Nonlocal theory of the third-order nonlinear optical response of confined excitons

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A nonlocal formalism of the nonlinear optical-response field has been developed, in which the additional-boundary-condition theory for linear response has been extended. In this theory, Maxwell's equations in terms of site-represented susceptibility up to the third order are solved. Calculations using this theory have been performed for a one-dimensional Frenkel exciton model with hard-wall boundary conditions. As a result, it has been made clear that the nonlocal effect appears in the spectra even when the system size is much smaller than the relevant light wavelengths. This is recognized as a clear difference between the results of fully nonlocal calculations and those obtained using the long-wavelength approximation. This result indicates that the local description is not sufficient when studying the nonlinear response of mesoscopic systems.

I. INTRODUCTION

In recent years, the nonlinear optical properties of mesoscopic systems have attracted much interest mainly because of their large potentiality for application in the field of optoelectronics. With the rapid advance of fabrication technologies to produce microstructures, a variety of electronic confined systems, such as thin films, fine particles, and quantum wells (wires and boxes) of semiconductors have become objects of research. Besides the application aspect, fundamental problems of optical response have appeared through detailed studies of mesoscopic systems.

One of the characteristic phenomena in the optical response of mesoscopic systems is the remarkable size dependence of the nonlinearity, which is never seen in bulk materials. This leads to a new aspect of nonlinear response in condensed matter where the interactions between sites are very strong in comparison with the cases of gas and impurity systems, and to a possible large nonlinear effect by manufacturing appropriate mesoscopic structures.

The origin of the size dependence of the nonlinear response is attributed to the nonlocal nature of the media. In general, exciton energy in condensed matter is transferred from one site to the other via interaction between the sites. The wave functions of excited states (exciton states) in such systems extend coherently over the whole crystal, and the energy eigenvalues are size quantized. Because of this transfer effect, the induced dipole moment at a site is determined by the electric field not only at that site, but also at other sites. Thus, it is called a nonlocal optical response. Materials are generally more or less nonlocal, and the local description is allowed only for the limiting case (transfer energy $\rightarrow 0$), though it has been used in most cases. Therefore, it is necessary to properly introduce the nonlocality in the theoretical description of the optical response in condensed matter.

In the early stages of the theoretical study of mesoscopic systems, a size-enhancement effect of $\chi^{(3)}$ was pointed out to be a dominant factor in the size dependence of the nonlinearity.[1-4] This effect was explained with the idea that the oscillator strength is enhanced in proportion to the coherent volume of the exciton wave function, which is basically the same idea as that of the giant oscillator strength of shallow bound excitons at impurity sites.[5,6] These theories can describe the size-enhancement effect in a limited (small) size region. However, they could not reach a consistent understanding of the size dependence (enhancement together with saturation) of $\chi^{(3)}$ and the nonlinearity in the response field because of insufficient consideration of the nonlocality.

In our previous works, we showed that the size enhancement of $\chi^{(3)}$ and its saturation can be described in a consistent way by explicitly introducing the transfer effect and relaxation of excitons into the model, and by proper consideration of the cancellation problem, namely, $\chi^{(3)}$ is enhanced in proportion to the system size in a small size region, and then it is saturated to a constant value by the cancellation between the terms of $\chi^{(3)}$ containing the two-exciton states and ground state as the second intermediate state of the third-order perturbation.[7] The size region for the enhancement is determined by the relative magnitudes of energy transfer and damping constant, which affect the extent of the cancellation.

On the other hand, it should be noted that the nonlocality appears not only in the size enhancement of the nonlinear susceptibility, but also in the magnitude and spatial distribution of the internal field. Since the internal field is determined via the self-consistent motion with the dipole moment, the optical spectrum contains the information of the internal field as well as $\chi^{(3)}$. Therefore, a study of the size dependence of susceptibility alone is not sufficient in general, and Maxwell's equations, explicitly

considering the site dependence of the susceptibility and the internal field, should be solved in order to totally understand the size-dependent nonlinear response.

If one neglects the site dependence of the internal field [long-wavelength approximation (LWA)], one can show that $\chi^{(3)}$ is enhanced in proportion to the sample volume as long as the volume is smaller than the coherent volume of the exciton. However, our previous treatments[8,9] explicitly show the existence of a size region where we get both the size enhancement of $\chi^{(3)}$ in the LWA and the strong site dependence of the internal field. This indicates the insufficiency of evaluating $\chi^{(3)}$ by the LWA. On the other hand, we have also shown that the internal field for a resonant light has a size-resonance behavior both in its amplitude[9] and in its spatial pattern.[10] These results show the absolute necessity of considering the site dependence of the internal field for the description of the "size, shape, internal structure" dependence of the optical response of mesoscopic systems.

The purpose of this paper is to formulate a nonlocal theory of the third-order nonlinear response and to demonstrate its application. In this method, nonlinear Maxwell's equations are solved in terms of the linear and third-order susceptibilities in the site representation. In the case of linear response, a similar method for the nonlocal calculation has been well developed as the additional boundary condition (ABC) theory,[11–14] and the ABC-free theory.[15–17] The essence of these theories is to solve Maxwell's equations containing the site-represented susceptibility which is calculated from the electronic states obtained by proper consideration of the quantum-mechanical boundary condition. Especially in the ABC-free theory, the use of the concept of the ABC (see Sec. II) is completely avoided. Our present method is an extension of the ABC-free theory. In the ABC-free theory, the general form of the susceptibility in the site representation, which is a sum of the products of functions of each coordinate, is used to rewrite the integrodifferential Maxwell's equations into a set of linear equations. In the case of the third-order nonlinearity, the separability of nonlinear susceptibility is again utilized and simultaneous cubic equations are obtained. This set of equations can be solved numerically if the number of bases is not too large.

The organization of the rest of this paper is as follows. In Sec. II, a general explanation of the theory is presented. Its application to the specific model, i.e., the model of one-dimensional Frenkel excitons, is explained in Sec. III. The results of numerical calculations and the discussions are given in Secs. IV and V, respectively. We summarize in the final section.

II. GENERAL THEORY

For nonlocal media specified by explicit wave-vector (k) dependence of the bulk dielectric function $\varepsilon(k,\omega)$, the dispersion relation of transverse polariton is given as

$$\varepsilon(k,\omega)=c^2k^2/\omega^2 . \tag{2.1}$$

The solutions of this equation are the multiple transverse-polariton modes. Therefore, the ABC's are usually required in addition to Maxwell's boundary conditions (MBC's) for the unique connection with an external field. Theoretical treatments of such a problem from the microscopic model are well established in the regime of linear response as the ABC theory[11–14] and the ABC-free theory.[15–17] In the former theory, the relations of polariton amplitudes which play the role of ABC's are derived from microscopic calculation, while in the latter the same equation is solved without using the concept of the ABC. These theories provide physically equivalent results.[16]

The basic idea of nonlocal theory which we develop here comes from the ABC-free theory. For the sake of a clear understanding, we outline this theory before the presentation of the general framework for the nonlinear response.

A. Outline of the ABC-free theory for linear response

The starting point of the ABC-free theory is Maxwell's equation for the ω-Fourier component,

$$\mathrm{rotrot}\mathbf{E}(\mathbf{r})-(\omega^2/c^2)\mathbf{E}(\mathbf{r}) -(4\pi\omega^2/c^2)\int d\mathbf{r}'\chi(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')=0 . \tag{2.2}$$

The essential point of this formulation is based on the general form of the linear susceptibility $\chi^{(1)}(\mathbf{r},\mathbf{r}';\omega)$ in the site representation which is to be used as the kernel in this integrodifferential equation (2.2). It is clear from the linear response theory[18] that $\chi^{(1)}(\mathbf{r},\mathbf{r}';\omega)$ (at 0 K) can generally be written as a sum of the products of functions of $\mathbf{r}$ and $\mathbf{r}'$, respectively, namely,

$$\chi^{(1)}_{\xi\eta}(\mathbf{r},\mathbf{r}';\omega)=\sum_{\lambda}\bar{\chi}^{(1)}_{\lambda}(\omega)\rho^{*}_{\lambda\xi}(\mathbf{r})\rho_{\lambda\eta}(\mathbf{r}') , \tag{2.3}$$

where

$$\bar{\chi}^{(1)}_{\lambda}(\omega)=1/(E_\lambda-\hbar\omega-i\gamma) , \tag{2.4}$$

$$\rho_{\lambda\xi}(\mathbf{r})=\langle\lambda|P_\xi(\mathbf{r})|0\rangle . \tag{2.5}$$

In the above expressions, E_λ and $|\lambda\rangle$ are the eigenenergy and eigenstate of the unperturbed system, respectively, (ξ,η) are the components of the Cartesian coordinate system. The nonresonant terms will be put aside as a background susceptibility proportional to $\delta(\mathbf{r}-\mathbf{r}')$. In (2.4), γ is a positive infinitesimal value representing the adiabatic switching of the radiation-matter interaction. When we treat scattering mechanisms phenomenologically, it is taken to be a positive finite value. In (2.5), $P_\xi(\mathbf{r})$ is the ξ component of the polarization density operator which is defined as

$$\mathbf{P}(\mathbf{r})=(-ie/m\omega)\sum_{l}\delta(\mathbf{r}-\mathbf{r}_l)\mathbf{p}_l , \tag{2.6}$$

where $\mathbf{r}_l$, $\mathbf{p}_l$ are the coordinate and momentum of the lth electron, respectively, m and e are the mass and charge of the electron, c the velocity of light, and ω the angular frequency. This definition of $\mathbf{P}(\mathbf{r})$ works together with the choice of the Coulomb gauge for the field, namely, $\mathrm{div}\mathbf{E}(\mathbf{r})=0$. All the information about the bulk and surfaces is included in $\{\hbar\omega_\lambda,|\lambda\rangle\}$.

With the expressions (2.3)–(2.5), the integrodifferential Maxwell's equation can be converted to a second-order differential equation, namely,

$$\mathrm{rotrot}\mathbf{E}(\mathbf{r})-(\omega^2/c^2)\mathbf{E}(\mathbf{r}) -(4\pi\omega^2/c^2)\sum_\lambda \bar{\chi}_\lambda^{(1)}(\omega)\boldsymbol{\rho}_\lambda^*(\mathbf{r})F_\lambda=0 , \quad (2.7)$$

where the definition of F_λ is

$$F_\lambda=\sum_\eta \int \rho_{\lambda\eta}(\mathbf{r})E_\eta(\mathbf{r})d\mathbf{r} . \quad (2.8)$$

Consider the case of the normal incidence of external light to a slab of thickness d for the sake of simplicity. In this case, we have only to deal with the surface-normal (z) dependence of $\mathbf{E}$, so that (2.7) can be replaced by

$$\frac{d^2\mathcal{E}(z)}{dz^2}+q^2\mathcal{E}(z)+Q^2\sum_\lambda \bar{\chi}_\lambda^{(1)}(\omega)\rho_\lambda^*(z)F_\lambda=0 , \quad (2.9)$$

where $\mathcal{E}$ is the transverse component of $\mathbf{E}$, and

$$F_\lambda=\int_0^d \rho_\lambda(z)\mathcal{E}(z)dz , \quad (2.10)$$

$$q^2=\varepsilon_b\omega^2/c^2, \quad Q^2=4\pi\omega^2/c^2 . \quad (2.11)$$

We have also introduced the background constant ε_b to which the nonresonant terms of polarizability contribute, and at the same time the summation over λ is restricted to resonant levels. In this one-dimensional formulation, $\rho_\lambda(z)$ should be redefined as (2.5) multiplied by a certain length. Thus, the problem is just to solve the second-order differential equation (2.9) in a consistent way with (2.10). If we regard $\{F_\lambda\}$ as given constants, the general solution of (2.9) can be written as

$$\mathcal{E}(z)=\mathcal{E}_1 e^{iqz}+\mathcal{E}_2 e^{iq\bar{z}}-\sum_\lambda \bar{G}_\lambda(z)F_\lambda , \quad (2.12)$$

where

$$\bar{G}_\lambda(z)=\{Q^2\bar{\chi}_\lambda^{(1)}(\omega)/2iq\}\int_0^d e^{iq|z-z'|}\rho_\lambda^*(z')dz' , \quad (2.13)$$

$$\bar{z}=d-z , \quad (2.14)$$

$\mathcal{E}_1$ and $\mathcal{E}_2$ are arbitrary constants, and we have used the identity

$$(d^2/dz^2+q^2)e^{iq|z-z'|}=2iq\delta(z-z') . \quad (2.15)$$

Substituting (2.12)–(2.14) in (2.10), we obtain the linear simultaneous equations to determine the expansion coefficients $\{F_\lambda\}$ of the electric field as

$$F_\lambda=\mathcal{E}_1\int \rho_\lambda(z)e^{iqz}dz+\mathcal{E}_2\int \rho_\lambda(z)e^{iq\bar{z}}dz -\sum_{\lambda'} F_{\lambda'}\int G_{\lambda'}(z)\rho_\lambda(z)dz . \quad (2.16)$$

The solution of this equation has the form

$$F_\lambda=a_\lambda\mathcal{E}_1+b_\lambda\mathcal{E}_2 . \quad (2.17)$$

When we substitute (2.17) into (2.12), the final expression of $\mathcal{E}(z)$ contains only the two arbitrary constants, $\mathcal{E}_1$ and $\mathcal{E}_2$. Because of the minimum number of arbitrary constants, just a set of MBC's is enough for a unique connection of the external and internal fields across the surface. The characteristic points of this theory are that the argument of the ABC is not necessary at all and that the presence of the bulk mode is not assumed. These points, together with the separable site dependence of linear and nonlinear susceptibilities, enable us to extend this theory to the nonlinear response as shown below.

B. Nonlocal theory of nonlinear response

In the case of the third-order nonlinear response, we calculate the third-order nonlinear polarization $P^{(3)}$ with the usual perturbation expansion of the density matrix as in Ref. 7. After decomposition of the threefold commutator in the integrand of $P^{(3)}$, $\chi^{(3)}$ turns out to be a sum of eight kinds of terms. They correspond to the eight terms in (A5) of Appendix A. Following the notations in Ref. 7, we denote them as $A_1, A_2, \ldots, B_4$ in the order of their appearance in (A5). Each of them can be classified into two, according to the type of the second intermediate state $|\mu\rangle$: $|\mu\rangle$ can be the ground state or the doubly excited states. The former and latter cases are denoted as $A_i(0)$, $B_i(0)$, and $A_i(2)$, $B_i(2)$, respectively. As argued in Ref. 7, cancellation between these two types of terms occurs. Therefore no term should be omitted without proper examination of its contribution.

The essential point is that each term is also written as a sum of the products of functions of respective coordinates as in the case of the linear susceptibility. In $\chi^{(3)}$, there appear dipole density matrix elements of the form $\langle\sigma|P_j|\tau\rangle$, where $\{|\sigma\rangle,|\tau\rangle\}$ are either a ground state or single or doubly excited states. If we define $F_{\sigma\tau}$ similarly as in (2.8), $P^{(3)}$ becomes a cubic polynomial of $\{F_{\sigma\tau}\}$, and so is the solution of Maxwell's equations. Then, the self-consistent equations to determine $\{F_{\sigma\tau}\}$ become simultaneous cubic equations, which is an extended version of Eq. (2.16). Though it may be difficult to solve these equations analytically, it is possible to solve them numerically in the case that a small number of states are required as the basis set.

Let us see this explicitly in terms of a simple model of Frenkel excitons. The wave functions of one- and two-exciton states are written as

$$|\lambda\rangle=\sum_l \phi_{\lambda,l}b_l^\dagger|0\rangle \quad (2.18)$$

and

$$|\mu\rangle=\sum_{lm}\Phi_{\mu,lm}b_l^\dagger b_m^\dagger|0\rangle , \quad (2.19)$$

respectively, where $b_l^\dagger$ is the operator to create an exciton on the lth site. With these expressions, the matrix element of P_j between the zero- and one-exciton states and one- and two-exciton states is calculated, respectively, as

$$\langle 0|P_j|\lambda\rangle=M\phi_{\lambda,j}^* , \quad (2.20)$$

$$\langle\lambda|P_j|\mu\rangle=2M\sum_n \phi_{\lambda,n}^*\Phi_{\mu,jn} \equiv 2M\bar{\Phi}_{\lambda\mu,j} , \quad (2.21)$$

where the definition of P_j is

$$P_j = M b_l + M^* b_l^\dagger \ , \tag{2.22}$$

M is the transition dipole moment per site, and b_l is the operator to annihilate an exciton on the lth site.

Using these expressions of the matrix element, we can write $P^{(3)}$ with the parameters like $\{F_\lambda\}$ defined by (2.8). We should note that they include F containing the matrix elements between the one-exciton states and two-exciton states besides those used in the linear response.

In the nonlinear case, we have to consider a set of Maxwell's equations for all the relevant frequency components of the field, and these components are coupled through the nonlinear terms. We suppose that there are altogether N_f frequency components of the field $(\omega_1, \omega_2, \ldots, \omega_{N_f})$. In the Maxwell equation for frequency ω_{n_f}, the expansion coefficients of the form

$$F_\lambda^{(n_f)} = \sum_l \phi_{\lambda,l} \mathcal{E}_l(n_f) \tag{2.23}$$

appear from the first-order polarization $P_j^{(1)}$, where $\mathcal{E}_l(n_f)$ is the amplitude of the electric field with the frequency ω_{n_f} at site l. The contribution from $P_j^{(3)}$ in the same equations contains the products of three expansion coefficients F. For example, the expression corresponding to $A_1(0)$ in $P_j^{(3)}$ is

$$P_j^{(3)}(t)|_{A_1(0)} = -\frac{M^4}{v_0} \sum_{p,q,s} \exp[-i(\omega_p+\omega_q+\omega_s+3i\gamma)t] \sum_\lambda \sum_\nu \frac{\phi_{\lambda,j} F_\lambda^{(p)*} F_\nu^{(q)} F_\nu^{(s)*}}{(E_{\lambda 0}-\Omega_3')\Omega_2'(E_{\nu 0}-\omega_s')} \ , \tag{2.24}$$

where $\sum_{p,q,s}$ means the summation over all the combinations of $(\omega_p, \omega_q, \omega_s)$ which satisfy the condition $\omega_p+\omega_q+\omega_s=\omega_{n_f}$, with ω_p, ω_q, and ω_s taken from the set $(\omega_1, \omega_2, \ldots, \omega_{N_f})$ and v_0 is the volume of a unit cell. In the practical calculation, the summation can be restricted to the combinations which satisfy the resonant conditions. The term corresponding to $A_1(2)$ is

$$P_j^{(3)}(t)|_{A_1(2)} = \frac{4M^4}{v_0} \sum_{p,q,s} \exp[-i(\omega_p+\omega_q+\omega_s+3i\gamma)t] \sum_\lambda \sum_\mu \sum_\nu \frac{\phi_{\lambda,j} F_{\lambda\mu}^{(p)} F_{\nu\mu}^{(q)*} F_\nu^{(s)*}}{(E_{\lambda 0}-\Omega_3')(E_{\mu 0}-\Omega_2')(E_{\nu 0}-\omega_s')} \ , \tag{2.25}$$

where

$$F_{\lambda\mu}^{(p)} = \sum_l \bar{\Phi}_{\lambda\mu,l} \mathcal{E}_l(p) \ . \tag{2.26}$$

The term corresponding to $B_2(2)$ is

$$P_j^{(3)}(t)|_{B_2(2)} = \frac{4M^4}{v_0} \sum_{p,q,s} \exp[-i(\omega_p+\omega_q+\omega_s+3i\gamma)t] \sum_\lambda \sum_\mu \sum_\nu \frac{\bar{\Phi}_{\nu\mu,j} F_\nu^{(q)} F_{\lambda\mu}^{(p)*} F_\lambda^{(s)*}}{(E_{\nu\mu}+\Omega_3')(E_{\nu\lambda}+\Omega_2')(E_{0\lambda}+\omega_s')} \ . \tag{2.27}$$

Writing the remaining 13 terms in a similar way, we see that $P_j^{(3)}$ is written in the linear combination of the functions $\{\phi_{\lambda,j}\}$ ($\{\phi_{\lambda,j}^*\}$) and $\{\bar{\Phi}_{\lambda\mu,j}\}$ ($\{\bar{\Phi}_{\lambda\mu,j}^*\}$). In the coefficients of these functions, there appear products of three F's from the following:

$$\begin{aligned}
&F_\lambda^{(1)} = \sum_l \phi_{\lambda,l} \mathcal{E}_l(1), \quad F_\lambda^{(1)*} = \sum_l \phi_{\lambda,l}^* \mathcal{E}_l(1) \\
&F_\lambda^{(2)} = \sum_l \phi_{\lambda,l} \mathcal{E}_l(2), \quad F_\lambda^{(2)*} = \sum_l \phi_{\lambda,l}^* \mathcal{E}_l(2) \\
&\quad\vdots \qquad\qquad \vdots \\
&F_\lambda^{(N_f)} = \sum_l \phi_{\lambda,l} \mathcal{E}_l(N_f), \quad F_\lambda^{(N_f)*} = \sum_l \phi_{\lambda,l}^* \mathcal{E}_l(N_f) \ ,
\end{aligned} \tag{2.28}$$

and

$$\begin{aligned}
&F_{\lambda\mu}^{(1)} = \sum_l \bar{\Phi}_{\lambda\mu,l} \mathcal{E}_l(1), \quad F_{\lambda\mu}^{(1)*} = \sum_l \bar{\Phi}_{\lambda\mu,l}^* \mathcal{E}_l(1) \\
&F_{\lambda\mu}^{(2)} = \sum_l \bar{\Phi}_{\lambda\mu,l} \mathcal{E}_l(2), \quad F_{\lambda\mu}^{(2)*} = \sum_l \bar{\Phi}_{\lambda\mu,l}^* \mathcal{E}_l(2) \\
&\quad\vdots \qquad\qquad \vdots \\
&F_{\lambda\mu}^{(N_f)} = \sum_l \bar{\Phi}_{\lambda\mu,l} \mathcal{E}_l(N_f), \quad F_{\lambda\mu}^{(N_f)*} = \sum_l \bar{\Phi}_{\lambda\mu,l}^* \mathcal{E}_l(N_f) \ .
\end{aligned} \tag{2.29}$$

If we regard $\{F_\lambda^{(n_f)}\}$ ($\{F_\lambda^{(n_f)*}\}$) and $\{F_{\lambda\mu}^{(n_f)}\}$ ($\{F_{\lambda\mu}^{(n_f)*}\}$) as given constants as in the case of the ABC-free theory of the linear response, the Maxwell equation for each frequency component becomes a second-order differential equation with inhomogeneous terms, which correspond to (2.7) or (2.9) in the ABC-free theory.

These equations can easily be solved in basically the same way as in the linear case. The forms of solutions $\{\mathcal{E}_j(n_f)\}$ are similar to that of (2.12) except that they include many kinds of functions of coordinate j corresponding to $\bar{G}_\lambda(z)$ in (2.12) and products of three F's. Substituting these solutions $\mathcal{E}_j(1), \mathcal{E}_j(2), \ldots, \mathcal{E}_j(N_f)$ in the definitions of the expansion coefficients (2.28) and (2.29), we obtain the simultaneous cubic equations for $(N_\lambda+N_\lambda\times N_\mu)\times N_f$ variables F in (2.28) and (2.29), where N_λ and N_μ are the numbers of the one- and two-exciton states. Since there are $(N_\lambda+N_\lambda\times N_\mu)\times N_f$ equations, we can obtain unique solutions. These equations contain $2N_f$ arbitrary amplitudes of the external fields $\mathcal{E}^1(n_f)$ and $\mathcal{E}^2(n_f)$ [which correspond to $\mathcal{E}_1$ and $\mathcal{E}_2$ in (2.12), respectively]. For each frequency, the field outside the medium is specified by three amplitudes (incident, reflected, and transmitted waves). Including the $2N_f$ arbitrary amplitudes in the medium, there are alto-

gether $5N_f$ amplitudes to be fixed. On the other hand, we can write four MBC's (two for the front and two for the back surfaces of the medium) for each frequency in terms of $5N_f$ amplitudes. Thus, if we give the N_f amplitudes of the incident fields, we can uniquely determine the remaining $4N_f$ amplitudes.

A problem to be encountered in practice is how to obtain the explicit expression of $\bar{\Phi}_{\lambda\mu,j}$ in (2.21). When the closed form of the two-exciton wave function $\Phi_{\mu,lm}$ [in (2.19)] cannot be obtained, we can perform the nonlocal calculation with numerically calculated $\Phi_{\mu,lm}$ in the following way. Generally, the function $\Phi_{\mu,lm}$ can be expanded in the sum of the products of a complete set of one-exciton wave functions $\{\phi_{\lambda,l}\}$ as

$$\Phi_{\mu,lm}=\sum_{\lambda,\nu} C_{\lambda\nu}^{(\mu)}\phi_{\lambda,l}\phi_{\nu,m} \ . \tag{2.30}$$

With this expression, the matrix element of P_j between the one-exciton state and the two-exciton state can be calculated as

$$\begin{aligned}\langle\lambda|P_j|\mu\rangle&=\sum_n \langle 0|b_n\phi_{\lambda,n}^* P_j \sum_{\nu_1,\nu_2} C_{\nu_1,\nu_2}^{(\mu)} \sum_{l,m}\phi_{\nu_1,l}\phi_{\nu_2,m} b_l^\dagger b_m^\dagger|0\rangle \\ &=2M\sum_\nu C_{\lambda\nu}^{(\mu)}\phi_{\nu,j} \ ,\end{aligned} \tag{2.31}$$

where λ, ν, ν_1, and ν_2 are the indices for the one-exciton states, and μ is that of the two-exciton states. If we use this expression, only $\{\phi_{\lambda,j}\}$ ($\{\phi_{\lambda,j}^*\}$) are enough as functions of coordinate j, and the number of the expansion coefficients is also reduced from $(N_\lambda+N_\lambda\times N_\mu)\times N_f$ to $N_\lambda\times N_f$ but the necessary summation over quantum indices increases. Thus, if we can calculate the eigenvalues and expansion coefficients $C_{\lambda\nu}^{(\mu)}$ of two-exciton wave functions, the nonlocal calculation of the nonlinear response is possible.

In the next section, we demonstrate the application of the above theory to a one-dimensional Frenkel exciton system of finite size, in which the eigenvalues and eigenfunctions of the two-exciton states are calculated numerically.

III. APPLICATION TO ONE-DIMENSIONAL FRENKEL EXCITONS

In this section, we consider the nonlinear response in a thin film consisting of a bundle of one-dimensional chains of size N, each of which confines Frenkel excitons. There is no interaction between each chain, and the array of the chains is periodic along the surface of the film. We assume the normal incidence of beams. The Hamiltonian of this system is

$$H=\sum_{l=0}^{N+1}\varepsilon_0 b_l^\dagger b_l - b\sum_{l=0}^{N+1}(b_{l-1}^\dagger b_l + b_l^\dagger b_{l-1}) \ , \tag{3.1}$$

where ε_0 is the excitation energy of each site, b is the transfer energy, and we introduce the imaginary sites at $l=0$ and $N+1$ on which the amplitudes of excitons are zero. The lattice constant in the chain is assumed to be unity.

The eigenvalues and eigenfunctions of one-exciton states are

$$E_1(k)=\varepsilon_0-2b\cos k \tag{3.2}$$

and

$$|k\rangle=\left[\frac{2}{N+1}\right]^{1/2}\sum_l \sin klb_l^\dagger|0\rangle \ , \tag{3.3}$$

respectively. The allowed values of k are

$$k=\frac{n\pi}{N+1}, \quad \{n=1,2,\ldots,N\} \ . \tag{3.4}$$

Then, to prepare the two-exciton states, we take a set of $\{|m,n)\}$ ($=\{b_m^\dagger b_n^\dagger|0\rangle\}$) as a base, where the case $m=n$ is excluded. Using this base, we expand the two-exciton states as

$$|\mu\rangle=\sum_{n<m} C_{n,m}^{(\mu)}|m,n) \ . \tag{3.5}$$

Inserting (3.1) and (3.5) into the Schrödinger equation, we get the following linear simultaneous equations to determine $\{C_{n,m}^{(\mu)}\}$ and the eigenvalues of the two-exciton states E_μ,

$$2\varepsilon_0 C_{l',l}-t(C_{l',l+1}+C_{l',l-1}+C_{l'+1,l}+C_{l'-1,l})=EC_{l',l} \ . \tag{3.6}$$

These equations are solved numerically. Then, we rewrite the two-exciton states as

$$|\mu\rangle=\frac{2}{N+1}\sum_{k,k'} C_{k,k'}^{(\mu)}\sum_{n,m}\sin kn\,\sin k'm b_n^\dagger b_m^\dagger|0\rangle \ , \tag{3.7}$$

where

$$C_{k,k'}^{(\mu)}=\frac{1}{N+1}\sum_{l'<l} C_{l,l'}^{(\mu)}(\sin kl\,\sin k'l'+\sin kl'\,\sin k'l) \ , \tag{3.8}$$

and in (3.7), the indices n,m run over all sites independently, and k,k' run over all allowed values in (3.4) independently. Hereafter, we use $\{C_{k,k'}^{(\mu)}\}$ and $\{E_\mu\}$ as known quantities. With the expressions (3.3), (3.7), the dipole matrix elements between the ground and the one-exciton states, and one- and two-exciton states are given as

$$\langle 0|P_l|k\rangle=M\left[\frac{2}{N+1}\right]^{1/2}\sin kl \ , \tag{3.9}$$

$$\langle K|P_l|\mu\rangle=M\left[\frac{2}{N+1}\right]^{1/2}\sum_k 2C_{k,K}^{(\mu)}\sin kl \ , \tag{3.10}$$

respectively. Making use of these results, we can get the explicit expression of $P_j^{(3)}$ for arbitrary frequencies as

$$P_j^{(3)}(t)=\frac{M^4}{v_0}\left[\frac{2}{N+1}\right]^{1/2}\sum_p\sum_q\sum_s \exp[-i(\omega_p+\omega_q+\omega_s)t]$$
$$\times\left[4\sum_K\sum_{K'}\sum_\mu\sum_k\sum_{k'}\frac{\sin Kj C_{kK}^{(\mu)}C_{K'k'}^{(\mu)}F_k^{(p)}F_{k'}^{(q)}F_{K'}^{(s)}}{[E_1(K)-\Omega_3-i\Gamma](E_\mu-\Omega_2-2i\Gamma)[E_1(K')-\omega_s-i\Gamma]}\right.$$
$$-4\sum_K\sum_{K'}\sum_\mu\sum_k\sum_{k'}\frac{\sin Kj C_{kk}^{(\mu)}C_{K'k'}^{(\mu)}F_k^{(p)}F_{k'}^{(q)}F_{K'}^{(s)}}{(E_{\mu k}-\Omega_3-i\Gamma)(E_\mu-\Omega_2-2i\Gamma)[E_1(K')-\omega_s-i\Gamma]}$$
$$+4\sum_K\sum_{K'}\sum_\mu\sum_k\sum_{k'}\frac{\sin Kj C_{kK}^{(\mu)}C_{K'k'}^{(\mu)}F_{k'}^{(p)}F_k^{(q)}F_{K'}^{(s)}}{(E_{\mu k}-\Omega_3-i\Gamma)(E_{kK'}+\Omega_2+i\Gamma_{kK'})[E_1(K')-\omega_s-i\Gamma]}$$
$$-\sum_K\sum_{K'}\frac{\sin Kj F_K^{(p)}F_{K'}^{(q)}F_{K'}^{(s)}}{[E_1(K)-\Omega_3-i\Gamma](\Omega_2+i\gamma)[E_1(K')-\omega_s-i\Gamma]}$$
$$-\sum_K\sum_{K'}\frac{\sin Kj F_K^{(p)}F_{K'}^{(q)}F_K^{(s)}}{[E_1(K)-\Omega_3-i\Gamma](E_{KK'}-\Omega_2-i\Gamma_{KK'})[E_1(K)-\omega_s-i\Gamma]}$$
$$-4\sum_K\sum_{K'}\sum_\mu\sum_k\sum_{k'}\frac{\sin Kj C_{Kk}^{(\mu)}C_{K'k'}^{(\mu)}F_{k'}^{(p)}F_{K'}^{(q)}F_k^{(s)}}{(E_{\mu k}-\Omega_3-i\Gamma)(E_{kK'}+\Omega_2+i\Gamma_{kK'})[E_1(k)+\omega_s+i\Gamma]}$$
$$+\sum_K\sum_{K'}\frac{\sin Kj F_{K'}^{(p)}F_K^{(q)}F_{K'}^{(s)}}{[E_1(K)-\Omega_3-i\Gamma](E_{KK'}-\Omega_2-i\Gamma_{KK'})[E_1(K')+\omega_s+i\Gamma]}$$
$$\left.+\sum_K\sum_{K'}\frac{\sin Kj F_K^{(p)}F_{K'}^{(q)}F_{K'}^{(s)}}{[E_1(K)-\Omega_3-i\Gamma](\Omega_2+i\gamma)[E_1(K')+\omega_s+i\Gamma]}\right]+\text{c.c.}\ , \tag{3.11}$$

where

$$F_k^{(p)}=\left[\frac{2}{N+1}\right]^{1/2}\sum_l \sin kl\,\mathcal{E}_l(p)\ , \tag{3.12}$$

$$E_{\mu K}=E_\mu-E_1(K)\ , \tag{3.13}$$

$$E_{KK'}=E_1(K)-E_1(K')\ , \tag{3.14}$$

$$\Omega_3=\omega_p+\omega_q+\omega_s\ , \tag{3.15}$$

$$\Omega_2=\omega_q+\omega_s\ , \tag{3.16}$$

and $\hbar$ is taken to be unity. We have introduced the phenomenological damping constant in the usual way as in Ref. 8, namely, the population decay constant γ, the phase decay constant Γ between the ground state and one-exciton states, 2Γ between the ground state and two-exciton states, and $\Gamma_{kk'}$ in (3.11) means γ when $k=k'$, and otherwise it means Γ.

Now, we consider the case of the pump-probe measurement, where the system is pumped at the frequency ω_2 and probed at the frequency ω_1, namely, we require $\omega_1=\omega_p+\omega_q+\omega_s$ and pick up the contribution of the most (triply) resonant [denoted as (tri. res.)] terms from the general expression of $P_j^{(3)}$, (3.11). For the frequency ω_1, the corresponding part of $P_j^{(3)}$ can be written in the following form:

$$P_j^{(3)}(t)|_{(\text{tri. res.})}=\frac{M^4}{v_0}\left[\frac{2}{N+1}\right]^{1/2}\sum_K \sin Kj$$
$$\times\left[\sum_{K'}|F_{K'}^{(1)}|^2F_K^{(1)}G_0(K,K';\omega_1)+\sum_{K'}\sum_k\sum_{k'}F_{K'}^{(1)*}F_k^{(1)}F_{k'}^{(1)}G_1(K,K',k,k';\omega_1)\right.$$
$$+\sum_{K'}|F_{K'}^{(2)}|^2F_K^{(1)}H_0(K,K';\omega_1,\omega_2)+\sum_{K'}\sum_k\sum_{k'}F_{K'}^{(2)*}F_{k'}^{(2)}F_k^{(1)}H_1(K,K',k,k';\omega_1,\omega_2)$$
$$+\sum_{K'}F_{K'}^{(2)*}F_K^{(2)}F_{K'}^{(1)}\bar{H}_0(K,K';\omega_1,\omega_2)$$
$$\left.+\sum_{K'}\sum_k\sum_{k'}F_{K'}^{(2)*}F_k^{(2)}F_{k'}^{(1)}\bar{H}_1(K,K',k,k';\omega_1,\omega_2)\right]e^{-i\omega_1 t}\ , \tag{3.17}$$

where the explicit expressions of G_0, G_1, H_0, H_1, $\bar{H}_0$, and $\bar{H}_1$ are given in Appendix B. By the replacement (ω_1, $F^{(1)} \rightleftharpoons \omega_2$, $F^{(2)}$) in (3.17), we can obtain the expression of $P_j^{(3)}(t)|_{(\text{tri. res.})}$ for the frequency ω_2. Then, we proceed to calculate the spectra along the procedure explained in the previous section. In Appendix C, we give Maxwell's equations in terms of the linear polarization,

$$P_j^{(1)} = \frac{M^2}{v_0}\left[\frac{2}{N+1}\right]^{1/2} \sum_K \frac{\sin KjF_K^{(1)}}{E_1(K)-\omega_1-i\Gamma} e^{-i\omega_1 t} , \tag{3.18}$$

and $P_j^{(3)}(t)|_{(\text{tri. res.})}$, (3.17), the general solutions of them, the simultaneous cubic equations for the expansion coefficients F, and the MBC's.

In case the intensity of the probe beam is much smaller than that of the pump beam, we can do the following. In Maxwell's equation for the frequency ω_2, there exist two types of terms, namely, those proportional to the cube of $F^{(2)}$ and those proportional to $[F^{(1)}]^2 \times F^{(2)}$. Under the above condition, the latter is negligible as compared with the former. Therefore, the $F^{(2)}$'s can be calculated independently of the $F^{(1)}$'s. On the other hand, in Maxwell's equation for the frequency ω_1, the terms which are proportional to the cube of the $F^{(1)}$ are negligible as compared with the terms proportional to $[F^{(2)}]^2 \times F^{(1)}$. Therefore, inserting the value of the $F^{(2)}$'s, which are determined independently, into Maxwell's equation for the frequency ω_1, we obtain a linear equation to determine the $F^{(1)}$'s with a renormalized linear susceptibility due to the pumping. This method remarkably saves the time for computing, and under the usual condition of the third-order pump-probe measurement, it is a valid approximation in most cases.

IV. THE RESULTS

In this section, we show (a) several examples of nonlinear optical spectra, (b) the size dependence of the nonlinearity in the spectra, and (c) a comparison between the nonlocal calculation and the LWA.

Throughout this section, the following values of the parameters are used:

$$\omega_t = 3202.2 \text{ meV}, \quad b = 57.0 \text{ meV} ,$$
$$\frac{4\pi|M|^2}{v_0} = 5.7 \text{ meV}, \quad \varepsilon_b = 5.6 , \tag{4.1}$$
$$a_0 = 5.4 \text{ Å}, \quad \Gamma = 0.6 \text{ meV}, \quad \gamma = 0.02 \text{ meV} ,$$

where ω_t is the energy of the bottom of the exciton band, namely, $\omega_t = \varepsilon_0 - 2b$. As for the amplitudes of the incident beam, we choose 2.4×10^5 V/m and 1.2×10^3 V/m for the pump and probe beams, respectively. In every spectrum shown below, the pump beam energy is tuned at the lowest one-exciton energy which varies with the size N.

A. Several examples of nonlinear optical spectra

As we mentioned in the previous section, the present nonlocal theory for the nonlinear response enables us to calculate the optical spectra such as reflectance $R(\omega_1)$ and transmittance $T(\omega_1)$ for the probe light. We show the pump-induced change of these spectra, $\delta R(\omega_1)$, $\delta T(\omega_1)$, and that of the normalized absorption $\delta \bar{A}(\omega_1)$, which are defined as

$$\begin{aligned} \delta R &= R^{(\text{nonlinear})} - R^{(\text{linear})} , \\ \delta T &= T^{(\text{nonlinear})} - T^{(\text{linear})} , \\ \delta \bar{A} &= \bar{A}^{(\text{nonlinear})} - \bar{A}^{(\text{linear})} , \end{aligned} \tag{4.2}$$

where

$$\bar{A} = \frac{1-R-T}{1-R} . \tag{4.3}$$

Figure 1 shows spectra for $N=6$. The upper tick mark(s) in each graph show the energy levels of size-quantized one-exciton states. In Figs. 1(a)–1(c), there exists a fine structure due to the small longitudinal damping (γ) just at the lowest one-exciton level, and broad structures due to the large transverse damping (Γ). Figure 2 is for $N=20$. The lower tick marks, indicating the energy differences of two-exciton levels and lowest one-exciton level, are added. The large structure near $\hbar\omega_1 = 3.207$ eV due to induced absorption from the lowest one-exciton level to the lowest two-exciton level is characteristic.

The spectra of imaginary $\chi^{(3)}$ which are calculated by the LWA in the same model are shown in Fig. 3 for the

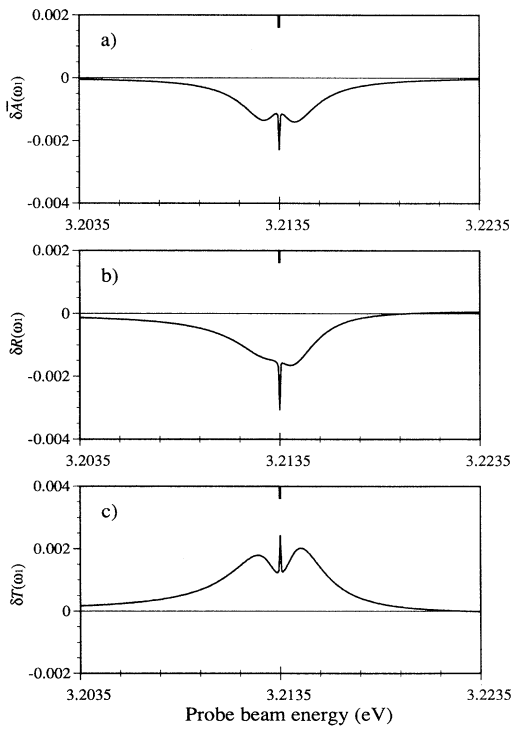

FIG. 1. Pump-induced change of normalized absorption (a), reflectance (b), and transmittance (c) for $N=6$. The tick mark in each graph indicates the one-exciton level. The values of the parameters used are given in the text.

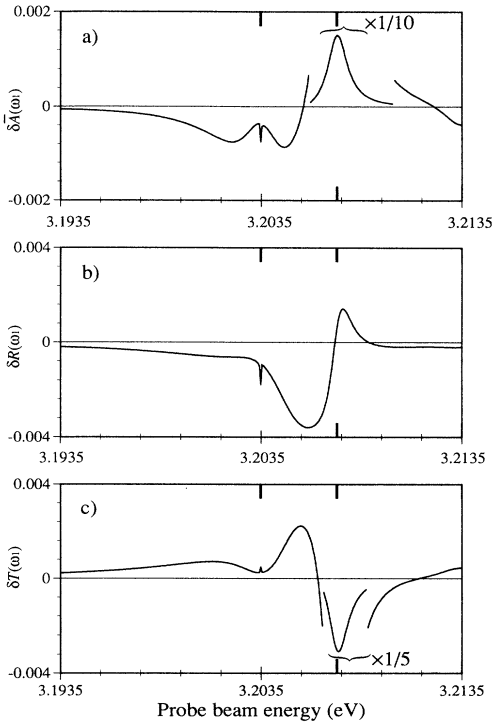

FIG. 2. The same as Fig. 1 for $N=20$. Tick marks, indicating the energy position of two-exciton level–lowest one-exciton level, are added at the bottom of each graph.

sake of comparison with Figs. 1(a) and 2(a). They are calculated in the following way: In expression (3.17), we pick up the terms which are proportional to $[F^{(2)}]^2 \times F^{(1)}$ and neglect the site dependence of $\mathcal{E}_l$, contained in each F. Then the summation over the site indices can be performed. As for the j-dependent factor $\sin Kj$, we replace it with an average value, namely, $\sum_j (\sin Kj)/N$. Dividing the result by $[\mathcal{E}(2)]^2\mathcal{E}(1)$, we obtain $\chi^{(3)}$ in the LWA. We recognize by comparison that there are remarkable differences between Fig. 1(a) and Fig. 3(a), and Fig. 2(a) and Fig. 3(b) especially in the shapes around the lowest one-exciton level and near the peak due to the induced absorption. We should note that the effect of nonlinear susceptibility appearing in the spectra depends very much on the magnitude of the linear susceptibility at the same energy point, which is to be expected from the renormalization procedure mentioned at the end of Sec. III.

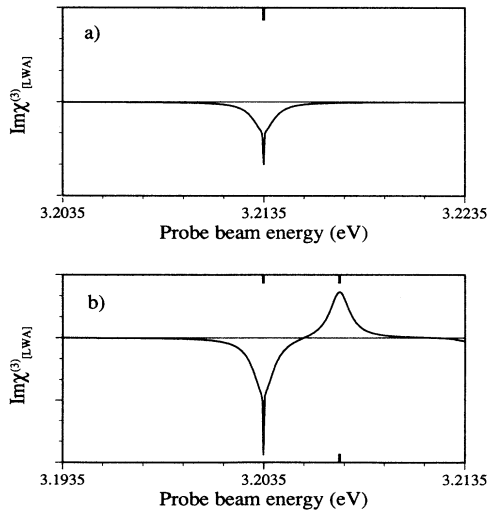

FIG. 3. Spectrum of $\mathrm{Im}\chi^{(3)}$ in LWA for $N=6$ (a) and $N=20$ (b). The meanings of tick marks are the same as in Figs. 1 and 2. The scale of the vertical axis is common to (a) and (b) in arbitrary units.

B. Size dependence of nonlinear optical spectra

Here, we see how the magnitude and shape of the spectra vary as N changes. Figures 4 and 5 show the size dependence of $\delta\overline{A}(\omega_1)$ and $\mathrm{Im}\chi^{(3)}$ in the LWA, respectively. It should be noted that the size dependence of $\delta\overline{A}(\omega_1)$ by nonlocal calculation is quite different from that of $\mathrm{Im}\chi^{(3)}$ in the LWA. In Fig. 5, we see the size enhancement of $\chi^{(3)}$, where the depth of the lowest-energy structure of $\mathrm{Im}\chi^{(3)}$ is kept developing within the range of N indicated in the figure. This is expected from the result of Ref. 8, in which we showed the size dependence of $\chi^{(3)}$ in the same model except that the boundary conditions for excitons were supposed to be periodic. On the other hand, the size enhancement of $\delta\overline{A}(\omega_1)$ in the nonlocal treatment (Fig. 4) is much suppressed, and for $N \geq 4$, the depth of the negative peak around the lowest one-exciton level starts to decrease. This is not due to the saturation of $\chi^{(3)}$, but to the size dependence of the amplitude of the pump field. As we pointed out in Ref. 9, the intensity of the internal field has a strong size dependence when it resonates with a size-quantized exciton level. In the present case, the amplitude of $\mathcal{E}(2)$ rapidly decreases as N increases in the size region indicated in the figure. Therefore, the size enhancement of $\delta\overline{A}(\omega_1)$ is suppressed at an earlier stage than that of $\chi^{(3)}$. To make it clearer, we calculate $\chi^{(3)}$ multiplied by the intensity of the internal field of the pump light averaged over the layers in the film $\langle I_{\mathrm{pump}} \rangle$. The size dependence of this quantity, shown in Fig. 6, follows well that of $\delta\overline{A}(\omega_1)$ in Fig. 4.

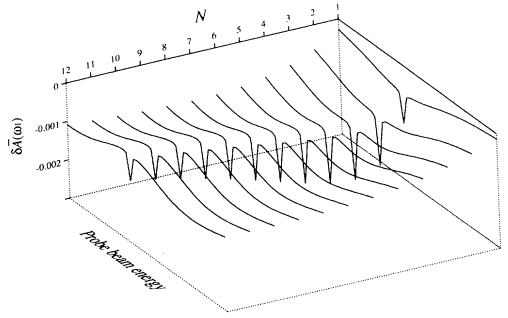

FIG. 4. The size dependence of $\delta\overline{A}$ near the lowest exciton level. The position of the lowest one-exciton state for each N is adjusted to a given energy. The full range of the probe beam energy is 3 meV.

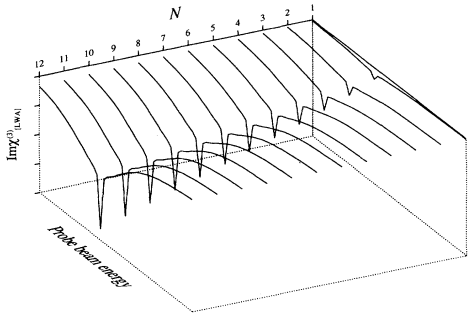

FIG. 5. The size dependence of Im$\chi^{(3)}$ in LWA near the lowest exciton level. The position of the lowest one-exciton state for each N is adjusted to a given energy. The full range of the probe beam energy is 3 meV. The scale of the vertical axes is common to Fig. 3 in arbitrary units.

C. Nonlocal calculation versus the LWA

Next, we compare the results of the fully nonlocal calculation and the LWA treatment. Their difference is expected to be seen as N increases. Our aim is to find out the critical region of N where their difference becomes appreciable. This comparison is necessary for both the linear and the nonlinear response. Since the case of the linear response was considered elsewhere,[19] we concentrate on the comparison of the nonlinear part in this paper, namely, the linear part of the probe beam response is calculated in the nonlocal way, and the nonlinear part is treated either nonlocally or in the LWA. The latter case is treated in the following way: In expression (3.17), we omit the terms which are proportional to the cube of $F^{(1)}$ because they are negligible as compared with the terms proportional to $[F^{(2)}]^2 \times F^{(1)}$. Then we neglect the site dependence of the pump field, namely,

$$\sum_l \sin(Kl)\mathcal{E}_l(2) \rightarrow \mathcal{E}(2)\sum_l \sin(Kl)\ , \tag{4.4}$$

and attribute $[\mathcal{E}(2)]^2$ to the pump field intensity averaged over the sites. The pump field itself is calculated in a fully nonlocal way by solving the nonlinear Maxwell's equation for the pump field alone. As for the probe field, we make the following replacement:

$$\sin(Kj)\sum_l \sin(kl)\mathcal{E}_l(1) \rightarrow f(K)\sum_l f(k)N\delta_{lj}\mathcal{E}_l(1)$$
$$= \mathcal{E}_j(1)Nf(K)f(k)\ , \tag{4.5}$$

where

$$f(K) = \frac{1}{N}\sum_n \sin(Kn)\ . \tag{4.6}$$

Thus, we can write the nonlinear term in Maxwell's equation for the probe field as

$$\bar{\chi}^{(3)}(-\omega_1;\omega_1,\omega_2,-\omega_2)|\mathcal{E}(2)|^2\mathcal{E}_j(1)e^{-i\omega_1 t}\ . \tag{4.7}$$

Since (4.7) has the form where the site-dependent field $\mathcal{E}_j(1)$ is multiplied by a site-independent constant, we can formally treat it as an additional term of the linear polarization.

This approximation means that the pump field is treated in the LWA and an effect of the probe field on the polarization is supposed to be local. In this approximation, the nonlocality is represented by the effect of the size enhancement of $\chi^{(3)}$ alone.

The result is shown in Fig. 7 for $N=20$ (108 Å). For larger N, the difference of the solid and dashed curves becomes more distinct. Even in this small size ($N=20$), which is much smaller than the wavelength of light, a clear difference between the nonlocal and approximated treatments begins to appear. If we do not neglect the site dependence of the pump field in the latter treatment, while keeping the local treatment of the probe beam, the result cannot be distinguished from the full nonlocal result until N becomes much larger.[20] Thus, the above difference should be attributed to the LWA of the pump beam. The reason why the LWA treatment starts to break down in such a small system size is that the internal field resonating with the exciton has quite a short wavelength and has a strong site dependence, which becomes appreciable already in this small size region.[9] This

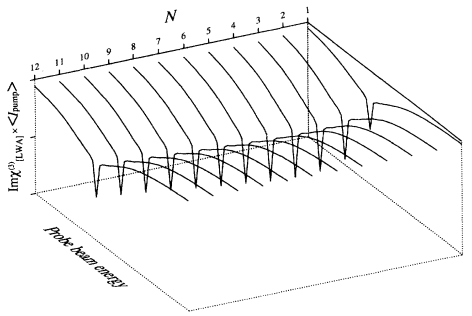

FIG. 6. The size dependence of Im$\chi^{(3)}$ in LWA multiplied by $\langle I_{\text{pump}} \rangle$ near the lowest exciton level. The position of the lowest one-exciton state for each N is adjusted to a given energy. The full range of the probe beam energy is 3 meV. The unit of the vertical axis is arbitrary.

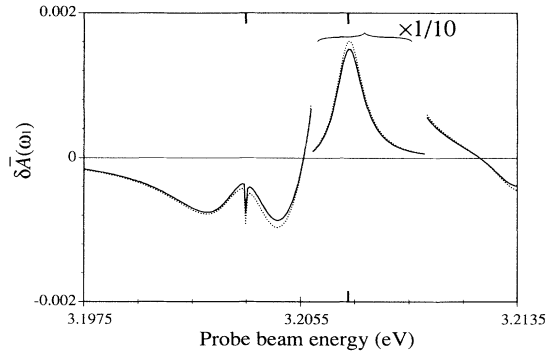

FIG. 7. Comparison of $\delta\bar{A}=20$ calculated by the fully nonlocal method (solid line) and by the method partly including LWA and LA (dotted line). The meaning of the tick marks is the same as in Figs. 1 and 2.

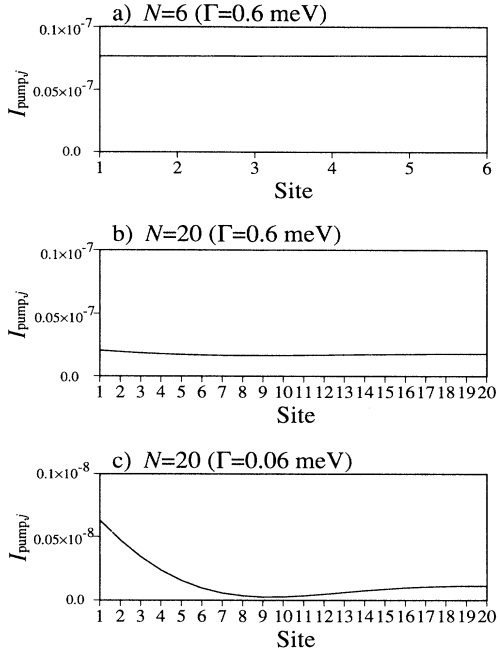

FIG. 8. The site dependence of $I_{\text{pump},j}$ for (a) $N=6$, $\Gamma=0.6$ meV, (b) $N=20$, $\Gamma=0.6$ meV, and (c) $N=20$, $\Gamma=0.06$ meV. The numbers on the horizontal axis denote the position of the layers in the film from the front to the back surface. The unit of the vertical axis is $(\text{V/cm})^2$.

becomes clear if we actually see the site dependence of the internal field. In Figs. 8(a) and 8(b), the site dependence of the intensity of the internal field $I_{\text{pump},j}$ for $N=6$ and 20 of the above model is shown. In the former case, the intensity of the internal field is almost constant in the media. In the latter case, on the other hand, the site dependence of the internal field begins to appear. For a smaller value of Γ ($=0.06$ meV), this is more obvious [Fig. 8(c)]. For such a small damping, the nonlinear signal shows a remarkable change, which we report in a subsequent publication.

V. DISCUSSION

In the preceding sections, we have given a formulation of the nonlinear response of nonlocal media by extension of the ABC-free theory for the linear response. In this extension, we use the fact that the general feature of the site-represented linear susceptibility also holds true in the nonlinear susceptibility, i.e., it is written in a sum of the products of functions of each coordinate. Further, we have shown the feasibility of the method by treating a simple example numerically. Though the system size is limited, we could obtain the complete solutions of the nonlocal and nonlinear Maxwell's equations, considering the microscopic details of the model exactly. The fields in the medium have been determined, not from the LWA, but by solving the simultaneous nonlinear equations, where the solution of each beam is affected by the presence of the other beams.

As to the intensities of the pump and probe beams, we have not made any assumption. However, if the former is larger than the latter by two orders of magnitude, the result cannot be distinguished from that of a simplified version where, the pump field being determined by itself, the equation for the probe field is linearized by employing the fixed pump field. This version requires much less time than the fully nonlinear treatment, and therefore is quite useful if the condition allows it.

The results of our demonstration show another factor for size dependence of nonlinearity besides nonlinear susceptibility. Since the amplitude of the internal field in resonance with an exciton has a strong size dependence in a mesoscopic system, it was expected that the size dependence of the nonlinearity appearing in the spectra would be much affected by this.[9] Actually, the size dependence of normalized absorption follows that of $\text{Im}\chi^{(2)}_{(\text{LWA})}\times\langle I_{\text{pump}}\rangle$ rather than $\text{Im}\chi^{(3)}_{(\text{LWA})}$ only. This fact indicates that the size dependence of the internal field should be taken into account when the resonant nonlinear response is analyzed. Though the above effect of the internal field in the case of small size can be described by the LWA to some extent, it can no longer be treated as an averaged quantity if its site dependence becomes stronger as the system size increases. This was demonstrated as the difference between the results of the LWA and the fully nonlocal calculation in the preceding section.

According to our result, the LWA is broken when the size exceeds 20 atomic layers. Though this may seem smaller than expected, it is not surprising, because the resonant internal field has the mesoscopic scale of a wavelength. Thus, the site variation of the internal field can be seen even in such a small size. When the site dependence of the internal field is not negligible, the response field can be obtained only by the fully nonlocal calculation because the polarization and the internal field as functions of sites are determined self-consistently with each other.

Though we have shown the validity limit of the LWA by the use of the nonlocal treatment, there are still more points to be studied about the nonlocal theory. First of all, we need to develop a more practical scheme which allows us to treat larger systems, since the size range treated in the present work is too small to cover many cases of actual interest in various materials.

In the present method, we treat all of the one- and two-exciton states in the model system. This needs a long computing time to prepare the nonlinear terms in $\chi^{(3)}$ in a large system. Omitting the higher nonresonant levels of the two-exciton states would be the simplest improvement. But the adoption of this method needs careful examination of the cancellation problem,[7] because the extent of the contribution of each term to the cancellation is quite delicately dependent on the material parameters.

If it becomes possible to calculate the nonlinear response of the larger system, we can treat an interesting problem: It is known that the internal field of a resonant light is resonantly size enhanced at a certain mesoscopic size due to its interference in a thin film.[9] We can expect a remarkably large and peculiar nonlocal response under such a condition. The question of how the nonlinear

response appears in this case can be answered concretely only by the fully nonlocal formalism for the nonlinear response. We are preparing the report of this calculation by an improved method.

The effect of exciton-exciton interaction $H_{\text{ex-ex}}$ in the nonlinear response is another remaining problem to study. As we discussed in Ref. 7, the presence of $H_{\text{ex-ex}}$ leads to bound two-exciton states (excitonic molecule states) and the poles of these states are separated from those of the two-exciton bands. This redistribution of poles must change the manner of the cancellation around the lowest one-exciton level, and the size dependence of $\chi^{(3)}$ in this region becomes different from that in the absence of $H_{\text{ex-ex}}$. How this effect is reflected in the nonlinear optical spectra is an interesting issue. Since many materials have excitonic molecule states, the introduction of $H_{\text{ex-ex}}$ into the model is desirable within the framework of the nonlocal theory. As for the present numerical method, it is relatively easy to introduce it, while it is difficult in the case of a rigorous analytical calculation such as that in Ref. 7. We will report on this problem elsewhere.

VI. SUMMARY

We have formulated a nonlocal theory of the nonlinear optical response by an extension of the ABC-free theory. In this formulation, Maxwell's equations in terms of the site-represented linear and third-order nonlinear susceptibilities are solved numerically, and the optical spectra such as reflectance and transmittance including the nonlinear effect can be obtained. We have demonstrated its application to the model of finite one-dimensional Frenkel excitons.

The calculations have been performed for small system size, and it has been made clear that the size dependence of the internal field in the mesoscopic system size has an important role in the size-dependent nonlinearity appearing in the optical spectra, and that the nonlocality appears in the spectra even in the case of a much smaller size than the relevant light wavelength. We have shown the former explicitly by the results that the size dependence of spectra of the normalized absorption including the nonlinear effect does not coincide with that of $\chi^{(3)}$ in the long-wavelength approximation, but almost follows that of $\chi^{(3)}$ in the LWA multiplied by the averaged intensity of the internal field. As for the latter, we compared the results of the fully nonlocal calculation and that by the LWA. As a result, the difference between the spectra by these methods begins to appear from the size of about 20 atomic layers (about 108 Å thickness).

Though the treated model is simple and the system size is limited, the necessity and feasibility of the nonlocal theory for the study of the nonlinear optical response in mesoscopic systems have been shown by these demonstrations.

ACKNOWLEDGMENTS

The authors are grateful to Professor A. Yoshimori for his support and to Dr. Y. Ohfuti for his useful discussions. This work was supported in part by Grant-in-Aid for Scientific Research on Priority Area, "Electron Wave Interference Effects in Mesoscopic Structures" from the Ministry of Education, Science and Culture of Japan.

APPENDIX A: THE EXPRESSION OF SITE-REPRESENTED THIRD-ORDER POLARIZATION $P_j^{(3)}$

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

$$P_j^{(3)}(t)=\frac{(-i)^3}{v_0}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\langle[[[P_j(t),H'(t_1)],H'(t_2)],H'(t_3)]\rangle\ , \tag{A1}$$

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 representation of the polarization operator and electron-radiation interaction, respectively,

$$P_j(t)=\exp(iH_0t)P_j\exp(-iH_0t)\ , \tag{A2}$$

$$H'(t)=\exp(iH_0t)\left[-\sum_n\sum_s P_n\mathcal{E}_n(s)\exp(-i\omega_s t+\gamma t)\right]\exp(-H_0t)\ , \tag{A3}$$

H_0 being the unperturbed Hamiltonian, $\gamma=0^+$ the factor for adiabatic switching of the electron-radiation interaction, and $\mathcal{E}_n(s)$ the amplitude of the electric field at site n with frequency ω_s. As the interaction term, we have neglected the term arising from $\sum_l(e^2/2mc^2)A(\mathbf{r}_l,t)^2$, since we are interested in resonant optical processes. Decomposing the threefold commutator and carrying out the integration in (A1), (A2), and (A3), we get the expression

$$P_j^{(3)}(t)=\sum_l\sum_m\sum_n\sum_p\sum_q\sum_s\exp[-i(\omega_p+\omega_q+\omega_s+3i\gamma)t]\mathcal{E}_l(p)\mathcal{E}_m(q)\mathcal{E}_n(s)\chi^{(3)}_{jlmn}(\omega_p,\omega_q,\omega_s)\ , \tag{A4}$$

where

$$\chi^{(3)}_{jlmn}(\omega_p,\omega_q,\omega_s)=(1/v_0)\sum_{\lambda}\sum_{\mu}\sum_{\nu}\left[\frac{\langle 0|P_j|\lambda\rangle\langle\lambda|P_l|\mu\rangle\langle\mu|P_m|\nu\rangle\langle\nu|P_n|0\rangle}{(E_{\lambda 0}-\Omega_3')(E_{\mu 0}-\Omega_2')(E_{\nu 0}-\omega_s')}\right.$$
$$+\frac{\langle 0|P_n|\lambda\rangle\langle\lambda|P_l|\mu\rangle\langle\mu|P_j|\nu\rangle\langle\nu|P_m|0\rangle}{(E_{\nu\mu}-\Omega_3')(E_{\nu\lambda}-\Omega_2')(E_{0\lambda}-\omega_s')}+\frac{\langle 0|P_n|\lambda\rangle\langle\lambda|P_m|\mu\rangle\langle\mu|P_j|\nu\rangle\langle\nu|P_l|0\rangle}{(E_{\nu\mu}-\Omega_3')(E_{0\mu}-\Omega_2')(E_{0\lambda}-\omega_s')}$$
$$+\frac{\langle 0|P_m|\lambda\rangle\langle\lambda|P_l|\mu\rangle\langle\mu|P_j|\nu\rangle\langle\nu|P_n|0\rangle}{(E_{\nu\mu}-\Omega_3')(E_{\nu\lambda}-\Omega_2')(E_{\nu 0}-\omega_s')}+\frac{\langle 0|P_n|\nu\rangle\langle\nu|P_m|\mu\rangle\langle\mu|P_l|\lambda\rangle\langle\lambda|P_j|0\rangle}{(E_{\lambda 0}+\Omega_3')(E_{\mu 0}+\Omega_2')(E_{\nu 0}+\omega_s')}$$
$$+\frac{\langle 0|P_m|\nu\rangle\langle\nu|P_j|\mu\rangle\langle\mu|P_l|\lambda\rangle\langle\lambda|P_n|0\rangle}{(E_{\nu\mu}+\Omega_3')(E_{\nu\lambda}+\Omega_2')(E_{0\lambda}+\omega_s')}+\frac{\langle 0|P_l|\nu\rangle\langle\nu|P_j|\mu\rangle\langle\mu|P_m|\lambda\rangle\langle\lambda|P_n|0\rangle}{(E_{\nu\mu}+\Omega_3')(E_{0\mu}+\Omega_2')(E_{0\lambda}+\omega_s')}$$
$$\left.+\frac{\langle 0|P_n|\nu\rangle\langle\nu|P_j|\mu\rangle\langle\mu|P_l|\lambda\rangle\langle\lambda|P_m|0\rangle}{(E_{\nu\mu}+\Omega_3')(E_{\nu\lambda}+\Omega_2')(E_{\nu 0}+\omega_s')}\right]. \tag{A5}$$

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

$$H_0|\xi\rangle=E_\xi|\xi\rangle,\quad \xi=0,\lambda,\mu,\nu\ , \tag{A6}$$
$$E_{\xi\eta}=E_\xi-E_\eta\ , \tag{A7}$$
$$\Omega_3'=\omega_p+\omega_q+\omega_s+3i\gamma\ , \tag{A8}$$
$$\Omega_2'=\omega_q+\omega_s+2i\gamma\ , \tag{A9}$$
$$\omega_s'=\omega_s+i\gamma\ . \tag{A10}$$

APPENDIX B: THE EXPLICIT EXPRESSIONS OF G_0, G_1, H_0, H_1, $\bar{H}_0$, and $\bar{H}_1$

$$G_0(K,K';\omega)=\frac{1}{[\omega+i\Gamma-E_1(K)][(E_1(K')-\omega)^2+\Gamma^2]}\frac{2\Gamma}{\gamma}$$
$$-\frac{1}{[\omega+i\Gamma-E_1(K)](i\Gamma_{KK'}-E_{KK'})}\left\{\frac{1}{E_1(K')-\omega+i\Gamma}+\frac{1}{\omega+i\Gamma-E_1(K)}\right\}, \tag{B1}$$

$$G_1(K,K',k,k';\omega)=\sum_{\mu}4C^{(\mu)}_{KK'}C^{(\mu)}_{kk'}\left\{-\frac{1}{[\omega+i\Gamma-E_1(K)](2\omega+2i\Gamma-E_\mu)[\omega+i\Gamma-E_1(k')]}\right.$$
$$+\frac{1}{(\omega+i\Gamma-E_{\mu K'})(i\Gamma_{k'K'}-E_{k'K'})[E_1(K')-\omega+i\Gamma]}$$
$$+\frac{1}{(\omega+i\Gamma-E_{\mu K'})(i\Gamma_{k'K'}-E_{k'K'})[\omega+i\Gamma-E_1(k')]}$$
$$\left.+\frac{1}{(\omega+i\Gamma-E_{\mu K'})(2\omega+2i\Gamma-E_\mu)[\omega+i\Gamma-E_1(k')]}\right\}, \tag{B2}$$

$$H_0(K,K';\omega_1,\omega_2)=\frac{1}{[\omega_1+i\Gamma-E_1(K)]\{[E_1(K')-\omega_2]^2+\Gamma^2\}}\frac{2\Gamma}{\gamma}-\frac{1}{[\omega_1+i\Gamma-E_1(K)](\omega_1-\omega_2+i\Gamma_{KK'}-E_{KK'})}$$
$$\times\left\{\frac{1}{E_1(K')-\omega_2+i\Gamma}+\frac{1}{\omega_1+i\Gamma-E_1(K)}\right\}, \tag{B3}$$

$$H_1(K,K',k,k';\omega_1,\omega_2)=\sum_{\mu}4C^{(\mu)}_{KK'}C^{(\mu)}_{kk'}\left\{\frac{-1}{[\omega_1+i\Gamma-E_1(K)](\omega_1+\omega_2+2i\Gamma-E_\mu)[\omega_2+i\Gamma-E_1(k')]}\right.$$
$$+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(i\Gamma_{k'K'}-E_{k'K'})[E_1(K')-\omega_2+i\Gamma]}$$
$$+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(i\Gamma_{k'K'}-E_{k'K'})[\omega_2+i\Gamma-E_1(k')]}$$
$$\left.+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(\omega_1+\omega_2+2i\Gamma-E_\mu)[\omega_2+i\Gamma-E_1(k')]}\right\}, \tag{B4}$$

$$\bar{H}_0(K,K';\omega_1,\omega_2)=-\frac{1}{[\omega_1+i\Gamma-E_1(K)](\omega_1-\omega_2+i\gamma)}\left\{\frac{1}{E_1(K')-\omega_2+i\Gamma}+\frac{1}{\omega_1+i\Gamma-E_1(K')}\right\}$$
$$-\frac{1}{[\omega_1+i\Gamma-E_1(K)](i\Gamma_{KK'}-E_{KK'})}\left\{\frac{1}{E_1(K')-\omega_2+i\Gamma}+\frac{1}{\omega_2+i\Gamma-E_1(K)}\right\}, \tag{B5}$$

$$\bar{H}_1(K,K',k,k';\omega_1,\omega_2)=\sum_{\mu}4C_{KK'}^{(\mu)}C_{kk'}^{(\mu)}$$
$$\times\left\{-\frac{1}{[\omega_1+i\Gamma-E_1(K)](\omega_1+\omega_2+2i\Gamma-E_\mu)[\omega_1+i\Gamma-E_1(k')]}\right.$$
$$+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(\omega_1-\omega_2+i\Gamma_{k'K'}-E_{k'K'})[E_1(K')-\omega_2+i\Gamma]}$$
$$+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(\omega_1-\omega_2+i\Gamma_{k'K'}-E_{k'K'})[\omega_1+i\Gamma-E_1(k')]}$$
$$\left.+\frac{1}{(\omega_1+i\Gamma-E_{\mu K'})(\omega_1+\omega_2+2i\Gamma-E_\mu)[\omega_1+i\Gamma-E_1(k')]}\right\}. \tag{B6}$$

APPENDIX C: MAXWELL'S EQUATIONS, GENERAL SOLUTIONS, SIMULTANEOUS EQUATIONS, AND MBC'S FOR THE NONLOCAL CALCULATION IN SEC. III

Maxwell's equation (for the discrete lattice model) in terms of $P_j^{(1)}(t)$ in (3.18), and $P_j^{(3)}(t)|_{(\text{tri. res.})}$ in (3.17) for the frequency ω_1 is

$$[\Delta^2-(2\cos q_1-2)]\mathcal{E}_j(1)-\sum_K \sin Kj\left[\left\{B_1^{(1)}\left[\frac{2}{N+1}\right]^{1/2}\frac{1}{\omega_1+i\Gamma-E_1(K)}\right.\right.$$
$$-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\sum_{K'}|F_{K'}^{(2)}|^2H_0(K,K';\omega_1,\omega_2)$$
$$\left.-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(2)}]H_1(K,k,K,k';\omega_1,\omega_2)\right\}F_K^{(1)}$$
$$-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\sum_{K'(\neq K)}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(2)}]H_1(K,k,K',k';\omega_1,\omega_2)F_{K'}^{(1)}$$
$$-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\left\{\sum_{K'}[F_{K'}^{(2)*}F_{K'}^{(1)}]\bar{H}_0(K,K';\omega_1,\omega_2)\right.$$
$$\left.+\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(1)}]\bar{H}_1(K,k,K,k';\omega_1,\omega_2)\right\}F_K^{(2)}$$
$$-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\sum_{K'(\neq K)}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(1)}]\bar{H}_1(K,k,K',k';\omega_1,\omega_2)F_{K'}^{(2)}$$
$$-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\left\{\sum_{K'}|F_{K'}^{(1)}|^2G_0(K,K';\omega_1)\right.$$
$$\left.+\sum_k\sum_{k'}[F_k^{(1)*}F_{k'}^{(1)}]G_1(K,k,K,k';\omega_1)\right\}F_K^{(1)}$$
$$\left.-B_1^{(3)}\left[\frac{2}{N+1}\right]^{1/2}\sum_{K'(\neq K)}\sum_k\sum_{k'}[F_k^{(1)*}F_{k'}^{(1)}]G_1(K,k,K',k';\omega_1)F_{K'}^{(1)}\right]=0\,, \tag{C1}$$

where

$$\Delta^2\mathcal{E}_j=\mathcal{E}_{j+1}-2\mathcal{E}_j+\mathcal{E}_{j-1}\ , \tag{C2}$$

$$q_1=a_0\frac{\omega_1}{c}\sqrt{\varepsilon_b}\ , \tag{C3}$$

$$B_1^{(1)}=Q_1^2\frac{M^2}{v_0}\ , \tag{C4}$$

$$B_1^{(3)}=Q_1^2\frac{M^4}{v_0}\ , \tag{C5}$$

in the above expressions,

$$Q_1^{(2)}=a_0^2\frac{4\pi\omega_1^2}{c^2}\ , \tag{C6}$$

and a_0 is the lattice constant. The corresponding equation for frequency ω_2 can be obtained by the replacements $[F^{(1)}, \mathcal{E}(1)\rightleftharpoons F^{(2)}, \mathcal{E}(2)]$ and $(\omega_1\rightleftharpoons\omega_2)$ in (C1) and (C3)–(C6).

The general solution of Eq. (C1) is written in the following form:

$$\mathcal{E}_j(1)=\mathcal{E}^1e^{iq_1j}+\overline{\mathcal{E}}^1e^{iq_1(N+1-j)}+\sum_K\frac{\sin Kj}{2\cos K-2\cos q_1}\tilde{A}(K)\ , \tag{C7}$$

where $\tilde{A}(K)$ is the quantity inside the large square brackets in (C1).

Inserting the above solution into the definition of F, (3.12), we obtain the simultaneous cubic equations for $\{F\}$:

$$\begin{aligned}
&\left[1-\frac{1}{2\cos K-2\cos q_1}\left\{B_1^{(1)}\frac{1}{\omega_1+i\Gamma-E_1(K)}-B_1^{(3)}\sum_{K'}|F_{K'}^{(2)}|^2H_0(K,K';\omega_1,\omega_2)\right.\right.\\
&\qquad -B_1^{(3)}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(2)}]H_1(K,k,K,k';\omega_1,\omega_2)-B_1^{(3)}\sum_{K'}|F_{K'}^{(1)}|^2G_0(K,K';\omega_1)\\
&\qquad \left.\left.-B_1^{(3)}\sum_k\sum_{k'}[F_k^{(1)*}F_{k'}^{(1)}]G_1(K,k,K,k';\omega_1)\right\}\right]F_K^{(1)}\\
&+\frac{1}{2\cos K-2\cos q_1}B_1^{(3)}\left\{\sum_{K'}[F_{K'}^{(2)*}F_{K'}^{(1)}]\bar{H}_0(K,K';\omega_1,\omega_2)+\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(1)}]\bar{H}_1(K,k,K,k';\omega_1,\omega_2)\right\}F_K^{(2)}\\
&+\frac{1}{2\cos K-2\cos q_1}\sum_{K'(\neq K)}\left\{B_1^{(3)}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(2)}]H_1(K,k,K',k';\omega_1,\omega_2)\right.\\
&\qquad \left.+B_1^{(3)}\sum_k\sum_{k'}[F_k^{(1)*}F_{k'}^{(1)}]G_1(K,k,K',k';\omega_1)\right\}F_{K'}^{(1)}\\
&+\frac{1}{2\cos K-2\cos q_1}\sum_{K'(\neq K)}\left\{B_1^{(3)}\sum_k\sum_{k'}[F_k^{(2)*}F_{k'}^{(1)}]\bar{H}_1(K,k,K',k';\omega_1,\omega_2)\right\}F_{K'}^{(2)}\\
&-\mathcal{E}^1\left[\frac{2}{N+1}\right]^{1/2}\frac{\sin K}{2\cos K-2\cos q_1}\{(-1)^ne^{iq_1(N+1)}-1\}\\
&\qquad -\overline{\mathcal{E}}^1\left[\frac{2}{N+1}\right]^{1/2}\frac{\sin K}{2\cos K-2\cos q_1}\{(-1)^n-e^{iq_1(N+1)}\}=0\ ,
\end{aligned} \tag{C8}$$

where the integer n is related with K through $K=n\pi/(N+1)$. By the replacements $(\omega_1,\ F^{(1)}\rightleftharpoons\omega_2,\ F^{(2)})$ and $(\mathcal{E}^1,\overline{\mathcal{E}}^1)\rightarrow(\mathcal{E}^2,\overline{\mathcal{E}}^2)$, we can obtain another set of simultaneous equations corresponding to Maxwell's equation for the frequency ω_2.

We write the MBC's for the general solution (C7). Let

$$\mathcal{E}^{1,i}\exp(ik_0^{(1)}j)+\mathcal{E}^{1,r}\exp(-ik_0^{(1)}j)\ , \tag{C9}$$

and

$$\mathcal{E}^{1,t}\exp[ik_0^{(1)}(j-N-1)]\ , \tag{C10}$$

be the external field at $j<0$ and $j>N+1$, respectively, where

$$k_0^{(1)}=a_0\frac{\omega_1}{c}\ . \tag{C11}$$

Then, the MBC's at $j=0$ are

$$\mathcal{E}^{1,i}+\mathcal{E}^{1,r}=\mathcal{E}^1+\overline{\mathcal{E}}^{\,1}e^{iq_1(N+1)}\ , \tag{C12}$$

$$\mathcal{E}^{1,i}(e^{ik_0^{(1)}}-1)+\mathcal{E}^{1,r}(e^{-ik_0^{(1)}}-1)=\mathcal{E}^1(e^{iq_1}-1)+\overline{\mathcal{E}}^{\,1}(e^{-iq_1}-1)e^{iq_1(N+1)}+\sum_K\frac{\sin K}{2\cos K-2\cos q_1}\tilde{A}(K)\ , \tag{C13}$$

and at $j=N+1$

$$\mathcal{E}^1e^{iq_1(N+1)}+\overline{\mathcal{E}}^{\,1}=\mathcal{E}^{1,t}\ , \tag{C14}$$

$$\mathcal{E}^1e^{iq_1(N+1)}(1-e^{-iq_1})+\overline{\mathcal{E}}^{\,1}(1-e^{iq_1})+\sum_K\frac{(-1)^n\sin K}{2\cos K-2\cos q_1}\tilde{A}(K)=\mathcal{E}^{1,t}(1-e^{-ik_0^{(1)}})\ . \tag{C15}$$

In a similar way, the MBC's for frequency ω_2 can also be obtained. Thus, if we give the amplitudes of incident fields for frequencies ω_1 and ω_2, Eqs. (C8), (C12), (C13), (C14), (C15), and corresponding equations for the frequency ω_2 become a complete set of simultaneous equations to determine the optical response.

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