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Topology of Energy Hypersurfaces

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Some of the basic notions of chemistry, associated with an energy function of several variables, are shown to be of topological character. Properties of potential energy hypersurfaces, structural relations, models for interconversion processes and transformations between such models suggest a topological theory (*reaction topology*) for the analysis of potential energy hypersurfaces. By introducing appropriate topologies into the nuclear configuration space R and equivalent topologies on the energy hypersurface E, rigorous definitions are given for fundamental chemical concepts such as *molecular structure* and *reaction mechanism*. These definitions are based on the properties of the expectation value of energy, a quantum mechanical observable. Topologies based on curvature, structural and energetic relations of the energy hypersurface are proposed for a theoretical interpretation of molecular processes.

Key words: Reaction topology – Potential energy surfaces – Reaction path – Chemical structure – Reaction mechanism.

1. Introduction

Energy hypersurfaces are of fundamental importance in chemistry for explaining molecular properties or chemical processes associated with an energy function of several (continuous) variables. Most often these variables are nuclear position coordinates and the associated Born–Oppenheimer energy functional [1] generates a potential energy hypersurface. Such potential surfaces of polyatomic molecules have been used extensively to explain molecular geometry, spectra, conformational properties and chemical reactions [2]. Computer-aided organic synthesis design and the study of chemical reaction networks [3, 4] are the areas where potential surfaces are expected to find an increasing number of applications.

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Energy hypersurfaces have distinct geometrical and topological properties. Reaction coordinates and local geometrical properties of minima and transition "states" on potential surfaces have been analyzed by several authors [5–28] and particular emphasis has been placed on reaction path properties [5, 9–20, 23–25]. The above studies, especially earlier results on the theory of intrinsic reaction coordinate [5, 23–25] have provided the basis for a global topological theory of multidimensional energy surfaces. A topological technique has been used in a study of the sign variation of wavefunctions about conical intersections of potential surfaces [28], and the topological features of triatomic potential surfaces have been discussed by Davidson [29]. Reviews of methods and models used in the analysis of conformational energy hypersurfaces may be found in references [17, 21, 22]. Some of the relevant aspects of differential geometry have been recently reviewed by Tachibana and Fukui [23].

The energy hypersurface model, however, is not restricted to the study of geometry changes. By considering more general parameters of the energy expectation value, e.g. orbital exponents of an approximate molecular wavefunction, an energy hypersurface may be defined over the space of such parameters [22]. By calculating the slope and curvature properties of the hypersurface (generalized "forces" and "force constants"), relations between optimum wavefunctions may be determined and utilized [30]. By further generalizing the energy expectation value functional, one may replace some of the integer parameters (e.g. quantum numbers or nuclear charges) by continuous variables. Whereas only those points of the resulting hypersurface over the space of such variables may correspond to true chemical structures where all variables take integer values, nevertheless, important relations between various chemical structures may be derived by utilizing properties of a continuous hypersurface. Such a technique has been applied to derive electronic energy inequalities for isoelectronic molecules [31].

Among the molecular expectation values that may be represented as a hypersurface (e.g. various one electron properties, absolute value of dipole moment, diamagnetic susceptibility, etc), the total energy is of unique importance. Physically, energy is one of the most influential factors determining conformational changes and chemical reactions. Powerful theorems, involving the molecular total energy or its components, such as the variation principle, Hellmann–Feynman theorem or the virial theorem, are routinely used to determine and analyse approximate molecular wavefunctions. Consequently, the theory of energy hypersurfaces is an underlying feature throughout most of theoretical chemistry.

Precise description of nuclear geometry changes within the Born–Oppenheimer model requires the introduction of a metric into the nuclear configuration space R. However, a full utilization of the advantages of a model based on a metric space is seldom possible, since accurate calculation of even small portions of potential hypersurfaces of polyatomic molecules may often present an immense computational problem. Fortunately, many chemical concepts are inherently topological in nature, e.g. molecular structure or reaction mechanism, what suggests the use of topological methods, with or without reference to metrization. Whereas in the interpretation of potential surface calculations reference has often been made to topological concepts, the expression, "topology", has been used in a very general sense of the word and a precise definition of the actual topology has usually been omitted. In most studies the emphasis has been placed on the metric properties of the nuclear configuration space R, although implicit in the application of a metric is the topology based on the ε-neighborhoods generated by the metric ("metric topology"). The metric topology, however, although powerful on its own right, does not offer significant departure from the original metric space model and does not lead to clear cut generalizations of certain chemical concepts.

2. Motivation and Objectives of a Topological Theory

Many of the common chemical concepts of stereochemistry, conformation analysis, or reaction mechanisms are usually described by *geometrical models*, with reference to nuclear positions in the 3-dimensional real space, or by referring to points in an abstract nuclear configuration space R. However, even within the framework of the Born–Oppenheimer approximation any solution for the nuclear wavefunction $\psi_{\text{nuc}}(\underline{r})$ in a potential field supplied by the electrons does result in a *distribution* of nuclear positions. Usually, the wave-package nature of nuclei is taken into account in an indirect way, e.g. as in vibrational analysis, nevertheless, the starting point of such an analysis is a geometrical model, the "equilibrium" nuclear geometry of the molecule. Although nuclei, being much heavier than electrons, are certainly more "particle-like" than electrons, nevertheless, by treating nuclei and electrons on an equal basis it is more justified to refer to nuclear distributions than to nuclear positions, just as one refers to electron distribution and not to electronic positions in a molecule. This suggests that *geometrical concepts* can be replaced by *topological concepts* in most of molecular physics.

Qualitatively speaking, topology can be described as "rubber geometry". The precise shape of a "topological object" is of little importance, the analysis is rather focussed on the way the parts are connected. A somewhat oversimplified example for a topological description of a molecule is the figure presenting the results of an X-ray structure determination, showing ellipsoids rather than precise nuclear positions. The topological counterparts of these ellipsoids are open sets of a topological space. One important property of these sets is that they cover and in fact include the entire space over which the topology is defined.

Up to date no comprehensive topological theory of energy hypersurfaces has been developed and this work is an attempt toward such a theory. Some earlier work on subsets of energy hypersurfaces may serve as a starting point for the development of a topological theory. Recently various partitioning schemes of the nuclear configuration space R have been proposed [32, 33]. The subsets of the nuclear configuration space R, involved in these partitionings, are directly related to familiar chemical concepts such as reaction mechanism, chemical structure, minimum energy path or energy of activation. Based on the curvature properties of the energy hypersurface E defined over R it is possible to determine those coordinate domains which are the most likely to contain the ideal, minimum energy reaction paths [32]. A complete partitioning of the space R may be given by a hierarchy of disjoint domains D^i_μ:

$$R = \bigcup_{\mu,i} D^i_\mu \cup D_{\text{excl}} \tag{1}$$

where index μ refers to the number of negative canonical curvatures in a locally defined subspace, orthogonal to the gradient, or to path vector $\underline{a}$ if the gradient vanishes [32]. The index i is the index of ordering for each D_μ type. D_0 domains are of special interest, since all minima and saddle points of transition "states" belong to D_0 domains, that is, D_0 domains reflect the distribution of the chemically most important critical points of E. Furthermore, minimum energy reaction paths are stable only in D_0 domains. The larger the index μ, the less likely that a minimum energy path enters D_μ. Domain D_{excl} contains all points where the energy hypersurface is a poor approximation to the Born–Oppenheimer energy expectation value.

A second partitioning scheme, proposed for the nuclear configuration space R, is based on the number and type of critical points of the $E(\underline{r})$ hypersurface [33], and is governed by Morse's critical point inequalities [34]. Steepest descent paths are ordered into equivalence classes according to their extremities which are either critical points or points in D_{excl}. These equivalence classes of steepest descent paths imply an equivalence relation for points of space R which leads to the definition of catchment regions $\{C^{\underline{r}^{(l)}_C}\}$ for all of the critical points $\{\underline{r}^{(l)}_C\}$, $\underline{r}^{(l)}_C \in R$. A complete partitioning of the R space is given as

$$R = \bigcup_{l} C^{\underline{r}^{(l)}_C} \cup C^{\bar{D}_{\text{excl}}} \cup \bar{D}_{\text{excl}} \tag{2}$$

where $C^{\bar{D}_{\text{excl}}}$ is the catchment region of the closure of the excluded domain D_{excl} [32]. It has been shown that both chemical structure and reaction mechanism, perhaps the two most fundamental concepts of chemistry, can be defined in terms of the $C^{\underline{r}^{(l)}_C}$ catchment regions, i.e. in terms of open sets of the underlying R space [33]. Whereas these definitions are strictly quantum mechanical since they are based on properties of a quantum mechanical observable, energy, and the associated expectation value functional $\underline{\underline{E}}(\underline{r})$, the fact that the typical $C^{(i)}$ catchment region of a minimum is a set *open* in the usual metric of R, clearly suggests a topological treatment.

The analysis of the molecular charge density in the real, Euclidean three space ^3R can be given in terms of catastrophe theory [35]. Based upon such an analysis [35, 36], a definition for molecular structure may be given by using molecular graphs, defined by "bond paths" of the charge density gradient field [36–37]. It has been conjectured [38] that a molecular structure definition, based on the three space topology of charge density is related to the definition given by the *catchment regions* [33], i.e. to the topological properties of the nuclear configuration space. One should note, however, that the catchment region definition of molecular structure [33] distinguishes between all stable conformers, optical isomers and *cis-trans* isomers, whereas the molecular structure concept based upon bond graphs of the charge density gradient field [36–38] does not, since it assigns identical graphs to some of the above structurally different chemical species.

The third partitioning of the nuclear configuration space results in subsets of R defined by equipotential contour hypersurfaces containing critical points of $E(\underline{r})$ [39]. These subsets generate the "critical level topology" $\boldsymbol{T}_F$ of $\boldsymbol{R}$. This topology is directly related to the number and distribution of various critical points of the hypersurface E and it is partially determined by critical point inequalities [34]. The topology $\boldsymbol{T}_F$ is ideally suited for the analysis of energy requirements of conformational or reaction processes.

Many of the topological features of the hypersurface are determined by the critical points $\{\underline{r}_C^{(l)}\}$. For a general hypersurface the relations between the number of various types of critical points are given by the Morse inequalities [34] and are extensively used in topological analysis [40–42]. Stronger relations, providing *both lower and upper bounds* for the number of critical points of a given type have been derived for an important class of energy hypersurfaces [43]. In chemical applications, various interrelations between critical points on energy hypersurfaces have been studied [5–17, 21–33, 43–46]. Following the notations of refs. 21 and 32 each critical point $\underline{r}_C$ is characterized by index λ, the number of negative eigenvalues of the Hessian matrix $\underline{\underline{H}}(\underline{r}_C)$ at $\underline{r}_C$. It has been demonstrated earlier [21] using a series of model surfaces that the *number*, *type* and *distribution* of critical points are the key features determining the fundamental morphology and the complexity of chemical processes on the hypersurface. Since the number of minima (index $\lambda = 0$), various saddle points ($0 < \lambda < n$) and maxima ($\lambda = n$) are interrelated, [34, 41–43], these relations place limits on the number of possible reaction mechanisms [21]. Besides the constraints on the number of various critical points, their distribution (relative position) is also of importance. Although precise determination of their location is a metric space problem rather than a topological one, a topological characterization of this distribution has been given in terms of catchment regions [33]. By regarding two critical points *neighbours* if and only if the corresponding catchment regions have a common boundary point [33], a neighbour relation may be defined:

$$N(\underline{r}_C^{(i)}, \underline{r}_C^{(j)}) = \begin{cases} 1 & \text{if } \bar{C}^{\underline{r}_C^{(i)}} \cap \bar{C}^{\underline{r}_C^{(j)}} \neq \varnothing. \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

That is, $N(\underline{r}_C^{(i)}, \underline{r}_C^{(j)})$ is 1 if $\underline{r}_C^{(i)}$ and $\underline{r}_C^{(j)}$ are neighbours and 0 if they are non-neighbours. This neighbour relation for the catchment region partitioning, combined with the general results of critical point theory [41–43] results in important inequalities governing the number of chemical structures and reaction mechanisms on a given hypersurface [33]. The same technique is applicable for studying the relative distribution of critical points on energy component hypersurfaces [21, 43, 44].

Homotopy theory of differential topology [41, 42, 47, 48] is simply described as the theory of continuous deformations. In the present work we shall apply the concept of homotopy of reaction paths to arrive at a topological definition of reaction mechanisms, and we shall show that this definition is consistent with the one given in an earlier study [33]. Homotopy theory is closely linked to catastrophe theory [49, 50]. Catastrophe theory deals with sudden, discontinuous changes of mathematical models caused by smooth, continuous changes in some control parameters. Its application to energy hypersurfaces provides an intuitively transparent interpretation of various catchment regions, since $C^{\underline{r}_C^{(l)}}$ may be regarded as the basin associated with critical point attractor $\underline{r}_C^{(l)}$ [33]. Boundaries of catchment regions form the catastrophe set of the hypersurface, since the assignment of a point moving smoothly in the nuclear configuration space changes abruptly from one critical point to another at the boundary of a catchment region. In addition to the analysis of structural stability and reaction path problems on a given hypersurface, catastrophe theory is applicable for the analysis of topological changes of the calculated hypersurface, caused by variations in the approximate wavefunctions. Orbital exponents or contraction coefficients or some other parameters of an approximate molecular wavefunction take the role of control parameters, and the topological changes induced by variations of these control parameters can be studied by catastrophe theory. In a topology based on the catchment region partitioning the disappearance or creation of critical point attractors $\underline{r}_C$ and a change in the neighbour relation (3) of two existing critical points correspond to elementary catastrophes of the bifurcation or conflict type. The family of hypersurfaces generated by variations in the control parameters, i.e. the *universal unfolding* of E, yields all topologically distinct descriptions of the molecular system, within the constraints of the given approximation for wavefunctions ψ.

In this study we analyse a *global topological* model of energy hypersurfaces, which unifies some earlier *geometrical* models into a single mathematical framework. In particular, we shall

(1) develop a model of the nuclear configuration space R in which *points of nuclear geometries*, as basic chemical entities, are replaced by *open sets* of R, where R is defined as a topological space,

(2) prove that partitionings of R based upon curvature or catchment region properties lead to mathematically rigorous global topologies of both R and the energy hypersurface E,

(3) show that the description of reaction mechanisms in terms of a sequence of catchment regions is equivalent to a description based on homotopically equivalent reaction paths

(4) propose topological definitions for chemical structure and reaction mechanisms as open sets of a topological space, *reaction topology* $(\boldsymbol{R}, \boldsymbol{T}_C)$

(5) show by the examples of the D_μ domain, catchment region and energy level topologies how a combination of a set of chemical properties leads to new topologies on R and E.

3. Topology of Potential Energy Hypersurfaces

Topology may be thought of as a generalization of geometry in which all structural features are swept away except those relevant to the preservation of the continuity of certain functions. General topology [51] is the abstract study of nearness, neighbourhoods, connectedness and continuity. In the present study we shall develop a topological model for a special class of hypersurfaces: potential energy hypersurfaces. In a subsequent study we shall consider more general hypersurfaces. For easy reference a short list of topological definitions is given in the Appendix.

The potential energy hypersurface $E(\underset{\sim}{r})$ of a molecular system is usually defined within the framework of the Born-Oppenheimer [1] or an equivalent approximation based on the separation of "slowly changing" and "rapidly changing" variables [52], and is not strictly valid. Nevertheless, it is an excellent approximation and gives insight into most low-energy chemical processes on the molecular level. $E(\underset{\sim}{r})$ is defined over the n-dimensional nuclear configuration space R. It is often convenient to choose R as the $n' = 3N$ dimensional space of the mass-weighted cartesian coordinates of the N nuclei present in the molecular system. In such a model special consideration must be given to the 3 translational and particularly to the 3 rotational degrees of freedom of the molecular system as a whole, by defining a rotating frame fulfilling the Eckart conditions [53, 54]. Similar conditions may be applied to give an equivalent description of the molecular system by using an $n = 3N - 6$ dimensional R space of some suitably chosen internal coordinates[1].

For special choices of the coordinates of the nuclear configuration space R subspaces ${}^{m}R$ of R may be defined which allow for substantial simplification of a topological analysis. These subspaces may allow various compactifications, e.g. transformations into circles or hyperspheres by the Alexandrov one-point compactification [47, 48]. For coordinates along which the energy hypersurface is periodic [21], conditions analogous to the Born–Kármán boundary conditions lead to a mapping of a subset onto a torus [40]. In such cases the topological analysis may be restricted to an energy function defined over a hypersphere or torus (see Fig. 1).

Throughout the following discussion we shall always refer to R, however, it should be kept in mind that the same topological analysis is applicable to subsets of the above types.

3.1. Metric Properties and the Metric Topologies

For the analysis of nuclear motions, using generalized coordinates, a metric may be introduced into space R by defining the element of arc ds as

$$ds^2 = g_{ij}\, dr^i\, dr^j, \tag{4}$$

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[1] In deviation from the common custom the left superscript, indicating the dimension of the space, will be usually omitted if this dimension is n, that is, we shall write simply R for ${}^{n}R$. On the other hand, the left superscript 1 will be always used for a one dimensional space ${}^{1}R$.

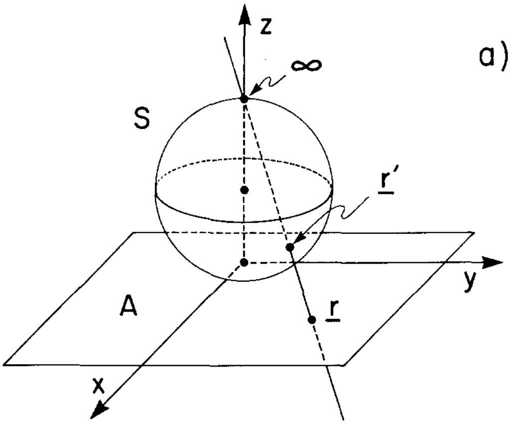

Fig. 1a. Sphere S is the Alexandrov one-point compactification of the (x, y) plane A. The line passing through the "north pole" assigns point $\underset{\sim}{r} \in A$ to point $r' \in S$. The "ideal point of infinity" of plane A is mapped onto "north pole" ∞ of the sphere

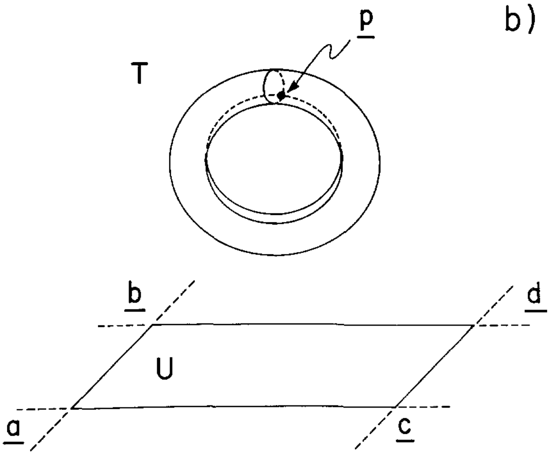

Fig. 1b. The unit cell U of a subspace ${}^2R \subset R$ over which E is periodic, is mapped onto torus T. Intervals $[\underset{\sim}{a}, \underset{\sim}{b}]$, $[\underset{\sim}{c}, \underset{\sim}{d}]$ and $[\underset{\sim}{a}, \underset{\sim}{c}]$, $[\underset{\sim}{b}, \underset{\sim}{d}]$, pairwise equivalent by periodicity, are mapped onto unique circles on the torus with common point p, the common image of equivalent points $\underset{\sim}{a}$, $\underset{\sim}{b}$, $\underset{\sim}{c}$, and $\underset{\sim}{d}$

and a related metric of the ${}^{n+1}R = R \otimes {}^1R$ space, embedding the energy hypersurface may be given [32] by

$$ {}^{n+1}ds^2 = {}^{n+1}g_{ij}\, {}^{n+1}dr^i\, {}^{n+1}dr^j. \tag{5}$$

Here g_{ij} and ${}^{n+1}g_{ij}$ are the corresponding Riemannian metric tensors. The elements of arc, ds and ${}^{n+1}ds$, are infinitesimal displacements along path $P \subset R$ and along the corresponding relief path ${}^{n+1}P \subset {}^{n+1}R$, respectively [32].

The hypersurface $E(\underset{\sim}{r})$ is assumed to be a continuous and infinitely differentiable function at most chemically important points $\underset{\sim}{r} \in R$. For polyatomic molecules, however, some of the derivatives of $E(\underset{\sim}{r})$ may become discontinuous at intersections of potential surfaces describing various excited electronic states [55, 28, 29], and most approximate solutions for the $E = \langle\Psi|\hat{H}|\Psi\rangle$ expectation value do not give physically meaningful results in the neighbourhood of coulomb singularities of coincident nuclear positions. A union of neighbourhoods of such points define the domain D_{excl}, which domain requires special treatment [32, 33].

In order to obtain a function $E'(\underline{r})$, twice continuously differentiable ($E'(\underline{r}) \in \boldsymbol{C}^2$) over the entire nuclear configuration space $\boldsymbol{R}$, we shall choose a bounded, continuous function $e(\underline{r})$ over the closure $\bar{\boldsymbol{D}}_{\text{excl}}$ with the following properties[1]:

(1) $e : \bar{\boldsymbol{D}}_{\text{excl}} \to {}^1\boldsymbol{R}$ (6)

(2) $e \in \boldsymbol{C}^2$ (7)

(3) $e(\underline{r}') = \lim\limits_{\substack{\underline{r} \to \underline{r}' \\ \underline{r} \in \boldsymbol{D}^c_{\text{excl}}}} E(\underline{r})$ (8)

for every element $\underline{r}'$ on the boundary of $\boldsymbol{D}_{\text{excl}}$.

(4) relations analogous to (3) are valid for all first order and

(5) for all second order partial deviatives of $e(\underline{r})$ and $E(\underline{r})$.

Such a function $e(\underline{r})$ is a twice continuously differentiable extension of $E(\underline{r})$ from $\boldsymbol{D}^c_{\text{excl}}$ to $\boldsymbol{D}_{\text{excl}}$.

In the following $E'(\underline{r})$ will be regarded as the hypersurface $E'(\underline{r}) : \boldsymbol{R} \to {}^1\boldsymbol{R}$, $E'(\underline{r}) \in \boldsymbol{C}^2$, defined as

$$E'(\underline{r}) = E(\underline{r}) \text{ if } \underline{r} \in \boldsymbol{D}^c_{\text{excl}} \tag{9a}$$

$$E'(\underline{r}) = e(\underline{r}) \text{ if } \underline{r} \in \boldsymbol{D}_{\text{excl}}. \tag{9b}$$

Furthermore, unless special distinction will be necessary, the extended $E'(\underline{r})$ hypersurface will be investigated and the distinguishing apostrophe will be omitted. Although not necessary for the present analysis, we may also require that at points $\underline{r}$ of coincident nuclear positions $e(\underline{r})$ takes the energy value of the isoelectronic molecular system in which the set of coincident nuclei is replaced by the nucleus of the corresponding united atom [29, 31].

An open sphere $S(\underline{p}, \delta)$ of radius δ about point $\underline{p}$ in the nuclear configuration space $\boldsymbol{R}$ is defined as

$$S(\underline{p}, \delta) = \{\underline{r} : \underline{r} \in \boldsymbol{R}, d(\underline{p}, \underline{r}) < \delta\}, \tag{10}$$

where $d(\underline{p}, \underline{r})$ is the distance function in the given metric [32]. The *metric topology* $\boldsymbol{T}$ on $\boldsymbol{R}$ is generated by the class of open spheres in $\boldsymbol{R}$ as subbase, thus $\boldsymbol{R}$ is a topological space $(\boldsymbol{R}, \boldsymbol{T})$ with a unique topology $\boldsymbol{T}$ *induced* by the metric. The metric topology ${}^{n+1}\boldsymbol{T}$ of ${}^{n+1}\boldsymbol{R}$ is defined similarly in terms of open spheres

$${}^{n+1}S({}^{n+1}\underline{p}, \delta) = \{{}^{n+1}\underline{r} : {}^{n+1}\underline{r} \in {}^{n+1}\boldsymbol{R}, {}^{n+1}d({}^{n+1}\underline{p}, {}^{n+1}\underline{r}) < \delta\}, \tag{11}$$

where ${}^{n+1}d({}^{n+1}\underline{p}, {}^{n+1}\underline{r})$ is the distance function in the metric of ${}^{n+1}\boldsymbol{R}$. The class of ${}^{n+1}S({}^{n+1}\underline{p}, \delta)$ open spheres in ${}^{n+1}\boldsymbol{R}$ form a subbase for the unique topology ${}^{n+1}\boldsymbol{T}$, thus $({}^{n+1}\boldsymbol{R}, {}^{n+1}\boldsymbol{T})$ is a topological space with the metric topology ${}^{n+1}\boldsymbol{T}$.

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[1] In the topological sense D_{excl} is not necessarily a domain since it may be disconnected. In spite of this, for sake of keeping the terminology simple D_{excl} will be referred to as a domain, unless its potential disconnectedness will have some significance in our analysis.

It is useful to remember that $E(\underline{r})$ with the extended interpretation has several intimately related but distinctly different meanings, depending on the context. Whenever necessary, different notations will be used to emphasise a particular interpretation.

$E(\underline{r})$ may refer to the energy *value* at point $\underline{r}$,

$$E(\underline{r}) \in {}^{1}\boldsymbol{R}. \tag{12}$$

$E(\underline{r})$ may also refer to the energy expectation value *functional*

$$\underline{\underline{E}}(\underline{r}) : \boldsymbol{R} \to {}^{1}\boldsymbol{R}, \qquad \underline{\underline{E}}(\underline{r}) \in C^{2}, \tag{13}$$

which assigns the above $E(\underline{r})$ values to points $\underline{r} \in \boldsymbol{R}$. $E(\underline{r})$ may also mean the energy *hypersurface* E embedded in the space ${}^{n+1}\boldsymbol{R}$, i.e. the point set $E \subset {}^{n+1}\boldsymbol{R}$,

$$E = \{{}^{n+1}\underline{r} : {}^{n+1}\underline{r} \in {}^{n+1}\boldsymbol{R},\ {}^{n+1}r^{i} = r^{i}(i \leq n),\ {}^{n+1}r^{n+1} = E(\underline{r}),\ \underline{r} \in \boldsymbol{R}\}. \tag{14}$$

Here on the right hand side of Eq. (14) $E(\underline{r})$ refers to the function value at point $\underline{r} \in \boldsymbol{R}$ whereas on the left hand side of the relation E means a point set in ${}^{n+1}\boldsymbol{R}$.

A mapping $\underline{E}$ between $\boldsymbol{R}$ and $E \subset {}^{n+1}\boldsymbol{R}$,

$$\underline{E} : \boldsymbol{R} \to E \tag{15}$$

is defined by the $\underline{\underline{E}}(\underline{r})$ functional as

$$\underline{E}(\underline{r}) = {}^{n+1}\underline{r}, \tag{16}$$

where

$${}^{n+1}r^{i} = r^{i}(i \leq n) \tag{17a}$$

and

$${}^{n+1}r^{n+1} = E(\underline{r}),\ \underline{r} \in \boldsymbol{R}. \tag{17b}$$

Since $E \subset {}^{n+1}\boldsymbol{R}$ is defined as the range of mapping $\underline{E} : \boldsymbol{R} \to {}^{n+1}\boldsymbol{R}$, which has domain the entire space $\boldsymbol{R}$, it is clear that $\underline{E}$ is continuous for any pairs of topologies $\boldsymbol{T}'$ of $\boldsymbol{R}$ and ${}^{n+1}\boldsymbol{T}'_{E}$ of $E \subset {}^{n+1}\boldsymbol{R}$ where the ${}^{n+1}\boldsymbol{T}'_{E}$-open sets in E are images of $\boldsymbol{T}'$-open sets in $\boldsymbol{R}$.

The metric topology ${}^{n+1}\boldsymbol{T}$ of ${}^{n+1}\boldsymbol{R}$ defines a *relative topology* ${}^{n+1}\boldsymbol{T}_{E}$ on the energy hypersurface E, $E \subset {}^{n+1}\boldsymbol{R}$:

$${}^{n+1}\boldsymbol{T}_{E} = \{{}^{n+1}G_{E} : {}^{n+1}G_{E} = {}^{n+1}G \cap E,\ {}^{n+1}G \in {}^{n+1}\boldsymbol{T}\} \tag{18}$$

that is, the ${}^{n+1}\boldsymbol{T}_{E}$-open subsets of E are the intersections of the ${}^{n+1}\boldsymbol{T}$-open subsets of ${}^{n+1}\boldsymbol{R}$ with the hypersurface $E(\underline{r})$. With this *relativization* of ${}^{n+1}\boldsymbol{T}$ to E, the topological space $(E, {}^{n+1}\boldsymbol{T}_{E})$ is a subspace of topological space $({}^{n+1}\boldsymbol{R}, {}^{n+1}\boldsymbol{T})$:

$$(E, {}^{n+1}\boldsymbol{T}_{E}) \subset ({}^{n+1}\boldsymbol{R}, {}^{n+1}\boldsymbol{T}). \tag{19}$$

In order to establish relations between topologies on R and topologies on the hypersurface E, we shall rely on the mapping $\underset{\sim}{E}$ and on the functional properties of $\underset{\sim}{E}(\underset{\sim}{r})$. The construction of space ${}^{n+1}R = R \otimes {}^{1}R$ as a product space is reflected in metric ${}^{n+1}g_{ij}$ and in the induced relative topology ${}^{n+1}\boldsymbol{T}_E$ on E. The extended $\underset{\sim}{E}(\underset{\sim}{r})$ functional is continuous in the metric of R by construction, consequently the mapping

$$\underset{\sim}{E}:(R, \boldsymbol{T}) \rightarrow (E, {}^{n+1}\boldsymbol{T}_E) \tag{20}$$

is continuous with respect to topologies $\boldsymbol{T}$ and ${}^{n+1}\boldsymbol{T}_E$. It should be noted however, that continuity depends on the actual topologies chosen and it is by no means guaranteed for arbitrary topologies. The inverse $\underset{\sim}{E}^{-1}$ of $\underset{\sim}{E}$ is clearly a projection from E to R,

$$\underset{\sim}{E}^{-1} = \underset{\sim}{\Pi}_E : E \rightarrow R, \tag{21}$$

where $\underset{\sim}{\Pi}_E$ is a restriction of projection

$$\underset{\sim}{\Pi} : {}^{n+1}R \rightarrow R \tag{22}$$

to subset $E \subset {}^{n+1}R$, and it is continuous since $\underset{\sim}{E} = \underset{\sim}{\Pi}_E^{-1}$ maps $\boldsymbol{T}$-open sets of R onto ${}^{n+1}\boldsymbol{T}_E$-open sets of E. The $\underset{\sim}{E}(\underset{\sim}{r})$ functional is single valued, and the $\underset{\sim}{E}: R \rightarrow E$ mapping is one-one and onto by definition. Consequently, $\underset{\sim}{E}$ is a homeomorphism between topological spaces $(R, \boldsymbol{T})$ and $(E, {}^{n+1}\boldsymbol{T}_E)$. That is, the above two spaces are topologically equivalent, which property will be utilized in analysing the *energy hypersurface* E in terms of topological properties of the *nuclear configuration space* R.

3.2. Topologies Based on Curvature Properties

The D_μ domain partitioning of the R nuclear configuration space, Eq. (1), reflects the relative importance of various coordinate domains in the analysis of minimum energy reaction paths. In particular, D_0 domains reflect the distribution of the two most important subsets of critical points: minima of equilibrium nuclear geometries and the saddle points of transition "states" [32]. Since the union of all D_μ^i domains with D_{excl} is the full R nuclear configuration space, Eq. (1), the union of their closures in the metric topology $\boldsymbol{T}$ is also R,

$$R = \bigcup_{\mu,i} \bar{D}_\mu^i \cup \bar{D}_{\mathrm{excl}}. \tag{23}$$

The D_μ domains and D_{excl} form a generating subbase

$$\boldsymbol{D}' = \{D_\mu^i\} \cup \{D_{\mathrm{excl}}\} \tag{24}$$

for a unique topology $\boldsymbol{T}_{D'}$ on R. Since elements of $\boldsymbol{D}'$ are disjoint sets, $\boldsymbol{D}'$ is also a base for topology $\boldsymbol{T}_{D'}$. Clearly, $R \in \boldsymbol{T}_{D'}$ due to Eq. (1), and $\varnothing \in \boldsymbol{T}_{D'}$, since $\varnothing$ is the *empty* union of sets in $\boldsymbol{D}'$.

The $(R, \boldsymbol{T}_{D'})$ topological space is closely related to a topology on the energy hypersurface E itself. The images of the D_μ^i and D_{excl} elements of subbase $\boldsymbol{D}'$, generated by mapping $\underset{\sim}{E}$, i.e. sets

$$D^i_{\mu E} = \underset{\sim}{E}(D^i_\mu), \qquad D^i_\mu \in \boldsymbol{D}', \qquad D^i_{\mu E} \subset E, \tag{25}$$

$$D_{\mathrm{excl}\,E} = \underset{\sim}{E}(D_{\mathrm{excl}}), \qquad D_{\mathrm{excl}} \in \boldsymbol{D}', \qquad D_{\mathrm{excl}\,E} \subset E \tag{26}$$

define a cover of the E energy hypersurface. By the definition of the hypersurface, and by virtue of Eq. (1), the union of all these images is the hypersurface E itself,

$$E = \bigcup_{\mu,i} D^i_{\mu E} \cup D_{\mathrm{excl}\,E}. \tag{27}$$

These images form a generating subbase $\boldsymbol{D}'_E$, defined as

$$\boldsymbol{D}'_E = \{D^i_{\mu E}\} \cup \{D_{\mathrm{excl}\,E}\}, \tag{28}$$

for a unique topology $\boldsymbol{T}_{D'E}$ on hypersurface E. $\boldsymbol{D}'_E$ itself is also a base for $T_{D'E}$. Since mapping $\underset{\sim}{E}: R \to E$ is used to define the subbase for the $\boldsymbol{T}_{D'E}$ topology, it is evident that $\underset{\sim}{E}$ is $\boldsymbol{T}_{D'} - \boldsymbol{T}_{D'E}$ continuous and its inverse mapping, projection $\underset{\sim}{\Pi}_E = \underset{\sim}{E}^{-1}$ is $\boldsymbol{T}_{D'E} - \boldsymbol{T}_{D'}$ continuous; they establish a one-one and onto assignment between subbases $\boldsymbol{D}'$ of $\boldsymbol{T}_{D'}$ and $\boldsymbol{D}'_E$ of $\boldsymbol{T}_{D'E}$, consequently, inverse images of $\boldsymbol{T}_{D'E}$-open sets are $\boldsymbol{T}_{D'}$-open and vice versa. Mapping $\underset{\sim}{E}: R \to E$ is pointwise one-one and onto, consequently, $\underset{\sim}{E}$ is a homeomorphism between topological spaces $(R, \boldsymbol{T}_{D'})$ and $(E, \boldsymbol{T}_{D'E})$. The pair of topological spaces $(R, \boldsymbol{T}_{D'})$ and $(E, \boldsymbol{T}_{D'E})$ may then be studied simultaneously since any topological property of $(R, \boldsymbol{T}_{D'})$ is also a topological property of $(E, \boldsymbol{T}_{D'E})$.

Another topology, $\boldsymbol{T}_{D''}$ on R, also defined in terms of domains D^i_μ and D_{excl} may be given by taking the set of $\boldsymbol{T}$-closures,

$$\boldsymbol{D}'' = \{\bar{D}^i_\mu\} \cup \{\bar{D}_{\mathrm{excl}}\} \tag{29}$$

as defining subbase.

$\underset{\sim}{E}$-images of elements of $\boldsymbol{D}''$ generate a defining subbase for topology $\boldsymbol{T}_{D''E}$ on E.

Particularly useful are the topology $\boldsymbol{T}_D$ of defining subbase $\boldsymbol{D}$, where

$$\boldsymbol{D} = \boldsymbol{D}' \cup \boldsymbol{D}'', \tag{30}$$

and the equivalent topology $\boldsymbol{T}_{DE}$ of defining subbase

$$\boldsymbol{D}_E = \boldsymbol{D}'_E \cup \boldsymbol{D}''_E. \tag{31}$$

Clearly, the mapping $\underset{\sim}{E}$ is a homeomorphism between topological spaces $(R, \boldsymbol{T}_D)$ and $(E, \boldsymbol{T}_{DE})$.

Every D^i_μ domain as well as every boundary set [32] $B_{D^{i_1}_{\mu_1}, D^{i_2}_{\mu_2} \cdots D^{i_k}_{\mu_k}}$ denoted in short as $B^{i_1 i_2 \cdots i_k}_{\mu_1 \mu_2 \cdots \mu_k}$ and defined as the intersection

$$B^{i_1 i_2 \cdots i_k}_{\mu_1 \mu_2 \cdots \mu_k} = \bigcap_{l=1}^{k} \bar{D}^{i_l}_{\mu_l}, \tag{32}$$

is a $\boldsymbol{T}_D$-open set in $\boldsymbol{R}$. Similarly, D_{excl} and any $B_{D^{i_1}_{\mu_1}\cdots D^{i_k}_{\mu_k}D_{\text{excl}}}$ boundary set

$$B_{D^{i_1}_{\mu_1}\cdots D^{i_k}_{\mu_k}D_{\text{excl}}} = \bigcap_{l=1}^{k} \bar{D}^{i_l}_{\mu_l} \cap \bar{D}_{\text{excl}} \tag{33}$$

is a $\boldsymbol{T}_D$-open set in $\boldsymbol{R}$.

Boundary sets $B_{ED_{\mu_1}\cdots D_{\mu_k}}$ and $B_{ED^{i_1}_{\mu_1}\cdots D_{\mu_k}D_{\text{excl}}}$ in topological space (E, $\boldsymbol{T}_{DE}$) are $\boldsymbol{T}_{DE}$-open sets and are defined by equations analogous to Eqs. (32)–(33).

The $\boldsymbol{T}_D$ topology in the nuclear configuration space $\boldsymbol{R}$ and the equivalent topology $\boldsymbol{T}_{DE}$ on the energy hypersurface E preserve only those structural features which are relevant to the curvature properties of equipotential contour surfaces, and treat any other property of $\boldsymbol{R}$ or E as irrelevant. This feature clearly shows the principle of a topological analysis, as such an analysis may concentrate on a set of particular properties designated as *topological* by the choice of open sets, and all other non-topological properties are swept away and disregarded. For example, in the ($\boldsymbol{R}$, $\boldsymbol{T}_D$) and (E, $\boldsymbol{T}_{DE}$) topological spaces energy relations such as relative stabilities of equilibrium nuclear arrangements are non-topological and are non-applicable. In spite of this, not all links with a metric space model are severed. By definition, a D_μ domain is a connected set with the general property that for every $\underline{r} \in \boldsymbol{R}$ in a locally defined ${}^{n-1}\boldsymbol{R}(\underline{r})$ subspace of *metric space* $\boldsymbol{R}$, where ${}^{n-1}\boldsymbol{R}(\underline{r})$ is orthogonal to the gradient $\underline{g}(\underline{r})$, the $n-1$ dimensional Hessian matrix ${}^{n-1}\underline{\underline{H}}(\underline{r})$ has exactly μ negative eigenvalues [32].

Topological space (E, $\boldsymbol{T}_{DE}$) has the following chemically significant properties:

(1) All energy minima of equilibrium nuclear geometries belong to sets D^{i}_{0E}, open in $\boldsymbol{T}_{DE}$.

(2) All saddle points of transition "state" geometries belong to the sets D^{i}_{0E}, open in $\boldsymbol{T}_{DE}$.

(3) Ideal, minimum energy reaction paths are stable with respect to displacements defined in the metric topology, only in sets D^{i}_{0E}, open in $\boldsymbol{T}_{DE}$. Note, that whereas the displacements are defined in the metric topology [32], nevertheless, the stability of minimum energy paths is a $\boldsymbol{T}_{DE}$-topological property.

(4) For any point of a $B_{ED^{i_1}_{\mu_1}\cdots D^{i_k}_{\mu_k}}$ boundary set or that of a boundary set $B_{ED^{i_1}_{\mu_1}\cdots D^{i_l}_{\mu_l}D_{\text{excl}}}$, where $l \geq 2$, the corresponding ${}^{n-1}\underline{\underline{H}}(\underline{r})$ Hessian matrix in the local ${}^{n-1}\boldsymbol{R}(\underline{r})$ subspace of $\boldsymbol{R}$ is singular. This result is a direct consequence of Theorem 2, Ref. [32].

This property (4) may be utilized for the determination of boundary sets in (E, $\boldsymbol{T}_{DE}$). A singularity-following algorithm applied on the locally defined ${}^{n-1}\underline{\underline{H}}(\underline{r})$ Hessian matrices in metric space $\boldsymbol{R}$ may be used to determine boundary contour hypersurfaces of D^{i}_{μ} domains in metric space $\boldsymbol{R}$.

Topology $\boldsymbol{T}_{D'}$ is coarser than $\boldsymbol{T}_D$, since every element of $\boldsymbol{D}'$ is a $\boldsymbol{T}_D$-open set. On the other hand, boundary sets given in Eqs. (32–33) are $\boldsymbol{T}_D$-open sets but not $\boldsymbol{T}_{D'}$-open sets. Similarly, topology $\boldsymbol{T}_{D''}$ is coarser than $\boldsymbol{T}_D$, whereas $\boldsymbol{T}_{D'}$ and $\boldsymbol{T}_{D''}$ are non-comparable.

3.3. *Catchment Region Topologies*; "*Reaction Topology*" $(\boldsymbol{R}, \boldsymbol{T}_C)$

In the metric topological spaces $(\boldsymbol{R}, \boldsymbol{T})$ and $({}^{n+1}\boldsymbol{R}, {}^{n+1}\boldsymbol{T})$ the steepest descent reaction path $P_{\underline{r}} \subset \boldsymbol{R}$ and steepest descent relief path ${}^{n+1}P_{{}^{n+1}\underline{r}} \subset {}^{n+1}\boldsymbol{R}$ are defined as the path with origin $\underline{r} \in \boldsymbol{R}$ which follows the negative gradient $-\underline{g}(\underline{r})$, and its image under the mapping $\underline{E}: \boldsymbol{R} \to E$, respectively [32, 33]. The set of all steepest descent paths $\{P_{\underline{r}}\}$ with origins *not* in the $\boldsymbol{T}$-closure $\bar{D}_{\mathrm{excl}}$, i.e. $\underline{r} \in \bar{D}^{c}_{\mathrm{excl}}$, is partitioned into equivalence classes by their extremities which are either critical points $\underline{r}_C$, $\underline{r}_C \in \boldsymbol{R}$ or points in $\bar{D}_{\mathrm{excl}}$ [33]:

$$P^{(\underline{r}_C)} = \{P_{\underline{r}}: \underline{r}_C \in P_{\underline{r}}\} \tag{34}$$

and

$$P^{(\bar{D}_{\mathrm{excl}})} = \{P_{\underline{r}}: P_{\underline{r}} \cap \bar{D}_{\mathrm{excl}} \neq \varnothing\}. \tag{35}$$

That is,

$$\{P_{\underline{r}}, P_{\underline{r}}: \underline{r} \in D^{c}_{\mathrm{excl}}\} = \bigcup_{\underline{r}_C} P^{(\underline{r}_C)} \cup P^{(\bar{D}_{\mathrm{excl}})} \tag{36}$$

where the sets on the right hand side are disjoint. This relation implies an equivalence class partitioning for the origin points and defines a function $\eta(\underline{r}) = \underline{r}_E$ which assigns to each origin point $\underline{r}$ the corresponding extremity $\underline{r}_E$. The catchment region $C^{(\underline{r}_C)}$ of critical point $\underline{r}_C$ is defined as

$$C^{(\underline{r}_C)} = \{\underline{r}_C, \underline{r}, \underline{r}: \underline{r}_C \in P_{\underline{r}}\} \tag{37}$$

i.e. the set of all origin points of steepest descent paths of equivalence class $P^{(\underline{r}_C)}$, or, equivalently, as the set of all points from where a steepest descent path terminates at critical point $\underline{r}_C$ [33]. Similarly, the catchment region of $\bar{D}_{\mathrm{excl}}$ is defined as

$$C^{(\bar{D}_{\mathrm{excl}})} = \{\underline{r}, \underline{r}: P_{\underline{r}} \cap \bar{D}_{\mathrm{excl}} \neq \varnothing\}. \tag{38}$$

By writing $\underline{r}_C^{(\lambda,k)}$ for the k^{th} critical point of index λ, the partitioning of the nuclear configuration space $\boldsymbol{R}$ into catchment regions, Eq. (2), may be written[1] as

$$\boldsymbol{R} = \bigcup_{\lambda,k} C^{\underline{r}_C^{(\lambda,k)}} \cup C^{\bar{D}_{\mathrm{excl}}} \cup \bar{D}_{\mathrm{excl}}. \tag{39}$$

Eq. (39) is a proper partitioning since the sets on the right hand side are disjoint, as a consequence of the equivalence class partitioning of steepest descent paths. Consequently, the union of the $\boldsymbol{T}$-closures of these sets,

$$\boldsymbol{R} = \bigcup_{\lambda,k} \bar{C}^{\underline{r}_C^{(\lambda,k)}} \cup \bar{C}^{\bar{D}_{\mathrm{excl}}} \cup \bar{D}_{\mathrm{excl}}, \tag{40}$$

is a cover of space $\boldsymbol{R}$. The sets on the right hand side of Eq. (39) form a defining subbase

$$\boldsymbol{C}' = \{C^{\underline{r}_C^{(\lambda,k)}}\} \cup \{C^{\bar{D}_{\mathrm{excl}}}\} \cup \{\bar{D}_{\mathrm{excl}}\} \tag{41}$$

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[1] Parentheses of superscript of C will be omitted. Also, when emphasis will not be necessary, subscript C of critical points $\underline{r}_C^{(\lambda,k)}$ will be omitted.

which is also a base for a unique topology $\boldsymbol{T}_{C'}$ in the nuclear configuration space $\boldsymbol{R}$.

Since elements of $\boldsymbol{C}'$ form a cover for the nuclear configuration space $\boldsymbol{R}$, their images generated by mapping $\underline{E}:\boldsymbol{R} \rightarrow E$ form a cover for the energy hypersurface E:

$$E = \bigcup_{\lambda,k} C_E^{\underline{r}^{(\lambda,k)}} \cup C_E^{\bar{D}_{\mathrm{excl}}} \cup \bar{D}_{\mathrm{excl}\,E} \tag{42}$$

where

$$C_E^{\underline{r}^{(\lambda,k)}} = \underline{E}(C^{\underline{r}^{(\lambda,k)}}), \tag{43a}$$

$$C_E^{\bar{D}_{\mathrm{excl}}} = \underline{E}(C^{\bar{D}_{\mathrm{excl}}}), \tag{43b}$$

$$\bar{D}_{\mathrm{excl}\,E} = \underline{E}(\bar{D}_{\mathrm{excl}}). \tag{43c}$$

The sets on the right hand side of Eq. (42) form a defining subbase for a unique topology $\boldsymbol{T}_{C'E}$ on the energy hypersurface E. Analogously to the case of D_μ domain topologies, the $(\boldsymbol{R}, \boldsymbol{T}_{C'})$ and $(E, \boldsymbol{T}_{C'E})$ topological spaces are homeomorphic as it is established by mapping $\underline{E}:\boldsymbol{R} \rightarrow E$, which is a homeomorphism between the two topological spaces.

A unique pair of topologies, $\boldsymbol{T}_{C''}$ and $\boldsymbol{T}_{C''E}$ is defined by the sets

$$\boldsymbol{C}'' = \{\bar{C}^{\underline{r}^{(\lambda,k)}}\} \cup \{\bar{C}^{\bar{D}_{\mathrm{excl}}}\} \cup \{\bar{D}_{\mathrm{excl}}\} \tag{44}$$

and

$$\boldsymbol{C}''_E = \{\bar{C}_E^{\underline{r}^{(\lambda,k)}}\} \cup \{\bar{C}_E^{\bar{D}_{\mathrm{excl}}}\} \cup \{\bar{D}_{\mathrm{excl}\,E}\} \tag{44a}$$

respectively, as defining subbases. Here the sets on the right hand side of Eq. (44a) are the respective images of sets on the right hand side of Eq. (44), generated by mapping $\underline{E}:\boldsymbol{R} \rightarrow E$. Clearly, mapping $\underline{E}$ is a homeomorphism between topological spaces $(\boldsymbol{R}, \boldsymbol{T}_{C''})$ and $(E, \boldsymbol{T}_{C''E})$.

A unique topology $\boldsymbol{T}_C$ on $\boldsymbol{R}$, finer than both $\boldsymbol{T}_{C'}$ and $\boldsymbol{T}_{C''}$ is generated by defining subbase $\boldsymbol{C}$, where

$$\boldsymbol{C} = \boldsymbol{C}' \cup \boldsymbol{C}''. \tag{45}$$

Homeomorphic $\underline{E}$-images of elements of $\boldsymbol{C}$ generate the defining subbase $\boldsymbol{C}_E$ for the unique topology $\boldsymbol{T}_{CE}$ on E.

Open sets of the $(\boldsymbol{R}, \boldsymbol{T}_{C'})$ topological space, i.e. the $C^{\underline{r}^{(\lambda,k)}}$ catchment regions and their unions, form the basis for a rigorous quantum mechanical analysis of structural relations between molecules. Since all steepest descent paths in a catchment region $C^{\underline{r}^{(\lambda,k)}} \in \boldsymbol{T}_{C'}$ lead to and terminate at critical point $\underline{r}^{(\lambda,k)}$, it is natural to associate the structural identity of a molecular system of any nuclear geometry $\underline{r}$ within catchment region $C^{\underline{r}^{(\lambda,k)}}$ with critical point $\underline{r}^{(\lambda,k)}$. There are compelling physical reasons for assigning a unique structural label to an entire catchment region $C^{\underline{r}^{(\lambda,k)}} \subset \boldsymbol{R}$. On the one hand, even within the Born–Oppenheimer approximation, no molecule may sustain a fixed nuclear geometry. The nuclear geometry of an energetically stable molecular species shows *incessant* *variations* within a *neighbourhood* of the equilibrium geometry. That is, the concept of chemical structure must correspond to an *open set* in the nuclear configuration space $\boldsymbol{R}$, and *not* to a discrete point. On the other hand, the limits on the nuclear geometry variations that still preserve the chemical identity of the molecule, i.e. that preserves the assignment of the nuclear geometry to that of a critical point, can be defined precisely by the catchment regions. As long as a geometry variation does not lead out of $C^{\underline{r}^{(\lambda,k)}}$, the eventual return of the molecular system to the nuclear geometry of $\underline{r}^{(\lambda,k)}$, is likely, and within $C^{\underline{r}^{(\lambda,k)}}$ one may regard the chemical identity of the molecule preserved.

Some of the chemically significant properties of catchment region topologies are listed below as **(1)** $\cdots$ **(6)**. The topological definition of molecular structure is ultimately based upon the topological properties of the $\underline{\underline{E}}(\underline{r}) = \langle\psi(\underline{r})|\hat{H}(\underline{r})|\psi(\underline{r})\rangle$ energy expectation value functional:

(1) *Chemical structure* is defined as an open set which is an element of base $\boldsymbol{C}'$ of the topological space $(\boldsymbol{R}, \boldsymbol{T}_{C'})$. Elements of base $\boldsymbol{C}'$ (Eq. (41)) represent all distinct molecular structures of nuclear configuration space $\boldsymbol{R}$ [33].

The subset of all catchment regions for minima $\{\underline{r}^{(0,k)}\}$ contains all *stable molecular structures*,

$$\textbf{(2)}\ \{C^{\underline{r}^{(0,k)}}\} \subset \boldsymbol{C}' \tag{46}$$

whereas the subset

$$\textbf{(3)}\ \{C^{\underline{r}^{(1,k)}}\} \subset \boldsymbol{C}' \tag{47}$$

contains all molecular structures that correspond to *transition "states"* of chemical reactions on E, since the $\boldsymbol{T}_{C'}$-open sets $C^{\underline{r}^{(1,k)}}$ are the catchment regions of saddle points $\{\underline{r}^{(1,k)}\}$ of index $\lambda = 1$.

Chemical structures $\{C^{\underline{r}^{(\lambda,k)}}\}$ with index $\lambda \geq 2$ are energetically unstable and are of lesser chemical importance, since none of the associated critical points $\{\underline{r}^{(\lambda,k)}\}$ $(\lambda \geq 2)$ can fall on minimum energy reaction paths [6]. Whereas a $C^{\underline{r}^{(\lambda,k)}}$ catchment region of $\lambda \geq 2$, i.e. the "basin" associated with attractor $\underline{r}^{(\lambda,k)}$, $\lambda \geq 2$, may have non-empty interior (similarly to the $\lambda = 1$ example of Ref. [33a], Fig. 5), a non-degenerate $\underline{r}^{(\lambda,k)}$ critical point $(\lambda \geq 1)$ must belong to the catastrophe set for another catchment region $C^{\underline{r}^{(\lambda',k')}}$, $\delta_{\lambda\lambda'}\delta_{kk'} = 0$. Function $\eta(\underline{r})$ (and, of course, the characteristic functions of all catchment regions involved) show instabilities in the neighbourhood of $\underline{r}^{(\lambda,k)}$.

The number of distinct chemical structures in $\boldsymbol{R}$ is equal to the number of elements in base $\boldsymbol{C}'$, Eq. (41). Disregarding sets $C^{\bar{D}_{\text{excl}}}$ and $\bar{D}_{\text{excl}}$, this number is equal to the number of critical points $\{\underline{r}^{(\lambda,k)}\}$ in $\bar{D}^{c}_{\text{excl}}$, i.e. those critical points which are in $\boldsymbol{R}$ but not in $\bar{D}_{\text{excl}}$. Furthermore, the number of stable molecular structures, i.e., the number of open sets $C^{\underline{r}^{(0,k)}}$ is clearly equal to m_0, the number of $\underline{r}^{(0,k)}$ critical points of index $\lambda = 0$ (minima), and the number of transition "state" structures is equal to m_1, the number of critical points of index $\lambda = 1$. In general, the set of all structures may be given as the union

$$\{C^{\underline{r}^{(\lambda,k)}}\} = \bigcup_{\lambda=0}^{n} \{C^{\underline{r}^{(\lambda,k)}}\}_{k=1}^{m_\lambda} \tag{48}$$

and similarly for critical points

$$\{\underline{r}^{(\lambda,k)}\} = \bigcup_{\lambda=0}^{n} \{\underline{r}^{(\lambda,k)}\}_{k=1}^{m_\lambda}. \tag{49}$$

The numbers $m_0, m_1, m_2 \cdots m_n$ of critical points of indices $\lambda = 0, 1, 2 \cdots n$, respectively, that is, the number of stable molecular structures (m_0), transition "states" (m_1) and the number of various unstable molecular structures $C^{\underline{r}^{(\lambda,k)}}$ of $\lambda \geq 2$ (m_λ, $\lambda \geq 2$), are not arbitrary and lower limits are established by the Morse inequalities [34, 42, 43]. These constraints in combination with the neighbour relation, Eq. (3), defines constraints on the total number of elementary reaction mechanisms on the hypersurface E [33]. The neighbour relation, however, involves the $\boldsymbol{T}$-closures of catchment regions, consequently, topological space $(\boldsymbol{R}, \boldsymbol{T}_C)$ with defining subbase containing the closures of catchment regions is more suitable for the analysis of neighbour relations and reaction mechanisms than topological space $\{\boldsymbol{R}, \boldsymbol{T}_{C'}\}$. Whereas $\{\boldsymbol{R}, \boldsymbol{T}_{C'}\}$ leads the most directly to a topological definition of *molecular structure*, the space $\{\boldsymbol{R}, \boldsymbol{T}_C\}$ is ideally suited for a topological study on structural *relations* and *reaction mechanisms* [33].

Consider three simply connected $\boldsymbol{T}_C$-open sets $C^{\underline{r}^{(0,i)}}$, $C^{\underline{r}^{(1,j)}}$ and $C^{\underline{r}^{(0,k)}}$, and for simplicity assume that $C^{\underline{r}^{(1,j)}} = W^{(i,j,k)}$, the common boundary of $C^{\underline{r}^{(0,i)}}$ and $C^{\underline{r}^{(0,k)}}$. Consider two different paths $P^{(0)}$ and $P^{(1)}$, both of which lie in the union

$$M^{(i,j,k)} = C^{\underline{r}^{(0,i)}} \cup W^{(i,j,k)} \cup C^{\underline{r}^{(0,k)}},$$

that is $P^{(0)}$, $P^{(1)} \subset M^{(i,j,k)}$. We shall assume that the origin and extremity are $\underline{r}^{(0,i)}$ and $\underline{r}^{(0,k)}$ for both paths, and that both $P^{(0)}$ and $P^{(1)}$ pass through $\underline{r}^{(1,j)} \in C^{\underline{r}^{(1,j)}}$. Assuming a parametrization for these paths, $P^{(0)}: I \to \boldsymbol{R}$, and $P^{(1)}: I \to \boldsymbol{R}$, where $I = [0, 1]$, the unit interval, there exists a (generally non-unique) homotopy $\underline{H}: I \otimes I \to \boldsymbol{R}$, such that $\underline{H}(t, 0) = P^{(0)}(t)$, $\underline{H}(t, 1) = P^{(1)}(t)$, and for every $\underline{H}(t, \alpha)$, $P^{(\alpha)} \subset M^{(i,j,k)}$. In the special case when $P^{(0)}$ is the minimum energy path between $\underline{r}^{(0,i)}$ and $\underline{r}^{(0,k)}$, the reaction paths generated by H are homotopically equivalent to the minimum energy path $P^{(0)}$ and they involve only the same set of chemical structures. In chemical terms, all these paths represent the same *reaction mechanism.*

This analysis may be extended by replacing the critical points by arbitrary three points $\underline{r}^{(i)}$, $\underline{r}^{(j)}$, $\underline{r}^{(k)}$, one in each of $C^{\underline{r}^{(0,i)}}$, $W^{(i,j,k)}$ and $C^{\underline{r}^{(0,k)}}$, respectively. Considering all homotopies $\underline{H}$ for all triplets $(\underline{r}^{(i)}, \underline{r}^{(j)}, \underline{r}^{(k)})$, *the point set union* of *all reaction paths* P which are in $M^{(i,j,k)}$ is $M^{(i,j,k)}$ itself. Consequently, it is natural to associate $M^{(i,j,k)}$ with the reaction mechanism involving the above three chemical structures[1].

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[1] By a geographical analogy, consider a *collection* of *all* paths passing through a fixed sequence of valleys and mountain ridges. As far as the general itinerary is concerned the exact details of these paths are unimportant, and any path which follows the given sequence of valleys and ridges corresponds to the same itinerary. That is, the itinerary can be represented by the collection of all these paths. The paths and the itinerary are static features of the terrain, as opposed to the dynamic concept of the journey itself, which is the realization of the itinerary by following a given path. On energy hypersurfaces the reaction mechanism corresponds to the itinerary, given as a collection of reaction paths or simply as a list of valleys and ridges (a static concept), whereas the chemical reaction is the journey itself (a dynamic concept).

In our topological treatment a reaction mechanism is defined as the point set union of all reaction paths involving precisely a given set of chemical structures.

A topological generalization of the minium energy path concept is the *elementary reaction mechanism* of index λ. It is defined as an open set $M^{(i,j_\lambda,k)} \in \boldsymbol{T}_C$ of the $\{R, \boldsymbol{T}_C\}$ topological space, given as

$$\textbf{(4)}\ M^{(i,j_\lambda,k)} = C^{\underline{r}^{(0,i)}} \cup W^{(i,j_\lambda,k)} \cup C^{\underline{r}^{(0,k)}} \tag{50}$$

where

$$N(\underline{r}_C^{(0,1)}, \underline{r}_C^{(\lambda,j_\lambda)}) = 1 \tag{50a}$$

$$N(r_C^{(\lambda,j_\lambda)}, \underline{r}_C^{(0,k)}) = 1 \tag{50b}$$

and $W^{(i,j_\lambda,k)}$ is defined as the $\boldsymbol{T}_C$-open set

$$W^{(i,j_\lambda,k)} = (\bar{C}^{\underline{r}^{(0,i)}} \cap \bar{C}^{\underline{r}^{(\lambda,j_\lambda)}}) \cup C^{\underline{r}^{(\lambda,j_\lambda)}} \cup (\bar{C}^{\underline{r}^{(\lambda,j_\lambda)}} \cap \bar{C}^{\underline{r}^{(0,k)}}). \tag{50c}$$

That is, $W^{(i,j_\lambda,k)}$ is the union of structure $C^{\underline{r}^{(\lambda,j_\lambda)}}$ with its boundary segments common with structures $C^{\underline{r}^{(0,i)}}$ and $C^{\underline{r}^{(0,k)}}$. Note that the $\boldsymbol{T}$-closures of the $C^{\underline{r}^{(\lambda,k)}}$ structures are $\boldsymbol{T}_C$-open sets. It is clear that the definition may be interpreted in the metric topology as well, where the interior of $C^{\underline{r}^{(\lambda,j_\lambda)}}$ may be a non-empty set for $1 \leq \lambda < n$. Consequently, relations (50a) and (50b) may be valid even if $C^{\underline{r}^{(0,i)}}$ and $C^{\underline{r}^{(0,k)}}$ are non-neighbours,

$$N(\underline{r}_C^{(0,i)}, \underline{r}_C^{(0,k)}) = 0. \tag{51}$$

The set of elementary reaction mechanisms of index $\lambda = 1$ contain a subset, elements of which are the most directly related to the minimum energy path concept. The condition $\lambda = 1$ is necessary, since for a minimum energy path the chemical structure involved as intermediate between structures $C^{\underline{r}^{(0,i)}}$ and $C^{\underline{r}^{(0,k)}}$ is a transition "state" structure $C^{\underline{r}^{(1,j)}}$, the catchment region of saddle point $\underline{r}_C^{(1,j)}$, $\lambda = 1$. Note, however, that even in this case the condition

$$N(\underline{r}_C^{(0,i)}, \underline{r}_C^{(0,k)}) = 1 \tag{52}$$

cannot replace conditions (50a) and (50b), since it is possible, in spite of (52), that the boundary segment $\bar{C}^{\underline{r}^{(0,i)}} \cap \bar{C}^{\underline{r}^{(0,k)}}$ does not contain a saddle point $\underline{r}_C^{(\lambda,j)}$ with $\lambda = 1$,

$$\bar{C}^{\underline{r}^{(0,i)}} \cap \bar{C}^{\underline{r}^{(0,k)}} \cap \{\underline{r}_C^{(1,j)}\} = \varnothing \quad \text{for all } j. \tag{53}$$

Two finger-holes next to each other on a bowling ball are examples for this case, whereas the description of the more common cases, Eqs. (50) and (51), is applicable to most actual chemical surfaces, e.g. those in refs. [44,45] or to model surfaces discussed in Refs. [17,33]. Consequently, if Eq. (53) is valid, then there is no minimum energy path interconnecting $\underline{r}_C^{(0,i)}$ and $\underline{r}_C^{(0,k)}$ directly.

An elementary mechanism $M^{(i,j_\lambda,k)} \in \boldsymbol{T}_C$ of index λ is *regular* if

$$\textbf{(5)}\ \underline{r}_C^{(\lambda,j_\lambda)} \in \bar{C}^{\underline{r}^{(0,i)}} \cap \bar{C}^{\underline{r}^{(0,k)}}. \tag{54}$$

A *regular elementary mechanism* $M^{(i,j_1,k)}$ of index $\lambda = 1$ does contain all points of the unique minimum energy path $P^{(\underline{r}^{(1,j)})}$ which contains the non-degenerate saddle point $\underline{r}_C^{(1,j)}$ of index $\lambda = 1$[1]. This is a special (although probably the most important) case, and a general elementary mechanism $M^{(i,j_\lambda,k)}$ may happen to contain no segment of a minimum energy path at all which would connect $\underline{r}_C^{(0,i)}$ and $\underline{r}_C^{(0,k)}$.

Any *complex reaction mechanism* $M^{(i\to k)}$ leading from reactant $C^{\underline{r}^{(0,i)}}$ to a product $C^{\underline{r}^{(0,k)}}$ can be defined as a $\boldsymbol{T}_C$-open set which is a union of elementary reaction mechanisms $M^{(i,j_\lambda,k')}$:

$$\textbf{(6)}\quad M^{(i\to k)} = \bigcup_{l=1}^{t} M^{(i_l,j_{\lambda,l},k_l)}. \tag{55}$$

The $\boldsymbol{T}_C$-open sets in the above union form a *t-member chain* of elementary reactions, defined by the union in Eq. (55) and by the following conditions:

$$i_1 = i \tag{55a}$$

$$i_l = k_{l-1} \quad (l>1) \tag{55b}$$

$$k_t = k \tag{55c}$$

$$i_l \neq i_{l'} \quad \text{if } l \neq l'. \tag{55d}$$

That is, molecular structures $C^{\underline{r}^{(0,i)}}$ and $C^{\underline{r}^{(0,k)}}$ are subsets of elementary mechanisms $M^{(i_1,j_{\lambda,1},k_1)}$ and $M^{(i_t,j_{\lambda,t},k_t)}$, respectively, and their intersection with any other $M^{(i_l,j_{\lambda,l},k_l)}$ elementary mechanism is the empty set whenever $i \neq k$:

$$C^{\underline{r}^{(0,i)}} \subset M^{(i_1,j_{\lambda,1},k_1)}, \tag{56}$$

$$C^{\underline{r}^{(0,k)}} \subset M^{(i_t,j_{\lambda,t},k_t)}, \tag{57}$$

$$C^{\underline{r}^{(0,i)}} \cap M^{(i_l,j_{\lambda,l},k_l)} = \varnothing \quad \text{for } l>1 \tag{58}$$

$$C^{\underline{r}^{(0,k)}} \cap M^{(i_l,j_{\lambda,l},k_l)} = \varnothing \quad \text{for } l<t. \tag{59}$$

For any other $C^{\underline{r}^{(0,m)}}$ molecular structure which is an intermediate in the complex mechanism $M^{(i\to k)}$ (Eq. (55)), that is, for $C^{\underline{r}^{(0,m)}}$ with

$$m = k_l \quad \text{for some } l,\ 1 \leq l < t-1, \tag{60}$$

the following two relations are valid:

$$C^{\underline{r}^{(0,m)}} \subset M^{(i_l,j_{\lambda,l},k_l)} \cap M^{(i_{l+1},j_{\lambda,l+1},k_{l+1})}, \tag{61}$$

and

$$C^{\underline{r}^{(0,m)}} \cap M^{(i_l,j_{\lambda,l'},k_{l'})} = \varnothing \text{ if } l' \neq l \text{ and } l' \neq l+1. \tag{62}$$

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[1] By far the most common minimum energy paths are those which interconnect two minima through a saddle point of index $\lambda = 1$. A descent from a saddle point, however, may lead to another saddle point on one or on both sides. When enumerating minimum energy paths by counting saddle points of index $\lambda = 1$, these generalized minimum energy paths are also counted.

The notation $M^{(i\to k)}$ for a complex mechanism does not specify the detailed course of the mechanism. For a detailed specification the

$$M^{(i\to k)} = M^{(i_1, j_{\lambda,1}, i_2, j_{\lambda,2} \cdots i_t, j_{\lambda,t}, k_t)} \tag{63}$$

notation is proposed.

A *t*-member chain of elementary mechanisms with the smallest number t for a given $M^{(i\to k)}$ interconversion process is called a *minimum chain.* For a fixed reactant and product there may exist several different minimum chains.

Conditions (55a–d) do not exclude the case of $i = k$, i.e. a *cycle.* The union of two different chains for $M^{(i\to k)}$ must contain a $\boldsymbol{T}_C$-open set which is a cycle; if

$$M_1^{(i\to k)} \neq M_2^{(i\to k)} \tag{64}$$

then exists $M^{(l\to l)} \subset \boldsymbol{T}_C$ such, that

$$M^{(l\to l)} \subset M_1^{(i\to k)} \cup M_2^{(i\to k)}. \tag{65}$$

Due to the topological equivalence of $(\boldsymbol{R}, \boldsymbol{T}_C)$ and $(E, \boldsymbol{T}_{CE})$, and to the equivalence of topological spaces $(\boldsymbol{R}, \boldsymbol{T}_{C'})$ and $(E, \boldsymbol{T}_{C'E})$, results **(1)** · · · **(6)** may be given an equivalent formulation with reference to the $\boldsymbol{T}_{CE}$ and $\boldsymbol{T}_{C'E}$ topologies.

3.4. Topologies Based on Energy Levels[1]

Consider all points ${}^{n+1}\underline{r}$ of the $E \subset {}^{n+1}R$ energy hypersurface, for which $E(\underline{r}) = A$, a constant. These points form a set E_A,

$$E_A = \{{}^{n+1}\underline{r}\colon {}^{n+1}r^{n+1} = E(\underline{r}) = A,\ {}^{n+1}\underline{r} = \underline{r} \oplus E(\underline{r})\}. \tag{66}$$

Any point ${}^{n+1}\underline{r} \in E_A$ is called a *point at level A*. A level C is called a *critical level* if there exists a critical point $\underline{r}_C^{(\lambda,k)}$ at this level,

$${}^{n+1}\underline{r}_C^{(\lambda,k)} \in E_C. \tag{67}$$

If a level set $E_A \subset E$ contains no critical point then A is called an *ordinary level.*

Each level set E_A may be given as a union of $E_A^{(i)}$ sets

$$E_A = \bigcup_i E_A^{(i)} \tag{68}$$

where each $E_A^{(i)}$ is a connected set and

$$\bar{E}_A^{(i)} \cap \bar{E}_A^{(j)} = \varnothing \quad \text{if } i \neq j. \tag{69}$$

If E_A is connected, then E_A itself is the only member of the union,

$$E_A = E_A^{(1)}. \tag{70}$$

In general, $E_A^{(i)}$ is a contour hypersurface of E at level A and is analogous to a contour level marking a given elevation on a geographical relief map. The actual

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[1] A detailed study on incidence matrices of the critical level topology has been given earlier [39].

calculation of the $E_A^{(i)}$ contour hypersurfaces may be based on contour following algorithms.

The set

$$\boldsymbol{C}_C = \{C^{(\lambda,k)}\} \tag{71}$$

of all critical levels is closed and also bounded by the absolute maximum and absolute minimum of $E(\underline{r})$ which are themselves elements of $\boldsymbol{C}_C$. More than one critical point may occur at the same level C and the set Q_C of all critical points at C will be called the *critical set* at level C.

Subsets $F_A, F_A^- \subset R$ are defined as

$$F_A = \{\underline{r}: E(\underline{r}) \leq A\} \tag{72}$$

$$F_A^- = \{\underline{r}: E(\underline{r}) < A\} \tag{73}$$

and are denoted as F_C and F_C^- if $A = C$, a critical level:

$$F_C = \{\underline{r}: E(\underline{r}) \leq C\} \tag{74}$$

$$F_C^- = \{\underline{r}: E(\underline{r}) < C\}. \tag{75}$$

Each of the sets F_A, F_A^- (and naturally F_C and F_C^-) can be given as a union, e.g.

$$F_A = \bigcup_i F_A^{(i)} \tag{76}$$

where each $F_A^{(i)}$ is connected and

$$\bar{F}_A^{(i)} \cap \bar{F}_A^{(j)} = \varnothing \text{ if } i \neq j. \tag{77}$$

Partitionings of F_A^- (and of F_C and F_C^-) are defined analogously, by including symbol $-$ or replacing A by C in Eqs. (76–77).

Topologies $\boldsymbol{T}_F$, $\boldsymbol{T}_{F^-}$, $\boldsymbol{T}_{F_C}$ and $\boldsymbol{T}_{F_C^-}$ in the nuclear configuration space R are defined by subbases

$$\boldsymbol{F}^A = \{F_A^{(i)}\}, \tag{78}$$

$$\boldsymbol{F}^{-A} = \{F_A^{-(i)}\}, \tag{79}$$

$$\boldsymbol{F}^C = \{F_C^{(i)}\}, \tag{80}$$

and

$$\boldsymbol{F}^{-C} = \{F_C^{-(i)}\}, \tag{81}$$

respectively. The elements of the $\boldsymbol{F}^A$ and $\boldsymbol{F}^{-A}$ subbases are partitioning sets for every level A, whereas the elements of the $\boldsymbol{F}^C$ and $\boldsymbol{F}^{-C}$ subbases are partitioning sets for all critical levels $C^{(\lambda,k)}$. All four subbases are actually bases for the respective topologies, since their elements are either pairwise disjoint sets or their intersection is one of the sets of the pair, thus it is an element of the subbase. For example,

$$F_A^{(i)} \neq F_B^{(j)} \tag{82}$$

and

$$F_A^{(i)} \cap F_B^{(j)} \neq \varnothing \tag{83}$$

is possible only if either

$$A > B \quad \text{and} \quad F_B^{(j)} \subset F_A^{(i)} \tag{84}$$

or

$$A < B \quad \text{and} \quad F_A^{(i)} \subset F_B^{(j)}. \tag{85}$$

Using the technique employed for the $\boldsymbol{T}_D$ and $\boldsymbol{T}_C$ topologies, images of the elements of the subbases, generated by mapping $\underline{E}$ on the hypersurface E, give defining subbases for four topologies on E, denoted by $\boldsymbol{T}_{FE}$, $\boldsymbol{T}_{F^-E}$, $\boldsymbol{T}_{F_CE}$ and $\boldsymbol{T}_{F_C^-E}$. Clearly, the topological spaces $(R, \boldsymbol{T}_F)$, $(R, \boldsymbol{T}_{F^-})$, $(R, \boldsymbol{T}_{F_C})$, $(R, \boldsymbol{T}_{F_C^-})$ and $(E, \boldsymbol{T}_{FE})$, (E, T_{F^-E}), $(E, \boldsymbol{T}_{F_CE})$, $(E, \boldsymbol{T}_{F_C^-E})$, respectively, are pairwise homeomorphic.

For fixed energy value A the union of the classically accessible regions of the nuclear configuration space R is precisely the $\boldsymbol{T}_F$-open set F_A. For disconnected F_A the $\boldsymbol{T}_F$-open sets $F_A^{(i)}$ of the union in Eq. (76) define all those subdomains among which no inter-conversion may take place at energy A. If A and B, $A < B$, are non-critical levels and if there is no critical level between A and B, then the number of subsets in the partitioning (76) of F_A and F_B is the same, that is, in

$$F_A = \bigcup_{i=1}^{k} F_A^{(i)} \tag{86}$$

$$F_B = \bigcup_{i=1}^{k'} F_B^{(i)} \tag{87}$$

the upper limits are the same,

$$k = k', \tag{88}$$

and one can choose the indices such that

$$F_A^{(i)} \subset F_B^{(i)}. \tag{89}$$

Consider a continuous change in energy as level B approaches a critical level C. A merger of two subdomains $F_B^{(i)}$ and $F_B^{(j)}$, may occur only at a critical level C as $B \to C$. However, such merger does not necessarily occur at every critical level. As an example, in a system of lakes the water level may rise to the top of a rock in the middle of one of the lakes (i.e. to a critical level $C^{(n,k)}$, corresponding to a local maximum, $\lambda = n = 2$), without the merger of two neighbour lakes. However, as pointed out above, a merger of two lakes implies a critical level (i.e. a $C^{(\lambda,k)}$ of a saddle point $\underline{r}_C^{(\lambda,k)}$, $\lambda = 1$).

When varying the energy value E, all topologically significant changes occur at critical levels, underlining the importance of critical level topologies $\boldsymbol{T}_{F_C}$ and

$\boldsymbol{T}_{F_C E}$. The $\boldsymbol{T}_{F_C}$-open $F_C^{(i)}$ sets of the nuclear configuration space R, with

$$C = C^{(1,k)} \tag{90}$$

are of particular importance, since points of these sets represent all classically accessible nuclear configurations in the particular case when the minimum activation energy for the reaction of an elementary mechanism $M^{(i,k_1,l)}$ is provided:

$$C^{(1,k)} = \text{absolute activation energy for } M^{(i,k_1,l)} \tag{91}$$

where

$$k = k_1. \tag{92}$$

Whereas $C^{(1,k)}$ is measured on an absolute energy scale, the differences $C^{(1,k)} - C^{(0,i)}$ and $C^{(1,k)} - C^{(0,l)}$ provide upper bounds for the minimum relative activation energies of the forward and reverse processes, respectively, provided that elementary reaction mechanism $M^{(i,k_1,l)}$ is followed.

3.5. *Topologies $\boldsymbol{T}_{CF_C}$, $\boldsymbol{T}_{DC}$ and $\boldsymbol{T}_{DCF_C}$*

As the last example indicates, a comparison of structural and interconversion properties (described by the $\boldsymbol{T}_C$ topologies) with energy relations (described by the $\boldsymbol{T}_F$ topologies) leads to comparisons between $\boldsymbol{T}_C$-open and (in the above case) $\boldsymbol{T}_{F_C}$-open sets. In the topological sense, however, topological spaces $(R, \boldsymbol{T}_C)$ and $(R, \boldsymbol{T}_{F_C})$ are non-comparable, since in general, $\boldsymbol{T}_C$-open sets are not $\boldsymbol{T}_{F_C}$-open and $\boldsymbol{T}_{F_C}$-open sets are not $\boldsymbol{T}_C$-open either, that is, neither topology is weaker than the other. Similarly, topologies $\boldsymbol{T}_D$, $\boldsymbol{T}_C$ and $\boldsymbol{T}_D$, $\boldsymbol{T}_{F_C}$ are also pairwise non-comparable, as shown by model surfaces analysed in Refs. [32, 33].

The nuclear configuration space R, however, may be topologized by a topology which is finer than both $\boldsymbol{T}_C$ and $\boldsymbol{T}_{F_C}$. In such a topology molecular structures, reaction mechanisms, as well as accessible domains defined by energy levels, are open sets. Their intersections define open sets with specific structural *and* energetic properties.

In general, there are infinitely many such topologies on R which fulfill the above requirements. However, a unique topology $\boldsymbol{T}_{CF_C}$ can be defined by subbase $\boldsymbol{C} \cup \boldsymbol{F}^C$, i.e. by the union

$$\boldsymbol{C} \cup \boldsymbol{F}^C = \{C^{\underline{r}^{(\lambda,k)}}\} \cup \{C^{\bar{D}_{\text{excl}}}\} \cup \{\bar{C}^{\underline{r}^{(\lambda,k)}}\} \cup \{\bar{C}^{\bar{D}_{\text{excl}}}\} \cup \{\bar{D}_{\text{excl}}\} \cup \{F_C^{(i)}\} \tag{93}$$

(compare Eqs. (45 and 80)). Clearly, topology $\boldsymbol{T}_{CF_C}$ of the above subbase is finer than both $\boldsymbol{T}_C$ and $\boldsymbol{T}_{F_C}$. Topology $\boldsymbol{T}_{CF_C E}$ on the energy hypersurface E is defined the usual way, by homeomorphic $\underline{E}$-images of $\boldsymbol{T}_{CF_C}$-open sets of R. Any given $\boldsymbol{T}_{CF_C}$-open set of R and the associated $\boldsymbol{T}_{CF_C E}$-open set of the energy hypersurface have well defined structural properties, admit a given set of reaction mechanisms and fulfill a well defined set of energy relations with other open sets. More importantly, these properties and relations are computable simply by generating the appropriate intersections with $\boldsymbol{T}_{CF_C}$-open sets $C^{\underline{r}^{(\lambda,k)}}$, $M^{(i,j_\lambda,k)}$,

$M^{(i_1,j_{\lambda,1}\cdots i_t,j_{\lambda,t},k_t)}$ and $F_C^{(i)}$, for molecular structure, elementary mechanism, complex reaction mechanism and energy level, respectively. For example, $\boldsymbol{T}_{CF_C}$-open set G has chemical structure $C^{\underline{r}^{(\lambda,k)}}$ if

$$G \cap C^{\underline{r}^{(\lambda,k)}} \neq \varnothing, \tag{94}$$

and $G \in \boldsymbol{T}_{CF_C}$ admits complex reaction mechanism $M^{(i_1,j_{\lambda,1}\cdots i_t,j_{\lambda,t},k_t)}$ if

$$G \cap M^{(i_1,j_{\lambda,1}\cdots i_t,j_{\lambda,t},k_t)} = M^{(i_1,j_{\lambda,1}\cdots i_t,j_{\lambda,t},k_t)}, \tag{95}$$

the latter being a sufficient but not a necessary condition.

Several other combinations of chemical properties of open sets in the $\boldsymbol{T}_D$, $\boldsymbol{T}_C$ and $\boldsymbol{T}_F$ topologies may be analysed by defining topologies using a union of the appropriate subbases. Topology $\boldsymbol{T}_{DC}$ of R is defined by subbase

$$\boldsymbol{D} \cup \boldsymbol{C} \tag{96}$$

(compare to Eqs. (32 and 45)), whereas topology $\boldsymbol{T}_{DCF_C}$ is defined by generating subbase

$$\boldsymbol{D} \cup \boldsymbol{C} \cup \boldsymbol{F}_C = \boldsymbol{D} \cup \boldsymbol{C} \cup \{F_C^{(i)}\}. \tag{97}$$

$\boldsymbol{T}_{DC}$ is finer than $\boldsymbol{T}_D$ and $\boldsymbol{T}_C$, whereas $\boldsymbol{T}_{DCF_C}$ is finer than $\boldsymbol{T}_{DC}$ and $\boldsymbol{T}_{F_C}$.

$\boldsymbol{T}_{DC}$-open sets of R correspond to well defined curvature properties of E and structural properties of the nuclear arrangement, and these sets are suitable for analysing the stability of reaction paths associated with a given reaction mechanism $M^{(i_1,j_{\lambda,1}\cdots i_t,j_{\lambda,t},k_t)}$, itself a $\boldsymbol{T}_{DC}$-open set of R. If reaction path stability, reaction mechanisms and energy relations are to be considered simultaneously, the $(R, \boldsymbol{T}_{DCF_C})$ topological space and the $G \in \boldsymbol{T}_{DCF_C}$ open sets define the collection of those nuclear configurations which exhibit a given combination of energetic, mechanistic and reaction path properties. $\underline{E}$-images of sets $H \in \boldsymbol{T}_{DC}$ and $G \in \boldsymbol{T}_{DCF_C}$ by homeomorphism $\underline{E}$ define the $\boldsymbol{T}_{DCE}$-open sets and $\boldsymbol{T}_{DCF_CE}$-open sets of topological spaces $(E, \boldsymbol{T}_{DCE})$ and $(E, \boldsymbol{T}_{DCF_CE})$ on the energy hypersurface E, equivalent to topological spaces $(R, \boldsymbol{T}_{DC})$ and $(R, \boldsymbol{T}_{DCF_C})$, respectively.

4. Applications

The topological theory of energy hypersurfaces is based on the replacement of individual *points* of the nuclear configuration space R, as fundamental chemical entities of the model, by *open sets* of R. One can compute all topological properties in the given topology by generating intersections of these open sets. Consequently, applications of the topological theory requires, at most, the actual calculation of the *boundaries of elements in the subbase only*, rather than the calculation of the energy hypersurface itself. The dimension of these boundaries is always lower than that of R itself what results in a considerable simplification of the computational problem. (Even with such simplifications, however, the required computational work can be extremely time consuming in higher dimensions).

As it has been pointed out earlier [32] the determination of the boundaries of sets in subbase of $\boldsymbol{T}_D$ is equivalent to the determination of point sets in R where the $^{n-1}\underline{\underline{H}}(\underline{r})$ Hessian matrix is singular. On the *ab initio* Hartree–Fock level of approximation this task can be accomplished by the use of available programs, such as the extended version of Gaussian 80, which can calculate analytical first and second derivatives of the hypersurface [56]. The calculation of boundaries of the $\boldsymbol{T}_C$ subbase elements is equivalent to the determination of the catastrophe set of function η [50], whereas one can obtain the boundaries in the $\boldsymbol{T}_F$ topology by using standard contour following algorithms.

The $(R, \boldsymbol{T}_C)$ "Reaction Topology" is the basis for the global analysis of *reaction networks*, comprising the set of *all possible reaction mechanisms* which involve a given set of nuclei and a fixed number of electrons [57]. Applying the results of the present work, several theorems are proven on relations between reaction mechanisms, reaction steps and activation energies, and in particular, on the properties and determination of "shortest" reaction mechanisms [57]. These results have a variety of possible applications in computer-aided synthesis planning.

The topological model of the present work has also been applied [58] to the analysis of the product space $R \otimes Z$, where Z is the abstract nuclear charge space, where the vector components are variable nuclear charges, as mentioned in the introduction. This product space has remarkable topological properties, which are summarized in two theorems [58], leading to geometry dependent and geometry independent lower and upper bounds for the electronic energy. Contrary to the applications for the analysis of reaction networks, which require considerable amount of computations, the applications of the above two theorems require only "back of the envelope" type calculations. Several numerical examples for actual molecules are presented in Ref. [58].

Symmetry in the metric space and properties of level set topologies of the nuclear charge space have been interrelated using a simple model of Hydrogen substituted molecules [59]. A topological inequality has been derived for general Hamiltonians with linear parameters, which inequality can be used as a simple test for the validity of perturbational expansions [60].

5. Summary

Primary concepts of chemistry, such as molecular structure, reaction mechanism, and reaction mixture of a given total energy, are shown to be of topological nature. By introducing appropriate topologies into the nuclear configuration space R, or equivalently, into the energy hypersurface E itself, a topological analysis may concentrate on a selected set of chemical properties. These properties are designated as topological by the choice of open sets, and all other properties of the energy hypersurface, being non-topological, are disregarded. A topologization of E, however, is not merely stripping away the disguise of a complicated multidimensional energy hypersurface: it also gives rigorous definitions for somewhat vague chemical notions, and at the same time forms the basis and raw material for a subsequent application of the powerful and elegant machinery of algebraic and differential topology.

A topological theory of potential energy hypersurfaces, "reaction topology", provides a common basis for structural chemistry, reaction mechanisms and many photochemical processes.

In a forthcoming paper we shall describe an application of homotopy theory to a family of energy hypersurfaces of various electronic excited states.

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Appendix

The following is a brief list of the most essential topological concepts and definitions employed in this paper. For more details the reader should consult the texts listed in the References.

Let X be a non-empty point set, and $\boldsymbol{T}$ is a class of subsets of X,

$$\boldsymbol{T} = \{T_\alpha\},\ T_\alpha \subset X.$$

$\boldsymbol{T}$ is called a *topology* on X if $\boldsymbol{T}$ satisfies the following criteria:

(1) set X and the empty set $\varnothing$ belong to $\boldsymbol{T}$,

$$X, \varnothing \in \boldsymbol{T}$$

(2) the union of any number of sets in $\boldsymbol{T}$ belongs to $\boldsymbol{T}$,

$$\bigcup_\beta T_\beta \in \boldsymbol{T}$$

(3) the intersection of any two sets in $\boldsymbol{T}$ belongs to $\boldsymbol{T}$,

$$T_\alpha \cap T_\beta \in \boldsymbol{T}.$$

The pair $(X, \boldsymbol{T})$, i.e. set X with the given $\boldsymbol{T}$ topology is called a *topological space*.

The sets in $\boldsymbol{T}$ are called the *$\boldsymbol{T}$-open sets*, or simply *open sets*. If $A \subset X$ is $\boldsymbol{T}$-open, its complement $A^c = X\backslash A$ is $\boldsymbol{T}$-closed. Whether a set is considered open or closed thus depends on the topology; if $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ are two different topologies on set X, a set $A \subset X$ may be $\boldsymbol{T}_1$-open but $\boldsymbol{T}_2$-closed. In fact, for topology $\boldsymbol{T}$ a topology $\boldsymbol{T}^c$, called *cotopology*, can be defined where the $\boldsymbol{T}^c$-open sets are precisely the $\boldsymbol{T}$-closed sets and vice versa.

Suppose that for two topologies $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ on X every $\boldsymbol{T}_1$-open subset of X is also $\boldsymbol{T}_2$-open. Then $\boldsymbol{T}_1$ is a subclass of $\boldsymbol{T}_2$, $\boldsymbol{T}_1 \subset \boldsymbol{T}_2$ and we say that topology $\boldsymbol{T}_1$ is *weaker* (*coarser*) than $\boldsymbol{T}_2$, or $\boldsymbol{T}_2$ is *stronger* (*finer*) than $\boldsymbol{T}_1$. Two topologies are *not comparable* if neither is weaker than the other.

$N \subset X$ is a neighbourhood of $\underline{r} \in X$ if there exists an open set $G \in \boldsymbol{T}$ such that $\underline{r} \in G \subset N$. A subclass $\boldsymbol{B} \subset \boldsymbol{T}$ is a *base* for topology $\boldsymbol{T}$ iff every open set $G \in \boldsymbol{T}$ is a union of sets in $\boldsymbol{B}$. A subclass $\boldsymbol{S} \subset \boldsymbol{T}$ is a *subbase* for topology $\boldsymbol{T}$ iff finite intersections of members of $\boldsymbol{S}$ form a base for $\boldsymbol{T}$. An important property of subbases will be often utilized in the forthcoming chemical applications: any class $\boldsymbol{A}$ of subsets of X is the subbase for a unique topology $\boldsymbol{T}$.

For topological spaces $(X_1, \boldsymbol{T}_1)$, $(X_2, \boldsymbol{T}_2)$ a function f from X_1 to X_2 is *continuous* iff the inverse image of every $\boldsymbol{T}_2$-open subset of X_2 is a $\boldsymbol{T}_1$-open subset of X_1,

$$f^{-1}(G) \in \boldsymbol{T}_1 \quad \text{if } G \in \boldsymbol{T}_2.$$

Topological spaces $(X_1, \boldsymbol{T}_1)$ and $(X_2, \boldsymbol{T}_2)$ are called *topologically equivalent* or *homeomorphic* if there exists a function $f: X_1 \rightarrow X_2$ which is bijective and both f and f^{-1} are continuous. A *bijective* function f is one-one and onto, that is, f assigns a unique element $\underline{p} \in X_2$ to each element $\underline{r} \in X_1$ and each element $\underline{p} \in X_2$ is assigned to an element $\underline{r} \in X_1$.

A property is called *topological* or *topological invariant* if it is a property for all topological spaces in an equivalence class generated by the equivalence relation "topologically equivalent". Length, boundedness, or being a Cauchy sequence are not topological properties, whereas *connectedness* and *compactness* are.

A topological space $(X, \boldsymbol{T})$ is *disconnected* iff X is a union of two, non-empty, disjoint open subsets,

$$X = A \cup B, A, B \neq \varnothing, A \cap B = \varnothing, A, B \in \boldsymbol{T}.$$

A topological space $(X, \boldsymbol{T})$ is *connected* if it is not disconnected. A connected open subset is also called a *domain*. A set X is simply connected if every closed path in X is contractible to a point.

Consider a general set X and a subset $A \subset X$. If $\boldsymbol{F} = \{F_i\}$ is a class of open subsets of set X such that $A \subset \bigcup_i F_i$ then $\boldsymbol{F}$ is called an *open cover* of A. If $\boldsymbol{F}$ contains only finite number of F_i subsets, then $\boldsymbol{F}$ is called a *finite cover*. Subset A of a topological space X is *compact* if every open cover of A contains a finite subcover. Compactness is a generalization of properties of closed and bounded intervals.

A general nuclear configuration space R, however, is not necessarily compact. Nevertheless, subsets of R may be "made" compact by various compactification techniques.

The topological space $(X_\infty, \boldsymbol{T}_\infty)$ is the Alexandrov one-point compactification of topological space, $(X, \boldsymbol{T})$, where $X_\infty = X \cup \{\infty\}$. One single point ∞, the "ideal point" of infinity, distinct from every other point of X is added to X, and topology $\boldsymbol{T}_\infty$ consists of the following sets:
(1) each set in $\boldsymbol{T}$,
(2) the complement in X_∞ of each closed and compact subset of X, that is

$$\boldsymbol{T}_\infty = \boldsymbol{T} \cup \{A : A = X_\infty \backslash B, X \backslash B \in \boldsymbol{T}, B \text{ compact in } X\}$$

By the above definitions, topological space $(X, \boldsymbol{T})$ is *embedded* in the compact topological space $(X_\infty, \boldsymbol{T}_\infty)$, since $(X, \boldsymbol{T})$ is homeomorphic to a subspace of $(\boldsymbol{X}_\infty, \boldsymbol{T}_\infty)$. An illustration of the one-point compactification S of the (x, y) plane A of the Euclidean 3-space, which is not compact, is shown in Fig. 1a. The center of sphere S of unit radius is located at point $(0, 0, 1)$. The straight line passing through the "north pole" $(0, 0, 2)$, denoted as ∞, and any point $\underline{r} \in A$, intersects the sphere S in exactly one point $\underline{r}' \neq \infty$, and thus assigns a unique point $\underline{r}' \in S$ to $\underline{r} \in A$. This assignment is a homeomorphism from A to $S \backslash \{\infty\}$, and generates an embedding of A in S. Consequently, since S is compact, S is a compactification of A.

The Alexandrov one-point compactification is applicable to subspaces ${}^mR$ of the nuclear configuration space R, if the same energy value E_∞ is obtained for any nuclear geometry change where $|{}^m\underline{r}| \to \infty$, ${}^m\underline{r} \in {}^mR$. A different transformation may be applied for subspaces ${}^pR$ of R, within which the energy hypersurface is periodic (e.g. the subspace of internal coordinates corresponding to bond rotations). A representative subdomain of ${}^pR$, analogous to the unit cell of crystal lattices, may be defined, within which no periodicity occurs [21, 22, 33]. For this unit cell U the Born–Kármán boundary conditions lead to a mapping of $U \subset {}^pR$ to a circle if $p = 1$, or in general to a torus if $p > 1$. In Fig. 1b the $p = 2$ case is illustrated. Note that in U points $\underline{a}$, $\underline{b}$, $\underline{c}$ and $\underline{d}$ are equivalent, and are transformed into a single point $\underline{p}$ of torus T. Line segments $[a, b]$, $[c, d]$ and $[a, c]$, $[b, d]$ are pairwise equivalent in U by periodicity, and these pairs of equivalent segments are transformed into unique lines on the torus T.

References

1. Born, M., Oppenheimer, J. R.: Ann. Phys. **84**, 457 (1927)
2. a. Proc. Conference on potential energy surfaces in chemistry, Santa Cruz, University of California, 1970 (Published by IBM Res. Lab., San Jose, Calif., 1971)
   b. Applications of electronic structure theory, ed. H. F. Schaefer III, New York: Plenum Press, 1977
3. a. Ugi, I.: Intra-Sci. Chem. Rep. **5**, 229 (1971)
   b. Ugi, I., Gillespie, P.: Angew. Chem. Int. Ed. Engl. **10**, 915 (1971)
4. a. Sinanoglu, O.: J. Am. Chem. Soc. **97**, 2309 (1975)
   b. Sinanoglu, O., Lee, L.-S.: Theoret. Chim. Acta (Berl.) **48**, 287 (1978)
5. a. Fukui, K.: J. Phys. Chem. **74**, 4161 (1970)
   b. Fukui, K.: Accounts Chem. Res. **14**, 363 (1981)
6. 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)
7. Basilevsky, M. V.: Mol. Phys. **23**, 161 (1972)
8. Stanton, R. E., McIver Jr., J. W.: J. Am. Chem. Soc. **97**, 3632 (1975)
9. Ezra, G. S.: Mol. Phys. **38**, 863 (1979)
10. Natanson, G. A.: Mol. Phys. **46**, 481 (1982)
11. Komornicki, A., McIver Jr., J. W.: J. Am. Chem. Soc. **95**, 4512 (1973); **96**, 5798 (1974); **98**, 4553 (1976)
12. Pechukas, P.: J. Chem. Phys. **64**, 1516 (1976)
13. Komornicki, A., Ishida, K., Morokuma, K., Ditchfield, R., Conrad, M.: Chem. Phys. Lett. **45**, 595 (1977)
14. Poppinger, D., Radom, L., Pople, J. A.: J. Am. Chem. Soc. **99**, 7806 (1977)
15. Rothman, M. J., Lohr Jr., L. L.: Chem. Phys. Lett. **70**, 405 (1980)

16. Halgren, T. A., Lipscomb, W. N.: Chem. Phys. Lett. **49**, 225 (1977)
17. Muller, K.: Angewandte Chemie, Internat Ed. **19**, 1 (1980)
18. Marcus, R. A.: J. Chem. Phys. **45**, 4493, 4500 (1966); **49**, 2610, 2617 (1968)
19. Polanyi, J. C., Schreiber, J. L.: Chem. Phys. Lett. **29**, 319 (1974)
20. Miller, W. H., Handy, N. C., Adams, J. E.: J. Chem. Phys. **72**, 99 (1980)
21. Mezey, P. G.: Analysis of conformational energy hypersurfaces. Progr. Theoret. Org. Chem. **2**, 127 (1977)
22. Mezey, P. G.: Optimization and analysis of energy hypersurfaces, in Computational Theoretical Organic Chemistry, New York: Reidel Publ. Co., 1981
23. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **49**, 321 (1978)
24. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **51**, 189 (1979)
25. Tachibana, A., Fukui, K.: Theoret. Chim. Acta (Berl.) **51**, 275 (1979), **57**, 81 (1980)
26. Nalewajski, R. F., Carlton, T. S.: Acta Phys. Pol. **A53**, 321 (1978)
27. Feller, D., Borden, W. T., Davidson, E. R.: J. Comput. Chem. **1**, 158 (1980)
28. Longuet-Higgins, H. C.: Proc. R. Soc. London Ser. A **344**, 147 (1975)
29. Davidson, E. R.: J. Am. Chem. Soc. **99**, 397 (1977)
30. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **53**, 183 (1979)
31. a. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **59**, 321 (1981)
    b. Mezey, P. G.: Intern. J. Quant. Chem. Symp. **15**, 279 (1981)
32. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **54**, 95 (1980)
33. a. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **58**, 309 (1981)
    b. Mezey, P. G.: Intern. J. Quant. Chem. Quant. Biol. Symp. **8**, 185 (1981)
34. Morse, M.: Calculus of variations in the large, Am. Math. Soc. Colloquium Publ. Vol. 18, 1934
35. Collard, K., Hall, G. G.: Intern. J. Quant. Chem. **12**, 623 (1977)
36. Bader, R. F. W., Anderson, S. G., Duke, A. J.: J. Am. Chem. Soc. **101**, 1389 (1979)
37. Bader, R. F. W., Nguyen-Dang, T. T., Tal, Y.: J. Chem. Phys. **70**, 4316 (1979)
38. Tal, Y., Bader, R. F. W., Nguyen-Dang, T. T., Ojha, M., Anderson, S. G.: J. Chem. Phys. **74**, 5162 (1981)
39. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **60**, 97 (1981)
40. Spanier, E. H.: Algebraic topology, New York: McGraw-Hill, 1966
41. Morse, M., Cairns, S. S.: Critical point theory in global analysis and differential topology, New York: Academic Press, 1969
42. Milnor: Morse theory, Annals of Math. Studies, Vol. **51**, Princeton Univ. Press. 1973
43. Mezey, P. G.: Chem. Phys. Lett. **82**, 100 (1981); **86**, 562 (1982)
44. Mezey, P. G.: Chem. Phys. Lett. **47**, 70 (1977)
45. Mezey, P. G., Kapur, A.: Can. J. Chem. **58**, 559 (1980)
46. Peterson, M.: Ph.D. Thesis, U. of Toronto, 1981
47. Munkres, J.: Elementary differential topology, Annals of Math. Studies, Vol. **54**, Princeton Univ. Press, 1963
48. Guillemin, V., Pollack, A.: Differential topology, Englewood Cliffs: Prentice Hall, 1974
49. Thom, R.: Structural stability and morphogenesis, Benjamin, 1975
50. Structural stability, the theory of catastrophes and applications in the sciences, ed. Hilton, P.: Lecture notes in Math. 525, New York: Springer, 1976
51. Simmons, G. F.: Introduction to topology and modern analysis, New York: McGraw-Hill, 1963
52. Essén, H.: Int. J. Quant. Chem. **12**, 721 (1977)
53. Eckart, C.: Phys. Rev. **47**, 552 (1935)
54. Louck, J. D., Galbraith, H. W.: Rev. Mod. Phys. **48**, 69 (1976)
55. Teller, E.: J. Phys. Chem. **41**, 109 (1937)
56. Binkley, J. S., Whiteside, R. A., Krishnan, R., Seeger, R., DeFrees, D. J., Schlegel, H. B., Topiol, S., Kahn, L. H., Pople, J. A.: GAUSSIAN 80, Carnegie-Mellon University 1980
57. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **60**, 409 (1982)
58. Mezey, P. G.: Int. J. Quant. Chem. **22**, 101 (1982)
59. Mezey, P. G.: Mol. Phys. **47**, 121 (1982)
60. Mezey, P. G.: Chem. Phys. Lett. **87**, 277 (1982)

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