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The topology of catchment regions of potential energy hypersurfaces*

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Abstract. A simple proof is presented for a fundamental topological property of catchment regions of potential energy hypersurfaces: each catchment region $C(\lambda, i)$, representing a chemical species and its conformational range on the potential energy hypersurface, is simply k-connected for each dimension $k = 1, 2, \ldots 3N - 6 - \lambda$, where λ is the index of the catchment region. The consequences of this property on the structure of the fundamental group of reaction mechanisms (the one-dimensional homotopy group of reaction paths) is discussed.

Key words: Catchment regions – Potential energy surfaces – Molecular conformation analysis – Fundamental group of reaction mechanisms

1 Introduction

The steepest descent path representation of the intrinsic reaction coordinate (IRC) concept of Fukui [1] and the meta-IRC concept of Tachibana and Fukui [2–4] have been strong motivating influences in the development of the topological model of potential energy hypersurfaces [5–11] and the associated topological description based on catchment regions [7–9, 11].

Catchment regions generate a partitioning of the $(3N - 6)$-dimensional "reduced", or internal nuclear configuration space M (which does not involve coordinates describing merely rigid translations and rigid rotations, motions which do not affect chemical identity). Note that for simplicity we shall assume that the number of nuclei, N, is 3 or more; for the rather trivial cases of diatomic and monoatomic species the formulas are somewhat different. Note, however, that for all finite N values, $N = 1, 2, 3, \ldots$, the internal configuration space M is a metric space that, contrary to some common assumptions, is not a vector space. These and some other counterintuitive properties of the nuclear configuration space are discussed in detail in Ref. [11]

Using the concept of the IRC, a catchment region $C(\lambda, i)$ of a potential energy hypersurface $E(K)$ is defined [7–9, 11] as the collection of all those nuclear configurations K of the reduced nuclear configuration space M from where an infinitely slow, vibrationless relaxation path, as expressed by the IRC of Fukui and Tachibana with respect to the given potential energy hypersurface $E(K)$, leads to a given critical point $K(\lambda, i)$ of the potential energy hypersurface. In these notations, λ is the index of the critical point (the number of negative eigenvalues of the local Hessian matrix of the potential energy hypersurface), whereas i is a simple index of ordering.

The concept of catchment regions is closely related to the potential surface cell concept, as suggested by Fukui and Tachibana [2, 3]. Based on the IRC, as discussed by Fukui [4], a cell of an n-dimensional Riemannian nuclear configuration space may involve several actual catchment regions of various dimensions, for example, those located on one side of an $(n - 1)$-dimensional ridge. In the topological model of catchment regions [7–9, 11], parts of such ridges are regarded as separate, $(n - 1)$-dimensional catchment regions, representing formal transition structures ("transition states") of various chemical interconversion processes (reactions or conformational changes). Within the topological model the IRC cells of potential surfaces can be generalized to catchment regions which include not only the most important attractors of potential energy minima but also lower-dimensional catchment regions of transition structures and even lower-dimensional formal entities [7–9, 11].

The catchment region and cell concepts have their origins in the inspired works of Cayley [12] and Maxwell [13], who used some of the mathematical properties of catchment regions for the description of geographical terrains, expressing the relations between hills, valleys, dales, and watersheds. A similar concept of catchment regions was used by Hoare [14] for the basins of potential minima of various microclusters, where the

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boundary points of neighboring catchment regions were assumed to belong to both basins; consequently, some of the nuclear configurations had no unique assignment to critical points of the potential. Basins of empirical potential functions for unit cells in melting ice, as studied by Stillinger and Weber [15] with regard to phase transitions, also show analogies with catchment regions.

A formal definition of a catchment region can be given as an equivalence class of internal nuclear configurations K in the reduced nuclear configuration space M. The assignment of each nuclear configuration K to some catchment region is based on the steepest decent path (with reference to mass-weighted nuclear displacements) leading from the actual configuration K to a critical point $K(\lambda, i)$ of the potential energy hypersurface $E(K)$. Each steepest descent path in the reduced nuclear configuration space M is represented by a mapping $P(K, u)$, where $P(K, u)$ maps the unit interval [0, 1] of parameter u to the configuration space M:

$$P(K, u) : [0, 1] \rightarrow M \tag{1}$$

and where the origin of the path,

$$P(K, 0) = K \tag{2}$$

corresponding to the parameter choice of $u = 0$ coincides with the actual point K, whereas the extremity of the steepest descent path corresponding to the parameter choice of $u = 1$ is the critical point $K(\lambda, i)$,

$$P(K, 1) = K(\lambda, i) \ . \tag{3}$$

The η-equivalence of nuclear configurations

$$K, K' \in M \tag{4}$$

is defined as follows:

$$K \, \eta \, K' \tag{5}$$

if and only if

$$P(K, 1) = P(K', 1) \ . \tag{6}$$

That is, the two nuclear configurations K and K' are η-equivalent if and only if the two steepest descent paths $P(K, u)$ and $P(K', u)$ starting from the points $K = P(K, 0)$ and $K' = P(K', 0)$, respectively, have a common extremity.

With respect to any twice continuously differentiable potential energy hypersurface $E(K)$ (or, with respect to any approximate energy hypersurface that can be made twice continuously differentiable by suitable local deformations near conical intersections or at other nonanalyticities), the η-equivalence relation generates an equivalence class partitioning of the nuclear configuration space M. The equivalence classes,

$$C_\eta(K) = C_\eta(K(\lambda, i)) \ , \tag{7}$$

where the representative element of each class can be chosen as the critical point $K(\lambda, i)$ itself, define the catchment regions

$$C(\lambda, i) = C_\eta(K) = C_\eta(K(\lambda, i)) \tag{8}$$

of the energy hypersurface $E(K)$.

Each catchment region contains precisely one critical point, hence it is justified to refer to the catchment region of a critical point.

The catchment region of an energy minimum, that (in the nondegenerate case) represents a stable molecular species, has the dimension $3N - 6$, whereas the catchment region of a saddle point of a transition structure has the dimension $3N - 7$. Lower-dimensional catchment regions of less direct physical significance complete the partitioning of the internal nuclear configuration space M into a stoichiometric family of catchment regions [7–9, 11]. The catchment regions are the faces of various dimensions of a topological structure called a "reaction polyhedron", representing the entire potential energy hypersurface [11].

One of the intuitively appealing aspects of the introduction of the IRC approach of Fukui was the generality of the definition that provided a natural, yet mathematically correct treatment of reaction paths, in a way that avoided the chances for most of the earlier, rather common misinterpretations of the multidimensional descriptions of concerted motions of nuclei. The potential energy hypersurfaces as well as the underlying nuclear configurational spaces have many counterintuitive properties, in part, as a consequence of their high dimensionality that lies beyond our usual imagination trained on the three-dimensional perception of the world. The precise definition of a reaction path, resulting in a one-dimensional line properly embedded in a multidimensional space, provided some safeguards against the pitfalls of presuming too many analogies with the three-dimensional world.

However, several counterintuitive properties of the nuclear configuration space M and the associated potential energy hypersurfaces $E(K)$ are independent of the representation of reaction paths, and among these counterintuitive features the lack of some of the vector space properties of the internal configuration space M is perhaps the most often misunderstood. This space not only lacks the closure property for the operation of combining elements (hence, it cannot be a vector space), but it also has a boundary beyond which no elements exist. Nevertheless, M is still a metric space, and by providing a suitable set of local coordinate systems and excluding degenerate conformations involving nuclear reactions, it can be turned into a manifold with a boundary [11]. A manifold structure is required for the use of sets of compatible internal coordinates and for the differentiation of the energy function in a consistent manner within the complete configuration space. This requirement is not always obvious as long as the family of conformations studied is essentially local, where simple, three-dimensional analogies and images still can be used for the interpretation of processes; for most local analyses of potential surface regions associated with a few chemical species involved in a reaction process or conformation change, the chemically motivated internal coordinates are suitable. For the usual, local descriptions of small amplitude motions, and selected large amplitude motions, where consistency with descriptions of very different arrangements of the same nuclei is not a concern, the choice of internal coordinates and differ-

entiation of the energy function are seldom problematic. However, by assuming too many analogies with the ordinary, three-dimensional space, a "nice" vector space, it is not universally appreciated that in most cases the local coordinate systems cannot be extended to the entire configuration space.

In fact, many of the concepts and tools which appear natural in the ordinary, three-dimensional space, are not automatically applicable within the internal configuration space and need to be checked before adapting them to the potential energy hypersurface problem, especially, if globally valid conclusions are needed. Based on the IRC approach of Fukui, these counterintuitive aspects of the internal configuration space have been analyzed in detail in Ref. [11] and in references quoted therein. In the present study we shall not repeat this analysis, but we shall take into acount all the relevant limitations, as well as some of the related properties of catchment regions.

Several topological as well as geometrical properties of catchment regions have been demonstrated in various studies [5–9, 11, 16–21]. These results include the catchment region point symmetry theorem [16], the vertical point symmetry theorem [16–18], the analogous framework group theorems, various symmetry constraints on relaxation and other deformation processes, surface crossings involving several potential energy hypersurfaces [19, 20], as well as results concerning the possible number of chemical species associated with regions of potential energy hypersurfaces [5, 6]. The catchment region approach also provides an alternative introduction to the symmetry as well as homotopy group properties of reaction mechanisms [21].

2 The topological structure of catchment regions

One question of some interest is the following: how complicated are the patterns of rearrangements of the nuclei and the associated electron density cloud allowed for a chemical species while preserving its chemical identity? Chemical identity can be defined in terms of catchment regions: two nuclear arrangements represent the same chemical species if these arrangements belong to the same catchment region. Consequently, this question can be phrased in terms of patterns of conformational rearrangement paths which are confined to a single catchment region. In general, if two paths are continuously deformable into one another within a given subset of the configurations, that is, if the paths are homotopically equivalent relative to this subset, then in a topological sense, these two paths describe the same internal rearrangement process [11]. This approach is consistent with quantum mechanics: whereas individual, formal reaction paths, represented by infinitely "thin" lines in a configuration space with no positional uncertainty for displacements perpendicular to the path are not compatible with the Heisenberg uncertainty relation, an entire equivalence class of homotopically equivalent (continuously interdeformable) reaction paths is compatible with the uncertainty relation [11]. In a more general sense, one may consider the interdeformability of not only paths but also of higher-dimensional objects of the configuration space, for example, two-dimensional "sheets" of nuclear arrangements, representing a "time-lapse photograph" of a deformation process of one formal reaction path into another, that is, representing a family of homotopically equivalent reaction paths within a two-dimensional surface of the nuclear configuration space. These sheets themselves are deformable, using two-dimensional homotopies, and the same principle applies to higher-dimensional objects in the configuration space M. Whereas the chemically most important deformability properties are those involving formal paths, the higher-dimensional deformations also provide important clues regarding the structure of the potential energy hypersurface in local regions of the configuration space. In this more general sense, here we are concerned with the one-, two-,... $(3N-7)$-dimensional connectedness properties of catchment regions, representing chemical species.

Although connectedness in high dimensions cannot be visualized, for one and two dimensions simple examples are available to illustrate the various cases of 1-connectedness and 2-connectedness. An object X is simply 1-connected if any loop (one-dimensional, topologically circular path) within X is contractible within the object X into a single point. Otherwise, X is multiply 1-connected. An object is simply 2-connected, if any closed sheet ("balloon", a two-dimensional, topological sphere) within X is contractible within the object X into a single point. Otherwise, X is multiply 2-connected. Higher-dimensional k-connectedness is defined analogously. A solid ball is simply 1-connected and simply 2-connected, the body of a doughnut is multiply 1-connected but simply 2-connected, whereas the rubber wall of a hollow ball is simply 1-connected but multiply 2-connected. In higher-dimensional subsets of a $(3N-6)$-dimensional configuration space M, many, complicated combinations of one-, two-,... $(3N-7)$-dimensional connectedness properties may occur. However, as shown later, catchment regions cannot have complicated connectedness properties in any dimension.

Since in most actual cases there are many catchment regions within the configuration space, our goal is to use a description that is general enough to handle all regions of this multidimensional space. Since M is not a vector space, the usual, chemically motivated internal coordinates are applicable only locally. On the other hand, the manifold-theoretical description provides proper families of compatible coordinate systems within space M, and by introducing a differentiable manifold structure, the potential energy hypersurface can globally represent the force field of the given stoichiometric family of the complete set of all the chemical species associated with the given set of nuclei which define the configuration space [11]. That is, the differentiable manifold description is universal enough to handle the force fields of all possible species, in all possible conformations, as long as the same set of nuclei is involved. These properties are essential for a mutually compatible representation of catchment regions, since steepest descent paths, hence gradients, are required for their definitions.

Intuitively, it is natural to expect that all catchment regions $C(\lambda, i)$ have relatively simple topological struc-

tures, and one might assume that each catchment region $C(\lambda, i)$ of index λ is homeomorphic to a λ-dimensional open ball. Although multidimensional potential energy hypersurfaces do provide surprises, in this case the expectation of simplicity is justified, and the following result can be proven:

2.1 Catchment region connectedness theorem

Consider a potential energy hypersurface $E(K)$ defined over an internal nuclear configuration space M, where $E(K)$ is assumed to be twice differentiable, and furthermore it is assumed to have no degenerate critical points. Then each catchment region $C(\lambda, i)$ of $E(K)$ is simply k-connected for each dimension $k, 0 \leq k \leq 3N - 6 - \lambda$.

2.1.1 Comments

The restriction on differentiability and the exclusion of degenerate critical points are not very severe constraints, since the potential energy hypersurface $E(K)$ for any set of a stoichiometric family of chemical species can be approximated arbitrarily closely by a function which satisfies these constraints [11]. In particular, at conical intersections or seams of intersections, where differentiability is locally violated, these properties can be ensured by a simple transformation involving arbitrarily small local deformations [11]. In fact, the potential energy hypersurface can be converted by such small deformations into a function that is a "Morse function" [22–24], fulfilling all these constraints, and also providing an opportunity to apply some of the powerful tools of calculus on manifolds and algebraic topology [25–27]. These methods lead to a quantum chemical interpretation of reaction mechanisms using an energy-dependent algebraic-topological structure, the fundamental group of reaction mechanisms [11]. Just like point symmetry groups represent some of the most essential information in molecular shape analysis, the energy-dependent fundamental groups of reaction mechanisms represent some of the most essential information on the interrelations between reaction mechanisms [11].

Based on the properties of differentiability and nondegeneracy of critical points, a simple combination of the critical level set topology [10] and the catchment region topology [7] provides the proof.

2.1.2 Proof

1. Each catchment region $C(\lambda, i)$ must be 1-connected, that is, it must be pathwise-connected, since according to the definition of catchment regions, each point K of the catchment region is the origin of a steepest descent path within $C(\lambda, i)$ that leads to the unique critical point $K(\lambda, i)$ within $C(\lambda, i)$.

Take any two conformations K and K' from a catchment region $C(\lambda, i)$,

$$K, K' \in C(\lambda, i) \ , \tag{9}$$

then

$$K \, \eta \, K' \tag{10}$$

which implies that for the two steepest descent paths $P(K, u)$ and $P(K', u)$ of origins $P(K, 0) = K$ and $P(K', 0) = K'$, respectively, the endpoints coincide with the unique critical point $K(\lambda, i)$ within $C(\lambda, i)$:

$$P(K, 1) = P(K'1) = K(\lambda, i) \ . \tag{11}$$

Consequently, point K is pathwise-connected to point K' within $C(\lambda, i)$ by a path $P(K, K', u)$ that is obtained as the path $P(K, u)$ followed by the inverse path $P^{-1}(K', u)$ of path $P(K, u)$, that is, by a so-called product path that leads from K to K'

$$P(K, K', u) = P(K, u)P^{-1}(K', u) \ . \tag{12}$$

Since this holds for all point-pairs K and K' within $C(\lambda, i)$, the catchment region $C(\lambda, i)$ is 1-connected.

2. In order to show that $C(\lambda, i)$ is not only 1-connected but simply k-connected for every dimension k, $0 \leq k \leq \lambda$, we shall use a combination of some of the open sets of the critical level topology [10] and the catchment region topology [7] of potential energy hypersurfaces. Furthermore, in order to be able to apply some of the tools we shall use in the proof, the part of the potential energy hypersurface studied must be defined on a compact, orientable manifold, whereas the internal configuration space M is not in general compact [11]. Nevertheless, level sets with sufficiently low energy bounds are compact, and the compactness property is either directly inherited, or can be achieved by a simple transformation for all those sets of nuclear configurations which are needed in the proof.

A closed level set $F_{E(K)}(A)$ of the nuclear configuration space M, with respect to a given potential energy hypersurface $E(K)$ and an energy bound A is defined as the collection of all those nuclear arrangements K in the nuclear configuration space M which have energies less than or equal to the energy threshold A:

$$F_{E(K)}(A) = \{K : E(K) \leq A\} \tag{13}$$

A level set restricted to a catchment region $C(\lambda, i)$ is the intersection of the two sets:

$$\begin{aligned} F_{E(K),C(\lambda,i)}(A) &= \{K : E(K) \leq A, \, K \in C(\lambda, i)\} \\ &= F_{E(K)}(A) \cap C(\lambda, i) \ . \end{aligned} \tag{14}$$

Such a restricted level set $F_{E(K),C(\lambda,i)}(A)$ is either compact, or can be converted into a compact set by a technique analogous to the Alexandrov one-point compactification, as described in Ref. [11]. If a compactification step is required, then the topological relations between the original, restricted level set $F_{E(K),C(\lambda,i)}(A)$ and its compactified counterpart are well defined, and are easily tractable [11]. Consequently, in the following it will be sufficient to consider the more common case of compact restricted level set $F_{E(K),C(\lambda,i)}(A)$.

A critical level set is a set $F_{E(K)}(A)$ where the energy threshold A is a value that corresponds to the energy of a critical point $K'(\lambda, i)$ of the potential energy hypersurface $E(K)$.

Within each catchment region $C(\lambda, i)$, the critical point $K(\lambda, i)$ of the catchment region $C(\lambda, i)$ is the nuclear arrangement of lowest energy:

$$E(K(\lambda, i)) \leq E(K),\ K \in C(\lambda, i)\ . \tag{15}$$

Consequently, for every energy bound for which the restricted level set $F_{E(K),C(\lambda,i)}(A)$ is nonempty, the critical point $K(\lambda, i)$ is an element of the restricted level set $F_{E(K),C(\lambda,i)}(A)$,

$$K(\lambda, i) \in F_{E(K),C(\lambda,i)}(A), \quad \text{if } F_{E(K),C(\lambda,i)}(A) \neq \varnothing\ . \tag{16}$$

Now we shall show that each restricted level set $F_{E(K),C(\lambda,i)}(A)$ is also pathwise-connected. If two conformations K and K' are chosen from the restricted level set $F_{E(K),C(\lambda,i)}(A)$, then

$$E(K) \leq A \tag{17}$$

and

$$E(K') \leq A\ . \tag{18}$$

Furthermore, since the catchment region $C(\lambda, i)$ itself is pathwise-connected and since the paths $P(K, u)$ and $P(K', u)$ of origins $P(K, 0) = K$ and $P(K', 0) = K'$ are steepest descent paths, it follows that any point of each path must have energy bounded by A. That is, if

$$K'' \in P(K, u) \tag{19}$$

or if

$$K'' \in P(K', u)\ , \tag{20}$$

then

$$E(K'') \leq A\ , \tag{21}$$

hence

$$K'' \in F_{E(K),C(\lambda,i)}(A)\ . \tag{22}$$

The endpoints of these paths $P(K, u)$ and $P(K', u)$ coincide with the unique critical point $K(\lambda, i)$ of $C(\lambda, i)$, that falls within $F_{E(K),C(\lambda,i)}(A)$:

$$P(K, 1) = P(K') = K(\lambda, i)\ . \tag{23}$$

Consequently, point K is pathwise-connected to point K' within $F_{E(K),C(\lambda,i)}(A)$ by a path $P(K, K', u)$ obtained as the path $P(K, u)$ followed by the inverse path $P^{-1}(K', u)$ of path $P(K', u)$, formally denoted as their product path:

$$P(K, K', u) = P(K, u)P^{-1}(K', u)\ . \tag{24}$$

This holds for all point-pairs K and K' within $F_{E(K),C(\lambda,i)}(A)$; consequently, the restricted level set $F_{E(K),C(\lambda,i)}(A)$ is 1-connected.

Since the critical point $K(\lambda, i)$ is nondegenerate, there must exist some small enough positive energy increment ΔA, $\Delta A > 0$, such that the restricted level set $F_{E(K),C(\lambda,i)}(A_0 + \Delta A)$, where

$$A_0 = E(K(\lambda, i))\ , \tag{25}$$

is simply k-connected for every dimension k, $0 \leq k \leq 3N - 6 - \lambda$.

Select one such dimension k. Contrary to the statement of the theorem, assume that $C(\lambda, i)$ is multiply k-connected. Take the energy threshold $A_1(k)$ as the lowest value where the k-connectedness of the restricted level set $F_{E(K),C(\lambda,i)}(A)$ changes from simply k-connected to multiply k-connected. If no such energy value exists, then the catchment region $C(\lambda, i)$ is simply k-connected. Otherwise, if such a lowest energy threshold $A_1(k)$ exists, then the corresponding restricted level set $F_{E(K),C(\lambda,i)}(A_1(k))$ must be a critical level set, such that $F_{E(K),C(\lambda,i)}(A_1(k))$ contains a critical point $K(\lambda', i')$, such that

$$K(\lambda', i') \neq K(\lambda, i)\ , \tag{26}$$

$$K(\lambda', i') \in F_{E(K),C(\lambda,i)}(A_1(k))\ , \tag{27}$$

and

$$E(K(\lambda', i')) = A_1(k)\ , \tag{28}$$

since for a Morse function, such as the energy function $E(K)$ within $F_{E(K),C(\lambda,i)}(A^1, (k))$, connectedness can change only at a critical level. However, each catchment region contains precisely one critical point, that must be $K(\lambda, i)$ in $C(\lambda, i)$; consequently, Eqs. (26) and (27) cannot hold simultaneously – a contradiction. Consequently, $C(\lambda, i)$ cannot be multiply k-connected. Since $F_{E(K),C(\lambda,i)}(A_0 + \Delta A)$ is simply k-connected, one concludes that $C(\lambda, i)$ is also simply k-connected.

This conclusion is general for all dimensions k, $0 \leq k \leq 3N - 6 - \lambda$, that proves the statement of the theorem: each catchment region $C(\lambda, i)$ is simply k-connected for all dimensions k, $0 \leq k \leq 3N - 6 - \lambda$.

Homotopy groups, among them the one-dimensional homotopy group of reaction mechanisms, or conformational rearrangement mechanisms, are algebraic-topological descriptors of the structure of various regions of the potential energy hypersurface [11]. These groups can be restricted to local ranges, for example, to individual catchment regions. The result concerning the connectedness types of catchment regions proven above implies that all the homotopy groups of catchment regions are very simple: they are all trivial groups, for all dimensions k, $0 \leq k \leq 3N - 6 - \lambda$. Specifically, the one-dimensional homotopy group, that is, the fundamental group of reaction mechanisms restricted to any catchment region is necessarily the trivial group. This is an intuitively satisfying result that coincides with the expectation of uninhibited conformational changes within a catchment region, that is, within the family of nuclear arrangements preserving chemical identity. In other words, within a catchment region there are no topological constraints beyond the topological relations between neighboring catchment regions and energy alone influences the pattern of conformational rearrangements. The universality of this result for all catchment regions provides a topological version of the unique extension property of local geometrical ranges of potential energy hypersurfaces to a global hypersurface.

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