

POLARITONS AND RETARDED INTERACTIONS IN NONLINEAR OPTICAL SUSCEPTIBILITIES

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In this paper we discuss the calculation of nonlinear optical susceptibilities in infinite crystals and in small molecular aggregates. In both cases, a systematic method is developed for treating the intermolecular interactions and the matter - field coupling. For the infinite crystal it is common to define the susceptibilities as the expansion coefficients of the polarization field in terms of the internal (Maxwell) electric field. This requires an analysis in which both the radiation field and the material variables are treated as degrees of freedom, which naturally leads to the introduction of polaritons: coupled field - matter eigenmodes. For molecular aggregates, it is more useful to define susceptibilities with respect to the external field, so that the problem may be analyzed in terms of material modes, such as excitons and biexcitons.

In the infinite crystal our method^[1] overcomes the difficulties associated with the local field, and the exciton or the external field approaches^[2-4]. Our approach is based on the derivation of a set of coupled reduced equations of motion for those material and radiation field variables that are relevant to the definition of susceptibilities. As stated above, the electromagnetic field is explicitly treated as a degree of freedom, and the coupled equations make it possible to account for polariton effects. The first problem we face is the proper choice of a Hamiltonian for charges interacting with radiation. This controversial issue has drawn considerable attention over the years.^[5,6] In the multipolar ($\mu \cdot \mathbf{D}$) Hamiltonian, the radiation-matter interaction is in the electric dipole approximation given by $-\mu \cdot \mathbf{D}$, where μ is the transition dipole moment and \mathbf{D} is the electric displacement field. This Hamiltonian can be obtained by a canonical transformation from the more fundamental minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian, in which the radiation-matter coupling is of the form $\mathbf{p} \cdot \mathbf{A} + A^2$, with \mathbf{p} the electronic momentum and \mathbf{A} the vector potential. Intermolecular forces enter both Hamiltonians in a profoundly different way. In the $\mu \cdot \mathbf{D}$ Hamiltonian there are no direct intermolecular interactions at all; instead they are mediated by exchange of photons. In the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian, however, instantaneous Coulomb interactions are explicitly present. On a formal level both Hamiltonians are equivalent, and in fact it has been shown that when intermolecular interactions are neglected, the susceptibilities predicted by them are identical. However, different predictions must be expected if these interactions are included, since in practice this can only be done using approximations, which may effect both Hamiltonians in a different way. The main dilemma in the choice of the Hamiltonian may be formulated as follows: In the $\mu \cdot \mathbf{D}$ Hamiltonian, the interaction between the radiation field and matter is more conveniently treated, which makes it most suitable for numerical work (e.g., the

propagation of Bloch-Maxwell equations), whereas in the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonian it is easier to incorporate intermolecular forces using physical intuition.

In the absence of a clear advantage to either of these Hamiltonians, we have derived reduced equations of motion in an infinite crystal starting from both the $\mu\cdot\mathbf{D}$ and the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonian. The nonlinear optical susceptibilities are obtained by solving the equations for the electronic variables iteratively in powers of the Maxwell electric field \mathbf{E} . Thus, the common introduction of intermediate susceptibilities with respect to the external or the local electric field is avoided. Our analysis within the $\mu\cdot\mathbf{D}$ Hamiltonian [1a,b] shows that up to second order in the matter-field coupling the material equations of motion coincide with the optical Bloch equations in which every molecule interacts with a microscopically defined local electric field, which includes the effects of retarded interactions with other molecules. Our calculation provides a microscopic derivation of the local field and shows limitations of this widely used concept, since we find that in higher order no local field can be defined. In our calculations within the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonian, we focussed in particular on microscopic polariton effects [1c]. Explicit forms for the linear ($\chi^{(1)}$) and nonlinear ($\chi^{(2)}$) susceptibilities are derived, which microscopically account for polariton-phonon scattering. This process is important in low temperature crystals, where the radiation-exciton interaction is stronger than the exciton-phonon coupling. Recent nonlinear experiments on low temperature aromatic crystals [7,8] have clearly demonstrated the importance of polariton effects and the necessity to formulate the microscopic theory of optical response in a way that systematically accounts for retardation. Small's group conducted detailed studies of one-photon absorption, second-harmonic generation and two-photon excited fluorescence in Naphtalene. [7] These experiments probe $\text{Im}(\chi^{(1)})$, $|\chi^{(2)}|^2$, and $\text{Im}(\chi^{(3)})$, respectively. It was found that the temperature dependent widths occurring in these susceptibilities differed dramatically for the linear and nonlinear experiments. This discrepancy violates the existing theories of nonlinear susceptibilities, in which the width is viewed as the exciton dephasing rate by phonons, for which the observed dramatic change cannot be understood. In contrast, the experiments clearly suggest that polariton-phonon scattering processes play a role in the susceptibilities. This addresses a very fundamental issue: Are the susceptibilities properties of the matter alone [which is the conventional viewpoint], or do they also contain an explicit signature of the transverse radiation field in the form of microscopic polariton effects? Our analysis resolves this question by showing how the polariton dynamics enters the material equations of motion. The experiments of Fayer's group [8] are also relevant in this context. They conducted transient grating spectroscopy in crystalline Anthracene at low temperatures with the hope of monitoring coherent exciton migration. Instead, they found a very fast incoherent motion which may be attributed to polariton effects. Most recently a dramatic variation of the transient grating signal as a function of detuning was observed, which could be attributed to polaritons as well. Again, conventional theories of $\chi^{(3)}$ predict that the experiment is probing exciton motion, whereas the proper incorporation of retarded interactions is essential for analyzing this experiment. This was pointed out by Agranovich, [9] but no systematic theory exists. Our microscopic theory for $\chi^{(3)}$ may be used towards the analysis of these polariton grating experiments.

Intermolecular interactions in molecular aggregates result in cooperative radiative dynamics. Some manifestations of the cooperativity are an enhanced oscillator strength, ultrafast radiative decay rates or superradiance [10,11] and the possible enhancement of nonlinear susceptibilities [12,13]. One important question is, How does the nonlinear susceptibility depend on aggregate size? To answer this, we have derived the third order susceptibility $\chi^{(3)}$ of a cyclic molecular aggregate consisting of N coupled two-level systems with transition frequency ω_0 . The coupling consists of a real, nearest neighbor dipole-dipole coupling V and an imaginary superradiant coupling γ , and we include excitons as well as biexcitons. For this model, we have:

$$\chi^{(3)}(-\omega_s; \omega_3, \omega_2, \omega_1) =$$

$$\begin{aligned}
& 8N^2\mu^4 \sum_P \frac{\omega(0)}{[\omega_1+\omega_2+\omega_3+i\frac{N\gamma}{2}] - \omega(0)^2} \frac{1}{\omega_1+\omega_2+iN\gamma} \frac{\omega_1+i\frac{N\gamma}{2}}{[\omega_1+i\frac{N\gamma}{2}] - \omega(0)^2} \\
& + 8N(N-1)\mu^4 \sum_P \sum_{q=1,3,5\dots}^{N-2} I_q \frac{[\omega(0) - \Omega(0,q)]}{[\omega_1+\omega_2+\omega_3+i(\Gamma(0,q)+\frac{N\gamma}{2})]^2 - [\omega(0) - \Omega(0,q)]^2} \\
& \quad \times \frac{1}{\omega_1+\omega_2+iN\gamma} \frac{\omega_1+i\frac{N\gamma}{2}}{[\omega_1+i\frac{N\gamma}{2}] - \omega(0)^2} \\
& - 2N(N-1)\mu^4 \sum_P \sum_{q=1,3,5\dots}^{N-2} I_q \left[\frac{1}{\omega_1+\omega_2+\omega_3+\omega(0) - \Omega(0,q) + i(\Gamma(0,q)+\frac{N\gamma}{2})} \right. \\
& \quad \left. - \frac{1}{\omega_1+\omega_2+\omega_3-\omega(0)+i\frac{N\gamma}{2}} \right] \frac{1}{\omega_1+\omega_2 - \Omega(0,q) + i\Gamma(0,q)} \frac{1}{\omega_1 - \omega(0) + i\frac{N\gamma}{2}} \\
& + 2N(N-1)\mu^4 \sum_P \sum_{q=1,3,5\dots}^{N-2} I_q \left[\frac{1}{\omega_1+\omega_2+\omega_3-\omega(0) + \Omega(0,q) + i(\Gamma(0,q)+\frac{N\gamma}{2})} \right. \\
& \quad \left. - \frac{1}{\omega_1+\omega_2+\omega_3+\omega(0)+i\frac{N\gamma}{2}} \right] \frac{1}{\omega_1+\omega_2 + \Omega(0,q) + i\Gamma(0,q)} \frac{1}{\omega_1 + \omega(0) + i\frac{N\gamma}{2}}
\end{aligned} \tag{1}$$

where $\omega(0)$ and $\Omega(0,q)$ are the exciton and q^{th} biexciton transition frequencies, $N\gamma/2$ and $\Gamma(0,q)$ are the exciton and biexciton superradiative decay rates, given by:

$$\omega(0) = \omega_0 + 2V \tag{2a}$$

$$\Omega(0,q) = 2\omega_0 + 4V\cos\left(\frac{\pi q}{N}\right) \tag{2b}$$

$$\Gamma(0,q) = \frac{2\gamma}{N} \left[\cot\left(\frac{\pi q}{2N}\right) \right]^2 \tag{2c}$$

The dimensionless factors I_q are given by:

$$I_q = \frac{2}{N(N-1)} \cot^2 \frac{q\pi}{2N} \tag{2d}$$

(We should point out that Eq.(1) is applicable for odd values of N which, in addition, satisfy

$N \geq 5$. For $N=3$, Eq.(1) is still valid provided one uses $I_1 = 1$, $\Omega(0,q) = 2\omega_0 + 2V$ and $\Gamma(0,1) = 2\gamma$. The first term in Eq.(1) represents the contribution to $\chi^{(3)}$ from all interaction processes which involve only the exciton state. The remaining terms involve exciton and biexciton states; the second term is resonantly enhanced for processes which involve biexciton formation through single photon absorption from an initial exciton population, while the last two terms involve biexciton formation via direct two photon absorption.

The aggregate size N appears in Eq.(1) as N^2 and $N(N-1)$ prefactors, arising from the enhanced exciton and exciton-biexciton transition dipole moments, and in the imaginary parts of all three denominators, due to the superradiant radiative decay of the exciton and biexciton states. Therefore, the scaling of $\chi^{(3)}$ with size depends on the particular nonlinear technique, for example, $\chi^{(3)}$ for degenerate four wave mixing will have a distinctly different N dependence than $\chi^{(3)}$ for third harmonic generation. There is, however, one very general limiting case which is the most important from a technological viewpoint, namely, when all three fields are far off resonance ($\omega_1 \pm \omega_2 \pm \omega_3 \pm \omega_0 \gg V$, $\omega_1 \pm \omega_2 \gg N\gamma$ and $\omega_1 \pm \omega_0 \gg V$). It was predicted in this case that there will be a universal cooperative enhancement of $\chi^{(3)}$ resulting in a giant nonlinear susceptibility [12]. In order to explore this point we take the off resonance limit of Eq.(1). This is done by substituting the approximations $\omega(0) \approx \omega_0$ and $\Omega(0,q) \approx 2\omega_0$ into Eq.(1) and neglecting the superradiant contribution in the denominators. It then appears, at first glance, that (when N is large) $\chi^{(3)}$ is enhanced by a factor of N^2 . Since, for N monomers $\chi^{(3)} \sim N$ we are led to the conclusion that the effect of aggregation, in this limit, is to enhance $\chi^{(3)}$ by a factor of N . This conclusion is however false. When all the terms in Eq.(1) are added in this limit we get:

$$\chi^{(3)}(\omega_s, \omega_3, \omega_2, \omega_1) = 8N\mu^4 \sum_p \frac{\omega_0}{[\omega_1 + \omega_2 + \omega_3]^2 - \omega_0^2} \frac{1}{\omega_1 + \omega_2} \frac{\omega_1}{\omega_1^2 - \omega_0^2} \quad (3)$$

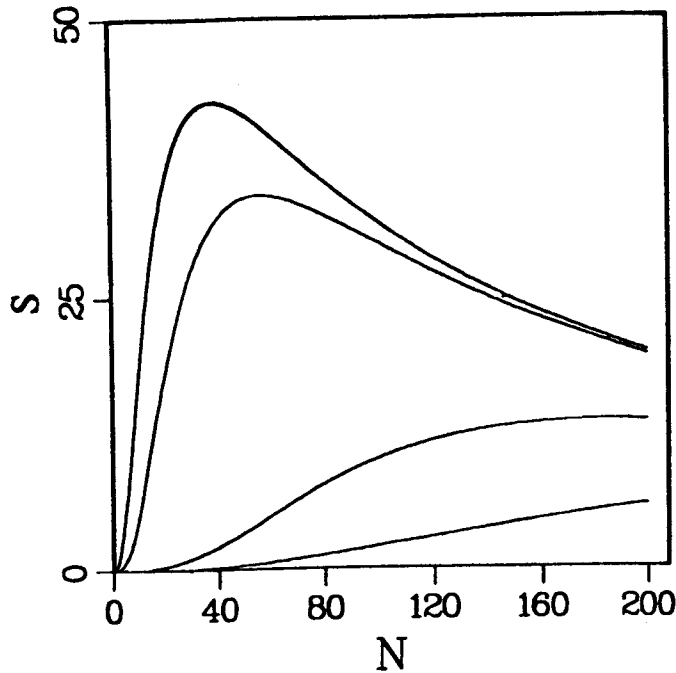


Figure 1: $S(N, \Gamma, \Delta\omega_1)$ for a phase conjugate DFWM configuration vs. aggregate size N for several values of pump laser detuning $\Delta\omega_1$ with $\omega_1 = \omega_0 + 2V$ and $\Gamma = 10\gamma$. The curves correspond to different detunings $\Delta\omega_1/\gamma = 0, 1, 10, 50$ and 100 . In all cases S decreases as $\Delta\omega_1$ increases. (Curves with $\Delta\omega_1/\gamma = 0$ and 1 overlap.)

The N^2 parts of Eq.(1) exactly cancel due to an interference between the first and second terms. In addition the third and fourth terms exactly cancel, leaving the monomer result given by Eq.(3). This is understandable since, under these far-off resonant conditions, the material response is very rapid and the molecules will not have time to interact with each other and establish aggregate properties. It is also important to note that the biexciton states, which contribute the last three terms in Eq.(1), are necessary to arrive at this result. It is not appropriate to treat the aggregate as a two-level system with an enhanced oscillator strength and radiative rate.

We have also investigated the effect of homogeneous or pure dephasing Γ and laser detuning on the nonlinear susceptibility. Since the pure dephasing competes directly with the size dependent superradiant damping [10] it also has a profound effect on the size dependence of $\chi^{(3)}$. In Figure 1 we show $|\chi^{(3)}(-2\omega_1+\omega_2; \omega_1, -\omega_2, \omega_1)|^2$ integrated over ω_2 for phase conjugate degenerate four-wave mixing (DFWM), defined as $S(N, \Gamma, \Delta\omega_1)$, plotted against aggregate size N . We have chosen $\Gamma = 10 \gamma$ and have set the counterpropagating pump beam frequencies equal to the exciton transition frequency, $\omega_1 = \omega(0)$ (or $\Delta\omega_1 = 0$ -the resonant case). Under these conditions $S(N, \Gamma, \Delta\omega_1)$ is both enhanced and degraded with size. Analysis of Eq.(1) shows that it ranges from an $\sim N^{-1}$ dependence to an $\sim N^4$ dependence as the homogeneous dephasing rate is increased from the superradiant limit ($\Gamma \ll N\gamma$) to the fast dephasing limit ($\Gamma \gg N\gamma$). In the nonresonant case ($\Delta\omega_1 \gg V$) the behavior is entirely different. In the superradiant limit, the size dependence becomes linear $\sim N$ while in the fast dephasing limit it reduces to $\sim N^2$, which is characteristic of N monomers. An important conclusion to be drawn from this work is that, in general, $\chi^{(3)}$ does not show a universal enhancement with size, and that under off resonant conditions it shows no enhancement at all.

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