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The topology of energy hypersurfaces III. The fundamental group of reaction mechanisms on potential energy hypersurfaces

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The family of all possible reaction mechanisms on a potential surface has an algebraic structure with potential applications in quantum chemical molecular design and synthesis planning.

Transformation properties and equivalence relations of reaction paths on potential energy hypersurfaces lead to a topological definition of reaction mechanisms. The family of all fundamental reaction mechanisms on the hypersurface has a group structure, the *fundamental group* of an appropriately defined topological space. Isomorphism and homomorphism relations between fundamental groups of reaction mechanisms are used to characterize the chemically important topological properties of various subsets of a hypersurface, or those of different excited state hypersurfaces.

Key words: Reaction mechanism—group theory of reaction mechanism—reaction topology—potential surfaces—reaction path—synthesis planning

1. Introduction

A reaction mechanism on a potential surface can be represented by collections of reaction paths which are equivalent in the following sense: they involve the same reactants, a fixed sequence of transition structures and intermediates, and they lead to the same product. Evidently, the general topological properties of the potential energy hypersurface fundamentally influence the properties of reaction mechanisms. Based upon this realization a topological model has been suggested as a possible mathematical framework for computer-aided quantum chemical synthesis design [1, 2]. It has also been suggested that a topological

model is more appropriate for the quantum-mechanical description of molecular structure and reaction mechanism, than the more conventional (and essentially classical-mechanical) geometrical model [1, 2]. Algebraic topology, applied in chemistry and physics, is somewhat reminiscent to applied group theory, since it also provides existence proofs and a clear description of some fundamental relations, in our case between all different chemical structures of a given overall constitution, as well as of all reaction mechanisms between them. General topology, however, has the promise of becoming an even more powerful tool than group theory, since it gives the most general mathematical description of open sets (needed in a quantum-mechanical model), continuity and continuous functions, such as potential energy hypersurfaces over nuclear configuration spaces.

Whereas the above mentioned topological concept of reaction mechanisms conforms with the conventional intuitive concept used by chemists, nevertheless, for equilibrium systems (and most reaction systems are such) a distinction between *alternative intermediates* that may easily interconvert into each other, is non-essential. For example, if compounds A, B, C, and D are related by the two formal reaction mechanisms

$$A \rightarrow C \rightarrow B$$

$$A \rightarrow D \rightarrow B$$

but there is also a direct $C \leftrightarrow D$ interconversion between the two alternative intermediates C and D, with an energy of activation *less* than that of any of the two overall reactions, then the distinction between the two formal mechanisms is non-essential.

As far as reaction mechanisms are concerned, at a given upper limit for the total energy of the system, there are essential differences only between those reaction paths which cannot be converted into each other below this energy value. On the other hand, all reaction paths which can be deformed into one another below this energy limit, represent the same reaction mechanism at the given energy bound. At a higher energy bound there are fewer distinguishable reaction mechanisms. At very high energy bounds all distinctions among chemical reaction mechanisms disappear, as nearly all nuclear configurations become accessible. Expressed differently, nearly all formal reaction paths become deformable into one another *below an energy bound* if this bound is high enough.

Using an upper limit for energy as the main criterion, it is intuitively obvious that all the essentially different reaction mechanisms are fully determined by the topology of potential energy hypersurfaces. We shall make the above statement more precise by a formal application of homotopy theory and we shall derive an underlying algebraic principle. In this work, as in earlier parts I–II, an effort has been made to make this series of studies as nearly self-contained as practical for journal papers. In particular, no previous knowledge of homotopy theory is needed to develop our model, and chemical terminology is often used when possible. The topological concepts used throughout are described in part in Refs.

[1, 2]. For a more detailed introduction into combinatorial and algebraic topology and to homotopy theory the reader may consult references [3–6].

In this study we shall investigate some universal properties of a general system of all fundamental reaction mechanisms on a potential energy hypersurface. We shall show that this system is highly structured and that the relevant algebraic structure is the *fundamental group* of an appropriately defined topological space. In doing this we shall rely on some earlier results. In a previous study [7] a general n-dimensional ($n = 3N$, where N is the number of nuclei) nuclear configuration space ${}^nR$ has been replaced with a metric space M, also referred to as metric topological space $(M, \boldsymbol{T}_d)$, by introducing a special metric d. This metric d, beyond giving internal structure to M, is consistent with the elimination of six degrees of freedom corresponding to the laboratory frame translations and rotations of the molecule as a whole. This metric preserves many features of the mass weighted Cartesian coordinates in the laboratory frame and is suitable for the introduction of reaction topology ("catchment region" topology) $\boldsymbol{T}_C$ into M, turning it into a topological space $(M, \boldsymbol{T}_C)$. The $(M, \boldsymbol{T}_C)$ topologization of M is suitable for a global analysis of energy hypersurfaces $E(K)$, $K \in M$, defined over the reduced nuclear configuration space M. For a local analysis of $\boldsymbol{T}_C$-open sets of M, representing individual chemical species, a differentiable manifold structure has been introduced [7].

It has been shown [8] that if certain open sets of the $(M, \boldsymbol{T}_C)$ topological space are multiply connected then the contribution of a single chemical structure to an overall reaction may lead to a variety of topologically non-equivalent reaction mechanisms. This is true even if the overall reaction involves a *fixed* sequence of chemical structures, and it leads to a fine classification of reaction mechanisms. This result has been obtained by considering homotopies (continuous deformations) of reaction paths [8]. Homotopy theory however, can also be used for a more general analysis of reaction mechanisms. In this study we shall analyse the internal structure of the set of all distinct fundamental reaction mechanisms on the hypersurface. We shall show that this structure is indeed the fundamental group of the topological space. Isomorphism and homomorphism relations of fundamental groups of various *energy dependent* relative topologies will be investigated. Relations between reaction mechanisms on various excited state hypersurfaces will be studied, in terms of relations between the representative fundamental groups. Finally, some interesting properties of higher dimensional homotopy groups of topological space $(M, \boldsymbol{T}'')$ will be pointed out.

2. Level sets and relative reaction topologies

The energy hypersurface $E(K)$ over M is generated by the continuous energy expectation value functional, implying that the actual mapping $M \to E(K)$ is a homeomorphism. Hence, each topological result in M has an equivalent counterpart on the energy hypersurface $E(K)$, consequently, we may refer to the topology of $E(K)$ although the actual analysis is carried out in M. In fact, instead of M, only suitably chosen subsets of M will be investigated.

Analogously to the critical level sets [9] of a general nuclear configuration space ${}^{n}R$, the level sets $F(A)$ and $F^{-}(A)$ of M, with respect to energy hypersurface $E(K)$ and energy value A, are defined as

$$F(A) = \{K: E(K) \leq A\} \tag{1}$$

$$F^{-}(A) = \{K: E(K) < A\}, \tag{2}$$

respectively. The reaction topology $\boldsymbol{T}_C$ on M is defined with respect to "catchment regions" $C(\lambda, i)$ of M, i.e. in terms of subsets of M, each containing one distinguished point $K(\lambda, i)$. These points are extremities of steepest descent paths on $E(K)$. A typical distinguished point $K(\lambda, i)$ is a critical point of $E(K)$ (i.e. a point where the gradient vanishes), where index λ is the number of negative canonical curvatures at $K(\lambda, i)$ and i is an index of ordering.

The relative topology $\boldsymbol{T}_{C/A}$ (reaction topology relative to level set $F^{-}(A)$) is defined by the following family of open sets in $F^{-}(A) \subset M$:

$$\boldsymbol{T}_{C/A} = \{G: G = F^{-}(A) \cap G_C,\ G_C \in \boldsymbol{T}_C\}. \tag{3}$$

Each set

$$C_A(\lambda, i) = F^{-}(A) \cap C(\lambda, i) \tag{4}$$

is a $\boldsymbol{T}_{C/A}$-open set by definition and each non-empty set of type (4) represents a chemical structure within level set $F^{-}(A)$. If $\boldsymbol{C} = \{B\}$ is a basis of topology $\boldsymbol{T}_C$ then $\boldsymbol{C}_A = \{B \cap F^{-}(A)\}$ is a basis for the relative reaction topology $\boldsymbol{T}_{C/A}$.

Note that for an arbitrary energy value A level set $F^{-}(A)$ may well be disconnected. Furthermore, its maximum connected components may be multiply connected, as a result of "cutting off" those parts of the energy hypersurface where it reaches or exceeds the value A.

The relative metric topology $\boldsymbol{T}_{d/A}$ on $F^{-}(A)$ is defined analogously to Eq. (3), by replacing $\boldsymbol{T}_C$ by $\boldsymbol{T}_d$. Intuitively, the metric d of M is simply "inherited" by $F^{-}(A)$.

The relative topology $\boldsymbol{T}_{C/A}$ has some advantageous properties when compared to topology $\boldsymbol{T}_C$: one may select a suitable energy value A and restrict the analysis of the hypersurface to the chemically most important low energy regions. It should be noted, however, that by formally taking $A = \infty$, $F^{-}(A)$ becomes M, i.e. the following treatment is applicable for the full space M. In this case $F^{-}(A) = M$ is simply connected. For the more interesting $A < \infty$ cases the actual determination of the $F^{-}(A)$ level sets is based on contour-following algorithms [2].

3. General homotopies on potential energy hypersurfaces

Consider two continuous mappings, $P^{(0)}$ and $P^{(1)}$, from a topological space $(S, \boldsymbol{T}')$ into space $(F^{-}(A), \boldsymbol{T}'')$:

$$P^{(0)}, P^{(1)}: (S, \boldsymbol{T}') \rightarrow (F^{-}(A), \boldsymbol{T}'') \tag{5}$$

where T' and T'' are some topologies, e.g. T'' can be chosen as $T_{d/A}$ or $T_{C/A}$. If there exists a continuous mapping

$$H:(S, T')\otimes(I, T)\to(F^{-}(A), T'') \tag{6}$$

for which I is the unit interval,

$$I=[0, 1] \tag{7}$$

provided with the usual metric topology T, and for every point, $\underline{s}$ of S

$$H(\underline{s}, 0)=P^{(0)}(\underline{s}) \quad \forall \underline{s}\in S \tag{8}$$

$$H(\underline{s}, 1)=P^{(1)}(\underline{s}) \quad \forall \underline{s}\in S \tag{9}$$

then mappings $P^{(0)}$ and $P^{(1)}$ are *homotopically equivalent*, denoted by $P^{(0)}\sim P^{(1)}$, and H is a *homotopy* (continuous deformation) from $P^{(0)}$ to $P^{(1)}$.

If for every $\underline{s}_0$ element of a subset S_0 of S the images of all $P^{(t)}$ mappings agree for every t, where

$$t\in I=[0, 1] \tag{10}$$

and

$$H(\underline{s}, t)=P^{(t)}(\underline{s}), \tag{11}$$

that is, if

$$P^{(0)}(\underline{s}_0)=P^{(t)}(\underline{s}_0)=P^{(1)}(\underline{s}_0), \quad \forall \underline{s}_0\in S_0\subset S, \quad \forall t\in I \tag{12}$$

then $P^{(0)}$ is *homotopic* to $P^{(1)}$, *relative to subset* S^0: $P^{(0)}\sim P^{(1)}$ rel S_0. If $S_0=\varnothing$, the empty set, then one obtains $P^{(0)}\sim P^{(1)}$, i.e. the "free" homotopy is a special case of the relative homotopy.

The following general result, (sometimes referred to as the "glueing" lemma) is often used in the analysis of various homotopies [4]:

If the (S, T') topological space is the union of two *closed* sets, V_1 and V_2,

$$S=V_1\cup V_2 \tag{13}$$

and if for the continuous (T', T''-continuous) mappings

$$P_1: V_1\to(M, T'') \tag{14}$$

$$P_2: V_2\to(M, T'') \tag{15}$$

their images agree on $V_1\cap V_2$,

$$P_1(\underline{s})=P_2(\underline{s}) \quad \forall \underline{s}\in V_1\cap V_2 \tag{16}$$

then the mapping P_3, defined as

$$P_3:(S, T')\to(M, T'') \tag{17}$$

$$P_3(\underline{s})=P_1(\underline{s}) \quad \forall \underline{s}\in V_1 \tag{18}$$

$$P_3(\underline{s})=P_2(\underline{s}) \quad \forall \underline{s}\in V_2 \tag{19}$$

i.e. the mapping obtained by "glueing" P_1 and P_2 together, is also $\boldsymbol{T}'$, $\boldsymbol{T}''$-continuous.

In particular, the $C_A(\lambda, i)$ relative chemical structures in level set $F^-(A)$ (i.e. the relative catchment regions) give a *partitioning* of $F^-(A)$, consequently their unions are open-closed sets within the relative topology $\boldsymbol{T}_{C/A}$. Such unions have been proposed earlier as an alternative definition of reaction mechanisms; a sequence of neighboring chemical structures in the reaction topology represents a reaction mechanism [2, 8]. Consequently, if S itself is a union of relative chemical structures, with the same $\boldsymbol{T}_{C/A}$ topology, then V_1 may be chosen as a reaction mechanism, (relative to $F^-(A)$) and V_2 as any $\boldsymbol{T}_{C/A}$-closed set containing the relative complement of V_1 in S. Now the above quoted general result (glueing lemma) is applicable and for *any pair of continuous functions* P_1 and P_2 defined on relative reaction mechanism V_1 and on set V_2, respectively, and fulfilling the "overlap condition" (condition (16)), the "unified" function P_3 is also continuous. In particular, if V_1 and V_2 are two overlapping reaction mechanisms, then the global continuity of P_3 on S is assured, no matter how strangely P_1 and P_2 behave in the non-overlapping regions. This property allows one to carry out extensive deformations of potential surfaces (e.g. if mappings to compact manifolds are required [8]) without altering the essential characteristics and mutual relations of reaction mechanisms.

The relative homotopy with respect to a subset $S_0 \subset S$ is an equivalence relation and all mappings P, P', ... that are related to each other by some homotopy relative to S_0, form an equivalence class $\boldsymbol{P}_\alpha$. Such equivalence classes generate a partitioning of the set $\boldsymbol{P}$ of all continuous mappings form S to $F^-(A)$ which agree on subset S_0:

$$\boldsymbol{P} = \{P: (S, \boldsymbol{T}') \to (F^-(A), \boldsymbol{T}''), P(\underline{s}) = P^0(\underline{s}) \quad \forall \underline{s} \in S_0 \subset S\} \tag{20}$$

for some specified $P^0(\underline{s})$ mapping on S_0, and

$$\boldsymbol{P}_\alpha = \{P: P \in \boldsymbol{P}, P \sim P_\alpha \text{ rel } S_0\} \tag{21}$$

where P_α is any representative from equivalence class $\boldsymbol{P}_\alpha$, and where

$$\boldsymbol{P} = \bigcup_\alpha \boldsymbol{P}_\alpha \tag{22}$$

and

$$\boldsymbol{P}_\alpha \cap \boldsymbol{P}_{\alpha'} = \varnothing \quad \forall_{\alpha \neq \alpha'}. \tag{23}$$

If $P \sim P'$ where P' maps the entire set S to a single point $K_0 \in F^-(A)$, then P is *homotopic to a constant.* If the $i: S \to S$ identity mapping is homotopic to a constant, then S is *contractible to a point.* If the level set $F^-(A)$ of the potential energy hypersurface is contractible to a point then *every* continuous

$$P: (S, \boldsymbol{T}') \to (F^-(A), \boldsymbol{T}'') \tag{24}$$

mapping is homotopic to a constant. If $(S, \boldsymbol{T}')$ is chosen as $(F^-(A), \boldsymbol{T}'')$ then contractibility of level set $F^-(A)$ implies that there is only *one* homotopy class,

$\boldsymbol{P}$ itself. This is indeed the simplest case and we are interested mostly in non-contractible $(F^{-}(A), \boldsymbol{T}'')$ topological spaces, where different homotopy classes have different chemical significance.

4. Reaction path homotopies

In order to introduce the fundamental group of general reaction mechanisms we need a description of the concepts of *homotopy type* and *homotopy invariants* in $(F^{-}(A), \boldsymbol{T}'')$. The fundamental group itself will be one such invariant. Furthermore, we also need a description of some homotopy properties of reaction paths and a definition of fundamental reaction mechanisms.

If for two topological spaces, $(S, \boldsymbol{T}')$ and $(F^{-}(A), \boldsymbol{T}'')$, there exist two continuous mappings

$$P: (S, \boldsymbol{T}') \to (F^{-}(A), \boldsymbol{T}'') \tag{25}$$

$$Q: (F^{-}(A), \boldsymbol{T}'') \to (S, \boldsymbol{T}') \tag{26}$$

such that the composition

$$Q \cdot P: (S, \boldsymbol{T}') \to (S, \boldsymbol{T}') \tag{27}$$

is homotopic to the identity mapping

$$i: (S, \boldsymbol{T}') \to (S, \boldsymbol{T}') \tag{28}$$

and similarly, if the composition

$$P \cdot Q: (F^{-}(A), \boldsymbol{T}'') \to (F^{-}(A), \boldsymbol{T}'') \tag{29}$$

is homotopic to the identity mapping

$$j: (F^{-}(A), \boldsymbol{T}'') \to (F^{-}(A), \boldsymbol{T}'') \tag{30}$$

then $(S, \boldsymbol{T}')$ and $(F^{-}(A), \boldsymbol{T}'')$ are of the same *homotopy type.* If the two spaces are homeomorphic, i.e. topologically equivalent, then they are necessarily of the same homotopy type, but the converse is not true. Belonging to the same homotopy type is also an equivalence relation with equivalence classes larger than the classes of topological equivalence, since the former is a weaker equivalence relation than the latter. In this study we are also interested in those cases, where the two homotopy types involved are *different.* In particular, we shall study the special case where S is an interval on the real line (e.g. I) provided with the usual metric, that space is evidently of different homotopy type than a general relative reaction topology $(F^{-}(A), \boldsymbol{T}_{C/A})$ or topological space $(F^{-}(A), \boldsymbol{T}_{d/A})$.

A *homotopical invariant* is an object that is the same for all topological spaces that are of the same homotopy type. Evidently, a homotopical invariant is also a topological invariant, but a topological invariant is not necessarily homotopically invariant. The most important homotopical invariants of the topological space $(F^{-}(A), \boldsymbol{T}_{d/A})$ are its *homotopy groups* $\Pi_n(F^{-}(A), \boldsymbol{T}_{d/A}, K_0)$, and in particular the one dimensional homotopy group, the *fundamental group of reaction*

mechanisms, $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_0)$. In order to give their definitions, we first give a very general definition of reaction paths, and describe some of their intuitively evident properties.

A *reaction path* P in topological space $(F^-(A), \boldsymbol{T}_{d/A})$ is a continuous mapping from $I=[0, 1]$ into $F^-(A)$:

$$P: (I, \boldsymbol{T}) \to (F^-(A), \boldsymbol{T}_{d/A}) \tag{31}$$

where $\boldsymbol{T}$ is the usual metric topology in I. That is, a reaction path is a special case of mappings (5), obtained by replacing $(S, \boldsymbol{T}')$ by $(I, \boldsymbol{T})$. Note that a topological reaction path P is not always a trajectory in the semiclassical sense, but all such trajectories are topological reaction paths. Any *single* path (irrespectively whether a semiclassical trajectory or not) is in a formal contradiction with the uncertainty principle, and we shall attempt to circumvent (at least in part) this contradiction and to obtain a *topological* representation by considering *families* of homotopically equivalent reaction paths.

Points $P(0)$ and $P(1)$ are the *origin* and *extremity*, resp., of reaction path P. The *inverse reaction path* P^{-1} of P is defined by

$$P^{-1}(u) = P(1-u) \quad \forall u \in I. \tag{32}$$

Evidently, the extremity of P coincides with the origin of P^{-1} and *vice versa*. P and P^{-1} define the same subset of $F^-(A)$, but they run through the same points in opposite sense. One should not confuse the inverse reaction path P^{-1} of path P with the inverse $(P)^{-1}$ of *mapping* P, the latter being a mapping itself:

$$(P)^{-1}: (F^-(A), \boldsymbol{T}'_{d/A})' \to (I, \boldsymbol{T}) \tag{33}$$

where $(F^-(A), \boldsymbol{T}'_{d/A})'$ is a subset of $(F^-(A), \boldsymbol{T}_{d/A})$.

If P_1 and P_2 are two reaction paths fulfilling the condition

$$P_1(1) = P_2(0) \tag{34}$$

i.e. the extremity of P_1 coincides with the origin of P_2, then the *product reaction path* P_1P_2 is the path P_3

$$P_3: (I, \boldsymbol{T}) \to (F^-(A), \boldsymbol{T}_{d/A}) \tag{35}$$

for which

$$P_3(u) = P_1(2u), \quad 0 \leq u \leq \tfrac{1}{2} \tag{36}$$

$$P_3(u) = P_2(2u-1), \quad \tfrac{1}{2} \leq u \leq 1. \tag{37}$$

In notation,

$$P_3 = P_1P_2. \tag{38}$$

Due to the general result ("gluing" lemma) quoted above (Eqs. 13–19), the product reaction path P_3 is also continuous, and it is also a reaction path itself. The product reaction path should not be confused with the product of the two

functions $P_1(u)$, (nor with the chemical product obtained after completion of the reaction). Intuitively, one may picture P_3 as the continuation of P_1 by P_2.

If for a reaction path P the entire image of I is a single element $K \in F^-(A)$,

$$P(I) = K \in F^-(A) \tag{39}$$

then P is called a *zero path.* (This name, as we shall see, is not very fortunate, but the name "unit reaction path" that may appear more consistent with the following group theoretical treatment, can be even more misleading.)

A path P is a *closed reaction path* if its origin coincides with its extremity:

$$P(0) = P(1). \tag{40}$$

For example, the product path PP^{-1} and $P^{-1}P$ are both closed reaction paths.

If P_1 and P_2 are two reaction paths with common origins and common extremities,

$$P_1(0) = P_2(0) \tag{41}$$

$$P_1(1) = P_2(1) \tag{42}$$

then we shall regard P_1 *path-homotopic* (or in short, *homotopic*) to P_2, $P_1 \sim P_2$, if they are homotopic *relative* to the subset $I_0 \subset I$

$$I_0 = \{0, 1\} \tag{43}$$

where in the general definition of relative homotopy [Eqs (6–11)] $(I, \boldsymbol{T})$, I_0, u and $\boldsymbol{T}_{d/A}$ are substituted for $(S, \boldsymbol{T}')$, S_0, $\underline{s}$ and $\boldsymbol{T}''$, respectively. Intuitively, P_1 and P_2 are homotopic *relative* to the fixed endpoints $P_1(0) = P_2(0)$ and $P_1(1) = P_2(1)$.

The following reaction path properties are intuitively evident and (what does not always follow) are relatively easy to prove (hence their proofs will be omitted):

(i) If for reaction paths P_1, P_2, P_3 and P_4

$$P_1 \sim P_3 \tag{44}$$

$$P_2 \sim P_4 \tag{45}$$

and the product path

$$P_1 P_2 \text{ exists,} \tag{46}$$

then the reaction path

$$P_3 P_4 \text{ exists,} \tag{47}$$

and

$$P_1 P_2 \sim P_3 P_4 \tag{48}$$

(ii) If two reaction paths are homotopic then their inverse reaction paths are also homotopic:

$$P_1 \sim P_2 \Rightarrow P_1^{-1} \sim P_2^{-1}. \tag{49}$$

(iii) If P_1 is an arbitrary reaction path and if P_2 is a zero reaction path

$$P_2(I) = K \in F^-(A) \tag{50}$$

such that

$$P_1P_2 \text{ exists} \tag{51}$$

then

$$P_1P_2 \sim P_1. \tag{52}$$

(Similarly, from the existence of P_2P_1 $P_2P_1 \sim P_1$ follows.)

(iv) If for reaction paths P_1, P_2 and P_3

$$P_1P_2 \text{ exists} \tag{53}$$

and

$$P_2P_3 \text{ exists} \tag{54}$$

then both

$$(P_1P_2)P_3,\ P_1(P_2P_3) \text{ exist} \tag{55}$$

and

$$(P_1P_2)P_3 \sim P_1(P_2P_3). \tag{56}$$

(v) For any reaction path P_1 there exists a zero path P_2,

$$P_2(I) = K \in F^-(A) \tag{57}$$

such, that

$$P_1P_1^{-1} \sim P_2. \tag{58}$$

(Evidently $P_1^{-1}P_1$ is also homotopic to a zero path.)

(vi) Let P_1 and P_2 be such a pair of reaction paths that

$$P_1P_2^{-1} \text{ exists} \tag{59}$$

and it is a closed reaction path:

$$P_1P_2^{-1}(0) = P_1P_2^{-1}(1). \tag{60}$$

In this case

$$P_1P_2^{-1} \sim P_3 \Leftrightarrow P_1 \sim P_2 \tag{61}$$

where P_3 is a zero reaction path. That is, a closed $P_1P_2^{-1}$ reaction path is homotopic to a zero path if and only if P_1 is homotopic to P_2.

We shall use the above properties (i)-(vi) to demonstrate the group properties of the fundamental group of reaction mechanisms, and to prove some isomorphism and homomorphism relations.

5. The fundamental group of reaction mechanisms

In a topological treatment of chemical reactions, and in fact in any quantum mechanical treatment, it is inappropriate to consider individual reaction paths only, just as it is inappropriate to consider a fixed nuclear geometry when describing a molecule. In the topological model chemical structure is defined as an *open set* of nuclear geometries (a catchment region $C(\lambda, i)$), hence it is natural to regard a topological reaction mechanism as a *set* of reaction paths, which paths are equivalent in certain sense. In this study we shall regard *homotopical equivalence of reaction paths* as the mathematical device that defines a general topological reaction mechanism.

Take an arbitrary point $K_0 \in F^{-}(A)$ and consider all closed reaction paths with extremity at K_0. If P_1 is such a reaction path, then denote the equivalence class of paths which are homotopic to P_1 by $[P_1]$:

$$[P_1] = \{P : P \sim P_1,\ P_1(0) = P_1(1) = K_0\}. \tag{62}$$

In the given level set $F^{-}(A)$ with upper limit A for energy, $[P_1]$ is a *closed topological reaction mechanism*, referred to as a *fundamental reaction mechanism.* Since any reaction path within level set $F^{-}(A)$ must occur as a segment of some P closed path, segments of the fundamental reaction mechanisms describe all possible reaction mechanisms in $F^{-}(A)$.

The product of such homotopy classes (i.e. the algebraic product of fundamental reaction mechanisms) is defined by

$$[P_1][P_2] = [P_1 P_2]. \tag{63}$$

According to property (i), this definition is independent of the actual choice of reaction paths P_1 and P_2 representing fundamental reaction mechanisms $[P_1]$ and $[P_2]$, respectively, since from $P_1 \sim P_3$ and $P_2 \sim P_4$ the homotopic equivalence $P_1 P_2 \sim P_3 P_4$ follows, hence

$$[P_3][P_4] = [P_3 P_4] = [P_1 P_2]. \tag{64}$$

That is, the product $[P_1][P_2]$ is uniquely determined by reaction mechnisms $[P_1]$ and $[P_2]$.

We show now that the above defined product generates a *group structure* in the family of homotopy classes (in the family of fundamental reaction mechanisms) of all reaction paths passing through point $K_0 \in F^{-}(A)$.

Closure property: the product is closed since $[P_1][P_2]$ is a fundamental reaction mechanism (homotopy class) of reaction paths passing through K_0, by definition.

Associative property: by definition (63)

$$[(P_1][P_2])[P_3] = [P_1 P_2][P_3] = [(P_1 P_2) P_3] \tag{65}$$

and

$$[P_1]([P_2][P_3]) = [P_1][P_2 P_3] = [P_1(P_2 P_3)]. \tag{66}$$

But from property (iv) $(P_1P_2)P_3 \sim P_1(P_2P_3)$ hence

$$([P_1][P_2])[P_3] = [P_1]([P_2][P_3]). \tag{67}$$

Unit element: let us denote by [1] the homotopy class of *zero reaction path* at point K_0:

$$[1] = \{P : P \sim P_{K_0},\ P_{K_0}(I) = K_0\}. \tag{68}$$

Then, property (iii) implies that for any reaction mechanism $[P_1]$

$$[P_1][1] = [P_1] \tag{69}$$

hence [1] is the *unit element.* (Since the multiplicative convention is used for groups throughout, for this reason one could, perhaps, find some justification calling the zero reaction paths "unit" reaction paths. These paths, however, refer to "no reaction" and we believe the name adopted is more appropriate.)

Inverse: According to property (v) for any reaction mechanism $[P_1]$

$$[P_1][P_1^{-1}] = [1] \tag{80}$$

hence $[P_1^{-1}]$ is the inverse reaction mechanism of $[P_1]$ every reaction mechanism $[P]$ has an inverse.

This proves that the family of fundamental reaction mechanisms defined by Eq. (62) is a *group*, with product defined by Eq. (63). We shall use the $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_0)$ notation (or in short, the Π_1 notation if no detailed specification is needed) for this group, and we shall refer to it as the *fundamental group of reaction mechanisms.*

Group Π_1 describes the internal structure of a family of reaction mechanisms which are indeed topological, i.e. free from the usual geometrical constraints of reaction paths, with one apparent exception: Π_1 refers to a *point* $K_0 \in F^-(A)$. This "geometrical remnant", however, can be removed relatively easily. We show that there is a considerable degree of freedom in choosing K_0, without affecting the group structure and the essential properties of reaction mechanisms.

More precisely, we show that if level set $F^-(A)$ is arcwise connected then the fundamental groups $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_0)$ and $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_1)$ are *isomorphic* for any two points $K_0, K_1 \in F^-(A)$.

Take any reaction path P_1 such that

$$P_1(0) = P_1(1) = K_0. \tag{71}$$

Since $F^-(A)$ is arcwise connected there exists a (generally non-unique) reaction path R_1 in $F^-(A)$ such that it leads from K_0 to K_1:

$$R_1(0) = K_0 \tag{72}$$

$$R_1(1) = K_1. \tag{73}$$

Then reaction path Q_1, defined as

$$Q_1 = (R_1^{-1} P_1) R_1 \tag{74}$$

is a closed path passing through K_1:

$$Q_1(0) = Q_1(1) = K_1. \tag{75}$$

Let us define a mapping V from homotopy classes $[P]$ based on K_0 to homotopy classes $[Q]$ based on K_1 by

$$V[P] = [Q]. \tag{76}$$

Then $[P]$ determines $V[P]$ uniquely. Conversely, $V[P]$ also determines $[P]$ uniquely, since from

$$(R_1^{-1} P_1) R_1 \sim (R_1^{-1} P_2) R_1 \tag{77}$$

the homotopy relation

$$P_1 \sim P_2 \tag{78}$$

follows, according to properties (iv) and (v). Furthermore, for any reaction path Q through point K_1

$$Q \sim R_1^{-1}((R_1 Q) R_1^{-1}) R_1 \tag{79}$$

hence any $[Q_1]$ homotopy class of reaction paths through point K_1 is of the form $V[P]$ for some $[P]$ reaction mechanism. Hence V is a one-to-one and onto mapping of the family of K_0-based reaction mechanism to the family of K_1-based reaction mechanisms. Since according to properties (iv) and (v)

$$V[P_1]V[P_2] = [(R_1^{-1} P_1) R_1][(R_1^{-1} P_2) R_1] = [(R_1^{-1}(P_1 P_2)) R_1] = V[P_1 P_2] \tag{80}$$

the product is "inherited" and the transformation V is an *isomorphism* between fundamental groups $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_0)$ and $\Pi_1(F^-(A), \boldsymbol{T}_{d/A}, K_1)$. Hence K_0 can be chosen freely within any arcwise connected level set $F^-(A)$ and the *resulting group structure of reaction mechanisms remains invariant.* For arcwise connected level sets of the potential energy hypersurface the specification of point K_0 can be omitted and we may write $\Pi_1(F^-(A), \boldsymbol{T}_{d/A})$ for the fundamental group of reaction mechanisms.

6. Isomorphism and homomorphism relations for groups of reaction mechanisms

If there are two level sets, $F_1^-(A)$ and $F_2^-(B)$ (on the same or possibly on two different potential energy hypersurfaces), provided with topologies $\boldsymbol{T}_1''$ and $\boldsymbol{T}_2''$, respectively, and if

$$f: (F_1^-(A), \boldsymbol{T}_1'') \to (F_2^-(B), \boldsymbol{T}_2'') \tag{81}$$

is a $\boldsymbol{T}_1''$, $\boldsymbol{T}_2''$—continuous mapping then for any point $K_0 \in F_1^-(A)$ there exists a *homomorphism*

$$f^*: \Pi_1(F_1^-(A), \boldsymbol{T}_1'', K_0) \to \Pi_1(F_2^-(B), \boldsymbol{T}_2'', f(K_0)) \tag{82}$$

between the corresponding fundamental groups of reaction mechanisms.

In order to show this, take two reaction paths P_1 and P_2 in $F_1^-(A)$, such that

$$P_1(0) = P_1(1) = P_2(0) = P_2(1) = K_0 \in F_1^-(A). \tag{83}$$

Define reaction paths Q_1 and Q_2 in $F_2^-(B)$ by the compositions

$$Q_1 = f \cdot P_1, \qquad Q_1(u) = f(P_1(u)), \quad \forall u \in I \tag{84}$$

and

$$Q_2 = f \cdot P_2, \qquad Q_2(u) = f(P_2(u)), \quad \forall u \in I. \tag{85}$$

Consequently,

$$Q_1(0) = Q_1(1) = Q_2(0) = Q_2(1) = f(K_0) \in F_2^-(B). \tag{86}$$

If $P_1 \sim P_2$ then there exists a $H_1 : I^2 \to (F_1^-(A), \boldsymbol{T}_1'')$ homotopy such, that

$$H_1(u, 0) = P_1(u) \tag{87}$$

$$H_1(u, 1) = P_2(u) \tag{88}$$

$$H_1(0, v) = H(1, v) = K_0 \quad \forall v \in I \tag{89}$$

where Eq. (83) has been taken into account. Define a mapping $H_2 : I^2 \to (F_2^-(B), \boldsymbol{T}_2'')$ by

$$H_2(u, v) = f(H_1(u, v)). \tag{90}$$

Then H_2 is continuous and

$$H_2(u, 0) = f(P_1(u)) = Q_1(u) \tag{91}$$

$$H_2(u, 1) = f(P_2(u)) = Q_2(u) \tag{92}$$

$$H_2(0, v) = H_2(1, v) = f(K_0) \quad \forall v \in I \tag{93}$$

hence reaction paths Q_1 and Q_2 of $F_2^-(B)$ are also homotopic:

$$Q_1 \sim Q_2. \tag{94}$$

If now we define a mapping f^* of reaction mechanisms as

$$f^*[P] = [f \cdot P] \tag{95}$$

then f^* is a unique assignment of all reaction mechanisms of $F_1^-(A)$ with reference to K_0 to some reaction mechanisms of $F_2^-(B)$ with reference to $f(K_0)$.

If $P_3 = P_1 P_2$ is the product reaction path as defined by Eqs. (36)–(37), and Q_3 is the reaction path in $F_2^-(B)$ defined by the composition

$$Q_3 = f \cdot P_3 \tag{96}$$

$$Q_3(u) = f(P_1(2u)), \qquad 0 \leq u \leq \tfrac{1}{2} \tag{97}$$

$$Q_3(u) = f(P_2(2u-1)), \qquad \tfrac{1}{2} \leq u \leq 1 \tag{98}$$

then Q_3 is also a product path

$$Q_3 = Q_1 Q_2 \tag{99}$$

and for the reaction mechanisms relation

$$f^*[P_1]f^*[P_2]=[Q_1][Q_2]=[Q_1Q_2]=f^*[P_1P_2] \tag{100}$$

follows, that is, the induced mapping f^* is indeed a *homomorphism* of fundamental group $\Pi_1(F_1^-(Q), \boldsymbol{T}_1'', K_0)$ to $\Pi_1(F_2^-(B), \boldsymbol{T}_2'', f(K_0))$.

From a general result of homotopy theory, i.e. from the fact that the fundamental groups of two spaces of the same homotopy type are isomorphic [4], it follows that if f is a *homeomorphism*, then *isomorphism* of the two groups follows. This latter result for the special case of the groups of reaction mechanism can also be shown by interchanging the roles of the two spaces in the above proof if f is a one-to-one and onto mapping.

Isomorphism of the two groups also follows from the following conditions: if there exist two continuous mappings f and g,

$$f:(F_1^-(A), \boldsymbol{T}_1'')\to(F_2^-(B), \boldsymbol{T}_2'') \tag{101}$$

$$g:(F_2^-(B), \boldsymbol{T}_2'')\to(F_1^-(A), \boldsymbol{T}_1'') \tag{102}$$

such that

$$g(f(K_0))=K_0\in F_1^-(A) \tag{103}$$

and

$$g\cdot f\sim i \text{ rel } K_0 \tag{104}$$

$$f\cdot g\sim j \text{ rel } f(K_0) \tag{105}$$

where i and j are the identity maps in $(F_1^-(A), \boldsymbol{T}_1'')$ and $(F_2^-(B), \boldsymbol{T}_2'')$, respectively, then the two fundamental groups of reaction mechanisms are isomorphic.

The above results have some interesting chemical implications. Let us consider a special case, where both $F_1^-(A)$ and $F_2^-(B)$ refer to the same energy hypersurface but the energy values A and B are different,

$$A<B. \tag{106}$$

Let us assume that both level sets are connected (simply or multiply connected). If during an $A\to B$ energy change *no critical level of* $E(K)$ *is encountered* (a critical level is the energy of a critical point, say that of $K(\lambda, i)$, of $E(K)$), then the connectedness properties of the level sets remain invariant [9]. Hence there exists a *homeophorphism* between the two level sets, consequently, the two fundamental groups of reaction mechanisms in the two level sets are *isomorphic.*

If, on the other hand, during the $A\to B$ energy change the connectedness properties of level sets also change, then, in general, no homeomorphism can be guaranteed between them, and it is possible that continuous mappings exist only from one space to a subset of the other. This implies only a homomorphism between the two fundamental groups of reaction mechanisms. Note that a *necessary condition* for a change in connectivity of level sets is the existence of a *critical level* within the $(A, B]$ open-closed energy interval [9]. Nevertheless,

the occurrence of critical levels, hence changes in connectedness, are *not sufficient conditions* for a difference between the two fundamental groups (i.e. for the nonexistence of an isomorphism). Using a simple geographical analogy, the connectedness of the level set of a lake (i.e. that of the flooded area) changes if the water level reaches the highest saddle point on the land behind a hill, turning the hill into an island. If this is the *only* topological change then no homeomorphism exists between the old and new level sets, hence there is only a homomorphism between the two fundamental groups. Evidently, there is a new route for boat trips behind the hill, hence the family of reaction mechanisms is "richer" in the new level set than in the old one. It is easy to see that in such a case $\Pi_1(F_1^-(A), T_1'', K_0)$ is a *subgroup* of $\Pi_1(F_2^-(B), T_2'', K_0)$, and in fact the same follows if the connectivity increases *monotonically* as $A \to B$.

However, if during the $A \to B$ flooding precisely one new island is formed, and in addition, the water level also covers the highest point of one old island, then the connectivity changes cancel out and in spite of the presence of critical levels within $(A, B]$ a homeomorphism can be given between the two level sets and the two fundamental groups of reaction mechanisms are *isomorphic.* Note, however, that in this example there is *no net change* in connectedness.

The fundamental groups of reaction mechanisms depend *indirectly* on the energy value A of level sets $F^-(A)$, through connectivity changes, and our conclusions can be summarized as follows:

(i) If there is no connectivity change during energy change $A \to B$ (for which a *sufficient* condition is that no critical level exists in $(A, B]$), then the fundamental groups of reaction mechanisms are *isomorphic* within $[A, B]$.
(ii) If the net connectivity of level sets changes (for which a *necessary* condition is the existence of a critical level in $(A, B]$) then in general only a *homomorphism* can be guaranteed between the two groups.
(iii) If in the $[A, B]$ interval the connectivity of level sets changes *monotonically,* then the fundamental group of reaction mechanisms in the level set of *lower* connectivity is a *subgroup* of the other group.

Another important example for the application of isomorphism - homomorphism conditions is the case of excited state energy hypersurfaces. Considering e.g. the ground state and one excited state hypersurface, a homeomorphism between the two relevant level sets assures that the main structural features of the two families of reaction mechanisms on the two surfaces are essentially the same, the two fundamental groups being isomorphic. If no homeomorphism, only continuous mappings exist between the two spaces, then the systems of reaction mechanisms are at most similar, one having a richer variety than the other, i.e. in this case only a homomorphism exists between the two groups. The simplest possible case is the *simply connected* level set $F^-(A)$ where every reaction path P is contractible to a point. In this case the fundamental group has one element only, [1], the "zero" reaction mechanism. The simplest example for this (uninteresting) case is the level set of a single basin with no internal features in it, hence without real reaction mechanisms.

7. *n*-Dimensional homotopy groups of energy level sets on hypersurfaces

We have obtained the definition of the fundamental group of reaction mechanisms by considering properties of reaction path homotopies. The concept of path, however is essentially a geometrical hence a classical mechanical one and it is in a formal contradiction with the uncertainty principle of quantum mechanics. This contradiction has been, at least in part, circumvented by considering *distributions* (open sets) of homotopically equivalent reaction paths. The question arises, however, is it possible to describe the fundamental topological - algebraic structure of potential energy hypersurfaces without relying on the concept of reaction paths? The n-dimensional homotopy groups appear to represent a step in the right direction. There is also a more practical reason for considering higher dimensional homotopy groups: they represent additional invariants which can be used for characterizing topological space $(F^{-}(A), \boldsymbol{T}_{d/A})$. We shall also see that in the special case of $n=1$, we get back the fundamental group of reaction mechanisms derived above.

Let I_n be an n-dimensional cube, the subset of the n-dimensional euclidean space containing all the points which have coordinates $(u_1, u_2, \ldots, u_n)$ fulfilling the

$$0 \leq u_i \leq 1 \qquad (i = 1, \ldots, n) \tag{107}$$

condition. The J_n boundary of I_n is the union of all points of I_n for which at least one coordinate u_i is either 0 or 1. We assume the usual topology $\boldsymbol{T}_n$ for I_n and we shall be particularly interested in its open interior.

Consider continuous mappings

$$P_1, P_2 : (I_n, \boldsymbol{T}_n) \to (F^{-}(A), \boldsymbol{T}'') \tag{108}$$

such that

$$P_1(J_n) = P_2(J_n) = K_0 \in F^{-}(A). \tag{109}$$

The *product* $P_0 = P_1 P_2$ is defined as

$$P_0(u_1, u_2, \ldots, u_n) = P_1(2u_1, u_2, \ldots, u_n), \qquad 0 \leq u_1 \leq \tfrac{1}{2} \tag{110}$$

$$P_0(u_1, u_2, \ldots, u_n) = P_2(2u_1 - 1, u_2, \ldots, u_n), \qquad \tfrac{1}{2} \leq u_1 \leq 1. \tag{111}$$

Evidently, P_0 is also continuous and

$$P_0(J_n) = K_0. \tag{112}$$

Consider two additional continuous mappings

$$P_3, P_4 : (I_n, \boldsymbol{T}_n) \to (F^{-}(A), \boldsymbol{T}'') \tag{113}$$

such that

$$P_3(J_n) = P_4(J_n) = K_0. \tag{114}$$

If $P_1 \sim P_3$ rel J_n then there exists continuous mapping

$$f : (I_n, \boldsymbol{T}_n) \otimes (I, \boldsymbol{T}) \to (F^{-}(A), \boldsymbol{T}'') \tag{115}$$

such that

$$f(u_1, u_2, \ldots, u_n, 0) = P_1(u_1, u_2, \ldots, u_n) \tag{116}$$

$$f(u_1, u_2, \ldots, u_n, 1) = P_3(u_1, u_2, \ldots, u_n) \tag{117}$$

$$f(z_1, z_2, \ldots, z_n, v) = K_0 \quad \forall v \tag{118}$$

where $(z_1, z_2, \ldots, z_n) \in J_n$ and $v \in I$. Similarly, if $P_2 \sim P_4$ rel J_n, then a mapping g is defined analogously.

Let us consider a third mapping,

$$h : (I_n, \boldsymbol{T}_n) \otimes (I, T) \to (F^-(A), \boldsymbol{T}'') \tag{119}$$

defined by

$$h(u_1, u_2, \ldots, u_n, v) = f(2u_1, u_2, \ldots, u_n, v), \qquad 0 \leq u_1 \leq \tfrac{1}{2} \tag{120}$$

$$h(u_1, u_2, \ldots, u_n, v) = g(2u_1 - 1, u_2, \ldots, u_n, v), \qquad \tfrac{1}{2} \leq u_1 \leq 1. \tag{121}$$

Then h is continuous and

$$h(u_1, u_2, \ldots, u_n, 0) = (P_1 P_2)(u_1, u_2, \ldots, u_n) \tag{122}$$

$$h(u_1, u_2, \ldots, u_n, 1) = (P_3 P_4)(u_1, u_2, \ldots, u_n) \tag{123}$$

$$h(z_1, z_2, \ldots, z_n, v) = K_0. \tag{124}$$

Consequently, if $P_1 \sim P_3$ rel J_n and $P_2 \sim P_4$ rel J_n then $P_1 P_2 \sim P_3 P_4$ rel J_n follows.

Consider the family $\{[P]\}$ of all homotopy classes $[P]$ of all P mappings satisfying

$$P : (I_n, \boldsymbol{T}_n) \to (F^-(A), \boldsymbol{T}'') \tag{125}$$

$$P(J_n) = K_0 \in F^-(A). \tag{126}$$

The *product* of homotopy classes $[P_1]$ and $[P_2]$ is defined uniquely by

$$[P_1][P_2] = [P_1 P_2], [P_1], [P_2] \in \{[P]\} \tag{127}$$

that definition is meaningful as it follows from the properties of mapping h. With respect to the above defined product the family $\{[P]\}$ of homotopy equivalence classes form a *group*, the *n-dimensional homotopy group* $\Pi_n(F^-(A), \boldsymbol{T}'', K_0)$.

Its group properties and other properties can be proven similarly to the case of the fundamental group of reaction mechanisms, in fact, if $n = 1$ this latter group is obtained. If $F^-(A)$ is arcwise connected then $\Pi_n(F^-(A), \boldsymbol{T}'', K_0)$ is isomorphic with $\Pi_n(F^-(A), \boldsymbol{T}'', K_1)$ for any choice of $K_0, K_1 \in F^-(A)$. The homotopy groups are homotopy invariants and homotopy groups of homeomorphic spaces are isomorphic, which properties can be utilized in comparing homotopy groups of various level sets and excited state energy hypersurfaces.

Higher dimensional ($n > 1$) homotopy groups describe the algebraic properties of interconversion processes of higher dimensional *subsets* of level set $F^-(A)$, as opposed to the fundamental group of reaction mechanisms which is based on the concept of reaction paths, i.e. on interconversion processes of one dimensional

subsets, themselves describing transformations of individual *points* of $F^{-}(A)$. As homotopical invariants, the n-dimensional homotopy groups give a detailed algebraic characterization of level sets of the potential energy hypersurface. Nevertheless, it is the special case of the one dimensional homotopy group, i.e. the fundamental group of reaction mechanisms, which is the algebraic - topological representation of quantum chemical reaction mechanisms, that retains the most of the conventional mechanistic concepts of chemistry.

In a subsequent study we shall describe some of the chemically important properties of fundamental groups of reaction mechanisms in terms of their generator sets. These generator sets contain certain distinguished reaction mechanisms as elements, which reaction mechanisms will be used for the actual construction of the fundamental groups, and for a detailed analysis of the relations between such groups at various upper bounds for energy.

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References

1. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **62**, 133 (1982); Theoret. Chim. Acta (Berl.) **63**, 9 (1983); J. Chem. Phys., **78**, 6182 (1983), and references therein
2. Mezey, P. G.: Reaction topology: Manifold theory of potential surfaces and quantum chemical synthesis design, in: Chemical applications of topology and graph theory. King, R. B., Ed. Amsterdam: Elsevier, Sci. Publ. Co. 1983
3. Munkres, J.: Elmentary differential topology, Annals of Math. Studies, Vol. 54. Princeton: Univ. Press 1963
4. Spanier, E. H.: Algebraic topology. New York: McGraw-Hill, 1966
5. Morse, M., Cairns, S. S.: Critical point theory in global analysis and differential topology. New York: Academic Press, 1969
6. Guillemin, A., Pollack, A.: Differential topology, Englewood Cliffs: Prentice Hall 1974
7. Mezey, P. G.: Int. J. Quantum Chem. Symp. **17**, 137 (1983)
8. Mezey, P. G.: Int. J. Quantum Chem. Symp. **17**, 453 (1983)
9. Mezey, P. G.: Theoret. Chim. Acta (Berl.) **60**, 97 (1981)

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