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Nonlinear optical susceptibilities, Raman efficiencies, and electro-optic tensors from first-principles density functional perturbation theory

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The nonlinear response of infinite periodic solids to homogenous electric fields and collective atomic displacements is discussed in the framework of density functional perturbation theory. The approach is based on the $2n+1$ theorem applied to an electric-field-dependent energy functional. We report the expressions for the calculation of the nonlinear optical susceptibilities, Raman scattering efficiencies, and electro-optic (EO) coefficients. Different formulations of third-order energy derivatives are examined and their convergence with respect to the **k**-point sampling is discussed. We apply our method to a few simple cases and compare our results to those obtained with distinct techniques. Finally, we discuss the effect of a scissors correction on the EO coefficients and nonlinear optical susceptibilities.

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I. INTRODUCTION

Nowadays, density functional theory[1,2] (DFT) is considered as a standard method in condensed matter physics, to study electronic, structural, and macroscopic properties of solids from first principles. Combined with adiabatic perturbation theory, it allows *a priori* the computation of derivatives of the energy and related thermodynamic potentials up to any order. At the second order, this approach has been applied to compute linear response functions such as phonon frequencies or Born effective charges with an accuracy of a few percent. The third-order derivatives are related to nonlinear properties such as phonon lifetimes, Raman tensors, or nonlinear optical susceptibilities.

The linear-response formalism has been implemented in various first-principles codes and is routinely applied to an increasing number of systems (see, for example, Ref. 3 and references therein). By contrast, the nonlinear response formalism has been mostly restricted to quantum chemistry problems. Although the hyperpolarizabilities of a huge number of molecules have been computed, taking into account both electronic and vibrational (ionic) contributions,[4,5] applications in condensed matter physics have focused on rather simple cases.[6–13]

Here, we present a methodology for the computation of nonlinear response functions and related physical quantities of periodic solids from density functional perturbation theory (DFPT). We focus on perturbations characterized by a zero wave vector and involving either three electric fields, or two electric fields and one atomic displacement. Following Nunes and Gonze,[14] our approach makes use of the $2n+1$ theorem applied to an electric-field-dependent energy functional.[15] We report the local density approximation (LDA) expressions, as implemented within the ABINIT package.[16]

Our paper is organized as follows. In Sec. II, we describe the theoretical background related to the $2n+1$ theorem and the electric field perturbation. In Sec. III, we describe the computation of the nonlinear optical susceptibilities, the nonresonant Raman scattering efficiencies of both transverse (TO) and longitudinal (LO) zone-center optical phonons and the linear electro-optic (EO) tensor. In Sec. IV, we illustrate the validity of the formalism by applying our methodology to some semiconductors and ferroelectric oxides and we briefly discuss the effect of a scissors correction on the EO coefficients and nonlinear optical susceptibilities.

Some of the tensors we consider in this work depend on static electric fields: they include contributions of both the electrons and the ions. Other quantities imply only the response of the valence electrons: they are defined for frequencies of the electric field high enough to get rid of the ionic contributions but sufficiently low to avoid electronic excitations. For clarity, we adopt the following convention. Static fields will be labeled by Greek indices $(\alpha,\beta,\ldots)$ while we will refer to optical fields with Latin symbols $(i,j,\ldots)$. To simplify the notation, we will also drop labels such as ∞ for quantities that do not involve the response of the ions. Using this convention, we can write ε_{ij} and $\varepsilon_{\alpha\beta}$, respectively, for the optical and static dielectric tensor, respectively, and $r_{ij\gamma}$ for the linear EO (Pockels) tensor that involves two optical and one static electric field.

II. FORMALISM

A. Mixed third-order energy derivatives

In this section, we present the general framework of the computation of third-order energy derivatives based on the $2n+1$ theorem.[17–19] Using the notation of Refs. 20 and 21, we consider three Hermitian perturbations labeled λ_1, λ_2, and λ_3. The mixed third-order derivatives

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{6}\left.\frac{\partial^3 E}{\partial\lambda_1\,\partial\lambda_2\,\partial\lambda_3}\right|_{\lambda_1=0,\lambda_2=0,\lambda_3=0} \qquad (1)$$

can be computed from the ground-state and first-order wave functions[19]

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{6}(\widetilde{E}^{\lambda_1\lambda_2\lambda_3} + \widetilde{E}^{\lambda_1\lambda_3\lambda_2} + \widetilde{E}^{\lambda_2\lambda_1\lambda_3} + \widetilde{E}^{\lambda_2\lambda_3\lambda_1} + \widetilde{E}^{\lambda_3\lambda_2\lambda_1} + \widetilde{E}^{\lambda_3\lambda_1\lambda_2}), \tag{2}$$

with

$$\begin{aligned}\widetilde{E}^{\lambda_1\lambda_2\lambda_3} = {} & \sum_\alpha [\langle \psi_\alpha^{\lambda_1} | (T + v_{ext})^{\lambda_2\lambda_3} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{\lambda_1} | (T + v_{ext} + v_{Hxc})^{\lambda_2} | \psi_\alpha^{\lambda_3} \rangle + \langle \psi_\alpha^{(0)} | (T + v_{ext})^{\lambda_1\lambda_2\lambda_3} | \psi_\alpha^{(0)} \rangle + \langle \psi_\alpha^{(0)} | (T + v_{ext})^{\lambda_1\lambda_2} | \psi_\alpha^{\lambda_3} \rangle] \\ & - \sum_{\alpha,\beta} \Lambda_{\beta\alpha}^{\lambda_2} \langle \psi_\alpha^{\lambda_1} | \psi_\beta^{\lambda_3} \rangle + \frac{1}{6} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \frac{\delta^3 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{\lambda_1}(\mathbf{r}) n^{\lambda_2}(\mathbf{r}') n^{\lambda_3}(\mathbf{r}'') \\ & + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{d}{d\lambda_2} \left. \frac{\delta^2 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right|_{\lambda=0} n^{\lambda_1}(\mathbf{r}) n^{\lambda_3}(\mathbf{r}') + \frac{1}{2} \int d\mathbf{r} \frac{d^2}{d\lambda_1 d\lambda_3} \left. \frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})} \right|_{\lambda=0} n^{\lambda_2}(\mathbf{r}) + \frac{1}{6} \left. \frac{d^3 E_{Hxc}[n^{(0)}]}{d\lambda_1 d\lambda_2 d\lambda_3} \right|_{\lambda=0}. \end{aligned} \tag{3}$$

T is the kinetic energy and E_{Hxc} (v_{Hxc}) is the sum of the Hartree and exchange-correlation energy (potential). The first-order potential $v_{Hxc}^{\lambda_2}$ can be computed as a second-order functional derivative of E_{Hxc}:[19]

$$v_{Hxc}^{\lambda_2} = \int \frac{\delta^2 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\lambda_2}(\mathbf{r}') d\mathbf{r}' + \frac{d}{d\lambda_2} \left. \frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})} \right|_{\lambda=0}. \tag{4}$$

Within the parallel gauge, the first-order Lagrange multipliers are given by

$$\Lambda_{\beta\alpha}^{\lambda_2} = \langle \psi_\beta^{(0)} | (T + v_{ext} + v_{Hxc})^{\lambda_2} | \psi_\alpha^{(0)} \rangle. \tag{5}$$

As a consequence of the $2n+1$ theorem, the evaluation of Eq. (3) requires no higher-order derivatives of the wave functions than the first one. These first-order wave functions are nowadays available in several first-principles codes. They can be computed from linear response by minimizing a stationary expression of the second-order energy[20] or equivalently by solving the corresponding Sternheimer equation.[22] It follows that the computation of third-order energy derivatives does not require additional quantities other than the calculation of second-order energy derivatives.

Equation (3) is the general expression of the third-order energy derivatives. In case at least one of the perturbations does not affect the explicit form of the kinetic energy or the Hartree and exchange-correlation energy, it can be simplified: some of the terms may be zero. This is the case for the electric field perturbations treated in this work as well as for phonon-type perturbations. Further simplifications can be made in case pseudopotentials without nonlinear exchange-correlation core correction are used.

B. The electric field perturbation

As mentioned in the Introduction, special care is required in case one of the perturbations λ_j is a macroscopic electric field $\boldsymbol{\mathcal{E}}$. In fact, as discussed in the literature, for infinite periodic solids, usually treated with Born–von Kármán boundary conditions, the scalar potential $\boldsymbol{\mathcal{E}} \cdot \mathbf{r}$ breaks the periodicity of the crystal lattice. Moreover, it is unbound from below: it is always possible to lower the energy by transferring electrons from the valence states to the conduction states in a distant region (Zener breakdown). However, for sufficiently small fields, the tunneling current through the band gap can be neglected and the system is well described by a set of electric-field-dependent Wannier functions $W_n(\mathbf{r})$. As shown by Nunes and Vanderbilt,[15] these Wannier functions minimize the energy functional

$$E[W_n; \boldsymbol{\mathcal{E}}] = E_0[W_n] - \Omega_0 \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{P}}, \tag{6}$$

where E_0 is the Kohn-Sham energy under zero field, Ω_0 the unit cell volume, and $\boldsymbol{\mathcal{P}}$ the macroscopic polarization that can be computed from the Wannier function centers. It is important to note that these Wannier functions do not correspond to the true ground state of the system but rather to a long-lived metastable state.

In practical applications, it is not mandatory to evaluate the functional equation (6) in a Wannier basis. It can equivalently be expressed using Bloch functions $u_{n\mathbf{k}}$ related to W_n by a unitary transform. In this case, the polarization can be computed as a Berry phase of the occupied bands[23]

$$\boldsymbol{\mathcal{P}} = -\frac{2ie}{(2\pi)^3} \sum_n^{occ} \int_{BZ} d\mathbf{k} \langle u_{n\mathbf{k}} | \boldsymbol{\nabla}_k | u_{n\mathbf{k}} \rangle, \tag{7}$$

where BZ is the Brillouin zone, e is the absolute value of the electronic charge, and the factor of 2 accounts for spin degeneracy. The Bloch functions are chosen to satisfy the periodic gauge condition

$$e^{i\mathbf{G}\cdot\mathbf{R}} u_{n\mathbf{k}+\mathbf{G}} = u_{n\mathbf{k}}. \tag{8}$$

In order to use Eq. (7) in practical calculations, the integration over the BZ, as well as the differentiation with respect to $\mathbf{k}$, has to be performed on a discrete mesh of N_k $\mathbf{k}$ points. In case of the ground-state polarization, the standard approach is to build strings of $\mathbf{k}$ points parallel to a vector of the reciprocal space $\mathbf{G}_\parallel$. The polarization can then be computed as a string-averaged Berry phase. Unfortunately, the adaptation of this method to the computation of the energy derivatives is plagued with several difficulties, like the following. The general form of the nonlinear optical susceptibility tensor of a compound is imposed by its symmetry. For example, in zinc-blende semiconductors, this tensor, expressed in *Cartesian coordinates*, reduces to $\chi^{(2)}_{ijl}=\chi^{(2)}|\epsilon_{ijl}|$, where ϵ is the Levi-Civita tensor. It follows that the *reduced coordinate* formulation of $\chi^{(2)}_{ijl}$ satisfies the relation

$$\left|\frac{\chi^{(2)}_{ijl}}{\chi^{(2)}_{iii}}\right| = \frac{1}{3}, \tag{9}$$

where at least one of the three indices i, j, and l are different from the two others. When we tried to use strings of **k** points to compute $\chi^{(2)}_{ijl}$, Eq. (9) was not satisfied. However, we were able to avoid these problems by using the finite difference formula of Marzari and Vanderbilt[24] on a regular grid of special **k** points (instead of strings),

$$\boldsymbol{\nabla} f(\mathbf{k}) = \sum_{\mathbf{b}} w_{\mathbf{b}}\mathbf{b}[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k})], \tag{10}$$

where **b** is a vector connecting a **k**-point to one of its nearest neighbors and $w_{\mathbf{b}}$ is a weight factor. The sum in Eq. (10) includes as many shells of first neighbors as necessary to satisfy the condition

$$\sum_{\mathbf{b}} w_{\mathbf{b}} b_\alpha b_\beta = \frac{g_{\alpha\beta}}{(2\pi)^2}, \tag{11}$$

where b_α are the reduced coordinates of **b** and $g_{\alpha\beta}$ is the metric tensor associated with the real space crystal lattice.

In the case of the ground-state polarization, we cannot apply the discretization equation (10) directly to Eq. (7). As shown by Marzari and Vanderbilt, the discretization of Eq. (7) does not transform correctly under the gauge transformation

$$u_{n\mathbf{k}}(\mathbf{r}) \to e^{-i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}}(\mathbf{r}). \tag{12}$$

Since Eq. (12) is equivalent to a shift of the origin by one lattice vector **R**, $\boldsymbol{\mathcal{P}}$ must change accordingly by one polarization quantum. In order to obtain a discrete expression that matches this requirement, we must combine Eq. (10) with the King-Smith and Vanderbilt formula[23,25]

$$\boldsymbol{\mathcal{P}} = \frac{2e}{N_k\Omega_0}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}\mathbf{b}\ \mathrm{Im}\ \ln\ \det\ [S(\mathbf{k},\mathbf{k}+\mathbf{b})], \tag{13}$$

where S is the overlap matrix between Bloch functions at **k** and $\mathbf{k}+\mathbf{b}$:

$$S_{n,m}(\mathbf{k},\mathbf{k}+\mathbf{b}) = \langle u_{n\mathbf{k}}|u_{m\mathbf{k}+\mathbf{b}}\rangle. \tag{14}$$

As discussed by Nunes and Gonze,[14] when we apply the perturbation expansion of the preceding section to the energy functional Eq. (6), we can adopt two equivalent approaches. The first possibility is the use of Eq. (7) for the polarization and a discretization after having performed the perturbation expansion. The second possibility is to apply the $2n+1$ theorem directly to Eq. (13) in which case no additional discretization is needed. Using the notations of Nunes and Gonze, we will refer to the first case as the discretization after perturbation expansion (DAPE) formulation and to the second one as the perturbation expansion after discretization (PEAD) formulation of the third-order energy. In the following sections, we will discuss both expressions. In addition, in Sec. IV B, we will compare their convergence with respect to the **k**-point sampling on a realistic example. The perturbation expansion of the first term (E_0) of Eq. (6) can easily be performed, as described in the Sec. II A. In contrast, the expansion of the second term ($-\Omega_0\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{P}}$) is more tricky since it explicitly depends on the polarization. In the two sections that follow, we will focus on the $-\Omega_0\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{P}}$ term of Eq. (6). It will be referred to as E_{pol}.

C. DAPE expression

According to the formalism of the preceding section, the $\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{P}}$ term acts as an additional external potential that has to be added to the ionic one. The $\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{P}}$ perturbation is linear in the electric field and does not depend explicitly on other variables such as the atomic positions. It just enters the terms of Eq. (3) that involve the first derivative of v_{ext} with respect to $\boldsymbol{\mathcal{E}}$. In other words, the only terms in Eq. (2) that involve the expansion of $\boldsymbol{\mathcal{P}}$ are of the form $\widetilde{E}^{\lambda_1\mathcal{E}_i\lambda_3}$, where λ_1 and λ_3 represent an arbitrary perturbation such as an electric field or an atomic displacement.

The DAPE expression of the third-order derivative of E_{pol} is written as follows[14]

$$\widetilde{E}^{\lambda_1\mathcal{E}_i\lambda_3}_{pol} = \frac{2ie\Omega_0}{(2\pi)^3}\int_{BZ} d\mathbf{k}\sum_{n}^{occ}\langle u^{\lambda_1}_{n\mathbf{k}}|\left(\frac{\partial}{\partial k_i}\sum_{m}^{occ}|u^{\lambda_3}_{m\mathbf{k}}\rangle\langle u^{(0)}_{m\mathbf{k}}|\right)|u^{(0)}_{n\mathbf{k}}\rangle, \tag{15}$$

where $u^{\lambda_j}_{n\mathbf{k}}$ are the projections of the first-order wave functions on the conduction bands. The complete expression of various third-order energy derivatives, taking into account the expansion of both E_0 and E_{pol}, are reported in Sec. III. Eq. (15) was derived first by Dal Corso and Mauri[26] in a slightly different context: they performed the perturbation expansion of the energy functional equation (6) using a Wannier basis. The resulting expression of the third-order energy was expressed in terms of Bloch functions by applying a unitary transform to the Wannier orbitals.

Using the finite difference expression of Marzari and Vanderbilt equation (10), Eq. (15) becomes

$$\begin{aligned}\widetilde{E}^{\lambda_1\mathcal{E}_i\lambda_3}_{pol} = \frac{2ie}{N_k}&\sum_{\mathbf{k}}\sum_{\mathbf{b}}\sum_{n,m}^{occ} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i)\\ &\times\{\langle u^{\lambda_1}_{n\mathbf{k}}|u^{\lambda_3}_{m\mathbf{k}+\mathbf{b}}\rangle\langle u^{(0)}_{m\mathbf{k}+\mathbf{b}}|u^{(0)}_{n\mathbf{k}}\rangle - \langle u^{\lambda_1}_{n\mathbf{k}}|u^{\lambda_3}_{m\mathbf{k}}\rangle\delta_{n,m}\},\end{aligned} \tag{16}$$

where $\mathbf{G}_i$ is a basis vector of the reciprocal lattice.

D. PEAD expression

Applying directly the $2n+1$ theorem to Eq. (13) we obtain the alternative PEAD formulation of the third-order energy:[14]

$$\begin{aligned}\widetilde{E}_{pol}^{\lambda_1\mathcal{E}_i\lambda_3} = \frac{-e}{N_k}\mathrm{Im}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i)\\ \times\Bigg[2\sum_{n,m}^{occ}\langle u_{n\mathbf{k}}^{\lambda_1}|u_{m\mathbf{k}+\mathbf{b}}^{\lambda_3}\rangle Q_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b})\\ -\sum_{n,m,l,l'}^{occ} S_{mn}^{\lambda_1}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{nl}(\mathbf{k},\mathbf{k}+\mathbf{b})\\ \times S_{ll'}^{\lambda_3}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{l'm}(\mathbf{k},\mathbf{k}+\mathbf{b})\Bigg]\end{aligned} \qquad (17)$$

where Q is the inverse of the overlap matrix S and S^{λ_j} its first-order perturbation expansion

$$S_{nm}^{\lambda_j}(\mathbf{k},\mathbf{k}+\mathbf{b}) = \langle u_{n\mathbf{k}}^{\lambda_j}|u_{m\mathbf{k}+\mathbf{b}}^{(0)}\rangle + \langle u_{n\mathbf{k}}^{(0)}|u_{m\mathbf{k}+\mathbf{b}}^{\lambda_j}\rangle. \qquad (18)$$

III. NONLINEAR OPTICAL PROPERTIES

In the preceding section we have discussed the general expressions of third-order energy derivatives. We now particularize them to the computation of selected nonlinear properties.

A. Nonlinear optical susceptibilities

In an insulator the polarization can be expressed as a Taylor expansion of the macroscopic electric field

$$\mathcal{P}_i = \mathcal{P}_i^s + \sum_{j=1}^{3}\chi_{ij}^{(1)}\mathcal{E}_j + \sum_{j,l=1}^{3}\chi_{ijl}^{(2)}\mathcal{E}_j\mathcal{E}_l + \cdots, \qquad (19)$$

where $\mathcal{P}_i^s$ is the zero-field (spontaneous) polarization, $\chi_{ij}^{(1)}$ the linear dielectric susceptibility (second-rank tensor), and $\chi_{ijl}^{(2)}$ the second-order nonlinear optical susceptibility (third-rank tensor). In the literature on nonlinear optics, one often finds another definition of the nonlinear optical susceptibility: instead of $\chi_{ijl}^{(2)}$, it is more convenient to rely on the **d** tensor defined as

$$d_{ijl} = \frac{1}{2}\chi_{ijl}^{(2)}. \qquad (20)$$

In general, the polarization depends on valence electrons as well as ions. In the present section, we deal only with the electronic contribution: we will consider the ionic cores as clamped to their equilibrium positions. This constraint will be relaxed in the following sections where we allow for ionic displacements.

Experimentally, the electronic contribution to the linear and nonlinear susceptibilities corresponds to measurements for electric fields at frequencies high enough to get rid of the ionic relaxation but low enough to avoid electronic excitations. In case of the second-order susceptibilities, this constraint implies that both the frequency of $\boldsymbol{\mathcal{E}}$, and its second harmonic, are lower than the fundamental absorption gap.

The general expression of the electronic nonlinear optical susceptibility depends on the frequencies of the optical electric fields (see, for example, Ref. 27). In the present context of the $2n+1$ theorem applied within the LDA to (static) DFT, we neglect the dispersion of $\chi_{ijl}^{(2)}$. As a consequence, $\chi_{ijl}^{(2)}$ satisfies Kleinman's[28] symmetry condition, which means that it is symmetric under a permutation of i, j, and l. In order to be able to investigate its frequency dependence, one would need either to apply the formalism of time-dependent DFT[9] or to use expressions that involve sums over excited states.[29–33] Following the work of Dal Corso and co-workers[9,26] we can relate the nonlinear optical susceptibilities to a third-order derivative of the energy with respect to an electric field,

$$\chi_{ijl}^{(2)} = -\frac{3}{\Omega_0}E^{\mathcal{E}_i\mathcal{E}_j\mathcal{E}_l}, \qquad (21)$$

where $E^{\mathcal{E}_i\mathcal{E}_j\mathcal{E}_l}$ is defined as the sum over the permutations of the three perturbations $\widetilde{E}^{\mathcal{E}_i\mathcal{E}_j\mathcal{E}_l}$ [Eq. (2)]. Using the PEAD formulation of Sec. II B we can express these terms as follows:

$$\begin{aligned}\widetilde{E}^{\mathcal{E}_i\mathcal{E}_j\mathcal{E}_l} = \frac{-e}{N_k}\mathrm{Im}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_j)\Bigg[2\sum_{n,m}^{occ}\langle u_{n\mathbf{k}}^{\mathcal{E}_i}|u_{m\mathbf{k}+\mathbf{b}}^{\mathcal{E}_l}\rangle Q_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b})\\ -\sum_{n,m,n',m'}^{occ} S_{mn}^{\mathcal{E}_i}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{nn'}(\mathbf{k},\mathbf{k}+\mathbf{b})S_{n'm'}^{\mathcal{E}_l}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{m'm}(\mathbf{k},\mathbf{k}+\mathbf{b})\Bigg]\\ +\frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}^{occ}[\delta_{m,n}\langle u_{n\mathbf{k}}^{\mathcal{E}_i}|v_{hxc}^{\mathcal{E}_j}|u_{m\mathbf{k}}^{\mathcal{E}_l}\rangle - \langle u_{m\mathbf{k}}^{(0)}|v_{hxc}^{\mathcal{E}_j}|u_{n\mathbf{k}}^{(0)}\rangle\langle u_{n\mathbf{k}}^{\mathcal{E}_i}|u_{m\mathbf{k}}^{\mathcal{E}_l}\rangle]\\ +\frac{1}{6}\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''\frac{\delta^3 E_{xc}[n^0]}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')\,\delta n(\mathbf{r}'')}n^{\mathcal{E}_i}(\mathbf{r})n^{\mathcal{E}_j}(\mathbf{r}')n^{\mathcal{E}_l}(\mathbf{r}'').\end{aligned} \qquad (22)$$

B. Raman susceptibilities of zone-center optical phonons

We now consider the computation of Raman scattering efficiencies of zone-center optical phonons. In the limit $\mathbf{q}\rightarrow 0$, the matrix of interatomic force constants $\widetilde{C}$ can be expressed as the sum of an analytical part and a nonanalytical term[21]

$$\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\rightarrow\mathbf{0}) = \widetilde{C}^{AN}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) + \widetilde{C}^{NA}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\rightarrow\mathbf{0}). \tag{23}$$

The analytical part corresponds to the second-order derivative of the energy with respect to an atomic displacement at $\mathbf{q}=\mathbf{0}$ under the condition of vanishing macroscopic electric field. The second term is due to the long-range electrostatic interactions in polar crystals. It is at the origin of the so-called LO-TO splitting and can be computed from the knowledge of the Born effective charges $Z^{*}_{\kappa\alpha\beta}$ and the electronic dielectric tensor[21] ε_{ij}. The phonon frequencies ω_m and eigendisplacements $u_m(\kappa\alpha)$ are solutions of the following generalized eigenvalue problem,

$$\sum_{\kappa',\beta} \widetilde{C}_{\kappa\alpha,\kappa'\beta} u_m(\kappa'\beta) = M_\kappa \omega_m^2 u_m(\kappa\alpha), \tag{24}$$

where M_κ is the mass of atom κ. As a convention, we choose the eigendisplacements to be normalized as

$$\sum_{\kappa,\alpha} M_\kappa u_m(\kappa\alpha) u_n(\kappa\alpha) = \delta_{m,n}. \tag{25}$$

In what follows we consider nonresonant Raman scattering where an incoming photon of frequency ω_0 and polarization $\mathbf{e}_0$ is scattered to an outgoing photon of frequency $(\omega_0 - \omega_m)$ and polarization $\mathbf{e}_S$ by creating a phonon of frequency ω_m (Stokes process). The scattering efficiency[34,35] (cgs units) corresponds to

$$\frac{dS}{d\Omega} = |\mathbf{e}_S \cdot R^m \cdot \mathbf{e}_0|^2 = \frac{(\omega_0-\omega_m)^4}{c^4} |\mathbf{e}_S \cdot \boldsymbol{\alpha}^m \cdot \mathbf{e}_0|^2 \frac{\hbar}{2\omega_m}(n_m+1), \tag{26}$$

where c is the speed of light in vacuum and n_m the boson factor

$$n_m = \frac{1}{\exp(\hbar\omega_m/k_B T) - 1}. \tag{27}$$

The Raman susceptibility $\boldsymbol{\alpha}^m$ is defined as

$$\alpha^m_{ij} = \sqrt{\Omega_0} \sum_{\kappa,\beta} \frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\beta}} u_m(\kappa\beta), \tag{28}$$

where $\chi^{(1)}_{ij}$ is the electronic linear dielectric susceptibility tensor. In Eq. (26), Ω is the angle of collection in which the outgoing photon is scattered. As discussed in Ref. 34, we have to be careful when we compare the theoretical and experimental scattering efficiencies. Due to Snell's law, the angle of collection is modified at the interface between the sample and the surrounding medium. Experimentally, the scattering efficiencies are measured with respect to the solid angle of the surrounding medium while Eq. (26) refers to the solid angle inside the sample. In order to relate theory and experiment, one has to take into account the different refractive indices of the sample and medium. For example, in case of an isotropic sample, Eq. (26) has to be multiplied[34] by $(n'/n)^2$ where n and n' are, respectively, the refractive indices of the sample and the medium. In contrast to the scattering efficiencies, the Raman susceptibilities defined in Eq. (28) are intrinsic properties of the sample and do not depend on the change in the angle of collection.

For pure transverse optical phonons, $\partial\chi^{(1)}_{ij}/\partial\tau_{\kappa\beta}$ can be computed as a mixed third-order derivative of the energy with respect to an electric field, twice, and to an atomic displacement under the condition of zero electric field

$$\left.\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\lambda}}\right|_{\mathcal{E}=0} = -\frac{6}{\Omega_0} E^{\tau_{\kappa\lambda}\mathcal{E}_i\mathcal{E}_j}. \tag{29}$$

In case of longitudinal optical phonons with wave vector $\mathbf{q}\rightarrow\mathbf{0}$ in a polar crystal, Eq. (28) must take into account the effect of the macroscopic electric field generated by the lattice polar vibration. This field enters the computation of the Raman susceptibilities at two levels. On one hand, it gives rise to the nonanalytical part of the matrix of interatomic force constants, Eq. (23), that modifies the frequencies and eigenvectors with respect to pure transverse phonons. On the other hand, the electric field induces an additional change in the dielectric susceptibility tensor related to the nonlinear optical coefficients $\chi^{(2)}_{ijk}$. For longitudinal optical phonons, Eq. (29) has to be modified as follows:[36]

$$\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\lambda}} = \left.\frac{\partial \chi^{(1)}_{ij}}{\partial \tau_{\kappa\lambda}}\right|_{\mathcal{E}=0} - \frac{8\pi}{\Omega_0} \frac{\sum_l Z^{*}_{\kappa\lambda l} q_l}{\sum_{l,l'} q_l \varepsilon_{ll'} q_{l'}} \sum_l \chi^{(2)}_{ijl} q_l. \tag{30}$$

The mixed third-order derivatives Eq. (29) can be computed from various techniques including finite differences of the dielectric tensor[37–39] or the second derivative of the electronic density matrix.[40,41] Here, we follow an approach similar to Deinzer and Strauch[10] based on the $2n+1$ theorem. The third-order energy can be computed as the sum over the 6 permutations, Eq. (2), of $\tau_{\kappa\lambda}$, $\mathcal{E}_i$, and $\mathcal{E}_j$. According to the discussion of Sec. II B, we have to distinguish between the terms that involve the discretization of the polarization such as $\widetilde{E}^{\tau_{\kappa\lambda}\mathcal{E}_i\mathcal{E}_j}$ or $\widetilde{E}^{\mathcal{E}_j\mathcal{E}_i\tau_{\kappa\lambda}}$ and those that can be computed from a straightforward application of the $2n+1$ theorem such as $\widetilde{E}^{\mathcal{E}_i\tau_{\kappa\lambda}\mathcal{E}_j}$. The former ones show an electric field as second perturbation. They can be computed from an expression analogous to Eq. (22):

$$\widetilde{E}^{\tau_{\kappa\lambda}\mathcal{E}_i\mathcal{E}_j} = \frac{-e}{N_k}\mathrm{Im}\sum_{\mathbf{k}}\sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b}\cdot\mathbf{G}_i)\left[2\sum_{n,m}^{occ}\langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}}|u_{m\mathbf{k}+\mathbf{b}}^{\mathcal{E}_j}\rangle Q_{mn}(\mathbf{k},\mathbf{k}+\mathbf{b}) - \sum_{n,m,l,l'}^{occ} S_{mn}^{\tau_{\kappa\lambda}}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{nl}(\mathbf{k},\mathbf{k}+\mathbf{b})S_{ll'}^{\mathcal{E}_j}(\mathbf{k},\mathbf{k}+\mathbf{b})Q_{l'm}(\mathbf{k},\mathbf{k}+\mathbf{b})\right]$$
$$+\frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}^{occ}[\delta_{m,n}\langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}}|v_{hxc}^{\mathcal{E}_i}|u_{m\mathbf{k}}^{\mathcal{E}_j}\rangle - \langle u_{m\mathbf{k}}^{(0)}|v_{hxc}^{\mathcal{E}_i}|u_{n\mathbf{k}}^{(0)}\rangle\langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}}|u_{m\mathbf{k}}^{\mathcal{E}_j}\rangle] + \frac{1}{6}\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''\frac{\delta^3 E_{xc}[n^0]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}n^{\tau_{\kappa\lambda}}(\mathbf{r})n^{\mathcal{E}_i}(\mathbf{r}')n^{\mathcal{E}_j}(\mathbf{r}''). \tag{31}$$

We obtain a similar expression for $\widetilde{E}^{\mathcal{E}_j\mathcal{E}_i\tau_{\kappa\lambda}}$. The remaining terms do not require any differentiation with respect to **k**. They can be computed from the first-order change of the ionic (pseudo-) potential with respect to an atomic displacement $v_{ext}^{\tau_{\kappa\lambda}}$:

$$\widetilde{E}^{\mathcal{E}_i\tau_{\kappa\lambda}\mathcal{E}_j} = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}^{occ}[\langle u_{n\mathbf{k}}^{\mathcal{E}_i}|v_{ext}^{\tau_{\kappa\lambda}} + v_{hxc}^{\tau_{\kappa\lambda}}|u_{m\mathbf{k}}^{\mathcal{E}_j}\rangle\delta_{n,m} - \langle u_{n\mathbf{k}}^{(0)}|v_{ext}^{\tau_{\kappa\lambda}} + v_{hxc}^{\tau_{\kappa\lambda}}|u_{m\mathbf{k}}^{(0)}\rangle\langle u_{m\mathbf{k}}^{\mathcal{E}_i}|u_{n\mathbf{k}}^{\mathcal{E}_j}\rangle]$$
$$+\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{d}{d\tau_{\kappa\lambda}}\frac{\delta^2 E_{Hxc}[n^0]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}n^{\mathcal{E}_i}(\mathbf{r})n^{\mathcal{E}_j}(\mathbf{r}') + \frac{1}{6}\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''\frac{\delta^3 E_{xc}[n^0]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')}n^{\tau_{\kappa\lambda}}(\mathbf{r})n^{\mathcal{E}_i}(\mathbf{r}')n^{\mathcal{E}_j}(\mathbf{r}''). \tag{32}$$

In pseudopotential calculations, the computation of the first-order ionic potential $v_{ext}^{\tau_{\kappa\lambda}}$ requires the derivative of local and nonlocal (usually separable) operators. These operations can be performed easily without any additional workload as described in Ref. 20.

In spite of the similarities between Eqs. (31) and (32) and the expression proposed by Deinzer and Strauch we can quote a few differences. First, our expression of the third-order energy derivatives makes use of the PEAD fomulation for the expansion of the polarization. Moreover, Eq. (32) is more general since it allows the use of pseudopotentials with nonlinear core correction through the derivative of the second-order exchange-correlation energy with respect to $\tau_{\kappa\lambda}$ (third term).

C. Sum rule

As in the cases of the Born effective charges and of the dynamical matrix,[42] the coefficients $\partial\chi_{ij}^{(1)}/\partial\tau_{\kappa\alpha}$ must vanish when they are summed over all atoms in the unit cell:

$$\sum_{\kappa}\frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\alpha}} = 0. \tag{33}$$

Physically, this sum rule guarantees that the macroscopic dielectric susceptibility remains invariant under a rigid translation of the crystal. In practical calculations, it is not always satisfied although the violation is generally less severe than in case of $\widetilde{C}$ or Z^*. Even in calculations that present a low degree of convergence, the deviations from this law can be quite weak. They can be corrected using similar techniques as in the case of the Born effective charges.[21] For example, we can define the mean excess of $\partial\chi_{ij}^{(1)}/\partial\tau_{\kappa\alpha}$ per atom

$$\overline{\frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\alpha}}} = \frac{1}{N_{at}}\sum_{\kappa}\frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\alpha}} \tag{34}$$

and redistribute it equally between the atoms:

$$\frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\alpha}} \rightarrow \frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\alpha}} - \overline{\frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\alpha}}}. \tag{35}$$

D. Electro-optic tensor

The optical properties of a compound usually depend on external parameters such as the temperature, electric fields, or mechanical constraints (stress, strain). In the present section we consider the variations of the refractive index induced by a static or low-frequency electric field $\mathcal{E}_{\gamma}$. At linear order, these variations are described by the linear EO coefficients (Pockels effect)

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r_{ij\gamma}\mathcal{E}_{\gamma}, \tag{36}$$

where $(\varepsilon^{-1})_{ij}$ is the inverse of the electronic dielectric tensor and $r_{ij\gamma}$ the EO tensor.

Within the Born-Oppenheimer approximation, the EO tensor can be expressed as the sum of three contributions: a bare electronic part $r_{ij\gamma}^{el}$, an ionic contribution $r_{ij\gamma}^{ion}$, and a piezoelectric contribution $r_{ij\gamma}^{piezo}$.

The electronic part is due to an interaction of $\mathcal{E}_{\gamma}$ with the valence electrons when considering the ions artificially as clamped at their equilibrium positions. It can be computed from the nonlinear optical coefficients. As can be seen from Eq. (19), $\chi_{ijl}^{(2)}$ defines the second-order change of the induced polarization with respect to $\mathcal{E}_{\gamma}$. Taking the derivative of Eq. (19), we also see that $\chi_{ijl}^{(2)}$ defines the first-order change of the linear dielectric susceptibility, which is equal to $(1/4\pi)\Delta\varepsilon_{ij}$. Since the EO tensor depends on $\Delta(\varepsilon^{-1})_{ij}$ rather than $\Delta\varepsilon_{ij}$, we have to transform $\Delta\varepsilon_{ij}$ to $\Delta(\varepsilon^{-1})_{ij}$ by the inverse of the zero-field electronic dielectric tensor[43]

$$\Delta(\varepsilon^{-1})_{ij} = -\sum_{m,n=1}^{3} \varepsilon^{-1}_{im} \Delta\varepsilon_{mn} \varepsilon^{-1}_{nj}. \tag{37}$$

Using Eq. (37) we obtain the following expression for the electronic EO tensor:

$$r^{el}_{ij\gamma} = -8\pi \sum_{l,l'=1}^{3} (\varepsilon^{-1})_{il} \chi^{(2)}_{ll'k} (\varepsilon^{-1})_{l'j} \bigg|_{k=\gamma}. \tag{38}$$

Equation (38) takes a simpler form when expressed in the principal axes of the crystal under investigation:[44]

$$r^{el}_{ij\gamma} = \frac{-8\pi}{n_i^2 n_j^2} \chi^{(2)}_{ijk} \bigg|_{k=\gamma}, \tag{39}$$

where the n_i coefficients are the principal refractive indices.

The origin of the ionic contribution to the EO tensor is the relaxation of the atomic positions due to the applied electric field $\mathcal{E}_\gamma$ and the variations of ε_{ij} induced by these displacements. It can be computed from the Born effective charges $Z^*_{\kappa,\alpha\beta}$ and the $\partial\chi^{(1)}_{ij}/\partial\tau_{\kappa\alpha}$ coefficients introduced in Sec. III B. As shown in the Appendix (see also Refs. 36 and 45), the ionic EO tensor can be computed as a sum over the transverse optic phonon modes at $\mathbf{q}=\mathbf{0}$:

$$r^{ion}_{ij\gamma} = -\frac{4\pi}{\sqrt{\Omega_0} n_i^2 n_j^2} \sum_m \frac{\alpha^m_{ij} p_{m,\gamma}}{\omega_m^2}, \tag{40}$$

where $\boldsymbol{\alpha}^m$ is the Raman susceptibility of mode m [Eq. (28)] and $p_{m,\gamma}$ the mode polarity

$$p_{m,\gamma} = \sum_{\kappa,\beta} Z^*_{\kappa,\gamma\beta} u_m(\kappa\beta), \tag{41}$$

which is directly linked to the mode oscillator strength

$$S_{m,\alpha\beta} = p_{m,\alpha} p_{m,\beta}. \tag{42}$$

For simplicity, we have expressed Eq. (40) in the principal axes while a more general expression can be derived from Eq. (37).

Finally, the piezoelectric contribution is due to a relaxation of the unit cell shape due to the converse piezoelectric effect.[46,47] As it is discussed in the Appendix, it can be computed from the elasto-optic coefficients $p_{ij\mu\nu}$ and the piezoelectric strain coefficients $d_{\gamma\mu\nu}$:

$$r^{piezo}_{ij\gamma} = \sum_{\mu,\nu=1}^{3} p_{ij\mu\nu} d_{\gamma\mu\nu}. \tag{43}$$

In the discussion of the EO effect, we have to specify whether we are dealing with strain-free (clamped) or stress-free (unclamped) mechanical boundary conditions. The clamped EO tensor $r^{\eta}_{ij\gamma}$ takes into account the electronic and ionic contributions but neglects any modification of the unit cell shape due to the converse piezoelectric effect:[46,47]

$$r^{\eta}_{ij\gamma} = r^{el}_{ij\gamma} + r^{ion}_{ij\gamma}. \tag{44}$$

Experimentally, it can be measured for frequencies of $\mathcal{E}_\gamma$ high enough to eliminate the relaxations of the crystal lattice but low enough to avoid excitations of optical phonon modes (usually above ~100 MHz). To compute the unclamped EO tensor $r^{\sigma}_{ij\gamma}$, we have to add the piezoelectric contribution to $r^{\eta}_{ij\gamma}$:

$$r^{\sigma}_{ij\gamma} = r^{\eta}_{ij\gamma} + r^{piezo}_{ij\gamma}. \tag{45}$$

Experimentally, $r^{\sigma}_{ij\gamma}$ can be measured for frequencies of $\mathcal{E}_\gamma$ below the (geometry-dependent) mechanical body resonances of the sample[47] (usually below ~1 MHz).

IV. RESULTS

A. Technical details

Our calculations have been performed within the local density approximation (LDA) to the density functional theory[1,2] (DFT). We used the ABINIT package,[16] a plane-wave, pseudopotential DFT code[48] in which we have implemented the formalism presented above. For reasons that will become obvious below, we chose the PEAD formulation, Eq. (17) , to perform the differentiation with respect to **k**. For the exchange-correlation energy E_{xc} we relied on the parametrization of Perdew and Wang[49] as well as the parametrization of Goedecker, Teter, and Hutter.[50] These expressions have the advantage of avoiding any discontinuities in the functional derivative of E_{xc}.

In case of the semiconductors Si, AlAs, and AlP, we used a $16\times16\times16$ grid of special **k** points, a plane-wave kinetic energy cutoff of 10 hartree, and Troullier-Martins[51] norm-conserving pseudopotentials. These calculations have been performed at the theoretical lattice constant. To perform the finite difference calculations of the Raman polarizabilities, changes of the electronic dielectric tensor were computed for atoms displaced by ±1% of the unit cell parameter along the Cartesian directions.

In case of rhombohedral $\mathrm{BaTiO_3}$, we used a $10\times10\times10$ grid of special **k** points, a plane-wave kinetic energy cutoff of 45 hartree, and extended norm-conserving pseudopotentials.[52] Since the ferroelectric instability is quite sensitive to the volume of the unit cell and tends to disappear due to the volume underestimation of the LDA,[53] we chose to work at the experimental lattice constants. In contrast to the lattice parameters, the atomic positions have been relaxed: the residual forces on the atoms were smaller than 5×10^{-5} hartree/bohr.

It was shown by Gonze, Ghosez, and Godby[54] that an accurate functional for the exchange-correlation energy in extended systems should depend on both the density and the polarization. The LDA used here neglects this polarization dependence and may consequently introduce significant relative errors when studying the response of a solid to an electric field. In case of the second-order derivatives, the LDA usually yields an overestimate of the dielectric tensor (as large as 20% in $\mathrm{BaTiO_3}$).[55] In contrast, no clear trends have been reported yet concerning nonlinear optical properties such as $\chi^{(2)}_{ijl}$.[9,29]

In LDA calculations, it is common practice to apply a *scissors correction*[57] to compensate for the lack of polarization dependence of the exchange-correlation functional. In case of nonlinear optical properties, such a correction can be applied at different levels. On one hand, we can compute the nonlinear optical susceptibilities [Eq. (22)] using a scissors operator for the first-order wave functions.[21] On the other hand, in the computation of the EO coefficients, we can use a scissors corrected refractive index in Eqs. (39) and (40). The influence of these corrections will be discussed below.

B. Nonlinear optical susceptibilities and Raman polarizabilities of semiconductors

In order to illustrate the computation of third-order energy derivatives, we performed a series of calculations on various cubic *AB* semiconductors where the atom *A* is located at the origin and *B* in (1/4,1/4,1/4). In these compounds, the nonlinear optical susceptibility tensor has only one independent element, d_{123},

$$d_{ijk} = d_{123}|\epsilon_{ijk}|, \tag{46}$$

where ε_{ijk} is the Levy-Civita tensor. The Raman susceptibilities are also defined by a single number, α_{12}. For phonons polarized along the Cartesian direction λ, the Raman susceptibility tensors are written as

$$\alpha_{ij}(\lambda) = \alpha_{12}|\epsilon_{ij\lambda}|. \tag{47}$$

In cubic semiconductors, it is customary to report the Raman polarizability[34,60] defined as

$$a = \sqrt{\mu\Omega_0}\alpha_{12} = \Omega_0 \frac{\partial \chi_{12}^{(1)}}{\partial \tau_{A,3}}, \tag{48}$$

where μ is the reduced mass of the two atoms in the unit cell and $\tau_{A,3}$ a displacement of atom *A* along the *z* direction.

The formalism of Sec. II involves an integration over the BZ and a differentiation with respect to **k**. In practical calculations, these operations must be performed on a discrete mesh of special **k** points. As we explained in Sec. II, the discretization can either be performed before (PEAD) or after (DAPE) the perturbation expansion of the energy functional equation (6). Up until now, the applications of the present formalism to real materials[9,10] made use of the DAPE formula of the third-order energy. The only application of the PEAD formula has been reported by Nunes and Gonze[14] on a one-dimensional model system. These authors observed that the PEAD formula converges better with respect to the **k**-point sampling than the DAPE formula. In order to compare the performance of these two approaches for a realistic case, we applied both of them to compute the nonlinear optical susceptibility d_{123} of AlAs. We performed a series of calculations on a $n \times n \times n$ grid of special **k** points. As can be seen in Fig. 1 the PEAD formula converges much faster than the DAPE formula. Therefore, the PEAD formulation has been applied to obtain the results presented below. It is the one that is actually available in the ABINIT code.

It is interesting to note that a different speed of convergence for distinct expressions has also been reported for the localization tensor. In Ref. 56 Sgiarovello and co-workers compared the convergence of two formulations based on different discretizations of the same **k** space integral.They observed that (i) both expressions converge to the same value in the limit of a large number of **k** points and (ii) that the expression used in their work converges faster than the expression used in Ref. 24.

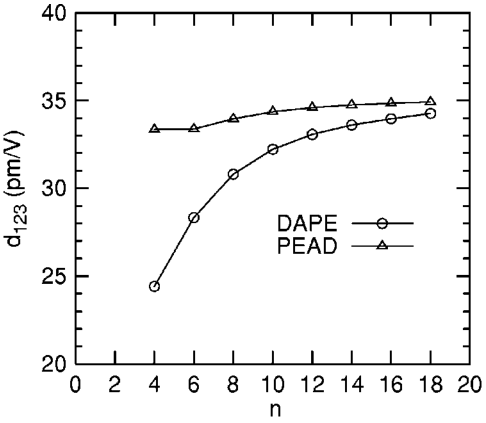

FIG. 1. Nonlinear optical susceptibility d_{123}(pm/V) of AlAs for various grids of $n \times n \times n$ special **k** points.

In Table I, we report the nonlinear optical susceptibilities of the cubic semiconductors AlAs and AlP. Our results are in close agreement with the values obtained by Dal Corso and co-workers[9] who applied the $2n+1$ theorem within the DAPE formalism, the results of Levine and Allan[29] who used a "sum over excited states" technique, and the values obtained by Souza and co-workers,[58] who followed a finite electric field approach. The values in the lower part of Table I have been obtained using a scissors correction. Our methodology provides a correction similar to that reported by Levine and Allan.[30]

The scissors correction decreases the value of the nonlinear optical susceptibilities in agreement with the discussion of Ref. 59. To the authors' knowledge, no experimental data are available for AlAs and AlP. For other cubic semiconductors, it is, however, not clear that the use of a scissors correction improves agreement with experiment[29] and will even have a negative effect when the LDA underestimates the experimental value. In addition, it is not straightforward to isolate the error of the LDA on the nonlinear response functions from other sources of errors. Other factors have a strong influence on $\chi_{ijl}^{(2)}$ similar to the scissors correction. For ex-

TABLE I. Nonlinear optical susceptibilities d_{123}(pm/V) of some semiconductors. The values in the lower part of the table have been obtained using a scissors (SCI) correction.

Method	AlAs	AlP
$2n+1$ theorem (present)	35	21
$2n+1$ theorem[a]	32	19
Finite fields[b]	32	19
Sum over states[c]	34	21
$2n+1$ theorem + SCI (present)	21	13
Sum over states + SCI[c]	21	13

[a] Reference 9.
[b] Reference 58.
[c] Reference 30.

TABLE II. Raman polarizabilities of the transverse (TO) and longitudinal (LO) optical modes (Å^2) of some semiconductors.

	Si	AlAs (TO)	AlAs (LO)	AlP (TO)	AlP (LO)
$2n+1$ theorem					
Present	20.02	8.48	12.48	4.30	7.46
DS[a]	23.56	7.39		5.13	
Finite differences					
Present	20.17	8.59		4.25	
DS[a]	20.44	5.64		4.44	
BR[b]	26.16				
Experiment	23±4[c]				

[a] Reference 10.
[b] Reference 37.
[c] Reference 60.

ample, the values of the nonlinear optical susceptibilities strongly depend on the pseudopotential[9] or on the error on the unit cell volume[29,59] that is usually underestimated in LDA calculations.

We also computed the Raman polarizabilities of the transverse (TO) and longitudinal optical (LO) phonons of various semiconductors. In addition, we performed finite difference calculations of the dielectric tensor with respect to atomic displacements. Our results are summarized in Table II where we also report the results of Deinzer and Strauch[10] (DS) and Baroni and Resta[37] (BR) as well as the experimental result of Wagner and Cardona[60] for Si. The agreement between our results and those obtained in previous works is quite good. In addition, the results we obtained from the $2n+1$ theorem closely agree with the finite difference calculations, giving us some indication of the numerical accuracy of the implementation.

The Raman polarizabilities of the TO and LO modes are different. As it is discussed in Sec. III B, this difference is attributed to the macroscopic electric field associated with a longitudinal polar lattice vibration. On the one hand, this field modifies the dynamical matrix at $\mathbf{q}\rightarrow\mathbf{0}$. The eventual related modification of the eigenvectors of the LO modes may imply a first change of the Raman susceptibility. On the other hand, the macroscopic electric field itself may induce an additional change of α related to the nonlinear optical coefficients $\chi^{(2)}_{ijl}$. In the cubic semiconductors, the eigenvectors of the TO and LO modes are identical. The difference between the polarizabilities of the TO and LO modes comes therefore exclusively from the second term of Eq. (30).

C. EO tensor in ferroelectric oxides

In the rhombohedral phase of BaTiO$_3$, the EO tensor has four independent elements: r_{13}, r_{33}, r_{22}, and r_{51}. In contrast to the dielectric tensor, the EO coefficients can either be positive or negative. The sign of these coefficients is often difficult to measure experimentally. Moreover, it depends on the choice of the Cartesian axes. Experimentally, these axes are chosen according to the *Standards on Piezoelectric Crystals*.[65,71] The z axis is along the direction of the spontaneous polarization and the y axis lies in a mirror plane. The z and y axes are both piezoelectric. Their positive ends are chosen in the direction that becomes negative under compression. The orientation of these axes can easily be found from pure geometrical arguments. Unfortunately, these arguments do not allow us to determine the direction of the y axis. Therefore, we applied the methodology of Ref. 61 to compute the piezoelectric tensor from finite differences of the Berry phase polarization. Our results are reported in the Cartesian axes where the piezoelectric coefficients e_{22} and e_{33} are positive.

These coefficients, as well as their decomposition on the individual phonon modes and their electronic part, are reported in Table III. All EO coefficients are positive. As is the case for the tetragonal phase,[46] the modes that have the strongest overlap with the soft mode of the paraelectric phase dominate the amplitude of the EO coefficients. Moreover, the electronic contribution is found to be quite small.

As we discussed in the previous sections, linear and nonlinear optical susceptibilities are sometimes relatively inaccurate within the LDA. In this context, it is interesting to investigate the error due to the use of the LDA optical dielectric constants in the transformation equation (37). Unfortunately, we could not find any experimental data on the EO coefficients in the rhombohedral phase of BaTiO$_3$. In Ref.

TABLE III. Decomposition of the clamped EO tensor (pm/V) in the rhombohedral phase of BaTiO$_3$. Reported are the contributions of individual zone-center phonon modes and the electronic contribution. The phonon frequencies are reported in cm^{-1}.

	A_1 modes			E modes		
	ω	r^{η}_{13}	r^{η}_{33}	ω	r^{η}_{22}	r^{η}_{51}
TO1	168	0.65	2.16	163	0.79	5.15
TO2	253	13.82	27.32	202	5.40	19.16
TO3	509	1.31	2.05	293	0.01	−0.02
TO4				469	0.24	0.65
Elect.		1.15	2.95		0.12	1.24
Tot.		16.93	34.48		6.56	26.18

TABLE IV. Effect of a scissors correction on the EO coefficients of $LiNbO_3$ (clamped and unclamped cases) and the tetragonal phases of $PbTiO_3$ and $BaTiO_3$ (clamped cases only). The dielectric tensor required to perform the transformation, Eq. (37), has been computed within the LDA (ε_{LDA}) and using the LDA with a scissors correction (ε_{SCI}). No scissors correction has been used to compute the nonlinear optical susceptibilities that determine the electronic contribution to the EO coefficients. In case of $PbTiO_3$, we also use the experimental dielectric tensor (ε_{expt}) to compute the EO coefficients. The values are compared to the experimental results.

		r_{13}	r_{33}	r_{22}	r_{51}
$LiNbO_3$	ε_{LDA}	9.67	26.93	4.55	14.93
(clamped)	ε_{SCI}	10.37	28.89	4.88	16.02
	Expt.[a]	8.6	30.8	3.4	28
$LiNbO_3$	ε_{LDA}	10.47	27.08	7.53	28.61
(unclamped)	ε_{SCI}	11.23	29.06	8.08	30.69
	Expt.[a]	10	32.2	6.8	32.6
	Expt.[b]			9.89	
$PbTiO_3$	ε_{LDA}	8.98	5.88		30.53
(clamped)	ε_{SCI}	14.24	8.94		47.39
	ε_{expt}	10.92	6.16		34.45
	Expt.[c]	13.8	5.9		
$BaTiO_3$	ε_{LDA}	8.91	22.27		
(clamped)	ε_{SCI}	12.68	30.84		
	Expt.[d]	10.2	40.6		
	Expt.[e]	8	28		

[a] Reference 71.
[b] Reference 72.
[c] Reference 73.
[d] Reference 74.
[e] Reference 47.

46, we studied the EO coefficients of ferroelectric $LiNbO_3$ and tetragonal $BaTiO_3$ and $PbTiO_3$ and found an overall good agreement between theory and experiment. In Table IV, we report the EO coefficients of these compounds as well as the values obtained using a scissors-corrected optical dielectric constant. No scissors correction has been applied for the nonlinear optical susceptibilities of these compounds that are required to compute the electronic contributions.

The effect of this correction is more important for the perovskite compounds than for $LiNbO_3$, for which the LDA band gap and optical dielectric constants are in reasonable agreement with experiment.[62] For $BaTiO_3$, we tested the optical dielectric tensor obtained from the scissors correction that modifies the LDA band gap to its experimental value:[21] we obtain $r_{13}^{\eta}=12.68$ pm/V and $r_{33}^{\eta}=30.84$ pm/V, in closer agreement with experimental data. However, such an improvement is not a general rule. In $PbTiO_3$, a scissors shift that corrects the LDA band gap fails to correct the LDA optical dielectric constant [we obtain $\varepsilon_{11}=5.81$ and $\varepsilon_{33}=5.51$, while the experimental values are 6.63 and 6.64 (Ref. 63)] and yields $r_{13}^{\eta}=14.24$ pm/V and $r_{33}^{\eta}=8.94$ pm/V. Using the experimental dielectric constants, we obtain $r_{13}^{\eta}=10.92$ pm/V and $r_{33}^{\eta}=6.16$ pm/V in better agreement with the experiment.

V. CONCLUSIONS AND PERSPECTIVES

In this paper, we presented the general framework for the computation of third-order energy derivatives within DFT. Our formalism makes use of the $2n+1$ theorem and the modern theory of polarization. Focusing on derivatives that are characterized by a zero wave vector and that involve either three electric fields or two electric fields and one atomic displacement, we described the computation of nonlinear optical susceptibilities, of Raman scattering efficiencies of TO and LO phonons, and of the EO tensor.

The computation of the Berry phase polarization involves a derivative of the wave functions with respect to their wave vector. In practice, this differentiation is computed on a grid of special **k** points. The perturbation expansion can either be performed before (DAPE) or after (PEAD) the discretization, leading to two mathematically distinct expressions of the third-order energies. We used both of them to compute the nonlinear optical susceptibility of AlAs, and we have shown that the PEAD formulation converges faster with respect to the **k**-point sampling.

We have computed the nonlinear optical susceptibilities and Raman polarizabilities of some cubic semiconductors as well as the EO tensor in the rhombohedral phase of $BaTiO_3$.

Finally, we have studied the effect of a scissors correction on the EO coefficients and the nonlinear optical susceptibilities. In contrast to the dielectric tensor, we did not find a systematic improvement of the results by using this correction.

We can figure out several applications of the methodology presented in this work. Combined with the calculation of phonon frequencies and infrared intensities, the computation of Raman efficiencies can be a useful complementary tool for the interpretation of experimental spectra. Furthermore, the computation of the EO tensor from first principles can guide the tuning of the EO properties and help in designing new efficient EO materials. This could be particularly helpful since accurate optical measurements require high-quality single crystals not always directly accessible.

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APPENDIX: EXPRESSIONS OF THE CLAMPED AND UNCLAMPED EO TENSORS

1. Macroscopic approach

As discussed in Sec. III D, the optical properties of a compound are modified by an electric field $\mathcal{E}_{\gamma}$ or a mechanical constraint (a stress $\sigma_{\mu\nu}$ or a homogeneous strain $\eta_{\mu\nu}$). At linear order, the variations of ε^{-1}_{ij} can be described using either the variables[64,65] $(\mathcal{E}_\gamma, \eta_{\mu\nu})$ or $(\mathcal{E}_\gamma, \sigma_{\mu\nu})$:

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\eta}_{ij\gamma}\mathcal{E}_\gamma + \sum_{\mu,\nu=1}^{3} p_{ij\mu\nu}\eta_{\mu\nu}, \tag{A1a}$$

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\sigma}_{ij\gamma}\mathcal{E}_\gamma + \sum_{\mu,\nu=1}^{3} \pi_{ij\mu\nu}\sigma_{\mu\nu}, \tag{A1b}$$

where $r^{\eta}_{ij\gamma}$ and $r^{\sigma}_{ij\gamma}$ are, respectively, the clamped (strain-free) and unclamped (stress-free) EO coefficients, $p_{ij\mu\nu}$ are the elasto-optic (strain-optic) coefficients, and $\pi_{ij\mu\nu}$ are the piezo-optical (stress-optical) coefficients. In order to relate Eqs. (A1a) and (A1b), we can express the strain as being induced by the stress or by the electric field (converse piezoelectric effect),

$$\eta_{\mu\nu} = \sum_{\mu',\nu'=1}^{3} S_{\mu\nu\mu'\nu'}\sigma_{\mu'\nu'} + \sum_{\gamma=1}^{3} d_{\gamma\mu\nu}\mathcal{E}_\gamma, \tag{A2}$$

where $S_{\mu\nu\mu'\nu'}$ are the elastic compliances and $d_{\gamma\mu\nu}$ the piezoelectric strain coefficients.

If we assume, for example, that the unit cell is free to relax within the electric field (stress-free mechanical boundary conditions) we can either use Eq. (A1b) (in which case the second term of the right-hand side is zero) or Eq. (A1a) to compute $\Delta(\varepsilon^{-1})_{ij}$. In the latter case, the strain induced by the electric field can be obtained from the second term of the right-hand side of Eq. (A2):

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\sigma}_{ij\gamma}\mathcal{E}_\gamma = \sum_{\gamma=1}^{3} r^{\eta}_{ij\gamma}\mathcal{E}_\gamma + \sum_{\mu,\nu=1}^{3}\sum_{\gamma=1}^{3} p_{ij\mu\nu}d_{\gamma\mu\nu}\mathcal{E}_\gamma. \tag{A3}$$

Using this identity, we obtain the following relation between the unclamped and the clamped EO coefficients:

$$r^{\sigma}_{ij\gamma} = r^{\eta}_{ij\gamma} + \sum_{\mu,\nu=1}^{3} p_{ij\mu\nu}d_{\gamma\mu\nu}. \tag{A4}$$

2. Microscopic approach

In order to derive the expressions of the clamped and unclamped EO tensor of Sec. III D, we use a Taylor expansion of the electric enthalpy[66] F. Similar developments have already been applied to determine the lattice contribution of the static dielectric tensor and of the piezoelectric tensor.[67,68] They are based on an expansion of F up to the second order in the atomic coordinates $R_{\kappa\alpha}$, the homogeneous strain $\eta_{\mu\nu}$, and the macroscopic electric field $\mathcal{E}_\gamma$. In this section, we extend these developments to the third order.

The electric enthalpy of a solid in an electric field is obtained by the minimization

$$F(\boldsymbol{\mathcal{E}}) = \min_{\mathbf{R},\eta} F(\mathbf{R},\eta,\boldsymbol{\mathcal{E}}). \tag{A5}$$

We denote $\mathbf{R}(\boldsymbol{\mathcal{E}})$ and $\eta(\boldsymbol{\mathcal{E}})$ the atomic positions and the strain that minimize F at constant $\boldsymbol{\mathcal{E}}$ and $\mathbf{R}_0$, $\eta_0(=0)$ their values at $\boldsymbol{\mathcal{E}}=\mathbf{0}$. For small fields, we can expand the function $F(\mathbf{R},\eta,\boldsymbol{\mathcal{E}})$ in powers of $\boldsymbol{\mathcal{E}}$ around $\boldsymbol{\mathcal{E}}=0$:

$$\begin{aligned} F(\mathbf{R},\eta,\boldsymbol{\mathcal{E}}) = F(\mathbf{R},\eta,0) &- \Omega_0\sum_{i=1}^{3}\mathcal{P}_i(\mathbf{R},\eta)\boldsymbol{\mathcal{E}}_i \\ &- \frac{\Omega_0}{8\pi}\sum_{i,j=1}^{3}\varepsilon_{ij}(\mathbf{R},\eta)\boldsymbol{\mathcal{E}}_i\boldsymbol{\mathcal{E}}_j \\ &- \frac{\Omega_0}{3}\sum_{i,j,k=1}^{3}\chi^{(2)}_{ijk}(\mathbf{R},\eta)\boldsymbol{\mathcal{E}}_i\boldsymbol{\mathcal{E}}_j\boldsymbol{\mathcal{E}}_k + \ldots \end{aligned} \tag{A6}$$

where Ω_0 is the volume of the primitive unit cell in real space and $\boldsymbol{\mathcal{P}}(\mathbf{R},\eta)$, $\varepsilon_{ij}(\mathbf{R},\eta)$, and $\chi^{(2)}_{ijk}(\mathbf{R},\eta)$ are the macroscopic polarization, electronic dielectric tensor, and nonlinear optical coefficients at zero macroscopic electric field and for a given configuration $(\mathbf{R},\eta)$. At nonzero field, these quantities are defined as partial derivatives of F with respect to $\boldsymbol{\mathcal{E}}$. For example, the electric-field-dependent electronic dielectric tensor can be computed from the expression

$$\varepsilon_{ij}(\mathbf{R}(\boldsymbol{\mathcal{E}}),\eta(\boldsymbol{\mathcal{E}}),\boldsymbol{\mathcal{E}}) = -\left.\frac{4\pi}{\Omega_0}\frac{\partial^2 F}{\partial\boldsymbol{\mathcal{E}}_i\,\partial\boldsymbol{\mathcal{E}}_j}\right|_{\mathbf{R}(\boldsymbol{\mathcal{E}}),\eta(\boldsymbol{\mathcal{E}}),\boldsymbol{\mathcal{E}}}. \tag{A7}$$

Let $\tau_{\kappa\alpha}=\mathbf{R}_{\kappa\alpha}-\mathbf{R}_{0,\kappa\alpha}$ be the displacement of atom κ along direction α and $\tau^{\lambda}_{\kappa\alpha}$ $(\eta^{\lambda}_{\mu\nu})$ the first-order modification of the atomic position (strain) induced by a perturbation λ:

$$\tau^{\lambda}_{\kappa\alpha} = \left.\frac{\partial\tau_{\kappa\alpha}}{\partial\lambda}\right|_{\lambda=0}, \quad \eta^{\lambda}_{\mu\nu} = \left.\frac{\partial\eta_{\mu\nu}}{\partial\lambda}\right|_{\lambda=0}. \tag{A8}$$

In the discussion that follows, we will study the effect of an electric field perturbation and a strain perturbation on the electric enthalpy F in order to obtain the formulas to compute the elasto-optic coefficients as well as the clamped and the unclamped EO tensors.

a. Elasto-optic coefficients ($\boldsymbol{\mathcal{E}}=\mathbf{0}$)

The elasto-optic tensor can be computed from the *total* derivative of the dielectric tensor with respect to $\eta_{\mu\nu}$ at zero electric field

$$\begin{aligned} \left.\frac{d\varepsilon_{ij}(\mathbf{R},\eta,0)}{d\eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0} &= \left.\frac{\partial\varepsilon_{ij}(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0} \\ &\quad + 4\pi\sum_{\kappa\alpha}\left.\frac{\partial\chi^{(1)}_{ij}(\mathbf{R},\eta)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_0,\eta_0}\tau^{\eta_{\mu\nu}}_{\kappa\alpha}. \end{aligned} \tag{A9}$$

The derivative in the first term of the right-hand side is computed considering the ionic cores as artificially clamped at their equilibrium positions. The remaining terms represent the ionic contribution to the elasto-optic tensor. They involve derivatives of the linear dielectric susceptibility $\chi^{(1)}_{ij}$ with respect to the atomic positions that have to be multiplied by the first-order strain-induced atomic displacements $\tau^{\eta_{\mu\nu}}_{\kappa\alpha}$ [Eq. (A8)]. To compute these quantities we use the fact that F is minimum at the equilibrium for an imposed strain η. This condition implies

$$\left.\frac{\partial F(\mathbf{R},\eta)}{\partial \tau_{\kappa\alpha}}\right|_{\mathbf{R}(\eta),\eta}=0. \tag{A10}$$

Since we are interested in first-order atomic displacements we can write $\tau_{\kappa\alpha}(\eta)=\Sigma_{\mu,\nu=1}^{3}\tau_{\kappa\alpha}^{\eta_{\mu\nu}}\eta_{\mu\nu}+O(\eta^2)$. Solving the extremum equation (A10) to the linear order in η, we obtain

$$\sum_{\kappa',\alpha'}\left.\frac{\partial^2 F(\mathbf{R},\eta)}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}\right|_{\mathbf{R}_0,\eta_0}\tau_{\kappa'\alpha'}^{\eta_{\mu\nu}}=-\left.\frac{\partial^2F(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}\,\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_0,\eta_0}. \tag{A11}$$

The second derivatives on the left side of Eq. (A11) define the matrix of interatomic force constants at zero macroscopic electric field, which enables the computation of the transverse phonon frequencies ω_m and eigendisplacements $u_m(\kappa\alpha)$. By decomposing $\tau_{\kappa\alpha}^{\eta_{\mu\nu}}$ in the basis of the zone-center phonon-mode eigendisplacements

$$\tau_{\kappa\alpha}^{\eta_{\mu\nu}}=\sum_m\tau_m^{\eta_{\mu\nu}}u_m(\kappa\alpha) \tag{A12}$$

and using Eqs. (24) and (25) we derive the following expression for the first-order strain-induced atomic displacements:

$$\tau_m^{\eta_{\mu\nu}}=\frac{-1}{\omega_m^2}\left.\frac{\partial^2F(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}\,\partial\tau_m}\right|_{\mathbf{R}_0,\eta_0}, \tag{A13}$$

where

$$\left.\frac{\partial^2F(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}\,\partial\tau_m}\right|_{\mathbf{R}_0,\eta_0}=\sum_{\kappa,\alpha}\left.\frac{\partial^2F(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}\,\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_0,\eta_0}u_m(\kappa\alpha). \tag{A14}$$

If we introduce Eqs. (A12) and (A13) into Eq. (A9) and use the definition of the Raman susceptibility, Eq. (28), and the transformation, Eq. (37), we finally obtain the formula to compute the elasto-optic tensor

$$p_{ij\mu\nu}=\frac{-1}{n_i^2n_j^2}\left.\frac{\partial\varepsilon_{ij}(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0}+\frac{4\pi}{n_i^2n_j^2\sqrt{\Omega_0}}\sum_m\frac{\alpha_{ij}^m}{\omega_m^2}\left.\frac{\partial^2F(\mathbf{R},\eta)}{\partial\eta_{\mu\nu}\,\partial\tau_m}\right|_{\mathbf{R}_0,\eta_0}. \tag{A15}$$

To simplify, we write Eq. (A15) in the principal axes of the crystal under investigation. A more general expression can be obtained from Eq. (37).

Equation (A15) is different from the approach used previously by Detraux and Gonze to study the elasto-optic tensor in α-quartz.[69] The authors of Ref. 69 used finite differences with respect to strains to compute the total derivative of ε_{ij}. In their approach, the atoms where relaxed to their equilibrium positions in the strained configurations. In case of Eq. (A15), the first term of the right-hand side is computed at clamped atomic positions while the effect of the strain-induced atomic relaxations is taken into account by the second term.

b. Clamped EO coefficients ($\boldsymbol{\eta}=\mathbf{0}$)

The clamped EO tensor can be computed from the *total* derivative of the electric field dependent dielectric tensor, Eq. (A7), with respect to $\mathcal{E}$

$$\left.\frac{d\varepsilon_{ij}(\mathbf{R},\eta_0,\boldsymbol{\mathcal{E}})}{d\mathcal{E}_\gamma}\right|_{\mathbf{R}_0,\mathcal{E}=0}=\left.\frac{\partial\varepsilon_{ij}(\mathbf{R}_0,\eta_0,\boldsymbol{\mathcal{E}})}{\partial\mathcal{E}_\gamma}\right|_{\mathcal{E}=0}+4\pi\sum_{\kappa\alpha}\left.\frac{\partial\chi_{ij}^{(1)}(\mathbf{R},\eta_0)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_0}\tau_{\kappa\alpha}^{\mathcal{E}_\gamma}. \tag{A16}$$

The derivative in the first term is computed considering the ionic cores as artificially clamped at their equilibrium positions. This term represents the bare electronic contribution to the EO tensor that can be computed from the nonlinear optical coefficients

$$\left.\frac{\partial\varepsilon_{ij}(\mathbf{R}_0,\eta_0,\boldsymbol{\mathcal{E}})}{\partial\mathcal{E}_\gamma}\right|_{\mathcal{E}=0}=8\pi\left.\chi_{ijk}^{(2)}\right|_{k=\gamma}, \tag{A17}$$

related to a third-order partial derivative of F:

$$\chi_{ijk}^{(2)}=\chi_{ijk}^{(2)}(\mathbf{R}_0,\eta_0)=\frac{-1}{2\Omega_0}\left.\frac{\partial^3F(\mathbf{R}_0,\eta_0,\boldsymbol{\mathcal{E}})}{\partial\mathcal{E}_i\,\partial\mathcal{E}_j\,\partial\mathcal{E}_k}\right|_{\mathcal{E}=0}. \tag{A18}$$

The remaining terms in Eq. (A16) represent the ionic contribution to the EO tensor. They involve derivatives of the linear dielectric susceptibility $\chi_{ij}^{(1)}$ with respect to the atomic positions that have to be multiplied by the first-order electric field induced atomic displacements $\tau_{\kappa\alpha}^{\mathcal{E}_\gamma}$ [Eq. (A8)]. To obtain these quantities, we proceed the same way as in case of the elasto-optic tensor. Using the equilibrium condition

$$\frac{\partial F}{\partial\tau_{\kappa\alpha}}=0=\left.\frac{\partial F(\mathbf{R},\eta_0,0)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}(\mathcal{E})}-\Omega_0\sum_{i=1}^{3}\left.\frac{\partial\mathcal{P}_i(\mathbf{R},\eta_0)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}(\mathcal{E})}\mathcal{E}_i-\frac{\Omega_0}{8\pi}\sum_{i,j=1}^{3}\left.\frac{\partial\varepsilon_{ij}(\mathbf{R},\eta_0)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}(\mathcal{E})}\mathcal{E}_i\mathcal{E}_j+\dots \tag{A19}$$

and expanding $\tau_{\kappa\alpha}$ to the first order in the electric field, we obtain

$$\sum_{\kappa',\alpha'}\left.\frac{\partial^2F(\mathbf{R},\eta_0,0)}{\partial\tau_{\kappa\alpha}\,\partial\tau_{\kappa'\alpha'}}\right|_{\mathbf{R}_0}\tau_{\kappa'\alpha'}^{\mathcal{E}_\gamma}=\Omega_0\left.\frac{\partial\mathcal{P}_\gamma(\mathbf{R},\eta_0)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_0}. \tag{A20}$$

This expression is similar to Eq. (A11). The second-order derivatives of F on the left side are the interatomic force constants and the derivative of the zero field polarization with respect to $\tau_{\kappa\alpha}$ on the right side is the Born effective charge tensor $Z_{\kappa,\gamma\alpha}^{*}$ of atom κ. Decomposing $\tau_{\kappa\alpha}^{\mathcal{E}_\gamma}$ in the basis of the zone-center phonon-mode eigendisplacements [Eq. (A12)] and using the orthonormality constraint Eq. (25) we derive the following expression for the first-order electric-field-induced atomic displacements:

$$\tau_m^{\mathcal{E}_\gamma} = \frac{1}{\omega_m^2} \sum_{\kappa,\alpha} Z^*_{\kappa,\gamma\alpha} u_m(\kappa\alpha). \tag{A21}$$

If we introduce Eqs. (A17) and (A21) into Eq. (A16) we finally obtain the formula to compute the total derivative of the dielectric tensor:

$$\left.\frac{d\varepsilon_{ij}(\mathbf{R},\boldsymbol{\mathcal{E}})}{d\mathcal{E}_\gamma}\right|_{\mathbf{R}_0,\mathcal{E}=0} = 8\pi \left.\chi^{(2)}_{ijk}\right|_{k=\gamma} + 4\pi \sum_m \frac{1}{\omega_m^2} \left(\sum_{\kappa,\alpha} \frac{\partial \chi^{(1)}_{ij}(\mathbf{R})}{\partial \tau_{\kappa\alpha}} u_m(\kappa\alpha) \right) \times \left(\sum_{\kappa',\beta} Z^*_{\kappa',\gamma\beta} u_m(\kappa'\beta) \right). \tag{A22}$$

Using the definition of the Raman susceptibility [Eq. (28)], the mode polarity [Eq. (41)] and the transformation [Eq. (37)], we obtain the expression of the clamped EO tensor

$$r^\eta_{ij\gamma} = \frac{-8\pi}{n_i^2 n_j^2} \left.\chi^{(2)}_{ijl}\right|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_m \frac{\alpha^m_{ij} p_{m,\gamma}}{\omega_m^2}. \tag{A23}$$

As in the case of the elasto-optic tensor [Eq. (A15)], we have written Eq. (A23) in the principal axes of the crystal under investigation.

c. Unclamped EO tensor ($\sigma=0$)

In order to compute the unclamped EO tensor, we have to take into account both the electric-field-induced atomic displacments $\tau^{\mathcal{E}_\gamma}_{\kappa\alpha}$ and the electric-field-induced strain $\eta^{\mathcal{E}_\gamma}_{\mu\nu}$ when computing the total derivative of ε_{ij}:

$$\left.\frac{d\varepsilon_{ij}(\mathbf{R},\eta,\boldsymbol{\mathcal{E}})}{d\mathcal{E}_\gamma}\right|_{\mathbf{R}_0,\eta_0,\mathcal{E}=0} = \left.\frac{\partial\varepsilon_{ij}(\mathbf{R}_0,\eta_0,\boldsymbol{\mathcal{E}})}{\partial\mathcal{E}_\gamma}\right|_{\mathcal{E}=0} + 4\pi \sum_{\kappa\alpha} \left.\frac{\partial \chi^{(1)}_{ij}(\mathbf{R},\eta_0)}{\partial \tau_{\kappa\alpha}}\right|_{\mathbf{R}_0} \tau^{\mathcal{E}_\gamma}_{\kappa\alpha} + 4\pi \sum_{\mu,\nu=1}^{3} \left.\frac{\partial \chi^{(1)}_{ij}(\mathbf{R}_0,\eta)}{\partial \eta_{\mu\nu}}\right|_{\eta_0} \eta^{\mathcal{E}_\gamma}_{\mu\nu}. \tag{A24}$$

The electronic contribution [first term of Eq. (A24)] is the same as for the clamped EO tensor. It can be computed from the nonlinear optical coefficients [Eq. (A17)]. To compute $\tau^{\mathcal{E}_\gamma}_{\kappa\alpha}$ and $\eta^{\mathcal{E}_\gamma}_{\mu\nu}$, we can use an equilibrium condition similar to Eq. (A19) where we require that the first-order derivatives of F with respect to $\tau_{\kappa\alpha}$ and $\eta_{\mu\nu}$ vanish. Expanding $\tau_{\kappa\alpha}$ and $\eta_{\mu\nu}$ to the first order in the electric field, we obtain the system of coupled equations (see also Ref. 70)

$$\sum_{\kappa',\alpha'} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa\alpha}\,\partial \tau_{\kappa'\alpha'}}\right|_{\mathbf{R}_0,\eta_0} \tau^{\mathcal{E}_\gamma}_{\kappa'\alpha'} + \sum_{\mu,\nu} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa\alpha}\,\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0} \eta^{\mathcal{E}_\gamma}_{\mu\nu} = \Omega_0 \left.\frac{\partial \mathcal{P}_\gamma(\mathbf{R},\eta)}{\partial \tau_{\kappa\alpha}}\right|_{\mathbf{R}_0,\eta_0}, \tag{A25a}$$

$$\sum_{\mu',\nu'} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \eta_{\mu\nu}\,\partial \eta_{\mu'\nu'}}\right|_{\mathbf{R}_0,\eta_0} \eta^{\mathcal{E}_\gamma}_{\mu'\nu'} + \sum_{\kappa',\alpha'} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa'\alpha'}\,\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0} \tau^{\mathcal{E}_\gamma}_{\kappa'\alpha'} = \Omega_0 \left.\frac{\partial \mathcal{P}_\gamma(\mathbf{R},\eta)}{\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0}. \tag{A25b}$$

Because of the coupling between $\tau^{\mathcal{E}_\gamma}_{\kappa\alpha}$ and $\eta^{\mathcal{E}_\gamma}_{\mu\nu}$, defined by the mixed second-order derivatives $\partial^2 F/\partial\tau_{\kappa\alpha}\eta_{\mu\nu}$, the second term of the right-hand side of Eq. (A24) is different from that of Eq. (A16). That means that the sum of the first and second terms of Eq. (A24) is not identical to the clamped EO coefficients $r^\eta_{ij\gamma}$. Moreover, the third term of Eq. (A24) is different from the piezoelectric contribution of Sec. A 1.

In order to obtain the decomposition of $r^\sigma_{ij\gamma}$ into electronic, ionic, and piezoelectric contributions defined previously, we can solve Eq. (A25a) for $\tau^{\mathcal{E}_\gamma}_{\kappa\alpha}$. In the basis of the zone-center phonon mode eigendisplacements we can write

$$\tau_n^{\mathcal{E}_\gamma} = \frac{p_{n,\gamma}}{\omega_n^2} - \frac{1}{\omega_n^2} \sum_{\mu\nu} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_n\,\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0} \eta^{\mathcal{E}_\gamma}_{\mu\nu}. \tag{A26}$$

If we insert this relation into Eq. (A24) and use the transformation equation (37) we obtain the following expression of the unclamped EO tensor in the principal axes:

$$r^\sigma_{ij\gamma} = \frac{-8\pi}{n_i^2 n_j^2} \left.\chi^{(2)}_{ijl}\right|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_m \frac{\alpha^m_{ij} p_{m,\gamma}}{\omega_m^2} - \frac{4\pi}{n_i^2 n_j^2} \sum_{\mu,\nu} \left[\left.\frac{\partial \chi^{(1)}_{ij}(\mathbf{R},\eta,\boldsymbol{\mathcal{E}})}{\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0,\mathcal{E}=0} - \frac{1}{\sqrt{\Omega_0}} \sum_m \frac{\alpha^m_{ij}}{\omega_m^2} \left.\frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_m\,\partial \eta_{\mu\nu}}\right|_{\mathbf{R}_0,\eta_0,\mathcal{E}=0} \right] \eta^{\mathcal{E}_\gamma}_{\mu\nu} \tag{A27}$$

The sum of the first and second term of the right-hand side of Eq. (A27) is equal to the clamped EO coefficient $r^\eta_{ij\gamma}$. The product of the conversion factor times the bracket in the third term of Eq. (A27) is equal to the elasto-optic coefficient $p_{ij\mu\nu}$ [Eq. (A15)]. Finally, by definition of the converse piezoelectric effect, $\eta^{\mathcal{E}_\gamma}_{\mu\nu}$ is equal to the piezoelectric strain coefficient $d_{\gamma\mu\nu}$. We thus obtain the following expression of the unclamped EO coefficients that is equal to the one derived in Sec. A 1 from pure macroscopic arguments:

$$r^\sigma_{ij\gamma} = r^\eta_{ij\gamma} + \sum_{\mu,\nu=1}^{3} p_{ij\mu\nu} d_{\gamma\mu\nu}. \tag{A28}$$

It is worth noting that the so-called piezoelectric contribution not only takes into account the change of the linear optical susceptibility with strain [third term of the right-hand side of Eq. (A24)] but also includes the modification of the ionic contribution, with respect to the clamped case, that is associated to the modification of the ionic relaxation induced by the strain.

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