

Intermolecular electronic coherences and local field effects in optical spectra of PPV-oligomer dimers

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Abstract

Optical spectra of an assembly of conjugated molecules are calculated using nonlocal molecular response functions which take into account electrostatic interactions with the surrounding molecules. The present approach provides a computationally efficient procedure for calculating the electrodynamics of interacting molecules with delocalized electronic states. Intramolecular and intermolecular electronic coherences are studied by examining the reduced single electron density matrix. Both electrostatic (multipolar) and chemical (exchange) interactions are incorporated in a unified formalism. Perturbative treatment of the latter allows a systematic extension of the local field approximation. Applications are made to dimers of PPV oligomers.

1. Introduction

The role of intermolecular interactions in the optical response of molecular aggregates and nanostructures is a fundamental problem whose solution is essential for the interpretation of linear and nonlinear spectroscopic measurements. In addition, it has important practical implications for the characterization of optical materials. Recent investigations of poly(*p*-phenylene vinylene) (PPV) have raised questions about the importance of interchain processes in conjugated polymers [1–4]. This problem was studied for polyacetylene [5–8], and 3D band structures for PPV have been calculated [9,10].

The local field approximation (LFA) is the simplest and most commonly used procedure to reduce the computational effort of such many-body problems [11]. This approach, which totally ignores molecular structure and shape, models molecules as point dipoles subject to a local field consisting of the external field and the field created by all other molecules. While the point dipole approximation may hold for the molecule–field interaction – since molecular sizes are usually smaller than the optical wavelength – this is clearly not the case for intermolecular forces. In addition, the LFA misses some important correlations and cooperative effects such as two-exciton states. A review of the LFA is given in Ref. [12].

In this work, we address the microscopic calculation of optical spectra of aggregates of conjugated molecules. We generalize the LFA in three respects. First we use nonlocal optical response functions in order to include the full Coulomb interaction between extended molecular charge distributions. Our approach further accounts for corrections to the molecular polarizabilities due to the electrostatic field of the ground state charge distribution of

neighboring molecules. Finally we account perturbatively for intermolecular electron exchange. We then explore the roles of intermolecular energy transfer and charge delocalization and their effects on the linear absorption. Our approach is based on the reduced single electron density matrix obtained by solving the time dependent Hartree–Fock (TDHF) equations of motion [13–15]. Using this density matrix, we calculate nonlocal optical response functions, which relate the optical polarization to the external driving field.

We begin with a review of the TDHF equations in Section 2, where we also define response functions and optical polarizabilities. Assuming that the charge distributions of different molecules do not overlap (no intermolecular charge exchange) we start from the equations of motion (EOM) for the density matrix of the entire system and derive a closed set of equations for the density matrix of each molecule by introducing a local field in Section 2.1. From the solution of these equations one immediately obtains the response functions, and hence the polarizabilities $\alpha(\omega)$ of the isolated molecules. In Section 2.2 we derive an expression for the aggregate polarizabilities in terms of the molecular polarizabilities, which is exact in the absence of intermolecular charge transfer. The latter is incorporated perturbatively in Section 2.3. Finally we present numerical computations for dimers of PPV oligomers in Section 3 and summarize our results in Section 4.

2. Response functions of molecular aggregates

In a recent study [15] we calculated the linear polarizabilities $\alpha(\omega)$ and nonlocal response functions $\tilde{\alpha}_{nm}$ of isolated conjugated molecules. Here we extend this study to a system of M interacting conjugated molecules, each having N_b , $b = 1, \dots, M$ carbon atoms at the positions $\mathbf{r}_{b,\beta}$, $b = 1, \dots, M$, $\beta = 1, \dots, N_b$. We will use a single, lower-case index $n = (b\beta)$ to denote the sites. The optical properties will be calculated using the Pariser–Parr–Pople (PPP) Hamiltonian for π -electrons [16]

$$\hat{H} = \sum_{n,m,\sigma} t_{nm} \hat{\rho}_{nm}^\sigma + \sum_n U \hat{\rho}_{nn}^\dagger \hat{\rho}_{nn}^\dagger + \frac{1}{2} \sum_{n,m,\sigma,\sigma'}^{n \neq m} U_{nm} \hat{\rho}_{nn}^\sigma \hat{\rho}_{mm}^{\sigma'} + \hat{H}_{\text{int}}, \quad (1)$$

where the density operator $\hat{\rho}$ is given by the creation and annihilation operators $\hat{c}_{n,\sigma}^\dagger$, $\hat{c}_{n,\sigma}$ for an electron with spin σ at site n :

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

U_{nm} is the electron–electron interaction between sites n and m given by Ohno's formula

$$U_{nm} = \frac{\bar{U}}{\sqrt{1 + (|\mathbf{r}_n - \mathbf{r}_m|/a_0)^2}}, \quad (3)$$

\bar{U} denotes the on-site (Hubbard) repulsion, and $a_0 = 1.2935 \text{ \AA}$. Diagonal matrix elements t_{nn} describe the site energies (interaction of nucleus n with all electrons in the system), and off-diagonal elements t_{nm} represent the Coulomb integrals between sites n and m . For intramolecular hopping t^{\parallel} we assume a nearest neighbor form [13,15], and for intermolecular hopping t^{\perp} an exponential dependence on intermolecular separation [10]:

$$t_{nn} = - \sum_l U_{nl}, \quad (4)$$

$$t_{nm}^{\parallel} = \bar{\beta} - \beta' (r_{nm} - \bar{x}), \quad (5)$$

$$t_{nm}^{\perp} = (1 - \delta_{nm}) a e^{-k|r_n - r_m|}. \quad (6)$$

Here \bar{x} is the average bond length, and the remaining parameters are given by $\bar{\beta} = -2.4 \text{ eV}$, $\beta' = -3.5 \text{ eV}$ [15], and $a = 2.75 \text{ eV}$, $k = 1.18 \text{ \AA}^{-1}$ [10].

The interaction with the electric field is given by [17]

$$\hat{H}_{\text{int}}(t) = - \int d\mathbf{r} \mathbf{E}(\mathbf{r}, t) \cdot \hat{\mathbf{P}}(\mathbf{r}), \quad (7)$$

where the polarization operator is [17]

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_{\alpha} q_{\alpha} (\hat{\mathbf{r}}_{\alpha} - \mathbf{R}) \int_0^1 d\lambda \delta(\mathbf{r} - \mathbf{R} - \lambda(\hat{\mathbf{r}}_{\alpha} - \mathbf{R})), \quad (8)$$

\mathbf{R} is an arbitrary reference point, and α runs over all charges in the system.

Using this Hamiltonian and dropping the spin index – thus restricting ourselves to the spin-symmetric case – we calculate the reduced one-electron density matrix

$$\rho_{nm}(t) = \langle \Psi(t) | \hat{\rho} | \Psi(t) \rangle, \quad (9)$$

assuming that the many electron wave function $|\Psi(t)\rangle$ can be expressed by a single Slater determinant (TDHF approximation) [15]. By expanding in powers of the electric field $\mathbf{E}(\mathbf{r}, t)$

$$\rho(t) = \bar{\rho} + \delta\rho(t), \quad (10)$$

$$\delta\rho(t) = \delta\rho^{(1)}(t) + \delta\rho^{(2)}(t) + \dots, \quad (11)$$

the TDHF equations can be written as

$$0 = [t, \bar{\rho}]_{nm} + \sum_l \Gamma_{nm}^l [\bar{\rho}_{nm} \bar{\rho}_{ll} - \bar{\rho}_{nl} \bar{\rho}_{lm}], \quad (12)$$

$$\begin{aligned} i\hbar \delta\dot{\rho}_{nm} = & [t, \delta\rho]_{nm} + \sum_l \Gamma_{nm}^l [\bar{\rho}_{nm} \delta\rho_{ll} + \bar{\rho}_{ll} \delta\rho_{nm} + \delta\rho_{nm} \delta\rho_{ll} - \bar{\rho}_{nl} \delta\rho_{lm} - \bar{\rho}_{lm} \delta\rho_{nl} - \delta\rho_{nl} \delta\rho_{lm}] \\ & + (V_n - V_m) (\bar{\rho}_{nm} + \delta\rho_{nm}). \end{aligned} \quad (13)$$

Here we defined

$$\Gamma_{nm}^l = U_{nl} - U_{ml}, \quad (14)$$

and introduced an effective potential V_n , which describes the interaction with the electric field

$$V_n(t) = \int d\mathbf{r} \mathcal{P}_n(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}, t), \quad (15)$$

where

$$\mathcal{P}_n(\mathbf{r}) = \langle \psi_n | \hat{\mathbf{P}}(\mathbf{r}) | \psi_n \rangle \quad (16)$$

are polarization densities defined by expanding the polarization operator $\hat{\mathbf{P}}(\mathbf{r})$ in the π -electron basis set $\{|\psi_n\rangle\}$ [15]

$$\hat{\mathbf{P}}(\mathbf{r}) = 2 \sum_n \hat{\rho}_{nn} \mathcal{P}_n(\mathbf{r}). \quad (17)$$

Eq. (12) defines the ground state single electron density matrix $\bar{\rho}_{nm}$. Its diagonal elements $\bar{\rho}_{nn}$ represent the charge on site n , and its off-diagonal elements $\bar{\rho}_{nm}$ measure the chemical bond strength (bond order) between sites n and m . Eq. (13) is the TDHF equation for the single electron density matrix $\delta\rho(t)$ induced

by the driving field. Diagonal elements represent induced charges, and off-diagonal elements constitute induced electronic coherences. These equations form the basis of the present theory [13].

The key quantity governing optical properties is the expectation value $\mathbf{P}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{P}}(\mathbf{r}) | \Psi(t) \rangle = 2 \sum_n \rho_{nn}(t) \mathcal{P}_n(\mathbf{r})$ of the polarization operator Eq. (17), whose computation requires the solution of Eq. (12) and Eq. (13). In analogy with ρ it can be expanded in the electric field, and the Fourier transform of the linear polarization is related to the electric field via

$$\tilde{\mathbf{P}}^{(1)}(\mathbf{r}, \omega) = \int d\mathbf{r}' \vec{\alpha}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \tilde{\mathbf{E}}(\mathbf{r}', \omega), \quad (18)$$

where the nonlocal optical polarizability $\vec{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ is given by [15]

$$\vec{\alpha}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{nm} \tilde{\alpha}_{nm}(\omega) \mathcal{P}_n(\mathbf{r}) \mathcal{P}_m(\mathbf{r}'). \quad (19)$$

Here the tilde indicates Fourier transformed quantities defined by

$$\tilde{A}(\omega) = \int d\omega e^{-i\omega t} A(t). \quad (20)$$

The polarizability factorizes into an orientation dependent tensorial product, which we write as a dyadic $\mathcal{P}_n(\mathbf{r}) \mathcal{P}_m(\mathbf{r}')$, times a purely position dependent nonlocal response tensor $\tilde{\alpha}_{nm}(\omega)$, which is defined by [15]

$$\delta \tilde{\rho}_{nn}^{(1)}(\omega) = \sum_l \tilde{\alpha}_{nl}(\omega) \tilde{V}_l(\omega). \quad (21)$$

Substitution of the power series expansion Eq. (11) into Eq. (13) yields a hierarchy of coupled linear equations for $\delta \rho^{(i)}$, $i = 1, 2, \dots$, which can be solved order by order. The linear density matrix can then be calculated using a generalized response function $\tilde{U}_{nm,l}$, which relates the induced density matrix to the external potential via

$$\delta \tilde{\rho}_{nm}^{(1)}(\omega) = \sum_l \tilde{U}_{nm,l}(\omega) \tilde{V}_l(\omega). \quad (22)$$

$\tilde{U}_{nm,l}$ is then given by [15]

$$\tilde{U}_{nm,l}(\omega) = \sum_r (\mathcal{G}_{nm,lr}(\omega) - \mathcal{G}_{nm,rl}(\omega)) \tilde{\rho}_{rl}, \quad (23)$$

and $\mathcal{G}_{nm,lr}$ is the Green's function of the homogeneous part of the linearized Eq. (13). Comparison to Eq. (21) immediately yields

$$\tilde{\alpha}_{nm}(\omega) = \tilde{U}_{nn,m}(\omega). \quad (24)$$

Assuming that the entire aggregate is small compared to the wavelength of the incident light, and choosing $\mathbf{R} = \mathbf{0}$ we may set [15]

$$\mathcal{P}_n(\mathbf{r}) = -2e\mathbf{r}_n \delta(\mathbf{r}), \quad (25)$$

so that

$$V_n(t) = -e\mathbf{r}_n \cdot \mathbf{E}(\mathbf{r} = \mathbf{0}, t). \quad (26)$$

The total polarizability, defined by integrating out the spatial coordinates of Eq. (19) is then

$$\vec{\alpha}(\omega) = \sum_{nm} \tilde{\alpha}_{nm}(\omega) \mathbf{r}_n \mathbf{r}_m. \quad (27)$$

Here the product $\mathbf{r}_n \mathbf{r}_m$ is again a dyadic. Eq. (27) is also obtained for $\mathbf{R} \neq \mathbf{0}$, as $\sum_n \tilde{\alpha}_{nm} = 0$ and $\tilde{\alpha}_{nm} = \tilde{\alpha}_{mn}$. This was the starting point for the calculation of the polarizabilities of isolated PPV oligomers using the TDHF method [15]. In the present work we are interested in nonlocal optical response functions defined by Eq. (21) for a system of M interacting molecules, each made of N carbon atoms. The method used in Refs. [13–15] allows the calculation of response functions to arbitrary order. However, since a Liouville operator needs to be diagonalized, the required memory scales as $(MN)^4$ and the CPU-time as $(MN)^6$, which makes application to large systems impractical. It would be most helpful to use the response functions of individual molecules as building blocks to construct the optical response of the assembly.

Assuming that charge distributions of different molecules do not overlap, we start from the EOM for the density matrix of the entire system and derive a closed EOM for the density matrix of each molecule in a local field. In this case intermolecular charge transfer is excluded, and the interaction between molecules is purely electrostatic, giving rise to excitation energy transfer (EET). From the solution of this equation one immediately obtains the response functions of the isolated molecules, i.e. the molecular polarizabilities $\vec{\alpha}(\omega)$. We then express the polarizabilities of the entire system in terms of these molecular polarizabilities. Intermolecular chemical (exchange) interactions may then be incorporated perturbatively.

2.1. Excitation energy transfer

Restricting ourselves to EET we next derive a closed EOM for a single (arbitrarily chosen) reference molecule of the aggregate. Indices with a prime run over the carbon atoms of this molecule (referred to as A), indices with a double prime run over the atoms of all other molecules (which can be regarded as a second molecule, labeled B), and unprimed indices run over all atoms. $\bar{\rho}$ then has the form

$$\bar{\rho} = \begin{pmatrix} \bar{\rho}^{AA} & \bar{\rho}^{AB} \\ \bar{\rho}^{BA} & \bar{\rho}^{BB} \end{pmatrix}, \quad (28)$$

where $\bar{\rho}^{AA} = (\bar{\rho}_{n'm'})$, $\bar{\rho}^{AB} = (\bar{\rho}_{n'm''})$, etc. Our calculation starts with setting the intermolecular t -matrix elements to zero, i.e.

$$t = t^0 = \begin{pmatrix} t^{AA} & 0 \\ 0 & t^{BB} \end{pmatrix}. \quad (29)$$

In this case the commutator of t^0 with an arbitrary matrix ρ assumes the simple form

$$[t^0, \rho] = \begin{pmatrix} [t^{AA}, \rho^{AA}] & t^{AA} \rho^{AB} - \rho^{AB} t^{BB} \\ t^{BB} \rho^{BA} - \rho^{BA} t^{AA} & [t^{BB}, \rho^{BB}] \end{pmatrix}. \quad (30)$$

Eq. (12) is solved by $\bar{\rho}_{l''n'} = (\bar{\rho}^T)_{n'l''} = 0$, which yields a closed set of equations in which $\bar{\rho}_{r's'}$ couples only to $\bar{\rho}_{r''s''}$. The absence of intermolecular electronic coherences $\bar{\rho}_{n'l''}$ makes the definition of a local field possible, so that Eq. (13) for molecule A, now assumes the form

$$\begin{aligned} i\hbar \delta \dot{\rho}_{n'm'} &= [(t_{r's'}), (\delta \rho_{u'v'})]_{n'm'} \\ &+ \sum_{l'} \Gamma_{n'm'}^{l'} [2\bar{\rho}_{n'l'} \delta \rho_{l'l'} + 2\bar{\rho}_{l'l'} \delta \rho_{n'm'} + 2\delta \rho_{n'm'} \delta \rho_{l'l'} - \bar{\rho}_{n'l'} \delta \rho_{l'm'} - \bar{\rho}_{l'm'} \delta \rho_{n'l'} - \delta \rho_{n'l'} \delta \rho_{l'm'}] \\ &+ \sum_{l''} \Gamma_{n'm'}^{l''} [2\bar{\rho}_{l''n'} \delta \rho_{n'm'} - \delta \rho_{n'l''} \delta \rho_{l''m'}] + (V_{n'}^{\text{loc}} - V_{m'}^{\text{loc}}) (\bar{\rho}_{n'm'} + \delta \rho_{n'm'}), \end{aligned} \quad (31)$$

where the local potential is defined by

$$V_n^{\text{loc}}(t) = V_n(t) + \sum_{l''} U_{n'l''} \delta\rho_{l''l''}(t) . \quad (32)$$

The first term in the sum over l'' in Eq. (31) is a simple charge correction to the second term in the sum over l' , and the product $\sum_{l''} \delta\rho_{n'l''} \delta\rho_{l''m'}$ is of higher order in the electromagnetic field than $\delta\rho$. Expanding $\delta\rho$ according to Eq. (11), and retaining only terms linear in the electric field, we find

$$\begin{aligned} i\hbar\delta\dot{\rho}_{n'm'}^{(1)} &= [(t_{r's'}, (\delta\rho_{u'v'})]_{n'm'} \\ &+ \sum_{l'} \Gamma_{n'm'}^{l'} [2\bar{\rho}_{n'm'} \delta\rho_{l'l'}^{(1)} + 2\bar{\rho}_{l'l'} \delta\rho_{n'm'}^{(1)} - \bar{\rho}_{n'l'} \delta\rho_{l'm'}^{(1)} - \bar{\rho}_{l'm'} \delta\rho_{n'l'}^{(1)}] \\ &+ 2 \sum_{l''} \Gamma_{n'm'}^{l''} \bar{\rho}_{l''l''} \delta\rho_{n'm'}^{(1)} + (V_n^{\text{loc}} - V_{m'}^{\text{loc}}) \bar{\rho}_{n'm'} . \end{aligned} \quad (33)$$

Since $\bar{\rho}_{n'm''} = 0$ we find, that the corresponding equations of motion for $\delta\rho_{n'm''}^{(1)}$ couple only to $\delta\rho_{n'm'}^{(1)}$, and hence

$$\delta\rho_{n'm''}^{(1)}(t) = \delta\rho_{n'm'}^{(1)}(t) = 0 \quad (34)$$

is the only solution satisfying the initial condition $\delta\rho_{n'm''}^{(1)}(t=0) = \delta\rho_{n'm'}^{(1)}(t=0) = 0$.

Eq. (33) yields the induced one-electron density matrix $\delta\rho_{n'm'}^{(1)}$. This equation is closed in the space of a single molecule, as the effects of intermolecular interactions are incorporated in V^{loc} by a mean field approach. The first two terms in the rhs. describe the evolution of the density matrix of the isolated molecule. The third term represents the interaction with the electrostatic field created by the static charge density of the other molecules, and the fourth term describes the interaction with the local field, which is the sum of the external field and the electric field created by the induced charge distribution of all other molecules. By solving this equation (in the frequency domain) we obtain for the induced charge density of the reference molecule

$$\delta\tilde{\rho}_{n'n'}^{(1)}(\omega) = \sum_{l'} \tilde{\alpha}_{n'l'}(\omega) V_l^{\text{loc}}(\omega) . \quad (35)$$

$\tilde{\alpha}$ represents the nonlocal response function of a single molecule in the electrostatic field created by the ground state charge distribution of the surrounding molecules. It can be calculated as $\tilde{\alpha}_{nm}(\omega)$ in Eq. (24) with the Green's function \mathcal{G}' of the homogeneous part of Eq. (33) obtained by setting $V^{\text{loc}} = 0$.

2.2. Aggregate response in terms of molecular response functions

In the following we shall replace the site indices n by double indices $c\gamma$, denoting the γ th atom in the c th molecule. Eq. (21) then assumes the form

$$\delta\rho_{c\gamma,c\gamma}^{(1)} = \sum_{d\mu} \tilde{\alpha}_{c\gamma,d\mu} \tilde{V}_{d\mu} \quad (36)$$

with the linear, nonlocal response function $\tilde{\alpha}_{c\gamma,d\mu}$ of the entire molecular assembly. As shown in the last section, the induced charges can also be expressed by the local field, and Eq. (35) in this notation reads

$$\delta\tilde{\rho}_{c\gamma,c\gamma}^{(1)} = \sum_{\mu} \tilde{\alpha}_{c\gamma,c\mu} \tilde{V}_{c\mu}^{\text{loc}} , \quad (37)$$

where the coefficients $\tilde{\alpha}_{c\gamma,c\mu}$ are the response functions for molecule c in the presence of the surrounding molecules.

Using the last relation when resolving the definition of the local field

$$\tilde{V}_{d\mu}^{\text{loc}} = \tilde{V}_{d\mu} + \sum_{r\rho} (1 - \delta_{dr}) U_{d\mu,r\rho} \delta \tilde{\rho}_{r\rho,r\rho} \quad (38)$$

for the external field $\tilde{V}_{d\mu}$, substituting into Eq. (36), and comparison to Eq. (35) yields an equation for $\tilde{\alpha}_{c\delta,d\beta}$, the solution of which is

$$\tilde{\alpha}_{c\delta,d\beta} = \sum_{\gamma} \tilde{\alpha}_{c\delta,c\gamma} S_{c\gamma,d\beta}, \quad (39)$$

with

$$S_{c\gamma,d\beta}^{-1} = \delta_{c,d} \delta_{\gamma,\beta} - \sum_{\sigma} U_{c\gamma,d\sigma} \tilde{\alpha}_{d\sigma,d\beta} (1 - \delta_{c,d}). \quad (40)$$

This equation relates the nonlocal, linear response functions of a system of interacting molecules to the nonlocal, linear polarizabilities of the individual molecules. The polarizability is obtained by replacing $n \rightarrow (c\delta)$ and $m \rightarrow (d\beta)$ in Eq. (19).

Eq. (39) provides a convenient procedure for computing the linear response functions of aggregates, based on the knowledge of individual molecular response functions. The required memory in this approach scales as MN^4 and CPU time as MN^6 , compared to $(MN)^4$ and $(MN)^6$, respectively, when solving the TDHF equations of the entire system. For large aggregates this makes a decisive difference, and a further reduction in computational cost can be achieved for ordered aggregates by assuming identical polarizabilities for all M molecules.

2.3. The role of intermolecular charge exchange

So far we have related the optical properties of aggregates to molecular properties, by neglecting chemical intermolecular interactions, i.e. neglecting the exchange integrals between different molecules. When intermolecular charge exchange is switched on, numerical solution of Eq. (13) for a dimer showed a wide range of distances, for which $\tilde{\rho}_{n'm''}$ is very small, but the response functions change considerably. Therefore it is interesting to compute the effects of intermolecular charge exchange perturbatively, in order to take advantage of the reduction in computational cost when using an equation like Eq. (39). The calculation of the polarizability of a reference molecule is presented in Appendix A, resulting in

$$\tilde{\alpha} = \tilde{\alpha}^{\text{EET}} + \lambda^2 \tilde{\alpha}^{\text{CHT}} + \text{O}(\lambda^3). \quad (41)$$

Here λ is the perturbation parameter defined in Eq. (44), $\tilde{\alpha}^{\text{EET}}$ is the linear polarizability in the absence of intermolecular charge exchange ($t^\perp = 0$), and the first correction is of second order in λ . As shown in Appendix A we find

$$\tilde{\alpha}_{n't'}^{\text{EET}} = \sum_{k'} (G_{n'n'k't'}^0(\omega) - G_{n'n't'k'}^0(\omega)) \tilde{\rho}_{k't'}^0, \quad (42)$$

$$\tilde{\alpha}_{n't'}^{\text{CHT}} = \sum_{k'l'} G_{n'n'k'l'}^0(\omega) \sum_{r's'} \mathcal{L}_{k'l'r's'}^0(0, \tilde{\rho}^{\Xi}) \tilde{U}_{r's',t'}(\omega) + \sum_{k'} (G_{n'm'k't'}^0(\omega) - G_{n'm't'k'}^0(\omega)) \tilde{\rho}_{k't'}^{\Xi}. \quad (43)$$

Substituting these results into Eq. (41), setting $\lambda = 1$, and utilizing Eq. (39) finally yields the aggregate polarizability to lowest order in the intermolecular hopping integrals.

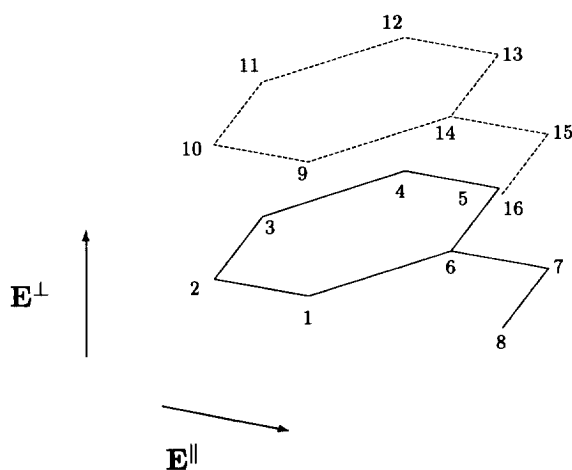


Fig. 1. Geometry of the dimer and atom labels. Bond angles are 120° , except $\alpha(r_{6,7}, r_{7,8}) = 128^\circ$, and distances are: $r_{1,2} = r_{2,3} = r_{3,4} = r_{4,5} = r_{5,6} = r_{6,1} = 1.39 \text{ \AA}$, $r_{6,7} = 1.44 \text{ \AA}$, $r_{7,8} = 1.33 \text{ \AA}$. Shown also are the two field orientations E^\perp and E^\parallel .

3. Application to dimers of PPV-oligomers

We now investigate a dimer of PPV oligomers, by applying the method used in Ref. [15]. All results are for a pair of parallel PPV oligomers at a distance d apart, and unless otherwise indicated we set $d = 2 \text{ \AA}$. The electric field vector of the incoming light be either parallel (E^\parallel) or perpendicular (E^\perp) to the molecular plane, and E^\parallel is assumed to be parallel to the long axis of the oligomers (see Fig. 1).

We first restrict ourselves to a reference system, in which the intermolecular hopping integrals t^\perp are set to zero. From Eq. (31) follows immediately, that $i\hbar \text{Tr}_A \delta \rho^{AA} = \text{Tr}_A [t^{AA}, \delta \rho^{AA}] = 0$, so that the total charge on each molecule is conserved, and we will refer to this situation as excitation energy transfer (EET). When invoking the dipole approximation, a perpendicular homogeneous field has no effect at all in the EET case, as the driving term in Eq. (13) vanishes (for intramolecular components $(r_n \cdot E - r_m \cdot E) = 0$, and for intermolecular components $\bar{\rho}_{n'm''}^{AB} = \delta \rho_{n'm''}^{AB}(t) = 0$).

Response functions depend on the orientation of the electric field relative to the molecular plane. Their magnitude is much larger, when the field vector lies in the PPV plane, which is a consequence of the chemical bond structure. In the absence of intermolecular coherences the electronic wave function is delocalized over one molecule, and – when responding to an external force – electrons can move only within each molecule (in the PPV plane). If the field lies in this plane, electrons move according to the concomitant force, resulting in a large polarization. As shown in Ref. [15], a field in the long axis of an oligomer produces the largest polarization responsible for the lowest lying absorption. Since electrons cannot move perpendicular to the PPV-plane, a field in this direction cannot dislocate electrons and no response is observed for the dimer if the hopping integrals are set to zero (α vanishes exactly). Even if intermolecular hopping is allowed, our numerical calculations show, that the response functions are smaller by 3 orders of magnitudes. Therefore we focus on the parallel case below.

The LFA models each molecule of an aggregate as a point dipole exposed to a local field, which is the sum of the external field and the induced field created by all other molecules. As shown in Appendix B the aggregate polarizability can then be expressed by the molecular polarizabilities. In Fig. 2 we show real (left) and imaginary (right) part of the linear polarizability $\alpha(\omega)$ for the distances $d = 2, 3$, and 4 \AA (from top to bottom). The solid curves show the exact results for EET, calculated by solving the TDHF equations of

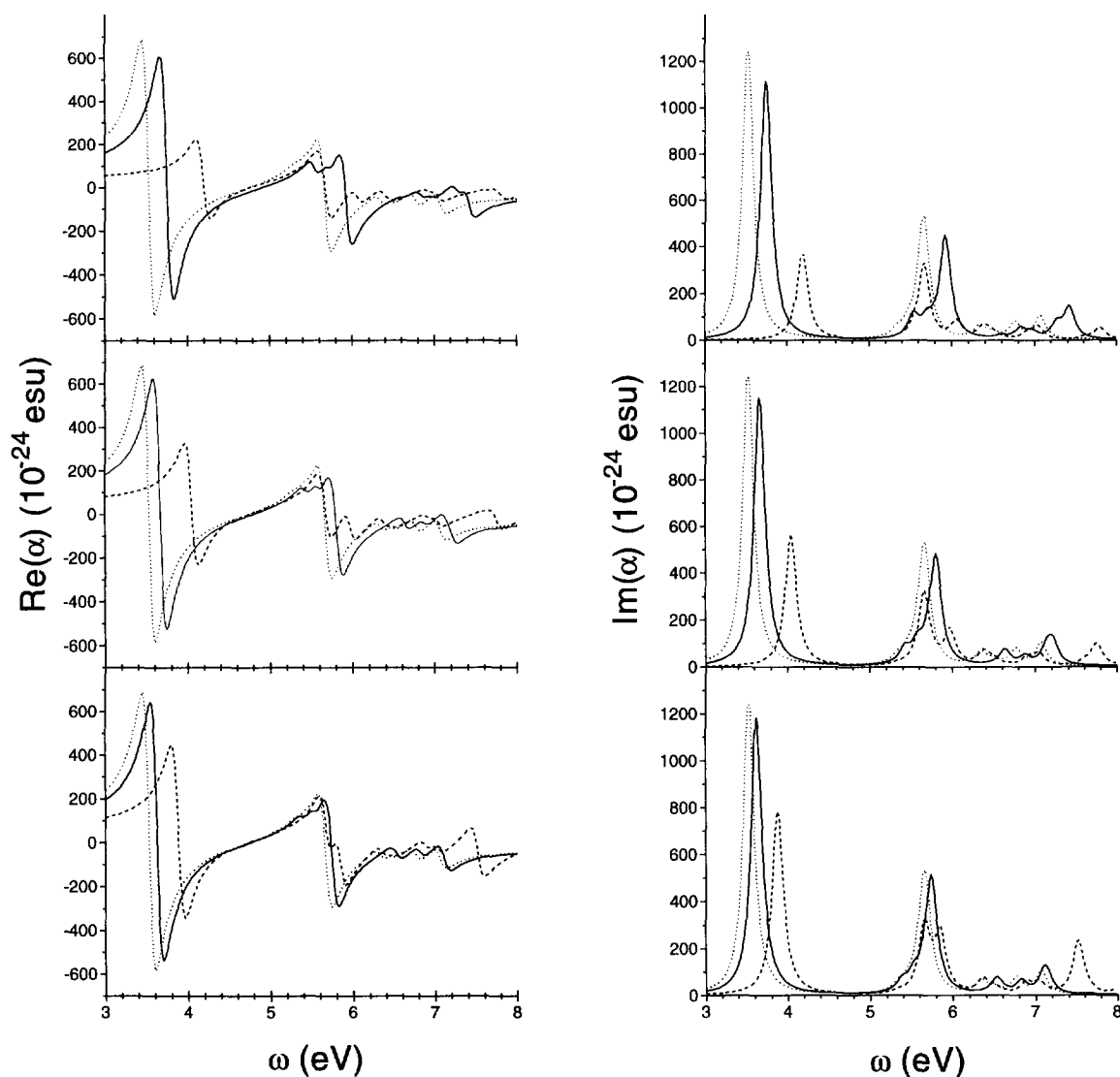


Fig. 2. Real (left) and imaginary (right) part of the frequency dependent linear polarizability $\alpha(\omega)$ as a function of distance ($d = 2, 3,$ and 4 \AA from top to bottom). Solid lines show the exact EET results, dashed lines the point-dipole approximation (see text), and the dotted lines serve as a reference for infinite distance (i.e. twice the monomer polarizabilities). The electric field is parallel to the PPV plane.

the entire system, and the dashed curves show LFA results, obtained by Eq. (67). For large distances both results converge towards twice the polarizability of isolated oligomers, which is also shown as dotted lines. Intermolecular EET affects the position and the height of peaks slightly, but leaves the overall shape of the spectra unchanged. In particular we observe a blue shift of the dimer absorption, which reflects the repulsive dipole-dipole interaction for this configuration. The point-dipole approximation overestimates this blue-shift. Furthermore part of the oscillator strength of the lowest absorption is redistributed, giving rise to higher lying absorptions, which are absent in the exact result. A distance of 6 \AA (not shown) already yields the monomer polarizability.

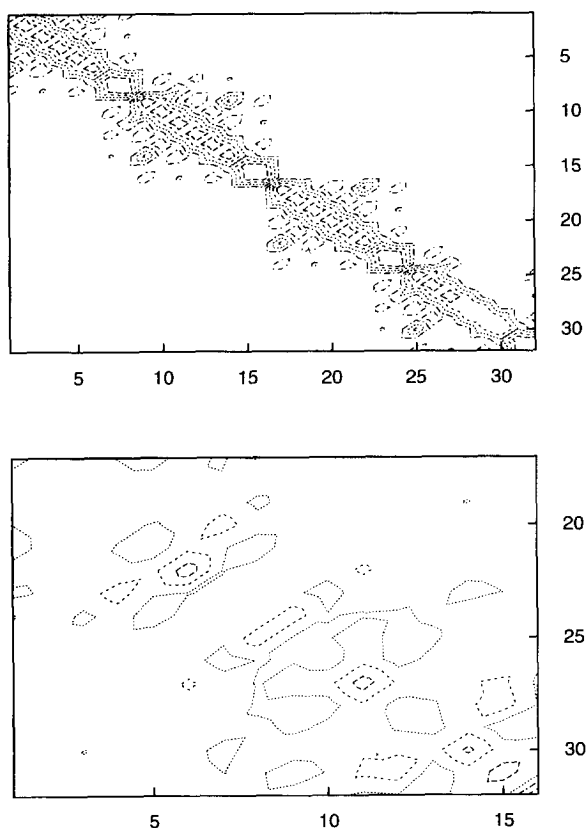


Fig. 3. Top: ground state density matrix $\bar{\rho}_{nm}$ of a dimer with intermolecular hopping integrals. Bottom: the magnified, intermolecular components $\bar{\rho}_{n'm''}$. The distance between molecules is $d = 2$ Å. For site labels see Fig. 1.

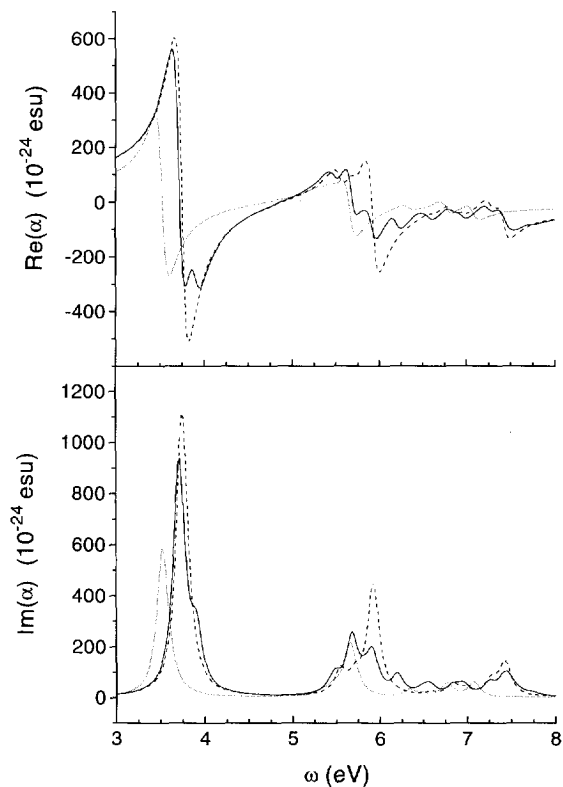


Fig. 4. Real (top) and imaginary (bottom) part of $\alpha(\omega)$ for a single oligomer with 2 units (dotted), a pair of these oligomers with intermolecular EET (dashed), and intermolecular EET and CHT (solid).

In order to examine the effects of intermolecular hopping, we next consider both, t^{\parallel} and t^{\perp} . The latter be given by the exponential form Eq. (6) for atoms facing each other ($t_{1\beta,2\beta}^{\perp}$). All other intermolecular hopping integrals ($t_{1\beta,2\delta}^{\perp}, \beta \neq \delta$) are set to zero. In this case, which we will refer to as charge transfer (CHT), weak chemical coherences between the two molecules representing the dimer develop, as can be seen from the reduced ground state single electron density matrix shown in Fig. 3. The stationary solution $\bar{\rho}_{nm}$ of Eq. (12) does not depend on the interaction V_n , i.e. the electric field, and therefore the result is the same for both orientations. As discussed in the derivation of the local field equation Eq. (31) for EET, intermolecular components $\bar{\rho}_{n'm''}$ vanish. First order corrections due to intermolecular hopping leave intramolecular components unchanged and give rise only to intermolecular components [see Eq. (47)]. This explains the negligible difference of intramolecular coherences for both situations (therefore we do not show $\bar{\rho}$ for EET here). Intramolecular components $\bar{\rho}^{AA}$ and $\bar{\rho}^{BB}$ are essentially identical to $\bar{\rho}$ of a monomer, telling us that charge distribution and intramolecular chemical bonds do not change very much upon dimerization. Intermolecular components $\bar{\rho}^{AB}$, which are shown in the bottom panel of Fig. 3 are smaller by two orders of magnitude, and the strongest intermolecular coherence occurs at the vinylene ends of the oligomers.

We next compare the linear polarizability $\alpha(\omega)$ of a single PPV oligomer, a dimer with intermolecular EET, and a dimer with both, intermolecular EET and CHT in Fig. 4. In order to show the effects of intermolecular

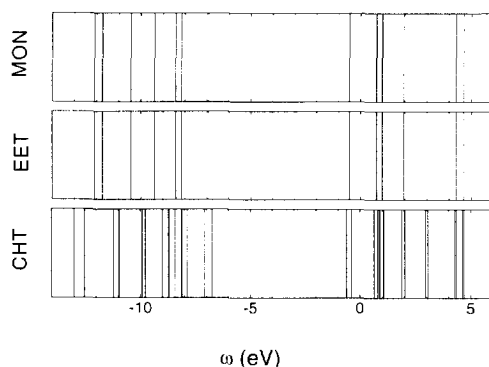


Fig. 5. Hartree-Fock energies for an oligomer with 2 units (top), a dimer of such oligomers with intermolecular EET (middle), and a dimer with intermolecular EET and CHT (bottom). Some of the levels are separated by 10–15 meV and thus appear as one line.

hopping integrals, which decrease exponentially with distance, we choose a relatively small separation of $d = 2$ Å. When charge transfer is switched on new peaks arise, and the lowest lying absorption is red shifted with respect to the EET case. This reflects the attractive chemical interaction, induced by the intermolecular hopping integrals. For larger separations $\alpha(\omega)$ converges towards twice the monomer polarizability, which is in accord with the macroscopic size scaling of an aggregate of non-interacting molecules.

In order to analyze the physical significance of these results we now apply the electronic oscillator analysis used in [15]. It was shown that the linearized TDHF equations can be transformed into the EOM of $N^2/2$ coupled electronic oscillators with coordinates Q_ν and momenta P_ν . Only few of these oscillators contribute significantly to the linear response, which makes this representation very attractive. By displaying the coordinates of these oscillators in the site representation and in the Hartree-Fock molecular orbital (HFMO) representation [13–15] we obtain information on intermolecular coherences and the states involved in each transition.

We first compare the Hartree-Fock energies of a monomer, a dimer with EET, and a dimer with EET and CHT in Fig. 5. The corresponding HFMOs are shown in Figs. 6, 7 and 8. The first observation is that the intermolecular Coulomb interaction does not change the Hartree-Fock (HF) energies. Monomer and dimer have the same HF-energies, each level being doubly degenerate. The corresponding two HF states are those with components of the monomer states on molecule A (B) and zero components on molecule B (A). Switching on intermolecular hopping breaks this degeneracy and leads to a splitting of the HF energies. The HFMOs for CHT are obtained by the linear combinations $c_{nm}^{0,a} \pm c_{nm}^{0,b}$, where $c_{nm}^{0,a}$ and $c_{nm}^{0,b}$ denote the two degenerate HFMOs for EET. As in the case of isolated oligomers, the unoccupied states ($L+i$) can be constructed from the occupied ones ($H-i$) by flipping the sign of every other component [15], which is a consequence of the pairing theorem [18]. Therefore we display only the occupied states.

We next show the five strongest oscillators (having an oscillator strength $f > 10\%$ of f_{\max}) for EET in Fig. 10 (HFMO representation) and Fig. 9 (site representation). Fig. 9 reveals, that the absence of intermolecular hopping integrals is reflected in vanishing intermolecular coherences of the oscillators. The HFMO representation Fig. 10 provides information on the molecular states involved in each transition. As for the monomers, the largest components of Q_1 correspond again to the HOMO–LUMO transition. The next strongest coherences indicate $(H-1, L+1)$ transitions. (Note, that all levels are doubly degenerate, so that both level 15 and 16 are HOMOs). Similarly, the next two oscillators (at 5.54 and 5.92 eV) are characterized by $(H-2, L+2)$ transitions, involving states with negligible components at the vinylene units. This indicates dynamics on the phenylene rings, and the corresponding absorption lines depend only weakly on the size of the oligomers.

The oscillators for CHT are more uniformly distributed, and we find eight oscillators, having an oscillator strength larger than 10% of the strongest transition. They are depicted in Fig. 12 (site representation) and Fig. 11 (HFMO representation). Due to the weak intermolecular bonds intramolecular coherences develop for

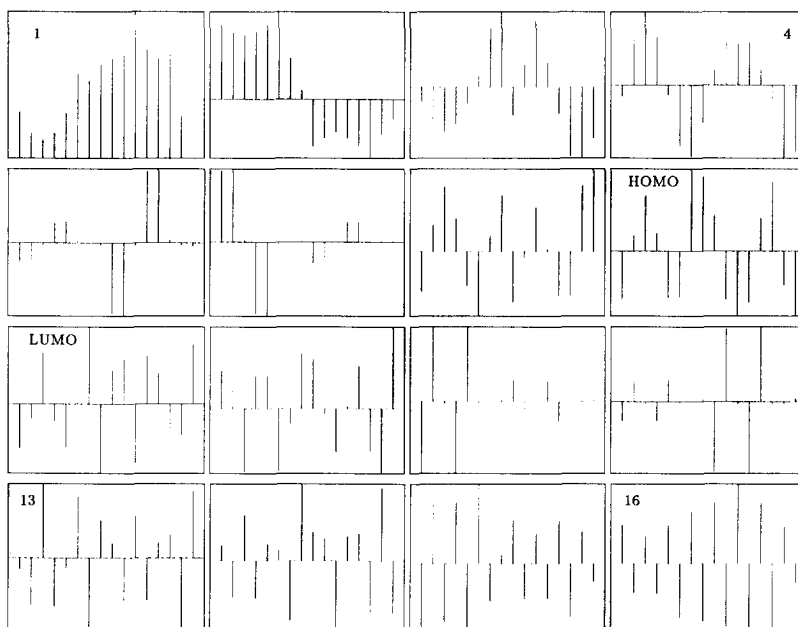


Fig. 6. HFMOs c_{ij} of an oligomer with 2 repeat units. The i th panel corresponds to the i th orbital and shows the components c_{ij} versus $j, j = 1, \dots, 16$.

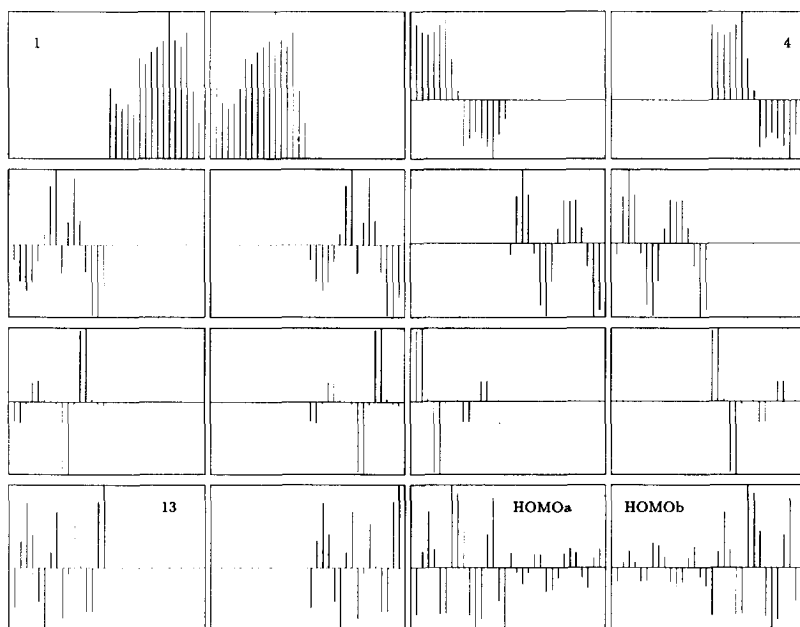


Fig. 7. The sixteen occupied HFMOs of a dimer with intermolecular EET. The sixteen unoccupied HFMOs are not shown, as they can be constructed from the occupied ones (see text).

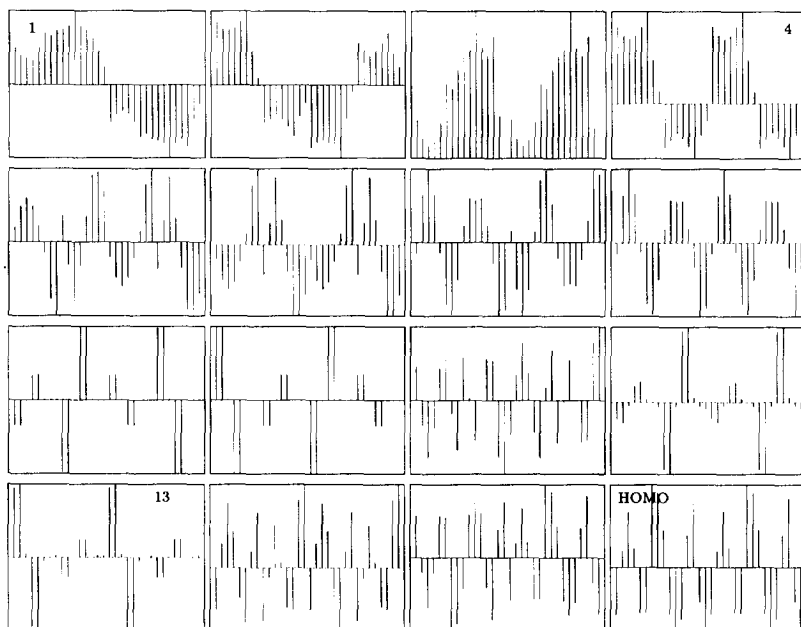


Fig. 8. The sixteen occupied HFMOs of a dimer with both, intermolecular EET and CHT.

all oscillators. The lowest absorptions are dominated by a $(H, L + 2)$ transition (3.71 eV) and a $(H - 1, L)$ transition (3.90 eV). The lines around 5.5 eV involve again states with negligible components on the vinylene rings.

Finally, the nonlocal polarizabilities at the frequencies of the dominant ($> 10\%$ of f_{\max}) oscillators discussed above are shown in Figs. 13 and 14. Since we study a dimer of small oligomers (2 repeat units) finite size effects still affect our results considerably [15]. At the lowest absorption frequency the inner vinylene units are strongly correlated. As in the monomer case, the absorptions around 5.5 eV show strong correlations between phenylene rings of the same molecule. Moreover, strong correlations between phenylene rings on different molecules occur. For EET 5.54 eV correlates the first rings of the monomers, and 5.92 the second rings. A similar pattern can be observed for CHT.

4. Discussion

Recent investigations of PPV and other conjugated molecules in thin films had raised the issue of the role of intermolecular charge transfer in their optical response [1–4]. This was the primary motivation for the present study of the effects of intermolecular Coulomb and exchange interactions on optical properties of aggregates of conjugated molecules. We calculated the frequency dependent local and nonlocal linear optical polarizabilities of a model system of M molecules, each having N carbon atoms. To reduce computational cost, it is customary to invoke the point-dipole (long wavelength) approximation and calculate the optical response using the local field approximation [12,19,20]. These approximations are avoided in the present study. Our analysis is based on the time dependent Hartree–Fock (TDHF) equations for the reduced one-electron density matrix $\rho_{nm}(t)$ derived for the Pariser–Parr–Pople (PPP) Hamiltonian for π electrons. Neglecting intermolecular exchange interaction by setting intermolecular hopping integrals ($t_{n'm''}$) to zero we formally eliminated the remaining intermolecular Coulomb interaction ($U_{n'm''}$) by introducing a local field, which is the sum of the external field, and the field

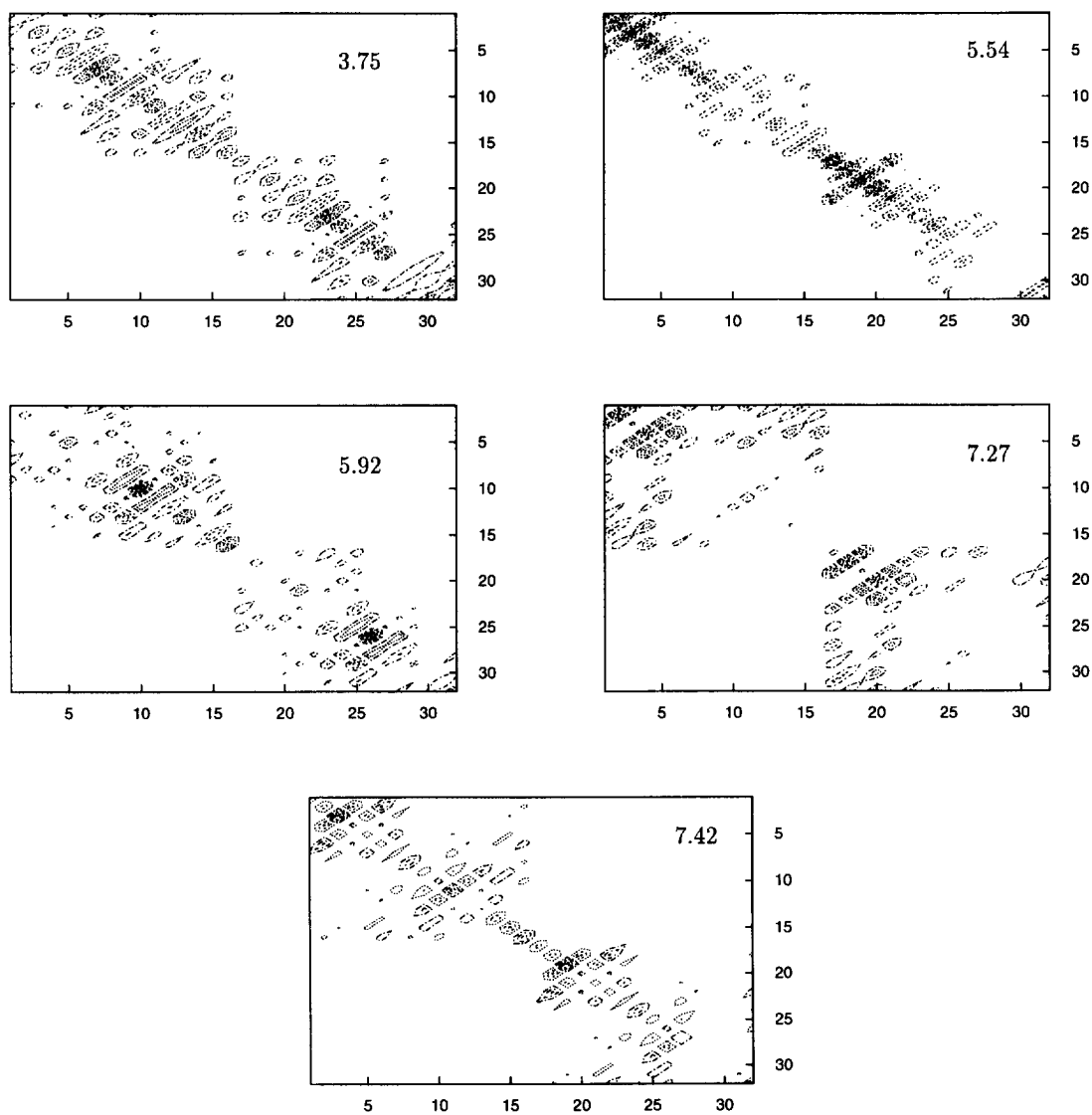


Fig. 9. EET: The strongest 5 oscillators, having an oscillator strength larger than 10% of the strongest transition, in the site representation. The corresponding oscillator frequencies in eV are indicated in each panel.

resulting from the induced charge distribution at all other molecules. This leads to the TDHF equations [Eq. (33)] for an arbitrarily chosen reference molecule of the aggregate, which are closed in the space of that molecule. These equations, which rigorously follow from the TDHF equations of the entire aggregate, differ from the TDHF equations for an isolated molecule by the third term on the rhs, which describes the interactions with the electric field of the ground state charge distribution of all other molecules. Their solution Eq. (35) defines the modified molecular nonlocal response functions $\bar{\alpha}_{c\beta,c\gamma}(\omega)$, $c = 1, \dots, M$. We next derived Eq. (39), which expresses the aggregate polarizability $\bar{\alpha}_{c\beta,d\gamma}$ in terms of the molecular polarizabilities $\bar{\alpha}_{c\beta,c\gamma}$. This was done by comparing the induced charges calculated in terms of both quantities. The evaluation of this formula requires the computation of M polarizabilities, so that required memory scales as $M N^4$, and CPU time as

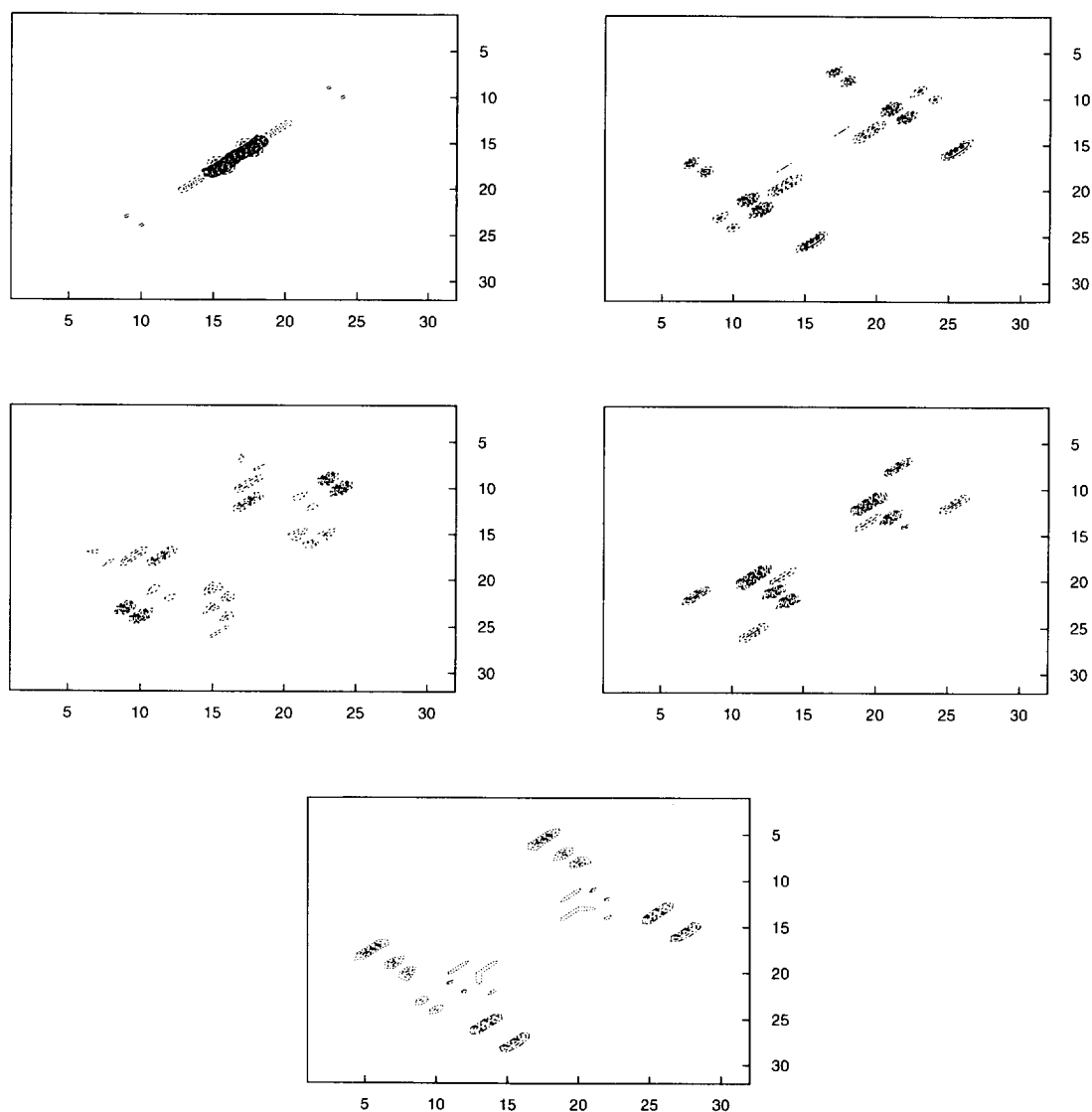


Fig. 10. EET: The strongest 5 oscillators in the HFMO representation numbered as in Fig. 9.

MN^6 . This leads to a considerably reduced computational cost, as the solution of the TDHF equations for the assembly scales as $(MN)^4$, and $(MN)^6$ respectively. For periodic systems with identical polarizabilities for all M molecules the computational effort is further reduced to N^4 (memory) and N^6 (CPU time), respectively.

We next investigated the effects of intermolecular charge exchange perturbatively. By expanding the molecular polarizabilities as a power series in the intermolecular components t^Δ of the t matrix [Eq. (41)] we found, that the lowest corrections to the local field result are second order in t^Δ . The modified aggregate polarizability is again determined by the molecular polarizabilities via Eq. (39).

In the present treatment we consider spatially extended molecules, so that the local field defined as the sum of the external field and the field of the induced charges of all other molecules is not uniform across each molecule. The resulting expression Eq. (39) for the aggregate polarizability is therefore applicable to an

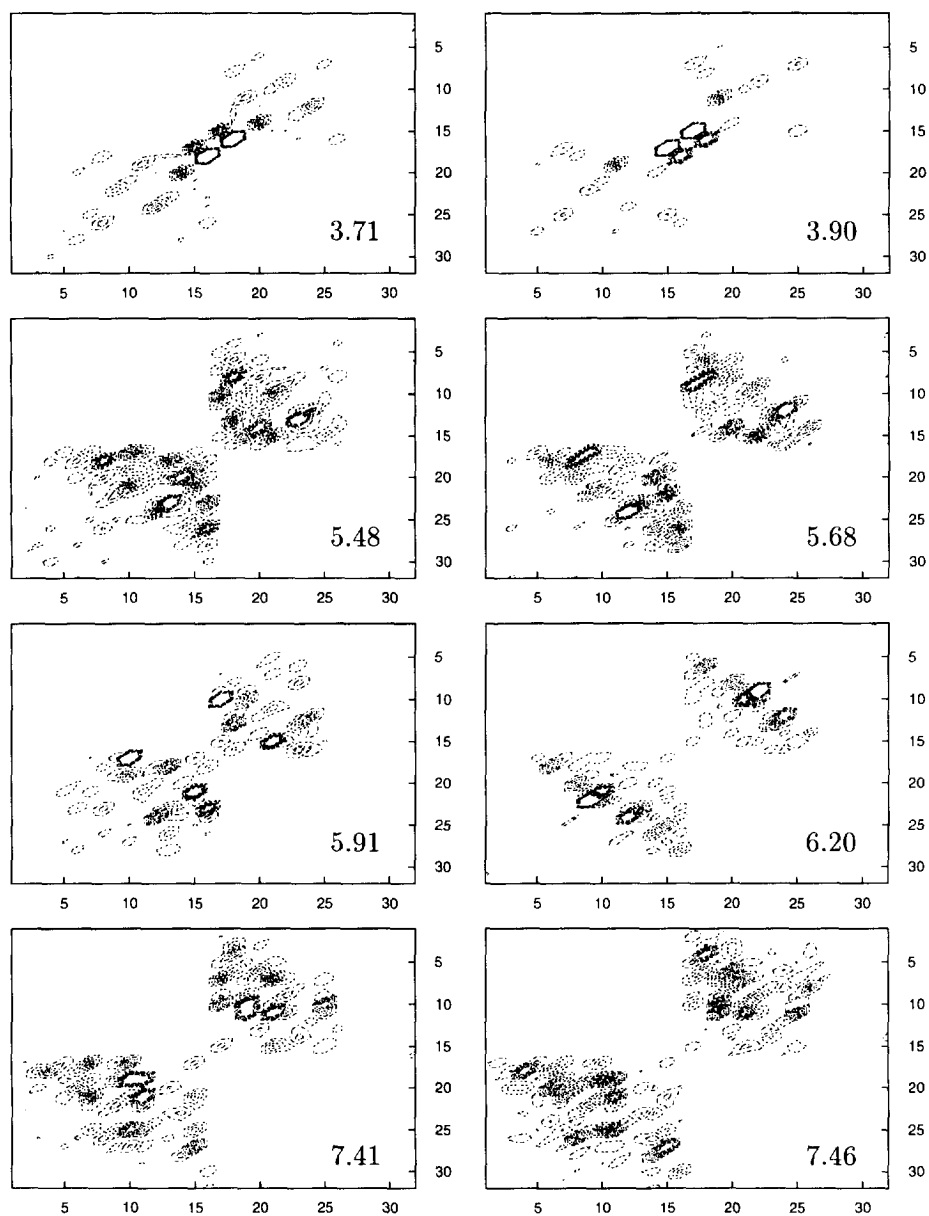


Fig. 11. CHT: The strongest 8 oscillators, having an oscillator strength larger than 10% of the strongest transition, in the HFMO representation. The corresponding oscillator frequencies in eV are indicated in each panel.

aggregate of spatially extended molecules at arbitrarily close separations. Furthermore the modification of the molecular polarizabilities by the ground state charge distribution of neighboring molecules is fully taken into account.

Finally we investigated a dimer of PPV oligomers numerically. Response functions are largest, if the field is parallel to the molecular plane. A perpendicular field results in response smaller by 3 orders of magnitude. When setting intermolecular hopping integrals to zero we found that intermolecular EET induces a blue-shift

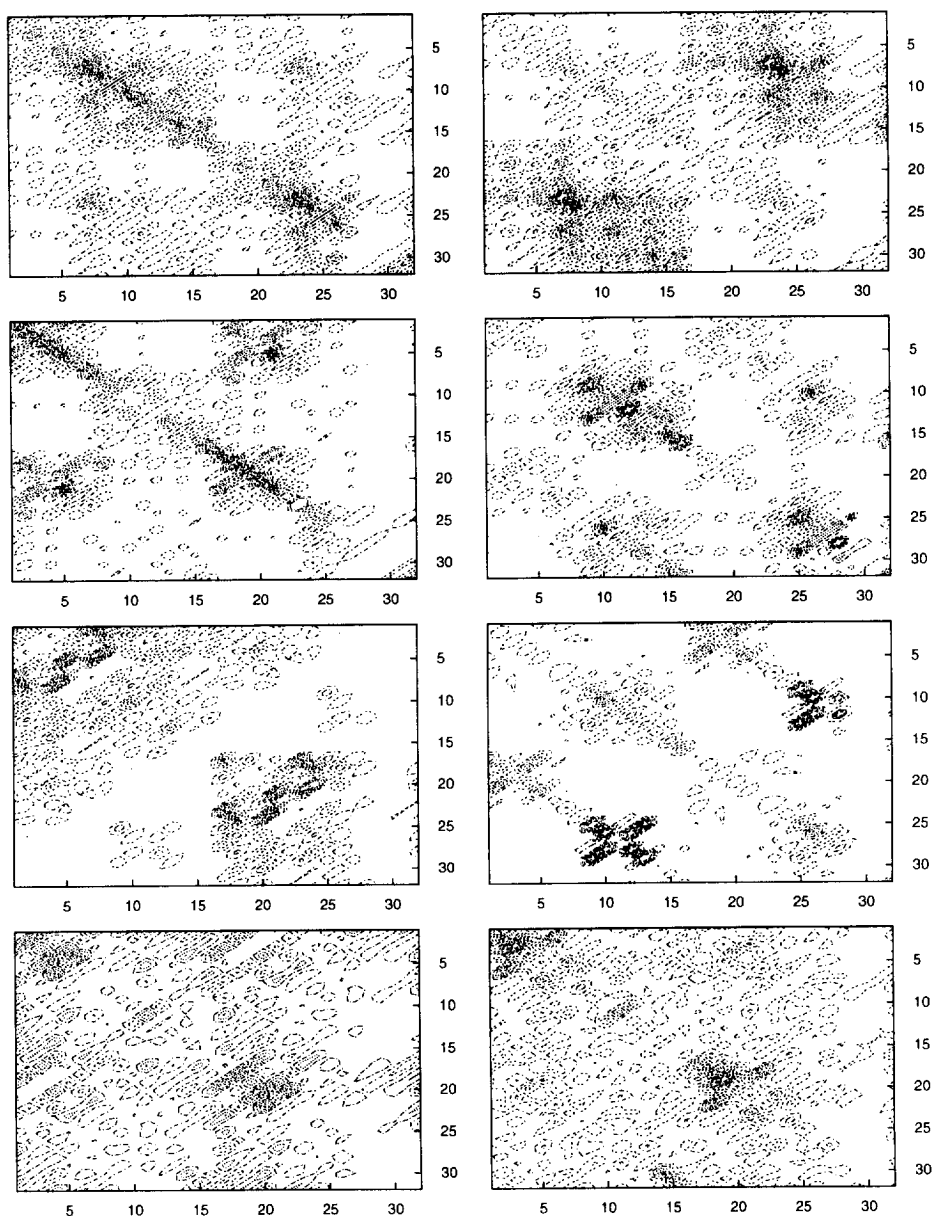


Fig. 12. CHT: The strongest 8 oscillators in the site representation numbered as in Fig. 11.

of the dimer absorption. Replacing the two interacting oligomers by point dipoles is a crude approximation, which considerably overestimates the blue-shift of the dominant absorption line (see Fig. 2). Since the oligomer separation is smaller than the oligomer size, the full interaction of the molecular charge distributions has to be taken into account in order to properly describe the dimer absorption.

When intermolecular hopping t^A is incorporated, the ground state density matrix did hardly change; Neither the charge distribution, nor the intramolecular bonding structure of the oligomers changed significantly. As shown in Fig. 3, the only effect was the appearance of weak intermolecular electronic coherences, which are

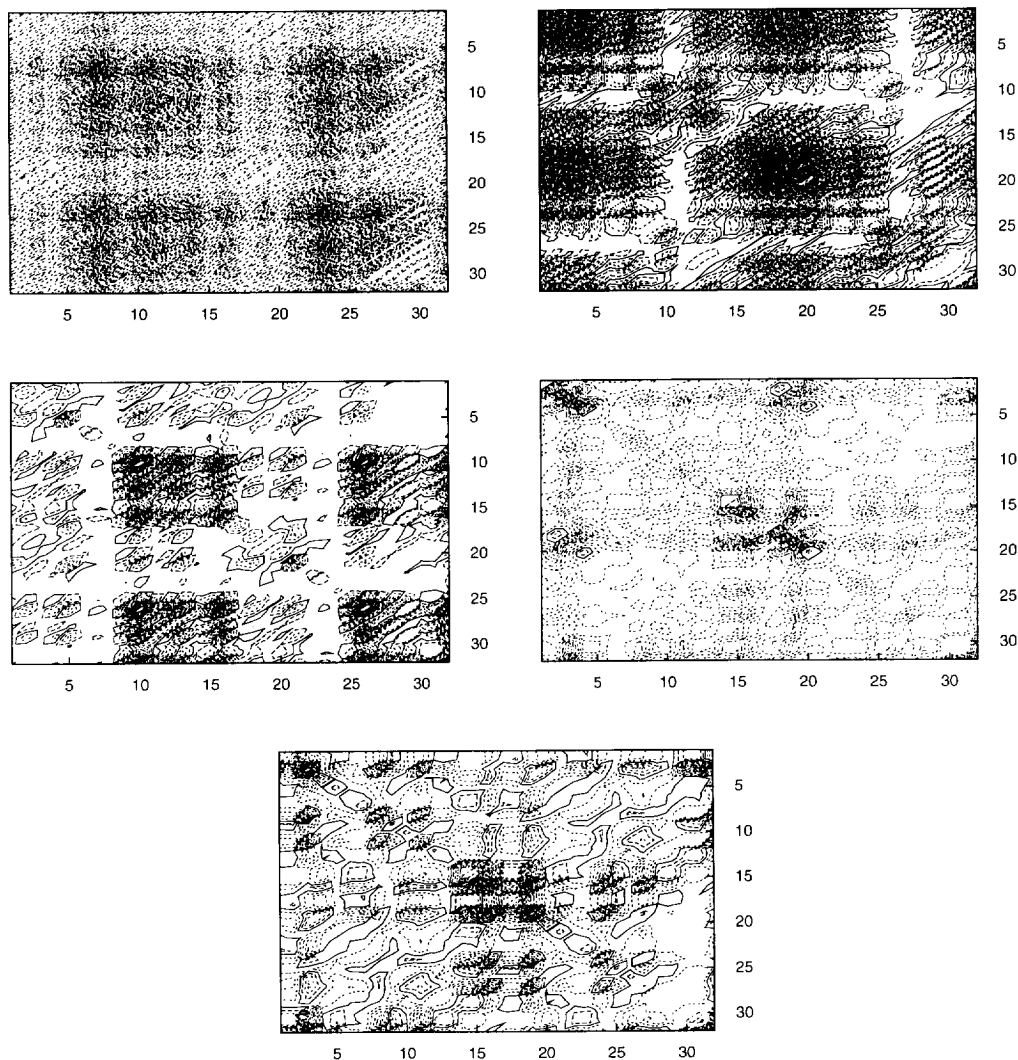


Fig. 13. EET: The nonlocal response functions $\text{Im}(\tilde{\alpha}_{nm}(\omega))$ at the frequencies of the strongest 5 oscillators numbered as in Fig. 9.

strongest at the vinylene ends. CHT results in a red shift of the dominant absorption and induces new absorption peaks at higher frequencies (Fig. 4).

We also analyzed our results in terms of the electronic oscillator representation, which provides information on electronic coherences and the relevant states for each transition. As shown in Refs. [13,14], all oscillators contributing to the linear response have B_u symmetry. Oscillators with A_g symmetry do not affect the linear response, but become important for higher order response functions. This issue and the extension of Eq. (39) to the nonlinear hyperpolarizabilities deserve a further study. The site representation of the dominant oscillators shows intermolecular coherences only in the presence of CHT (Figs. 9 and 12). In this case the number of dominant oscillators is larger, compared to the EET case. An analysis of the HFMO showed that intermolecular EET does not change the energy levels of the monomer (Fig. 5). The orbitals of the dimer are direct products of the monomer orbitals (Figs. 7 and 8), and hence are doubly degenerate. Charge transfer removes this degeneracy (Fig. 5), and the HFMOs are linear combinations of the degenerate states of EET (Fig. 8). By depicting the

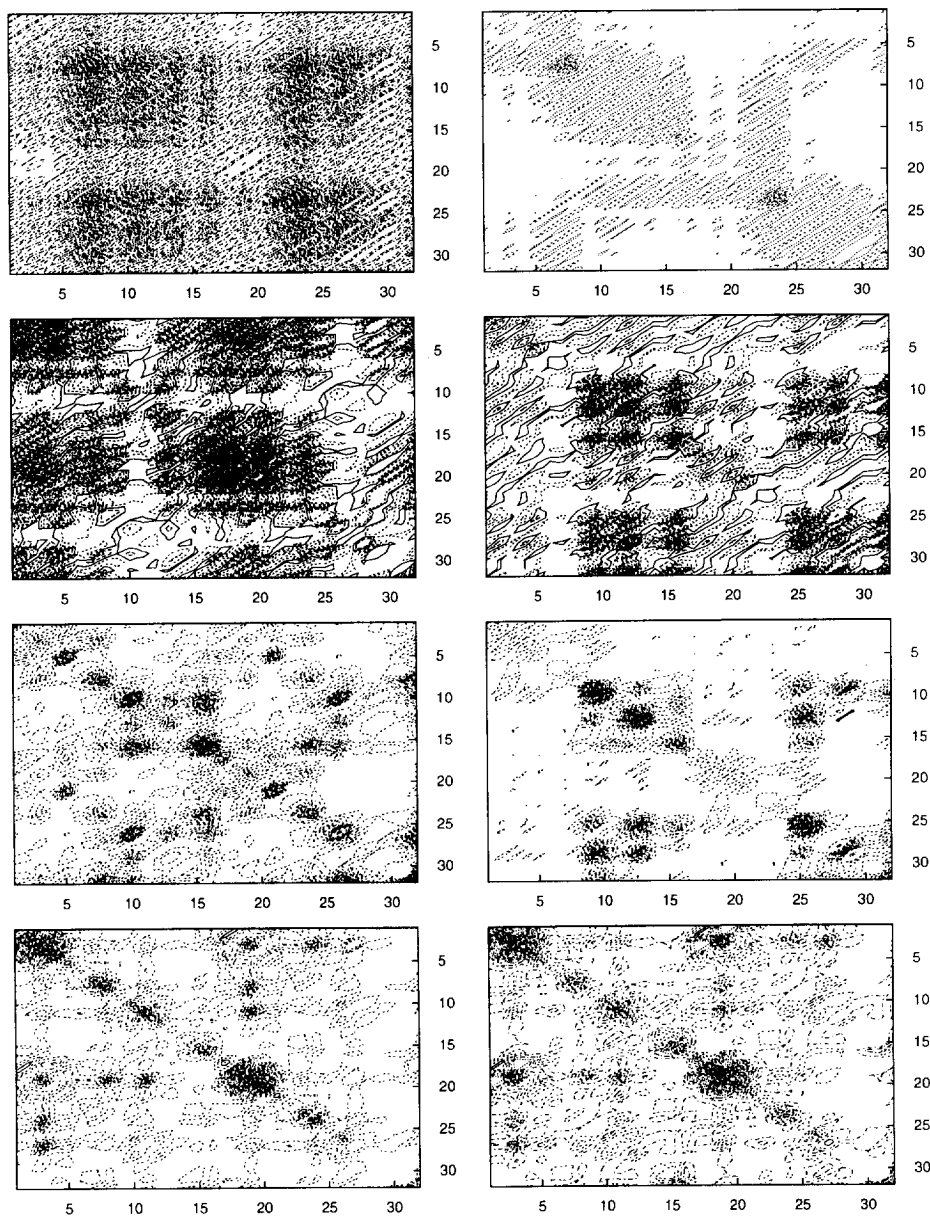


Fig. 14. CHT: The nonlocal response functions $\text{Im}(\tilde{\alpha}_{nm})$ at the frequencies of the strongest 8 oscillators numbered as in Fig. 11.

dominant oscillators in the HFMO representation we identified the states involved in each transition and studied their localization properties. The calculated nonlocal polarizabilities for EET (Fig. 13) and CHT (Fig. 13) helped identifying the parts of the molecule, which are relevant for the various optical transitions.

Acknowledgements

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Appendix A. The role of intermolecular charge exchange

In this section we describe the perturbative expansion of the molecular polarizabilities in the intermolecular t -matrix. Our goal is the derivation of EOMs for the density matrix, which are closed in the coordinates of a reference molecule. Hereby we obtain a molecular polarizability, which can again be used to construct the aggregate polarizability according to Eq. (39).

We assume an intermolecular hopping term of the form

$$t = t^0 + \lambda t^\Delta, \quad (44)$$

where

$$t^\Delta = \begin{pmatrix} 0 & t^{\Delta B} \\ t^{\Delta A} & 0 \end{pmatrix}. \quad (45)$$

The solution of Eq. (12) can then be expanded as

$$\bar{\rho} = \bar{\rho}^0 + \lambda \bar{\rho}^\Delta + \lambda^2 \bar{\rho}^\Xi + O(\lambda^3), \quad (46)$$

where $\bar{\rho}^0$ is the solution of Eq. (12) for $t = t^0$. Substituting Eq. (44) and Eq. (46) into Eq. (12) and solving to first order in λ yields

$$\bar{\rho}^\Delta = \begin{pmatrix} 0 & \bar{\rho}^{\Delta, AB} \\ \bar{\rho}^{\Delta, BA} & 0 \end{pmatrix}, \quad (47)$$

and $\bar{\rho}^{\Delta, AB}$ is the solution of the following inhomogeneous system of linear equations:

$$\begin{aligned} \sum_{r'} \bar{\rho}_{n'r', r'm''}^0 t_{r'm''}^\Delta - \sum_{r''} t_{n'r'', r'm''}^\Delta \bar{\rho}_{r''m''}^0 &= \sum_{r'} t_{n'r', r'm''}^0 \bar{\rho}_{r'm''}^\Delta - \sum_{r''} \bar{\rho}_{n'r'', r'm''}^\Delta t_{r''m''}^0 \\ &+ \sum_l \Gamma_{n'm'', l}^l \bar{\rho}_{ll}^0 \bar{\rho}_{n'm''}^\Delta - \sum_{l'} \Gamma_{n'm'', l'}^{l'} \bar{\rho}_{n'l'}^0 \bar{\rho}_{l'm''}^\Delta - \sum_{l''} \Gamma_{n'm'', l''}^{l''} \bar{\rho}_{l''m''}^0 \bar{\rho}_{n'l''}^\Delta. \end{aligned} \quad (48)$$

Hence the first order corrections of intermolecular charge exchange give rise to electronic coherences between molecules, but do not affect existing, intramolecular bonds or the ground state charge distribution (i.e. $\bar{\rho}^{AA}$, $\bar{\rho}^{BB}$). The second order correction $\bar{\rho}^\Xi$ has nonzero components AA, AB, BA, BB and modifies both, intra- and intermolecular bonding.

The modified equations of motion to first order in the electromagnetic field follow from Eq. (13) after substitution of Eq. (44), Eq. (46). Collecting terms to first order in the field yields:

$$\begin{aligned}
i\hbar\delta\dot{\rho}_{nm}^{(1)} = & \sum_{rs} \mathcal{L}_{nmrs}^0(t^0, \bar{\rho}^0) \delta\rho_{rs}^{(1)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^0 \delta\rho_{l''m}^{(1)} + \bar{\rho}_{l''m}^0 \delta\rho_{nl''}^{(1)} \right) + (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^0 \\
& + \lambda \left[\sum_{rs} \mathcal{L}_{nmrs}^0(t^\Delta, \bar{\rho}^\Delta) \delta\rho_{rs}^{(1)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^\Delta \delta\rho_{l''m}^{(1)} + \bar{\rho}_{l''m}^\Delta \delta\rho_{nl''}^{(1)} \right) + (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^\Delta \right] \\
& + \lambda^2 \left[\sum_{rs} \mathcal{L}_{nmrs}^0(0, \bar{\rho}^\Xi) \delta\rho_{rs}^{(1)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^\Xi \delta\rho_{l''m}^{(1)} + \bar{\rho}_{l''m}^\Xi \delta\rho_{nl''}^{(1)} \right) + (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^\Xi \right] \\
& + \text{O}(\lambda^3), \tag{49}
\end{aligned}$$

where

$$\begin{aligned}
\sum_{rs} \mathcal{L}_{nmrs}^0(t, \phi) \delta\rho_{rs} = & [t, \delta\rho]_{nm} + \sum_{l'} \Gamma_{nm}^{l'} [2\bar{\phi}_{nm} \delta\rho_{l'l'} + 2\bar{\phi}_{l'l'} \delta\rho_{nm} - \bar{\phi}_{nl'} \delta\rho_{l'm} - \bar{\phi}_{l'm} \delta\rho_{nl'}] \\
& + 2 \sum_{l''} \Gamma_{nm}^{l''} \bar{\phi}_{l''l''} \delta\rho_{nm}. \tag{50}
\end{aligned}$$

We next expand $\delta\rho^{(1)}$ in powers of λ according to

$$\delta\rho_{nm}^{(1)}(t) = \delta\rho_{nm}^{(1,0)}(t) + \lambda\delta\rho_{nm}^{(1,1)}(t) + \lambda^2\delta\rho_{nm}^{(1,2)}(t) + \text{O}(\lambda^3) \tag{51}$$

and find

$$\begin{aligned}
i\hbar\delta\dot{\rho}_{nm}^{(1,0)} - \sum_{rs} \mathcal{L}_{nmrs}^0(t^0, \bar{\rho}^0) \delta\rho_{rs}^{(1,0)} + \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^0 \delta\rho_{l''m}^{(1,0)} + \bar{\rho}_{l''m}^0 \delta\rho_{nl''}^{(1,0)} \right) \\
= (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^0, \tag{52}
\end{aligned}$$

$$\begin{aligned}
i\hbar\delta\dot{\rho}_{nm}^{(1,1)} - \sum_{kl} \mathcal{L}_{nmkl}^0(t^0, \bar{\rho}^0) \delta\rho_{kl}^{(1,1)} + \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^0 \delta\rho_{l''m}^{(1,1)} + \bar{\rho}_{l''m}^0 \delta\rho_{nl''}^{(1,1)} \right) \\
= \sum_{kl} \mathcal{L}_{nmkl}^0(t^\Delta, \bar{\rho}^\Delta) \delta\rho_{kl}^{(1,0)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^\Delta \delta\rho_{l''m}^{(1,0)} + \bar{\rho}_{l''m}^\Delta \delta\rho_{nl''}^{(1,0)} \right) + (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^\Delta, \tag{53}
\end{aligned}$$

$$\begin{aligned}
i\hbar\delta\dot{\rho}_{nm}^{(1,2)} - \sum_{kl} \mathcal{L}_{nmkl}^0(t^0, \bar{\rho}^0) \delta\rho_{kl}^{(1,2)} + \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^0 \delta\rho_{l''m}^{(1,2)} + \bar{\rho}_{l''m}^0 \delta\rho_{nl''}^{(1,2)} \right) \\
= \sum_{kl} \mathcal{L}_{nmkl}^0(t^\Delta, \bar{\rho}^\Delta) \delta\rho_{kl}^{(1,1)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^\Delta \delta\rho_{l''m}^{(1,1)} + \bar{\rho}_{l''m}^\Delta \delta\rho_{nl''}^{(1,1)} \right) \\
+ \sum_{kl} \mathcal{L}_{nmkl}^0(0, \bar{\rho}^\Xi) \delta\rho_{kl}^{(1,0)} - \sum_{l''} \Gamma_{nm}^{l''} \left(\bar{\rho}_{nl''}^\Xi \delta\rho_{l''m}^{(1,0)} + \bar{\rho}_{l''m}^\Xi \delta\rho_{nl''}^{(1,0)} \right) + (V_n^{\text{loc}} - V_m^{\text{loc}}) \bar{\rho}_{nm}^\Xi. \tag{54}
\end{aligned}$$

Eq. (52) is identical to Eq. (33) and defines $\delta\rho^{(1,0)}$ as the unperturbed (t^\perp) induced density matrix. The solution of the second equation Eq. (53) yields the first order corrections due to nonzero hopping integrals between different molecules. Using $\delta\rho_{n'm'}^{(1,0)} = 0$ from Section (2.1), the source term in Eq. (53) due to $\delta\rho^{(1,0)}$ simplifies, the EOM for $\delta\rho_{n'm'}^{(1,1)}$ reduces to

$$i\hbar\delta\dot{\rho}_{n'm'}^{(1,1)} = \sum_{k'l'} \mathcal{L}_{n'm'k'l'}^0(t^0, \bar{\rho}^0) \delta\rho_{k'l'}^{(1,1)}, \tag{55}$$

and has only the trivial solution $\delta\rho_{n'm'}^{(1,1)}(t) = 0$, satisfying the initial condition $\delta\rho_{n'm'}^{(1,1)}(t=0) = 0$. Therefore the first nonvanishing correction due to intermolecular hopping is of second order in the t -matrix. With these results, the EOM for $\delta\rho_{n'm'}^{(1,2)}(t)$ reads

$$i\hbar\delta\rho_{n'm'}^{(1,2)} = \sum_{k'l'} \mathcal{L}_{n'm'k'l'}^0(t^0, \bar{\rho}^0) \delta\rho_{k'l'}^{(1,2)} + \sum_{k'l'} \mathcal{L}_{n'm'k'l'}^0(0, \bar{\rho}^{\Xi}) \delta\rho_{k'l'}^{(1,0)} + (V_{n'}^{\text{loc}} - V_{m'}^{\text{loc}}) \bar{\rho}_{n'm'}^{\Xi}, \quad (56)$$

This equation is closed in the subspace of molecule A and can be solved using the Green's function for this molecule. Upon transforming to the frequency domain we obtain

$$\rho_{n'm'}^{(1,2)}(\omega) = \sum_{k'l'} G_{n'm'k'l'}^0(\omega) \sum_{r's'} \mathcal{L}_{k'l'r's'}^0(0, \bar{\rho}^{\Xi}) \delta\rho_{r's'}^{(1,0)}(\omega) + \sum_{k'l'} G_{n'm'k'l'}^0(\omega) (V_{k'}^{\text{loc}} - V_{l'}^{\text{loc}}) \bar{\rho}_{k'l'}^{\Xi}. \quad (57)$$

This result allows the computation of the lowest order corrections due to intermolecular hopping using a local field like equation. The computation of $\bar{\rho}_{kl}^{\Xi}$ is not more expensive than the computation of the Hartree-Fock ground state, which was already necessary in order to formulate the local field equations for non-overlapping charge distributions (see Section 2.1). Hence the molecular polarizability needed for the computation of the aggregate polarizability according to Eq. (39) can be written as

$$\tilde{\alpha} = \tilde{\alpha}^{\text{EET}} + \lambda^2 \tilde{\alpha}^{\text{CHT}} + O(\lambda^3). \quad (58)$$

Here α^{EET} is the linear polarizability without intermolecular chemical bonds, and the lowest correction is of second order in λ . A brief glance at Eqs. (21) and (23) reveals

$$\tilde{\alpha}_{n'l'}^{\text{EET}} = \sum_{k'} (G_{n'n'k'l'}^0(\omega) - G_{n'n'l'k'}^0(\omega)) \bar{\rho}_{k'l'}^0, \quad (59)$$

$$\tilde{\alpha}_{n'l'}^{\text{CHT}} = \sum_{k'l'} G_{n'n'k'l'}^0(\omega) \sum_{r's'} \mathcal{L}_{k'l'r's'}^0(0, \bar{\rho}^{\Xi}) \tilde{U}_{r's',l'}(\omega) + \sum_{k'} (G_{n'n'k'l'}^0(\omega) - G_{n'n'l'k'}^0(\omega)) \bar{\rho}_{k'l'}^{\Xi}. \quad (60)$$

Appendix B. LFA for point-dipoles

The easiest approach to the computation of aggregate polarizabilities consists in replacing the molecules by point dipoles and applying the LFA to the so obtained aggregate [19,20]. Analogous to Eqs. (36) and (37) one can write the i th component of the polarization vector at site n in terms of the molecular polarizability α_n^{ij} or the nonlocal aggregate polarizability α_{nm}^{ij} :

$$P_n^i = \sum_j \alpha_n^{ij} E_n^{\text{loc},j}, \quad (61)$$

$$P_n^i = \sum_{m,j} \tilde{\alpha}_{nm}^{ij} E_m^j, \quad (62)$$

where the local field $E_n^{\text{loc},j}$ is now given by

$$E_n^{\text{loc},j} = E_n^j + \sum_m \overleftrightarrow{T}_{nm} \cdot P_m, \quad (63)$$

and

$$\vec{T}_{nm} = (1 - \delta_{nm}) \frac{3\mathbf{r}_n \mathbf{r}_m - \mathbf{1}}{r_{nm}^3}. \quad (64)$$

This local field is the sum of the external field and the fields of the surrounding induced dipoles at site n .

Following the steps, leading to Eq. (39) we find

$$\alpha_{nm}^{ij} = \sum_l S_{nm}^{il} \bar{\alpha}_n^{lj}, \quad (65)$$

where

$$(S^{-1})_{nm}^{il} = \delta_{nm} \delta_{il} - \sum_j \bar{\alpha}_n^{ij} T_{nm}^{jl}. \quad (66)$$

The total aggregate polarizability is obtained by summing over all site indices:

$$\alpha^{ij} = \sum_{nm} \alpha_{nm}^{ij}. \quad (67)$$

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