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Theory of Excitation Broadening using Time-Dependent Density Functional Theory for Open Quantum Systems

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The Casida equations of linear response TDDFT are extended to calculate linear spectra of open quantum systems evolving according to a Markovian master equation. By mapping a many-body open quantum system onto an open, non-interacting Kohn-Sham system, extrinsic line broadening due to electron-bath coupling can be described exactly within TDDFT. The structure of the resulting matrix equations are analyzed for the generic case of electrons linearly coupled to a harmonic bath within Redfield theory. An approximate form of the exchange-correlation kernel based on first-order Görling-Levy perturbation theory is derived.

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Due to its attractive balance between accuracy and efficiency, time-dependent density functional theory (TDDFT) has seen a tremendous growth of applications in recent years. These range from optical properties of molecules, clusters and solids, to optimal control theory and real time dynamics of species in intense laser fields [1–5]. A majority of applications concern molecular excitation energies and oscillator strengths extracted from Casida’s matrix formulation of linear response TDDFT [4]. In the usual formulation, one considers the density response of an isolated molecule without coupling to its environment. The resulting excitations are infinitely long lived, which unrealistically correspond to perfectly sharp peaks in the frequency spectrum. In reality, excited states of molecular systems decay due to relaxation and dephasing induced by the surrounding environment. Information about the environment is contained in the experimental shape and width of the excitation peaks in addition to their location.

In contrast to usual TDDFT methods, the theory of open quantum systems (OQS) provides a systematic way to describe spectral line broadening due to environmental effects. Accurate models exist to describe diverse phenomena ranging from pressure broadening due to intermolecular collisions in the gas phase, to vibrational relaxation of molecules in solid matrices and liquids in the condensed phase [14–17]. However, a majority of the OQS models require knowledge of the molecular many-body eigenstates which are in general too complex to explicitly calculate. This precludes a strictly *ab initio* treatment of spectral lineshapes using OQS, since without knowledge of the molecular eigenstates, the broadening must be semi-empirically modeled.

In the present letter, we use a recent extension of TDDFT for OQS (OQS-TDDFT) [6–8] to formulate matrix response equations yielding the exact spectral lineshapes of a Markovian many-body OQS model without requiring explicit a priori knowledge of the many-body eigenstates. We focus on electronic systems whose density operator in the absence of an external driving field evolves toward equilibrium according to a general memoryless (Markovian) master equation

$$\frac{d}{dt}\hat{\rho}(t) = -i[\hat{H}_{el}, \hat{\rho}(t)] + \check{D}[\hat{\rho}(t)], \quad (1)$$

which is more conveniently expressed in a basis of eigenstates of \hat{H}_{el} :

$$\frac{d}{dt}\rho_{ab}(t) = -i\omega_{ab}\rho_{ab}(t) + \sum_{cd} R_{ab,cd}\rho_{cd}(t). \quad (2)$$

With appropriate choice of the tetratic matrix, $R_{ab,cd}$, Eq. (2) encompasses master equations of the Lindblad form or those derived from Redfield theory. We consider an N -electron system having an electronic Hamiltonian $\hat{H}_{el} = -\frac{1}{2}\sum_{i=1}^N \nabla_i^2 + \sum_{i<j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N V_{ext}(\mathbf{r}_i)$, where $V_{ext}(\mathbf{r})$ is the static external potential of the nuclei. \hat{H}_{el} has a complete set of eigenstates satisfying $\hat{H}_{el}|\Psi_a\rangle = E_a|\Psi_a\rangle$ and $\omega_{ab} = E_a - E_b$ are the system transition frequencies. Here $\rho_{ab}(t) = \langle \Psi_a | \hat{\rho}(t) | \Psi_b \rangle$ and $\sum_{cd} R_{ab,cd}\rho_{cd}(t) = \langle \Psi_a | \check{D}[\hat{\rho}(t)] | \Psi_b \rangle$ are respectively matrix elements of the coarse-grained reduced system density operator and the dissipative superoperator between eigenstates of the full many-body electronic Hamiltonian.

We assume the system to be initially in thermal equilibrium with its environment at temperature T such that $\omega_{01} \gg K_B T$ is satisfied and hence all excited-state populations are negligible. The initial equilibrium density matrix is then $\rho_{ab}(0) = \delta_{a0}\delta_{b0}$ i.e. we start the system in the ground-state. This restriction is not necessary as one could start from the Kohn-Sham-Mermin density matrix when formulating the OQS-TDDFT response equations. However, for molecular electronic excitations, assuming a ground-state density is usually a very reasonable approximation. Applying a weak time-dependent external potential $\delta V_{appl}(\mathbf{r}, t)$, adiabatically switched on at $t = -\infty$, we expand the density response to first order in the perturbing potential:

$$\delta n(\mathbf{r}, t) = \int d^3\mathbf{r}' \int_{-\infty}^{\infty} dt' \chi_{nn}(\mathbf{r}, \mathbf{r}', t - t') \delta V_{appl}(\mathbf{r}', t'). \quad (3)$$

Here, $\delta n(\mathbf{r}, t) = \sum_{ab} n_{ab}(\mathbf{r}) \delta \rho_{ba}(t)$ where $n_{ab}(\mathbf{r}) = \langle \Psi_a | \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i) | \Psi_b \rangle$ are the matrix elements of the density operator and $\delta \rho_{ba}(t)$ is the deviation of the system density matrix from its equilibrium value to first order in the applied

field. $\chi_{nn}(\mathbf{r}, \mathbf{r}', \tau)$ is the OQS density-density response function whose Fourier transform to the frequency domain is:

$$\chi_{n,n}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{a \neq 0} \left[\frac{n_{0a}(\mathbf{r})n_{a0}(\mathbf{r}')}{\omega - (\omega_{a0} - iR_{a0,a0})} - \frac{n_{a0}(\mathbf{r})n_{0a}(\mathbf{r}')}{\omega - (\omega_{0a} - iR_{0a,0a})} \right] \quad (4)$$

In Eq. (4), transition frequencies lie at the poles of the density-density response function, while oscillator strengths are obtained from the residues. In the vicinity of a transition, the imaginary part

$$\Im m \chi_{n,n}(\mathbf{r}, \mathbf{r}', \omega) \approx \frac{n_{0a}(\mathbf{r})n_{a0}(\mathbf{r}') \Re e R_{a0,a0}}{(\omega - \omega_{a0} - \Im m [R_{a0,a0}])^2 + (\Re e R_{a0,a0})^2} \quad (5)$$

shows that each isolated transition acquires a Lorentzian lineshape. The presence of the bath shifts the excitation frequencies of the isolated molecule by $\Im m [R_{a0,a0}]$ while broadening the peak to a width at half maximum given by $\Re e [R_{a0,a0}]$. The dephasing rates $R_{a0,a0}$ depend on the specific bath model, but in general are proportional to the correlation time of the bath and the second power of the strength of the system-bath coupling. The Lorentzian lineshape is a generic feature of Markovian systems and is expected to hold for realistic systems in the long-time limit. Experimentally, this corresponds to frequencies near the center of a given spectral line in Fourier space [15]. Corrections to the Lorentzian shape can be obtained by including non-Markovian effects and will be discussed in future work.

As discussed in [6–8], one can define a unique non-interacting, but open Kohn-Sham system with an effective one-particle local potential $V_s^{open}(\mathbf{r}, t)$ and Hamiltonian $\hat{H}(t)^{ks} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + V_s^{open}(\mathbf{r}_i, t)$ such that when it's density operator $\hat{\rho}^{ks}$ evolves under the master equation,

$$\frac{d}{dt} \hat{\rho}(t)^{ks} = -i[\hat{H}(t)^{ks}, \hat{\rho}(t)^{ks}] + \check{D}^{ks}[\hat{\rho}^{ks}(t)] \quad (6)$$

the density of the correlated OQS is reproduced for all times. This implies that $Tr[\hat{\rho}(t)^{ks} \hat{n}(\mathbf{r})] = Tr[\hat{\rho}(t) \hat{n}(\mathbf{r})]$ is always satisfied, where Tr denotes a trace over the 3N system degrees of freedom. In Eq. (6), the dissipative superoperator \check{D}^{ks} is derived using the same approximations to derive \check{D} in the original master equation (Eq. (1)), but evaluated using Kohn-Sham eigenvalues and determinants in place of many-body states. This is the procedure employed in [7]. We now exploit the fact that the linear density response of the open Kohn-Sham system matches that of the interacting open system and develop a set of matrix equations whose solution yields the correct spectrum.

With the system initially in it's ground-state, we begin by performing a self-consistent ground-state DFT calculation, yielding a static Kohn-Sham Hamiltonian $\hat{H}_{gs}^{ks} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + V_s(\mathbf{r}_i)$ where $V_s(\mathbf{r})$ is the ground-state Kohn-Sham potential corresponding to the density of the initial many-body state

$\rho_{ab}(0) = \delta_{a0}\delta_{b0}$. Denoting the spectrum of Slater determinants of \hat{H}_{gs}^{ks} by $\{|\Phi_\alpha\rangle\}$, the initial non-interacting density matrix is $\rho_{\alpha\beta}^{ks}(0) = \delta_{\alpha0}\delta_{\beta0}$. Here greek indices will be used for Kohn-Sham determinants and latin indices for many-body states. We have assumed $\omega_{01} \gg K_B T$ is also satisfied for the first Kohn-Sham excited-state. Applying $\delta V_{appl}(\mathbf{r}, t)$ to the open Kohn-Sham system yields the linear density response:

$$\delta n(\mathbf{r}, t) = \int d^3 \mathbf{r}' \int_{-\infty}^{\infty} \chi_{nn}^s(\mathbf{r}, \mathbf{r}', t-t') \delta V_s^{open}(\mathbf{r}', t) \quad (7)$$

Where $\delta V_s^{open}(\mathbf{r}, t) = \delta V_{appl}(\mathbf{r}, t) + \int d^3 \mathbf{r}' \frac{\delta n(\mathbf{r}', t)}{|\mathbf{r}-\mathbf{r}'|} + \delta V_{xc}^{open}(\mathbf{r}, t)$ and $\delta V_{xc}^{open}(\mathbf{r}, t)$ is the response of the unknown OQS exchange-correlation potential. Here, $\chi_{nn}^s(\mathbf{r}, \mathbf{r}', \tau)$ is the Kohn-Sham density-density response function whose Fourier transform has the same form as Eq. (4), but the matrix elements and energies are taken with respect to Kohn-Sham determinants while replacing the many-body dephasing rates $R_{a0,a0}$ are the Kohn-Sham dephasing rates $R_{\alpha0,\alpha0}^{ks}$. In general, the system-bath interaction will only involve one-body system operators and therefore couple Kohn-Sham determinants differing by a single orbital. In this case, $R_{\alpha0,\alpha0}^{ks} = \gamma_{ij}$, where the Kohn-Sham singly-excited determinant Φ_α is obtained from the ground-state Φ_0 by replacing an occupied orbital ϕ_i by an unoccupied orbital ϕ_j . Additionally, γ_{ij} represents the dephasing rate between the two orbitals involved. This procedure is discussed in more detail below for a specific system-bath model.

By matching the response of the interacting and Kohn-Sham systems and following a similar procedure to the formulation used by Casida [4], one finds the squares of the excitation energies as solutions to the pseudo-eigenvalue equation

$$\tilde{\Omega}(\omega)F = \omega^2 F. \quad (8)$$

The operator on the left hand side is written as a matrix in a basis of ground-state Kohn-Sham molecular orbitals:

$$\begin{aligned} \tilde{\Omega}_{ij,kl}(\omega) &= \delta_{ik}\delta_{jl}(\omega_{ik}^2 - \frac{1}{4}(\gamma_{kl} - \gamma_{ik})^2) \\ &+ 2\sqrt{(f_i - f_j)(\omega_{jk} + \frac{1}{2}(\gamma_{ij} - \gamma_{ji})K_{ij,kl}(\omega) \times} \\ &\sqrt{(f_k - f_l)(\omega_{lk} + \frac{1}{2}(\gamma_{kl} - \gamma_{lk})} \\ &- i\omega\delta_{ik}\delta_{jl}(\gamma_{kl} + \gamma_{ik}) + \frac{1}{4}\delta_{ik}\delta_{jl}(\gamma_{kl} + \gamma_{ik})^2. \end{aligned} \quad (9)$$

Equations (8) and (9) are the first central result of the paper. The Kohn-Sham eigenvalues ω_{ij} and dephasing rates γ_{ij} are mixed by the (in general, imaginary and frequency-dependent) exchange-correlation kernel to yield the real and imaginary parts of the energies of the interacting OQS. For each eigenvalue solution in Eq. (8), the real part gives the center of the excitation peak while its

imaginary part gives the width at half maximum. The $\{f_i\}$ are orbital occupation numbers, which will be 0 or 1 in the groundstate, but may be fractional if higher temperatures are involved and Kohn-Sham-Mermin theory becomes necessary. The coupling matrix is given by $K_{ij,kl}(\omega) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) f_{hxc}^{open}(\mathbf{r}, \mathbf{r}', \omega) \phi_k(\mathbf{r}') \phi_l(\mathbf{r}')$ with $f_{hxc}^{open}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta V_{xc}^{open}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)}$ the Hartree kernel plus open system exchange-correlation kernel.

Since $\gamma_{ij} = \gamma_{ji}^*$, one notices that all terms in the operator $\tilde{\Omega}(\omega)$ are real except for the coupling matrix and the term $-2i\omega\delta_{ik}\delta_{jl}\Re(\gamma_{kl})$. The structure of Eq. (8) is most easily analyzed within a single-pole approximation, in which we zoom into a subspace spanned by a single Kohn-Sham transition from an occupied orbital ϕ_1 to an unoccupied orbital ϕ_2 and further assume $\omega_{12} \gg K_{12,12}(\omega)$ i.e. the correction from the kernel is small relative to the bare Kohn-Sham transition. In this case, one finds a single solution to Eq. (8):

$$\omega \approx -i\Re\gamma_{12} + \sqrt{\omega_{12}^2 + (\Im m\gamma_{12})^2} + (\omega_{12} + \Im m\gamma_{12})K_{12,12}. \quad (10)$$

If one uses a standard adiabatic approximation for f_{hxc}^{open} , the elements of the coupling matrix in Eq. (10), $K_{12,12}$ are real and independent of ω . In this case, we get a TDDFT correction to the location of the peak given by $\Re(\omega)$, but the width is given by $\Im m(\omega)$ and the peak still has its bare Kohn-Sham value of $\Re\gamma_{12}$. This simple analysis suggests that an adiabatic functional may be sufficient if the bare Kohn-Sham linewidth is close to that of the interacting system. For more accuracy, a frequency-dependent and imaginary functional is required. In the remainder of the paper, we propose such a functional, which starting from the bare Kohn-Sham linewidth at zeroth-order, systematically provides corrections through perturbation theory.

However, before discussing approximations to $f_{xc}^{open}(\mathbf{r}, \mathbf{r}', \omega)$, we generalize the adiabatic connection perturbation theory of [9–13] to OQS. Following a generalization of the theorems proven in [6–8] and detailed in the appendix, it is possible to consider an entire class of master equations:

$$\frac{d}{dt}\hat{\rho}(t, \alpha) = -i[\hat{H}(t, \alpha), \hat{\rho}(t, \alpha)] + \check{D}^\alpha[\hat{\rho}(t, \alpha)] \quad (11)$$

where $0 \leq \alpha \leq 1$ is the electron-electron adiabatic coupling constant and where the Hamiltonian is

$$\hat{H}(t, \alpha) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j=1}^N \frac{\alpha}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N V(\mathbf{r}_i, t, \alpha). \quad (12)$$

Here, $V(\mathbf{r}, t, \alpha)$ is a unique, local, one-body potential chosen such that $Tr[\hat{\rho}(t, \alpha)\hat{n}(\mathbf{r})] = n(\mathbf{r}, t, \alpha) = n(\mathbf{r}, t)$ yields the physical open system density for all times independent of α . Considering linear response only, $V(\mathbf{r}, t, \alpha) = V(\mathbf{r}, \alpha) + \delta V(\mathbf{r}, t, \alpha)$, where $V(\mathbf{r}, \alpha)$ is the potential lying on the static

adiabatic connection at coupling constant α and $\delta V(\mathbf{r}, t, \alpha)$ is the linear response of this potential to the applied field. Here, $V(\mathbf{r}, t, \alpha = 1) = V_{ext}(\mathbf{r}) + \delta V_{appl}(\mathbf{r}, t)$ while $V(\mathbf{r}, t, \alpha = 0) = V_s(\mathbf{r}) + \delta V_s^{open}(\mathbf{r}, t)$. We further specify the initial condition $\hat{\rho}(t = -\infty, \alpha) = |\Psi_0(\alpha)\rangle\langle\Psi_0(\alpha)|$ where $|\Psi_0(\alpha)\rangle$ is the ground-state that lies on the stationary adiabatic connection between the Kohn-Sham groundstate determinant $|\Psi_0(\alpha = 0)\rangle = |\Phi_0\rangle$ and the interacting groundstate of \hat{H}_{el} , $|\Psi_0(\alpha = 1)\rangle = |\Psi_0\rangle$. As detailed in [13], one can also consider excited states $\{|\Psi_i(\alpha)\rangle\}$ with corresponding energy $\{E_i(\alpha)\}$ lying on the adiabatic connection between the i th Kohn-Sham excited determinant and the i th many-body excited state. The density response at coupling constant α can be formally written in terms of these states as

$$\delta n(\mathbf{r}, \omega, \alpha) = \sum_{a \neq 0}^{\infty} \frac{2\omega_{0a}(\alpha)}{\omega_{0a}(\alpha)^2 + R_{0a0a}(\alpha)^2 - \omega^2 - 2i\omega R_{0a0a}(\alpha)} \times \langle \psi_0(\alpha) | \hat{n}(\mathbf{r}) | \psi_a(\alpha) \rangle \langle \psi_a(\alpha) | \delta \hat{V}(\alpha, \omega) | \psi_0(\alpha) \rangle, \quad (13)$$

where the quantities $R_{0a0a}(\alpha)$ are obtained from matrix elements of the dissipative superoperator at coupling constant α , $\sum_{cd} R_{ab,cd}(\alpha) \rho_{cd}(t, \alpha) = \langle \Psi_a(\alpha) | \check{D}^\alpha[\hat{\rho}(t, \alpha)] | \Psi_b(\alpha) \rangle$ and $\delta \hat{V}(\alpha, \omega)$ is the operator that generates $\delta V(\mathbf{r}, \omega, \alpha)$. As in the Kohn-Sham case, \check{D}^α is obtained by making the same approximations used in obtaining \check{D} , but with eigenstates and energies of the stationary adiabatic connection Hamiltonian at coupling constant α . We now expand all functions of α appearing in Eq. (13) in a Taylor series in α . The expansions of quantities in Eq. (13) are given by Görling-Levy perturbation theory as in [9–13], but we now also expand the elements of the relaxation matrix as $R_{0a0a}(\alpha) = \sum_{i=0}^{\infty} \alpha^i R_{0a0a}^i$. This is justified, since for a given superoperator \check{D}^α , the elements $R_{0a0a}(\alpha)$ will depend on eigenstates and energies of the stationary adiabatic connection Hamiltonian at coupling constant α , which can be systematically expanded order by order to construct the set of coefficients $\{R_{0a0a}^i\}$.

Taylor expanding both sides of Eq. (13) and equating terms of equal-order in alpha, at zeroth-order recovers Eq. (7). At first-order in α one obtains,

$$\int d^3\mathbf{r}_2 \chi_{nn}^s(\omega, \mathbf{r}_1, \mathbf{r}_2) V^1(\omega, \mathbf{r}_2) = - \int d^3\mathbf{r}_2 h_1^{open}(\omega, \mathbf{r}_1, \mathbf{r}_2) \delta V_s^{open}(\omega, \mathbf{r}_2). \quad (14)$$

The exact form of $h_1^{open}(\omega, \mathbf{r}_1, \mathbf{r}_2)$ together with a detailed derivation of Eq. (14) is given in the appendix. $V^1(\omega, \mathbf{r}_2) = - \int d^3\mathbf{r}' \frac{\delta n(\mathbf{r}', \omega)}{|\mathbf{r}-\mathbf{r}'|} - \delta V_x^{open}(\mathbf{r}, \omega)$ is the first-order potential in the Görling-Levy perturbation theory expansion of the OQS response potential and $\delta V_x^{open}(\mathbf{r}, \omega)$ generalizes the time-dependent exact-exchange response potential of TDDFT to OQS-TDDFT. Defining the OQS exact-exchange kernel by $f_x^{open}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\delta V_x^{open}(\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)}$ and inserting $V^1(\omega, \mathbf{r}) = - \int d^3\mathbf{r}' [\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_x^{open}(\mathbf{r}, \mathbf{r}', \omega)] \delta n(\mathbf{r}', \omega)$ together with $\delta V_s^{open}(\omega, \mathbf{r}) = \int d^3\mathbf{r}' (\chi_{nn}^s)^{-1}(\omega, \mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}', \omega)$ into Eq. (14), one finds:

$$f_x^{open}(\omega, \mathbf{r}, \mathbf{r}') + \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ = \int d^3 \mathbf{r}'' d^3 \mathbf{r}''' (\chi_{nm}^s)^{-1}(\omega, \mathbf{r}, \mathbf{r}'') h_1^{open}(\omega, \mathbf{r}'', \mathbf{r}''') (\chi_{nm}^s)^{-1}(\omega, \mathbf{r}''', \mathbf{r}') \text{ is:} \quad (15)$$

This is the second main result of the paper. The functional $f_x^{open}(\omega, \mathbf{r}, \mathbf{r}')$ provides an approximate imaginary and frequency-dependent OQS kernel to be implemented in solving Eq. (8). All quantities are computed in terms of ground-state Kohn-Sham orbitals and eigenvalues together with a specified bath model. $(\chi_{nm}^s)^{-1}(\omega, \mathbf{r}, \mathbf{r}')$ is the inverse Kohn-Sham density-density response function. Appearing in the final expression for $f_x^{open}(\omega, \mathbf{r}, \mathbf{r}')$ (see appendix) are R_{0a0a}^0 and R_{0a0a}^1 which are respectively the zeroth and first-order coefficients of the Görling-Levy expansion of the relaxation matrix. To be more concrete, we now proceed to construct these coefficients for a generic system-bath model: electrons linearly coupled to a bath of linear harmonic oscillators treated within Redfield theory.

The full hamiltonian before tracing over bath degrees of freedom for this model is:

$$\hat{H} = \hat{H}_{el} + \xi \sum_i r_i \cdot \sum_{\zeta} R_{\zeta} + \sum_{\zeta} \omega_{\zeta} (c_{\zeta}^{\dagger} c_{\zeta} + \frac{1}{2}). \quad (16)$$

In Eq. (16), r_i and R_{ζ} are respectively the position operator of the i th electron in the system and ζ th oscillator of frequency ω_{ζ} in the bath and ξ is a coupling constant characterizing the strength of the system-bath interaction. c_{ζ}^{\dagger} and c_{ζ} are raising and lowering operators for each bath mode. Performing the standard reduction to the multilevel Redfield equations [18], one arrives at Eq. (2), with:

$$R_{ab,ab} = -\frac{\pi}{2\omega_{ab}} f\left(\frac{\omega_{ab}}{K_B T}\right) (\tilde{\xi}^{ab})^2 D(\omega_{ab}), \quad (17)$$

where $\tilde{\xi}^{ab} = N \xi \langle \Psi_a | r | \Psi_b \rangle$, $D(\omega)$ is the harmonic oscillator bath density of states and $f(x) = \frac{1+e^{-x}}{1-e^{-x}}$. Applying the same dissipative superoperator for this model, but at intermediate coupling constant as in Eq. (11), one finds

$$R_{ab,ab}(\alpha) = -\frac{\pi}{2\omega_{ab}(\alpha)} f\left(\frac{\omega_{ab}(\alpha)}{K_B T}\right) \tilde{\xi}^{ab}(\alpha)^2 D(\omega_{ab}(\alpha)) \quad (18)$$

with $\tilde{\xi}^{ab}(\alpha) = N \xi \langle \Psi_a(\alpha) | r | \Psi_b(\alpha) \rangle$. Expanding to first order in the coupling constant, $R_{ab,ab}(\alpha) \approx R_{ab,ab}^0 + \alpha R_{ab,ab}^1$, one finds

$$R_{ab,ab}^0 = -\frac{\pi}{2\omega_{ab}(0)} f\left(\frac{\omega_{ab}(0)}{K_B T}\right) \tilde{\xi}^{ab}(0)^2 D(\omega_{ab}(0)) \quad (19)$$

as the dephasing rate between Kohn-Sham determinants Φ_a and Φ_b . $\tilde{\xi}_{\zeta}^{ab}(0)$ is zero unless these two determinants differ by

a single occupied-unoccupied orbital transition and so $R_{ab,ab}^0$ reduces to the dephasing rate between these two orbitals as discussed earlier. Eq. (19) is analogous to Eq. (12) in [7], but for a different system-bath model. The first order coefficient

$$R_{ab,ab}^1 = \frac{\pi \omega_{ab}^1}{2\omega_{ab}(0)^2} f\left(\frac{\omega_{ab}(0)}{K_B T}\right) \tilde{\xi}^{ab}(0)^2 D(\omega_{ab}(0)) \\ - \frac{\pi}{2\omega_{ab}(0)} f' \left(\frac{\omega_{ab}(0)}{K_B T}\right) \tilde{\xi}^{ab}(0)^2 D(\omega_{ab}(0)) \\ - \frac{\pi}{\omega_{ab}(0)} f\left(\frac{\omega_{ab}(0)}{K_B T}\right) \tilde{\xi}^{ab}(0) \tilde{\xi}^{ab,1} D(\omega_{ab}(0)) \\ - \frac{\pi}{\omega_{ab}(0)} f\left(\frac{\omega_{ab}(0)}{K_B T}\right) \tilde{\xi}^{ab}(0)^2 \omega_{ab}^1 D'. \quad (20)$$

Primes denote derivatives of the respective functions and the quantities ω_{ab}^1 and $\tilde{\xi}^{ab,1}$ are obtained from Görling-Levy first order perturbation theory and given explicitly in the Appendix for completeness.

The density functional formalism we have presented allows one to calculate spectra starting from a many-body Markovian OQS model, without requiring the many-body molecular eigenstates as input. By explicitly coupling a system of non-interacting electrons with the same Markovian bath model used for the interacting system, the dissipation is explicitly accounted for in the response equations to zeroth-order in Görling-Levy perturbation theory. Since the Kohn-Sham eigenvalues and wavefunctions are different from those of the interacting system, the Kohn-Sham dissipation will in general be different as well. The task of the open-system exchange-correlation kernel is to correct the Kohn-Sham dissipation to that of the interacting system. We have presented a frequency dependent and imaginary functional that explicitly incorporates the first order correction to the Kohn-Sham dissipation.

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APPENDIX - DERIVATION OF OQS EXACT-EXCHANGE FUNCTIONAL

The functional we present in Eq. (15) is based on a generalization of perturbation theory along the adiabatic connection [9–13]. This was originally formulated for time-dependent closed systems in [12]. The generalization to non-unitary evolution follows directly once a one-to-one mapping between densities and potentials is established for an open system at any electron-electron interaction strength. Although this is not the main point of [8], such a mapping follows directly from the theorems proven therein.

The main point of the perturbation theory employed in [9–13] is to use the Kohn-Sham Hamiltonians as solutions to the unperturbed problem. This means $\hat{H}(t)^{ks} = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 +$

$V_s^{open}(\mathbf{r}_i, t)$ is the zeroth-order Hamiltonian for the evolution and $\hat{H}_{gs}^{ks} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + V_s(\mathbf{r}_i)$ is the zeroth-order Hamiltonian for the initial state. We wish to include corrections due to finite coupling constant α in the exchange-correlation kernel perturbatively. In the context of OQS-TDDFT, these corrections will also include corrections to the Kohn-Sham dissipation which plays the role of a zeroth-order dissipation in the theory. The starting point of the derivation of the functional is Eq. (13) for the linear density response of an OQS at coupling constant α :

$$\delta n(\mathbf{r}, \omega, \alpha) = \sum_{a \neq 0}^{\infty} \frac{2\omega_{0a}(\alpha)}{\omega_{0a}(\alpha)^2 + R_{0a0a}(\alpha)^2 - \omega^2 - 2i\omega R_{0a0a}(\alpha)} \times \langle \psi_0(\alpha) | \hat{n}(r) | \psi_a(\alpha) \rangle \langle \psi_a(\alpha) | \delta \hat{V}(\alpha, \omega) | \psi_0(\alpha) \rangle. \quad (21)$$

All quantities are then expanded in a Taylor series in α . For the density response this yields:

$$\delta n(\mathbf{r}, \omega, \alpha) = \sum_{i=0}^{\infty} \alpha^i \delta n^i(\mathbf{r}, \omega). \quad (22)$$

By construction, the density response is invariant with respect to α . This implies that $\delta n^0(\mathbf{r}, \omega) = \delta n(\mathbf{r}, \omega)$, is the physical density response while $\delta n^i(\mathbf{r}, \omega) = 0$ for $i \geq 1$. Consider now the Taylor series expansion of the response potential operator:

$$\delta \hat{V}(\alpha, \omega) = \sum_{i=0}^{\infty} \alpha^i \delta \hat{V}^i(\omega). \quad (23)$$

The potential operator at zero coupling constant, $\delta \hat{V}(\alpha = 0, \omega) = \delta \hat{V}^0(\omega)$, generates the Kohn-Sham response potential $\delta V_s^{open}(\mathbf{r}, t)$, while $\delta \hat{V}(\alpha = 1, \omega) = \sum_{i=0}^{\infty} \delta \hat{V}^i(\omega)$ generates the true applied field $\delta V_{appl}(\mathbf{r}, t)$. Of particular interest, is the first order coefficient $\delta \hat{V}^1(\omega)$ which generates the negative of the Hartree and exchange potential response $-\int d^3\mathbf{r}' \frac{\delta n(\mathbf{r}', \omega)}{|\mathbf{r}-\mathbf{r}'|} - \delta V_x^{open}(\mathbf{r}, \omega)$. The higher-order terms $\sum_{i=2}^{\infty} \delta \hat{V}^i(\omega)$ give the response of the negative of the correlation potential and will be neglected here.

At $t = -\infty$, the system is in the groundstate of \hat{H}_{el} with ground-state density $n_0(\mathbf{r})$. There exists an entire set of Hamiltonians with ground-state density $n_0(\mathbf{r})$ at different interaction strengths α :

$$\hat{H}(\alpha) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j=1}^N \frac{\alpha}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N V(\mathbf{r}_i, \alpha). \quad (24)$$

The Hamiltonian $\hat{H}(\alpha = 1) = \hat{H}_{el}$ is the many-body Hamiltonian while $\hat{H}(\alpha = 0) = \hat{H}_{gs}^{ks}$ is the Kohn-Sham ground-state Hamiltonian. Assuming the eigenstates of $\hat{H}(\alpha)$, $\{|\Psi_i(\alpha)\rangle\}$, do not cross as α is varied between 0 and 1, there is a continuous one-to-one adiabatic connection between the many-body eigenstates and the Kohn-Sham determinants. Expanding the i th excited state of $\hat{H}(\alpha)$ in a Taylor series

$|\Psi_i(\alpha)\rangle = \sum_{k=0}^{\infty} \alpha^k |\Psi_i^k\rangle$, we find $|\Psi_i(\alpha = 0)\rangle = |\Psi_i^0\rangle = |\Phi_i\rangle$ is the i th Kohn-Sham excited determinant while $|\Psi_i(\alpha = 1)\rangle = \sum_{k=0}^{\infty} |\Psi_i^k\rangle = |\Psi_i\rangle$ is the i th many-body excited state. The first order coefficient in the expansion $|\Psi_i^1\rangle$ is obtained from perturbation theory according to:

$$|\Psi_i^1\rangle = \sum_{j=1, j \neq i}^{\infty} \frac{\langle \Psi_j(0) | \hat{v}_{ee} - \hat{v}_H - \hat{v}_x | \Psi_i(0) \rangle}{\omega_{ij}(0)} |\Psi_j(0)\rangle. \quad (25)$$

In Eq. (25), \hat{v}_{ee} generates the electron-electron repulsion $\sum_{i < j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ while \hat{v}_H generates the ground-state Hartree potential $\int d^3\mathbf{r}' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ and \hat{v}_x the local exchange potential of ground-state DFT. The sum is over all excited Kohn-Sham determinants differing from the i th determinant and $\omega_{ij}(0)$ is the energy difference between these two determinants. Eq. (25) follows from expanding the Hamiltonian in Eq. (24) in a Taylor series in α and treating the term linear in α , $\hat{v}_{ee} - \hat{v}_H - \hat{v}_x$ within usual Rayleigh-Schrodinger perturbation theory [9, 10].

Similarly, the energies are expanded as $E_i(\alpha) = \sum_{k=0}^{\infty} \alpha^k E_i^k$. The first-order correction to the energies are obtained from first order perturbation theory as well:

$$E_i^1 = \langle \Psi_i(0) | \hat{v}_{ee} - \hat{v}_H - \hat{v}_x | \Psi_i(0) \rangle. \quad (26)$$

Since the relaxation matrix $R_{ab,ab}(\alpha)$ depends on the energies and wavefunctions, $\{E_i(\alpha)\}$ and $\{|\Psi_i(\alpha)\rangle\}$, it can also be systematically expanded in a Taylor series in α . The result of such an expansion to first order is Eq. (20), for the specific system-bath model considered. In Eq. (20), $\omega_{ab}^1 = E_a^1 - E_b^1$ and $\xi^{ab,1} = N \xi \langle \Psi_a(0) | r | \Psi_b^1 \rangle$.

Now, with the expansions of the energies, wavefunctions and relaxation matrix elements, we can systematically expand both sides of Eq. (13) and equate coefficients of equal powers in α . If we keep only the terms of first-order in α , the right hand side of Eq. (13) contains only Kohn-Sham determinants and eigenvalues as well as the first-order corrections E_i^1 and $|\Psi_i^1\rangle$. As a result, all quantities in Eq. (13) are expressed in terms of ground-state Kohn-Sham orbitals and eigenvalues. The result of the first-order expansion is Eq. (14), where:

$$\chi_{nn}^s(\omega, \mathbf{r}, \mathbf{r}') = \sum_{s=N}^{\infty} \sum_{a=1}^N \frac{2\omega_{as}}{\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as}} \phi_a(\mathbf{r}) \phi_s(\mathbf{r}) \phi_a(\mathbf{r}') \phi_s(\mathbf{r}') \quad (27)$$

is the Kohn-Sham response function and:

$$h_1^{open}(\omega, \mathbf{r}, \mathbf{r}') = \sum_{ijkl=1}^{\infty} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) g(\omega, i, j, k, l) \phi_k(\mathbf{r}') \phi_l(\mathbf{r}') \quad (28)$$

The non-zero elements of the matrix $g(\omega, i, j, k, l)$ are given as follows:

$$g(\omega, a, s, a, b) = \frac{2\omega_{as}}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})\omega_{bs}} \times \left[-\sum_{c=1}^N \langle bc|cs \rangle - \langle s|\hat{v}_x|b \rangle \right] \quad (29)$$

$$g(\omega, a, s, t, s) = \frac{2\omega_{as}}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})\omega_{at}} \times \left[-\sum_{c=1}^N \langle ac|ct \rangle - \langle t|\hat{v}_x|a \rangle \right] \quad (30)$$

$$g(\omega, a, s, a, a) = g(\omega, a, s, s, s) = \frac{1}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})} \times \left[-\sum_{c=1}^N \langle ac|cs \rangle - \langle s|\hat{v}_x|a \rangle \right] \quad (31)$$

$$g(\omega, a, s, b, s) = \frac{2\omega_{as}}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})\omega_{ba}} \times \left[-\sum_{c=1}^N \langle ab|cc \rangle - \langle a|\hat{v}_x|b \rangle \right] \quad (32)$$

$$g(\omega, a, s, a, t) = \frac{2\omega_{as}}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})\omega_{st}} \times \left[-\sum_{c=1}^N \langle ts|cc \rangle - \langle t|\hat{v}_x|s \rangle \right] \quad (33)$$

$$g(\omega, a, s, b, t) = \frac{2\omega_{as}}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})(\omega_{sa} - \omega_{tb})} \times [\langle as|bt \rangle - \langle at|bs \rangle] \quad (34)$$

$$g(\omega, a, s, a, s) = \left[-\frac{1}{2} \sum_{cb=1}^N (\langle cc|bb \rangle + \langle cb|bc \rangle) - \sum_{c=1}^N \langle c|\hat{v}_x|c \rangle - \frac{1}{2} (\langle aa|ss \rangle - \langle as|sa \rangle) + \sum_{c=1}^N \langle as|cc \rangle + \langle a|\hat{v}_x|s \rangle \right] \frac{1}{\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as}} - \left[-\frac{1}{2} \sum_{cb=1}^N (\langle cc|bb \rangle + \langle cb|bc \rangle) - \sum_{c=1}^N \langle c|\hat{v}_x|c \rangle - \frac{1}{2} (\langle aa|ss \rangle - \langle as|sa \rangle) + \sum_{c=1}^N \langle as|cc \rangle + \langle a|\hat{v}_x|s \rangle \right] \times \left[\frac{4\omega_{as}^2}{\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as}} - \frac{4\omega_{as}\gamma_{as}^1(\gamma_{as} - i\omega)}{(\omega_{as}^2 + \gamma_{as}^2 - \omega^2 - 2i\omega\gamma_{as})^2} \right] \quad (35)$$

In the above, we use the notation of [11] where indices a,b and c are used to represent occupied Kohn-Sham orbitals while s and t are for unoccupied orbitals. As in [11], all matrix elements of $g(\omega, i, j, k, l)$ not specified above are zero. In the above notation, matrix elements of the Coulomb and non-local exchange operators are defined as (and assuming real molecular orbitals) $\langle ij|kj \rangle = \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\phi_i(\mathbf{r})\phi_j(\mathbf{r})\phi_k(\mathbf{r}')\phi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$. In the above expression, γ_{as} is the dephasing rate between two determinants differing by a transition from an occupied orbital ϕ_a to an unoccupied orbital ϕ_s as discussed in Eq. (19) for a specific system-bath model. γ_{as}^1 represents the first order correction to this dephasing rate as shown in Eq. (20). Thus, we obtain the generalization of the exact-exchange functional of TDDFT derived in [11] to the OQS-TDDFT case. In the limit that $\gamma_{as} = \gamma_{as}^1 = 0$, we recover the result of [11] as expected.

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