First-principles calculations of nonlinear optical susceptibility of inorganic materials

First-principles calculations of nonlinear optical susceptibility of inorganic materials

Michel Rérat[1], Wen-Dan Cheng[2,3] and Ravindra Pandey[2]

[1] Laboratoire de Chimie Structurale, UMR 5624, Université de Pau, IFR, rue J-Ferry, 64000 Pau, France
[2] Department of Physics, Michigan Technological University, Houghton, MI 49931, USA

Abstract
A method for calculations of the frequency-dependent nonlinear susceptibility of inorganic materials is implemented in the velocity gauge using a linear combination of atomic orbitals (LCAO) method within the framework of either the Hartree–Fock approximation or density functional theory. It is based on the standard time-dependent diagrammatic perturbation theory and has previously been applied successfully for atoms and molecules. For inorganic materials, it requires the eigenvalues and position operator matrix elements at several k points in the Brillouin zone. A quantitative assessment of the predictability of the method was made on cubic GaN for which the results of previous theoretical studies are available.

1. Introduction

Calculations based on quantum mechanical methods have now been routinely applied for the quantitative prediction of the nonlinear optical (NLO) properties of atomic and molecular systems [1–4]. In general, these methods are based on perturbation theory methods where the unperturbed molecular ground state provides a complete set of eigenfunctions in terms of which the perturbed state can be expanded. These methods generally use the expressions derived from the theory of Ward [5] and Orr and Ward [6] to calculate the frequency-dependent NLO properties from the matrix elements of the dipole operator and the energies of molecular orbitals that are expanded in the LCAO (linear combination of atomic orbitals) scheme.

In this paper, we now propose to implement the Ward theory to calculate nonlinear susceptibilities of inorganic materials using the LCAO scheme where the electronic structure can be described in the framework of either the Hartree–Fock (HF) approximation or density functional theory (DFT). In the LCAO scheme, linear combinations of Gaussian orbitals are used to construct a localized atomic basis from which Bloch functions are constructed by a further linear combination with plane-wave phase factors. The LCAO–HF or LCAO–DFT methods as implemented in the CRYSTAL95 program [7] have been shown to provide a reliable

---

[3] Permanent address: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, People's Republic of China.

description of the structural and electronic properties of a wide variety of ionic and semi-ionic materials.

It may be noted here that a number of theoretical models have previously been proposed for second-order susceptibility calculations for semiconducting materials [8–21]. Based on the first-principles band structure methods, Levine and Allan [13, 14] and Chen *et al* developed the formalism which included the local-field corrections. It led to the successful prediction of static values of the linear and nonlinear susceptibilities of binary semiconductors, for example GaAs. On the other hand, the Sipe's group, see [16–18], employed the uncoupled treatment of the Hamiltonian using the standard time-dependent perturbation theory for the frequency-dependent susceptibility calculations of semiconductors. Rearranging the terms in the susceptibility expressions of Aversa and Sipe [16], Rashkeev *et al* [19–21] reported the frequency-dependent linear and nonlinear susceptibilities of various binary and ternary semiconductors, which are in good agreement with the corresponding experimental values.

In the standard time-dependent perturbation theory, the susceptibility calculations can be performed in either length- or velocity-gauge formulations depending on the form of the interaction between the long-wavelength electromagnetic field and the crystalline solid considered. In the former approach, the interaction is taken to be $\boldsymbol{E} \cdot \boldsymbol{r}$ in which $\boldsymbol{r}$ is the position operator and $\boldsymbol{E}$ is the electric field. The latter approach, on the other hand, considers the interaction to be $\boldsymbol{A} \cdot \boldsymbol{p}$ where $\boldsymbol{p}$ is the momentum operator and $\boldsymbol{A}$ is the vector potential of the field. Although these two formulations are proven to be equivalent through a unitary transformation [22], each formulation has its own disadvantages [16]. The susceptibility expressions in the velocity-gauge formulation appear to diverge in the static limit while the position operator matrix elements can only be used for long wavelengths, for which the spatial variation of $\boldsymbol{A}(\boldsymbol{r}, t)$ (and $\boldsymbol{E}(\boldsymbol{r}, t)$) in the Hamiltonian can be neglected. That is, $\boldsymbol{A}(\boldsymbol{r}, t)$ (or $\boldsymbol{E}(\boldsymbol{r}, t)$) can be replaced by $\boldsymbol{A}(\boldsymbol{R}, t)$ (or $\boldsymbol{E}(\boldsymbol{R}, t)$) in the kinetic energy term, where $\boldsymbol{R}$ is a point taken in the interior of the system of charges.

We begin with the expressions derived by Ward [5] in the standard time-dependent perturbation theory in the length-gauge formulation, i.e. the perturbation interaction Hamiltonian between the independent particle and the applied field is treated in the electronic dipole approximation ($\boldsymbol{E} \cdot \boldsymbol{r}$). The susceptibility is then directly proportional to the product of the moment matrix elements between a pair of occupied valence and unoccupied conduction bands and inversely proportional to the transition energy.

Although the analytical expressions for the nonlinear susceptibilities are derived in the length gauge by Aversa and Sipe [16], these expressions can also be written in terms of the velocity matrix element rather than the matrix elements of the position operator. In fact, the position and momentum operator matrix elements are related, i.e. $\boldsymbol{p}_{mn}/m = \mathrm{i}\omega_{mn}\boldsymbol{r}_{mn}$ when m and n are exact eigenvectors of the 'true' zeroth-order Hamiltonian, H_0. This is the reason why the susceptibilities calculated by the $\boldsymbol{A} \cdot \boldsymbol{p}$ and $\boldsymbol{E} \cdot \boldsymbol{r}$ interaction Hamiltonians are identical when summation over the complete band states is performed. In practice, however, it is often impossible to perform the summation over a complete band states space. It is thus useful to know about the convergence behaviour of these two interaction Hamiltonians. The convergence of the susceptibility calculations with respect to the number of excited states is generally much slower in the velocity-gauge formulation than that using the length-gauge formulation for a static electric field or an electric field with long wavelengths. This is illustrated by Cohen-Tannoudji *et al* [22] for a classic example of the 1s–2s hydrogen transition in evaluating the contributions of summations over different intermediate np levels. Accordingly, the most satisfactory results were obtained from the $\boldsymbol{E} \cdot \boldsymbol{r}$ Hamiltonian if an incomplete summation over the excited-state space is performed.

In the following, we choose $\boldsymbol{R}$ as the origin of the coordinates $\boldsymbol{R} = \boldsymbol{0}$ in the $\boldsymbol{E} \cdot \boldsymbol{r}$ gauge to derive the expressions of linear and nonlinear susceptibilities for the bulk crystal. Here, the matrix elements in these expressions are those of the velocity operator and the r_{mn} transition moments will be calculated using the velocity formula as discussed above. Under these conditions, we can determine the electric dipole moment of the charge distribution with respect to the origin [22]. The transition energies and moments in the susceptibility expressions are calculated at the HF or DFT level, where the operator takes an effect on the crystal orbital functions which are constructed by a LCAO. The susceptibility calculations in our approach, we believe, has the ability to identify specific virtual excitation processes among the crystalline bands of a system that make the most significant contributions to the susceptibilities, along with the advantage of a faster convergence in the summation over a truncated excited-state space.

In the following section, we give the analytical expressions of the linear and nonlinear susceptibilities. In section 3, we briefly describe the LCAO method which has been used to obtain the electronic structure of the material considered here. The convergence test of the numerical procedure employed here along with the results for the linear and nonlinear susceptibilities are given in section 4. The summary of the present work is given in section 5.

2. Expressions for susceptibilities

We define the bulk electronic susceptibilities by an expression of the macroscopic polarization $\boldsymbol{P}$ in terms of the applied electric field $\boldsymbol{E}$:

$$\boldsymbol{P} = \chi^{(1)} \cdot \boldsymbol{E} + \chi^{(2)} \cdot \boldsymbol{EE} + \chi^{(3)} \cdot \boldsymbol{EEE} + \cdots \tag{1}$$

where $\chi^{(n)}$ is the nth-order susceptibility of the medium.

The total electric field and polarization in terms of their frequency component can also be written [5] as follows:

$$E(t) = \sum_n E(\omega_n) \exp(-\mathrm{i}\omega_n t) \qquad \text{and} \qquad P(t) = \sum_n P(\omega_n) \exp(-\mathrm{i}\omega_n t) \tag{2}$$

where the summation extends over all positive and negative frequencies ω_n.

In the one-electron approximation, the wavefunction is taken as an antisymmetrized product of one-electron orbitals. Assuming that the excited states are due to monoexcitations from occupied to unoccupied orbitals at each $\boldsymbol{k}$ point, the ground ($|g\rangle$) and excited states ($|m\rangle$ and $|n\rangle$) in terms of Bloch functions can be written as:

$$|g\rangle = |O_1(1, \boldsymbol{k}_1) O_2(2, \boldsymbol{k}_2) \cdots O_a(A, \boldsymbol{k}_a) O_b(B, \boldsymbol{k}_b) \cdots O_n(N, \boldsymbol{k}_n)|$$
$$|m\rangle = |O_1(1, \boldsymbol{k}_1) \cdots U_a(A, \boldsymbol{k}_a) O_b(B, \boldsymbol{k}_b) \cdots O_n(N, \boldsymbol{k}_n)|$$
$$|n\rangle = |O_1(1, \boldsymbol{k}_1) \cdots O_a(A, \boldsymbol{k}_a) U_b(B, \boldsymbol{k}_b) \cdots O_n(N, \boldsymbol{k}_n)|. \tag{3}$$

where O_i and U_j are the occupied and unoccupied orbitals in the ground state.

The matrix elements over the Block functions are then written as:

$$\langle g|\boldsymbol{r}|m\rangle = \sum_{A_{m,O_a \to U_a}} \langle O_a(\boldsymbol{k})|\boldsymbol{r}|U_a(\boldsymbol{k}')\rangle$$

$$\langle n|\boldsymbol{r}|g\rangle = \sum_{A_{n,O_b \leftarrow U_b}} \langle U_b(\boldsymbol{k}')|\boldsymbol{r}|O_b(\boldsymbol{k})\rangle$$

and

$$\langle m|\boldsymbol{r}|n\rangle = \sum_{A_{n,O_b \to U_b} A_{m,O_a \leftarrow U_a}} [\langle U_a(\boldsymbol{k})|\boldsymbol{r}|U_b(\boldsymbol{k}')\rangle \delta_{O_a O_b} - \langle O_b(\boldsymbol{k})|\boldsymbol{r}|O_a(\boldsymbol{k}')\rangle \delta_{U_a U_b}]. \tag{4}$$

Recall that the matrix element involving the positon operator (e.g. $\langle O_a(\mathbf{k})|\mathbf{r}|U_a(\mathbf{k}')\rangle$) is, in fact, calculated using the velocity operator (e.g. $\langle O_a(\mathbf{k})|\nabla|U_a(\mathbf{k}')/\omega_{U_a O_a}\rangle$) in this study.

In the LCAO scheme, a Bloch function is constructed from a linear combination of the basis functions $\varphi_\mu(\mathbf{k})$ as follows:

$$O_a(\mathbf{k}) = \sum_\mu c_a\mu(\mathbf{k})\varphi_\mu(\mathbf{k}) \qquad \text{with} \qquad \varphi_\mu(\mathbf{k}) = 1/\sqrt{N}\sum_g \chi^\mu(\mathbf{g})\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{g}} \tag{5}$$

where χ^μ is an atomic orbital in the $\mathbf{g}$ cell and N is the number of $\mathbf{g}$ cells.

The first-order susceptibility of a crystalline state can then be written as follows:

$$\chi^{(1)}(-\omega;\omega)_{ij} = e^2/(2\hbar V)\sum_k \Omega(\mathbf{k})$$
$$\times \sum_{O,U}\left[\left(\frac{\langle O|r^i|U\rangle\langle U|r^j|O\rangle}{\omega_{uo}+\omega-\mathrm{i}\Gamma_u/2} + \frac{\langle O|r^j|U\rangle\langle U|r^i|O\rangle}{\omega_{uo}-\omega+\mathrm{i}\Gamma_u/2}\right)\right.$$
$$\left.+\left(\frac{\langle O|r^i|U\rangle\langle U|r^j|O\rangle}{\omega_{uo}-\omega-\mathrm{i}\Gamma_u/2} + \frac{\langle O|r^j|U\rangle\langle U|r^i|O\rangle}{\omega_{uo}+\omega-\mathrm{i}\Gamma_u/2}\right)\right] \tag{6}$$

where V is the unit cell volume and $\Omega(\mathbf{k})$ is the geometrical weight factor associated with the $\mathbf{k}$ points of the irreducible Brillouin zone. The energy of the orbital O at wave vector $\mathbf{k}$ is $\hbar\omega_O$ and the frequency difference is defined as $\omega_{UO} \equiv \omega_U - \omega_O$. Spin degeneracy is not included here.

Omitting the resonance case with ($\Gamma = 0$) and rearranging the terms in equation (6), we arrive at the following expression:

$$\chi^{(1)}(-\omega;\omega)_{ij} = e^2/(\hbar V)\sum_k \Omega(\mathbf{k})$$
$$\times \sum_{O,U}\left(\frac{\mathrm{Re}\,\langle O|r^i|U\rangle\langle U|r^j|O\rangle}{\omega_{uo}+\omega} + \frac{\mathrm{Re}\,\langle O|r^j|U\rangle\langle U|r^i|O\rangle}{\omega_{uo}-\omega}\right). \tag{7}$$

Owing to the fact that the Bloch functions are expressed in terms of the basis functions (equation (5)), which in turn are taken as a LCAO expressed as a set of Gaussian-type orbitals, the dipole transition integrals between the crystalline orbitals become those of between Gaussian-type functions. It may be noted here the dipole transition integrals over Bloch functions in a periodic solid are not defined uniquely in the length gauge. This problem, as described before, can be solved by setting the original cell of $\mathbf{g}$ to be zero [23, 24]. That is, we can write

$$\langle O|\mathbf{r}|U\rangle = \sum C_{O\mu}^* C_{U\nu}\sum_g \langle\chi_\mu(\mathbf{0})|\mathbf{r}|\chi_\nu(\mathbf{g})\rangle \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{g}). \tag{8}$$

Similarly, the expression for the second-order optical susceptibility can be written as:

$$\chi^{(2)}(-\omega_3;\omega_1,\omega_2) = -\frac{1}{2}\frac{e^3}{\hbar^2}\frac{K}{V}\sum_k \Omega(\mathbf{k})\sum_{O_a,O_b}\sum_{U_a,U_b}\{\langle O_a|r^i|U_a\rangle[\langle U_a|r^k|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^k|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^j|O_b\rangle W_1 + \langle O_a|r^i|U_a\rangle[\langle U_a|r^k|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^k|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^i|O_b\rangle W_2 + \langle O_a|r^i|U_a\rangle[\langle U_a|r^j|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^j|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^k|O_b\rangle W_3 + \langle O_a|r^k|U_a\rangle[\langle U_a|r^j|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^j|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^i|O_b\rangle W_4 + \langle O_a|r^k|U_a\rangle[\langle U_a|r^i|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^i|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^j|O_b\rangle W_5 + \langle O_a|r^j|U_a\rangle[\langle U_a|r^i|U_b\rangle\delta_{O_a O_b}$$
$$-\langle O_b|r^i|O_a\rangle\delta_{U_a U_b}]\langle U_b|r^k|O_b\rangle W_6\} \tag{9}$$

where

$$W_1 = [(\omega_{U_a O_a} + \omega_1 + \omega_2)(\omega_{U_b O_b} + \omega_1)]^{-1} + [(\omega_{U_a O_a} - \omega_1 - \omega_2)(\omega_{U_b O_b} - \omega_1)]^{-1}$$
$$W_2 = [(\omega_{U_a O_a} - \omega_1)(\omega_{U_b O_b} - \omega_1 - \omega_2)]^{-1} + [(\omega_{U_a O_a} + \omega_1)(\omega_{U_b O_b} + \omega_1 + \omega_2)]^{-1}$$
$$W_3 = [(\omega_{U_a O_a} + \omega_1 + \omega_2)(\omega_{U_b O_b} + \omega_2)]^{-1} + [(\omega_{U_a O_a} - \omega_1 - \omega_2)(\omega_{U_b O_b} - \omega_2)]^{-1}$$
$$W_4 = [(\omega_{U_a O_a} - \omega_2)(\omega_{U_b O_b} - \omega_1 - \omega_2)]^{-1} + [(\omega_{U_a O_a} + \omega_2)(\omega_{U_b O_b} + \omega_1 + \omega_2)]^{-1}$$
$$W_5 = [(\omega_{U_a O_a} - \omega_2)(\omega_{U_b O_b} + \omega_1)]^{-1} + [(\omega_{U_a O_a} + \omega_2)(\omega_{U_b O_b} - \omega_1)]^{-1}$$
$$W_6 = [(\omega_{U_a O_a} - \omega_1)(\omega_{U_b O_b} + \omega_2)]^{-1} + [(\omega_{U_a O_a} + \omega_1)(\omega_{U_b O_b} - \omega_2)]^{-1}. \tag{10}$$

The second-order NLO susceptibility of a crystalline state can therefore be computed using (9). Depending on the combination of frequencies ω_1 and ω_2, we can obtain values of the coefficient of various NLO processes, for example second harmonic generation, linear electro-optic effect and sum and difference frequency generation.

To obtain the contributions from interband and intraband transitions for $\chi^{(2)}$ we consider the following three cases:

(i) $O_a = O_b$ and $U_a = U_b$

$$\chi_{vc}^{(2)}(-\omega_3; \omega_1, \omega_2) = -\frac{1}{2}\frac{e^3}{\hbar^2}\frac{K}{V}\sum_{\boldsymbol{k}}\Omega(\boldsymbol{k})$$
$$\times \sum_{O_a, U_a} \{\langle O_a|r^i|U_a\rangle[\langle U_a|r^k|U_a\rangle - \langle O_a|r^k|O_a\rangle]\langle U_a|r^j|O_a\rangle W_1'$$
$$+\langle O_a|r^j|U_a\rangle[\langle U_a|r^k|U_a\rangle - \langle O_a|r^k|O_a\rangle]\langle U_a|r^i|O_a\rangle W_2'$$
$$+\langle O_a|r^i|U_a\rangle[\langle U_a|r^j|U_a\rangle - \langle O_a|r^j|O_a\rangle]\langle U_a|r^k|O_a\rangle W_3'$$
$$+\langle O_a|r^k|U_a\rangle[\langle U_a|r^j|U_a\rangle - \langle O_a|r^j|O_a\rangle]\langle U_a|r^i|O_a\rangle W_4'$$
$$+\langle O_a|r^k|U_a\rangle[\langle U_a|r^i|U_a\rangle - \langle O_a|r^i|O_a\rangle]\langle U_a|r^j|O_a\rangle W_5'$$
$$+\langle O_a|r^j|U_a\rangle[\langle U_a|r^i|U_a\rangle - \langle O_a|r^i|O_a\rangle]\langle U_a|r^k|O_a\rangle W_6'\} \tag{11}$$

where we replace $\omega_{U_b O_b}$ by $\omega_{U_a O_a}$ in W_i to write W_i' since the summation indices are limited to $O_a = O_b$ and $U_a = U_b$;

(ii) $O_a = O_b$ and $U_a \neq U_b$

$$\chi_{vcc}^{(2)}(-\omega_3; \omega_1, \omega_2) = -\frac{1}{2}\frac{e^3}{\hbar^2}\frac{K}{V}\sum_{\boldsymbol{k}}\Omega(\boldsymbol{k})$$
$$\times \sum_{O_a}\sum_{U_a, U_b} \{\langle O_a|r^i|U_a\rangle\langle U_a|r^k|U_b\rangle\langle U_b|r^j|O_a\rangle W_1''$$
$$+\langle O_a|r^j|U_a\rangle[\langle U_a|r^k|U_b\rangle\langle U_b|r^i|O_a\rangle W_2''$$
$$+\langle O_a|r^i|U_a\rangle[\langle U_a|r^j|U_b\rangle\langle U_b|r^k|O_a\rangle W_3''$$
$$+\langle O_a|r^k|U_a\rangle[\langle U_a|r^j|U_b\rangle\langle U_b|r^i|O_a\rangle W_4''$$
$$+\langle O_a|r^k|U_a\rangle[\langle U_a|r^i|U_b\rangle\langle U_b|r^j|O_a\rangle W_5''$$
$$+\langle O_a|r^j|U_a\rangle[\langle U_a|r^i|U_b\rangle\langle U_b|r^k|O_a\rangle W_6''\} \tag{12}$$

where we replace $\omega_{U_b O_b}$ by $\omega_{U_b O_a}$ in W_i to write W_i'' since the summation indices are limited to $O_a = O_b$;

(iii) $O_a \neq O_b$ and $U_a = U_b$

$$\chi_{vvc}^{(2)}(-\omega_3; \omega_1, \omega_2) = \frac{1}{2}\frac{e^3}{\hbar^2}\frac{K}{V}\sum_{\boldsymbol{k}}\Omega(\boldsymbol{k})$$

$$\times \sum_{O_a, O_b} \sum_{U_a} \{\langle O_a | r^i | U_a \rangle \langle O_b | r^k | O_a \rangle \langle U_a | r^j | O_b \rangle W_1'''$$

$$+ \langle O_a | r^j | U_a \rangle \langle O_b | r^k | O_a \rangle \langle U_a | r^i | O_b \rangle W_2'''$$

$$+ \langle O_a | r^i | U_a \rangle \langle O_b | r^j | O_a \rangle \langle U_a | r^k | O_b \rangle W_3'''$$

$$+ \langle O_a | r^k | U_a \rangle \langle O_b | r^j | O_a \rangle \langle U_a | r^i | O_b \rangle W_4'''$$

$$+ \langle O_a | r^k | U_a \rangle \langle O_b | r^i | O_a \rangle \langle U_a | r^j | O_b \rangle W_5'''$$

$$+ \langle O_a | r^j | U_a \rangle \langle O_b | r^i | O_a \rangle \langle U_a | r^k | O_b \rangle W_6'''\} \tag{13}$$

where we replace $\omega_{U_b O_b}$ by $\omega_{U_a O_b}$ in W_i to write W_i''' since the summation indices are limited to $U_a = U_b$.

Combining equations (11)–(13), we can write

$$\chi^{(2)}(-\omega_3; \omega_1, \omega_2) = \chi_{vcc}^{(2)} + \chi_{vvc}^{(2)} + \chi_{vc}^{(2)} \tag{14}$$

where the double or triple summation indices are unequal for the terms $\chi_{vcc}^{(2)}$, $\chi_{vvc}^{(2)}$ and $\chi_{vc}^{(2)}$. Here, $\chi_{vc}^{(2)}$ represents contributions from the pure interband processes that result in electronic transitions from the valence to the conduction bands. The $\chi_{vcc}^{(2)}$ term includes contributions from the polarization effects associated with the interband transition, whereas $\chi_{vvc}^{(2)}$ includes the relaxation effects of the (occupied) valence bands associated with the interband transition. The contributions from $\chi_{vcc}^{(2)}$ and $\chi_{vvc}^{(2)}$ generally tend to cancel each other and therefore, in the length gauge, $\chi_{vc}^{(2)}$ with a high symmetrical tensor index contributes substantially to the second-order susceptibility of crystalline materials. Note that $\chi_{vc}^{(2)}$ is zero in the velocity gauge.

3. Computational details

The periodic LCAO scheme as implemented in the CRYSTAL95 program [7] was used for electronic structure calculations. It may be noted here that this program package offers a unique feature which allows a direct comparison of the HF and DFT results employing the same computational conditions for a given material. Here, the Bloch functions, $O_i(r)$, are solutions of the one-particle equations:

$$H_0 O_i(r) = \varepsilon_i O_i(r) \tag{15}$$

where

$$H_0(\text{HF}) = T + V + J + K \tag{16}$$

or

$$H_0(\text{DFT}) = T + V + J + v^{x-c}. \tag{17}$$

Here T, V and J are the kinetic, external potential and Coulomb operators, respectively. The exchange operator K of the HF method is replaced by the exchange–correlation potential v^{x-c} in the DFT method. The exchange term is calculated exactly and the correlation term is ignored in the HF calculations. On the other hand, the DFT calculations describe the exchange and correlation terms in a generalized gradient approximation (GGA) corresponding to non-local exchange and correlation potentials of Becke [25] and Perdew and Wang [26].

It is well known that both the HF and DFT methods suffer from the so-called band-gap problem; the HF method systematically overestimates the gap between the occupied (i.e. valence band) and unoccupied orbitals (i.e. conduction band) while the DFT method underestimates the gap. To correct the band-gap problem, we follow the approach of Levine and Allan [13] who used the scissor-operator approximation to reproduce the experimental value of the gap for a given material. The justification of this approach comes from the fact

that first-principles calculations that include self-energy corrections generally yield a rigid shift (Δ) of the conduction bands in most zinc-blende semiconductors [27]. In the present work, the transition energy $\hbar\omega_{UO}$ was replaced by $\hbar\omega_{UO} + \Delta/\hbar$, while the matrix elements of the position operator remain unchanged in the scissor-operator approximation.

The accuracy and reliability of the present method is now assessed by considering gallium nitride (GaN) in the cubic (zinc blende) phase. We note here that GaN is not only a prototype of a number of theoretical investigations [18, 19, 28], but is also a technologically important material for applications in tunable electro-optical devices [29–31].

4. Results and discussion

4.1. Convergence

In the present method, the crystalline state functions are first obtained by solving self-consistently either the HF or Kohn–Sham one-electron equations and are then used to calculate susceptibilities as outlined in section 2. Since the summation over excited states is replaced by a sum over the occupied (O) and virtual (U) orbitals and over k with a geometrical weight $\Omega(k)$ in (9), we need to study the convergence issues associated with the summations over orbitals and k points for the susceptibility calculations.

The sum-over-states expansion, in principle, requires a mixing of the ground state with several excited states under an applied field. In practice, a truncation of the expansion over the unoccupied orbitals (i.e. conduction bands) is, however, performed. Therefore, a test of apparent convergence of $\chi^{(2)}$ is required with respect to this truncation. The second convergence parameter is the number of k points considered for the irreducible Brillouin zone integration in the numerical procedure used here for susceptibility calculations.

For the cubic GaN, $\chi^{(2)}_{xyz}$ appears to converge in calculations that used at least 50 or more k points for the irreducible Brillouin zone integration. Likewise, a faster convergence of $\chi^{(2)}$ with respect to a number of crystal bands was seen, indicating that fact that the inclusion of only few conduction bands in the summation series can yield reliable values of $\chi^{(2)}$. In the following discussion we have considered 104 k points for the cubic GaN and have included all of the valence and conduction bands generated by our LCAO model in the susceptibility calculations.

4.2. Comparison with previous calculations

Table 1 lists the calculated values of the dielectric constant and the susceptibilities for GaN in the zinc blende phase and, also, compares these with the corresponding values obtained in previous first-principles studies. We also list the ε and $\chi^{(2)}$ values calculated at 1064 nm in table 1 in order to facilitate a comparison with the experimental data usually obtained at this wavelength. As discussed earlier, the scissor operator was used to match the calculated gap to the experimental value. It is found to be +1.24 and −7.87 eV for the gaps calculated using the DFT and HF approximations, respectively, for the cubic GaN. It may be noted here that the DFT calculations generally underestimate the gap whereas the HF calculations overestimate the gap in most of the semiconducting materials.

Although the 'corrected' gap of the cubic GaN is the same in both the HF and the GGA–DFT calculations, the HF values (see table 1) appear to be higher for ε and lower for χ_{xyz} relative to the corresponding GGA values. Overall, the agreement of the susceptibility values obtained in the present study with the calculated values obtained using the local density approximation with the pseudopotentials or muffin-tin orbitals method appears to be good. We do not include

Table 1. Calculated static and frequency-dependent values of the dielectric function (ε) and the susceptibility (χ, in pm V^{-1}) for the cubic GaN. The scissor-operator approximation was used to reproduce the experimental value of the band gap.

Method	$\varepsilon_{xx}(0)$	$\varepsilon_{xx}(\lambda = 1064 \text{ nm})$	$\chi_{xyz}(0)$	$\chi_{xyz}(\lambda = 1064 \text{ nm})$
This work				
GGA–LCAO, no scissor operator	4.91	5.06	13.3	14.48
GGA–LCAO, scissor operator	3.41	3.45	8.06	8.52
HF–LCAO, scissor operator	6.62	6.74	7.04	7.08
Chen *et al* [15]				
LDA–pseudopotential[a], no scissor operator	5.74	—	16.9	—
Rashkeev, Lambrecht and Segall [19]				
LDA–LMTO, no scissor operator	—	—	18.3	—
LDA–LMTO, scissor operator	—	—	10.6	—

[a] The calculated results include local field corrections.

the local field corrections in the present calculations which are generally known to increase the values by 10% in the zero frequency limit [14].

Finally, we identify the distinct physical contributions arising from the optical perturbation to the crystal susceptibility. In general, the derived formulae for the second-order response include various terms, and their partition into the so-called intraband and interband terms is rather conventional and depends somewhat on the formulation of the problem [2, 5, 23]. In the present model, χ_{vc} represents an interband process of transitions from the valence to conduction bands (see equation (11)) and its value is directly related to changes in the crystal orbital dipole moments occurring during the transition (i.e. $-\Delta\mu_a = e[\langle U_a|\boldsymbol{R}|U_a \rangle - \langle O_a|\boldsymbol{R}|O_a \rangle]$). It may be noted here that its value is zero in the velocity gauge. The terms χ_{vvc} and χ_{vcc}, as defined in equation (14), described mixed interband and intraband processes that include one and two conduction band states in the spectral sum. It is expected that the so-called polarization effects introduced by the electrons in the conduction bands upon excitation can be described by the χ_{vcc} term. On the other hand, the χ_{vvc} term includes the so-called relaxation effects of the valence bands occurring due to the promotion of electrons to conduction bands. For the cubic GaN, both the χ_{vvc} and χ_{vcc} terms are found to provide an almost equal contribution to the calculated second harmonic generation (SHG) susceptibilities, in agreement with the results of previous calculations [14] on the similar cubic semiconductors, namely AlP, AlAs, GaP and GaAs.

5. Summary

We have developed a method to calculate the linear and second-order NLO susceptibilities for a crystalline material in the velocity-gauge Hamiltonian employing either the HF theory or the DFT. The state wavefunction can be described by a simple configuration function, in which the determinable function is constructed by one-electron crystal orbitals which are a LCAO in this formalism. The reliability of the calculated results are evaluated using cubic GaN for which the results of several previous theoretical studies are available.

References

[1] Karna S P 1996 *J. Chem. Phys.* **104** 6590
    Karna S P and Yeates A T (eds) 1994 *Nonlinear Optical Materials: Theory and Modeling (ACS Symposium Series 628)* (Washington, DC: American Chemical Society)
[2] Kanis D R, Ratner M A and Marks T J 1994 *Chem. Rev.* **94** 195

[3] Bishop D M 1990 *Rev. Mod. Phys.* **62** 343
[4] Chemla D S and Zyss J (eds) 1987 *Nonlinear Optical Properties of Organic Molecules and Crystals* vol 1–3 (New York: Academic)
[5] Ward J F 1965 *Rev. Mod. Phys.* **37** 1
[6] Orr B J and Ward J F 1971 *Mol. Phys.* **20** 527
    Pugh D and Morley J O 1987 *Nonlinear Optical Properties of Organic Molecules and Crystals* vol 1, ed D S Chemla and J Zyss (New York: Academic)
[7] Dovesi R, Saunders V R, Roetti C, Causà M, Harrison N M, Orlando R and Aprà E 1996 *CRYSTAL95 User's Manual* (Torino: University of Torino)
[8] Levine B F 1973 *Phys. Rev.* B **7** 2600
[9] Fong C Y and Shen Y R 1975 *Phys. Rev.* B **12** 2325
[10] Choy M M, Ciraci S and Byer R L 1975 *IEEE J. Quantum Electron.* **11** 40
[11] Moss D J, Ghahramani E and Sipe J E 1991 *Phys. Status Solidi* b **164** 587
[12] Ching W Y and Huang M-Z 1993 *Phys. Rev.* B **47** 9479
[13] Levine Z H and Allan D C 1991 *Phys. Rev. Lett.* **66** 41
[14] Levine Z H and Allan D C 1991 *Phys. Rev.* **44** 12 781
[15] Chen J, Levine Z H and Wilkins J W 1995 *Appl. Phys. Lett.* **66** 1129
[16] Aversa C and Sipe J E 1995 *Phys. Rev.* B **52** 14 636
[17] Hughes J L P and Sipe J E 1996 *Phys. Rev.* B **53** 10 751
[18] Hughes J L P, Wang Y and Sipe J E 1997 *Phys. Rev.* B **55** 13 630
[19] Rashkeev S N, Lambrecht W R L and Segall B 1998 *Phys. Rev.* B **57** 3905
[20] Rashkeev S N, Lambrecht W R L and Segall B 1998 *Phys. Rev.* B **57** 9705
[21] Rashkeev S N, Limpijumnong S and Lambrecht W R L 1999 *Phys. Rev.* B **59** 2737
[22] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1997 *Photons and Atoms: Introduction to Quantum Electrodynamics* (New York: Wiley) pp 253–342
[23] Ayma D, Campillo J P, Rérat M and Causà M 1997 *J. Comput. Chem.* **18** 1253
[24] Ayma D, Rérat M and Lichanot A 1998 *J. Phys.: Condens. Matter* **10** 557
[25] Becke A 1988 *Phys. Rev.* A **88** 1053
[26] Perdew J P and Wang Y 1991 *Phys. Rev.* B **45** 13 244
[27] Zhu X and Louie S G 1991 *Phys. Rev.* B **43** 14 142
[28] Pandey R, Jaffe J and Harrison N 1994 *J. Phys. Chem. Solids* **219**
[29] Strite S and Morkoc H 1992 *J. Vac. Sci. Technol.* B **10** 1238
[30] Miragliotta J, Wickenden D K, Kistenmacher T J and Bryden W A 1993 *J. Opt. Soc. Am.* B **10** 1447
[31] Nakamura S and Fasol G 1997 *The Blue Laser Diode* (Berlin: Springer)