THE ELECTRONIC NON-ADIABATIC COUPLING TERM IN MOLECULAR SYSTEMS: A THEORETICAL APPROACH

MICHAEL BAER

Applied Physics Division, Soreq NRC, Yavne, Israel

CONTENTS

I.   INTRODUCTION

Electronic non-adiabatic effects are an outcome of the Born–Oppenheimer–Huang treatment and as such are a result of the distinction between the fast moving electrons and the slow moving nuclei [1,2]. The non-adiabatic coupling terms, together with the adiabatic potential energy surfaces (which are also an outcome of this treatment) form the origin for the driving forces that govern the

motion of the atoms in the molecular system. Still they differ from the potential energy surfaces because they are, as we shall show, *derivative coupling* and as such they are vectors, in contrast to adiabatic potential energy surfaces, which are scalars.

The ordinary way to get acquainted with objects like the non-adiabatic coupling terms is to derive them from first principles, via ab initio calculations [4–6], and study their spatial structure—somewhat reminiscent of the way potential energy surfaces are studied. However, this approach is not satisfactory because the non-adiabatic coupling terms are frequently singular (in addition to being vectors), and therefore theoretical means should be applied in order to understand their role in molecular physics. During the last decade, we followed both courses but our main interest was directed toward studying their physical–mathematical features [7–13]. In this process, we revealed (1) the necessity to form sub-Hilbert spaces [9,10] in the region of interest in configuration space and (2) the fact that the non-adiabatic coupling *matrix* has to be *quantized* for this sub-space [7–10].

In the late 1950s and the beginning of the 1960s Longuet-Higgins and colleagues [14–17] discovered one of the more interesting features in molecular physics related to the Born–Oppenheimer–Huang electronic adiabatic eigenfunctions (which are parametrically dependent on the nuclear coordinates). They found that these functions, when surrounding a point of degeneracy in configuration space, may acquire a phase that leads to a flip of sign of these functions. Later, this feature was explicitly demonstrated by Herzberg and Longuet-Higgins [16] for the Jahn–Teller conical intersection model [18–29] (see also Appendix A). This interesting observation implies that if a molecular system possesses a conical intersection at a point in configuration space the relevant electronic eigenfunctions that are parametrically dependent on the nuclear coordinates, are multivalued (this finding was later confirmed for a real case following ab initio calculations [30]). No hints were given to the fact that this phenomenon is associated with the electronic non-adiabatic coupling terms. In this chapter, we not only discuss this connection but also extend the two-state case to the multistate cases.

In molecular physics, one distinguishes between (1) the adiabatic framework that is characterized by the adiabatic surfaces and the above-mentioned non-adiabatic coupling terms [31–46] and (2) the diabatic framework that is characterized by the smoothly behaving potential couplings (and the nonexistence of non-adiabatic couplings) [31–53]. The adiabatic framework is in most cases inconvenient for treating the nuclear Schrödinger equation because of two reasons. (1) The non-adiabatic coupling terms are usually spiky [3,54] and frequently singular [3,36,55,56] so that any numerical recipe for solving this equation becomes unstable. (2) The singular feature of the non-adiabatic coupling terms dictates certain boundary conditions that may not be easily implemented for deriving the solution within this framework [56]. Therefore,

transforming to the diabatic framework, to be termed *diabatization*, is essentially enforced when treating the multistate problem as created by the Born–Oppenheimer–Huang approach.

The diabatization can be carried out in various ways—and we discuss some of them here—but the way recommended in the present composition is based on the following two-step process: (1) Forming the Schrödinger equation within the adiabatic framework (which also includes the non-adiabatic coupling terms) and (2) employing a unitary transformation that eliminates these terms from the adiabatic Schrödinger equation and replacing them with the relevant potential coupling terms [34–36,57]. This two-step process creates, as will be shown, an opportunity to study the features of the non-adiabatic coupling terms and the results of this study constitute the main subject of this chapter.

The theoretical foundations for this study were laid in a 1975 publication [34] in which this transformation matrix, hence to be termed the adiabatic-to-diabatic transformation matrix, was shown to be a solution of an integral equation defined along a given contour. In what follows, this equation will be termed as a *line integral*. The line integral reduces, for the two-state case, to an ordinary integral over the corresponding non-adiabatic coupling term, and yields the adiabatic-to-diabatic transformation angle [34–36]. In addition, the sufficient conditions that guarantee the existence and the single-valuedness of the integral-equation solution (along a contour in a given region in configuration space) were derived. In this context, it was shown that these conditions, hence termed the *curl* conditions, are fulfilled by the system of Born–Oppenheimer–Huang eigenfunctions that span a full-Hilbert space [34], and sometimes, under certain conditions, also span a sub-Hilbert space [8–10].

These two findings form a connection of the theory of the electronic non-adiabatic coupling terms with the Yang–Mills isotopic gauge transformation [58,59]. The existence of the *curl* conditions may lead to nonzero Yang–Mills fields as will be proposed in Section XIV. Still, it is important to emphasize that the curl condition as it emerges from our theory and the Yang–Mills field that is a quantum mechanical extension of the classical electromagnetic theory are far from being identical or of the same origin.

In 1992, Baer and Englman [55] suggested that Berry's topological phase [60–62], as derived for molecular systems, and likewise the Longuet-Higgins phase [14–17], should be related to the adiabatic-to-diabatic transformation angle as calculated for a two-state system [56] (see also [63]). Whereas the Baer–Englman suggestion was based on a study of the Jahn–Teller conical intersection model, it was later supported by other studies [11,12,64–75]. In particular, it can be shown that these two angles are related by comparing the "extended" Born–Oppenheimer *approximation*, once expressed in terms of the gradient of the Longuet-Higgins phase (see Appendix A) and once in terms of the two-state non-adiabatic coupling term [75].

Although the two angles seem to serve the same purpose, there is one fundamental difference between the two: The Longuet-Higgins phase (or the molecular Berry phase), when followed along a closed contour becomes, due to an *ansatz*, a multiple of π. Contrary to this ansatz, the situation with respect to the adiabatic-to-diabatic transformation angle is much more fundamental, because of the close relationship between the non-adiabatic coupling terms and the *diabatic* potentials. It was proved that the corresponding non-adiabatic coupling *matrix* has to be ''quantized'' (see Section IV) in order to yield single-valued diabatic potentials. This ''quantized'' non-adiabatic coupling matrix yields, in the case of a two-state isolated system, an adiabatic-to-diabatic transformation angle, with features as demanded by the Longuet-Higgins ansatz. In other words, the adiabatic-to-diabatic transformation angle when calculated along closed contours becomes, just like the Longuet-Higgins phase, a multiple of π (or zero).

The next question asked is whether there are any indications, from ab initio calculations, to the fact that the non-adiabatic transformation angles have this feature. Indeed such a study, related to the H_3 system, was reported a few years ago [64]. However, it was done for circular contours with exceptionally small radii (at most a few tenths of an atomic unit). Similar studies, for circular and noncircular contours of much larger radii (sometimes up to five atomic units and more) were done for several systems showing that this feature holds for much more general situations [11,12,74]. As a result of the numerous numerical studies on this subject [11,12,64–75] the quantization of a quasi-isolated two-state non-adiabatic coupling term can be considered as established for realistic systems.

Like the curl condition is reminiscent of the Yang–Mills field, the quantization just mentioned is reminiscent of a study by Wu and Yang [76] for the quantization of Dirac's magnetic monopole [77–78]. As will be shown, the present quantization conditions just like the Wu and Yang conditions result from a *phase factor*, namely, the exponential of a phase and not just from a *phase*.

As mentioned above, the starting point in this field is the Born–Oppenheimer–Huang treatment. However in the first derivations [34] it was always assumed that the corresponding Born–Oppenheimer–Huang eigenfunctions form a full-Hilbert space. Here, the derivation is repeated for a finite sub-Hilbert space, which is defined by employing features of the non-adiabatic coupling terms. It will be shown that this particular sub-space behaves, for all practical purposes, as a full-Hilbert space [8–10]. These subjects are treated in Sections II and III. The connection between the non-adiabatic coupling matrix and the uniqueness of the relevant diabatic potential matrix is presented in Section IV; the quantization of the non-adiabatic coupling matrix is discussed in Section V and the conditions for breaking up the complete

Hilbert space into sub-Hilbert spaces and sub-sub-Hilbert spaces are given in Section VI. Three subjects related to topological effects are presented in Sections VII–IX, and multidegeneracy at a point is further (briefly) discussed in Section X. Section XI is devoted to a practical aspect of the theory, namely, how and when one may/can *diabatize* an electronic adiabatic framework. An interesting relationship between the adiabatic-to-diabatic transformation matrix and Wigner's rotation matrix is discussed in Section XII. Two "exotic" subjects—one related to pseudomagnetic fields in molecular systems and the other related to the possibility of calculating the non-adiabatic coupling terms from the curl equations—are presented in Sections XIII and XIV, respectively. Throughout the review, we show results as derived from ab initio calculations. However, more situations and examples are given in Section XV. A summary and conclusions are presented in Section XVI.

II.   THE BORN–OPPENHEIMER–HUANG TREATMENT

A.   The Born–Oppenheimer Equations for a Complete Hilbert Space

The Hamiltonian, $\mathbf{H}$, of the nuclei and the electrons is usually written in the following form:

$$\mathbf{H} = \mathbf{T}_n + \mathbf{H}_e(e \mid n) \tag{1}$$

where $\mathbf{T}_n$ is the nuclear kinetic energy, $\mathbf{H}_e(e \mid n)$ is the electronic Hamiltonian that also contains the nuclear Coulombic interactions and depends parametrically on the nuclei coordinates, and e and n stand for the electronic and the nuclear coordinates, respectively.

The Schrödinger equation to be considered is of the form:

$$(\mathbf{H} - E)\Psi(e, n) = 0 \tag{2}$$

where E is the total energy and $\Psi(e,n)$ is the complete wave function that describes the motions of both the electrons and the nuclei. Next, we employ the Born–Oppenheimer–Huang expansion:

$$\Psi(e, n) = \sum_{i=1}^{N} \psi_i(n)\zeta_i(e \mid n) \tag{3}$$

where the $\psi_i(n)$, $i = 1, \ldots, N$ are nuclear-coordinate dependent coefficients (recognized later as the nuclear wave functions) and $\zeta_i(e \mid n), i = 1, \ldots, N$ are the electronic eigenfunctions of the above introduced electronic Hamiltonian:

$$[\mathbf{H}_e(e \mid n) - u_i(n)]\zeta_i(e \mid n) = 0 \qquad i = 1, \ldots, N \tag{4}$$

Here $u_i(n), i = 1, \ldots, N$ are the electronic eigenvalues recognized, later, as the (adiabatic) potential energy surfaces (PES) that governs the motion of the nuclei. In this treatment, we assume that the Hilbert space is of dimension N. Substituting Eq. (3) in Eq. (2), multiplying it from the left by $\zeta_j(e \mid n)$, and integrating over the electronic coordinates while recalling Eqs. (1) and (4), yields the following set of coupled equations:

$$\sum_{i=1}^{N} \langle \zeta_j | \mathbf{T}_n \psi_i(n) | \zeta_i \rangle + (u_j(n) - E)\psi_j(n) = 0 \qquad j = 1, \ldots, N \qquad (5)$$

where the bra–ket notation means integration over electronic coordinates. To continue, we recall that the kinetic operator $\mathbf{T}_n$ can be written (in terms of mass-scaled coordinates) as

$$\mathbf{T}_n = -\frac{1}{2m}\mathbf{V}^2 \qquad (6)$$

where m is the mass of the system and $\mathbf{V}$ is the gradient (vector) operator. By substituting Eq. (6) in Eq. (5) yields the more explicit form of the Born–Oppenheimer–Huang system of coupled equations:

$$-\frac{1}{2m}\nabla^2\psi_j + (u_j(n) - E)\psi_j - \frac{1}{2m}\sum_{i=1}^{N}(2\tau_{ji}^{(1)} \cdot \nabla\psi_i + \tau_{ji}^{(2)}\psi_i) = 0$$
$$j = 1, \ldots, N \qquad (7)$$

where $\tau^{(1)}$ is the non-adiabatic (vector) matrix of the first kind with the elements:

$$\tau_{ji}^{(1)} = \langle \zeta_j | \nabla \zeta_i \rangle \qquad (8a)$$

and $\tau^{(2)}$ is non-adiabatic (scalar) matrix of the second kind, with the elements:

$$\tau_{ji}^{(2)} = \langle \zeta_j | \nabla^2 \zeta_i \rangle \qquad (8b)$$

For a system of real electronic wave functions, $\tau^{(1)}$ is an antisymmetric matrix.

Equation (7) can also be written in a matrix form as follows:

$$-\frac{1}{2m}\nabla^2\mathbf{\Psi} + (\mathbf{u} - E)\mathbf{\Psi} - \frac{1}{2m}(2\tau^{(1)} \cdot \nabla + \tau^{(2)})\mathbf{\Psi} = 0 \qquad (9)$$

where $\mathbf{\Psi}$ is column vector that contains nuclear functions.

B.   The Born–Oppenheimer–Huang Equation for a (Finite) Sub-Hilbert Space

Next, the full-Hilbert space is broken up into two parts—a finite part, designated as the P space, with dimension M, and the complementary part, the Q space (which is allowed to be of an infinite dimension). The breakup is done according to the following criteria [8–10]:

$$\tau_{ij}^{(1)} \cong 0 \qquad \text{for} \qquad i \leq M \qquad j > M \tag{10}$$

In other words, the non-adiabatic coupling terms between P and Q states are all assumed to be zero. These requirements will later be reconsidered for a relaxed situation where these coupling terms are assumed to be not necessarily identically zero but small, that is, of the order ε in regions of interest.

To continue, we define the following two relevant Feshbach projection operators [79], namely, P_M, the projection operator for the P space

$$\mathrm{P}_M = \sum_{j=1}^{M} |\zeta_j\rangle \langle \zeta_j| \tag{11a}$$

and Q_M, the projection operator for the Q space

$$\mathrm{Q}_M = I - P_M \tag{11b}$$

Having introduced these operators, we are now in a position to express the P part of the $\tau^{(2)}$ matrix (to be designated as $\tau_M^{(2)}$) in terms of the P part of $\tau^{(1)}$ (to be designated as $\tau_M^{(1)}$). To do that, we consider Eq. (8a) and derive the following expression:

$$\nabla \tau_{ji}^{(1)} = \nabla \langle \zeta_j | \nabla \zeta_i \rangle = \langle \nabla \zeta_j \nabla \zeta_i \rangle + \langle \zeta_j | \nabla^2 \zeta_i \rangle$$

or, by recalling Eq. (8b), we get

$$\tau_{ji}^{(2)} = -\langle \nabla \zeta_j | \nabla \zeta_i \rangle + \nabla \tau_{ji}^{(1)} \tag{12}$$

The first term on the right-hand side can be further treated as follows:

$$\langle \nabla \zeta_j | \nabla \zeta_i \rangle = \langle \nabla \zeta_j P_M + Q_M | \nabla \zeta_i \rangle$$

which for $i, j \leq M$ becomes

$$\langle \nabla \zeta_j | \nabla \zeta_i \rangle |_M = \langle \nabla \zeta_j | P_M | \nabla \zeta_i \rangle = \sum_{k=1}^{M} \langle \nabla \zeta_j | \zeta_k \rangle \langle \zeta_k | \nabla \zeta_i \rangle \tag{13}$$

(the contribution due to Q_M can be shown to be zero), or also:

$$\langle \nabla \zeta_j | \nabla \zeta_i \rangle |_M = (\tau_M^{(1)})_{ij}^2 \qquad i,j \leq M \tag{13a}$$

where $\tau_M^{(1)}$ is, as mentioned above, of dimension M. Therefore within the Pth subspace the matrix $\tau_M^{(2)}$ can be presented in terms of $\tau_M^{(1)}$ in the following way:

$$\tau_M^{(2)} = (\tau_M^{(1)})^2 + \nabla \tau_M^{(1)} \tag{14}$$

Substituting the matrix elements of Eq. (14) in Eq. (7) yields the final form of the Born–Oppenheimer–Huang equation for the P subspace:

$$-\frac{1}{2m} \nabla^2 \Psi + \left(u - \frac{1}{2m} \tau_M^2 - E \right) \Psi - \frac{1}{2m} (2\tau_M \cdot \nabla + \nabla \tau_M) \Psi = 0 \tag{15}$$

where the dot designates the scalar product, Ψ is a column matrix that contains the nuclear functions $\{\psi_i; \ i = 1, \ldots, M\}$, $\mathbf{u}$ is a diagonal matrix that contains the adiabatic potentials, and τ_M, for reasons of convenience, replaces $\tau_M^{(1)}$. Equation (15) can also be written in the form [9]:

$$-\frac{1}{2m} (\nabla + \tau_M)^2 \Psi + (u - E) \Psi = 0 \tag{16}$$

which is writing the Schrödinger equation more compactly. (A similar Hamiltonian was employed by Pacher et al. [41] within their block-diagonalized approach to obtain quasidiabatic states.)

III. THE ADIABATIC-TO-DIABATIC TRANSFORMATION

A. The Derivation of the Adiabatic-to-Diabatic Transformation Matrix

The aim in performing what is termed the adiabatic-to-diabatic transformation is to eliminate from Eq. (16) the eventually problematic matrix, τ_M, which is done by replacing the column matrix Ψ in Eq. (16) by another column matrix Φ where the two are related as follows:

$$\Psi = A\Phi \tag{17}$$

At this stage, we would like to emphasize that the same transformation has to be applied to the electronic adiabatic basis set in order not to affect the total wave function of both the electrons and the nuclei. Thus if ξ is the electronic basis set that is attached to Φ then ζ and ξ are related to each other as

$$\xi = \zeta \mathbf{A}^\dagger \tag{18}$$

Here, $\mathbf{A}$ is an undetermined matrix of the coordinates ($\mathbf{A}^\dagger$ is its Hermitian conjugate). Our next step is to obtain an $\mathbf{A}$ matrix, which will eventually simplify Eq. (16) by eliminating the τ_M matrix. For this purpose, we consider the following expression:

$$
\begin{aligned}
(\nabla + \tau_M)^2 \mathbf{A}\mathbf{\Phi} &= (\nabla + \tau_M)(\nabla + \tau_M)\mathbf{A}\mathbf{\Phi} \\
&= (\nabla + \tau_M)(\mathbf{A}\nabla\mathbf{\Phi} + (\nabla\mathbf{A})\mathbf{\Phi} + \tau_M\mathbf{A}\mathbf{\Phi}) \\
&= 2(\nabla\mathbf{A}) \cdot \nabla\mathbf{\Phi} + \mathbf{A}\nabla^2\mathbf{\Phi} + (\nabla^2\mathbf{A})\mathbf{\Phi} + (\nabla\tau_M)\mathbf{A}\mathbf{\Phi} \\
&\quad + 2\tau_M(\nabla\mathbf{A})\mathbf{\Phi} + 2\tau_M\mathbf{A}(\nabla\mathbf{\Phi}) + \tau_M^2\mathbf{A}\mathbf{\Phi}
\end{aligned}
$$

which can be further developed to become

$$
\therefore = \mathbf{A}\nabla^2\mathbf{\Phi} + 2(\nabla\mathbf{A} + \tau_M\mathbf{A}) \cdot \nabla\mathbf{\Phi} + \{(\tau_M + \nabla) \cdot (\nabla\mathbf{A} + \tau_M\mathbf{A})\}\mathbf{\Phi}
$$

where the ∇ parameters, in the third term, do not act beyond the curled parentheses { }. Now, if $\mathbf{A}$ (henceforth to be designated as $\mathbf{A}_M$ in order to remind us that it belongs to the M-dimensional P subspace) is chosen to be a solution of the following equation:

$$
\nabla\mathbf{A}_M + \tau_M\mathbf{A}_M = 0 \tag{19}
$$

then the above (kinetic energy) expression takes the simplified form:

$$
(\nabla + \tau_M)^2 \mathbf{A}\mathbf{\Phi} = \mathbf{A}_M\nabla^2\mathbf{\Phi} \tag{20}
$$

and therefore Eq. (16) becomes

$$
-\frac{1}{2m}\nabla^2\mathbf{\Phi} + (W_M - E)\mathbf{\Phi} = 0 \tag{21}
$$

where we used the fact that $\mathbf{A}_M$ is a unitary matrix (seen Appendix B) and $\mathbf{W}_M$, the diabatic potential matrix, is given in the form:

$$
\mathbf{W}_M = (\mathbf{A}_M)^\dagger \mathbf{u}_M \mathbf{A}_M \tag{22}
$$

Equation (21) is the diabatic Schrödinger equation.

In what follows, the $\mathbf{A}$ matrix (or the $\mathbf{A}_M$ matrix) will be called the adiabatic-to-diabatic transformation matrix.

B.   The Necessary Condition for Having a Solution for the Adiabatic-to-Diabatic Transformation Matrix

The $\mathbf{A}$ matrix has to fulfill Eq. (19). It is obvious that all features of $\mathbf{A}$ are dependent on the features of the τ-matrix elements. Thus, for example, if we

want the adiabatic-to-diabatic transformation matrix to have second derivatives or more in a given region, the τ-matrix elements have to be analytic functions in this region, namely, they have to have well-defined derivatives. However, this is not enough to guarantee the analyticity of $\mathbf{A}$. In order for it to be analytic, there are additional conditions that the elements of this matrix have to fulfill, namely, that the result of two (or more) mixed derivatives should not depend on the order of the differentiation. In other words, if p and q are any two coordinates then the following condition has to hold:

$$\frac{\partial^2}{\partial p \partial q}\mathbf{A} = \frac{\partial^2}{\partial q \partial p}\mathbf{A} \tag{23}$$

The conditions for that to happen are derived in Appendix B (under Analyticity) and are given here:

$$\frac{\partial}{\partial p}\tau_q - \frac{\partial}{\partial q}\tau_p - [\tau_q, \tau_p] = 0 \tag{24}$$

which can also be written more compact as a vector equation:

$$\operatorname{curl} \tau - [\tau \times \tau] = 0 \tag{25}$$

For a two-state system Eq. (25) simplifies significantly to become

$$\operatorname{curl} \tau = 0 \tag{26}$$

In what follows, Eq. (25) [and Eq. (26)] will be referred to as the *curl* condition. In Appendix C it is proved, employing the integral representation [see Eq. (27)], that the fulfillment of this condition at every point throughout a given region, guarantees the *single valuedness* of the $\mathbf{A}$ matrix throughout this region.

The importance of the adiabatic-to-diabatic transformation matrix is in the fact that given the adiabatic potential matrix it yields the diabatic potential matrix. Since the potentials that govern the motion of atomic species have to be analytic and *single valued*, and since the adiabatic potentials usually have these features, we expect the adiabatic-to-diabatic transformation to yield diabatic potentials with the same features. Whereas the analyticity feature is guaranteed because the adiabatic-to-diabatic transformation matrix is usually analytic it is more the uniqueness requirement that is of concern. The reason being that in cases where the electronic eigenfunctions become degenerate in configuration space the corresponding non-adiabatic coupling terms become singular (as is well known from the Hellmann–Feynman theorem [3,36]) and this as is proved in Appendix C, may cause the adiabatic-to-diabatic transformation matrix to become multivalued. Thus we have to make sure that the relevant diabatic potentials will

also stay single-valued in cases where the adiabatic-to-diabatic transformation matrix is not. All these aspects will be discussed in Section IV.

By returning to the diabatic potentials as defined in Eq. (22), the condition expressed in Eq. (25) also guarantees well-behaved (namely, single-valued) diabatic potentials. However, it is known (as was already discussed above) that the τ-matrix elements are not always well behaved because they may become singular, implying that in such regions Eq. (25) is not satisfied at *every point*. In such a situation the analyticity of the adiabatic-to-diabatic transformation matrix may still be guaranteed (except at the close vicinity of these singular points) but no longer its single-valuedness. The question is to what extent this "new" difficulty is going to affect the single-valuedness of the diabatic potentials (which have to be single valued if a solution for the corresponding Schrödinger equation is required). Section IV is devoted to this issue.

IV.   THE ADIABATIC-TO-DIABATIC TRANSFORMATION MATRIX AND THE LINE INTEGRAL APPROACH

From now on, the index M will be omitted and it will be understood that any subject to be treated will refer to a finite sub-Hilbert space of dimension M.

Equation (19) can also be written as an integral equation along a contour in the following way [34–36]:

$$\mathbf{A}(s, s_0 \mid \Gamma) = \mathbf{A}(s_0 \mid \Gamma) - \int_{s_0}^{s} \mathbf{ds}' \cdot \boldsymbol{\tau}(s' \mid \Gamma) \mathbf{A}(s', s_0 \mid \Gamma) \tag{27}$$

where Γ is the given contour in the multidimensional configuration space, the points s and s_0 are located on this contour, $\mathbf{ds}'$ is a differential vector along this contour, and the dot is a scalar product between this differential vector and the (vectorial) non-adiabatic coupling matrix $\boldsymbol{\tau}$. Note that the $\boldsymbol{\tau}$ matrix is the kernel of this equation and since, as mentioned above, some of the non-adiabatic coupling terms may be singular in configuration space (but not necessarily along the contour itself), it has implication on the multivaluedness of both the $\mathbf{A}$ matrix and the diabatic potentials.

A.   The Necessary Conditions for Obtaining Single-Valued Diabatic Potentials and the Introduction of the Topological Matrix

The solution of Eq. (19) can be written in the form [57]:

$$\mathbf{A}(s, s_0) = \wp \exp\left(-\int_{s_0}^{s} ds \cdot \boldsymbol{\tau}\right) \mathbf{A}(s_0) \tag{28}$$

where the symbol $\wp$ is introduced to indicate that this integral has to be carried out in a given order [57,80]. In other words, $\wp$ is a path ordering operator. The solution in Eq. (28) is well defined as long as τ, along Γ, is well defined. However, as mentioned earlier, the solution may not be *uniquely* defined at every point in configuration space. Still, we claim that under certain conditions such a solution is of importance because it will lead to uniquely defined diabatic potentials. This claim brings us to formulate the necessary condition for obtaining uniquely defined diabatic potentials.

Let us consider a closed path Γ defined in terms of a continuous parameter λ so that the starting point s_0 of the contour is at $\lambda = 0$. Next, β is defined as the value attained by λ once the contour completes a full cycle and returns to its starting point. For example, in the case of a circle, λ is an angle and $\beta = 2\pi$.

With these definitions we can now look for the necessary condition(s). Thus, we assume that at *each point* s_0 in configuration space the diabatic potential matrix $\mathbf{W}(\lambda)$ [$\equiv \mathbf{W}(s, s_0)$] fulfills the condition:

$$\mathbf{W}(\lambda = 0) = \mathbf{W}(\lambda = \beta) \tag{29}$$

Following Eq. (22), this requirement implies that for every point s_0 we have

$$\mathbf{A}^\dagger(0)u(0)\mathbf{A}(0) = \mathbf{A}^\dagger(\beta)u(\beta)\mathbf{A}(\beta) \tag{30}$$

Next, we introduce another transformation matrix, $\mathbf{B}$, defined as

$$\mathbf{B} = \mathbf{A}(\beta)\mathbf{A}^\dagger(0) \tag{31}$$

which, for every s_0 and a given contour Γ, connects $u(\beta)$ with $u(0)$:

$$u(\beta) = \mathbf{B}u(0)\mathbf{B}^\dagger \tag{32}$$

The $\mathbf{B}$ matrix is, by definition, a unitary matrix (it is a product of two unitary matrices) and at this stage except for being dependent on Γ and, eventually, on s_0, it is rather arbitrary. In what follows, we shall derive some features of $\mathbf{B}$.

Since the electronic eigenvalues (the adiabatic PESs) are uniquely defined at each point in configuration space we have $u(0) \equiv u(\beta)$, and therefore Eq. (32) implies the following commutation relation:

$$[\mathbf{B}, u(0)] = 0 \tag{33}$$

or more explicitly:

$$\sum_{j=1}(\mathbf{B}_{kj}^*\mathbf{B}_{kj} - \delta_{kj})u_j(0) = 0 \tag{34}$$

Equation (34) has to hold for every arbitrary point s_0 ($\equiv \lambda = 0$) on the path Γ and for an essential, arbitrary set of nonzero adiabatic eigenvalues, $u_j(s_0)$; $j = 1, \ldots, M$. Due to the arbitrariness of s_0, and therefore also of the $u_j(s_0)$ values, Eqs. (34) can be satisfied if and only if the **B**-matrix elements fulfill the relation:

$$\mathbf{B}_{kj}^* \mathbf{B}_{kj} = \delta_{kj} \qquad j, k \leq M \tag{35}$$

or

$$\mathbf{B}_{jk} = \delta_{jk} \exp(i\chi_k) \tag{36}$$

Thus **B** is a diagonal matrix that contains in its diagonal (complex) numbers whose norm is 1 (this derivation holds as long as the adiabatic potentials are nondegenerate along the path Γ). From Eq. (31), we obtain that the **B**-matrix transforms the **A**-matrix from its initial value to its final value while tracing a closed contour:

$$\mathbf{A}(\beta) = \mathbf{B}\mathbf{A}(0) \tag{37}$$

Let us now return to Eq. (28) and define the following matrix:

$$\mathbf{D} = \wp \exp\left(-\oint_\Gamma ds \cdot \boldsymbol{\tau}\right) \tag{38}$$

Notice from Eq. (28) that if the contour Γ is a closed loop (which returns to s_0) the **D** matrix transforms $\mathbf{A}(s_0)$ to its value $\mathbf{A}(s = s_0|s_0)$ at the end of the closed contour, namely;

$$\mathbf{A}(s = s_0 \mid s_0) = \mathbf{D}\mathbf{A}(s_0) \tag{39}$$

Now, by comparing Eq. (37) with Eq. (39) it is noticed that **B** and **D** are identical, which implies that all the features that were found to exist for the **B** matrix also apply to the matrix **D** as defined in Eq. (38).

Returning to the beginning of this section, we established the following: The *necessary* condition for the **A** matrix to yield single-valued diabatic potentials is that the **D** matrix, defined in Eq. (38), be diagonal and has, in its diagonal, numbers of norm 1. Since we consider only real electronic eigenfunctions these numbers can be either $(+1)$ or (-1) established. By following Eq. (39), it is also obvious that the **A** matrix is not necessarily single-valued because the **D** matrix, as was just proved, is not necessarily a unit matrix. In what follows, the number of (-1) values in a given matrix **D** will be designated as **K**.

The **D** matrix plays an important role in the forthcoming theory because it contains all topological features of an electronic manifold in a region surrounded by a contour Γ as will be explained next.

That the electronic adiabatic manifold can be multivalued is a well-known fact, going back to Longuet-Higgins et al. [14–17]. In this section, we just proved that the same applies to the adiabatic-to-diabatic transformation matrix and for this purpose we introduced the diabatic framework. The diabatic manifold is, by definition, a manifold independent of the nuclear coordinates and therefore single-valued in configuration space. Such a manifold always exists for a complete Hilbert space [36b] (see Appendix D). Next, we assume that an *approximate* (partial) diabatic manifold like that can be found for the present sub-Hilbert space defined with respect to a certain region in configuration space. This approximate diabatic manifold is, by definition, single valued. Then, we consider Eq. (18), in which the electronic diabatic manifold is presented in terms of the product $\zeta \mathbf{A}^\dagger$, where ζ is the adiabatic electronic manifold. Since this product is singled valued in configuration space (because it produces a diabatic manifold) it remains single valued while tracing a closed contour. In order for this product to remain single valued, the number of wave functions that flip sign in this process has to be identical to the topological number K. Moreover the positions of the $(-1)s$ in the **D** matrix have to match the electronic eigenfunctions that flip their sign. Thus, for example, if the third element in the **D** matrix is (-1) this implies that the electronic eigenfunction that belongs to the third state flips sign.

It is known that multivalued adiabatic electronic manifolds create topological effects [23,25,45]. Since the newly introduced **D** matrix contains the information relevant for this manifold (the number of functions that flip sign and their identification) we shall define it as the *Topological Matrix*. Accordingly, K will be defined as the *Topological Number*. Since **D** is dependent on the contour Γ the same applies to K thus: $K = K(\Gamma)$.

B. The Quasidiabatic Framework

In Section IV.A, the adiabatic-to-diabatic transformation matrix as well as the diabatic potentials were derived for the relevant sub-space without running into theoretical conflicts. In other words, the conditions in Eqs. (10) led to a *finite* sub-Hilbert space which, for all practical purposes, behaves like a full (infinite) Hilbert space. However it is inconceivable that such strict conditions as presented in Eq. (10) are fulfilled for real molecular systems. Thus the question is to what extent the results of the present approach, namely, the adiabatic-to-diabatic transformation matrix, the curl equation, and first and foremost, the diabatic potentials, are affected if the conditions in Eq. (10) are replaced by more realistic ones? This subject will be treated next.

The quasidiabatic framework is defined as the framework for which the conditions in Eqs. (10) are replaced by the following less stricked ones [81]:

$$\tau_{ij}^{(1)} \cong O(\varepsilon) \qquad \text{for} \qquad i \leq M \qquad j > M \qquad (40)$$

Thus, we still relate to the same sub-space but it is now defined for *P*-states that are weakly coupled to *Q*-states. We shall prove the following *lemma*: If the interaction between any *P*- and *Q*-state measures like $O(\varepsilon)$, the resultant *P*-diabatic potentials, the *P*-adiabatic-to-diabatic transformation matrix elements and the *P*-curl τ equation are all fulfilled up to $O(\varepsilon^2)$.

1. The Adiabatic-to-Diabatic Transformation Matrix and the Diabatic Potentials

We prove our statement in two steps: First, we consider the special case of a Hilbert space of three states, the two lowest of which are coupled strongly to each other but the third state is only weakly coupled to them. Then, we extend it to the case of a Hilbert space of *N* states where *M* states are strongly coupled to each other, and $L (= N - M)$ states, are only loosely coupled to these *M* original states (but can be strongly coupled among themselves).

We start with the first case where the components of two of the τ-matrix elements, namely, τ_{13} and τ_{23}, are of the order of $O(\varepsilon)$ [see Eq. (40)].

The 3×3 **A** matrix has nine elements of which we are interested in only four, namely, a_{11}, a_{12}, a_{21}, and a_{22}. However, these four elements are coupled to a_{31} and a_{32} and, therefore, we consider the following *six* line integrals [see Eq. (27)]:

$$a_{ij}(s) = a_{ij}(s_0) - \sum_{k=1}^{3} \int_{s_0}^{s} ds \cdot \tau_{ik}(s) a_{kj}(s) \qquad i = 1, 2, 3 \qquad j = 1, 2 \qquad (41)$$

Next, we estimate the magnitudes of a_{31} and a_{32} and for this purpose we consider the equations for a_{31} and a_{32}. Thus, assuming a_{1j} and a_{2j} are given, the solution of the relevant equations in Eq. (41), is

$$a_{3j}(s) = a_{3j}(s_0) - \int_{s_0}^{s} ds' \cdot (\tau_{31} a_{1j} + \tau_{32} a_{2j}) \qquad (42)$$

For obvious reasons, we assume $a_{3j}(s_0) = 0$. Since both, a_{1j} and a_{2j}, are at most (in absolute values) unity, it is noticed that the magnitude of a_{31} and a_{32} are of the order of $O(\varepsilon)$ just like the assumed magnitude of the components of τ_{i3} for $i = 1, 2$. Now, returning to Eq. (41) and substituting Eq. (42) in the last term in each summation, one can see that the integral over $\tau_{i3} a_{3j}; j = 1, 2$ is of the second

order in ε, which can be specified as $O(\varepsilon^2)$. In other words, ignoring the coupling between the two-state system and a third state introduces a second-order error in the calculation of each of the elements of the two-state **A** matrix.

To treat the general case, we assume **A** and τ to be of the following form:

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{(M)} & \mathbf{A}^{(M,L)} \\ \mathbf{A}^{(L,M)} & \mathbf{A}^{(L)} \end{pmatrix} \tag{43a}$$

and

$$\tau = \begin{pmatrix} \tau^{(M)} & \tau^{(M,L)} \\ \tau^{(L,M)} & \tau^{(L)} \end{pmatrix} \tag{43b}$$

where we recall that M is the dimension of the P sub-space. As before, the only parts of the **A** matrix that are of interest for us are $\mathbf{A}^{(M)}$ and $\mathbf{A}^{(L,M)}$. By substituting Eqs. (43) in Eq. (27), we find for $\mathbf{A}^{(M)}$ the following integral equation:

$$\mathbf{A}^{(M)} = \mathbf{A}_0^{(M)} - \int_{s_0}^{s} ds \cdot \tau^{(M)} \mathbf{A}^{(M)} - \int_{s_0}^{s} ds \cdot \tau^{(M,L)} \mathbf{A}^{(L,M)} \tag{44}$$

where **A** stands for $\mathbf{A}(s)$ and $\mathbf{A}_0$ for $\mathbf{A}(s_0)$. Our next task is to get an estimate for $\mathbf{A}^{(L,M)}$. For this purpose, we substitute Eqs. (43) in Eq. (19) and consider the first-order differential equation for this matrix:

$$\nabla \mathbf{A}^{(L,M)} + \tau^{(L,M)} \mathbf{A}^{(M)} + \tau^{(L)} \mathbf{A}^{(L,M)} = 0 \tag{45a}$$

which will be written in a slightly different form:

$$\nabla \mathbf{A}^{(L,M)} + \tau^{(L)} \mathbf{A}^{(L,M)} = -\tau^{(L,M)} \mathbf{A}^{(M)} \tag{45b}$$

in order to show that it is an inhomogeneous equation for $\mathbf{A}^{(L,M)}$ (assuming the elements of $\mathbf{A}^{(M)}$ are known). Equation (45b) will be solved for the initial conditions where the elements of $\mathbf{A}^{(L,M)}$ are zero (this is the obvious choice in order for the isolated sub-space to remain as such in the diabatic framework as well). For these initial conditions, the solution of Eq. (45a) can be shown to be

$$\mathbf{A}^{(L,M)} = \exp\left(-\int_{s_0}^{s} ds' \cdot \tau^{(L)}\right) \left\{ \int_{s_0}^{s} \exp\left(\int_{s_0}^{s'} ds'' \cdot \tau^{(L)}\right) ds' \cdot \tau^{(L,M)} \mathbf{A}^{(M)} \right\} \tag{46}$$

In performing this series of integrations, it is understood that they are carried out in the correct order and always for consecutive infinitesimal sections along

the given contour Γ [57]. Equation (46) shows that all elements of $\mathbf{A}^{(L,M)}$ are linear combinations of the (components of the) $\tau^{(L,M)}$ elements, which are all assumed to be of first order in ε. We also reiterate that the absolute values of all elements of $\mathbf{A}^{(M)}$ are limited by the value of the unity.

Now, by returning to Eq. (44) and replacing $\mathbf{A}^{(L,M)}$ by the expression in Eq. (46) we find that the line integral to solve $\mathbf{A}^{(M)}$ is perturbed to the second order, namely,

$$\mathbf{A}^{(M)} = \mathbf{A}_0^{(M)} - \int_{s_0}^{s} ds \cdot \tau^{(M)} \mathbf{A}^{(M)} + O(\varepsilon^2) \tag{47}$$

This concludes our derivation regarding the adiabatic-to-diabatic transformation matrix for a finite N. The same applies for an infinite Hilbert space (but finite M) if the coupling to the higher Q-states decays fast enough.

Once there is an estimate for the error in calculating the adiabatic-to-diabatic transformation matrix it is possible to estimate the error in calculating the *diabatic potentials*. For this purpose, we apply Eq. (22). It is seen that the error is of the second order in ε, namely, of $O(\varepsilon^2)$, just like for the adiabatic-to-diabatic transformation matrix.

2. *The Curl Condition*

Next, we analyze the P-curl condition with the aim of examining to what extent it is affected when the weak coupling is ignored as described in Section IV.B.1 [81]. For this purpose, we consider two components of the (unperturbed) τ matrix, namely, the matrices τ_q and τ_p, which are written in the following form [see Eq. (43)]:

$$\tau_x = \begin{pmatrix} \tau_x^{(M)} & \tau_x^{(M,L)} \\ \tau_x^{(L,M)} & \tau_x^{(L)} \end{pmatrix} \qquad x = q,p \tag{48}$$

Here, $\tau_x^{(M)}$ (and eventually $\tau_x^{(L)}$); $x = p,q$ are the matrices that contain the strong non-adiabatic coupling terms, whereas $\tau_x^{(M,L)}$ [and $\tau_x^{(L,M)}$]; $x = p,q$ are the matrices that contain the weak non-adiabatic coupling terms, all being of the order $O(\varepsilon)$. Employing Eqs. (24) and (25) and by substituting Eq. (48) for τ_q and τ_p, it can be seen by algebraic manipulations that the following relation holds:

$$\frac{\partial \tau_p^{(M)}}{\partial q} - \frac{\partial \tau_q^{(M)}}{\partial p} - [\tau_p^{(M)}, \tau_q^{(M)}] = \{\tau_p^{(M,L)}\tau_q^{(L,M)} - \tau_q^{(M,L)}\tau_p^{(L,M)}\} \tag{49}$$

Notice, all terms in the curled parentheses are of $O(\varepsilon^2)$, which implies that the curl condition becomes

$$\text{curl}\,\tau^{(M)} - [\tau^{(M)} \times \tau^{(M)}] = O(\varepsilon^2) \tag{50}$$

namely, the curl condition within the sub-space, is fulfilled up to $O(\varepsilon^2)$.

Obviously, the fact that the solution of the adiabatic-to-diabatic transformation matrix is only perturbed to second order makes the present approach rather attractive. It not only results in a very efficient approximation but also yields an estimate for the error made in applying the approximation.

V. THE QUANTIZATION OF THE NON-ADIABATIC COUPLING MATRIX

One of the main outcomes of the analysis so far is that the topological matrix $\mathbf{D}$, presented in Eq. (38), is identical to an adiabatic-to-diabatic transformation matrix calculated at the end point of a closed contour. From Eq. (38), it is noticed that $\mathbf{D}$ does not depend on any particular point along the contour but on the contour itself. Since the integration is carried out over the non-adiabatic coupling matrix, τ, and since $\mathbf{D}$ has to be a diagonal matrix with numbers of norm 1 for *any* contour in configuration space, these two facts impose severe restrictions on the non-adiabatic coupling terms.

In Section V.A, we present a few analytical examples showing that the restrictions on the τ-matrix elements are indeed quantization conditions that go back to the early days of quantum theory. Section V.B will be devoted to the general case.

A. The Quantization as Applied to Model Systems

In this section, we intend to show that for a certain type of models the above imposed ''restrictions'' become the ordinary well-known Bohr–Sommerfeld quantization conditions [82]. For this purpose, we consider the following non-adiabatic coupling matrix τ:

$$\tau(s) = \mathbf{g}\mathbf{t}(s) \tag{51}$$

where $\mathbf{t}(s)$ is a vector whose components are functions in configuration space and $\mathbf{g}$ is a *constant* antisymmetric matrix of dimension M. For this case, one can evaluate the ordered exponential in Eq. (38). Thus substituting Eq. (51) in Eq. (38) yields the following solution for the $\mathbf{D}$ matrix:

$$\mathbf{D} = \mathbf{G} \exp\left(-\omega \oint_{\Gamma} ds \cdot \mathbf{t}(s)\right) \mathbf{G}^{\dagger} \tag{52}$$

where ω is a diagonal matrix that contains the eigenvalues of the $\mathbf{g}$ matrix and $\mathbf{G}$ is a matrix that diagonalizes g ($\mathbf{G}^{\dagger}$ is the Hermitian conjugate of $\mathbf{G}$). Since $\mathbf{g}$ is an antisymmetric matrix all its eigenvalues are either imaginary or zero.

Next, we concentrate on a few special cases.

1.   The Two-State Case

The **g** matrix in this case is given in the form:

$$\mathbf{g} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{53}$$

The matrix **G** that diagonalizes it is

$$\mathbf{G} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \tag{54}$$

and the corresponding eigenvalues are $\pm i$. Substituting Eq. (54) in Eq. (52) and replacing the two ω parameters by $\pm i$ yields the following **D** matrix:

$$\mathbf{D} = \begin{pmatrix} \cos\left(\oint_{\Gamma} \mathbf{t}(s) \cdot ds\right) & -\sin\left(\oint_{\Gamma} \mathbf{t}(s) \cdot ds\right) \\ \sin\left(\oint_{\Gamma} \mathbf{t}(s) \cdot ds\right) & \cos\left(\oint_{\Gamma} \mathbf{t}(s) \cdot ds\right) \end{pmatrix} \tag{55}$$

Next, we refer to the requirements to be fulfilled by the matrix **D**, namely, that it is diagonal and that it has the diagonal numbers that are of norm 1. In order for that to happen, the vector-function $\mathbf{t}(s)$ has to fulfill along a given (closed) path Γ the condition:

$$\oint_{\Gamma} \mathbf{t}(s) \cdot ds = n\pi \tag{56}$$

where n is an *integer*. These conditions are essentially the Bohr–Sommerfeld quantization conditions [82] (as applied to the single term of the two-state τ matrix).

Equation (56) presents the condition for the extended conical intersection case. It is noticed that if n is an odd integer the diagonal of the **D** matrix contains two (-1) terms, which means that the elements of the adiabatic-to-diabatic transformation matrix flip sign while tracing the closed contour in Eq. (56) [see Eq. (39)]. This case is reminiscent of what happened in the simplified Jahn–Teller model as was studied by Herzberg–Longuet–Higgins [16] in which they showed that if two eigenfunctions that belong to the two states that form a conical intersection, trace a closed contour around that conical intersection, both of them flip sign (see Appendix A).

If the value of n in Eq. (56), is an even integer, the diagonal of the **D** matrix contains two $(+1)$ terms, which implies that in this case none of the elements of

the adiabatic-to-diabatic transformation matrix flip sign while tracing the closed contour. This situation will be identified as the case where the above mentioned two eigenfunctions trace a closed contour but do not flip sign—the case known as the Renner–Teller model [15,83]. Equation (56) is the extended version of the Renner–Teller case.

In principle, we could have a situation where one of the diagonal elements is $(+1)$ and one (-1) but from the structure of the $\mathbf{D}$ matrix one can see that this case can never happen.

In our introductory remarks, we said that this section would be devoted to model systems. Nevertheless it is important to emphasize that although this case is treated within a group of model systems this *model* stands for the general case of a two-state sub-Hilbert space. Moreover, this is the only case for which we can show, analytically, for a nonmodel system, that the restrictions on the $\mathbf{D}$ matrix indeed lead to a quantization of the relevant non-adiabatic coupling term.

2.   The Three-State Case

The non-adiabatic coupling matrix $\boldsymbol{\tau}$ will be defined in a way similar to that in the Section V.A [see Eq. (51)], namely, as a product between a vector-function $\mathbf{t}(s)$ and a constant antisymmetric matrix $\mathbf{g}$ written in the form

$$\mathbf{g} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & \eta \\ 0 & -\eta & 0 \end{pmatrix} \tag{57}$$

where η is a (constant) parameter. By employing this form of $\mathbf{g}$, we assumed that g_{13} and g_{31} are zero (the more general case is treated elsewhere [80]). The eigenvalues of this matrix are

$$\omega_{1,2} = \pm i\omega \qquad \omega_3 = 0 \qquad \omega = \sqrt{1 + \eta^2} \tag{58}$$

and the corresponding matrix, $\mathbf{G}$, that diagonalizes the matrix $\mathbf{g}$ is

$$\mathbf{G} = \frac{1}{\omega\sqrt{2}} \begin{pmatrix} 1 & 1 & \eta\sqrt{2} \\ i\omega & -i\omega & 0 \\ -\eta & -\eta & \sqrt{2} \end{pmatrix} \tag{59}$$

By again employing Eq. (52), we find the following result for the $\mathbf{D}$ matrix

$$\mathbf{D} = \omega^{-2} \begin{pmatrix} \eta^2 + C & \omega S & \eta(1 - C) \\ \omega S & \omega^2 C & -\eta\omega S \\ \eta(1 - C) & \eta\omega S & 1 + \eta^2 C \end{pmatrix} \tag{60}$$

where

$$C = \cos\left(w\oint_\Gamma \mathbf{t}(s)\cdot ds\right) \qquad \text{and} \qquad S = \sin\left(w\oint_\Gamma \mathbf{t}(s)\cdot ds\right) \qquad (61)$$

Notice that the necessary and sufficient condition for this matrix to become diagonal is that the following condition:

$$\omega\oint_\Gamma \mathbf{t}(s)\cdot ds = \sqrt{1+\eta^2}\oint_\Gamma \mathbf{t}(s)\cdot ds = 2n\pi \qquad (62)$$

be fulfilled. Moreover, this condition leads to a **D** matrix that contains in its diagonal numbers of norm 1 as required. However, in contrast to the previously described two-state case, they, all three of them, are positive, namely, $(+1)$. In other words the "quantization" of the matrix τ as expressed in Eq. (62) leads to a **D** matrix that is a unit matrix, and therefore will maintain the adiabatic-to-diabatic transformation matrix single valued along any contour that fulfills this quantization. This is, to a certain extent, an unexpected result but, as we shall see in the Section V.A.3, it is not the typical result. Still it is an interesting result and we shall return to it in Sections X and XII.

3. The Four-State Case

The **g** matrix in this case will be written in the form

$$\mathbf{g} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & \eta & 0 \\ 0 & -\eta & 0 & \sigma \\ 0 & 0 & -\sigma & 0 \end{pmatrix} \qquad (63)$$

where η and σ are two parameters. The matrix **G** that diagonalizes **g** is

$$\mathbf{G} = \frac{1}{\sqrt{2}}\begin{pmatrix} i\lambda_q & i\lambda_q & -i\lambda_p & -i\lambda_p \\ p\lambda_q & -p\lambda_q & -q\lambda_p & q\lambda_p \\ i\lambda_p & i\lambda_p & i\lambda_q & i\lambda_q \\ q\lambda_p & -q\lambda_p & p\lambda_q & -p\lambda_q \end{pmatrix} \qquad (64)$$

where p and q are defined as

$$\begin{aligned} p &= \frac{1}{\sqrt{2}}(\varpi^2 + \sqrt{\varpi^4 - 4\sigma^2})^{(1/2)} \\ q &= \frac{1}{\sqrt{2}}(\varpi^2 - \sqrt{\varpi^4 - 4\sigma^2})^{(1/2)} \end{aligned} \qquad (65)$$

and λ_p and λ_q are defined as

$$\lambda_p = \sqrt{\frac{p^2 - 1}{p^2 - q^2}} \qquad \lambda_q = \sqrt{\frac{1 - q^2}{p^2 - q^2}} \tag{66}$$

and ϖ as

$$\varpi = \sqrt{(1 + \eta^2 + \sigma^2)} \tag{67}$$

From Eq. (65), it is obvious that $p > q$. The four eigenvalues are

$$(\omega_1, \omega_2, \omega_3, \omega_4) \equiv (ip, -ip, iq, -iq) \tag{68}$$

Again, by employing Eq. (52) we find the following expressions for the **D**-matrix elements:

$$
\begin{aligned}
&\mathbf{D}_{11}(\alpha) = \lambda_q^2 C_p + \lambda_p^2 C_q & &\mathbf{D}_{12}(\alpha) = p\lambda_q^2 S_p + q\lambda_p^2 S_q \\
&\mathbf{D}_{13}(\alpha) = \lambda_p \lambda_q (-C_p + C_q) & &\mathbf{D}_{14}(\alpha) = \lambda_p \lambda_q (-qS_p + pS_q) \\
&\mathbf{D}_{22}(\alpha) = p^2 \lambda_q^2 C_p + q^2 \lambda_p^2 C_q & &\mathbf{D}_{23}(\alpha) = \lambda_p \lambda_q (pS_p - qS_q) \\
&\mathbf{D}_{24}(\alpha) = pq\lambda_p \lambda_q (C_p - C_q) & &\mathbf{D}_{33}(\alpha) = (\lambda_p^2 C_p + \lambda_q^2 C_q \\
&\mathbf{D}_{34}(\alpha) = -(q\lambda_p^2 S_p + p\lambda_q^2 S_q) & &\mathbf{D}_{44}(\alpha) = q^2 \lambda_p^2 C_p + p^2 \lambda_q^2 C_q \\
&\mathbf{D}_{21}(\alpha) = -\mathbf{D}_{12}(\alpha) \quad \mathbf{D}_{31}(\alpha) = \mathbf{D}_{13}(\alpha) & &\mathbf{D}_{32}(\alpha) = -\mathbf{D}_{23}(\alpha) \\
&\mathbf{D}_{41}(\alpha) = -\mathbf{D}_{14}(\alpha) \quad \mathbf{D}_{42}(\alpha) = \mathbf{D}_{24}(\alpha) & &\mathbf{D}_{43}(\alpha) = -\mathbf{D}_{34}(\alpha)
\end{aligned}
\tag{69}
$$

where

$$C_p = \cos(p\alpha) \qquad \text{and} \qquad S_p = \sin(p\alpha) \tag{70}$$

and similar expressions for C_q and S_q. Here α stands for

$$\alpha = \oint_\Gamma \mathbf{t}(s') \cdot ds' \tag{71}$$

Next, we determine the conditions for this matrix to become diagonal (with numbers of norm 1 in the diagonal), which will happen if and only if when p and q fulfill the following relations:

$$p\alpha = p\oint_\Gamma \mathbf{t}(s') \cdot ds' = 2\pi n \tag{72a}$$

$$q\alpha = q\oint_\Gamma \mathbf{t}(s') \cdot ds' = 2\pi \ell \tag{72b}$$

where n (>1) and ℓ, defined in the range $n > \ell \geq 0$, are allowed to be either integers or half-integers but m ($= n - \ell$) can only attain *integer* values. The difference between the case where n and ℓ are integers and the case where both are half-integers is as follows: By examining the expressions in Eq. (69), notice that in the first case all diagonal elements of $\mathbf{D}$ are ($+1$), so that, $\mathbf{D}$ is, in fact, the unit matrix and therefore the elements of the adiabatic-to-diabatic transformation matrix are single valued in configuration space. In the second case, we get from Eq. (69), that all four diagonal elements are (-1). In this case, when the adiabatic-to-diabatic transformation traces a closed contour all its elements flip sign.

Since p and q are directly related to the non-adiabatic coupling terms η and σ [see Eqs. (65) and (66)] the two conditions in Eqs. (72) imply, again, "quantization" conditions for the values of the τ-matrix elements, namely, for η and σ, as well as for the vectorial function $\mathbf{t}(s)$.

It is interesting to note that this is the first time that in the present framework the quantization is formed by two quantum numbers: a number n to be termed the principal quantum number and a number ℓ, to be termed the secondary quantum number. This case is reminiscent of the two quantum numbers that characterize the hydrogen atom.

4. *Comments Concerning Extensions*

In Sections V.A.1–V.A.3, we treated one particular group of τ matrices as presented in Eq. (51), where $\mathbf{g}$ is an antisymmetric matrix with constant elements. The general theory demands that the matrix $\mathbf{D}$ as presented in Eq. (52) be diagonal and that as such it contains ($+1$) and (-1) values in its diagonal. In the three examples that were worked out, we found that for this particular class of τ matrices the corresponding $\mathbf{D}$ matrix contains either ($+1$) or (-1) terms but never a mixture of the two types. In other words, the $\mathbf{D}$ matrix can be represented in the following way:

$$\mathbf{D} = (-1)^k \mathbf{I} \tag{73}$$

where k is either even or odd and $\mathbf{I}$ is the unit matrix. Indeed, for the two-state case k was found to be either odd or even, for the three-state case it was found to be only even, and for the four-state case it was again found to be either odd or even. It seems to us (without proof) that this pattern applies to any dimension. If this really is the case, then we can make the following two statements:

1. In case the dimension of the τ matrix is an odd number, the $\mathbf{D}$ matrix will always be the unit matrix $\mathbf{I}$, namely, k must be an even number. This is so because an odd dimensional $\mathbf{g}$ matrix, always has the zero as an eigenvalue and this eigenvalue produces the ($+1$) in the $\mathbf{D}$ matrix that dictates the value of k in Eq. (73).

2. In case the dimension of the τ matrix is an even number, the **D** matrix will (always) be equal either to **I** or to $(-\mathbf{I})$.

3. These two facts imply that in case of an odd dimension the quantization is characterized by (a series of) integers only [as in Eq. (62)] but in case of an even dimension it is characterized either by (a series of) integers or by (a series of) half-integers [as in Eqs. (72)].

B. The Treatment of the General Case

The derivation of the **D** matrix for a given contour is based on first deriving the adiabatic-to-diabatic transformation matrix, **A**, as a function of s and then obtaining its value at the end of the arbitrary closed contours (when s becomes s_0). Since **A** is a real unitary matrix it can be expressed in terms of cosine and sine functions of given angles. First, we shall consider briefly the two special cases with $M = 2$ and 3.

The case of $M = 2$ was treated in Section V.A.4. Here, this treatment is repeated with the aim of emphasizing different aspects and also for reasons of completeness. The matrix $\mathbf{A}^{(2)}$ takes the form:

$$\mathbf{A}^{(2)} = \begin{pmatrix} \cos\gamma_{12} & \sin\gamma_{12} \\ -\sin\gamma_{12} & \cos\gamma_{12} \end{pmatrix} \tag{74}$$

where γ_{12}, the adiabatic-to-diabatic transformation angle, can be shown to be [34]

$$\gamma_{12} = \int_{s_0}^{s} \tau_{12}(s') \cdot ds' \tag{75}$$

Designating α_{12} as the value of γ_{12} for a closed contour, namely,

$$\alpha_{12} = \oint_{\Gamma} \tau_{12}(s') \cdot ds' \tag{76}$$

the corresponding $\mathbf{D}^{(2)}$ matrix becomes accordingly [see also Eq. (55)]:

$$\mathbf{D}^{(2)} = \begin{pmatrix} \cos\alpha_{12} & \sin\alpha_{12} \\ -\sin\alpha_{12} & \cos\alpha_{12} \end{pmatrix} \tag{77}$$

Since for any closed contour $\mathbf{D}^{(2)}$ has to be a diagonal matrix with $(+1)$ and (-1) terms, it is seen that $\alpha_{12} = n\pi$ where n is either odd or even (or zero) and therefore the only two possibilities for $\mathbf{D}^{(2)}$ are as follows:

$$\mathbf{D}^{(2)} = (-1)^k \mathbf{I} \tag{78}$$

where **I** is the unit matrix and k is either even or odd.

The case of $M = 3$ is somewhat more complicated because the corresponding orthogonal matrix is expressed in terms of three angles, namely, γ_{12}, γ_{13}, and γ_{23} [36,84,85]. This case was recently studied by us in detail [85] and here we briefly repeat the main points.

The matrix $\mathbf{A}^{(3)}$ is presented as a product of three rotation matrices of the form:

$$\mathbf{Q}_{13}^{(3)}(\gamma_{13}) = \begin{pmatrix} \cos\gamma_{13} & 0 & \sin\gamma_{13} \\ 0 & 1 & 0 \\ -\sin\gamma_{13} & 0 & \cos\gamma_{13} \end{pmatrix} \tag{79}$$

[the other two, namely, $\mathbf{Q}_{12}^{(3)}(\gamma_{12})$ and $\mathbf{Q}_{23}^{(3)}(\gamma_{23})$, are of a similar structure with the respective cosine and sine functions in the appropriate positions) so that $\mathbf{A}^{(3)}$ becomes:

$$\mathbf{A}^{(3)} = \mathbf{Q}_{12}^{(3)}\mathbf{Q}_{23}^{(3)}\mathbf{Q}_{13}^{(3)} \tag{80}$$

or, following the multiplication, the more explicit form:

$$\mathbf{A}^{(3)} = \begin{pmatrix} c_{12}c_{13} - s_{12}s_{23}s_{13} & s_{12}s_{23} & c_{12}s_{13} + c_{12}s_{23}c_{13} \\ -s_{12}c_{13} - c_{12}s_{23}s_{13} & c_{12}c_{23} & -s_{12}s_{13} + c_{12}s_{23}c_{13} \\ -c_{23}s_{13} & -s_{23} & c_{23}c_{13} \end{pmatrix} \tag{81}$$

Here, $c_{ij} = \cos(\gamma_{ij})$ and $s_{ij} = \sin(\gamma_{ij})$. The three angles are obtained by solving the following three coupled first-order differential equations, which follow from Eq. (19) [36,84,85]:

$$\begin{aligned} \nabla\gamma_{12} &= \tau_{12} - \tan\gamma_{23}(-\tau_{13}\cos\gamma_{12} + \tau_{23}\sin\gamma_{12}) \\ \nabla\gamma_{23} &= -(\tau_{23}\cos\gamma_{12} + \tau_{13}\sin\gamma_{12}) \\ \nabla\gamma_{13} &= -(\cos\gamma_{23})^{-1}(-\tau_{13}\cos\gamma_{12} + \tau_{23}\sin\gamma_{12}) \end{aligned} \tag{82}$$

These equations were integrated as a function of φ (where $0 \le \varphi \le 2\pi$), for a *model* potential [85] along a circular contour of radius ρ (for details see Appendix E). The φ-dependent γ angles, that is, $\gamma_{ij}(\varphi \mid \rho)$, for various values of ρ and $\Delta\varepsilon$ ($\Delta\varepsilon$ is the potential energy shift defined as the shift between the two original coupled adiabatic states and a third state, at the origin, i.e., at $\rho = 0$.) are presented in Figure 1. Thus for each φ we get, employing Eq. (81), the $\mathbf{A}^{(3)}(\varphi)$ matrix elements. The relevant $\mathbf{D}^{(3)}$ matrix is obtained from $\mathbf{A}^{(3)}$ by substituting $\varphi = 2\pi$. If α_{ij} are defined as

$$\alpha_{ij} = \gamma_{ij}(\varphi = 2\pi) \tag{83}$$

then, as is noticed from Figure 1, the values of α_{ij} are either zero or π. A simple analysis of Eq. (81), for these values of α_{ij}, shows that $\mathbf{D}^{(3)}$ is a diagonal matrix with two (-1) terms and one $(+1)$ in the diagonal.
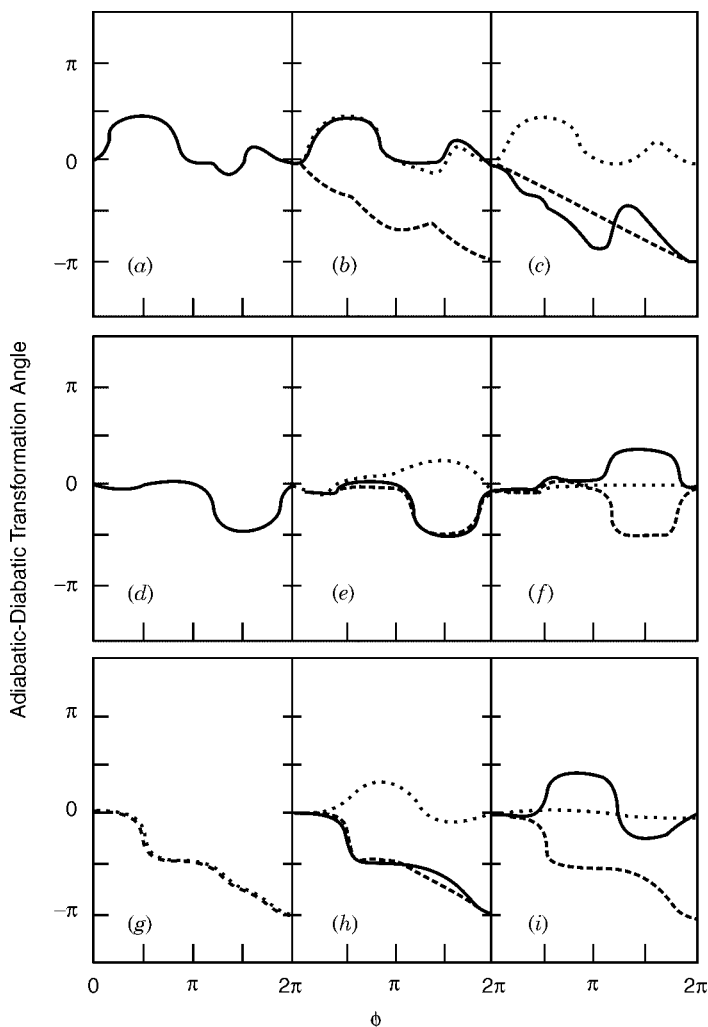
Figure 1. The three adiabatic–diabatic transformation angles [obtained by solving Eqs. (77) for a 3×3 diabatic model potential presented in Section XIII.B] $\gamma_{12}(\varphi)$, $\gamma_{23}(\varphi)$, $\gamma_{13}(\varphi)$ as calculated for different values of ρ and $\Delta\varepsilon$: (a) $\gamma = \gamma_{12}$, $\Delta\varepsilon = 0.0$; (b) $\gamma = \gamma_{12}$, $\Delta\varepsilon = 0.05$; (c) $\gamma = \gamma_{12}$, $\Delta\varepsilon = 0.25$; (d) $\gamma = \gamma_{23}$, $\Delta\varepsilon = 0.0$; (e) $\gamma = \gamma_{23}$, $\Delta\varepsilon = 0.05$; (f) $\gamma = \gamma_{23}$, $\Delta\varepsilon = 0.25$; (g) $\gamma = \gamma_{13}$, $\Delta\varepsilon = 0.0$; (h) $\gamma = \gamma_{13}$, $\Delta\varepsilon = 0.05$; (i) $\gamma = \gamma_{13}$, $\Delta\varepsilon = 0.25$. ——— $\rho = 0.01$; - - - - - - - $\rho = 0.1$; .... $\rho = 0.5$.

This result will now be generalized for an arbitrary $\mathbf{D}^{(3)}$ matrix in the following way: Since a general $\mathbf{A}^{(3)}$ matrix can always be written as in Eq. (81) the corresponding $\mathbf{D}^{(3)}$ matrix becomes diagonal if and only if:

$$\alpha_{ij} = \gamma_{ij}(\varphi = 2\pi) = n_{ij}\pi \tag{84}$$

the diagonal terms can, explicitly, be represented as

$$\mathbf{D}_{ij}^{(3)} = \delta_{ij} \cos\alpha_{jn} \cos\alpha_{jm} \qquad j \neq n \neq m \quad j = 1,2,3 \qquad (85)$$

This expression shows that the $\mathbf{D}^{(3)}$ matrix, in the most general case, can have either three $(+1)$ terms in the diagonal or two (-1) terms and one $(+1)$. In the first case, the contour does not surround any conical intersection, whereas in the second case it surrounds either one or two conical intersections (a more general discussion related to the solution of the corresponding line integral is given in Section VIII and a discussion regarding the ''geometrical'' aspect is given in Section IX).

It is important to emphasize that this analysis, although it is supposed to hold for a general three-state case, contradicts the analysis we performed of the three-state model in Section V.A.2. The reason is that the ''general (physical) case'' applies to an (arbitrary) aggregation of conical intersections whereas the previous case applies to a special (probably unphysical) situation. The discussion on this subject is extended in Section X. In what follows, the cases for an aggregation of conical intersections will be termed the ''breakable'' situations (the reason for choosing this name will be given later) in contrast to the type of models that were discussed in Sections V.A.2 and V.A.3 and that are termed as the ''unbreakable'' situation.

Before discussing the general case, we would like to refer to the present choice of the rotation angles. It is well noticed that they differ from the ordinary *Euler* angles that are routinely used to present three-dimensional (3D) orthogonal matrices [86]. In fact, we could apply the Euler angles for this purpose and get identical results for $\mathbf{A}^{(3)}$ (and for $\mathbf{D}^{(3)}$). The main reason we prefer the ''democratic'' choice of the angles is that this set of angles can be extended to an arbitrary number of dimensions as will be done next.

The M-dimensional adiabatic-to-diabatic transformation matrix $\mathbf{A}^{(M)}$ will be written as a product of elementary rotation matrices similar to that given in Eq. (80) [9]:

$$\mathbf{A}^{(M)} = \prod_{i=1}^{M-1} \prod_{j>i}^{M} \mathbf{Q}_{ij}^{(M)}(\gamma_{ij}) \qquad (86)$$

where $\mathbf{Q}_{ij}^{(M)}(\gamma_{ij})$ [like in Eq. (79)] is an $M \times M$ matrix with the following terms: In its (ii) and (jj) positions (along the diagonal) are located the two relevant cosine functions and at the rest of the $(M-2)$ positions are located $(+1)s$; in the (ij) and (ji) off-diagonal positions are located the two relevant $\pm$sine functions and at all other remaining positions are zeros. From Eq. (86), it can be seen that the number of matrices contained in this product is $M(M-1)/2$ and that this is also the number of independent γ_{ij} angles that are needed to describe an $M \times M$

unitary matrix (we recall that the missing $M(M + 1)/2$ conditions follow from the ortho-normal conditions). The matrix $\mathbf{A}^{(M)}$ as presented in Eq. (86) is characterized by two important features: (1) Every *diagonal* element contains at least one term that is a product of cosine functions only. (2) Every *off-diagonal* element is a summation of products of terms where each product contains at least one sine function. These two features will lead to conditions to be imposed on the various γ_{ij} angles to ensure that the topological matrix, $\mathbf{D}^{(M)}$, is diagonal as discussed in the Section IV.A.

To obtain the γ_{ij} angles one usually has to solve the relevant first-order differential equations of the type given in Eq. (82). Next, like before, the α_{ij} angles are defined as the γ_{ij} angles at the end of a closed contour. In order to obtain the matrix $\mathbf{D}^{(M)}$, one has to replace, in Eq. (86), the angles γ_{ij} by the corresponding α_{ij} angles. Since $\mathbf{D}^{(M)}$ has to be a *diagonal* matrix with $(+1)$ and (-1) terms in the diagonal, this can be achieved if and only if *all* α_{ij} angles are zero or multiples of π. It is straightforward to show that with this structure the elements of $\mathbf{D}^{(M)}$ become [9]:

$$\mathbf{D}_{ij}^{(M)} = \delta_{ij} \prod_{k \neq i}^{M} \cos \alpha_{ik} = \delta_{ij}(-1)^{\sum_{k \neq i}^{M} n_{ik}} \qquad i = 1, \ldots, M \qquad (87)$$

where n_{ik} are integers that fulfill $n_{ik} = n_{ki}$. From Eq. (87), it is noticed that along the diagonal of $\mathbf{D}^{(M)}$ we may encounter K numbers that are equal to (-1) and the rest that are equal to $(+1)$. It is important to emphasize that in case a contour does not surround any conical intersection the value of K is zero.

VI.   THE CONSTRUCTION OF SUB-HILBERT SPACES AND SUB-SUB-HILBERT SPACES

In Section II.B, it was shown that the condition in Eq. (10) or its relaxed form in Eq. (40) enables the construction of sub-Hilbert space. Based on this possibility we consider a prescription first for constructing the sub-Hilbert space that extends to the full configuration space and then, as a second step, constructing of the sub sub-Hilbert space that extends only to (a finite) portion of configuration space.

In the study of (electronic) curve crossing problems, one distinguishes between a situation where two electronic curves, $E_j(R)$, $j = 1, 2$, approach each other at a point $R = R_0$ so that the difference $\Delta E(R = R_0) = E_2(R = R_0) - E_1$ is relatively small and a situation where the two electronic curves interact so that $\Delta E(R) \sim$ Const is relatively large. The first case is usually treated by the Landau–Zener formula [87–92] and the second is based on the Demkov approach [93]. It is well known that whereas the Landau–Zener type interactions are

strong enough to cause transitions between two adiabatic states, the Demkov-type interactions are usually weak and affect the motion of the interacting molecular species relatively slightly. The Landau–Zener situation is the one that may become the Jahn–Teller conical intersection in two dimensions [15–21]. We shall also include the Renner–Teller parabolic intersection [15,22,26,83], although it is characterized by two interacting potential energy surfaces that behave quadratically (and not linearly as in the Landau–Zener case) in the vicinity of the above mentioned degeneracy point.

A.   The Construction of Sub-Hilbert Spaces

By following Section II.B, we shall be more specific about what is meant by "strong" and "weak" interactions. It turns out that such a criterion can be assumed, based on whether two *consecutive* states do, or do not, form a conical intersection or a parabolical intersection (it is important to mention that only consecutive states can form these intersections). The two types of intersections are characterized by the fact that the nonadiabatic coupling terms, at the points of the intersection, become infinite (these points can be considered as the "black holes" in molecular systems and it is mainly through these "black holes" that electronic states interact with each other.). Based on what was said so far we suggest breaking up complete Hilbert space of size N into L sub-Hilbert spaces of varying sizes $N_P, P = 1, \ldots, L$ where

$$N = \sum_{P=1}^{L} N_P. \tag{88}$$

(L may be finite or infinite.)

Before we continue with the construction of the sub-Hilbert spaces, we make the following comment: Usually, when two given states form conical intersections, one thinks of isolated points in configuration space. In fact, conical intersections are not points but form (finite or infinite) seams that "cut" through the molecular configuration space. However, since our studies are carried out for planes, these planes usually contain isolated conical intersection points only.

The criterion according to which the break-up is carried out is based on the non-adiabatic coupling term τ_{ij} as were defined in Eq. (8a). In what follows, we distinguish between two kinds of non-adiabatic coupling terms: (1) The intra-non-adiabatic coupling terms $\tau_{ij}^{(P)}$, which are formed between two eigenfunctions belonging to a given sub-Hilbert space, namely, the Pth sub-space:

$$\tau_{ij}^{(P)} = \langle \zeta_i^{(P)} | \nabla \zeta_j^{(P)} \rangle \qquad i,j = 1, \ldots, N_P \tag{89}$$

and (2) Inter-non-adiabatic coupling terms $\tau_{ij}^{(P,Q)}$, which are formed between two eigenfunctions, the first belonging to the Pth sub-space and the second to the Qth sub-space:

$$\tau_{ij}^{(P,Q)} = \langle \zeta_i^{(P)} | \nabla \zeta_j^{(Q)} \rangle \qquad i = 1, \ldots, N_P \qquad j = 1, \ldots, N_Q \qquad (90)$$

The Pth sub-Hilbert space is defined through the following two requirements:

1. All N_p states belonging to the Pth sub-space interact strongly with each other in the sense that each pair of *consecutive* states have at least one point where they form a Landau–Zener type interaction. In other words, all $\tau_{jj+1}^{(P)}$; $j = 1, \ldots, N_P - 1$ form at least at one point in configuration space, a conical (parabolical) intersection.
2. The range of the Pth sub-space is defined in such a way that the lowest (or the first) state and the highest (the N_Pth) state that belong to this sub-space form Demkov-type interactions with the highest state belonging to the lower $(P - 1)$th sub-space and with the lowest state belonging to the upper $(P + 1)$th sub-space, respectively (see Fig. 2). In other words, the two non-adiabatic coupling terms fulfill the conditions:

$$\tau_{N_{P-1}1}^{(P-1,P)} \sim O(\varepsilon) \qquad \text{and} \qquad \tau_{N_P1}^{(P,P+1)} \sim O(\varepsilon) \qquad (91)$$

At this point, we make two comments: (a) Conditions (1) and (2) lead to a well-defined sub-Hilbert space that for any further treatments (in spectroscopy or scattering processes) has to be treated as a whole (and not on a ''state by state'' level). (b) Since all states in a given sub-Hilbert space are adiabatic states, strong interactions of the Landau–Zener type can occur between two consecutive states only. However, Demkov-type interactions may exist between any two states.

B.   The Construction of Sub-Sub-Hilbert Spaces

As we have seen, the sub-Hilbert spaces are defined for the whole configuration space and this requirement could lead, in certain cases, to situations where it will be necessary to include the complete Hilbert space. However, it frequently happens that the dynamics we intend to study takes place in a given, isolated, region that contains only part of the conical intersection points and the question is whether the effects of the other conical intersections can be ignored?

The answer to this question can be given following a careful study of these effects employing the line integral approach presented in terms of Eq. (27). For this purpose, we analyze what happens along a certain line Γ that surrounds
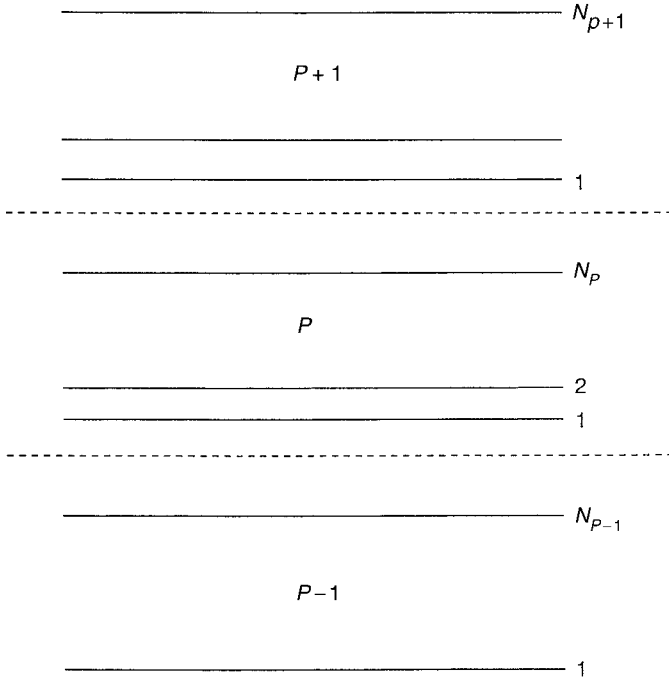
Figure 2. A schematic picture describing the three consecutive sub-Hilbert spaces, namely, the $(P-1)$th, the Pth, and the $(P+1)$th. The dotted lines are separation lines.

one or several conical intersections. To continue, we employ the same procedure as discussed in Section IV.B: We break up the adiabatic-to-diabatic transformation matrix **A** and the τ matrix as written in Eq. (43). In this way, we can show that if, along the particular line Γ, the noninteresting parts of the τ matrix are of order ε the error expected for the interesting part in the **A** matrix is of order $O(\varepsilon^2)$ [81]. If this happens for any contour in this region, then we can ignore the effects of conical intersection that are outside this region and carry out the dynamic calculations employing the reduced set of states.

VII.   THE TOPOLOGICAL SPIN

Before we continue and in order to avoid confusion, two matters have to be clarified: (1) We distinguished between two types of Landau–Zener situations, which form (in two dimensions) the Jahn–Teller conical intersection and the Renner–Teller parabolical intersection. The main difference between the two is

that the parabolical intersections do not produce topological effects and therefore, as far as this subject is concerned, they can be ignored. Making this distinction leads to the conclusion that the more relevant magnitude to characterize topological effects, for a given sub-space, is not its dimension M but N_J, the number of conical intersections. (2) In general, one may encounter more than one conical intersection between a pair of states [12,22,26,66,74]. However, to simplify the study, we assume one conical intersection for a pair of states so that $(N_J + 1)$ stands for the *number of states* that form the conical intersections.

So far, we introduced three different integers M, N_J, and K. As mentioned earlier, M is a characteristic number of the sub-space (see Section VI.B) but is not relevant for topological effects; instead N_J, as just mentioned, is a characteristic number of the sub-space and relevant for topological effects, and K, the number of (-1) terms in the diagonal of the topological matrix $\mathbf{D}$ (or the number of eigenstates that flip sign while the electronic manifold traces a closed contour) is relevant for topological effects but may vary from one contour to another, and therefore is not a characteristic feature for a given sub-space.

Our next task is to derive all possible K values for a given N_J. First, we refer to a few special cases: It was shown before that in case of $N_J = 1$ the $\mathbf{D}$ matrix contains two (-1) terms in its diagonal in case the contour surrounds the conical intersection and no (-1) terms when the contour does not surround the conical intersection. Thus the allowed values of K are either 2 or 0. The value $K = 1$ is not allowed. A similar inspection of the case $N_J = 2$ reveals that K, as before, is equal either to 2 or to 0 (see Section V.B). Thus the values $K = 1$ or 3 are not allowed. From here, we continue to the general case and prove the following statement:

In any molecular system, K can attain only *even* integers in the range [9]:

$$K = \{0, 2, \ldots, K_J\} \quad \begin{cases} K_J = N_J & N_J = 2p \\ K_J = (N_J + 1) & N_J = 2p + 1 \end{cases} \qquad (92)$$

where p is an integer.

The proof is based on Eq. (87). Let us assume that a certain closed contour yields a set of α_{ij} angles that produce a number K. Next, we consider a slightly different closed contour, along which one of these α_{ij} parameters, say α_{st}, changed its value from zero to π. From Eq. (87), it can be seen that only two $\mathbf{D}$ matrix elements contain $\cos(\alpha_{st})$, namely, $\mathbf{D}_{ss}$ and $\mathbf{D}_{tt}$. Now, if these two matrix elements were positive following the first contour, then changing α_{st} from $0 \to \pi$ would produce two additional (-1) terms, thus increasing K to $K + 2$; if these two matrix elements were negative, this change would cause K to decrease to $K - 2$; and if one of these elements was positive and the other negative, then

changing α_{st} from $0 \rightarrow \pi$ would not affect K. Thus, immaterial to the value of N_J, the various K values *differ* from each other by even integers only. Now, since any set of K values also contains the value $K = 0$ (the case when the closed loop does not surround any conical intersections), this implies that K can attain only even integers. The final result is the set of values presented in Eq. (92).

The fact that there is a one-to-one relation between the (-1) terms in the diagonal of the topological matrix and the fact that the eigenfunctions flip sign along closed contours (see discussion at the end of Section IV.A) hints at the possibility that these sign flips are related to a kind of a spin quantum number and in particular to its magnetic components.

The spin in quantum mechanics was introduced because experiments indicated that individual particles are not completely identified in terms of their three spatial coordinates [87]. Here we encounter, to some extent, a similar situation: A system of items (i.e., distributions of electrons) in a given point in configuration space is usually described in terms of its set of eigenfunctions. This description is incomplete because the existence of conical intersections causes the electronic manifold to be multivalued. For example, in case of two (isolated) conical intersections we may encounter at a given point in configuration space four different sets of eigenfunctions (see Section VIII).

$$
\begin{array}{ll}
\text{(a)} & (\zeta_1, \zeta_2, \zeta_3) \\
\text{(b)} & (-\zeta_1, -\zeta_2, \zeta_3) \\
\text{(c)} & (\zeta_1, -\zeta_2, -\zeta_3) \\
\text{(d)} & (-\zeta_1, \zeta_2, -\zeta_3)
\end{array}
\tag{93}
$$

In case of three conical intersections, we have as many as eight different sets of eigenfunctions, and so on. Thus we have to refer to an additional characterization of a given sub-sub-Hilbert space. This characterization is related to the number N_J of conical intersections and the associated possible number of sign flips due to different contours in the relevant region of configuration space, traced by the electronic manifold.

In [7,8,80], it was shown that in a two-state system the nonadiabatic coupling term, τ_{12}, has to be "quantized" in the following way:

$$
\oint_\Gamma \tau_{12}(s') \cdot ds' = n\pi
\tag{94}
$$

where n is an integer (in order to guarantee that the 2×2 diabatic potential be single valued in configuration space). In case of conical intersections, this number has to be an odd integer and for our purposes it is assumed to be $n = 1$. Thus each conical intersection can be considered as a "spin." Since in a given

sub-space N_J conical intersections are encountered, we could define the spin J of this sub-space as $(N_J/2)$. However, this definition may lead to more sign flips than we actually encounter (see Section VIII). In order to make a connection between J and N_J as well as with the "magnetic components" M_J of J and the number of the actual sign flips, the spin J has to be defined as [9]:

$$J = \frac{1}{2}\frac{K_J}{2} \qquad \begin{cases} K_J = N_J & N_J = 2p \\ K_J = (N_J + 1) & N_J = 2p + 1 \end{cases} \qquad (95)$$

and, accordingly, the various M_J values are defined as

$$M_J = J - K/2 \qquad \text{where} \qquad K = \{0, 2, \ldots, K_J\} \qquad (96)$$

For the seven lowest N_J values, we have the following assignments:

$$\begin{aligned}
&\text{For } N_J = 0 && \{J = 0 && M_J = 0\} \\
&\text{For } N_J = 1 && \{J = 1/2 && M_J = 1/2, -1/2\} \\
&\text{For } N_J = 2 && \{J = 1/2 && M_J = 1/2, -1/2\} \\
&\text{For } N_J = 3 && \{J = 1 && M_J = 1, 0, -1\} \\
&\text{For } N_J = 4 && \{J = 1 && M_J = 1, 0, -1\} \\
&\text{For } N_J = 5 && \{J = 3/2 && M_J = 3/2, 1/2, -1/2, -3/2\} \\
&\text{For } N_J = 6 && \{J = 3/2 && M_J = 3/2, 1/2, -1/2, -3/2\} \\
&\text{For } N_J = 7 && \{J = 2 && M_J = 2, 1, 0, -1, -2\}
\end{aligned} \qquad (97)$$

The general formula and the individual cases as presented in Eq. (97) indicate that indeed the number of conical intersections in a given sub-space and the number of possible sign flips within this sub-sub-Hilbert space are interrelated, similar to a spin J with respect to its magnetic components M_J. In other words, each decoupled sub-space is now characterized by a spin quantum number J that connects between the number of conical intersections in this system and the topological effects which characterize it.

VIII. AN ANALYTICAL DERIVATION FOR THE POSSIBLE SIGN FLIPS IN A THREE-STATE SYSTEM

In Section IX, we intend to present a geometrical analysis that permits some insight with respect to the phenomenon of sign flips in an M-state system ($M > 2$). This can be done without the support of a parallel mathematical study [9]. In this section, we intend to supply the mathematical foundation (and justification) for this analysis [10,12]. Thus employing the line integral approach, we intend to prove the following statement:
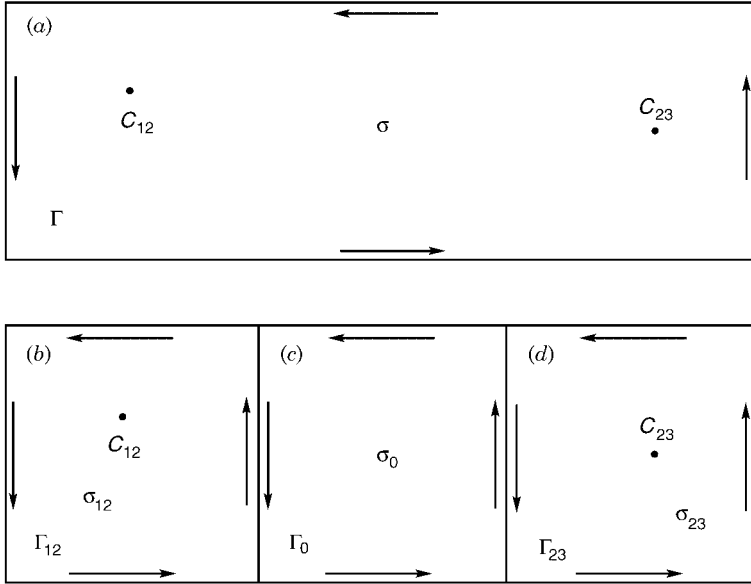
Figure 3. The breaking up of a region σ, which contains two conical intersections (at C_{12} and C_{23}), into three subregions: (*a*) The full region σ defined in terms of the closed contour Γ. (*b*) The region σ_{12}, which contains a conical intersection at C_{12} and is defined by the closed contour Γ_{12}. (*c*) The region σ_0, which is defined by the closed contour Γ_0 and does not contain any conical intersection. (*d*) The region σ_{23}, which contains a conical intersection at C_{23} and is defined by the closed contour Γ_{23}. It can be seen that $\Gamma = \Gamma_{12} + \Gamma_0 + \Gamma_{23}$.

If a contour in a given plane surrounds two conical intersections belonging to two different (adjacent) pairs of states, only two eigenfunctions flip sign—the one that belongs to the lowest state and the one that belongs to the highest one.

To prove this, we consider the following three regions (see Fig. 3): In the first region, designated σ_{12}, is located the main portion of the interaction, t_{12}, between states 1 and 2 with the point of the conical intersection at C_{12}. In the second region, designated as σ_{23}, is located the main portion of the interaction, t_{23}, between states 2 and 3 with the point of the conical intersection at C_{23}. In addition, we assume a third region, σ_0, which is located in-between the two and is used as a buffer zone. Next, it is assumed that the intensity of the interactions due to the components of t_{23} in σ_{12} and due to t_{12} in σ_{23} is ~ 0. This situation can always be achieved by shrinking $\sigma_{12}(\sigma_{23})$ toward its corresponding center $C_{12}(C_{23})$. In σ_0, the components of both t_{12} and t_{23} may be of arbitrary magnitude but no conical intersection of any pair of states is allowed to be there.

To prove our statement, we consider the line integral [see Eq. (27)]:

$$\mathbf{A} = \mathbf{A}_0 - \oint_{\Gamma} ds \cdot \boldsymbol{\tau} \mathbf{A} \tag{98}$$

where the integration is carried out along a closed contour Γ, $\mathbf{A}$ is the 3×3 adiabatic-to-diabatic transformation matrix to be calculated, the dot stands for a scalar product, and $\boldsymbol{\tau}$ is the matrix of 3×3 that contains the two non-adiabatic coupling terms, namely,

$$\boldsymbol{\tau}(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \tag{99}$$

Note the components of $t_{13} \sim 0$. This assumption is not essential for the proof, but simplifies the derivation.

The integral in Eq. (98) will now be presented as a sum of three integrals (for a detailed discussion on that subject: see Appendix C), namely,

$$\mathbf{A} = \mathbf{A}_0 - \oint_{\Gamma_{12}} ds \cdot \boldsymbol{\tau} \mathbf{A} - \oint_{\Gamma_0} ds \cdot \boldsymbol{\tau} \mathbf{A} - \oint_{\Gamma_{23}} ds \cdot \boldsymbol{\tau} \mathbf{A} \tag{100}$$

Since there is no conical intersection in the buffer zone, σ_0, the second integral is zero and can be deleted so that we are left with the first and the third integrals. In general, the calculation of each integral is independent of the other; however, the two calculations have to yield the same result, and therefore they have to be interdependent to some extent. Thus we do each calculation separately but for different (yet unknown) boundary conditions: The first integral will be done for $\mathbf{G}_{12}$ as a boundary condition and the second for $\mathbf{G}_{23}$. Thus $\mathbf{A}$ will be calculated twice:

$$\mathbf{A} = \mathbf{G}_{ij} - \oint_{\Gamma_{ij}} ds \cdot \boldsymbol{\tau} \mathbf{A} \tag{101}$$

Next are introduced the topological matrices $\mathbf{D}$, $\mathbf{D}_{12}$, and $\mathbf{D}_{23}$, which are related to $\mathbf{A}$ in the following way [see Eq. (39)]:

$$\mathbf{A} = \mathbf{D}\mathbf{A}_0 \tag{102a}$$

$$\mathbf{A} = \mathbf{D}_{12}\mathbf{G}_{12} \tag{102b}$$

$$\mathbf{A} = \mathbf{D}_{23}\mathbf{G}_{23} \tag{102c}$$

The three equalities can be fulfilled if and only if the two $\mathbf{G}$ matrices, namely, $\mathbf{G}_{12}$ and $\mathbf{G}_{23}$, are chosen to be

$$\mathbf{G}_{12} = \mathbf{D}_{23}\mathbf{A}_0 \qquad \text{and} \qquad \mathbf{G}_{23} = \mathbf{D}_{12}\mathbf{A}_0 \qquad (103)$$

Since the $\mathbf{D}$ matrices are diagonal the same applies to $\mathbf{D}_{12}$ and $\mathbf{D}_{23}$ so that $\mathbf{D}$ becomes

$$\mathbf{D} = \mathbf{D}_{13} = \mathbf{D}_{12}\mathbf{D}_{23} \qquad (104)$$

Our next task will be to obtain $\mathbf{D}_{12}$ and $\mathbf{D}_{23}$. For this purpose, we consider $\boldsymbol{\tau}_{12}$ and $\boldsymbol{\tau}_{23}$—the two partial $\boldsymbol{\tau}$ matrices—defined as follows:

$$\boldsymbol{\tau}_{12}(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \text{and} \qquad \boldsymbol{\tau}_{23}(s) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \qquad (105)$$

so that

$$\boldsymbol{\tau} = \boldsymbol{\tau}_{12} + \boldsymbol{\tau}_{23} \qquad (106a)$$

We start with the first of Eqs. (101), namely,

$$\mathbf{A} = \mathbf{G}_{12} - \oint_{\Gamma_{ij}} ds \cdot \boldsymbol{\tau}_{12}\mathbf{A} \qquad (107)$$

where $\boldsymbol{\tau}_{12}$ replaces $\boldsymbol{\tau}$ because $\boldsymbol{\tau}_{23}$ is assumed to be negligibly small in σ_{12}. The solution and the corresponding $\mathbf{D}$ matrix, namely, $\mathbf{D}_{12}$ are well known (see discussion in Sections V.A.1 and V.B). Thus

$$\mathbf{D}_{12} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (108)$$

which implies (as already explained in Section IV.A) that the first (lowest) and the second functions flip sign. In the same way, it can be shown that $\mathbf{D}_{23}$ is equal to

$$\mathbf{D}_{23} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (109)$$

which shows that the second and the third (the highest) eigenfunctions flip sign. Substituting Eqs. (108) and (109) in Eq. (104) yields the following result for $\mathbf{D}_{13}$:

$$\mathbf{D}_{13} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (110)$$

In other words, surrounding the two conical intersections indeed leads to the flip of sign of the first and the third eigenfunctions, as was claimed.

This idea can be extended, in a straightforward way, to various situations as will be done in Section IX.

IX. THE GEOMETRICAL INTERPRETATION FOR SIGN FLIPS

In Sections V and VII, we discussed the possible K values of the $\mathbf{D}$ matrix and made the connection with the number of signs flip based on the analysis given in Section IV.A. Here, we intend to present a geometrical approach in order to gain more insight into the phenomenon of signs flip in the M-state system ($M > 2$).

As was already mentioned, conical intersections can take place only between two adjacent states (see Fig. 4). Next, we make the following definitions:

1. Having two consecutive states j and $(j + 1)$, the two form the conical intersection to be designated as C_j as shown in Figure 4, where N_J conical intersection are presented.
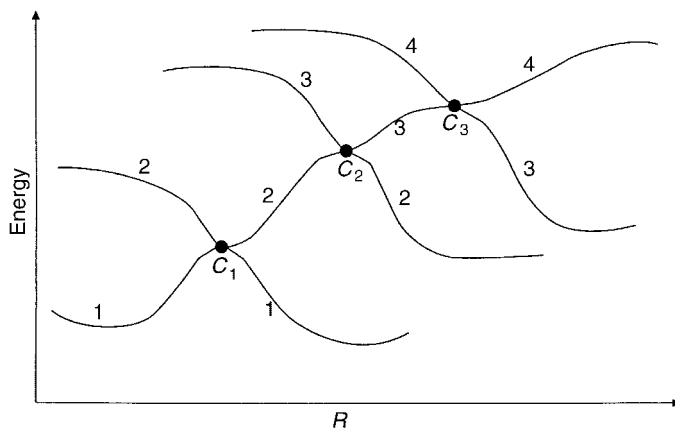

Figure 4. Four interacting adiabatic surfaces presented in terms of four adiabatic curves. The points C_j; $j = 1,2,3$, stand for the three conical intersections.

2. The contour that surrounds a conical intersection at C_j will be designated as Γ_{jj+1} [see Fig. 5(a)].

3. A contour that surrounds two consecutive conical intersections that is, C_j and C_{j+1} will be designated as Γ_{jj+2} [see Fig. 5(b)]. In the same way a contour that surrounds n consecutive conical intersections namely C_j, $C_{j+1} \ldots C_{j+n}$ will be designated as Γ_{jj+n} [see Fig. 5(c) for $N_J = 3$].

4. In case of three conical intersections or more, a contour that surrounds C_j and C_k but not the in-between conical intersections will be designated as $\Gamma_{j,k}$. Thus, for example, $\Gamma_{1,3}$ surrounds C_1 and C_3 but not C_2 (see Fig. 5d).

We also introduce an algebra of closed contours based on the analysis given in Section VIII (see also Appendix C):

$$\Gamma_{jn} = \sum_{k=j}^{n-1} \Gamma_{kk+1} \tag{111}$$

and also

$$\Gamma_{j,k} = \Gamma_{jj+1} + \Gamma_{kk+1} \qquad \text{where} \qquad (k > j+1) \tag{112}$$

This algebra implies that in case of Eq. (111) the only two functions (out of n) that flip sign are ζ_1 and ζ_n because all in-between ζ functions get their sign flipped twice. In the same way, Eq. (112) implies that all four electronic functions mentioned in the expression, namely, the jth and the $(j+1)$th, the kth and the $(k+1)$th, all flip sign. In what follows, we give a more detailed explanation based on the mathematical analysis of the Section VIII.

In Sections VII and VIII, it was mentioned that K yields the number of eigenfunctions that flip sign when the electronic manifold traces certain closed paths. In what follows, we shall show how this number is formed for various N_J values.

The situation is obvious for $N_J = 1$. Here, the path either surrounds or does not surround a C_1. In case it surrounds it, two functions, that is, ζ_1 and ζ_2, flip sign so that $K = 2$ and if it does not surround it no ζ function flips sign and $K = 0$. In case of $N_J = 2$, we encounter two conical intersections, namely, C_1 and the C_2 (see Fig. 5a and 5b). Moving the electronic manifold along the path Γ_{12} will change the signs of ζ_1 and ζ_2, whereas moving it along the path Γ_{23} will change the signs ζ_2 and ζ_3. Next, moving the electronic manifold along the path, Γ_{13} (and Fig. 5b) causes the sign of ζ_2 to be flipped twice (once when surrounding C_1 and once when surrounding C_2) and therefore, altogether, its sign remains unchanged. Thus in the case of $N_J = 2$ we can have either no change of sign (when the path does not surround any conical intersection) or three cases where two different functions change sign.
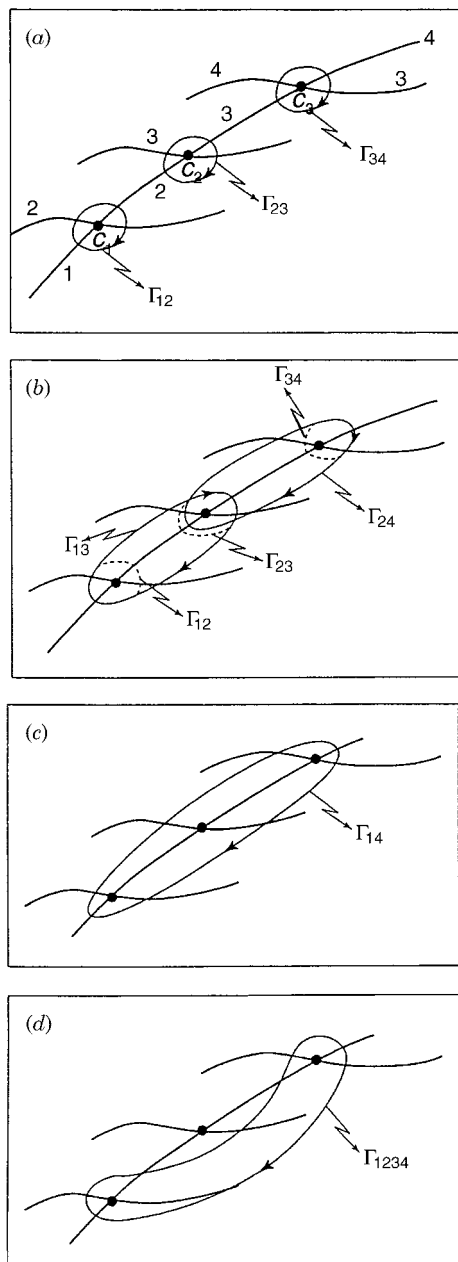
Figure 5. The four interacting surfaces, the three points of conical intersection and the various contours leading to sign conversions: (a) The contours Γ_{jj+1} surrounding the respective C_j; $j = 1, 2, 3$ leading to the sign conversions of the jth and the $(j + 1)$th eigenfunctions. (b) The contours Γ_{jj+2} surrounding the two (respective) conical intersections namely C_j and C_{j+1}; $j = 1, 2$ leading to the sign conversions of the jth and the $(j + 2)$th eigenfunctions but leaving unchanged the sign of the middle, the $(j + 1)$, eigenfunction. Also shown are the contours Γ_{jj+1} surrounding the respective C_j; $j = 1, 2, 3$ using partly dotted lines. It can be seen that $\Gamma_{jj+2} = \Gamma_{jj+1} + \Gamma_{j+1j+2}$. (c) The contour Γ_{14} surrounding the three conical intersections, leading to the sign conversions of the first and the fourth eigenfunctions but leaving unchanged the signs of the second and the third eigenfunctions. Based on Figure (5b) we have $\Gamma_{14} = \Gamma_{12} + \Gamma_{23} + \Gamma_{34}$. (d) The contour $\Gamma_{1,3}$ surrounding the two external conical intersections but not the middle one, leading to the sign conversions of all four eigenfunctions, that is, $(\zeta_1, \zeta_2, \zeta_3, \zeta_4); \rightarrow (-\zeta_1, -\zeta_2, -\zeta_3, -\zeta_4)$. Based on Figure (5b) we have $\Gamma_{1,3} = \Gamma_{12} + \Gamma_{34}$.

A somewhat different situation is encountered in case of $N_J = 3$, and therefore we shall briefly discuss it as well (see Fig. 5d). It is now obvious that contours of the type Γ_{jj+1}; $j = 1, 2, 3$ surround the relevant C_j (see Fig. 5a) and will flip the signs of the two corresponding eigenfunctions. From Eq. (111), we get that surrounding two consecutive conical intersections, namely, C_j and C_{j+1}, with Γ_{jj+2}; $j = 1, 2$ (see Fig. 5b), will flip the signs of the two external eigenfunctions, namely, ζ_j and ζ_{j+2}, but leave the sign of ζ_{j+1} unchanged. We have two such cases—the first and the second conical intersections and the second and the third ones. Then we have a contour Γ_{14} that surrounds all three conical intersections (see Fig. 5c) and here, like in the previous where $N_J = 2$ [see also Eq. (111)], only the two external functions, namely, ζ_1 and ζ_4 flip sign but the two internal ones, namely, ζ_2 and ζ_3, will be left unchanged. Finally, we have the case where the contour $\Gamma_{1,3}$ surrounds C_1 and C_3 but not C_2 (see Fig. 5d). In this case, all four functions flip sign [see Eq. (112)].

We briefly summarize what we found in this $N_J = 3$ case: We revealed six different contours that led to the sign flip of six (different) pairs of functions and one contour that leads to a sign flip of all four functions. The analysis of Eq. (87) shows that indeed we should have seven different cases of sign flip and one case without sign flip (not surrounding any conical intersection).

X.   THE MULTIDEGENERATE CASE

The emphasis in our previous studies was on isolated two-state conical intersections. Here, we would like to refer to cases where at a given point three (or more) states become degenerate. This can happen, for example, when two (line) seams cross each other at a point so that at this point we have three surfaces crossing each other. The question is: How do we incorporate this situation into our theoretical framework?

To start, we restrict our treatment to a tri-state degeneracy (the generalization is straightforward) and consider the following situation:

1. The two lowest states form a conical intersection, presented in terms of $\tau_{12}(\rho)$, located at the origin, namely, at $\rho = 0$.
2. The second and the third states form a conical intersection, presented in terms of $\tau_{23}(\rho, \varphi \mid \rho_0, \varphi_0)$, located at $\rho = \rho_0$, $\varphi = \varphi_0$ [24].
3. The tri-state degeneracy is formed by letting $\rho_0 \to 0$, namely,

$$\lim_{\rho_0 \to 0} \tau_{23}(\rho, \varphi \mid \rho_0, \varphi_0) = \tau_{23}(\rho, \varphi) \tag{113}$$

so that the two conical intersections coincide. Since the two conical intersections are located at the same point, every closed contour that surrounds one of them will surround the other so that this situation is the case of one contour $\Gamma(= \Gamma_{13})$

surrounding two conical intersections (see Fig. 5*b*). According to the discussion of Section IX, only two functions will flip signs (i.e., the lowest and the highest one). Extending this case to an intersection point of *n* surfaces will not change the final result, namely, only two functions will flip signs, the lowest one and the highest one.

This conclusion contradicts the findings discussed in Sections V.A.2 and V.A.3. In Section V.A.2, we treated a three-state model and found that functions can *never* flip signs. In Section V.A.3, we treated a four-state case and found that either all four functions flip their sign or none of them flip their sign. The situation where two functions flip signs is not allowed under any conditions.

Although the models mentioned here are of a very specialized form (the non-adiabatic coupling terms have identical spatial dependence), still the fact that such contradictory results are obtained for the two situations could hint to the possibility that in the transition process from the nondegenerate to the degenerate situation, in Eq. (113), something is not continuous.

To date, this contradiction has not been resolved but we still would like to make the following suggestion. In molecular physics, we may encounter two types of multidegeneracy situations: (1) The one described above is formed from an aggregation of two-state conical intersections and depends on external coordinates (the coordinates that form the seam). Thus this multidegeneracy is created by varying these external coordinates in a proper way. In the same way, the multidegeneracy can be removed by varying these coordinates. Note that this kind of a degeneracy is not an essential degeneracy because the main features of the individual conical intersections are unaffected while assembling or disassembling this degeneracy. We shall term this degeneracy as a *breakable* multidegeneracy. (2) The other type mentioned above is the one that is not formed from an aggregation of conical intersections and therefore will not breakup under any circumstances. Therefore, this degeneracy is termed the *unbreakable* multidegeneracy.

XI. THE NECESSARY CONDITIONS FOR A RIGOROUS MINIMAL DIABATIC POTENTIAL MATRIX

This Section considers one of the more important dilemmas in molecular physics: Given a Born–Oppenheimer–Huang system, what is the minimal sub-Hilbert space for which diabatization is still valid.

A. Introductory Comments

When studying molecular systems one encounters two almost insurmountable difficulties: (1) That of numerically treating the non-adiabatic coupling terms that are not only spiky—a feature that is in itself a ''recipe'' for numerical

instabilities—but also, singular. (2) That of having to consider large portions of the Hilbert space. As we will show in this section, the two apparently unrelated difficulties are strongly interrelated. Moreover, we will show that resolving the first difficulty may, in many cases, also settle the second.

As discussed earlier, one distinguishes between (1) the adiabatic framework that is characterized by the adiabatic surfaces and the non-adiabatic (derivative) coupling terms and (2) the diabatic framework that is characterized by the fact that derivative couplings are eliminated and replaced by (smoothly behaving) potential couplings. Because of the unpleasant features of the non-adiabatic coupling terms the dynamics is expected to be more easily carried out within the diabatic framework. Therefore, transforming to the diabatic framework (also to be termed *diabatization*) is the right thing to do when treating the multistate problem as created by the Born–Oppenheimer–Huang approach [1,2]. However, because the non-adiabatic coupling terms are frequently singular functions may cause difficulties and therefore the diabatization becomes more of a theoretical–mathematical problem rather than a numerical one.

In 1975, Baer suggested that the diabatic arrangement be reached by first forming the adiabatic framework and then transforming it to the diabatic one by employing the non-adiabatic coupling terms [34]. This approach becomes particularly simple when applied to two states, because it amounts to the calculation of an angle (related to a 2×2 orthogonal matrix), which is formed by integration over the (1,2) non-adiabatic coupling term along a given contour [34–36]. This approach was successfully employed to treat charge-transfer processes [54,94–97], which until that time were solely carried out using classical trajectories [3,98,99], reactive exchange processes between neutrals [100–102] and photodissociation processes [103,104].

Because of difficulties in calculating the non-adiabatic coupling terms, this method did not become very popular. Nevertheless, this approach, was employed extensively in particular to simulate spectroscopic measurements, with a ''modification'' introduced by Macias and Riera [47,48]. They suggested looking for a symmetric operator that behaves ''violently'' at the vicinity of the conical intersection and use it, instead of the non-adiabatic coupling term, as the integrand to calculate the adiabatic-to-diabatic transformation. Consequently, a series of operators such as the electronic dipole moment operator, the transition dipole moment operator, the quadrupole moment operator, and so on, were employed for this purpose [49,52,53,105]. However, it has to be emphasized that immaterial to the success of this approach, it is still an ad hoc procedure.

For example, there are also other approaches by Pacher et al. [106], Romero et al. [107], Sidis [40], and Domcke and Stock [42], which developed recipes for construction ab initio diabatic states. These methods can be efficient as long as one encounters, *at most*, one isolated conical intersection in a given region in

configuration space but have to be further developed, if several conical intersections are located at the region of interest.

Now we intend to present the purpose of this section. In order to do this in a comprehensive way, we need to explain what is meant, within the *present* framework, by the statement that "the diabatization is non-physical." The procedure discussed above is based on a transformation matrix of a dimension M derived within a sub-Hilbert space of the same dimension. The statement "a diabatization is non-physical" implies that some of the elements of the diabatic matrix formed in this process are *multivalued* in configuration space. (In this respect, it is important to emphasize that the nuclear Schrödinger equation cannot be solved for multivalued potentials.) We show that if an M-dimensional sub-Hilbert space is not large enough, some elements of the diabatic potential matrix will not be single valued. Thus a resolution to this difficulty seems to be in increasing the dimension of the sub-Hilbert space, that is, the value of M. However, increasing M indefinitely will significantly increase the computational volume. Therefore it is to everyone's interest to keep M as small as possible. Following this explanation, we can now state the purpose of this section:

We intend to show that an adiabatic-to-diabatic transformation matrix based on the non-adiabatic coupling matrix can be used not only for reaching the diabatic framework but also as a mean to determine the *minimum* size of a sub-Hilbert space, namely, the minimal M value that still guarantees a valid diabatization.

For example: one forms, within a two-dimensional (2D) sub-Hilbert space, a 2×2 diabatic potential matrix, which is not single valued. This implies that the 2D transformation matrix yields an invalid diabatization and therefore the required dimension of the transformation matrix has to be at least three. The same applies to the size of the sub-Hilbert space, which also has to be at least three. In this section, we intend to discuss this type of problems. It also leads us to term the conditions for reaching the minimal relevant sub-Hilbert space as "the necessary conditions for diabatization."

In this section, diabatization is formed employing the adiabatic-to-diabatic transformation matrix $\mathbf{A}$, which is a solution of Eq. (19). Once $\mathbf{A}$ is calculated, the diabatic potential matrix $\mathbf{W}$ is obtained from Eq. (22). Thus Eqs. (19) and (22) form the basis for the procedure to obtain the diabatic potential matrix elements.

Note that since the *adiabatic* potentials are single valued by definition, the single valuedness of $\mathbf{W}$ (viz, the single valuedness of each of its terms) depends on the features of the $\mathbf{A}$ matrix [see Eq. (22)]. It is also obvious that if $\mathbf{A}$ is single valued, the same applies to $\mathbf{W}$ [the single valuedness of the $\mathbf{A}$ matrix in a given region is guaranteed if Eq. (25) is fulfilled throughout this region]. However, in Section (IV.A) we showed that $\mathbf{A}$ does not have to be single valued in order to guarantee the single valuedness of $\mathbf{W}$. In fact, it was proved that the necessary condition for having single-valued diabatic potentials along a given

contour Γ is that the **D** matrix introduced in Eq. (38) is *diagonal* with numbers of norm 1, namely, numbers that are either $(+1)$ or (-1). If this condition is fulfilled for every contour in the region of interest, then we may say that for this particular dimension M the diabatic potential is single valued or in other words the diabatization is valid. However, if this condition is fulfilled for a give value M but not for $(M - 1)$, then M is the minimal value for which diabatization is valid in this particular case.

According to Section VI, the size M of the sub-Hilbert space is determined whether the respective M states form an isolated set of states fulfilling Eqs. (91). In this case, diabatization is always valid for this subsystem. However, it can happen that under certain geometrical situations the size of the sub-Hilbert space for which diabatization is valid is even smaller than this particular M
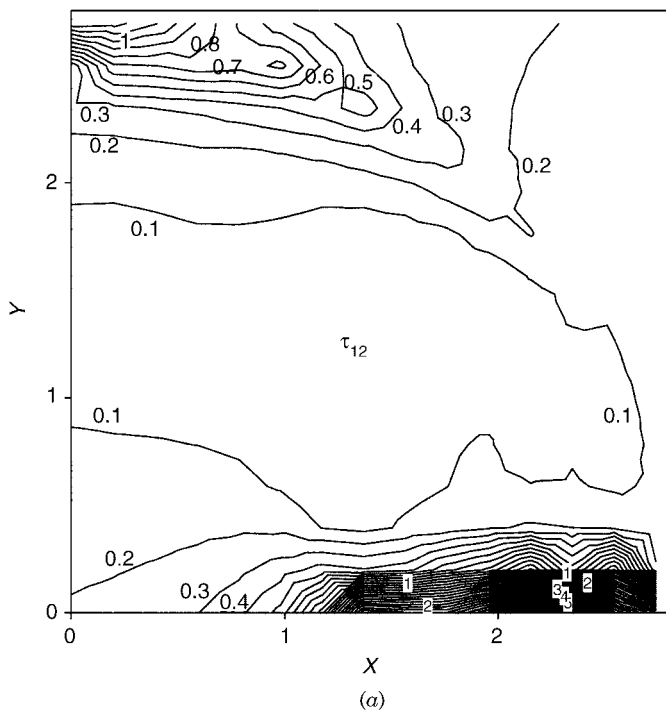
Figure 6. Equi-nonadiabatic coupling lines for the terms $\tau_{12}(x, y)$ and $\tau_{23}(x, y)$ as calculated for the C_2H molecule for a fixed C–C distance, that is, $r_{CC} = 1.35$ Å. (*a*) Equi-non-adiabatic coupling term lines for the $\tau_{12}(x, y)$. (*b*) Equi-non-adiabatic coupling term lines for $\tau_{23}(x, y)$. The Cartesian coordinates (x, y) are related to (q, θ) as follows: $x = q \cos \theta$; $y = q \sin \theta$, where q and θ are measured with respect to the midpoint between the two carbons.

value. These geometrical situations are considered in Section XI.B, and to simplify the discussion we refer to $M = 3$.

B. The Noninteracting Conical Intersections

Let us consider a system of three states where the two lower states are coupled by $\tau_{12}(s)$ and the two upper ones by $\tau_{23}(s)$ (see Section VIII for details). By the concept "noninteracting conical intersections" we mean the case where the spatial distribution of $\tau_{12}(s)$ and $\tau_{23}(s)$ is such that they overlap only slightly at the region of interest. As an example we may consider a case where the main intensity of $\tau_{12}(s)$ is concentrated along one ridge and the main intensity of $\tau_{23}(s)$ is concentrated along another ridge. Next, we assume that these two ridges are approximately parallel and located far enough apart so that the overlap between $\tau_{12}(s)$ and $\tau_{23}(s)$ is minimal (see Figs. 6 and 7).

We are interested in calculating the diabatic potentials for a region in configuration space, that contains the two conical intersections. According
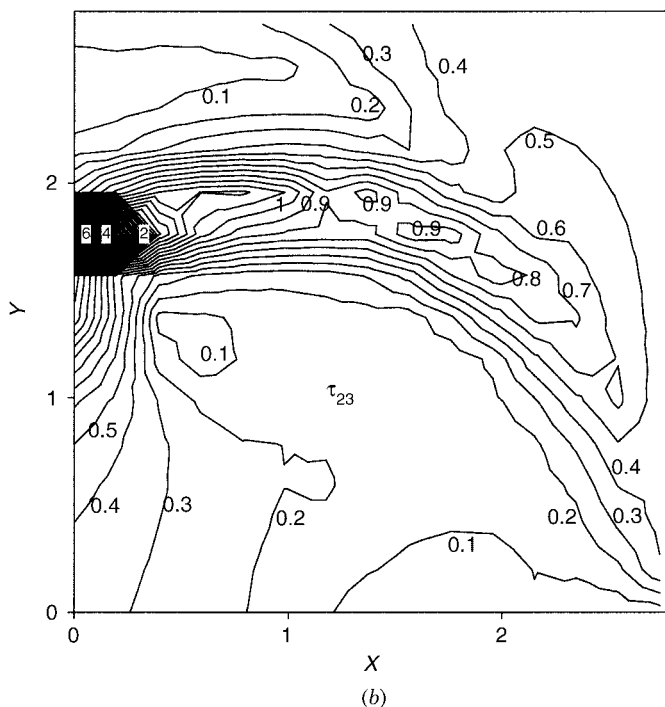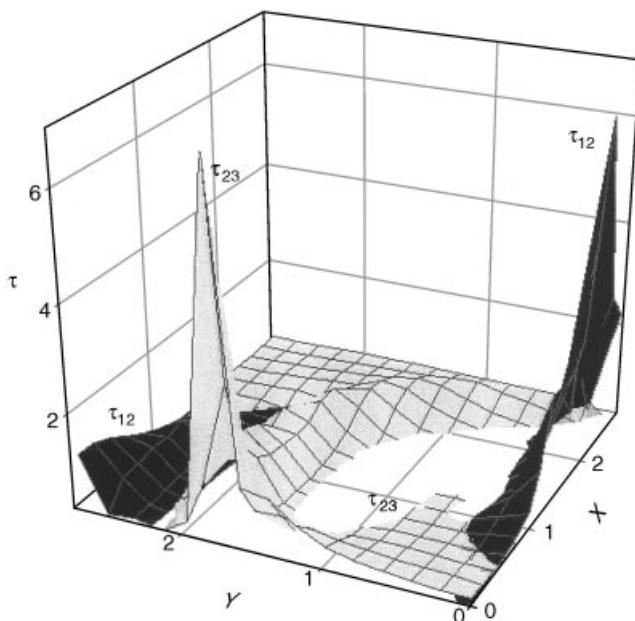

Figure 6   (*Continued*)

Figure 7. The geometrical positions (with respect to the *CC* axis) of $\tau_{12}(x, y)$ and $\tau_{23}(x, y)$. All distances are in angstroms (Å). The Cartesian coordinates (x, y) are related to (q, θ) as follows: $x = q \cos \theta$; $y = q \sin \theta$, where q and θ are measured with respect to the midpoint between the two carbons.

to Section VI, for this purpose we need the *three* states because the two lowest states (1 and 2) and the two highest states (2 and 3) are *strongly* coupled to each other. Next, we examine to see if under these conditions this is really necessary or could the diabatization be achieved with only the two lowest states.

For this purpose, we consider Figure 8 with the intention of examining what happens along the contour Γ, in particularly when it gets close to C_{23}. Note that some segments of the contour Γ are drawn as full lines and others are as dashed lines. The full lines denote segments along which $\tau_{12}(s)$ is of a strong intensity but $\tau_{23}(s)$ is negligibly weak. The dashed lines denote segments along which $\tau_{12}(s)$ is negligibly weak.

Next, consider the following line integral [see Eq. (27)]:

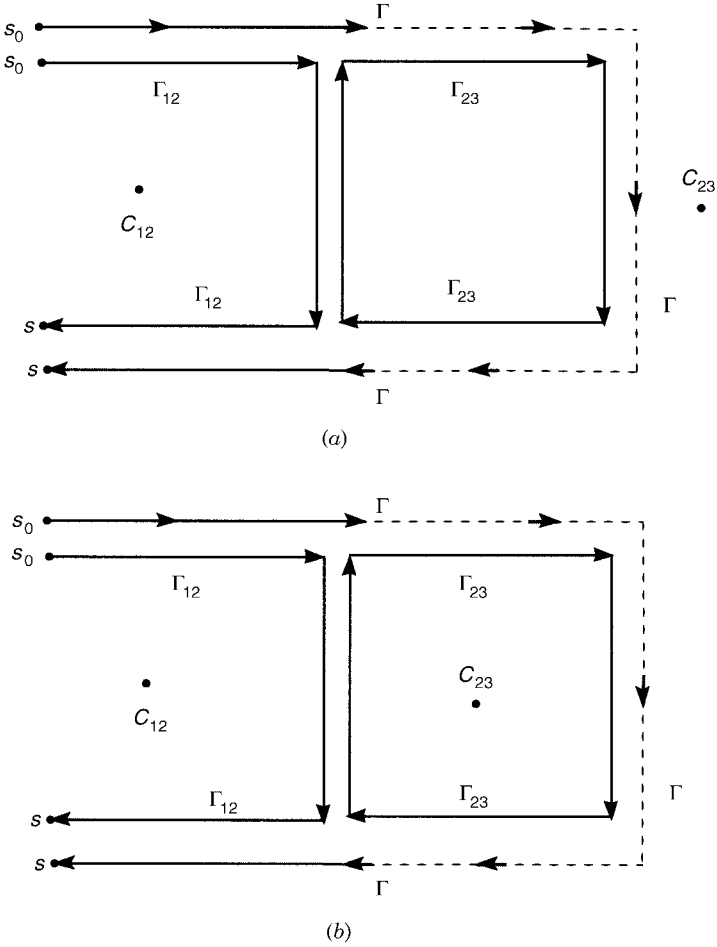$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{s_0}^{s} ds \cdot \mathbf{\tau A} \qquad (114)$$

Figure 8. The representation of an open contour Γ in terms of an open contour Γ_{12} in the vicinity of the conical intersection at C_{12} and a closed contour Γ_{23} at the vicinity of a conical intersection at C_{23}: $\Gamma = \Gamma_{12} + \Gamma_{23}$. It is assumed that the intensity of τ_{12} is strong along Γ_{12} (full line) and weak along Γ_{23} (dashed line). (*a*) The situation when C_{23} is outside the closed contour Γ_{23}. (*b*) The situation when C_{23} is inside the closed contour Γ_{23}.

where $\mathbf{A}(s)$ and $\boldsymbol{\tau}(s)$ are of dimensions 3×3 [the explicit form of $\boldsymbol{\tau}(s)$ is given in Eq. (99)]. We also consider the two other $\boldsymbol{\tau}$ matrices, namely, $\boldsymbol{\tau}_{12}(s)$ and $\boldsymbol{\tau}_{23}(s)$ (see Eq. (105)] and it is easy to see that

$$\boldsymbol{\tau}(s) = \boldsymbol{\tau}_{12}(s) + \boldsymbol{\tau}_{23}(s) \tag{106b}$$

To continue, the contour Γ, along which the integration in Eq. (114) is carried out, is assumed to be the sum of two contours [see Fig. 8]:

$$\Gamma = \Gamma_{12} + \Gamma_{23} \tag{115}$$

where Γ_{23} is a closed contour in the vicinity of C_{23} that may or may not surround it and Γ_{12} is an open contour near C_{12}. By substituting Eq. (115) in (114) we get

$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{\Gamma_{12}} ds' \cdot \boldsymbol{\tau}(s')\mathbf{A}(s') - \oint_{\Gamma_{23}} ds' \cdot \boldsymbol{\tau}(s')\mathbf{A}(s') \tag{116}$$

Next, by recalling the assumptions concerning the intensities of $\boldsymbol{\tau}_{12}(s)$ and $\boldsymbol{\tau}_{23}(s)$ we replace $\boldsymbol{\tau}(s)$, in the second term of Eq. (116) with $\boldsymbol{\tau}_{12}(s)$ and in the third term with $\boldsymbol{\tau}_{23}(s)$. As a result Eq. (116) becomes

$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{\Gamma_{12}} ds' \cdot \boldsymbol{\tau}_{12}(s')\mathbf{A}(s') - \oint_{\Gamma_{23}} ds' \cdot \boldsymbol{\tau}_{23}(s')\mathbf{A}(s') \tag{117}$$

By defining $\mathbf{A}_{23}$ as the following (constant) matrix,

$$\mathbf{A}_{23} = \mathbf{A}(s_0) - \oint_{\Gamma_{23}} ds' \cdot \boldsymbol{\tau}_{23}(s')\mathbf{A}(s') \tag{118}$$

Eq. (117) becomes

$$\mathbf{A}(s) = \mathbf{A}_{23} - \int_{\Gamma_{12}} ds' \cdot \boldsymbol{\tau}_{12}(s')\mathbf{A}(s') \tag{119}$$

where the matrix $\mathbf{A}_{23}$ is the corresponding "boundary" value matrix. As for $\mathbf{A}_{23}$, it is noticed to be the solution of Eq. (118), namely, the outcome of an integration performed along a closed contour (Γ_{23}) where $\boldsymbol{\tau}_{23}$ is the kernel. Consequently, this matrix can be presented as [see Eq. (39)]:

$$\mathbf{A}_{23} = \mathbf{D}_{23}\mathbf{A}(s_0) \tag{120}$$

where from the analysis in Section VIII we get that $\mathbf{D}_{23}$ will have a $(+1)$ at position $(1,1)$ and a (-1) at positions $(2,2)$ and $(3,3)$ when it surrounds the conical intersection at C_{23}.

Now, by returning to Eq. (119) it can be shown that if $\mathbf{A}_{12}$ is the solution of the equation

$$\mathbf{A}_{12}(s) = \mathbf{A}_0 + \int_{\Gamma_{12}} ds' \cdot \boldsymbol{\tau}_{12}(s')\mathbf{A}_{12}(s') \tag{121}$$

where the contour Γ_{12} can be any contour, then

$$\mathbf{A}(s) = \mathbf{D}_{23}\mathbf{A}_{12}(s) \tag{122}$$

To summarize: Following the theory presented above, we have to distinguish between two situations. (1) As long as Γ does not surround C_{23} the matrix $\mathbf{A}(s)$ is given in the form

$$\mathbf{A}(s) = \begin{pmatrix} \cos\gamma_{12} & \sin\gamma_{12} & 0 \\ -\sin\gamma_{12} & \cos\gamma_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{123}$$

where $\gamma_{12}(s)$ is given in the form

$$\gamma_{12}(s) = \gamma_{12}(s_0) - \int_{s_0}^{S} ds \cdot \tau_{12}(s) \tag{124}$$

(2) In the case where Γ surrounds the C_{23} conical intersection, the value of $\gamma_{12}(s)$ may change its sign (for more details see Ref. [108]).

Since for any assumed contour the most that can happen, due to C_{23}, is that $\gamma_{12}(s)$ flips its sign, the corresponding 2×2 diabatic matrix potential, $\mathbf{W}(s)$, will not be affected by that as can be seen from the following expressions:

$$\begin{aligned} W_{11}(s) &= u_1(s)\cos^2\gamma_{12}(s) + u_2(s)\sin^2\gamma_{12}(s) \\ W_{22}(s) &= u_1(s)\sin^2\gamma_{12}(s) + u_2(s)\cos^2\gamma_{12}(s) \\ W_{12}(s) &= W_{21}(s) = \frac{1}{2}(u_2(s) - u_1(s))\sin(2\gamma_{12}(s)) \end{aligned} \tag{125}$$

In other words, the calculation of $\mathbf{W}$ can be carried out by ignoring C_{23} [or $\tau_{23}(s)$] altogether.

XII. THE ADIABATIC-TO-DIABATIC TRANSFORMATION MATRIX AND THE WIGNER ROTATION MATRIX

The adiabatic-to-diabatic transformation matrix in the way it is presented in Eq. (28) is somewhat reminiscent of the Wigner rotation matrix [109a] (assuming that $\mathbf{A}(s_0) \equiv I$). In order to see this, we first present a few well-known facts related to the definition of ordinary angular momentum operators (we follow the presentation by Rose [109b] and the corresponding Wigner matrices and then return to discuss the similarities between Wigner's $\mathbf{d}^j(\beta)$ matrix and the adiabatic-to-diabatic transformation matrix.

A. Wigner Rotation Matrices

The ordinary angular rotation operator $R(\mathbf{k},\theta)$ in the limit $\theta \rightarrow 0$ is written as

$$R(\mathbf{k}, \theta) = \exp(-iS(\mathbf{k}, \theta)) \tag{126}$$

where $\mathbf{k}$ is a unit vector in the direction of the axis of rotation, θ is the angle of rotation, and $S(\mathbf{k},\theta)$ is an operator that has to fulfill the condition $S(\mathbf{k}, \theta) \rightarrow 0$ for $\theta \rightarrow 0$ to guarantee that in this situation (i.e., when $\theta \rightarrow 0$) $R(\mathbf{k}, \theta) \rightarrow \mathbf{I}$. Moreover, since $R(\mathbf{k}, \theta)$ has to be unitary, the operator $S(\mathbf{k}, \theta)$ has to be Hermitian. Next, it is shown that $S(\mathbf{k}, \theta)$ is related to the total angular momentum operator, $\mathbf{J}$, in the following way:

$$S(\mathbf{k}, \theta) = (\mathbf{k} \cdot \mathbf{J})\theta \tag{127}$$

where the dot stands for scalar product. By substituting Eq. (127) in Eq. (126) we get the following expression for $R(\mathbf{k}, \theta)$:

$$R(\mathbf{k}, \theta) = \exp(-i(\mathbf{k} \cdot \mathbf{J})\theta) \tag{128}$$

It has to be emphasized that in this framework $\mathbf{J}$ is the angular momentum operator in ordinary coordinate space (i.e., configuration space) and θ is a (differential) ordinary angular polar coordinate.

Next, Euler's angles are employed for deriving the outcome of a general rotation of a system of coordinates [86]. It can be shown that $R(\mathbf{k}, \theta)$ is accordingly presented as

$$R(\mathbf{k}, \theta) = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} \tag{129}$$

where J_y and J_z are the y and the z components of $\mathbf{J}$ and α, β, and γ are the corresponding three Euler angles. The explicit matrix elements of the rotation operator are given in the form:

$$\mathbf{D}_{m'm}^{j}(\theta) = \langle jm'|R(k, \theta)|jm \rangle = e^{-i(m'\alpha + m\gamma)}\langle jm'|e^{-i\beta J_y}|jm \rangle \tag{130}$$

where m and m' are the components of $\mathbf{J}$ along the J_z and $J_{z'}$ axes, respectively, and $|jm\rangle$ is an eigenfunction of the Hamiltonian of J^2 and of J_z. Equation (130) will be written as

$$\mathbf{D}_{m'm}^{j}(\theta) = e^{-i(m'\alpha + m\gamma)}\mathbf{d}_{m'm}^{j}(\beta) \tag{131}$$

The $\mathbf{D}^j$ matrix as well as the $\mathbf{d}^j$ matrix are called the Wigner matrices and are the subject of this section. Note that if we are interested in finding a relation between the adiabatic-to-diabatic transformation matrix and Wigner's matrices, we should mainly concentrate on the $\mathbf{d}^j$ matrix. Wigner derived a formula for

these matrix elements [see [109b], Eq. (4.13)] and this formula was used by us to obtain the explicit expression for $j = \frac{3}{2}$ (the matrix elements for $j = 1$ are given in [109b], p. 72).

B.   The Adiabatic-to-Diabatic Transformation Matrix and the Wigner $\mathbf{d}^j$ Matrix

The obvious way to form a similarity between the Wigner rotation matrix and the adiabatic-to-diabatic transformation matrix defined in Eqs. (28) is to consider the (unbreakable) multidegeneracy case that is based, just like Wigner rotation matrix, on a single axis of rotation. For this sake, we consider the particular set of $\boldsymbol{\tau}$ matrices as defined in Eq. (51) and derive the relevant adiabatic-to-diabatic transformation matrices. In what follows, the degree of similarity between the two types of matrices will be presented for three special cases, namely, the two-state case which in Wigner's notation is the case, $j = \frac{1}{2}$, the tri-state case (i.e., $j = 1$) and the tetra-state case (i.e., $j = \frac{3}{2}$).

However, before going into a detail comparison between the two types of matrices it is important to remind the reader what the elements of the $\mathbf{J}_y$ matrix look like. By employing Eqs (2.18) and (2.28) of [109b] it can be shown that

$$\langle jm | J_y | jm + k \rangle = \boldsymbol{\delta}_{1k} \frac{1}{2i} \sqrt{(j + m + 1)(j - m)} \tag{132a}$$

$$\langle jm + k | J_y | jm \rangle = -\boldsymbol{\delta}_{1k} \frac{1}{2i} \sqrt{(j - m + 1)(j + m)} \tag{132b}$$

Now, by defining $\tilde{\mathbf{J}}_y$ as

$$\tilde{\mathbf{J}}_y = \mathbf{i} J_y \tag{133}$$

it is seen that the $\tilde{\mathbf{J}}_y$ matrix is an antisymmetric matrix just like the $\boldsymbol{\tau}$ matrix. Since the $\mathbf{d}^j$ matrix is defined as

$$\mathbf{d}^j(\beta) = \exp(-i\beta J_y) = \exp(\beta \tilde{\mathbf{J}}_y) \tag{134}$$

It is expected that for a certain choice of parameters (that define the $\boldsymbol{\tau}$ matrix) the adiabatic-to-diabatic transformation matrix becomes identical to the corresponding Wigner rotation matrix. To see the connection, we substitute Eq. (51) in Eq. (28) and assume $\mathbf{A}(s_0)$ to be the unity matrix.

The three matrices of interest were already derived and presented in Section V.A. There they were termed the $\mathbf{D}$ (topological) matrices (not related to the above mentioned Wigner $\mathbf{D}^j$ matrix) and were used to show the kind of quantization one should expect for the relevant non-adiabatic coupling terms. The only difference between these topological matrices and the

adiabatic-to-diabatic transformation matrices requested here, is that in Eqs. (55), (61), and (72) the closed-line integral [see Eq. (76)] is replaced by $\gamma(s)$ defined along an (open) contour [see Eq. (75)]:

For the three cases studied in Section V.A, the similarity to the three corresponding Wigner matrices is achieved in the following way:

1. For the two-state case (i.e., $j = \frac{1}{2}$), $\mathbf{d}^{1/2}(\beta)$ is identified with the corresponding adiabatic-to-diabatic transformation matrix [see Eq. (74)] for which $\beta = \gamma$.

2. For the tri-state case ($j = 1$), we consider Eq. (60). The corresponding $\mathbf{d}^1(\beta)$ matrix is obtained by assuming $\eta = 1$ [see Eq. (57)], and therefore $\omega = \sqrt{2}$. From Eq. (61) or (62), it is seen that $\beta = \gamma\sqrt{2}$. For the sake of completeness we present the corresponding $\mathbf{d}^1(\beta)$ matrix [109b]:

$$\mathbf{d}^1(\beta) = \frac{1}{2} \begin{pmatrix} 1 + C(\beta) & \sqrt{2}S(\beta) & 1 - C(\beta) \\ \sqrt{2}S(\beta) & 2C(\beta) & -\sqrt{2}S(\beta) \\ 1 - C(\beta) & \sqrt{2}S(\beta) & 1 + C(\beta) \end{pmatrix} \qquad (135)$$

where $C(\beta) = \cos\beta$ and $S(\beta) = \sin\beta$.

3. For the tetra-state case ($j = \frac{3}{2}$), we consider Eq. (69). The corresponding $\mathbf{d}^{3/2}(\beta)$ matrix is obtained by assuming $\eta = \sqrt{4/3}$ and $\sigma = 1$ [see Eq. (63)]. This will yield for ϖ the value $\varpi = \sqrt{10/3}$ [see Eq. (67)]. Since $\beta = p\gamma$ [see Eqs. (72)] we have to determine the value of p, which can be shown to be $p = \sqrt{3}$ [see Eq. (65)] and therefore $\beta = \gamma\sqrt{3}$. For the sake of completeness, we present the $\mathbf{d}^{3/2}(\beta)$ matrix:

$$\mathbf{d}^{3/2}(\beta') = \begin{pmatrix} C^3 & -\sqrt{3}C^2S & -\sqrt{3}S^2C & S^3 \\ \sqrt{3}C^2S & C(1 - 3S^2) & -S(1 - 3C^2) & -\sqrt{3}S^2C \\ -\sqrt{3}S^2C & S(1 - 3C^2) & C(1 - 3S^2) & -\sqrt{3}C^2S \\ -S^3 & -\sqrt{3}S^2C & \sqrt{3}C^2S & C^3 \end{pmatrix} \quad (136)$$

where $C = \cos(\beta/2)$ and $S = \sin(\beta/2)$.

The main difference between the adiabatic-to-diabatic transformation and the Wigner matrices is that whereas the Wigner matrix is defined for an ordinary spatial coordinate the adiabatic-to-diabatic transformation matrix is defined for a rotation coordinate in a different space.

XIII.   CURL CONDITION REVISITED: INTRODUCTION OF THE YANG–MILLS FIELD

In this section, the curl condition is extended to include the points of singularity as discussed in Appendix C. The study is meant to shed light as to the origin of

the non-adiabatic coupling terms and to connect them with pseudomagnetic fields.

A. The Non-Adiabatic Coupling term as a Vector Potential

In Section III.B, and later in Appendix C, it was shown that the sufficient condition for the adiabatic-to-diabatic transformation matrix $\mathbf{A}$ to be single valued in a given region in configuration space is the fulfillment of the following "curl" condition [8,34]:

$$\text{curl } \boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] = 0 \tag{137}$$

This condition is fulfilled as long as the components of $\boldsymbol{\tau}$ are analytic functions at the point under consideration (in case part of them become singular at this point, curl $\boldsymbol{\tau}$ is not defined).

The expression in Eq. (137) is reminiscent of the Yang–Mills field, however, it is important to emphasize that the Yang–Mills field was introduced for a different physical situation [58,59]. In fact, what Eq. (137) implies is that for molecular systems the Yang–Mills field is zero if the following two conditions are fulfilled:

1. The group of states, for which Eq. (137) is expected to be valid, forms a sub-Hilbert space that is isolated with respect to other portions of the Hilbert space following the definition in Eqs. (40).
2. The $\boldsymbol{\tau}$-matrix elements are analytic functions (vectors) in the above-mentioned region of configuration space.

In what follows, we assume that indeed the group of states form an isolated sub-Hilbert space, and therefore have a Yang–Mills field that is zero or not will depend on whether or not the various elements of the $\boldsymbol{\tau}$ matrix are singular.

In order to extend the existence of Eq. (137) for the singular points as well we write it as follows:

$$\text{curl } \boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] = \mathbf{H} \tag{138}$$

where $\mathbf{H}$ is zero at the regular points.

In order to get more insight, we return to the Born–Oppenheimer–Huang equation [1,2] as written in Eq. (16) and, for simplicity, limit ourselves to the two-state case:

$$-\frac{1}{2m}(\nabla + \boldsymbol{\tau})^2 \Psi + (u - E)\Psi = 0 \tag{139}$$

so that $\boldsymbol{\tau}$ is given in the form

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & \tau \\ -\tau & 0 \end{pmatrix} \tag{140}$$

Although Eq. (139) looks like a Schrödinger equation that contains a vector potential τ, it cannot be interpreted as such because τ is an *antisymmetric* matrix (thus, having diagonal terms that are equal to zero). This "inconvenience" can be "repaired" by employing the following unitary transformation:

$$\Psi = \mathbf{G}\Phi \tag{141}$$

where $\mathbf{G}$ is the (constant) matrix

$$\mathbf{G} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \tag{142}$$

By substituting Eq. (141) in Eq. (139) and multiplying it from the left by $G^\dagger$ yields

$$\frac{1}{2m}(-i\nabla + \mathbf{t})^2\Phi + (\mathbf{w} - E)\Phi = 0 \tag{143}$$

where $\mathbf{t}$ is now a diagonal matrix

$$\mathbf{t} = \begin{pmatrix} \tau & 0 \\ 0 & -\tau \end{pmatrix} \tag{144}$$

and $\mathbf{w}$ is an ordinary potential matrix of the kind

$$\mathbf{w} = \frac{1}{2} \begin{pmatrix} u_1 + u_2 & -(u_2 - u_1) \\ -(u_2 - u_1) & u_1 + u_2 \end{pmatrix} \tag{145}$$

The important outcome from this transformation is that now the non-adiabatic coupling term τ is incorporated in the Schrödinger equation in the same way as a vector potential due to an external magnetic field. In other words, τ behaves like a vector potential and therefore is expected to fulfill an equation of the kind [111a]

$$\text{curl } \tau = \mathbf{H} \tag{146}$$

where $\mathbf{H}$ is a pseudomagnetic field. Equation (146) looks similar to Eq. (138) but is in fact identical to it because in the case of two states the cross-term $[\tau \times \tau]$ is zero. Now, by returning to the Yang–Mills field we recall that $\mathbf{H} \neq 0$ at the singular points of τ. In the present study, we consider a case of *one* singular point.

The question is if in reality such magnetic fields exist. It turns out that such fields can be formed by long and narrow solenoids [111b]. It is well known that in this case the magnetic fields are nonzero only inside the solenoid but zero

outside it [111b]. Moreover, it has a nonzero component along the solenoid axis only. Thus simulating the molecular *seam* [36,54,110] as a solenoid we can identify the non-adiabatic coupling term as a vector potential produced by an infinitesimal narrow solenoid.

The quantum mechanical importance of a vector potential **A**, in regions where the magnetic field is zero, was first recognized by Aharonov and Bohm in their seminal 1959 paper [112].

B. The Pseudomagnetic Field and the Curl Equation

To continue, we assume the following situation: We concentrate on an x–y plane, which is chosen to be perpendicular to the seam. In this way, the pseudomagnetic field is guaranteed to be perpendicular to the plane and will have a nonzero component in the z direction only. In addition, we locate the origin at the point of the singularity, that is, at the crossing point between the plane and the seam. With these definitions the pseudomagnetic field is assumed to be of the form [113].

$$H = H_z = 2\pi \frac{\delta(q)}{q} f(\theta) \tag{147}$$

Here, $\delta(q)$ is the Dirac δ function and $f(\theta)$ is an arbitrary function to be determined [it can be shown that any function of the type $f(q,\theta)$ leads to the same result because of the $\delta(q)$ function]. By considering Eq. (146) for the z component, we obtain (employing polar coordinates):

$$\frac{1}{q}\left(\frac{\partial \tau_\theta}{\partial q} - \frac{\partial \tau_q}{\partial \theta}\right) = 2\pi \frac{\delta(q)}{q} f(\theta) \tag{148}$$

Here, (τ_q, τ_θ) are the radial and the angular components of τ (the z component, i.e., the out-of-plane component, is by definition equal to zero). Equation (148) can be shown (by substitution) to have the following solution:

$$\tau_\theta(q,\theta) - \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \pi h(q) f(\theta) \tag{149}$$

where $h(q)$ is the Heaviside function

$$h(q) = \begin{cases} 1 & q \geq 0 \\ 0 & q < 0 \end{cases} \tag{150}$$

Since q is a radius it is always positive, and therefore Eq. (149) can be written, without loss of generality, as

$$\tau_\theta(q,\theta) - \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \pi f(\theta) \tag{151}$$

Next, we consider the "quantization" condition introduced earlier [see Eq. (94)]. Assuming Γ to be a circle with radius q, Eq. (94) implies

$$\int_0^{2\pi} \tau_\theta(q, \theta)d\theta = n\pi \tag{152}$$

A similar integration over θ along the $(0, 2\pi)$ range can be carried out for Eq. (151). Thus, let us first consider the integration over the second term

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \int_0^q dq \int_0^{2\pi} \frac{\partial \tau_q}{\partial \theta} d\theta = \int_0^q dq(\tau_q(q, \theta = 2\pi) - \tau_q(q, \theta = 0))$$

In Section XIV.A, it is proved that $\tau_q(q, \theta)$ is, for every value of q, single valued with respect to θ so that we have

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = 0 \tag{153}$$

Combining Eqs. (151)–(153) yields the following outcome:

$$\int_0^{2\pi} f(\theta)\, d\theta = n \tag{154}$$

In other words, the quantization that was encountered for the non-adiabatic coupling terms is associated with the "quantization" of the *intensity* of the "magnetic" field along the seam. Moreover, Eq. (154) reveals another feature, namely, that there are fields for which n is an odd integer, namely, conical intersections and there are fields for which n is an even integer, namely, parabolical intersections.

Equation (151) can be applied to obtain $f(\theta)$. Ab initio calculation for small enough q values will yield $\tau_\theta(\theta, q \sim 0)$ and these, as is seen from Eq. (151), can be directly related to $f(\theta)$:

$$f(\theta) \sim \frac{1}{\pi} \tau_\theta(q \sim 0, \theta) \tag{155}$$

where the contribution of the second term on the left-hand side (for small enough q values) is ignored.

C. Conclusions

This section is devoted to the idea that the electronic non-adiabatic coupling terms can be simulated as vector potentials. For this purpose, we considered

a two-state system, shifted (rigorously) the off-diagonal non-adiabatic coupling terms to the diagonal and employed the relevant Maxwell equation. As is also noticed, the simulation created a connection between the ''curl'' condition as fulfilled by the non-adiabatic coupling terms and the Yang–Mills field.

As noticed, a pseudomagnetic field is assumed to exist along the seam formed by varying indirect coordinates (i.e., coordinates not related to the plane for which the vector potential is not zero) of a given molecular system. In this respect, we want to suggest that eventually the pseudomagnetic field is ''formed,'' semiclassically, by the zero-point vibrational motion of the indirect coordinates. For this purpose, we consider a three-atom molecular system ABC and assume the AB distance to be the *indirect* coordinate. Varying the AB distance builds up, semiclassically, a motion along the seam. Consequently, the zero-point vibrational motion along the AB bond creates, semiclassically, a periodic motion along the seam. This motion eventually causes charges that are concentrated along the seam (or its vicinity) to oscillate and in this way to form a pseudoelectromagnetic field.

XIV.   A THEORETIC-NUMERIC APPROACH TO CALCULATE THE ELECTRONIC NON-ADIABATIC COUPLING TERMS

In this section, we discuss the possibility that the electronic non-adiabatic coupling terms will be derived, not by ab initio treatments but, by solving the curl equations for a given set of boundary conditions obtained from ab initio calculations [114,115]. In other words, instead of performing an ab initio calculation at any point in configuration space we suggest solving the relevant differential equations for boundary conditions obtained from a (limited) ab initio calculation [64–74] or perturbation theory [66,67].

A.   The Treatment of the Two-State System in a Plane

1.   The Solution for a Single Conical Intersection

The curl equation for a two-state system is given in Eq. (26):

$$\operatorname{curl} \tau = 0 \tag{26}$$

Equation (26) is fulfilled at any point in configuration space for which the components of τ are analytic functions.

Equation (26) is a set of partial first-order differential equations. Each component of the Curl forms an equation and this equation may or may not be ''coupled'' to the other equations. In general, the number of equations is equal to the number of components of the Curl equations. At this stage, to solve this set of equation in its most general case seems to be a formidable task.

In what follows, we shall limit ourselves to the following situation. Assuming a system of N coordinates $(z_1, z_2, \ldots, z_N)$, with the following components:

$$\tau_{z_j} = \tau_{z_j}(z_1, z_2, \ldots z_N) \qquad j = 1, 2, \ldots, N \qquad (156a)$$

and assume that two of them, that is, τ_{z_1} and τ_{z_2} depend only on their own coordinates, namely, (z_1, z_2), thus

$$\tau_{z_j} = \tau_{z_j}(z_1, z_2) \qquad j = 1, 2 \qquad (156b)$$

then the following partial curl equation

$$\frac{\partial \tau_{z_1}}{\partial z_2} - \frac{\partial \tau_{z_2}}{\partial z_1} = 0$$

is the only equation to be considered within the (z_1, z_2) space because due to Eq. (156b) all the other relevant components lead to the results

$$\frac{\partial \tau_{z_n}}{\partial z_1} = \frac{\partial \tau_{z_n}}{\partial z_2} 0 \qquad n = 3, \ldots, N$$

In what follows, the 2D space is assumed to be a plane, and therefore we apply either the polar coordinates (q, θ) or the Cartesian coordinates (x, y).

We start treating the curl equation expressed in terms of polar coordinates:

$$\frac{1}{q}\left(\frac{\partial \tau_\theta}{\partial q} - \frac{\partial \tau_q}{\partial \theta}\right) = 0 \Rightarrow \frac{\partial \tau_\theta}{\partial q} - \frac{\partial \tau_q}{\partial \theta} = 0 \qquad (157)$$

Integrating the second equation with respect to q along the interval $[0, q]$ yields

$$\tau_\theta(q, \theta) - \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \tau_\theta(q \sim 0, \theta) \qquad (158a)$$

Next, Eq. (158a) is integrated with respect to θ along the interval $[0, 2\pi]$ and we get

$$\int_0^{2\pi} \tau_\theta(q, \theta)d\theta - \int_0^{2\pi}\int_0^q dq \frac{\partial \tau_q}{\partial \theta} d\theta = \int_0^{2\pi} \tau_\theta(q \sim 0, \theta)d\theta \qquad (158b)$$

which due to the fact that $\tau_\theta(q, \theta)$ is quantized (for every value of q) in the following way [see Eq. (94)]:

$$\int_0^{2\pi} \tau_\theta(q, \theta)d\theta = n\pi \qquad (159)$$

yields the result:

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = 0 \tag{160}$$

If we evaluate the integrand and change the order of integration we get

$$\int_0^{2\pi} d\theta \int_0^q dq \frac{\partial \tau_q}{\partial \theta} = \int_0^q dq \int_0^{2\pi} \frac{\partial \tau_q}{\partial \theta} d\theta = \int_0^q dq (\tau_q(q, \theta = 2\pi) - \tau_q(q, \theta = 0))$$

This result implies that $\tau_q(q, \theta)$ is, for every value of q, single valued with respect to θ.

In what follows, we assume that the second term in Eq. (158a) is *negligibly small* and as a result $\tau_\theta(q, \theta)$ becomes independent of q. Thus

$$\tau_\theta(q, \theta) = \tau_\theta(q = q_0, \theta) \tag{161a}$$

where q_0 is a fixed q value and $\tau_\theta(q = q_0, \theta)$ is a boundary value (at $q_0 \sim 0$) for $\tau_\theta(q, \theta)$ determined either by ab initio calculations or perturbation theory. We also recall that $\tau_\theta(q, \theta)$ fulfills the quantization condition as written in Eq. (159).

To examine our assumption regarding the dependence of $\tau_\theta(q, \theta)$ on q, we consider the well-known (collinear) conical intersection of the C_2H molecule formed by the two lowest states, namely, the $1^2A'$ and the $2^2A'$ states [12,72,105]. Figure 9 presents $\tau_\theta(q, \theta)$ as calculated for a fixed C–C distance, that is, $R_{CC} = 1.35$ Å and for different q values. It is seen that the basic shape of $\tau_\theta(q, \theta)$ is approximately preserved although q is varied along a relative large interval, that is, the [0.05, 1.0 Å] interval. It is noticed that the shape $\tau_\theta(q, \theta)$ is significantly affected only when $q = 1$ Å and $\theta \sim \pi$. The reason is that in this situation the point $(q = 1 \text{ Å}, \theta = \pi)$ gets very close to one of the carbons (the distance becomes ~ 0.3 Å) and therefore the ab initio values for $\tau_\theta(q, \theta)$ are not for an isolated conical intersection anymore as it should be [12].

In Section XIV.A.2, we intend to obtain the vector function $\tau(q, \theta)$ for a given *distribution* of conical intersections. Thus, first we have to derive an expression for a conical intersection removed from the origin, namely, assumed to be located at some point, (q_{j0}, θ_{j0}), in the plane.

Combining Eqs. (151), (158a), and (161a) we get that $\tau_\theta(q, \theta)$ can be writtern as:

$$\tau_\theta(q, \theta) = \pi f(\theta) \tag{161b}$$

To shift it to some arbirtrary point (q_{j0}, θ_{j0}) we first express Eq. (161b) in terms of *Cartesian* coordinates, and then shift the solution to the point of interest, namely, to $(x_{j0}, y_{j0})[\equiv (q_{j0}, \theta_{j0})]$. Once completed, the solution is transformed back to polar coordinates (for details see Appendix F). Following
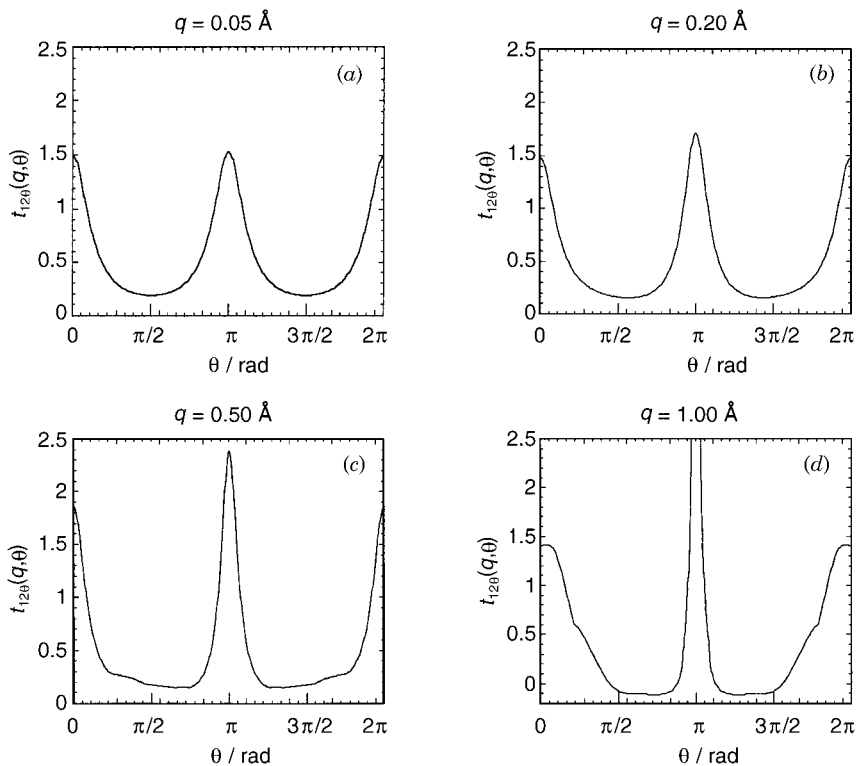
Figure 9. The $\tau_\theta(q, \theta)$—the angular non-adiabatic coupling term as a function of θ—as calculated for different q values. (a) $q = 0.05$ Å; (b) $q = 0.2$ Å; (c) $q = 0.5$ Å; (d) $q = 1.0$ Å.

this procedure, $\tau_\theta(q, \theta)$ and $\tau_q(q, \theta)$ (which is now different from zero) become

$$\tau_q(q, \theta) = -f_j(\theta_j) \frac{1}{q_j} \sin(\theta - \theta_j)$$

$$\tau_\theta(q, \theta) = f_j(\theta_j) \frac{q}{q_j} \cos(\theta - \theta_j)$$
(162)

where q_j and θ_j are the coordinates of an arbitrary point, $P(q, \theta)$, with respect to the conical intersection position. The coordinates (q_j, θ_j) are related to (q, θ) as follows:

$$q_j = \sqrt{(q \cos\theta - q_{j0} \cos\theta_{j0})^2 + (q \sin\theta - q_{j0} \sin\theta_{j0})^2}$$

$$\cos\theta_j = \frac{q \cos\theta - q_{j0} \cos\theta_{j0}}{q_j}$$
(163)

and $f_j(\theta_j)$ is defined as

$$f_j(\theta_j) \equiv \tau_{j\theta}(q_j \sim 0, \theta_j) \qquad (164)$$

In Eq. (162) [as well as in Eq. (164)], we attached a subscript j to $f(\theta)$ to indicate that each conical intersection (in this case the jth one) may form a different spatial (angular) distribution.

Note that for $q_{j0} = 0$ the solution in Eq. (161b) is restored (and τ_q becomes zero).

2. The Solution for a Distribution of Conical Intersections

With the modified expression we can now extend the solution of Eq. (162) to any number of conical intersections. The solution in Eq. (162) stands for a single conical intersection located at an arbitrary point (q_{j0}, θ_{j0}). Since $\tau_\theta(q, \theta)$ and $\tau_q(q, \theta)$ are scalars the solution in case of N conical intersections located at the points $(q_{j0}, \theta_{j0}); j = 1, \ldots, N$ are obtained by summing up the individual contributions [114]:

$$
\begin{aligned}
\tau_q(q, \theta) &= -\sum_{j=1}^{N} f_j(\theta_j) \frac{1}{q_j} \sin(\theta - \theta_j) \\
\tau_\theta(q, \theta) &= q \sum_{j=1}^{N} f_j(\theta_j) \frac{1}{q_j} \cos(\theta - \theta_j)
\end{aligned}
\qquad (165)
$$

Equation (165) yields the two components of $\tau(q, \theta)$, the vectorial non-adiabatic coupling term, for a distribution of two-state conical intersections expressed in terms of the values of the *angular* component of each individual non-adiabatic coupling term at the *closest* vicinity of each conical intersection. These values have to be obtained from ab initio treatments (or from perturbation expansions); however, all that is needed is a set of these values along a single closed circle, each surrounding one conical intersection.

To summarize our findings so far, we may say that if indeed the radial component of a single completely *isolated* conical intersection can be assumed to be negligible small as compared to the angular component, then we can present, almost fully analytically, the 2D "field" of the non-adiabatic coupling terms for a two-state system formed by any number of conical intersections. Thus, Eq. (165) can be considered as the non-adiabatic coupling field in the case of two states.

In Section XIV.B, this derivation is extended to a three-state system.

B. The Treatment of the Three-State System in a Plane

To study the three-state case, we consider two non-adiabatic coupling terms: one, between the lowest and the intermediate state, designated as τ_{12} with its origin located at $P_a(q_a, \theta_a)$, and the other between the intermediate and the highest state, designated as τ_{23} with its origin located at $P_b(q_b, \theta_b)$. As will be seen, in addition to τ_{12} and τ_{23} we also have to consider τ_{13}, although no degeneracy point

exists between the lowest and the highest states. In other words, we shall show how the interaction between the above mentioned two conical intersections builds up τ_{13}, which does not have a source of its own. Thus the τ matrix for the most general case has to be of the form:

$$\tau = \begin{pmatrix} 0 & \tau_{12} & \tau_{13} \\ -\tau_{12} & 0 & \tau_{23} \\ -\tau_{13} & -\tau_{23} & 0 \end{pmatrix} \tag{166}$$

The curl equation for three (or more) states is given in Eq. (25) and is presented here again for the sake of completeness:

$$\text{curl } \tau - [\tau \times \tau] = 0 \tag{25}$$

It is well noted that, in contrast to the two-state equation [see Eq. (26)], Eq. (25) contains an additional, nonlinear term. This nonlinear term enforces a perturbative scheme in order to solve the required τ-matrix elements.

The derivation of the τ-matrix elements will be done in two steps: (1) first by considering each of the conical intersection as being isolated, namely, the one independent of the other; and (2) secondly by employing Eq. (20) to treat the two conical intersections as one complete system. Thus within the first step we obtain zeroth-order expressions for τ_{12} and τ_{23}, that is, τ_{012} and τ_{023}, respectively, whereas within the second step we not only correct these expressions so that Eq. (25), is ($\sim$) fulfilled for three states, but also derive the missing τ_{13} term. The study is done, as before, for a plane in configuration space employing polar coordinates.

To study the two isolated conical intersections, we have to treat two-state curl equations that are given in Eq. (26). Here, the first 2×2 τ matrix contains the (vectorial) element, that is, τ_{012} and the second 2×2 τ matrix contains τ_{023}. As before each of the non-adiabatic coupling terms, τ_{012} and τ_{023} has the following components:

$$\tau_{0jj+1} = (\tau_{0qjj+1}, \tau_{0\theta jj+1}) \qquad j = 1, 2 \tag{167}$$

where τ_{0qjj+1} and $\tau_{0\theta jj+1}$; $j = 1, 2$, were derived in Section XIV.A [see Eqs. (165)], and therefore no further treatment is necessary.

In Section XI.B, we discussed situations (based on ab initio calculations) where the two non-adiabatic coupling terms τ_{12} and τ_{23} slightly overlap [12,108]. Based on ab initio calculations (as were carried out for the C_2H molecule) it was found that in many cases the non-adiabatic coupling is not evenly distributed around its point of degeneracy but rather is concentrated along a radial ridge that starts at the point of degeneracy (see Figs. 6 and 7). Therefore, in these cases, only slight overlaps are expected, in particular, when the two points of degeneracy $P_x(q_x, \theta_x)$; $x = a, b$ are located far enough from each other [108].

Thus if τ_{jj+1}—the full non-adiabatic coupling term—and the unperturbed non-adiabatic coupling term, τ_{0jj+1}, are assumed to be related to each other as

$$\tau_{jj+1} = \tau_{0jj+1} + \delta\tau_{jj+1} \qquad j = 1, 2 \tag{168}$$

then it follows, from the above discussion, that the components of the two vectorial perturbations (i.e., $\delta\tau_{qjj+1}$ and $\delta\tau\theta_{jj+1}$) are likely to be (much) smaller than the corresponding components, namely, τ_{0qjj+1} and τ_{00jj+1}.

Next, we return to Eq. (25) and recall that we are interested only in the components of τ_{jj+1} $j = 1, 2$ in a plane perpendicular to the z axis. It can be shown that if τ_{0jj+1}, $j = 1, 2$ do not posses a z component, the same applies to the perturbations $\delta\tau_{jj+1}$ $j = 1, 2$, as well as to τ_{13}.

Substituting Eq. (168) in Eq. (166) and the result in Eq. (25) yields the (inhomogeneous) differential equations for the components of $\delta\tau_{jj+1}$; $j = 1, 2$

$$
\begin{aligned}
\mathrm{curl}(\delta_{12}) &= \frac{\partial(\delta\tau_{q12})}{\partial\theta} - \frac{\partial(\delta\tau_{012})}{\partial q} = \tau_{\theta13}\tau_{0q23} - \tau_{q13}\tau_{0\theta23} \\
\mathrm{curl}(\delta\tau_{23}) &= \frac{\partial(\delta\tau_{q23})}{\partial\theta} - \frac{\partial(\delta\tau_{023})}{\partial q} = \tau_{q13}\tau_{0\theta12} - \tau_{\theta13}\tau_{0q12}
\end{aligned}
\tag{169}
$$

where the second-order terms were deleted. In this derivation, we employed the fact that:

$$\mathrm{curl}\,\tau_{012} = \mathrm{curl}\,\tau_{023} = 0 \tag{170}$$

In the same way, with similar assumptions, we obtain the (inhomogeneous) differential equation for the components of τ_{13}

$$\mathrm{curl}\,\tau_{13} = \frac{\partial\tau_{q13}}{\partial\theta} - \frac{\partial\tau_{013}}{\partial q} = \tau_{0\theta12}\tau_{0q23} - \tau_{0q12}\tau_{0\theta23} \tag{171}$$

Equation (171) is the an explicit "curl" equation for a coupling that does not has a "source" of its own but is formed due to the interaction between two "real" conical intersection.

Equations (169) and (171), together with Eqs. (170), form the basic equations that enable the calculation of the non-adiabatic coupling matrix. As is noticed, this set of equations creates a hierarchy of approximations starting with the assumption that the cross-products on the right-hand side of Eq. (171) have small values because at any point in configuration space at least one of the multipliers in the product is small [115].

XV.   STUDIES OF SPECIFIC SYSTEMS

In this section, we concentrate on a few examples to show the degree of relevance of the theory presented in the previous sections. For this purpose, we analyze the conical intersections of two *real* two-state systems and one *real* system resembling a tri-state case.

A.   The Study of *Real* Two-State Molecular Systems

We start by mentioning the studies of Yarkony et al. [64] who were the first to apply the line integral approach to reveal the existence of a conical intersection for a ''real'' molecular system—the H_3 system—by calculating the relevant non-adiabatic coupling terms from first principles and then deriving the topological angle α [see Eq. (76)]. Later Yarkony and co-workers applied this approach to study other tri-atom system such as AlH_2 [65], CH_2 [66,69], H_2S [66], HeH_2 [68], and Li_3 [70].

Recently, Xu et al. [11] studied in detail the H_3 molecule as well as its two isotopic analogues, namely, H_2D and D_2H, mainly with the aim of testing the ability of the line integral approach to distinguish between the situations when the contour surrounds or does not surround the conical intersection point. Some time later Mebel and co-workers [12,72–74,116] employed *ab initio* non-adiabatic coupling terms and the line-integral approach to study some features related to the C_2H molecule.

Some results of these studies will be presented in Sections XV.A.1–XV.A.3.

1.   *The H_3-System and Its Isotopic Analogues*

Although the study to be described is for a ''real'' system, the starting point was not the ab initio adiabatic potential energy surfaces and the ab initio non-adiabatic coupling terms but a diabatic potential [117], which has its origin in the LSTH potential [118] improved by including three-center terms [119]. These were used to calculate the adiabatic-to-diabatic transformation angle γ by employing the Hellmann–Feynman theorem [3,36]. However, we present our results in term of the diabatic-to-adiabatic transformation angle β, which is also know as the *mixing angle*. We start by proving, analytically that these two angles are identical up to an integration constant.

We consider a 2D diabatic framework that is characterized by an angle, $\beta(s)$, associated with the orthogonal transformation that diagonalizes the diabatic potential matrix. Thus, if $\mathbf{V}$ is the diabatic potential matrix and if $\mathbf{u}$ is the adiabatic one, the two are related by the orthogonal transformation matrix $\mathbf{A}$ [34]:

$$\mathbf{u} = \mathbf{A}^{\dagger}\mathbf{V}\mathbf{A} \qquad (172)$$

where $\mathbf{A}^{\dagger}$ is the complex conjugate of the $\mathbf{A}$ matrix. For the present two-state case, $\mathbf{A}$ can be written in the form:

$$\mathbf{A} = \begin{pmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{pmatrix} \qquad (173)$$

where β—the above mentioned mixing angle—is given by [36a]:

$$\beta = \frac{1}{2}\tan^{-1}\frac{2V_{12}}{V_{11} - V_{22}} \qquad (174)$$

Recalling $\gamma(s)$, the adiabatic-to-diabatic transformation angle [see Eqs. (74) and (75)] it is expected that the two angles are related. The connection is formed by the Hellmann–Feynman theorem, which yields the relation between the s component of the non-adiabatic coupling term, τ, namely, τ_s, and the characteristic diabatic magnitudes [13]

$$\tau_s(s) = (u_2 - u_1)^{-1}\mathbf{A}_1^*\frac{\partial\mathbf{V}}{\partial s}\mathbf{A}_2 = \frac{\sin 2\beta}{2W_{12}}\mathbf{A}_1^*\frac{\partial\mathbf{V}}{\partial s}\mathbf{A}_2 \qquad (175)$$

where $\mathbf{A}_i, i = 1, 2$ are the two columns of the $\mathbf{A}$ matrix in Eq. (173). By replacing the two $\mathbf{A}_i$ columns by their explicit expressions yields for τ_s the expression

$$\tau_s(s) = \frac{\sin 2\beta}{2V_{12}}\left[\frac{-\sin 2\beta}{2}\frac{\partial}{\partial s}(V_{11} - V_{22}) + \cos 2\beta\frac{\partial}{\partial s}V_{12}\right] \qquad (176)$$

Next, by differentiating Eq. (174) with respect to s

$$\frac{\partial}{\partial s}(V_{11} - V_{22}) = 2\left(V_{12}\frac{\partial}{\partial s}\cot 2\beta + \cot 2\beta\frac{\partial}{\partial s}V_{12}\right) \qquad (177)$$

and by substituting Eq. (177) in Eq. (176), yields the following result for $\tau_s(s)$:

$$\tau_s(s) = \frac{\partial\beta}{\partial s} \qquad (178)$$

Comparing this equation with Eq. (75), it is seen that the mixing angle β is, up to an additive constant, identical to the relevant adiabatic-to-diabatic transformation—angle γ:

$$\gamma(s) = \beta(s) - \beta(s_0) \qquad (179)$$

This relation will be used to study geometrical phase effects within the diabatic framework for the H_3 system and its two isotopic analogues. What is meant by

this is that since our starting point is the 2×2 diabatic potential matrix, we do not need to obtain the adiabatic-to-diabatic transformation angle by solving a line integral; it will be obtained simply by applying Eqs. (174) and (178). The forthcoming study is carried out by presenting $\beta(\varphi)$ as a function of an angle φ to be introduced next.

In the present study, we are interested in finding the locus of the seam defined by the conditions $r_{AB} = r_{BC} = r_{AC}$ [14–17] where r_{AB}, r_{BC}, and r_{AC} are the interatomic distances. Since we intend to study the geometrical properties produced by this seam we follow a suggestion by Kuppermann and co-workers [29,120,121] and employ the hyperspherical coordinates (ρ, θ, φ) that were found to be suitable for studying topological effects for the H—H$_2$ (and its isotopic analogues) because one of the hyperspherical (angular) coordinates surrounds the seam in case of the pure-hydrogenic case. Consequently, following previous studies [29,122–124], we express the three above-mentioned distances in terms of these coordinates, that is,

$$
\begin{aligned}
r_{AB}^2 &= \frac{1}{2} d_C \rho^2 \left[1 + \sin \frac{\theta}{2} \cos (\varphi + \chi_{AC}) \right] \\
r_{BC}^2 &= \frac{1}{2} d_A \rho^2 \left[1 + \sin \frac{\theta}{2} \cos (\varphi) \right] \\
r_{AC}^2 &= \frac{1}{2} d_B \rho^2 \left[1 + \sin \frac{\theta}{2} \cos (\varphi - \chi_{AB}) \right]
\end{aligned}
\tag{180}
$$

where

$$
\begin{aligned}
d_X^2 &= \frac{m_X}{\mu} \left(1 - \frac{m_X}{M} \right) \qquad \chi_{XY} = 2 \tan^{-1} \left(\frac{m_Z}{\mu} \right) \\
\mu &= \sqrt{\frac{m_A m_B m_C}{M}} \qquad\qquad M = m_A + m_B + m_C
\end{aligned}
\tag{181}
$$

Here X,Y,Z stand for A,B,C and

$$
\rho = \sqrt{r_{AB}^2 + r_{AC}^2 + r_{BC}^2}
\tag{182}
$$

By equating the three interatomic distances with each other, we find that the seam is a straight line, for which ρ is arbitrary but φ and θ have fixed values φ_s and θ_s determined by the masses only.

$$
\varphi_s = \tan^{-1} \left\{ \frac{\cos \chi_{AC} - t \cos \chi_{AB} - \left(\dfrac{d_A}{d_C} \right)^2 + t \left(\dfrac{d_A}{d_B} \right)^2}{\sin \chi_{AC} - t \sin \chi_{AB}} \right\}
\tag{183}
$$

and

$$\theta_s = 2\sin^{-1}\left\{\frac{\left(\frac{d_A}{d_B}\right)^2 - 1}{\cos\left(\varphi_s - \chi_{AB}\right) - \left(\frac{d_A}{d_B}\right)^2\cos\varphi_s}\right\} \tag{184}$$

where t is given in the form

$$t = \left[\left(\frac{d_A}{d_C}\right)^2 - 1\right]\left[\left(\frac{d_A}{d_B}\right)^2 - 1\right]^{-1} \tag{185}$$

Equations (182)–(185) are valid when all three masses are different. In case two masses are equal, namely, $m_B = m_C$, we get for θ_s the simplified expression

$$\theta_s = 2\sin^{-1}\left\{\left|\frac{m_B - m_A}{m_B + 2m_A}\right|\right\} \tag{186}$$

and for φ_s the value π when $m_A > m_B$ and the value zero when $m_A < m_B$. In case all three masses are equal (then $t = 1$), we get $\theta_s = 0$ and $\varphi_s = \pi$.

In what follows, we discuss the H_2D system. For this purpose Eq. (186) is employed for which it is obtained that the straight line seam is defined for the following values of θ_s and φ_s, namely, $\theta_s = 0.4023$ rad, and $\varphi_s = \pi$. In the H_3 case, the value of θ_s is zero and this guarantees that all the circles with constant ρ and θ encircle the seam. The fact that θ_s is no longer zero implies that not all the circles with constant ρ and θ encircle the seam; thus, circles for which $\theta > \theta_s$ will encircle the seam and those with $\theta < \theta_s$ will not.

In Figure 10 are presented $\beta(\varphi)$ curves for H_2D, all calculated for $\rho = 6a_0$. In this calculation, the hyperspherical angle φ, defined in along the $[0,2\pi]$ interval, is the independent angular variable. Figure 10a shows two curves for the case where the line integral does not encircle the seam, namely, for $\theta = 0.2$ and 0.4 rad and in Figure 10b for the case where the line integral encircles the seam, namely, for $\theta = 0.405$ and 2.0 rad. Notice that the curves in Figure 10a reach the value of zero and those in Figure 10b reach the value of π. In particular, two curves, that in Figure 10a for $\theta = 0.4$ rad and the other in Figure 10b for $\theta = 0.405$ rad, were calculated along very close contours (that approach the locus of the seam) and indeed their shapes are similar—they both yield an abrupt step—but one curve reaches the value of zero and the other the value π. Both types of results justify the use of the line integral to uncover the locus of the seam. More detailed results as well as the proper analysis can be found in [11].

These results as well as others presented in [11] are important because on various occasions it was implied that the line integral approach is suitable only
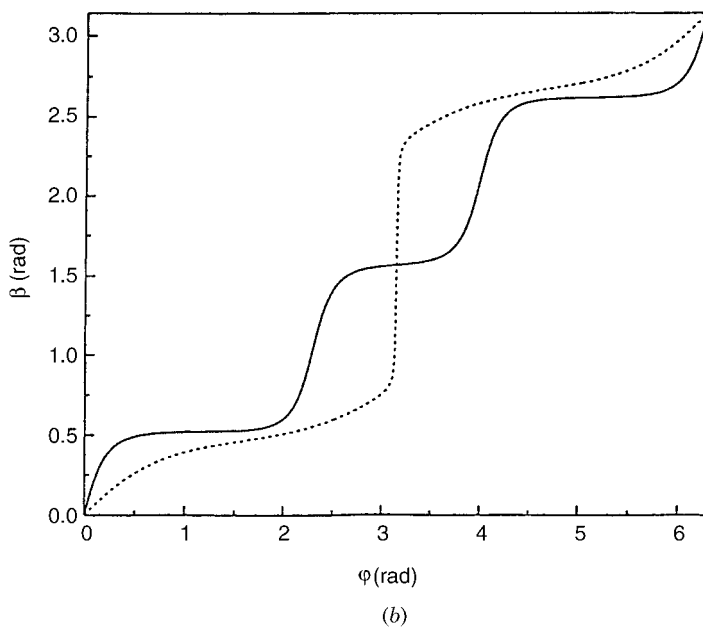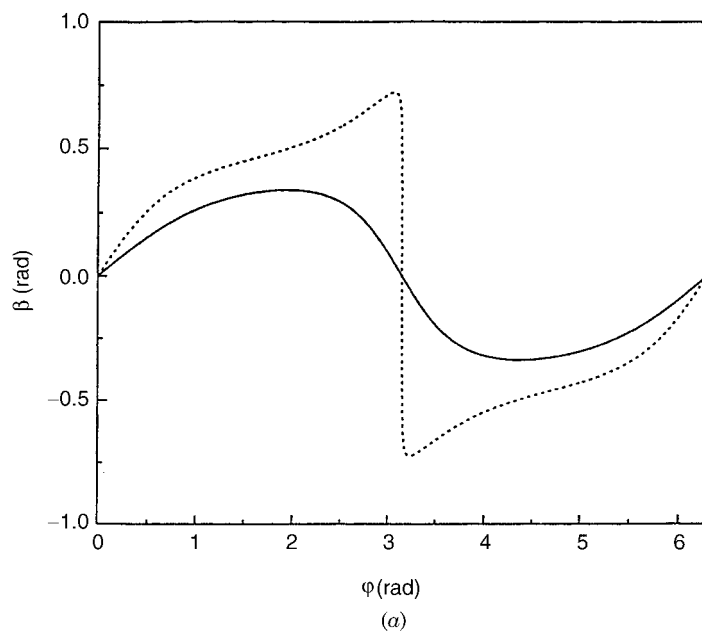
MICHAEL BAER

Figure 10. The mixing angle β, for the H_2D system, as a function of hyperspherical angle φ, calculated for hyperspherical radius $\rho = 6$ a_0: (*a*) Results for $\theta = 0.2$ rad ———— and $\theta = 0.4$ rad .... (*b*) The same as (*a*) but for $\theta = 2.0$ rad ————; and $\theta = 0.405$ rad ....

for cases when relatively small radii around the conical intersection are applied [64]. In [11], it is shown for the first time that this approach can be useful even for large radii, which does not mean that it is relevant for any assumed contour surrounding a conical intersection (or for that matter a group of conical intersections) but means that we can always find contours with large radii that will reveal the conical intersection location for a given pair of states.

2. The C₂H-Molecule: The Study of the (1,2) and the (2,3) Conical Intersections

In the first part of this study, we were interested in non-adiabatic coupling terms between the $1^2A'$ and $2^2A'$ and between the $2^2A'$ and $3^2A'$ electronic states. The calculations were done employing MOLPRO [6], which yield the six relevant non-adiabatic coupling elements as calculated with respect to the Cartesian center-of-mass coordinates of each atom. These coupling terms were then transformed, employing chain rules [12,73], to non-adiabatic coupling elements with respect to the internal coordinates of the C_2H molecule, namely, $\langle \zeta_i | \partial \zeta_j / \partial r_1 \rangle$ $(= \tau_{r_1})$, $\langle \zeta_i | \partial \zeta_j / \partial r_2 \rangle (= \tau_{r_2})$, and $\langle \zeta_i | \partial \zeta_j / \partial \varphi \rangle (= \tau_\varphi)$. Here r_1 and r_2 are the C—C and C—H distances, respectively, and φ is the relevant $CC \cdots CH$ angle. The adiabatic-to-diabatic transformation angle, $\gamma(\varphi | r_1, r_2)$, is derived next employing the following line integral [see Eq. (75)], where the contour is an arc of a circle with radius r_2:

$$\gamma(\varphi \mid r_1, r_2) = \int_0^\varphi d\varphi' \tau_\varphi(\varphi' \mid r_1, r_2) \tag{187}$$

The corresponding topological phase, $\alpha(r_1, r_2)$ [see Eq. (76)] defined as $\gamma(\varphi = 2\pi \mid r_1, r_2)$, was also obtained for various values of r_1 and r_2.

First, we refer to the (1,2) conical intersection. A detailed inspection of the non-adiabatic coupling terms revealed the existence of a conical intersection between these two states, for example, at the point $\{\varphi = 0, r_1 = 1.35\,\text{Å}, r_2 = 1.60\,\text{Å}\}$ as was established before [105]. More conical intersections of this kind are expected at other r_1 values. Next, were calculated the $\gamma(\varphi \mid r_1, r_2)$ angles as a function of φ for various r_2. The $\tau_\varphi(\varphi \mid r_1, r_2)$ functions as well as the adiabatic-to-diabatic transformation angles are presented in Figure 11 for three different r_2 values, namely, $r_2 = 1.8, 2.0, 3.35\,\text{Å}$. Mebel et al. [12] also calculated the topological angle $\alpha(r_1, r_2)$ for these three r_2 values employing Eq. (76) and got, for the first two r_2 values, the values 3.136 and 3.027 rad, respectively—thus, in both cases, values close to the expected π value. A different situation is encountered in the third case when the circle surrounds the two (symmetrical) CIs as can be seen from the results presented in the third panel of Figure 11e and f. In such a case, the angle α is expected to be either an even multiple of π or zero. The integration according to Eq. (76) yields the value
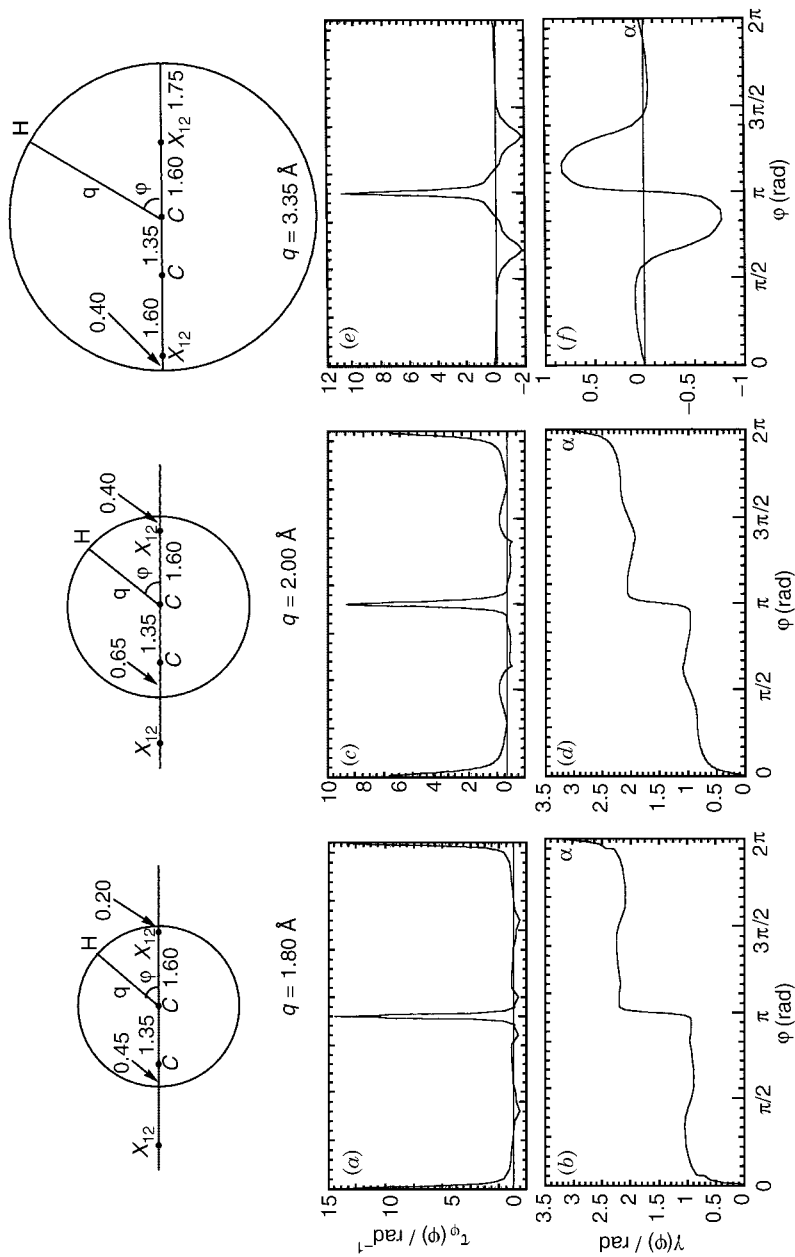
Figure 11. Results for the C_2H molecule as calculated along a circle surrounding the $1^2A'-2^2A'$ conical intersection. Shown are the geometry, the non-adiabatic coupling matrix elements $\tau\varphi(\varphi \,|\, r_2)$ and the adiabatic-to-diabatic transformation angles $\gamma(\varphi \,|\, r_2)$ as calculated for r_1 (=CC distance) = 1.35 Å and for three r_2 values (r_2 is the CH distance): (a) and (b) r_2 = 1.80 Å; (c) and (d) r_2 = 2.00 Å; (e) and (f) r_2 = 3.35 Å. (Note that $q \equiv r_2$.)

of 0.048 rad, namely, a value close to zero. It is important to mention that we also performed integrations along closed circles that do not surround any conical intersections and got the value zero as was proved in Appendix C (for more details about these calculations see [12]).

In this series of results, we encounter a somewhat unexpected result, namely, when the circle surrounds two conical intersections the value of the line integral is zero. This does not contradict any statements made regarding the general theory (which asserts that in such a case the value of the line integral is either a multiple of 2π or *zero*) but it is still somewhat unexpected, because it implies that the two conical intersections behave like *vectors* and that they arrange themselves in such a way as to reduce the effect of the non-adiabatic coupling terms. This result has important consequences regarding the cases where a pair of electronic states are coupled by more than one conical intersection.

On this occasion, we want also to refer to an incorrect statement that we made more than once [72], namely, that the (1,2) conical intersection results indicate ''that for any value of r_1 and r_2 the two states under consideration form an *isolated* two-state sub-Hilbert space.'' We now know that in fact they do not form an isolated system because the second state is coupled to the third state via a conical intersection as will be discussed next. Still, the fact that the series of topological angles, as calculated for the various values of r_1 and r_2, are either multiples of π or zero indicates that we can form, for this adiabatic two-state system, *single-valued* diabatic potentials. Thus if for some numerical treatment only the two lowest adiabatic states are required, the results obtained here suggest that it is possible to form from these two adiabatic surfaces single-valued diabatic potentials employing the line-integral approach. Indeed, recently Billing et al. [104] carried out such a photodissociation study based on the two lowest adiabatic states as obtained from ab initio calculations. The complete justification for such a study was presented in Section XI.

Reference [73] presents the first line-integral study between two excited states, namely, between the second and the third states in this series of states. Here, like before, the calculations are done for a fixed value of r_1 (results are reported for $r_1 = 1.251$ Å) but in contrast to the previous study the origin of the system of coordinates is located at the point of this particular conical intersection, that is, the (2,3) conical intersection. Accordingly, the two polar coordinates (φ, q) are defined. Next is derived the φ-th non-adiabatic coupling term i.e. $\tau_\varphi \; (= \langle \zeta_2 | \partial \zeta_3 / \partial \varphi \rangle)$ again employing chain rules for the transformation $(\tau_\gamma, \tau_{r2}) \to \tau_\varphi (\tau_q$ is not required because the integrals are performed along a circle with a fixed radius q—see Fig. 12).

Figure 12 presents $\tau_\varphi(\varphi \mid q)$ and $\gamma(\varphi \mid q)$ for three values of q, that is, $q = 0.2, 0.3, 0.4$ Å. The main features to be noticed are (1) The function $\tau_\varphi(\varphi \mid q)$ exhibits the following symmetry properties: $\tau_\varphi(\varphi) = \tau_\varphi(\pi - \varphi)$ and
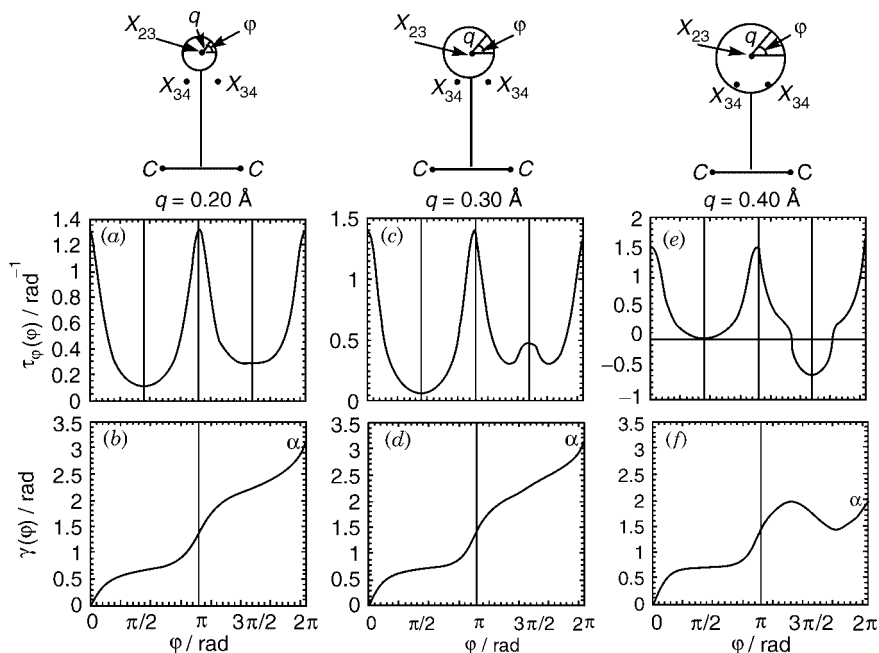
Figure 12. Results for the C_2H molecule as calculated along a circle surrounding the $2^2A'-3^2A'$ conical intersection. The conical intersection is located on the C_{2v} line at a distance of 1.813 Å from the CC axis, where r_1 (=CC distance) = 1.2515 Å. The center of the circle is located at the point of the conical intersection and defined in terms of a radius q. Shown are the non-adiabatic coupling matrix elements $\tau\varphi(\varphi|q)$ and the adiabatic-to-diabatic transformation angles $\gamma(\varphi|q)$ as calculated for (a) and (b) where $q = 0.2$ Å; (c) and (d) where $q = 0.3$ Å; (e) and (f) where $q = 0.4$ Å. Also shown are the positions of the two close-by (3,4) conical intersections (designated as X_{34}).

$\tau_\varphi(\pi + \varphi) = \tau_\varphi(2\pi - \varphi)$, where $0 \le \varphi \le \pi$. In fact, since the origin is located on the C_{2v} axis we should expect only $|\tau_\varphi(\varphi)| = |\tau_\varphi(\pi - \varphi)|$ and $|\tau_\varphi(\pi + \varphi)| = |\tau_\varphi(2\pi - \varphi)|$, where $0 \le \varphi \le \pi$ but due to continuity requirements these relations also have to be satisfied without the absolute signs. (2) It is seen that the adiabatic-to-diabatic transformation angle, $\gamma(\varphi \mid q)$, increases, for the two smaller q-values, monotonically to become $\alpha(\Gamma \mid q)$, with the value of π (in fact, we got 0.986π and 1.001π for $q = 0.2$ and 0.3 Å, respectively). The two-state assumption seems to break down in case $q = 0.4$ Å because the calculated value of $\alpha(\Gamma \mid q)$ is not anymore π but only 0.63π. The reason being that the $q = 0.4$-Å circle not only passes too close to two (3,4) conical intersections—the distances at the closest points are ~ 0.04 Å—and so the (2,3) system can not be considered anymore as an isolated sub-Hilbert space but in fact surrounds these two conical intersections (see third panel of Fig. 12). More details are given in Section XV.B [116].

B.   The Study of a *Real* Three-State Molecular System: Strongly Coupled (2,3) and (3,4) Conical Intersections

We ended Section XV.A by claiming that the value $\alpha(\Gamma \mid q = 0.4 \text{ Å})$ is only 0.63π instead of π (thus damaging the two-state quantization requirement) because, as additional studies revealed, of the close locations of two (3,4) conical intersections. In this section, we show that due to these two conical intersections our sub-space has to be extended so that it contains three states, namely, the second, the third, and the fourth states. Once this extension is done, the quantization requirement is restored but for the three states (and not for two states) as will be described next.

In Section IV, we introduced the topological matrix $\mathbf{D}$ [see Eq. (38)] and showed that for a sub-Hilbert space this matrix is diagonal with $(+1)$ and (-1) terms a feature that was defined as quantization of the non-adiabatic coupling matrix. If the present three-state system forms a sub-Hilbert space the resulting $\mathbf{D}$ matrix has to be a diagonal matrix as just mentioned. From Eq. (38) it is noticed that the $\mathbf{D}$ matrix is calculated along contours, Γ, that surround conical intersections. Our task in this section is to calculate the $\mathbf{D}$ matrix and we do this, again, for circular contours.

The numerical part is based on two circles, C_3 and C_4, related to two different centers (see Fig. 13). Circle C_3, with a radius of 0.4 Å, has its center at the position of the (2,3) conical intersection (like before). Circle C_4, with a radius 0.25 Å, has its center (also) on the C_{2v} line, but at a distance of 0.2 Å from the (2,3) conical intersection and closer to the two (3,4) conical intersections. The computational effort concentrates on calculating the exponential in Eq. (38) for the given set of ab initio 3×3 τ matrices computed along the above mentioned two circles. Thus, following Eq. (28) we are interested in calculating the following expression:

$$\mathbf{A}(\varphi \mid q) = \wp \exp\left(-\int_0^\varphi \tau_\varphi(\varphi' \mid q)d\varphi'\right) \tag{188}$$

where value of q determines the circular contour. The matrix $\mathbf{D}(q)$ is, accordingly:

$$\mathbf{D}(q) = \mathbf{A}(\varphi = 2\pi \mid q) \tag{189}$$

To calculate $\mathbf{A}(\varphi \mid q)$ the angular interval $\{0, \varphi\}$ is divided into n (small enough) segments with $\{\varphi_0(= 0), \varphi_1, \ldots, \varphi_n(= \varphi)\}$ as division points, so that the $\mathbf{A}$ matrix can be presented as

$$\mathbf{A}(\varphi = \varphi_n) = \prod_{k=1}^n \exp\left(-\int_{\varphi_{k-1}}^{\varphi_k} \tau(\varphi')d\varphi'\right) \tag{190}$$
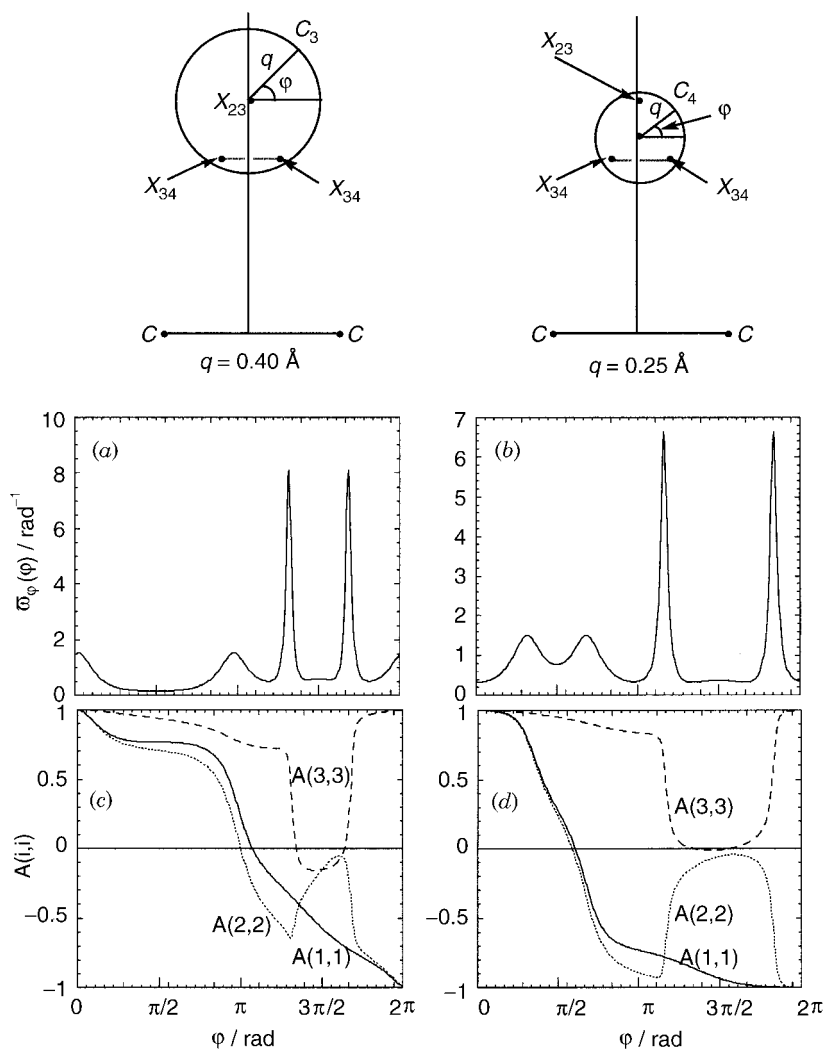
Figure 13. The NACT $\varpi(\varphi)$ (see text) and the ADT matrix diagonal elements $A_{ii}(\varphi)$; $i = 1,2,3$, as calculated for two contours surrounding all three CIs: (*a*) and (*c*) Results for the C_3 contour ($q = 0.4$ Å). (*b*) and (*d*) Results for the C_4 contour ($q = 0.25$ Å). The upper panels present the geometrical situation for each case: The contour C_3 has its center at the point of the (2,3) CI and its radius is $q = 0.4$ Å. The contour C_4 has its center (at a distance of 0.2 Å) in-between the (2,3) CI point and the two (3,4) CIs axis and its radius is $q = 0.25$ Å.

where the variable q is deleted. By following the procedure described in [57], one presents $\mathbf{A}(\varphi_n)$ as

$$\mathbf{A}(\varphi_n) = \prod_{k=1}^{n} \mathbf{G}_k^{\dagger}\mathbf{E}(\varphi_k)\mathbf{G}_k \qquad (191)$$

where $\mathbf{G}_k$ is a unitary matrix that diagonalizes $\tau(\varphi)$ at the mid-point of the kth segment: $\tilde{\varphi}_k = (\varphi_k + \varphi_{k-1})/2$ and $\mathbf{E}(\varphi_k)$ is a diagonal matrix with elements $(m = 1, 2, \ldots, M)$:

$$\mathbf{E}_m(\varphi_k) = \exp\left(-\int_{\varphi_k}^{\varphi_{k+1}} t_m(\varphi)d\varphi\right) = \exp(-t_m(\tilde{\varphi}_k)\Delta\varphi) \qquad (192)$$

Here, $t_m(\tilde{\varphi})$; $m = 1, 2, \ldots, M$ are the eigenvalues of $\tau(\tilde{\varphi})$ and $\Delta\varphi$ is the angular grid size. The order of the multiplication in Eq. (191) is such that the $k = 0$ term is the first term from the right-hand side in the product. With these definitions the matrix $\mathbf{D}$ is defined as $\mathbf{D}(q) = A(\varphi = \varphi_N \mid q)$, where $\varphi_N = 2\pi$ [see Eq. (189)].

Going back to our case and recalling that $\tau(\varphi \mid q)$ is a 3×3 antisymmetric matrix it can be shown that one of its eigenvalues is always zero and the others are two imaginary conjugate functions, namely, $\pm i\varpi(\varphi)$ where $\varpi(\varphi) = \sqrt{\tau_{12}^2 + \tau_{23}^2 + \tau_{13}^2}$. In Figure 13a and b we present $\varpi(\varphi)$ functions as calculated for the two circles C_3 and C_4 (see the relevant upper panels of Fig. 13). The two strong spikes are due to the two (3,4) conical intersections and they occur at points where the circles cross their axis line.

To perform the product in Eq. (191) we need the $\mathbf{G}$ matrices and, for this 3×3 matrix, these can be obtained analytically [7,80]. Thus

$$\mathbf{G} = \frac{1}{\varpi\lambda\sqrt{2}}\begin{pmatrix} i\tau_{13}\varpi - \tau_{23}\tau_{12} & -i\tau_{13}\varpi - \tau_{23}\tau_{12} & \tau_{23}\lambda\sqrt{2} \\ i\tau_{23}\varpi + \tau_{13}\tau_{12} & -i\tau_{23}\varpi + \tau_{13}\tau_{12} & -\tau_{13}\lambda\sqrt{2} \\ \lambda^2 & \lambda^2 & \tau_{12}\lambda\sqrt{2} \end{pmatrix} \qquad (193)$$

where $\lambda = \sqrt{\tau_{23}^2 + \tau_{13}^2}$.

In Figure 13c and d we present the three diagonal elements of the corresponding adiabatic-to-diabatic transformation matrices $\mathbf{A}(\varphi \mid q)$ as calculated for the two circles. Note that $\mathbf{A}_{11}(\varphi \mid q)$, in both cases, behaves smoothly while varying essentially undisturbed, from $(+1)$ to (-1). The second diagonal term in each case, that is, $\mathbf{A}_{22}(\varphi \mid q)$, follows the relevant $\mathbf{A}_{11}(\varphi \mid q)$, until the contour enters the region of the (3,4) conical intersections. There the $\mathbf{A}_{22}(\varphi \mid q)$ terms start to increase like they would do if only one (3,4) conical intersection were present. However, once they have reached the region of the second (3,4) conical intersection this conical intersection pushes the curve down again so that

finally the $A_{22}(\varphi \mid q)$ terms become (-1), instead of $(+1)$. The third term, $A_{33}(\varphi \mid q)$ in each case, proceeds undisturbed as long as it is out of the range of the two $(3,4)$ conical intersections. Once it enters the region of the first conical intersection, the curve starts to decrease and eventually becomes (-1) as it should if only one conical intersection was present. However, as the contour reaches the region of the second conical intersection, $A_{33}(\varphi \mid q)$ is pushed back and ends up with the value of $(+1)$, instead of (-1). The value of each term $A_{ii}(\varphi = 2\pi \mid q), i = 1, 2, 3$ constitutes the diagonal of the $\mathbf{D}$ matrix for the particular contour:

The results for $C_4(q = 0.25 \text{ Å})$ are as follows:

$$\mathbf{D}_{11} = -0.9998; \quad \mathbf{D}_{22} = -0.9999; \quad \mathbf{D}_{33} = 0.9997.$$

The results for $C_3(q = 0.4 \text{ Å})$ are as follows:

$$\mathbf{D}_{11} = -0.990; \quad \mathbf{D}_{22} = -0.988; \quad \mathbf{D}_{33} = 0.997.$$

While studying these results we have to pay attention to two features: (1) In each case, these numbers must, in absolute value, be as close as possible to 1; and (2) two of these numbers have to be negative. Then, we also have to be able to justify the fact that it is the first two diagonal elements that have to be negative and it is the third one that must be positive. Note that these $\mathbf{D}_{ii}$ terms are reasonably close to fulfilling the expected features just mentioned:

For the three relevant (absolute) numbers, the two different calculations yielded $\mathbf{D}_{jj}$ values (three for each case) all in the range $0.99 \leq |\mathbf{D}_{jj}| \leq 0.9999$— thus the quantization is fulfilled to a very high degree.

The values due to the two separate calculations are of the same quality we usually get from (pure) two-state calculations, that is, very close to 1.0 but two comments have to be made in this respect: (1) The quality of the numbers are different in the two calculations: The reason might be connected with the fact that in the second case the circle surrounds an area about three times larger than in the first case. This fact seems to indicate that the deviations are due "noise" caused by CIs belonging to neighbor states [e.g., the $(1,2)$ and the $(4,5)$ CIs]. (2) We would like to remind the reader that the diagonal element in case of the two-state system was only $(-)0.39$ [73] [instead of $(-)1.0$] so that incorporating the third state led, indeed, to a significant improvement.

The requirement of having two negative values and one positive is also fulfilled. Since this subject has been treated several times before (see Sections VIII and IX) it will be discussed within the next subject, related to the locations of the negative terms, that requires some analysis.

The positions of the (-1) terms in the diagonal indicate which of the electronic eigenfunction flips sign upon tracing the closed contour under

consideration [see Section (IV.A)]. The results of this study show that in both cases the eigenfunctions of the two lower states (i.e., $2^2A'$ and $3^2A'$) flip sign, whereas the sign of the third function (i.e., $4^2A'$) remains the same. In situations where we have a single conical intersection between *each* consecutive pair of states it is the first and the third eigenfunctions that flip sign (see Section VIII). Here, we encounter the situation of one conical intersection between the lower pair of states but *two* (not one) conical intersections between the upper pair of states.

To analyze this case, we employ, as before, "contour algebra" (see Section IX): From Figure 14, it is noticed that Γ_{23} is a contour that surrounds the (2,3) conical intersection, Γ_{34} is the contour that surrounds the two (3,4) conical intersections, and Γ_{24} is a contour that surrounds all three conical intersections. According to "contour algebra" the event that "takes place" along Γ_{24} is the sum of the events along each individual contour. Thus,

$$\Gamma_{24} = \Gamma_{23} + \Gamma_{34} \tag{194}$$

Next, we are aware of the fact that if the system traces Γ_{23} it will be the two lower eigenfunctions that flip signs. If the system traces Γ_{34}, then no function flips its sign because two such conical intersections cancel each other [12,22,26,74,125]. Now, if the system traces Γ_{24} then, from Eq. (194) it follows that again, only the two lowest functions flip their sign, so that the effect due to the single lower CI will be preserved. In other words, the *two-state* topological effects are not disturbed along those contours that surround all three CIs. The results will be different once we choose a contour that surrounds, in addition to the lower CI, only one of the two upper CIs [see Ref. (117b)].
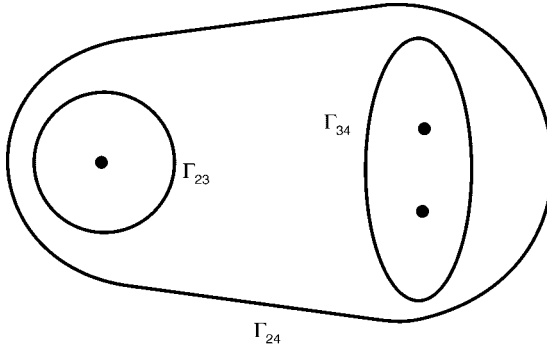
Figure 14. The three contours for the three situations discussed in the text: Γ_{23} surrounds the (2,3) CI, Γ_{34} surrounds the two (3,4) CIs, and Γ_{24} surrounds all three CIs.

XVI.   SUMMARY AND CONCLUSIONS

This field currently differs from others fields in molecular physics mainly in two ways: (1) It is a highly theoretical field and as such it requires chemical–physical intuition and mathematical skill. (2) This field is still open to new developments that could significantly affect chemistry when treated on the molecular level. In this chapter, we tried to summarize the various findings related to this field and to give the reader its state of the art. Some of the subjects presented here were already discussed in previous reviews [8,13]. Still, due to last year's intensive efforts, we managed to include several new issues—some of them may open new venues for more research in this field. Since, as mentioned, part of the subjects presented here were already summarized in a previous review [13], in this section we will mainly concentrate on the implications of new subjects thus avoiding unnecessary repetition. We distinguish between two kinds of topics: (1) Practical ones that are associated with the possibility of treating dynamical processes related to excited states, namely, the *diabatization* process. (2) Less practical ones, which are interesting from a theoretical point of view but with potential prospects.

We start summarizing our findings regarding diabatization. There is no doubt that diabatization is essential for any dynamical study that involves electronically excited states. Diabatization is applied (on and off) for almost three decades mainly for studying charge-transfer processes between ion and molecules [54,94–97,125,127–131] and sporadically for other purposes [100–104]. However, only recently the conditions for a *correct* diabatization, subject to minimal numerical efforts, were formulated [108]. This subject is discussed in Section XI. The diabatization as presented here is shown to be closely connected with the fact that the non-adiabatic coupling matrix has to be quantized to guarantee single-valued diabatic potentials. One of the more fundamental answers regarding the quantization of the nonadiabatic coupling matrix were given in a series of ab initio calculations for different molecules [64–74]. The quantization for two-state systems for real systems was discussed in our previous reviews [8,13] but here, in Section XV.B, we extended the discussion to a three-state case found to exist for the second, third, and fourth states of the C_2H molecule [117]. This study is particularly important because it produces, for first time, the proof that the quantization is a general feature that goes beyond the two-state systems.

The two other subjects, as we already mentioned, are more theoretical but eventually may lead to interesting practical findings.

In Section XIII, we made a connection between the *curl* condition that was found to exist for Born–Oppenheimer–Huang systems and the Yang–Mills field. Through this connection we found that the non-adiabatic coupling terms can be considered as vector potentials that have their source in pseudomagnetic

fields defined along *seams*. We speculated that these fields could be, semiclassically, associated with the zero-point vibrational motion [113].

Another subject with important potential application is discussed in Section XIV. There we suggested employing the *curl* equations (which any Bohr–Oppenheimer–Huang system has to obey for the for the relevant sub-Hilbert space), instead of ab initio calculations, to derive the non-adiabatic coupling terms [113,114]. Whereas these equations yield an analytic solution for any two-state system (the abelian case) they become much more elaborate due to the nonlinear terms that are unavoidable for any realistic system that contains more than two states (the non-abelian case). The solution of these equations is subject to boundary conditions that can be supplied either by ab initio calculations or perturbation theory.

This chapter centers on the mathematical aspects of the non-adiabatic coupling terms as single entities or when grouped in matrices, but were it not for the available ab initio calculation, it would have been almost impossible to proceed thus far in this study. Here, the ab initio results play the same crucial role that experimental results would play in general, and therefore the author feels that it is now appropriate for him to express his appreciation to the groups and individuals who developed the numerical means that led to the necessary numerical outcomes.

APPENDIX A: THE JAHN–TELLER MODEL AND THE LONGUET–HIGGINS PHASE

We consider a case where in the vicinity of a point of degeneracy between two electronic states the diabatic potentials behave linearly as a function of the coordinates in the following way [16–21]

$$\mathbf{W} = k \begin{pmatrix} y & x \\ x & -y \end{pmatrix} \tag{A.1}$$

where (x, y) are some generalized nuclear coordinates and k is a force constant. The aim is to derive the eigenvalues and the eigenvectors of this potential matrix. The eigenvalues are the adiabatic potential energy states and the eigenvectors form the columns of the adiabatic-to-diabatic transformation matrix. In order to perform this derivation, we shall employ polar coordinates (q, φ), namely,

$$y = q \cos \varphi \quad \text{and} \quad x = q \sin \varphi \tag{A.2}$$

By substituting for x and y, we get φ-*independent* eigenvalues of the form

$$u_1 = kq \quad \text{and} \quad u_2 = -kq \quad \text{where} \quad q = \{0, \infty\} \quad \text{and} \quad \varphi = \{0, 2\pi\}$$
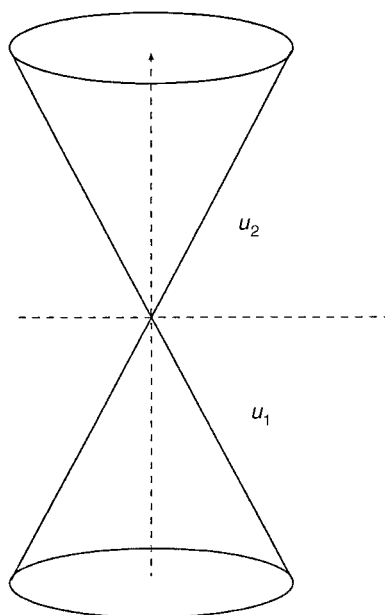
Figure 15.   The two interacting cones within the Jahn–Teller model.

As noticed from Figure 15, the two surfaces u_1 and u_2 are conelike potential energy surfaces with a common apex. The corresponding eigenvectors are

$$\zeta_1 = \left(\cos\frac{\varphi}{2}, \quad \sin\frac{\varphi}{2}\right)$$
$$\zeta_2 = \left(\sin\frac{\varphi}{2}, \quad -\cos\frac{\varphi}{2}\right)$$

$$(A.3)$$

The components of the two vectors (ξ_1, ξ_2), when multiplied by the electronic (diabatic) basis set $(|\phi_1\rangle, |\phi_2\rangle)$, form the corresponding electronic adiabatic basis set $(|\eta_1\rangle, |\eta_2\rangle)$:

$$|\eta_1\rangle = \cos\frac{\varphi}{2}|\phi_1\rangle + \sin\frac{\varphi}{2}|\phi_2\rangle$$
$$|\eta_2\rangle = \sin\frac{\varphi}{2}|\phi_1\rangle - \cos\frac{\varphi}{2}|\phi_2\rangle$$

$$(A.4)$$

The adiabatic functions are characterized by two interesting features: (1) they depend only on the angular coordinate (but not on the radial coordinate) and (2) they are not single valued in configuration space because when φ is replaced by $(\varphi + 2\pi)$—a rotation that brings the adiabatic wave functions back to their

initial position—*both* of them change sign. This last feature, which was revealed by Longuet-Higgins [14–17], may be, in certain cases, very crucial because multivalued electronic eigenfunctions cause the corresponding nuclear wave functions to be multivalued as well, a feature that has to be incorporated explicitly (through specific boundary conditions) while solving the nuclear Schrödinger equation. In this respect, it is important to mention that ab initio electronic wave functions indeed, possess the multivaluedness feature as described by Longuet–Higgins [30].

One way to eliminate the multivaluedness of the electronic eigenfunctions is by multiplying it by a phase factor [15], namely,

$$\zeta_j(\varphi) = \exp(i\vartheta)\eta_j(\varphi) \qquad j = 1, 2 \tag{A.5}$$

where a possible choice for ϑ is

$$\vartheta = \varphi/2 \tag{A.6}$$

Note that $\zeta_j(\varphi)$; $j = 1, 2$ are indeed single-valued eigenfunctions; however, instead of being real, they become complex.

The fact that the electronic eigenfunctions are modified as presented in Eq. (A.5) has a direct effect on the non-adiabatic coupling terms as introduced in Eqs. (8a) and (8b). In particular, we consider the term $\tau_{11}^{(1)}$ (which for the case of real eigenfunctions is identically zero) for the case presented in Eq. (A.5):

$$\tau_{11}^{(1)} = \langle\zeta_1|\nabla\zeta_1\rangle = i\nabla\vartheta + \langle\eta_1|\nabla\eta_1\rangle$$

but since

$$\langle\eta_1|\nabla\eta_1\rangle = 0$$

it follows that $\tau_{11}^{(1)}$ becomes

$$\tau_{11}^{(1)} = i\nabla\vartheta \tag{A.7}$$

In the same way, we obtain

$$\tau_{11}^{(2)} = i\nabla^2\vartheta - (\nabla\vartheta)^2 \tag{A.8}$$

The fact that now $\tau_{11}^{(1)}$ is not zero will affect the ordinary Born–Oppenheimer approximation. To show that, we consider Eq. (15) for $M = 1$, once for a real

eigenfunction and once for a complex eigenfunction. In the first case, we get from Eq. (15) the ordinary Born–Oppenheimer equation:

$$-\frac{1}{2m}\nabla^2\psi + (u - E)\psi = 0 \qquad (A.9)$$

because for real electronic eigenfunctions $\tau_{11}^{(1)} \equiv 0$ but in the second case for which $\tau_{11}^{(1)} \neq 0$ the Born–Oppenheimer approximation becomes

$$-\frac{1}{2m}(\nabla + i\nabla\vartheta)^2\psi + (u - E)\psi = 0 \qquad (A.10)$$

which can be considered as an 'extended' Born–Oppenheimer approximation for a case of a single isolated state expressed in terms of a complex electronic eigenfunction [132]. This equation was interpreted for some time as the adequate Schrödinger equation to describe the effect of the conical intersection that originate from the two interacting states. As it stands it contains an effect due to an ad hoc phase attached to a ground-state electronic eigenfunction [63].

The extended Born–Oppenheimer approximation based on the nonadiabatic coupling terms was discussed on several occasions [23,25,26,55,56,133,134] and is also presented here by Adhikari and Billing (see Chapter 3).

APPENDIX B: THE SUFFICIENT CONDITIONS FOR HAVING AN ANALYTIC ADIABATIC-TO-DIABATIC TRANSFORMATION MATRIX

The adiabatic-to-diabatic transformation matrix, $\mathbf{A}_p$, fulfills the following first-order differential vector equation [see Eq. (19)]:

$$\nabla\mathbf{A}_M + \tau_M\mathbf{A}_M = 0 \qquad (B.1)$$

In order for $\mathbf{A}_M$ to be a regular matrix at every point in the assumed region of configuration space it has to have an inverse and its elements have to be analytic functions in this region. In what follows, we prove that if the elements of the components of τ_M are analytic functions in this region and have derivatives to any order and if the P subspace is decoupled from the corresponding Q subspace then, indeed, $\mathbf{A}_M$ will have the above two features.

I.   ORTHOGONALITY

We start by proving that $\mathbf{A}_M$ is a unitary matrix and as such it will have an inverse (the proof is given here again for the sake of completeness). Let us consider the

complex conjugate of Eq. (B.1):

$$\nabla \mathbf{A}_M^\dagger - \mathbf{A}_M^\dagger \tau_M = 0 \tag{B.2}$$

where we recall that τ_M, the non-adiabatic coupling matrix, is a real anti-symmetric matrix. By multiplying Eq. (B.2) from the right by $\mathbf{A}_M$ and Eq. (B.1) from the left by $\mathbf{A}_M^\dagger$ and combining the two expressions we get

$$\mathbf{A}_M^\dagger \nabla \mathbf{A}_M + (\nabla \mathbf{A}_M^\dagger)\mathbf{A}_M = (\nabla \mathbf{A}_M^\dagger \mathbf{A}_M) = 0 \Rightarrow \qquad \mathbf{A}_M^\dagger \mathbf{A}_M = \text{constant}$$

For a proper choice of boundary conditions, the above mentioned constant matrix can be assumed to be the identity matrix, namely,

$$\mathbf{A}_M^\dagger \mathbf{A}_M = I \tag{B.3}$$

Thus $\mathbf{A}_P$ is a unitary matrix at any point in configuration space.

II.   ANALYTICITY

From basic calculus, it is known that a function of a single variable is analytic at a given interval if and only if it has well-defined derivatives, to any order, at any point in that interval. In the same way, a function of several variables is analytic in a region if at any point in this region, in addition to having well-defined derivatives for all variables to any order, the result of the differentiation with respect to any *two* different variables does not depend on the order of the differentiation.

The fact that the $\mathbf{A}_M$ matrix fulfills Eq. (B.1) ensures the existence of derivatives to any order for any variable, at a given region in configuration space, if τ_M is analytic in that region. In what follows, we assume that this is, indeed, the case. Next, we have to find the conditions for a mixed differentiation of the $\mathbf{A}_M$ matrix elements to be independent of the order.

For that purpose, we consider the p and the q components of Eq. (B.1) (the subscript M will be omitted to simplify notation):

$$\frac{\partial}{\partial p}\mathbf{A} + \tau_p \mathbf{A} = 0$$
$$\frac{\partial}{\partial q}\mathbf{A} + \tau_q \mathbf{A} = 0 \tag{B.4}$$

By differentiating the first equation according to q we find

$$\frac{\partial}{\partial q}\frac{\partial}{\partial p}\mathbf{A} + \left(\frac{\partial}{\partial q}\tau_p\right)\mathbf{A} + \tau_p \frac{\partial}{\partial q}\mathbf{A} = 0$$

or

$$\frac{\partial}{\partial q}\frac{\partial}{\partial p}\mathbf{A} + \left(\frac{\partial}{\partial q}\boldsymbol{\tau}_p\right)\mathbf{A} - \boldsymbol{\tau}_p\boldsymbol{\tau}_q\mathbf{A} = 0 \qquad \text{(B.5a)}$$

In the same way, we get from the second equation the following expression:

$$\frac{\partial}{\partial p}\frac{\partial}{\partial q}\mathbf{A} + \left(\frac{\partial}{\partial p}\boldsymbol{\tau}_q\right)\mathbf{A} - \boldsymbol{\tau}_q\boldsymbol{\tau}_p\mathbf{A} = 0 \qquad \text{(B.5b)}$$

Requiring that the mixed derivative is independent of the order of the differentiation yields

$$\left(\frac{\partial}{\partial p}\boldsymbol{\tau}_q - \frac{\partial}{\partial q}\boldsymbol{\tau}_p\right)\mathbf{A} = (\boldsymbol{\tau}_q\boldsymbol{\tau}_p - \boldsymbol{\tau}_p\boldsymbol{\tau}_q)\mathbf{A} \qquad \text{(B.6)}$$

or (since **A** is a unitary matrix):

$$\frac{\partial}{\partial p}\boldsymbol{\tau}_q - \frac{\partial}{\partial q}\boldsymbol{\tau}_p = [\boldsymbol{\tau}_q, \boldsymbol{\tau}_p] \qquad \text{(B.7)}$$

Thus, in order for the **A** matrix to be analytic in a region, any two components of $\boldsymbol{\tau}$, locally, have to fulfill Eq. (B.7). Equation (B.7) can also be written in a more compact way

$$\text{curl } \boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] = 0 \qquad \text{(B.8)}$$

where $\times$ stands for a vector product.

The question to be asked is: Under what conditions (if at all) do the components of $\boldsymbol{\tau}$ fulfill Eq. (B.8)? In [34] it is proved that this relation holds for any full Hilbert space. Here, we shall show that this relation holds also for the P sub-Hilbert space of dimension M, as defined by Eq. (10). To show that we employ, again, the Feshbach projection operator formalism [79] [see Eqs. (11)].

We start by considering the pth and the qth components of Eqs. (8a)

$$\left(\frac{\partial\boldsymbol{\tau}_q}{\partial p}\right)_{jk} = \left\langle\frac{\partial\zeta_j}{\partial p}\bigg|\frac{\partial\zeta_k}{\partial q}\right\rangle + \left\langle\zeta_j\bigg|\frac{\partial^2\zeta_k}{\partial p\partial q}\right\rangle \qquad j,k \leq M \qquad \text{(B.9a)}$$

and

$$\left(\frac{\partial\boldsymbol{\tau}_p}{\partial q}\right)_{jk} = \left\langle\frac{\partial\zeta_{kj}}{\partial q}\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle + \left\langle\zeta_j\bigg|\frac{\partial^2\zeta_k}{\partial q\partial p}\right\rangle \qquad j,k \leq M \qquad \text{(B.9b)}$$

Subtracting Eq. (B.9b) from Eq. (B.9a) and assuming that the electronic eigen-functions are *analytic* functions with respect to the nuclear coordinates yields the following result:

$$\left(\frac{\partial}{\partial p}\tau_q - \frac{\partial}{\partial q}\tau_p\right)_{jk} = \left\langle\frac{\partial\zeta_{kj}}{\partial p}\bigg|\frac{\partial\zeta_k}{\partial q}\right\rangle - \left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle \qquad j,k \leq M \qquad (B.10)$$

Equation (B.10) stands for the (j,k) matrix element of the left-hand side of Eq. (B.7). Next, we consider the (j,k) element of the first term on the right-hand side of Eq. (B.7), namely,

$$(\tau_q\tau_p)_{jk} = \sum_{i=1}^{M}\left\langle\zeta_j\bigg|\frac{\partial\zeta_i}{\partial q}\right\rangle\left\langle\zeta_i\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle$$

Since for real functions

$$\left\langle\zeta_j\bigg|\frac{\partial\zeta_i}{\partial q}\right\rangle = -\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\zeta_i\right\rangle$$

we get for this matrix element the result

$$(\tau_q\tau_p)_{jk} = -\sum_{i=1}^{M}\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\zeta_i\right\rangle\left\langle\zeta_i\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle = -\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\left(\sum_{i=1}^{M}|\zeta_i\rangle\langle\zeta_i|\right)\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle$$

Recalling that the summation within the round parentheses can be written as $[1 - Q_M]$, where Q_M is the projection operator for Q subspace, we obtain

$$(\tau_q\tau_p)_{jk} = -\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle - \sum_{i=M+1}^{N}\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\zeta_i\right\rangle\left\langle\zeta_i\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle \qquad j,k \leq M$$

Since under the summation sign each term is zero (no coupling between the inside and the outside subspaces) [see Eq. (10)] we finally get

$$(\tau_q\tau_p)_{jk} = -\left\langle\frac{\partial\zeta_j}{\partial q}\bigg|\frac{\partial\zeta_k}{\partial p}\right\rangle \qquad\qquad (B.11a)$$

A similar result will be obtained for Eq. (B.7), namely,

$$(\tau_p\tau_q)_{jk} = -\left\langle\frac{\partial\zeta_j}{\partial p}\bigg|\frac{\partial\zeta_k}{\partial q}\right\rangle \qquad\qquad (B.11b)$$

Subtracting Eq. (B.11b) from Eq. (B.11a) yields Eq. (B.10), thus proving the existence of Eq. (B.7).

Summary: In a region where the τ_M elements are analytic functions of the coordinates, A_M is an orthogonal matrix with elements that are analytic functions of the coordinates.

APPENDIX C: ON THE SINGLE/MULTIVALUEDNESS OF THE ADIABATIC-TO-DIABATIC TRANSFORMATION MATRIX

In this appendix, we discuss the case where two components of τ_M, namely, τ_{Mp} and τ_{Mq} (p and q are Cartesian coordinates) are singular in the sense that at least one element in each of them is singular at the point $B(p = a, q = b)$ located on the plane formed by p and q. We shall show that in such a case the adiabatic-to-diabatic transformation matrix *may* become multivalued.

We consider the integral representation of the two relevant first-order differential equations [namely, the p and the q components of Eq. (19)]:

$$
\frac{\partial}{\partial p}\mathbf{A}_M + \tau_{Mp}\mathbf{A}_M = 0
$$
$$
\frac{\partial}{\partial q}\mathbf{A}_M + \tau_{Mq}\mathbf{A}_M = 0
$$

(C.1)

In what follows, the subscript M will be omitted to simplify the notations. If the initial point is $P(p_0, q_0)$ and we are interested in deriving the value of $\mathbf{A}(\equiv \mathbf{A}_M)$ at a final point $Q(p, q)$ then one integral equation to be solved is

$$
\mathbf{A}(p,q) = \mathbf{A}(p_0, q_0) - \int_{p_0}^{p} dp'\,\tau_p(p', q_0)\mathbf{A}(p', q_0) - \int_{q_0}^{q} dq'\,\tau_q(p, q')\mathbf{A}(p, q')
$$

(C.2a)

Another way of obtaining the value of $\mathbf{A}(p, q)$ [we shall designate it as $\tilde{\mathbf{A}}(p, q)$] is by solving the following integral equation:

$$
\tilde{\mathbf{A}}(p,q) = \mathbf{A}(p_0, q_0) - \int_{q_0}^{q} dq'\,\tau_q(p_0, q')\tilde{\mathbf{A}}(p_0, q') - \int_{p_0}^{p} dp'\,\tau_p(p', q)\tilde{\mathbf{A}}(p', q)
$$

(C.2b)

In Eq. (C.2a), we derive the solution by solving it along the path Γ' characterized by two straight lines and three points (see Fig. 16a):

$$
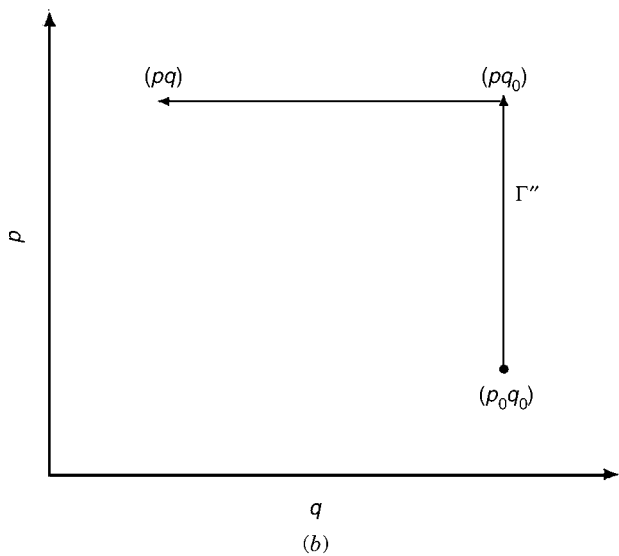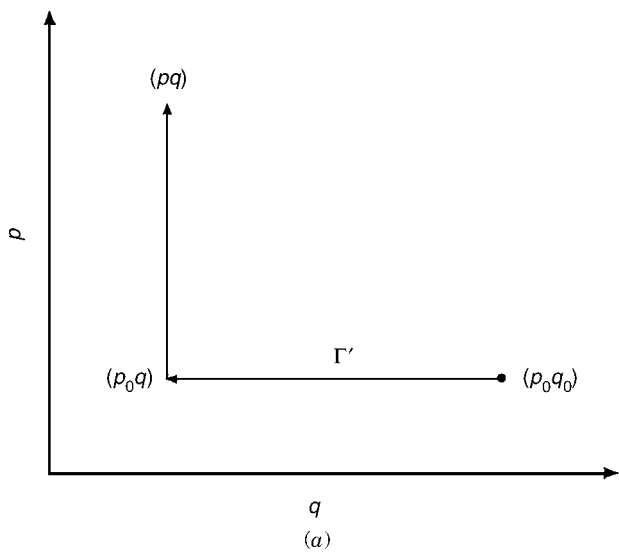\Gamma': \quad P(p_0, q_0) \rightarrow P'(p_0, q) \rightarrow Q(p, q)
$$

(C.3a)

(pq)

(p_0q) Γ' (p_0q_0)

q

(a)

(pq) (pq_0)

Γ''

(p_0q_0)

q

(b)

Figure 16. The rectangular paths Γ' and Γ'' connecting the points (p_0, q_0) and (p, q) in the (p, q) plane.

and in Eq. (C.2b) by solving it along the path Γ'' also characterized by two (different) straight lines and the three points (see Fig. 16b)

$$\Gamma'': \quad P(p_0, q_0) \to Q'(p, q_0) \to Q(p, q) \tag{C.3b}$$

Note that Γ, formed by Γ' and Γ'' written schematically as

$$\Gamma = \Gamma' - \Gamma'' \tag{C.4}$$

is a closed path.

Since the two solutions of Eq. (C.1) presented in Eqs. (C.2a) and (C.2b) may not be identical we shall derive the sufficient conditions for that to happen.

To start this study, we assume that the four points P, P', Q', and Q are at small distances from each other so that if

$$p = p_0 + \Delta p \qquad q = q_0 + \Delta q$$

then Δp and Δq are small enough distances as required for the derivation.

Subtracting Eq. (C.2b) from Eq. (C.2a) yields the following expression:

$$
\begin{aligned}
\Delta \mathbf{A}(p, q) = -&\int_{q_0}^{q_0 + \Delta q} dq' (\tau_q(p_0, q') \mathbf{A}(p_0, q') - \tau_q(p, q') \mathbf{A}(p, q')) \\
+ &\int_{p_0}^{p_0 + \Delta p} dp' (\tau_p(p', q_0) \mathbf{A}(p', q_0) - \tau_p(p', q) \mathbf{A}(p', q))
\end{aligned}
\tag{C.5}
$$

where

$$\Delta \mathbf{A}(p, q) = \mathbf{A}(p, q) - \tilde{\mathbf{A}}(p, q) \tag{C.6}$$

Next, we consider two cases.

1. The case where the point $B(a, b)$ is not surrounded by the path Γ (see Fig. 17a). In this case, both τ_p and τ_q are *analytic* functions of the coordinates in the region enclosed by Γ, and therefore the integrands of the two integrals can be replaced by the corresponding derivatives calculated at the respective intermediate points, namely,

$$
\begin{aligned}
\Delta \mathbf{A}(p, q) = \Delta p \int_{q_0}^{q_0 + \Delta q} dq' \frac{\partial (\tau_q(\tilde{p}, q') \mathbf{A}(\tilde{p}, q'))}{\partial p} \\
- \Delta q \int_{p_0}^{p_0 + \Delta p} dp' \frac{\partial (\tau_p(p', \tilde{q}) \mathbf{A}(p', \tilde{q}))}{\partial q}
\end{aligned}
\tag{C.7}
$$

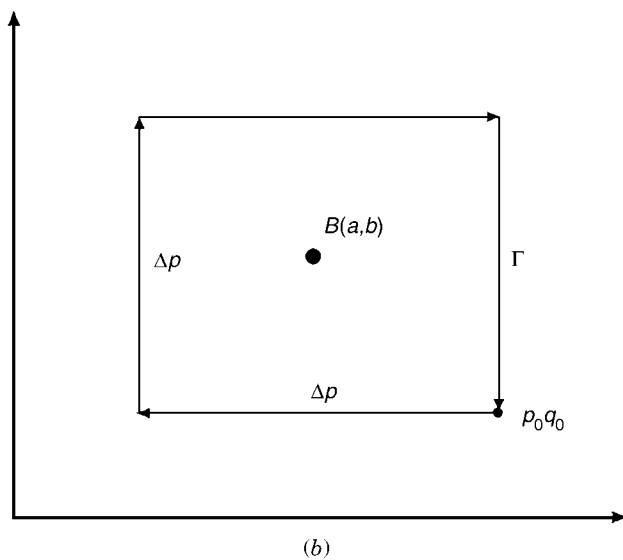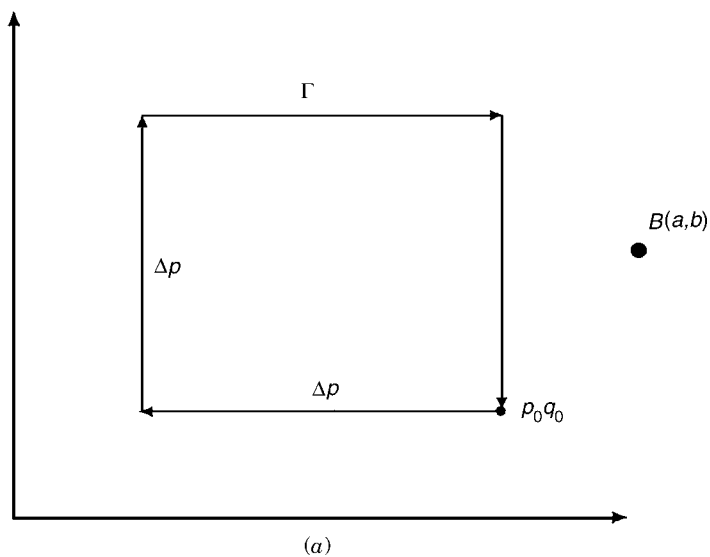**Figure 17.** The differential closed paths Γ and the singular point $B(a, b)$ in the (p, q) plane: (a) The point B is not surrounded by Γ. (b) The point B is surrounded by Γ.

To continue the derivation, we recall that Δp and Δq are small enough so that the two integrands vary only slightly along the interval of integration so, that ΔA becomes

$$\Delta \mathbf{A}(p, q) = \Delta p \Delta q \left\{ \frac{\partial (\tau_q(\tilde{p}, \tilde{\tilde{q}}) \mathbf{A}(\tilde{p}, \tilde{\tilde{q}}))}{\partial p} - \frac{\partial (\tau_p(\tilde{\tilde{p}}, \tilde{q}) \mathbf{A}(\tilde{\tilde{p}}, \tilde{q}))}{\partial q} \right\} \quad \text{(C.8)}$$

If we assume again that all relevant functions are smooth enough, the expression in the curled parentheses can be evaluated further to become

$$\Delta \mathbf{A}(p, q) = \left\{ \left(\frac{\partial \tau_q(p, q)}{\partial p} - \frac{\partial \tau_p(p, q)}{\partial q} \right) - [\tau_q, \tau_p] \right\} \mathbf{A}(p, q) \Delta p \Delta q \quad \text{(C.9)}$$

where Eqs. (C.1) were used to express the derivatives of $\mathbf{A}(p, q)$. Since the expression within the curled parentheses is identically zero due to Eq. (24), ΔA becomes identically zero or in other words the two infinitesimal paths Γ' and Γ'' yield identical solutions for the $\mathbf{A}$ matrix. The same applies to ordinary (viz., not necessarily small) closed paths because they can be constructed by ''integrating'' over closed infinitesimal paths (see Fig. 18).

2. The case when one of the differential closed paths surrounds the point $B(a, b)$ (see Fig. 17b). Here the derivation breaks down at the transition from Eqs. (C.5)–(C.7) and later, from Eqs. (C.7)–(C.8), because τ_p and τ_q become infinitely large in the close vicinity of $B(a, b)$, and therefore their
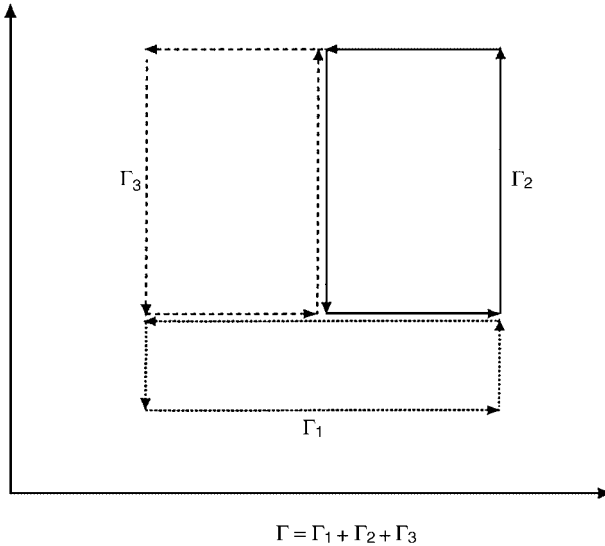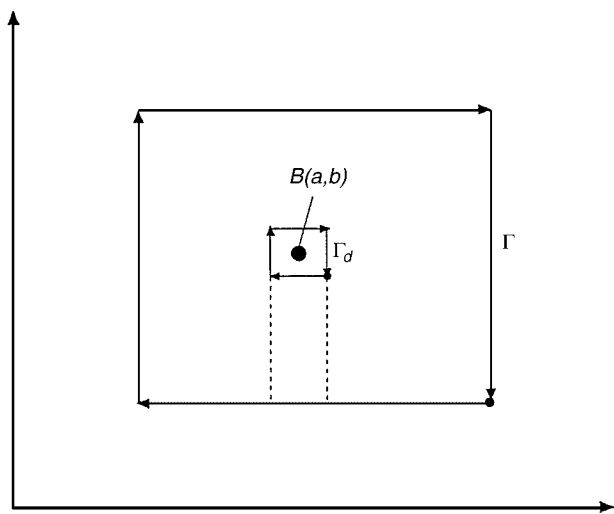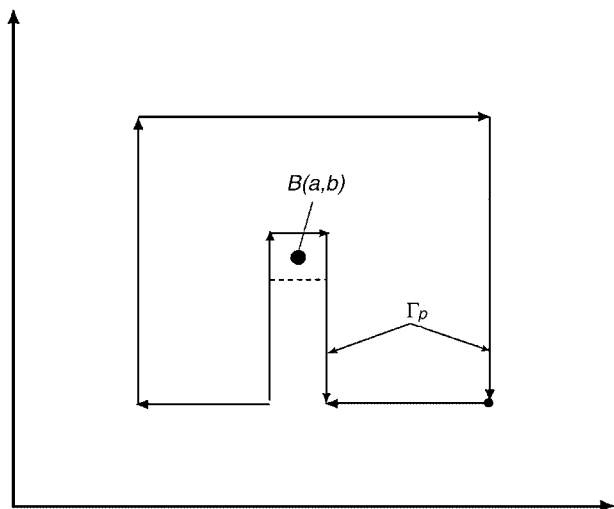

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3$$

Figure 18.   The closed (rectangular) path Γ as a sum of three partially closed paths Γ_1, Γ_2, Γ_3.

(a)

(b)

$$\Gamma = \Gamma_p + \Gamma_i + \Gamma_d$$

Figure 19. The closed path Γ as a sum of three closed paths Γ_d, Γ_p, Γ_i. (a) The closed (rectangular) paths, that is, the large path Γ and the differential path Γ_d both surrounding the singular point $B(a, b)$. (b) The closed path Γ_p that does not surround the point $B(a, b)$. (c) The closed path Γ_i that does not surround the point $B(a, b)$.
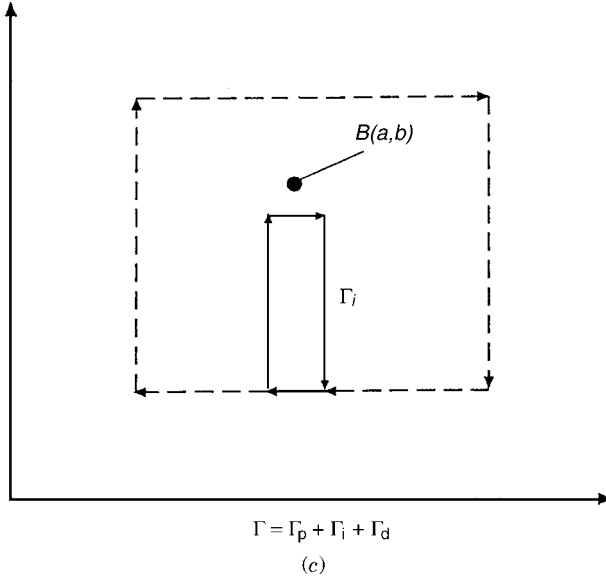
$$\Gamma = \Gamma_p + \Gamma_i + \Gamma_d$$

(c)

Figure 19 (*Continued*)

intermediate values cannot be estimated. As a result it is not clear whether the two solutions of the **A** matrix calculated along the two different differential paths are identical or not. The same applies to a regular size (i.e., not necessarily small) path Γ that surrounds the point $B(a,b)$. This closed path can be constructed from a differential path Γ_d that surrounds $B(a,b)$, a path Γ_p that does not surround $B(a,b)$, and a third, a connecting path Γ_i, which, also, does not surround $B(a,b)$ (see Fig. 19). It is noted that the small region surrounded by Γ_d governs the features of the **A** matrix in the entire region surrounded by Γ, immaterial of how large Γ is.

APPENDIX D: THE DIABATIC REPRESENTATION

Our starting equation is Eq. (3) in Section II.A with one difference, namely, we replace $\zeta_i(e \mid n)$ by $\zeta_i(e \mid n_0)$; $i = 1, \ldots, N$, where n_0 stands for a fixed set of nuclear coordinates. Thus

$$\Psi(e, n \mid n_0) = \sum_{i=1}^{N} \psi_i(n)\zeta_i(e \mid n_0) \tag{D.1}$$

Here, $\zeta_i(e \mid n_0)$, like $\zeta_i(e \mid n)$, is an eigenfunction of the following Hamiltonian

$$(\mathbf{H}_e(e \mid n_0) - u_i(n_0))\zeta_i(e \mid n_0) = 0 \qquad i = 1, \ldots, N \tag{D.2}$$

where $u_i(n_0), i = 1, \ldots, N$ are the electronic eigenvalues as calculated for this (fixed) set of nuclear coordinates. Substituting Eqs. (1) and (D.1) in Eq. (2) yields the following expression:

$$\sum_{i=1}^{N} \mathbf{T}_n \psi_i(n) |\zeta_i(e \mid n_0)\rangle + \sum_{i=1}^{N} \psi_i(n) [\mathbf{H}_e(e \mid n) - E] |\zeta_i(e \mid n_0)\rangle = 0 \qquad \text{(D.3)}$$

It has to be emphasized that whereas n_0 is fixed, n is a variable. Substituting Eq. (6) for T_n, multiplying Eq. (D.3) by $\langle \zeta_j(e \mid n_0)|$, and integrating over the electronic coordinates yields the following result:

$$\left(-\frac{1}{2m}\nabla^2 - E \right) \psi_j(n) + \sum_{i=1}^{N} \langle \zeta_j(e \mid n_0) | \mathbf{H}_e(e \mid n) | \zeta_i(e \mid n_0)\rangle \psi_i(n) = 0 \qquad \text{(D.4)}$$

Recalling

$$\mathbf{H}_e(e \mid n) = \mathbf{T}_e + \mathbf{u}(e \mid n) \qquad \text{(D.5a)}$$

and, therefore, also

$$\mathbf{H}_e(e \mid n_0) = \mathbf{T}_e + \mathbf{u}(e \mid n_0) \qquad \text{(D.5b)}$$

where $u(e \mid n)$ is the Coulombic field, we can replace $H_e(e \mid n)$ in Eq. (D.4) by the following expression:

$$\mathbf{H}_e(e \mid n) = \mathbf{H}_e(e \mid n_0) + \{\mathbf{u}(e \mid n) - \mathbf{u}(e \mid n_0)\} \qquad \text{(D.6)}$$

Equation (D.6) is valid because the electronic coordinates are independent of the nuclear coordinates. Having this relation, we can calculate the following matrix element:

$$\langle \chi_j(e \mid n_0) | \mathbf{H}_e(e \mid n) | \chi_i(e \mid n_0)\rangle = u_j(n_0)\delta_{ji} + v_{ij}(n \mid n_0) \qquad \text{(D.7)}$$

where

$$v_{ij}(n \mid n_0) = \langle \chi_j(e \mid n_0) | \mathbf{u}(e \mid n) - \mathbf{u}(e \mid n_0) | \chi_i(e \mid n_0)\rangle \qquad \text{(D.8)}$$

Defining

$$\mathbf{V}_{ij}(n \mid n_0) = v_{ij}(n \mid n_0) + u_j(n_0)\delta_{ji} \qquad \text{(D.9)}$$

and recalling Eq. (D.7), we get for Eq. (D.4) the expression

$$\left(-\frac{1}{2m}\nabla^2 - E\right)\psi_j(\mathbf{n}) + \sum_{i=1}^{N} V_{ji}(\mathbf{n} \mid \mathbf{n}_0)\psi_i(\mathbf{n}) = 0 \qquad \text{(D.10)}$$

This equation can be also written in matrix form

$$-\frac{1}{2m}\nabla^2\Psi + (\mathbf{V} - E)\Psi = 0 \qquad \text{(D.11)}$$

Here, $\mathbf{V}$ is the diabatic potential matrix and, in contrast to $\mathbf{u}$ in Eq. (9) of Section (II.A), it is a full matrix. Thus Eq. (D.11) is the Schrödinger equation within the diabatic representation.

APPENDIX E: A NUMERICAL STUDY OF A THREE-STATE MODEL

In Section V.B, we discussed to some extent the 3×3 adiabatic-to-diabatic transformation matrix $\mathbf{A}(\equiv \mathbf{A}^{(3)})$ for a tri-state system. This matrix was expressed in terms of three (Euler-type) angles $\gamma_{ij}, i = 1, 2, 3$ [see Eq. (81)], which fulfill a set of three coupled, first-order, differential equations [see Eq. (82)].

In what follows, we treat a tri-state model system defined in a plane in terms of two polar coordinates (ρ, φ) [85]. In order to guarantee that the non-adiabatic matrix τ, yields single-valued diabatic potentials we shall start with a 3×3 *diabatic* potential matrix and form, employing the Hellmann–Feynman theorem [3,36,85], the corresponding non-adiabatic coupling matrix τ. The main purpose of studying this example is to show that the $\mathbf{A}$ matrix may not be uniquely defined in configuration space although the diabatic potentials are all single valued.

The tri-state diabatic potential that is employed in this study is closely related (but not identical) to the one used by Cocchini et al. [39,135] to study the excited states of Na$_3$. It is of the following form (for more details see [85]):

$$\mathbf{V} = \begin{pmatrix} \varepsilon_E + U_1 & U_2 & W_1 - W_2 \\ U_2 & \varepsilon_E - U_1 & W_1 + W_2 \\ W_1 - W_2 & W_1 + W_2 & \varepsilon_A \end{pmatrix} \qquad \text{(E.1)}$$

Here ε_E and ε_A are the values of two electronic states (an E-type state and an A-type state, respectively), $U_i; i = 1, 2$ are two potentials defined as

$$U_1 = k\rho\cos\varphi + \frac{1}{2}g\rho^2\cos(2\varphi) \qquad \text{(E.2a)}$$

and

$$U_2 = k\rho \sin\varphi - \frac{1}{2}g\rho^2 \sin(2\varphi) \qquad (\text{E.2b})$$

W_i; $i = 1, 2$ are potentials of the same functional form as the U_i parameters but defined in terms of a different set of parameters f and p, which replace g and k, respectively. The numerical values for these four parameters are [135]

$$k = \sqrt{2}p = 5.53 \text{ a.u.} \qquad \text{and} \qquad g = \sqrt{2}f = 0.152 \text{ a.u.}$$

Equation (82) is solved, for fixed ρ values, but for a varying angular coordinate, φ, defined along the interval $(0, 2\pi)$. Thus ρ serves as a parameter and the results will be presented for different ρ values. A second parameter that will be used is the potential energy shift, $\Delta\varepsilon(= \varepsilon_E - \varepsilon_A)$, defined as the shift between the two original coupled adiabatic states and the third state at the origin, that is, at $\rho = 0$ (in case $\Delta\varepsilon = 0$, all three states are degenerate at the origin). The results will be presented for several of its values. In Figure 20 are shown the three non-adiabatic coupling terms $\tau_{\varphi ij}(\varphi)$; $i, j = 1, 2, 3(i > j)$ as calculated for different values of ρ and $\Delta\varepsilon$. The main feature to be noticed is the well-defined (sharp) tri-peak structure of $\tau_{\varphi 12}$ and $\tau_{\varphi 23}$ as a function of φ. There are other interesting features to be noticed but these are of less relevance to the present study (for a more extensive discussion see [85]).

Figure 1 presents the three γ angles as a function of φ for various values of ρ and $\Delta\varepsilon$. The two main features that are of interest for the present study are (1) following a full cycle, all three angles in all situations obtain the values either of π or of zero. (2) In each case (viz., for each set of ρ and $\Delta\varepsilon$), following a full cycle, two angles become zero and one becomes π. From Eq. (81) notice that the $\mathbf{A}$ matrix is diagonal at $\varphi = 0$ and $\varphi = 2\pi$ but in the case of $\varphi = 0$ the matrix $\mathbf{A}$ is the unit matrix and in the second case it has two (-1) terms and one $(+1)$ in its diagonal. Again recalling Eq. (39), this implies that the $\mathbf{D}$ matrix is indeed diagonal and has in its diagonal numbers of norm 1. However, the most interesting fact is that $\mathbf{D}$ is not the unit matrix. In other words, the adiabatic-to-diabatic transformation matrix presented in Eq. (81) is not single valued in configuration space although the corresponding diabatic *potential* matrix is single valued, by definition [see Eqs. (E.1) and (E.2)]. The fact that $\mathbf{D}$ has two (-1) terms and one $(+1)$ in its diagonal implies that the present $\mathbf{\tau}$ matrix produces topological effects, as was explained in the last two paragraphs of Section IV.A: Two electronic eigenfunctions flip sign upon tracing a closed path and one electronic function remains with its original sign.

As much as the results in the last section (Appendix D) are interesting the rather more interesting case is the one for $\Delta\varepsilon = 0$, namely, the case where the three states degenerate at one point. Here we find that even in this case $\mathbf{D}$ is *not*
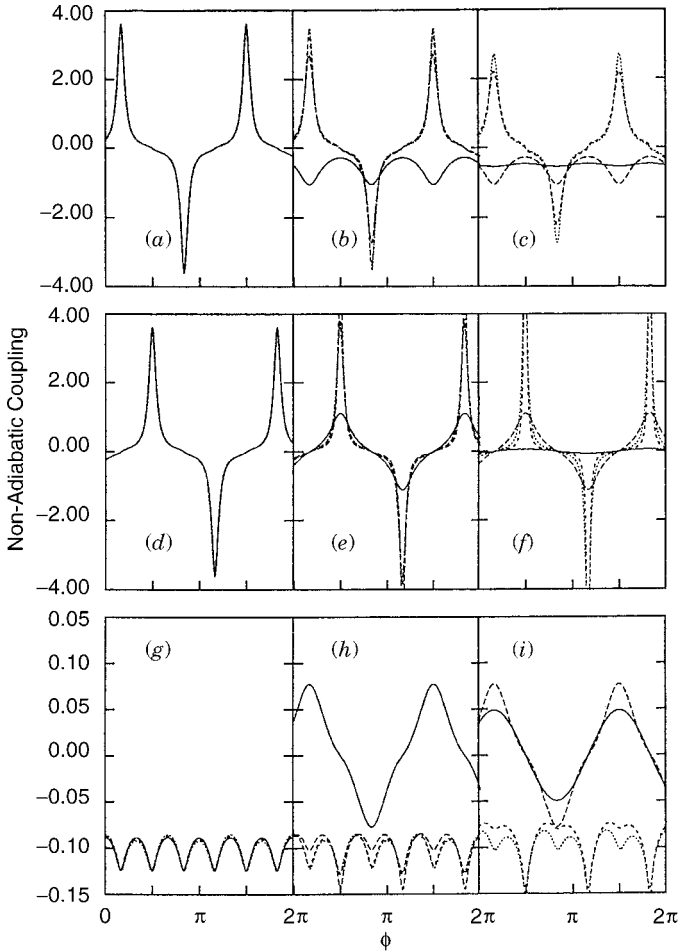
Figure 20. The three non-adiabatic coupling terms (obtained for the model potential described in Appendix E, see also Section V.B) $\tau_{12\varphi}(\varphi), \tau_{23\varphi}(\varphi), \tau_{13\varphi}(\varphi)$ as a function φ calculated for different values of ρ and $\Delta\varepsilon$: (a) $\tau = \tau_{12}$, $\Delta\varepsilon = 0.0$; (b) $\tau = \tau_{12}$, $\Delta\varepsilon = 0.05$; (c) $\tau = \tau_{12}$, $\Delta\varepsilon = 0.5$; (d) $\tau = \tau_{23}$, $\Delta\varepsilon = 0.0$; (e) $\tau = \tau_{23}$, $\Delta\varepsilon = 0.05$; (f) $\tau = \tau_{23}$, $\Delta\varepsilon = 0.5$; (g) $\tau = \tau_{13}$, $\Delta\varepsilon = 0.0$; (h) $\tau = \tau_{13}$, $\Delta\varepsilon = 0.05$; (i) $\tau = \tau_{13}$, $\Delta\varepsilon = 0.5$. ———— $\rho = 0.01$; – – – – – – $\rho = 0.1$; - - - - - - - $\rho = 0.5$; .... $\rho = 1.0$.

the unit matrix but it keeps the features it encountered for $\Delta\varepsilon \neq 0$. In other words, the transition from the $\Delta\varepsilon \neq 0$ situation to the $\Delta\varepsilon = 0$ situation is continuous as was discussed in Section X. However, the present $\Delta\varepsilon = 0$ **D** matrix is in contradiction with the **D** matrix in Section V.A.2, which was derived for a particular type of a 3×3 τ matrix that also refers to a trifold degeneracy at

a single point. In this case, as we may recall, it was proved that it has to be a unit matrix if it is expected to yield single-valued diabatic potentials. These two examples support the finding of Section X where we distinguished between breakable and unbreakable multidegeneracy. The Cocchini et al. [135] model belongs, of course, to those models that yield the breakable degeneracy.

APPENDIX F: THE TREATMENT OF A CONICAL INTERSECTION REMOVED FROM THE ORIGIN OF COORDINATES

We start by writing the curl equation in Eq. (157) for a vector $\mathbf{t}(x, y)$ in Cartesian coordinates.

$$\frac{\partial t_x}{\partial y} - \frac{\partial t_y}{\partial x} = 0 \tag{F.1}$$

The solution to Eq. (F.1)

$$\mathbf{t}(x, y) = f\left(\frac{y}{x}\right) \frac{-y\mathbf{i_x} + x\mathbf{i_y}}{x^2 + y^2} \tag{F.2}$$

where $\mathbf{i_x}$ and $\mathbf{i_y}$ are unit vectors along the x and the y axes, respectively. To shift this solution from the origin to some given point (x_{j0}, y_{j0}) the variable x is replaced by $(x - x_{j0})$ and the variable y by $(y - y_{j0})$ so that the solution of Eq. (F.1) is given in the form

$$\mathbf{t}(x, y) = f\left(\frac{y - y_{j0}}{x - x_{j0}}\right) \frac{-(y - y_{j0})\mathbf{i_x} + (x - x_{j0})\mathbf{i_y}}{(x - x_{j0})^2 + (y - y_{j0})^2} \tag{F.3}$$

Next, we are interested in expressing this equation in terms of polar coordinates (q, θ). For this purpose, we recall the following relations:

$$x = q \cos \theta \qquad y = q \sin \theta \tag{F.4}$$

and introduce the following definitions:

$$x - x_{j0} = q_j \cos \theta_j \qquad y - y_{j0} = q_j \sin \theta_j \tag{F.5}$$

Since we are interested in the polar components of $\mathbf{t}(q, \theta)$, that is, t_q and t_θ, we need to know their relation with t_x and t_y as well, which was derived sometime

ago [84].

$$t_q = \left\langle \chi_1 \left| \frac{\partial}{\partial q} \chi_2 \right. \right\rangle = \cos\theta t_x + \sin\theta t_y$$

$$t_\theta = \left\langle \chi_1 \left| \frac{\partial}{\partial \theta} \chi_2 \right. \right\rangle = q(-\sin\theta t_x + \cos\theta t_y) \tag{F.6}$$

where χ_1 and χ_2 are the two lowest electronic adiabatic wave functions. By employing Eqs. (F.3), (F.5), and (F.6), we finally get

$$t_q(q,\theta) = -f(\theta_j)\frac{1}{q_j}\sin(\theta - \theta_j)$$

$$t_\theta(q,\theta) = \frac{q}{q_j}f(\theta_j)\cos(\theta - \theta_j) \tag{F.7}$$

Equations (F.7) are the equations employed in the text [see Eqs. (164)].

Acknowledgments

References

1. M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)* **84**, 457 (1927).

2. M. Born and K. Huang, *Dynamical theory of Crystal Lattices*, Oxford University Press, New York, 1954.

3. R. K. Preston and J. C. Tully, *J. Chem. Phys.* **54**, 4297 (1971).

4. A. Kuppermann and R. Abrol (Chapter 5 in this volume).

5. R. Krishnan, M. Frisch, J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980).

6. MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

7. M. Baer and A. Alijah, *Chem. Phys. Lett.* **319**, 489 (2000).

8. M. Baer,*Chem. Phys.* **259**, 123 (2000).

9. M. Baer,*Chem. Phys. Lett.* **329**, 450 (2000).

10. M. Baer, *J. Chem. Phys. Chem. A* **105**, 2198 (2001).

11. Z. R. Xu, M. Baer, and A. J. C. Varandas, *J. Chem. Phys.* **112**, 2746 (2000).

12. A. Mebel, A. Yahalom, R. Englman, and M. Baer, *J. Chem. Phys.* **115**, 3673 (2001).

13. M. Baer, *Phys. Reps.* **358**, 75 (2002).

14. H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, *Proc. R. Soc. London, Ser. A* **244**, 1 (1958).

15. H. C. Longuet-Higgins, *Adv. Spectrosc.* **2**, 429 (1961).

16. G. Herzberg and H. C. Longuet-Higgins, *Discuss. Faraday Soc.* **35**, 77 (1963).

17. H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A* **344**, 147 (1975).

18. H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A* **161**, 220 (1937).

19. E. Teller, *J. Phys. Chem.* **41**, 109 (1937).

20. E. Teller, *Isr. J. Chem.* **7**, 227 (1969).

21. R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, John Wiley & Sons, Inc., Interscience, New York, 1972; I. B. Bersucker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer Verlag, 1989.

22. J. W. Zwanziger and E.R. Grant, *J. Chem. Phys.* **87**, 2954 (1987).

23. R. Baer, D. Charutz, R. Kosloff, and M. Baer, *J. Chem. Phys.* **105**, 9141 (1996).

24. M. Baer, A. Yahalom, and R. Englman, *J. Chem. Phys.* **109**, 6550 (1998).

25. S. Adhikari and G. D. Billing, *J. Chem. Phys.* **111**, 40 (1999).

26. M. Baer, *J. Chem. Phys.* **107**, 10662 (1997).

27. M. Baer, R. Englman, and A. J. C Varandas, *Mol. Phys.* **97**, 1185 (1999).

28. R. Englman, A. Yahalom, and M. Baer, *Eur. Phys. J* **D8**, 1 (2000).

29. A. Kuppermann, in *Dynamics of Molecules and Chemical Reactions*, R. E. Wyatt and J. Z. H. Zhang, eds., Marcel, Dekker, New York, 1996, p. 411.

30. A. J. C. Varandas, J. Tennyson, and J. N. Murrell, *Chem. Phys. Lett.* **61**, 431 (1979).

31. W. D. Hobey and A. D. Mclachlan, *J. Chem. Phys.* **33**, 1695 (1960).

32. W. Lichten, *Phys. Rev.* **164**, 131 (1967).

33. F. T. Smith, *Phys. Rev.* **179**, 111 (1969).

34. M. Baer, *Chem. Phys. Lett.* **35**, 112 (1975).

35. M. Baer, *Chem. Phys.* **15**, 49 (1976).

36. (a) M. Baer, in *Theory of Chemical Reaction Dynamics*, M. Baer, ed., CRC, Boca Raton, FL, 1985, Vol. II, Chap. 4; (b) M. Baer, *Adv. Chem. Phys.* **49**, 191 (1982) (see Chap. VI).

37. H. Köppel, W. Domcke, and L. S. Cederbaum, *Adv. Chem. Phys.* **57**, 59 (1984).

38. T. Pacher, L. S. Cederbaum, and H. Köppel, *J. Chem. Phys.* **89**, 7367 (1988).

39. R. Meiswinkel and H. Köppel, *Chem. Phys.* **144**, 117 (1990).

40. V. Sidis, in *State-to-State Ion Molecule Reaction Dynamics*, M. Baer and C. Y. Ng, eds., Vol. II p. 73; *Adv. Chem. Phys.* **82**, 73 (1992).

41. T. Pacher, L. S. Cederbaum, and H. Köppel, *Adv. Chem. Phys.* **84**, 293 (1993).

42. W. Domcke and G. Stock, *Adv. Chem. Phys.* **100**, 1 (1997).

43. A. Thiel and H. Köppel, *J. Chem. Phys.* **110**, 9371 (1999).

44. D. A. Micha, *Adv. Chem. Phys.* **30**, 7 (1975).

45. B. Lepetit, and A. Kuppermann, *Chem. Phys. Lett.* **166**, 581 (1990); Y.-S. M. Wu, B. Lepetit, and A. Kuppermann, *Chem. Phys. Lett.* **186**, 319 (1991); Y.-S. M. Wu and A. Kuppermann, *Chem. Phys. Lett.* **201**, 178 (1993); A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett.* **205**, 577 (1993); Y.-S. M. Wu and A. Kuppermann, *Chem. Phys. Lett.* **235**, 105 (1995).

46. R. Abrol, A. Shaw, A. Kuppermann, and D. R. Yarkony, *J. Chem. Phys.* **115**, 4640 (2001); R. Abrol and A. Kuppermann, *J. Chem. Phys.* **116**, 1035 (2002).

47. A. Macias and A. Riera, *J. Chem. Phys. B* **11**, L489 (1978).

48. A. Macias and A. Riera, *Int. J. Quantum Chem.* **17**, 181 (1980).

49. H.-J. Werner and W. Meyer, *J. Chem. Phys.* **74**, 5802 (1981).

50. X. Chapuisat, A. Nauts, and D. Dehareug-Dao, *Chem. Phys. Lett.* **95**, 139 (1983).

51. D. Hehareug-Dao, X. Chapuisat, J. C. Lorquet, C. Galloy, and G. Raseev, *J. Chem. Phys.* **78**, 1246 (1983).

52. C. Petrongolo, G. Hirsch, and R. Buenker, *Mol. Phys.* **70**, 825 (1990).

53. C. Petrongolo, G. Hirsch, and R. Buenker, *Mol. Phys.* **70**, 835 (1990).

54. Z. H. Top and M. Baer, *Chem. Phys.* **25**, 1 (1977).

55. M. Baer and R. Englman, *Mol. Phys.* **75**, 293 (1992).

56. M. Baer and R. Englman, *Chem. Phys. Lett.* **265**, 105 (1997).

57. M. Baer, *Mol. Phys.* **40**, 1011 (1980).

58. C. N. Yang and R. L. Mills, *Phys. Rev.* **96**, 191 (1954).

59. L. O'Raifeartaigh, *The Dawning of Gauge Theory*, Princeton University Press, Princeton, N. J., 1997.

60. M. V. Berry, *Proc. R. Soc. London. Ser. A* **392**, 45 (1984).

61. B. Simon, *Phys. Rev. Lett.* **51**, 2167 (1983).

62. Y. Aharonov and J. Anandan, *Phys. Rev. Lett.* **58**, 1593 (1987).

63. Y. Aharonov, E. Ben-Reuven, S. Popescu, and D. Rohrlich, *Nucl. Phys. B* **350**, 818 (1991).

64. D. R. Yarkony, *J. Chem. Phys.* **105**, 10456 (1996).

65. G. Chaban, M. S. Gordon, and D. R. Yarkony, *J. Phys. Chem.* **101A**, 7953 (1997).

66. N. Matsunaga and D. R. Yarkony, *J. Chem. Phys.* **107**, 7825 (1997).

67. N. Matsunaga and D. R. Yarkony, *Mol. Phys.* **93**, 79 (1998).

68. R. G. Sadygov and D. R. Yarkony, *J. Chem. Phys.* **109**, 20 (1998).

69. D. R. Yarkony, *J. Chem. Phys.* **110**, 701 (1999).

70. R. G. Sadygov and D. R. Yarkony, *J. Chem. Phys.* **110**, 3639 (1999).

71. D. R. Yarkony, *J. Chem. Phys.* **112**, 2111 (2000).

72. A. Mebel, M. Baer, and S. H. Lin, *J. Chem. Phys.* **112**, 10703 (2000).

73. A. Mebel, M. Baer, V. M. Rozenbaum, and S. H. Lin, *Chem. Phys. Lett.* **336**, 135 (2001).

74. A. Mebel, M. Baer, and S. H. Lin, *J. Chem. Phys.* **114**, 5109 (2001).

75. M. Baer, *J. Chem. Phys.* **107**, 2694 (1997).

76. T. T. Wu and C. N. Yang, *Phys. Rev. D* **12**, 3845 (1975).

77. P. A. M. Dirac, *Proc. R. Soc., London Ser. A* **133**, 60 (1931).

78. J. D. Jackson, *Classical Electrodynamics*, 3rd ed., John Wiley & Sons, Inc., 1998, p. 275.

79. H. Feshbach, *Ann. Phys. (N.Y.)* **5**, 357 (1958).

80. M. Baer, *J. Phys. Chem. A* **104**, 3181 (2000).

81. M. Baer and R. Englman, *Chem. Phys. Lett*. **335**, 85 (2001).

82. D. Bohm, *Quantum Theory*, Dover Publications, Inc., N.Y., 1989, p. 41.

83. R. Renner, *Z. Phys*. **92**, 172 (1934).

84. Z. H. Top and M. Baer, *J. Chem. Phys*. **66**, 1363 (1977).

85. A. Alijah and M. Baer, *J. Phys. Chem. A* **104**, 389 (2000).

86. H. Goldstein, *Classical Mechanics*, Addison-Wesley Publishing Company, 1966, p.107.

87. L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, Pergamon Press, Oxford, U.K., 1965, p. 188.

88. C. Zener, *Proc. R. Soc. London Ser. A* **137**, 696 (1932).

89. L. D. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932).

90. H. Nakamura and C. Zhu, *Comments At. Mol. Phys*. **32**, 249 (1996).

91. D. Elizaga, L. F. Errea, A. Macias, L. Mendez, A. Riera, and A. Rojas, *J. Phys. B* **32**, L697 (1999).

92. A. Alijah and E. E. Nikitin, *Mol. Phys.* **96**, 1399 (1999).

93. Yu. N. Demkov, *Sov. Phys. JETP* **18**, 138 (1964).

94. M. Baer and A. J. Beswick, *Phys. Rev. A* **19**, 1559 (1979).

95. M. Baer, G. Niedner-Schatteburg, and J. P. Toennies, *J. Chem. Phys*. **91**, 4169 (1989).

96. M. Baer, C-L. Liao, R. Xu, G. D. Flesch, S. Nourbakhsh, and C. Y. Ng, *J. Chem. Phys*. **93**, 4845 (1990); M. Baer and C. Y. Ng, *J. Chem. Phys*. **93**, 7787 (1990).

97. I. Last, M. Gilibert, and M. Baer, *J. Chem. Phys*. **107**, 1451 (1997).

98. A. Bjerre and E. E. Nikitin, *Chem. Phys. Lett*. **1**, 179 (1967).

99. S. Chapman, in *State-to-State Ion Molecule Reaction Dynamics*, M. Baer and C. Y. Ng, eds., Vol. II; *Adv. Chem. Phys*. **82** (1992).

100. P. Halvick and D. G. Truhlar, *J. Chem. Phys*. **96**, 2895 (1992).

101. G. J. Tawa, S. L. Mielke, D. G. Truhlar, and D. W. Schwenke, in *Advances in Molecular Vibrations Collision Dynamics*, J. M. Bowman, ed., JAI Press, Greenwich, CT, 1993, Vol. 2B, p. 45.

102. S. L. Mielke, D. G. Truhlar, and D. W. Schwenke, *J. Phys. Chem.* **99**, 16210 (1995).

103. T. Suzuki, H. Katayanagi, S. Nanbu, and M. Aoyagi, *J. Chem. Phys*. **109**, 5778 (1998).

104. G. D. Billing, M. Baer, and A. M. Mebel, *Chem. Phys. Lett.* (in press).

105. H. Thümmel, M. Peric, S. D. Peyerimhoff, and R. J. Buenker, *Z. Phys. D: At. Mol. Clusters* **13**, 307 (1989).

106. T. Pacher, H. Koppel, and L. S. Cederbaum, *J. Chem. Phys*. **95**, 6668 (1991).

107. T. Romero, A. Aguilar, and F. X. Gadea,, *J. Chem. Phys*. **110**, 6219 (1999).

108. M. Baer, A. M. Mebel, and G. D. Billing, *J. Phys. Chem. A* (in press).

109a. E. P. Wigner, *Gruppentheorie*, FriedrichVieweg und son, Braunschweig, 1931.

109b. 109M. E. Rose, *Elementary Theory of Angular Momentum*, John Wiley & Sons, Inc., New York, 1957.

110. M. Baer, *Chem. Phys. Lett*. **347**, 149 (2001).

111. (a) R. P. Feynman, R. B Leighton, and M. Sands, *The Feynman Lectures on Physics*, Addison-Wesley Publishing Co., 1964, Vol. II, Sect. 14.1; (b) *ibid*. Sect. 14.4.

112. Y. Aharonov and D. Bohm, *Phys. Rev.* **115**, 485 (1959).

113. M. Baer, *Chem. Phys. Lett*. **349**, 84 (2001).

114. J. Avery, M. Baer, and G. D. Billing, *Mol. Phys.* **100**, 1011 (2002).

115. M. Baer, A. M. Mebel, and G. D. Billing (submitted for publication).

116. M. Baer and A. M. Mebel, *Int. J. Quant. Chem.* (in press); A. M. Mebel, G. Halasz, A. Vibok, and M. Baer (submitted for publication).

117. A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blaise, *J. Chem. Phys*. **86**, 6258 (1987).

118. S. Liu and P. Siegbahn, *J. Chem. Phys*. **68**, 2457 (1978); D. G. Truhlar and C. J. Horowitz, *J. Chem. Phys*. **68**, 2466 (1978).

119. I. Last and M. Baer, *J. Chem. Phys*. **75**, 288 (1981); ibid. **80**, 3246 (1984).

120. Y.-S. M. Wu, B. Lepetit, and A. Kuppermann, *Chem. Phys. Lett*. **186**, 319 (1991).

121. A. Kuppermann and Y.-S. M. Wu, *Chem. Phys. Lett*. **241**, 229 (1995).

122. R. C. Whitten and F. T. Smith, *J. Math. Phys*. **9**, 1103 (1968).

123. B. R. Johnson, *J. Chem. Phys*. **73**, 5051 (1980).

124. G. D. Billing and N. Markovic, *J. Chem. Phys*. **99**, 2674 (1993).

125. M. Baer, in *State Selected and State-to-Sate Ion-Molecule Reaction Dynamics: Theory*, M. Baer and C. Y. Ng, eds., Vol. II, p. 187; *Adv. Chem. Phys*. **82**, 1992.

126. R. Englman, A. Yahalom, A. M. Mebel, and M. Baer, *Int. J. Quant. Chem.* (in press).

127. M. Chajia and R. D. Levine, *Phys. Chem. Chem. Phys*. **1**, 1205 (1999).

128. T. Takayanki, Y. Kurasaki, and A. Ichihara, *J. Chem. Phys*. **112**, 2615 (2000).

129. L. C. Wang, *Chem. Phys*. **237**, 305 (1998).

130. C. Shin and S. Shin, *J. Chem. Phys*. **113**, 6528 (2000).

131. T. Takayanki and Y. Kurasaki, *J. Chem. Phys*. **113**, 7158 (2000).

132. C. A. Mead, *Chem. Phys*. **49**, 23 (1980).

133. M. Baer, S. H. Lin, A. Alijah, S. Adhikari, and G. D. Billing. *Phys. Rev. A* **62**, 032506-1 (2000).(*)

134. S. Adhikari and G. D. Billing, A. Alijah, S. H. Lin, and M. Baer, *Phys. Rev. A* **62**, 032507-1 (2000).

135. F. Cocchini, T. H. Upton, and W. J. Andreoni, *Chem. Phys*. **88**, 6068 (1988).