Cancellation of size-linear terms in the third-order nonlinear susceptibility: Frenkel excitons in a periodic chain

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For a system of noninteracting Frenkel excitons in a one-dimensional lattice of size N with periodic boundary conditions, the third-order optical susceptibility $\chi^{(3)}$ has been calculated rigorously in a nonlocal form with arbitrary dependence on external-field frequencies. Among the various terms in $\chi^{(3)}$ (per unit volume), those explicitly proportional to N in the long-wavelength approximation have been shown to cancel out completely for arbitrary N. The remaining terms, including the effect of nonlocality, reduce to the well-known result of a two-level system in the limit of vanishing transfer energy. There remain N-dependent factors in $\chi^{(3)}$, with different functional forms for even and odd N, but they all approach unity in the limit of large N.

I. INTRODUCTION

There has recently been a great deal of interest in the nonlinear optical properties of confined systems of excitons, because they apparently show an explicit size-enhancement effect,[1,2] which would be attractive from an applicational, as well as a fundamental, point of view. The effect is related to the coherent extension of exciton wave functions, treated in the long-wavelength approximation (LWA), where one neglects the position dependence of the electric fields and the polarization in calculating $\chi^{(3)}$. It is claimed that there occurs a factor of system size in the expression of $\chi^{(3)}$ per unit volume. One cannot of course extrapolate the effect to bulk systems. Usually the growth of $\chi^{(3)}$ in proportion to system size is supposed to be suppressed, either by the breakdown of the LWA, or by the existence of the so-called coherent length, which limits the coherent extension of the wave function of excited states, due to the various scattering mechanisms in samples.

A question arises as to the validity of the explicit size-enhancement effect mentioned above: Though one can expect some size-dependent effects for small systems, the appearance of system size as a multiplicative factor is rather strange. The answer to this question seems to be closely connected to the presence of strange terms in the standard expression of susceptibility based on the perturbation expansion of density matrix. They are strange, or unphysical, in the sense that their contribution to the third-order nonlinear polarization at site j, affected by three electric fields at site l, m, and n, depends on one of them (say l) in a normal way, but on the other two (m and n) through their mere presence, without specific dependence on the relative positions between j and (m,n). Such a site dependence is certainly unphysical, and if one treats the system in LWA, these terms can be shown to give an explicit size dependence. Since unphysical terms should make no contribution to the final result of $\chi^{(3)}$, they are expected to vanish somehow. Actually, it has been demonstrated that they cancel one another in certain limited situations by Banyai *et al.*[3] and Spano and Mukamel.[4] Though their results agree with our expectation, the conditions they used for the proof are too restricted: noninteracting bosons and LWA in the former and the complete off-resonance condition and LWA in the latter. The purpose of the present work is to show the cancellation in a more general situation. Namely, for a system of noninteracting Frenkel excitons (i.e., nonideal bosons) in a periodic one-dimensional chain, the cancellation is demonstrated for the nonlocal expression of $\chi^{(3)}$, i.e., without the use of LWA, and for arbitrary frequencies of external fields. This result encourages us to expect the occurrence of the cancellation in general: Since the unphysical nature of the above-mentioned terms does not change in more general situations, including the case of Wannier excitons, exciton-exciton interaction, the effect of higher dimension, and relaxation effects, they should be canceled out. The form of $\chi^{(3)}$ after the cancellation does not include the system size N as a multiplicative factor. But it contains N-dependent factors which tend to become unity for large N. This means that there can be some size-dependent effects for small systems.

The rest of this paper is organized as follows. In Sec. II, the form of $\chi^{(3)}$ in site representation is introduced, and a discussion is given about the unphysical nature of certain terms. The cancellation of the unphysical terms is shown for a local, two-level system in Sec. III, and for a noninteracting Frenkel exciton on a linear periodic chain in Sec. IV. In Sec. V discussions are given, including comments to related works.

II. THIRD-ORDER NONLINEAR SUSCEPTIBILITY IN THE SITE REPRESENTATION

We start with a standard expression of the third-order nonlinear polarization at site j and time t:

$$P_j^{(3)}(t)=\frac{(-i)^3}{V_0}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\langle[[[P_j(t),H'(t_1)],H'(t_2)],H'(t_3)]\rangle\ , \tag{2.1}$$

where the angular brackets mean a statistical average, V_0 is the volume of a unit cell, $\hbar$ is taken to be unity, $P(t)$ and $H'(t)$ are the interaction representations of the polarization operator and electron-radiation interaction, respectively,

$$P_j(t)=\exp(iH_0t)P_j\exp(-iH_0t)\ , \tag{2.2}$$

$$H'(t)=\exp(iH_0t)\left[-\sum_n\sum_s P_nF_n(s)\exp(-i\omega_st+\gamma t)\right]\exp(-iH_0t)\ , \tag{2.3}$$

H_0 being the unperturbed Hamiltonian, $\gamma=0^+$ the factor for adiabatic switching of the electron-radiation interaction, and $F_n(s)$ the amplitude of the electric field at site n with frequency ω_s.

The commutators in (2.1) give eight terms, four of which are denoted as

$$\begin{aligned}A_1&=\langle P_j(t)H'(t_1)H'(t_2)H'(t_3)\rangle\ ,\\ A_2&=\langle H'(t_3)H'(t_1)P_j(t)H'(t_2)\rangle\ ,\\ A_3&=\langle H'(t_3)H'(t_2)P_j(t)H'(t_1)\rangle\ ,\\ A_4&=\langle H'(t_2)H'(t_1)P_j(t)H'(t_3)\rangle\ .\end{aligned} \tag{2.4}$$

Each of the remaining four terms, denoted as B_i $(i=1,2,3,4)$, has a reversed order of operators of that in A_i and is multiplied by -1. Expression (2.1) can be rewritten as

$$P_j^{(3)}(t)=\sum_l\sum_m\sum_n\sum_p\sum_q\sum_s\exp[-i(\omega_p+\omega_q+\omega_s+3i\gamma)t]F_l(p)F_m(q)F_n(s)G_{jlmn}(\omega_p,\omega_q,\omega_s)\ . \tag{2.5}$$

The function G is merely $\chi^{(3)}$ in site representation, and consists of a sum of eight terms arising from (A_i,B_i). In order to save space, we now show only two typical terms out of eight:

$$A_2:\ (1/V_0)\sum_\lambda\sum_\mu\sum_\nu\frac{\langle 0|P_n|\lambda\rangle\langle\lambda|P_l|\mu\rangle\langle\mu|P_j|\nu\rangle\langle\nu|P_m|0\rangle}{(E_{\nu\mu}-\Omega_3')(E_{\nu\lambda}-\Omega_2')(E_{0\lambda}-\omega_s')}\ , \tag{2.6}$$

$$B_2:\ (1/V_0)\sum_\lambda\sum_\mu\sum_\nu\frac{\langle 0|P_m|\nu\rangle\langle\nu|P_j|\mu\rangle\langle\mu|P_l|\lambda\rangle\langle\lambda|P_n|0\rangle}{(E_{\nu\mu}+\Omega_3')(E_{\nu\lambda}+\Omega_2')(E_{0\lambda}+\omega_s')}\ . \tag{2.7}$$

In these expressions we assume $T=0$ K, and

$$H_0|\xi\rangle=E_\xi|\xi\rangle\quad(\xi=0,\lambda,\mu,\nu)\ , \tag{2.8}$$

$$E_{\xi\eta}=E_\xi-E_\eta\ , \tag{2.9}$$

$$\Omega_3'=\omega_p+\omega_q+\omega_s+3i\gamma\ , \tag{2.10}$$

$$\Omega_2'=\omega_q+\omega_s+2i\gamma\ , \tag{2.11}$$

$$\omega_s'=\omega_s+i\gamma\ . \tag{2.12}$$

At this stage, one might notice that each of the expressions (2.6) and (2.7) contains problematic terms: Consider the terms in (2.6), for example, with the second intermediate state $|\mu\rangle$ being $|0\rangle$. Such terms give rise to particular site correlations between n and l (j and m) through the form of the wave function $|\lambda\rangle$ ($|\nu\rangle$), but no correlation between the two groups (n,l) and (j,m), except for the site-independent weighting factor $1/(E_{\nu\lambda}-\Omega_2')$. This means that $P_j^{(3)}$ is affected by F_n and F_l through their presence alone (even at a very remote position), which is quite an unphysical situation. This is found in all of (A_i,B_i). If one treats the response in LWA, that is, if one neglects the site dependence of the field amplitudes F in (2.5), each of these unphysical terms leads to an explicitly size-dependent factor: Since the center-of-mass position of the set of coordinates (n,l) can take all the sites (N) in the system independently from that of (j,m), the summations over site indices in (2.5) lead to the factor N.

In the simplest case of noninteracting boson system, it is rather well known that all the contributions cancel out, leading to the absence of nonlinear effects in such a system. On the other hand, in the case of a local two-, three-, or any level system, a commonly used expression of $\chi^{(3)}$ is one that resembles (2.5) with the restriction $j=l=m=n$, namely, none of the unphysical terms inherent to each of the A_i and B_i contribute to the final expression of $\chi^{(3)}$. This will be shown explicitly in the next section.

III. A LOCAL TWO-LEVEL SYSTEM

This system consists of an assembly of noninteracting atoms, each of which has only one excited state. Then, the excited states of the system are specified by the positions of excited atoms. The one- and two-atom excited states, necessary for the calculation of $\chi^{(3)}$ at $T=0$ K, are denoted as $|l\rangle$ and $|l,m\rangle$ respectively, where l and m indicate the positions of the excited atoms. One should note that $|l,m\rangle=|m,l\rangle$ in the following calculations. The exclusion principle forbids the state $|l,l\rangle$ for any l. The states with more excited atoms are required only for the calculation of higher-order susceptibilities than $\chi^{(3)}$. For the subspace of one- and two-atom excited states, the Hamiltonian and polarization operator are given as

$$H_0=\sum_l E_1|l\rangle\langle l|+\sum_{l>m}\sum 2E_1|l,m\rangle\langle l,m|\ , \tag{3.1}$$

$$P_l=M|0\rangle\langle l|+\sum_{m\ (\neq l)}M|m\rangle\langle l,m|+\text{H.c.}\ , \tag{3.2}$$

where E_1 is the excitation energy of each atom and M the corresponding transition dipole moment. From these definitions, we can explicitly calculate expressions such as (2.6) and (2.7), where we find a large amount of cancellation among the terms with $|\mu\rangle=|0\rangle$ and the terms with $|\mu\rangle=$two-atom excited states, where $|\mu\rangle$ is the second intermediate state in expressions such as (2.6) or (2.7). If we denote the contributions from $|\mu\rangle=|0\rangle$ and two-atom excited states as $[A_i(0),B_i(0)]$ and $[A_i(2),B_i(2)]$, respectively, the cancellation occurs in each of the following six sets:

$$A_1(2)+B_3(2)\ , \tag{3.3a}$$

$$B_1(2)+A_3(2)\ , \tag{3.3b}$$

$$A_2(2)+B_1(0)+B_4(0)\ , \tag{3.3c}$$

$$B_2(2)+A_1(0)+A_4(0)\ , \tag{3.3d}$$

$$A_4(2)+B_2(0)+B_3(0)\ , \tag{3.3e}$$

$$B_4(2)+A_2(0)+A_3(0)\ . \tag{3.3f}$$

The first two groups [(3.3a) and (3.3b)] having energy denominators

$$(E_1-\Omega_3')(2E_1-\Omega_2')(E_1-\omega_s')\ , \tag{3.4a}$$

$$(E_1+\Omega_3')(2E_1+\Omega_2')(E_1+\omega_s')\ , \tag{3.4b}$$

respectively, vanish completely due to the mutual cancellation within each group. The remaining four groups have contributions (in units of M^4/V_0) as

$$[(-\delta_{jl}\delta_{mn}-\delta_{jn}\delta_{lm})+\delta_{jl}\delta_{mn}+\delta_{jn}\delta_{lm}]/(E_1+\Omega_3')\Omega_2'(E_1+\omega_s')\ , \tag{3.4c}$$

$$[(\delta_{jl}\delta_{mn}+\delta_{jn}\delta_{lm})-\delta_{jl}\delta_{mn}-\delta_{jn}\delta_{lm}]/(E_1-\Omega_3')\Omega_2'(E_1-\omega_s')\ , \tag{3.4d}$$

$$[(\delta_{jl}\delta_{mn}+\delta_{jm}\delta_{ln})-\delta_{jm}\delta_{ln}-\delta_{jl}\delta_{mn}]/(E_1+\Omega_3')\Omega_2'(E_1-\omega_s')\ , \tag{3.4e}$$

$$[(-\delta_{jl}\delta_{mn}-\delta_{jm}\delta_{ln})+\delta_{jm}\delta_{ln}+\delta_{jl}\delta_{mn}]/(E_1-\Omega_3')\Omega_2'(E_1+\omega_s')\ . \tag{3.4f}$$

The Kronecker δ's in the parentheses originate from the $|\mu\rangle=$two-atom excited states and, therefore, the case $j=l=m=n$ should be avoided, i.e., two-particle state at one site is forbidden as $|\mu\rangle$. The other Kronecker δ's in (3.4) arise from $|\mu\rangle=|0\rangle$ and, therefore, the case $j=l=m=n$ can be included. Hence, the only terms escaping the cancellation in each of the above expressions are those with $j=l=m=n$. This result is merely the usual expression of $\chi^{(3)}$ for a two-level system. This argument applies, not only to a two-level system, but also to any-level (local) systems.

IV. NONINTERACTING FRENKEL EXCITONS ON A PERIODIC CHAIN

In the case of a nonlocal system where the wave functions of all the intermediate states are extended and the eigenvalues form bands for one- and two-particle excited states, it is not so simple to show how the cancellation works. As a model system which allows us an exact treatment, we take a one-dimensional, noninteracting Frenkel exciton with periodic boundary condition.

Using the definition of one- and two-atom excited states $|l\rangle$ and $|l,m\rangle$ in Sec. III, we define H_0 and P, within the subspace contributing to $\chi^{(3)}$ at 0 K, as

$$H_0=\varepsilon_0\sum_l |l)(l|-b\sum_{l\neq m}{}'\sum_{l\neq m}{}' |l)(m|+2\varepsilon_0\sum_{l>m}\sum |l,m)(l,m| -b\sum_{n\ (\neq l,m)}\ \sum_{l\neq m}{}'\sum_{l\neq m}{}' |l,n)(m,n|\ , \tag{4.1}$$

$$P_l=M|0)(l|+M\sum_{m\ (\neq l)}|m)(l,m|+\text{H.c.} \tag{4.2}$$

The summation $\sum'\sum'$ in (4.1) is limited to the nearest neighbors. Here again, the states $\{|l,l)\}$ are forbidden due to the Pauli exclusion principle. The periodic condition is expressed as

$$|l+N)=|l),\quad |l+N,m)=|l,m+N)=|l,m)\ . \tag{4.3}$$

Then, the energy and wave function of the one-exciton eigenstates, $|\lambda\rangle$ and $|\nu\rangle$ in (2.6) and (2.7), are

$$E_1(k)=\varepsilon_0-2b\cos k\ , \tag{4.4}$$

$$|k\rangle=(1/\sqrt{N})\sum_l \exp(ikl)|l)\ , \tag{4.5}$$

respectively, where the lattice constant is taken as the unit of length. The two-particle eigenstate, $|\mu\rangle$ in (2.6) and (2.7), is determined by the condition that two excitons cannot stay at a single site but otherwise are free and noninteracting, as

$$|K,\kappa\rangle=(2/N)\sum_{l>m}\sum \exp[iK(l+m)]\sin(\kappa|l-m|)|l,m)\ . \tag{4.6}$$

The eigenvalue of the two-exciton state, (4.6), is

$$E_2(K,\kappa)=E_1(K+\kappa)+E_1(K-\kappa)\ . \tag{4.7}$$

The requirement of periodic boundary condition to the wave functions (4.5) and (4.6) leads to the allowed values of k, K, and κ as

$$(k,K,\kappa)=(2n,2\bar{m},2m'-1)\pi/N\ , \quad \{n,\bar{m}=1,2,\ldots,N;m'=1,2,\ldots,(N-1)/2\}\ . \tag{4.8}$$

The quantization conditions for K and κ apply to the case of odd N. The following calculation is done for this case. The necessary alterations for the case of even N are given in the Appendix. The dipole matrix elements are given as

$$\langle k|P_l|0\rangle=M\exp(-ikl)/\sqrt{N}\ , \tag{4.9}$$

$$\langle K,\kappa|P_l|k\rangle=M(2/\sqrt{N}^{\,3})\sin\kappa\, e^{-i(2K-k)l}/[\cos(k-K)-\cos\kappa]\ , \tag{4.10}$$

In terms of the energy eigenvalues (4.4) and (4.7) and the dipole matrix elements (4.9) and (4.10), we can write down all the terms (A_i, B_i) in the expression of $\chi^{(3)}$. As in the local case, there occurs a large amount of cancellation among various terms. The combination of the cancelling terms is the same as (3.3). We show the case of $B_4(2)+A_3(0)+A_2(0)$ explicitly:

$$B_4(2):\ \sum_k \sum_{k'} \sum_K \sum_\kappa \frac{\langle 0|P_n|k'\rangle\langle k'|P_j|K\kappa\rangle\langle K\kappa|P_l|k\rangle\langle k|P_m|0\rangle}{[E_{k'(K\kappa)}+\Omega_3'](E_{k'k}+\Omega_2')[E_1(k')+\omega_s']}\ , \tag{4.11}$$

$$A_3(0):\ \sum_k \sum_{k'} \frac{\langle 0|P_n|k\rangle\langle k|P_m|0\rangle\langle 0|P_j|k'\rangle\langle k'|P_l|0\rangle}{[E_1(k')-\Omega_3']\Omega_2'[E_1(k)+\omega_s']}\ , \tag{4.12}$$

$$A_2(0):\ \sum_k \sum_{k'} \frac{\langle 0|P_n|k\rangle\langle k|P_l|0\rangle\langle 0|P_j|k'\rangle\langle k'|P_m|0\rangle}{[E_1(k')-\Omega_3'](E_{kk'}+\Omega_2')[E_1(k)+\omega_s']}\ , \tag{4.13}$$

where

$$E_{k'(K\kappa)}=E_1(k')-E_2(K,\kappa)\ , \tag{4.14}$$

$$E_{kk'}=E_1(k)-E_1(k')\ . \tag{4.15}$$

The κ summation in (4.11) has the form

$$\sum_\kappa \frac{\sin^2\kappa}{(\Omega_3'-\varepsilon_0+4b\cos K\cos\kappa-2b\cos k')[\cos(k-K)-\cos\kappa][\cos(k'-K)-\cos\kappa]} \tag{4.16}$$

and can be evaluated by an integral in the complex κ plane. Depending on the conditions (a) $k=k'$, (b) $k-K=K-k'$, and (c) otherwise, the last two factors in the denominator do [(a),(b)] or do not [(c)] contribute as poles to the contour integral. Exact evaluation shows that the contributions from (a) and (b) just cancel the terms $A_3(0)$ and $A_2(0)$, respectively, and the remaining term, arising from the pole due to the first factor in the denominator of (4.16), is given as

$$\frac{2M^4}{N^3}\sum_k \sum_{k'} \sum_K \frac{S(k,k',K)e^{ikn}e^{i(2K-k)j}e^{-i(2K-k')l}e^{-ik'm}}{(\Omega_2'-E_{k'k})[\omega_s'+E_1(k)]}\bar{A}(K,k,\Omega_3')\ , \tag{4.17}$$

where

$$S(k,k',K)=\frac{[(\varepsilon_0+2b\cos k-\Omega_3')^2-16b^2\cos^2K]^{1/2}}{[\Omega_3'-E_1(2K-k)][\Omega_3'-E_1(2K-k')-E_{k'k}]}\ . \tag{4.18}$$

In the last expression, the branch of the square-root term is chosen so that, in the limit of $b\to 0$, it reduces to $\varepsilon_0-\Omega_3'$. This choice leads us automatically to the correct expression of the local $\chi^{(3)}$ in the limit of $b\to 0$. The factor $\bar{A}(K,k,\Omega_3')$ in (4.17) is defined as

$$\bar{A}(K,k,\Omega_3')=-i\,\mathrm{sgn}(\bar{b})\tan[N(\bar{a}+i\bar{b})/2]\ , \tag{4.19}$$

where

$$\bar{a}+i\bar{b}=\cos^{-1}[(\varepsilon_0+2b\cos k-\Omega_3')/4b\cos K]\quad(\bar{a}>0)\ . \tag{4.20}$$

The other contributions to $\chi^{(3)}$ can be calculated in a similar way: $B_2(2)$ gives rise to the terms cancelling $A_1(0)$ and $A_4(0)$, and the remainder is

$$\frac{2M^4}{N^3}\sum_k \sum_{k'} \sum_K \frac{S(k,k',K)e^{ikm}e^{i(2K-k)j}e^{-i(2K-k')l}e^{-ik'n}}{(\Omega_2'-E_{k'k})[\omega_s'-E_1(k')]}\bar{A}(K,k,\Omega_3')\ . \tag{4.21}$$

$A_1(2)+B_3(2)$ cancels out completely in the case of local two-level system ($b=0$), but, in the presence of energy transfer, the following terms remain:

$$\frac{2M^4}{N^3}\sum_k \sum_{k'} \sum_K \left[-\frac{T(k,k',K)e^{ikj}e^{i(2K-k)l}e^{-i(2K-k')m}e^{-ik'n}}{[\Omega_3'-E_1(k)][\omega_s'-E_1(k')]}\bar{B}(K,\Omega_2') \right.$$
$$-\frac{S(k,k',K)e^{ikl}e^{i(2K-k)j}e^{-i(2K-k')m}e^{-ik'n}}{[\Omega_3'-\Omega_2'+E_1(k)][\omega_s'-E_1(k')]}\bar{A}(K,k,\Omega_3')$$
$$\left.+\frac{T(k,k',K)e^{ikl}e^{i(2K-k)j}e^{-i(2K-k')m}e^{-ik'n}}{[\Omega_3'-\Omega_2'+E_1(k)][\omega_s'-E_1(k')]}\bar{B}(K,\Omega_2') \right]\ , \tag{4.22}$$

where

$$T(k,k',K)=\frac{[(2\varepsilon_0-\Omega_2')^2-16b^2\cos^2K]^{1/2}}{[\Omega_2'-E_2(2K-k,k)][\Omega_2'-E_2(2K-k',k')]}\ , \tag{4.23}$$

$$\bar{B}(K,\Omega_2')=-i\,\mathrm{sgn}(\bar{d})\tan[N(\bar{c}+i\bar{d})/2]\ , \tag{4.24}$$

$$\bar{c}+i\bar{d}=\cos^{-1}[(2\varepsilon_0-\Omega_2')/4b\cos K]\quad(\bar{c}>0)\ . \tag{4.25}$$

The contributions from $[A_4(2)+B_3(0)+B_2(0)]$, $[A_2(2)+B_1(0)+B_4(0)]$, and $[B_1(2)+A_3(2)]$ can be obtained from (4.17), (4.21), and (4.22), respectively, by the following replacement: $(K,k,k',\Omega_3',\Omega_2',\omega_s')$ $\rightarrow(-K,-k',-k,-\Omega_3',-\Omega_2',-\omega_s')$. The sum of all these terms is the function $G_{jlmn}(\omega_p,\omega_q,\omega_s)$ in (2.5), namely $\chi^{(3)}$ in site representation for this model system.

The above result is obtained in the absence of damping effect. The only source of the imaginary parts of $\chi^{(3)}$ is the factor γ $(=0^+)$ arising from the adiabatic switching of the electron-radiation interaction. In realistic systems, one must always consider the effect of damping. The simplest way to introduce a damping effect is to regard γ as a positive finite quantity instead of 0^+. In general, one must consider the coupling of each electronic state with heat bath, and derive a self-energy correction to each factor of the denominators of $\chi^{(3)}$. This recipe might be necessary for a detailed discussion of damping effect, but here we will skip all the details and consider the damping through a single parameter γ. Then, the imaginary parts $\bar{b}$ and $\bar{d}$ become finite, and (4.19) and (4.24) lead to

$$\bar{A},\bar{B}\rightarrow 1\quad(N\rightarrow\infty)\ . \tag{4.26}$$

This completes our demonstration that the $\chi^{(3)}$ of this model does not contain N as a multiplicative factor.

V. DISCUSSIONS

In the preceding sections, we have shown that all the unphysical parts in $A_i(0)$ and $B_i(0)$ $(i=1,2,3,4)$ are canceled out by the corresponding parts in $A_i(2)$ and $B_i(2)$. The remarkable points in our demonstration of the cancellation are that we have made no assumption about the resonance or off-resonance conditions of the source field frequencies, and that the argument is made in the nonlocal form of $\chi^{(3)}$ without using LWA, i.e., in a form applicable to any sample size (N). Though we have used a particular model for the explicit calculation, we can expect this type of cancellation also in most other systems from the unphysical nature of the canceled terms and from the general character of our demonstration. Since our $\chi^{(3)}$ is expressed only in terms of the quantities per unit volume, its magnitude does not diverge in the limit of $N\rightarrow\infty$. Therefore, it is not necessary to introduce such a concept as coherent region[5] to avoid the divergence.

An important factor missing in our treatment is the interaction between excitons, $H_{\text{ex-ex}}$, in the two-particle states. But we did include the Pauli exclusion effect, which eliminates N degrees of freedom from the $N(N+1)/2$ for the free two-particle states. Because of this, the cancellation becomes incomplete, and we obtain the remaining terms which agree, in the limit of zero transfer effect, with those of the well-known case of the two-level system. In the presence of $H_{\text{ex-ex}}$, the energy scheme and the wave functions of the two-exciton states are different from those in its absence. However, in view of the unphysical nature of all the $[A_i(0),B_i(0)]$ as discussed in the preceding section, we believe that they are all canceled out by a part of $[A_i(2),B_i(2)]$ even in the presence of $H_{\text{ex-ex}}$. The remaining part of $\sum_i[A_i(2)+B_i(2)]$ is different from that in the absence of $H_{\text{ex-ex}}$. The poles in the expressions (4.17), (4.21), and (4.22) form bands of eigenvalues in different energy regions for different frequency components: for ω_s', ω_p' $(=\Omega_3'-\Omega_2')$ and Ω_3' in the region of the one-exciton energy, and for $\Omega_2'(=\omega_q+\omega_s)$ in the region of the sum and difference of the two one-exciton energies [$E_{kk'}$ or $E_2(2K-k,k)$, etc.]. The factor $\bar{A}$ $(\bar{B})$ has poles, as a function of Ω_3' (Ω_2'), at the energies $E_2(K,\kappa)-E_1(k)$ $[E_2(K,\kappa)]$. In the presence of $H_{\text{ex-ex}}$, there can be poles isolated from these bands, especially those for the excitonic molecule states. Therefore, $H_{\text{ex-ex}}$ will redistribute the poles of (4.17), (4.21), and (4.22) in such a way that, in addition to the above-mentioned bands, there are isolated poles of excitonic molecules. How this redistribution should occur depends, of course, on the microscopic model of the system, and should be worked out in the near future.

The existence of the cancellation also in the presence of $H_{\text{ex-ex}}$ is obvious from the following argument: For noninteracting boson system, both of the operators $P(t)$ and $H'(t)$ in Eq. (2.1) are linear in boson creation and annihilation operators. Therefore, the innermost commutator of the threefold ones gives a c number, so that the next commutator becomes zero. This is the most general proof of the absence of nonlinearity in the noninteracting boson systems. In the presence of interaction, the operators $P(t)$ and $H'(t)$ consist of terms linear and higher-order terms of boson creation and annihilation operators. A similar argument of vanishing commutators mentioned above can also be made in this case: The linear and a part of the quadratic terms contribute to the vanishing of commutators. If we evaluate the eight expanded terms of the threefold commutators separately, those linear and quadratic terms make a finite contribution in each term. Therefore, the vanishing of commutators is equivalent to a certain cancellation. This argument suggests the existence of a different method of calculating nonlinear susceptibilities, where one eliminates the cancelling terms from the beginning. Such a scheme is now being studied by us.

It is interesting that the present model needs a separate treatment for even and odd N. The quantum numbers (K,κ) for the translational and relative motions of the two-particle states must be chosen in different ways corresponding to even and odd N. The result of the different choices appears in the factors $\bar{A}(K)$ and $\bar{B}(K)$ in (4.17), (4.21), and (4.22), and $\bar{C}(K)$ and $\bar{D}(K)$ in (A4) and (A5) in the Appendix. Note that they all give the same value $+1$ in the limit of large N. Therefore, the $\chi^{(3)}$ in this limit is the same for even and odd N, as it should be.

Now we compare the present result with those of the existing theories about the cancellation problem. There are three groups of them: those by Hanamura,[1,2] Banyai *et al.*,[3] and Spano and Mukamel.[4] In an earlier pioneering work,[1] Hanamura made an argument to classify $[A_i(0),B_i(0),A_i(2),B_i(2)]$ into groups so that they cancel one another in the case of pure bosons. However, his grouping $[A_1(2)+A_1(0)]$, $[B_1(2)+B_1(0)]$, $[A_2(0)+A_3(0)+A_4(0)]$, $[B_2(0)+B_3(0)+B_4(0)]$ is totally different from ours, [(3.3a)–(3.3f)]. The grouping should be unique, even in the resonant condition, as seen from the characteristic energy denominator for each group in (3.4), and we believe ours is correct. In his later paper,[2] he proposes a different scheme to calculate a "very large $\chi^{(3)}$" for a weakly confined exciton system. In this case, he picks up the combination, $B_2(0)+B_1(2)+B_4(0)$, as the terms giving finite contribution to $\chi^{(3)}(\omega;-\omega,\omega,-\omega)$. This new grouping, again being different from ours, leads to the expression of $\chi^{(3)}$ which, in the limit of pure bosons, does not have the expected behavior that it should vanish completely irrespective of resonant or off-resonant condition. This means that the cancellation of the leading-order terms (with respect to the size N) is not properly taken into account in his theory, so that the expression of "very large $\chi^{(3)}$" can possibly be a big overestimate.

Banyai *et al.*[3] discussed a similar cancellation in a simplified system of excitons and biexcitons as a basis for the analysis of size-dependent nonlinear susceptibility of microcrystals. For a source field with a single frequency component, they showed that the contributions from the one- and two-exciton states, treated as pure bosons, cancel one another. In this treatment the energy dispersions of one- and two-exciton states are neglected. Their result remains finite due to the extra contribution from biexciton states. But their expression of $\chi^{(3)}$ stays finite even in the limit of zero binding energy of biexcitons, which is not consistent with the well-known fact that the noninteracting bosons do not show any nonlinearity. As they notice, this is due to their approximate way of introducing biexciton states: The properly introduced biexciton states should affect the wave functions and the number of states of the two-exciton continuum, but this effect is neglected in their treatment.

Spano and Mukamel[4] have treated essentially the same model as ours in LWA, i.e., with the assumption that the sample size (N times the lattice constant) is much smaller than the light wavelength. With this assumption, they introduce a radiative decay width, as well as the nonradiative one, of the exciton states. Except for these decay widths, their expression of $\chi^{(3)}$ is the same as ours when we take $k=k'=K=0$ in (4.17), (4.21), and (4.22). (Their $\chi^{(3)}$ corresponds to ours multiplied by N.) Their calculation is restricted to the case of odd N, and they did not carry out the summation over the quantum number of the relative motion of the two-exciton states (κ in our notation). Thus, their argument about the cancellation was possible only for the complete off-resonance condition, in contrast to ours where the site dependence of the electric fields is retained and the frequencies of the source fields are arbitrary. The explicit κ dependence of their radiative decay constant for two-exciton states might possibly cause a difficulty in carrying out the κ summation. The radiative decay constant does not show up in our formulation. The corresponding effect should appear in the process of solving the Maxwell equations with boundary conditions, in a nonlocal manner, with our $\chi^{(3)}$, together with the linear response $\chi^{(1)}$, as integral kernels. Since we have derived $\chi^{(3)}$ for arbitrary (even and odd) N, including the effect of nonlocality, it allows a detailed study of its consequences in a wider range of N. The result of such a study will be published elsewhere.

Note added in proof. In the most-recent publication [Solid State Commun. **73**, 551 (1990)], Hanamura revised his calculation by taking the contribution of all the terms of (A_i and B_i), but still the result does not have the proper limit of the pure boson case, namely, the vanishing of $\chi^{(3)}$ is attained only in the off-resonant condition. The idea of a coherent region in Ref. 5, as a mechanism to suppress the infinite growth of $\chi^{(3)}$, has been withdrawn in a recent publication [T. Ishihara, Phys. Status Solidi B **159**, 111 (1990)].

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APPENDIX: THE CASE OF EVEN N

The form of the two-particle eigenstate (4.6) is common to both even and odd N, but the allowed values of the quantum numbers K and κ are different from (4.8) for even N:

$$K=\pi\bar{n}/N \quad (\bar{n}=1,2,\ldots,N) \tag{A1}$$

and

$$\kappa=\frac{\pi}{N}(2m'-1) \quad \left[m'=1,2,\ldots,\frac{N}{2}\right] \quad \text{for even } \bar{n}\ , \tag{A2}$$

$$\kappa=\frac{\pi}{N}2m'' \quad \left[m''=1,2,\ldots,\frac{N}{2}-1\right] \quad \text{for odd } \bar{n}\ . \tag{A3}$$

For odd N, similar $\bar{n}$ dependence occurs, but we can rearrange both of the K and κ using the odd character of the modulus N in the way given in (4.8), which allows the κ

summation independent of the value of K. This kind of rearrangement is, however, not possible for the case of even N, and there remains the correlation between the even and odd natures of K and κ. Because of this complication, the κ summation in (4.16) must be done separately for even and odd $\bar{n}$. The cancellation of the terms $[A_1(0),B_i(0)]$ occurs in a similar way as before, and the remaining terms can be written as (4.17), (4.21), and (4.22) except that the factors $\bar{A}(K,k,\Omega_3')$ and $\bar{B}(K,\Omega_2')$ must be replaced by

$$\bar{C}(K,k,\Omega_3')=\begin{cases}-i\tan[N(\bar{a}+i\bar{b})/2] & \text{for even } \bar{n}\\ i\cot[N(\bar{a}+i\bar{b})/2] & \text{for odd } \bar{n}\end{cases} \tag{A4}$$

and

$$\bar{D}(K,\Omega_2')=\begin{cases}-i\tan[N(\bar{c}+i\bar{d})/2] & \text{for even } \bar{n}\\ i\cot[N(\bar{c}+i\bar{d})/2] & \text{for odd } \bar{n}\end{cases}, \tag{A5}$$

respectively, where $\bar{n}$ refers to K in (4.20) and (4.25) through definition (A1).

[1]E. Hanamura, Solid State Commun. **62**, 465 (1987).
[2]E. Hanamura, Phys. Rev. B **37**, 1273 (1988).
[3]L. Banyai, Y. Z. Hu, M. Lindberg, and S. W. Koch, Phys. Rev. B **38**, 8142 (1988).
[4]F. C. Spano and S. Mukamel, Phys. Rev. A **40**, 5783 (1989).
[5]T. Ishihara and T. Goto, J. Phys. Soc. Jpn. **57**, 2191 (1988).