

Quantum Chemical Reaction Networks, Reaction Graphs and the Structure of Potential Energy Hypersurfaces

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Global properties of the Born–Oppenheimer energy expectation value functional, defined over the nuclear configuration space R , are analyzed. Quantum chemical reaction graphs and reaction networks are defined in terms of intersection graphs of connected sets of nuclear geometries, representing various chemical structures. The set of all possible reaction mechanisms on the given energy hypersurface and the associated activation energy conditions are analyzed using reachability matrices defined over digraphs $D^s(\lambda)$ and $D^s(\lambda, E)$.

Key Words: Potential energy surfaces – Reaction topology – Reaction graphs – Reaction networks – Reaction path.

1. Introduction

Potential energy hypersurfaces are of fundamental importance in the analysis of chemical reactions and conformational changes. Whereas thousands of studies, both experimental and theoretical, have been reported in recent years on *local* analysis of potential surfaces of various molecular systems, only very few studies have been carried out to date on the *global* topological properties of potential surfaces of polyatomic molecules [1–4]. Recent topological analysis of potential energy hypersurfaces resulted in consistent quantum-mechanical definitions of molecular structure and reaction mechanism [2–4]. Based on the topological properties of the energy hypersurface E , equivalence classes of nuclear geometries are defined on the nuclear configuration space R which lead to topologizations of both R and E . Chemical structures and reaction mechanisms

are defined as open sets of the resulting (R, T_C) topological space [4]. Based upon this topology, a neighbour relation is introduced for critical points of the energy hypersurface E . In the present study we shall consider a selected subset of the topological properties of the energy hypersurface leading to a subsequent level of abstraction: to reaction networks and graphs. In order to generate a complete reaction network of the hypersurface we shall utilize the above mentioned neighbour relation as applied to various pointed open sets of the topological space (R, T_C) .

Theoretical studies on chemical reaction networks may, in principle, lead to the determination of all possible reaction mechanisms for a given overall chemical process. In particular, theoretical models may aid the development of computer assisted methods for organic synthesis design. In many of these studies [5–12], the initial data on some of the possible reaction pathways, individual synthetic steps and intermediate species have been assumed to be given as experimental information, although for a partial analysis symmetry relations and quantum chemical results have also been utilized [13–17].

In the quantum mechanical model the nuclear configuration space R is assumed to be provided with a metric ρ . The ε -neighbourhoods of points $\mathbf{r} \in R$ define the metric topology T in this metric. (Throughout this study the same notations will be used as in Refs. [2–4]. An introduction to the topological concepts used in this work may be found in Refs. [3, 4, 18–20].) Since the energy hypersurface E , defined over R , is bounded from below, all steepest descent paths on E must terminate either at a critical point $\mathbf{r}_C \in R$, or at a point $\mathbf{r} \in D_{\text{excl}}$. Here D_{excl} is the union of neighbourhoods of all points where the energy hypersurface E is a poor approximation to the energy expectation value [2–3].

To each non-critical point $\mathbf{r} \in R$, $\mathbf{r} \notin D_{\text{excl}}$, a steepest descent path P_r is assigned. The \mathbf{r} origin points are ordered into equivalence classes according to the extremities of the P_r paths. For extremity $\mathbf{r}_C^{(i)}$ the equivalence class has been defined [3] as the catchment region

$$C^{r_C^{(i)}} = \{\mathbf{r}_C^{(i)}, \mathbf{r}, \mathbf{r}: \mathbf{r}_C^{(i)} \in P_r\} \quad (1)$$

and for extremities in D_{excl} a single such catchment region has been given:

$$C^{\bar{D}_{\text{excl}}} = \{\mathbf{r}, \mathbf{r}: P_r \cap \bar{D}_{\text{excl}} \neq \emptyset\}. \quad (2)$$

These catchment regions generate a unique partitioning of the nuclear configuration space R , by

$$R = \bigcup_i C^{r_C^{(i)}} \cup C^{\bar{D}_{\text{excl}}} \cup \bar{D}_{\text{excl}}. \quad (3)$$

Catchment regions appearing in the union of Eq. (3) and their T -closures form a generating subbase for a unique topology T_C on the nuclear configuration space R [3–4]. Chemical structure is defined as an open set $C^{r_C^{(i)}}$ of topological space (R, T_C) . Similarly, elementary and complex reaction mechanisms are defined as open sets of (R, T_C) [4]. The above topological definitions express

the fact that molecules are inherently topological objects rather than geometrical entities. In a topological model, the precise geometrical arrangement of the nuclei is irrelevant (topology \approx "rubber geometry") and the concept of distance is of no importance. Nearness and connectedness, neighbourhoods and continuity are the primary concepts of topology. These are precisely the concepts of primary importance to molecular behaviour on the microscopic level, since even in semi-classical treatments of molecular motion (e.g. vibrational analysis) an open set of nuclear geometries must be considered and no molecule can exist with any fixed nuclear geometry for any length of time. A purely quantum mechanical model goes even beyond this, since nuclei, just as electrons, are described by probability distributions, which clearly favour a topological model over a geometrical one.

The topological model of chemical structures and reaction mechanisms circumvents the fundamental incompatibility of geometrical models of molecules with the Heisenberg uncertainty principle, since points of R , representing rigid nuclear geometries, are replaced by open sets of R . The definition of "reaction topology" is based upon the properties of the Born–Oppenheimer energy functional [4]. Consequently, the generalization of reaction topology, the proposed theory of reaction networks is also inherently quantum-mechanical since it is also based on an observable, energy, and on the corresponding expectation value functional.

In a previous extension of the topological model, local coordinate systems and metrization have been re-introduced into open sets of topological space (R, T_C) in a special way, leading to a manifold theoretical model of energy hypersurfaces [4]. In the present work we start again with the topological model; metric, however, will be re-introduced only on reaction graphs and reaction networks as distance of vertices. The reaction graphs will be defined as intersection graphs for a subset of the generating subbase for topology T_C , and their subgraphs. The relations between various models of potential energy hypersurfaces are shown in Fig. 1.

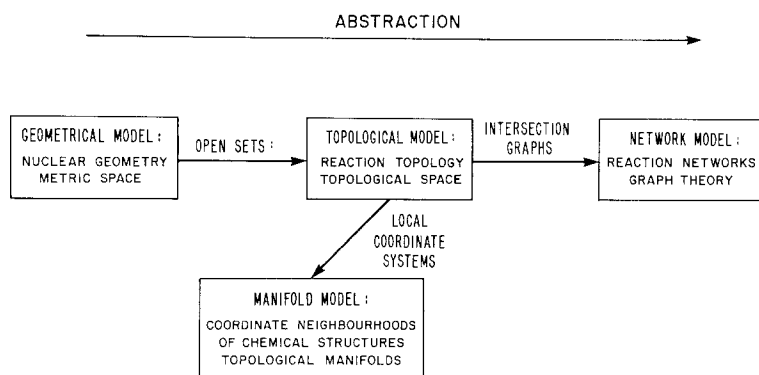


Fig. 1. Interrelations between geometrical, topological, manifold, and graph theoretical models of potential energy hypersurfaces

Network theory and graph theory appear especially suitable for the analysis of the most essential features of a topological model of energy hypersurfaces. In this study we shall present such an analysis. For concepts and definitions of graph theory the reader should consult references [21, 22]. A sample of selected chemical applications of graph theory is discussed in the work by Randić [23] and in Refs. [24, 25].

2. Pointed Sets of the Nuclear Configuration Space R and Reaction Networks

In order to reduce the topological model (R, T_C) of R to a graph, preserving the most essential information on the chemically important features of the energy expectation value functional, we shall utilize neighbour relations of catchment regions and the properties of mapping $\eta(\mathbf{r})$ [4]. To each non-critical point $\mathbf{r} \in R$ the mapping $\eta(\mathbf{r})$ assigns the extremity \mathbf{r}_E of steepest descent path P_r :

$$\eta(\mathbf{r}) = \mathbf{r}_E(P_r). \quad (4)$$

By virtue of $\eta(\mathbf{r})$ each catchment region $C^{(l)}$ (Eq. (1)) is a *pointed set* with *distinguished element* $\mathbf{r}_C^{(l)}$, the critical point in the catchment region. The neighbour relation which has been proposed for the catchment regions [3] defines a neighbour relation for the distinguished elements (critical points) $\mathbf{r}_C^{(l)} \in C^{(l)}$ and $\mathbf{r}_C^{(l')} \in C^{(l')}$:

$$N(\mathbf{r}_C^{(l)}, \mathbf{r}_C^{(l')}) = \begin{cases} 1 & \text{if } \bar{C}^{\mathbf{r}_C^{(l)}} \cap \bar{C}^{\mathbf{r}_C^{(l')}} \neq \emptyset, \quad l \neq l' \\ 0 & \text{otherwise,} \end{cases} \quad (5)$$

where the closure refers to the metric topology T on R [4].

In general, the excluded domain D_{excl} may be disconnected, then D_{excl} is not a proper domain in the topological sense. In such a case, a unique partitioning of D_{excl} may be given in terms of disjoint connected subsets $D_{\text{excl}}^{(d)}$ which are the maximum connected components of D_{excl} :

$$D_{\text{excl}} = \bigcup_d D_{\text{excl}}^{(d)}. \quad (6)$$

Here

$$D_{\text{excl}}^{(d)} \cap D_{\text{excl}}^{(d')} = \emptyset \quad \text{if } d \neq d' \quad (7)$$

and each $D_{\text{excl}}^{(d)}$ is connected.

Partitioning (6) of D_{excl} implies a partitioning of $C^{\bar{D}_{\text{excl}}}$, by

$$C^{\bar{D}_{\text{excl}}} = \bigcup C^{\bar{D}_{\text{excl}}^{(d)}}, \quad (8)$$

where each $C^{\bar{D}_{\text{excl}}^{(d)}}$ is the union of all origin points from where the steepest descent paths leads into $\bar{D}_{\text{excl}}^{(d)}$.

One may designate one point, $\mathbf{r}_D^{(d)}$, in each $D_{\text{excl}}^{(d)}$ as the distinguished element, and formally regard the union

$$C^{\mathbf{r}_D^{(d)}} = D_{\text{excl}}^{(d)} \cup C^{\bar{D}_{\text{excl}}^{(d)}} \quad (9)$$

as the catchment region for $\mathbf{r}_D^{(d)}$. The mapping η may then be extended from $R \setminus (C^{\bar{D}_{\text{excl}}} \cup D_{\text{excl}})$ to R by defining $\eta(\mathbf{r})$ for every $\mathbf{r} \in C^{\bar{D}_{\text{excl}}} \cup D_{\text{excl}}$ as

$$\eta(\mathbf{r}) = \mathbf{r}_D^{(d)} \quad (10)$$

where

$$\mathbf{r} \in C^{\mathbf{r}_D^{(d)}} \subset D_{\text{excl}} \cup C^{\bar{D}_{\text{excl}}}. \quad (11)$$

The neighbour relation (5) may also be extended to these $\mathbf{r}_D^{(d)}$ points by

$$N(\mathbf{r}_E^{(i)}, \mathbf{r}_{E'}^{(j)}) = \begin{cases} 1 & \text{if } \bar{C}^{\mathbf{r}_E^{(i)}} \cap \bar{C}^{\mathbf{r}_{E'}^{(j)}} \neq \emptyset, \quad i \neq j \\ 0 & \text{otherwise,} \end{cases} \quad (12)$$

where $E, E' = D$ or C .

In this study, we shall assume that topological space (R, T_C) is defined in terms of all $C^{\mathbf{r}_E^{(i)}}$ catchment regions that is, sets $C^{\mathbf{r}_D^{(d)}}$ and their T -closures are also elements of the defining subbase of T_C [4]. The subset of T -closed elements of the defining subbase may then be used for the definition of the reaction graph G as an *intersection graph*. More explicitly, by taking all distinguished elements as the vertex set V and all vertex pairs with a non-zero neighbour relation as the edge set E , we may define the *reaction graph* G of the potential energy hypersurface E :

$$V(G) = \{\mathbf{r}_E^{(i)}\}, \quad (13)$$

$$E(G) = \{(\mathbf{r}_E^{(i)}, \mathbf{r}_{E'}^{(j)}) : N(\mathbf{r}_E^{(i)}, \mathbf{r}_{E'}^{(j)}) = 1\}. \quad (14)$$

Graph G has several equivalent interpretations. Vertex set V may be interpreted as the family of catchment regions,

$$V(G) = \{C^{\mathbf{r}_E^{(i)}}\} \quad (13a)$$

and the edge set E as the set representing neighbour relations of the catchment regions themselves,

$$E(G) = \{(C^{\mathbf{r}_E^{(i)}}, C^{\mathbf{r}_{E'}^{(j)}}) : \bar{C}^{\mathbf{r}_E^{(i)}} \cap \bar{C}^{\mathbf{r}_{E'}^{(j)}} \neq \emptyset\}. \quad (14a)$$

By using the terminology of Thom's catastrophe theory [26], as applied to the stability of function $\eta : R \rightarrow R$, the $\{C^{\mathbf{r}_E^{(i)}}\}$ catchment regions are the basins associated with critical point attractors $\{\mathbf{r}_C^{(i)}\}$ [3] and attractors $\{\mathbf{r}_D^{(j)}\}$. The vertex set $V(G)$ of the reaction graph G is the reduction of the nuclear configuration space R to a discrete set of the attractors. The edge set $E(G)$ represents the neighbour relations between these attractors.

To facilitate the chemical interpretation of the results, we shall adopt the following terminology: an open set $C^{\mathbf{r}^{(\lambda,k)}}$, where critical point index λ is also specified, or a set $C^{\mathbf{r}_D^{(d)}}$ will be referred to as chemical structure. A structure $C^{\mathbf{r}^{(0,k)}}$, with $\lambda = 0$, will be called a molecule. A structure $C^{\mathbf{r}^{(1,k)}}$, with $\lambda = 1$, will be referred to as transition structure. Each structure $C^{\mathbf{r}^{(\lambda,k)}}$, or $C^{\mathbf{r}_D^{(d)}}$, can be represented by the corresponding distinguished geometry $\mathbf{r}^{(\lambda,k)}$ or $\mathbf{r}_D^{(d)}$. It is evident that graph G may be interpreted in chemical terms either as one describing the

neighbour relations between chemical structures or one describing neighbour relations between distinguished geometries. Whenever the interpretation is of no immediate concern, i.e. when purely graph theoretical relations will be considered, $\mathbf{r}_E^{(i)}$ in Eqs. (13) and (14) (and $C^{\mathbf{r}_E^{(i)}}$ in Eqs. (13a) and (14a)) will be replaced by general vertex symbol v_i .

In an earlier graph theoretical representation of multidimensional potential surfaces [27], the vertex set has been chosen similarly, as the set of critical points, which is a subset of $V(G)$. However, an edge set has been given using a different criterion, based upon a one dimensional ordering of vertices. Although the assumption in Ref. [27], that all equipotential contours are homeomorphic to circles or hyperspheres, is not generally valid for an arbitrary energy hypersurface, nevertheless, a somewhat modified construction for an edge set may be given which leads to similar graphs. This particular edge set may be defined by regarding precisely those vertices v_i and v_j interconnected by an edge which are not separated by an equipotential contour hypersurface containing another vertex v_k . Such a graph, may be derived from G as a special case of subgraph, which contains less information about the energy surface E than does G itself.

Energy relations between various distinguished points of R , together with graph G , define a *digraph* D where each edge $e_k(v_i, v_j) \in E(G)$, [$v_i, v_j \in V(G)$] is given the direction of non-increasing energy. That is, by interpreting vertices as the distinguished points, for the *arc* $v_i v_j$ of D ,

$$E(v_i) \geq E(v_j). \quad (15)$$

If the equality holds in Eq. (15), then we shall assume two arcs, one from v_i to v_j and one from v_j to v_i . The arcs of digraph D may be *labeled* by the non-negative energy difference ΔE_{ij} ,

$$\Delta E_{ij} = E(v_i) - E(v_j). \quad (16)$$

The labeled digraph D will be referred to as *reaction network*.

For the purposes of a detailed analysis, the neighbour relation (12) is much too general, and it is useful to introduce the concept of *strong neighbour*. Chemical structure $C^{\mathbf{r}_E^{(i)}}$ is a strong neighbour of chemical structure $C^{\mathbf{r}_E^{(j)}}$ if

$$\bar{C}^{\mathbf{r}_E^{(i)}} \cap C^{\mathbf{r}_E^{(j)}} \neq \emptyset. \quad (17)$$

The implied strong neighbour relation for the distinguished elements is defined by

$$N^s(\mathbf{r}_E^{(i)}, \mathbf{r}_E^{(j)}) = \begin{cases} 1 & \text{if } \bar{C}^{\mathbf{r}_E^{(i)}} \cap C^{\mathbf{r}_E^{(j)}} \neq \emptyset, \quad i \neq j \\ 0 & \text{otherwise.} \end{cases} \quad (18)$$

Note that the strong neighbour relation is not symmetric, in contrast to the neighbour relation, which is symmetric. It is possible that an $\mathbf{r}_C^{(1,k)}$ critical point is an element of the closure of catchment region for another $\mathbf{r}_C^{(1,l)}$ critical point,

$$\mathbf{r}_C^{(1,k)} \in \bar{C}^{\mathbf{r}_C^{(1,l)}}, \quad (19)$$

nevertheless, relation (17) does not hold if indices k and l are interchanged. Chemical structure $C^{\mathbf{r}_c^{(1,i)}}$ is a strong neighbour of $C^{\mathbf{r}_c^{(1,k)}}$, but the latter is not a strong neighbour of the former. Saddle points of the model surface shown in Fig. 4, Ref. [28], are examples for such a relation. It is also clear, that the strong neighbour relation implies the neighbour relation, but not *vice versa*.

Note that both the neighbour and the strong neighbour relations can be expressed by intersections involving open sets of the (R, T_C) topological space, that is, both relations are topological in (R, T_C) .

A symmetric variant of the strong neighbour relation, the s -neighbour relation, may be defined as

$$\tilde{N}^s(v_i, v_j) = \begin{cases} 1 & \text{if } N^s(v_i, v_j) + N^s(v_j, v_i) \geq 1 \\ 0 & \text{otherwise,} \end{cases} \quad (20)$$

that is, \tilde{N}^s is 1 if either of the two vertices is a strong neighbour of the other.

Graph G^s and digraph D^s are defined by vertex set (13),

$$\mathbf{V}(G^s) = \mathbf{V}(G) \quad (21)$$

and by edge set $\mathbf{E}(G^s)$ where neighbour relation N is replaced by the symmetric strong neighbour relation \tilde{N}^s in Eq. (14). For digraph D^s directions (and labels) are given by the same relations, (15) and (16), as for digraph D . Since

$$\mathbf{E}(G^s) \subset \mathbf{E}(G), \quad (22)$$

it is clear that G^s and D^s are subgraphs of G and D , respectively. Note that in the typical case of two molecules, $C^{\mathbf{r}_c^{(0,k)}}$ and $C^{\mathbf{r}_c^{(0,i)}}$, separated by a transition structure $C^{\mathbf{r}_c^{(1,i)}}$, all three structures are pairwise neighbours, that is, the corresponding three edges are all elements of $\mathbf{E}(G)$,

$$e(v_k, v_i), e(v_k, v_j), e(v_i, v_j) \in \mathbf{E}(G). \quad (23)$$

However, neither of the two molecules is a strong neighbour of the other, and only two of the above edges are in $\mathbf{E}(G^s)$:

$$e(v_k, v_j), e(v_i, v_j) \in \mathbf{E}(G^s) \quad (24)$$

$$e(v_k, v_i) \notin \mathbf{E}(G^s). \quad (25)$$

Consequently, graph G^s [digraph D^s] is a proper subgraph of graph G [digraph D , respectively].

Neighbour relation matrix \mathbf{N} and strong neighbour relation matrix $\mathbf{N}^{(s)}$ for the distinguished geometries (and equivalently for chemical structures) are defined by

$$N_{ij} = N(\mathbf{r}_E^{(i)}, \mathbf{r}_E^{(j)}) \quad (26)$$

and

$$N_{ij}^{(s)} = N^{(s)}(\mathbf{r}_E^{(i)}, \mathbf{r}_E^{(j)}), \quad (27)$$

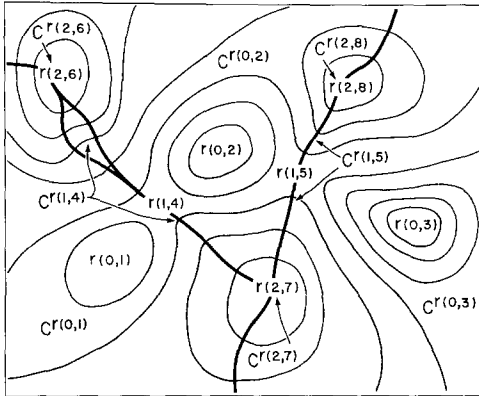


Fig. 2. Part of a model surface showing critical points $r^{(\lambda,i)}$ equipotential contours, and catchment regions $C^{r^{(\lambda,i)}}$

respectively. Note that \mathbf{N} is symmetric whereas $\mathbf{N}^{(s)}$ is not in general symmetric matrix. It is evident that \mathbf{N} is nothing else but the adjacency matrix $\mathbf{A}(G)$ for vertices of G ,

$$\mathbf{N} = \mathbf{A}(G). \tag{28}$$

Matrix $\mathbf{N}^{(s)}$, however, is not in general equal to the adjacency matrix $\mathbf{A}(G^s)$ of G^s :

$$\mathbf{N}^{(s)} \neq \mathbf{A}(G^s). \tag{29}$$

Nevertheless, $\mathbf{A}(G^s)$, (which is identical to $\bar{\mathbf{N}}^{(s)}$) may be obtained from $\mathbf{N}^{(s)}$ by

$$A_{ij}(G^s) = \text{sign}(N_{ij}^{(s)} + N_{ji}^{(s)}). \tag{30}$$

In Fig. 2, a part of a two dimensional model surface is shown. Boundaries of catchment regions are shown by heavy lines. Some of these lines are themselves one dimensional catchment regions for saddle points. Note, however, that catchment region $C^{r^{(1,4)}}$ of saddle point $r^{(1,4)}$ has a non-empty two dimensional interior. The catchment regions for maxima are one-point sets [3]. For the distinguished elements shown in Fig. 2 the neighbour relation matrices are

$$\mathbf{N} = \begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \\ 1 & 0 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 0 & 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{N}^{(s)} = \begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

and

$$\bar{\mathbf{N}}^{(s)} = \begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \end{vmatrix}$$

Adjacency matrices $\mathbf{A}(D)$ and $\mathbf{A}(D^s)$ for digraphs D and D^s are given by

$$A_{ij}(D) = A_{ij}(G) \cdot p_{ij} \quad (31)$$

and

$$A_{ij}(D^s) = A_{ij}(G^s) \cdot p_{ij}, \quad (32)$$

respectively, where p_{ij} is defined in terms of condition (15):

$$p_{ij} = \begin{cases} 1 & \text{if } E(v_i) \geq E(v_j) \\ 0 & \text{otherwise.} \end{cases} \quad (33)$$

Graph $G(\lambda)$ is defined as the subgraph of G , obtained by eliminating all vertices corresponding to catchment regions $C_{D^s}^{(d)}$ and to all chemical structures $C_C^{(\lambda,k)}$ where $\bar{\lambda} > \lambda$. Expressed in terms of distinguished geometries,

$$\mathbf{V}(G(\lambda)) = \{\mathbf{r}_C^{(\lambda',k)} : \lambda' \leq \lambda\} \quad (34)$$

and

$$\mathbf{E}(G(\lambda)) = \{(\mathbf{r}_C^{(\lambda',k)}, \mathbf{r}_C^{(\lambda'',l)}) : \lambda', \lambda'' \leq \lambda, N(\mathbf{r}_C^{(\lambda',k)}, \mathbf{r}_C^{(\lambda'',l)}) = 1\}. \quad (35)$$

For sake of notational convenience we shall use the $G(n+1)$ symbol for G itself. Note that $\mathbf{V}(G(n))$ contains all critical points as vertices, but none of the $\mathbf{r}_D^{(d)}$ distinguished geometries, consequently $G(n) \neq G$ whenever $D_{\text{excl}} \neq \emptyset$. Graphs $G^s(\lambda)$ and digraphs $D(\lambda)$ and $D^s(\lambda)$, which are subgraphs of G^s , D and D^s , respectively, are defined analogously. In Fig. 3 subgraphs of reaction graph G of model surface given in Fig. 2 and some of the associated $G(\lambda)$ and $G^s(\lambda)$ graphs are shown.

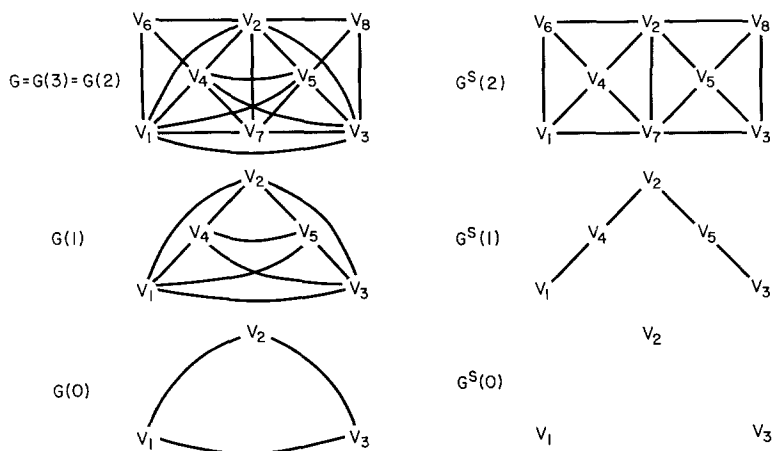


Fig. 3. Subgraphs of reaction graph G and graphs $G(1)$, $G(0)$, $G^s(2)$, $G^s(1)$ and $G^s(0)$ of model surface shown in Fig. 2

3. Analysis of Reaction Graphs and Networks of Reaction Mechanisms

In reaction topology [3–4] a reaction mechanism is defined as an open set of the (R, T_C) topological space, which open set is a union of a sequence of chemical structures, involved either as reactant, transition structures, intermediate structures or product. The reaction graphs, defined above, retain the most essential relations between such open sets, and are suitable for the analysis of reaction mechanisms on E .

Graphs $G(0)$, $D(0)$, $G^s(1)$ and $D^s(1)$ express the most directly some familiar chemical concepts. $G(0)$ and $D(0)$ describe the relations between stable molecular structures, i.e. molecules. $D(0)$ also contains information on energy relations. $G^s(1)$ and $D^s(1)$ represent the relations between all molecules and transition structures. Whereas graphs with $\lambda = 0$ and $\lambda = 1$ are by far the most important in our analysis, most of the results will be formulated for a general λ parameter. Whenever the "closeness" of chemical structures is our only concern, then the analysis of E may be given in terms of graphs $G(\lambda)$ and $D(\lambda)$. However, when sequences of chemical structures, encountered along a reaction mechanism, are studied, then graphs $G^s(\lambda)$ and digraphs $D^s(\lambda)$ are more suitable for the analysis. In particular, one should recall that two molecules separated by a transition structure are not in general adjacent in $G^s(\lambda)$, even if they are adjacent in $G(\lambda)$. This feature of $G^s(\lambda)$ is compatible with the classical concept of reaction paths which explicitly involves all three structures, and does not formally allow tunneling.

Consider a graph $G^s(\lambda)$ of the energy hypersurface E . It is evident that each path on graph $G^s(\lambda)$ represents a set of infinitely many paths on the energy hypersurface E , and each element of this set involves the same sequence of chemical structures. That is, the path on the graph represents a reaction mechan-

ism. (Unless otherwise stated, in this paper path means a path on a graph.) Since $G^s(\lambda)$ describes the symmetric strong neighbour relations between all chemical structures of critical point index less or equal to λ , all reaction mechanisms involving such structures can be specified by paths in $G^s(\lambda)$. In the context of reaction mechanisms, an edge of $G^s(\lambda)$, or equivalently, the incident vertex-pair $\mathbf{r}^{(\lambda',i)}$, $\mathbf{r}^{(\lambda'',j)}$ corresponds to a *reaction step*. A *general reaction mechanism* in $G^s(\lambda)$ is a path composed of steps involving arbitrary λ' and λ'' indices, the only restriction besides adjacency is

$$\lambda', \lambda'' \leq \lambda. \quad (36)$$

Apparently, the chemically most important *reaction mechanisms* are those with paths along which every vertex with an odd serial number has index $\lambda^{(i)} = 0$. That is, usually only *one* unstable ($\lambda^{(i)} > 0$) structure is involved in a transformation between two nearest stable ($\lambda^{(i)} = 0$) molecules along the path.

A reaction step or a mechanism will be referred to as a λ -step or λ -mechanism, respectively, if the highest critical point index involved is λ . By considering interconversions between unstable ($\lambda^{(i)} > 0$) structures as well, it is clear that every path in $G^s(\lambda)$ corresponds to a unique general mechanism. The set of all paths in $G^s(\lambda)$ represents the set of all λ' -mechanisms on E , for all λ' values permitted by condition (36).

An *elementary reaction mechanism* of index λ corresponds to a vertex sequence

$$\mathbf{r}^{(0,i)}, \mathbf{r}^{(\lambda,j)}, \mathbf{r}^{(0,k)} \quad (37)$$

along a path, where $\mathbf{r}^{(0,i)}$ and $\mathbf{r}^{(\lambda,j)}$, and also $\mathbf{r}^{(\lambda,j)}$ and $\mathbf{r}^{(0,k)}$ are neighbours. Each *minimum energy path* on E is a representation of an elementary mechanism of index 1, where

$$N^s(\mathbf{r}^{(0,i)}, \mathbf{r}^{(1,j)}) = 1, \quad (38)$$

$$N^s(\mathbf{r}^{(0,k)}, \mathbf{r}^{(1,j)}) = 1. \quad (39)$$

Each sequence of minimum energy paths on E corresponds to a unique 1-mechanism on a graph $G^s(\lambda)$, $\lambda \geq 1$. This explains the special importance of $G^s(1)$, which is the simplest graph with the above property.

The number of neighbours and their types i.e. their λ indices, are crucial in determining the importance of a chemical structure $C_{E}^{r^{(\lambda,i)}}$ in various reaction mechanisms. The total number of neighbours is the *degree* $d(v_i)$ of the corresponding vertex v_i of graph $G(n+1)$. The total number of incident reaction steps is the degree $d(v_i)$ in graph $G^s(n+1)$. The number $\nu_\lambda(v_i)$ of *incident λ -steps* for the i th chemical structure $C_{E}^{r^{(\lambda,i)}}$ is given by

$$\nu_\lambda(v_i) = d(v_i(G_i^s(\lambda))) - d(v_i(G_i^s(\lambda - 1))) \quad (40)$$

where graph $G_i^s(\lambda)$ is defined by

$$V(G_i^s(\lambda)) = V(G^s(\lambda)) \cup \{\mathbf{r}_E^{(\lambda',i)}\}, \quad (41a)$$

$$E(G_i^s(\lambda)) = E(G^s(\lambda)) \cup \{(\mathbf{r}_E^{(\lambda',i)}, \mathbf{r}_E^{(\lambda'',k)}): \lambda'' \leq \lambda, \bar{N}^s(\mathbf{r}_E^{(\lambda',i)}, \mathbf{r}_E^{(\lambda'',k)}) = 1\} \quad (41b)$$

This definition implies the following interpretation: $\nu_{n+1}(v_i)$ is the number of strong neighbour relations involving structure v_i and structures in $D_{\text{excl}} \cup C_{\text{excl}}^{\text{D}}$.

Definition (40) also implies that the sum of the $\nu_{\lambda'}(v_i)$ λ' -step numbers for $\lambda' = 0, 1, \dots, \lambda$ is the degree of v_i in graph $G^s(\lambda)$:

$$d(v_i(G^s(\lambda))) = \sum_{\lambda'=0}^{\lambda} \nu_{\lambda'}(v_i). \quad (42)$$

The total number of reaction steps of index λ or less, $q(G^s(\lambda))$, is the number of edges in set $E(G^s(\lambda))$. The number $q(G^s(\lambda))$ and the numbers $\nu_{\lambda'}(v_i)$ of λ' -steps, $\lambda' \leq \lambda$, $v_i \in V(G^s(\lambda))$ are interrelated by the following

Theorem 1:

$$\sum_i \sum_{\lambda'=0}^{\lambda} \nu_{\lambda'}(v_i) = 2q(G^s(\lambda)). \quad (43)$$

The proof follows directly from relation (42) and from Euler's relation for the number of edges and vertices [21].

The *distance* $d(v_i, v_j)$, in $G^s(\lambda)$, of chemical structures $v_i, v_j \in V(G^s(\lambda))$ is the length of the shortest $G^s(\lambda)$ -path between them, that is, the minimum number of elementary reaction steps separating v_i and v_j in $G^s(\lambda)$. If there is no such path (consequently, $G^s(\lambda)$ is disconnected), then $d(v_i, v_j) = \infty$ by definition.

The following concept of *eccentricity* $e(v_i)$ has a certain relation to the importance of chemical structure v_i in various reaction mechanisms. For a connected reaction graph $G^s(\lambda)$ $e(v_i)$ is defined as

$$e(v_i) = \max_{v_j \in V(G^s(\lambda))} d(v_i, v_j). \quad (44)$$

The *radius* $r(G^s(\lambda))$ is defined as

$$r(G^s(\lambda)) = \min_{v_i \in V(G^s(\lambda))} e(v_i) \quad (45)$$

whereas the maximum eccentricity is the *diameter* $d(G^s(\lambda))$ of $G^s(\lambda)$:

$$d(G^s(\lambda)) = \max_{v_i \in V(G^s(\lambda))} e(v_i). \quad (46)$$

A chemical structure v_i is a *central structure* in $G^s(\lambda)$ if

$$e(v_i) = r(G^s(\lambda)). \quad (47)$$

The *center* of reaction graph $G^s(\lambda)$ is the set of all central structures. Central chemical structures are likely to have central role in many reaction mechanisms.

Particularly important are those chemical structures which correspond to a cutpoint v_i of a graph $G^s(\lambda)$, since the formal removal of v_i from $G^s(\lambda)$ increases the number of components of $G^s(\lambda)$. If A and B are two blocks of $G^s(\lambda)$, held together by cutpoint v_i , then every λ' -mechanism, $\lambda' \leq \lambda$, interconverting a

molecule in block A and one in block B must pass through v_i . The vertex – connectivity $k(G^s(\lambda))$ is the minimum number of vertices whose removal results in a disconnected graph.

The reaction graph $G^s(\lambda)$ is m -connected if

$$k(G^s(\lambda)) \geq m. \quad (48)$$

Elementary reaction steps corresponding to edges $e_k \in E(G^s(\lambda))$ which are bridges, have similar importance, since all λ -mechanisms between fragments of $G^s(\lambda)$, held together by bridge e_k , must pass through e_k . The edge-connectivity $l(G^s(\lambda))$ is the minimum number of edges whose removal results in a disconnected graph.

The minimum degree $\delta(G^s(\lambda))$ is an upper bound for both $k(G^s(\lambda))$ and $l(G^s(\lambda))$:

$$k(G^s(\lambda)) \leq l(G^s(\lambda)) \leq \delta(G^s(\lambda)). \quad (49)$$

Furthermore, if the number of chemical structures and the number of elementary reaction steps are p and q , respectively, then

$$\max k(G^s(\lambda)) = \max l(G^s(\lambda)) = [2q/p], \quad (50)$$

when $q \geq p - 1$ [21]. Here $[x]$ denotes the entire function, i.e. the greatest integer not exceeding the real number x .

Two reaction mechanisms, interconverting chemical structures v_i and v_j , are said to be disjoint if their paths on graph $G^s(\lambda)$ have no chemical structures other than v_i and v_j in common. For a given v_i and v_j pair of molecules, the number of disjoint reaction mechanisms is of certain practical importance in synthesis planning. This number can be determined by the following

Theorem 2:

The minimum number of chemical structures in $G^s(\lambda)$, separating two non- s -neighbour molecules v_i and v_j , is equal to the maximum number of disjoint $v_i - v_j$ reaction mechanisms in $G^s(\lambda)$.

It is clear that if m chemical structures separate molecules v_i and v_j then there can exist no more than m disjoint reaction mechanisms. The proof then follows from Dirac's proof of Menger's theorem on disjoint paths [21].

There are three important corollaries of Theorem 2:

- (1) $G^s(\lambda)$ is m -connected if and only if every pair of chemical structures $v_i, v_j \in V(G^s(\lambda))$ can be interconverted into each other by at least m disjoint reaction mechanisms.
- (2) If V_1 and V_2 are two disjoint non-empty sets of chemical structures, where no chemical structure in V_1 is an s -neighbour of any one in V_2 , then the maximum number of disjoint reaction mechanisms between V_1 and V_2 is equal to the minimum number of chemical structures separating V_1 and V_2 .
- (3) A graph $G^s(\lambda)$ of at least $2m$ chemical structures is m -connected if and only if for any two disjoint sets V_1 and V_2 of m chemical structures each, there exist m disjoint reaction mechanisms between V_1 and V_2 .

The local connectivity of two non-adjacent chemical structures v_i and v_j is denoted by $k(v_i, v_j)$ and is defined as the minimum number of chemical structures whose formal removal separates v_i and v_j . From Theorem 2 it follows that

$$k(G(\lambda)) = \min_{v_i, v_j \in \mathbf{V}(G(\lambda))} k(v_i, v_j). \quad (51)$$

If the maximum number of disjoint reaction mechanisms interconverting v_i and v_j is denoted by $\mu(v_i, v_j)$, then Theorem 2 may be re-stated as

$$k(v_i, v_j) = \mu(v_i, v_j). \quad (52)$$

Two reaction mechanisms interconverting chemical structures v_i and v_j are *step-disjoint* if their paths have no edges in common. The result for step disjoint mechanisms, analogous to Theorem 2, is stated as

Theorem 3:

For any two chemical structures v_i and v_j in $G^s(\lambda)$, the maximum number of step-disjoint reaction mechanisms is equal to the minimum number of elementary reaction steps separating them in $G^s(\lambda)$.

Theorem 3 has the following interesting corollary:

(1) $G^s(\lambda)$ is m -step-connected if and only if every pair of chemical structures v_i and $v_j \in \mathbf{V}(G^s(\lambda))$ can be interconverted into each other by at least m step-disjoint reaction mechanisms in $G^s(\lambda)$.

4. Theorems on Shortest Reaction Mechanisms and Reachability Matrices

Just as the neighbour relations of all chemical structures are presented by elements of adjacency matrix $\mathbf{A}(G)$, Eq. (28), the set of all s -neighbour relations for chemical structures of index λ' , $\lambda' \leq \lambda$, can be given in terms of elements of adjacency matrix $\mathbf{A}(G^s(\lambda))$ of reaction graph $G^s(\lambda)$.

The following graph-theoretical theorem on the k -th power of adjacency matrices [21] is the basis for two theorems on reaction mechanisms.

Theorem 4:

The number $w_{ij}(k)$ of walks of length k from v_i to v_j in $G^s(\lambda)$ is equal to the i, j element of the k th power of adjacency matrix $\mathbf{A}(G^s(\lambda))$:

$$w_{ij}(k) = \mathbf{A}_{ij}^k(G^s(\lambda)). \quad (53)$$

This theorem, as formulated for reaction graph $G^s(\lambda)$, is not always applicable directly for chemical problems since walks which are not paths on $G^s(\lambda)$ are generally of lesser importance than paths. Non-path walks usually do not correspond to "economical" reaction mechanisms, since they involve repetitions of one or more chemical structures along the walk. For the special case of paths of length 2, however, the following, chemically more important result is obtained:

Theorem 5:

The number $p_{ij}(2)$ of paths of length 2 between two different chemical structures v_i and v_j in $G^s(\lambda)$ is equal to the i, j ($i \neq j$) element of matrix $\mathbf{A}^2(G^s(\lambda))$:

$$p_{ij}(2) = A_{ij}^2(G^s(\lambda)). \quad (54)$$

The proof follows immediately from the observation that for two different chemical structures every walk of length 2 which interconnects them, must be a path. Then $p_{ij}(2) = w_{ij}(2)$ and Theorem 4 can be applied. In the special case of two molecules $C^{r(0,i)}$ and $C^{r(0,i)}$, the number $p_{ij}(2)$ is the total number of elementary reaction mechanisms of index λ' , $\lambda' \leq \lambda$, leading from one molecule to the other.

A reaction mechanism leading from chemical structure v_i to v_j is a *shortest* mechanism if it consists of the minimum number of elementary reaction steps. The length of a shortest reaction mechanism can be given in terms of adjacency matrices, as established by

Theorem 6:

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

$$A_{ij}^k(G^s(\lambda)) \neq 0. \quad (55)$$

The proof follows from Theorem 4 and from the observation that a shortest walk between two chemical structures v_i and v_j on $G^s(\lambda)$ is necessarily a path, consequently

$$p_{ij}(k) = w_{ij}(k). \quad (56)$$

Connectedness of $G^s(\lambda)$ can also be verified by inspecting $\mathbf{A}(G^s(\lambda))$, since $G^s(\lambda)$ is connected if and only if no re-labeling of vertices can bring $\mathbf{A}(G^s(\lambda))$ into block-diagonal form. In fact, any property of graph $G^s(\lambda)$ is reflected in adjacency matrix $\mathbf{A}(G^s(\lambda))$ due to the one-to-one correspondence between graphs of labeled vertices and binary square matrices of zero diagonal.

Similar theorems are valid for adjacency matrices of digraphs $D^s(\lambda)$, representing reaction networks on the energy hypersurface. Adjacency matrix $\mathbf{A}(D^s(\lambda))$ is not in general symmetric matrix, as a consequence of the orientations given to arcs in $D^s(\lambda)$ (Eq. 15). The outdegree $\text{od}(v_i)$ of chemical structure v_i in $D^s(\lambda)$ is the number of arcs originating at v_i , whereas the indegree $\text{id}(v_i)$ is the number of arcs leading to v_i . The outdegree and indegree of v_i in $D^s(\lambda)$ can be given by the following sums of elements of the adjacency matrix:

$$\text{od}(v_i) = \sum_t A_{it}(D^s(\lambda)) \quad (57)$$

and

$$\text{id}(v_i) = \sum_t A_{ti}(D^s(\lambda)). \quad (58)$$

The elements of reachability matrix $\mathbf{R}(D^s(\lambda))$ are defined by

$$R_{ij} = \begin{cases} 1 & \text{if there is a (directed) path in } D^s(\lambda) \text{ leading from } v_i \text{ to } v_j \\ 0 & \text{otherwise.} \end{cases} \quad (59)$$

Chemical structure v_j is said to be reachable from v_i (that is, $R_{ij} = 1$) if and only if there is a sequence

$$v_i = v_{k_0}, v_{k_1}, \dots, v_{k_l} = v_j \quad (60)$$

of chemical structures where for each pair $v_{k_m}, v_{k_{m+1}}$

$$\bar{N}^s(v_{k_m}, v_{k_{m+1}}) = 1 \quad (61)$$

and for the above distinguished geometries

$$E(v_{k_m}) - E(v_{k_{m+1}}) \geq 0. \quad (62)$$

That is, the energy values in sequence (60) of distinguished geometries form a monotonic non-increasing series. Along the corresponding reaction mechanism, each reaction step is associated with either preserving or lowering the total energy. If $R_{ij} = 1$, such chemical reactions occur spontaneously with no activation energy.

In order to investigate reaction mechanisms involving non-zero activation energy, we shall introduce the concept of *relative* and *absolute E-reachability*. For this end we shall define two digraphs, both derived from $D^s(\lambda)$.

Digraph $D^s(\lambda, E)$ is defined by the vertex set of $D^s(\lambda)$,

$$\mathbf{V}(D^s(\lambda, E)) = \mathbf{V}(D^s(\lambda)) \quad (63)$$

and an arc set¹ obtained by adding an arc $v_j v_i$ to the arc set $\mathbf{A}(D^s(\lambda))$ for every arc $v_i v_j \in \mathbf{A}(D^s(\lambda))$ where

$$0 < E(v_i) - E(v_j) \leq E. \quad (64)$$

That is, for each pair of chemical structures which are adjacent (with *any* orientation) in $D^s(\lambda)$, and which differ by energy less or equal to E , there are two arcs with opposite orientations in $\mathbf{A}(D^s(\lambda, E))$. Due to this construction

$$\mathbf{A}(D^s(\lambda)) \subset \mathbf{A}(D^s(\lambda, E)) \quad (65)$$

and

$$D^s(\lambda) \subset D^s(\lambda, E). \quad (66)$$

Digraph $D^s(\lambda, \bar{E})$ is defined by

$$\mathbf{V}(D^s(\lambda, \bar{E})) = \mathbf{V}(D^s(\lambda)) \quad (67)$$

and an arc set obtained by adding an arc $v_j v_i$ to the arc set $\mathbf{A}(D^s(\lambda))$ of $D^s(\lambda)$ for every arc $v_i v_j \in \mathbf{A}(D^s(\lambda))$ where

$$0 < E(v_i) - E(v_j) \quad (68)$$

¹ Whereas $\mathbf{A}(D^s(\lambda))$ stands for the adjacency matrix, $\mathbf{A}(D^s(\lambda))$ slants for the arc set.

and

$$E(v_i), E(v_j) \leq E. \quad (69)$$

Due to this construction

$$\mathbf{A}(D^s(\lambda)) \subset \mathbf{A}(D^s(\lambda, \bar{E})) \quad (70)$$

and

$$D^s(\lambda) \subset D^s(\lambda, \bar{E}). \quad (71)$$

In $\mathbf{A}(D^s(\lambda, \bar{E}))$ there are two arcs with opposite orientation for every arc of $\mathbf{A}(D^s(\lambda))$ interconnecting vertices of different energy not exceeding E .

The relative and absolute E -reachability matrices of digraph $D^s(\lambda)$ are defined as the reachability matrices of digraphs $D^s(\lambda, E)$ and $D^s(\lambda, \bar{E})$:

$$\mathbf{R}(D^s(\lambda, E)) \quad (72)$$

and

$$\mathbf{R}(D^s(\lambda, \bar{E})), \quad (73)$$

respectively.

Their physical meaning is as suggested by the terminology. Chemical structure v_j is relative E -reachable from chemical structure v_i by a λ' -mechanism, $\lambda' \leq \lambda$, if and only if there is a (directed) path in $D^s(\lambda, E)$ from v_i to v_j . This implies that, in each reaction step along such a reaction mechanism, the activation energy cannot exceed the value E .

Chemical structure v_j is absolute E -reachable from chemical structure v_i by a λ' -mechanism, $\lambda' \leq \lambda$, if and only if there is a (directed) path in $D^s(\lambda, \bar{E})$ from v_i to v_j . This implies that none of the critical points \mathbf{r}_C representing various chemical structures encountered along such a reaction mechanism has total energy larger than the value E .

The connectedness properties of digraph $D^s(\lambda)$ are reflected in the relative and absolute E -reachability matrices. Digraph $D^s(\lambda)$ is *strongly connected* if every two chemical structures v_i and v_j are mutually reachable. $D^s(\lambda)$ is *unilaterally connected* if for every two structures, at least one is reachable from the other. $D^s(\lambda)$ is *weakly connected* if every two chemical structures are joined by a semipath of $D^s(\lambda)$, i.e. by a path of the corresponding $G^s(\lambda)$. Digraph $D^s(\lambda)$ is *disconnected* if it is not even weakly connected. Relative and absolute (strong, unilateral and weak) E -connectedness are defined analogously in terms of digraphs $D^s(\lambda, E)$ and $D^s(\lambda, \bar{E})$, respectively.

The relative and absolute E -reachability matrices are E and \bar{E} dependent, respectively. We are interested in those E values at which the E -reachability of a chemical structure v_j from chemical structure v_i , that is, element R_{ij} of \mathbf{R} , changes. These are the minimum energy values at which a $v_i \rightarrow v_j$ interconversion becomes possible in the classical sense, i.e. when excluding tunneling. This

E -dependence of reachability matrices represents the mathematical link between the theory of reaction networks and the critical level topology (R , T_{FC}) of energy hypersurfaces [29] and it is directly related to the enumeration problem of various critical points on such hypersurfaces [30].

It is evident that an only (relative or absolute) weakly E -connected digraph $D^s(\lambda)$ becomes (relative or absolute, resp.) unilaterally E -connected and eventually (relative or absolute, resp.) strongly E -connected when the E value is sufficiently increased.

Theorems analogous to Theorems 4–6 are valid for digraphs $D^s(\lambda, E)$ and $D^s(\lambda, \bar{E})$, where ordinary walks and paths must be replaced by (directed) walks and paths on digraphs. In particular, the digraph version of Theorem 6 shows how to obtain reachability matrices $\mathbf{R}(D^s(\lambda))$, $\mathbf{R}(D^s(\lambda, E))$ and $\mathbf{R}(D^s(\lambda, \bar{E}))$ from the respective adjacency matrices $\mathbf{A}(D^s(\lambda))$, $\mathbf{A}(D^s(\lambda, E))$ and $\mathbf{A}(D^s(\lambda, \bar{E}))$:

- (1) $R_{ii} = 1$ for every i
- (2) $R_{ij} = 1$ if and only if there exists k such that

$$A_{ij}^k > 0, \quad i \neq j \quad (74)$$

which construction is valid for all three types of reachability matrices.

In the example of Fig. 4, digraph $D^s(2)$ of the portion of model surface of Fig. 2 is shown, where the arcs are labeled by the energy difference between the incident distinguished elements. The energy values of the distinguished points are also given in parentheses after each vertex. The reachability matrix $\mathbf{R}(D^s(\lambda)) = \mathbf{R}(D^s(\lambda, 0.0))$ and the relative E -reachability matrices obtained from digraphs $D^s(2, 1.0)$ and $D^s(2, 2.0)$ are the following:

$$\mathbf{R}(D^s(2)) = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \end{vmatrix}$$

$$\mathbf{R}(D^s(2, 1.0)) = \begin{vmatrix} 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \end{vmatrix}$$

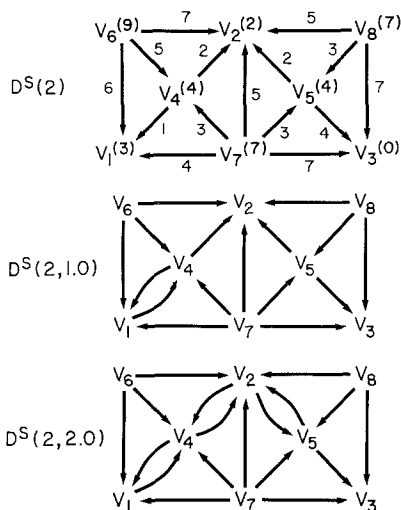


Fig. 4. Subgraphs of digraph $D^S(2)$ and digraphs $D^S(2, 1 \cdot 0)$ and $D^S(2, 2 \cdot 0)$, used in the determination of relative E -reachability matrices of model potential surface shown in Fig. 2

and

$$\mathbf{R}(D^S(2, 2 \cdot 0)) = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 1 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 & 1 \end{pmatrix}$$

In the simple case of the two dimensional surface of the example these results may be obtained easily by inspection of the surface or digraph $D^S(2)$. However, for more complicated multidimensional cases simple inspection as an analytic tool rapidly becomes inapplicable and useless, and in such cases one must rely on graph theoretical relations between adjacency and reachability matrices which provide easily programmable algorithms.

5. Summary

Quantum chemical reaction networks are defined by utilizing topological properties of potential energy hypersurfaces. By exploiting a one-to-one correspondence between graphs and binary matrices of zero diagonal, the fundamental structural properties of energy hypersurfaces, reaction mechanisms and certain energy relations are described in matrix-algebraic terms: by powers of adjacency matrices and reachability matrices. In particular, E -reachability matrices derived from adjacency matrices of reaction digraphs are of some importance whenever the feasibility of various reaction mechanisms cannot be decided by simple

inspection of complicated multidimensional hypersurfaces. Further work on reaction graphs and reaction topology is in progress.

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