

## Efficient algorithm for calculating two-photon absorption spectra

Toshiaki Iitaka and Toshikazu Ebisuzaki

*The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

(Received 10 May 1999)

We propose an efficient time-dependent algorithm for nonlinear response function that requires CPU time proportional to the system size, and study the size effects in two-photon absorption spectra of Si nanocrystallites by using this algorithm. [S1063-651X(99)51808-4]

PACS number(s): 02.70.-c, 42.65.-k, 78.40.-q, 78.20.Bh

### I. INTRODUCTION

The two-photon absorption (TPA) spectrum is an important optical property of solids. It brings information complementary to the one-photon absorption spectrum because their process and selection rules are different. Therefore, many physicists have studied the TPA spectrum of solids by using various band structure models such as the two-parabolic-band model and the Kane band-structure model [1,2]. However, if we try to apply the microscopic band structure model [3,4] to very large systems, such as amorphous systems and nanocrystallites, calculation of TPA spectra becomes computationally very demanding since the CPU time for diagonalization grows in proportion to the cube of system size. Therefore, one must employ new numerical schemes such as the Green's function methods [5] and the time-dependent methods [6].

In this Rapid Communication, we describe an efficient algorithm for calculating TPA spectra by combining the *particle source method* [7,8] for the product of Green's function, and the *projection method* [9,10] for summation over all occupied states of Fermi degenerate electron system. We use semiempirical local pseudopotentials [12], the finite difference method in real space [13] for constructing the Hamiltonian matrix, and the *leap frog method* [14] for the time evolution of the state vectors. This efficient algorithm makes it possible to calculate the size effect on the TPA spectra of very large nanocrystallites without using effective-mass approximation. In the following we describe the algorithm and its application to hydrogenated Si nanocrystallites.

### II. FORMULATION

The nondegenerate TPA coefficient  $\beta_{ab}(\omega_1, \omega_2)$  describes absorption of the probe light with frequency  $\omega_1$  and polarization  $\mathbf{e}_a$  in the presence of the excite light with frequency  $\omega_2$  and polarization  $\mathbf{e}_b$ . In the transparent region ( $\omega_1, \omega_2 < E_g$ ) it is related to the third-order nonlinear susceptibility  $\text{Im} \chi_{abba}^{(3)}$  by

$$\beta_{ab}(\omega_1, \omega_2) = \frac{6(2\pi)^2 \omega_1}{c^2 \eta_{aa}(\omega_1) \eta_{bb}(\omega_2)} \times \text{Im} \chi_{abba}^{(3)}(-\omega_1; -\omega_2, \omega_2, \omega_1), \quad (1)$$

where  $\eta_{aa}(\omega_1)$  and  $\eta_{bb}(\omega_2)$  are the real part of the linear refractive index. A simple form of

$\text{Im} \chi_{abba}^{(3)}(-\omega_1; -\omega_2, \omega_2, \omega_1)$  for TPA is provided by the second-order time-dependent perturbation theory [15],

$$\chi_{abba}^{(3)}(-\omega_1; -\omega_2, \omega_2, \omega_1) = \sum_{v,c} \frac{1}{6\epsilon_0 V} \frac{\alpha_{cv}^*(\omega_1, \omega_2) \alpha_{cv}(\omega_1, \omega_2)}{\omega_{cv} - i\gamma - \omega_1 - \omega_2}, \quad (2)$$

where the composite matrix elements are defined by

$$\alpha_{cv}(\omega_1, \omega_2) = \sum_m \left[ \frac{(\mathbf{e}_a \cdot \mathbf{r}_{cm})(\mathbf{e}_b \cdot \mathbf{r}_{mv})}{\omega_{mv} - \omega_2} + \frac{(\mathbf{e}_b \cdot \mathbf{r}_{cm})(\mathbf{e}_a \cdot \mathbf{r}_{mv})}{\omega_{mv} - \omega_1} \right]. \quad (3)$$

The subscripts  $v$  and  $c$  in the summation run over all occupied states (valence-band states in case of semiconductors) and all unoccupied states (conduction-band states), respectively. The subscript  $m$  for the intermediate states runs over both occupied and unoccupied states.

The degenerate TPA coefficient  $\beta(\omega, \omega)$  is defined by substituting  $\omega_1 = \omega_2 = \omega$  and  $\mathbf{e}_a = \mathbf{e}_b = \mathbf{e}_x$  in Eq. (1)–Eq. (3). Therefore, the main quantity we should calculate becomes

$$\chi^{(3)}(\omega) = \frac{2}{3\epsilon_0 V} \sum_{v,c,m,m'} \frac{x_{vm}}{\omega_{mv} - \omega} x_{mc} \frac{1}{\omega_{cv} - i\gamma - 2\omega} \times x_{cm'} \frac{x_{m'v}}{\omega_{m'v} - \omega}. \quad (4)$$

As seen in the above equations, nonlinear response functions, such as  $\chi^{(3)}$ , can be written as a product of Green's functions and perturbation operators summed over contributions from each occupied state of the Fermi degenerate electron system. Therefore, they can be calculated by combining the *particle source method* [7,8] and the *projection method* [9,10]. In the following, we describe the computational procedure for calculating the *degenerate* TPA coefficient for simplicity. However, the extension to the nondegenerate TPA coefficient is straightforward.

We define a *random vector* by

$$|\Phi\rangle \equiv \sum_{n=1}^N |n\rangle \xi_n = \sum_{n=1}^N |E_n\rangle \zeta_n, \quad (5)$$

where  $\{|n\rangle\}$  are the basis set used in the computation and  $\{\xi_n\}$  are the pseudorandom numbers generated by the library routines that satisfy the statistical relation

$$\langle\langle \xi_n^*, \xi_n \rangle\rangle = \delta_{n'n}, \quad (6)$$

where  $\langle\langle \cdot \rangle\rangle$  indicates the statistical average. The second equality in Eq. (5) is the expansion of the random vector by the energy eigenstates  $\{|E_n\rangle\}$ , where  $\zeta_n$  are their coefficients. Although we do not know the exact eigenstates or their coefficients, it is easily proven that the coefficients  $\zeta_n$  satisfy the same statistical relation as that of  $\xi$ ,

$$\langle\langle \zeta_n^*, \zeta_n \rangle\rangle = \delta_{n'n}, \quad (7)$$

since the two sets of random variables  $\xi_n$  and  $\zeta_n$  are related to each other by the unitary transformation (5). Applying the projection operator  $\theta(E_f - H)$  to the random vector, we obtain the *projected random vector* [11] representing the Fermi degenerate ground state,

$$|\Phi_{E_f}\rangle \equiv \theta(E_f - H)|\Phi\rangle = \sum_{E_v \leq E_f} |E_v\rangle \zeta_v, \quad (8)$$

where  $E_f$  is the Fermi energy. Then the statistical average of  $\langle\Phi_{E_f}|X|\Phi_{E_f}\rangle$  gives the sum of contributions from each occupied state [9]. Time evolution of a projected random vector

$$|\Phi_{E_f}; t\rangle = e^{-iHt}|\Phi_{E_f}\rangle \quad (9)$$

can be calculated by the *leap frog method* [14].

Then it is easy to show that Eq. (4) is reformulated as

$$\chi^{(3)}(\omega) = \left\langle\left\langle \int_{-\infty}^0 dt e^{+i\omega t} \delta B(t) \right\rangle\right\rangle, \quad (10)$$

where  $\delta B(t)$  is the response of the system defined by

$$\delta B(t) = \frac{2}{3\epsilon_0 V} \langle \delta\Phi_{E_f}; t | x | \delta\Phi_{E_f}^{(2)}; t \rangle, \quad (11)$$

where  $|\delta\Phi_{E_f}; t\rangle$  and  $|\delta\Phi_{E_f}^{(2)}; t\rangle$  are the first- and the second-order perturbed state vectors. The first-order perturbed state vector

$$|\delta\Phi_{E_f}; t\rangle = (-i) \int_{-\infty}^t dt' e^{-iH(t-t')} (x e^{-i(\omega+i\gamma)t'}) |\Phi_{E_f}; t'\rangle \quad (12)$$

$$\approx \sum_{m,v} |m\rangle \frac{x_{mv}}{\omega_{mv} - \omega} \times (-e^{-i(E_v + \omega + i\gamma)t}) \zeta_v \quad (13)$$

is calculated as the solution of the inhomogeneous time-dependent Schrödinger equation,

$$i \frac{d}{dt} |\delta\Phi_{E_f}; t\rangle = H |\delta\Phi_{E_f}; t\rangle + x e^{-i(\omega+i\gamma)t} |\Phi_{E_f}; t\rangle, \quad (14)$$

with the initial condition  $|\delta\Phi_{E_f}; t = -\infty\rangle = 0$ . The imaginary part of frequency  $\gamma$  is introduced to replace  $-\infty$  in Eq. (10) by a large negative number  $T \approx \ln \delta/\gamma$ , where  $\delta$  is the relative numerical accuracy we need. The second-order perturbed state vector is defined as

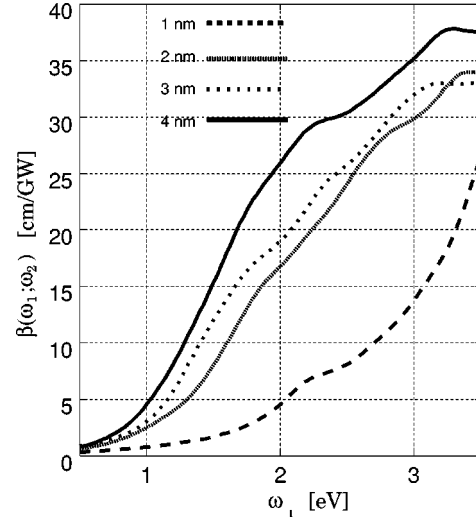


FIG. 1. The nondegenerate TPA coefficient  $\beta_{xx}(\omega_1, \omega_2)$  of Si nanocrystallites as a function of  $\omega_1$  with a fixed excite light frequency,  $\omega_2 = 2.4$  eV.

$$|\delta\Phi_{E_f}^{(2)}; t\rangle = (-i) e^{-iHt} \theta(H - E_f) x |\delta\Phi_{E_f}; t = 0\rangle, \quad (15)$$

where  $\theta(H - E_f)$  is a projection operator to extract the Fermi unoccupied states.

### III. RESULTS

Figure 1 shows the nondegenerate TPA coefficient  $\beta_{xx}(\omega_1, \omega_2)$  of hydrogenated cubic Si nanocrystallites of size  $l = 1-4$  nm as a function of probe light frequency,  $\omega_1$ , with a fixed excite light frequency,  $\omega_2 = 2.4$  eV. In the calculation, we used the Hamiltonian matrix discretized into  $N = L^3$  cubic meshes in real space ( $L = 32-80$ ), which consists of the semiempirical local pseudopotential [12], the kinetic energy operator in the finite difference form [13]. The results were averaged over 2-16 random vectors depending on the crystallite size. The energy resolution is set to  $\gamma = 0.2$  eV, which may not be small enough to resolve the fine structures in the spectra but small enough to study the size effects on the magnitude of  $\text{Im } \chi^{(3)}$ . The size effects on the TPA coefficient is evident in the figure. The absorption increases as the crystallite size increases, and approaches to the bulk value when  $l = 4$  nm. The tail extending below the TPA absorption edge 0.8 eV in the spectrum is due to the Lorentzian distribution with the finite width  $\gamma$  in the time-dependent calculation.

Figure 2 shows the degenerate TPA spectra  $\beta_{xx}(\omega, \omega)$  of Si nanocrystallites of  $l = 1.5-4$  nm,  $L = 40-80$ . Other parameters are the same as in Fig. 1. The results were averaged over 8-64 random vectors depending on the crystallite size, so that the typical value of statistical error becomes less than 2%. As the size of nanocrystallite becomes larger, the degenerate TPA spectra approaches to that of bulk Si calculated by the diagonalization method [3], which is evidence that our algorithm works properly.

### IV. DISCUSSION

An advantage of this method is that we can calculate the nondegenerate TPA coefficient  $\beta_{ab}(\omega_1, \omega_2)$  over the whole range of  $\omega_1$  for a fixed  $\omega_2$  at one program run, as in the case

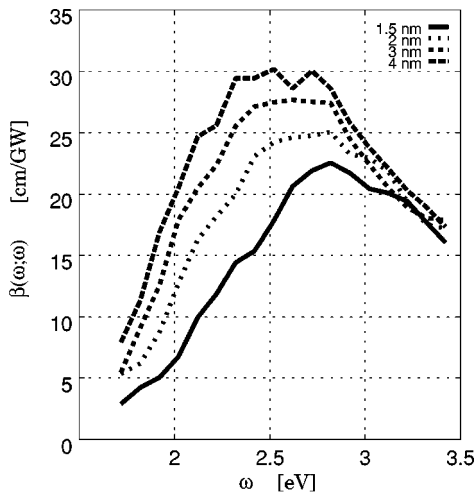


FIG. 2. The degenerate TPA coefficient  $\beta(\omega, \omega)$  of Si nanocrystallites as a function of  $\omega$ .

of the linear-response functions [9], by using an impulse probe light instead of a monochromatic one and calculating the Fourier transform of the induced polarization. This is possible because the induced polarization in the nondegenerate TPA is a *linear* function of the probe light field. Therefore, the computational cost for the nondegenerate coefficient is  $O(MN)$ , where  $M \propto T/\Delta t \propto E_{max}/\gamma$  is the number of time steps in time domain or the number of  $\omega_1$  points in energy domain. The computational cost for the degenerate coefficient becomes  $O(M^2N)$  because only one data point of  $\beta_{aa}(\omega_1 = \omega_2, \omega_2)$  is obtained from the nondegenerate spectrum data  $\beta_{aa}(\omega_1, \omega_2)$  at a fixed  $\omega_2$ . Note that the large-scale calculation in this article became possible only after the invention of our linear scaling time-dependent methods, which are much more efficient than the conventional *equation of motion* methods [6] whose computational effort is

$O(M^2N)$  for the linear-response function and  $O(M^3N)$  for the third order susceptibility.

Recently, Kurokawa *et al.* [16] have proposed another algorithm for calculating the TPA coefficient by using projected random vectors. The main difference between their algorithm and ours lies in the calculation of the double integral in the time domain that appears in the second-order time-dependent perturbation theory. While we factorize this double integral to a product of Green's functions in energy domain by Fourier transformation, they factorize it to the product of two single integrals in time domain by inserting an additional random vector. Let us compare the efficiency of the two algorithms. The CPU time for our algorithm to calculate the degenerate TPA spectrum of nanocrystallite with mesh  $N=64^3$  and the typical statistical error less than 2% is equivalent to 2400 hours on a single processor of Fujitsu VPP500 machine. The CPU time for their algorithm to calculate the degenerate TPA spectrum of *harmonic oscillator* with mesh  $N=16^3$  and the statistical error less than 7% was 19 hours, which scales to 15 000 hours for  $N=64^3$  and the typical statistical error less than 2%. The origin of the slow convergence probably originates from the additional random vector they introduced.

## V. SUMMARY

In summary, we have established an efficient time-dependent algorithm for the nonlinear response function whose computational cost scales linearly to the system size, and studied the size effects on the two-photon absorption spectra of Si nanocrystallites.

## ACKNOWLEDGMENTS

We wish to thank M. Murayama and D.C. Hutchings for their useful comments. The numerical results in this article were computed by using Fujitsu VPP computers at RIKEN, ISSP, and NIG.

- 
- [1] D.C. Hutchings and E.W. Van Stryland, *J. Opt. Soc. Am. B* **9**, 2065 (1992).
- [2] J.A. Bolger *et al.*, *Opt. Commun.* **97**, 203 (1993).
- [3] M. Murayama and T. Nakayama, *Phys. Rev. B* **49**, 5737 (1994); **52**, 4986 (1995).
- [4] J. Li *et al.*, *Phys. Rev. B* **57**, 2222 (1998).
- [5] G. Duan *et al.*, *Phys. Rev. B* **57**, 10 (1998).
- [6] D. Hobbs *et al.*, *J. Phys.: Condens. Matter* **8**, 4691 (1996), and references therein.
- [7] T. Iitaka, in *High Performance Computing in RIKEN 1995* [Institute of Physical and Chemical Research (RIKEN), Wako, 1996], p. 241 (e-print physics/9802021), and references therein.
- [8] H. Tanaka, *Phys. Rev. B* **57**, 2168 (1998); H. Tanaka and M. Itoh, *Phys. Rev. Lett.* **81**, 3727 (1998).
- [9] T. Iitaka *et al.*, *Phys. Rev. E* **56**, 1222 (1997); T. Iitaka, *ibid.* **56**, 7318 (1997); “Fast” Algorithms for Quantum Physics in *RIKEN*, Review No. 19 [Institute of Physical and Chemical Research (RIKEN), Wako, 1998].
- [10] S. Nomura *et al.*, *Phys. Rev. B* **56**, 4348 (1997); **59**, 10 309 (1999).
- [11] O.F. Sankey, D.A. Drabold, and A. Gibson, *Phys. Rev. B* **50**, 1376 (1994).
- [12] L.W. Wang and A. Zunger, *J. Phys. Chem.* **98**, 2158 (1994).
- [13] J. Chelikowsky, N. Troullier, and Y. Saad, *Phys. Rev. Lett.* **72**, 1240 (1994).
- [14] T. Iitaka, *Phys. Rev. E* **49**, 4684 (1994); T. Iitaka, N. Carjan, and D. Strottman, *Comput. Phys. Commun.* **90**, 251 (1995); T. Iitaka, *Introduction to Quantum Dynamics* (Maruzen, Tokyo, 1994) (in Japanese).
- [15] P.N. Butcher and D. Cotter, *The Elements of Nonlinear Optics* (Cambridge University Press, Cambridge, England, 1990).
- [16] Y. Kurokawa *et al.*, *Phys. Rev. E* **59**, 3694 (1999); Y. Kurokawa (private communication).