

Cooperative radiative decay in the nonlinear optical response of excitonic nanostructures

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The nonlinear susceptibility $\chi^{(3)}$ and the four-wave mixing signal from assemblies of molecules with nonoverlapping charge distributions and an arbitrary geometry are calculated using Green's-function techniques. At low molecular density and under off-resonant excitation we recover the local-field approximation. The role of retarded interactions and cooperative spontaneous emission in the electro-dynamics of confined excitons in molecular quantum wells is discussed.

I. INTRODUCTION

The study of excitons in systems with restricted geometries such as molecular multilayers (quantum wells),¹⁻³ chains,⁴⁻⁷ and clusters⁸⁻¹⁰ is currently drawing considerable attention. One of the main effects of interest is the possibility of enhanced nonlinearities due to increased exciton-exciton interactions resulting from the confinement.^{4,6} This effect is totally missed by the conventional local-field approximation. For extended nanostructures whose size is larger than the optical wavelength one has to take into account retardation effects.¹ A dramatic manifestation of retardation is the possibility of cooperative spontaneous emission. In three-dimensional (3D) crystals the radiation and material (polarization) modes combine to form joint normal modes (polaritons) which have no radiative decay.¹¹⁻¹⁴ This is no longer the case in nanostructures with lower dimensionality. These systems show radiative decay of excitons due to the fact that photons created in the material system can leave it. It was pointed out by Agranovich and Dubovsky in 1966 that in 2D systems there are two polariton branches one of which is nonradiative and the second has a finite lifetime due to spontaneous emission.¹⁵ In further investigations different methods were used for describing polaritons in systems with lower dimensionality. These include projection operators,^{1,13} and canonical transformation of creation and annihilation operators in the joint matter-field space.^{11,12,14} Both methods lead to correct dispersion relations for polaritons but the issue of *nonlinear response* of polaritons in confined systems remains an open question.

A different approach for calculating the optical response of systems with restricted geometries is based on introducing optical susceptibilities calculated with respect to the transverse Maxwell electric field. It was shown in Ref. 16 that the linear susceptibility $\chi^{(1)}$ is not affected by retardation. The effects of retardation (including spontaneous emission) for the optical *signal* from such a system, which is calculated in terms of the external field, are contained in the relationship between the transverse (Maxwell) and the external fields.

In the present paper we use this approach for calculating the nonlinear signal from molecular assemblies with arbitrary geometry. In the following section we present the Frenkel exciton model and the Hamiltonian. In Sec.

II we derive the expression for $\chi^{(3)}$ for a system of interacting two-level systems with arbitrary geometry. In Sec. IV we express the transverse Maxwell field in terms of the external field and calculate the nonlinear signal. In Sec. V we apply the results of Sec. IV to frequency-domain four-wave mixing from a molecular monolayer and in Sec. VI we show how cooperative spontaneous emission in this system may be probed using the transient grating technique. Conclusions and discussion are given in Sec. VII.

II. THE MODEL AND THE HAMILTONIAN

We consider an assembly of neutral molecules with nonoverlapping charge distributions. The total Hamiltonian in the Coulomb gauge and the multipolar form (neglecting magnetic terms) is^{14,16}

$$\hat{H}_{\text{mult}} = \hat{H}_{\text{mat}} + \hat{H}_{\text{rad}} - \int d\mathbf{r} \hat{\mathbf{P}}(\mathbf{r}) \cdot \hat{\mathbf{D}}^\perp(\mathbf{r}) + 2\pi \int d\mathbf{r} |\hat{\mathbf{P}}^\perp(\mathbf{r})|^2. \quad (2.1)$$

We denote an operator by a caret, e.g., \hat{O} and write $\langle \hat{O}(t) \rangle$ or simply $O(t)$ for its expectation value at time t , and we set $\hbar=1$. \hat{H}_{mat} is the material Hamiltonian with Coulomb interactions included. In our case it is the Hamiltonian of two-level molecules with dipole-dipole interactions. We represent the material Hamiltonian \hat{H}_{mat} in the form

$$\hat{H}_{\text{mat}} = \sum_m \Omega_m \hat{B}_m^\dagger \hat{B}_m + \sum_{m \neq n} J_{mn} \hat{B}_m^\dagger \hat{B}_n. \quad (2.2)$$

Here Ω_m is the transition frequency of the m th molecule and J_{mn} is the dipole-dipole intermolecular interaction. The operators \hat{B}_m are transition operators of the m th molecule, transforming its excited state to the ground state, and \hat{B}_m^\dagger is its Hermitian conjugate which induces the reverse transition. They satisfy the commutation relations

$$[\hat{B}_m, \hat{B}_{m'}^\dagger] = (1 - 2\hat{B}_m^\dagger \hat{B}_m) \delta_{mm'}. \quad (2.3)$$

The first term in (2.2) represents the noninteracting two-level molecules, whereas the second term describes the Coulomb (dipole-dipole) intermolecular interactions in the Heitler-London approximation where we neglect terms of the form $\hat{B}_m \hat{B}_n$ on $\hat{B}_m^\dagger \hat{B}_n^\dagger$. This approximation is

valid provided $\Omega_n \gg J_{mn}$. \hat{H}_{rad} is a free radiation field Hamiltonian

$$\hat{H}_{\text{rad}} = \frac{1}{8\pi} \int d\mathbf{r} \{ \hat{\mathbf{D}}^{\perp 2}(\mathbf{r}) + [\nabla \times \hat{\mathbf{A}}(\mathbf{r})]^2 \}, \quad (2.4)$$

where $\hat{\mathbf{A}}(\mathbf{r})$ is the vector potential in the Coulomb gauge $\nabla \cdot \hat{\mathbf{A}}(\mathbf{r}) = 0$, $\hat{\mathbf{D}}^{\perp}(\mathbf{r})$ is the operator of the transverse part of electric displacement $\nabla \cdot \hat{\mathbf{D}}^{\perp}(\mathbf{r}) = 0$. For the present (multipolar) form of the Hamiltonian, $\hat{\mathbf{D}}^{\perp}(\mathbf{r})$ is the momentum conjugate to $\hat{\mathbf{A}}(\mathbf{r})$, i.e., it commutes with all material operators and

$$[\hat{D}_i^{\perp}(\mathbf{r}), \hat{A}_j(\mathbf{r}')] = 4\pi ic \delta_{ij}^{\perp}(\mathbf{r} - \mathbf{r}'). \quad (2.5a)$$

$\delta_{ij}^{\perp}(\mathbf{r} - \mathbf{r}')$ is the transverse δ function [projection of the function $\delta_{ij}\delta(\mathbf{r} - \mathbf{r}')$ onto the space of transverse functions]. The commutation relations (2.5a) can be rewritten also in the form

$$\{ \hat{D}_i^{\perp}(\mathbf{r}), [\nabla \times \hat{A}(\mathbf{r}')]_j \} = 4\pi ic \sum_m \epsilon_{ijm} \frac{\partial}{\partial r'_m} \delta(\mathbf{r} - \mathbf{r}'). \quad (2.5b)$$

Here ϵ_{ijm} is the antisymmetric tensor with $\epsilon_{123} = 1$. It changes sign upon the permutation of any pair of indices. The Latin indices ijm denote the Cartesian components, and x, y, z are 1, 2, 3, respectively.

The transverse electromagnetic field $\hat{\mathbf{E}}^{\perp}(\mathbf{r})$ is related to the electric displacement operator $\hat{\mathbf{D}}^{\perp}(\mathbf{r})$ by the relation

$$\hat{\mathbf{E}}^{\perp}(\mathbf{r}) \equiv \hat{\mathbf{D}}^{\perp}(\mathbf{r}) - 4\pi \hat{\mathbf{P}}^{\perp}(\mathbf{r}), \quad (2.6)$$

where $\hat{\mathbf{P}}^{\perp}(\mathbf{r})$ is the transverse part of polarization. Since $\hat{\mathbf{P}}^{\perp}(\mathbf{r})$ is a purely material operator, it commutes with all field operators such as $\hat{\mathbf{D}}^{\perp}(\mathbf{r}')$ and $\hat{\mathbf{A}}(\mathbf{r}')$.

The polarization operator $\hat{\mathbf{P}}(\mathbf{r})$ can be represented in the following form:

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_m \hat{\mathbf{P}}_m(\mathbf{r}), \quad (2.7)$$

$$\frac{d\hat{B}_m(t)}{dt} = -i\Omega_m \hat{B}_m(t) - i \sum_{n \neq m} J_{mn} [1 - 2\hat{B}_m^{\dagger}(t)\hat{B}_m(t)] + \frac{i}{2} |\mu| \int d\mathbf{r} \rho(\mathbf{r} - \mathbf{R}_m) \cdot [\hat{\mathbf{E}}^{\perp}(\mathbf{r}, t), 1 - 2\hat{B}_m^{\dagger}(t)\hat{B}_m(t)]_+, \quad (3.2)$$

where $[\]_+$ denotes an anticommutator.

In the present paper we adopt a semiclassical approximation whereby the material system is treated quantum mechanically and the electromagnetic field is considered classical. In Eq. (3.2) we thus replace the transverse electromagnetic field operator by its expectation value $E^{\perp}(\mathbf{r}, t)$. We further introduce the following definitions:

$$E_m(t) \equiv \int d\mathbf{r} E^{\perp}(\mathbf{r}, t) \cdot \rho(\mathbf{r} - \mathbf{R}_m). \quad (3.3)$$

Equation (3.2) then takes the form

$$\begin{aligned} \frac{d\hat{B}_m(t)}{dt} = & -i\Omega_m \hat{B}_m(t) - i \sum_{n \neq m} J_{mn} [1 - 2\hat{B}_m^{\dagger}(t)\hat{B}_m(t)] \hat{B}_n(t) \\ & + i|\mu| E_m(t) [1 - 2\hat{B}_m^{\dagger}(t)\hat{B}_m(t)]. \end{aligned} \quad (3.4)$$

Equation (3.4) is very similar to the equation of motion for \hat{B} operators derived in Ref. 10. The only difference is

with

$$\hat{\mathbf{P}}_m(\mathbf{r}) = |\mu| \rho(\mathbf{r} - \mathbf{R}_m) (\hat{B}_m + \hat{B}_m^{\dagger}).$$

Here R_m is the position of the m th molecule, μ is the transition dipole, and $\rho(\mathbf{r})$ is the polarization density for the optical transition. A precise microscopic definition of $\rho(\mathbf{r})$ was given in Ref. 16. We have made here a slight change in notation and our $|\mu| \rho(\mathbf{r} - \mathbf{R}_m)$ is equal to $\rho(\mathbf{r} - \mathbf{R}_m)$ of Ref. 16. With this definition we have the normalization

$$\left| \int \rho(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} \right| = 1,$$

and the dipole approximation is simply obtained by setting

$$\rho(\mathbf{r} - \mathbf{R}_m) = \mu_m |\mu|^{-1} \delta(\mathbf{r} - \mathbf{R}_m).$$

III. LINEAR AND NONLINEAR OPTICAL SUSCEPTIBILITIES

The present approach is based on the derivation of equations of motion in the Heisenberg representation which map the system onto a set of coupled anharmonic oscillators.^{14,16} The equation of motion for an arbitrary operator \hat{Q} is

$$\frac{d\hat{Q}(t)}{dt} = -i[\hat{Q}(t), \hat{H}]. \quad (3.1)$$

Equation (3.1) for electromagnetic field operators results in the Maxwell equations.¹⁶ The solution of these equations relates the expectation value of the electromagnetic field to the total polarization. In order to express the polarization in terms of the transverse electromagnetic field, we apply Eq. (3.1) to the material operators \hat{B} and \hat{B}^{\dagger} , and obtain

that there the material system was treated in the dipole approximation and E_m was simply the electric field at the position R_m of the m th molecule. Here E_m is the transverse field averaged over the polarization density of the m th molecule. We next follow the steps used in Refs. 10 and 16 to solve this system of equations and calculate the nonlinear susceptibility $\chi^{(3)}$. This procedure is outlined in Appendix A. We adopt the following convention for a Fourier transform throughout this paper:

$$F(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) F(t). \quad (3.5)$$

We separate the polarization in the frequency domain into a linear and a nonlinear part

$$\mathbf{P}(\mathbf{r}, \omega) = \mathbf{P}^L(\mathbf{r}, \omega) + \mathbf{P}^{\text{NL}}(\mathbf{r}, \omega). \quad (3.6)$$

For the linear part we get

$$\mathbf{P}^L(\mathbf{r}, \omega) = \int d\mathbf{r}_1 \chi^{(1)}(\mathbf{r}, \mathbf{r}_1, \omega) \mathbf{E}^L(\mathbf{r}_1, \omega), \quad (3.7)$$

where the linear susceptibility is given by

$$\chi^{(1)}(\mathbf{r}, \mathbf{r}_1; \omega) = \sum_{n,m} \rho(\mathbf{r} - \mathbf{R}_n) \rho(\mathbf{r}_1 - \mathbf{R}_m) \hat{\chi}_{nm}^{(1)}(\omega) \quad (3.8)$$

and

$$\hat{\chi}_{nm}^{(1)}(\omega) = |\mu|^2 [G_{nm}(\omega) + G_{nm}^*(-\omega)]. \quad (3.9)$$

Here G_{nm} is the one-exciton Green's function,

$$G_{nm}(\omega) = \sum_{\alpha} \frac{\psi_{\alpha}^*(n) \psi_{\alpha}(m)}{\omega - \varepsilon_{\alpha} + i\eta}. \quad (3.10a)$$

It is expressed in the terms of the one-exciton wave functions $\psi_{\alpha}(n)$:

$$\Psi_{\alpha} = \sum_n \psi_{\alpha}(n) \hat{B}_n^{\dagger} |0\rangle, \quad (3.10b)$$

which satisfy the equation

$$\hat{H}_{\text{mat}} \Psi_{\alpha} = \varepsilon_{\alpha} \Psi_{\alpha}. \quad (3.10c)$$

For brevity we hereafter write ω instead of $\omega + i\eta$. The third-order nonlinear polarization \mathbf{P}^{NL} is

$$\begin{aligned} \mathbf{P}^{\text{NL}}(\mathbf{r}, \omega_s) &= \frac{1}{(2\pi)^2} \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_s - \omega_1 - \omega_2 - \omega_3) \\ &\quad \times \sum_{n, m_1, m_2, m_3} \rho(\mathbf{r} - \mathbf{R}_n) \hat{R}_{nm_1 m_2 m_3}^{\perp}(\omega_s, \omega_1, \omega_2, \omega_3) E_{m_1}(\omega_1) E_{m_2}(\omega_2) E_{m_3}(\omega_3), \end{aligned} \quad (3.11a)$$

with the nonlinear response function

$$\begin{aligned} \hat{R}_{nm_1 m_2 m_3}^{\perp}(\omega_s, \omega_1, \omega_2, \omega_3) &= |\mu|^4 \sum_{n', n''} \{ G_{nn'}(\omega_s) G_{n'm_3}^*(-\omega_3) G_{n''m_2}(\omega_2) G_{n'm_1}(\omega_1) \bar{\Gamma}_{n'n''}(\omega_1 + \omega_2) \\ &\quad + G_{nn'}^*(-\omega_s) G_{n'm_3}(\omega_3) G_{n''m_2}^*(-\omega_2) G_{n'm_1}^*(-\omega_1) \bar{\Gamma}_{n'n''}^*(-\omega_1 - \omega_2) \}. \end{aligned} \quad (3.11b)$$

Here $\bar{\Gamma}$ is a two-exciton scattering matrix

$$\bar{\Gamma}_{n'n''}(\omega) = -2[F^{-1}(\omega)]_{n'n''}, \quad (3.12a)$$

$$F_{n'n''}(\omega) = \sum_{\alpha', \alpha} \frac{\psi_{\alpha'}^*(n') \psi_{\alpha'}^*(n'') \psi_{\alpha}(n') \psi_{\alpha}(n'')}{\omega - \varepsilon_{\alpha'} - \varepsilon_{\alpha}}. \quad (3.12b)$$

Finally, the third-order susceptibility is given by

$$\chi^{(3)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \omega_s, \omega_1, \omega_2, \omega_3) = \sum_{n, m_1, m_2, m_3} \rho(\mathbf{r} - \mathbf{R}_n) \rho(\mathbf{r}_1 - \mathbf{R}_{m_1}) \rho(\mathbf{r}_2 - \mathbf{R}_{m_2}) \rho(\mathbf{r}_3 - \mathbf{R}_{m_3}) \hat{\chi}_{nm_1 m_2 m_3}^{(3)}(\omega_s, \omega_1, \omega_2, \omega_3), \quad (3.13)$$

where $\hat{\chi}^{(3)}$ can be expressed in terms of \hat{R}^{\perp} :

$$\begin{aligned} \hat{\chi}_{nm_1 m_2 m_3}^{(3)}(\omega_s, \omega_1, \omega_2, \omega_3) \\ = \frac{1}{8} \sum_p \hat{R}_{nm_1 m_2 m_3}^{\perp}(\omega_s, \omega_1, \omega_2, \omega_3), \end{aligned} \quad (3.14)$$

and the p sum is over all six permutations of the indices $m_j \omega_j$.

These expressions extend the results of Leegwater and Mukamel¹⁰ beyond the dipole approximation. Note that $\chi^{(1)}$ and $\chi^{(3)}$ do not depend on retardation and contain no signature of spontaneous emission. However, retardation is included in the actual signal through the relation between the transverse field and the external field, as will be shown below.

IV. THE NONLINEAR OPTICAL SIGNAL

The optical susceptibilities which relate the polarization to the transverse electric field provide a convenient

intermediate step in the calculation of the optical signal. The transverse field is the sum of the external field and the field generated by the material system. In practice it is the external field rather than the transverse field that can be controlled experimentally. The final step in connecting our results to experiment is thus to relate the transverse field to the external field. This can be done using the Green's-function solution of the Maxwell equation in the linear approximation.

From Eq. (3.11) we see that the nonlinear polarization may be expressed in terms of the average field variables E_n [Eq. (3.3)]. We then get

$$\begin{aligned} E_n &= |\mu|^{-1} \mu_n \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_n) + \sum_{n' \neq n} |\mu|^{-1} \mu_n \cdot \mathcal{G}(\mathbf{R}_n - \mathbf{R}_{n'}, \omega) \cdot \mathbf{P}_{n'} \\ &\quad + |\mu|^{-1} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \cdot \mathcal{G}(\mathbf{r} - \mathbf{r}', \omega) \cdot \rho(\mathbf{r}') \mathbf{P}_n \cdot \mu_n, \end{aligned} \quad (4.1a)$$

where

$$\mathbf{P}_n \equiv \int d\mathbf{r} \langle \hat{\mathbf{P}}_n(\mathbf{r}) \rangle \quad (4.1b)$$

is the total polarization of the n th molecule, and \mathcal{G} is the Green's function of the transverse electromagnetic field in vacuum,

$$\mathcal{G}(\mathbf{r}, \omega) = (2\pi)^{-3} \int_{-\infty}^{\infty} d^3q e^{i\mathbf{q}\cdot\mathbf{r}} \mathcal{G}(\mathbf{q}, \omega), \quad (4.1c)$$

$$\mathcal{G}_{ij}(\mathbf{q}, \omega) = \frac{4\pi\omega^2}{\omega^2 - \mathbf{q}^2 c^2} \left[\delta_{ij} - \frac{q_i q_j}{\mathbf{q}^2} \right]. \quad (4.1d)$$

Here \mathbf{q} is a 3D momentum conjugate to \mathbf{r} . We have assumed that the size of the molecular charge distribution is much smaller than the intermolecular distance and the wavelength of the external field. In the second term in Eq. (4.1a) we have thus invoked the dipole approximation. The last term in (4.1a) describing the electric field due to the polarization of a molecule in the region of its charge distribution (self-energy) cannot be calculated in the dipole approximation, and was taken into account exactly.

We next introduce the material self-energy matrix

$$\phi(\omega) = \phi^{\text{mol}}(\omega) + \phi^c(\omega),$$

$\phi^{\text{mol}}(\omega)$ and $\phi^c(\omega)$ are the single molecule and cooperative contributions to the self-energy, i.e.,

$$\phi_{mn}^{\text{mol}}(\omega) = \delta_{mm} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \mathcal{G}(\mathbf{r} - \mathbf{r}', \omega) \rho(\mathbf{r}'), \quad (4.2)$$

$$\phi_{mn}^c(\omega) = |\mu|^{-2} \boldsymbol{\mu}_m \cdot \mathcal{G}(\mathbf{R}_m - \mathbf{R}_n, \omega) \cdot \boldsymbol{\mu}_n [1 - \delta_{nm}].$$

We further use Eq. (3.8) and get

$$\mathbf{P}_n = \mu_n |\mu|^{-1} \sum_m \hat{\chi}_{nm}^{(1)} E_m. \quad (4.3)$$

Substituting (4.3) into (4.1a) we obtain

$$\begin{aligned} \mathbf{P}_n^s(\omega_s) &= \frac{1}{(2\pi)^2} \int \int \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_s - \omega_1 - \omega_2 - \omega_3) \\ &\quad \times \sum_{m_1 m_2 m_3} \hat{R}_{nm_1 m_2 m_3}(\omega_s; \omega_1, \omega_2, \omega_3) |\mu|^{-4} \boldsymbol{\mu}_n \boldsymbol{\mu}_{m_1} \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_{m_1}, \omega_1) \boldsymbol{\mu}_{m_2} \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_{m_2}, \omega_2) \boldsymbol{\mu}_{m_3} \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_{m_3}, \omega_3), \end{aligned} \quad (4.8)$$

where

$$\begin{aligned} \hat{R}_{nm_1 m_2 m_3}(\omega_s; \omega_1, \omega_2, \omega_3) &= |\mu|^4 \sum_{n', n''} \{ \hat{G}_{nn'}(\omega_s) \hat{G}_{n'm_3}^*(-\omega_3) \hat{G}_{n''m_2}(\omega_2) \hat{G}_{n''m_1}(\omega_1) \bar{\Gamma}_{n'n''}(\omega_1 + \omega_2) \\ &\quad + \hat{G}_{nn'}^*(\omega_s) \hat{G}_{n'm_3}(\omega_3) \hat{G}_{n''m_2}^*(-\omega_2) \hat{G}_{n''m_1}^*(-\omega_1) \bar{\Gamma}_{n'n''}^*(-\omega_1 - \omega_2) \}, \end{aligned} \quad (4.9)$$

with the modified Green's function

$$\hat{G}_{mn}(\omega) \equiv (G(\omega) \{ 1 - |\mu|^2 \phi(\omega) [G(\omega) + G^*(-\omega)] \}^{-1})_{mn}. \quad (4.10)$$

$$\begin{aligned} E_n - \sum_{n' \neq n} \phi_{nn'}^c(\omega) \hat{\chi}_{n'm}^{(1)}(\omega) E_m - \sum_m \phi_{nm}^{\text{mol}}(\omega) \hat{\chi}_{nm}^{(1)}(\omega) E_m \\ = |\mu|^{-1} \boldsymbol{\mu}_n \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_n). \end{aligned} \quad (4.4a)$$

Adopting a matrix notation, the solution of Eq. (4.4a) is given by

$$E_n = \sum_m [1 - \phi(\omega) \hat{\chi}^{(1)}(\omega)]_{nm}^{-1} |\mu|^{-1} \boldsymbol{\mu}_m \cdot \mathbf{E}^{\text{ext}}(\mathbf{R}_m). \quad (4.4b)$$

For a system with N molecules, the calculation of E_n requires the inversion of a $3N \times 3N$ matrix.

Let $\mathbf{P}_n^{\text{NL}}(\mathbf{r})$ be the nonlinear polarization of the n th molecule. We further introduce the total polarization of the n th molecule $\mathbf{P}_n^s(\mathbf{r})$, defined as the sum of $\mathbf{P}_n^{\text{NL}}(\mathbf{r})$ and the linear polarization induced by the electromagnetic field of the nonlinear signal

$$\mathbf{P}_n^s(\mathbf{r}, \omega) \equiv \mathbf{P}_n^{\text{NL}}(\mathbf{r}, \omega) + \int d\mathbf{r}' \chi^{(1)}(\mathbf{r}, \mathbf{r}', \omega) \mathbf{E}^s(\mathbf{r}', \omega). \quad (4.5)$$

We shall be interested in calculating the nonlinear signal field $\mathbf{E}^s(\mathbf{r}, \omega)$ outside the region of the molecular charge distribution. Using the Green's-function solution of the Maxwell equation we obtain for the signal field

$$\mathbf{E}^s(\mathbf{r}, \omega) = \sum_n \mathcal{G}(\mathbf{r} - \mathbf{R}_n, \omega) \mathbf{P}_n^s(\omega), \quad (4.6)$$

where

$$\mathbf{P}_n^s \equiv \int \mathbf{P}_n^s(\mathbf{r}') d\mathbf{r}'.$$

In complete analogy with the derivation of Eq. (4.4b) we may express \mathbf{P}^s in terms of \mathbf{P}^{NL} :

$$\mathbf{P}_n^s(\omega) = \mu_n \sum_m [1 - \phi(\omega) \hat{\chi}(\omega)]_{nm}^{-1} |\mu|^{-2} \boldsymbol{\mu}_m \mathbf{P}_m^{\text{NL}}, \quad (4.7)$$

where

$$\mathbf{P}_m^{\text{NL}} \equiv \int d\mathbf{r}' \mathbf{P}_m^{\text{NL}}(\mathbf{r}').$$

Combining (3.11), (4.4b), and (4.7) and making use of the symmetry $\phi(-\omega) = \phi^*(\omega)$, we finally have

Equations (4.6)–(4.10) provide an explicit expression of the nonlinearly generated field in terms of the external electromagnetic field.

We next introduce a different susceptibility defined with respect to the external field

$$\hat{\chi}_{nm_1m_2m_3}^{\text{ext}}(\omega_s, \omega_1, \omega_2, \omega_3) \equiv \frac{1}{8} \sum_p \hat{R}_{nm_1m_2m_3}(\omega_s, \omega_1, \omega_2, \omega_3). \quad (4.11)$$

It can be easily verified using Eqs. (4.8) and (4.11) that $\hat{\chi}^{\text{ext}}$ expresses the polarization which forms the nonlinear signal in four wave mixing in terms of the external electromagnetic field and the intensity of the signal is related to the absolute square of $\hat{\chi}^{\text{ext}}$, not $\hat{\chi}^{(3)}$. However, comparing (4.11) and (4.9) with (3.11b) and (3.14) we see that

we can obtain $\hat{\chi}^{\text{ext}}$ from $\hat{\chi}^{(3)}$ by simply substituting the modified Green's functions \hat{G} (4.10) into (3.11b) instead of the one-exciton Green's functions G . As can be seen from (4.10), \hat{G} is significantly different from G only when the self-energy ϕ is not small, which is the case near resonances. Thus only in the off-resonant regime is the nonlinear signal directly related to the third-order nonlinear susceptibility.

In order to treat time-domain four-wave-mixing measurements involving short pulses it is preferable to recast the nonlinear response in the time domain. We then have

$$\begin{aligned} P_n^s(t) = \frac{1}{|\mu|^4} \mu_n \int_0^\infty \int_0^\infty \int_0^\infty dt_1 dt_2 dt_3 \sum_{m_1, m_2, m_3} \hat{R}_{nm_1m_2m_3}(t_1, t_2, t_3) \mu_1 \cdot E^{\text{ext}}(\mathbf{R}_{m_1}, t - t_1 - t_2 - t_3) \\ \times \mu_2 \cdot E^{\text{ext}}(\mathbf{R}_{m_2}, t - t_2 - t_3) \mu_3 \cdot E^{\text{ext}}(\mathbf{R}_{m_3}, t - t_3) \end{aligned} \quad (4.12)$$

with the nonlinear response function

$$\hat{R}_{nm_1m_2m_3}(t_1, t_2, t_3) = \frac{1}{(2\pi)^3} \iiint d\omega_1 d\omega_2 d\omega_3 \left[\sum_p \hat{R}_{nm_1m_2m_3}(\omega_s; \omega_1, \omega_2, \omega_3) \right] \exp[-i\omega_1(t_1 + t_2 + t_3) - i\omega_2(t_2 + t_3) - i\omega_3 t_3]. \quad (4.13)$$

This expression is a convenient starting point for analyzing ultrafast techniques such as the transient grating, which will be considered in Sec. VI.

V. APPLICATION TO FOUR-WAVE MIXING FROM A MOLECULAR MONOLAYER

In this section we apply the general results of the previous section for calculating the four wave mixing signal from a 2D molecular assembly.^{1-3,17}

Consider a periodic monolayer in which the molecules occupy a square lattice with lattice constant a . Each lattice site is occupied by a two-level molecule with a transition dipole moment μ oriented in the z direction perpendicular to the monolayer. The generalization of the

present results to account for an arbitrary direction of the transition dipoles is straightforward.

To make use of the translational symmetry of the problem we recast the expressions of Sec. III in momentum (\mathbf{k}) space. We first perform a two-dimensional Fourier transform of the z component of the external field in the plane of the monolayer. We thus have

$$E_z^{\text{ext}}(\omega, \mathbf{k}) \equiv \sum_n E_z^{\text{ext}}(\omega, \mathbf{R}_n) e^{-i\mathbf{k} \cdot \mathbf{R}_n}, \quad (5.1)$$

where the wave vector \mathbf{k} with components k_1 and k_2 , $\mathbf{k} = (k_1, k_2)$ is defined in the first Brillouin zone $0 \leq k_1, k_2 \leq 2\pi/a$. Equations (4.8) and (4.9) then assume the form

$$\begin{aligned} P^s(\omega_s, \mathbf{k}_s) = \frac{a^4}{(2\pi)^6} \int d\omega_1 d\omega_2 d\omega_3 d^2k_1 d^2k_2 d^2k_3 \delta(\omega_s - \omega_1 - \omega_2 - \omega_3) \delta(\mathbf{k}_s - \mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) E_z^{\text{ext}}(\omega_1, \mathbf{k}_1) \\ \times E_z^{\text{ext}}(\omega_2, \mathbf{k}_2) E_z^{\text{ext}}(\omega_3, \mathbf{k}_3) \hat{R}(-\omega_s, -\mathbf{k}_s; \omega_1 \mathbf{k}_1, \omega_2 \mathbf{k}_2, \omega_3 \mathbf{k}_3), \end{aligned} \quad (5.2a)$$

$$\begin{aligned} \hat{R}(-\omega_s, -\mathbf{k}_s; \omega_1 \mathbf{k}_1, \omega_2 \mathbf{k}_2, \omega_3 \mathbf{k}_3) = -2|\mu|^4 \{ \hat{G}(\omega_s, \mathbf{k}_s) \hat{G}^*(-\omega_3, -\mathbf{k}_3) \hat{G}(\omega_1, \mathbf{k}_1) \hat{G}(\omega_2, \mathbf{k}_2) \bar{\Gamma}(\omega_1 + \omega_2, \mathbf{k}_1 + \mathbf{k}_2) \\ + \hat{G}^*(-\omega_s, -\mathbf{k}_s) \hat{G}(\omega_3, \mathbf{k}_3) \hat{G}^*(-\omega_1, -\mathbf{k}_1) \hat{G}^*(-\omega_2, -\mathbf{k}_2) \\ \times \bar{\Gamma}^*(-\omega_1 - \omega_2, -\mathbf{k}_1 - \mathbf{k}_2) \}. \end{aligned} \quad (5.2b)$$

Here the signal field has a frequency ω_s and in-plane momentum \mathbf{k}_s . The Green's function is given by

$$\hat{G}(\omega, \mathbf{k}) \equiv \sum_m \hat{G}_{mn}(\omega) \exp[-i\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)]. \quad (5.3)$$

We can similarly introduce the transverse response function \hat{R}^\perp in \mathbf{k} space by equations similar to (5.2) where all field components E^{ext} are replaced by the Maxwell field E . \hat{R} is simply related to \hat{R}^\perp in \mathbf{k} space by

$$\hat{R}(-\omega_s, -\mathbf{k}_s; \omega_1 \mathbf{k}_1, \omega_2 \mathbf{k}_2, \omega_3 \mathbf{k}_3) = S(\omega_s, \mathbf{k}_s) S(\omega_1, \mathbf{k}_1) S(\omega_2, \mathbf{k}_2) S(\omega_3, \mathbf{k}_3) \hat{R}^\perp(-\omega_s, -\mathbf{k}_s; \omega_1 \mathbf{k}_1, \omega_2 \mathbf{k}_2, \omega_3 \mathbf{k}_3), \quad (5.4a)$$

where

$$S(\omega, \mathbf{k}) \equiv \{1 - |\mu|^2 \phi(\omega, \mathbf{k}) [G(\omega, \mathbf{k}) + G^*(-\omega, -\mathbf{k})]\}^{-1}. \quad (5.4b)$$

Since we consider a periodic geometry, the single-exciton states have a well-defined momentum \mathbf{k} and energy $\Omega_{\mathbf{k}}$

$$\psi_{\alpha}(\mathbf{n}) = \exp(i\mathbf{k} \cdot \mathbf{R}_n), \quad \alpha = \mathbf{k}, \quad (5.5a)$$

$$\Omega_{\mathbf{k}} = \Omega + \sum_n \exp(-i\mathbf{k} \cdot \mathbf{R}_n) J_{n0}.$$

We then have

$$G(\omega, \mathbf{k}) = \frac{1}{\omega - \Omega_{\mathbf{k}}}, \quad (5.5b)$$

$$\hat{\chi}^{(1)}(\omega, \mathbf{k}) = -\frac{2\Omega_{\mathbf{k}}|\mu|^2}{\omega^2 - \Omega_{\mathbf{k}}^2}, \quad (5.5c)$$

$$\bar{\Gamma}(\omega, \mathbf{k}) = \left[\frac{2\pi}{a} \right]^2 \left[\int d^2\mathbf{k}_1 (\omega - \Omega_{\mathbf{k}_1} - \Omega_{\mathbf{k} - \mathbf{k}_1})^{-1} \right]^{-1}, \quad (5.5d)$$

which gives for the modified Green's function

$$\hat{G}(\omega, \mathbf{k}) = \frac{\omega + \Omega_{\mathbf{k}}}{\omega^2 - \Omega_{\mathbf{k}}^2 - 2\Omega_{\mathbf{k}}\phi(\omega, \mathbf{k})} \quad (5.5e)$$

Equation (4.2) in k space takes the form

$$\phi(\omega, \mathbf{k}) = \phi^{\text{mol}}(\omega) + \phi^c(\omega, \mathbf{k}), \quad (5.6a)$$

$$\phi^{\text{mol}}(\omega) = \frac{2}{(2\pi)^2} \pi |\mu|^2 \int_{-\infty}^{\infty} d^3q \left[\frac{(\omega^2/c^2) \bar{\rho}(\mathbf{q}) \cdot \rho(\mathbf{q}) - |\mathbf{q} \cdot \rho(\mathbf{q})|^2}{\omega^2/c^2 - q^2} - \frac{|\mathbf{q} \cdot \rho(\mathbf{q})|^2}{q^2} \right], \quad (5.6b)$$

$$\begin{aligned} \phi^c(\omega, \mathbf{k}) = |\mu|^2 \left[\frac{2\pi}{a^2} \sum_{G_1, G_2} \left[i \frac{(k_1 + G_1)^2 + (k_2 + G_2)^2}{\sqrt{\omega^2/c^2 - (k_1 + G_1)^2 - (k_2 + G_2)^2}} - \sqrt{(k_1 + G_1)^2 + (k_2 + G_2)^2} \right] \right. \\ \left. - \frac{1}{2\pi} \int_{-\infty}^{\infty} d^2q \left[i \frac{q^2}{\sqrt{\omega^2/c^2 - q^2}} - |\mathbf{q}| \right] \right], \quad \text{for } \omega > 0. \quad (5.6c) \end{aligned}$$

Note that

$$\phi^c(-\omega, \mathbf{k}) = \phi^{c*}(\omega, \mathbf{k}). \quad (5.6d)$$

$G_1 \equiv 2\pi m_1/a$ and $G_2 \equiv 2\pi m_2/a$ are reciprocal-lattice vectors, m_1, m_2 are integer numbers, k_1 and k_2 are the components of the momentum \mathbf{k} in the first Brillouin zone, and $\rho(\mathbf{q})$ is the continuous Fourier transform of $\rho(\mathbf{r})$

$$\rho(\mathbf{q}) \equiv \int_{-\infty}^{\infty} \rho(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r. \quad (5.7)$$

A few limiting cases can be obtained from these results.

When we are far from one-photon resonances we can neglect the radiative corrections altogether (setting $\phi=0$), we can then use the one-exciton Green's functions $G(\omega, \mathbf{k})$ instead of the modified Green's functions $\hat{G}(\omega, \mathbf{k})$ in Eq. (5.2b). For frequencies detuned far off the two-photon resonance ($\omega - 2\Omega$ is much larger than the two-exciton band width) we get from (5.5d) $\bar{\Gamma}(\omega, \mathbf{k}) \rightarrow \omega - 2\Omega$, and recover the local-field approximation for the nonlinear signal.¹⁴ These limiting cases show that the effects of retardation are significant only near resonances.

We next consider limiting cases for the molecular density. In the low-density limit, $a \rightarrow \infty$, we have $\Omega_q \rightarrow \Omega$, $\bar{\Gamma}(\omega, \mathbf{k}) \rightarrow \omega - 2\Omega$ [see Eq. (5.5d)] and we again get the local-field approximation. For high molecular density $a \ll \lambda_j$, where the λ_j is the optical wavelength $\lambda_j = 2\pi c/\omega_j$, we can simplify expression (5.6) for the self-energy by taking into account only the term with

$m_1 = m_2 = 0$ in the sum (5.6c) and neglecting the integral in (5.6c) and the self-interaction term $\phi^{\text{mol}}(\omega)$ in (5.6a). This gives

$$\phi(\omega, \mathbf{k}) = i \frac{2\pi |\mu|^2}{a^2} \frac{k^2}{\sqrt{\omega^2/c^2 - k^2}}, \quad \omega > 0. \quad (5.8)$$

This result corresponds to the continuum limit, where the monolayer is treated as a homogeneous 2D medium.

VI. COOPERATIVE RADIATIVE DECAY PROBED BY TRANSIENT GRATING SPECTROSCOPY

Consider a transient grating experiment with two coherent resonant pump beams incident on the monolayer with a common incident angle θ . We denote the projections of the two-pump wave vectors in the monolayer plane by \mathbf{k}_1 and \mathbf{k}_2 ($|\mathbf{k}_2| = |\mathbf{k}_1|$) and their (common) electric field envelop $\zeta_1(\tau)$. After a delay period τ_d , a third pulse (the probe) with in-plane wave vector \mathbf{k}_3 and incident angle θ_3 is scattered off the system and the Bragg diffracted signal with the in-plane momentum $\mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ is being detected in the direction θ_s . The probe pulse with envelope $\zeta_3(\tau - \tau_d)$ is taken to be off resonant with frequency ω_3 . The duration of all pulses is assumed to be much shorter than the decay time of the grating. We further assume that we are in the high-density limit and we use Eq. (5.8) for the self-energy ϕ .

To calculate the transient grating signal we decompose the external electric field in (5.2a) into a sum of two-pump pulses and the probe pulse, taking into account only the terms in (5.2a) which contain a product of the envelopes of all three pulses. We then substitute (5.2b) into (5.2a) using the expression (5.5d) for $\bar{\Gamma}(\omega, \mathbf{k})$ and (5.5e) with $\phi(\omega, \mathbf{k})$ from (5.8) for $\hat{G}(\omega, \mathbf{k})$. Switching to real space and to the time domain we can make use of the fact that the probe and the signal pulses are off resonant

$$P_n^s(t) = 8|\mu|^4 \frac{\Omega \sin^2 \theta}{\Omega^2 - \omega_3^2} \left| \int_{-\infty}^{\infty} \zeta_1(t) dt \right|^2 \exp(-t/2\tau_{\text{TG}}) \zeta_3(t - \tau_d) \exp(-i\omega_3 t + i\mathbf{k}_s \cdot \mathbf{R}_n), \quad (6.1)$$

where \mathbf{k}_s is the projection of the wave vector of the signal pulse onto the x - y plane.

The electric field of the signal is related to polarization P^s by means of the Green's function (4.1c) [see (4.6)]. This enables us to express the envelope of the electric field in the signal pulse $\zeta_s(t)$ in terms of P^s . We are interested in the dependence of the integrated intensity of the signal pulse I^s on the integrated intensity of the probe pulse I_3 and the delay time τ_d where

$$I_{\text{TG}}(\tau_d) = \int_{-\infty}^{\infty} |\zeta^s(\tau)|^2 d\tau. \quad (6.2)$$

Straightforward calculation of Eq. (6.1) gives

$$I_{\text{TG}}(\tau_d) = A \exp(-\tau_d/\tau_{\text{TG}}), \quad (6.3)$$

with

$$A = 256\pi^2 \frac{|\mu|^8}{a^4} \left[\frac{\Omega\omega_3}{\Omega^2 - \omega_3^2} \right]^2 \frac{\sin^4 \theta \sin^2 \theta_3 \sin^2 \theta_s}{\cos^2 \theta_s} \times \int_{-\infty}^{\infty} |\zeta_3(\tau)|^2 d\tau \left| \int_{-\infty}^{\infty} \zeta_1(\tau) dt \right|^4. \quad (6.4)$$

Here τ_{TG} represents the transient grating radiative decay time

$$\tau_{\text{TG}} = \tau_m \frac{\cos \theta}{24\pi^3 \sin^2 \theta} \left[\frac{a}{\lambda} \right]^2, \quad (6.5)$$

where λ is the wavelength of the pump beams and τ_m the decay time of a single molecule,

$$\tau_m = \frac{3}{4} \frac{c^3}{\omega^3 |\mu|^2}. \quad (6.6)$$

The $(a/\lambda)^2$ factor in τ_{TG} shows the effect of cooperative spontaneous emission in the grating decay. Note that the grating decay time τ_{TG} does not depend on the grating wave vector $\mathbf{k}_1 - \mathbf{k}_2$. This can be explained by the fact that it depends on retardation on the linear optics level, since Eq. (4.4b), which expresses the transverse Maxwell field in terms of external field, is linear.

VII. CONCLUSIONS

We have calculated both the nonlinear susceptibility $\chi^{(3)}$ and the nonlinear signal for a system of interacting two-level molecules of arbitrary geometry. The calculation is based on two main assumptions: (i) we use the

and the pump pulses are much shorter than the transition grating decay time τ_{TG} . Consequently, when performing integrations in (5.2a) with \hat{K} from (5.2b) we can take the scattering matrix $\bar{\Gamma}(\omega, \mathbf{k})$ and the Green's functions $\hat{G}(\omega, \mathbf{k})$, corresponding to the probe and signal pulses at some average frequencies and wave vectors of the pulses and we can also take the electric field of the pump pulses at the resonant frequency. We then obtain the following expression for the polarization:

Heitler-London Hamiltonian for the material system, and (ii) we do not take into account the quantum nature of the transverse electromagnetic field. The first assumption implies that we work in first-order perturbation theory in the parameter J/Ω , where J is the interaction energy between molecules and Ω is the molecular excited-state energy. It is possible to develop a perturbation theory and calculate corrections of higher order. As a result of the second assumption, the nonlinear susceptibility $\chi^{(3)}$ has the form of a product of four one-exciton Green's functions G and a two-exciton Green's function $\bar{\Gamma}$ [see (3.11)]. We can calculate the nonlinear signal [(4.8) and (4.9)] by replacing the Green's function G in Eq. (3.11) with the modified Green's functions \hat{G} [Eq. (4.10)], without changing $\bar{\Gamma}$. This results from expressing the transverse electromagnetic field in terms of the external field, and the total polarization P^s in terms of the nonlinear part P^{NL} in the framework of linear optics. Therefore all retardation effects are contained in the modified Green's functions \hat{G} . Stated differently, this assumption implies that we neglect radiative (retardation) effects in the calculation of the linear and nonlinear susceptibilities. Nevertheless we have retardation effects in the nonlinear signal due to radiative effects in linear optics, where it makes no difference whether we treat the field classically or quantum mechanically. To incorporate rigorously the effects of radiative decay of two-exciton states we have to take into account nonlinear polariton effects related to the interaction of excitons¹⁴ which result in radiative corrections to $\chi^{(3)}$. This requires relaxing the second assumption and will be discussed in a future publication.¹⁸ Generalization of the results obtained in the present paper to the case of multilevel molecules is possible. Further generalizations of the present approach to other techniques such as $\chi^{(2)}$ are of interest as well.^{3,19,20}

As is clearly seen from (4.10) the modification of the one-exciton Green's functions is determined by the self-energy $\phi_{mn}(\omega)$ which is a sum of an intramolecular contribution and an intermolecular cooperative contribution which depends on the geometry of the system. We evaluated the self-energy for a two-dimensional monolayer. The real part of ϕ defines the radiative shift of the exciton energy, and the imaginary part is responsible for the finite radiative lifetime of excitons. For $a \ll \lambda$, the lifetime is determined by the cooperative contribution and is reduced by a factor $(a/\lambda)^2$ compared with the lifetime of a single molecule. This means that the cooperative

length is $\sim \lambda$.¹⁶ This effect of cooperativity in the nonlinear signal can be observed using the transient grating technique [Eq. (6.3)] with the decay time given by (6.5).

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APPENDIX: CALCULATION OF $\chi^{(3)}$

Although we can proceed with the Hamiltonian, Eq. (2.2), it will be easier to consider a different Hamiltonian,

$$\hat{H}'_{\text{mat}} = \sum_m \Omega_m \hat{C}_m^\dagger \hat{C}_m + \sum_{m \neq n} J_{mn} \hat{C}_m^\dagger \hat{C}_n + g \sum_m (\hat{C}_m^\dagger)^2 \hat{C}_m^2, \quad (\text{A1})$$

where the operators $\hat{C}_m, \hat{C}_m^\dagger$, obey the Bose commutation relations

$$[\hat{C}_m, \hat{C}_{m'}^\dagger] = \delta_{mm'}, \quad (\text{A2})$$

and the polarization is given by

$$\mathbf{P}_n(r) = |\mu| \rho(r - R_n) (\hat{C}_m + \hat{C}_m^\dagger). \quad (\text{A3})$$

The Hamiltonian (A1) describes a system of oscillators with repulsion on the same site (we take $g > 0$). In the limit $g \rightarrow \infty$, (A1), (A2), and (A3) describe the same model as (2.2), (2.3), and (2.7) due to the fact that the excited states higher than the first on each molecule have an infinite energy and should not be taken into account, so that the exciton dynamics described by (A1) and (A2) with infinite number of states in each site is identical to our original model of two-level molecules. The Hamiltonian (A1) is more convenient for calculations, as the Bose commutation relations (A2) are simpler. We will use this form of the Hamiltonian for calculation of susceptibilities $\chi^{(1)}$ and $\chi^{(3)}$. $\chi^{(3)}$ will be calculated using the Hamiltonian (A1) and then we shall take the $g \rightarrow \infty$ limit.

The equation of motion (3.1) for the \hat{C} operators is

$$\frac{d\hat{C}_m(t)}{dt} = -i\Omega_m \hat{C}_m(t) - i \sum_{n \neq m} J_{mn} \hat{C}_n(t) - i2g \hat{C}_m^\dagger(t) \hat{C}_m^2(t) + i\mu E_m(t). \quad (\text{A4})$$

Taking the expectation value of (A4) we get

$$\frac{dC_m(t)}{dt} = -i\Omega_m C_m(t) - i \sum_{n \neq m} J_{mn} C_n(t) - i2g \langle \hat{C}_m^\dagger(t) \hat{C}_m^2(t) \rangle + i\mu E_m(t). \quad (\text{A5})$$

We are interested in evaluating $C_m(t)$ up to third order in electromagnetic field. In this case we can make use of the fact that the expansion of expectation values of the form $\langle \hat{C}_{n_1}^\dagger \hat{C}_{n_1} \hat{C}_{n_2}^\dagger \hat{C}_{n_2} \dots \hat{C}_{n_m} \rangle$ in powers of the electric field start at m th order, and for this order we have

$$\langle \hat{C}_{n_1}^\dagger \hat{C}_{n_1} \hat{C}_{n_2}^\dagger \hat{C}_{n_2} \dots \hat{C}_{n_m} \rangle^{(m)} = \langle \hat{C}_{n_1}^\dagger \dots \hat{C}_{n_i}^\dagger \rangle^{(i)} \langle \hat{C}_{n_{i+1}} \dots \hat{C}_{n_m} \rangle^{(m-i)}. \quad (\text{A6})$$

The relations (A6) are valid due to the Heitler-London form of the Hamiltonian (A1), which conserves the number of excitons, and the ground state is the vacuum state with no excitons. Using (A6) we get from (A5)

$$\frac{dC_m^{(1)}(t)}{dt} = -i\Omega_m C_m^{(1)}(t) - i \sum_{n \neq m} J_{mn} C_n^{(1)}(t) + i\mu E_n(t), \quad (\text{A7a})$$

$$\frac{dC_m^{(3)}(t)}{dt} = -i\Omega_m C_m^{(3)}(t) - i \sum_{n \neq m} J_{mn} C_n^{(3)}(t) - 2iG \bar{C}_m^{(1)}(t) \langle \hat{C}_m^2(t) \rangle^{(2)}. \quad (\text{A7b})$$

To get a closed system of equations we use Eq. (A5) to write down the equation of motion for the variables $\langle \hat{C}_m(t) \hat{C}_n(t) \rangle$. Making use of (A6) we finally get

$$\frac{d}{dt} \langle \hat{C}_n(t) \hat{C}_m(t) \rangle^{(2)} = -i(\Omega_m + \Omega_n) \langle \hat{C}_n(t) \hat{C}_m(t) \rangle^{(2)} - i \sum_{n' \neq n} J_{nn'} \langle \hat{C}_{n'}(t) \hat{C}_m(t) \rangle^{(2)} - i \sum_{m' \neq m} J_{mm'} \langle \hat{C}_n(t) \hat{C}_{m'}(t) \rangle^{(2)} - 2ig \delta_{mn} \langle \hat{C}_n^{(2)}(t) \rangle^{(2)} + i\mu E_n(t) C_m^{(1)}(t) + i\mu E_n(t) C_m^{(1)}(t). \quad (\text{A8})$$

Equations (A7) and (A8) form a closed set. Their solution, which yields the optical polarization in terms of the transverse electromagnetic field, is exact up to third order, and gives the susceptibilities $\chi^{(1)}$, $\chi^{(3)}$, and \hat{R}^\perp [Eqs. (3.8), (3.9), (3.13), (3.14), and (3.11b)] with

$$\bar{\Gamma}_{mn}(\omega) = 4g [(1 - 2gF)^{-1}]_{mn}. \quad (\text{A9})$$

Upon sending g to infinity in Eq. (A9) we obtain Eq. (3.12a).

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