

## Nonlinear-optical properties of biexcitons: Single-beam propagation

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A nonperturbational method is developed for the calculation of the nonlinear-optical susceptibility of a system composed of two types of bosons: excitons and biexcitons. When applied to CuCl, this calculation accounts for the renormalization of the polariton dispersion relation due to the presence of the biexciton transition. It also gives a two-photon absorption towards the biexciton, with a resonance frequency which shifts with intensity. The calculated transmission spectrum for a light beam propagating through CuCl reproduces the features of the experimental spectrum. It contains an asymmetric dip at half the biexciton frequency, with a width dependent on the incident intensity. The nonperturbational treatment suggests that this width is due essentially to the shift of the absorption frequency during propagation, rather than to the collisional mechanism postulated within the perturbational framework of nonlinear optics.

### I. INTRODUCTION

The nonlinear-optical response of a material system has traditionally been expressed in terms of a perturbational expansion of the induced polarization in powers of the incident electromagnetic field. Several methods have been developed for the calculation of the corresponding coefficients, called the optical susceptibilities.<sup>1</sup> Clearly, the domain of validity of the perturbation expansion is limited only to those situations in which the infinite series of the successive orders of the induced polarization converges. Thus, the description of some near-resonant nonlinear-optical phenomena may not be possible within the perturbational framework, since the successive orders of the susceptibility diverge due to their resonance denominators.

A case in point is the description of the nonlinear susceptibility of a semiconductor in the vicinity of the two-photon biexciton resonance: At relatively low light intensities the resonance-enhanced nonlinear-optical response of CuCl is so strong that forward degenerate "four-wave" mixing cannot be distinguished from higher-order  $(4 + 2n)$ -wave processes.<sup>2</sup> In the perturbational language of nonlinear optics this can be expressed as a renormalization of the third-order susceptibility  $\chi^{(3)}$  by the higher-odd-order  $\chi$ 's. The corresponding calculation, however, presents many difficulties since it involves the summation of an infinite series in which each term is divergent (near resonance) while at the same time the bookkeeping of high-order mixing processes involving three distinct waves represents a formidable task.<sup>3</sup> The nonlinear-optical response of CuCl in the vicinity of the biexciton resonance must therefore be expressed within a nonperturbational framework.

In the light of this observation the interpretation of experiments based on a perturbational analysis of such systems may need to be reconsidered. An example is the "two-photon" absorption line shape of biexcitons in CuCl. In contrast to conventional two-photon absorption the biexciton linewidth was found to be intensity dependent and was thus attributed to "collisional broadening" in the

biexciton gas whose density increases with intensity.<sup>4</sup> The collisional mechanism, however, could not be corroborated by different experiments.<sup>5</sup> A reexamination of the absorption line shape within a nonperturbational theory is thus in order. Another example concerns the spectral line shape of the four-wave-mixing signal resonant with the two-photon biexciton transition.<sup>6</sup> The observed asymmetry could not be accounted for by the third-order susceptibility obtained from a simple exciton-biexciton model. Thus a Fano interference effect between the sharp biexciton level and the two-polariton continuum was invoked to explain it. The nonperturbational description of four-wave mixing, however, may require that this mechanism be revised.

In this paper we address the problem of the nonperturbational calculation of the nonlinear-optical response of an exciton-biexciton system using CuCl as a reference. To keep the physics and the algebra simple we limit our description to single-beam experiments (such as transmission or reflexion spectroscopy) by (1) calculating the nonlinear intensity-dependent dielectric function of the medium, and (2) by accounting for the nonlinear propagation of light through such a medium. Some of our conclusions are applicable also in multibeam experiments; a more thorough examination of such experimental configurations is left for a planned future publication. The calculation of the nonlinear dielectric function and the corresponding renormalization of the polariton dispersion relation near the two-photon biexciton resonance has been addressed also by other authors using a variety of formal approaches: Green's-function techniques,<sup>7</sup> the summation of perturbational (infinite) series,<sup>3</sup> or the solution of Bloch-type equations of motion.<sup>8</sup> Our results reduce to theirs under the appropriate approximations. The paper is organized as follows. Section II reviews the basic concepts of nonlinear optics relevant to the nonperturbational treatment. The physical model for an exciton-biexciton system and the unitary transformations diagonalizing its Hamiltonian are presented in Sec. III. Section IV contains the calculation of the nonlinear susceptibility and discusses

the effects observable in the propagation of a light beam through such a system. Finally, Sec. V contains the conclusions of this study.

## II. GENERAL CONSIDERATIONS

### A. Optical susceptibility

We consider a semiconductor described by a Hamiltonian  $H_0$  and interacting with the electromagnetic field. Within the dipolar approximation the interaction Hamiltonian is

$$H_1 = -\hat{\mu} \cdot \hat{E}(r, t), \quad (2.1)$$

where  $\hat{\mu}$  is the dipole operator, while  $\hat{E}$  is the electric field operator. In what follows we shall adopt a semiclassical treatment by using an effective Hamiltonian which deals only with the occupied modes of the electromagnetic field and treats the corresponding electric field as a  $c$ -number  $E$ . The interaction with the unoccupied modes is included through its lowest-order term: the dipole-dipole interaction among the polarizable units in the system.<sup>9</sup> This produces a renormalization of the electric field felt by the individual polarizable units, which in classical optics (and electrostatics) is known as the "local-field correction."<sup>10</sup> For an isotropic polarizable medium, the local field at a point  $r$  is given by the field produced by the induced polarization at all other points, in addition to the externally applied field. That is, it can be written as

$$E_{\text{loc}} = E_{\text{appl}} + \frac{4\pi}{3} \sum_i \gamma_i P_i, \quad (2.2)$$

where  $p_i$  is the polarization induced on the  $i$ th-type polarizable unit (excited state) while  $\gamma_i$  is a parameter ( $0 \leq \gamma_i \leq 1$ ) which depends on the degree of delocalization of the electrons associated to excitation  $i$ . For completely delocalized electrons (e.g., in metals),  $\gamma = 0$ , while for excitations confined to a single unit cell  $\gamma = 1$ . Under these considerations the full electromagnetic interaction of Eq. (2.1) can be rewritten as

$$H_1 = -\hat{\mu} \cdot E_{\text{loc}}(r, t) \quad (2.3)$$

where  $E_{\text{loc}}$  is a  $c$  number and is given by Eq. (2.2),

We assume that at  $t = -\infty$  the system is found in the  $n$ th eigenstate of  $H_0$ ,  $|n\rangle$  and that the field is turned on adiabatically to attain the value  $E$  at  $t=0$  so as to avoid transients in the response of the system. The state of the system after the turn on of the field is

$$|\tilde{n}\rangle = U(-\infty, t=0) |n\rangle, \quad (2.4)$$

where  $U$ , the time-evolution operator, can be expressed in the interaction picture as a time-ordered exponential of  $H_1$ . Clearly,  $U$  is the transformation that diagonalizes the full Hamiltonian

$$H = H_0 + H_1, \quad (2.5)$$

since  $|\tilde{n}\rangle$  is the eigenstate of  $H$  that is reached when  $H_1$  is turned on adiabatically.

The optical response of the system is given by the polarization induced on it by the electromagnetic field. It cor-

responds to the expectation value of  $\hat{\mu}$  per unit volume after the field has been turned on. That is

$$P = \langle \tilde{n} | (\hat{\mu}/V) | \tilde{n} \rangle \\ = \langle n | U^\dagger(-\infty, 0) (\hat{\mu}/V) U(-\infty, 0) | n \rangle. \quad (2.6)$$

At this point it is customary to expand  $U$  and  $U^\dagger$  in a perturbational series in powers of the field and obtain the optical susceptibilities of different orders. Clearly, however, a calculation of  $U$  through a nonperturbational scheme would give the optical response of the material to all orders, without distinction among the effects due to the different susceptibilities. The result of Eq. (2.6) may then be written formally as

$$P = \alpha(E_{\text{loc}})E_{\text{loc}}, \quad (2.7)$$

defining thus  $\alpha$ , the nonlinear polarizability. The induced polarization may also be calculated in terms of the externally applied field, by explicitly introducing the local-field correction, and by solving Eqs. (2.2) and (2.7) self-consistently. The solution can then be expressed formally as

$$P = \chi(E_{\text{appl}})E_{\text{appl}}, \quad (2.8)$$

defining thus  $\chi$ , the (macroscopic) nonlinear susceptibility. The nonlinear susceptibility (rather than the nonlinear polarizability) is the quantity relevant to an experiment, since the applied (rather than the local) field is one of the experimental parameters.

A major problem in the description of the optical response of a real material system is the inclusion of the effects of relaxation processes. Such processes are most often treated phenomenologically by the addition of a small imaginary part ( $i\gamma$ ) to the corresponding frequency. In such a case, however, care must be exercised since the phenomenological Hamiltonian is not Hermitian, and its eigenstates cannot be properly defined (e.g., they do not remain normalized as they evolve in time). It has been shown<sup>11</sup> that with such a Hamiltonian the calculation of the expectation value of the induced polarization can still be performed, if the time evolution of the bra and the ket are correlated at all times through the *simultaneous* time ordering of both  $U(-\infty, 0)$  and  $U^\dagger(-\infty, 0)$  in Eq. (2.6). This double time ordering is generally possible only when both  $U$  and  $U^\dagger$  are expanded in a perturbation series. However, if both the real and imaginary parts of the frequency follow the same combination rule,

$$\omega_{nn'} + \omega_{n'n''} = \omega_{nn''} \quad (2.9)$$

(where  $\omega_{ij}$  is the frequency difference between the  $i$ th and  $j$ th states), the same result is obtained whether the evolution operator and its conjugate are time-ordered simultaneously or independently.<sup>11</sup> This implies that when Eq. (2.9) is satisfied for all complex frequencies associated with a material system, the evolution operator  $U(-\infty, 0)$  can be calculated (separately from its conjugate) through nonperturbational techniques as the unitary transformation that diagonalizes  $H$ .

### B. Nonlinear propagation

An optical experiment involves the observation of a light beam traversing a material system and is thus described by the Maxwell equations for the generation and/or propagation of the beam through the oscillating induced polarization of the medium. For  $z$ -axis propagation of a single beam, the Maxwell equations reduce to

$$\frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} (E + 4\pi P), \quad (2.10)$$

where  $P$  is the induced polarization. The conventional procedure<sup>1</sup> consists of separating  $P$  into linear and nonlinear parts, solving the problem of linear propagation, and calculating the effects of the nonlinear part of  $P$  as a deviation from linear propagation within the slowly varying envelope approximation. The nonperturbational treatment of the induced polarization, however, requires that both the linear and nonlinear parts of  $P$  be treated on the same footing. We shall examine such a treatment for the simple case in which the only time dependence of both  $E$  and  $P$  is an oscillation at frequency  $\omega$ . In such a case, differentiating with respect to time in Eq. (2.10) we have

$$\frac{\partial^2 E}{\partial z^2} = -\frac{\omega^2}{c^2} (E + 4\pi P) = -\frac{\omega^2}{c^2} \epsilon(E) E, \quad (2.11)$$

where we define formally the nonlinear dielectric function

$$\epsilon(E) = 1 + 4\pi\chi(E), \quad (2.12)$$

and  $\chi(E)$  is the macroscopic susceptibility. For the case in which  $\epsilon(E)$  does not change its value with distance, Maxwell's equations permit us to reduce Eq. (2.11) to the first-order equation

$$\frac{\partial E}{\partial z} = -ikE, \quad (2.13)$$

where

$$k = (\omega/c)\sqrt{\epsilon} \quad (2.14)$$

is the wave vector. Equation (2.13) is rigorous when  $\epsilon$  is independent of the incident light field (linear propagation) or when  $\epsilon$  depends on the incident intensity (or the absolute value of  $E$ ) but that latter parameter remains constant throughout the sample (i.e., there is no absorption). In such cases Eq. (2.14) permits the definition of the nonlinear dispersion relation.

When  $\epsilon$  is a weak function of  $z$ , as in the case in which light is weakly absorbed while it propagates in the nonlinear medium, passage from Eq. (2.11) to (2.13) is still possible, as in the theory of propagation through media with weak refractive-index variations.<sup>12</sup> In that case, however, Eq. (2.13) involves a small error which may be evaluated by redifferentiating Eq. (2.13) to obtain Eq. (2.11). The error is small when

$$\left| \frac{dk}{dz} \right| \ll |k^2|, \quad (2.15a)$$

or rearranging,

$$\left| \frac{d}{dz} \left[ \frac{1}{k} \right] \right| \ll 1, \quad (2.15b)$$

that is, when the fractional variation of the wave vector is small over a wavelength or, in other words, when a wave vector (and a wavelength) can be defined locally. We note that if the nonlinear part of the susceptibility is small compared to the linear part, the dispersion relation (2.14) can be expanded as

$$k = \frac{\omega}{c} \sqrt{\epsilon_L + \chi_{NL}} \approx \frac{\omega}{c} \sqrt{\epsilon_L} + \frac{\omega}{c} \frac{\chi_{NL}}{2\sqrt{\epsilon_L}}, \quad (2.16)$$

so that Eq. (2.13) reduces to the familiar slowly varying envelope approximation.

### III. MODEL HAMILTONIAN

A semiconductor interacting with an electromagnetic field in the vicinity of the two-photon biexciton resonance can be described as an idealized system involving two types of quasiparticles: excitons and biexcitons. The reason is that in the vicinity of that resonance the electrostatic and exchange interactions among excitons can be simply represented by the formation of a new quasiparticle, the biexciton. Both excitons and biexcitons behave approximately as bosons when they are created at low densities.

The Hamiltonian of the crystal may be written as

$$H_0 = \sum_q \omega_0(q) b_q^\dagger b_q + \sum_Q \Omega(Q) B_Q^\dagger B_Q, \quad (3.1)$$

where the operators  $b_q^\dagger$  and  $b_q$  ( $B_Q^\dagger$  and  $B_Q$ ) create and annihilate, respectively, an exciton (a biexciton) of wave vector  $q$  ( $Q$ ) and frequency  $\omega_0(\Omega)$ . If we assume that excitons are active in one-photon absorption while biexcitons can be accessed through a two-photon transition with the exciton as an intermediate state, the interaction of the crystal with an electric field of the form

$$E e^{-i\omega t + ikr} + E^* e^{i\omega t - ikr}$$

can be written as

$$H_1 = -\sqrt{N} \mu_1 (E e^{-i\omega t} b_k^\dagger + E^* e^{i\omega t} b_k) - \sum_q \mu_2 (E' e^{-i\omega t} B_{k+q}^\dagger b_q + E'^* e^{i\omega t} B_{k+q} b_q^\dagger), \quad (3.2)$$

where  $\mu_1$  is the transition dipole per unit cell for the exciton transition, and  $N$  is the number of unit cells in the crystal, while  $\mu_2$  is the dipole matrix element for the exciton-biexciton transition. The spatial part of the phase factor for the electromagnetic wave  $e^{ikr}$  is incorporated in the definition of the exciton or biexciton operators with the corresponding wave vector.

In writing Eq. (3.2) the rotating-wave approximation has been invoked by eliminating the antiresonant terms of the interaction Hamiltonian; this approximation limits the calculation only to the resonant features of the nonlinear-optical response. We note also that a prime ( $E'$ ) has been used to denote the possibility that the electric field felt by the exciton and by the biexciton are not exactly the same.

This may arise from local-field effects on the two quasi-particles, given that the extension of their Wannier functions differ greatly: In CuCl the exciton radius ( $\sim 7 \text{ \AA}$ ) is of the order of the lattice spacing while the volume of the biexciton is  $\sim 300$  times larger,<sup>13</sup> indicating that the local-field produced by the exciton polarization varies rapidly over the dimensions of the biexciton. Thus, the biexciton is subject to an average field which essentially excludes the contribution of the exciton polarization and conversely it does not contribute to the local field felt by the exciton. In other words, in considering local-field effects according to Eq. (2.2) we may take  $\gamma=1$  for the excitons and  $\gamma=0$  for the biexcitons.

The full Hamiltonian of a crystal interacting with a laser beam (plane wave) of wave vector  $k$  is, of course,

$$H = H_0 + H_1. \quad (3.3)$$

Equations of motion under this Hamiltonian are somewhat difficult to solve because of the time dependence in the interaction Hamiltonian  $H_1$ . They are, however, greatly simplified if they are recast in a rotating frame of reference such that the explicit oscillations of the interaction Hamiltonian are eliminated, as is routinely done in the theory of NMR or coherent optics. Since there are two types of excitations it is necessary to use a "double" rotating frame<sup>14</sup> composed of one reference frame for the excitons rotating at  $\omega$  (the frequency of the radiation field) and one for the biexcitons rotating at twice that frequency,  $2\omega$ . The transformation to this doubly rotating frame, then, is essentially equivalent to a transformation into an interaction picture in which the overall Hamiltonian of Eq. (3.3) is partitioned into a "zeroth-order" Hamiltonian of the form

$$H' = \omega \sum_q b_q^\dagger b_q + 2\omega \sum_Q B_Q^\dagger B_Q, \quad (3.4a)$$

and an "interaction"

$$H'' = H - H'. \quad (3.4b)$$

Equations of motion in this interaction picture, then, involve the Hamiltonian

$$\tilde{H} = e^{iH't} H'' e^{-iH't} = \tilde{H}_0 + \tilde{H}_1, \quad (3.5a)$$

with

$$\tilde{H}_0 = \sum_q \delta(q) b_q^\dagger b_q + \sum_Q \Delta(Q) B_Q^\dagger B_Q \quad (3.5b)$$

and

$$\begin{aligned} \tilde{H}_1 = & -\sqrt{N} \mu_1 (E b_k^\dagger + E^* b_k) \\ & -\mu_2 \sum_q (E' B_{q+k}^\dagger b_k + E'^* B_{q+k} b_k^\dagger), \end{aligned} \quad (3.5c)$$

where  $\delta(q) = \omega_0(q) - \omega$  and  $\Delta(Q) = \Omega(Q) - 2\omega$  are, respectively, the detunings of the exciton relative to the one-photon transition and of the biexciton relative to the two-photon transition.

Relaxation processes may be included phenomenologically in the equations of motion by allowing the exciton and biexciton frequencies (or the corresponding detunings)

to be complex. For the equations of motion of the operators  $b_q$  and  $B_Q$  we may thus write

$$\omega_0(q) \rightarrow \omega_0(q) - i\gamma, \quad (3.6a)$$

$$\Omega(Q) \rightarrow \Omega(Q) - i\Gamma. \quad (3.6b)$$

For the creation operators  $b^\dagger$  and  $B^\dagger$  the conjugate frequencies must be used. Clearly, for the different levels within each Bose oscillator, the combination rule of Eq. (2.5) is always satisfied: The decay rates of  $(b)^\dagger$  and  $(B)^\dagger$  are  $4\gamma$  and  $4\Gamma$ , respectively. In order to be able to calculate the induced polarization without the need for double time-ordering procedures we must postulate that Eq. (2.6) holds even between exciton and biexciton states.

When  $E$  is turned on adiabatically the equations of motion of any operator under the Hamiltonian (3.5) can be solved in a very straightforward manner, by simply applying to that operator the unitary transformation that diagonalizes Eq. (3.5) and then introducing an imaginary part to all detunings, positive for creation operators and negative for annihilation operators. Since the Hamiltonian involves only Bose operators and is quadratic, the unitary transformation that diagonalizes it can be obtained in analytic form. The calculation is easiest performed in two stages: First, the linear terms in  $(b^\dagger + b)$  can be eliminated through a translation of both exciton and biexciton operators, and then the quadratic cross terms in  $(B^\dagger b + B b^\dagger)$  can be diagonalized away through a rotation in exciton-biexciton coordinate space. That is the diagonalization procedure can be written as

$$U^{-1} \tilde{H} U = e^{-S_2} (e^{-S_1} \tilde{H} e^{S_1}) e^{S_2}, \quad (3.7)$$

where the anti-Hermitian operators  $S_1$  and  $S_2$  are linear and quadratic, respectively, in the Bose creation and annihilation operators. The translational part can be written

$$S_1 = \sum_q (x_q b_q^\dagger - x_q^* b_q) + \sum_Q (y_Q B_Q^\dagger - y_Q^* B_Q), \quad (3.8a)$$

so that when applied on the exciton and biexciton operators the translational part gives

$$e^{-S_1} b_q e^{S_1} = b_q + x_q, \quad (3.8b)$$

$$e^{-S_1} B_Q e^{S_1} = B_Q + y_Q, \quad (3.8c)$$

and so on. As shown in the Appendix, the values

$$x_k = \sqrt{N} \frac{(\mu_1 E) \Delta}{\Delta \delta - |\mu_2 E'|^2}, \quad (3.9a)$$

$$y_{2k} = \sqrt{N} \frac{\mu_1 E (\mu_2 E')}{\Delta \delta - |\mu_2 E'|^2}, \quad (3.9b)$$

$$x_q = 0 \quad \text{for } q \neq k \quad (3.9c)$$

$$y_Q = 0 \quad \text{for } Q \neq 2k \quad (3.9d)$$

with  $\Delta = \Delta(2k)$ ,  $\delta = \delta(k)$ , eliminate the linear terms of the Hamiltonian. The partially transformed Hamiltonian now reads

$$e^{-S_1} \tilde{H} e^{S_1} = \sum_q \delta(q) b_q^\dagger b_q + \sum_Q \Delta(Q) B_Q^\dagger B_Q - \mu_2 \sum_q (E' B_{q+k}^\dagger b_q + E'^* B_{q+k} b_q^\dagger), \quad (3.10)$$

where the constant term (order zero in the operators) resulting from the translational transformation has been dropped.

We note that Eq. (3.10) can be separated into  $N$  independent and mutually commuting partial Hamiltonians, each of which involves one exciton ( $q$ ) and one biexciton ( $Q=q+k$ ) linked through the radiative interaction. Each one of these Hamiltonians may be diagonalized through a rotational transformation of the form

$$S_2^{(q)} = \theta_q B_{q+k} b_q^\dagger - \theta_q^* B_{q+k}^\dagger b_q, \quad (3.11a)$$

such that

$$U^{-1} \tilde{H} U = \sum_q \left\{ \frac{\Delta' + \delta'}{2} + \left[ \left( \frac{\Delta' - \delta'}{2} \right)^2 + |\mu_2 E'|^2 \right]^{1/2} \right\} b_q^\dagger b_q + \left\{ \frac{\Delta' + \delta'}{2} - \left[ \left( \frac{\Delta' - \delta'}{2} \right)^2 + |\mu_2 E'|^2 \right]^{1/2} \right\} B_{k+q}^\dagger B_{k+q}, \quad (3.14)$$

where  $\delta' = \delta(q)$  and  $\Delta' = \Delta(q+k)$  for brevity.

#### IV. PROPAGATION OF A SINGLE BEAM

We consider a plane electromagnetic wave of wave vector  $k$  and frequency  $\omega$  propagating through the crystal. Such an experiment, of course, involves the observation of the transmitted radiation of the same wave vector. The experimental observable thus consists of the induced polarization of wave vector  $k$ , which is given by the expectation value over the adiabatic state of the total dipole operator,

$$\hat{\mu}^k = \hat{\mu}_1^k + \hat{\mu}_2^k = \sqrt{N} \mu_1 b_k + \mu_2 B_{k+q} b_q^\dagger, \quad (4.1)$$

where  $\hat{\mu}_1^k, \hat{\mu}_2^k$  distinguish the direct contributions of the exciton and biexciton transitions for the sake of clarity: The expectation value of  $\hat{\mu}_1^k$  corresponds to the probability that a photon of wave vector  $k$  is emitted while the system undergoes a transition in which an exciton is annihilated, while the expectation value of  $\hat{\mu}_2^k$  gives the probability that the experimental observation of a photon occurs when a biexciton-to-exciton transition takes place.

With the use of the unitary transformation obtained in Sec. III and Eq. (2.6) the direct contribution of the exciton transition to the induced polarization is

$$P_1 = \langle i | U^{-1} (\hat{\mu}_1 / V) U | i \rangle = \frac{N \mu_1^2 E \Delta}{V \Delta \delta - |\mu_2 E'|^2} \quad (4.2a)$$

for all initial states  $|i\rangle$ . The detunings are taken to be complex,

$$\Delta = \Delta(2k) - i\Gamma, \quad \delta = \delta(k) - i\gamma.$$

We note that for  $E'=0$ , Eq. (4.2a) gives the linear polarization corresponding to the exciton transition. For finite

$$e^{-S_2^{(q)}} b_q e^{S_2^{(q)}} = \cos |\theta_q| b_q + (\theta_q / |\theta_q|) \sin |\theta_q| B_{q+k}, \quad (3.11b)$$

$$e^{-S_2^{(q)}} B_{q+k} e^{S_2^{(q)}} = \cos |\theta_q| B_{q+k} - (\theta_q^* / |\theta_q|) \sin |\theta_q| b_q. \quad (3.11c)$$

It can easily be shown (see Appendix) that for

$$\theta_q = -\frac{1}{2} \frac{E'^*}{|E'|} \arctan \frac{2|\mu_2 E'|}{\Delta(q+k) - \delta(q)}, \quad (3.12)$$

each partial Hamiltonian is diagonalized. The overall rotational transformation is, of course,

$$S_2 = \sum_q S_2^{(q)}, \quad (3.13)$$

giving for the overall diagonalized Hamiltonian

$E'$  this polarization is renormalized (by its denominator) for all virtual biexciton-to-exciton transitions, so that it gives the probability that the exciton transition occurs as part of the two-photon biexciton-to-ground transition. The direct biexciton contribution is

$$P_2 = \langle i | U^{-1} (\hat{\mu}_2 / V) U | i \rangle = \frac{N \Delta^* \mu_1^2 \mu_2^2 |E|^2 E'}{V |\Delta \delta - |\mu_2 E'|^2|^2} + \frac{\mu_2^2 E'}{2V} \sum_q \frac{\langle i | b_q^\dagger b_q - B_{q+k}^\dagger B_{q+k} | i \rangle}{\left[ \left( \frac{\Delta(q+k) - \delta(q)}{2} \right)^2 + |\mu_2 E'|^2 \right]^{1/2}}, \quad (4.2b)$$

and corresponds to the probability that the photon emitted by the oscillating induced polarization is associated with the biexciton-to-exciton part of the two-photon biexciton transition. The first term in Eq. (4.2b) is due to the translational part of the unitary transformation and is the same for all initial states. The second term results from the rotational part; it is essentially proportional to the exciton-biexciton population difference and displays a resonance at approximately the exciton-to-biexciton transition frequency. This term thus corresponds to the case in which the exciton-to-biexciton transition occurs because of the presence of a real population of excitons and biexcitons while the translational term is associated with the probability that the exciton-to-biexciton transition occurs as part of a coherent two-photon (rather than two-step) process.

In most experimental situations the initial state of the crystal contains no excitons or biexcitons, i.e.,  $|i\rangle = |0\rangle$ , so that only the first term in Eq. (4.2b) need be considered.

This is the case that will be considered in this paper. However, when the initial state is prepared experimentally, as in time-resolved pump-and-probe-type experiments, the second term has to be explicitly included.

The nonlinear polarizability may be immediately obtained from Eqs. (4.2) through its definition (2.7). Neglecting the local-field corrections, the polarizability of a semiconductor initially in its ground state can be written as

$$\alpha = \alpha_1 + \alpha_2 = \frac{P_1 + P_2}{E} = \frac{N}{V} \frac{\mu_1^2 (\Delta\Delta^* \delta^* + 2i\Gamma |\mu_2 E|^2)}{|\Delta\delta - |\mu_2 E|^2|^2}. \quad (4.3)$$

In order to relate these calculations to experimental observations, however, it is more convenient to calculate the nonlinear *susceptibility* in which all local-field factors are included explicitly so that the induced polarization is expressed as a function of the applied fields. As was discussed in an earlier publication,<sup>15</sup> if both the excitons and biexcitons are affected by the same local field the nonlinear susceptibility becomes a multivalued function of the incident electric field and thus may give rise to a bistability in the refractive index and in the reflectivity of the medium. Such an intrinsic bistability (without an optical cavity) due to dipole-dipole interactions which introduce an "internal" feedback in the material has also been discussed by other authors in different systems.<sup>9</sup> However, although this effect may in principle be observable in exciton-biexciton systems, it is questionable whether CuCl can exhibit such intrinsic bistable behavior. The reason lies in the large extension of the biexciton wave function which implies that these quasiparticles are affected by the externally applied electric field directly, rather than the local field [ $\gamma_{\text{biex}} \approx 0$  in Eq. (2.2)]. Using this "size" argument, we may thus assume that only the exciton is subject to local-field considerations ( $\gamma_{\text{ex}} \approx 1$ ). We may further assume that we also have  $\gamma \approx 1$  for the background polarization which arises from all nonresonant transition processes (i.e., to all states other than the exciton and the biexciton). Under these assumptions we have

$$E' = E_{\text{appl}}, \quad (4.4a)$$

$$E = E_{\text{loc}} = E_{\text{appl}} + \frac{4\pi}{3} (\alpha_{\infty} + \alpha_1) E_{\text{loc}}, \quad (4.4b)$$

where  $\alpha_{\infty}$  is the background polarizability while  $\alpha_1$  is the direct exciton contribution to the polarizability corresponding to Eq. (4.2a). Equation (4.4b) can be rewritten as

$$E_{\text{loc}} = f E_{\text{appl}}, \quad (4.5a)$$

with the local-field factor  $f$  given by

$$f = \frac{(\epsilon_{\infty} + 2)/3}{1 - (4\pi\alpha_1/3)(\epsilon_{\infty} + 2)/3}, \quad (4.5b)$$

where the Lorentz-Lorenz relationship

$$\frac{4\pi}{3} \alpha_{\infty} = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \quad (4.5c)$$

has been used. Thus, if local-field considerations are included, the nonlinear susceptibility is given by

$$\chi = \alpha_{\infty} f + \alpha_1 f + \alpha_2 f f^*. \quad (4.6)$$

Substituting  $\alpha_1$  and  $\alpha_2$  from Eq. (4.2) we obtain an expression similar to Eq. (4.3), the only difference being that the exciton frequency gets shifted to

$$\delta \rightarrow \delta - \frac{4\pi}{3} \frac{N}{V} \mu_1^2 \left[ \frac{\epsilon_{\infty} + 2}{3} \right].$$

Thus, as in the case of the linear susceptibility of polaritons,<sup>16</sup> inclusion of local-field effects for excitons *only*, simply produces a shift of the exciton frequency, an effect which cannot be measured independently.

By expanding  $\chi$  (or  $\alpha$ ) in powers of the incident electric field, we can verify that we obtain the standard expressions for the fully resonant terms in the different orders of the susceptibility. For example,

$$\chi^{(1)} = \frac{N\mu_1^2}{V} \frac{1}{\delta} \quad (4.7a)$$

is the one-photon absorption coefficient (or dispersion), while

$$\chi^{(3)} = \frac{N}{V} \mu_1^2 \mu_2^2 \left[ \frac{1}{\Delta\delta^2} + \frac{1}{\Delta\delta\delta^*} \right] \quad (4.7b)$$

corresponds to the sum of *all* fully resonant third-order terms, as, for example, diagrams  $D_1$  and  $(D_4 + D_{11} + D_{18})$  in Ref. 6. Alternatively, each order of the susceptibility could have been obtained by the standard diagrammatic techniques (limited to fully resonant terms) and the summation of the infinite series would have yielded<sup>3</sup> Eq. (4.3). From that point of view, Eq. (4.3) may be considered as representing the "renormalization" of the first-order susceptibility by the inclusion of higher-order processes involving many photons. Individual optical processes of different orders, however, cannot be distinguished experimentally in a one-beam experiment. Thus the conceptual distinction of different orders and the description of the nonlinear-optical response of the system in a perturbational language are not very meaningful: A one-beam experiment is described by a propagation equation for the electromagnetic field and thus the relevant quantity for such a treatment is the dielectric function in which all orders of the susceptibility are treated on the same footing. That is,

$$\epsilon = \epsilon_{\infty} + 4\pi\chi = \epsilon_{\infty} \left[ 1 + \frac{\omega_{\text{LT}} (\Delta\Delta^* \delta^* + 2i\Gamma |\mu_2 E|^2)}{|\Delta\delta - |\mu_2 E|^2|^2} \right], \quad (4.8)$$

where  $\epsilon_{\infty}$  is the background dielectric constant, while  $\omega_{\text{LT}} = 4\pi N \mu_1^2 / V \epsilon_{\infty}$  is the longitudinal-transverse polariton splitting. It is straightforward to verify that at low light intensities Eq. (4.8) gives the well-known polariton dispersion relationship in the rotating-wave approximation (RWA),

$$\epsilon = \epsilon_{\infty} \frac{\delta + \omega_{\text{LT}}}{\delta} = \epsilon_{\infty} \left[ \frac{\omega_{\text{L}} - \omega}{\omega_{\text{T}} - \omega} \right]. \quad (4.9)$$

It should be remembered that within the RWA the Lydane-Sachs-Teller relationship,

$$\omega_L = \omega_T \left( \frac{\epsilon_0}{\epsilon_\infty} \right)^{1/2} = \omega_T \left( 1 + 8\pi \frac{N}{V} \frac{\mu_1^2}{\epsilon_\infty \omega_T} \right)^{1/2} \quad (4.10a)$$

reduces to

$$\omega_L = \omega_T \left( 1 + 4\pi \frac{N}{V} \frac{\mu_1^2}{\epsilon_\infty \omega_T} \right), \quad (4.10b)$$

which is a good approximation as long as

$$\omega_{LT} \ll \omega_T, \quad (4.10c)$$

and thus justifies *a posteriori* the use of the RWA.

At high intensities, of course, the polariton dispersion relation is greatly modified, and effect which in the perturbational viewpoint is attributed to the renormalization of the susceptibility. Since our model neglects all exciton-exciton interactions other than biexciton formation, Eq. (4.8) can be expected to provide a good description of the renormalization and the dispersion modifications only in the vicinity of the two-photon biexciton resonance.

In the vicinity of that resonance, i.e., at  $\Delta \approx (\mu_2 E)^2 / \delta$ , the dielectric function diverges if there is no damping. This implies that the reflectivity experienced by a plane electromagnetic wave propagating in the direction perpendicular to the surface of the sample and given by

$$R = \left| \frac{\sqrt{\epsilon - 1}}{\sqrt{\epsilon + 1}} \right|^2 \quad (4.11)$$

becomes unity. This corresponds to a two-photon polariton effect since the electromagnetic waves cannot enter the crystal. The "forbidden" spectral region, however, is limited to a single point: the frequency for which  $\epsilon = \infty$ . This is in contrast to the well-known one-photon polariton effect in which light is totally reflected because the dielectric constant is *negative* over a relatively wide spectral frequencies. As the incident intensity increases the two-photon polariton divergence is displaced to lower frequencies while the dispersion relation around the divergence becomes less steep. Thus, as the intensity increases the effective gap of the two-photon polariton (i.e., the region in which the reflectivity is larger than a given value  $R_0$ ) widens. This effect is presented in Figs. 1 and 2. In all figures the following parameters of CuCl are used<sup>13,17</sup>:  $\epsilon_\infty = 4.1$ ,  $\omega_0 = 3.204$  eV,  $\Omega = 6.372$  eV,  $\omega_{LT} = 5.4$  meV, and  $\mu_2 = 1 \times 10^{-17}$  esu. The value for  $\mu_1$  is taken from Ref. 13. Since it is the product  $\mu_2 E$  that enters in all formulas, a different value of  $\mu_2$  would simply change the intensity scales.

The problem of the nonlinear dielectric function in an exciton-biexciton system has been examined also by other workers.<sup>7,8</sup> A detailed comparison of the assumptions and the severity of the approximations used in the different approaches is published elsewhere.<sup>18</sup> Here it suffices to point out the main difference in the results of our treatment compared to the theory of März *et al.*<sup>7</sup> In the vicin-

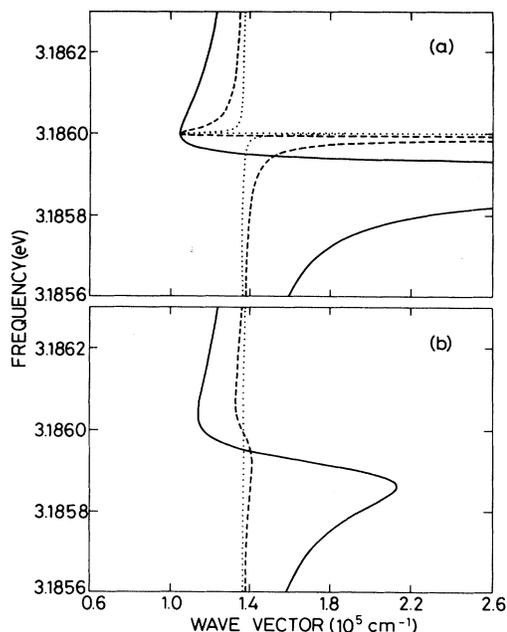


FIG. 1. Polariton dispersion in the vicinity of the two-photon biexciton absorption in CuCl (3.186 eV) at different incident intensities (a) with no damping and (b) with damping ( $\gamma = 0.05$  and  $\Gamma = 0.15$  meV). Solid line (—) is for 30 MW/cm<sup>2</sup>, dashed line (---) is for 3 MW/cm<sup>2</sup>, and dotted line (⋯) is for 0.3 MW/cm<sup>2</sup>.

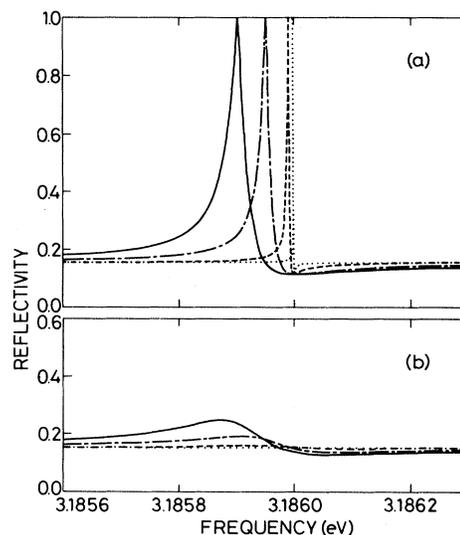


FIG. 2. Reflectivity of CuCl in the vicinity of the two-photon biexciton absorption (a) with no damping and (b) with damping ( $\gamma = 0.05$  and  $\Gamma = 0.15$  meV). Solid line (—) is for 30 MW/cm<sup>2</sup>, dashed-dotted line (---) is for 15 MW/cm<sup>2</sup>, dashed line (---) is for 3 MW/cm<sup>2</sup>, and dotted line (⋯) is for 0.3 MW/cm<sup>2</sup>.

ity of the two-photon biexciton resonance the März formula for the susceptibility can be written as

$$\chi = \frac{\epsilon_0 - \epsilon_\infty}{4\pi} \frac{\omega_0 \Delta / 2}{\Delta \delta - 2n_p M^2}, \quad (4.12)$$

where  $n_p$  is the polariton density, while  $M$  represents the exciton-biexciton-transition matrix element. For a given polariton density this equation corresponds to a dispersion curve which displays a polaritonlike gap (i.e., a region in which  $\epsilon < 0$ ) in the vicinity of the two-photon biexciton resonance.<sup>7,15</sup> This behavior is in contrast to that of our model in which  $\epsilon$  is always positive and diverges at only one point. This difference is due to the neglect of the direct biexciton contribution to the polarization in the derivation of Eq. (4.12): Our results reduce to the same equation if the biexciton contribution [Eq. (4.2b)] is not included in the calculation of the susceptibility.

If damping is included, the divergence of the dielectric function disappears, thus closing the effective gap of the two-photon polariton and smoothing out the sharp peak in reflectivity. This is shown in Figs. 1 and 2 for  $\gamma = 0.05$  meV and  $\Gamma = 0.15$  meV. These values, although probably not very accurate, were chosen so that they verify the relation  $2\gamma + \Gamma = 0.25$  meV found experimentally.<sup>13</sup> At the same time, a "two-photon" absorption towards the biexciton state occurs, with an intensity-dependent effective two-photon absorption coefficient given essentially by the imaginary part of the overall nonlinear susceptibility. As should be expected the imaginary part of the susceptibility in Eq. (4.3) is never negative, indicating that a single incident beam propagating through a nonlinear medium can only undergo absorption and is never amplified. Figure 3 presents the real and imaginary parts of the dielectric function of CuCl at different intensities. We note that the width of the absorption peak ( $\text{Im}\chi$ ) is essentially constant at all intensities and approximately equal to the biexciton damping constant. Its height and its position, however, vary linearly with intensity. The same is of course true for the effective dispersion relation ( $\text{Re}\chi$ ), which, at the same time, displays a marked asymmetry.

The spectral characteristics of the dispersive and absorptive parts of the susceptibility, however, are not directly accessible in an experiment on a macroscopic crystal. What is measured experimentally is the transmission of the sample which (in the nonlinear case) is not very simply related to the susceptibility. The transmission spectrum of a light beam propagating through a sample of finite thickness may be calculated by inserting the nonlinear dielectric function of Eq. (4.3) into the equation of propagation (2.11). If the dielectric function (which depends on the beam intensity) varies little along the propagation length, the propagation equation may be simplified to Eq. (2.13), which can be rewritten to yield directly the transmitted intensity  $I$ ,

$$\frac{dI}{dz} = -2 \frac{\omega}{c} I \text{Im}\sqrt{\epsilon(I)}. \quad (4.13)$$

The condition of validity (2.15) of the above equation may be rewritten in terms of the dielectric function as

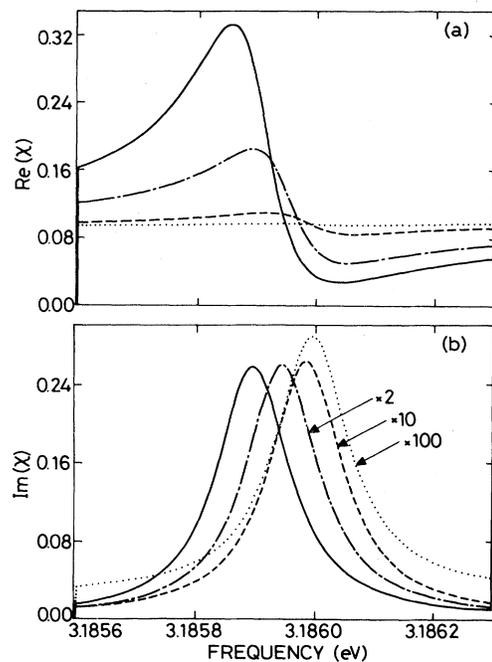


FIG. 3. (a) Real and (b) imaginary parts of the nonlinear-optical susceptibility of CuCl for damping constants  $\gamma = 0.05$  meV and  $\Gamma = 0.15$  meV. Solid line (—) is for 30 MW/cm<sup>2</sup>, dashed-dotted line (- · - · -) is for 15 MW/cm<sup>2</sup>, dashed line (---) is for 3 MW/cm<sup>2</sup>, and dotted line (· · ·) is for 0.3 MW/cm<sup>2</sup>.

$$I \left| \frac{d\epsilon}{dI} \frac{\text{Im}\sqrt{\epsilon}}{\epsilon^{3/2}} \right| \ll 1. \quad (4.14)$$

This equation is verified at all frequencies for CuCl with damping parameters of the order of 0.1 meV and intensities of up to a few tens of MW/cm<sup>2</sup>, thus justifying the use of the approximate propagation equations (2.13) and (4.13) under such conditions.

Figure 4 presents the calculated transmission spectrum observable by a tunable narrow-line laser passing through a 0.50- $\mu\text{m}$  film of CuCl obtained through the numerical solution of Eq. (4.13) at different frequencies. For incident intensities higher than  $\sim 50$  MW/cm<sup>2</sup>, the full propagation equation (2.11) should of course be used. We note that at all intensities this spectrum presents a dip at half the biexciton frequency, whose depth and width increase with intensity. At high intensities the dip becomes asymmetric, and its low-frequency side becomes less steep. The decrease of transmittance with increasing intensity can easily be related to the increase of the effective two-photon absorption coefficient (the imaginary part of the susceptibility) as shown in Fig. 3. However, the justification for the width and the asymmetry of the transmission spectrum is a little less obvious, since the imaginary part of the susceptibility displays a totally different behavior: Its width is essentially constant and its asymmetry barely perceivable while its peak undergoes a displacement towards lower frequencies, essentially proportional to the in-

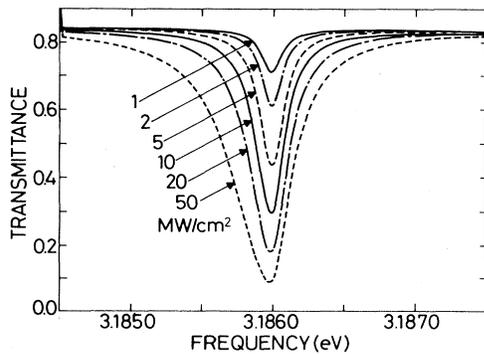


FIG. 4. Calculated transmission spectra of CuCl in the vicinity of the two-photon biexciton absorption. Intensities are given in  $\text{MW}/\text{cm}^2$ .

cident intensity. Part of the width of the transmission spectra of Fig. 4 is due to a trivial cause: The flattening out of the spectrum at low transmittances. The overall appearance of the transmission spectrum and its relationship to the imaginary part of the susceptibility may be understood if we consider that the absorption process is "chirped," that is, its peak frequency changes. For example, an incident beam of  $\sim 50 \text{ MW}/\text{cm}^2$  experiences an absorption spectrum centered  $\sim 0.15 \text{ meV}$  below  $\Omega/2$  (half the biexciton frequency). As the beam propagates in the material it gets attenuated due to (linear or two-photon) absorption. This attenuation causes the absorption maximum to shift to higher frequencies and brings about a depletion of a new spectral region of the beam and so on. In the limit of full attenuation of the beam the absorption maximum moves back to  $\Omega/2$ . The shift of the absorption peak therefore produces an apparent width to the transmission, an asymmetry towards the low-frequency side of  $\Omega/2$ , and a transmission at  $\Omega/2$  for sufficiently long propagation distances.

It is possible, thus, that the intensity-dependent absorption width of the two-photon biexciton resonance, observed experimentally and attributed to biexciton density and collisional effects,<sup>4</sup> may be due, at least in part, to the interplay of propagation, intensity attenuation, and the chirping of the absorption peak.

## V. SUMMARY AND CONCLUSIONS

The optical behavior of interacting excitons cannot be treated successfully through the perturbational formulation of nonlinear optics as the large oscillator strengths involved and the near-resonance conditions cause the perturbational series to diverge. The interpretation of optical experiments on biexcitons, therefore, through the traditional perturbational framework of nonlinear optics, has led to dubious conclusions.

In order to account for the optical properties of excitons and biexcitons in a semiconductor such as CuCl without recourse to the perturbational methods of nonlinear optics, we have adopted a model which is based on a quantum-mechanical description of excitons and biexcitons as bosons and a classical description of the light field. This permits us to express the Hamiltonian as a quadratic form

of Bose operators which can easily be diagonalized through a unitary transformation. The unitary transformation is then used to calculate the induced polarization and the nonlinear susceptibility relevant to the experimental observation. This nonperturbational method automatically enumerates all  $n$ th-order processes through the algebraic properties of the Bose creation and annihilation operators. It can easily be generalized to account for the nonlinear-optical response relevant to multibeam experiments.

The nonlinear susceptibility thus obtained can account for the observations of one-beam experiments through the Maxwell equations. If damping is not included, the dielectric function obtainable from the nonlinear susceptibility gives directly the renormalization of the polariton dispersion curve in the vicinity of the two-photon biexciton resonance. This renormalization is manifested by the divergence of the dispersion relation at one only point which is at half the biexciton frequency for low intensities but gets displaced to lower frequencies as the incident intensity increases. The opening of a polaritonlike gap associated to the renormalization of the dispersion, found by other authors, can be obtained only if the direct biexciton contribution to the susceptibility is neglected.

Inclusion of damping removes the two-photon divergence of the renormalized polariton dispersion relation and introduces an imaginary part to the linear susceptibility which corresponds to an effective two-photon absorption coefficient. This absorption coefficient presents a sharp resonance at the same frequency as the divergence of the renormalized polariton dispersion relation. With increasing intensity, thus, its peak shifts to lower frequencies while its width remains constant.

The intensity-dependent transmission spectrum corresponding to this two-photon absorption coefficient, however, exhibits a different behavior. For crystals of finite thickness, its peak is located at half the biexciton frequency (independent of intensity), while its width and asymmetry increase with increasing intensity. The appearance of the transmission spectrum is due to the fact that the absorption of a propagating beam is chirped, since the absorption maximum experienced by a light beam depends on the beam intensity. Thus attenuation of the beam due to absorption implies that the absorption spectrum seen by the beam shifts to higher frequencies as the beam propagates in the medium. This gives an apparent width and an asymmetry to the transmission spectrum. Strictly speaking, our results are applicable only to one-beam experiments. We may however, expect that similar conclusions are valid also in multibeam experiments if allowance is made for modifications due to multibeam effects, such as induced absorption or four-wave mixing.

The intensity-dependent width observed experimentally for the two-photon biexciton transition has been attributed to collisional broadening brought about by the intensity-dependent density of the biexciton gas. This mechanism was postulated to account for the unconventional behavior of the third-order susceptibility  $\chi^{(3)}$  obtained in the interpretation of these experiments within the traditional perturbational formulation of nonlinear optics. The results obtained from the nonperturbational treatment of non-

linear susceptibility and of propagation, however, suggest that the chirped nature of absorption of a propagating beam may account, at least in part, for the intensity-dependent width observed in the biexciton absorption spectrum.

#### ACKNOWLEDGMENTS

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#### APPENDIX: DIAGONALIZATION OF THE HAMILTONIAN

The rotating-frame Hamiltonian of Eq. (3.5),

$$\tilde{H} = \sum_q \delta(q) b_q^\dagger b_q + \sum_Q \Delta(Q) B_Q^\dagger B_Q - \sqrt{N} \mu_1 (E b_k^\dagger + E^* b_k) - \mu_2 \sum_q (E' B_{q+k}^\dagger b_q + E'^* B_{q+k} b_q^\dagger), \quad (\text{A1})$$

may be diagonalized through the successive application of two unitary transformations: a translation and a rotation, as in Eq. (3.7). Application of the translation adds a displacements to each operator as in Eqs. (3.8b) so that the transformed Hamiltonian reads

$$e^{-S_1} \tilde{H} e^{S_1} = \sum_q \delta(q) (b_q^\dagger + x_q)(b_q + x_q) + \sum_Q \Delta(Q) (B_Q^\dagger + y_Q)(B_Q + y_Q) - \sqrt{N} \mu_1 [E(b_k^\dagger + x_k^*) + E^*(b_k + x_k)] - \mu_2 \sum_q [E'(B_{q+k}^\dagger + y_{q+k}^*)(b_q + x_q) + E'^*(B_{q+k} + y_{q+k})(b_q^\dagger + x_q^*)]. \quad (\text{A2})$$

Collecting terms, we note that the coefficients of  $b^\dagger$  and  $B^\dagger$  vanish, respectively, when

$$\delta(q)x_q - \sqrt{N} \mu_1 E \delta_{kq} - \mu_2 E'^* y_{q+k} = 0 \quad (\text{A3a})$$

and

$$\Delta(q+k)y_{q+k} - \mu_2 E' x_q = 0, \quad (\text{A3b})$$

where  $\delta_{kq}$  is the Kronecker  $\delta$  symbol. Similar expressions [the complex conjugates of Eqs. (A3)] are obtained for the coefficients of the corresponding annihilation operators.

For  $q=k$ , the solution of the system of two linear equations (A3) is

$$x_k = \sqrt{N} \frac{(\mu_1 E) \Delta(2k)}{\Delta(2k) \delta(k) - |\mu_2 E'|^2}, \quad (\text{A4a})$$

$$y_{2k} = \sqrt{N} \frac{(\mu_1 E)(\mu_2 E')}{\Delta(2k) \delta(k) - |\mu_2 E'|^2}, \quad (\text{A4b})$$

while for  $q \neq k$  and  $Q \neq 2k$  we obtain

$$x_q = 0, \quad (\text{A4c})$$

$$y_Q = 0. \quad (\text{A4d})$$

It is thus for these values that the translational transformation diagonalizes away the linear terms of the Hamiltonian. The partially diagonalized Hamiltonian is given in Eq. (3.10) and can be written as

$$e^{-S_1} \tilde{H} e^{S_1} = \sum_q \tilde{\tilde{H}}_q, \quad (\text{A5a})$$

where

$$\tilde{\tilde{H}}_q = \delta(q) b_q^\dagger b_q + \Delta(q+k) B_{q+k}^\dagger B_{q+k} - \mu_2 (E' B_{q+k}^\dagger b_q + E'^* B_{q+k} b_q^\dagger). \quad (\text{A5b})$$

When applying the rotational transformation (3.11) we have

$$e^{-S_2(q)} \tilde{\tilde{H}}_q e^{S_2(q)} = \delta(q) (c b_q^\dagger + s^* B_{q+k}^\dagger)(c b_q + s B_{q+k}) + \Delta(q+k) (c B_{q+k}^\dagger - s b_q^\dagger)(c B_q - s^* b_{q+k}) - \mu_2 [E'(c B_{q+k} - s b_q)(c b_q^\dagger + s B_{q+k}^\dagger) + E'^*(c B_{q+k} - s^* b_q)(c b_q^\dagger + s^* B_{q+k}^\dagger)], \quad (\text{A6})$$

where

$$c = \cos |\theta_q|,$$

$$s = (\theta_q / |\theta_q|) \sin |\theta_q|$$

for brevity. Collecting terms in Eq. (A6) we obtain, for the coefficient of  $Bb^\dagger$ ,

$$[\delta(q) - \Delta(q+k)]cs + \mu_2(E's^2 - E'^*c^2), \quad (\text{A7})$$

and its complex conjugate for the coefficient of  $B^\dagger b$ . Clearly, these coefficients vanish for

$$\theta_q = \frac{1}{2} \frac{E'^*}{|E'|} \arctan \frac{2|\mu_2 E'|}{\delta(q) - \Delta(q+k)}, \quad (\text{A8})$$

and thus the Hamiltonian (A5b) is diagonalized for this value of  $\theta_q$ . The overall Hamiltonian, after application of the translational and rotational transformations, is given by Eq. (3.14).

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