

Density-matrix representation of nonadiabatic couplings in time-dependent density functional (TDDFT) theories

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Closed expressions for nonadiabatic coupling between the ground and an excited electronic state of a molecule are derived by representing the time-dependent density functional (TDDFT) equations in a form of classical dynamics for the Kohn-Sham (KS) single-electron density matrix. Applicability of Krylov-space-type fast algorithms to nonadiabatic TDDFT as well as the representivity of the time-dependent charge density of a driven system are discussed. © 2000 American Institute of Physics. [S0021-9606(00)01608-1]

I. INTRODUCTION

Photoisomerization processes that play an important role in photoinduced dynamics of various chemical and biological systems¹ usually involve four steps. (i) A molecule initially in its ground state is excited by interaction with a laser field. If the excitation pulse is short compared to the molecular dynamics time scale, the molecular geometry remains the same and a nuclear wave packet is formed on an excited state adiabatic surface. (ii) The wave packet evolves on the excited state adiabatic surface. (iii) When the nuclear configuration approaches a region where the ground-state and excited-state adiabatic surfaces come close or even intersect, the wave packet transfers from the excited state to the ground-state adiabatic surface. (iv) The last step involves nuclear relaxation on the ground-state adiabatic surface toward a stable or a metastable state different from the ground state. Computation of molecular dynamics during stages (i), (ii) and (iv) requires the adiabatic surfaces as an input, whereas molecular dynamics at stage (iii) involves the nonadiabatic coupling terms as well.

For a given molecular geometry \mathbf{R} , the nonadiabatic coupling matrix element is a single number. However, its calculation using standard expressions requires the entire many-body wave functions of the ground and excited states. Obviously much of the information contained in these wave functions is redundant.

In this paper we derive closed expressions for the nonadiabatic coupling matrix elements based on computing the electronic response of the system to an external field. The present direct computation totally avoids the expensive and unnecessary calculation of the many-electron wave functions and opens up an attractive new computational scheme for photochemical processes. Time-dependent density functional theory (TDDFT)²⁻⁴ that extends the stationary density functional theory (DFT)⁵⁻⁸ constitutes a powerful tool for studying the dynamics of many-electron systems. Its capability to calculate the dynamical linear⁹⁻¹¹ as well as nonlinear dynamical response¹² has been demonstrated by numerous studies. By applying the TDDFT to the linear optical response we derive closed expressions of the nonadiabatic cou-

pling between the ground and excited states in terms of the exchange-correlation functional.

We start in Sec. II by formulating the DFT in the Kohn-Sham (KS) form using the KS single-electron density matrix ρ rather than the KS single-electron orbitals. This allows us to formulate the TDDFT in a way that closely resembles time-dependent Hartree-Fock (TDHF) equations. We can then use our earlier results for the optical response, and in particular, the Lanczos-type density-matrix spectral moments algorithm (DSMA), originally developed for the TDHF,¹³ to the TDDFT calculations. The DSMA offers an extremely efficient algorithm with minimal memory and computational time requirements. We further formulate the stationary DFT using the KS density matrix and extend it to the adiabatic TDDFT. In Sec. III we formulate the procedure for obtaining the nonadiabatic coupling by computing the linear response using the adiabatic TDDFT and obtain closed expressions for the coupling in terms of the stationary exchange-correlation functional. The nonadiabatic TDDFT (which uses a frequency-dependent exchange-correlation functional) is formulated in terms of the KS density matrix in Appendices A and B. In Appendix C we obtain closed expressions for nonadiabatic coupling using the nonadiabatic TDDFT. Finally, in Sec. IV we discuss our results and compare with the TDHF approach.

II. DENSITY MATRIX FORMULATION OF TDDFT

In this section we introduce the basic notation and formulate DFT using the single-electron density matrix. We start with the Hamiltonian of a many-electron system,

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (2.1)$$

where \hat{H}_0 is the single-particle part that includes the electron kinetic energy and the external potential, while \hat{V} represents the Coulomb interaction among electrons. When it does not cause confusion, we shall also denote by \hat{H}_0 the Hamiltonian of the single-electron space, as opposed to Eq. (2.1), where \hat{H}_0 acts in the many-electron space.

Let $\rho(\mathbf{r}, \mathbf{r}')$ be the single-electron density matrix represented by an operator in the single-electron space. The elec-

tron density will be denoted $n(\mathbf{r}) \equiv \rho(\mathbf{r}, \mathbf{r})$. We start with the ground-state DFT. Using the elegant formulations of Levy and Lieb for the Hohenberg-Kohn DFT,^{6,14,15} we have for the Hohenberg-Kohn density functional (DF),

$$E[n] \equiv \min_{\Psi \in V[n]} \langle \Psi | \hat{H} | \Psi \rangle, \quad (2.2)$$

where $V[n]$ denotes the subspace of many-body states Ψ subjected to the constraint that the expectation value of the electronic density at point \mathbf{r} is given by $n(\mathbf{r})$. The ground-state energy E_0 is given by

$$E_0 = \min_n E[n]. \quad (2.3)$$

To introduce the Kohn-Sham exchange-correlation functional $E_{xc}[n]$, we define the DF $E_0[n]$ of a system of non-interacting electrons,

$$E_0[n] = \min_{\rho \in M[n]} \text{Tr}(\hat{H}_0 \rho), \quad (2.4)$$

where $M[n] \subset M$ is the subspace of the space M of the single Slater determinants represented by the single-electron density matrices with $\rho^2 = \rho$, which satisfy the constraint $\rho(\mathbf{r}, \mathbf{r}) = n(\mathbf{r})$. Stated differently, $E_0[n]$ is the minimal energy of the many-body Hamiltonian \hat{H}_0 computed using single Slater determinants with the constraint that they reproduce the charge distribution $n(\mathbf{r})$. According to the representivity theorem, $M[n] \neq \emptyset$ for any $n(\mathbf{r})$.

The exchange-correlation functional is defined as

$$E_{xc}[n] \equiv E[n] - E_0[n] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.5)$$

We now introduce the functional $E[\rho]$ on M by

$$E[\rho] \equiv \text{Tr}(\hat{H}_0 \rho) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}, [\rho])n(\mathbf{r}', [\rho])}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n, [\rho]], \quad (2.6)$$

with $n(\mathbf{r}, [\rho]) \equiv \rho(\mathbf{r}, \mathbf{r})$. Applying the operation $\min_{\rho \in M[n]}$ to Eq. (2.6), making use of the fact that the last two terms in the right-hand side (rhs) of Eq. (2.6) are constants on $M[n]$, and using the definitions of $E_{xc}[n]$ and $E_0[n]$ [Eqs. (2.5) and (2.4)], we obtain

$$E[n] = \min_{\rho \in M[n]} E[\rho]. \quad (2.7)$$

Combining Eqs. (2.7) and (2.3) immediately yields

$$E_0 = \min_{\rho \in M} E[\rho], \quad n_0(\mathbf{r}) = \rho_0(\mathbf{r}, \mathbf{r}), \quad (2.8)$$

where ρ_0 is the density matrix which minimizes $E[\rho]$, and $n_0(\mathbf{r})$ is the ground-state electron charge distribution. Equations (2.6) and (2.8) constitute a density-matrix formulation of the KS DFT, where $\rho \in M$ is a single-electron density matrix representing the Slater determinant constructed using the KS orbitals, hereafter referred to as the KS density matrix.

Next we turn to TDDFT. The density-matrix formulation of the ordinary TDDFT is presented in Appendix A. In this section we consider the adiabatic TDDFT that can be formulated as classical dynamics in the phase space M of single Slater determinants parametrized through their density matrices.

This is based on the fact that the dynamical adiabatic TDDFT equations can be formally derived by applying the dynamical variational principle (DVP), where the many-body wave function is restricted to be a single Slater determinant representing the occupied KS orbitals. The expectation value of the energy on a single Slater determinant entering the action that needs to be minimized should be set to $E[\rho]$ given by Eq. (2.6), where ρ is the single-electron density matrix corresponding to the single Slater determinant. Since the DVP is based on the minimal action principle, the resulting equations represent a classical Lagrangian dynamics. The corresponding classical Hamiltonian form of the dynamics is derived starting with the Lagrange formulation in a standard way.¹⁶ The Poisson bracket for the resulting Hamiltonian dynamics which constitutes an equivalent representation of the DVP equations can be expressed in terms of the scalar products of the trial wave functions (in our case, Slater determinants). The procedure is briefly outlined in Sec. III of Ref. 17. Since Slater determinants may be viewed as generalized coherent states,¹⁸ the Poisson bracket can be represented in an algebraic rather than a differential form. This is known as the Kirillov form.¹⁹ The algebraic formulation of the Poisson bracket in the space of Slater determinants is given in Ref. 20 for a discrete basis set in the single-electron orbital space. For a continuous representation, this immediately yields

$$\{\rho(\mathbf{r}_1, \mathbf{r}'_1), \rho(\mathbf{r}_2, \mathbf{r}'_2)\} \equiv i \delta(\mathbf{r}'_1 - \mathbf{r}_2) \rho(\mathbf{r}_1, \mathbf{r}'_2) - i \delta(\mathbf{r}'_2 - \mathbf{r}_1) \rho(\mathbf{r}_2, \mathbf{r}'_1). \quad (2.9)$$

The adiabatic TDDFT equations of motion thus may be represented in the Hamilton-Liouville form,

$$\frac{d\rho}{d\tau} = \{H, \rho\}, \quad (2.10)$$

with

$$H(\rho) \equiv E[\rho], \quad (2.11)$$

and $E[\rho]$ in Eq. (2.11) is given by Eq. (2.6).

Finally we note that we have adopted a nonstandard definition of the exchange-correlation functional. In a standard formulation, $E_0[n]$ is defined as

$$E_0[n] = \min_{\Psi \in V[n]} \langle \Psi | \hat{H}_0 | \Psi \rangle. \quad (2.12)$$

Applying the Lagrange procedure for finding the conditional minimum in Eq. (2.12) gives the minimum achieved on the ground state of some⁸ system of noninteracting electrons. If the ground state of this system⁸ is nondegenerate, it is necessarily given by a single Slater determinant, and both definitions coincide. In case of degeneracy, the minimum can be obtained for any linear combination of Slater determinants and the two definitions may be different. In this case Eq. (2.4) should be used to recover the KS theory.

III. NONADIABATIC COUPLING TERMS FROM THE ADIABATIC TDDFT

In this section we outline the procedure for computing the nonadiabatic coupling terms between the ground and an excited state using the adiabatic TDDFT. Generalization to

the nonadiabatic TDDFT is given in Appendix C and a similar procedure based on the TDHF is described in Sec. IV.

We denote by $\hat{H}(\mathbf{R})$ the many-body electronic Hamiltonian that depends parametrically on the set of nuclear coordinates \mathbf{R} . Its eigenstates are denoted $\nu_0(\mathbf{R}), \nu_1(\mathbf{R}), \dots$ with energies $\varepsilon_0(\mathbf{R}), \varepsilon_1(\mathbf{R}), \dots$,

$$\hat{H}(\mathbf{R})|\nu_j(\mathbf{R})\rangle = \varepsilon_j(\mathbf{R})|\nu_j(\mathbf{R})\rangle. \quad (3.1)$$

$\varepsilon_j(\mathbf{R})$ for $j=0,1,\dots$ thus represent the adiabatic surfaces. The nonadiabatic coupling terms may be represented by a set of matrices $A_{ij,\mu}(\mathbf{R})$ defined by

$$A_{ij,\mu}(\mathbf{R}) \equiv -\langle \nu_i(\mathbf{R}) | \partial_\mu \nu_j(\mathbf{R}) \rangle, \quad (3.2)$$

where $\partial_\mu \equiv \partial/\partial R_\mu$. Each matrix is a vector field (with components μ) in nuclear configuration space.

When time-reversal symmetry is satisfied, the states $\nu_j(\mathbf{R})$ can be taken to be real, and the matrices $A_{ij,\mu}(\mathbf{R})$ are real and antisymmetric, i.e., $A_{ji,\mu}(\mathbf{R}) = -A_{ij,\mu}(\mathbf{R})$. Standard quantum mechanical perturbation theory gives

$$\partial_\mu |\nu_i(\mathbf{R})\rangle = \sum_{j \neq i} |\nu_j(\mathbf{R})\rangle \frac{\langle \nu_j(\mathbf{R}) | \partial_\mu \hat{H}(\mathbf{R}) | \nu_i(\mathbf{R}) \rangle}{\varepsilon_j(\mathbf{R}) - \varepsilon_i(\mathbf{R})}. \quad (3.3)$$

Substituting Eq. (3.3) into Eq. (3.2) immediately yields

$$A_{ij,\mu}(\mathbf{R}) = -\frac{\langle \nu_j(\mathbf{R}) | \hat{h}_\mu(\mathbf{R}) | \nu_i(\mathbf{R}) \rangle}{\varepsilon_j(\mathbf{R}) - \varepsilon_i(\mathbf{R})}, \quad (3.4)$$

with $\hat{h}_\mu(\mathbf{R}) = \partial_\mu \hat{H}(\mathbf{R})$. Since a change in molecular geometry affects the electrons only by changing the external potential, the operators $\hat{h}_\mu(\mathbf{R})$ can always be represented in a form

$$\hat{h}_\mu(\mathbf{R}) = \int d\mathbf{r} \bar{h}_\mu(\mathbf{r}, \mathbf{R}) \hat{\rho}(\mathbf{r}, \mathbf{r}), \quad (3.5)$$

where $\hat{\rho}(\mathbf{r}, \mathbf{r}')$ denotes an operator representing the single-electron density matrix.

To compute the nonadiabatic coupling terms $A_{ij,\mu}(\mathbf{R})$ within the adiabatic TDDFT, we introduce an external driving field $\mathcal{E}_\mu(\mathbf{R}, \tau)$ and consider the following total Hamiltonian \hat{H}_T of the driven electronic system,

$$\hat{H}_T(\mathbf{R}, \tau) = \hat{H}(\mathbf{R}) - \sum_\mu \mathcal{E}_\mu(\mathbf{R}, \tau) \hat{h}_\mu(\mathbf{R}). \quad (3.6)$$

Equation (3.6) describes a set of purely electronic time-dependent Hamiltonians parametrized by \mathbf{R} .

We next introduce the time-domain linear response function $R_{\mu\nu}^{(1)}(t, \mathbf{R})$ with respect to the driving field,

$$\langle \hat{h}_\mu(\mathbf{R}, \tau) \rangle = \int_{-\infty}^{\tau} d\tau' \sum_\nu R_{\mu\nu}^{(1)}(\mathbf{R}, \tau - \tau') \mathcal{E}_\nu(\mathbf{R}, \tau'), \quad (3.7)$$

and the corresponding frequency-domain linear polarizability,

$$\alpha_{\mu\nu}(\mathbf{R}, \omega) \equiv \int_0^\infty dt \exp(i\omega t) R_{\mu\nu}^{(1)}(\mathbf{R}, t). \quad (3.8)$$

This polarizability can be obtained using the TDDFT approach by solving the classical Liouville equation for the single-electron density matrix,

$$\frac{d\rho}{d\tau} = \{H_T, \rho\}, \quad (3.9)$$

with the classical Hamiltonian H_T of the externally driven system,

$$H_T(\mathbf{R}; \rho, \tau) = H(\mathbf{R}, \rho) - \sum_\mu \mathcal{E}_\mu(\mathbf{R}, \tau) h_\mu(\mathbf{R}, \rho). \quad (3.10)$$

The Poisson bracket was defined in Eq. (2.9), $H(\rho)$ is given by Eq. (2.11), and

$$h_\mu(\mathbf{R}, \rho) \equiv \int d\mathbf{r} \bar{h}_\mu(\mathbf{r}, \mathbf{R}) \rho(\mathbf{r}, \mathbf{r}). \quad (3.11)$$

Since \hat{h}_μ is linear in the charge density [Eq. (3.5)], the TDDFT may be used for computing the linear response. In the case of adiabatic TDDFT, as stated in Sec. II, it follows the TDHF procedure of solving Eq. (3.9) with H_T given by Eqs. (3.10) and (3.11), $H(\rho)$ is given by Eq. (2.11) and $E[\rho]$ is determined by Eq. (2.6). In what follows we treat the density matrices $\rho(\mathbf{r}, \mathbf{r}')$ as operators acting in the space of functions $\varphi(\mathbf{r})$,

$$\rho\varphi(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \varphi(\mathbf{r}'), \quad (3.12)$$

and treat adiabatic TDDFT in the same way as the TDHF, making use of their close formal analogy. We can, therefore, use the expressions for the linear susceptibilities derived using the TDHF approach.²⁰

We denote by $\bar{\rho}(\mathbf{R})$ the ground-state density matrix for the configuration \mathbf{R} that minimizes the classical Hamiltonian $H(\mathbf{R}, \rho)$. $L(\mathbf{R})$ is the superoperator of the linearized dynamical equation that acts in the space of the particle-hole density matrices ξ , i.e., the ones that satisfy the constraint

$$[\bar{\rho}(\mathbf{R}), [\bar{\rho}(\mathbf{R}), \xi]] = \xi. \quad (3.13)$$

For the adiabatic TDDFT, $L(\mathbf{R})$ has the form

$$L(\mathbf{R})\xi = [t(\mathbf{R}) + V(\bar{\rho}(\mathbf{R})) - \mathcal{P}_{xc}^{(0)}(\mathbf{R}), \xi] + [V(\xi), \bar{\rho}(\mathbf{R})] - [\delta\mathcal{P}_{xc}^{(a)}(\mathbf{R}, \xi), \bar{\rho}], \quad (3.14)$$

where the matrix elements of t are defined by Eq. (B6), V is given by Eq. (B8), the matrix elements of $\mathcal{P}_{xc}^{(0)}$ are given by Eq. (B7), with $v_{xc}^{(0)}$ defined by Eq. (B3). The matrix elements $\mathcal{P}_{xc}^{(a)}(\mathbf{R}, \xi, \mathbf{r}, \mathbf{r}')$ of the density-matrix-type operator $\mathcal{P}_{xc}^{(a)}(\mathbf{R}, \xi)$ have the form

$$\begin{aligned} \mathcal{P}_{xc}^{(a)}(\mathbf{R}, \xi, \mathbf{r}, \mathbf{r}') \\ = \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{r}'' \frac{\delta v_{xc}^{(0)}(\mathbf{r}, [n])}{\delta n(\mathbf{r}'')} \Big|_{n(\mathbf{r}) = \bar{\rho}(\mathbf{r}, \mathbf{r}, \mathbf{R})} \xi(\mathbf{r}'', \mathbf{r}''). \end{aligned} \quad (3.15)$$

We denote the eigenmodes of the superoperator $L(\mathbf{R})$ by $\xi_j(\mathbf{R})$, with the eigenfrequencies $\Omega_j(\mathbf{R})$. $j = \pm 1, \pm 2, \dots$,

$$L(\mathbf{R})\xi_j(\mathbf{R}) = \Omega_j(\mathbf{R})\xi_j(\mathbf{R}). \quad (3.16)$$

As demonstrated in Ref. 20, $\xi_{-j} = \xi_j^+$, $\Omega_{-j} = -\Omega_j$.

The linear response $\alpha_{\mu\nu}(\mathbf{R}, \omega)$ can be expressed in terms of $\xi_j(\mathbf{R})$ and $\Omega_j(\mathbf{R})$ by solving the dynamical equation [Eq. (3.9)] to first order in the driving field $\mathcal{E}_\mu(\mathbf{R}, \tau)$, which yields²⁰

$$\alpha_{\mu\nu}(\omega) = \sum_{j>0} \text{Tr}(\xi_j^+ h_\mu) \text{Tr}(\xi_j^+ h_\nu) \frac{2\Omega_j}{\Omega_j^2 - \omega^2}, \quad (3.17)$$

where $\alpha_{\mu\nu}, \xi_j, \Omega_j$, and h_μ depend parametrically on \mathbf{R} . $h_\mu(\mathbf{R})$ is a density-matrix-type operator with matrix elements

$$h_\mu(\mathbf{R}, \mathbf{r}, \mathbf{r}') = \bar{h}_\mu(\mathbf{R}, \mathbf{r}) \delta(\mathbf{r}, \mathbf{r}'). \quad (3.18)$$

The eigenmodes in Eq. (3.17) are normalized as

$$\text{Tr}(\bar{\rho}[\xi_j^+, \xi_j]) = 1, \quad (3.19)$$

and are chosen to be real. This implies, in particular, that $\text{Tr}(\xi_j^+ h_\nu)$ are real.

The nonadiabatic coupling terms $A_{j0,\mu}(\mathbf{R})$ are obtained immediately by comparing Eq. (3.17) with the standard expression for $\alpha_{\mu\nu}$ in terms of the many-electron eigenstates, i.e.,

$$\alpha_{\mu\nu}(\omega) = \sum_j \langle \nu_j | \hat{h}_\mu | \nu_0 \rangle \langle \nu_j | \hat{h}_\nu | \nu_0 \rangle \frac{2\Omega_j}{\Omega_j^2 - \omega^2}, \quad (3.20)$$

where $\Omega_j = \varepsilon_j - \varepsilon_0$. Comparing Eq. (3.17) with (3.20) and making use of Eq. (3.4) yields

$$A_{j0,\mu}(\mathbf{R}) = - \frac{1}{\Omega_j(\mathbf{R})} \text{Tr}[\xi_j^+(\mathbf{R}) h_\mu(\mathbf{R})]. \quad (3.21)$$

Equation (3.21) constitutes a closed expression for the nonadiabatic coupling terms between the ground and an excited state in terms of quantities that can be calculated using the adiabatic TDDFT.

Equation (3.21) involves the transition frequencies $\Omega_j(\mathbf{R})$ and the derivatives $h_\mu(\mathbf{R})$ of the electronic Hamiltonian with respect to the nuclear configuration. This equation can be recast in an alternative form that only involves the modes $\xi_j(\mathbf{R})$ and the derivatives $\partial_\mu \bar{\rho}(\mathbf{R})$ of the ground-state density matrix. To that end, we note that an infinitesimal shift can be evaluated as a linear response to a static field $\mathcal{E}_\mu(\mathbf{R})$. This yields

$$\partial_\mu \bar{\rho}(\mathbf{R}) = \sum_{j>0} [\text{Tr}(\xi_j^+ h_\mu) \xi_j - \text{Tr}(\xi_j h_\mu) \xi_j^+] \frac{1}{\Omega_j}. \quad (3.22)$$

Making use of the orthogonality of the eigenmodes,²⁰ we obtain

$$\text{Tr}(\xi_j^+ h_\mu) = \Omega_j \text{Tr}(\bar{\rho}[\xi_j^+, \partial_\mu \bar{\rho}]). \quad (3.23)$$

Substituting Eq. (3.23) into Eq. (3.21) we finally obtain

$$A_{j0,\mu}(\mathbf{R}) = - \text{Tr}\{\bar{\rho}(\mathbf{R})[\xi_j^+(\mathbf{R}), \partial_\mu \bar{\rho}(\mathbf{R})]\}. \quad (3.24)$$

The nonadiabatic coupling terms can therefore be calculated in the framework of the adiabatic TDDFT using Eqs. (3.21) or (3.24). In Appendix C we derive an analog of Eq. (3.21) for the nonadiabatic TDDFT. A nonadiabatic TDDFT analog of Eq. (3.24) does not exist.

IV. DISCUSSION

In this paper we have formulated both DFT and TDDFT in terms of the KS density matrix ρ and applied these results to obtain the closed expression for the nonadiabatic coupling between the ground and an excited electronic state. The density matrix formulation establishes a close resemblance between the HF and the DFT theories. The HF is equivalent to DFT in the KS formulation, provided we use the following exchange-correlation functional that depends on ρ (rather than only on n):

$$E_{xc}^{\text{HF}}[\rho] = - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (4.1)$$

The dynamical TDDFT equations are thus formulated in a way that closely resembles the TDHF equations, i.e., in a form of classical dynamics in a Grassman manifold¹⁸ of single Slater determinants. This allows us to use all the properties of the Grassman manifold dynamics established earlier for the TDHF equations toward the TDDFT.²⁰

The nonadiabatic coupling can also be computed using the TDHF approximation in a way similar to that described in Sec. III. The only difference is that $H(\rho)$ in Eq. (3.10) is given by Eq. (2.11), with $E[\rho]$ given by Eq. (2.6), where $E_{xc}^{\text{HF}}[\rho]$ is given by Eq. (4.1). In particular this leads to the linearized operator $L(\mathbf{R})$ given in Ref. 20 rather than Eq. (3.14) for the adiabatic TDDFT.

A very important consequence of the close similarity between the TDDFT and TDHF approach is that one can use the fast DSMA¹³ developed for the latter. Its extension to the adiabatic TDDFT is straightforward. Extension to the general (nonadiabatic) TDDFT is somewhat less obvious. For the adiabatic TDDFT or TDHF approach we have a standard eigenvalue problem

$$L\xi = \Omega\xi, \quad (4.2)$$

whereas in the nonadiabatic TDDFT we encounter a more general spectral problem,

$$L(\Omega)\xi = \Omega\xi. \quad (4.3)$$

The iterative DSMA¹³ can treat both spectral problems. The output of the n th iteration in the iterative DSMA is an approximation $\xi^{(n)}$ for the eigenmode and $\Omega^{(n)}$ for its frequency. $\xi^{(n)}$ is then used as an input for the next iteration. The n th iteration uses $\xi^{(n-1)}$ and the operator L as an input. The iterative DSMA can be reformulated for the spectral problem of Eq. (4.3) in the following way. We start by setting $L = L(\Omega_0)$ for some reasonable Ω_0 . For the n th iteration we use $\xi^{(n-1)}$ as an input and set $L = L(\Omega^{(n-1)})$. Provided the procedure converges it yields the solution of the spectral problem of Eq. (4.3). This method may be used for solving the nonadiabatic TDDFT equations using the frequency-dependent functional proposed by Gross and Kohn.²¹

We have demonstrated how the nonadiabatic coupling between the ground and excited electronic states can be obtained by computing the linear response. Computing the coupling between excited states requires the second-order nonlinear response. A procedure for computing the matrix elements of relevant operators between two excited states

using the TDHF approach has been outlined in Ref. 22. A similar procedure can be developed for the TDDFT.

Finally, we note that the adiabatic TDDFT not only constitutes a fair, although uncontrolled, approximation, but it becomes asymptotically exact as the transition frequency is decreased. It therefore constitutes an excellent approximation for curve crossing and conical intersection events.¹

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APPENDIX A: TDDFT THEORY USING THE KS DENSITY MATRIX

In this Appendix we formulate the TDDFT using the KS single-electron density matrix ρ introduced in Sec. II.

The TDDFT is based on the invertibility properties first demonstrated by Runge and Gross.² The invertibility theorems² were proved by expanding the time-dependent quantities in the Taylor series in the vicinity of some $\tau = \tau_0$. The proof of Ref. 2 has been criticized by Xu and Rajagopal,³ who found counterexamples for which the invertibility theorems do not hold. It was later demonstrated by Dhara and Ghosh⁴ that the results of Ref. 2 are valid provided the relevant distributions decay sufficiently fast at large values of \mathbf{r} .

It is easy to show that the proof of Ref. 2 actually rests on a physically reasonable assumption about the differential operator $D(n)$ that depends parametrically on the charge density distribution $n(\mathbf{r})$,

$$D(n) = \sum_{\mu} \frac{\partial}{\partial r_{\mu}} \left[n(\mathbf{r}) \frac{\partial}{\partial r_{\mu}} \right]. \quad (\text{A1})$$

The assumption is that $D(n)$ does not have zero-eigenvalue modes [except for $\varphi_0(\mathbf{r}) = \text{const}$] for relevant charge density distributions $n(\mathbf{r})$. It is important to realize that the results of Refs. 2–4 are related to the uniqueness of the representation of the time-dependent density $n(\mathbf{r}, \tau)$ by a time-dependent driving field (potential) $\mathcal{E}(\mathbf{r}, \tau)$, i.e., if $\mathcal{E}_1(\mathbf{r}, \tau)$ and $\mathcal{E}_2(\mathbf{r}, \tau)$ represent the same $n(\mathbf{r}, \tau)$, then $\mathcal{E}_1(\mathbf{r}, \tau) - \mathcal{E}_2(\mathbf{r}, \tau)$ is a function of time only. However, to prove the invertibility of the map $\mathcal{E}(\mathbf{r}, \tau) \rightarrow n(\mathbf{r}, \tau)$ introduced in Ref. 2 one needs to further demonstrate the representability of any relevant $n(\mathbf{r}, \tau)$ with $\mathcal{E}(\mathbf{r}, \tau)$.

We start with demonstrating both the representability and uniqueness $n(\mathbf{r}, \tau)$. Our arguments use the general idea of Ref. 2, but as opposed to Ref. 2 they are based on the existence and uniqueness of the solutions of differential equations²³ rather than expanding the time-dependent quantities in a Taylor series.

We first note that the problem of surface terms outlined in Ref. 3 can be eliminated by compactification of the R^3 space, e.g., by considering the system on a sphere S^3 of a large radius, so that one can neglect its curvature in the region where the charge is concentrated. This is equivalent to imposing the conditions of fast decay of the charge densities and potentials at large \mathbf{r} , as was done in Ref. 4. Second, we emphasize that we call what follows “arguments” or “dem-

onstrations,” rather than the “proof,” for the following reasons. To convert the following into a proof of a theorem one needs to implement delicate techniques of functional analysis,²⁴ such as defining the convergence and topology in infinite-dimensional Hilbert spaces, defining the regions of the Hilbert space where differential operators, e.g., $D(n)$ are defined, and introducing the proper Hermitian extensions of symmetric operators. This goes beyond the scope of this paper. On the other hand, in quantum chemistry calculations the space of the single-electron states is in practice chosen to be finite-dimensional. In this case all dynamical spaces considered below are not only finite-dimensional but compact as well, and the following arguments can be converted into a proof of a theorem in a straightforward way.

To demonstrate the one-to-one correspondence $\mathcal{E}(\mathbf{r}, \tau) \rightarrow n(\mathbf{r}, \tau)$, we consider $n(\mathbf{r}, \tau)$ with $n(\mathbf{r}, \tau) = n_0(\mathbf{r})$ for $\tau \leq \tau_0$, where $n_0(\mathbf{r})$ is the ground-state charge-density distribution of the nondriven system. We assume that the operator $D(n_0)$ does not have zero-eigenvalue modes except for a constant function. This implies that this property holds for $D(n)$ for all $n \in W_{n_0}$, where W_{n_0} is some neighborhood of the ground-state distribution $n_0(\mathbf{r})$. We further assume that $n(\tau) \in W_{n_0}$ at all times τ . For the sake of computing optical response functions, these assumptions are always justified, since we can take the driving field to be infinitesimally weak.

The Hamiltonian $\hat{H}_T(\tau)$ of the driven system has the form

$$\hat{H}_T(\tau) = \hat{H} - \int d\mathbf{r} \mathcal{E}(\mathbf{r}, \tau) \hat{n}(\mathbf{r}). \quad (\text{A2})$$

We further introduce the following notation:

$$\dot{n}(\mathbf{r}, \tau) = \frac{\partial}{\partial \tau} n(\mathbf{r}, \tau), \quad \ddot{n}(\mathbf{r}, \tau) \equiv \frac{\partial^2 n(\mathbf{r}, \tau)}{\partial \tau^2}, \quad (\text{A3})$$

and

$$n(\mathbf{r}, \Omega) \equiv \langle \Omega | \hat{n}(\mathbf{r}) | \Omega \rangle, \quad j(\mathbf{r}, \Omega) \equiv \langle \Omega | \hat{j}(\mathbf{r}) | \Omega \rangle, \quad (\text{A4})$$

where $|\Omega\rangle$ is a many-body wave function and $\hat{j}(\mathbf{r})$ is the current density operator.

Let $|\Omega(\tau)\rangle$ be the solution of the dynamical Schrodinger equation,

$$i \frac{\partial}{\partial \tau} |\Omega(\tau)\rangle = \hat{H}_T(\tau) |\Omega(\tau)\rangle, \quad (\text{A5})$$

with $|\Omega(\tau)\rangle = |\Omega_0\rangle$ for $\tau \leq \tau_0$, where $|\Omega_0\rangle$, represents the ground state. It follows from the continuity equation that

$$\frac{\partial}{\partial \tau} \sum_{\mu} \partial_{\mu} j_{\mu}(\mathbf{r}, \Omega(\tau)) = -\ddot{n}(\mathbf{r}, \tau). \quad (\text{A6})$$

On the other hand, the Heisenberg equation for the current density operator yields

$$\begin{aligned} \frac{\partial}{\partial \tau} j_{\mu}(\mathbf{r}, \Omega(\tau)) &= -i \langle \Omega(\tau) | [\hat{j}_{\mu}(\mathbf{r}), \hat{H}] | \Omega(\tau) \rangle \\ &\quad - n(\mathbf{r}, \Omega(\tau)) \partial_{\mu} \mathcal{E}(\mathbf{r}, \tau). \end{aligned} \quad (\text{A7})$$

Substituting Eq. (A7) into Eq. (A6), and making use of Eq. (A1), yields

$$D(n(\Omega(\tau)))\mathcal{E}(\mathbf{r},\tau) = \ddot{n}(\mathbf{r},\tau) - i \sum_{\mu} \langle \Omega(\tau) | [\partial_{\mu} \hat{j}_{\mu}(\mathbf{r}), \hat{H}] | \Omega(\tau) \rangle. \quad (\text{A8})$$

We next introduce $\bar{\mathcal{E}}(\mathbf{r},\tau,\Omega)$,

$$\bar{\mathcal{E}}(\mathbf{r},\tau,\Omega) \equiv D^{-1}(n(\Omega)) \left\{ \ddot{n}(\mathbf{r},\tau) - i \sum_{\mu} \partial_{\mu} \langle \Omega | [\hat{j}_{\mu}(\mathbf{r}), \hat{H}] | \Omega \rangle \right\}. \quad (\text{A9})$$

The field $\bar{\mathcal{E}}(\mathbf{r},\tau,\Omega)$ is correctly defined by Eq. (A9) for all $|\Omega\rangle$ that satisfy the condition $n(\Omega) \in W_{n_0}$, since the integral over \mathbf{r} of the expression in the curly brackets in Eq. (A9) vanishes, which implies that this expression is orthogonal to the only zero mode of the operator $D(n(\Omega))$. $\bar{\mathcal{E}}(\mathbf{r},\tau,\Omega)$ is thus correctly defined and

$$\int d\mathbf{r} \bar{\mathcal{E}}(\mathbf{r},\tau,\Omega) = 0. \quad (\text{A10})$$

Let $|\bar{\Omega}(\tau)\rangle$ be the solution of the differential equation,

$$i \frac{d}{d\tau} |\bar{\Omega}(\tau)\rangle = \hat{H} |\bar{\Omega}(\tau)\rangle - \int d\mathbf{r} \bar{\mathcal{E}}(\mathbf{r},\tau, \bar{\Omega}(\tau)) \hat{n}(\mathbf{r}) |\bar{\Omega}(\tau)\rangle. \quad (\text{A11})$$

Setting

$$\mathcal{E}(\mathbf{r},\tau) \equiv \bar{\mathcal{E}}(\mathbf{r},\tau,\Omega(\tau)), \quad (\text{A12})$$

we see by combining Eqs. (A9) and (A11) that $\mathcal{E}(\mathbf{r},\tau)$ defined by Eq. (A12) satisfies Eq. (A8), and therefore represents $n(\mathbf{r},\tau)$. It is also obvious from our construction that $\mathcal{E}(\mathbf{r},\tau)$ defined by Eq. (A12) is the only driving field that represents $n(\mathbf{r},\tau)$ and satisfies the condition Eq. (A10). We have thus established a one-to-one correspondence between $\mathcal{E}(\mathbf{r},\tau)$ and $n(\mathbf{r},\tau)$, provided $n(\tau) \in W_{n_0}$ for all τ , which is always the case when looking for the response functions.

We are now in a position to formulate the TDDFT using the KS density matrix. The equation for the KS orbitals² can be recast as an equation for the KS density matrix ρ introduced in Sec. II, in the following way. The KS density matrix ρ satisfies Eq. (3.9) with H_T given by

$$H_T(\rho,\tau) = H_0(\rho) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r},\mathbf{r})\rho(\mathbf{r}',\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r} \mathcal{E}(\mathbf{r},\tau) \rho(\mathbf{r},\mathbf{r}) - \int d\mathbf{r} v_{xc}(\mathbf{r},\tau) \rho(\mathbf{r},\mathbf{r}), \quad (\text{A13})$$

where H_0 is the classical counterpart of the single-particle Hamiltonian \hat{H}_0 in Eq. (2.1), and the exchange-correlation potential $v_{xc}(\mathbf{r},\tau)$ depends on the charge density $n(\mathbf{r}',\tau')$ for $\tau' < \tau$.

The exchange-correlation potential $v_{xc}(\mathbf{r},\tau)$ can be found using the following procedure: Given $n(\mathbf{r},\tau)$ we first find $\mathcal{E}(\mathbf{r},\tau)$ as described above. $v_{xc}(\mathbf{r},\tau)$ can be obtained in a

similar way we found $\mathcal{E}(\mathbf{r},\tau)$, with the only difference that the dynamics is described by Eqs. (3.9) and (A13) and the wave function $|\bar{\Omega}(\tau)\rangle$ is assumed to be a single Slater determinant at all times, described by a KS density matrix $\rho(\tau)$.

APPENDIX B: RESPONSE THEORY USING TDDFT IN TERMS OF THE KS DENSITY MATRIX

Following Ref. 20 we represent the KS density matrix ρ as

$$\rho = \bar{\rho} + \xi + T(\xi), \quad (\text{B1})$$

where $\bar{\rho}$ is the ground-state KS density matrix, ξ and $T(\xi)$ are the particle-hole and intraband component of $(\rho - \bar{\rho})$, respectively. We also represent the exchange-correlation potential in a form

$$v_{xc}(\mathbf{r},\tau) = v_{xc}^{(0)}(\mathbf{r}) + \delta v_{xc}(\mathbf{r},\tau), \quad (\text{B2})$$

where

$$v_{xc}^{(0)}(\mathbf{r}) \equiv \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r}') = \bar{\rho}(\mathbf{r}',\tau')}, \quad (\text{B3})$$

is its ground-state form.

Substituting Eq. (B2) into Eq. (A13) and subsequently Eq. (A13) into Eq. (3.9), and making use of Eqs. (B1) and (2.9), yields after some straightforward transformations,

$$i \frac{d\xi}{d\tau} = [t + V(\bar{\rho}) - \mathcal{P}_{xc}^{(0)}, \xi] + [V(\xi), \bar{\rho}] - [\delta \mathcal{P}_{xc}, \bar{\rho}] - [\mathcal{P}, \bar{\rho}] + \xi^{(2)} + \xi^{(3)}, \quad (\text{B4})$$

with

$$\begin{aligned} \xi^{(2)} &\equiv [\bar{\rho}, [\bar{\rho}, [V(\xi), \xi]]] + [V(T(\xi)), \bar{\rho}] \\ &\quad - [\bar{\rho}, [\bar{\rho}, [\mathcal{P}_{xc}^{(0)}, T(\xi)]]] - [\bar{\rho}, [\bar{\rho}, [\delta \mathcal{P}_{xc}, \xi]]] \\ &\quad - [\bar{\rho}, [\bar{\rho}, [\mathcal{P}, \xi]]], \end{aligned} \quad (\text{B5})$$

and $\xi^{(3)}$ denotes terms that do not contribute to the optical response to second order in the driving field. In Eqs. (B4) and (B5) we have used the following notation. $\xi, \bar{\rho}, t, \mathcal{P}_{xc}^{(0)}, \delta \mathcal{P}_{xc}$, and \mathcal{P} are single-electron density operators determined by their matrix elements, e.g., $\xi(\mathbf{r},\mathbf{r}')$ etc. t represents the single-particle part \hat{H}_0 of the many-body Hamiltonian [see Eq. (2.1)],

$$\hat{H}_0 = \int d\mathbf{r} d\mathbf{r}' t(\mathbf{r},\mathbf{r}') \hat{\psi}^{\dagger}(\mathbf{r}) \hat{\psi}(\mathbf{r}'). \quad (\text{B6})$$

We further have

$$\begin{aligned} \mathcal{P}_{xc}^{(0)}(\mathbf{r},\mathbf{r}') &= v_{xc}^{(0)}(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}'), \\ \delta \mathcal{P}_{xc}(\mathbf{r},\mathbf{r}',\tau) &= \delta v_{xc}(\mathbf{r},\tau) \delta(\mathbf{r}-\mathbf{r}'), \\ \mathcal{P}(\mathbf{r},\mathbf{r}',\tau) &= \mathcal{E}(\mathbf{r}) \delta(\mathbf{r}-\mathbf{r}'). \end{aligned} \quad (\text{B7})$$

V is a linear superoperator acting in the space of single-electron density operators, defined by

$$V(\mathbf{r},\mathbf{r}',\rho) = \delta(\mathbf{r}-\mathbf{r}') \int d\mathbf{r}'' \frac{\rho(\mathbf{r}'',\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|}. \quad (\text{B8})$$

To close the system of equations for the optical response we expand δv_{xc} in the deviation $\delta n(\mathbf{r}, \tau)$ of the charge-density from its ground-state value,

$$\begin{aligned} \delta v_{xc}(\mathbf{r}, \tau) = & \int_{-\infty}^{\tau} d\tau' \int d\mathbf{r}' f^{(1)}(\mathbf{r}-\mathbf{r}'; \tau-\tau') \delta n(\mathbf{r}', \tau') \\ & + \int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau} d\tau'' \int d\mathbf{r}'' \\ & \times f^{(2)}(\mathbf{r}-\mathbf{r}', \mathbf{r}-\mathbf{r}''; \tau-\tau', \tau-\tau'') \\ & \times \delta n(\mathbf{r}', \tau') \delta n(\mathbf{r}'', \tau'') + \dots \end{aligned} \quad (\text{B9})$$

Equation (B4), together with Eq. (B9), constitutes a closed system of equations for the optical response. The response functions and optical susceptibilities are obtained by solving these equations order-by-order in the driving field.

APPENDIX C: TDDFT LINEAR RESPONSE AND THE NONADIABATIC COUPLING TERMS

In this Appendix we formulate the KS scheme for the TDDFT linear response using the density matrix and compute the nonadiabatic coupling terms.

To compute the linear response we consider the following equation:

$$i \frac{d\xi(\tau)}{d\tau} - L_0 \xi(\tau) - \int_{-\infty}^{\tau} d\tau' L_1(\tau-\tau') \xi(\tau') = -[\mathcal{P}, \bar{\rho}], \quad (\text{C1})$$

where the superoperators L_0 and $L_1(t)$ are defined by

$$L_0 \xi \equiv [t + V(\bar{\rho}) - \mathcal{P}_{xc}^{(0)}, \xi] + [V(\xi), \bar{\rho}], \quad (\text{C2})$$

and

$$\begin{aligned} L_1(\mathbf{r}, \mathbf{r}'; t) \xi \equiv & -\bar{\rho}(\mathbf{r}, \mathbf{r}') \int d\mathbf{r}'' [f^{(1)}(\mathbf{r}-\mathbf{r}'', t) \\ & - f^{(1)}(\mathbf{r}'-\mathbf{r}'', t)] \xi(\mathbf{r}'', \mathbf{r}''). \end{aligned} \quad (\text{C3})$$

The linear response function is defined by

$$\delta n(\mathbf{r}, \tau) = \int_{-\infty}^{\tau} d\tau' \int d\mathbf{r}' R^{(1)}(\mathbf{r}, \mathbf{r}'; \tau-\tau') \mathcal{E}(\mathbf{r}', \tau'). \quad (\text{C4})$$

The linear susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ which is related to $R^{(1)}$ through Eq. (3.8), can be obtained by solving Eq. (C1), resulting in

$$\alpha(\mathbf{r}, \mathbf{r}'; \omega) = -\text{Tr}\{\mu(\mathbf{r})[\omega - L(\omega)]^{-1}[\mu(\mathbf{r}'), \bar{\rho}]\}, \quad (\text{C5})$$

where $\mu(\mathbf{r})$ is a single-electron density operator that depends parametrically on \mathbf{r} and has the matrix elements $\mu(\mathbf{r}'', \mathbf{r}'; \mathbf{r}) = \delta(\mathbf{r}''-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r})$. The frequency-dependent superoperator $L(\omega)$ is defined by

$$L(\omega) \equiv L_0 + \int_0^{\infty} dt L_1(t) \exp(i\omega t). \quad (\text{C6})$$

To derive an analog of Eq. (3.21) we first demonstrate how to use Eq. (C5) to compute the matrix elements $\langle v_j | \hat{\rho}(\mathbf{r}, \mathbf{r}) | v_0 \rangle$ of the charge-density operator $\hat{\rho}(\mathbf{r}, \mathbf{r})$ be-

tween the ground and an excited states. Comparison of the sum-over-states expression for the linear susceptibility,

$$\begin{aligned} \alpha(\mathbf{r}, \mathbf{r}'; \omega) = & \sum_j \langle v_j | \hat{\rho}(\mathbf{r}, \mathbf{r}) | v_0 \rangle \\ & \times \langle v_j | \hat{\rho}(\mathbf{r}', \mathbf{r}') | v_0 \rangle \frac{2\Omega_j}{\Omega_j^2 - \omega^2}, \end{aligned} \quad (\text{C7})$$

where $\Omega_j = \varepsilon_j - \varepsilon_0$ with Eq. (C5), shows that the operator $B(\omega) \equiv \omega - L(\omega)$ has a zero-eigenvalue mode at $\omega = \Omega_j$, hereafter referred to as ξ_j . We now consider Eq. (C5) at $\omega \rightarrow \Omega_j$ and neglect that the terms have a finite limit when $\omega \rightarrow \Omega_j$,

$$\alpha(\mathbf{r}, \mathbf{r}'; \omega) \approx -\frac{1}{\omega - \Omega_j} \frac{\text{Tr}[\mu(\mathbf{r}) \xi_j] \langle \xi_j | [\mu(\mathbf{r}'), \bar{\rho}] \rangle}{\langle \xi_j | B'(\Omega_j) \xi_j \rangle}, \quad (\text{C8})$$

where $B'(\Omega_j) \equiv [dB/d\omega]_{\omega=\Omega_j}$, and $\langle \xi_j |$ denotes the projection onto the mode ξ_j when expanding the vector in the eigenmodes of an operator $B(\Omega_j)$. Comparison of Eqs. (C7) and (C8) immediately yields

$$\langle \xi_j | \zeta \rangle = c \text{Tr}\{\bar{\rho}[\xi_j^+, \zeta]\}, \quad (\text{C9})$$

for any ζ that has the form

$$\zeta = \int d\mathbf{r} \zeta(\mathbf{r}) [\mu(\mathbf{r}), \bar{\rho}], \quad (\text{C10})$$

with $\zeta(\mathbf{r})$ being an arbitrary function. In Eq. (C9), c is a constant that does not depend on ζ . Since $[\mu(\mathbf{r}'), \bar{\rho}]$ and $B'(\Omega_j)\zeta = [1 - L'(\omega)]\zeta$ for any vector ζ can be represented in the form of Eq. (C10), we can recast Eq. (C8) in the form

$$\alpha(\mathbf{r}, \mathbf{r}'; \omega) \approx -\frac{1}{\omega - \Omega_j} \frac{\text{Tr}[\mu(\mathbf{r}) \xi_j] \text{Tr}[\mu(\mathbf{r}') \xi_j]}{1 - \text{Tr}\{\bar{\rho}[\xi_j^+, L'(\Omega_j) \xi_j]\}}, \quad (\text{C11})$$

and the constant c is canceled out. A comparison of Eq. (C11) and Eq. (C7) finally gives

$$\langle v_j | \hat{\rho}(\mathbf{r}, \mathbf{r}) | v_0 \rangle = \frac{\text{Tr}[\mu(\mathbf{r}) \xi_j]}{(1 - \text{Tr}\{\bar{\rho}[\xi_j^+, L'(\Omega_j) \xi_j]\})^{1/2}}. \quad (\text{C12})$$

Making use of Eq. (C3), we can recast Eq. (C12) in the form

$$\begin{aligned} \langle v_j | \hat{\rho}(\mathbf{r}, \mathbf{r}) | v_0 \rangle & = \frac{\xi_j(\mathbf{r}, \mathbf{r})}{\left\{ 1 - \int d\mathbf{r} d\mathbf{r}' \frac{d}{d\omega} [f^{(1)}(\mathbf{r}-\mathbf{r}', \omega)] \xi_j(\mathbf{r}, \mathbf{r}) \xi_j(\mathbf{r}', \mathbf{r}') \right\}^{1/2}}. \end{aligned} \quad (\text{C13})$$

Combining Eqs. (C12), (3.11), and (3.4) finally yields

$$\begin{aligned} A_{j0, \mu}(\mathbf{R}) & = -\frac{1}{\Omega_j(\mathbf{R})} \frac{\text{Tr}[\xi_j^+(\mathbf{R}) h_{\mu}(\mathbf{R})]}{(1 - \text{Tr}\{\bar{\rho}(\mathbf{R})[\xi_j^+(\mathbf{R}), L'(\Omega_j, \mathbf{R}) \xi_j(\mathbf{R})]\})^{1/2}} \end{aligned} \quad (\text{C14})$$

Equation (C14) constitutes our final expression for the nonadiabatic coupling terms between the ground and excited states in terms of quantities that can be calculated using the general (as opposed to adiabatic) TDDFT. The adiabatic limit [Eq. (3.21)] can be obtained from Eq. (C14) by setting $L'(\Omega_j; \mathbf{R})=0$, since L does not depend on the frequency in the adiabatic case.

- ¹W. Domcke and D. Stock, *Adv. Chem. Phys.* **100**, 1 (1997).
- ²E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- ³B.-X. Xu and A. K. Rajagopal, *Phys. Rev. A* **31**, 2682 (1985).
- ⁴A. K. Dhara and S. K. Ghosh, *Phys. Rev. A* **35**, 442 (1987).
- ⁵M. E. Casida, *Recent Advances in Density Functional Methods, Part I*, edited by D. P. Chong (Singapore, World Scientific, 1995), p. 155.
- ⁶R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ⁷P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ⁸W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁹A. Zangwill and P. Soven, *Phys. Rev. A* **21**, 1561 (1980).
- ¹⁰E. K. U. Gross and W. Kohn, *Phys. Rev. Lett.* **55**, 2850 (1985).
- ¹¹T. K. Ng, *Phys. Rev. Lett.* **62**, 2417 (1989).
- ¹²G. Senatore and K. R. Subbaswamy, *Phys. Rev. A* **35**, 2440 (1987).
- ¹³S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.* **119**, 11408 (1997).
- ¹⁴M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979).
- ¹⁵E. H. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).
- ¹⁶V. I. Arnold, *Mathematical Methods in Classical Mechanics* (Springer-Verlag, New York, 1978).
- ¹⁷V. Chernyak and S. Mukamel, *J. Chem. Phys.* **111**, 4383 (1999).
- ¹⁸A. Perelomov, *Generalized Coherent States and their Applications* (Springer, Berlin, 1986).
- ¹⁹A. A. Kirillov, *Elements of the Theory of Representations* (Springer, Berlin, 1976).
- ²⁰V. Chernyak and S. Mukamel, *J. Chem. Phys.* **104**, 444 (1996).
- ²¹E. K. U. Gross and W. Kohn, *Adv. Quantum Chem.* **21**, 255 (1990).
- ²²S. Tretiak, V. Chernyak, and S. Mukamel, *Int. J. Quantum Chem.* **70**, 711 (1998).
- ²³V. I. Arnold, *Ordinary Differential Equations* (MIT Press, Cambridge, 1973); *Geometrical Methods in the Theory of Ordinary Differential Equations* (Springer-Verlag, New York, 1988).
- ²⁴M. Reed and B. Simon, *Methods of Modern Mathematical Physics* (Academic, New York, 1972–1979), Vols. 1–4.