

Self-consistent density matrix algorithm for electronic structure and excitations of molecules and aggregates

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An *ab initio* density matrix algorithm for electronic structure computations of many-electron systems is proposed. The reduced single-electron density matrices are derived by mapping the density functional theory nonlinear optical response functions onto an effective multilevel system. These density matrices are then used as a zeroth order iteration into self-consistent equations whose solution should yield the exact energies and the complete set of (transition and diagonal) single-electron density matrices. Higher order (n electron) density matrices are not computed explicitly. The linear and nonlinear optical response functions may be obtained at a low computational cost. Application is made to constructing an exciton Hamiltonian for molecular aggregates using density matrices of isolated molecules, avoiding electronic structure calculations of the entire aggregate. © 2003 American Institute of Physics. [DOI: 10.1063/1.1625365]

I. INTRODUCTION

Computing many-electron wave functions is numerically expensive and can only be carried out at the *ab initio* level for small molecules.^{1,2} The major difficulty stems from the fact that these wave functions carry an enormous amount of information, most of it is unnecessary for computing ordinary molecular properties (energies, optical response, etc.). Considerable effort has thus been devoted to developing *reduced descriptions*, which eliminate redundant information from the outset and only retain the essential information.³

Density functional theory^{4–8} is one of the most notable examples for such approaches. DFT focuses on the charge density but does not offer a recipe for computing the necessary exchange correlation functional. Including more information, in addition to the charge density, may provide more flexibility, particularly for excited state computations. Green function (propagator) techniques,^{9–11} for example, include coherence in Fock space between states with different number of electrons. Variational techniques such as the generator coordinate approach^{12–14} provide useful approximations, but it is hard to make them exact.

The single-electron density matrix provides an attractive level of reduction.^{3,15,16} Let us denote the Fermi creation (annihilation) operators for electron on the basis function n by c_n^+ (c_n) and the many-electron eigenstates by ν, ν' . The long standing goal of developing a closed algorithm for density matrices has been hindered by the N representability problem, i.e., the difficult task of securing that an approximate density matrix is compatible with an N -electron wave function. We shall focus on the complete set of single-electron density matrices

$$\rho_{nm}^{\nu\nu'} \equiv \langle \nu | c_n^+ c_m | \nu' \rangle. \quad (1)$$

For $\nu = \nu'$ this is the density matrix of state ν whereas for $\nu \neq \nu'$ this is the transition density matrix between two states. For $\nu = \nu'$ and $n = m$, $\rho_{nn}^{\nu\nu}$ is the charge density in state

ν . ρ is thus a natural extension of the charge density to include spatial coherence ($n \neq m$) and coherence between different many-electron states ($\nu \neq \nu'$).

Spatial coherence is the key for describing collective excitations in, e.g., Bose Einstein condensates.¹⁷ Recent interest in quantum computing and information is based on controlling the many-body wave function. Correlation (entanglement) allows to store and retrieve large amounts of information. The single-electron density matrix provides a direct measure of the degree of coherence and correlations and may be useful for these applications.¹⁸ N -electron density matrices satisfy the usual many-body hierarchy and considerable effort has been made to truncate this hierarchy at the 2 or 3 electron level.^{16,19–21} Memory requirements grow rapidly with N so that there is an obvious advantage to staying at the one-electron level. Density matrix renormalization group techniques whose numerical effort grows linearly with size (N scaling) have been successfully applied.^{22,23}

TDDFT provides a convenient way for generating approximations for transition density matrices $\rho_{nm}^{g\nu\nu'}$ involving the ground state g . The method assumes that the many-electron wave function is given by a single Slater determinant at all times, and takes some correlation effects into account. The computations are very fast and efficient but have a limited accuracy. In this paper we propose a new practical method for extending the TDDFT calculations, making them exact. A closed system of equations for $\rho_{nm}^{\nu\nu'}$ and the energy levels E_ν are derived, whose iterative solution starting with the TDDFT matrices $\rho_{nm}^{g\nu\nu'}$ can lead to the exact quantities, fully including all exchange and correlation effects. The proposed algorithm consists of the following steps. (i) Start with a Hartree–Fock ground state calculation. This results in ρ^{gg} and the energy E_g . (ii) Solve the TDDFT equations for the linear optical response, using ρ^{gg} as an input. This yields a subset of approximate transition density matrices involving the ground state $\rho^{g\nu}$ as well as the transition energies $\Omega_{g\nu} \equiv E_g - E_\nu$. (iii) Construct approximate expressions for the

density matrices $\rho^{\nu\nu'}$ between any pair of excited states. This is done by mapping the TDDFT linear and nonlinear response functions into an effective multilevel system, yielding a complete set of approximate density matrix $\rho_{nm}^{\nu\nu'}$ that are consistent with the TDDFT response. This approach and the necessary Poisson bracket algebra and scalar product^{24,25} were developed in Refs. 26 and 27. (iv) Solve an exact self-consistent equation for $\rho^{\nu\nu'}$ and E_ν , Eqs. (C3) and (48) using the TDDFT quantities as a zero-order iteration.

The TDDFT equations of motion for the single-electron density matrix and the CEO (collective electron oscillator), quasiparticle, representation of the density matrix are reviewed in Sec. II. A corresponding classical Hamiltonian describing fluctuations in the vicinity of the ground state density matrix $\bar{\rho}$ is derived in Sec. III. The TDDFT response is then mapped onto a quantum oscillator model, and the complete set of transition density matrices is obtained in Sec. IV. An application to computing the Frenkel-exciton Hamiltonian for molecular aggregates in terms of the transition density matrices of individual molecules is made in Sec. V, and our results are discussed in Sec. VI.

II. THE TDDFT EQUATIONS

The favorable scaling of TDDFT with molecular size has made it very effective for computing electronic spectra of large molecules.^{6,28–30} Formulating the TDDFT equations for the single-electron density matrix in Liouville space (rather than for the Kohn–Sham orbitals) yields a quasiparticle, collective electronic oscillators (CEO), representation of the density response functions.³⁰ The key ingredients in this formulation are the reduced single-electron density matrices.¹⁶

Consider a molecule with N electrons, occupying Kohn–Sham orbitals $\psi_j(\mathbf{r}, t)$. The ground state density matrix is given by^{30,31}

$$\rho^{gs}(\mathbf{r}, \mathbf{r}') \equiv \bar{\rho}(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^N \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}'). \quad (2)$$

More generally, we define for every pair of electronic states ν, ν' ,

$$\rho^{\nu\nu'}(\mathbf{r}, \mathbf{r}', t) \equiv \langle \nu | \hat{\psi}^\dagger(\mathbf{r}, t) \hat{\psi}(\mathbf{r}', t) | \nu' \rangle. \quad (3)$$

Here $\hat{\psi}^\dagger$ ($\hat{\psi}$) is the creation (annihilation) field operator for an electron at \mathbf{r} .

Expanding in a single-electron basis set $\phi_n(\mathbf{r})$, we have

$$\hat{\psi}^\dagger(\mathbf{r}, t) = \sum_n \phi_n^*(\mathbf{r}) c_n^\dagger(t), \quad (4)$$

$$\hat{\psi}(\mathbf{r}, t) = \sum_n \phi_n(\mathbf{r}) c_n(t).$$

Substitution in Eq. (3) gives

$$\rho^{\nu\nu'}(\mathbf{r}, \mathbf{r}', t) = \sum_{mn} \rho_{nm}^{\nu\nu'} \phi_n^*(\mathbf{r}) \phi_m(\mathbf{r}'), \quad (5)$$

where

$$\rho_{nm}^{\nu\nu'} \equiv \langle \nu | c_n^\dagger c_m | \nu' \rangle. \quad (6)$$

Here c_n^\dagger (c_m) is the Fermi creation (annihilation) operator. $|\nu\rangle$ and $|\nu'\rangle$ represent global electronic states, whereas n and m denote the atomic basis functions. $\rho^{\nu\nu'}$ constitute a natural generalization of the ground state density matrix. $\rho^{\nu\nu}$ is the reduced single-electron density matrix of state ν . For $\nu \neq \nu'$, $\rho^{\nu\nu'}$ is the density-matrix associated with the transition between ν and ν' . These quantities carry more information than $\bar{\rho} \equiv \rho^{gs}$ (the ground state density matrix ρ^{gs} will be denoted $\bar{\rho}$ throughout this paper), yet considerably less than the complete set of many-electron eigenstates.

We start with the general electronic Hamiltonian in second quantization,^{1,31}

$$\hat{H} = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} \langle ij|kl \rangle c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{k\sigma'} c_{l\sigma} - E(t) \sum_{i,j,\sigma} \mu_{ij} c_{i\sigma}^\dagger c_{j\sigma}, \quad (7)$$

where the indices i, j, k , and l run over all basis electronic orbitals, and σ and σ' denote the spin. c_m^\dagger (c_m) is the creation (annihilation) operator for an electron at orbital m , and spin indices are omitted for brevity. These operators satisfy the Fermi commutation rules,

$$[c_m^\dagger, c_n]_+ = \delta_{mn}, \quad [c_m^\dagger, c_n^\dagger]_+ = [c_m, c_n]_+ = 0. \quad (8)$$

The single-electron matrix element, t_{ij} given by

$$t_{ij} = \int d\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m_e} + V_N(\mathbf{r}) \right) \phi_j(\mathbf{r}). \quad (9)$$

$\phi_i(\mathbf{r})$ are orthonormal spatial atomic basis functions, $V_N(\mathbf{r})$ is the nuclear potential, and

$$\langle ij|kl \rangle = e^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2) \quad (10)$$

represents the Coulomb interaction; $\langle ij|kl \rangle$ are invariant to permutations of indexes ij and kl .

The interaction between the electrons and the external electric field $E(t)$ polarized along the z axis is given by the last term in Eq. (7), where $\hat{\mu}$ is the dipole operator,

$$\mu_{ij} = \langle i | \mu_z | j \rangle \equiv \int d\mathbf{r} \phi_i^*(\mathbf{r}) z \phi_j(\mathbf{r}). \quad (11)$$

We will hereafter only consider closed-shell configurations and for brevity eliminate the spin indices.

The TDDFT equations of motion for the reduced single-electron density matrix $\hat{\rho}$ with matrix elements $\rho_{nm} \equiv \langle \Psi(t) | c_n^\dagger c_m | \Psi(t) \rangle$, where $\Psi(t)$ is the time-dependent Kohn–Sham many-electron state, are³⁰

$$i \frac{\partial \hat{\rho}}{\partial t} = [\hat{t} + \hat{V}(\hat{\rho}) - E(t) \hat{\mu}, \hat{\rho}], \quad (12)$$

where

$$\hat{V}(\hat{\rho}) = \hat{V}^f(\hat{\rho}) + \hat{V}^g(\hat{\rho}) + \hat{V}^h(\hat{\rho}), \quad (13)$$

here

$$V_{mn}^f(\hat{\rho}(t)) = \sum_{kl} \rho_{kl} \langle mk | f'_{xc}[\bar{\rho}] | nl \rangle, \quad (14)$$

$$\langle mk | f'_{xc}[\bar{\rho}] | nl \rangle = \int d\mathbf{r} \int d\mathbf{r}' \left(f_{xc}^*(\mathbf{r}, \mathbf{r}') \phi_n^*(\mathbf{r}) \phi_l(\mathbf{r}') + f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') \right) \phi_n(\mathbf{r}) \phi_l(\mathbf{r}'), \quad (15)$$

and $f_{xc}[\bar{\rho}]$ is the first-order adiabatic exchange–correlation kernel⁶

$$f_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}') = \left. \frac{\delta U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t')} \right|_{\bar{\rho}}, \quad (16)$$

$U_{xc}[\rho](\mathbf{r})$ is the TDDFT adiabatic exchange–correlation potential, and we denote $\delta\rho(\mathbf{r}', t') \equiv \delta\rho(\mathbf{r}', \mathbf{r}', t')$,

$$V_{mn}^g(\hat{\rho}\hat{\rho}) = \sum_{kl ij} \rho_{kl} \rho_{ij} \langle mki | g_{xc}[\bar{\rho}] | nlj \rangle, \quad (17)$$

where

$$\begin{aligned} \langle mki | g_{xc}[\bar{\rho}] | nlj \rangle &= \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \\ &\times \phi_m^*(\mathbf{r}) \phi_k^*(\mathbf{r}') \phi_i^*(\mathbf{r}'') \\ &\times g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'') \phi_n(\mathbf{r}) \phi_l(\mathbf{r}') \phi_j(\mathbf{r}''). \end{aligned} \quad (18)$$

$g_{xc}[\bar{\rho}]$ is the second-order adiabatic exchange–correlation kernel,⁶

$$g_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \left. \frac{\delta^2 U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t') \delta \rho(\mathbf{r}'', t'')} \right|_{\bar{\rho}}, \quad (19)$$

$$V_{mn}^h(\hat{\rho}\hat{\rho}\hat{\rho}) = \sum_{kl ij pq} \rho_{kl} \rho_{ij} \rho_{pq} \langle mkip | h_{xc}[\bar{\rho}] | nljq \rangle, \quad (20)$$

where

$$\begin{aligned} \langle mkip | h_{xc}[\bar{\rho}] | nljq \rangle &= \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \\ &\times \phi_m^*(\mathbf{r}) \phi_k^*(\mathbf{r}') \\ &\times \phi_i^*(\mathbf{r}'') \phi_p^*(\mathbf{r}''') \\ &\times h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') \phi_n(\mathbf{r}) \phi_l(\mathbf{r}') \phi_j(\mathbf{r}'') \phi_q(\mathbf{r}'''), \end{aligned} \quad (21)$$

and $h_{xc}[\bar{\rho}]$ is the third-order adiabatic exchange–correlation kernel⁶

$$h_{xc}[\bar{\rho}](\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{r}''') = \left. \frac{\delta^3 U_{xc}[\rho](\mathbf{r})}{\delta \rho(\mathbf{r}', t') \delta \rho(\mathbf{r}'', t'') \delta \rho(\mathbf{r}''', t''')} \right|_{\bar{\rho}}. \quad (22)$$

Here and below, we will label with carets matrices of dimension $K \times K$, where K is the basis set size, i.e., the number of spin–orbitals. These matrices represent spin-independent operators acting in the single-electron Hilbert space. $\hat{\rho}$ is such a matrix of rank $(\hat{\rho}) = N$, where N is the number of electrons. Since $N < K$, we can reduce the dimen-

sionality of the TDDFT equations²⁶ by introducing independent variables $\hat{\xi}$. These variables represent the particle–hole components of deviations $\delta\rho(t) = \hat{\rho}(t) - \bar{\rho}$ from the ground-state density matrix $\bar{\rho}$. $\hat{\rho}$ may then be decomposed as

$$\hat{\rho} = \bar{\rho} + \hat{\xi} + \hat{T}(\hat{\xi}), \quad (23)$$

where $\hat{T}(\hat{\xi})$ represents the particle–particle and hole–hole components

$$\hat{T}(\hat{\xi}(t)) = \left(\bar{\rho} - \frac{\hat{I}}{2} \right) (\hat{I} - \sqrt{I - 4\hat{\xi}^2(t)}), \quad (24)$$

and \hat{I} is the unit matrix. Equation (24) can be expanded in powers of $\hat{\xi}$,

$$\hat{T}(\hat{\xi}(t)) = (\hat{I} - 2\bar{\rho}) [\hat{\xi}^2(t) + \hat{\xi}^4(t) + 2\hat{\xi}^6(t) + \dots]. \quad (25)$$

Substituting Eq. (23) into Eq. (12), we obtain the closed equation of motion for $\hat{\xi}$,

$$\begin{aligned} i \frac{\partial \hat{\xi}}{\partial t} &= \mathcal{L}\hat{\xi} + [\hat{V}(\hat{\xi}), \hat{\xi} + \hat{T}(\hat{\xi})] + [\hat{V}(\hat{T}(\hat{\xi})), \bar{\rho} + \hat{\xi}] \\ &\quad - E(t)[\hat{\mu}, \hat{\rho}], \end{aligned} \quad (26)$$

where \mathcal{L} is the linearized TDDFT Liouville superoperator³⁰

$$\mathcal{L}\hat{\xi} \equiv [\hat{t}, \hat{\xi}] + [\hat{V}'(\hat{\xi}), \bar{\rho}], \quad (27)$$

Eqs. (24) and (25) form the basis for our subsequent calculations.

III. CLASSICAL HAMILTONIAN IN THE VICINITY OF $\bar{\rho}$

To establish a quasiparticle picture of electronic excitations it will be useful to recast Eq. (21) in the form of the classical Hamilton equations where the matrix elements of $\hat{\xi}$ act as classical oscillators.^{26,29} To that end we first introduce the eigenmodes of the linearized TDDFT equation for $\hat{\xi}$,

$$\mathcal{L}\hat{\xi}_\alpha = \Omega_\alpha \hat{\xi}_\alpha. \quad (28)$$

The CEO modes $\hat{\xi}_\alpha$ and the corresponding oscillator frequencies Ω_α satisfy

$$\hat{\xi}_{-\alpha} = \hat{\xi}_\alpha^\dagger, \quad \Omega_{-\alpha} = -\Omega_\alpha. \quad (29)$$

These modes are orthonormal with respect to the following scalar product:

$$\text{Tr}[\bar{\rho}[\hat{\xi}_{-\alpha}, \hat{\xi}_\beta]] = \text{sgn}(\alpha) \delta_{\alpha\beta}. \quad (30)$$

Any electron–hole density matrix $\hat{\xi}$ may be expanded using $\hat{\xi}_\alpha$ which constitute a complete set of modes

$$\hat{\xi}(t) = \sum_\alpha z_\alpha(t) \hat{\xi}_\alpha. \quad (31)$$

Here the CEO dynamical variables $z_\alpha \equiv \text{Tr}[\bar{\rho}[\hat{\xi}_{-\alpha}, \hat{\xi}]]$ satisfy $z_{-\alpha} = z_\alpha^*$ and the summation runs over both positive and negative α .

We next recast the TDDFT equations in terms of the CEO amplitudes $z_\alpha(t)$. To that end we first substitute the expansion of $\hat{\xi}$, Eq. (31) into Eq. (26), and use the orthonormality condition Eq. (30) to get

$$i \frac{\partial z_\alpha}{\partial t} = \Omega_\alpha z_\alpha + \sum_{\beta\gamma} V_{-\alpha,\beta\gamma} z_\beta z_\gamma + \sum_{\beta\gamma\delta} V_{-\alpha,\beta\gamma\delta} z_\beta z_\gamma z_\delta - E(t) \left[\mu_{-\alpha} + \sum_{\beta} \mu_{-\alpha,\beta} z_\beta + \sum_{\beta\gamma} \mu_{-\alpha,\beta\gamma} z_\beta z_\gamma \right]. \quad (32)$$

Here $V_{\alpha,\beta\gamma}$ and $V_{\alpha,\beta\gamma\delta}$ have been symmetrized with respect to all permutations of indices β, γ and β, γ, δ , respectively. These anharmonicities describe couplings among electronic oscillators mediated by Coulomb (V) and dipole (μ) interactions. All indices α, β, γ , and δ run over positive and negative modes.

The time-dependent polarization $P(t)$ is

$$P(t) = \text{Tr}(\mu \hat{\rho}(t)) = \text{Tr}(\mu \hat{\xi}(t)) + \text{Tr}(\mu \hat{T}(\hat{\xi}(t))). \quad (33)$$

Using Eqs. (24) and (31), it may be expanded in terms of the CEO amplitudes as follows:²⁷

$$P = \sum_{\alpha} \mu_{\alpha} z_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} z_{\alpha} z_{\beta} + \frac{1}{3} \sum_{\alpha\beta\gamma} \mu_{\alpha\beta\gamma} z_{\alpha} z_{\beta} z_{\gamma}. \quad (34)$$

In Eqs. (32) and (34) μ describes optical transitions between oscillators whereas V describes scattering among oscillators induced by the many-body Coulomb interactions. The anharmonic coefficients can be calculated using the ground state density matrix $\bar{\rho}$ together with the eigenmodes ξ_ν of the linearized TDHF equation. Closed expressions for all the coefficients in Eqs. (32) and (34) are given in Appendix A. In these equations we have only retained terms which contribute up to the third order optical response.³⁰ Higher order terms can be calculated similarly.

Equations (32) map the derivation of the optical response of the original many-electron system onto finding the oscillators and the nonlinear couplings μ and V . The equations of motion for the CEO amplitudes $z_\alpha(t)$, Eq. (32), are classical in the sense that they are closed nonlinear equations, in contrast with the quantum many-body equations of motion, which form a hierarchy of equations with different numbers of operators.^{12,13,32-39} The nonlinear equations of motion are closed, because in the TDDFT framework we are

working in a space of single Slater determinants which form coherent states,^{12,13,25,40,41} and the idempotent property of single Slater determinants ($\hat{\rho}^2 = \hat{\rho}$) was used for developing the CEO algebra.^{26,29,30} We can, therefore, treat z_α as classical dynamical variables, and introduce a classical Poisson bracket as a binary operation for our dynamical variables z_α which is required to satisfy the following properties: $\{z_\alpha, z_\beta\} = i \text{sgn}(\alpha) \delta_{\alpha,-\beta}$, $\{z_\alpha, z_\beta\} = -\{z_\beta, z_\alpha\}$, and $\{z_\alpha, z_\beta z_\gamma\} = \{z_\alpha, z_\beta\} z_\gamma + z_\beta \{z_\alpha, z_\gamma\}$.

Using this Poisson bracket, we can recast Eq. (32) in the form of the classical Liouville equation

$$\dot{z}_\alpha = \{H, z_\alpha\}, \quad (35)$$

with the Hamiltonian

$$H = \sum_{\alpha>0} \Omega_\alpha z_\alpha z_{-\alpha} + \frac{1}{3} \sum_{\alpha\beta\gamma} V_{\alpha\beta\gamma} z_\alpha z_\beta z_\gamma + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} z_\alpha z_\beta z_\gamma z_\delta - E(t) P, \quad (36)$$

and P is given in Eq. (34).

IV. CONSTRUCTING THE COMPLETE SET OF TDDFT DENSITY MATRICES

The system described by the classical oscillator Hamiltonian $H(z)$ [Eq. (36)] can be considered as a classical limit of a quantum boson system of oscillators.^{27,41} We require this quantum oscillator model (QOM) to have the same response functions as the original quantum TDDFT equations [Eq. (12)] for the many-electron Hamiltonian given by Eq. (7). However, the QOM is much simpler and offers a convenient exciton-like description of the original electronic system. The classical Hamiltonian Eq. (36) will be quantized by substituting each z_α and $z_{-\alpha}$ ($\alpha>0$) with creation and annihilation operators a_α and a_α^\dagger , respectively, which satisfy the boson commutation relations,

$$[a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta}. \quad (37)$$

The quantum Hamiltonian corresponding to Eq. (36), written in a normally ordered form, is

$$H_{\text{QOM}} = \sum_{\alpha>0} \Omega_\alpha a_\alpha^\dagger a_\alpha + \sum_{\alpha,\beta,\gamma>0} \left(\frac{1}{3} V_{\alpha,\beta,\gamma} a_\alpha a_\beta a_\gamma + V_{-\alpha,\beta,\gamma} a_\alpha^\dagger a_\beta a_\gamma + V_{-\alpha,-\beta,\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma + \frac{1}{3} V_{-\alpha,-\beta,-\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger \right) + \sum_{\alpha,\beta,\gamma,\delta>0} \left(\frac{1}{4} V_{\alpha,\beta,\gamma,\delta} a_\alpha a_\beta a_\gamma a_\delta + V_{-\alpha,\beta,\gamma,\delta} a_\alpha^\dagger a_\beta a_\gamma a_\delta + \frac{3}{2} V_{-\alpha,-\beta,\gamma,\delta} a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta + V_{-\alpha,-\beta,-\gamma,\delta} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger a_\delta \right) + \frac{1}{4} V_{-\alpha,-\beta,-\gamma,-\delta} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger a_\delta^\dagger - E(t) P_1(a_\alpha^\dagger, a_\alpha), \quad (38)$$

where

$$P_{\text{QOM}}(a_\alpha^\dagger, a_\alpha) = \sum_{\alpha>0} (\mu_\alpha a_\alpha + \mu_{-\alpha} a_\alpha^\dagger) + \sum_{\alpha, \beta>0} (\frac{1}{2} \mu_{\alpha, \beta} a_\alpha a_\beta + \mu_{-\alpha, \beta} a_\alpha^\dagger a_\beta + \frac{1}{2} \mu_{-\alpha, -\beta} a_\alpha^\dagger a_\beta^\dagger) + \frac{1}{2} \sum_{\alpha, \beta, \gamma>0} (\frac{1}{3} \mu_{\alpha, \beta, \gamma} a_\alpha a_\beta a_\gamma + \mu_{-\alpha, \beta, \gamma} a_\alpha^\dagger a_\beta a_\gamma + \mu_{-\alpha, -\beta, \gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma + \frac{1}{3} \mu_{-\alpha, -\beta, -\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger). \quad (39)$$

In Eq. (38) we have expanded the Kohn–Sham adiabatic exchange–correlation potential to second order in the external field $E(t)$.

The search for a multilevel system which has the same response functions as the TDDFT³⁰ will be done order by order. Higher order response functions carry gradually more information about additional states. By comparing Eq. (7) and Eqs. (38), (39) we find

$$\sum_{mn\sigma} \mu_{mn} c_{m\sigma}^\dagger c_{n\sigma} = \sum_{\alpha>0} (\mu_\alpha a_\alpha + \mu_{-\alpha} a_\alpha^\dagger) + \sum_{\alpha, \beta>0} (\frac{1}{2} \mu_{\alpha, \beta} a_\alpha a_\beta + \mu_{-\alpha, \beta} a_\alpha^\dagger a_\beta + \frac{1}{2} \mu_{-\alpha, -\beta} a_\alpha^\dagger a_\beta^\dagger). \quad (40)$$

Since Eq. (40) should hold for any μ_{mn} , and recalling the definitions of μ_α and $\mu_{\alpha\beta}$ [Eqs. (A1) and (A2)], we can write

$$\sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} = \sum_{\alpha>0} \{(\hat{\xi}_\alpha)_{mn} a_\alpha + (\hat{\xi}_\alpha^\dagger)_{mn} a_\alpha^\dagger\} + \frac{1}{2} \sum_{\alpha, \beta>0} \{([\hat{\xi}_\alpha, \bar{\rho}], \hat{\xi}_\beta)_{mn} a_\alpha a_\beta + 2([\hat{\xi}_\alpha^\dagger, \bar{\rho}], \hat{\xi}_\beta)_{mn} a_\alpha^\dagger a_\beta + ([[\hat{\xi}_\alpha^\dagger, \bar{\rho}], \hat{\xi}_\beta^\dagger])_{mn} a_\alpha^\dagger a_\beta^\dagger\}. \quad (41)$$

The QOM has an infinite number of states. We shall focus on a subgroup of *physical* states and require that the sum over states response obtained with this subgroup should coincide with the TDDFT. The remaining states of the QOM have no physical relevance and should be ignored. This approach is common in bosonization schemes.^{12,13,24,32–38}

Let us start with the effective multilevel system consistent with the linear response. The reduced single-electron transition density matrix elements involving the ground state are

$$\langle \phi^{(0)} | \sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} | \phi^{(0)} \rangle = \bar{\rho}_{mn}. \quad (42)$$

Assuming that there are M CEO modes, the TDDFT linear response $\chi^{(1)}(\omega)$ is³¹

$$\chi^{(1)}(\omega) = \sum_{\alpha=-M, \dots, M} \frac{s_\alpha \mu_{-\alpha} \mu_\alpha}{\Omega_\alpha - \omega} = \sum_{\alpha=1, \dots, M} \frac{2\Omega_\alpha |\mu_\alpha|^2}{\Omega_\alpha^2 - \omega^2}, \quad (43)$$

where $s_\alpha \equiv \text{sign}(\alpha)$. The M reduced single-electron transition density matrix elements involving the single excited states, contributing to the linear response, can be obtained from Eq. (41), using Eqs. (B1), (B2) (see Appendix B),

$$\langle \phi^{(0)} | \sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} | \phi_\alpha^{(1)} \rangle = (\hat{\xi}_\alpha)_{mn}. \quad (44)$$

Here $\phi^{(0)}$ and $\phi_\alpha^{(1)}$ represent the ground state and the single excitation of QOM α , respectively. The linear response thus gives M excited states with energies Ω_α as well as M transition elements of the density matrix Eq. (44).

We next turn to transition density matrix elements contributing to the second-order response.²⁷ We denote the binomial coefficient $C_M^K \equiv M!/K!(M-K)!$, which is a number of K permutations taken from the set of size M . From Eq. (41), using Eqs. (B1), (B2), and (B3) for the eigenstates of the quantum oscillator Hamiltonian H_{QOM} we obtain the following C_M^2 transition density matrix elements:

$$\langle \phi^{(0)} | \sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} | \phi_{\alpha\beta}^{(2)} \rangle = \frac{1}{\sqrt{1 + \delta_{\alpha\beta}}} \left[([[\hat{\xi}_\alpha, \bar{\rho}], \hat{\xi}_\beta])_{mn} + 2 \sum_{\gamma>0} \left(\frac{V_{\alpha, \beta, -\gamma}(\hat{\xi}_\gamma)_{mn}}{\Omega_\alpha + \Omega_\beta - \Omega_\gamma} - \frac{V_{\alpha, \beta, \gamma}(\hat{\xi}_\gamma^\dagger)_{mn}}{\Omega_\alpha + \Omega_\beta + \Omega_\gamma} \right) \right]. \quad (45)$$

Another group of C_M^2 transition density matrix elements,

$$\langle \phi_\alpha^{(1)} | \sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} | \phi_\beta^{(1)} \rangle = \bar{\rho}_{mn} \delta_{\alpha\beta} + ([[\hat{\xi}_\alpha^\dagger, \bar{\rho}], \hat{\xi}_\beta])_{mn} + 2 \sum_{\gamma>0} \left(\frac{V_{-\alpha, \beta, -\gamma}(\hat{\xi}_\gamma)_{mn}}{\Omega_\beta - \Omega_\alpha - \Omega_\gamma} - \frac{V_{-\alpha, \beta, \gamma}(\hat{\xi}_\gamma^\dagger)_{mn}}{\Omega_\beta - \Omega_\alpha + \Omega_\gamma} \right), \quad (46)$$

and MC_M^2 transition density matrix elements

$$\langle \phi_\alpha^{(1)} | \sum_{\sigma} c_{m\sigma}^\dagger c_{n\sigma} | \phi_{\beta\gamma}^{(2)} \rangle = \frac{1}{\sqrt{1 + \delta_{\beta\gamma}}} [(\hat{\xi}_\beta)_{mn} \delta_{\alpha\gamma} + (\hat{\xi}_\gamma)_{mn} \delta_{\alpha\beta}]. \quad (47)$$

The effective level scheme necessary to reproduce the second-order response thus consists of M single excited states and C_M^2 doubly excited states.

Taking higher-order anharmonicities into account should allow us to obtain additional density matrix elements involving new states. However, it will not affect the transition density matrix elements already obtained from lower-order responses, because those elements already reproduce the

lower-order TDDFT responses.³⁰ For example, the third-order response involves the following higher lying excitations: C_M^3 excitations with transitions $\langle \phi^{(0)} | c_m^\dagger c_n | \phi_{\alpha\beta\gamma}^{(3)} \rangle$; $M C_M^3$ excitations with transitions $\langle \phi_\alpha^{(1)} | c_m^\dagger c_n | \phi_{\beta\gamma\delta}^{(3)} \rangle$; $C_M^2 C_M^3$ excitations with transitions $\langle \phi_{\alpha\beta}^{(2)} | c_m^\dagger c_n | \phi_{\gamma\delta\zeta}^{(3)} \rangle$; $C_M^2 C_M^2$ excitations with transitions $\langle \phi_{\alpha\beta}^{(2)} | c_m^\dagger c_n | \phi_{\gamma\delta}^{(2)} \rangle$. The effective level scheme consistent with the third-order response is thus M singly excited states, C_M^2 doubly excited states, and C_M^3 triply excited states. Substituting these QOM formulas for into the sum-over-states formulas⁴² for the linear and nonlinear responses [see Eqs. (3.6) and (3.7) of Ref. 27 and Ref. 42], we recover the TDDFT response functions in the CEO representation.³⁰

TDDFT computations directly yield the density matrix elements $\rho^{g\nu}$, corresponding to the electronic transitions from the ground state to any excited state ν . All other elements between arbitrary molecular excited states $\rho^{\nu\nu'}$ may be calculated using this set of transition density matrices.²⁷ These density matrices are not exact since they are obtained at the TDDFT level which is approximate for excited states. An exact self-consistent procedure for computing the density matrices was given in Ref. 19 and is outlined in Appendix C using our notation. The resulting self-consistent equations for the density matrices are¹⁹

$$\Omega^{\nu' \nu} \rho_{ab}^{\nu' \nu} = \sum_n \hat{t}_{an} \rho_{nb}^{\nu' \nu} - \rho_{an}^{\nu' \nu} \hat{t}_{nb} + \sum_{\lambda n} [G_{an}^{\nu' \lambda} \rho_{nb}^{\lambda \nu} - \rho_{an}^{\nu' \lambda} G_{nb}^{\lambda \nu}], \quad (48)$$

where

$$G_{an}^{\nu\nu'} = \sum_{mk} (V_{mnak} - V_{mnka}) \rho_{mk}^{\nu\nu'} \quad (49)$$

the energies are given by Eq. (C3). In Eq. (48) each element $\rho^{\nu\nu'}$ is an $K \times K$ matrix where K is the basis set size. By considering the complete set of $\rho^{\nu\nu'}$ we obtain closed equations and avoid the expensive computation of higher (two electron, etc.) quantities.

The TDDFT density matrices may be used as a first iteration in solving these equations. The practical implementation of this procedure requires a truncation of the summations over excited states. This was shown in Ref. 19 to be problematic for small atoms and diatomic molecules like beryllium dimer. However, its applicability to large conjugated chromophore aggregates has not been tested yet.

V. APPLICATION TO HAMILTONIANS OF MOLECULAR AGGREGATES

We now apply the density matrices obtained in the preceding sections to calculate electronic excitations of molecular aggregates made out of spatially well separated molecules with nonoverlapping charge distributions, so that their interaction is purely Coulombic and internuclear exchange is negligible. The exchange correlation DFT functionals applicable to systems with nonoverlapping charges become complicated and nonlocal, making it very hard to compute directly the electronic excitations of the entire aggregate. Indeed, even modelling the electrostatic van der Waals interaction⁴³ be-

comes quite involved within DFT.^{44–47} Exciton Hamiltonians provide then an attractive route for computing electronic excitations. Exciton models have been widely used in the computation of optical excitations of extended molecular assemblies.^{48–55} The elementary excitations of molecular aggregate are then known as Frenkel excitons.⁵⁶ We provide an affordable *ab initio* algorithm for computing electronic excitations of aggregates by connecting the exciton models with DFT techniques. A Frenkel-exciton Hamiltonian is constructed using TDDFT calculations performed on individual chromophores.

The study of aggregates is of considerable fundamental and technological interest. Issues related to the delocalization properties of excitations such as the degree of intermolecular coherence, coherence lengths, and the collective nature have been the subject of considerable activity in molecular crystals,^{50–52} J -aggregates,^{57–59} dendrimers,^{60–63} photosynthetic complexes (antennae and reaction centers),^{43,64–69} and in supramolecular structures.⁷⁰ The design of devices based on organic materials (light emitting diodes, molecular wires, nonlinear optical switches)^{71–74} depends on the ability to compute and characterize these excitations. The modelling of these excitations poses a formidable computational challenge. While it is usually feasible to compute electronic spectra of individual chromophores in a complex using higher-level quantum-chemistry methods like the time-dependent density functional (TDDFT)^{4,6,28} or time-dependent Hartree–Fock (TDHF) techniques,^{26,43,75} the cost becomes prohibitive for large chromophore complexes.⁶⁷

We shall construct the Frenkel-exciton Hamiltonian for an aggregate⁵³ using the transition density matrices for individual chromophores obtained in Sec. IV and Appendix C. Since the overlap of electronic orbitals on different chromophores is negligible, $\langle i | j | k | l \rangle$ vanishes unless orbital i is located on the same chromophore as orbital k , and orbital j is located on the same chromophore as orbital l . It is then possible to partition \hat{H} as

$$\hat{H} = \sum_{\alpha} \hat{H}_{\alpha} + \sum_{\alpha, \beta \neq \alpha} \hat{V}_{\alpha\beta}, \quad (50)$$

where \hat{H}_{α} contains terms of \hat{H} involving only chromophore α , whereas $\hat{V}_{\alpha\beta}$ includes the terms which couple chromophore α with chromophore β .

As a first step in constructing a basis set for the many-chromophore system, we solve the single-chromophore eigenvalue problem

$$\hat{H}_{\alpha} |m^{(\alpha)}\rangle = E_m^{(\alpha)} |m^{(\alpha)}\rangle, \quad (51)$$

where $|m^{(\alpha)}\rangle$ is the m th state of the isolated chromophore α and $E_m^{(\alpha)}$ is its energy. The eigenstate $\{|g^{(\alpha)}\rangle, |1^{(\alpha)}\rangle, |2^{(\alpha)}\rangle, \dots\}$ where $|g^{(\alpha)}\rangle$ is the ground state of chromophore α and $|m^{(\alpha)}\rangle$ is its m th single excited state, then constitutes a basis for the space ν_{α} of electronic states on chromophore α . Since we have assumed that electronic orbitals on different chromophores do not overlap, the space ν of electronic states on an N -chromophore aggregate is sim-

ply the direct product of the spaces of single-chromophore electronic states, $\nu = \otimes_{\alpha=1}^N \nu_{\alpha}$, with a many-chromophore basis state

$$|m_1^{(1)}, \dots, m_N^{(N)}\rangle \equiv |m_1^{(1)}\rangle \otimes \dots \otimes |m_N^{(N)}\rangle. \quad (52)$$

In this basis, the electronic Hamiltonian \hat{H} may be written as

$$\begin{aligned} \hat{H} = & \sum_{\alpha} \sum_{\nu \in \alpha} E_{\nu}^{(\alpha)} |\nu^{(\alpha)}\rangle \langle \nu^{(\alpha)}| \\ & + \sum_{\alpha < \beta} \sum_{\substack{\nu, \lambda \in \alpha \\ \mu, \tau \in \beta}} M_{\nu\lambda\mu\tau}^{(\alpha, \beta)} (|\nu^{(\alpha)}\rangle \langle \lambda^{(\alpha)}|) (|\mu^{(\beta)}\rangle \langle \tau^{(\beta)}|), \end{aligned} \quad (53)$$

where the transition density matrix between states ν and λ of chromophore α is

$$\rho_{jl}^{\nu\lambda(\alpha)} \equiv \langle \nu^{(\alpha)} | \sum_{\sigma} c_{j\sigma}^{(\alpha)\dagger} c_{l\sigma}^{(\alpha)} | \lambda^{(\alpha)} \rangle \quad (54)$$

and the intermolecular Coulomb coupling matrix element is given by

$$\begin{aligned} M_{\nu\lambda\mu\tau}^{(\alpha, \beta)} = & \sum_{\substack{k, l \in \alpha \\ m, n \in \beta}} \langle km | ln \rangle \rho_{kl}^{\nu\lambda(\alpha)} \rho_{mn}^{\mu\tau(\beta)} \\ = & \sum_{\substack{k, l \in \alpha \\ m, n \in \beta}} \int d\mathbf{r} \int d\mathbf{r}' \phi_k^*(\mathbf{r}) \phi_m^*(\mathbf{r}') \\ & \times M_{\nu\lambda\mu\tau}^{(\alpha, \beta)}(\mathbf{r}, \mathbf{r}') \phi_l(\mathbf{r}) \phi_n(\mathbf{r}'), \end{aligned} \quad (55)$$

where $M_{\nu\lambda\mu\tau}^{(\alpha, \beta)}(\mathbf{r}, \mathbf{r}')$ is the intermolecular Coulomb coupling matrix element in real space

$$M_{\nu\lambda\mu\tau}^{(\alpha, \beta)}(\mathbf{r}, \mathbf{r}') = \frac{e^2 \rho^{\nu\lambda(\alpha)}(\mathbf{r}, \mathbf{r}) \rho^{\mu\tau(\beta)}(\mathbf{r}', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (56)$$

The first sum in Eq. (53), runs over all chromophores α and the ground and all single excited states ν on α , and the second sum includes all pairs of states ν and λ on α , and all pairs of states μ and τ on β . In Eq. (55), the sum is performed over all orbitals j on chromophore α and all orbitals l on chromophore β .

Comparing Eq. (54) with Eqs. (42) and (44) we see that for the transition density matrices involving the ground state of a chromophore, $\hat{\rho}^{g g(\alpha)} = \bar{\rho}^{(\alpha)}$, $\hat{\rho}^{g \nu(\alpha)} = \hat{\xi}_{\nu}^{(\alpha)}$, and $\hat{\rho}^{\nu g(\alpha)} = \hat{\xi}_{\nu}^{(\alpha)\dagger}$. Transition density matrices between the single excited states of the same chromophore $\hat{\rho}^{\nu\lambda(\alpha)}$ are given by Eq. (46).

We next recast the Hamiltonian (53) in a second-quantized form^{54,76} by introducing the creation and annihilation operators $B_{\nu}^{(\alpha)} = |g^{(\alpha)}\rangle \langle \nu^{(\alpha)}|$ and $B_{\nu}^{(\alpha)\dagger} = |\nu^{(\alpha)}\rangle \langle g^{(\alpha)}|$. Equation (53) then becomes

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}'. \quad (57)$$

\hat{H}_1 is a single-molecule part of a Hamiltonian,

$$\begin{aligned} \hat{H}_1 = & \sum_{\nu \in \alpha} \left(\Omega_{\nu}^{(\alpha)} - \sum_{\beta \neq \alpha} (M_{g g g g}^{(\alpha, \beta)} + N_{g g}^{(\alpha, \beta)}) \right) B_{\nu}^{(\alpha)\dagger} B_{\nu}^{(\alpha)} \\ & + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha}} M_{\nu g g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha}} M_{g \nu g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)} \\ & + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu, \lambda \in \alpha}} M_{\nu\lambda g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\lambda}^{(\alpha)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha}} N_{\nu g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} \\ & + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha}} N_{g \nu}^{(\alpha, \beta)} B_{\nu}^{(\alpha)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu, \lambda \in \alpha}} N_{\nu\lambda}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\lambda}^{(\alpha)}. \end{aligned} \quad (58)$$

The terms with $N_{\nu\lambda}^{(\alpha, \beta)}$ represent the Coulomb attraction to the nuclei of other molecules and

$$N_{\nu\lambda}^{(\alpha, \beta)} = \sum_{\substack{k, l \in \alpha \\ B \in \beta}} \int d\mathbf{r} \phi_k^*(\mathbf{r}) N_{\nu\lambda B}^{(\alpha, \beta)}(\mathbf{r}) \phi_l(\mathbf{r}), \quad (59)$$

where $N_{\nu\lambda B}^{(\alpha, \beta)}(\mathbf{r})$ is the intermolecular Coulomb electron-nuclei coupling matrix element in real space (\mathbf{r}_B is the coordinate vector of a nucleus B in a molecule β)

$$N_{\nu\lambda B}^{(\alpha, \beta)}(\mathbf{r}) = - \frac{e^2 \rho^{\nu\lambda(\alpha)}(\mathbf{r}, \mathbf{r})}{|\mathbf{r} - \mathbf{r}_B|}. \quad (60)$$

\hat{H}_2 is the intermolecular part of the Hamiltonian

$$\begin{aligned} \hat{H}_2 = & \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \tau \in \beta}} M_{\nu g g \tau}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\tau}^{(\beta)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \tau \in \beta}} M_{g \nu \tau g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)} B_{\tau}^{(\beta)\dagger} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \tau \in \beta}} M_{\nu g \tau g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\tau}^{(\beta)\dagger} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \tau \in \beta}} M_{g \nu g \tau}^{(\alpha, \beta)} B_{\nu}^{(\alpha)} B_{\tau}^{(\beta)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \mu, \tau \in \beta}} (M_{\nu g \mu \tau}^{(\alpha, \beta)} \\ & - \delta_{\mu\tau} M_{\nu g g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\mu}^{(\beta)\dagger} B_{\tau}^{(\beta)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu \in \alpha \\ \mu, \tau \in \beta}} (M_{g \nu \mu \tau}^{(\alpha, \beta)} - \delta_{\mu\tau} M_{g \nu g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)} B_{\mu}^{(\beta)\dagger} B_{\tau}^{(\beta)} + \sum_{\substack{\alpha, \beta \neq \alpha \\ \nu, \lambda \in \alpha \\ \mu, \tau \in \beta}} (M_{\nu\lambda \mu \tau}^{(\alpha, \beta)} - \delta_{\mu\tau} M_{\nu\lambda g g}^{(\alpha, \beta)} - \delta_{\nu\lambda} M_{g g \mu \tau}^{(\alpha, \beta)} \\ & + \delta_{\nu\lambda} \delta_{\mu\tau} M_{g g g g}^{(\alpha, \beta)} B_{\nu}^{(\alpha)\dagger} B_{\mu}^{(\beta)\dagger} B_{\tau}^{(\beta)} B_{\lambda}^{(\alpha)}). \end{aligned} \quad (61)$$

Finally \hat{H}' represents the interaction with the external field

$$\begin{aligned} \hat{H}' = & E(t) \sum_{\nu \in \alpha} P_{gg}^{(\alpha)} B_{\nu}^{(\alpha)\dagger} B_{\nu}^{(\alpha)} - E(t) \sum_{\nu \in \alpha} P_{\nu g}^{(\alpha)} B_{\nu}^{(\alpha)\dagger} \\ & - E(t) \sum_{\nu \in \alpha} P_{g\nu}^{(\alpha)} B_{\nu}^{(\alpha)} - E(t) \sum_{\nu, \lambda \in \alpha} P_{\nu\lambda}^{(\alpha)} B_{\nu}^{(\alpha)\dagger} B_{\lambda}^{(\alpha)} \end{aligned} \quad (62)$$

with the polarization matrix elements

$$P_{\nu\lambda}^{(\alpha)} = e \sum_{k,l \in \alpha} \int d\mathbf{r} \mathbf{r} \phi_k^*(\mathbf{r}) \rho^{\nu\lambda(\alpha)}(\mathbf{r}, \mathbf{r}) \phi_l(\mathbf{r}). \quad (63)$$

In Eqs. (58), (61), and (62), g denotes a ground state, the indices ν, λ, μ , and τ run over excited states, and $\Omega_{\nu}^{(\alpha)} \equiv E_{\nu}^{(\alpha)} - E_g^{(\alpha)}$ is the excitation energy of chromophore α . All parameters of the full Frenkel-exciton Hamiltonian may thus be obtained directly from *ab initio* computations performed on the uncoupled chromophores. This is because the coefficients $\Omega_{\nu}^{(\alpha)}$ and $M_{\nu\lambda\mu\tau}^{(\alpha,\beta)}$ depend only on individual chromophore quantities. For $M_{\nu\lambda\mu\tau}^{(\alpha,\beta)}$, this follows from Eq. (55), which relates $M_{\nu\lambda\mu\tau}^{(\alpha,\beta)}$ to the single-chromophore transition density matrix elements. A similar procedure has been employed for constructing a simpler Frenkel-exciton model for an assembly of two-level chromophores using the TDHF formalism.^{43,44} We have extended these earlier results in several ways: First we use the TDDFT rather than the TDHF. Second, we obtain all types of matrix elements of the full exciton Hamiltonian, not only the resonant exchange terms which dominate exciton transport. Third, we give explicitly the ground and single excited states of the chromophores, and outline a procedure for systematically extending the excited state space size to include all double excited, triple excited, etc., states as well as the corresponding transition density matrices.

VI. DISCUSSION

This paper provides a practical algorithm for constructing the complete set of single-electron density matrices. First, the ground-state reduced single electron density matrix $\bar{\rho}$ is derived at the DFT level.^{6,28} A set of CEO eigenmodes $\hat{\xi}_{\nu}$ and eigenfrequencies Ω_{ν} is then obtained by solving Eq. (28) where the linearized Liouville operator given in Eq. (27). It is possible to avoid direct diagonalization of the huge Liouville matrix, and obtain a few lowest-frequency modes using Krylov space techniques such as the density-matrix-spectral-moment algorithm (DSMA)³¹ or oblique Lanczos algorithms.⁷⁷ The CEO modes give the reduced single-electron transition density matrices for the transitions between the ground state and an excited state. All other transition density matrices between the single excited states of each chromophore are calculated subsequently using Eq. (46).

While the states in the QOM exciton and TDDFT are defined in a completely different space, and even their number is different, they give the same response functions. This is because the response is determined by the CEO amplitudes

$z_{\alpha}(t)$,³⁰ and, since the QOM exciton Hamiltonian Eq. (38) was derived directly from the TDDFT equation of motion Eq. (32) for $z_{\alpha}(t)$, both representations yield the same response functions. We have used the TDDFT ansatz that the electron density matrix is a single Slater determinant, whose has idempotent property ($\hat{\rho}^2 = \hat{\rho}$), allowed us to introduce the CEO representation, resulting in the closed nonlinear equation of motion Eq. (32) for the amplitudes $z_{\alpha}(t)$.

The time-dependent Hartree–Fock TDHF (also known as RPA) is an alternative, widely used, approximation for computing response functions.^{12,13,31,40,78} The present procedure can be applied to derive the transition density matrices in the TDHF approach. In that case we use for electron–electron interaction potential instead of Eq. (13). We then obtain the following matrix representation of the effective single particle Coulomb electronic operator $\hat{V}(\hat{\rho})$ in the atomic basis set $\{\phi_i(\mathbf{r})\}$:

$$V_{mn}(\hat{\rho}) = \sum_{kl} \rho_{kl} \left[\langle mk|nl \rangle - \frac{1}{2} \langle mn|kl \rangle \right], \quad (64)$$

and for the linearized Liouville superoperator we replace Eq. (27) by²⁶

$$\mathcal{L}\hat{\xi} = [\hat{t} + \hat{V}(\bar{\rho}), \hat{\xi}] + [\hat{V}(\hat{\xi}), \bar{\rho}]. \quad (65)$$

The main difference between TDDFT and TDHF equations is that in the former each order of the perturbed density matrix satisfies its own equation of motion with a different electron–electron interaction potential, because the TDDFT exchange–correlation potential, expanded in terms of exchange–correlation kernels, is different in each order. In contrast, in the TDHF the electron–electron interaction is the same for all orders.

In the adiabatic TDDFT used here^{4,6} the Liouville superoperator is the same for the responses of all orders³⁰ and the corresponding CEO excitation frequencies ω_{α} for each order coincide with the first-order excitation frequencies. The next order in the expansion of the exchange–correlation potential will result in new higher excited states compared to Eqs. (B1)–(B3), which contribute to higher-order responses (see Sec. IV), but the excitation frequencies will remain the same as long as we use the adiabatic exchange–correlation potential. Frequency-dependent (nonadiabatic) exchange–correlation potentials predict different excitation frequencies for each order of the response.²⁹ It will be interesting to use the nonlinear response for construction of new exchange correlation functionals. By mapping the nonlinear response of the actual and a reference system it should be possible to construct new exchange correlation kernels.⁷⁹ As higher-order nonlinearities are taken into account, the kernels may be improved since additional information about excited states is revealed.

The approximate TDDFT electronic density matrices are then inserted in nonlinear SCF equations whose solution should yield the exact quantities. We thus obtain an exact, yet practical generalization of the TDDFT. The closed equations for the density matrix are equivalent to constructing a density matrix functional. Starting with a set of approximate matrices $\rho^{\nu\nu'}$ obtained by mapping the TDDFT response

functions into a set of states,^{26,27} Eqs. (C3) and (48) can be solved iteratively for E_ν and $\rho^{\nu\nu'}$. The TDDFT $\rho^{\nu\nu'}$ and E_ν may be substituted in the nonlinear parts of these equations to generate a new set of $\rho^{\nu\nu'}$. These can then be used to compute E_ν and the procedure is repeated until satisfactory convergence is achieved. It is reasonable to expect that the summations over ν' and λ may be truncated since high energy states should make a negligible contribution to lower states. Such truncations could provide a low cost self-consistent systematic hierarchy of approximations for the energies as well as the ground state, excited state and transition density matrices. Even though in earlier applications to small atoms the truncations were not very accurate,¹⁹ they may work for large conjugated systems.

Since the dipole is a single-body operator, the density matrices contain all the necessary information for computing the optical response to arbitrary order in external field.²⁶ Furthermore, the real space description of the density matrix allows to make use of the finite coherence size and only retain elements ρ_{nm} with n and m centered at sufficiently close atoms. This will greatly reduce memory requirements and ultimately gives an N scaling of numerical effort.^{22,23} Ordinarily, the many-body hierarchy is closed approximately

by factorizing some N electron quantity into lower order products. In contrast, the closure of the hierarchy [Eqs. (48) and (49)] is exact, provided we include the complete family of density matrices $\rho^{\nu\nu'}$ for all $\nu\nu'$.

Section V shows how to construct a Frenkel-exciton Hamiltonian for molecular aggregates using the transition density matrices of isolated chromophores and the two-electron Coulomb integrals. We derive the intermolecular coupling coefficients $M_{\nu\lambda,\mu\tau}^{(\alpha,\beta)}$ which together with the transition frequencies $\Omega_\nu^{(\alpha)}$, define the form Frenkel-exciton Hamiltonian Eq. (57).

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APPENDIX A: PARAMETERS FOR THE COLLECTIVE ELECTRONIC OSCILLATOR EQUATIONS OF MOTION

The parameters of Eq. (32) are^{30,31}

$$\mu_\alpha = \text{Tr}([\bar{\rho}, \xi_\alpha][\mu, \bar{\rho}]) = \text{Tr}(\mu \xi_\alpha), \quad (\text{A1})$$

$$\mu_{\alpha\beta} = \text{Tr}([\bar{\rho}, \xi_\alpha][\mu, \xi_\beta]) = \text{Tr}(\mu(I - 2\bar{\rho})(\xi_\alpha \xi_\beta + \xi_\beta \xi_\alpha)), \quad (\text{A2})$$

$$\mu_{\alpha,\beta\gamma} = \text{Tr}([\bar{\rho}, \xi_\alpha][\mu, \frac{1}{2}[[\xi_\beta, \bar{\rho}], \xi_\gamma]]) = -\frac{1}{2} \text{Tr}((\mu \xi_\alpha + \xi_\alpha \mu)(\xi_\beta \xi_\gamma + \xi_\gamma \xi_\beta)), \quad (\text{A3})$$

$$V_{\alpha,\beta\gamma} = \frac{1}{2!} \sum_{\beta\gamma}^{\text{perm}} (\text{Tr}([\bar{\rho}, \xi_\alpha][V^{fg}(\xi_\beta), \xi_\gamma]) + \text{Tr}([\bar{\rho}, \xi_\alpha][V^{fg}(\frac{1}{2}[[\xi_\beta, \bar{\rho}], \xi_\gamma]), \bar{\rho}])) \\ = \frac{1}{2} \text{Tr}((I - 2\bar{\rho}) \times ((\xi_\beta \xi_\gamma + \xi_\gamma \xi_\beta) V^{fg}(\xi_\alpha) + (\xi_\alpha \xi_\beta + \xi_\beta \xi_\alpha) V^{fg}(\xi_\gamma) + (\xi_\alpha \xi_\gamma + \xi_\gamma \xi_\alpha) V^{fg}(\xi_\beta))), \quad (\text{A4})$$

$$V_{\alpha,\beta\gamma\delta} = \frac{1}{3!} \sum_{\beta\gamma\delta}^{\text{perm}} (\text{Tr}([\bar{\rho}, \xi_\alpha][V(\frac{1}{2}[[\xi_\beta, \bar{\rho}], \xi_\gamma]), \xi_\delta]) + \text{Tr}([\bar{\rho}, \xi_\alpha][V(\xi_\delta), \frac{1}{2}[[\xi_\beta, \bar{\rho}], \xi_\delta]])) \\ = \frac{1}{6} \text{Tr}((I - 2\bar{\rho})(\xi_\alpha \xi_\delta + \xi_\delta \xi_\alpha) V((I - 2\bar{\rho})(\xi_\beta \xi_\gamma + \xi_\gamma \xi_\beta))) + \frac{1}{6} \text{Tr}((I - 2\bar{\rho})(\xi_\alpha \xi_\gamma + \xi_\gamma \xi_\alpha) V((I - 2\bar{\rho})(\xi_\delta \xi_\beta + \xi_\beta \xi_\delta))) \\ + \frac{1}{6} \text{Tr}((I - 2\bar{\rho})(\xi_\alpha \xi_\beta + \xi_\beta \xi_\alpha) V((I - 2\bar{\rho})(\xi_\delta \xi_\alpha + \xi_\gamma \xi_\delta))) - \frac{1}{6} \text{Tr}((\xi_\alpha V(\xi_\beta) + V(\xi_\beta) \xi_\alpha)(\xi_\gamma \xi_\delta + \xi_\delta \xi_\gamma)) \\ - \frac{1}{6} \text{Tr}((\xi_\alpha V(\xi_\gamma) + V(\xi_\gamma) \xi_\alpha)(\xi_\beta \xi_\delta + \xi_\delta \xi_\beta)) - \frac{1}{6} \text{Tr}((\xi_\alpha V(\xi_\beta) + V(\xi_\beta) \xi_\alpha)(\xi_\beta \xi_\gamma + \xi_\gamma \xi_\beta)), \quad (\text{A5})$$

where $V^{fg} = V^f + V^g$.

APPENDIX B: THE QUANTUM-OSCILLATOR EXCITATIONS

Here we calculate the ground, single excited, and double excited eigenstates of the QOM [$E(t) = 0$] to first order in $V_{\alpha\beta\gamma}$. We use first-order perturbation theory in the Kohn-Sham exchange-correlation potential V , using only the terms of the exciton Hamiltonian Eq. (38), which result in getting the same second-order response as can be obtained for the CEO system^{27,30} (see Sec. III):

$$|\phi^{(0)}\rangle = \left[1 - \frac{1}{3} \sum_{\alpha,\beta,\gamma>0} \frac{V_{-\alpha,-\beta,-\gamma}}{\Omega_\alpha + \Omega_\beta + \Omega_\gamma} a_\alpha^\dagger a_\beta^\dagger a_\gamma^\dagger \right] |g_0\rangle, \quad (\text{B1})$$

$$|\phi_{\alpha}^{(1)}\rangle = \left[a_{\alpha}^{\dagger} + \sum_{\beta, \gamma > 0} \frac{V_{-\beta, -\gamma, \alpha}}{\Omega_{\alpha} - \Omega_{\beta} - \Omega_{\gamma}} a_{\beta}^{\dagger} a_{\gamma}^{\dagger} - \frac{1}{3} \sum_{\beta, \gamma, \delta > 0} \frac{V_{-\beta, -\gamma, -\delta}}{\Omega_{\beta} + \Omega_{\gamma} + \Omega_{\delta}} a_{\beta}^{\dagger} a_{\gamma}^{\dagger} a_{\delta}^{\dagger} \right] |g_0\rangle, \quad (\text{B2})$$

$$|\phi_{\alpha\beta}^{(2)}\rangle = \frac{1}{\sqrt{1 + \delta_{\alpha\beta}}} \left[a_{\alpha}^{\dagger} a_{\beta}^{\dagger} - \sum_{\gamma > 0} \frac{2V_{-\gamma, \alpha, \beta}}{\Omega_{\gamma} - \Omega_{\alpha} - \Omega_{\beta}} a_{\gamma}^{\dagger} - \sum_{\gamma, \delta > 0} \left(\frac{V_{-\gamma, -\delta, \beta} a_{\alpha}^{\dagger}}{\Omega_{\beta} - \Omega_{\gamma} - \Omega_{\delta}} + \frac{V_{-\gamma, -\delta, \alpha} a_{\beta}^{\dagger}}{\Omega_{\alpha} - \Omega_{\gamma} - \Omega_{\delta}} \right) a_{\gamma}^{\dagger} a_{\delta}^{\dagger} - \frac{1}{3} \sum_{\gamma, \delta, \eta > 0} \frac{V_{-\gamma, -\delta, -\eta}}{\Omega_{\gamma} + \Omega_{\delta} + \Omega_{\eta}} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\gamma}^{\dagger} a_{\delta}^{\dagger} a_{\eta}^{\dagger} \right] |g_0\rangle. \quad (\text{B3})$$

Here $|g_0\rangle$ is the ground state of the uncoupled system (with $V_{\alpha\beta\gamma} = 0$). All the eigenstates $|\phi^{(0)}\rangle$, $|\phi_{\alpha}^{(1)}\rangle$, and $|\phi_{\alpha\beta}^{(2)}\rangle$ are normalized. Note that $|\phi_{\alpha\beta}^{(2)}\rangle$ and $|\phi_{\beta\alpha}^{(2)}\rangle$ represent the same state, so we can restrict the indices in $|\phi_{\alpha\beta}^{(2)}\rangle$ by the condition $\alpha \leq \beta$. Equations (B1), (B2), and (B3) can be verified by directly substituting those expressions into the eigenvalue problems

$$H_1 |\phi^{(0)}\rangle = 0, \quad (\text{B4})$$

$$H_1 |\phi_{\alpha}^{(1)}\rangle = \Omega_{\alpha} |\phi_{\alpha}^{(1)}\rangle, \quad (\text{B5})$$

$$H_1 |\phi_{\alpha\beta}^{(2)}\rangle = (\Omega_{\alpha} + \Omega_{\beta}) |\phi_{\alpha\beta}^{(2)}\rangle. \quad (\text{B6})$$

APPENDIX C: SELF-CONSISTENT EQUATIONS FOR THE DENSITY MATRICES

In this Appendix we briefly summarize the derivation of the self-consistent density matrix equations following Ref. 19, using our notation.

Using the commutation relations [Eq. (8)] we can represent the Hamiltonian Eq. (10) in the form¹⁹

$$H = \sum_{mn} t'_{mn} \hat{\rho}_{mn} - \sum_{mnl} V_{mnl} \hat{\rho}_{mk} \hat{\rho}_{nl}. \quad (\text{C1})$$

Here $V_{ijkl} \equiv \langle ij | kl \rangle$ and

$$t'_{mn} \equiv t_{mn} + \sum_k V_{mkn}, \quad (\text{C2})$$

is the renormalized single-body part. We further denote the many-electron wave function $|\nu\rangle$ (where $|g\rangle$ is the ground state). Taking the $\nu\nu$ matrix element of Eq. (C1) gives the first group of self-consistent equations for $\rho^{\nu\nu}$

$$\sum_{mn} t'_{mn} \rho_{mn}^{\nu\nu} = E_{\nu} + \sum_{mnl\nu'} V_{mnl} \rho_{mk}^{\nu\nu'} \rho_{nl}^{\nu'\nu}. \quad (\text{C3})$$

Here $\rho_{mk}^{\nu\nu'} \equiv \langle \nu | \hat{\rho}_{mk} | \nu' \rangle$. These equations are not closed since the rhs depends on the transition density matrices $\rho^{\nu'\nu}$ with $\nu \neq \nu'$. To derive equations for the latter quantities we start with the Heisenberg equation for $\hat{\rho}_{ab}$,

$$\dot{\hat{\rho}}_{ab} = \frac{-i}{\hbar} [H, \hat{\rho}_{ab}]. \quad (\text{C4})$$

Using the commutation relations it is possible to recast the rhs in the form of products of $\hat{\rho}_{mn}$ operators in the same way we obtained Eq. (6) from Eq. (2). This gives

$$\dot{\hat{\rho}} = \frac{-i}{\hbar} [\hat{t}, \hat{\rho}] - \frac{i}{\hbar} [\hat{G}(\hat{\rho}), \hat{\rho}], \quad (\text{C5})$$

where

$$\hat{t}_{am} = t_{ma} + \sum_k V_{mkka} - \sum_l V_{mlal}, \quad (\text{C6})$$

$$\hat{G}_{an}(\hat{\rho}) = \sum_{mk} (V_{mnak} - V_{mnka}) \hat{\rho}_{mk}. \quad (\text{C7})$$

These equations can be readily closed by expanding them in the exact eigenstates ν' , ν . Note that $\langle \nu' | \hat{\rho} | \nu \rangle = -i\Omega_{\nu'\nu} \hat{\rho}_{\nu'\nu}$ and $\Omega_{\nu'\nu} \equiv E_{\nu'} - E_{\nu}$. Equation (C5) then assumes the form

$$\Omega^{\nu'\nu} \hat{\rho}^{\nu'\nu} = \langle \nu' | [\hat{t}, \hat{\rho}] | \nu \rangle + \langle \nu' | [\hat{G}(\hat{\rho}), \hat{\rho}] | \nu \rangle. \quad (\text{C8})$$

Taking matrix elements of Eq. (C8) results in Eqs. (48) and (49).

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