lambda(\boldsymbol{r}_C) = 0, \boldsymbol{r}_C \notin M, \boldsymbol{r}_C \notin \bar{\boldsymbol{D}}_{\text{excl}}\} \tag{16}$$

i.e. S' contains all shoulder points in addition to all saddle points, that are not in $\bar{\boldsymbol{D}}_{\text{excl}}$.

Points $\boldsymbol{z} \in Z$ and $\boldsymbol{s} \in S'$ do not belong to any of the above catchment regions,

$$\boldsymbol{z}, \boldsymbol{s} \notin C^{(i)}, \quad \text{for any } i, \tag{17}$$

since no steepest descent path P_z or P_s is defined. Furthermore, if for an ordinary point $\boldsymbol{r}$ the P_r path terminates at a point $\boldsymbol{s}$, $\boldsymbol{s} \in S'$, or at point $\boldsymbol{r}'$, $\boldsymbol{r}' \in \bar{\boldsymbol{D}}_{\text{excl}}$, then $\boldsymbol{r}$ does not belong to any of the $C^{(i)}$ catchment regions either:

$$\boldsymbol{r} \notin C^{(i)} \text{ for any } i \text{ if } \boldsymbol{r} \in \{\boldsymbol{r}: P_r \cap S' \neq \varnothing\} = C^{(S')} \tag{18a}$$

$$\text{or, if } \boldsymbol{r} \in \{\boldsymbol{r}: P_r \cap \bar{\boldsymbol{D}}_{\text{excl}} \neq \varnothing\} = C^{(\bar{D}_{\text{excl}})}. \tag{18b}$$

The set of all points not covered by catchment regions $C^{(i)}$ will be denoted by W:

$$W = \boldsymbol{R} - \bigcup_i C^{(i)} = Z \cup S' \cup C^{(S')} \cup C^{(\bar{D}_{\text{excl}})} \cup \bar{\boldsymbol{D}}_{\text{excl}} \tag{19}$$

where sets $C^{(S')}$ and $C^{(D_{\text{excl}})}$ are defined by (18a) and (18b), respectively. Set W contains all boundary points of all catchment regions $C^{(i)}$.

The definition of the $C^{(i)}$ catchment regions implies that a typical $C^{(i)}$ is an open set. The $W^{(i)}$ boundary of catchment region $C^{(i)}$ is an $n-1$ dimensional hypersurface that separates minimum $\boldsymbol{m}^{(i)}$ from every minimum $\boldsymbol{m}^{(i')}$ of index $i' \neq i$. (A connected point set of degenerate minima share the same serial index i, and these minima are not separated by boundaries). If $\bar{C}^{(i)}$ is the closure of catchment region $C^{(i)}$, then $W^{(i)}$ may be defined as

$$W^{(i)} = \bar{C}^{(i)} \cap W. \tag{20}$$

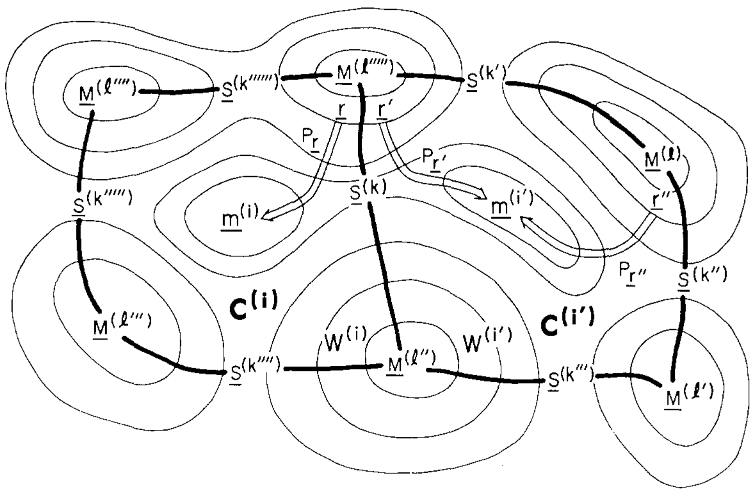

Fig. 1. Model surface with catchment regions $C^{(i)}$ and $C^{(i')}$ of minima $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$, respectively. Boundaries of catchment regions (shown by heavy lines) pass through various saddle points $\boldsymbol{s}$ and maxima $\boldsymbol{M}$

In Fig. 1, catchment regions $C^{(i)}$ and $C^{(i')}$ of a model surface are shown. Path P_r with origin at point $\boldsymbol{r}$ terminates at minimum $\boldsymbol{m}^{(i)}$, whereas path $P_{r'}$ with origin at point $\boldsymbol{r}'$ terminates at extremity $\boldsymbol{m}^{(i')}$. The $W^{(i)}$ and $W^{(i')}$ boundaries of catchment regions $C^{(i)}$ and $C^{(i')}$, respectively, have a common segment containing saddle points $\boldsymbol{s}^{(k)}$ and separating the two catchment regions. Points $\boldsymbol{r}$ and $\boldsymbol{r}'$ fall on opposite sides of this common segment. Path $P_{r''}$ with origin at point $\boldsymbol{r}'' \in C^{(i')}$ has the same extremity ($\boldsymbol{m}^{(i')}$) as path $P_{r'}$ and both belong to the same equivalence class,

$$P_{r'}, P_{r''} \in P^{(\boldsymbol{m}^{(i')})}.$$

None of the above steepest descent paths is a part of a minimum energy path, since such a path must enter a $C^{(i)}$ catchment region at one of the saddle points $\boldsymbol{s}$, $\lambda(\boldsymbol{s}) = 1$.

In order to show that definitions (19) and (20) are chemically meaningful, we prove that no minimum point $\boldsymbol{m}^{(i')}$ may fall on the boundary of catchment region $C^{(i)}$ of a non-degenerate minimum or an isolated degenerate minimum $\boldsymbol{m}^{(i)}$. Whereas for the simplest case of isolated minima this follows directly from $C^{(i)} \cap C^{(i')} = \emptyset$, we present here a proof that is easier to generalize for pathological cases.

Let us consider a critical point $\boldsymbol{r}_C$ in the point set

$$W'^{(i)} = \bar{C}^{(i)} - C^{(i)} \tag{21}$$

on the boundary of $C^{(i)}$, that is,

$$\boldsymbol{r}_C \in \bar{C}^{(i)} \tag{21a}$$

and

$$\boldsymbol{r}_C \not\in C^{(i)}. \tag{21b}$$

As a consequence of relation (12), $\boldsymbol{r}_C$ cannot belong to a set of connected degenerate minima with serial index i, and no $\boldsymbol{m}'^{(i)}$ exists for which

$$\boldsymbol{m}'^{(i)} = \boldsymbol{r}_C \tag{22}$$

since $\boldsymbol{m}^{(i)}$ is an isolated minimum. Contrary to the proposition, let us assume that $\boldsymbol{r}_C$ is a minimum, $\boldsymbol{r}_C = \boldsymbol{m}^{(i')}$. Since $\boldsymbol{m}^{(i')} \in \bar{C}^{(i)}$, it is possible to find a point series $\{\boldsymbol{r}^{(j)}\}$ in $C^{(i)}$ that converges to boundary point $\boldsymbol{m}^{(i')} = \boldsymbol{r}_C \in W'^{(i)}$:

$$\lim_{j} \boldsymbol{r}^{(j)} = \boldsymbol{r}_C = \boldsymbol{m}^{(i')} \tag{23}$$

where

$$\{\boldsymbol{r}^{(j)}\} \subset C^{(i)} \tag{24}$$

and

$$\boldsymbol{r}^{(j)} \neq \boldsymbol{m}^{(i)}. \tag{24a}$$

Property (24) implies that

$$P_{\boldsymbol{r}^{(j)}} \in P^{(\boldsymbol{m}^{(i)})} \tag{25}$$

for any index j. On the other hand, by applying relations (11a, b) we may write for any point $\boldsymbol{r}$ in an open ball $G(\boldsymbol{m}^{(i')}, \rho)$ of a small enough radius ρ, $\rho > 0$, that

$$E(\boldsymbol{r}) \geq E(\boldsymbol{m}^{(i')}). \tag{26}$$

There must exist index j' such, that

$$\boldsymbol{r}^{(j')} \in G(\boldsymbol{m}^{(i')}, \rho). \tag{27}$$

Since $\boldsymbol{r}^{(j')} \in C^{(i)}$ and $\boldsymbol{r}^{(j')} \neq m^{(i)}$, $\boldsymbol{r}^{(j')}$ itself cannot be a critical point. Consequently, even if $\boldsymbol{m}^{(i')}$ belongs to a set of connected degenerate minima, $\boldsymbol{r}^{(j')}$ cannot belong to the same set. Consequently, if ρ is small enough, then for the $\boldsymbol{r}^{(j')}$, $\boldsymbol{m}^{(i')}$ point pair inequality (12) applies, i.e.

$$E(\boldsymbol{r}^{(j')}) > E(\boldsymbol{m}^{(i')}) \tag{28}$$

and

$$P_{\boldsymbol{r}(j')} \in P^{(\boldsymbol{m}^{(i')})}. \tag{29}$$

However, relation (25) implies that

$$P_{\boldsymbol{r}^{(j')}} \in P^{(\boldsymbol{m}^{(i)})}, \tag{30}$$

a contradiction, since $\boldsymbol{m}^{(i)} \neq \boldsymbol{m}^{(i')}$. That is, $\boldsymbol{r}_C \in W'^{(i)}$ cannot be a minimum.

Essentially the same proof applies to the catchment region of a connected set of degenerate minima if this set has no points in $\bar{D}_{\mathrm{excl}}$. However, if the second derivative is discontinuous at any of these minimum points, then $W^{(i)}$ may also

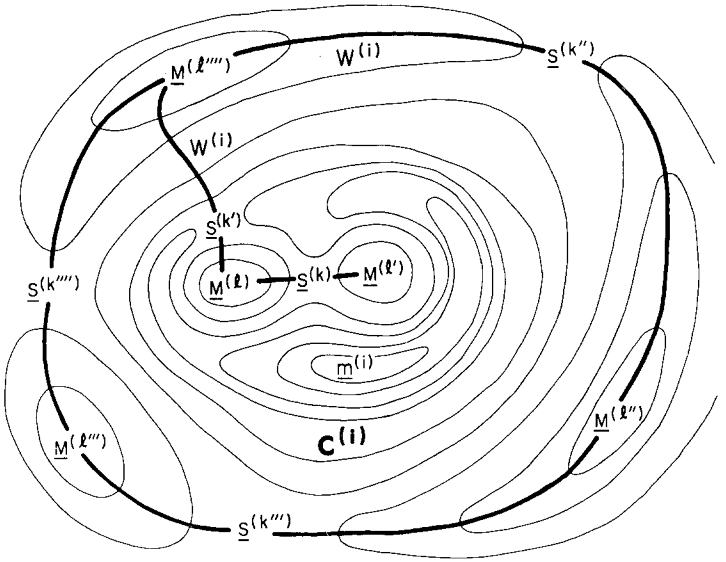

Fig. 2. Model surface showing various segments of the $W^{(i)}$ boundary of $C^{(i)}$. The $(\boldsymbol{M}^{(l'''')}, \boldsymbol{M}^{(l')}]$ segment of $W^{(i)}$ falls into the interior of $\bar{C}^{(i)}$

contain points from this degenerate set. Such degenerate cases, however, are not likely to occur in the chemically important regions of energy hypersurfaces.

Boundary $W^{(i)}$ may include points $\boldsymbol{r}$ that are not boundary points of any other catchment region $C^{(i')}$, $\boldsymbol{r} \notin W^{(i')}$ for any $i' \neq i$. Such an example is shown on Fig. 2, where a ridge stretching from $\boldsymbol{M}^{(l'''')}$ to $\boldsymbol{M}^{(l')}$ through $\boldsymbol{s}^{(k')}$, $\boldsymbol{M}^{(l)}$ and $\boldsymbol{s}^{(k)}$ falls into the interior of $\bar{C}^{(i)}$.

Formally, points on this ridge do not belong to $C^{(i)}$, since a P_r path from any point $\boldsymbol{r}$ of the ridge terminates at one of the saddle points $\boldsymbol{s}^{(k)}$ and $\boldsymbol{s}^{(k')}$, rather than at minimum $\boldsymbol{m}^{(i)}$. In the geographical sense, however, only the boundary points of the closure $\bar{C}^{(i)}$ may be regarded as true boundary points of catchment region $C^{(i)}$.

The entire space R may be partitioned into a set of mutually exclusive domains $C^{(1)}, C^{(2)}, \ldots, C^{(i)}, \ldots, W$. Catchment regions $C^{(i)}$ and $C^{(i')}$ are called *neighbours* if $W^{(i)} \cap W^{(i')} \neq \emptyset$. The catchment regions are ordered by relation (2) and for any pair $C^{(i)}, C^{(i')}$, $(i < i')$ of catchment regions for which the inequality holds in (2), a product-reactant assignment can be made by labelling $C^{(i)}$ as product region and $C^{(i')}$ as reactant region. It is clear that this labelling reflects the relative stabilities of the corresponding equilibrium geometries $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$ in terms of total energies.

A similar relation does not necessarily hold for arbitrary point pairs from $C^{(i)}$ and $C^{(i')}$, and it may be possible to find points $\boldsymbol{r} \in C^{(i)}$, $\boldsymbol{r}' \in C^{(i')}$ far enough from the minima such that $E(\boldsymbol{r}) > E(\boldsymbol{r}')$.

A given catchment region $C^{(i)}$ may contain points that correspond to highly unlikely nuclear configurations, even if index i is small, i.e. $\boldsymbol{m}^{(i)}$ is one of the lowest few minima. Such points usually belong to D_μ domains of large index μ. On the other hand, points $\boldsymbol{r}$ along minimum energy paths are likely to have smaller $\mu(\boldsymbol{r})$ indices than points representing chemically unlikely nuclear arrangements [1]. The relations between catchment regions $\{C^{(i)}\}$ and domains $\{D_\mu\}$ reflect the relative importance of various subdomains of the $C^{(i)}$ regions.

For $\boldsymbol{m}^{(i)} \in C^{(i)}$ the critical point indices $\lambda(\boldsymbol{m}^{(i)}) = \mu(\boldsymbol{m}^{(i)}) = 0$, and there must exist a domain $D_0^{(i)}$ such that $\boldsymbol{m}^{(i)} \in D_0^{(i)}$. If there is any other minimum $\boldsymbol{m}^{(i')}$ on the hypersurface, and $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$ are not elements of a connected set of degenerate minima, that is $i \neq i'$, then $\boldsymbol{m}^{(i')}$ belongs to a different catchment region $\boldsymbol{m}^{(i')} \in C^{(i')}$. There must exist a domain $D_0^{(i')}$ such that $\boldsymbol{m}^{(i')} \in D_0^{(i')}$. Usually, these two minima may be interconnected by a minimum energy path P, if there is a saddle point $\boldsymbol{s}$ such, that $\lambda(\boldsymbol{s}) = 1$ and $\boldsymbol{s} \in W^{(i)} \cap W^{(i')}$, or, by a series of minimum energy paths, joined at their extremities at one or more intermediate minima $\{\boldsymbol{m}^{(j)}\}$, $i, i' \neq j$. In all cases, $D_0^{(i)}$ must contain at least one saddle point $\boldsymbol{s}$, $\lambda(\boldsymbol{s}) = 1$, $\boldsymbol{s} \in D_0^{(i)}$ such that $\boldsymbol{s} \in W^{(i)}$. Consequently, $D_0^{(i)}$ and $W^{(i)}$ must have at least one common point,

$$\boldsymbol{s} \in W^{(i)} \cap D_0^{(i)}. \tag{31}$$

Similarly, there must exist a saddle point $\boldsymbol{s}'$, $\lambda(\boldsymbol{s}') = 1$, such that

$$\boldsymbol{s}' \in W^{(i')} \cap D_0^{(i')}. \tag{31a}$$

If the minimum energy path (or a series of such paths) does not pass through an instability domain D_μ, $\mu \geq 1$, then the connectedness property of D_0 domains [1] implies that $D_0^{(i')} = D_0^{(i)}$. Domains $D_0^{(i)}$ and $D_0^{(i')}$ may be different only if there are points $\boldsymbol{r}$, $\mu(\boldsymbol{r}) \geq 1$ along the minimum energy path(s) interconnecting $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$. On the model surface shown in Fig. 3 the boundaries of D_μ domains are

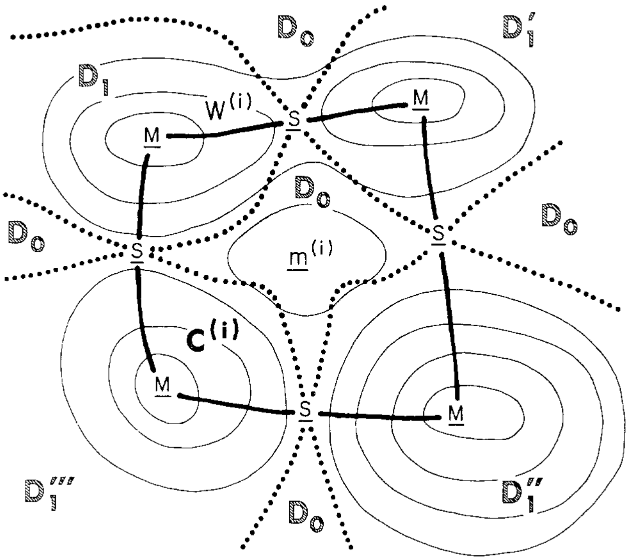

Fig. 3. Typical model surface showing the interrelations between $C^{(i)}$ and various D_μ domains. Boundaries of the latter are shown by dotted line

indicated by dotted lines, whereas the $W^{(i)}$ boundary of catchment region $C^{(i)}$ is shown as solid line. Since all four saddle points have indices $\mu(\boldsymbol{s})=0$, they all belong to the D_0 domain containing minimum point $\boldsymbol{m}^{(i)}$. Consequently, all points with index $\mu(\boldsymbol{r})=0$, shown on the figure, belong to the same D_0 domain. Portions of four different D_1 domains are also shown in the figure. Catchment region $C^{(i)}$ contains subdomains of all five domains D_0, D_1, D_1', D_1'' and D_1'''. With the exception of the four saddle points, all points of the $W^{(i)}$ boundary fall into the D_1 domains,

$$\mu(\boldsymbol{r})=1 \quad \text{if } \boldsymbol{r}\in W^{(i)}, \qquad \boldsymbol{r}\neq \boldsymbol{s}. \tag{32}$$

Whereas this example might suggest the contrary, it is *not* true that

$$\mu(\boldsymbol{r})>0 \quad \text{if } \boldsymbol{g}(\boldsymbol{r})\neq \boldsymbol{0}, \qquad \boldsymbol{r}\in W^{(i)}$$

for boundary points of all catchment regions. As the example in Fig. 4 shows, non-critical points with index $\mu(\boldsymbol{r})=0$ may also belong to the boundary. Any point $\boldsymbol{r}$ within the closed segment $[\boldsymbol{a},\boldsymbol{b}]$ on the $W^{(i')}$ boundary belongs to D_0, that is, $\mu(\boldsymbol{r})=0$. This example shows two more unusual features: domain D_1 contains no critical point at all, and the two minima, $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$ may be interconnected by a (non-steepest-descent) path that lies in the interior of D_0 and does *not* pass through a saddle point ($\boldsymbol{s}^{(k)}$). In fact, an entire D_0 domain may be contained in W, as in the model surface shown in Fig. 5, where $D_0'\subset W$.

Whereas not every point $\boldsymbol{r}\in W^{(i)}$ of $\mu(\boldsymbol{r})=0$ must be a saddle point $\boldsymbol{s}$, it is true that every saddle point $\boldsymbol{s}$, $\mu(\boldsymbol{s})=0$ must belong to W, $\boldsymbol{s}\in W$, by virtue of definition (19).

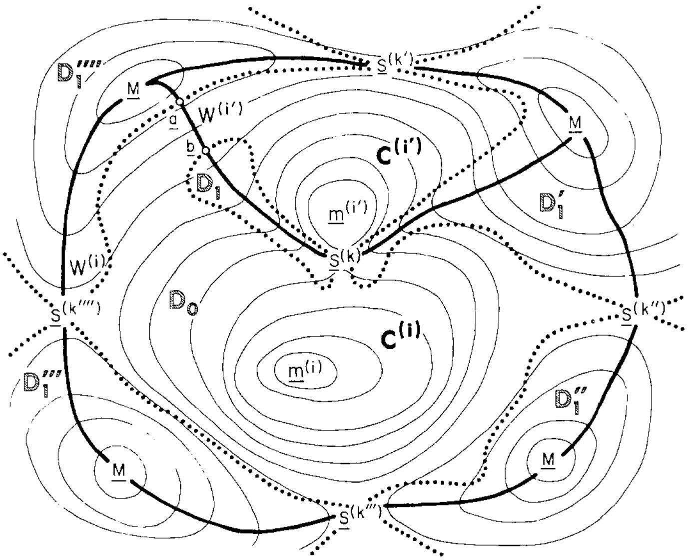

Fig. 4. Atypical model surface with ordinary $\boldsymbol{r}\in D_0$ points on the $[\boldsymbol{a},\boldsymbol{b}]$ segment of the $W^{(i')}$ boundary. D_1 does not contain critical point and minima $\boldsymbol{m}^{(i)}$ and $\boldsymbol{m}^{(i')}$ may be interconnected within D_0 without passing through a saddle point

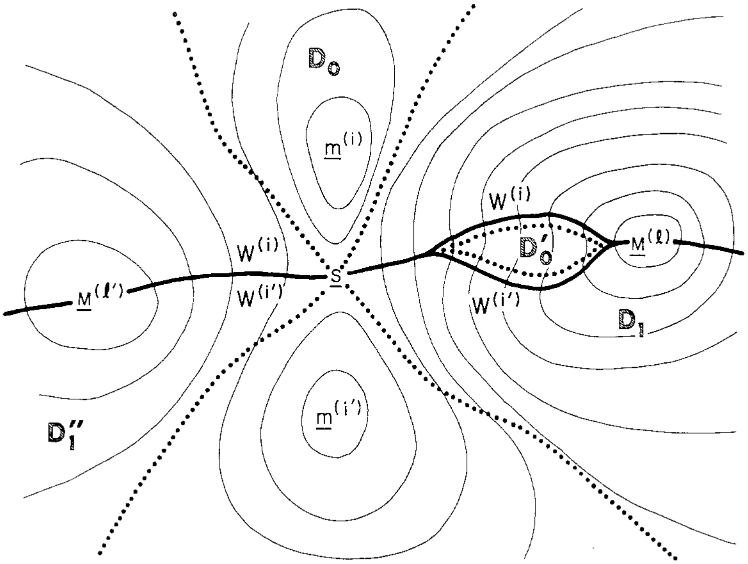

Fig. 5. Atypical model surface with an entire D_0 domain (D'_0) contained in W. Domain D'_0 does not have a minimum

Let us consider all minimum energy paths with the common extremity $\boldsymbol{m}^{(i)}$. These are the only minimum energy paths entering catchment region $C^{(i)}$. Since each minimum energy path contains exactly one saddle point $\boldsymbol{s}$, $\lambda(\boldsymbol{s})=1$, these saddle points must also belong to the boundary $W^{(i)}$ of $C^{(i)}$. Also, to each isolated saddle point $\boldsymbol{s}\in W^{(i)}$, $\lambda(\boldsymbol{s})=1$, one may assign a minimum energy path; consequently there is a one to one correspondence between these saddle points and minimum energy paths,

$$P^{(k)} \leftrightarrow \boldsymbol{s}^{(k)} \tag{33}$$

where

$$P^{(k)}\colon \boldsymbol{m}^{(i)} \in P^{(k)} \tag{34a}$$

and

$$\boldsymbol{s}^{(k)}\colon \boldsymbol{s}^{(k)} \in W^{(i)} \quad \text{and} \quad \lambda(\boldsymbol{s}^{(k)})=1. \tag{34b}$$

For any such $\boldsymbol{s}^{(k)}$ the equivalence class of steepest descent paths,

$$P^{(s^{(k)})} = \{P_r\colon \boldsymbol{s}^{(k)} \in P_r\} \tag{35}$$

is composed of paths P_r with their origins in W:

$$\boldsymbol{r}\in W \quad \text{if } P_r \in P^{(s^{(k)})}. \tag{36}$$

Since all such P_r paths terminate at saddle point $\boldsymbol{s}^{(k)}$, the set of all their origin points $\boldsymbol{r}$ may be regarded a "catchment region" for saddle point $\boldsymbol{s}^{(k)}$:

$$C^{(s^{(k)})} = \{\boldsymbol{s}^{(k)}, \boldsymbol{r}\colon \boldsymbol{s}^{(k)} \in P_r\}. \tag{37}$$

Relation (36) may be re-stated as

$$C^{(s^{(k)})} \subset W. \tag{38}$$

Since a steepest descent path P_r contains only one critical point, that is the extremity, the entire set $C^{(s^{(k)})}$ contains only one critical point, $s^{(k)}$. The closure $\bar{C}^{(s^{(k)})}$, however, may contain additional critical points that must be elements of the $\bar{C}^{(s^{(k)})} - C^{(s^{(k)})}$ boundary. It is always possible to find a point series $\{r^{(j)}\}$ within $C^{(s^{(k)})}$ that converges to a given point r on the boundary,

$$\lim_{j} r^{(j)} = r \tag{39}$$

$$r^{(j)} \in C^{(s^{(k)})} \tag{39a}$$

$$r \in \bar{C}^{(s^{(k)})} - C^{(s^{(k)})}. \tag{39b}$$

Since these $r^{(j)}$ points are origins of steepest descent paths $P_r(j)$ from the equivalence class $P^{(s^{(k)})}$, it can be shown, similarly to the case of the $W^{(i)}$ boundary, that boundary point r cannot be a minimum. Point r, however, may be a saddle point or maximum, $1 \leq \lambda(r) \leq n$.

Definition (37) is applicable for any element of set S', i.e. for saddle points of any index, $1 \leq \lambda(s) < n$, or to shoulders, and relation (38) is also valid for any element $s \in S'$, as a direct consequence of definition (19). Consequently, set W itself may be partitioned into catchment regions of all elements of set S', set Z of all maxima, and $\bar{D}_{\text{excl}}$:

$$W = \bigcup_{\substack{k \\ s^{(k)} \in S'}} C^{(s^{(k)})} \cup Z \cup C^{(\bar{D}_{\text{excl}})} \cup \bar{D}_{\text{excl}} \tag{40}$$

where $C^{(\bar{D}_{\text{excl}})}$ may be regarded the catchment region for $\bar{D}_{\text{excl}}$. Similarly to property (8) of $C^{(i)}$ catchment regions, the $C^{(s^{(k)})}$ regions are disjoint:

$$C^{(s^{(k)})} \cap C^{(s^{(k')})} \neq \varnothing, \quad \text{if } k \neq k' \tag{41}$$

and also

$$C^{(s^{(k)})} \cap C^{(\bar{D}_{\text{excl}})} = \varnothing. \tag{41a}$$

A complete catchment region partitioning of space R may be given as

$$R = \bigcup_{i} C^{(i)} \bigcup_{k} C^{(s^{(k)})} \bigcup Z \bigcup C^{(\bar{D}_{\text{excl}})} \bigcup \bar{D}_{\text{excl}} \tag{42}$$

or more concisely

$$R = \bigcup_{l} C^{(r^{(l)})} \bigcup C^{(\bar{D}_{\text{excl}})} \bigcup \bar{D}_{\text{excl}} \tag{43}$$

where index l runs over all non-degenerate and isolated degenerate critical points as well as over all *sets* of connected degenerate critical points, that are not contained in the closure of the excluded domain D_{excl}

$$r_C^{(l)} \notin \bar{D}_{\text{excl}}. \tag{44}$$

Here the "catchment regions" for maxima are defined as one-point sets:

$$C^{(z^{(l)})} = \{z^{(l)}\}, \qquad \lambda(z^{(l)}) = n \tag{45}$$

and are used purely for the sake of a uniform treatment of all critical points.

5. The Concept of Molecular Structure and Catchment Regions of Critical Points

The concept of chemical structure has undergone a considerable development since the early models of "atoms interconnected by chemical bonds". The classical concept of structure is often associated with a rigid nuclear arrangement, corresponding to an equilibrium geometry. This structural model is clearly an oversimplification, since even within the Born–Oppenheimer approximation a vibrating molecule spends no time at the equilibrium configuration. Furthermore, by treating electrons and nuclei on equal footing, it appears more appropriate to refer to nuclear distributions rather than to nuclear positions, just as one refers to electron distributions, rather than to electronic positions in a given molecule. Nevertheless, the classical structural concept of molecules is very successful in correlating geometrical features of "equilibrium configurations" with macroscopic chemical properties, and stereochemistry, symmetry properties and the very identity of molecules are usually discussed in terms of such "equilibrium configurations". A great variety of spectroscopic phenomena may be described with satisfactory accuracy by quantum mechanical treatments involving approximate potentials in the neighbourhoods of such "equilibrium points".

It has been argued that even extensions of the classical concept of "structure" are incompatible with rigorous quantum mechanics, and recently several authors have given theoretical discussions of the underlying quantum mechanical concepts and of the interpretation of "structure" in chemistry [15–21].

In any practical sense, molecules do have some identity and different molecules, even if composed of the same set of atoms, do exhibit different "structural" features. Apparently, the problem of the quantum chemical structure concept is a matter of definition. Whereas a structure concept defined only for discrete points, e.g. for minima $\boldsymbol{m}^{(i)}$ of R is clearly unsatisfactory, on intuitive basis one may expect that a quantum mechanical definition retains some reference to such points, or it is even based on them. Alternatively as Bader and co-workers have demonstrated [20–21], chemical structure may be defined in terms of molecular graphs, determined by the topological properties of molecular charge density, a quantum mechanical observable. It is conjectured, that a homeomorphism exists between the structure diagram of the charge density and the nuclear potential [21].

The definition of catchment regions offers an intuitively straightforward definition for chemical structures, that assigns an open set of points to a given structural label. Within the framework of the Born–Oppenheimer energy hypersurface model the surface points have a simple geometric interpretation and each point is associated with a rigid nuclear arrangement. Considering two different points in the immediate vicinity of a stationary point, the associated geometrical structures may be derived by small distortions of the "equilibrium structure", that is associated with the stationary point (critical point). Since the structural characterization of the "equilibrium structure" itself is only an approximation, there is little justification for considering these three geometries fundamentally different, and one may regard an entire neighbourhood of a critical point as one that describes essentially the same, if somewhat distorted, "molecular structure". Such an "approximate classification" of molecular structure is indeed well established in chemical practice. E.g. various vibrational states of *cis*-1,2-difluoroethene are all considered *cis*-1,2-difluoroethene, in spite of differences even between classical "time averaged" geometries that are due to anharmonicity. On the other hand, all these geometries are well distinguished from various states of the *trans* compound.

In the energy hypersurface model it is convenient to regard the nuclear geometries associated with various critical points as "reference structures" ("equilibrium structures") and consider any geometry in the close neighbourhood of these points as a distorted nuclear arrangement, i.e. essentially the same compound ("chemical structure") as that at the critical point. It is natural then to classify these distorted nuclear arrangements according to catchment regions of various critical points. In this classification the nuclear arrangement of point $\boldsymbol{r}$, $\boldsymbol{r} \in C^{(i)}$, is regarded a distorted form of reference structure represented by the equilibrium nuclear arrangement of minimum point $\boldsymbol{m}^{(i)}$. Similarly, point $\boldsymbol{r} \in C^{(s^{(k)})}$ is regarded a distorted form of the chemical structure at the "transition state", described by saddle point $\boldsymbol{s}^{(k)}$. As long as at point $\boldsymbol{r}$ there is a steepest descent path P_r leading to critical point $\boldsymbol{r}_C$, the actual difference between geometric arrangements at points $\boldsymbol{r}$ and $\boldsymbol{r}_C$ may be considered a "distortion", and precisely the same condition has been used in the definition of catchment region $C^{(r_C)}$. However, if a steepest descent path P_r leads to a different critical point, $\boldsymbol{r}'_C$, then the structural differences between points $\boldsymbol{r}$ and $\boldsymbol{r}_C$ are certainly sufficient to regard an $\boldsymbol{r}_C \to \boldsymbol{r}$ distortion "large" in a chemical sense. Such a distortion may be classified as a chemical (conformational or reaction) process, since the geometry at point $\boldsymbol{r}$ is likely to get converted into one at point $\boldsymbol{r}'_C$, rather than into one at point $\boldsymbol{r}_C$.

The classification of chemical structures may then follow the ordering of steepest descent paths into equivalence classes $\{P^{(r_C)}\}$, and the identity of a given structure (with limited distortions allowed) is decided on the basis of catchment regions $C^{(r_C)}$. The limitations on distortions that are considered small enough to preserve the fundamental features (chemical identity) of a structure are precisely defined in terms of the $W^{(r_C)}$ boundaries of $C^{(r_C)}$ catchment regions about critical points $\boldsymbol{r}_C$.

6. Reaction Mechanisms and Catchment Regions

The classical concept of chemical structure is only an approximation in the rigorous quantum mechanical sense, and the qualitative description of the interconversion processes between such structures involves similar approximations.

Although in chemical practice it is usually possible to identify some distinguishing features of the structural changes during a reaction, usually referred to as the reaction mechanism, nevertheless, in the rigorous quantum mechanical sense, no reaction follows a unique course of geometry changes. The concept of minimum energy reaction path is an approximation to the steric course of a chemical process, just as a critical point (e.g. "equilibrium configuration") is an approximation to a chemical structure, and the two concepts represent a consistent set of approximations. Within the framework of the Born–Oppenheimer energy surface model it is convenient to distinguish between reaction mechanisms according to minimum energy paths, i.e. two mechanisms are considered different if they may be associated with two different minimum energy paths. There is a one-to-one correspondence between minimum energy paths and saddle points $s^{(k)}$, $\lambda(s^{(k)}) = 1$; consequently, the ideal reaction mechanisms (i.e. those hypothetical processes following minimum energy paths) may be identified by the corresponding saddle points. However, even within the Born–Oppenheimer model, infinitely many different trajectories may pass through a neighbourhood of saddle point, $s^{(k)}$, associated with the given "ideal" reaction mechanism, and all these trajectories may be regarded as "distorted" versions of the ideal minimum energy path $P^{(k)}$. Considering a given *pair of minima* and a set of interconnecting trajectories, $\{P\}$, it is natural to regard the subset $\{P\}^{C^{(s^{(k)})}} \subset \{P\}$ of all those paths that pass through the catchment region $C^{(s^{(k)})}$ of saddle point $s^{(k)}$, as representing essentially the same, if somewhat distorted, reaction mechanism. On the other hand, if a path P' is distorted beyond the $W^{(s^{(k)})}$ boundary of catchment region $C^{(s^{(k)})}$, then a "relaxation" of this path would lead to a different minimum energy path $P^{(k')}$, that passes through a saddle point $s^{(k')} \in W$, different from $s^{(k)}$. That is, path P' has more common "chemical features" with minimum energy path $P^{(k')}$ at $s^{(k')}$ than with the original minimum energy path, $P^{(k)}$ at $s^{(k)}$ and it shows more similarities with the ideal reaction mechanism corresponding to saddle point $s^{(k')}$ than with the one corresponding to $s^{(k)}$ (cf. Fig. 6).

This classification of reaction mechanisms according to catchment regions $C^{(s^{(k)})}$ of saddle points $s^{(k)}, \lambda(s^{(k)}) = 1$, may also be interpreted as a classification according to transition state structures, since the same $C^{(s^{(k)})}$ catchment regions are proposed for the identification of chemical structures approximately corresponding to saddle points of index $\lambda = 1$, i.e. to classical transition states.

The stability of ideal steepest descent and minimum energy paths with respect to small perturbations, e.g. vibrational motion across the reaction path, depends on index $\mu(r)$ of points r along the path [1]. A sufficient condition for stability is $\mu(r) = 0$, that is, steepest descent and minimum energy paths are stable in D_0 domains. Usually a large perturbation of a minimum energy path $P^{(k)}$ is required to change the basic features of the reaction mechanism, i.e. to convert it from an "$s^{(k)}$ dominated" mechanism into one that is dominated by another saddle point, e.g. $s^{(k')}$, $k \neq k'$. Such an example is shown in Fig. 6, where the entire $P^{(k)}$ minimum energy path is contained in a D_0 domain, $\mu(r) = 0$ if $r \in P^{(k)}$. However, if minimum energy path $P^{(k)}$ does pass through an instability domain D_μ, $\mu > 0$, such as the domain D_1 shown in Fig. 7, then small perturbations may cause large

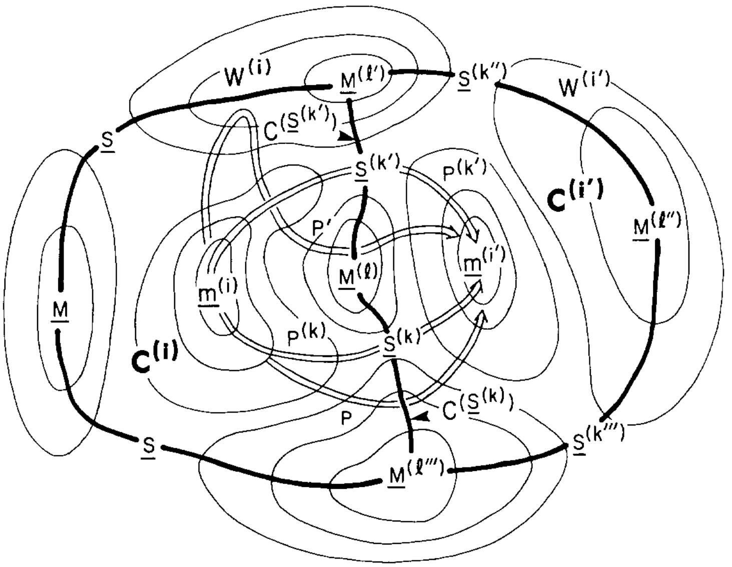

Fig. 6. Model surface with minimum energy paths $P^{(k)}$ and $P^{(k')}$ and distorted paths P and P'

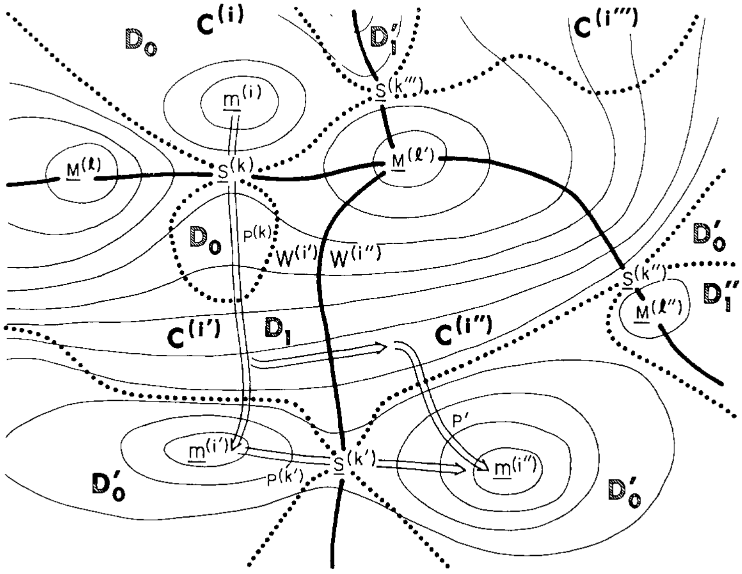

Fig. 7. Surface model with instability domain D_1 extending over several catchment regions. Small perturbations may cause a branching of the reaction mechanism

changes in the path, and, depending on the actual surface the new path may lead to a different product [1].

For the simplest case of one isolated instability domain D_μ, $\mu > 0$, a necessary condition for such instability-induced change of reaction mechanisms may be given in terms of catchment regions. It is possible for a small (infinitesimal) perturbation of the ideal minimum energy path $P^{(k)}$ to alter the outcome of the reaction from product $\boldsymbol{m}^{(i')}$ to product $\boldsymbol{m}^{(i'')}$, $i' \neq i''$, only if conditions a, and b, are fulfilled:

a) $P^{(k)}$ passes through the instability domain

$$D_\mu, \mu > 0. \tag{45}$$

b) The $W^{(i')}$ and $W^{(i'')}$ boundaries of catchment regions $C^{(i')}$ and $C^{(i'')}$ do have common points with D_μ

$$W^{(i')} \cap D_\mu \neq \varnothing, \tag{46a}$$

$$W^{(i'')} \cap D_\mu \neq \varnothing. \tag{46b}$$

The minimum energy path $P^{(k)}$ on the model surface shown in Fig. 7 is an example for such a path. In domain D_1, $P^{(k)}$ is not stable, since any displacement of the path, orthogonal to the gradient is associated with a lowering of the energy $E(\boldsymbol{r})$; consequently, small perturbations may cause extensive displacements. The shift across the $W^{(i')}/W^{(i'')}$ boundary symbolizes the perturbation that diverts the path from $\boldsymbol{m}^{(i')}$ to $\boldsymbol{m}^{(i'')}$. The actual process P' is equivalent to an $\boldsymbol{m}^{(i)} \to \boldsymbol{s}^{(k)} \to \boldsymbol{m}^{(i')} \to \boldsymbol{s}^{(k')} \to \boldsymbol{m}^{(i'')}$ transformation, i.e. to two consecutive processes, along $P^{(k)}$ followed by $P^{(k')}$. The reaction mechanisms may be referred to by the corresponding saddle points $\boldsymbol{s}^{(k)}$ and $\boldsymbol{s}^{(k')}$. The contribution of the second mechanism to the actual process P' is a consequence of the crossing of path P' through the $W^{(i')}/W^{(i'')}$ boundary, since this crossing point $\boldsymbol{r}$,

$$\boldsymbol{r} \in P' \cap W^{(i')} \cap W^{(i'')} \tag{47}$$

is also an element of catchment region $C^{(s^{(k')})}$,

$$\boldsymbol{r} \in C^{(s^{(k')})} \tag{48}$$

and the chemical structure associated with point $\boldsymbol{r}$ is a transition state structure of type $\boldsymbol{s}^{(k')}$.

Since in this model surface both conditions a) and b) are satisfied for the ideal path $P^{(k)}$, the net result is an actual "branching" of the reaction mechanism. Besides $\boldsymbol{m}^{(i')}$, the product of the ideal single step process $P^{(k)}$, product $\boldsymbol{m}^{(i'')}$ also appears, that is ideally a product of a two-step process, $P^{(k)}$ followed by $P^{(k')}$.

7. Conclusions

The geographical concept of catchment regions is generalized for multidimensional energy hypersurfaces of polyatomic chemical systems. The R space of internal coordinates is partitioned into catchment regions $C^{(r_C)}$ of critical points of various indices $\lambda(\boldsymbol{r}_C)$ and a domain $\bar{D}_{\text{excl}}$, where the energy hypersurface concept is a poor approximation to the energy expectation value. The catchment region partitioning is based on equivalence classes, defined for steepest descent paths $\{P_r\}$. Properties of $C^{(r_C)}$ catchment regions and their $W^{(r_C)}$ boundaries are analysed and their relations to the chemically most important D_μ domains with small μ indices are investigated. Catchment regions $C^{(m^{(i)})}$ and $C^{(s^{(k)})}$ of minima $\boldsymbol{m}^{(i)}$ and saddle points $\boldsymbol{s}^{(k)}$, $\mu(\boldsymbol{s}^{(k)})=0$, are proposed for the classification of chemical structures and reaction mechanisms, respectively. A necessary condition for instability-induced branching of reaction mechanisms is given in terms of the relations between D_μ domains and catchment regions.

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