Homology of Potential Energy Surfaces

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Z. Naturforsch. **41 a,** 1118 – 1122 (1986); received February 26, 1986

It is shown that all the adjacency relations for the basins of attraction of stable chemical species and transition states can be derived from the topology of the pattern of intrinsic-reaction-coordinate-and-separatrix trajectories in the nuclear configuration space.

The results are applied to thermal [1, 3] sigmatropic rearrangements and they show that even the symmetry-forbidden path proceeds concertedly. The corresponding homological formulas giving the adjacency relations are derived.

1. Definitions and Motivations

In this work we shall deal with 2-dimensional cross-sections $U = U(\boldsymbol{X})$ $(\boldsymbol{X} = (X_1, X_2))$ of potential energy surfaces (PES's). The X_i-coordinate is tangent to some vibrational mode at a fixed critical nuclear configuration. The structural stability (SS) is a condition which holds for any vector field (VF) $\boldsymbol{Y}(\boldsymbol{X})$ such that the "qualitative" (topological) features of the set of integral curves (tangent at point $\boldsymbol{X}$ to the vector $\boldsymbol{Y}(\boldsymbol{X})$) remain unchanged when $\boldsymbol{Y}(\boldsymbol{X})$ is perturbed by a "sufficiently small" (in the C^1-norm [1]) VF $\boldsymbol{\Theta}(\boldsymbol{X})$ [2, 3]. More precisely, let us assume that we can find a domain $\mathscr{D}$ in the $\boldsymbol{X}$-configuration space such that $\boldsymbol{Y}(\boldsymbol{X})$ points inwards at the boundary $\partial\mathscr{D}$ ($\mathscr{D}$ is $\boldsymbol{Y}$-invariant), then, if $\boldsymbol{Y}$ has SS there exists a number $\delta > 0$ such that for any perturbation $\boldsymbol{\Theta}$ with $\|\boldsymbol{\Theta}\|_1 < \delta$, there exists a homeomorphism (a bijective and bicontinuous map) that maps the trajectories of $\boldsymbol{Y}(\boldsymbol{X})$ onto the trajectories of $(\boldsymbol{Y} + \boldsymbol{\Theta})(\boldsymbol{X})$.

The trajectories are the solutions $\boldsymbol{X}(t)$ of the problem $\dot{\boldsymbol{X}} = \boldsymbol{Y}(\boldsymbol{X})$ and their support set are the integral curves. In what follows, $\boldsymbol{Y}(\boldsymbol{X})$ is taken as $\boldsymbol{Y}(\boldsymbol{X}) = -\operatorname{grad}_{\boldsymbol{X}} U$. The $\boldsymbol{Y}$-invariance of a region $\mathscr{D}$ will be verified later.

We can alternatively state that if $\boldsymbol{Y}(\boldsymbol{X})$ has SS, then there exists a C^1-neighbourhood ($\boldsymbol{Z}(\boldsymbol{X})$ such that $\|\boldsymbol{Z} - \boldsymbol{Y}\|_1 < \delta$), of $\boldsymbol{Y}(\boldsymbol{X})$ such that every $\boldsymbol{Z}(\boldsymbol{X})$ in it has the same topology as $\boldsymbol{Y}(\boldsymbol{X})$.

The analysis of the topology of a model with SS is systematic, however the same cannot be stated when the VF does not enjoy that property [2]. Two questions naturally emerge:

1) Is it possible to approximate any (smooth) gradient field $\boldsymbol{Y}(\boldsymbol{X})$ by a structurally stable one $\boldsymbol{Y}_0(\boldsymbol{X})$ as close as desired?

2) For which domains of a PES and for which electronic state sheets is such an approximation of any physical meaning?

The answer to the first question is affirmative: given a domain $\mathscr{D}$, the set of structurally stable VF leaving $\mathscr{D}$ invariant is dense in the set of all VF's that leave $\mathscr{D}$ invariant [3, 4]. (For technical aspects concerning the smoothness required of the VF's the reader is referred to [3]; it suffices, for the scope of this work, to be able to warrant fourth-order continuous derivatives.) The word dense means, precisely, that in any neighbourhood (with the C^1-norm) of a given VF there is a structurally stable one. The same result is not valid if we are considering higher dimensional cross sections of the PES which involve more than two vibrational degrees of freedom at a given critical configuration.

Since the kinetic energy is always coupled to the nuclear motion relative to the center of mass, it becomes physically irrelevant to consider a fixed gradient field $\boldsymbol{Y}$ *as a model for a chemical rearrangement. The mechanistic-determining features of the PES are not the paths of steepest descent but rather the contiguity relations of the basins of attraction of stable species and transition states. Therefore one should consider a neighbourhood (with* C^1*-norm) of a gradient field. We do not know a priori how big this neighbourhood can be taken but if two internal degrees of freedom are involved in the rearrangement,*

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we know that any such neighbourhood contains a structurally-stable VF $\boldsymbol{Y}_0$. *It is warranted (by definition) that there exists a neighbourhood of* $\boldsymbol{Y}_0$ *such that any VF in it is topologically equivalent to* $\boldsymbol{Y}_0$, *and therefore also structurally stable. Hence, if there is evidence that the course of a thermal process proceeds along the singlet sheet of a PES, it is only possible to model the process with a* C^1*-neighbourhood of a structurally stable vector field (SSVF) whose integral curves are the trajectories in the nuclear configuration space. Since all SSVF's in such a neighbourhood will have the same contiguity relations for the basins of attraction of the species involved, it suffices to take one SSVF.*

2. Intrinsic Reaction Coordinate and Separatrix Graph

The aim is now to show that in a SSVF $\boldsymbol{Y}_0$, the contiguity (or adjacency) relations which give the distribution of the basins of attraction of all the species involved in a chemical process is determined by the topology of a set of integral curves which consists on a few trajectories: the integral curves that join critical configurations [5, 6]. These curves are: a) The path of steepest descent [7] which joins a simple saddle point (a transition state in the PES [8]) with a sink (a minimum in the PES). This is called an intrinsic reaction coordinate trajectory (IRC [9]). b) The path of steepest descent which joins a source (a configuration for which the Hessian-force constant-matrix has two negative eigenvalues) with a saddle point. This is called a separatrix (S) [5, 10, 11], since it separates the basins of attraction of sinks.

The SS condition imposes certain restrictions on VF $\boldsymbol{Y}_0$: a′) *There are no direct saddle-saddle connections by trajectories of* $\boldsymbol{Y}_0$, *or, in other words, the path of steepest descent from a transition state cannot terminate at another transition state.* b′) *There are no critical configurations for which the Hessian matrix is singular* [12].

This author [13, 14] has considered associating to $\boldsymbol{Y}_0$ a graph which represents the way in which the pattern of IRC's and that of S's are coupled: the IRCS graph. (See also work [6, 12] with Sinanoğlu.)

These graphs enjoy the following property: if two VF's $\boldsymbol{Y}_1$ *and* $\boldsymbol{Y}_2$ *have the same IRCS graph, they are topologically equivalent in the sense that the trajectory-preserving map H as defined in the previous section exists.*

The IRCS graphs are build as follows:

Rule I – Each critical configuration is represented by a vertex and each IRC or S, by an edge joining vertices. There are three levels of vertices, one (for instance, the upper level) for sources, one for saddles and one for sinks.

Rule II – $\partial\mathcal{D}$ is considered a source since $\mathcal{D}$ is $\boldsymbol{Y}_0$-invariant (cf. section 1).

Rule III – There are no source-sink edges except for the IRCS graph representing the dissociation of a diatomic molecule.

Rule IV – There are always two incoming and two outgoing edges for every saddle vertex.

Rule V – The IRCS graph has Euler characteristic 2: (# sinks) – (# saddles) + (# sources) = 2.

It is important to keep in mind that given an IRCS graph, the VF $\boldsymbol{Y}_0(\boldsymbol{X})$ can be constructed modulo homeomorphisms H's.

3. Example: A Structurally Stable IRCS Graph for the [1, 3] Sigmatropic Thermal Rearrangements

The rules of symmetry control for thermal [1, 3] sigmatropic rearrangements of the type

$$\begin{tikzcd}[column sep=small] & & \mathbf{SR} & & \\ & \mathbf{1} \arrow[rr, leftrightarrow] \arrow[dr, leftrightarrow] & & \mathbf{2} \arrow[dl, leftrightarrow] & \\ \mathbf{SI} & & \mathbf{3} & & \mathbf{8} \end{tikzcd}$$

(see Fig. 1) required the suprafacial participation of the π-allylic portion of the molecules and the inversion of configuration at the migrating group. (For reviews of these processes, cf. [15] and [16].) The possibility of a biradical transition state alternative for the symmetry-forbidden ($\mathbf{1} \rightleftarrows \mathbf{2}$) path has been invoked [17–19]. *We shall prove that the forbidden pathway also should be concerted. A model in which the forbidden path is not concerted is structurally unstable (since it contains a saddle-saddle connection) and, in view of the density property of the set of SSVF's, should be regarded as an isolated or singular case, it does not represent a mechanism of reaction (cf. Section 1).* This situation could only occur if some steric hindrance prevents the transannular C_2-C_4 orbital interaction destabilizing the "anti-aromatic" transition state **SR**.

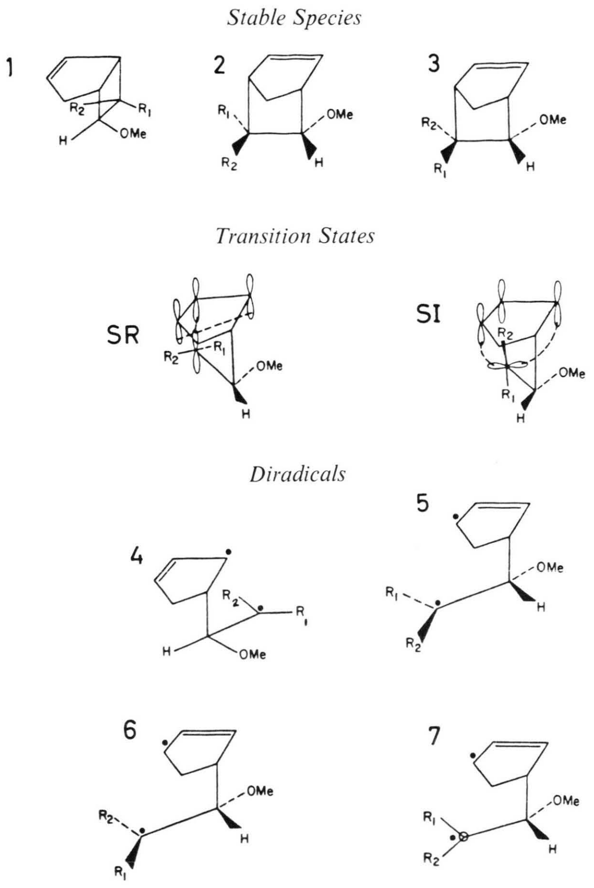

Fig. 1. Critical configurations for the 1,3-sigmatropic rearrangement.

Fig. 2. The IRCS graph.

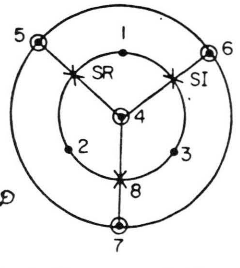

Fig. 3. The vector field realization of the IRCS graph up to homeomorphisms H's.

The generic coordinates X_1, X_2 are defined as tangent at the biradical configuration **4** to the unstable modes leading to the distortions **4** → **SR** and **4** → **SI**, respectively. By pursuing these distortions even further we obtain biradicals **5** and **6**. The calculations indicate [19–21] that the "symmetry forbidden" transition state **SR** is substantially stabilized with respect to the biradical by transannular overlap of the p-orbital of C_4 and the p-orbital of C_2 in the allylic framework.

The only possible IRCS graph with three sinks (**1, 2, 3**), three saddles (**SR, SI, 8**) and two sources (**4**, $\partial\mathscr{D}$) is displayed in Figure 2. We are interested in a realization of this graph (modulo H's) in terms of a SSVF $\boldsymbol{Y}_0(\boldsymbol{X})$. This will be performed in the next section but fully justified in Section 5.

4. The Homology of the Surface is Obtained from the IRCS Graph

Given any critical configuration **a**, we shall denote $M^{\mathrm{s}}(\mathbf{a})$ ($M^{\mathrm{u}}(\mathbf{a})$) the stable (unstable) manifold or set of trajectories which are tangent at **a** to the stable (unstable) vibrational degrees of freedom. Property a′) of a SSVF can be stated as follows: If $\mathbf{a}_1, \mathbf{a}_2$ are two different transition states, then

$$M^{\mathrm{s}}(\mathbf{a}_1) \cap M^{\mathrm{u}}(\mathbf{a}_2) = \emptyset$$

($\cap$ = intersection of sets, $\emptyset \equiv$ empty set).

The M^{s} of any transition state is an S and the M^{u} is an IRC. So the IRCS graph represents the stable and unstable (one-dimensional) manifolds of all the transition states and this suffices to derive the relative distribution of the stable and unstable manifolds of dimensions two, one and zero. This is given by a theorem by Smale [3]: The boundaries of a stable manifold of dimension p are stable manifolds of dimension < p.

Thus, the boundaries of the stable 2-dim. manifold of a stable configuration are the S's (stable 1-dim. manifolds of transition states) and the boundaries of the unstable 2-dim. manifold of a source (like the diradical species **4** in our example) are the IRC's (the unstable 1-dim. manifolds of the transition states).

Figure 3 is the realization modulo H's of the IRCS graph for our example.

In general intuition is a shaky ground for the construction of $\boldsymbol{Y}_0$ starting from the IRCS graph; therefore, in the next section, an algebraic method is developed which formalizes the process of such a construction. The results are tested vis a vis Figure 3. We can see that $\partial\mathcal{D}$ joins the three biradicals **5, 6** and **7** (not three different configurations but conformers of each other). $\mathcal{D}$ is Y_0-invariant. The behaviour of VF's at the boundaries of invariant regions is crucial for the SS problem. (For a related problem in far from equilibrium kinetics and in closed systems the reader is referred to the papers by Fernández and Sinanoğlu [2, 12, 22, 23].)

5. Homological Groups of IRCS Graphs

We now view the manifolds M^{s}, M^{u} as abstract objects and consider the formal expressions of the form

$$\sum_{j=1}^{N} \pm M^{\mathrm{s}}(\mathbf{a}_j) \tag{5a}$$

for critical configurations $\mathbf{a}_j$ such that

$$\dim M^{\mathrm{s}}(\mathbf{a}_i) = \dim M^{\mathrm{s}}(\mathbf{a}_j)_{i,j=1,\ldots,N} \tag{1}$$

or

$$\sum_{j}^{P} \pm M^{\mathrm{u}}(\mathbf{a}_j) \tag{5b}$$

if

$$\dim M^{\mathrm{u}}(\mathbf{a}_i) = \dim M^{\mathrm{u}}(\mathbf{a}_j)_{i,j=1,\ldots,P}\,. \tag{2}$$

We define the *r-stable homology group* H_{s}^{r} $(r=0,1,2)$ as the set of expressions (5a) together with the operation "+" if dim. $M^{\mathrm{s}}(\mathbf{a}_j)=r$. The generators of this free group [21] are the stable manifolds of dimension r: $H_{\mathrm{s}}^{r}=\langle\{M^{\mathrm{s}}(\mathbf{a}_j)\}_j\rangle$ ($\langle\,\rangle \equiv$ generated by). Analogously we define the *r-unstable homology group* H_{u}^{r}. Thus we have

$$H_{\mathrm{u}}^{1}=\langle \text{IRC's}\rangle\,,$$
$$H_{\mathrm{s}}^{1}=\langle \text{S's}\rangle\,. \tag{3}$$

Since the stable manifolds of dimension 2 correspond to the stable configurations, by abuse of notation we can write

$$H_{\mathrm{s}}^{2}\cong\langle \text{stable configurations}\rangle\,, \tag{4}$$

($\cong$ denotes group isomorphism).

Analogously:

$$H_{\mathrm{u}}^{2}\cong\langle \text{sources}\rangle\,, \tag{5}$$

also

$$H_{\mathrm{u}}^{1}\cong H_{\mathrm{s}}^{1}\cong\langle \text{transition states}\rangle \tag{6}$$

and

$$H_{\mathrm{u}}^{2}\cong H_{\mathrm{s}}^{2}\,, \tag{7}$$

$$H_{\mathrm{u}}^{2}\cong H_{\mathrm{s}}^{0}\,. \tag{8}$$

We should now define an orientation in the manifolds in the following way: Taking into account the result by Smale [3] quoted in Sect. 4, we define the boundary operator ∂,

$$\partial_2^{\mathrm{s}}: H_{\mathrm{s}}^{2}\to H_{\mathrm{s}}^{1},\quad \partial_1^{\mathrm{s}}: H_{\mathrm{s}}^{1}\to H_{\mathrm{s}}^{0}\,, \tag{9}$$

$$\partial_2^{\mathrm{u}}: H_{\mathrm{u}}^{2}\to H_{\mathrm{u}}^{1},\quad \partial_1^{\mathrm{u}}: H_{\mathrm{u}}^{1}\to H_{\mathrm{u}}^{0}\,, \tag{10}$$

by first defining an orientation on the manifolds M^{s}, M^{u}: If the separatrix $M^{\mathrm{s}}(\boldsymbol{b})$ for a transition state $\boldsymbol{b}$ is in the boundaries of two different attraction basins of stable species $M^{\mathrm{s}}(\boldsymbol{a}_1)$, $M^{\mathrm{s}}(\boldsymbol{a}_2)$ then

$$\partial_2^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{a}_1)=-\,\partial_2^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{a}_2) \tag{11}$$

and we can arbitrarily choose

$$\partial_2^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{a}_1)=+M^{\mathrm{s}}(\boldsymbol{b})\quad\text{or}\quad \partial_2^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{a}_2)=+M^{\mathrm{s}}(\boldsymbol{b})\,. \tag{12}$$

Analogously, if $M^{\mathrm{u}}(\boldsymbol{b})$ is the IRC which is in the boundary of two unstable manifolds $M^{\mathrm{u}}(\boldsymbol{c}_1)$, $M^{\mathrm{u}}(\boldsymbol{c}_2)$ for two sources $\boldsymbol{c}_1$, $\boldsymbol{c}_2$, then also

$$\partial_2^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{c}_1)=-\,\partial_2^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{c}_2) \tag{13}$$

and

$$\partial_2^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{c}_1)=(+\text{ or }-)\,M^{\mathrm{u}}(\boldsymbol{b})\,. \tag{14}$$

If $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the boundaries of the IRC joining them and passing through the transition state $\boldsymbol{b}$, we have

$$\partial_1^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{b})=(+\text{ or }-)\,(\boldsymbol{a}_2-\boldsymbol{a}_1)\,. \tag{15}$$

If the stable configuration $\boldsymbol{a}$ is in the boundary of two IRC's $M^{\mathrm{u}}(\boldsymbol{b}_1)$, $M^{\mathrm{u}}(\boldsymbol{b}_2)$, then

$$\partial_1^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{b}_1)=-\,\partial_1^{\mathrm{u}}M^{\mathrm{u}}(\boldsymbol{b}_2)\,, \tag{16}$$

and also we have the dual relations

$$\partial_1^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{b})=(+\text{ or }-)\,(\boldsymbol{c}_2-\boldsymbol{c}_1) \tag{17}$$

if $\boldsymbol{c}_2$ and $\boldsymbol{c}_1$ are the boundaries of an S $M^{\mathrm{s}}(\boldsymbol{b})$; and we get

$$\partial_1^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{b}_1)=-\,\partial_1^{\mathrm{s}}M^{\mathrm{s}}(\boldsymbol{b}_2) \tag{18}$$

(if $M^s(\boldsymbol{b}_1)$ and $M^s(\boldsymbol{b}_2)$ share the same boundary). The kernel (Ker) of a group homomorphism $h\colon \sigma_1 \to \sigma_2$ is defined as the set $\{g_1 \in \sigma_1,\ h(g_1) = 0\} = \operatorname{Ker} h$. The image of h is $\operatorname{Im} h = h(\sigma_1)$. A sequence $\sigma_1 \xrightarrow{h} \sigma_2 \xrightarrow{f} \sigma_3$ is called exact if $\operatorname{Im} h = \operatorname{Ker} f$ (cf. [24]). In view of the relations (6)–(18) we can state the following:

Theorem: the sequence given by (19) is exact.

$$\begin{gathered}
0 \to A_{\mathrm{u}} \xrightarrow{i_{\mathrm{u}}} H^2_{\mathrm{u}} \xrightarrow{\partial^{\mathrm{u}}_2} H^1_{\mathrm{u}} = \langle \text{IRC's} \rangle \xrightarrow{\partial^{\mathrm{u}}_1} H^0_{\mathrm{u}} \xrightarrow{\pi_{\mathrm{u}}} H^0_{\mathrm{u}}/B_{\mathrm{s}} \to 0\,, \\
0 \leftarrow H^0_{\mathrm{s}}/B_{\mathrm{u}} \underset{\pi_{\mathrm{s}}}{\leftarrow} H^0_{\mathrm{s}} \underset{\partial^{\mathrm{s}}_1}{\leftarrow} H^1_{\mathrm{s}} = \langle \text{S's} \rangle \underset{\partial^{\mathrm{s}}_2}{\leftarrow} H^2_{\mathrm{s}} \underset{i_{\mathrm{s}}}{\leftarrow} A_{\mathrm{s}} \leftarrow 0\,,
\end{gathered} \tag{19}$$

where

$$A_{\mathrm{u}} = \Big\langle \sum_{\boldsymbol{C}_i \text{ all u.c.}} \boldsymbol{C}_i \Big\rangle, \quad \begin{aligned} &\text{u.c.} = \text{unstable configurations} \\ &\text{s.c.} = \text{stable configurations}\,, \end{aligned} \tag{20}$$

$$B_{\mathrm{u}} = \Big\langle \{\boldsymbol{C} - \boldsymbol{C}_i\}_{\substack{\boldsymbol{C},\ \text{u.c.} \\ \boldsymbol{C}_i,\ \text{all u.c.}}} \Big\rangle\,, \tag{21}$$

$$A_{\mathrm{s}} = \Big\langle \sum_{\boldsymbol{a}_j \text{ all s.c.}} \boldsymbol{a}_j \Big\rangle\,, \tag{22}$$

$$B_{\mathrm{s}} = \Big\langle \{\boldsymbol{a} - \boldsymbol{a}_j\}_{\substack{\boldsymbol{a},\ \text{s.c.} \\ \boldsymbol{a}_j,\ \text{all s.c.}}} \Big\rangle\,. \tag{23}$$

i_{u}, i_{s} are the injection maps for the subgroups A_{u}, A_{s} of the groups H^2_{u}, H^2_{s}, respectively.

$$\operatorname{Im} i_{\mathrm{u}} = A_{\mathrm{u}}\,; \qquad \operatorname{Im} i_{\mathrm{s}} = A_{\mathrm{s}}\,. \tag{24}$$

π_{u}, π_{s} are the canonical maps of H^0_{u} and H^0_{s} onto the quotient groups $H^0_{\mathrm{u}}/B_{\mathrm{s}}$, $H^0_{\mathrm{s}}/B_{\mathrm{u}}$.

$$\operatorname{Ker} \pi_{\mathrm{u}} = B_{\mathrm{s}}\,, \qquad \operatorname{Ker} \pi_{\mathrm{s}} = B_{\mathrm{u}}\,. \tag{25}$$

The groups A_{s}, A_{u}, $H^0_{\mathrm{u}}/B_{\mathrm{s}}$, $H^0_{\mathrm{s}}/B_{\mathrm{u}}$ are generated by a single element, and therefore they are isomorphic to Z (the additive group of the integers). The isomorphisms $H^{2-p}_{\mathrm{u}} \cong H^p_{\mathrm{s}}$, $p = 0, 1, 2$ form the Poincaré duality [3].

The exact sequence for the thermal rearrangement of our example follows:

$$\begin{gathered}
0 \to Z \to \langle \mathbf{4}, \partial\mathscr{D} \rangle \to \left\langle \begin{matrix} \text{IRC}\,(\mathbf{1\text{-}SR\text{-}2}), \\ \text{IRC}\,(\mathbf{1\text{-}SI\text{-}3}), \\ \text{IRC}\,(\mathbf{2\text{-}8\text{-}3}) \end{matrix} \right\rangle \to \\
\to \langle \mathbf{1}, \mathbf{2}, \mathbf{3} \rangle \to Z \to 0\,, \\
\leftarrow \langle \mathbf{1}, \mathbf{2}, \mathbf{3} \rangle \leftarrow Z \leftarrow 0\,. \\
0 \leftarrow Z \leftarrow \langle \mathbf{4}, \partial\mathscr{D} \rangle \leftarrow \left\langle \begin{matrix} \text{S}\,(\partial\mathscr{D}\text{-}\mathbf{SI\text{-}4}), \\ \text{S}\,(\partial\mathscr{D}\text{-}\mathbf{SR\text{-}4}), \\ \text{S}\,(\partial\mathscr{D}\text{-}\mathbf{8\text{-}4}) \end{matrix} \right\rangle \leftarrow
\end{gathered} \tag{26}$$

This sequence defines all the homological relations that formalized the process of construction of our VF $\boldsymbol{Y}_0$ given in Fig. 3 from the IRCS graph obtained a priori in Figure 2. Several applications of this exact sequence techniques are presently being accomplished and will appear in forthcoming papers.

[1] The C^1-norm is defined as follows:

$$\|\boldsymbol{Y}\|_1 = \sup_{\substack{\boldsymbol{X} \text{ in } \mathscr{D} \\ j = 1, 2}} \left(\|\boldsymbol{Y}(\boldsymbol{X})\|,\ \left\| \frac{\partial \boldsymbol{Y}}{\partial \boldsymbol{X}_j}(\boldsymbol{X}) \right\| \right).$$

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