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Hamiltonian operators including both symmetric and antisymmetric vibrational modes for vibronic coupling and intervalence charge-transfer applications

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Abstract

Corrections are provided to our previous treatment [Chem. Phys. 208 (1996) 177] of generalized Hamiltonian operators for the description of the non-adiabatic interaction of two potential-energy surfaces coupled by collections of both symmetric and anti-symmetric vibrational modes that restore invariance to unitary transformation of the operators. The form of other important projection and dipole-moment operators are also provided. These Hamiltonians are appropriate to a wide range of problems ranging from vibronic coupling in small aromatic molecules to intervalence charge-transfer phenomena to the operation of the special-pair solar to electrical energy converter in natural photosynthesis.
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1. Introduction

Previously [1] we have provides a generalized description for intervalence and related spectroscopies in which two electronic states are tightly coupled. Applications were developed therein to mixed-valence systems such as the Creutz–Taube ion [2] and the intervalence hole-transfer band of the special-pair radical cation from photosynthetic reaction centres [3]. The description includes provision for electronic coupling J acting between the two states, for geometrical relaxations λ' and λ'' in symmetric and antisymmetric modes, and for asymmetry E_0 in the energy of the two states; it was the first theory to include all of this complexity. Subsequently, we have expanded the approach to include up to four coupled electronic states with vibrations of two classes (symmetric and antisymmetric) [4]

and three electronic states with vibrations of three classes (totally symmetric and two different types of modes of reduced symmetry) [5]. This later application is particularly significant as it demonstrates that our theory, designed initially to describe mixed-valence spectroscopy, provides the simplest possible description for the nature of the triplet (π, π^*) states of pyridine, and subsequently we will show that, this result applies for benzene and indeed all simple aromatic hydrocarbons. The theory also encompasses that used in previous treatments of the Stark-effect on mixed-valence compounds [6] and hence provides a powerful and widely applicable methodology.

Our work claimed to develop a range of equivalent Hamiltonian operators for the depiction of problems of this type, Treynor, Andrews and Boxer [7] through numerical evaluation shown that some of the Hamiltonians in fact do not have the desired properties. Here, we correct these inadequacies and in addition present a number of additional important projection and dipole-moment operators.

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2. The vibronic coupling model

The method introduced [1] was based, as has been usual in mixed-valence spectroscopy [8], on the introduction of diabatic potential-energy surfaces rather than direct exploitation of Born–Oppenheimer adiabatic surfaces. Diabatic surfaces are not unique, however, and, for the first time, a method was constructed for the generation of an infinite number of distinct yet completely equivalent diabatic representations. Their equivalence is demonstrated in that application of the Born–Oppenheimer approximation to any of the diabatic forms of the electronic-vibrational coupling Hamiltonian results in the same adiabatic potential-energy surface, which solution of the full vibronic coupling problem leads to identical results in the limit of a complete vibrational basis set. The different diabatic representations vary significantly in terms of their suitability for use in analytical theories and in the size of the vibrational basis sets required to achieve convergence of the vibronic coupling problem, however, as well as in the ease by which vibronic matrix elements may be evaluated. A key conceptual development was the demonstration of the equivalence of the diabatic representations traditionally used to describe mixed-valence spectroscopy with the diabatic forms traditionally used to describe the high-resolution spectroscopy of small organic molecules such as benzene; this has led through cross fertilization to the development of more powerful methods for application in both fields [4,5,9]. In particular, we have exploited these transformation properties to introduce fully localized ($\mathbf{H}^L$) and fully delocalized ($\mathbf{H}^D$) diabatic representations

$$\mathbf{H}^L = \begin{bmatrix} H_{11}^L & H_{12}^L \\ H_{12}^L & H_{22}^L \end{bmatrix} \quad \text{and} \quad \mathbf{H}^D = \begin{bmatrix} H_{11}^D & H_{12}^D \\ H_{12}^D & H_{22}^D \end{bmatrix}, \qquad (1)$$

where the labels 1 and 2 refer to the two diabatic states and the matrix elements are given by

$$H_{11}^L = -\frac{E_0}{2} - \frac{\lambda''}{4} + \frac{1}{2}\sum_{j=1}^{n''} hv_j''[(\dot{q}_j'')^2 + (q_j'' + \delta_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} hv_i'[(\dot{q}_i')^2 + (q_i')^2],$$

$$H_{22}^L = \frac{E_0}{2} - \frac{\lambda''}{4} + \frac{1}{2}\sum_{j=1}^{n''} hv_j''[(\dot{q}_j'')^2 + (q_j'' - \delta_j'')^2] \qquad (2)$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} hv_i'[(\dot{q}_i')^2 + (q_i')^2],$$

$$H_{12}^L = J - \sum_{i=1}^{n'} \alpha_i' q_i',$$

and

$$H_{11}^D = -J - \frac{\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} hv_j''[(\dot{q}_j'')^2 + (q_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} hv_i'[(\dot{q}_i')^2 + (q_i' + \delta_i')^2],$$

$$H_{22}^D = J - \frac{\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} hv_j''[(\dot{q}_j'')^2 + (q_j'')^2] \qquad (3)$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} hv_i'[(\dot{q}_i')^2 + (q_i' - \delta_i')^2],$$

$$H_{12}^D = -\frac{E_0}{2} + \sum_{j=1}^{n''} \alpha_j'' q_j'',$$

where q' and q'' are symmetric and antisymmetric normal vibrational coordinates, respectively, in n' and n'' vibrational modes, δ' are displacements in the symmetric modes and α'' are vibronic coupling constants in the antisymmetric normal modes that can be transformed into effective vibrationic couplings and displacements according to

$$\alpha_i' = hv_i'\delta_i' \quad \text{and} \quad \delta_j'' = \frac{\alpha_j''}{hv_j''}, \qquad (4)$$

and the antisymmetric-mode and symmetric-mode reorganization energies defined by

$$\lambda'' = 2\sum_{j=1}^{n''} hv_j''(\delta_j'')^2 = 2\sum_{j=1}^{n''} \frac{(\alpha_j'')^2}{hv_j''},$$
$$\lambda' = 2\sum_{i=1}^{n'} hv_i'(\delta_i')^2 = 2\sum_{i=1}^{n'} \frac{(\alpha_i')^2}{hv_i'}, \qquad (5)$$

respectively. These two Hamiltonians are linked through a rotation of the electronic basis functions

$$\mathbf{H}^D = \frac{1}{2}\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}, \quad \mathbf{H}^L \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}, \qquad (6)$$

and the key result of our original paper [1] is that an infinite number of diabatic Hamiltonians can be produced simply by choosing different (coordinate independent) rotation matrices. Originally [1], the reported Hamiltonians were expressed in a manner that minimized the off-diagonal matrix elements and hence produced Hamiltonians that were best suited to analytical expansion. These representations also have optimal convergence properties in vibronic coupling calculations as a function of the truncation of the vibrational basis set; they are produced using the rotations [1]

$$\mathbf{H}^{D'} = \frac{1}{2}\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}, \quad \mathbf{H}^{L'} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} = \mathbf{R}\,\mathbf{H}^L\,\mathbf{R}^{TRANSP}, \qquad (7)$$

where

$$\mathbf{R} = [2\Delta(\Delta - E_0)]^{-1/2} \begin{bmatrix} 2J & \Delta - E_0 \\ E_0 - \Delta & 2J \end{bmatrix}, \qquad (8)$$

with

$$\Delta = [4J^2 + E_0^2]^{1/2}, \qquad (9)$$

designed to eliminate the energy asymmetry E_0 from the off-diagonal position of the delocalized Hamiltonian. This produces Hamiltonians of pseudo-localized and pseudo-delocalized nature of the form

$$\mathbf{H}^{L'} = \begin{bmatrix} H_{11}^{L'} & H_{12}^{L'} \\ H_{12}^{L'} & H_{22}^{L'} \end{bmatrix} \quad \text{and} \quad \mathbf{H}^{D'} = \begin{bmatrix} H_{11}^{D'} & H_{12}^{D'} \\ H_{12}^{D'} & H_{22}^{D'} \end{bmatrix}, \qquad (10)$$

where

$$H_{11}^{L'} = -\frac{a^2\lambda'' + b^2\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} h v_j''[(\dot{q}_j'')^2 + (q_j'' + a\delta_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} h v_i'[(\dot{q}_i')^2 + (q_i' - b\delta_i')^2],$$

$$H_{22}^{L'} = -\frac{a^2\lambda'' + b^2\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} h v_j''[(\dot{q}_j'')^2 + (q_j'' - a\delta_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} h v_i'[(\dot{q}_i')^2 + (q_i' + b\delta_i')^2],$$

$$H_{12}^{L'} = \frac{\Delta}{2} - b\sum_{j=1}^{n''} \alpha_j'' q_j'' - a\sum_{j=1}^{n'} \alpha_j' q_j',$$

$$(11)$$

and

$$H_{11}^{D'} = -\Delta/2 - \frac{b^2\lambda'' + a^2\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} h v_j''[(\dot{q}_j'')^2 + (q_j'' + b\delta_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} h v_i'[(\dot{q}_i')^2 + (q_i' + a\delta_i')^2],$$

$$H_{22}^{D'} = \Delta/2 - \frac{b^2\lambda'' + a^2\lambda'}{4} + \frac{1}{2}\sum_{j=1}^{n''} h v_j''[(\dot{q}_j'')^2 + (q_j'' - b\delta_j'')^2]$$
$$+ \frac{1}{2}\sum_{i=1}^{n'} h v_i'[(\dot{q}_i')^2 + (q_i' + a\delta_i')^2],$$

$$H_{12}^{D'} = a\sum_{j=1}^{n''} \alpha_j'' q_j'' - b\sum_{j=1}^{n'} \alpha_j' q_j',$$

$$(12)$$

where the coefficients a and b indicate that the purely displacement or purely-vibronic forms of the original couplings have been mixed together with coefficients

$$a = \frac{2J}{\Delta} \quad \text{and} \quad b = \frac{E_0}{\Delta}. \qquad (13)$$

Unfortunately, in the original manuscript, some of the contributions involving these dampings were omitted from Eqs. (21) and (22) of that manuscript. As a result, the published Hamiltonians do not display the required invariance properties, contrary to the claims made therein and elsewhere. We thank Treynor, Andrews and Boxer [7] for bringing this discrepancy to our attention.

3. Projection operators and dipole-moment operators

In order to simulate observed spectra, the related dipole moment operators are required. These are

$$\mathbf{M}^L = \frac{eR}{2}\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \mathbf{M}^D = \frac{eR}{2}\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix},$$
$$\mathbf{M}^{L'} = \frac{eR}{2}\begin{bmatrix} -a & b \\ b & a \end{bmatrix} \quad \text{and} \quad \mathbf{M}^{D'} = \frac{eR}{2}\begin{bmatrix} -b & -a \\ -a & b \end{bmatrix}, \qquad (14)$$

where R is the effective distance between the centres of the electron-transfer sites [1,10]. Note that the off-diagonal elements of these operators are in fact the electronic transition moments. Also, it is possible to define projection operators which give the contribution to any particular electronic basis state from all of the different diabatic representations. As an example, we give the projection operators for the first of the two electronic states in the fully localized representation as [1,4,9]

$$\mathbf{P}^L = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad \mathbf{P}^D = \frac{1}{2}\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix},$$
$$\mathbf{P}^{L'} = \frac{1}{2}\begin{bmatrix} 1+a & -b \\ -b & 1-a \end{bmatrix} \quad \text{and} \quad \mathbf{P}^{D'} = \frac{1}{2}\begin{bmatrix} 1+b & a \\ a & 1-b \end{bmatrix}. \qquad (15)$$

4. Conclusions

Problems involving the non-adiabatic interaction between two or more electronic states are ubiquitous in chemical spectroscopy. While for applications involving small molecules such as benzene, the azines, etc., it has been usual to cast this interaction in terms of vibronic couplings acting between diabatic states of high-symmetry, the usual approach for applications involving intervalence charge-transfer has been to use electronic couplings acting between localized low-symmetry diabatic states. Through the construction of various unitary transformations of the respective Hamiltonian operators used in each case, we demonstrate the equivalence of the two methods and generate a scheme by which arbitrary, conceptually equivalent, formulations can be generated. This is a powerful tool in practical applications as different formulations lead to very different implementational requirements.

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