Charge-transfer excitons and $\chi^{(2)}$ of molecular monolayers

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The second-order nonlinear susceptibility $\chi^{(2)}$ is calculated for a monolayer of donor-acceptor substituted molecules, using equations of motion which map the problem onto the dynamics of coupled anharmonic (exciton) oscillators. New exciton resonances, which may change in character from Frenkel through charge transfer to Wannier excitons, are predicted as the intermolecular charge-transfer coupling is turned on.

I. INTRODUCTION

The elementary optical excitations in molecular assemblies are Frenkel excitons which describe the coherent migration of the optical excitation among the molecules. In molecular crystals the exciton states form a band whose width reflects the strength of intermolecular interactions.¹ In semiconductors, on the other hand, the elementary excitations are electron-hole pairs.^{2,3} Depending on the strength of the Coulomb interactions, these pairs can either form bound states (Wannier excitons) which show up as a Rydberg series in the optical spectra, or move as free carriers in the valence and in the conduction band. Adopting the electron-hole terminology, Frenkel excitons can be considered as strongly bound electron-hole pairs which are confined to the same molecule. Wannier excitons are more complex than their Frenkel counterparts since their description involves both the relative and the center-of-mass coordinates of the pair, whereas for Frenkel excitons we need consider only the center-of-mass coordinate.⁴ When molecules with electron donor and acceptor substituents are assembled, we have an intermediate situation in which the electron and the hole strongly attract each other, but the charges can still separate on a length scale of a few molecules.^{5,6} These intermediatetype elementary excitations are denoted charge-transfer excitons.⁷⁻¹³ Conjugated polymers are a beautiful example of a system with intermediate excitons.^{14,15} The nonlinear optical response of intermediate excitons is an open theoretical problem.

In this paper we develop a theory for the second-order susceptibility $\chi^{(2)}$ of organized assemblies of molecules with donor and acceptor substituents. Such systems are of considerable current interest as $\chi^{(2)}$ materials. Polled polymers^{16,17} form a one-dimensional assembly, whereas molecmonolayers (whether self-assembled, 16,17 ular Langmuir-Blodgett,^{18,19} or epitaxially grown²⁰) constitute a two-dimensional system. The optical response of these systems is primarily determined by intramolecular and possibly also intermolecular charge-transfer processes. Using equations of motion,²¹ we map the problem onto the dynamics of coupled anharmonic oscillators, which represent intermediate excitons. We derive a general electron-hole Green-function expression for $\chi^{(2)}$ and apply it to two-dimensional assemblies. Previous theoretical treatments of this problem only allowed for intramolecular charge transfer, and intermolecular interactions were included through a local-field correction factor which represents the dipole–dipole interactions.^{16,22}

In Sec. II we present the model Hamiltonian which describes a monolayer of molecules with intramolecular and intermolecular charge transfer. In Sec. III we derive the equations of motion which map the problem of calculating the nonlinear optical response onto the dynamics of coupled anharmonic oscillators. In Sec. IV we present formal expressions for $\chi^{(1)}$ and $\chi^{(2)}$ using a Green function which describes both the relative and the translational motion of the electron-hole pair. In Sec. V we show how the Frenkel and the Wannier exciton limits are obtained using the present Green-function expression. Finally, in Sec. VI we present numerical calculations and explore the role of intermolecular charge transfer.

II. THE MODEL

We consider a two-dimensional assembly of donor-acceptor substituted molecules (Fig. 1). Each molecule can be found in one of four possible states representing the ground state, a single additional electron, a single hole, or an electron-hole pair. For the *n*th molecule we denote these states as $|1,n\rangle$, $|2,n\rangle$, $|3,n\rangle$, and $|4,n\rangle$, respectively. Hereafter, we adopt a second quantization representation of these states. We thus denote $|1,n\rangle$ as the vacuum $|0\rangle$ state, and introduce an electron (hole) creation operator c_n^+ (d_n^+) and the corresponding annihilation operators c_n and d_n . We then write



FIG. 1. Geometry of the donor-acceptor molecular monolayer.

$$|1,n\rangle \equiv |0\rangle, \quad |2,n\rangle \equiv c_n^{\dagger}|0\rangle; |3,n\rangle \equiv d_n^{\dagger}|0\rangle, \quad |4,n\rangle \equiv c_n^{\dagger}d_n^{\dagger}|0\rangle.$$
(2.1)

The c and the d operators are defined by the relations

$$c_{n} \equiv |1,n\rangle \langle n,2| + |3,n\rangle \langle n,4|,$$

$$d_{n} \equiv |1,n\rangle \langle n,3| + |2,n\rangle \langle n,4|.$$
(2.2)

It follows from Eqs. (2.2) that c_n and d_n are Pauli operators which satisfy the commutation relations

$$\begin{bmatrix} c_n, c_m^{\dagger} \end{bmatrix} = \delta_{nm} (1 - 2c_n^{\dagger}c_n), \begin{bmatrix} d_n, d_m^{\dagger} \end{bmatrix} = \delta_{nm} (1 - 2d_n^{\dagger}d_n), \begin{bmatrix} c_n, c_m \end{bmatrix} = \begin{bmatrix} d_n, d_m \end{bmatrix} = \begin{bmatrix} c_n, d_m \end{bmatrix} = \begin{bmatrix} c_n, d_m^{\dagger} \end{bmatrix} = 0.$$
(2.3)

It will be useful to further introduce exciton creation (annihilation) operators B^{\dagger}_{nm} (B_{nm}) defined by

$$B_{nm} \equiv c_n d_m. \tag{2.4}$$

These operators satisfy the commutation relations

$$\begin{bmatrix} B_{nm}, B_{n'm'}^{\dagger} \end{bmatrix} = \delta_{nn'} \delta_{mm'} + \delta_{mm'} \zeta_{nn'} C_{n'n} + \delta_{nn'} \zeta_{m'm} D_{m'm} + (\zeta_{nn'} \zeta_{mm'} - 1) C_{n'n} D_{m'm}, \qquad (2.5)$$

where $\zeta_{nn'} \equiv 1 - 2\delta_{nn'}$, and the operators $C_{n'n}$, $D_{m'm}$ are defined by $C_{n'n} \equiv c_n^{\dagger} c_n$, $D_{m'm} \equiv d_{m'}^{\dagger} d_m$.

Using these definitions, we can now introduce our model Hamiltonian:

$$H = H_{\rm ex} + H_{\rm CT} + H_{\rm int}.$$
 (2.6)

 $H_{\rm ex}$ represents the exciton part of the Hamiltonian, $H_{\rm CT}$ the charge-transfer processes, and $H_{\rm int}$ represents the interaction with the radiation field. The exciton part can be written by a straightforward generalization of the Hamiltonian of molecular crystals,²³

$$H_{ex} = (\hbar\omega_{0} + D) \sum_{nm} B^{\dagger}_{nm} B_{nm} + \sum_{nm} V^{(2)}_{nm,n'm'} \times \left[B^{\dagger}_{nm} B_{n'm'} + \frac{1}{2} (B^{\dagger}_{nm} B^{\dagger}_{n'm'} + B_{nm} B_{n'm'}) \right] + \sum_{nm} V^{(3)}_{nm,n'm'} (B^{\dagger}_{nm} + B_{nm}) B^{\dagger}_{n'm'} B_{n'm'}.$$
(2.7)

Here $\hbar\omega_0$ is the optical excitation energy of the isolated molecule. In order to introduce the remaining terms of the Hamiltonian, we consider first the dipole operator for the system

$$\hat{P} = \sum_{n,m} \hat{P}_{nm}, \qquad (2.8)$$

where \hat{P}_{nm} is the dipole moment operator associated with the B_{nm} electron-hole pair,

$$\widehat{P}_{nm} \equiv \mu_{nm} c_n d_m + \mu_{nm} c_n^{\dagger} d_m^{\dagger} + \Delta_{nm} c_n^{\dagger} d_m^{\dagger} c_n d_m. \quad (2.9)$$

Here μ_{nm} is the transition dipole matrix element for creating an electron and a hole on the *n*th and on the *m*th molecules, respectively,

$$\mu_{nm} \equiv \langle 0|\hat{P}_{nm}B^{\dagger}_{nm}|0\rangle, \qquad (2.10a)$$

and Δ_{nm} is the difference between permanent dipole moments in the excited and in the ground states,

$$\Delta_{nm} \equiv \langle 0|B_{nm}\widehat{P}_{nm}B_{nm}^{\dagger}|0\rangle - \langle 0|\widehat{P}_{nm}|0\rangle. \qquad (2.10b)$$

Equation (2.9) can alternatively be written using the exciton operators

$$\widehat{P}_{nm} \equiv \mu_{nm} \left(B_{nm} + B_{nm}^{\dagger} \right) + \Delta_{nm} B_{nm}^{\dagger} B_{nm}.$$
(2.11)

The dipole–dipole operator which represents the interaction of the nm and the n'm' pairs is then given by

$$\widehat{V}_{nm,n',m'} = \frac{\widehat{\mathbf{P}}_{nm}\widehat{\mathbf{P}}_{n'm'}|\mathbf{r}|^2 - 3(\widehat{\mathbf{P}}_{nm}\cdot\mathbf{r})(\widehat{\mathbf{P}}_{n'm'}\cdot\mathbf{r})}{|\mathbf{r}|^5},$$
(2.12)

where r denotes the radius vector between the centers of the nm and n'm' pairs. D is given by

$$D = \sum_{n'm'} \{ \langle 0 | B_{n'm'} \hat{V}_{nm,n'm'} B_{n'm'}^{\dagger} | 0 \rangle - \langle 0 | \hat{V}_{nm,n'm'} | 0 \rangle \}.$$
(2.13)

The matrix element $V_{nm,n'm'}^{(2)}$ is responsible for the exciton transfer between the *nm* and the *n'm'* sites

$$V_{nm,n'm'}^{(2)} = \langle 0|B_{n'm'} \hat{V}_{nm,n'm'} B_{nm}^{\dagger}|0\rangle. \qquad (2.14a)$$

 $V_{nm,n'm'}^{(3)}$ is the difference of the matrix elements

$$V_{nm,n'm'}^{(3)} = \langle 0|B_{n'm'} \hat{V}_{nm,n'm'} B_{nm}^{\dagger} B_{n'm'}^{\dagger} |0\rangle - \langle 0|B_{nm} \hat{V}_{nm,n'm'} |0\rangle.$$
(2.14b)

It follows from this definition that $V_{nm,n'm'}^{(3)}$ is proportional to the difference of permanent dipole moments in the excited and the ground states, which is an important factor that determines the second-order nonlinear susceptibility [see Eq. (3.7)].

We next turn to the charge-transfer part of the Hamiltonian:

$$H_{\rm CT} = I \sum_{n} c_{n}^{\dagger} c_{n} - A \sum_{n} d_{n}^{\dagger} d_{n} + \sum_{nm} U^{e} (n-m) c_{n}^{\dagger} c_{m}$$
$$+ \sum_{nm} U^{h} (n-m) d_{n}^{\dagger} d_{m} + \sum_{nm} U^{c}_{n-m} c_{n}^{\dagger} d_{m}^{\dagger} c_{n} d_{m}.$$
(2.15)

Here *I* is the molecular ionization energy, *A* is its electron affinity, $U^e(n-m)$ is the matrix element which represents electron hopping between sites *n* and *m*, and $U^h(n-m)$ represents the hole hopping between these sites. U_{n-m}^c represents the Coulomb interaction between electrons and holes. For the present two-dimensional (monolayer) geometry (Fig. 1), it is given by

$$U_{n-m}^{(c)} = -\frac{\eta}{\left[d^2 + (n_x - m_x)^2 + (n_y - m_y)^2\right]^{1/2}},$$

$$n = (n_x, n_y), \quad m = (m_x, m_y), \quad (2.16)$$

where d is the intramolecular distance between the donor and the acceptor, in units of the lattice constant a, and η represents the strength of electron-hole Coulomb interaction. Finally, the dipolar interaction with the radiation field is given by

$$H_{\rm int} = -\sum_{n>m} E\left(\frac{n+m}{2}\right) \cdot \hat{P}_{nm}, \qquad (2.17)$$

where E[(n + m)/2] is the electric field at the electronhole pair mean coordinate (n + m)/2.

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III. EQUATIONS OF MOTION AND THE ANHARMONIC-OSCILLATOR PICTURE

The optical response of the system will be calculated by solving the Heisenberg equations of motion for the optical polarization. We start by considering the Heisenberg equation of B_{nm} ,

$$\frac{\hbar}{i}\frac{d}{dt}B_{nm} = [H,B_{nm}]. \tag{3.1}$$

The commutator may be evaluated using Eq. (2.5), and it can be expressed in terms of products of B_{nm} and B_{nm}^{\dagger} operators. These operators are then recast in a normally ordered form, i.e., all B_{nm}^{\dagger} operators are moved to the right and B_{mn} operators to the left, e.g., $B^{\dagger}BB$. In this form, the expectation value of an operator with jB or B^{\dagger} factors will be to jth order in the field. Since we are interested in calculating $\chi^{(2)}$, we can therefore neglect all products involving three or more normally ordered B operators. We then get

$$\frac{\hbar}{i}\frac{d}{dt}B_{nm} = -(\hbar\omega_{0} + D + I - A)B_{nm} - \sum_{n'm'} V^{(2)}_{nm,n'm'}(B_{n'm'} + B^{\dagger}_{n'm'})$$

$$-\sum_{n'm'} V^{(3)}_{n'm',nm}(B^{\dagger}_{n'm'} + B_{n'm'})B_{nm} - \sum_{n'm'} V^{(3)}_{nm,n'm'}B^{\dagger}_{n'm'}B_{n'm'} - \sum_{m'} U^{e}(n - m')B_{m'm}$$

$$-\sum_{m'} U^{h}(m - m')B_{nm'} - U^{(c)}_{n-m}B_{nm} + E\left(\frac{n + m}{2}\right)\mu_{nm} + E\left(\frac{n + m}{2}\right)\Delta_{nm}B_{nm}.$$
(3.2)

We next assume the following factorization for the expectation value of a product of operators:²⁴

$$\langle B_{n'm'}^{\dagger} B_{nm} \rangle = \langle B_{n'm'}^{\dagger} \rangle \langle B_{nm} \rangle. \tag{3.3}$$

This factorization is justified in the absence of pure dephasing where the system is in a pure state. Since our main goal is to study the effects of intermolecular charge transfer, we shall treat the exciton–exciton interactions within the localfield approximation. We have shown earlier in our study of Frenkel excitons^{21,24,25} that this can be accomplished using the following factorization:

$$\langle B_{n'm'}B_{nm}\rangle = \langle B_{n'm'}\rangle\langle B_{nm}\rangle \quad \frac{n'+m'}{2} \neq \frac{n+m}{2}.$$
(3.4)

By employing this factorization (and neglecting factorizations of the type $\langle B_{n'm} \rangle \langle B_{nm'} \rangle$) we have reduced the complex four-particle problem to the simpler problem of two interacting excitons (*nm* and *n'm'*). We shall now change variables from *n* and *m* to *r* and *s* where $r \equiv (n + m)/2$ is the average position of the electron-hole pair, and $s \equiv n - m$ is their relative coordinate,

$$B_{rs} \equiv c_{r+s/2} d_{r-s/2}.$$
 (3.5)

Using this notation, we have for the optical polarization

$$\hat{P} = \sum_{rs} \hat{P}_{rs}, \qquad (3.6a)$$

$$\widehat{P}_{rs} = \mu_s (B_{rs} + B_{rs}^{\dagger}) + \Delta_s B_{rs}^{\dagger} B_{rs}.$$
(3.6b)

We further have

$$V_{n'm',nm}^{(2)} = \mu_{s'}\mu_{s}U_{r'r}^{s's}$$
(3.7a)

$$V_{n'm',nm}^{(3)} = \mu_{s'} \Delta_s U_{r'r}^{s's}, \qquad (3.7b)$$

where the function $U_{rr}^{s's}$ is given by

$$U_{rr}^{s's} = \frac{R^2(\mathbf{s}\cdot\mathbf{s}') - 3(\mathbf{s}\cdot\mathbf{R})(\mathbf{s}'\cdot\mathbf{R})}{a^3|\mathbf{R}|^5}$$
(3.8)

with $\mathbf{R} \equiv \mathbf{r}' - \mathbf{r}$. In the following calculations we shall neglect the dependence of $U_{r'r}^{s's}$ on the s,s' indexes, adopting the approximation

$$U_{r'r}^{s's} \equiv U^{x}(r - r'). \tag{3.9}$$

The superscript x indicates that this is exciton-exciton coupling.

Making use of the factorizations, Eqs. (3.3) and (3.4), and the new notation, and taking the expectation value, Eq. (3.2) becomes

$$\frac{\hbar}{i}\frac{d}{dt}\langle B_{rs}\rangle = -\epsilon_{s}\langle B_{rs}\rangle - \sum_{s'}U^{e}(s-s')\langle B_{r-s/2+s/2,s'}\rangle$$
$$-\sum_{s'}U^{h}(s'-s)\langle B_{r+s/2-s'/2,s'}\rangle$$
$$+E_{L}(r)\mu_{s} + E_{L}(r)\Delta_{s}\langle B_{rs}\rangle, \qquad (3.10)$$

where $E_L(r)$ is the local field at point r

$$E_L(r) \equiv E(r) - \sum_{r's'} U^x(r - r')\mu_{s'} \left[\langle B_{r's'} \rangle + \langle B_{r's'}^{\dagger} \rangle \right]$$

$$-\sum_{r's'} U^{x}(r-r')\Delta_{s'} \langle B_{r's'}^{\dagger} \rangle \langle B_{r's'} \rangle. \qquad (3.11)$$

Here

$$\epsilon_{s} \equiv \hbar \Omega_{0} - \eta / (d^{2} + s^{2})^{1/2}$$
 (3.12a)

and

$$\Omega_0 \equiv \omega_0 + (D + I - A)/\hbar - i\gamma. \qquad (3.12b)$$

 Ω_0 is the molecular frequency shifted by exciton interactions, whereas ϵ_s includes also the Coulomb interactions, and γ is a phenomenological exciton dephasing rate. Within the present model, $\langle B_{rs} \rangle$ (and its complex conjugate $\langle B_{rs}^{\dagger} \rangle$) are the only relevant dynamical variables necessary for the calculation of $\chi^{(1)}$ and $\chi^{(2)}$. The polarization is given by

$$\langle \hat{P}_{rs} \rangle = \mu_s \left[\langle B_{rs} \rangle + \langle B_{rs}^{\dagger} \rangle \right] + \Delta_s \langle B_{rs}^{\dagger} \rangle \langle B_{rs} \rangle. \quad (3.13)$$

Equation (3.10) maps the calculation of $\chi^{(2)}$ of an N-molecule assembly, onto the dynamics of N^2 -coupled anharmonic oscillators. In the next section we shall present the solution of Eq. (3.10) in terms of the electron-hole Green function.

IV. CALCULATION OF OPTICAL SUSCEPTIBILITIES

We shall be interested in calculating the linear and the second-order nonlinear susceptibilities. To that end we decompose of the field and the polarization into modes:

$$E(r) = \sum_{j=1,2} E_{j} (e^{i(k_{j}r - \omega_{j}t)} + e^{i(-k_{j}r + \omega_{j}t)}), \qquad (4.1)$$

$$\langle \hat{P} \rangle = \frac{1}{(aN)^{2}} \sum_{s} \langle \hat{P}_{rs} \rangle$$

$$= \sum_{j} \chi^{(1)}(\omega_{j}, k_{j}) E_{j}$$

$$+ \sum_{j,j_{2}} \chi^{(2)}(-\omega_{\sigma} - k_{\sigma}; \omega_{j_{1}}k_{j_{1}}, \omega_{j_{2}}k_{j_{2}}) E_{j_{1}} E_{j_{2}} + \cdots, \qquad (4.2)$$

where the lattice size is $N \times N$, and *a* is the lattice constant. We shall expand all quantities $\langle B_{rs} \rangle$, $\langle \hat{P}_{rs} \rangle$, etc. in powers of the electric field. We start with the linear response. Linearizing Eq. (3.10), we get

$$\frac{\hbar}{i} \frac{d}{dt} \langle B_{rs} \rangle^{(1)} = -\epsilon_s \langle B_{rs} \rangle^{(1)} - \sum_{s'} U^e(s-s') \langle B_{r-s/2+s/2,s'} \rangle^{(1)} - \sum_{s'} U^h(s'-s) \langle B_{r+s/2-s'/2,s'} \rangle^{(1)} + E_L^{(1)}(r) \mu_s,$$
(4.3)

with the linearized local field

$$E_{L}^{(1)}(r) = E(r) - \sum_{r's'} \mu_{s'} U^{x}(r - r') \\ \times \left[\langle B_{r's'} \rangle^{(1)} + \langle B_{r's'}^{\dagger} \rangle^{(1)} \right].$$
(4.4)

The linear polarization is then given by

$$\langle P_{rs} \rangle^{(1)} = \mu_s (\langle B_{rs} \rangle^{(1)} + \langle B_{rs}^{\dagger} \rangle^{(1)}).$$
(4.5)

The superscript in Eqs. (4.2)–(4.5) denotes the order with respect to the field. Expanding $\langle B_{rs} \rangle^{(1)}$ in Fourier components, we get

$$\langle B_{rs} \rangle^{(1)} = \sum_{j=1,2} \left[b_{sj}^{(1)} e^{i(k_j r - \omega_j t)} + \tilde{b}_{sj}^{(1)} e^{i(-k_j r + \omega_j t)} \right].$$
(4.6)

Substituting Eqs. (4.6) and (4.4) into Eq. (4.3), we can solve for $b_{sj}^{(1)}$. The equation is expressed in terms of the electron-hole Green function $G_{ss}(\omega,k)$,

$$b_{sj}^{(1)} = \left[\sum_{s'} G_{ss'}(\omega_{j}, k_{j}) \mu_{s'}\right] \times \left\{ E_{j} - J_{k_{j}} \sum_{s_{1}} \mu_{s_{1}} \left[\langle b_{s_{1}j} \rangle^{(1)} + \langle b_{s_{1}j}^{\dagger(1)} \rangle \right] \right\}$$
(4.7a)

with

$$J_{k_j} \equiv \sum_{r'} U^{x}(r-r')e^{ik_j(r-r')}.$$
 (4.7b)

The Green function $G_{ss'}(\omega_i, k_i)$ satisfies the equation

$$\sum_{s^{*}} \left[-(\hbar\omega - \epsilon_{s})\delta_{ss^{*}} + U^{e}(s - s^{*})e^{i(k_{j}/2)(s^{*} - s)} + U^{h}(s^{*} - s)e^{i(k_{j}/2)(s - s^{*})} \right] G_{s^{*}s^{*}}(\omega_{j}, k_{j}) = \delta_{ss^{*}}.$$
 (4.8)

When the solution of Eq. (4.7a) together with Eq. (4.6) is substituted in Eq. (4.4), we obtain for the local field

$$E_{L}^{(1)}(\omega_{j},k_{j}) = S(\omega_{j},k_{j})E_{j},$$
 (4.9a)

where the local-field factor $S(\omega_j, k_j)$ is given by $S(\omega_j, k_j)$

$$= \frac{1}{1 + J_{k_j} \sum_{ss'} \mu_s \mu_s \left[G_{ss'}(\omega_j, k_j) + G_{ss'}(-\omega_j, k_j) \right]}$$
(4.9b)

We finally obtain for the linear susceptibility

$$\chi^{(1)}(\omega_j, k_j) = \rho S(\omega_j, k_j)$$

$$\times \sum_{ss'} \mu_s \mu_{s'} [G_{ss'}(\omega_j, k_j) + G_{ss'}(-\omega_j, k_j)], \quad (4.10)$$

where $\rho \equiv 1/a^2$ is the number density of molecules per unit area.

We next turn to the calculation of $\chi^{(2)}$. We start with Eqs. (3.10) and (3.13) expanded to second order:

$$\langle P_{rs} \rangle^{(2)} = \mu_s \left(\langle B_{rs} \rangle^{(2)} + \langle B_{rs}^{\dagger} \rangle^{(2)} \right) + \Delta_s \langle B_{rs}^{\dagger} \rangle^{(1)} \langle B_{rs} \rangle^{(1)}, \qquad (4.11)$$

$$\frac{\hbar}{i} \frac{d}{dt} \langle B_{rs} \rangle^{(2)} = -\epsilon_{s} \langle B_{rs} \rangle^{(2)} -\sum_{s'} U^{e}(s-s') \langle B_{r+s/2-s'/2,s'} \rangle^{(2)} -\sum_{s'} U^{h}(s'-s) \langle B_{r+s/2-s'/2,s'} \rangle^{(2)} +E_{L}^{(2)}(r)\mu_{s} + E_{L}^{(1)}(r)\Delta_{s} \langle B_{rs} \rangle^{(1)},$$
(4.12a)

 $E_{L}^{(2)}(r)$

$$= -\sum_{r's'} \mu_{s'} U^{x}(r-r') \left[\langle B_{r's'} \rangle^{(2)} + \langle B_{r's'}^{\dagger} \rangle^{(2)} \right]$$
$$- \sum_{r's'} \Delta_{s'} U^{x}(r-r') \langle B_{r's'} \rangle^{(1)} \langle B_{r's'}^{\dagger} \rangle^{(1)}.$$
(4.12b)

Equations (4.12) are solved in the Appendix, resulting in

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$$\chi^{(2)}(-\omega_3-k_3;\omega_1k_1,\omega_2k_2)$$

$$= \frac{\rho}{2} S(\omega_{3},k_{3})S(\omega_{1},k_{1})S(\omega_{2},k_{2}) \sum_{ss's''} \Delta_{s}\mu_{s'}\mu_{s''} \left[G_{s's}(\omega_{3},k_{3})G_{ss''}(\omega_{2},k_{2}) + G_{s's}(\omega_{3},k_{3})G_{ss''}(\omega_{1},k_{1}) + G_{s's}(-\omega_{3},k_{3})G_{ss''}(-\omega_{1},k_{3})G_{ss''}(-\omega_{1},k_{1}) + G_{ss'}(-\omega_{1},k_{1})G_{ss''}(-\omega_{2},k_{2}) + G_{ss'}(-\omega_{2},k_{2})G_{ss''}(\omega_{1},k_{1}) \right],$$

$$(4.13)$$

where $\omega_3 \equiv \omega_1 + \omega_2$ and $k_3 \equiv k_1 + k_2$. Equations (5.10) and (4.13) constitute our final formal expression for the first- and for the second-order optical response. The microscopic information regarding the dynamics of the electrons and holes is contained in the Green function $G_{ss}(\omega,k)$, which will be evaluated in the forthcoming sections.

V. THE FRENKEL AND THE WANNIER EXCITON LIMITS

Equations (4.10) and (4.13) are valid for arbitrary types of elementary excitations and interpolate all the way from Frenkel, through charge-transfer, to Wannier excitons. We shall now illustrate how the Frenkel and the Wannier exciton limits are obtained as the strength of the Coulomb interaction is varied. In the Frenkel limit we neglect the possibility of charge transfer. We then set s = s' = s'' = 0, $\eta = U^e = U^h = 0$ in Eqs. (4.10) and (4.13), and obtain

$$G_{00}(\omega,k) = \frac{1}{-\hbar(\omega - \Omega_0)}.$$
(5.1)

Note that this Green function is independent on the wave vector k. When Eq. (5.1) is substituted in Eqs. (4.10) and (4.13), we get

$$\chi^{(1)}(k,\omega) = \frac{2\rho\mu_0^2 \Omega_0/\hbar^2}{-\omega^2 + \Omega_0^2 + (2\mu_0^2 J_k^2 \Omega_0/\hbar^2)},$$
(5.2)

and

$$\begin{aligned} &= \frac{1}{9} \rho S(\omega_{3},k_{3}) S(\omega_{1},k_{1}) S(\omega_{2},k_{2}) \Delta_{0} \mu_{0}^{2} \bigg[\frac{1}{(\Omega_{0} - \omega_{3})(\Omega_{0} - \omega_{2})} + \frac{1}{(\Omega_{0} - \omega_{3})(\Omega_{0} - \omega_{1})} + \frac{1}{(\Omega_{0} + \omega_{3})(\Omega_{0} + \omega_{2})} \\ &+ \frac{1}{(\Omega_{0} + \omega_{3})(\Omega_{0} + \omega_{1})} + \frac{1}{(\Omega_{0} + \omega_{1})(\Omega_{0} - \omega_{2})} + \frac{1}{(\Omega_{0} + \omega_{2})(\Omega_{0} - \omega_{1})} \bigg]. \end{aligned}$$

$$(5.3)$$

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Equations (5.2) and (5.3) recover the well-known results¹⁶ whereby the nonlinear susceptibility is given by the hyperpolarizability of a single molecule multiplied by local-field correction factors. Equation (5.3) can be rearranged in the form

$$\chi^{(2)}(-\omega_{3}-k_{3};\omega_{1}k_{1},\omega_{2}k_{2}) = \rho S(\omega_{3},k_{3})S(\omega_{1},k_{1})S(\omega_{2},k_{2})\Delta_{0}(\mu_{0})^{2} \\ \times \frac{3\Omega_{0}^{2} \left[\Omega_{0}^{2}-\frac{1}{3}(\omega_{3}^{2}-\omega_{1}\omega_{2})\right]}{\left[\Omega_{0}^{2}-\omega_{3}^{2}\right]\left[\Omega_{0}^{2}-\omega_{1}^{2}\right]\left[\Omega_{0}^{2}-\omega_{2}^{2}\right]}.$$
(5.4)

In particular, for second-harmonic generation^{16,22} (SHG) we set

$$\omega_1 = \omega_2 = \frac{1}{2}\omega_3 = \omega, \quad k_1 = k_2 = \frac{1}{2}k_3 = k,$$

and obtain

$$\chi^{(2)}(-2\omega 2k;\omega k,\omega k)$$

$$=\rho S(2\omega,2k)S^{2}(\omega,k)\Delta_{0}\mu_{0}^{2}$$

$$\times \frac{3\Omega_{0}^{2}}{\left[\Omega_{0}^{2}-4\omega^{2}\right]\left[\Omega_{0}^{2}-\omega^{2}\right]}.$$
(5.5)

We next turn to the Wannier exciton limit. For simplicity, we consider here only the long-wavelength limit and set all wave vectors $k_j = 0$. In order to obtain the Wannier excitons, we make a continuum approximation to Eq. (4.8) and transform it to a differential form:

$$\begin{bmatrix} -\hbar(\omega - \tilde{\Omega}_{s}) - \frac{\hbar^{2}}{2ma^{2}} \left(\frac{\partial^{2}}{\partial s_{x}^{2}} + \frac{\partial^{2}}{\partial s_{y}^{2}} \right) \end{bmatrix} G_{ss'}(\omega)$$
$$= \delta(s - s''), \qquad (5.6)$$

where m_e and m_h are effective masses of the electron and the hole,

$$U^{e} \equiv U^{e}(1) \equiv -\frac{\hbar}{2m_{e}a^{2}}, \quad U^{h} \equiv U^{h}(1) \equiv -\frac{\hbar^{2}}{2m_{h}a^{2}},$$
(5.7a)

m is reduced mass of the electron-hole pair

$$1/m \equiv 1/m_e + 1/m_h,$$
 (5.7b)

and

$$\widetilde{\Omega}_{s} \equiv \epsilon_{s}/\hbar - (\hbar/2ma^{2}).$$
(5.7c)

Equation (5.6) is the equation for the Green function for the following Schrödinger equation,

$$-\frac{\hbar^2}{2ma^2} \left(\frac{\partial^2}{\partial s_x^2} + \frac{\partial^2}{\partial s_y^2}\right) \phi_l(s) - \frac{\eta}{(s_x^2 + s_y^2 + d^2)^{1/2}} \phi_l(s)$$
$$= E_l \phi_l(s). \tag{5.8}$$

Substitution of the solution of Eq. (5.8) in Eq. (4.13) gives the susceptibilities $\chi^{(2)}$ in terms of a sum over eigenstates.^{16,26} The *l* index denotes both bound and unbound electron-hole pair states, with energies E_l and eigenfunc-

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tions $\phi_i(s)$. The permanent and the transition dipole matrix elements are given by

$$\Delta_{l_1 l_2} = \sum_{s} \Delta_s \phi_{l_1}^*(s) \phi_{l_2}(s), \qquad (5.9a)$$

$$\mu_I = \sum_{s} \mu_s \phi_I(s). \tag{5.9b}$$

Since we adopt the k = 0 limit, we shall hereafter delete all wave-vector variables from the quantities defined below, e.g., $G_{ss'}(\omega) \equiv G_{ss'}(k = 0, \omega)$, etc. The Green function, which is the solution of Eq. (5.6), is then given by

$$G_{ss'}(\omega) = \sum_{l} \frac{\phi_{l}(s)\phi_{l}^{*}(s')}{-\hbar(\omega - \widetilde{\Omega}_{0}) + E_{l}}.$$
 (5.10)

Upon the substitution of this result in Eq. (4.10), we obtain the following expression for $\chi^{(1)}$:

$$\chi^{(1)}(\omega_j) = \rho S(\omega_j) \sum_{l} \frac{2|\mu_l|^2 (\hbar \tilde{\Omega}_0 + E_l)}{-\hbar^2 \omega_j^2 + (\hbar \tilde{\Omega}_0 + E_l)^2}, (5.11)$$

and for the local-field correction factor,

$$S(\omega_j) = \left[1 + J_0 \sum_l \frac{2|\mu_l|^2 (\hbar \widetilde{\Omega}_0 + E_l)}{-\hbar^2 \omega_j^2 + (\hbar \widetilde{\Omega}_0 + E_l)^2}\right]^{-1}.$$
(5.12)

Substituting of Eq. (5.10) in Eq. (4.13), we finally obtain the following expression for $\chi^{(2)}$:

$$\begin{split} \chi^{(r')}(-\omega_{3};\omega_{1},\omega_{2}) &= \frac{\rho}{2} S(\omega_{3}) S(\omega_{1}) S(\omega_{2}) \sum_{l_{1}l_{2}} \mu_{l_{1}} \mu_{l_{2}} \Delta_{l_{1}l_{2}} \left\{ \frac{1}{\left[-\hbar(\omega_{3} - \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[-\hbar(\omega_{2} - \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} \right. \\ &+ \frac{1}{\left[-\hbar(\omega_{3} - \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[-\hbar(\omega_{1} - \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} + \frac{1}{\left[-\hbar(-\omega_{3} - \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[-\hbar(-\omega_{2} - \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} \\ &+ \frac{1}{\left[\hbar(\omega_{3} + \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[\hbar(\omega_{1} + \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} \\ &+ \frac{1}{\left[\hbar(\omega_{1} + \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[-\hbar(\omega_{2} - \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} \\ &+ \frac{1}{\left[\hbar(\omega_{2} + \widetilde{\Omega}_{0}) + E_{l_{1}} \right] \left[\hbar(\omega_{1} - \widetilde{\Omega}_{0}) + E_{l_{2}} \right]} \right\}. \end{split}$$

$$(5.13)$$

The Schrödinger equation [Eq. (5.8)] for Wannier-Mott excitons, for an infinite system in the continuum limit with d = 0, was solved by Merrifield⁷ in one dimension. The bound-state energies were found to be

$$E_{n_0}^{(1)} = -\left[E_0^2 + (R/n_0)^2\right]^{1/2}, \quad n_0 = 1, 2, \dots .(5.14a)$$

Equation (5.14a) represents a family of odd states. In addition, he found another family of even states with no simple expression for the eigenvalues. The eigenvalue problem in two dimensions for a molecular monolayer was solved by Shinada and Sugano,²⁷ who found for the bound states

$$E_{n_0}^{(2)} = -R'/(n_0 + \frac{1}{2})^2, \quad n_0 = 0, 1, 2, ...,$$
 (5.14b)

where R, R', and E_0 are given parameters. The electron-hole pair bound-exciton eigenstates in two dimensions are given by Laguerre polynomials. The unbound states are given by a hypergeometric function.²⁷ Realistic molecular monolayers with donor-acceptor substituents are intermediate between the Frenkel and the Wannier limits discussed here.^{5,6,16,20} In the next section we present numerical calculations which show the role of charge-transfer excitons in the nonlinear optical response of molecular assemblies.

VI. CALCULATIONS AND DISCUSSION

In Fig. 1 we display the geometry of the donor-acceptor molecular assembly. Molecules with donor substituents (D) and with acceptor substituents (A) are assembled in a monolayer, and form a two-dimensional crystal with lattice constant a. The molecular length (separation of the donor and the acceptor units) is da. We have calculated the electronhole Green function by a numerical solution of Eq. (4.8), and used it to calculate $\chi^{(1)}$ and $\chi^{(2)}$. Since we expect the elementary excitations to be charge-transfer excitons, we have restricted the s summation by truncating it to $s = 0, 1, \dots, M$. M is a truncation parameter which will be varied. The convergence of the calculation with M will demonstrate the exciton size. We further specialized to the longwavelength limit $k_1 = k_2 = k_3 = 0$, and set $\omega_1 = \omega_2 = \omega_3/2 \equiv \omega$ (second-harmonic generation) in all calculations. The evaluation of the Green function [Eq. (4.18)] thus reduces to the inversion of an $(M + 1)^2 \times (M + 1)^2$ matrix. We have adopted typical parameters of anthracene. Since anthracene crystals have two molecules in unit cell, they have different types of chargetransfer excitons. The band structure of charge-transfer excitons, with electrons and holes in the *a-b* plane, propagating in the b direction with energy $\hbar\Omega_0 = 3.4 \,\mathrm{eV}$, was investigated in Ref. 12. The Frenkel exciton bandwidth in the b direction was estimated as ~ 100 meV. Therefore, for the parameter $V_0 \equiv \mu_0^2 J_0$ that defines the local-field correction factor $S(\omega, k = 0)$ we assume the value of $V_0 = 25$ meV. The electron-hole Coulomb coupling constant η for anthracene crystal is 0.5 eV.5 There is a broad range of values for carrier mobility and the corresponding electron and hole bandwidths in organic crystals.^{8,10–12} The electron and the hole bandwidth in the *a-b* plane of the anthracene crystal was

(2) .

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⁹²⁰⁶

estimated to be in the range of 0.1–0.2 eV.¹⁰ We have therefore used the values $U^e = -0.13$ eV and $U^h = 0.2$ eV for the parameters that define electron and hole mobilities. Note that the electron effective mass is positive and the hole mass is negative. The ratio U^e/U^h agrees with the estimates of Ref. 12. The exciton dephasing rate $\hbar \gamma = 34$ meV is taken to reproduce the linear absorption linewidth in anthracene crystals.⁵ Since the electronic wave functions in molecular crystals are tightly bound, we have taken the transition dipole moments μ_s and permanent dipole moments Δ_s to be finite only for the same site (s = 0) and nearest neighbors s = 1. We thus set $\mu_1/\mu_0 = 0.3$, $\Delta_1/\Delta_0 = 0.3$, and $\mu_s = \Delta_s = 0$ for s > 1. Finally, we took the donor-acceptor separation to be equal to the lattice constant and set d = 1.

In Fig. 2 we display the absorption line shapes Im $\chi^{(1)}(\omega)$ for various values of M. For M = 0 (solid line, top panel) we see the spectrum in the absence of charge transfer. The absorption peak is then at $\omega = \Omega_0 - V_0 - \eta$. Neglecting Coulomb interactions, the exciton peak appears on the low-frequency edge of the Frenkel exciton band, $\omega = \Omega_0 - V_0$ (dotted curve). We then note the appearance of extra resonances related to charge-transfer excitons as Mis increased. The calculation rapidly converges with the



FIG. 3. Frequency dependence of the linear (top frame) and nonlinear (bottom frame) susceptibility. Solid lines, with charge transfer; dotted lines, in the absence of charge transfer $\eta = U^* = U^h = 0$ and M = 8. For other parameters see text.



FIG. 2. Frequency dependence of the linear susceptibility $[\operatorname{Im} \chi^{(1)}(\omega)]$ in the resonance region $\omega \sim \Omega_0$ for different values of the truncation size M as indicated in each frame. The dotted line is for M = 8, with no charge transfer $\eta = U^c = U^h = 0$. The parameters used are given in the text.

truncation size. The M = 12 calculation (not shown) is very close to the M = 8 calculation. In Fig. 3 we display the absolute magnitude of the susceptibility responsible for secondharmonic generation $|\chi_{\text{SHG}}^{(2)}| = |\chi^{(2)}(-2\omega;\omega,\omega)|$, and Im $\chi^{(1)}$ with and without charge transfer, over a broad frequency range, including the $\omega \sim \Omega_0/2$ and $\omega \sim \Omega_0$ regions. The linear absorption is similar to that shown in Fig. 2, with a single-exciton absorption line when charge transfer is absent, and a series of red-shifted charge-transfer resonances. For second-harmonic generation, we notice two resonances in the absence of charge transfer: at the one-photon resonance frequency $\omega \sim \Omega_0$ and the two-photon resonance frequency $\omega \sim \Omega_0/2$. The amplitude of the resonance at $\omega \sim \Omega_0/2$ is approximately twice that for frequency $\omega \sim \Omega_0$. When charge transfer is turned on, both resonances change into a series of charge-transfer exciton lines with approximately the same ratio of amplitudes at $\omega \sim \Omega_0$ and $\omega \sim \Omega_0/2$. model, with a higher spectral resolution. The charge-transfer excitons are seen at both the single photon $\omega \sim \Omega_0$ [Fig. 4(a)] and the two-photon $\omega \sim \Omega_0/2$ [Fig. 4(b)] resonances. The variation and the convergence with M shown in this figure is similar to that of Fig. 2. In Fig. 5 we show the effect of varying various parameters on $\chi^{(1)}$ and in Figs. 6 and 7 we repeat these calculations for $\chi^{(2)}_{SHG}$. We have varied



FIG. 4. Frequency dependence of the nonlinear susceptibility $|\chi_{SHG}^{(2)}|$ for different truncation sizes M, as indicated in each frame. Solid lines, with charge transfer; dotted line, in the absence of charge transfer $\eta = U^e = U^h = 0$ and M = 8. (a) The single-photon resonance region $\omega \sim \Omega_0$. (b) The two-photon resonance region $\omega \sim \Omega_0/2$.





FIG. 5. Frequency dependence of the linear susceptibility $[\operatorname{Im} \chi^{(1)}(\omega)]$ in the resonance region $\omega \sim \Omega_0$ for different values of the parameters η , d, V_0 , U^{ϵ} , and U^{h} . (a) Uses the basic parameters discussed in the text. $\Omega_0 = 3.4$ eV, $V_0 = -25$ meV, $\eta = 0.5$ eV, $U^{\epsilon} = -0.13$ eV, $U^{h} = 0.2$ eV, d = 1. (b) Same as (a) except that we neglected charge transfer and set $\eta = U^{\epsilon} = U^{h} = 0$. (c) Same as (a) except that we increased the donor-acceptor separation and set d = 5. (d) Same as (a) except that we reduced the exciton bandwidth, setting $V_0 = -2.5$ meV.

FIG. 6. Frequency dependence of the nonlinear susceptibility $(|\chi_{3HG}^{(S)}|)$ for the same set of parameters η , d, V_0 , U^{ϵ} , U^{h} (M = 8, $\gamma = 34$ meV) used in Fig. 5. Shown is the single-photon resonance region $\omega \sim \Omega_0$.



0.8 0.4 0.2 0.3 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.1 0.9 0.9 0.1 0.9 0.9 0.9 0.1 0.9 0.9 0.1 0.9 0.1 0.9 0.1 0.9 0.1 0.9 0.1 0.9 0.1 0.1 0.9 0.1 0.9 0.1 0.9 0.1 0.1 0.9 0.1 0.1 0.9 0.1

FIG. 7. Same as Fig. 6 but in the two-photon resonance region $\omega \sim \Omega_0/2$.

 $\bar{\chi}_{\rm SHG}^{(2)}$ includes the sum in Eq. (4.13), whereas $f(\omega)$ is the local-field correction factor. In the last two figures, we display separately the two factors contributing to the nonlinear susceptibility: $|\bar{\chi}_{\rm SHG}^{(2)}|$ and $|f(\omega)|$, as well as the total $|\chi_{\rm SHG}^{(2)}|$. Calculations were made in the vicinity of the single-photon resonance (Fig. 8) and the two-photon resonance (Fig. 9). We note that the local-field factor $|f(\omega)|$ has a minimum at the frequency where the other term $|\bar{\chi}_{\rm SHG}^{(2)}|$ has a maximum. This results in a spectral redshift of $|\chi_{\rm SHG}^{(2)}|$ with respect to $|\bar{\chi}_{\rm SHG}^{(2)}|$.

In conclusion, we note that there are several other techniques which are particularly suitable for monitoring intermolecular charge transfer. Photoinduced charge-transfer processes can be identified by following the strong dependence of the absorption line shape on an applied electric field.²⁸ This technique, known as electroabsorption, is related to $\chi^{(3)}$. Analysis of saturation spectroscopy (another $\chi^{(3)}$ -related technique) in molecular aggregates has also suggested the existence of intermediate excitons.²⁹ In addition,

the key coupling parameters of this problem, i.e., the electron-hole coupling constant (η) , electron (U^e) and hole (U^h) mobilities, the Frenkel-exciton bandwidth (V_0) , and the donor-acceptor distance d. Changing the charge dynamical parameters $(\eta, U^e, \text{ and } U^h)$ affects the charge-transfer exciton structure, whereas varying V_0 results in a spectral shift of the exciton band. All of these features may be ration-

FIG. 8. Influence of the local-field correction factor $f(\omega)$ [Eq. (6.2)] on the frequency dependence of the nonlinear susceptibility $(|\chi_{SHG}^{(2)}|)$ in a monolayer with (bottom frame) and without (upper frame) charge transfer. (a) $|\chi_{SHG}^{(2)}|$; (b) $|f(\omega)| \times 10$; (c) $|\bar{\chi}_{SHG}^{(2)}|$. Shown is the single-photon resonance region $\omega \sim \Omega_0$.

alized from Eqs. (4.10) and (4.13). The role of the localfield factors is illustrated in Figs. 8 and 9. To that end we recast Eq. (4.13) for second-harmonic generation in the long-wavelength (k = 0) limit in the form

$$\chi_{\rm SHG}^{(2)}(-2\omega;\omega,\omega) \equiv \overline{\chi}_{\rm SHG}^{-(2)}(-2\omega;\omega,\omega)f(\omega), \qquad (6.1)$$

where

$$f(\omega) \equiv S^{2}(\omega)S(2\omega). \tag{6.2}$$

 $\tilde{\chi}_{\rm SHG}^{(2)}$ includes the sum in Eq. (4.13), whereas $f(\omega)$ is the local-field correction factor. In the last two figures, we display separately the two factors contributing to the nonlinear susceptibility: $|\tilde{\chi}_{\rm SHG}^{(2)}|$ and $|f(\omega)|$, as well as the total $|\chi_{\rm SHG}^{(2)}|$. Calculations were made in the vicinity of the single-photon resonance (Fig. 8) and the two-photon resonance (Fig. 9). We note that the local-field factor $|f(\omega)|$ has a minimum at the frequency where the other term $|\tilde{\chi}_{\rm SHG}^{(2)}|$ has a maximum. This results in a spectral redshift of $|\chi_{\rm SHG}^{(2)}|$ with respect to $|\tilde{\chi}_{\rm SHG}^{(2)}|$.

In conclusion, we note that there are several other techniques which are particularly suitable for monitoring intermolecular charge transfer. Photoinduced charge-transfer processes can be identified by following the strong depend-



FIG. 9. Same as Fig. 8 but in the two-photon resonance region $\omega \sim \Omega_0/2$.

ence of the absorption line shape on an applied electric field.²⁸ This technique, known as electroabsorption, is related to $\chi^{(3)}$. Analysis of saturation spectroscopy (another $\chi^{(3)}$ -related technique) in molecular aggregates has also sug-

gested the existence of intermediate excitons.²⁹ In addition. direct measurements of photoconductivity can be used for identifying charge-transfer transitions.³⁰ The combination of $\gamma^{(2)}$ measurements analyzed in this article with these techniques may be used to explore the role of charge-transfer processes in the optical response of molecular assemblies. The rapid progress in the fabrication of molecular nanostructures, such as monolayers and thin films,²⁰ stimulates an increasing interest in the microscopic understanding and the manipulation of primary photochemical events such as charge transfer. An important aspect of the present formulation is that it interpolates between the molecular and the semiconductor pictures,³¹ and can therefore be used for a detailed comparison of different types of nanostructures including semiconductor quantum dots,³² polled and conjugated polymers,^{14,15} and molecular assemblies.

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APPENDIX: CALCULATION OF $\chi^{(2)}$

In this appendix we present the derivation of Eq. (4.13). We start with Eq. (4.11) and expand $\langle B_{rs} \rangle^{(2)}$ in Fourier components resulting in

$$\langle B_{rs} \rangle^{(2)} = b_{s,k_{\sigma}}^{(2)} e^{i(k_{\sigma}r - \omega_{\sigma}t)} + \tilde{b}_{s,k_{\sigma}}^{(2)} e^{i(-k_{\sigma}r + \omega_{\sigma}t)}.$$
 (A1)

When Eq. (A1) is substituted in Eq. (4.12) we obtain the following equations for amplitudes $b_{s,k_2}^{(2)}$:

$$-\omega_{\sigma}b_{s,k_{\sigma}}^{(2)} = -\Omega_{s}b_{s,k_{\sigma}}^{(2)} - \sum_{s'}U^{e}(s-s')e^{i(k_{\sigma}/2)(s'-s)}b_{s',k_{\sigma}}^{(2)} - \sum_{s'}U^{h}(s'-s)e^{i(k_{\sigma}/2)(s-s')}b_{s',k_{\sigma}}^{(2)}$$

$$-\mu_{s}J_{k_{\sigma}}\sum_{s'}\mu_{s'}\left[b_{s',k_{\sigma}}^{(2)} + \tilde{b}_{s',k_{\sigma}}^{*(2)}\right] - \mu_{s}J_{k_{\sigma}}\sum_{s'}\Delta_{s'}\sum_{j_{j_{\sigma}}}\tilde{b}_{s',j_{1}}^{*(1)}b_{s',j_{2}}^{(1)} + \sum_{j_{j_{\sigma}}}E_{j_{1}}S(\omega_{j_{1}},k_{j_{1}})\Delta_{s}b_{s,j_{2}}^{(1)}$$
(A2)

and a similar equation for $b_{s,k_{\alpha}}^{(2)*}$. Using the Green function $G_{ss'}(\omega,k)$ [Eq. (4.8)] we solve these equations resulting in

$$b_{s,k_{\sigma}}^{(2)} = \sum_{s'} G_{ss'}(\omega_{\sigma},k_{\sigma}) \bigg[-\mu_{s'}J_{k_{\sigma}} \sum_{s''} \mu_{s''}(b_{s'',k_{\sigma}}^{(2)} + \tilde{b}_{s'',k_{\sigma}}^{*(2)}) - \mu_{s'}J_{k_{\sigma}} \sum_{s''} \Delta_{s''}t_{s''}^{(2)} + \sum_{j_{1}j_{2}} E_{j_{1}}S(\omega_{j_{1}},k_{j_{1}})\Delta_{s'} \sum_{s''} G_{s's''}(\omega_{j_{2}},k_{j_{2}})E_{j_{2}}S(\omega_{j_{2}},k_{j_{2}})\mu_{s''}\bigg],$$
(A3)

where

$$t_{s^*}^{(2)} \equiv \sum_{j_1 j_2} E_{j_1} E_{j_2} S(\omega_{j_1}, k_{j_1}) S(\omega_{j_2}, k_{j_2}) \sum_{s_1 s_2} G_{s^* s_1} (-\omega_{j_1}, k_{j_1}) G_{s^* s_2} (\omega_{j_2}, k_{j_2}) \mu_{s_1} \mu_{s_2}.$$
(A4)

We next expand $\langle P_{rs}^{(2)} \rangle$, Eq. (4.11), in Fourier components

$$\langle P_{rs} \rangle^{(2)} = a_{s,k_{\sigma}}^{(2)} e^{i(k_{r}r - \omega_{\sigma}t)} + \tilde{a}_{s,k_{\sigma}}^{(2)} e^{i(-k_{r}r - \omega_{\sigma}t)}.$$
(A5)

Upon the substitution of Eqs. (A1), (A3), and (A4) in (4.11), we obtain the following for the amplitude [Eq. (A5)]:

$$a_{s,k_{\sigma}}^{(2)} = \mu_{s} \sum_{s'} G_{ss'}(\omega_{\sigma},k_{\sigma}) \bigg\{ -\mu_{s'}J_{k_{\sigma}} \sum_{s''} \big[\mu_{s''}(b_{s'',k_{\sigma}}^{(2)} + \tilde{b}_{s'',k_{\sigma}}^{*(2)}) + \Delta_{s''}t_{s''}^{(2)} \big] \\ + \sum_{j_{1}j_{2}} E_{j_{1}}S(\omega_{j_{1}},k_{j_{1}})\Delta_{s'} \sum_{s''} G_{s's''}(\omega_{j_{2}},k_{j_{2}})E_{j_{2}}S(\omega_{j_{2}},k_{j_{2}})\mu_{s''} \bigg\}$$

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$$+ \mu_{s} \sum_{s'} G_{ss'} (-\omega_{\sigma}, k_{\sigma}) \left\{ -\mu_{s'} J_{k_{\sigma}} \sum_{s''} \left[\mu_{s''} (b_{s'', k_{\sigma}}^{(2)} + \tilde{b}_{s', k_{\sigma}}^{*(2)}) + \Delta_{s''} t_{s''}^{(2)} \right] \right\} + \sum_{j, j_{2}} E_{j_{1}} S(\omega_{j_{1}}, k_{j_{1}}) \Delta_{s'} \sum_{s''} G_{ss''} (-\omega_{j_{2}}, k_{j_{2}}) E_{j_{2}} S(\omega_{j_{2}}, k_{j_{2}}) \mu_{s''} + \Delta_{s} \sum_{j, j_{2}} E_{j_{1}} E_{j_{2}} S(\omega_{j_{1}}, k_{j_{1}}) S(\omega_{j_{2}}, k_{j_{2}}) \sum_{s_{1}s_{2}} G_{ss_{1}} (-\omega_{j_{1}}, k_{j_{1}}) G_{ss_{2}} (-\omega_{j_{2}}, k_{j_{2}}) \mu_{s_{1}} \mu_{s_{2}}.$$
(A6)

Substituting Eq. (A6) and (A5) in Eq. (3.6a) and using the definition of $\chi^{(2)}$ [Eq. (4.2)], we finally obtain Eq. (4.13).

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