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## Electronic Diabatic Framework: Restrictions Due to Quantization of the Nonadiabatic Coupling Matrix

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In this article, two issues related to the size of the electronic diabatic potential energy matrix are treated. (a) We frequently mention the fact that the dimension of a diabatic matrix obtained by a unitary transformation from the adiabatic framework is determined by the way the nonadiabatic coupling matrix  $\tau$  breaks up into blocks. In this article, we prove for the first time that the size of the diabatic matrix as obtained in a direct way is determined in the same way. In other words, if the dimension of the above-mentioned decoupled block is  $N$ , then the dimension of any diabatic potential energy matrix with physical relevance has to be  $N$  as well, regardless of how it was derived. This number,  $N$ , is also equal to the number of coupled diabatic–Schrödinger equations to be solved. (b) The second issue is, consequently, related to the actual required number of coupled Schrödinger equations to be solved to obtain a well-converged solution. Starting with the earlier introduced number  $N$ , we show that this number can be reduced, and in fact, it is most likely equal to the number of energetically open adiabatic states (for a given energy). While doing that, we rigorously derived the relevant diabatic potential matrix for this reduced case. We also worked out in detail an example related to a three-state case and derived the relevant  $2 \times 2$  diabatic potential matrix.

### I. Introduction

The quantum mechanical study of electronic nonadiabatic processes becomes more and more a subject of major importance.<sup>1–64</sup> Most of the quantum-mechanical treatments of molecular systems during the last four decades took place on the lowest adiabatic Born–Oppenheimer potential energy surface (PES). This applies to both the derivation of the PES and the dynamical studies. The pace of similar treatments for several PESs was rather slow, and only during the 1990s did interest in electronic nonadiabatic effects start to become significant mainly because of the pioneering dynamical studies of Kuppermann et al.<sup>6–11</sup> and the ability to calculate ab initio nonadiabatic coupling terms (NACT).<sup>32</sup>

One of the main obstacles in the study of electronic nonadiabatic transitions is the existence of conical intersections (ci),<sup>64–67</sup> a phenomenon that is responsible for the existence of singular NACTs.<sup>68,69c</sup> As it turns out, it is not the singularity per se but the fact that these singularities are poles and therefore create nonlocal effects that extend to infinity. It is, of course, well known that poles of this kind (similarly to potentials that behave asymptotically like  $(1/r)$ ) cannot be treated by numerical recipes but have to be approached rigorously.

The existence of the singularities in general and the infinite long-range effect of the NACTs' poles in particular slowed the process of studying electronic nonadiabatic effects. In the 1970s, it was revealed that one can transform the adiabatic framework to the diabatic one (namely, the framework where the NACTs are zero) by an orthogonal matrix called the adiabatic-to-diabatic transformation (ADT) matrix.<sup>69</sup> In this process, the adiabatic

diagonal potential energy matrix becomes a full matrix of dimensions  $N \times N$  (where  $N$  is the number of states included in the transformation, see section II), which is known as the diabatic potential matrix (or simply the diabatic matrix).<sup>69,70</sup> However, it was soon revealed that this procedure is numerically time-consuming, and other “more efficient” methods were proposed.<sup>15,17,18,22,24,28</sup> One procedure where the diabatic matrix is formed directly is presented in section II.3. Now, having (at least) two different ways to form the diabatic matrix, the question is whether these two procedures lead to identical results for the diabatic matrix (up to a constant orthogonal transformation). If the two matrices are the same at each point in the region of interest, then we may conclude that we found the correct diabatic matrix. If not, then the natural question to ask is, which of the two (if either of them) is the correct diabatic matrix? This question is unresolved for many; however, it is our opinion that neither of them is the correct potential matrix. In other words, the only way to ensure that, indeed, we have the correct diabatic potential matrix is if  $N$  is such that the two procedures yield the same diabatic matrix.

In this article, we also address another issue that is of similar importance. The above-mentioned (minimal) number  $N$  required for diabaticization, also, determines the number of coupled nuclear Schrödinger equations (SE) that have to be solved to treat the nuclear dynamics. It is known from previous theoretical studies and numerical calculations that to guarantee the accurate diabatic potential matrix the required number  $N$  may become relatively large. In this article, we discuss the possibility of reducing  $N$  in a rigorous way while still obtaining converged scattering calculations.

The article is arranged as follows. In the next section, we present the background required for our theoretical study. In the third section, we discuss the intimate connection between the diabatic and the adiabatic frameworks for a given number

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of states,  $N$ . In sections IV, V and VI, we discuss the second issue related to the reduction in size of the set of coupled SEs for a given energy  $E$ . In particular, we present (in section VI) such a reduction for a three-state system and obtain the relevant 2-D diabatic potential matrix. In the last section, we summarize the conclusions.

## II. Theoretical Background

**II.1. Introductory Remarks.** In this article, we consider the general Schrödinger equation that describes the motion of both the electrons and the nuclei<sup>69,71</sup>

$$(\mathbf{H} - E)\Psi = 0 \quad (1)$$

where  $E$  is the total energy,  $\Psi$  is the total wave function of the system, and  $\mathbf{H}$  is the complete Hamiltonian given in the form

$$\mathbf{H} = \mathbf{T}_\nu + \mathbf{H}_e \quad \mathbf{T}_\nu = -\frac{\hbar^2}{2m}\nabla^2 \quad (2)$$

Here,  $\nu$  and  $e$  stand for nuclear and electronic coordinates, respectively,  $\mathbf{H}_e$  is the electronic Hamiltonian to be discussed later,  $\mathbf{T}_\nu$  is the kinetic operator of the nuclei expressed in mass-scaled coordinates,  $m$  is the mass of the system, and  $\nabla$  is the gradient operator.

**II.2. Adiabatic Framework and Adiabatic-to-Diabatic Transformation.** The starting point is the Born–Oppenheimer–Huang (BOH)<sup>72</sup> close-coupling expansion

$$\Psi(e, \nu) = \sum_{j=1}^N \psi_j(\nu) \zeta_j(e|\nu) \quad (3)$$

where  $\psi_j(\nu)$  is the ( $j$ th) nuclear-coordinate-dependent coefficient (recognized as the  $j$ th nuclear wave functions) and  $\zeta_j(e|\nu)$ , is the  $j$ th electronic wave function, assumed to be the  $j$ th eigenfunction of the electronic Hamiltonian  $\mathbf{H}_e(e|\nu)$ :

$$(\mathbf{H}_e(e|\nu) - u_j(\nu))\zeta_j(e|\nu) = 0 \quad j = 1, \dots, N \quad (4)$$

Here,  $u_j(\nu)$  ( $j = 1, \dots, N$ ) are the electronic eigenvalues that serve as the adiabatic potential energy surfaces that govern the motion of the nuclei in this system. Equation 3 can also be written in matrix notation as follows:

$$\Psi(e, \nu) = \zeta^T(e|\nu) \psi(\nu) \quad (5)$$

where  $\zeta^T$  is the corresponding row vector. Next, we introduce the nonadiabatic coupling matrix elements (NACME),  $\tau_{ji}$ , the principal magnitudes considered in this article, which are defined as

$$\tau_{ji} = \langle \zeta_j | \nabla \zeta_i \rangle \quad i, j = \{1, \dots\} \quad (6)$$

where the gradient operator is expressed with respect to the (mass-scaled) nuclear coordinates,  $\nu$ , and the  $\zeta_k(e|\nu)$  functions ( $k = j, i$ ) are the above-mentioned eigenfunctions. The NACTs become apparent following the derivation of the SE that describes the motion of the nuclei. Substituting eqs 2 and 3 into eq 1, recalling eq 4 and assuming that the electronic manifold forms a complete Hilbert space, this nuclear equation can be shown to take the form<sup>69,70b</sup>

$$-\frac{\hbar^2}{2m}(\nabla + \boldsymbol{\tau})^2\Psi + (\mathbf{u} - E)\Psi = 0 \quad (7)$$

where  $\tau$  is the above-mentioned antisymmetric NACM,  $\mathbf{u}$  is a diagonal matrix that contains the adiabatic PESs (introduced

through eq 4), and  $\Psi$  is a column vector that contains the nuclear wave functions to be solved (introduced in eq 3). Equation 7 is known as the adiabatic SE for the nuclei.

Equation 7 can be shown to be approximately valid for a group of states that do not necessarily form a Hilbert space but are strongly coupled to themselves and, at most, weakly coupled to other states belonging to this manifold (see the discussion below<sup>73</sup>). In what follows, such a group of states is termed a Hilbert subspace. We return to this issue later.

As mentioned earlier, the NACTs may possess unpleasant features that can prevent the solution of eq 7 as such. To overcome this difficulty, the idea is to eliminate the NACTs, and this is done by applying the following (unitary) transformation:<sup>69</sup>

$$\Psi = \mathbf{A}^\dagger \Phi \quad (8)$$

Inserting eq 8 in eq 7 yields the following diabatic equation:<sup>69</sup>

$$-\frac{\hbar^2}{2m}\nabla^2\Phi + (\mathbf{W} - E)\Phi = 0 \quad (9)$$

where  $\mathbf{W}$ , the diabatic potential matrix, is given in the form

$$\mathbf{W} = \mathbf{A}\mathbf{u}\mathbf{A}^\dagger \quad (10)$$

and  $\mathbf{A}$ , the adiabatic-to-diabatic transformation (ADT) matrix, has to be a solution of the following first-order differential equation:<sup>69</sup>

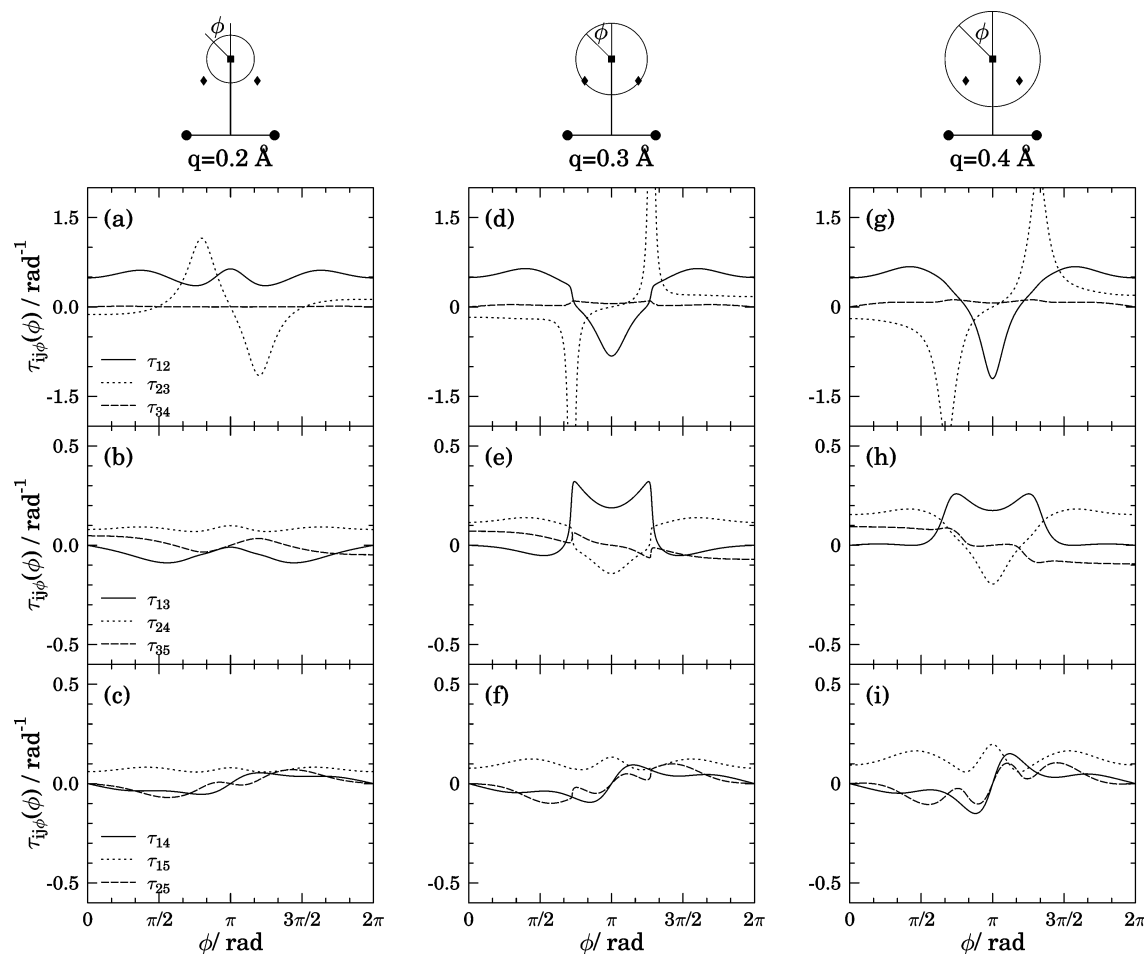
$$\nabla\mathbf{A} + \boldsymbol{\tau}\mathbf{A} = 0 \quad (11)$$

The solution of eq 11, namely, matrix  $\mathbf{A}$ , has to yield a single-valued diabatic PES matrix  $\mathbf{W}$ , a feature not guaranteed by an arbitrary  $\boldsymbol{\tau}$  matrix. We will not go into the full details regarding the required features of the  $\boldsymbol{\tau}$  matrix for this purpose but will just summarize them as follows. To guarantee a single-valued  $\mathbf{W}$  matrix of (finite) dimensions  $N \times N$  in a given region  $\Lambda$ , the  $\boldsymbol{\tau}$  matrix has to be of the following form<sup>58,62a,b,74</sup>

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & \tau_{12} & \tau_{13} & \tau_{1N} & & & & & & \\ -\tau_{12} & 0 & \tau_{23} & \tau_{2N} & & & & & & \\ -\tau_{13} & -\tau_{23} & 0 & \tau_{3N} & & & & & & \\ & & & 0 & & & & & & \\ -\tau_{1N} & -\tau_{2N} & -\tau_{3N} & & 0 & -\tau_{N+1N+2} & -\tau_{N+1N+3} & & & \\ & & & & -\tau_{N+1N+2} & 0 & -\tau_{N+2N+3} & & & \\ & & & & -\tau_{N+1N+3} & -\tau_{N+2N+3} & 0 & & & \\ & & & & & & & 0 & & \\ & & & & & & & & 0 & \\ & & & & & & & & & 0 \end{pmatrix} \mathbf{O}(\epsilon) \quad (12)$$

at every point in that region. Here, the off-diagonal elements at positions ( $j, k$ ) where  $j \leq N$  and  $k \geq N$  (the same applies to the ( $k, j$ ) positions) are on the order of  $\epsilon$ , namely,  $\mathbf{O}(\epsilon)$ , and  $\epsilon$  is a given small number. In other words the  $\boldsymbol{\tau}$  matrix has to be of the above “block” structure.<sup>75</sup> The  $N$  states that produce this block structure are those mentioned earlier as the ones that form the Hilbert subspace. From now on,  $N$  stands for the dimension of the lowest block in the  $\boldsymbol{\tau}$  matrix in eq 12, and the block itself is designated as  $\boldsymbol{\tau}_N$ .

The breakup of the  $\boldsymbol{\tau}$  matrix in eq 12 is frequently under scrutiny; therefore, to show that it happens in realistic cases,



**Figure 1.** Angular nonadiabatic coupling terms,  $\tau_{ij}(\phi|q)$  ( $i < j$ ) as calculated for the  $\text{H} + \text{H}_2$  system for  $R_{\text{HH}} = 0.74 \text{ \AA}$ : (a–c) circle located at the (1,2)  $D_{3h}$  ci with radius  $q = 0.2 \text{ \AA}$ ; (d–f) circle located at the (1,2)  $D_{3h}$  ci with radius  $q = 0.3 \text{ \AA}$ ; (g–i) circle located at the (1,2)  $D_{3h}$  ci with radius  $q = 0.4 \text{ \AA}$ . Full circles stand for the two fixed hydrogens; full squares stand for (1,2) ci's; and the circles describe the contours along which the  $\tau_{ij}(\phi|q)$  were calculated. The straight line perpendicular to the HH axis connects the midpoint between the two hydrogens and the  $D_{3h}$  ci point. Notice the small values of  $\tau_{q34}(\phi|q)$  in a, d, and g as compared to those of  $\tau_{q12}(\phi|q)$  and  $\tau_{q23}(\phi|q)$ . Also note the change in scale of b, c, e, f, h, and i as compared to the scale in a, d, and g. Note the increased scale in b, c, e, f, h, and i as compared to the scale in a, d, and g.

we present a few results related to the  $\text{H} + \text{H}_2$  system. This system was recently studied by us,<sup>58</sup> and it was found that its three lower states form, in the region surrounding its  $D_{3h}$  ci's, a Hilbert subspace; in other words, its  $\tau$  matrix breaks up exactly as shown in eq 12 where  $N = 3$ . This would imply that all  $\tau$  elements  $\tau_{jk}$  where  $j \leq 3$  and  $k > 3$  are much smaller than  $\tau_{12}$  and  $\tau_{23}$  (and sometimes even  $\tau_{13}$ ). In Figure 1, we present the angular components of nine  $\tau$ -matrix elements,  $\tau_{12}$ ,  $\tau_{13}$ ,  $\tau_{14}$ ,  $\tau_{15}$ ,  $\tau_{23}$ ,  $\tau_{24}$ ,  $\tau_{25}$ ,  $\tau_{35}$ , and  $\tau_{34}$  calculated along three different circles (all centered at the  $D_{3h}$  ci point) with radii  $q = 0.2, 0.3, 0.4 \text{ \AA}$ . The results in Figure 1 are presented as a function of the angle  $\phi$  (defined in the Figure). The details regarding such calculations are given in ref 58a. Here, we just mention that they were derived, employing MOLPRO, for a fixed distance  $R_{\text{HH}} (= 0.74 \text{ \AA})$  between two hydrogens. The third hydrogen is the test particle for probing the  $\tau$  elements so that the variables ( $q, \phi$ ) are the coordinates of this third hydrogen.

Out of these nine elements, only two are relatively large, namely,  $\tau_{12}$  and  $\tau_{23}$ ; one—the  $\tau_{13}$  element—is of an intermediate size, and the rest (namely, those that couple the  $3 \times 3$  block to the rest of the  $\tau$  matrix) are at least one order of magnitude smaller. In particular, we call attention to  $\tau_{34}$ . In general, the main coupling between two (adjacent) states,  $j$  and  $(j + 1)$ , is due to the corresponding tridiagonal matrix element  $\tau_{jj+1}$ . The fact that the value of such a matrix element is small is an

indication that these two states are not coupled via a ci in the considered region. This is what happens to the third and the fourth states of the  $\text{H} + \text{H}_2$  system; they are not coupled via a ci,<sup>58c</sup> and it is this missing ci that is the main cause for the breakup of the  $\text{H} + \text{H}_2$   $\tau$  matrix into a  $(3 \times 3 \text{ matrix} + \text{rest})$  as shown in eq 12.

It is not always possible to determine whether at a given region  $\Lambda$  the  $\tau$  matrix breaks up as in eq 12 by just inspecting the various  $\tau$ -matrix elements at each point. Instead, we devised the following  $\mathbf{D}$  matrix defined in terms of the exponentiated line integral<sup>74</sup>

$$\mathbf{D}(\Gamma) = \rho \exp(\oint_{\Gamma} \text{ds} \cdot \tau_N) \quad (13)$$

where  $\Gamma$  is a closed contour in  $\Lambda$ ,  $\rho$  is an ordering operator,  $\text{ds}$  is a differential increment along  $\Gamma$ , and the dot stands for a scalar product. It was shown that in the case in which the  $\tau$  matrix has the structure in eq 12 at every point in the region  $\Lambda$ , the corresponding  $\mathbf{D}$  matrix is approximately a diagonal matrix for every closed contour  $\Gamma$  in this region. Moreover, it was also shown that matrix  $\mathbf{D}$  is a unitary matrix; therefore, its values along the diagonal are  $\pm 1$  (for real eigenfunctions). We called this unique feature the “quantization of the  $\tau$ -matrix” because in case the decoupled block in eq 12 is of dimension  $N = 2$ ,

the corresponding (only nonzero) element of the  $\tau$  matrix; namely,  $\tau_{12}$  fulfills the Bohr–Sommerfeld quantization law.<sup>47,74</sup>

The quantization of the  $\mathbf{D}$  matrix in relatively large regions of configuration space (namely, regions much too large to be treated by perturbation treatments) is established in a series of ab initio studies related to  $\{\text{C}_2\text{H}\}$ ,<sup>55</sup>  $\{\text{H}, \text{H}_2\}$ ,<sup>58a,c</sup>  $\{\text{Na}, \text{H}_2\}$ ,<sup>62a</sup> and  $\{\text{C}_2\text{H}, \text{H}\}$ <sup>58c</sup> and recently also to  $\{\text{O}, \text{H}_2\}$ .<sup>76</sup>

Let us summarize our finding so far. The electronic ab initio calculations usually supply the adiabatic PES matrix,  $\mathbf{u}$ , and the NACM,  $\tau$ . Therefore, to study electronic nonadiabatic processes one has to solve the SE given in eq 3. However, it is now known that the  $\tau$  matrix is frequently singular and in particular may possess poles—features that cause difficulties in solving this equation. One way to overcome these difficulties is to diabaticize eq 3, namely, rigorously eliminate the troublesome NACTs. In this process, one forms eq 9, which contains the diabatic PES  $\mathbf{W}$  given in eq 10. However, in doing so we may encounter the situation in which  $\mathbf{W}$  is multivalued. It was revealed that a meaningful diabaticization (namely, the one that produces single-valued diabatic potentials) cannot be achieved for an arbitrary number of states  $N$ . It can be achieved if and only if this group of states yields the quasi-decoupled block  $\tau_N$  of the NACTs matrix (see eq 12). It is important to emphasize that this demand is not based on any energy considerations but results from nonlocal effects (or topological effects) formed by the poles of the various NACTs.

**II.3. Diabatic Framework.** As was discussed in the Introduction, we consider a different way of forming diabatic states—an approach that does not involve the NACTs. As was already mentioned in the Introduction, there are many approaches to forming diabatic states.<sup>15,17,18,22,24,28</sup> In the present section, we refer to one of the simplest procedures that also allows us to “stay analytic all the way”.

Our starting equation is eq 3 with one difference; namely, we replace  $\zeta_i(\mathbf{e}|\nu)$  by  $\zeta_i(\mathbf{e}|\nu_0)$  ( $i = 1, \dots$ ) where  $\nu_0$  stands for a fixed set of nuclear coordinates. Thus, instead of expansion in eq 3 we consider

$$\tilde{\Phi}(\mathbf{e}, \nu|\nu_0) = \sum_{j=1}^L \tilde{\phi}_j(\nu) \zeta_j(\mathbf{e}|\nu_0) \quad (14)$$

Here,  $\zeta_i(\mathbf{e}|\nu_0)$ , just like  $\zeta_i(\mathbf{e}|\nu)$ , is an eigenfunction of the following Hamiltonian

$$(\mathbf{H}_e(\mathbf{e}|\nu_0) - u_j(\nu_0))\zeta_j(\mathbf{e}|\nu_0) = 0 \quad j = 1, \dots, L \quad (15)$$

where  $u_i(\nu_0)$  ( $i = 1, \dots, L$ ) are the electronic eigenvalues as calculated for this (fixed) set of nuclear coordinates. Continuing in the usual manner,<sup>77</sup> we obtain the following diabatic SE:

$$-\frac{1}{2m}\nabla^2\tilde{\Phi} + (\mathbf{V} - \mathbf{E})\tilde{\Phi} = 0 \quad (16)$$

where

$$\mathbf{V}_{ij}(\nu|\nu_0) = \langle \zeta_i(\mathbf{e}|\nu_0) | \mathbf{H}_e(\mathbf{e}|\nu) | \zeta_j(\mathbf{e}|\nu_0) \rangle \quad (17)$$

which can be shown to be<sup>77</sup>

$$\mathbf{V}_{ij}(\nu|\nu_0) = \langle \zeta_i(\mathbf{e}|\nu_0) | U(\mathbf{e}|\nu) - U(\mathbf{e}|\nu_0) | \zeta_j(\mathbf{e}|\nu_0) \rangle + \mathbf{u}_j(\nu_0)\delta_{ji} \quad (18)$$

In eq 18, the potential  $U(\mathbf{e}|\nu)$  (and also  $U(\mathbf{e}|\nu_0)$ ) is the sum of the Coulomb potentials between the electrons, between the electrons and the nuclei, and between the nuclei all calculated at the spatial point  $\nu$ .

Equation 16 is similar to eq 9 except that the diabatic potential  $\mathbf{V}$  is not necessarily identical to the diabatic potential matrix  $\mathbf{W}$ . The main difference is that the dimension of  $\mathbf{W}$  (i.e.,  $N$ ), unlike the dimension  $L$  of  $\mathbf{V}$ , is not arbitrary but is determined by the structure of the  $\tau$  matrix. Consequently, it is expected that if eqs 9 and 16 are solved for matrices of different dimensions the results will be different. In the next section, we show that if the dimensions of  $\mathbf{V}$  and  $\mathbf{W}$  are the same (namely,  $N$ ) then the two matrices contain identical elements.

### III. Unification of the Two Diabatic Frameworks

We start with the  $\mathbf{W}$  matrix. Considering eq 9, the  $(i, j)$  matrix element of  $\mathbf{W}$  is given in the form

$$\mathbf{W}_{ij} = \sum_{k=1}^N \mathbf{A}_{ik} \mathbf{u}_{kk} \mathbf{A}_{jk}^* \quad (19)$$

or recalling eq 4, this equation can also be written as

$$\mathbf{W}_{ij} = \sum_{k=1}^N \mathbf{A}_{ik}(\nu) \langle \zeta_k(\mathbf{e}|\nu) | \mathbf{H}_e(\mathbf{e}|\nu) | \zeta_k(\mathbf{e}|\nu) \rangle \mathbf{A}_{jk}^*(\nu) = \sum_{k=1}^N \sum_{k'=1}^N \mathbf{A}_{ik}(\nu) \langle \zeta_k(\mathbf{e}|\nu) | \mathbf{H}_e(\mathbf{e}|\nu) | \zeta_{k'}(\mathbf{e}|\nu) \rangle \mathbf{A}_{jk'}^*(\nu) \quad (20)$$

where the double sum in the second row is allowed because the off-diagonal elements of the  $\mathbf{H}_e(\mathbf{e}|\nu)$  matrix are all identically zero. To continue, we recall eqs 3 and 8. Just like the electronic basis set,  $\zeta$  is associated with  $\psi$  so that the scalar product forms the total wave function  $\Psi$  (eq 3); there exists an electronic basis set  $\chi$  that is associated with  $\Phi$  so that their scalar product also forms  $\Psi$ , namely,

$$\Psi(\mathbf{e}, \nu) = \chi^T(\mathbf{e}|\nu) \Phi(\nu) \quad (21)$$

Next, equating eqs 3 and 21 and recalling eq 8, it is seen that  $\zeta$  and  $\chi$  are connected through the same unitary transformation as  $\psi$  and  $\Phi$ , namely,

$$\zeta^T = \chi^T \mathbf{A}^\dagger \Rightarrow \chi^T = \zeta^T \mathbf{A}$$

or

$$\zeta = \mathbf{A}\chi \Rightarrow \chi = \mathbf{A}^\dagger \zeta \quad (22)$$

However the two basis sets  $\zeta$  and  $\chi$  differ in one essential feature; namely, in contrast to  $\zeta$ , the  $\chi$  eigenfunctions do not depend on the nuclear coordinates. This can be seen from the substitution of eq 21, together with eqs 2 and 4, in eq 1 and by repeating the same procedure as in the derivation of eq 16. Because  $\Phi$  has to fulfill eq 9, this requires the corresponding  $\tau$ -matrix elements, namely,  $\tilde{\tau}_{ij}$ , to be all identically zero:

$$\tilde{\tau}_{ji} = \langle \chi_j | \nabla \chi_i \rangle \equiv 0 \quad i, j = \{1, \dots, N\} \quad (23)$$

Next, it can be shown that Eq 23 implies that all of the  $N$  relevant  $\chi$  functions are independent of the nuclear coordinates, thus  $\chi \equiv \chi(\mathbf{e})$

Having made all of the preparations, we are now in the position to treat the second row in eq 20. Employing eqs 22, we replace the  $\zeta(\mathbf{e}, \nu)$  functions in this expression by the  $\chi$  functions so that we get for  $\mathbf{W}_{ij}$  the following result:

$$\mathbf{W}_{ij} = \langle \chi_i(\mathbf{e}) | \mathbf{H}_e(\mathbf{e}|\nu) | \chi_j(\mathbf{e}) \rangle$$



Because both the  $\chi(e)$  and the  $\zeta(e|\nu_0)$  functions are sets of  $N$  electronic independent functions, they may not be identical but are at most related by a constant unitary matrix of dimension  $N$  (see also eq 22). We replace the  $\chi(e)$  functions by the  $\zeta(e|\nu_0)$  functions so that  $\mathbf{W}_{ij}$  becomes

$$\mathbf{W}_{ij}(\nu|\nu_0) = \langle \zeta_i(e|\nu_0) | \mathbf{H}_e(e|\nu) | \zeta_j(e|\nu_0) \rangle \quad (24)$$

Equation 24 is identical to eq 17.

In summary, it is important to realize that we are not proposing here a new way to form diabatic potentials. Our intention is to show that it is immaterial which way one chooses to form diabatic potentials because the dimension of the respective diabatic potential matrix cannot be smaller than  $N$  (see eq 12). In other words, there exists this belief that one can find an “efficient” diabatic framework for which, for example, the number of states is 2 whereas the minimal number  $N$  is 5. What we are saying is that this belief is not supported by theory because the minimal number  $N$  is determined by the system and not by the user. To determine the value of  $N$ , one has to calculate the NACTs and then form the  $\mathbf{D}$  matrix (eq 13) to examine whether it is diagonal for the contour that surrounds the region of interest. This examination has to be repeated until the smallest value of  $N$ , that still guarantees the diagonal  $\mathbf{D}$  matrix, is found.

#### IV. Reduced Born–Oppenheimer Diabatic Matrix for Dynamical Calculations

We realize that diabatization overcomes one difficulty (namely, eliminates the unpleasant NACTs) but then may create a new difficulty, eventually, increasing significantly the number of coupled SEs (in eq 9) to be solved. As mentioned earlier, this difficulty is inherent and is not connected to the way the diabatization is achieved. In the present section, we discuss an approach that reduces the size of this set of equations and still guarantees well-converged dynamical calculations.

In what follows, we adopt the following notation:  $\mathbf{Z}_N^p$  labels a rectangular matrix  $\mathbf{Z}$  with  $p$  columns and  $N$  rows. In other words, the superscript index designates the number of columns, and the subscript index indicates the number of rows.

With this notation, the diabatic SE in eq 9 takes the form

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi_N^1 + (\mathbf{W}_N^N - E) \Phi_N^1 = 0 \quad (25)$$

where  $\Phi_N^1$  is a column vector that contains the diabatic (nuclear) wave functions and  $\mathbf{W}_N^N$  is the diabatic potential matrix (eq 10):

$$\mathbf{W}_N^N = \mathbf{A}_N^N \mathbf{u}_N \mathbf{A}_N^{\dagger N} \quad (26)$$

Next, we recall that the connection between the diabatic wave functions in  $\Phi_N^1$  and the adiabatic ones in  $\Psi_N^1$  is given as follows (eq 8):

$$\Phi_N^1 = \mathbf{A}_N^N \Psi_N^1 \quad (27)$$

We continue, assuming that for a given energy  $E$  only  $q$  adiabatic states are classically allowed (i.e., open). This implies that out of the  $N$  nuclear adiabatic wave functions ( $\psi_1, \dots, \psi_N$ ) only the  $q$  lowest ones differ (significantly) from zero for any practical application. Because of that, the row vector  $\Psi^T$  takes the form  $\Psi^T \equiv (\psi_1, \dots, \psi_q, 0, \dots, 0)$ . Consequently, eq 27 can also be written in the form

$$\Phi_N^1 = \mathbf{A}_N^q \Psi_q^1 \quad (28)$$

On the basis of this observation, we assume that the diabatic framework is, similarly, presented in terms of  $p$  ( $q \leq p \leq N$ ) functions so that  $\Phi^T \equiv (\phi_1, \dots, \phi_p, 0, \dots, 0)$  where  $p$  is yet an undetermined value. As a result, eq 28 becomes

$$\Phi_p^1 = \mathbf{A}_p^q \Psi_q^1 \quad (28')$$

In what follows, we treat only the first  $p$  equation of eq 25:

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi_p^1 + (\mathbf{W}_p^N - E) \Phi_p^1 = 0 \quad (29)$$

where  $\Phi_N^1$ , in the second term, is still unchanged but is replaced by employing eq 28 so that eq 29 becomes

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi_p^1 + (\mathbf{W}_p^N - E) \mathbf{A}_N^q \Psi_q^1 = 0 \quad (30)$$

Recalling eq 28',  $\Psi_q^1$  is replaced by the expression

$$\Psi_q^1 = (\mathbf{A}_q^q)^{-1} \Phi_p^1 = \mathbf{C}_q^p \Phi_p^1 \quad (31)$$

so that the equation for  $\Phi_p^1$  takes the form

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi_p^1 + (\mathbf{W}_p^N - E) \mathbf{B}_N^p \Phi_p^1 = 0 \quad (32)$$

where

$$\mathbf{B}_N^p = \mathbf{A}_N^q \mathbf{C}_q^p \quad (33)$$

It is important to emphasize that  $\mathbf{C}_q^p$  is the right-hand-side inverse matrix of the rectangular matrix  $\mathbf{A}_q^p$ ; namely, it fulfills the condition

$$\mathbf{A}_q^p \mathbf{C}_q^p = \mathbf{I}_p^p \quad (34)$$

where  $\mathbf{I}_p^p$  is the unit matrix of dimensions  $p \times p$ . Consequently, eq 32 can be further simplified to become

$$-\frac{\hbar^2}{2m} \nabla^2 \Phi_p^1 + (\tilde{\mathbf{W}}_p^p - E) \Phi_p^1 = 0 \quad (35)$$

where the elements of  $\tilde{\mathbf{W}}_p^p$  are

$$(\tilde{\mathbf{W}}_p^p)_{kn} = (\mathbf{W}_p^p)_{kn} + \sum_{j=p+1}^N (\mathbf{W}_p^N)_{kj} (\mathbf{B}_N^p)_{jn} \quad (36)$$

Here, both  $k$  and  $n$  are limited by  $p$ . Thus, although we treat only  $p$  equations (instead of  $N$ ) we still employ all the  $N^2$  elements of  $\mathbf{W}$  (recall that  $\mathbf{W}$  is a symmetric matrix).

The main numerical difficulty to be encountered is in deriving the inverse of the rectangular matrix  $\mathbf{A}_q^p$ . It is obvious that if  $p$  can be chosen to be equal to  $q$  then this difficulty disappears. However,  $p$  is a parameter to be varied until convergence is attained. However,  $q$ , which is assumed to be a fixed number, can be made equal to  $p$  as long as its value is larger than (or equal to) the number of open adiabatic states for the assumed energy  $E$ . In numerical treatments,  $q$  is assumed to be equal to  $p$ ; therefore, both  $\mathbf{A}_p^q$  ( $\equiv \mathbf{A}_p^p$ ) and  $\mathbf{C}_q^p$  ( $\equiv \mathbf{C}_p^p$ ) become square matrices. It is important to emphasize that making  $q$  equal to  $p$  does not affect the number of SE to be solved.

To continue the derivation, we examine in more detail the potential matrix elements  $(\tilde{\mathbf{W}}_p^p)_{nk}$  given in eq 36, which from now on are designated as  $\tilde{\mathbf{W}}_{nk}$  (recalling that  $\tilde{\mathbf{W}} \equiv \tilde{\mathbf{W}}_p^p$ ). For this purpose, we consider first the ordinary potential matrix element  $\mathbf{W}_{nk}$  that is given in the form (eq 26)

$$\mathbf{W}_{nk} = \sum_{j=1}^N \mathbf{A}_{nj} \mathbf{u}_{jj} (\mathbf{A}^\dagger)_{jk} = \sum_{j=1}^N \mathbf{A}_{nj} \mathbf{u}_j \mathbf{A}_{kj}^* \quad (37)$$

where the star, as before, labels the complex conjugate. Along the same lines, we remember that because of unitarity

$$\sum_{j=1}^N \mathbf{A}_{jk}^* \mathbf{A}_{jn} = \delta_{kn} \quad (38)$$

Returning to eq 36, we consider the second term on the right-hand side

$$\begin{aligned} \sum_{j=p+1}^N (\mathbf{W}_p^N)_{kj} (\mathbf{B}_N^p)_{jn} &= \sum_{j=p+1}^N \left[ \sum_{s=1}^N (\mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{A}_{js}^*) \sum_{t=1}^p (\mathbf{A}_{jt} \mathbf{C}_m) \right] \\ &= \sum_{s=1}^N \{ \mathbf{A}_{ks} \mathbf{u}_{ss} \sum_{t=1}^p \sum_{j=p+1}^N (\mathbf{A}_{js}^* \mathbf{A}_{jt}) \mathbf{C}_m \} \\ &= \sum_{s=1}^N \{ \mathbf{A}_{ks} \mathbf{u}_{ss} \sum_{t=1}^p [\delta_{st} - \sum_{j=1}^p (\mathbf{A}_{js}^* \mathbf{A}_{jt})] \mathbf{C}_m \} \\ &= \sum_{s=1}^p (\mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{C}_{sn}) - \\ &\quad \sum_{s=1}^N \{ \mathbf{A}_{ks} \mathbf{u}_{ss} \sum_{j=1}^p [\mathbf{A}_{js}^* \sum_{t=1}^p (\mathbf{A}_{jt} \mathbf{C}_m)] \} \end{aligned}$$

We continue by analyzing the second term (following the last equal sign). Because of eq 34, the last summation term (over  $t$ ) yields the Kronecker  $\delta$  function (i.e.,  $\delta_{jn}$ ) so that the final form of the above expression is

$$\begin{aligned} \sum_{j=p+1}^N (\mathbf{W}_p^N)_{kj} (\mathbf{B}_N^p)_{jn} &= \\ \sum_{s=1}^p \mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{C}_{sn} - \sum_{s=1}^N \mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{A}_{ns}^* &= \sum_{s=1}^p \mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{C}_{sn} - (\mathbf{W}_p^p)_{kn} \quad (39) \end{aligned}$$

Substituting eq 39 in eq 36, we obtain for  $\tilde{\mathbf{W}}_{kn}$  the result

$$\tilde{\mathbf{W}}_{kn} = \sum_{s=1}^p \mathbf{A}_{ks} \mathbf{u}_{ss} \mathbf{C}_{sn} \quad (40)$$

where all four matrices are of dimensions  $p \times p$ . Equation 40 can also be written as a matrix equation

$$\tilde{\mathbf{W}} = \mathbf{A} \mathbf{u} \mathbf{C} = \mathbf{A} \mathbf{u} \mathbf{A}^{-1} \quad (41)$$

which is our final result.

Equation 41 is, in fact, somewhat of a surprise because we managed to show that the modified diabatic potential matrix  $\tilde{\mathbf{W}}$  ( $\equiv \tilde{\mathbf{W}}_p^p$ ) is similar to the ordinary diabatic potential  $\mathbf{W}$  as given in eq 10 except that  $\mathbf{A}$  ( $\equiv \mathbf{A}_p^p$ ) is not the full  $N \times N$  ADT matrix but the reduced one of dimensions  $p \times p$  (where  $p < N$ ). Consequently, we do not encounter in eq 41 the complex conjugate matrix  $(\mathbf{A}_p^p)^\dagger$  but  $\mathbf{A}^{-1}$ , the inverse matrix of  $\mathbf{A}_p^p$ .

We are aware of the fact that because  $\tilde{\mathbf{W}}$  ( $\equiv \tilde{\mathbf{W}}_p^p$ ) is not a symmetrical matrix the Hamiltonian is not Hermitian (and therefore, for instance, in a scattering calculation the  $\mathbf{S}$  matrix is not guaranteed to be a unitary matrix), but it is our belief that this fact does not necessarily affect the results significantly, at least not those related to the lower states. Non-Hermitian Hamiltonians are frequently applied in molecular dynamics (see, for instance, those that contain imaginary potentials to form absorbing boundary conditions<sup>78–89</sup>); nevertheless, the results are practically correct. In any case, the final results are subject to convergence tests; therefore, to achieve convergence, we may need to vary  $p$ , as in any other scattering or spectroscopic cross-section calculation.

## V. Example: Formation of a $2 \times 2$ Diabatic Potential Matrix for a Three Coupled-State System

To show the relevance and the efficiency of the present approach, we work out, to some extent, the three-state case. In other words, we show how, according to the above procedure, a two-state ADT matrix is formed from an original three-state ADT matrix and, consequently, the two-state diabatic potential matrix.

For this purpose the three-state ADT matrix,  $\mathbf{A}^{(3)}$ , is assumed to be obtained from the following product:<sup>48,90</sup>

$$\mathbf{A}^{(3)} = \mathbf{Q}_{13}^{(3)} \mathbf{Q}_{23}^{(3)} \mathbf{Q}_{12}^{(3)} \quad (42)$$

where, for instance,  $\mathbf{Q}_{12}^{(3)}$  is defined as

$$\mathbf{Q}_{12}^{(3)}(\gamma_{12}) = \begin{pmatrix} \cos \gamma_{12} & \sin \gamma_{12} & 0 \\ -\sin \gamma_{12} & \cos \gamma_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (43)$$

and the two other matrices are defined accordingly.

Substituting eq 43 as well as the two other matrices into eq 42 yields the quasi-Euler matrix

$$\mathbf{A} = \begin{pmatrix} c_{12}c_{13} + s_{12}s_{13}s_{23} & c_{13}s_{12} - c_{12}s_{13}s_{23} & c_{23}s_{13} \\ -c_{23}s_{12} & c_{12}c_{23} & -s_{23} \\ -c_{12}s_{13} + c_{13}s_{12}s_{23} & -s_{12}s_{13} - c_{12}c_{13}s_{23} & c_{13}c_{23} \end{pmatrix} \quad (44)$$

where  $(c_{kj}, s_{kj}) = \{\cos(\gamma_{kj}), \sin(\gamma_{kj})\}$  and  $\gamma_{12}$ ,  $\gamma_{23}$ , and  $\gamma_{13}$  are the three Euler angles. Substituting eq 44 in eq 11 yields the three first-order differential equations for these angles:

$$\begin{aligned} \nabla \gamma_{12} &= -\tau_{12} - \tan \gamma_{23} (\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12}) \\ \nabla \gamma_{23} &= -\tau_{23} \cos \gamma_{12} + \tau_{13} \sin \gamma_{12} \\ \nabla \gamma_{13} &= -(\cos \gamma_{23})^{-1} (\tau_{13} \cos \gamma_{12} + \tau_{23} \sin \gamma_{12}) \quad (45) \end{aligned}$$

where  $\tau_{12}$ ,  $\tau_{23}$ , and  $\tau_{13}$  are the corresponding elements of the  $3 \times 3$  NACT matrix. To apply the  $\mathbf{A}$  matrix in eq 44 to the reduced  $2 \times 2$  case, we have to cut out the  $2 \times 2$  submatrix located in the upper left corner of  $\mathbf{A}$ , namely,  $\mathbf{A}^{(2)}$ :

$$\mathbf{A}^{(2)} = \begin{pmatrix} c_{12}c_{13} + s_{12}s_{13}s_{23} & c_{13}s_{12} - c_{12}s_{13}s_{23} \\ -c_{23}s_{12} & c_{12}c_{23} \end{pmatrix} \quad (46)$$

Next, according to the theory we have to form its inverse:

$$(\mathbf{A}^{(2)})^{-1} = \frac{1}{c_{13}c_{23}} \begin{pmatrix} c_{12}c_{23} & -c_{13}s_{12} + c_{12}s_{13}s_{23} \\ c_{23}s_{12} & c_{12}c_{13} + s_{12}s_{13}s_{23} \end{pmatrix} \quad (47)$$

Consequently, the corresponding  $2 \times 2$  diabatic matrix  $\tilde{\mathbf{W}}$  is given in the form

$$\tilde{\mathbf{W}} = \mathbf{A}^{(2)} \begin{pmatrix} u_1 & 0 \\ 0 & u_2 \end{pmatrix} (\mathbf{A}^{(2)})^{-1} \quad (48)$$

which can be written as

$$\tilde{\mathbf{W}} = \mathbf{W}^{(2)} - \Delta\mathbf{W} \quad (49)$$

where  $\mathbf{W}^{(2)}$ , the principal part, is given in the form

$$\mathbf{W}^{(2)} = \begin{pmatrix} c_{12}^2 u_1 + s_{12}^2 u_2 & c_{12} s_{12} (u_2 - u_1) \\ c_{12} s_{12} (u_2 - u_1) & s_{12}^2 u_1 + c_{12}^2 u_2 \end{pmatrix} \quad (50)$$

and  $\Delta\mathbf{W}$ , the correction term, is given in the form

$$\Delta\mathbf{W} = \frac{1}{c_{13}c_{23}} \begin{pmatrix} v_{11} & v_{12} \\ v_{21} & v_{22} \end{pmatrix} (u_2 - u_1) \quad (51)$$

The missing elements are

$$\begin{aligned} v_{11} &= -v_{22} = -s_{12}s_{13}s_{23}c_{12}c_{23} \\ v_{21} &= (c_{13} - c_{23})c_{12}c_{23}s_{12} \\ v_{12} &= (c_{13} - c_{23})c_{12}c_{13}s_{12} + \\ &\quad s_{13}s_{23}(-c_{12}s_{12} + c_{13}s_{12}^2 - c_{13}c_{12}^2) \end{aligned} \quad (52)$$

The main outcome of this derivation is that in situations in which the elements of  $\Delta\mathbf{W}$  are small the diabatic potential matrix  $\mathbf{W}^{(2)}$  is of the usual form but is expressed in terms of an ADT angle (i.e.,  $\gamma_{12}$ ) that results from a three-state calculation and therefore is guaranteed to be a multiple of  $\pi$ . This, as is well known, ensures the single valuedness of the diabatic potentials.

Equation 50 implies that  $\Delta\mathbf{W}$  can be ignored as long as the two other angles, namely,  $\gamma_{23}$  and  $\gamma_{13}$ , are small enough. However, this approximation breaks down when one of these two angles (in this case,  $\gamma_{13}$ ) becomes  $\pi/2$ , namely, when the contour gets close enough to any of the (2,3) ci's.

## VI. Analysis of the Final Results

Equation 41 yields the (diabatic) potential matrix for the modified (reduced) diabatic framework. At the beginning of our analytical derivation, we assumed that the Hilbert subspace is made up of  $N$  states; therefore, one expects a diabatic potential matrix to be of dimensions  $N \times N$  and the number of equations to be solved as  $N$ . Following the analytical study presented in the previous section, we reduced this number to  $p$ , which can be increased until convergence is attained ( $p \leq N$ ). We recall that  $p$  is limited not only from above (by  $N$ ) but also from below by  $q$ , where  $q$  is the number of open (adiabatic) states for a given energy (and a given region).

Equation 41 clearly exhibits the two aspects that affect most electronic nonadiabatic processes, namely, energy and topology. The energy aspect enters through the  $\mathbf{u}$  matrix, which contains the adiabatic PESs, because the energy controls the number,  $p$ , of adiabatic PESs to be included in the calculation. The topological aspect enters through the reduced  $\mathbf{A}$  matrix (and its inverse) because its derivation, although it is of dimensions  $p \times p$ , involves all of the  $N$  eigenstates of the Hilbert subspace. This is also well demonstrated in the example that was worked out in section V.

The derivation is characterized by two important features.

(1) For  $p = N$ , eq 41 yields the ordinary result given in eq 26. The reason is that for  $p = N$  the matrix  $(\mathbf{A}_p^p)^{-1}$  becomes

$$(\mathbf{A}_p^p)^{-1} = (\mathbf{A}_N^N)^{-1} = (\mathbf{A}_N^N)^\dagger \quad (53)$$

as one would expect. This implies that in this case  $N$  SEs have to be solved.

(2) For  $q = p = 1$ , the (single) potential term is  $u_1$  (namely, the lowest adiabatic potential), and the corresponding Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \nabla^2 \varphi + (u_1 - E)\varphi = 0 \quad (54)$$

In other words, eq 53 is the ordinary adiabatic BO–Schrödinger equation. It is important to emphasize that to apply eq 53 to systems with conical intersections (systems that possess singular NACTs) eq 53 has to be solved for the relevant boundary conditions.

## VII. Conclusions

In this article, we treat two issues related to the electronic diabatic potential energy matrix.

(a) From scanning through the published literature, we notice that the dimension of the diabatic matrices is arbitrary and not subject to any limitations. We proved on various occasions<sup>74</sup> (see also refs 58(a), 58(c), 62(a), and 62(b)) that the dimension of a diabatic matrix that follows from the adiabatic framework by employing the ADT is determined to the extent that the nonadiabatic coupling matrix,  $\tau$ , breaks up into blocks. This implies that if the size of the decoupled block belonging to the  $\tau$  matrix (i.e.,  $\tau_N$ ) is  $N$  then the dimension of this diabatic potential energy matrix has to be  $N$  as well. In this article, we prove for the first time that the size of a diabatic matrix obtained in any other way (direct or indirect) has to be  $N$  as well.

(b) One of the main obstacles in treating electronic nonadiabatic processes is the fact that the just-mentioned number  $N$ , which also stands for the number of diabatic SEs to be solved, can be rather large. This fact causes many dynamical treatments to be carried out with an arbitrarily reduced number of equations (usually two), essentially without any justification. In the present article, we consider this issue in detail and show how the number of SEs to be solved can be reduced rigorously from its original value  $N$  (which is energy-independent) to a smaller number, labeled as  $p$ , which is expected to be energy-dependent and most likely equals the number of energetically open adiabatic states.

As a final issue, we refer to a different method, due to Kuppermann,<sup>6,11</sup> that is also devised to overcome the problem of an enlarged system of diabatic states. According to this method, one considers only the two lowest adiabatic states and derives the corresponding ADT angle by solving a Poisson equation based on the removable part of the (1,2) NACT. In this way, the newly formed diabatic potential matrix (eq 50) is guaranteed to be single valued as it should be.

The two approaches differ significantly from each other. The Kuppermann approach considers only two states; in other words, all magnitudes are related to the single (1,2) NACT. This is its advantage but mainly its limitation because it is not clear how to incorporate topological features of higher states. Our approach demands a knowledge of the  $N \times N$   $\tau$  matrix where  $N$  is usually larger than 2, but then, at the stage of treating the system of  $N$  diabatic (nuclear) Schrödinger equations, this number is reduced to  $p$ , where  $p$  ( $\leq N$ ) is now energy-dependent. The main



advantage of our approach is that it enables a series of iterations to obtain the converged results. Because this part seems to be missing in the Kuppermann approach, our method can be considered to be complimentary to his when it turns out that keeping only two equations may lead to inadequate results.

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