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# INTRODUCTION TO THE THEORY OF ELECTRONIC NON-ADIABATIC COUPLING TERMS IN MOLECULAR SYSTEMS

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# Introduction to the theory of electronic non-adiabatic coupling terms in molecular systems

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## Abstract

The Born–Oppenheimer treatment leads to the adiabatic framework where the non-adiabatic terms are the physical entities responsible for the coupling between adiabatic states. The main disadvantage of this treatment is in the fact that these coupling terms frequently become singular thus causing difficulties in solving the relevant Schroedinger equation for the motion of the nuclei that make up the molecular systems. In this review, we present the line integral approach which enables the formation of the adiabatic-to-diabatic transformation matrix that yields the friendlier diabatic framework. The review concentrates on the mathematical conditions that allow the rigorous derivation of the adiabatic-to-diabatic transformation matrix and its interesting physical properties. One of the findings of this study is that the non-adiabatic coupling terms have to be *quantized* in a certain manner in order to yield single-valued diabatic potentials. Another important feature revealed is the existence of the topological matrix, which contains all the topological features of a given molecular system related to a closed contour in configuration space. Finally, we present an approximation that results from the Born–Oppenheimer treatment which, in contrast to the original Born–Oppenheimer approximation, contains the effect of the non-adiabatic coupling terms. The various derivations are accompanied by examples which in many cases are interesting by themselves. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Electronic non-adiabatic effects are an outcome of the Born–Oppenheimer (BO) 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 (NACT), together with the potential energy surfaces (PES), which are also an outcome of the BO treatment, are the origin for the driving forces which govern the motion of the atoms in molecular systems. The NACTs couple the various adiabatic PESs just like potential coupling terms do within a diabatic framework. Indeed, they are considered as such for instance while studying charge transfer processes during atomic and molecular collisions [3].

In the late 1950s and the beginning of the 1960s Longuet-Higgins (LH) and colleagues [4–7] discovered one of the more fundamental features in molecular physics related to the BO electronic adiabatic eigenfunctions. They found that these functions, when surrounding a point of degeneracy, in configuration space (CS), may acquire a phase which leads to a flip of sign of these functions. Later this feature was explicitly demonstrated by Herzberg and Longuet-Higgins [6] for the Jahn–Teller conical intersection (CI) model [8–11] (see Appendix A). This interesting observation implies that if a molecular system possesses a CI at a point in CS, the relevant electronic eigenfunctions which are parametrically dependent on the nuclear coordinates, are multi-valued (this finding was later confirmed in a numerical calculation [12]). No hints were given to the fact that this phenomenon is connected, in some way, to the BO NACTs.

In 1960, Hobe and McLachlan [13] discussed a transformation (henceforth to be termed, as the ‘adiabatic-to-diabatic transformation’ or concisely, the ADT) to eliminate the NACTs from the BO close-coupling equations with the aim of reaching (what a few years later was termed) the diabatic framework [14] and got as far as generating the first order differential equations to determine the transformation matrix elements. In a subsequent publication, McLachlan [15] dropped the whole idea as being ‘inconsistent’ and tried other ways to achieve his goal.

In 1969, Smith [16] considered a di-atom system, eliminated the radial NACT from the BO close coupling equations and obtained the corresponding diabatic representation.

In 1975, the present author suggested deriving the ADT matrix for a tri-atom system by solving an integral equation along a two-dimensional contour [17]. This integral equation, hence to be termed the line integral, reduces, for the two-state case, to an ordinary integral along a contour, over the corresponding NACT, to calculate the ADT angle. In addition, the sufficient conditions that guarantee the existence and uniqueness of the integral equation solution (along a contour in a given region in CS) were derived. Moreover, it was shown that these conditions, later termed the ‘Curl’ conditions, are fulfilled by the system of BO eigenfunctions which span a full Hilbert space.

In 1980, the LH phase [5] was employed in order to form what can be termed as an extended BO approximation [19]. In 1982, Mead and Truhlar [20], who followed the foot steps of McLachlan [15], stated that the diabatic framework is out of reach because the ‘Curl’ condition, just mentioned, can never be fulfilled in a molecular system since the electronic manifold forms an *unbreakable* infinite Hilbert space.

In 1984, the LH phase got a tremendous boost by the exciting exposure of the novel adiabatic phase—termed the topological (Berry) phase [21]—an unavoidable feature for a system which contains fast moving parts (e.g. electrons) and which is driven by a slowly moving external

field (e.g. vibrating/rotating molecules). Berry suggested that the LH phase is a good example for the existence of such a phase in molecular systems.

In 1988, Pacher et al. [18] made the *ansatz* that one can always find a group of states which are strongly coupled to each other but only weakly coupled to states outside this group.

In 1992, Baer and Englman suggested that the topological phase related to molecular systems, as well as the LH phase, should be identified with the ADT angle as calculated for a two-state system [22]. A similar idea was expressed, independently, by Aharonov et al. [23].

In 1997, Baer and Englman [24] presented their version of the extended BO approximation expressed in terms the NACTs and following that the present author showed that, up to an additive constant, the ADT angle is identical to the LH phase [25].

In 2000, Baer and Alijah [26] showed that in order for the ADT to yield single-valued diabatic potentials, the corresponding NACT matrix cannot be arbitrary but has to be ‘quantized’ (as will be discussed later). The ‘quantized’ NACT for the two-state system yields an ADT angle, with features identical to the LH phase. In other words, demanding single-valuedness for the diabatic potentials forces the NACT to yield an ADT angle, once it is calculated along a closed contour, to be a multiple of  $\pi$  (or zero).

In 1996, the first verification of the relevance of the line integral approach for a realistic molecular system was published by Yarkony [27]. He calculated *ab initio* NACTs for the two lowest states of the  $H_3$  system and used them to obtain the corresponding ADT angle along a circle with a given radius centered at the point of the CI. The calculations were done for circles of different radii. He found that as long as the radius is smaller than 0.7 Bohr the final ADT angle is, up to third decimal place, equal to  $\pi$ . Increasing the radius led to values smaller than  $\pi$  which he interpreted as a drawback of the theory. In a more recent publication, Alijah and Baer [28] showed that these deviations from  $\pi$  are most likely due to a third electronic state interfering with the two-state system and therefore one has to apply the line integral approach for a three-state system [28].

We return now to LH findings regarding the multi-valuedness of the electronic eigenfunctions. LH proposed to correct for this ‘deficiency’ by multiplying the wave functions of the two states responsible for forming the CI by an *identical* phase factor which ensures their uniqueness without affecting the ortho-normal features of the original eigenfunctions [5]. This modification seemed to be the right thing to do, at least at that time, but two questions arise: (a) Was it really necessary to incorporate into the quantum mechanical theory of atoms and molecules an ad hoc correction of this type? (b) Is it guaranteed that such a modification will not lead, in some cases, to conflicting results? Among other things we shall try to answer these questions. At this stage we just ascertain that irrespective of what the answers will be the importance of the LH observation is in pointing out that something *may* go wrong if the whole system of the electrons and nuclei is not treated with care. This is essential in particular if, once the electronic eigenvalue problem is solved, the resulting nuclear Schroedinger equation (SE) is treated employing approximations.

As mentioned above, the starting point in this field is the Born–Oppenheimer (BO) treatment. Here, this derivation is carried out for a finite sub-Hilbert space (SHS), which is defined by making use of the NACTs. It will be shown that this particular SHS behaves for all practical purposes as a full Hilbert space [29]. Among other things it is characterized by a well-defined ADT matrix. These subjects are treated in Sections 2 and 3. The connection between the

non-adiabatic coupling matrix (NACM) and the uniqueness of the relevant diabatic potential matrix is presented in Section 4; the quantization of the NACM is discussed in Section 5 and the conditions for breaking up the complete Hilbert space into sub-Hilbert spaces (SHS) and sub-sub-Hilbert spaces (SSHS) are given in Section 6. Three subjects related to topological effects are presented in Sections 7–9, the multi-degenerate case is discussed in Section 10, the extended BO approximation is treated in Section 11 and the relation between the ADT matrix and Wigner's rotation matrix is elaborated in Section 12. Analytic and numerical examples are given in Section 13 and a summary and conclusions are presented in Section 14.

## 2. The Born–Oppenheimer treatment

### 2.1. The Born–Oppenheimer equations for a complete Hilbert space

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

$$H = T_n + H_e(e | n) , \quad (1)$$

where  $T_n$  is the nuclear kinetic energy, and  $H_e(e | n)$  the electronic Hamiltonian which also contains the nuclear Coulomb interactions and depends parametrically on the nuclei coordinates, and  $e$  and  $n$  stand for the electronic and the nuclear coordinates, respectively.

The Schroedinger equation (SE) to be considered is of the form

$$(H - E)\Psi(e, n) = 0 , \quad (2)$$

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

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

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

$$(H_e(e | n) - u_i(n))\zeta_i(e | n) = 0, \quad i = 1, \dots, N . \quad (4)$$

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

$$\sum_{i=1}^N \langle \zeta_j | T_n \psi_i(n) | \zeta_i \rangle + (u_j(n) - E)\psi_j(n) = 0, \quad j = 1, \dots, N , \quad (5)$$

where the bracket notation means integration over electronic coordinates. To continue we recall that the kinetic operator  $T_n$  can be written (in terms of mass-scaled coordinates) as

$$T_n = -\frac{1}{2m}\nabla^2, \quad (6)$$

where  $m$  is the mass of the system and  $\nabla$  is the gradient (vector) operator. Substituting Eq. (6) into Eq. (5) yields the more explicit form of the BO system of coupled equations:

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

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

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

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

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

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

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

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

where  $\Psi$  is the column vector that contains nuclear functions.

## 2.2. The Born–Oppenheimer 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 [29]:

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

In other words, the non-adiabatic coupling terms between  $P$ -states 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, i.e., of the order  $\varepsilon$  in regions of interest.

To continue we define the following two relevant Feshbach projection operators [30], namely,  $P_M$ , the projection operator for the  $P$ -space

$$P_M = \sum_{j=1}^M |\zeta_j\rangle\langle\zeta_j| \quad (11a)$$



and  $Q_M$ , the projection operator for the  $Q$ -space

$$Q_M = I - P_M . \quad (11b)$$

Having introduced these operators we are now in a position to express the  $P$ -part of the  $\tau^{(2)}$ -matrix (to be designated as  $\tau_P^{(2)}$ ) in terms of the  $P$ -part of  $\tau^{(1)}$  (to be designated as  $\tau_P^{(1)}$ ). 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, recalling Eq. (8b), we get

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

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

$$\langle \nabla \zeta_j | \nabla \zeta_i \rangle_P = \langle \nabla \zeta_j | P_M | \nabla \zeta_i \rangle = \sum_{k=1}^M \langle \nabla \zeta_j | \zeta_k \rangle \langle \zeta_k | \nabla \zeta_i \rangle \quad (13)$$

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

$$\langle \nabla \zeta_j | \nabla \zeta_i \rangle_P = (\tau_P^{(1)})_{ij}^2, \quad i, j \leq M , \quad (13')$$

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

$$\tau_P^{(2)} = (\tau_P^{(1)})^2 + \nabla \tau_P^{(1)} . \quad (14)$$

Substituting the matrix elements of Eq. (14) into Eq. (7) yields the final form of the BO equation for the  $P$ -subspace:

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

where the dot designates the scalar product,  $\Psi$  is a column matrix which contains the nuclear functions  $\{\psi_i; i=1, \dots, M\}$ ,  $u$  is a diagonal matrix which contains the adiabatic potentials and  $\tau_P$ , for reasons of convenience, replaces  $\tau_P^{(1)}$ . Eq. (15) can also be written in the form

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

which is writing the SE more compactly (a similar Hamiltonian was employed by Pacher et al. [31] within their block-diagonalized approach to obtain quasi-diabatic states).

### 3. The adiabatic-to-diabatic transformation

#### 3.1. The derivation of the adiabatic-to-diabatic transformation matrix

The aim in performing what is termed the ADT is to eliminate from Eq. (16) the somewhat problematic matrix,  $\tau_P$ . This is done by replacing, in Eq. (16), the column matrix  $\Psi$  by another column matrix  $\Phi$  where the two are related as follows:

$$\Psi = A\Phi . \quad (17)$$

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  $\xi$  is the electronic basis set that is attached to  $\Phi$  then  $\zeta$  and  $\xi$  are related to each other as

$$\xi = \zeta A^\dagger . \quad (18)$$

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

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

which can be further developed to become

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

where the  $\nabla$ 's, in the third term, do not act beyond the curled parentheses  $\{ \}$ . Now, if  $A$  (henceforth to be designated as  $A_P$  in order to remind us that it belongs to the  $P$ -sub-space) is chosen to be a solution of the following equation:

$$\nabla A_P + \tau_P A_P = 0 , \quad (19)$$

then the above (kinetic energy) expression becomes

$$\therefore = A_P \nabla^2 \Phi$$

and so Eq. (16) becomes

$$-\frac{1}{2m} A_P \nabla^2 \Phi + (u_P - E) A_P \Phi = 0 . \quad (16')$$

In Appendix B,  $A_P$  is proved to be an orthogonal matrix. Consequently, Eq. (16') becomes

$$-\frac{1}{2m} \nabla^2 \Phi + (W_P - E) \Phi = 0 , \quad (20)$$

where  $W_P$ , the diabatic potential matrix is

$$W_P = (A_P)^\dagger u_P A_P . \quad (21)$$

Eq. (20) is the diabatic Schroedinger equation.

In what follows, the  $A$ -matrix (or the  $A_P$ -matrix) will be called the ADT matrix.

### 3.2. The necessary condition for having a solution for the adiabatic-to-diabatic transformation matrix

The  $A$ -matrix has to fulfill Eq. (19). It is obvious that all features of  $A$  are dependent on the features of the  $\tau$ -matrix elements. Thus, for instance, if we want the ADT matrix to have second derivatives or more in a given region, the  $\tau$ -matrix elements have to be analytic functions in this region namely, they themselves have to have well defined derivatives. However, this is not enough to guarantee the analyticity of  $A$ . In order for it to be fully 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:

$$\frac{\partial^2}{\partial p \partial q} A = \frac{\partial^2}{\partial q \partial p} A . \quad (22)$$

We derived the conditions for that to happen on various occasions [17,32] and this derivation is repeated in Appendix B (under Section B.2). The result is the fulfillment of the following relation:

$$\frac{\partial}{\partial p} \tau_q - \frac{\partial}{\partial q} \tau_p = [\tau_q, \tau_p] \quad (23)$$

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

$$\text{Curl } \tau = [\tau \times \tau] \quad (24)$$

In what follows, Eq. (24) will be referred to as the ‘Curl’ condition. In Appendix C, it is proved, employing the integral representation, that the same condition guarantees that the  $A$ -matrix will be *single-valued* throughout this region.

The importance of the ADT 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 ADT to yield diabatic potentials with the same features. Whereas the analyticity feature is guaranteed because the ADT 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 CS, the corresponding NACT terms become singular (as is well known from the Hellman–Feynman theorem [32]) and this as is proved in Appendix C, may cause the ADT to become multi-valued. Thus we have to make sure that the relevant diabatic potentials will stay single-valued also in cases where the ADT matrix is not. All these aspects will be discussed in the next section.

Returning to the diabatic potentials as defined in Eq. (21), the condition expressed in Eq. (24) also guarantees well behaved (namely single-valued) diabatic potentials. However, it is known (as was already discussed above) that the  $\tau$ -matrix elements are not always well behaved because they may become singular, implying that in such regions Eq. (24) is not satisfied at *every point*. Such a situation still guarantees an analytic ADT matrix (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 SE is required). The next section is devoted to this problem.

#### 4. The adiabatic-to-diabatic transformation matrix and the line integral approach

Eq. (19) is the main subject of this section. From now on the index  $P$  will be omitted and it will be understood that any subject to be treated will refer to a finite SHS of dimension  $M$ .

Eq. (19) can also be written as an integral equation along a contour in the following way:

$$A(s, s_0 | \Gamma) = A(s_0 | \Gamma) - \int_{s_0}^s ds' \cdot \tau(s' | \Gamma) A(s', s_0 | \Gamma), \quad (25)$$

where  $\Gamma$  is a contour in the multi-dimensional CS, the points  $s$  and  $s_0$  are located on this contour,  $ds'$  is a differential vector along this contour and the dot is a scalar product between this differential vector and the (vectorial) NACM  $\tau$ . It is noticed that the  $\tau$ -matrix is the kernel of this equation and since, as mentioned above, some of the NACTs may be singular in CS (but not necessarily along the contour itself) it has implication on the multi-valuedness of both the  $A$ -matrix and the diabatic potentials.

##### 4.1. 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 [32,33]:

$$A(s, s_0) = \wp \exp \left( - \int_{s_0}^s ds \cdot \tau \right) A(s_0), \quad (26)$$

where the symbol  $\wp$  is introduced to indicate that this integral has to be carried out in a given order [33] (see also Ref. [31]). In other words,  $\wp$  is a path ordering operator. The solution in Eq. (26) is well defined as long as  $\tau$ , along  $\Gamma$ , is well defined. However, as mentioned earlier, the solution may not be *uniquely* defined at every point in CS. 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  $\Gamma$  defined in terms of a continuous parameter  $\lambda$  so that the starting point  $s_0$  of the contour is at  $\lambda = 0$ . Next,  $\beta$  is defined as the value attained by  $\lambda$  once the contour completes a full cycle and returns to its starting point. For instance, in case of a circle  $\lambda$  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 CS, the diabatic potential matrix  $W(\lambda)$  ( $\equiv W(s, s_0)$ ) fulfills the condition:

$$W(\lambda=0) = W(\lambda=\beta) \quad (27)$$

Following Eq. (21) this requirement implies that for every point  $s_0$ , we have

$$A^+(0)u(0)A(0) = A^+(\beta)u(\beta)A(\beta) . \quad (28)$$

Next is introduced another transformation matrix,  $B$ , defined as

$$B = A(\beta)A^+(0) \quad (29)$$

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

$$u(\beta) = Bu(0)B^+ . \quad (30)$$

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

Since the electronic eigenvalues (the adiabatic PESs) are uniquely defined at each point in CS we have:  $u(0) \equiv u(\beta)$  and therefore Eq. (30) implies the following commutation relation:

$$[B, u(0)] = 0 \quad (31)$$

or more explicitly:

$$\sum_{j=1} (B_{kj}^* B_{kj} - \delta_{kj}) u_j(0) = 0 \quad (32)$$

Eq. (32) has to hold for every arbitrary point  $s_0 (\equiv \lambda=0)$  on the path  $\Gamma$  and for an essential, arbitrary set of non-zero adiabatic eigenvalues,  $u_j(s_0)$ ;  $j=1, \dots, M$ . Due to the arbitrariness of  $s_0$  and therefore also of the  $u_j(s_0)$ 's Eq. (32) can be satisfied if and only if the  $B$ -matrix elements fulfill the relation:

$$B_{kj}^* B_{kj} = \delta_{kj}, \quad j, k \leq M \quad (33)$$

or

$$B_{jk} = \delta_{jk} \exp(i\chi_k) . \quad (34)$$

Thus  $B$  is a diagonal matrix which contains in its diagonal (complex) numbers whose norm is 1 (this derivation holds as long as the adiabatic potentials are non-degenerate along the path  $\Gamma$ ). From Eq. (29) we obtain that the  $B$ -matrix transforms the  $A$ -matrix from its initial value to its final value while tracing a closed contour:

$$A(\beta) = BA(0) . \quad (35)$$

Let us now return to Eq. (26) and define the following matrix:

$$D = \wp \exp \left( - \oint_{\Gamma} ds \cdot \tau \right) . \quad (36)$$

From Eq. (26) it is noticed that if the contour  $\Gamma$  is a closed loop (which returns to  $s_0$ ) the  $D$ -matrix transforms  $A(s_0)$  to its value  $A(s=s_0 | s_0)$  obtained, once we reached the end of the closed contour, namely:

$$A(s=s_0 | s_0) = DA(s_0) . \quad (37)$$

Now comparing Eq. (35) with Eq. (37), it is noticed that  $B$  and  $D$  are identical. This implies that all the features that were found to exist for the  $B$ -matrix also apply to the matrix  $D$  as defined in Eq. (36).

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. (36), be diagonal and has, in its diagonal, numbers of norm 1. Since we consider only real electronic eigenfunctions these numbers can be either  $(+1)$ s or  $(-1)$ s. Following Eq. (37) 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  $(-1)$ s 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 its contour  $\Gamma$  as will be explained next.

That the electronic adiabatic manifold can be multi-valued is a well known fact, going back to LH et al. [4–7]. In this section, we just proved that the same applies to the ADT matrix and for this purpose is introduced the diabatic framework. The diabatic manifold is, by definition, a manifold independent of the nuclear coordinates and therefore single-valued in CS. Such a manifold always exists for a complete Hilbert space [32] (see Appendix D). Next we assume that an *approximate* (partial) diabatic manifold like that can be found for the present SHS defined with respect to a certain (usually finite) region in CS. This approximate diabatic manifold is, by definition, single-valued. Next we consider Eq. (18), in which the electronic diabatic manifold is presented in terms of the product  $\zeta A^+$  where  $\zeta$  is the adiabatic electronic manifold. Since this product is single-valued in CS (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 correspond with the electronic eigenfunctions that flip their sign. Thus, for instance, if the third element in the  $D$ -matrix is  $(-1)$  this implies that the electronic eigenfunction that belongs to the third state has to flip sign.

It is known that multi-valued adiabatic electronic manifolds create topological effects [34]. Since the newly introduced  $D$ -matrix contains the information relevant for this manifold (the number 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  $\Gamma$  the same applies to  $K$  thus:  $K = K(\Gamma)$ .

## 4.2. The approximate adiabatic-to-diabatic transformation matrix

In the previous section, the ADT matrix as well as the diabatic potentials were derived for the relevant SHS without running into any theoretical conflicts. In other words, the conditions in Eq. (10) led to a *finite* SHS which, for all practical purposes, behaves like a full (infinite) Hilbert space. However, it is unconceivable 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 diabatic potentials as well as the ADT matrix and the ‘Curl’ relations will be affected if the conditions in Eq. (10) are replaced by more realistic ones? This subject will be treated next. We shall also briefly discuss other approaches and examine their ability to yield relevant diabatic potentials.

### 4.2.1. The quasi-diabatic framework

The quasi-diabatic framework is defined as the framework for which the conditions in Eq. (10) are replaced by the following more realistic ones [35]:

$$\tau_{ij}^{(1)} \cong O(\varepsilon) \quad \text{for } i \leq M, \quad j > M. \quad (10')$$

Thus, we still relate to the same SHS but it is now defined for  $P$ -states which are weakly coupled to  $Q$ -states. We shall prove the following lemma: If the interaction between any  $P$ -state and  $Q$ -state is measured like  $O(\varepsilon)$  the resultant  $P$ -ADT matrix elements and the diabatic potentials become perturbed to  $O(\varepsilon^2)$ . The same applies to the Curl  $\tau$  conditions in Eqs. (23) and (24) which, in this case, are fulfilled up to  $O(\varepsilon^2)$ .

**4.2.1.1. The ADT matrix and the diabatic potentials.** We prove our statement in two steps: First, we consider the special case of a (finite) 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 complete 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  $\tau$ -matrix elements, namely,  $\tau_{13}$  and  $\tau_{23}$ , are of the order of  $O(\varepsilon)$  (see Eq. (10')).

The  $3 \times 3$   $A$ -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. (22)):

$$a_{ij}(s) = a_{ij}(s_0) - \sum_{k=1}^3 \int_{s_0}^s ds \cdot \tau_{ik}(s) a_{kj}(s), \quad i = 1, 2, 3, \quad j = 1, 2. \quad (38)$$

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. (38), is

$$a_{3j}(s) = a_{3j}(s_0) - \int_{s_0}^s ds' \cdot (\tau_{31} a_{1j} + \tau_{32} a_{2j}). \quad (39)$$

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  $\tau_{i3}$  for  $i = 1, 2$ . Now, returning to Eq. (38) and substituting Eq. (39) 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  $\varepsilon$  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 get to the general case we assume  $A$  and  $\tau$  to be of the following form:

$$A = \begin{pmatrix} A^{(M)} & A^{(M,L)} \\ A^{(L,M)} & A^{(L)} \end{pmatrix} \quad (40a)$$

and

$$\tau = \begin{pmatrix} \tau^{(M)} & \tau^{(M,L)} \\ \tau^{(L,M)} & \tau^{(L)} \end{pmatrix}, \quad (40b)$$

where we recall that  $M$  is the dimension of the  $P$ -SHS. As before, the only parts of the  $A$ -matrix which are of interest to us are  $A^{(M)}$  and  $A^{(L,M)}$ . Substituting Eqs. (40) into Eq. (22) we find for  $A^{(M)}$  the following integral equation:

$$A^{(M)} = A_0^{(M)} - \int_{s_0}^s ds \cdot \tau^{(M)} A^{(M)} - \int_{s_0}^s ds \cdot \tau^{(M,L)} A^{(L,M)}, \quad (41)$$

where  $A$  stands for  $A(s)$  and  $A_0$  for  $A(s_0)$ . Our next task is to get an estimate for  $A^{(L,M)}$ . For this purpose, we substitute Eqs. (40) into Eq. (19) and consider the first order differential equation for this matrix:

$$\nabla A^{(L,M)} + \tau^{(L,M)} A^{(M)} + \tau^{(L)} A^{(L,M)} = 0 \quad (42)$$

which will be written in a slightly different form

$$\nabla A^{(L,M)} + \tau^{(L)} A^{(L,M)} = -\tau^{(L,M)} A^{(M)} \quad (42')$$

in order to show that it is an inhomogeneous equation for  $A^{(L,M)}$  (assuming the elements of  $A^{(M)}$  are known). Eq. (42') will be solved for the initial conditions where the elements of  $A^{(L,M)}$  are zero (this is the obvious choice in order for the isolated SHS to remain as such in the diabatic framework as well). For these initial conditions, the solution of Eq. (42') can be shown to be

$$A^{(L,M)} = \exp\left(-\int_{s_0}^s ds' \cdot \tau^{(L)}\right) \left\{ \int_{s_0}^s \exp\left(\int_{s_0}^{s'} ds'' \cdot \tau^{(L)}\right) ds' \cdot \tau^{(L,M)} A^{(M)} \right\}. \quad (43)$$

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  $\Gamma$  [17,33]. Eq. (43) shows that all elements of  $A^{(L,M)}$  are linear combinations of the (components of the)  $\tau^{(L,M)}$  elements which are all assumed to be of first order in  $\varepsilon$ . We also reiterate that the absolute values of all elements of  $A^{(M)}$  are limited by the value of the unity.



Returning now to Eq. (41) and replacing  $A^{(L,M)}$  by the expression in Eq. (43) we find that the line integral to solve  $A^{(M)}$  is perturbed to the second order, namely:

$$A^{(M)} = A_0^{(M)} - \int_{s_0}^s ds \cdot \tau^{(M)} A^{(M)} + O(\varepsilon^2). \quad (44)$$

This concludes our derivation regarding the ADT 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 ADT matrix, it is possible to estimate the error in calculating the *adiabatic potentials*. For this purpose we apply Eq. (21). It is seen that the error is of the second order in  $\varepsilon$  namely of  $O(\varepsilon^2)$ , just like for the ADT-matrix.

**4.2.1.2. 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 the previous section [35]. For this purpose, we consider two components of the (unperturbed)  $\tau$ -matrix, namely, the matrices  $\tau_q$  and  $\tau_p$  which are written in the following form (see Eq. (40b)):

$$\tau_x = \begin{pmatrix} \tau_x^{(M)} & \tau_x^{(M,L)} \\ \tau_x^{(L,M)} & \tau_x^{(L)} \end{pmatrix}, \quad x = q, p. \quad (45)$$

Here  $\tau_x^{(M)}$  (and eventually  $\tau_x^{(L)}$ );  $x = p, q$  are the matrices that contain the strong NACTs whereas  $\tau_x^{(M,L)}$  (and  $\tau_x^{(L,M)}$ );  $x = p, q$  are the matrices that contain the weak NACTs, all being of the order  $O(\varepsilon)$ . Employing Eqs. (23,24) and substituting Eq. (45) for  $\tau_q$  and  $\tau_p$ , it can be seen by algebraic manipulations that the following relation holds:

$$\frac{\partial \tau_p^{(M)}}{\partial q} - \frac{\partial \tau_q^{(M)}}{\partial p} = [\tau_p^{(M)}, \tau_q^{(M)}] + \{\tau_p^{(M,L)} \tau_q^{(L,M)} - \tau_q^{(M,L)} \tau_p^{(L,M)}\}. \quad (46)$$

As is noticed, all terms in the curled parentheses are of order  $\varepsilon^2$  which implies that the Curl condition becomes

$$\text{Curl } \tau^{(M)} = [\tau^{(M)} \times \tau^{(M)}] + O(\varepsilon^2) \quad (47)$$

or, in other words, the Curl condition within the SHS is fulfilled up to  $O(\varepsilon^2)$ .

Obviously, the fact that the solution of the ADT matrix is only perturbed to the 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.

#### 4.2.2. The diabatization due to other approaches

Although the procedure described so far, to reach the diabatic framework (to be termed ‘diabatization’), is, in principle, the most straightforward one still other approaches were also developed [36–45]. As is noticed, the present approach is based on the NACTs which are computationally expensive to obtain and quite often are not available. Other methods were developed to achieve approximate diabatization without explicitly referring to the NACTs.

One procedure due to Macias and Riera [36] is based on the behavior of certain operators around the avoided crossing region (it was originally suggested for diatomic molecules). The main idea is to expose a symmetric operator which some of its terms behave ‘violently’ at the vicinity of this region but following the ADT become mild. Meyer and Werner [37] while applying this approach to LiF considered the electronic dipole moment operator, Peric et al. [38,39], while studying the C<sub>2</sub>H system, suggested for this purpose the transition dipole moment operator and Petrongolo et al. [40], while studying the NH<sub>2</sub> system, considered the quadrupole moment and for NO<sub>2</sub>, one of the dipole moments. These studies were all performed for two-state systems and since the ADT matrix is expressed, in such cases, by a single angle—the ADT angle (to be discussed later)—the information available from the regular ab initio calculation suffices to determine, in this way, the ADT matrix. In all cases reported so far the calculated ADT angles exhibit a reasonable functional form. In particular, this procedure yields the value of  $\pi$  while passing directly through the avoided crossing point. This is very clearly shown in Fig. 15 of Ref. [39]. However, it has to be emphasized that these calculations were carried out for two-state systems having in the region of interest one isolated CI. Thus, additional studies are necessary to find out whether this approach can be extended to a system with several CIs.

A different approach is utilized by Pacher et al. [41], Romero et al. [42], Sidis [43], and others [44,45] which developed recipes for construction ab initio diabatic states. These methods can be efficient as long as one encounters, at most, one isolated CI in a given region in CS but have to be further developed, if several CIs are located at the region of interest.

## 5. The quantization of the non-adiabatic coupling matrix

One of the main outcomes of the analysis so far is that the topological matrix  $D$ , presented in Eq. (36), is identical to an ADT matrix calculated at the end point of a closed contour. From Eq. (36) it is noticed that  $D$  does not depend on any particular point along the contour but on the contour itself. Since the integration is carried out over the NACM,  $\tau$ , and since  $D$  has to be a diagonal matrix with numbers of norm 1 for *any* contour in CS, these two facts impose severe restrictions on the NACTs.

In the next section, we present a few analytical examples showing that the restrictions on the  $\tau$ -matrix elements are indeed quantization conditions that go back to the early days of quantum theory. Section 5.2 will be devoted to the general case.

### 5.1. 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 [46]. For this purpose we consider the following NACM  $\tau$ :

$$\tau(s) = gt(s), \quad (48)$$

where  $t(s)$  is a vector whose components are functions in CS and  $g$  is a *constant* antisymmetric matrix of dimension  $M$ . For this case, one can evaluate the ordered exponential in Eq. (36).

Thus substituting Eq. (48) into Eq. (36) yields the following solution for the  $D$ -matrix:

$$D = G \exp \left( -\omega \oint_{\Gamma} ds \cdot t(s) \right) G^{\dagger}, \quad (49)$$

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

Next we concentrate on a few special cases:

### 5.1.1. The two-state case

The  $g$ -matrix in this case is given in the form

$$g = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \quad (50a)$$

The matrix  $G$  that diagonalizes it is

$$G = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \quad (50b)$$

and the corresponding eigenvalues are  $\pm i$ . Substituting Eq. (50b) in Eq. (49) and replacing the two  $\omega$ 's by  $\pm i$  yields the following  $D$ -matrix:

$$D = \begin{pmatrix} \cos \left( \oint_{\Gamma} t(s) \cdot ds \right) & -\sin \left( \oint_{\Gamma} t(s) \cdot ds \right) \\ \sin \left( \oint_{\Gamma} t(s) \cdot ds \right) & \cos \left( \oint_{\Gamma} t(s) \cdot ds \right) \end{pmatrix}. \quad (51)$$

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

$$\oint_{\Gamma} t(s) \cdot ds = n\pi, \quad (52)$$

where  $n$  is an integer. These conditions are essentially the Bohr–Sommerfeld quantization conditions [46] (as applied to the single term of the two-state  $\tau$ -matrix).

Eq. (52) presents the condition for the extended CI case. It is noticed that if  $n$  is an odd integer, the diagonal of the  $D$ -matrix contains two  $(-1)$ s, which means that the elements of the ADT matrix flip sign while tracing the closed contour in Eq. (52) (see Eq. (37)). This case is reminiscent of what happened in the simplified Jahn–Teller model as was studied by HLH [6] in which they showed that if two eigenfunctions that belong to the two states that form a CI, trace a closed contour around that CI, both of them flip sign (see Appendix A).

If the value of  $n$ , in Eq. (52), is an even integer the diagonal of the  $D$ -matrix contains two  $(+1)$ s, which implies that in this case none of the elements of the ADT 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 [5,47]. Eq. (52) 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  $D$ -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 SHS. Moreover, this is the only case for which we can show, analytically, for a non-model system, that the restrictions on the  $D$ -matrix indeed lead to a quantization of the relevant NACT.

### 5.1.2. The three-state case

The NACM  $\tau$  will be defined in a way similar to that in the previous section (see Eq. (48)), namely, as a product between a vector-function  $t(s)$  and a constant antisymmetric matrix  $g$  written in the form

$$g = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & \eta \\ 0 & -\eta & 0 \end{pmatrix}, \quad (53)$$

where  $\eta$  is a (constant) parameter. Employing this form of  $g$  we assumed that  $g_{13}$  and  $g_{31}$  are zero. (The more general case is treated elsewhere [29].) The eigenvalues of this matrix are

$$\omega_{1,2} = \pm i\omega, \quad \omega_3 = 0, \quad \omega = \sqrt{1 + \eta^2} \quad (54)$$

and the corresponding matrix,  $G$ , that diagonalizes the matrix  $g$  is

$$G = \frac{1}{\omega\sqrt{2}} \begin{pmatrix} 1 & 1 & \eta\sqrt{2} \\ i\omega & -i\omega & 0 \\ -\eta & -\eta & \sqrt{2} \end{pmatrix}. \quad (55)$$

Employing, again, Eq. (49) we find for the  $D$ -matrix the following result:

$$D = \omega^{-2} \begin{pmatrix} \eta^2 + C & \omega S & \eta(1 - C) \\ \omega S & \omega^2 C & -\eta\omega S \\ \eta(1 - C) & \eta\omega S & 1 + \eta^2 C \end{pmatrix} \quad (56)$$

where

$$C = \cos\left(\omega \oint_{\Gamma} t(s) \cdot ds\right) \quad \text{and} \quad S = \sin\left(\omega \oint_{\Gamma} t(s) \cdot ds\right). \quad (57)$$

It is well noticed that the necessary and sufficient condition for this matrix to become diagonal is that the following condition

$$\omega \oint_{\Gamma} t(s) \cdot ds = \sqrt{1 + \eta^2} \oint_{\Gamma} t(s) \cdot ds = 2n\pi \quad (58)$$

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 previous two-state case, they, all three of them, are positive, namely (+1). In other words, the ‘quantization’ of the matrix  $\tau$  as expressed in Eq. (58) leads to a  $D$ -matrix that is a unit matrix and therefore will maintain the ADT 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 next section, it is not the typical result. Still it is an interesting result and we shall return to it in Sections 10 and 12.

### 5.1.3. The four-state case

The  $g$ -matrix in this case will be written in the form

$$g = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & \eta & 0 \\ 0 & -\eta & 0 & \sigma \\ 0 & 0 & -\sigma & 0 \end{pmatrix}, \quad (59)$$

where  $\eta$  and  $\sigma$  are the two parameters. The matrix  $G$  that diagonalizes  $g$  is

$$G = \frac{1}{\sqrt{2}} \begin{pmatrix} i\lambda_q & i\lambda_q & -i\lambda_p & -i\lambda_p \\ p\lambda_q & -p\lambda_q & -q\lambda_p & q\lambda_p \\ i\lambda_p & i\lambda_p & i\lambda_q & i\lambda_q \\ q\lambda_p & -q\lambda_p & p\lambda_q & -p\lambda_q \end{pmatrix}, \quad (60)$$

where  $p$  and  $q$  are defined as

$$\begin{aligned} p &= \frac{1}{\sqrt{2}}(\varpi^2 + \sqrt{\varpi^4 - 4\sigma^2})^{1/2}, \\ q &= \frac{1}{\sqrt{2}}(\varpi^2 - \sqrt{\varpi^4 - 4\sigma^2})^{1/2} \end{aligned} \quad (61)$$

and  $\lambda_p$  and  $\lambda_q$  are defined as

$$\lambda_p = \sqrt{\frac{p^2 - 1}{p^2 - q^2}}, \quad \lambda_q = \sqrt{\frac{1 - q^2}{p^2 - q^2}} \quad (62a)$$

and  $\varpi$  as

$$\varpi = \sqrt{1 + \eta^2 + \sigma^2}. \quad (62b)$$

From Eq. (61) it is obvious that  $p > q$ . The four eigenvalues are:

$$(\omega_1, \omega_2, \omega_3, \omega_4) \equiv (ip, -ip, iq, -iq). \quad (63)$$

Again employing Eq. (49) we find for the  $D$ -matrix elements, the following expressions:

$$\begin{aligned}
 D_{11}(\alpha) &= \lambda_q^2 C_p + \lambda_p^2 C_q, & D_{12}(\alpha) &= p\lambda_q^2 S_p + q\lambda_p^2 S_q, \\
 D_{13}(\alpha) &= \lambda_p \lambda_q (-C_p + C_q), & D_{14}(\alpha) &= \lambda_p \lambda_q (-qS_p + pS_q), \\
 D_{22}(\alpha) &= p^2 \lambda_q^2 C_p + q^2 \lambda_p^2 C_q, & D_{23}(\alpha) &= \lambda_p \lambda_q (pS_p - qS_q), \\
 D_{24}(\alpha) &= pq \lambda_p \lambda_q (C_p - C_q), & D_{33}(\alpha) &= \lambda_p^2 C_p + \lambda_q^2 C_q, \\
 D_{34}(\alpha) &= -(q\lambda_p^2 S_p + p\lambda_q^2 S_q), & D_{44}(\alpha) &= q^2 \lambda_p^2 C_p + p^2 \lambda_q^2 C_q, \\
 D_{21}(\alpha) &= -D_{12}(\alpha), \quad D_{31}(\alpha) = D_{13}(\alpha), \quad D_{32}(\alpha) = -D_{23}(\alpha), \\
 D_{41}(\alpha) &= -D_{14}(\alpha), \quad D_{42}(\alpha) = D_{24}(\alpha), \quad D_{43}(\alpha) = -D_{34}(\alpha),
 \end{aligned} \tag{64}$$

where

$$C_p = \cos(p\alpha) \quad \text{and} \quad S_p = \sin(p\alpha) \tag{65}$$

and similar expressions for  $C_q$  and  $S_q$ . Here  $\alpha$  stands for

$$\alpha = \oint_{\Gamma} f(s') \cdot ds'. \tag{66}$$

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

$$p\alpha = p \oint_{\Gamma} f(s') \cdot ds' = 2\pi n, \tag{67a}$$

$$q\alpha = q \oint_{\Gamma} f(s') \cdot ds' = 2\pi \ell, \tag{67b}$$

where  $n(>1)$  and  $\ell$  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  $\ell$  are the integers and the case where both are half-integers is as follows: Examining the expressions in Eq. (64), it is noticed that in the first case all diagonal elements of  $D$  are (+1), so that,  $D$  is, in fact, the unit matrix and therefore the elements of the ADT matrix are single-valued in CS. In the second case, we get from Eq. (64), that all four diagonal elements are (−1). In this case, when the ADT traces a closed contour all its elements flip sign.

Since  $p$  and  $q$  are directly related to the NACTs  $\eta$  and  $\sigma$  (see Eqs. (61) and (62)), the two conditions in Eqs. (67) imply, again, ‘quantization’ conditions for the values of the  $\tau$ -matrix elements, namely for  $\eta$  and  $\sigma$ , as well as for the vectorial function  $f(s)$ . 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  $\ell$ , to be termed the secondary quantum number. This case is reminiscent of the two quantum numbers that characterize the hydrogen atom.

#### 5.1.4. Comments concerning extensions

In the last three sub-sections, we treated one particular group of  $\tau$ -matrices as presented in Eq. (48) where  $g$  is an antisymmetric matrix with constant elements. The general theory demands that the matrix  $D$  as presented in Eq. (49) be diagonal and that as such it contains  $(+1)$ s and  $(-1)$ s in its diagonal. In the three examples that were worked out, we found that for this particular class of  $\tau$ -matrices the corresponding  $D$ -matrices contained either  $(+1)$ s or  $(-1)$ s but never a mixture of the two types. In other words, the  $D$ -matrix can be represented in the following way:

$$D = (-1)^n I, \quad (68)$$

where  $n$  is either even or odd and  $I$  the unit matrix. Indeed, for the two-state case,  $n$  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:

(a) In case the dimension of the  $\tau$ -matrix is an odd number, the  $D$ -matrix will always be the unit matrix  $I$ , namely  $n$  must be an even number. This is so because an odd dimensional  $g$ -matrix, always has zero as an eigenvalue and this eigenvalue produces the  $(+1)$  in the  $D$ -matrix which ‘dictates’ the value of  $n$  in Eq. (68).

(b) In case the dimension of the  $\tau$ -matrix is an even number the  $D$ -matrix will (always) be equal either to  $I$  or to  $(-I)$ .

(c) These two facts lead to the conclusions that in case of an odd dimension the ‘quantization’ is characterized by (a series of) integers only but in case of an even dimension it is characterized either by (a series of) integers or by (a series of) half-integers.

#### 5.2. The treatment of the general case

The derivation of the  $D$ -matrix for the general case is based on first deriving the ADT matrix,  $A$ , as a function of  $\lambda$  and then obtaining its value at the end of the arbitrary closed contours (when  $\lambda$  becomes  $\beta$ ). Since  $A$  is a real unitary matrix, it can be expressed in terms of cosine and sine functions of given angles [32,48,49]. We shall, first, briefly consider the two special cases with  $M=2$  and 3.

The case of  $M=2$  was treated by us in the previous section. Here this treatment is repeated with the aim of emphasizing different aspects and also for reasons of completeness. The matrix  $A^{(2)}$  takes the form

$$A^{(2)} = \begin{pmatrix} \cos \gamma_{12} & \sin \gamma_{12} \\ -\sin \gamma_{12} & \cos \gamma_{12} \end{pmatrix}, \quad (69)$$

where  $\gamma_{12}$ , the ADT angle, can be shown to be [17]

$$\gamma_{12} = \int_{s_0}^s \tau_{12}(s') \cdot ds'. \quad (70)$$

Designating  $\alpha_{12}$  as the value of  $\gamma_{12}$  for a closed contour, namely:

$$\alpha_{12} = \oint_{\Gamma} \tau_{12}(s') \cdot ds', \quad (71)$$

the corresponding  $D^{(2)}$  matrix becomes accordingly (see also Eq. (51)):

$$D^{(2)} = \begin{pmatrix} \cos \alpha_{12} & \sin \alpha_{12} \\ -\sin \alpha_{12} & \cos \alpha_{12} \end{pmatrix}. \quad (72)$$

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

$$D^{(2)} = (-1)^n I, \quad (73)$$

where  $I$  is the unit matrix and  $n$  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,  $\gamma_{12}$ ,  $\gamma_{13}$ , and  $\gamma_{23}$  [32,48]. This case was recently studied by us in detail [28] and here we briefly repeat the main points.

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

$$Q_{13}^{(3)}(\gamma_{13}) = \begin{pmatrix} \cos \gamma_{13} & 0 & \sin \gamma_{13} \\ 0 & 1 & 0 \\ -\sin \gamma_{13} & 0 & \cos \gamma_{13} \end{pmatrix} \quad (74)$$

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

$$A^{(3)} = Q_{12}^{(3)} Q_{23}^{(3)} Q_{13}^{(3)} \quad (75)$$

or, following the multiplication, the more explicit form

$$A^{(3)} = \begin{pmatrix} c_{12}c_{13} - s_{12}s_{23}s_{13} & s_{12}s_{23} & c_{12}s_{13} + c_{12}s_{23}c_{13} \\ -s_{12}c_{13} - c_{12}s_{23}s_{13} & c_{12}c_{23} & -s_{12}s_{13} + c_{12}s_{23}c_{13} \\ -c_{23}s_{13} & -s_{23} & c_{23}c_{13} \end{pmatrix}. \quad (76)$$

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) [28,48]:

$$\begin{aligned} \nabla \gamma_{12} &= -\tau_{12} - \tan \gamma_{23}(-\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12}), \\ \nabla \gamma_{23} &= -(\tau_{23} - \cos \gamma_{12} + \tau_{13} \sin \gamma_{12}), \\ \nabla \gamma_{13} &= -(\cos \gamma_{23})^{-1}(-\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12}). \end{aligned} \quad (77)$$

These equations were integrated as a function of  $\varphi$  (where  $0 \leq \varphi \leq 2\pi$ ), for a *model* potential [28] along a circular contour of radius  $\rho$  (for details see Section 13.2). The  $\varphi$ -dependent  $\gamma$  angles, i.e.,  $\gamma_{ij}(\varphi|\rho)$ , for various values of  $\rho$  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 Fig. 1. Thus for each  $\varphi$  we get, employing Eq. (76), the  $A^{(3)}(\varphi)$ -matrix elements. The relevant  $D^{(3)}$ -matrix is obtained from  $A^{(3)}$  by substituting  $\varphi=2\pi$ . If  $\alpha_{ij}$  are defined as

$$\alpha_{ij} = \gamma_{ij}(\varphi=2\pi), \quad (78)$$



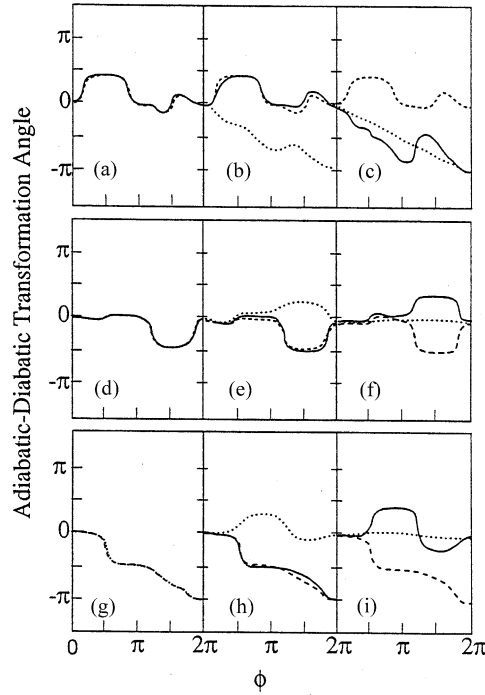


Fig. 1. The three adiabatic–diabatic-transformation angles (obtained by solving Eqs. (77) for a  $3 \times 3$  diabatic model potential presented in Section 13.2)  $\gamma_{12}(\phi), \gamma_{23}(\phi), \gamma_{13}(\phi)$  as calculated for different values of  $\rho$  and  $\Delta\epsilon$ : (a)  $\gamma = \gamma_{12}$ ,  $\Delta\epsilon = 0.0$ ; (b)  $\gamma = \gamma_{12}$ ,  $\Delta\epsilon = 0.05$ ; (c)  $\gamma = \gamma_{12}$ ,  $\Delta\epsilon = 0.25$ ; (d)  $\gamma = \gamma_{23}$ ,  $\Delta\epsilon = 0.0$ ; (e)  $\gamma = \gamma_{23}$ ,  $\Delta\epsilon = 0.05$ ; (f)  $\gamma = \gamma_{23}$ ,  $\Delta\epsilon = 0.25$ ; (g)  $\gamma = \gamma_{13}$ ,  $\Delta\epsilon = 0.0$ ; (h)  $\gamma = \gamma_{13}$ ,  $\Delta\epsilon = 0.05$ ; (i)  $\gamma = \gamma_{13}$ ,  $\Delta\epsilon = 0.25$ . (—)  $\rho = 0.01$ ; (---)  $\rho = 0.1$ ; (-----)  $\rho = 0.5$ .

then, as is noticed from Fig. 1, the values of  $\alpha_{ij}$  are either zero or  $\pi$ . A simple analysis of Eq. (76), for these values of  $\alpha_{ij}$ , shows that  $D^{(3)}$  is a diagonal matrix with two  $(-1)$ s and one  $(+1)$  in the diagonal.

This result will now be generalized for an arbitrary  $D^{(3)}$ -matrix in the following way: Since a general  $A^{(3)}$ -matrix can always be written as in Eq. (76) the corresponding  $D^{(3)}$ -matrix will become diagonal if and only if:

$$\alpha_{ij} = \gamma_{ij}(\phi = 2\pi) = n_{ij}\pi \quad (79)$$

the diagonal terms can, explicitly, be represented as

$$D_{ij}^{(3)} = \delta_{ij} \cos \alpha_{jn} \cos \alpha_{jm}, \quad j \neq n \neq m; \quad j = 1, 2, 3. \quad (80)$$

This expression shows that the  $D^{(3)}$ -matrix, in the most general case, can have either three  $(+1)$ s in the diagonal or two  $(-1)$ s and one  $(+1)$ . In the first case, the contour does not surround any CI whereas in the second case, it surrounds either one or two CIs (a more general discussion regarding this ‘geometrical’ aspect will be given in Section 9).

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 5.1.2. The reason is that the ‘general (physical) case’ applies to an (arbitrary) aggregation of CIs

whereas the previous case applies to a special (probably unphysical) situation. In Section 10, the discussion on this subject is extended. In what follows, the cases for an aggregation of CIs will be termed the ‘breakable’ situations (the reason for choosing this name will be given later) in contrast to the type of models which were discussed in Sections 5.1.2 and 5.1.3 and which 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 which are routinely used to present three-dimensional orthogonal matrices [50]. In fact, we could apply the Euler angles for this purpose and get identical results for  $A^{(3)}$  (and for  $D^{(3)}$ ). The main reason we prefer the ‘democratic’ choice of the angles is that this set of angles can be extended to an arbitrary dimension without any difficulty as will be done next.

The  $M$ -dimensional ADT matrix  $A^{(M)}$  will be written as a product of elementary rotation matrices similar to that given in Eq. (75) [32]:

$$A^{(M)} = \prod_{i=1}^{M-1} \prod_{j>i}^M Q_{ij}^{(M)}(\gamma_{ij}), \quad (81)$$

where  $Q_{ij}^{(M)}(\gamma_{ij})$  (like in Eq. (74)) 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. (81) 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  $\gamma_{ij}$ -angles which are needed to describe an  $M \times M$  unitary matrix (we recall that the missing  $M(M+1)/2$  conditions follow from the orthonormality conditions). The matrix  $A^{(M)}$  as presented in Eq. (81) is characterized by two important features: (a) Every *diagonal* element contains at least one term which is a product of cosine functions only. (b) 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  $\gamma_{ij}$ -angles to ensure that the topological matrix,  $D^{(M)}$ , is diagonal as discussed in Section 4.1.

To obtain the  $\gamma_{ij}$ -angles, one usually has to solve the relevant first order differential equations of the type given in Eq. (77). Next, like before, the  $\alpha_{ij}$ -angles are defined as the  $\gamma_{ij}$ -angles at the end of a closed contour. In order to obtain the matrix  $D^{(M)}$  one has to replace, in Eq. (81), the angles  $\gamma_{ij}$  by the corresponding  $\alpha_{ij}$ -angles. Since  $D^{(M)}$  has to be a *diagonal* matrix with  $(+1)$ s and  $(-1)$ s in the diagonal this can be achieved if and only if *all*  $\alpha_{ij}$ -angles are zero or multiples of  $\pi$ . It is straightforward to show that with this structure the elements of  $D^{(M)}$  become

$$D_{ij}^{(M)} = \delta_{ij} \prod_{k \neq i}^M \cos \alpha_{ik} = \delta_{ij} (-1)^{\sum_{k \neq i}^M n_{ik}}, \quad i = 1, \dots, M, \quad (82)$$

where  $n_{ik}$  are integers which fulfill  $n_{ik} = n_{ki}$ . From Eq. (82), it is noticed that along the diagonal of  $D^{(M)}$  we may encounter  $K$  numbers which are equal to  $(-1)$  and the rest which are equal to  $(+1)$ . It is important to emphasize that in case a contour does not surround any CI the value of  $K$  is 0.

## 6. The construction of sub-Hilbert spaces and sub-sub-Hilbert spaces

In Section 2.2, it was shown that the condition in Eq. (10) or its relaxed form in Eq. (10') (in Section 4) enables the construction of SHS. Based on this possibility we consider a prescription first for constructing the SHS which extends to the full CS and then, as a second step, constructing the sub-SHS that extends only to (a finite) portion of CS.

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  $\Delta E(R=R_0) = E_2(R=R_0) - E_1(R=R_0) \equiv 0$ , and a situation where the two electronic curves interact so that  $\Delta E(R) \sim \text{Const.} (> 0)$ . The first case is usually treated by the Landau–Zener (LZ) formula [52–56] and the second is based on the Demkov-approach [57]. It is well known that whereas the LZ-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 LZ situation is the one that becomes the Jahn–Teller conical intersection (CI) in two dimensions [5–11]. We shall also include the Renner–Teller parabolic intersection (PI) [5,58,61], although it is characterized by two interacting potential energy surfaces which behave quadratically (and not linearly as in the LZ case) in the vicinity of the above mentioned degeneracy point.

### 6.1. The construction of sub-Hilbert spaces

Following Section 2.2 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 CI or a PI (it is important to mention that only consecutive states can form CI/PIs). The two types of intersections are characterized by the fact that the non-adiabatic 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 a complete Hilbert space of size  $N$  into  $L$  SHSs of varying sizes  $N_P$ ,  $P=1, \dots, L$ , where

$$N = \sum_{P=1}^L N_P \quad (83)$$

with  $L$  being finite or infinite.

Before we continue with the construction of the SHSs we would like to make the following comment: Usually, when two given states form CI/PIs, one thinks of isolated points in CS. In fact, CI/PI points are not isolated points but form (finite or infinite) seams which ‘cut’ through the molecular CS. However, since our studies are carried out for planes, these planes, usually, contain isolated CI/PI points only.

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

$$\tau_{ij}^{(P)} = \left\langle \zeta_i^{(P)} \left| \nabla \zeta_j^{(P)} \right. \right\rangle, \quad i \cdot j = 1, \dots, N_P \quad (84)$$

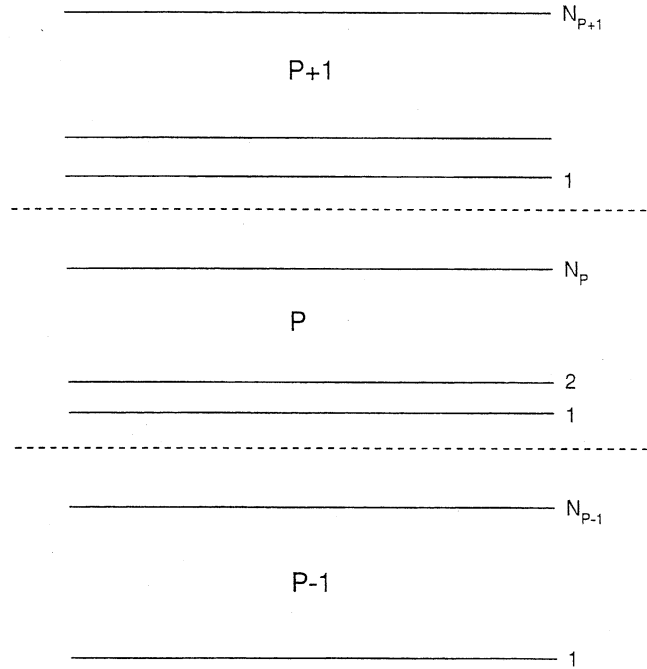


Fig. 2. A schematic picture describing the three consecutive sub-Hilbert spaces, namely, the  $(P-1)$ th, the  $P$ th and the  $(P+1)$ th. The dotted lines are separation lines.

and (b) Inter non-adiabatic coupling terms  $\tau_{ij}^{(P,Q)}$  which are formed between two eigenfunctions, the first belonging to the  $P$ th SHS and the second to the  $Q$ th SHS:

$$\tau_{ij}^{(P,Q)} = \left\langle \zeta_i^{(P)} \left| \nabla \zeta_j^{(Q)} \right. \right\rangle, \quad i = 1, \dots, N_P, \quad j = 1, \dots, N_Q. \quad (85)$$

The  $P$ th SHS is defined through the following two requirements:

- (1) All  $N_P$  states belonging to the  $P$ th SHS interact strongly with each other in the sense that each pair of *consecutive* states have at least one point where they form an LZ-type interaction. In other words, all  $\tau_{jj+1}^{(P)}$ ,  $j = 1, \dots, N_P - 1$  form, at least at one point in CS, a CI/PI.
- (2) The range of the  $P$ th SHS, is defined in such a way that the lowest (or the first) state and the highest (the  $N_P$ th) state which belong to this SHS form Demkov-type interactions with the highest state belonging to the lower  $(P-1)$ th SHS and with the lowest state belonging to the upper  $(P+1)$ th SHS, respectively (see Fig. 2). In other words, the two non-adiabatic coupling terms fulfill the conditions (see Eq. (10') in Section (4.2)):

$$\tau_{N_P-1,1}^{(P-1,P)} \sim O(\varepsilon) \quad \text{and} \quad \tau_{N_P,1}^{(P,P+1)} \sim O(\varepsilon). \quad (86)$$

At this point we make two comments: (a) Conditions (1) and (2) lead to a well defined SHS which 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 SHS are adiabatic

states strong interactions of the LZ-type can occur between two consecutive states only. However Demkov-type interactions may exist between any two states.

## 6.2. The construction of sub-sub-Hilbert spaces

As we have seen the sub-Hilbert spaces are defined for the whole CS 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 which contains only part of the CI/PI points and the question is whether the effects of the other CI/PIs can be ignored?

The answer to this question can be given following a careful study of these effects employing the line integral approach as presented in terms of Eq. (25). For this purpose we analyze what happens along a certain line  $\Gamma$  which surrounds one CI or more. To continue we employ the same procedure as discussed in Section 4.2: We break up the ADT matrix and the  $\tau$ -matrix as written in Eq. (40) and then continue like in Eq. (41), etc. In this way we can show that if, along the particular line  $\Gamma$ , the ‘non-interesting’ parts of the  $\tau$ -matrix are of order  $\varepsilon$  the error expected for the interesting part in the ADT matrix is of order  $O(\varepsilon^2)$ . If this happens for any contour in this region then we can just ignore the affects of CI which are outside this region and carry out the dynamic calculations with this reduced set of states.

## 7. The topological spin

Before we continue and in order to avoid confusion two matters have to be clarified: (a) We distinguished between two types of LZ situations, which form (in two dimensions) the Jahn–Teller CI and the Renner–Teller PI. The main difference between the two is that the PIs 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 SSHS, is not its dimension  $M$  but  $N_J$ , the number of CIs. (b) In general, one may encounter more than one CI between a pair of states [76,80]. However, to simplify the study, we assume one CI for a pair of states so that  $(N_J + 1)$  stands for the *number of states* that form the CIs.

So far we introduced three different integers  $M$ ,  $N_J$  and  $K$ . As mentioned earlier,  $M$  is a characteristic number of the SSHS (see Section 6.2) but is not relevant for topological effects; instead  $N_J$ , as just mentioned, is a characteristic number of the SSHS and relevant for topological effects, and  $K$ , the number of  $(-1)$ s in the diagonal of the topological matrix  $D$  (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 SSHS.

Our next task is to derive all possible  $K$ -values for a given  $N_J$ . Let us first refer to a few special cases: It was shown before that in case of  $N_J = 1$  the  $D$ -matrix contains two  $(-1)$ s in its diagonal in case the contour surrounds the CI<sup>(29)</sup> and no  $(-1)$ s when the contour does not surround the CI. Thus the allowed values of  $K$  are either 2 or zero. 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 zero (see Section 5.2). 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:

$$K = \{0, 2, \dots, K_J\}, \quad \begin{cases} K_J = N_J, & N_J = 2P, \\ K_J = (N_J + 1), & N_J = 2P + 1, \end{cases} \quad (87)$$

where  $p$  is an integer.

The proof is based on Eq. (82). Let us assume that a certain closed contour yields a set of  $\alpha_{ij}$ -angles which produce a number  $K$ . Next we consider a slightly different closed contour, along which one of these  $\alpha_{ij}$ 's, say  $\alpha_{st}$ , changed its value from zero to  $\pi$ . From Eq. (82) it can be seen that only two  $D$ -matrix elements contain  $\cos(\alpha_{st})$ , namely,  $D_{ss}$  and  $D_{tt}$ . Now if these two matrix elements were, following the first contour, positive then changing  $\alpha_{st}$  from  $0 \rightarrow \pi$  would produce two additional  $(-1)$ s, 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  $\alpha_{st}$  from  $0 \rightarrow \pi$  would not affect  $K$ . Thus, immaterial the value of  $N_J$ , the various  $K$  values *differ* from each other by even integers only. Now since any set of  $K$ 's also contains the value  $K=0$  (the case when the closed loop does not surround any CIs), this implies that  $K$  can attain only even integers. The final result is the set of values presented in Eq. (87).

The fact that there is a one-to-one relation between the  $(-1)$ s 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 4.1) 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 [51]. Here we encounter, to some extent, a similar situation: A system of items (i.e., distributions of electrons) in a given point in CS is usually described in terms of its set of eigenfunctions. This description is incomplete because the existence of CIs causes the electronic manifold to be multi-valued. For instance, in case of two (isolated) CIs we may encounter at a given point in CS four different sets of eigenfunctions (see next section):

$$(a) (\zeta_1, \zeta_2, \zeta_3), \quad (b) (-\zeta_1, -\zeta_2, \zeta_3), \quad (c) (\zeta_1, -\zeta_2, -\zeta_3), \quad (d) (-\zeta_1, \zeta_2, -\zeta_3). \quad (88)$$

In case of three CIs we have as many as eight different sets of eigenfunctions, etc. Thus, we have to refer to an additional characterization of a given SSHS. This characterization is related to the number  $N_J$  of CIs and the associated possible number of sign flips due to different contours in the relevant region of CS, traced by the electronic manifold.

In Refs. [26,29], it was shown that in a two-state system the non-adiabatic coupling term,  $\tau_{12}$ , has to be ‘quantized’ in the following way:

$$\oint_{\Gamma} \tau_{12}(s') \cdot ds' = n\pi, \quad (89)$$

where  $n$  is an integer (in order to guarantee that the  $2 \times 2$  diabatic potential be single-valued in configuration space). In case of CIs 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 SSHS  $N_J$  conical intersections are encountered, we could define the spin,  $J$ , of this SSHS as  $(N_J/2)$ . However, this definition may lead to more sign flips than we actually encounter (see next section). 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

$$J = \frac{1}{2} \frac{K_J}{2}, \quad \begin{cases} K_J = N_J, & N_c = 2p, \\ K_J = (N_J + 1), & N_J = 2p + 1 \end{cases} \quad (90a)$$

and, accordingly, the various  $M_J$ -values will be defined as

$$M_J = J - K/2 \quad \text{where} \quad K = \{0, 2, \dots, K_J\}. \quad (90b)$$

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

$$\begin{aligned} \text{For } N_J = 0: & \quad \{J = 0, M_J = 0\}, \\ \text{for } N_J = 1: & \quad \{J = 1/2, M_J = 1/2, -1/2\}, \\ \text{for } N_J = 2: & \quad \{J = 1/2, M_J = 1/2, -1/2\}, \\ \text{for } N_J = 3: & \quad \{J = 1, M_J = 1, 0, -1\}, \\ \text{for } N_J = 4: & \quad \{J = 1, M_J = 1, 0, -1\}, \\ \text{for } N_J = 5: & \quad \{J = 3/2, M_J = 3/2, 1/2, -1/2, -3/2\}, \\ \text{for } N_J = 6: & \quad \{J = 3/2, M_J = 3/2, 1/2, -1/2, -3/2\}, \\ \text{for } N_J = 7: & \quad \{J = 2, M_J = 2, 1, 0, -1, -2\}. \end{aligned} \quad (90c)$$

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

## 8. An analytical derivation for the possible sign flips in a three-state system

In the next section, we intend to present a geometrical analysis to permit us to gain 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 [60]. In this section, we intend to supply the mathematical foundation (and justification) for this analysis [59]. Thus employing the LI approach, we intend to prove the following statement:

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

To prove this we consider the three following regions (see Fig. 3): In the first region, designated  $\sigma_{12}$ , is located the main portion of the interaction,  $t_{12}$ , between states 1 and 2 with the point of the CI/PI at  $C_{12}$ . In the second region, designated as  $\sigma_{23}$ , is located the main

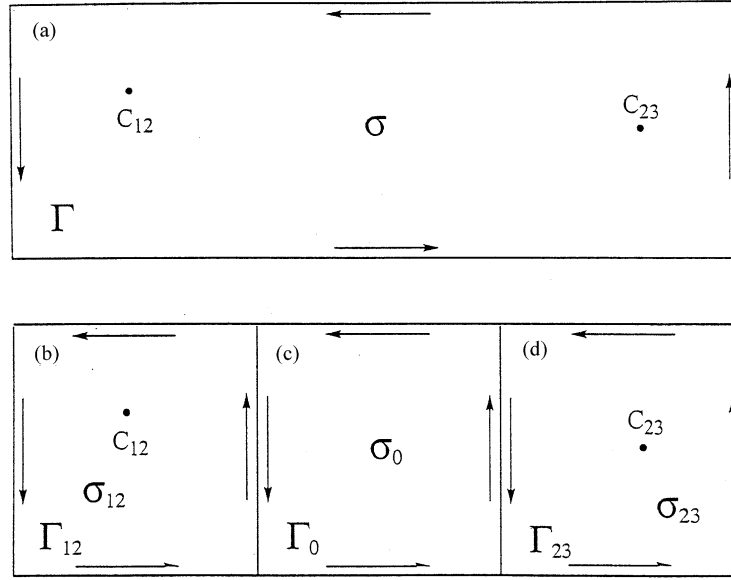


Fig. 3. The breaking up of a region  $\sigma$ , that contains two CIs (at  $C_{12}$  and  $C_{23}$ ), into three sub-regions: (a) The full region  $\sigma$  defined in terms of the closed contour  $\Gamma$ . (b) The region  $\sigma_{12}$  which contains a CI at  $C_{12}$  and is defined by the closed contour  $\Gamma_{12}$ . (c) The region  $\sigma_0$ , which is defined by the closed contour  $\Gamma_0$  and does not contain any CI. (d) The region  $\sigma_{23}$  which contains a CI at  $C_{23}$  and is defined by the closed contour  $\Gamma_{23}$ . It can be seen that  $\Gamma = \Gamma_{12} + \Gamma_0 + \Gamma_{23}$ .

portion of the interaction,  $t_{23}$ , between states 2 and 3 with the point of the CI/PI at  $C_{23}$ . In addition, we assume a third region,  $\sigma_0$ , 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  $\sigma_{12}$  and due to  $t_{12}$  in  $\sigma_{23}$  is  $\sim 0$ . This situation can always be achieved by shrinking  $\sigma_{12}$  ( $\sigma_{23}$ ) towards its corresponding center  $C_{12}$  ( $C_{23}$ ). In  $\sigma_0$  the components of both,  $t_{12}$  and  $t_{23}$ , may be of arbitrary magnitude but no CI/PI of any pair of states is allowed to be there.

To prove our statement, we consider the line integral (see Eq. (25)):

$$A = A_0 - \oint_{\Gamma} ds \cdot \tau A, \quad (91)$$

where the integration is carried out along a closed contour  $\Gamma$ ,  $A$  is the  $3 \times 3$  ADT matrix to be calculated, the dot stands for a scalar product and  $\tau$  is the matrix of  $3 \times 3$  that contains the two non-adiabatic coupling terms, namely:

$$\tau(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix}. \quad (92)$$

(It is noticed the components of  $t_{13} \sim 0$ .) This assumption is not essential for the proof, but makes it more straightforward.



The integral in Eq. (91) will now be presented as a sum of three integrals (for a detailed discussion on that subject: see Appendix C), namely:

$$A = A_0 - \oint_{\Gamma_{12}} ds \cdot \tau A - \oint_{\Gamma_0} ds \cdot \tau A - \oint_{\Gamma_{23}} ds \cdot \tau A . \quad (93)$$

Since there is no CI in the buffer zone,  $\sigma_0$ , 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  $G_{12}$  as a boundary condition and the second for  $G_{23}$ . Thus  $A$  will be calculated twice:

$$A = G_{ij} - \oint_{\Gamma_{ij}} ds \cdot \tau A . \quad (94)$$

Next, the topological matrices  $D$ ,  $D_{12}$  and  $D_{23}$  are introduced which are related to  $A$  in the following way (see Eq. (37)):

$$A = DA_0 , \quad (95a)$$

$$A = D_{12}G_{12} , \quad (95b)$$

$$A = D_{23}G_{23} . \quad (95c)$$

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

$$G_{12} = D_{23}A_0 \quad \text{and} \quad G_{23} = D_{12}A_0 . \quad (96)$$

Since the all  $D$ -matrices are diagonal the same applies to  $D_{12}$  and  $D_{23}$  so that  $D$  becomes

$$D = D_{13} = D_{12}D_{23} . \quad (97)$$

Our next task will be to obtain  $D_{12}$  and  $D_{23}$ . For this purpose, we consider the two partial  $\tau$ -matrices,  $\tau_{12}$  and  $\tau_{23}$ :

$$\tau_{12}(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \tau_{23}(s) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} , \quad (98)$$

so that

$$\tau = \tau_{12} + \tau_{23} . \quad (99)$$

We start with the first of Eq. (94), namely:

$$A = G_{12} - \oint_{\Gamma_{ij}} ds \cdot \tau_{12} A , \quad (100)$$

where  $\tau_{12}$  replaces  $\tau$  because  $\tau_{23}$  is assumed to be negligibly small in  $\sigma_{12}$ . The solution and the corresponding  $D$ -matrix, namely,  $D_{12}$  are well known (see discussion in Section 5.1.1). Thus,

$$D_{12} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (101)$$

which implies (as already explained in Section 4.1) that the first (lowest) and the second functions flip sign. In the same way, it can be shown that  $D_{23}$  is equal to

$$D_{23} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (102)$$

which shows that the second and the third (the highest) eigenfunctions flip sign. Substituting Eqs. (101) and (102) into Eq. (97) yields the following result for  $D_{13}$ :

$$D_{13} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (103)$$

In other words, surrounding the two CIs 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, indeed, be done in the next section.

## 9. The geometrical interpretation for sign flips

In Sections 5 and 7, we discussed the possible  $K$ -values of the  $D$ -matrix and made the connection to the number of sign flips based on the analysis given in Section 4.1. Here we intend to present a geometrical approach in order to gain more insight into the phenomenon of sign flips in the  $M$ -state system ( $M > 2$ ).

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

- (a) Having two consecutive states  $j$  and  $(j+1)$ , the two form the CI to be designated as  $C_j$  as shown in Fig. 5, where  $N_J$  CI are presented.
- (b) The contour that surrounds a CI at  $C_j$  will be designated as  $\Gamma_{jj+1}$  (see Fig. 5a).
- (c) A contour that surrounds two consecutive CIs, i.e.,  $C_j$  and  $C_{j+1}$  will be designated as  $\Gamma_{jj+2}$  (see Fig. 5b). In the same way, a contour that surrounds  $n$  consecutive CIs namely  $C_j, C_{j+1}, \dots, C_{j+n}$  will be designated as  $\Gamma_{jj+n}$  (see Fig. 5c for  $N_J = 3$ ).
- (d) In case of three CIs or more: a contour that surrounds  $C_j$  and  $C_k$  but not the in-between CIs will be designated as  $\Gamma_{j,k}$ . Thus, for instance,  $\Gamma_{1,3}$  surrounds  $C_1$  and  $C_3$  but not  $C_2$  (see Fig. 5d).

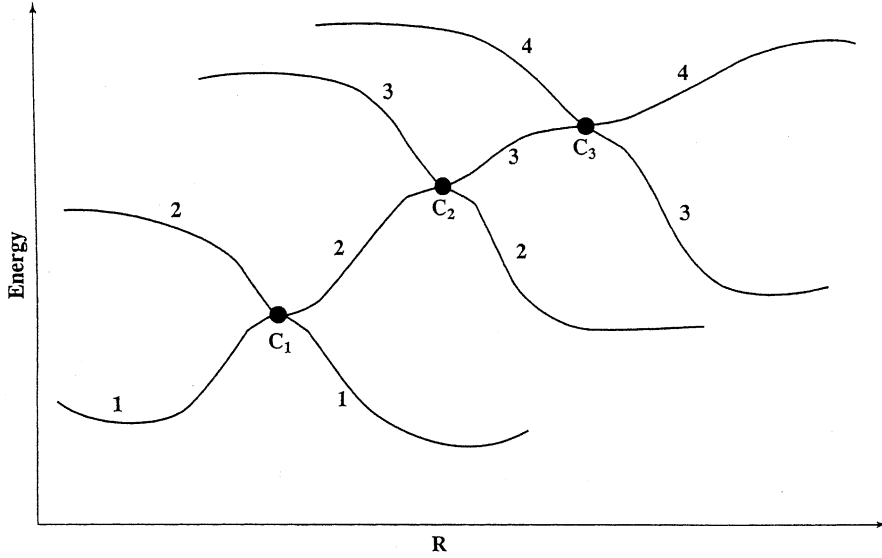


Fig. 4. Four interacting adiabatic surfaces presented in terms of four adiabatic Landau–Zener-type curves. The points  $C_j$ ;  $j=1,2,3$ , stand for the three conical intersections.

We also introduce an ‘algebra’ of closed contours based on previous section (see also Appendix C):

$$\Gamma_{jn} = \sum_{k=j}^{n-1} \Gamma_{kk+1} \quad (104)$$

and also:

$$\Gamma_{j,k} = \Gamma_{jj+1} + \Gamma_{kk+1} \quad \text{where } k > j + 1. \quad (105)$$

This algebra implies that in case of Eq. (104) the only two functions that flip sign are  $\zeta_1$  and  $\zeta_n$  because all in-between  $\zeta$ -functions get their sign flipped twice. In the same way, Eq. (105) implies that all four electronic functions mentioned in the expression, namely, the  $j$ th and the  $(j+1)$ th, the  $k$ th and the  $(k+1)$ th, all flip sign. In what follows, we give a more detailed explanation based on the mathematical analysis of Section 8.

In the last two sections, it was mentioned that  $K$  yields the number of eigenfunctions which 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, i.e.,  $\zeta_1$  and  $\zeta_2$  flip sign so that  $K=2$  and if it does not surround it, no  $\zeta$ -function flips sign and  $K=0$ . In case of  $N_J=2$ , we encounter two CIs, namely,  $C_1$  and the  $C_2$  (see Fig. 5a and b). Moving the electronic manifold along the path  $\Gamma_{12}$  will change the signs of  $\zeta_1$  and  $\zeta_2$  whereas moving it along the path  $\Gamma_{23}$  will change the signs  $\zeta_2$  and  $\zeta_3$ . Next moving the electronic manifold along the path,  $\Gamma_{13}$  (and Fig. 5b) causes the sign of  $\zeta_2$  to be flipped twice (once when surrounding  $C_1$  and once when surrounding  $C_2$ ) and

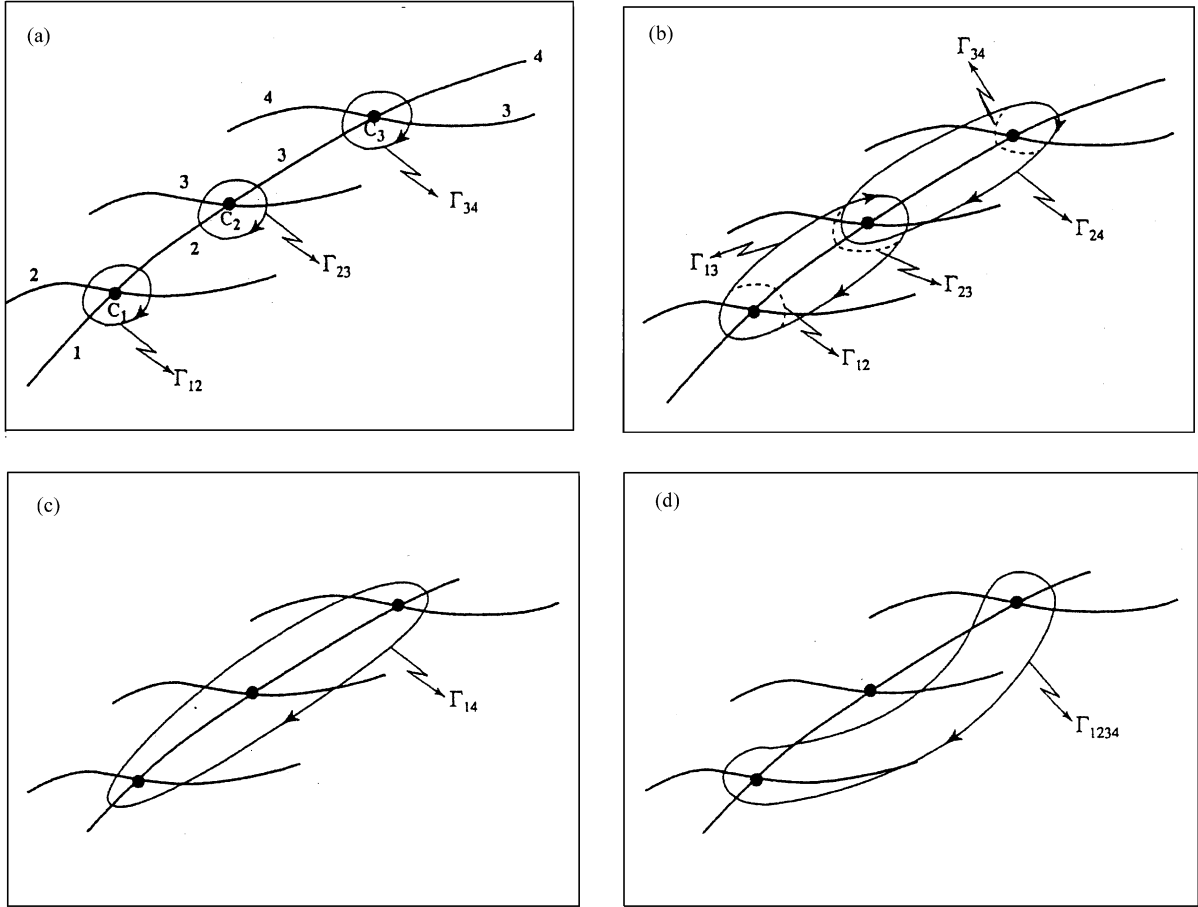


Fig. 5. The four interacting surfaces, the three points of conical intersection and the various contours leading to sign conversions: (a) The contours  $\Gamma_{jj+1}$  surrounding the respective  $C_j$ ;  $j=1,2,3$  leading to the sign conversions of the  $j$ th and the  $(j+1)$ th eigenfunctions. (b) The contours  $\Gamma_{jj+2}$  surrounding the two (respective) conical intersections namely  $C_j$  and  $C_{j+1}$ ;  $j=1,2$  leading to the sign conversions of the  $j$ th and the  $(j+2)$ th eigenfunctions but leaving unchanged the sign of the middle, the  $(j+1)$ , eigenfunction. Also shown are the contours  $\Gamma_{jj+1}$  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  $\Gamma_{14}$  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 Fig. 4b) 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, i.e.,  $(\zeta_1, \zeta_2, \zeta_3, \zeta_4) \rightarrow (-\zeta_1, -\zeta_2, -\zeta_3, -\zeta_4)$ . Based on Fig. 5(b) we have:  $\Gamma_{1,3} = \Gamma_{12} + \Gamma_{34}$ .

therefore, altogether, its sign remains unchanged. Thus in case of  $N_J=2$ , we can have either no change of sign (when the path does not surround any CI) or three cases where two different functions change sign.

A somewhat different situation is encountered in case  $N_J=3$  and therefore we shall briefly discuss it as well (see Fig. 5d). It is now obvious that contours of the type  $\Gamma_{jj+1}$ ;  $j=1,2,3$  surround the relevant  $C_j$  (see Fig. 5a) and will flip the signs of the two corresponding

eigenfunctions. From Eq. (104) we get that surrounding two consecutive CIs namely,  $C_j$  and  $C_{j+1}$ , with  $\Gamma_{jj+2}$ ;  $j=1,2$  (see Fig. 5b), will flip the signs of the two external eigenfunctions, namely,  $\zeta_j$  and  $\zeta_{j+2}$ , but leave the sign of  $\zeta_{j+1}$  unchanged. We have two such cases—the first and the second CIs and the second and the third ones. Then we have a contour  $\Gamma_{14}$  that surrounds all three CIs (see Fig. 5c) and here, like in the previous where  $N_J=2$  (see also Eq. (104), only the two external functions, namely,  $\zeta_1$  and  $\zeta_4$  flip sign but the two internal ones, namely,  $\zeta_2$  and  $\zeta_3$ , 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. (105)).

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. (82) shows that indeed we should have seven different cases of sign flip and one case without sign flip (not surrounding any CI).

## 10. The multi-degenerate case

The emphasis in our previous studies, was on isolated two-state CIs. Here we would like to refer to cases where at a given point three (or more) states become degenerate.

This can happen, for instance, when two seams cross each other at a point so that at this point we have three surfaces crossing each other. The question is: how to incorporate this situation into our theoretical framework?

To start with, 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 CI, presented in terms of  $\tau_{12}(\rho)$ , located at the origin, namely, at  $\rho=0$ .
- (2) The second and the third states form a CI, presented in terms of  $\tau_{23}(\rho, \varphi | \rho_0, \varphi_0)$ , located at  $\rho=\rho_0$ ,  $\varphi=\varphi_0$  [61].
- (3) The tri-state degeneracy is formed by letting  $\rho_0 \rightarrow 0$ , namely

$$\lim_{\rho_0 \rightarrow 0} \tau_{23}(\rho, \varphi | \rho_0, \varphi_0) = \tau_{23}(\rho, \varphi) \quad (106)$$

so that the two CIs coincide. Since the two CIs 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 CIs (see Fig. 5b) According to the discussion of the previous section, 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 5.1.2 and 5.1.3. In Section 5.1.2, we treated a three-state model and found that in this case the functions can *never* flip signs. In Section 5.1.3, we treated a similar four-state case and found that either all four functions flip sign or none of them flips 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 (all the non-adiabatic coupling terms ought to 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 non-degenerate to the degenerate situation, in Eq. (106), something is not continuous.

This contradiction is not resolved so far but still we would like to make the following suggestion. We may encounter in molecular physics two types of multi-degeneracy situations: (1) The one, described above, is formed from an aggregation of two-state CIs and depends on ‘outside’ coordinates (the coordinates that yield the seam). Thus this multi-degeneracy is formed by varying these external coordinates in a proper way. In the same way, the multi-degeneracy can be removed by varying these coordinates. It is noticed that this kind of a degeneracy is not an essential degeneracy because the main features of the individual CIs are expected to be unaffected while assembling this degeneracy or disassembling it. We shall term this degeneracy as the *breakable* multi-degeneracy. (2) The other type, mentioned above, is the one which is not formed from an aggregation of CIs and probably will not breakup under any circumstances. Therefore this degeneracy is termed as the *unbreakable* multi-degeneracy.

## 11. The extended approximate Born–Oppenheimer equation

### 11.1. Introductory remarks

In this section, we derive the (extended) BO approximation which, in contrast to the original BO approximation, contains the effect of the non-adiabatic coupling term [64–67].

The starting point of approximate treatments of molecular dynamics is the BO treatment, which is based on the fact that within molecular systems the fast moving electrons can be distinguished from the slow moving nuclei. Within the BO approximation, one assumes that the non-adiabatic coupling terms are negligibly small and that therefore the upper electronic states do not affect the nuclear wave function on the lower surface. The relevance of this assumption is not considered to be dependent on the energy of the system. However, the ordinary BO approximation was also employed for cases where these coupling terms are not necessarily small, assuming that the energy can be made as low as required. The justification for applying the approximation in such cases is that for a low enough energy the upper adiabatic surfaces are classically forbidden, implying that the components of the total wave function related to these states are negligibly small. As a result, the terms that contain the product of these components with the non-adiabatic coupling terms are also small and will have a minor effect on the dynamical process. This assumption, which underlies many of the single-state dynamical calculations performed during the last three decades, becomes questionable when some of the non-adiabatic coupling terms are large or *infinitely* large. The reason is that although the components of the total wave function may be negligibly small, their product with the large non-adiabatic coupling terms will result in non-negligible values, sometimes even indefinitely large values. In that case, this aspect of the BO approximation will break down for any energy, no matter how low.

As is well known (and as follows from their definition), the non-adiabatic coupling terms appear in the off-diagonal positions in the SE (see Eq. (7)). In order to form a single approximate BO equation that contains the non-adiabatic coupling terms, these terms must first be shifted from their original off-diagonal positions to the diagonal. In a first publication on this subject the present author and Englman [64] showed that such a possibility exists and they derived, for the two-state case, an approximate version of the BO equation which indeed contains the non-adiabatic coupling term. There are also two other, additional, derivations [65,66]. In particular, the latest version [66] treats an  $M$ -state model which is an extension of the two-state (general) case. Here, we shall briefly present this last derivation with some modifications. Particular emphasis will be placed on the two-state case.

### 11.2. The Born–Oppenheimer approximation as applied to an $M$ -dimensional model

Our starting equation is the BO equation as presented in Eq. (15) or more compactly in Eq. (16):

$$-\frac{1}{2m}(\nabla + \tau)^2 \Psi + (u - E)\Psi = 0. \quad (107)$$

As we may recall the matrix  $u$  is a diagonal matrix and  $\tau$  is an antisymmetric vector matrix. The model aspect of this system is with regard to the form of the  $\tau$ -matrix. This matrix is assumed to be of the type presented in Eq. (48), in Section 5.1, namely

$$\tau(s) = gt(s), \quad (48')$$

where  $t(s)$  is a *vector* whose components are functions of the coordinates and  $g$  a *constant* antisymmetric matrix. Due to its particular form, it presents the multi-degeneracy case as discussed in Section 10. The advantage of this choice is that the unitary matrix that diagonalizes it, is a constant matrix  $G$ . Thus, returning to Eq. (107), replacing  $\Psi$  by  $\chi$  where the two are related as

$$\Psi = G\chi \quad (108)$$

and continuing in the usual way leads to the following equation:

$$-\frac{1}{2m}(\nabla + i\lambda t)^2 \chi + (W - E)\chi = 0 \quad (109)$$

for  $\chi$ . Here  $\lambda$  is a diagonal matrix which contains the eigenvalues of the  $g$ -matrix and  $W$  is the matrix that contains the diabatic potentials, thus:

$$W = G^\dagger u G, \quad (110)$$

where  $G^\dagger$  is complex conjugate of  $G$ .

Considering Eq. (110), it is seen that the first term in front of the (column) vector  $\chi$  is a diagonal matrix because  $t$  is a vector of functions (not of matrices) and  $\lambda$ , as mentioned above, is a diagonal matrix. However due to the transformation a new non-diagonal matrix is formed, i.e., the potential matrix  $W$ , which couples the various differential equations. It is important to emphasize that so far the derivation has been rigorous and no approximations have been imposed. Thus, the solution of Eq. (109) will be the same as the solution of Eq. (107). Having

arrived at Eq. (109) we are now in a position to impose the BO approximation. As was already stated earlier, since for low enough energies, all upper adiabatic states are energetically closed, each of the corresponding *adiabatic* functions  $\psi_j$ ,  $j = 2, \dots, N$  is expected to fulfill the condition

$$|\psi_1| \gg |\psi_j|; \quad j = 2, \dots, N \quad (111)$$

in those regions of CS where the lower surface is energetically allowed. This assumption has to be employed with some care because so far it was proven, numerically, to hold for a two-state system ( $N = 2$ ) only [62,63]. (In Ref. [67] we showed, employing this assumption in a three-state model, that it is also fulfilled there as well.)

Our next step is to analyze the product  $W\chi$  for the  $j$ th equation of Eq. (109). Recalling Eqs. (108) and (110), we have

$$\begin{aligned} (W\chi)_j &= \{(G^*uG)(G^*\Psi)\}_j = (G^*u\Psi)_j = \sum_{k=1}^N G_{jk}^* u_k \psi_k \\ &= u_i \chi_j - u_1 \sum_{k=1}^N G_{jk}^* \psi_k + \sum_{k=1}^N G_{jk}^* u_k \psi_k \end{aligned}$$

or

$$(W\chi)_j = u_1 \chi_j + \sum_{k=2}^N G_{jk}^* (u_j - u_1) \psi_k, \quad j = 1, \dots, N. \quad (112)$$

It is noticed from Eq. (112) that for each  $j$  ( $= 1, \dots, N$ ) this equation contains the product of the function  $\chi_j$  and the lowest *adiabatic* potential surface  $u_1$  and a summation of products of the negligibly small  $\psi_k$ 's (namely, only those for  $k \geq 2$ ) with potential terms. Substituting Eq. (112) into Eq. (109) and deleting these summations in each of the equations yields the following system of equations:

$$-\frac{1}{2m}(\nabla + i\omega_j)^2 \chi_j + (u_1 - E) \chi_j = 0, \quad j = 1, \dots, N. \quad (113)$$

It is well noticed that this system of  $N$  equations for the  $N$   $\chi$ -functions is uncoupled and therefore each equation stands on its own and can be solved independently of all other equations. However, it is also to be noticed that all these equations are solved for the same (adiabatic) potential energy surface  $u_1$  but for different  $\lambda_j$ 's.

Once the  $\chi$ -functions are derived the final adiabatic vector  $\Psi_f$  is obtained from Eq. (108) when applied to  $\chi_f$ . In particular, the final nuclear wave function  $\psi_{1f}$  follows from the explicit expression:

$$\psi_{1f} = \sum_{k=1}^N G_{1k} \chi_{kf}. \quad (114)$$

A potential difficulty associated with this approach is due to the fact that the calculated  $\chi$ -functions yield, through the transformation in Eq. (108), also all other  $\psi_f$ -functions, namely  $\psi_{jf}$ ;  $j > 1$ . These functions, by definition, have to be identically zero at all asymptotes, because they belong to the upper adiabatic states which are classically forbidden at all these regions. At this stage nothing in the theory guarantees that the calculated  $\chi$ -functions fulfill this demand.



There is, however, at least one case for which the calculated  $\chi$ -functions will produce  $\psi_{jf}$ 's;  $j > 1$  which are all identically zero and that is the case when Eq. (113) are gauge invariant [68–70] (we shall elaborate on the gauge invariance property in the next section). At this stage let us assume that the functions  $(t\lambda_j)$ ;  $j = 1, \dots, N$  (if  $\lambda_j$  are the eigenvalues of the  $\tau$ -matrix) are such that these equations are gauge invariant so that the various  $\chi$ -functions, if calculated for the same boundary conditions, are all identical. Thus, our next step will be to determine the boundary conditions for the  $\chi$ -functions in order to solve Eq. (113). To find those we need to impose boundary conditions on the  $\psi$ -functions. We assume that at the given (initial) asymptote all  $\psi$ -functions are zero except for the ground state function  $\psi_{1in}$ . Thus,

$$\psi_1 = \psi_{1in}, \quad \psi_j = \psi_{jin} = 0, \quad j = 2, \dots, N. \quad (115)$$

Due to Eq. (108) the boundary conditions for the  $\chi$ -functions are given in the form

$$\chi_{jin} = G_{j1}^* \psi_{1in}, \quad j = 1, \dots, N. \quad (116)$$

It is seen that the boundary conditions for the  $\chi$ -functions are all identical, up to a constant ( $= G_{j1}^*$ ), and therefore the same applies to the  $\chi$ -functions at every point in CS. Thus if at a given asymptotic region we define  $\chi_f$  as the  $\chi$ -function calculated for a  $\chi_{in}$  which is identical to  $\psi_{in}$  (not proportional to it) then it can be shown (see also Eq. (114)) that the  $\psi$ -functions at this particular asymptote, namely  $\psi_{jf}$ ,  $j = 1, \dots, N$  become

$$\psi_{1f} = \chi_f, \quad \psi_j = 0, \quad j = 2, \dots, N. \quad (117)$$

Thus, for the particular case of a gauge invariant set of uncoupled equations, we indeed obtain a solution, which is compatible with the assumptions.

### 11.3. The gauge invariance condition for the approximate Born–Oppenheimer equations and the Bohr–Sommerfeld quantization of the non-adiabatic coupling matrix

The system of uncoupled equations presented in Eq. (113) do not necessarily yield solutions which are related to each other. In other words, if we do not produce the conditions that will guarantee that all these equations yield the same solution this procedure cannot be accepted. In what follows we show, based on studies performed and assumptions made in Section 5.1 (in particular, in Section 5.1.4), that if solved for the same initial conditions all equations indeed yield identical results.

As was already mentioned, the various equations differ only because their imaginary components, i.e.,  $\lambda_j t(s)$ ;  $j = 1, \dots, M$  are not necessarily identical. However, it is well known that if this set of functions are related to each other in a way that will be discussed next, Eq. (113) are gauge invariant [68–70] and their solutions, therefore, are all identical. The gauge invariance condition is fulfilled if the products  $\lambda_j t(s)$  satisfy the following condition:

$$\lambda_j \oint_{\Gamma} ds \cdot t(s) = 2\pi n_j, \quad j = 1, \dots, M, \quad (118)$$

where the  $n_j$  numbers form either a series of integers or of a series of half-integers (i.e.,  $2p_j + 1)/2$ ;  $p_j$  is an integer). These conditions are very similar to those discussed in Section 5.1.4 for the type of  $\tau$ -matrices treated in the previous section. In Section 5.1 we found

that in order for the topological matrix  $D$  to be diagonal (which also implies that it must have  $(+1)$ s and  $(-1)$ s in its diagonal) these the products  $\lambda_j t(s)$ ;  $j = 1, \dots, M$  have to fulfill Eq. (118). Moreover, for the cases  $M = 2, 4$  the series has to be either of integers or of half-integers (but not a mixture of them) and in case of  $M = 3$  it has to be a series of integers only. In Section 5.1.4 we speculated (but did not prove) that these features will apply for any  $M$ -value, namely, in case of even  $M$ -values we have both series (of integers and half-integers) but in case of odd  $M$ -values we have only integers. The difference between having a series of integers and half-integers is that in the first case, all electronic eigenfunctions are singled-valued and in the second case *all* of them are multi-valued. Thus in the first case, while tracing any closed contour these functions do not produce topological effects whereas in the second case, *all* of them produce topological effects (see Section 5.1).

To conclude this subject we would like to refer to two subjects: (1) For the model treated in this section, we derived an extended BO approximated equation, i.e. Eq. (113). Its validity is guaranteed by the fact that the eigenvalues of non-adiabatic coupling matrix  $\tau$  have to fulfill the Bohr–Sommerfeld quantization rules. (2) For the case  $M = 2$ , the model presents, in fact, the realistic, most general, case.

## 12. The adiabatic-to-diabatic transformation matrix and the Wigner rotation matrix

The ADT matrix in the way it is presented in Eq. (26) is somewhat reminiscent of the Wigner rotation matrix [71] (assuming that  $A(s_0) \equiv I$ ). In order to see that we first present a few well known facts related to the definition of ordinary angular momentum operators (we follow the presentation by Rose [72]) and the corresponding Wigner matrices and then return to discuss the similarities between Wigner's  $d^j(\beta)$  matrix and the ADT matrix.

### 12.1. Wigner rotation matrices

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

$$R(k, \theta) = \exp(-iS(k, \theta)) , \quad (119)$$

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

$$S(k, \theta) = (k \cdot J)\theta , \quad (120)$$

where the dot stands for scalar product. Substituting Eq. (120) in Eq. (119) yields, for  $R(k, \theta)$ , the following expression:

$$R(k, \theta) = \exp(-i(k \cdot J)\theta) . \quad (119')$$

It has to be emphasized that in this framework,  $J$  is the angular momentum operator in the ordinary coordinates space (i.e., CS) and  $\theta$  is a (differential) ordinary angular polar coordinate.

Next, the Euler's angles are employed for deriving the outcome of a general rotation of a system of coordinates [50]. It can be shown that  $R(k, \theta)$  is, accordingly, presented as

$$R(k, \theta) = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z}, \quad (121)$$

where  $J_y$  and  $J_z$  are the  $y$  and  $z$  components of  $J$  and  $\alpha$ ,  $\beta$  and  $\gamma$  are the corresponding three Euler angles. The explicit matrix elements of the rotation operator are given in the form

$$D_{m'm}^j(\theta) = \langle jm' | R(k, \theta) | jm \rangle = e^{-i(m'\alpha + m\gamma)} \langle jm' | e^{-i\beta J_y} | jm \rangle, \quad (122)$$

where  $m$  and  $m'$  are the components of  $J$  along the  $J_z$  and  $J_{z'}$  axes, respectively, and  $|jm\rangle$  is an eigenfunction of the Hamiltonian, of  $J^2$  and of  $J_z$ . Eq. (122) will be written as

$$D_{m'm}^j(\theta) = e^{-i(m'\alpha + m\gamma)} d_{m'm}^j(\beta). \quad (123)$$

The  $D^j$ -matrix as well as the  $d^j$ -matrix are called the Wigner matrices and they are the subject of the present section. It is noticed that if we are interested in finding a relation between the ADT matrix and Wigner's matrices, we should mainly concentrate on the  $d^j$ -matrix. Wigner derived a formula for these matrix elements (see Ref. [72], 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 Ref. [72], p. 72).

## 12.2. The adiabatic-to-diabatic transformation matrix and Wigner's $d^j$ -matrix

The obvious way to form a similarity between Wigner rotation matrix and the ADT matrix defined in Eqs. (26) is to consider the (unbreakable) multi-degeneracy case which is based, just like Wigner rotation matrix, on a single axis of rotation. For this sake, we consider the particular set of  $\tau$ -matrices as defined in Eq. (48) and derive the relevant ADT 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 detailed comparison between the two types of matrices, it is important to remind the reader what the elements of the  $J_y$ -matrix look like. Employing Eqs. (2.18) and (2.28) of Ref. [72], it can be shown that

$$\langle jm | J_y | jm + k \rangle = \delta_{1k} \frac{1}{2i} \sqrt{(j + m + 1)(j - m)}, \quad (124a)$$

$$\langle jm + k | J_y | jm \rangle = -\delta_{1k} \frac{1}{2i} \sqrt{(j - m + 1)(j + m)}. \quad (124b)$$

Defining now  $\tilde{J}_y$  as

$$\tilde{J}_y = iJ_y, \quad (125)$$

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

$$d^j(\beta) = \exp(-i\beta J_y) = \exp(\beta \tilde{J}_y). \quad (126)$$

It is expected that for a certain choice of parameters (that define the  $\tau$ -matrix) the ADT matrix becomes identical to the corresponding Wigner rotation matrix. To see the connection, we substitute Eq. (48) into Eq. (26) and assume  $A(s_0)$  to be the unity matrix.

The three matrices of interest were already derived and presented in Section 5.1. There they were termed the  $D$ -(topological) matrices (not related to the above mentioned Wigner  $D^j$ -matrix) and were used to show the kind of quantization one should expect for the relevant NACTs. The only difference between these topological matrices and the ADT matrices requested here is that in Eqs. (51), (57) and (67), the closed line integral (see Eq. (71) is replaced by  $\gamma(s)$  defined along an (open) contour (see Eq. (70)):

For the three cases studied in Section 5.1, the similarity to the three corresponding Wigner matrices is achieved in the following way:

(1) For the two-state case (i.e.  $j = \frac{1}{2}$ ), the  $d^{1/2}(\beta)$  is identified with the corresponding ADT matrix (see Eq. (69)) for which  $\beta = \gamma$ .

(2) For the tri-state case ( $j = 1$ ) we consider Eq. (56). The corresponding  $d^1(\beta)$ -matrix is obtained by assuming  $\eta = 1$  (see Eq. (53)) and therefore  $\omega = \sqrt{2}$ . From Eq. (57) or (58) it is seen that  $\beta = \gamma\sqrt{2}$ . For the sake of completeness, we present the corresponding  $d^1(\beta)$ -matrix [72]:

$$d^1(\beta) = \frac{1}{2} \begin{pmatrix} 1 + C(\beta) & \sqrt{2}S(\beta) & 1 - C(\beta) \\ \sqrt{2}S(\beta) & 2C(\beta) & -\sqrt{2}S(\beta) \\ 1 - C(\beta) & \sqrt{2}S(\beta) & 1 + C(\beta) \end{pmatrix}, \quad (127)$$

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

(3) For the tetra-state case ( $j = \frac{3}{2}$ ), we consider Eq. (64). The corresponding  $d^{3/2}(\beta)$  is obtained by assuming  $\eta = \sqrt{4/3}$  and  $\sigma = 1$  (see Eq. (59)). This will yield for  $\varpi$  the value  $\varpi = \sqrt{\frac{10}{3}}$  (see Eq. (62b)). Since  $\beta = p\gamma$  (see Eqs. (67)), we have to determine the value of  $p$  which can be shown to be  $p = \sqrt{3}$  (see Eq. (61)) and therefore:  $\beta = \gamma\sqrt{3}$ . For the sake of completeness we present the  $d^{3/2}(\beta)$  matrix:

$$d^{3/2}(\beta) = \begin{pmatrix} C^3 & -\sqrt{3}C^2S & -\sqrt{3}S^2C & S^3 \\ \sqrt{3}C^2S & C(1 - 3S^2) & -S(1 - 3C^2) & -\sqrt{3}S^2C \\ -\sqrt{3}S^2C & S(1 - 3C^2) & C(1 - 3S^2) & -\sqrt{3}C^2S \\ -S^3 & -\sqrt{3}S^2C & \sqrt{3}C^2S & C^3 \end{pmatrix}, \quad (128)$$

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

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

### 13. 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 model-system resembling a tri-state case.

### 13.1. The study of ‘real’ two-state molecular systems

We start by mentioning the pioneering studies of Yarkony et al. Yarkony was the first to apply the line integral approach to reveal the existence of a CI for a ‘real’ molecular system—the  $H_3$  system [27]—by calculating the relevant NACTs from first principles and then deriving the topological angle  $\alpha$  (see Eq. (71)). Later he and co-workers applied this approach to study other tri-atom system such as  $CH_2$  [73,76],  $Li_3$  [74],  $HeH_2$  [75],  $H_2S$  [76] and  $AlH_2$  [77]. Such studies could be materialized only due to the efficient methods developed by Yarkony et al. [78] to calculate the NACT.

Recently, Xu et al. [79] studied in detail the  $H_3$  molecule as well as its two isotopic analogs 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 and/or does not surround the CI point. Some time later Mebel et al. [80,81] employed ab initio NACTs and the line integral approach to study some features related to the  $C_2H$  molecule.

In the next two sections the results of these two studies will be presented.

#### 13.1.1. The $H_3$ -system and its isotopic analogs

Although the study to be described is for a ‘real’ systems, the starting point were not the ab initio adiabatic PESs and the ab initio NACTs but the diabatic double-many-body-expansion (DMBE) potentials [82–84]. These were used to calculate the ADT angle  $\gamma$  by employing the Hellman–Feynman theorem [32,85]. However, we shall present our results in term of the Diabatic-to-adiabatic transformation (DAT) angle  $\beta$  (as will be explained next). So we have to prove that the two angles are identical.

We consider a two-dimensional diabatic framework which is characterized by an angle,  $\beta(s)$ , associated with the orthogonal transformation which diagonalizes the diabatic potential matrix. Thus, if  $V$  is the diabatic potential matrix and if  $u$  is the adiabatic one, the two are related by the orthogonal transformation matrix  $A$  [32,85]:

$$u = A^\dagger V A, \quad (129)$$

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

$$A = \begin{pmatrix} \cos \beta & -\sin \beta \\ \sin \beta & \cos \beta \end{pmatrix}, \quad (130)$$

where  $\beta$ —the above mentioned DAT angle (or mixing angle as it is recently termed)—is given by [32]

$$\beta = \frac{1}{2} \tan^{-1} \frac{2V_{12}}{V_{11} - V_{22}}. \quad (131)$$

Recalling  $\gamma(s)$ , the ADT angle (see Eqs. (69) and (70)) it is expected that the two angles are related. The connection is formed by the Hellman–Feynman [32,85] theorem which yields the relation between the  $s$  component of the NACT,  $t$ , namely,  $t_s$ , and the characteristic diabatic magnitudes:

$$t_s(s) = (u_2 - u_1)^{-1} A_1^* \frac{\partial V}{\partial s} A_2 = \frac{\sin 2\beta}{2W_{12}} A_1^* \frac{\partial V}{\partial s} A_2, \quad (132)$$

where  $A_i$ ,  $i = 1, 2$  are the two columns of the  $A$ -matrix in Eq. (130). Replacing the two  $A_i$ -columns by their explicit expressions yields for  $t_s$  the expression [86]:

$$t_s(s) = \frac{\sin 2\beta}{2V_{12}} \left[ -\frac{\sin 2\beta}{2} \frac{\partial}{\partial s} (V_{11} - V_{22}) + \cos 2\beta \frac{\partial}{\partial s} V_{12} \right] \quad (133)$$

Next, differentiating Eq. (131) with respect to  $s$ :

$$\frac{\partial}{\partial s} (V_{11} - V_{22}) = 2 \left( V_{12} \frac{\partial}{\partial s} \cot 2\beta + \cot 2\beta \frac{\partial}{\partial s} V_{12} \right) \quad (134)$$

and substituting Eq. (134) into Eq. (133) yields the following result for  $t_s(s)$ :

$$t_s(s) = \frac{\partial \beta}{\partial s} . \quad (135)$$

Comparing this equation with Eq. (70) it is seen that the DAT angle  $\beta$  is, up to an additive constant, identical to the relevant ADT-angle  $\gamma$ :

$$\gamma(s) = \beta(s) - \beta(s_0) . \quad (136)$$

This relation will be used to study geometrical phase effects within the diabatic framework for the  $H_3$  system and its two isotopic analogs. What is meant by this is that since our starting point is the  $2 \times 2$  diabatic potential matrix, we do not need to obtain the ADT angle by solving a line integral; it will be obtained, simply by applying Eqs. (131) and (136). The forthcoming study is carried out by presenting  $\beta(\varphi)$  as a function of an angle  $\varphi$  to be introduced next:

In what follows, we shall be interested in the location of the seam defined by the conditions  $r_{AB} = r_{BC} = r_{AC}$  [4–7] where  $r_{AB}$ ,  $r_{BC}$  and  $r_{AC}$  are the inter-atomic distances. Since we intend to study the geometrical properties produced by this seam we follow a suggestion by Kuppermann and coworkers [34,90] and employ the hyperspherical coordinates  $(\rho, \theta, \varphi)$  which are known to be convenient to carry out quantum mechanical reactive (i.e. exchange) processes. These coordinates were found to be suitable for this purpose as well because one of the angular coordinates surrounds the seam in case of the pure hydrogenic case. Consequently, following previous studies [87–90], we express the three above mentioned distances in terms of these coordinates, i.e.

$$\begin{aligned} r_{AB}^2 &= \frac{1}{2} d_C \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos(\varphi + \chi_{AC}) \right] , \\ r_{BC}^2 &= \frac{1}{2} d_A \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos(\varphi) \right] , \\ r_{AC}^2 &= \frac{1}{2} d_B \rho^2 \left[ 1 + \sin \frac{\theta}{2} \cos(\varphi - \chi_{AB}) \right] , \end{aligned} \quad (137)$$

where

$$\begin{aligned} d_X^2 &= \frac{m_X}{\mu} \left( 1 - \frac{m_X}{M} \right), \quad \chi_{XY} = 2 \tan^{-1} \left( \frac{m_Z}{\mu} \right) , \\ \mu &= \sqrt{\frac{m_A m_B m_C}{M}}, \quad M = m_A + m_B + m_C . \end{aligned} \quad (138)$$

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

$$\rho = \sqrt{r_{AB}^2 + r_{AC}^2 + r_{BC}^2}. \quad (139)$$

Equating the three inter-atomic distances with each other, we find that the seam is a straight line, for which  $\rho$  is arbitrary but  $\varphi$  and  $\theta$  have fixed values  $\varphi_s$  and  $\theta_s$  determined by the masses only:

$$\varphi_s = \tan^{-1} \left\{ \frac{\cos \chi_{AC} - t \cos \chi_{AB} - (d_A/d_C)^2 + t(d_A/d_B)^2}{\sin \chi_{AC} - t \sin \chi_{AB}} \right\} \quad (140)$$

and

$$\theta_s = 2 \sin^{-1} \left\{ \frac{(d_A/d_B)^2 - 1}{\cos(\varphi_s - \chi_{AB}) - (d_A/d_B)^2 \cos \varphi_s} \right\}, \quad (141)$$

where  $t$  is given in the form

$$t = \left[ \left( \frac{d_A}{d_C} \right)^2 - 1 \right] \left[ \left( \frac{d_A}{d_B} \right)^2 - 1 \right]^{-1}. \quad (142)$$

Eqs. (139)–(142) are valid when all three masses are different. In case two masses are equal, namely,  $m_B = m_C$ , we get for  $\theta_s$  the simplified expression:

$$\theta_s = 2 \sin^{-1} \left\{ \left| \frac{m_B - m_A}{m_B + 2m_A} \right| \right\} \quad (143)$$

and for  $\varphi_s$  the value  $\pi$  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  $\text{H}_2\text{D}$  system. For this purpose is employed Eq. (143) for which it is obtained that the straight-line-seam is defined for the following values of  $\theta_s$  and  $\varphi_s$ , namely  $\theta_s = 0.4023$  rad, and  $\varphi_s = \pi$ . In the  $\text{H}_3$  case, the value of  $\theta_s$  is zero and this guarantees that all the circles with constant  $\rho$  and  $\theta$  encircle the seam. The fact that  $\theta_s$  is no longer zero implies that not all the circles with constant  $\rho$  and  $\theta$  encircle the seam; thus, circles for which  $\theta > \theta_s$  will encircle the seam and those with  $\theta < \theta_s$  will not.

In Fig. 6 are presented  $\beta(\varphi)$  curves for  $\text{H}_2\text{D}$ , all calculated for  $\rho = 6a_0$ . In this calculation, the hyperspherical angle  $\varphi$ , defined along the  $[0, 2\pi]$  interval, is the independent angular variable. In Fig. 6a are shown 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 Fig. 6b for the case the line integral encircles the seam namely, for  $\theta = 0.405$  and  $2.0$  rad. It is noticed that the curves in Fig. 6a reach the value of zero and those in Fig. 6b the value of  $\pi$ . In particular, two curves, one in Fig. 6a for  $\theta = 0.4$  rad and the other in Fig. 6b 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  $\pi$ . 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 Ref. [79].

These results as well as others presented in Ref. [79] are important because on various occasions, it was implied that the line integral approach is suitable only for cases when relatively short radii around the CI are applied. In Ref. [79], it was shown for the first time that this

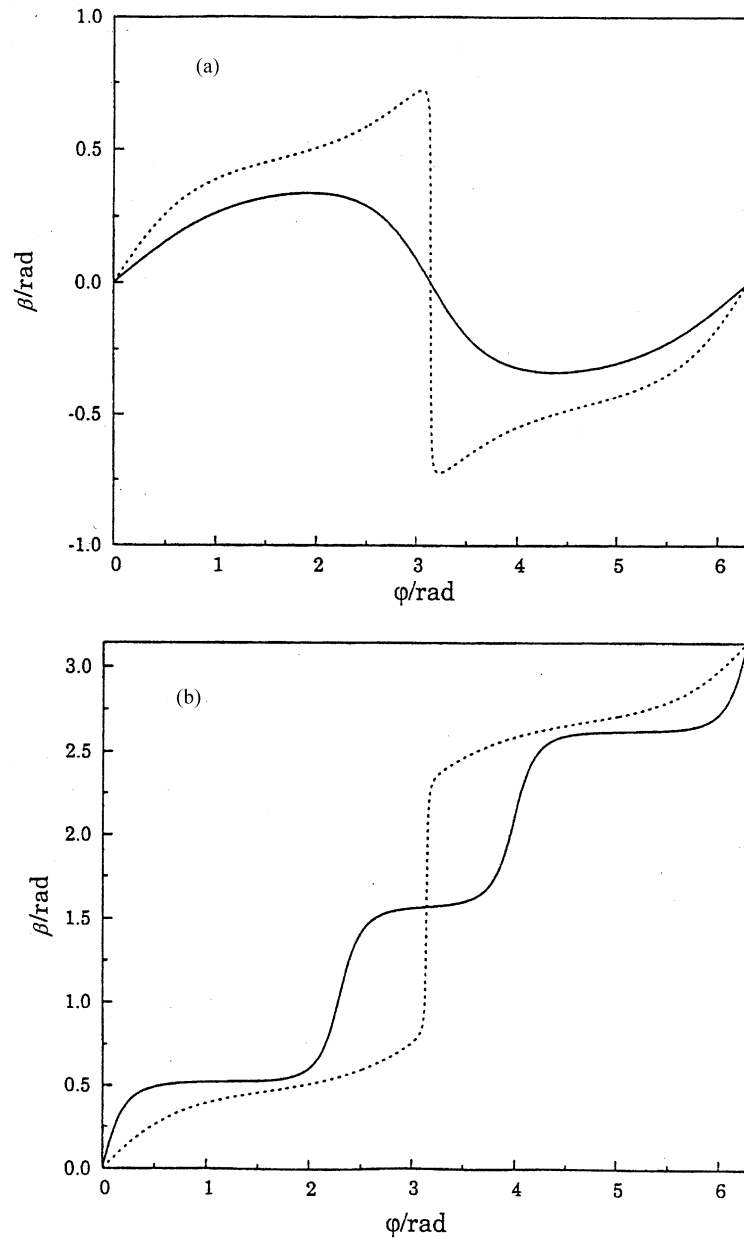


Fig. 6. The mixing angle  $\beta$ , for the  $\text{H}_2\text{D}$  system, as a function of hyperspherical angle  $\phi$ , calculated for hyperspherical radius  $\rho = 6a_0$ : (a) Results for  $\theta = 0.2$  rad (—) and  $\theta = 0.4$  rad (-----). (b) The same as (a) but for  $\theta = 2.0$  rad (—) and  $\theta = 0.405$  rad (-----).

approach can be useful even for large radii. This does not mean that it is relevant for any assumed contour surrounding a CI (or for that matter a group of CIs) but it means that we can always find contours with large radii that will reveal the CI location for a given pair of states. We shall return to this problem in our next section.



### 13.1.2. The C<sub>2</sub>H molecule

As expected, the molecule C<sub>2</sub>H is the focus of intensive studies experimental [91–96] as well as theoretical/numerical [80,81,97–105]. As far as our subject is concerned, it was Peyerimhoff and coworkers [97–102], who revealed the existence of a CI between the 1<sup>2</sup>A' and the 2<sup>2</sup>A' states (to be designated the (1,2) CI) in the collinear configuration and Cui and Morokuma [103], who found a CI between the 2<sup>2</sup>A' and the 3<sup>2</sup>A' states in the C<sub>2v</sub> configuration (henceforth designated the (2,3) CI). Recently, Mebel et al. found two twins CI between the 3<sup>2</sup>A' and the 4<sup>2</sup>A' states [105] (henceforth designated (3,4) CIs). These twins are located on the two sides of the C<sub>2v</sub> line at relatively short distances [0.0, 0.3 Å]. Since the study of the twins has not yet been completed, we refer to the two lower CIs only.

Employing the MOLPRO program package [106], the six relevant (Cartesian) non-adiabatic coupling terms between the two states, the 1<sup>2</sup>A' and 2<sup>2</sup>A' as well as between the 2<sup>2</sup>A' and 3<sup>2</sup>A' electronic states were calculated for the configurations of interest. These non-adiabatic coupling elements were then transformed, employing chain rules [48], to non-adiabatic coupling elements with respect to the internal coordinates of the C<sub>2</sub>H molecule, namely,  $\langle \zeta_i | \partial \zeta_j / \partial r_1 \rangle (= \tau_{r_1})$ ,  $\langle \zeta_i | \partial \zeta_j / \partial r_2 \rangle (= \tau_{r_2})$ ,  $\langle \zeta_i | \partial \zeta_j / \partial \varphi \rangle (= \tau_\varphi)$ , where  $r_1$  and  $r_2$  are the CC and CH distances, respectively, and  $\varphi$  is the relevant CC...CH angle. Next, is derived the ADT angle,  $\gamma(\varphi|r_1, r_2)$ , employing the following line integral (see Eq. (70)), where the contour is an arc of a circle with radius  $r_2$ :

$$\gamma(\varphi|r_1, r_2) = \int_0^\varphi d\varphi' \tau_\varphi(\varphi'|r_1, r_2). \quad (144)$$

The corresponding topological phase,  $\alpha(r_1, r_2)$ —see Eq. (71)—defined as  $\gamma(\varphi = 2\pi|r_1, r_2)$ , was also obtained for various values of  $r_1$  and  $r_2$ .

First we refer to the (1,2) CI. A detailed inspection of the non-adiabatic coupling terms revealed, indeed, the existence of a CI between these two states, for instance, at the point  $\{\varphi = 0, r_1 = 1.35 \text{ Å}, r_2 = 1.60 \text{ Å}\}$  as was established before [97,102]. More CIs, of this kind, are expected at other  $r_1$  values. Next were calculated the  $\gamma(\varphi|r_1, r_2)$  angles as a function of  $\varphi$  for various  $r_2$ . The  $\tau_\varphi(\varphi|r_1, r_2)$  functions as well as the ADT angles are presented in Figs. 7a–c for three different  $r_2$ -values namely,  $r_2 = 1.8, 2.0, 3.35 \text{ Å}$ . Mebel et al. also calculated the topological angle  $\alpha(r_1, r_2)$  for these three  $r_2$ -values as well as for other  $r_2$ -values. In all cases, they got for  $\alpha(r_1, r_2)$  either the value of  $\pi$  (when  $r_2$  was in the interval  $\{r_2\} = \{1.60, 2.95 \text{ Å}\}$ ) or zero (when  $r_2$  was outside it). The reason is that as long as  $r_2$  is in this interval, it forms a circle that contains one single CI (see also Figs. 7a and b for the cases  $r_2 = 1.8, 2.0 \text{ Å}$ ); however, when  $r_2 > 2.95 \text{ Å}$ , it forms a circle that contains two (symmetric) CIs (see Fig. 7c) and in case  $r_2 < 1.60 \text{ Å}$ , it forms a circle that does not contain any CI [105]. The fact that the value of the integral is zero when no CIs are surrounded by the circle was proved in Appendix C. Thus, in this sense the present calculation confirms this derivation. In this series of results, we encounter a somewhat unexpected result namely when the circle surrounds two CIs 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  $2\pi$  or zero) but it is still somewhat unexpected, because it implies that the two CIs behave like vectors and that they arrange themselves in such a way as to reduce the effect of the NACTs. This result has important consequences regarding the cases where a pair of electronic states are coupled by more than one CI [105].

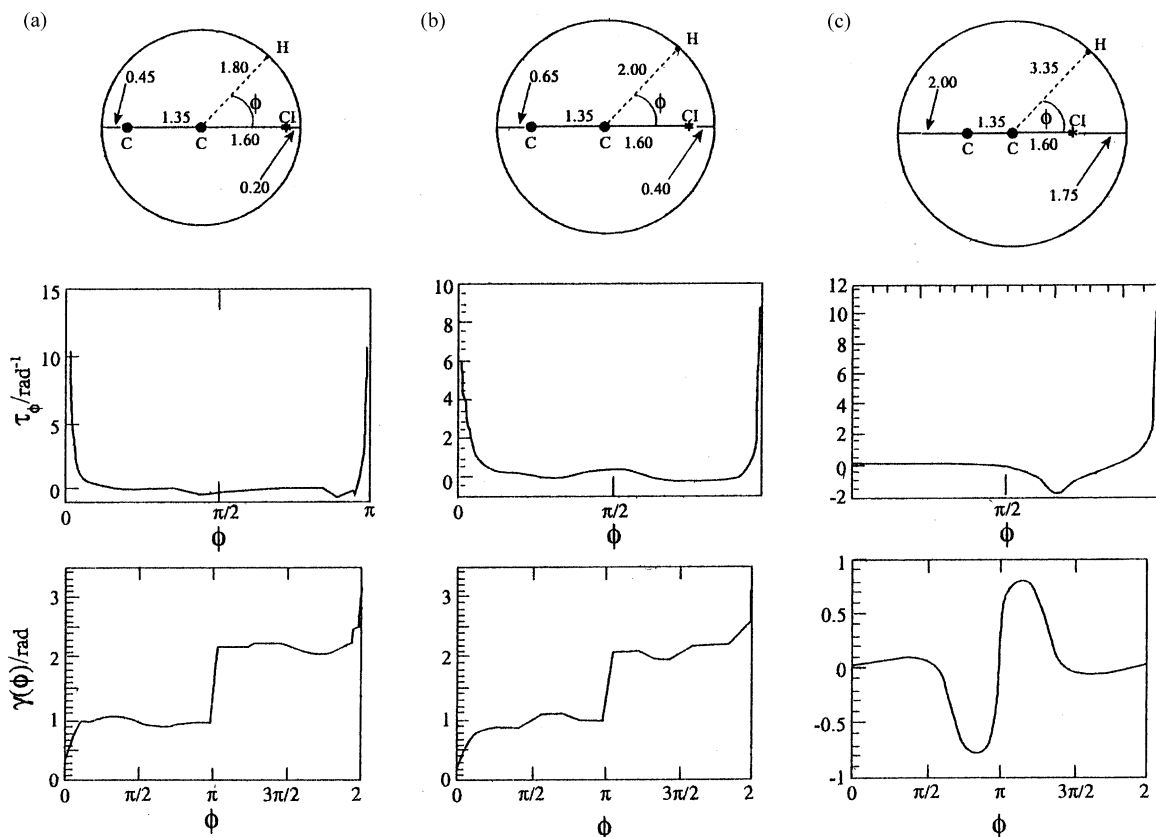


Fig. 7. Results for the  $C_2H$  molecule as calculated along a circle surrounding the  $1^2A'-2^2A'$  conical intersection. Shown are the geometry, the non-adiabatic coupling matrix elements  $\tau_\phi(\phi|r_2)$  and the ADT angles  $\gamma(\phi|r_2)$  as calculated for  $r_1$  (= CC distance) = 1.35 Å and for three  $r_2$ -values ( $r_2$  is the CH distance): (a)  $r_2 = 1.80$  Å; (b)  $r_2 = 2.00$  Å; (c)  $r_2 = 3.35$  Å.

On this occasion, we want also to refer to a wrong statement that we made more than once, [32b,80], namely that the (1,2) results indicate ‘that for any value of  $r_1$  and  $r_2$  the two states under consideration form an *isolated* two-state SHS’. 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 CI 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  $2\pi$  or zero indicates that we can form, for this adiabatic two-state system, *single-valued*, namely physical, 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.

In Ref. [81] is presented the first line integral study between the 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 the CI. Accordingly,

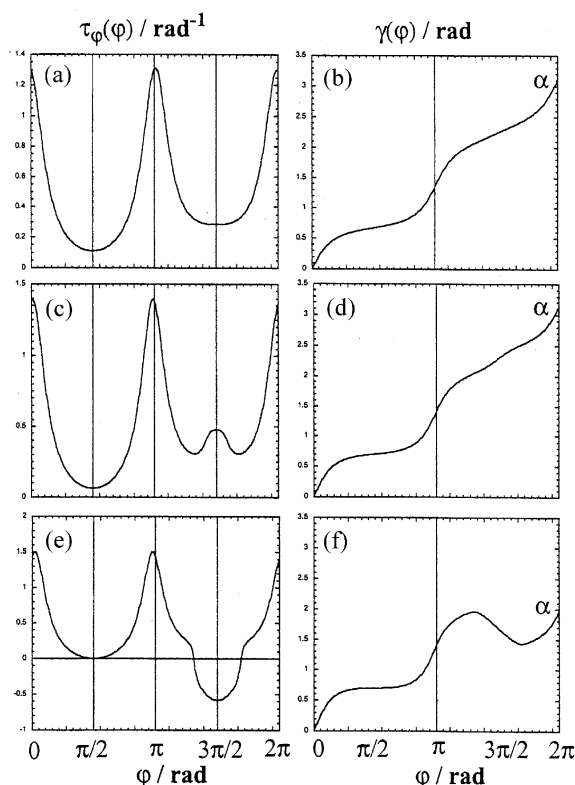


Fig. 8. Results for the  $C_2H$  molecule as calculated along a circle surrounding the  $2^2A'-3^2A'$  conical intersection. The CI is located on the  $C_{2v}$  line at a distance of 1.813 Å from the CC axis where  $r_1 (=CC)=1.2515$  Å. The circle is located at the point of the CI and defined in terms of a radius  $q$ . Shown are the non-adiabatic coupling matrix elements  $\tau_\varphi(\varphi|q)$  and the ADT angles  $\gamma(\varphi|q)$  as calculated for: (a) and (b) for  $q=0.2$  Å; (c) and (d) for  $q=0.3$  Å; (e) and (f) for  $q=0.4$  Å.

the two polar coordinates  $(\varphi, q)$  are defined. Next is derived the  $\varphi$ th non-adiabatic coupling term, i.e.,  $\tau_\varphi(=\langle \zeta_1 | \partial \zeta_2 / \partial \varphi \rangle)$  again employing chain rules for the transformation  $(\tau_\gamma, \tau_{r_2}) \rightarrow \tau_\varphi$  ( $\tau_q$  is not required because the integral is performed along a circle with a fixed radius  $q$ ).

In Fig. 8 are presented  $\tau_\varphi(\varphi|q)$  and  $\gamma(\varphi|q)$  for three values of  $q$ , i.e.,  $q=0.2, 0.3, 0.4$  Å. The main features to be noticed are: (1) The function  $\tau_\varphi(\varphi|q)$  exhibits the following symmetry properties:  $\tau_\varphi(\varphi) = \tau_\varphi(\pi - \varphi)$  and  $\tau_\varphi(\pi + \varphi) = \tau_\varphi(2\pi - \varphi)$  where  $0 \leq \varphi \leq \pi$ . 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  $0 \leq \varphi \leq \pi$  but since the line integral has to supply the value of  $\pi$ , this function cannot allow itself to be with alternating signs. (2) The ADT angle,  $\gamma(\varphi|q)$ , increases, for the two smaller  $q$ -values, monotonically to become  $\alpha(\Gamma|q)$ , with the value of  $\pi$  (in fact we got  $0.986\pi$  and  $1.001\pi$  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  $\alpha(\Gamma|q)$  is only  $0.63\pi$ . The reason being that the  $q=0.4$  Å circle passes very close to the two (3,4) CIs (the distance at the closest points is  $\sim 0.04$  Å). A detailed analysis of this situation is given elsewhere [81].

### 13.2. The study of a tri-state model system

In Section 5.2 we discussed to some extent the  $3 \times 3$  ADT matrix  $A$  ( $\equiv A^{(3)}$ ) for a tri-state system. This matrix was expressed in terms of three (Euler-type) angles  $\gamma_{ij}$ ,  $i > j = 1, 2, 3$  (see Eq. (76)) which fulfill a set of three coupled, first order, differential equations (see Eq. (77)).

In what follows, we treat a tri-state model system defined in a plane in terms of two polar coordinates  $(\rho, \varphi)$  [28]. In order to guarantee that the non-adiabatic matrix  $\tau$ , yields single-valued diabatic potentials we shall start with a  $3 \times 3$  *diabatic* potential matrix and form, employing the Hellman–Feynman theorem [32,85], the corresponding non-adiabatic coupling matrix  $\tau$ . The main purpose of studying this example is to show that the  $A$ -matrix may not be uniquely defined in CS 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. [107,108] to study the excited states of  $Na_3$ . It is of the following form (for more details see Ref. [28]):

$$V = \begin{pmatrix} \varepsilon_E + U_1 & U_2 & W_1 - W_2 \\ U_2 & \varepsilon_E - U_1 & W_1 + W_2 \\ W_1 - W_2 & W_1 + W_2 & \varepsilon_A \end{pmatrix}. \quad (145)$$

Here  $\varepsilon_E$  and  $\varepsilon_A$  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

$$U_1 = k\rho \cos \varphi + \frac{1}{2}g\rho^2 \cos(2\varphi) \quad (146a)$$

and

$$U_2 = k\rho \sin \varphi - \frac{1}{2}g\rho^2 \sin(2\varphi). \quad (146b)$$

$W_i$ ;  $i = 1, 2$  are potentials of the same functional form as the  $U_i$ 's 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 [107]

$$k = \sqrt{2}p = 5.53 \text{ a.u.} \quad \text{and} \quad g = \sqrt{2}f = 0.152 \text{ a.u.}$$

Eqs. (77) are solved, for fixed  $\rho$ -values, but for a varying angular coordinate,  $\varphi$ , defined along the interval  $(0, 2\pi)$ . Thus,  $\rho$  serves as a parameter and the results will be presented for different  $\rho$ -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, i.e., 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 Fig. 9 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  $\rho$  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  $\varphi$ . There are other interesting features to be noticed but these are of less relevance to the present study (for a more extensive discussion see Ref. [28]).

In Fig. 1 are presented the three  $\gamma$ -angles as a function of  $\varphi$  for various values of  $\rho$  and  $\Delta\varepsilon$ . The two main features which are of interest for the present study are: (1) Following

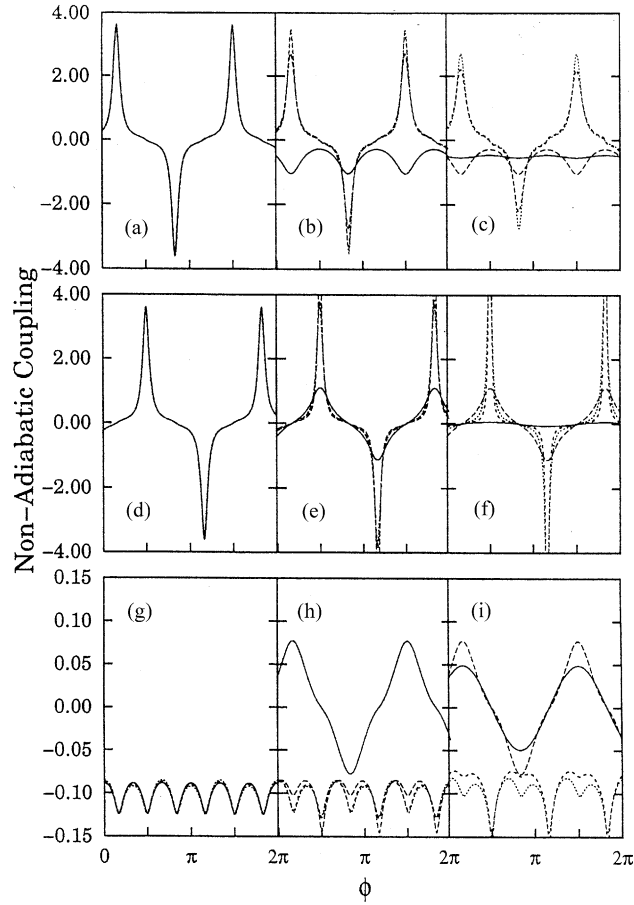


Fig. 9. The three non-adiabatic coupling terms (obtained for the model potential described in Section 13.2)  $\tau_{12\phi}(\phi)$ ,  $\tau_{23\phi}(\phi)$ ,  $\tau_{13\phi}(\phi)$  as a function  $\phi$  calculated for different values of  $\rho$  and  $\Delta\epsilon$ : (a)  $\tau = \tau_{12}$ ,  $\Delta\epsilon = 0.0$ ; (b)  $\tau = \tau_{12}$ ,  $\Delta\epsilon = 0.05$ ; (c)  $\tau = \tau_{12}$ ,  $\Delta\epsilon = 0.5$ ; (d)  $\tau = \tau_{23}$ ,  $\Delta\epsilon = 0.0$ ; (e)  $\tau = \tau_{23}$ ,  $\Delta\epsilon = 0.05$ ; (f)  $\tau = \tau_{23}$ ,  $\Delta\epsilon = 0.5$ ; (g)  $\tau = \tau_{13}$ ,  $\Delta\epsilon = 0.0$ ; (h)  $\tau = \tau_{13}$ ,  $\Delta\epsilon = 0.05$ ; (i)  $\tau = \tau_{13}$ ,  $\Delta\epsilon = 0.5$ . (—)  $\rho = 0.01$ ; (-----)  $\rho = 0.1$ ; (-·-·-)  $\rho = 0.5$ ; (·····)  $\rho = 1.0$ .

a full cycle, all three angles in all situations obtain the values either of  $\pi$  or of zero. (2) In each case (namely for each set of  $\rho$  and  $\Delta\epsilon$ ), following a full cycle, two angles become zero and one becomes  $\pi$ . From Eq. (76) it is noticed that the  $A$ -matrix is diagonal at  $\phi = 0$  and  $\phi = 2\pi$  but in case of  $\phi = 0$  the matrix  $A$  is the unit matrix and in the second case, it has two  $(-1)$ s and one  $(+1)$  in its diagonal. Again recalling Eq. (37), this implies that the  $D$ -matrix is indeed diagonal and has in its diagonal numbers of norm 1. However, the most interesting fact is that  $D$  is not the unit matrix. In other words, the ADT matrix presented in Eq. (76) is not single-valued in CS although the corresponding diabatic *potential* matrix is single-valued, by definition (see Eqs. (145) and (146)). The fact that  $D$  has two  $(-1)$ s and one  $(+1)$  in its diagonal implies that the present  $\tau$ -matrix produces topological effects, as was explained in the last two paragraphs of Section 4.1: Two electronic eigenfunctions flip sign upon tracing a closed path and one electronic function remains with its original sign.

Much as the results in the last section 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. What we found is that even in this case  $D$  is not 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 11. However, the present  $\Delta\varepsilon=0$   $D$ -matrix is in contradiction with the  $D$ -matrix in Section 5.1.2 which was derived for a particular type of a  $3\times 3$   $\tau$ -matrix which also refers to a tri-fold 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 11 where we distinguished between breakable and unbreakable multi-degeneracy. The Cocchini et al. model [107] belongs, of course, to those models that yield the breakable degeneracy.

## 14. Summary and conclusions

Part of the subjects presented here have already been discussed in a previous review article [32b], but since the time that article was published not only was progress made but also, having gained perspective, we can now weight various ideas in a different way. Moreover, in this composition we have been able to verify some of the assumptions which, in previous publications, looked more like *ansatz*. In what follows, we shall summarize the main points.

(1) In the previous review article [32b], the diabatic framework was derived, employing projection operators, for a sub-space of a Hilbert space which was assumed to be decoupled from the remaining part of the Hilbert space. In other words, it was assumed that the coupling terms between the internal states of the SHS and outside states are zero. Here we showed that if these coupling terms are small enough, e.g. of  $O(\varepsilon)$  all equations derived for establishing the SHS diabatic presentation are correct to the  $O(\varepsilon^2)$  level. In particular, the diabatic potentials (as calculated by the present approach) are perturbed only to the second order. This important feature and the fact that the calculation of NACTs, once a formidable task, has recently become more of a routine [78,106] (although, still, very time consuming and quite approximate) make the combined approach an attractive procedure to eliminate the unpleasant NACTs and in this way to form the diabatic framework. We, also, briefly referred to other approaches [36–45] which were developed to achieve the same goal without explicitly employing the NACTs. Their obvious advantage is in avoiding the troublesome NACTs, however their accuracy cannot always be estimated and the extension to three (or more) states is not guaranteed.

(2) In the previous review article [29], the topological  $D$ -matrix was introduced. Here its topological features were presented in much more detail than before. We discussed the explicit connection between the number of  $(-1)$ s and their positions along the diagonal of this matrix with the particular electronic eigenfunctions that flip sign while tracing a closed contour. For instance one interesting finding is that only an *even* number of functions can flip sign and another one is, that in case of a multi-degeneracy, at most two functions will flip sign. As a by-product we derived the topological spin and discussed to some extent the idea of a new assignment for molecular systems.

(3) Another subject discussed at some length is the extended BO approximation. This type of the BO approximation, in contrast to the ordinary one, contains the effect of the NACTs.

In the previous review article [29], this approximation was presented for a two-state case. Here the derivation is extended to a model system of  $M$ -states. The extension can be accomplished if and only if the NACTs fulfill certain gauge conditions as discussed in Section 11. In contrast to the previous review we omitted the results of a numerical example. The numerical study for a two state and a tri-state model is described in Ref. [67].

(4) In the present review, we considered the case of multi-degeneracy (namely, situations where more than two states cross at one point in CS) and we distinguished between a *breakable* and an *unbreakable* degeneracy. The breakable degeneracy is formed by an aggregation of conical intersections which originally were located at different points in CS but, were, then, shifted one with respect to the other (for instance by varying one of the indirect coordinates of the molecular system) to form the one single point of degeneracy. The unbreakable degeneracy, is a situation where the multi-fold degeneracy is treated as a *fait accompli* (see Section 5.1). Within this context (i.e., the unbreakable degeneracy), we discussed to some extent the fact that the ADT matrix may become, for a certain chosen set of parameters, the corresponding Wigner's rotation matrix [71,72] (see Section 12).

(5) A few examples are presented in order to clarify the ideas and strengthen the confidence in the derivations and their outcome. For this sake we studied analytically various models (as presented in Section 5.1) and also solved, numerically, a well known tri-state model (see Section 13.2) which led to the first three calculated ADT-angles. This approach was also applied to realistic cases in particular to tri-atom molecules (as well as other types of tri-atom systems). One important example which was mentioned is the first successful application of the line integral approach to a realistic system for the  $H_3$  system [27]. A study of the  $H_3$  system and its isotopic analogs was also performed by Xu et al. [79], who pointed out the capability of the line integral to distinguish between (closed) contours that surround and do not surround a CI. Mebel et al. [80,81] considered the CIs between the two lowest states and between the second and the third states of the  $C_2H$  molecule. In particular, in the first study it was demonstrated that although the second state is strongly coupled to the third state the two lower *adiabatic* states can be transformed, *correctly*, to the corresponding two *diabatic* states. This can be accomplished because the two strong interaction regions (namely the interaction region between the first and the second states and the region between the second and the third states) do not overlap. In this way, the two-state 'Curl' condition is approximately fulfilled throughout CS (see Section 4.2) which ensures the single-valuedness of the resulting diabatic potentials.

We shall finish this review with some practical conclusions:

The subject of topological effects has its roots in the interesting studies of Longuet-Higgins (LH) and his collaborators [4–7]. The importance of these studies in revealing the unusual phenomenon related to the possible non-uniqueness of the electronic eigenfunctions in configuration space is incontrovertible. However, we question the way this subject was subsequently treated. Our main hesitation is connected with the ad hoc correction of the deficiency by the introduction of a phase factor to restore the uniqueness of the electronic wave function [5]. Such modifications, eventually, help to temporarily overcome encountered difficulties but then may cause confusion and prevent uncovering the real cause for the observed phenomenon. Indeed, for two or three decades, the LH phase was often treated as an independent self-standing entity and this in spite of the fact that no recipe was given for its calculation. In the present review,

it is shown that the LH phase has its origin in the NACTs and that it should be identified, in case of an isolated two-state system, with the ADT angle.

The study of NACTs has to be considered as an important topic in molecular systems. Nevertheless, the NACTs are still ignored in many studies mainly because of difficulties in obtaining them numerically. The inclusion of the NACTs will produce topological effects which may affect some of the measured magnitudes [34], but their main importance is that in many cases they couple adiabatic states to such an extent, that they cannot be treated as isolated states. This, however, does not imply that every time they show up they have to be incorporated. In order to be able to decide when NACTs have to be included and in what way to include them we first have to know their locations and to be aware of their spatial dependence. At this stage, it is accepted that the strong NACTs have their origin in a CI/PI. Here were presented means to expose the point of the CI/PI in given situations. Moreover, it was proved that, in case of a single CI/PI, they decrease as  $q^{-1}$ . However, information on their dependence on other nuclear coordinates is very scarce.

One of the most common ways to include NACTs is to transform to the diabatic framework. (In fact, this is the only way to guarantee their correct inclusion because not eliminating them from the SE enforces solving differential equations that contain singularities.) Indeed, there are many publications that report on numerical studies for diabatic potentials (a sample is also given here [17,31–33,36–45,48,79,97,109–125]) and a variety of methods were proposed to derive them, but the relevance of these potentials was only rarely tested. For instance, these potentials, when transformed back to the adiabatic framework, have to produce not only the correct adiabatic potentials but also the correct NACTs.

Finally, we would like to call attention to the recent study of the NACTs between the two lowest states of the  $C_2H$  system [80] already mentioned earlier. It was shown employing ab initio numerical results that immaterial which closed contour one may assume (large or small), the result of the two-state line integral is, either  $\sim 0.0$  or  $\sim \pi$ . This does not necessarily mean that the two-state system is decoupled from the other states, but it means that it is coupled with these higher states in such a way that the transformation to the (two-state) diabatic framework can be made by, simply, ignoring these additional coupling terms. In other words, the line integral approach is not only a way to produce the correct diabatic potentials but it also probes to what extent a given system of adiabatic states can be safely transformed to the diabatic framework.

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## 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 [8–10]:

$$\mathbf{W} = k \begin{pmatrix} y & x \\ x & -y \end{pmatrix},$$

where  $(x, y)$  are some generalized nuclear coordinates and  $k$  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 ADT matrix. In order to perform this derivation, we shall employ polar coordinates  $(q, \varphi)$ , namely:

$$y = q \cos \varphi \quad \text{and} \quad x = q \sin \varphi. \quad (\text{A.1})$$

Substituting for  $x$  and  $y$  we get  $\varphi$ -independent eigenvalues of the form

$$u_1 = kq \quad \text{and} \quad u_2 = -kq \quad \text{where } q = \{0, \infty\} \quad \text{and} \quad \varphi = \{0, 2\pi\}. \quad (\text{A.2})$$

As noticed from Fig. 10, the two surfaces  $u_1$  and  $u_2$  are cone-like PESs with a common apex. The corresponding eigenvectors are

$$\begin{aligned} \xi_1 &= \left( \frac{1}{\sqrt{\pi}} \cos \frac{\varphi}{2}, \frac{1}{\sqrt{\pi}} \sin \frac{\varphi}{2} \right), \\ \xi_2 &= \left( \frac{1}{\sqrt{\pi}} \sin \frac{\varphi}{2}, -\frac{1}{\sqrt{\pi}} \cos \frac{\varphi}{2} \right). \end{aligned} \quad (\text{A.3})$$

The components of the two vectors  $(\xi_1, \xi_2)$ , when multiplied by the electronic (diabatic) basis set  $(|\phi_1\rangle, |\phi_2\rangle)$ , form the corresponding electronic adiabatic basis set  $(|\eta_1\rangle, |\eta_2\rangle)$ :

$$\begin{aligned} |\eta_1\rangle &= \frac{1}{\sqrt{\pi}} \cos \frac{\varphi}{2} |\phi_1\rangle + \frac{1}{\sqrt{\pi}} \sin \frac{\varphi}{2} |\phi_2\rangle, \\ |\eta_2\rangle &= \frac{1}{\sqrt{\pi}} \sin \frac{\varphi}{2} |\phi_1\rangle - \frac{1}{\sqrt{\pi}} \cos \frac{\varphi}{2} |\phi_2\rangle. \end{aligned} \quad (\text{A.4})$$

The adiabatic functions are characterized by two interesting features: (a) they depend only on the angular coordinate (but not on the radial coordinate) and (b) they are not single-valued in CS because when  $\varphi$  is replaced by  $(\varphi + 2\pi)$ —a rotation which brings the adiabatic wave functions back to their initial position—*both* of them change sign. This last feature, which was revealed by LH [4–7], may be, in certain cases, very crucial because multi-valued electronic eigenfunctions cause the corresponding nuclear wave functions to be multi-valued as well, a feature which has to be incorporated explicitly (through specific boundary conditions) while

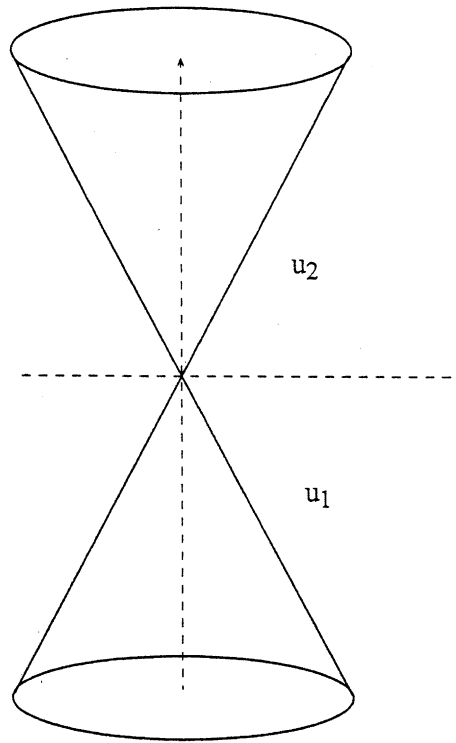


Fig. 10. The two interacting cones within the Jahn–Teller model.

solving the nuclear SE. In this respect, it is important to mention that ab initio electronic wave functions indeed, possess the multi-valuedness feature as described by LH [12].

One way to get rid of the multi-valuedness of the electronic eigenfunctions is by multiplying it by a phase factor [5], namely:

$$\zeta_j(\varphi) = \exp(i\alpha)\eta_j(\varphi), \quad j = 1, 2, \quad (\text{A.5})$$

where

$$\alpha = \varphi/2. \quad (\text{A.6})$$

It is noticed 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):

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

but since

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

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

$$\tau_{11}^{(1)} = i \nabla \alpha . \quad (\text{A.7})$$

In the same way, we obtain

$$\tau_{11}^{(2)} = i \nabla^2 \alpha - (\nabla \alpha)^2 . \quad (\text{A.8})$$

The fact that now  $\tau_{11}^{(1)}$  is not zero will affect the ordinary BO 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. (16) the ordinary BO equation:

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

because for real electronic eigenfunctions  $\tau_{11}^{(1)} \equiv 0$  but in the second case for which  $\tau_{11}^{(1)} \neq 0$  the BO-SE becomes

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

which can be considered as an extended BO approximation [19] for a case of a single isolated state expressed in terms of a complex electronic eigenfunction. This equation was interpreted for some time as the adequate SE to describe the effect of the Jahn–Teller CI which originates from the two interacting states. As it stands, it contains an effect due to an ad hoc phase related to a *single* (the lowest-state) electronic eigenfunction. Moreover, no prescription is given how to calculate it. If no other information is available it is inconceivable that this equation bears any relevance to non-adiabatic coupling effects [23].

## Appendix B. The sufficient conditions for having an analytic adiabatic-to-diabatic transformation matrix

The adiabatic-to-diabatic transformation matrix (ADT),  $A_P$ , fulfills the following first order differential vector equation (see Eq. (19)):

$$\nabla A_P + \tau_P A_P = 0 . \quad (\text{B.1})$$

In order for  $A_P$  to be a regular matrix at every point in the assumed region of CS, 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  $\tau_P$  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,  $A_P$  will have the above two features.

### B.1. Orthogonality

We start by proving that  $A_P$  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):

$$\nabla A_P^\dagger - A_P^\dagger \tau_P = 0, \quad (\text{B.2})$$

where we recall that  $\tau_P$ , the non-adiabatic coupling matrix, is a real antisymmetric matrix. Multiplying Eq. (B.2) from the right by  $A_P$  and Eq. (B.1) from the left by  $A_P^\dagger$  and combining the two expressions, we get

$$A_P^\dagger \nabla A_P + (\nabla A_P^\dagger) A_P = (\nabla A_P^\dagger A_P) = 0 \Rightarrow A_P^\dagger A_P = \text{Const}.$$

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

$$A_P^\dagger A_P = I. \quad (\text{B.3})$$

Thus  $A_P$  is a unitary matrix at any point in CS.

### B.2. 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  $A_P$  matrix fulfills Eq. (B.1) ensures the existence of derivatives to any order for any variable, at a given region in CS, if  $\tau_P$  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  $A_P$  matrix elements to be independent of the order.

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

$$\begin{aligned} \frac{\partial}{\partial p} A + \tau_p A &= 0, \\ \frac{\partial}{\partial q} A + \tau_q A &= 0. \end{aligned} \quad (\text{B.4})$$

Differentiating the first equation with respect to  $q$ , we find

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

or

$$\frac{\partial}{\partial q} \frac{\partial}{\partial p} A + \left( \frac{\partial}{\partial q} \tau_p \right) A - \tau_p \tau_q A = 0. \quad (\text{B.5a})$$

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

$$\frac{\partial}{\partial p} \frac{\partial}{\partial q} A + \left( \frac{\partial}{\partial p} \tau_q \right) A - \tau_q \tau_p A = 0 . \quad (\text{B.5b})$$

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

$$\left( \frac{\partial}{\partial p} \tau_q - \frac{\partial}{\partial q} \tau_p \right) A = (\tau_q \tau_p - \tau_p \tau_q) A \quad (\text{B.6})$$

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

$$\frac{\partial}{\partial p} \tau_q - \frac{\partial}{\partial q} \tau_p = [\tau_q, \tau_p] . \quad (\text{B.7})$$

Thus, in order for the  $A_P$  matrix to be analytic in a region, any two components of  $\tau_P$  have to fulfill Eq. (B.7). Eq. (B.7) can also be written in a more compact way:

$$\text{Curl } \tau_P = [\tau_P x \tau_P] , \quad (\text{B.8})$$

where  $x$  stands for a vector product.

The question to be asked is: Under what conditions (if at all) do the components of  $\tau_P$  fulfill Eq. (B.8)? In Ref. [17], it is proved that this relations holds for any full Hilbert space. Here we shall show that this relation holds also for the  $P$ -SHS of dimension  $M$ , as defined by Eq. (10) in Section 2.2. To show that we employ, again, the Feshbach projection operator formalism [30] (see Eqs. (11)).

We start by considering the  $p$ th and  $q$ th components of Eqs. (8) in Section 2.1:

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

$$\left( \frac{\partial \tau_p}{\partial q} \right)_{jk} = \left\langle \frac{\partial \zeta_j}{\partial q} \left| \frac{\partial \zeta_k}{\partial p} \right\rangle + \left\langle \zeta_j \left| \frac{\partial^2 \zeta_k}{\partial q \partial p} \right\rangle , \quad j, k \leq M . \quad (\text{B.9b})$$

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

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

Eq. (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:

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

Since for real functions:

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

we get for this matrix element the result:

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

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

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

Since under the summation sign each term is zero (no coupling between the inside and the outside subspaces—see Eq. (10) in Section 2.2—we finally get that

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

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

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

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  $\tau_p$  elements are analytic functions of the coordinates,  $A_p$  is an orthogonal matrix with elements which are analytic functions of the coordinates.

## Appendix C. On the single/multi-valuedness of the adiabatic-to-diabatic transformation matrix

In this appendix, we discuss the case where two components of  $\tau_p$ , namely  $\tau_p$  and  $\tau_q$  ( $p$  and  $q$  are the 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 ADT matrix *may* become multi-valued.

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

$$\begin{aligned} \frac{\partial}{\partial p} A_p + \tau_{p_p} A_p &= 0, \\ \frac{\partial}{\partial q} A_p + \tau_{p_q} A_p &= 0 . \end{aligned} \quad (\text{C.1})$$

In what follows, the subscript  $P$  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  $A(=A_P)$  at a final point  $Q(p, q)$  then one integral equation to be solved is

$$A(p, q) = A(p_0, q_0) - \int_{p_0}^p dp' \tau_p(p', q_0) A(p', q_0) - \int_{q_0}^q dq' \tau_q(p, q') A(p, q'). \quad (\text{C.2a})$$

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

$$\tilde{A}(p, q) = A(p_0, q_0) - \int_{q_0}^q dq' \tau_q(p_0, q') \tilde{A}(p_0, q') - \int_{p_0}^p dp' \tau_p(p', q) \tilde{A}(p', q). \quad (\text{C.2b})$$

In Eq. (C.2a), we derive the solution by solving it along the path  $\Gamma'$  characterized by two straight lines and three points (see Fig. 11a):

$$\Gamma': P(p_0, q_0) \rightarrow P'(p_0, q) \rightarrow Q(p, q) \quad (\text{C.3a})$$

and in Eq. (C.2b) by solving it along the path  $\Gamma''$  also characterized by two (different) straight lines and the three points (see Fig. 11b):

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

It is noticed that  $\Gamma$ , formed by  $\Gamma'$  and  $\Gamma''$  written schematically as:

$$\Gamma = \Gamma' - \Gamma'' \quad (\text{C.4})$$

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

$$p = p_0 + \Delta p, \quad q = q_0 + \Delta q$$

then  $\Delta p$  and  $\Delta q$  are small enough distances as required for the derivation.

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

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

where

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

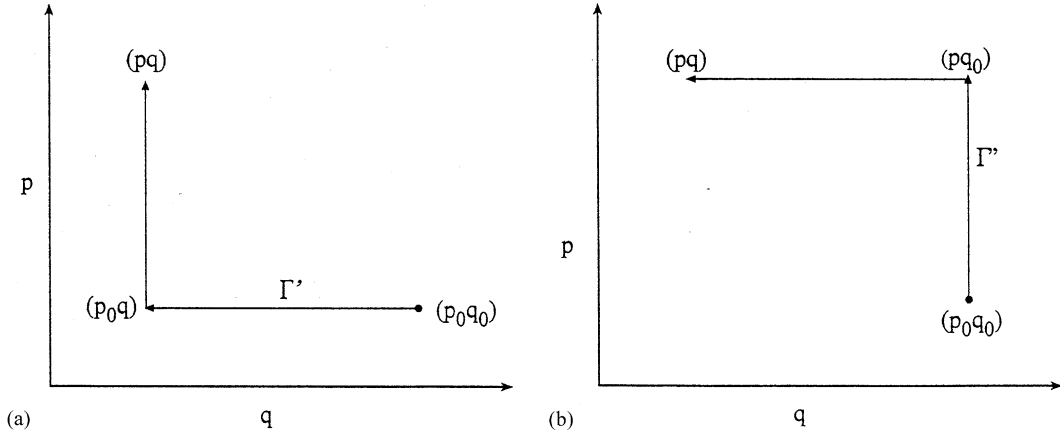


Fig. 11. The rectangular paths  $\Gamma'$  and  $\Gamma''$  connecting the points  $(p_0, q_0)$  and  $(p, q)$  in the  $(p, q)$  plane.

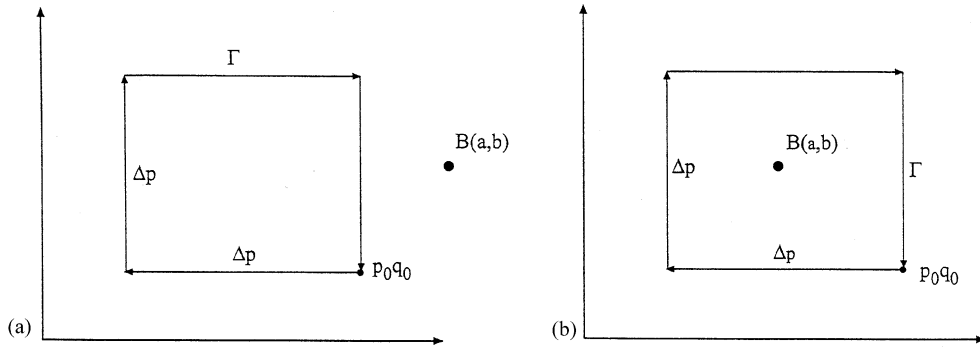


Fig. 12. The differential closed paths  $\Gamma$  and the singular point  $B(a, b)$  in the  $(p, q)$  plane: (a) The point  $B$  is not surrounded by  $\Gamma$ . (b) The point  $B$  is surrounded by  $\Gamma$ .

Next we consider two cases:

(a) The case where the point  $B(a, b)$  is not surrounded by the path  $\Gamma$  (see Fig. 12a). In this case, both  $\tau_p$  and  $\tau_q$  are *analytic* functions of the coordinates in the region enclosed by  $\Gamma$  and therefore the integrands of the two integrals can be replaced by the corresponding derivatives calculated at the respective intermediate points, namely:

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



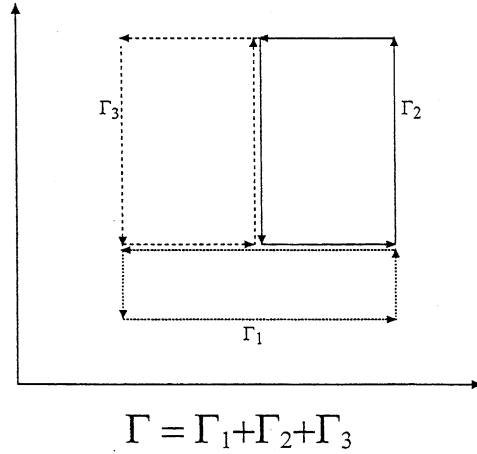


Fig. 13. The closed (rectangular) path  $\Gamma$  as a sum of three partially closed paths  $\Gamma_1, \Gamma_2, \Gamma_3$ .

To continue the derivation we recall that  $\Delta p$  and  $\Delta q$  are small enough so that the two integrands vary only slightly along the interval of integration so, that  $\Delta A$  becomes

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

Assuming again that all relevant functions are smooth enough the expression in the curled parentheses can be evaluated further to become:

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

where Eqs. (C.1) were used to express the derivatives of  $A(p, q)$ . Since the expression within the curled parentheses is identically zero due to Eq. (23),  $\Delta A$  becomes identically zero or in other words, the two infinitesimal paths  $\Gamma'$  and  $\Gamma''$  yield identical solutions for the  $A$  matrix. The same applies to ordinary (namely not necessarily small) closed paths because they can be constructed by ‘integrating’ over closed infinitesimal paths (see Fig. 13).

(b) The case when one of the differential closed paths surrounds the point  $B(a, b)$  (see Fig. 12b). Here the derivation breaks down at the transition from Eq. (C.5) to (C.7) and later, from Eq. (C.7) to (C.8), because  $\tau_p$  and  $\tau_q$  become infinitely large in the close vicinity of  $B(a, b)$  and therefore their 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  $\Gamma$  that surrounds the point  $B(a, b)$ . This closed path can be constructed from a differential path  $\Gamma_d$  that surrounds  $B(a, b)$ , a path  $\Gamma_p$  that does not surround  $B(a, b)$ , and a third, a connecting path  $\Gamma_i$ , which, also, does not surround  $B(a, b)$  (see Fig. 14). It is noted that the small region surrounded by  $\Gamma_d$  governs the features of the  $A$  matrix in the entire region surrounded by  $\Gamma$ , immaterial how large is  $\Gamma$ .

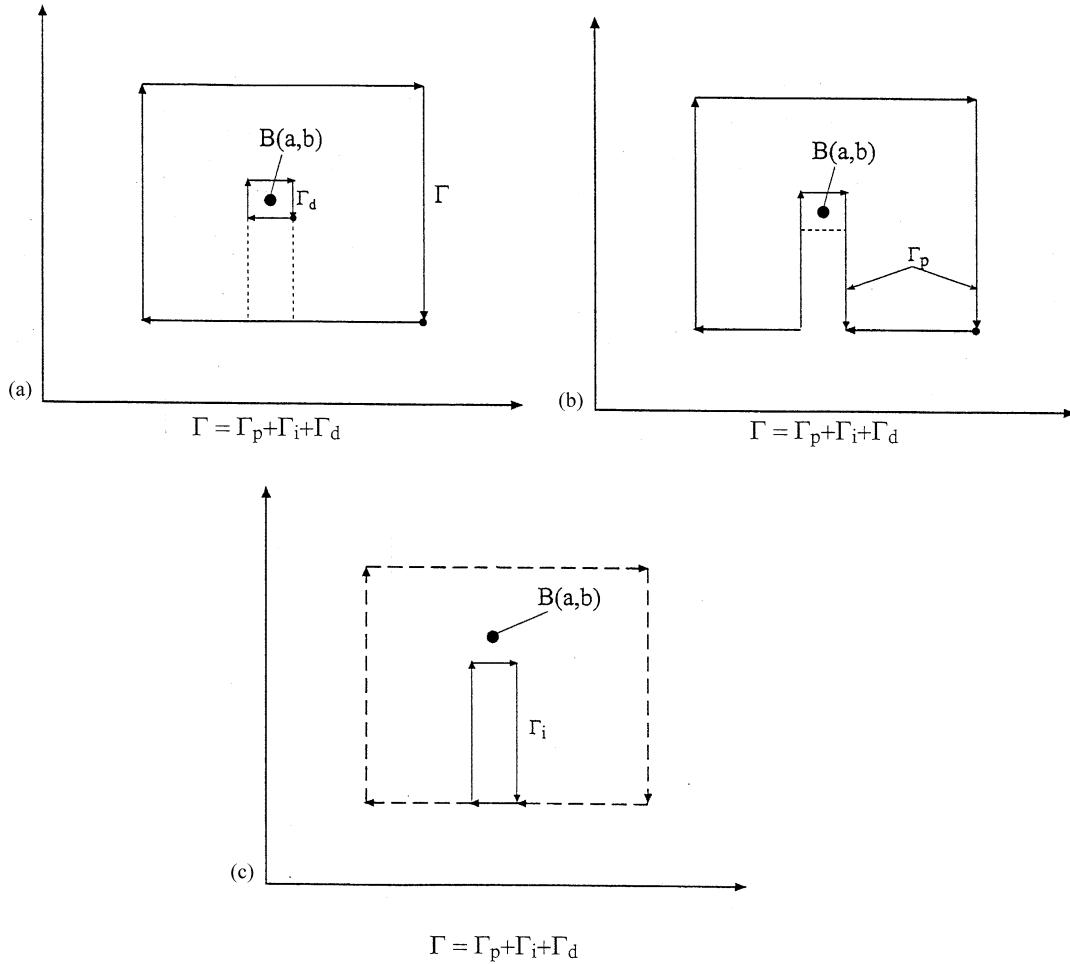


Fig. 14. The closed path  $\Gamma$  as a sum of three closed paths  $\Gamma_d, \Gamma_p, \Gamma_i$ . (a) The closed (rectangular) paths, i.e., the large path  $\Gamma$  and the differential path  $\Gamma_d$  both surrounding the singular point  $B(a,b)$ . (b) The closed path  $\Gamma_p$  which does not surround the point  $B(a,b)$ . (c) The closed path  $\Gamma_i$  which does not surround the point  $B(a,b)$ .

#### Appendix D. The diabatic representation

Our starting equation is Eq. (3) in Section 2.1 with one difference namely we replace  $\zeta_i(e|n)$  by  $\zeta_i(e|n_0)$ ,  $i = 1, \dots, N$ , where  $n_0$  stands for a fixed set of nuclear coordinates. Thus

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

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

$$(H_e(e|n_0) - u_i(n_0)) \zeta_i(e|n_0) = 0, \quad i = 1, \dots, N, \quad (\text{D.2})$$

where  $u_i(n_0)$ ,  $i = 1, \dots, N$  are the electronic eigenvalues at this fixed set of nuclear coordinates. Substituting Eq. (1) (of Section 2.1) and Eq. (D.1) in Eq. (2) yields the following expression:

$$\sum_{i=1}^N T_n \psi_i(n) |\zeta_i(e|n_0)\rangle + \sum_{i=1}^N \psi_i(n) [H_e(e|n) - E] |\zeta_i(e|n_0)\rangle = 0. \quad (\text{D.3})$$

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  $\langle \zeta_j(e|n_0)|$  and integrating over the electronic coordinates yields the following result:

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

Recalling

$$H_e(e|n) = T_e + u(e|n) \quad (\text{D.5})$$

and also

$$H_e(e|n_0) = T_e + u(e|n_0), \quad (\text{D.5}')$$

we can replace  $H_e(e|n)$  in Eq. (D.4) by the following expression:

$$H_e(e|n) = H_e(e|n_0) + \{u(e|n) - u(e|n_0)\}. \quad (\text{D.6})$$

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

$$\langle \chi_j(e|n_0) | H_e(e|n) | \chi_i(e|n_0) \rangle = u_j(n_0) \delta_{ji} + v_{ij}(n|n_0), \quad (\text{D.7})$$

where

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

Defining

$$V_{ij}(n|n_0) = v_{ij}(n|n_0) + u_j(n_0) \delta_{ji} \quad (\text{D.9})$$

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

$$\left( -\frac{1}{2m} \nabla^2 - E \right) \psi_j(n) + \sum_{i=1}^N V_{ji}(n|n_0) \psi_i(n) = 0. \quad (\text{D.10})$$

This equation can be also written in the matrix form

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

Here  $V$ , the diabatic potential matrix, in contrast to  $u$ , in Eq. (9) of Section 2.1, is a full matrix. Thus Eq. (D.11) is the SE within the diabatic representation.

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