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First-principles responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm

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The changes in density, wave functions, and self-consistent potentials of solids, in response to small atomic displacements or infinitesimal homogeneous electric fields, are considered in the framework of the density-functional theory. A variational principle for second-order derivatives of the energy provides a basis for efficient algorithmic approaches to these linear responses, such as the state-by-state conjugate-gradient algorithm presented here in detail. The phase of incommensurate perturbations of periodic systems, that are, like phonons, characterized by some wave vector, can be factorized: the incommensurate problem is mapped on an equivalent one presenting the periodicity of the unperturbed ground state. The singularity of the potential change associated with an homogeneous field is treated by the long-wave method. The efficient implementation of these theoretical ideas using plane waves, separable pseudopotentials, and a nonlinear exchange-correlation core correction is described in detail, as well as other technical issues. [S0163-1829(97)05016-9]

I. INTRODUCTION

The accurate prediction of material properties is one of the pivotal goals of computational condensed matter physics. Current efforts aim at increasing the accuracy of the predictions, the complexity of the systems studied, and the number of properties predicted, altogether for a decreasing computational cost. I will focus on the efficient prediction of *responses* of periodic systems to different perturbations, using the local-density approximation (LDA) to density-functional theory[1] (DFT) as a basic underlying tool. With this technique, changes in total energy due to adiabatic perturbations are obtained within a few percent of experimental data.[2] Exceptions to this gratifying picture are well characterized and discussed in the literature.[2,3]

The perturbations that will be considered belong to the following two classes: (a) collective displacements of atoms characterized by a wave vector, either commensurate or incommensurate with the underlying lattice, that altogether generate a basis for the description of phonons, and (b) homogeneous static electric fields. The present paper describes the computation of the first-order derivatives of the wave functions, density, and self-consistent potential with respect to these perturbations. The subsequent computation of various second-order derivatives of the total energy is described in an accompanying paper (P2).[4]

The responses of crystalline solids to external perturbations, like electric fields or atomic displacements, have been calculated within the DFT using various methods.[5–12] The simplest is a direct approach[5] in which one freezes a finite-amplitude perturbation into the system and compares the perturbed system with the corresponding unperturbed one (e.g., the frozen-phonon technique). However, in this approach, it is was impossible to handle perturbations incommensurate with the periodic lattice, or potentials linear in space (corresponding to homogeneous electric fields), while commensurate perturbations were handled through the use of supercells, sometimes with a considerable increase of computing time. Still, its simplicity has attracted many research groups.[13] The recent appearance of O(N) algorithms for phonons[14] as well as Wannier function approach to the dielectric constant[15] could reduce the above-mentioned disadvantages.

There is also a dielectric-matrix approach in which one calculates dielectric matrices from the unperturbed ground-state wave functions.[6–8] Incommensurability is not a problem in this technique. However, the whole spectrum of the valence- and conduction-band wave functions is required, which can be computationally demanding, and responses to atomic displacements cannot be obtained when the electron-ion interaction is represented by a nonlocal pseudopotential.

Baroni, Giannozzi, and Testa[10,16] (BGT) demonstrated the power of a perturbative approach, appearing also in Ref. 9, in which the linear responses are calculated self-consistently. It combines the advantages of the two previous methods, without their drawbacks. Baroni and coworkers, as well as other research groups[17–19] used this formalism with plane waves and pseudopotentials. Linear muffin tin orbital[20–22] (LMTO) and linear augmented plane-wave[23] (LAPW) versions of this linear-response approach have also been proposed and implemented. Applications have been numerous, and included computations of dynamical matrices, Born effective charge tensors and dielectric permittivity tensors for bulk materials, surfaces or large molecules, as well as computation of elastic constants, piezoelectric tensors, photoelastic tensors, internal strain, deformation potential, electron-phonon coupling, thermodynamical properties, atomic temperature factors, and phase transitions.[18,24–35]

It was also realized that the BGT approach was derived from an interesting merging of DFT and perturbation theory, and that it could be extended very efficiently to nonlinear responses, thanks to the $2n+1$ theorem.[36–43] From the same point of view, often referred to as density-functional perturbation theory (DFPT), one can infer the existence of a variational principle for the second-order derivatives of the total energy.[12,20] This variational principle, its higher-order generalizations, and the $2n+1$ theorem for DPFT, are thoroughly discussed in Ref. 42. Thanks to the second-order variational principle, efficient minimization techniques, like the conjugate-gradient algorithm,[12,44,45] can be used for the evaluation of the first-order changes of the wave functions, charge densities, and self-consistent potentials. Moreover, second-order derivatives of the total energy converge more rapidly to the correct answers than in the BGT approach. Like the BGT technique, the variational approach has been widely used for studies of dynamical and dielectric properties of various materials [SiO_2-quartz,[12,46–48] SiO_2-stishovite,[48–52] Si,[53] TiO_2,[54,55] $BaTiO_3$,[56–60] $PbTiO_3$,[61] $PbZrO_3$,[62] Al_2Ru,[63] and PbTe (Ref. 64)]. The use of a variational principle was also instrumental in the LMTO implementation of the linear-response approach.[20,22]

Since the presentation of the technique that was used for the computation of dielectric and dynamical properties of solids was rather limited in these previous papers, an extensive description of the method will be given in the present paper and in P2,[4] from the basic determination of the responses, to the computation of phonon band structures. In common with BGT,[16] the implementation of this scheme is done using plane waves and pseudopotentials, but, at variance, fast Fourier transforms are used (in the spirit of the Car-Parrinello technique[65]) as well as elaborate separable pseudopotentials,[66] in order to enhance the efficiency of the calculation. Since nonlinear exchange-correlation core corrections[67,31] have been used in the above-mentioned applications[12,46–50,53–60] the consequences of this technical feature will also be described. Specific aspects related to metals that cannot sustain static electric fields, and for which a Fermi surface is present, will be briefly mentioned when appropriate. By definition, all nonadiabatic as well as nonharmonic effects are ignored.

This paper is organized as follows. In Sec. II, some basic results of DFPT are recalled. In Sec. III, I describe the preconditioned conjugate-gradient gradient algorithm that can be used to find the first-order changes in wave functions, charge densities, and the self-consistent potential with respect to a generic perturbation. Section IV contains a general analysis of response to perturbations that are characterized by a wave vector incommensurate with the periodicity of the underlying lattice. The factorization of the incommensurability is shown. In Sec. V, one finds the developments needed to obtain the first-order change in wave functions and densities with respect to collective atomic displacements, in the plane-wave implementation with separable pseudopotentials and a nonlinear exchange-correlation core correction. Section VI describes the treatment of homogeneous electric fields, using the long-wave method, then its implementation. In Sec. VII, I mention some technical considerations, and present perspectives in Sec. VIII. Atomic (Hartree) units are used throughout this paper.

II. BASICS OF DENSITY-FUNCTIONAL PERTURBATION THEORY

A. DFT equations

In the DFT, the ground-state energy of the electronic system is derived from the following minimum principle:[2]

$$E_{\mathrm{el}}\{\psi_\alpha\}=\sum_{\alpha}^{\mathrm{occ}}\langle\psi_\alpha|T+v_{\mathrm{ext}}|\psi_\alpha\rangle+E_{\mathrm{Hxc}}[n], \tag{1}$$

where the ψ_α's are the Kohn-Sham orbitals (to be varied until the minimum is found), T is the kinetic energy operator, v_{ext} is the potential external to the electronic system that includes the one created by nuclei (or ions), E_{Hxc} is the Hartree and exchange-correlation energy functional of the electronic density $n(\mathbf{r})$, and the summation runs over the occupied states α. The occupied Kohn-Sham orbitals are subject to the orthonormalization constraints,

$$\int \psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r})d\mathbf{r}=\langle\psi_\alpha|\psi_\beta\rangle=\delta_{\alpha\beta}, \tag{2}$$

where α and β label occupied states. The density is generated from

$$n(\mathbf{r})=\sum_{\alpha}^{\mathrm{occ}}\psi_\alpha^*(\mathbf{r})\psi_\alpha(\mathbf{r}). \tag{3}$$

The minimization of $E_{\mathrm{el}}\{\psi\}$ under the orthonormality constraints Eq. (2) can be achieved using the Lagrange multiplier method. The problem turns into the minimization of

$$E_{\mathrm{el}}^{+}\{\psi\}=\sum_{\alpha}^{\mathrm{occ}}\langle\psi_\alpha|T+v_{\mathrm{ext}}|\psi_\alpha\rangle+E_{\mathrm{Hxc}}[n] -\sum_{\alpha\beta}^{\mathrm{occ}}\epsilon_{\beta\alpha}(\langle\psi_\alpha|\psi_\beta\rangle-\delta_{\alpha\beta}), \tag{4}$$

where $\epsilon_{\alpha\beta}$ are the Lagrange multipliers corresponding to the set of constraints Eq. (2). The canonical Euler-Lagrange equations are

$$H|\psi_\alpha\rangle=\sum_{\beta}^{\mathrm{occ}}\epsilon_{\beta\alpha}|\psi_\beta\rangle, \tag{5}$$

where the Hamiltonian operator is

$$H=T+v_{\mathrm{ext}}+\frac{\delta E_{\mathrm{Hxc}}}{\delta n}=T+v_{\mathrm{ext}}+v_{\mathrm{Hxc}}. \tag{6}$$

Since H is Hermitian, it is always possible to make a unitary transformation of Eq. (5) in such a way that

$$H|\psi_\alpha\rangle=\epsilon_\alpha|\psi_\alpha\rangle. \tag{7}$$

B. Perturbation expansion

Having defined the DFT equations for the possible external potentials v_{ext}, we now choose a reference (unperturbed) external potential $v_{\mathrm{ext}}^{(0)}$ and expand the perturbed potential v_{ext} in terms of a small parameter λ, as follows:

$$v_{\mathrm{ext}}(\lambda)=v_{\mathrm{ext}}^{(0)}+\lambda v_{\mathrm{ext}}^{(1)}+\lambda^2 v_{\mathrm{ext}}^{(2)}+\cdots. \tag{8}$$

We are interested in the change of physical quantities, due to the perturbation of the external potential.[68] So, we expand all of the exact perturbed quantities $X(\lambda)$ in the same form as $v_{\mathrm{ext}}(\lambda)$,

$$X(\lambda)=X^{(0)}+\lambda X^{(1)}+\lambda^2X^{(2)}+\cdots, \tag{9}$$

where X can be $E_{\rm el}$, $\psi_\alpha(\mathbf{r})$, $n(\mathbf{r})$, $\epsilon_{\alpha\beta}$, or H. For example, the lowest-order expansion of Eq. (7) is simply

$$H^{(0)}|\psi_\alpha^{(0)}\rangle=\epsilon_\alpha^{(0)}|\psi_\alpha^{(0)}\rangle. \tag{10}$$

Because $E_{\rm el}$ satisfies a variational principle under constraints, it is possible to derive a constrained variational principle for the $2n$th order derivative of $E_{\rm el}$ with respect to the nth order derivative of ψ_α:[69,70,42] when the expansion of the wave function of up to an order of $n-1$ is known, the variational (minimum) principle for the $2n$th order derivative of $E_{\rm el}$ is as follows:

$$E_{\rm el}^{(2n)}=\min_{\psi_\alpha^{(n)}}\left(E_{\rm el}^{+}\left\{\sum_{i=0}^{n}\lambda^i\psi_\alpha^{(i)}\right\}\right)^{(2n)}, \tag{11}$$

under constraints (in the parallel transport gauge[42])

$$\sum_{i=0}^{n}\langle\psi_\alpha^{(n-i)}|\psi_\beta^{(i)}\rangle=0 \tag{12}$$

for all occupied states α and β. The explicit expressions for $E_{\rm el}^{(2n)}$ can be worked out by introducing Eq. (4) into Eq. (11).

For the second order, we obtain that $E_{\rm el}^{(2)}$ is the minimum of the following expression:[12,20,42]

$$\begin{aligned}E_{\rm el}^{(2)}\{\psi^{(0)};\psi^{(1)}\}=&\sum_{\alpha}^{\rm occ}\,[\langle\psi_\alpha^{(1)}|H^{(0)}-\epsilon_\alpha^{(0)}|\psi_\alpha^{(1)}\rangle+(\langle\psi_\alpha^{(1)}|v_{\rm ext}^{(1)}|\psi_\alpha^{(0)}\rangle+\langle\psi_\alpha^{(0)}|v_{\rm ext}^{(1)}|\psi_\alpha^{(1)}\rangle)+\langle\psi_\alpha^{(0)}|v_{\rm ext}^{(2)}|\psi_\alpha^{(0)}\rangle]\\&+\frac{1}{2}\int\int\left.\frac{\delta^2E_{\rm Hxc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n^{(0)}}n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'+\int\frac{d}{d\lambda}\left.\frac{\delta E_{\rm Hxc}}{\delta n(\mathbf{r})}\right|_{n^{(0)}}n^{(1)}(\mathbf{r})d\mathbf{r}+\frac{1}{2}\left.\frac{d^2E_{\rm Hxc}}{d\lambda^2}\right|_{n^{(0)}},\end{aligned} \tag{13}$$

where the first-order changes in wave functions $\psi_\alpha^{(1)}$ (these quantities will be referred to as the first-order wave functions, for brevity) are varied under the constraints

$$\langle\psi_\alpha^{(0)}|\psi_\beta^{(1)}\rangle=0 \tag{14}$$

for all occupied states α and β, while the first-order density is given by

$$n^{(1)}(\mathbf{r})=\sum_{\alpha}^{\rm occ}\,\psi_\alpha^{*(1)}(\mathbf{r})\psi_\alpha^{(0)}(\mathbf{r})+\psi_\alpha^{*(0)}(\mathbf{r})\psi_\alpha^{(1)}(\mathbf{r}). \tag{15}$$

By virtue of Eq. (14), the first-order wave functions are orthogonal to the unperturbed wave functions of the occupied states. This is a specific advantage of the parallel-transport gauge.[71]

Since $E_{\rm el}^{(2)}\{\psi^{(0)};\psi^{(1)}\}$ is variational with respect to $\psi^{(1)}$,[72] we deduce the Euler-Lagrange equations (also called self-consistent Sternheimer equations in this particular case),[73,42]

$$P_c(H^{(0)}-\epsilon_\alpha^{(0)})P_c|\psi_\alpha^{(1)}\rangle=-P_cH^{(1)}|\psi_\alpha^{(0)}\rangle, \tag{16}$$

where P_c is the projector upon the unoccupied states (conduction bands), $H^{(0)}$, $\epsilon_\alpha^{(0)}$, and $\psi^{(0)}$ are obtained from Eq. (10), and the first-order Hamiltonian $H^{(1)}$ is given by

$$\begin{aligned}H^{(1)}=v_{\rm ext}^{(1)}+v_{\rm Hxc}^{(1)}=v_{\rm ext}^{(1)}+\int\left.\frac{\delta^2E_{\rm Hxc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n^{(0)}}n^{(1)}(\mathbf{r}')d\mathbf{r}'\\+\frac{d}{d\lambda}\left.\frac{\delta E_{\rm Hxc}}{\delta n(\mathbf{r})}\right|_{n^{(0)}}.\end{aligned} \tag{17}$$

One defines also

$$v_{\rm Hxc0}^{(1)}=\frac{d}{d\lambda}\left.\frac{\delta E_{\rm Hxc}}{\delta n(\mathbf{r})}\right|_{n^{(0)}}, \tag{18}$$

not to be confused with $v_{\rm Hxc}^{(1)}$, that contains one more term, see Eq. (17). $v_{\rm ext}^{(1)}$ and $v_{\rm Hxc0}^{(1)}$ do not depend on the first-order wave functions. Equation (16) can be solved by algorithms based on Green's functions or, within some basis set, by standard algorithms for dealing with inhomogeneous systems of equations.[16]

In Eq. (13), the contributions

$$\sum_{\alpha}^{\rm occ}\,\langle\psi_\alpha^{(0)}|v_{\rm ext}^{(2)}|\psi_\alpha^{(0)}\rangle+\frac{1}{2}\left.\frac{d^2E_{\rm Hxc}}{d\lambda^2}\right|_{n^{(0)}}, \tag{19}$$

that will be denoted by $E_{\rm non\text{-}var}^{(2)}$, also do not depend on the first-order wave functions, and will not change in the course of the minimization procedure or in the self-consistent procedure.

For the first-order wave functions that satisfy Eqs. (14)–(17), or equivalently minimize Eq. (13) under constraints Eq. (14), $E_{\rm el}^{(2)}$ can also be computed from

$$\begin{aligned}E_{\rm el}^{(2)}=\frac{1}{2}\sum_{\alpha}^{\rm occ}\,(\langle\psi_\alpha^{(1)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\alpha^{(0)}\rangle\\+\langle\psi_\alpha^{(0)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\alpha^{(1)}\rangle)+E_{\rm non\text{-}var}^{(2)},\end{aligned} \tag{20}$$

instead from Eq. (13). Taking into account the time-reversal symmetry, other expressions for $E_{\rm el}^{(2)}$ can be found:

$$E_{\rm el}^{(2)}=\sum_{\alpha}^{\rm occ}\,\langle\psi_\alpha^{(0)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\alpha^{(1)}\rangle+E_{\rm non\text{-}var}^{(2)}, \tag{21}$$

or its Hermitian conjugate. However, if the wave functions are not exactly the ones that minimize Eq. (13) and satisfy

Eqs. (14)–(17), the error in Eqs. (20) and (21) is larger than the error in Eq. (13), since Eq. (13) is variational, while Eqs. (20) and (21) are not.

III. A CONJUGATE-GRADIENT ALGORITHM FOR THE COMPUTATION OF THE FIRST-ORDER RESPONSES

Equations (14)–(17) are used in the BGT approach.[9,10,16] They can be solved self-consistently: one fixes first a basis set, then, supposing $H^{(1)}$ to be known, Eq. (16) is treated as a linear system of equations for $\psi^{(1)}$, whose solution can be obtained by different standard numerical techniques; once $\psi^{(1)}$ is found, it can be used to build a new $H^{(1)}$ through Eqs. (15) and (17).

In a different spirit, direct minimization of Eq. (13) is performed in the variational approach described here. These two possible approaches are directly connected to the two approaches that have been used to compute the *ground-state* properties of materials. Indeed, until 1985, the DFT ground-state wave functions were usually computed using a two-level procedure: at the lower level, Eq. (7) was solved using standard diagonalization procedures, while at the upper level, a loop used the output of this diagonalization to generate a new density through Eq. (3), and a new Hamiltonian through Eq. (6), thus a new Eq. (7). Self-consistency was enforced, if needed, by the use of some convergence accelerator.[74] This is, in spirit, similar to the BGT technique.

By contrast, Car and Parrinello[65] suggested the insertion of the quantity defined in Eq. (4) in a fictitious Lagrangian (that also included the classical kinetic energy of nuclei), giving a unified approach to molecular dynamics and DFT. As a further step, the direct minimization of the functional Eq. (4) under the orthonormalization constraints Eq. (2) was proposed. For this purpose, Teter, Payne and Allan[45] (TPA) designed a band-by-band (or state-by-state) conjugate-gradient algorithm. Other global minimization algorithms were proposed in Refs. 75–78. The Car-Parrinello and the band-by-band conjugate-gradient algorithms have been presented in considerable detail in a review article by Payne *et al.*[44] All these techniques are particularly effective with plane-wave basis sets, since the corresponding Hamiltonian is sparse when fast Fourier transforms and separable pseudopotentials are used.[79]

Since Eq. (13) is also a minimum principle, it is possible to use the same global minimization techniques for the second-order derivative of the energy $E_{\rm el}^{(2)}$ as for the ground-state energy. Moreover, the expression for $E_{\rm el}^{(2)}$, Eq. (13), is an exact quadratic form in the space of the first-order wave functions, unlike the ground-state energy functional Eq. (4). This feature leads to an easier implementation of the state-by-state conjugate-gradient algorithm for response functions than for ground-state energy, that we will now describe.

A. State-by-state decomposition of the energy functional

In a state-by-state conjugate-gradient algorithm, each wave function is considered successively, and the energy functional is minimized with respect to variations of this wave function, in the potential created by the density of the others, the latter being temporarily frozen. Let us suppose that the state β, with first-order wave function $\psi_\beta^{(1)}$, is varied. One writes the minimum principle Eq. (13) as

$$E_{\rm el}^{(2)}=E_\beta^{(2)}+E_{{\rm no}\ \beta}^{(2)}+E_{\text{non-var}}^{(2)}, \tag{22}$$

where the term $E_\beta^{(2)}$ is the only one that depends on $\psi_\beta^{(1)}$. This first term is

$$\begin{aligned}E_\beta^{(2)}=&\langle \psi_\beta^{(1)}|H^{(0)}-\epsilon_\beta^{(0)}|\psi_\beta^{(1)}\rangle+(\langle \psi_\beta^{(1)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\beta^{(0)}\rangle+\langle \psi_\beta^{(0)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\beta^{(1)}\rangle)\\&+\int\int \left.\frac{\delta^2 E_{\rm Hxc}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')}\right|_{n^{(0)}}\left(\frac{1}{2}n_\beta^{(1)}(\mathbf{r})n_\beta^{(1)}(\mathbf{r}')+n_\beta^{(1)}(\mathbf{r})\sum_{\alpha\neq\beta}^{\rm occ} n_\alpha^{(1)}(\mathbf{r}')\right)d\mathbf{r}\,d\mathbf{r}'\ ,\end{aligned} \tag{23}$$

where $n_\beta^{(1)}$, the density change due to the first-order wave function $\psi_\beta^{(1)}$, is

$$n_\beta^{(1)}(\mathbf{r})=\psi_\beta^{*(1)}(\mathbf{r})\psi_\beta^{(0)}(\mathbf{r})+\psi_\beta^{*(0)}(\mathbf{r})\psi_\beta^{(1)}(\mathbf{r}). \tag{24}$$

The second term of Eq. (22),

$$\begin{aligned}E_{{\rm no}\ \beta}^{(2)}=&\sum_{\alpha\neq\beta}^{\rm occ}\left(\langle \psi_\alpha^{(1)}|H^{(0)}-\epsilon_\alpha^{(0)}|\psi_\alpha^{(1)}\rangle+(\langle \psi_\alpha^{(1)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\alpha^{(0)}\rangle+\langle \psi_\alpha^{(0)}|v_{\rm ext}^{(1)}+v_{\rm Hxc0}^{(1)}|\psi_\alpha^{(1)}\rangle)\right)\\&+\frac{1}{2}\int\int \left.\frac{\delta^2 E_{\rm Hxc}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')}\right|_{n^{(0)}}\left(\sum_{\alpha\neq\beta}^{\rm occ} n_\alpha^{(1)}(\mathbf{r})\right)\left(\sum_{\alpha\neq\beta}^{\rm occ} n_\alpha^{(1)}(\mathbf{r}')\right)\,d\mathbf{r}\,d\mathbf{r}',\end{aligned} \tag{25}$$

does not depend on $\psi_\beta^{(1)}$, but on all the first-order wave functions for the states other than β. The third term of Eq. (22), $E_{\text{non-var}}^{(2)}$, is given by Eq. (19) and does not depend on first-order wave functions. Thus, only the first term must be considered in the minimization procedure with respect to $\psi_\beta^{(1)}$. Once the first-order wave function $\psi_\beta^{(1)}$ is sufficiently converged (via the conjugate-gradient algorithm described in the next paragraph), another first-order wave function is varied, and so on. As soon as the last wave function has been varied, the algorithm goes on with varying the first wave function again, and then the others as well. Indeed, the wave functions were minimized in the potential created by the others while these were not yet converged. Thus, there is still a self-consistency loop, although the second-order electronic energy is always decreased. Because of the latter property, the algorithm is unconditionally stable.

B. Optimization of one state

A basic description of the conjugate-gradient algorithms can be found in Ref. 80. The procedure of minimization of Eq. (23) follows closely Eqs. (5.10)–(5.38) of Ref. 44, valid for the minimization of the ground-state functional (the TPA algorithm). Except for a few details, the flow diagram of this update of a single state is very similar to the flow diagram of the TPA algorithm, shown in Fig. 17 of Ref. 44.

In the initial step $(m=1)$, a trial $\psi_\beta^{m(1)}$ is used, which is either the null vector [it obviously satisfies the constraints Eq. (14)], or the vector determined from the previous self-consistency loop.

Then, an improved $\psi_\beta^{m+1(1)}$ is determined by the following operations (iterated over m, which runs from 1 to $m_{\max}$).

(1) The steepest-descent vector ζ_β^m [minus half the gradient of Eq. (23) with respect to changes of $\psi_\beta^{m(1)}$, projected on the conduction bands] is

$$\zeta_\beta^m = -P_c[(H^{(0)}-\epsilon_\beta^{(0)})|\psi_\beta^{m(1)}\rangle + H^{m(1)}|\psi_\beta^{(0)}\rangle], \tag{26}$$

with

$$H^{m(1)} = v_{\text{ext}}^{(1)} + v_{\text{Hxc0}}^{(1)} + \int \left.\frac{\delta^2 E_{\text{Hxc}}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')}\right|_{n^{(0)}} \left[n_\beta^{m(1)}(\mathbf{r}') + \sum_{\alpha\neq\beta} n_\alpha^{(1)}(\mathbf{r}') \right] d\mathbf{r}', \tag{27}$$

where $n_\beta^{m(1)}(\mathbf{r})$ is inferred from Eq. (24), updated for each m.

(2) The preconditioned steepest-descent vector η_β^m is as follows: $\eta_\beta^m = P_c K \zeta_\beta^m$, where the preconditioning operator K is similar to the one defined in Eq. (5.16) of Ref. 44.

(3) The conjugate-gradient (or search) direction ϕ_β^m is $\phi_\beta^m = \eta_\beta^m + \gamma_\beta^m\ \phi_\beta^{m-1}$, with $\gamma_\beta^m = \langle \eta_\beta^m|\phi_\beta^m\rangle / \langle \eta_\beta^{m-1}|\phi_\beta^{m-1}\rangle$ and $\gamma_\beta^1 = 0$.

(4) An improved trial first-order $\psi_\beta^{m+1(1)}$ will be obtained by mixing $\psi_\beta^{m(1)}$ with ϕ_β^m: $\psi_\beta^{m+1(1)} = \psi_\beta^{m(1)} + \theta\ \phi_\beta^m$, where the parameter θ is to be determined by the minimization requirement, as follows. The energy Eq. (23), as a function of θ, becomes

$$E_\beta^{(2)}(\theta) = E_\beta^{(2)}(0) + \left.\frac{dE_\beta^{m(2)}}{d\theta}\right|_{\theta=0} \theta + \frac{1}{2} \left.\frac{d^2 E_\beta^{m(2)}}{d\theta^2}\right|_{\theta=0} \theta^2, \tag{28}$$

where

$$\left.\frac{dE_\beta^{m(2)}}{d\theta}\right|_{\theta=0} = -2\ \text{Re}\ \langle \phi_\beta^m|\zeta_\beta^m\rangle, \tag{29}$$

$$\left.\frac{d^2 E_\beta^{m(2)}}{d\theta^2}\right|_{\theta=0} = 2\ \langle \phi_\beta^m|H^{(0)}-\epsilon_\beta^{(0)}|\phi_\beta^m\rangle + \int\int \left.\frac{\delta^2 E_{\text{Hxc}}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')}\right|_{n^{(0)}} \Delta n_\beta^m(\mathbf{r}) \times \Delta n_\beta^m(\mathbf{r}')\,d\mathbf{r}\ d\mathbf{r}'\ , \tag{30}$$

with $\Delta n_\beta^m(\mathbf{r}) = \phi_\beta^{m*}(\mathbf{r})\psi_\beta^{(0)}(\mathbf{r}) + \psi_\beta^{*(0)}(\mathbf{r})\phi_\beta^m(\mathbf{r})$. The expression Eq. (28) is minimal when

$$\theta = -\left.\frac{dE_\beta^{m(2)}}{d\theta}\right|_{\theta=0} \left(\left.\frac{d^2 E_\beta^{m(2)}}{d\theta^2}\right|_{\theta=0} \right)^{-1}, \tag{31}$$

a value that allows one to generate $\psi_\beta^{m+1(1)}$.

In step 3, unlike for the ground-state minimization algorithm, no further orthonormalization or orthogonalization is needed [compare with Eqs. (5.21) and (5.22) of Ref. 44], since the constraint Eq. (14) is linear in $\psi_\beta^{(1)}$ and fulfilled by ϕ_β^m. In step 4, the search for the minimum of the second-order energy is simplified with respect to the ground-state minimization algorithm, because Eq. (23) is a quadratic form in $\psi_\beta^{(1)}$.

Usually, $m_{\max}$ is on the order of 4–6, while the error in the second derivative of the energy decreases by a factor of 3 or more after each set of all-state optimizations. Figure 2 of Ref. 42 shows a typical convergence of this algorithm.

In this state-by-state conjugate-gradient algorithm, only one wave function is varied at a time. Giannozzi and Baroni[33] have recently proposed to treat the minimization of Eq. (13) by simultaneous variation of all the first-order wave functions. No supplementary self-consistency loop is then needed. The latter approach requires more disk space, and a comparative study would be useful in order to assert the relative merits of both methods in terms of computational efficiency.

IV. RESPONSE TO INCOMMENSURATE PERTURBATIONS OF PERIODIC SYSTEMS

The conventions for the treatment of the unperturbed periodic system (e.g., normalization of Bloch's wave functions) are presented in Appendix A.

A. Incommensurate perturbations

One considers perturbations of the system that are incommensurate with the unperturbed periodic lattice, and characterized by a wave vector $\mathbf{q}$. In order to be able to treat nonlocal pseudopotentials, the general form of a perturbation (a linear operator and not simply a local function in space) is taken into account. The *ground-state potential* operator is periodic, with

$$v_{\text{ext}}^{(0)}(\mathbf{r}+\mathbf{R}_a,\mathbf{r}'+\mathbf{R}_a)=v_{\text{ext}}^{(0)}(\mathbf{r},\mathbf{r}'), \tag{32}$$

where $\mathbf{R}_a$ is a vector of the real space lattice, while the *perturbing potential* operator is such that

$$v_{\text{ext},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a,\mathbf{r}'+\mathbf{R}_a)=e^{i\mathbf{q}\cdot\mathbf{R}_a}\, v_{\text{ext},\mathbf{q}}^{(1)}(\mathbf{r},\mathbf{r}'). \tag{33}$$

Actually, when $\mathbf{q}$ is not equal to half a vector of the reciprocal lattice, such a perturbing potential is non-Hermitian, and should be always used in conjunction with its Hermitian conjugate counterpart. However, at the level of the linear response, there is no consequence of working only with the non-Hermitian $v_{\text{ext},\mathbf{q}}^{(1)}$, since the response to the sum of $v_{\text{ext},\mathbf{q}}^{(1)}$ and its Hermitian conjugate is simply the sum of the response to each perturbation separately. Nevertheless we are also interested in the variational property of the second-order change in energy, for which we cannot afford a non-Hermitian external potential. This difficulty is solved as follows. One considers both $v_{\text{ext},\mathbf{q}}$ and its Hermitian conjugate, written $v_{\text{ext},-\mathbf{q}}$ (since its wave vector is $-\mathbf{q}$), as well as a complex expansion parameter λ, such that

$$v_{\text{ext}}(\lambda)=v_{\text{ext}}^{(0)}+(\lambda v_{\text{ext},\mathbf{q}}^{(1)}+\lambda^* v_{\text{ext},-\mathbf{q}}^{(1)})+\ (\lambda^2 v_{\text{ext},\mathbf{q},\mathbf{q}}^{(2)} +\lambda\lambda^* v_{\text{ext},\mathbf{q},-\mathbf{q}}^{(2)}+\lambda^*\lambda\ v_{\text{ext},-\mathbf{q},\mathbf{q}}^{(2)}+\lambda^{*2} v_{\text{ext},-\mathbf{q},-\mathbf{q}}^{(2)}) +\cdots. \tag{34}$$

This definition is a generalization of Eq. (8). Since both $v_{\text{ext}}(\lambda)$ and $v_{\text{ext}}^{(0)}$ are Hermitian, the Hermitian conjugates of $v_{\text{ext},\mathbf{q}}^{(1)}$ and $v_{\text{ext},\mathbf{q},\mathbf{q}}^{(2)}$ are $v_{\text{ext},-\mathbf{q}}^{(1)}$ and $v_{\text{ext},-\mathbf{q},-\mathbf{q}}^{(2)}$, respectively. One also has the freedom to impose that $v_{\text{ext},\mathbf{q},-\mathbf{q}}^{(2)}$ is Hermitian and equal to $v_{\text{ext},-\mathbf{q},\mathbf{q}}^{(2)}$ (sometimes they will be noted $v_{\text{ext},\mathbf{0}}^{(2)}$ in what follows).

Applying a translation to the first-order wave functions and densities, one observes the following behaviors:

$$\psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a)=e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_a}\ \psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) \tag{35}$$

and

$$n_{\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a)=e^{i\mathbf{q}\cdot\mathbf{R}_a}\, n_{\mathbf{q}}^{(1)}(\mathbf{r}). \tag{36}$$

An expansion similar to Eq. (34) applies also to the energy, with

$$E(\lambda)=E^{(0)}+(\lambda E_{\mathbf{q}}^{(1)}+\lambda^* E_{-\mathbf{q}}^{(1)})+(\lambda^2 E_{\mathbf{q},\mathbf{q}}^{(2)}+2\lambda\lambda^* E_{\mathbf{q},-\mathbf{q}}^{(2)} +\lambda^{*2}E_{-\mathbf{q},-\mathbf{q}}^{(2)})+\cdots. \tag{37}$$

Due to the requirement of invariance under translation of the whole system, one derives, when $\mathbf{q}$ is not a vector of the reciprocal lattice,[81]

$$E_{\mathbf{q}}^{(1)}=E_{-\mathbf{q}}^{(1)}=0, \tag{38}$$

while for $2\mathbf{q}$ which is not a vector of the reciprocal lattice,[81]

$$E_{\mathbf{q},\mathbf{q}}^{(2)}=E_{-\mathbf{q},-\mathbf{q}}^{(2)}=0. \tag{39}$$

Thanks to these equations, it can be shown that $E_{\mathbf{q},-\mathbf{q}}^{(2)}$ is a real quantity, variational with respect to change in the first-order wave functions. This property will allow one to apply the above-mentioned minimization algorithm to the case of incommensurate perturbations.

B. Factorization of the phase

The factorization of the phase, in order to map the incommensurate problem to an equivalent one presenting the periodicity of the unperturbed problem is the crucial point in the treatment of perturbations characterized by a wave vector $\mathbf{q}$, like $v_{\text{ext},\mathbf{q}}^{(1)}$. For this purpose, inspired by Eqs. (35) and (36), one defines the *periodic* functions (see Appendix A for the notations)

$$u_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})=(N\Omega_0)^{1/2}e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\ \psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) \tag{40}$$

and

$$\overline{n}_{\mathbf{q}}^{(1)}(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\ n_{\mathbf{q}}^{(1)}(\mathbf{r}), \tag{41}$$

in which case Eq. (13) becomes

$$E_{\text{el},-\mathbf{q},\mathbf{q}}^{(2)}\{u^{(0)};u^{(1)}\}=\frac{\Omega_0}{(2\pi)^3}\int_{\text{BZ}}\sum_m^{\text{occ}} s\ (\langle u_{m\mathbf{k},\mathbf{q}}^{(1)}|H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)}-\epsilon_{m\mathbf{k}}^{(0)}|u_{m\mathbf{k},\mathbf{q}}^{(1)}\rangle+\langle u_{m\mathbf{k},\mathbf{q}}^{(1)}|v_{\text{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}^{(1)}+v_{\text{Hxc0},\mathbf{k}+\mathbf{q},\mathbf{k}}^{(1)}|u_{m\mathbf{k}}^{(0)}\rangle \\ +\langle u_{m\mathbf{k}}^{(0)}|v_{\text{ext},\mathbf{k},\mathbf{k}+\mathbf{q}}^{(1)}+v_{\text{Hxc0},\mathbf{k}+\mathbf{q},\mathbf{k}}^{(1)}|u_{m\mathbf{k},\mathbf{q}}^{(1)}\rangle+\langle u_{m\mathbf{k}}^{(0)}|v_{\text{ext},\mathbf{k},\mathbf{k}}^{(2)}|u_{m\mathbf{k}}^{(0)}\rangle)d\mathbf{k} \\ +\frac{1}{2}\int_{\Omega_0}\int \left.\frac{\delta^2 E_{\text{Hxc}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n^{(0)}} \overline{n}_{\mathbf{q}}^{(1)*}(\mathbf{r})\ \overline{n}_{\mathbf{q}}^{(1)}(\mathbf{r}')e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{r}\ d\mathbf{r}'+\frac{1}{2}\left.\frac{d^2E_{\text{Hxc}}}{d\lambda\ d\lambda^*}\right|_{n^{(0)}}, \tag{42}$$

satisfying a minimum principle with respect to variations of the first-order wave functions $u_{n,\mathbf{k},\mathbf{q}}^{(1)}$ under constraints

$$\langle u_{m,\mathbf{k}+\mathbf{q}}^{(0)}|u_{n,\mathbf{k},\mathbf{q}}^{(1)}\rangle=0, \tag{43}$$

where the index n runs over the occupied states, while the first-order change in density is given by[82]

$$\overline{n}_{\mathbf{q}}^{(1)}(\mathbf{r})=\frac{2}{(2\pi)^3}\int_{\text{BZ}}\sum_m^{\text{occ}} s u_{m\mathbf{k}}^{(0)*}(\mathbf{r})u_{m\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})d\mathbf{k}. \tag{44}$$

The Euler-Lagrange equations associated with the minimization of Eq. (42) under constraints Eq. (43) are

$$P_{c,\mathbf{k}+\mathbf{q}}(H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}-\epsilon^{(0)}_{m,\mathbf{k}})P_{c,\mathbf{k}+\mathbf{q}}\,|u^{(1)}_{m,\mathbf{k},\mathbf{q}}\rangle$$
$$=-P_{c,\mathbf{k}+\mathbf{q}}H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}|u^{(0)}_{m,\mathbf{k}}\rangle, \tag{45}$$

with

$$H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}=v^{(1)}_{\text{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}+v^{(1)}_{\text{Hxc0},\mathbf{k}+\mathbf{q},\mathbf{k}}+\int\left.\frac{\delta^2E_{\text{Hxc}}}{\delta n(\mathbf{r})\,\delta n(\mathbf{r}')}\right|_{n^{(0)}}$$
$$\times\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r}')e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\,d\mathbf{r}'. \tag{46}$$

Finally, there are simpler, but nonvariational, expressions for $E^{(2)}_{\text{el},-\mathbf{q},\mathbf{q}}$, in the spirit of Eq. (21):[82]

$$E^{(2)}_{\text{el},-\mathbf{q},\mathbf{q}}\{u^{(0)};u^{(1)}\}$$
$$=\frac{\Omega_0}{(2\pi)^3}\int_{\text{BZ}}\sum_m^{\text{occ}} s\,\big(\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|v^{(1)}_{\text{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}+v^{(1)}_{\text{Hxc0},\mathbf{k}+\mathbf{q},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle$$
$$+\langle u^{(0)}_{m\mathbf{k}}|v^{(2)}_{\text{ext},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle\big)d\mathbf{k}+\frac{1}{2}\left.\frac{d^2E_{\text{Hxc}}}{d\lambda\;d\lambda^*}\right|_{n^{(0)}}, \tag{47}$$

its Hermitian conjugate, or their mean. All the quantities that appear in Eqs. (42)–(47) have the periodicity of the unperturbed lattice. Note that the ground-state wave functions at $\mathbf{k}$ and at $\mathbf{k}+\mathbf{q}$ are needed to determine $u^{(1)}_{m\mathbf{k},\mathbf{q}}$: $u^{(0)}_{m\mathbf{k}}$ appear in Eqs. (42), (44), and (45), while the orthonormalization constraint Eq. (43) makes use of $u^{(0)}_{m\mathbf{k}+\mathbf{q}}$.

V. RESPONSE TO COLLECTIVE ATOMIC DISPLACEMENTS

We now focus on a first class of perturbations, directly connected to phonons. In this section and the next ones, the responses are treated in view of the implementation of the formalism with a plane-wave basis set, separable pseudopotentials, and taking into account the nonlinear exchange-correlation core correction. The notations (definitions of local and separable potentials, exchange-correlation functional) are described in Appendix A. The different quantities will be given either in the real space or in the reciprocal space, whichever is the most appropriate.[83]

A. First- and second-order changes in potential operators

One considers unit displacements of atoms in sublattice κ, along the α axis, multiplied by the infinitesimal λ (eventually, a complex quantity) and by a phase varying with the cell to which the atoms belong: the α component of their vector position is changed from $\tau_{\kappa,\alpha}+R_{a,\alpha}$ to $\tau_{\kappa,\alpha}+R_{a,\alpha}+\lambda e^{i\mathbf{q}\cdot\mathbf{R}_a}$. Atoms in the other sublattices are not displaced. Note that all of these collective displacements can be generated from $\mathbf{q}$ wave vectors restricted inside the Brillouin zone, the only ones that will be considered. Also, for reasons given in Sec. VII A and in the next paper (P2), we consider nonzero $\mathbf{q}$ wave vectors.

The first-order change in the potential operator Eq. (A12) (see Appendix A) is

$$v^{(1)}_{\text{ext},\mathbf{q}}(\mathbf{r},\mathbf{r}')=\sum_a e^{i\mathbf{q}\cdot\mathbf{R}_a}\frac{\partial}{\partial\tau_{\kappa,\alpha}}v_\kappa(\mathbf{r}-\boldsymbol{\tau}_\kappa-\mathbf{R}_a,\mathbf{r}'-\boldsymbol{\tau}_\kappa-\mathbf{R}_a), \tag{48}$$

while the second-order $v^{(2)}_{\text{ext},\mathbf{0}}(\mathbf{r},\mathbf{r}')$, needed in Eqs. (42) and (47), is as follows:

$$v^{(2)}_{\text{ext}}(\mathbf{r},\mathbf{r}')=\sum_a\frac{1}{2}\frac{\partial^2}{\partial\tau^2_{\kappa,\alpha}}v_\kappa(\mathbf{r}-\boldsymbol{\tau}_\kappa-\mathbf{R}_a,\mathbf{r}'-\boldsymbol{\tau}_\kappa-\mathbf{R}_a). \tag{49}$$

Their evaluation, based on Eqs. (A15) and (A19), leads to the following expressions

(1) The first-order change of the local potential is

$$\overline{v^{(1)}_{\text{loc},\mathbf{q}}}(\mathbf{G})=\frac{1}{\Omega_0}\frac{\partial}{\partial\tau_{\kappa\alpha}}(e^{-i(\mathbf{G}+\mathbf{q})\cdot\boldsymbol{\tau}_\kappa})\;v^{\text{loc}}_\kappa(\mathbf{G}+\mathbf{q})$$
$$=\frac{1}{\Omega_0}(-i)(\mathbf{G}+\mathbf{q})_\alpha e^{-i(\mathbf{G}+\mathbf{q})\cdot\boldsymbol{\tau}_\kappa}\;v^{\text{loc}}_\kappa(\mathbf{G}+\mathbf{q}), \tag{50}$$

where $v^{\text{loc}}_\kappa(\mathbf{G}+\mathbf{q})$ can be found from Eq. (A16), and where the definition of the phase-factorized, periodic potential

$$\overline{v^{(1)}_{\text{loc},\mathbf{q}}}(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\;v^{(1)}_{\text{loc},\mathbf{q}}(\mathbf{r}), \tag{51}$$

has been used [compare with Eq. (41)]. Note that, unlike in Eqs. (A15) and (A27), $\overline{v^{(1)}_{\text{loc},\mathbf{q}}}$ includes the $\mathbf{G}=0$ contribution: there is no associated divergence since we have supposed $\mathbf{q}$ to be nonzero.

(2) The second-order change of the local potential is[84,85]

$$v'^{(2)}_{\text{loc}}(\mathbf{G})=-\frac{1}{\Omega_0}\frac{1}{2}G^2_\alpha(e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_\kappa})\;v^{\text{loc}}_\kappa(\mathbf{G})\quad\text{when}\quad\mathbf{G}\neq\mathbf{0}$$
$$=0\quad\text{when}\quad\mathbf{G}=\mathbf{0}. \tag{52}$$

(3) The first-order change of the nonlocal potential is

$$v^{(1)}_{\text{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{\Omega_0}\sum_\mu e_{\mu\kappa}\frac{\partial}{\partial\tau_{\kappa\alpha}}$$
$$\times\left[\left(\sum_G e^{-i(\mathbf{k}+\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{q}+\mathbf{G})\right)\right.$$
$$\left.\times\left(\sum_{G'} e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_\kappa}\zeta^*_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\right)\right]. \tag{53}$$

(4) The second-order change of the nonlocal potential is

$$v^{(2)}_{\text{sep},\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{\Omega_0}\sum_\mu e_{\mu\kappa}\frac{1}{2}\frac{\partial^2}{\partial\tau^2_{\kappa\alpha}}$$
$$\times\left[\left(\sum_G e^{-i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{G})\right)\right.$$
$$\left.\times\left(\sum_{G'} e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_\kappa}\zeta^*_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\right)\right]. \tag{54}$$

The efficient use of $v^{(1)}_{\text{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}$ as well as $v^{(2)}_{\text{sep},\mathbf{k},\mathbf{k}}$ is accomplished thanks to a further manipulation, an example of which is given here for the first-order separable part: Eq. (53) becomes

$$v^{(1)}_{\mathrm{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{\Omega_0}\sum_{\mu} e_{\mu\kappa}\Bigg[\Bigg(\sum_{G}(-i)(\mathbf{k}+\mathbf{q}+\mathbf{G})_{\alpha}e^{-i(\mathbf{k}+\mathbf{q}+\mathbf{G})\cdot\boldsymbol{\tau}_{\kappa}}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{q}+\mathbf{G})\Bigg)\Bigg(\sum_{G'}e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_{\kappa}}\zeta^{*}_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\Bigg)$$
$$+\Bigg(\sum_{G}e^{-i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{\tau}_{\kappa}}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{q}+\mathbf{G})\Bigg)\Bigg(\sum_{G'}i(\mathbf{k}+\mathbf{q}+\mathbf{G}')_{\alpha}e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_{\kappa}}\zeta^{*}_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\Bigg)\Bigg]. \tag{55}$$

In this way, the sums on the reciprocal vectors $\mathbf{G}$ or $\mathbf{G}'$ are well separated. The same manipulation can be performed on Eq. (54).

B. First- and second-order changes in the exchange and correlation energy functional

The phase-factorized first-order change of pseudocore charge density is given by

$$\overline{n^{(1)}_{\mathrm{c},\mathbf{q}}}(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{a}e^{i\mathbf{q}\cdot\mathbf{R}_a}\frac{\partial}{\partial\tau_{\kappa,\alpha}}n_{c,\kappa}(\mathbf{r}-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_a), \tag{56}$$

while the second-order change is

$$n^{(2)}_{\mathrm{c}}(\mathbf{r})=\sum_{a}\frac{1}{2}\frac{\partial^2}{\partial\tau^2_{\kappa,\alpha}}n_{c,\kappa}(\mathbf{r}-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_a). \tag{57}$$

These expressions allow us to build $\overline{v^{(1)}_{\mathrm{xc}0,\mathbf{q}}}$ and $\frac{1}{2}(d^2E_{\mathrm{xc}}/d\lambda\ d\lambda^*)|_{n^{(0)}}$:[31]

$$\overline{v^{(1)}_{\mathrm{xc}0,\mathbf{q}}}(\mathbf{r})=\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}\overline{n^{(1)}_{\mathrm{c},\mathbf{q}}}(\mathbf{r}) \tag{58}$$

and

$$\frac{1}{2}\frac{d^2E_{\mathrm{xc}}}{d\lambda\ d\lambda^*}\bigg|_{n^{(0)}}=\frac{1}{2}\int_{\Omega_0}\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}|\overline{n^{(1)}_{\mathrm{c},\mathbf{q}}}(\mathbf{r})|^2d\mathbf{r}$$
$$+\int_{\Omega_0}v_{\mathrm{xc}}(n^{(0)}(\mathbf{r}))n^{(2)}_{\mathrm{c}}(\mathbf{r})d\mathbf{r}. \tag{59}$$

C. Variational principle

Having obtained the first and second derivatives of the potentials and exchange-correlation energy functional, we are able to write the second-order electronic energy:

$$E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}\{u^{(0)};u^{(1)}\}=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_{m}^{\mathrm{occ}}s\,(\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}-\epsilon^{(0)}_{m\mathbf{k}}|u^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle+\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|v^{(1)}_{\mathrm{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle+\langle u^{(0)}_{m\mathbf{k}}|v^{(1)}_{\mathrm{sep},\mathbf{k},\mathbf{k}+\mathbf{q}}|u^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle$$
$$+\langle u^{(0)}_{m\mathbf{k}}|v^{(2)}_{\mathrm{sep},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle)d\mathbf{k}+\frac{1}{2}\int_{\Omega_0}([\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r})]^*[\overline{v^{(1)}_{\mathrm{loc},\mathbf{q}}}(\mathbf{r})+\overline{v^{(1)}_{\mathrm{xc}0,\mathbf{q}}}(\mathbf{r})]+[\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r})][\overline{v^{(1)}_{\mathrm{loc},\mathbf{q}}}(\mathbf{r})+\overline{v^{(1)}_{\mathrm{xc}0,\mathbf{q}}}(\mathbf{r})]^*)d\mathbf{r}$$
$$+\frac{1}{2}\int_{\Omega_0}\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}|\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r})|^2d\mathbf{r}+2\pi\Omega_0\sum_{\mathbf{G}}\frac{|\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{G})|^2}{|\mathbf{q}+\mathbf{G}|^2}+\int_{\Omega_0}(n^{(0)}(\mathbf{r})v'^{(2)}_{\mathrm{loc}}(\mathbf{r}))d\mathbf{r}+\frac{1}{2}\frac{d^2E_{\mathrm{xc}}}{d\lambda\ d\lambda^*}\bigg|_{n^{(0)}}. \tag{60}$$

In this expression, as for $\overline{v^{(1)}_{\mathrm{loc},\mathbf{q}}}$ in Eq. (50), the $\mathbf{G}=\mathbf{0}$ contribution is included in the Hartree term: there is no associated divergence since we have supposed $\mathbf{q}$ to be nonzero.

Equation (60) is to be minimized under the constraints Eq. (43), with the first-order change in density given by Eq. (44). The associated Euler-Lagrange equation is still Eq. (45), with a more explicit first-order Hamiltonian operator:

$$H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}=v^{(1)}_{\mathrm{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}+\overline{v^{(1)}_{\mathrm{loc},\mathbf{q}}}+\overline{v^{(1)}_{\mathrm{H},\mathbf{q}}}+\overline{v^{(1)}_{\mathrm{xc},\mathbf{q}}}, \tag{61}$$

where

$$\overline{v^{(1)}_{\mathrm{H},\mathbf{q}}}(\mathbf{G})=4\pi\frac{\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{G})}{|\mathbf{G}+\mathbf{q}|^2} \tag{62}$$

and

$$\overline{v^{(1)}_{\mathrm{xc},\mathbf{q}}}(\mathbf{r})=\Bigg(\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r})\Bigg)+\overline{v^{(1)}_{\mathrm{xc}0,\mathbf{q}}}(\mathbf{r}). \tag{63}$$

Finally, there exists simpler, but nonvariational expressions for $E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}$, derived from Eq. (47): for example,

$$E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\ (\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|v^{(1)}_{\mathrm{sep},\mathbf{k}+\mathbf{q},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle$$
$$+\langle u^{(0)}_{m\mathbf{k}}|v^{(2)}_{\mathrm{sep},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle)d\mathbf{k}$$
$$+\frac{1}{2}\int_{\Omega_0}([\overline{n^{(1)}_{\mathbf{q}}}(\mathbf{r})]^*[\overline{v^{(1)}_{\mathrm{loc},\mathbf{q}}}(\mathbf{r})+\overline{v^{(1)}_{\mathrm{xc0},\mathbf{q}}}(\mathbf{r})])d\mathbf{r}$$
$$+\int_{\Omega_0}(n^{(0)}(\mathbf{r})v'^{(2)}_{\mathrm{loc}}(\mathbf{r}))d\mathbf{r}+\frac{1}{2}\left.\frac{d^2E_{\mathrm{xc}}}{d\lambda\ d\lambda^*}\right|_{n^{(0)}}. \tag{64}$$

At this stage, we have written all the theoretical ingredients needed for the computation of the response to a collective displacement of atoms on one sublattice, in which the vector position $\tau_{\kappa,\alpha}+R_{a,\alpha}$ is changed into $\tau_{\kappa,\alpha}+R_{a,\alpha}+\lambda e^{i\mathbf{q}\cdot\mathbf{R}_a}$. In further sections, in order not to confuse them with the response to other perturbations, the first-order quantities related to this perturbation will be written $X^{\tau_{\kappa\alpha}}_{\mathbf{q}}$ instead of $X^{(1)}_{\mathbf{q}}$, while the corresponding second-order quantities will be denoted by $X^{\tau^*_{\kappa\alpha}\tau_{\kappa\alpha}}_{-\mathbf{q},\mathbf{q}}$ instead of $X^{(2)}_{-\mathbf{q},\mathbf{q}}$.

VI. RESPONSE TO AN HOMOGENEOUS, STATIC ELECTRIC FIELD

Two important problems arise when one attempts to deal with the response to an homogeneous, static electric field. The first problem comes from the fact that the potential energy of the electron, placed in such a field, is linear in space, and breaks the periodicity of the crystalline lattice:[86]

$$v_{\mathrm{scr}}(\mathbf{r})=\sum_\alpha \mathcal{E}_{\mathrm{mac},\alpha}\ r_\alpha. \tag{65}$$

Second, this macroscopic electric field corresponds to a screened potential: the change of macroscopic electric field is the sum of an external change of field and an internal change of field, the latter being induced by the response of the electrons (the polarization of the material). In order to indicate this fact, the subscript ''scr'' has been used in Eq. (65). In the theory of classical electromagnetism,[87] the connection between the macroscopic displacement, electric, and polarization fields is

$$\mathcal{D}_{\mathrm{mac}}(\mathbf{r})=\mathcal{E}_{\mathrm{mac}}(\mathbf{r})+4\pi\mathcal{P}_{\mathrm{mac}}(\mathbf{r}), \tag{66}$$

where $\mathcal{P}_{\mathrm{mac}}(\mathbf{r})$ is related to the macroscopic charge density by

$$n_{\mathrm{mac}}(\mathbf{r})=-\nabla\mathcal{P}_{\mathrm{mac}}(\mathbf{r}). \tag{67}$$

It is important to emphasize that these fields are *macroscopic* fields: the microscopic fluctuations (local fields) have been averaged out in this description.[87]

The long-wave method is commonly used to deal with the first problem: a potential linear in space is obtained as the limit for $\mathbf{q}$ tending to $\mathbf{0}$ of

$$v(\mathbf{r})=\lim_{\mathbf{q}\to 0}\lambda\frac{2\sin\mathbf{q}\cdot\mathbf{r}}{|\mathbf{q}|}=\lim_{\mathbf{q}\to 0}\lambda\left(\frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{i|\mathbf{q}|}-\frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{i|\mathbf{q}|}\right), \tag{68}$$

where $\mathbf{q}$ is in the direction of the homogeneous field. This method has its drawback: the homogeneous field and the wave vector are always parallel. In other words, the electric field is longitudinal. The treatment of transverse fields should be done by considering not only a scalar potential, but a vector potential. However, for our purpose, the scalar theory will be sufficient.[26]

The detailed theoretical treatment of the response to an electric field, using the long-wave method, and treating the screening adequately (in order to solve the above-mentioned second problem) is given in Appendix B. It is found that an auxiliary quantity is needed: the derivative of the ground-state wave functions with respect to their wave vector. Once this quantity has been obtained, the computation of the response to an homogeneous electric field *per se* can be performed.

A. Derivative of the wave functions with respect to their wave vector

We will use the shorthand notation

$$u^{k_\alpha}_{m\mathbf{k}}=\frac{du^{(0)}_{m\mathbf{k}}}{dk_\alpha}. \tag{69}$$

In the parallel-transport gauge,[42] the $u^{k_\alpha}_{m\mathbf{k}}$ at each $\mathbf{k}$ can be determined by the minimization of the following expression:

$$E^{k_\alpha k_\alpha}_{m,\mathbf{k}}=\langle u^{k_\alpha}_{m\mathbf{k}}|H^{(0)}_{\mathbf{k},\mathbf{k}}-\epsilon^{(0)}_{m\mathbf{k}}|u^{k_\alpha}_{m\mathbf{k}}\rangle+\langle u^{k_\alpha}_{m\mathbf{k}}|T^{k_\alpha}_{\mathbf{k},\mathbf{k}}-v^{k_\alpha}_{\mathrm{sep},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle$$
$$+\langle u^{(0)}_{m\mathbf{k}}|T^{k_\alpha}_{\mathbf{k},\mathbf{k}}-v^{k_\alpha}_{\mathrm{sep},\mathbf{k},\mathbf{k}}|u^{k_\alpha}_{m\mathbf{k}}\rangle, \tag{70}$$

with the constraints

$$\langle u^{(0)}_{m\mathbf{k}}|u^{k_\alpha}_{n\mathbf{k}}\rangle=0. \tag{71}$$

$T^{k_\alpha}_{\mathbf{k},\mathbf{k}}$ and $v^{k_\alpha}_{\mathrm{sep},\mathbf{k},\mathbf{k}}$ are the first derivative of kinetic energy operator and external potential with respect to the wave vector k_α:

$$T^{k_\alpha}_{\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}')=(G_\alpha+k_\alpha)\,\delta_{\mathbf{G}\mathbf{G}'} \tag{72}$$

and

$$v^{k_\alpha}_{\mathrm{sep},\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{\Omega_0}\sum_{\mu\kappa} e_{\mu\kappa}\frac{\partial}{\partial k_\alpha}$$
$$\times\left[\left(\sum_G e^{-i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{\tau}_\kappa}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{G})\right)\right.$$
$$\left.\times\left(\sum_{G'} e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_\kappa}\zeta^*_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\right)\right]. \tag{73}$$

The Euler-Lagrange equation associated with the minimization procedure Eq. (70) is

$$P_{c,\mathbf{k}}(H^{(0)}_{\mathbf{k},\mathbf{k}}-\epsilon^{(0)}_{m,\mathbf{k}})P_{c,\mathbf{k}}\,|u^{k_\alpha}_{m,\mathbf{k}}\rangle=-P_{c,\mathbf{k}}(T^{k_\alpha}_{\mathbf{k},\mathbf{k}}+v^{k_\alpha}_{\mathrm{sep},\mathbf{k},\mathbf{k}})|u^{(0)}_{m,\mathbf{k}}\rangle. \tag{74}$$

B. Derivative of the wave functions with respect to an electric field

Having obtained the derivative of the wave functions with respect to their wave vector, one is able to compute the response of the system with respect to the change of the long-wave screened potential

$$\Delta v_{\mathrm{scr}}(\mathbf{r})=\lim_{\mathbf{q}\rightarrow 0}\left(\mathcal{E}_\alpha\frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{i|\mathbf{q}|}+\mathcal{E}_\alpha^{*}\frac{e^{-i\mathbf{q}\cdot\mathbf{r}}}{(-i)|\mathbf{q}|}\right). \tag{75}$$

In the parallel-transport gauge,[42] the derivative of the wave functions with respect to $\mathcal{E}_\alpha$ is obtained through the minimization of the following expression (for which, as at the end of Sec. V, we rationalize our notation in view of the multiplicity of perturbations that are examined):

$$\begin{aligned}E_{\mathrm{el}}^{\mathcal{E}_\alpha^{*}\mathcal{E}_\alpha}\{u^{(0)};u^{\mathcal{E}_\alpha}\}=&\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s(\langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha}|H_{\mathbf{k},\mathbf{k}}^{(0)}-\epsilon_{m\mathbf{k}}^{(0)}|u_{m\mathbf{k}}^{\mathcal{E}_\alpha}\rangle\\&+\langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha}|iu_{m\mathbf{k}}^{k_\alpha}\rangle+\langle iu_{m\mathbf{k}}^{k_\alpha}|u_{m\mathbf{k}}^{\mathcal{E}_\alpha}\rangle)d\mathbf{k}\\&+\frac{1}{2}\int_{\Omega_0}\left.\frac{dv_{\mathrm{xc}}}{dn}\right|_{n^{(0)}(\mathbf{r})}|n^{\mathcal{E}_\alpha}(\mathbf{r})|^2\\&+2\pi\Omega_0\sum_{\mathbf{G}\neq\mathbf{0}}\frac{|n^{\mathcal{E}_\alpha}(\mathbf{G})|^2}{|\mathbf{G}|^2},\end{aligned} \tag{76}$$

with

$$n^{\mathcal{E}_\alpha}(\mathbf{r})=\frac{2}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} su_{m\mathbf{k}}^{(0)*}(\mathbf{r})u_{m\mathbf{k}}^{\mathcal{E}_\alpha}(\mathbf{r})d\mathbf{k}, \tag{77}$$

under the constraints

$$\langle u_{m,\mathbf{k}}^{(0)}|u_{n\mathbf{k}}^{\mathcal{E}_\alpha}\rangle=0, \tag{78}$$

where the indices m and n run over occupied states, and $\langle iu_{m\mathbf{k}}^{k_\alpha}|=(-i)\langle u_{m\mathbf{k}}^{k_\alpha}|$.[88]

The associated Euler-Lagrange equations are

$$\begin{aligned}&P_{c,\mathbf{k}}(H_{\mathbf{k},\mathbf{k}}^{(0)}-\epsilon_{m,\mathbf{k}}^{(0)})P_{c,\mathbf{k}}\;|u_{m,\mathbf{k}}^{k_\alpha}\rangle\\&\qquad=-P_{c,\mathbf{k}}\left(i\frac{\partial}{\partial k_\alpha}+v_{\mathrm{H}}^{\prime\mathcal{E}_\alpha}+v_{\mathrm{xc}}^{\mathcal{E}_\alpha}\right)|u_{m,\mathbf{k}}^{(0)}\rangle\end{aligned} \tag{79}$$

with[84,85]

$$\begin{aligned}v_{\mathrm{H}}^{\prime\mathcal{E}_\alpha}(\mathbf{G})&=4\pi\frac{n^{\mathcal{E}_\alpha}(\mathbf{G})}{|\mathbf{G}|^2}\quad\text{when}\quad\mathbf{G}\neq\mathbf{0}\\&=0\quad\text{when}\quad\mathbf{G}=\mathbf{0}\end{aligned} \tag{80}$$

and

$$v_{\mathrm{xc}}^{\mathcal{E}_\alpha}(\mathbf{r})=\left.\frac{dv_{\mathrm{xc}}}{dn}\right|_{n^{(0)}(\mathbf{r})}n^{\mathcal{E}_\alpha}(\mathbf{r}). \tag{81}$$

The nonvariational expressions for $E_{\mathrm{el}}^{\mathcal{E}_\alpha^{*}\mathcal{E}_\alpha}$ can be obtained as well: for example,

$$E_{\mathrm{el}}^{\mathcal{E}_\alpha^{*}\mathcal{E}_\alpha}=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\;\langle iu_{m\mathbf{k}}^{k_\alpha}|u_{m\mathbf{k}}^{\mathcal{E}_\alpha}\rangle d\mathbf{k}. \tag{82}$$

In Eqs. (76) and (79), the operator $i(\partial/\partial k_\alpha)$ acts on the wave functions $u_{m,\mathbf{k}}^{(0)}$ to replace the operator r_α, which should have been considered if there was no problem of compatibility between the linear potential Eq. (65) and the periodicity of the crystal. This result had been also obtained by other mathematical transformations.[89]

VII. TECHNICALITIES

A. Linear combination of perturbations

In Secs. V and VI, we have examined the responses with respect to two important classes of perturbations: wave-vector-characterized collective atomic displacements, and homogeneous electric fields. We were also lead to consider derivatives of the wave functions with respect to their wave vector. These perturbations will be considered as basic perturbations. Since we are at the level of the linear response, the response of the system to a linear combination of these perturbations will be the linear combination of the responses of the system to each perturbation: for example, if a first-order change of potential is described by

$$v_{\mathbf{q}}^{(1)}=C_1v_{\mathbf{q}}^{\tau_\kappa,\alpha}+C_2v_{\mathbf{q}}^{\tau_{\kappa'},\beta}, \tag{83}$$

then the density response will be

$$n_{\mathbf{q}}^{(1)}=C_1n_{\mathbf{q}}^{\tau_\kappa,\alpha}+C_2n_{\mathbf{q}}^{\tau_{\kappa'},\beta}. \tag{84}$$

This rule also applies to a linear combination of perturbations incommensurate with each other, or of different types.

As such, it gives a powerful approach to the treatment of the $\mathbf{q}\rightarrow\mathbf{0}$ limit of the response to collective atomic displacements. Indeed, the singularities observed in Eqs. (60) and (62) in the $\mathbf{q}\rightarrow\mathbf{0}$ limit can be treated separately, as an homogeneous electric field associated with the collective atomic displacements. Thus, for $\mathbf{q}\rightarrow\mathbf{0}$, we will first compute the response to a collective atomic displacement without associated electric field [by considering Eq. (60) without the $\mathbf{G}=\mathbf{0}$ contribution in the local potential and the Hartree term], and then combines it with the response to an electric field, as elaborated on in Ref. 16 and P2.[4]

As a complementary advantage of working with linear combination of perturbations, in the case where one does not want to compute the response to these basic perturbations, but would like to compute directly the response to one, specific perturbation not contained in this set of basic perturbations, one can tailor a variational expression by inserting the correct first-order change of potential into the expression Eq. (42), the latter being eventually worked out along the lines developed in Sec. VI.

Interestingly, the computations of the responses to a different set of perturbations are completely independent of each other, and offer a trivial way to parallelize the code. The amount of computation to be done to get the response to one perturbation is rather large compared to the time needed to initialize or gather the results of the different response computations, and there is no communication during the computation of responses. Thus the parallelization will be rather efficient, as soon as the number of perturbations to be treated is sufficiently large compared to the number of independent processors.[90] This part of the overall process of computing dynamical and dielectric properties is by far the most computing intensive. The steps explained in the P2 (Ref. 4) are at least one order of magnitude less time consuming, and can be easily parallelized as well.

B. Method of solution

Although the atomic displacement and electric field types of perturbations are different, we arrive at strikingly similar variational principles [Eqs. (60) and (76)] under the same type of constraints [Eqs. (43) and (78)], and the same rule for the formation of the density change from wave functions changes [Eqs. (44) and (77)]. The state-by-state conjugate-gradient algorithm previously described (Sec. III) can be applied straightforwardly to all of these minimization problems. Most of the routines of the code will be common to all the perturbations, because of the common form of the variational principle.

The computation of the steepest-descent vector, Eq. (26), will be the most time-consuming step in the state-by-state iterations. As already mentioned, the use of the fast Fourier transform allows us to make it tractable. In particular, when the zero-order Hamiltonian $H^{(0)}$ is to be applied to the change in first-order wave function, (a) the latter, available in the reciprocal space, is Fourier transformed to the real space; (b) the local potential part of $H^{(0)}$ is applied to it; (c) the remaining of the right-hand side of Eq. (26) is added; (d) the sum is backtransformed to the reciprocal space; (e) finally, one adds the result of applying the kinetic operator and separable potentials to the first-order wave function, since these operations are less time consuming (at the level of a few atoms per unit cell). Fast Fourier transforms are also needed to evaluate and update the Hartree potential Eqs. (27) and (30).

The computation of the derivative of the wave functions with respect to their wave vector can also be done using the same methodology. The quantity to be minimized, Eq. (70), is even simpler than those contained in Eqs. (60) and (76). The routines will be also similar.

C. Sampling of the Brillouin zone and symmetries

In view of the practical implementation of Eqs. (60) and (76), other comments must still be made. First, the integral over the Brillouin zone must be replaced by a summation, through discretization of the **k** space. For insulators, one can use the special **k** point technique of Ref. 91. This replacement is well-known in ground-state calculations. Its use in perturbed situations does not lead to technical problems. For metals, the existence of the Fermi surface, and occupied or unoccupied states below or above it, raises interesting questions. The techniques described by de Gironcoli[32] and Savrasov[22] can be adapted to the present variational approach.

Although it is a usual practice to fix the grid of **k** points, and then perform the computation of phonons only for the **q**-wave vectors that are differences between two **k** points in this grid, this attitude is not mandatory, as shown by the present theory. Though, some additional small error might appear when this rule is not followed,[92] although likely not larger than the error associated with the replacement of the integral over the Brillouin zone by a summation on a discrete set of points.

In the ground-state calculations, one is able to reduce the number of **k** points by folding the Brillouin zone to its irreducible part, using the spatial symmetries and the time-reversal symmetry, with a considerable reduction in computing time. In general, it will not be possible to achieve the same gain in response calculations with respect to a perturbation of the atomic displacement or electric field type, because some symmetries will usually be broken by the perturbation. The collective atomic displacements are characterized by their **q** wave vector, the sublattice κ that is displaced, and the direction of the displacement α. Only when all of these elements are left invariant by some symmetry operation, will it be possible to reduce the number of **k** wave vectors for the summation on the Brillouin zone, for this perturbation. Nevertheless, all the other symmetry operations can be used to deduce the response with respect to another, symmetry-related one.

By the time-reversal symmetry, the wave vector **q** is mapped to $-\mathbf{q}$. So, the response to a $-\mathbf{q}$ perturbation can be deduced from the response to a **q** perturbation. Also, the number of **k** points can be decreased by a factor of two, when $2\mathbf{q}$ is equal to a reciprocal-space **G** vector.

The electric field perturbation is characterized by its direction α. It is left invariant by the time-reversal symmetry, so that the number of **k** wave vectors for the summation on the Brillouin zone can usually be halved. If, moreover, point-group symmetries leave the α direction invariant, the number of **k** wave vectors can be further decreased. If not, the other symmetries can be used to relate the response with respect to an electric field along some direction with the response with respect to an electric field along another direction.

The computation of the derivative of wave functions with respect to their wave vector **k** can also benefit from symmetry operations. However, this computation is rather fast, since there is no self-consistency step in the conjugate-gradient minimization.

VIII. PERSPECTIVES

The aim of the present paper was to present a formalism (theory and algorithm) based on a variational principle within the DFPT, which allows one to obtain responses to atomic displacements and homogeneous electric fields. P2 (Ref. 4) describes the further manipulations needed to determine the dynamical matrices, interatomic force constant, Born effective charges, and dielectric permittivity tensors. Other papers mentioned in the Introduction give examples of the application of this technique.

The technical advantages that are characteristics of the perturbative approaches, like the one developed by Baroni, Giannozzi, and Testa,[10,16] have been shown to be also valid in the present variational approach: a periodic problem to which an incommensurable perturbation is imposed can be mapped on an unperturbed unit-cell problem, amounting to a considerable reduction of computing time; an homogeneous electric field, whose potential breaks the periodicity of the lattice, can be treated by the long-wave method; because the formalism is very similar for the different perturbations, the implementation of codes for all these properties requires reasonable human work. The state-by-state conjugate-gradient algorithm has the nice property of being unconditionally convergent, since the trial second-order derivative of the energy is always decreased, and its convergence is easy to monitor, the right value being approached from above.

The present technique can be extended to cover more perturbations, especially those derived from modifications of the unit-cell size and shape,[93] or from alchemical transformation of atoms.[94,28] A variational principle for second-order derivatives of the total energy will be equally valid for these other perturbations, and the same conjugate-gradient algorithm can be used efficiently for these.

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APPENDIX A: CONVENTIONS FOR THE UNPERTURBED PERIODIC SYSTEM

The present appendix describes the conventions on which the perturbed expressions developed in this paper are based: Fourier transform, the relation between real and reciprocal space, the local and separable parts of pseudopotentials, exchange-correlation functional in the LDA with nonlinear core correction.

1. Periodic system: Real and reciprocal space

By Bloch's theorem, each wave function can be decomposed in a product of a phase factor by a periodic function. Explicitly, we write the ground-state unperturbed wave functions as

$$\psi^{(0)}_{m\mathbf{k}}(\mathbf{r})=(N\Omega_0)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}u^{(0)}_{m\mathbf{k}}(\mathbf{r}), \tag{A1}$$

where N is the number of unit cells repeated in the Born–von Karman periodic box, and Ω_0 the volume of the unperturbed unit cell. m and $\mathbf{k}$ label the number of the band and the wave vector of the wave function, respectively. The periodic function can be expanded in terms of plane waves as follows:[95]

$$u^{(0)}_{m\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}u^{(0)}_{m\mathbf{k}}(\mathbf{G}), \tag{A2}$$

where the coefficients $u^{(0)}_{m\mathbf{k}}(\mathbf{G})$ are the Fourier transform of $u^{(0)}_{m\mathbf{k}}(\mathbf{r})$, defined for each vector $\mathbf{G}$ of the reciprocal lattice,

$$u^{(0)}_{m\mathbf{k}}(\mathbf{G})=\frac{1}{\Omega_0}\int_{\Omega_0} e^{-i\mathbf{G}\cdot\mathbf{r}}u^{(0)}_{m\mathbf{k}}(\mathbf{r})d\mathbf{r}. \tag{A3}$$

Equation (A1) is such that the orthonormalization condition of the $u^{(0)}_{m\mathbf{k}}(\mathbf{r})$ functions is

$$\langle u^{(0)}_{m\mathbf{k}}|u^{(0)}_{n\mathbf{k}}\rangle=\delta_{mn}, \tag{A4}$$

where the scalar product of *periodic functions*, either represented in real space or in reciprocal space, is defined as

$$\langle f|g\rangle=\frac{1}{\Omega_0}\int_{\Omega_0} f^*(\mathbf{r})g(\mathbf{r})d\mathbf{r}=\sum_{\mathbf{G}} f^*(\mathbf{G})g(\mathbf{G}). \tag{A5}$$

This definition of scalar product for periodic functions is different from Eq. (2) which was valid for nonextended wave functions. Equation (A4) must be fulfilled only between periodic functions characterized by the same wave vector $\mathbf{k}$.

The density of the electronic system is obtained by performing an integral over the whole Brillouin zone, and summing on all the occupied bands:

$$n^{(0)}(\mathbf{r})=\frac{1}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_{m}^{\mathrm{occ}} s u^{(0)*}_{m\mathbf{k}}(\mathbf{r})u^{(0)}_{m\mathbf{k}}(\mathbf{r})d\mathbf{k}. \tag{A6}$$

Since we will consider only nonmagnetic materials, the spin degeneracy factor s is 2. For insulators, the number of occupied bands is independent of the wave vector $\mathbf{k}$, which simplifies the practical implementation of these calculations.

For metals, the number of occupied bands will depend on the wave vector $\mathbf{k}$. Instead of making a sharp transition from the occupied states and the unoccupied ones, a convenient practice involves introducing a smeared occupation function.[97] An alternative approach invokes the linear tetrahedron method.[98] The present formalism could be modified in order to incorporate the effect of these modifications, following de Gironcoli[32] or Savrasov.[22]

The ground-state wave functions can be obtained from the minimization of the electronic energy per unit cell; Eq. (1) becomes

$$E_{\mathrm{el}}\{u^{(0)}\}=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_{m}^{\mathrm{occ}} s\ \langle u^{(0)}_{m\mathbf{k}}|T^{(0)}_{\mathbf{k},\mathbf{k}}+v^{(0)}_{\mathrm{ext},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle d\mathbf{k} + E_{\mathrm{Hxc}}[n^{(0)}]. \tag{A7}$$

In order to keep the amount of different symbols sufficiently low, in Eq. (A7) and in Secs. IV–VIII, we redefine E_{el} and E_{Hxc} to be energies *per unit cell*, unlike in Eq. (1) where these quantities were defined *for the whole system*. We have also redefined the kinetic and potential operators that act now on the periodic part of the Bloch functions, according to the following rule, valid for a generic operator O [this definition is coherent with Eq. (A1)]:

$$O_{\mathbf{k},\mathbf{k}'}=e^{-i\mathbf{k}\cdot\mathbf{r}}\ O\ e^{i\mathbf{k}'\cdot\mathbf{r}'}. \tag{A8}$$

For example, we obtain the following expression for the kinetic operator in reciprocal space, for $\mathbf{k}=\mathbf{k}'$:

$$T^{(0)}_{\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{2}(\mathbf{G}+\mathbf{k})^2\delta_{\mathbf{G}\mathbf{G}'}. \tag{A9}$$

The Euler-Lagrange equations associated with the minimization of Eq. (A7) under constraint Eq. (A4), followed by a unitary transformation, as to get Eq. (7), give

$$H^{(0)}_{\mathbf{k},\mathbf{k}}|u^{(0)}_{m,\mathbf{k}}\rangle=\epsilon^{(0)}_{m,\mathbf{k}}|u^{(0)}_{m,\mathbf{k}}\rangle, \tag{A10}$$

where

$$H^{(0)}_{\mathbf{k},\mathbf{k}}=T^{(0)}_{\mathbf{k},\mathbf{k}}+v^{(0)}_{\text{ext},\mathbf{k},\mathbf{k}}+\left.\frac{\delta E_{\text{Hxc}}}{\delta n}\right|_{n^{(0)}}. \tag{A11}$$

2. Description of the potential operator

In applications based on plane waves, the bare nuclear potential operator is replaced by a pseudopotential made of local and nonlocal contributions from all atoms inside each repeated cell with lattice vector $\mathbf{R}_a$:

$$v_{\text{ext}}(\mathbf{r},\mathbf{r}')=\sum_{a\kappa} v_{\kappa}(\mathbf{r}-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_a,\mathbf{r}'-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_a), \tag{A12}$$

where $\boldsymbol{\tau}_{\kappa}$ is the vector position of the atoms inside the cell, and each atom contribution is

$$v_{\kappa}(\mathbf{r},\mathbf{r}')=v_{\kappa}^{\text{loc}}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')+v_{\kappa}^{\text{sep}}(\mathbf{r},\mathbf{r}'). \tag{A13}$$

I consider here only nonlocal parts of the separable type,[66,96,44]

$$v_{\kappa}^{\text{sep}}(\mathbf{r},\mathbf{r}')=\sum_{\mu} e_{\mu\kappa}\zeta_{\mu\kappa}(\mathbf{r})\zeta^{*}_{\mu\kappa}(\mathbf{r}'), \tag{A14}$$

where only a few separable terms, labeled by μ, are present. The functions $\zeta_{\mu\kappa}$ are short ranged, and should not overlap for adjacent atoms. Because of their different mathematical expressions, the local and nonlocal parts are treated in different ways. A local potential is naturally applied on the wave functions in the real space, since it is a diagonal operator in that representation. A separable potential could be treated efficiently either in reciprocal space or in real space. For small systems (on the order of ten atoms, or less), it is more efficient to apply the separable potential in the reciprocal space. The transformations of the wave functions between the real and reciprocal space are carried out by means of fast Fourier transforms.[65]

Let us first treat the local part. For each atom, this local part is long ranged, with asymptotic behavior $-Z_{\kappa}/r$, where Z_{κ} is the charge of the (pseudo) ion. It is well known that, in a periodic geometry, this long-ranged part creates a divergence in the ionic potential that must be treated together with a similar divergence in the Hartree potential (the divergences cancel each other, but give also a residue, usually incorporated in the ion-ion energy).[2] In the reciprocal space, these divergences are associated with terms at $\mathbf{G}=\mathbf{0}$, constant in real space. Thus in any case these compensating divergences are of no importance for the generation of the wave functions and the density, since only the mean of the potential is affected. Although the local potential operator as well as its derivatives are applied to the wave function in the real space, we will give their (simpler) expression in the reciprocal space. Their expression in the real space can be obtained by a Fourier transform, similar to Eq. (A2). We define[84,85]

$$\begin{aligned} v'_{\text{loc},\mathbf{k},\mathbf{k}}(\mathbf{G})&=\frac{1}{\Omega_0}\sum_{\kappa} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\kappa}}\,v_{\kappa}^{\text{loc}}(\mathbf{G}) \quad \text{when} \quad \mathbf{G}\neq\mathbf{0}\\ &=0 \quad \text{when} \quad \mathbf{G}=\mathbf{0}. \end{aligned} \tag{A15}$$

In this expression,

$$v_{\kappa}^{\text{loc}}(\mathbf{K})=\int e^{-i\mathbf{K}\cdot\mathbf{r}}v_{\kappa}^{\text{loc}}(\mathbf{r})d\mathbf{r}, \tag{A16}$$

where the latter integral is performed throughout all the space. The limiting behavior of $v_{\kappa}^{\text{loc}}(\mathbf{K})$ for $\mathbf{K}$ tending to zero diverges

$$v_{\kappa}^{\text{loc}}(\mathbf{K}\rightarrow 0)=-\frac{4\pi Z_{\kappa}}{K^2}+C_{\kappa}+O(K^2), \tag{A17}$$

with

$$C_{\kappa}=\int\left(v_{\kappa}^{\text{loc}}(\mathbf{r})+\frac{Z_{\kappa}}{r}\right)d\mathbf{r}. \tag{A18}$$

For the separable part, one obtains

$$\begin{aligned} v^{(0)}_{\text{sep},\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}')=\frac{1}{\Omega_0}\sum_{\mu\kappa} e_{\mu\kappa}&\left(\sum_{G} e^{-i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{\tau}_{\kappa}}\zeta_{\mu\kappa}(\mathbf{k}+\mathbf{G})\right)\\ &\times\left(\sum_{G'} e^{i(\mathbf{k}+\mathbf{G}')\cdot\boldsymbol{\tau}_{\kappa}}\zeta^{*}_{\mu\kappa}(\mathbf{k}+\mathbf{G}')\right), \end{aligned} \tag{A19}$$

where

$$\zeta_{\mu\kappa}(\mathbf{K})=\int e^{-i\mathbf{K}\cdot\mathbf{r}}\zeta_{\mu\kappa}(\mathbf{r})d\mathbf{r}. \tag{A20}$$

The special form of the matrix of separable potential, Eq. (A19), allows for its efficient application to any wave function.

3. Exchange and correlation energy and potential in the LDA

In the LDA, the exact exchange-correlation energy, a functional of the density everywhere, is replaced by the integral of the density $n(\mathbf{r})$ times the mean exchange-correlation energy per particle $\epsilon_{\text{xc}}(\mathbf{r})$ of the homogeneous electron gas at the point $\mathbf{r}$. However, when combined with pseudopotentials, this simple definition is to be modified, in order to take into account that only valence states are used to build the density: the contribution of the core electrons should be included, because of the nonlinear character of the exchange-correlation energy functional.[67] The functional then is

$$E_{\text{xc}}[n(\mathbf{r})]=\int_{\Omega_0}[n(\mathbf{r})+n_c(\mathbf{r})]\epsilon_{\text{xc}}[n(\mathbf{r})+n_c(\mathbf{r})]d\mathbf{r}, \tag{A21}$$

where the pseudocore density n_c is made of nonoverlapping contributions from each atom,

$$n_c(\mathbf{r})=\sum_{a\kappa} n_{c,\kappa}(\mathbf{r}-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_a). \tag{A22}$$

The pseudocore density from each atom $n_{c,\kappa}$ is built at the same time as the pseudopotential.[67,99] It has spherical symmetry, and is specified by a one-dimensional function. The corresponding exchange-correlation potential is

$$v_{\mathrm{xc}}(n(\mathbf{r}))=\left.\frac{d[(n+n_c)\epsilon_{\mathrm{xc}}(n+n_c)]}{dn}\right|_{n=n(\mathbf{r});n_c=n_c(\mathbf{r})}, \tag{A23}$$

and its derivative with respect to the density

$$\frac{dv_{\mathrm{xc}}(n(\mathbf{r}))}{dn}=\left.\frac{d^2[(n+n_c)\epsilon_{\mathrm{xc}}(n+n_c)]}{dn^2}\right|_{n=n(\mathbf{r});n_c=n_c(\mathbf{r})}. \tag{A24}$$

4. Unperturbed energy and Hamiltonian in the LDA

With these definitions, the electronic energy is

$$E_{\mathrm{el}}\{u^{(0)}\}=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\,\langle u^{(0)}_{m\mathbf{k}}|T^{(0)}_{\mathbf{k},\mathbf{k}}+v^{(0)}_{\mathrm{sep},\mathbf{k},\mathbf{k}}|u^{(0)}_{m\mathbf{k}}\rangle d\mathbf{k}+\int_{\Omega_0} n^{(0)}(\mathbf{r})v'^{(0)}_{\mathrm{loc}}(\mathbf{r})d\mathbf{r}$$
$$+\int_{\Omega_0}[n^{(0)}(\mathbf{r})+n^{(0)}_c(\mathbf{r})](\epsilon_{\mathrm{xc}}[n^{(0)}(\mathbf{r})+n^{(0)}_c(\mathbf{r})])d\mathbf{r}+2\pi\Omega_0\sum_{\mathbf{G}\neq 0}\frac{|n^{(0)}(\mathbf{G})|^2}{|\mathbf{G}|^2}. \tag{A25}$$

The Hartree energy [last term of Eq. (A25)] can also be computed as

$$E_{\mathrm{H}}=\int_{\Omega_0} n^{(0)}(\mathbf{r})v'^{(0)}_{\mathrm{H}}(\mathbf{r})d\mathbf{r}, \tag{A26}$$

with the Hartree potential being defined as[84,85]

$$v'^{(0)}_{\mathrm{H}}(\mathbf{G})=2\pi\Omega_0\sum_{\mathbf{G}\neq 0}\frac{n^{(0)}(\mathbf{G})}{|\mathbf{G}|^2}\quad \text{when}\quad \mathbf{G}\neq\mathbf{0}$$
$$=0\quad\text{when}\quad \mathbf{G}=\mathbf{0}. \tag{A27}$$

The Hamiltonian is given by

$$H^{(0)}_{\mathbf{k},\mathbf{k}}=T^{(0)}_{\mathbf{k},\mathbf{k}}+v^{(0)}_{\mathrm{sep},\mathbf{k},\mathbf{k}}+(v'^{(0)}_{\mathrm{loc}}+v'^{(0)}_{\mathrm{H}}+v^{(0)}_{\mathrm{xc}}). \tag{A28}$$

The local, Hartree, and exchange-correlation (XC) potentials are operators local in the real space which are independent of **k**.

APPENDIX B: RESPONSE TO AN HOMOGENEOUS, STATIC ELECTRIC FIELD BY THE LONG-WAVE METHOD: DETAILED TREATMENT

1. Small-wave-vector limit of the response to an incommensurate perturbation

Inspired by Eq. (68), we write the following first-order potential operator change:

$$v^{(1)}_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\mathbf{r}')=e^{i\mathbf{q}\cdot\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}'), \tag{B1}$$

which corresponds to the simple change of phase-factorized local potential

$$\bar{v}^{(1)}_{\mathrm{loc},\mathbf{q}}=1. \tag{B2}$$

The supplementary constant $1/i|\mathbf{q}|$, present in Eq. (68), will be taken into account afterwards. No second-order potential change, first-order separable potential change, or nonlinear exchange-correlation core correction is present. This leads to important simplifications of the variational principle [compare with Eq. (60), which was obtained for collective atomic displacements]:

$$E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}\{u^{(0)};u^{(1)}\}$$
$$=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\,\langle u^{(1)}_{m\mathbf{k},\mathbf{q}}|H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}-\epsilon^{(0)}_{m\mathbf{k}}|u^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle d\mathbf{k}$$
$$+\frac{\Omega_0}{2}[\bar{n}^{*(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})+\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})]$$
$$+\frac{1}{2}\int_{\Omega_0}\left.\frac{dv_{\mathrm{xc}}}{dn}\right|_{n^{(0)}(\mathbf{r})}|\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{r})|^2\,d\mathbf{r}$$
$$+2\pi\Omega_0\sum_{\mathbf{G}}\frac{|\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{G})|^2}{|\mathbf{q}+\mathbf{G}|^2}, \tag{B3}$$

where we have taken advantage of

$$\int_{\Omega_0}\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{r})d\mathbf{r}=\Omega_0\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0}). \tag{B4}$$

The corresponding nonvariational expressions are simple:

$$E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}=\frac{\Omega_0}{2}\bar{n}^{*(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=\frac{\Omega_0}{2}\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0}). \tag{B5}$$

The associated first-order Hamiltonian operator is a local potential operator, here written in the reciprocal space,

$$\bar{H}^{(1)}_{\mathbf{q}}(\mathbf{G})=\delta_{\mathbf{G},\mathbf{0}}+4\pi\frac{\bar{n}^{(1)}_{\mathbf{q}}(\mathbf{G})}{|\mathbf{G}+\mathbf{q}|^2}+\bar{v}^{(1)}_{\mathrm{xc},\mathbf{q}}(\mathbf{G}). \tag{B6}$$

The exchange-correlation contribution $\bar{v}^{(1)}_{\mathrm{xc},\mathbf{q}}(\mathbf{G})$ is obtained from the knowledge of $\bar{n}^{(1)}_{\mathbf{q}}$ through Eq. (63). This local potential operator includes a long-wave part (for $\mathbf{G}=\mathbf{0}$), but also local fields (for $\mathbf{G}\neq\mathbf{0}$), the latters being of electrostatic origin (the Hartree part) as well as exchange-correlation origin.

From Eq. (B6) one can infer that the long-wave (macroscopic) potential, for $\mathbf{G}=\mathbf{0}$ in the limit of $\mathbf{q}\rightarrow\mathbf{0}$, is made of the bare applied potential and the electronic screening, due to the Hartree term:

$$\overline{H}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=1+4\pi\frac{\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})}{|\mathbf{q}|^2}. \tag{B7}$$

In the derivation of this equation, we have neglected the exchange-correlation contribution in comparison to the Hartree term in the limit of $\mathbf{q}\rightarrow\mathbf{0}$, because of the $1/q^2$ divergence of the latter while in the LDA, the exchange-correlation energy functional is well behaved in this limit.[100]

2. Analytical treatment of the Hartree divergence

The divergence of the Hartree term in Eq. (B3) can be treated analytically, thanks to the Sherman-Morrison formula for connecting two inversion (or minimization) problems.[101] The following auxiliary variational expression is first minimized [this expression would be equal to Eq. (B3) if it were not for the removal of the divergent $\mathbf{G}=\mathbf{0}$ Hartree contribution]:

$$\begin{aligned}\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}&\{u^{(0)};\widetilde{u}^{(1)}\}\\&=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\,\langle\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}|H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}-\epsilon^{(0)}_{m\mathbf{k}}|\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle d\mathbf{k}\\&\quad+\frac{\Omega_0}{2}[\widetilde{n}^{*(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})+\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})]\\&\quad+\frac{1}{2}\int_{\Omega_0}\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}|\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{r})|^2+2\pi\Omega_0\sum_{\mathbf{G}\neq\mathbf{0}}\frac{|\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G})|^2}{|\mathbf{q}+\mathbf{G}|^2},\end{aligned} \tag{B8}$$

with

$$\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{r})=\frac{2}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\,u^{(0)*}_{m\mathbf{k}}(\mathbf{r})\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}(\mathbf{r})d\mathbf{k} \tag{B9}$$

under constraints

$$\langle u^{(0)}_{m,\mathbf{k}+\mathbf{q}}|\widetilde{u}^{(1)}_{n,\mathbf{k},\mathbf{q}}\rangle=0, \tag{B10}$$

where the indices m and n runs over occupied states. The associated nonvariational expressions give

$$\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}=\frac{\Omega_0}{2}\widetilde{n}^{*(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=\frac{\Omega_0}{2}\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0}). \tag{B11}$$

The quantity $\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})$ has the following expression in terms of the scalar products of zeroth- and first-order wave functions:

$$\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=\frac{2}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\,\langle u^{(0)}_{m\mathbf{k}}|\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle d\mathbf{k}. \tag{B12}$$

The associated first-order Hamiltonian operator, in the limit $\mathbf{q}\rightarrow\mathbf{0}$ is

$$\begin{aligned}\widetilde{H}^{(1)}_{\mathbf{q}}(\mathbf{G})&=4\pi\frac{\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G})}{|\mathbf{G}+\mathbf{q}|^2}+\widetilde{v}^{(1)}_{\mathrm{xc},\mathbf{q}}(\mathbf{G})\quad\text{when }\ \mathbf{G}\neq\mathbf{0}\\&=1\quad\text{when }\ \mathbf{G}=\mathbf{0}.\end{aligned} \tag{B13}$$

That is, the screening by the Hartree term has been removed when $\mathbf{G}=\mathbf{0}$.

By the Sherman-Morrison formula, at the minimum of both Eq. (B8) and Eq. (B3) one gets the following relationships:

$$\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=\frac{\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})}{1+\frac{4\pi}{q^2}\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})}, \tag{B14}$$

$$\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})=\frac{\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})}{1-\frac{4\pi}{q^2}\widetilde{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})}, \tag{B15}$$

$$E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}=\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}\left(1+\frac{4\pi}{q^2}\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})\right), \tag{B16}$$

$$|u^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle=|\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}\rangle\left(1+\frac{4\pi}{q^2}\overline{n}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})\right). \tag{B17}$$

These equations are especially important in that, when compared with Eq. (B7), they show that the rate of change of $E^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}$ with respect to an electric field [the long-wave part of $\overline{H}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})$], is the same as the rate of change of $\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}$ with respect to a bare applied field $\widetilde{H}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})$.

3. The limit $\mathbf{q}\rightarrow\mathbf{0}$

We now chose a particular direction $\mathbf{q}$ along which the limit $\mathbf{q}\rightarrow\mathbf{0}$ is taken. Let it be the α direction. We have $\mathbf{q}=q\mathbf{e}_\alpha$, where $\mathbf{e}_\alpha$ is a unit vector along direction α, and q is the norm of the $\mathbf{q}$ vector, tending to zero. We expand the zeroth-order and first-order wave functions in powers of the small parameter q:

$$u^{(0)}_{m\mathbf{k}+\mathbf{q}}=u^{(0)}_{m\mathbf{k}}+q\,\frac{du^{(0)}_{m\mathbf{k}}}{dk_\alpha}+O(q^2) \tag{B18}$$

and

$$\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{q}}=\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{0}}+q\,\frac{d\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{0}}}{dq_\alpha}+O(q^2). \tag{B19}$$

At the lowest order in q, the Euler-Lagrange equation derived from Eq. (B8), with the Hamiltonian Eq. (B13), is satisfied by taking

$$\widetilde{u}^{(1)}_{m\mathbf{k},\mathbf{0}}=0, \tag{B20}$$

which constitutes the unique solution of them, because the whole quadratic form in Eq. (B8) is definite positive (see the discussion in Sec. IV B of Ref. 42). This means that the expansion of $\widetilde{n}\,{}^{(1)}_{\mathbf{q}}$, $\widetilde{v}\,{}^{(1)}_{\mathrm{xc},\mathbf{q}}$, or $\widetilde{H}^{(1)}_{\mathbf{q}}$ in powers of q only begins with the linear term.

From Eq. (B20), at the first order in q, the constraints Eq. (B10) give

$$\left\langle u^{(0)}_{m,\mathbf{k}} \middle| \frac{d\widetilde{u}\,{}^{(1)}_{n\mathbf{k},\mathbf{0}}}{dq_\alpha} \right\rangle = 0, \tag{B21}$$

where the indices m and n run over occupied states. Because of Eqs. (B9), (B20), and (B21), the expansion of $\widetilde{n}\,{}^{(1)}_{\mathbf{q}}(\mathbf{G}=\mathbf{0})$ will even begin at the second order only. The same is true for the expansion of $\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}$.

Finally, taking into account the second-order expansion of Eq. (B10),

$$\left\langle u^{(0)}_{m,\mathbf{k}} \middle| \frac{d^2\widetilde{u}\,{}^{(1)}_{n\mathbf{k},\mathbf{0}}}{dq_\alpha^2} \right\rangle + \left\langle \frac{d\widetilde{u}\,{}^{(0)}_{m,\mathbf{k}}}{dk_\alpha} \middle| \frac{d\widetilde{u}\,{}^{(1)}_{n\mathbf{k},\mathbf{0}}}{dq_\alpha} \right\rangle = 0, \tag{B22}$$

as well as its complex conjugate, we obtain a variational expression with respect to the quantities $d\widetilde{u}\,{}^{(1)}_{n\mathbf{k},\mathbf{0}}/dq_\alpha$:

$$\begin{aligned}
\frac{1}{2}\,\frac{d^2\widetilde{E}^{(2)}_{\mathrm{el},-\mathbf{q},\mathbf{q}}}{dq_\alpha^2}\bigg|_{q\to 0}&\left\{u^{(0)};\frac{d\widetilde{u}\,{}^{(1)}}{dq_\alpha}\right\} \\
=\frac{\Omega_0}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s\Bigg(&\left\langle \frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{q}}}{dq_\alpha}\middle| H^{(0)}_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}} - \epsilon^{(0)}_{m\mathbf{k}} \middle| \frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{q}}}{dq_\alpha}\right\rangle \\
&-\left\langle \frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{q}}}{dq_\alpha}\middle|\frac{du^{(0)}_{m\mathbf{k}}}{dk_\alpha}\right\rangle - \left\langle \frac{du^{(0)}_{m\mathbf{k}}}{dk_\alpha}\middle|\frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{q}}}{dq_\alpha}\right\rangle d\mathbf{k} \\
&+\frac{1}{2}\int_{\Omega_0}\frac{dv_{\mathrm{xc}}}{dn}\bigg|_{n^{(0)}(\mathbf{r})}\left|\frac{d\widetilde{n}\,{}^{(1)}_{\mathbf{q}}(\mathbf{r})}{dq_\alpha}\right|^2 \\
&+2\pi\Omega_0\sum_{\mathbf{G}\neq\mathbf{0}}\frac{\left|\dfrac{d\widetilde{n}\,{}^{(1)}_{\mathbf{q}}(\mathbf{G})}{dq_\alpha}\right|^2}{|\mathbf{G}|^2},
\end{aligned} \tag{B23}$$

with

$$\frac{d\widetilde{n}\,{}^{(1)}_{\mathbf{q}}(\mathbf{r})}{dq_\alpha} = \frac{2}{(2\pi)^3}\int_{\mathrm{BZ}}\sum_m^{\mathrm{occ}} s u^{(0)*}_{m\mathbf{k}}(\mathbf{r})\frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{0}}(\mathbf{r})}{dq_\alpha}d\mathbf{k} \tag{B24}$$

under constraints Eq. (B21).

The connection with the equations presented in Secs. VI A and VI B is now possible, thanks to the identification

$$u^{\mathcal{E}_\alpha}_{m\mathbf{k}} = \frac{q_\alpha}{i|\mathbf{q}|}\,\frac{d\widetilde{u}\,{}^{(1)}_{m\mathbf{k},\mathbf{0}}(\mathbf{r})}{dq_\alpha}\,. \tag{B25}$$

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[82] In order to obtain Eqs. (44) and (47), the time-reversal symmetry has been used in order to get rid of the first-order wave functions for $-\mathbf{q}$ using the following equalities:

$$u^{(1)}_{m\mathbf{k},\mathbf{q}}(\mathbf{r}) = \eta\, u^{(1)*}_{m(-\mathbf{k}),(-\mathbf{q})}(\mathbf{r}) \tag{B26}$$

and

$$u^{(0)}_{m\mathbf{k}}(\mathbf{r}) = \eta\, u^{(0)*}_{m(-\mathbf{k})}(\mathbf{r}) \tag{B27}$$

(where η is a complex number of module unity), or using a generalization of these equalities when degeneracies are present. Other equations were also simplified thanks to this symmetry: all those giving the first-order densities in terms of the first-order wave functions, and the nonvariational expressions for the second-order derivatives of the energy.

[83] The transformation of wave functions, the density, and potential between the real space and the reciprocal space will be often performed in an efficient way thanks to the fast Fourier transform algorithm.

[84] The local potential $v'_{\mathrm{loc},\mathbf{k},\mathbf{k}}$ does not depend on **k** and will be usually written v'_{loc}. This shortening of the notation will be used for all occurrences of a **k** independent quantity.

[85] The prime symbol indicates that the $\mathbf{G}=\mathbf{0}$ term is excluded.

[86] In this expression, it is taken into account that the electronic charge is -1 in the atomic units.

[87] L. D. Landau and E. M. Lifshits, *Electrodynamics of Continuous Media* (Pergamon, London, 1960).

[88] These equations differ from those given in Ref. 55, because of different choices of conventions.

[89] See, for example, E. I. Blount, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 306; S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).

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[100] However, in the ‘‘exact’’ DFT, an exchange-correlation electric field exists in the limit $\mathbf{q}\rightarrow\mathbf{0}$, which is totally absent in the LDA (Ref. 3).

[101] Page 67 in Ref. 80.