Space-Time Contours to Treat the Interaction between an Intense Electric Field and a Molecular System

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A few years ago, we developed an approach to treat molecular systems exposed to an external, intense, time-dependent field (*J. Phys. Chem. A* **2003**, *107*, 4724; *J. Chem. Phys*. **2003**, *119*, 6998). Within this study, we encountered two novel concepts: the dressed (namely, *field* affected) time-dependent nonadiabatic coupling term and the space-time contours. In the present article, we analyze the newly introduced nonadiabatic coupling term and discuss its importance for dynamical studies. We also refer to the just mentioned space-time contour and present the *more* efficient contour for realistic situations. The scope of the above-mentioned articles is extended with the aim of defining quasi-adiabatic states for such situations. Strictly speaking, molecular systems exposed to *intense*, fast oscillating fields are not expected to form *adiabatic* states. Still we consider such a situation and end up with three possibilities for quasi-adiabatical time-dependent states eventually to be used within the Born–Oppenheimer approximation.

I. Introduction

The treatment of molecular systems exposed to electromagnetic fields (e.g., laser fields) has become along the years one of the main subjects in theoretical chemistry. This subject has its origin in studies during the 1970s and the 1980s which centered on time-independent treatments[1-4] but then were extended to the time domain.[5-12] To treat such a time-dependent Schrödinger equation (SE), one follows the usual same pattern, namely, first solving the electronic time-independent (TID) eigenvalue problem to derive the TID adiabatic eigenvalues and in particular the TID eigenfunctions which are then employed to form the time-dependent (TD) coupling matrix that is added to the adiabatic Hamiltonian. This procedure, for a system that contains conical intersections (ci), is described elsewhere.[13]

Several years ago, we presented the theory to treat the TD Born–Oppenheimer (BO) molecular system exposed to *intense* external TD fields.[13-15] We use the word *intense* to distinguish it from a weak field, which is considered as a perturbation, and treated as is briefly described in the previous paragraph.[13] In the present article, we intend to discuss a few issues that are closely connected with this preliminary study: (a) While treating the TD electron–nuclear Hamiltonian, we became acquainted with a novel magnitude, that is, the *dressed* (namely, *field* affected) TD nonadiabatic coupling term (NACT); this magnitude is analyzed in the present publication. (b) In this and other publications,[13-15] we introduced a novel contour—a *space-time* contour—to form the TD adiabatic-to-diabatic transformation (ADT) matrix **A**. In the present article, the discussion on this issue is extended to end up with an *efficient* network of *space-time* contours to be applied in realistic situations. (c) In previous publications, we referred to external fields in general; in the present one, we discuss explicitly the electric field (recalling that we consider an intense electric field). (d) Recently, Balint-Kurti et al.[12] developed a time-dependent BO *approximation* which is somewhat related to our formalism. To achieve that

purpose, they solve an ordinary electronic eigenvalue problem while considering time as a parameter (similar to the BO assumption concerning the nuclear coordinates).[16-21] In a subsequent step, while forming the time derivative, $i\hbar \partial \Psi / \partial t$, the time parameter becomes again a variable. Part of the present article is devoted to a similar issue, and we end up with three definitions for quasi-adiabatical time-dependent states (where the lowest one can be used within the BO approximation) which are in the spirit of our general framework.[13]

II. Diabatic Potential Matrix for Intense Electric Fields

In a previous publication,[13] we presented a recipe for rigorously deriving the diabatic SE in the case of an *intense* external field. We also made the distinction between a treatment of a *weak* external field and a treatment of an *intense* external field. The main difference between the two situations is that in the case of a weak field the perturbation can be presented in terms of a small number of basis functions whereas in the second case the perturbation requires a large basis set. Thus, if L is the number of basis functions required to present the perturbation and if N is the actual number of states required to solve the nuclear SEs, then within the perturbation approach it is usually assumed that $L = N$; in other words, there is no distinction between the two numbers. However, in the case of an *intense* field (thus, a large perturbation), for which a large number, L, of basis sets is required, assuming $L = N$ enforces also treating a large number of SEs. In the above-mentioned publications, we managed to separate between the two issues, namely, to distinguish between L and N: we left L to be as large as required for presenting the field, whereas N is determined, independently, until a converged solution is attained. In general, we expect $L \gg N$.

In the present article, we concentrate again on the effect of intense fields on molecular systems, where now the aim is 2-fold: (1) to analyze some of the expressions derived in the previous publications and (2) to present practical ideas for future applications.

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II.1. Dressed TD Nonadiabatic Coupling Term. The distinction between L and N enforces a different treatment of the TD electron−nuclear interaction in molecular systems than the usual. The details of this study are given in ref 13, but for convenience of the reader, we listed the relevant findings (without proofs) in Appendix A. The main difference is in the way the electronic part is treated within the BO framework. Thus, instead of deriving the electronic basis set by solving a TID eigenvalue problem, the TD eigenfunctions are obtained by solving a TD equation for the electronic basis set

$$i\hbar \frac{\partial \zeta(\mathbf{s}_e|\mathbf{s},t)}{\partial t} = \mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)\zeta(\mathbf{s}_e|\mathbf{s},t) \quad (1)$$

where $\zeta_j(\mathbf{s}_e|\mathbf{s},t)$; $j = 1,N$ are the required electronic basis functions ($\mathbf{s}_e$ and $\mathbf{s}$ are the corresponding electronic and nuclear coordinates) and $\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)$ is the electronic TD Hamiltonian. Having the TD electronic basis functions, we are in the position to form the relevant *dressed* TD nonadiabatic coupling matrix (NACM), $\tilde{\tau}$, which can be shown to be of the form

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

Here, τ is the original (TID) $L \times L$ NACM with its elements defined as

$$\tau_{jk}(\mathbf{s}) = \langle \zeta_j(\mathbf{s}_e|\mathbf{s},t{=}0)|\nabla\zeta_k(\mathbf{s}_e|\mathbf{s},t{=}0)\rangle; \quad j = \{1,L\}; k = \{1,L\} \quad (3)$$

where the functions $\zeta_i(\mathbf{s}_e|\mathbf{s},t{=}0)$ ($\equiv \zeta_i(\mathbf{s}_e|\mathbf{s})$); $i = j,k$ are the ordinary (TID) eigenfunctions (see eq A.2) and $\omega(\mathbf{s}|t)$ is a $L \times N$ *rectangular* matrix related to the potential matrix $\tilde{\mathbf{H}}_e$ as

$$\omega(\mathbf{s}|t) = \mathscr{P}\exp\left(-\frac{i}{\hbar}\int_0^t \tilde{\mathbf{H}}_e(\mathbf{s}|t')dt'\right)\mathbf{I}_L^N \quad (4)$$

where $\tilde{\mathbf{H}}_e(\mathbf{s}|t)$ is the *square* TD matrix of dimensions $L \times L$

$$\tilde{\mathbf{H}}_{jk}(\mathbf{s},t) = \langle \zeta_j(\mathbf{s}_e|\mathbf{s},t{=}0)|\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)|\zeta_k(\mathbf{s}_e|\mathbf{s},t{=}0)\rangle \quad (5)$$

$\mathbf{I}_L^N$ is a rectangular unit matrix of L rows and N columns ($\mathbf{I}_L^N$ guarantees the corresponding *rectangular* structure of $\omega(\mathbf{s}|t)$) and $\mathscr{P}$ is a path ordering operator. It is important to realize that the external field is turned on at $t = 0$ which implies that for any time $t \leq 0$ the system is not exposed to an external field.

It is important to realize that, although τ is of dimensions $L \times L$, the (*dressed*) $\tilde{\tau}$ is of dimensions $N \times N$, namely, of a smaller dimension than τ.

The matrix $\tilde{\tau}$ is one of the more characteristic magnitudes that emerge from this TD treatment. Although it may vary under a gauge transformation (just like the TID NACM, τ[22]), it is of major importance because this dressed NACM not only is responsible for forming the TD ADT matrix (the ADT matrix is a solution of eq A.8) but also fulfills the *four-dimensional* space-time Curl equation.[13]

One of the more important features that characterizes the (TID) NACTs, τ_{jk}, is the fact that at points of degeneracy some of them become *singular*.[22] There exists a belief that intense external fields (either electric or magnetic) are capable of affecting the positions of these *singularities*. In fact, the structure of the dressed NACM as given in eq 2 shows that this possibility does not exist.

As a final issue in this section, we analyze the second term, $\omega^\dagger \nabla \omega$, in eq 2. Thus, if ω is written in the form

$$\omega(\mathbf{s}|t) = \exp\left(-\frac{i}{\hbar}\mathbf{Z}\right)\mathbf{I}_L^N \Rightarrow \omega^\dagger(\mathbf{s}|t) = \mathbf{I}_N^L \exp\left(\frac{i}{\hbar}\mathbf{Z}\right) \quad (6)$$

(see eq 4 for the definition of the matrix $\mathbf{Z}(\mathbf{s},t)$), then to evaluate $\omega^\dagger \nabla \omega$ we have to present ω (and $\omega^\dagger$) in terms of its eigenvalues and eigenvectors

$$\omega(\mathbf{s}|t) = \mathbf{G} \exp\left(-\frac{i}{\hbar}\mathbf{R}\right)\mathbf{G}^\dagger\mathbf{I}_L^N \Rightarrow \omega^\dagger(\mathbf{s}|t) = \mathbf{I}_N^L\mathbf{G} \exp\left(\frac{i}{\hbar}\mathbf{R}\right)\mathbf{G}^\dagger \quad (7)$$

where $\mathbf{G}(\mathbf{s},t)$ is a square matrix of dimensions $L \times L$ which diagonalizes $\mathbf{Z}$ and $\mathbf{R}(\mathbf{s},t)$ is a diagonal matrix which contains the (L) eigenvalues of $\mathbf{Z}$. Next, we derive the matrix, $\nabla\omega$

$$\nabla\omega(\mathbf{s}|t) = \left[\nabla\mathbf{G} \exp\left(-\frac{i}{\hbar}\mathbf{R}\right)\mathbf{G}^\dagger - \frac{i}{\hbar}\mathbf{G}\nabla\mathbf{R} \exp\left(-\frac{i}{\hbar}\mathbf{R}\right)\mathbf{G}^\dagger + \mathbf{G}\exp\left(-\frac{i}{\hbar}\mathbf{R}\right)\nabla\mathbf{G}^\dagger\right]\mathbf{I}_L^N \quad (8)$$

which, when multiplied, from the right-hand side by $\omega^\dagger$ (see eq 7), forms the desired result.

II.2. Adiabatic-to-Diabatic Transformation Matrix and the Efficient Networks of Space-Time Contours. The diabatic potential matrix $\mathbf{W}(\mathbf{s},t)$ is written in the form[13]

$$\mathbf{W}(\mathbf{s},t) = \mathbf{A}^\dagger(\mathbf{s},t)\tilde{\mathbf{H}}_e(\mathbf{s},t)\mathbf{A}(\mathbf{s},t) \quad (9)$$

Here, two matrices are encountered, that is, the TD potential matrix, $\tilde{\mathbf{H}}_e$, and the corresponding ADT matrix, $\mathbf{A}$. As for $\tilde{\mathbf{H}}_e$, it was derived in ref 13 and is presented again, for the sake of convenience, in eq A.7. In what follows, our main interest is in the ADT matrix.

At this stage, two comments are to be made based on TID studies: (1) In general, $\mathbf{W}$ is calculated along the contours, but this happens only because $\mathbf{A}$ is derived by solving line integrals along the *contours*[21,23,24,28] (as for $\tilde{\mathbf{H}}_e$, it is derived just like the adiabatic potential $\mathbf{u}$, point-wise at every required grid point). (2) It is important to emphasize that in case the N states form, in the considered region, a Hilbert *subspace* $\mathbf{W}$ *does not* depend on the chosen contour Γ along which $\mathbf{A}$ is calculated.[25−27] To illustrate this, we refer the reader to Figure 1: The two contours shown in Figure 1 (and for this sake any other contour) are expected to yield the same value for the diabatic potential matrix at the crossing point of the two contours (i.e., the point $(\tilde{\bar{\mathbf{s}}},\tilde{t})$).

The ADT matrix is usually calculated along *spatial* contours. In ref 13, it was shown that within the TD framework (characterized by intense fields) this matrix has to be calculated along *space-time* contours. Although these contours are discussed in ref 13 (see also eqs A.11 and A.12), here, we extend this discussion with the purpose of gaining more insight.

Since for a Hilbert subspace the calculation of $\mathbf{W}(\mathbf{s},t)$ does not depend on any specific set of contours, we are free to choose the more convenient ones for this purpose. In the forthcoming paragraphs, we propose such contours.

To discuss this issue in a comprehensive way, we break it up into two parts. In the first part, we present the preferred contour that leads from an initial point $(\mathbf{s}_0,t_0)$ to some other point $(\mathbf{s},t)$, and in the second, we discuss specific contours that lead from an initial point $(\mathbf{s}_0,t_0)$ to a grid of points $(\mathbf{s}_j,t_k)$ (see Figure 2). To simplify the discussion, we assume the initial point to be $(\mathbf{s}_0,t_0) \equiv (\mathbf{0},0)$ and recall that $\mathbf{s}_0$ just like $\mathbf{s}$ is a point in configurational space.

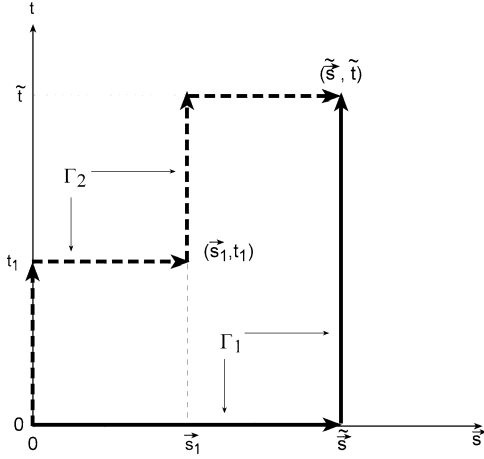The contour Γ we suggest is made up of two segments, one segment, $\Gamma_\mathbf{s}$, is defined as

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Figure 1. Space-time system of coordinates. Shown are two different space-time contours Γ_1 and Γ_2 connecting $(\mathbf{s}=\mathbf{0},t=0)$ with $(\mathbf{s}=\tilde{\mathbf{s}},t=\tilde{t})$.

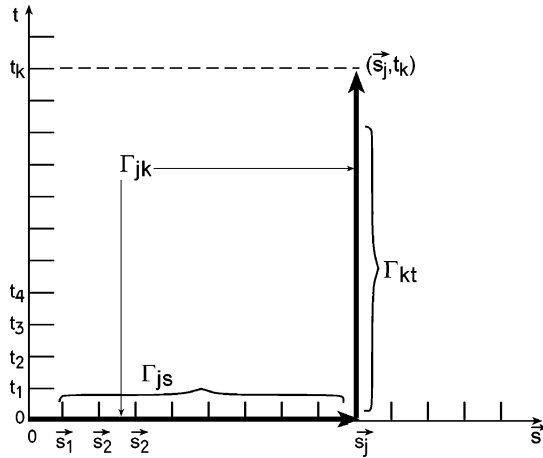**Figure 2.** Space-time system of coordinates. Shown is the contour $\Gamma_{jk} = \Gamma_{js} + \Gamma_{kt}$ connecting $(\mathbf{s}=\mathbf{0},t=0)$ with $(\mathbf{s}=\tilde{\mathbf{s}}_j,t=t_k)$.

$$\Gamma_s: \quad (\mathbf{0},0) \rightarrow (\mathbf{s},0) \qquad (10a)$$

and it is noticed that this contour is essentially a spatial contour (calculated for time $t =$ constant).

To calculate $\mathbf{A}$ along the spatial segment, we employ eq A.8a, and solving it the usual way (just like within the TID framework[21,23,24]) yields

$$\mathbf{A}\left(\mathbf{s},t=0\middle|\Gamma_s\right) = \mathscr{P}\exp\left\{-\int_{\mathbf{0}}^{\mathbf{s}} \boldsymbol{\tau}(\mathbf{s}',t=0|\Gamma_s)\cdot d\mathbf{s}'\right\}\mathbf{A}\left(\mathbf{s}=\mathbf{0},t=0\right) \quad (11a)$$

(in writing eq 11a, we assumed that $\mathbf{z} \equiv \mathbf{s}$.)

The second segment, Γ_t, is defined as

$$\Gamma_t: \quad (\mathbf{s},0) \rightarrow (\mathbf{s},t) \qquad (10b)$$

and to calculate $\mathbf{A}$ along this segment, we employ eq A.8b and solve it for the case that $z \equiv t$ where $\mathbf{s}$ is held constant

$$\mathbf{A}(\mathbf{s},t|\Gamma_t) = \mathscr{P}\exp\left\{\frac{i}{\hbar}\int_{\mathbf{0}}^{t} \tilde{\boldsymbol{\tau}}_e(\mathbf{s},t'|\Gamma_t)dt'\right\}\mathbf{A}(\mathbf{s},t=0) \quad (11b)$$

It is easy to see that $\Gamma = \Gamma_s + \Gamma_t$ (the contour Γ_1, in Figure 1, is such a contour), and consequently, we obtain for $\mathbf{A}(\mathbf{s},t)$ (by substitution of eq 11a into eq 11b) the following expression

$$\mathbf{A}(\mathbf{s},t|\Gamma) = \mathscr{P}\left[\exp\left\{\frac{i}{\hbar}\int_{\mathbf{0}}^{t} \tilde{\mathbf{H}}_e(\mathbf{s},t'|\Gamma_t)dt'\right\} \times\right.$$

$$\left.\exp\left\{-\int_{\mathbf{0}}^{\mathbf{s}} \boldsymbol{\tau}(\mathbf{s}',t=0|\Gamma_s)\cdot d\mathbf{s}'\right\}\right] \quad (12)$$

It is important to realize that at $t = 0$ (namely, just slightly before the field is turned on) the time-dependent dressed NACM, $\tilde{\tau}$, is identical to the ordinary undressed NACM, $\boldsymbol{\tau}$ (see eqs 2 and 3). Thus, the *spatial* phase factor (on the right-hand side) is identical to the one encountered within the TID framework[21,23,24] for contours given in eq 10a. It is only the time phase factor (on the left-hand side) that introduces explicitly the time (formed along the time segment of the contour in eq 10b). The calculations to derive this phase factor are simple not only because the corresponding integration is performed for a scalar (instead for a vector) but also because the elements of $\tilde{\mathbf{H}}_e$ are *analytic* functions of t and $\mathbf{s}$ (in other words, $\tilde{\mathbf{H}}_e$ is not expected to be affected by singularities).

Next, we limit ourselves to a specific space-time grid $(\mathbf{s}_j,t_k)$, where $j = \{0,n_s\}$ and $k = \{0,n_t\}$. On the basis of eq 12, $\mathbf{A}$, at such a grid point, is given by following the expression

$$\mathbf{A}(\mathbf{s}_j,t_k|\Gamma_{jk}) = \left[\mathscr{P}\prod_{l=0}^{k} \exp\left\{\frac{i}{\hbar}\int_{t_{l-1}}^{t_l} \tilde{\mathbf{H}}_e(\mathbf{s}_j,t'|\Gamma_{kt})\cdot dt'\right\}\right]$$

$$\left[\mathscr{P}\prod_{l=0}^{j} \exp\left\{-\int_{\mathbf{s}_{l-1}}^{\mathbf{s}_l} \boldsymbol{\tau}(\mathbf{s}',t=0|\Gamma_{js})\cdot d\mathbf{s}'\right\}\right] \quad (13)$$

As for the meaning of the three contours Γ_{jk}, Γ_{kt}, and Γ_{js}, see Figure 2. We remind the reader that all matrices, in particular $\tilde{\mathbf{H}}_e$ (see eq A.7), are N-dimensional square matrices.

II.3. Topological D(Γ) within the Space-Time Framework. We just briefly refer to the topological matrix because it will become a major issue in our next article that will present numerical results as derived for a realistic model (formed by the Mathieu equation[29]). The main reason for our interest in the topological matrix (see eq A.13) is because it "*measures*" the ability of a group of N states to yield a *single-valued* diabatic potential matrix. It is proven elsewhere that, for the diabatic potential matrix $\mathbf{W}(\mathbf{s})$ to become single-valued, the $\mathbf{D}$ matrix has to be diagonal for *any* closed contour in that region.[23−28] The new aspect that we encounter here is that it is not enough that $\mathbf{D}$ is diagonal along *any spatial* contour in the region but has to be diagonal for *any space-time* contour.

From eq 12, it is quite obvious that any group of states that yields a single-valued diabatic potential matrix in a space-time region has to form a single-valued diabatic potential matrix in configurational space. Thus

$$\mathbf{D}(\Gamma_s) = \mathscr{P}\exp\left\{-\oint_{\Gamma_s} \boldsymbol{\tau}(\mathbf{s}',t=0|\Gamma_s)\cdot d\mathbf{s}'\right\} \qquad (13')$$

This condition is not necessarily sufficient for the group of states to yield the single-valued diabatic potential in the space-time region because there exists the possibility that other space-time contours may form $\mathbf{D}$ matrices which are not diagonal (the $\mathbf{D}$ matrix in eq 13′ is just calculated for one particular contour). In the forthcoming numerical study, this issue will be studied in detail.

III. Intense (External) Electric Fields

III.1. General Nuclear Schrödinger Equation. In Appendix B, we derived the SE for a molecular system exposed to an

intense electric field (see eq B.28). At this stage, we just mention that the derivation was done for an intense *electromagnetic* field, but in the forthcoming application, we assume that the *magnetic* component is weak enough so that it can be ignored. As for the *electric* field, we assume it to be homogeneous so that $\mathbf{E} = \mathbf{E}(t)$. Consequently, eq B.28 takes the somewhat simplified form

$$i\hbar \frac{\partial \Psi(\mathbf{s}_e,\mathbf{s}|t)}{\partial t} = \left(-\sum_\gamma \frac{\hbar^2}{2m_\gamma} \nabla_\gamma^2 - \sum_\gamma (\mathbf{E}_\gamma(t)\cdot\mathbf{M}_\gamma(\mathbf{s}_e|\mathbf{s})) + V(\mathbf{s}_e|\mathbf{s})\right)\Psi(\mathbf{s}_e,\mathbf{s}|t) \quad (14)$$

or

$$i\hbar \frac{\partial \Psi(\mathbf{s}_e,\mathbf{s}|t)}{\partial t} = \left(-\frac{\hbar^2}{2m_n}\nabla^2 + \mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)\right)\Psi(\mathbf{s}_e,\mathbf{s}|t) \quad (15)$$

The first term on the right-hand side of eq 15 is the nuclear kinetic energy expressed in terms of mass-dependent coordinates (m_n is the reduced mass of the nuclear system), and the second term, $\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)$, is the electronic Hamiltonian given in the form

$$\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t) = -\frac{\hbar^2}{2m}\sum_\alpha \nabla_\alpha^2 - \sum_\alpha (\mathbf{E}_\alpha(t)\cdot\mathbf{M}_\alpha(\mathbf{s}_e|\mathbf{s})) + V(\mathbf{s}_e|\mathbf{s}) \quad (16)$$

where $V(\mathbf{s}_e|\mathbf{s})$ is the sum of Coulombic potentials that govern the motion of the nuclei and the electrons. For simplicity, we ignore the direct effect of the field on the nuclei. Having $\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)$, we are in the position to form $\tilde{\mathbf{H}}_e(\mathbf{s},t)$ (see eq 5)

$$\tilde{\mathbf{H}}_e(\mathbf{s},t) = \mathbf{u}(\mathbf{s}) + \mathbf{E}(t)\cdot\mathbf{M}(\mathbf{s}) \quad (17)$$

and the corresponding explicit expression for $\boldsymbol{\omega}(\mathbf{s},t)$ (see eq 6)

$$\boldsymbol{\omega}(\mathbf{s},t) = \mathscr{P}\exp\left[-\frac{i}{\hbar}\left(\mathbf{u}(\mathbf{s})t + \mathbf{M}(\mathbf{s})\cdot\int_0^t \mathbf{E}(t')dt'\right)\right]\mathbf{I}_L^N \quad (18)$$

Here, $\mathbf{u}(\mathbf{s})$ is an L-dimensional diagonal matrix that contains the (TID) adiabatic potentials, $\mathbf{M}(\mathbf{s})$ is an L-dimensional square matrix which contains the (TID) various dipole moments, $\mathbf{E}(t)$ is the TD external field, and $\mathbf{I}_L^N$ is a *rectangular* unit matrix of L rows and N columns. Substituting eqs 17 and 18 into eq A.7 yields the corresponding potential matrix, $\tilde{\mathbf{H}}_e$ which is then employed to form the diabatic potential matrix, $\mathbf{W}(\mathbf{s},t)$. Having $\mathbf{W}(\mathbf{s},t)$, we are in the position to solve the relevant diabatic SE given in the form

$$i\hbar \frac{\partial\Phi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathbf{W}(\mathbf{s},t)\right)\Phi \quad (19)$$

It is important to remind the reader that $\mathbf{W}(\mathbf{s},t)$ is the $N \times N$ diabatic potential matrix and that $\Phi(\mathbf{s},t)$ is an N-dimensional column vector that contains the (diabatic) *nuclear* wave functions to be solved.

III.2. Born–Oppenheimer Approximation for a Strongly Perturbed Time-Dependent Hamiltonian. One of the more peculiar outcomes of treating the strongly perturbed TD molecular system is the following adiabatic SE for $\psi(\mathbf{s},t)$, the N-dimensional vector that contains the (adiabatic) nuclear components ψ_j: $j = \{1,N\}$,[13-15] namely

$$i\hbar \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}(\nabla + \tilde{\boldsymbol{\tau}})^2\psi \quad (20)$$

where $\tilde{\boldsymbol{\tau}}$ the TD, dressed NACM is given in eq 2. Equation 20 is peculiar in the sense that it is governed only by NACTs but lacks the expected (adiabatic) potentials. In fact, it is not surprising that eq 20 lacks the *adiabatic* potentials because, strictly speaking, a molecular TD system (at least a fast oscillating system) does not have adiabatic potentials or, in other words, these potentials are identically zero.

Still we may be able to produce, at least, quasi-adiabatic TD potentials by diagonalizing the TD Hermitean diabatic potential matrix, $\mathbf{W}(\mathbf{s},t)$, discussed earlier and presented in eq 9. With this idea in mind, we may produce the lowest quasi-adiabatic state which in turn can be used to form the BO approximation.[12,16,18-20,30]

This definition of the lowest eigenvalue is not straightforward because the convergence of the eigenvalues of $\mathbf{W}(\mathbf{s},t)$ depends on two numbers L and N and not on just one of them as is usually the case (the dependence on one number happens when $L = N$). In other words, to attach to the lowest (BO) adiabatic potential of $\mathbf{W}(\mathbf{s},t)$ a physical meaning, we have to understand the meaning of this eigenvalue.

From eq 9, it is noticed that the eigenvalues of $\mathbf{W}(\mathbf{s},t)$ are identical to those of $\tilde{\tilde{\mathbf{H}}}_e$ which is derived elsewhere[13-15] and presented in eq A.7. Thus, our next task is to derive the eigenvalues of $\tilde{\tilde{\mathbf{H}}}_e$. To do that, eq A.7 is presented in a slightly different form

$$\tilde{\tilde{\mathbf{H}}}_e = (\mathbf{B}^\dagger\boldsymbol{\omega})^\dagger(\mathbf{B}^\dagger\tilde{\mathbf{H}}_e\mathbf{B})(\mathbf{B}^\dagger\boldsymbol{\omega}) = \Omega^\dagger(\mathbf{B}^\dagger\tilde{\mathbf{H}}_e\mathbf{B})\Omega \quad (21)$$

where $\mathbf{B} = \mathbf{B}(\mathbf{s},t)$ is an L-dimensional orthogonal matrix which diagonalizes $\tilde{\mathbf{H}}_e$ (see eq 5) and $\Omega(\mathbf{s},t)$ (= $\mathbf{B}^\dagger\boldsymbol{\omega}$), just like $\boldsymbol{\omega}(\mathbf{s},t)$, is a rectangular $L \times N$ matrix. Defining $\mathbf{V}(\mathbf{s},t)$ as the diagonal matrix that contains the eigenvalues of $\tilde{\mathbf{H}}_e$, we obtain

$$\mathbf{V} = \mathbf{B}^\dagger\tilde{\mathbf{H}}_e\mathbf{B} \quad (22)$$

The convergence of $\mathbf{V}(\mathbf{s},t)$ to the desired level is achieved by increasing L. Before analyzing the eigenvalues of $\tilde{\tilde{\mathbf{H}}}_e$, we refer briefly to $\mathbf{V}(\mathbf{s},t)$. It is noticed that in the case where $\boldsymbol{\omega}$ is a square matrix (i.e., when $L = N$) $\boldsymbol{\omega}$ becomes an orthogonal matrix. In such a case, Ω becomes orthogonal as well and therefore the eigenvalues of $\tilde{\mathbf{H}}_e$, $\tilde{\tilde{\mathbf{H}}}_e$, and $\mathbf{W}$ are all the same and are contained along the diagonal of $\mathbf{V}$ (such a situation we encountered while studying the *weak field* case (see eq 18 in ref 13). We also mention that these quasi-adiabatic potentials are identical to those discussed in ref 12. Returning to the BO approximation, we find that the BO state (in the case that $L = N$) is the lowest diagonal element of $\mathbf{V}(\mathbf{s},t)$ and therefore is well defined.

The situation becomes more complicated in case of the *intense* field. Here, our approach allows L to differ from N, and in this situation, $\boldsymbol{\omega}$ is rectangular and the same applies to Ω so that the eigenvalues of $\tilde{\tilde{\mathbf{H}}}_e$ differ from those of $\tilde{\mathbf{H}}_e$ and therefore also from $\mathbf{V}$. Consequently, the adiabatic (lowest) state to be employed within the BO approximation is not uniquely defined anymore. This situation opens up two additional possibilities:

(1) Assuming $N = 1$, we get that $\tilde{\tilde{\mathbf{H}}}_e$ is a 1×1 matrix and this single matrix element takes the form

$$(\tilde{\tilde{\mathbf{H}}}_e)_{11} = \sum_{k=1}^L \Omega^\dagger_{1k}\mathbf{V}_{kk}\Omega_{k1} \quad (23)$$

(2) Assuming $N \neq 1$, we recall that $\tilde{\tilde{\mathbf{H}}}_e$ is a square Hermitian matrix which can be diagonalized. Thus, we may employ the lowest eigenvalue of this matrix for the BO approximation.

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IV. Discussion and Conclusions

The TD (nonperturbative) approach to study molecular systems exposed to external, *intense* TD fields was presented sometime ago.[13] In the present article, this study is extended to cover the following issues:

(a) We elaborated on the novel *dressed* TD NACM: We not only emphasized its importance for dynamic studies but also analyzed the meaning of the algebraic expression.

(b) We discussed in some detail how to choose efficiently the network of space-time contours to obtain the corresponding ADT matrix (see eq 13) which is then employed to calculate the TD diabatic potential matrix $\mathbf{W}(\mathbf{s},t)$ (see eq 9).

(c) Next, we referred to the possibility of forming the lowest quasi-adiabatic potential with the aim of applying it within the BO approximation to treat molecular systems exposed to intense electromagnetic fields.

(d) As a side issue (see Appendix B), we studied the connection between a molecular Hamiltonian expressed in terms of an external *vector potential* and the one expressed in terms of corresponding external *electric* and *magnetic* field components. This derivation is performed with the aim of revealing the conditions for which this connection can be formed in the case of *intense* electromagnetic fields.

Our main outcome is that whereas the adiabatic states in general and the lowest BO state in particular are uniquely defined within the TID framework, the situation within the TD framework is more complicated. Strictly speaking, adiabatic states in general and the lowest (BO) one in particular do not exist for a system exposed to an (external) TD field (e.g., a laser field). In this article, we study this situation in detail and end up with three definitions of TD quasi-adiabatical states. It still remains to be seen if indeed these states, in numerical applications, can be considered as being (quasi-) adiabatic states and then, if so, which of the definitions applies best in realistic cases.

Before the conclusion, we would like to make two comments:

(1) To solve eq 1, we use the relevant TID BO basis set with time-dependent coefficients. It is very likely that in such a procedure we may have to include continuous, namely, non-discrete eigenfunctions extracted from the continuum. Although it seems as if such eigenfunctions may cause numerical difficulties, these are very likely to be overcome by employing negative imaginary potential (NIPs) to form absorbing boundary conditions.[30−32]

(2) Next, we refer to the fact that in the present study we ignored the wavelength (frequency) of the field. It is true that in an actual numerical treatment this feature of the field has to be incorporated as is done routinely in many theoretical and numerical treatments (see, e.g., refs 1−12 and in particularly ref 4). We decided to ignore this issue, at this stage, mainly to emphasize the new ingredients as given here.

Appendix A. Time-Dependent System: The General Formulation

The diabatic SE is characterized by the diabatic potential matrix $\mathbf{W}(\mathbf{s},t)$ which is written in the form

$$\mathbf{W}(\mathbf{s},t) = \mathbf{A}^\dagger(\mathbf{s},t)\tilde{\mathbf{H}}_e(\mathbf{s},t)\mathbf{A}(\mathbf{s},t) \tag{A.1}$$

Here two matrices are encountered, that is, the (extended) potential matrix, $\tilde{\mathbf{H}}_e$, and the corresponding ADT matrix, $\mathbf{A}$. In what follows, both are briefly discussed and we start with $\tilde{\mathbf{H}}_e$.

To relate to a realistic case, we assume that the external field is turned on at $t = 0$ which implies that for $t \leq 0$ the system is unperturbed and therefore described in terms of the electronic Hamiltonian $\mathbf{H}_e(\mathbf{s}_e|\mathbf{s})$ ($\equiv \mathbf{H}_e(t=0)$) which is TID. Consequently, for $t \leq 0$, the eigenfunctions, $\zeta_j(\mathbf{s}_e|\mathbf{s})$; $j = \{1,L\}$ of $\mathbf{H}_e(t=0)$), are also TID. Thus

$$(\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t=0) - u_j(\mathbf{s}))|\zeta_j(\mathbf{s}_e|\mathbf{s},t=0)\rangle = 0; \, j = 1,...,L \tag{A.2}$$

where $u_j(\mathbf{s})$; $j = \{1,L\}$ are TID adiabatic potentials.

At $t \geq 0$, the electronic molecular system becomes TD, and consequently, the corresponding basis set $\zeta_j(\mathbf{s}_e|\mathbf{s},t)$; $j = \{1,N\}$ becomes, as well, TD because it is a solution of the following eigenvalue problem

$$i\hbar \frac{\partial \zeta(\mathbf{s}_e|\mathbf{s},t)}{\partial t} = \mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)\zeta(\mathbf{s}_e|\mathbf{s},t) \tag{A.3}$$

The TD eigenfunctions can be presented in terms of the previous, TID eigenfunctions

$$|\zeta(\mathbf{s}_e|\mathbf{s},t)\rangle = \boldsymbol{\omega}(\mathbf{s}|t)|\zeta(\mathbf{s}_e|\mathbf{s},t=0)\rangle \tag{A.4}$$

where the $\boldsymbol{\omega}(\mathbf{s}|t)$ matrix contains the TD expansion coefficients:

As discussed in the last paragraph in the Introduction, we expect $L \neq N$ and, consequently, $\boldsymbol{\omega}(\mathbf{s}|t)$ becomes a rectangular matrix of dimensions $L \times N$ (it reduces to a rectangular "unit" matrix for $t \leq 0$). It can be shown that $\boldsymbol{\omega}(\mathbf{s}|t)$ is related to the potential matrix $\tilde{\mathbf{H}}_e$ as

$$\boldsymbol{\omega}(\mathbf{s}|t) = \mathscr{P}\exp\left(-\frac{i}{\hbar}\int_0^t \tilde{\mathbf{H}}_e(\mathbf{s}|t')dt'\right)\mathbf{I}_L^N \tag{A.5}$$

where $\mathbf{I}_L^N$ is a rectangular unit matrix of L rows and N columns ($\mathbf{I}_L^N$ guarantees the relevant structure of $\boldsymbol{\omega}(\mathbf{s}|t)$), $\mathscr{P}$ is a path ordering operator, and $\tilde{\mathbf{H}}_e(\mathbf{s}|t)$ is the square matrix of dimensions $L \times L$

$$\tilde{\mathbf{H}}(\mathbf{s},t)_{jk} = \langle \zeta_j(\mathbf{s}_e|\mathbf{s},t=0)|\mathbf{H}_e(\mathbf{s}_e|\mathbf{s},t)|\zeta_k(\mathbf{s}_e|\mathbf{s},t=0)\rangle \tag{A.6}$$

It is noticed that for $t \leq 0$ this matrix reduces to a diagonal matrix that contains the adiabatic potential energy surfaces (see eq A.2).

To continue the derivation of eq A.1, we still need the explicit expression for $\tilde{\mathbf{H}}_e$ which, like all other expressions, can be found in ref 13. Thus

$$\tilde{\tilde{\mathbf{H}}}_e = \boldsymbol{\omega}^\dagger\tilde{\mathbf{H}}_e\boldsymbol{\omega} \tag{A.7}$$

It is noticed that, in contrast to the *rectangular* matrix $\boldsymbol{\omega}$ and in contrast to the L-dimensional square matrix $\tilde{\mathbf{H}}_e$, the matrix $\tilde{\tilde{\mathbf{H}}}_e$ is an N-dimensional square matrix. However, the value of N is still not determined and will be discussed below.

The second issue to be considered is the ADT matrix, $\mathbf{A}$. In ref 13, we showed that $\mathbf{A}$ is a solution of a set of first-order differential equations in a four-dimensional space, namely, within space-time

$$\nabla\mathbf{A} + \tilde{\boldsymbol{\tau}}\mathbf{A} = \mathbf{0} \tag{A.8a}$$

$$i\hbar \frac{\partial\mathbf{A}}{\partial t} + \tilde{\tilde{\mathbf{H}}}_e\mathbf{A} = \mathbf{0} \tag{A.8b}$$

where $\tilde{\boldsymbol{\tau}}$, the dressed nonadiabatic coupling matrix (NACM), is

given in the form

$$\tilde{\boldsymbol{\tau}} = \boldsymbol{\omega}^\dagger \boldsymbol{\tau} \boldsymbol{\omega} + \boldsymbol{\omega}^\dagger \nabla \boldsymbol{\omega} \tag{A.9}$$

Here, $\boldsymbol{\tau}$ is the original NACM defined in terms of the time-independent basis set $\zeta(\mathbf{s}_e|\mathbf{s}, t=0)$

$$\boldsymbol{\tau}_{jk} = \langle \zeta_j(t=0)|\nabla \zeta_k(t=0)\rangle; \quad j = \{1,L\}; k = \{1,L\} \tag{A.10}$$

and $\boldsymbol{\omega}$ is introduced through eq A.5. It is important to emphasize that $\tilde{\boldsymbol{\tau}}(\mathbf{s}, t)$, just like $\mathbf{A}(\mathbf{s}, t)$ and $\tilde{\tilde{\mathbf{H}}}_e(\mathbf{s}, t)$ (but *unlike* $\boldsymbol{\tau}(\mathbf{s}, t)$), is an N-dimensional square matrix.

The solution of eq A.8 leads to a single-valued diabatic potential matrix, $\mathbf{W}(\mathbf{s}, t)$, if and only if the vector, $\tilde{\tilde{\boldsymbol{\tau}}}$, defined in terms of its space-time components

$$\tilde{\tilde{\boldsymbol{\tau}}} = \{ \tilde{\boldsymbol{\tau}}_{s1}, \tilde{\boldsymbol{\tau}}_{s2}, ..., \tilde{\boldsymbol{\tau}}_{sn}, \tilde{\boldsymbol{\tau}}_e\} \tag{A.11}$$

fulfills the space-time Curl condition/equation.[13] Here, $\tilde{\boldsymbol{\tau}}_{sj}; j = \{1,n\}$ are the relevant spatial components of $\tilde{\boldsymbol{\tau}}$ (and therefore also of $\tilde{\tilde{\boldsymbol{\tau}}}$) and $\tilde{\tilde{\mathbf{H}}}_e$ is the corresponding (N-dimensional) potential matrix defined in eq A.7 and applies as the time component (see eq A.7). These conditions are extensively discussed for the TID system.[21,23,26,27] Here, we just briefly refer to the parallel conditions to be fulfilled for the TD system.

The solution of eqs A.8 is given in terms of an exponentiated line integral along a space-time contour Γ[13]

$$\mathbf{A}(\mathbf{z}|\Gamma) = \mathscr{P}\exp\left\{-\int_{\mathbf{s}_0}^{\mathbf{s}} \tilde{\tilde{\boldsymbol{\tau}}}(\mathbf{z}'|\Gamma)\cdot d\mathbf{z}'\right\} \tag{A.12}$$

where $\mathscr{P}$ is an extended ordering operator, $\tilde{\tilde{\boldsymbol{\tau}}}$ is the space-time vector defined in eq A.11, $\mathbf{z}$ is the space-time coordinate, and the dot stands for the corresponding scalar product.

The space-time contour, Γ, contains a mixture of segments related to various spatial coordinates $\mathbf{s}_j: j = \{1,n\}$ and to time (the time variable is, in fact, not t but $(i/\hbar)t$). In Figure 1, two such contours are presented, Γ_1 and Γ_2, connecting the initial point ($\mathbf{s}=\mathbf{0}, t=0$) and some arbitrary point ($\mathbf{s}=\tilde{\mathbf{s}}, t=\tilde{t}$).

Having introduced the two matrices, $\tilde{\tilde{\mathbf{H}}}_e$ and $\mathbf{A}$, we are in a position to derive the diabatic potential matrix $\mathbf{W}$ (see eq A.1).

Next, we briefly refer to the topological matrix $\mathbf{D}(\Gamma)$ which is closely related to the ADT matrix but defined for a *closed* space-time contour Γ, namely

$$\mathbf{D}(\Gamma) = \mathscr{P}\exp\left\{-\oint_\Gamma \tilde{\tilde{\boldsymbol{\tau}}}(\mathbf{z}'|\Gamma)\cdot d\mathbf{z}'\right\} \tag{A.13}$$

The feature that most characterizes the topological matrix is that it becomes diagonal when the Curl equation is fulfilled[21,23] (this happens when the N states form a Hilbert subspace). A closed contour is formed when two open contours, for example, Γ_1 and Γ_2, cross at two (different) points. In such a case, $\Gamma = \Gamma_1 - \Gamma_2$ (see Figure 1).

Appendix B. Molecular Schrödinger Equation in an Electromagnetic Field

1. Molecular Schrödinger Equation and the Vector Potential. Our starting point is the molecular Hamiltonian which describes the interaction between a molecular system made up of electrons and nuclei and an external electromagnetic field[34,35]

$$\mathbf{H} = \frac{1}{2m}\sum_\alpha \left(-i\hbar\nabla_\alpha + \frac{e}{c}\mathbf{a}_\alpha\right)^2 + \\ \sum_\beta \frac{1}{2m_\beta}\left(-i\hbar\nabla_\beta + \frac{eZ_\beta}{c}\mathbf{a}_\beta\right)^2 + V(\mathbf{s}_{e\alpha}, \mathbf{s}_\beta) \tag{B.1}$$

Here, $V(\mathbf{s}_{e\alpha}, \mathbf{s}_\beta)$ is the sum of Coulombic potentials that govern the motion of the nuclei and the electrons, $\mathbf{a}_\gamma, \gamma = \alpha,\beta$ are the values of the vector potential $\mathbf{a}$ at the position of the α electron when $\gamma = \alpha$ or at the position of the β nucleus when $\gamma = \beta$ (consequently, α and β are the summation indices for the electrons and the nuclei, respectively), m_β and Z_β are the mass and the charge of the β nucleus, m is the mass of the electron, $\mathbf{s}_{e\alpha}$ is the coordinate of the electron α, and $\mathbf{s}_\beta$ is the coordinate of the nucleus β.

Our aim is to solve the following time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Theta(\mathbf{s}_e, \mathbf{s})}{\partial t} = \mathbf{H}\Theta(\mathbf{s}_e, \mathbf{s}) \tag{B.2}$$

For this purpose, we examine the possibility to eliminate parts of the vector potential and in this way to simplify the equation that finally has to be solved. For this purpose, we introduce a phase factor and try the following substitution[4,36]

$$\Theta(\mathbf{s}_e, \mathbf{s}) = \exp\{i\Omega(\mathbf{s}_e, \mathbf{s})\}\Psi(\mathbf{s}_e, \mathbf{s}) \tag{B.3}$$

where $\Omega(\mathbf{s}_e, \mathbf{s})$ is assumed to be of the form[4]

$$\Omega(\mathbf{s}_e, \mathbf{s}) = \sum_\alpha \Omega_\alpha(\mathbf{s}_{e\alpha}) + \sum_\beta \Omega_\beta(\mathbf{s}_\beta) \tag{B.4}$$

but the explicit expressions of $\Omega_\alpha(\mathbf{s}_{e\alpha})$ and $\Omega_\beta(\mathbf{s}_\beta)$ are still to be determined.

To simplify the forthcoming derivation, we introduce the canonical momentum operator π_γ

$$\pi_\gamma = -i\hbar\nabla_\gamma + \frac{Z_\gamma e}{c}\mathbf{a}_\gamma; \quad \gamma = \alpha,\beta \tag{B.5}$$

and consider the following expression

$$\pi_\gamma^2 \exp\{i\Omega(\mathbf{s}_e, \mathbf{s})\} = \exp\{i\Omega(\mathbf{s}_e, \mathbf{s})\}\Big\{-\hbar^2\nabla_\gamma^2 - 2i\hbar \\ \left(\hbar\nabla_\gamma\Omega_\gamma + \frac{Z_\gamma e}{c}\mathbf{a}_\gamma\right)\cdot\nabla_\gamma - i\hbar\frac{Z_\gamma e}{c}\nabla_\gamma\mathbf{a}_\gamma - i\hbar^2\nabla_\gamma^2\Omega_\gamma + \\ (\hbar\nabla_\gamma\Omega_\gamma)^2 + \hbar\frac{2Z_\gamma e}{c}\mathbf{a}_\gamma\cdot\nabla_\gamma\Omega_\gamma + \left(\frac{Z_\gamma e}{c}\right)^2\mathbf{a}_\gamma^2\Big\} \tag{B.6}$$

To continue, we remind the reader of the Helmholtz theorem[20,37] that states that a given vector $\mathbf{G}$ can be shown to be a sum of two components, that is, a longitudal component $\mathbf{G}_{lo}$ and a transversal component, $\mathbf{G}_{tr}$

$$\mathbf{G} = \mathbf{G}_{lo} + \mathbf{G}_{tr} \tag{B.7}$$

where $(\mathbf{G}_{lo}, \mathbf{G}_{tr})$ fulfill the following conditions

$$\text{curl}\,\mathbf{G}_{lo} = \nabla \times \mathbf{G}_{lo} = \mathbf{0} \tag{B.8a}$$

and

$$\text{Div}\,\mathbf{G}_{tr} = \nabla\cdot\mathbf{G}_{tr} = 0 \tag{B.8b}$$

In what follows, we assume this decomposition to exist also

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for **a** so that at each point, $\mathbf{a}_\gamma$, $\gamma = \alpha,\beta$ can be presented as

$$\mathbf{a}_\gamma = \mathbf{a}_{\gamma\text{lo}} + \mathbf{a}_{\gamma\text{tr}} \tag{B.9}$$

where the longitudal and the transversal components fulfill eqs B.8a and B.8b, respectively.

Substituting eq B.9 into eq B.6 and choosing the phases $\Omega_\alpha(\mathbf{s}_e\alpha)$ and $\Omega_\beta(\mathbf{s}_\beta)$ to fulfill the first-order vector equation

$$\nabla_\gamma\Omega_\gamma + \frac{Z_\gamma e}{\hbar c}\mathbf{a}_{\gamma\text{lo}} = \mathbf{0}; \quad \gamma = \alpha,\beta \tag{B.10}$$

we find that eq B.6 simplifies to become

$$\pi_\gamma{}^2 \exp\{i\Omega(\mathbf{s}_e,\mathbf{s})\} = \\ \exp\{i\Omega(\mathbf{s}_e,\mathbf{s})\}(-\hbar^2\nabla_\gamma{}^2 + \Lambda(\mathbf{a}_{\gamma\text{tr}})) \tag{B.11}$$

where $\Lambda(\mathbf{a}_{\gamma\text{tr}})$ is the sum of the terms that contain the transversal components $\mathbf{a}_{\gamma\text{tr}}$. While deriving eq B.11, we assumed that eq B.10 has an analytic solution. The condition for that to happen is that $\mathbf{a}_{\text{lo}}$ fulfills eq B.8a at every point. Indeed $\mathbf{a}_{\text{lo}}$, by its definition, satisfies eq B.8a (see the statement that follows eq B.9).

To complete the derivation, we have to evaluate $\Lambda(\mathbf{a}_{\gamma\text{tr}})$. Following a few simple algebraic manipulations, we obtain

$$\Lambda(\mathbf{a}_{\gamma\text{tr}}) = \\ -i\hbar\frac{Z_\gamma e}{c}(2\mathbf{a}_{\gamma\text{tr}}\cdot\nabla_\gamma - \nabla_\gamma\cdot\mathbf{a}_{\gamma\text{tr}}) + \left(\frac{Z_\gamma e}{c}\right)^2\mathbf{a}_{\gamma\text{tr}}{}^2 \tag{B.12}$$

where $\nabla_\gamma\,\mathbf{a}_{\gamma\text{tr}}$ is an operator that does not act on functions beyond the parentheses. However, recalling that $\mathbf{a}_{\gamma\text{tr}}$, by its definition, satisfies eq B.8b, the expression for $\Lambda(\mathbf{a}_{\gamma\text{tr}})$ simplifies to become

$$\Lambda(\mathbf{a}_{\gamma\text{tr}}) = -2i\hbar\frac{Z_\gamma e}{c}\mathbf{a}_{\gamma\text{tr}}\cdot\nabla_\gamma + \left(\frac{Z_\gamma e}{c}\right)^2\mathbf{a}_{\gamma\text{tr}}{}^2 \tag{B.12$'$}$$

Returning now to eq B.2 and replacing $\Theta(\mathbf{s}_e,\mathbf{s})$ according to eq B.3, we have

$$i\hbar\frac{\partial\Psi(\mathbf{s}_e,\mathbf{s})}{\partial t} = \exp(-i\Omega(\mathbf{s}_e,\mathbf{s}))\left(\mathbf{H} + \hbar\frac{\partial\Omega}{\partial t}\right)\exp(i\Omega(\mathbf{s}_e,\mathbf{s})) \times \\ \Psi(\mathbf{s}_e,\mathbf{s}) \tag{B.13}$$

which, following the incorporation of eqs B.1, B.4, B.5, and B.11, yields the following relevant SE

$$i\hbar\frac{\partial\Psi(\mathbf{s}_e,\mathbf{s})}{\partial t} = \left(-\sum_\gamma\frac{\hbar^2}{2m_\gamma}\nabla_\gamma{}^2 + \sum_\gamma\frac{1}{2m_\gamma}\Lambda(\mathbf{a}_{\gamma\text{tr}}) + \right. \\ \left. \hbar\sum_\gamma\frac{\partial\Omega_\gamma}{\partial t} + V(\mathbf{s}_e,\mathbf{s})\right)\Psi(\mathbf{s}_e,\mathbf{s}) \tag{B.14}$$

namely, a SE to study any molecular system affected by an external electromagnetic field.

2. Introducing the Electric and Magnetic Fields. 2.1. Electric Field. When introducing the electric field, we consider the following Maxwell equation

$$\text{curl}\mathbf{E}_\gamma = \frac{1}{c}\frac{\partial\mathbf{B}_\gamma}{\partial t}; \quad \gamma = \alpha,\beta \tag{B.15}$$

Since $\mathbf{B}_\gamma$ can be presented in terms of a vector potential

$$\mathbf{B}_\gamma = \text{curl}\mathbf{a}_\gamma; \quad \gamma = \alpha,\beta \tag{B.16}$$

Substituting eq B.16 into eq B.15 and solving it we get

$$\mathbf{E}_\gamma = -\frac{\partial}{\partial t}\left[\frac{1}{c}(\mathbf{a}_{\gamma\text{tr}} + \mathbf{a}_{\gamma\text{lo}}) - \nabla\chi_\gamma\right] \equiv -\frac{\partial}{\partial t}\left(\frac{1}{c}\mathbf{a}_{\gamma\text{tr}}\right) - \\ \frac{\partial}{\partial t}\left(\frac{1}{c}\mathbf{a}_{\gamma\text{lo}} + \nabla\chi_\gamma\right) \tag{B.17}$$

where χ is an undetermined analytic function. Since $\mathbf{a}_{\text{lo}}$ is determined up to a function of the type $\nabla\chi$, we can define the expression $((1/c)\mathbf{a}_{\text{lo}} + \nabla\chi)$ as a new longitudal component, that is, $\mathbf{a}_{\text{lo}}{}^{(n)}$ which is an analytic, but yet, undefined function. In what follows, we assume that this new longitudal component is such that for all cases to be considered here

$$\left|\frac{\partial}{\partial t}\left(\frac{1}{c}\mathbf{a}_{\gamma\text{lo}}\right)\right| \gg \left|\frac{\partial}{\partial t}\left(\frac{1}{c}\mathbf{a}_{\gamma\text{tr}}\right)\right| \tag{B.18}$$

where we dropped the upper index, n. With this assumption in mind, we may form, for $\mathbf{E}_\gamma$, the following expression

$$\mathbf{E}_\gamma = \frac{1}{c}\frac{\partial\mathbf{a}_{\gamma\text{lo}}}{\partial t}; \quad \gamma = \alpha,\beta \tag{B.19}$$

To make the connection between Ω_γ and $\mathbf{E}_\gamma$, we employ eq B.10. For this purpose, we first derive the solution of this equation which is presented in terms of an integral along a contour, Γ

$$\Omega_\gamma = \Omega_\gamma 0 - \frac{Z_\gamma e}{\hbar c}\int_\Gamma d\mathbf{s}_\gamma\cdot\mathbf{a}_{\gamma\text{lo}}; \quad \gamma = \alpha,\beta \tag{B.20}$$

where $\mathbf{s}_\gamma$ is defined as

$$\mathbf{s}_\gamma = \begin{cases} \mathbf{s}_{e\alpha}; & \gamma = \alpha \\ \mathbf{s}_\beta; & \gamma = \beta \end{cases} \tag{B.21}$$

It is important to remind the reader that each of the integrals in eq B.20 (like each of the differential equations in eq B.10) yields an analytic, single-valued function of Ω_γ because $\text{curl}\mathbf{a}_{\text{lo}} \equiv \mathbf{0}$.

Next, differentiating eq B.20 with respect to time and recalling eq B.19, we obtain

$$\frac{\partial\Omega_\gamma}{\partial t} = -\frac{Z_\gamma e}{\hbar}\int_\Gamma d\mathbf{s}_\gamma\cdot\mathbf{E}_\gamma; \quad \gamma = \alpha,\beta \tag{B.22}$$

Finally, substituting eq B.22 into eq B.14 yields the explicit incorporation of the electric field in the molecular SE

$$i\hbar\frac{\partial\Psi(\mathbf{s}_e,\mathbf{s})}{\partial t} = \left(-\sum_\gamma\frac{\hbar^2}{2m_\gamma}\nabla_\gamma{}^2 + \sum_\gamma\frac{1}{2m_\gamma}\Lambda(\mathbf{a}_{\gamma\text{tr}}) - \right. \\ \left. \sum_\gamma Z_\gamma e\int_\Gamma d\mathbf{s}_\gamma\cdot\mathbf{E}_\gamma + V(\mathbf{s}_e,\mathbf{s})\right)\Psi(\mathbf{s}_e,\mathbf{s}) \tag{B.23}$$

As a special case, we consider a homogeneous electric field. Consequently, $\mathbf{E}_\gamma$ can be moved in front of the integral and eq B.23 takes a more familiar form

$$i\hbar\frac{\partial\Psi(\mathbf{s}_e,\mathbf{s})}{\partial t} = \left(-\sum_\gamma\frac{\hbar^2}{2m_\gamma}\nabla_\gamma{}^2 + \sum_\gamma\frac{1}{2m_\gamma}\Lambda(\mathbf{a}_{\gamma\text{tr}}) - \right. \\ \left. \sum_\gamma(\mathbf{E}_\gamma\cdot\mathbf{M}_\gamma) + V(\mathbf{s}_e,\mathbf{s})\right)\Psi(\mathbf{s}_e,\mathbf{s}) \tag{B.24}$$

where $\mathbf{M}_\gamma$ is the electronic (nuclear) dipole moment

$$\mathbf{M}_\gamma = Z_\gamma \mathrm{e} \int_\Gamma \mathbf{ds}_\gamma = Z_\gamma \mathrm{e}\mathbf{s}_\gamma \tag{B.25}$$

In this presentation, $\mathbf{s}_\gamma$ is a vector that connects the γ-particle with the chosen origin of coordinates.

II.2.2. Magnetic Field. To obtain a more explicit expression for the effect of the magnetic field, we consider the simplified case where the magnetic field, $\mathbf{B}$, is homogeneous (see paragraph 126 in Landau and Lifshitz).[34] In such a case, the γ-transversal vector potential $\mathbf{a}_{\gamma\mathrm{tr}}$ can be presented as

$$\mathbf{a}_{\gamma\mathrm{tr}} = \frac{1}{2} \mathbf{B}_\gamma \times \mathbf{s}_\gamma \tag{B.26}$$

where $\mathbf{B}_\gamma$ is the magnetic field affecting the γ-particle (see also eq B.21). Recalling eq B.12′, we obtain for $\Lambda(\mathbf{a}_{\gamma\mathrm{tr}})$ the result

$$\Lambda(\mathbf{a}_{\gamma\mathrm{tr}}) = -i\hbar \frac{Z_\gamma \mathrm{e}}{c} \mathbf{B}_\gamma \times \mathbf{s}_\gamma \cdot \nabla_\gamma + \left(\frac{Z_\gamma \mathrm{e}}{2c}\right)^2 (\mathbf{B}_\gamma \times \mathbf{s}_\gamma)^2 \tag{B.27}$$

Next, we recall that

$$\mathbf{B}_\gamma \times \mathbf{s}_\gamma \cdot \nabla_\gamma = \mathbf{B}_\gamma \cdot \mathbf{s}_\gamma \times \nabla_\gamma = -i\mathbf{B}_\gamma \cdot \mathbf{L}_\gamma$$

so that eq B.23 becomes

$$\Lambda(\mathbf{a}_{\gamma\mathrm{tr}}) = \frac{Z_\gamma \mathrm{e}\hbar}{c} \mathbf{B}_\gamma \cdot \mathbf{L}_\gamma + \left(\frac{Z_\gamma \mathrm{e}}{2c}\right)^2 (\mathbf{B}_\gamma \times \mathbf{s}_\gamma)^2 \tag{B.27′}$$

where $\mathbf{L}$ is the angular momentum operator. Substituting eq 27′ into eq 24 leads to the final expression for the SE of the electrons and the nuclei in a given electromagnetic field.

$$i\hbar \frac{\partial \Psi(\mathbf{s}_\mathrm{e},\mathbf{s})}{\partial t} = \left(-\sum_\gamma \frac{\hbar^2}{2m_\gamma} \nabla_\gamma{}^2 + \sum_\gamma \frac{Z_\gamma \mathrm{e}\hbar}{c} \mathbf{H}_\gamma \cdot \mathbf{L}_\gamma - \right.$$
$$\left. \sum_\gamma (\mathbf{E}_\gamma \cdot \mathbf{M}_\gamma) + V(\mathbf{s}_\mathrm{e},\mathbf{s})\right)\Psi(\mathbf{s}_\mathrm{e},\mathbf{s}) \tag{B.28}$$

where for simplicity we ignored the term that is quadratic in the intensity of the magnetic field (in other words eq B.28 applies for weak magnetic fields).

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