Nonlocality-induced anomalous input-intensity dependence of optical response for weakly confined excitons in an ultrathin film

Hajime Ishihara*
Department of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
(Received 13 March 2002; published 6 March 2003)

By means of the nonlocal theory of the nonlinear optical response, an anomalous input-intensity dependence of the optical response was demonstrated for an ultrathin film confining the center-of-mass motion of excitons. We showed that (i) the inverted type of input-output characteristics arise from the peculiar input-intensity dependence of the nanoscale spatial structure of the internal field due to the uneven feedback effect of the different components in the field relevant to the confined excitonic levels, and (ii) the nanoscale Fabry-Pérot interference of polaritons gives rise to a bistability, even in an ultrathin film with a thickness of about 20 nm.

DOI: 10.1103/PhysRevB.67.113302 PACS number(s): 78.66.−w, 78.20.Bh, 42.65.−k

One of the most interesting aspects in the optical response of confined excitonic systems is that the coherence of a single quantum state is manifested as the sample-size, shape, and internal structure dependence of observed quantities. The size quantization is a result of the coherence of quantum states in a whole volume of the sample, which has been discussed thoroughly for the various types of confinement geometry such as quantum wells[1] and quantum dots,[2] through the studies of the size-dependent spectral structures of optical responses. In contrast to this aspect, the nonlocal response, which also arises from the coherent extension of the quantum states, has not been studied sufficiently, especially for the nonlinear-response regime. If the coherent length of a quantum state reaches the wavelength of the resonant light, the nonlocal response plays an important role, and a proper description of the induced polarization is necessary. For the linear response, for example, the induced polarization should be written

$$\mathbf{P}^{(1)}(\mathbf{r};\omega)=\int \chi^{(1)}(\mathbf{r},\mathbf{r}';\omega)\mathbf{E}(\mathbf{r}')d\mathbf{r}', \tag{1}$$

where $\chi^{(1)}$ and $\mathbf{E}(\mathbf{r})$ are the linear susceptibility and the field amplitude, respectively. Since the radiation is determined self-consistently with the induced polarization, the internal field generally contains components with a spatial structure similar to that of the wave functions of the excited states. It has been shown that a particular component is resonantly enhanced due to the nanoscale Fabry-Pérot interference if certain conditions of size and energy are met.[3] Such behavior of the internal field brings about anomalous size dependence of the nonlinear response[4–6] in a mesoscopic regime, which is beyond the previously discussed size dependence of the nonlinear response based on the long-wavelength approximation.[7–9]

In addition to the size dependence of nonlinearity, input-intensity dependence for nonlocal media is also expected to be different from that for local media because of the nanoscale Fabry-Pérot interference and the uneven feedback effect of the different components of the internal field. One of the attracting nonlinear input-output characteristics is the bistability effect, which was extensively studied during the 1980s. As discussed in an early paper by Gibbs *et al.*,[10] nonlinearity and a certain feedback mechanism should work in a bistable system. Since the excitonic resonance provides effective nonlinearity, a number of schemes of bistability by excitonic systems plus some feedback mechanisms have been proposed, both experimentally and theoretically.[11] (For more recent works, see Refs. 12–16). However, similar studies which considered the nonlocal response have been poorly performed, though nonlocality is an essential element of the excitonic resonance in confined systems.

In this report, we demonstrate an anomalous nonlinear input-intensity dependence of the optical response by means of the nonlocal theory of the nonlinear response,[17] where the nanoscale spatial structure of the internal field is properly treated. The point of this theory is to solve the Maxwell equations containing the linear and third-order polarizations written in a nonlocal form. These polarizations can be rewritten in terms of the quantities defined as $F_\lambda=\int \rho_\lambda(\mathbf{r})\mathbf{E}(\mathbf{r})d\mathbf{r}$ and a similar one, $F_{n\nu}$ for a (one excitons $\rightarrow$ two excitons) transition by use of the separable form of the susceptibility in respect to the coordinates,[17] where $\rho_\lambda(\mathbf{r})$ is the dipole density relevant to the excitonic state labeled by λ. Using this result, the Maxwell equations are reduced to the simultaneous cubic equations for $\{F\}$, which can be solved together with Maxwell's boundary conditions at the surfaces of the medium (related to the background dielectric constant), and all the amplitudes of the internal and external fields are fixed.

For a numerical demonstration, we use the simplified model of a thin film consisting of a bundle of independent one-dimensional chains of size N (lying perpendicular to the surface) confining Frenkel-type excitons. The transfer effect along the direction parallel to the surface is neglected in this model. We assume the normal incidence of beams. The unperturbed Hamiltonian is

$$\mathcal{H}=\sum_{l=0}^{N+1}\varepsilon_0 b_l^\dagger b_l - b\sum_{l=1}^{N+1}(b_{l-1}^\dagger b_l + b_l^\dagger b_{l-1}), \tag{2}$$

where $b_l^\dagger$ and b_l are the creation and annihilation operators of an exciton on the lth site, ε_0 is the excitation energy of each site, b is the transfer energy, and we suppose the amplitudes of excitons to be zero at $l=0$ and $N+1$. The eigenenergies and eigenfunctions are those of typical Frenkel excitons. Two-exciton states are numerically calculated by

expanding them with the products of the one-exciton states.[17] Although the exciton-exciton interaction generally affects the absolute value of the nonlinear signal at one-exciton resonance through the cancellation effect between the one-exciton and two-exciton contributions,[18,19] we omit it because we are studying in the small size regime, where the cancellation is ineffective due to the wider level spacing than that of the peak widths in the spectrum, which allows us to concentrate our attention on the problem of how the spatial structure of the internal field affects the intensity dependence of the response.

The procedure of the calculation is as follows. First, by use of the eigenvalues and eigenfunctions of one- and two-exciton states, we calculated the site represented linear polarization $P_j^{(1)}$ and the third-order polarization $P_j^{(3)}$ for arbitrary frequencies according to the usual perturbation expansion method of the density matrix.[18] In this stage, we introduced the phenomenological damping constants γ for the population decay and Γ for the phase decay in the usual way.[20] Among the terms in the nonlinear polarization, we picked up the contribution of the most (triply) resonant terms for the frequency that is the same as the incident frequency ω. The third-order polarization $P_j^{(3)}$ can be written in the following form:

$$P_j^{(3)}(\omega)\big|_{(\text{tri res})} = \frac{M^4}{v_0}\sqrt{\frac{2}{N+1}}\sum_n \sin K_n j\left[\sum_{n'} |F_{n'}|^2 F_n G_0(n,n';\omega) + \sum_{n'}\sum_{m}\sum_{m'} F_{n'}^* F_m F_{m'} G_1(n,n',m,m';\omega)\right], \quad (3)$$

where M is the transition dipole moment per unit cell, v_0 is the unit-cell volume, and K_n is the wave number of the quantized center-of-mass (c.m.) motion of excitons. Its allowed values are $K_n = n\pi/(N+1), \{n=1,2,\ldots,N\}$. The definition of F_n is

$$F_n = \sqrt{\frac{2}{N+1}}\sum_j \sin K_n j \mathcal{E}_j, \quad (4)$$

where $\mathcal{E}_j$ is the electric field at site j. In Eq. (3), G_0 has the poles for one-exciton resonance and G_1 has those for the two-exciton resonance in addition to the poles for one-exciton resonance [see Eqs. (B1) and (B2) in Ref. 17].

Although we can obtain the formal solution of the above Maxwell equations in the form including $\{F_n\}$, it contains the internal field $\mathcal{E}_j$ in itself through the definition (4). If we substitute this solution into the definition (4), we obtain the simultaneous cubic equations for the unknown parameters $\{F_n\}$ which can be solved numerically together with Maxwell's boundary conditions. (See Appendix C in Ref. 17.)

We used the iterative method to solve the cubic equations of $\{F_n\}$. In sweeping the input intensity, we started from the intensity near the linear-response region, employing the solutions of $\{F_n\}$ for the linear response as the zeroth-order solutions, because the deviation of the convergent solutions from the linear one is not very large. After the convergent solutions were obtained, we moved to the higher input intensity and performed the iterative calculation employing the previous solutions as zeroth-order solutions. Repeating such steps, we swept in the input-intensity domain. Interestingly, we can find another set of solutions by sweeping from the higher intensity to the lower, if the bistable solutions are possible. It is difficult to obtain such solutions in a general way, because the simultaneous equations for unknown parameters $\{F_n\}$ have many dimensions, and mathematically a large number of solutions exist.

In the following, we show the results with the material parameters for the Z_3 exciton in CuCl, which is a typical single-component exciton with a large binding energy (213 meV). Namely, $\hbar\omega_T = 3202.2$ meV, $b = 57.0$ meV, $4\pi|M|^2/v_0 = 5.7$ meV, $\varepsilon_b = 5.6$, $a_0 = 5.4$ Å, and $\Gamma(\gamma) = 0.06\ (0.02)$ meV, where $\hbar\omega_T$ is the energy of the bottom of the exciton band for $N\to\infty$ ($\hbar\omega_T = \varepsilon_0 - 2b$), ε_b is the background dielectric constant, and a_0 the lattice constant.

Recently, a bistability effect within the total reflection region between $\hbar\omega_T$ and the longitudinal frequency $\hbar\omega_L$ has been discussed with a similar model of linear Frenkel chains.[12,16] Although the nonlocality was not considered there, the influence of the spatial structure of the field due to the finite penetration depth was studied. Within the penetration region, the saturation of the field-dependent refractive index occurs. This gives rise to multiple reflections within the same region, which leads to the feedback to increase the penetration depth. In contrast to this case, we consider the thinner film where the polariton interference occurs even within the longitudinal and transverse energy splitting (LT splitting). This interference causes the spatial structure reflecting the c.m. wave function of excitons, which can be described only by the nonlocal framework. First, we see the transmittance spectrum $T(\omega)$ in the linear response and the energy dependence of F_n. To discuss the spatial structure of the internal field, it is useful to see the behavior of F_n instead of the electric field $\mathcal{E}_j$, where F_n is nothing but the amplitude of the component of the internal field relevant to the nth quantized exciton, which is easily understood if we see the inverse transformation of Eq. (4). (Note that $\mathcal{E}_j$ written in such an expansion does not define $\mathcal{E}_0$ and $\mathcal{E}_{N+1}$.) Figure 1 shows the spectra of $T(\omega)$ and F_n in the excitonic resonance region for the film with $N=42$ (226.8 Å). Note that the peaks of the transmittance appear below the second and third excitonic levels. The former peak corresponds to the enhancement of $|F_2|^2$ [Fig. 1(b)]. It should be remarked that the F_2 component is relevant to the nondipole-type ($n=2$) excitonic state, namely, the wave function of the $|K_2\rangle$ state has a node in the surface normal direction, which is a specific feature to the nonlocal response. The peak position corresponds with the resonance energy of the $n=2$ exciton, including the radiative correction.[3] In contrast to the negative radiative shift of the $n=2$ exciton, the shift of the lowest exciton is generally positive for the film geometry.[21] The corresponding structure of $|F_1|^2$ can be seen between the $n=2$ and $n=3$ excitonic levels.

We noted the energy region just above the first peak of transmittance because a strong feedback to increase the internal field is expected, as in the case of the usual Fabry-Pérot etalon. In Fig. 2, the transmitted intensities as functions

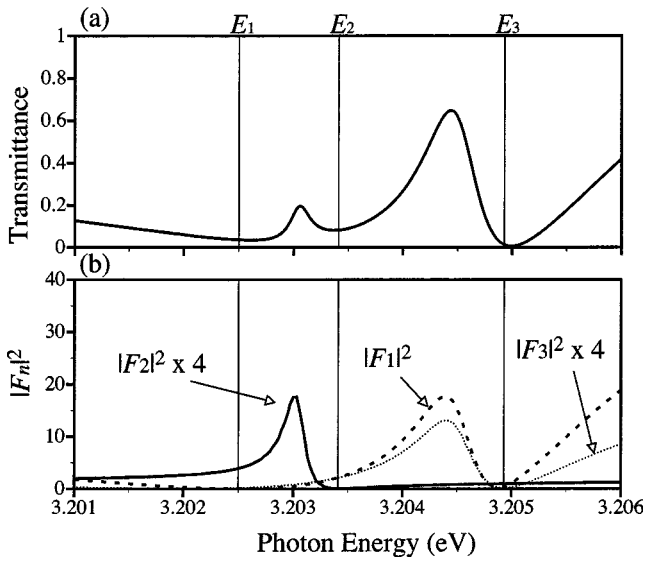

FIG. 1. Spectra of (a) transmittance and (b) $|F_n|^2$ for a CuCl thin film with $N=42$ (226.8 Å). The parameter values are given in the text. The vertical lines represent the energy positions of one-exciton levels.

of the incident intensity for the beam with $\hbar\omega = 3.203\,22$ eV are given for the intensity regime where the boson approximation is fairly good, i.e., the averaged interparticle distance is much longer than the excitonic Bohr radius (less than 7 Å for CuCl). Two curves are obtained by sweeping from the lower input intensity and from the higher intensity, respectively. The remarkable points are as follows: (i) The inverted region of the input-output characteristic appears and (ii) the bistable solutions are obtained due to

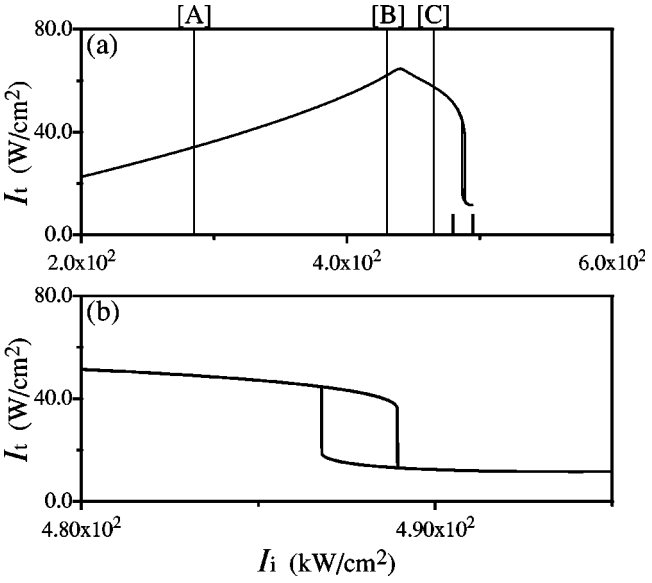

FIG. 2. Transmitted intensity I_t vs input intensity I_i for the beam with $\hbar\omega = 3.203\,22$ eV. The parameters are the same as in Fig. 1. (b) is the enlargement of (a), whose range of the horizontal axis is the same as the distance of two tick marks on the horizontal axis of (a). The input intensities [A], [B], and [C] in (a) are referred to in Fig. 4.

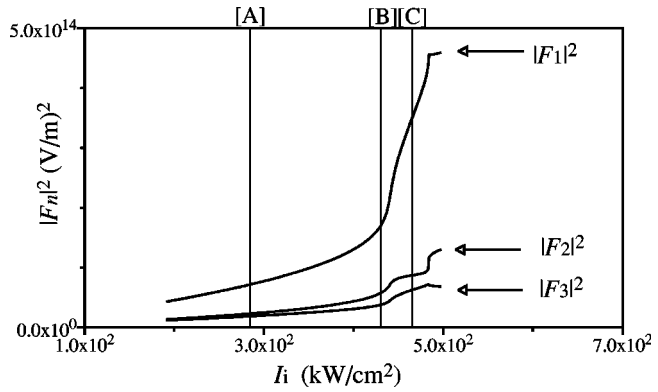

FIG. 3. $|F_n|^2$ vs input intensity I_i. The parameters are the same as in Fig. 1. The input intensities [A], [B], and [C] are referred to in Fig. 4.

Fabry-Pérot-type feedback, even for the considerably thin film. The inverted type of input-output characteristic usually appears in the induced absorption type of nonlinear response. In the present effect, however, this type of nonlinearity is not essential. Actually, the same characteristic can be obtained qualitatively even if we deliberately omit the two-exciton states in the calculation. As for the bistable effect in an ultrathin film, the nanoscale spatial structure of the internal field is essential, because it allows Fabry-Pérot-type feedback in the nanoscale thin film.

The above two effects can be understood by considering the resonant enhancement of the internal field and the input-intensity dependence of its spatial structure. In the third-order polarization, the terms that dominantly contribute to the above nonlinear response are proportional to the following factor,[4]

$$\frac{4\Gamma|F_n|^2}{(\omega+i\Gamma-E_n)[(E_n-\omega)^2+\Gamma^2]\gamma}, \tag{5}$$

where E_n is the eigenenergy of the nth exciton state. When F_n is resonantly enhanced near the pole of the bare nth excitonic state, the strong nonlinear effect arises due to the double resonance in the internal field and the energy denominator of the nonlinear susceptibility.[4,5] Since this enhancement of the internal field originates from the interference of polaritons, the positive feedback strongly works to enhance F_n in the higher-energy side of the peak. Actually, as shown in Fig. 3, the main components $|F_1|^2$ and $|F_2|^2$ in the internal field increase in the entire region of intensity in Fig. 2. This is consistent with the positive feedback to increase the nonlinearity. However, the inverted input-output characteristic is strange at a glance from the behavior of $|F_n|^2$ indicated in Fig. 3. This can be explained from the behavior of the spatial structure of the internal field with the change of the input intensity. Figure 4 shows the position dependence of the internal field for the values of input intensities [A], [B], and [C] indicated in Figs. 2 and 3. For input intensity [A], at which the input-output characteristic is almost linear, the spatial distribution is almost symmetric, but it becomes asymmetric as the intensity increases due to the nondipole-type contribution from F_2. For [C], the intensity at the back

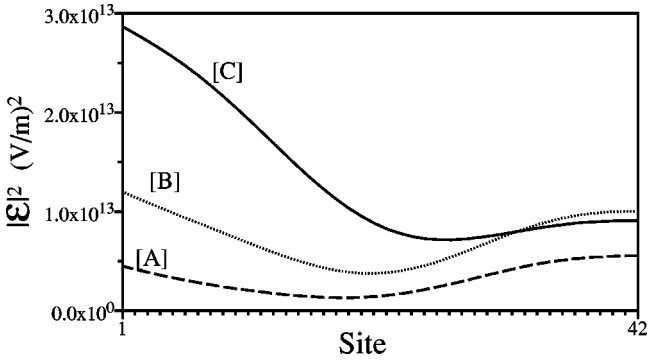

FIG. 4. Spatial distributions of the intensity of the internal field for the beam intensities indicated in Figs. 2 and 3 by [A], [B], and [C].

surface is less than that for [B], which means that the transmitted intensity for the former case is less than that for the latter case. Namely, we have a condition in which the intensity of each component F_n increases, which leads to an increase in the averaged internal field over the film and nonlinearity, while the intensity at the back surface decreases, which leads to a decrease of the transmitted intensity. Such variation of symmetry of the spatial structure with the input intensity originates from the uneven feedback strength on the different component F_n, which changes the weight of each component, as seen in Fig. 3. In particular, it should be mentioned that the nondipole-type contribution from F_2 is essential, and that the above effect never occurs if we neglect the $n=2$ exciton in the calculation.

In conclusion, an anomalous input-intensity dependence of the optical response with the inverted type of input-output characteristics and the bistability arises in an ultrathin film due to the peculiar intensity dependence of the nanoscale spatial structure of the internal field, where uneven feedback occurs on the different components in the field relevant to the confined excitonic levels. Although we treated a particular model system for the numerical demonstrations, a similar effect is generally expected for nonlocal systems where the nanoscale spatial structure of the internal field plays a central role. Thus, we believe that similar studies for the various types of model systems will provide important contributions to the comprehensive understanding of the nonlocal response in a nonlinear regime.

The author is grateful to Professor K. Cho for his fruitful discussions and support. Thanks are also due to Dr. Y. Ohfuti, Dr. Y. Nomura, and Dr. H. Sugimoto for their useful discussions. This work was supported in part by Grants-in-Aid for Scientific Research (Grant No. 14540301) and for COE Research (Grant No. 10CE2004) from the Ministry of Education, Science, Sports, and Culture of Japan.

*Electronic address: ishi@mp.es.osaka-u.ac.jp

[1] For an example, see *Excitons in Confined Systems*, edited by R. Del Sole, A. D'Andrea, and A. Lapiccirella (Springer, Berlin, 1988), Vol. 25.
[2] S. V. Gaponenko, *Optical Properties of Semiconductor Nanocrystals* (Cambridge University, Cambridge, England, 1998), and references therein.
[3] K. Cho, H. Ishihara, and Y. Ohfuti, Solid State Commun. **87**, 1105 (1993).
[4] H. Ishihara and K. Cho, Phys. Rev. B **53**, 15 823 (1996).
[5] H. Ishihara, T. Amakata, and K. Cho, Phys. Rev. B **65**, 035305 (2002).
[6] H. Ishihara, K. Cho, K. Akiyama, N. Tomita, Y. Nomura, and T. Isu, Phys. Rev. Lett. **89**, 017402 (2002).
[7] T. Takagahara, Phys. Rev. B **36**, 9293 (1987).
[8] E. Hanamura, Phys. Rev. B **37**, 1273 (1988).
[9] T. Takagahara, Phys. Rev. B **39**, 10 206 (1989).
[10] H.M. Gibbs, S.L. McCall, and T.N.C. Venkatesan, Phys. Rev. Lett. **36**, 1135 (1976).
[11] See *From Optical Bistability Towards Optical Computing*, The EJOB Project, edited by P. Mandel, S.D. Smith, and B.S. Wherrett (North-Holland, Amsterdam, 1987).
[12] V.A. Malyshev and E. Conejero Jarque, J. Opt. Soc. Am. B **12**, 1868 (1995); **14**, 1167 (1997).
[13] V.Z. Tronciu and A.H. Rotaru, Phys. Status Solidi B **212**, 383 (1999).
[14] V.A. Malyshev, H. Glaeske, and K.-H. Feller, J. Chem. Phys. **113**, 1170 (2000).
[15] H. Glaeske, V.A. Malyshev, and K.-H. Feller, J. Chem. Phys. **114**, 1966 (2001).
[16] E. Conejero Jarque and V.A. Malyshev, J. Chem. Phys. **115**, 4275 (2001).
[17] H. Ishihara and K. Cho, Phys. Rev. B **48**, 7960 (1993).
[18] H. Ishihara and K. Cho, Phys. Rev. B **42**, 1724 (1990).
[19] H. Ishihara and T. Amakata, Int. J. Mod. Phys. B **15**, 3809 (2001).
[20] Y.S. Shen, *The Principle of Nonlinear Optics* (Wiley, New York, 1984), p. 13.
[21] H. Ishihara, H. Asakawa, and K. Cho, Physica E (Amsterdam) **7**, 671 (2000).