

Second-order susceptibility from a tight-binding Hamiltonian

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Using a new formalism that modifies a tight-binding Hamiltonian to include interaction with a time-dependent electromagnetic field, we have obtained an analytical expression for the second-order susceptibility. This expression has been used to calculate the energy dependence of $\chi^{(2)}(\omega)$ for GaAs. The results are in agreement with previous calculations and with available experimental data. [S0163-1829(98)01848-7]

I. INTRODUCTION

Nonlinear optical phenomena in semiconductors are of considerable interest for both applications and understanding of the fundamental physics. For this reason there have been several previous theoretical studies of the second-order nonlinear susceptibility $\chi^{(2)}(\omega)$.¹⁻³ An additional motivation involves experiments in which semiconductors are subjected to intense subpicosecond laser pulses.⁴⁻⁶ Measurements of second harmonic generation (SHG) provide information about the dynamics of the structural changes that take place in the material between pump and probe pulses.^{7,8} It would be very useful to have a formalism that permits calculations of nonlinear effects from a tight-binding Hamiltonian, since tight-binding methods provide a versatile approach to many problems involving real materials.⁹ For example, tight-binding molecular dynamics has been used to simulate the coupled dynamics of electrons and ions in semiconductors that are subjected to ultrafast and ultraintense laser pulses.¹¹ In this context, and others, an efficient tight-binding technique for evaluating the SHG susceptibility $\chi^{(2)}(\omega)$ would be very useful.

Our calculation is based on the formalism introduced by Graf and Vogl,¹² who first recognized that a time-dependent Peierls substitution can be used to couple electrons to an electromagnetic field without the need of any additional parameters. In their approach, each element of the unperturbed tight-binding Hamiltonian is multiplied by a phase factor containing the vector potential associated with an arbitrarily intense and time-dependent electromagnetic field. They employed this idea in obtaining an analytical expression for the linear dielectric function in a tight-binding representation, and performing a calculation for GaAs that yielded satisfactory agreement with the experimental measurements. In Sec. II of this paper we summarize the essential features of their formalism. In Sec. III we then extend it to obtain an analytical expression for the second-order nonlinear susceptibility $\chi^{(2)}(\omega)$. This expression is then employed in Sec. IV, where results are given for the real and imaginary parts of $\chi^{(2)}(\omega)$ in the case of GaAs. These results are in good agreement with previous calculations and with the available experimental data.

II. TIGHT-BINDING HAMILTONIAN IN AN EXTERNAL ELECTROMAGNETIC FIELD

Let us begin with a Bloch sum over the localized Löwdin¹⁰ orbitals $|\alpha, L\rangle$:

$$|\alpha, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_L e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha L}} |\alpha, L\rangle. \quad (1)$$

Here L labels the unit cell and α labels a specific atomic orbital on a specific site. There are N unit cells labeled by lattice vectors $\mathbf{R}_{\alpha L}$. The matrix elements of the tight-binding Hamiltonian are

$$\begin{aligned} \langle \alpha', \mathbf{k} | H | \alpha, \mathbf{k} \rangle &= \sum_L e^{i\mathbf{k}\cdot(\mathbf{R}_{\alpha' L} - \mathbf{R}_{\alpha L})} \\ &\times t_{\alpha', \alpha}(\mathbf{R}_{\alpha', L} - \mathbf{R}_{\alpha L}) + \epsilon_{\alpha} \delta_{\alpha', \alpha} \end{aligned} \quad (2)$$

where $R_{\alpha} = R_{\alpha, 0}$. Here $t_{\alpha', \alpha}$ and ϵ_{α} are the usual off-site and on-site matrix elements. Each eigenstate $|n, \mathbf{k}\rangle$ is a superposition of Bloch sums (1) with appropriate coefficients $\mathbf{C}_{\alpha}(n\mathbf{k})$:

$$|n\mathbf{k}\rangle = \sum_{\alpha} C_{\alpha}(n\mathbf{k}) |\alpha\mathbf{k}\rangle, \quad (3)$$

where n is the band index.

When $\mathbf{k}\cdot\mathbf{p}$ theory is adapted to the tight-binding form, an effective momentum operator \mathbf{P} and a kinetic energy operator \mathbf{T} can be defined.¹² In matrix form these operators are

$$\mathbf{p}_{n, n'}(\mathbf{k}) = \frac{m_0}{\hbar} \mathbf{C}_{\alpha}^{\dagger}(n\mathbf{k}) \nabla_{\mathbf{k}} \mathbf{H}(\mathbf{k}) \mathbf{C}(n'\mathbf{k}), \quad (4)$$

$$\mathbf{T}_{n, n'}(\mathbf{k}) = \frac{m_0}{\hbar^2} \mathbf{C}_{\alpha}^{\dagger}(n\mathbf{k}) \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \mathbf{H}(\mathbf{k}) \mathbf{C}(n'\mathbf{k}). \quad (5)$$

Here $\mathbf{H}(\mathbf{k})$ is the Hamiltonian matrix whose elements are defined in Eq. (2), and $\mathbf{C}_{\alpha}(n\mathbf{k})$ is the vector whose components are defined in Eq. (3).

Interaction with an electromagnetic field requires an appropriate modification of the Hamiltonian (2). The most efficient approach in a tight-binding picture is to use the Peierls substitution,¹³ which has long been a useful tool for time-independent fields and has been generalized to the time-dependent case.¹² The familiar minimal coupling substitution $\mathbf{p} \rightarrow \mathbf{p} - (e/c)\mathbf{A}$, where e is the charge of the electron and \mathbf{A} is the vector potential, is equivalent to the replacement

$$t_{\alpha',\alpha}(\mathbf{R}'-\mathbf{R})=t_{\alpha',\alpha}^0(\mathbf{R}'-\mathbf{R})\exp\left[-\frac{ie}{\hbar c}(\mathbf{R}'-\mathbf{R})\cdot\mathbf{A}(t)\right]. \quad (6)$$

The tight-binding expression for the current-density operator \mathbf{J} can be written in terms of the effective momentum and kinetic-energy matrices defined above:¹²

$$\mathbf{J}_{n',n}=\frac{e}{m_0}\mathbf{p}_{n',n}+\frac{e^2}{m_0c}\mathbf{T}_{n',n}(\mathbf{k})\cdot\mathbf{A}(t). \quad (7)$$

III. SECOND-ORDER SUSCEPTIBILITY IN A TIGHT-BINDING REPRESENTATION

In an intense field, the macroscopic current density contains contributions to all orders in the electric field. In particular, the second-order contribution will be related to the electric fields $\mathbf{E}_\beta(\omega_1)$ and $\mathbf{E}_\gamma(\omega_2)$ via the second-order conductivity tensor $\sigma_{\alpha\beta\gamma}^{(2)}(\omega_1,\omega_2)$:

$$J_\alpha^{(2)}(\omega_1,\omega_2)=\sigma_{\alpha\beta\gamma}^{(2)}(\omega_1,\omega_2)E_\beta(\omega_1)E_\gamma(\omega_2). \quad (8)$$

Here α , β , and γ represent Cartesian coordinates. The second-order susceptibility tensor is related to the conductivity tensor by

$$\chi_{\alpha\beta\gamma}^{(2)}(\omega_1,\omega_2)=\frac{i}{2\omega}\sigma_{\alpha\beta\gamma}^{(2)}(\omega_1,\omega_2). \quad (9)$$

For simplicity, we will limit the calculation to second-harmonic generation when the two frequencies ω_1,ω_2 are equal.

Standard response theory extended to second order in the interaction¹⁴ involves the thermodynamic average of the current-density operator:

$$\begin{aligned} \langle J_\alpha(t) \rangle &= \langle J_\alpha(t) \rangle_0 + \frac{i}{c\hbar} \int_{-\infty}^t dt_1 \langle [\tilde{J}_\alpha(t), \tilde{J}_\beta(t_1)] \rangle_0 A_\beta(t_1) \\ &+ \left(\frac{i}{c\hbar} \right)^2 \int_{-\infty}^t dt_1 \\ &\times \int_{-\infty}^{t_1} dt_2 \langle [[\tilde{J}_\alpha(t), \tilde{J}_\beta(t_1)], \tilde{J}_\gamma(t_2)] \rangle_0 \\ &\times A_\beta(t_1) A_\gamma(t_2). \end{aligned} \quad (10)$$

Tildes are used to denote operators in the interaction picture, and $\langle \rangle_0$ indicates an equilibrium average.

If the completeness relation satisfied by the eigenvectors $|n,\mathbf{k}\rangle$ is inserted on the right-hand side of Eq. (10), one obtains a product of current-density matrices. The terms that are second-order in the electric field can be sorted out using Eq. (7). We note that the current operators on the right-hand side of Eq. (10) result from the interaction Hamiltonian¹⁴

$$H' = -\frac{1}{c} J_\alpha A_\alpha. \quad (11)$$

This expression is correct to only the first order in the vector potential \mathbf{A} ; however, the term that is neglected (involving \mathbf{A}^2) does not give rise to electronic transitions in the long-wavelength approximation, since it can be eliminated

through a unitary transformation.¹⁵ Only the last term in Eq. (10) gives a contribution that is second-order in the electric field, since the subscript ‘‘0’’ indicates that the current operator (7) is evaluated in the unperturbed system, with $\mathbf{A}=0$. The second-order susceptibility tensor must be symmetric¹⁶ in the last two Cartesian coordinates β and γ , so we permute the times t_1 and t_2 in Eq. (10). The resulting expression is

$$\begin{aligned} \chi_{\alpha\beta\gamma}^{(2)} &= \frac{i}{2\hbar^2\Omega} \left(\frac{e}{m_0} \right)^3 \\ &\times \sum_{m,n,l,\mathbf{k}} \frac{p_{nm}^\alpha [p_{ml}^\beta p_{ln}^\gamma]}{\omega^3 (2\omega - \omega_{mn})} \left(\frac{f_{ln}}{\omega - \omega_{ln}} + \frac{f_{ml}}{\omega - \omega_{ml}} \right) \end{aligned} \quad (12)$$

where Ω is the crystal volume and $[p_{nl}^\beta p_{ln}^\gamma]$ indicates a symmetrized form. Expression (12) is a general one, in the sense that it is not simplified by any symmetry of the material. As in the case of the linear dielectric tensor,¹² the tight-binding expression for the second-order susceptibility is similar to the classical one, but the matrix elements \mathbf{p}_{nm} are given by Eq. (4). A general result of $\mathbf{k}\cdot\mathbf{p}$ theory is that the average of $\nabla_{\mathbf{k}}H(\mathbf{k})$ for any Bloch state [with $H(\mathbf{k})$ the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian] equals the average of the momentum operator $(\hbar/i)\nabla$. The above result is, therefore, not unexpected.

Invoking time-reversal symmetry, and adding an infinitesimal imaginary part to the frequency, $\omega + i\eta$ with $\eta \rightarrow 0$, one can separate the real and imaginary parts of $\chi^{(2)}(\omega)$:

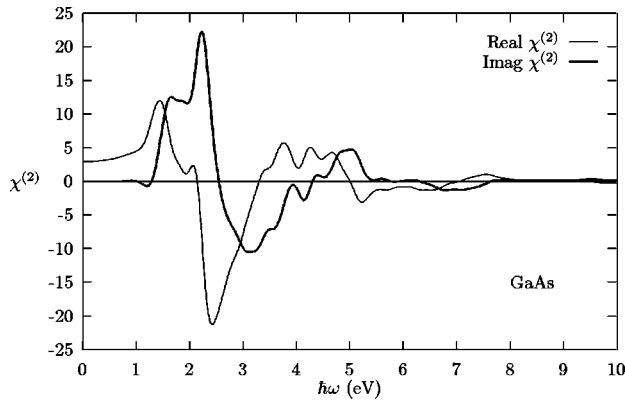
$$\begin{aligned} \text{Re}[\chi_{\alpha\beta\gamma}^{(2)}] &= \frac{i}{2\hbar^2\Omega} \left(\frac{e}{m_0\omega} \right)^3 \sum_{m,n,l,\mathbf{k}} p_{nm}^\alpha [p_{ml}^\beta p_{ln}^\gamma] \\ &\times \left[\frac{f_{ln}}{\omega - \omega_{ml}} \left(\frac{1}{\omega - \omega_{ln}} - \frac{1}{2\omega - \omega_{mn}} \right) \right. \\ &\left. + \frac{f_{ml}}{\omega - \omega_{ln}} \left(\frac{1}{\omega - \omega_{ml}} - \frac{1}{2\omega - \omega_{mn}} \right) \right], \end{aligned} \quad (13)$$

$$\begin{aligned} \text{Im}[\chi_{\alpha\beta\gamma}^{(2)}] &= \frac{i\pi}{2\hbar^2\Omega} \left(\frac{e}{m_0\omega} \right)^3 \sum_{m,n,l,\mathbf{k}} p_{nm}^\alpha [p_{ml}^\beta p_{ln}^\gamma] \\ &\times \left[f_{ln} \frac{\delta(2\omega - \omega_{mn}) - \delta(\omega - \omega_{ln})}{\omega - \omega_{ml}} \right. \\ &\left. + f_{ml} \frac{\delta(2\omega_{mn} - \omega_{mn}) - \delta(\omega - \omega_{ml})}{\omega - \omega_{ln}} \right]. \end{aligned} \quad (14)$$

The apparent divergence at $\omega=0$ can be cured in the same way as in Ref. 17. For computational purposes, however, the above expressions are quite sufficient.

IV. CALCULATION OF $\chi^{(2)}(\omega)$ FOR GaAs

A dielectric function is determined by the eigenvalues and eigenvectors at many points in the Brillouin zone. In addition, both the ground state and relevant excited states are important. For this reason we follow Ref. 18 in extending the minimal sp^3 orbital basis with an additional orbital s^* , which models the manifold of d states and other higher-lying

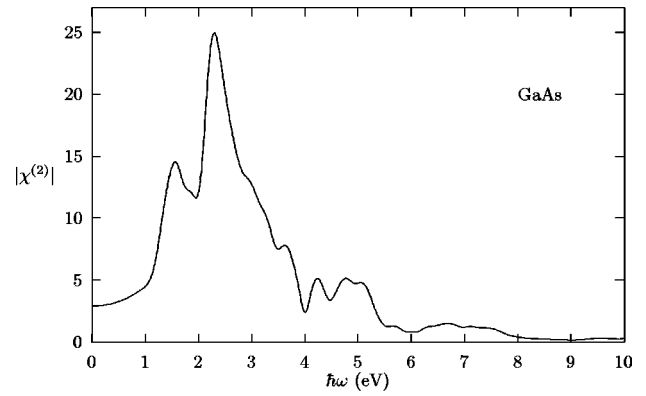
FIG. 1. Real and imaginary parts of $\chi^{(2)}(\omega)$.

excited states that are omitted in a minimal basis. It has been shown that the Vogl sp^3s^* model provides a good description of the bands in both direct and indirect-band semiconductors, including GaAs and Si,¹⁸ and of the linear dielectric function.^{11,12}

Because of its noncentrosymmetric structure, it is appropriate to apply our formalism to GaAs. The analytic formula for $\chi^{(2)}(\omega)$ involves virtual electron processes (with n the valence-band state and m, l the conduction-band states) and virtual hole processes (with n, m the valence-band states and l the conduction-band state). Aspnes¹⁹ showed that the latter type of contribution can be neglected. We therefore include only the virtual electron transitions. We also choose to evaluate the imaginary part of Eq. (14), and then use the Kramers-Kronig relation to obtain the real part:

$$\text{Re}[\chi^{(2)}(\omega)] = \frac{2}{\pi} \mathbf{P} \int_0^\infty \frac{\omega'}{\omega'^2 - \omega^2} \text{Im}[\chi^{(2)}(\omega')] d\omega'. \quad (15)$$

The numerical calculation employs an adaptation of the method used to calculate the linear dielectric function. Details of this method have been published¹¹ and will not be repeated here. The results for the real and imaginary parts of $\chi_{xyz}^{(2)}$ (the only independent component) are presented in Fig. 1. Due to the nondissipative character of the second-order susceptibility, the experimentally measured quantity is $|\chi^{(2)}(\omega)|$, and the results for that quantity are shown in Fig. 2. Our results compare well with those calculated using other methods.¹⁻³ The major features in the structure of our calculated dispersion curves clearly resemble those obtained in a first-principles calculation.³ There is also good agreement with experiment:^{20,21} In the data for $|\chi^{(2)}(\omega)|$, the first peak

FIG. 2. Magnitude of $\chi^{(2)}(\omega)$.

at 1.5 eV agrees with the present results, and the deep minimum and the second peak at 2.3 eV appear to be only slightly shifted.

The results presented in Figs. 1 and 2 are in arbitrary units. As in the case of the linear dielectric function,¹² the overall scale is too low by about a factor of 2, but the energy dependence of $\chi^{(2)}$ is correct, as noted above. Another check is provided by a set of sum rules.²² Those that weight the higher frequencies heavily (by some power of ω) are not well satisfied by the present model, which is only valid for excitations with energies up to a few eV. On the other hand, the sum rule

$$\int_0^\infty \text{Re}[\chi^{(2)}(\omega)] d\omega = 0 \quad (16)$$

is a valid test. Our numerical results give

$$\int_0^\infty \text{Re}[\chi^{(2)}(\omega)] d\omega = 0.35, \quad (17)$$

which is quite satisfactory for a function that varies over a range of about -20 to $+10$ in Fig. 1.

V. CONCLUSION

We have obtained an expression for the SHG susceptibility $\chi^{(2)}(\omega)$, which can be employed with a tight-binding Hamiltonian. This expression has been tested for GaAs, and the results agree with previous calculations and with experiment.

ACKNOWLEDGMENT

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