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Isostationary functions for multimode and multilevel Jahn–Teller systems

A. Ceulemans, L.F. Chibotaru*

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium, FAX 32-16-327992

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Summary. The method of isostationary functions, first introduced for linear Jahn–Teller problems within a single electronic term, is generalized to multimode and multilevel problems. Analytic expressions are obtained for the case of linear vibronic coupling of a general form, including both simply and non-simply reducible groups. It is shown that the static multimode Jahn–Teller problem for non-simply reducible groups can always be reduced to an ideal single-mode problem.

Key words: Jahn–Teller effect – Potential energy surface

1 Introduction

The method of the isostationary function [1] provides a suitable tool for investigating the topology of the potential energy surface in the vicinity of a Jahn–Teller (JT) instability [2]. In this method the usual representation of the surface in the space of nuclear configurations is mapped onto a projective representation in the space of electronic functions. In this space the isostationary function is defined as a very simple analytic function which has the same stationary structure as the JT potential. It thus allows to derive exactly all extremal points of the actual energy surface, and forms the key to understanding the deep symmetry grounds of the JT topology, as expressed in the epikernel principle [1, 3].

Originally the method was derived for linear JT problems and successfully applied to the cases of fourfold and fivefold orbital degeneracies in icosahedral molecules [4, 5]. In the present paper two further results of a more general nature are reported. In Sect. 2 it is shown that the method of the isostationary function also holds for the more general Hamiltonian, which extends over a manifold of electronic states and contains second-order terms and multimode coupling. In Sect. 3 explicit expressions for the isostationary function are obtained in the most important particular case of linear vibronic coupling of general form, including both simply and non-simply reducible groups. It is shown that the static multimode

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* On leave of the Institute of Chemistry, Academy of Sciences, Kishinev, Moldova

Jahn–Teller problem for non-simply reducible groups can be reduced to a single-mode problem, exactly as in the case of simply reducible groups [2, 6]. In Sect. 4 these results are briefly discussed in the perspective of vibronic instabilities in the excited and ionic forms of C_{60}, where the Jahn–Teller effects are essentially multimode and extend over several quasi-degenerate states [7–17].

2 Generalization of the isostationary functions

Consider the general case of vibronic coupling, described by the following Hamiltonian:

$$H = \sum_i \varepsilon_i C^i_{A_1} + \frac{1}{2} \sum_{\mu\Gamma\gamma} K_{\mu\gamma} Q^2_{\mu\Gamma\gamma} + H^{(1)} + H^{(2)}, \tag{1}$$

where the first term describes the energies of the electronic states, the second term is the elastic energy of the vibrations, and the last two terms are contributions of the first- (linear) and second-order vibronic coupling. The linear coupling part may be expressed explicitly as follows:

$$H^{(1)} = \sum_{\mu\Gamma\gamma} \sum_{aij} V^{aij}_{\mu\Gamma} C^{aij}_{\Gamma\gamma} Q_{\mu\Gamma\gamma}. \tag{2}$$

The index μ counts repeated irreducible representations Γ of the vibrational modes. The linear coupling constants V are reduced matrix elements that link electronic levels i and j, characterized by corresponding irreducible representations Γ_i and Γ_j, under vibronic coupling to the $\mu\Gamma$ mode. They are independent of the mode component γ. Finally C's denote electronic operators in the space of electronic states. Their matrix elements correspond to Clebsch–Gordan coefficients for the appropriate symmetry group [18–20]:

$$\langle \Gamma_i\gamma_i | C^{aij}_{\Gamma\gamma} | \Gamma_j\gamma_j \rangle = \langle \Gamma_i\gamma_i | \Gamma\gamma\Gamma_j\gamma_j \rangle^a, \tag{3}$$

where γ_i, γ_j are components of the corresponding irreducible representations Γ_i, Γ_j. The superscript a in the above equations denotes repeating representations in the product $\Gamma_i \times \Gamma_j$ and can be dropped for simply reducible groups. The short notation $C^i_{A_1}$ stands for the unity operator, defined in the electronic space of the term Γ_i.

The extremal points of the energy surfaces, which are eigenvalues of the Hamiltonian (1), can be found as solutions of the Oepik and Pryce equations [21]:

$$\langle \Psi | \frac{\partial H(\{Q_{\mu\Gamma\gamma}\})}{\partial Q_{\mu\Gamma\gamma}} | \Psi \rangle = 0, \tag{4a}$$

$$H(\{Q^{(0)}_{\mu\Gamma\gamma}\}) | \Psi \rangle = E(\{Q^{(0)}_{\mu\Gamma\gamma}\}) | \Psi \rangle, \tag{4b}$$

$$\langle \Psi | \Psi \rangle = 1, \tag{4c}$$

where $|\Psi\rangle$ is a column vector describing the eigenfunction in the basis of electronic states, $|\Gamma_i\gamma_i\rangle$:

$$|\Psi\rangle = \sum_i \sum_{\gamma_i} x^i_{\gamma_i} | \Gamma_i\gamma_i \rangle. \tag{5}$$

From Eq. (4a) the values of nuclear coordinates in the extremal points, $Q^{(0)}_{\mu\Gamma\gamma}$, can be expressed as functions of the electronic space coordinates, $\{x^i_{\gamma_i}\}$. Upon substitution in Eq. (4b) one then obtains a system of non-linear equations in the x coefficients, subject to the normalization condition of Eq. (4c). The solution of this system yields the extremal configurations and hence the extremal points of the energy surface. In a further development the Oepik and Pryce conditions may be identified as the extrema conditions for a function in electronic space. This function simply corresponds to the average of H over $|\Psi\rangle$ in the extremal points:

$$\langle H\rangle^{(0)} = \sum_{ij}\sum_{\gamma_i\gamma_j} x^i_{\gamma_i} x^j_{\gamma_j} \langle \Gamma_i\gamma_i | H(\{Q^{(0)}_{\mu\Gamma\gamma}\}) | \Gamma_j\gamma_j\rangle, \tag{6}$$

where a real electronic basis was supposed and $Q^{(0)}_{\mu\Gamma\gamma}$ are conceived as functions of unknown parameters $x^i_{\gamma_i}$. In [1] it was shown that the minimization of $\langle H\rangle^{(0)}$ in the space of electronic functions indeed generates the Oepik and Pryce conditions in Eq. (3). The function thus has the same stationary structure as the adiabatic potential in Q-space, and is therefore denoted as the *isostationary* function. However the proof in [1] was limited to the simple case of a linear Jahn–Teller problem associated with a single electronic term. We now proceed with a more general proof adapted to the arbitrary Hamiltonian in Eq. (1). To show the isostationary nature of $\langle H\rangle^{(0)}$ we first minimize the following expression,

$$\langle H\rangle^{(0)} - \lambda\sum_{i}\sum_{\gamma_i}(x^i_{\gamma_i})^2, \tag{7}$$

with respect to the coordinates x. The first term in Eq. (7) corresponds to the function (6), derived for the Hamiltonian (1). The second term was added in order to satisfy the normalization condition for the electronic function; λ is the corresponding Lagrange multiplier. Minimization of Eq. (7) leads to the following set of equations:

$$\sum_{j\gamma_j} x^j_{\gamma_j}\langle\Gamma_k\gamma_k|H(\{Q^{(0)}_{\mu\Gamma\gamma}\})|\Gamma_j\gamma_j\rangle + \frac{1}{2}\sum_{ij}\sum_{\gamma_i\gamma_j} x^i_{\gamma_i}x^j_{\gamma_j}\left\langle\Gamma_i\gamma_i\left|\frac{\partial H(\{Q^{(0)}_{\mu\Gamma\gamma}\})}{\partial x^k_{\gamma_k}}\right|\Gamma_j\gamma_j\right\rangle - \lambda x^k_{\gamma_k} = 0, \tag{8}$$

where k runs through the entire electronic manifold. In deriving this result use was made of the hermiticity of the Hamiltonian. The second term on the left-hand side of Eq. (8) can be presented as follows:

$$\sum_{\mu\Gamma\gamma}\left[\sum_{ij}\sum_{\gamma_i\gamma_j} x^i_{\gamma_i}x^j_{\gamma_j}\left\langle\Gamma_i\gamma_i\left|\frac{\partial H(\{Q_{\mu\Gamma\gamma}\})}{\partial Q_{\mu\Gamma\gamma}}\right|\Gamma_j\gamma_j\right\rangle\right]^{(0)}\frac{\partial Q^{(0)}_{\mu\Gamma\gamma}}{\partial x^k_{\gamma_k}}. \tag{9}$$

The expression contained within the brackets in Eq. (9) is nothing but

$$\left\langle\Psi\left|\frac{\partial H(\{Q_{\mu\Gamma\gamma}\})}{\partial Q_{\mu\Gamma\gamma}}\right|\Psi\right\rangle,$$

which vanishes in the extremal points in conformity with Eq. (4a). Accordingly, Eq. (8) becomes

$$\sum_{j\gamma_j} x^j_{\gamma_j}\langle\Gamma_k\gamma_k|H(\{Q^{(0)}_{\mu\Gamma\gamma}\})|\Gamma_j\gamma_j\rangle = \lambda x^k_{\gamma k}, \tag{10}$$

which coincides with Eq. (4b).

This completes the proof that the minimization of the expression (7) is consistent with the Oepik and Pryce equations (4). We thus have shown that the isostationary function also is defined in the case of a more general vibronic Hamiltonian, involving non-linear and multimode coupling over several electronic states. The analytic form of this function can be obtained by solving the system of equations (4a) with respect to $Q^{(0)}_{\mu\Gamma\gamma}$. For the Hamiltonian (1) these equations are always linear. In the absence of second-order coupling this system can easily be solved to yield simple expressions in the coordinates x. A further examination of this simplified case is presented in the next section.

3 Multimode and multiterm linear vibronic coupling

By dropping the $H^{(2)}$ term, Eq. (1) reduces to the linear JT Hamiltonian in a multimode and multiterm system. To obtain the isostationary function in this case, we first derive the stationary coordinate expressions, using Eq. (4a).

$$Q^{(0)}_{\mu\Gamma\gamma} = -\sum_{aij}\sum_{\gamma_i\gamma_j}\frac{V^{aij}_{\mu\Gamma}}{K_{\mu\Gamma}}\,x^i_{\gamma_i}x^j_{\gamma_j}\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle^a. \tag{11}$$

By inserting these coordinates in Eq. (6), the isostationary function is obtained at once:

$$\langle H\rangle^{(0)} = \sum_i \varepsilon_i R^{ii}_{A_1} - \frac{1}{2}\sum_{\Gamma}\sum_{aij}\sum_{blm}\left[\sum_{\mu}\frac{V^{aij}_{\mu\Gamma}V^{blm}_{\mu\Gamma}}{K_{\mu\Gamma}}\right]\sum_{\gamma}R^{aij}_{\Gamma\gamma}R^{blm}_{\Gamma\gamma}, \tag{12}$$

where the R coefficients denote tensors in electronic space:

$$R^{aij}_{\Gamma\gamma} = \sum_{\gamma_i\gamma_j}x^i_{\gamma_i}x^j_{\gamma_j}\langle\Gamma_i\gamma_i|\Gamma\gamma\Gamma_j\gamma_j\rangle^a. \tag{13}$$

Equation (12) is a generalization over the multimode and multilevel case of the isostationary function introduced in Ref. [1]. The expressions $R^{aij}_{\Gamma\gamma}$ are bilinear combinations of x coordinates, transforming as irreducible representations Γ under symmetry transformations of the point group. By summing over γ in Eq. (12) one realizes a totally symmetric convolution of these functions. This confirms that the isostationary function is an invariant of the point group.

The result further indicates that the multimode aspect of the Hamiltonian does not really represent a complication, since the individual mode contributions are absorbed by an inner sum over μ. This is not surprising since the isostationary function represents a projection in electronic function space and therefore integrates the coupling strengths of the individual modes.

In the space of normal coordinates the situation is less straightforward. For the case of a single electronic term in a group with no product multiplicities it is known that the coordinate space can be divided into one interacting mode of each symmetry type and a remainder space of non-JT coordinates. Hence in this case the multimode effect essentially reduces to the ideal JT effect, at least as far as the adiabatic surface is concerned. In general though such a simplification will no longer be possible.

To illustrate this, we first pass to frequency-weighted nuclear coordinates, following Toyozawa and Inoue [22].

$$q_{\mu\Gamma\gamma} = \sqrt{K_{\mu\Gamma}}\,Q_{\mu\Gamma\gamma}. \tag{14}$$

In this way the harmonic energy operator in Eq. (1) is transformed to an isotropic form. A further coordinate transformation is now introduced in the frequency-weighted vibrational space of each symmetry type Γ:

$$q_{\Gamma\gamma}^{aij} = \frac{1}{F_{\Gamma}^{aij}} \sum_{\mu} \frac{V_{\mu\Gamma}^{aij}}{\sqrt{K_{\mu\Gamma}}} q_{\mu\Gamma\gamma}. \tag{15}$$

The normalization coefficients in Eq. (15), F_{Γ}^{aij}, are given by the following equation,

$$F_{\Gamma}^{aij} = \left[\sum_{\mu} (V_{\mu\Gamma}^{aij})^2 / K_{\mu\Gamma} \right]^{1/2}, \tag{16}$$

and represent effective linear vibronic constants in the frequency-weighted space, corresponding to the a-type coupling of the terms Γ_i and Γ_j by the vibrations $q_{\mu\Gamma\gamma}$. Hence each different scheme $\Gamma_i \times \Gamma_j$ that can be realized in the multilevel manifold will give rise to a set of effective coordinates spanning the entire $\Gamma_i \times \Gamma_j$ product representation. In principle the number of effective modes of type Γ will thus be equal to the number of times Γ occurs in the symmetrized direct product of the reducible representation of the total manifold. However all these effective modes need not be orthogonal to each other. In fact their mutual overlap is easily calculated:

$$S_{aij}^{blm}(\Gamma) \equiv \langle q_{\Gamma\gamma}^{aij} | q_{\Gamma\gamma}^{blm} \rangle = \frac{1}{F_{\Gamma}^{aij} F_{\Gamma}^{blm}} \sum_{\mu} V_{\mu\Gamma}^{aij} V_{\mu\Gamma}^{blm} / K_{\mu\Gamma}. \tag{17}$$

As a result it may well be possible to project out a number of inactive modes by applying unitary transformations within subspaces of all modes of a given symmetry type according to standard procedures. In this way one can obtain an effective vibronic Hamiltonian with a minimal number of active modes. We have to accept though that – unlike in the case of a single level in a simple reducible group – this number may be larger than one per allowed symmetry representation. In the next section this will be illustrated for the case of a single level system in a non-simply reducible group.

4 Examples

Buckminsterfullerene is characterized by a fivefold degenerate HOMO transforming as the H_u representation in the icosahedral point group. The LUMO and next-LUMO are both threefold degenerate and transform respectively as T_{1u} and T_{1g} [10]. These high degeneracies give rise to several new and interesting JT problems. The cationic ground state, C_{60}^{+}, exemplifies the multimode $^2H_u \times (2a_g + 6g_g + 8h_g)$ system, which has a product multiplicity in the h_g modes. The anionic ground state, C_{60}^{-}, should in principle be described by a multimode multilevel system of the type $(^2T_{1u} + {}^2T_{1g}) \times (2a_g + 8h_g + a_u + 4t_{1u} + 7h_u)$. Finally vibronic interactions in the excited state of the neutral molecule are even more involved since they combine the cationic and anionic instabilities. All these problems are at the focus of intense research activity [7–17], and the isostationary function method in its multimode and multilevel form proves to be a powerful tool to explore the topology of these complicated JT surfaces. As an example, in a recent paper we have analysed the $^2T_{1u} + {}^2T_{1g}$ problem of the fulleride C_{60}^{-}, using precisely the functional expressions of Eq. (12) [23]. It was found that this problem may exhibit high symmetries that can be described by generalized rotation groups.

Here we will briefly investigate the multimode $H \times (nh)$ problem as an example of the use of the isostationary function in a non-simply reducible group under multimode coupling.

Since the h representation appears twice in the $H \times H$ product there are two effective $q^{aij}_{\Gamma\gamma}$ sets in the frequency-weighted vibrational space, which we will denote as $q^a_{H\gamma}$ and $q^b_{H\gamma}$. Their overlap is given by

$$S^b_a(H) = \frac{1}{F^a_H F^b_H} \sum_{\mu=1}^{n} V^a_{\mu H} V^b_{\mu H} / K_{\mu H}. \tag{18}$$

In all these symbols we have omitted the repeating $H \times H$ upper indices. In the space of h modes we can now carry out a unitary transformation to $\tilde{q}$ coordinates, as defined below:

$$\tilde{q}_{\nu H\gamma} = \sum_{\mu=1}^{n} c^H_{\nu\mu} q_{\mu H\gamma}. \tag{19}$$

Let the effective coordinates $q^a_{H\gamma}$ and $q^b_{H\gamma}$ be described by unit vectors $\tilde{q}_{1H\gamma}$ and $\tilde{q}_{2H\gamma}$, i.e.

$$\begin{aligned} q^a_{H\gamma} &= \cos\alpha\, \tilde{q}_{1H\gamma} + \sin\alpha\, \tilde{q}_{2H\gamma} \\ q^b_{H\gamma} &= \cos\beta\, \tilde{q}_{1H\gamma} + \sin\beta\, \tilde{q}_{2H\gamma}, \end{aligned} \tag{20}$$

where the direction cosines are largely arbitrary except for the requirement

$$\cos(\alpha - \beta) = S^b_a(H).$$

The vibronic Hamiltonian may then be expressed as follows:

$$\begin{aligned} H = {} & \frac{1}{2} \sum_{\gamma} \sum_{\nu=1}^{\mu} \tilde{q}^2_{\nu H\gamma} + \sum_{\gamma} [(F^a_H \cos\alpha\, C^a_{H\gamma} + F^b_H \cos\beta\, C^b_{H\gamma})\, \tilde{q}_{1H\gamma} \\ & + (F^a_H \sin\alpha\, C^a_{H\gamma} + F^b_H \sin\beta\, C^b_{H\gamma})\, \tilde{q}_{2H\gamma}]. \end{aligned} \tag{21}$$

This expression clearly indicates that the coordinate space is now divided in a non-active harmonic part $\{\tilde{q}_{\nu H\gamma}\}$, $\nu = 3, \cdots, n$ and a JT active part $\{\tilde{q}_{\nu H\gamma}\}$, $\nu = 1, 2$. Unlike in simply reducible groups, this active part now contains two modes instead of one. The equilibrium values of these modes are given by

$$\begin{aligned} \tilde{q}^{(0)}_{1H\gamma} &= -\cos\alpha\, F^a_H R^a_{H\gamma} - \cos\beta\, F^b_H R^b_{H\gamma}, \\ \tilde{q}^{(0)}_{2H\gamma} &= -\sin\alpha\, F^a_H R^a_{H\gamma} - \sin\beta\, F^b_H R^b_{H\gamma}. \end{aligned} \tag{22}$$

By inserting these values in $\langle H \rangle$ we immediately obtain the isostationary function:

$$\langle H \rangle^{(0)} = -\frac{1}{2} \left[(F^a_H)^2 \sum_{\gamma} (R^a_{H\gamma})^2 + (F^b_H)^2 \sum_{\gamma} (R^b_{H\gamma})^2 + 2 F^a_H F^b_H S^b_a(H) \sum_{\gamma} R^a_{H\gamma} R^b_{H\gamma} \right]. \tag{23}$$

Using the appropriate substitution for F and S symbols as given in Eqs. (16) and (18), one verifies that this result exactly coincides with the general expression for the isostationary function, as given in Eq. (12). The $R^a_{H\gamma}$ and $R^b_{H\gamma}$ tensors are found to be orthogonal, which implies that the cross product in Eq. (23) vanishes:

$$\sum_\gamma R^a_{H\gamma} R^b_{H\gamma} = 0.$$

This is a general result for the coupling in a single level, which originates from the properties of the corresponding Clebsch–Gordan coefficients. Indeed the rank of the matrix described by these coefficients always equals the multiplicity of the product involved [24]. Hence coupling coefficients, corresponding to different branches a and b in the same product decomposition, can always be chosen to be orthogonal under the inner sum over γ in the cross product. In consequence the isostationary function further reduces to

$$\langle H \rangle^{(0)} = -\frac{1}{2}\left[(F^a_H)^2 \sum_\gamma (R^a_{H\gamma})^2 + (F^b_H)^2 \sum_\gamma (R^b_{H\gamma})^2\right]. \tag{24}$$

Essentially the same function appears when examining the ideal $H \times (g + 2h)$ JT problem in the single mode limit [5]. This illustrates that the method of the isostationary function completely integrates the multimode effect, even if the coordinate space representation cannot be reduced to an ideal system.

5 Conclusions

In this paper the method of the isostationary function is generalized to Hamiltonians that deviate from the ideal JT case. In addition an analytic expression for the isostationary function is derived for the important case of linear vibronic coupling. This function is of a general form and allows the full description of the topology of energy surfaces by means of Eqs. (12), (13) and (11), provided the corresponding coupling and force constants are known. It is shown that the multimode vibronic coupling requires some additional parameters to describe the topology of extremal points. The minimal number of these parameters and their expression through the parameters of the vibronic Hamiltonian are established by Eq. (12). The linear multimode vibronic problem within a single electronic term for both simply and non-simply reducible groups is equivalent to the one-mode problem as far as the topology of extremal points is concerned.

The inclusion of quadratic vibronic coupling leads to small changes of the energy surfaces in accordance with much smaller values of quadratic vibronic constants as compared with zeroth-order force constants [2]. The main effect of quadratic coupling thus consists in a symmetry lowering of the adiabatic potential through the warping of energy surfaces obtained within the linear approximation [2, 6]. This effect can usually be taken into account by adding second-order perturbation terms to the isostationary function.

The present theory proves to be especially useful in the treatment of complex vibronic problems, such as appear in the study of fullerene compounds.

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