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Born−Oppenheimer Time-Dependent Systems: Perturbative vs Nonperturbative Diabatization

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In this article a *time-dependent* molecular system is considered. The theoretical treatment is characterized by the fact that here, for the first time, the adiabatic framework is assumed to contain singular nonadiabatic coupling terms or, in other words, *conical intersections*. The aim is to derive under these conditions, from first principles and in a rigorous manner, the time-dependent nuclear Schroedinger equations to be solved. We arrived at two different versions: (1) the "ordinary" version, which is essentially similar to the one encountered within the time-independent scheme and demands the fulfillment of the spatial Curl condition (Baer, M. *Chem. Phys. Lett.* **1975,** *35,* 112), and (2) a novel version, which introduces the time−space configuration and consequently demands the fulfillment of a "four"-component Curl condition, reminiscent of the one in special relativity (R. Baer, M. Baer, D. K. Hoffman, and D. J. Kouri, to be published). Both versions lead to the same number of Schroedinger equations, but within the second version, the time-dependent interaction is treated much more reliably.

I. Introduction

As more and more groups show interest in treating molecular interactions which involve electronic transitions,[1] I thought it would be useful to discuss some difficulties in treating such processes and present theoretical ways to handle them. There is no doubt that treating molecular interactions affected by electronic nonadiabatic coupling terms (NACT) is much more complicated than treating interactions where these effects are ignored. The main reason is that NACTs are frequently singular,[2] and this is believed to introduce insurmountable numerical difficulties. Scanning through the published literature, one will notice that in many cases the NACTs are not as seriously considered as they should be. In contrast to the familiar vib-rotational coupling terms which are well understood and usually handled correctly, the NACTs are kinds of physical magnitudes which in most cases are either ignored or circumvented without proper justifications. If ignored, not much can be added except to say that the results have to be considered unreliable and eventually nonrelevant. More serious difficulties are encountered with treatments that circumvent the need to consider NACTs and give the inexperienced user the impression that these treatments are well established and numerically sound. As it turns out it is impossible to circumvent the NACTs because in treating electronic transitions one has *to know* the size of the Hilbert subspace (namely the number of strongly coupled eigenstates) in the region of interest, and this can be obtained only by studying the NACTs.[3,4] This statement may be more confusing than enlightening but we elaborate on this subject in the next two paragraphs. A NACT is a vector characterized by two features: it has its origin in a degeneracy point (i.e., where two electronic eigenstates become identical),[2] known also as a conical intersection (*ci*)[5] and it has a spatial distribution which decreases like q^{-1} where q is a the distance from the *ci*.[6] Conical intersections are well-established concepts in solid-state phys-

ics[7,8] but were shown to play a dominant role in molecular dynamics as well.[1−4]

The starting point of any study of electronic effects in molecular systems is the Born−Oppenheimer (BO) assumption that electrons are moving much faster than nuclei and therefore, theoretically, one can treat first the dynamics of the electrons and then consider the motion of the nuclei.[9] To continue, one may choose either the adiabatic framework which consists of the adiabatic potential energy surfaces (PES) and the NACTs, or the diabatic framework which is expressed in terms of the diabatic potential matrix. Since the elements of the diabatic PES matrix are smooth functions of the coordinates (and NACTs are usually not) the diabatic framework is preferred for treating the nuclear dynamics of the nuclei and indeed all rigorous quantum mechanical treatments aim at reaching it.[1,10−12] The diabatic framework can be formed in three ways: (1)The first is the *direct* way, namely, deriving an electronic basis set as well as a set of eigenvalues calculated at a given (one, single) point in configuration space and applying them to calculate the diabatic potential matrix at any requested point (see, for instance, ref 4a, Appendix D); (2) The second is the *indirect* way, namely, deriving for *each* point in configuration space the electronic eigenvalues (which are recognized as the adiabatic potentials) and the electronic eigenfunctions needed to calculate the NACTs and, then, employing these NACTs, to form the transformation to the diabatic framework.[11] This transformation is termed as the adiabatic-to-diabatic transformation, or by its acronym ADT, and as was discussed on many other occasions the ADT yields a meaningful diabatic potential matrix if and only if certain conditions (to be discussed below) are fulfilled. (3) There is also a third way which is similar to the previous one as it is based on an ADT matrix, but the relevant matrix elements are not calculated from the NACTs but employing other considerations.[1c,d,e,12] It is important to mention that there are other approaches, nonrigorous, which differ significantly from the ones just mentioned. Such are the quasi-classical,[13] semiclassical,[14] mixed electronic-nuclear quantum-classical[15] and nuclear quantum-

classical approaches.[16] These approaches are usually approximate and are mainly designed to treat larger molecular systems which are beyond the capability of the pure quantum methods. In the present article, we consider the rigorous quantum mechanical methods only.

There is no doubt that on the face of it the *direct* way of reaching the diabatic framework is more convenient. Indeed, as long as the various NACTs are regular functions at every point in configuration space (or at least in that part of interest) this procedure is valid and simple. However, in case certain NACTs become singular, as for instance in the case of the H + H_2 system,[17,18] this procedure is most likely to fail and therefore is expected to yield irrelevant results. To find out if such singular NACTs exist one has to "move" into the adiabatic framework and calculate them for a highly dense grid of points which, in turn, makes this procedure (i.e., the *direct* one) essentially redundant. Another difficulty associated with the *direct* approach has to do with the size of the required group of states that has to be included in the calculations (which is equivalent to the smallest number of *adiabatic* states which can be considered as being *isolated* from the rest of the Hilbert space − see the detailed discussion on this subject in ref 19). We showed in numerous articles that dynamic calculations are meaningless unless they are carried out for *such* a Hilbert subspace but the size of this Hilbert subspace (in a given region) can be obtained only by employing the NACTs. The reason for this is associated with the ability to form *single-valued* diabatic potentials. Such potentials are guaranteed if and only if the Hilbert subspace is not coupled (or, at most, weakly coupled) to the rest of the Hilbert space.[3,4,19] To find out whether a given Hilbert subspace forms an isolated group of states we need the relevant NACT matrix of the same size (i.e., dimension). In summary, whatever approach one uses to treat the nuclear system a detailed study of the NACTs is required first. Thus, in order to carryout a reliable dynamical treatment of a molecular system (e.g., scattering processes, photodissociation, unimolecular processes), the adiabatic framework can never be circumvented. In other words any diabatization process has to be started in the adiabatic framework and the diabatic framework is best reached applying the ADT matrix. In what follows, whenever we mention a Hilbert subspace we refer to an *isolated* group of states.

The subject to be treated in the present article is related to the diabatization to be carried out for a BO system exposed to an external time-dependent (TD) electric field.[20] We assume an electric field and not an electromagnetic field in order to avoid the electromagnetic vector potential, which, for our purpose unnecessarily complicates the theoretical derivations. We discuss two procedures: (a) the perturbative approach which can be considered as the traditional approach; (b) the nonperturbative approach which introduces novel ideas such as a "four"-component curl equation ("four" in the sense of field theory or special theory of relativity). This particular issue was addressed in a review article by Englman and Yahalom,[21] whereas the more general aspect is discussed in two more recent articles.[22]

The two procedures yield different expressions (but the same number of nuclear equations) for the final diabatic (nuclear) TD Schrödinger equations (SE) to be solved. Following the theoretical presentation, we discuss to some extent the advantages and disadvantages of each approach.

The article is arranged in the following way: In the next section we briefly summarize the theoretical background related to the present subject (essentially summarizing the theory for the time-independent framework), in the third section is

presented the perturbative approach for treating the TD−BO equation, in the fourth the nonperturbative approach is discussed, and in the last section the conclusions are discussed and summarized.

II. Theoretical Background: The Time-Independent System

The nonadiabatic coupling matrix element, τ_{ji}, the central magnitude of this article, is defined as

$$\tau_{ji} = \langle \zeta_j | \nabla \zeta_i \rangle; \quad i,j = \{ 1, ... \} \tag{1}$$

where the grad operator is expressed with respect to the nuclear coordinates, ν, and the $\zeta_k(e|\nu)$ functions, $k = j,i$, are the eigenfunctions of the time-independent (TID) electronic Hamiltonian $\mathbf{H}_e(e|\nu)$:

$$(\mathbf{H}_e(e|\nu) - u_k(\nu))\zeta_k(e|\nu) = 0; \quad k = j,i \tag{2}$$

Here, e stands for the electronic coordinates and $u_k(\nu)$ is the kth (adiabatic) PES. The NACTs become apparent, at a somewhat later stage, following the BO treatment which leads to the nuclear SE. Assuming we encounter the situation of a Hilbert subspace (as briefly defined in the Introduction) the nuclear SE becomes:[3c]

$$-\frac{\hbar^2}{2m}(\nabla + \boldsymbol{\tau})^2 \boldsymbol{\Psi} + (\mathbf{u} - E)\boldsymbol{\Psi} = \mathbf{0} \tag{3}$$

where $\boldsymbol{\tau}$ is an antisymmetric matrix which contains the NACTs defined in eq 1, $\mathbf{u}$ is a diagonal matrix that contains the nuclear PESs (introduced through eq 2), $\boldsymbol{\Psi}$ is a column vector that contains the nuclear wave functions to be solved, E is the energy, and m is the mass of the system (it is assume that the grad operator is defined with respect to mass-scaled coordinates).

The $\boldsymbol{\tau}$ matrix is characterized by two important features:

(1) Some of its elements can become singular. The singularity follows from the Hellmann−Feynman theorem which also yields an explicit expression for each matrix element τ_{ji}:[2]

$$\tau_{ji} = \frac{\langle \zeta_j | \nabla \mathbf{H}_e | \zeta_i \rangle}{u_j - u_i} \tag{4}$$

Here u_k, $k = j,i$ are the corresponding eigenvalues defined in eq 2. It is well noticed that when the ith and the jth eigenvalues become degenerate the corresponding $\boldsymbol{\tau}$ matrix element, i.e., τ_{ji} becomes singular. This is expected, when it happens, between two consecutive states, namely the jth and the $(j+1)$th one.

(2) The components of the $\boldsymbol{\tau}$ matrix fulfill (in the case of a Hilbert subspace) the following set of equations:[11]

$$\frac{\partial}{\partial p}\boldsymbol{\tau}_q - \frac{\partial}{\partial q}\boldsymbol{\tau}_p - [\boldsymbol{\tau}_q, \boldsymbol{\tau}_p] = 0; \quad \{ p,q;K \} \tag{5}$$

where q and p are any of the K components of $\boldsymbol{\tau}$ (K is equal to the number of internal nuclear coordinates). This set can be written also in a more compact way:

$$Curl\boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] = 0 \tag{6}$$

Equation 5 (or eq 6) is sometimes called the Curl condition or also the Curl equation.

The next subject is related to the adiabatic-to-diabatic transformation. Again we just scan through the main expressions. The aim of the diabatization is to eliminate the unpleasant singular NACTs from eq 3, and for this purpose, we perform

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the following transformation:[11]

$$\mathbf{\Psi} = \mathbf{A\Phi} \qquad (7)$$

Substituting eq 7 into eq 3, performing the usual algebra, and demanding the elimination of the $\boldsymbol{\tau}$ matrix yields the following results:

(a) The new (diabatic) SE is

$$-\frac{\hbar^2}{2m}\nabla^2\mathbf{\Phi} + (\mathbf{W} - E)\mathbf{\Phi} = 0 \qquad (8)$$

where the diabatic potential $\mathbf{W}$ is given in the following form:

$$\mathbf{W} = \mathbf{A}^\dagger\mathbf{uA} \qquad (9)$$

(b) The ADT matrix, $\mathbf{A}$, which is a solution of the first-order differential equation, is[9]

$$\nabla\mathbf{A} + \boldsymbol{\tau}\mathbf{A} = 0 \qquad (10)$$

Equation 10 is solved along contours, Γ.[11]

As a final point in this section we mention that fulfillment of the Curl equation (eqs 5 or 6) in a given region is a sufficient condition for eq 10 to have a solution in that region. More about this subject can be found in ref 4.

III. The Time-Dependent Perturbative Approach

The starting point is the TD−SE for the total wave function, $\mathbf{\Psi}$, of the electrons and the nuclei:[20,22b]

$$i\hbar\frac{\partial\mathbf{\Psi}}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathbf{H}_e\right)\mathbf{\Psi} \qquad (11)$$

where the electronic Hamiltonian, $\mathbf{H}_e$, is time dependent for $t \geq 0$, i.e., $\mathbf{H}_e = \mathbf{H}_e(t)$. Following Born and Oppenheimer, $\mathbf{\Psi}$ is presented in the following form:

$$\mathbf{\Psi}(e|t,\nu) = \zeta^{\mathbf{T}}(e|\nu)\psi(t,\nu) \qquad (12)$$

(here $\zeta^{\mathbf{T}}(e|\nu)$ is a row vector, in contrast to $\zeta(e|\nu)$ which is a column vector) and we assume that $\zeta(e|\nu)$ is a TID basis set which fulfills eq 2, but only for t ≤ 0. Substituting eq 12 into eq 11 yields the following TD equation for the nuclear wave functions:

$$i\hbar\zeta^{\mathbf{T}}\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2(\zeta^{\mathbf{T}}\psi) + \mathbf{H}_e(\zeta^{\mathbf{T}}\psi) \qquad (13)$$

or

$$i\hbar\zeta^{\mathbf{T}}\frac{\partial\psi}{\partial t} =$$
$$-\frac{\hbar^2}{2m}\{\zeta^{\mathbf{T}}\nabla^2\psi + 2\nabla\zeta^{\mathbf{T}}\nabla\psi + (\nabla^2\zeta^{\mathbf{T}})\psi\} + (\mathbf{H}_e\zeta^{\mathbf{T}})\psi \quad (14)$$

Multiplying eq 14 (from the left-hand side) by $\zeta^\dagger(e|\nu)$ and integrating over the electronic coordinates, we obtain, in a similar way, as within the TID framework, the (adiabatic) nuclear TD−SE:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}(\nabla + \tau)^2\psi + \tilde{\mathbf{H}}_e\psi \qquad (15)$$

where $\boldsymbol{\tau}$, introduced in eq 1, is a *TID* matrix, but $\tilde{\mathbf{H}}_e$ is the TD potential matrix defined as

$$\tilde{\mathbf{H}}_e(t|\nu)_{jk} = \langle\zeta_j(e|\nu)|\mathbf{H}_e(e|t,\nu)|\zeta_k(e|\nu)\rangle \qquad (16)$$

It is important to mention that $\tilde{\mathbf{H}}_e$, for $t \leq 0$ is a diagonal matrix which is identical to the adiabatic potential matrix $\mathbf{u}$ introduced in eq 3 but becomes nondiagonal at $t > 0$.

The next step is to perform the ADT in order to eliminate the $\boldsymbol{\tau}$ matrix which is done in a similar way as within the TID framework,[11] namely replacing $\mathbf{\Psi}$ by $\mathbf{A\Phi}$, (see eq 7) and performing the usual algebra (see, also, eqs 8−10). This derivation yields the following TD nuclear SE:

$$i\hbar\frac{\partial\mathbf{\Phi}}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\mathbf{\Phi} + \mathbf{W}_e\mathbf{\Phi} \qquad (17)$$

where the diabatic potential $\mathbf{W}_e$ is similar to $\mathbf{W}$ in eq 9 but defined with respect to $\tilde{\mathbf{H}}_e$, given in eq 16:

$$\mathbf{W}_e = \mathbf{A}^\dagger\tilde{\mathbf{H}}_e\mathbf{A} \qquad (18)$$

and $\mathbf{A}$ is the solution of eq 10. Since the electronic basis set is TID the same applies to the $\boldsymbol{\tau}$ matrix as well as to the $\mathbf{A}$ matrix so that the time dependence of the diabatic potential $\mathbf{W}_e$ follows, solely, from $\tilde{\mathbf{H}}_e$.

At this stage we want to call attention to the following difficulty. It is noticed that the number of coupled (nuclear) SEs to be solved is equal to the number of electronic eigenstates, designated as L, employed in the derivation of $\tilde{\mathbf{H}}_e$. However this number has to equal N, the size of the Hilbert subspace, because otherwise, based on numerous studies, *multivalued* diabatic potentials are encountered.[3,4,19] Thus, L is forced to be equal to N. However if the perturbation is too strong so that N states may not suffice to present it properly, this procedure is expected to fail (this is also why we termed this approach *perturbative*).

To summarize this section: The perturbative approach may not be robust because the dimension of the Hilbert subspace dictates the dimension of the perturbation.

IV. The Time-Dependent Nonperturbative Approach

IV.1. Introductory Comments. The starting point is, like in the previous section, the TD−SE for the total wave function, $\mathbf{\Psi}$:[20,22a,b]

$$i\hbar\frac{\partial\mathbf{\Psi}}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathbf{H}_e\right)\mathbf{\Psi} \qquad (11)$$

and $\mathbf{\Psi}$ is presented, as usual, in the following form:

$$\mathbf{\Psi}(e|t,\nu) = \zeta^{\mathbf{T}}(e|t,\nu)\psi(t,\nu) \qquad (19)$$

(we recall that $\zeta^{\mathbf{T}}$, as in the previous section, is a row vector corresponding to ζ). The number of (time-dependent) eigenfunctions included in the expansion is N which, as was emphasized in the previous section, is equal to the size of the Hilbert subspace. In what follows we assume that the $\zeta(e|t,\nu)$ functions fulfill the following TD equation, namely:

$$i\hbar\frac{\partial\zeta^{\mathbf{T}}(e|t,\nu)}{\partial t} = \zeta^{\mathbf{T}}(e|t,\nu)\mathbf{H}_e(e|t,\nu) \qquad (20)$$

Substituting eqs 19 and 20 into eq 11 yields the following TD equation for the nuclear wave functions:[22a,b]

$$i\hbar\zeta^{\mathbf{T}}(e|t,\nu)\frac{\partial\psi(e|t,\nu)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2(\zeta^{\mathbf{T}}(e|t,\nu)\psi(e|t,\nu)) \quad (21)$$

As can be noticed, this equation is entirely dominated by the kinetic operator.

IV.2. The Time-Dependent Equation for the Electronic Components. Our next step is to write eq 20 in a more explicit way. In what follows, we are allowed, without losing the generality, to assume that each electronic "adiabatic" wave function fulfills the following TD equation:[22a,b]

$$i\hbar\frac{\partial|\zeta_k(e|t,\nu)\rangle}{\partial t} = \mathbf{H}_e|\zeta_k(e|t,\nu)\rangle \qquad (22)$$

Equation 22 is solved for the initial function which is identified with the kth electronic eigenfunction of $\mathbf{H}_e$ at $t = 0$, i.e., $|\zeta_k(e|t = 0,\nu)\rangle$—as given in eq 2. To solve eq 22 each of the TD $|\zeta_k(e|t,\nu)\rangle$ functions is expanded in terms of L eigenfunctions of $\mathbf{H}_e$ as calculated at $t = 0$. Thus

$$|\zeta_k(e|t,\nu)\rangle = \sum_{j=1}^{L}|\zeta_j(e|t = 0,\nu)\rangle\omega_{jk}(t|\nu) \qquad (23)$$

Since the number of $|\zeta_k(e|t,\nu)\rangle$ functions is N (which is the size of the Hilbert subspace) which is not necessarily equal to L—in what follows $N \leq L$—it is noticed that the $\omega(t|\nu)$ matrix can be a rectangular (not square) matrix with N columns and L rows, thus, of dimensions $L \times N$.

Substituting eq 23 into eq 22 yields the differential equation for $\omega(t|\nu)$:

$$i\hbar\frac{\partial\omega(t|\nu)}{\partial t} = \tilde{\mathbf{H}}_e(t|\nu)\omega(t|\nu) \qquad (24)$$

where:

$$\tilde{\mathbf{H}}_e(t|\nu)_{jk} = \langle\zeta_j(e|t = 0,\nu)|\mathbf{H}_e(e|t,\nu)|\zeta_k(e|t = 0,\nu)\rangle \quad (25)$$

The solution of eq 24 is given in the form:

$$\omega(t|\nu) = \rho\exp\left(-\frac{i}{\hbar}\int_0^t\tilde{\mathbf{H}}_e(t'|\nu)dt'\right)\tilde{\mathbf{I}} \qquad (26)$$

where ρ is now the time ordering operator (see also ref 11b) and $\tilde{\mathbf{I}}$ is a rectangular matrix with the elements δ_{jk} and dimensions identical to those in $\omega(t|\nu)$, i.e., $L \times N$. It can be seen that at $t = 0$ the matrix $\omega(t = 0|\nu)$ is equal to $\tilde{\mathbf{I}}$.

As a final subject in this subsection we emphasize that although $\omega(t|\nu)$ is not a square matrix, it is a unitary matrix in the sense that

$$\omega^\dagger(t|\nu)\omega(t|\nu) = \mathbf{I} \qquad (27)$$

where $\omega^\dagger(t|\nu)$ is of dimension $N \times L$ and is the (right-hand-side) complex conjugate of $\omega(t|\nu)$ and $\mathbf{I}$ is the unit matrix of dimension $N \times N$.

As is noticed, the present derivation (in contrast to the previous, perturbative, one) does not require the size of the employed TID basis set, L, to be identical to N, the size of the Hilbert subspace. This is an important feature because the perturbation can now be of any magnitude and still be treated reliably without significantly increasing the numerical effort (as will be shown next).

IV.3. The Adiabatic Time-Dependent Equation for the Nuclear Wave Functions. Returning to eq 21 and evaluating the right-hand side, one obtains the following:

$$i\hbar\zeta^{\mathbf{T}}\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\zeta^{\mathbf{T}}\nabla^2\psi + 2\nabla\zeta^{\mathbf{T}}\nabla\psi + (\nabla^2\zeta^{\mathbf{T}})\psi\} \quad (28)$$

Multiplying eq 28 (from the left side) by $\zeta^\dagger(e|t,\nu)$ and integrating over the electronic coordinates, we obtain (see Appendix I)[22]

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}(\nabla + \tilde{\tau})^2\psi \qquad (29)$$

where $\tilde{\tau}$ is a TD, *dressed*, nonadiabatic coupling matrix given in the form:

$$\tilde{\tau} = \omega^\dagger\tau\omega + \omega^\dagger\nabla\omega \qquad (30)$$

It is well noticed that although $\omega(t|\nu)$ is a rectangular matrix, $\tilde{\tau}$ is a square matrix of dimensions $N \times N$ and therfore the size of the system of SEs in eq 29 remains N (and not L).

Equation 29 stands for the general adiabatic time-dependent nuclear SE. It is of an unusual interesting form because it is expressed in terms of (dressed) NACTs only and lacks the expected PES matrix. A similar form was encountered in a simplified version of the present treatment[22c] when we attached to the electronic eigenfunctions time-dependent phases worked out, originally, earlier.[23]

Equation 29 will be diabatized in the next section.

IV.4. The Time-Dependent Adiabatic-to-Diabatic Transformation. We apply again the ADT as presented in eq 7 but to distinguish this case from the previous one we labeled it $\tilde{\mathbf{A}}$. Substituting eq 7 into eq 29 yields the following expression:

$$i\hbar\tilde{\mathbf{A}}\frac{\partial\Phi}{\partial t} = -\frac{\hbar^2}{2m}[\tilde{\mathbf{A}}\nabla^2 + 2(\mathbf{G}\tilde{\mathbf{A}})\nabla + (\mathbf{G}^2\tilde{\mathbf{A}})]\Phi - i\hbar\frac{\partial\tilde{\mathbf{A}}}{\partial t}\Phi \tag{31}$$

Here $\mathbf{G}$ is an operator which acts only on $\tilde{\mathbf{A}}$ and is given in the form:

$$\mathbf{G} = \nabla + \tilde{\tau} \qquad (32)$$

To continue we add and subtract an undetermined matrix $\mathbf{B}$ multiplied by $\tilde{\mathbf{A}}\Phi$, so that eq 31 becomes

$$i\hbar\tilde{\mathbf{A}}\frac{\partial\Phi}{\partial t} = $$
$$-\frac{\hbar^2}{2m}[\tilde{\mathbf{A}}\nabla^2 + 2(\mathbf{G}\tilde{\mathbf{A}})\nabla + (\mathbf{G}^2\tilde{\mathbf{A}})]\Phi - (\mathbf{F} - \mathbf{B})\tilde{\mathbf{A}}\Phi \quad (33)$$

where $\mathbf{F}$ is an operator which acts on $\tilde{\mathbf{A}}$ only and is defined as

$$\mathbf{F} = i\hbar\frac{\partial}{\partial t} + \mathbf{B} \qquad (34)$$

The $\tilde{\mathbf{A}}$ matrix is chosen to be a simultaneous solution of the two following equations:

$$\mathbf{G}\,\tilde{\mathbf{A}} = \mathbf{0} \qquad (35a)$$

and

$$\mathbf{F}\,\tilde{\mathbf{A}} = 0 \qquad (35b)$$

The derivation of this matrix follows by demanding that the elements of the solution matrix of eq 35, once derived, have to be analytic functions at every point in a given "four-dimensional" configuration time−space. This means that each element of the $\tilde{\mathbf{A}}$ matrix has to be differentiable to any order with respect to all the spatial coordinates and with respect to time. In addition, analyticity requires the fulfillment of the following two conditions:

(1) The results of two consecutive differentiations of the $\tilde{\mathbf{A}}$ matrix with respect to two spatial coordinates, p and q, does

not depend on the order of differentiation.[11] This requirement can be shown to lead to Curl conditions similar to those given in eq 5 (or 6) but where $\boldsymbol{\tau}$ is replaced by its TD counterpart, $\tilde{\boldsymbol{\tau}}$ (see eq 30).

(2) The results of two consecutive differentiations of the $\tilde{\mathbf{A}}$ matrix, one with respect to *time* and the other with respect to any spatial coordinate p, does not depend on the order of differentiation. This requirement implies

$$\frac{\partial}{\partial t}(\nabla\tilde{\mathbf{A}}) - \nabla\left(\frac{\partial}{\partial t}\tilde{\mathbf{A}}\right) = \mathbf{0} \qquad (36)$$

In Appendix II, is proved that the condition for this equality to hold is that the **B** matrix (introduced earlier, in eqs 33 and 34, but not yet determined) has to be

$$\mathbf{B} \equiv \tilde{\tilde{\mathbf{H}}}_e = \boldsymbol{\omega}^\dagger \tilde{\mathbf{H}}_e \boldsymbol{\omega} \qquad (37)$$

Having this result, we find for eq 35:

$$\nabla\tilde{\mathbf{A}} + \tilde{\boldsymbol{\tau}}\tilde{\mathbf{A}} = \mathbf{0}$$

$$i\hbar\frac{\partial\tilde{\mathbf{A}}}{\partial t} + \tilde{\boldsymbol{\tau}}_e\tilde{\mathbf{A}} = \mathbf{0} \qquad (38)$$

which can be written in terms of a "four"-component vector:[22a,b]

$$\tilde{\nabla}\tilde{\mathbf{A}} + \tilde{\tilde{\boldsymbol{\tau}}}\tilde{\mathbf{A}} = \mathbf{0} \qquad (39)$$

where $\tilde{\nabla}$ is a "four"-component grad operator (reminiscent of special relativity):[21,22a,b,24,25]

$$\tilde{\nabla} = \left\{\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, ..., \frac{\partial}{\partial q_n}, i\hbar\frac{\partial}{\partial t}\right\} \qquad (40)$$

and, similarly, $\tilde{\tilde{\boldsymbol{\tau}}}$ is recognized as a "four"-component vector matrix:

$$\tilde{\tilde{\boldsymbol{\tau}}} = \{\tilde{\boldsymbol{\tau}}_{q_1}, \tilde{\boldsymbol{\tau}}_{q_2}, ..., \tilde{\boldsymbol{\tau}}_{qn}, \tilde{\tilde{\mathbf{H}}}_e\} \qquad (41)$$

Here $\tilde{\tilde{\mathbf{H}}}_e$ is the time component of $\tilde{\tilde{\boldsymbol{\tau}}}$. It is important to mention that in our case we do not necessarily have "four" components but in general $(K + 1)$ components.

The corresponding "four"-component non-Abelian Curl equation which guarantees the existence of a solution for eq 39 takes the form

$$\frac{\partial}{\partial\mu'}\tilde{\tilde{\boldsymbol{\tau}}}_\mu - \frac{\partial}{\partial\mu}\tilde{\tilde{\boldsymbol{\tau}}}_{\mu'} - [\tilde{\tilde{\boldsymbol{\tau}}}_\mu, \tilde{\tilde{\boldsymbol{\tau}}}_{\mu'}] = \mathbf{0}; \quad \{\mu, \mu' = p, q, t/(i\hbar)\} \quad (42)$$

where p and q are spatial coordinates and $\tilde{\tilde{\boldsymbol{\tau}}}_t$, stands for the time component of $\tilde{\tilde{\boldsymbol{\tau}}}$, namely, $\tilde{\tilde{\mathbf{H}}}_e$. Equation 42 is reminiscent of the "four-component" Yang-Mills non-Abelian Curl equation.[24] We would like also to mention that Englman and Yahalom briefly discussed the possibility to extend the present author's spatial Curl equation to include the relevant time component[21] similar to eq 42.

It can be shown that the solution of eq 38, namely, the $\tilde{\mathbf{A}}$ matrix is a unitary matrix and as a result the diabatic SE (see eq 33) takes the simplified form

$$i\hbar\frac{\partial\mathbf{\Phi}}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + \tilde{\mathbf{W}}_e\right)\mathbf{\Phi} \qquad (43)$$

where $\tilde{\mathbf{W}}_e$ is the "missing" potential matrix:

$$\tilde{\mathbf{W}}_e = \tilde{\mathbf{A}}^\dagger\tilde{\mathbf{H}}_e\tilde{\mathbf{A}} \qquad (44)$$

The potential matrix $\tilde{\mathbf{W}}_e$ is similar, in some respect, to $\mathbf{W}_e$ in eq 18 because at time $t \leq 0$, both $\tilde{\mathbf{H}}_e$ and $\tilde{\tilde{\mathbf{H}}}_e$ are diagonal matrices that contain the adiabatic potentials. However at $t > 0$, $\tilde{\mathbf{H}}_e$ and $\tilde{\tilde{\mathbf{H}}}_e$ become nondiagonal and in general differ from each other so that the same applies to $\mathbf{W}_e$ and $\tilde{\mathbf{W}}_e$.

V. Discussion and Conclusions

In this article are presented two different diabatization schemes for a molecular system perturbed by a time-dependent perturbation. We termed the first, the simplified version, as the perturbative approach and the second, the more general one, as the nonperturbative approach. In both treatments we end up with a unitary ADT matrix (reminiscent of the one encountered in the TID framework) calculated by solving a vectorial first-order differential equation along contours.

The main difference between the two approaches is: Within the first approach a *time-independent* electronic basis set is used so that the ADT matrix is TID and the resulting diabatic PES matrix is similar to the one encountered for a TID interaction. Within the second approach we apply a *time-dependent* electronic basis set so that we end up with a TD-ADT matrix which leads to a somewhat more complicated diabatic PES matrix.

There is no doubt that on the face of it the first approach, due to its simplified ADT, should be preferred. However this version may have its disadvantages due to two contradictory requirements: (1) To have a correct ADT matrix, one has to apply a Hilbert subspace which contains N states (which results in a system of N nuclear SEs to be solved). (2) Given a TD interaction one may need L (TID) electronic eigenfunctions to present it reliably (where L can be larger than N). Within the first approach L has to be equal to N even though a set of N $(=L)$ electronic eigenfunctions may not be sufficient to present satisfactorily the TD perturbation. Within the second approach the two numbers N and L are *independent*; namely, the number of SEs to be solved is, as before, N, but this approach allows to apply a (much) larger electronic basis set to represent the perturbation. It is true that within this process one encounters rectangular (as opposed to square) matrices, but the theory, as presented here, overcomes this obstacle in a reliable, coherent and consistent way. Thus, the final outcome is a set of N (not L) nuclear SEs just like in the previous case and the inconvenience as encountered within the second approach is mainly in constructing the diabatic potential matrix but not in solving the nuclear SEs.

Appendix I. Derivation of $\tilde{\tau}$, the Dressed Nonadiabatic Coupling Matrix

Our starting point is eq 28:

$$i\hbar\zeta^{\mathbf{T}}(e|t,\nu)\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\zeta^{\mathbf{T}}(e|t,\nu)\nabla^2\psi + 2\nabla\zeta^{\mathbf{T}}(e|t,\nu)\nabla\psi +$$
$$(\nabla^2\zeta^{\mathbf{T}}(e|t,\nu))\psi\} \quad (I.1)$$

Employing eq 23 to present $\zeta^{\mathbf{T}}(e|t,\nu)$ we get

$$i\hbar\zeta^{\mathbf{T}}(e|t=0,\nu)\boldsymbol{\omega}(t|\nu)\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\zeta^{\mathbf{T}}(e|t=0,\nu)\boldsymbol{\omega}(t|\nu)\nabla^2\psi +$$

$$2\nabla(\zeta^{\mathbf{T}}(e|t=0,\nu)\boldsymbol{\omega}(t|\nu))\cdot\nabla\psi + \nabla^2(\zeta^{\mathbf{T}}(e|t=0,\nu)\boldsymbol{\omega}(t|\nu))\psi\} \tag{I.2}$$

Multiplying eq I.2 each time by one of the $|\zeta_k(e|t=0,\nu)\rangle$ functions, $k = 1, ..., L$, and integrating the result with respect to e, the electronic coordinates, and multiplying through by $\boldsymbol{\omega}^{\dagger}(t|\nu)$ yield the following outcome:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\nabla^2\psi + 2\boldsymbol{\omega}^{\dagger}(\boldsymbol{\tau}\boldsymbol{\omega}+\nabla\boldsymbol{\omega})\cdot\nabla\psi +$$

$$\boldsymbol{\omega}^{\dagger}(\boldsymbol{\tau}^{(2)}\boldsymbol{\omega}+2\boldsymbol{\tau}\cdot\nabla+\nabla^2\boldsymbol{\omega})\psi\} \tag{I.3}$$

where $\boldsymbol{\omega}$ replaces $\boldsymbol{\omega}(t|\nu)$, $\boldsymbol{\tau}$ is TID, namely, $\boldsymbol{\tau}=\boldsymbol{\tau}(\nu)$ and $\boldsymbol{\tau}^{(2)}$ (which is also TID) stands for

$$\tau^{(2)}{}_{jk} = \langle\zeta^{\mathbf{T}}_j(e|t=0,\nu)|\nabla^2\zeta^{\mathbf{T}}_k(e|t=0,\nu)\rangle \tag{I.4}$$

Recalling that for a Hilbert subspace the following relation holds:[1g]

$$\boldsymbol{\tau}^{(2)} = \nabla\boldsymbol{\tau} + \boldsymbol{\tau}^2 \tag{I.5}$$

we get for eq I.3 the following result:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\nabla^2\psi + 2\boldsymbol{\omega}^{\dagger}(\boldsymbol{\tau}\boldsymbol{\omega}+\nabla\boldsymbol{\omega})\cdot\nabla\psi +$$

$$\boldsymbol{\omega}^{\dagger}(\boldsymbol{\tau}^2\boldsymbol{\omega}+\nabla\boldsymbol{\tau}\boldsymbol{\omega}+2\boldsymbol{\tau}\cdot\nabla\boldsymbol{\omega}+\nabla^2\boldsymbol{\omega})\psi\} \tag{I.6}$$

Next we consider eq 29 and evaluate the following squared expression:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\{\nabla^2\psi + 2\tilde{\boldsymbol{\tau}}\cdot\nabla\psi + (\nabla\tilde{\boldsymbol{\tau}}+\tilde{\boldsymbol{\tau}}^2)\psi\} \tag{I.7}$$

Recalling eq 30, it is noticed that the two first terms on the rhs in eqs I.6 and I.7 are identical, and in order to complete the proof for the derivation of eq 28, we still have to prove the following identity:

$$\nabla\tilde{\boldsymbol{\tau}} + \tilde{\boldsymbol{\tau}}^2 = \boldsymbol{\omega}^{\dagger}(\boldsymbol{\tau}^2\boldsymbol{\omega}+\nabla\boldsymbol{\tau}\boldsymbol{\omega}+2\boldsymbol{\tau}\cdot\nabla\boldsymbol{\omega}+\nabla^2\boldsymbol{\omega}) \tag{I.8}$$

For this purpose we *assume* that indeed $\tilde{\boldsymbol{\tau}}$ is correctly presented in eq 30 and, accordingly, we evaluate the lhs of eq I.8 in terms of $\tilde{\boldsymbol{\tau}}$ to verify this assumption:

$$\nabla\tilde{\boldsymbol{\tau}} + \tilde{\boldsymbol{\tau}}^2 = \nabla(\boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\boldsymbol{\omega}+\boldsymbol{\omega}^{\dagger}\nabla\boldsymbol{\omega}) +$$

$$(\boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\boldsymbol{\omega}+\boldsymbol{\omega}^{\dagger}\nabla\boldsymbol{\omega})(\boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\boldsymbol{\omega}+\boldsymbol{\omega}^{\dagger}\nabla\boldsymbol{\omega}) \tag{I.9}$$

It is seen that the main obstacle for the expressions of the rhs of eqs I.8 and I.9 to become equal is the fact that in eq I.9 we encounter terms that contain $\nabla\boldsymbol{\omega}^{\dagger}$ which is missing on the rhs of eq I.8. To overcome this difficulty we activate the grad operator on eq 27:

$$\nabla(\boldsymbol{\omega}^{\dagger}\boldsymbol{\omega}) = (\nabla\boldsymbol{\omega}^{\dagger})\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\nabla\boldsymbol{\omega} = 0 \tag{I.10}$$

which allows one to express $\nabla\boldsymbol{\omega}^{\dagger}$ as follows:

$$\nabla\boldsymbol{\omega}^{\dagger} = -\boldsymbol{\omega}^{\dagger}(\nabla\boldsymbol{\omega})\boldsymbol{\omega}^{\dagger} \tag{I.11}$$

Evaluating the first term on the rhs in eq I.9 and substituting eq I.11 in the relevant expressions, finally, yields the verification for eq 30.

It is important to emphasize that this derivation is valid immaterial if $\boldsymbol{\omega}$ is a square or a rectangular matrix.

Appendix II. On the Analyticity of the Ã Matrix in Configuration Time−Space

In the present appendix we intend to derive the matrix **B** (introduced in eqs 33 and 34) that will yield an analytic **Ã** matrix in the time−space configuration which (besides being differentiable with respect to all coordinates) has to satisfy the following condition (see eq 36):

$$i\hbar\frac{\partial}{\partial t}(\nabla\tilde{\mathbf{A}}) - \nabla\left(i\hbar\frac{\partial}{\partial t}\tilde{\mathbf{A}}\right) = \mathbf{0} \tag{II.1}$$

From eq 35, we can see that **Ã** has to fulfill two first-order differential equations:

$$\nabla\tilde{\mathbf{A}} + \tilde{\boldsymbol{\tau}}\tilde{\mathbf{A}} = \mathbf{0}$$

$$i\hbar\frac{\partial\tilde{\mathbf{A}}}{\partial t} + \mathbf{B}\tilde{\mathbf{A}} = \mathbf{0} \tag{II.2}$$

Activating the grad operator on the second equation in eq II.2, differentiating the first with respect to t (and multiplying it by $(i\hbar)$), subtracting the second from the first, and assuming eq I.1, we obtain the following expression that has to be fulfilled:

$$i\hbar\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t}\tilde{\mathbf{A}} + \tilde{\boldsymbol{\tau}}i\hbar\frac{\partial\tilde{\mathbf{A}}}{\partial t} - (\nabla\mathbf{B})\tilde{\mathbf{A}} - \mathbf{B}\nabla\tilde{\mathbf{A}} = \mathbf{0} \tag{II.3}$$

Substituting eq II.2 for the relevant terms in eq II.3 yields

$$\left(i\hbar\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t} - \tilde{\boldsymbol{\tau}}\mathbf{B} - \nabla\mathbf{B} + \mathbf{B}\tilde{\boldsymbol{\tau}}\right)\tilde{\mathbf{A}} = \mathbf{0}$$

or since **A** can be shown to be regular (in fact, even, unitary) we also have

$$i\hbar\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t} - \tilde{\boldsymbol{\tau}}\mathbf{B} - \nabla\mathbf{B} + \mathbf{B}\tilde{\boldsymbol{\tau}} = \mathbf{0} \tag{II.4}$$

Recalling eq 30, we evaluate the first term in eq II.4, namely

$$\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t} = \frac{\partial\boldsymbol{\omega}^{\dagger}}{\partial t}\boldsymbol{\tau}\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\frac{\partial\boldsymbol{\omega}}{\partial t} + \frac{\partial\boldsymbol{\omega}^{\dagger}}{\partial t}\nabla\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\nabla\left(\frac{\partial\boldsymbol{\omega}}{\partial t}\right) \tag{II.5}$$

where we remember that by definition the $\boldsymbol{\tau}$ matrix is TID. To continue, we recall eq 24 and replace, accordingly, the various time derivatives so that we get:

$$i\hbar\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t} = -\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\tau}\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\tilde{\mathbf{H}}_e\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}(\nabla\tilde{\mathbf{H}}_e)\boldsymbol{\omega} \tag{II.5'}$$

The next step is to evaluate $\nabla(\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\omega})$ while incorporating the fact that

$$\nabla\boldsymbol{\omega}^{\dagger} = -\boldsymbol{\omega}^{\dagger}(\nabla\boldsymbol{\omega})\boldsymbol{\omega}^{\dagger} \tag{II.6}$$

As a result one obtains:

$$\nabla(\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\omega}) = -\boldsymbol{\omega}^{\dagger}(\nabla\boldsymbol{\omega})\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}(\nabla\tilde{\mathbf{H}}_e)\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\nabla\boldsymbol{\omega}$$

This expression is used to replace, in eq II.5′, the term $\boldsymbol{\omega}^{\dagger}(\nabla\tilde{\mathbf{H}}_e)\boldsymbol{\omega}$. Therefore, eq II.5′ becomes

$$i\hbar\frac{\partial\tilde{\boldsymbol{\tau}}}{\partial t} = -\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\tau}\boldsymbol{\omega} + \boldsymbol{\omega}^{\dagger}\boldsymbol{\tau}\tilde{\mathbf{H}}_e\boldsymbol{\omega} + \nabla\tilde{\mathbf{H}}_e + \boldsymbol{\omega}^{\dagger}(\nabla\boldsymbol{\omega})\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\boldsymbol{\omega} -$$

$$\boldsymbol{\omega}^{\dagger}\tilde{\mathbf{H}}_e\nabla\boldsymbol{\omega} \tag{II.7}$$

To continue, we first introduce a new definition, i.e., $\tilde{\tilde{\mathbf{H}}}_e$:

$$\tilde{\tilde{\mathbf{H}}}_e = \boldsymbol{\omega}^\dagger \tilde{\mathbf{H}}_e \boldsymbol{\omega} \tag{II.8}$$

and secondly, we substitute eqs II.7 and II.8 into eq II.4 so that following a few algebraic manipulations we get

$$-\tilde{\tilde{\mathbf{H}}}_e \tilde{\boldsymbol{\tau}} + \tilde{\boldsymbol{\tau}}\tilde{\tilde{\mathbf{H}}}_e + \nabla\tilde{\tilde{\mathbf{H}}}_e - \tilde{\boldsymbol{\tau}}\mathbf{B} - \nabla\mathbf{B} + \mathbf{B}\tilde{\boldsymbol{\tau}} = 0 \tag{II.9}$$

It is well noticed that this expression becomes identically zero assuming $\mathbf{B} \equiv \tilde{\tilde{\mathbf{H}}}$.

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