

On the Conical Intersection and the Possibility of a New Assignment for Molecular Systems[†]

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In this article we discuss new ideas regarding the effect of conical intersections on a multielectronic adiabatic manifold of eigenfunctions: (a) The conical intersections are used to break up the Hilbert space into sub-Hilbert spaces by demanding that these subspaces do not have common conical intersections with each other (in other words electronic states belonging to different subspaces do not form conical intersections). (b) A new concept, the topological spin, is introduced; it is shown that its value is closely related to the number of (Jahn–Teller) conical intersections in a given sub-Hilbert-space and that the values of the components are related to the possible number of electronic eigenfunctions that flip sign while surrounding the conical intersections. (c) A geometrical description for the above-mentioned sign conversions is introduced, and it is, also, shown that this description agrees nicely with the results obtained from the topological matrix D . This geometrical, qualitative-type picture is supported by a quantitative analysis based again on the line integral.

I. Introduction

In our recent publications^{1–3} was revealed an interesting relation between the electronic nonadiabatic coupling terms and the diabatic potentials formed via the adiabatic-to-diabatic transformation (ADT). We found that if a certain electronic manifold can be isolated from the full Hilbert space, then the relevant ADT matrix, calculated along a *closed* contour in configuration space (CS), ‘returns to itself’ to guarantee that resulting *diabatic* potentials are uniquely defined in every point in CS. This finding, as derived for a general case, is interesting as such, but surprising results are obtained for some simplified models for which these findings led to ordinary *quantization conditions* with respect to nonadiabatic coupling terms, of the type introduced by Bohr and Sommerfeld almost a century ago.⁴ Once this fundamental relation was established we were able to perform more detailed studies of topological effects within molecular systems. In this respect topological effects are defined as the number of electronic eigenfunctions that flip sign while the electronic manifold traces a closed loop.

One of the main difficulties in molecular physics is to be able to define rigorous sub-Hilbert spaces (SHS). There were several attempts to do that, but the borders of these SHSs were, rigorously, not satisfying.^{3,5,6} It is important to emphasize that without being able to form finite SHSs, it is not only that the study of topological effects will be harmed, but, in fact, the entire field of molecular physics will be doomed. In the next section we shall present a new approach which enables a rigorous study of topological effects, but we think that this approach can be a solution for other purposes as well.

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 $\Delta E(R = R_0) = E_2(R = R_0) - E_1(R = R_0) \cong 0$ 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^{7–11} and the second is based on the Demkov approach.¹² 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.^{13–16} We shall also include the Renner–Teller parabolic intersection (PI),^{17,18} 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 degeneracy point. The distinction between the (extended) LZ situation and the Demkov situation enables the rigorous construction of SHS as will be presented in the following section.

For the sake of completeness, we present, in sections III and IV, respectively the ADT^{19,20} matrix and the topological matrix,^{1–3} which contains the topological information related to a given closed contour.

Another subject that will be discussed to some extent is the fact that the existence of CIs leads to a situation where knowledge of the electronic manifold is not sufficient to characterize a molecular system. The fact that CIs cause electronic eigenfunctions to be multivalued makes it necessary to determine the size of the relevant SHS and the number of CIs it contains. This necessity leads to the introduction of a topological spin which is proposed for a further assignment of the molecular system. This subject is discussed in section V and its geometrical interpretation in section VI. Section VII is devoted to topological effects in case two CIs coincide, namely, when three surfaces have their CIs at the same point. Conclusions are given in the last section.

The subject of topological effects caused by electronic nonadiabatic coupling is not new and goes back to studies by Longuet-Higgins and his colleagues^{21,22} in particular to the Herzberg–Longuet-Higgins 1975 paper.²² Although this subject attracted some attention for about a decade,^{5,6} it became of minor interest for chemists later on (although it attracted interest among physicists due to Berry’s seminal 1984 paper).²³ It was only

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due to Kuppermann and his colleagues^{24,25} that this subject earned, recently, renewed attention. At the beginning of the 1990s, Kupperman et al. published their state-to-state integral and differential cross sections for the various triatom hydrogenic reactive systems, presenting the nuclear wave functions in terms of antiperiodic basis sets. By doing that they showed that some of these cross sections, at certain energies, are governed by topological effects.²⁵

II. Construction of Sub-Hilbert Spaces

In our recent articles we suggested^{1–3} reconsidering the almost well-established belief that the electronic manifold is an unbreakable system of electronic adiabatic eigenfunctions which form a full Hilbert space.²⁶ In general it may not be easy to contradict this claim because, indeed, almost every state interacts with any other state to some extent. The question is only whether we can distinguish between the intensity of the various interactions. In other words: is there a criterion according to which we can form subsets of functions that strongly interact with each other but interact rather “weakly” with the states belonging to other subsets? Hence it was suggested to probe the nonadiabatic coupling terms with the aim of finding such a criterion. 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 (only consecutive states can form CIs and/or PIs). The two types of intersections are characterized by the fact that the nonadiabatic coupling terms, at the points of the intersections, 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 “know” of each other.) Based on what was said so far we shall, accordingly, form L SHSs of varying sizes N_P , $P = 1, \dots, L$.

Before we continue with the construction of the SHSs we would like to make the following comment: Usually, when two given states form CIs and/or PIs, one thinks of isolated points in CS. In fact, CI/PIs are not isolated 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.

We start by introducing the electronic nonadiabatic coupling terms τ_{ij} , defined as

$$\tau_{ij} = \langle \zeta_i | \nabla \zeta_j \rangle \quad (1)$$

where ζ_k , $k = i, j$ is the k th electronic adiabatic eigenfunction and ∇ is the grad operator (the bra and the ket notation is applied for integration with respect to the electronic coordinates). In what follows we distinguish between two kinds of nonadiabatic coupling terms: (a) intra nonadiabatic coupling terms $\tau_{ij}^{(P)}$ which are formed between two eigenfunctions belonging to a given SHS, namely, the P th SHS

$$\tau_{ij}^{(P)} = \langle \zeta_i^{(P)} | \nabla \zeta_j^{(P)} \rangle; \quad i, j = 1, \dots, N_P \quad (2)$$

and (b) inter nonadiabatic coupling terms $\tau_{ij}^{(P,Q)}$ which are formed between two eigenfunctions belonging to two different SHSs, namely, the P th SHS and the Q th SHS

$$\tau_{ij}^{(P,Q)} = \langle \zeta_i^{(P)} | \nabla \zeta_j^{(Q)} \rangle; \quad i = 1, \dots, N_P \quad j = 1, \dots, N_Q \quad (3)$$

The P th SHS is defined through the following requirements:

Each *pair* of consecutive states, namely, the j th and the $(j + 1)$ th, belonging to the P th SHS, form, at least at one point in CS, a CI^{14–16} or a PI.^{17,18}

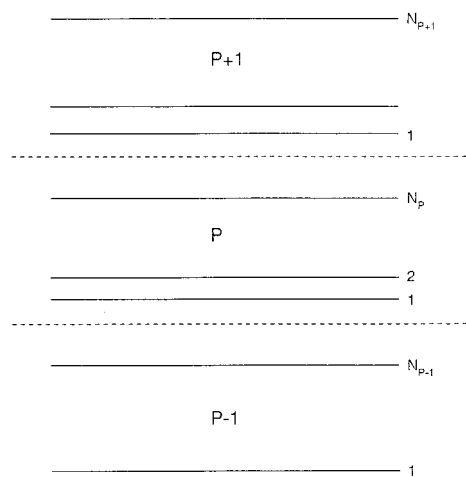


Figure 1. Schematic picture describing the three consecutive sub-Hilbert spaces, namely, the $(P - 1)$ th, the P th, and the $(P + 1)$ th. The dotted lines are separation lines.

The size of the P th SHS is determined in such a way that the lowest (the first) state and the highest (the N_P th) state do not form CIs or PIs with their corresponding neighbors belonging to the $(P - 1)$ th SHS and the $(P + 1)$ th SHS, respectively (see Figure 1). In other words the two nonadiabatic coupling terms

$$\tau_{N_{P-1}}^{(P-1,P)} \quad \text{and} \quad \tau_{N_P}^{(P,P+1)} \quad (4)$$

are assumed not to become singular in any point in CS.

III. Adiabatic-to-Diabatic Matrix

It was shown, employing projection operators,³ that the Born–Oppenheimer treatment yields for each SHS the following set of coupled adiabatic Schroedinger equations (SE):

$$-\frac{1}{2m}(\nabla + \tau^{(P)})^2 \Psi^{(P)} + (u^{(P)} - E)\Psi^{(P)} = 0 \quad (5)$$

where $u^{(P)}$ is a diagonal matrix which contains the above-mentioned N_P adiabatic potential energy surfaces and $\Psi^{(P)}$ is a column vector which contains the relevant adiabatic nuclear wave functions $\psi_j^{(P)}$; $j = 1, \dots, N_P$ (see also refs 5 and 6).

To study the topological features of the P th SHS, it is essential first to obtain the adiabatic-to-diabatic transformation (ADT) matrix $\mathbf{A}^{(P)}$: Thus if $\Phi^{(P)}$ is the column vector which contains the *diabatic* nuclear wave functions (these are the solutions to the corresponding diabatic SE), the $\mathbf{A}^{(P)}$ -matrix is defined through the relation

$$\Psi^{(P)} = \mathbf{A}^{(P)} \Phi^{(P)} \quad (6)$$

One can show, again employing projection operators, that for each separate SHS, the corresponding \mathbf{A} -matrix fulfills the following first-order differential equation:^{3,19,20}

$$\nabla \mathbf{A} + \tau \mathbf{A} = 0 \quad (7)$$

where τ is an antisymmetric matrix with the elements defined in eq 2. In what follows we drop the subscript P and discuss one particular SHS of dimension N . (Since many referees and others questioned the existence of a solution for this equation we presented in Appendix I of ref 38 a detailed discussion on this subject. Still for the sake of completeness we say the following: A valid solution for this equation can be derived

along a given contour, if and only if along this contour the corresponding Curl condition¹⁹ is fulfilled. In all our theoretical publications it was assumed that this condition is satisfied)

The more relevant feature of the \mathbf{A} -matrix, for our purposes, is the fact that it also transforms the electronic adiabatic basis set, ζ , to the electronic diabatic basis set, χ :¹⁹

$$\chi = \mathbf{A}\zeta \quad (8)$$

In what follows we show that topological effects become apparent through this transformation.

To solve eq 7 one has to assume a path (contour), Γ , and a solution will be obtained for this particular path. If s and s_0 are two points on this path, we find for $\mathbf{A}(s)$ the result:^{1-3,27,28}

$$\mathbf{A}(s) = \exp\left(-\int_{s_0}^s ds \cdot \boldsymbol{\tau}\right) \mathbf{A}(s_0) \quad (9)$$

where ds is a differential vector along the path, the dot stands for a scalar product, and $\mathbf{A}(s_0)$ is a given initial or boundary value. The solution in eq 9 is well-defined along this particular path as long as the elements of the $\boldsymbol{\tau}$ -matrix are analytic functions in the close vicinity of the path. Next we introduce the \mathbf{D} -matrix defined as¹⁻³

$$\mathbf{D} = \exp\left(-\oint_{\Gamma} ds \cdot \boldsymbol{\tau}\right) \quad (10)$$

which by its definition is only dependent on the path Γ . As will be shown, this matrix contains the topological features of the system and was therefore is termed the *topological* matrix.³

The next subject is the diabatic potential matrix $\mathbf{W}(s)$ that follows from the ADT given in eq 7: namely,

$$\mathbf{W}(s) = \mathbf{A}^\dagger(s) u(s) \mathbf{A}(s) \quad (11)$$

where \mathbf{A}^\dagger is the complex conjugate of \mathbf{A} . The main feature that will be used in the ongoing presentation is the uniqueness of $\mathbf{W}(s)$. Thus it is assumed that at each point in CS $\mathbf{W}(s)$ attains one single value, or, in other words $\mathbf{W}(s)$ is uniquely defined throughout CS.

As a final point in this section and mainly for the sake of completeness we shall introduce the diabatic SE. Replacing Ψ in eq 5 by Φ (see eq 6) and recalling eq 7 yield the diabatic SE:

$$-\frac{1}{2m} \nabla^2 \Phi + (\mathbf{W} - E) \Phi = 0 \quad (12)$$

where \mathbf{W} is a full potential matrix. It is important to emphasize that eq 12 can be solved only when $\mathbf{W}(s)$ is *uniquely* defined throughout CS.

IV. Topological Matrix

The \mathbf{D} -matrix is defined in eq 7 and it is noticed that its definition is based on a closed path Γ . Thus let us consider such a path, defined in terms of a continuous parameter λ , so that the starting point s_0 of the path is at $\lambda = 0$. Next we define β as the value attained by λ once the path completes a full cycle and returns to its starting point. Thus, for instance, in case of a circle, λ is an angle and $\beta = 2\pi$.^{1,2}

Having introduced these definitions we can now express our assumption regarding the uniqueness of $\mathbf{W}(s, s_0)$ in the following way: At *each point* s_0 in CS the diabatic potential matrix $\mathbf{W}(\lambda)$ ($\equiv \mathbf{W}(s, s_0)$) has to fulfill the relation:

$$\mathbf{W}(\lambda = 0) = \mathbf{W}(\lambda = \beta) \quad (13)$$

Following eq 11 this requirement implies that for every point s_0 we have

$$\mathbf{A}^\dagger(0) u(0) \mathbf{A}(0) = \mathbf{A}^\dagger(\beta) u(\beta) \mathbf{A}(\beta) \quad (14)$$

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

$$\mathbf{B} = \mathbf{A}(\beta) \mathbf{A}^\dagger(0) \quad (15)$$

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

$$u(\beta) = \mathbf{B} u(0) \mathbf{B}^\dagger \quad (16)$$

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

Since the adiabatic eigenvalues are uniquely defined at each point in CS, we have $u(0) \equiv u(\beta)$, and therefore eq 16 implies the existence of the following commutation relation:

$$[\mathbf{B}, u(0)] = 0 \quad (17)$$

Equation 17 yields the following system of equations between the adiabatic eigenvalues $u_j(0)$ and the \mathbf{B} -matrix elements:

$$\sum_{j=1}^M (\mathbf{B}_{kj}^* \mathbf{B}_{kj} - \delta_{kj}) u_j(0) = 0 \quad (18)$$

Equation 18 has to hold at every arbitrary point s_0 ($\equiv \lambda = 0$) on the path Γ and for an essential, arbitrary set of nonzero adiabatic eigenvalues, $u_j(s_0)$; $j = 1, \dots, N$. Due to the arbitrariness of s_0 (and therefore also of the set $u(s_0)$), eq 18 can be satisfied, if and only if, the \mathbf{B} -matrix elements fulfill the relation

$$\mathbf{B}_{kj}^* \mathbf{B}_{kj} = \delta_{kj}; \quad j, k \leq M \quad (19)$$

or

$$\mathbf{B}_{kj} = \delta_{kj} \exp(i\eta_k) \quad (20)$$

Thus \mathbf{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 singled-valued, i.e., nondegenerate along the path Γ). In case of real eigenfunctions the matrix \mathbf{B} contains in its diagonal (+1)s and (-1)s. The number of (-1)s is the main subject of the article.

Recalling eq 15, we obtain that

$$\mathbf{A}(\beta) = \mathbf{B} \mathbf{A}(0) \quad (21)$$

Equation 21 is similar to eq 9; it becomes identical if we close the contour so that the upper limit of the integral becomes s_0 and identify \mathbf{B} with \mathbf{D} as defined in eq 10. Therefore the features just derived for \mathbf{B} , namely, its being diagonal, having only (+1)s and (-1)s in the diagonal, and in particular fulfilling eq 21, will apply to \mathbf{D} as well. In addition, based on its derivation in the previous section, we know that \mathbf{D} depends only on the contour along which it is calculated but does not depend on any particular point on this contour. Rewriting eq 21 gives

$$\mathbf{A}(\beta) = \mathbf{D} \mathbf{A}(0) \quad (22)$$

It is noticed that \mathbf{D} transforms $\mathbf{A}(0)$ to \mathbf{A} at the same point, namely, $\mathbf{A}(\beta)$ as calculated from eq 7 (or eq 9) following the integration along the same closed contour. However, since \mathbf{D}

does not have to be the unit matrix and since $\lambda = 0$ and $\lambda = \beta$ describe the same point in CS, eq 22 implies that $\mathbf{A}(s)$ is not necessarily uniquely defined in CS. This, eventually, could be an unpleasant situation, but since the diabatic potential matrix $\mathbf{W}(s)$, for which the diabatic SE (see eq 12) has to be solved, is uniquely defined in space, no difficulties are expected.

Our next task is to reveal the meaning of (-1) s in the diagonal of matrix \mathbf{D} . For that purpose we consider eq 8 and assume that $\mathbf{A}(s_0)$ is the unit matrix. Replacing, in eq 8, matrix \mathbf{A} by matrix \mathbf{D} , namely,

$$\chi = \mathbf{D}\zeta \quad (8')$$

yields the following χ -functions:

$$\chi_j = \pm \zeta_j; \quad j = 1, \dots, N \quad (23)$$

namely, \mathbf{D} transforms the original ζ -adiabatic eigenfunctions back on themselves but with some of the functions flipping their sign. It is to be remembered that diabatic eigenfunctions are single valued in CS. Moreover, if \mathbf{D} contains K (-1) s in its diagonal then, due to the transformation in eq 8', K functions flip sign. Making the electronic manifold trace different (closed) contours several things can happen: (1) A different number of functions may flip signs, or, in other words, K may vary. (2) It also may happen, whether K varies or not, that a *different* set of functions may flip sign. Thus the conclusion is that altogether the electronic manifold might be multivalued and the rate of increase in the multivaluedness, as will be discussed later, depends on the number of CIs.

The fact that an adiabatic electronic wave function flips its sign while following a closed contour is called a topological effect. Since the \mathbf{D} -matrix contains the information regarding the number of functions that flip sign, the \mathbf{D} -matrix will be defined as the *topological matrix*.

V. Derivation of the Topological Matrix

To derive the topological matrix we first have to obtain the ADT matrix, \mathbf{A} , as introduced in eq 8. Since \mathbf{A} is a real unitary matrix it can be expressed in terms of cosine and sine functions of given angles.^{20,29,30} We shall, first, briefly consider the two special cases with $N = 2$ and 3.

In case of $N = 2$ the matrix \mathbf{A}^2 takes the form

$$\mathbf{A}^{(2)} = \begin{pmatrix} \cos \gamma_{12} & \sin \gamma_{12} \\ -\sin \gamma_{12} & \cos \gamma_{12} \end{pmatrix} \quad (24)$$

where γ_{12} , the ADT angle, can be shown to be¹⁹

$$\gamma_{12} = \int_{s_0}^s \tau_{12}(s') ds' \quad (25)$$

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

$$\alpha_{12} = \oint_{\Gamma} \tau_{12}(s') ds' \quad (25')$$

the corresponding $\mathbf{D}^{(2)}$ matrix becomes accordingly:

$$\mathbf{D}^{(2)} = \begin{pmatrix} \cos \alpha_{12} & \sin \alpha_{12} \\ -\sin \alpha_{12} & \cos \alpha_{12} \end{pmatrix} \quad (24')$$

Since $\mathbf{D}^{(2)}$ has to be, for any closed contour, 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 $\mathbf{D}^{(2)}$ are as follows:

$$\mathbf{D}^{(2)} = (-1)^n \mathbf{I} \quad (26)$$

where \mathbf{I} is the unit matrix. The case where n is an odd number is recognized as the Jahn–Teller case.^{13–16} The reason is that in this case $K = 2$, and therefore, according to our analysis in the previous section, the two eigenfunctions ζ_1 and ζ_2 flip signs for this particular closed contour.²² From other numerous studies it is well-known that this happens when the contour surrounds a conical intersection (for a detailed study on this subject see ref 31). In case the contour does not surround any CI³² or surrounds a PI,^{9,10} n must be an even number (or zero) and no eigenfunction flips its sign.

The case of $N = 3$ is somewhat more complicated because the corresponding orthogonal matrix is expressed in terms of three angles, namely, γ_{12} , γ_{13} , and γ_{23} . This case was recently studied by us³³ in detail and here we will briefly repeat the main points.

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

$$\mathbf{Q}_{13}^{(3)}(\gamma_{13}) = \begin{pmatrix} \cos \gamma_{13} & 0 & \sin \gamma_{13} \\ 0 & 1 & 0 \\ -\sin \gamma_{13} & 0 & \cos \gamma_{13} \end{pmatrix} \quad (27)$$

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

$$\mathbf{A}^{(3)} = \mathbf{Q}_{12}^{(3)} \mathbf{Q}_{23}^{(3)} \mathbf{Q}_{13}^{(3)} \quad (28)$$

or, following the multiplication, the more explicit form

$$\mathbf{A}^{(3)} = \begin{pmatrix} c_{12}c_{13} - s_{12}s_{23}s_{13} & s_{12}s_{23} & c_{12}s_{13} + c_{12}s_{23}c_{13} \\ -s_{12}c_{13} - c_{12}s_{23}s_{13} & c_{12}c_{23} & -s_{12}s_{13} + c_{12}s_{23}c_{13} \\ -c_{23}s_{13} & -s_{23} & c_{23}c_{13} \end{pmatrix} \quad (29)$$

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 7:^{20,29}

$$\nabla \gamma_{12} = -\tau_{12} - \tan \gamma_{23}(-\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12})$$

$$\nabla \gamma_{23} = -(\tau_{23} \cos \gamma_{12} + \tau_{13} \sin \gamma_{12})$$

$$\nabla \gamma_{13} = -(\cos \gamma_{23})^{-1}(-\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12}) \quad (30)$$

These equations were integrated, for a model potential and for fixed values of the radial coordinate ρ , along the angular interval $0 \leq \varphi \leq 2\pi$. The φ -dependent γ 's, for various values ρ and $\Delta\epsilon$ are presented in Figure 2. $\Delta\epsilon$ 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., $\rho = 0$. In case $\Delta\epsilon = 0.0$ all three states become degenerate at the origin. The relevant $\mathbf{D}^{(3)}$ -matrix is obtained from $\mathbf{A}^{(3)}$ by replacing, in eq 29, the angle γ_{ij} with α_{ij} where

$$\alpha_{ij} = \gamma_{ij}(\varphi = 2\pi) \quad (31)$$

As is noticed from Figure 2 the values of α_{ij} are either zero or π . A brief analysis of eq 29, for these values of α_{ij} , shows that $\mathbf{D}^{(3)}$ is a diagonal matrix with two (-1) s and one $(+1)$ in the diagonal. This result can be generalized in the following way: Since the $\mathbf{D}^{(3)}$ -matrix will become diagonal if and only if

$$\alpha_{ij} = n_{ij}\pi \quad (31')$$

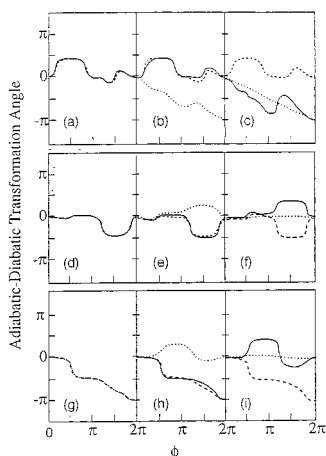


Figure 2. Three adiabatic–diabatic–transformation angles $\gamma_{ij}(\varphi|\rho)$ (obtained by solving eqs 30) as a function φ calculated for different values of ρ (and $\Delta\epsilon$). Here ρ is a radial coordinate with respect to the assumed origin but serves as a parameter (not a variable) and all calculations are done for fixed ρ -values. As for $\Delta\epsilon$, it 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., $\rho = 0$. (In the case $\Delta\epsilon = 0.0$, all three states are degenerate at the origin.) For more clarifications, see ref 33. (a) $\theta = \theta_{12}$, $\Delta\epsilon = 0.0$; (b) $\theta = \theta_{12}$, $\Delta\epsilon = 0.05$; (c) $\theta = \theta_{12}$, $\Delta\epsilon = 0.25$; (d) $\theta = \theta_{23}$, $\Delta\epsilon = 0.0$; (e) $\theta = \theta_{23}$, $\Delta\epsilon = 0.05$; (f) $\theta = \theta_{23}$, $\Delta\epsilon = 0.25$; (g) $\theta = \theta_{13}$, $\Delta\epsilon = 0.0$; (h) $\theta = \theta_{13}$, $\Delta\epsilon = 0.05$; (i) $\theta = \theta_{13}$, $\Delta\epsilon = 0.25$. (—) $\rho = 0.01$; (---) $\rho = 0.1$; (- - -) $\rho = 0.5$.

the diagonal terms can, explicitly, be represented as

$$\mathbf{D}_{ij}^{(3)} = \delta_{ij} \cos \alpha_{jn} \cos \alpha_{jm}; \quad j \neq n \neq m; \quad j = 1, 2, 3 \quad (32)$$

This presentation shows, unambiguously, that the $\mathbf{D}^{(3)}$ -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 VI).

Before moving to the general case we would like to refer to our choice of the rotation angles. It is well noticed that they differ from the ordinary *Euler* angles, which are routinely used whenever a general 3-dimensional orthogonal matrix is discussed.³⁴ In fact we could apply the Euler angles for this purpose and get identical results for $\mathbf{A}^{(3)}$ (and for $\mathbf{D}^{(3)}$). The main reason we prefer the “democratic” choice (with respect to the angles) is that this set of angles can be extended to an arbitrary value of \mathbf{N} without any difficulty as will be done next.

The matrix $\mathbf{A}^{(N)}$ will be written as a product of elementary rotation matrixes similar to the one given in eq 28:

$$\mathbf{A}^{(N)} = \prod_{i=1}^{N-1} \prod_{j>i}^N Q_{ij}^{(N)}(\gamma_{ij}) \quad (33)$$

where $Q_{ij}^{(N)}(\gamma_{ij})$ (see eq 27) is an $N \times N$ matrix, which in its (ii) and (jj) positions in the diagonal are the two relevant cosine functions and the rest of the $(N - 2)$ elements are (+1)’s, in the (ij) and (ji) off-diagonal positions we have the two relevant \pm sine functions and the rest are zeros. From eq 33 it can be seen that the number of matrixes contained in this product is $N(N - 1)/2$ and that this is also the number of independent γ_{ij} -angles which are needed to describe an $N \times N$ unitary matrix (we recall that the missing $N(N + 1)/2$ conditions follow from the orthogonality and normality conditions). The matrix $\mathbf{A}^{(N)}$ as presented in eq 33 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. For a rigorous proof see Appendix I. These two features will lead to conditions to be imposed on the various γ_{ij} -angles to ensure that the topological matrix, $\mathbf{D}^{(N)}$, is diagonal (and all its diagonal elements are of norm 1) as discussed in the previous section.

To obtain the γ_{ij} -angles one usually has to solve the relevant first-order differential equations of the type given in eq 30. Next, like before, the α_{ij} -angles are defined as the γ_{ij} -angles at the end of a closed loop. To obtain the matrix $\mathbf{D}^{(N)}$ all one has to do is to replace, in eq 33, the angles γ_{ij} by the corresponding α_{ij} -angles. Since $\mathbf{D}^{(N)}$ has to be a *diagonal* matrix with (+1)s and (−1)s in the diagonal, this can be achieved if and only if all α_{ij} -angles are multiples of π (see eq 31’). It is straightforward to show that with this structure the elements of $\mathbf{D}^{(N)}$ become

$$\mathbf{D}_{ij}^{(N)} = \delta_{ij} \prod_{k \neq i}^N \cos \alpha_{ik} = \delta_{ij} (-1)^{\sum_{k \neq i} n_{ik}}; \quad i = 1, \dots, N \quad (34)$$

where n_{ik} are integers and we have $n_{ik} = n_{ki}$. From eq 20 it is noticed that along the diagonal of \mathbf{D} we may encounter K numbers which are equal to (−1) and $(N - K)$ numbers which are equal to (+1). We recall that K is also equal to the *number of electronic eigenfunctions which flip sign when tracing a closed contour around one CI or more*. It is important to emphasize that in case a contour does not surround any CI (but may surround one or more PIs) the value of $K = 0$.

VI. Topological Spin

Before we continue, two matters have to be clarified in order to avoid confusion: (a) We distinguished between two types of LZ situations, which form (in two dimensions) the Jahn–Teller CI and the Renner–Teller PI. (Thus, if the subset contains N_J CIs and N_R PIs then N , the dimension of the SHS, is $N = N_J + N_R + 1$.) 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 SHS, is not its dimension N but N_J , the number of CIs. (b) In general one may encounter more than one CI between *two* given states. Nevertheless, the above-defined number, N_J , will not be affected by that and will remain the same. In other words $(N_J + 1)$ stands for the *number of states* that form the CIs.

In the present treatment we assume, for simplicity, that any two (consecutive) states have one CI only; the extension to the more general case is relatively straightforward and will not affect any of the findings below.

So far we introduced three different integers N , N_J , and K . As mentioned earlier, indeed, N is a characteristic number of the SHS but is not relevant for topological effects, instead N_J , as just mentioned, is a characteristic number of the SHS and relevant for topological effects, and K , the number of eigenstates that flip sign while the electronic manifold traces a closed loop, is relevant for topological effects but may vary from one path to another and therefore is not, as such, a characteristic feature for a given SHS.

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 above that when $N_J = 1$ we have two sign conversions, in the case where the loop surrounds the CI,²² and no conversion of signs

when the loop does not surround the CI.³² 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 either equal to 2 or zero (for details see Appendix II). 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

$$K = \{0, 2, \dots, K_J\} \begin{cases} K_J = N_J; & N_J = 2p \\ K_J = (N_J + 1); & N_J = 2p + 1 \end{cases} \quad (35)$$

where p is an integer (in deriving eq 35 it is assumed that two consecutive surfaces have, *at most*, one conical intersection).

The proof is based on calculating the possible numbers of (-1) s in the various **D**-matrixes and recalling that this number is equal to the number of sign-conversions as discussed in Appendix II. Let us assume that a certain closed path yields a set of α_{ij} -angles which produce the number K (see eq 34). Next we consider a slightly different path, along which one of these α_{ij} 's, say α_{st} , changed its value from zero to π . From eq 34 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 path, positive then changing α_{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 were positive and the other negative, then changing α_{st} from $0 \rightarrow \pi$ would not affect K . Thus, for all N (or N_J), the various K values *differ* from each other by even integers only. Now since any set of K 's contains also 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 as presented in eq 34.

The fact that eigenfunctions may flip sign along closed contours hints at the possibility that these sign conversions are related to a kind of 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.³⁵ Here we encounter, to some extent, a similar situation: A system of particles (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 multivalued. For instance, in the case of two (isolated) CIs, we may encounter at a given point in CS four different sets of eigenfunctions (see Appendix II):

$$\begin{aligned} \text{(a)} & (\zeta_1, \zeta_2, \zeta_3); & \text{(b)} & (-\zeta_1, -\zeta_2, \zeta_3); & \text{(c)} & (\zeta_1, -\zeta_2, -\zeta_3); \\ & & \text{(d)} & (-\zeta_1, \zeta_2, -\zeta_3) \end{aligned} \quad (36)$$

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

In refs 1 and 2 we showed that in a two-state system the nonadiabatic coupling term, τ_{12} , has to be "quantized" in the following way:

$$\oint_{\Gamma} \tau_{12}(s') ds' = n\pi \quad (37)$$

where n is an integer (in order to guarantee that the 2×2 diabatic potential be single-valued in configuration space). Thus each (isolated) conical intersection can be considered as a "spin". Since in a given sub-Hilbert space N_J conical intersections are encountered, we could define the spin, J , of this subspace as $(N_J/2)$. However, this definition may lead to more sign flips than we actually encounter (see next section). To make a connection between J and N_J as well as with the "magnetic components" M of J and the number of the actual sign flips, the spin J has to be defined as

$$J = \frac{1}{2} \frac{K_J}{2}, \begin{cases} K_J = N_J; & N_J = 2p \\ K_J = (N_J + 1); & N_J = 2p + 1 \end{cases} \quad (38a)$$

and, accordingly, the various M -values will be defined as

$$M = J - K/2; \quad \text{where } K = \{0, 2, \dots, K_J\} \quad (38b)$$

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

$$\begin{aligned} \text{for } N_J = 0 & \quad \{J = 0; \quad M = 0\} \\ \text{for } N_J = 1 & \quad \{J = 1/2; \quad M = 1/2, -1/2\} \\ \text{for } N_J = 2 & \quad \{J = 1/2; \quad M = 1/2, -1/2\} \\ \text{for } N_J = 3 & \quad \{J = 1; \quad M = 1, 0, -1\} \\ \text{for } N_J = 4 & \quad \{J = 1; \quad M = 1, 0, -1\} \\ \text{for } N_J = 5 & \quad \{J = 3/2; \quad M = 3/2, 1/2, -1/2, -3/2\} \\ \text{for } N_J = 6 & \quad \{J = 3/2; \quad M = 3/2, 1/2, -1/2, -3/2\} \\ \text{for } N_J = 7 & \quad \{J = 2; \quad M = 2, 1, 0, -1, -2\} \end{aligned} \quad (38c)$$

The general formula and the individual cases as presented in the above list indicate that indeed the number of conical intersections in a given sub-Hilbert space and the numbers of possible sign flips within this sub-space are interrelated in a similar way as a spin J is related to its magnetic components M . In other words each decoupled sub-Hilbert space 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.

VII. Geometrical Approach

The closed contours that were discussed in previous sections take place in multidimensional CSs. It will be difficult to get some insight if, at this stage, we try to follow what happens along these multidimensional contours. Therefore, in the present article, we assume that all the CIs are located in a plane so that all paths considered here are assumed to be in the same plane. Another simplifying assumption is that the various CIs take place at different points, so that no more than two states may cross at a given point (the case where three or more states cross at a given point will be discussed in the next section). Thus having the two consecutive states j and $(j + 1)$, the two form the CI to be designated as C_j (see Figure 3).

In the last two sections it was mentioned that K yields the number of eigenfunctions which change sign when the electronic manifold traces certain closed paths. The situation is relatively simple in case of $N_J = 1$ where $K = 0, 2$. We also discussed to some extent the case of $N_J = 2$ and found, again, that either $K = 2$ or $K = 0$.³ However, we would like to be able to say

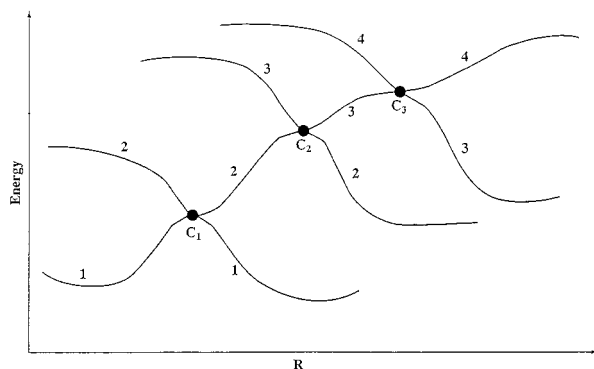


Figure 3. Four interacting adiabatic surfaces presented in terms of four adiabatic Landau–Zener-type curves. The points C_j , $j = 1, 2, 3$, stand for the three conical intersections.

more about that case. Here are encountered two CIs, namely, C_1 and the C_2 (see Figure 4a). In what follows Γ_{jj+1} is a contour that surrounds only the corresponding C_j .

Moving the electronic manifold along the path Γ_{12} will change the signs of ζ_1 and ζ_2 , whereas moving it along the path Γ_{23} will change the signs ζ_2 and ζ_3 . Next is examined the situation where a path, Γ_{13} , surrounds both C_1 and C_2 . It turns out that tracing that path will, again, cause a flip of sign of two eigenfunctions only, because we already know that for $N_j = 2$, K can be, at most, equal to 2. However, we shall analyze this case and for that purpose we refer to Figure 4b in which it is shown that the contour Γ_{13} that surrounds the two CIs can be presented as the sum $\Gamma_{13} = \Gamma_{12} + \Gamma_{23}$ of two contours, each surrounding one of the relevant CIs. Thus, surrounding the two CIs will cause the sign of ζ_2 to flip twice and 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. It is important to mention that all four possibilities are predicted by the products in eq 34 (for $N = 3$ or $N_j = 2$). So far we presented a qualitative picture of what happens in the three-state system. A more mathematical analysis is given in Appendix III.

A somewhat different situation is encountered in the case of $N_j = 3$ and therefore we shall briefly discuss it as well (see Figure 4). In this case we have three CIs. It is now obvious that each contour of the type Γ_{jj+1} , $j = 1, 2, 3$, surrounds the relevant C_j (see Figure 4a) and will flip the signs of the two relevant eigenfunctions. Surrounding with Γ_{jj+2} , $j = 1, 2$ the two consecutive CIs, namely, C_j and C_{j+1} (see Figure 4b), will flip the signs of the two external eigenfunctions, namely, ζ_j and ζ_{j+2} , but leave the sign of ζ_{j+1} unchanged. We have two such cases—the first and the second CIs and the second and the third ones. Then we have a contour Γ_{14} that surrounds all three CIs (see Figure 4c) and here, like in the previous, $N_j = 2$ case, only the two external functions, namely, ζ_1 and ζ_4 , change signs but as for the two internal ones, namely, ζ_2 and ζ_3 , their signs will remain unchanged. Finally we have the case where the contour Γ_{1234} surrounds C_1 and C_3 but not C_2 (see Figure 4d). In this case all four functions flip sign.

We briefly summarize what we found in this particular case: We revealed six types of contours that led to sign changes of six (different) pairs of functions and one type that leads to a sign conversion of four functions. Inspection of eq 33 shows that indeed we should have seven cases of flipped sign and one case where no sign change takes place (no surrounding of any CI).

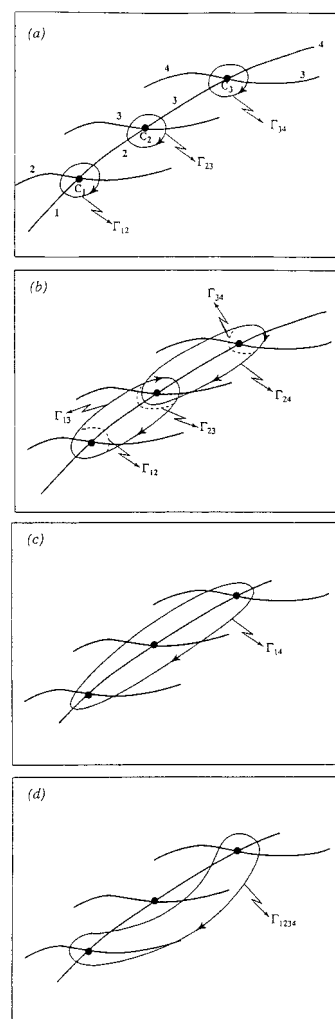


Figure 4. Four interacting surfaces, the three points of conical intersections, and the various contours leading to sign conversions: the contours Γ_{jj+1} surrounding the respective C_j , $j = 1, 2, 3$, leading to the sign conversions of the j th and the $(j + 1)$ th eigenfunctions. The contours Γ_{jj+2} surrounding the two (respective) conical intersections, namely, C_j and C_{j+1} , $j = 1, 2$, leading to the sign conversions of the j th and the $(j + 2)$ th eigenfunctions but leaving unchanged the sign of the middle, $(j + 1)$, eigenfunction. Also shown are the contours Γ_{jj+1} surrounding the respective C_j , $j = 1, 2, 3$, using partly dotted lines. It can be seen that $\Gamma_{jj+2} = \Gamma_{jj+1} + \Gamma_{j+1j+2}$. The contour Γ_{14} surrounding the three conical intersections, leading to the sign conversions of the first and the fourth eigenfunctions but leaving unchanged the signs of the second and the third eigenfunctions. Based on (b), we have $\Gamma_{14} = \Gamma_{12} + \Gamma_{23} + \Gamma_{34}$. The contour Γ_{1234} 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 (4b), we have $\Gamma_{1234} = \Gamma_{12} + \Gamma_{34}$.

VIII. Multidegeneracy Case

In the previous section it was emphasized that a case where three states degenerate at the same point is excluded from discussion. Here we would like to refer to that case (the case $\Delta\epsilon = 0$; see Figures 2a,d,g) in order to show that complications can be expected. In what follows we restrict our treatment to a tristate degeneracy.

The straightforward theory presented so far can be applied here by considering 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 $\rho =$

ρ_0 , $\varphi = \varphi_0$.³² (3) The tristate degeneracy is formed by letting $\rho_0 \rightarrow 0$, namely,

$$\lim_{\rho_0 \rightarrow 0} \tau_{23}(\rho, \varphi | \rho_0, \varphi_0) = \tau_{23}(\rho, \varphi) \quad (39)$$

so that the two CIs coincide. Now if the contour Γ_{13} in Figure 4b surrounds the two CIs then, following the discussion in the previous section, the \mathbf{D} -matrix will contain two (-1) s, which are formed whenever one of the three topological angles α_{ij} attains the value of π and the other two are equal to zero (or 2π). Inspection of Figures 2a,d,g shows for the tristate degeneracy case (namely, the case for which $\Delta\epsilon = 0$) that, indeed, α_{12} and α_{23} are equal to zero but $\alpha_{13} = \pi$ (we remind the reader that $\alpha_{ij} = \gamma_{ij}(\varphi = 2\pi)$). Moreover, the fact that $\alpha_{13} = \pi$, but not the other two angles, indicates that the two functions that flip sign are ζ_1 and ζ_3 as was discussed in the previous section—see also Figure 4b (if, for instance, we had $\alpha_{12} = \pi$, this would imply that ζ_1 and ζ_2 flipped sign—see Figure 4a). Thus, so far, the theory presented in previous sections and the calculations performed much earlier²⁹ yield identical results.

However, we also have other findings which are not so easily understood. In refs 1 and 2 we studied a tristate model presented in terms of the following τ -matrix:

$$\tau = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \quad (40)$$

where t_{ij} ; $i < j = 2, 3$ are defined as follows:

$$t_{ij}(s) = \sigma_{ij}\tau(s); \quad i < j = 2, 3 \quad (41)$$

Here σ_{ij} are constants and $\tau(s)$ is a (vector) function of the nuclear coordinates s . It is noticed that in this case we again have a situation where the three surfaces form a common CI at one point. The corresponding \mathbf{D} -matrix can be derived, directly, by applying eq 10. It was established that, no matter which contour is followed, the \mathbf{D} -matrix contains three $(+1)$ s in the diagonal. This situation can be attained if and only if the following condition is fulfilled:

$$(\sigma_{12}^2 + \sigma_{23}^2)^{1/2} \oint_{\Gamma} \tau ds = 2n\pi \quad (42)$$

where n is an integer. Thus in contrast to the previous case here none of the electronic functions will ever flip sign no matter which contour is followed.

Although the model presented here is of a very specialized form (the two nonadiabatic coupling terms have an identical spatial dependence), still the fact that such contradictory results are obtained for the two situations could hint to the possibility that in the transition process from the nondegenerate to the degenerate situation, in eq 39, something is not continuous. The conflicting results are not resolved within the present article.

IX. Conclusions

In this article new ideas are discussed regarding topological effects due to several CIs belonging to a multistate system. These are the main findings:

(a) In past publications^{3,31} we suggested to break-up the entire electronic manifold into sub-Hilbert spaces (termed SHSs) according to the strength of the nonadiabatic coupling terms between the relevant states. This division is now refined by demanding that the two border states of such a subset form,

neither Jahn–Teller CIs nor Renner–Teller PIs, with their respective neighbor states belonging to the next lower and the upper SHSs, respectively (see Figure 1).

(b) The ADT and the topological matrixes were introduced previously but here we not only discussed their derivations or emphasized their importance but also referred to some new features, in particular, the meaning of the number K —the number of (-1) s in the \mathbf{D} -matrix's diagonal—which is shown to be identical to the number of functions that flip sign while the electronic manifold is tracing a closed contour.

(c) A novel concept to assign electronic manifolds belonging to a given SHS, namely, the topological spin, is introduced and it is shown that the spin number is closely related to the number, N_j , of CIs in a given SHS (see eq 37a). Moreover, its components are related to the possible number of sign conversions, K , in this system (see eq 37b).

(d) A geometrical description of the possible sign conversions for a given SHS was presented and it is shown that this description corresponds nicely with the results obtained from the topological matrix \mathbf{D} .

(e) The case of two *degenerate* CIs was discussed to some extent. It was found that two different approaches—each well justified—yield different values for K . These contradictory results (that were not resolved within this article) seem to indicate that a discontinuity is involved in the transition from the nondegenerate to the degenerate situation.

Before completing this article we would like to refer briefly to an example for a real system, namely, the C_2H system. For this system Mebel et al. recently studied the lower states of the C_2H molecule,³⁶ and employing the MOLPRO program package³⁷ they calculated the six relevant (Cartesian) nonadiabatic coupling terms between the two following states: $X^2\Sigma^+(1^2A')$ and the $A^2\Pi(2^2A' + 1^2A'')$. They found that the corresponding line integral in eq 25' yields for α_{12} the value of π when the closed paths (of varying radii) surround the point of the CI or yields the value zero when they do not surround it or surround two of them. This system is now under further investigation to reveal more CIs in particular between higher states, namely, the second and the third, the third and the fourth, etc.

Appendix I. On the Trigonometric Structure of the Adiabatic-to-Diabatic Matrix

For the present purposes the ADT matrix will be presented (see eq 32) as the following product of rotation matrixes:

$$\mathbf{A} = \prod_{i=1}^{N-1} \prod_{j>i}^N Q^{(ij)}(\gamma_{ij}) \quad (\text{I.1})$$

where $Q^{(ij)}(\gamma_{ij})$ is an $N \times N$ matrix which in its (ii) and (jj) positions (in the diagonal) are the two relevant cosine functions and the rest of the $(N - 2)$ elements are $(+1)$ s, in the (ij) and (ji) off-diagonal positions we have the two relevant \pm sine functions, and the rest are zeros. It is noticed that eq I.1 is written in a somewhat different manner from eq 32. An example for such a matrix is given in eq 27. In what follows we drop the variable γ_{ij} , to simplify the notations. To continue we consider first a general diagonal term of the \mathbf{A} -matrix and later an odd diagonal term.

(1) The k th diagonal term of \mathbf{A} can be written as:

$$\mathbf{A}_{kk} = \sum_{\substack{l, n, \dots, p, \\ q, \dots, t}}^N Q_{kl}^{(12)} Q_{ln}^{(13)} \dots Q_{pq}^{(uv)} \dots Q_{tk}^{(xy)} \quad (\text{I.2})$$

where the upper indices run over all possible matrixes included in eq I.1. Among the various terms in eq I.2 there is, for each k , also one single term of the form

$$C_{kk} = Q_{kk}^{(12)} Q_{kk}^{(13)} \dots Q_{kk}^{(uv)} \dots Q_{kk}^{(xy)} \quad (\text{I.3})$$

which is the only term in eq I.2 that contains (only) diagonal terms of the various \mathbf{Q} -matrixes. This product is made up of N terms (one term from each matrix) which are either cosine functions of the various angles γ_{ij} or $(+1)$ s but not sine functions. In fact we can be more specific and it can be shown that C_{kk} is of the form

$$C_{kk} = \prod_{j \neq k}^N Q_{kk}^{(kj)} \quad (\text{I.4})$$

or

$$C_{kk} = \prod_{j \neq k}^N \cos(\gamma_{jk}) \quad (\text{I.5})$$

which proves our first assertion.

(2) For this case we consider a general *off-diagonal* (kj) element which can be written as

$$\mathbf{A}_{kj} = \sum_{\substack{l, n, \dots, p, \\ q, \dots, t}}^N Q_{kl}^{(12)} Q_{ln}^{(13)} \dots Q_{pq}^{(uv)} \dots Q_{tj}^{(xy)}, \quad k \neq j \quad (\text{I.6})$$

where, as before, the upper indices run over all possible matrixes included in eq I.1. We claim that each term in (I.6) has to have in its product at least one sine function. So let us assume that this assertion is wrong and there exists a product of pure cosine functions (or $(+1)$ s). Cosine functions or $(+1)$ s are located only in the diagonal of each matrix and therefore the lowest indices of each term in the product in eq I.6 have to be equal. Making the two corresponding indices, of each term, equal, we get

$$\mathbf{A}_{kj} = Q_{kk}^{(12)} Q_{kk}^{(13)} \dots Q_{kk}^{(uv)} \dots Q_{kj}^{(xy)}, \quad k \neq j \quad (\text{I.7})$$

It is noticed that changing the indices in order to obtain a product of diagonal elements only is impossible, because among other things the two indices of the last term have also to be made equal. However, replacing j by k contradicts our assumption that $j \neq k$.

Appendix II. On the Possible Sign Conversions and Diagonal Elements of the Topological Matrix

The topological matrix, \mathbf{D} , is a diagonal matrix which contains K (-1) s (and $(N - K)$ $(+1)$ s) in its diagonal. This number is dependent on the closed contour, Γ , along which \mathbf{D} is calculated. In this Appendix we show that K is equal to the number of electronic eigenfunctions that change sign when the electronic manifold of the SHS moves along Γ .

The adiabatic-to-diabatic transformation is carried out along a path Γ and as a result the adiabatic basis set, ζ , transforms to χ , the corresponding diabatic basis set (see eq 8')

$$\chi = \mathbf{A}\zeta \quad (\text{II.1})$$

A similar transformation will be applied to the complementary nuclear wave functions (see eq 8).

Next we consider the point s_0 on Γ , for which we have

$$\chi(s_0) = \mathbf{A}(s_0)\zeta(s_0) \quad (\text{II.2})$$

and designating $\tilde{\chi}(s_0)$ as the χ -column that is derived by employing $\tilde{\mathbf{A}}(s_0)$, which is the matrix \mathbf{A} calculated at $s = s_0$ following the integration of eq 7 along the (closed) contour Γ , namely,

$$\tilde{\mathbf{A}}(s_0) = \exp\left(-\oint_{\Gamma} ds \tau\right) \mathbf{A}(s_0) \quad (\text{II.3})$$

Thus

$$\tilde{\chi}(s_0) = \tilde{\mathbf{A}}(s_0)\zeta(s_0) = \exp\left(-\oint_{\Gamma} ds \tau\right) \mathbf{A}(s_0)\zeta(s_0) \quad (\text{II.4})$$

If now $\mathbf{A}(s_0)$ is chosen to be the *unit* matrix then the new *adiabatic* basis set formed at $s = s_0$ is

$$\tilde{\chi}(s_0) = \exp\left(-\oint_{\Gamma} ds \tau\right) \zeta(s_0) = D^* \zeta(s_0) \quad (\text{II.5})$$

where we made use of eq 10. Since \mathbf{D}^\dagger is a diagonal matrix which contains $(N - K)$ $(+1)$ s and K (-1) s in its diagonal, the column-vector $\tilde{\chi}(s_0)$ is identical to the original column-vector, $\zeta(s_0)$, except that K of its components flipped their sign.

Since along each path a different set of eigenfunctions may (or also may not) flip sign the column vector is not just double-valued as in case of $N = 2$ but multivalued. For instance, in the case of $N = 3$ the multivaluedness is 4. We may encounter the following four different eigenvectors:

$$\begin{aligned} \text{(a)} & (\zeta_1, \zeta_2, \zeta_3); & \text{(b)} & (-\zeta_1, -\zeta_2, \zeta_3); & \text{(c)} & (\zeta_1, -\zeta_2, -\zeta_3); \\ & & \text{(d)} & (-\zeta_1, \zeta_2, -\zeta_3) \end{aligned} \quad (\text{II.6})$$

It is interesting to mention that the eigenvector $(-\zeta_1, -\zeta_2, -\zeta_3)$ cannot be formed.

For a more complete discussion on this subject we refer the reader to section VI.

Appendix III. Quantitative Analysis of Possible Sign Flips in a Three-State System

In this Appendix we intend to prove mathematically, employing the LI approach, that if a contour in a given plane surrounds two CIs belonging to two different pairs of states, the two eigenfunctions that flip signs are the one that belongs to the lowest state and the one that belongs to the highest one.

Let us consider a case with three region as follows: In the first region, designated as σ_{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 σ_{23} , is located the main 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, σ_0 , which is located between the two and is used as a buffer zone (see Figure 5). Next is assumed that the intensity of the interactions due to the components of t_{23} in σ_{12} and due to t_{12} in σ_{23} is practically zero. In σ_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.

As mentioned above to prove our statement we consider the line integral

$$\mathbf{A} = \mathbf{A}_0 - \oint_{\Gamma} da \tau \mathbf{A} \quad (\text{III.1})$$

where the integration is carried out along a closed contour Γ , \mathbf{A} is the ADT matrix to be calculated, the dot stands for a scalar product, and τ is the matrix of 3×3 that contains the two nonadiabatic coupling terms, namely,

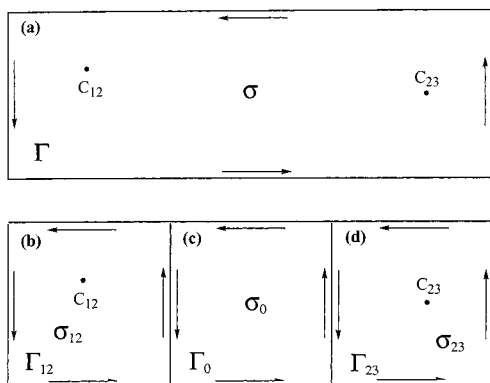


Figure 5. Breaking up of a region σ , that contains two CIs (at C_{12} and C_{23}) and is defined in terms of a closed contour Γ , into three subregions. (a) The full region σ . (b) The region σ_{12} , which contains a CI at C_{12} and is defined by the closed contour Γ_{12} . (c) The region σ_0 , which is defined by the closed contour Γ_0 and does not contain any CI. (d) The region σ_{23} , which contains a CI at C_{23} and is defined by the closed contour Γ_{23} . It can be seen that $\Gamma = \Gamma_{12} + \Gamma_0 + \Gamma_{23}$.

$$\tau(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \quad (\text{III.2})$$

(It is noticed that the components of t_{13} are assumed to be negligibly small—an assumption which is made for reasons of convenience only.)

The integral in eq 1 will now be presented as a sum of three integrals (for a detailed discussion on that subject: see ref 31), namely,

$$\mathbf{A} = \mathbf{A}_0 - \oint_{\Gamma_{12}} ds \tau \mathbf{A} - \oint_{\Gamma_0} ds \tau \mathbf{A} - \oint_{\Gamma_{23}} ds \tau \mathbf{A} \quad (\text{III.3})$$

Since there is no CI in the buffer zone, σ_0 , the second integral does not contribute 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 are dependent to some extent. Thus we do each calculation separately but for different (yet unknown) boundary conditions: the first integral for \mathbf{G}_{12} as a boundary condition and the second for \mathbf{G}_{23} . Thus \mathbf{A} will be calculated twice:

$$\mathbf{A} = \mathbf{G}_{ij} - \oint_{\Gamma_{ij}} ds \tau \mathbf{A} \quad (\text{III.4})$$

Next are introduced the topological matrixes \mathbf{D} , \mathbf{D}_{12} , and \mathbf{D}_{23} , which are related to \mathbf{A} in the following way (see eq 22):

$$\mathbf{A} = \mathbf{D}\mathbf{A}_0; \quad \mathbf{A} = \mathbf{D}_{12}\mathbf{G}_{12}; \quad \mathbf{A} = \mathbf{D}_{23}\mathbf{G}_{23} \quad (\text{III.5})$$

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

$$\mathbf{G}_{12} = \mathbf{D}_{23}\mathbf{A}_0 \quad \text{and} \quad \mathbf{G}_{23} = \mathbf{D}_{12}\mathbf{A}_0 \quad (\text{III.6})$$

Since all \mathbf{D} -matrixes are diagonal the same applies to \mathbf{D}_{12} and \mathbf{D}_{23} , so that \mathbf{D} becomes

$$\mathbf{D} = \mathbf{D}_{13} = \mathbf{D}_{12}\mathbf{D}_{23} \quad (\text{III.7})$$

Our next task will be to obtain \mathbf{D}_{12} and \mathbf{D}_{23} . For this sake we consider the two partial τ -matrixes, τ_{12} and τ_{23}

$$\tau_{12}(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \tau_{23}(s) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \quad (\text{III.8})$$

so that

$$\tau = \tau_{12} + \tau_{23} \quad (\text{III.9})$$

We start with the first of eqs III.4, namely,

$$\mathbf{A} = \mathbf{G}_{12} - \oint_{\Gamma_{ij}} ds \tau_{12} \mathbf{A} \quad (\text{III.10})$$

where τ_{12} replaces τ because τ_{23} is identically zero in σ_{12} . The solution and the corresponding \mathbf{D} -matrix, namely, \mathbf{D}_{12} are well-known (see discussion in section IV). Thus

$$\mathbf{D}_{12} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (\text{III.11})$$

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

$$\mathbf{D}_{23} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (\text{III.12})$$

which shows that the second and the third (the highest) eigenfunctions flip sign. Substituting eqs III.11 and III.12 in eq 7 yields for \mathbf{D}_{13} the result

$$\mathbf{D}_{13} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (\text{III.13})$$

In other words, surrounding the two CIs, indeed, leads to the flip of sign of the first and the third eigenfunctions.

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