

Quasiparticle density-matrix representation of nonlinear time-dependent density-functional response functions

Oleg Berman¹ and Shaul Mukamel^{1,2}¹*Department of Chemistry, University of Rochester, Rochester, New York 14627-0216*²*Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627-0216*

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The time-dependent density-functional (TDDFT) equations may be written either for the Kohn-Sham orbitals in Hilbert space or for the single-electron density matrix in Liouville space. A collective-oscillator, quasiparticle, representation of the density response of many-electron systems which explicitly reveals the relevant electronic coherence sizes is developed using the Liouville-space representation of adiabatic TDDFT. Closed expressions for the nonlinear density-density response are derived, eliminating the need to solve nonlinear integral equations, as required in the Hilbert-space formulation of the response.

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I. INTRODUCTION

Time-dependent density-functional theory (TDDFT) offers a computationally tractable framework for calculating response functions of many-electron systems (such as molecules, semiconductors and metals) to electrical or optical perturbations [1–14]. The linear and nonlinear response functions (NRF) may then be used to extract useful information about electronic excited states (energies, transition and permanent dipole moments, etc.). The standard TDDFT algorithm involves the computation of the Kohn-Sham orbitals $\psi_n(\mathbf{r})$ in Hilbert space [11], and the response functions are calculated in two steps. First, a reference response is calculated for noninteracting electrons. Then a nonlinear integral equation is solved for the actual response function. The complexity of these calculations increases rapidly with the nonlinear order of the response. Alternatively, the Kohn-Sham equations may be written for the single-electron density matrix $\rho(\mathbf{r}, \mathbf{r}')$ and its evolution in Liouville space. We shall denote these as time-dependent Hilbert-space (TDHS) and time-dependent Liouville-space (TDLS) representations, respectively. The reduced single-electron density matrix for N electron pairs $\psi_n(\mathbf{r}, t)$ is given by [15]

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_{n=1}^N \psi_n(\mathbf{r}, t) \psi_n^*(\mathbf{r}', t). \quad (1)$$

A density matrix approach to the response was developed for the time-dependent Hartree-Fock approximation (TDHF) [17–20], which is formally very similar to TDDFT [21]. A closed algebra of quasiparticles which satisfy a somewhat unusual scalar product, which allows a systematic order by order expansion of the density matrix in the field [18]. In this paper, we extend this approach to TDDFT and provide closed expressions for density-density response functions using the adiabatic exchange-correlation potential.

Doubling the space dimensionality in Liouville space compared to Hilbert space [$\rho(\mathbf{r}, \mathbf{r}')$ vs. $\psi_n(\mathbf{r})$] seems computationally prohibitive, in particular since within the Kohn-Sham approximation $\rho(\mathbf{r}, \mathbf{r}')$ may be computed using $\psi_n(\mathbf{r})$ using Eq.(1). However, recasting reduced descriptions of

many-body systems using density matrices [15,16] has many numerical advantages, as will be discussed later. In addition, the TDLS representation offers following valuable physical insight:

(i) A quasiparticle picture of the response is naturally obtained in terms of the eigenstates of the linearized TDDFT.

(ii) Closed expressions for response functions may be derived. In contrast, in the TDHS approach one needs to solve a chain of integral equations for each order self-consistently.

(iii) The density-matrix carries explicit information about electronic coherence sizes. Molecular (e.g., Kohn-Sham) orbitals can be arbitrarily transformed to be localized or delocalized, without affecting the many-electron state. Their coherence length is, therefore, ill defined and does not carry a meaningful physical information. The density matrix is, on the other hand, uniquely defined. Optical excitations involve the creation of electron-hole pairs (excitons). The diagonal length of $\rho(\mathbf{r}, \mathbf{r}')$ along $\mathbf{r} = \mathbf{r}'$ reflects the center-of-mass motion of excitons whereas the off-diagonal length (along $\mathbf{r} - \mathbf{r}'$) shows the size associated with the relative electron-hole pairs motion. Plotting the density matrix provides physical insights and offers a real space N scaling description of electronic excitations when the density matrix is localized along $\mathbf{r} - \mathbf{r}'$, which is typically the case [22].

(iv) The response functions for any single-electron operator (e.g., current) can be readily obtained. This allows to compute, for example, conductivities.

This paper is organized as follows. The time-dependent Kohn-Sham equations of motion for the single-electron density matrix are presented in Sec. II. The CEO (collective electron oscillator), quasiparticle, representation of the TD-DFT density matrix is derived in Sec. III. The linear density-density response function is calculated in Sec. IV and the second-order and the third-order responses are given in Appendices B and C, respectively. The advantages of the TDLS approach for computations of linear and nonlinear time-dependent response functions, as well as possible extensions are summarized in Sec. V.

II. TIME-DEPENDENT KOHN-SHAM EQUATIONS FOR THE SINGLE-ELECTRON DENSITY MATRIX

The time-dependent Kohn-Sham equations of motion for the density matrix [21] are

$$i \frac{\partial \rho(\mathbf{r}, \mathbf{r}', t)}{\partial t} = \hat{L}_{KS}[\rho(\mathbf{r}, \mathbf{r}', t)](\mathbf{r}, \mathbf{r}', t) \rho(\mathbf{r}, \mathbf{r}', t), \quad (2)$$

where we set $\hbar = 1$, and

$$\rho(\mathbf{r}, t) = \rho(\mathbf{r}, \mathbf{r}, t) \equiv n(\mathbf{r}, t) \quad (3)$$

is the exact time-dependent charge density of electrons; $\hat{L}_{KS}[\rho(\mathbf{r}, \mathbf{r}', t)](\mathbf{r}, \mathbf{r}', t)$ is the superoperator in Liouville space corresponding to the Kohn-Sham Hamiltonian:

$$\begin{aligned} \hat{L}_{KS}[\rho(\mathbf{r}, \mathbf{r}', t)](\mathbf{r}, \mathbf{r}', t) &\equiv \hat{H}_{KS}[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}, t) \\ &- \hat{H}_{KS}^*[\rho(\mathbf{r}', \mathbf{r}', t)](\mathbf{r}', t), \end{aligned} \quad (4)$$

\hat{H}_{KS} is the Kohn-Sham Hamiltonian

$$\hat{H}_{KS} = \hat{H}_{KS}^0 + U_1(\mathbf{r}, t), \quad (5)$$

\hat{H}_{KS}^0 is the Hamiltonian of the isolated model and U_1 represents the coupling to an external optical field,

$$\hat{H}_{KS}^0[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}, t) = -\frac{\nabla_{\mathbf{r}}^2}{2m} + U_{KS}^0[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}) + U_0(\mathbf{r}), \quad (6)$$

m is an effective electron mass and the Kohn-Sham external potential is a functional of the charge density,

$$U_{KS}^0[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', \mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + U_{xc}[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}), \quad (7)$$

$U_0(\mathbf{r})$ is the field created by nuclei and $U_{xc}[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r})$ is the exchange-correlation potential in the adiabatic approximation. We further define the time-dependent external potential, given by $U_{ext}(\mathbf{r}, t) = U_0(\mathbf{r})$ at time $t \leq t_0$ and $U_{ext}(\mathbf{r}, t) = U_0(\mathbf{r}) + U_1(\mathbf{r}, t)$ for $t > t_0$.

III. QUASIPARTICLE REPRESENTATION OF DENSITY RESPONSE FUNCTIONS

The TDDFT equations describe the evolution of the reduced single-electron density matrix of a many-electron system driven by an external field. The calculation starts by computing the ground-state single-electron density matrix $\bar{\rho}(\mathbf{r}, \mathbf{r}')$ in real space, which is determined by the stationary solution of the Kohn-Sham equation [Eq. (2)]. $\bar{\rho}$ is a key input to the TDDFT calculations. We then set $\rho(\mathbf{r}, \mathbf{r}', t) = \bar{\rho}(\mathbf{r}, \mathbf{r}') + \delta\rho(\mathbf{r}, \mathbf{r}', t)$, where $\delta\rho(\mathbf{r}, \mathbf{r}', t)$ represents the changes induced by the external field, described by the potential $U_1(\mathbf{r}, t)$. The diagonal elements $\delta\rho(\mathbf{r}, \mathbf{r}, t)$ give the changes in charge density, whereas the off-diagonal elements $\rho(\mathbf{r}, \mathbf{r}', t)$ represent the changes in electronic coherences between two points. Eq. (2) is then recast in the form

$$\begin{aligned} i \frac{\partial \delta\rho(\mathbf{r}, \mathbf{r}', t)}{\partial t} &= (\hat{H}_{KS}^0[\rho(\mathbf{r}, \mathbf{r}, t)](\mathbf{r}) - \hat{H}_{KS}^{0*}[\rho(\mathbf{r}', \mathbf{r}', t)](\mathbf{r}')) \\ &+ [U_1(\mathbf{r}, t) - U_1^*(\mathbf{r}', t)] \rho(\mathbf{r}, \mathbf{r}', t). \end{aligned} \quad (8)$$

This equation may be solved for $\delta\rho(\mathbf{r}, \mathbf{r}', t)$ either in the frequency or in the time domain.

In order to calculate linear and nonlinear response functions, we expand $\delta\rho(\mathbf{r}, \mathbf{r}', t)$ in powers of $U_1(\mathbf{r}, t)$: $\delta\rho(\mathbf{r}, \mathbf{r}', t) = \delta\rho_1(\mathbf{r}, \mathbf{r}', t) + \delta\rho_2(\mathbf{r}, \mathbf{r}', t) + \delta\rho_3(\mathbf{r}, \mathbf{r}', t) + \dots$ and solve the resulting equations of motion successively order by order. To that end we first expand U_{KS}^0 in Taylor series in the vicinity of $\bar{\rho}$ to third order in $\delta\rho$:

$$\begin{aligned} U_{KS}^0[\rho(\mathbf{r}, t)](\mathbf{r}) &= U_{KS}^0[\bar{\rho}](\mathbf{r}) + V_f + V_g + V_h, \\ V_f &= \int d\mathbf{r}' \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') \right) \delta\rho(\mathbf{r}', t), \\ V_g &= \int d\mathbf{r}' \int d\mathbf{r}'' g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'') \delta\rho(\mathbf{r}', t) \delta\rho(\mathbf{r}'', t), \\ V_h &= \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' h_{xc}[\bar{\rho}] \\ &\quad \times (\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') \delta\rho(\mathbf{r}', t) \delta\rho(\mathbf{r}'', t) \delta\rho(\mathbf{r}''', t), \end{aligned} \quad (9)$$

where for brevity we denote $\delta\rho(\mathbf{r}, \mathbf{r}, t)$ as $\delta\rho(\mathbf{r}, t)$; e is the electron charge and $f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}')$, $g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, and $h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''')$ are the first-, the second-, and the third-order adiabatic exchange-correlation kernels [11] (we consider the commonly used adiabatic approximation where they are assumed time independent)

$$f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') = \left. \frac{\delta U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t')} \right|_{\bar{\rho}}, \quad (10)$$

$$g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \left. \frac{\delta^2 U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t') \delta \rho(\mathbf{r}'', t'')} \right|_{\bar{\rho}}, \quad (11)$$

$$h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \left. \frac{\delta^3 U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t') \delta \rho(\mathbf{r}'', t'') \delta \rho(\mathbf{r}''', t''')} \right|_{\bar{\rho}}. \quad (12)$$

We further define

$$f'_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') \equiv f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') + \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \quad (13)$$

and introduce the following notation for the product of two real-space matrices ζ and η :

$$(\zeta * \eta)(\mathbf{r}, \mathbf{r}') \equiv \int \zeta(\mathbf{r}, \mathbf{r}'') \eta(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' \quad (14)$$

For an operator $A[\zeta(\mathbf{r},\mathbf{r})](\mathbf{r})$ and a matrix $\eta(\mathbf{r},\mathbf{r}')$, we denote

$$[A, \eta](\mathbf{r},\mathbf{r}') \equiv (A[\zeta(\mathbf{r},\mathbf{r})](\mathbf{r}) - A^*[\zeta(\mathbf{r}',\mathbf{r}')](\mathbf{r}'))\eta(\mathbf{r},\mathbf{r}'), \quad (15)$$

and the commutator of two single-electron matrixes ζ and η is [the $*$ operation was defined by Eq. (14)]

$$[\zeta, \eta](\mathbf{r},\mathbf{r}') \equiv (\zeta * \eta)(\mathbf{r},\mathbf{r}') - (\eta * \zeta)(\mathbf{r},\mathbf{r}'). \quad (16)$$

Since $\rho(\mathbf{r},\mathbf{r}',t)$ represents a single Slater determinat, it must be idempotent, and, consequently, not all elements of $\delta\rho(\mathbf{r},\mathbf{r}',t)$ are independent [18]. When expanded using the ground-state Kohn-Sham orbitals, $\delta\rho$ can be divided into four blocks: electron-hole and hole-electron (interband) and electron-electron and hole-hole (inraband). Only the interband elements of $\xi(\mathbf{r},\mathbf{r}',t)$ are independent and the intraband blocks T can be expressed in terms of these elements [24–26]. We thus decompose $\delta\rho(\mathbf{r},\mathbf{r}',t)$ as (see Appendix A)

$$\delta\rho(\mathbf{r},\mathbf{r}',t) \equiv \xi(\mathbf{r},\mathbf{r}',t) + T(\xi(\mathbf{r},\mathbf{r}',t)). \quad (17)$$

It will be desirable to remain in real space and avoid switching back and forth to the orbital basis. Fortunately, this goal can be accomplished and ξ can be computed directly in real space using the double commutator:

$$\xi(\mathbf{r},\mathbf{r}',t) \equiv [[\delta\rho(t), \bar{\rho}], \bar{\rho}](\mathbf{r},\mathbf{r}'). \quad (18)$$

The operation in the right-hand side (rhs) is a *projection operator* that projects $\delta\rho$ into the interband subspace [see Eq. (A1)] [18]. Once ξ is calculated, we obtain for T (see Appendix A)

$$T(\xi(\mathbf{r},\mathbf{r}',t)) = (I - 2\bar{\rho}) * [\xi(t) * \xi(t) + \xi(t) * \xi(t) * \xi(t) * \xi(t) + \dots](\mathbf{r},\mathbf{r}'), \quad (19)$$

where all $\xi(\mathbf{r},\mathbf{r}',t)$ are taken at time t .

The next step is to develop a convenient quasiparticle algebra for the independent dynamical variables ξ which represent collective electronic excitations. To that end we start with the eigenvalue equation corresponding to the linearized Kohn-Sham equations

$$L\xi_\alpha(\mathbf{r},\mathbf{r}') = \Omega_\alpha \xi_\alpha(\mathbf{r},\mathbf{r}'), \quad (20)$$

where

$$L = H_f(\mathbf{r}) - H_f^*(\mathbf{r}'), \quad (21)$$

$$H_f(\mathbf{r})\xi_\alpha(\mathbf{r},\mathbf{r}') = -\frac{\nabla_{\mathbf{r}}^2 \xi_\alpha(\mathbf{r},\mathbf{r}')}{2m} + \left(\int d\mathbf{r}'' \int d\mathbf{r}''' f'_{xc}[\bar{\rho}] \times (\mathbf{r},\mathbf{r}',\mathbf{r}'')\xi_\alpha(\mathbf{r}',\mathbf{r}''') \right) \bar{\rho}(\mathbf{r},\mathbf{r}'), \quad (22)$$

and

$$f'_{xc}[\bar{\rho}](\mathbf{r},\mathbf{r}',\mathbf{r}'') = f'_{xc}[\bar{\rho}](\mathbf{r},\mathbf{r}')\delta(\mathbf{r}' - \mathbf{r}''). \quad (23)$$

The eigenmodes ξ_α come in pairs. Each pair of conjugated modes $\xi_\alpha(\mathbf{r},\mathbf{r}')$ and $\xi_\alpha^\dagger(\mathbf{r},\mathbf{r}')$ forms a collective electronic oscillator α (where $\alpha = 1, 2, \dots$). We define $\xi_{-\alpha}(\mathbf{r},\mathbf{r}') = \xi_\alpha^\dagger(\mathbf{r},\mathbf{r}')$ and $\Omega_{-\alpha} = -\Omega_\alpha$, where $\alpha = \pm 1, \pm 2, \dots$. The algebraic properties of these oscillators were developed in Ref. [18] and reviewed in Ref. [20].

We further introduce the following scalar product of any two interband matrixes ξ and η :

$$\langle \xi | \eta \rangle \equiv \int d\mathbf{r} \int d\mathbf{r}' \bar{\rho}[\xi^\dagger, \eta](\mathbf{r},\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}'). \quad (24)$$

The bra (ket) notation underscores the similarity with Dirac's Hilbert-space notation. Eq. (24) satisfies the following relation:

$$\langle \xi | \eta \rangle = \langle \eta^\dagger | \xi^\dagger \rangle^* = -\langle \eta | \xi \rangle. \quad (25)$$

Using this scalar product, we shall normalize these modes as follows:

$$\langle \xi_\alpha^\dagger | \xi_\beta \rangle = \delta_{\alpha\beta}, \quad \langle \xi_\alpha | \xi_\beta \rangle = 0. \quad (26)$$

Equations (25) and (26) show that this is an unusual scalar product: for one thing, the norm of a vector is zero. Nevertheless, it has one important property: it allows us to expand $\xi(\mathbf{r},\mathbf{r}',t)$ in terms of CEO modes $\xi_\alpha(\mathbf{r},\mathbf{r}')$:

$$\xi(\mathbf{r},\mathbf{r}',t) = \sum_{\alpha=\pm 1, \pm 2, \dots} \xi_\alpha(\mathbf{r},\mathbf{r}')z_\alpha(t), \quad (27)$$

where $z_\alpha(t) = \langle \xi_\alpha^\dagger | \xi(t) \rangle$ and its complex conjugate $z_{-\alpha}(t) = z_\alpha^*(t)$ constitute complex oscillator amplitudes. ξ_α thus form a complete basis for representing an arbitrary interband matrix.

Combining Eqs. (27) and (17), we get

$$\begin{aligned} \delta\rho(\mathbf{r},\mathbf{r}',t) &= \sum_\alpha \rho_\alpha(\mathbf{r},\mathbf{r}')z_\alpha(t) + \frac{1}{2} \sum_{\alpha\beta} \rho_{\alpha\beta}(\mathbf{r},\mathbf{r}')z_\alpha(t)z_\beta(t) \\ &+ \frac{1}{3} \sum_{\alpha\beta\gamma} \rho_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}')z_\alpha(t)z_\beta(t)z_\gamma(t), \\ &\alpha, \beta, \gamma = \pm 1, \pm 2, \dots, \end{aligned} \quad (28)$$

where we only retained terms that contribute to the third-order response. The expansion coefficients in the rhs are given by

$$\rho_\alpha(\mathbf{r},\mathbf{r}') = \xi_\alpha(\mathbf{r},\mathbf{r}'), \quad (29)$$

$$\rho_{\alpha\beta}(\mathbf{r},\mathbf{r}') = (I - 2\bar{\rho}) * (\xi_\alpha * \xi_\beta + \xi_\beta * \xi_\alpha)(\mathbf{r},\mathbf{r}'), \quad (30)$$

$$\rho_{\alpha\beta\gamma}(\mathbf{r},\mathbf{r}') = -\xi_\alpha * (\xi_\beta * \xi_\gamma + \xi_\gamma * \xi_\beta)(\mathbf{r},\mathbf{r}'). \quad (31)$$

The amplitudes of the adjoint (negative frequency) variables are simply the complex conjugates ($z_{-\alpha} = z_\alpha^*$).

Upon the substitution of Eqs. (28), (29), (30), and (31) into Eq. (8), we obtain the equation of motion for the CEO amplitude $z(t)$ to third order in the external field:

$$\begin{aligned}
i \frac{\partial z_\alpha(t)}{\partial t} &= \Omega_\alpha z_\alpha(t) + K_{-\alpha} + \sum_\beta K_{-\alpha\beta} z_\beta(t) \\
&+ \sum_{\beta\gamma} K_{-\alpha\beta\gamma} z_\beta(t) z_\gamma(t) \\
&+ \sum_{\beta\gamma\delta} K_{-\alpha\beta\gamma\delta} z_\beta(t) z_\gamma(t) z_\delta(t), \\
\alpha, \beta, \gamma, \delta &= \pm 1, \pm 2, \dots,
\end{aligned} \tag{32}$$

where

$$\begin{aligned}
K_{-\alpha} &= \int U_1(\mathbf{r}, t) \rho_{-\alpha}(\mathbf{r}) d\mathbf{r}, \quad \rho_{-\alpha}(\mathbf{r}) \equiv \rho_{-\alpha}(\mathbf{r}, \mathbf{r}), \\
K_{-\alpha\beta} &= \int U_1(\mathbf{r}, t) \rho_{-\alpha, \beta}(\mathbf{r}) d\mathbf{r}, \quad \rho_{-\alpha, \beta}(\mathbf{r}) \equiv \rho_{-\alpha, \beta}(\mathbf{r}, \mathbf{r}), \\
K_{-\alpha\beta\gamma} &= U_{KS(-\alpha\beta\gamma)}^0 + \int U_1(\mathbf{r}, t) \rho_{-\alpha, \beta\gamma}(\mathbf{r}) d\mathbf{r}, \\
\rho_{-\alpha, \beta\gamma}(\mathbf{r}) &\equiv \rho_{-\alpha, \beta\gamma}(\mathbf{r}, \mathbf{r}), \\
K_{-\alpha\beta\gamma\delta} &= U_{KS(-\alpha\beta\gamma\delta)}^0,
\end{aligned} \tag{33}$$

U_{KS}^0 is the Kohn-Sham external potential, expanded to the third-order kernel Eq. (9), and $U_{KS(-\alpha\beta\gamma)}^0$ and $U_{KS(-\alpha\beta\gamma\delta)}^0$ are given in Eq. (B6) and Eq. (C5), respectively.

Eqs. (32) together with Eq. (28) constitute the quasiparticle algorithm for computing density response functions. These nonlinear equations that map the system onto coupled collective classical oscillators, may be solved by expanding $z(t)[z^*(t)]$ in powers of the external field $U_1(\mathbf{r}, t)$:

$$z(t) = z^{(1)}(t) + z^{(2)}(t) + z^{(3)}(t) + \dots \tag{34}$$

Substituting this in Eq. (32), we can successively solve for $z^{(j)}$ order by order which when substituted in Eq (28) will give $\delta\rho_j$. The present truncation of Eqs. (28) and (32) allows to compute response functions up to third order. However, this approach may be extended to NRF of arbitrary order by simply adding higher terms to Eqs. (28) and (32).

IV. THE LINEAR DENSITY RESPONSE

The following calculation of the linear response illustrates the strategy for computing response functions. The first-order density matrix [Eq. (8)] satisfies

$$\begin{aligned}
i \frac{\partial \delta\rho_1(\mathbf{r}, \mathbf{r}', t)}{\partial t} &= L \delta\rho_1(\mathbf{r}, \mathbf{r}', t) \\
&+ [U_1(\mathbf{r}, t) - U_1^*(\mathbf{r}', t)] \delta\rho_1(\mathbf{r}, \mathbf{r}', t).
\end{aligned} \tag{35}$$

The equation of motion for $z_\alpha^{(1)}(t)$ is obtained from Eq. (35) together with Eq. (17) and the expansion (19):

$$\begin{aligned}
i \frac{\partial z_\alpha^{(1)}(t)}{\partial t} &= \Omega_\alpha z_\alpha^{(1)}(t) + \int U_1(\mathbf{r}, t) \rho_{-\alpha}(\mathbf{r}) d\mathbf{r}, \\
\alpha &= \pm 1, \pm 2, \dots
\end{aligned} \tag{36}$$

The solution of this equation can be represented as

$$z_\alpha^{(1)}(t) = i s_\alpha \int_{-\infty}^t d\tau \int d\mathbf{r} U_1(\mathbf{r}, \tau) \rho_{-\alpha}(\mathbf{r}) G_\alpha(t - \tau), \tag{37}$$

where positive and negative α correspond to $z_\alpha^{(1)}(t)$ and $z_\alpha^{*(1)}(t)$, respectively, $s_\alpha \equiv \text{sign}(\alpha)$, and we have introduced the time-domain Green function

$$G_\alpha(t) = \theta(t) e^{-i\Omega_\alpha t}, \quad G_{-\alpha}(t) = \theta(t) e^{-i\Omega_{-\alpha} t} = \theta(t) e^{i\Omega_\alpha t}, \tag{38}$$

where $\theta(t)$ is the Heavyside step function.

Inserting Eq. (37) into Eq. (28), we obtain for the density to linear order

$$\delta\rho_1(\mathbf{r}, t) = \delta\rho_1(\mathbf{r}, \mathbf{r}, t) = \sum_{\alpha=\pm 1, \pm 2, \dots} z_\alpha^{(1)}(t) \rho_\alpha(\mathbf{r}). \tag{39}$$

This can be recast in the form

$$\delta\rho_1(\mathbf{r}, t) = \int_{-\infty}^t d\tau \int d\mathbf{r}' U_1(\mathbf{r}', \tau) \chi^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}'), \tag{40}$$

where the first-order time-domain linear density-density response function is given by [11]

$$\chi^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}') = i \sum_{\alpha=\pm 1, \pm 2, \dots} i s_\alpha \rho_{-\alpha}(\mathbf{r}') \rho_\alpha(\mathbf{r}) G_\alpha(t - \tau). \tag{41}$$

The corresponding frequency-domain density-density linear-response function $\chi^{(1)}(-\omega_s; \omega)$ is defined by

$$\delta\rho_1(\mathbf{r}, \omega_s) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int d\mathbf{r}' \chi^{(1)}(-\omega_s; \omega, \mathbf{r}, \mathbf{r}') U_1(\mathbf{r}', \omega). \tag{42}$$

Here $U_1(\mathbf{r}, \omega)$ is the Fourier transform of the time-dependent external field $U_1(\mathbf{r}, t)$ defined as

$$f(\mathbf{r}, \omega) \equiv \int dt f(\mathbf{r}, t) e^{i\omega t}, \quad f(\mathbf{r}, t) \equiv \frac{1}{2\pi} \int d\omega f(\mathbf{r}, \omega) e^{-i\omega t}. \tag{43}$$

By comparing Eqs. (40) with Eqs. (42) and using Eq. (43) [16,27] we have

$$\chi^{(1)}(-\omega_s; \omega, \mathbf{r}, \mathbf{r}') = \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau e^{-i\omega\tau} \chi^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}'). \tag{44}$$

The linear order response functions is usually denoted [27] by

$$\chi^{(1)}(\omega_s = \omega; \omega, \mathbf{r}, \mathbf{r}') = 2\pi \delta(-\omega_s + \omega) \chi^{(1)}(\omega, \mathbf{r}, \mathbf{r}'). \quad (45)$$

Using Eqs. (44) and (45), we obtain the linear density-density response function

$$\begin{aligned} \chi^{(1)}(\omega, \mathbf{r}, \mathbf{r}') &= \sum_{\alpha=\pm 1, \pm 2, \dots} \frac{s_\alpha \rho_{-\alpha}(\mathbf{r}') \rho_\alpha(\mathbf{r})}{\Omega_\alpha - \omega} \\ &= \sum_{\alpha=1, 2, \dots} \frac{2\Omega_\alpha \rho_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}')}{\Omega_\alpha^2 - \omega^2}. \end{aligned} \quad (46)$$

Here and below, Ω_α is positive (negative) for all $\alpha > 0$ ($\alpha < 0$), following the convention $\Omega_{-\alpha} = -\Omega_\alpha$.

Finally, the static linear density-density response can be obtained from Eq. (46) by setting $\omega = 0$:

$$\chi^{(1)}(0, \mathbf{r}, \mathbf{r}') = \sum_{\alpha=1, 2, \dots} \frac{2\rho_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}')}{\Omega_\alpha}. \quad (47)$$

Higher-order response functions may be computed in the same way and depend on the same ingredients: the CEO modes. Closed expressions for the second-order density-density response functions are given in Appendix B [Eqs. (B12), (B19), and (B20)] and the third-order response is presented in Appendix C [Eqs. (C10), (C23), and (C32)].

V. DISCUSSION

The density-matrix TDLS representation of linear and nonlinear TDDFT density-density response functions has several notable computational advantages compared with the Hilbert-space (orbital) TDHS representation. To facilitate the comparison, we have outlined the TDHS in Appendix D. In the TDLS approach, we need to solve the CEO eigenfunction and eigenvalue problem in Liouville space [Eq. (20)] to obtain the quasiparticle spectrum of excitations (the CEO modes) [18]. Eqs. (46), (B19) and (C23) can then be directly used to calculate time-dependent response functions in a single step. In TDHS, in contrast, we proceed in two steps: we first solve K Kohn-Sham equations Eq. (D1) with Eq. (D2) for the Kohn-Sham orbitals, and calculate the linear response for noninteracting particles Eq. (D3) and as a second step, we solve the Dyson-type integral equation [Eq. (D4)] to obtain linear response [11]. Calculating the nonlinear response in this approach is even more complicated. For example, obtaining the second-order response requires solving the Dyson-type integral equation [Eq. (D7)] using the integral equation for the linear response [Eq. (D6)]. Similarly, obtaining the third-order response requires the solution of Dyson-type integral equation [Eq. (D11)] using the integral equations for the second [Eq. (D10)] and linear response [Eq. (D6)]. The computation of nonlinear higher-order response thus involves the chain of self-consistent integral equations for all previous responses, while the TDLS provides a closed expression for the response functions. Clearly, the TDLS approach provides a much faster one-step algorithm for computations of response functions.

The CEO modes are nonlocal and act in a six-dimensional

space $(\mathbf{r}, \mathbf{r}')$ compared to the three-dimensional space (\mathbf{r}) of the Kohn-Sham orbitals. However, several points help reduce the computational cost. First, we can reduce the number of Liouville-space equations by solving only for particle-hole (interband) density matrix ξ instead of the entire density matrix $\delta\rho$: the particle-particle and hole-hole (intra-band) density matrix $T(\xi)$ can be obtained from Eq. (19), which follows from the idempotent property of single Slater determinant. For a basis set of K orbitals, the number of elements is the KN rather than K^2 . Moreover, the density matrices have nonvanishing elements only when $|\mathbf{r} - \mathbf{r}'|$ is less than a coherence size, which is typically very short. This allows to neglect many density-matrix elements, further reducing the size. It is not possible to include the coherent size in TDHS computations.

The present work can be extended in several ways. Even though we have derived closed expressions for the response up to third order, the computation of higher-order responses is straightforward and merely involves carrying out the expansions in Eqs. (28) and (32). The procedure, used here to compute response functions of the charge density, can be used to obtain response functions for any single-electron operator. For example, conductivities may be computed from the paramagnetic current response [28,29]

$$j_p^{(i)}(\mathbf{r}, t) = \text{Tr}\{[\mathbf{v} \delta\rho^{(i)}(t)](\mathbf{r}, \mathbf{r}')\}, \quad (48)$$

where $\mathbf{v}(\mathbf{r}, \mathbf{r}') = -(1/2m)(\nabla_{\mathbf{r}'} - \nabla_{\mathbf{r}})$ is the velocity operator.

Another interesting possible extension of this work is to include nonadiabatic exchange-correlation potentials, as outlined recently for the linear response [21]. In general, the exchange-correlation potential and exchange-correlation kernels are time dependent [23]. This time dependence has been neglected within the adiabatic approximation used here. If we relax this approximation, the eigenvalue equation for the Liouville superoperator L , Eq. (20), should be replaced by [21]

$$L(\Omega_\alpha) \xi_\alpha(\mathbf{r}, \mathbf{r}') = \Omega_\alpha \xi_\alpha(\mathbf{r}, \mathbf{r}'). \quad (49)$$

Methods for solving Eq. (49) using the frequency-dependent functional of Gross and Kohn [23] were described in Ref. [21].

The time dependent Hartree-Fock TDHF (also known as Random-phase approximation) is an alternative widely used approximation for computing response functions [24–26]. Within the density matrix representation, the TDHF is formally equivalent to TDDFT, provided we use the following exchange-correlation potential that depends on the density matrix (rather than merely on the charge density) [21]:

$$\begin{aligned} U_{KS-TDHF}^0[\rho](\mathbf{r}) &= -\frac{1}{2} \frac{\delta}{\delta n(\mathbf{r})} \left[\int d\mathbf{r}' \right. \\ &\quad \left. \times \int d\mathbf{r}'' \frac{\rho(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}'')}{|\mathbf{r} - \mathbf{r}''|} \right] \Bigg|_{n(\mathbf{r}') = \bar{\rho}(\mathbf{r}', \mathbf{r}')} \end{aligned} \quad (50)$$

By substituting $U_{KS}^0[\rho](\mathbf{r}) = U_{KS-TDHF}^0[\rho](\mathbf{r})$ from Eq. (50) into Eq. (9), we obtain the TDHF density-density responses. The TDLS formalism and the associated CEO algebra were first derived for the TDHF [18,20] and this paper extends these results to TDDFT. The difference between TD-DFT and TDHF equations is that in the former each order of the perturbed density matrix has its own equation of motion with a different electron-electron interaction potential, because the TDDFT exchange-correlation potential, expanded in terms of exchange-correlation kernels, is different in each order, while in TDHF the electron-electron interaction is the same for all orders [20].

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APPENDIX A: PROJECTION OF THE DENSITY MATRIX INTO THE INTERBAND SUBSPACE

Since the many-electron wave function is represented at all times by a single Slater determinant, the total density matrix $\rho(\mathbf{r}, \mathbf{r}', t)$ must be a projector. The idempotent property $[(\bar{\rho})^2(\mathbf{r}, \mathbf{r}') = \bar{\rho}(\mathbf{r}, \mathbf{r}')] allows us to project any single-particle matrix ζ into the interband (p - h) subspace [18]:$

$$\zeta_{p-h}(\mathbf{r}, \mathbf{r}') = [[\zeta, \bar{\rho}], \bar{\rho}](\mathbf{r}, \mathbf{r}'). \quad (\text{A1})$$

Consequently, not all elements of the density matrix are independent [18]. The idempotent property gives

$$[(\bar{\rho} + \delta\rho(t)) * (\bar{\rho} + \delta\rho(t))](\mathbf{r}, \mathbf{r}') = \bar{\rho}(\mathbf{r}, \mathbf{r}') + \delta\rho(\mathbf{r}, \mathbf{r}', t). \quad (\text{A2})$$

The number of degrees of freedom of $\delta\rho$ subject to the condition Eq. (A2) is precisely the number of its particle-hole matrix elements, and $T(\xi(\mathbf{r}, \mathbf{r}', t))$ can, therefore, be expressed in terms of $\xi(\mathbf{r}, \mathbf{r}', t)$. Using Eq. (A2) and Eq. (17) we get

$$\begin{aligned} & [(\bar{\rho} + \xi(t) + T(\xi(t))) * (\bar{\rho} + \xi(t) + T(\xi(t)))](\mathbf{r}, \mathbf{r}') \\ & = \bar{\rho}(\mathbf{r}, \mathbf{r}') + \xi(\mathbf{r}, \mathbf{r}', t) + T(\xi(\mathbf{r}, \mathbf{r}', t)). \end{aligned} \quad (\text{A3})$$

To simplify this expression we use the following relations, which follow from Eq. (A1): $\bar{\rho}(\mathbf{r}, \mathbf{r}') = (\bar{\rho} * \bar{\rho})(\mathbf{r}, \mathbf{r}')$, $\xi(\mathbf{r}, \mathbf{r}', t) = \bar{\rho} * \xi(t)(\mathbf{r}, \mathbf{r}') + \xi(t) * \bar{\rho}(\mathbf{r}, \mathbf{r}')$, and $T(t) * \bar{\rho}(\mathbf{r}, \mathbf{r}') = \bar{\rho} * T(t)(\mathbf{r}, \mathbf{r}')$. The following rule may be applied to separate the remaining terms: product of two interband (or two intraband) matrices gives an intraband matrix, whereas product of interband into intraband (or intraband into interband) matrices results in an interband matrix. Finally, the intraband part of Eq. (A3) is

$$\begin{aligned} & [T(\xi(t)) * T(\xi(t))](\mathbf{r}, \mathbf{r}') + (2\bar{\rho} - I) * T(\xi(t))(\mathbf{r}, \mathbf{r}') \\ & + [\xi(t) * \xi(t)](\mathbf{r}, \mathbf{r}') = 0, \end{aligned} \quad (\text{A4})$$

where I is the unit matrix in the real space $[I(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')]$. The formal solution of this quadratic equation, with the condition $T(\xi(\mathbf{r}, \mathbf{r}', t) = 0) = 0$ yields

$$T(\xi(\mathbf{r}, \mathbf{r}', t)) = \left(\bar{\rho} - \frac{I}{2} \right) * (I - \sqrt{I - 4\xi(t) * \xi(t)})(\mathbf{r}, \mathbf{r}'). \quad (\text{A5})$$

Equation (19) is obtained by expanding Eq. (A5) in powers of ξ .

APPENDIX B: THE SECOND-ORDER DENSITY RESPONSE

Expanding Eq. (8) to second order, we obtain

$$\begin{aligned} i \frac{\partial \delta\rho_2(\mathbf{r}, \mathbf{r}', t)}{\partial t} & = L \delta\rho_2(\mathbf{r}, \mathbf{r}', t) + (V_f[\delta\rho_1])(\mathbf{r}, t) \\ & - V_f^*[\delta\rho_1](\mathbf{r}', t) \delta\rho_1(\mathbf{r}, \mathbf{r}', t) \\ & + (V_g'[\delta\rho_1 \delta\rho_1])(\mathbf{r}, t) \\ & - V_g^*[\delta\rho_1 \delta\rho_1](\mathbf{r}', t) \bar{\rho}(\mathbf{r}, \mathbf{r}') + [U_1(\mathbf{r}, t) \\ & - U_1^*(\mathbf{r}', t)] \delta\rho_1(\mathbf{r}, \mathbf{r}', t), \end{aligned} \quad (\text{B1})$$

where

$$V_f[\delta\rho_1](\mathbf{r}, t) = \int d\mathbf{r}'' f'_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'') \delta\rho_1(\mathbf{r}', \mathbf{r}'', t) \quad (\text{B2})$$

and

$$V_g'[\delta\rho_1 \delta\rho_1](\mathbf{r}, t) = \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \int d\mathbf{r}'''' g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''', \mathbf{r}'''') \delta\rho_1(\mathbf{r}', \mathbf{r}'', t) \delta\rho_1(\mathbf{r}''', \mathbf{r}'''' , t), \quad (\text{B3})$$

where

$$g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''', \mathbf{r}'''') = g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}''') \delta(\mathbf{r}' - \mathbf{r}'') \delta(\mathbf{r}''' - \mathbf{r}''''). \quad (\text{B4})$$

Using Eq. (32), the equation of motion for $z_\alpha^{(2)}$ is

$$i \frac{\partial z_\alpha^{(2)}(t)}{\partial t} = \Omega_\alpha z_\alpha^{(2)}(t) + \sum_\beta z_\beta^{(1)}(t) \int U_1(\mathbf{r}, t) \rho_{-\alpha, \beta}(\mathbf{r}) d\mathbf{r} \\ + \sum_{\beta\gamma} V_{g(-\alpha\beta\gamma)} z_\beta^{(1)}(t) z_\gamma^{(1)}(t), \\ \alpha, \beta, \gamma = \pm 1, \pm 2, \dots, \quad (\text{B5})$$

where

$$V_{g(\alpha, \beta\gamma)} = \frac{1}{2} \text{Tr}[(I - 2\bar{\rho}) * ((\xi_\beta * \xi_\gamma + \xi_\gamma * \xi_\beta) \\ \times V_g(\xi_\alpha) + (\xi_\alpha * \xi_\beta + \xi_\beta * \xi_\alpha) \\ \times V_g(\xi_\gamma) + (\xi_\alpha * \xi_\gamma + \xi_\gamma * \xi_\alpha) V_g(\xi_\beta))], \quad (\text{B6})$$

where

$$V_g(\xi_\alpha)(\mathbf{r}) \xi_\beta = V_f[\xi_\alpha](\mathbf{r}) \xi_\beta + V'_g[\xi_\alpha \xi_\alpha](\mathbf{r}) \bar{\rho}, \quad (\text{B7})$$

and

$$\text{Tr}[\zeta(\mathbf{r}, \mathbf{r}')] = \int d\mathbf{r} \int d\mathbf{r}' \zeta(\mathbf{r}, \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \\ = \int \zeta(\mathbf{r}, \mathbf{r}) d\mathbf{r} \\ = \int \zeta(\mathbf{r}) d\mathbf{r}. \quad (\text{B8})$$

The solution of Eq. (B5) is

$$z_\alpha^{(2)}(t) = i \int_{-\infty}^t d\tau_1 \int d\mathbf{r} \int d\mathbf{r}' s_\alpha G_\alpha(t - \tau_1) \Gamma_\alpha^{(2)}(\tau_1, \mathbf{r}, \mathbf{r}'), \quad (\text{B9})$$

where

$$\Gamma_\alpha^{(2)}(\tau_1, \mathbf{r}, \mathbf{r}') = \sum_{\beta\gamma} V_{g(-\alpha\beta\gamma)} \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_1} d\tau_3 U_1(\mathbf{r}, \tau_1) U_1(\mathbf{r}', \tau_2) \rho_{-\beta}(\mathbf{r}) \rho_{-\gamma}(\mathbf{r}') s_\beta s_\gamma G_\beta(\tau_1 - \tau_2) G_\gamma(\tau_1 - \tau_3) \\ + \sum_\beta i U_1(\mathbf{r}, \tau_1) \rho_{-\alpha\beta}(\mathbf{r}) \int_{-\infty}^{\tau_1} d\tau_2 U_1(\mathbf{r}', \tau_2) \rho_{-\beta}(\mathbf{r}') s_\beta G_\beta(\tau_1 - \tau_2). \quad (\text{B10})$$

The time domain second-order density-density response function $\chi^{(2)}(t, \tau_1, \tau_2)$ is defined [11] by

$$\delta\rho_2(\mathbf{r}, t) = \delta\rho_2(\mathbf{r}, \mathbf{r}, t) = \frac{1}{2} \int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_2 \int d\mathbf{r}' \int d\mathbf{r}'' U_1(\mathbf{r}', \tau_1) U_1(\mathbf{r}'', \tau_2) \chi^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (\text{B11})$$

Inserting Eqs. (37) and (B9) into Eq. (28) and keeping all terms up to the second order, we find that the second-order response function finally has three contributions:

$$\chi^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = \chi_{\text{I}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') + \chi_{\text{II}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') + \chi_{\text{III}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}''), \quad (\text{B12})$$

where

$$\chi_{\text{I}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = 2 \sum_{\alpha\beta} \rho_{-\alpha, \beta}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_{-\beta}(\mathbf{r}'') s_\alpha s_\beta G_\alpha(t - \tau_1) G_\beta(\tau_1 - \tau_2), \quad (\text{B13})$$

$$\chi_{\text{II}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = 2i \int_{\tau_2}^t d\tau \sum_{\alpha\beta\gamma} V_{g(-\alpha\beta\gamma)} \rho_\alpha(\mathbf{r}) \rho_{-\beta}(\mathbf{r}') \rho_{-\gamma}(\mathbf{r}'') s_\alpha s_\beta s_\gamma G_\alpha(t - \tau) G_\beta(\tau - \tau_1) G_\gamma(\tau - \tau_2), \quad (\text{B14})$$

$$\chi_{\text{III}}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = 2 \sum_{\alpha\beta} \rho_{\alpha\beta}(\mathbf{r}) \rho_{-\alpha}(\mathbf{r}') \rho_{-\beta}(\mathbf{r}'') s_\alpha s_\beta G_\alpha(t - \tau_1) G_\beta(t - \tau_2). \quad (\text{B15})$$

The corresponding frequency domain density-density response function $\chi^{(2)}(-\omega_s; \omega_1, \omega_2)$ is defined by

$$\delta\rho_2(\mathbf{r}, \omega_s) = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \int d\mathbf{r}' \int d\mathbf{r}'' \chi^{(2)}(-\omega_s; \omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') U_1(\mathbf{r}', \omega_1) U_1(\mathbf{r}'', \omega_2). \quad (\text{B16})$$

The relation between response functions and charge densities are obtained by comparing Eq. (B11) with Eq. (B16) and using the Fourier transform Eq. (43):

$$\chi^{(2)}(-\omega_s; \omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau_1 e^{-i\omega_1 \tau_1} \int_{-\infty}^{\tau_1} d\tau_2 e^{-i\omega_2 \tau_2} \chi^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (\text{B17})$$

The second order response function is usually denoted by

$$\chi^{(2)}(\omega_s = \omega_1 + \omega_2, \omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = 2\pi \delta(-\omega_s + \omega_1 + \omega_2) \chi^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (\text{B18})$$

Using Eq. (B17) we finally obtain the second-order density-density response function that is symmetric with respect to ω_1 and ω_2 permutations:

$$\begin{aligned} \chi^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') &= 2 \sum_{\alpha\beta\gamma} \frac{V_{g(-\alpha\beta\gamma)} \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') \rho_\gamma(\mathbf{r}'') s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)(\Omega_\gamma - \omega_2)} + \sum_{\alpha\beta} \frac{\rho_{-\alpha\beta}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_\beta(\mathbf{r}'') s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)} \\ &+ \sum_{\alpha\beta} \frac{\rho_{-\alpha\beta}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_\beta(\mathbf{r}'') s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_2)} + \sum_{\alpha\beta} \frac{\rho_{\alpha\beta}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_\beta(\mathbf{r}'') s_\alpha s_\beta}{(s_\alpha \Omega_\alpha - \omega_1)(s_\beta \Omega_\beta - \omega_2)}, \\ &\alpha, \beta, \gamma = \pm 1, \pm 2, \dots \end{aligned} \quad (\text{B19})$$

Here and below Ω_ν , $\nu = \alpha, \beta$ is positive (negative) for all $\nu > 0$ ($\nu < 0$) following to the convention $\Omega_{-\nu} = -\Omega_\nu$.

By setting ω_1 and ω_2 to zero and using the identities $s_\nu \Omega_\nu = |\Omega_\nu|$ and $\rho_{-\nu} = \rho_\nu$, we obtain the second-order static density-density response

$$\chi^{(2)}(0, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = 2 \sum_{\alpha\beta\gamma} \frac{V_{g(\alpha\beta\gamma)} \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') \rho_\gamma(\mathbf{r}'')}{|\Omega_\alpha \Omega_\beta \Omega_\gamma|} + 3 \sum_{\alpha\beta} \frac{\rho_{\alpha\beta}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_\beta(\mathbf{r}'')}{|\Omega_\alpha \Omega_\beta|}, \quad \alpha, \beta, \gamma = \pm 1, \pm 2, \dots \quad (\text{B20})$$

APPENDIX C: THE THIRD-ORDER DENSITY RESPONSE

Expanding Eq. (8) to third order, we obtain

$$\begin{aligned} i \frac{\partial \delta \rho_3(\mathbf{r}, \mathbf{r}', t)}{\partial t} &= L \delta \rho_3(\mathbf{r}, \mathbf{r}', t) + (V_f[\delta \rho_1](\mathbf{r}, t) - V_f^*[\delta \rho_1](\mathbf{r}', t)) \delta \rho_2(\mathbf{r}, \mathbf{r}', t) + (V_f[\delta \rho_2](\mathbf{r}, t) - V_f^*[\delta \rho_2](\mathbf{r}', t)) \delta \rho_1(\mathbf{r}, \mathbf{r}', t) \\ &+ (V'_g[\delta \rho_1, \delta \rho_1](\mathbf{r}, t) - V'_g^*[\delta \rho_1, \delta \rho_1](\mathbf{r}', t)) \delta \rho_1(\mathbf{r}, \mathbf{r}', t) + (V'_g[\delta \rho_1, \delta \rho_2](\mathbf{r}, t) - V'_g^*[\delta \rho_1, \delta \rho_2](\mathbf{r}', t)) \\ &+ V'_g[\delta \rho_2, \delta \rho_1](\mathbf{r}, t) - V'_g^*[\delta \rho_2, \delta \rho_1](\mathbf{r}', t)) \bar{\rho}(\mathbf{r}, \mathbf{r}') + (V_h[\delta \rho_1, \delta \rho_1, \delta \rho_1](\mathbf{r}, t) \\ &- V_h^*[\delta \rho_1, \delta \rho_1, \delta \rho_1](\mathbf{r}', t)) \bar{\rho}(\mathbf{r}, \mathbf{r}') + [U_1(\mathbf{r}, t) - U_1^*(\mathbf{r}', t)] \delta \rho_3(\mathbf{r}, \mathbf{r}', t), \end{aligned} \quad (\text{C1})$$

where

$$\begin{aligned} V_h[\delta \rho_1 \delta \rho_1 \delta \rho_1](\mathbf{r}, t) &= \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \int d\mathbf{r}'''' \int d\mathbf{r}''''' h_{xc}[\bar{\rho}] \\ &\times (\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''', \mathbf{r}''''', \mathbf{r}''''''') \delta \rho_1(\mathbf{r}', \mathbf{r}'', t) \delta \rho_1(\mathbf{r}''', \mathbf{r}''''', t) \delta \rho_1(\mathbf{r}''''', \mathbf{r}''''''', t), \end{aligned} \quad (\text{C2})$$

where

$$h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''', \mathbf{r}''''', \mathbf{r}''''''') = h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''''') \delta(\mathbf{r}' - \mathbf{r}'') \delta(\mathbf{r}''' - \mathbf{r}''''') \delta(\mathbf{r}'''''' - \mathbf{r}'''''''). \quad (\text{C3})$$

Using Eq. (32), the equation of motion for $z_\alpha^{(3)}$ is

$$\begin{aligned} i \frac{\partial z_\alpha^{(3)}(t)}{\partial t} &= \Omega_\alpha z_\alpha^{(3)}(t) + z_\beta^{(2)}(t) \sum_\beta \int U_1(\mathbf{r}, t) \rho_{-\alpha\beta}(\mathbf{r}) d\mathbf{r} + \sum_{\beta\gamma} z_\beta^{(1)}(t) z_\gamma^{(1)}(t) \int U_1(\mathbf{r}, t) \rho_{-\alpha\beta\gamma}(\mathbf{r}) d\mathbf{r} \\ &+ 2 \sum_{\beta\gamma} V_{g(-\alpha\beta\gamma)} z_\beta^{(1)}(t) z_\gamma^{(2)}(t) + \sum_{\beta\gamma\delta} V_{h(-\alpha\beta\gamma\delta)} z_\beta^{(1)}(t) z_\gamma^{(1)}(t) z_\delta^{(1)}(t), \quad \alpha, \beta, \gamma, \delta = \pm 1, \pm 2, \dots, \end{aligned} \quad (\text{C4})$$

where

$$\begin{aligned}
 V_{h(\alpha,\beta\gamma\delta)} = & \frac{1}{6} \text{Tr}[(I-2\bar{\rho})^*(\xi_\alpha^*\xi_\delta + \xi_\delta^*\xi_\alpha) V_h((I-2\bar{\rho})^*(\xi_\beta^*\xi_\gamma + \xi_\gamma^*\xi_\beta))] \\
 & + \frac{1}{6} \text{Tr}[(I-2\bar{\rho})^*(\xi_\alpha^*\xi_\gamma + \xi_\gamma^*\xi_\alpha) V_h((I-2\bar{\rho})^*(\xi_\delta^*\xi_\beta + \xi_\beta^*\xi_\delta))] \\
 & + \frac{1}{6} \text{Tr}[(I-2\bar{\rho})^*(\xi_\alpha^*\xi_\beta + \xi_\beta^*\xi_\alpha) V_h((I-2\bar{\rho})^*(\xi_\delta^*\xi_\alpha + \xi_\gamma^*\xi_\delta))] \\
 & - \frac{1}{6} \text{Tr}[(\xi_\alpha V_h(\xi_\beta) + V_h(\xi_\beta)\xi_\alpha)^*(\xi_\gamma^*\xi_\delta + \xi_\delta^*\xi_\gamma)] \\
 & - \frac{1}{6} \text{Tr}[(\xi_\alpha V_h(\xi_\gamma) + V_h(\xi_\gamma)\xi_\alpha)^*(\xi_\beta^*\xi_\delta + \xi_\delta^*\xi_\beta)] \tag{C5}
 \end{aligned}$$

$$- \frac{1}{6} \text{Tr}[(\xi_\alpha V_h(\xi_\beta) + V_h(\xi_\beta)\xi_\alpha)^*(\xi_\beta^*\xi_\gamma + \xi_\gamma^*\xi_\beta)]. \tag{C6}$$

The solution of Eq. (C4) is

$$z_\alpha^{(3)}(t) = i \int_{-\infty}^t d\tau_1 \int d\mathbf{r} s_\alpha G_\alpha(t-\tau_1) \Gamma_\alpha^{(3)}(\tau_1, \mathbf{r}), \tag{C7}$$

where

$$\begin{aligned}
 \Gamma_\alpha^{(3)}(\tau_1, \mathbf{r}) = & \sum_\beta U_1(\mathbf{r}, \tau_1) \rho_{-\alpha\beta}(\mathbf{r}) z_\beta^{(2)}(\tau_1) + \sum_{\beta\gamma} U_1(\mathbf{r}, \tau_1) \rho_{-\alpha\beta\gamma}(\mathbf{r}) z_\beta^{(1)}(\tau_1) z_\gamma^{(1)}(\tau_1) + 2 \sum_{\beta\gamma} V_{g(-\alpha\beta\gamma)} z_\beta^{(1)}(\tau_1) z_\gamma^{(2)}(\tau_1) \\
 & + \sum_{\beta\gamma\delta} V_{h(-\alpha\beta\gamma\delta)} z_\beta^{(1)}(\tau_1) z_\gamma^{(1)}(\tau_1) z_\delta^{(1)}(\tau_1), \tag{C8}
 \end{aligned}$$

where $z^{(1)}(\tau_1)$ and $z^{(2)}(\tau_1)$ are given by Eqs. (37) and (B9).

Time domain third-order density-density response function $\chi^{(3)}(t, \tau_1, \dots, \tau_3)$ is defined [11] by

$$\begin{aligned}
 \delta\rho_3(\mathbf{r}, t) = & \delta\rho_3(\mathbf{r}, \mathbf{r}, t) \\
 = & \frac{1}{6} \int_{-\infty}^t d\tau_1 \int_{-\infty}^t d\tau_2 \int_{-\infty}^t d\tau_3 \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' U_1(\mathbf{r}', \tau_1) U_1(\mathbf{r}'', \tau_2) U_1(\mathbf{r}''', \tau_3) \chi^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}'''). \tag{C9}
 \end{aligned}$$

Inserting Eqs. (37), (B9), and (C7) into Eq. (28) and retaining all terms to third order, we obtain the final expression for the third-order response function

$$\chi^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \chi_{\text{I}}^{(3)} + \chi_{\text{II}}^{(3)} + \chi_{\text{III}}^{(3)} + \chi_{\text{IV}}^{(3)} + \chi_{\text{V}}^{(3)} + \chi_{\text{VI}}^{(3)} + \chi_{\text{VII}}^{(3)} + \chi_{\text{VIII}}^{(3)}, \tag{C10}$$

where

$$\chi_{\text{I}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = -6i \sum_{\alpha\beta\gamma} \rho_{-\alpha\beta}(\mathbf{r}) \rho_{-\beta\gamma}(\mathbf{r}') \rho_\alpha(\mathbf{r}'') \rho_{-\gamma}(\mathbf{r}''') s_\alpha s_\beta s_\gamma G_\alpha(t-\tau_1) G_\beta(\tau_1-\tau_2) G_\gamma(\tau_2-\tau_3), \tag{C11}$$

$$\begin{aligned}
 \chi_{\text{II}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = & 12 \sum_{\alpha\beta\gamma\delta} \rho_{-\alpha\beta}(\mathbf{r}) V_{g(-\beta\gamma\delta)} \rho_\alpha(\mathbf{r}') \rho_{-\gamma}(\mathbf{r}'') \rho_{-\delta}(\mathbf{r}''') s_\alpha s_\beta s_\gamma s_\delta \\
 & \times \int_{\tau_3}^t d\tau G_\alpha(t-\tau_1) G_\beta(\tau_1-\tau) G_\gamma(\tau-\tau_2) G_\delta(\tau-\tau_3), \tag{C12}
 \end{aligned}$$

$$\chi_{\text{III}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = -6i \sum_{\alpha\beta\gamma} \rho_{-\alpha\beta\gamma}(\mathbf{r}) \rho_\alpha(\mathbf{r}') \rho_{-\beta}(\mathbf{r}'') \rho_{-\gamma}(\mathbf{r}''') s_\alpha s_\beta s_\gamma G_\alpha(t-\tau_1) G_\beta(\tau_1-\tau_2) G_\gamma(\tau_1-\tau_3), \tag{C13}$$

$$\begin{aligned} \chi_{\text{IV}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= 12 \sum_{\alpha\beta\gamma\delta} V_{g(-\alpha\beta\gamma)} \rho_{-\gamma\delta}(\mathbf{r}) \rho_{\alpha}(\mathbf{r}') \rho_{-\beta}(\mathbf{r}'') \rho_{-\delta}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta} \\ &\quad \times \int_{\tau_3}^t d\tau G_{\alpha}(t-\tau) G_{\beta}(\tau-\tau_1) G_{\gamma}(\tau-\tau_2) G_{\delta}(\tau_2-\tau_3), \end{aligned} \quad (\text{C14})$$

$$\begin{aligned} \chi_{\text{V}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= 12i \sum_{\alpha\beta\gamma\delta\eta} V_{g(-\alpha\beta\gamma)} V_{g(-\gamma\delta\eta)} \rho_{\alpha}(\mathbf{r}) \rho_{-\beta}(\mathbf{r}') \rho_{-\delta}(\mathbf{r}'') \rho_{-\eta}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta} s_{\eta} \\ &\quad \times \int_{\tau_3}^t d\tau \int_{\tau_3}^{\tau} d\tau' G_{\alpha}(t-\tau) G_{\beta}(\tau-\tau_1) G_{\gamma}(\tau-\tau') G_{\delta}(\tau'-\tau_2) G_{\eta}(\tau'-\tau_3), \end{aligned} \quad (\text{C15})$$

$$\begin{aligned} \chi_{\text{VI}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= 6 \sum_{\alpha\beta\gamma\delta} V_{h(-\alpha\beta\gamma\delta)} \rho_{\alpha}(\mathbf{r}) \rho_{-\beta}(\mathbf{r}') \rho_{-\gamma}(\mathbf{r}'') \rho_{-\delta}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta} \\ &\quad \times \int_{\tau_3}^t d\tau G_{\alpha}(t-\tau) G_{\beta}(\tau-\tau_1) G_{\gamma}(\tau-\tau_2) G_{\delta}(\tau-\tau_3), \end{aligned} \quad (\text{C16})$$

$$\begin{aligned} \chi_{\text{VII}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= -12i \sum_{\alpha\beta\gamma} \rho_{\alpha\beta}(\mathbf{r}) \rho_{-\beta\gamma}(\mathbf{r}') \rho_{-\alpha}(\mathbf{r}'') \rho_{-\gamma}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} G_{\alpha}(t-\tau_1) G_{\beta}(\tau-\tau_2) G_{\gamma}(\tau_2-\tau_3), \end{aligned} \quad (\text{C17})$$

$$\begin{aligned} \chi_{\text{VIII}}^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= 12 \sum_{\alpha\beta\gamma\delta} \rho_{\alpha\beta}(\mathbf{r}) V_{g(-\beta\gamma\delta)} \rho_{-\alpha}(\mathbf{r}') \rho_{\gamma}(\mathbf{r}'') \rho_{-\delta}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta} \\ &\quad \times \int_{\tau_3}^t d\tau G_{\alpha}(t-\tau_1) G_{\beta}(t-\tau) G_{\gamma}(\tau-\tau_2) G_{\delta}(\tau-\tau_3). \end{aligned} \quad (\text{C18})$$

The corresponding frequency domain density-density response function $\chi^{(3)}(-\omega_s; \omega_1, \dots, \omega_3)$ is defined by

$$\begin{aligned} \delta\rho_3(\mathbf{r}, \omega_s) &= \frac{1}{6} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \chi^{(3)}(-\omega_s; \omega_1, \omega_2, \mathbf{r}, \mathbf{r}', \mathbf{r}'') U_1(\mathbf{r}', \omega_1) U_1(\mathbf{r}'', \omega_2) U_1(\mathbf{r}''', \omega_3). \end{aligned} \quad (\text{C19})$$

The relation between response functions and charge densities are obtained by comparing Eq. (C9) with Eqs. (C20) and using the Fourier transform Eq. (43):

$$\begin{aligned} \chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= \int_{-\infty}^{\infty} dt e^{i\omega_s t} \int_{-\infty}^t d\tau_1 e^{-i\omega_1 \tau_1} \int_{-\infty}^t d\tau_2 e^{-i\omega_2 \tau_2} \int_{-\infty}^t d\tau_3 e^{-i\omega_3 \tau_3} \chi^{(3)}(t, \tau_1, \tau_2, \tau_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}'''). \end{aligned} \quad (\text{C20})$$

The third-order response function is usually denoted by

$$\chi^{(3)}(\omega_s = \omega_1 + \omega_2 + \omega_3, \omega_1, \omega_2, \omega_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = 2\pi \delta(-\omega_s + \omega_1 + \omega_2 + \omega_3) \chi^{(3)}(\omega_1, \omega_2, \omega_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}'''). \quad (\text{C21})$$

Using Eqs. (C21) and (C22), we obtain the following eight-term expression for the third-order density response function (symmetrized with respect to ω_1, ω_2 , and ω_3 permutations):

$$\chi^{(3)}(\omega_1, \omega_2, \omega_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \sum_{\omega_1 \omega_2 \omega_3}^{perm} (\chi_{\text{I}}^{(3)} + \chi_{\text{II}}^{(3)} + \chi_{\text{III}}^{(3)} + \dots + \chi_{\text{VIII}}^{(3)}), \quad (\text{C22})$$

where

$$\chi_{\text{I}}^{(3)} = \sum_{\alpha\beta\gamma} \frac{\rho_{-\alpha\beta}(\mathbf{r}) \rho_{-\beta\gamma}(\mathbf{r}') \rho_{\alpha}(\mathbf{r}'') \rho_{-\gamma}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_3)}, \quad (\text{C23})$$

$$\chi_{\text{II}}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{\rho_{-\alpha\beta}(\mathbf{r}) V_{g(-\beta\gamma\delta)} \rho_{\alpha}(\mathbf{r}') \rho_{-\gamma}(\mathbf{r}'') \rho_{-\delta}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta}}{(\Omega_{\alpha} - \omega_1 - \omega_2 - \omega_3)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_2)(\Omega_{\delta} - \omega_3)}, \quad (\text{C24})$$

$$\chi_{\text{III}}^{(3)} = \sum_{\alpha\beta\gamma} \frac{\rho_{-\alpha\beta\gamma}(\mathbf{r})\rho_{\alpha}(\mathbf{r}')\rho_{-\beta}(\mathbf{r}'')\rho_{-\gamma}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_3)}, \quad (\text{C26})$$

$$\chi_{\text{IV}}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{2V_{g(-\alpha\beta\gamma)}\rho_{-\gamma\delta}(\mathbf{r})\rho_{\alpha}(\mathbf{r}')\rho_{-\beta}(\mathbf{r}'')\rho_{-\delta}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2-\omega_3)(\Omega_{\delta}-\omega_3)}, \quad (\text{C27})$$

$$\chi_{\text{V}}^{(3)} = \sum_{\alpha\beta\gamma\delta\eta} \frac{2V_{g(-\alpha\beta\gamma)}V_{g(-\gamma\delta\eta)}\rho_{\alpha}(\mathbf{r})\rho_{-\beta}(\mathbf{r}')\rho_{-\delta}(\mathbf{r}'')\rho_{-\eta}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s s_{\eta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2-\omega_3)(\Omega_{\delta}-\omega_2)(\Omega_{\eta}-\omega_3)}, \quad (\text{C28})$$

$$\chi_{\text{VI}}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{V_{h(-\alpha\beta\gamma\delta)}\rho_{\alpha}(\mathbf{r})\rho_{-\beta}(\mathbf{r}')\rho_{-\gamma}(\mathbf{r}'')\rho_{-\delta}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2)(\Omega_{\delta}-\omega_3)}, \quad (\text{C29})$$

$$\chi_{\text{VII}}^{(3)} = \sum_{\alpha\beta\gamma} \frac{\rho_{\alpha\beta}(\mathbf{r})\rho_{-\beta\gamma}(\mathbf{r}')\rho_{-\alpha}(\mathbf{r}'')\rho_{-\gamma}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s}{(\Omega_{\alpha}-\omega_1)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_3)}, \quad (\text{C30})$$

$$\chi_{\text{VIII}}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{\rho_{\alpha\beta}(\mathbf{r})V_{g(-\beta\gamma\delta)}\rho_{-\alpha}(\mathbf{r}')\rho_{-\gamma}(\mathbf{r}'')\rho_{-\delta}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_2)(\Omega_{\delta}-\omega_3)}. \quad (\text{C31})$$

Here $\nu = \alpha, \beta, \gamma, \delta, \eta = \pm 1, \pm 2, \dots$ and Ω_{ν} is positive (negative) for all $\nu > 0$ ($\nu < 0$) according to the convention $\Omega_{-\nu} = -\Omega_{\nu}$. Note, that in Eq. (B19) the permutations over ω_1 and ω_2 were written explicitly. Finally, by setting ω_1 , ω_2 , and ω_3 to zero and using identities $s_{\nu}\Omega_{\nu} = |\Omega_{\nu}|$ and $\rho_{-\nu} = \rho_{\nu}$, we obtain the third-order static density-density response

$$\begin{aligned} \chi^{(3)}(0, \mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') &= 6 \sum_{\alpha\beta\gamma} \frac{\rho_{\alpha\beta\gamma}(\mathbf{r})\rho_{\alpha}(\mathbf{r}')\rho_{\beta}(\mathbf{r}'')\rho_{\gamma}(\mathbf{r}''')}{|\Omega_{\alpha}\Omega_{\beta}\Omega_{\gamma}|} \\ &+ 6 \sum_{\alpha\beta\gamma} \frac{2\rho_{\alpha\beta}(\mathbf{r})\rho_{-\beta\gamma}(\mathbf{r}')\rho_{\alpha}(\mathbf{r}'')\rho_{\gamma}(\mathbf{r}''')}{|\Omega_{\alpha}\Omega_{\beta}\Omega_{\gamma}|} \\ &+ 6 \sum_{\alpha\beta\gamma\delta} \frac{4\rho_{\alpha\beta}(\mathbf{r})V_{g(-\beta\gamma\delta)}\rho_{\alpha}(\mathbf{r}')\rho_{\gamma}(\mathbf{r}'')\rho_{\delta}(\mathbf{r}''')}{|\Omega_{\alpha}\Omega_{\beta}\Omega_{\gamma}\Omega_{\delta}|} \\ &+ 6 \sum_{\alpha\beta\gamma\delta\eta} \frac{2V_{g(\alpha\beta\gamma)}V_{g(-\gamma\delta\eta)}\rho_{\alpha}(\mathbf{r})\rho_{\beta}(\mathbf{r}')\rho_{\delta}(\mathbf{r}'')\rho_{\eta}(\mathbf{r}''')}{|\Omega_{\alpha}\Omega_{\beta}\Omega_{\gamma}\Omega_{\delta}\Omega_{\eta}|} \\ &+ 6 \sum_{\alpha\beta\gamma\delta} \frac{V_{h(\alpha\beta\gamma\delta)}\rho_{\alpha}(\mathbf{r})\rho_{\beta}(\mathbf{r}')\rho_{\gamma}(\mathbf{r}'')\rho_{\delta}(\mathbf{r}''')}{|\Omega_{\alpha}\Omega_{\beta}\Omega_{\gamma}\Omega_{\delta}|}, \\ &\alpha, \beta, \gamma, \delta, \eta = \pm 1, \pm 2, \dots \end{aligned} \quad (\text{C32})$$

APPENDIX D: THE TIME-DEPENDENT HILBERT-SPACE REPRESENTATION OF RESPONSE FUNCTIONS

The ordinary ground-state Kohn-Sham equations in Hilbert space are [2,11] ($\hbar = 1$)

$$\hat{H}_{KS}[n_0(\mathbf{r})](\mathbf{r})\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}), \quad (\text{D1})$$

$$\sum_{j=1}^K |\varphi_j(\mathbf{r})|^2 = n_0(\mathbf{r}), \quad (\text{D2})$$

where $n_0(\mathbf{r})$ is a true initial ground-state charge density of electrons (the charge of an electron $e = 1$); $\hat{H}_{KS}[n_0(\mathbf{r})](\mathbf{r})$ is the Kohn-Sham Hamiltonian Eq. (6) with the time-independent external field $U_{ext}(\mathbf{r}) = U_0(\mathbf{r})$.

The density-density linear response Eqs. (40), (B11), and (C9) in the TDHS framework can be calculated in two steps, using a perturbative expansion in the electron-electron interaction [11]. The first step is the calculation of the response function $\chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{r}')$ of non-interacting particles with unperturbed density n_0 in terms of the static unperturbed Kohn-Sham orbitals $\phi_k(\mathbf{r})$:

$$\chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{r}') = \sum_{j,k} (f_k - f_j) \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta}. \quad (\text{D3})$$

Here, (f_k, f_j) are the occupation numbers (0 or 1) of the Kohn-Sham orbitals; ε_j and ε_k are corresponding energy levels of the noninteracting particles. The summation in Eq. (D3) extends over both occupied and unoccupied orbitals, including the continuum states.

The linear response function for the system of interacting particles $\chi^{(1)}(\omega, \mathbf{r}, \mathbf{r}')$ is obtained in a second step by solving Dyson-type integral equation:

$$\chi^{(1)}(\omega, \mathbf{r}, \mathbf{r}') = \chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{r}') + \int d\mathbf{x} \int d\mathbf{x}' \chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{x}) \left(\frac{e^2}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}[n_0](\omega, \mathbf{x}, \mathbf{x}') \right) \chi^{(1)}(\omega, \mathbf{x}', \mathbf{r}'), \quad (\text{D4})$$

where $f_{xc}[n_0](\omega, \mathbf{r}, \mathbf{r}')$ is a Fourier transform with respect to time of the time-dependent exchange-correlation kernel $f_{xc}[n_0](\mathbf{r}, t, \mathbf{r}', t')$

$$f_{xc}[n_0](\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta U_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n_0}, \quad (\text{D5})$$

and the exact frequency-dependent linear density response is given by

$$\begin{aligned} n_1(\omega, \mathbf{r}) = & \int d\mathbf{y} \chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{y}) U_1(\mathbf{y}, \omega) \\ & + \int d\mathbf{y} \int d\mathbf{y}' \chi_s^{(1)}(\omega, \mathbf{r}, \mathbf{y}) \\ & \times \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc}[n_0](\omega, \mathbf{y}, \mathbf{y}') \right) n_1(\omega, \mathbf{y}'). \end{aligned} \quad (\text{D6})$$

The Bethe-Salpeter-type integral equation for the second-order density-density response is represented in four-dimensional coordinate-time space:

$$\begin{aligned} \chi^{(2)}(x, y, y') = & \int dz \int dz' \chi_s^{(2)}(x, z, z') \left. \frac{\delta U_{KS}(z)}{\delta U_{ext}(y)} \right|_{n_0} \\ & \times \left. \frac{\delta U_{KS}(z')}{\delta U_{ext}(y')} \right|_{n_0} + \int dz \chi_s^{(1)}(x, z) \int dz' \\ & \times \int dz'' g_{xc}(z, z', z'') \chi_s^{(1)}(z', y) \chi_s^{(1)}(z'', y') \\ & + \int dz \chi_s^{(1)}(x, z) \int dz' (w(z, z')) \end{aligned}$$

$$+ f_{xc}(z, z') \chi^{(2)}(z', y, y'), \quad (\text{D7})$$

where the time-dependent second-order exchange-correlation kernel g_{xc} is defined as

$$g_{xc}(z, z', z'') = \left. \frac{\delta^2 U_{xc}(z)}{\delta n(z') \delta n(z'')} \right|_{n_0}; \quad (\text{D8})$$

the kernel of the (instantaneous) Coulomb interaction $w(x, x')$ is

$$w(x, x') = \frac{e^2 \delta(t - t')}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{D9})$$

The time-dependent Kohn-Sham equations for the second-order density response are finally obtained by inserting Eq. (D7) into Eq. (B11):

$$\begin{aligned} n_2(x) = & \frac{1}{2} \int dz \int dz' \chi_s^{(2)}(x, z, z') U_{KS}[n_1](z) U_{KS}[n_1](z') \\ & + \frac{1}{2} \int dz \int dz' \int dz'' \chi_s^{(1)}(x, z) g_{xc}(z, z', z'') \\ & \times n_1(z') n_1(z'') + \int dz \int dz' \chi_s^{(1)}(x, z) (w(z, z') \\ & + f_{xc}(z, z')) n_2(z'). \end{aligned} \quad (\text{D10})$$

Solving Eq. (D6) first, allows for the subsequent solution of the self-consistent Eq. (D10) that is quadratic in the (effective) perturbing potential $U_{KS}[n_1(\mathbf{r}, t)](\mathbf{r}, t)$.

Proceeding in a similar fashion, one can set up the Dyson-type integral equation for the third-order density response Eq. (C9):

$$\begin{aligned} n_3(x) = & \frac{1}{6} \int dy \int dy' \int dy'' \chi_s^{(3)}(x, y, y', y'') U_{KS}[n_1](y) U_{KS}[n_1](y') U_{KS}[n_1](y'') \\ & + \frac{1}{2} \int dy \int dy' \int dz \int dz' \chi_s^{(2)}(x, y, y') U_{KS}[n_1](y) g_{xc}(y', z, z') n_1(z) n_1(z') \\ & + \int dy \int dy' \int dy'' \chi_s^{(2)}(x, y, y') U_{KS}[n_1](y) (w(y', y'') + f_{xc}(y', y'')) n_2(y'') \\ & + \frac{1}{6} \int dy \int dz \int dz' \int dz'' \chi_s^{(1)}(x, y) h_{xc}(y, z, z', z'') n_1(z) n_1(z') n_1(z'') \\ & + \int dy \int dy' \int dy'' \chi_s^{(1)}(x, y) g_{xc}(y, y', y'') n_1(y') n_2(y'') \\ & + \int dy \int dy' \chi_s^{(1)}(x, y) (w(z, z') + f_{xc}(y, y')) n_3(y'), \end{aligned} \quad (\text{D11})$$

where h_{xc} is the third-order functional derivative of the time-dependent exchange-correlation potential with respect to the time-dependent densities

$$h_{xc}(y, z, z', z'') = \frac{\delta^3 U_{xc}(y)}{\delta n(z) \delta n(z') \delta n(z'')} \Big|_{n_0}. \quad (\text{D12})$$

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