Homology of a Structurally Stable Chemical Rearrangement

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The structural stability in the sense of Adronov and Pontriagin is proved to be a property of any rearrangement occurring in a single electronic state sheet of the potential energy surface if such a rearrangement involves two internal degrees of freedom. It is then shown that features of no dynamical significance (the paths of steepest descent joining critical configurations) determine completely those of dynamical significance: The topology of the set of paths of steepest descent determines the triangulation of the nuclear configuration space which is rigorously derived from homology theory.

Key words: Structural stability of dynamical systems – Intrinsic reaction coordinate – 1,3-sigmatropic rearrangement.

1. The Suitable Models are Gradient-Like Morse-Smale Vector Fields on the 2-Sphere (M-S VF's)

We shall consider chemical rearrangements which follow a single electronic state sheet and involve only 2 internal degrees of freedom. Examples of such processes are: 1,3-sigmatropic thermal rearrangements which occur with suprafacial participation of the π-allylic framework and inversion of configuration at the migrating group [1 – 3]; interconversion of Jahn-Teller isomers in the lower energy manifold of the surface when the electronic state degeneracy is lifted by the strong coupling of two degenerate Jahn-Teller modes to the electronic energy [4, 5], etc. Consider the cross section $U = U(\boldsymbol{X})$ where the components X_1, X_2 are tangent at a fixed critical nuclear configuration to two independent vibrational modes respectively. It has been shown that it is always possible to find a domain Ω in the $\boldsymbol{X}$-space so that the region Ω is invariant under the flow of the vector field $\boldsymbol{Y}(\boldsymbol{X}) = -\operatorname{grad}_{\boldsymbol{X}} U$ since the vector field points inwards along the boundary. The only exception to this situation occurs if the potential energy surface is repulsive at the bond dissociation limit [6].

The topology of the set of paths of steepest descent that join critical configurations determines, as we shall prove, the mechanism of the reaction although these paths are by themselves, taken individually, of no dynamical significance [7].

It is not physically meaningful to consider an individual model $\boldsymbol{Y}(\boldsymbol{X})$ for a rearrangement, the reason being the impossibility to uncouple the kinetic energy from the changes in the nuclear configuration. Therefore a suitable model should involve an (open) neighborhood of $\boldsymbol{Y}(\boldsymbol{X})$ in the C^1-norm.

But the set of structurally stable vector fields (the MSVF's) on the domain Ω is *dense and open* in the set of possible smooth models $\boldsymbol{Y}(\boldsymbol{X})$'s [8, 9]. (For related problems of structural stability in chemical kinetics, the reader is referred to (10), (11).)

2. An Indexing Theorem for MSVF's

The description of the Poincaré group $\pi_0(W)$ which gives all the connected (open) components of the set of structurally stable gradient fields of PES's was obtained by this author and Sinanoğlu [8, 12].

Each connected component is associated to an IRCS-graph (intrinsic reaction coordinate and separatrix graph): Each edge of the graph represents an intrinsic reaction coordinate trajectory (IRC) (joining a transition state-saddle point with a stable species configuration represented by a sink vertex) or a separatrix (a steepest descent path which joins a configuration which Hessian matrix has two negative eigenvalues with a saddle point). The IRCS is referred, of course, to a representative of a connected component of W.

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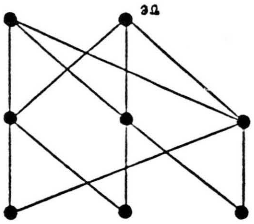

Fig. 1.

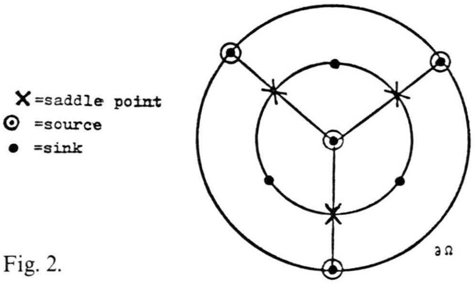

Fig. 2.

$$\begin{tikzcd}
0 \arrow[r] & Z \arrow[r, "i"] \arrow[d, dashed, leftrightarrow, "\psi"'] & C_2^{\mathrm{s}} \arrow[r, "d_2"] \arrow[d, dashed, leftrightarrow, "\psi"'] & C_1^{\mathrm{s}} \arrow[r, "d_1"] \arrow[d, dashed, leftrightarrow, "\psi"'] & C_0^{\mathrm{s}} \arrow[r, "p"] \arrow[d, dashed, leftrightarrow, "\psi"'] & Z \arrow[r] \arrow[d, dashed, leftrightarrow, "\psi"'] & 0 \\
0 & Z \arrow[l] & C_0^{\mathrm{u}} \arrow[l, "p"'] & C_1^{\mathrm{u}} \arrow[l, "d_1"'] & C_2^{\mathrm{u}} \arrow[l, "d_2"'] & Z \arrow[l, "i"'] & 0 \arrow[l]
\end{tikzcd} \tag{1}$$

$$H_1(\Omega, Z) = \frac{\operatorname{Ker} d_1}{\operatorname{Im} d_2} = 0 \, . \tag{2}$$

Fig. 3. Homology sequence for a two-dimensional cross section Ω of the PES involving two internal degrees of freedom.

The following property holds: *every vector field in the same element of* $\pi_0(W)$ *has the same IRCS graph*. Or: *the group* $\pi_0(W)$ *is described by the set of IRCS graphs.*

In Fig. 1, we give the IRCS graph for the connected component of gradient fields on Ω with three stable configurations, three transition states and two configurations one of which is the source $\partial\Omega$ and the other, a critical configuration for which the force constant matrix has two negative eigenvalues (another source). A representative model for gradient field of a PES in this connected component is given in the Figure 2.

Vector fields which are transversal to the boundary of the domain Ω can be also regarded as vector fields of the 2-sphere [13]. This result is useful when one considers the homological relations defined for a connected component of $\pi_0(W)$:

We define the stable manifold of a nuclear configuration $\boldsymbol{a}$ (denoted $M^{\mathrm{s}}(\boldsymbol{a})$) as the set of trajectories in the nuclear configuration space which are tangent at $\boldsymbol{a}$ to the space generated by the stable vibrational degrees of freedom of $\boldsymbol{a}$. Dually, we denote $M^{\mathrm{u}}(\boldsymbol{a})$ the set of trajectories tangent at $\boldsymbol{a}$ to the space of unstable degrees of freedom. For example, if a $\boldsymbol{a}$ represents a transition state, $M^{\mathrm{s}}(\boldsymbol{a})$ is a separatrix and $M^{\mathrm{u}}(\boldsymbol{a})$, an IRC trajectory.

C_2^{s} represents the abelian free group of 2-stable chains [14] that is the abelian free group with generators $M^{\mathrm{s}}(\boldsymbol{a}_j)$, the basins of attraction of all the stable chemical configurations $\boldsymbol{a}_j$'s. Analogously, C_i^{s}, C_i^{u} represent, respectively, the free abelian groups of i-stable and i-unstable chains respectively. For example, C_1^{u} is generated by all the IRC trajectories.

The kernel of the boundary operator d_2: $C_2^{\mathrm{s}} \to C_1^{\mathrm{s}}$ is the free group generated by only one element, the sum of all the stable manifolds. Then its kernel is isomorphic to Z, the additive group of the integers. Analogously, it can be shown that Ker d_2: $C_2^{\mathrm{u}} \to C_1^{\mathrm{u}}$ is isomorphic to Z. Similarly one can show that $C_0^{\mathrm{s}}/\operatorname{Ker} d_1$ is isomorphic to Z and that the same holds in the dual quotient group $C_0^{\mathrm{u}}/\operatorname{Ker} d_1$.

If i represents the natural inclusions i: $Z \to C_2^{\mathrm{s}}$, and the dual i: $Z \to C_2^{\mathrm{u}}$ and p the canonical epimorphism p: $C_0^{\mathrm{s}} \to C_0^{\mathrm{s}}/\operatorname{Ker} d_1$ and the dual p: $C_0^{\mathrm{u}} \to C_0^{\mathrm{u}}/\operatorname{Ker} d_1$, then, the sequence given in the (1) is exact since the first homology group of the 2-sphere vanishes (as expressed in (2)). Moreover, the correspondence $\psi(M^{\mathrm{s}}(\boldsymbol{a})) = M^{\mathrm{u}}(\boldsymbol{a})$ induces the Poincaré duality group isomorphism $H^{2-j} \simeq H_j$ for $j = 0, 1, 2$ [14].

The reaction mechanism is not defined by the pattern of IRC's and the pattern of separatrices but rather by the contiguity and adjacency relations between the basins of attraction of the stable configurations and of the transition states. These relations, however, are determined by the topology of the pattern of IRC's and separatrices which is given by the IRCS graph.

Summarizing, we have the following one-to-one correspondences:

$$\begin{tikzcd}
\text{Reaction mechanism} \arrow[r] & \text{IRCS graph} \arrow[r] & \text{Connected component of } W \arrow[r] & \text{Element of } \pi_0(W)
\end{tikzcd}$$

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