Original Investigations

Critical Level Topology of Energy Hypersurfaces

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Topologies are introduced into the nuclear configuration space R of molecular systems, based upon equipotential contour hypersurfaces on the potential energy hypersurface E. Critical level topologies T_{F_C} and $T_{F_{C'}}$, based upon the number and distribution of various critical points of E, are of particular importance, since they represent convenient yet rigorous mathematical models for relations between elementary reaction mechanisms, and for relations between open sets of nuclear geometries which are classically accessible at a given total energy.

Key words: Reaction topology – Potential surfaces – Reaction mechanisms – Critical points.

1. Introduction

The energy hypersurface model of chemical reactions and conformational changes is one of the most powerful tools of theoretical chemistry. Within the Born–Oppenheimer approximation this model gives a detailed description of energetic relations governing chemical changes on the molecular level. By introducing a suitable metric into the nuclear configuration space R over which the $E(r)$ hypersurface is defined[1], it is possible in principle to obtain detailed numerical information about all possible chemical processes on the given hypersurface. Whereas this approach is not always feasible due to the often enormous computational work that would be required for a full analysis, *topological* analysis of the hypersurface, applied in combination with, or replacing a metric space

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[1] In this paper the same notations will be used as in Ref. [1]. In particular, for the n-dimensional nuclear configuration space symbol n will be omitted and we shall write R for ^nR. All other dimensions, including dimension 1, will be always shown, e.g. ^1R.

approach, may lead to significant simplifications and a better understanding of the general features of such chemical processes. A topological model is strongly suggested by many familiar chemical concepts, since concepts like chemical structure or reaction mechanism are inherently topological in nature [2].

Recently two schemes have been proposed for the partitioning of the nuclear configuration space R into mutually exclusive subsets [1, 2]. In the first partitioning the subsets $D_\mu^i \subset R$ are defined in terms of the curvature properties of the hypersurface $E \subset {}^{n+1}R$ over tangent spaces of equipotential contour maps [1]. These subsets may be ordered into a hierarchy according to an index μ where μ is the critical point index of ${}^{n+1}r \in E$ in the tangent space. The larger the index μ, the less likely that a minimum energy path enters D_μ. D_0 domains have the important property that all energy minima and transition states belong to such D_0 domains and minimum energy reaction paths are stable only in the interior of D_0 domains. A complete partitioning of the nuclear configuration space R is given by

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

where "excluded" domain D_{excl} contains neighborhoods of all points where the hypersurface is a poor approximation to the energy expectation value.

Another partitioning of the nuclear configuration space has been given, based upon the number and type of critical points of the $E(r)$ hypersurface [2]. The number of minima and the number of other critical points, e.g. saddle points of transition states are not independent, these numbers are governed by the Morse inequalities [3]. Critical points $r_C \in R$ may be characterized by the rank and the number λ of negative eigenvalues of the Hessian matrix $H(r_C)$. If the rank of the Hessian matrix is equal to the dimension n of space R, i.e. the critical point r_C is non-degenerate, then index λ may be used as a single-index classification. Only critical points with index $\lambda = 0$ (minimum) or index $\lambda = 1$ (saddle point with *one* negative canonical curvature, usually referred to as transition state) are of primary importance on potential energy hypersurfaces, and no minimum energy path may pass through any critical point with $\lambda \geq 2$ [4]. Nevertheless, as it has been pointed out, the number and position of *all* critical points, even those not located along minimum energy paths, give important information on reaction paths [5]. Information on the relative position and number of various critical points may also aid the solution of optimization problems on energy hypersurfaces [6]. In the partitioning scheme an important property of critical points is utilized: since the Born–Oppenheimer energy expectation value functional is bounded from below, the extremity of every steepest descent path P_r is either a critical point r_C or a point in the excluded domain D_{excl}. Consequently, the steepest descent paths may be ordered into equivalence classes according to the number and type of critical points [2], which, in turn, leads to the ordering of the $r \in R$ origin points of steepest descent paths P_r into catchment regions $\{C^{r_C^{(l)}}\}$ of critical points $\{r_C^{(l)}\}$, $r_C^{(l)} \in R$, $r_C^{(l)} \notin \bar{D}_{\text{excl}}$. A complete partitioning of the

nuclear configuration space R is given by

$$R = \bigcup_l C^{r_c^{(l)}} \cup C^{\bar{D}_{\text{excl}}} \cup \bar{D}_{\text{excl}}. \tag{2}$$

Here $C^{\bar{D}_{\text{excl}}}$ is defined as the catchment region of $\bar{D}_{\text{excl}}$, where $\bar{D}_{\text{excl}}$ is the closure of excluded domain D_{excl} [2]. It has been shown that the catchment regions $\{C^{r_c^{(l)}}\}$ give mutually consistent and quantum mechanically rigorous definitions for two of the most fundamental chemical concepts: molecular structure and reaction mechanism [2]. It has been suggested [7] that the molecular structure definition, based upon catchment regions in the n-dimensional nuclear configuration space R is closely related to the molecular structure definition based on molecular graphs of "bond paths", in the real, Euclidean three dimensional space ^3R, determined from charge density calculations [8].

Short of a global analytic representation it is a rather difficult task to analyze the global properties of the Born–Oppenheimer energy hypersurface. Sets of grid points of varying density in the nuclear configuration space, or point series converging to a critical point (usually to a minimum) are used most often to construct approximations to a portion of the hypersurface.

Alternatively, equipotential contours of E may be determined using contour following algorithms. This approach, which leads to *subsets* of E, complements the usual optimization techniques, which have the primary aim of locating *critical points* of E. These subsets of E are of considerable value in the analysis of chemical processes, since they can be used for a global characterization of E. The dimension of equipotential contours is $n - 1$ and for large n their determination is a complicated task. An analysis of the topological properties of these contours, however, can decide which contours can provide the most chemically useful information, and it leads to relations which simplify their determination. Topological properties of contour sets are of fundamental importance in the analysis of chemical reactions and conformational changes. In this paper we shall study some of these topological properties, with special emphasis on contours containing *non-degenerate critical points* of E.

2. Critical Points, Ordinary Levels, and Critical Levels

Both the D_μ domain and $C^{r_c^{(l)}}$ catchment region partitionings of the nuclear configuration space R, Eqs. (1) and (2), resp., involve disjoint subsets of R, and both lead in a natural way to chemically meaningful topologizations of space R. Whereas the properties of the corresponding (R, T_D) and (R, T_C) topological spaces are discussed elsewhere [9], in the present study we shall introduce a topology into the R space which is suitable for the analysis of the energy requirements of molecular processes. This topologization, just as the T_C topology [9], is based upon the critical points of the hypersurface, however, it utilizes properties of equipotential contour hypersurfaces rather than those of catchment regions. This topology, just as the T_D and T_C topologies, is global in the sense suggested by Davidson in a topological study on triatomic systems [10], and it

is expected to be applicable for the analysis of interrelations between energy component hypersurfaces [11, 12] as well.

Critical points of the energy hypersurfaces determine many of the topological features including the distribution and type of catchment regions [2]. Using a series of model surfaces, depicting various topologically distinct cases, it has been demonstrated that the *number* and *type* of critical points are of primary import- ance in determining the fundamental morphology of the hypersurface [5]. It has been pointed out that the number of possible reaction mechanisms is limited by relations governing the number of minima ($\lambda = 0$), saddle points, (including transition states with $\lambda = 1$), and maxima [5]. For the most general hypersurfaces these relations are given by the Morse inequalities [3], however, for special cases simpler inequalities may apply [13]. The same model surfaces have also indicated that the distribution (relative location) of various critical points along the hyper- surface plays an equally important role and in special cases it may indeed be the dominant influencing factor[2]. Whereas the determination of the precise location of critical points is an optimization problem in a metric space [6] and cannot be solved in general by purely topological means, nevertheless, a topologi- cal characterization of this distribution may be given in terms of catchment regions by defining a neighbour relation $N(r_C^{(i)}, r_C^{(j)})$ for critical points $r_C^{(i)}$ and $r_C^{(j)}$:

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

The catchment region partitioning and the above neighbour relation extends the applicability of the critical point theory [3, 14, 15] from a set of discrete points to chemically identifiable connected point sets of the entire hypersurface. The combination of catchment region analysis and critical point theory leads to important inequalities governing the number of chemical structures and the number of possible reaction mechanisms on energy hypersurfaces [2, 13]. These relations describe constraints on the number of critical points of the entire hypersurface, or of a unit cell of a periodic hypersurface. However, they do not provide sufficient information on the accessibility of catchment regions of various critical points. Accessibility depends on the energy values associated with critical points. A systematic study of the classically accessible regions of the energy hypersurface, subject to an upper bound on the energy value, is based on homeomorphic level set topologies introduced into the nuclear configuration space R and energy hypersurface E.

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[2] Periodicity in the occurrence of critical points may greatly simplify the analysis, although the boundaries of a representative subdomain (unit cell) [5, 6] must be chosen with care, particularly in higher dimensions n. In example D of Ref. [5] (Fig. 3) the model for a linear chain of alternating minima and maxima has a unit cell which contains one maximum and one minimum and there is no regular saddle point only degenerate saddle point at infinity. That is, all minimum energy paths on this surface extend to infinity. In example C the unit cell contains six minima and six maxima, five ordinary saddle points and one "four valleys" degenerate saddle point at the boundary of the unit cell. Here, besides the minimum energy paths passing through the non-degenerate saddle points and "four valleys" degenerate saddle point, there are also minimum energy paths that extend to infinity.

For a given constant A, all points ${}^{n+1}r$ of the energy hypersurface E, ${}^{n+1}r \in E \subset {}^{n+1}R$ for which ${}^{n+1}r^{\,n+1} = A$, form the *level set* E_A:

$$E_A = \{{}^{n+1}r: {}^{n+1}r \in E, {}^{n+1}r = r \oplus E(r), {}^{n+1}r^{n+1} = E(r) = A\}. \tag{4}$$

If there is no critical point r_C of $E(r)$ for which $r_C \oplus E(r_C)$ belongs to E_A, that is, if

$$E(r_C) \neq A \quad \text{for any } r_C \in R, \tag{5}$$

then A is called an *ordinary level*. If there is a critical point r_C for which

$$E(r_C) = C \tag{6}$$

then C is called a *critical level*. The corresponding level set is a special case of level sets defined by Eq. (4), explicitly:

$$E_C = \{{}^{n+1}r: {}^{n+1}r \in E, {}^{n+1}r = r \oplus E(r), {}^{n+1}r^{n+1} = E(r) = C\} \tag{7}$$

is a *critical level set* of the energy hypersurface E. The calculation of equipotential hypersurface E_A requires a contour following algorithm. Such algorithms are the most efficient when based upon the energy gradient and on the Hessian matrix of the second derivatives.

Level sets E_A and E_C are analogous to contour lines on geographical relief maps, marking a given elevation A or C. Projections of these level sets onto the nuclear configuration space R lead to subsets F_A and F_C:

All points of R for which

$$E(r) \leq A \tag{8}$$

form the set F_A, $F_A \subset R$:

$$F_A = \{r, r: E(r) \leq A\}. \tag{9}$$

Set F_C is a special case of sets defined by Eq. (9), that is

$$F_C = \{r, r: E(r) \leq C\}. \tag{10}$$

Set F_A is the set of all nuclear geometries with total energies less or equal to A. Two associated sets, F_A^- and F_C^- are defined similarly by replacing symbol $\leq$ by $<$ in Eqs. (9) and (10), respectively.

If a level set E_A is disconnected, it may be given as a unique union of disjoint connected subsets:

$$E_A = \bigcup_i E_A^{(i)}, \tag{11}$$

where the $E_A^{(i)}$ sets are the maximum connected components of E_A.

A similar partitioning may be given for set F_A (and similarly for sets F_A^-, F_C, and F_C^-):

$$F_A = \bigcup_i^k F_A^{(i)}. \tag{12}$$

If sets E_A and F_A are themselves connected, then

$$E_A = E_A^{(1)} \tag{13}$$

and

$$F_A = F_A^{(1)}, \tag{14}$$

respectively.

Level sets $E_A^{(i)} \subset E$ and sets $F_A^{(i)} \subset R$ have important chemical properties. Sets $\{E_A^{(i)}\}_{i=1}^k$ enclose all domains of the hypersurface E which are classically accessible if the total energy of the molecular system is A, and the associated nuclear configurations are precisely the elements of sets $\{F_A^{(i)}\}_{i=1}^{k'}$. It is clear, that $k = k'$ and that index i may be assigned consistently, that is, if

$$E(r) = A \quad \text{for } r \in F_A^{(i)} \tag{15}$$

then

$$^{n+1}r \in E_A^{(i)}, \quad \text{where } ^{n+1}r = r \oplus E(r). \tag{16}$$

The energy expectation value functional $E(r)$ is bounded from both below and above, consequently the set

$$C_C = \{C^{(\lambda,k)}\} \tag{17}$$

of all critical levels is closed and bounded by the absolute minimum and absolute maximum of $E(r)$. The absolute maximum and absolute minimum themselves are elements of C_C. In Eq. (17) λ and k refer to critical point index and serial index of the critical point $r^{(\lambda,k)}$, respectively. If for a given critical level C there are l isolated critical points, that is, the *critical set* Q_C contains l isolated points, then C_C contains l copies of level C. If E_C contains a connected subset of critical points, then a single index k is assigned to the entire subset, similarly to the index of catchment regions of such connected degenerate critical points [2]. Index λ is given as the smallest critical point index in the subset. With the above interpretation the set C_C is assumed to be a countable set.

3. Energy Level Topologies

Sets $F_A^{(i)}$ and $F_B^{(j)}$ are either disjoint or one contains the other, since for

$$F_A^{(i)} \neq F_B^{(j)} \tag{18}$$

their intersection may be non-empty,

$$F_A^{(i)} \cap F_B^{(j)} \neq \emptyset \tag{19}$$

only if either

$$F_A^{(i)} \subset F_B^{(j)}, \qquad (A < B) \tag{20}$$

or

$$F_B^{(j)} \subset F_A^{(i)}, \qquad (B < A). \tag{21}$$

Consequently, by considering the family $\boldsymbol{F}^A$ of all $F_A^{(i)}$ sets for all A values, that is

$$\boldsymbol{F}^A = \{F_A^{(i)}\}, \tag{22}$$

the family generated by all finite intersections of elements of $\boldsymbol{F}^A$ is $\boldsymbol{F}^A$ itself. It is also clear that $\boldsymbol{F}^A$ contains the nuclear configuration space R,

$$R \in \boldsymbol{F}^A, \tag{23}$$

since

$$R = F_A^{(1)} \tag{24}$$

for any level A which is an upper bound for the energy expectation value functional $E(r)$. Similarly, the empty set is an element of $\boldsymbol{F}^A$,

$$\emptyset \in \boldsymbol{F}^A, \tag{25}$$

since

$$\emptyset = F_B^{(1)} \tag{26}$$

for any lower bound B of $E(r)$.

Family $\boldsymbol{F}^A$ is a *defining subbase* for a unique topology $\boldsymbol{T}_F$ of the nuclear configuration space R. Since any finite intersection of elements of $\boldsymbol{F}^A$ is also an element of $\boldsymbol{F}^A$, subbase $\boldsymbol{F}^A$ is also a *base* for topology $\boldsymbol{T}_F$, and the open sets of the $(R, \boldsymbol{T}_F)$ topological space are the unions of sets in $\boldsymbol{F}_A$. The class $\boldsymbol{T}_F$, containing all such unions, satisfies the conditions for a topology on R:

(i) the empty set $\emptyset$ and the nuclear configuration space R belong to $\boldsymbol{T}_F$,

$$\emptyset, R \in \boldsymbol{T}_F, \tag{27}$$

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

$$\bigcup_\beta T_\beta \in \boldsymbol{T}_F, \quad \text{if } T_\beta \in \boldsymbol{T}_F, \tag{28}$$

(iii) the intersection of every finite class of sets in $\boldsymbol{T}_F$ is a set in $\boldsymbol{T}_F$:

$$\bigcap_{i=1}^m T_i \in \boldsymbol{T}_F, \quad \text{if } T_i \in \boldsymbol{T}_F. \tag{29}$$

The energy functional $E(r)$ generates a one-one and onto mapping $\boldsymbol{E}$ between the nuclear configuration space R and the energy hypersurface $E \subset {}^{n+1}R$

$$\boldsymbol{E} : R \to E. \tag{30}$$

This mapping is continuous in the usual metric at every point $r \in R \backslash D_{\text{excl}}$, and may be extended continuously over D_{excl} [9]. The inverse of mapping $\boldsymbol{E}$, that is, projection $\Pi_E = \boldsymbol{E}^{-1}$

$$\Pi_E : E \to R \tag{31}$$

is also continuous, consequently, mapping E is a homeomorphism between R and E. The E-images of the elements of the F^A subbase generate a subbase F^{AE} for a unique topology T_{FE} on the energy hypersurface E:

$$F_{AE}^{(i)} = E(F_A^{(i)}), \qquad F_A^{(i)} \in F^A, \qquad F_{AE}^{(i)} \subset E \tag{32}$$

and

$$F^{AE} = \{F_{AE}^{(i)}\}. \tag{33}$$

Just as the F^A subbase is a base for topology T_F on R, the defining subbase, F^{AE} is also a base for unique topology T_{FE} on the energy hypersurface E. Mapping $E : R \to E$ is a homeomorphism between topological spaces (R, T_F) and (E, T_{FE}) which topological spaces, being homeomorphic, are topogically equivalent. That is, any topological property of (R, T_F) is also a topological property of (E, T_{FE}) and the two spaces may be studied simultaneously.

The T_F-open sets in the partitioning $\{F_A^{(i)}\}_{i=1}^k$ of T_F-open set F_A, given by Eq. (12), are precisely those domains of the nuclear configuration space, which are the unions of all classically accessible nuclear configurations at or below energy A, but among which no interconversion may take place. Number k is then the number of different "autonomic" chemical systems, which may exist independently at energy A. If A and B are two non-critical levels, $B > A$, and if there is no critical level between A and B, then an energy increase $A \to B$ will not change the number of the above independent domains. That is, in

$$F_A = \bigcup_{i=1}^k F_A^{(i)} \tag{34}$$

and

$$F_B = \bigcup_{i=1}^{k'} F_B^{(i)} \tag{35}$$

the upper limit of indices must be the same,

$$k = k'. \tag{36}$$

Furthermore, due to properties (18–20), the indices in (34) and (35) may be chosen consistently, that is,

$$F_A^{(i)} \subset F_B^{(i)}. \tag{37}$$

The upper limits k and k' for index i may be different only if there is a critical level C such that

$$A < C \le B, \tag{38}$$

since a "merger" of two $F_D^{(i)}$ and $F_D^{(j)}$ domains may occur only at a critical level $D = C$, when the energy is increased from A to B.

A geographical example may illustrate the behavior of $F_A^{(i)}$ sets during a continuous $A \to B$ energy change. F_A may be taken as the flooded area over a relief map, A is the water level. Sets $F_A^{(i)}$ are disjoint lakes separated by dry land. It

is assumed that the water level is the same in all these lakes, and may change only simultaneously, e.g. by free exchange of ground water. If the water rises from level A to level B, and no critical point exists on the relief map for which the elevation would fall between A and B, i.e.

$$C \leq A \tag{39}$$

or

$$B < C \tag{40}$$

for all critical levels C, then the number of lakes will not change $(k = k')$ during the flooding, $A \rightarrow B$. A merger of two lakes may take place only at a critical level C. However,

$$A < C \leq B \tag{41}$$

is only a necessary but not a sufficient condition for a merger to take place, since reaching a $C^{(2, l)}$ critical level, e.g. the highest point of an island in the middle of one lake, does not imply a merger of two lakes. Nevertheless, the topological properties (connectedness) of the lake have changed when the island has disappeared among the waves.

4. Critical Level Topologies

It is apparent that all topologically significant changes occur when a critical level is encountered during an $A \rightarrow B$ energy change. This underlines the importance of the F_C sets (Eq. 10) and their partitionings, which are special cases of those given by Eq. (12):

$$F_C = \bigcup_i^k F_C^{(i)} \tag{42}$$

where connected sets $F_C^{(i)}$ are disjoint.

The family $\boldsymbol{F}^C$ of all $F_C^{(i)}$ sets for all critical values C,

$$\boldsymbol{F}^C = \{F_C^{(i)}\} \tag{43}$$

is a defining subbase for a unique topology $\boldsymbol{T}_{F_C}$ on the nuclear configuration space R. Since subbase $\boldsymbol{F}^C$ is a subset of subbase $\boldsymbol{F}^A$,

$$\boldsymbol{F}^C \subset \boldsymbol{F}^A, \tag{44}$$

any two elements of $\boldsymbol{F}^C$ are either disjoint or one contains the other. Consequently, $\boldsymbol{F}^C$ is also a base for topology $\boldsymbol{T}_{F_C}$.

Homeomorphic $\boldsymbol{E}$-images of elements of $\boldsymbol{F}^C$ generate a family $\boldsymbol{F}^{CE}$ of subsets of the energy hypersurface E, where

$$F_{CE}^{(i)} = \boldsymbol{E}(F_C^{(i)}), \qquad F_C^{(i)} \in \boldsymbol{F}^C, \qquad F_{CE}^{(i)} \subset E \tag{45}$$

and

$$\boldsymbol{F}^{CE} = \{F_{CE}^{(i)}\}. \tag{46}$$

Family F^{CE} is a defining subbase for a unique topology $T_{F_C E}$ on the energy hypersurface E. Topological spaces (R, T_{F_C}) and $(E, T_{F_C E})$ are homeomorphic by virtue of homeomorphism

$$E : (R, T_{F_C}) \to (E, T_{F_C E}), \tag{47}$$

and thus are topologically equivalent.

Since F^C is a subset of F^A, Eq. (44), and similarly F^{CE} is a subset of F^{AE}, $F^{CE} \subset F^{AE}$, it follows that topological space (R, T_{F_C}) is a subspace of (R, T_F), $(R, T_{F_C}) \subset (R, T_F)$, and similarly $(E, T_{F_C E}) \subset (E, T_{FE})$. Topology T_{F_C} is coarser than T_F, $T_{F_C} \subset T_F$, and $T_{F_C E}$ is coarser than T_{FE}, $T_{F_C E} \subset T_{FE}$.

By the choice of open sets of topological spaces (R, T_{F_C}) and $(E, T_{F_C E})$ the T_{F_C} and $T_{F_C E}$ topologies preserve only those chemical properties of the nuclear configuration space R and the energy hypersurface E, respectively, which are related to the classically accessible nuclear configurations at various critical energy values $\{C^{(\lambda, k)}\}$. All other properties are non-topological in the above topological spaces and are disregarded. Energy relations between various T_{F_C}-open (or $T_{F_C E}$-open) sets may be computed by generating intersections of these sets.

For studying such intersections it is useful to introduce the concept of incidence matrix M^{pq}. Assume that an ordering of critical levels is given as

$$\{C^{(p)}\}_{p=1}^{p_{\max}} \tag{48}$$

where for every p $(1 < p \le p_{\max})$

$$C^{(p)} > C^{(p-1)}. \tag{49}$$

The matrix element M_{ij}^{pq} of incidence matrix M^{pq} is defined as

$$M_{ij}^{pq} = [F_{C^{(p)}}^{(i)} ; F_{C^{(q)}}^{(j)}] = \begin{cases} 1 & \text{if } F_{C^{(q)}}^{(j)} \subset F_{C^{(p)}}^{(i)} \\ 0 & \text{otherwise.} \end{cases} \tag{50}$$

In the above definition

$$F_{C^{(p)}}^{(i)} \subset F_{C^{(p)}} \tag{51}$$

and

$$F_{C^{(q)}}^{(j)} \subset F_{C^{(q)}} \tag{52}$$

i.e. they appear as one of the subsets in the appropriate unions given by Eq. (42). Since for levels $C^{(p)}$ and $C^{(q)}$ indices i and j in Eq. (42) run from 1 to k_p and from 1 to k_q, respectively, consequently, incidence matrix M^{pq} is k_p by k_q. For levels $C^{(p)}$, $C^{(q)}$ and $C^{(r)}$, where

$$C^{(p)} > C^{(q)} > C^{(r)}, \tag{53}$$

the incidence matrices M^{pq} and M^{qr} are compatible for matrix multiplication. Furthermore,

$$M^{pq} M^{qr} = M^{pr}, \tag{54}$$

that is, the matrix product of incidence matrices for level pairs $C^{(p)}$, $C^{(q)}$ and $C^{(q)}$, $C^{(r)}$ is precisely the incidence matrix for level pair $C^{(p)}$, $C^{(r)}$. To prove relation (54) one has to observe only that in order to have

$$M_{il}^{pr} = 1 \tag{55}$$

that is,

$$F_{C^{(r)}}^{(l)} \subset F_{C^{(p)}}^{(i)}, \tag{56}$$

it is both sufficient and necessary to have precisely one $F_{C^{(q)}}^{(j)}$ set, such that

$$F_{C^{(r)}}^{(l)} \subset F_{C^{(q)}}^{(j)} \subset F_{C^{(p)}}^{(i)}. \tag{57}$$

Due to properties (19–21) there can exist at most one such $F_{C^{(q)}}^{(j)}$ set. Consequently, if $F_{C^{(q)}}^{(j)}$ fulfills (57), then

$$M_{ij'}^{pq} M_{j'l}^{qr} = \delta_{jj'} \tag{58}$$

and

$$\sum_{j'=1}^{k_q} M_{ij'}^{pq} M_{j'l}^{qr} = 1. \tag{59}$$

That is

$$(\boldsymbol{M}^{pq}\boldsymbol{M}^{qr})_{il} = 1 = M_{il}^{pr}, \tag{60}$$

which relation is an expression of the transitivity of inclusion.

The above incidence matrices and relations between them are not restricted to critical levels, and may be applied to ordinary levels $A^{(p)}$, $A^{(q)}$ and $A^{(r)}$, where

$$A^{(p)} > A^{(q)} > A^{(r)}. \tag{61}$$

Consider T_{F_C}-open set $F_C(\lambda, l)$ and its partitioning by Eq. (42):

$$F_C(\lambda, l) = \bigcup_i^{k_{\lambda,l}} F_{C^{(\lambda,l)}}^{(i)}. \tag{62}$$

It is clear, that there is exactly one index i' such, that

$$r^{(\lambda,l)} \in F_{C(\lambda,l)}^{(i')}. \tag{63}$$

It is useful to introduce the critical point characteristic function $\gamma : \boldsymbol{F}^C \to I$, defined as

$$\gamma(F_{C^{(\lambda,l)}}^{(i)}) = \begin{cases} 1 & \text{if } r^{(\lambda,l)} \in F_{C^{(\lambda,l)}}^{(i)} \\ 0 & \text{otherwise.} \end{cases} \tag{64}$$

For set $F_{C^{(\lambda,l)}}^{(i')}$ of relation (63) the characteristic function gives unity:

$$\gamma(F_{C^{(\lambda,l)}}^{(i')}) = 1 \tag{65}$$

and $F_{C^{(\lambda,l)}}^{(i')}$ is regarded a *pointed set* with distinguished element $r^{(\lambda,l)}$.

The subclass $\boldsymbol{F}^{C'}$ of all these pointed sets, i.e. all $F_C^{(i')}$ elements of subbase $\boldsymbol{F}^C$ for which

$$\gamma(F_C^{(i')}) = 1, \tag{66}$$

is a defining subbase for a unique topology $\boldsymbol{T}_{F_{C'}}$ on the nuclear configuration space R. Since

$$\boldsymbol{F}^{C'} \subset \boldsymbol{F}^C, \tag{67}$$

it follows that topology $\boldsymbol{T}_{F_{C'}}$ is weaker than both $\boldsymbol{T}_{F_C}$ and $\boldsymbol{T}_F$:

$$\boldsymbol{T}_{F_{C'}} \subset \boldsymbol{T}_{F_C} \subset \boldsymbol{T}_F. \tag{68}$$

Homeomorphic $\boldsymbol{E}$-images of $\boldsymbol{T}_{F_{C'}}$-open sets of R define a topology $\boldsymbol{T}_{F_{C'E}}$ on the energy hypersurface, for which

$$\boldsymbol{T}_{F_{C'E}} \subset \boldsymbol{T}_{F_CE} \subset \boldsymbol{T}_{FE}. \tag{69}$$

In the subbase $\boldsymbol{F}^{C'}$ each critical level $C^{(\lambda, l)}$ (in case of coincident levels each *copy*) is represented by exactly one set $F_C^{(i')}$. Thus the enumeration problem of critical points [13] may be converted into the enumeration problem of sets in subbase $\boldsymbol{F}^{C'}$, which may be formulated in terms of intersections. The number $m(C, \lambda)$ of critical points of index λ which are elements of set $F_C^{(i')}$, is equal to the number of sets $F_{C^{(\lambda, l)}}^{(j')} \in \boldsymbol{T}_{F_{C'}}$ contained in $F_C^{(i')}$. Considering the subclass $\boldsymbol{F}^{C'_\lambda}$ of all λ-sets,

$$\boldsymbol{F}^{C'_\lambda} = \{F_{C^{(\lambda, l)}}^{(i')}\} \subset \boldsymbol{F}^{C'} \tag{70}$$

of subbase $\boldsymbol{F}^{C'}$ for a fixed λ, the elements of $\boldsymbol{F}^{C'_\lambda}$ may be ordered according to index l, by

$$C^{(\lambda, l)} > C^{(\lambda, l-1)}. \tag{71}$$

It is clear that incidence matrices $\boldsymbol{M}^{pq}$ of the $(R, \boldsymbol{T}_{F_{C'}})$ topological space are one by one, due to condition (66) on the elements of subbase $\boldsymbol{F}^{C'}$. That is, in $(R, \boldsymbol{T}_{F_{C'}})$

$$\boldsymbol{M}^{pq} = M^{pq}. \tag{72}$$

These M^{pq} incidence numbers, however, may be ordered into a matrix $\boldsymbol{M}$ by taking p and q as row and column indices, respectively. Matrix $\boldsymbol{M}$ is a lower triangle matrix, by virtue of definition (50).

The incidence matrix $\boldsymbol{M}_{(\lambda)}$ is defined similarly for subset $F^{C'_\lambda}$ (Eq. 70), subject to ordering (71), and it may be obtained by eliminating all rows p and columns q of $\boldsymbol{M}$ except those which refer to critical levels $C^{(p)}$ and $C^{(q)}$ of index λ. Among the $\boldsymbol{M}_{(\lambda)}$ matrices $\boldsymbol{M}_{(0)}$ is unique, since it is the m_0 by m_0 null-matrix, as a consequence of the definition of one-point sets $F_{C^{(0,l)}}^{(1')}$ (Eq. 65):

$$\boldsymbol{M}_{(0)} = \boldsymbol{0}. \tag{73}$$

Particularly important is the matrix $\boldsymbol{M}_{(1)}$ since it describes the inclusion relations for sets $F_{C^{(1,l)}}^{(i')}$ of saddle points $r^{(1,l)}$, which correspond to classical transition states of chemical reactions. The critical level $C^{(1,l)}$ itself corresponds to the classical

minimum absolute activation energy necessary to bring about *all* chemical processes within $T_{F_{C'}}$-open set $F_{C^{(1,l)}}^{(i')}$ The adjective "absolute" indicates that these energies are measured with reference to an energy scale common for all $T_{F_{C'}}$-open sets.

Each non-degenerate saddle point $r^{(\lambda, l)}$ with $\lambda = 1$ can be assigned to one and only one elementary minimum energy path [1, 2], representing a distinct elementary reaction mechanism [9], and the sum of all matrix elements in row l of $\boldsymbol{M}_{(1)}$ corresponds to $M_{1(l)}$, the total number of ($\lambda = 1$) elementary reaction mechanisms within set $F_{C^{(1,l)}}^{(i')}$:

$$m_{1(l)} = \sum_q M_{(1)}^{lq}. \tag{74}$$

Those generalized minimum energy paths are also counted along which a steepest descent from a saddle point leads to another saddle point.

By referring to the single-index ordering (48) of critical levels $C^{(q)}$ and to incidence matrix $\boldsymbol{M}$, the total number of $T_{F_{C'}}$-open elements of class $F^{C_\lambda'}$ of a fixed λ, which elements are contained in $T_{F_{C'}}$-open set $F_{C^{(p)}}^{(i')}$, is given by the general expression

$$m_{\lambda(p)} = \sum_q M^{pq} \delta_{\lambda, \lambda_q}. \tag{75}$$

Here λ refers to the critical point index of class $F^{C_\lambda'}$ (Eq. 70) and λ_q is that of critical level $C^{(q)}$. In particular, the total number of stable nuclear geometries (energy minima) within a $T_{F_{C'}}$-open set $F_{C^{(p)}}^{(i')}$ is

$$m_{0(p)} = \sum_q M^{pq} \delta_{0, \lambda_q} \tag{76}$$

and the number of $F_{C^{(r)}}^{(i')}$ sets of critical level index $\lambda_r = 1$, (and equivalently, the number of distinct elementary ($\lambda = 1$) reaction mechanisms) contained within $F_{C^{(p)}}^{(i')}$ is given by

$$m_{1(p)} = \sum_q M^{pq} \delta_{1, \lambda_q}. \tag{77}$$

Due to the construction of matrix $\boldsymbol{M}_{(1)}$, result (77) is equivalent to Eq. (74).

5. Summary

Energy level topologies, in particular the critical level topologies T_{F_C} and $T_{F_{C'}}$ of the nuclear configuration space R are the natural mathematical models for studying interrelations between classically accessible regions of the potential energy hypersurface at various upper limits of the total molecular energy. Activation energies for chemical processes are directly related to open sets in the $(R, T_{F_{C'}})$ topological space. The enumeration of stable nuclear geometries and elementary reaction mechanisms, below a fixed total energy value, may be

formulated in terms of incidence matrices $\boldsymbol{M}^{pq}$ and $\boldsymbol{M}$, defined for elements of the generating subbases $\boldsymbol{F}^C$ and $\boldsymbol{F}^{C'}$ of topolgies $\boldsymbol{T}_{F_C}$ and $\boldsymbol{T}_{F_{C'}}$, respectively.

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