

N-State Adiabatic-to-Diabatic Transformation Angle: Theory and Application

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In this article is discussed a new diabatization procedure which is expected to be reliable and, also, relatively easy to implement. This procedure takes into account the two main ingredients related to diabatization: (1) The size N of the smallest (relevant) group of states that forms a Hilbert subspace (this fact enforces the dimension of the adiabatic-to-diabatic transformation matrix to be N). (2) The total energy E which determines the number of open states, p , within this group of N states. The main emphasis in this manuscript is on the case that N is arbitrary but p is equal to 2. The various derivations as well as the final results are accompanied by numerical examples extracted from three- to five-state ab initio calculations for the $\text{H} + \text{H}_2$ system.

I. Introduction

It is well accepted that in order to study electronic non-adiabatic processes the treatment has to be carried out within the diabatic framework.^{1–15,29} The main difficulty with the diabatic framework is that its size, N , may become too large (and eventually even infinitely large) to prevent any sensible quantum mechanical treatment for the molecular system of interest. In a recent publication, we discussed the possibility to rigorously reduce the size N by employing energy arguments.¹⁶ To be more specific, we suggested to use an energy criterion to determine the size of the diabatic potential matrix that has to be employed for solving the relevant nuclear Schrödinger equation (SE). The energy criterion is introduced while being in the *adiabatic* framework and it recommends limiting the size of the *diabatic* manifold to be $\sim q$ where q is the number of *adiabatic* states which, for a given energy E , are classically reachable. Although, to be more flexible, it was suggested to carry out the calculations employing p states where p is an integer along the interval $q \leq p \leq N$. In what follows, the leading dimension is p ; however, we expect $p \sim q$.

As a result of a rigorous, but not trivial, theoretical treatment, the following was established.¹⁶ Assuming that the $N \times N$ adiabatic-to-diabatic transformation (ADT) matrix \mathbf{A} is given, it is enough to consider only the upper, left-hand side, square sub-matrix, $\mathbf{A}^{(p)}$ (which is of dimension $p \times p$) so that the corresponding *diabatic* potential matrix, $\mathbf{W}^{(p)}$ becomes

$$\mathbf{W}^{(p)} = \mathbf{A}^{(p)} \mathbf{u}^{(p)} (\mathbf{A}^{(p)})^{-1} \quad (1)$$

where $\mathbf{u}^{(p)}$ is the (diagonal) adiabatic potential matrix. Since $\mathbf{W}^{(p)}$ in eq 1, is in general not symmetric (unless $p = N$), this outcome contradicts a basic requirement of quantum mechanics, namely that the potential matrix has to be Hermitean. Although

one way to correct for this mishap is to symmetrize $\mathbf{W}^{(p)}$ this is not what we have in mind.

This issue is the main subject to be considered in the present article. Our treatment is limited to the case that $p = 2$ but N is arbitrary; in the numerical examples are considered values of $3 \leq N \leq 5$. In the next section is introduced a novel, two-state ADT angle, which, in principle is valid for any N (thus is N -dependent). This angle is then applied to perform the relevant ADT – a treatment accompanied by a numerical study applied to the five lower adiabatic states of the $\text{H} + \text{H}_2$ system, namely, to the $1^2A'$, $2^2A'$, $3^2A'$, $4^2A'$, and $5^2A'$ electronic states (see section III). The resulting diabatic matrices are analyzed in section IV and the conclusions are summarized in section V.

II. The Extended Euler Matrix as a Model for the ADT Matrix

II.1. Introductory Comments. In deriving a model for the \mathbf{A} -matrix, we have to make sure that it is able to form a matrix with the following features:

- (1) The matrix has to be orthogonal at any point in configuration space.
- (2) Its elements are cyclic functions with respect to a single given parameter, λ , so that starting with a diagonal (unit) matrix the model-matrix has to become diagonal again after one cycle (it does not have to be the unit matrix)
- (3) While becoming diagonal it has to contain an *even* number (-1 s) along the diagonal.

The first condition is due to the fact that \mathbf{A} is a solution of the following first order differential equation:^{14,17}

$$\nabla \mathbf{A}(\mathbf{s}) + \boldsymbol{\tau}(\mathbf{s}) \mathbf{A}(\mathbf{s}) = \mathbf{0} \quad (2)$$

where $\boldsymbol{\tau}(\mathbf{s})$ is the $N \times N$ matrix which contains the electronic nonadiabatic coupling terms (NACTs):

$$\boldsymbol{\tau}_{ji} = \langle \zeta_j | \nabla \zeta_i \rangle; \quad i, j = \{1, N\} \quad (3)$$

Here the grad-operator is expressed in terms of (mass-scaled) nuclear coordinates and $\zeta_k(\mathbf{s}_e | \mathbf{s})$; $k = j, i$ are the relevant adiabatic eigenfunctions.

Equation 2 has to be solved along contours to be designated as Γ . Its solution is given in the form:^{14a,17c}

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$$\mathbf{A}(\mathbf{s}|\Gamma) = \mathcal{P}\exp\left\{-\int_{\mathbf{s}_0}^{\mathbf{s}} \boldsymbol{\tau}(\mathbf{s}'|\Gamma) d\mathbf{s}'\right\} \quad (4)$$

where it is assumed that its initial matrix, $\mathbf{A}(\mathbf{s} = \mathbf{s}_0)$, is the unit matrix and \mathcal{P} is the ordering operator. For a closed contour, the relevant ADT matrix, $\mathbf{A}(\Gamma)$, becomes independent of any particular point along Γ but depends on Γ itself. This final matrix along the closed contour is designated as the **D**-matrix and takes the form

$$\mathbf{D}(\Gamma) = \mathcal{P}\exp\left\{-\oint_{\Gamma} \boldsymbol{\tau}(\mathbf{s}'|\Gamma) d\mathbf{s}'\right\} \quad (5)$$

It was shown that this matrix is diagonal (like the initial unit matrix) but is not necessarily a unit matrix. For a real basis set the diagonal elements of $\mathbf{D}(\Gamma)$ are ± 1 .^{13,18} In addition it was shown that the number of (-1) 's, to be labeled as *K*, has to be even (or zero).¹⁹

In this article we intend to present the general $N \times N$ ADT matrix \mathbf{A} as a product of single angle $N \times N$ rotation matrices. The resulting matrix becomes, in case of $N = 3$, similar to the Euler matrix,²⁰ and therefore will be termed, for $N > 3$, as the extended Euler matrix.¹⁹ In what follows this matrix is labeled as $\mathbf{A}^{(N)}$ or simply \mathbf{A} .

Before we relate to the general case we discuss two cases, namely, $N = 2$ and $N = 3$.

II.2. The Two-Dimensional System. $\mathbf{A}^{(2)}(\gamma_{12})$ is well-known to be of the form¹⁷

$$\mathbf{A}^{(2)}(\gamma_{12}(\mathbf{s}|\Gamma)) = \begin{pmatrix} \cos \gamma_{12}(\mathbf{s}|\Gamma) & \sin \gamma_{12}(\mathbf{s}|\Gamma) \\ -\sin \gamma_{12}(\mathbf{s}|\Gamma) & \cos \gamma_{12}(\mathbf{s}|\Gamma) \end{pmatrix} \quad (6)$$

where $\gamma_{12}(\mathbf{s}|\Gamma)$ is¹⁷

$$\gamma_{12}(\mathbf{s}|\Gamma) = -\int_{\mathbf{s}_0}^{\mathbf{s}} d\mathbf{s} \boldsymbol{\tau}_{12}(\mathbf{s}|\Gamma) \quad (7)$$

Next we consider what happens when the contour Γ becomes a closed contour. For this particular case, we define the angle $\alpha_{12}(\Gamma)$, which is given in the form:

$$\gamma_{12}(\mathbf{s}_0|\Gamma) \equiv \alpha_{12}(\Gamma) = \oint_{\Gamma} d\mathbf{s} \boldsymbol{\tau}_{12}(\mathbf{s}|\Gamma) \quad (8)$$

The angle $\alpha_{12}(\Gamma)$ is also known as the *topological* phase. In case the two states are isolated from the rest of the states that form the Hilbert space (this happens if in the given region all the NACTs that connect these two states with rest of the Hilbert space are small enough)^{21,22} $\alpha_{12}(\Gamma)$ becomes i.e., $\alpha_{12}(\Gamma) = n\pi$ where n is an integer or zero. This situation is termed by us as *quantization* condition—reminiscent of the Bohr–Sommerfeld quantization law^{13,18} but more relevant for spin states.

The above-mentioned **D**-matrix is obtained by replacing, in eq 6, the phase, $\gamma_{12}(\mathbf{s}|\Gamma)$, by its value at the end of the closed contour, namely, $\alpha_{12}(\Gamma)$. For the isolated case just mentioned, the **D**-matrix becomes¹⁸

$$\mathbf{D}^{(2)}(\Gamma) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad (9)$$

where we assumed that the contour Γ , in eq 8, surrounds one point of conical intersection (*ci*).

II.3. The Three-Dimensional System. In case of $N = 3$ we encounter the matrix $\mathbf{A}^{(3)}$, with nine elements. However, $\mathbf{A}^{(3)}$ has to be an orthogonal matrix where the ortho-normality conditions require the fulfillment of six relations. This leaves three free unknowns which, according to Euler, are three angles of rotation, namely, γ_{12} , γ_{13} , and γ_{23} . Consequently, it was suggested to construct the 3-state **A**-matrix as a product of three

rotation matrices. For this purpose we define the following three matrices, $\mathbf{Q}_{12}^{(3)}(\gamma_{12})$, $\mathbf{Q}_{23}^{(3)}(\gamma_{23})$, and $\mathbf{Q}_{13}^{(3)}(\gamma_{13})$ where for instance, $\mathbf{Q}_{13}^{(3)}(\gamma_{13})$ is given in the form:

$$\mathbf{Q}_{13}^{(3)}(\gamma_{13}) = \begin{pmatrix} \cos \gamma_{13} & 0 & \sin \gamma_{13} \\ 0 & 1 & 0 \\ -\sin \gamma_{13} & 0 & \cos \gamma_{13} \end{pmatrix} \quad (10)$$

(the other two are of a similar structure with the respective cosine and sine functions at the appropriate positions). One way of presenting $\mathbf{A}^{(3)}$ is²⁰

$$\mathbf{A}^{(3)} = \mathbf{Q}_{12}^{(3)} \mathbf{Q}_{13}^{(3)} \mathbf{Q}_{23}^{(3)} \quad (11a)$$

which following the multiplication takes the form:

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

Here (and elsewhere) $c_{kj} = \cos(\gamma_{kj})$ and $s_{kj} = \sin(\gamma_{kj})$. It is important to notice that deriving the matrix $\mathbf{A}^{(3)}$ in this way guarantees that the matrix is orthogonal (as it is a product of three orthogonal matrixes).

The relevant **D**⁽³⁾-matrix is obtained from $\mathbf{A}^{(3)}$, as before, by replacing the γ_{ij} angles calculated at the end point of the closed contour (i.e., $\gamma_{kj}(\mathbf{s}=\mathbf{s}_0|\Gamma)$) by $\alpha_{kj}(\Gamma)$.

As mentioned earlier the **D**⁽³⁾-matrix is expected to be diagonal, a condition that can be achieved if and only if $\alpha_{kj}(\Gamma) = n_{kj}\pi$ where n_{kj} are integers (or zero).

To obtain the three γ_{jk} angles, eq 12a is substituted in eq 2 and it can be shown that the three angles have to satisfy the following three coupled first order differential equations²⁰

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

Next we examine, briefly, the possible signs of the diagonal elements of **D**⁽³⁾. Because of the product in eq 11a, these diagonal elements take the form¹⁹

$$\mathbf{D}_{ij}^{(3)} = \delta_{ij}\cos \alpha_{jn}\cos \alpha_{jm}; \quad j \neq n \neq m; \quad j = 1,2,3 \quad (14)$$

where all the terms that contain sine-functions are, obviously, zero ($\sin(\pm n\pi) \equiv 0$)

This expression shows that the **D**⁽³⁾-matrix, may have either three (+1)s in the diagonal (it happens when all cosine functions are either positive or negative) or two (-1)s and one (+1) (which happens when one or two of the three cosine functions are negative). For the first case to happen, the contour has to surround an even number of *cis* for each pair of *adjacent* states (or not to surround any *ci*) whereas the second case applies for all other situations. It is straightforward to see that according to this model, *K* is either 2 or 0 as, indeed, is required. It is important to mention that eqs 14 were successfully applied for model systems^{20b} as well as for ab initio ones.^{20c}

The **A**-matrix can be written also in a slightly different form

$$\mathbf{A}^{(3)} = \mathbf{Q}_{12}^{(3)} \mathbf{Q}_{23}^{(3)} \mathbf{Q}_{13}^{(3)} \quad (11b)$$

which due to the lack of commutation relations yields a different presentation for the **A**-matrix

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

and a different set of equations for the three angles γ_{12} , γ_{13} , and γ_{23} :

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

In general, the two sets of equations yield different results for the three angles, γ_{12} , γ_{13} , and γ_{23} ; however, as long as we are interested only in the elements of the \mathbf{A} -matrix, eq 13a and 13b are expected to yield identical results. In what follows eqs 13a and 13b are applied to derive *approximate* solutions for the \mathbf{A} -matrix and in this case we may get different results due to the two presentations, but as will be seen, each of the solutions applies for a different *physical* situation.

In principle we may derive more sets of equations (for other permutations see ref 20b) but here, and in what follows, we are interested only in those permutations where the first matrix on the left-hand side is $\mathbf{Q}_{12}^{(N)}(\gamma_{12})$. This choice guarantees that γ_{12} is *privileged* by a differential equation where its own NACT, τ_{12} is the isolated *free* term. This fact ensures that whenever the region under consideration contains one or several (1,2) *cis*, the corresponding γ_{12} angle has features which connect it, in a straightforward way, with τ_{12} . This feature is, of course, expected when the region, surrounded by Γ , is dominated by τ_{12} but, as will be shown here, even in cases when τ_{12} is not the only NACT in the region, still this particular γ_{12} is dominated by τ_{12} .

II.4. The N -Dimensional System. Like in the previous three-state case, here too, we are interested in products similar to those given in eq 11a or 11b, namely, where the first matrix on right-hand side is $\mathbf{Q}_{12}^{(N)}(\gamma_{12})$. Therefore, we treat the N -dimensional case for an \mathbf{A} -matrix given in the form

$$\mathbf{A}^{(N)}(\gamma_{12}, \gamma_{13}, \dots, \gamma_{N-1N}) = \mathbf{Q}_{12}^{(N)}(\gamma_{12})\tilde{\mathbf{A}}^{(N)}(\gamma_{13}, \dots, \gamma_{N-1N}) \quad (15)$$

where we recall that in general we have $N(N-1)/2$ angles of the type γ_{kj} ; $k > j$ as unknowns and that $\mathbf{Q}_{12}^{(N)}(\gamma_{12})$ is, for instance for $N=5$, of the form:

$$\mathbf{Q}_{12}^{(N=5)}(\gamma_{12}) = \begin{pmatrix} \cos(\gamma_{12}) & \sin(\gamma_{12}) & 0 & 0 & 0 \\ -\sin(\gamma_{12}) & \cos(\gamma_{12}) & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad (16)$$

Our next task is not to present the first order differential equations for all the $N(N-1)/2$ angles but only to derive the equation for γ_{12} . To achieve that we substitute eq 15 in eq 2,

$$\nabla(\mathbf{Q}_{12}^{(N)}(\gamma_{12})\tilde{\mathbf{A}}^{(N)}(\gamma_{13}, \dots, \gamma_{N-1N})) + \tau\mathbf{Q}_{12}^{(N)}(\gamma_{12})\tilde{\mathbf{A}}^{(N)}(\gamma_{13}, \dots, \gamma_{N-1N}) = \mathbf{0}$$

perform the necessary differentiations, and then multiply the outcome from the right-hand side by $(\tilde{\mathbf{A}}^{(N)})^\dagger$; thus

$$\nabla(\mathbf{Q}_{12}^{(N)}(\gamma_{12})) + \tau\mathbf{Q}_{12}^{(N)}(\gamma_{12}) + \mathbf{Q}_{12}^{(N)}(\gamma_{12})(\nabla\tilde{\mathbf{A}}^{(N)}(\gamma_{13}, \dots))\tilde{\mathbf{A}}^{(N)}(\gamma_{13}, \dots)^\dagger = \mathbf{0} \quad (17)$$

where we mention that $\tilde{\mathbf{A}}^{(N)}$ is itself an orthogonal matrix (it is a product of orthogonal matrices) so that $\tilde{\mathbf{A}}^{(N)}(\tilde{\mathbf{A}}^{(N)})^\dagger = \mathbf{I}^{(N)}$. Equation 17 can be further simplified by multiplying it from the left-hand side by $\mathbf{Q}_{12}^{(N)}(\gamma_{12})^\dagger$. Next considering any of the two equations for γ_{12} (we have only two equations but the values of γ_{12} are not necessarily the same), we get

$$\nabla\gamma_{12}^{(i)} = -\tau_{12} - \sum_{jk} Z_{jk}^{(i)} \nabla\gamma_{jk}; \quad i = 1, 2 \quad (18)$$

where $Z_{jk}^{(i)} \equiv Z_{jk}^{(i)}(\gamma_{13}, \dots, \gamma_{N-1N})$, namely none of them depend on γ_{12} and the prime sign (under the summation symbol) implies that the summation does not contain the term $(jk) = (12)$ (in other words $Z_{12}^{(i)} \equiv 0$).

As mentioned we have two different equations for γ_{12} . As an example we consider, explicitly, what happens in the case of $N=3$.

(1) For the case $\tilde{\mathbf{A}}^{(3)}(\gamma_{13}, \gamma_{23}) = \mathbf{Q}_{13}^{(3)}(\gamma_{13})\mathbf{Q}_{23}^{(3)}(\gamma_{23})$, it can be shown, employing eq 12a, that

$$\nabla\gamma_{12}^{(1)} = -\tau_{12} + \sin\gamma_{13}\nabla\gamma_{23} \quad (19a)$$

(2) For the (permuted) case, $\tilde{\mathbf{A}}^{(3)}(\gamma_{23}, \gamma_{13}) = \mathbf{Q}_{23}^{(3)}(\gamma_{23})\mathbf{Q}_{13}^{(3)}(\gamma_{13})$, it can be shown, employing eq 12b, that

$$\nabla\gamma_{12}^{(2)} = -\tau_{12} + \sin\gamma_{23}\nabla\gamma_{13} \quad (19b)$$

Although eq 18 is an interesting result (and, following it, the same applies to eq 19a and eq 19b), it is not in a practical form for an arbitrary value of N . The main reason being that, for $N > 3$ *deriving* the differential equations for the $N(N-1)/2$ angles is a formidable task. In fact it is much easier to derive the \mathbf{A} -matrix by solving the exponentiated line integral as given in eq 4. However having the explicit elements of the \mathbf{A} -matrix does not necessarily yield the angle γ_{12} . Still while considering the algebraic expressions of the elements of the various matrices for $N=3$, we revealed some interesting features which seem to yield the required γ_{12} angle. In particular we get from eq 12a the following result:

$$\gamma_{12} = \gamma_{12}^{(1)} = -\tan^{-1}(\mathbf{A}_{21}/\mathbf{A}_{11}) \quad (20a)$$

As a result of this finding we may encounter two difficulties.

(1) From eq 12b we find another relation for γ_{12} , namely:

$$\gamma_{12} = \gamma_{12}^{(2)} = \tan^{-1}(\mathbf{A}_{12}/\mathbf{A}_{22}) \quad (20b)$$

Since there is no reason to believe that the two expressions yield, in general, identical numerical values, the question to be asked is which of the two values should be preferred. (2) The second possible difficulty is related to the extension of these relations for $N > 3$, or in other words: do these relations hold for $N > 3$?

These two questions will be treated in the next section. For this purpose we employ results obtained from a recent five-state study related to the $\text{H} + \text{H}_2$ system.

III. The Derivation of the γ_{12} -Angle for an N -State System

III.1. Comments Concerning *ab Initio* Calculations. The NACTs and the potential energy surfaces (PES) required for

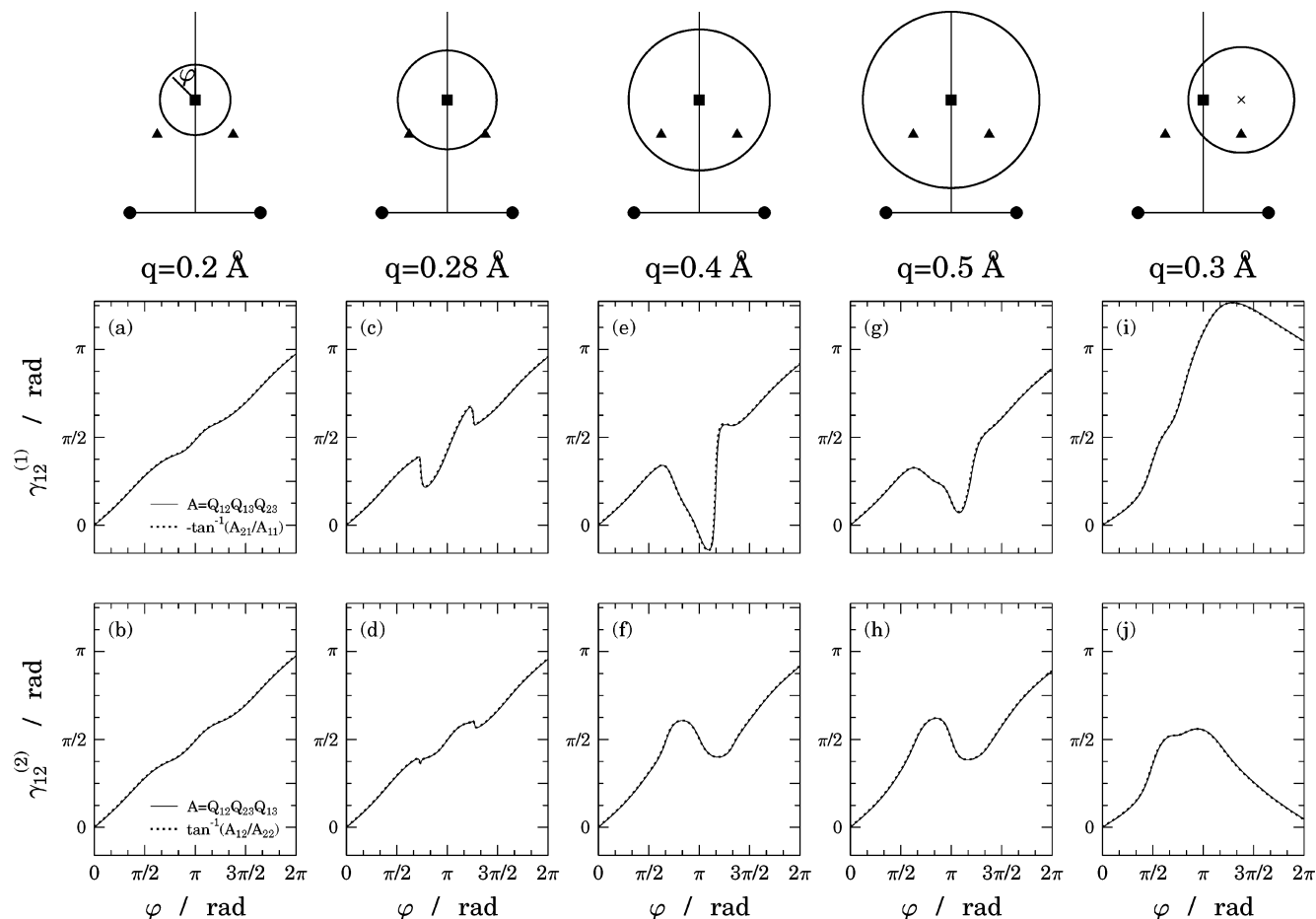


Figure 1. ADT angles, $\gamma_{12}^{(1)}$ (see eq 20a and presented in the upper row of parts) and $\gamma_{12}^{(2)}$ (see eq 20b and presented in the lower row of parts), as obtained for a three-state Hilbert subspace. The calculations are done for the contours shown in the schematic section of the figure and the results are presented as a function of φ (the polar coordinate). In each part are presented two curves one as obtained from eq 20 (the dashed line) and one as solved by eq 13 (the full line). The more interesting results are shown in parts i and j, emphasizing the different characters of the two ADT angles, $\gamma_{12}^{(1)}$ and $\gamma_{12}^{(2)}$: the first ends up with a *topological* phase π and the second with zero. As for the schematic section: we show the contours along which were performed the calculations, the position of the two fixed hydrogens (\bullet) and the position of the two different types of *cis*: The single (1,2) *ci* is presented in terms of a full square, and the two (2,3) *cis* are shown in terms of full triangles.

the present studies are calculated at the state-average CASSCF level using 6-311G** (3df,3pd) basis set^{23a} extended with additional diffuse functions. In order properly to take into account the Rydberg states we added, to the basis set, one *s* diffuse function and one *p* diffuse function in an even tempered manner,^{23b} with the exponents of 0.0121424 and 0.046875, respectively. We used the active space including all three electrons distributed on 9 orbitals. Usually five different electronic states (depending on the case) namely, $1^2A'$, $2^2A'$, $3^2A'$, $4^2A'$, and $5^2A'$ were computed by the state-average CASSCF method with equal weights. Convergence test were carried out with respect to the number of states. All ab initio calculations were carried out employing MOLPRO. Previous studies on this system were presented in refs 22, 24, and 25.

We report here on results as calculated for the situation where two Hydrogen atoms are fixed so that their interatomic distance is $R_{\text{HH}} = 0.74 \text{ \AA}$ and the third atom is free to move to probe the values of the NACTs at the various points in configuration space. With this approach we detected the well-known *equilateral* D_{3h} *ci* that couples the two lower states of this system, the *two* C_{2v} *cis* that couple the second and the third states and a second D_{3h} *ci* that couples the fourth and the fifth state. It is important to mention that in the region inspected by us we did not find any (3,4) *cis*. The positions of the various *cis* are, schematically, shown in Figure 1.

We usually report on results along circular contours and consequently, in the present article, are discussed results related to five circles. Four of them are centered at the D_{3h} point (the position of the (1,2) *ci*) with radii $q = 0.2, 0.28, 0.4, 0.5 \text{ \AA}$. The fifth circle has a radius $q = 0.3 \text{ \AA}$ and is centered at a point shifted toward the right from the (1,2) *ci*-point (designated as \times in Figure 1). The first two (out of the five) circles surround only the (1,2) *ci*, the third and the fourth circles surround the (1,2) *ci* and the *two* (2,3) *cis* and the fifth circle surrounds the (1,2) *ci* and *one* of the (2,3) *cis*.

The results of the various calculations are presented as a function of the polar coordinate, φ . We recall that the NACTs are vectors but we are interested only in their *angular* component $\tau_{\varphi jk}(\varphi|q)/q$ where $\tau_{\varphi jk}(\varphi|q)$ is given in the form:

$$\tau_{\varphi jk} = \left\langle \xi_j \left| \frac{\partial}{\partial \varphi} \xi_k \right. \right\rangle; j, k = \{1, N\} \quad (21)$$

It is important to mention that the points $(q, \varphi = 0)$ and $(q, \varphi = \pi)$ are the ‘northern’ and the ‘southern’ poles, respectively, both located on the symmetry line (which is perpendicular to the HH axis). The various figures and mainly parts c–h of Figure 1 indicate that most of the ‘action’ (i.e., strong variations in the NACTs) takes place around $\varphi = \pi$ the point closest to the HH axis.

III.2. The γ_{12} -Angle for a Three-State System. The numerical study in this section is related to $\gamma_{12}^{(1)}$ as calculated for the product in eq 11a (presented in the upper row of sub figures) and $\gamma_{12}^{(2)}$ as calculated for the product in eq 11b (presented in the lower row of parts). In parts a, c, e, g, and i of Figure 1 are compared results as derived by solving eq 13a—full line—with those obtained by applying eq 20a—dashed line. In parts b, d, f, h, and j of Figure 1 are compared results as derived by solving eq 13b with those obtained by applying eq 20b. The two main features to be noticed are as follows: (a) The two curves in each part overlap *completely*, indicating that the simple solutions in eqs 20a and 20b are relevant for deriving γ_{12} in each of the situations. In other words, once the **A**-matrix is given (namely, calculated employing eq 4) there is no need to solve eq 13 to derive the γ_{12} angles. (b) The curves in the upper parts of Figure 1 differ—in most cases—significantly from their counterparts given in the lower parts indicating that the two γ_{12} angles, as obtained for the two permuted products in eq 11, relate to different physical situations.

To understand the source for these differences it is best to compare the results presented in Figure 1, parts i and j. It is noticed that the curves in sub-Figure 1i behave similar to those in the other eight parts presented in Figure 1, namely, their topological phases (their values at the end of the closed contour) become $\alpha_{12}(q) \sim \pi$ whereas the curves in Figure 1j end up with $\alpha_{12}(q) \sim 0$. The explanation is as follows: The variation of each of the angles along a contour, known as the *open phase*, is associated with a given eigenfunction and the value of such a phase, at the end of a closed contour, is the corresponding *topological phase*^{26,27} (also called the Berry phase). With this interpretation in mind the γ_{12} -curves presented in the upper parts of Figure 1 are the open phases related to the ground-state eigenfunction and the curves presented in the lower parts of Figure 1 are the open phases related to the upper, first excited, eigenfunction. Next, in the first four cases presented in parts a, c, e, and g (see also parts b, d, f, and h) the contours surround the single (1,2) *ci* and the *two* (2,3) *cis*. In these situations the topological phases of both, the lower and the upper eigenfunctions become $\sim \pi$, as indeed is the case (this particular aspect of the line integral is best explained in ref 20c; see Figure 5 in that reference and the relevant discussion). However, a different situation is encountered for parts i and j. Here the contour surrounds, like before, the (1,2) *ci* but only *one* (2,3) *ci*. On the basis of previous studies,^{14a,19} the topological phase for the lower state, like in the previous cases, is $\sim \pi$ but it becomes zero for the second, upper, state, as is expected in this situation (in this case, due to the (1,2) and the (2,3) *cis*, the sign of the second topological phase is flipped twice).

The fact that our procedure can distinguish between the two kinds of the γ_{12} angle is encouraging because it enables to apply the correct ADT angle for each process. To study the (1 \rightarrow 2) transition we employ $\gamma_{12}^{(1)}$, as obtained from the product (1,2)-(1,3)(2,3) and to study the (2 \rightarrow 1) transition we apply $\gamma_{12}^{(2)}$ as obtained from the (1,2)(2,3)(1,3) product.

III.3. The γ_{12} -Angle for Four and Five-State Systems. Whereas all the details regarding the three-state γ_{12} angle could be verified analytically (because the 3×3 **A**-matrix is given explicitly—see eq 12) this advantage is usually not available for those cases that $N > 3$. For instance to derive the relevant **A**-matrix for a four-state system is already a formidable task because this case is defined in terms of *six* angles, and therefore it requires solving six first order differential equations (one for each angle) that have to be derived from a matrix that is formed by a product of six 4×4 rotational matrices. In what follows

we somewhat extend the previous three-state case to cases which contain four and five states. However, this extension is limited for certain aspects.

In what follows we consider products of the type given in eq 15, namely products that have the rotation matrix for γ_{12} located on the left-hand side for any of the possible permutations. As was shown in section II.3, this arrangement guarantees that the differential equation for any γ_{12} contains τ_{12} as the leading term a fact that yields the required information on the way γ_{12} is formed primarily by the τ_{12} NACT (subject to disturbances caused by other NACTs).

In contrast to the $N = 3$ case here we intend to extract the two different γ_{12} angles from eqs 20a and 20b only. Before doing that we verified two facts: (1) For $N = 4$ we produced all the 120 permutations of $\tilde{\mathbf{A}}^{(N=4)}$ and the corresponding $\mathbf{A}^{(N=4)}$ -matrices to see that indeed some of the permutations yield eq 20a and some others yield eq 20b. For instance we find that numerous permutations yield, for the two first elements of the first column, the following terms:

$$\mathbf{A}_{11} = \cos \gamma_{12} \cos \gamma_{13} \cos \gamma_{14}; \quad \mathbf{A}_{21} = \sin \gamma_{12} \cos \gamma_{13} \cos \gamma_{14} \quad (22a)$$

and others yield

$$\mathbf{A}_{12} = -\sin \gamma_{12} \cos \gamma_{23} \cos \gamma_{24}; \quad \mathbf{A}_{22} = \cos \gamma_{12} \cos \gamma_{23} \cos \gamma_{24} \quad (22b)$$

but not the ones in eq 22a. It is well noticed that eq 22a yields eq 20a and eq 22b yields eq 20b.

We also made sure that no other equations of the above type exist from which one can derive, solely, γ_{12} angles. The same procedure was repeated for $N = 5$ and we obtained a similar outcome, namely eqs 20a and 20b are also valid for this case.

It is important to realize that these derivations are valid because each permutation within the product (12)(13)(14)(23)-(24)(34) is expected to yield, numerically, the same **A**-matrix.

In Figure 2 are presented the angles γ_{12} as calculated once employing eq 20a (Figure 2, parts a, c, e, and g) and once employing eq 20b (Figure 2, parts b, d, f, and h) for four different N values, namely, $N = 2, 3, 4$, and 5. The results are presented in four columns—each column refers to a different contour as shown in the schematic drawings at the top of each column.

Two main features are to be noticed: (1) The γ_{12} -functions are seen, approximately, to converge as N increases a feature to be expected. Fast convergence is achieved in case the contour surrounds only one *ci* (see Figure 2, parts a and b). In all other cases, the convergence is slower: It is noticed that the γ_{12} -functions for $N = 2$ are always inadequate, but then already for $N = 3$, relatively well converged γ_{12} -functions are obtained. The only exceptions are $\gamma_{12}^{(1)}$ -functions as calculated for $q = 0.4, 0.5 \text{ \AA}$ along the short interval: $\pi - \delta \leq \varphi \leq \pi + \delta$, mainly because of the strong interaction between the τ_{12} -NACT and τ_{23} -NACT along that interval. This interaction affects also the convergence for $\gamma_{12}^{(2)}$ but to a smaller extent.

IV. The Diabatic Potential Energy Surface

In what follows we concentrate on forming the two-dimensional diabatic PES matrix according to the prescription given in eq 1 where the required two-dimensional **A**-matrix is obtained from $\mathbf{A}^{(3)}$ -matrices presented in eq 12a or (12b). The decision which of the two matrices to apply is made as follows. If the aim is to study the 1 \rightarrow 2 transition (namely the transition

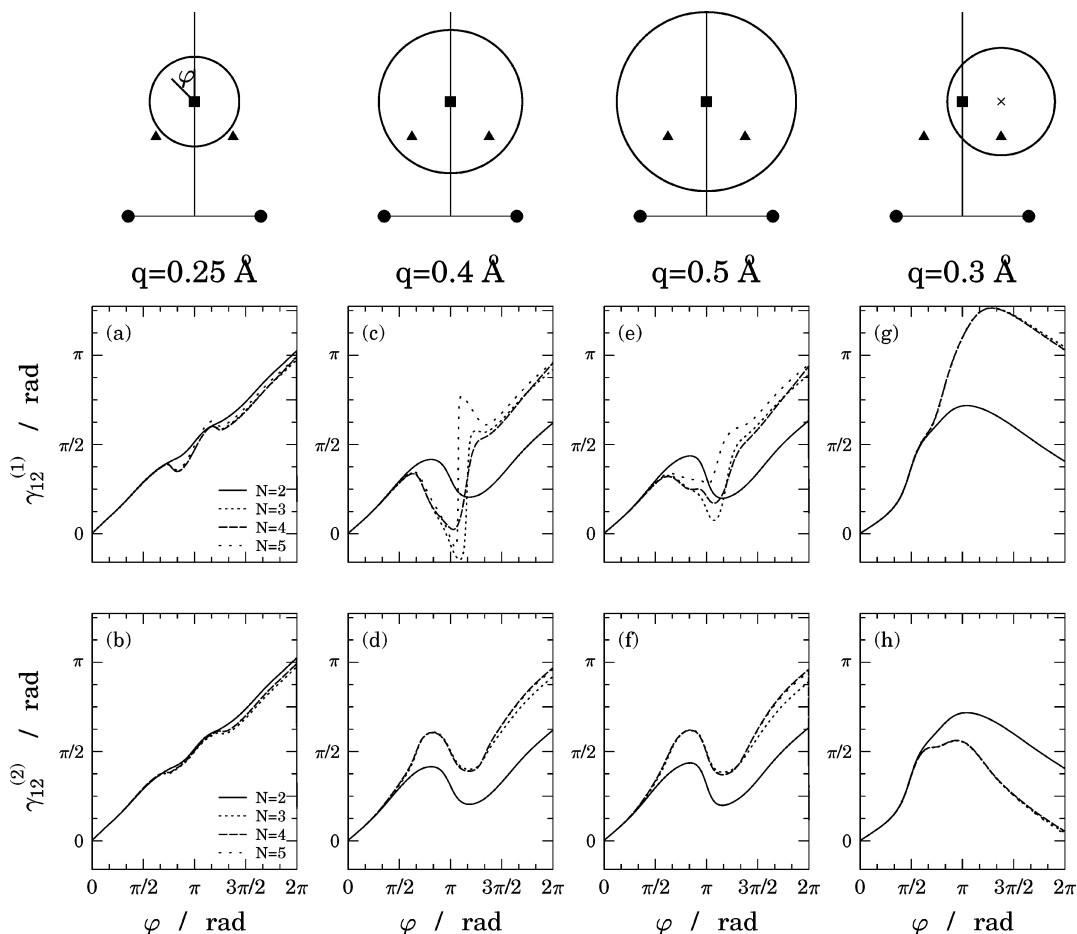


Figure 2. ADT angles $\gamma_{12}^{(1)}$ (upper row of parts) and $\gamma_{12}^{(2)}$ (lower row of parts) as a function of φ calculated along the contours. The different curves in each part were calculated for different N values where N is the dimension of the Hilbert subspace. Results are shown for $N = 2, 3, 4$, and 5 . The more important issue here is the large difference between the curves as calculated for $N = 2$ and those for $N > 2$. Compare with Figure 1.

from the ground-state to the (first) excited state) then the $\mathbf{A}^{(3)}$ given in eq 12a and the $\gamma_{12}^{(1)}$ angle given in eq 20a should be employed. If the aim is to study the $2 \rightarrow 1$ transition (namely the transition from the (first) excited state to the ground-state) then the $\mathbf{A}^{(3)}$ in eq 12b and the $\gamma_{12}^{(2)}$ angle in eq 20b has to be employed (see discussion at the last paragraph of section III.2). We are aware that this procedure does not necessarily fulfill microscopic reversibility but it is not clear to what extent microscopic reversibility is really damaged. This has to be tested in actual applications.

IV.1. The Two-State Diabatic PES Matrix To Study the $1 \rightarrow 2$ Transition. To study this case we employ $\mathbf{A}^{(3)}$ given in eq 12a from which $\mathbf{A}^{(2)}$ is formed by extracting the 2×2 sub-matrix in the upper left corner of $\mathbf{A}^{(3)}$. Thus

$$\mathbf{A}^{(2)} = \begin{pmatrix} c_{12}c_{13} & s_{12}c_{23} - c_{12}s_{13}s_{23} \\ -s_{12}c_{13} & c_{12}c_{23} + s_{12}s_{13}s_{23} \end{pmatrix} \quad (23a)$$

Next is formed the corresponding inverse matrix, $(\mathbf{A}^{(2)})^{-1}$:

$$(\mathbf{A}^{(2)})^{-1} = \frac{1}{c_{13}c_{23}} \begin{pmatrix} c_{12}c_{23} + s_{12}s_{13}s_{23} & -s_{12}c_{23} + c_{12}s_{13}s_{23} \\ s_{12}c_{13} & c_{12}c_{13} \end{pmatrix} \quad (24a)$$

According to eq 1 the relevant 2×2 diabatic potential matrix results from the expression

$$\tilde{\mathbf{W}}^{(2)} = \mathbf{A}^{(2)} \begin{pmatrix} \mathbf{u}_1 & 0 \\ 0 & \mathbf{u}_2 \end{pmatrix} (\mathbf{A}^{(2)})^{-1} \quad (25)$$

In what follows $\tilde{\mathbf{W}}^{(2)}$ is presented as a sum of two matrices:

$$\tilde{\mathbf{W}}^{(2)} = \mathbf{W}^{(2)} + \Delta\mathbf{W}^{(2)} \quad (26)$$

Here

$$\mathbf{W}^{(2)} = \begin{pmatrix} c_{12}^2 u_1 + s_{12}^2 u_2 & c_{12}s_{12}(u_2 - u_1) \\ c_{12}s_{12}(u_2 - u_1) & c_{12}^2 u_2 + s_{12}^2 u_1 \end{pmatrix} \quad (27)$$

and

$$\Delta\mathbf{W}^{(2)} = \frac{s_{13}s_{23}}{c_{23}} \begin{pmatrix} -c_{12}s_{12} & -c_{12}^2 \\ s_{12}^2 & c_{12}s_{12} \end{pmatrix} (u_2 - u_1) \quad (28a)$$

It is well noticed that as long as γ_{23} is not too close to $\pi/2$ (so that c_{23} does not become too small) the elements of $\Delta\mathbf{W}^{(2)}$ are expected to be small (because $\gamma_{13} \sim 0$), and consequently $\mathbf{W}^{(2)}$ becomes the *ordinary* diabatic potential matrix defined in terms of a (single) ADT $\gamma_{12}^{(1)}$ angle:

$$\mathbf{W}^{(2)} = \begin{pmatrix} c_{12}^2 u_1 + s_{12}^2 u_2 & c_{12}s_{12}(u_2 - u_1) \\ c_{12}s_{12}(u_2 - u_1) & c_{12}^2 u_2 + s_{12}^2 u_1 \end{pmatrix} \quad (29)$$

It is because of this interesting outcome that we decided to define $\gamma_{12}^{(1)}$ (and accordingly, later, also $\gamma_{12}^{(2)}$) the N -state ADT angle (see title of the article).

IV.2. The Two-State Diabatic PES Matrix To Study the $2 \rightarrow 1$ Transition. To study this case we employ $\mathbf{A}^{(3)}$ given in

eq 12b from which $\mathbf{A}^{(2)}$ is formed, as in the previous case, by extracting the 2×2 submatrix in the upper left corner of $\mathbf{A}^{(3)}$. Thus

$$\mathbf{A}^{(2)} = \begin{pmatrix} c_{12}c_{13} - s_{12}s_{13}s_{23} & s_{12}c_{23} \\ -s_{12}c_{13} - c_{12}s_{13}s_{23} & c_{12}c_{23} \end{pmatrix} \quad (23b)$$

and the corresponding inverse matrix $(\mathbf{A}^{(2)})^{-1}$, is

$$(\mathbf{A}^{(2)})^{-1} = \frac{1}{c_{13}c_{23}} \begin{pmatrix} c_{12}c_{23} & -s_{12}c_{23} \\ s_{12}c_{13} + c_{12}s_{13}s_{23} & c_{12}c_{13} - s_{12}s_{13}s_{23} \end{pmatrix} \quad (24b)$$

Continuing in the same manner as in the previous section we get for $\mathbf{W}^{(2)}$ a similar expression (except that the angle $\gamma_{12}^{(1)}$ is replaced by $\gamma_{12}^{(2)}$) but a somewhat different expression for $\Delta\mathbf{W}^{(2)}$

$$\Delta\mathbf{W}^{(2)} = \frac{s_{13}s_{23}}{c_{13}} \begin{pmatrix} c_{12}s_{12} & -s_{12}^2 \\ c_{12}^2 & -c_{12}s_{12} \end{pmatrix} (u_2 - u_1) \quad (28b)$$

It is well noticed that as long as γ_{13} is not too close to $\pi/2$ (so that c_{13} is not too small) the elements of $\Delta\mathbf{W}^{(2)}$ are expected to be small (because $\gamma_{23} \sim 0$) and consequently $\mathbf{W}^{(2)}$ becomes, as in the previous section (see eq 29), the *ordinary* diabatic potential matrix defined in terms of a (single) ADT $\gamma_{12}^{(2)}$ angle:

It is important to realize that in eq 28b it is not only that $\gamma_{12}^{(2)}$ differs from $\gamma_{12}^{(1)}$ but also the two other angles, namely, γ_{13} and γ_{23} differ from the respective ones mentioned in section IV.1.

IV.3. Analysis. Usually the numerical part is devoted to comparisons between *accurate* and *approximate* results. In our study this implies comparing the approximate and the correct diabatic potential matrix elements. However from the presentation of the approximate diabatic potential matrix (see eq 1) it is obvious that the elements of this matrix and the corresponding elements of the so-called *accurate* $N \times N$ matrix are not necessarily similar. Moreover going over the derivation, the relevant elements of the two matrices *cannot* be similar because we ignored all those *adiabatic* potentials which, for a given energy E , are unreachable (or classically “closed”) arguing that doing that does not affect the *solution* of the diabatic (nuclear) SE. No claims were made regarding the resulting *diabatic* potential matrix elements. Therefore, comparing the two kinds of diabatic matrix elements is meaningless.

As is noticed the procedure developed here for the case of $N = 3$ yields two 2×2 diabatic potential matrices: (a) the one given in eqs 26–28a with the main disadvantage of being nonsymmetrical; (b) the one given in eq 29 which is symmetrical but with the main disadvantage of being only approximate. Similar situations are expected for $N > 3$.

No doubt, that for practical purposes, one would prefer the symmetrical diabatic potential matrix given in eq 29. The question is if we can establish simple means to determine to what extent this matrix is relevant. For instance one way to achieve that is to calculate the elements of $\Delta\mathbf{W}^{(2)}$ and compare them with \mathbf{u}_1 and \mathbf{u}_2 in the regions of interest. However the matrix elements of $\Delta\mathbf{W}^{(2)}$ are, in general, not available (in particular when $N > 3$), and therefore, this approach cannot be considered as practical. Nevertheless we suggest to carry out this study in case for $N = 3$ (the case for which we have these elements available), mainly in order to reveal where and to what extent the elements of $\Delta\mathbf{W}^{(2)}$ are large and in this way eventually to be able to estimate the relevance of the proposed diabatization.

To study this issue we consider eq 28a (and/or eq 28b) and concentrate mainly on $c_{23} \equiv \cos \gamma_{23}$ (because c_{23} appears in the *denominator* of eq 28a). Since $(\cos \gamma_{23})^{-1}$ is the only function which may attain large values (eventually even infinite values, in case $\gamma_{23} = \pi/2$) we follow γ_{23} along various contours in configuration space. From the second equation in eq 13a it is obvious that if τ_{23} is zero or small enough along such a contour, γ_{23} is expected to be small and most likely stays (far) away from $\pi/2$. (we remind the reader that, based on our experience, $\tau_{13} \ll \tau_{23}$,²⁸ so that, τ_{13} can be ignored). In other words we expect γ_{23} to approach $\pi/2$ only along those contours where τ_{23} –NACT is large enough and this can happen only in the vicinity of a (2,3) *ci*. Therefore, as long as the contour of interest does not get too close to a (2,3) *ci*, γ_{23} is expected not to change significantly and remains ~ 0 . From eq 28a it follows that not only the denominator is finite in such a case but the numerator $\rightarrow 0$. Similar arguments apply for γ_{13} .

The next question is related to the case that, indeed, the contour gets close to the (2,3) *ci*. Can we justify ignoring $\Delta\mathbf{W}^{(2)}$ in such a situation? Including the close vicinity of the (2,3) *ci* implies including the region where \mathbf{u}_2 is large. We remind the reader that at the vicinity of (2,3) *ci points* the surface \mathbf{u}_2 , most likely, reaches its highest values. Consequently, for the case under consideration, these (highest) values of \mathbf{u}_2 , are assumed to be classically closed (if this assumption is not valid then the approximate diabatization has to be carried out for a three-state system) and therefore adding the large values of $\Delta\mathbf{W}^{(2)}$ to the large values of $\mathbf{W}^{(2)}$ (see eq 26) is not expected to affect the results.

The conclusion of this analysis is that in general the elements of $\Delta\mathbf{W}^{(2)}$ are small enough as long as the contours do not get too close to a (2,3) *ci*. It is true that being in a region that contains such a *ci*, causes $\Delta\mathbf{W}^{(2)}$ to attain large values but this kind of a region is most likely classically closed so that the exact values of the potentials are not expected to affect results, such as scattering cross sections or spectroscopic cross sections. In other words since such a region (near the (2,3) *ci*) is already excluded by the original *adiabatic* potential \mathbf{u}_2 adding the values of $\Delta\mathbf{W}^{(2)}$ is not expected to significantly affect the calculations.

In the next section the above analysis is carried out for the {H,H₂} system.

IV.4. A Numerical Study of the New Way of Diabatization. To perform the numerical study, we use the two (1,2) ADT angles given in eqs 20a and 20b, for $N = 3$, and calculate the elements of $\Delta\mathbf{W}^{(2)}$ at several regions of interest (see eq 28a and eq 28b). To calculate $\Delta\mathbf{W}^{(2)}$ we need all three angles $\gamma_{12}^{(1)}$, γ_{23} , and γ_{13} (or $\gamma_{12}^{(2)}$, γ_{23} , and γ_{13} for the second case). Having, for instance, $\gamma_{12}^{(1)}$ we employ the second and the third equations in eq 13a, to calculate γ_{23} and γ_{13} which are then employed, together with $\gamma_{12}^{(1)}$, to calculate $\Delta\mathbf{W}^{(2)}$ (see eq 28a).

The results, to be discussed next, are presented in a series of parts of Figure 3. In the parts along the upper row of Figure 3 are given the two lower *adiabatic* PESs of the H + H₂ system as calculated along five different circular contours (see Figure 1). In the second and third rows are presented the corresponding four elements of the $\Delta\mathbf{W}^{(2)}$ matrix as calculated along the same contours. In the intermediate row of parts are shown the matrix elements as calculated employing $\gamma_{12}^{(1)}$ (and the corresponding γ_{23} and γ_{13} angles) and in the lower (third) row those calculated employing $\gamma_{12}^{(2)}$ (and the corresponding γ_{23} and γ_{13} angles).

The following is to be noticed:

(1) The two first *columns* are related to situations where the circular contour (which is centered at the (1,2) *ci*) does not surround any of the (2,3) *cis*. As a result the elements of $\Delta\mathbf{W}^{(2)}$

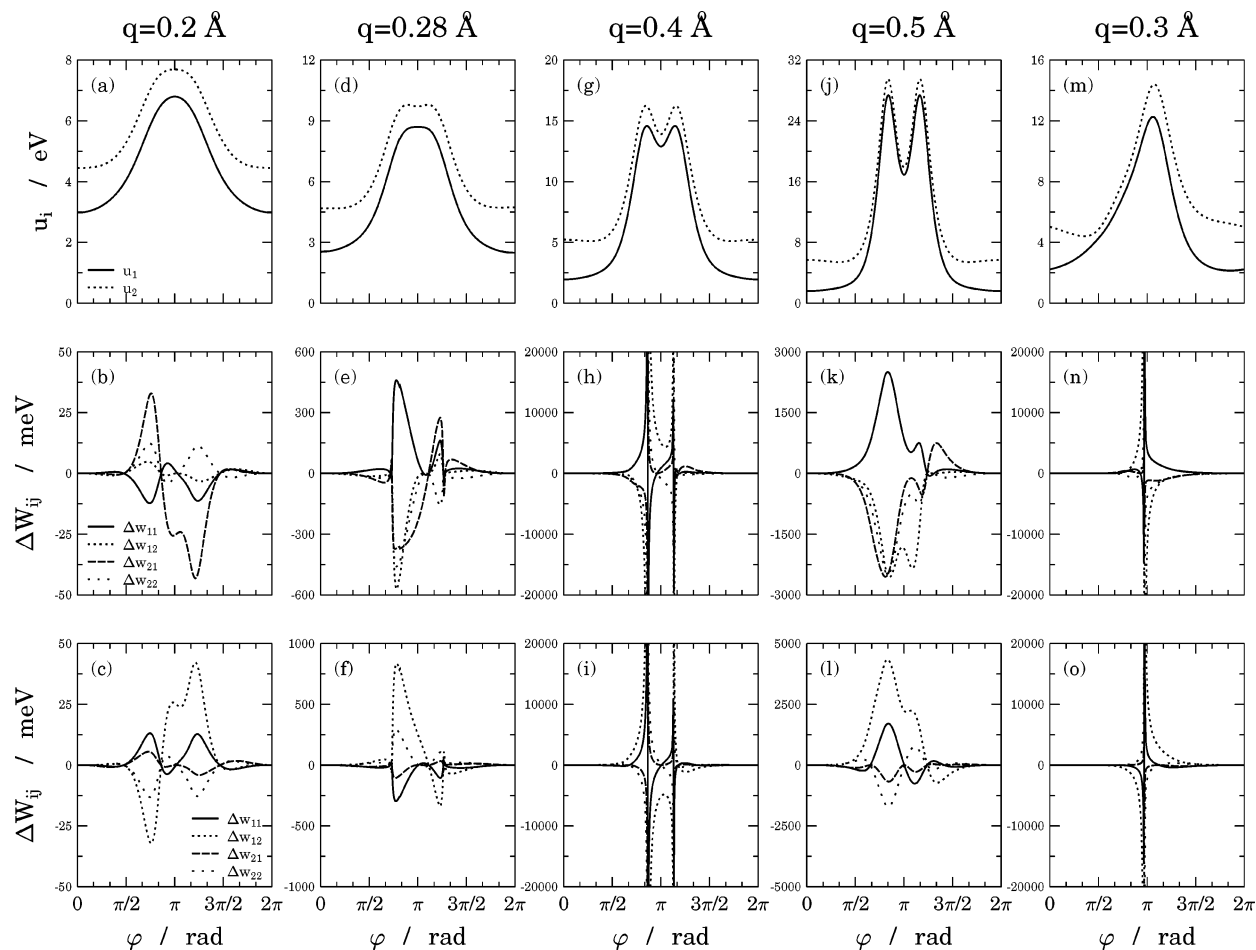


Figure 3. Adiabatic potentials \mathbf{u}_1 and \mathbf{u}_2 and the elements of the diabatic correction matrix, $\Delta\mathbf{W}^{(2)}$ as calculated along the contours presented in Figure 1. The first (upper) row contains in each part, two curves related to $\mathbf{u}_1(\varphi|q)$ and $\mathbf{u}_2(\varphi|q)$; in the next two rows are presented, in each part, four curves describing $\Delta W_{11}(\varphi|q)$, $\Delta W_{12}(\varphi|q)$, $\Delta W_{21}(\varphi|q)$ and $\Delta W_{22}(\varphi|q)$, respectively. The curves in the intermediate row were calculated, employing eq 28a, for $\gamma_{12}^{(1)}$ and the corresponding γ_{13} and γ_{23} angles (obtained from eq 13a) and the curves in the last row were calculated, employing eq 28b, for $\gamma_{12}^{(2)}$ and the respective γ_{13} and γ_{23} angles (obtained from eq 13b). The calculations are done for contours given in Figure 1.

are relatively small—a few millielectronvolts for the inner circle and, at most, a few hundreds of millielectronvolts for the second circle. These values have to be compared with values of \mathbf{u}_1 and \mathbf{u}_2 , calculated along the same contours. It is well noticed that in general the largest values of $\Delta\mathbf{W}^{(2)}$, are located along the same angular interval $\pi - \delta \leq \varphi \leq \pi + \delta$ where the largest values of \mathbf{u}_1 and \mathbf{u}_2 are to be found. It is important to mention that the values of \mathbf{u}_1 and \mathbf{u}_2 are between one and 2 orders of magnitude larger than those of $\Delta\mathbf{W}^{(2)}$.

(2) The next three columns are related to situations where the circular contours surround the two (2,3) *cis*. We encounter, here, the same situations as in the previous case except that the values of both, those of \mathbf{u}_1 and \mathbf{u}_2 and those of $\Delta\mathbf{W}^{(2)}$ are much larger. Again, the values of $\Delta\mathbf{W}^{(2)}$ become large only along the above-mentioned angular interval but are, always at least, 1 order of magnitude smaller than those of \mathbf{u}_1 and \mathbf{u}_2 . The only exceptions are the rare cases where γ_{23} or γ_{13} become (exactly) $\pi/2$ which happens only along circles that approach very closely any of the (2,3) *cis* as for instance when $q = 0.3, 0.4$ Å. (see Figure 1) but not anymore along the circle for which $q = 0.5$ Å (in this case the contour is located further away from the (2,3) *cis* so that γ_{23} (γ_{13}) cannot become $\pi/2$ anymore).

V. Conclusions

In this article we discussed a new diabaticization procedure which is expected to be reliable and, also, relatively easy to

implement. This procedure takes into account the two main ingredients related to diabaticization: (1) The size N of the smallest (relevant) group of states that forms a Hilbert subspace (this fact enforces the dimension of the ADT matrix to be $N^{16,22}$). (2) The total energy E which determines the number of open states, p , within this group of N states. The main emphasis in this manuscript is on the case that N is arbitrary but p is equal to 2. The various derivations as well as the final results are accompanied by numerical examples extracted from ab initio calculations carried out for three- to five-states of the $\text{H} + \text{H}_2$ system.

In many situations where the energy is not too high it is enough to solve only two coupled SEs and for this purpose it is required one ADT angle. However the ADT angle and in particular the topological (Berry) phase depend on other states within the Hilbert subspace. Our procedure is unique in the sense that it is capable to incorporate correctly, within the two-state diabaticization, the effect of all the states that form the Hilbert subspace.

It is important to mention that other two-state diabaticization procedures are available for systems where $N > 2$.²⁵ However, in contrast to our procedure, they do not include in the calculations the effect, of upper states. In other words, they solely depend on the two states under consideration. This fact may lead to inadequate results due the application of the inappropriate ADT angle. Consider, for instance, a three-state

system governed by one (1,2) *ci* and one (2,3) *ci*. If we treat only the two lower states (and ignore the third state) then the topological (Berry) phase related to the second state is identical to the topological phase related to the first state namely, it is equal to π (for contours that surround the (1,2) *ci*). However if we consider all the three states then, for those contours that surround both, the (1,2) *ci* and the (2,3) *ci*, the topological phase, related to the (same) second state, is either zero or a multiple of 2π but not π (or an odd multiple of π).¹⁹ This fact does not affect the $1 \rightarrow 2$ transition probabilities but, is expected to affect the calculated $2 \rightarrow 1$ transition probabilities.

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