

Density-functional approach to nonlinear-response coefficients of solids

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We propose a general scheme, within the density-functional theory, for an accurate computation of a large class of nonlinear-response coefficients of solids. The scheme is applicable to all kinds of adiabatic perturbations of the crystal ground state, such as the application of mechanical strains, static electric fields of any wavelength, or individual atomic displacements, and allows the study of coefficients which describe anharmonicities or coupling of simultaneously applied disturbances. Total-energy changes as a function of the perturbation wavelength, as needed to obtain phonon group velocities, can also be considered. The formalism, which avoids the use of supercells and large-matrix inversions, contains as a special case the treatment of linear-response coefficients recently suggested by Baroni, Giannozzi, and Testa. The central ingredient in our scheme is an efficient use of the “ $2n+1$ ” theorem of the perturbation theory, which allows us to obtain the third-order derivatives of the total energy by using only byproducts of a first-order perturbation calculation.

I. INTRODUCTION

The density-functional approach^{1,2} underlies many present theoretical studies of crystalline solids. While limited to the study of electronic ground states, it has been successfully applied to the evaluation of the total energy of even rather complex atomic aggregates, with or without an applied external field.

The study of response coefficients of solids (or derivatives of total energy) has often been performed, in the framework of density-functional theory (DFT), through a brute-force finite-difference method: a small modification of the atomic coordinates or of the intensity of the applied field, and iterations of the density toward an accurate self-consistency in the perturbed geometry, allows one, in principle, to obtain the tiny total-energy differences needed to assess the value of the response coefficients. This is not always easily achieved in practice; the calculation of most phonon frequencies in the Brillouin zone, for instance, will require the use of prohibitively large supercells, as the small-size supercells carry information on only a few discretely distributed wavelengths.³⁻¹¹

Another approach aims at performing the derivation by analytical means; a first derivative of the total energy can be reached by applying the Hellman-Feynman theorem¹² or the stress theorem.¹³ For computing the dielectric tensor a density-functional-formalism version of the analytical Adler-Wiser random-phase approximation (RPA) formula was written, but this approach shows the disadvantage of requiring the inversion of large matrices.¹⁴⁻¹⁶ The advantages sought in such methods are

usually to escape from restriction on wavelengths, to avoid the need for supercell construction, and to generate fewer computational uncertainties. Analytical methods have, however, to cope with the loss of stability found in the direct evaluation of the total energy by variational methods.⁷

Baroni, Giannozzi, and Testa (BGT) recently proposed a scheme which combines the advantages of both methods, and used it for assessing phonon frequencies and dielectric constants,¹⁸ as well as elastic constants.¹⁹ The same approach should also be efficient on problems involving piezoelectric tensors, and with sufficient Brillouin-zone sampling of phonon frequencies, should allow the study of thermal properties involving vibrational degrees of freedom: internal energy, entropy, and thermal capacity. The BGT method is particularly efficient for well-defined wavelength perturbations, as they can be mapped onto an unperturbed periodic problem, with the original small primitive cell.

One byproduct of the BGT method is, for each point in the Brillouin zone, the set of first derivatives of the eigenfunctions. It has been known for a long time²⁰ that, in the case of a one-body problem, the first $2n+1$ derivatives of the eigenenergies are directly related to the first n derivatives of the corresponding eigenfunction. The extension of this result to a many-body problem is not straightforward; it has been considered in the Hartree-Fock scheme, as well as within a general variational formulation, with explicit formulas up to the fifth order.²⁰ In what follows, we will prove the corresponding theorem for DFT, with no local-density approximation and give explicit general formulas without restriction on order.

Using this result, we are able to find expressions for the third-order nonlinear-response coefficients with a computational effort virtually identical to that required by the second-order-coefficients calculation via the BGT method. Third-order coefficients are related to the following physical properties: phonon-phonon coupling, the electro-optical effect (nonlinear electrical susceptibility), nonlinear elasticity, change in the phonon frequencies with applied stress (Grüneisen parameters) or applied electromagnetic fields (Raman cross section), and photoelastic and electrostrictive effects. The thermal properties obtained at the same perturbation order by integration over phonon degrees of freedom are phonon-limited thermal conductivity, thermal expansion, and pyroelectricity.^{21,22} Another important outcome of this scheme lies in the possibility of analytic derivation of the second-order coefficients with respect to the perturbation wavelength. This allows a closer interpolation of the phonon spectrum in the whole Brillouin zone or the calculation of the phonon group velocity.

The fourth- and fifth-order coefficients are obtained with the second derivatives of each eigenfunction. Their range of application is also very wide (combination of strains, static electric fields or phonons of any wavelength, and derivation with respect to this wavelength: the Kerr effect, or four-phonon coupling constants, for example). It is worth noting that recent studies, using finite difference methods, have already dealt with third or fourth derivatives of energy.⁷⁻¹¹

II. "2n + 1" THEOREM IN THE DENSITY-FUNCTIONAL THEORY

The total energy, in the Born-Oppenheimer approximation, can be split into the nuclei (or ionic) Coulomb repulsion, and the stabilizing electronic energy.²³ The derivatives of the Madelung term are easily found by Ewald summation techniques (see Maradudin *et al.*²⁴) while the electronic contribution requires more attention.

In the framework of the DFT, the ground-state electronic energy is given by⁴

$$E_{el} = \sum_{\alpha} \varepsilon_{\alpha} + \left[E_I[n] - \int \frac{\delta E_I[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r} \right], \quad (1)$$

where E_I is the interaction energy and the ε_{α} are the energies of the Kohn-Sham orbitals, determined self-consistently by the Kohn-Sham equations:

$$H = T + v_{\text{ext}} + \frac{\delta E_I[n]}{\delta n(\mathbf{r})}, \quad (2)$$

$$H|\Psi_{\alpha}\rangle = \varepsilon_{\alpha}|\Psi_{\alpha}\rangle, \quad \langle\Psi_{\alpha}|\Psi_{\alpha}\rangle = 1 \quad (3)$$

$$n(\mathbf{r}) = \sum_{\alpha} \Psi_{\alpha}^*(\mathbf{r})\Psi_{\alpha}(\mathbf{r}). \quad (4)$$

In Eqs. (1) and (4), the summation on α extends over the occupied orbitals only. The interaction functional $E_I[n]$ is usually written as the sum of a Hartree energy and an exchange-correlation contribution (eventually considered in the local-density approximation).² We now perform the perturbative development of those quantities and equations as a function of the small parameter λ :

$$H = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)} + \dots \quad (5)$$

The equation of Schrödinger and normalization condition Eq. (3) become, at order i ,

$$\sum_{j=0}^i (H - \varepsilon_{\alpha})^{(j)} |\Psi_{\alpha}^{(i-j)}\rangle = 0, \quad (6)$$

$$\sum_{j=0}^i \langle\Psi_{\alpha}^{(j)}|\Psi_{\alpha}^{(i-j)}\rangle = 0, \quad i \neq 0. \quad (7)$$

Before proceeding to the expansion of Eqs. (2) and (4), let us write and prove the $2n + 1$ theorem in our notations for the one-particle eigenvalue equation: premultiplying Eq. (3) by the eigenfunction Ψ_{α} , we have the identity

$$\langle\Psi_{\alpha}|(H - \varepsilon_{\alpha})|\Psi_{\alpha}\rangle = 0, \quad (8)$$

which translates into the perturbation expansion as

$$\sum_{j=0}^i \sum_{k=0}^i \langle\Psi_{\alpha}^{(j)}|(H - \varepsilon_{\alpha})^{(i-j-k)}|\Psi_{\alpha}^{(k)}\rangle = 0. \quad (9)$$

From this expression we can form triangular tables similar to the following one, associated with third-order terms:

$$\begin{aligned} 0 = & \langle\Psi_{\alpha}^{(3)}|H^{(0)} - \varepsilon_{\alpha}^{(0)}|\Psi_{\alpha}^{(0)}\rangle \\ & + \langle\Psi_{\alpha}^{(2)}|H^{(1)} - \varepsilon_{\alpha}^{(1)}|\Psi_{\alpha}^{(0)}\rangle + \langle\Psi_{\alpha}^{(2)}|H^{(0)} - \varepsilon_{\alpha}^{(0)}|\Psi_{\alpha}^{(1)}\rangle \\ & + \langle\Psi_{\alpha}^{(1)}|H^{(2)} - \varepsilon_{\alpha}^{(2)}|\Psi_{\alpha}^{(0)}\rangle + \langle\Psi_{\alpha}^{(1)}|H^{(1)} - \varepsilon_{\alpha}^{(1)}|\Psi_{\alpha}^{(1)}\rangle + \langle\Psi_{\alpha}^{(1)}|H^{(0)} - \varepsilon_{\alpha}^{(0)}|\Psi_{\alpha}^{(2)}\rangle \\ & + \langle\Psi_{\alpha}^{(0)}|H^{(3)} - \varepsilon_{\alpha}^{(3)}|\Psi_{\alpha}^{(0)}\rangle + \langle\Psi_{\alpha}^{(0)}|H^{(2)} - \varepsilon_{\alpha}^{(2)}|\Psi_{\alpha}^{(1)}\rangle + \langle\Psi_{\alpha}^{(0)}|H^{(1)} - \varepsilon_{\alpha}^{(1)}|\Psi_{\alpha}^{(2)}\rangle + \langle\Psi_{\alpha}^{(0)}|H^{(0)} - \varepsilon_{\alpha}^{(0)}|\Psi_{\alpha}^{(3)}\rangle. \end{aligned} \quad (10)$$

Equation (6) shows that the sum of the terms on any horizontal line vanishes, and the complex conjugate of the same equation gives the same result, for any vertical line. Moreover, Eq. (7) can be used to perform partial summations along diagonal lines. We eliminate the two first lines as zeros, and, similarly, the two last columns. $\varepsilon_{\alpha}^{(2)}$ disappears from the equation, as a result of condition (7). We finally isolate $\varepsilon_{\alpha}^{(3)}$:

$$\begin{aligned} \varepsilon_{\alpha}^{(3)} = & \langle\Psi_{\alpha}^{(1)}|H^{(2)}|\Psi_{\alpha}^{(0)}\rangle + \langle\Psi_{\alpha}^{(1)}|H^{(1)} - \varepsilon_{\alpha}^{(1)}|\Psi_{\alpha}^{(1)}\rangle \\ & + \langle\Psi_{\alpha}^{(0)}|H^{(3)}|\Psi_{\alpha}^{(0)}\rangle + \langle\Psi_{\alpha}^{(0)}|H^{(2)}|\Psi_{\alpha}^{(1)}\rangle. \end{aligned} \quad (11)$$

For a *non-self-consistent* perturbative Hamiltonian, known at any order, the knowledge of the unperturbed and first-order eigenfunctions gives us the third-order eigenenergy. This is the $2n + 1$ theorem for the case

$n = 1$. Using the same steps with the $(2n + 1)$ th triangular table easily shows that the first n perturbative eigenfunctions are sufficient to produce the first $2n + 1$ eigenenergy derivatives.²⁵ The Appendix states general formulas valid for any order.

In the *many-body* case, $H^{(i)}$ functionally depends on all $n^{(j)}$ for $j \leq i$ which, in turn, come from eigenfunctions of every order up to and including order i . These wave functions are found from Eq. (9) which requires knowledge of the Hamiltonian to order i .²⁶

$$H^{(i)} = v_{\text{ext}}^{(i)} + \left[\frac{\delta E_I \left[n^{(0)} + \sum_{j=1}^i \lambda^j n^{(j)} \right]}{\delta n(\mathbf{r})} \right]^{(i)}, \quad (12)$$

$$n^{(i)}(\mathbf{r}) = \sum_{\alpha} \sum_{j=0}^i \Psi_{\alpha}^{(j)*}(\mathbf{r}) \Psi_{\alpha}^{(i-j)}(\mathbf{r}). \quad (13)$$

It is not possible to obtain each particular perturbative *one-electron* energy to order $2n + 1$ in the many-body problem (except for the trivial case of noninteracting particles) without the resolution of the whole problem at order $2n + 1$. By contrast, as we shall now prove, an exact cancellation of terms happens in the *total-energy* expression, which restores the $2n + 1$ theorem for this quantity. We refer to Appendix A for the all-order formulas, and establish here the result for the third-order derivative of total energy.

We first treat the sum of third-order eigenvalues in Eq. (1), using Eq. (11), and develop the interaction term in Eq. (12) by Taylor expansion:

$$\begin{aligned} \sum_{\alpha} \varepsilon_{\alpha}^{(3)} = & \sum_{\alpha} \left(\langle \Psi_{\alpha}^{(1)} | v_{\text{ext}}^{(2)} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(1)} | H^{(1)} - \varepsilon_{\alpha}^{(1)} | \Psi_{\alpha}^{(1)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{(3)} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{(2)} | \Psi_{\alpha}^{(1)} \rangle \right) \\ & + \int \int \frac{\delta^2 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(2)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \int \int \int \frac{\delta^3 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') n^{(1)}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \\ & + \int \int \frac{\delta^2 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(3)}(\mathbf{r}) n^{(0)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \int \int \int \frac{\delta^3 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{(1)}(\mathbf{r}) n^{(2)}(\mathbf{r}') n^{(0)}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \\ & + \frac{1}{6} \int \int \int \int \frac{\delta^4 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'') \delta n(\mathbf{r}''')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') n^{(1)}(\mathbf{r}'') n^{(0)}(\mathbf{r}''') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''. \end{aligned} \quad (14)$$

The procedure is similar for the second part of Eq. (1):

$$\begin{aligned} & \left[E_I[n] - \int \frac{\delta E_I[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r} \right]^{(3)} \\ & = - \left[\int \int \frac{\delta^2 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(2)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \right. \\ & \quad + \frac{1}{3} \int \int \int \frac{\delta^3 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') n^{(1)}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \\ & \quad + \int \int \frac{\delta^2 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(3)}(\mathbf{r}) n^{(0)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \int \int \int \frac{\delta^3 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{(1)}(\mathbf{r}) n^{(2)}(\mathbf{r}') n^{(0)}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \\ & \quad \left. + \frac{1}{6} \int \int \int \int \frac{\delta^4 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'') \delta n(\mathbf{r}''')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') n^{(1)}(\mathbf{r}'') n^{(0)}(\mathbf{r}''') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \right]. \end{aligned} \quad (15)$$

We finally obtain

$$\begin{aligned} E^{(3)} = & \sum_{\alpha} \left(\langle \Psi_{\alpha}^{(1)} | v_{\text{ext}}^{(2)} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(1)} | H^{(1)} - \varepsilon_{\alpha}^{(1)} | \Psi_{\alpha}^{(1)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{(3)} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{(2)} | \Psi_{\alpha}^{(1)} \rangle \right) \\ & + \frac{1}{6} \int \int \int \frac{\delta^3 E_I [n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') n^{(1)}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' , \end{aligned} \quad (16)$$

an expression which shows no explicit dependence on the perturbative corrections to the particle density and one-electron wave functions, except the first-order terms. This expression will be somewhat simplified if, to begin with, the potential has no second- or third-order contribution. This is often the case: the external potential arising from the application of an electric perturbation, for

instance, depends only linearly on the applied electric field.

The nontrivial cancellation of high-order corrections is not restricted to the third-order expression. The general formula can be found in Appendix A. The extension of Eqs. (16) or (A3) to simultaneous different perturbations is straightforward, and can be written out in a systematic

manner, along the same lines as above.

The first-order corrections to the wave function, needed to evaluate the third-order perturbation to the total energy, are summarized in the following self-consistent procedure:

$$\varepsilon_\alpha^{(1)} = \langle \Psi_\alpha^{(0)} | H^{(1)} | \Psi_\alpha^{(0)} \rangle, \quad (17)$$

$$(H^{(0)} - \varepsilon_\alpha^{(0)}) | \Psi_\alpha^{(1)} \rangle = - (H^{(1)} - \varepsilon_\alpha^{(1)}) | \Psi_\alpha^{(0)} \rangle, \quad (18)$$

$$\text{Re} \langle \Psi_\alpha^{(0)} | \Psi_\alpha^{(1)} \rangle = 0, \quad (19)$$

$$n^{(1)}(\mathbf{r}) = \sum_\alpha \Psi_\alpha^{(1)*}(\mathbf{r}) \Psi_\alpha^{(0)}(\mathbf{r}) + \Psi_\alpha^{(0)*}(\mathbf{r}) \Psi_\alpha^{(1)}(\mathbf{r}), \quad (20)$$

$$H^{(1)} = v_{\text{ext}}^{(1)} + \int \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}') d\mathbf{r}'. \quad (21)$$

The first iteration usually starts with $H^{(1)} = v_{\text{ext}}^{(1)}$ and Eq. (18) is subsequently solved for all first-order corrections of valence states α , respecting the constraint expressed by Eq. (19). The first-order charge-density correction is then computed by Eq. (20) and this allows us to construct a relaxed first-order Hamiltonian (21). This Hamiltonian is then reinserted into Eqs. (17) and (18) and the whole process is repeated until self-consistency is reached. The special case of a degenerate unperturbed eigenvalue can be handled using perturbation-adapted eigenvectors in the usual way:

$$\varepsilon_\alpha^{(1)} \delta_{\alpha\beta} = \langle \Psi_\alpha^{(0)} | H^{(1)} | \Psi_\beta^{(0)} \rangle. \quad (22)$$

This procedure is no more than a slight generalization of the technique used by BGT to the case where first-order corrections on the one-particle eigenvalues are present. In BGT, this scheme is only exploited to provide the first- and second-order total-energy corrections, leading to linear-response coefficients and various harmonic force constants. Equation (16) emphasizes the important result that the same scheme provides full access to third-order corrections to the total energy, and anharmonic response functions. The third-order self-consistent computation of the total energy generates a large number of relevant pieces of information about the system response, especially if the number of different external perturbations considered is large. The $1 + N + N(N+1)/2 + N(N+1)(N+2)/6$ zeroth-, first-, second-, and third-order perturbation energies arising from N external perturbations can all be found by only one zeroth-order and N independent first-order self-consistent calculations of the unrelaxed system.

Also, it is quite conceivable to use a similar scheme to obtain higher-order wave-function corrections to access still-higher-order hyperpolarizabilities, anharmonicities, and coupling constants. The formulas needed to achieve such a generalized scheme have already been obtained in the present paper: for order i (i.e., order $2i+1$ for the total energy) Eqs. (17)–(21) are simply replaced by (A1), (6), (9), (13), and (12), respectively, and the total-energy corrections are obtained through Eq. (A3).

III. INCOMMENSURATE PERIODIC PERTURBATIONS

In view of the importance of the problem, we will now specialize our formalism to the case of a periodic pertur-

bation applied to a perfect crystal. The wavelength of this perturbation is not necessarily commensurate with the crystalline lattice structure. To take a well-defined problem as reference, we consider the perturbation arising from a static displacement field (frozen phonon) of wave vector \mathbf{q} and polarization vector $e_\gamma(\mathbf{q}, j)$ which takes the special form

$$v_{\text{ph}} = \sum_n V(\mathbf{r} - (\mathbf{a}_n + \mathbf{R}_n)) - V(\mathbf{r} - \mathbf{a}_n) \quad (23)$$

with

$$R_{n\gamma} = \lambda 2e_\gamma(\mathbf{q}, j) \cos(\mathbf{q} \cdot \mathbf{a}_n), \quad (24)$$

where \mathbf{a}_n is the equilibrium position of the atom in cell n (we simplify the discussion by considering only one atom per unit cell, as well as a real polarization vector), while \mathbf{R}_n is the displacement of the same atom in the distorted crystal.

The external local potential depends on the displacement amplitude λ in a nonlinear way, and a systematic Taylor expansion of the potential with respect to the displacement amplitude λ must be explicitly carried out to comply with the perturbative scheme defined above. The first-order correction becomes

$$v_{\text{ph}}^{(1)} = \left[\sum_\gamma e_\gamma(\mathbf{q}, j) \sum_n \frac{dV}{dr_\gamma}(\mathbf{r} - \mathbf{a}_n) e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{a}_n)} \right] e^{i\mathbf{q} \cdot \mathbf{r}} + \left[\sum_\gamma e_\gamma(\mathbf{q}, j) \sum_n \frac{dV}{dr_\gamma}(\mathbf{r} - \mathbf{a}_n) e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{a}_n)} \right] e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (25)$$

In expression (25) the noncommensurate phase factors $e^{i\mathbf{q} \cdot \mathbf{r}}$ and $e^{-i\mathbf{q} \cdot \mathbf{r}}$ appear as envelopes to specific potentials which exhibit the same periodicity as the perfect crystal. For higher-order perturbations, this is still true of the phase factors $e^{2i\mathbf{q} \cdot \mathbf{r}}$, $e^{-2i\mathbf{q} \cdot \mathbf{r}}$, $e^{3i\mathbf{q} \cdot \mathbf{r}}$, $e^{-3i\mathbf{q} \cdot \mathbf{r}}$, etc. [see Eq. (41), for example]. We will now show that, though the perturbation effectively breaks the perfect-crystal translational invariance, the computation of the nonlinear-response coefficients, along the lines described above, can be mapped onto a periodic problem with the original small primitive cell.

Let us focus on the third-order total energy for a perturbation of the form (23)–(25). The first-order corrections $v^{(1)}(\mathbf{r})$, $n^{(1)}(\mathbf{r})$, and $H^{(1)}(\mathbf{r})$ all have the same generic form

$$A^{(1)} = A_{\mathbf{q}}^{(1)} e^{i\mathbf{q} \cdot \mathbf{r}} + A_{-\mathbf{q}}^{(1)} e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (26)$$

where $A_{\mathbf{q}}^{(1)}$ and $A_{-\mathbf{q}}^{(1)}$ have the periodicity of the perfect lattice, and are mutually complex conjugate.²⁷ The Bloch functions (leaving out the band index for simplicity) are written as

$$|\Psi_{\mathbf{k}}^{(0)}\rangle = e^{i\mathbf{k} \cdot \mathbf{r}} |u_{\mathbf{k}}^{(0)}\rangle, \quad (27)$$

$$|\Psi_{\mathbf{k}}^{(1)}\rangle = e^{i\mathbf{k} \cdot \mathbf{r}} (e^{i\mathbf{q} \cdot \mathbf{r}} |u_{\mathbf{k}, \mathbf{q}}^{(1)}\rangle + e^{-i\mathbf{q} \cdot \mathbf{r}} |u_{\mathbf{k}, -\mathbf{q}}^{(1)}\rangle), \quad (28)$$

$$\langle \Psi_{\mathbf{k}}^{(1)} | = (\langle u_{\mathbf{k}, \mathbf{q}}^{(1)} | e^{-i\mathbf{q} \cdot \mathbf{r}} + \langle u_{\mathbf{k}, -\mathbf{q}}^{(1)} | e^{i\mathbf{q} \cdot \mathbf{r}}) e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (29)$$

When \mathbf{q} is different from any reciprocal-lattice vector, the

first-order eigenvalue vanishes and the orthogonality condition (19) is always satisfied. We are thus left with a set of self-consistent equations which specialize Eqs. (17)–(21):

$$(H_{\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{\mathbf{k}}^{(0)})|u_{\mathbf{k},\mathbf{q}}^{(1)}\rangle = -H_{\mathbf{q}}^{(1)}|u_{\mathbf{k}}^{(0)}\rangle, \quad (30)$$

$$n_{\mathbf{q}}^{(1)}(\mathbf{r}) = \sum_{\text{occ bands}} \sum_{\mathbf{k}} u_{\mathbf{k}}^{(0)*}(\mathbf{r})u_{\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) + u_{\mathbf{k},-\mathbf{q}}^{(1)*}(\mathbf{r})u_{\mathbf{k}}^{(0)}(\mathbf{r}), \quad (31)$$

$$H_{\mathbf{q}}^{(1)} = v_{\mathbf{q}}^{(1)} + \int e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n_{\mathbf{q}}^{(1)}(\mathbf{r}') d\mathbf{r}'. \quad (32)$$

It is easy to verify that all the quantities needed to perform the self-consistent procedure defined by the above equations have the periodicity of the unperturbed lattice. Following the above scheme, an incommensurate perturbation does not require reference to any supercell calculations. This is an obvious advantage, already noticed by BGT,¹⁸ over previous approaches of *ab initio* phonon spectra.

In its main features, the resolution of the system Eqs. (30)–(32) is rather similar to that of the usual self-consistent problem Eqs. (2)–(4). A linear algebra system Eq. (30) replaces the eigenvalue problem Eq. (3). For both, modern iterative algorithms will require a number of floating-point operations proportional to the square of the size of the matrix.¹⁸ Recently, special treatments of pseudopotential Hamiltonians have been proposed to speed up the resolution of the eigenvalue problem.^{28,29} Those treatments could also work in the case of Eq. (30). For each band, this equation must be solved at some \mathbf{k} vectors in the Brillouin zone. Except for high-symmetry \mathbf{q} wave vectors, this Brillouin-zone sampling cannot be performed only in its irreducible part, as the perturbation breaks the original symmetry. This drawback arises from the otherwise advantageous use of a small cell.

The Hartree part of the interaction potential in Eq. (32) is easily obtained in the reciprocal space, for a plane-wave basis set, while its LDA exchange-correlation part is naturally formulated in the real space. A Fourier transform will provide the relation between the two representations. One should be careful with the Perdew-Zunger parametrization of Ceperley-Alder exchange-correlation energy,³⁰ often used for semiconductor calculations, as it generates a discontinuity at $n^{(0)} = 3/4\pi$ in Eq. (32), and even a δ function in the third-order expression that will be needed for the evaluation of phonon-phonon interaction.

It is well known that forces calculated using the

$$\bar{E}^{\lambda_1\lambda_2} = \sum_{\alpha} (\langle \Psi_{\alpha}^{\lambda_1} | v_{\text{ext}}^{\lambda_2} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{\lambda_1} | H^{(0)} - \epsilon_{\alpha}^{(0)} | \Psi_{\alpha}^{\lambda_2} \rangle$$

$$+ \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{\lambda_1\lambda_2} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{\lambda_1} | \Psi_{\alpha}^{\lambda_2} \rangle) + \frac{1}{2} \int \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n^{\lambda_1}(\mathbf{r}) n^{\lambda_2}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (37)$$

and

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{6} (\bar{E}^{\lambda_1\lambda_2\lambda_3} + \bar{E}^{\lambda_2\lambda_1\lambda_3} + \bar{E}^{\lambda_1\lambda_3\lambda_2} + \bar{E}^{\lambda_3\lambda_1\lambda_2} + \bar{E}^{\lambda_3\lambda_2\lambda_1} + \bar{E}^{\lambda_2\lambda_3\lambda_1}) \quad (38)$$

with

Hellman-Feynman theorem require better convergence with respect to density self-consistency and numerical cutoffs than do corresponding total-energy calculations. We might expect that as higher-order derivatives of the total energy are considered, the requirements for accuracy would become progressively more stringent.

As soon as the convergence of the system (30)–(32) is appropriate, the density and the functions $|u_{\mathbf{k},\mathbf{q}}^{(1)}\rangle$ for each occupied band are stored, and the whole process can reinitialize for another first-order perturbation. After the treatment of a complete set of perturbations, we are able to obtain the related second- and third-order perturbative coefficients.

IV. PHONON FREQUENCY, GROUP VELOCITY, AND INTERACTION

This section presents explicit formulas for the electronic part of the dynamical matrix $\mathcal{A}_{\gamma\gamma'}(\mathbf{q})$, its gradient $\nabla_{\mathbf{q}}\mathcal{A}_{\gamma\gamma'}(\mathbf{q})$, and the third-order anharmonic coefficients $b_{j_1,j_2,j_3}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)$, a basic quantity in the theory of phonon-interaction. We follow Gurevich³¹ for the notations and definitions. The phonon frequency and polarization are derived from

$$\Omega^2(\mathbf{q},j)M e_{\gamma}(\mathbf{q},j) = \sum_{\gamma'} \mathcal{A}_{\gamma\gamma'}(\mathbf{q}) e_{\gamma'}(\mathbf{q},j), \quad (33)$$

where M is the atom mass, while the phonon group velocity for the phonon with wave vector \mathbf{q} and polarization j is related to the following quantity:

$$\nabla_{\mathbf{q}}\Omega^2(\mathbf{q},j)M = \sum_{\gamma,\gamma'} e_{\gamma}(\mathbf{q},j)\nabla_{\mathbf{q}}[\mathcal{A}_{\gamma\gamma'}(\mathbf{q})]e_{\gamma'}(\mathbf{q},j). \quad (34)$$

As we will work with two or three different small parameters and perturbations, we must generalize some equations. We define

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{(i+j+k)!} \frac{\partial^{i+j+k} E}{\partial \lambda_1^i \partial \lambda_2^j \partial \lambda_3^k} \Big|_{\lambda_1=0, \lambda_2=0, \lambda_3=0}, \quad (35)$$

which for only one perturbation, or for identical perturbations, reduces to Eq. (5). For zeroth-order quantities, we will keep the previously defined notation $E^{(0)}$.

The second-order and third-order expressions for energy generalize as

$$E^{\lambda_1\lambda_2} = \frac{1}{2} (\bar{E}^{\lambda_1\lambda_2} + \bar{E}^{\lambda_2\lambda_1}) \quad (36)$$

with

$$\begin{aligned} \tilde{E}^{\lambda_1\lambda_2\lambda_3} = & \sum_{\alpha} (\langle \Psi_{\alpha}^{\lambda_1} | v_{\text{ext}}^{\lambda_2\lambda_3} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{\lambda_1} | H^{\lambda_2} - \varepsilon_{\alpha}^{\lambda_2} | \Psi_{\alpha}^{\lambda_3} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{\lambda_1\lambda_2\lambda_3} | \Psi_{\alpha}^{(0)} \rangle + \langle \Psi_{\alpha}^{(0)} | v_{\text{ext}}^{\lambda_1\lambda_2} | \Psi_{\alpha}^{\lambda_3} \rangle) \\ & + \frac{1}{6} \int \frac{\delta^3 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')\delta n(\mathbf{r}'')} n^{\lambda_1}(\mathbf{r})n^{\lambda_2}(\mathbf{r}')n^{\lambda_3}(\mathbf{r}'') d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' . \end{aligned} \quad (39)$$

We consider now two different frozen phonons of wave vector \mathbf{q}_1 and \mathbf{q}_2 and polarization j_1 and j_2 . The related atomic displacements are written

$$R_{n\gamma} = 2\lambda_1 e_{\gamma}(\mathbf{q}_1, j_1) \cos(\mathbf{q}_1 \cdot \mathbf{a}_n - \alpha_1) + 2\lambda_2 e_{\gamma}(\mathbf{q}_2, j_2) \cos(\mathbf{q}_2 \cdot \mathbf{a}_n - \alpha_2) , \quad (40)$$

where the phase shifts α_i can have any value.

At second order Eq. (26) becomes

$$A^{\lambda_1\lambda_2} = A_{\mathbf{q}_1\mathbf{q}_2}^{j_1j_2} e^{i(\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}} + A_{-\mathbf{q}_1\mathbf{q}_2}^{j_1j_2} e^{i(-\mathbf{q}_1+\mathbf{q}_2)\cdot\mathbf{r}} + A_{\mathbf{q}_1-\mathbf{q}_2}^{j_1j_2} e^{i(\mathbf{q}_1-\mathbf{q}_2)\cdot\mathbf{r}} + A_{-\mathbf{q}_1-\mathbf{q}_2}^{j_1j_2} e^{i(\mathbf{q}_1-\mathbf{q}_2)\cdot\mathbf{r}} . \quad (41)$$

For example, the particular second-order external potential $v_{-\mathbf{q}_1\mathbf{q}_2}$ (with $\alpha_i = 0^\circ$) is given by

$$v_{-\mathbf{q}_1\mathbf{q}_2}^{j_1j_2} = \left[\sum_{\gamma} e_{\gamma}(\mathbf{q}_1, j_1) \sum_{\gamma'} e_{\gamma'}(\mathbf{q}_2, j_2) \sum_n \frac{d^2 V}{dr_{\gamma} dr_{\gamma'}}(\mathbf{r} - \mathbf{a}_n) e^{-i(-\mathbf{q}_1+\mathbf{q}_2)\cdot(\mathbf{r}-\mathbf{a}_n)} \right] , \quad (42)$$

which for $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{q}$ is independent of \mathbf{q} . This will be used later to establish Eq. (47).

Using the corresponding energy variation $E^{\lambda_1\lambda_2}$ for $\mathbf{q}_1 = \mathbf{q}_2 = \mathbf{q}$ together with Eqs. (1.2) and (1.13) of Gurevich³¹ gives the following expression:

$$\sum_{\gamma, \gamma'} e_{\gamma}(\mathbf{q}, j_1) \lambda \mathcal{A}_{\gamma\gamma'}^{\text{el}}(\mathbf{q}) e_{\gamma'}(\mathbf{q}, j_2) = A^{j_1j_2}(\mathbf{q}) + A^{j_2j_1}(-\mathbf{q}) , \quad (43)$$

where

$$\begin{aligned} N A^{j_1j_2}(\mathbf{q}) = & \sum_{\mathbf{k}, \text{occ bands}} (\langle u_{\mathbf{k}, \mathbf{q}}^{j_1} | v_{\mathbf{q}}^{j_2} | u_{\mathbf{k}}^{(0)} \rangle + \langle u_{\mathbf{k}, \mathbf{q}}^{j_1} | H_{\mathbf{k}+\mathbf{q}}^{(0)} - \varepsilon_{\mathbf{k}}^{(0)} | u_{\mathbf{k}, \mathbf{q}}^{j_2} \rangle + \langle u_{\mathbf{k}}^{(0)} | v_{-\mathbf{q}, \mathbf{q}}^{j_1j_2} | u_{\mathbf{k}}^{(0)} \rangle + \langle u_{\mathbf{k}}^{(0)} | v_{-\mathbf{q}}^{j_1} | u_{\mathbf{k}, \mathbf{q}}^{j_2} \rangle) \\ & + \frac{1}{2} \int \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} [n_{-\mathbf{q}}^{j_1}(\mathbf{r})n_{\mathbf{q}}^{j_2}(\mathbf{r}') e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}] d\mathbf{r} d\mathbf{r}' . \end{aligned} \quad (44)$$

N is the number of unit cells in the whole crystal.³² The first-order quantities correspond to the external potential given by Eqs. (23)–(25), the second-order quantity to Eq. (42) (zero phase shift). With three first-order calculations, one for each orthogonal polarization, we get the nine matrix element of the dynamical matrix for a particular vector \mathbf{q} .

The combination of this last result, Eq. (44), with Eqs. (30)–(32) gives a much simpler expression:

$$N \sum_{\gamma, \gamma'} e_{\gamma}(\mathbf{q}, j_1) \lambda \mathcal{A}_{\gamma\gamma'}^{\text{el}}(\mathbf{q}) e_{\gamma'}(\mathbf{q}, j_2) = \text{Re} \left[\int \frac{1}{2} v_{\mathbf{q}}^{j_1}(\mathbf{r}) n_{-\mathbf{q}}^{j_2}(\mathbf{r}) + \frac{1}{2} v_{\mathbf{q}}^{j_2}(\mathbf{r}) n_{-\mathbf{q}}^{j_1}(\mathbf{r}) + 2v_{-\mathbf{q}, \mathbf{q}}^{j_1j_2}(\mathbf{r}) n_{(\mathbf{r})}^{(0)} d\mathbf{r} \right] . \quad (45)$$

This expression requires only the first-order densities, and not the set of first-order wave functions. A similar expression, for nonlocal pseudopotentials, was used by BGT in their work on optical phonons and dielectric constants.¹⁸

Nevertheless, the way to get the simplest expression for the group velocity starts from Eqs. (43) and (44). We apply the gradient operator to each side of this equation: the term containing the second-order potential vanishes, then we use identities similar to

$$\langle \nabla_{\mathbf{q}}(u_{\mathbf{k}, \mathbf{q}}^{j_1}) | v_{\mathbf{q}}^{j_2} | u_{\mathbf{k}}^{(0)} \rangle + \langle \nabla_{\mathbf{q}}(u_{\mathbf{k}, \mathbf{q}}^{j_1}) | H_{\mathbf{k}+\mathbf{q}}^{(0)} - \varepsilon_{\mathbf{k}}^{(0)} | u_{\mathbf{k}, \mathbf{q}}^{j_2} \rangle = - \left\langle \nabla_{\mathbf{q}}(u_{\mathbf{k}, \mathbf{q}}^{j_1}) \left| \int \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n_{\mathbf{q}}^{j_2}(\mathbf{r}') e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{r} \right| u_{\mathbf{k}}^{(0)} \right\rangle , \quad (46)$$

and finally sum the terms containing either the gradient of first-order potential or the gradient of first-order wave functions:

$$\begin{aligned} N \sum_{\gamma, \gamma'} e_{\gamma}(\mathbf{q}, j_1) \nabla_{\mathbf{q}}[\mathcal{A}_{\gamma\gamma'}(\mathbf{q})] e_{\gamma'}(\mathbf{q}, j_2) = & \sum_{\mathbf{k}, \text{occ bands}} [\langle u_{\mathbf{k}, \mathbf{q}}^{j_1} | \nabla_{\mathbf{q}}(H_{\mathbf{k}+\mathbf{q}}^{(0)}) | u_{\mathbf{k}, \mathbf{q}}^{j_2} \rangle + \langle u_{\mathbf{k}, -\mathbf{q}}^{j_1} | \nabla_{\mathbf{q}}(H_{\mathbf{k}-\mathbf{q}}^{(0)}) | u_{\mathbf{k}, -\mathbf{q}}^{j_2} \rangle] \\ & + \int \nabla_{\mathbf{q}}[v_{-\mathbf{q}}^{j_1}(\mathbf{r})] n_{\mathbf{q}}^{j_2}(\mathbf{r}) + \nabla_{\mathbf{q}}[v_{-\mathbf{q}}^{j_2}(\mathbf{r})] n_{\mathbf{q}}^{j_1}(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \frac{\delta^2 E_I[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n_{-\mathbf{q}}^{j_1}(\mathbf{r}) n_{\mathbf{q}}^{j_2}(\mathbf{r}') \nabla_{\mathbf{q}}(e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}) d\mathbf{r} d\mathbf{r}' . \end{aligned} \quad (47)$$

Neither gradients of first-order wave functions nor gradients of wave functions appear in this expression. We obtain the remarkable result that gradients of phonon frequencies can be found from the self-consistent first-order calculations needed to obtain those frequencies. For a local potential Hamiltonian, the gradient of the Hamiltonian reduces to the gradient of its kinetic part, which is diagonal in the reciprocal space. The exchange-correlation part of the interaction term, in the local-density approximation, vanishes and the Hartree part of the same term also diagonalizes in the reciprocal space. It is thus very easy to include this expression in a computer program which already solves the first-order self-consistent problem.

Besides providing the phonon group velocities, this formula can also be used to improve the efficiency of inter-

polation schemes for the frequency spectrum in the Brillouin zone.

To establish the expression for the third-order anharmonic coefficient, we must start from the following perturbation:

$$\begin{aligned} R_{n\gamma} = & 2\lambda_1 e_\gamma(\mathbf{q}_1, j_1) \cos(\mathbf{q}_1 \cdot \mathbf{a}_n - \alpha_1) \\ & + 2\lambda_2 e_\gamma(\mathbf{q}_2, j_2) \cos(\mathbf{q}_2 \cdot \mathbf{a}_n - \alpha_2) \\ & + 2\lambda_3 e_\gamma(\mathbf{q}_3, j_3) \cos(\mathbf{q}_3 \cdot \mathbf{a}_n - \alpha_3). \end{aligned} \quad (48)$$

We consider the related energy $E^{\lambda_1 \lambda_2 \lambda_3}$, in connection with Eqs. (6.3) and (6.5) of Gurevich.³⁰ For $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = \mathbf{G}$, where \mathbf{G} is some reciprocal-lattice vector,

$$\begin{aligned} b_{j_1 j_2 j_3}^{\text{el}}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = & [\tilde{b}_{j_1 j_2 j_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) + \tilde{b}_{j_2 j_1 j_3}(\mathbf{q}_2, \mathbf{q}_1, \mathbf{q}_3) + \tilde{b}_{j_1 j_3 j_2}(\mathbf{q}_1, \mathbf{q}_3, \mathbf{q}_2) \\ & + \tilde{b}_{j_3 j_1 j_2}(\mathbf{q}_3, \mathbf{q}_1, \mathbf{q}_2) + \tilde{b}_{j_2 j_3 j_1}(\mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_1) + \tilde{b}_{j_3 j_2 j_1}(\mathbf{q}_3, \mathbf{q}_2, \mathbf{q}_1)] \end{aligned} \quad (49)$$

with

$$\begin{aligned} \tilde{b}_{j_1 j_2 j_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = & \frac{1}{NM} \left[\sum_{\mathbf{k}, \text{occ bands}} \langle u_{\mathbf{k}, -\mathbf{q}_1}^{j_1} | e^{i\mathbf{G} \cdot \mathbf{r}} H_{\mathbf{q}_2}^{j_2} | u_{\mathbf{k}, \mathbf{q}_3}^{j_3} \rangle + \int e^{i\mathbf{G} \cdot \mathbf{r}} [v_{\mathbf{q}_1 \mathbf{q}_2}^{j_1 j_2}(\mathbf{r}) n_{\mathbf{q}_3}^{j_3}(\mathbf{r}) + v_{\mathbf{q}_1 \mathbf{q}_2 \mathbf{q}_3}^{j_1 j_2 j_3}(\mathbf{r}) n^{(0)}(\mathbf{r})] d\mathbf{r} \right. \\ & \left. + \frac{1}{6} \frac{\delta^3 E_I[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}'')} n_{\mathbf{q}_1}^{j_1}(\mathbf{r}) n_{\mathbf{q}_2}^{j_2}(\mathbf{r}') n_{\mathbf{q}_3}^{j_3}(\mathbf{r}'') e^{i(\mathbf{q}_1 \cdot \mathbf{r} + \mathbf{q}_2 \cdot \mathbf{r}' + \mathbf{q}_3 \cdot \mathbf{r}'')} d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \right]. \end{aligned} \quad (50)$$

The different first-, second-, and third-order quantities correspond to Eq. (48), where $\alpha_i = 0^\circ$. The Hartree part of the interaction term vanishes, while the exchange-correlation part of it, in the local-density approximation, will be very easy to evaluate in the real space. This expression of the phonon-phonon interaction parameters uses only the first-order wave functions and densities needed to find the phonon frequencies. The CPU time gain with respect to supercell calculations is obvious.

In this last section, we have obtained explicit formulas for second- and third-order quantities related to the frozen-phonon perturbations. We could also consider the long-wavelength limit of periodic perturbations, which corresponds to uniform strains or electric fields. The long-wavelength limit of the self-consistent system (30)–(32) and the related properties will be developed in a subsequent paper.³³ We also note that the scaled-Hamiltonian technique suggested by BGT (Ref. 19) is easily implemented within the nonlinear-response-function formalism.

V. CONCLUSION

This paper deals with the construction of the derivatives of the total energy of solids to an arbitrary order, on a first-principles basis, within density-functional theory. The response coefficients which can be computed cover the nonlinear hyperpolarizabilities, the anharmonic

effects in static or dynamic lattice deformation, and different types of coupling between strains, phonons, and static electric fields of any range of wavelengths. In essence, the method generalizes the approach described by Baroni *et al.*^{18,19} and uses the $2n + 1$ theorem adapted to many-body quantum mechanics in the framework of the DFT to obtain, for instance, third-order nonlinear-response functions with virtually the same computational effort as for the calculation of the linear coefficients. Higher-order coefficients can also be analytically obtained using the same approach: a second-order perturbation treatment will provide all fifth-order response coefficients.

In contrast to the usual brute-force supercell approaches, the present scheme is based on a high-order analytic derivative of the total energy, instead of finite-difference estimations.

Another important advantage of this scheme is that it allows one to treat periodic perturbations applied to a crystal without resorting to the generation of large supercells, and to consider explicitly the perturbation wavelength incommensurate with the periodic structure of the perfect crystal. Derivatives with respect to the perturbation wavelength can also be considered.

Finally, we have explicitly written the expressions for the electronic part of the dynamical matrix, of its gradient with respect to the wavelength, and of the third-order anharmonic coefficients. These quantities give ac-

cess to phonon frequency, group velocity, and phonon-phonon interaction.

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APPENDIX: $2n + 1$ THEOREM TO ANY ORDER

This appendix gives the explicit formulas for the energy corrections to any perturbation order, as obtained from the application of the $2n + 1$ theorem.

For the one-electron Schrödinger equation, the generalization of Eq. (11) reads

$$\varepsilon_{\alpha}^{(i)} = \sum_{j=0}^{[i/2]} \sum_{k=0}^{[i/2]} \sum_{l=[(i+1)/2]}^i \delta(i-j-k-l) \langle \Psi_{\alpha}^{(j)} | H^{(l)} | \Psi_{\alpha}^{(k)} \rangle + \sum_{j=0}^{[i/2]} \sum_{k=0}^{[i/2]} \sum_{l=0}^{[(i-1)/2]} \delta(i-j-k-l) \langle \Psi_{\alpha}^{(j)} | H^{(l)} - \varepsilon_{\alpha}^{(l)} | \Psi_{\alpha}^{(k)} \rangle, \quad (\text{A1})$$

where $[x]$ means the integer part of x . If we turn to the many-body problem, the second term and the external-potential part of the first term in Eq. (A1) present no contribution from perturbative self-consistent corrections of order higher than $[i/2]$. After summation on α , in the expression of the total energy, Eq. (1) at order i , the other part will become

$$\sum_{l=[(i+1)/2]}^i \int n^{(i-l)}(\mathbf{r}) \left[\frac{\delta E_I[n]}{\delta n(\mathbf{r})} \right]^{(l)} d\mathbf{r}. \quad (\text{A2})$$

We then combine this expression with the electron-electron interaction in Eq. (1), expanded at order i , to find

$$E_{\text{el}}^{(i)} = \sum_{j=0}^{[i/2]} \sum_{k=0}^{[i/2]} \sum_{l=0}^{[(i-1)/2]} \sum_{\alpha} \delta(i-j-k-l) \langle \Psi_{\alpha}^{(j)} | H^{(l)} - \varepsilon_{\alpha}^{(l)} | \Psi_{\alpha}^{(k)} \rangle + \int \sum_{l=0}^{[i/2]} v_{\text{ext}}^{(i-l)}(\mathbf{r}) n^{(l)}(\mathbf{r}) d\mathbf{r} + \frac{1}{i!} \frac{d}{d\lambda^{(i)}} E_I \left[n^{(0)} + \sum_{j=1}^{[i/2]} \lambda^j n^{(j)} \right] \Big|_{\lambda=0}. \quad (\text{A3})$$

Here, all quantities, except v_{ext} , enter with maximum order $[i/2]$. The $2n + 1$ theorem is then proved to all orders in the DFT treatment of the many-body problem.

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