

Real-space coupled-oscillator approach to the radiative decay of conjugated polymers

M. Hartmann, V. Chernyak, and S. Mukamel

Department of Chemistry, University of Rochester, Rochester, New York 14627

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The optical response of conjugated polymers is calculated using a one-dimensional tight-binding model with Coulomb interactions, and adopting the multipolar form for the electromagnetic field Hamiltonian. By formulating the problem using the reduced single-electron density matrix and its evolution in Liouville space, we obtain a real-space description for the elementary electronic excitations. A unified expression for the linear response including radiative decay, which is valid for arbitrary chain size compared with the optical wavelength, is described. For small sizes it shows exciton confinement effects on the radiative decay and for larger sizes it fully incorporates polariton effects.

I. INTRODUCTION

The linear and nonlinear optical properties of conjugated molecules and polymers are currently drawing considerable attention.¹⁻⁸ Their strong off-resonant optical nonlinearities make them ideal candidates for device applications. In addition, these materials possess rather complicated electronic properties that show up in resonant optical measurements. Since polymers are one-dimensional structures with delocalized electronic states, strong Coulomb interactions and electron correlations dominate their optical properties.^{7,9} Conjugated polymers are semiconductorlike materials, which have unique electronic properties, since the Coulomb coupling and correlation effects are very large compared to semiconductors. Consequently, the two-band approximation, based on neglecting all processes which do not conserve the number of electrons and holes, and which works well for undoped semiconductors,¹⁰ cannot be applied for these systems. By studying oligomers of different length, one can address the interplay of different coherent sizes, which are responsible for interesting scaling behavior of the linear absorption and cooperative radiative decay.

Since optical response involves a large number of eigenstates of the interacting many-body system, and since the optical field interacts with the charge density, it is much more natural to think about the optical response in terms of the motion of the charge density in real space rather than using properties of individual eigenstates.⁴ Such a theoretical approach is the Green-function technique¹¹ or its simplified version based on the reduced density matrix.⁴

In this paper, we study the linear absorption and the radiative decay of conjugated polymers and oligomers.¹²⁻¹⁵ The factors affecting the fluorescence quantum yield¹⁶⁻¹⁸ are of considerable current interest, in particular, due to recent electroluminescence studies of large conjugated systems and multilayer structures.

In Sec. II, we start with a tight-binding model, the Pariser-Parr-Pople (PPP) Hamiltonian by invoking the time-dependent Hartree-Fock (TDHF) approximation,^{19,20} the optical response and the radiative decay are described using the evolution of the reduced (single-

electron) density matrix in the real space. The TDHF method takes into account approximately some effects of electron correlations both for the ground state and for the excited states, and enables us to compute the optical response directly from the dynamics of the charges. The eigenmodes of the linearized TDHF equation describe the resonant structure of the optical response, and suggest a real-space physical picture in terms of coupled nonlocal harmonic oscillators as an alternative to the conventional description in terms of global molecular eigenstates. In addition, these modes can be used as a starting point for incorporating higher-order electron correlations. In Sec. III, we apply the general formalism to the radiative decay of conjugated polymers. Numerical results are presented in Sec. IV and discussed in Sec. V.

II. GENERAL FORMALISM

We consider an electronic system described by a one-dimensional nearest-neighbor tight-binding Hamiltonian with electron-electron interaction,

$$\hat{H}_0 = \sum_{n,m} \sum_{\sigma} t_{nm} \hat{\rho}_{nm,\sigma} + \frac{1}{2} \sum_{nmkl} \sum_{\sigma,\sigma'} V_{nmkl} \hat{\rho}_{nl,\sigma} \hat{\rho}_{m,k\sigma'} \quad (1)$$

Here, the density-matrix operator $\hat{\rho}_{nm,\sigma}$ is given by

$$\hat{\rho}_{nm,\sigma} = \hat{c}_{n,\sigma}^\dagger \hat{c}_{m,\sigma} \quad (2)$$

where $\hat{c}_{n,\sigma}^\dagger$ ($\hat{c}_{n,\sigma}$) denotes the creation (annihilation) operator of an electron at the n th orbital with spin σ . These operators obey the Fermi commutation rules $[\hat{c}_{n,\sigma}^\dagger, \hat{c}_{m,\sigma'}]_+ = \delta_{n,m} \delta_{\sigma,\sigma'}$, and all other anticommutators vanish. t_{nm} denotes the hopping matrix elements, and the Coulomb interaction matrix elements read

$$V_{nmkl} \equiv \int d\mathbf{r} \int d\mathbf{r}' \Psi_n^*(\mathbf{r}) \Psi_m^*(\mathbf{r}') \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \Psi_k(\mathbf{r}') \Psi_l(\mathbf{r}) \quad (3)$$

where Ψ_n are the atomic wave functions. This Hamiltonian with a specific parametrized form for V [see Eq. (38)] is known as the PPP Hamiltonian. The properties of this Hamiltonian have been studied extensively using

various methods, and exact numerical calculations of the eigenstates have been reported for small chains.^{4,8,9}

The interaction of the radiation field with the system in the Coulomb gauge and the multipolar form (neglecting magnetic terms) is

$$\hat{H}_{\text{int}} = \int d\mathbf{r} \hat{\mathbf{P}}(\mathbf{r}, t) \cdot \hat{\mathbf{D}}(\mathbf{r}, t) + 2\pi \int d\mathbf{r} |\hat{\mathbf{P}}(\mathbf{r}, t)|^2, \quad (4)$$

where $\hat{\mathbf{D}}(\mathbf{r})$ is the electric displacement field [$\nabla \cdot \hat{\mathbf{D}}(\mathbf{r}) = 0$], which is related to the transverse electromagnetic field $\hat{\mathbf{E}}(\mathbf{r})$ by

$$\hat{\mathbf{E}}(\mathbf{r}, t) \equiv \hat{\mathbf{D}}(\mathbf{r}, t) - 4\pi \hat{\mathbf{P}}(\mathbf{r}, t). \quad (5)$$

Note that $\hat{\mathbf{E}}(\mathbf{r}, t)$ and $\hat{\mathbf{D}}(\mathbf{r}, t)$ are defined to be purely transverse. This multipolar form can be obtained by performing a gauge transformation on the more conventional minimal coupling ($\hat{\mathbf{p}} \cdot \hat{\mathbf{A}}$) Hamiltonian.²¹ It has several advantages for calculating linear and nonlinear optical properties.^{22,23} It focuses on the field rather than on the vector potential, and local field and semiclassical approximations are then easier to implement. It also provides a convenient way to incorporate polariton effects and spontaneous emission. Finally, the polarization operator is given by

$$\hat{\mathbf{P}}(\mathbf{r}, t) = \sum_{\sigma} \sum_{n, m} \mu_{nm}(\mathbf{r}) \hat{\rho}_{nm, \sigma}(t), \quad (6)$$

where the dipole density is

$$\mu_{nm}(\mathbf{r}) = \int_0^1 d\lambda \int d\mathbf{r}' \Psi_n^*(\mathbf{r}') e^{i\lambda \mathbf{r} \cdot \mathbf{r}'} \Psi_m(\mathbf{r}') \delta(\mathbf{r} - \lambda \mathbf{r}'). \quad (7)$$

Here, the origin $\mathbf{r} = 0$ is an arbitrary reference point. Note that we have not invoked the dipole approximation; Eq. (6) allows us to model an arbitrary system as a continuous distribution of dipoles, and the λ integration ensures the correct coefficients of the entire multipolar expansion of the polarization operator if we choose to make such an expansion. The dipole approximation simply implies replacing this distribution by a single dipole. In conventional treatments of semiconductors,²⁴ the dipole approximation is made from the outset.

The dynamics of the optically driven system can be obtained by considering the density matrix,

$$\rho_{nm, \sigma}(t) \equiv \text{Tr}[W_0 \hat{\rho}_{nm, \sigma}(t)] \equiv \langle \hat{\rho}_{nm, \sigma}(t) \rangle, \quad (8)$$

where W_0 is the density operator of the initial state. Using the Heisenberg equation and Eqs. (1) and (4), we obtain the equation of motion for the density matrix,

$$i\hbar \frac{\partial}{\partial t} \rho_{nn', \sigma}(t) = \sum_m [h_{nm, \sigma}(t) \rho_{mn', \sigma}(t) - \rho_{nm, \sigma}(t) h_{mn', \sigma}(t)] \\ + \sum_m [\rho_{nm, \sigma}(t) E_{mn'}(t) - E_{nm}(t) \rho_{mn', \sigma}(t)]. \quad (9)$$

Here, the kernel $h_{nm, \sigma}$ is given by

$$h_{nm, \sigma}(t) = t_{nm} + \sum_{kl, \sigma'} V_{nkml} \rho_{lk, \sigma'}(t) - \sum_{kl} V_{nlmk} \rho_{kl, \sigma}(t), \quad (10)$$

and we have defined

$$E_{nm}(t) \equiv \int d\mathbf{r} \mu_{nm}(\mathbf{r}) \langle \hat{\mathbf{E}}(\mathbf{r}, t) \rangle. \quad (11)$$

To obtain Eq. (9), we have used the Hartree-Fock approximation to truncate higher-order correlation functions,

$$\langle \hat{\rho}_{nm} \hat{\rho}_{kl} \rangle = \delta_{mk} \rho_{nl} + \rho_{nl} \rho_{mk} - \rho_{nm} \rho_{kl}, \quad (12)$$

and in the last sum of Eq. (9), we have treated the Maxwell field $\hat{\mathbf{E}}(\mathbf{r}, t)$ classically. The linear response of the system can now be calculated by diagonalizing Eq. (9) and linearizing with respect to the Maxwell field E_{nm} . Since Eq. (9) does not contain relaxation processes, it yields sharp resonances at the excitonic transition frequencies. We will now show that radiative decay can be incorporated by defining the linear response, with respect to the external field E_{nm}^{ex} rather than the Maxwell field E_{nm} . Consider the solution of the Maxwell equation,

$$\hat{\mathbf{E}}(\mathbf{r}, t) = \mathbf{E}^{\text{ex}}(\mathbf{r}, t) + \int dt' d\mathbf{r}' \mathcal{G}(\mathbf{r} - \mathbf{r}', t - t') \hat{\mathbf{P}}(\mathbf{r}', t'), \quad (13)$$

where $\mathbf{E}^{\text{ex}}(\mathbf{r}, t)$ represents the external field, and $\mathcal{G}(\mathbf{r} - \mathbf{r}', t - t')$ is the Green function of the transverse electromagnetic field in vacuum, with the tensor components,

$$\mathcal{G}_{ij}(\mathbf{r} - \mathbf{r}', t - t') = \int \frac{d\omega}{2\pi} \frac{d\mathbf{k}}{(2\pi)^3} \\ \times \mathcal{G}_{ij}(\mathbf{k}, \omega) e^{i[\mathbf{k}(\mathbf{r} - \mathbf{r}') - \omega(t - t')]}, \quad (14)$$

$$\mathcal{G}_{ij}(\mathbf{k}, \omega) = \frac{4\pi\omega^2}{\omega^2 - k^2 c^2} \left[\delta_{ij} - \frac{k_i k_j}{k^2} \right]. \quad (15)$$

From Eq. (11), we obtain

$$E_{nm}(t) = E_{nm}^{\text{ex}}(t) + \int dt' \sum_{lk} \sum_{\sigma} \mathcal{D}_{nm lk}^0(t - t') \rho_{lk, \sigma}(t'), \quad (16)$$

where

$$\mathcal{D}_{nm lk}^0(t - t') = \int d\mathbf{r} d\mathbf{r}' \mu_{nm}(\mathbf{r}) \mathcal{G}(\mathbf{r} - \mathbf{r}', t - t') \mu_{lk}(\mathbf{r}'). \quad (17)$$

Putting Eq. (16) into Eq. (9), transforming to the frequency domain, considering the spin symmetric situation $\rho_{nm, \uparrow} = \rho_{nm, \downarrow}$, and linearizing with respect to E_{nm}^{ex} , we obtain the equation

$$\hbar\omega \rho_{nm}(\omega) - \sum_{lk} A_{nm, lk}(\omega) \rho_{lk}(\omega) \\ + i \sum_{lk} \Gamma_{nm, lk}(\omega) \rho_{lk}(\omega) = F_{nm}(\omega), \quad (18)$$

where the tetradic $N^2 \times N^2$ matrices A and Γ , and the dyadic $N \times N$ matrix F are given by

$$A_{nn',lk}(\omega) = \sum_m \{ t_{nm} \delta_{lm} \delta_{kn'} - t_{mn} \delta_{ln} \delta_{km} - \sum_{k'l'} [(2V_{nk'l'm} - V_{nk'm'l'}) \delta_{lm} \delta_{kn'} - (2V_{mk'l'n'} - V_{mk'n'l'}) \delta_{ln} \delta_{km}] \bar{\rho}_{l'k'} + \bar{\rho}_{nm} [2V_{mkl'n'} - V_{mkn'l}] - [2V_{nkml} - V_{nkml}] \bar{\rho}_{mn} \}, \quad (19)$$

$$\Gamma_{nn',lk}(\omega) = \text{Im} \left\{ \sum_m [\mathcal{D}_{nmkl}^0(\omega) \bar{\rho}_{mn'} - \bar{\rho}_{nm} \mathcal{D}_{mn'lk}^0(\omega)] \right\}, \quad (20)$$

$$F_{nn'}(\omega) = \sum_m [\bar{\rho}_{nm} E_{mn'}^{\text{ex}}(\omega) - E_{nm}^{\text{ex}}(\omega) \bar{\rho}_{mn'}]. \quad (21)$$

Here, the zeroth-order density matrix $\bar{\rho}_{nm}$ is calculated from the stationary Hartree-Fock equation,

$$\frac{\partial}{\partial t} \bar{\rho}_{nm}(t) = 0. \quad (22)$$

As can be seen from Eq. (18) and will become more clear below, the excitonic resonances are now broadened by radiative decay, which is contained in the matrix $\Gamma_{nn',lk}$. The matrix A can be diagonalized using a tetradic (Liouville space) transformation, matrix \mathcal{S} ,

$$\sum_{nm,kl} \mathcal{S}_{\alpha,nm}^{-1} A_{nm,kl} \mathcal{S}_{kl,\alpha'} = \varepsilon_{\alpha} \delta_{\alpha\alpha'}, \quad (23)$$

or in matrix form

$$\mathcal{S}^{-1} A \mathcal{S} = \varepsilon I. \quad (24)$$

The resulting eigenmodes (labeled α) are normalized as

$$\sum_{nm} \bar{\rho}_{nm} (\mathcal{S}_{mm',\alpha}^* \mathcal{S}_{nm',\alpha} - \mathcal{S}_{m',\alpha} \mathcal{S}_{m',n,\alpha}^*) = 1, \quad \alpha > 0. \quad (25)$$

Note that since the Liouville space matrix A is not Hermitian, \mathcal{S} is not unitary, and $\mathcal{S}^{\dagger} \neq \mathcal{S}^{-1}$. The nonhermiticity of the operator A is the consequence of the fact that we include processes which do not conserve the number of electron-hole pairs, i.e., that we go beyond the two-band model. The solution of Eq. (18) then assumes the form (see Appendix A)

$$\rho_{nm}(\omega) = \sum_{\alpha} \sum_{kl} \frac{\mathcal{S}_{nm,\alpha} \mathcal{S}_{\alpha,kl}^{-1} F_{kl}(\omega)}{\hbar\omega - \varepsilon_{\alpha} + i\Gamma_{\alpha}(\omega)}, \quad (26)$$

and the radiative damping Γ becomes (see Appendix B)

$$\Gamma_{\alpha}(\omega) = \sum_{nm,kl} \mathcal{S}_{nm,\alpha}^* \text{Im}(\mathcal{D}_{nm,kl}^0(\omega)) \mathcal{S}_{kl,\alpha}, \quad (27)$$

We now define the linear-response function $\chi(\mathbf{r}, \mathbf{r}')$ as

$$P(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; \omega) E^{\text{ex}}(\mathbf{r}', \omega). \quad (28)$$

Combining Eqs. (6) and (26), we obtain

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\alpha > 0} \left\{ \frac{\mu_{\alpha}(\mathbf{r}) \mu_{\alpha}^*(\mathbf{r}')}{\hbar\omega - \varepsilon_{\alpha} + i\Gamma_{\alpha}(\omega)} - \frac{\mu_{\alpha}^*(\mathbf{r}) \mu_{\alpha}(\mathbf{r}')}{\hbar\omega + \varepsilon_{\alpha} + i\Gamma_{\alpha}(\omega)} \right\}, \quad (29)$$

where $\sum_{\alpha > 0}$ means summation over "physical" (particle-hole) modes with $\varepsilon_{\alpha} > 0$. The dipole moment density μ_{α} is defined as [see Eq. (B12)]

$$\mu_{\alpha}(\mathbf{r}) = \sum_{mn} \mu_{mn}(\mathbf{r}) \mathcal{S}_{mn,\alpha}. \quad (30)$$

Integrating Eq. (29) over space (\mathbf{r} and \mathbf{r}'), and using the sum rule²⁵

$$\frac{m_0}{e^2} \lim_{\omega \rightarrow \infty} \omega^2 \chi(\omega) = N. \quad (31)$$

We find that the oscillator strength

$$f_{\alpha} \equiv \frac{2m_0 \varepsilon_{\alpha}}{e^2 \hbar^2} |\mu_{\alpha}|^2, \quad (32)$$

where the dipole moment is

$$\mu_{\alpha} \equiv \int d\mathbf{r} \mu_{\alpha}(\mathbf{r}), \quad (33)$$

satisfies the Thomas-Reiche-Kuhn sum rule,

$$\sum_{\alpha} f_{\alpha} = N, \quad (34)$$

where N is the number of electrons.

Equation (29) together with Eqs. (30) and (27) is our final result for the linear-response function. This result is very general, and holds regardless of the nature of the material (molecular, semiconductor, or metallic). Moreover, since we have not made the dipole approximation, it applies to systems of arbitrary size (small clusters, nanostructures, as well as bulk materials). In the derivation of Eq. (29), we assumed that the eigenvalues ε_{α} of the matrix A are well separated compared with their widths Γ_{α} . This allowed us to diagonalize the matrix A and treat Γ perturbatively. When this is not the case, we need to calculate the eigenstates of $A + i\Gamma$; the final formal results remain, however, very similar. Finally, we note that our eigenvalue problem requires the diagonalization of an $N^2 \times N^2$ matrix A . This implies that the calculation is done in Liouville space rather than Hilbert space.^{26,27} The need to work in Liouville space is highlighted if we recast Eq. (19) in the form $A = A^{(0)} + A^{(1)}$. A has one part $A^{(0)}$,

$$A_{nn',lk}^{(0)}(\omega) = \sum_m \left\{ t_{nm} \delta_{lm} \delta_{kn'} - t_{mn} \delta_{ln} \delta_{km} - \sum_{k'l'} [(2V_{nk'l'm} - V_{nk'm'l'}) \delta_{lm} \delta_{kn'} - (2V_{mk'l'n'} - V_{mk'n'l'}) \delta_{ln} \delta_{km}] \bar{\rho}_{l'k'} \right\}, \quad (35)$$

that can be written as a commutator, and another part $A^{(1)}$,

$$A_{nn',lk}^{(1)}(\omega) = \sum_m \{ \bar{\rho}_{nm} [2V_{mkin'} - V_{mkn'l}] - [2V_{nklm} - V_{nkml}] \bar{\rho}_{mn'} \}, \quad (36)$$

that cannot be written in this form. It is the latter part, that originates from the Fock operator linear in the field that makes it essential to work in Liouville space. $A^{(0)}$ could be diagonalized in Hilbert space using $N \times N$ matrices. Physically, Liouville space is most natural for the description of electrodynamics and optical response, since excited states involve the creation of at least two particles (an electron and a hole), and their correlated dynamics is treated explicitly in Liouville space.

III. APPLICATION TO RADIATIVE DECAY OF CONJUGATED POLYMERS

As is common in the description of conjugated polymers, we focus on the π electrons, which are confined to a periodic chain of atoms formed by the σ electrons, and consider the half filled band case (one electron per atom). These materials (e.g., Polyacetylene, Polydiacetylene, PPV, etc.) are usually described using the Pariser-Parr-Pople Hamiltonian,^{28,29} which can be obtained from Eq. (1) by specifying the matrix elements of the hopping integrals, the Coulomb interaction, and the dipole moment,

$$t_{nm} = \begin{cases} \beta + \beta'(u_n - u_{n+1}), & m = n + 1 \\ -\sum_l V_{nl}, & n = m \\ \beta + \beta'(u_{n-1} - u_n), & m = n - 1 \\ 0 & \text{otherwise.} \end{cases} \quad (37)$$

$$V_{nmkl} = \delta_{nl} \delta_{mk} V_{nk} = \delta_{nl} \delta_{mk} \frac{U_0}{\epsilon \sqrt{1 + [|\mathbf{r}_{nk}|/r_0]^2}}. \quad (38)$$

$$\mu_{nm}(\mathbf{r}) = \delta_{nm} \mu_n(\mathbf{r}) = \delta_{nm} \int_0^1 d\lambda \int d\mathbf{r}' |\Psi_n(\mathbf{r}')|^2 e \mathbf{r}' \delta(\mathbf{r} - \lambda \mathbf{r}'). \quad (39)$$

Here, β is the nearest-neighbor hopping integral and β' represents the electron-phonon interaction. u_n denotes the displacement of the position of atom n , with respect to a reference chain with a uniform (average) bond length. It can be determined from the force equilibrium condition,

$$\kappa(u_n - u_{n+1}) = 4\beta' \bar{\rho}_{n,n+1}, \quad (40)$$

where κ is the force constant. In expression (38), we have adopted Ohno's formula for the matrix element of the Coulomb interaction, where U_0 is the on-site Hubbard potential, and ϵ is the static dielectric constant. We now

obtain for the dipole moment density Eq. (30),

$$\mu_\alpha(\mathbf{r}) = \sum_n \mu_n(\mathbf{r}) \mathcal{S}_{nn,\alpha}, \quad (41)$$

and for the radiative decay Γ_α from Eqs. (27), (20), and (17),

$$\Gamma_\alpha(\omega) = \sum_{nl} \mathcal{S}_{nn,\alpha}^* \text{Im} \mathcal{D}_{nl}^0(\omega) \mathcal{S}_{ll,\alpha}, \quad (42)$$

where

$$\mathcal{D}_{nl}^0(\omega) = \int d\mathbf{r} d\mathbf{r}' \mu_n(\mathbf{r}) \mathcal{G}(\mathbf{r} - \mathbf{r}', \omega) \mu_l(\mathbf{r}'). \quad (43)$$

Substituting Eq. (43) into Eq. (42) and making use of Eqs. (41) and (27), we obtain

$$\Gamma_\alpha(\omega) = \int d\mathbf{r} d\mathbf{r}' \frac{d\mathbf{k}}{(2\pi)^3} \mu_\alpha(\mathbf{r}) \mu_\alpha^*(\mathbf{r}') e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} \text{Im} \mathcal{G}(\mathbf{k}, \omega). \quad (44)$$

When the molecular size is much smaller than the optical wavelength, we can set $e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} \approx 1$ in the right-hand side of Eq. (44) and obtain

$$\Gamma_\alpha(\omega) = \frac{2e^2 \hbar^2 \omega^3}{3m_0 c^3 \epsilon_\alpha} f_\alpha. \quad (45)$$

We will now consider chains with sizes much larger than the exciton (the composite particle representing an electron and a hole) size. In this case, the relative and the center-of-mass motions of the electron-hole pair are separable. We can then factorize the quantum number α as $\alpha = q, \nu$, where q represents the center-of-mass momentum and ν stands for the relative motion. We further assume that the chain lies in the z direction and introduce the longitudinal and the transverse coordinates,

$$\mathbf{r} = (\mathbf{r}_\perp, z). \quad (46)$$

Translational symmetry results in the following properties,

$$\bar{\rho}_{k+2n, l+2n} = \bar{\rho}_{kl}; \quad \mu_{l+2n}(\mathbf{r}_\perp, z + 2na) = \mu_l(\mathbf{r}_\perp, z), \quad (47)$$

$$\mathcal{S}_{k+2n, l+2n; q\nu} = e^{i2naq} \mathcal{S}_{kl; q\nu}. \quad (48)$$

Since the only contribution to Eq. (44) is from \mathbf{k} with $|\mathbf{k}| = \omega/c$, and $\omega a/c \ll 1$, we can recast it in the form

$$\Gamma_{q\nu}(\omega) = \frac{e^2 \hbar^2}{2m_0 \epsilon_{q\nu}} \times \sum_{nm} \int \frac{d\mathbf{k}}{(2\pi)^3} f_{q\nu; mn} e^{i2k_z a(m-n)} \text{Im} \mathcal{G}(\mathbf{k}, \omega), \quad (49)$$

with

$$f_{q\nu; mn} = \frac{2m_0 \epsilon_{q\nu}}{e^2 \hbar^2} \int d^2 r_\perp d^2 r'_\perp \int_{R_{2m}}^{R_{2m+2}} dz \int_{R_{2n}}^{R_{2n+2}} dz' \mu_{q\nu}(\mathbf{r}_\perp, z) \mu_{q\nu}^*(\mathbf{r}'_\perp, z'). \quad (50)$$

It follows from Eqs. (47), (48), and (41) that

$$f_{qv,m+l,n+s} = e^{i2lqa - i2sqa} f_{qv,mn}, \quad (51)$$

which allows us to write $f_{qv,mn}$ in the form

$$f_{qv,mn} = e^{i2qa(m-n)} \left[\frac{N}{2} \right]^{-1} \bar{f}_{qv}, \quad (52)$$

where \bar{f} is the oscillator strength per unit cell (see discussion). Substituting Eq. (52) into Eq. (49), we obtain

$$\Gamma_{qv}(\omega) = \frac{e^2 \hbar^2 \bar{f}_{qv}}{2m_0 \epsilon_{qv}} \left[\frac{N}{2} \right]^{-1} \sum_{nm} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i2(k_z - q)a(m-n)} \times \text{Im} \mathcal{G}(\mathbf{k}, \omega). \quad (53)$$

Summing over m and n , we get

$$\sum_{nm} e^{i2(k_z - q)a(m-n)} = \begin{cases} \left[\frac{N}{2} \right]^2 \delta_{q,0} & \text{for } Na \ll \lambda \\ \frac{N}{2} 2\pi \delta[2a(k_z - q)] & \text{for } Na \gg \lambda \end{cases} \quad (54)$$

Combining Eqs. (53) and (54), we obtain the limiting expressions

$$\Gamma_{0v}(\omega) = \frac{e^2 \hbar^2}{2m_0 \epsilon_{0v}} \frac{N}{2} \bar{f}_{0v} \int \frac{d\mathbf{k}}{(2\pi)^3} \text{Im} \mathcal{G}(\mathbf{k}, \omega), \quad Na \ll \lambda, \quad (55)$$

$$\Gamma_{qv}(\omega) = \frac{e^2 \hbar^2}{2m_0 \epsilon_{qv}} \bar{f}_{qv} \int \frac{d\mathbf{k}}{(2\pi)^3} 2\pi \delta[2a(k_z - q)] \times \text{Im} \mathcal{G}_{zz}(\mathbf{k}, \omega), \quad Na \gg \lambda. \quad (56)$$

Performing the \mathbf{k} integration in Eqs. (55) and (56), and utilizing the fact that for optical wave vectors q , ϵ_{qv} , and \bar{f}_{qv} depend only weakly on q and we can set $\epsilon_{qv} \approx \epsilon_v$, $\bar{f}_{qv} \approx \bar{f}_v$, we obtain for the radiative decay,

$$\Gamma_v(\omega) = \frac{2e^2 \hbar^2 \omega^3 \bar{f}_v}{3m_0 c^3 \epsilon_v} N_c, \quad (57)$$

with

$$N_c = \begin{cases} \frac{N}{2} & \text{for } Na \ll \lambda \\ \frac{3}{8} \frac{\lambda}{2a} \sin^2 \theta & \text{for } Na \gg \lambda \end{cases} \quad (58)$$

Here, $\cos \theta \equiv qc/\omega$ and N_c is the coherence number (i.e., is a number of unit cells radiating coherently); for $Na \ll \lambda$, it is equal to the number of the unit cells in the chain, for $Na \gg \lambda$, it is the superradiance coherence size.

IV. NUMERICAL RESULTS

We have performed numerical calculations using the PPP model with the following parameters: $\beta = -2.4$ eV,

$\beta' = -3.5$ eV/Å, $\kappa = 30$ eV/Å², and $U_0 = 11.13$ eV. The absorption line shape calculated with these parameters gives an optical transition frequency of 2 eV for a large polyacetylene chain (more than 100 atoms). We first determined the stationary solutions $\bar{\rho}_{nm}$ by calculating the one-particle Hartree-Fock (HF) wave functions (molecular orbitals) and energies from

$$\sum_m \bar{h}_{nm} c_{mk} = E_k c_{nk}. \quad (59)$$

The coefficients c_{mk} satisfy the orthonormality and closure relations,

$$\sum_m c_{mk} c_{mk'} = \delta_{k,k'}, \quad (60)$$

$$\sum_k c_{mk} c_{nk} = \delta_{n,m}. \quad (61)$$

Using the coefficients c_{mk} , we construct the density matrix $\bar{\rho}_{nm}$,

$$\bar{\rho}_{nm} = \sum_k^{\text{occ}} c_{mk} c_{nk}, \quad (62)$$

where the summation runs over all occupied levels k . From Eq. (40), we obtain the dimerization parameter u_n , which can be used to calculate the new $\bar{\rho}_{nm}$ according to the above procedure. Repeating the calculations until the old and the new \bar{u}_n converge, we finally obtain the geometry optimized HF solution for $\bar{\rho}_{nm}$ and \bar{u}_n .

The total electron-hole excitation spectrum for a 30 atom chain is obtained by solving the eigenvalue problem (23) for the matrix A . Since this matrix is defined in Liouville space, the excitation spectrum includes the contribution of the center of mass, as well as the relative motions of electrons and holes. However, only very few modes of this spectrum are relevant for the linear optical properties of the chain. This is demonstrated in Fig. 1(a), where we have plotted the oscillator strength Eq. (41) versus the energy ϵ_a for a 30 atom chain. As can be seen, 45% of the oscillator strength is carried by lowest peak, which is excitonic nature, due to the long-range Coulomb interaction. The influence of the Coulomb interaction on the linear optical response can be illustrated by comparing with the independent electron (Huckel) model, obtained by setting $U_0 = 0$. In that case, the Peierls gap is caused only by chain dimerization. To retain the same transition frequency, we need to modify the parameters of the model to $\beta' = -4.437$ eV/Å, $\kappa = 21$ eV/Å². As can be seen in Fig. 1(b), for the Huckel model the oscillator strength is more uniformly distributed over the chain. This behavior is also reflected in the linear absorption, which is determined by the oscillator strength. In Figs. 2(a) and 2(b), we show the imaginary and real parts of the linear polarizability,

$$\bar{\chi}(\omega) = \int d\mathbf{r} \int d\mathbf{r}' \chi(\mathbf{n}, \mathbf{n}', \omega) \quad (63)$$

for the PPP and the Huckel model, respectively. In the calculations, we have added a nonradiative damping $\gamma = 0.1$ eV to Γ . As can be seen from Figs. 2(a), the excitonic peak is clearly much stronger compared with the

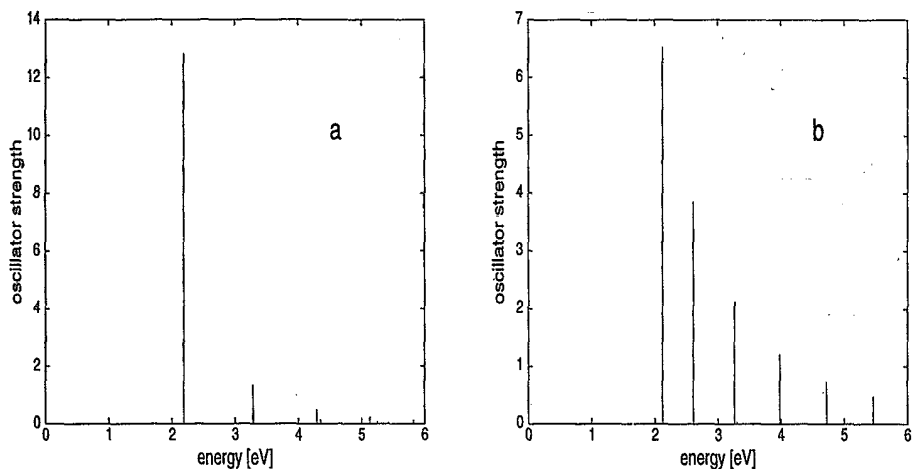


FIG. 1. Oscillator strength of a 30-atom chain for (a) the PPP model and (b) the Huckel model. Note that the sum of all oscillator strengths is equal to the number of electrons, Eq. (34).

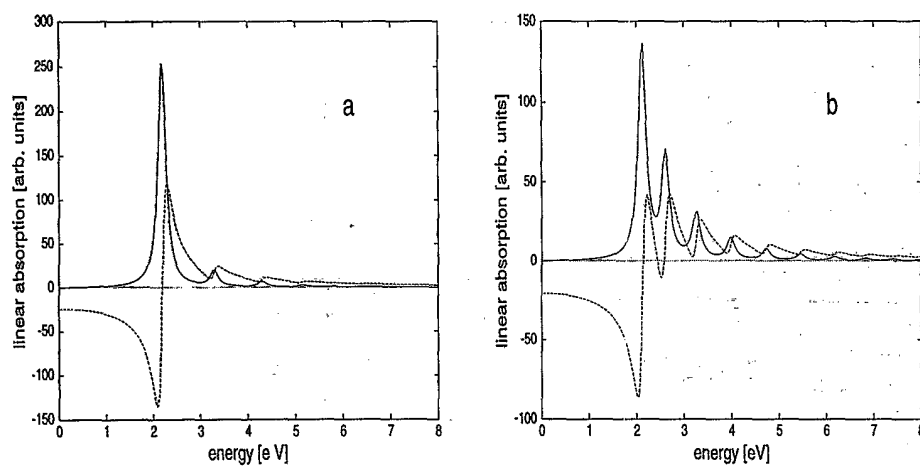


FIG. 2. Imaginary part (solid line) and real part (dashed line) of the linear polarizability, Eq. (63), of a 30-atom chain for (a) the PPP model and (b) the Huckel model.

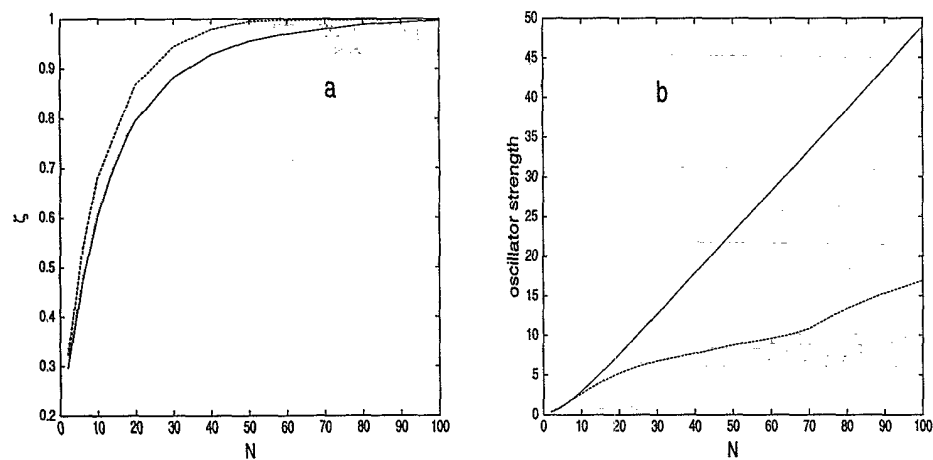


FIG. 3. (a) Saturation of the lowest optical transition frequency ($\zeta = E_0/E_{N \rightarrow \infty}$, with size N for the PPP (solid) and the Huckel (dashed) models; (b) oscillator strength of the lowest transition as function of size N for the PPP (solid) and the Huckel (dashed) models.

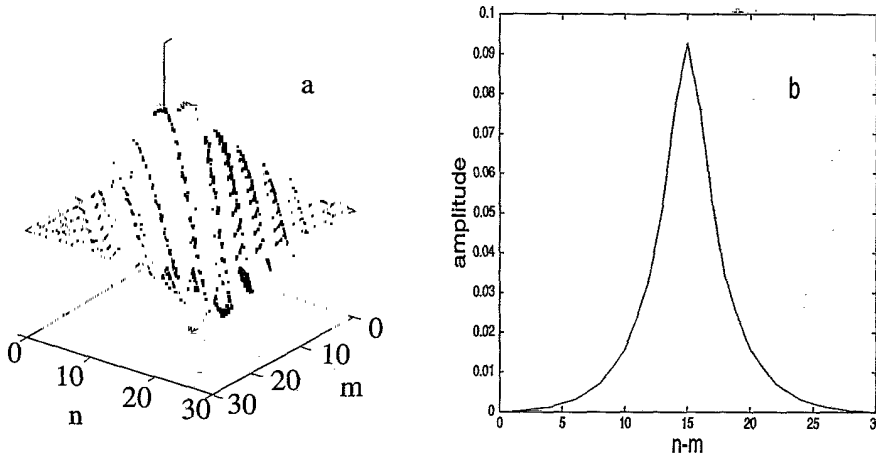


FIG. 4. (a) The eigenvector corresponding to the lowest optical transition in a 30-atom chain as a function of size n and m ; (b) an antidiagonal cross section of (a) plotted versus the relative coordinate $n-m$ for fixed center-of-mass coordinate $n+m=31$.

Huckel (free electron) case [Fig. 2(b)], which shows a more uniform distribution of oscillator strength. We have also studied the variation of the linear optical properties with chain size. In Fig. 3, we display the size dependence of the lowest transition and its oscillator strength for the PPP model (full lines) and for the Huckel model (dashed lines). In both cases, the transition frequency saturates with size. However, the corresponding oscillator strengths show different behavior. The Huckel model shows a strong size dependence of the oscillator strengths, indicating that the dynamics of the lowest transition is influenced by oscillators of higher frequencies. In contrast, for the PPP model, we obtain a simple linear scaling for sizes larger than 20 atoms. This reflects the fact that the excitonic peak is well separated, and no other transitions are involved in the dynamics of this state. For sizes below 20 atoms, a slight deviation from linear scaling can be observed, since the chain size is comparable to the exciton radius and therefore, exciton confinement effects become important. The exciton size can be visualized by considering the eigenvectors α of the \mathcal{A} matrix, whose components are given by the transformation matrix $\mathcal{S}_{nm,\alpha}$. The eigenvector corresponding to the lowest line in a 30-atom chain is displayed as a function of n and m in Fig. 4(a). Figure 4(b) shows an “antidiagonal” cross section of that eigenvector plotted versus the relative coordinate $n-m$ (electron-hole separation) for fixed center-of-mass coordinate $n+m=31$. As can be clearly seen from this figure, the exciton size is of the order of 20 atoms.

V. DISCUSSION

In conclusion, we now discuss the present method and the numerical results, and outline some of the key open problems in the optical studies of conjugated polymers. We start by examining our expression for the linear response Eqs. (29), (30). Neglecting the radiative width, the derivation of Eqs. (29), (30) is based on inverting the operator $\hbar\omega - A$, using a spectral decomposition through the eigenstates of A [see Eq. (23)]. The matrix form of the operator A in the site basis set is given by Eq. (19).

As indicated in Sec. V, the operator A is not Hermitian, and \mathcal{S}^{-1} is different from \mathcal{S}^\dagger . We will now show that the nonhermiticity of the operator A is a consequence of the inclusion of processes which do not conserve the number of electron-hole pairs, i.e., that go beyond the two-band model. To illustrate this let us examine the following free boson Hamiltonian, which does not conserve the number of particles,

$$H_0 = \varepsilon B^\dagger B + \frac{\Delta}{2} (B^\dagger B^\dagger + BB), \quad (64)$$

with

$$[B, B^\dagger] = 1. \quad (65)$$

One way to deal with this system is to make the Bogolubov transformation, which eliminates the terms, which do not conserve the number of particles. Alternatively, we can use the Green-function approach, and then one needs to diagonalize or invert a Hermitian matrix $L(\omega)$,

$$L(\omega) = \hbar\omega\Lambda - \mathcal{L}, \quad (66)$$

with

$$\Lambda = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad (67)$$

$$\mathcal{L} = \begin{bmatrix} \varepsilon & \Delta \\ \Delta & \varepsilon \end{bmatrix}. \quad (68)$$

The poles of the L^{-1} matrix yield the well-known spectrum,

$$\hbar\omega = \sqrt{\varepsilon^2 - \Delta^2}. \quad (69)$$

The matrix $L^{-1}(\omega)$ can be alternatively recast in the form

$$L^{-1}(\omega) = (\hbar\omega - \mathcal{A})^{-1} \Lambda, \quad (70)$$

with the non-Hermitian matrix \mathcal{A} ,

$$\mathcal{A} \equiv \Lambda \mathcal{L}. \quad (71)$$

This illustrates that in systems which do not conserve the number of particles, one needs to invert a matrix of the type $\hbar\omega - \mathcal{A}$, where \mathcal{A} is non-Hermitian. This example applies qualitatively to the system considered in Sec. V, provided we allow ε and Δ to be operators rather than numbers.

We denote by W the space of the single-particle states and decompose it into the valence and conduction subspaces W_v and W_c , respectively:

$$W = W_v \oplus W_c, \quad (72)$$

$$W_v \equiv \ker(1 - \bar{\rho}), \quad W_c \equiv \ker \bar{\rho}. \quad (73)$$

Here \ker denotes the kernel, i.e., the subspace of vectors with zero eigenvalue. Then, since in the time-dependent Hartree-Fock approach $\rho^2 = 1$ and hence

$$\bar{\rho} \rho^{(1)} + \rho^{(1)} \bar{\rho} = \rho^{(1)}, \quad (74)$$

it follows from Eq. (74) that $\rho^{(1)}$ belongs to the subspace \bar{W} of $W \otimes W$,

$$\bar{W} \equiv (W_v \otimes W_c) \oplus (W_c \otimes W_v), \quad (75)$$

and the linear response $\chi^{(1)}$ is nonzero on the subspace \bar{W} . The linear response can then be written in the form of Eq. (70), with $L(\omega)$ being a 2×2 matrix with operator matrix elements. This structure is imposed by the decomposition (75). In particular, the operator Λ has the form

$$\Lambda = \bar{\rho} \otimes (1 - \bar{\rho}) - (1 - \bar{\rho}) \otimes \bar{\rho}, \quad (76)$$

which leads to the last factor $F_{kl}(\omega)$ in the numerator of Eq. (26).

Another manifestation of the nonhermiticity of the operator \mathcal{A} , which is connected with the nonconservation of the number of electron-hole pairs, is in the structure of oscillators in the decoupled oscillator picture of the linear response. To obtain this picture, we first note that the density matrix ρ involved in the time-dependent Hartree-Fock procedure obeys

$$\rho^\dagger = \rho; \quad \rho^2 = 1. \quad (77)$$

It then operates on the Grassman manifold $G_N(N/2, C)$ on which we can consider a canonical Poisson bracket, associated with the canonical symplectic Kähler structure on a Grassman manifold.³⁰ Next, we introduce a classical Hamiltonian $h(\rho)$,

$$h(\rho) \equiv \langle \Omega(\rho) | \hat{H} | \Omega(\rho) \rangle, \quad (78)$$

where \hat{H} is our original quantum Hamiltonian, and $\Omega(\rho)$ is a Slater determinant associated with a subspace $\ker \rho$ of W . The time-dependent Hartree-Fock equations can then be written in the form of equations of motion for a classical Hamiltonian system,

$$\partial_t \rho = \{h, \rho\}, \quad (79)$$

and $\bar{\rho}$ is the minimum of the function h . Expanding in the vicinity of $\bar{\rho}$

$$\rho = \bar{\rho} + \xi, \quad (80)$$

$$h = \sum_{i,j} \frac{1}{2} \frac{\partial^2 h(\bar{\rho})}{\partial \rho_i \partial \rho_j} \xi_i \xi_j, \quad (81)$$

$$\{\xi_i, \xi_j\} = w_{ij}(\bar{\rho}), \quad (82)$$

we can switch to the independent harmonic oscillator picture. Since in Eq. (81) canonical coordinates and momenta are mixed, this requires the diagonalization of a non-Hermitian matrix. In other words, the mixed form of Eq. (81) makes it necessary to work in Liouville space.

We next discuss our numerical results for the properties of the ground state and the linear-response function. The solution of the Hartree-Fock equation shows spontaneous symmetry breaking in the bond order, i.e.,

$$\bar{\rho}_{m,m+j} \neq \bar{\rho}_{m+1,m+j+1} \quad \text{for } j \neq 0, \quad (83)$$

which leads to the formation of gap in the single-particle excitation spectrum. Two mechanisms contribute to this effect: the Coulomb interactions and the dependence of electron energy on nuclear positions (exciton-phonon coupling). The ground state is obtained by first calculating the Hartree-Fock energy of electrons as a function of nuclear configuration, and then minimizing the total energy (which is a sum of the Hartree-Fock electron energy and the potential energy of nuclei), with respect to nuclear positions. Our numerical results for polyacetylene show that the ground state reduced density matrix is not sensitive to bond-length alternation. Stated differently, if we start with a regular chain with no bond-length alternation, the ground-state density matrix will be virtually identical to that obtained when allowing for geometry optimization. The reason is the strong Coulomb interaction in polyacetylene, which seems to dominate the ground-state bonding. This means that we can neglect the effect of geometric rearrangement on electronic properties. To reproduce the bond-length alternation, we need to minimize the energy of the nuclei (which depends on $\bar{\rho}_{m,n}$) using $\bar{\rho}_{m,n}$, obtained from the solution of the electronic problem. This conclusion depends on the parameters used. For example, for the Huckel model, where the Coulomb interaction is neglected, the entire bond order alternation is induced by the bond-length alternation resulting from exciton-phonon (lattice) coupling.

Based on the analogy with semiconductors, one could expect several sharp peaks in the absorption (related to the exciton states) accompanied by a broad feature related to the continuous spectrum of the electron and hole states. Instead, we get four sharp peaks with most oscillator strength concentrated in a single peak. This can be very important in interpreting the experimental absorption of conjugated polymers. Absorption experiments show a broad shoulder with a width of several eV.³¹ This could be explained by a broad band spectrum of electronic states contributing to the absorption. However, our numerical calculations show a quite different picture. Since typical values of optical phonons are of the order of 2000 cm^{-1} , and the phonon linewidths are of the order of hundreds of wave numbers, homogeneous broadening cannot lead to such a broad absorption spectrum. Inhomogeneous broadening seems to be the most likely mechanism. For example, the main peak energy in our calcu-

lations is around 2 eV for N in the range from 10 to 100. Optical experiments that can eliminate inhomogeneous broadening, such as fluorescence line narrowing, photon echo, and hole burning, can, therefore, be very useful in the studies of conjugated polymers.

Let us turn now to the size scaling of the absorption and the radiative decay rates. When the chain size is much smaller than the optical wavelength, one can invoke the dipole approximation. There are three possible length scales, which could be connected with the validity of the dipole approximation: the lattice constant a , the exciton size which is about $15a$ in our calculations, and the chain length Na . The linear scaling of the absorption with size for $N > 20$ shows that the dipole approximation is not connected with the physical size of the molecule. This allows us to use the dipole approximation even for $Na \gg \lambda$ and account for superradiance. We will show that the dipole approximation is connected with the length a , i.e., the unit cell in the dimerized polymer. To that end, we first note that the interaction with the transverse field can be written in the following form,

$$H_{\text{int}} = - \int_C d\mathbf{r} \rho(\mathbf{r}) \mathcal{U}(\mathbf{r}), \quad (84)$$

with

$$\mathcal{U}(\mathbf{r}) \equiv \int_{C_r} E(\mathbf{r}') d\mathbf{r}', \quad (85)$$

where C_r is a segment $[0, \mathbf{r}]$. The integration here starts at some arbitrary origin. The following results do not depend on the choice of origin. This follows directly from the orthogonality of the Bloch basis functions [see Eq. (88)]. For molecules oriented in the z direction, Eq. (85) yields

$$E_z = \frac{\partial \mathcal{U}}{\partial z}. \quad (86)$$

For rather long chains, we can switch to a basis set of the Bloch functions, which are determined by momentum k , and by a two-dimensional vector $w_i(k)$ ($i=c, v$ denotes the bands), which describes the Bloch function in a unit cell. Switching to the momentum domain, we obtain the interaction in the Bloch basis set,

$$H_{\text{int}} = - \int dq \mathcal{U}(-q) \int dk (w_i(k+q), w_j(k)) \times c_{i,k+q}^\dagger c_{j,k}, \quad (87)$$

where (w_i, w_j) stands for the scalar product of the Bloch functions in a unit cell, and c_{ik}^\dagger and c_{ik} are the electron creation and annihilation operators in the Bloch basis set. Since we consider the states of the subspace \overline{W} [see Eq. (75)], we always have a factor $(w_c(k+q), w_v(k))$ in the interaction. The states in different bands are orthogonal,

$$(w_c(k), w_v(k)) = 0, \quad (88)$$

and for $qa \ll 1$, we can write

$$(w_c(k+q), w_v(k)) \approx \mu(k)q, \quad (89)$$

with

$$\mu(k) \equiv \left[\frac{\partial w_c(k)}{\partial k}, w_v(k) \right]. \quad (90)$$

Substituting Eq. (90) into (87) and making use of Eq. (86), we obtain (omitting the indices)

$$H_{\text{int}} = \int dk \int dq E_z(q) \mu(k) c_{k+q}^\dagger c_k. \quad (91)$$

Equation (91) shows that for $a \ll \lambda$, the interaction has the form of the dipole approximation and $\mu(k)$ can be treated as a k -dependent dipole moment of a unit cell. One can also see from Eq. (90) that the oscillator strength of the α eigenstate is determined by its dipole moment μ_α , defined as

$$\mu_\alpha \equiv \int dk \mu(k) \varphi_\alpha(k), \quad (92)$$

with $\varphi_\alpha(k)$ being the wave function of the relative electron-hole motion, corresponding to the state α in the momentum representation.

Finally, we discuss the role of screening in the linear response of conjugated polymers. We emphasize that although polymers are formally similar to semiconductors, their properties are very different, due to different magnitudes of parameters. For ordinary semiconductors, the band gap E_g is typically much larger than the Coulomb interaction V_0 ,

$$E_g \gg V_0. \quad (93)$$

This implies that many-body effects as reflected in the parameter V_0/E_g are weak, and screening is important only if we add carriers (by doping or pumping with a strong field). In our calculations for polymers $E_g \approx 2$ eV. $V_0 \approx 10$ eV and the many-body effects (in particular screening) are not only important, but seem to be dominant and to change the ground state drastically. This means that there should be some different justification for starting with the Hartree-Fock ground state as a zero approximation. Since screening is provided by electron-hole pairs, interaction of the longitudinal field with these pairs always contains the factor given by (89). This leads to the following form of the interaction in this channel in the momentum domain for small q ,

$$V(q) \sim (qa)^2 \ln(qa) V_0. \quad (94)$$

Equation (94) implies that screening effects are important on short distances. A typical value of q for excitons is $qa \sim 0.1$ and we get $V(q) \sim 0.2$ eV, which is smaller than the gap. Effects of screening can be still very important, since they contain retardation, which can destroy the sharp peaks in absorption. As indicated above, this may be very important in interpreting the experimental absorption spectra. The study of screening effects should clarify whether the calculated sharp peak structure of linear absorption is a genuine property of the system or a result of the approximations made in the present calculations.

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APPENDIX A: THE DENSITY MATRIX IN LIOUVILLE SPACE

In this Appendix we derive Eq. (26), which is the solution of Eq. (18) for the density matrix ρ_{mn} . Using an operator notation, we can write the solution of Eq. (18) in the form

$$\rho = (\hbar\omega - A + i\Gamma)^{-1}F. \quad (\text{A1})$$

Expanding the right-hand side (rhs) of Eq. (A1) in powers of Γ , we obtain

$$\begin{aligned} \rho = & (\hbar\omega - A)^{-1}I + (\hbar\omega - A)^{-1}(-i\Gamma)(\hbar\omega - A)^{-1}F \\ & + (\hbar\omega - A)^{-1}(-i\Gamma)(\hbar\omega - A)^{-1} \\ & \times (-i\Gamma)(\hbar\omega - A)^{-1}F + \dots \end{aligned} \quad (\text{A2})$$

Making use of Eq. (23), we can represent the operator $(\hbar\omega - A)^{-1}$ in the form

$$\{(\hbar\omega - A)^{-1}\}_{nm,kl} = \sum_{\alpha} \frac{\mathcal{S}_{nm,\alpha} \mathcal{S}_{\alpha,kl}^{-1}}{\hbar\omega - \varepsilon_{\alpha}}. \quad (\text{A3})$$

We consider a situation when the resonances are well separated, i.e., the radiative width is much smaller than the energy spacings between the resonances. In this case, if $\hbar\omega$ is far from all ε_{α} , we can neglect Γ in Eq. (A1) and obtain using (A3),

$$\rho_{nm} = \sum_{\alpha} \sum_{kl} \frac{\mathcal{S}_{nm,\alpha} \mathcal{S}_{\alpha,kl}^{-1}}{\hbar\omega - \varepsilon_{\alpha}} F_{kl}. \quad (\text{A4})$$

In the vicinity of a resonance $\hbar\omega \approx \varepsilon_{\alpha}$, we can retain only the resonant terms in the spectral decomposition of the rhs of Eq. (A2). Performing the summation over resonant terms, we then get

$$\rho_{nm} \approx \sum_{kl} \frac{\mathcal{S}_{nm,\alpha} \mathcal{S}_{\alpha,kl}^{-1}}{\hbar\omega - \varepsilon_{\alpha} + i\Gamma_{\alpha}} F_{kl}, \quad (\text{A5})$$

with Γ_{α} defined by Eq. (27). Note that Γ_{α} is a number, not an operator.

APPENDIX B: MATRIX RELATIONS

From Appendix A, we obtain the following form of χ (written in matrix form):

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\alpha} \frac{\text{Tr}(\mu(\mathbf{r})\mathcal{S}_{\alpha})\text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')])}{\hbar\omega - \varepsilon_{\alpha} + i\Gamma_{\alpha}}, \quad (\text{B1})$$

where

$$\Gamma_{\alpha}(\omega) = \text{Tr}(\mathcal{S}_{\alpha}^{-1}(\Gamma(\omega)\mathcal{S}_{\alpha})). \quad (\text{B2})$$

The matrix \mathcal{A} acting in Liouville space has certain properties which can be checked directly from the Hamiltonian.

First, we define an antisymmetric scalar product in Liouville space

$$\begin{aligned} \{u, v\} & \equiv \text{Tr}(\bar{\rho}[u, v]), \\ \{u, v\} & = -\{v, u\}. \end{aligned} \quad (\text{B3})$$

Note that $\{u, v\} = 0$ if u or v belong to the particle-particle or hole-hole subspace. The matrix \mathcal{A} has the following properties:

$$\{\mathcal{A}u, v\} = -\{u, \mathcal{A}v\}, \quad (\text{B4})$$

$$(\mathcal{A}u)^{\dagger} = -\mathcal{A}u^{\dagger}, \quad (\text{B5})$$

and all eigenvalues of \mathcal{A} are real. It follows from these properties that for two eigenmodes $\mathcal{A}u = \lambda_{\mu}u$, $\mathcal{A}v = \lambda_{\nu}v$ it is $\{u, v\} = 0$ if $\lambda_{\mu} \neq -\lambda_{\nu}$ and $\mathcal{A}u^{\dagger} = -\lambda_{\mu}u^{\dagger}$, if $\mathcal{A}u = \lambda_{\mu}u$. Therefore, in the physical subspace (particle-hole modes), we have eigenmodes \mathcal{S}_{α} , $\alpha > 0$ with eigenvalues ε_{α} and $\mathcal{S}_{-\alpha}^{\dagger} \equiv \mathcal{S}_{\alpha}^{\dagger}$ with eigenvalues $-\varepsilon_{\alpha}$. The normalization Eq. (25) means $\{\mathcal{S}_{\alpha}^{\dagger}, \mathcal{S}_{\alpha}\} = 1$ for $\alpha > 0$, which leads to

$$\{\mathcal{S}_{\alpha}, \mathcal{S}_{\beta}\} = \text{sgn}(\beta)\delta_{-\alpha, \beta}. \quad (\text{B6})$$

Since $[\bar{\rho}, \mu(\mathbf{r}')]_{\alpha}$ always belongs to the particle-hole subspace, we can recast Eq. (B1) in the form

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) = & \sum_{\alpha > 0} \left\{ \frac{\text{Tr}(\mu(\mathbf{r})\mathcal{S}_{\alpha})\text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')])}{\hbar\omega - \varepsilon_{\alpha} + i\Gamma_{\alpha}} \right. \\ & \left. + \frac{\text{Tr}(\mu(\mathbf{r})\mathcal{S}_{-\alpha})\text{Tr}(\mathcal{S}_{-\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')])}{\hbar\omega + \varepsilon_{\alpha} + i\Gamma_{\alpha}} \right\}. \end{aligned} \quad (\text{B7})$$

The expansion of $[\bar{\rho}, \mu(\mathbf{r}')]_{\alpha}$ in eigenmodes has the form

$$\begin{aligned} [\bar{\rho}, \mu(\mathbf{r}')]_{\alpha} = & \sum_{\alpha > 0} \{ \text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')])\mathcal{S}_{\alpha} \\ & + \text{Tr}(\mathcal{S}_{-\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')])\mathcal{S}_{-\alpha} \}. \end{aligned} \quad (\text{B8})$$

Taking the scalar products of Eq. (B8) with the eigenmodes \mathcal{S}_{α} , making use of Eq. (B6) and Eq. (B3), we obtain

$$\text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')]) = \text{sgn}(\alpha)\text{Tr}(\bar{\rho}[\mathcal{S}_{\alpha}^{\dagger}[\bar{\rho}, \mu(\mathbf{r}')]]), \quad (\text{B9})$$

or using in the rhs of Eq. (B9) a well-known equality

$$\text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')]) = \text{sgn}(\alpha)\text{Tr}(\mathcal{S}_{\alpha}^{\dagger}[\bar{\rho}, [\bar{\rho}, \mu(\mathbf{r}')]]). \quad (\text{B10})$$

It is easy to verify that the operator $[\bar{\rho}, [\bar{\rho}, \dots]]$ is the projector onto the particle-hole subspace. Then we have for a particle-hole mode \mathcal{S}_{α}

$$\text{Tr}(\mathcal{S}_{\alpha}^{-1}[\bar{\rho}, \mu(\mathbf{r}')]) = \text{sgn}(\alpha)\text{Tr}^*(\mu(\mathbf{r}')\mathcal{S}_{\alpha}). \quad (\text{B11})$$

Substituting Eq. (B11) into Eq. (B7), we obtain Eq. (29) with

$$\mu_{\alpha}(\mathbf{r}) = \text{Tr}(\mu(\mathbf{r})\mathcal{S}_{\alpha}). \quad (\text{B12})$$

Writing Eq. (B12) in the index form, we obtain Eq. (30). Expressing $\Gamma(\omega)$ in terms of $\mathcal{D}^0(\omega)$ in Eq. (B2) and expressing $\mathcal{S}_{\alpha}^{-1}$ in the same manner, we obtain

$$\Gamma_{\alpha}(\omega) = \text{Tr}(\mathcal{S}_{\alpha}^{\dagger}(\text{Im}\mathcal{D}^{(0)}(\omega)\mathcal{S}_{\alpha})), \quad (\text{B13})$$

which gives in the index form Eq. (27).

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