Non-degenerate Two Photon Absorption Spectra of Si Nanocrystallites

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We propose an efficient linear-scaling time-dependent method for calculating nonlinear response function, and study the size effects in non-degenerate two photon absorption spectra of Si nanocrystallites by using semi-empirical pseudopotentials.

1. INTRODUCTION

The two-photon absorption (TPA) spectrum is an important optical property of semiconductors. It brings valuable information complementary to the one-photon absorption spectrum, gives the limits to the optical transparency of materials, and causes laser-induced damages.

Recently, the TPA spectrum of direct-gap nanocrystallites was calculated by Cotter et al. [1] by using the effective-mass approximation to predict a strong effect of the nanocrystallites size. However the experimental result [2] does not support this result. Since then TPA spectra of nanocrystallites has been attracting attention of researchers.

In this paper, we develop a new algorithm for calculating TPA spectra by using semi-empirical local pseudopotentials [3], finite difference method in real space [4], and a linear-scaling time-dependent method which has been applied to the calculation of the linear-response functions [5, 6, 7, 8]. This efficient algorithm made it possible, for the first time, to calculate the size effect on the TPA spectra of very large nanocrystallites without using effective-mass approximation. In the following we show the effectiveness of this algorithm by applying it to the TPA spectra of indirect-gap nanocrystallites. Though this result does not solve the controversy related to direct-gap nanocrystallites [1, 2], it will be an important step toward it.

2. TPA COEFFICIENT

The non-degenerate TPA coefficient $\beta_{ab}(\omega_1, \omega_2)$ describes absorption of the probe light with the frequency $\omega_1$ and the polarization $e_a$ in the presence of the excite light with the frequency $\omega_2$ and the polarization $e_b$, and, in the transparent region ($\omega_1, \omega_2 < E_g$), it is related to the third order nonlinear susceptibility $\chi^{(3)}_{abba}$ by

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

where $\eta_{aa}(\omega_1)$ and $\eta_{bb}(\omega_2)$ are the real part of linear refractive index. A simple form of $\chi^{(3)}$ for TPA is provided by the second-order time-dependent perturbation theory [9],

$$\chi^{(3)}_{abba}(-\omega_1; -\omega_2, \omega_2, \omega_1) = \sum_{v,c} \frac{1}{6\hbar\epsilon_0 V} \frac{\alpha_{vc}(\omega_1, \omega_2)\alpha^*_{vc}(\omega_1, \omega_2)}{\omega_{cv} - i\gamma - \omega_1 - \omega_2}$$
where the composite matrix element is defined by

$$\alpha_{vc}(\omega_1, \omega_2) = \frac{e^2}{\hbar} \sum_m \left( \frac{(e_a \cdot r_{cm})(e_b \cdot r_{mv})}{\omega_{mv} - \omega_2} + \frac{(e_b \cdot r_{cm})(e_a \cdot r_{mv})}{\omega_{mv} - \omega_1} \right).$$  \hspace{1cm} (3)$$

The subscripts \(v\) and \(c\) in the summation run over all valence-band states and all conduction-band states, respectively. The subscript \(m\) for the intermediate states runs over both valence- and conduction-band states.

It is worth to note that the form Eq. (2) looks very similar to that of the linear-response function, and that, therefore, we may calculate \(\chi^{(3)}\) by using the linear-scaling time-dependent method for the linear-response functions [7, 8],

$$\chi^{(1)}_{bc}(\omega) = \sum_{v,c} -\frac{e^2}{\hbar \epsilon_0 V} \left\{ \frac{(e_b \cdot r_{vc})(e_a \cdot r_{cv})}{\omega_{cv} - i\gamma - \omega} - \frac{(e_b \cdot r_{vc})(e_a \cdot r_{cv})}{\omega_{cv} + i\gamma + \omega} \right\} = \langle \langle \int_0^T dt \ e^{+i(\omega+i\gamma)t} \delta B(t) \rangle \rangle$$  \hspace{1cm} (4)$$

where \langle\langle \cdot \rangle\rangle\) indicates the statistical average over random vectors, and \(\delta B(t)\) is the response of the system defined by

$$\delta B(t) = 2 \ \text{Im} \langle \Phi_{E_f} \ e^{+iHt}(e_b \cdot r)e^{-iHt}\theta(H - E_f)(e_a \cdot r)\Phi_{E_f} \rangle.$$

The ket \(\ket{\Phi_{E_f}}\) is a random vector projected onto the Fermi occupied states, and \(\theta(H - E_f)\) is a projection operator to extract the Fermi unoccupied states. The imaginary part of frequency \(\gamma\) is introduced to limit the integration time in Eq. (3) to a finite value \(T = -\ln \delta/\gamma\) with \(\delta\) being the relative numerical accuracy we need. The main difference of \(\chi^{(3)}\) from \(\chi^{(1)}\) is the composite matrix elements in place of the dipole matrix elements, which we can calculate with the help of the particle source method [5, 6].

3. RESULT

Figure 1 shows the non-degenerate TPA coefficient \(\beta_{xx}(\omega_1, \omega_2)\) of hydrogenated cubic Si nanocrystallites of size \(l = 1 \sim 4\) (nm) as a function of \(\omega_1\) with a fixed excite light frequency, \(\omega_2 = 2.4(eV)\). In the calculation, we used the Hamiltonian matrix discretized into \(N = L^3\) (\(L = 32 \sim 80\)) cubic meshes in real space, which consists of the semi-empirical local pseudopotential [3] the kinetic energy operator in the finite difference form [4]. The results were averaged over 2 – 16 random vectors depending on the system size. The energy resolution is set to \(\gamma = 200(m\text{eV})\), which may not small enough to resolve the fine structures in the spectra but small enough to study the size effects on the magnitude of \(\text{Im}\chi^{(3)}\).

Fig. 1 \(\beta_{xx}(\omega_1, \omega_2)\) of Si nanocrystallites with \(\omega_2 = 2.4(eV)\).
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 \( l \approx 4 \) (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.

4. DISCUSSIONS AND SUMMARY

The computational cost of our method is \( O(MN) \) for the linear response function and the non-degenerate TPA coefficient and \( O(M^2N) \) for the degenerate TPA coefficient. The large number \( M \propto T/\Delta t \propto E_{\text{max}}/\gamma \ll N \) is the number of time steps in a time evolution or the number of the frequency \( \omega_1 \) to be calculated, where \( E_{\text{max}} \) is the range of the eigenenergy. Therefore our method is much more efficient than the \( O(N^3) \) diagonalization method [1] and the equation of motion methods [1] whose computational effort is \( O(M^2N) \) for the linear-response function and \( O(M^3N) \) for the third order susceptibility.

In summary, we have established an efficient linear-scaling time-dependent method for nonlinear response function, and studied the size effects on the two photon absorption spectra of Si nanocrystallites. Such a large scale calculation has been impossible with conventional algorithms. Therefore the present result will be an important step to solve the controversy related to direct-gap nanocrystallites [1, 2].

The calculation in this article has been done on the supercomputer Fujitsu VPP500 at RIKEN and NIG.

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