

Triangulation of the Lowest Energy Sheet for Jahn-Teller Potential Energy Surfaces

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The topology of the lower energy sheet for the Potential Energy Surface corresponding to the dynamic Jahn-Teller effect is obtained by means of homological techniques.

Key words: Structurally – stable dynamical system – Jahn-Teller effect.

1. Introduction

When the stabilization energy corresponding to a Jahn-Teller distortion is much smaller than the zero point energy of the associated vibrational mode there is a continual dynamical interconversion of the distorted isomers [1]. The breakdown of the Born-Oppenheimer approximation implies that the paths of steepest descent in the lowest energy sheet of the potential energy surface (LPES) $U = U(X)$ are not the features of dynamical significance (see for example, Pechukas [2]). However, we shall prove that the pattern of paths of steepest descent determines uniquely those topological features of the LPES which are dynamically relevant. That is, it defines adjacency or contiguity relations for the basins of attraction of the Jahn-Teller stable isomers and of the saddles that surround the symmetric critical configuration (the undistorted arrangement).

A well known example of this dynamic effect is the $C_6H_6^+$ ion (with an odd number of π -electrons) in its ground state [3]. The relative distribution of the basins of attraction in the LPES is preserved under small perturbations if the model for the LPES is structurally stable in the sense of Adronov and Pontriagin [4, 5]. This restriction then guarantees the permanence of the adjacency relations. Its validity will be proven in the next section. Two kinds of paths of steepest descent need to be considered: those trajectories in the X -space which join the symmetric critical configuration to the saddle points (the separatrices) and the intrinsic reaction coordi-

nate curves (IRC's) which were formally defined by Fukui [6]; these last ones join saddles to minima. A convenient representation of the pattern of paths of steepest descent is the IRCS graph [7–10]. Each vertex represents a critical configuration and each edge, a path of steepest descent. This device allows one to calculate the possible a priori patterns from certain input data:

a) The number of critical configurations with two, one and zero unstable degrees of freedom (saddles of index 2, 1 and minima of $U(X)$ respectively).

b) The specification of those critical configurations to which the saddles of index 2 decay without activation energy. This essentially means that given a pattern of separatrices, the possible associated patterns of IRC's are determined by the possible IRCS graphs.

2. Triangulation of the Surface Determined by the IRCS Graph

We shall apply the structural stability restriction to the LPES of the $C_6H_6^+$ ion to illustrate the technique. In this case, a degenerate vibration with e_{2g} symmetry and zero point energy of approximately 800 cm^{-1} (cf. [1] and [11]) constantly overcomes the barriers for the interconversion of the Jahn-Teller isomers. The X -space giving the cross-section of interest is therefore the Q_A, Q_B -cross-section. Q_A, Q_B are the Jahn-Teller distortion coordinates corresponding to the two components of the e_{2g} symmetry coordinate S_8 for carbon-carbon bond stretching modes. Let X_0 denote the configuration with degenerate ground state and $Y(X) = -\text{gradient } U_x$.

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There exists a region \mathcal{D} containing X_0 in the X -space such that $Y(X)$ points inwards at the boundary $\partial\mathcal{D}$. That is so since $U(X)$ tends asymptotically and from below to the bond dissociation limits as $\|X - X_0\| \rightarrow \infty$. (For details, the reader is referred to [7–10].)

The structural stability restriction can be now properly stated as follows: there exists $\delta > 0$ such that for any perturbation Ω of Y which obeys:

$$\|\Omega\|_1 = \sup_{X \in \mathcal{D}, j} \left(\|\Omega(X)\|, \left\| \frac{\partial \Omega}{\partial X_j}(X) \right\| \right) < \delta$$

there exists a homeomorphism $H: \mathcal{D} \rightarrow \mathcal{D}$ (a bijective and bicontinuous map) such that H maps trajectories of $Y(X)$ onto trajectories of $Y(X) + \Omega(X)$.

The structural stability restriction implies that there are no direct connections between saddles of index 1 given by trajectories of $Y(X)$ [7, 12]. The following property holds: if Y_1 and Y_2 are structurally stable and they have isomorphic IRCS graphs, they are topologically equivalent in the sense that the trajectory-preserving homeomorphism H exists (see Peixoto, [12]).

To build the corresponding IRCS graph for our example, we first notice that it should contain three sinks which correspond to the three stable $J-T$ isomers **1**, **2** and **3** [1, 11]. The interconversion of these species and the separation of their basins of attraction requires three saddles (denoted a_1, a_2, a_3) and from the structural stability restriction, X_0 cannot correspond to a classical transition state (a saddle of index 1, see Murrell and Laidler [13]), but it should be a source (saddle of index 2) in \mathcal{D} . This being so since X_0 is directly connected to the saddles and it lies higher in energy than them.

The IRCS graphs are derived following seven rules:

I) There are three levels of vertices: on four sources, one for classical transition states and one for sinks (minima in $U(X)$).

II) an IRC is represented by an edge from a saddle vertex to a sink vertex.

III) A separatrix is represented by an edge from a source to a saddle.

IV) There are no source-sink edges except for the case of a diatomic molecule.

V) The boundary $\partial\mathcal{D}$ is regarded as a source.

VI) There are exactly two incoming and two outgoing edges for every saddle vertex.

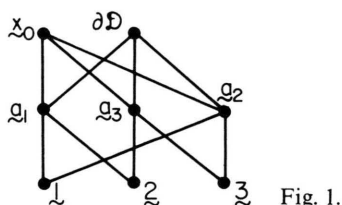


Fig. 1.

VII) The IRCS graph has Euler characteristic 2: $\# \text{sources} - \# \text{saddles} + \# \text{sinks} = 2$. The only possible IRCS graph for our example is displayed in Figure 1.

To discuss in detail the triangulation that it defines in the nuclear configuration space, we need to introduce the following definitions.

A stable (unstable) manifold of a critical configuration a : $M^s(a)$ ($M^u(a)$) is the set of trajectories of $Y(X)$ tangent at a to the space generated by the stable (unstable) vibrational degrees of freedom.

The physical meaning of these manifolds for critical configurations follows:

$$M^s(a_j) = \text{Separatrix} [\partial\mathcal{D} \rightarrow a_j \leftarrow X_0];$$

$$j = 1, 2, 3. \quad (1)$$

$$M^u(a_1) = \text{IRC} [1 \leftarrow a_1 \rightarrow 2],$$

$$M^u(a_2) = \text{IRC} [1 \leftarrow a_2 \rightarrow 3],$$

$$M^u(a_3) = \text{IRC} [2 \leftarrow a_3 \rightarrow 3]. \quad (2)$$

$$M^s(X_0) = \{X_0\}, \quad M^s(\partial\mathcal{D}) = \{\partial\mathcal{D}\}. \quad (3)$$

$$M^u(i) = \{i\}; \quad i = 1, 2, 3. \quad (4)$$

A result by Smale (14) ensures that, for structurally stable vector fields, the boundary of a stable manifold of dimension p is the union of stable manifolds of dimension $< p$. Thus,

$$\partial M^s(1) = M^s(a_1) \cup M^s(a_2) \cup \{X_0\} \cup \{\partial\mathcal{D}\}$$

$$= \text{Separatrix} [\partial\mathcal{D} \rightarrow a_1 \leftarrow X_0 \rightarrow a_2 \leftarrow \partial\mathcal{D}], \quad (5)$$

$$\partial M^s(2) = M^s(a_1) \cup M^s(a_3) \cup \{X_0\} \cup \{\partial\mathcal{D}\}$$

$$= \text{Separatrix} [\partial\mathcal{D} \rightarrow a_1 \leftarrow X_0 \rightarrow a_3 \leftarrow \partial\mathcal{D}], \quad (6)$$

$$\partial M^s(3) = M^s(a_2) \cup M^s(a_3) \cup \{X_0\} \cup \{\partial\mathcal{D}\}$$

$$= \text{Separatrix} [\partial\mathcal{D} \rightarrow a_2 \leftarrow X_0 \rightarrow a_3 \leftarrow \partial\mathcal{D}], \quad (7)$$

$$\partial M^s(a_j) = \{X_0\} \cup \{\partial\mathcal{D}\}; \quad j = 1, 2, 3. \quad (8)$$

As we have shown, the application of the boundary operator ∂ to a stable manifold gives a sum of stable manifolds of lower dimension. Dually, the following

relations hold:

$$\partial: \left(\begin{array}{c} \text{unstable} \\ 2\text{-homology} \end{array} \right) \rightarrow \left(\begin{array}{c} \text{unstable} \\ 1\text{-homology} \end{array} \right)$$

and $\partial: \left(\begin{array}{c} \text{unstable} \\ 1\text{-homology} \end{array} \right) \rightarrow \left(\begin{array}{c} \text{unstable} \\ 0\text{-homology} \end{array} \right).$

(Here we will understand by i -homology the collection of i -dimensional faces)

$$\partial M^u(X_0) = \bigcup_{j=1}^3 M^u(a_j) \cup \bigcup_{i=1}^3 U\{i\} = \text{IRC} [1 \leftrightarrow 2 \leftrightarrow 3]. \quad (9)$$

Equation (9) tells us literally that *the intrinsic reaction coordinate trajectory for the interconversion of the three Jahn-Teller isomers 1, 2, 3, determines the boundary of the unstable manifold of the totally symmetric configuration X_0 .*

$$\partial M^u(a_1) = \{1\} \cup \{2\}, \quad (10)$$

$$\partial M^u(a_2) = \{1\} \cup \{3\}, \quad (11)$$

$$\partial M^u(a_3) = \{2\} \cup \{3\}. \quad (12)$$

Still another more convenient way of stating the structural stability condition is: *The stable manifold of a transition state a_i cannot be a piece of the unstable manifold of another transition state a_j .*

$$M^s(a_i) \cap M^u(a_j) = \emptyset \quad \text{if } i \neq j. \quad (13)$$

To test the validity of the structural stability assumption, we first notice that from the relations

(5)–(13), the sets $\{M^s(b)\}_b$, $\{M^u(b)\}_b$ (where b runs over all critical configurations) determine two triangulations of the $Q_A - Q_B$ cross section.

Hence, the following Euler-Poincaré relations [4, 14] are valid:

$$(\# \text{ 2-dimensional faces}) - (\# \text{ 1-dimensional faces}) + (\# \text{ 0-dimensional faces}) = 2, \quad (14)$$

$$\begin{aligned} &(\# \text{ stable 2-dimensional manifolds}) \\ &- (\# \text{ stable 1-dimensional manifolds}) \\ &+ (\# \text{ stable 0-dimensional manifolds}) = 2, \end{aligned} \quad (15)$$

$$\begin{aligned} &(\# \text{ stable chemical species}) - (\# \text{ transition states}) \\ &+ (\# \text{ sources}) = 2. \end{aligned} \quad (16)$$

This is in agreement with the classical picture of Liehr [11] in which each of the three displacements leads to a minimum and a conjugated transition state and the interconversion of the three $J - T$ isomers occurs via these transition states. At the bottom of the LPES there are three wells and three humps. Moreover, our technique shows how to couple the pattern of IRC's to the given separatrix framework.

A dual relation with unstable manifolds equivalent to (15) can be written. Formula (16) is obviously valid since the l.h.s. of the equality is the Euler-Poincaré characteristic of the IRCS graph.

The application of the IRCS graph technique provides a rigorous derivation of the topology of the PES given by relations (5), (6), (7) and (9).

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