

# Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory

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(Received 7 November 1996)

Starting from the knowledge of first-order changes of wave functions and density with respect to small atomic displacements or infinitesimal homogeneous electric fields within the density-functional theory, we write the expressions for the diagonal or mixed second-order derivatives of the total energy with respect to these perturbations: dynamical matrices for different wave vectors, Born effective-charge tensors and electronic dielectric permittivity tensors. Interatomic force constants and the phonon-band structure are then obtained by computing the Fourier transform of dynamical matrices on a regular mesh of wave vectors, with an eventual, separate treatment of the long-range dipole-dipole interaction. The same ingredients also allow one to compute the low-frequency response of the crystal to homogeneous electric fields. [S0163-1829(97)05116-3]

## I. INTRODUCTION

Nowadays, the density-functional theory<sup>1,2</sup> (DFT) is considered as the method of choice for simulating solids from the first principles. The present paper focuses on the computation, from perturbation theory within DFT (actually within the local-density approximation to DFT), of second derivatives of the total energy of periodic solids with respect to (a) collective displacements of atoms with different wave vectors, either commensurate or incommensurate with the underlying lattice; and (b) homogeneous static electric fields. In the preceding paper (P1),<sup>3</sup> it was shown how to compute the corresponding first-order changes in density, wave functions, and self-consistent potentials, thanks to a conjugate-gradient algorithm, with plane waves and pseudopotentials. The further second-order derivatives of the energy are directly linked to the dynamical matrices at any wave vector, the low-frequency (ion-clamped) dielectric permittivity tensor  $\epsilon^\infty$ , and the Born effective-charge tensors  $Z^*$  (mixed second-order derivative with respect to atomic displacement and electric field).

As for the calculation of the first-order responses, the methods used for the second-order derivatives of the energy are of two types: the direct approaches, and the perturbative approaches. In the frozen-phonon method (a direct approach), a small, but finite, perturbation is frozen in the system, allowing us to compute, e.g., interatomic force constants.<sup>4</sup> It is also possible to extract phonon eigenfrequencies and eigenmodes from molecular dynamic trajectories,<sup>5</sup> which is another direct method. Recent progress in polarization theory has open the way to direct approaches of Born effective charges,<sup>6</sup> and dielectric permittivity tensors.<sup>7</sup>

However, in the frozen-phonon or the molecular dynamics methods, one has to deal with supercells, whose size depends on the commensurability of the perturbation with the unperturbed periodic cell. When the original cell is small (a few atoms), the supercells to take into account will be typically four or eight times larger, with a considerable increase

in computer time. A recently proposed order  $N$  approach to the computation of phonon bands and interatomic force constant could partially waive this drawback.<sup>8</sup>

By contrast, for wave-vector-characterized perturbations, perturbation theory allows one to map the computation of the responses onto an equivalent problem presenting the periodicity of the unperturbed periodic ground state, which is an obvious advantage over direct methods. Baroni, Giannozzi and Testa<sup>9</sup> (BGT) have popularized this type of method, as described in P1.<sup>10</sup> Many perturbative implementations of the computation of the first-order responses have been realized. When the first-order responses have been obtained, the generation of the diagonal (two derivatives with respect to the same perturbation) or mixed (one derivative with respect to one perturbation, one more derivative with respect to another) second-order derivatives of the total energy, can be performed. This supplementary step is rather easy, compared to the computation of the first-order responses. Actually, from the latter, even the mixed third-order derivatives of the energy can be computed easily.<sup>11</sup>

There are different formulas connecting the first-order responses to second-order derivatives of the energy. Some of them are *stationary* with respect to the errors made in the first-order responses. Others, inherently less accurate, have, in the case of mixed second-order derivatives of the total energy, the advantage of using the knowledge of the first-order responses with respect to *only one* of the two perturbations. This property, in a different context, was called the ‘‘interchange theorem.’’<sup>12</sup> The stationarity of some formulas, as well as the interchange theorem, is a consequence of the existence of the variational principle for the total energy of the system.<sup>2</sup> In this paper, the different formulas, nonstationary,<sup>13</sup> as well as stationary, will be developed, for the above-mentioned perturbations, in the framework of a plane-wave-pseudopotential method. Like in P1, efficient separable pseudopotentials,<sup>14</sup> as well as the nonlinear exchange-correlation core correction,<sup>15,16</sup> are considered. Results obtained with these formulas were exhibited in Refs.

17–22, with restricted presentation of the underlying theory.

For insulators, once the analytic part of the dynamical matrix at  $\mathbf{q}=\mathbf{0}$  as well as  $\epsilon^\infty$  and  $Z^*$  are available, it is possible to compute the LO-TO splitting of phonon frequencies at  $\mathbf{q}=\mathbf{0}$ , the low-frequency dielectric permittivity tensor, including the effect of ionic motion, and also the infrared reflectivity. These formulas will be derived in the present context, explicitly taking into account the anisotropy of  $\epsilon^\infty$  and  $Z^*$ .

When the dynamical matrices are known for a sufficiently fine grid of wave vectors in the irreducible Brillouin zone, one can generate easily the interatomic force constants (IFC's) using a Fourier transformation, as well as dynamical matrices and phonon frequencies interpolated for any wave vectors. The efficiency of these transformations can benefit from a separate, analytic, treatment of the long-ranged dipole-dipole interactions, made possible by the knowledge of  $\epsilon^\infty$  and  $Z^*$ . This treatment, in the case of isotropic  $\epsilon^\infty$  and  $Z^*$  is rather easy to formulate, while the generalization to anisotropic quantities was only recently proposed.<sup>17</sup> It has been used to compute the phonon band structure of SiO<sub>2</sub> stishovite,<sup>18–20,23,24</sup> SiO<sub>2</sub> quartz,<sup>17,19</sup> and to analyze the instabilities in cubic and rhombohedral BaTiO<sub>3</sub>.<sup>21</sup> A comprehensive description of this technique is presented here.

Once the complete phonon-band structure is available, one can compute the phonon density of states, some thermodynamical properties, and the atomic temperature factors. The corresponding formulas have been recalled in Ref. 19.

This paper is organized as follows. In Sec. II, we present the different generic formulas (stationary and nonstationary), that allow us to compute mixed second derivatives of the total energy from the knowledge of the first-order responses. In Sec. III, the second-order derivatives of the total energy with respect to atomic displacements are presented, within the plane-wave-pseudopotential implementation: they allow us to compute the dynamical matrices and phonon frequencies. The derivatives with respect to homogeneous electric fields, which allow us to compute dielectric permittivity tensors are developed in Sec. IV. Section V focuses on mixed derivatives with respect to atomic displacements and homogeneous electric fields: the Born effective charges. Then, we discuss the implementation of these equations (Sec. VI) and detail the sum rules to be checked for accuracy (Sec. VII). The two last sections of the paper build upon the results obtained in the previous sections: the computation of the low-frequency dielectric permittivity tensor and the associated LO-TO splitting (Sec. VIII), and the computation of interatomic force constants and phonon-band structures (Sec. IX). Some perspectives are presented in Sec. X. Appendix A describes briefly the computation of the dielectric permittivity tensors using different approximations: the ‘‘local density plus scissors’’ approach, the random phase approximation, and the neglect of local fields.

Throughout this paper, we use the atomic (Hartree) units. The notations and conventions are described in P1 (Ref. 3) and Ref. 25.

## II. MIXED DERIVATIVES OF THE TOTAL ENERGY

We consider two or more simultaneous Hermitian perturbations, combined in a Taylor-like expansion of the following type:

$$v_{\text{ext}}(\boldsymbol{\lambda}) = v_{\text{ext}}^{(0)} + \sum_{j_1} \lambda_{j_1} v_{\text{ext}}^{j_1} + \sum_{j_1 j_2} \lambda_{j_1} \lambda_{j_2} v_{\text{ext}}^{j_1 j_2} + \dots \quad (1)$$

(the indices  $j_1$  and  $j_2$  are not exponents, but label the different perturbations). The mixed derivative of the energy of the electronic system

$$E_{\text{el}}^{j_1 j_2} = \frac{1}{2} \frac{\partial^2 E_{\text{el}}}{\partial \lambda_{j_1} \partial \lambda_{j_2}} \quad (2)$$

is obtained in the local-density approximation to DFT from<sup>25,26</sup>

$$E_{\text{el}}^{j_1 j_2} = \frac{1}{2} (\tilde{E}_{\text{el}}^{j_1 j_2} + \tilde{E}_{\text{el}}^{j_2 j_1}), \quad (3)$$

with

$$\begin{aligned} & \tilde{E}_{\text{el}}^{j_1 j_2} \{ \psi^{(0)}, \psi^{j_1}, \psi^{j_2} \} \\ &= \sum_{\alpha} [ \langle \psi_{\alpha}^{j_1} | H^{(0)} - \epsilon_{\alpha}^{(0)} | \psi_{\alpha}^{j_2} \rangle + ( \langle \psi_{\alpha}^{j_1} | v_{\text{ext}}^{j_2} + v_{\text{Hxc0}}^{j_2} | \psi_{\alpha}^{(0)} \rangle \\ & \quad + \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{j_1} + v_{\text{Hxc0}}^{j_1} | \psi_{\alpha}^{j_2} \rangle ) + \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{j_1 j_2} | \psi_{\alpha}^{(0)} \rangle ] \\ & \quad + \frac{1}{2} \int \int \frac{\delta^2 E_{\text{Hxc}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Big|_{n^{(0)}} n^{j_1}(\mathbf{r}) n^{j_2}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ & \quad + \frac{1}{2} \frac{d^2 E_{\text{Hxc}}}{d\lambda_{j_1} d\lambda_{j_2}} \Big|_{n^{(0)}}. \end{aligned} \quad (4)$$

The derivatives of the wave functions and density with respect to one perturbation can be obtained from the technique explained in P1, or from the BGT technique,<sup>27–29</sup> applied to the case of that particular perturbation.

Supposing that the first-order wave functions and densities are not exact, then Eqs. (3) and (4) give an estimation of  $E_{\text{el}}^{j_1 j_2}$  that has an error proportional to the *product* of errors made in the first-order quantities for the first and second perturbations. It is a *stationary* expression. If these errors are small, their product will be much smaller. However, the sign of the error is undetermined, unlike for the variational expressions<sup>30,31</sup> presented in detail in P1 [see Eq. (13) of Ref. 3].

The following expressions do not have these interesting properties (their error is on the order of the errors made on the first-order wave functions or densities, and not their product), but allows us to evaluate  $E_{\text{el}}^{j_1 j_2}$  from the knowledge of the derivative of wave functions with respect to *only one* of the perturbations:

$$\begin{aligned}
E_{\text{el}}^{j_1 j_2} &= \frac{1}{2} \sum_{\alpha}^{\text{occ}} \left( \langle \psi_{\alpha}^{j_2} | v_{\text{ext}}^{j_1} + v_{\text{Hxc}0}^{j_1} | \psi_{\alpha}^{(0)} \rangle \right. \\
&\quad \left. + \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{j_1} + v_{\text{Hxc}0}^{j_1} | \psi_{\alpha}^{j_2} \rangle \right) + E_{\text{non-var}}^{j_1 j_2} \\
&= \sum_{\alpha}^{\text{occ}} \langle \psi_{\alpha}^{j_2} | v_{\text{ext}}^{j_1} + v_{\text{Hxc}0}^{j_1} | \psi_{\alpha}^{(0)} \rangle + E_{\text{non-var}}^{j_1 j_2} \\
&= \sum_{\alpha}^{\text{occ}} \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{j_1} + v_{\text{Hxc}0}^{j_1} | \psi_{\alpha}^{j_2} \rangle + E_{\text{non-var}}^{j_1 j_2}, \quad (5)
\end{aligned}$$

where

$$E_{\text{non-var}}^{j_1 j_2} = \sum_{\alpha}^{\text{occ}} \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{j_1 j_2} | \psi_{\alpha}^{(0)} \rangle + \frac{1}{2} \left. \frac{d^2 E_{\text{Hxc}}}{d\lambda_{j_1} d\lambda_{j_2}} \right|_{n(0)}. \quad (6)$$

In the expressions Eq. (5),  $|\psi_{\alpha}^{j_1}\rangle$  is not needed, while the computation of  $v_{\text{ext}}^{j_1}$  and  $v_{\text{Hxc}0}^{j_1}$  takes little time. Similar expressions that do not involve  $|\psi_{\alpha}^{j_2}\rangle$  but  $|\psi_{\alpha}^{j_1}\rangle$  are also available.

The time-reversal symmetry allows us to simplify further these expressions. For example,

$$E_{\text{el}}^{j_1 j_2} = \sum_{\alpha}^{\text{occ}} \langle \psi_{\alpha}^{j_2} | v_{\text{ext}}^{j_1} + v_{\text{Hxc}0}^{j_1} | \psi_{\alpha}^{(0)} \rangle + E_{\text{non-var}}^{j_1 j_2}. \quad (7)$$

These results Eqs. (5)–(7) are generalizations of the so-called ‘‘interchange theorem,’’<sup>12</sup> and will be exploited in the next three sections.<sup>13</sup> We will, moreover, suppose that we have been able to compute the first-order responses (i.e., changes in wave functions and densities) to the basic perturbations described previously.<sup>27,28,3,29</sup>

### III. DYNAMICAL MATRIX AND PHONON FREQUENCIES

The total energy of a periodic crystal with small lattice distortions from the equilibrium positions can be expressed as

$$\begin{aligned}
E_{\text{tot}}(\{\Delta \boldsymbol{\tau}\}) &= E_{\text{tot}}^{(0)} + \sum_{\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left( \frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right) \Delta \tau_{\kappa\alpha}^a \Delta \tau_{\kappa'\beta}^b \\
&\quad + \dots, \quad (8)
\end{aligned}$$

where  $\Delta \tau_{\kappa\alpha}^a$  is the displacement along direction  $\alpha$  of the atom  $\kappa$  in the cell labeled  $a$  (with vector  $\mathbf{R}_a$ ), from its equilibrium position  $\boldsymbol{\tau}_{\kappa}$ .

The matrix of the IFC’s is defined as

$$C_{\kappa\alpha, \kappa'\beta}(a, b) = \left( \frac{\partial^2 E_{\text{tot}}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right), \quad (9)$$

its Fourier transform is

$$\begin{aligned}
\tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) &= \frac{1}{N} \sum_{ab} C_{\kappa\alpha, \kappa'\beta}(a, b) e^{-i\mathbf{q} \cdot (\mathbf{R}_a - \mathbf{R}_b)} \\
&= \sum_b C_{\kappa\alpha, \kappa'\beta}(0, b) e^{i\mathbf{q} \cdot \mathbf{R}_b}, \quad (10)
\end{aligned}$$

where  $N$  is the number of cells of the crystal in the Born–von Karman approach.<sup>32</sup> It is connected to the dynamical matrix  $\tilde{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q})$  by

$$\tilde{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) / (M_{\kappa} M_{\kappa'})^{1/2}. \quad (11)$$

The squares of the phonon frequencies  $\omega_{m\mathbf{q}}^2$  at  $\mathbf{q}$  are obtained as eigenvalues of the dynamical matrix  $\tilde{D}_{\kappa\alpha, \kappa'\beta}(\mathbf{q})$ , or as solutions of the following generalized eigenvalue problem:

$$\sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) U_{m\mathbf{q}}(\kappa'\beta) = M_{\kappa} \omega_{m\mathbf{q}}^2 U_{m\mathbf{q}}(\kappa\alpha). \quad (12)$$

From Eqs. (8)–(10), the matrix  $\tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q})$  can be linked to the second-order derivative of the total energy with respect to collective atomic displacements of the type described in P1:

$$\tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) = 2E_{\text{tot}, -\mathbf{q}, \mathbf{q}}^{\tau_{\kappa\alpha}^* \tau_{\kappa'\beta}}. \quad (13)$$

$E_{\text{tot}}$  is made of a contribution from the electron system and a contribution from the electrostatic energy between ions. Similarly, the  $\tilde{C}$  matrix is split in two parts:

$$\tilde{C}_{\kappa\alpha, \kappa'\beta}(\mathbf{q}) = \tilde{C}_{\text{el}, \kappa\alpha, \kappa'\beta}(\mathbf{q}) + \tilde{C}_{\text{EW}, \kappa\alpha, \kappa'\beta}(\mathbf{q}). \quad (14)$$

The tools developed in P1 would allow us to build the diagonal part of the  $\tilde{C}_{\text{el}}(\mathbf{q})$  matrix, in a plane wave basis, with efficient separable pseudopotentials and a nonlinear exchange–correlation core correction. In the following subsections, these results are generalized to the nondiagonal part of this matrix, and the ion–ion term is also computed.

#### A. The electronic contribution

The use of the mixed derivative formulas, shown in Sec. II, gives the following stationary expression (see P1 for the notations):

$$\begin{aligned}
E_{\text{el},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}\{u^{(0)};u_{\mathbf{q}}^{\tau_{\kappa\alpha}},u_{\mathbf{q}}^{\tau_{\kappa'\beta}}\} &= \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left( \langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} | H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa'\beta}} \rangle + \langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} | v_{\text{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}^{\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \right. \\
&+ \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}+\mathbf{q}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa'\beta}} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \left. \right) d\mathbf{k} \\
&+ \frac{1}{2} \int_{\Omega_0} \{ [\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* [\bar{v}_{\text{loc},\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) + \bar{v}_{\text{xc0},\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r})] + \bar{n}_{\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) [\bar{v}_{\text{loc},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r}) + \bar{v}_{\text{xc0},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* \} d\mathbf{r} \\
&+ \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* \bar{n}_{\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) d\mathbf{r} + 2\pi\Omega_0 \sum_{\mathbf{G}} \frac{[\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{G})]^* \bar{n}_{\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} \\
&+ \int_{\Omega_0} (n^{(0)}(\mathbf{r}) v'_{\text{loc}}{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{r})) d\mathbf{r} + \frac{1}{2} \frac{d^2 E_{\text{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}} d\tau_{\kappa'\beta,\mathbf{q}}} \Big|_{n^{(0)}}. \tag{15}
\end{aligned}$$

The corresponding nonstationary expressions are

$$\begin{aligned}
E_{\text{el},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}\{u^{(0)};u_{\mathbf{q}}^{\tau_{\kappa\alpha}}\} &= \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left( \langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} | v_{\text{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}^{\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \right) d\mathbf{k} \\
&+ \frac{1}{2} \int_{\Omega_0} \{ [\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* [\bar{v}_{\text{loc},\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) + \bar{v}_{\text{xc0},\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r})] \} d\mathbf{r} \\
&+ \int_{\Omega_0} (n^{(0)}(\mathbf{r}) v'_{\text{loc}}{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{r})) d\mathbf{r} + \frac{1}{2} \frac{d^2 E_{\text{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}} d\tau_{\kappa'\beta,\mathbf{q}}} \Big|_{n^{(0)}} \tag{16}
\end{aligned}$$

and

$$\begin{aligned}
E_{\text{el},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}\{u^{(0)};u_{\mathbf{q}}^{\tau_{\kappa'\beta}}\} &= \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left( \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}+\mathbf{q}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa'\beta}} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \right) d\mathbf{k} \\
&+ \frac{1}{2} \int_{\Omega_0} \{ \bar{n}_{\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) [\bar{v}_{\text{loc},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r}) + \bar{v}_{\text{xc0},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* \} d\mathbf{r} \\
&+ \int_{\Omega_0} (n^{(0)}(\mathbf{r}) v'_{\text{loc}}{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{r})) d\mathbf{r} + \frac{1}{2} \frac{d^2 E_{\text{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}} d\tau_{\kappa'\beta,\mathbf{q}}} \Big|_{n^{(0)}}. \tag{17}
\end{aligned}$$

Using Eqs. (16) and (17), a whole column or a whole row of the dynamical matrix  $\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$  can be obtained from the knowledge of the first-order wave functions with respect to only one perturbation, either  $u_{\mathbf{q}}^{\tau_{\kappa\alpha}}$  or  $u_{\mathbf{q}}^{\tau_{\kappa'\beta}}$ , respectively.

The mixed second derivatives of the local and nonlocal potentials (given here in reciprocal space), and the second derivatives of the exchange-correlation functional are obtained from

$$\begin{aligned}
v'_{\text{loc}}{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{G}) &= -\frac{\delta_{\kappa\kappa'}}{2\Omega_0} G_{\alpha} G_{\beta} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\kappa}} v_{\kappa}^{\text{loc}}(\mathbf{G}) \quad \text{when } \mathbf{G} \neq \mathbf{0} \\
&= 0 \quad \text{when } \mathbf{G} = \mathbf{0}, \tag{18}
\end{aligned}$$

$$v'_{\text{sep},\mathbf{k},\mathbf{k}}{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{G},\mathbf{G}') = \frac{\delta_{\kappa\kappa'}}{2\Omega_0} \sum_{\mu} e_{\mu\kappa} \frac{\partial^2}{\partial\tau_{\kappa\alpha}\partial\tau_{\kappa'\beta}} \left[ \left( \sum_{\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{\tau}_{\kappa}} \zeta_{\mu\kappa}(\mathbf{k}+\mathbf{G}) \right) \left( \sum_{\mathbf{G}'} e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_{\kappa}} \zeta_{\mu\kappa}^*(\mathbf{k}+\mathbf{G}') \right) \right], \tag{19}$$

$$\frac{1}{2} \frac{d^2 E_{\text{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}} d\tau_{\kappa'\beta,\mathbf{q}}} \Big|_{n^{(0)}} = \delta_{\kappa\kappa'} \left( \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [\bar{n}_{c,\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* [\bar{n}_{c,\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r})] d\mathbf{r} + \int_{\Omega_0} v_{\text{xc}}(n^{(0)}(\mathbf{r})) \bar{n}_c{}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{r}) d\mathbf{r} \right), \tag{20}$$

with

$$\bar{n}_{c,0}^{\tau_{\kappa\alpha}\tau_{\kappa\beta}}(\mathbf{r}) = \sum_a \frac{1}{2} \frac{\partial^2}{\partial \tau_{\kappa,\alpha} \partial \tau_{\kappa,\beta}} n_{c,\kappa}(\mathbf{r} - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_a). \quad (21)$$

### B. The ion-ion contribution

Following the Ewald summation method,<sup>2</sup> the ion-ion contribution to the unperturbed total energy per unit cell (to which the residue of the cancellation of the divergences mentioned in Sec. IV B of P1 is added) is obtained as

$$\begin{aligned} E_{\text{Ew}} = & \frac{1}{2} \sum_{\kappa\kappa'} Z_{\kappa} Z_{\kappa'} \left[ \sum_{\mathbf{G} \neq \mathbf{0}} \frac{4\pi}{\Omega_0 G^2} e^{i\mathbf{G} \cdot (\boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'})} \exp\left(-\frac{G^2}{4\Lambda^2}\right) \right. \\ & \left. - \sum_a \Lambda e^{i\mathbf{q} \cdot \mathbf{R}_a} H(\Lambda d_{a,\kappa\kappa'}) - \frac{2}{\sqrt{\pi}} \Lambda \delta_{\kappa\kappa'} - \frac{\pi}{\Omega_0 \Lambda^2} \right] \\ & + \frac{1}{2} \sum_{\kappa\kappa'} \frac{Z_{\kappa} C_{\kappa'}}{\Omega_0}, \end{aligned} \quad (22)$$

with  $H(y) = \text{erfc}(y)/y$ ,  $d_{a,\kappa\kappa'} = |\mathbf{d}_{a,\kappa\kappa'}|$ , and  $\mathbf{d}_{a,\kappa\kappa'} = \mathbf{R}_a + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_{\kappa}$ . The parameter  $\Lambda$  can assume any value, and is adjusted to obtain the fastest convergence of both reciprocal- and real-space sums.

The contribution of the second derivative of the ion-ion energy to the matrix  $\bar{C}_{\text{Ew}}(\mathbf{q})$  can be computed following Ref. 33,

$$\tilde{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \bar{C}_{\text{Ew},\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0}). \quad (23)$$

$\bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q})$  can be split into three parts: a rapidly convergent sum in reciprocal space; a rapidly convergent sum in real space; and a rather simple residual contribution,<sup>34</sup>

$$\bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q})$$

$$\begin{aligned} & = Z_{\kappa} Z_{\kappa'} \left[ \sum_{\mathbf{G} \text{ with } \mathbf{K}=\mathbf{G}+\mathbf{q}} \frac{4\pi}{\Omega_0} \frac{K_{\alpha'} K_{\beta'}}{K^2} e^{i\mathbf{K} \cdot (\boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'})} \right. \\ & \quad \times \exp\left(-\frac{K^2}{4\Lambda^2}\right) - \sum_a \Lambda^3 e^{i\mathbf{q} \cdot \mathbf{R}_a} H_{\alpha'\beta'}^{\text{iso}}(\Lambda \mathbf{d}_{a,\kappa\kappa'}) \\ & \quad \left. - \frac{4}{3\sqrt{\pi}} \Lambda^3 \delta_{\kappa\kappa'} \right], \end{aligned} \quad (24)$$

with

$$\begin{aligned} H_{\alpha\beta}^{\text{iso}}(\mathbf{x}) = & \frac{x_{\alpha} x_{\beta}}{x^2} \left[ \frac{3}{x^3} \text{erfc}(x) + \frac{2}{\sqrt{\pi}} e^{-x^2} \left( \frac{3}{x^2} + 2 \right) \right] \\ & - \delta_{\alpha\beta} \left( \frac{\text{erfc}(x)}{x^3} + \frac{2}{\sqrt{\pi}} \frac{e^{-x^2}}{x^2} \right). \end{aligned} \quad (25)$$

The superscript ‘‘iso’’ is used in order to distinguish this quantity from its anisotropic generalization, needed in Sec. IX.

### C. The $\mathbf{q}=\mathbf{0}$ case

As mentioned in Sec. VII A of P1, the limit  $\mathbf{q} \rightarrow \mathbf{0}$  must be performed carefully. By the separate treatment of the electric field associated with phonons in this limit, one sees that a ‘‘bare’’  $\mathbf{q}=\mathbf{0}$  dynamical matrix must be computed, to which a ‘‘nonanalytical’’ part will be added, in order to reproduce correctly the  $\mathbf{q} \rightarrow \mathbf{0}$  behavior along different directions (see Sec. VIII B). The bare dynamical matrix is obtained from the following electronic contribution:

$$\begin{aligned} E_{\text{el},\mathbf{0},\mathbf{0}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}} \{u_{\mathbf{q}=\mathbf{0}}^{(0)}, u_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}, u_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}\} = & \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left( \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}} \rangle + \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \right. \\ & \left. + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \right) d\mathbf{k} \\ & + \frac{1}{2} \int_{\Omega_0} \{ [\bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* [\bar{v}_{\text{loc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}(\mathbf{r}) + \bar{v}_{\text{xc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}(\mathbf{r})] + \bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}(\mathbf{r}) [\bar{v}_{\text{loc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r}) + \bar{v}_{\text{xc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* \} d\mathbf{r} \\ & + \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [\bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* \bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}(\mathbf{r}) d\mathbf{r} + 2\pi\Omega_0 \sum_{\mathbf{G} \neq \mathbf{0}} \frac{[\bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{G})]^* \bar{n}_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa'\beta}}(\mathbf{G})}{|\mathbf{G}|^2} \\ & + \int_{\Omega_0} [n^{(0)}(\mathbf{r}) v_{\text{loc}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}(\mathbf{r})] d\mathbf{r} + \frac{1}{2} \frac{d^2 E_{\text{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}=\mathbf{0}} d\tau_{\kappa'\beta,\mathbf{q}=\mathbf{0}}} \Big|_{n^{(0)}}, \end{aligned} \quad (26)$$

combined with the modified ion-ion contribution

$$\begin{aligned} \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) &= Z_\kappa Z_{\kappa'} \left[ \sum_{\mathbf{G} \neq \mathbf{0}} \frac{4\pi}{\Omega_0} \frac{G_\alpha G_{\beta'}}{G^2} e^{i\mathbf{G} \cdot (\tau_\kappa - \tau_{\kappa'})} \right. \\ &\quad \times \exp\left(-\frac{G^2}{4\Lambda^2}\right) - \sum_a \Lambda^3 H_{\alpha'\beta'}^{\text{iso}}(\Lambda \mathbf{d}_{a,\kappa\kappa'}) \\ &\quad \left. - \frac{4}{3\sqrt{\pi}} \Lambda^3 \delta_{\kappa\kappa'} \right]. \end{aligned} \quad (27)$$

Note the absence of the  $\mathbf{G}=\mathbf{0}$  contributions in the Hartree contribution to Eq. (26) and in the first term of Eq. (27). Equation (26) is a stationary expression. Simpler, nonstationary expressions exist as well, and are similar to Eqs. (16) and (17).

#### IV. ELECTRONIC DIELECTRIC PERMITTIVITY TENSOR

For insulators, the dielectric permittivity tensor is the coefficient of proportionality between the macroscopic displacement field and the macroscopic electric field, in the linear regime:

$$\mathcal{D}_{\text{mac},\alpha} = \sum_\beta \epsilon_{\alpha\beta} \mathcal{E}_{\text{mac},\beta}. \quad (28)$$

It can be obtained as

$$\epsilon_{\alpha\beta} = \frac{\partial \mathcal{D}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\beta}} = \delta_{\alpha\beta} + 4\pi \frac{\partial \mathcal{P}_{\text{mac},\alpha}}{\partial \mathcal{E}_{\text{mac},\beta}}. \quad (29)$$

In general, the displacement  $\mathcal{D}_{\text{mac}}$ , or the polarization  $\mathcal{P}_{\text{mac}}$ , will include contributions from ionic displacements. In the present section, we examine only the contribution to the dielectric permittivity tensor from the electronic polarization, and for low frequencies of the applied field. This contribution is usually noted  $\epsilon_{\alpha\beta}^\infty$ . In Sec. VIII A, we will take care of the supplementary contributions from the ionic displacements.

We connect the dielectric permittivity tensor to the polarizability matrix, following Refs. 35 and 36. The polarizability of a solid describes the density response to an applied potential. In real space, one has

$$n^{(1)}(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') v_{\text{ext}}^{(1)}(\mathbf{r}') d\mathbf{r}'. \quad (30)$$

In the reciprocal space, for a periodic solid,

$$n_{\mathbf{q}}^{(1)}(\mathbf{G}) = \sum_{\mathbf{G}'} \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) v_{\text{ext},\mathbf{q}}^{(1)}(\mathbf{G}'). \quad (31)$$

Since the density is the first-order derivative of the total energy with respect to a change of potential,

$$n(\mathbf{r}) = \frac{\partial E_{\text{tot}}}{\partial v_{\text{ext}}(\mathbf{r})}, \quad (32)$$

the polarizability is related to the second-order derivative of the total energy:

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{\partial^2 E_{\text{tot}}}{\partial v_{\text{ext}}(\mathbf{r}) \partial v_{\text{ext}}(\mathbf{r}')}. \quad (33)$$

The connection with the dielectric permittivity tensor, following Ref. 35, proceeds through the definition of the inverse dielectric matrix, with

$$\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q}) = \delta_{\mathbf{G},\mathbf{G}'} + \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}), \quad (34)$$

and, for  $\mathbf{q}$  approaching to zero, one finds<sup>35</sup>

$$\sum_{\alpha\beta} \hat{q}_\alpha \epsilon_{\alpha\beta}^\infty \hat{q}_\beta = \frac{1}{\epsilon_{0,0}^{-1}(\mathbf{q})}, \quad (35)$$

where  $\hat{\mathbf{q}}$  is the unit vector in the direction of  $\mathbf{q}$ .

These theoretical definitions give the following approach to the electronic contribution to the dielectric permittivity tensor:<sup>37</sup>

$$\epsilon_{\alpha\beta}^\infty = \delta_{\alpha\beta} - \frac{4\pi}{\Omega_0} 2E_{\text{el}}^{\epsilon_\alpha^* \epsilon_\beta}, \quad (36)$$

where  $E_{\text{el}}^{\epsilon_\alpha^* \epsilon_\beta}$  is the mixed derivative generalization of the Eq. (76) of the preceding paper:<sup>3</sup>

$$\begin{aligned} E_{\text{el}}^{\epsilon_\alpha^* \epsilon_\beta} \{u^{(0)}; u^{\epsilon_\alpha}, u^{\epsilon_\beta}\} &= \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle u_{m\mathbf{k}}^{\epsilon_\alpha} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\epsilon_\beta} \rangle \\ &\quad + \langle u_{m\mathbf{k}}^{\epsilon_\alpha} | iu_{m\mathbf{k}}^{k\beta} \rangle + \langle iu_{m\mathbf{k}}^{k\alpha} | u_{m\mathbf{k}}^{\epsilon_\beta} \rangle d\mathbf{k} \\ &\quad + \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [n^{\epsilon_\alpha}(\mathbf{r})]^* n^{\epsilon_\beta}(\mathbf{r}) d\mathbf{r} \\ &\quad + 2\pi\Omega_0 \sum_{\mathbf{G} \neq \mathbf{0}} \frac{[n^{\epsilon_\alpha}(\mathbf{G})]^* n^{\epsilon_\beta}(\mathbf{G})}{|\mathbf{G}|^2}. \end{aligned} \quad (37)$$

A much simpler nonstationary formula also gives  $E_{\text{el}}^{\epsilon_\alpha^* \epsilon_\beta}$ :

$$E_{\text{el}}^{\epsilon_\alpha^* \epsilon_\beta} \{u^{(0)}; u^{\epsilon_\alpha}\} = \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle u_{m\mathbf{k}}^{\epsilon_\alpha} | iu_{m\mathbf{k}}^{k\beta} \rangle d\mathbf{k}. \quad (38)$$

By this last expression, the knowledge of  $u^{\epsilon_\alpha}$ , the first-order derivative of the wave functions with respect to an electric field along direction  $\alpha$ , allows us to compute the elements of the dielectric permittivity tensor  $\epsilon_{\alpha\beta}$ , for any value of  $\beta$ , *provided* that the derivative of the unperturbed wave function with respect to their wave vector along  $\beta$  is also known.

#### V. BORN EFFECTIVE CHARGES

For insulators, the Born effective charge tensor  $Z_{\kappa,\beta\alpha}^*$  (Ref. 38) is defined as the proportionality coefficient relating,

at linear order, the polarization per unit cell, created along the direction  $\beta$ , and the displacement along the direction  $\alpha$  of the atoms belonging to the sublattice  $\kappa$ , under the condition of a zero electric field. The same coefficient also describes the linear relation between the force on an atom and the macroscopic electric field, because both can be connected to the mixed second-order derivative of the energy with respect to atomic displacements and a macroscopic electric field:

$$Z_{\kappa,\beta\alpha}^* = \Omega_0 \frac{\partial \mathcal{P}_{\text{mac},\beta}}{\partial \tau_{\kappa\alpha}(\mathbf{q}=\mathbf{0})} = \frac{\partial F_{\kappa,\alpha}}{\partial \mathcal{E}_\beta}. \quad (39)$$

In the present formalism, this quantity can be obtained from

$$Z_{\kappa,\beta\alpha}^* = Z_\kappa \delta_{\beta\alpha} + \Delta Z_{\kappa,\beta\alpha}, \quad (40)$$

where  $Z_\kappa$  is the charge of the (pseudo-)ion  $\kappa$ , and the electronic screening  $\Delta Z_{\kappa,\beta\alpha}$  is

$$\begin{aligned} \Delta Z_{\kappa,\beta\alpha} = & 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\mathcal{E}_\beta} \rangle \right. \\ & + \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | i u_{m\mathbf{k}}^{k_\beta} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}'}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k}'}^{\mathcal{E}_\beta} \rangle d\mathbf{k} \\ & + \frac{1}{2} \int_{\Omega_0} \{ [v_{\text{loc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r}) + v_{\text{xc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})] [\bar{n}^{\mathcal{E}_\beta}(\mathbf{r})]^* \} d\mathbf{r} \\ & + \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [n_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* n^{\mathcal{E}_\beta}(\mathbf{r}) d\mathbf{r} \\ & \left. + 2\pi\Omega_0 \sum_{\mathbf{G} \neq \mathbf{0}} \frac{[n_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{G})]^* n^{\mathcal{E}_\beta}(\mathbf{G})}{|\mathbf{G}|^2} \right]. \quad (41) \end{aligned}$$

In this stationary expression, the basic ingredients are the first-order derivative of the wave functions with respect to a  $\mathbf{q}=\mathbf{0}$  collective displacement, and the first-order derivatives of the wave functions with respect to an electric field and to their wave vector. By contrast, in the following nonstationary expressions, more sensitive to wave function convergence errors, the derivative with respect to an electric field is not needed:

$$\Delta Z_{\kappa,\beta\alpha} = 2 \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | i u_{m\mathbf{k}}^{k_\beta} \rangle d\mathbf{k} \quad (42)$$

or only its knowledge is required:

$$\begin{aligned} \Delta Z_{\kappa,\beta\alpha} = & 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle u_{m\mathbf{k}}^{(0)} | v_{\text{sep},\mathbf{k},\mathbf{k}'}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k}'}^{\mathcal{E}_\beta} \rangle d\mathbf{k} \right. \\ & \left. + \frac{1}{2} \int_{\Omega_0} \{ [v_{\text{loc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r}) + v_{\text{xc},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})] [\bar{n}^{\mathcal{E}_\beta}(\mathbf{r})]^* \} d\mathbf{r} \right]. \quad (43) \end{aligned}$$

## VI. IMPLEMENTATION NOTES

The stationary formulas Eqs. (15), (26), (37), (41), (A1), (A3), and (A5), to be considered for the computation of the

second-order derivatives of the energy are all similar. This fact strongly reduces the time needed to implement this formalism. The similarity is also observed for the nonstationary formulas Eqs. (16), (17), (38), (42), and (43).

In order to compute the above-mentioned *stationary* expressions, one needs to know the first-order derivative of the wave functions with respect to the *two* perturbations defining the second-order derivative, and eventually the auxiliary derivative of the wave functions with respect to their wave vector. By contrast, for the *nonstationary* Eqs. (16), (17), (38), (42), and (43), the derivative of the wave functions with respect to only *one* of these perturbations is needed (and eventually the derivative with respect to the wave vector). This latter advantage can prove useful if, for example, the set of Born effective charges must be computed, while the dynamical matrix at  $\mathbf{q}=\mathbf{0}$  is not needed: even if the number of atoms on the unit cell is large, all the effective charges can be easily found from the knowledge of the first-order responses with respect to the electric field only.

The parallelization of these formulas is easily achieved by considering the mixed derivatives one at a time: all the  $N^2$  mixed derivatives with respect to the  $N$  perturbations can be computed in parallel, when all the first-order wave functions and densities have been computed. Also, the evaluation of the nonstationary expressions could be done at the end of the parallel computation of the first-order wave functions, using only one set of the first-order wave functions, since no information is required from the other processors.

In any case, the amount of computational work to evaluate these expressions is rather small compared with the work needed to obtain the first-order derivatives of the wave functions through the conjugate-gradient algorithm described in P1, or from the BGT procedure.<sup>27</sup>

## VII. SUM RULES

A few sum rules are available to monitor whether the calculation is well converged with respect to numerical parameters, like the number of plane waves, the sampling of the Brillouin zone, and the number of points of the exchange-correlation grid.

The first is the acoustic-sum rule:<sup>32</sup> the dynamical matrix at the zone center should admit the homogeneous translations of the solid as an eigenvector, with a zero eigenfrequency, because of the invariance of the total energy with respect to translation. From Eq. (12), this gives

$$\sum_{\kappa'} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) = 0. \quad (44)$$

Since the dynamical matrix is symmetric, the transpose relation is also valid. In the implementation of the formalism explained here, this relation is slightly broken because of the presence of the exchange-correlation grid in the real space, on which the exchange-correlation potential and energies are evaluated: if all the atoms are translated by a given vector, while the exchange-correlation grid is unchanged, the energies will slightly change, and induce the breaking of the sum rule. All of the other terms can be implemented in a translation-invariant way. If needed, this problem can be bypassed by the following simple modification:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{New}}(\mathbf{q}=\mathbf{0}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \tilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0}). \quad (45)$$

However, by this operation, the eigenfrequencies at  $\mathbf{q}=\mathbf{0}$  will change, and will not be the limit of the eigenfrequencies obtained by making  $\mathbf{q}\rightarrow\mathbf{0}$ , unless the other dynamical matrices, for  $\mathbf{q}\neq\mathbf{0}$ , are also corrected. The generalization of Eq. (45) for  $\mathbf{q}\neq\mathbf{0}$  will be discussed in Sec. IX.

The second sum rule guarantees that the charge neutrality is also fulfilled at the level of the Born effective charges. For every direction  $\alpha$  and  $\beta$ , one must have<sup>39</sup>

$$\sum_{\kappa} Z_{\kappa,\alpha\beta}^* = 0, \quad (46)$$

i.e., the sum of the Born effective charges of all atoms in one cell must vanish, element by element. This sum rule will be broken because of the finiteness of the number of plane waves or special points, or because of the discretization of the real-space integral (needed for the evaluation of the exchange-correlation energies and potentials). This problem could be corrected as follows. We define the mean effective charge excess per atom

$$\bar{Z}_{\alpha\beta}^* = \frac{1}{N_{\text{at}}} \sum_{\kappa} Z_{\kappa,\alpha\beta}^*. \quad (47)$$

This excess can be redistributed equally among the atoms as follows:<sup>27</sup>

$$Z_{\kappa,\alpha\beta}^{*,\text{New}} = Z_{\kappa,\alpha\beta}^* - \bar{Z}_{\alpha\beta}^*, \quad (48)$$

or can be redistributed among them in proportion to their mean electronic effective charge,

$$Z_{\kappa,\alpha\beta}^{*,\text{New}} = Z_{\kappa,\alpha\beta}^* - \frac{N_{\text{at}} \sum_{\alpha\beta} \Delta Z_{\kappa,\alpha\beta} \bar{Z}_{\alpha\beta}^*}{\sum_{\kappa,\alpha\beta} \Delta Z_{\kappa,\alpha\beta}}. \quad (49)$$

Other weighting schemes for the redistribution of this excess could be designed. Finally, in the case of the response to an electric field, one can also monitor the fulfillment of the  $f$ -sum rule, as described in Ref. 40.

We define the components of the mode-effective charge vector  $\mathbf{Z}_m^*$  as

$$Z_{m,\alpha}^* = \frac{\sum_{\kappa\beta} Z_{\kappa,\alpha\beta}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa\beta)}{(\sum_{\kappa\beta} [U_{m\mathbf{q}=\mathbf{0}}(\kappa\beta)]^* U_{m\mathbf{q}=\mathbf{0}}(\kappa\beta))^{1/2}}. \quad (53)$$

Note that with this definition, the mode-effective charge of a pure translation of the solid vanishes, unlike with the definition given in Ref. 41. The mode-oscillator strength tensor  $S_{m,\alpha\beta}$  is defined as

## VIII. LOW-FREQUENCY DIELECTRIC PERMITTIVITY TENSOR AND LO-TO SPLITTING

In this section, we discuss two phenomena that arise from the same basic mechanism: the coupling between the macroscopic electric field and the polarization associated with the  $\mathbf{q}\rightarrow\mathbf{0}$  atomic displacements. In the computation of the low-frequency (infrared) dielectric permittivity tensor, one has to include the response of the ions, whose motion will be triggered by the force due to the electric field, and whose polarization will be created by their displacement. The Born effective charges are involved in both mechanisms.

Also, in the computation of the long-wavelength limit of phonons, a macroscopic polarization and electric field will be associated with the atomic displacements. At the simplest level, the eigenfrequencies of phonons will depend on the direction along which the limit is taken as well as on the polarization of the phonon. This gives birth to the LO-TO splitting, and to the Lyddane-Sachs-Teller relation.<sup>32</sup> This phenomenon is also directly described by the Born effective charges.

### A. Low-frequency dielectric permittivity tensor

The macroscopic low-frequency (static) dielectric permittivity tensor  $\epsilon_{\alpha\beta}(\omega)$  is calculated by adding to  $\epsilon_{\alpha\beta}^{\infty}$  the ionic contribution, following Maradudin *et al.*<sup>33</sup> In our notations, we obtain

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_{\kappa\kappa'} \sum_{\alpha'\beta'} Z_{\kappa,\alpha\alpha'}^* [\tilde{C}(\mathbf{q}=\mathbf{0}) - M\omega^2]_{\kappa\alpha',\kappa'\beta'}^{-1} Z_{\kappa',\beta\beta'}^*. \quad (50)$$

Using the knowledge of the eigendisplacements  $U_{m\mathbf{q}}(\kappa\beta)$  of  $\tilde{C}(\mathbf{q}=\mathbf{0})$  from Eq. (12), normalized as

$$\sum_{\kappa\beta} M_{\kappa} [U_{m\mathbf{q}}(\kappa\beta)]^* U_{n\mathbf{q}}(\kappa\beta) = \delta_{mn}, \quad (51)$$

one derives

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{(\sum_{\kappa\alpha'} Z_{\kappa,\alpha\alpha'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa\alpha')) (\sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa'\beta'))}{\omega_m^2 - \omega^2}. \quad (52)$$

$$S_{m,\alpha\beta} = \left( \sum_{\kappa\alpha'} Z_{\kappa,\alpha\alpha'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa\alpha') \right) \times \left( \sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa'\beta') \right), \quad (54)$$

so that

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2 - \omega^2}. \quad (55)$$



One can also evaluate the value of the dielectric permittivity constant along the direction  $\hat{\mathbf{q}}$ , by

$$\begin{aligned}\epsilon_{\hat{\mathbf{q}}}(\omega) &= \sum_{\alpha\beta} \hat{q}_\alpha \epsilon_{\alpha\beta}(\omega) \hat{q}_\beta \\ &= \sum_{\alpha\beta} \hat{q}_\alpha \epsilon_{\alpha\beta}^\infty \hat{q}_\beta + \frac{4\pi}{\Omega_0} \sum_m \frac{\sum_{\alpha\beta} \hat{q}_\alpha S_{m,\alpha\beta} \hat{q}_\beta}{\omega_m^2 - \omega^2} \\ &= \sum_{\alpha\beta} \hat{q}_\alpha \epsilon_{\alpha\beta}^\infty \hat{q}_\beta \\ &\quad + \frac{4\pi}{\Omega_0} \sum_m \frac{|\mathbf{Z}_m^* \cdot \mathbf{q}|^2}{\omega_m^2 - \omega^2} \left( \sum_{\kappa\beta} [U_{m\mathbf{q}=\mathbf{0}}(\kappa\beta)]^* U_{n\mathbf{q}=\mathbf{0}}(\kappa\beta) \right).\end{aligned}\quad (56)$$

The reflectivity of optical waves normal to the surface, with their electric field along an optical axis of the crystal  $\mathbf{q}$ , is given by

$$R(\omega) = \left| \frac{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) - 1}{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) + 1} \right|^2. \quad (58)$$

More general expressions for the reflectivity may be found in classical textbooks.<sup>42</sup>

Equation (56) shows that, if the vector  $Z_m^*$  is perpendicular to  $\mathbf{q}$ , the mode  $m$  does not contribute to the dielectric permittivity constant along  $\mathbf{q}$ . For each mode  $m$ , there will thus be one direction along which the mode contributes to the dielectric permittivity constant, in which case it is referred to as longitudinal, while for the perpendicular directions, the mode will be referred to as transverse. We recover the usual distinction between LO and TO modes, confirmed by the following analysis of the  $\mathbf{q} \rightarrow \mathbf{0}$  limit of the dynamical matrix.

### B. LO-TO splitting

The macroscopic electric field that accompanies the collective atomic displacements at  $\mathbf{q}=\mathbf{0}$  can be treated separately, as mentioned in Sec. III C and in Sec. VII A of P1. After a careful treatment, one is able to recover the important result,<sup>39,27</sup>

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q} \rightarrow \mathbf{0}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) + \tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{NA}}(\mathbf{q} \rightarrow \mathbf{0}), \quad (59)$$

where the nonanalytical, direction-dependent term  $\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{NA}}(\mathbf{q} \rightarrow \mathbf{0})$  is given by

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{NA}}(\mathbf{q} \rightarrow \mathbf{0}) = \frac{4\pi}{\Omega_0} \frac{(\sum_{\gamma} q_\gamma Z_{\kappa,\gamma\alpha}^*)(\sum_{\gamma'} q_{\gamma'} Z_{\kappa',\gamma'\beta}^*)}{\sum_{\alpha\beta} q_\alpha \epsilon_{\alpha\beta}^\infty q_\beta}. \quad (60)$$

In general, the eigenvectors of the  $\tilde{C}(\mathbf{q} \rightarrow \mathbf{0})$  matrix will not be identical to those of the  $\tilde{C}(\mathbf{q}=\mathbf{0})$ . However, the modes that are transverse to the direction of  $\mathbf{q}$  are common to

both. Indeed, the NA term in Eq. (59) acts in a space that is perpendicular to the space spanned by the TO modes (for which  $\mathbf{Z}_m^* \cdot \mathbf{q} = 0$ ):

$$\sum_{\kappa'\beta} \left( \sum_{\gamma'} q_{\gamma'} Z_{\kappa',\gamma'\beta}^* \right) U_{m\mathbf{q}=\mathbf{0}}(\kappa'\beta) = 0. \quad (61)$$

Sometimes, symmetry constraints will be sufficient to guarantee that some LO eigendisplacements of  $\tilde{C}(\mathbf{q} \rightarrow \mathbf{0})$  will be identical to those of  $\tilde{C}(\mathbf{q}=\mathbf{0})$ , even if the eigenfrequencies are not the same. In this case, the following relationship, linking LO and TO modes, holds:

$$\omega_m^2(\mathbf{q} \rightarrow \mathbf{0}) = \omega_m^2(\mathbf{q}=\mathbf{0}) + \left( \frac{4\pi}{\Omega_0} \right) \frac{\sum_{\alpha\beta} q_\alpha S_{m,\alpha\beta} q_\beta}{\sum_{\alpha\beta} q_\alpha \epsilon_{\alpha\beta}^\infty q_\beta}. \quad (62)$$

By summing on all modes, and using the orthonormalization of eigenvectors Eq. (51), one gets

$$\begin{aligned}\sum_m \omega_m^2(\mathbf{q} \rightarrow \mathbf{0}) - \omega_m^2(\mathbf{q}=\mathbf{0}) \\ = \left( \frac{4\pi}{\Omega_0} \right) \sum_{\kappa} \frac{1}{M_{\kappa}} \frac{\sum_{\alpha\beta\gamma} q_\alpha Z_{\kappa,\alpha\beta}^* Z_{\kappa,\gamma\beta} q_\gamma}{\sum_{\alpha\beta} q_\alpha \epsilon_{\alpha\beta}^\infty q_\beta}.\end{aligned}\quad (63)$$

Finally, let us mention an interesting generalization of the Lyddane-Sachs-Teller relationship, linking dielectric properties and phonon frequencies, in the harmonic approximation:<sup>43</sup>

$$\frac{\sum_{\alpha\beta} q_\alpha \epsilon_{\alpha\beta}(\omega) q_\beta}{\sum_{\alpha\beta} q_\alpha \epsilon_{\alpha\beta}^\infty q_\beta} = \prod_m \frac{\omega_m^2(\mathbf{q} \rightarrow \mathbf{0}) - \omega^2}{\omega_m^2(\mathbf{q}=\mathbf{0}) - \omega^2}. \quad (64)$$

### IX. INTERATOMIC FORCE CONSTANTS, PHONON-BAND STRUCTURES

If the dynamical matrices were known everywhere in the Brillouin zone, the IFC's could be built by inverting Eq. (10), which defines the dynamical matrix from the IFC's:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{\text{BZ}} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_b} d\mathbf{q}. \quad (65)$$

Unfortunately, the dynamical matrices are not known everywhere in the Brillouin zone: for computational reasons they are only obtained for a small set of wave vectors. In this case, a numerical integration technique must be used to perform the integration appearing in Eq. (65). For that purpose, the use of a discrete Fourier transform is tempting: the dynamical matrices on a regular grid of  $(l \times m \times n)$  points in the Brillouin zone<sup>44</sup> will generate approximate IFC's in a large box, made of  $(l \times m \times n)$  periodic cells. Outside of this box, the IFC's, are supposed to vanish.<sup>45</sup>

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{1}{N} \sum_{\mathbf{q} \in \text{grid}(l \times m \times n)} \widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{R}_b} \text{ if } \mathbf{R}_b + \boldsymbol{\tau}_\kappa - \boldsymbol{\tau}'_{\kappa'} \in \text{box } (l \times m \times n)$$

$$= 0 \text{ if } \mathbf{R}_b + \boldsymbol{\tau}_\kappa - \boldsymbol{\tau}'_{\kappa'} \notin \text{box } (l \times m \times n). \quad (66)$$

The vanishing of the IFC's beyond some distance is intrinsic to this discrete Fourier transform technique. If the integrand in Eq. (65) were infinitely differentiable, then the IFC's would decrease exponentially fast, and this intrinsic limitation would not be a practical concern. However, for insulators with nonvanishing effective charges, Eqs. (59) and (60) shows that, close to  $\mathbf{q}=\mathbf{0}$ , the behavior of the dynamical matrices is strongly nonanalytical: it depends on the direction along which  $\mathbf{q}=\mathbf{0}$  is attained. In the real space, it can be seen that this nonanalytical behavior corresponds to long-ranged IFC's, with an average  $1/d^3$  decay ( $d$  being the distance between atoms), corresponding to dipole-dipole interactions.

Indeed, a dipole is created when an atom is displaced from its original position, and the proportionality coefficient between the dipole and the displacement is the Born effective charge. Even if the Born effective charge vanishes (this may be imposed by symmetry constraints, in elemental crystals), the atomic displacement will create a quadrupole or an octupole (the latter cannot be forbidden for symmetry reasons), with corresponding quadrupole-quadrupole  $1/d^5$  decay, or octupole-octupole  $1/d^7$  decay. However, the non-analyticity corresponding to the dipole-dipole interaction is the strongest, and in the context of the present paper, even the dipole-quadrupole interaction, with  $1/d^4$  decay, will be neglected. Thus, if the Born effective charges of all atoms in a crystal vanish, we consider that Eq. (66) will give an adequate description of the IFC's.

For metals, the electrostatic interactions are screened for sufficiently large distances. On the other hand, Friedel oscillations, due to the abrupt change of the occupation number at the Fermi level, cause a long-ranged decay of the IFC's. In a simple isotropic model, the decay of the IFC's is given by  $\cos 2k_F d / k_F^3 d^3$ , where  $k_F$  is the Fermi wave vector.<sup>46</sup> In more realistic situations, the decay will still be inversely proportional to the cube of the distance, but the oscillatory behavior will be more complex, and determined by the shape of the Fermi surface. In many practical applications, this long-range decay of metallic interatomic force constants in the real space, and the associated singularity in the reciprocal space are of little importance.

For insulators with nonvanishing Born effective charges, the nonanalytical behavior of the dynamical matrices close to  $\mathbf{q}=\mathbf{0}$  is perfectly defined from the knowledge of the Born effective charges and the electronic dielectric permittivity tensor, as shown in Eq. (60). This term cannot be neglected in practical applications. In a *homogeneous* material with an isotropic dielectric permittivity tensor  $\epsilon \delta_{\alpha\beta}$  (the superscript  $\infty$  of the  $\epsilon^\infty$  tensor will be omitted in the remainder of this paper, for brevity), the dipole-dipole interaction created by the displacement of atoms with (isotropic) charges  $Z_\kappa$  and  $Z'_\kappa$  will be described by the following force constants:<sup>27</sup>

$$C_{\kappa\alpha,\kappa'\beta}(0,a) = \frac{Z_\kappa Z'_\kappa}{\epsilon} \left( \frac{\delta_{\alpha\beta}}{d^3} - 3 \frac{d_\alpha d_\beta}{d^5} \right), \quad (67)$$

where

$$\mathbf{d} = \mathbf{R}_a + \boldsymbol{\tau}_{\kappa'} - \boldsymbol{\tau}_\kappa. \quad (68)$$

The Fourier transform of these force constants exhibits the following nonanalytical behavior:

$$\widetilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{NA}}(\mathbf{q} \rightarrow \mathbf{0}) = \frac{4\pi}{\Omega_0} \frac{Z_\kappa Z'_\kappa}{\epsilon} \frac{q_\alpha q_\beta}{q^2}. \quad (69)$$

Comparing the nonanalytical behaviors of Eqs. (60) and (69), it appears that, in the former, the  $\epsilon$  tensor is present as a metric in the reciprocal space. In order to reproduce the nonanalytical behavior of the dynamical matrix in the case of a material with anisotropic dielectric permittivity tensor and anisotropic effective-charge tensor, the following generalization of the dipole-dipole force constants Eq. (67) can be used, where the  $(\epsilon)^{-1}$  tensor is used as a metric in the real space:

$$C_{\kappa\alpha,\kappa'\beta}^{\text{DD}}(0,a) = \sum_{\alpha'\beta'} Z_{\kappa,\alpha\alpha'}^* Z_{\kappa',\beta\beta'}^* \left( \frac{(\epsilon^{-1})_{\alpha'\beta'}}{D^3} - 3 \frac{\Delta_{\alpha'} \Delta_{\beta'}}{D^5} \right) \times (\det \epsilon)^{-1/2}, \quad (70)$$

where  $\Delta_\alpha = \sum_\beta (\epsilon^{-1})_{\alpha\beta} d_\beta$  is the conjugate of the vector  $\mathbf{d}$  relating nuclei, while the norm of the latter in this metrics is  $D = \sqrt{\boldsymbol{\Delta} \cdot \mathbf{d}}$ . The supplementary factor  $(\det \epsilon)^{-1/2}$  is needed to get Eq. (60), and is connected to the Jacobian of the transformation between real and reciprocal space. The  $a=0$  and  $\kappa=\kappa'$  case is obtained by imposing the acoustic-sum rule on the first or the second indices. The contribution  $\widetilde{C}_{\text{Ew}}^{\text{DD}}$  of these dipole-dipole IFC's to the dynamical matrix can be calculated<sup>17</sup> using the Ewald summation technique as follows.<sup>47</sup>

$$(1) \quad \widetilde{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}) = \widehat{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \widehat{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}=\mathbf{0}). \quad (71)$$

(2) The effective charge tensors can be factored out from  $\widehat{C}_{\text{Ew}}^{\text{DD}}$ ,

$$\widehat{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}) = \sum_{\alpha'\beta'} Z_{\kappa,\alpha\alpha'}^* Z_{\kappa',\beta\beta'}^* \widetilde{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}). \quad (72)$$

(3)  $\bar{C}_{\text{Ew}}^{\text{DD}}$ , the remaining quantity, is split into three parts: a rapidly convergent sum in the reciprocal space; a rapidly convergent sum in the real space; and the limiting contribution (as usual in Ewald summation techniques),

$$\begin{aligned} \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}) &= \sum_{\mathbf{G} \text{ with } \mathbf{K}=\mathbf{G}+\mathbf{q}} \frac{4\pi}{\Omega_0} \frac{K_{\alpha'}K_{\beta'}}{\sum_{\gamma\gamma'} K_{\gamma}\epsilon_{\gamma\gamma'}K_{\gamma'}} \\ &\times e^{i\mathbf{K}\cdot(\boldsymbol{\tau}_{\kappa}-\boldsymbol{\tau}_{\kappa'})} \exp\left(-\sum_{\gamma\gamma'} \frac{K_{\gamma}\epsilon_{\gamma\gamma'}K_{\gamma'}}{4\Lambda^2}\right) \\ &- \sum_a \Lambda^3 e^{i\mathbf{q}\cdot\mathbf{R}_a} H_{\alpha'\beta'}(\Lambda\Delta,\Lambda D) \\ &\times (\det\boldsymbol{\epsilon})^{-1/2} \\ &- \frac{4}{3\sqrt{\pi}} \Lambda^3 \delta_{\kappa\kappa'} (\boldsymbol{\epsilon}^{-1})_{\alpha'\beta'} (\det\boldsymbol{\epsilon})^{-1/2}, \end{aligned} \quad (73)$$

with

$$\begin{aligned} \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}) &= \sum_{\mathbf{G} \text{ with } \mathbf{K}=\mathbf{G}+\mathbf{q}} \frac{4\pi}{\Omega_0} \frac{(\sum_{\alpha'} K_{\alpha'} Z_{\kappa,\alpha'}^*)(\sum_{\beta'} K_{\beta'} Z_{\kappa',\beta'}^*)}{\sum_{\gamma\gamma'} K_{\gamma}\epsilon_{\gamma\gamma'}K_{\gamma'}} e^{i\mathbf{K}\cdot(\boldsymbol{\tau}_{\kappa}-\boldsymbol{\tau}_{\kappa'})} \\ &- \delta_{\kappa\kappa'} \sum_{\kappa''} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{4\pi}{\Omega_0} \frac{(\sum_{\alpha'} G_{\alpha'} Z_{\kappa,\alpha'}^*)(\sum_{\beta'} G_{\beta'} Z_{\kappa'',\beta'}^*)}{\sum_{\gamma\gamma'} G_{\gamma}\epsilon_{\gamma\gamma'}G_{\gamma'}} e^{i\mathbf{G}\cdot(\boldsymbol{\tau}_{\kappa}-\boldsymbol{\tau}_{\kappa''})}. \end{aligned} \quad (75)$$

The nonanalytical behavior of this expression, for  $\mathbf{q}\rightarrow\mathbf{0}$ , is found to be Eq. (60), as expected.<sup>48</sup>

With the help of the dipole-dipole expressions for the dynamical matrix and the IFC's, we are now able to bypass the problems mentioned at the beginning of the present section. Indeed, the long-range behavior of the IFC's for real materials should not be different from the long-range behavior of the dipole-dipole IFC's characterized by the same  $Z^*$  and  $\boldsymbol{\epsilon}$ . So, we remove, from the dynamical matrices of real materials, determined on a homogeneous set of wave vectors in the Brillouin zone with the grid ( $l\times m\times n$ ), the dynamical matrices of the dipole-dipole system for the same wave vectors, shown in Eq. (75):

$$\bar{C}_{\kappa\alpha,\kappa'\beta}^{\text{SR}}(\mathbf{q}) = \bar{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}). \quad (76)$$

It is expected that their inverse Fourier transform, approximated by

$$\begin{aligned} C_{\kappa\alpha,\kappa'\beta}^{\text{SR}}(0,b) &= \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q} \in \text{grid}} \sum_{(l\times m\times n)} \bar{C}_{\kappa\alpha,\kappa'\beta}^{\text{SR}}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_b} \\ &\text{if } \mathbf{R}_b + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'} \in \text{box } (l\times m\times n) \\ &= 0 \text{ if } \mathbf{R}_b + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa'} \notin \text{box } (l\times m\times n) \end{aligned} \quad (77)$$

$$\begin{aligned} H_{\alpha\beta}(\mathbf{x},y) &= \frac{x_{\alpha}x_{\beta}}{y^2} \left[ \frac{3}{y^3} \text{erfc}(y) + \frac{2}{\sqrt{\pi}} e^{-y^2} \left( \frac{3}{y^2} + 2 \right) \right] \\ &- (\boldsymbol{\epsilon}^{-1})_{\alpha\beta} \left[ \frac{\text{erfc}(y)}{y^3} + \frac{2}{\sqrt{\pi}} \frac{e^{-y^2}}{y^2} \right]. \end{aligned} \quad (74)$$

This expression is invariant under the change of the parameter  $\Lambda$ , which can be adjusted to obtain the fastest convergence of both the reciprocal- and real-space sums.

If  $\Lambda$  is made equal to 0, the reciprocal-space sum in Eq. (73) vanishes, as well as the limiting contribution. The complementary error functions in Eq. (74) will have the value 1, while the contributions from the Gaussians in the same equation will vanish. Altogether, one finds that the dynamical matrices described by Eqs. (71)–(74) are indeed the Fourier transform of the IFC's, Eq. (70).

Alternatively, putting  $\Lambda$  to infinity allows us to make the real-space sum vanish. The limiting behavior is suppressed, due to Eq. (71), and finally one finds

decays like  $1/d^4$  or faster. The total IFC's, following this technique, is given by

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C_{\kappa\alpha,\kappa'\beta}^{\text{SR}}(0,b) + C_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(0,b), \quad (78)$$

where the short-ranged part is given by Eq. (77), and the dipole-dipole part is given by Eq. (70).

This technique not only allows us to get the IFC's, but also allows an easy interpolation of the dynamical matrix across the full Brillouin zone, with

$$\begin{aligned} \bar{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) &= \sum_{\mathbf{d}_b \in \text{box } (l\times m\times n)} C_{\kappa\alpha,\kappa'\beta}^{\text{SR}}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} \\ &+ \bar{C}_{\text{Ew},\kappa\alpha,\kappa'\beta}^{\text{DD}}(\mathbf{q}). \end{aligned} \quad (79)$$

Thus, it is possible to build the IFC's, and the full phonon spectrum, from the knowledge of the Born effective charge tensor, the dielectric permittivity tensor, and a few dynamical matrices, which sample adequately the whole Brillouin zone. Moreover, the use of the symmetries of the material (spatial operations of symmetries, as well as the time-reversal symmetry), allows us to sample the dynamical matrices only in the irreducible part of the Brillouin zone, with a considerable reduction of computing time (see Sec. VI).

As mentioned previously, the dynamical matrix at  $\mathbf{q}=\mathbf{0}$  computed from the formulas of Sec. III C does not satisfy

exactly the acoustic-sum rule. In term of the IFC's, the following relationship [Fourier transform of Eq. (44)], is not satisfied:

$$\sum_{\kappa'b} C_{\kappa\alpha,\kappa'\beta}(a,b) = 0. \quad (80)$$

This problem can be bypassed by generalizing, to every  $\mathbf{q}$  wave vector, the recipe of Eq. (45) for  $\mathbf{q}=\mathbf{0}$ .<sup>39,27</sup>

$$\widetilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{New}}(\mathbf{q}) = \widetilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \widetilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0}). \quad (81)$$

In this case, a wave-vector-independent, site-diagonal ( $\delta_{\kappa\kappa'}$ ) correction is applied to the dynamical matrices. In the real space, only the ‘‘on-site’’ IFC's are affected. For every  $a$  and  $\kappa$ ,

$$C_{\kappa\alpha,\kappa\beta}^{\text{New}}(a,a) = - \sum_{(\kappa'',b) \neq (\kappa,a)} C_{\kappa\alpha,\kappa''\beta}(a,b). \quad (82)$$

Other correction schemes are possible. At this stage, one is able to compute the full phonon-band structure, and use it to predict thermodynamical properties by occupying the phonon modes following the Bose-Einstein statistics.

## X. PERSPECTIVES

In the present paper, different equations that allow one to investigate the dynamical matrices, interatomic force constants, Born effective charge and dielectric permittivity tensor, have been presented in detail. Papers mentioned in the Introduction give examples of the application of this technique.

At the level of the second-order derivatives of the energy, these equations can be extended to cover more perturbations, especially those derived from the consideration of modifications of the unit cell, like the elastic constants, and the connected mixed derivatives, like the internal strain or the piezoelectricity. The extension to nonlinear properties is also possible, following the ideas contained in Refs. 25,11. The number of properties covered by such generalizations is very large: mode-Grüneisen parameters, nonlinear optical coefficients, phonon-phonon interaction, Raman scattering cross section, nonlinear piezoelectricity, nonlinear elasticity, etc.

The technique of Fourier interpolation of dynamical matrices takes advantage of the known asymptotic behavior of the IFC's. This technical point, combined with the advances described in P1,<sup>3</sup> have allowed us to obtain full phonon-band structures for moderately complex materials such as SiO<sub>2</sub>  $\alpha$  quartz and stishovite.<sup>18,17</sup>

A few thermodynamical properties, like constant-volume specific heats and entropy, have been derived from this knowledge, based upon the Bose-Einstein occupation of the phonon degrees of freedom. Other properties, like the thermal expansion or thermal conductivity, are also in the reach of this method.

## ACKNOWLEDGMENTS

The authors acknowledge interesting discussions with D. C. Allan, K. Rabe, Ph. Ghosez, and G.-M. Rignanese, as well

as with participants to the '96 CECAM workshop on Ab Initio Phonons, especially P. Giannozzi, H. Krakauer, and S. Baroni. We also thanks Ph. Ghosez and G.-M. Rignanese for a careful reading of the manuscript. X.G. thanks S. Savrasov for a copy of Ref. 29 prior to publication. X.G. acknowledges financial support from FNRS-Belgium and C.L. acknowledges support from Korea Science and Engineering Foundation Grant No. 961-0207-043-2, Ministry of Education Grant No. BSRI-96-2428, Center for Theoretical Physics in Seoul National University.

## APPENDIX A: THE COMPUTATION OF THE DIELECTRIC PERMITTIVITY TENSOR IN DIFFERENT APPROXIMATIONS

In Sec. IV, the computation of the dielectric permittivity tensor in the local-density approximation (LDA) was presented. Other approximate schemes are amenable to similar formulas.

### 1. Electronic dielectric permittivity tensor in the ‘‘local-density plus scissor’’ approximation

Because the agreement between the LDA dielectric permittivity tensor and the experiment was not satisfactory, Levine and Allan have introduced the scissor operator correction to the LDA.<sup>40</sup> This correction leads to an improved agreement between theory and experiment for many semiconductors, although some cases of negative results have been reported. The reasons of the partial failure of LDA have been discussed in Ref. 49.

The modifications of the equations appearing in Sec. VI B of the preceding paper,<sup>3</sup> needed to incorporate a scissor correction, are rather simple. Supposing that the gap between the valence and conduction states must be increased from  $E_g^{\text{LDA}}$  to  $E_g^{\text{LDA}} + \Delta$ , then Eq. (37) is slightly modified and becomes

$$\begin{aligned} E_{\text{SCI}}^{\varepsilon_\alpha^* \varepsilon_\beta} \{ u^{(0)}; u^{\text{SCI},\varepsilon_\alpha}, u^{\text{SCI},\varepsilon_\beta} \} \\ = \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s \langle \langle u_{m\mathbf{k}}^{\text{SCI},\varepsilon_\alpha} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} + \Delta | u_{m\mathbf{k}}^{\text{SCI},\varepsilon_\beta} \rangle \rangle \\ + \langle u_{m\mathbf{k}}^{\text{SCI},\varepsilon_\alpha} | i u_{m\mathbf{k}}^{k\beta} \rangle + \langle i u_{m\mathbf{k}}^{k\alpha} | u_{m\mathbf{k}}^{\text{SCI},\varepsilon_\beta} \rangle d\mathbf{k} \\ + \frac{1}{2} \int_{\Omega_0} \frac{dv_{\text{xc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [n_{\text{SCI}}^{\varepsilon_\alpha}(\mathbf{r})]^* n_{\text{SCI}}^{\varepsilon_\beta}(\mathbf{r}) d\mathbf{r} \\ + 2\pi\Omega_0 \sum_{\mathbf{G} \neq \mathbf{0}} \frac{[n_{\text{SCI}}^{\varepsilon_\alpha}(\mathbf{G})]^* n_{\text{SCI}}^{\varepsilon_\beta}(\mathbf{G})}{|\mathbf{G}|^2}. \quad (\text{A1}) \end{aligned}$$

The minimization problem appearing in Sec. VI B of the preceding paper<sup>3</sup> is to be replaced by Eq. (A1), where  $\beta = \alpha$ . The associated Euler-Lagrange equation is

$$\begin{aligned} P_{c,\mathbf{k}} (H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)} + \Delta) P_{c,\mathbf{k}} | u_{m,\mathbf{k}}^{\text{SCI},\varepsilon_\alpha} \rangle \\ = - P_{c,\mathbf{k}} \left( i \frac{\partial}{\partial k_\alpha} + v_{\text{H}}^{\text{SCI},\varepsilon_\alpha} + v_{\text{xc}}^{\text{SCI},\varepsilon_\alpha} \right) | u_{m,\mathbf{k}}^{(0)} \rangle. \quad (\text{A2}) \end{aligned}$$

The other equations are unchanged, except for the replacement of  $|u_{m,\mathbf{k}}^{\varepsilon_\alpha}\rangle$  by  $|u_{m,\mathbf{k}}^{\text{SCI},\varepsilon_\alpha}\rangle$ ,  $n^{\varepsilon_\alpha}$  by  $n_{\text{SCI}}^{\varepsilon_\alpha}$ ,  $v_{\text{H}}^{\varepsilon_\alpha}$  by  $v_{\text{H}}^{\text{SCI},\varepsilon_\alpha}$ , and  $v_{\text{xc}}^{\varepsilon_\alpha}$  by  $v_{\text{xc}}^{\text{SCI},\varepsilon_\alpha}$ .

Because of the positive definiteness of the term governed by  $\Delta$  in the quadratic form underlying  $E_{\text{el}}^{\varepsilon_\alpha^* \varepsilon_\alpha}$ , it is straightforward that if  $\Delta$  is positive, the dielectric permittivity constant along any direction is *always* smaller in the ‘‘local-density plus scissor’’ approximation than in the local-density approximation.

## 2. Electronic dielectric permittivity tensor in the random phase approximation

In the random phase approximation (RPA), described in the classical papers by Adler and Wiser,<sup>50</sup> one neglects the exchange and correlation effects. In the present variational approach, the RPA dielectric permittivity tensor is obtained by the following modifications to the LDA expressions Eq. (37):

$$\begin{aligned} E_{\text{RPA}}^{\varepsilon_\alpha^* \varepsilon_\beta} \{u^{(0)}; u^{\text{RPA},\varepsilon_\alpha}, u^{\text{RPA},\varepsilon_\beta}\} \\ = \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s(\langle u_{m\mathbf{k}}^{\text{RPA},\varepsilon_\alpha} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\text{RPA},\varepsilon_\beta} \rangle \\ + \langle u_{m\mathbf{k}}^{\text{RPA},\varepsilon_\alpha} | iu_{m\mathbf{k}}^{k_\beta} \rangle + \langle iu_{m\mathbf{k}}^{k_\alpha} | u_{m\mathbf{k}}^{\text{RPA},\varepsilon_\beta} \rangle) d\mathbf{k} \\ + 2\pi\Omega_0 \sum_{\mathbf{G} \neq 0} \frac{[n_{\text{RPA}}^{\varepsilon_\alpha}(\mathbf{G})]^* n_{\text{RPA}}^{\varepsilon_\beta}(\mathbf{G})}{|\mathbf{G}|^2}, \end{aligned} \quad (\text{A3})$$

where the first-order  $u^{\text{RPA},\varepsilon_\alpha}$  are to be obtained from the minimization of the same expression, for  $\beta = \alpha$ , and the associated Euler-Lagrange equation is

$$\begin{aligned} P_{c,\mathbf{k}}(H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)}) P_{c,\mathbf{k}} |u_{m,\mathbf{k}}^{\text{SCI},\varepsilon_\alpha}\rangle \\ = -P_{c,\mathbf{k}} \left( i \frac{\partial}{\partial k_\alpha} + v_{\text{H}}^{\text{RPA},\varepsilon_\alpha} \right) |u_{m,\mathbf{k}}^{(0)}\rangle. \end{aligned} \quad (\text{A4})$$

The other equations are unchanged, except for the replacement of  $|u_{m,\mathbf{k}}^{\varepsilon_\alpha}\rangle$  by  $|u_{m,\mathbf{k}}^{\text{RPA},\varepsilon_\alpha}\rangle$ ,  $n^{\varepsilon_\alpha}$  by  $n_{\text{RPA}}^{\varepsilon_\alpha}$ , and  $v_{\text{H}}^{\varepsilon_\alpha}$  by  $v_{\text{H}}^{\text{RPA},\varepsilon_\alpha}$ , respectively.

Because the contribution of the LDA exchange-correlation term to the quadratic form underlying  $E_{\text{el}}^{\varepsilon_\alpha^* \varepsilon_\alpha}$  is negative definite, it is straightforward that the dielectric permittivity constant along any direction is *always* smaller in the RPA than in the LDA.

## 3. Electronic dielectric permittivity tensor without local fields

It is also possible to neglect the effect of all local fields, not only those connected to the exchange-correlation effects. This approach<sup>51</sup> has been also heavily used. In the variational density-functional perturbation theory (DFPT), the computations performed in this approximation rely on the following modifications to the LDA expressions Eq. (37):

$$\begin{aligned} E_{00}^{\varepsilon_\alpha^* \varepsilon_\beta} \{u^{(0)}; u^{00,\varepsilon_\alpha}, u^{00,\varepsilon_\beta}\} \\ = \frac{\Omega_0}{(2\pi)^3} \int_{\text{BZ}} \sum_m^{\text{occ}} s(\langle u_{m\mathbf{k}}^{00,\varepsilon_\alpha} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{00,\varepsilon_\beta} \rangle \\ + \langle u_{m\mathbf{k}}^{00,\varepsilon_\alpha} | iu_{m\mathbf{k}}^{k_\beta} \rangle + \langle iu_{m\mathbf{k}}^{k_\alpha} | u_{m\mathbf{k}}^{00,\varepsilon_\beta} \rangle) d\mathbf{k}, \end{aligned} \quad (\text{A5})$$

where the first-order wave functions  $u^{00,\varepsilon_\alpha}$  are to be obtained from the minimization of the same expression, for  $\beta = \alpha$ , and the associated Euler-Lagrange equation is

$$P_{c,\mathbf{k}}(H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)}) P_{c,\mathbf{k}} |u_{m,\mathbf{k}}^{00,\varepsilon_\alpha}\rangle = -P_{c,\mathbf{k}} \left( i \frac{\partial}{\partial k_\alpha} \right) |u_{m,\mathbf{k}}^{(0)}\rangle. \quad (\text{A6})$$

The other equations are unchanged, except for the replacement of  $|u_{m,\mathbf{k}}^{\varepsilon_\alpha}\rangle$  by  $|u_{m,\mathbf{k}}^{00,\varepsilon_\alpha}\rangle$ .

Because the contribution of the Hartree term to the quadratic form underlying  $E_{\text{el}}^{\varepsilon_\alpha^* \varepsilon_\alpha}$  is positive definite and usually larger than the negative-definite exchange-correlation contribution (this is not always true, see Ref. 52), it is *expected* that the dielectric permittivity constant along any direction is larger in the approximation without local fields than in the LDA.

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