First-principles perturbative computation of dielectric and Born charge tensors in finite electric fields

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We present a perturbative treatment of the response properties of insulating crystals under a dc bias field, and use this to study the effects of such bias fields on the Born effective charge tensor and dielectric tensor of insulators. We start out by expanding a variational field-dependent total-energy functional with respect to the electric field within the framework of density-functional perturbation theory. The second-order term in the expansion of the total energy is then minimized with respect to the first-order wave functions, from which the Born effective charge tensor and dielectric tensor are easily computed. We demonstrate an implementation of the method and perform illustrative calculations for the III-V semiconductors AlAs and GaAs under finite bias field.

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I. INTRODUCTION

The dielectric tensor and Born (or dynamical) effective charge tensor are of fundamental importance in understanding and modeling the response of an insulator to an electric field.[1] They give, respectively, the first-order polarization and atomic force appearing in response to a first-order change in the macroscopic electric field. While one is most often interested in evaluating these response tensors at zero field, there is increasing interest in finite-field properties. For example, the study of bulk ferroelectrics[2–4] and of ferroelectric films[5] and superlattices[4,6] in finite field, and of lattice vibrations in polar crystals in finite field,[7] have recently generated interest. While it may sometimes be reasonable to model the dielectric behavior by assuming that the dielectric and Born effective charge tensors have a negligible dependence on the bias field, it is important to be able to quantify such approximations and to compute the field dependence when it is physically important to do so (e.g., for describing non-linear optical phenomena such as second-harmonic generation).

Density-functional perturbation theory (DFPT)[8,9] provides a powerful tool for calculating the second-order derivatives of the total energy of a periodic solid with respect to external perturbations such as atomic sublattice displacements or a homogeneous electric field. In contrast to the case of sublattice displacements, for which the perturbing potential remains periodic, the treatment of homogeneous electric fields is subtle because the corresponding potential acquires a term that is linear in real space, thereby breaking the translational symmetry and violating the conditions of Bloch's theorem. For this reason, electric-field perturbations have often been studied in the past using the long-wave method, in which the linear potential resulting from the applied electric field is obtained by considering a sinusoidal potential in the limit that its wave vector goes to zero. In this approach, however, the response tensor can only evaluated at zero electric field, and it also requires as an ingredient the calculation of the derivatives of the ground-state wave functions with respect to wave vector.

Recently, Nunes and Gonze introduced an electric-field-dependent energy functional expressed in terms of the Berry-phase polarization.[10] This approach was initially introduced in order to provide an alternative framework for the DFPT treatment of electric-field perturbations (evaluated at zero field) in which the long-wave method is entirely avoided. More recently, it has been pointed out that the Nunes-Gonze functional could also serve as the basis for a calculation of the "ground-state" properties in *finite* electric field.[11,12] (Here, the phrase "ground state" is used advisedly; because of Zener tunneling, the state of interest is actually a long-lived resonance.[13]) In this approach, the energy functional is minimized with respect to a set of field-polarized Bloch functions that form a natural representation of the one-particle density matrix even though they are no longer eigenstates of the Hamiltonian.[11,13] The introduction of this approach has also made possible the calculation of the dielectric and Born effective charge tensors at finite electric fields using finite-difference methods.[11]

In a recent paper[7] we developed a perturbative method, within this framework, for computing the phonon properties of insulators at finite electric fields. The starting point was the Nunes-Gonze electric-field-dependent energy functional, which represents the effect of the electric field by including its coupling to the Berry-phase polarization.[10] This total-energy functional was expanded up to second order in atomic displacements. The linear response of the field-polarized Bloch functions to the atomic displacements was obtained by minimizing the second-order term in the expansion of the total-energy functional with respect to the first-order changes in the Bloch functions. Finally, the force-constant matrix was constructed based on these first-order Bloch functions. This method provides a tractable and efficient computational scheme for computing phonon properties at finite electric field, and suggests that a similar treatment of other response properties of insulators in finite electric field should be possible.

In this paper, we follow the approach of Ref. 7 to de-

velop a method for computing the dielectric and Born effective charge tensors at finite electric field. Again using the Nunes-Gonze energy functional,[10] we compute the first-order responses of the electronic wave functions to a small change in the electric field. We then use these to construct the second-order derivatives of the total energy with respect to electric field (to give the dielectric tensors evaluated at non-zero field) and the mixed derivatives with respect to electric field and atomic sublattice displacement (to give the Born effective charge tensors evaluated at non-zero field).

The paper is organized as follows. In Sec. II, the second-order perturbation expansion of the total energy functional with respect to electric fields is derived and the steepest-descent directions are identified. The expressions for computing the dielectric and Born effective charge tensors are also given. In Sec. III, we describe the implementation of the approach in the `ABINIT` code package,[14] and present test calculations for the III-V semiconductors AlAs and GaAs. (Since we are mainly interested in the purely electronic effects here, we do not include the strains or sublattice displacements that might occur in response to the electric field; these could easily be included by employing structural-relaxation methods at finite field.[11]) By comparing with the results of finite-differences calculations, we demonstrate the correctness of the new formulation and the internal consistency of the theory. A brief summary and conclusion are presented in Sec. IV.

II. METHOD

A. Perturbation expansion of the enthalpy functional

We start from the electric enthalpy functional[10,11]

$$F[\mathbf{R};\psi;\mathcal{E}] = E_{\rm KS}[\mathbf{R};\psi] - \Omega\mathcal{E}\cdot\mathbf{P}[\psi] \ , \tag{1}$$

where $\mathbf{R}$, $\mathcal{E}$, Ω and $\mathbf{P}$ are, respectively, the atomic coordinates, the electric field, the cell volume, and the macroscopic polarization, $E_{\rm KS}$ is Kohn-Sham energy functional at zero electric field, and atomic units are used throughout. After minimizing this functional, the field-polarized Bloch functions ψ may be regarded as depending implicitly on the electric field $\mathcal{E}$. Our treatment of this functional will parallel the treatment given in our previous Ref. 7.

In the present case, we take the electric field $\mathcal{E}$ to consist of two parts, a finite part $\mathcal{E}^{(0)}$ and a small variation $\delta\mathcal{E}$. In the following, we consider the perturbation expansion of the functional in Eq. (1) with respect to the small variation $\delta\mathcal{E}$ under the orthonormality constraints

$$\langle\psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle = \delta_{mn} \ . \tag{2}$$

The wave functions are to be relaxed, subject to these constraints, in such a way as to minimize the electric enthalpy functional

$$F = F_{\rm KS} + F_{\rm BP} + F_{\rm LM} \ , \tag{3}$$

where $F_{\rm KS} = E_{\rm KS}$ is the Kohn-Sham energy (as it would be calculated at $\mathcal{E} = 0$), $F_{\rm BP} = -\Omega\mathcal{E}\cdot\mathbf{P}$ contains the coupling of the Berry-phase polarization $\mathbf{P}$ to the electric field, and the constraint is implemented by the inclusion of the Lagrange-multiplier term $F_{\rm LM}$. The first and last of these terms are given by

$$F_{\rm KS} = \frac{f}{N_k}\sum_{\mathbf{k}n}^{\rm occ}\langle\psi_{n\mathbf{k}}|T + v_{\rm ext}|\psi_{n\mathbf{k}}\rangle + E_{\rm Hxc}[n] \tag{4}$$

and

$$F_{\rm LM} = -\frac{f}{N_k}\sum_{\mathbf{k},mn}^{\rm occ}\Lambda_{\mathbf{k},mn}(\langle\psi_{m\mathbf{k}}|\psi_{n\mathbf{k}}\rangle - \delta_{mn}) \tag{5}$$

where f is the spin degeneracy (normally f=2), N_k is the number of k-points, and $\Lambda_{\mathbf{k},mn}$ is the matrix of Lagrange multipliers. In a notation similar to that of Ref. 7, the second term may be written as

$$F_{\rm BP} = -\frac{ef}{2\pi}\sum_{i=1}^{3}\frac{\mathcal{E}\cdot\mathbf{a}_i}{N_\perp^{(i)}}\sum_{\mathbf{k}} D_{\mathbf{k},\mathbf{k}+\mathbf{g}_i} \ . \tag{6}$$

Here $\mathbf{a}_i$ are the three primitive real-space lattice vectors, and the mesh of N_k k-points is defined by mesh vectors $\mathbf{g}_i = \mathbf{b}_i/N^{(i)}$ where $\mathbf{b}_i$ is the reciprocal lattice vector dual to $\mathbf{a}_i$. Thus, $N_k = N^{(1)}N^{(2)}N^{(3)}$, and we also define $N_\perp^{(i)} = N_k/N^{(i)}$ as the number of k-point strings running in direction i. Finally,

$$D_{\mathbf{k}\mathbf{k}'} = {\rm Im}\ln\det S_{\mathbf{k}\mathbf{k}'} \tag{7}$$

where the overlap matrix is defined as

$$(S_{\mathbf{k}\mathbf{k}'})_{mn} \ = \ \langle u_{m\mathbf{k}}|u_{n\mathbf{k}'}\rangle \ . \tag{8}$$

In order to obtain the desired response properties, we now wish to expand the finite-field enthalpy functional $F_{\rm KS}$ up to second order in the electric field. We shall assume for the moment that the electric field is applied in Cartesian direction α only. The expansion of $F_{\rm KS}$ with respect to atomic displacements was already obtained in Ref. 7, and the expansion with respect to electric field can be carried through in a very similar way. Indeed, the second-order expansions of $F_{\rm KS}$ and $F_{\rm LM}$ can essentially be transcribed from Ref. 7 with the first-order wave functions with respect to displacement replaced here by the first-order wave functions with respect to electric field, giving

$$\begin{aligned} F_{\rm KS}^{(2)} \ &= \ \frac{1}{2}\frac{\partial^2 F_{\rm KS}}{\partial\mathcal{E}_\alpha^2} \\ &= \ \frac{f}{N_k}\sum_{\mathbf{k}}\sum_{n=1}^{occ}\langle u_{n\mathbf{k}}^{\mathcal{E}_\alpha}|T + v_{ext}|u_{n\mathbf{k}}^{\mathcal{E}_\alpha}\rangle \\ &\qquad + E_{\rm Hxc}^{\mathcal{E}_\alpha\mathcal{E}_\alpha} \end{aligned} \tag{9}$$

and

$$F^{(2)}_{\rm LM} \;=\; -\frac{f}{N_k}\sum_{\mathbf{k},n}^{\rm occ}\Lambda^{(0)}_{\mathbf{k},nn}\langle u^{\mathcal{E}_\alpha}_{n\mathbf{k}}|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle\;. \tag{10}$$

As in Ref. 7, terms that can be eliminated by use of the "$2n+1$ theorem" (e.g., $\langle u^{\mathcal{E}_\alpha\mathcal{E}_\alpha}_{n\mathbf{k}}|T+v_{ext}|u^{(0)}_{n\mathbf{k}}\rangle$) have been dropped. The the first-order wave functions are

$$|u^{\mathcal{E}_\alpha}_{n\mathbf{k}_j}\rangle = \frac{\partial|u_{n\mathbf{k}_j}\rangle}{\partial\mathcal{E}_\alpha} \tag{11}$$

and the second-order $E_{\rm Hxc}$ are

$$E^{\mathcal{E}_\alpha\mathcal{E}_\alpha}_{\rm Hxc} = \frac{\partial^2 E_{\rm Hxc}}{2\partial\mathcal{E}_\alpha\partial\mathcal{E}_\alpha}\;. \tag{12}$$

In these and subsequent equations, the partial derivatives indicate that the *structural* coordinates $\mathbf{R}$ are being held fixed (while, however, the *wave functions* $|u_{n\mathbf{k}}\rangle$ are allowed to vary).

The second-order expansion of $F_{\rm BP}$ with respect to electric field requires somewhat more care. We find

$$\begin{aligned} F^{(2)}_{\rm BP} \;&=\; \frac{1}{2}\frac{\partial^2 F_{\rm BP}}{\partial\mathcal{E}^2_\alpha} \\ &=\; -\frac{\Omega}{2}\frac{\partial^2(\mathcal{E}\cdot\mathbf{P})}{\partial\mathcal{E}^2_\alpha} \\ &=\; -\Omega(\hat{\mathbf{e}}_\alpha\cdot\mathbf{P}^{\mathcal{E}_\alpha}+\mathcal{E}^{(0)}\cdot\mathbf{P}^{\mathcal{E}_\alpha\mathcal{E}_\alpha})\;, \end{aligned} \tag{13}$$

where $\hat{\mathbf{e}}_\alpha$ is the unit vector along Cartesian direction α. The first term in the last line of Eq. (13) is special to the case of the electric-field perturbation, while the second term can be derived in close correspondence to the case of displacement perturbations in Ref. 7. The first-order variation of $\mathbf{P}$ with field $\mathcal{E}_\alpha$ is

$$\mathbf{P}^{\mathcal{E}_\alpha} = -\frac{ef}{2\pi\Omega}\sum_{i=1}^{3}\frac{\mathbf{a}_i}{N^{(i)}_\perp}\sum_{\mathbf{k}}D^{(1)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i} \tag{14}$$

and its second-order variation is

$$\mathbf{P}^{\mathcal{E}_\alpha\mathcal{E}_\alpha} = -\frac{ef}{4\pi\Omega}\sum_{i=1}^{3}\frac{\mathbf{a}_i}{N^{(i)}_\perp}\sum_{\mathbf{k}}D^{(2)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i}\;, \tag{15}$$

where

$$D^{(1)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i} = {\rm ImTr}\left[S^{(1)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i}Q_{\mathbf{k}+\mathbf{g}_i,\mathbf{k}}\right] \tag{16}$$

and

$$\begin{aligned} D^{(2)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i} \;=\; {\rm ImTr}\Big[&2S^{(2)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i}Q_{\mathbf{k}+\mathbf{g}_i,\mathbf{k}} \\ &-S^{(1)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i}Q_{\mathbf{k}+\mathbf{g}_i,\mathbf{k}}S^{(1)}_{\mathbf{k},\mathbf{k}+\mathbf{g}_i}Q_{\mathbf{k}+\mathbf{g}_i,\mathbf{k}}\Big]\;. \end{aligned} \tag{17}$$

In these equations, 'Tr' indicates a trace of the bracketed matrix over band indices, and Q, $S^{(1)}$, and $S^{(2)}$ are defined with respect to the series expansion of the overlap matrix via

$$S_{\mathbf{k}\mathbf{k}'}(\mathcal{E}_\alpha) = S^{(0)}_{\mathbf{k}\mathbf{k}'}+\mathcal{E}_\alpha S^{(1)}_{\mathbf{k}\mathbf{k}'}+\mathcal{E}^2_\alpha S^{(2)}_{\mathbf{k}\mathbf{k}'}+... \tag{18}$$

and

$$Q_{\mathbf{k}\mathbf{k}'} \;=\; [S^{(0)}_{\mathbf{k}'\mathbf{k}}]^{-1}\;. \tag{19}$$

The first- and second-order expansions of the overlap matrix take the form

$$S^{(1)}_{\mathbf{k},\mathbf{k}',mn} = \langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|u^{(0)}_{n\mathbf{k}'}\rangle+\langle u^{(0)}_{m\mathbf{k}}|u^{\mathcal{E}_\alpha}_{n\mathbf{k}'}\rangle \tag{20}$$

and

$$S^{(2)}_{\mathbf{k},\mathbf{k}',mn} = \langle u^{\mathcal{E}_\alpha}_{m\mathbf{k}}|u^{\mathcal{E}_\alpha}_{n\mathbf{k}'}\rangle\;. \tag{21}$$

In the last equation above, terms like $\langle u^{\mathcal{E}_\alpha\mathcal{E}_\alpha}_{m\mathbf{k}}|u^{(0)}_{n\mathbf{k}'}\rangle$ have again been dropped by virtue of the "$2n+1$ theorem."

B. First-order wave functions with respect to electric-field perturbation

The second-order term in the expansion of the energy functional, given by the sum $F^{(2)} = F^{(2)}_{\rm KS}+F^{(2)}_{\rm BP}+F^{(2)}_{\rm LM}$ of the expressions in Eqs. (9), (13), and (10) respectively, is minimized with respect to the first-order wave functions $|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle$ using standard conjugate-gradient methods. The steepest-descent direction is obtained from the gradient of $F^{(2)}$ with respect to $\langle u^{\mathcal{E}_\alpha}_{n\mathbf{k}}|$, whose contributions take the form

$$\frac{\delta F^{(2)}_{\rm KS}}{\delta u^{\mathcal{E}_\alpha *}_{n\mathbf{k}}} \;=\; \frac{f}{N_k}\left[\left(T+v^{(0)}_{ext}\right)|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle+\frac{\delta E^{\mathcal{E}_\alpha\mathcal{E}_\alpha}_{\rm Hxc}}{\delta u^{\mathcal{E}_\alpha *}_{n\mathbf{k}}}\right]\;, \tag{22}$$

$$\begin{aligned} \frac{\delta F^{(2)}_{\rm BP}}{\delta u^{\mathcal{E}_\alpha *}_{n\mathbf{k}}} \;&=\; \frac{ief}{4\pi}\sum_{i=1}^{3}\frac{\mathcal{E}^{(0)}\cdot\mathbf{a}_i}{N^{(i)}_\perp}\big(\,|\mathcal{C}_{m\mathbf{k},\mathbf{k}+\mathbf{g}_i}\rangle-|\mathcal{C}_{m\mathbf{k},\mathbf{k}-\mathbf{g}_i}\rangle\,\big) \\ &+\; \frac{ief}{4\pi}\sum_{i=1}^{3}\frac{\hat{\mathbf{e}}_\alpha\cdot\mathbf{a}_i}{N^{(i)}_\perp}\big(\,|\mathcal{D}_{m\mathbf{k},\mathbf{k}+\mathbf{g}_i}\rangle-|\mathcal{D}_{m\mathbf{k},\mathbf{k}-\mathbf{g}_i}\rangle\,\big)\;, \end{aligned} \tag{23}$$

and

$$\frac{\delta F^{(2)}_{\rm LM}}{\delta u^{\mathcal{E}_\alpha *}_{n\mathbf{k}}} = \frac{f}{N_k}\epsilon^{(0)}_{n\mathbf{k}}|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle\;. \tag{24}$$

Here

$$\mathcal{C}_{m\mathbf{k}\mathbf{k}'} = \Big(\,|u^{\mathcal{E}_\alpha}_{\mathbf{k}'}\rangle Q_{\mathbf{k}'\mathbf{k}}-|u^{(0)}_{\mathbf{k}'}\rangle Q_{\mathbf{k}'\mathbf{k}}S^{(1)}_{\mathbf{k}\mathbf{k}'}Q_{\mathbf{k}'\mathbf{k}}\Big)_m\;, \tag{25}$$

$$\mathcal{D}_{m\mathbf{k}\mathbf{k}'} = \Big(\,|u^{(0)}_{\mathbf{k}'}\rangle Q_{\mathbf{k}'\mathbf{k}}\Big)_m\;, \tag{26}$$

and $\epsilon^{(0)}_{n\mathbf{k}}$ is the diagonal zero-order matrix of Lagrange multipliers. Convergence of the conjugate-gradient procedure yields a set of first-order wave functions $|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle$. These then become the essential ingredients for constructing the dielectric and Born charge tensors as discussed below.

C. Dielectric permittivity tensor

The dielectric permittivity tensor can be written as

$$\epsilon^{\infty}_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi\chi_{\alpha\beta} \tag{27}$$

where the electric susceptibility tensor $\chi_{\alpha\beta}$ at a *finite* electric field is defined as

$$\begin{aligned}\chi_{\alpha\beta} &= -\frac{1}{\Omega}\frac{\partial^2 F(\mathcal{E})}{\partial\mathcal{E}_\alpha\partial\mathcal{E}_\beta}\bigg|_{\mathcal{E}=\mathcal{E}^{(0)}} \\ &= \frac{\partial P_\alpha}{\partial\mathcal{E}_\beta}\bigg|_{\mathcal{E}=\mathcal{E}^{(0)}} = \hat{\mathbf{e}}_\alpha\cdot\mathbf{P}^{\mathcal{E}_\beta} \ . \end{aligned} \tag{28}$$

The derivative $\mathbf{P}^{\mathcal{E}_\beta}$ of the polarization with respect to electric field is already given by Eq. (14). Since the first-order wave functions $|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle$ have already been obtained in Sec. II B, it is straightforward to evaluate Eq. (28) and thus obtain the polarizability and permittivity.

The dielectric responses above are the static responses computed with atomic coordinates frozen. That is, they correspond to the dielectric response that would be measured at frequencies low compared to electronic frequencies but high compared to any infrared-active phonon modes. The true static susceptibility could be computed by including the lattice displacements (and, if appropriate, the piezoelectric strains) using, e.g., the methods of Ref. 15.

D. Born effective charge tensor

The electronic contribution to the Born effective charge tensor at finite electric field takes the form

$$Z^*_{\kappa,\alpha\beta} = -\frac{\partial^2 F(\mathcal{E})}{\partial\mathcal{E}_\alpha\partial\tau_{\kappa,\beta}}\bigg|_{\mathcal{E}=\mathcal{E}^{(0)}} . \tag{29}$$

This expression can be calculated equivalently in two different ways. First, introducing the force $f_{\kappa,\alpha} = -\partial F(\mathcal{E})/\partial\tau_{\kappa,\alpha}$ acting on atom κ in direction α, it can be written as

$$Z^*_{\kappa,\alpha\beta} = \frac{\partial f_{\kappa,\beta}}{\partial\mathcal{E}_\alpha} \ . \tag{30}$$

Using the Hellmann-Feynman theorem, the expression for the force is given as

$$f_{\kappa,\beta} = \frac{f}{N_k}\sum_{\mathbf{k}}\sum_{n=1}^{occ}\langle u^{(0)}_{n\mathbf{k}}|(T+v_{ext})^{\tau_{\kappa,\beta}}|u^{(0)}_{n\mathbf{k}}\rangle \ , \tag{31}$$

and taking an additional derivative with respect to electric field yields

$$Z^*_{\kappa,\alpha\beta} = \frac{2f}{N_k}\sum_{\mathbf{k}}\sum_{n=1}^{occ}\langle u^{(0)}_{n\mathbf{k}}|(T+v_{ext})^{\tau_{\kappa,\beta}}|u^{\mathcal{E}_\alpha}_{n\mathbf{k}}\rangle \ . \tag{32}$$

This has essentially the same form as Eq. (43) in Ref. 9, except that here the zero-order wave functions are already polarized by the preexisting finite electric field.

Alternatively, Eq. (29) can be computed as the derivative of the polarization with respect to the displacement,

$$Z^*_{\kappa,\alpha\beta} = \Omega\frac{\partial P_\alpha}{\partial\tau_{\kappa,\beta}} = \Omega\hat{\mathbf{e}}_\alpha\cdot\mathbf{P}^{\tau_{\kappa,\beta}} \ . \tag{33}$$

Here $\mathbf{P}^{\tau_{\kappa,\beta}}$ takes a form very similar to that of Eq. (14), except that the first-order changes $|u^{\mathcal{E}_\alpha}_{n\mathbf{k}_j}\rangle$ in the wave functions in response to an electric field are replaced by the corresponding changes $|u^{\tau_{\kappa,\beta}}_{n\mathbf{k}_j}\rangle$ in response to a sublattice displacement. The computation of the $|u^{\tau_{\kappa,\beta}}_{n\mathbf{k}_j}\rangle$ has already been described in detail in Ref. 7.

The computation of the first-order derivatives of the wave functions is typically the most time-consuming step of the linear-response calculation. Therefore, for a complicated unit cell with many atoms M per cell, the computation of the three derivatives $|u^{\mathcal{E}_\alpha}\rangle$ will be much cheaper than that of the $3M$ derivatives $|u^{\tau_{\kappa,\beta}}\rangle$, and the method of Eq. (32) will therefore be significantly faster than the method of Eq. (33). In the special case that the displacement derivatives $|u^{\tau_{\kappa,\beta}}\rangle$ have already been computed for some other reason (e.g., for the purpose of computing the phonon frequencies in finite field), the use of the latter method may be advantageous. In any case, a comparison of the two methods should provide a useful check on the internal consistency of the theory and its computational implementation.

III. TEST CALCULATIONS FOR III-V SEMICONDUCTORS

In order to check our method, we have performed test calculations on two prototypical III-V semiconductors, AlAs and GaAs, for which the electronic contribution to the polarization is typically comparable to the ionic contribution.[4] The calculation is carried out using the planewave-pseudopotential method based on density-functional theory with local-density approximation (LDA). We use Troullier-Martins norm-conserving pseudopotentials[16] in which the $3d$ states on the Ga and As atoms are treated as core states. (The omission of the semicore $3d$ states from the valence on the Ga atom may limit the accuracy of the Ga pseudopotential somewhat.) A $16\times16\times16$ Monkhorst-Pack mesh is used for the k-point sampling. More computational details can be found in our preceding paper.[7]

The calculation of the dielectric permittivity tensor and the Born effective charge tensor is carried out in three steps. First, a ground-state calculation at finite electric field is performed using the Berry-phase approach[11] implemented in the `ABINIT` code, and the field-polarized Bloch functions are stored for the later linear response calculation. Second, the linear response calculation is carried out to obtain the first-order response of Bloch functions. Third, the matrix elements of the dielectric and Born effective charge tensors are computed using these first-order responses.

TABLE I: Calculated electronic dielectric constants of AlAs and GaAs at zero field, and changes resulting from an electric field of 3.08×10^8 V/m along the [100] direction. 'LR' and 'FD' denote the results of linear-response [Eq. (28)] and finite-difference calculations, respectively.

		ϵ_∞	$\Delta\epsilon_{\infty,23}$	$\Delta\epsilon_{\infty,11}$	$\Delta\epsilon_{\infty,33}$
AlAs	LR	9.681	0.039	0.027	0.013
	FD	9.681	0.040	0.027	0.013
GaAs	LR	13.315	0.202	0.211	0.104
	FD	13.319	0.203	0.207	0.098

TABLE II: Calculated cation Born effective charges of AlAs and GaAs at zero field, and changes resulting from an electric field of 3.08×10^8 V/m along the [100] direction. 'LR' and 'FD' denote the results of linear-response [Eq. (32)] and finite-difference calculations, respectively.

		Z^*	ΔZ^*_{23} ($\times 10^{-3}$)	ΔZ^*_{11} ($\times 10^{-3}$)	ΔZ^*_{33} ($\times 10^{-3}$)
AlAs	LR	2.110	17.23	−0.06	−0.13
	FD	2.110	17.22	−0.05	−0.11
GaAs	LR	2.186	52.88	−3.42	−3.17
	FD	2.186	52.83	−3.36	−3.14

The first column of Table I shows the calculated electronic dielectric constants of AlAs and GaAs at zero electric field, and the remaining ones show the nonzero changes in the dielectric tensor elements after the application of an electric field $\mathcal{E}^{(0)}$ of 3.08×10^8 V/m along the [100] direction. The results obtained with the linear-response approach of Eq. (28) are compared with those calculated by finite differences. In the latter case, polarizations are computed at several values of the electric field in steps of 3.08×10^5 V/m, and the dielectric tensor is calculated using a finite-difference version of Eq. (28). It can be seen that the agreement between the linear-response and the finite-difference results is excellent, demonstrating the internal consistency between the two approaches.

In Table II we present similar results for the cation Born effective charges of the same two materials, first at zero field and then again under application of a field of $\mathcal{E}^{(0)}$ of 3.08×10^8 V/m along the [100] direction. The linear-response results were obtained using Eq. (32), but we also computed the corresponding values using Eq. (33) and found agreement between the two linear-response approaches with a maximum fractional error smaller than 10^{-6} for all values reported. For the finite-difference comparison, the polarizations were computed at several values of the atomic displacements in steps of 10^{-3} Bohr and the Born charge tensors were calculated using a finite-difference version of Eq. (33). It can again be seen the agreement between the linear-response and the finite-difference results is excellent.

We emphasize that the values of $\Delta\epsilon_\infty$ and ΔZ^* reported in Tables I and II are purely electronic or "frozen-ion" ones – that is, the sublattice displacements that would be induced by a truly static electric field $\mathcal{E}^{(0)}$ are not included.

The values of ϵ_∞ and Z^* reported in Tables I and II are in good agreement with other theoretical values in the literature[17–19] and with experiment. The symmetry is such that the applied electric field along x breaks the degeneracy between the diagonal elements of the ϵ_∞ and Z^* tensors so that $\epsilon_{\infty,11} \neq \epsilon_{\infty,22} = \epsilon_{\infty,33}$ and $Z^*_{11} \neq Z^*_{22} = Z^*_{33}$, and introduces non-zero off-diagonal elements $\epsilon_{\infty,23} = \epsilon_{\infty,32}$ and $Z^*_{23} = Z^*_{32}$.

Symmetry considerations also imply that $\epsilon_{\infty,23}$ and Z^*_{23} should appear to first order in $\mathcal{E}^{(0)}$, while $\Delta\epsilon_{\infty,11}$, $\Delta\epsilon_{\infty,33}$, ΔZ^*_{11}, and ΔZ^*_{33} should be quadratic in $\mathcal{E}^{(0)}$. This is confirmed by our numerical calculations. Indeed, by repeating calculations like those shown in Tables I and II for several values of $\mathcal{E}^{(0)}$ and fitting to obtain the coefficients of the linear and quadratic dependence, we can extract information about the nonlinear dielectric response and the Raman tensor. The second- and third-order nonlinear dielectric tensors are defined as

$$\chi^{(2)}_{123} = \frac{1}{2}\frac{\partial^2 P_2}{\partial\mathcal{E}_1\partial\mathcal{E}_3} = \frac{1}{2}\frac{\partial\chi_{23}}{\partial\mathcal{E}_1} \tag{34}$$

and

$$\chi^{(3)}_{1111} = \frac{1}{6}\frac{\partial^3 P_1}{\partial\mathcal{E}_1^3} = \frac{1}{6}\frac{\partial^2\chi_{11}}{\partial\mathcal{E}_1^2}\,, \tag{35}$$

while the Raman polarizability tensor is defined by

$$\alpha_{\rm TO} = \frac{\partial^2 f_2}{\partial\mathcal{E}_1\partial\mathcal{E}_3} = \frac{\partial Z_{23}}{\partial\mathcal{E}_1} \tag{36}$$

where $\mathbf{f}$ is the force on the cation sublattice induced by the electric field. In practice, we calculate χ_{23}, χ_{11}, and Z^*_{23} for a series of finite electric fields oriented along the x-axis with values of $\mathcal{E}^{(0)}$ ranging from zero to 5.14×10^8V/m in increments of one-fifth of the maximum value. Fitting these data to a polynomial in $\mathcal{E}^{(0)}$ then gives the values of $\chi^{(2)}_{123}$, $\chi^{(3)}_{1111}$, and $\alpha_{\rm TO}$. Note that $\alpha_{\rm TO}$ can alternatively be expressed as

$$\alpha_{\rm TO} = \Omega\frac{\partial\chi_{23}}{\partial\tau_1} \tag{37}$$

where τ_1 is a cation sublattice displacement and χ_{23} is computed at zero field. We have also computed $\alpha_{\rm TO}$ by fitting to a series of calculations of this type, and find values of $\alpha_{\rm TO}$ that agree with those obtained from Eq. (36) within 0.3%.

The results for the $\chi^{(2)}_{123}$ and $\alpha_{\rm TO}$ values as computed from Eqs. (34) and (36) are presented in Table III for AlAs, together with some previous theoretical and experimental values for comparison. In view of the fact that the calculation of higher-order tensor elements tends to be delicate, the agreement is generally quite good. In

TABLE III: Values of second-order dielectric susceptibility and Raman matrix elements in AlAs, as defined by Eqs. (34) and (36) respectively, compared with previous theory and experiment.

	$\chi^{(2)}_{123}$ (pm/V)	$\lvert\alpha_{\rm TO}\rvert$ (Å^2)
Present work	62	8.0
Theory,[a] Ref. 11	64	
Theory,[b] Ref. 20	70	8.5
Theory,[a] Ref. 21	79	9.0
Theory,[b] Ref. 22		7.4
Experiment, Ref 23	78±20	

[a]Using finite-difference approach.
[b]Using $(2n+1)$-theorem approach.

particular, Veithen et al.[20] have shown (see their Fig. 1) that the results for $\chi^{(2)}_{123}$ can be quite sensitive to the method of discretization in k-space and the fineness of the k-point mesh. For GaAs we find $\chi^{(2)}_{123} = 293\,\text{pm/V}$ and $\alpha_{\rm TO} = -24.1\,\text{Å}^2$ (which is close to the value in Ref. 22), but these numbers are of questionable accuracy because of our use of a Ga pseudopotential that does not include the $3d$ semicore orbitals in the valence. We obtain $\chi^{(3)}_{1111}$ values of 3.90 and 33.8×10^{-11} esu for AlAs and GaAs, respectively. We are not aware of previous theoretical values of $\chi^{(3)}_{1111}$ with which to compare; this quantity is beyond the reach of the "$2n+1$" theorem using first-order wave function responses only, and so is difficult to compute by pure DFPT methods. Experimental values ranging from 3.9 to 18×10^{-11} esu for GaAs[24] can be found in the literature.

The discrepancies noted above between theory and theory, and between theory and experiment, may have many possible causes. In addition to some of the computational and convergence issues mentioned above, the adequacy of the LDA approximation itself is also a serious question. Because the LDA tends to underestimate gaps, some authors have included a so-called "scissors correction" in order to widen the gap artificially; this tends to decrease the magnitude of response tensors.[25] On the experimental side, the difficulty in obtaining reproducible results is surely also an issue. Nevertheless, we emphasize that the *relative* accuracy of the values reported in Tables I and II, which were done under the *same* computational conditions (same pseudopotentials, k-point meshes, etc.), demonstrates the correctness of our new finite-field linear-response formulation and the internal consistency of the computational framework that we employ.

IV. SUMMARY

We have developed a linear-response method for computing dielectric constants and Born effective charges in the presence of a *finite* electric field. We have demonstrated the reliability of our approach by implementing it in the context of the `ABINIT` code package[14] and performing test calculations on two III-V semiconductors, AlAs and GaAs. We have confirmed that the results calculated using the new linear-response approach are consistent with those obtained from finite-difference calculations carried out within the same framework. In general, our results are also in good agreement with other theoretical calculations and with experiment.

A major advantage of the present approach is that, unlike the conventional long-wave linear-response method,[8] it can be applied to obtain response tensors in finite electric field. While it is possible to obtain similar information from a set of finite-difference calculations carried out for some chosen set of applied electric fields, the linear-response approach is more direct, and it avoids the troublesome truncation errors that may arise in a finite-difference approach. In the future, it may be of interest to extend the finite-field DFPT treatment not just to phonon perturbations (presented in Ref. 7) and electric-field perturbations (presented here), but also to other perturbations such as those associated with strain or chemical composition. Taken together, these developments should allow for much greater flexibility in the calculation of materials properties of insulators under electrical bias and facilitate the study of higher-order nonlinear dielectric properties.

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