

Resonant nonlinear polarizabilities in the time-dependent density functional theory

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The response of the density matrix to an external field is calculated in the adiabatic time-dependent density functional (TDDFT) theory by mapping the equation of motion for the driven single-electron density matrix into the dynamics of coupled harmonic oscillators. The resulting nonlinear response functions and the closed expressions for nonlinear frequency-dependent polarizabilities are derived. These expressions include transition densities and frequencies calculated in the linear response TDDFT, and higher order functional derivatives of the exchange-correlation functional. Limitations of the applicability of the traditional sum over states approach for computing the nonlinear response to the TDDFT are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1614240]

I. INTRODUCTION

Quantum-chemical calculations of nonlinear optical response of molecular systems require extensive numerical effort. The complete information on the optical response of a quantum multielectron system is contained in its set of many-electron eigenstates. Since the number of states increases exponentially with the number of electrons in the finite basis set, exact calculations become impractical even for fairly small molecules with a few atoms. An approximation at some level of many-body perturbation theory [Møller–Plesset (MP) technique] and configuration interaction (CI) are frequently used to compute the ground and excited states, respectively.^{1–3}

Off-resonant nonlinear response can then be calculated by a perturbative treatment of the ground state in the presence of a static electric field. In such coupled perturbed (CP) approaches the off-resonant polarizabilities are obtained by evaluating derivatives of the ground-state energy with respect to an external field.^{4–7} On the other hand, resonant optical responses imply a significant involvement of the specific excited electronic states. Time-dependent perturbation theory, which relates optical response to the properties of the excited states, is then typically used to evaluate nonlinear frequency-dependent responses. For example, the sum over states (SOS) method based on the expansion of the Stark energy of the molecule in powers of the electric field, involves the calculations of both the ground and excited states wavefunctions and the transition dipole moments between them.^{8,9} The CI/SOS calculations are computationally expensive.^{6,7} Therefore, this approach is usually based on simplified semiempirical model Hamiltonians such as the intermediate neglect of differential overlap/spectroscopy

(INDO/S) model, fitted to reproduce UV-visible absorption spectra at the CI Singles (CIS) level (i.e., accounting only for single-particle electronic correlations).^{10–12} This technique usually calculates excited states contributing to the linear optical response fairly accurately.^{13,14} However, the situation is very different for the electronic states, which contribute to the nonlinear responses. Accurate calculation of such states may require accounting for higher order electronic correlations^{15,16} (a typical example is A_g states in the conjugated polymers which have significant double excitation character^{17,18}). Semiempirical techniques accounting solely for single-particle electronic correlations result in a significant blue-shift of transition frequencies compared to the experiment. Methods including higher-order correlations [such as multireference (MR) CI] are computationally expensive and result in the overcorrelated ground-state wavefunction.^{15,16} In addition, size consistency is not guaranteed and special care needs to be taken when choosing the right configurations.^{19–21}

Even though the many-electron wavefunctions contain a complete information about quantum system, most of it is rarely used in the calculation of common observables (such as energies, dipole moments, spectra, etc.), which only depend on the expectation values of one- and two-electron quantities.²² A reduced description, which only keeps a small amount of the relevant information, is possible and could be built on the single-electron density matrix in the time-dependent methods based the time-dependent variational principle (TDVP).^{23–27} An example of such approach is the time-dependent Hartree–Fock (TDHF) theory, where the excited state wavefunctions are never calculated.^{28,29} However, the set of transition densities computed in the TDHF is sufficient for calculating all linear and nonlinear optical responses.^{14,25,30–32}

The time-dependent density functional theory

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(TDDFT)^{33–35} in the Kohn–Sham (KS) form^{36,37} is a relatively new and increasingly popular approach for computing molecular excited states.^{38–42} This method may be formulated as a response of the single-electron density matrix of the noninteracting time-dependent KS system to an external field. This leads to the equations similar to that in the TDHF technique and can be interpreted as the dynamics of a single Slater determinant driven by an external field.^{26,43,44} However, compared to the TDHF, the TDDFT is not an approximation to the many-electron wave function. Rather, the level of an approximation is limited by our knowledge of the density functional and, in principle, an exact solution for excited states of many-electron system is possible within the nonadiabatic TDDFT approach.^{26,45,46} It is instructive to emphasize that although both TDDFT and TDHF approaches use a time-dependent many-body wave function in a form of a single Slater determinant the meaning of this many-body wave function is very different in these two approaches. While in TDHF the single Slater determinant constitutes an approximation to the wave functions of a driven system (dynamical variational approach), in the TDDFT it is rather an auxiliary object that represents a system of fictitious KS noninteracting particles that are, however, capable of reproducing the exact values of the electron density of the driven system at all times.

The linear response TDDFT is well developed and matured technique which currently became a method of choice for computing excited states in extended molecules.^{35,39,42,47–52} Even though an application of the TDDFT for calculating nonlinear responses is a subject of great interest (e.g., the extensions to the second-order properties have been explored in several studies^{43,53,54}), a systematic study of the nonlinear responses in the TDDFT method is yet to be done.

In this article we study the nonlinear optical responses up to the third order in the driving field in the adiabatic TDDFT approach. Sections II and III introduce the density matrix formulation of the TDDFT. In Sec. IV equation of motion for the single electron density matrix is mapped into the dynamics of a system of weakly anharmonic oscillators. This establishes the same mathematical formulation of the adiabatic TDDFT and the TDHF methods in any order of optical response and allows to derive compact expressions for frequency dependent polarizabilities. In Sec. V we analyze the nonlinear response in the TDDFT using an effective quantum multilevel system and show why the standard SOS expansion cannot be applied directly for calculating nonlinear optical polarizabilities in the adiabatic TDDFT and TDHF methods. Finally, we discuss the trends that emerge and summarize our results in Sec. VI.

II. DENSITY MATRIX FORMULATION OF ADIABATIC TDDFT EQUATIONS

We start with the time-dependent Kohn–Sham (KS) equation

$$i \frac{\partial \psi_p(\mathbf{r}, t)}{\partial t} = \left[-\frac{1}{2} \nabla^2 + v^{\text{eff}}(\mathbf{r}, t) \right] \psi_p(\mathbf{r}, t), \quad (2.1)$$

which can be derived assuming the existence of a potential $v^{\text{eff}}(\mathbf{r}, t)$ for a system of non-interacting electrons, whose single-particle orbitals $\psi_p(\mathbf{r}, t)$ produce the same charge density $n(\mathbf{r}, t) = \rho(\mathbf{r}, t)$ as for the interacting particle system,^{33–35,45} and

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_p^N \psi_p(\mathbf{r}, t) \psi_p^*(\mathbf{r}', t) \quad (2.2)$$

is the single electron density matrix, which is not necessary the same as one-particle density matrix of the interacting system, and N being the number of electrons. $v^{\text{eff}}(\mathbf{r}, t)$ is given by

$$v^{\text{eff}}(\mathbf{r}, t) = \mathcal{P}(\mathbf{r}, t) + v^{\text{ext}}(\mathbf{r}) + v^{\text{cl}}(\mathbf{r}, t) + v^{\text{xc}}(\mathbf{r}, t), \quad (2.3)$$

where $\mathcal{P}(\mathbf{r}, t)$ is an external perturbation (e.g., applied electric field) turned on adiabatically, and $v^{\text{ext}}(\mathbf{r})$ is an external potential typically mediated by the interactions of electrons with nuclei

$$v^{\text{ext}}(\mathbf{r}) = \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|}, \quad (2.4)$$

Z_{α} and R_{α} being the charge and the coordinate of α th nucleus, respectively. $v^{\text{cl}}(\mathbf{r}, t)$ represents a Coulomb interaction between electrons

$$v^{\text{cl}}(\mathbf{r}, t) = \int \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.5)$$

Finally the exchange-correlation potential $v^{\text{xc}}(\mathbf{r}, t)$ is given by a functional derivative of the exchange-correlation action A^{xc} as

$$v^{\text{xc}}(\mathbf{r}, t) = \frac{\delta A^{\text{xc}}[n]}{\delta n(\mathbf{r}, t)}. \quad (2.6)$$

We will limit our discussion to the adiabatic approximation^{33–35,43,48} where the retardation effects in the exchange-correlation potential are neglected and the functional A^{xc} of $n(\mathbf{r}, t)$ over both space and time is approximated by E^{xc} (the exchange-correlation functional of the time-independent Kohn–Sham theory) which is a functional of n_t of space with fixed t :

$$v^{\text{xc}}(\mathbf{r}, t) \approx \frac{\delta E^{\text{xc}}[n_t]}{\delta n_t(\mathbf{r}, t)}. \quad (2.7)$$

The nonadiabatic extensions of the TDDFT have been extensively discussed in the literature.^{45,26,46,55}

The stationary point is defined by a solution of the static Kohn–Sham equations [$\mathcal{P}(\mathbf{r}, t) = 0$]

$$\left[-\frac{1}{2} \nabla^2 + v^{\text{ext}}(\mathbf{r}) + v^{\text{cl}}[\bar{n}](\mathbf{r}) + v^{\text{xc}}[\bar{n}](\mathbf{r}) \right] \varphi_p(\mathbf{r}) = \varepsilon_p \varphi_p(\mathbf{r}), \quad (2.8)$$

where ε_p and $\varphi_p(\mathbf{r})$ denote energies and wave functions of occupied single particle states (molecular orbitals, MOs), respectively, and $\bar{n}(\mathbf{r}) = \bar{\rho}(\mathbf{r}) = \sum_p^N |\varphi_p(\mathbf{r})|^2$ is the ground-state charge density. The respective energy of the electronic system at stationary point is then given by a functional

$$E[\bar{n}] = T[\bar{n}] + E^{\text{ext}}[\bar{n}] + E^{\text{cl}}[\bar{n}] + E^{\text{xc}}[\bar{n}], \quad (2.9)$$

where the terms in the rhs of the equation correspond to the kinetic, external potential, Coulomb, and exchange-correlation energies, respectively, and $E_g = E[\bar{n}] = \min_{\rho \in N} E[\rho]$ is a minimum of the functional $E[\rho]$ in the space N of single Slater determinants (defined up to a phase) known as the Grassman manifold $\mathbf{M} = \mathbf{G}(N; K; C)$, K being the basis set size and N is the number of electrons. This can be represented as the space of Hermitian $K \times K$ single-electron density matrices with $\rho^2 = \rho$ and $\text{rank}(\rho) = N$.²⁵

Subsequently, the TDDFT can be formulated as classical dynamics in the phase space N with equations of motion for density matrix ρ ^{26,43,44} satisfying the Hamilton–Liouville form and equivalent to Eq. (2.1):

$$i \frac{d\rho}{dt} = \{H_T, \rho\}, \quad (2.10)$$

where the classical Hamiltonian $H_T = E[n] + \int d\mathbf{r} \mathcal{P}(\mathbf{r}, t) n(\mathbf{r}, t)$, $n(\mathbf{r}, t) = \rho(\mathbf{r}, \mathbf{r}, t)$ and $\rho = \bar{\rho} + \delta\rho(t)$.

Equation (2.10) can be conveniently represented and solved in the matrix form by introducing the atomic basis set of single-particle spin orbitals (AOs) $\chi_{i\sigma}(\mathbf{r})$ and expanding MOs as a linear combination of AOs (LCAO method):^{1–3} $\varphi_{p\sigma}(\mathbf{r}) = \sum_i C_{ip\sigma} \chi_{i\sigma}(\mathbf{r})$ where index σ refers to the spin space and C is a matrix of the expansion coefficients. For clarity, we will assume the AO basis functions are orthonormal [$\int d\mathbf{r} \chi_{i\sigma}^*(\mathbf{r}) \chi_{j\sigma'}(\mathbf{r}) = \delta_{ij} \delta_{\sigma\sigma'}$] and linearly independent. Otherwise, for example, the Löwdin’s transformation may be used ($\tilde{\chi} = S^{-\frac{1}{2}} \chi$, S being the overlap matrix) for basis set orthogonalization.² Modern quantum chemical codes handle efficiently nonorthogonality and linear dependency of atomic basis functions.^{56–58}

Equation (2.10) in the matrix form can be written as

$$i \frac{d\delta\rho}{dt} = [F(\rho), \rho] + [\mathcal{P}(t), \rho]. \quad (2.11)$$

Here all quantities are $K \times K$ matrices, K being the basis set size, and the square brackets denote a commutator of two operators. Equation (2.11) is identical to the time-dependent Hartree–Fock (TDHF) equation of motion.^{14,59} We will define all variables in Eq. (2.11) in a generic way to treat simultaneously pure TDDFT and TDHF, and mixed approaches that use hybrid functionals.

$\mathcal{P}(t)$ is an external perturbation operator which in the case of the driving electric field is given by

$$\mathcal{P}_{ij\sigma}(t) = -\mathcal{E}(t) \cdot \boldsymbol{\mu}_{ij\sigma} = -\sum_{s=x,y,z} \mathcal{E}^{(s)}(t) \mu_{ij\sigma}^{(s)}, \quad (2.12)$$

where $\mathcal{E}^{(s)}(t)$ is an external field along s -direction and $\mu_{ij\sigma}^{(s)}$ is a respective dipole matrix calculated in the AO basis set as $\mu_{ij\sigma}^{(s)} = \int d\mathbf{r} \chi_{i\sigma}^*(\mathbf{r}) \mathbf{r}^{(s)} \chi_{j\sigma}(\mathbf{r})$.

$F(\rho)$ is a Fock operator given by

$$F_{ij\sigma}(\rho) = t_{ij\sigma} + V_{ij\sigma}(\rho) + v_{ij\sigma}^{\text{xc}}(\rho), \quad (2.13)$$

where $t_{ij\sigma}$ are one-electron integrals accounting for the kinetic energy and nuclear attraction of an electron corresponding to $-\frac{1}{2}\nabla^2$ and v^{ext} kernels, respectively, and $V(\rho)$ is a Coulomb-exchange operator

$$V_{ij\sigma}(\rho) = \sum_{kl\sigma'} ((ij\sigma|kl\sigma') \rho_{kl\sigma'} - c_x (ik\sigma|jl\sigma) \rho_{kl\sigma} \delta_{\sigma\sigma'}). \quad (2.14)$$

Here $(ij\sigma|kl\sigma')$ are two-electron integrals representing electron–electron Coulomb interactions corresponding to the v^{cl} kernel. For practical purposes, modern computational software codes use the same AO basis sets and the matrix elements for the single-electron integrals ($t_{ij\sigma}$) and the two-electrons integrals $(ij\sigma|kl\sigma')$ are usually the same in both *ab initio* and DFT computations. The hybrid mixing parameter c_x accounts for the amount of Hartree–Fock exchange in $F(\rho)$. Introduced by Becke in 1993,^{60,61} this parameter allows to interpolate between pure DFT ($c_x = 0$) and Hartree–Fock ($c_x = 1$ and $E_{\text{xc}} = 0$) theories.

Finally, $v_{ij\sigma}^{\text{xc}}(\rho)$ is a matrix element corresponding to the exchange–correlation $v^{\text{xc}}[n]$ kernel which could be a complicated function with unknown exact form. We will use a Taylor expansion of $v^{\text{xc}}(\rho)$ given by

$$v^{\text{xc}}(\rho) = v^{(0)} + v^{(1)}(\delta\rho) + v^{(2)}(\delta\rho, \delta\rho) + v^{(3)}(\delta\rho, \delta\rho, \delta\rho) \quad (2.15)$$

which is sufficient for computing the nonlinear optical response to the third order in the driving field. Here

$$v_{ij\sigma}^{(1)}(\delta\rho) = \sum_{kl\sigma'} f_{ij\sigma,kl\sigma'} \delta\rho_{kl\sigma'}, \quad (2.16)$$

$$v_{ij\sigma}^{(2)}(\delta\rho, \delta\rho) = \frac{1}{2!} \sum_{kl\sigma', mn\sigma''} g_{ij\sigma,kl\sigma',mn\sigma''} \delta\rho_{kl\sigma'} \delta\rho_{mn\sigma''}, \quad (2.17)$$

$$v_{ij\sigma}^{(3)}(\delta\rho, \delta\rho, \delta\rho) = \frac{1}{3!} \sum_{kl\sigma', mn\sigma'', pq\sigma'''} h_{ij\sigma,kl\sigma',mn\sigma'',pq\sigma'''} \times \delta\rho_{kl\sigma'} \delta\rho_{mn\sigma''} \delta\rho_{pq\sigma'''}. \quad (2.18)$$

In Eqs. (2.15)–(2.18) quantities $v_{ij\sigma}^{(0)}$, $f_{ij\sigma,kl\sigma'}$, $g_{ij\sigma,kl\sigma',mn\sigma''}$, and $h_{ij\sigma,kl\sigma',mn\sigma'',pq\sigma'''}$ are the matrix elements of kernels corresponding to the functional derivatives

$$v_{\sigma}^{(0)}(\mathbf{r}) = \frac{\delta E^{\text{xc}}}{\delta n_{\sigma}(\mathbf{r})}, \quad (2.19)$$

$$f_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E^{\text{xc}}}{\delta n_{\sigma}(\mathbf{r}) \delta n_{\sigma'}(\mathbf{r}')}, \quad (2.20)$$

$$g_{\sigma\sigma'\sigma''}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \frac{\delta^3 E^{\text{xc}}}{\delta n_{\sigma}(\mathbf{r}) \delta n_{\sigma'}(\mathbf{r}') \delta n_{\sigma''}(\mathbf{r}'')}, \quad (2.21)$$

$$h_{\sigma\sigma'\sigma''\sigma'''}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \frac{\delta^4 E^{\text{xc}}}{\delta n_{\sigma}(\mathbf{r}) \delta n_{\sigma'}(\mathbf{r}') \delta n_{\sigma''}(\mathbf{r}'') \delta n_{\sigma'''}(\mathbf{r}''')}, \quad (2.22)$$

calculated, for example, as

$$f_{ij\sigma,kl\sigma'} = \int d\mathbf{r} d\mathbf{r}' f_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \mathcal{D}_{ij\sigma}(\mathbf{r}) \mathcal{D}_{kl\sigma'}(\mathbf{r}'),$$

$$g_{ij\sigma,kl\sigma',mn\sigma''} = \int d\mathbf{r}d\mathbf{r}'d\mathbf{r}'' g_{\sigma\sigma'\sigma''}(\mathbf{r},\mathbf{r}',\mathbf{r}'') \times \mathcal{D}_{ij\sigma}(\mathbf{r})\mathcal{D}_{kl\sigma'}(\mathbf{r}')\mathcal{D}_{mn\sigma''}(\mathbf{r}''), \quad (2.23)$$

with $\mathcal{D}_{ij\sigma}(\mathbf{r})$ denoting the derivatives of the electron density with respect to the matrix elements of the KS density matrix

$$\mathcal{D}_{ij\sigma}(\mathbf{r}) = \frac{\delta n_{\sigma}(\mathbf{r})}{\delta \rho_{ij\sigma}} = \chi_{i\sigma}^*(\mathbf{r})\chi_{j\sigma}(\mathbf{r}), \quad (2.24)$$

where $\chi_{i\sigma}$ are orthonormal single-particle spin orbitals (e.g., AOs or MOs). Using expressions (2.15)–(2.18), the Fock operator [Eq. (2.13)] can be represented as

$$F(\rho) = \tilde{t} + \tilde{V}(\rho) + v^{(2)}(\delta\rho, \delta\rho) + v^{(3)}(\delta\rho, \delta\rho, \delta\rho), \quad (2.25)$$

where $\tilde{t} = t + v^{(0)}$ is an effective one-electron operator, $\tilde{V}(\rho) = V(\rho) + v^{(1)}(\delta\rho)$ term is linear in ρ , and $v^{(2)}$ and $v^{(3)}$ terms are quadratic and cubic in $\delta\rho$, respectively. From Eq. (2.25) immediately follows that

$$F(\bar{\rho}) = \tilde{t} + V(\bar{\rho}). \quad (2.26)$$

The stationary solution of Eq. (2.11) (ground state) is given by

$$[F(\bar{\rho}), \bar{\rho}] = 0, \quad (2.27)$$

Being equivalent to Eq. (2.11), Eq. (2.27) is nonlinear and may be readily solved iteratively using the self-consistent field (SCF) procedure.² The ground-state energy can be calculated as

$$E_g = \frac{1}{2} \text{Tr}((\tilde{t} + F(\bar{\rho}))\bar{\rho}), \quad (2.28)$$

where trace includes both spatial and spin variables.

III. PROPERTIES AND ALGEBRA OF TDDFT EQUATIONS

The elements of the driven density matrix $\delta\rho(t)$ in Eq. (2.11) are not independent variables. Following^{14,25,26} we decompose $\delta\rho(t)$ into two components

$$\delta\rho(t) = \xi(t) + T(\xi(t)), \quad (3.1)$$

where ξ represents the particle–hole (interband) and $T(\xi)$ represents the particle–particle and the hole–hole (intra-band) parts. Since the many-electron wave function is represented by a single Slater determinant, the total density matrix $\rho(t)$ must be a projector at all times satisfying $\rho^2 = \rho$. This idempotent property allows us to express intra-band components $T(t)$ through interband part $\xi(t)$ using power series as shown in Appendix A

$$T(\xi) = (I - 2\bar{\rho})(\xi^2 + \xi^4 + 2\xi^6 + \dots). \quad (3.2)$$

In addition the idempotent property of $\bar{\rho}$ permits us to project any single-electron matrix η into the interband ($p-h$) subspace in an arbitrary orthonormal basis set^{14,25,26}

$$\eta_{p-h} = [[\eta, \bar{\rho}], \bar{\rho}]. \quad (3.3)$$

Formally, interband and intra-band subspaces of $K \times K$ density matrices have $2N(K-N)$ and $N^2 + (K-N)^2$ dimensions, respectively (K being the basis set size and N is the

number of electrons). These subspaces are clearly decomposed only in the MO representation. Equations (3.2) and (3.3) provide a convenient way of separating interband and intra-band subspaces in an arbitrary (e.g., AO) orthonormal basis set.

Using expressions (3.1), (2.25), and (2.27), the TDDFT equation of motion (2.11) after projecting onto the interband subspace using Eq. (3.3), can be written as

$$i \frac{\partial \xi}{\partial t} - L\xi = R(\xi)_{p-h} - \mathcal{E}(t) \cdot [\boldsymbol{\mu}, \bar{\rho}], \quad (3.4)$$

where L is a linear operator in Liouville space (i.e., superoperator) given by

$$L\xi = [F(\bar{\rho}), \xi] + [\tilde{V}(\xi), \bar{\rho}]. \quad (3.5)$$

Note that, compared to TDHF, the TDDFT Liouville operator involves the functional derivative $f_{ij\sigma,kl\sigma'}$ (Eq. (2.20)) of exchange–correlation functional included in $\tilde{V}(\xi)$. Finally

$$R(\xi) = -\mathcal{E}(t) \cdot [\boldsymbol{\mu}, \xi + T(\xi)] + [\tilde{V}(\xi), \xi + T(\xi)] + [\tilde{V}(T(\xi)), \bar{\rho} + \xi] + [v^{(2)}(\xi, \xi), \bar{\rho} + \xi] + 2[v^{(2)}(T(\xi), \xi), \bar{\rho}] + [v^{(3)}(\xi, \xi, \xi), \bar{\rho}] \quad (3.6)$$

is the nonlinear part of the TDDFT equation of motion (up to the third order in the driven field) projected onto the particle–hole subspace with Eq. (3.3), which contains higher functional derivatives $g_{ij\sigma,kl\sigma',mn\sigma''}$, and $h_{ij\sigma,kl\sigma',mn\sigma'',pq\sigma'''}$ [Eqs. (2.21), and (2.22)]. The operators \tilde{V} , $F(\bar{\rho})$, $v^{(2)}$, and $v^{(3)}$ were defined by Eqs. (2.25), (2.26), (2.17), and (2.18), respectively. The equations of motion for ξ [Eq. (3.4)] have fewer variables than those for $\delta\rho$ [Eq. (2.11)] but contain additional nonlinearities. However, ξ is the set of truly independent variables which are required to uniquely represent $\delta\rho$.²⁵

We start with the analysis of the solution of the linearized TDDFT equation (3.4) with $R=0$, which defines linear response of the electronic system to the driving field. Since Eq. (3.4) is formally identical to the TDHF equation of motion, it has the same properties which were analyzed in details (e.g., in Ref. 14). Here we briefly overview the essentials. Equation (3.4) can be solved by diagonalizing the Liouville operator $L\xi = \Omega\xi$. Since only particle–hole and hole–particle components of ξ are computed, this is an eigenvalue problem of dimension $2M \times 2M$, $M = N_{\text{occ}} \times N_{\text{vir}} = N \times (K-N)$, which in the MO basis set representation may be recast in the form^{28,29}

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \Omega \begin{bmatrix} X \\ Y \end{bmatrix}. \quad (3.7)$$

This is known as the RPA eigenvalue equation,^{62–67} where X and Y are, respectively, the particle–hole and hole–particle components of the eigenvector $\xi = \begin{bmatrix} X \\ Y \end{bmatrix}$ in the MO representation. In Eq. (3.7) the matrix A is Hermitian and identical to the configuration interaction singles (CIS) matrix. Neglecting B results in the diagonalization of A operator and is known as Tamm–Dancoff approximation (TDA).^{52,62,68} The matrix elements of A and B could be immediately obtained from Eq. (3.5) written in the canonical MO basis set^{35,39,48}

$$A_{ia\sigma,jb\sigma'} = (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) \delta_{ij} \delta_{ab} \delta_{\sigma\sigma'} + (ia\sigma|jb\sigma') + f_{ia\sigma,jb\sigma'} - c_x(ab\sigma|ij\sigma) \delta_{\sigma\sigma'}, \quad (3.8)$$

$$B_{ia\sigma,jb\sigma'} = (ia\sigma|jb\sigma') + f_{ia\sigma,jb\sigma'} - c_x(ja\sigma|ib\sigma) \delta_{\sigma\sigma'}, \quad (3.9)$$

where indices i, j (a, b) run over the occupied (virtual) space.

From Eqs. (3.5) and (3.7) follows that the eigenmodes ξ_ν and eigenfrequencies Ω_ν of L come in conjugated pairs:

$$L\xi_\nu = \Omega_\nu \xi_\nu \quad L\xi_\nu^\dagger = -\Omega_\nu \xi_\nu^\dagger \quad \nu = 1, \dots, M. \quad (3.10)$$

Each vector ξ_ν with frequency Ω_ν has a counterpart $\xi_{-\nu} = \xi_\nu^\dagger$ with frequency $\Omega_{-\nu} = -\Omega_\nu$. Ω_ν represents vertical transition energy from the ground state $|g\rangle$ to the excited state $|\nu\rangle$. In molecules with unstable ground state (saddle point), eigenvalues Ω_ν may be complex which correspond to singlet or triplet instabilities.^{62,69-71} ξ_ν is the correspondent transition density matrix, which represent the changes in the ground-state density matrix upon the electronic excitation, and may be represented as¹⁴

$$(\xi_\nu)_{ij} = \langle g|c_j^\dagger c_i|\nu\rangle, \quad (3.11)$$

where $|g\rangle$ ($|\nu\rangle$) is the ground (excited) state many-electron wave function and c_j^\dagger (c_j) are creation (annihilation) operators of an electron at the j th one-particle orbital satisfying the Fermi anticommutation relationships

$$[c_j^\dagger c_i]_+ = \delta_{ij}; \quad [c_j^\dagger c_i^\dagger]_+ = [c_j c_i]_+ = 0. \quad (3.12)$$

Since L is real, the transition densities can be taken to be real as well.

This block-diagonal structure of operator L [Eq. (3.7)] (known as the symplectic structure²⁵) allow to introduce the following scalar product of any two interband matrices ξ and η :^{14,25,59,72}

$$\langle \xi|\eta \rangle \equiv Tr[\bar{\rho}[\xi^\dagger, \eta)], \quad (3.13)$$

which obeys

$$\langle \xi|\eta \rangle = \langle \eta^\dagger|\xi^\dagger \rangle^* = -\langle \eta|\xi \rangle. \quad (3.14)$$

Here and below we use the angular brackets to denote this scalar product. Equation (3.13) can further be expressed through the particle-hole (X) and hole-particle (Y) components of the interband density matrix in MO representation as^{14,35,39}

$$\langle \xi|\eta \rangle \equiv (X_\xi, X_\eta) - (Y_\xi, Y_\eta), \quad (3.15)$$

where $\xi = \begin{bmatrix} X_\xi \\ Y_\xi \end{bmatrix}$, $\eta = \begin{bmatrix} X_\eta \\ Y_\eta \end{bmatrix}$, and the round brackets denote standard (Hermitian) scalar product of two vectors. We also note that the commutator of $\bar{\rho}$ with an arbitrary interband matrix $\xi = \begin{bmatrix} X_\xi \\ Y_\xi \end{bmatrix}$ corresponds to the transformation $\begin{bmatrix} X_\xi \\ Y_\xi \end{bmatrix} \rightarrow \begin{bmatrix} X_\xi \\ -Y_\xi \end{bmatrix}$.

The Liouville operator L defined by Eq. (3.5) is Hermitian with respect to this scalar product^{14,25}

$$\langle L\xi|\eta \rangle = \langle \xi|L\eta \rangle, \quad (3.16)$$

and the eigenvectors obey the following normalization conditions:

$$\langle \xi_\alpha|\xi_\beta \rangle = Tr[\bar{\rho}[\xi_\alpha^\dagger, \xi_\beta]] = \delta_{\alpha\beta}, \quad (3.17)$$

$$\langle \xi_\alpha|\xi_\beta^\dagger \rangle = Tr[\bar{\rho}[\xi_\alpha^\dagger, \xi_\beta^\dagger]] = \langle \xi_\alpha^\dagger|\xi_\beta \rangle = Tr[\bar{\rho}[\xi_\alpha, \xi_\beta]] = 0. \quad (3.18)$$

Transition densities $\{\xi_\alpha\}$ provide a complete basis set in the interband space.

A scalar product [Eq. (3.13)] also suggests a variational principle formulated by Thouless back in 1961, that yields the lowest positive eigenvalue of Eq. (3.10)⁷³

$$\Omega_{\min} = \min_{\{X, Y\}} \frac{[X, Y] \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}}{|(XX) - (YY)|}. \quad (3.19)$$

The minimum always exists, since the HF stability condition Eq. (2.27) keeps the numerator positive. The denominator can be arbitrarily small, and therefore, the expression has no maximum.

The product of Eq. (3.5) can be calculated directly without constructing and storing the full matrix L in the computer memory. In addition, the existence of a scalar product Eq. (3.13) and a variational principle Eq. (3.19) make possible development of fast Krylov space methods^{74,75} for solution of the RPA eigenproblem, such as modified Lanczos⁷⁶⁻⁷⁸ and Davidson algorithms,^{39,67,79,80} the IDSMA procedure,⁵⁹ etc., which show a formal scaling $\sim K^3$ in time and $\sim K^2$ in memory of computational effort with system size. These algorithms became standard in computational chemistry codes^{56,58} allowing efficient calculations of the excited states with effort comparable to the ground-state calculations.

Finally, we formulate several useful identities which hold for any interband matrices ξ and ζ and directly follow from Eqs. (A1), (3.2), and (3.13):

$$\xi = \rho\xi + \xi\rho, \quad (3.20)$$

$$\rho\xi^2 = \xi^2\rho, \quad (3.21)$$

$$[\xi, \rho] = (I - 2\rho)\xi, \quad (3.22)$$

$$\xi(I - 2\rho)\xi = -(I - 2\rho)\xi^2, \quad (3.23)$$

$$\frac{1}{2}[[\xi, \rho], \xi] = (I - 2\rho)\xi^2, \quad (3.24)$$

$$[[\xi, \rho], \zeta] = (I - 2\rho)(\xi\zeta + \zeta\xi). \quad (3.25)$$

The effective linear Coulomb-exchange operator \tilde{V} is Hermitian and, therefore, obeys

$$(\xi|\tilde{V}(\zeta)) = (\tilde{V}(\xi)|\zeta), \quad (3.26)$$

where the round brackets denote the standard (Hermitian) scalar product of two vectors.

IV. NONLINEAR RESPONSE OF A COUPLED SYSTEM OF ELECTRONIC OSCILLATORS

Equation (3.4) can be envisioned as an equation of motion for coupled harmonic oscillators. In particular, the TDHF approximation is usually considered as a classical limit of the original many-electron system. Each oscillator α is described by two conjugated modes ξ_α and ξ_α^\dagger . We define^{14,81,82} $\xi_{-\alpha} = \xi_\alpha^\dagger$ and $\Omega_{-\alpha} = -\Omega_\alpha$, so that equation $L\Omega_\alpha = \Omega_\alpha \xi_\alpha$ would hold for $\alpha = -M, \dots, M$, $M = N \times (K$

– N). To transform Eq. (3.4) into the oscillator variables we will further introduce complex oscillator amplitudes z_α as

$$\xi(t) = \sum_{\alpha} \xi_{\alpha} z_{\alpha}(t) \quad \alpha = -M, \dots, M. \quad (4.1)$$

Inserting expansion (4.1) into Eq. (3.4) and using Eq. (3.2) we obtain the following equations for the complex amplitudes, when the retained terms that contribute to the third-order optical response:^{14,81}

$$\begin{aligned} i \frac{\partial z_{\alpha}}{\partial t} = & \Omega_{\alpha} z_{\alpha} - \mathcal{E}(t) \cdot \boldsymbol{\mu}_{-\alpha} - \mathcal{E}(t) \cdot \sum_{\beta} \boldsymbol{\mu}_{-\alpha, \beta} z_{\beta} \\ & - \mathcal{E}(t) \cdot \sum_{\beta \gamma} \boldsymbol{\mu}_{-\alpha, \beta \gamma} z_{\beta} z_{\gamma} + \sum_{\beta \gamma} V_{-\alpha, \beta \gamma} z_{\beta} z_{\gamma} \\ & + \sum_{\beta \gamma \delta} V_{-\alpha, \beta \gamma \delta} z_{\beta} z_{\gamma} z_{\delta}, \\ \alpha = & 1, \dots, M, \quad \beta, \gamma, \delta = -M, \dots, M. \end{aligned} \quad (4.2)$$

The amplitudes for the adjoint variables are simply the complex conjugates. Equation (4.2) is the same for both TDDFT and TDHF, and all information about the underlying density functional (or Hamiltonian) is hidden in the excitation energies Ω_{α} and the anharmonicities $\boldsymbol{\mu}_{\alpha}$, $\boldsymbol{\mu}_{\alpha\beta}$, $\boldsymbol{\mu}_{\alpha\beta\gamma}$, $V_{\alpha\beta\gamma}$, and $V_{\alpha\beta\gamma\delta}$, which describe coupling among the electronic oscillators mediated by Coulomb-exchange-correlation \tilde{V} and dipole $\boldsymbol{\mu}$ interactions. These quantities are given by

$$\boldsymbol{\mu}_{\alpha} = Tr([\bar{\rho}, \xi_{\alpha}][\boldsymbol{\mu}, \bar{\rho}]), \quad (4.3)$$

$$\boldsymbol{\mu}_{\alpha\beta} = Tr([\bar{\rho}, \xi_{\alpha}][\boldsymbol{\mu}, \xi_{\beta}]), \quad (4.4)$$

$$\boldsymbol{\mu}_{\alpha\beta\gamma} = Tr([\bar{\rho}, \xi_{\alpha}][\boldsymbol{\mu}, \frac{1}{2}[[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]]), \quad (4.5)$$

$$\begin{aligned} V_{\alpha\beta\gamma} = & Tr([\bar{\rho}, \xi_{\alpha}][\tilde{V}(\xi_{\beta}), \xi_{\gamma}] + [\tilde{V}(\frac{1}{2}[[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]), \bar{\rho}] \\ & + [v^{(2)}(\xi_{\beta}, \xi_{\gamma}, \bar{\rho})]), \end{aligned} \quad (4.6)$$

$$\begin{aligned} V_{\alpha\beta\gamma\delta} = & Tr([\bar{\rho}, \xi_{\alpha}][V(\frac{1}{2}[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}), \xi_{\delta}] \\ & + [V(\xi_{\delta}), \frac{1}{2}[[\xi_{\beta}, \bar{\rho}], \xi_{\delta}]] + [v^{(2)}(\xi_{\beta}, \xi_{\gamma}, \xi_{\delta})] \\ & + [v^{(2)}(\frac{1}{2}[[\xi_{\beta}, \bar{\rho}], \xi_{\gamma}]), \xi_{\delta}, \bar{\rho}] \\ & + [v^{(3)}(\xi_{\beta}, \xi_{\gamma}, \xi_{\delta}, \bar{\rho})]). \end{aligned} \quad (4.7)$$

Here \tilde{V} , $v^{(2)}$, and $v^{(3)}$ are given by Eqs. (2.25), (2.17), and (2.18), respectively. Note that tensors $\boldsymbol{\mu}_{\alpha}$, $\boldsymbol{\mu}_{\alpha\beta}$, $\boldsymbol{\mu}_{\alpha\beta\gamma}$ are vectors with the spatial x , y , and z components (e.g., $\boldsymbol{\mu}_{\alpha}$ is the transition dipole from the ground state to the α excited state). Using identities (3.21)–(3.26) these expressions can be written in a compact form

$$\boldsymbol{\mu}_{\alpha} = Tr(\boldsymbol{\mu} \xi_{\alpha}), \quad (4.8)$$

$$\boldsymbol{\mu}_{\alpha\beta} = \sum_{\alpha\beta}^{\text{perm}} Tr(\boldsymbol{\mu}(I-2\bar{\rho})\xi_{\alpha}\xi_{\beta}), \quad (4.9)$$

$$\boldsymbol{\mu}_{\alpha\beta\gamma} = -\frac{1}{3} \sum_{\alpha\beta\gamma}^{\text{perm}} Tr(\boldsymbol{\mu}\xi_{\alpha}\xi_{\beta}\xi_{\gamma}), \quad (4.10)$$

$$\begin{aligned} V_{\alpha\beta\gamma} = & \frac{1}{2} \sum_{\alpha\beta\gamma}^{\text{perm}} Tr((I-2\bar{\rho})\xi_{\alpha}\xi_{\beta}\tilde{V}(\xi_{\gamma})) \\ & + \frac{1}{6} \sum_{\alpha\beta\gamma}^{\text{perm}} Tr(\xi_{\alpha}v^{(2)}(\xi_{\beta}, \xi_{\gamma})), \end{aligned} \quad (4.11)$$

$$\begin{aligned} V_{\alpha\beta\gamma\delta} = & \frac{1}{12} \sum_{\alpha\beta\gamma\delta}^{\text{perm}} Tr((I-2\bar{\rho})\xi_{\alpha}\xi_{\beta}\tilde{V}((I-2\bar{\rho})\xi_{\gamma}\xi_{\delta})) \\ & - \frac{1}{12} \sum_{\alpha\beta\gamma\delta}^{\text{perm}} Tr(\xi_{\alpha}\xi_{\beta}\xi_{\gamma}\tilde{V}(\xi_{\delta})) \\ & + \frac{1}{12} \sum_{\alpha\beta\gamma\delta}^{\text{perm}} Tr((I-2\bar{\rho})\xi_{\alpha}\xi_{\beta}v^{(2)}(\xi_{\gamma}, \xi_{\delta})) \\ & + \frac{1}{12} \sum_{\alpha\beta\gamma\delta}^{\text{perm}} Tr(\xi_{\alpha}v^{(2)}(((I-2\bar{\rho})\xi_{\beta}\xi_{\gamma}), \xi_{\delta})) \\ & + \frac{1}{24} \sum_{\alpha\beta\gamma\delta}^{\text{perm}} Tr(\xi_{\alpha}v^{(3)}(\xi_{\beta}, \xi_{\gamma}, \xi_{\delta})), \end{aligned} \quad (4.12)$$

where all tensors have been symmetrized with respect to all permutations of their indices.

The response of this effective oscillator system is equivalent to the response of the original electronic system within the underlying TDDFT (or TDHF) approximation. In particular, the time-dependent polarization which determines all optical properties is given by

$$\mathbf{P}(t) = Tr(\boldsymbol{\mu} \delta \rho(t)). \quad (4.13)$$

Using Eqs. (4.1) and (3.2) and retaining terms that contribute to the third-order optical response, the optical polarization in terms of the oscillator amplitudes can be represented as^{14,81}

$$\mathbf{P}(t) = \sum_{\beta} \boldsymbol{\mu}_{\beta} z_{\beta} + \frac{1}{2} \sum_{\beta\gamma} \boldsymbol{\mu}_{\beta\gamma} z_{\beta} z_{\gamma}, \quad \beta, \gamma = -M, \dots, M. \quad (4.14)$$

Linear and nonlinear optical responses are defined in the Appendix B and may be calculated by expanding $z(t)$ in powers of the external field $\mathcal{E}(t)$ to solve Eq. (4.2) as

$$z(t) = z^{(1)}(t) + z^{(2)}(t) + z^{(3)}(t) + \dots \quad (4.15)$$

The expressions for the polarizabilities have been derived in Ref. 14. Here we give the results and outline derivations in Appendices C–E. Frequency dependent first $\alpha(\omega)$, second $\beta(\omega_1, \omega_2)$, and third $\gamma(\omega_1, \omega_2, \omega_3)$ order optical polarizabilities are given by

$$\begin{aligned} \alpha_{ij}(\omega) = & \sum_{\alpha=-M, \dots, M} \frac{S_{\alpha} \mu_{-\alpha}^{(i)} \mu_{\alpha}^{(j)}}{\Omega_{\alpha} - \omega} \\ = & \sum_{\alpha=1, \dots, M} \frac{2\Omega_{\alpha} \mu_{-\alpha}^{(i)} \mu_{\alpha}^{(j)}}{\Omega_{\alpha}^2 - \omega^2}, \end{aligned} \quad (4.16)$$

$$\begin{aligned} \beta_{ijk}(\omega_1, \omega_2) = & - \sum_{\alpha\beta\gamma} \frac{V_{-\alpha\beta\gamma} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(j)} \mu_{-\gamma}^{(k)} S_{\alpha} S_{\beta} S_{\gamma}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_1)(\Omega_{\gamma} - \omega_2)} + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{\alpha\beta}^{(i)} \mu_{-\alpha}^{(j)} \mu_{-\beta}^{(k)} S_{\alpha} S_{\beta}}{(\Omega_{\alpha} - \omega_1)(\Omega_{\beta} - \omega_2)} \\ & + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{-\alpha\beta}^{(j)} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(k)} S_{\alpha} S_{\beta}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_1)} + \frac{1}{2} \sum_{\alpha\beta} \frac{\mu_{-\alpha\beta}^{(j)} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(k)} S_{\alpha} S_{\beta}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_2)}, \end{aligned} \quad (4.17)$$

$$\gamma(\omega_1, \omega_2, \omega_3) = \frac{1}{3!} \sum_{\text{perm}} (\gamma^{(I)} + \gamma^{(II)} + \gamma^{(III)} + \dots + \gamma^{(VIII)}), \quad (4.18)$$

where

$$\gamma_{ijkl}^{(I)} = \sum_{\alpha\beta\gamma} \frac{\mu_{-\alpha\beta}^{(j)} \mu_{-\beta\gamma}^{(k)} \mu_{\alpha}^{(i)} \mu_{-\gamma}^{(l)} S_{\alpha} S_{\beta} S_{\gamma}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_3)}, \quad (4.19)$$

$$\gamma_{ijkl}^{(II)} = \sum_{\alpha\beta\gamma\delta} \frac{-\mu_{-\alpha\beta}^{(j)} V_{-\beta\gamma\delta} \mu_{\alpha}^{(i)} \mu_{-\gamma}^{(k)} \mu_{-\delta}^{(l)} S_{\alpha} S_{\beta} S_{\gamma} S_{\delta}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_2)(\Omega_{\delta} - \omega_3)}, \quad (4.20)$$

$$\gamma_{ijkl}^{(III)} = \sum_{\alpha\beta\gamma} \frac{\mu_{-\alpha\beta\gamma}^{(j)} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(k)} \mu_{-\gamma}^{(l)} S_{\alpha} S_{\beta} S_{\gamma}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_3)}, \quad (4.21)$$

$$\gamma_{ijkl}^{(IV)} = \sum_{\alpha\beta\gamma\delta} \frac{-2V_{-\alpha\beta\gamma} \mu_{-\gamma\delta}^{(k)} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(j)} \mu_{-\delta}^{(l)} S_{\alpha} S_{\beta} S_{\gamma} S_{\delta}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_1)(\Omega_{\gamma} - \omega_2 - \omega_3)(\Omega_{\delta} - \omega_3)}, \quad (4.22)$$

$$\gamma_{ijkl}^{(V)} = \sum_{\alpha\beta\gamma\delta\eta} \frac{2V_{-\alpha\beta\gamma} V_{-\gamma\delta\eta} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(j)} \mu_{-\delta}^{(k)} \mu_{-\eta}^{(l)} S_{\alpha} S_{\beta} S_{\gamma} S_{\delta} S_{\eta}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_1)(\Omega_{\gamma} - \omega_2 - \omega_3)(\Omega_{\delta} - \omega_2)(\Omega_{\eta} - \omega_3)}, \quad (4.23)$$

$$\gamma_{ijkl}^{(VI)} = \sum_{\alpha\beta\gamma\delta} \frac{-V_{-\alpha\beta\gamma\delta} \mu_{\alpha}^{(i)} \mu_{-\beta}^{(j)} \mu_{-\gamma}^{(k)} \mu_{-\delta}^{(l)} S_{\alpha} S_{\beta} S_{\gamma} S_{\delta}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_1)(\Omega_{\gamma} - \omega_2)(\Omega_{\delta} - \omega_3)}, \quad (4.24)$$

$$\gamma_{ijkl}^{(VII)} = \sum_{\alpha\beta\gamma} \frac{\mu_{\alpha\beta}^{(i)} \mu_{-\beta\gamma}^{(k)} \mu_{-\alpha}^{(j)} \mu_{-\gamma}^{(l)} S_{\alpha} S_{\beta} S_{\gamma}}{(\Omega_{\alpha} - \omega_1)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_3)}, \quad (4.25)$$

$$\gamma_{ijkl}^{(VIII)} = \sum_{\alpha\beta\gamma\delta} \frac{-\mu_{\alpha\beta}^{(i)} V_{-\beta\gamma\delta} \mu_{-\alpha}^{(j)} \mu_{-\gamma}^{(k)} \mu_{-\delta}^{(l)} S_{\alpha} S_{\beta} S_{\gamma} S_{\delta}}{(\Omega_{\alpha} - \omega_1)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_2)(\Omega_{\delta} - \omega_3)}. \quad (4.26)$$

Here indices $s = i, j, k, l$ label the spatial directions ($x, y,$ and z), indices $\nu = \alpha, \beta, \gamma, \delta, \eta = -M, \dots, M$ run over the excited states, and Ω_{ν} is positive (negative) for all $\nu > 0$ ($\nu < 0$) according to the convention $\Omega_{-\nu} = -\Omega_{\nu}$, $S_{\alpha} = \text{sign}(\alpha)$, and the other variables are given by Eqs. (4.8)–(4.12). Note, that in Eq. (4.17) the permutations over ω_1 and ω_2 are written explicitly.

Using Eqs. (4.16)–(4.18) for computing frequency-dependent polarizabilities in the adiabatic TDDFT formalism involves several steps:

- (1) Solve the ground state Kohn–Sham equations (2.8) and (2.27) for ground-state density matrix $\bar{\rho}$ using the SCF procedure;
- (2) obtain a set of transition densities $\{\xi_{\alpha}\}$ and transition frequencies $\{\Omega_{\alpha}\}$ from the RPA eigenproblems (3.10) and (3.7) using the fast Krylov diagonalizers;
- (3) calculate anharmonicity tensors (4.8)–(4.12) using $\{\xi_{\alpha}\}$ and functional derivatives given by Eqs. (2.25), (2.17), and (2.18);
- (4) perform summation over states using Eqs. (4.16)–(4.26) to compute the desired response.

Steps (3) and (4) may be combined together to compute the response on the fly at reduced numerical cost.

V. EXCITED-STATE DIPOLE MOMENTS AND THE SOS EXPANSION

Expressions (4.16)–(4.18) for polarizabilities remind the standard sum-over-states equations by Ward and Orr^{8,9} for computing resonant polarizabilities [e.g., the expansion for β is given by Eq. (G18) in Appendix G] since they include the summation over the contributions from the individual excited electronic states, however, there are significant differences. Equations (4.16)–(4.18) do not include the dipole moments between the excited states. Instead, the coupling among the electronic states enters indirectly through dipolar μ and Coulomb-exchange-correlation terms \tilde{V} defined by Eqs. (4.8)–(4.12), where μ_{α} is the transition dipole between ground and $|\alpha\rangle$ excited states and the other terms describe couplings between two (or more) states.

On the other hand, all first order properties, including the dipole moments between the excited states, can be calculated variationally using the analytic gradient technique for the TDDFT linear response properties developed in Refs. 43 and

48 Appendix F outlines this derivation to obtain the excited state dipole moments in a modified form. In principle, these dipole moments could be further used in the SOS expressions to obtain nonlinear polarizabilities of any order, instead of Eqs. (4.16)–(4.18). To clarify the subtleties and the limitations of the SOS approach for TDDFT (or TDHF) we outline in the Appendix G an alternative way of obtaining the transition dipole moments among the excited states. Namely, we could calculate the excited electronic states wave functions in the quantum oscillator system associated with the TDDFT equation of motion (4.2). Subsequently, the dipoles in this auxiliary system that reproduce the second order response Eq. (4.17) using the SOS expressions can be calculated following⁸² as well (Appendix G). Finally, we end up with a complete set of the oscillator states required for the second-order response. These states include all excited states $\{|\alpha\rangle\}$ calculated using the linear response theory by diagonalizing Eq. (3.10). In particular, the expressions for the dipole moments of the excited states derived in Appendices F and G are identical. However, in addition to the states that show up in the linear response we observe the appearance of the states $|1\alpha1\beta\rangle$ with the transition frequencies $\Omega_\alpha + \Omega_\beta$ that correspond to the doubly excited oscillators⁸² and contribute to the second-order response with nonzero dipoles as well.

To understand the significance of these new $|1\alpha1\beta\rangle$ states we further appeal to the interpretation of the SOS expression as the summation over the Liouville space paths.^{6,7,22} Figures 1(A) and 1(B) show paths corresponding to $\mu_{gn}\mu_{nn'}\mu_{n'g}$ and $\mu_{gn}\mu_{nn}\mu_{ng}$ dipole combinations, respectively, in the SOS expression Eq. (G18). Similar interpretation can be applied to Eqs. (4.16)–(4.18) using the effective oscillator system. Using our notation, we define that for $\alpha > 0$ μ_α with Ω_α ($\mu_{-\alpha}$ with $\Omega_{-\alpha} = -\Omega_\alpha$) corresponds to a transition from the ground state to the $|\alpha\rangle$ excited state (from the $|\alpha\rangle$ excited state to the ground state) to interpret positive and negative indices. For example, Fig. 1(C) shows the paths for the linear response corresponding to Eq. (4.16). Subsequently, the terms in the second-order response [Eq. (4.17)] that involve $\mu_{\alpha\beta}$, can be described by the paths shown in Figs. 1(D)–1(F). Here Figs. 1(D) and 1(E) are related to the contributions from the linear response states whereas Fig. 1(E) show the contributions from the doubly excited effective oscillators. These extra terms may not be derived from the linear response theory. We rather need to tailor a specific manifold of the excited states to interpret the exact second-order response Eq. (4.17) with the adiabatic TDDFT theory. The $|1\alpha1\beta\rangle$ states are no longer relevant within the Tamm–Dancoff approximation⁵² when the matrices B and Y [Eq. (3.7)] are set to zero. This leads to vanishing of the $\mu_{\alpha\beta}$ terms when both indices are either positive or negative. In addition, the Coulomb terms $V_{\alpha\beta\gamma}$ also vanish. Subsequently, the unrelaxed density $[[\xi_\alpha^\dagger, \bar{\rho}], \xi_\beta]$ becomes an exact transition density between the excited states $|\alpha\rangle$ and $|\beta\rangle$ with the corresponding transition dipole $\mu_{-\alpha\beta}$, and Eq. (4.17) coincides with Eq. (G18).

The third-order response Eq. (4.18) in the TDDFT include a new manifold of contributing oscillator states $|1\alpha1\beta1\gamma\rangle$. Furthermore, we also note that the expressions

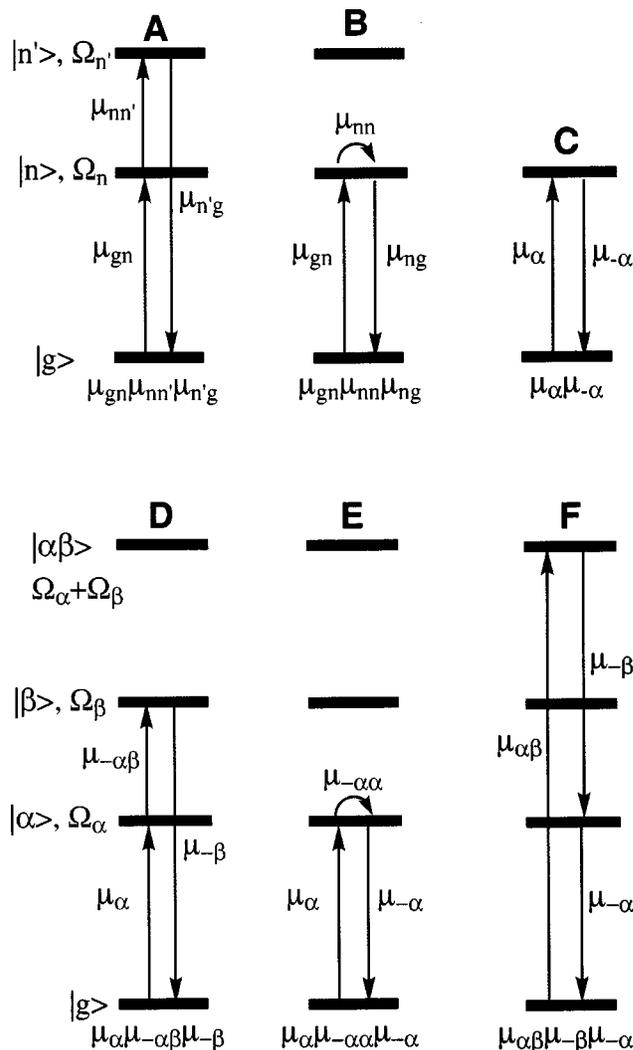


FIG. 1. Liouville space pathways. (A) and (B) show the interpretation of the SOS for the second-order response, (C) displays the representation of the linear TDDFT response [Eq. (4.16)], (D) and (E) show paths over the states from the linear response theory and (F) shows paths over the doubly excited oscillator states contributing to the second-order TDDFT response [Eq. (4.17)].

for the excited state dipole moments and the transition dipoles between the excited states do not include specific anharmonicities $\mu_{\alpha\beta\gamma}$ and $V_{\alpha\beta\gamma\delta}$ [Eqs. (4.9) and (4.12)] characteristic for the third-order optical response. Repeating the procedure outlined in the Appendix G for the third-order response will result in the additional terms in equations for the transition dipoles between the excited states, including $\mu_{\alpha\beta\gamma}$, $V_{\alpha\beta\gamma\delta}$, and second order cross terms $\mu_{\alpha\beta}\mu_{\beta\gamma}$, $\mu_{\alpha\beta}V_{\beta\gamma\delta}$, and $V_{\alpha\beta\gamma}V_{\gamma\delta\eta}$. The higher-order optical responses will modify the expressions for the dipole moments [Eqs. (G10)–(G12)] even further and add a new set of dipoles associated with the higher oscillator states (e.g., $|1\alpha1\beta1\gamma\rangle$). The same arguments are applicable to the respective transition densities [Eqs. (G13)–(G17)]. Thus, each order of the nonlinear optical response will be associated with the different expressions for the excited state dipole moments (densities) and transition dipoles (densities) between the states. In addition the manifold of the contributing excited state would extend with each next order of the re-

sponse. A study of the role of multiply excited states in the higher-order optical responses, in particular within the nonadiabatic TDDFT approach, will be published elsewhere.

VI. CONCLUSION

The density matrix formulation of the time-dependent Kohn–Sham equations^{26,43,44} allows to treat the adiabatic TDDFT on the same footing as TDHF theory, not only within the linear response theory, but also to an arbitrary order in the external perturbation. This originates from the fact that the adiabatic TDDFT evolution can be interpreted as a Hamilton classical mechanics, whose phase space is represented by a Grassman manifold with a canonical Poisson bracket in it (that corresponds to the canonical symplectic structure in a Grassman manifold).²⁶ The same is true for the TDHF dynamics.²⁵ The difference is due to different classical Hamiltonians (these, according to the Hamilton picture of classical mechanics, are just functions in phase space represented by idempotent $\rho^2 = \rho$ single-electron density matrices). In the TDHF case, the classical Hamiltonian is represented by first- and second-order terms in ρ . Whereas in the adiabatic TDDFT case, the expansion of the classical Hamiltonian in powers of ρ contains generally all orders because of a nontrivial form of the exchange-correlation functional. Even though both TDDFT and TDHF are described by exactly the same equations of motion for a driven density matrix [Eq. (3.4)], which originates from the same dynamical structure of the phase space, special care should be taken to account for a complex nature of exchange-correlation functional $E^{xc}[n]$ that enters the equation coefficients as higher-order functional derivatives [Eqs. (2.20)–(2.22)].

Subsequently, in terms of response, Eq. (3.4) can be treated as dynamics of a set of weakly coupled classical harmonic oscillators [Eq. (4.2)],^{14,81,82} where the transition densities provide a convenient coordinate system in the vicinity of a stationary point that describes the relevant ground-state properties. Linear and nonlinear response of a real electronic system is thus mapped by adiabatic TDDFT (or TDHF) to the corresponding response of this effective oscillator system. This allows us to obtain closed expressions for the linear [Eq. (4.16)], second [Eq. (4.17)], and third [Eq. (4.18)] order frequency-dependent optical polarizabilities. The quasiparticle representation is universal and very convenient for computing the spectroscopic probes (such as four-wave-mixing spectra),⁸¹ building related effective reduced models, and coupling molecular system to the thermostat.²² Our subsequent studies show that the results of calculations, which use these equations for computing the third-order optical response in extended molecular systems, agree well with experiment, in particular, for two-photon absorption properties.^{83,84} Further applications of the adiabatic TDDFT for computing nonlinear molecular properties will be reported elsewhere.

Expressions (4.16)–(4.18) require a set of transition densities $\{\xi_\alpha\}$ with the corresponding frequencies $\{\Omega_\alpha\}$, that can be obtained from the linear response theory by diagonalizing the Liouville operator [Eq. (3.10)], and the corresponding functional derivatives [Eq. (2.15)]. Application of the traditional SOS expressions^{8,9} [e.g., Eq. (G18)] for calculat-

ing nonlinear responses is problematic since the dipole moments of the excited states and the transition dipoles between excited states are not well defined, i.e., quantities obtained within the linear response theory are suitable for calculating the second order response, whereas treatment of the higher order responses in the frame of the SOS approach requires redefinition of the dipoles. In addition, the manifold of contributing states includes states $(|1\alpha1\beta\rangle$ and $|1\alpha1\beta1\gamma\rangle)$ ⁸² that may not be obtained in the linear response theory.

The variation of the number of excited states with an order of nonlinear response is an indication of the fundamental limitation of the adiabatic TDDFT theory. This deficiency is lifted in the nonadiabatic TDDFT formulation where the solution of the spectral problem instead of the eigenvalue problem [Eq. (3.10)] has the number of electronic states equals to the number of states in the related many-electron problem.^{26,55} This is accounted for by a complex frequency dependence of the Liouville operator $\hat{L}(\omega)$ in the case of the nonadiabatic spectral problem $\hat{L}(\omega)\xi = \omega\xi$.

Finally we note that, as opposed to the approximate case of the adiabatic TDDFT, the transition dipoles between the excited states should be naturally well-defined in the case of exact TDDFT. This creates a set of requirements that can be interpreted as sum rules the exact time-dependent density functional should satisfy. These sum rules can be either used as a test for approximate time-dependent density functionals, or, alternatively, they can be applied for building time-dependent density functionals with the sum rules built in. This will be published elsewhere.

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APPENDIX A: RELATIONS BETWEEN THE INTER- AND INTRABAND COMPONENTS OF THE DENSITY MATRIX

The single-electron reduced density matrix satisfies the idempotency condition $\rho^2 = \rho$, i.e.,

$$(\bar{\rho} + \xi(t) + T(\xi(t)))^2 = \bar{\rho} + \xi(t) + T(\xi(t)), \quad (\text{A1})$$

at all times.

To simplify this expression it is possible to use following relations: $\bar{\rho}^2 = \bar{\rho}$, $\xi = \bar{\rho}\xi + \xi\bar{\rho}$, and $T\bar{\rho} = \bar{\rho}T$. A simple rule may be applied to separate the remaining terms: Product of two inter- (or two intra-) band matrices gives an intraband matrix, whereas product of inter- into intra- (or intra- into inter-) band matrices results in an interband matrix. Finally, the intraband part of Eq. (A1) is

$$(T(\xi))^2 + (2\bar{\rho} - I)T(\xi) + \xi^2 = 0, \quad (\text{A2})$$

where I is a unit matrix. The formal solution of this quadratic equation, with the condition $T(\xi=0) = 0$ yields¹⁴

$$T(\xi) = \left(\frac{I}{2} - \bar{\rho} \right) (I - \sqrt{I - 4\xi^2}). \quad (\text{A3})$$

A Taylor series expansion of this expression in ξ finally gives

$$T(\xi) = (I - 2\bar{\rho}) \sum_{m=1}^{\infty} \frac{2^m (2m-3)!!}{2m!} \xi^{2m}. \quad (\text{A4})$$

An alternative expansion is^{25,59}

$$T(\xi) = \frac{1}{2!} [[\xi, \bar{\rho}], \xi] + \frac{1}{4!} [[\xi, \bar{\rho}], [[\xi, \bar{\rho}], [[\xi, \bar{\rho}], \xi]]] + \dots \quad (\text{A5})$$

When ξ is small

$$T(\xi) \approx (I - 2\bar{\rho}) \xi^2 = \frac{1}{2!} [[\xi, \bar{\rho}], \xi], \quad (\text{A6})$$

is quadratic in ξ which is sufficient for calculating nonlinear responses up to the third order in the driving field.

APPENDIX B: DEFINITION OF NONLINEAR RESPONSE FUNCTIONS

Optical polarizabilities are induced by the deviation of the one electron density matrix from its equilibrium value $\bar{\rho}$ expanded in powers of the external field $\mathcal{E}(t)$. Following Refs. 22, 25 we define time domain response functions $R^{(q)}(t, \tau_1, \dots, \tau_j)$ up to the third order ($q=1,2,3$):

$$P^{(1)}(t) = \int_{-\infty}^t d\tau \mathcal{E}(\tau) R^{(1)}(t, \tau), \quad (\text{B1})$$

$$P^{(2)}(t) = \int_{-\infty}^t \int_{-\infty}^t d\tau_1 d\tau_2 \mathcal{E}(\tau_1) \mathcal{E}(\tau_2) R^{(2)}(t, \tau_1, \tau_2), \quad (\text{B2})$$

$$P^{(3)}(t) = \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t d\tau_1 d\tau_2 d\tau_3 \mathcal{E}(\tau_1) \mathcal{E}(\tau_2) \mathcal{E}(\tau_3) \times R^{(3)}(t, \tau_1, \tau_2, \tau_3). \quad (\text{B3})$$

The corresponding frequency domain polarizabilities $R^{(q)}(-\omega_s; \omega_1, \dots, \omega_j)$ ($q=1,2,3$) are given by

$$P^{(1)}(\omega_s) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} R^{(1)}(-\omega_s; \omega) \mathcal{E}(\omega), \quad (\text{B4})$$

$$P^{(2)}(\omega_s) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \times R^{(2)}(-\omega_s; \omega_1, \omega_2) \mathcal{E}(\omega_1) \mathcal{E}(\omega_2), \quad (\text{B5})$$

$$P^{(3)}(\omega_s) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \frac{d\omega_3}{2\pi} \times R^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) \mathcal{E}(\omega_1) \mathcal{E}(\omega_2) \mathcal{E}(\omega_3). \quad (\text{B6})$$

Here $\mathcal{E}(\omega)$ is the Fourier transform of the time-dependent external field $\mathcal{E}(t)$ defined as

$$f(\omega) \equiv \int dt f(t) e^{i\omega t}, \quad f(t) \equiv \frac{1}{2\pi} \int d\omega f(\omega) e^{-i\omega t}. \quad (\text{B7})$$

For clarity in Appendices B–E we suppress the indices of the spatial directions (x, y, z) . One spatial index tensors (vectors) are $P^{(q)}$, \mathcal{E} , μ_α , $\mu_{\alpha\beta}$, and $\mu_{\alpha\beta\gamma}$. $R^{(1)}[\alpha(\omega)]$, $R^{(2)}[\beta(\omega_1, \omega_2)]$, and $R^{(3)}[\gamma(\omega_1, \omega_2, \omega_3)]$ are two, three, and four indices tensors, respectively. The multiplication of these tensors assumes the summation over the respective spatial indices according to the usual convention in the tensor algebra [e.g., $P_k^{(2)}(\omega_s) \sim R^{(2)}(-\omega_s; \omega_1, \omega_2) \mathcal{E}(\omega_1) \mathcal{E}(\omega_2) = \sum_{ij} R_{ijk}^{(2)}(-\omega_s; \omega_1, \omega_2) \mathcal{E}^{(i)}(\omega_1) \mathcal{E}^{(j)}(\omega_2)$, where i, j , and k run over the spatial $(x, y, \text{ and } z)$ components].

The relations between response functions and polarizabilities are obtained by comparing Eqs. (B1)–(B3) with Eqs. (B4)–(B6) and using the Fourier transform Eq. (B7)

$$R^{(1)}(-\omega_s; \omega) = \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau e^{-i\omega\tau} R^{(1)}(t, \tau), \quad (\text{B8})$$

$$R^{(2)}(-\omega_s; \omega_1, \omega_2) = \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau_1 e^{-i\omega_1\tau_1} \times \int_{-\infty}^t d\tau_2 e^{-i\omega_2\tau_2} R^{(2)}(t, \tau_1, \tau_2), \quad (\text{B9})$$

$$R^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau_1 e^{-i\omega_1\tau_1} \times \int_{-\infty}^t d\tau_2 e^{-i\omega_2\tau_2} \times \int_{-\infty}^t d\tau_3 e^{-i\omega_3\tau_3} R^{(3)}(t; \tau_1, \tau_2, \tau_3). \quad (\text{B10})$$

The linear, second- and third-order polarizabilities are usually denoted α , β , and γ , respectively,

$$R^{(1)}(\omega_s = \omega; \omega) = 2\pi \delta(-\omega_s + \omega) \alpha(\omega), \quad (\text{B11})$$

$$R^{(2)}(\omega_s = \omega_1 + \omega_2, \omega_1, \omega_2) = 2\pi \delta(-\omega_s + \omega_1 + \omega_2) \beta(\omega_1, \omega_2), \quad (\text{B12})$$

$$R^{(3)}(\omega_s = \omega_1 + \omega_2 + \omega_3; \omega_1, \omega_2, \omega_3) = 2\pi \delta(-\omega_s + \omega_1 + \omega_2 + \omega_3) \gamma(\omega_1, \omega_2, \omega_3), \quad (\text{B13})$$

where $\delta(\omega)$ is the Dirac delta function.

APPENDIX C: LINEAR RESPONSE

To calculate the linear response we start with the equation of motion for $z_\alpha^{(1)}$ obtained from Eq. (4.2) using expansion Eq. (4.15)

$$i \frac{\partial z_\alpha^{(1)}}{\partial t} = \Omega_\alpha z_\alpha^{(1)} - \mathcal{E}(t) \mu_{-\alpha}, \quad \alpha = 1, \dots, M. \quad (\text{C1})$$

The solution of this equation for $z_\alpha^{(1)}$ and its complex conjugate $z_\alpha^{*(1)}$ is

$$z_\alpha^{(1)} = i \int_{-\infty}^t \mathcal{E}(\tau) \mu_{-\alpha} G_\alpha(t - \tau), \quad \alpha > 0, \quad (\text{C2})$$

$$z_{\alpha}^{*(1)} = z_{-\alpha}^{(1)} = -i \int_{-\infty}^t \mathcal{E}(\tau) \mu_{\alpha} G_{\alpha}^{*}(t-\tau), \quad \alpha > 0, \quad (C3)$$

where we introduce time-domain Green function

$$G_{\alpha}(t) = \theta(t) e^{-i\Omega_{\alpha} t},$$

$$G_{-\alpha}(t) = \theta(t) e^{-i\Omega_{-\alpha} t} = \theta(t) e^{i\Omega_{\alpha} t}, \quad (C4)$$

and $\theta(t)$ is the Heavyside step function. Using the notation $S_{\alpha} = \text{sign}(\alpha)$, Eqs. (4.2) and (4.2) can be represented in a compact notation.

$$z_{\alpha}^{(1)} = i S_{\alpha} \int_{-\infty}^t \mathcal{E}(\tau) \mu_{-\alpha} G_{\alpha}(t-\tau), \quad \alpha = -M, \dots, M, \quad (C5)$$

where positive and negative α correspond to $z_{\alpha}^{(1)}$ and $z_{\alpha}^{*(1)}$, respectively.

Inserting Eq. (C5) into Eq. (4.14) we finally obtain for the linear polarizability

$$P^{(1)}(t) = \sum_{\alpha=-M, \dots, M} z_{\alpha}^{(1)} \mu_{\alpha}$$

$$= \sum_{\alpha=-M, \dots, M} i S_{\alpha} \int_{-\infty}^t \mathcal{E}(\tau) \mu_{-\alpha} \mu_{\alpha} G_{\alpha}(t-\tau). \quad (C6)$$

The linear response function [Eq. (B1)] is then

$$R^{(1)}(t, \tau) = i \sum_{\alpha=-M, \dots, M} i S_{\alpha} \mu_{-\alpha} \mu_{\alpha} G_{\alpha}(t-\tau). \quad (C7)$$

Using Eqs. (B8) and (B11) we obtain the linear polarizability given by Eq. (4.16).

APPENDIX D: SECOND-ORDER RESPONSE

The equation of motion for $z_{\alpha}^{(2)}$ is

$$i \frac{\partial z_{\alpha}^{(2)}}{\partial t} = \Omega_{\alpha} z_{\alpha}^{(2)} - \mathcal{E}(t) \sum_{\beta} \mu_{-\alpha, \beta} z_{\beta}^{(1)}$$

$$+ \sum_{\beta, \gamma} V_{-\alpha \beta \gamma} z_{\beta}^{(1)} z_{\gamma}^{(1)},$$

$$\alpha = 1, \dots, M, \quad \beta, \gamma = -M, \dots, M. \quad (D1)$$

and its solution, which includes complex conjugate, is

$$z_{\alpha}^{(2)} = i \int_{-\infty}^t d\tau_1 S_{\alpha} G_{\alpha}(t-\tau_1) \Gamma_{\alpha}^{(2)}(\tau_1), \quad \alpha = -M, \dots, M, \quad (D2)$$

where

$$\Gamma_{\alpha}^{(2)}(\tau_1) = \sum_{\beta \gamma} V_{-\alpha \beta \gamma} \int_{-\infty}^{\tau_1} \int_{-\infty}^{\tau_1} d\tau_2 d\tau_3 \mathcal{E}(\tau_2) \mathcal{E}(\tau_3)$$

$$\times \mu_{-\beta} \mu_{-\gamma} S_{\beta} S_{\gamma} G_{\beta}(\tau_1 - \tau_2) G_{\gamma}(\tau_1 - \tau_3)$$

$$+ i \mathcal{E}(\tau_1) \sum_{\beta} \mu_{-\alpha \beta} \int_{-\infty}^{\tau_1} \mathcal{E}(\tau_2) \mu_{-\beta} S_{\beta} G_{\beta}(\tau_1 - \tau_2),$$

$$\alpha, \beta, \gamma = -M, \dots, M. \quad (D3)$$

Inserting Eqs. (C5) and (D2) into Eq. (4.14) and keeping all terms up to the second order we find that the second-order response function has three contributions:

$$R^{(2)}(t, \tau_1 \tau_2) = R_I^{(2)} + R_{II}^{(2)} + R_{III}^{(2)}, \quad (D4)$$

where

$$R_I^{(2)}(t, \tau_1 \tau_2) = - \sum_{\alpha \beta} \mu_{-\alpha, \beta} \mu_{\alpha} \mu_{-\beta} S_{\alpha} S_{\beta} G_{\alpha}(t-\tau_1)$$

$$\times G_{\beta}(\tau_1 - \tau_2), \quad (D5)$$

$$R_{II}^{(2)}(t, \tau_1 \tau_2) = i \int_{\tau_2}^t d\tau \sum_{\alpha \beta \gamma} V_{-\alpha \beta \gamma} \mu_{\alpha} \mu_{-\beta} \mu_{-\gamma} S_{\alpha} S_{\beta} S_{\gamma}$$

$$\times G_{\alpha}(t-\tau) G_{\beta}(\tau - \tau_1) G_{\gamma}(\tau - \tau_2), \quad (D6)$$

$$R_{III}^{(2)}(t, \tau_1 \tau_2) = - \sum_{\alpha \beta} \mu_{\alpha \beta} \mu_{-\alpha} \mu_{-\beta} S_{\alpha} S_{\beta} G(t-\tau_1) G(t-\tau_2). \quad (D7)$$

Using Eq. (B9) we finally obtain the second-order polarizability [Eq. (4.17)].

APPENDIX E: THIRD-ORDER RESPONSE

The equation of motion for $z_{\alpha}^{(3)}$ is

$$i \frac{\partial z_{\alpha}^{(3)}}{\partial t} = \Omega_{\alpha} z_{\alpha}^{(3)} - \left[\mathcal{E}(t) \sum_{\beta} \mu_{-\alpha \beta} z_{\beta}^{(2)} \right.$$

$$+ \mathcal{E}(t) \sum_{\beta \gamma} \mu_{-\alpha \beta \gamma} z_{\beta}^{(1)} z_{\gamma}^{(1)} - 2 \sum_{\beta \gamma} V_{-\alpha \beta \gamma} z_{\beta}^{(1)} z_{\gamma}^{(2)}$$

$$\left. - \sum_{\beta \gamma \delta} V_{-\alpha \beta \gamma \delta} z_{\beta}^{(1)} z_{\gamma}^{(1)} z_{\delta}^{(1)} \right],$$

$$\alpha = 1, \dots, M, \quad \beta, \gamma, \delta = -M, \dots, M. \quad (E1)$$

and its solution, which includes the complex conjugate, is

$$z_{\alpha}^{(3)} = i \int_{-\infty}^t d\tau_1 S_{\alpha} G_{\alpha}(t-\tau_1) \Gamma_{\alpha}^{(3)}(\tau_1), \quad \alpha = -M, \dots, M, \quad (E2)$$

where

$$\Gamma_{\alpha}^{(3)}(\tau_1) = \mathcal{E}(\tau_1) \sum_{\beta} \mu_{-\alpha \beta} z_{\beta}^{(2)}(\tau_1)$$

$$+ \mathcal{E}(\tau_1) \sum_{\beta \gamma} \mu_{-\alpha \beta \gamma} z_{\beta}^{(1)}(\tau_1) z_{\gamma}^{(1)}(\tau_1)$$

$$- 2 \sum_{\beta \gamma} V_{-\alpha \beta \gamma} z_{\beta}^{(1)}(\tau_1) z_{\gamma}^{(2)}(\tau_1)$$

$$- \sum_{\beta \gamma \delta} V_{-\alpha \beta \gamma \delta} z_{\beta}^{(1)}(\tau_1) z_{\gamma}^{(1)}(\tau_1) z_{\delta}^{(1)}(\tau_1). \quad (E3)$$

Here $\alpha, \beta, \gamma, \delta = -M, \dots, M$ and $z^{(1)}(\tau_1)$ and $z^{(2)}(\tau_1)$ are given by Eqs. (C5) and (D2). Inserting Eqs. (C5), (D2), and (E2) into Eq. (4.14) and keeping all terms up to third order we obtain the following 8 term expression for the third-order response function:

$$R^{(3)}(t, \tau_1 \tau_2 \tau_3) = R_I + R_{II} + R_{III} + R_{IV} + R_V + R_{VI} + R_{VII} + R_{VIII}, \quad (\text{E4})$$

where

$$R_I^{(3)}(t, \tau_1 \tau_2 \tau_3) = -i \sum_{\alpha\beta\gamma} \mu_{-\alpha\beta} \mu_{-\beta\gamma} \mu_{\alpha\mu} \mu_{-\gamma} S_\alpha S_\beta S_\gamma \times G_\alpha(t - \tau_1) G_\beta(\tau_1 - \tau_2) G_\gamma(\tau_2 - \tau_3), \quad (\text{E5})$$

$$R_{II}^{(3)}(t, \tau_1 \tau_2 \tau_3) = - \sum_{\alpha\beta\gamma\delta} \mu_{-\alpha\beta} V_{-\beta\gamma\delta} \mu_{\alpha\mu} \mu_{-\gamma} \mu_{-\delta} S_\alpha S_\beta S_\gamma S_\delta \times \int_{\tau_3}^t d\tau G_\alpha(t - \tau) G_\beta(\tau_1 - \tau) \times G_\gamma(\tau - \tau_2) G_\delta(\tau - \tau_3), \quad (\text{E6})$$

$$R_{III}^{(3)}(t, \tau_1 \tau_2 \tau_3) = -i \sum_{\alpha\beta\gamma} \mu_{-\alpha\beta\gamma} \mu_{\alpha\mu} \mu_{-\beta} \mu_{-\gamma} S_\alpha S_\beta S_\gamma \times G_\alpha(t - \tau_1) G_\beta(\tau_1 - \tau_2) G_\gamma(\tau_1 - \tau_3), \quad (\text{E7})$$

$$R_{IV}^{(3)}(t, \tau_1 \tau_2 \tau_3) = -2 \sum_{\alpha\beta\gamma\delta} V_{-\alpha\beta\gamma} \mu_{-\gamma\delta} \mu_{\alpha\mu} \mu_{-\beta} \mu_{-\delta} S_\alpha S_\beta S_\gamma S_\delta \times \int_{\tau_3}^t d\tau G_\alpha(t - \tau) G_\beta(\tau - \tau_1) \times G_\gamma(\tau - \tau_2) G_\delta(\tau_2 - \tau_3), \quad (\text{E8})$$

$$R_V^{(3)}(t, \tau_1 \tau_2 \tau_3) = 2i \sum_{\alpha\beta\gamma\delta\eta} V_{-\alpha\beta\gamma} V_{-\gamma\delta\eta} \mu_{\alpha\mu} \mu_{-\beta} \mu_{-\delta} \mu_{-\eta} \times S_\alpha S_\beta S_\gamma S_\delta S_\eta \int_{\tau_3}^t d\tau \int_{\tau_3}^{\tau} d\tau' G_\alpha(t - \tau) \times G_\beta(\tau - \tau_1) G_\gamma(\tau - \tau') G_\delta(\tau' - \tau_2) \times G_\eta(\tau' - \tau_3), \quad (\text{E9})$$

$$R_{VI}^{(3)}(t, \tau_1 \tau_2 \tau_3) = \sum_{\alpha\beta\gamma\delta} V_{-\alpha\beta\gamma} \mu_{\alpha\mu} \mu_{-\beta} \mu_{-\gamma} \mu_{-\delta} S_\alpha S_\beta S_\gamma S_\delta \times \int_{\tau_3}^t d\tau G_\alpha(t - \tau) G_\beta(\tau - \tau_1) \times G_\gamma(\tau - \tau_2) G_\delta(\tau - \tau_3), \quad (\text{E10})$$

$$R_{VII}^{(3)}(t, \tau_1 \tau_2 \tau_3) = -2i \sum_{\alpha\beta\gamma} \mu_{\alpha\beta} \mu_{-\beta\gamma} \mu_{-\alpha} \mu_{-\gamma} S_\alpha S_\beta S_\gamma \times G_\alpha(t - \tau_1) G_\beta(\tau - \tau_2) G_\gamma(\tau_2 - \tau_3), \quad (\text{E11})$$

$$R_{VIII}^{(3)}(t, \tau_1 \tau_2 \tau_3) = -2 \sum_{\alpha\beta\gamma\delta} \mu_{\alpha\beta} V_{-\beta\gamma\delta} \mu_{-\alpha} \mu_{\gamma} \mu_{-\delta} S_\alpha S_\beta S_\gamma S_\delta \times \int_{\tau_3}^t d\tau G_\alpha(t - \tau) G_\beta(t - \tau) \times G_\gamma(\tau - \tau_2) G_\delta(\tau - \tau_3). \quad (\text{E12})$$

Using Eqs. (B10) and (B13) we obtain 8 term expression for the third-order polarizability (symmetrized with respect to ω_1 , ω_2 , and ω_3 permutations) given by Eq. (4.18)

APPENDIX F: VARIATIONAL DERIVATION OF THE EXCITED-STATE DIPOLE MOMENTS

To derive the excited-state dipoles we use the variational formulation of the TDDFT introduced in Refs. 43 and 48. However, instead of varying the MO coefficients, we show that the same result could be obtained by varying the density matrix. The excited states are obtained variationally from the functional

$$\Lambda(\xi, \Omega, Z, \bar{\rho}) = \langle \xi | L \xi \rangle - \Omega (\langle \xi | \xi \rangle - 1) + \langle Z | [F, \bar{\rho}] \rangle, \quad (\text{F1})$$

required to be stationary with respect to all parameters (ξ, Ω, Z , and $\bar{\rho}$). Here the angular brackets denote the scalar product Eq. (3.13). Variation of Λ with respect to ξ leads to the eigenvalue problem Eq. (3.10) and the Lagrangian multiplier Ω ensures the RPA scalar product Eq. (3.13). In addition, the Hartree-Fock condition Eq. (2.27) is satisfied by Lagrangian multiplier Z . (The orthonormality of the basis set imposes an additional condition which is important for analytic gradient technique but not essential for the purposes of current paper. For clarity we postulated the second condition from the beginning and refer to the full derivation given in Refs. 43 and 48.) Subsequently, the derivatives of the excited-state energy Ω with respect to an external perturbation x (e.g., an external field $x = \mathcal{E}$) can be expressed in terms of Λ as

$$\Omega^x = \Lambda^x = \langle \xi | L^x \xi \rangle, \quad (\text{F2})$$

where the derivatives of ξ vanish due to the variational principle at stationary point of Λ .

Variation of Λ with respect to $\bar{\rho}$ determines Z

$$\delta\Lambda(\bar{\rho}) = \langle \xi | \delta L \xi \rangle + \langle Z | \delta [F, \bar{\rho}] \rangle = 0. \quad (\text{F3})$$

Using

$$\delta[F, \bar{\rho}] = [F(\bar{\rho}), \delta\rho] + [\tilde{V}(\delta\rho), \bar{\rho}], \quad (\text{F4})$$

$$\delta L \xi = [\tilde{V}(\delta\rho), \xi] + [\tilde{V}(\xi), \delta\rho] + [v^{(2)}(\xi, \delta\rho), \bar{\rho}], \quad (\text{F5})$$

and after rearranging the terms under the scalar product, Eq. (F3) can be written as

$$\langle \delta\rho | [([[\bar{\rho}, \xi^\dagger], \tilde{V}(\xi)] + \tilde{V}(\frac{1}{2}[[\xi^\dagger, \bar{\rho}], \xi]) + [v^{(2)}(\xi, \delta\rho), \bar{\rho}]) + \langle \delta\rho | LZ \rangle = 0. \quad (\text{F6})$$

In turn, this leads to the linear equation for Z

$$LZ = -([[\bar{\rho}, \xi^\dagger], \tilde{V}(\xi)] + \tilde{V}(\frac{1}{2}[[\xi^\dagger, \bar{\rho}], \xi]) + [v^{(2)}(\xi, \delta\rho), \bar{\rho}]), \quad (\text{F7})$$

which is identical to Eq. (18) in Ref. 48 given in the basis set of the momentum $|X - Y\rangle$ coordinate $|X + Y\rangle$ variables. Note that the variation of the stationary point Eq. (2.27) leads to the linear Liouville operator L in Eq. (F6) and the variation of the linear Liouville operator results in the second-order terms [compare the r.h.s. of Eq. (F7) with the second order terms in Eq. (3.4)]. Using an expansion (4.1), the interband matrix Z for the state α can be further expanded into a set of transition densities $\{\xi_\beta\}$ as

$$Z_\alpha = - \sum_\beta \frac{V_{-\alpha\beta}}{|\Omega_\beta|} \xi_{-\beta}, \quad \beta = -M, \dots, M. \quad (\text{F8})$$

Finally, the derivative of the excited-state energy Ω_α [Eq. (F2)] becomes

$$\Omega_\alpha^x = \Lambda^x = Tr(\tilde{t}^{(x)} p_\alpha) + Tr(V^{(x)}(\bar{\rho}) p_\alpha) + Tr(\tilde{V}^{(x)}(\xi_\alpha^\dagger) \xi_\alpha), \quad (F9)$$

where

$$p_\alpha = [[\xi_\alpha^\dagger, \bar{\rho}], \xi_\alpha] + Z_\alpha = [[\xi_\alpha^\dagger, \bar{\rho}], \xi_\alpha] - \sum_\beta \frac{V_{-\alpha\beta}}{\Omega_\beta}, \quad (F10)$$

$$\beta = -M, \dots, M,$$

and (x) denotes the derivative of the Hamiltonian matrix elements while holding $\bar{\rho}$ constant.

The difference between excited- and ground-state dipole moments is defined as $\partial\Omega_\alpha/\partial\mathcal{E}$ and $\partial\tilde{t}_{ij}/\partial\mathcal{E} = \mu_{ij}$ [assuming that the perturbation $\mathcal{E}(t) \cdot \mu$ is included in the one electron part \tilde{t}]. Subsequently, $p_\alpha + \bar{\rho}$ is the density matrix of the excited state α . Even though this route represents a simple and convenient way for computing the excited-state dipole moments and the transition dipoles between states in the TD-DFT, the current derivation was obtained with the linear response theory [i.e., R term in Eq. (3.4) was neglected altogether] and, therefore, holds only up to the second-order optical responses.

APPENDIX G: SECOND-ORDER OPTICAL RESPONSE OF THE EFFECTIVE MULTILEVEL SYSTEM

Following Ref. 82, Eq. (4.2) can be interpreted as the classical Hamilton equation of motion $\dot{z} = \{H, z\}$ of the system of classical coupled oscillators with the Hamiltonian (up to the second order)

$$H(z) = \sum_{\alpha>0} \Omega_\alpha z_{-\alpha} z_\alpha + \frac{1}{3} \sum_{\alpha\beta\gamma=-M, \dots, M} V_{\alpha,\beta\gamma} z_\alpha z_\beta z_\gamma - \mathcal{E}(t) \cdot \mathbf{P}(z), \quad (G1)$$

with the polarization \mathbf{P} given by Eq. (4.14) and tensor $V_{\alpha\beta\gamma}$ is given by Eq. (4.11).

A quantum oscillator model whose classical limit is given by Eqs. (4.2) and (G1) can be obtained by association with each classical variable z_α an annihilation operator a_α ($z_\alpha = \langle a_\alpha \rangle$, $\alpha > 0$), and $z_{-\alpha} = z_\alpha^*$ is a creation operator a_α^\dagger ($z_\alpha^* = \langle a_\alpha^\dagger \rangle$).⁸² a_α and a_α^\dagger satisfy the boson commutation relations:

$$[a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta}; \quad [a_\alpha^\dagger, a_\beta^\dagger] = [a_\alpha, a_\beta] = 0. \quad (G2)$$

The respective quantum Hamiltonian H_1 , when preserving normal ordering, is given by

$$H_1 = \sum_{\alpha>0} \Omega_\alpha a_\alpha^\dagger a_\alpha + \frac{1}{3!} \left(\sum_{\alpha\beta\gamma>0} V_{\alpha\beta\gamma} a_\alpha a_\beta a_\gamma + 3 \sum_{\alpha\beta\gamma>0} V_{-\alpha\beta\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger + h.c. \right) - \mathcal{E}(t) \cdot \mathbf{P}(a_\alpha^\dagger, a_\alpha), \quad (G3)$$

with

$$\mathbf{P}(a_\alpha^\dagger, a_\alpha) = \sum_{\alpha>0} (\mu_\alpha a_\alpha + h.c.) + \frac{1}{2!} \left(\sum_{\alpha\beta>0} \mu_{\alpha\beta} a_\alpha a_\beta + \sum_{\alpha\beta>0} \mu_{-\alpha\beta} a_\alpha^\dagger a_\beta^\dagger + h.c. \right), \quad (G4)$$

where $h.c.$ denotes Hermitian conjugate. The H_1 Hamiltonian represents M quantum oscillators with the harmonic frequencies Ω_α that are subject to inter oscillator couplings $V_{\alpha\beta\gamma}$ and the polarizability operator $\mathbf{P}(a_\alpha^\dagger, a_\alpha)$. Using the perturbation theory we next calculate the wavefunctions of this oscillator system to first order in V :⁸²

$$\phi^{(0)} = |g\rangle_0 - \frac{1}{3!} \sum_{\alpha\beta\gamma>0} \frac{V_{-\alpha-\beta-\gamma}}{\Omega_\alpha + \Omega_\beta + \Omega_\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger |g\rangle_0, \quad (G5)$$

$$\phi_\alpha^{(1)} = a_\alpha^\dagger |g\rangle_0 + \frac{1}{2!} \sum_{\beta\gamma>0} \frac{V_{\alpha-\beta-\gamma}}{\Omega_\alpha - \Omega_\beta - \Omega_\gamma} a_\beta^\dagger a_\gamma^\dagger |g\rangle_0, \quad (G6)$$

$$\phi_{\beta\gamma}^{(2)} = a_\beta^\dagger a_\gamma^\dagger |g\rangle_0 + \frac{1}{2!} \sum_{\alpha>0} \frac{2V_{-\alpha\beta\gamma}}{-\Omega_\alpha + \Omega_\beta + \Omega_\gamma} a_\alpha^\dagger |g\rangle_0 + \frac{1}{2!} \sum_{\delta\zeta>0} \left(\frac{V_{\gamma-\delta-\zeta}}{\Omega_\gamma - \Omega_\delta - \Omega_\zeta} a_\delta^\dagger + \frac{V_{\beta-\delta-\zeta}}{\Omega_\beta - \Omega_\delta - \Omega_\zeta} a_\zeta^\dagger \right) a_\delta^\dagger a_\zeta^\dagger |g\rangle_0, \quad (G7)$$

where $|g\rangle_0$, $a_\alpha^\dagger |g\rangle_0$, $a_\alpha^\dagger a_\beta^\dagger |g\rangle_0$, and $a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger |g\rangle_0$ denote the ground, single, double, and triple excited states of the uncoupled system, respectively.

The transition dipoles among the ground and the first two excited states (to the first order in V) are given by

$$\langle \phi^{(0)} | \mathbf{P} | \phi^{(0)} \rangle = 0, \quad (G8)$$

$$\langle \phi^{(0)} | \mathbf{P} | \phi_\alpha^{(1)} \rangle = \mu_\alpha, \quad (G9)$$

$$\langle \phi^{(0)} | \mathbf{P} | \phi_{\alpha\beta}^{(2)} \rangle = \mu_{\alpha\beta} + \sum_{\gamma>0} \left(\frac{V_{\alpha\beta-\gamma} \mu_\gamma}{\Omega_\alpha + \Omega_\beta - \Omega_\gamma} - \frac{V_{\alpha\beta\gamma} \mu_{-\gamma}}{\Omega_\alpha + \Omega_\beta + \Omega_\gamma} \right), \quad (G10)$$

$$\langle \phi_\alpha^{(1)} | \mathbf{P} | \phi_\beta^{(1)} \rangle = \mu_{-\alpha\beta} + \sum_{\gamma>0} \left(\frac{V_{-\alpha\beta-\gamma} \mu_\gamma}{-\Omega_\alpha + \Omega_\beta - \Omega_\gamma} + \frac{V_{\alpha-\beta-\gamma} \mu_{-\gamma}}{\Omega_\alpha - \Omega_\beta - \Omega_\gamma} \right), \quad (G11)$$

$$\langle \phi_\alpha^{(1)} | \mathbf{P} | \phi_{\alpha\beta}^{(2)} \rangle = \mu_\beta. \quad (G12)$$

Using our notation, the respective transition densities are represented as

$$\langle g | c_j^\dagger c_i | g \rangle = (\bar{\rho})_{ij}, \quad (G13)$$

$$\langle g | c_j^\dagger c_i | \alpha \rangle = (\xi_\alpha)_{ij}, \quad (G14)$$

$$\langle g | c_j^\dagger c_i | \alpha \beta \rangle = ([[\xi_\alpha, \bar{\rho}], \xi_\beta])_{ij} - \sum_{\gamma=-M, \dots, M} \frac{V_{\alpha\beta\gamma} S_\gamma}{\Omega_\alpha + \Omega_\beta + \Omega_\gamma} (\xi_{-\gamma})_{ij}, \quad (\text{G15})$$

$$\langle \alpha | c_j^\dagger c_i | \beta \rangle = (\bar{\rho})_{ij} \delta_{\alpha\beta} + ([[\xi_{-\alpha}, \bar{\rho}], \xi_\beta])_{ij} - \sum_{\gamma=-M, \dots, M} \frac{V_{-\alpha\beta\gamma} S_\gamma}{-\Omega_\alpha + \Omega_\beta + \Omega_\gamma} (\xi_{-\gamma})_{ij}, \quad (\text{G16})$$

$$\langle \alpha | c_j^\dagger c_i | \beta \gamma \rangle = (\xi_\gamma)_{ij} \delta_{\alpha\beta} + (\xi_\beta)_{ij} \delta_{\alpha\gamma}. \quad (\text{G17})$$

Here Eq. (G14) is identical to Eq. (3.11) which defines the transition densities of the linear response. Setting $\alpha = \beta$ in Eq. (G16) recovers the excited state $|\alpha\rangle$ density $p_\alpha + \bar{\rho}$ given by Eq. (F10).

Finally, substituting the transitions dipoles Eqs. (G8)–(G12) in the usual SOS expression for the second-order response given by^{8,9}

$$\beta(\omega_1, \omega_2) = -\frac{1}{4} \sum_{\omega_1, \omega_2}^{\text{perm}} \sum_{n, n'} \mu_{gn} \mu_{nn'} \mu_{n'g} \times \left(\frac{1}{(\omega_{n'g} + \omega_1 + \omega_2)(\omega_{ng} + \omega_1)} + \frac{1}{(\omega_{n'g} - \omega_1 - \omega_2)(\omega_{ng} - \omega_1)} + \frac{1}{(\omega_{n'g} + \omega_1)(\omega_{ng} + \omega_1 + \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_1)(\omega_{ng} - \omega_1 - \omega_2)} + \frac{1}{(\omega_{n'g} - \omega_2)(\omega_{ng} + \omega_1)} + \frac{1}{(\omega_{n'g} + \omega_2)(\omega_{ng} - \omega_1)} \right), \quad (\text{G18})$$

we obtain expressions for the second-order polarizability which coincide with Eq. (4.17). This proves the equivalence of the second-order response of the quantum oscillator system calculated in the classical limit and using the sum-over-states expression.

¹D. B. Cook, *Handbook of Computational Quantum Chemistry* (Oxford University Press, New York, 1998).

²A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).

³C. J. Cramer, *Essentials of Computational Chemistry* (Wiley, West Sussex, England, 2002).

⁴*Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by J. Zyss and D. S. Chemla (Academic, Florida, 1987), Vol. 1 and 2.

⁵C. Flytzanis and J. Huttler, in *Contemporary Nonlinear Optics*, edited by G. P. Agrawal and R. W. Boyd (Academic, San Diego, 1992).

⁶D. R. Kanis, M. A. Ratner, and T. J. Marks, *Chem. Rev.* **94**, 195 (1994).

⁷J. L. Brédas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, *Chem. Rev.* **94**, 243 (1994).

⁸J. F. Ward, *Rev. Mod. Phys.* **37**, 1 (1965).

⁹B. J. Orr and J. F. Ward, *Mol. Phys.* **20**, 513 (1971).

¹⁰J. Ridley and M. C. Zerner, *Theor. Chim. Acta* **32**, 111 (1973).

¹¹G. Karlsson and M. C. Zerner, *Int. J. Quantum Chem.* **7**, 35 (1973).

¹²M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **102**, 589 (1980).

¹³G. R. Hutchison, M. A. Ratner, and T. J. Marks, *J. Phys. Chem. A* **106**, 10596 (2002).

¹⁴S. Tretiak and S. Mukamel, *Chem. Rev.* **102**, 3171 (2002).

¹⁵M. Albota, D. Beljonne, J. L. Brédas *et al.*, *Science* **281**, 1653 (1998).

¹⁶S. J. K. Pond, M. Rumi, M. D. Levin, T. C. Parker, D. Beljonne, M. W. Day, J. L. Bredas, S. R. Marder, and J. W. Perry, *J. Phys. Chem. A* **106**, 11470 (2002).

¹⁷Z. G. Soos, S. Ramasesha, and D. S. Galvao, *Phys. Rev. Lett.* **71**, 1609 (1993).

¹⁸Z. G. Soos, D. S. Galvao, and S. Etemad, *Adv. Mater. (Weinheim, Ger.)* **6**, 280 (1994).

¹⁹D. C. Rodenberger, J. R. Heflin, and A. F. Garito, *Nature (London)* **359**, 309 (1992).

²⁰J. R. Heflin, K. Y. Wong, O. Zamanikhamiri, and A. F. Garito, *Phys. Rev. B* **38**, 1573 (1988).

²¹D. Yaron, *Phys. Rev. B* **54**, 4609 (1996).

²²S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford, New York, 1995).

²³B. Weiner and S. B. Trickey, *Adv. Quantum Chem.* **35**, 217 (1999).

²⁴B. Weiner and S. B. Trickey, *J. Mol. Struct.: THEOCHEM* **501**, 65 (2000).

²⁵V. Chernyak and S. Mukamel, *J. Chem. Phys.* **104**, 444 (1996).

²⁶V. Chernyak and S. Mukamel, *J. Chem. Phys.* **112**, 3572 (2000).

²⁷J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory*, edited by D. Yarkoni (VCH, New York, 1995), Vol. II.

²⁸D. J. Thouless, *The Quantum Mechanics Of Many-Body Systems* (Academic, New York, 1972).

²⁹J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, London, 1973).

³⁰H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **85**, 976 (1986).

³¹H. Sekino and R. J. Bartlett, *J. Chem. Phys.* **94**, 3665 (1991).

³²S. Mukamel, A. Takahashi, H. X. Wang, and G. H. Chen, *Science* **266**, 250 (1994).

³³E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).

³⁴M. Petersilka, U. J. Gossmann, and E. K. U. Gross, *Phys. Rev. Lett.* **76**, 1212 (1996).

³⁵M. E. Casida, in *Recent Advances in Density-Functional Methods*, Vol. 3 of Part I, edited by D. A. Chong (World Scientific, Singapore, 1995).

³⁶P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).

³⁷W. Kohn and L. J. Sham, *Phys. Rev. A* **137**, 1697 (1965).

³⁸H. Appel, E. K. U. Gross, and K. Burke, *Phys. Rev. Lett.* **90**, 043005 (2003).

³⁹R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998).

⁴⁰C. Jamorski, M. E. Casida, and D. R. Salahub, *J. Chem. Phys.* **104**, 5134 (1996).

⁴¹P. Deglmann and F. Furche, *J. Chem. Phys.* **117**, 9535 (2002).

⁴²R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.* **256**, 454 (1996).

⁴³F. Furche, *J. Chem. Phys.* **114**, 5982 (2001).

⁴⁴H. Larsen, P. Jørgensen, J. Olsen, and T. Helgaker, *J. Chem. Phys.* **113**, 8908 (2000).

⁴⁵E. K. U. Gross, J. F. Dobson, and M. Petersilka, *Top. Curr. Chem.* **181**, 81 (1996).

⁴⁶P. Hessler, N. T. Maitra, and K. Burke, *J. Chem. Phys.* **117**, 72 (2002).

⁴⁷M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.* **108**, 4439 (1998).

⁴⁸F. Furche and R. Ahlrichs, *J. Chem. Phys.* **117**, 7433 (2002).

⁴⁹R. Bauernschmitt, R. Ahlrichs, F. H. Hennrich, and M. M. Kappes, *J. Am. Chem. Soc.* **120**, 5052 (1998).

⁵⁰K. B. Wiberg, R. E. Stratmann, and M. J. Frisch, *Chem. Phys. Lett.* **297**, 60 (1998).

⁵¹C. P. Hsu, G. R. Fleming, M. Head-Gordon, and T. Head-Gordon, *J. Chem. Phys.* **114**, 3065 (2001).

⁵²S. Hirata, M. Head-Gordon, and R. J. Bartlett, *J. Chem. Phys.* **111**, 10774 (1999).

⁵³P. Salek, O. Vahtras, T. Helgaker, and H. Agren, *J. Chem. Phys.* **117**, 9630 (2002).

⁵⁴S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **109**, 10644 (1998).

⁵⁵R. Baer, *Chem. Phys. Lett.* **364**, 75 (2002).

- ⁵⁶M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98 (Revision A.11) (Gaussian, Inc., Pittsburgh PA, 2002).
- ⁵⁷M. W. Schmidt, K. K. Baldridge, J. A. Boatz *et al.*, *J. Comput. Chem.* **14**, 1347 (1993).
- ⁵⁸R. Ahlrichs, M. Bar, M. Haser, H. Horn, and C. Kolmel, *Chem. Phys. Lett.* **162**, 165 (1989).
- ⁵⁹S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.* **119**, 11408 (1997).
- ⁶⁰A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ⁶¹A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).
- ⁶²T. H. Dunning and V. McKoy, *J. Chem. Phys.* **47**, 1735 (1967).
- ⁶³T.-I. Shibuya, J. Rose, and V. McKoy, *J. Chem. Phys.* **58**, 500 (1973).
- ⁶⁴J. Paldus and J. Čížek, *J. Chem. Phys.* **60**, 149 (1974).
- ⁶⁵J. Oddershede and P. Jorgensen, *J. Chem. Phys.* **66**, 1541 (1977).
- ⁶⁶J. Linderberg and E. W. Thulstrup, *J. Chem. Phys.* **49**, 710 (1968).
- ⁶⁷S. Rettrup, *J. Comput. Phys.* **45**, 100 (1982).
- ⁶⁸T. H. Dunning and V. McKoy, *J. Chem. Phys.* **48**, 5263 (1967).
- ⁶⁹P. Jorgensen and Y. Öhrn, *Chem. Phys. Lett.* **18**, 261 (1973).
- ⁷⁰J. Čížek and J. Paldus, *Phys. Rev. A* **3**, 525 (1971).
- ⁷¹J. Paldus and J. Čížek, *Chem. Phys. Lett.* **3**, 1 (1969).
- ⁷²V. Chernyak and S. Mukamel, *J. Chem. Phys.* **111**, 4383 (1999).
- ⁷³D. J. Thouless, *Nucl. Phys.* **22**, 78 (1961).
- ⁷⁴Y. Saad, *Numerical Methods for Large Eigenvalue Problems* (Manchester, University Press, 1992).
- ⁷⁵B. N. Parlett, *Symmetric Eigenvalue Problem* (Prentice Hall, Englewood Cliffs, NJ, 1980).
- ⁷⁶V. Chernyak, M. F. Schulz, S. Mukamel, S. Tretiak, and E. V. Tsiper, *J. Chem. Phys.* **113**, 36 (2000).
- ⁷⁷E. V. Tsiper, *J. Phys. B* **34**, L401 (2001).
- ⁷⁸E. V. Tsiper, *JETP Lett.* **70**, 751 (1999).
- ⁷⁹E. R. Davidson, *J. Comput. Phys.* **17**, 87 (1975).
- ⁸⁰J. Olsen, H. J. A. Jensen, and P. Jorgensen, *J. Comput. Phys.* **74**, 265 (1988).
- ⁸¹T. Meier, S. Tretiak, V. Chernyak, and S. Mukamel, *Phys. Rev. B* **55**, 4960 (1997).
- ⁸²S. Tretiak, V. Chernyak, and S. Mukamel, *Int. J. Quantum Chem.* **70**, 711 (1998).
- ⁸³G. P. Bartholomew, M. Rumi, S. J. K. Pond, J. W. Perry, S. Tretiak, and G. C. Bazan (in preparation).
- ⁸⁴A. Masunov and S. Tretiak (in preparation).