Necessary Conditions for a Rigorous Minimal Diabatic Potential Matrix

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In this article, one of the more important dilemmas in molecular physics is considered: given a matrix of the nonadiabatic coupling terms of any desired dimension, what is the minimal sub-Hilbert space for which diabatization is still valid. This problem was addressed by one of us before (Baer, M. *Chem. Phys. Lett.* **2000**, *329*, 450), but it was recently established that the suggested criteria therein lead to subspaces that are too large to be of any use. In this article, we discuss the conditions that have to be satisfied to reach the minimal subspace. We have found that these conditions are related to the spatial distribution of the various nonadiabatic coupling terms. Thus, if nonadiabatic coupling terms for the relevant states overlap only slightly in configuration space, the required size of the subspace for diabatization can be reduced significantly. As an example, we consider the C_2H molecule.

I. Introduction

When studying molecular systems, one encounters two almost insurmountable difficulties: (1) that of treating the nonadiabatic coupling terms, which are not only spiky—a feature that is a "recipe" for numerical instabilities—but also singular and (2) that of having to consider large configuration subspaces. As will be shown in this article, the two apparently unrelated types of difficulties are, in fact, interrelated. Moreover, it will be shown that resolving the first difficulty may, in many cases, also settle the second.

In molecular physics, one distinguishes between (i) the adiabatic framework that is characterized by the adiabatic surfaces and the above-mentioned nonadiabatic coupling terms, which arise from derivative coupling and (ii) the diabatic framework that is characterized by the fact that derivative couplings are replaced by (smoothly behaving) potential couplings. Because of the unpleasant features of the nonadiabatic coupling terms, the dynamics is more easily carried out within the diabatic framework. Therefore, transforming to the diabatic framework, which is to be termed diabatization, is appropriate when treating the multi-state problem as created by the Born–Oppenheimer approach.[1,2] However, the fact that the nonadiabatic coupling terms become singular ("dressed" as conical intersections[3,4] or parabolical intersections,[5,6]) causes difficulties. There exists a belief that conical intersections are rare events in molecular systems; therefore, one is expected to achieve diabatization without essential difficulties. Indeed, in many earlier formulations, the transformation to the diabatic framework was done by ignoring the effect—the topological effect—of the singularities of the nonadiabatic coupling terms.[7] However, more recently, it became clear that conical intersections are very common[8–22] and that while diabatizing one must treat the singularities of the nonadiabatic coupling terms with care.

In 1975, one of the present authors[23] suggested a way to reach the diabatic framework indirectly by first forming the adiabatic framework and then transforming to the diabatic framework by employing the nonadiabatic coupling terms. This procedure becomes particularly simple when applied to two states because it amounts to the calculation of an angle (related to a 2×2 orthogonal matrix) by integration over a nonadiabatic coupling term along an assumed contour.[23–26] This approach was later employed to treat charge-transfer processes[27–31] (studies which until that time were solely carried out using semiclassical surface-hopping-trajectories[32–33]) and reactive exchange processes between neutrals[34–36] and, most recently, photodissociation.[37] In the following discussion, this angle is termed the adiabatic-to-diabatic transformation angle, and the integral along the contour is termed the line integral. The concept "line integral" is also used in the more general situation (i.e., in the case of more than two coupled adiabatic states for which the above-mentioned integral becomes an integral equation along a contour).

Because of difficulties in calculating the nonadiabatic coupling terms, this method did not become very popular. Nevertheless, this approach, as such, was employed extensively, in particular, to simulate spectroscopic measurements, with a modification by Macias and Riera.[38a] They suggested looking for a symmetric operator that behaves "violently" at the vicinity of the conical intersection and using it instead of the nonadiabatic coupling term as the kernel to calculate the adiabatic-to-diabatic transformation angle via the line integral. As a result, a series of operators such as the electronic dipole moment operator, the transition dipole moment operator, the quadrupole moment operator, etcetera were employed for this purpose.[16,18,38b] However, we emphasize that, immaterial to the success of this approach, it is still an ad hoc procedure; therefore, sooner or later, the adiabatic-to-diabatic transformation angles will have to be formed from the nonadiabatic coupling terms to guarantee reliable results. Another difficulty associated with the Macias–Riera approach is that it cannot be extended to multisurface systems (or at least was never suggested for this purpose).

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Before discussing the main subject of this article, we consider the problem of finite subspaces and the corresponding finite Curl condition (see eqs 6 and 7). This is always an important issue when treating a finite number of electronic states but is particularly important when considering the adiabatic-to-diabatic transformation. The transformation is guaranteed to be meaningful if the Curl condition is fulfilled. However ,the Curl condition was derived for an electronic manifold that forms a very large and even an infinite Hilbert space.[23] The question to be asked in this respect is whether a reduced Curl condition can be formulated for a finite subspace. This subject was addressed some time ago by Mead and Truhlar[39] while referring to the possibility of constructing diabatic states, and it was claimed that strictly diabatic states cannot be formed because a Curl condition cannot be formulated for a finite subspace except in case of atom−atom systems (where it is trivially fulfilled for any number of states). However, it is known from numerous studies, whether based on perturbation theory or on ab initio treatment, that if one considers regions close enough to a given conical intersection, the size of the sub-Hilbert space (see below for definition) shrinks significantly and may be reduced even to two states.[8−13,15,19,20,22] This implies that diabatic states, not necessarily strictly diabatic states but those that are accurate enough for any practical numerical application, can be formed in given finite regions of configuration space and that the "reduced" Curl condition holds approximately in these regions. This reduced Curl condition was recently addressed in several articles,[40] and they can be summarized as follows: A sub-Hilbert space (or a subspace of a Hilbert space) is considered in which the states belonging to it are strongly coupled to each other, but none of them is strongly coupled to states outside it (see section III). It was proved[40a,b] that if the weak interaction between any two states—one internal and one external—measures as $O(\epsilon)$ then the Curl condition related to the sub-Hilbert space (i.e., the reduced Curl condition) is fulfilled up to an error of $O(\epsilon^2)$.[40a,b]

In the last paragraph, we present the purpose of this article. To do so in a comprehensive way, we need to explain what is meant, within the present study, by the statement that a diabatic potential matrix is *nonphysical*. The procedure discussed above is based on a transformation matrix of dimension *M* derived within a subspace of the same dimension. When we say that the diabatic potential matrix, obtained via this transformation matrix, is nonphysical, we mean that some of its elements are multivalued in configuration space. (It is important to emphasize that the nuclear Schrödinger equation cannot be solved for multivalued potentials.) We shall show that if an *M*-dimensional subspace is not large enough some elements of the diabatic potential matrix will not be single-valued. On the other hand, we have to guarantee that *M* is kept as small as possible.

Finally, we refer to recent efforts to form diabatic states by overcoming the incompleteness of the two-state subspace as encountered in the H_3 system. Kuppermann and Abrol[41] present an interesting approach in which the nonadiabatic coupling matrix is decomposed into two matrixes (i.e., the longitudinal matrix, which fulfills a reduced Curl condition, and the transversal matrix). Next, they suggest the determination of the longitudinal part in such a way as to minimize the average effect of the transversal matrix.

Following these introductory remarks, we can now state the purpose of this paper. We intend to show that an adiabatic-to-diabatic transformation matrix based on the nonadiabatic coupling matrix can be used not only to reach the diabatic

framework (for which, a priori, it was designed) but also to determine the minimum size of a subspace for which diabatization is still physically meaningful.

We explain this subject by considering the two-state situation: following a 2×2 adiabatic-to-diabatic transformation, a 2-D, multivalued diabatic potential matrix is formed. This implies that the 2-D transformation matrix yields a nonphysical diabatic potential matrix; therefore, the required dimension of the transformation matrix has to be increased to three or more dimensions. The same situation applies to the size of the subspace, which also must be at least 3-D. In the present article, we intend to discuss these types of problems. We refer to the conditions for forming the minimal relevant subspace as "the necessary conditions for diabatization".

The paper is arranged as follows: In section II, we present a summary of the theoretical background that leads to "quantization" of the nonadiabatic coupling matrix. In section III, we discuss the conditions for a "reduced" diabatization, which is obtained by considering the spatial distribution of the relevant nonadiabatic coupling terms, and in section IV, we consider the C_2H molecule to show that the two lowest states can indeed be diabatized although the relevant sub-Hilbert space contains more than two states in the region of interest. Conclusions are given in section V.

II. Theoretical Background

In their treatment of the mixed systems of nuclei and electrons, Born and Oppenheimer derived the Schrödinger equation for the nuclei, which can be written as[7,42,43]

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

where ∇ is the usual gradient operator (here and in the following discussion, all coordinates are internal, mass-scaled Jacoby coordinates), E is the total energy, Ψ is a column matrix that contains the nuclear functions $\{\Psi_i; i = 1,2...\}$, $\mathbf{u}$ is a diagonal matrix that contains the adiabatic potentials, and $\boldsymbol{\tau}$ is the nonadiabatic coupling matrix with the (vectorial) elements t_{ij} defined as

$$t_{ij} = \langle \zeta_j | \nabla \zeta_i \rangle \qquad (2)$$

In eq 2, the differentiation is with respect to the nuclear coordinates, and the integration, with respect to the electronic coordinates. Note that each element of the $\boldsymbol{\tau}$ matrix is a vector of n components where n is the number of internal coordinates (this number will be 1 for a diatomic system, 3 for a triatomic system, etc.). In what follows, we assume that the dimension of the (complete) Hilbert space is N, which, therefore, is also the dimension of the $\boldsymbol{\tau}$ matrix. For real molecular systems, N is very large and may even become infinite. However, it can be shown that eq 1 also holds for a subspace of finite, much-reduced dimension M, provided that certain conditions (to be discussed in section IV) are fulfilled. In what follows, we assume that a finite sub-Hilbert space can be constructed.[40,43−45]

In this article, the diabatic states are obtained from the adiabatic-to-diabatic transformation matrix $\mathbf{A}$, which is a solution of the following first-order differential equation:[23−26]

$$\nabla \mathbf{A} + \tau \mathbf{A} = 0 \qquad (3)$$

It has been shown that the diabatic potential matrix $\mathbf{W}$ is obtained from the expression

$$\mathbf{W} = \mathbf{A}^\dagger \mathbf{u} \mathbf{A} \qquad (4)$$

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where $\mathbf{A}^{\dagger}$ is the Hermitian conjugate of the unitary matrix $\mathbf{A}$.

Before considering $\mathbf{W}$, we shall briefly discuss the conditions for eq 3 to have a solution. To solve eq 3, we assume a contour and then solve it along this contour. The condition for the existence of a solution along such a contour is the fulfillment of the Curl condition[23,43-46] in a region along this contour and that contains the contour. Thus, if p and q are any two (Cartesian) coordinates, then the Curl condition implies that

$$\frac{\partial}{\partial p}\boldsymbol{\tau}_q - \frac{\partial}{\partial q}\boldsymbol{\tau}_p = [\boldsymbol{\tau}_q, \boldsymbol{\tau}_p] \tag{5}$$

This equation can be written more compactly as

$$\mathrm{Curl}\boldsymbol{\tau} = [\boldsymbol{\tau} \times \boldsymbol{\tau}] \tag{6}$$

Let us now return to eqs 3 and 4, which form the basis of the procedure used to obtain the diabatic potential matrix elements. If this procedure is mathematically valid, then the diabatic potentials produced in this way have to be single-valued. We notice that because the adiabatic potentials are single-valued, by definition, the single-valuedness of $\mathbf{W}$ depends on the features of the $\mathbf{A}$ matrix (see eq 4). It is also obvious that if $\mathbf{A}$ is single-valued the same applies to $\mathbf{W}$. In Appendix C of ref 43, it is shown that the condition for having a single-valued $\mathbf{A}$ matrix is the fulfillment of the Curl condition in the region of interest. However, it turns out that $\mathbf{A}$ does not have to be single-valued to guarantee the single-valuedness of $\mathbf{W}$. In fact, it was proved that the necessary condition for having single-valued diabatic potentials in the region surrounded by a given contour Γ is that the $\boldsymbol{\tau}$ matrix fulfills a certain quantization condition.[46,47] This condition will be discussed next.

If we assume that the Curl condition (i.e., eq 6) is fulfilled along a given contour Γ, then eq 3 has the following solution:[25]

$$\mathbf{A}(s, s_0) = \tilde{P} \exp(-\int_{s_0}^{s} \mathrm{d}s\, \boldsymbol{\tau})\, \mathbf{A}(s_0) \tag{7}$$

s and s_0 are two points on Γ, and $\mathbf{A}(s_0)$ is the boundary condition for the solution (in this article, it is assumed to be the unit matrix $\mathbf{I}$). A path-ordering operator $\tilde{P}$ is introduced to indicate that this integral has to be carried out in a certain order.[25] In other words, the contour Γ has to be broken into segments so that the integration and the exponentiation are done independently for each segment and that the final result is obtained, following a series of products to be performed in the correct order.

Next, we introduce a matrix $\mathbf{D}$, hence termed the topological matrix.[47] The $\mathbf{D}$ matrix is defined as

$$\mathbf{D} = \mathbf{A}(s_0, s_0)\, \mathbf{A}^{\dagger}(s_0) \tag{8}$$

where $\mathbf{A}(s_0, s_0)$ is the value of $\mathbf{A}$ as calculated at the end point of the closed contour. It has been proved that $\mathbf{D}$ does not depend on the boundary matrix $\mathbf{A}(s_0)$ but depends only on the assumed contour Γ. From eq 7, the $\mathbf{D}$ matrix for a closed contour can be presented as[47]

$$\mathbf{D} = \tilde{P} \exp(-\oint_{\Gamma} \mathrm{d}s\, \boldsymbol{\tau}) \tag{9}$$

which shows explicitly that $\mathbf{D}$ depends only on the contour Γ, not on any particular point along this contour.

Now returning to the diabatic potentials, it was proved that the necessary condition for having single-valued diabatic potentials is that the $\mathbf{D}$ matrix is diagonal with numbers of norm equal to 1, namely, numbers that are either $(+1)s$ or $(-1)s$ (the norm 1 is guaranteed by the fact that the $\mathbf{D}$ matrix is a unitary
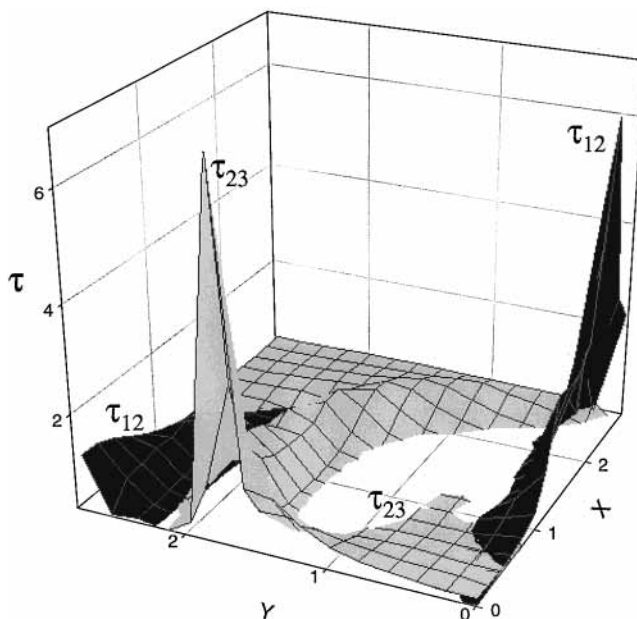
Figure 1. 3-D plot for the nonadiabatic coupling terms $t_{12}(x, y)$ and $t_{23}(x, y)$ (see eq 29) as calculated for the C$_2$H molecule for a fixed CC distance of $r_{CC} = 1.35$ Å τ_{12} stands for t_{12}, and τ_{23} stands for t_{23}.

matrix). In this sense, eq 9 is a quantization condition. In other words, if in a given region the calculated $\mathbf{D}$ matrices of dimension M are diagonal for any closed contour in this region, then this implies that the corresponding M-dimensional diabatic potential matrix in this region is single-valued and therefore can be employed to solve the diabatic Schrödinger equation.

III. Noninteracting Conical Intersections

III.1. Introductory Comments. We use the term "noninteracting conical intersections" to mean a situation where the spatial distribution of two conical intersections (in a given region), presented in terms of $t_{12}(s)$ and $t_{23}(s)$, is such that they overlap slightly, at most, in the region of interest. As an example, we consider a 2-D (planar) case where the highest intensity of $t_{12}(s)$ is concentrated along one straight line that is reminiscent of a ridge and the highest intensity of $t_{23}(s)$ is concentrated along another straight line. Next, if these two lines are parallel and located far enough apart, the overlap will be minimal. In Figures 1 and 2, we present a situation similar to the one that was revealed while we were studying the C$_2$H molecule (see section IV for more details)

In some recent publications,[40a,b,43,48] we examined conditions under which certain subspaces belonging to a Hilbert space can be treated independently of other (external) parts of the Hilbert space. To simplify the discussion, we consider two subspaces, namely, the P space with dimension M and the complementary Q space, which is allowed to be of an infinite dimension. It was suggested that we use the following criteria for constructing the P subspace in a given region:[40]

$$t_{ij} \cong O(\epsilon) \qquad \text{for } i \leq M, j > M \tag{10}$$

In other words, the P states are all assumed to be weakly coupled to Q states. Next, an interaction between two states is strong when they are coupled via a conical intersection.[40a,b] Because a conical intersection can be formed between two successive states only, the P subspace is seen to be composed of M states where each two adjacent states, j and $j + 1$, are coupled via a strong nonadiabatic coupling term, t_{jj+1}, which is a conical
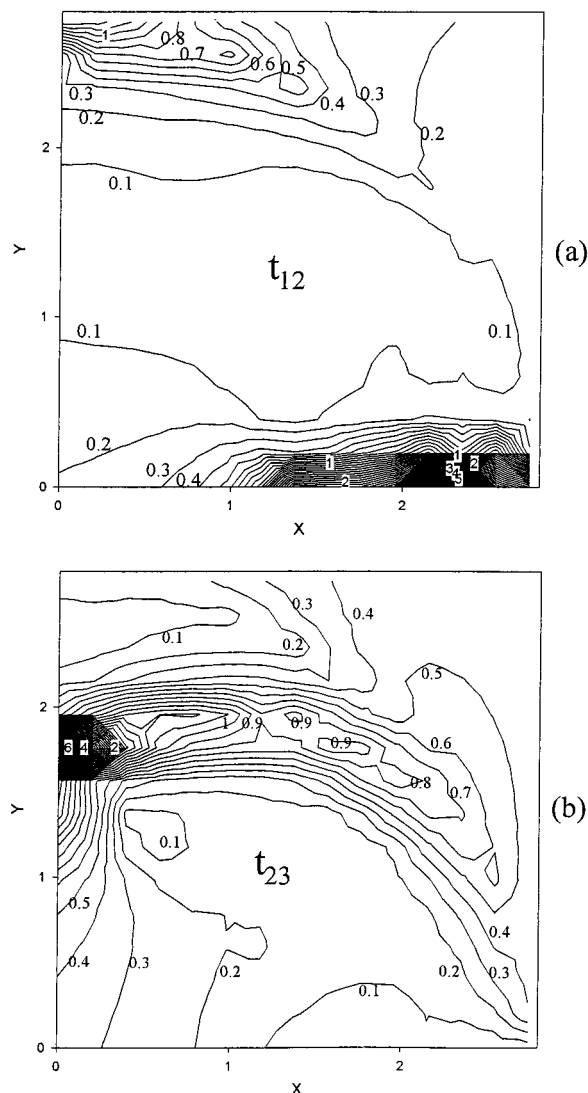
Figure 2. Equi-nonadiabatic coupling-term lines for $|t_{12}(x, y)|$ and $|t_{23}(x, y)|$ (see eq 29) as calculated for the C_2H molecule for a fixed CC distance of $r_{CC} = 1.35$ Å.

intersection (or stands for a sum of several conical intersections). For such P subspaces, we showed that one can form a rigorous diabatic framework characterized by an $M \times M$ diabatic potential matrix.[40a,b,43,48]

The main difficulty with this procedure is that the above definition for an isolated P subspace can be too extensive; in particular, we suspect that almost every adiabatic state is coupled via a conical intersection to its neighbor states at some point(s) in configuration space. If this is indeed the case, then the suggested breakup of the Hilbert space is not useful, even if M is finite but too large.

Knowing that, the question to be asked is whether one can reach the diabatic framework using requirements that are not as strict but are still rigorous. In other words, what are the necessary conditions to reach the diabatic framework and obtain the relevant (dimensionally reduced) potential matrix? We shall not treat this issue for a general M-dimensional subspace but shall limit ourselves to a 3-D space where each two adjacent states, namely, the two lower states 1 and 2 and the two higher states 2 and 3, are strongly coupled to each other in the region of interest. We shall examine the conditions necessary to reach a 2-D diabatic framework for which the 2×2 diabatic potential matrix is single-valued.
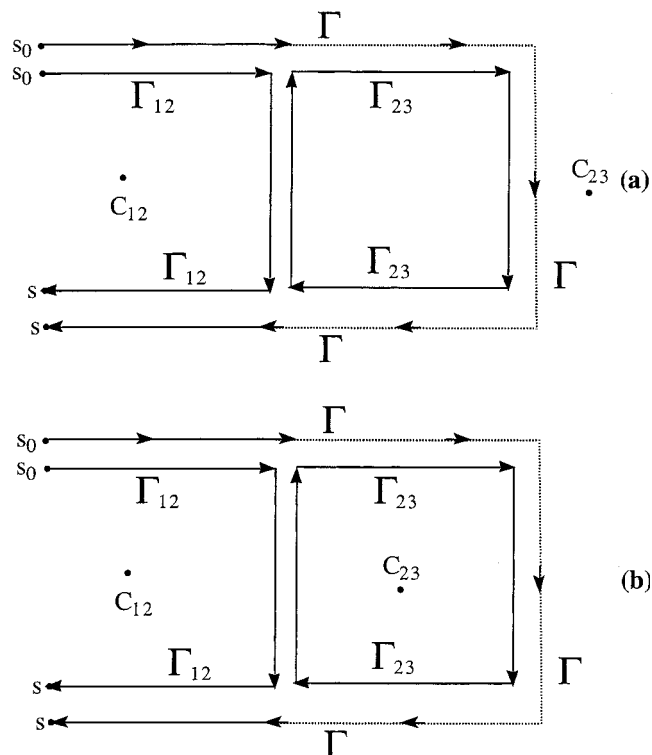
Figure 3. Representation of an open contour Γ in terms of an open contour Γ_{12} in the vicinity of the conical intersection at C_{12} and a closed contour Γ_{23} at the vicinity of a conical intersection at C_{23}. $\Gamma = \Gamma_{12} + \Gamma_{23}$. It is assumed that the intensity of t_{12} is strong along those segments of Γ that coincide with Γ_{12} (—) and weak along those segments of Γ that coincide with Γ_{23} (···). (a) C_{23} is outside the closed contour Γ_{23}. (b) C_{23} is inside the closed contour Γ_{23}.

III.2. Treatment of the Line Integral. For this purpose, we consider a 2-D configuration space (see Figure 3) in which two conical intersections are located at C_{12} and C_{23}. The two corresponding nonadiabatic coupling terms are $t_{12}(s)$ for the two lower states and $t_{23}(s)$ for the two higher two states. Although we consider here only two conical intersections, the treatment can be extended to any number of conical intersections (among the three just-mentioned states). In addition, we present a contour Γ that is located mainly in the vicinity of C_{12}, and we are interested to follow what happens along this contour, in particular, when it gets closer to C_{23}.

Note that some segments of the contour Γ are drawn as solid lines and others, as dashed lines. The solid lines denote segments along which the intensity of $t_{12}(s)$ is strong but that of $t_{23}(s)$ is negligibly weak. The dashed lines denote segments along which $t_{12}(s)$ is negligible weak.

Next, we consider the following line integral[23]

$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{s_0}^{s} ds \, \boldsymbol{\tau}(s) \, \mathbf{A}(s) \tag{11}$$

where $\mathbf{A}(s)$ is a 3-D matrix and $\boldsymbol{\tau}(s)$ is given in the form

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

Note that the t_{13} term is missing because in realistic cases it was found to be negligibly small; it is ignored to shorten the algebra, and it is not essential to the derivation that follows.

We also consider two other $\boldsymbol{\tau}$ matrixes, namely, $\tilde{\boldsymbol{\tau}}_{12}(s)$

$$\tilde{\boldsymbol{\tau}}_{12}(s) = \begin{pmatrix} 0 & t_{12} & 0 \\ -t_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{13a}$$

and $\tilde{\boldsymbol{\tau}}_{23}(s)$

$$\tilde{\boldsymbol{\tau}}_{23}(s) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & t_{23} \\ 0 & -t_{23} & 0 \end{pmatrix} \tag{13b}$$

and it is easy to see that

$$\boldsymbol{\tau}(s) = \tilde{\boldsymbol{\tau}}_{12}(s) + \tilde{\boldsymbol{\tau}}_{23}(s) \tag{14}$$

To continue, the contour Γ along which the integration in eq 11 is carried out is assumed to be the sum of two contours (see Figure (3))

$$\Gamma = \Gamma_{12} + \Gamma_{23} \tag{15}$$

where Γ_{23} is a closed contour in the vicinity of C_{23} that may surround it and Γ_{12} is an open contour near C_{12}. By substituting eq 15 into eq 11, we get

$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{\Gamma_{12}} ds' \, \boldsymbol{\tau}(s') \, \mathbf{A}(s') - \oint_{\Gamma_{23}} ds' \, \boldsymbol{\tau}(s') \, \mathbf{A}(s') \tag{16}$$

Next, recalling the assumptions concerning the intensities of $t_{12}(s)$ and $t_{23}(s)$, we replace the $\boldsymbol{\tau}(s)$ in the second term of eq 16 with $\tilde{\boldsymbol{\tau}}_{12}(s)$ and in the third term, with $\tilde{\boldsymbol{\tau}}_{23}(s)$. As a result, eq 16 becomes

$$\mathbf{A}(s) = \mathbf{A}(s_0) - \int_{\Gamma_{12}} ds' \, \tilde{\boldsymbol{\tau}}_{12}(s') \, \mathbf{A}(s') - \oint_{\Gamma_{23}} ds' \, \tilde{\boldsymbol{\tau}}_{23}(s') \, \mathbf{A}(s') \tag{17}$$

Defining $\mathbf{A}_{23}$ as the following (constant) matrix

$$\mathbf{A}_{23} = \mathbf{A}(s_0) - \oint_{\Gamma_{23}} ds' \, \tilde{\boldsymbol{\tau}}_{23}(s') \, \mathbf{A}(s') \tag{18}$$

eq 17 becomes

$$\mathbf{A}(s) = \mathbf{A}_{23} - \int_{\Gamma_{12}} ds' \, \tilde{\boldsymbol{\tau}}_{12}(s') \, \mathbf{A}(s') \tag{19}$$

where the matrix $\mathbf{A}_{23}$ is now the corresponding boundary condition for this equation.

To continue, we first consider $\mathbf{A}_{23}$ and we notice that because it is defined via an integration along a closed contour (Γ_{23}) where $\tilde{\boldsymbol{\tau}}_{23}(s)$ is the kernel, it can be written as (see eq 8)

$$\mathbf{A}_{23} = \mathbf{D}_{23} \, \mathbf{A}(s_0) \tag{20}$$

where $\mathbf{D}_{23}$ is the corresponding topological matrix and is assumed to be diagonal.

Next, we treat eq 19, and for this purpose, we consider the following equation

$$\tilde{\mathbf{A}}_{12}(s) = \mathbf{A}(s_0) \mp \int_{\Gamma_{12}} ds' \, \tilde{\boldsymbol{\tau}}_{12}(s') \, \tilde{\mathbf{A}}_{12}(s') \tag{21}$$

which is similar to eq 19, where the only difference is the inhomogeneous (matrix) term. To obtain eq 19 from eq 21, we use the following manipulation: (a) multiply it from the left by $\mathbf{D}_{23}$ and (b) introduce into the integrand (between $\tilde{\boldsymbol{\tau}}_{12}(s)$ and

$\tilde{\mathbf{A}}_{12}(s)$) the product $\mathbf{D}_{23}\mathbf{D}_{23}$ ($\equiv \mathbf{I}$). Because $\mathbf{D}_{23} \, \tilde{\boldsymbol{\tau}}_{12}(s) \, \mathbf{D}_{23} = \pm\tilde{\boldsymbol{\tau}}_{12}(s)$, eq 19 is fulfilled for the following $\mathbf{A}(s)$ matrix:

$$\mathbf{A}(s) = \mathbf{D}_{23}\tilde{\mathbf{A}}(s) \tag{22}$$

Returning to eq 21, we notice that this is the line integral for a 2×2 $\tilde{\mathbf{A}}_{12}(s)$ matrix because $\tilde{\boldsymbol{\tau}}_{12}(s)$, its kernel, is (essentially) a 2×2 matrix (see eq 13a).

We shall now summarize our findings. We proved that if the two interactions $t_{12}(s)$ and $t_{23}(s)$ overlap even slightly along any segment of a chosen contour Γ in the region of interest, then it is enough to solve eq 21 where Γ_{12} is the contour along which $t_{23}(s) \approx 0$. However, a solution is needed along the given contour Γ, and to find this solution, we arbitrarily extend Γ_{12} to Γ because $t_{12}(s) \approx 0$ along the missing segment. To obtain the final solution $\mathbf{A}(s)$, we employ eq 22.

Next, we consider the equation for the diabatic potential $\mathbf{W}(s)$ (see eq 4). After substituting eq 22 in eq 4 and recalling that $\mathbf{D}_{23}$ and $\mathbf{u}(s)$ are diagonal matrixes, we find that

$$\mathbf{W} = \tilde{\mathbf{A}}_{12}^{\dagger}\mathbf{u}\tilde{\mathbf{A}}_{12} \tag{23}$$

This implies that whenever the above requirements are fulfilled we do not have to solve a 3×3 matrix. In fact, we are allowed to assume an $\mathbf{A}(s)$ matrix of the form

$$\mathbf{A}(s) = \tilde{\mathbf{A}}_{12}(s) = \begin{pmatrix} \cos \gamma_{12} & \sin \gamma_{12} & 0 \\ -\sin \gamma_{12} & \cos \gamma_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{24}$$

where γ_{12} ($= \gamma_{12}(s|\Gamma_{12})$) is obtained from the integral over the (1, 2) nonadiabatic coupling term

$$\gamma_{12}(s|\Gamma_{12}) = \gamma_{12}(s_0) \mp \int_{s_0}^{s} ds \, t_{12}(s|\Gamma_{12}) \tag{25}$$

In other words, we are essentially back to the two-state case.

Finally, we have three comments:

(1) In eq 25, we have a $\mp$ sign. It is important to emphasize that the minus sign applies to those contours that do not surround the (2, 3) conical intersection and that the plus sign applies to those contours that do surround it. The only potential matrix element affected by this sign is the off-diagonal term (see eq 23), but this sign will not affect the solution of the final nuclear Schrödinger equation.

(2) We limited the derivation to a case where the Γ_{12} contour is close to C_{12}, the point of the (1, 2) conical intersection. This treatment can be extended to any number of C_{12} locations as long as the specified conditions are fulfilled.

(3) It could very well be that in realistic cases $\mathbf{D}_{23}$ is not diagonal because the third state may be strongly coupled to a fourth state, etcetera. If this is the case, the theoretical treatment just described has to be extended to four states (or for that matter, to any number of states). This extension will not affect our final result as expressed in eqs 22−25.

III.3. Curl Condition. The theory presented in the previous section ended by stating that if for a given three-state system the nonadiabatic coupling terms between the two lower states and between the two upper states do not interact we can form a 2×2 diabatic potential by calculating the adiabatic-to-diabatic transformation angle as presented in eq 25. The question to be asked is whether the corresponding reduced Curl condition is fulfilled along every contour in the region of interest. Before answering this question, we have to remind the reader of two facts:
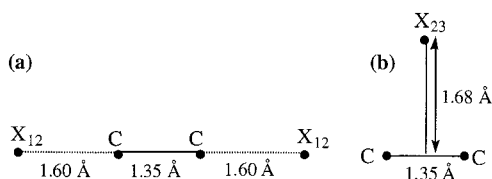
Figure 4. Geometrical positions (with respect to the CC axis) of the two conical intersections studied in this article. The planes on which the conical intersections are located are formed by freezing the CC distances. X_{ij} designates the conical intersection formed by the ith and the jth states. All distances are in Å. (a) (1,2) conical intersection; (b) (2,3) conical intersection.

(1) The Curl condition as presented in eqs 5 and 6 simplifies significantly for the case of two states. First, the commutator on the right side of eq 5 is identically zero; second, the Curl condition between matrixes becomes the Curl condition between the matrix elements t_{p12}, t_{q12}, etcetera. Thus, in a two-state system, we have

$$\text{Curl} t_{12} = 0 \qquad (26)$$

(2) In the case of three states, each nonadiabatic coupling matrix contains three nonzero elements, and its components form a nonzero commutation relation. To probe whether the Curl condition for (the vector) t_{12} holds while also considering the three-state system, we have to evaluate the commutation relation of eq 5 for our planar system composed of the coordinates (p, q). Thus,

$$[\boldsymbol{\tau} \times \boldsymbol{\tau}] =$$

$$\begin{pmatrix} 0 & -t_{13p}t_{23q} + t_{13q}t_{23p} & t_{12p}t_{23q} - t_{12q}t_{23p} \\ -(-t_{13p}t_{23q} + t_{13q}t_{23p}) & 0 & -t_{12p}t_{13q} + t_{12q}t_{13p} \\ -(t_{12p}t_{23q} - t_{12q}t_{23p}) & -(-t_{12p}t_{13q} + t_{12q}t_{13p}) & 0 \end{pmatrix}$$
$$(27)$$

Returning now to eq 5, we notice that for the Curl condition (for the matrixes) produced for the two components of the t_{12} element, the following condition must be fulfilled:

$$\text{Curl} t_{12} = -t_{13p}\,t_{23q} + t_{13q}\,t_{23p} \qquad (28)$$

We see that the right-hand side of eq 28 is equal to zero when $|t_{23}| = 0$. However, we assumed that $|t_{23}| \approx 0$ whenever $|t_{12}| > 0$. Consequently, eq 26 holds in all regions where $|t_{12}| > 0$ and is trivially fulfilled in those regions where $|t_{12}| \approx 0$.

IV. C$_2$H Molecule as a Test Case

As an example, we discuss the three lowest $^2A'$ states of the C$_2$H molecule. The ab initio calculations of the nonadiabatic coupling terms were carried out at the state-averaged CASSCF level with the 6-311G** basis set.[50] The three $^2A'$ states were calculated using the active space, including all nine valence electrons distributed on nine orbitals (full-valence active space). Depending on the targeted electronic states, up to five states were computed by the state-averaged CASSCF with equal weights. The nonadiabatic coupling terms were calculated by using MOLPRO program.[51]

All calculations were made for a fixed CC distance, namely, $r_{CC} = 1.35$ Å. For this CC distance, the (1, 2) conical intersection is located at the linear configuration at a distance of 1.3 Å from the closest carbon.[16] Because of symmetry, we encounter two conical intersections—one on each side (see Figure 4). As for the (2, 3) conical intersection, it is located at

a distance of 1.68 Å from the CC axis[17] on the C_{2v} line (see Figure 4). Here also, because of symmetry, we encounter another conical intersection "below" the CC axis (not shown in the Figure).

To show the spatial distribution of each of the nonadiabatic coupling terms, we employed a Cartesian system of coordinates with its origin at the midpoint between the two carbons on the CC axis. The relevant nonadiabatic coupling terms for this presentation were defined as follows.

Employing chain rules,[11,13] we calculated for the above fixed CC distance and a given set of (x, y) grid points the Cartesian nonadiabatic coupling terms $t_{jj+1x}(x, y)$ and $t_{jj+1y}(x,y)$ with $j = 1, 2$. We continued the calculations to obtain absolute values of $t_{jj+1}(x, y)$, namely, $|t_{jj+1}(x, y)|$:

$$|t_{jj+1}(x, y)| = \sqrt{t_{jj+1x}(x, y)^2 + t_{jj+1y}(x, y)^2} \qquad j = 1, 2 \quad (29)$$

The values of the two functions are presented twice: in Figure 1, the 3-D plot for the two nonadiabatic coupling terms for both $|t_{12}(x, y)|$ and $|t_{23}(x, y)|$ as defined above is presented, and in Figures 2a and b, equi-nonadiabatic coupling lines for these two functions, respectively, are presented. We have noticed (in particular, in Figure (2)) that the regions for which either $|t_{12}(x, y)|$ or $|t_{23}(x, y)|$ differ from zero are indeed well-separated. This implies that any contour assumed in the above (x, y) plane will have segments for which $|t_{12}(x, y)| > 0$ but $|t_{23}(x, y)| \approx 0$ and vice versa, namely, segments for which $|t_{12}(x, y)| \approx 0$ but $|t_{23}(x, y)| > 0$ (we may also have segments along which both functions are ~0). We have hardly any segments along which both $|t_{12}(x, y)|$ and $|t_{23}(x, y)|$ are significantly different from zero. According to the theory presented in the previous section, the necessary condition that ensures the replacement of the three-state line integral by a two-state line integral is that along any segment of an assumed contour for which $|t_{12}(x, y)| > 0$ we have $|t_{23}(x, y)| \approx 0$. If this condition is fulfilled along any contour in a given region, we can safely employ the two-state line integral for the entire region under consideration. From Figures 1 and 2, it seems that this condition is satisfied by the three lowest states of the C$_2$H molecule.

Next, we prove numerically that this is indeed the case. For this purpose, we performed a series of line integral calculations of the kind given in eq 25. All line integral calculations were made for circular contours, namely, the adiabatic-to-diabatic transformation angles were calculated from the expression

$$\gamma_{12}(q, \varphi) = \int_0^\varphi d\varphi'\, t_{12\varphi}(q, \varphi') \qquad (30)$$

The test for the above-discussed decoupling is based on $\alpha_{12}(q)$, the topological angle, which is defined as

$$\alpha_{12}(q) = \gamma_{12}(q, \varphi = 2\pi) \qquad (31)$$

Having this angle, the (1, 2) system is assumed to be "decoupled" from other states if and only if for any circle $\alpha_{12}(q)$ can be written as

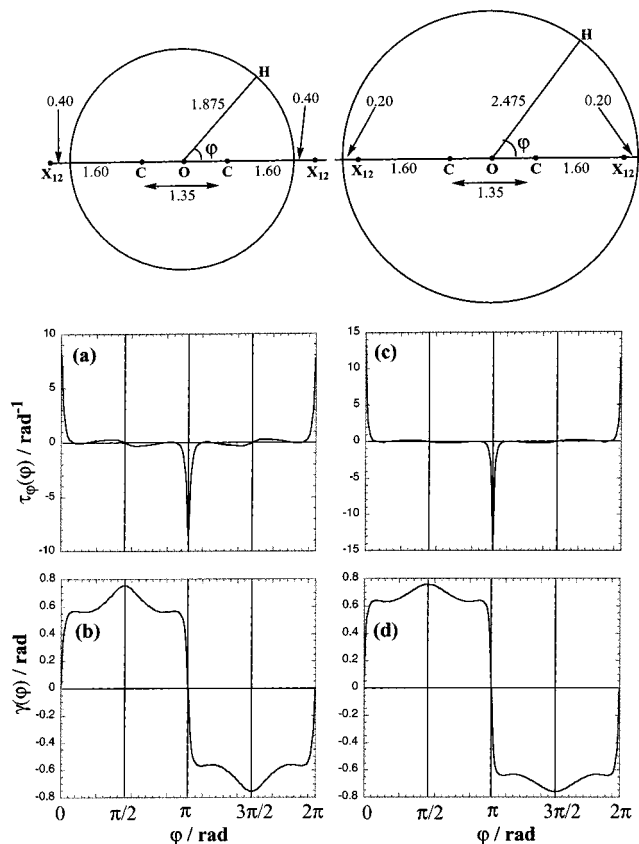$$\alpha_{12}(q) = n\pi \qquad (32)$$

where n is an integer (or zero).

In Figures 5−7, angular nonadiabatic coupling terms and the relevant adiabatic-to-diabatic transformation angles as calculated for seven cases are presented. We show the results obtained for three different systems of coordinates, each time for a different radius q (some of these radii are large enough for their circles to surround the entire configuration space of interest).

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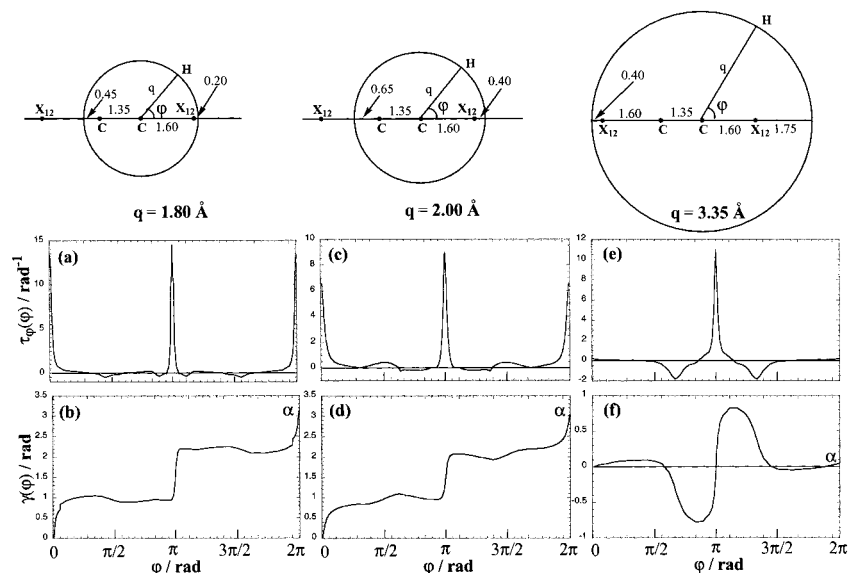
Figure 5. Results as calculated along circles located at the carbon position and surrounding the (1, 2) conical intersections. Shown are the geometry, the nonadiabatic coupling-matrix elements $\tau_\varphi(\varphi|q)$, and the adiabatic-to-diabatic transformation angles $\gamma(\varphi|q)$ as calculated for $r_{CC} = 1.35$ Å and for three q values (q is the CH distance). (a) and (b) $q = 1.80$ Å; (c) and (d) $q = 2.00$ Å; (e) and (f) $q = 3.35$ Å. The first two circles surround one conical intersection, and the third circle surrounds the two conical intersections.
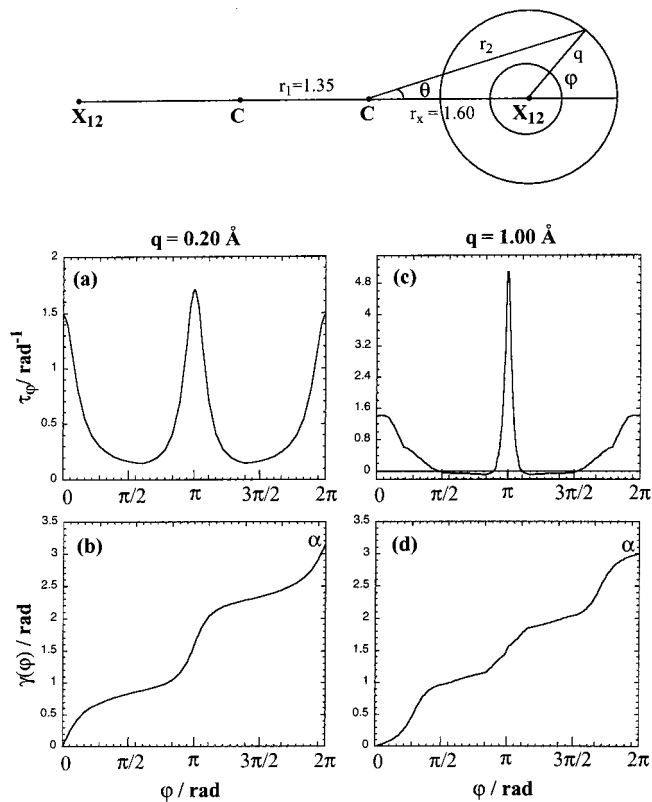
Figure 6. Results as calculated along circles located at the (1, 2) conical intersection position and defined in terms of a radius q. Shown are the geometry, the nonadiabatic coupling-matrix elements $\tau_\varphi(\varphi|q)$ ((a) and (c)), and the adiabatic-to-diabatic transformation angles $\gamma(\varphi|q)$ ((b) and (d)) as calculated for $r_{CC} = 1.35$ Å and for two q values. (a) and (b) $q = 0.2$ Å; (c) and (d) $q = 1.00$ Å.

In Table 1 are listed the n values as calculated for these circular closed contours. We have noticed that in all cases the n value of eq 29 is either ~1.0 when only one conical intersection is surrounded or ~0.0 when the circle surrounds two conical intersections or none of them. More information about the various n values can be found in ref 13.

Figure 7. Results as calculated along circles located at the midpoint between the two carbon atoms and defined in terms of a radius q. Shown are the geometry, the nonadiabatic coupling-matrix elements $\tau_\varphi(\varphi|q)$ ((a) and (c)) and the adiabatic-to-diabatic transformation angles $\gamma(\varphi|q)$ ((b) and (d)) as calculated for $r_{CC} = 1.35$ Å and for two q values. (a) and (b) $q = 2.475$ Å (in this case, the contour does not surround any (1, 2) conical intersection); (c) and (d) $q = 2.875$ Å (in this case, the contour surrounds the two (1, 2) conical intersections).

Before concluding this section, we have to make the following comment to avoid any reservations regarding these results: all contours considered here are symmetrical with respect to the

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TABLE 1: *n* Values as Calculated for Various Circles[a]

no.	center of circle	radius (Å)	no. of surrounded (1, 2) conical intersections	n
1	carbon atom	1.8	1	0.998
2	carbon atom	2.0	1	0.963
3	carbon atom	3.35	2	0.048
4	conical intersection	0.2	1	1.007
5	conical intersection	1.0	1	0.956
6	midpoint between two carbons	1.875	none	$\sim 10^{-4}$
7	midpoint between two carbons	2.475	2	$\sim 10^{-4}$

[a] See eqs 30–32.

two sides ("above" and "below") of the CC axis; therefore, one may suspect that effects due to the third state produced along segments located above this axis may cancel those produced along segments located below this axis. This possibility always exists, but because for practical purposes the components of $t_{12} \approx 0$ along these segments, as is shown in Figures 1, 2, and 5–7, it is not conceivable that the third state is capable of enhancing them significantly, if at all.

To avoid any confusion or ambiguity, all line integral calculations reported here have been carried out properly, namely, by employing the relevant components of t_{12} and not the absolute value of t_{12} (i.e., $|t_{12}|$).

V. Conclusions

In this article, we have tried to answer the following question. Considering a nonadiabatic coupling-term matrix of a given dimension, what is the minimal subspace for which diabatization is still valid? We proved that the actual size might be smaller than the size of the P sub-Hilbert space as defined in eq 10. The conditions for that to happen—they were referred to as the necessary conditions for diabatization—are dependent on the spatial distribution of the various nonadiabatic coupling terms. It was found that if the relevant nonadiabatic coupling terms do not overlap in configuration space (or overlap only slightly) then the subspace for diabatization can be reduced significantly. As an example, we considered the three lowest states of the C_2H molecule and showed that although the subspace is 3-D (in fact, we know it is larger than 5-D) we are (rigorously) allowed to employ, for diabatization purposes, the two lowest (adiabatic) states only. To show that this approach is valid, we calculated various line integrals along closed contours and examined the n values as presented in eq 32. In all cases, our results were close to 1 or 0 (see Table 1).

The fact that for any assumed contour the value of n is either 1 or 0 guarantees that any 2×2 diabatic matrix potential, $\mathbf{W}(s)$, calculated from eq 4 will be single-valued and can be used for any dynamic calculations. In other words, the following four potential matrix elements

$$W_{11}(s) = u_1(s) \cos^2 \gamma_{12}(s) + u_2(s) \sin^2 \gamma_{12}(s)$$

$$W_{22}(s) = u_1(s) \sin^2 \gamma_{12}(s) + u_2(s) \cos^2 \gamma_{12}(s)$$

$$W_{12}(s) = W_{21}(s) = \frac{1}{2}(u_2(s) - u_1(s)) \sin(2\gamma_{12}(s)) \quad (33)$$

are reliable as long as the $\gamma_{12}(s)$ angles are calculated by employing contours that start at the same point s_0 with the same given initial value of $\gamma_{12} = \gamma_{12}(s = s_0)$ (see eq 25).

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