

Exciton-scattering mechanism for enhanced nonlinear response of molecular nanostructures

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We study the nonlinear optical response of molecular assemblies consisting of coupled two-level molecules with arbitrary geometry including inhomogeneous broadening and exciton dephasing. An analytical expression for the third-order optical susceptibility is derived based on a certain closure of the equation-of-motion hierarchy. An exact expression for the third-order response of small crystalline aggregates with exciton population relaxation is derived, and used to show that for low relaxation rate Γ the cooperative part of the nonlinear response scales as $\Gamma^{-1/2}$ in $d=1$, and up to logarithmic corrections, as Γ^{-1} in $d=2$ and 3. We show that cooperative enhancement is caused by exciton scattering. This is to be contrasted to other cooperative effects such as superradiance, which are related to the size of molecular coherence domains and therefore scale as $\Gamma^{-d/2}$. In a numerical study for dipole-dipole interactions in $d=1, 2$, and 3 dimensions we find that the local-field approximation is valid only in selected cases, and in general fails to reproduce the magnitude and the resonance structure of $\chi^{(3)}$.

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I. INTRODUCTION

In recent years a number of studies have appeared investigating the optical response of molecular and semiconductor nanostructures. A main point of focus has been the effects of exciton confinement on the magnitude of the nonlinear optical response [1–7].

Previous theoretical works considered the nonlinear optical response of a system of N coupled two-level molecules [8,9]. The nonlinear susceptibility was expressed as the sum of Liouville pathways, and it was found that there are two contributions, both of order N^2 . These contributions interfere destructively for moderate to rapid dephasing rates, resulting in a susceptibility proportional to the number of molecules N . In a subsequent study [10], the same results were obtained using an equation-of-motion approach which rigorously maps the system onto a collection of coupled anharmonic oscillators which represent one or more excitons. In the oscillator picture the interference is built in naturally and we obtain a starting harmonic reference system in which the excitons are bosons: cooperative enhancement is then obtained through exciton-exciton interactions.

Using equations of motion for the oscillators themselves (instead of the N -molecule exciton states), it has been shown that the nonlinear response contains two contributions. The first contribution is a *local* nonlinearity, that is also present even with no coupling between the molecules and is proportional to N . The second contribution is caused by the coupling of molecules and represents a nonlocal nonlinearity. The magnitude of the nonlocal contribution depends on the laser detuning as well as the exciton dephasing rate, and may become of the order of N^2 .

So far the theories used to study cooperativity concerned themselves with one-dimensional regular lattices with nearest-neighbor interactions [8–11]. The main purpose of the present work is to remove these limita-

tions by considering a molecular assembly with arbitrary geometry, and to incorporate the more realistic dipole-dipole interactions. We derive a general expression for the nonlocal contribution in terms of a specific matrix element of the two-exciton Green function, which, in turn, can be related to a matrix element of the two-exciton scattering (T) matrix [12]. For a small crystalline aggregate this particular matrix element of the T matrix is inversely proportional to the amplitude of returning to the origin for a particle that is hopping over the lattice. Mathematically, the Schrödinger equation is closely related to the diffusion equation. Making an analytical continuation to imaginary times we can therefore establish a general formal connection between enhanced nonlinearities and the probability of returning to the origin in a random walk. Apart from being an interesting theoretical observation, this connection immediately shows that the dimensionality is going to be of prime importance, as the total number of returns to the origin in a random walk diverges in one and two dimensions, and is finite in three dimensions [13].

An apparently related cooperative effect is the enhanced radiative decay rate (superradiance) observed in molecular assemblies [4,14–16]. Superradiance can be most conveniently described using the concept of a molecular coherence size (coherent domains). In the absence of dephasing it was shown [10] that both the superradiance and the enhanced nonlinearity are limited by the coherence size λ , the optical wavelength. The present study of the effects of dephasing points out a fundamental difference between the two phenomena. Enhanced nonlinearities are best described in terms of the coherence among elementary excitations (excitons) whereas superradiance is related to the coherence among molecules (coherence domains). This difference is clearly shown by examining the scaling of both phenomena with the dephasing rate in various dimensionalities.

The rest of the paper is organized as follows. In Sec. II

we define the model studied and present the equations of motion for the oscillators. In Sec. III we calculate the nonlinear optical response of this system, and in Sec. IV we specialize to a frequency-domain third-order ($\chi^{(3)}$) measurement. In Sec. V a further simplification is presented resulting from the study of small crystalline aggregates. In Sec. VI we study the cooperativity enhancement factor, and in particular its behavior in various dimensions. Here we show that exciton scattering rather than coherent domains is the more appropriate picture for cooperative enhancement. In Sec. VII we present numerical results for the nonlinear susceptibilities of periodic structures with dipole-dipole interactions.

II. THE FRENKEL EXCITON MODEL

We consider a molecular assembly containing N coupled two-level molecules with an arbitrary geometry and dimensionality. We start with the Frenkel exciton Hamiltonian [17–19]

$$H = \hbar \sum_n \Omega_n B_n^\dagger B_n + \frac{\hbar}{2} \sum_{n,m} J_{nm} (B_m^\dagger B_n + B_n^\dagger B_m) - \sum_n E_n(t) P_n. \quad (1)$$

The B_n operators are Pauli creation (B^\dagger) and annihilation (B) operators for excitons at molecule, or site, n . The index n runs over all the molecules in the system, and may also run over internal degrees of freedom. The B 's commute, except when acting on the same site. So we have

$$[B_n, B_m] = [B_n^\dagger, B_m^\dagger] = B_n^2 = (B_n^\dagger)^2 = 0, \quad (2)$$

and

$$[B_n, B_m^\dagger] = \delta_{nm} (1 - 2B_n^\dagger B_n), \quad (3)$$

where δ_{nm} is the Kronecker delta.

Ω_n is the isolated-molecule transition frequency, and J is the coupling between two molecules. By convention we take $J_{nn} = 0$, $J_{nm} = J_{mn}$ and real. The coupling allows for exciton migration among molecules but does not change the number of excitations. In molecular crystal language this is known as the Heitler-London approximation [17]. J_{nm} can represent dipole-dipole interactions as well as short-range exchange exciton couplings. Finally E is the external field, $P_n = \mu_n (B_n + B_n^\dagger)$ is the dipole operator, and μ_n is the transition dipole moment of molecule n .

Equation (3) states that there can only be one exciton on a molecule. Excitons are therefore not true bosons; instead they can be thought of as hard-core bosons. As an interesting note: superfluid helium is also not an ideal Bose fluid, but rather a hard-core Bose fluid, since ^4He atoms have short-range repulsive forces. Pushing this analogy to high exciton density, excitons may be expected to undergo a Bose condensation in intense laser fields [20]. Recent experiments have attempted to observe Bose condensation of Wannier exciton systems in semiconductors [21], but no firm evidence for a condensation has been given yet. We feel that Frenkel exciton systems are

more promising candidates for observing Bose condensation, as much higher exciton densities can be attained without destroying their boson character. The treatment of Bose condensation is beyond the scope of the present article which is restricted to weak excitations and third-order response. However, we believe that the exciton coupling mechanism and Green-function approach developed here could be used in a future microscopic theoretical treatment of this important problem.

We use the Heisenberg picture throughout this paper. The Heisenberg equation of motion for an operator $A(t)$, $\hbar dA(t)/dt = i[H, A]$, yields

$$\frac{1}{i} \frac{d}{dt} B_n = -\Omega_n B_n - \sum_m J_{nm} B_m + 2 \sum_m J_{nm} B_n^\dagger B_n B_m + \mu_n \frac{E_n(t)}{\hbar} (1 - 2B_n^\dagger B_n). \quad (4)$$

There are two nonlinear terms in Eq. (4). The source of nonlinearities is that two-level molecules are not harmonic oscillators. The nonlinear terms correct for the difference. The last term in Eq. (4) implies that an excited molecule cannot be excited again, and therefore constitutes a local, or intramolecular nonlinearity. This type of nonlinearity has been referred to in semiconductors as phase-space filling [3]. The Bloch equations commonly used in the calculation of the nonlinear response contain only this nonlinearity. There is one additional nonlinearity; the coupling *between* sites is also nonlinear due to the on-site exclusion. This additional term states that the interaction between molecules n and m depends on whether the molecule at n is excited or not, since the molecule can only be excited once. We will refer to this term as the nonlocal or intermolecular nonlinearity [10].

Equation (4) contains no relaxation mechanism. In order to make the model more realistic, we incorporate exciton population relaxation and pure-dephasing mechanisms into the equations of motion. We first introduce a simple model for exciton dephasing corresponding to relaxation of population resulting in a finite exciton lifetime. The model assumes a coupling to a heat bath (Q_n) with a coupling $\sum_n [V_n^\dagger(Q_n) B_n^\dagger + V_n(Q_n) B_n]$. The coupling operators V_n at different sites are assumed to be uncorrelated, so that each molecule has its own heat bath. Using standard procedures from the theory of relaxation [19], we can then incorporate the effects of the baths by adding a damping term to the equations of motion. To second order in V_n , and assuming a very short correlation time of the bath, we find that the following relaxation term has to be added to the equations of motion:

$$\left. \frac{d}{dt} \right|_{\text{lifetime}} B_{n_1}^\dagger \cdots B_{n_i}^\dagger B_{n_{i+1}} \cdots B_{n_m} = -\frac{m}{2} \gamma B_{n_1}^\dagger \cdots B_{n_i}^\dagger B_{n_{i+1}} \cdots B_{n_m}, \quad (5a)$$

where the (site-independent) population relaxation rate γ is given by

$$\gamma = \int_0^\infty d\tau \langle V_n(\tau) V_n(0) \rangle_{\text{bath}} \exp(i\Omega_n \tau). \quad (5b)$$

It should be emphasized that the relaxation term may only be added to the time evolution of a normally ordered product, that is, all the B^\dagger are to the left of the B 's. As we can bring any product of operators to a normally ordered form using the commutation relations, this is not a limitation. It can easily be verified that this relaxation model guarantees conservation of probability, i.e., $(d/dt)(B_n^\dagger B_n + B_n B_n^\dagger) = 0$.

The second relaxation mechanism corresponds to pure dephasing resulting from fluctuations of the isolated-molecule frequency. For this use the Haken-Strobl model [19,22], which assumes a coupling to another heat bath, (Q'_n) with a coupling $\sum_n [V'_n(Q'_n) B_n^\dagger B_n]$. Again each molecule has its own heat bath which has a very short correlation time. This will introduce an additional damping term, such as Eq. (5), but now the right-hand side depends on whether different indices are equal. The pure-dephasing contributions to the equations of motion occurring in this paper are

$$\left. \frac{d}{dt} \right|_{PD} \langle B_{n_1} \rangle = -\frac{\hat{\Gamma}}{2} \langle B_{n_1} \rangle, \quad (6a)$$

$$\left. \frac{d}{dt} \right|_{PD} \langle B_{n_1} B_{n_2} \rangle = -\hat{\Gamma} \langle B_{n_1} B_{n_2} \rangle, \quad (6b)$$

$$\left. \frac{d}{dt} \right|_{PD} \langle B_{n_1}^\dagger B_{n_2} \rangle = -\hat{\Gamma}(1 - \delta_{n_1, n_2}) \langle B_{n_1}^\dagger B_{n_2} \rangle, \quad (6c)$$

$$\left. \frac{d}{dt} \right|_{PD} \langle B_{n_1}^\dagger B_{n_2} B_{n_3} \rangle = -\hat{\Gamma} \left(\frac{3}{2} - \delta_{n_1, n_2} - \delta_{n_1, n_3} \right) \times \langle B_{n_1}^\dagger B_{n_2} B_{n_3} \rangle, \quad (6d)$$

where

$$\hat{\Gamma} = 2 \int_0^\infty d\tau \langle V'_n(\tau) V'_n(0) \rangle_{\text{bath}} \quad (6e)$$

is the pure-dephasing rate. We use the notation $\Gamma \equiv \hat{\Gamma} + \gamma$ for the total dephasing rate in the sequel. Equation (4) together with Eqs. (5) and (6) form the basis for the theory and calculations developed in this paper.

III. THE NONLINEAR OPTICAL RESPONSE

For weak fields, the polarization (and the expectation values of the B_n and B_n^\dagger operators) is small, so to find the nonlinear response we can make a perturbation expansion in the number of B 's provided they are normally ordered. We are interested in the response of the system to external electric fields, in particular in the expectation value of the dipole operator $\langle P_n(t) \rangle$ as this is what is observed in optical measurements. In the Heisenberg picture the expectation value of an operator is taken with respect to the state without excitons (vacuum), so $\langle \rangle = \langle 0 | \cdot | 0 \rangle$. In Eq. (4) we then need the expectation value of a product of three B 's. It is possible to derive entirely general formulas for the nonlinear response in terms of Green functions for up to three excitons. For the sake of simplicity we will not do this, but rather use a certain factorization de-

scribed below. If we set the pure-dephasing rate $\hat{\Gamma}$ to zero, the only dephasing mechanism is population relaxation, so that the system is in a pure state, and therefore

$$\langle B^\dagger \cdots B^\dagger B \cdots B \rangle = \langle B^\dagger \cdots B^\dagger \rangle \langle B \cdots B \rangle, \quad (7)$$

for any number of exciton creation and annihilation operators. On the other hand, note that

$$\langle B_n B_m(t) \rangle \neq \langle B_n(t) \rangle \langle B_m(t) \rangle \quad (8)$$

as can be seen by taking, for instance, $n = m$. If pure dephasing is present, the factorization Eq. (7) no longer holds. Recently Dubovsky and Mukamel [11] proposed the factorization

$$\begin{aligned} \langle B_n^\dagger B_n B_m \rangle &= \langle B_n^\dagger \rangle \langle B_n B_m \rangle + \langle B_n^\dagger B_n \rangle \langle B_m \rangle \\ &+ \langle B_n^\dagger B_m \rangle \langle B_n \rangle - 2 \langle B_n^\dagger \rangle \langle B_m \rangle \langle B_n \rangle. \end{aligned} \quad (9)$$

This factorization generalizes Eq. (7) so that also the exciton population $\langle B^\dagger B \rangle$ is treated explicitly, which is needed in order to describe, e.g., extra resonances in degenerate four-wave mixing and coherent Raman spectroscopy. The specific form of Eq. (9) follows from a maximization of entropy argument. An attractive feature of this factorization is that it allows us to obtain simple numerical calculations for small crystalline aggregates.

Before proceeding with the calculation let us first comment on the local-field approximation [1,23–25] which is commonly used in nonlinear optics, and will be a convenient reference in the following calculation. By taking expectation values of all operators in Eq. (4) and factorizing $\langle B_n^\dagger B_n B_m \rangle = \langle B_n^\dagger \rangle \langle B_n \rangle \langle B_m \rangle$ and $\langle B_n^\dagger B_n \rangle = \langle B_n^\dagger \rangle \langle B_n \rangle$ we can recast Eq. (4) in the form

$$\begin{aligned} \frac{d}{dt} \langle B_n \rangle &= -i\Omega_n \langle B_n \rangle + i\mu_n \frac{E_n^{(l)}(t)}{\hbar} (1 - 2 \langle B_n^\dagger \rangle \langle B_n \rangle) \\ &- \frac{\Gamma}{2} \langle B_n \rangle, \end{aligned} \quad (10)$$

with the local field at site n

$$E_n^{(l)}(t) \equiv E_n(t) + \sum_{m (\neq n)} J_{nm} \langle B_m(t) \rangle. \quad (11)$$

In Eq. (10) we have converted the dynamics to that of a single molecule in a local field. Equation (10) is closed and can be solved for the nonlinear response [11,19]. We shall refer to that solution in Sec. IV.

When solving the equations of motion we find that we have to solve for single (one B) and double (two B 's) exciton operators; for the triple B term we can use Eq. (9). Denoting the order with respect to the applied field as a superscript, we have to first order

$$\frac{1}{i} \frac{d}{dt} \langle B_n \rangle^{(1)} = \sum_m F_{nm} \langle B_m \rangle^{(1)} + \mu_n \frac{E_n(t)}{\hbar}, \quad (12)$$

where we used the notation

$$F_{nm} \equiv -\Omega_n \delta_{nm} - J_{nm} + i \frac{\Gamma}{2} \delta_{nm}. \quad (13)$$

For the Hermitian conjugate we find

$$i \frac{d}{dt} \langle B_n^\dagger \rangle^{(1)} = \sum_m F_{nm}^* \langle B_m^\dagger \rangle^{(1)} + \mu_n \frac{E_n(t)}{\hbar} \quad (14)$$

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} \langle B_n \rangle^{(3)} = & \sum_m F_{nm} \langle B_m \rangle^{(3)} + 2 \sum_m J_{nm} (\langle B_n^\dagger \rangle^{(1)} \langle B_n B_m \rangle^{(2)} + \langle B_n \rangle^{(1)} \langle B_n^\dagger B_m \rangle^{(2)} \\ & + \langle B_m \rangle^{(1)} \langle B_n^\dagger B_n \rangle^{(2)} - 2 \langle B_n^\dagger \rangle^{(1)} \langle B_n \rangle^{(1)} \langle B_m \rangle^{(1)}) \\ & - 2 \mu_n \frac{E_n(t)}{\hbar} \langle B_n^\dagger \rangle^{(1)} \langle B_n \rangle^{(1)}. \end{aligned} \quad (15)$$

We therefore also need the equation of motion for the expectation value of two exciton operators $\langle BB \rangle$ as well as $\langle B^\dagger B \rangle$. Equations of motion for higher-order moments of B can be derived trivially using $[AB, H] = A[B, H] + [A, H]B$. For the product of two B 's we find, to second order in the external electric fields,

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} \langle B_n B_m \rangle^{(2)} = & \sum_{n', m'} F_{nm, n'm'}^{(2)} \langle B_{n'} B_{m'} \rangle^{(2)} \\ & + \mu_{n, m} \frac{E_n(t)}{\hbar} \langle B_m \rangle^{(1)} \\ & + \mu_{m, n} \frac{E_m(t)}{\hbar} \langle B_n \rangle^{(1)}, \end{aligned} \quad (16)$$

where we introduced transition elements $\mu_{n, m} = (1 - \delta_{nm})\mu_n$, and the two-exciton operator $F^{(2)}$,

$$F_{nm, n'm'}^{(2)} = \bar{F}_{nm, n'm'}^{(2)} + D_{nm, n'm'}, \quad (17)$$

where $\bar{F}^{(2)}$ describes the dynamics of noninteracting bosons

$$\bar{F}_{nm, n'm'}^{(2)} = F_{nn'} \delta_{mm'} + F_{mm'} \delta_{nn'} \quad (18)$$

whereas D takes care of the on-site exclusion

$$\begin{aligned} D_{nm, n'm'} = & -F_{nm}(\delta_{nn'} + \delta_{mm'})\delta_{n'm'} - 2\delta_{nm}\delta_{nn'}F_{n'm'} \\ & + 2\delta_{nm}\delta_{nn'}\delta_{mm'}F_{n'm'}. \end{aligned} \quad (19)$$

As a check, we note that if $\langle B_n B_n(t=0) \rangle = 0$ then the equations of motion give $\langle B_n B_n(t) \rangle = 0$ at all times as it should.

In the calculations we use a different way of accounting for the on-site exclusion in the dynamics, which is to make the hard-core-on-site exclusion into a soft core and to take the hard-core limit in the end. To derive the new equations of motion, we change the Hamiltonian H , Eq. (1), by assuming that the B 's are Bose (rather than Pauli) operators and satisfy the standard Bose commutation relations $[B_n, B_m^\dagger] = \delta_{n, m}$ instead of Eq. (3). To account for the exciton repulsion we add an interaction $V_\lambda = \sum_n \lambda B_n^\dagger B_n^\dagger B_n B_n$ to the Hamiltonian. For finite λ we have a soft-core model of excitons. By taking the $\lambda \rightarrow \infty$ limit in the end we recover the hard-core boson model.

Deriving the equations of motion using this modified Hamiltonian we find that all the expressions given so far

For the third-order expectation value we find, using the equation of motion for B , Eq. (4) and the factorization Eq. (9),

hold, except that instead of the exclusion operator D we have to use

$$D_{nm, n'm'}^{(\lambda)} = \lambda \delta_{nm} \delta_{nn'} \delta_{mm'}. \quad (20)$$

This is a much simpler operator than D , a diagonal $N \times N$ matrix.

In the local-field approximation we simply factorize $\langle B_n B_m \rangle^{(2)} = \langle B_n \rangle^{(1)} \langle B_m \rangle^{(1)}$ in Eq. (15), and set $D = 0$. We thus do not need Eq. (16). The additional dynamical variable describing the deviations from the local-field approximation is thus $\langle B_n B_m \rangle^{(2)} - \langle B_n \rangle^{(1)} \langle B_m \rangle^{(1)}$.

The equation of motion for the exciton population $\langle B^\dagger B \rangle$ is

$$\begin{aligned} \frac{1}{i} \frac{d}{dt} \langle B_n^\dagger B_m \rangle = & \sum_{n', m'} F_{nm, n'm'}^{(2')} \langle B_{n'}^\dagger B_{m'} \rangle - \frac{\mu_n E_n(t)}{\hbar} \langle B_m \rangle \\ & + \frac{\mu_m E_m(t)}{\hbar} \langle B_n^\dagger \rangle, \end{aligned} \quad (21)$$

where we have used the notation $(2')$ to indicate that we are dealing with the two-exciton operator $\langle B^\dagger B \rangle$, which is different from the two-exciton operators defined before. We have

$$F_{nm, n'm'}^{(2')} = \bar{F}_{nm, n'm'}^{(2')} + D_{nm, n'm'}^{(\hat{\Gamma})} \quad (22)$$

with the noninteracting operator \bar{F} ,

$$\bar{F}_{nm, n'm'}^{(2')} = i\Gamma \delta_{nn'} \delta_{mm'} - J_{nn'} \delta_{mm'} + J_{mm'} \delta_{nn'} \quad (23)$$

and the interaction operator is

$$D_{nm, n'm'}^{(\hat{\Gamma})} = -i\delta_{nm}\delta_{nn'}\delta_{mm'}\hat{\Gamma}. \quad (24)$$

This again is a diagonal $N \times N$ matrix. The equations of motion (12), (15), (16), and (21) map the problem of the nonlinear response onto that of $N + N(N-1)/2 + N^2$ coupled oscillators.

Before proceeding to calculate the optical response we note the following. The equations of motion (12), (15), and (16) depend only on the dephasing rate $\hat{\Gamma} + \gamma$ (whether it comes from pure dephasing or finite lifetime makes no difference). The only place where it makes a difference is Eq. (21) since $D^{(\hat{\Gamma})}$ depends only on the pure-dephasing rate. If $\hat{\Gamma} = 0$ we can factorize $\langle B_n^\dagger B_m \rangle = \langle B_n^\dagger \rangle \langle B_m \rangle$ and Eq. (21) is not needed. Pure dephasing thus introduces a new class of relevant variables, $\langle B_n^\dagger B_m \rangle$ [26,27].

IV. FREQUENCY-DOMAIN RESPONSE

We shall now calculate the third-order response of the system for a cw experiment, that is, we take for the external field

$$E_n(t) = \frac{1}{2} \sum_{i=1}^3 (E_n^{(i)} e^{i\omega_i t} + E_n^{(i)*} e^{-i\omega_i t}) \quad (25)$$

and solve the equations of motion for the term proportional to $E^{(1)} E^{(2)} E^{(3)}$. We will solve the equations of motion in terms of one- and two-exciton Green functions.

To first order in the applied fields, the expectation values are found to be

$$\langle B_n \rangle^{(1)} = \frac{1}{2\hbar} \sum_i \left[\sum_m G_{nm}(\omega_i) \mu_m E_m^{(i)} \right], \quad (26)$$

$$\langle B_n B_m \rangle^{(2)} = \frac{1}{2\hbar} \sum_{i,j} \left[\sum_{n',m'} G_{nm,n'm'}^{(2)}(\omega_i + \omega_j) [\mu_{n',m'} E_{n'}^{(i)} \langle B_m(\omega_j) \rangle^{(1)} + \mu_{m',n'} E_m^{(j)} \langle B_{n'}(\omega_i) \rangle^{(1)}] \right]. \quad (29)$$

Here the two-exciton Green function $G^{(2)}$ is given by

$$G_{nm,n'm'}^{(2)}(\omega_1 + \omega_2) = \left[\frac{1}{\omega_1 + \omega_2 + F^{(2)}} \right]_{nm,n'm'}. \quad (30)$$

It is desirable to express the two-exciton Green function in terms of a scattering (T) matrix, using the noninteracting Green function $\bar{G}^{(2)}$ [12]. In this way we can pin down the contribution caused by the on-site repulsion of the two excitons. The T matrix is defined through

$$G^{(2)}(\omega_1 + \omega_2) = \bar{G}^{(2)}(\omega_1 + \omega_2) - \bar{G}^{(2)}(\omega_1 + \omega_2) T(\omega_1 + \omega_2) \bar{G}^{(2)}(\omega_1 + \omega_2). \quad (31)$$

We have dropped the indices here, all the products are understood to be matrix products. We have the Green function for noninteracting bosons

$$\bar{G}^{(2)}(\omega_1 + \omega_2) = \left[\frac{1}{\omega_1 + \omega_2 + \bar{F}^{(2)}} \right]. \quad (32)$$

The T matrix is given by [12]

$$T(\omega_1 + \omega_2) = D [1 + D \bar{G}^{(2)}(\omega_1 + \omega_2)]^{-1}. \quad (33)$$

It represents the scattering of two excitons. All two-exciton operators $\bar{F}^{(2)}$, D , T , and $\bar{G}^{(2)}$ are $N^2 \times N^2$ matrices. In the soft-core treatment of the on-site exclusion, however, the operator $D^{(\lambda)}$ is an $N \times N$ matrix, and hence also $T^{(\lambda)}$ is an $N \times N$ matrix, a considerable simplification. Next we define a new $N \times N$ Green function \hat{G} which is a projection of the full noninteracting Green function

$$\hat{G}_{n,n'}^{(2)} = \bar{G}_{nn,n'n'}^{(2)}. \quad (34)$$

We find that $T^{(\lambda)}$ is given by

$$T_{nm,n'm'}^{(\lambda)} = \delta_{nm} \delta_{n'm'} \lambda (1 + \lambda \hat{G}_{n,n'}^{(2)})^{-1}, \quad (35)$$

where the one-exciton Green function G is the inverse of the F_{nm} matrix, i.e.,

$$G_{nm}(\omega) = \left[\frac{1}{\omega + F} \right]_{nm}. \quad (27)$$

The linear response is then given by

$$\langle P_n(\omega_1) \rangle = \sum_m \alpha_{n,m}(\omega_1) E_m^{(1)}, \quad (28a)$$

with

$$\alpha_{n,m}(\omega_1) = \frac{1}{2\hbar} \mu_n [G_{nm}(\omega_1) + G_{nm}^*(-\omega_1)] \mu_m. \quad (28b)$$

To second order we have

where the inverse is the inverse of an $N \times N$ matrix. In the limit $\lambda \rightarrow \infty$ we have $T^{(\infty)} = T$. Notice the structure of the Green function relevant for T : the matrix elements needed represent two excitons initially at the same site, moving over the molecules independently, both excitons ending up at the same site again.

The Green function for noninteracting bosons $\bar{G}^{(2)}$ can be expressed as a convolution of one-exciton Green functions. Alternatively, if we compute the single-exciton eigenstates $|\psi_j\rangle$ we have

$$G(\omega) = \sum_j \frac{|\psi_j\rangle \langle \psi_j|}{\omega - \lambda_j + i\Gamma/2} \quad (36)$$

and

$$\bar{G}^{(2)}(\omega) = \sum_{j,j'} \frac{|\psi_j\rangle \langle \psi_{j'}| \langle \psi_{j'}| \langle \psi_j|}{\omega - \lambda_j - \lambda_{j'} + i\Gamma}. \quad (37)$$

For the exciton population $\langle B^\dagger B \rangle$ we have the solution

$$\begin{aligned} \langle B_n^\dagger B_m \rangle^{(2)} &= \frac{1}{4\hbar^2} \sum_{n',m'} G_{nm,n'm'}^{(2')}(\omega_1 - \omega_3) \\ &\quad \times [\delta_{n'n_1} G_{m',m_1}(\omega_1) - \delta_{m'm_1} G_{n',n_1}^*(-\omega_3)] \\ &\quad \times \mu_{m_1} E_{m_1}(\omega_1) \mu_{n_1} E_{n_1}(\omega_3), \end{aligned} \quad (38)$$

with a new Green function, as indicated by the prime. This Green function is the inverse of $F^{(2')}$, in a way entirely similar to $G^{(2)}$. We then define the noninteracting two-exciton Green function

$$\bar{G}_{nm,n'm'}^{(2')}(\omega_1 - \omega_3) = (\omega_1 - \omega_3 + \bar{F}^{(2')})_{nm,n'm'}^{-1} \quad (39)$$

and interaction part $D^{(\Gamma)}$ is given by Eq. (24). Again we introduce the corresponding $T^{(\Gamma)}$ matrix through

$$G^{(2')} = (1 + \bar{G}^{(2')} T^{(\Gamma)}) \bar{G}^{(2')}. \quad (40)$$

In terms of the projected Green function \hat{G} ,

$$\hat{G}_{n,n'}^{(2')} = \bar{G}_{nn,n'n'}^{(2')}, \quad (41)$$

the T matrix is now given by

$$T_{n_1 n_1, n_2 n_2}^{(\hat{\Gamma})}(\omega_1 - \omega_3) = -i \hat{\Gamma} [1 - i \hat{\Gamma} \hat{G}^{(2')}(\omega_1 - \omega_3)]_{n_1, n_2}^{-1}. \quad (42)$$

The inverse, again, is that of an $N \times N$ matrix.

The third-order response is given by the solution to Eq. (15) using the factorization Eq. (9). As a note of caution we point out that the expressions of the optical susceptibility are often misleading and due to interference effects the true resonances in our expressions are not always the ones suggested by the Green functions. For example, we

can use the identity

$$\begin{aligned} \sum_{n'm'} \bar{G}_{nm,n'm'}^{(2')}(\omega_2 - \omega_3) [\delta_{n'n_1} G_{m',m_1}(\omega_2) \\ - \delta_{m'm_1} G_{n',n_1}^*(-\omega_3)] \\ = G_{m,m_1}(\omega_2) G_{n,n_1}^*(-\omega_3). \end{aligned} \quad (43)$$

In contrast to $G^{(2')}$, the combination at the right-hand side has no resonance at $\omega_2 = \omega_3$. Applying this equation makes the actual resonances more apparent, a desirable goal.

Putting together all the Green functions introduced above, the expectation value of the nonlinear polarization with frequency $\omega_s = \omega_1 + \omega_2 + \omega_3$, at site n , is finally given by

$$\langle P_n(\omega_s) \rangle = -\frac{1}{4\hbar^3} \sum_{\text{perm } m_1, m_2, m_3} \sum E_{m_1}^{(1)} E_{m_2}^{(2)} E_{m_3}^{(3)} [\gamma_{n,m_1,m_2,m_3}(\omega_1, \omega_2, \omega_3) + \gamma_{n,m_1,m_2,m_3}^*(-\omega_1, -\omega_2, -\omega_3)], \quad (44)$$

where we have a sum over permutations of the applied electric fields and the third-order hyperpolarizability γ is given by

$$\gamma_{n,m_1,m_2,m_3} = \mu_n \mu_{m_1} \mu_{m_2} \mu_{m_3} \sum_{n_1, n_2, n_3} G_{n,n_1}(\omega_s) G_{n_3,m_3}^*(-\omega_3) G_{n_2,m_1}(\omega_1) A_{n_1,n_2,n_3,m_2}(\omega_1, \omega_2, \omega_3) \quad (45)$$

with the *cooperative enhancement factor* A ,

$$A_{n_1,n_2,n_3,m_2}(\omega_1, \omega_2, \omega_3) = \delta_{n_1,n_2} \delta_{n_1,m_2} \delta_{n_1,n_3} + 2\delta_{n_1,n_3} \sum_m J_{n_1,m} G_{n_1,m,n_2,m_2}^{(2)}(\omega_1 + \omega_2)(1 - \delta_{n_2,m_2}) + A_{n_1,n_2,n_3,m_2}^{(p)}(\omega_1 - \omega_3, \omega_2), \quad (46)$$

where the pure-dephasing contribution is

$$\begin{aligned} A_{n_1,n_2,n_3,m_2}^{(p)}(\omega_1 - \omega_3, \omega_2) = \delta_{n_2,n_3} \sum_{n_4, n_5} \bar{G}_{n_1 n_5, n_4 n_4}^{(2')}(\omega_1 - \omega_3) T_{n_4 n_4, n_2 n_2}^{(\hat{\Gamma})}(\omega_1 - \omega_3) \\ \times \left[\delta_{n_1 n_5} + J_{n_1, n_5} G_{n_5, m_2}(\omega_2) + \delta_{n_1 n_5} \sum_{n_6} J_{n_1, n_6} G_{n_6, m_2}(\omega_2) \right]. \end{aligned} \quad (47)$$

The local nonlinearities give the δ term in Eq. (46), the nonlocal nonlinearities result in the second and third terms. We call A an enhancement factor as it gives the polarization of the entire system compared to the polarization resulting from the use of only the local nonlinearities of Eq. (4). The reference system used here seems to be a natural choice. The one-exciton Green function can be measured in an experiment as the linear response, see Eq. (26). The cooperativeness-enhancement factor as defined here can then in principle be extracted from experiment.

Let us try to give an explanation of the derivation of Eqs. (45) and (46). For this discussion we neglect the pure-dephasing contributions for which a similar description can be given. We do this using a hypothetical time ordering, hypothetical since this results holds for a cw experiment, and a sum over certain time orderings has been performed in order to arrive at Eqs. (45) and (46). First the ω_3 field creates at B^\dagger exciton at site m_3 . This exciton propagates through the system ending up at $n_3 = n_1$.

Due to the factorization Eq. (7) this exciton does not interact with other excitons. Next an exciton is created at m_1 by ω_1 . This exciton propagates to n_2 and then two processes occur, corresponding to the first two terms in Eq. (46). In the first term the two excitons are at the same site, $n_1 = n_2$, creating an exciton population. Now comes the ω_2 electric field, which interacts with the population at $m_2 = n_1$ to create an exciton with energy ω_s that propagates to site n where it is observed. In the second contribution to Eq. (46), the ω_2 field excites a molecule at m_2 , which can be any molecule, except n_2 , since a molecule can be excited only once. The two excitons then propagate from (n_2, m_2) to (n_1, m) . The system is then in a state that can be described as exciton population at n_1 , exciton at m . Finally the collection of three (two plus one rather) excitons interact through the nonlocal nonlinearity, creating an exciton at n_1 which propagates to n and is observed there.

Using the T matrix [Eq.(31)], Eq. (46) can be recast in

the form

$$A_{n_1, n_2, n_3, m_2}(\omega_1, \omega_2, \omega_3) = A^{(1)} + A^{(l)} + A^{(x)} + A^{(p)}, \quad (48)$$

where

$$A^{(1)} = \delta_{n_1, n_2} \delta_{n_1, m_2} \delta_{n_1, n_3}, \quad (49)$$

the factor $A^{(l)}$ gives the local-field correction

$$A^{(l)} = J_{n_1, n_2} G_{n_1 m_1}(\omega_2) \delta_{n_1, n_3}, \quad (50)$$

and the on-site exclusion gives rise to

$$A_{n_1, n_2, n_3, m_2}^{(x)}(\omega_1 + \omega_2) = 2\delta_{n_1 n_3} \sum_{m, n_4, n_5} J_{n_1, m} \bar{G}_{n_1 m, n_4 n_5}^{(2)}(\omega_1 + \omega_2) T_{n_4 n_4, n_5 n_5}(\omega_1 + \omega_2) \bar{G}_{n_5 n_5, n_2 m_2}^{(2)}(\omega_1 + \omega_2). \quad (51)$$

We used here an equation such as (43) in order to obtain the one-exciton Green function in $A^{(l)}$. We also used the fact that $J_{nn} = 0$ in order to simplify the results by setting $\mu_{n, m} \rightarrow \mu_n$.

$A^{(1)}$ gives us the nonlinear optical response of the reference system in which we neglect the $B^\dagger BB$ contribution and pure dephasing altogether. It has a local nonlinearity but as far as the dynamics goes the excitons are treated as noninteracting bosons. Note that we cannot write a simple zero-order Hamiltonian for this reference system using the Pauli operators B since we include the couplings J_{nm} in the linear terms and neglect them in the nonlinear terms. Writing a Hamiltonian will require transferring to the Bose operators as is done for the soft-core treatment of the two-exciton dynamics. However, by considering the equations of motion the reference set of oscillators emerges naturally. The first and second terms in Eq. (48), $A^{(1)} + A^{(l)}$, combine to the traditional local-field approximation [1,10] and the other two terms $A^{(x)}$ and $A^{(p)}$ describe the contribution due to exciton-exciton interactions. Both of these contributions are due to exciton scattering described by the T matrix.

Equations (45) and (48) are a generalization to arbitrary geometry and couplings of results due to Spano, Dubovsky, and Mukamel [8,10,11]. These equations provide a clear physical picture of cooperative effects which, apart from the local-field term, depend on certain matrix elements of the scattering T matrices. These in turn depend only on two-photon resonances as they depend only on the combinations $\omega_1 + \omega_2$ and $\omega_1 - \omega_3$. In the absence of pure dephasing, a variety of different experiments should be measuring the same quantities, $A^{(x)}(\omega_1 + \omega_2)$.

Finally Eq. (46) can be generalized in a straightforward way to time-dependent couplings, as would be required for considering nonlinear optical properties of liquids where the motion of the nuclei is included, or systems with phonons. Inhomogeneous broadening is present in the expressions derived so far. In the present oscillator picture there is no mysterious canceling of very large terms [8,9] since the cancellation is naturally built in. Similar advantages of the oscillator picture exist also for

conjugate polymers where the elementary excitations are electrons and holes rather than excitons [28–30].

V. OPTICAL SUSCEPTIBILITIES OF SMALL PERIODIC STRUCTURES

The expressions for the optical susceptibilities simplify considerably if we consider an aggregate with a size small compared to optical wavelengths. In this case we can treat the entire system as a single point particle as far as the radiation field is concerned. We can then define the total polarization $\langle P(\omega) \rangle$ as the sum of $\langle P_n(\omega) \rangle$ over all sites n . We can further drop the m_1, m_2 , and m_3 indices of the fields in Eq. (44) since the field can be considered uniform. In addition we consider a regular cubic lattice of identical molecules, so that the system is translationally invariant. Using these assumptions, Eqs. (28) assume the form

$$\langle P(\omega_1) \rangle = \alpha(\omega_1) E^{(1)}(\omega_1) \quad (52a)$$

and

$$\alpha(\omega_1) = \frac{\mu^2}{2\hbar} [G(\omega_1) + G^*(-\omega_1)], \quad (52b)$$

where the relevant combination of matrix elements of the one-exciton Green function is

$$G(\omega) = \sum_m G_{nm}(\omega) = \frac{1}{\omega - \Omega_s + i\Gamma/2}, \quad (52c)$$

where $\Omega_s = \Omega + \bar{J}$, and $\bar{J} = \sum_m J_{nm}$. Due to the translational variance, G_{nm} depends only on the distance $|n - m|$ (note that n and m are to be considered vectors in more than one dimension). The one-exciton resonance is shifted from the single molecule frequency Ω to Ω_s .

The third-order polarization is given by

$$\langle P(\omega_s) \rangle = \chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) E^{(1)}(\omega_1) E^{(2)}(\omega_2) E^{(3)}(\omega_3), \quad (53)$$

where $\chi^{(3)}$ is given by

$$\begin{aligned} \chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = & -N\mu^4 \sum_{\text{perm}} [G(\omega_s) G(\omega_1) G^*(-\omega_3) A(\omega_1, \omega_2, \omega_3) \\ & + G^*(-\omega_s) G^*(-\omega_1) G(\omega_3) A^*(-\omega_1, -\omega_2, -\omega_3)], \end{aligned} \quad (54)$$

where we still have to perform the sum over permutations of the applied electric fields. In order to express the two-exciton quantities we define

$$\tilde{G}_{s,s_1}^{(2)} = \sum_m \tilde{G}_{nn+s,mm+s_1}^{(2)} \quad (55)$$

s and s_1 denote the relative distance vectors for the initial and final two excitons. This matrix is simplified from $N^2 \times N^2$ matrices to an $N \times N$ matrix as the center-of-mass motion of the two excitons can be factorized out. The T matrix is now a 1×1 matrix given by

$$T(\omega_1 + \omega_2) = [\tilde{G}_{0,0}^{(2)}(\omega_1 + \omega_2)]^{-1} \quad (56)$$

The T matrix is inversely proportional to the Fourier transform of the amplitude of the return of the two excitons to the origin. The noninteracting Green function for pure dephasing is

$$\tilde{G}_{s,s_1}^{(2')}(\omega_1 - \omega_3) = \delta_{ss_1} \frac{1}{\omega_1 - \omega_3 + i\gamma} \quad (57)$$

For the cooperative enhancement factor we find in this case

$$A(\omega_1, \omega_2, \omega_3) = A^{(1)} + A^{(l)} + A^{(x)} + A^{(p)} \quad (58)$$

where

$$A^{(1)} = 1 \quad (59)$$

and

$$A^{(l)} = \bar{J}G(\omega_2) \quad (60)$$

The contribution of pure dephasing to the enhancement factor is

$$A^{(p)}(\omega_1 - \omega_3; \omega_2) = \frac{-i\hat{\Gamma}}{\omega_1 - \omega_3 - i\Gamma} \left[1 + \frac{\bar{J}}{\omega_2 - \Omega_s + i\Gamma/2} \right] \quad (61)$$

An important aspect of this expression is that the structure of the underlying lattice has completely disappeared. In order to probe the structure of the lattice using pure dephasing a nonuniform initial condition is needed.

Finally

$$A^{(x)}(\omega_1 + \omega_2 + i\Gamma) = 2 \sum_{s_1, s_2} J_{s_1} \tilde{G}_{s_1,0}^{(2)}(\omega_1 + \omega_2) T(\omega_1 + \omega_2) \times \tilde{G}_{0,s_2}^{(2)}(\omega_1 + \omega_2) \quad (62)$$

As shown here, the interaction contribution $A^{(x)}$ depends only on a single complex quantity $\omega_1 + \omega_2 + i\Gamma$. We can find more explicit results using Eq. (37) for the non-

interacting two-exciton Green function. The eigenfunctions of the one-exciton evolution are simply plane waves, $\psi_s^{(k)} = \exp(ik \cdot s) / \sqrt{N}$. The noninteracting two-exciton Green function is given by

$$\tilde{G}_{s,s_1}^{(2)}(\omega_1 + \omega_2) = \frac{1}{N} \sum_k e^{ik(s_1 - s)} \frac{1}{z - 2J(k)} \quad (63)$$

where $z = \omega_1 + \omega_2 - 2\Omega + i\Gamma$ and $J(k)$ is the Fourier transform of J_{nm} ,

$$J(k) = \sum_s e^{ik \cdot s} J_{n,n+s} \quad (64)$$

The scattering operator is given by

$$T(\omega_1 + \omega_2) = N \left[\sum_k \frac{1}{z - 2J(k)} \right]^{-1} \quad (65)$$

and the total cooperative enhancement factor [Eq. (58)] is

$$A(\omega_1, \omega_2, \omega_3) = \tilde{A}(z) + A^{(p)} \quad (66)$$

with

$$\tilde{A}(z) = \frac{N}{z - 2J(0)} \left[\sum_k \frac{1}{z - 2J(k)} \right]^{-1} \quad (67)$$

Notice that $J(0) = \bar{J}$. Equation (66) expresses the cooperative enhancement factor in any dimension entirely in terms of one-exciton energies. It is exact for a lattice; apart from the factorization assumption, which is exact if there is no pure dephasing, no further approximation is made. The function $\tilde{A}(z)$ is the quantity of prime importance to cooperative enhancement in small crystalline aggregates.

VI. COOPERATIVE ENHANCEMENT: EXCITON SCATTERING OR COHERENCE DOMAINS?

In this section we analyze the origin of the cooperative enhancement obtained in the previous sections. For the sake of clarity we consider a simple cubic lattice in one, two, or three dimensions and assume that all the transition dipoles μ point in the same direction. We take the infinite lattice limit (but still smaller than optical wavelengths) and we restrict the interaction to the nearest neighbor. Since the effect of pure dephasing is to add a single, noncooperative contribution [Eq. (66)] we shall hereafter neglect pure dephasing; we set $\hat{\Gamma} = 0$. Under this assumption our expression for the hyperpolarizability γ is actually exact since we no longer need the factorization approximation Eq. (9). We then find [31]

$$\tilde{A}(z) = \frac{-1}{z - 2\bar{J}} \left[\frac{1}{8\pi^3} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \int_{-\pi}^{\pi} dk_z [-z + 2\bar{J} + J_x(\cos k_x - 1) + J_y(\cos k_y - 1) + J_z(\cos k_z - 1)]^{-1} \right]^{-1} \quad (68)$$

The one- and two-dimensional cases are contained in this by setting $J_y = J_z = 0$ or $J_z = 0$, respectively.

In one dimension the (single) integral can be performed and we obtain

$$\tilde{A}(z) = \left[1 - \frac{8J}{z - 2\bar{J}} \right]^{1/2} \quad (69)$$

For low dephasing rates Γ ($\Gamma < \bar{J}$), the enhancement factor on resonance scales as $\Gamma^{-1/2}$, agreeing with previous results [10]. The next question is what the analogous behavior is for two and three dimensions, and in what way it depends on the interactions. Actually \tilde{A} can be expressed in terms of elliptic integrals [12], but this gives little information about its behavior. We are most interested in the maximum enhancement. For this we have to be on resonance, so we consider $z = z_R = 2\bar{J} + i\Gamma$. We need only to consider the behavior of the integral for small wave vectors k . In three dimensions we readily find

$$\tilde{A}(z_R) \approx \frac{-1}{i\Gamma} \int d^3k \frac{1}{-i\Gamma + k^2} = \frac{-C_3}{i\Gamma} + \text{const} \quad (70)$$

and in two dimensions

$$\tilde{A}(z_R) \approx \frac{C_2}{\Gamma \ln \Gamma} + \text{const}. \quad (71)$$

In practical cases, the value of the logarithm changes only slightly. These dephasing dependencies are due to the structure of Eq. (67) which tells us that \tilde{A} is proportional to $1/z$ divided by the number of times the exciton, which has a lifetime $1/\Gamma$, returns to the origin. In one dimension this number diverges as $\Gamma^{-1/2}$, in two dimensions it is proportional to $-\ln \Gamma$, and in three dimensions it is finite.

This scaling of the optical nonlinearities with Γ reveals

an important characteristic of the nature of enhancement. It is tempting to think of it in terms of coherence domains—the simplest way of thinking about enhancement is in terms of collections of molecules reacting coherently to the electric fields. Based on the one-dimensional result, the length of this coherent region is then assumed to be proportional to $\Gamma^{-1/2}$. In d dimensions a signal proportional to the coherence volume $\Gamma^{-d/2}$ is then expected. The enhanced radiative decay rate in molecular assemblies (superradiance) [16] indeed scales as $\Gamma^{-d/2}$. Our analysis based on the exact solution of γ shows a very different scaling [$\Gamma^{-1/2}$, $(\Gamma \ln \Gamma)^{-1}$, and Γ^{-1} for $d=1, 2, 3$, respectively] which suggests that the coherence domain picture is not applicable for optical nonlinearities. Instead of coherences between the molecules, coherences between the elementary excitations (excitons) are underlying the cooperative enhancement. Coherences among molecules provide two large terms that cancel [8]. Therefore the more natural picture is in terms of the elementary excitations.

In the next section we shall analyze the full dipole-dipole coupling. One characteristic of that coupling is that it can change sign upon direction. In concluding this section we therefore consider nearest-neighbor couplings with a variation of sign which should provide a qualitative feeling for the effects of dipolar couplings. As the couplings have a different sign there is potentially a divergence of the integral. We have in two dimensions

$$\begin{aligned} \int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \frac{1}{-i\Gamma + J \cos k_x - J \cos k_y} &= f(\Gamma) + \int_{-J}^J \frac{1}{-i\Gamma + x} dx \\ &= f(\Gamma) + \ln(-i\Gamma/J + 1) - \ln(-i\Gamma/J - 1), \end{aligned} \quad (72)$$

where $f(\Gamma)$ is a regular function for $\Gamma \rightarrow 0$. Equation (72) shows that for an interaction with different signs

$$\tilde{A}(z_r) = \frac{C}{\Gamma} + \text{const} \quad (\Gamma \rightarrow 0), \quad (73)$$

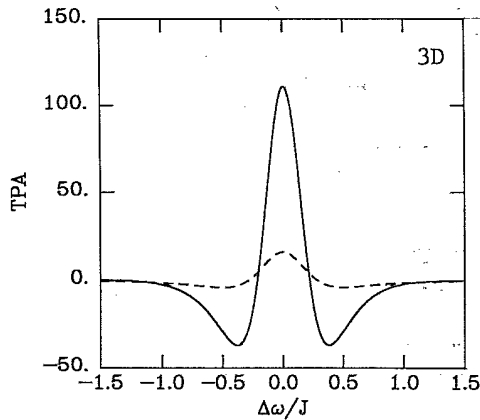


FIG. 1. Two-photon absorption $\text{Im}\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ for dipoles in three dimensions, $\Delta\omega = \omega - \Omega_s$, at dephasing rate $\Gamma/J=1$, $\Omega_s/J=10^4$. Solid line: numerical results for a $79 \times 79 \times 79$ lattice. Dashed line: local-field approximation, note that $\bar{J}=0$. The absorption is enhanced by a factor 7.

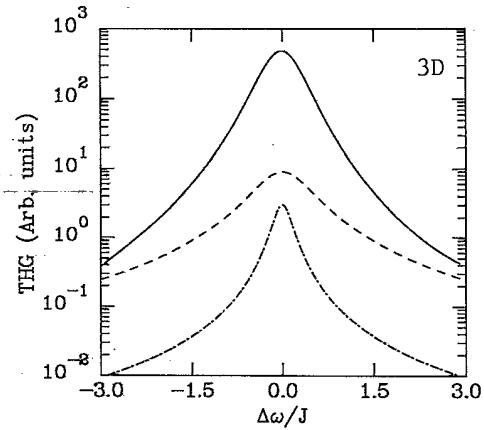


FIG. 2. The third-harmonic signal $|\chi^{(3)}(-3\omega; \omega, \omega, \omega)|^2$ for dipoles in three dimensions at dephasing $\Gamma/J=1$. Solid line: Numerical results for the response near the single-photon resonance Ω_s , $\Delta\omega = \omega - \Omega_s$. Dashed line: local-field result at the same resonance. The enhancement now is 48, the square of the enhancement of the TPA (Fig. 1). The dot-dashed curve shows the three-photon resonance ($\Delta\omega = \omega - \Omega_s/3$). It is actually a superposition of two curves, one dashed, the other dotted corresponding to the numerical solution and the local-field results, respectively. Note the complete absence of enhancement for this resonance.

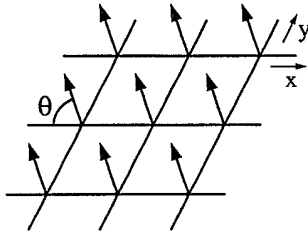


FIG. 3. The geometry of the two-dimensional lattice. The arrows denote the direction of the transition dipole of the two-level molecules. The dipoles only have a component along the x axis, the component along the y axis is zero. In this paper we study three cases for the angle θ : (i) $\theta=90^\circ$ (H aggregates), so the dipoles are perpendicular to the plane; (ii) $\theta=0^\circ$ (J aggregates), the dipoles lie in the plane; (iii) skew to the plane at the "magic angle" $\theta=35^\circ$, or more accurately $(\cos\theta)^2=\frac{2}{3}$. For the magic angle the one-exciton energy shift is $\bar{J}=0$, and the local-field approximation gives no enhancement.

which is valid in both two and three (or more) dimensions. Even though the integrand can be very large, the integral is finite. Notice the behavior of \tilde{A} : in two or more dimensions we find an enhancement, but (up to logarithmic corrections) it is *always* proportional to Γ^{-1} . In the local-field approximation we find an enhancement which is also proportional to Γ^{-1} , but with a different prefactor that may be zero. We expect the results of this section to hold also for long-range interactions. This is supported by our numerical results.

VII. NUMERICAL CALCULATIONS FOR PERIODIC STRUCTURES WITH DIPOLAR INTERACTIONS

In this section we consider dipole-dipole interactions

$$J_{nm} = J \mu_n \cdot \frac{3\hat{r}\hat{r} - 1}{r^3} \cdot \mu_m, \quad (74)$$

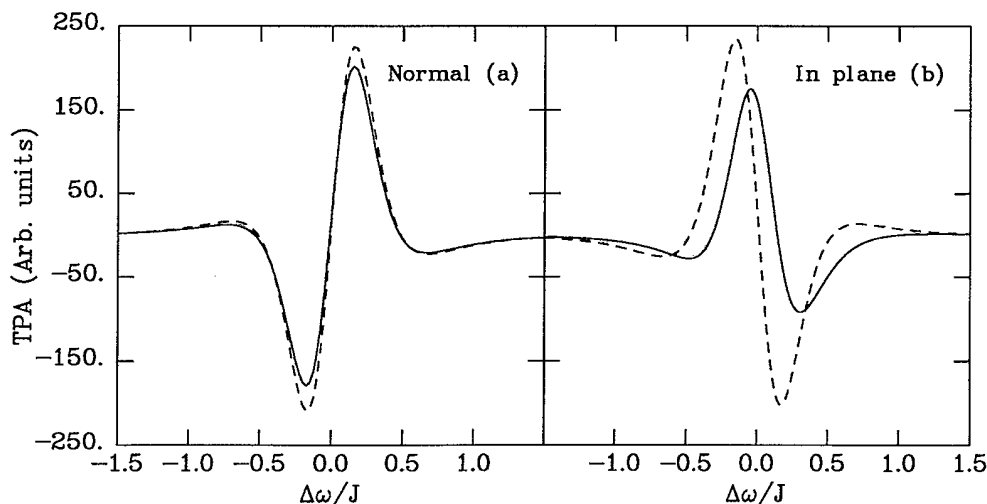


FIG. 4. Two-photon absorption $\text{Im}\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ for dipoles in two dimensions, $\Delta\omega = \omega - \Omega$, at dephasing rate $\Gamma/J=1$. In both figures the solid line is the numerical result for a 199×199 lattice, and the dashed line is the local-field result. In (a) the dipole moments are normal to the plane (H aggregates). In (b) the dipoles are in the plane (J aggregates). The crucial difference between (a) and (b) is that for J aggregates the couplings have different signs. The TPA for dipoles at the magic angle is very similar to the three-dimensional result, Fig. 1.

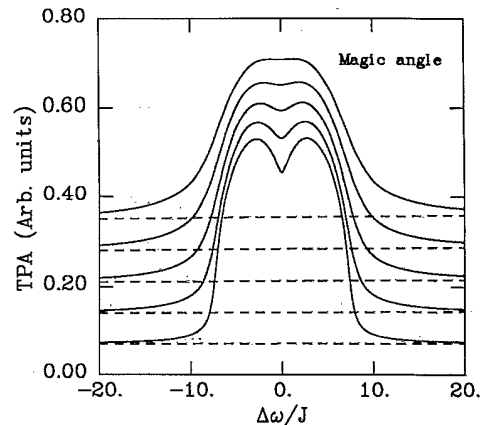


FIG. 5. Two-photon absorption $\text{Im}\chi^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1)$. The solid lines are numerical results for two-dimensional dipoles at the magic angle for a 199×199 lattice, the dashed line is the local-field approximation. Here we have taken $\omega_1 = 0.7\Omega_s + \Delta\omega$, and $\omega_2 = 1.3\Omega_s$. For these frequencies the one-photon frequencies are nonresonant, but the two-exciton term in the cooperativity-enhancement factor is resonant. We have plotted the signal for five dephasing rates, from bottom to top $\Gamma/J = 0.5, 1, 1.5, 2$, and 2.5 . The TPA probes the two-exciton resonances which are missed completely by the local-field approximation.

where \mathbf{r} is the vector pointing from site n to m and $\hat{\mathbf{r}} = \mathbf{r}/r$. We express energies in units of $J \equiv \mu^2/a^3$, where a is the lattice spacing. We start with the three-dimensional lattice.

In the following calculations we aim for the infinite lattice, but our numerical results use finite lattices with periodic boundary conditions. For the three-dimensional calculations we have taken a $79 \times 79 \times 79$ simple cubic lattice, using the minimal-image convention [32]. The

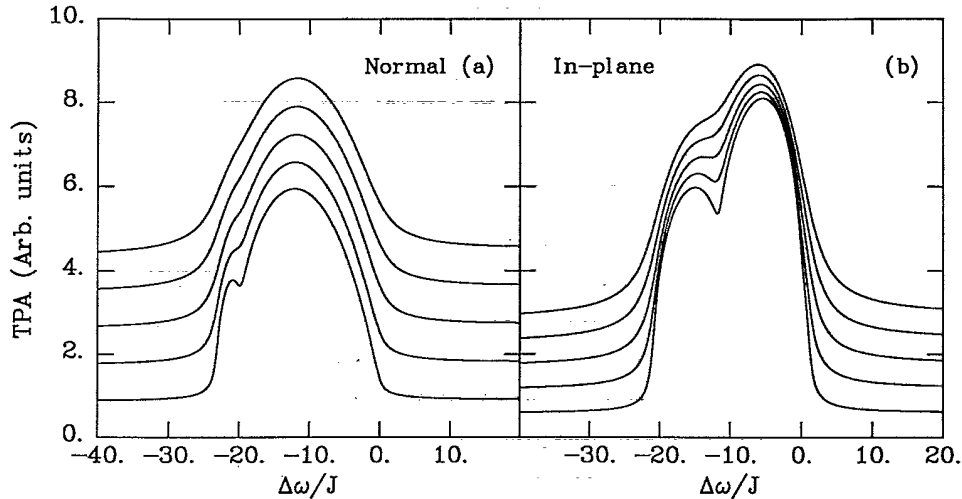


FIG. 6. As in Fig. 5 for (a) H aggregates $\theta=90^\circ$, and (b) J aggregates $\theta=0^\circ$. The dephasing rates shown range from $\Gamma/J=0.5$ (lowest) to $\Gamma/J=2.5$ (highest).

two-photon absorption as well as third-harmonic generation depends in a trivial way on the isolated-molecule transition frequency Ω . We have taken $\Omega=10^4 J$ in the following calculations.

We first consider two-photon absorption (TPA) $\text{Im}\chi^{(3)}(-\omega; \omega, -\omega, \omega)$. We calculate the signals near a resonance, and find that for TPA we have to take only two, identical terms in the sum over permutations in Eq. (44). Other contributions are off resonant and can be neglected using the rotating-wave approximation. There is one resonance for TPA. In Fig. 1 we present results comparing the TPA signal for dipoles in three dimensions. We see that the cooperativity gives a large enhancement of the signal, even for the quite strong damping $\Gamma/J=1$, and essentially no shift of the reso-

nance. Since the signal depends on the detuning we have expressed all frequencies in units of J .

We next consider third-harmonic generation (THG), $|\chi^{(3)}(-3\omega; \omega, \omega, \omega)|^2$. For THG all six terms in Eq. (54) are identical. In this case there are two resonances in the model, a single-photon resonance at $\omega=\Omega$ and a three-photon resonance at $\omega=\Omega/3$. In Fig. 2 we plotted the THG signal near these two resonances. Note the absence of cooperativity near $\omega=\Omega/3$. For this resonance the two-photon levels are nonresonant, so only the first term in Eq. (58) contributes and $A^{(x)}=0$, to a very good approximation. This argument is valid irrespective of the dimensionality of the model, and the couplings. As the aggregate is much smaller than an optical wavelength we have $\bar{J}=0$ which no longer holds if the system size is larger. In both Figs. 1 and 2 the local-field approximation misses the enhancement entirely as $\bar{J}=0$.

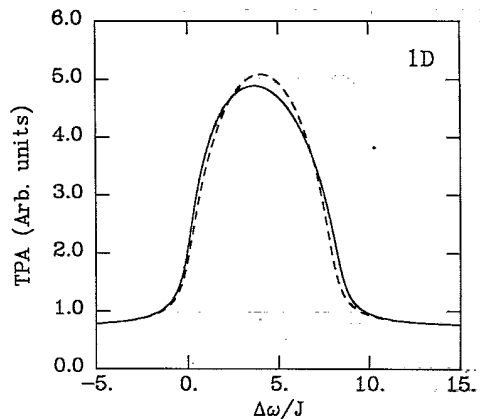


FIG. 7. Same as in Fig. 5 for one dimension, $\Gamma/J=0.5$. The solid line is the TPA for a dipole-dipole interaction $J_{nm}=J|n-m|^{-3}$. The dotted line is the result of using a nearest-neighbor interaction with strength J , so that A is given by Eq. (69).

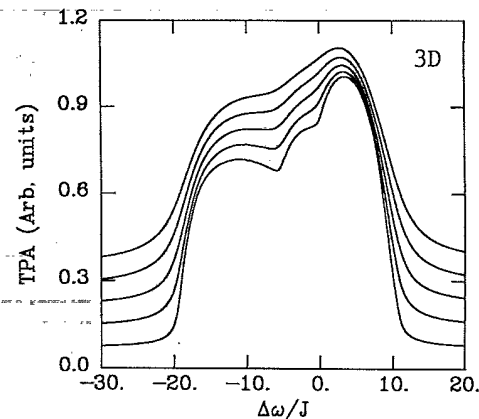


FIG. 8. Same as Fig. 5 for three-dimensional dipoles. From top to bottom: $\Gamma/J=5.5, 4.5, 3.5, 2.5$.

We next turn to two-dimensional aggregates where we consider three different orientations of the transition dipole (Fig. 3) [14–16,33]: (i) perpendicular to the plane (H aggregates), (ii) in the plane (J aggregates), and (iii) skew to the plane at the “magic angle” so that $\mu \cdot \hat{r}_x = 0$, and $(\mu \cdot \hat{r}_x)^2 = \frac{2}{3}$. The magic angle is $\theta = 35^\circ$. For the magic angle the one-exciton energy shift $\bar{J} = 0$, and the local-field approximation gives no enhancement. In the following we used the minimal-image convention and a square 199×199 lattice.

In Fig. 4 we show that the relative signs of the couplings J in the x and y directions are very important in determining the accuracy of the local-field approximation, at moderate to high Γ . In Fig. 4(a) all the signs are equal, in Fig. 4(b) they are not, and even though \bar{J} is nonzero, the local-field approximation is not very accurate.

In order to observe directly the cooperative enhancement factor we consider a two-color experiment first for two-photon absorption. We took frequencies such that single-photon transitions are off resonant so we see only the two-photon resonances in the cooperative enhancement factor. In Figs. 5 and 6 we show results for the three models in two dimensions. Notice in particular the complete absence of a resonance in the local-field approximation. We expect the dip at $\Delta\omega$ in Fig. 5 to be much more pronounced at lower dephasing rates, but $\Gamma/J = 1$ is about the lowest value for which we have reliable results. In Fig. 7 we show similar TPA results in one dimension, and in Fig. 8 the three-dimensional case. In Fig. 7 we also compare the difference between taking a nearest-neighbor interaction and dipole-dipole interactions.

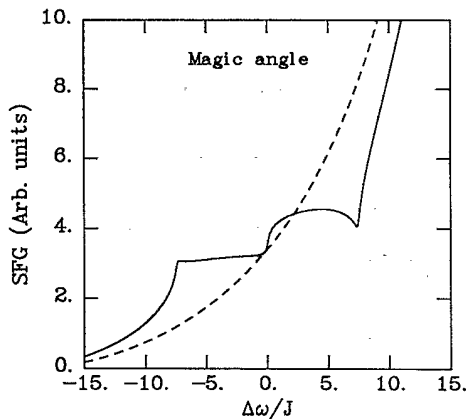


FIG. 9. Sum-frequency generation (SFG) $|\chi^{(3)}(-\omega_2; \omega_2, \omega_1, -\omega_1)|^2$. The solid lines are numerical results for two-dimensional dipoles at the magic angles for a 59×59 lattice and $\Gamma = 0.1J$. The dashed line is the local-field approximation result. We have taken $\omega_1 = 0.7\Omega_s + \Delta\omega$, and $\omega_2 = 1.3\Omega_s$. For these frequencies the one-photon frequencies are non-resonant, but the two-exciton term with the cooperativity-enhancement factor is resonant. These curves depend also on the isolated-molecule transition frequency; we have taken $\Omega = 100J$. The local-field approximation misses the two-photon resonances.

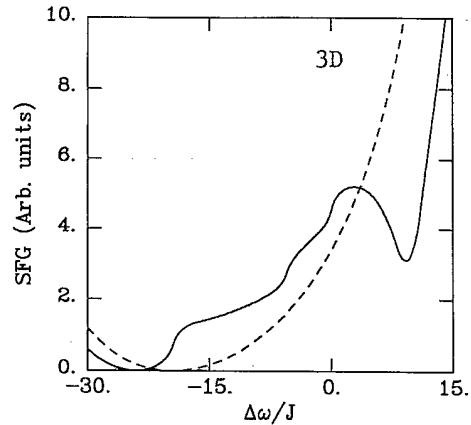


FIG. 10. Sum-frequency generation (SFG) in a three-dimensional lattice with dipole-dipole interactions, as in Fig. 9 now with $\Gamma = 0.3J$. Solid line: numerical results for a $(79 \times 79 \times 79)$ lattice. Dashed line: local-field result.

tions. We did similar calculations in two and three dimensions, reaching similar results.

Another experiment that addresses the cooperativity-enhancement factor is sum-frequency generation (SFG) for single frequencies off resonance. For SFG we find that we have to consider all six terms in the sum over permutations, so that the resulting spectrum is more complex and moreover depends on the ratio Ω/J . In Figs. 9 and 10 typical results are shown. The line shape of the SFG resonance is dispersive, unlike the previous resonances.

We have used periodic boundary conditions in all our numerical calculations. This is an approximation for the infinite system, but it is not intended to represent a true finite system. We varied the lattice size in order to estab-

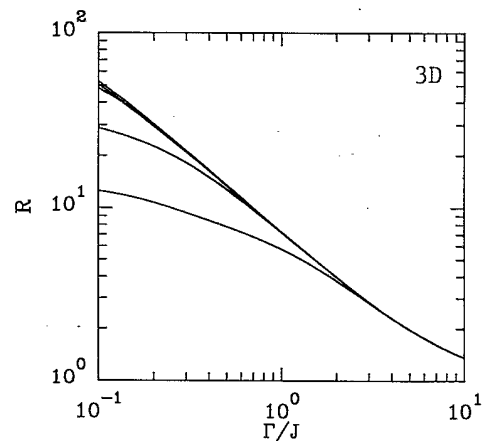


FIG. 11. The ratio R of the maximum two-photon absorption signal for three-dimensional dipoles to the local-field result for various $L \times L \times L$ lattices. From bottom to top at $\Gamma/J = 0.1$: $L = 7, 13, 19, 25, 31$. For $\Gamma/J > 0.3$ we have reliable, converged results for the infinite lattice.

lish how good a finite lattice approximates the infinite lattice. This depends on the dephasing rate; in Fig. 11 we plot the maximum of the two-photon absorption versus the local-field maximum for various dephasing rates. For $\Gamma/J \geq 1$ our results are valid, for lower dephasing rates larger lattices are needed.

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