Fast algorithm for calculating two-photon absorption spectra

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We report a numerical calculation of the two-photon absorption coefficient of electrons in a binding potential using the real-time real-space higher-order difference method. By introducing random vector averaging for the intermediate state, the task of evaluating the two-dimensional time integral is reduced to calculating two one-dimensional integrals. This allows a reduction of the computation load down to the same order as that for the linear response function. The relative advantage of the method compared to the straightforward multidimensional time integration is greater for the calculation of nonlinear response functions of higher order at higher energy resolution. [S1063-651X(99)00603-0]

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The measurement of the two-photon absorption coefficient [1] yields different information from the single-photon absorption measurement, since the physical processes involved and selection rules are different. Because of this, there has always been a lot of interest in two-photon absorption of various molecules, crystals, and solids [2–9]. To compare against the experimental data, one would like to have theorerical calculations based on some realistic model of the material. However, since the two-photon absorption is a typical nonlinear optical process, its realistic modeling has always proved difficult for large complex systems [2–6].

A powerful method that has come to be used widely for large quantum systems is the real time real space higher-order difference method [10,11], in which the real space is represented by discrete mesh points, and the time development of a system is solved by numerically integrating the Schrödinger equation for discrete time steps. The energy levels and energy eigenstates are obtained by Fourier analyzing the numerical solution. The memory requirement scales linearly with the number of basis states, N, compared to N^2 for matrix diagonalization, and the method has proved effective in solving large quantum systems that cannot be solved by conventional methods [11,12]. So far, the large computation load has meant that the actual application of the method has been made primarily to the calculation of linear response functions of one-particle systems [10,11]. Nevertheless, the potential scale advantage of the method when applied to large systems invites the speculation that development of the method will be essential in making the calculation of nonlinear response functions of complex many-body quantum systems feasible.

In this paper, we report a trial application of the method to the calculation of the two-photon absorption coefficient of noninteracting electrons trapped by a binding potential and exposed to monochromatic light of frequency ω.

The two-photon absorption coefficient is given by [1]

$$\alpha^{(2)}(\omega) = \left(\frac{e}{\hbar}\right)^4 \sum_{E_f > E_F} \sum_{E_i < E_F}$$

$$\times \left| \frac{1}{V} \int_0^\infty dt_1 \int_0^{t_1} dt_2 e^{-i(\omega - i\eta)(t_1 + t_2)} \right.$$

$$\times \left. \langle E_f | e^{iHt_1/\hbar} \mathbf{r} e^{-iH(t_1 - t_2)/\hbar} \mathbf{r} e^{-iHt_2/\hbar} | E_i \rangle \right|^2, \quad (1)$$

where H is the unperturbed Hamiltonian of the system, $\mathbf{r}$ is the electron coordinate operator, η is the frequency resolution, V is the volume of the system, the summation with respect to the initial state $|E_i\rangle$ must be taken over all states below the Fermi level E_F, and the summation with respect to $|E_f\rangle$ must be taken over the states $E_f > E_F$.

An important ingredient of the real-time real-space higher-order difference method is the use of random vectors as probes to scan the Hilbert space [10,11,13–16]. Among various types of random vector is the uniform amplitude random phase vector

$$|\Phi\rangle = \sum_{n=1}^N |n\rangle e^{i\phi_n}, \quad (2)$$

whose effectiveness has been amply demonstrated [10,11,13–16]. Here, the phases ϕ_n are independent random variables with uniform distribution in the range $[-\pi, \pi)$, and $|n\rangle$ ($n = 1, N$) are the orthonormal basis states which are localized at the mesh points in the real space. Using the property of completeness

$$\langle |\Phi\rangle\langle\Phi| \rangle_\Phi = I \quad \text{(identity operator)}, \quad (3)$$

which obtains after averaging over random realizations of $|\Phi\rangle$ denoted above by the brackets $\langle \cdots \rangle_\Phi$, the two-photon absorption coefficient, Eq. (1), can be rewritten as

$$\alpha^{(2)}(\omega) = \left(\frac{e}{\hbar}\right)^4 \left\langle \left| \frac{1}{V} \int_0^\infty dt_1 \right.\right.$$

$$\times \int_0^{t_1} dt_2 e^{-i(\omega - i\eta)(t_1 + t_2)} \left\langle \Phi \right| \theta(H - E_F)$$

$$\times e^{iHt_1/\hbar} \mathbf{r} e^{-iH(t_1 - t_2)/\hbar} \mathbf{r} e^{-iHt_2/\hbar}$$

$$\times \left.\left. \theta(E_F - H) \left| \Phi \right\rangle \right|^2 \right\rangle_\Phi. \quad (4)$$

The operator step function [15]

$$\theta(X) = \sum_{X_i} |X_i\rangle \theta(X_i)\langle X_i| \quad (5)$$

can be explicitly constructed for any bounded Hermitian operator X without solving for the eigenvalues X_i and eigenvectors $|X_i\rangle$. In our calculation, we used an algorithm based on Chebyshev polynomial expansion, which yields $\theta(X)$ as a polynomial of the operator X [10,11,15–18].

If Eq. (4) were to be numerically implemented straightforwardly, the matrix element inside the integral would have to be obtained for all necessary combinations of time variables t_1 and t_2. One would then start with a random vector $|\Phi\rangle$, solve the time development according to the Schrödinger equation, mutiplying operators (**r**'s and θ's) along the way as required, and take the inner product with $|\Phi\rangle$ at the end. The number of discrete time steps required for a calculation of energy resolution η scales as η^{-1}, so that the direct implementation of Eq. (4) requires a computation load that grows as η^{-2}. On top of it, the calculation has to be repeated for a number of different realizations of $|\Phi\rangle$ for random averaging. This is necessary to reduce the fluctuation arising from the use of random vectors, whose amplitude can be of the same order in magnitude as the final result itself. The scale of such a computation can easily overwhelm the capacity of any computing facility in existence.

However, the computational load can be greatly reduced by inserting the completeness relation (3) in the matrix element of Eq. (4) to decompose it into two factors. The absorption coefficient is then given by

$$\alpha_2^{(2)}(\omega)=\left(\frac{e}{\hbar}\right)^4\left\langle\left|\frac{1}{V}\int_0^\infty dt_1\int_0^{t_1}dt_2 e^{-i(\omega-i\eta)(t_1+t_2)}\right.\right.$$
$$\times\langle\langle\Phi|\,\theta(H-E_F)e^{iHt_1/\hbar}\mathbf{r}e^{-iHt_1/\hbar}\theta(E_c-H)|\Phi'\rangle$$
$$\times\left.\left.\langle\Phi'|e^{iHt_2/\hbar}\mathbf{r}e^{-iHt_2/\hbar}\theta(E_F-H)|\Phi\rangle\rangle_{\Phi'}\right|^2\right\rangle_\Phi ,$$

$$(6)$$

where $|\Phi\rangle$ and $|\Phi'\rangle$ are mutually independent random vectors, and E_c is the cutoff energy to be explained below. The most costly process of integrating the Schrödinger equation is now used only to obtain two complex functions of a single time variable instead of a bivariate function with two time variables. Once the necessary complex-valued functions have been calculated and stored, the two-dimensional time integration may easily be done with a small computer. The computational load therefore scales only as η^{-1} with the energy resolution.

The benefit must be weighed against the increased cost of having to average over random realizations of intermediate states $|\Phi'\rangle$. The statistical variance arising from the random sampling is independent of the number of time steps used in the calculation, but is controlled only by the number of random samples taken. Therefore, the relative advantage of the use of Eq. (6) over the straightforward integration of Eq. (4) increases as higher energy resolution is required. For the actual numerical implementation of the random sampling, it is essential that one have control over the extent of the Hilbert space to be probed. In Eq. (6), the extra cutoff factor $\theta(E_c-H)$ is inserted for this purpose. The final result should be independent of the cutoff energy E_c if it is taken sufficiently large. However, a large value of E_c entails a large random fluctuation, so that a larger number of samples will
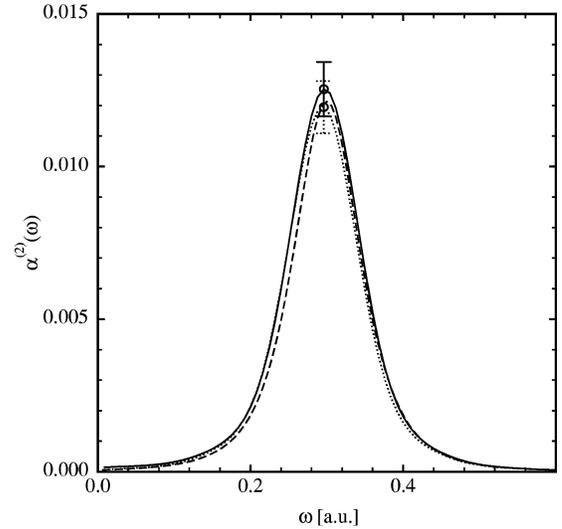

FIG. 1. Two-photon absorption coefficient $\alpha^{(2)}(\omega)$ of electrons trapped in a parabolic potential. The results obtained by the use of Eqs. (4) and (6) are shown by the dotted curve and the solid curve, respectively. The analytical result is shown by the dashed line.

be required to average out the noise to achieve the same accuracy. Therefore, the value of E_c must be set as small as possible provided that its interference with the final result is kept within the margin of tolerance.

In order to compare the CPU time for the two methods, we have computed Eqs. (4) and (6) for the case of a parabolic binding potential,

$$V(r)=\frac{m\omega_0^2}{2}r^2 , \qquad (7)$$

with $\omega_0=0.3$ a.u. and m being the electron mass. The real space was represented by 16^3 mesh points to cover a cubic volume of linear dimension 16 a.u. For the time development, discrete time steps with $\Delta t=0.05$ a.u. were used for integration of the Schrödinger equation. The Fermi energy was set at $E_F=3\hbar\omega_0$ and the frequency resolution was $\eta=8\times10^{-2}$ a.u.

In Fig. 1 we compare the results of Eqs. (4) and (6) with the analytical result for electrons in the parabolic potential. Both numerical results well reproduce the analytical curve with the standard deviation standing at 7% at the peak ($\omega_0=0.3$ a.u.) for both cases.

The result for the straightforward implementation of Eq. (4) is an average over 200 runs with different $|\Phi\rangle$'s. The CPU time on a single processing unit of Fujitsu VPP500 was 1.5×10^3 sec for each run, totaling 3.0×10^5 sec ($\simeq$ 83 h) to achieve 7% accuracy. For the calculation according to Eq. (6), an average was first taken over 50 different samples of $|\Phi'\rangle$ with a fixed $|\Phi\rangle$. The result was then averaged over 100 different samples of $|\Phi\rangle$. The total of 5000 runs of integrating the Schrödinger equation took 6.8×10^4 sec ($\simeq$ 19 h) to achieve the same 7% accuracy at the peak. If the statistical standard deviation is to be brought down to 1%, an average over $7^2=49$ times more samples will have to be taken, which translates to 1.5×10^7 sec ($\simeq$174 days) and 3.3×10^6 sec ($\simeq$38 days) for Eqs. (4) and (6), respectively.
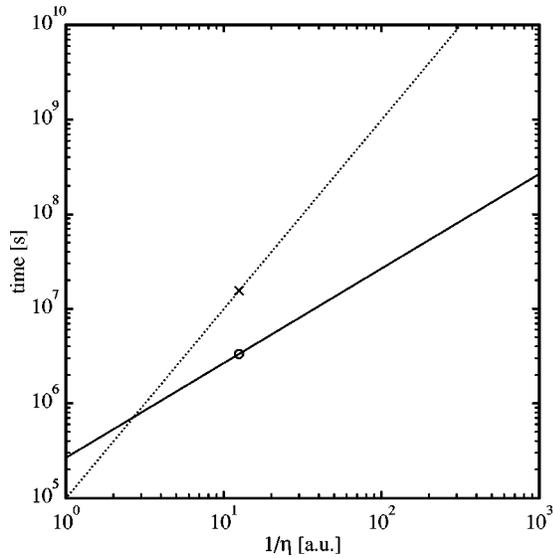
FIG. 2. Relation between the energy resolution and the total CPU time for calculating the two-photon absorption coefficient to 1% statistical accuracy. The solid line and the dotted line are for calculation according to Eqs. (6) and (4) of the text, respectively. The cross and the circle are the projected CPU time for energy resolution $\eta = 8 \times 10^{-2}$ a.u. based on the actual calculation performed with the same resolution but to 7% accuracy.

In Fig. 2, we show the estimated CPU time to achieve 1% statistical accuracy for various values of frequency resolution. The relative advantage of the use of random vectors for the intermediate state should grow as higher frequency resolution is required. The actual lapse time of computation can be reduced nearly by an order of magnitude if the computation is parallelized to use all the 30 processing units on Fujitsu VPP500 at RIKEN.

The present calculation was done for the specific case of noninteracting electrons trapped in a parabolic potential, only in order to test the relative advantage of the algorithm and to compare against the analytical result. The computer code admits an arbitrary potential, and work is under way to extend the present calculation to electrons in various pseudo-potentials. Extension of the algorithm itself to deal with an interacting M-particle system is straightforward, although solution of the Schrödinger equation in the $3M$-dimensional space soon becomes unmanageable with increasing M. Of more significance is the potential of the present strategy to be used to facilitate the calculation of nonlinear response functions of higher order. A numerical calculation of a nonlinear response function of order n typically involves computing an n-dimensional integral of the type

$$\int_0^\infty dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n e^{i(\omega_1 t_1 + \omega_2 t_2 + \cdots + \omega_n t_n)}$$

$$\times \langle\!\langle \Phi | \hat{O}_f e^{iHt_1/\hbar} \hat{O}_1 e^{-iH(t_1-t_2)/\hbar} \hat{O}_2 e^{-iH(t_2-t_3)/\hbar}$$

$$\cdots e^{-iH(t_{n-1}-t_n)/\hbar} \hat{O}_n e^{-iHt_n/\hbar} \hat{O}_i | \Phi \rangle\!\rangle_\Phi , \tag{8}$$

where each $\hat{O}$ represents some operator. While the straightforward evaluation requires computation time proportional to η^{-n}, it may be possible to reduce the CPU time as far down as to n times that for the linear response function by inserting the completeness relation (3) and decomposing the matrix element into n factors. This may be regarded as a version of the quantum Monte Carlo method, and the use of importance sampling techniques [14,19] will be vital in reducing the evaluation time. In fact, the use of $\theta(E_c - H)$ in Eq. (6) is one rudimentary method of improving the sampling efficiency.

The insertion of random intermediate vectors is not the only way to reduce the CPU time of evaluation of the n-dimensional integral. For example, the standard Monte Carlo random sampling technique may be applied directly to the evaluation of the integral (8). If one adopts uniform random sampling in the n-dimensional time space, the CPU time for integration of the Schrödinger equation scales as η^{-1} times the number of samples required for the statistical averaging, which is precisely the same as for the case of random vector insertion above. In either case, the statistical method of evaluation suffers from the familiar negative sign problem [19], so that some scheme needs to be devised to improve the sampling efficiency. Nevertheless, it remains true that the size of statistical variance is independent of the energy resolution, so that it should be advantageous to employ statistical methods for the calculation of high-order nonlinear coefficients at a high resolution of frequency.

All calculations reported here were performed on a Fujitsu VPP500 at RIKEN.

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