

Constructing approximately diabatic states from LCAO-SCF-CI calculations

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We consider here two approaches which have been proposed in the literature to obtain diabatic states from *ab initio* calculations. First, by calculating explicitly the coupling vector $\mathbf{g} = \langle \psi_2 | \nabla \psi_1 \rangle$ which describes the nonadiabatic interaction between two adiabatic states ψ_1 and ψ_2 . Second, by some extrapolation process of the wave functions obtained at a particular reference point. The coupling vector \mathbf{g} is the sum of three contributions:

$\mathbf{g} = \mathbf{g}_{\text{CI}} + \mathbf{g}_{\text{LCAO}} + \mathbf{g}_{\text{AO}}$. The first two represent the change in character of the adiabatic states in the region of nonadiabatic coupling due to the variation of the CI and LCAO coefficients, whereas \mathbf{g}_{AO} results from the translation of the atomic orbitals with the moving nuclear centers. Criteria have been given to recognize when it is possible to transform a set of CI wave functions into a pair of useful diabatic states. A particularly favorable situation is obtained when the interacting electronic states are doubly excited with respect to each other. Within the two-state approximation, \mathbf{g}_{CI} is strictly irrotational and never gives rise to problems. One can expect situations in which this is also true for \mathbf{g}_{LCAO} . However, that part of the coupling represented by \mathbf{g}_{AO} can never be described as a rotation of two diabatic functions. Nevertheless, the latter contribution can frequently be neglected, at least when the nonadiabatic coupling is strong. The theory of the electron translation factors (ETF's) provides further insight into the problem and confirms our conclusions.

I. INTRODUCTION

It is well known that as long as adiabatic potential energy surfaces remain separated by an energy gap which is much larger than the nuclear kinetic energy, the Born-Oppenheimer method is a good approximation. It is then sufficient to consider a single potential energy surface to describe the nuclear motion. When this is not the case, nonadiabatic coupling takes place. The literature on the subject is really enormous¹⁻⁵ (see especially the recent review by Köppel *et al.*⁵). Since the problem can be treated from several points of view, we have to restrict the scope of the present contribution right at the beginning. Our objective is to study the general rules which control the nonadiabatic transitions and to obtain simple analytical expressions for the probabilities of hopping between potential energy surfaces. For that purpose, the simplest level of approximation will be adopted throughout the present paper.

(i) We assume that a LCAO-SCF-CI calculation has been carried out which has generated a set of N eigenstates. For simplicity we assume all electronic wave functions to be real.

(ii) We restrict our attention to a limited portion of configuration space in which it is meaningful to assume that only two electronic states out of N interact. In the first sections of this paper, we assume that the corresponding potential energy surfaces come close to each other but do not intersect. This restriction is lifted in Sec. V.

(iii) We restrict ourselves to a classical trajectory formulation in which the nuclear motion is described by a classical equation of motion.^{1,2,7-9} Nuclear wave functions thus never appear in the present treatment. The time-dependent electronic wave function is then expressed as a two-state expansion:

$$\Psi(q,t) = \sum_{j=1}^2 a_j(t) |j[q, \mathbf{Q}(t)]\rangle \exp \left[- (i/\hbar) \int^t H_{jj} dt' \right], \quad (1.1)$$

where $|1\rangle$ and $|2\rangle$ are the electronic functions used as a basis set (thus not necessarily the eigenfunctions of the electronic Hamiltonian); H_{ij} are the elements of the electronic Hamiltonian matrix in this representation; q and $\mathbf{Q}(t)$ are the electronic and nuclear coordinates, respectively. The time-dependent coefficients $a_j(t)$ are solution of a system of two coupled differential equations

$$\dot{a}_1(t) = a_2(t) \left[- (i/\hbar) H_{12} + \langle 2 | \nabla | 1 \rangle \cdot \dot{\mathbf{Q}} \right] \times \exp \left[- (i/\hbar) \int^t (H_{22} - H_{11}) dt' \right] \quad (1.2)$$

and a similar equation for \dot{a}_2 .

In the adiabatic representation, the basis functions are the eigenfunctions of the electronic Hamiltonian H (in other words the CI wave functions) and the dynamical coupling results from the term $\langle \psi_2 | \nabla \psi_1 \rangle \cdot \dot{\mathbf{Q}}$. It is then convenient to introduce a coupling vector $\mathbf{g}(\mathbf{Q})$:

$$\mathbf{g} \equiv \langle \psi_2 | \nabla \psi_1 \rangle \quad (1.3)$$

whose components are

$$g_k = \langle \psi_2 | \frac{\partial}{\partial Q_k} | \psi_1 \rangle. \quad (1.4)$$

What has been consistently looked for is a so-called diabatic representation^{1-3,5,7-16} in which the coupling results from the off-diagonal H_{12} only. The diabatic basis [hereafter denoted $\chi_1(q, \mathbf{Q})$, $\chi_2(q, \mathbf{Q})$] is required to obey two conditions:

(1) It should be related to the adiabatic basis by an orthogonal transformation

$$\begin{pmatrix} \chi_1(q, \mathbf{Q}) \\ \chi_2(q, \mathbf{Q}) \end{pmatrix} = \begin{pmatrix} \cos \theta(\mathbf{Q}) & \sin \theta(\mathbf{Q}) \\ -\sin \theta(\mathbf{Q}) & \cos \theta(\mathbf{Q}) \end{pmatrix} \begin{pmatrix} \psi_1(q, \mathbf{Q}) \\ \psi_2(q, \mathbf{Q}) \end{pmatrix}. \quad (1.5)$$

(2) The second *a priori desirable* property would be

$$\langle \chi_2 | \nabla \chi_1 \rangle = 0. \quad (1.6)$$

The significance of this requirement is that their physical character (ionic, covalent, Rydberg, $n-\pi^*$, etc.) should remain unaltered as the nuclear geometry changes. However, the diabatic states we are looking for are allowed to move along with the nuclei.^{11,12} They are not the fixed functions commonly referred to as “crude adiabatic.”^{17,18} Hence, they will be denoted $\chi_i(q, \mathbf{Q})$ to emphasize the fact that $\nabla \chi_i \neq 0$.

From Eq. (1.3) one gets

$$\langle \chi_2 | \nabla \chi_1 \rangle = \nabla \theta + \mathbf{g}. \quad (1.7)$$

Hence, if it is possible to satisfy simultaneously conditions (1.5) and (1.6), the angle $\theta(\mathbf{Q})$ is a solution of a differential equation:

$$\nabla \theta = -\mathbf{g}. \quad (1.8)$$

However, as pointed out by Mead and Truhlar,¹⁵ following up previous discussions by McLachlan¹¹ and by Baer,¹³ Eq. (1.8) admits a solution only if

$$\text{curl } \mathbf{g} = 0. \quad (1.9)$$

Unfortunately, this condition cannot, in general, be rigorously fulfilled in a multidimensional \mathbf{Q} space, and one has to look for approximate diabatic basis sets. Our objective is to analyze this problem within the context of *ab initio* calculations.

It is possible to calculate for polyatomic molecules matrix elements of the type (1.4) when ψ_1 and ψ_2 are configuration interaction (CI) wave functions.^{16,19,20} We assume that a particular pair (ψ_1, ψ_2) gives rise locally to a large value of \mathbf{g} , whereas the coupling with the other adiabatic states ψ_α ($\alpha \neq 1, 2$) is negligible. More precisely, we assume that within the region of interest one has

$$|\hbar \dot{\mathbf{Q}} \cdot \langle \psi_i | \nabla \psi_\alpha \rangle| \ll |E_\alpha - E_i|. \quad (1.10)$$

As discussed by Mead and Truhlar,¹⁵ approximate diabatic states can be constructed only when the irrotational part of \mathbf{g} is large with respect to the remainder. This leads to two questions. First, can one expect situations in which this is the case? It would be impractical to calculate the components of $\text{curl } \mathbf{g}$ by numerical double differentiations. For similar reasons, we have to abandon the study of an equation¹⁵ which is equivalent to condition (1.9):

$$\sum_{\alpha=3}^n \left[\left\langle \frac{\partial \psi_2}{\partial Q_j} \middle| \psi_\alpha \right\rangle \left\langle \psi_\alpha \middle| \frac{\partial \psi_1}{\partial Q_k} \right\rangle - \left\langle \frac{\partial \psi_2}{\partial Q_k} \middle| \psi_\alpha \right\rangle \left\langle \psi_\alpha \middle| \frac{\partial \psi_1}{\partial Q_j} \right\rangle \right] = 0, \quad (1.11)$$

but which requires in principle the *ab initio* calculation of an enormous number of matrix elements. Thus, our first question transforms into: “Is it possible to recognize the favorable situations by inspecting the characteristics of the output of an *ab initio* calculation?” Second, since the construction of

diabatic states necessarily involves approximations, “is it possible to define tolerance parameters?”

An answer to the first question will be proposed in the next section. As far as the second question is concerned, tolerance thresholds can be found in Eqs. (1.2). Consider a particular region of strong nonadiabatic coupling and let $\Delta E^{\min} = 2H_{12}$ be the smallest energy gap between adiabatic surfaces, g_a^{\max} the maximum value of the coupling matrix element along coordinate Q_a , and ξ_a the corresponding Massey parameter.⁹ Then, if the conditions

$$\left| \left\langle \chi_2 \middle| \frac{\partial \chi_1}{\partial Q_a} \right\rangle \right| \ll \Delta E^{\min} / \hbar \dot{Q}_a = \xi_a g_a^{\max} \quad (1.12)$$

are fulfilled for all a , the basis set $\{\chi_1, \chi_2\}$ can be considered “diabatic enough” for a classical trajectory calculation of the transition probabilities. Conditions (1.12) thus replace Eq. (1.6). Note that the tolerance thresholds depend on the internal energy through the nuclear velocities.

In summary, the concept of diabatic states involves a certain vagueness since approximate solutions have to be looked for. In the remainder of the paper we discuss two possible approaches which have been proposed to extract approximate but acceptable solutions from *ab initio* calculations. The present analysis is an extension of a previous discussion given by Mead and Truhlar¹⁵ recast in the language appropriate to *ab initio* calculations. It should also be useful in the discussion of the interesting alternative procedures developed by Werner and Meyer²¹ and by Hendeković.²² Numerical applications to specific cases will be presented in forthcoming papers.

II. METHOD INVOLVING A DIFFERENTIATION OF THE WAVE FUNCTION

In a CI calculation, the adiabatic wave functions $\psi_i(q, \mathbf{Q})$ are expanded⁶ in a set of N configuration state functions (CSF's) $\eta_i(q, \mathbf{Q})$:

$$\begin{pmatrix} \psi_1(q, \mathbf{Q}) \\ \psi_2(q, \mathbf{Q}) \\ \vdots \\ \psi_N(q, \mathbf{Q}) \end{pmatrix} = \mathbf{C}(\mathbf{Q}) \begin{pmatrix} \eta_1(q, \mathbf{Q}) \\ \eta_2(q, \mathbf{Q}) \\ \vdots \\ \eta_N(q, \mathbf{Q}) \end{pmatrix}, \quad (2.1)$$

where \mathbf{C} is the orthogonal matrix of the CI coefficients. Then

$$\mathbf{g} = \mathbf{g}_{\text{CI}} + \mathbf{g}_{\text{MO}} \quad (2.2)$$

with

$$\mathbf{g}_{\text{CI}} = \sum_j C_{2j} \nabla C_{1j}, \quad (2.3)$$

and

$$\mathbf{g}_{\text{MO}} = \sum_{j \neq k} \sum C_{2j} C_{1k} \langle \eta_j | \nabla \eta_k \rangle. \quad (2.4)$$

Since ∇ is a one-electron operator, expansion (2.4) is severely limited by the fact that η_j and η_k should be singly excited with respect to each other.²³

However, according to the previous discussion, another decomposition is required. The problem is to express \mathbf{g} as the

sum of two vectors. First, an irrotational component which can be equated to a gradient. The second component which has a nonzero curl is the residual quantity $\langle \chi_2 | \nabla \chi_1 \rangle$. This leads to two questions.

(1) Is \mathbf{g}_{CI} an irrotational vector?

Mead and Truhlar¹⁵ have shown this to be the case within a two-state approximation. This means that in a CI calculation, the matrix \mathbf{C} should have the following form:

$$\mathbf{C}(\mathbf{Q}) = \begin{pmatrix} \cos \theta & -\sin \theta & | & 0 \\ \sin \theta & \cos \theta & | & 0 \\ \hline 0 & 0 & | & \mathbf{U}^I(\mathbf{Q}) \end{pmatrix} \cdot \mathbf{U}, \quad (2.5)$$

where \mathbf{U} is an orthogonal constant matrix and $\mathbf{U}^I(\mathbf{Q})$ is a nonconstant $(N-2) \times (N-2)$ orthogonal matrix. The vector \mathbf{g}_{CI} is then strictly irrotational and is equal to $-\nabla \theta$.

(2) Similarly, when is \mathbf{g}_{MO} an irrotational vector?

The answer to that question is much less straightforward. One has, from density-matrix theory,²⁴

$$\mathbf{g}_{\text{MO}} = \sum_i^M \sum_m^M T_{im}(\mathbf{Q}) \langle \phi_i | \nabla \phi_m \rangle, \quad (2.6)$$

where ϕ_i and ϕ_m are MO's and $T_{im}(\mathbf{Q})$ is the first-order transition matrix for states ψ_1 and ψ_2 . Each element of this matrix can be expressed as a sum of products of CI coefficient times fixed coefficients expressing the CSF's in terms of Slater determinants. The MO's are expanded in a basis of nonorthogonal AO's:

$$\begin{pmatrix} \phi_1 \\ \vdots \\ \phi_M \end{pmatrix} = \mathbf{A}(\mathbf{Q}) \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_M \end{pmatrix}. \quad (2.7)$$

Then

$$\mathbf{g}_{\text{MO}} = \mathbf{g}_{\text{LCAO}} + \mathbf{g}_{\text{AO}} \quad (2.8)$$

with

$$\mathbf{g}_{\text{LCAO}} = \sum_i^M \sum_m^M T_{im} \sum_p^M \sum_q^M a_{ip} a_{mq} \langle \xi_p | \xi_q \rangle, \quad (2.9)$$

$$\mathbf{g}_{\text{AO}} = \sum_i^M \sum_m^M T_{im} \sum_p^M \sum_q^M a_{ip} a_{mq} \langle \xi_p | \nabla \xi_q \rangle. \quad (2.10)$$

The first contribution results from the nonconstancy of the LCAO coefficients, whereas the second is due to the fact that the AO's translate with the moving nuclear centers.¹²

Let us now return to curl \mathbf{g} and consider the following particular cases.

(a) The first-order transition matrix is negligible because the terms which dominate the CI expansion of ψ_1 are doubly excited with respect to those which dominate the expression of ψ_2 . Then, \mathbf{g}_{MO} is negligible, i.e., $\mathbf{g} \approx \mathbf{g}_{\text{CI}}$ which is irrotational if condition (2.5) is satisfied. The constant orthogonal matrix \mathbf{U} (or at least its first two rows) determines the CI expansion of the diabatic states. This result is of course independent of the nature of the AO basis set which is used (cf. Sec. VI).

The argument is again valid in the limit since the first-order transition matrix never strictly vanishes in practice.

The leading term of wave function is always contaminated by additional singly excited configurations which are the only ones to have a nonzero component on the gradient of the other function.²³

(b) The LCAO coefficients a_{lm} happen to be constant across the region of strong nonadiabatic interaction. Then, $\mathbf{g}_{\text{LCAO}} = 0$ and $\mathbf{g}_{\text{MO}} = \mathbf{g}_{\text{AO}}$. It will be shown in Sec. IV that the curl of \mathbf{g}_{AO} does not, in general, vanish. Thus, the main source of the difficulties encountered in the definition of the diabatic states is to be found in the properties of the basis set of AO's. However, orders of magnitude will be given in Sec. IV and it will be found that it is often safe to neglect \mathbf{g}_{AO} with respect to \mathbf{g}_{CI} and \mathbf{g}_{LCAO} .

(c) The coupling vector \mathbf{g}_{MO} can be expected to be dominated by a single (l, m) contribution. This circumstance results from the fact²³ that $\nabla \phi_m$ has a nonzero component on ϕ_l only if ϕ_l is an occupied and ϕ_m an unoccupied spin orbital or vice versa. If ψ_1 and ψ_2 were SCF wave functions, they should be singly excited with respect to each other. For CI wave functions, a similar but less stringent condition can be expressed in the language of density matrix theory. The sets of occupation numbers of ψ_1 and ψ_2 should differ roughly by the transfer of one electron only, say from ϕ_1 to ϕ_2 . Then, the transition matrix has a single large element $T_{12}(\mathbf{Q})$.

It is appropriate to expand the MO's in a set of orthogonalized AO's:

$$\begin{pmatrix} \phi_1 \\ \vdots \\ \phi_M \end{pmatrix} = \mathbf{B}(\mathbf{Q}) \begin{pmatrix} \xi_1 \\ \vdots \\ \xi_M \end{pmatrix} \quad (2.11)$$

with

$$\langle \xi_p | \xi_q \rangle = \delta_{pq}. \quad (2.12)$$

\mathbf{B} is now an orthogonal matrix equal to

$$\mathbf{B} = \mathbf{A}(\mathbf{1} - \mathbf{S})^{-1}, \quad (2.13)$$

where \mathbf{S} is the overlap matrix defined by Löwdin.²⁵ Then

$$\mathbf{g}_{\text{MO}} = \mathbf{g}_{\text{LCAO}}^{\text{orth}} + \mathbf{g}_{\text{AO}}^{\text{orth}}, \quad (2.14)$$

each term having an expression analogous to Eqs. (2.9) and (2.10).

Let us now assume that \mathbf{B} can be block diagonalized as follows:

$$\mathbf{B}(\mathbf{Q}) = \begin{pmatrix} \cos \omega & -\sin \omega & | & 0 \\ \sin \omega & \cos \omega & | & 0 \\ \hline 0 & 0 & | & \mathbf{U}^{\text{III}}(\mathbf{Q}) \end{pmatrix} \cdot \mathbf{U}^{\text{III}}, \quad (2.15)$$

where the angle ω and the elements of the orthogonal matrix \mathbf{U}^{II} depend on the nuclear coordinates \mathbf{Q} , whereas \mathbf{U}^{III} is a constant orthogonal matrix. In the particular case where \mathbf{U}^{II} is also a constant matrix, then

$$\mathbf{g}_{\text{LCAO}}^{\text{orth}} = T_{12}(\mathbf{Q}) \nabla \omega. \quad (2.16)$$

If \mathbf{U}^{II} is not constant, $\mathbf{g}_{\text{LCAO}}^{\text{orth}}$ is a sum of several pair contributions. However, as argued above, T_{12} is the leading term and it is often a good approximation to neglect the

others. Note that, even if Eq. (2.16) is strictly valid, $\mathbf{g}_{\text{LCAO}}^{\text{orth}}$ is not necessarily an irrotational vector because the element of the transition matrix T_{12} is a function of \mathbf{Q} . Nevertheless, it is easily seen that when the CI coefficients are given by Eq. (2.5) one has

$$\partial_a T_{12} = \left(\frac{dT_{12}}{d\theta} \right) \partial_a \theta, \quad (2.17)$$

where the symbol ∂_a represents the partial derivative operator with respect to a particular degree of freedom Q_a . The vector $\mathbf{g}_{\text{LCAO}}^{\text{orth}}$ is irrotational if

$$\partial_a \theta \partial_b \omega - \partial_b \theta \partial_a \omega = 0. \quad (2.18)$$

This will be the case if either \mathbf{g}_{CI} or \mathbf{g}_{LCAO} is equal to zero. For example, in the Renner-Teller coupling (see Sec. V), $\mathbf{g}_{\text{CI}} = 0$ and $\partial_a \theta = \partial_b \theta = 0$. When this is not so, we can use the fact that both angles θ and ω parametrize a 2×2 orthogonal transformation.²⁶ Hence, they have the functional form

$$\theta = k \arctan[f_1(\mathbf{Q})/f_2(\mathbf{Q})], \quad (2.19)$$

$$\omega = k' \arctan[f_3(\mathbf{Q})/f_4(\mathbf{Q})], \quad (2.20)$$

so that condition (2.18) becomes

$$\partial_a f_i \partial_b f_j - \partial_b f_i \partial_a f_j = 0, \quad 1 \leq i, j \leq 4. \quad (2.21)$$

In practice, it is not unreasonable to expect this condition to be fulfilled. For example, if f_1 and f_3 are constant, whereas f_2 and f_4 are linear functions of the coordinates \mathbf{Q} . This implies that the loci of the angles θ and ω are a set of parallel straight lines. One is then dealing with an avoided crossing.¹⁶ Conditions (2.18) and (2.21) will be fulfilled if both sets are parallel to a common direction. At first sight this may seem an extremely restrictive condition. However, this simply means that this common direction has some simple physical significance determined, e.g., by a low-energy dissociation process. Then, the variation of both the CI and LCAO coefficients is naturally controlled by the orientation in \mathbf{Q} space of the reaction coordinate. This is especially clear if the avoided crossing takes place at fairly large distances along the reaction coordinate, i.e., if the region of strong nonadiabatic interaction corresponds to a weak interaction between both fragments. Then, the internal degrees of freedom can hardly be expected to change the nature of the wave function and the loci of both θ and ω are quite naturally oriented along the reaction coordinate.

(d) A similar discussion is possible if several pairs of MO's give rise to nonnegligible elements of the transition matrix. The condition is then that the first matrix of the right-hand side of Eq. (2.15) be block diagonal for each (l, m) pair having a nonnegligible T_{lm} and that each block be parametrized by the same angle ω .

In summary, there exist a number of particular cases in which \mathbf{g}_{CI} and \mathbf{g}_{LCAO} are to a good approximation irrotational vectors. From a mathematical point of view, these cases are very special if not exceptional. However, this is not so in practice because they correspond to standard physical situations having a simple interpretation. When these conditions are not satisfied, a detailed mathematical treatment is necessary to see whether $\text{curl } \mathbf{g}$ does not vanish by the combination of other circumstances. If not, the concept of diabatic state loses much of its interest.

In addition, it should be kept in mind that, unless \mathbf{g}_{MO} vanishes [case 2(a)], there always subsists a contribution to \mathbf{g} due to the displacement in space of the nuclei on which the AO's are centered. In general, \mathbf{g}_{AO} cannot be equated with a gradient because its curl does not in general vanish (Sec. IV). It is then crucial to compare its magnitude with that of \mathbf{g}_{CI} and \mathbf{g}_{LCAO} . This will be done in Sec. IV.

III. DIRECT CONSTRUCTION OF DIABATIC STATES

The calculation of the coupling vector \mathbf{g} is a tedious task.^{19,20,27,28} Therefore, one often finds in the literature, especially that relative to diatomic molecules and atom-atom collisions,³ attempts to obtain directly (sometimes to guess) an expression of the diabatic states, e.g., by assuming that they retain everywhere their asymptotic expression or by approximating them by a single configuration state function. In this section, we examine the rationale of this approach in the case of polyatomic molecules.

The diabatic functions $\chi_1(q, \mathbf{Q})$ and $\chi_2(q, \mathbf{Q})$ should obey Eq. (1.5). However, we start from their expansion in a complete set: that of the adiabatic functions at some reference point \mathbf{Q}_0 , right in the middle of the region of strong nonadiabatic interaction. (This is much more satisfactory than considering their asymptotic expression since there is vagueness in the definition of the boundaries of the coupling region.)

$$\begin{pmatrix} \chi_1(q, \mathbf{Q}) \\ \chi_2(q, \mathbf{Q}) \end{pmatrix} = \mathbf{R} \begin{pmatrix} \psi_1(q, \mathbf{Q}_0) \\ \psi_2(q, \mathbf{Q}_0) \\ \vdots \\ \psi_N(q, \mathbf{Q}_0) \end{pmatrix} = \mathbf{R}\mathbf{C}(\mathbf{Q}_0) \begin{pmatrix} \eta_1(q, \mathbf{Q}_0) \\ \eta_2(q, \mathbf{Q}_0) \\ \vdots \\ \eta_N(q, \mathbf{Q}_0) \end{pmatrix}, \quad (3.1)$$

\mathbf{C} being a $(N \times N)$ orthogonal matrix [Eq. (2.1)], whereas \mathbf{R} is a $(2 \times N)$ matrix whose structure will now be discussed.

(1) The fixed set (crude adiabatic) approximation^{17,18} is the zero-order approximation in which \mathbf{R} is the upper part of a block-diagonal orthogonal matrix:

$$\begin{pmatrix} \mathbf{D} & \mathbf{0} \\ \mathbf{0} & \mathbf{U}^{\text{IV}} \end{pmatrix}. \quad (3.2)$$

This form ensures that χ_1 and χ_2 are expressed in terms of only adiabatic functions. \mathbf{D} is a 2×2 constant matrix for which various expressions can be proposed: either the unit matrix or, more appropriately for an avoided crossing:

$$(2)^{-1/2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}.$$

As argued by Mead and Truhlar¹⁵ among others,⁵ with such a definition, the adiabatic states calculated by inverting Eq. (3.1) will agree with the genuine states only in a very restricted range of configuration space.

(2) Much less crude is the approximation in which a basis set is used that follows the nuclei but does not otherwise distort.^{12,29} This amounts to keeping the block-diagonal character of \mathbf{R} while allowing the CSF's to follow the nuclei. Equation (3.1) is now replaced by

$$\begin{pmatrix} \chi_1(q, \mathbf{Q}) \\ \chi_2(q, \mathbf{Q}) \end{pmatrix} = \mathbf{RC}(\mathbf{Q}_0) \begin{pmatrix} \eta_1(q, \mathbf{Q}) \\ \eta_2(q, \mathbf{Q}) \\ \vdots \\ \eta_N(q, \mathbf{Q}) \end{pmatrix} \quad (3.3)$$

with \mathbf{R} being the same constant ($2 \times N$) matrix as in Eq. (3.1). In contradistinction to the fixed set approximation, the CSF's are now allowed to follow the nuclear displacements.

According to this definition, the diabatic functions χ_1 and χ_2 are now expressed as an orthogonal linear combination with constant coefficients of nonconstant CSF's. The constant CI coefficients are those of the adiabatic functions at \mathbf{Q}_0 transformed by the posited 2×2 matrix. The LCAO coefficients are determined variationally and the AO's follow the nuclear positions.

With this definition, there is no difficulty in calculating the Hamiltonian matrix in the diabatic representation and in defining therefrom an angle $\theta(\mathbf{Q})$:

$$\theta(\mathbf{Q}) = (1/2) \arctan \{ 2H_{12}(\mathbf{Q}) / [H_{22}(\mathbf{Q}) - H_{11}(\mathbf{Q})] \}. \quad (3.4)$$

The diabatic functions resulting from the present procedure are acceptable if two conditions are fulfilled:

(a) Inserting these functions into the inverted Eq. (1.5) with θ given by Eq. (3.4) should generate adiabatic functions in good agreement with those calculated *ab initio*. This condition also implies that the calculated quantity $[(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}$ should agree with the energy gap ΔE calculated *ab initio*. How large the region where these two equivalent conditions are fulfilled is a question which has to be examined in each particular case (orders of magnitude will be suggested in the next section).

(b) The second condition is that $\langle \chi_2 | \nabla \chi_1 \rangle$ should be smaller than the threshold given by Eq. (1.12). There is no contribution to this term due to the CI coefficients which are now constant. The LCAO coefficients give rise to a contribution which, according to the discussion given in Sec. II, is sometimes negligible. Note that in the present case the transition matrix is constant which simplifies the discussion.

However, unless $\langle \chi_2 | \nabla \chi_1 \rangle$ is zero or negligible because one of the wave functions is doubly excited with respect to the other, a third contribution subsists which results from the fact that the atomic orbitals follow the nuclear motion.

When criteria (a) and (b) are both fulfilled the set of diabatic states can be used to calculate transition probabilities.

As a final remark, we note that the present procedure is simpler than that of Sec. II but also less general. The two gradients $\nabla\theta$ (resulting from the CI coefficients) and $\nabla\omega$ (due to the LCAO coefficients) have to be added to give a total gradient which, if \mathbf{g}_{AO} is negligible, should be equal to

the coupling vector \mathbf{g} . It is sometimes observed that the two gradients have opposite signs, e.g., when the CI coefficients try to compensate the inadequacies of the LCAO coefficients obtained from an inappropriate SCF calculation.²⁰ (This results from the fact that both wave functions have to be built on the same set of MO's and that it is sometimes hard to find a SCF calculation which is adequate for both.) In such a case, the second approach leads to great difficulties.

IV. PROPERTIES OF THE AO BASIS SET

Consider a basis set of nonorthogonal AO's $|\xi_r\rangle$. It is readily seen that $\langle \xi_r | \nabla \xi_s \rangle$ is not, in general, an irrotational vector. Let Q_a and Q_b denote two particular degrees of freedom and let $\xi(\Delta a, \Delta b)$ represent an AO centered on point $(\Delta a, \Delta b)$. The quantity

$$\begin{aligned} \partial_a \langle \xi_r | \partial_b \xi_s \rangle - \partial_b \langle \xi_r | \partial_a \xi_s \rangle \\ = \langle \partial_a \xi_r | \partial_b \xi_s \rangle - \langle \partial_b \xi_r | \partial_a \xi_s \rangle \end{aligned} \quad (4.1)$$

does not, in general, vanish. This is easily seen if derivatives are replaced by finite differences. One has, e.g. (see Fig. 1),

$$\begin{aligned} \langle 2s(0, \Delta b) | 2p_x(\Delta a, 0) \rangle \\ = - \langle 2s(\Delta a, 0) | 2p_x(0, \Delta b) \rangle. \end{aligned} \quad (4.2)$$

We have calculated numerically about 200 integrals $\langle \xi_r | \nabla \xi_s \rangle$ with the most commonly used $2s$ and $2p$ AO's of carbon and oxygen and $1s$ hydrogen orbitals centered at reasonable distances. These integrals were found to range between 0.01 and 0.8 \AA^{-1} for valence displacements and between 10^{-4} and 10^{-2} deg^{-1} for bending motions. These values are useful in determining the thresholds of tolerance mentioned in the previous sections. However, it should be kept in mind that what matters is the total value of \mathbf{g}_{AO} which [cf. Eq. (2.10)] is given by a multiple summation of terms with different signs. It thus seems reasonable to admit as a rule of thumb that \mathbf{g}_{AO} can be neglected for strong nonadiabatic interactions with \mathbf{g}^{max} substantially larger than 1.0 \AA^{-1} or 10^{-2} deg^{-1} . This concurs with Mead and Truhlar's estimates according to which the nonremovable part of the coupling is of the order unity in atomic units. In the two-state approximation, the components of \mathbf{g} are nearly always^{16,19,20,27} close to Lorentzian functions with an area equal to $\pi/2$. (This is no longer true if more than two states interact.³⁰) Therefore, a large value of \mathbf{g}^{max} implies a small extension of the region of strong nonadiabatic coupling. Thus, the methods described in Secs. II and III will be satisfactory for strong and localized coupling and will fail when

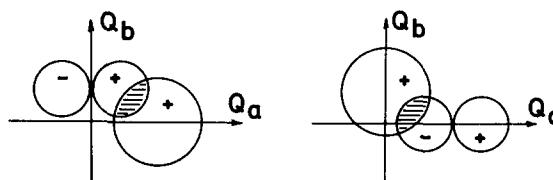


FIG. 1. The translation of atomic basis functions along with the nuclear centers does not give rise to an irrotational coupling vector (see the text).

the coupling is weak and operates over a large region (in practice, larger than a few tenths of an Å).

The only way to get rid of \mathbf{g}_{AO} would be to work with a basis set of fixed AO's frozen at some point \mathbf{Q}_0 . This gives rise to another estimate which confirms the previous orders of magnitude. Let us carry out the LCAO expansion in a basis set consisting of M AO's which we assume orthogonal for simplicity. In general, such a set centered on point \mathbf{Q}_0 is not complete at a neighboring point \mathbf{Q} and one has to include a number n of additional AO's. Then

$$\xi_r(\mathbf{Q}) = \sum_{i=1}^{M+n} v_{ri} \xi_i(\mathbf{Q}_0), \quad 1 \leq r \leq M \quad (4.3)$$

with

$$v_{ri} = \langle \xi_r(\mathbf{Q}) | \xi_i(\mathbf{Q}_0) \rangle. \quad (4.4)$$

Substituting into Eq. (2.11) one has

$$\begin{aligned} \langle \phi_i | \nabla \phi_j \rangle &= \sum_r \sum_s^M b_{ir}(\mathbf{Q}) \nabla b_{js}(\mathbf{Q}) \\ &+ \sum_r \sum_s^M b_{ir}(\mathbf{Q}) b_{js}(\mathbf{Q}) \sum_t^{M+n} v_{rt} \nabla v_{st}. \end{aligned} \quad (4.5)$$

The first term of the right-hand side contributes to \mathbf{g}_{LCAO} and has been discussed in Sec. II(2). The troublesome terms are $v_{rt} \nabla v_{st}$ which typically are of the order of 0.4 Å^{-1} . This confirms our previous estimates.

V. GENUINE CROSSINGS

Our considerations have so far been restricted to avoided crossings and have excluded genuine intersections of the conical, Jahn–Teller, and Renner–Teller type. The reason is that in the latter cases θ becomes a multivalued function^{16–18} (modulo π or 2π), at least in the framework of the semiclassical approximation where vibrational wave functions are not introduced.³¹ In fact, θ is single valued in an exceptional case only: that of the avoided crossing with parallel energy contours. The loci of θ are then a set of parallel straight lines.¹⁶

However, our previous discussion still applies if a branch cut is introduced. Consider a system with two nuclear degrees of freedom Q_a , Q_b (Fig. 2). When the polar angle γ varies from 0 to 2π , θ varies from 0 to π (conical and Jahn–Teller intersections) or from 0 to 2π (Renner–Teller interactions).^{16–18,20} In order to keep θ single valued, one sets up a branch cut along the positive part of axis Q_a . The numerical integrations of \mathbf{g} which is necessary to calculate θ ^{13,14,16,20} should be carried out along closed loops which do not cross this branch cut. As in our previous discussion, such calculations require either that $\mathbf{g}_{\text{MO}} = 0$ or that \mathbf{g}_{AO} be sufficiently small.

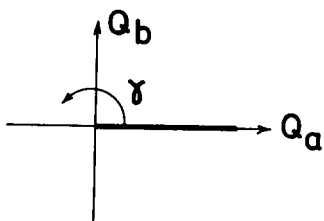


FIG. 2. Branch cut not to be crossed during the numerical integrations leading to the angle θ .

VI. THE ELECTRON TRANSLATION FACTOR

It has been seen repeatedly that the main source of the difficulties encountered in the definition of the diabatic states is to be found in the properties of the basis set of AO's. The problem is well known in the theory of diatomic collisions and has given rise to an important literature.^{12,28,32} As shown by Delos and Thorson,¹² the use of a basis set which properly describes the translation of the electrons along with the nuclei increases the insight into the problem and provides a much more satisfactory definition of the diabatic representation. A clear distinction is introduced between the change of character of the adiabatic wave functions near a crossing or an avoided crossing and the simple translation of the basis functions along with the moving nuclei.

Let us introduce a new basis set of AO's $|\tilde{\xi}_p\rangle$, each member of which is equal to an ordinary AO multiplied by a so-called electron translation factor (ETF) F_p whose expression will be specified later on:

$$|\tilde{\xi}_p\rangle = F_p |\xi_p\rangle. \quad (6.1)$$

Throughout this section, the quantities to which a tilde is appended represent wave functions built on this ETF-modified basis set. Thus, $\tilde{\psi}_i$ is a linear combination of Slater determinants built on MO's which are linear combinations of these $\tilde{\xi}_p$'s.

A convenient form of the coupled equations in this ETF-modified basis set has been derived by Delos and Thorson for the diatomic one-electron case. They introduced approximations, adequate for low nuclear velocities, which consist in expanding the F_p 's in a power series, in neglecting all terms of order v^2 and higher, and also those containing accelerations. We now wish to show briefly that the main results of their analysis are transferable to polyatomic molecules. This can be seen as follows.

Let X_S, Y_S, Z_S represent the Cartesian coordinates of a particular nucleus S . Then, the single-center ETF associated with the AO ξ_s centered on S can be written, within this approximation:

$$F_S = 1 + (im/\hbar)(\dot{X}_S x + \dot{Y}_S y + \dot{Z}_S z). \quad (6.2)$$

The velocity-dependent operator can either be written as the time-derivative operator or as the nuclear kinetic energy operator:

$$\frac{i\hbar\partial}{\partial t} = i\hbar\dot{\mathbf{Q}} \cdot \nabla. \quad (6.3)$$

Then, the term $\langle \tilde{\psi}_2 | i\hbar\partial/\partial t | \tilde{\psi}_1 \rangle$ can be split into three terms $\tilde{\mathbf{g}}_{\text{CI}}$, $\tilde{\mathbf{g}}_{\text{LCAO}}$, and $\tilde{\mathbf{g}}_{\text{AO}}$, exactly as in the previous sections.

To keep the formulas as simple as possible, the cumbersome CI and LCAO expansions will not be repeated in what follows. The products of LCAO coefficients, the elements of the transition matrix, and the relevant summation signs in front of the expression of each matrix element involving AO's are to be understood. Then, following Delos and Thorson:

$$\begin{aligned}
& \left\langle \tilde{\zeta}_r \left| \frac{i\hbar\partial}{\partial t} \right| \tilde{\zeta}_s \right\rangle \\
&= \left\langle F_r \tilde{\zeta}_r \left| i\hbar \left(\frac{\partial F_s}{\partial t} \right) \tilde{\zeta}_s \right\rangle + \left\langle \tilde{\zeta}_r F_r F_s^* \left| i\hbar \frac{\partial \tilde{\zeta}_s}{\partial t} \right\rangle \right. \\
&\approx 0 + i\hbar \left\langle \dot{X}_s \left| \tilde{\zeta}_r \left| \frac{\partial}{\partial X_s} \right| \tilde{\zeta}_s \right\rangle + \dot{Y}_s \left\langle \tilde{\zeta}_r \left| \frac{\partial}{\partial Y_s} \right| \tilde{\zeta}_s \right\rangle \right. \\
&\quad \left. + \dot{Z}_s \left\langle \tilde{\zeta}_r \left| \frac{\partial}{\partial Z_s} \right| \tilde{\zeta}_s \right\rangle \right\}. \quad (6.4)
\end{aligned}$$

Each of these terms, which represents a particular element in the expansion of $\tilde{\mathbf{g}}_{\text{AO}} \cdot \mathbf{Q}$, can be shown to cancel out with similar terms deriving from the matrix element $\langle \tilde{\psi}_2 | H | \tilde{\psi}_1 \rangle$ which also appears in the coupled equations. Let us consider a particular element generated by the one-electron part of H :

$$\langle \tilde{\zeta}_r | H_1 | \tilde{\zeta}_s \rangle = \langle \tilde{\zeta}_r F_r F_s^* | H_1 | \tilde{\zeta}_s \rangle + \langle \tilde{\zeta}_r F_r | [H_1, F_s] | \tilde{\zeta}_s \rangle. \quad (6.5)$$

Adopting Delos and Thorson's terminology, the first term of the right-hand side gives rise to the ordinary matrix element $\langle \tilde{\zeta}_r | H_1 | \tilde{\zeta}_s \rangle$ plus an element of the matrix γ , whereas the commutator term is an element of the matrix A . Substituting Eqs. (6.2) and (6.3) into the latter, one finds

$$\begin{aligned}
\langle \tilde{\zeta}_r F_r | [H_1, F_s] | \tilde{\zeta}_s \rangle &= \langle \tilde{\zeta}_r | [\dot{X}_s p_x + \dot{Y}_s p_y + \dot{Z}_s p_z] | \tilde{\zeta}_s \rangle \\
&= i\hbar \left\langle \tilde{\zeta}_r \left| \dot{X}_s \left(\frac{\partial}{\partial X_s} \right) + \dot{Y}_s \left(\frac{\partial}{\partial Y_s} \right) + \dot{Z}_s \left(\frac{\partial}{\partial Z_s} \right) \right| \tilde{\zeta}_s \right\rangle, \quad (6.6)
\end{aligned}$$

since $\tilde{\zeta}_r$ and $\tilde{\zeta}_s$ are "fixed one-center orbitals" in the sense defined by Delos and Thorson, i.e., they depend upon the nuclear coordinates X, Y, Z , as

$$\tilde{\zeta}_s(q; Q) = \tilde{\zeta}_s(x - X_s, y - Y_s, z - Z_s).$$

Then

$$\frac{\partial \tilde{\zeta}_s}{\partial x} = - \frac{\partial \tilde{\zeta}_s}{\partial X_s}. \quad (6.7)$$

Since the quantities (6.4) and (6.6) appear with opposite signs in the coupled equations, they cancel each other out. This means that part of the coupling which derives from the displacement of the electrons as they follow the nuclear motion is canceled by the inclusion of the ETF's.

Thus, the simplest way of incorporating the major ETF correction consists in simply ignoring the component \mathbf{g}_{AO} . However, this procedure is not exact: the ETF's also introduce a further first-order correction (called γ by Delos and Thorson), which results from the expansion of $F_r F_s^*$ and which gives rise to an additional velocity-dependent coupling term. The latter has a double origin. Products $F_r F_s^*$ appear both in the expansion of $\langle \tilde{\zeta}_p | H | \tilde{\zeta}_q \rangle$ and in the expansion of $\tilde{\mathbf{g}}_{\text{LCAO}}$. They give rise to the terms denoted as η and σ ,¹² respectively. Since the calculation of this additional coupling term would raise great difficulties, it is interesting to look for circumstances under which it spontaneously vanishes.

(i) As shown by Delos and Thorson, γ vanishes in a basis where the Hamiltonian is diagonal. Now, the theory of molecular ETF's is intrinsically more complicated than that of their atomic counterparts. Even if the calculations could

be done, γ would indeed be found to vanish, but the value of A would be modified, and the cancellation between Eqs. (6.4) and (6.6) would be lost.

(ii) There exists another case where γ is found to vanish. This happens in precisely the most favorable circumstance recognized in Sec. II, i.e., when ψ_1 and ψ_2 are doubly excited with respect to each other. Then, $\langle \tilde{\psi}_1 | i\hbar\partial/\partial t | \tilde{\psi}_2 \rangle$ reduces to its first term $\tilde{\mathbf{g}}_{\text{CI}}$ only. Furthermore, $\langle \tilde{\psi}_1 | H | \tilde{\psi}_2 \rangle$ can be split into a one-electron part which obviously vanishes, and a two-electron part: $\langle \tilde{\psi}_1 | (r_{12})^{-1} | \tilde{\psi}_2 \rangle$, which can be shown to reduce to $\langle \tilde{\psi}_1 | (r_{12})^{-1} | \tilde{\psi}_2 \rangle$.

All the two-center atomic integrals: $[\tilde{\zeta}_A \tilde{\zeta}_A' | \tilde{\zeta}_B \tilde{\zeta}_B']$, where $\tilde{\zeta}_A$ and $\tilde{\zeta}_A'$ are two possibly different AO's centered on atom A (i.e., all the Coulombic plus some other two-electron integrals) reduce identically to their usual counterpart

$$\begin{aligned}
& [\tilde{\zeta}_A \tilde{\zeta}_A' | \tilde{\zeta}_B \tilde{\zeta}_B'] \\
& [\tilde{\zeta}_A \tilde{\zeta}_A' | \tilde{\zeta}_B \tilde{\zeta}_B'] \\
&= \int \int F_A^*(1) F_A(1) F_B^*(2) F_B(2) \tilde{\zeta}_A(1) \tilde{\zeta}_A'(1) \\
&\quad \times \tilde{\zeta}_B(2) \tilde{\zeta}_B'(2) (r_{12})^{-1} d\tau_1 d\tau_2 \\
&= \int \int \tilde{\zeta}_A(1) \tilde{\zeta}_A'(1) \tilde{\zeta}_B(2) \tilde{\zeta}_B'(2) (r_{12})^{-1} d\tau_1 d\tau_2 \\
&= [\tilde{\zeta}_A \tilde{\zeta}_A' | \tilde{\zeta}_B \tilde{\zeta}_B']. \quad (6.8)
\end{aligned}$$

Similarly, the expansion of the exchange-like integrals $[\tilde{\zeta}_A \tilde{\zeta}_B' | \tilde{\zeta}_B \tilde{\zeta}_A']$ contains a term $F_A^*(1) F_A(2) F_B^*(1) F_B(2) = 1 + [(im/\hbar) [(\mathbf{Q}_A - \mathbf{Q}_B) \cdot (\mathbf{p}_2 - \mathbf{p}_1)]]$. This introduces into a symmetric integrand a first-order term which is antisymmetric with respect to the exchange of two electrons. The integral then reduces to its zeroth-order term $[\tilde{\zeta}_A \tilde{\zeta}_B' | \tilde{\zeta}_B \tilde{\zeta}_A']$.

The three- and four-center integrals can be reduced by expansion techniques to two-center integrals.

Therefore, when the problem consists in an interplay between two electronic states which are doubly excited with respect to each other, the velocity-dependent coupling term results exclusively from the change of physical character of the states and can be calculated very simply by differentiation of the CI coefficients only.

VII. CONCLUSIONS

It has been repeatedly seen that, as was to be expected from Mead and Truhlar's analysis,¹⁵ the construction of approximately diabatic states requires a combination of circumstances. The problem is to recognize when this is possible in practice. Two approaches have been discussed. One of them starts when the other ends up but in the favorable cases they both should lead to the same diabatic basis set.

We have proposed a set of criteria to examine whether a set of CI wave functions calculated *ab initio* can be transformed into a pair of useful diabatic states. Since these conditions are sufficient but not necessary, it might be possible to find additional circumstances which allow diabatic states to be constructed. However, the underlying reasons would then be obscure and it is best not to depend on them. We believe that the cases which are most frequently encountered in practice have been considered here. On the other hand,

counterexamples have been published in the literature³³ where the only solution which could be extracted from an *ab initio* calculation was the trivial solution,¹⁵ valid in an extremely restricted range of internuclear distances. It would be useful to discuss these cases as indicated in Sec. II in order to determine the origin of the breakdown.

As pointed out by several authors,^{5,11,12,15} it is not possible to satisfy Eqs. (1.6) and (1.9) exactly. Neither is it desirable: $\nabla\chi_i$ should not vanish because we want the electronic wave functions to follow the nuclear centers. The problem thus consists in detecting those cases where in a limited region the irrotational part of \mathbf{g} becomes large with respect to its other component.¹⁵ The conditions which have been proposed are never rigorously satisfied, even in the most favorable situations listed in Sec. II. They should be considered as a mathematical limit to be approached. The closer these conditions are obeyed, the larger the irrotational part of \mathbf{g}_{CI} and \mathbf{g}_{LCAO} and the clearer the rôle played by the different components of \mathbf{g} . As the limit is approached, \mathbf{g}_{CI} and \mathbf{g}_{LCAO} become irrotational vectors which describe the change of character of the electronic adiabatic wave functions as one goes across the coupling region, whereas \mathbf{g}_{AO} accounts for the fact that the electronic wave functions follow the nuclear centers.

In summary, the conclusions reached by Delos and Thorson¹² for diatomic systems remain valid for polyatomic molecules. Approximate diabatic states can be obtained when "that portion of the derivative coupling matrix that represents merely the translation of basis functions along with moving nuclei" is negligible with respect to the part "representing actual change of character..., i.e.,... the part that really is responsible for nonadiabatic transitions." For diatomic molecules, the strategy to be adopted has been given by Mead and Truhlar.¹⁵ For polyatomic molecules, the sufficient criteria can only be approximately fulfilled. It is, therefore, to be expected that each of the three components will contain a nonirrotational part (of the order unity in atomic units). As explained by Mead and Truhlar,¹⁵ approximate diabatic states can be constructed when this part is much smaller than the other one associated with the change in the nature of the wave function. The stronger and the more localized the coupling, the easier it will be the case.²

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