Application of Green's-function technique to the calculation of multiphoton absorption coefficients of crystalline solids

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The Green's-function method is introduced to avoid the sums over intermediate states occurring in the calculation of multiphoton absorption coefficients of crystalline solids. Up to four-photon absorption coefficients of NaCl are obtained by this method. The results are in accord with those obtained by carrying out the summations directly. The advantages of the method and its further applications are also discussed in the paper. [S0163-1829(98)00102-7]

I. INTRODUCTION

The multiphoton absorption (MPA) processes in crystalline solids have attracted a great deal of experimental and theoretical attention[1] because of many technical applications and the important role in providing information which cannot be obtained by the usual single-photon spectroscopy due to the different selection rules. MPA can be used to generate the color centers in alkali halides and pump the semiconductor laser.[2] Experimental research revealed that MPA processes are of great importance to laser-induced modification and intrinsic bulk damage of wide-gap optical materials.[3] This invoked the interest of the theoretical calculation of MPA coefficients of crystalline solids. However, it is not trivial to evaluate the multiphoton transition rate, because the evaluation involves the time-consuming summations over a complete set of intermediate states, including the high conduction-band states. The large discrepancy between earlier attempts and the experimental values showed that the reliable results must be based on band-structure calculations. This was done by Vaidynathan et al.[4] using empirical pseudopotential method. They calculated the two-photon absorption coefficients of some semiconductors. By means of the *ab initio* linear augmented plane-wave method, Zhang et al.[5] studied the MPA for several alkali halides and semiconductors, and obtained more reliable results than those of earlier works.

In this paper we present the result of calculation on MPA of NaCl using the first-principles self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method[6] in the local-density approximation (LDA) of the density-functional theory (DFT). The Green's-function technique was used in the calculation to reduce the summations over intermediate states to the solutions of the inhomogeneous linear equations. This technique was introduced and applied by Baroni and Quattropani[7] to two-photon transitions in the hydrogen atom. Inspired by its successful application,[8] we extended this approach to MPA processes in crystalline

solids. Up to four-photon absorption coefficients of NaCl were obtained by this method and compared with the results from the conventional method using the direct summations.

II. FORMALISM

According to higher-order perturbation theory, the l-photon absorption coefficient from initial valence-band states $|v\rangle$ to conduction-band states $|c\rangle$ is given by (atomic units are used throughout the paper)

$$\alpha^{(l)}(\omega) = \frac{4\pi l\omega}{\Omega}\left(\frac{2\pi}{nc\omega^2}\right)^l \sum_{\vec{k}} |T_{cv}^{(l)}(\vec{k},\omega)|^2 \delta(E_c - E_v - l\omega),$$

(1)

where E_c and E_v are energies for state $|c\rangle$ and $|v\rangle$, ω, Ω, n, and c denote the photon energy, cell volume, refractive index, and velocity of light, respectively, and

$$T_{cv}^{(l)}(\vec{k},\omega) = \sum_n \sum_m \cdots \sum_j \sum_i \frac{\langle c|M|n\rangle\langle n|M|m\rangle}{[E_n - E_v - (l-1)\omega]} \cdots$$
$$\frac{\langle j|M|i\rangle}{[E_j - E_v - 2\omega]} \frac{\langle i|M|v\rangle}{[E_i - E_v - \omega]},$$

(2)

here $M = \vec{e}\cdot\vec{p}$, $\vec{e}$ is the polarization vector of photon, and $\vec{p}$ is the momentum operator for electron. The Green's function is defined as

$$G(E) = (H - E)^{-1},$$

(3)

here H is the Hamiltonian of the system.

We define functions $|\Psi_v^{(m)}\rangle$ in a recursive way:

$$|\Psi_v^{(m+1)}\rangle = G(E_v + m\omega)|\widetilde{\Psi}_v^{(m)}\rangle, \quad \text{for} \quad m = 1,2,\ldots,l-1$$
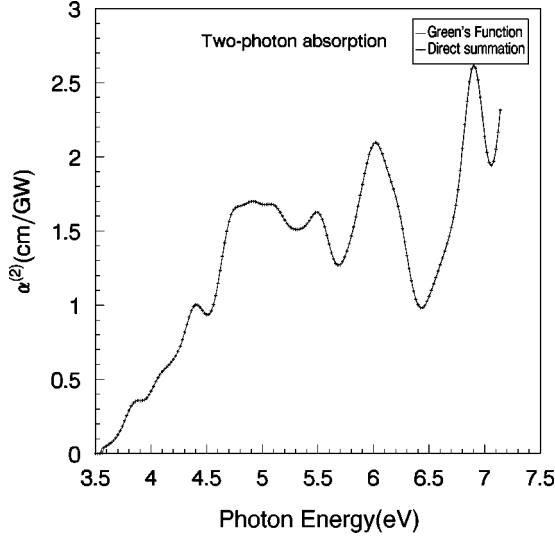
(4)

where

FIG. 1. The calculated two-photon absorption coefficients of NaCl.

$$|\widetilde{\Psi}_v^{(m)}\rangle = M|\Psi_v^{(m)}\rangle \qquad (5)$$

with

$$|\Psi_v^{(1)}\rangle = |v\rangle. \qquad (6)$$

Then the transition amplitude $T_{cv}^{(l)}$ [Eq. (2)] can be simply written as a scalar product

$$T_{cv}^{(l)} = \langle c|\widetilde{\Psi}_v^{(l)}\rangle. \qquad (7)$$

It is easy to justify this formalism by substituting Eqs. (4) and (5) into Eq. (7) recursively and comparing with Eq. (2).

According to the definitions of $G(E)$ [Eq. (3)], functions $|\Psi_v^{(m+1)}\rangle$ are obtained by solving the inhomogeneous linear equation

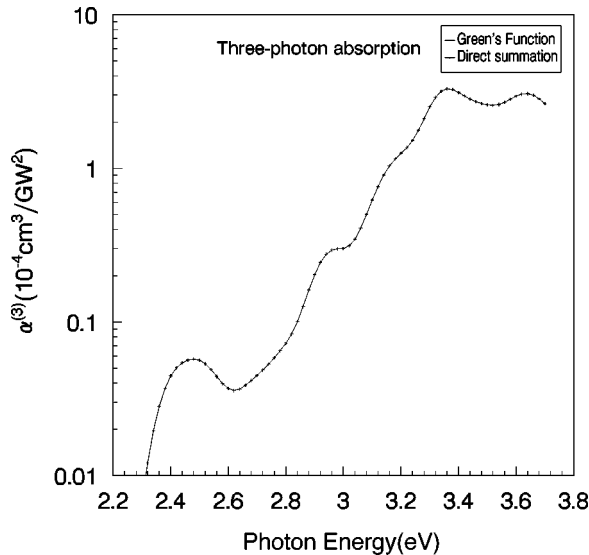$$(H - E_v - m\omega)|\Psi_v^{(m+1)}\rangle = |\widetilde{\Psi}_v^{(m)}\rangle, \qquad (8)$$

FIG. 2. The calculated three-photon absorption coefficients of NaCl.
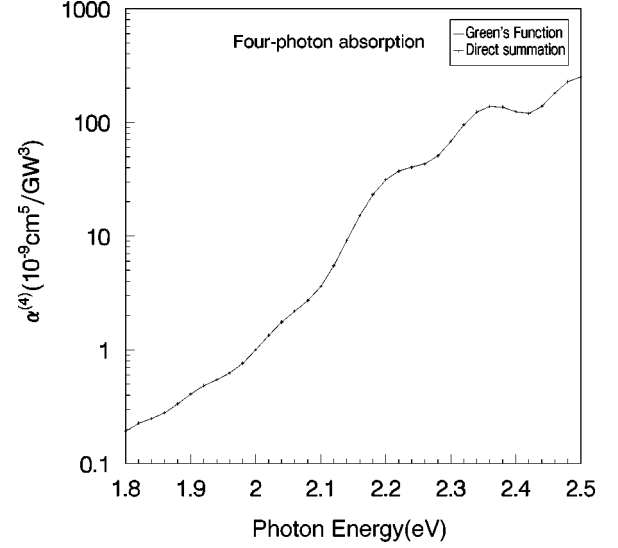

FIG. 3. The calculated four-photon absorption coefficients of NaCl.

iteratively to any designed order. In solids, all states are expanded in terms of the Bloch basis $\{|\chi_i\rangle\}$, i.e.,

$$|\Psi_v^{(m)}\rangle = \sum_i D_i^{(m)}|\chi_i\rangle. \qquad (9)$$

Substituting this expression into Eq. (8) and rewritten in a matrix form, we have an inhomogeneous linear equation for column vector $D^{(m)}$, i.e.,

$$[H - (E_v + m\omega)S]D^{(m+1)} = MD^{(m)}, \qquad (10)$$

in which H, S, and M stand for the Hamiltonian, overlap, and momentum matrices respectively, in the Bloch basis $|\chi_i\rangle$. The coefficient $D^{(m+1)}$ then can be obtained by factorization technique.

The role played by $|\widetilde{\Psi}_v^{(m)}\rangle$ is twofold: it forms the inhomogeneous term in Eq. (8) for the next iteration, and forms the scalar product with $\langle c|$ to extract the m-photon absorption amplitude $T_{cv}^{(m)}$, as was indicated in Eq. (7). Therefore, all MPA coefficients up to the lth order can be obtained during iterations when H, S, and M matrices are given in the Bloch basis and the conduction and valence bands are solved.

III. TEST ON NaCl

NaCl is an important optical material. Because of its interesting optical properties, wide gap and low cost in crystal growth, NaCl has been subjected to numerous experimental studies and become a typical material for MPA and laser-induced damage studies.[9] On the other hand, NaCl has simple crystal structure with only two atoms per unit cell. Thus, a thorough theoretical study on its electronic structure and optical properties is easy to perform. These are the reasons why we choose NaCl as the object of our theoretical calculations.

In the OLCAO method,[6] the basis functions for band and

TABLE I. Comparison of the results of two methods and available experimental data at a given wavelength λ. Unit for $\alpha^{(l)}$ is cm^{2l-3}/GW^{l-1}. (We give our results in five digits only to show the difference of the two theoretical calculations.)

Name	λ (μm)	Photon No.	Experiments $\alpha^{(l)}$	Direct summation $\alpha^{(l)}$	Green's function $\alpha^{(l)}$
NaCl	0.266	2	[a]3.5	1.4185	1.4181
	0.397	3	[a]6.9×10^{-4}	0.75987×10^{-4}	0.75978×10^{-4}
	0.532	4	[b]$(3.45-69) \times 10^{-9}$	9.5365×10^{-8}	9.5365×10^{-8}

[a]Reference 1.
[b]Reference 13.

optical calculations are orthogonalized Bloch sums, which are constructed from atomiclike function $\phi_\alpha(\vec{r} - \vec{\tau}_i - \vec{R}_\mu)$ centered at the ith atom in the μth unit cell through

$$\chi'_{iv}(\vec{k},\vec{r}) = \chi_{iv}(\vec{k},\vec{r}) - \sum_c \langle \chi_{ic}(\vec{k},\vec{r}) | \chi_{iv}(\vec{k},\vec{r}) \rangle \chi_{ic}(\vec{k},\vec{r}) \tag{11}$$

with

$$\chi_{i\alpha}(\vec{k},\vec{r}) = \sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu} \phi_\alpha(\vec{r} - \vec{\tau}_i - \vec{R}_\mu) \quad (\alpha = c,v), \tag{12}$$

where c, v represent the core and valence orbitals, respectively. In the present calculations, $3s$, $4s$, $3p$, $4p$, and $3d$ of Na and Cl are treated as valence orbitals. All atomic orbitals were composed of 16 Gaussian-type functions with decaying exponents ranging from 0.15 to 50 000. In the self-consistent iterations, the potential and the charge density of crystal are represented by the superpositions of atom-centered functions consisting of simple Gaussians, which were carefully chosen to ensure that the fitting error to valence charge density was small enough and the calculated electronic structure was accurate. The sums over the Brillouin zone (BZ) were performed using 60 Chadi-Cohen special k points in the irreducible BZ.[10] A direct gap E_g of 7.2 eV at Γ was obtained which is smaller than the experimental value of 8.6 eV,[3] as was expected for the LDA of the DFT.[11] At each k point, only the valence-band states and a few conduction-band states with energies less than $2E_g$ were concerned with multiphoton transitions (the top of the valence band was taken as the energy zero). It can be understood by the fact that the transition probability of the l-photon process is several orders of magnitude lower than the $(l-1)$-photon processes and consequently the detection of l-photon processes can only be realized in a situation in which $(l-1)$-photon processes are not possible. Thus the interested photon energies for l-photon processes will range from E_g/l to $E_g/(l-1)$, and the final conduction-band states of the transitions induced by the l-photon process will be in the range $E_g/(l-1)$ above the conduction-band minimum. This is the great advantage of Green's-function approach. The Hamiltonian matrix H and overlap matrix S were given during self-consistent band calculation and then used in the establishment of the coefficient determinant of the linear equation for $|\Psi_v^{(l)}\rangle$. The momentum matrix M was also computed in advance before calculating $|\Psi_v^{(l)}\rangle$ to construct the inhomogeneous term in Eq. (8). In order to smooth MPA

spectroscopy, the δ function in Eq. (1) was approximated by a Gaussian function with a width of 0.24 eV. The refractive index n, as an input parameter to the MPA coefficient in Eq. (1), was separately evaluated in the formalism of linear optical theory. The calculated refractive index at zero frequency is 1.53 in close agreement with the experimental value of 1.52.[12]

Following the steps described above, two-, three-, and four-photon absorption spectroscopies of NaCl in the interested range of frequency were calculated by using the Green's-function approach. For comparison purposes, they were also computed using the conventional method by direct sum as given by Eq. (2). Both results are given in Figs. 1–3. The accordance between the two results shows not only the equivalence of Eq. (2) and Eq. (7), but also the numerical error in our computation is negligible. Table I lists the MPA coefficients calculated at a given wavelength λ, along with the available experimental data for comparison.

We should mention that the experimentally deduced MPA coefficients are significantly effected by many factors, such as temporal and spacial distribution of the laser intensity, sample thickness and temperature, type and concentration of impurities, and so on.[1,4] Due to those factors, the experimental data may range over one or two orders of magnitude.[14]. While the theoretical evaluations also have some uncertainties, e.g., the limitation of the LDA and the neglecting of some factors, such as the modification of the solid structure by the external field, excitonic effects, and the finite-temperature effect, etc. Based on the above observations, we think the agreement between our theoretical evaluations and the experimental measurements is fairly good.

IV. CONCLUSION AND DISCUSSION

We have extended the Green's-function technique to the investigation of multiphoton transitions in crystalline solids. Testing calculations on MPA coefficients of NaCl indicates that it is an efficient and accurate method. A multiple sum over the intermediate states has been converted to solving the corresponding inhomogeneous linear equations recursively. Unlike the Green's-function approach, the conventional method requires the knowledge of all the eigenstates and the momentum matrix elements between these eigenstates to carry out the summations over all intermediate states. While in the Green's-function approach, only the initial valence-band states $|v\rangle$ and a few final conduction-band states within the range of E_g above the conduction-band minimum are involved in the calculations. Moreover, the application of

variational techniques to time-dependent perturbation theory[15] and the iterative conjugate-gradient method[16] are very efficient to solve the inhomogeneous equation [Eq. (8)], especially when large basis sets are used or when the solution is required as a function of a free parameter (here, the frequency of the photon). The application of variational techniques would further enhance the use of the Green's-function method.

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