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The Topology of Energy Hypersurfaces II. Reaction Topology in Euclidean Spaces

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By introducing equivalence classes of critical points of potential energy hypersurfaces a unique topological space, Reaction Topology $({}^{3N}E, \mathbf{T}_C)$ is defined over an *Euclidean nuclear configuration space* ${}^{3N}E$ for a system of N nuclei and k electrons. Relations between the topological concepts of molecular structure and reaction mechanism are analyzed. Topological equivalences between Euclidean and Riemannian representations of nuclear configuration spaces are exploited for the analysis of quantum mechanical reaction networks of all possible chemical reactions over the given potential energy hypersurface.

Key words: Potential energy surfaces – Computer-aided synthesis design – Quantum chemical synthesis design – Reaction mechanism – Reaction networks.

1. Introduction

Differential and algebraic topology form a powerful and nearly encompassing framework for modern mathematics, suitable for providing the foundations for many, seemingly most diverse branches of mathematical disciplines [1, 2]. In this study we shall describe an application of topology to a quantum chemical problem: to the global analysis of the Born–Oppenheimer [3] energy functional of chemically reacting systems [4–8][1]. For this end, we shall choose a conceptually and mathematically simpler approach than in earlier Riemannian space studies[4–6], as topologies and the notions of chemical structure and reaction mechanisms will be introduced in an *Euclidean* nuclear configuration space

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[1] See Ref. [8] for part I of this study.

where some difficulties associated with an internal coordinate description can be avoided.

In the rigorous quantum mechanical description of molecules and chemical reactions electrons and nuclei are treated on an equal basis as quantal particles or wave-packets. In general, quantum mechanical probability distributions and expectation values replace the classical concept of *position*, consequently, the primary quantum chemical concepts are nuclear and electronic probability distributions rather than nuclear and electronic "positions". Such probability distributions can be represented as *open sets* of an abstract configuration space. The most general mathematical theory of open sets is *topology*, suggesting that classical *geometrical concepts* can be replaced by *topological concepts* in most areas of molecular physics [4–8]. Topology is the most natural mathematical framework for the *global analysis* and interpretation of the results of molecular quantum mechanics, relevant to stereochemistry, conformational analysis and reaction mechanisms.

The purpose of our studies is the development of a global topological theory of conformational changes and chemical reactions. The underlying principle is the replacement of *points* of the nuclear configuration space, as fundamental entities, by *open sets* of the space [4–6, 8]. In the resulting topologization only the fundamental *global* properties and relations, relevant to conformational processes and chemical reactions, are retained, and some of the geometrical information is ignored. Nevertheless, by introducing a differentiable manifold structure into the topological space [6, 7] all the desired geometrical concepts can be re-introduced in a consistent and convenient way, suitable e.g. for a vibrational normal coordinate analysis within various open sets. Thus we may have the best of both worlds: a *topological model* for the *global analysis* of the maze of all possible reaction mechanisms over a multidimensional potential energy hypersurface [8], and a *manifold model* of *local coordinate neighbourhoods* for the utilization of geometrical and metric concepts in a vibrational analysis of small domains of the hypersurface [6, 7].

The motivation for the development of a topological theory is twofold: on the one hand, the topological model gives a convenient quantum mechanical interpretation of molecular structure and reaction mechanism [4–6, 8], and on the other hand, it has predictive potential in determining suitable synthetic routes in complex reaction networks [5].

The topological model of molecules is much closer to the quantum mechanical reality than the usual geometrical model. The conventional geometrical model of molecules, often visualized as nuclear masses interconnected by springs representing chemical bonds, gives the false impression of strong analogies with macroscopic vibrating systems where classical mechanics applies. A variety of correction terms (anharmonic correction, libration correction, etc.) is required to make the classical concepts of "bond length" and "bond angle", *and their values measured* using various techniques, compatible with the quantum mechanical description of vibrating molecules. In the quantum mechanical model the wave packet representation of nuclei and the probabilistic interpretation of bond length and bond angle are very different from the analogous concepts based on the essentially classical, geometrical model. Most figures depicting the results of X-ray diffraction studies of molecular structures show ellipsoids (open sets!) rather than precise nuclear positions. A topological interpretation of such experimental results is certainly more appropriate than a geometrical one. Topology gives clear-cut quantum mechanical definitions for molecular structure and reaction mechanism, [4, 6] which are the two most fundamental concepts of chemistry.

The predictive power of the topological model stems from its exceptional potential to simplify complicated mathematical structures. The vast complexity of various features of potential energy hypersurfaces of higher dimensions renders both their direct calculation and their subsequent analysis by conventional geometrical methods extremely time consuming and cumbersome. The topological model, however, has several advantages. Whereas on the one hand it offers only a modest simplification in the computations (instead of the energy hypersurface of dimension n, only the *boundaries of open sets* need to be calculated, which have dimensions at most $n-1$), on the other hand, the subsequent analysis of the chemically important global features becomes quite simple. The results of the global analysis are expected to find important applications in experimental chemistry and chemical industry. The global topological description of potential energy hypersurfaces of higher dimensions is the natural basis for the determination and analysis of *reaction networks* [5], important in *computer aided synthesis design*, whenever simple inspection fails due to our inability to visualize highly interwoven multidimensional networks several theorems have been proven on topological reaction networks and on properties of "shortest" reaction mechanisms [5]. These theorems lead to easily programmable algorithms for the determination of feasible synthetic routes [5].

Topology ("rubber geometry") also appears to be an ideal mathematical tool to describe the most essential features of non-rigid systems in semi-classical theory. It has been shown [4–8] that a topological model arising naturally in abstract configuration spaces of rigorous quantum mechanics can be implemented at the approximate level of the Born–Oppenheimer model [3]. In the proposed model the concepts of molecular structure and reaction mechanism correspond to open sets of a topological space $({}^{n}R, \mathbf{T}_C)$, defined over a Riemannian nuclear configuration space ${}^{n}R$ [4, 6]. Properties of differentiable manifolds [6] have been exploited to derive upper and lower bounds for the numbers of all possible molecular structures and reaction mechanisms on energy hypersurfaces [7].

In the present study we shall analyze the topological properties of an *Euclidean* nuclear configuration space. In the earlier manifold theoretical model of energy hypersurfaces [6] homeomorphisms were defined which linked the Riemannian representation of the nuclear configuration space ${}^{n}R$ to *local* Euclidean representations by defining suitable differentiable manifolds and their submanifolds. In the present work a more direct approach will be used: direct topologization of a ${}^{3N}E$ Euclidean nuclear configuration space. This model has a more direct physical interpretation than the Riemannian space referred to above[4], and it has some further advantages. In contrast to the Riemannian representation, analogies with the familiar 3-dimensional real space are readily exploited. In the Euclidean configuration space model the topological concepts of molecular structure and reaction mechanism are easier to develop and much simpler to visualize. Furthermore, in the Euclidean representation a conceptually simple algorithm can be given for the actual construction of a unique Reaction Topology.

In particular, in this study we shall investigate the following problems:

(1) *equivalence classes of critical points* of energy hypersurfaces defined over a $3N$ dimensional Euclidean nuclear configuration space ${}^{3N}E$, where N is the number of nuclei,

(2) conditions for the determination of subsets of ${}^{3N}E$ which correspond to the above equivalence classes,

(3) homotopy classes in the set of *all possible reaction paths* over the energy hypersurface E

(4) the existence of a *unique Reaction Topology* $({}^{3N}E, \mathbf{T}_C)$ on ${}^{3N}E$ for each specified electronic state

(5) conditions for the *topological equivalence* of Reaction Topology $({}^{3N}E, \mathbf{T}_C)$ in ${}^{3N}E$ and the catchment region topology [8] $({}^{n}R, \mathbf{T}_C)$ in Riemannian space ${}^{n}R$.

(6) topological definitions of *reaction mechanisms* and *quantum mechanical reaction networks* in Euclidean space ${}^{3N}E$ and the utilization of the topological equivalence noted in (5) for the analysis of the set of all possible reactions on the energy hypersurface.

Most of the elementary topological and manifold-theoretical definitions and concepts used in this study are given in Refs. [4–8]; for a more thorough exposition of the relevant mathematics the reader should consult Refs. [1, 2]. Some of the present (and earlier) results are built upon the differential-geometrical studies of Fukui [9, 10] and Tachibana and Fukui [11, 12], as well as on some general results of differential geometry [13]. Intersection properties of energy hypersurfaces, important in earlier [4–8] and in the present topologizations, are discussed in references [14–16].

2. Equivalence Classes of Critical Points in Euclidean Space ${}^{3N}E$

Following the familiar definition of coordinate systems used in molecular dynamics studies [17, 18], we assume that the $3N$ dimensional Euclidean nuclear configuration space ${}^{3N}E$ is spanned by the mass-weighted Cartesian coordinates $\{\boldsymbol{e}_i\}$ of the N nuclei. The (unweighted) Cartesian coordinates of the individual nuclei refer to a fixed laboratory frame. The component x^i of point $\boldsymbol{x} \in {}^{3N}E$ along coordinate $\boldsymbol{e}_i$ is given by

$$x^i = \sqrt{m_\alpha}\, A_{\alpha j}, \tag{1}$$

$$i = 3(\alpha - 1) + j, \qquad j = 1, 2, 3. \tag{2}$$

Here the laboratory-frame Cartesian coordinates of nucleus α are

$$A_{\alpha 1} = X_\alpha \tag{3}$$

$$A_{\alpha 2} = Y_\alpha \tag{4}$$

$$A_{\alpha 3} = Z_\alpha, \tag{5}$$

for each $\alpha = 1, \ldots N$, and m_α is the mass of nucleus α.

The usual Euclidean metric defines the metric topology [1, 2] $\mathbf{T}$ on ${}^{3N}E$, and distance, angles, orthogonality, and open sets will refer to this metric unless stated otherwise.

The Born–Oppenheimer energy functional $E(\boldsymbol{x})$ for a given electronic state of the molecule of N nuclei is assumed to be defined above ${}^{3N}E$. We shall also assume that $E(\boldsymbol{x})$ is twice continuously differentiable at all points of ${}^{3N}E \backslash D_{\text{excl}}$ where subset $D_{\text{excl}} \subset {}^{3N}E$, is defined by

$$D_{\text{excl}} = \bigcup_{\gamma} G(\boldsymbol{x}_\gamma, \rho). \tag{6}$$

Here $\boldsymbol{x}_\gamma$ is either a point corresponding to identical three-space (laboratory frame) positions for two or more nuclei, or a point where $E(\boldsymbol{x})$ is not twice continuously differentiable (e.g. $\boldsymbol{x}_\gamma$ is a point where a conical intersection of two potential hypersurfaces [12–14] occurs). The ρ radius of open balls $G(\boldsymbol{x}_\gamma, \rho)$ is a small positive value. (The analogous definition for D_{excl} in Riemannian space ${}^{n}R$ has been given elsewhere [4], where openness has been defined in terms of Riemannian metric g_{ij}, rather than in terms of an Euclidean metric.)

At every point $\boldsymbol{x} \in {}^{3N}E \backslash D_{\text{excl}}$ the gradient

$$\boldsymbol{g}(\boldsymbol{x}) = \boldsymbol{\nabla} E(\boldsymbol{x}) \tag{7}$$

is well defined. Due to the choice of the mass weighted coordinates, $-\boldsymbol{g}(\boldsymbol{x})$ represents the direction of steepest descent on the energy hypersurface, i.e. the "force" acting upon a hypothetical "particle" at point $\boldsymbol{x}$, moving infinitely slowly. The components of this $3N$ dimensional "force" vector correspond to the components of all the laboratory-frame forces of relaxation acting upon the nuclei in the 3-space conformation specified by point $\boldsymbol{x} \in {}^{3N}E$.

Points $\boldsymbol{c} \in {}^{3N}E$, where

$$\boldsymbol{g}(\boldsymbol{c}) = \boldsymbol{0} \tag{8}$$

are the critical points of $E(\boldsymbol{x})$. The critical points are of particular importance, since the corresponding three-space nuclear configurations represent stationary conformations (energy minima, various saddle points, e.g. transition structures, or maxima) of the molecule.

All critical points $\boldsymbol{c}$ can be characterized by the Hessian matrix $\boldsymbol{H}(\boldsymbol{c})$ of the second derivatives of $E(\boldsymbol{x})$ at $\boldsymbol{x}=\boldsymbol{c}$,

$$H_{ij}(\boldsymbol{c})=\left.\frac{\partial^2 E(\boldsymbol{x})}{\partial x^i \partial x^j}\right|_{\boldsymbol{x}=\boldsymbol{c}}. \tag{9}$$

If the rank of $\boldsymbol{H}(\boldsymbol{c})$ is $3N-k$ $(k>0)$ then $\boldsymbol{c}$ is a k-fold degenerate critical point. Index λ of $\boldsymbol{c}$ is the number of negative eigenvalues of $\boldsymbol{H}(\boldsymbol{c})$. Index values $\lambda=0,1,2,\ldots,3N$ for a general function $E(\boldsymbol{x})$ defined over a $3N$-dimensional space correspond to minimum, saddle point of transition structure ("transition state"), saddle point of index $2,\ldots$, maximum, respectively. However, as it is easily shown, for a general polyatomic molecule in the Euclidean representation, no non-degenerate maximum of energy $E(\boldsymbol{x})$ (as defined by $\lambda=3N$) can exist, in fact $\lambda\leq 3N-6$ for every λ.

In the limit of infinitely slow nuclear motion no isolated critical point $\boldsymbol{c}\in {}^{3N}E$ can exist. If $\boldsymbol{c}$ is a critical point of index λ then $\boldsymbol{c}$ must belong to an at least 6 dimensional connected subset $K_c\subset {}^{3N}E$, every element of which is also a critical point of the same index λ:

$$\boldsymbol{g}(\boldsymbol{x})=\boldsymbol{0}, \qquad \lambda(\boldsymbol{x})=\lambda(\boldsymbol{c}) \quad \text{if } \boldsymbol{x}\in K_c. \tag{10}$$

(Throughout the paper number 6 appearing in various expressions should be replaced by 5 if diatomics are considered). The existence of such subset K_c follows immediately from the observation, that the three translational and three rotational degrees of freedom of the molecule as a whole do not affect the Born-Oppenheimer energy. Consequently, each critical point $\boldsymbol{c}\in {}^{3N}E$ must be at least 6-fold degenerate. If this degeneracy is *only* 6-fold, then K_c is a 6-dimensional connected subset in ${}^{3N}E$ which can be generated from *any* critical point $\boldsymbol{c}\in K_c$ by the following procedure:

(1) A 3-dimensional hyperplane L_c containing $\boldsymbol{c}$ is defined by

$$L_c=\{\boldsymbol{x}:\boldsymbol{x}=\boldsymbol{c}+\sum_{j=1}^{3}\beta_j\boldsymbol{y}_j\}. \tag{11}$$

Here parameters β_j can take any real values,

$$-\infty\leq\beta_j\leq\infty, \qquad j=1,2,3 \tag{12}$$

and vectors $\boldsymbol{y}_1$, $\boldsymbol{y}_2$ and $\boldsymbol{y}_3$ correspond to unit vectors of translation in the laboratory frame, along X, Y and Z, respectively, as applied simultaneously to *all* nuclei. Vectors $\{\boldsymbol{y}_j\}$ are given by

$$\boldsymbol{y}_1'=(\sqrt{m_1},0,0,\sqrt{m_2},0,0,\ldots,\sqrt{m_N},0,0) \tag{13}$$

$$\boldsymbol{y}_2'=(0,\sqrt{m_1},0,0,\sqrt{m_2},0,\ldots,0,\sqrt{m_N},0) \tag{14}$$

and

$$\boldsymbol{y}_3'=(0,0,\sqrt{m_1},0,0,\sqrt{m_2},\ldots,0,0,\sqrt{m_N}) \tag{15}$$

where ′ means transpose. Alternatively, in tensorial notation the formal contravariant components of vectors $\boldsymbol{y}_j = \boldsymbol{y}_{(j)}$ ($j = 1, 2, 3$) can be written as

$$y^i_{(j)} = \sqrt{m_\alpha}\delta_{jk} \tag{16}$$

where

$$\alpha = [(i-1)/3]+1, \tag{17}$$

$$k = i - 3(\alpha - 1), \tag{18}$$

and $[x]$ is the largest integer not exceeding x (entier function). Clearly, vectors $\boldsymbol{y}_1$, $\boldsymbol{y}_2$ and $\boldsymbol{y}_3$ are pairwise orthogonal in ${}^{3N}E$, hence are linearly independent. Consequently, L_c is indeed a 3-dimensional hyperplane in ${}^{3N}E$.

Hyperplanes L_c are used in the construction of sets K_c:

(2) K_c is given as the subset of points in ${}^{3N}E$ obtained by *all* possible rotations (within the laboratory frame) of the 3-space nuclear arrangements corresponding to *all* points $\boldsymbol{x} \in L_c$. The overall effect of an arbitrary translation and rotation about an arbitrary axis by any angle in the laboratory frame can always be reproduced by a translation in the same frame and three subsequent rotations about the three *cartesian axes* of the laboratory frame.

It is convenient to replace the 3-space rotations along the 3 coordinate axes of the laboratory frame by 3 transformations, denoted by $T_j(\theta_j)$, $j = 1, 2, 3$, acting directly on the $3N$ dimensional vectors $\boldsymbol{x} \in L$. The corresponding $\boldsymbol{T}_j(\theta_j)$ matrices are block-diagonal with 3×3 blocks representing 3-dimensional rotations by angle θ_j along laboratory frame axes X, Y, Z for $j = 1, 2, 3$, respectively:

$$\begin{aligned}(\boldsymbol{T}_j(\theta_j))_{rp} = {} & \delta_{rp}(\cos\theta_j + (1-\cos\theta_j)\delta_{kq}) + \sin\theta_j(\delta_{1j}(\delta_{rp+1}\delta_{0q} - \delta_{r+1p}\delta_{0s}) \\ & + \delta_{2j}(\delta_{rp+2}\delta_{0q} - \delta_{r+2p}\delta_{0s}) + \delta_{3j}(\delta_{rp+1}\delta_{2q} - \delta_{r+1p}\delta_{2s}))\end{aligned} \tag{19}$$

where

$$k = j \bmod 3 \tag{20}$$

$$q = r \bmod 3 \tag{21}$$

$$s = p \bmod 3. \tag{22}$$

With the above notations, K_c is obtained as

$$K_c = \{\boldsymbol{x} : \boldsymbol{x} = \boldsymbol{T}_1(\theta_1)\boldsymbol{T}_2(\theta_2)\boldsymbol{T}_3(\theta_3)\boldsymbol{x}_L,\ \boldsymbol{x}_L \in L_c,\ 0 \leq \theta_1, \theta_2, \theta_3 < 2\pi\}. \tag{23}$$

In each K_c set we may choose *one* critical point $\boldsymbol{c}^{(\tau)}$ and we may regard the corresponding $K_c(\tau)$ set a pointed set with distinguished element $\boldsymbol{c}^{(\tau)}$,

$$\boldsymbol{c}^{(\tau)} \in K_c(\tau). \tag{24}$$

Since each critical point of $E(\boldsymbol{x})$ belongs to one and to only one of the $K_c(\tau)$ sets, the set C of all critical points can be partitioned into equivalence classes by

$$C = \bigcup_{\tau} K_c(\tau) \tag{25}$$

where $\tau \in t$ for an index set t.

Set D_{excl} (Eq (6)) is not necessarily a connected subset of ${}^{3N}E$, and in general it may be partitioned into its maximum connected components:

$$D_{\text{excl}} = \bigcup_{\kappa} D_{\text{excl}}^{(\kappa)}. \tag{26}$$

One may choose one point $\boldsymbol{d}^{(\kappa)}$ in each $D_{\text{excl}}^{(\kappa)}$,

$$\boldsymbol{d}^{(\kappa)} \in D_{\text{excl}}^{(\kappa)} \tag{27}$$

and regard maximum connected components $D_{\text{excl}}^{(\kappa)}$ as pointed sets with distinguished elements $\boldsymbol{d}^{(\kappa)}$.

The following topological treatment is the simplest if we assume that for finite molecular systems indices τ and κ form countable sets. This assumption is valid if the maximum connected components of set C are the sets $K_c(\tau)$ of the union in Eq. (25). This condition is realized e.g. if the maximum degeneracy for critical points of $E(\boldsymbol{x})$ is 6-fold, since then necessarily

$$\bar{K}_c(\tau) \bigcap \bar{K}_c(\tau') = \emptyset \tag{28}$$

for every τ, τ', $\tau \neq \tau'$. On the other hand, if Eq. (28) is not satisfied for certain $K_c(\tau)$ sets of highly degenerate critical points then partitioning (25) may be re-defined in terms of maximum connected components $K'_c(\tau)$ of set C as

$$C = \bigcup_{\tau'} K'_c(\tau'). \tag{29}$$

Here each $K'_c(\tau')$ can be represented as a union of some of the original $K_c(\tau)$ sets:

$$K'_c(\tau') = \bigcup_{\tau \in t'} K_c(\tau) \tag{30}$$

where t' is a subset of index set t. By choosing *one* of the critical points of set $\{\boldsymbol{c}^{(\tau)}\}_{\tau \in t'}$ as distinguished element $\boldsymbol{c}^{(\tau')}$, $K'_c(\tau')$ is a pointed set. For such highly degenerate cases we shall assume countability for sets in union (29) rather than for those of union (25).

Eq. (25), or for highly degenerate cases Eq. (29)[2], corresponds to a countable equivalence class partitioning of the set C of all critical points of $E(\boldsymbol{x})$, defined over ${}^{3N}E$. These equivalence classes, together with maximum connected components $D_{\text{excl}}^{(\kappa)}$ of D_{excl}, will serve as the starting point for the introduction of a unique Reaction Topology $({}^{3N}E, \mathbf{T}_C)$ into the Euclidean nuclear configuration space ${}^{3N}E$.

3. Molecular Structures as Equivalence Classes in Euclidean Space ${}^{3N}E$

The gradient $\boldsymbol{g}(\boldsymbol{x})$ of energy hypersurface $E(\boldsymbol{x})$ is well defined and non-zero at every point $\boldsymbol{x}$ in the complement of $C \cup D_{\text{excl}}$,

$$\boldsymbol{x} \in {}^{3N}E \backslash (C \cup D_{\text{excl}}) \tag{31}$$

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[2] In the following discussion no direct reference will be made to union (29) with the understanding that sets in union (29) are to replace sets in union (25) in all highly degenerate cases.

furthermore, to every such point $\boldsymbol{x}$ a unique steepest descent path $P_{\boldsymbol{x}}$ can be assigned. Since $E(\boldsymbol{x})$ is bounded from below, each path $P_{\boldsymbol{x}}$ must have its extremity $\boldsymbol{e}(P_{\boldsymbol{x}})$ in set $C \cup D_{\text{excl}}$,

$$\boldsymbol{e}(P_{\boldsymbol{x}}) \in C \cup D_{\text{excl}}. \tag{32}$$

Due to partitionings (25) and (26) for any given $P_{\boldsymbol{x}}$ either

$$\boldsymbol{e}(P_{\boldsymbol{x}}) \in K_c(\tau) \tag{33}$$

or

$$\boldsymbol{e}(P_{\boldsymbol{x}}) \in D_{\text{excl}}^{(\kappa)} \tag{34}$$

for one and only one index τ or κ, respectively.

The set P of all steepest descent paths

$$P = \{P_{\boldsymbol{x}} : \boldsymbol{x} \in {}^{3N}E \backslash (C \cup D_{\text{excl}})\} \tag{35}$$

can be partitioned into equivalence classes according to the equivalence classes $K_c(\tau)$ of critical points and maximum connected components $D_{\text{excl}}^{(\kappa)}$ of D_{excl}. The set of all steepest descent paths with extremities in a given $K_c(\tau)$ or $D_{\text{excl}}^{(\kappa)}$ forms the equivalence class $P(\boldsymbol{c}^{(\tau)})$ or, $P(\boldsymbol{d}^{(\kappa)})$, respectively:

$$P(\boldsymbol{c}^{(\tau)}) = \{P_{\boldsymbol{x}} : \boldsymbol{e}(P_{\boldsymbol{x}}) \in K_c(\tau)\} \tag{36}$$

$$P(\boldsymbol{d}^{(\kappa)}) = \{P_{\boldsymbol{x}} : \boldsymbol{e}(P_{\boldsymbol{x}}) \in D_{\text{excl}}^{(\kappa)}\}. \tag{37}$$

Paths from a given equivalence class $P(\boldsymbol{c}^{(\tau)})$ are physically equivalent in the sense that they all lead to the same set $K(\boldsymbol{c}^{(\tau)})$ of critical points, which points are physically equivalent if one disregards translation and rotation of the molecule *as a whole* in the laboratory frame. An analogous interpretation is valid for paths from any equivalence class of the $P(\boldsymbol{d}^{(\kappa)})$ type.

The above equivalence classes of set P induce an equivalence class partitioning of the entire Euclidean nuclear configuration space ${}^{3N}E$. These equivalence classes are defined as

$$C(\boldsymbol{c}^{(\tau)}) = \{\boldsymbol{x} : P_{\boldsymbol{x}} \in P(\boldsymbol{c}^{(\tau)})\} \cup K_c(\tau) \tag{38}$$

and

$$C(\boldsymbol{d}^{(\kappa)}) = \{\boldsymbol{x} : P_{\boldsymbol{x}} \in P(\boldsymbol{d}^{(\kappa)})\} \cup D_{\text{excl}}^{(\kappa)} \tag{39}$$

for the two types of sets of extremities, respectively.

From any point $\boldsymbol{x}$ within $C(\boldsymbol{c}^{(\tau)})$ either there is a unique steepest descent path $P_{\boldsymbol{x}}$ which leads into set $K_c(\tau)$ or point $\boldsymbol{x}$ itself is an element of set $K_c(\tau)$. Consequently, equivalence class $C(\boldsymbol{c}^{(\tau)})$ can be regarded as the *catchment region for set* $K_c(\tau)$ in the Euclidean space ${}^{3N}E$. Similarly, equivalence class $C(\boldsymbol{d}^{(\kappa)})$ is the *catchment region for set* $D_{\text{excl}}^{(\kappa)}$. The catchment region terminology follows from a direct analogy with geographical catchment regions and watersheds.

The above definitions of catchment regions in the ${}^{3N}E$ Euclidean nuclear configuration space model, Eqs. (38), (39), reflect the principal differences between the present and the earlier Riemannian space models [4]. Whereas catchment regions in Riemannian space ${}^nR$ are basins associated with *point attractors* [4], in the present model the formal point attractors are replaced by entire *sets of equivalent critical points*. More importantly, in the ${}^{3N}E$ Euclidean space model there is a direct correspondence and a simple and unique transformation between the actual physical paths of the nuclei in the laboratory frame and paths $P_x \subset {}^{3N}E$.

Transformations within equivalence classes $K_c(\tau)$ and $D_{\text{excl}}^{(\kappa)}$ can be given explicitly be defining translation operators $Y_i(\beta_i)$, $i = 1, 2, 3$ and $Y(\boldsymbol{\beta})$ as

$$Y_i(\beta_i)\boldsymbol{x} = \boldsymbol{x} + \beta_i \boldsymbol{y}_i, \qquad i = 1, 2, 3 \tag{40}$$

and

$$Y(\boldsymbol{\beta})\boldsymbol{x} = Y_1(\beta_1)Y_2(\beta_2)Y_3(\beta_3)\boldsymbol{x}. \tag{41}$$

Here vectors $\boldsymbol{y}_i$, $i = 1, 2, 3$, are those given in Eqs. (13), (41), (15), respectively, and vector $\boldsymbol{\beta}$ is given as

$$\boldsymbol{\beta}' = (\beta_1, \beta_2, \beta_3). \tag{42}$$

By analogy with Eq. (41) a general rotation $T(\boldsymbol{\theta})$ is given by

$$T(\boldsymbol{\theta})\boldsymbol{x} = T_1(\theta_1)T_2(\theta_2)T_3(\theta_3)\boldsymbol{x} \tag{43}$$

where the $T_j(\theta_j)$ transformations are those defined in Eq. (19), and vector $\boldsymbol{\theta}$ is given by

$$\boldsymbol{\theta}' = (\theta_1, \theta_2, \theta_3). \tag{44}$$

A general point transformation within any equivalence class $K_c(\tau)$ has the form

$$\boldsymbol{x}^{(2)} = T(\boldsymbol{\theta})Y(\boldsymbol{\beta})\boldsymbol{x}^{(1)}. \tag{45}$$

Evidently, for any point

$$\boldsymbol{x}^{(1)} \in K_c(\tau), \tag{46}$$

and parameters

$$-\infty < \beta_j < \infty, \qquad j = 1, 2, 3 \tag{47}$$

$$0 \leq \theta_i < 2\pi, \qquad i = 1, 2, 3 \tag{48}$$

the resulting point $\boldsymbol{x}^{(2)}$ is also an element of the same class,

$$\boldsymbol{x}^{(2)} \in K_c(\tau) \tag{49}$$

by virtue of definitions (11) and (23). In fact, definition (23) can be given in an equivalent form as

$$K_c(\tau) = \{\boldsymbol{x} : \boldsymbol{x} = T(\boldsymbol{\theta})Y(\boldsymbol{\beta})\boldsymbol{c}^{(\tau)}, \qquad -\infty < \beta_j < \infty, 0 \leq \theta_j < 2\pi, j = 1, 2, 3\}. \tag{50}$$

In chemical practice structural information of molecules is usually interpreted in terms of *geometrical models*, corresponding to conformations of minimum energy, or saddle points, i.e. in terms of *points* of the nuclear configuration space which are *critical points* of the energy hypersurface. This interpretation, however, is valid only in the classical model of molecules and is incompatible with the Heisenberg uncertainty principle. In the quantum mechanical model no molecule can exist with a fixed nuclear configuration $\boldsymbol{x} \in {}^{3N}E$ and it is more appropriate to define molecular structure in terms of an open set of nuclear configurations, rather than in terms of rigid nuclear geometries. From any point $\boldsymbol{x}$ in a given catchment region $C(\boldsymbol{c}^{(\tau)})$ a spontaneous relaxation of the nuclear configuration along a classical steepest descent path necessarily leads to a point $\boldsymbol{c}$ in set $K_c(\tau)$. Since this is a universal property of all points in the catchment region, any distortion of the nuclear configuration *within* $C(\boldsymbol{c}^{(\tau)})$ retains a direct physical relation to the set $K_c(\tau)$ of equivalent critical points. It is natural then to choose the $C(\boldsymbol{c}^{(\tau)})$ and $C(\boldsymbol{d}^{(\kappa)})$ catchment regions for a structural classification. Such a structural classification retains the reference to critical points, i.e. it may be regarded as a generalization of the classical structural model and at the same time it circumvents the incompatibility of the geometrical point models with the uncertainty principle.

In the ${}^{3N}E$ Euclidean nuclear configuration space model a unique definition can be given for *molecular structure*:

Each distinct molecular structure is a catchment region $C(\boldsymbol{p}^{(\sigma)})$, ($\boldsymbol{p}^{(\sigma)} = \boldsymbol{c}^{(\tau)}$ or $\boldsymbol{d}^{(\tau)}$) *of the nuclear configuration space* ${}^{3N}E$*. Each molecular structure corresponds to a subset of nuclear geometries in the space* ${}^{3N}E$, and *not* to distinct points of individual nuclear geometries. Note that,

(1) the above structure definition refers to a specified energy hypersurface $E(\boldsymbol{x})$ over ${}^{3N}E$, that is, to a given electronic state. Different energy hypersurfaces of different electronic states imply different catchment regions i.e. different chemical structures over the same nuclear configuration space ${}^{3N}E$.

(2) The definition of sets $K_c(\tau)$ and $D^{(\kappa)}_{\text{excl}}$ and that of catchment regions $C(\boldsymbol{p}^{(\sigma)})$ imply that the catchment regions of ${}^{3N}E$ are disjoint:

$$C(\boldsymbol{p}^{(\sigma)}) \cap C(\boldsymbol{p}^{(\sigma')}) = \emptyset \quad \text{if } \sigma \neq \sigma'. \tag{51}$$

(3) The boundedness of energy hypersurface $E(\boldsymbol{x})$ and the definition of catchment regions imply that the latter form a cover of the entire space ${}^{3N}E$:

$$\bigcup_{\sigma} C(\boldsymbol{p}^{(\sigma)}) = {}^{3N}E \tag{52}$$

(4) Since the catchment regions are disjoint, Eq. (51), property (3) also implies that the union in Eq. (52) represents a *unique partitioning* of space ${}^{3N}E$.

One may restate the above observations in chemical terms: chemical structure is well defined in terms of a *set* of nuclear geometries, and the nuclear configuration space is nothing else than a collection of chemical structures of a specified electronic state.

The above properties lead to a well defined *topological* description of the nuclear configuration space ${}^{3N}E$.

4. Homotopy Classes of set *P* of All Steepest Descent Paths

Transformations of the form $T(\boldsymbol{\theta})\ Y(\boldsymbol{\beta})$ are not limited to critical points. These are transformations of the most general form which interrelate those position vectors in the Euclidean space ${}^{3N}E$ which correspond to equivalent nuclear arrangements in the 3-dimensional physical space of the laboratory frame. This property implies the following important relations:

(1) if $\boldsymbol{x}^{(0)} \in C(\boldsymbol{p}^{(\sigma)}), \boldsymbol{p}^{(\sigma)} = \boldsymbol{c}^{(\tau)}$ or $\boldsymbol{d}^{(\kappa)}$ then

$$T(\boldsymbol{\theta})Y(\boldsymbol{\beta})\boldsymbol{x}^{(0)} = \boldsymbol{x}^{(1)} \in C(p^{(\sigma)}) \tag{53}$$

(2) if $P_{\boldsymbol{x}}(0) \in P(\boldsymbol{p}^{(\sigma)}), \boldsymbol{p}^{(\sigma)} = \boldsymbol{c}^{(\tau)}$ or $\boldsymbol{d}^{(\kappa)}$ then

$$T(\boldsymbol{\theta})Y(\boldsymbol{\beta})P_{\boldsymbol{x}}(0) = P_{\boldsymbol{x}}(1) \in P(\boldsymbol{p}^{(\sigma)}) \tag{54}$$

where in Eq. (54) the transformations of paths are taken in the pointwise sense. Transformation (54) defines homotopies between paths $P_{\boldsymbol{x}}(0)$ and $P_{\boldsymbol{x}}(1)$ of equivalence class $P(\boldsymbol{p}^{(\sigma)})$. The simplest such homotopy is given in terms of a continuous parameter w, $0 \leq w \leq 1$, as

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, w) = T(w\boldsymbol{\theta})Y(w\boldsymbol{\beta}) \tag{55}$$

for which

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, 0)P_{\boldsymbol{x}}(0) = P_{\boldsymbol{x}}(0) \tag{56}$$

and

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, 1)P_{\boldsymbol{x}}(0) = P_{\boldsymbol{x}}(1). \tag{57}$$

A more general homotopy $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, \boldsymbol{w})$ is given in terms of two continuous vector functions $\boldsymbol{t}(w)$ and $\boldsymbol{b}(w)$,

$$\boldsymbol{t}:[0, 1] \to {}^{3}E \tag{58}$$

$$\boldsymbol{b}:[0, 1] \to {}^{3}E, \tag{59}$$

for which the only restrictions besides continuity are

$$\boldsymbol{t}(0) = \boldsymbol{b}(0) = \boldsymbol{0} \tag{60}$$

and

$$\boldsymbol{t}(1) = \boldsymbol{b}(1) = \boldsymbol{1}. \tag{61}$$

This homotopy is defined by

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w) = T(t_1(w)\theta_1, t_2(w)\theta_2, t_3(w)\theta_3)Y(b_1(w)\beta_1, b_2(w)\beta_2, b_3(w)\beta_3). \tag{62}$$

Clearly,

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, 0)P_{\boldsymbol{x}}(0) = P_{\boldsymbol{x}}(0) \tag{63}$$

and

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, 1)P_{\boldsymbol{x}}(0) = P_{\boldsymbol{x}}(1). \tag{64}$$

In the special case of

$$t'(w) = b'(w) = (w, w, w) \tag{65}$$

homotopy $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$ becomes $h(\boldsymbol{\theta}, \boldsymbol{\beta}, w)$ of Eq. (55).

Homotopies given by Eq. (62) represent continuous deformations of steepest descent paths in equivalence class $P(\boldsymbol{p}^{(\sigma)})$, the two extreme cases being $P_x(0)$ and $P_x(1)$ as w varies $0 \to 1$. Paths $P_x(w)$ generated by a given homotopy $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$ belong to the same homotopy class and are homotopically equivalent. Any combinations of simultaneous rotation and translation in the laboratory frame which leave the path of actual nuclear rearrangement physically invariant, *relative to the molecule*, correspond to a homotopy class of paths *within* equivalence class $P(\boldsymbol{p}^{(\sigma)}) \subset {}^{3N}E$. That is, homotopy classes of paths induced by homotopies $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$ generate a "fine" classification of paths within the "large" equivalence class $P(\boldsymbol{p}^{(\sigma)})$, which finer classification refers to specific displacements of a distorted geometry of the *molecule as a whole, together with its relaxation path* in the laboratory frame. In particular, homotopies $h(\boldsymbol{0}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$ and $h(\boldsymbol{\theta}, \boldsymbol{0}, \boldsymbol{t}, \boldsymbol{b}, w)$ correspond to homotopy classes of paths which are related to each other within a class by pure translation and pure rotation, respectively, in the laboratory frame.

Note, that the above homotopy classes are more numerous than the possible Eckart frames of the molecular system [19, 20]. In order to obtain a homotopy compatible with any given Eckart frame, it is necessary for *both* $P_x(0)$ and $P_x(1)$ to be paths compatible with the same Eckart frame, which is not in general valid for arbitrary paths $P_x(0)$ and $P_x(1)$ of equivalence class $P(\boldsymbol{p}^{(\sigma)})$. Consequently, the characterization of molecular deformations in terms of the above homotopies is finer than the one given in terms of Eckart frames. Homotopies of the above form will be used in the following analysis of reaction mechanisms.

5. Reaction Topology: Topological Structure of Energy Hypersurfaces Based upon Catchment Regions in Euclidean Space ${}^{3N}E$

The metric topology **T** on ${}^{3N}E$ is defined by the ε-neighbourhoods of points $\boldsymbol{x} \in {}^{3N}E$ as open sets, where the metric is the usual Euclidean metric of ${}^{3N}E$. The induced metric topological space $({}^{3N}E, \mathbf{T})$ reflects the usual concept of openness, since the **T**-open sets of $({}^{3N}E, \mathbf{T})$ are precisely those subsets of ${}^{3N}E$ which are open in the conventional sense.

The catchment region partitioning, Eq. (52) of ${}^{3N}E$, however, induces several *different* topologies, which are more closely related to the chemical concepts of molecular structure and reaction mechanisms.

Family **C**′ of all catchment regions,

$$\mathbf{C}' = \{C(\boldsymbol{p}^{(\sigma)})\} = \{C(\boldsymbol{c}^{(\tau)})\} \cup \{C(\boldsymbol{d}^{(\kappa)})\} \tag{66}$$

is a defining subbase for a unique topology $\mathbf{T}_{C'}$ on Euclidean space ${}^{3N}E$. That **C**′ is indeed a proper subbase, it follows from the fact that elements of **C**′ form a cover for ${}^{3N}E$, Eq. (52), and from the observation that the empty union of elements of $\mathbf{C}'$ is the empty set $\emptyset$. Note, that finite intersections of elements of $\mathbf{C}'$ are also elements of $\mathbf{C}'$, consequently $\mathbf{C}'$ is also a base for the same topology $\mathbf{T}_{C'}$.

Set $\mathbf{T}_{C'}$ is the family of all sets which are unions of sets from the base. Thus $\mathbf{T}_{C'}$ is indeed a topology on ${}^{3N}E$, since

(1) the whole space ${}^{3N}E$ and the empty set $\emptyset$ belong to $\mathbf{T}_{C'}$

$$ {}^{3N}E, \emptyset \in \mathbf{T}_{C'} \tag{67}$$

(2) the union of any number of sets from $\mathbf{T}_{C'}$ also belongs to $\mathbf{T}_{C'}$

$$\bigcup_{\beta} T_\beta \in \mathbf{T}_{C'} \quad \text{if each } T_\beta \in \mathbf{T}_{C'} \tag{68}$$

(3) the intersection of any finite class of sets in $\mathbf{T}_{C'}$ is also a set in $\mathbf{T}_{C'}$

$$\bigcap_{i=1}^{m} T_i \in \mathbf{T}_{C'} \quad \text{if each } T_i \in \mathbf{T}_{C'} \text{ and } m \text{ is finite.} \tag{69}$$

Family $\mathbf{C}''$, defined as

$$\mathbf{C}'' = \{\bar{C}(\boldsymbol{p}^{(\sigma)})\} \tag{70}$$

where the closure symbol $^{-}$ refers to the metric topology $\mathbf{T}$, is a defining subbase for a different topology, $\mathbf{T}_{C''}$. Evidently, elements of $\mathbf{C}''$ also form a cover for ${}^{3N}E$. Note however, that finite intersections of elements of $\mathbf{C}''$ are not necessarily elements of the same family $\mathbf{C}''$ (see e.g. example of Fig. 2, Ref. [5]), consequently family $\mathbf{C}''$ itself is not necessarily a base for topology $\mathbf{T}_{C''}$.

The third, and possibly the most important topology, $\mathbf{T}_C$, is defined in terms of defining subbase $\mathbf{C}$, where

$$\mathbf{C} = \mathbf{C}' \bigcup \mathbf{C}''. \tag{71}$$

That $\mathbf{T}_{C''}$ and $\mathbf{T}_C$ are proper topologies on ${}^{3N}E$ can be shown easily by proving relations analogous to (67)-(69).

By introducing topology $\mathbf{T}_{C'}$, $\mathbf{T}_{C''}$ or $\mathbf{T}_C$, Euclidean space ${}^{3N}E$ becomes a topological space $({}^{3N}E, \mathbf{T}_{C'})$, $({}^{3N}E, \mathbf{T}_{C''})$ or $({}^{3N}E, \mathbf{T}_C)$, respectively.

In topological space $({}^{3N}E, \mathbf{T}_{C'})$ the open sets are the chemical structures and their unions, as a consequence of the definition of catchment regions of the Euclidean representation of the nuclear configuration space. For the analysis of *interrelations* between various chemical structures topological space $({}^{3N}E, \mathbf{T}_{C''})$ and particularly, $({}^{3N}E, \mathbf{T}_C)$ are more suitable since in these spaces various *neighbour relations* between chemical structures can be defined as *topological relations*, which lead to a suitable topological description of reaction mechanisms. Before analyzing such relations, we shall introduce a series of topologies on the energy hypersurface $E(\boldsymbol{x})$ defined over Euclidean space ${}^{3N}E$, which topologies are pairwise equivalent to $\mathbf{T}_{C'}$, $\mathbf{T}_{C''}$, and $\mathbf{T}_C$ on ${}^{3N}E$.

We shall assume that $E(\boldsymbol{x})$, $E(\boldsymbol{x}): {}^{3N}E \to {}^{1}E$ is a continuous functional in the usual sense, that is, it is $\mathbf{T}$, $\mathbf{T}'$ continuous in the metric topology $\mathbf{T}$ of ${}^{3N}E$ and metric topology $\mathbf{T}'$ of ${}^{1}E$. In fact, we shall assume more: that $E(\boldsymbol{x})$ is twice continuously differentiable in all of ${}^{3N}E$.[3] Functional $E(\boldsymbol{x})$ defines a mapping $\boldsymbol{E}$

$$\boldsymbol{E}: {}^{3N}E \to E \subset {}^{3N+1}E. \tag{72}$$

Here the energy hypersurface E is regarded a subset of an Euclidean space ${}^{3N+1}E$,

$${}^{3N+1}E = {}^{3N}E \otimes {}^{1}E \tag{73}$$

which latter is a direct product of nuclear configuration space ${}^{3N}E$ and ${}^{1}E$, a one dimensional space containing the range of functional $E(\boldsymbol{x})$.

The properties of functional $E(\boldsymbol{x})$ imply that the inverse of mapping $\boldsymbol{E}$, i.e. projection $\boldsymbol{\pi} = \boldsymbol{E}^{-1}$

$$\boldsymbol{\pi}: E \to {}^{3N}E, \qquad E \subset {}^{3N+1}E \tag{74}$$

is also continuous in the metric topologies of the above spaces. Consequently, $\boldsymbol{E}$ is a homeomorphism from ${}^{3N}E$ to E.

Mapping $\boldsymbol{E}$ as applied to a set $X \subset {}^{3N}E$ generates the homeomorphic image X_E on hypersurface E:

$$\boldsymbol{E}X = X_E \subset E \subset {}^{3N+1}E \tag{75}$$

$$\boldsymbol{\pi}X_E = X. \tag{76}$$

Consider the following families of sets

$$\mathbf{C}'_E = \{C_E(\boldsymbol{p}^{(\sigma)})\} \tag{77}$$

$$\mathbf{C}''_E = \{\bar{C}_e(\boldsymbol{p}^{(\sigma)})\} \tag{78}$$

and

$$\mathbf{C}_E = C'_E \bigcup C''_E \tag{79}$$

where elements of families $\mathbf{C}'_E$, $\mathbf{C}''_E$ and $\mathbf{C}_E$ are the homeomorphic $\boldsymbol{E}$-images of elements of families $\mathbf{C}'$, $\mathbf{C}''$ and $\mathbf{C}$, respectively. Since elements of either one of $\mathbf{C}'$, $\mathbf{C}''$, or $\mathbf{C}$ form a cover of ${}^{3N}E$, elements of either one of $\mathbf{C}'_E$, $\mathbf{C}''_E$ or $\mathbf{C}_E$ form a cover of energy hypersurface E.

Families $\mathbf{C}'_E$, $\mathbf{C}''_E$ and $\mathbf{C}_E$ are defining subbases for three topologies, $\mathbf{T}_{C'E}$, $\mathbf{T}_{C''E}$ and $\mathbf{T}_{CE}$, respectively, on the energy hypersurface E. By the above definitions, mapping $\boldsymbol{E}$, as a homeomorphism, establishes pairwise topological equivalences (denoted by $\sim$) between the induced topological spaces $(E, \mathbf{T}_{C'E})$, $(E, \mathbf{T}_{C''E})$, and $(E, \mathbf{T}_{CE})$ of the energy hypersurface E and topological spaces $({}^{3N}E, \mathbf{T}_{C'})$, $({}^{3N}E, \mathbf{T}_{C''})$ and $({}^{3N}E, \mathbf{T}_{C})$ of Euclidean space ${}^{3N}E$, respectively:

$$(E, \mathbf{T}_{C'E}) \sim ({}^{3N}E, \mathbf{T}_{C'}) \tag{80}$$

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[3] The above conditions are not necessarily fulfilled in domain D_{excl}, however, $E(\boldsymbol{x})$ always can be extended continuously and differentiably from ${}^{3N}E \backslash D_{\text{excl}}$ to ${}^{3N}E$ using a method described in Ref. [8], part I of our study.

$$(E, \mathbf{T}_{C''E}) \sim ({}^{3N}E, \mathbf{T}_{C''}) \tag{81}$$

and

$$(E, \mathbf{T}_{CE}) \sim ({}^{3N}E, \mathbf{T}_{C}). \tag{82}$$

The above relations (80)–(82) allow one to carry out a topological analysis in either one of a pair of topological spaces, since all topological properties are necessarily transferrable from one space to the other. In the present study we shall choose topologies in Euclidean space ${}^{3N}E$ as the primary subject of our investigations.

Any $\mathbf{T}_{C'}$-open or $\mathbf{T}_{C''}$-open set is also open in the $\mathbf{T}_C$ topology, however, $\mathbf{T}_C$-open sets are not necessarily $\mathbf{T}_{C'}$-open or $\mathbf{T}_{C''}$-open. That is, topology $\mathbf{T}_C$ is finer than either the $\mathbf{T}_{C'}$ or $\mathbf{T}_{C''}$ topology. Topologies $\mathbf{T}_{C'}$ and $\mathbf{T}_{C''}$ on the other hand, are non-comparable, that is, neither one is finer than the other. Analogous relations are valid for the respective $\mathbf{T}_{C'E}$, $\mathbf{T}_{C''E}$ and $\mathbf{T}_{CE}$ topologies on the energy hypersurface E:

$$({}^{3N}E, \mathbf{T}_{C'}) \subset ({}^{3N}E, \mathbf{T}_{C}) \tag{83}$$

$$({}^{3N}E, \mathbf{T}_{C''}) \subset ({}^{3N}E, \mathbf{T}_{C}) \tag{84}$$

$$(E, \mathbf{T}_{C'E}) \subset (E, \mathbf{T}_{CE}) \tag{85}$$

$$(E, \mathbf{T}_{C''E}) \subset (E, \mathbf{T}_{CE}). \tag{86}$$

Open sets in the above topological spaces have important chemical interpretations.

Chemical structure is a $\mathbf{T}_{C'}$-open set which is an element of base C' of topological space $({}^{3N}E, \mathbf{T}_{C'})$. Note that each chemical structure is also a $\mathbf{T}_C$-open set.

A stable molecule is a chemical structure $C(\boldsymbol{p}^{(\sigma)})$, where

$$\boldsymbol{p}^{(\sigma)} = \boldsymbol{c}^{(\tau)} \tag{87}$$

a critical point with index 0,

$$\lambda(\boldsymbol{c}^{(\tau)}) = 0, \tag{88}$$

i.e. $\boldsymbol{p}^{(\sigma)}$ is a minimum.

A transition structure ("transition state") is a chemical structure $C(\boldsymbol{p}^{(\sigma)})$ where

$$\boldsymbol{p}^{(\sigma)} = \boldsymbol{c}^{(\tau)}, \tag{89}$$

a critical point with index 1,

$$\lambda(\boldsymbol{c}^{(\tau)}) = 1, \tag{90}$$

i.e. $\boldsymbol{p}^{(\sigma)}$ is a saddle point of index 1.

Chemical structures $C(\boldsymbol{p}^{(\sigma)})$ with distinguished element $\boldsymbol{p}^{(\sigma)}$ being a critical point $\boldsymbol{c}^{(\tau)}$ of index larger than 1,

$$\lambda(\boldsymbol{c}^{(\tau)}) > 1 \tag{91}$$

are of somewhat lesser chemical importance than the above two types, since such critical points do not occur along ideal minimum energy reaction paths [21].

The number of all possible chemical structures of various types, with reference to a given set of nuclei and electrons, and regarding a specified electronic state, can be determined by enumerating the distinguished critical points $\boldsymbol{c}^{(\tau)}$. The enumeration problem of critical points is a central problem of topology [22–24], and for special cases of chemical energy hypersurfaces it has been discussed in references [4, 7].

6. Relations Between Reaction Topologies in Euclidean Space $^{3N}\boldsymbol{E}$ and Riemannian Space $^{n}\boldsymbol{R}$

In the earlier Riemannian nuclear configuration space model [4–6, 8] partitioning of space ^{n}R and various topologies in ^{n}R have been introduced, based upon the definition of the intrinsic reaction coordinate of Fukui [9, 10] and Fukui and Tachibana [11, 12]. This definition gives the intuitively straightforward description of an ideal, vibrationless reaction path as a path in Riemannian space ^{n}R which is orthogonal to every equipotential surface crossed. Orthogonality can be defined in a coordinate-invariant way in Riemannian spaces [13] as long as condition (a) is met:

(a) the Jacobian determinant of the coordinate transformation is non-zero. Clearly, infinitely many coordinate systems fulfill this condition.

For a physically correct model it is also necessary to satisfy condition (b):

(b) there is a correspondence between the vibrationless relaxation paths of nuclear displacements in the laboratory frame ^{3}E and the ideal reaction paths in subsets of ^{n}R. Such correspondence implies a correspondence between the vectors of laboratory frame forces acting upon the nuclei and the n-dimensional gradient vector of the potential energy hypersurface over ^{n}R [4–6, 8].

Note that it is sufficient if condition (b) can be satisfied in locally defined Euclidean spaces generated in a manifold representation of Riemannian space ^{n}R [6], as long as the coordinate domains $G^{(i)}$ of ^{n}R contain the inverse images of catchment regions defined in the local Euclidean spaces. Equivalently, it is sufficient if diffeomorphic images $H^{(i)}$ of coordinate domains $G^{(i)}$ [6] contain catchment regions $C^{(i)}$ in the local Euclidean space.

Let us assume that the Riemannian representation (in fact an infinite set of such representations) fulfills the above conditions. Consider a set of N paths representing simultaneous nuclear relaxations in laboratory frame ^{3}E and the corresponding ideal reaction path P in ^{n}R. This correspondence is in general not one to one since for $n = 3N - 6$ there are infinitely many sets of N paths in ^{3}E with the common image P, as translation and rotation of the molecule as a whole, *together* with the set of N paths in ^{3}E, do not affect P.

In any such Riemannian representation the paths of steepest descent in $^{n}R \backslash D_{\text{excl}}$ have well defined extremities [4] which are physically equivalent in *all* such representations. Consequently, the resulting catchment region topologies are also equivalent in all representations which fulfill conditions (a) and (b).

By comparison, in the ${}^{3N}E$ Euclidean nuclear configuration space model conditions (a) and (b) are replaced by features inherent in the model and are automatically satisfied. Consequently, the catchment region reaction topologies defined in Riemannian spaces ${}^{n}R$ (subject to conditions (a) and (b)) and reaction topologies in ${}^{3N}E$ are topologically equivalent:

$$({}^{3N}E, \mathbf{T}_{C'}) \sim ({}^{n}R, \mathbf{T}_{C'}) \tag{92}$$

$$({}^{3N}E, \mathbf{T}_{C''}) \sim ({}^{n}R, \mathbf{T}_{C''}) \tag{93}$$

$$({}^{3N}E, \mathbf{T}_{C}) \sim ({}^{n}R, \mathbf{T}_{C}). \tag{94}$$

The above topological equivalences enable one to transfer all results obtained for topological space $({}^{n}R, \mathbf{T}_{C})$ [6, 8] directly to topological space $({}^{3N}E, \mathbf{T}_{C})$. Most of the results in the rest of the present study can be obtained directly by the above device. However, we shall follow a more consistent route to these results by giving the necessary definitions in ${}^{3N}E$ and by pointing out direct relations between reaction path properties in ${}^{3N}E$ and in the laboratory frame ${}^{3}E$. On the other hand, for abstract relations between quantum chemical reaction networks and reaction graphs, where the laboratory frame interpretation of results is no longer feasible, we shall adopt a formal transfer of results from $({}^{n}R, \mathbf{T}_{C})$ to $({}^{3N}E, \mathbf{T}_{C})$.

7. The Topological Model of Reaction Mechanisms in Euclidean Space ${}^{3N}E$

The classical interpretation of an elementary reaction step is a direct interconversion of "reactants" into "products" without involving any other chemical species. In the geometrical model this corresponds to a direct change of the nuclear configuration of the reactant to that of the product. In our topological model reactants and products are represented by open sets of a topological space, and a *direct* interconversion implies that these open sets must be related in a simple way, they must be "neighbours" in certain sense.

We need a topological definition for a neighbour relation of chemical structures in ${}^{3N}E$. By taking advantage of equivalences (92)–(94), one could rely on neighbour relations in space ${}^{n}R$ and relations induced by them in ${}^{3N}E$. It seems more appropriate, however, to define neighbour relations directly in ${}^{3N}E$. Such a definition can be given most conveniently in topological space $({}^{3N}E, \mathbf{T}_{C})$. For any two chemical structures $C(\boldsymbol{p}^{(\sigma)})$ and $C(\boldsymbol{p}^{(\sigma')})$,

$$C(\boldsymbol{p}^{(\sigma)}), C(\boldsymbol{p}^{(\sigma')}) \in \mathbf{T}_{C} \tag{95}$$

a neighbour relation is defined as

$$N(C(\boldsymbol{p}^{(\sigma)}), C(\boldsymbol{p}^{(\sigma')})) = \begin{cases} 1 & \text{if } \bar{C}(\boldsymbol{p}^{(\sigma)}) \cap \bar{C}(\boldsymbol{p}^{(\sigma')}) \neq \emptyset \\ 0 & \text{otherwise} \end{cases} \tag{96}$$

where

$$\sigma \neq \sigma' \tag{97}$$

and evidently,

$$\bar{C}(\boldsymbol{p}^{(\sigma)}),\ \bar{C}(\boldsymbol{p}^{(\sigma')}) \in \mathbf{T}_C \tag{98}$$

For simplicity, in writing relation N the actual open sets will be often replaced by the distinguished elements, e.g. $N(\boldsymbol{p}^{(\sigma)}, \boldsymbol{p}^{(\sigma')})$.

Two further relations, the strong neighbour relation N^s and the symmetric strong neighbour relation (s-neighbour relation) $\bar{N}^s$ are defined as

$$N^s(\boldsymbol{p}^{(\sigma)}, \boldsymbol{p}^{(\sigma')}) = \begin{cases} 1 & \text{if } \bar{C}(\boldsymbol{p}^{(\sigma)}) \cap C(\boldsymbol{p}^{(\sigma')}) \neq \emptyset \\ 0 & \text{otherwise} \end{cases} \tag{99}$$

and

$$\bar{N}^s(\boldsymbol{p}^{(\sigma)}, \boldsymbol{p}^{(\sigma')}) = \begin{cases} 1 & \text{if } N^s(\boldsymbol{p}^{(\sigma)}, \boldsymbol{p}^{(\sigma')}) + N^s(\boldsymbol{p}^{(\sigma')}, \boldsymbol{p}^{(\sigma)} \geq 1 \\ 0 & \text{otherwise} \end{cases} \tag{100}$$

respectively.

Note that if chemical structure $C(\boldsymbol{p}^{(\sigma)})$ is a strong neighbour of chemical structure $C(\boldsymbol{p}^{(\sigma')}$ then the two structures are s-neighbours and also neighbours, since N^s implies $\bar{N}^s$ and $\bar{N}^s$ implies N:

$$N^s \rightarrow \bar{N}^s \tag{101}$$

$$\bar{N}^s \rightarrow N \tag{102}$$

and evidently

$$N^s \rightarrow N. \tag{103}$$

However, none of the converse statements is valid in general:

$$\bar{N}^s \nrightarrow N^s \tag{104}$$

$$N \nrightarrow \bar{N}^s \tag{105}$$

$$N \nrightarrow N^s. \tag{106}$$

Note that relations N and $\bar{N}^s$ are symmetric whereas N^s is not in general symmetric:

$$N(\boldsymbol{p}^{(\tau)}, \boldsymbol{p}^{(\tau')}) = N(\boldsymbol{p}^{(\tau')}, \boldsymbol{p}^{(\tau)}) \tag{107}$$

$$\bar{N}^s(\boldsymbol{p}^{(\tau)}, \boldsymbol{p}^{(\tau')}) = \bar{N}^s(\boldsymbol{p}^{(\tau')}, \boldsymbol{p}^{(\tau)}) \tag{108}$$

for all $\boldsymbol{p}^{(\tau)}$, $\boldsymbol{p}^{(\tau')}$ pairs, whereas

$$N^s(\boldsymbol{p}^{(\tau)}, \boldsymbol{p}^{(\tau')}) \neq N^s(\boldsymbol{p}^{(\tau')}, \boldsymbol{p}^{(\tau)}) \tag{109}$$

for some pairs of structures.

Consider the example of two stable molecules $C(\boldsymbol{c}^{(\tau)})$ and $C(\boldsymbol{c}^{(\tau')})$,

$$\lambda(\boldsymbol{c}^{(\tau)}) = \lambda(\boldsymbol{c}^{(\tau')}) = 0 \tag{110}$$

separated by a transition structure $C(\boldsymbol{c}^{(\tau'')})$,

$$\lambda(\boldsymbol{c}^{(\tau'')}) = 1. \tag{111}$$

Typically all these structures are pairwise neighbours,

$$N(\boldsymbol{c}^{(\tau)}, \boldsymbol{c}^{(\tau')}) = N(\boldsymbol{c}^{(\tau)}, \boldsymbol{c}^{(\tau'')}) = N(\boldsymbol{c}^{(\tau')}, \boldsymbol{c}^{(\tau'')}) = 1 \tag{112}$$

but only the transition structure is an s-neighbour of the two molecules,

$$\bar{N}^s(\boldsymbol{c}^{(\tau'')}, \boldsymbol{c}^{(\tau)}) = \bar{N}^s(\boldsymbol{c}^{(\tau'')}, \boldsymbol{c}^{(\tau')}) = 1 \tag{113}$$

$$\bar{N}^s(\boldsymbol{c}^{(\tau)}, \boldsymbol{c}^{(\tau')}) = 0, \tag{114}$$

and only the transition structure has strong neighbours:

$$N^s(\boldsymbol{c}^{(\tau)}, \boldsymbol{c}^{(\tau'')}) = N^s(\boldsymbol{c}^{(\tau')}, \boldsymbol{c}^{(\tau'')}) = 1, \tag{115}$$

$$N^s(\boldsymbol{c}^{(\tau'')}, \boldsymbol{c}^{(\tau)}) = N^s(\boldsymbol{c}^{(\tau'')}, \boldsymbol{c}^{(\tau')}) = N^s(\boldsymbol{c}^{(\tau)}, \boldsymbol{c}^{(\tau')}) = N^s(\boldsymbol{c}^{(\tau')}, \boldsymbol{c}^{(\tau)}) = 0. \tag{116}$$

Eqs. (115) and (116) are examples for asymmetric strong neighbour relations. Consider the set $\mathbf{Q}(\boldsymbol{a}, \boldsymbol{b})$ of all paths interconnecting points $\boldsymbol{a}, \boldsymbol{b} \in {}^{3N}E$,

$$\boldsymbol{a} \in C(\boldsymbol{p}^{(\tau_0)}) \tag{117}$$

$$\boldsymbol{b} \in C(\boldsymbol{p}^{(\tau_k)}). \tag{118}$$

Take two paths, $Q_0(\boldsymbol{a}, \boldsymbol{b})$ and $Q_1(\boldsymbol{a}, \boldsymbol{b})$

$$Q_0(\boldsymbol{a}, \boldsymbol{b}), Q_1(\boldsymbol{a}, \boldsymbol{b}) \in \mathbf{Q}(\boldsymbol{a}, \boldsymbol{b}) \tag{119}$$

of the following properties:

(1) Both Q_0 and Q_1 pass through the same sequence of catchment regions

$$C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_1)}), C(\boldsymbol{p}^{(\tau_2)}) \cdots C(\boldsymbol{p}^{(\tau_k)}) \tag{120}$$

(2) There exists a homotopy

$$h(\boldsymbol{a}, \boldsymbol{b}, w): \mathbf{Q}(\boldsymbol{a}, \boldsymbol{b}) \otimes [0, 1] \rightarrow \mathbf{Q}(\boldsymbol{a}, \boldsymbol{b}) \tag{121}$$

such, that

$$h(\boldsymbol{a}, \boldsymbol{b}, 0) Q_0(\boldsymbol{a}, \boldsymbol{b}) = Q_0(\boldsymbol{a}, \boldsymbol{b}) \tag{122}$$

$$h(\boldsymbol{a}, \boldsymbol{b}, 1) Q_0(\boldsymbol{a}, \boldsymbol{b}) = Q_1(\boldsymbol{a}, \boldsymbol{b}) \tag{123}$$

and for every $w \in [0, 1]$ the path $Q_w(\boldsymbol{a}, \boldsymbol{b})$, given by

$$Q_w(\boldsymbol{a}, \boldsymbol{b}) = h(\boldsymbol{a}, \boldsymbol{b}, w) Q_0(\boldsymbol{a}, \boldsymbol{b}), \tag{124}$$

passes through exactly the same sequence of catchment regions as given in Eq. (120). Note, that this homotopy is in general *not* unique for a given pair of $\boldsymbol{a}$, $\boldsymbol{b} \in {}^{3N}E$.

Property (1) implies that each catchment region in sequence (120) is an *s*-neighbour (hence a neighbour) of the two catchment regions immediately preceding and following it in the sequence.

Evidently, all homotopically equivalent paths, thus the entire set $\{Q_w(\boldsymbol{a}, \boldsymbol{b})\}$ of these paths, represent the same sequence of chemical structures. Regarding $C(\boldsymbol{p}^{(\tau_0)})$ the *reactant* and $C(\boldsymbol{p}^{(\tau_k)})$ the *product*, each element of the set $\{Q_w(\boldsymbol{a}, \boldsymbol{b})\}$,

$$\{Q_w(\boldsymbol{a}, \boldsymbol{b})\} \subset \mathbf{Q}(\boldsymbol{a}, \boldsymbol{b}), \tag{125}$$

is a representation of the same *reaction mechanism*, consisting of k elementary reaction steps.

Set

$$\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}, C(\boldsymbol{p}^{(\tau_k)})) = \bigcup \{Q\} \tag{126}$$

is the collection of all paths Q satisfying condition (120) for every $\boldsymbol{a}$, $\boldsymbol{b}$ pair which in turn fulfill conditions (117) and (118), respectively. Homotopies given by Eq. (121) are continuous mappings on *subsets* of $\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)}))$

$$\mathbf{Q}(\boldsymbol{a}, \boldsymbol{b}) \subset \mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})). \tag{127}$$

The entire $\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)}))$ set can be generated as the union

$$\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) = \bigcup_{\substack{\boldsymbol{a} \in C(\boldsymbol{p}^{(\tau_0)}) \\ \boldsymbol{b} \in C(\boldsymbol{p}^{(\tau_k)})}} \bigcup_{\substack{Q_0(\boldsymbol{a}, \boldsymbol{b}) \\ Q_1(\boldsymbol{a}, \boldsymbol{b})}} \bigcup_{h(\boldsymbol{a}, \boldsymbol{b}, w)} \{Q_w(\boldsymbol{a}, \boldsymbol{b})\}. \tag{128}$$

whereas sets $\{Q_w(\boldsymbol{a}, \boldsymbol{b})\}$ with different $\boldsymbol{a}$, $\boldsymbol{b}$ pairs are disjoint

$$\{Q_w(\boldsymbol{a}, \boldsymbol{b})\} \bigcap \{Q_w(\boldsymbol{a}', \boldsymbol{b}')\} = \emptyset, \tag{129}$$

if either

$$\boldsymbol{a} \neq \boldsymbol{a}' \tag{130}$$

or

$$\boldsymbol{b} \neq \boldsymbol{b}', \tag{131}$$

and sets differing only in the choice of paths $Q_0(\boldsymbol{a}, \boldsymbol{b})$ and $Q_1(\boldsymbol{a}, \boldsymbol{b})$, or in the actual choice of homotopies $h(\boldsymbol{a}, \boldsymbol{b}, w)$, are not in general disjoint. Consequently, the right side of Eq. (128) is a cover but not a partitioning of set given in Eq. (126).

Eq. (128) is a special representation of the set given in Eq. (126), in terms of sets of homotopically equivalent paths, all of which represent the *same reaction mechanism*. Since set of Eq. (126) contains *all* paths compatible with sequence (120), it is a *general* representation of the corresponding reaction mechanism.

Homotopical equivalences in ${}^{3N}E$ reflecting the physical equivalences of paths in laboratory frame ${}^{3}E$ can be introduced for general paths in set $\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)}))$ in the same way as for steepest descent paths P. Homotopies $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$, defined in Eq. (62) as applied to path

$$Q(\boldsymbol{a}^{(0)}, \boldsymbol{b}^{(0)}) \in \mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) \tag{132}$$

cause a continuous deformation of path $Q(\boldsymbol{a}^{(0)}, \boldsymbol{b}^{(0)})$to a path

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)Q(\boldsymbol{a}^{(0)}, \boldsymbol{b}^{(0)}) = Q(\boldsymbol{a}^{(w)}, \boldsymbol{b}^{(w)}) \tag{133}$$

where

$$Q(\boldsymbol{a}^{(w)}, \boldsymbol{b}^{(w)}) \in \mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) \tag{134}$$

that is, to a path belonging to the same reaction mechanism. In particular,

$$\boldsymbol{a}^{(w)} \in C(\boldsymbol{p}^{(\tau_0)}) \tag{135}$$

and

$$\boldsymbol{b}^{(w)} \in C(\boldsymbol{p}^{(\tau_k)}) \tag{136}$$

for every $w \in [0, 1]$, and

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, 0)Q(\boldsymbol{a}^{(0)}, b^{(0)}) = Q(\boldsymbol{a}^{(0)}, b^{(0)}) \tag{137}$$

$$h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, 1)Q(\boldsymbol{a}^{(0)}, \boldsymbol{b}^{(0)}) = Q(a^{(1)}, \boldsymbol{b}^{(1)}). \tag{138}$$

The effect of homotopy $h(\boldsymbol{\theta}, \boldsymbol{\beta}, \boldsymbol{t}, \boldsymbol{b}, w)$ as parameter w sweeps through the interval [0, 1], is to generate all paths in $\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}, C(\boldsymbol{p}^{(\tau_k)}))$ which correspond to continuous displacement of the entire deformation paths of all nuclei in laboratory frame ^3E. In other words, this homotopy generates a particular "path of a path" in ^{3N}E, specified by vector functions $\boldsymbol{t}(w)$ and $\boldsymbol{b}(w)$. Each path along this "path of a path" belongs to the same reaction mechanism, furthermore, they are all ^{3N}E-space images of physically equivalent laboratory frame deformations.

Let

$$\mathbf{Q}'(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) = \bigcup Q, \qquad Q \in \mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) \tag{139}$$

be defined as the point-set union of elements of set given in Eq. (126).

It is evident from the union representation (128) of $\mathbf{Q}(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)}))$ that this point-set union is an open set in the $(^{3N}E, \mathbf{T}_{C'})$ topological space, hence an open set in the $(^{3N}E, \mathbf{T}_C)$ topological space. In particular, it can be given as the union

$$\mathbf{Q}'(C(\boldsymbol{p}^{(\tau_0)}), C(\boldsymbol{p}^{(\tau_k)})) = \bigcup_{i=0}^{k} C(\boldsymbol{p}^{(\tau_i)}) \tag{140}$$

as follows from condition (120).

Comparison of Eqs. (128) and (140) implies that a general k-step reaction mechanism can be represented as open sets of both the $(^{3N}E, \mathbf{T}_{C'})$ and $(^{3N}E, \mathbf{T}_C)$ topological spaces, that is, *reaction mechanisms and relations between them are topological properties in the above two spaces.*

It is of some importance to decide which open sets correspond to topological reaction mechanisms. The neighbour relations, in particular the s-neighbour relation $\bar{N}^s$ in topological space $({}^{3N}E, \mathbf{T}_C)$ yields a simple definition for reaction mechanism.

Reaction Mechanism: the union of a sequence of **T**-open sets of subbase **C** of topology $\mathbf{T}_C$ on ${}^{3N}E$ (Eq. 71) is a general reaction mechanism in topological space $({}^{3N}E, \mathbf{T}_C)$ if and only if every two **T**-open sets adjacent in the sequence are s-neighbours.

The above definition of reaction mechanisms in Euclidean space ${}^{3N}E$, in combination with the s-neighbour relation in $({}^{3N}E, \mathbf{T}_C)$, lead to the definition of reaction networks on the energy hypersurface. The network of all possible chemical reactions on a given energy hypersurface can be defined by the *intersection graph* of sets of subbase **C**. Note, that the various neighbour relations themselves have been defined in terms of intersections, consequently, property (120) implies that *a general reaction mechanism in* $({}^{3N}E, \mathbf{T}_C)$ *corresponds to a walk on the intersection graph.*

The above observations indicate that in spite of the differences in dimension and in the definitions and physical concepts of catchment regions in ${}^{3N}E$ and ${}^{n}R$, conditions (a) and (b) for the topological equivalence of $({}^{3N}E, \mathbf{T}_C)$ and $({}^{n}R, \mathbf{T}_C)$ ensure that the chemically important fundamental features of energy hypersurfaces are the same over ${}^{3N}E$ and ${}^{n}R$. In particular, if conditions (a) and (b) are met, all differences disappear for intersection graphs, and the induced reaction networks and reaction graphs are the same in ${}^{3N}E$ and in ${}^{n}R$. Consequently, *the analysis of reaction networks, given for* ${}^{n}R$ *in reference* [5] *is equally applicable to the* $({}^{3N}E, \mathbf{T}_C)$ *reaction topology and Theorems* 1–6 [5] *are equally valid for quantum chemical reaction networks defined on energy hypersurfaces over Euclidean space* ${}^{3N}E$.

8. Conclusions

Topologies $\mathbf{T}_{C'}$, $\mathbf{T}_{C''}$ and $\mathbf{T}_C$ introduced into the Euclidean nuclear configuration space ${}^{3N}E$ give unique definitions of the two most fundamental chemical concepts: *molecular structure* and *reaction mechanism*. It is shown that the above topologies are equivalent to topologies introduced earlier into Riemannian representations of the nuclear configuration space [4–8] and also to topologies defined on the energy hypersurface itself. In the case of the Euclidean representation, however, a direct relation can be established between molecular deformations in the laboratory frame and homotopies in the nuclear configuration space.

Neighbour relations in topological space $({}^{3N}E, \mathbf{T}_C)$ lead to the definition of reaction networks in terms of intersection graphs of $\mathbf{T}_C$-open sets. The $\mathbf{T}_C$-open sets themselves can be determined directly by the calculation of their *boundaries*, which have dimensions always less than the dimension of the energy hypersurface. That is, for the actual topologization no direct calculation of the hypersurface itself is required, and some computational savings can be realized.

Topological equivalences (92)–(94) establish the general validity of theorems derived for quantum chemical reaction networks [5], two of which are of particular importance in *computer-aided synthesis planning*:

Theorem (Theorem 3, Ref. [5]):
For any two chemical structures v_i and v_j in $G^s(\lambda)$, the maximum number of step-disjoint reaction mechanisms is equal to the minimum number of elementary reaction steps separating them in $G^s(\lambda)$. (Using the terminology of the Euclidean representation of the nuclear configuration space as given in the present work, $G^s(\lambda)$ is a subgraph of reaction graph defined by the $\mathbf{T}_C$-topological s-neighbour relation of Eq. 100).

Theorem (Theorem 6, Ref. [5])
If $G^s(\lambda)$ is a connected graph, then a shortest reaction mechanism between two chemical structures v_i and v_j consists of k elementary reaction steps, where k is the smallest integer such that

$$A^k_{ij}(G^s(\lambda)) \neq 0.$$

(Here $\boldsymbol{A}$ is the adjacency matrix.)

The same topological equivalences, Eq. (92)–(94) ensure that the topological properties of product space ${}^n\boldsymbol{R} \otimes {}^wZ$, are equally valid in the product space defined as ${}^{3N}E \otimes {}^wZ$, where ${}^wZ$ is the abstract nuclear charge space [25]. Lower and upper energy bounds, as well as electronic energy inequality relations derived in ${}^n\boldsymbol{R} \otimes {}^wZ$ [25–29] are equally valid in ${}^{3N}E \otimes {}^wZ$. Note that the application of these topological inequality relations require much less calculations than that needed for the boundaries of $\mathbf{T}_C$-open sets. In fact the application of most ${}^wZ$-space results require only "back of an envelope" type calculations [25–29].

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References

1. Guillemin, V., Pollack, A.: Differential topology. Englewood Cliffs: Prentice Hall, Inc., 1974
2. Spanier, E. H.: Algebraic topology. New York: McGraw-Hill, 1966
3. Born, M., Oppenheimer, J. R.: Ann. Phys. **84**, 457 (1927)
4. Mezey, P. G.: Theor. Chim. Acta (Berl.) **54**, 95 (1980), **58**, 309 (1981), **60**, 97 (1981)
5. Mezey, P. G.: Theor. Chim. Acta (Berl.) **60**, 409 (1982)
6. Mezey, P. G.: Internat. J. Quantum Chem. QBS **8**, 185 (1981)
7. Mezey, P. G.: Chem. Phys. Letters **82**, 100 (1981), **86**, 562 (1982)
8. Mezey, P. G.: Theor. Chim. Acta (Berl.) **62**, 133 (1982)
9. Fukui, K.: J. Phys. Chem. **74**, 4161 (1970)
10. Fukui, K.: Accounts Chem. Res. **14**, 363 (1981)
11. Tachibana, A., Fukui, K.: Theor. Chim. Acta (Berl.) **49**, 321 (1978)
12. Tachibana, A., Fukui, K.: Theor. Chim. Acta (Berl.) **51**, 189, 275 (1979), **57**, 81 (1980)
13. Eisenhart, L. P.: Riemannian geometry. Princeton: University Press, Princeton, 1963
14. Teller, E.: J. Phys. Chem. **41**, 109 (1937)
15. Longuet-Higgins, H. C.: Proc. Roy. Soc. London, Ser. A, **344**, 147 (1975)

16. Davidson, E. R.: J. Am. Chem. Soc. **99**, 397 (1977)
17. Marcus R. A.: J. Chem. Phys., **45**, 4493, 4500 (1966), **49**, 2610, 2617 (1968)
18. Miller, W. H., Handy, N. C., Adams, J. E.: J. Chem. Phys. **72**, 99 (1980)
19. Eckart, C.: Phys. Rev. **47**, 552 (1935)
20. Louck, J. D., Galbraith, H. W.: Rev. Mod. Phys. **48**, 69 (1976)
21. a. Murrell, J. N., Laidler, K. J.: Trans. Faraday Soc. **64**, 371 (1968) b. Murrell, J. N., Pratt, G. L.: Trans. Faraday Soc. **66**, 1680 (1974)
22. Morse, M.: Calculus of variations in the large. Amer. Math. Soc. Colloq. Publ. Vol. **18**, 1934
23. Morse, M., Cairns S. S.: Critical point theory in global analysis and differential topology. New York: Academic Press, 1969
24. Milnor, J.: Morse Theory, Annals of Math. Studies, Vol. **51**, Princeton: Univ. Press, Princeton, 1973
25. Mezey, P. G.: Internat. J. Quantum Chem. QCS **15**, 279 (1981)
26. Mezey, P. G.: Theor. Chim. Acta (Berl.) **59**, 321 (1981)
27. Mezey, P. G.: Internat. J. Quantum Chem. **22**, 101 (1982)
28. Mezey, P. G.: Chem. Phys. Letters **87**, 277 (1982)
29. Mezey, P. G.: Mol. Phys. **47**, 121 (1982)

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