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Efficient linear-response method circumventing the exchange-correlation kernel: Theory for molecular conductance under finite bias

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An iterative approach for calculating the frequency domain linear response of molecular systems within time-dependent density-functional theory is presented. The method completely avoids computing the exchange-correlation kernel which is typically the most expensive step for large systems. In particular, virtual orbitals are not needed. This approach may be useful for treating the response of large systems. We give an outline of the theory and a demonstration on a jellium model of an elliptic gold cluster. A detailed theory is appended discussing the computation of conductance and ac impedance of molecular junctions under bias. © *2005 American Institute of Physics*.
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I. INTRODUCTION

Time-dependent density-functional theory [1] (TDDFT) is a framework for calculating the response of molecular systems to temporal perturbations.[2–10] In the linear-response domain the method has been used extensively in recent years, especially in its frequency form.[10–18]

In a recent paper we derived a real-time approach for propagating the TDDFT Kohn-Sham equations in their linearized form.[4] For the commonly used adiabatic functionals, the linearization makes the kernel of the equations time independent so that one can use the efficient approaches developed for time-dependent Schrödinger equations for propagation.[19]

In the time domain, the linearized response may suffer from instabilities due to the complex eigenvalues of the linearized propagator. This problem is absent in real-time calculations that are not linearized, since the full time-dependent Kohn-Sham equations are gauge invariant and therefore norm conserving. A common way to sidestep this difficulty in linear response is to treat the system in the frequency domain. This gives a formalism which is analogous to the well-established random-phase approximation (RPA) for time-dependent mean-field theories.[20]

Most of the approaches to linear response in TDDFT (Refs. 11, 12, and 18) involve, in one way or the other, calculation of the exchange-correlation kernel[3] $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';t-t')=\delta v_{\mathrm{XC}}[n](\mathbf{r},t)/\delta n(\mathbf{r}',t')$ [where $v_{\mathrm{XC}}(\mathbf{r},t)$ and $n(\mathbf{r},t)$ are, respectively, the time-dependent exchange-correlation potential and the electronic number density] or its Fourier-transformed frequency domain counterpart $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';\omega)$. For local exchange-correlation functionals the kernel $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';\omega)$ is proportional to the delta function $\delta(\mathbf{r}-\mathbf{r}')$. This is no longer true for hybrid functionals, such as the often used B3LYP,[21] which mix in nonlocal explicit exchange. However, even when local functionals are used, most applications of linear response compute the kernel within a nonorthogonal atomic-orbital basis, where it assumes a four-indexed nondiagonal form. In particular, most applications use the Kohn-Sham occupied and virtual orbitals which must all be computed, a relatively expensive operation for large systems.

A physical advantage of the resulting formalism (which is absent from a fully-time-dependent formulation without linearization) is that it is suitable for calculating molecular conductance,[22,23] or in general for cases where the underlying static density is extended. This is exactly the case in the calculation of molecular impedance. In this case, a weak perturbation is applied which starts up an electron current. Since only a finite part of the system is actually represented (on a grid, for example), this current needs to be absorbed at the boundaries, while the other part of the electron density must not be absorbed. When treated in linear response, this different boundary conditions for different parts of the electron density are naturally enforced, as discussed in Appendix A.

The balance of the paper is as follows. In Sec. II we present the linear-response formalism starting from time domain moving into frequency domain. We emphasize the potential efficiency of our approach for large systems. In Sec. III we present an example on a model system, followed by conclusions in Sec. IV.

An integral part of the paper is given in the appendixes. Appendix A discusses the extension of the formalism to an unbounded ground state. This could be a conducting ground state, in which case the formulation gives the necessary information for calculating the impedance. Specifically the most natural application would be to calculate the impedance of a conducting system under a dc bias (so that the ac per-

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turbation is applied in addition to the possibly strong dc bias). The static system would be evaluated typically by a nonequilibrium Green's function method while the dc perturbation would be calculated by a linearized TDDFT as presented here.

Appendix B then extends the derivation to the use of a density matrix, rather than using the molecular orbitals. Such a formulation may be useful when large systems are treated and the density matrix is easier to compute than the molecular orbitals, as in some linear scaling density-functional theory algorithms.[24]

II. FORMALISM

In this section we present the linear-response method. A real-time formalism is first presented and then extended to frequency domain. We emphasize the fact that the present method can completely circumvent the computation of the exchange-correlation kernel.

A. Time picture

We start with a Kohn-Sham (KS) Hamiltonian H, which depends nonlinearly on the particle density and therefore on the set of occupied KS orbitals or density matrix. For simplicity, we develop the formalism in terms of orbitals, and extend the theoretical treatment to a density-matrix picture in Appendix B.

We imagine a system of interacting electrons in its ground state. The electronic density $n_0(\mathbf{r})$ is described by a set of N Kohn-Sham spatial orbitals $\phi_k(\mathbf{r})$ and corresponding occupation numbers f_k:

$$n_0(\mathbf{r}) = \sum_k f_k \phi_k(\mathbf{r})^2. \tag{1}$$

These ground-state orbitals (assumed real, for simplicity) are eigenfunctions of the stationary Kohn-Sham Hamiltonian, $H_0 \equiv H_{\mathrm{KS}}[n_0]$:

$$H_0 \phi_k = \varepsilon_k \phi_k, \tag{2}$$

where ε_k are the corresponding eigenvalues.

At time $t=0$ a small instantaneous external perturbation is applied to the system for an infinitesimal amount of time. The time-dependent perturbation is described by the operator $\eta\hat{\lambda}\delta(t)$, where η is, in principle, an infinitesimal (of the correct units), but in practice, a small quantity which serves as the linear-response parameter. $\hat{\lambda}$ is any one-electron operator of interest [for example (but not limited to), a component of the electronic dipole moment er_α, where $\alpha=x$, y, or z, of the quadrupole moment or even of the current density $\hat{J}_\alpha(\mathbf{r})$]. The ground-state orbitals serve to build the initial wave functions $\psi_k(\mathbf{r},t=0)=e^{-i\eta\hat{\lambda}}\phi_k(\mathbf{r})$ which then evolve according to the time-dependent Kohn-Sham equations,[1] which are written here as

$$i\frac{d\psi_k}{dt} = (H[n] - \varepsilon_k)\psi_k. \tag{3}$$

Clearly $e^{-i\varepsilon_k t}\psi_k(\mathbf{r},t)$ are the time-dependent Kohn-Sham orbitals describing the time-dependent electronic density:

$$n[\psi](\mathbf{r},t) = \sum_k f_k |\psi_k(\mathbf{r},t)|^2. \tag{4}$$

Note that there is freedom in the description of the initial density. It could be a ground-state density, when spectroscopic applications for isolated systems are studied. Alternately, it could be the zero-order nonequilibrium Green's function[25] density for current-carrying system, which means, in practice, simply that it would be composed of a different amount of scattering orbitals from each lead. The determination of the initial set of orbitals and therefore of n_0 would be done by standard techniques.

In preparation for the linear-response treatment, we write each orbital in terms of the original Kohn-Sham orbital and a response:

$$\psi_k(t=0^+) = \phi_k + \nu_k(t=0), \tag{5}$$

where the small initial response orbital is obtained by linearizing the propagator $e^{-i\eta\hat{\lambda}}=1-i\eta\hat{\lambda}+O(\eta^2)$:

$$\nu_k(t=0) = -i\eta\hat{\lambda}\phi_k. \tag{6}$$

At any later time we then *define* $\nu_k(\mathbf{r},t)$ by its relation to $\psi_k(\mathbf{r},t)$:

$$\psi_k(\mathbf{r},t) = \phi_k(\mathbf{r}) + \nu_k(\mathbf{r},t). \tag{7}$$

Note that $\nu_k(\mathbf{r},t)$ is "small" (i.e., of order η). We further separate ν into its real and imaginary parts so that (suppressing the orbital index k)

$$\nu = \nu' + i\nu''. \tag{8}$$

From Eq. (3), the equation governing the evolution of the "small" response ν is, to first order,

$$i\frac{d\nu}{dt} = [H_0 - \varepsilon]\nu + (H[n[\phi+\nu']] - H_0)\phi, \tag{9}$$

where n depends, to first order, only on the real part of the orbital perturbation ν' since from Eq. (4),

$$\begin{aligned} n[\phi+\nu'] &= \sum_{k=1}^{N} f_k |\phi_k + \nu_k' + i\nu_k''|^2 \\ &= \sum_{k=1}^{N} f_k (\phi_k + \nu_k')^2 + O((\nu)^2). \end{aligned} \tag{10}$$

Equation (9) can be written as a coupled equation for the real and imaginary parts of ν:

$$\frac{d}{dt}\begin{pmatrix}\nu' \\ \nu''\end{pmatrix} = \mathbf{A}\begin{pmatrix}\nu' \\ \nu''\end{pmatrix}, \tag{11}$$

where the action of the operator $\mathbf{A}$ is defined implicitly by

$$\mathbf{A}\begin{pmatrix}\nu' \\ \nu''\end{pmatrix} = (H-\varepsilon)\begin{pmatrix}\nu'' \\ -\nu'\end{pmatrix} - \begin{pmatrix}0 \\ (H[n[\phi+\nu']] - H_0)\phi\end{pmatrix}. \tag{12}$$

Equation (12) is crucial for our-derivation. The important point to notice is that the operator $\mathbf{A}$ is formally a *linear operator* as long as ν is small (we refer the reader to Ref. 4 concerning the technical details of the meaning of linearity of **A**). In practice this latter condition can always be assured by selecting η small enough. The point we emphasize is that only the difference $(H[n[\phi+\nu]]-H_0)\phi$ needs to be computed, and thus it is not necessary to compute the functional derivatives of the exchange-correlation potential. Thus the computation of $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';t-t')$ is completely circumvented.

The time development of Eq. (12) was discussed in our previous paper on this subject,[4] where we have shown how to employ a Chebyshev propagator[19] to study this equation in real time. However, in many systems, there is an underlying problem. The equations possess some complex eigenvalues which make the calculation inherently unstable at long times. This is not a problem if one is interested only in the (linear) behavior at short times. This is not the case for spectroscopic applications and thus they require further development, which we pursue in Sec. II B.

B. Frequency picture

When the frequency response is needed, the singularity in time propagation can be avoided by noticing that the half-Fourier-transform at a specific frequency

$$\nu_k(\mathbf{r},\omega)=\int_0^\infty \nu_k(\mathbf{r},t)e^{(i\omega-\gamma)t}dt \tag{13}$$

can be regularized by an appropriate damping constant γ. Thus, the frequency response of the system can always be defined.

Continuing our derivation, we emphasize an important technical point: even though $\nu'(t)$ is real, $\nu'(\omega)$ is not since the latter is the half-Fourier-transform:

$$\nu_k'(\mathbf{r},\omega)=\int_0^\infty \nu_k'(\mathbf{r},t)e^{i\omega t}dt,$$

$$\nu_k''(\mathbf{r},\omega)=\int_0^\infty \nu_k''(\mathbf{r},t)e^{i\omega t}dt. \tag{14}$$

From $\nu'(\omega)$ we can compute the frequency-dependent linear density response [see Eq. (10)],

$$\delta n(\mathbf{r},\omega)=2\sum_k f_k\nu_k'(\mathbf{r},\omega)\phi_k(\mathbf{r}). \tag{15}$$

Combining Eqs. (11) and (13) leads to the formal equality

$$\begin{aligned}\begin{pmatrix}\nu'(\omega)\\ \nu''(\omega)\end{pmatrix}&=\int_0^\infty \exp(i(\omega+i\gamma-\mathbf{A})t)\begin{pmatrix}\nu'(t=0)\\ \nu''(t=0)\end{pmatrix}\\ &=\frac{i}{\omega+i\gamma-\mathbf{A}}\begin{pmatrix}\nu'(t=0)\\ \nu''(t=0)\end{pmatrix}=\frac{-i}{\omega+i\gamma-\mathbf{A}}\begin{pmatrix}0\\ \eta\lambda\phi\end{pmatrix}.\end{aligned} \tag{16}$$

This equation involves the operation of the inverse of a linear complex operator $\omega+i\gamma-\mathbf{A}$ on a two-spinor. For large systems, the inverse operation can be obtained by a standard iterative approach, for example, the Lanczos or quasi-minimal-residue (QMR) algorithm.[26] The Lanczos method can give for this case many energies at once; however, if one intends to calculate the results for a smaller number of energies, it is possible to significantly reduce the number of iterations by using a preconditioner, labeled q, so that

$$\begin{pmatrix}\nu'(\omega)\\ \nu''(\omega)\end{pmatrix}=q\frac{-i}{q(\omega+i\gamma-\mathbf{A})q}q\begin{pmatrix}0\\ \eta\lambda\phi\end{pmatrix}. \tag{17}$$

The simplest preconditioner is the kinetic energy K which is diagonal in reciprocal (k) space,

$$q\equiv\frac{1}{\sqrt{K+a}}, \tag{18}$$

and a is a small positive regularization constant.

With the preconditioner, the inversion of the modified operator amounts to applying an iterative algorithm (such as QMR) which only requires the ability to apply the modified operator, $q(\omega+i\gamma-\mathbf{A})q$, on any given spinor. There is a fine point here, however. The application of the only nontrivial part, **A**, needs to be done on a general complex spinor. Specifically, we need to be able to perform

$$\mathbf{A}\begin{pmatrix}\nu'\\ \nu''\end{pmatrix}=(H_0-\varepsilon)\begin{pmatrix}\nu''\\ -\nu'\end{pmatrix}-\begin{pmatrix}0\\ (H[n(\phi+\nu')]-H_0)\phi\end{pmatrix}, \tag{19}$$

where, unlike Eq. (12), the components of this spinor, $\nu_k'(\mathbf{r})$ and $\nu_k''(\mathbf{r})$, are complex. In other words, the components lose their original meaning of a real part and an imaginary part and become complex.

A corollary is that $n[\phi+\nu']$ is now a complex quantity since it is defined in Eq. (10) as $n[\phi+\nu']=\Sigma_k f_k(\phi_k+\nu_k')^2$. In order to use a regular density-functional program, which is defined for real functions, we simply use the underlying linearity in the perturbation so that

$$\begin{aligned}(H[n[\phi+\nu']]-H_0)\phi=&(H[n[\phi+\mathrm{Re}\ \nu']]-H_0)\phi\\ &+i(H[n[\phi+\mathrm{Im}\ \nu']]-H_0)\phi\\ &+O(\nu'^2).\end{aligned} \tag{20}$$

The final, technical ingredient is to ensure the linearity of the **A** operator (by making sure ν stays small). For this, we scale ν, prior to the application of **A**, by a normalization factor:

$$\nu\to\alpha\nu\quad \alpha=\frac{10^{-m}}{|\nu|}, \tag{21}$$

where the parameter m is typically taken as $m\sim 6-7$ (at this value α is small enough for linearity and is not too small so that there are no numerical stability problems). The final algorithm for applying the preconditioned iterative operator is then

$$q(\omega+i\gamma-\mathbf{A})a\begin{pmatrix}\nu'\\ \nu''\end{pmatrix}=\begin{pmatrix}\nu'_{\mathrm{out}}\\ \nu''_{\mathrm{out}}\end{pmatrix}, \tag{22}$$

where

$$\nu'_{\mathrm{out}}=q(\omega+i\gamma)q\nu'-q(H_0-\varepsilon)q\nu'',$$

$$\begin{aligned}\nu''_{\mathrm{out}}=&q(\omega+i\gamma)q\nu''+q(H_0-\varepsilon)q\nu'\\ &+\alpha^{-1}q(H[n[\phi+\alpha\,\mathrm{Re}(q\nu')]]\phi-H_0\phi)\\ &+i\alpha^{-1}q(H[n[\phi+\alpha\,\mathrm{Im}(q\nu')]]\phi-H_0\phi).\end{aligned} \tag{23}$$

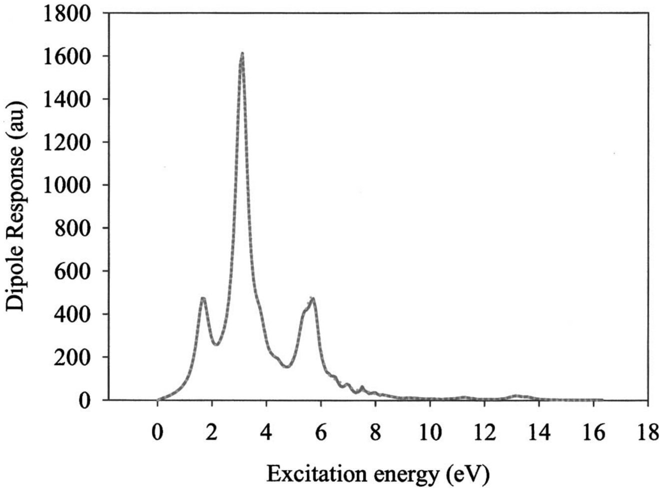

FIG. 1. The dipole-dipole linear response of an elliptical ball of jellium described in the text. Two calculations are shown, which are almost indistinguishable: a Fourier-transformed dipole response from the direct solution of the Kohn-Sham equations (not linearized) and the present frequency domain method.

Equations (22) and (23) serve as the basic ingredient in the application of the numerical algorithm.

III. RESULTS

We have used Eqs. (22) and (23) to study a simple model system, similar to that used in a previous study on this subject: An elliptical ball of jellium matter with a density of $n=0.0088a_0^{-3}$, corresponding to the Wigner-Seitz radius of $r_s=3a_0$. This is a model for a small elliptic gold cluster. The elliptical cluster had extensions of $\Delta z=10.64$ a.u., $\Delta y=1.1\Delta z$, and $\Delta x=1.2\Delta z$.

For the numerical simulation, we used a plane-wave basis spanned by a grid of $16\times 16\times 16$ points with plane-wave cutoff of $E_{\max}\approx 0.8\ E_{\mathrm{h}}$. The number of iterations required for converging the QMR algorithm was less than 128, although the calculation needs to be repeated for each energy. In comparison, a full time-dependent simulation requires a total propagation time of at least 3000 a.u. with a time step of about 0.1 a.u. or less, i.e., a minimum of 30 000 steps. Of course, the time-dependent simulation gets all energies at once while in the QMR approach each energy must be calculated separately. We could have used information from one energy as a starting vector for calculating other energies, thereby reducing further significantly the number of iterations, but have not done it in this model study.

The spectrum of the model cluster is shown in Fig. 1, where a few resonances appear around a surface plasmon mode at ~3 eV. By comparing with a real-time (nonlinear) propagation, we find the results captured by the simulations using Eqs. (22) and (23) are virtually the same.

IV. CONCLUSIONS

In conclusion, the paper and the appendixes develop an approach to the calculation of frequency-dependent response of an electronic system, which is iterative and requires only the calculation of the Kohn-Sham potential. This approach has the potential to be applicable to large systems, where the calculation exchange-correlation kernel $f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}';\omega)$ is prohibitive. The approach is extended in the appendixes to treat an extended system in which absorbing potentials are needed, but they do not affect the underlying static density. Such an approach is appropriate to the calculation of the frequency-dependent impedance of a conducting system in a finite bias.

In future papers this work would be used to study the impedance and frequency-dependent response of molecular current conducting systems.

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APPENDIX A: LINEAR RESPONSE FOR SYSTEMS WITH A FINITE BIAS

The formalism presented gives also a practical recipe for systems with a finite bias in which the initial state is a nonequilibrium scattering states. These states serve as equivalent to ground states in the calculation of coherent current conducting systems, i.e., the underlying system is described by the nonequilibrium Green's function method (as noted in Ref. 27 there are still formal difficulties with this approach). The formalism here would be used to calculate the impedance of such systems.

As a precursor to the calculation of the impedance, one calculates the initial orbitals. Briefly, each initial DFT state is presented as

$$\phi_k(\mathbf{r}) = \phi_{in,k}(\mathbf{r}) + \chi_k(\mathbf{r}), \tag{A1}$$

where k is the vector of the incoming state from one of the leads. The state includes an incoming known part, and an outgoing part χ_k, which includes both the components reflected into the original lead and the components transmitted into the other leads; it is determined as part of the self-consistent evaluation of the density of states. The final equation is then

$$(H-\varepsilon_k-\Sigma_k)\phi_k(\mathbf{r}) = S_k(\mathbf{r}), \tag{A2}$$

where we introduced the self energy (Σ_k) and the source term (S_k), which are both localized as the edges of the grid. These equations are solved self-consistently by standard techniques.

Next one solves the time-dependent equations. These equations are only modified by the presence of an imaginary potential which is located at the edges of the grid; specifically, these equations become

$$i\frac{d\nu_k}{dt}[H_0-\varepsilon_k-iV_I]\nu_k + (H[n(\phi+\nu')]-H_0)\phi_k, \tag{A3}$$

where we introduced a complex imaginary potential which absorbs the time-dependent wavefunction at the edges of the grid. It is important to differentiate between this imaginary potential, iV_I, which acts on the time-dependent perturbation, and the energy-dependent self-energy which acts on the time-independent part of the wave function. The reason for the difference is that the imaginary potential absorbs wave functions which have many energy components while the self-energy is optimized for wave functions of specific kinetic energy. Furthermore, note that we assume that the perturbation ν is absorbed way before the edges of the grid so that there is no need to insert the self energy into Eq. (A3).

The absorbing potential modifies the equations for **A** and for the QMR solution in a trivial way. Assuming, for simplicity, that it is purely imaginary (i.e., that V_I is a real function), it follows that

$$\mathbf{A}\begin{pmatrix} \nu' \\ \nu'' \end{pmatrix} = (H_0 - \varepsilon)\begin{pmatrix} \nu'' \\ -\nu' \end{pmatrix} - V_1\begin{pmatrix} \nu' \\ \nu'' \end{pmatrix} - \begin{pmatrix} 0 \\ (H[n(\phi + \nu')] - H_0)\phi \end{pmatrix} \tag{A4}$$

so that the QMR or Lanczos iteration, Eqs. (23), is modified to

$$\begin{aligned} \nu'_{\text{out}} &= q(\omega + i(\gamma + V_I))q\nu' - q(H_0 - \varepsilon)q\nu'', \\ \nu''_{\text{out}} &= q(\omega + i(\gamma + V_I))q\nu'' + q(H_0 - \varepsilon)q\nu' \\ &\quad + \alpha^{-1}q(H[n[\phi + \alpha\,\mathrm{Re}(q\nu')]]\phi - H_0\phi) \\ &\quad + i\alpha^{-1}q(H[n[\phi + \alpha\,\mathrm{Im}(q\nu')]]\phi - H_0\phi). \end{aligned} \tag{A5}$$

This constitutes the complete methodology for extracting the frequency-dependent orbitals for a finite bias. An alternate approach for extracting the density-dependent matrix directly without using orbitals is outlined in the next appendix.

The last stage is the extraction of impedance information from the time-dependent orbitals; this is detailed, e.g., in Ref. 22. The electric conductivity tensor between two points **r** and **r**′ can be calculated as the correlation function[28]

$$\sigma_{\alpha\beta}(\mathbf{r},\mathbf{r}',\omega) = \frac{e^2}{\hbar\omega}\langle[J_\alpha(\mathbf{r},\omega),J_\beta(\mathbf{r}')]\rangle, \tag{A6}$$

where α and β are Cartesian directions (x, y, or z) and $J_\alpha(\mathbf{r},\omega)$ is the α component of the current density. In order to compute this expression in our method, we take advantage of the fact that the commutator in Eq. (A6) is equal to the expectation value of $\langle\hat{J}_\alpha(\mathbf{r},\omega)\rangle$ when the perturbation is the current density, i.e., $\hat{\lambda} \equiv J_\beta(\mathbf{r}')$. This expectation value is given by

$$\langle J_\alpha(\mathbf{r},\omega)\rangle = 2\sum_k f_k\langle\phi_k|\hat{J}_\alpha(\mathbf{r})|\nu'_k(\omega)\rangle. \tag{A7}$$

APPENDIX B: A DENSITY-MATRIX DESCRIPTION

Since much of the methodology, especially in basis-set language, uses directly the density matrix rather than the specific orbitals, we write the equivalent description in this appendix.

The time-dependent density matrix, in linear response, is now written as

$$\rho(t) = \rho_0 + \zeta + \xi, \tag{B1}$$

where

$$\rho_0 = \sum_k f_k|\phi_k\rangle\langle\phi_k| \tag{B2}$$

and

$$\zeta = \sum_k f_k|\nu_k\rangle\langle\phi_k|,$$

$$\xi = \zeta^\dagger. \tag{B3}$$

Here, we neglected the second-order term $\Sigma_k f_k|\nu_k\rangle\langle\nu_k|$.

A simple multiplication of Eq. (A3) by $f_k\langle\phi_k|$ followed by summation over occupied states yields

$$i\frac{d\zeta}{dt} = [H_0,\zeta] - iV_l\zeta + \delta H\rho_0, \tag{B4}$$

where $\delta H \equiv H(n(\rho_0 + \zeta + \xi)) - H_0$, and we used

$$\sum_k f_k\varepsilon_k|\nu_k\rangle\langle\phi_k| = \sum_k f_k|\nu_k\rangle\langle\phi_k|H_0 = \zeta H_0. \tag{B5}$$

(Note that if there are no absorbing potentials, the equations for ζ can be added to its Hermitian conjugate to yield an equation involving only the Hermitian part of ζ; however, the presence of the absorbing potentials yields additional terms mixing the Hermitian and anti-Hermitian parts of ζ.)

The equation for ζ and the associated one for ξ are then combined in a superoperator language,

$$\frac{d}{dt}\begin{pmatrix} \zeta \\ \xi \end{pmatrix} = L\begin{pmatrix} \zeta \\ \xi \end{pmatrix}, \tag{B6}$$

where we write the evolution equation for the density as

$$L\begin{pmatrix} \zeta \\ \xi \end{pmatrix} = i\begin{pmatrix} (H - iV_I)\zeta + \delta H\rho_0 \\ -\xi(H - iV_I) - \rho_0\delta H \end{pmatrix}. \tag{B7}$$

In frequency space this equation becomes

$$\begin{pmatrix} \zeta(\omega) \\ \xi(\omega) \end{pmatrix} = \frac{1}{\gamma - i\omega - L}\begin{pmatrix} \zeta_0 \\ \xi_0 \end{pmatrix}, \tag{B8}$$

where

$$\begin{aligned} \zeta(\omega) &= \int_0^t \exp((i\omega - \gamma)t')\zeta(t')dt', \\ \xi(\omega) &= \int_0^t \exp((i\omega - \gamma)t')\xi(t')dt', \end{aligned} \tag{B9}$$

and

$$\begin{pmatrix} \zeta_0 \\ \xi_0 \end{pmatrix} = \begin{pmatrix} -i\eta\lambda\rho_0 \\ i\eta\rho_0\lambda \end{pmatrix}. \tag{B10}$$

The evolution equations in can be solved by QMR completely analogously to the orbital case.

Equations (B7)–(B10) are the final equations determining the frequency-dependent response of the density matrix.

In this density-matrix formalism, the conductivity of Eq. (A6) can be calculated by replacing Eq. (A7) with

$$\langle J_\alpha(\mathbf{r},\omega)\rangle = 2\,\mathrm{Re}\,\mathrm{Tr}[\zeta(\omega)J_\alpha(\mathbf{r})]. \tag{B11}$$

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