

Time-dependent quasiparticle current-density-functional theory of x-ray nonlinear response functions

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A real-space representation of the current response of many-electron systems with possible applications to x-ray nonlinear spectroscopy and magnetic susceptibilities is developed. Closed expressions for the linear, quadratic, and third-order response functions are derived by solving the adiabatic time dependent current density functional (TDCDFT) equations for the single-electron density matrix in Liouville space.

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I. INTRODUCTION

Time-dependent current-density-functional theory (TDCDFT) offers a computationally tractable framework for computing currents and response functions of many-electron systems in response to external electric and magnetic perturbations.¹ The time-dependent linear paramagnetic susceptibilities are calculated as the linear response of a noninteracting Kohn-Sham reference system to an effective vector-potential, which consists of the external field, together with the Hartree and the exchange-correlation contributions.¹ For the sake of computing current-related properties, it is natural to consider the effective potential to be a functional of both current and charge density rather than charge density alone, as in standard time-dependent density-functional-theory (TDDFT).² Another reason for applying TDCDFT to crystals is connected with the recent argument that there is a one-to-one correspondence between time-varying periodic potentials and the current density but not with the charge density.³ TDCDFT was successfully used for calculating the polarizability of conjugated polymers.^{4,5} Current density functional theory (CDFT) yields exact response functions⁶ to static external potentials and TDCDFT is thus expected to provide reasonable approximations for time-dependent current properties.

The linear magnetic susceptibility (the response of the current to an external vector-potential) of the Kohn-Sham noninteracting system has been calculated using the local current density exchange correlation kernel for the electron gas.¹ However, computing the response functions of the interacting system (where the quasiparticle energies cannot be expressed as differences between Kohn-Sham energy levels), requires the solution of a chain of integral equations,¹ whose computational cost rapidly increases with the nonlinear order of the response. In this paper we compute current response functions by recasting the TDCDDT equations in terms of the reduced single electron density matrix for an N electron system $\rho(\mathbf{r}, \mathbf{r}_1, t) = \sum_{n=1}^N \psi_n(\mathbf{r}, t) \psi_n^*(\mathbf{r}_1, t)$,⁷ where $\psi_n(\mathbf{r})$ are the Kohn-Sham orbitals. Closed expressions are derived for the linear, quadratic, and third-order response functions^{2,8,9} (the response of the total polarization current to the external electric field) by solving an eigenvalue equation in Liouville space. The quasiparticle frequencies are not given simply as

differences of Kohn-Sham orbital energies.⁶ Current response functions should also be particularly suitable for computing the resonant nonlinear response to x-ray fields.¹⁰ Due to the short wavelength, the dipole approximation does not generally hold, and x-ray susceptibilities may be expressed in terms of multitime correlation functions of currents and charge densities.^{10,11} TDCDFT thus provides a natural direct computational approach for nonlinear x-ray spectroscopy.

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

TDCDFT maps the original system of interacting electrons onto an effective system of noninteracting electrons subjected to an exchange-correlation scalar and vector potentials,¹ constructed to yield the same charge density and current profiles as the interacting system. The Kohn-Sham TDCDFT equations of motion for the time-dependent density matrix are

$$i \frac{\partial \rho(\mathbf{r}, \mathbf{r}_1, t)}{\partial t} = [\hat{H}_{\text{KS}}^0(\mathbf{r}, t) - \hat{H}_{\text{KS}}^{0*}(\mathbf{r}_1, t)] \rho(\mathbf{r}, \mathbf{r}_1, t) - [\mathbf{j}(\mathbf{r}, t) \mathbf{A}(\mathbf{r}, t) - \mathbf{j}^*(\mathbf{r}_1, t) \mathbf{A}^*(\mathbf{r}_1, t)] + \left(\frac{e^2}{2mc} A^2(\mathbf{r}, t) n(\mathbf{r}, t) - \frac{e^2}{2mc} A^{2*}(\mathbf{r}_1, t) n^*(\mathbf{r}_1, t) \right), \quad (1)$$

where $e(m)$ is the electron charge (mass), and we set $\hbar = 1$. The time-dependent charge density and paramagnetic electronic current are given by

$$n(\mathbf{r}, t) = \rho(\mathbf{r}, \mathbf{r}, t), \quad \mathbf{j}(\mathbf{r}, t) = - \frac{ie}{2m} [(\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}}) \delta \rho(\mathbf{r}, \mathbf{r}_1, t)]_{\mathbf{r}=\mathbf{r}_1}. \quad (2)$$

The observed (physical) current, which enters the continuity equation, is given by

$$\mathbf{J}(\mathbf{r},t) = \mathbf{j}(\mathbf{r},t) - \frac{e^2}{2mc} \mathbf{A}(\mathbf{r},t)n(\mathbf{r},t); \quad (3)$$

\hat{H}_{KS}^0 is the Kohn-Sham Hamiltonian $\hat{H}_{\text{KS}}^0(\mathbf{r},t) \equiv \hat{H}_{\text{KS}}^0[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$. The remaining terms in Eq. (1) represent the coupling to an external vector potential

$$\hat{H}_{\text{KS}}^0[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)] = -\frac{1}{2m} \nabla_{\mathbf{r}}^2 + U_{\text{KS}}(\mathbf{r},t), \quad (4)$$

where the potential $U_{\text{KS}}(\mathbf{r},t) = U_{\text{KS}}[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$ is

$$U_{\text{KS}}(\mathbf{r},t) = -\frac{e}{c} \nabla_{\mathbf{r}} \mathbf{A}_{\text{xc}}(\mathbf{r},t) - \frac{e}{c} \mathbf{A}_{\text{xc}}(\mathbf{r},t) \nabla_{\mathbf{r}} + U_{\text{KS}}^0(\mathbf{r},t) + U_0(\mathbf{r}). \quad (5)$$

The exchange-correlation vector potential $\mathbf{A}_{\text{xc}}[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$ and the Kohn-Sham scalar external potential $U_{\text{KS}}^0[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$ are functionals of both the charge density and the current.¹ The scalar potential is given by

$$U_{\text{KS}}^0(\mathbf{r},t) = \int d\mathbf{r}_1 \frac{n(\mathbf{r}_1,t)e^2}{|\mathbf{r}-\mathbf{r}_1|} + U_{\text{xc}}(\mathbf{r},t); \quad (6)$$

$U_0(\mathbf{r})$ is the field created by nuclei and $U_{\text{xc}}[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)](\mathbf{r})$ is the exchange-correlation potential in the adiabatic approximation. The time-dependent external potential is $U_{\text{ext}}(\mathbf{r},t) = U_0(\mathbf{r})$ at time $t \leq t_0$ and $U_{\text{ext}}(\mathbf{r},t) = U_0(\mathbf{r}) + U_1(\mathbf{r},t)$ for $t > t_0$. \mathbf{A}_{xc} adds a magnetic field induced by the exchange-correlation interaction between electrons. Note that unlike the paramagnetic canonical current, \mathbf{J} is gauge invariant.¹

The stationary solution of Eq. (1) gives the ground-state single electron density matrix $\bar{\rho}(\mathbf{r}, \mathbf{r}_1)$ which carries no current. We then write $\rho(\mathbf{r}, \mathbf{r}_1, t) \equiv \bar{\rho}(\mathbf{r}, \mathbf{r}_1) + \delta\rho(\mathbf{r}, \mathbf{r}_1, t)$ where $\delta\rho$ represents the changes induced by $U_1(\mathbf{r},t)$. Its diagonal elements $\delta n(\mathbf{r}) = \delta\rho(\mathbf{r}, \mathbf{r}, t)$ give the changes in charge density, whereas the off-diagonal elements represent the changes in electronic coherences between two points. The physical current may be obtained by expanding $\delta\rho$ in powers of the external vector potential $\mathbf{A}(\mathbf{r},t)$: $\delta\rho = \delta\rho_1 + \delta\rho_2 + \dots$ and solving Eqs. (1) and (2) self-consistently for $\delta\rho$ order by order. To that end we first recast $U_{\text{KS}}[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$ as a functional of the paramagnetic current $\mathbf{j}(\mathbf{r},t)$ alone. This is done by substituting the total current $\mathbf{J}(\mathbf{r},t)$ [Eq. (3)] into the continuity relation between the charge density and the total current

$$\delta n(\mathbf{r},t) = -\frac{1}{e} \int_0^t \nabla_{\mathbf{r}} \cdot \mathbf{J}(\mathbf{r},\tau) d\tau. \quad (7)$$

Solving Eq. (7) self-consistently for the charge density $n(\mathbf{r},t)$ in terms of the paramagnetic current $\mathbf{j}(\mathbf{r},t)$, and substituting it in $U_{\text{KS}}[n(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]$ eliminates the explicit dependence on the charge density. Expanding U_{KS} around $\bar{\rho}$ to second order in \mathbf{j} , we obtain

$$U_{\text{KS}}[\mathbf{j}(\mathbf{r},t)](\mathbf{r}) = U_{\text{KS}}^0[\bar{\rho}](\mathbf{r}) + \int d\mathbf{r}_1 \left(\frac{e^2}{|\mathbf{r}-\mathbf{r}_1|} + \tilde{f}_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1) \right) \mathbf{j}(\mathbf{r}_1, t) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \times \tilde{g}_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \mathbf{j}(\mathbf{r}_1, t) \mathbf{j}(\mathbf{r}_2, t), \quad (8)$$

where $\tilde{f}_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1)$ and $\tilde{g}_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2)$ are the first and the second order adiabatic exchange-correlation kernels. We have made the commonly used adiabatic approximation where we assume that the kernels are time independent.

III. QUASIPARTICLE REPRESENTATION OF X-RAY NONLINEAR RESPONSE FUNCTIONS

We next separate $\delta\rho$ into an electron-hole, interband (ξ), and intraband (T) components $\delta\rho(\mathbf{r}, \mathbf{r}_1, t) = \xi(\mathbf{r}, \mathbf{r}_1, t) + T[\xi(\mathbf{r}, \mathbf{r}_1, t)]$. It follows from the idempotent property of ρ , that T is uniquely determined by ξ .⁸ The matrix elements of ξ , unlike those of $\delta\rho$, constitute independent variables, that can be used to construct a quasiparticle representation.

The quasiparticle spectrum is obtained by solving the linearized Kohn-Sham eigenvalue equation

$$L\xi_{\alpha}(\mathbf{r}, \mathbf{r}_1) = \Omega_{\alpha} \xi_{\alpha}(\mathbf{r}, \mathbf{r}_1), \quad (9)$$

where

$$L\xi_{\alpha}(\mathbf{r}, \mathbf{r}_1) = -\frac{(\nabla_{\mathbf{r}}^2 - \nabla_{\mathbf{r}_1}^2) \xi_{\alpha}(\mathbf{r}, \mathbf{r}_1)}{2m} + \bar{\rho}(\mathbf{r}, \mathbf{r}_1) \times \left(\int d\mathbf{r}_1 \int d\mathbf{r}_2 f'_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) \xi_{\alpha}(\mathbf{r}_1, \mathbf{r}_2) - \bar{\rho}^*(\mathbf{r}_1, \mathbf{r}) \left(\int d\mathbf{r} \int d\mathbf{r}_2 \times f'_{\text{xc}} * [\bar{\rho}](\mathbf{r}_1, \mathbf{r}, \mathbf{r}_2) \xi_{\alpha}(\mathbf{r}_2, \mathbf{r}) \right) \right), \quad (10)$$

$$f'_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) = \tilde{f}'_{\text{xc}}[\bar{\rho}](\mathbf{r}, \mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \hat{v}(\mathbf{r}_1, \mathbf{r}_2), \quad (11)$$

and \hat{v} is the velocity operator

$$\hat{v}(\mathbf{r}, \mathbf{r}_1) = -\frac{i}{2m} (\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}}). \quad (12)$$

The quasiparticle modes ξ_{α} come in pairs $\alpha = \pm 1, \pm 2, \dots$, with $\Omega_{-\alpha} \equiv \Omega_{\alpha}$. Their orthonormality and algebraic properties make it possible to expand an arbitrary interband matrix⁸ in the form

$$\xi(\mathbf{r}, \mathbf{r}_1, t) = \sum_{\alpha} \xi_{\alpha}(\mathbf{r}, \mathbf{r}_1) z_{\alpha}(t), \quad (13)$$

where $z_{\alpha}(t) = \langle \xi_{\alpha}^{\dagger} | \xi(t) \rangle$ and the scalar product of any two interband matrices ξ and η is defined by⁹

$$\langle \xi | \eta \rangle \equiv \int d\mathbf{r} \int d\mathbf{r}' \bar{\rho}[\xi^\dagger, \eta](\mathbf{r}, \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (14)$$

The bra (ket) notation underscores the similarity with Dirac's Hilbert space notation. $z_{-\alpha}(t) = z_\alpha^*(t)$ constitute complex oscillator amplitudes. We shall denote their perturbative expansion in the external vector-potential $\mathbf{A}(\mathbf{r}, t)$ by $z_\alpha^{(1)}, z_\alpha^{(2)}, \dots$.

The paramagnetic current is calculated by taking the expectation value of the velocity $\hat{v}(\mathbf{r}, \mathbf{r}_1)$ with respect to the time-dependent density matrix

$$\begin{aligned} \mathbf{j}(\mathbf{r}, t) = & \sum_\alpha \mathbf{j}_\alpha(\mathbf{r}) z_\alpha(t) + \frac{1}{2} \sum_{\alpha\beta} \mathbf{j}_{\alpha\beta}(\mathbf{r}) z_\alpha(t) z_\beta(t) \\ & + \frac{1}{3} \sum_{\alpha\beta\gamma} \mathbf{j}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}') z_\alpha(t) z_\beta(t) z_\gamma(t), \end{aligned} \quad (15)$$

where $(\alpha, \beta, \gamma = \pm 1, \pm 2, \dots)$ and we only retained terms that contribute to the third order response. Here

$$\mathbf{j}_\alpha(\mathbf{r}) = -\frac{ie}{2m} \int d\mathbf{r}_1 [\delta(\mathbf{r} - \mathbf{r}_1) (\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}}) \xi_\alpha(\mathbf{r}, \mathbf{r}_1)], \quad (16)$$

$$\begin{aligned} \mathbf{j}_{\alpha\beta}(\mathbf{r}) = & -\frac{ie}{2m} \int d\mathbf{r}_1 \left(\delta(\mathbf{r} - \mathbf{r}_1) (\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}}) \int d\mathbf{r}_2 \right. \\ & \times \left\{ [\delta(\mathbf{r}_2 - \mathbf{r}) - 2\bar{n}(\mathbf{r}, \mathbf{r}_2)] \int d\mathbf{r}_3 [\xi_\alpha(\mathbf{r}_2, \mathbf{r}_3) \right. \\ & \left. \left. \times \xi_\beta(\mathbf{r}_3, \mathbf{r}_1) + \xi_\beta(\mathbf{r}_2, \mathbf{r}_3) \xi_\alpha(\mathbf{r}_3, \mathbf{r}_1)] \right\} \right), \end{aligned} \quad (17)$$

$$\begin{aligned} \mathbf{j}_{\alpha\beta\gamma}(\mathbf{r}) = & \frac{ie}{2m} \int d\mathbf{r}_1 \left(\delta(\mathbf{r} - \mathbf{r}_1) (\nabla_{\mathbf{r}_1} - \nabla_{\mathbf{r}}) \int d\mathbf{r}_2 \right. \\ & \times \left\{ \xi_\alpha(\mathbf{r}, \mathbf{r}_2) \int d\mathbf{r}_3 [\xi_\alpha(\mathbf{r}_2, \mathbf{r}_3) \xi_\beta(\mathbf{r}_3, \mathbf{r}_1) \right. \\ & \left. \left. + \xi_\beta(\mathbf{r}_2, \mathbf{r}_3) \xi_\alpha(\mathbf{r}_3, \mathbf{r}_1)] \right\} \right). \end{aligned} \quad (18)$$

The collective electronic oscillator (CEO) expansion for the charge density $n(\mathbf{r}, t)$ is given by⁹

$$\begin{aligned} \delta n(\mathbf{r}, t) = & \sum_\alpha n_\alpha(\mathbf{r}) z_\alpha(t) + \frac{1}{2} \sum_{\alpha\beta} n_{\alpha\beta}(\mathbf{r}) z_\alpha(t) z_\beta(t) \\ & + \frac{1}{3} \sum_{\alpha\beta\gamma} n_{\alpha\beta\gamma}(\mathbf{r}) z_\alpha(t) z_\beta(t) z_\gamma(t), \\ & \alpha, \beta, \gamma = \pm 1, \pm 2, \dots \end{aligned} \quad (19)$$

The coefficients of this expansion are given by Eqs. (29)–(31) in Ref. 9.

The equations of motion for ξ can be obtained from Eq. (1) by expressing the density matrix in terms of ξ and $T(\xi)$.⁹ Equations of motions for $z^{(1)}(t)$ are derived in terms of

$\mathbf{A}(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r})$ by substituting the mode expansion of ξ into these equations. Substituting the solution $z^{(1)}(t)$ into Eq. (15), gives

$$j_{\lambda_s}^{(1)}(\mathbf{r}, t) = \int_{-\infty}^t d\tau \int d\mathbf{r}_1 \sum_{\mu=x,y,z} \tilde{\chi}_{\lambda_1 \lambda_s}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1) A_{\lambda_1}(\mathbf{r}_1, \tau), \quad (20)$$

where $\tilde{\chi}^{(1)}$ is the linear paramagnetic susceptibility, and λ_s, λ_1 are Cartesian tensor components.

We further introduce the observed susceptibility $\chi_{\lambda\mu}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1)$ defined by replacing the paramagnetic current $\mathbf{j}(\mathbf{r}, t)$ with the physical current $\mathbf{J}(\mathbf{r}, t)$ in Eq. (20). Substituting $\mathbf{j}^{(1)}(\mathbf{r}, t)$ from Eq. (3) into Eq. (20), we obtain

$$\begin{aligned} \chi_{\lambda\mu}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1) = & \tilde{\chi}_{\lambda\mu}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1) - \frac{1}{mc} \bar{n}(\mathbf{r}_1) \\ & \times \delta(\mathbf{r}_1 - \mathbf{r}) \delta(\tau - t) \delta_{\lambda\mu}. \end{aligned} \quad (21)$$

We next derive equations of motions for $z^{(1)}(t)$ in terms of $\mathbf{A}(\mathbf{r}, t)$ and $\mathbf{j}_\alpha(\mathbf{r})$, by substituting the CEO expansion of ξ from Eq. (13) into the equation of motion for ξ , which can be obtained from Eq. (1) by expansion of the density matrix on ξ and $T(\xi)$.⁹ Solving these equations we substitute $z^{(1)}(t)$ into Eq. (15).

$$\tilde{\chi}_{\lambda\mu}^{(1)}(\omega, \mathbf{r}, \mathbf{r}_1) = \sum_{\alpha=1,2,\dots} \frac{2\Omega_{\alpha} j_{\alpha\lambda}(\mathbf{r}) j_{\alpha\mu}(\mathbf{r}_1)}{\Omega_{\alpha}^2 - \omega^2}. \quad (22)$$

Optical and x-ray signals are most conveniently expressed using response functions which connect the polarization with the electric field. For example, the linear response function $\sigma_{\lambda_1 \lambda_s}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1)$ to first order in the external field $E(\mathbf{r}, t)$ is defined as

$$P_{\lambda_s}^{(1)}(\mathbf{r}, t) = \int_{-\infty}^t d\tau \int d\mathbf{r}_1 \sum_{\mu=x,y,z} \sigma_{\lambda_1 \lambda_s}^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1) E_{\lambda_1}(\mathbf{r}_1, \tau), \quad (23)$$

where $\mathbf{P}(\mathbf{r}, t)$ is the total polarization.¹¹ $\sigma^{(1)}(t, \tau, \mathbf{r}, \mathbf{r}_1)$ can be obtained from Eq. (20) by noting that \mathbf{j} is connected to \mathbf{J} through Eq. (3); \mathbf{J} is connected to \mathbf{P} through¹¹ $\mathbf{P}(\mathbf{r}, t) = \int_{-\infty}^t d\tau \mathbf{J}(\mathbf{r}, \tau)$ and $\mathbf{A}(\mathbf{r}, \omega) = -ic\mathbf{E}(\mathbf{r}, \omega)/\omega$. Using these relations we obtain¹¹

$$\begin{aligned} \sigma^{(n)}(\omega, \mathbf{r}, \mathbf{r}_n, \dots, \mathbf{r}_1, \omega_n, \dots, \omega_1) \\ = \frac{i^{1-n}}{\omega_1 \omega_2 \dots \omega_n \omega} \chi^{(n)}(\omega, \mathbf{r}, \mathbf{r}_n, \dots, \mathbf{r}_1, \omega_n, \dots, \omega_1), \end{aligned} \quad (24)$$

which gives for the linear response

$$\begin{aligned}\sigma_{\lambda_1\lambda_s}^{(1)}(\omega, \mathbf{r}, \mathbf{r}_1) &= \frac{1}{\omega^2} \chi_{\lambda_1\lambda_s}^{(1)}(\omega = \omega_1, \mathbf{r}, \mathbf{r}_1) \\ &= \frac{1}{\omega^2} 2\pi \left(\sum_{\alpha = \pm 1, \pm 2, \dots} \frac{2\Omega_\alpha j_\alpha^{\lambda_s}(\mathbf{r}) j_\alpha^{\lambda_1}(\mathbf{r}_1)}{\Omega_\alpha^2 - \omega^2} \right. \\ &\quad \left. - \frac{e^2}{2mc} \bar{n}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}) \delta_{\lambda_s\lambda_1} \right),\end{aligned}\quad (25)$$

where the first term in the bracket is $\tilde{\chi}_{\lambda_s\lambda_1}^{(1)}(\omega, \mathbf{r}, \mathbf{r}_1)$, and $\bar{n}(\mathbf{r})$ is the ground state charge density. Equation (25) provides a microscopic algorithm for computing the Kubo formula;¹² all quantities are obtained from the quasiparticle modes.

To calculate the second order response function $\sigma^{(2)}$

$$\begin{aligned}P_{\lambda_s}^{(2)}(\mathbf{r}, t) &= \frac{1}{2} \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 E_{\lambda_1}(\mathbf{r}_1, \tau_1) \\ &\quad \times E_{\lambda_2}(\mathbf{r}_2, \tau_2) \sigma_{\lambda_1\lambda_2\lambda_s}^{(2)}(t, \tau_1, \tau_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_2),\end{aligned}\quad (26)$$

we introduce the second-order exchange-correlation kernel g_{xc} , obtained by expanding the exchange correlation potential $U_{KS}[j(\mathbf{r}, t)](\mathbf{r})$ to the second order by $\delta\mathbf{j}$ [Eq. (8)]

$$\begin{aligned}g_{xc}[\bar{n}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_2, \mathbf{r}_4) &= \tilde{g}_{xc}[\bar{n}](\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) \delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &\quad \times \delta(\mathbf{r}'_2 - \mathbf{r}_4) \hat{v}(\mathbf{r}_1, \mathbf{r}_2) \hat{v}(\mathbf{r}'_2, \mathbf{r}_4).\end{aligned}\quad (27)$$

Repeating the procedure used for $\sigma^{(1)}$ to the next order we obtain the second order paramagnetic susceptibility¹³

$$\begin{aligned}\tilde{\chi}_{\lambda_1\lambda_2\lambda_s}^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) &= -2 \sum_{\alpha\lambda_s\beta\gamma} \frac{V_{g(-\alpha\beta\gamma)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) j_\alpha^{\lambda_s}(\mathbf{r}) j_{-\beta}^{\lambda_1}(\mathbf{r}_1) j_{-\gamma}^{\lambda_2}(\mathbf{r}_2) s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)(\Omega_\gamma - \omega_2)} + \sum_{\alpha\beta} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r}) j_\alpha^{\lambda_1}(\mathbf{r}_1) j_{-\beta}^{\lambda_2}(\mathbf{r}_2) s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_1)} \\ &\quad + \sum_{\alpha\beta} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r}) j_\alpha^{\lambda_1}(\mathbf{r}_1) j_{-\beta}^{\lambda_2}(\mathbf{r}_2) s_\alpha s_\beta}{(\Omega_\alpha - \omega_1 - \omega_2)(\Omega_\beta - \omega_2)} + \sum_{\alpha\beta} \frac{j_{\alpha\beta}^{\lambda_s}(\mathbf{r}) j_\alpha^{\lambda_1}(\mathbf{r}_1) j_{-\beta}^{\lambda_2}(\mathbf{r}_2) s_\alpha s_\beta}{(\Omega_\alpha - \omega_1)(\Omega_\beta - \omega_2)},\end{aligned}\quad \alpha, \beta, \gamma = \pm 1, \pm 2, \dots, \quad (28)$$

where $s_\alpha \equiv \text{sgn}(\alpha)$. $V_{g(-\alpha\beta\gamma)}$ is obtained by substituting the exchange-correlation kernels f_{xc} from Eq. (11) and g_{xc} into the expression for $V_{g(-\alpha\beta\gamma)}$ given in Ref. 9.

Similar to the linear response function, the second-order response function is finally obtained by expanding of the charge density $n(\mathbf{r}, t)$ in the modes [Eq. (19)]

$$\begin{aligned}\sigma_{\lambda_1\lambda_2\lambda_s}^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) &= -\frac{i}{\omega_1\omega_2(\omega_1 + \omega_2)} 2\pi \left[\tilde{\chi}_{\lambda_s\lambda_1\lambda_2}^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_2) - \frac{e^2}{2mc} \left(\sum_{\alpha} \frac{2\Omega_\alpha j_\alpha^{\lambda_s}(\mathbf{r}) n_\alpha(\mathbf{r}_1)}{\Omega_\alpha^2 - (\omega_1 + \omega_2)^2} \delta(\mathbf{r}_2 - \mathbf{r}_1) \delta_{\lambda_2\lambda_1} \right. \right. \\ &\quad \left. \left. + \sum_{\alpha} \frac{2\Omega_\alpha n_\alpha(\mathbf{r}) j_\alpha^{\lambda_1}(\mathbf{r}_1)}{\Omega_\alpha^2 - (\omega_1 + \omega_2)^2} \delta(\mathbf{r} - \mathbf{r}_2) \delta_{\lambda_2\lambda_s} \right) \right].\end{aligned}\quad (29)$$

Higher response functions can be computed similarly.⁹ The third-order response function is given in Appendix A.

IV. DISCUSSION

To get the high-order paramagnetic susceptibilities via the standard Hilbert space TDDCDT approach one needs to self-consistently solve a chain of integral equations for each order.¹ The linear paramagnetic susceptibility in the standard approach is given by Eqs. (8), (9) in Ref. 1. In contrast, the closed expressions for the linear [Eq. (22)], second-order [Eq. (28)], and third-order [Eq. (A12)] susceptibilities derived in this paper use the CEO representation in Liouville space. A similar representation was developed in Ref. 14.

Correlation-function expressions for the linear, second-order and third-order x-ray response functions were derived in Eqs. (B1), (B2), (B3a)–(B3d) in Ref. 11. Equations (25), (29), and (A1) express these TDCDFT response functions in the CEO representation, and provide a computational scheme

for nonlinear x-ray response functions.

TDDFT exchange-correlation functionals are better developed and more widely used than their TDCDFT counterparts. TDDFT currents can be obtained by simply modifying Eqs. (11) by setting $\hat{v} = 1$, and using the TDDFT exchange-correlation kernels^{2,9} where the scalar exchange-correlation potential depends only on charge density.

Finally we note that this work can be extended to include nonadiabatic exchange-correlation potentials, as outlined recently for the linear response.¹⁵ In general, the exchange-correlation potential and exchange-correlation kernels are time dependent.¹⁶ 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. (9), should be replaced by¹⁵

$$L(\Omega_\alpha)\xi_\alpha(\mathbf{r},\mathbf{r}')=\Omega_\alpha\xi_\alpha(\mathbf{r},\mathbf{r}'). \quad (30)$$

Methods for solving Eq. (30) using the frequency-dependent functional of Gross and Kohn¹⁶ were described in Ref. 15.

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APPENDIX A: THE THIRD-ORDER RESPONSE

For the third-order response function we obtain

$$\begin{aligned} \sigma_{\lambda_1\lambda_2\lambda_3\lambda_s}^{(3)}(\omega_1,\omega_2,\omega_3,\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = & -\frac{1}{\omega_1\omega_2\omega_3(\omega_1+\omega_2+\omega_3)}2\pi\left[\tilde{\chi}_{\lambda_1\lambda_2\lambda_3\lambda_s}^{(3)}(\omega_1,\omega_2,\omega_3,\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \right. \\ & +\frac{e^2}{2mc}\{F[j^{\lambda_s}(\mathbf{r})n(\mathbf{r}_3)j^{\lambda_1}(\mathbf{r}_1)]\delta(\mathbf{r}_2-\mathbf{r}_3)\delta_{\lambda_2\lambda_3}+F[j^{\lambda_s}(\mathbf{r})n(\mathbf{r}_3)j^{\lambda_1}(\mathbf{r}_1)]\delta(\mathbf{r}_2-\mathbf{r}_3)\delta_{\lambda_2\lambda_3} \\ & +F[n(\mathbf{r})j^{\lambda_2}(\mathbf{r}_3)j^{\lambda_1}(\mathbf{r}_1)]\delta(\mathbf{r}-\mathbf{r}_3)\delta_{\lambda_2\lambda_1}\delta_{\lambda_3\lambda_s}\} \\ & \left. +\left(\frac{e^2}{2mc}\right)^2R^{(1)}(\omega_1+\omega_2+\omega_3,\mathbf{r},\mathbf{r}_2)\delta(\mathbf{r}-\mathbf{r}_3)\delta(\mathbf{r}_2-\mathbf{r}_1)\delta_{\lambda_3\lambda_s}\delta_{\lambda_2\lambda_1}\right], \end{aligned} \quad (A1)$$

where $R^{(1)}(\omega_1+\omega_2+\omega_3,\mathbf{r},\mathbf{r}_2)$ is the linear density-density response given by Eq. (46) in Ref. 9; $\tilde{\chi}_{\lambda_1\lambda_2\lambda_3\lambda_s}^{(3)}(\omega_1,\omega_2,\omega_3,\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is the third-order paramagnetic susceptibility given by the right-hand side of Eqs. (C23)–(C31) in Ref. 9 by replacing ρ by j :

$$\tilde{\chi}_{\lambda_1\lambda_2\lambda_3\lambda_s}^{(3)}(\omega_1,\omega_2,\omega_3,\mathbf{r},\mathbf{r}',\mathbf{r}'',\mathbf{r}''') = \sum_{\omega_1\omega_2\omega_3}^{\text{perm}} (\tilde{\chi}_I^{(3)} + \tilde{\chi}_{II}^{(3)} + \tilde{\chi}_{III}^{(3)} + \dots + \tilde{\chi}_{VIII}^{(3)}), \quad (A2)$$

where

$$\tilde{\chi}_I^{(3)} = \sum_{\alpha\beta\gamma} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r})j_{-\beta\gamma}^{\lambda_1}(\mathbf{r}')j_{\alpha}^{\lambda_2}(\mathbf{r}'')j_{-\gamma}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_3)}, \quad (A3)$$

$$\tilde{\chi}_{II}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r})V_{g(-\beta\gamma\delta)}j_{\alpha}^{\lambda_1}(\mathbf{r}')j_{-\gamma}^{\lambda_2}(\mathbf{r}'')j_{-\delta}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_2)(\Omega_{\delta}-\omega_3)}, \quad (A4)$$

$$\tilde{\chi}_{III}^{(3)} = \sum_{\alpha\beta\gamma} \frac{j_{-\alpha\beta\gamma}^{\lambda_s}(\mathbf{r})j_{\alpha}^{\lambda_1}(\mathbf{r}')j_{-\beta}^{\lambda_2}(\mathbf{r}'')j_{-\gamma}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_3)}, \quad (A5)$$

$$\tilde{\chi}_{IV}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{2V_{g(-\alpha\beta\gamma)}j_{-\gamma\delta}^{\lambda_s}(\mathbf{r})j_{\alpha}^{\lambda_1}(\mathbf{r}')j_{-\beta}^{\lambda_2}(\mathbf{r}'')j_{-\delta}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2-\omega_3)(\Omega_{\delta}-\omega_3)}, \quad (A6)$$

$$\tilde{\chi}_V^{(3)} = \sum_{\alpha\beta\gamma\delta\eta} \frac{2V_{g(-\alpha\beta\gamma)}V_{g(-\gamma\delta\eta)}j_{\alpha}^{\lambda_s}(\mathbf{r})j_{-\beta}^{\lambda_1}(\mathbf{r}')j_{-\delta}^{\lambda_2}(\mathbf{r}'')j_{-\eta}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s s_{\eta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2-\omega_3)(\Omega_{\delta}-\omega_2)(\Omega_{\eta}-\omega_3)}, \quad (A7)$$

$$\tilde{\chi}_{VI}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{V_{h(-\alpha\beta\gamma\delta)}j_{\alpha}^{\lambda_s}(\mathbf{r})j_{-\beta}^{\lambda_1}(\mathbf{r}')j_{-\gamma}^{\lambda_2}(\mathbf{r}'')j_{-\delta}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s s_{\delta}^s}{(\Omega_{\alpha}-\omega_1-\omega_2-\omega_3)(\Omega_{\beta}-\omega_1)(\Omega_{\gamma}-\omega_2)(\Omega_{\delta}-\omega_3)}, \quad (A8)$$

$$\tilde{\chi}_{VII}^{(3)} = \sum_{\alpha\beta\gamma} \frac{j_{\alpha\beta}^{\lambda_s}(\mathbf{r})j_{-\beta\gamma}^{\lambda_1}(\mathbf{r}')j_{-\alpha}^{\lambda_2}(\mathbf{r}'')j_{-\gamma}^{\lambda_3}(\mathbf{r}''')s_{\alpha}^s s_{\beta}^s s_{\gamma}^s}{(\Omega_{\alpha}-\omega_1)(\Omega_{\beta}-\omega_2-\omega_3)(\Omega_{\gamma}-\omega_3)}, \quad (A9)$$

$$\tilde{\chi}_{\text{VIII}}^{(3)} = \sum_{\alpha\beta\gamma\delta} \frac{j_{\alpha\beta}^{\lambda_s}(\mathbf{r}) V_{g(-\beta\gamma\delta)} j_{-\alpha}^{\lambda_1}(\mathbf{r}') j_{-\gamma}^{\lambda_2}(\mathbf{r}'') j_{-\delta}^{\lambda_3}(\mathbf{r}''') s_{\alpha} s_{\beta} s_{\gamma} s_{\delta}}{(\Omega_{\alpha} - \omega_1)(\Omega_{\beta} - \omega_2 - \omega_3)(\Omega_{\gamma} - \omega_2)(\Omega_{\delta} - \omega_3)}. \quad (\text{A10})$$

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 $\Omega_{-\nu} = -\Omega_{\nu}$.

$F[j^{\lambda_s}(\mathbf{r})n(\mathbf{r}_3)j^{\lambda_1}(\mathbf{r}_1)]$ is determined by the right-hand side of Eq. (29) by replacing $j^{\lambda_1}(\mathbf{r}_1)$ by $n(\mathbf{r}_3)$:

$$F[j^{\lambda_s}(\mathbf{r})n(\mathbf{r}_3)j^{\lambda_1}(\mathbf{r}_1)] = -\frac{i}{\omega_1\omega_2(\omega_1 + \omega_2)} 2\pi \left[\hat{\chi}_{\lambda_s\lambda_1\lambda_2}^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) - \frac{e^2}{2mc} \left(\sum_{\alpha} \frac{2\Omega_{\alpha} j_{\alpha}^{\lambda_s}(\mathbf{r}) n_{\alpha}(\mathbf{r}_1)}{\Omega_{\alpha}^2 - (\omega_1 + \omega_2)^2} \delta(\mathbf{r}_3 - \mathbf{r}_1) \delta_{\lambda_2\lambda_1} \right. \right. \\ \left. \left. + \sum_{\alpha} \frac{2\Omega_{\alpha} n_{\alpha}(\mathbf{r}) n(\mathbf{r}_3)}{\Omega_{\alpha}^2 - (\omega_1 + \omega_2)^2} \delta(\mathbf{r} - \mathbf{r}_3) \delta_{\lambda_2\lambda_s} \right) \right], \quad (\text{A11})$$

where

$$\hat{\chi}_{\lambda_1\lambda_2\lambda_s}^{(2)}(\omega_1, \omega_2, \mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) = -2 \sum_{\alpha\lambda_s\beta\gamma} \frac{V_{g(-\alpha\beta\gamma)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_3) j_{\alpha}^{\lambda_s}(\mathbf{r}) n_{-\beta}(\mathbf{r}_3) j_{-\gamma}^{\lambda_1}(\mathbf{r}_1) s_{\alpha} s_{\beta}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_1)(\Omega_{\gamma} - \omega_2)} + \sum_{\alpha\beta} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r}) n_{\alpha}(\mathbf{r}_3) j_{-\beta}^{\lambda_1}(\mathbf{r}_1) s_{\alpha} s_{\beta}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_1)} \\ + \sum_{\alpha\beta} \frac{j_{-\alpha\beta}^{\lambda_s}(\mathbf{r}) n_{\alpha}(\mathbf{r}_3) j_{-\beta}^{\lambda_1}(\mathbf{r}_1) s_{\alpha} s_{\beta}}{(\Omega_{\alpha} - \omega_1 - \omega_2)(\Omega_{\beta} - \omega_2)} + \sum_{\alpha\beta} \frac{j_{\alpha\beta}^{\lambda_s}(\mathbf{r}) n_{\alpha}(\mathbf{r}_3) j_{-\beta}^{\lambda_1}(\mathbf{r}_1) s_{\alpha} s_{\beta}}{(\Omega_{\alpha} - \omega_1)(\Omega_{\beta} - \omega_2)}, \quad \alpha, \beta, \gamma = \pm 1, \pm 2, \dots, \quad (\text{A12})$$

where $s_{\alpha} \equiv \text{sgn}(\alpha)$.

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