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Variational Approach to Diabatic States*

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Avoided crossings and conical intersections of adiabatic potential energy surfaces are considered. Defects of the adiabatic representation at conical intersections are ascribed to an improper expansion of a continuous molecular wavefunction over a locally discontinuous set of functions. The purpose of diabatic states in this context is to regularize the adiabatic representation. A novel variational definition of diabatic states is introduced, and a simple general algorithm for an adiabatic-diabatic transformation is derived.

INTRODUCTION

The significance of adiabatic potential energy surfaces for chemistry in general, and for organic chemistry in particular, is well recognized. However, only well-behaved potential surfaces are commonly considered. Their distinct features are local minima and saddle points interpreted as stable molecular structures and transition states respectively. Only recently more attention has been paid to dynamically very significant avoided crossings of potential energy surfaces.[1-4] True surface crossings (conical intersections) are seldomly discussed,[5-8] except in the very special context of the Jahn-Teller effect,[9] although they are very common in triatomics and polyatomics.[10,11]

Since avoided and true intersections are related to the break-down of the adiabatic Born-Oppenheimer approximation, difficulties are often encountered in the theoretical treatment of nuclear motion.[4] These difficulties are particularly serious at conical intersections where nonadiabatic coupling becomes infinite.[8] On the other hand, results of atomic and molecular scattering experiments reveal that adiabatic potential energy surfaces do not provide an optimal representation for a description of molecular scattering, since the system passes from one potential surface to another in the region of avoided crossing.[3,4] As a more natural representation Lichten[1] introduced the concept of diabatic states, i. e. states dominated by a well defined electronic configuration which tends to be conserved in the scattering process. How to determine diabatic states and related diabatic potential energy surfaces remained, however, an open problem, which attracted subsequently very much attention,[2,6,13-21] but was not satisfactorily solved.

In order to reach a better understanding of the theoretical difficulties springing from the adiabatic representation we shall closely examine assum-

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ptions and common practices in solving the molecular Shrödinger equation. Finally, a recently proposed[22] very general variational scheme for generating diabatic states from adiabatic ones will be presented.

ADIABATIC REPRESENTATION

In the attempt to solve the molecular Schrödinger equation

$$\hat{H}\,\Psi_r(q,Q) = E_r\,\Psi_r(q,Q) \tag{1}$$

where q and Q stand for electronic and nuclear coordinates, the molecular wavefunction $\Psi_r(q,Q)$ is usually developed in a complete set of known electronic functions $\{\varphi_k(q,Q)\}$:

$$\Psi_r(q,Q) = \sum_k \xi_k^r(Q)\,\varphi_k(q,Q) \tag{2}$$

The set $\{\varphi_k(q,Q)\}$ defines a *representation*.

Among infinitely many representations one should choose that one which simplifies the original problem as much as possible. Good results are usually obtained in the *adiabatic representation,* defined by the set $\{\varphi_k(q,Q)\}$ which diagonalizes the electronic part of the Hamiltonian, $\hat{H}^{el}(q,Q) = \hat{H} - \hat{T}_Q$:

$$\hat{H}^{el}(q,Q)\,\varphi_k(q,Q) = \varepsilon_k(Q)\,\varphi_k(q,Q) \tag{3}$$

Nuclear coordinates Q appear here only as parameters while $\hat{T}_Q$ stands for the nuclear kinetic energy operator. Eigenvalue $\varepsilon_k(Q)$, as a function of nuclear coordinates Q, represents the *adiabatic potential energy surface* of the »electronic state« $\varphi_k(q,Q)$. This terminology springs form the very drastic Born-Oppenheimer approximation in which expansion (2) is truncated to a single leading term. In this highly successful approximation $\varepsilon_k(Q)$ indeed defines a potential field governing the vibrational motion of nuclei about the equilibrium configuration. Furthermore, even if this approximation becomes invalid for certain values of nuclear coordinates Q, it provides a reference model and terminology for discussing the non-adiabatic effects.

Somewhat less drastic is the *two-state approximation* in which the molecular wavefunction in eq. (2) is truncated to only two leading terms:

$$\Psi_r(q,Q) \simeq \xi_1^r(Q)\,\varphi_1(q,Q) + \xi_2^r(Q)\,\varphi_2(q,Q) \tag{4}$$

Since nuclear and electronic motion are here inseparable, such states are usually called vibronic.

AVOIDED POTENTIAL CROSSING IN DIATOMICS

To simplify the analysis we shall temporarily discuss only diatomics with a single internuclear coordinate $Q \equiv R$. In this case the original Schrödinger equation (1) reduces in the two-state approximation to the following coupled equations for the amplitudes $\xi_k^r(Q)$:

$$\begin{pmatrix} \hat{T}_R + \varepsilon_1(R) + G(R) & \hat{F}(R) \\ -\hat{F}(R) & \hat{T}_R + \varepsilon_2(R) + G(R) \end{pmatrix} \begin{pmatrix} \xi_1^r(R) \\ \xi_2^r(R) \end{pmatrix} = E_r \begin{pmatrix} \xi_1^r(R) \\ \xi_2^r(R) \end{pmatrix} \tag{5}$$

Here $\wedge$ marks differential operators. The non-adiabatic terms $G(R)$ and $F(R)$ are given by

$$G(R) = \frac{\hbar^2}{2\mu}[f(R)]^2, \qquad \hat{F}(R) = \frac{\hbar^2}{\mu} f(R) \frac{d}{dR}, \tag{6}$$

where μ is the reduced mass. They depend on a single *non-adiabatic coupling function* $f(R)$ defined by

$$f(R) = \int \varphi_1(q, R) \frac{d}{dR} \varphi_2(q, R)\, dq \tag{7}$$

This function plays the central role in discussing the Born-Oppenheimer approximation and its break-down reflected in the non-adiabatic effects.

If the electronic wavefunctions $\varphi_1(q, R)$ and $\varphi_2(q, R)$ vary slowly with R everywhere, $f(R)$ in eq. (7) may be neglected. This justifies the Born-Oppenheimer approximation. However, if the electronic wavefunctions suddenly change their character in a certain domain of R, then $f(R)$ in this domain will not be negligible and equations (5) remain coupled. The fact that the generated coupling operator $\hat{F}(R)$ is a differential operator causes difficulties in the numerical treatment of these equations. Closer inspection reveals also that the adiabatic potential curves, which exhibit an avoided crossing in the critical region of R, often do not provide an optimal representation for the description of scattering processes. For example, the CsBr molecule dissociates into the ionic channel[23] although the adiabatic potential curve would imply its dissociation into neutral atoms. In this case the non-adiabatic coupling function $f(R)$ is large in the avoided crossing region. It has the role of a *switching function* between two adiabatic potential curves.

In CsBr dissociation the system follows the ionic potential curve ignoring the adiabatic non-crossing rule in diatomics.[24,25] If this ionic potential curve is interpreted as one basic entity, and covalent curve as another entity, no switching functions are required to describe CsBr dissociation. Such electronic states, which are dominated by a well-defined configuration (i. e. ionic, or covalent), and which do not obey the adiabatic non-crossing rule for diatomics, were named *diabatic* by Lichten.[1]

Quite generally, the two-state approximation in any (unspecified) representation leads to the following coupled equations

$$\begin{pmatrix} \hat{T}_Q + H_{11}(Q) + G(Q) & H_{12}(Q) + \hat{F}(Q) \\ H_{12}(Q) - \hat{F}(Q) & \hat{T}_Q + H_{22}(Q) + G(Q) \end{pmatrix} \begin{pmatrix} \xi_1(Q) \\ \xi_2(Q) \end{pmatrix} = E \begin{pmatrix} \xi_1(Q) \\ \xi_2(Q) \end{pmatrix} \tag{8}$$

where

$$H_{kl}(Q) = \int \varphi_k^*(q, Q)\, \hat{H}^{el}(q, Q)\, \varphi_l(q, Q)\, dq \equiv \langle \Phi_k | \hat{H}^{el} | \Phi_l \rangle \tag{9}$$

where $G(Q)$ and $\hat{F}(Q)$ are non-adiabatic terms.

If $H_{12}(Q)$ vanishes, the representation is adiabatic. The representation is diabatic if $\hat{F}(Q)$ is negligibly small. Diabatic states are often defined by the requirement that $\hat{F}(Q)$ vanish.[26,2,15,16] While in diatomics this requirement may be justified, in polyatomics additional constraints appear which are rarely fulfilled.[27,28] In the general multi-state case this requirement is certainly too strong.[29]

TRUE POTENTIAL SURFACE CROSSING IN POLYAOTMICS

In polyatomics, where the potential non-crossing rule does not hold, defects of the addiabatic representation are more serious then in diatomics.[24,25,5]

1. At the crossing point electronic wavefunctions are discontinuous.
2. At the crossing point non-adiabatic coupling functions f(Q) are *infinite.*
3. Along a path around the crossing point electronic wavefunctions *change the sign.*

Since the adiabatic electronic wavefunctions are essentially discontinuous at the potential crossing point they should not be used as basis functions in the expansion of the molecular wavefunction, eq. (2). Instead, one should find two well-behaved functions spanning the same twodimensional manifold as two locally degenerate adiabatic wavefunctions. In general, keeping resulting functions orthogonal, the new functions $|\Phi_1(q, Q)\rangle$ and $|\Phi_2(q, Q)\rangle$ are given by a 2 × 2 Q-dependent orthogonal transformation.[26,27,9,8]

$$\begin{pmatrix} |\Phi_1(q, Q)\rangle \\ |\Phi_2(q, Q)\rangle \end{pmatrix} = \begin{pmatrix} \cos\Theta(Q) & -\sin\Theta(Q) \\ \sin\Theta(Q) & \cos\Theta(Q) \end{pmatrix} \begin{pmatrix} |\varphi_1(q, Q)\rangle \\ |\varphi_2(q, Q)\rangle \end{pmatrix} \tag{10}$$

Since there are infinitely many ways to choose the continuous functions $|\Phi_1(q, Q)\rangle$ and $|\Phi_2(q, Q)\rangle$ in a given 2-dimensional manifold, one may impose an additional requirement to make the choice unique. Diabatic functions, dominated by well-defined configurations, and coinciding with adiabatic wavefunctions at the dissociation limit, would certainly represent a physically significant choice. Thus, one should find such $\Theta(Q)$ in the complete space of nuclear coordinates Q, which generates diabatic functions by the transformation (10). In the avoided crossing problem of diatomics several schemes for the adiabatic-diabatic transformation were proposed,[6,15,16,18–20] but they are neither general enough nor sufficiently suited for the problem of conical intersections in polyatomics. In the next two sections we shall present the recently proposed[22] general variational method for the adiabatic-diabatic transformation.

VARIATIONAL DEFINITION OF DIABATIC STATES

Accepting Lichten's original concept of diabatic states[1] as states dominated by certain simple electronic configuration (ionic, covalent, single-determinant, etc.) the problem is — how to extract such two orthogonal states from a given 2-dimensional manifold of adiabatic wavefunctions?

As a first step, of heuristic value only, let us consider two »perfect« orthogonal diabatic states $|\Phi_1\rangle$ and $|\Phi_2\rangle$, each given by a single Slater determinant in a certain orbital basis set. Suppose that two »adiabatic« states $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are produced by a 2 × 2 orthogonal transformation

$$\begin{pmatrix} |\varphi_1\rangle \\ |\varphi_2\rangle \end{pmatrix} = \begin{pmatrix} \cos\Theta & \sin\Theta \\ -\sin\Theta & \cos\Theta \end{pmatrix} \begin{pmatrix} |\Phi_1\rangle \\ |\Phi_2\rangle \end{pmatrix} \tag{11}$$

Suppose further that the recorded »adiabatic« states are expressed in a certain unnatural orbital basis set, in which they have a large number of configuration interaction components. How to recover the original single-determinant »diabatic« states from this record? Clearly, one should find an inverse transformation of (11), as in eq. (10), by changing the angle Θ until one of the resulting functions $|\Phi\rangle$ is recognized to be a Slater determinant. However, how to recognize a Slater determinant $|\Phi\rangle$ if it is expressed (in an unnatural orbital set) by thousands of CI components? This can be done by finding the natural spin-orbitals Z_α of $|\Phi\rangle$ and their occupation nubers γ_α from the relevant reduced density matrix[30] (with $c_\mu^\dagger$ an electron creation operator):

$$\sum_\nu R_{\mu\nu} Z_{\nu\alpha} = \gamma_\alpha Z_{\mu\alpha}, \quad R_{\mu\nu} \equiv \langle \Phi | c_\mu^\dagger c_\nu | \Phi \rangle \tag{12}$$

If all nonvanishing occupation numbers γ_α are equal to one, the function $|\Phi\rangle$ is a Slater determinant.

Although this procedure solves the problem of finding diabatic states in our model case, it cannot be applied to a more realistic situation when the diabatic states are not »perfect« pure configurations. An algorithm is required which would generate diabatic states of the best possible structure in a given manifold. Again, our simple model of two Slater determinants will help to find such an algorithm.

Recall that our »diabatic« (single-determinant) states are identified by inspecting the occupation numbers of their natural spin-orbitals. What happens to the occupation numbers if one mixes a little these two Slater determinants? The sum of the occupation numbers does not change since it equals the number of electrons, $\sum_\alpha \gamma_\alpha = N$. However, the sum of squared occupation numbers diminishes. Namely, $\sum_\alpha \gamma_\alpha^2 \leq N$, since $\gamma_\alpha^2 \leq \gamma_\alpha$ for all $0 \leq \gamma_\alpha \leq 1$, and it reaches the maximum value N for a Slater determinant. Thus, in our model case one may generate »diabatic« states by requiring that the sum of squared occupation numbers of their natural spin-orbitals be the largest possible.

This variational procedure may be applied also to more general adiabatic states. It will tend to transform them into vectors which are dominated by one or several pure configurations — to the extent permitted by the original manifold. States obtained by this variational procedure will be called diabatic.

TWO-DIMENSIONAL MANIFOLD

The crossing or avoided crossing of only two adiabatic potential surfaces represents the most common case of the break-down of the Born-Oppenheimer approximation. Multiple surface crossing could be treated as a sequence of twosurface problems.

If $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are two orthonormal adiabatic electronic wavefunctions, the equivalent diabatic orthonormal states $|\Phi_1\rangle$ and $|\Phi_2\rangle$ are locally given by that 2×2 transformation, eq. (10), which maximizes the sum F of squared occupation probabilities of the natural spin-orbitals of the resulting diabatic states:

$$F = \sum_\alpha [\gamma_\alpha^2(1) + \gamma_\alpha^2(2)] = max. \tag{13}$$

From the defining equation (12) for the natural spin-orbitals using their orthogonality, we have

$$\gamma_\alpha (i)\, \delta_{\alpha\beta} = \sum_{\mu\nu} Z_{\mu\alpha} (i)\, Z_{\nu\beta} (i)\, R_{\mu\nu} (i), \qquad i = 1, 2 \tag{14}$$

This gives

$$F = \sum_{\mu\nu} [R_{\mu\nu}{}^2 (1) + R_{\mu\nu}{}^2 (2)] = max. \tag{15}$$

or

$$F = \sum_{\mu\nu} [R_{\mu\nu} (1) + R_{\mu\nu} (2)]^2 - 2 \sum_{\mu\nu} R_{\mu\nu} (1)\, R_{\mu\nu} (2) = max. \tag{16}$$

It may be easily verified that $\overline{R} = R\,(1) + R\,(2)$ remains invariant on the transformation (10). This matrix could be named the one-electron reduced density matrix of the manifold. Thus, from eq. (16) we obtain

$$\sum_{\mu\nu} R_{\mu\nu} (1)\, R_{\mu\nu} (2) = min. \tag{17}$$

Expressing the reduced density matrices R of diabatic states in terms of reduced density and transition matrices $\varrho\,(ij)$ of the original adiabatic states,

$$\varrho_{\mu\nu} (ij) = \langle \varphi_i \,|\, c_\mu{}^\dagger\, c_\nu \,|\, \varphi_j \rangle \tag{18}$$

we obtain

$$4\, R_{\mu\nu} (1)\, R_{\mu\nu} (2) = \overline{R}_{\mu\nu}{}^2 - [A_{\mu\nu} \cos 2\,\Theta + B_{\mu\nu} \sin 2\,\Theta]^2 \tag{19}$$

with

$$A_{\mu\nu} = \varrho_{\mu\nu} (22) - \varrho_{\mu\nu} (11), \qquad B_{\mu\nu} = \varrho_{\mu\nu} (12) + \varrho_{\mu\nu} (21) \tag{20}$$

From eqs. (17) and (19) it follows that

$$\sum_{\mu\nu} [A_{\mu\nu} \cos 2\,\Theta + B_{\mu\nu} \sin 2\,\Theta]^2 = max. \tag{21}$$

where Θ is a variational parameter. This gives

$$A \cos^2 2\,\Theta + B \sin^2 2\,\Theta + C \sin 4\,\Theta = max. \tag{22}$$

with

$$A = \sum_{\mu\nu} A_{\mu\nu}{}^2, \quad B = \sum_{\mu\nu} B_{\mu\nu}{}^2, \quad C = \sum_{\mu\nu} A_{\mu\nu} B_{\mu\nu} \tag{23}$$

Finally, the function in eq. (22) reaches its maximum for the following value Θ_0 of Θ:

$$\tan (4\,\Theta_o) = 2\,C/(A-B), \quad (A-B)/\cos (4\,\Theta_o) > 0. \tag{24}$$

This is equivalent to the equations

$$\sin 4\,\Theta_o = 2\,C/a^2, \qquad \cos 4\,\Theta_o = (A - B)/a^2 \tag{25}$$

with

$$a^2 = 4\,C^2 + (A - B)^2 \tag{26}$$

Requiring the continuity of Θ_o along any path around the conical intersection, equations (25) fully define this angle. This prescription determines completely the 2 × 2 adiabatic-diabatic transformation in eq. (10) for every nuclear configuration separately.

The adiabatic-diabatic transformation (10) generates the following potential matrix

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} \overline{E} - \Delta \cos 2\,\Theta & -\Delta \sin 2\,\Theta \\ -\Delta \sin 2\,\Theta & \overline{E} + \Delta \cos 2\,\Theta \end{pmatrix} \tag{27}$$

expressed in terms of the adiabatic energies ε_1 and ε_2:

$$\overline{E} = (\varepsilon_1 + \varepsilon_2)/2, \qquad \Delta = (\varepsilon_2 - \varepsilon_1)/2. \tag{28}$$

CONCLUSIONS

The variational scheme for the 2 × 2 adiabatic-diabatic transformation, discussed in this paper, represents a precise mathematical expression of Lichten's original concept of diabatic states. This scheme is very general, simple to apply, and equally valid for avoided and true adiabatic surface crossings. It requires only one-electron reduced spin-density and transition matrices of relevant adiabatic states, so that non-adiabatic coupling functions need not be computed at all.

In the resulting diabatic representation non-adiabatic coupling functions do not vanish exactly They should be, however, equally negligible as in the domain where the Born-Oppenheimer approximation is valid.

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SAŽETAK

Varijacijski pristup dijabatskim stanjima

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Razmotrena su izbjegnuta križanja i konična presijecanja ploha adijabatske potencijalne energije. Defekti adijabatske reprezentacije na koničnim presjecima pripisani su nepravilnom razvoju kontinuirane molekulske valne funkcije s pomoću skupa lokalno diskontinuiranih funkcija. Svrha dijabatskih stanja u ovom kontekstu jest uređenje adijabatske reprezentacije. Uvedena je nova varijacijska definicija dijabatskih stanja i izveden je jednostavan opći algoritam za adijabatsko-dijabatsku transformaciju.