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Projector augmented-wave approach to density-functional perturbation theory

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The density-functional theory total energy within the projector-augmented wave formalism is expressed in a form suitable for application of the variation-perturbation formalism. We derive the corresponding expressions up to the third order. The much deeper complexity of the projector-augmented wave formalism, compared to the norm-conserving pseudopotential case, implies the introduction of several new notations. However, the structure of the resulting formalism is quite similar, and should be as useful, accurate, and widely applicable.

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I. INTRODUCTION

The computation of properties of condensed matter, based on first-principles within density functional theory (DFT),[1] involves choices related to the representation of electronic wavefunctions as well as to the treatment of core electrons. Several methodologies are well-established, like those based on pseudopotentials or those based on "augmented waves."

Pseudopotentials allow one to ignore the core electrons, at the expense of the replacement of the strong nuclear Coulomb potential of the all-electron system by a weak pseudopotential, designed to mimick the scattering due to the combined effect of nuclei and core electrons. This replacement leads to a somewhat uncontrolled approximation of the all-electron system. However, with a weak pseudopotential, a plane-wave basis can be used to represent the electronic wavefunctions, with many computational advantages. The norm-conserving[2] separable[3] pseudopotential method, thanks to its simplicity, elegance, and computational efficiency, is widely used in present-day research. For systems that include elements in the transition metal series, or for actinides, or even for elements in the right-side of first row of the periodic table, the size of the plane wave basis has been further decreased by the introduction of ultra-soft pseudopotentials (USPP),[4] at the expense of the loss of simplicity.

Borrowing ideas from the augmented-waves methodology, Blöchl designed a formalism[5] called projector augmented waves (PAW), in which an accurate, all-electron, representation of the electronic system is placed in one-to-one correspondence with a pseudopotential-like treatment of the valence and conduction electrons.[5–7] In particular, the electronic system can be represented by a small set of plane-waves, of a size comparable to the USPP case. Actually, the USPP treatment can even be derived from the PAW treatment, provided some terms are assumed to be constants.[6] Of course, the PAW formalism has the conceptual advantage of being directly derived from an all-electron approach thanks to a well-controlled approximation. As such, it seems to gather all advantages from the different methodologies, and would be the method of choice, if it were not for its complexity.

First-principles approaches, considered both within the pseudopotential framework or the augmented waves framework, provide a direct approach to total energy and charge densities of electronic systems. However, many other properties of such systems are derivatives of the total energy with respect to perturbations, like an electric field, an atomic displacement, the change of the primitive vectors, or combinations thereof. First-order derivatives can be computed straighforwardly from the Hellmann-Feynman theorem,[1] providing forces, stresses, or polarization. For higher-order derivatives, like interatomic force constants (leading to phonon band structures), dielectric tensors, Raman tensors, Grüneisen parameters, etc., the simplest approach would be to rely on finite-differences of first-order derivatives. However, by mixing perturbation theory with density-functional theory, it is possible to obtain a much more powerful, computationally efficient, and systematic treatment of the derivatives, as realized by Baroni and co-workers.[8]

The resulting framework, called density perturbation functional theory (DFPT),[9] has been extensively studied, and used for practical applications. Expressions have been obtained to all orders of perturbation.[10] The existence of a variational principle for the total energy as a functional of wavefunctions[11,12] is at the heart of this framework. An interplay between expansions of the wavefunctions and the total energy allows one to get, for example, all mixed second-order[13] and third-order[14] derivatives of the total energy from the knowledge of the first-order derivative wavefunctions, the latter being determined by the minimization of a second-order total energy, or the resolution of a generalized Sternheimer equation.[9]

This framework, when considered up to the second-order of total energy derivatives only, has been implemented in numerous softwares, most of them based on norm-conserving pseudopotentials (NCPP) and plane waves, with the noticeable exceptions of the USPP implementation of PWSCF/PHONON,[15] based on the derivation by Dal Corso and co-workers,[16,17] the LMTO implementation of Savrasov,[18] the LAPW implementation of Yu and Krakauer,[19] and the local orbital approach of Heid and Bohnen.[20] To our knowledge, only the linear response to the very specific external field perturbation has been examined within PAW.[21]

Concerning third-order derivatives of the total energy, they have only been established and implemented within the norm-conserving pseudopotential framework.[10,15,22–25]

The PAW formalism complexity contrast with the simplicity of the norm-conserving pseudopotential framework. Moreover, the density-functional perturbation theory, even in the case of norm-conserving pseudopotentials, can become rapidly quite complex. It will be the purpose of the present paper to establish the equations for the density-functional perturbation theory within PAW, up to the third-order derivative of the total energy, for generic perturbations (except those perturbations affecting the space metric, like the strain perturbation).

The chain of dependencies that link the PAW total energy to the wavefunctions includes several levels. Our first task will be to identify correctly the dependences and the levels. Then, in order to present the expressions in a systematic way, new notations will be introduced see, e.g., Eqs. (29), (37), (52), (84), (85), and (87). We have checked that such equations and the corresponding new notations can be generalized to the case of mixed perturbations (see Appendix G).

In Sec. II, after a short summary of the main results of variation-perturbation theory, we present a formulation of the PAW total energy as a variational functional of the wavefunctions, depending on some parameter λ, taking into account the constraints thanks to Lagrange parameters. The chain of dependencies is analyzed carefully. Our notations and basic PAW "usual" expressions are presented in Appendix A. The formulas for the first-order derivatives are presented in Sec. III, and follow quite straighforwardly from the Hellmann-Feynman theorem. Although these are mostly known results,[5,6] the notations and equations in this section will prove useful in the next ones. The variational principle for the second-order derivative of the total energy, quadratic in the pseudo-wave functions, is presented in Sec. IV. The associated Euler-Lagrange equations, also called generalized Sternheimer equations, are presented in Sec. V. In the same section, Lagrange multipliers and gauge freedom are briefly discussed. We derive a nonvariational form of the second-order derivative of the total energy, linear in the wavefunctions, in Sec. VI. In the Sec. VII, we establish the notation and expressions for the third-order derivative of the total energy. In the body of the text, we have tried to focus on the new notations and correspondences between important formulas. Additional detailed expressions are given in Appendices B–F. An even more extensive account of the present theory in given in Ref. 26.

Throughout this article, we will use atomic (Hartree) units.

II. THE PAW TOTAL ENERGY AS A VARIATIONAL FUNCTIONAL

In order to apply the well-established perturbation theory of a variational principle,[11] we must build an expression of the PAW total energy (see Appendix A), as a variational functional of a set of pseudo-wave wavefunctions $\tilde{\psi}_i$. Generalized orthonormalization constraints should be taken into account thanks to Lagrange multipliers. We want also to keep track from the very start, of the possible dependencies of the different terms in this total energy expression upon some parameter λ, describing the perturbation. In this section, we will adopt the convention that square brackets indicate the different λ and/or $\tilde{\psi}_i$-dependencies of the term preceding them. The **x**-dependence of densities and potentials will not be indicated, except when there is a risk of confusion.

Let us denote such a variational PAW total energy expression, that includes the constraint terms, as $E^{+}_{tot}[\tilde{\psi}_i,\lambda]$. The minimization procedure will select among the trial pseudo-wavefunctions $\tilde{\psi}_i$, those giving the lowest energy. Such a minimization procedure can be performed for different values of λ, and will select different optimized pseudo-wavefunctions. The pseudo-wavefunctions, determined variationally, acquire thus a λ-dependence, $\tilde{\psi}_i[\lambda]$.

In the variation-perturbation theory,[11] all physical quantities X (like densities, energy, atomic datas, etc.) are expanded in terms of λ:

$$X[\tilde{\psi}_i[\lambda],\lambda] = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \cdots \tag{1}$$

with $X^{(n)} = \frac{1}{n!}\left(\frac{d^n}{d\lambda^n}X\right)\big|_{\lambda=0}$. A first theorem of variation-perturbation theory states that the knowledge of the expansion of $\tilde{\psi}_i[\lambda]$ up to order n allows one to determine the expansion of $E^{+}_{tot}[\tilde{\psi}_i,\lambda]$ up to order $2n+1$. Explicitly,

$$E^{+(2n+1)}_{tot} = \left(E^{+}_{tot}\left[\sum_{j=0}^{n}\lambda^j\tilde{\psi}_i^{(j)},\lambda\right]\right)^{(2n+1)} \tag{2}$$

For even orders, one finds a variational (minimum) principle:

$$E^{+(2n)}_{tot} = \min_{\tilde{\psi}^{(n)}_{i,trial}}\left(E^{+}_{tot}\left[\sum_{j=0}^{n-1}\lambda^j\tilde{\psi}_i^{(j)} + \lambda^n\tilde{\psi}^{(n)}_{i,trial},\lambda\right]\right)^{(2n)} \tag{3}$$

At the minimum, $\tilde{\psi}^{(n)}_{i,trial}$ is equal to $\tilde{\psi}^{(n)}_{i}$.

From the PAW standard expressions (Appendix A), one can build the requested PAW total energy expression, suitable for the application of the variation-perturbation theory whose critical terms will be detailed in Eqs. (6)–(16):

$$\begin{aligned}E^{+}_{tot}[\tilde{\psi}_i,\lambda] = {} & \sum_{j=1}^{N}\langle\tilde{\psi}_j|\tilde{H}_{KV}[\lambda]|\tilde{\psi}_j\rangle - \sum_{j,j'=1}^{N}\Lambda_{jj'}[\tilde{\psi}_i,\lambda](\langle\tilde{\psi}_j|\tilde{S}[\lambda]|\tilde{\psi}_{j'}\rangle - \delta_{jj'}) \\ & + \tilde{E}_{Hxc}\Big[\tilde{\rho}[\tilde{\psi}_i],\hat{\rho}[\tilde{\psi}_i,\lambda],\rho^k_1[\tilde{\psi}_i,\lambda],\tilde{\rho}^k_1[\tilde{\psi}_i,\lambda],\hat{\rho}^k[\tilde{\psi}_i,\lambda],\tilde{\rho}_c[\lambda],\rho^k_c[\lambda],\tilde{\rho}^k_c[\lambda]\Big] \\ & + \sum_{k=1}^{K}\int_{\Omega_k} V_{ext}[\lambda]\rho^k_{\mathcal{Z}_c}[\lambda]d\mathbf{x} + \frac{1}{2}\sum_{k=1}^{K}\int_{\Omega_k}\int_{\Omega_k}\frac{\rho^k_{\mathcal{Z}_c}[\lambda](\mathbf{x})\rho^k_{\mathcal{Z}_c}[\lambda](\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x}d\mathbf{y} + U[\lambda]\end{aligned} \tag{4}$$

This expression, considered for some value of λ should be minimized by varying the pseudo-wavefunctions $\tilde{\psi}_i$, for all i between 1 and N. The N^2 constraints describing the generalized orthonormalization conditions

$$\langle\tilde{\psi}_j|\tilde{S}[\lambda]|\tilde{\psi}_{j'}\rangle - \delta_{jj'} = 0 \tag{5}$$

should be enforced, after the minimization, by the adequate choice of the Lagrange multipliers $\Lambda_{jj'}[\tilde{\psi}_i,\lambda]$, see the second term of Eq. (4).

Equation (4) does not take into account metallic occupancies (the pseudo-wavefunctions are all occupied wavefunctions), as well as the possible spin-polarization of the system. Also, it does not take into account the possibility that the very expressions of scalar products or Hartree convolutions, might be λ-dependent. The generalization to metals and spin-polarized systems can be done in a way very similar to the one followed in the NCPP and USPP cases,[27] without any additional complication specifically due to the PAW. By contrast, the possible additional λ-dependencies in scalar products or Hartree convolutions, would lead to much more intricate formulas. Actually, such dependences are needed only in the case of perturbations acting on the space metrics (the only useful case in the present practice being the strain-type perturbation). The corresponding formalism has been developed only very recently,[28] in the NCPP case. To avoid unneeded complexity, we will ignore the possibility a λ-dependence mediated by the metrics. In the same spirit, the Laplacian as well as atomic orbitals ϕ^k_p, $\tilde{\phi}^k_p$ (see Appendix A) can be considered as λ-independent.

The last line of Eq. (4) includes contributions that do not depend on the wavefunctions. Hence, the computation of their derivative should not pose any specific problem. The first of these terms takes into account a possible applied external potential, also present in the forthcoming Eqs. (6) and (7).

The three first terms of Eq. (4) will now be detailed, one after the other. In order to deal with the operator $\tilde{H}_{KV}$ and the overlap one $\tilde{S}$ in a compact notation, we replace the dyadic product $|\tilde{p}^k_p\rangle\langle\tilde{p}^k_q|$ by the slightly shorter $(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)$. The operator $\tilde{H}_{KV}$, related to the kinetic energy and the attractive potential between electrons and nuclei, is defined by:

$$\begin{aligned}\tilde{H}_{KV}[\lambda] = {} & -\frac{1}{2}\nabla^2 + V_H[\tilde{\rho}_{\mathcal{Z}_c}[\lambda]] + V_{ext}[\lambda] \\ & + \sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}} E_{kpq}[\lambda](\tilde{p}^k_p\tilde{p}^{k\dagger}_q)[\lambda]\end{aligned} \tag{6}$$

with

$$\begin{aligned}E_{kpq}[\lambda] = {} & \sum_{LM}\int_{\mathbb{R}^3}(V_H[\tilde{\rho}_{\mathcal{Z}_c}[\lambda]] + V_{ext}[\lambda])\hat{Q}^{LM}_{kpq}[\lambda]d\mathbf{x} \\ & + \langle\phi^k_p| -\frac{1}{2}\nabla^2 + V_{H_{|\Omega_k}}[\rho^k_{\mathcal{Z}_c}[\lambda]] + V_{ext}[\lambda]|\phi^k_q\rangle_k \\ & - \langle\tilde{\phi}^k_p| -\frac{1}{2}\nabla^2 + V_{H_{|\Omega_k}}[\tilde{\rho}^k_{\mathcal{Z}_c}[\lambda]] + V_{ext}[\lambda]|\tilde{\phi}^k_q\rangle_k \\ & - \sum_{LM}\int_{\Omega_k}(V_{H_{|\Omega_k}}[\tilde{\rho}^k_{\mathcal{Z}_c}[\lambda]] + V_{ext}[\lambda])\hat{Q}^{LM}_{kpq}[\lambda]d\mathbf{x}.\end{aligned} \tag{7}$$

These expressions, Eqs. (6) and (7), do not depend on the pseudo-wavefunctions. Hence, as for the last three terms of Eq. (4), the computation of their derivative should not pose any specific problem, see Appendix B.

Let us come to the Hartree and exchange-correlation energy. We write[29]

$$\begin{aligned}& \tilde{E}_{Hxc}[\tilde{\rho}[\tilde{\psi}_i],\hat{\rho}[\tilde{\psi}_i,\lambda],\rho^k_1[\tilde{\psi}_i,\lambda],\tilde{\rho}^k_1[\tilde{\psi}_i,\lambda],\hat{\rho}^k[\tilde{\psi}_i,\lambda],\tilde{\rho}_c[\lambda],\rho^k_c[\lambda],\tilde{\rho}^k_c[\lambda]] \\ & = E_{Hxc}[\tilde{\rho}[\tilde{\psi}_i] + \hat{\rho}[\tilde{\psi}_i,\lambda];\tilde{\rho}_c[\lambda]] + \sum_{k=1}^{K}(E_{Hxc}[\rho^k_1[\tilde{\psi}_i,\lambda];\rho^k_c[\lambda]] - E_{Hxc}[\tilde{\rho}^k_1[\tilde{\psi}_i,\lambda] + \hat{\rho}^k[\tilde{\psi}_i,\lambda];\tilde{\rho}^k_c[\lambda]])_{|\Omega_k}\end{aligned} \tag{8}$$

in which we have combined the Hartree and exchange-correlation contributions, on the basis of the following notation

$$E_{Hxc}[\rho;\rho_c] = E_H[\rho] + E_{xc}[\rho+\rho_c]. \tag{9}$$

The different densities are:

$$\hat{\rho}[\tilde{\psi}_i,\lambda] = \sum_{k=1}^{K} \hat{\rho}^k[\tilde{\psi}_i,\lambda], \tag{10}$$

$$\tilde{\rho}[\tilde{\psi}_i] = \sum_{j=1}^{N} |\tilde{\psi}_j|^2, \tag{11}$$

$$\rho_1^k[\tilde{\psi}_i,\lambda] = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}[\tilde{\psi}_i,\lambda]\phi_p^k\phi_q^{k*}, \tag{12}$$

$$\tilde{\rho}_1^k[\tilde{\psi}_i,\lambda] = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}[\tilde{\psi}_i,\lambda]\tilde{\phi}_p^k\tilde{\phi}_q^{k*} \tag{13}$$

and

$$\hat{\rho}^k[\tilde{\psi}_i,\lambda] = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} \rho_{kpq}[\tilde{\psi}_i,\lambda]\hat{Q}_{kpq}^{LM}[\lambda] \tag{14}$$

with the coefficients

$$\rho_{kpq}[\tilde{\psi}_i,\lambda] = \sum_{i=1}^{N} \langle\tilde{\psi}_i|(\tilde{p}_q^k\tilde{p}_p^{k\dagger})[\lambda]|\tilde{\psi}_i\rangle_k \tag{15}$$

We come now to the second term in Eq. (4). It is made of two factors. The Lagrange multipliers $\Lambda_{jj'}[\tilde{\psi}_i,\lambda]$ that guarantee the fulfillment of the constraints, are obtained from

$$\Lambda_{jj'}[\tilde{\psi}_i,\lambda] = \langle\tilde{\psi}_{j'}|\tilde{H}[\tilde{\psi}_i,\lambda]|\tilde{\psi}_j\rangle \tag{16}$$

The Hamiltonian $\tilde{H}[\tilde{\psi}_i,\lambda]$ also appears in the Euler-Lagrange equations derived from Eq. (4):

$$\tilde{H}\tilde{\psi}_j = \sum_{j'=1}^{N} \Lambda_{jj'}\tilde{S}\tilde{\psi}_{j'}. \tag{17}$$

After a unitary rotation of the pseudo-wavefunctions $\tilde{\psi}_i$, one can deduce the Kohn-Sham equations from Eq. (17).

This Hamiltonian $\tilde{H}[\tilde{\psi}_i,\lambda]$ depends itself on the pseudo-wavefunctions and on λ. Indeed,

$$\begin{aligned}\tilde{H}[\tilde{\psi}_i,\lambda] = &-\frac{1}{2}\nabla^2 + V_H[\tilde{\rho}_{\mathcal{Z}_c}[\lambda]] + V_{Hxc}[\tilde{\rho}[\tilde{\psi}_i] + \hat{\rho}[\tilde{\psi}_i,\lambda];\tilde{\rho}_c[\lambda]] + V_{ext}[\lambda] \\ &+ \sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}} (\tilde{D}_{kpq}[\tilde{\psi}_i,\lambda] + D_{kpq}^1[\tilde{\psi}_i,\lambda] - \tilde{D}_{kpq}^1[\tilde{\psi}_i,\lambda])(\tilde{p}_p^k\tilde{p}_q^{k\dagger})[\lambda]\end{aligned} \tag{18}$$

with

$$\tilde{D}_{kpq}[\tilde{\psi}_i,\lambda] = \int_{\mathbb{R}^3} (V_H[\tilde{\rho}_{\mathcal{Z}_c}[\lambda]] + V_{Hxc}[\tilde{\rho}[\tilde{\psi}_i] + \hat{\rho}[\tilde{\psi}_i,\lambda];\tilde{\rho}_c[\lambda]] + V_{ext}[\lambda])\left(\sum_{LM}\hat{Q}_{kpq}^{LM}[\lambda]\right)d\mathbf{x}, \tag{19}$$

$$D_{kpq}^1 = \langle\phi_p^k| - \frac{1}{2}\nabla^2 + V_{H_{|\Omega_k}}[\rho_{\mathcal{Z}_c}^k[\lambda]] + V_{Hxc_{|\Omega_k}}[\rho_1^k[\tilde{\psi}_i,\lambda];\rho_c^k[\lambda]] + V_{ext}[\lambda]|\phi_q^k\rangle_k \tag{20}$$

and

$$\begin{aligned}\tilde{D}_{kpq}^1 = &\langle\tilde{\phi}_p^k| - \frac{1}{2}\nabla^2 + V_{H_{|\Omega_k}}[\tilde{\rho}_{\mathcal{Z}_c}^k[\lambda]] + V_{Hxc_{|\Omega_k}}[\tilde{\rho}_1^k[\tilde{\psi}_i,\lambda] + \hat{\rho}^k[\tilde{\psi}_i,\lambda];\tilde{\rho}_c^k[\lambda]] + V_{ext}[\lambda]|\tilde{\phi}_q^k\rangle_k \\ &+ \int_{\Omega_k} (V_{H_{|\Omega_k}}[\tilde{\rho}_{\mathcal{Z}_c}^k[\lambda]] + V_{Hxc_{|\Omega_k}}[\tilde{\rho}_1^k[\tilde{\psi}_i,\lambda] + \hat{\rho}^k[\tilde{\psi}_i,\lambda];\tilde{\rho}_c^k[\lambda]] + V_{ext}[\lambda])\left(\sum_{LM}\hat{Q}_{kpq}^{LM}[\lambda]\right)d\mathbf{x}.\end{aligned} \tag{21}$$

To simplify the notations in the previous expressions, we have combined the Hartree and exchange-correlation potentials as follows [see Eq. (9)]:

$$V_{Hxc}[\rho;\rho_c] = V_H[\rho] + V_{xc}[\rho + \rho_c]. \tag{22}$$

The second factor in the third term in Eq. (4) relies on the definition of the overlap operator

$$\tilde{S}[\lambda] = I + \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} S_{kpq}(\tilde{p}_p^k \tilde{p}_q^{k\dagger})[\lambda] \tag{23}$$

with

$$S_{kpq} = \langle \phi_p^k | \phi_q^k \rangle_k - \langle \tilde{\phi}_p^k | \tilde{\phi}_q^k \rangle_k. \tag{24}$$

Equations (23) and (24) are independent of the pseudo-wavefunctions.

In view of the perturbation expansion, we will add two hypotheses to our formulation. First, we suppose that the zero-order pseudo-wavefunctions have been unitary transformed such as to satisfy Kohn-Sham eigenequations, instead of the nondiagonal Eqs. (17). Thus,

$$\Lambda_{jj'}^{(0)} = \varepsilon_j^{(0)} \delta_{jj'} \tag{25}$$

Second, the external potential $V_{ext}[\lambda]$ vanishes at $\lambda=0$, and is a linear function of the parameter λ:

$$V_{ext}[\lambda] = \lambda V_{ext}^{(1)} \tag{26}$$

Thus, our PAW formulation is made of Eqs. (4)–(26). It is significantly more complex than the corresponding NCPP total energy.[10]

Let us analyze the dependencies, with respect to pseudo-wavefunctions, of the six terms in Eq. (4). The first term (based on $\tilde{H}_{KV}$), and the second factor of the second term, have an explicit quadratic dependence on the pseudo-wavefunctions $\tilde{\psi}_i$, while the last three terms have no dependences on the pseudo-wavefunctions. The longest chain of dependencies for the exchange-correlation term $\tilde{E}_{Hxc}$ is as follows:

$$\{\tilde{\psi}_i\} \rightarrow \{\rho_{kpq}\} \rightarrow \{\rho_1^k, \tilde{\rho}_1^k, \hat{\rho}^k\} \rightarrow \{\tilde{E}_{Hxc}\} \tag{27}$$

The longest chain of dependencies for the Lagrange multipliers in the second term of Eq. (4) is even longer (and, moreover, the Lagrange multipliers must be multiplied by the second factor in this second term):

$$\{\tilde{\psi}_i\} \rightarrow \{\rho_{kpq}\} \rightarrow \{\rho_1^k, \tilde{\rho}_1^k, \hat{\rho}^k\} \rightarrow \{D_{kpq}^1, \tilde{D}_{kpq}^1\} \rightarrow \{\tilde{H}\} \rightarrow \{\Lambda_{jj'}\} \tag{28}$$

In this framework, we are going to build the expressions of $E_{tot}^{+(1)}$, $E_{tot}^{+(2)}$ and $E_{tot}^{+(3)}$.

III. FIRST-ORDER CHANGE OF TOTAL ENERGY

Due to the complex dependencies of the PAW total energy Eq. (4), we will benefit a lot from notations that takes into account the limited wavefunction expansion that is needed in Eqs. (2) and (3). We define, for all the quantities $X[\tilde{\psi}_i[\lambda],\lambda]$, the incomplete terms of the series expansion:

$$X^{(\underline{2n+1})} = \left(X\left[\sum_{j=0}^{n} \lambda^j \tilde{\psi}_i^{(j)}, \lambda \right] \right)^{(2n+1)} \tag{29}$$

and

$$X^{(\underline{2n})} = \left(X\left[\sum_{j=0}^{n} \lambda^j \tilde{\psi}_i^{(j)}, \lambda \right] \right)^{(2n)}. \tag{30}$$

For the specific case of the total energy, Eqs. (2) and (3) imply, for all m:

$$E_{tot}^{+(m)} = E_{tot}^{+(\underline{m})} \tag{31}$$

But this equality is true only for the total energy.

Let us focus on the first-order incomplete terms (terms for higher orders will be found in the following sections). We have

$$X^{(\underline{1})} = (X[\tilde{\psi}_i^{(0)},\lambda])^{(1)} = \frac{\partial X}{\partial \lambda}, \tag{32}$$

so that, $X^{(\underline{1})}$ is equal to the partial derivative of X with respect to λ, and

$$X^{(1)} = \frac{dX}{d\lambda} = \sum_{i=1}^{N} \frac{\delta X}{\delta \tilde{\psi}_i} \tilde{\psi}_i^{(1)} + X^{(\underline{1})}, \tag{33}$$

Eq. (2) taken with $n=0$ gives the first-order term in the expansion of the energy, for which the knowledge of $\tilde{\psi}_i^{(0)}$ is sufficient. For the unperturbed wavefunctions, and evaluated at $\lambda=0$, the Lagrange constraint term $(\langle \tilde{\psi}_i | \tilde{S}[\lambda] | \tilde{\psi}_j \rangle - \delta_{ij})$ vanish.

From Eqs. (2) and (4), we derive thus

$$\begin{aligned} E_{tot}^{+(1)} = & \sum_{i=1}^{N} \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)} | \tilde{\psi}_i^{(0)} \rangle + (\tilde{E}_{Hxc})^{(\underline{1})} \\ & + \sum_{k=1}^{K} \int_{\Omega_k} V_{ext}^{(1)} \rho_{\mathcal{Z}_c}^{k(0)} d\mathbf{x} \\ & + \left(\frac{1}{2} \sum_{k=1}^{K} \int_{\Omega_k} \int_{\Omega_k} \frac{\rho_{\mathcal{Z}_c}^k(\mathbf{x}) \rho_{\mathcal{Z}_c}^k(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{x} d\mathbf{y} + U \right)^{(1)}. \end{aligned} \tag{34}$$

$\tilde{H}_{KV}^{(1)}$ and $\tilde{S}^{(1)}$ are specified in Appendix B.

The exchange-correlation energy derivative is the most embarrassing term. Using the fact that only the $\tilde{\psi}_i^{(0)}$ are needed for the knowledge of $(\tilde{E}_{Hxc})^{(\underline{1})}$, we introduce the following decomposition:

$$(E_{Hxc}[\rho(\lambda);\rho_c(\lambda)])^{(\underline{1})} = E'_{Hxc}[\rho^{(0)};\rho_c^{(0)}] \cdot (\rho^{(\underline{1})};\rho_c^{(1)}) \tag{35}$$

where we have set

$$E'_{Hxc} = \frac{\delta E_{Hxc}}{\delta \rho} = V_H + V_{xc} = V_{Hxc} \tag{36}$$

and abbreviate further the final expression thanks to the definition

$$\begin{aligned} E'_{Hxc}[\rho^{(0)};\rho_c^{(0)}] \cdot (\rho^{(1)};\rho_c^{(1)}) &= \int V_{Hxc}[\rho^{(0)};\rho_c^{(0)}](\rho^{(1)};\rho_c^{(1)}) \\ &= \int V_H[\rho^{(0)}]\rho^{(1)} d\mathbf{x} + \int V_{xc}[(\rho+\rho_c)^{(0)}](\rho+\rho_c)^{(1)} d\mathbf{x}. \end{aligned} \tag{37}$$

We also need first-order derivatives of the different densities. In the norm-conserving formalism, the electronic density ρ only depends on the wavefunctions, implying that $\rho^{(\underline{1})}=0$. In the PAW formalism, we have the same thing for $\tilde{\rho}$, which depends on λ only in an implicit way:

$$\tilde{\rho}^{(1)} = \sum_{i=1}^{N} (\tilde{\psi}_i^{(0)*}\tilde{\psi}_i^{(1)} + \tilde{\psi}_i^{(1)*}\tilde{\psi}_i^{(0)}), \tag{38}$$

meaning also that $\tilde{\rho}^{(\underline{1})}=0$. For ρ_1, $\tilde{\rho}_1$, and $\hat{\rho}$, the dependence of λ are both implicit and explicit. We have gathered all the equations defining derivatives of densities in Appendix C.

Thanks to Eqs. (35) and (38), Eq. (34) becomes:

$$\begin{aligned} E_{tot}^{+(1)}[\tilde{\psi}_i^{(0)}] = {} & \sum_{i=1}^{N} \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)}\tilde{S}^{(1)} | \tilde{\psi}_i^{(0)} \rangle + \int_{\mathbb{R}^3} V_{Hxc}[(\tilde{\rho}+\hat{\rho})^{(0)};\tilde{\rho}_c^{(0)}](\hat{\rho}^{(\underline{1})};\tilde{\rho}_c^{(1)}) d\mathbf{x} \\ & + \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[\rho_1^{k(0)};\rho_c^{k(0)}](\rho_1^{k(\underline{1})};\rho_c^{k(1)}) d\mathbf{x} - \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[(\rho_1^{k}+\hat{\rho}^{k})^{(0)};\tilde{\rho}_c^{k(0)}]((\tilde{\rho}_1^{k}+\hat{\rho}^{k})^{(\underline{1})};\tilde{\rho}_c^{k(1)}) d\mathbf{x} \\ & + \sum_{k=1}^{K} \int_{\Omega_k} V_{ext}^{(1)} \rho_{\mathcal{Z}_c}^{k(0)} d\mathbf{x} + \left(\frac{1}{2} \sum_{k=1}^{K} \int_{\Omega_k} \int_{\Omega_k} \frac{\rho_{\mathcal{Z}_c}^{k}(\mathbf{x})\rho_{\mathcal{Z}_c}^{k}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{x} d\mathbf{y} + U \right)^{(1)}. \end{aligned} \tag{39}$$

In the case of perturbation caused by atomic displacements, Blöchl,[5] as well as Kresse and Joubert[6] have derived a PAW expression for the forces. The correspondence with the present formalism will be derived now. We have to consider in a different way the change of atomic positions in the "real" space, on one hand, and in the spaces Ω_k attached to the atomic spheres, on the other hand. Indeed, for the space attached to the sphere, there is no direct effect of an atomic position change: The positions are relative to the origin of the sphere. By contrast, the atomic position changes will affect all the atomic functions in the "real" space. So, the changes of core densities in the space "attached" to the spheres vanish: $\rho_c^{k(1)}=\tilde{\rho}_c^{k(1)}=0$. By contrast, this is not the case for the changes of core densities in real space $\tilde{\rho}_c^{(1)}$. The external potential change vanishes also, $V_{ext}^{(1)}[\mathbf{x}]=0$, as well as the change of self-interaction of core charge $\rho_{\mathcal{Z}_c}^{k}$.

For $\tilde{H}_{KV}^{(1)}$, the general expression Eq. (B1), presented in Appendix B, simplifies to

$$\begin{aligned} \tilde{H}_{KV}^{(1)} = {} & V_H[\tilde{\rho}_{\mathcal{Z}_c}^{(1)}] + \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} E_{kpq}^{(0)} (\tilde{p}_p^{k}\tilde{p}_q^{k\dagger})^{(1)} \\ & + \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} \left[\sum_{LM} \int_{\mathbb{R}^3} (V_H[\tilde{\rho}_{\mathcal{Z}_c}]\hat{Q}_{kpq}^{LM})^{(1)} dx \right] (\tilde{p}_p^{k}\tilde{p}_q^{k\dagger})^{(0)}. \end{aligned} \tag{40}$$

Now, we can reformulate Eq. (39) to make exactly appear the different forces according to Ref. 6:

$$E_{tot}^{+(1)} = -(F^1 + F^2 + F^3 + F^{nlcc}) + U^{(1)}, \tag{41}$$

with

$$F^1 = -\int_{\mathbb{R}^3} (V_H[\tilde{\rho}_{\mathcal{Z}_c}^{(1)}])(\tilde{\rho}+\hat{\rho})^{(0)} d\mathbf{x}, \tag{42}$$

$$F^2 = -\sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} \sum_{LM} \int_{\mathbb{R}^3} \rho_{kpq}^{(0)} (V_H[\tilde{\rho}_{\mathcal{Z}_c}^{(0)}] + V_{Hxc}[(\tilde{\rho}+\hat{\rho})^{(0)};\tilde{\rho}_c^{(0)}])(\hat{Q}_{kpq}^{LM})^{(1)} d\mathbf{x}, \tag{43}$$

$$F^3 = -\sum_{i=1}^{N}\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}} (\tilde{D}_{kpq} + D^1_{kpq} - \tilde{D}^1_{kpq} - \varepsilon_i S_{kpq})^{(0)} \langle \tilde{\psi}_i^{(0)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(1)} | \tilde{\psi}_i^{(0)} \rangle \tag{44}$$

and

$$F^{nlcc} = -\int_{\mathbb{R}^3} V_{xc}[(\tilde{\rho} + \hat{\rho} + \tilde{\rho}_c)^{(0)}] \tilde{\rho}_c^{(1)} d\mathbf{x}. \tag{45}$$

IV. SECOND-ORDER CHANGE OF TOTAL ENERGY

The second-order energy term $E_{tot}^{+(2)}$ is given by Eq. (3) for $n=1$, also a variational principle with respect to the first-order wavefunctions $\tilde{\psi}_i^{(1)}$. Higher-order pseudo-wavefunctions are not needed.

To get $E_{tot}^{+(2)}$, we have to characterize perturbation terms up to the second order. We introduce quantities $X^{(\underline{2})}$, following Eq. (30), or equivalently, from the following expansion:

$$X[\tilde{\psi}_i^{(0)} + \lambda \tilde{\psi}_i^{(1)}, \lambda] = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(\underline{2})} + \lambda^3 X^{(\underline{3})} + \cdots \tag{46}$$

To build $X^{(\underline{2})}$, only first-order and zero-order wavefunctions $\tilde{\psi}_i$ are needed; the exact second-perturbation term $X^{(2)}$ would need at least an expansion up to the second-order $\tilde{\psi}_i^{(2)}$, except for $E_{tot}^{+(2)} = E_{tot}^{+(\underline{2})}$.

The variational principle can now be written as follows:

$$E_{tot}^{+(2)} = \min_{\tilde{\psi}_i^{(1)}} \left\{ \sum_{i=1}^{N} (\langle \tilde{\psi}_i | \tilde{H}_{KV} | \tilde{\psi}_i \rangle)^{(\underline{2})} - \sum_{j,j'=1}^{N} \Lambda_{jj'}^{(0)} (\langle \tilde{\psi}_j | \tilde{S} | \tilde{\psi}_{j'} \rangle)^{(\underline{2})} + (\tilde{E}_{Hxc})^{(\underline{2})} \right\}$$
$$+ \sum_{k=1}^{K} \int_{\Omega_k} V_{ext}^{(1)} \rho_{\mathcal{Z}_c}^{k(1)} d\mathbf{x} + \left(\frac{1}{2} \sum_{k=1}^{K} \int_{\Omega_k} \int_{\Omega_k} \frac{\rho_{\mathcal{Z}_c}^k(\mathbf{x}) \rho_{\mathcal{Z}_c}^k(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y} + U \right)^{(2)}. \tag{47}$$

under the constraints

$$\langle \tilde{\psi}_j^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_{j'}^{(0)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_{j'}^{(1)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_{j'}^{(0)} \rangle = 0. \tag{48}$$

The first two terms are expanded as follows

$$(\langle \tilde{\psi}_i | \tilde{H}_{KV} | \tilde{\psi}_i \rangle)^{(\underline{2})} = \langle \tilde{\psi}_i^{(1)} | \tilde{H}_{KV}^{(0)} | \tilde{\psi}_i^{(1)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(1)} | \tilde{\psi}_i^{(1)} \rangle$$
$$+ \langle \tilde{\psi}_i^{(1)} | \tilde{H}_{KV}^{(1)} | \tilde{\psi}_i^{(0)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(2)} | \tilde{\psi}_i^{(0)} \rangle. \tag{49}$$

and

$$(\langle \tilde{\psi}_j | \tilde{S} | \tilde{\psi}_{j'} \rangle)^{(\underline{2})} = \langle \tilde{\psi}_j^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_{j'}^{(1)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_{j'}^{(1)} \rangle$$
$$+ \langle \tilde{\psi}_j^{(1)} | \tilde{S}^{(1)} | \tilde{\psi}_{j'}^{(0)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(2)} | \tilde{\psi}_{j'}^{(0)} \rangle \tag{50}$$

In the second term, we will need only the $j=j'$ contribution, due to Eq. (25).

In order to cope with the long chain of dependencies, e.g., Eqs. (27) and (28), we will need one more notational handle. Suppose that one quantity X depends on λ, as well as on another quantity Y, that depends also on λ. Then,

$$X^{(2)} = \frac{1}{2} \left(\frac{d^2}{d\lambda^2} X[Y(\lambda), \lambda] \right)_{|\lambda=0}$$
$$= \frac{\delta X}{\delta Y} Y^{(2)} + \frac{1}{2} \frac{\delta^2 X}{\delta Y^2} (Y^{(1)})^2 + \left(\frac{\partial}{\partial \lambda} \frac{\delta X}{\delta Y} \right)_{|\lambda=0} Y^{(1)} + \frac{1}{2} \left(\frac{\partial^2 X}{\partial \lambda^2} \right)_{|\lambda=0}. \tag{51}$$

An even more complex expression is found for the third-order expressions, see Sec. VII. We aim at a concise and systematic identification of the four terms in Eq. (51). One can distinguish them on the basis of the set of superscripts of Y factors in each term.[30] For Eq. (51), we write

$$X^{(2)} = X^{(2:2)} + X^{(2:1,1)} + X^{(2:1)} + X^{(2:0)}. \tag{52}$$

with

$$X^{(2:2)} = \frac{\delta X}{\delta Y} Y^{(2)}, \tag{53}$$

$$X^{(2:1,1)} = \frac{1}{2} \frac{\delta^2 X}{\delta Y^2} (Y^{(1)})^2, \tag{54}$$

$$X^{(2:1)} = \left(\frac{\partial}{\partial\lambda}\frac{\delta X}{\delta Y}\right)_{|\lambda=0} Y^{(1)} \tag{55}$$

and

$$X^{(2:0)} = \frac{1}{2}\left(\frac{\partial^2 X}{\partial\lambda^2}\right)_{|\lambda=0}. \tag{56}$$

Such a decomposition easily generalizes to higher-order expansions. In particular, we have

$$X^{(k:0)} = \frac{1}{k!}\left(\frac{\partial^k X}{\partial\lambda^k}\right)_{|\lambda=0}, \tag{57}$$

and

$$X^{(k:k)} = \left(\frac{\delta X}{\delta Y}\right)_{|\lambda=0} Y^{(k)}. \tag{58}$$

It generalizes also easily to more than one Y argument, by collecting the superscripts in a set, as previously, without taking care of the different arguments.

In the particular case where $Y(\lambda)=\tilde{\psi}(\lambda)$, where $\tilde{\psi}$ is a pseudo-wavefunction, we find

$$X^{(\underline{2})} = X^{(\underline{2}:1,1)} + X^{(\underline{2}:1)} + X^{(\underline{2}:0)}, \tag{59}$$

because the expansion of the pseudowavefunctions up to the first order only is needed (so, the contribution that would be labelled $X^{(\underline{2}:2)}$ vanishes).

The exchange-correlation term $\tilde{E}_{Hxc}$, Eq. (9), does not depend directly of the $\tilde{\psi}_i$ but on the different PAW densities, and does not depend explicitly on λ. We can use the decomposition Eq. (52), generalized to more than one argument, but without explicit λ-dependence:

$$(\tilde{E}_{Hxc})^{(\underline{2})} = \tilde{E}_{Hxc}^{(\underline{2}:2)} + \tilde{E}_{Hxc}^{(\underline{2}:1,1)}. \tag{60}$$

with

$$\begin{aligned}\tilde{E}_{Hxc}^{(\underline{2}:2)} = {} & V_{Hxc}[(\tilde{\rho}+\hat{\rho})^{(0)};\tilde{\rho}_c^{(0)}]\cdot(\tilde{\rho}^{(\underline{2})}+\hat{\rho}^{(\underline{2})};\tilde{\rho}_c^{(2)}) \\ & + \sum_{k=1}^{K} V_{Hxc_{|\Omega_k}}[\rho_1^{k(0)};\rho_c^{k(0)}]\cdot(\rho_1^{k(\underline{2})};\rho_c^{k(2)}) \\ & - \sum_{k=1}^{K} V_{Hxc_{|\Omega_k}}[(\tilde{\rho}_1^k+\hat{\rho}^k)^{(0)};\tilde{\rho}_c^{k(0)}]\cdot((\tilde{\rho}_1^k+\hat{\rho}^k)^{(\underline{2})};\tilde{\rho}_c^{k(2)})\end{aligned} \tag{61}$$

and

$$\begin{aligned}\tilde{E}_{Hxc}^{(\underline{2}:1,1)} = \frac{1}{2}\Bigg[& E''_{Hxc}[(\tilde{\rho}+\hat{\rho})^{(0)};\tilde{\rho}_c^{(0)}]\cdot((\tilde{\rho}+\hat{\rho};\tilde{\rho}_c)^{(1)},(\tilde{\rho}+\hat{\rho};\tilde{\rho}_c)^{(1)}) \\ & + \sum_{k=1}^{K} E''_{Hxc_{|\Omega_k}}[\rho_1^{k(0)};\rho_c^{k(0)}]\cdot((\rho_1^k;\rho_c^k)^{(1)},(\rho_1^k;\rho_c^k)^{(1)}) \\ & - \sum_{k=1}^{K} E''_{Hxc_{|\Omega_k}}[(\tilde{\rho}_1^k+\hat{\rho}^k)^{(0)};\tilde{\rho}_c^{k(0)}]\cdot((\tilde{\rho}_1^k+\hat{\rho}^k;\tilde{\rho}_c^k)^{(1)},(\tilde{\rho}_1^k+\hat{\rho}^k;\tilde{\rho}_c^k)^{(1)})\Bigg],\end{aligned} \tag{62}$$

where we have used the convention

$$A\cdot(f,g) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} A(\mathbf{x},\mathbf{y})f(\mathbf{x})g(\mathbf{y})d\mathbf{x}d\mathbf{y}, \tag{63}$$

so that

$$\begin{aligned}& \frac{1}{2}E''_{Hxc}[\rho^{(0)};\rho_c^{(0)}]\cdot((\rho;\rho_c)^{(1)},(\rho;\rho_c)^{(1)}) \\ & \quad = E_H[\rho^{(1)}] + \frac{1}{2}\int E''_{xc}[(\rho+\rho_c)^{(0)}](\rho+\rho_c)^{(1)}(\rho+\rho_c)^{(1)}d\mathbf{x},\end{aligned} \tag{64}$$

$E^{Hxc}_{''}$ being the second differential of E_{Hxc} with respect to $\rho(\mathbf{x})$.

Taking into account the expressions (C1)–(C3) of $\rho_1^{k(\underline{2})}$, $\tilde{\rho}_1^{k(\underline{2})}$, $\hat{\rho}^{(\underline{2})}$, and others in Appendix C, one shows that in Eq. (47), we can recover the term

$$\sum_{i=1}^{N} \langle \tilde{\psi}_i^{(1)} | \tilde{H}^{(0)} | \tilde{\psi}_i^{(1)} \rangle, \tag{65}$$

involving the unperturbed PAW Hamiltonian $\tilde{H}^{(0)}$ defined by Eq. (18). For this, we split $\rho_{kpq}^{(\underline{2})}$ given by Eq. (C17) of Appendix C into

$$\rho_{kpq}^{(\underline{2})} = \rho_{kpq}^{(\underline{2}:1,1)} + \rho_{kpq}^{(\underline{2}:1)} + \rho_{kpq}^{(\underline{2}:0)}. \tag{66}$$

The decomposition Eq. (59) can be considered here because ρ_{kpq} directly depends on the $\tilde{\psi}_i$. One can then verify that quantities belonging to $\tilde{E}_{Hxc}^{(\underline{2}:2)}$, gathered with $\Sigma_{i=1}^{N} \langle \tilde{\psi}_i^{(1)} | \tilde{H}_{KV}^{(0)} | \tilde{\psi}_i^{(1)} \rangle$, finally give the relation Eq. (65).

Equation (47) can thus be written in a way that makes more apparent its variational character, with some terms being quadratic in the first-order wavefunctions, some terms being linear in them, and the remaining being constant with respect to them.

$$\begin{aligned}
E_{tot}^{+(2)} = \min_{\tilde{\psi}_i^{(1)}} \Bigg\{ & \sum_{i=1}^{N} [\langle \tilde{\psi}_i^{(1)} | (\tilde{H} - \varepsilon_i \tilde{S})^{(0)} | \tilde{\psi}_i^{(1)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)} | \tilde{\psi}_i^{(1)} \rangle + \langle \tilde{\psi}_i^{(1)} | \tilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)} | \tilde{\psi}_i^{(0)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)} \tilde{S}^{(2)} | \tilde{\psi}_i^{(0)} \rangle] \\
& + \tilde{E}_{Hxc}^{(\underline{2}:1,1)} + \int_{\mathbb{R}^3} V_{Hxc}[(\tilde{\rho} + \hat{\rho})^{(0)}; \tilde{\rho}_c^{(0)}](\hat{\rho}^{(\underline{2}:1)} + \hat{\rho}^{(\underline{2}:0)}; \tilde{\rho}_c^{(\underline{2})}) d\mathbf{x} + \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[\rho_1^{k(0)}; \rho_c^{k(0)}](\rho_1^{k(\underline{2}:1)} + \rho_1^{k(\underline{2}:0)}; \rho_c^{k(2)}) d\mathbf{x} \\
& - \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[(\tilde{\rho}_1^k + \hat{\rho}^k)^{(0)}; \tilde{\rho}_c^{k(0)}]((\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{2}:1)} + (\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{2}:0)}; \tilde{\rho}_c^{k(2)}) d\mathbf{x} \Bigg\} \\
& + \sum_{k=1}^{K} \int_{\Omega_k} V_{ext}^{(1)} \rho_{\mathcal{Z}_c}^{k(1)} d\mathbf{x} + \left(\frac{1}{2} \sum_{k=1}^{K} \int_{\Omega_k} \int_{\Omega_k} \frac{\rho_{\mathcal{Z}_c}^k(\mathbf{x}) \rho_{\mathcal{Z}_c}^k(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y} + U \right)^{(2)}
\end{aligned} \tag{67}$$

with the first-order perturbations on the constraints Eqs. (48). In the variational formulation Eq. (67), we have used expressions $\hat{\rho}^{(\underline{2}:1)}$, $\hat{\rho}^{(\underline{2}:0)}$, $\rho_1^{k(\underline{2}:1)}$, $\rho_1^{k(\underline{2}:0)}$, $\tilde{\rho}_1^{k(\underline{2}:1)}$, $\tilde{\rho}_1^{k(\underline{2}:0)}$, $\hat{\rho}^{k(\underline{2}:1)}$, and $\hat{\rho}^{k(\underline{2}:0)}$, which are parts of $\hat{\rho}^{(\underline{2})}$, $\rho_1^{(\underline{2})}$,$\tilde{\rho}_1^{(\underline{2})}$. These quantities are defined in Appendix C. The first term of Eq. (67) is quadratic in the pseudo-wavefunctions. Other quadratic parts are also found in each of the three terms of $\tilde{E}_{Hxc}^{(\underline{2}:1,1)}$, see Eq. (62). All the other contributions are either linear in $\tilde{\psi}_i^{(1)}$ or do not depend on them.

V. THE GENERALIZED STERNHEIMER EQUATION

The resolution of this variational principle might rely on self-consistent minimization techniques, like conjugate gradient ones described, for example, in Refs. 33 and 34, or on the Euler-Lagrange equations corresponding to the minimization problem Eq. (67). These Euler-Lagrange equations are called generalized Sternheimer equations, and write:

$$(\tilde{H}^{(0)} - \varepsilon_i^{(0)} \tilde{S}^{(0)}) \tilde{\psi}_i^{(1)} + (\tilde{H}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)}) \tilde{\psi}_i^{(0)} = \sum_j \Lambda_{ij}^{(1)} \tilde{S}^{(0)} \tilde{\psi}_j^{(0)}, \tag{68}$$

where the operator $\tilde{H}^{(1)}$ will be detailed later. In Appendix D, we define the generalization to the PAW method of the parallel-transport gauge for NCPP (see Sec. III C of Ref. 10). Thanks to gauge freedom, one can impose the more restrictive constraints

$$\langle \tilde{\psi}_i^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(0)} \rangle = \langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(1)} \rangle, \tag{69}$$

which lead also to

$$\langle \tilde{\psi}_i^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(0)} \rangle = -\frac{1}{2} \langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_j^{(0)} \rangle. \tag{70}$$

As in the USPP formalism,[16,17] the projector operators P_c and $P_c^{\dagger}$ can be defined, as

$$P_c = I - \sum_{i=1}^{N} | \tilde{\psi}_i^{(0)} \rangle \langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(0)}, \tag{71}$$

$$P_c^{\dagger} = I - \sum_{i=1}^{N} \tilde{S}^{(0)} | \tilde{\psi}_i^{(0)} \rangle \langle \tilde{\psi}_i^{(0)} |. \tag{72}$$

In particular, we have $P_c^{\dagger}(\tilde{S}^{(0)} \tilde{\psi}_i^{(0)}) = 0$. We finally get (see Appendix D) the generalized Sternheimer equations:

$$P_c^{\dagger} (\tilde{H}^{(0)} - \varepsilon_i^{(0)} \tilde{S}^{(0)}) P_c \tilde{\psi}_i^{(1)} = - P_c^{\dagger} (\tilde{H}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)}) \tilde{\psi}_i^{(0)}. \tag{73}$$

We checked[26] that the operator $P_c^\dagger(\widetilde{H}^{(0)}-\varepsilon_i^{(0)}\widetilde{S}^{(0)})P_c$ of the Eq. (73) is positive-definite, as in the norm-conserving case. In particular, the different assumptions required in the PAW formalism play an important role: Using the completeness relation Eq. (A3) of Appendix A, assuming the fact that the support of the projectors $\widetilde{p}_j^k$ are inside Ω_k and that each monoatomic operator $I+T_k$ is invertible, the application

$$(u,v)\mapsto\langle u|\widetilde{S}^{(0)}|v\rangle$$

is a scalar product. Therefore, the operator of the generalized Sternheimer Eqs. (73) is positive-definite with respect to the norm defined by $\widetilde{S}^{(0)}$, provided that there exists an energy gap $\varepsilon_{N+1}^{(0)}\rangle\varepsilon_N^{(0)}$: for all u, we have

$$\begin{aligned}\langle u|P_c^\dagger(\widetilde{H}^{(0)}-\varepsilon_i^{(0)}\widetilde{S}^{(0)})P_c|u\rangle &= \left\langle\sum_{j\geqslant N+1}\langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(0)}|u\rangle\widetilde{\psi}_j^{(0)}|(\widetilde{H}^{(0)}-\varepsilon_i^{(0)}\widetilde{S}^{(0)})|\sum_{k\geqslant N+1}\langle\widetilde{\psi}_k^{(0)}|\widetilde{S}^{(0)}|u\rangle\widetilde{\psi}_k^{(0)}\right\rangle\\ &=\sum_{j\geqslant N+1}(\langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(0)}|u\rangle)^2(\varepsilon_j^{(0)}-\varepsilon_i^{(0)})\geqslant(\varepsilon_{N+1}^{(0)}-\varepsilon_i^{(0)})\sum_{j\geqslant N+1}(\langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(0)}|u\rangle)^2\\ &=(\varepsilon_{N+1}^{(0)}-\varepsilon_i^{(0)})\langle P_cu|\widetilde{S}^{(0)}|P_cu\rangle.\end{aligned}\tag{74}$$

Thus, we can transfer to the PAW case (with the appropriate modifications) the discussion on the variational properties of the corresponding NCPP expression, as given in Sec. IV B of Ref. 10.

To achieve the description of the Sternheimer equations, we give the form of the operator $\widetilde{H}^{(1)}$. Directly from the relation Eq. (18), we get the expression

$$\begin{aligned}\widetilde{H}^{(1)} &= V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(1)}]+(V_{Hxc}[\widetilde{\rho}+\hat{\rho};\widetilde{\rho}_c])^{(1)}+V_{ext}^{(1)}\\ &\quad+\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}(\widetilde{D}_{kpq}+D_{kpq}^1-\widetilde{D}_{kpq}^1)^{(1)}(\widetilde{p}_p^k\widetilde{p}_q^{k\dagger})^{(0)}\\ &\quad+\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}(\widetilde{D}_{kpq}+D_{kpq}^1-\widetilde{D}_{kpq}^1)^{(0)}(\widetilde{p}_p^k\widetilde{p}_q^{k\dagger})^{(1)},\end{aligned}\tag{75}$$

with

$$\begin{aligned}(V_{Hxc}[\widetilde{\rho}+\hat{\rho};\widetilde{\rho}_c])^{(1)} &= V_H[(\widetilde{\rho}+\hat{\rho})^{(1)}]\\ &\quad+E_{xc}''[(\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(0)}](\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(1)}.\end{aligned}\tag{76}$$

From the Eqs. (19)–(21), the first-order perturbations of the coefficients $\widetilde{D}_{kpq}$, D_{kpq}^1, $\widetilde{D}_{kpq}^1$ stand for

$$\begin{aligned}\widetilde{D}_{kpq}^{(1)} &= \sum_{LM}\int_{\mathbb{R}^3}(V_H[(\widetilde{\rho}+\hat{\rho})^{(1)}]+V_{ext}^{(1)})\hat{Q}_{kpq}^{LM(0)}d\mathbf{x}\\ &\quad+\sum_{LM}\int_{\mathbb{R}^3}E_{xc}''[(\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(0)}](\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(1)}\hat{Q}_{kpq}^{LM(0)}d\mathbf{x}\\ &\quad+\sum_{LM}\int_{\mathbb{R}^3}(V_H[\widetilde{\rho}_{\mathcal{Z}_c}]\hat{Q}_{kpq}^{LM})^{(1)}d\mathbf{x}\\ &\quad+\sum_{LM}\int_{\mathbb{R}^3}V_{Hxc}[(\widetilde{\rho}+\hat{\rho})^{(0)};\widetilde{\rho}_c^{(0)}]\hat{Q}_{kpq}^{LM(1)}d\mathbf{x},\end{aligned}\tag{77}$$

$$\begin{aligned}D_{kpq}^{1(1)} &= \int_{\Omega_k}(V_{H_{|\Omega_k}}[\rho_1^{k(1)}]+V_{ext}^{(1)})\phi_p^k\phi_q^{k*}d\mathbf{x}\\ &\quad+\int_{\Omega_k}E_{xc}''[(\rho_1^k+\rho_c^k)^{(0)}](\rho_1^k+\rho_c^k)^{(1)}\phi_p^k\phi_q^{k*}d\mathbf{x}\\ &\quad+\int_{\Omega_k}(V_{H_{|\Omega_k}}[\rho_{\mathcal{Z}_c}^k])^{(1)}\phi_p^k\phi_q^{k*}d\mathbf{x},\end{aligned}\tag{78}$$

$$\begin{aligned}\widetilde{D}_{kpq}^{1(1)} &= \int_{\Omega_k}(V_{H_{|\Omega_k}}[(\widetilde{\rho}_1^k+\hat{\rho}^k)^{(1)}]+(V_{H_{|\Omega_k}}[\widetilde{\rho}_{\mathcal{Z}_c}^k])^{(1)}+V_{ext}^{(1)})\left(\widetilde{\phi}_p^k\widetilde{\phi}_q^{k*}+\sum_{LM}(\hat{Q}_{kpq}^{LM})^{(0)}\right)d\mathbf{x}\\ &\quad+\int_{\Omega_k}E_{xc}''[(\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c^k)^{(0)}](\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c^k)^{(1)}\left(\widetilde{\phi}_p^k\widetilde{\phi}_q^{k*}+\sum_{LM}(\hat{Q}_{kpq}^{LM})^{(0)}\right)d\mathbf{x}\\ &\quad+\int_{\Omega_k}(V_{H_{|\Omega_k}}[\widetilde{\rho}_{\mathcal{Z}_c}^{k(0)}]+V_{Hxc_{|\Omega_k}}[(\widetilde{\rho}_1+\hat{\rho})^{k(0)};\widetilde{\rho}_c^{k(0)}])\sum_{LM}(\hat{Q}_{kpq}^{LM})^{(1)}d\mathbf{x}.\end{aligned}\tag{79}$$

Alternatively, one can obtain the perturbed operator $\widetilde{H}^{(1)}$ by deriving the expression of $E_{tot}^{+(2)}$ by respect to the $\widetilde{\psi}_i^{(1)}$, taking into account of all dependences in $\widetilde{\psi}_i^{(1)}$ of $\widetilde{\rho}^{(1)}$, $\hat{\rho}^{(1)}$, $\rho_1^{k(1)}$, $\widetilde{\rho}_1^{k(1)}$, $\hat{\rho}^{k(1)}$, $\rho_1^{k(\underline{2}:1)}$, $\widetilde{\rho}_1^{k(\underline{2}:1)}$, and $\hat{\rho}^{k(\underline{2}:1)}$.

VI. NONVARIATIONAL FORM OF THE SECOND-ORDER ENERGY CHANGE

We can also give a nonvariational form of $E_{tot}^{+(2)}$, as in the norm-conserving formalism. Coming back to the Eq. (39), we calculate $\frac{1}{2}\left(\frac{d}{d\lambda}E_{tot}^{+(1)}[\widetilde{\psi}_i^{(0)}+\lambda\widetilde{\psi}^{(1)}]\right)_{\lambda=0}$ to obtain:

$$\begin{aligned}E_{tot,not-var}^{+(2)} = \sum_{i=1}^{N} &[\langle\widetilde{\psi}_i^{(1)}|\widetilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)}\widetilde{S}^{(1)}|\widetilde{\psi}_i^{(0)}\rangle \\ &+ \langle\widetilde{\psi}_i^{(0)}|\widetilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)}\widetilde{S}^{(2)}|\widetilde{\psi}_i^{(0)}\rangle] \\ &- \frac{1}{2}\sum_{j,j'=1}^{N} \Lambda_{jj'}^{(1)}\langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(1)}|\widetilde{\psi}_{j'}^{(0)}\rangle \\ &+ \widetilde{E}_{Hxco}^{(\underline{2}:2)} + \widetilde{E}_{Hxco}^{(\underline{2}:1,1)} + \sum_{k=1}^{K}\int_{\Omega_k} V_{ext}^{(1)}\rho_{\mathcal{Z}_c}^{k(1)}d\mathbf{x} \\ &+ \left(\frac{1}{2}\sum_{k=1}^{K}\int_{\Omega_k}\int_{\Omega_k}\frac{\rho_{\mathcal{Z}_c}^{k}(\mathbf{x})\rho_{\mathcal{Z}_c}^{k}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x}d\mathbf{y} + U\right)^{(2)}\end{aligned} \tag{80}$$

where $\widetilde{E}_{Hxco}^{(\underline{2}:2)}$ and $\widetilde{E}_{Hxco}^{(\underline{2}:1,1)}$ are detailed in Appendix E. This nonvariational expression is *linear* with respect to the $\widetilde{\psi}_i^{(1)}$, contrary to the variational principle Eq. (67) which is a *quadratic* form. We have derived the same expression by substituting the Euler-Lagrange Eqs. (68) into Eq. (67), thanks to the expression Eq. (75) of $\widetilde{H}^{(1)}$, see Ref. 26.

The perturbed Lagrange multipliers $\Lambda_{jj'}^{(1)}$ that appear in Eq. (80) can be obtained, within the parallel gauge, as:

$$\Lambda_{jj'}^{(1)} = \langle\widetilde{\psi}_{j'}^{(0)}|\widetilde{H}^{(0)}|\widetilde{\psi}_j^{(1)}\rangle + \langle\widetilde{\psi}_{j'}^{(1)}|\widetilde{H}^{(0)}|\widetilde{\psi}_j^{(0)}\rangle + \langle\widetilde{\psi}_{j'}^{(0)}|\widetilde{H}^{(1)}|\widetilde{\psi}_j^{(0)}\rangle. \tag{81}$$

Finally, Eq. (80) can be compared to the Eqs. (20) and (21) of Ref. 11 given in the norm-conserving case.[31]

VII. THIRD-ORDER CHANGE OF TOTAL ENERGY

Thanks to the $2n+1$ theorem with $n=1$, we get the following relation:

$$\begin{aligned}E_{tot}^{+(3)} = \sum_{i=1}^{N} &[\langle\widetilde{\psi}_i^{(1)}|\widetilde{H}_{KV}^{(1)} - \varepsilon_i^{(0)}\widetilde{S}^{(1)}|\widetilde{\psi}_i^{(1)}\rangle \\ &+ \langle\widetilde{\psi}_i^{(0)}|\widetilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)}\widetilde{S}^{(2)}|\widetilde{\psi}_i^{(1)}\rangle + \langle\widetilde{\psi}_i^{(1)}|\widetilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)}\widetilde{S}^{(2)}|\widetilde{\psi}_i^{(0)}\rangle \\ &+ \langle\widetilde{\psi}_i^{(0)}|\widetilde{H}_{KV}^{(3)} - \varepsilon_i^{(0)}\widetilde{S}^{(3)}|\widetilde{\psi}_i^{(0)}\rangle] \\ &- \sum_{j,j'=1}^{N} \Lambda_{jj'}^{(1)}[\langle\widetilde{\psi}_j^{(1)}|\widetilde{S}^{(0)}|\widetilde{\psi}_{j'}^{(1)}\rangle \\ &+ \langle\widetilde{\psi}_j^{(1)}|\widetilde{S}^{(1)}|\widetilde{\psi}_{j'}^{(0)}\rangle + \langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(1)}|\widetilde{\psi}_{j'}^{(1)}\rangle + \langle\widetilde{\psi}_j^{(0)}|\widetilde{S}^{(2)}|\widetilde{\psi}_{j'}^{(0)}\rangle] \\ &+ (\widetilde{E}_{Hxc})^{(\underline{3})} + \sum_{k=1}^{K}\int_{\Omega_k} V_{ext}^{(1)}\rho_{\mathcal{Z}_c}^{k(2)}d\mathbf{x} \\ &+ \left(\frac{1}{2}\sum_{k=1}^{K}\int_{\Omega_k}\int_{\Omega_k}\frac{\rho_{\mathcal{Z}_c}^{k}(\mathbf{x})\rho_{\mathcal{Z}_c}^{k}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x}d\mathbf{y} + U\right)^{(3)}.\end{aligned} \tag{82}$$

To explicit the exchange-correlation term, we use, as in Sec. IV, the following developments:

$$\begin{aligned}X^{(3)} &= \frac{1}{6}\left(\frac{d^3}{d\lambda^3}X[Y(\lambda),\lambda]\right)_{|\lambda=0} \\ &= \frac{\delta^2 X}{\delta Y^2}Y^{(2)}Y^{(1)} + \frac{1}{6}\frac{\delta^3 X}{\delta Y^3}(Y^{(1)})^3 + \left(\frac{\partial}{\partial\lambda}\frac{\delta X}{\delta Y}\right)_{|\lambda=0}Y^{(2)} + \frac{\delta X}{\delta Y}Y^{(3)} \\ &+ \frac{1}{2}\left(\frac{\partial}{\partial\lambda}\frac{\delta^2 X}{\delta Y^2}\right)_{|\lambda=0}(Y^{(1)})^2 + \frac{1}{2}\left(\frac{\partial^2}{\partial\lambda^2}\frac{\delta X}{\delta Y}\right)_{|\lambda=0}Y^{(1)} \\ &+ \frac{1}{6}\left(\frac{\partial^3 X}{\partial\lambda^3}\right)_{|\lambda=0}\end{aligned} \tag{83}$$

that is to say, using the previous notations introduced in Sec. IV:

$$\begin{aligned}X^{(3)} = {} & X^{(3:2,1)} + X^{(3:1,1,1)} + X^{(3:2)} + X^{(3:3)} + X^{(3:1,1)} + X^{(3:1)} \\ & + X^{(3:0)}.\end{aligned} \tag{84}$$

For the special case $Y(\lambda)=\psi(\lambda)$, we define as before the quantities

$$X^{(\underline{3})} = X^{(\underline{3}:1,1,1)} + X^{(\underline{3}:1,1)} + X^{(\underline{3}:1)} + X^{(\underline{3}:0)}, \tag{85}$$

corresponding to the development in Eq. (46).

For example, the third-order perturbation term of ρ_{kpq} stands

$$\rho_{kpq}^{(\underline{3})} = \rho_{kpq}^{(\underline{3}:1,1)} + \rho_{kpq}^{(\underline{3}:1)} + \rho_{kpq}^{(\underline{3}:0)}, \tag{86}$$

where $\rho_{kpq}^{(\underline{3}:1,1)}$, $\rho_{kpq}^{(\underline{3}:1)}$, and $\rho_{kpq}^{(\underline{3}:0)}$ are presented explicitly in Appendix C.

Using a Taylor development we get:

$$\frac{1}{6}\frac{d^3}{d\lambda^3}(E_{Hxc}[\rho(\lambda),\lambda])_{|\widetilde{\psi}_i=\widetilde{\psi}_i^{(0)}+\lambda\widetilde{\psi}_i^{(1)},\lambda=0} = E_{Hxc}^{(\underline{3}:1,1,1)} + E_{Hxc}^{(\underline{3}:2,1)} + E_{Hxc}^{(\underline{3}:3)} \tag{87}$$

where the term $E_{Hxc}^{(\underline{3}:1,1,1)}$ is detailed in Appendix F.

As in the Sec. IV, in the expression of $E_{tot}^{+(3)}$ we gather all terms depending on $\rho_{kpq}^{(\underline{3}:1,1)}$ and $\rho_{kpq}^{(\underline{2}:1,1)}$ with $\Sigma_{i=1}^{N}\langle\widetilde{\psi}_i^{(1)}|\widetilde{H}_{KV}^{(1)}|\widetilde{\psi}_i^{(1)}\rangle$, to make appear $\Sigma_{i=1}^{N}\langle\widetilde{\psi}_i^{(1)}|\widetilde{H}^{(1)}|\widetilde{\psi}_i^{(1)}\rangle$. It leads to the introduction of the following quantities, $\rho_1^{k(\underline{3}:1)}$, $\rho_1^{k(\underline{3}:0)}$, $\widetilde{\rho}_1^{k(\underline{3}:1)}$, $\widetilde{\rho}_1^{k(\underline{3}:0)}$, $\hat{\rho}^{(\underline{3}:1)}$, $\hat{\rho}^{(\underline{3}:0)}$, $\hat{\rho}^{k(\underline{3}:1)}$, and $\hat{\rho}^{k(\underline{3}:0)}$, all defined in Appendix C.

We finally get the expression of $E_{tot}^{+(3)}$:

$$
\begin{aligned}
E_{tot}^{+(3)} = {} & \sum_{i=1}^{N} [\langle \tilde{\psi}_i^{(1)} | \tilde{H}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)} | \tilde{\psi}_i^{(1)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)} \tilde{S}^{(2)} | \tilde{\psi}_i^{(1)} \rangle + \langle \tilde{\psi}_i^{(1)} | \tilde{H}_{KV}^{(2)} - \varepsilon_i^{(0)} \tilde{S}^{(2)} | \tilde{\psi}_i^{(0)} \rangle + \langle \tilde{\psi}_i^{(0)} | \tilde{H}_{KV}^{(3)} - \varepsilon_i^{(0)} \tilde{S}^{(3)} | \tilde{\psi}_i^{(0)} \rangle] \\
& - \sum_{j,j'=1}^{N} \Lambda_{jj'}^{(1)} [\langle \tilde{\psi}_j^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_{j'}^{(1)} \rangle + \langle \tilde{\psi}_j^{(1)} | \tilde{S}^{(1)} | \tilde{\psi}_{j'}^{(0)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_{j'}^{(1)} \rangle + \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(2)} | \tilde{\psi}_{j'}^{(0)} \rangle] \\
& + \sum_{k=1}^{K} \int_{\Omega_k} V_{ext}^{(1)} \rho_{\mathcal{Z}_c}^{k(2)} d\mathbf{x} + \left(\frac{1}{2} \sum_{k=1}^{K} \int_{\Omega_k} \int_{\Omega_k} \frac{\rho_{\mathcal{Z}_c}^{k}(\mathbf{x}) \rho_{\mathcal{Z}_c}^{k}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y} + U \right)^{(3)} + \tilde{E}_{Hxc}^{(\underline{3}:1,1,1)} \\
& + \int_{\mathbb{R}^3} V_{Hxc}[(\tilde{\rho} + \hat{\rho})^{(0)}; \tilde{\rho}_c^{(0)}](\hat{\rho}^{(\underline{3}:1)} + \hat{\rho}^{(\underline{3}:0)}; \tilde{\rho}_c^{(3)}) d\mathbf{x} + \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[\rho_1^{k(0)}; \rho_c^{k(0)}](\rho_1^{k(\underline{3}:1)} + \rho_1^{k(\underline{3}:0)}; \rho_c^{k(3)}) d\mathbf{x} \\
& - \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc_{|\Omega_k}}[(\tilde{\rho}_1^k + \hat{\rho}^k)^{(0)}; \tilde{\rho}_c^{k(0)}]((\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{3}:1)} + (\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{3}:0)}; \tilde{\rho}_c^{k(3)}) d\mathbf{x} \\
& + E''_{Hxc}[(\tilde{\rho} + \hat{\rho})^{(0)}; \tilde{\rho}_c^{(0)}] \cdot (((\tilde{\rho} + \hat{\rho})^{(1)}; \tilde{\rho}_c^{(1)}), (\hat{\rho}^{(\underline{2}:1)} + \hat{\rho}^{(\underline{2}:0)}; \tilde{\rho}_c^{(2)})) \\
& + \sum_{k=1}^{K} E''_{Hxc_{|\Omega_k}}[\rho_1^{k(0)}; \rho_c^{k(0)}] \cdot ((\rho_1^{k(1)}; \rho_c^{k(1)}), (\rho_1^{k(\underline{2}:1)} + \rho_1^{k(\underline{2}:0)}; \tilde{\rho}_c^{k(2)})) \\
& - \sum_{k=1}^{K} E''_{Hxc_{|\Omega_k}}[(\tilde{\rho}_1^k + \hat{\rho}^k)^{(0)}; \tilde{\rho}_c^{k(0)}] \cdot (((\tilde{\rho}_1^k + \hat{\rho}^k)^{(1)}; \tilde{\rho}_c^{k(1)}), ((\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{2}:1)} + (\tilde{\rho}_1^k + \hat{\rho}^k)^{(\underline{2}:0)}; \tilde{\rho}_c^{k(2)})) \qquad (88)
\end{aligned}
$$

This expression, which only involves the wavefunctions $\tilde{\psi}_i^{(0)}$ and the perturbations $\tilde{\psi}_i^{(1)}$, can be compared with Eq. (111) given in Ref. 10.

In Eq. (88), the terms in lines five to seven come from $\tilde{E}_{Hxc}^{(\underline{3}:3)}$ in Eq. (87), while the terms in lines eight to ten come from $\tilde{E}_{Hxc}^{(\underline{3}:2,1)}$ in the same equation. The additional contributions from $\tilde{E}_{Hxc}^{(\underline{3}:3)}$ and $\tilde{E}_{Hxc}^{(\underline{3}:2,1)}$ have been absorbed in the first term of Eq. (88).

VIII. CONCLUSIONS AND PERSPECTIVES

Despite the PAW approach being much more complex than the norm-conserving pseudopotential approach, their structures is formally very similar. A careful analysis of dependencies of the PAW total energy, in Sec. II, has been performed. The variation-perturbation theorems have been applied to the formulation Eqs. (4)–(26), and have yield first-, second-, and third-order derivatives of the total energy.

At the level of the second-order derivative, the minimization principle allows to determine the first-order derivative of the wavefunctions. An alternative nonstationary expression allows the second-order derivative of the total energy to be computed as a linear function of the first-order derivative of the wavefunctions, plus constant terms.

As such, all the interesting applications of this method for NCPP or USPP can be expected to be implemented in the PAW case. At this stage, a real implementation is needed, to assert the kind of accuracy that can be obtained. In the NCPP case, finite-difference and variation-perturbation expressions have been shown to match numerically at the level of seven digits for the second-order derivative of the total energy, and at the level of four digits for the third-order derivative. At first sight, a similar accuracy should be obtained in the PAW case.

We expect the amount of developer time needed to implement the PAW-DFPT formalism up to second-order, starting from an existing (and reliable) PAW implementation, to be similar to the one needed to implement from scratch the PAW formalism. Availability of routines for DFPT calculation in the case of norm-conserving pseudopotentials should greatly facilitate this task: The same code structure could be used, and datastructures could be derived from PAW ones, thanks to appropriate generalization to first-order quantities, similar to those done in the norm-conserving pseudopotential case.

Finally, it is worth discussing briefly the CPU demand of PAW-DFPT calculations. We can compare it, as well, to the one needed for norm-conserving pseudopotentials. Usually, PAW calculations (nonperturbed) need a much smaller plane wave basis set than norm-conserving pseudopotential calculations, although the factor of improvement depends very much on the system under investigation. Like the USPP methodology, and even more than it, the PAW technique implies adding several calculations, compared to the norm-conserving pseudopotential technique. However, all the added steps are related to the treatment inside atomic spheres, and the overlap matrix. Such steps are already present in USPP, and are known to account only for a small fraction of the CPU time.

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APPENDIX A: THE PAW METHOD

The PAW method connects the Kohn-Sham wave functions ψ_i to pseudo-wavefunctions $\tilde{\psi}_i$ thanks to:

$$\psi_i = (I+T)\tilde{\psi}_i, \tag{A1}$$

where the index i runs over N, the number of occupied electronic states. For a molecular system composed of K nuclei, the linear operator T is defined by

$$T = \sum_{k=1}^{K}\sum_{j=1}^{N_{p_k}} (|\phi_j^k\rangle - |\tilde{\phi}_j^k\rangle)\langle\tilde{p}_j^k| = \sum_{k=1}^{K} T_k, \tag{A2}$$

where ϕ_j^k, $\tilde{\phi}_j^k$, and $\tilde{p}_j^k$ are atomic datas obtained for the k reference atom: ϕ_j^k and $\tilde{\phi}_j^k$ are all-electron and pseudo *atomic* wavefunctions which coincide outside the augmentation region, Ω_k, $\tilde{p}_j^k$ are projectors functions which are dual to the $\tilde{\phi}_j^k$ and whose support is in Ω_k. Here, the exponent k means that the functions ϕ_j^k, $\tilde{\phi}_j^k$, and $\tilde{p}_j^k$ are centered on the kth atomic site $\bar{x}_k$ (see Refs. 5–7 for details of such functions). By construction, the operator T only acts in the spheres Ω_k, which implies that $\psi_i = \tilde{\psi}_i$ outside the region $\Omega = \cup_{k=1}^{K}\Omega_k$.

It can be shown[26,32] that the operator $I+T$ is invertible, provided that each monoatomic operator $I+T_k$ is so and that the augmented zones are disjoined.

In each zone Ω_k, the projectors are supposed to satisfy the following completeness relation:

$$\sum_{j=1}^{N_{p_k}} |\tilde{\phi}_j^k\rangle\langle\tilde{p}_j^k| = I. \tag{A3}$$

Therefore, for each local operator A, the associated operator $\tilde{A} = (I+T)^{\dagger}A(I+T)$ such that $\langle\psi_i|A|\psi_j\rangle = \langle\tilde{\psi}_i|\tilde{A}|\tilde{\psi}_j\rangle$, can be written:

$$\tilde{A} = A + \sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}} |\tilde{p}_p^k\rangle\langle\tilde{p}_q^k|[\langle\phi_p^k|A|\phi_q^k\rangle_k - \langle\tilde{\phi}_p^k|A|\tilde{\phi}_q^k\rangle_k]. \tag{A4}$$

The pseudo-wavefunctions $\tilde{\psi}_i$ satisfy in that way the generalized constraints

$$\langle\tilde{\psi}_i|\tilde{S}|\tilde{\psi}_j\rangle = \delta_{ij} \tag{A5}$$

where the overlap operator is defined by

$$\tilde{S} = I + \sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}} S_{kpq}|\tilde{p}_p^k\rangle\langle\tilde{p}_q^k|, \tag{A6}$$

with S_{kpq} defined in Eq. (24) The notations $\langle|\,|\rangle$ or $\langle|\rangle$ mean matrix elements or scalar products over all space $\mathbb{R}^3$, while $\langle|\,|\rangle_k$ or $\langle|\rangle_k$ are defined over the sphere Ω_k only.

Following the notations of Ref. 6, the total charge density ρ is decomposed in:

$$\rho = (\tilde{\rho} + \hat{\rho} + \tilde{\rho}_{\mathcal{Z}_c}) + (\rho_1 + \rho_{\mathcal{Z}_c}) - (\tilde{\rho}_1 + \hat{\rho} + \tilde{\rho}_{\mathcal{Z}_c}), \tag{A7}$$

where $\tilde{\rho}+\rho_1-\tilde{\rho}_1$ represents the electronic valence density; $\rho_{\mathcal{Z}_c}=\rho_{\mathcal{Z}}+\rho_c$ is the core charge (core electrons and nuclei charge) and $\tilde{\rho}_{\mathcal{Z}_c}$ the pseudo core charge density. The compensation charge $\hat{\rho}$, built to have the same multipole moments as $\rho_1+\rho_{\mathcal{Z}_c}-(\tilde{\rho}_1+\tilde{\rho}_{\mathcal{Z}_c})$, allows to separate the potential and the Hartree terms of the total energy into two contributions, one estimated on a regular Fourier grid in the whole space, and other ones on radial grids in the regions Ω_k. Let us note that the scalar products in the sphere Ω_k of functions that are centered on the k atomic site do not change if this atom is moved.

The different densities of Eq. (A7) are given by:

$$\tilde{\rho}(\mathbf{x}) = \sum_{i=1}^{N} |\tilde{\psi}_i(\mathbf{x})|^2 \tag{A8}$$

which is calculated on the regular grid, while $\rho_1(\mathbf{x}) = \Sigma_{k=1}^{K}\rho_1^k(\mathbf{x})$ and $\tilde{\rho}_1(\mathbf{x}) = \Sigma_{k=1}^{K}\tilde{\rho}_1^k(\mathbf{x})$ are estimated on the radial grids in Ω_k. Each atomic component is defined by

$$\rho_1^k(\mathbf{x}) = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}\phi_p^k(\mathbf{x})\phi_q^{k*}(\mathbf{x}) \tag{A9}$$

and

$$\tilde{\rho}_1^k(\mathbf{x}) = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}\tilde{\phi}_p^k(\mathbf{x})\tilde{\phi}_q^{k*}(\mathbf{x}), \tag{A10}$$

with

$$\rho_{kpq} = \sum_{i=1}^{N} \langle\tilde{p}_p^k|\tilde{\psi}_i\rangle_k\langle\tilde{\psi}_i|\tilde{p}_q^k\rangle_k = \sum_{i=1}^{N} \langle\tilde{\psi}_i|(\tilde{p}_q^k\tilde{p}_p^{k\dagger})|\tilde{\psi}_i\rangle_k. \tag{A11}$$

The compensation charge is given by

$$\hat{\rho}(\mathbf{x}) = \sum_{k=1}^{K} \hat{\rho}^k(\mathbf{x}) \tag{A12}$$

with

$$\hat{\rho}^k(\mathbf{x}) = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}\sum_{LM} \hat{Q}_{kpq}^{LM}(\mathbf{x}), \tag{A13}$$

where $\hat{Q}_{kpq}^{LM}$ are atomic datas, the indices L,M being the angular momentum numbers. The whole density $\hat{\rho}$ is calculated on the regular grid while the atomic-centered density $\hat{\rho}^k$ is computed on the radial ones. Finally, the core charge is given by $\rho_{\mathcal{Z}_c}(\mathbf{x})=\Sigma_{k=1}^{K}\rho^k_{\mathcal{Z}_c}(\mathbf{x})$ with $\rho^k_{\mathcal{Z}_c}(\mathbf{x})=\rho^k_{\mathcal{Z}}(\mathbf{x})+\rho^k_c(\mathbf{x})$ and $\rho^k_{\mathcal{Z}}(\mathbf{x})=\mathcal{Z}_k\delta(\mathbf{x}-\bar{x}_k)$, $\mathcal{Z}_k$ being the nucleus charge of the kth atom; the pseudo core density is just an atomic data

$$\tilde{\rho}_{\mathcal{Z}_c}(\mathbf{x})=\sum_{k=1}^{K}\tilde{\rho}^k_{\mathcal{Z}_c}(\mathbf{x}). \tag{A14}$$

Here we introduce the notation "∘" for the repulsive Coulomb interaction between two densities charges u and v as follows:

$$(u)\circ(v)=\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{u(\mathbf{x})v(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x}d\mathbf{y}. \tag{A15}$$

The total energy E_{tot} of the system can be split into:[5–7,26]

$$E_{tot}=\tilde{E}+E_1-\tilde{E}_1 \tag{A16}$$

with

$$\tilde{E}=\sum_{i=1}^{N}\langle\tilde{\psi}_i|-\frac{1}{2}\nabla^2|\tilde{\psi}_i\rangle+\frac{1}{2}(\tilde{\rho}+\hat{\rho})\circ(\tilde{\rho}+\hat{\rho})+(\tilde{\rho}_{\mathcal{Z}_c})\circ(\tilde{\rho}+\hat{\rho})$$
$$+U+E_{xc}[\tilde{\rho}+\hat{\rho}+\tilde{\rho}_c]+\int_{\mathbb{R}^3}V_{ext}(\mathbf{x})(\tilde{\rho}+\hat{\rho})(\mathbf{x})d\mathbf{x}, \tag{A17}$$

$$\begin{aligned}E_1=&\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}\rho_{kpq}\langle\phi^k_p|-\frac{1}{2}\nabla^2|\phi^k_q\rangle_k+\frac{1}{2}\sum_{k=1}^{K}(\rho^k_1)\circ(\rho^k_1)_{|\Omega_k}\\&+\sum_{k=1}^{K}(\rho^k_{\mathcal{Z}_c})\circ(\rho^k_1)_{|\Omega_k}+\frac{1}{2}\sum_{k=1}^{K}(\rho^k_{\mathcal{Z}_c})\circ(\rho^k_{\mathcal{Z}_c})_{|\Omega_k}\\&+\sum_{k=1}^{K}E_{xc}[\rho^k_1+\rho^k_c]_{|\Omega_k}+\sum_{k=1}^{K}\int_{\Omega_k}V_{ext}(\mathbf{x})(\rho^k_1+\rho^k_{\mathcal{Z}_c})(\mathbf{x})d\mathbf{x}\end{aligned} \tag{A18}$$

and

$$\begin{aligned}\tilde{E}_1=&\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}\rho_{kpq}\langle\tilde{\phi}^k_p|-\frac{1}{2}\nabla^2|\tilde{\phi}^k_q\rangle_k\\&+\frac{1}{2}\sum_{k=1}^{K}(\tilde{\rho}^k_1+\hat{\rho}^k)\circ(\tilde{\rho}^k_1+\hat{\rho}^k)_{|\Omega_k}+\sum_{k=1}^{K}(\tilde{\rho}^k_{\mathcal{Z}_c})\circ(\tilde{\rho}^k_1+\hat{\rho}^k)_{|\Omega_k}\\&+\sum_{k=1}^{K}E_{xc}[\tilde{\rho}^k_1+\hat{\rho}^k+\tilde{\rho}^k_c]_{|\Omega_k}+\sum_{k=1}^{K}\int_{\Omega_k}V_{ext}(\mathbf{x})(\tilde{\rho}^k_1+\hat{\rho}^k)(\mathbf{x})d\mathbf{x}.\end{aligned} \tag{A19}$$

The atomic electrostatic repulsion term U of the Eq. (A17) is given by

$$U=\frac{1}{2}\sum_{k\neq l}\frac{N^k_vN^l_v}{|\bar{x}_k-\bar{x}_l|}, \tag{A20}$$

where N^k_v represents the number of valence electrons of the kth atom; in the Eq. (A18), ρ^k_c indicates the density of core electrons of the kth atom. Finally, V_{ext} represents an external linear potential (for example, an electric field) in which the molecular system is set.

If we consider the Euler-Lagrange equations associated with the minimization of the energy Eq. (A16), under the generalized constraints Eq. (A5), then we get the equations

$$\tilde{H}\tilde{\psi}_i=\varepsilon_i\tilde{S}\tilde{\psi}_i. \tag{A21}$$

APPENDIX B: EXPANSIONS OF $\tilde{H}_{KV}$ AND $\tilde{S}$

In the first term, $\tilde{H}^{(1)}_{KV}$ and $\tilde{S}^{(1)}$ are readily expressed as

$$\begin{aligned}\tilde{H}^{(1)}_{KV}=&V_H[\tilde{\rho}^{(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext}\\&+\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}(E^{(0)}_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(1)}+E^{(1)}_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(0)})\end{aligned} \tag{B1}$$

$$\begin{aligned}E^{(1)}_{kpq}=&\sum_{LM}\int_{\mathbb{R}^3}(V_H[\tilde{\rho}^{(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext})\hat{Q}^{LM(0)}_{kpq}+V_H[\tilde{\rho}^{(0)}_{\mathcal{Z}_c}]\hat{Q}^{LM(1)}_{kpq}d\mathbf{x}\\&-\sum_{LM}\int_{\Omega_k}(V_{H_{|\Omega_k}}[\tilde{\rho}^{(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext})\hat{Q}^{LM(0)}_{kpq}\\&+V_{H_{|\Omega_k}}[\tilde{\rho}^{(0)}_{\mathcal{Z}_c}]\hat{Q}^{LM(1)}_{kpq}d\mathbf{x}\\&+\langle\phi^k_p|V_{H_{|\Omega_k}}[\rho^{k(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext}|\phi^k_q\rangle_k\\&-\langle\tilde{\phi}^k_p|V_{H_{|\Omega_k}}[\tilde{\rho}^{k(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext}|\tilde{\phi}^k_q\rangle_k\end{aligned} \tag{B2}$$

and

$$\tilde{S}^{(1)}=\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}S_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(1)}, \tag{B3}$$

where the coefficients S_{kpq} and $E^{(0)}_{kpq}$ are defined by Eqs. (24) and (7), respectively, taken at $\lambda=0$.

The second-order terms $\tilde{H}^{(2)}_{KV}$ and $\tilde{S}^{(2)}$ are defined by

$$\begin{aligned}\tilde{H}^{(2)}_{KV}=&V_H[\tilde{\rho}^{(2)}_{\mathcal{Z}_c}]+\sum_{k=1}^{K}\sum_{p,q=1}^{N_{p_k}}(E^{(0)}_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(2)}+E^{(1)}_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(1)}\\&+E^{(2)}_{kpq}(\tilde{p}^k_p\tilde{p}^{k\dagger}_q)^{(0)})\end{aligned} \tag{B4}$$

$$\begin{aligned}E^{(2)}_{kpq}=&\sum_{LM}\int_{\mathbb{R}^3}V_H[\tilde{\rho}^{(0)}_{\mathcal{Z}_c}]\hat{Q}^{LM(2)}_{kpq}+(V_H[\tilde{\rho}^{(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext})\hat{Q}^{LM(1)}_{kpq}\\&+V_H[\tilde{\rho}^{(2)}_{\mathcal{Z}_c}]\hat{Q}^{LM(0)}_{kpq}d\mathbf{x}+\langle\phi^k_p|V_{H_{|\Omega_k}}[\rho^{k(2)}_{\mathcal{Z}_c}]|\phi^k_q\rangle_k\\&-\langle\tilde{\phi}^k_p|V_{H_{|\Omega_k}}[\tilde{\rho}^{k(2)}_{\mathcal{Z}_c}]|\tilde{\phi}^k_q\rangle_k-\sum_{LM}\int_{\Omega_k}V_{H_{|\Omega_k}}[\tilde{\rho}^{(0)}_{\mathcal{Z}_c}]\hat{Q}^{LM(2)}_{kpq}\\&+(V_{H_{|\Omega_k}}[\tilde{\rho}^{(1)}_{\mathcal{Z}_c}]+V^{(1)}_{ext})\hat{Q}^{LM(1)}_{kpq}+V_{H_{|\Omega_k}}[\tilde{\rho}^{(2)}_{\mathcal{Z}_c}]\hat{Q}^{LM(0)}_{kpq}d\mathbf{x}\end{aligned} \tag{B5}$$

and

$$\widetilde{S}^{(2)} = \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} S_{kpq} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(2)}. \tag{B6}$$

Finally, $\widetilde{H}_{KV}^{(3)}$ and $\widetilde{S}^{(3)}$ are given by

$$\begin{aligned}\widetilde{H}_{KV}^{(3)} = V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(3)}] + \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} (E_{kpq}^{(0)} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(3)} + E_{kpq}^{(1)} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(2)} \\ + E_{kpq}^{(2)} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(1)} + E_{kpq}^{(3)} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(0)})\end{aligned} \tag{B7}$$

$$\begin{aligned}E_{kpq}^{(3)} = \sum_{LM} \int_{\mathbb{R}^3} V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(0)}] \hat{Q}_{kpq}^{LM(3)} + (V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(1)}] + V_{ext}^{(1)}) \hat{Q}_{kpq}^{LM(2)} \\ + V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(2)}] \hat{Q}_{kpq}^{LM(1)} + V_H[\widetilde{\rho}_{\mathcal{Z}_c}^{(3)}] \hat{Q}_{kpq}^{LM(0)} d\mathbf{x} \\ + \langle \phi_p^k | V_{H_{|\Omega_k}} [\rho_{\mathcal{Z}_c}^{k(3)}] | \phi_q^k \rangle_k - \langle \widetilde{\phi}_p^k | V_{H_{|\Omega_k}} [\widetilde{\rho}_{\mathcal{Z}_c}^{k(3)}] | \widetilde{\phi}_q^k \rangle_k \\ - \sum_{LM} \int_{\Omega_k} V_{H_{|\Omega_k}} [\widetilde{\rho}_{\mathcal{Z}_c}^{(0)}] \hat{Q}_{kpq}^{LM(3)} + (V_{H_{|\Omega_k}} [\widetilde{\rho}_{\mathcal{Z}_c}^{(1)}] + V_{ext}^{(1)}) \hat{Q}_{kpq}^{LM(2)} \\ + V_{H_{|\Omega_k}} [\widetilde{\rho}_{\mathcal{Z}_c}^{(2)}] \hat{Q}_{kpq}^{LM(1)} + V_{H_{|\Omega_k}} [\widetilde{\rho}_{\mathcal{Z}_c}^{(3)}] \hat{Q}_{kpq}^{LM(0)} d\mathbf{x}\end{aligned} \tag{B8}$$

and

$$\widetilde{S}^{(3)} = \sum_{k=1}^{K} \sum_{p,q=1}^{N_{p_k}} S_{kpq} (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(3)}. \tag{B9}$$

APPENDIX C: EXPANSIONS OF THE DIFFERENT DENSITIES

In this Appendix, we examine the terms of the expansions of the different densities that depend on the wavefunctions, namely, $\widetilde{\rho}[\widetilde{\psi}_i]$, $\hat{\rho}[\widetilde{\psi}_i, \lambda]$, $\rho_1^k[\widetilde{\psi}_i, \lambda]$, $\widetilde{\rho}_1^k[\widetilde{\psi}_i, \lambda]$, $\hat{\rho}^k[\widetilde{\psi}_i, \lambda]$, as well as the coefficients $\rho_{kpq}[\widetilde{\psi}_i, \lambda]$, see Eqs. (10)–(15).

The computation of these terms is quite straightforward, following the different definitions in the present paper. In particular, in Eqs. (10), (12), and (13) the density on the l.h.s. is simply linear in the factor that depends on the pseudo-wavefunctions and λ. Thus, for any index *index*, be it a simple number ($index = 1,2,3\ldots$), an underlined number ($index = \underline{1}, \underline{2}, \underline{3}, \ldots$), or even a composite index, like 2: 1,3: 1, 1, or $\underline{2}:1,1$, the following relations apply:

$$\rho_1^{k(index)} = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}^{(index)} \phi_p^k \phi_q^{k*}, \tag{C1}$$

$$\widetilde{\rho}_1^{k(index)} = \sum_{p,q=1}^{N_{p_k}} \rho_{kpq}^{(index)} \widetilde{\phi}_p^k \widetilde{\phi}_q^{k*}, \tag{C2}$$

$$\hat{\rho}^{(index)} = \sum_{k=1}^{K} \hat{\rho}^{k(index)}. \tag{C3}$$

Despite being systematic, the expansion of Eqs. (11), (14), and (15) is not as trivial. We start with Eq. (11):

$$\widetilde{\rho}^{(1)} = \sum_{i=1}^{N} (\widetilde{\psi}_i^{(0)*} \widetilde{\psi}_i^{(1)} + \widetilde{\psi}_i^{(1)*} \widetilde{\psi}_i^{(0)}), \tag{C4}$$

$$\widetilde{\rho}^{(\underline{2})} = \sum_{i=1}^{N} |\widetilde{\psi}_i^{(1)}|^2, \tag{C5}$$

$$\widetilde{\rho}^{(\underline{3})} = 0. \tag{C6}$$

Equation (14) gives

$$\hat{\rho}^{k(1)} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(1)} \hat{Q}_{kpq}^{LM(0)}), \tag{C7}$$

$$\hat{\rho}^{k(\underline{1})} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(\underline{1})} \hat{Q}_{kpq}^{LM(0)}), \tag{C8}$$

$$\hat{\rho}^{k(\underline{2})} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(2)} + \rho_{kpq}^{(1)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(\underline{2})} \hat{Q}_{kpq}^{LM(0)}), \tag{C9}$$

$$\hat{\rho}^{k(\underline{2}:1)} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(1:1)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(\underline{2}:1)} \hat{Q}_{kpq}^{LM(0)}), \tag{C10}$$

$$\hat{\rho}^{k(\underline{2}:0)} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(2)} + \rho_{kpq}^{(1:0)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(\underline{2}:0)} \hat{Q}_{kpq}^{LM(0)}), \tag{C11}$$

$$\begin{aligned}\hat{\rho}^{k(\underline{3})} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(3)} + \rho_{kpq}^{(1)} \hat{Q}_{kpq}^{LM(2)} + \rho_{kpq}^{(\underline{2})} \hat{Q}_{kpq}^{LM(1)} \\ + \rho_{kpq}^{(\underline{3})} \hat{Q}_{kpq}^{LM(0)}),\end{aligned} \tag{C12}$$

$$\hat{\rho}^{k(\underline{3}:1)} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(1:1)} \hat{Q}_{kpq}^{LM(2)} + \rho_{kpq}^{(\underline{2}:1)} \hat{Q}_{kpq}^{LM(1)} + \rho_{kpq}^{(\underline{3}:1)} \hat{Q}_{kpq}^{LM(0)}), \tag{C13}$$

$$\begin{aligned}\hat{\rho}^{k(\underline{3}:0)} = \sum_{p,q=1}^{N_{p_k}} \sum_{LM} (\rho_{kpq}^{(0)} \hat{Q}_{kpq}^{LM(3)} + \rho_{kpq}^{(1:0)} \hat{Q}_{kpq}^{LM(2)} + \rho_{kpq}^{(\underline{2}:0)} \hat{Q}_{kpq}^{LM(1)} \\ + \rho_{kpq}^{(\underline{3}:0)} \hat{Q}_{kpq}^{LM(0)}).\end{aligned} \tag{C14}$$

Finally, the expansion of Eq. (15) gives:

$$\begin{aligned}\rho_{kpq}^{(1)} = \sum_{i=1}^{N} [\langle \widetilde{\psi}_i^{(0)} | (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(1)} | \widetilde{\psi}_i^{(0)} \rangle + \langle \widetilde{\psi}_i^{(1)} | (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(0)} | \widetilde{\psi}_i^{(0)} \rangle \\ + \langle \widetilde{\psi}_i^{(0)} | (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(0)} | \widetilde{\psi}_i^{(1)} \rangle],\end{aligned} \tag{C15}$$

$$\rho_{kpq}^{(\underline{1})} = \sum_{i=1}^{N} \langle \widetilde{\psi}_i^{(0)} | (\widetilde{p}_p^k \widetilde{p}_q^{k\dagger})^{(1)} | \widetilde{\psi}_i^{(0)} \rangle, \tag{C16}$$

$$\rho_{kpq}^{(\underline{2})} = \sum_{i=1}^{N} (\langle \tilde{\psi}_i^{(1)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(0)} | \tilde{\psi}_i^{(1)} \rangle) + \rho_{kpq}^{(\underline{2:1})} + \rho_{kpq}^{(\underline{2:0})}, \quad \text{(C17)}$$

$$\rho_{kpq}^{(\underline{2}:1)} = \sum_{i=1}^{N} (\langle \tilde{\psi}_i^{(1)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(1)} | \tilde{\psi}_i^{(0)} \rangle + \langle \tilde{\psi}_i^{(0)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(1)} | \tilde{\psi}_i^{(1)} \rangle), \quad \text{(C18)}$$

$$\rho_{kpq}^{(\underline{2}:0)} = \sum_{i=1}^{N} \langle \tilde{\psi}_i^{(0)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(2)} | \tilde{\psi}_i^{(0)} \rangle, \quad \text{(C19)}$$

$$\rho_{kpq}^{(\underline{3}:1,1)} = \sum_{i=1}^{N} \langle \tilde{\psi}_i^{(1)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(1)} | \tilde{\psi}_i^{(1)} \rangle, \quad \text{(C20)}$$

$$\rho_{kpq}^{(\underline{3}:1)} = \sum_{i=1}^{N} (\langle \tilde{\psi}_i^{(1)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(2)} | \tilde{\psi}_i^{(0)} \rangle + \text{c.c.}), \quad \text{(C21)}$$

$$\rho_{kpq}^{(\underline{3}:0)} = \sum_{i=1}^{N} \langle \tilde{\psi}_i^{(0)} | (\tilde{p}_p^k \tilde{p}_q^{k\dagger})^{(3)} | \tilde{\psi}_i^{(0)} \rangle. \quad \text{(C22)}$$

APPENDIX D: ABOUT THE GAUGE FREEDOM AND THE GENERALIZED STERNHEIMER EQUATIONS

We first explain why the Eqs. (69) can be imposed.[26] In the PAW formalism, the unperturbed energy is invariant under any unitary transformation on the wavefunctions $\tilde{\psi}_i$, because so are the densities $\tilde{\rho}$, ρ_1, $\tilde{\rho}_1$, and $\hat{\rho}$. From the unperturbed KS equations

$$\tilde{H}^{(0)} \tilde{\psi}_i^{(0)} = \sum_{j=1}^{N} \Lambda_{ij}^{(0)} \tilde{S}^{(0)} \tilde{\psi}_j^{(0)}, \quad \text{(D1)}$$

we can consider a unitary matrix $U^{(0)}$, such that $U^{(0)} \Lambda^{(0)} U^{(0)\dagger} = \mathrm{diag}(\varepsilon_i^{(0)})$. A natural choice is to take $U^{(0)} = I$ and $\Lambda_{ij}^{(0)} = \varepsilon_i^{(0)} \delta_{ij}$, leading to consider the problem $\tilde{H}^{(0)} \tilde{\psi}_i^{(0)} = \varepsilon_i^{(0)} \tilde{S}^{(0)} \tilde{\psi}_i^{(0)}$.

For the perturbed KS problem with wavefunctions $\tilde{\psi}_i(\lambda)$, let us consider a λ-dependent unitary transform denoted by $U(\lambda) = I + \lambda U^{(1)} + \cdots$. The unitary transformation on each wavefunction reads

$$\tilde{\psi}_i'(\lambda) = \sum_{j=1}^{N} U_{ij}(\lambda) \tilde{\psi}_j(\lambda). \quad \text{(D2)}$$

At the first order, we have $\tilde{\psi}_i'^{(0)} = \tilde{\psi}_i^{(0)}$ and

$$\tilde{\psi}_i'^{(1)} = \psi_i^{(1)} + \sum_{j=1}^{N} U_{ij}^{(1)} \tilde{\psi}_j^{(0)}, \quad \text{(D3)}$$

with $U_{ji}^{(1)\dagger} = -U_{ij}^{(1)}$.

Therefore, the relations

$$\langle \tilde{\psi}_i'^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_j'^{(0)} \rangle = \langle \tilde{\psi}_j'^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_j'^{(1)} \rangle \quad \text{(D4)}$$

are equivalent to

$$\langle \tilde{\psi}_i^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(0)} \rangle + U_{ji}^{(1)\dagger} = \langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(1)} \rangle - U_{ij}^{(1)}. \quad \text{(D5)}$$

So, for the particular choice of gauge

$$U_{ij}^{(1)} = \frac{1}{2} [\langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(1)} \rangle - \langle \tilde{\psi}_i^{(1)} | \tilde{S}^{(0)} | \tilde{\psi}_j^{(0)} \rangle], \quad \text{(D6)}$$

the Eqs. (69) are valid.

With this choice of gauge we can obtain the generalized Sternheimer equations. The projector operator $P_c^{\dagger}$ defined by Eq. (72) is such that $P_c^{\dagger}(\tilde{S}^{(0)} \tilde{\psi}_i^{(0)}) = 0$. Applying $P_c^{\dagger}$ to Eqs. (68), we get

$$P_c^{\dagger} (\tilde{H} - \varepsilon_i \tilde{S})^{(0)} \tilde{\psi}_i^{(1)} = - P_c^{\dagger} (\tilde{H}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)}) \tilde{\psi}_i^{(0)}. \quad \text{(D7)}$$

Let us define the adjunct projector operator

$$P_c = I - \sum_{i=1}^{N} \tilde{\psi}_i^{(0)} \langle \tilde{\psi}_i^{(0)} | \tilde{S}^{(0)}, \quad \text{(D8)}$$

we have

$$\begin{aligned} P_c \tilde{\psi}_i^{(1)} &= \tilde{\psi}_i^{(1)} - \sum_{j=1}^{N} \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(0)} | \tilde{\psi}_i^{(1)} \rangle \tilde{\psi}_j^{(0)} \\ &= \tilde{\psi}_i^{(1)} + \frac{1}{2} \sum_{j=1}^{N} \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_i^{(0)} \rangle \tilde{\psi}_j^{(0)}. \end{aligned} \quad \text{(D9)}$$

From Eqs. (D7) we deduce

$$\begin{aligned} & P_c^{\dagger} (\tilde{H} - \varepsilon_i \tilde{S})^{(0)} \left(P_c \tilde{\psi}_i^{(1)} - \frac{1}{2} \sum_{j=1}^{N} \langle \tilde{\psi}_j^{(0)} | \tilde{S}^{(1)} | \tilde{\psi}_i^{(0)} \rangle \tilde{\psi}_j^{(0)} \right) \\ & \quad = - P_c^{\dagger} (\tilde{H}^{(1)} - \varepsilon_i^{(0)} \tilde{S}^{(1)}) \tilde{\psi}_i^{(0)}. \end{aligned} \quad \text{(D10)}$$

Thus

$$P_c^{\dagger} (\tilde{H} - \varepsilon_i \tilde{S})^{(0)} \tilde{\psi}_j^{(0)} = (\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) P_c^{\dagger} (\tilde{S}^{(0)} \tilde{\psi}_j^{(0)}) = 0, \quad \text{(D11)}$$

from which we finally get the generalized Sternheimer Eqs. (73).

APPENDIX E: EXPRESSIONS NEEDED FOR $E_{tot,not-var}^{+(2)}$

The following equations are needed to complete the results of Sec. VI:

$$\begin{aligned} \tilde{E}_{Hxco}^{(\underline{2}:2)} = & \int_{\mathbb{R}^3} V_{Hxc}[(\tilde{\rho} + \hat{\rho})^{(0)}; \tilde{\rho}_c^{(0)}](\hat{\rho}_o^{(\underline{2})}; \tilde{\rho}_c^{(2)}) d\mathbf{x} + \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc}{}_{|\Omega_k} [\rho_1^{k(0)}; \rho_c^{k(0)}](\rho_1^{k(\underline{2}:1)} + \rho_1^{k(\underline{2}:0)}; \rho_c^{k(2)}) d\mathbf{x} \\ & - \sum_{k=1}^{K} \int_{\Omega_k} V_{Hxc}{}_{|\Omega_k} [(\tilde{\rho}_1^k + \hat{\rho}^k)^{(0)}; \tilde{\rho}_c^{k(0)}](\tilde{\rho}_1^{k(\underline{2}:1)} + \tilde{\rho}_1^{k(\underline{2}:0)} + \hat{\rho}_o^{k(\underline{2})}; \tilde{\rho}_c^{k(2)}) d\mathbf{x}, \end{aligned} \quad \text{(E1)}$$

$$\widetilde{E}_{Hxco}^{(\underline{2}:1,1)} = \frac{1}{2}\int_{\mathbb{R}^3} E''_{Hxc}[(\widetilde{\rho}+\hat{\rho})^{(0)};\widetilde{\rho}_c^{(0)}]((\widetilde{\rho}+\hat{\rho})^{(1)};\widetilde{\rho}_c^{(1)})(\hat{\rho}^{(\underline{1})};\widetilde{\rho}_c^{(1)})d\mathbf{x} + \frac{1}{2}\sum_{k=1}^{K}\int_{\Omega_k} E''_{Hxc_{|\Omega_k}}[\rho_1^{k(0)};\rho_c^{k(0)}](\rho_1^{k(1)};\rho_c^{k(1)})(\rho_1^{k(\underline{1})};\rho_c^{k(1)})d\mathbf{x}$$
$$-\frac{1}{2}\sum_{k=1}^{K}\int_{\Omega_k} E''_{Hxc_{|\Omega_k}}[(\widetilde{\rho}_1^k+\hat{\rho}^k)^{(0)};\widetilde{\rho}_c^{k(0)}]((\widetilde{\rho}_1^k+\hat{\rho}^k)^{(1)};\widetilde{\rho}_c^{k(1)})((\widetilde{\rho}_1^k+\hat{\rho}^k)^{(\underline{1})};\widetilde{\rho}_c^{k(1)})d\mathbf{x}. \tag{E2}$$

In Eq. (E2), we have defined the following quantity:

$$\hat{\rho}_o^{k(\underline{2})} = \sum_{p,q=1}^{N_{p_k}}\sum_{LM}\left(\rho_{kpq}^{(0)}\hat{Q}_{kpq}^{LM(\underline{2})} + \frac{1}{2}(\rho_{kpq}^{(1)}+\rho_{kpq}^{(\underline{1})})\hat{Q}_{kpq}^{LM(1)} + \left(\frac{1}{2}\rho_{kpq}^{(\underline{2}:1)}+\rho_{kpq}^{(\underline{2}:0)}\right)\hat{Q}_{kpq}^{LM(0)}\right). \tag{E3}$$

APPENDIX F: EXPRESSIONS NEEDED FOR $E_{tot}^{+(3)}$

We complete here Eq. (87). First, we define the notation $E'''_{xc}[\rho^{(0)}]\cdot(\rho^{(1)},\rho^{(1)},\rho^{(1)})$:

$$E'''_{xc}[\rho^{(0)}]\cdot(\rho^{(1)},\rho^{(1)},\rho^{(1)}) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} E'''_{Hxc}[\rho^{(0)};\mathbf{x},\mathbf{y},\mathbf{z}]\rho^{(1)}(\mathbf{x})\rho^{(1)}(\mathbf{y})\rho^{(1)}(\mathbf{z})d\mathbf{x}d\mathbf{y}d\mathbf{z} \tag{F1}$$

Then, in the expression of $E_{tot}^{+(3)}$ [see Eq. (88)], we have the following quantity:

$$\widetilde{E}_{Hxc}^{(\underline{3}:1,1,1)} = \frac{1}{6}E'''_{xc}[(\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(0)}]\cdot(((\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(1)}),((\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(1)}),((\widetilde{\rho}+\hat{\rho}+\widetilde{\rho}_c)^{(1)}))$$
$$+\frac{1}{6}\sum_{k=1}^{K}E'''_{xc_{|\Omega_k}}[\rho_1^{k(0)}+\rho_c^{k(0)}]\cdot((\rho_1^{k(1)}+\rho_c^{k(1)}),(\rho_1^{k(1)}+\rho_c^{k(1)}),(\rho_1^{k(1)}+\rho_c^{k(1)}))$$
$$-\frac{1}{6}\sum_{k=1}^{K}E'''_{xc_{|\Omega_k}}[(\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c)^{(0)}]\cdot(((\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c^k)^{(1)}),((\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c^k)^{(1)}),((\widetilde{\rho}_1^k+\hat{\rho}^k+\widetilde{\rho}_c^k)^{(1)})). \tag{F2}$$

E'''_{xc} is the third-order differential of E_{xc} with respect to the density. Note that E_H is quadratic in ρ, hence $E'''_H=0$.

APPENDIX G: MIXED PERTURBATIONS

As an example, we give here the generalization of the Eqs. (52)–(56) for mixed perturbations introduced in Ref. 13:

$$X^{(j_1j_2)} = \frac{1}{2}\left(\frac{d^2}{d\lambda_{j_1}d\lambda_{j_2}}X[Y(\lambda_{j_1},\lambda_{j_2}),\lambda_{j_1},\lambda_{j_2}]\right)_{|\lambda_{j_1}=\lambda_{j_2}=0}$$
$$= X^{(j_1j_2:2)} + X^{(j_1j_2:1,1)} + X^{(j_1j_2:1)} + X^{(j_1j_2:0)} \tag{G1}$$

with

$$X^{(j_1j_2:2)} = \frac{1}{2}\frac{\delta X}{\delta Y}Y^{(j_1j_2)} + \frac{1}{2}\frac{\delta X}{\delta Y}Y^{(j_2j_1)}, \tag{G2}$$

$$X^{(j_1j_2:1,1)} = \frac{1}{2}\frac{\delta^2 X}{\delta Y^2}Y^{(j_1)}Y^{(j_2)}, \tag{G3}$$

$$X^{(j_1j_2:1)} = \frac{1}{2}\left(\frac{\partial}{\partial\lambda_{j_1}}\frac{\delta X}{\delta Y}\right)_{|\lambda_{j_1}=0}Y^{(j_2)} + \frac{1}{2}\left(\frac{\partial}{\partial\lambda_{j_2}}\frac{\delta X}{\delta Y}\right)_{|\lambda_{j_2}=0}Y^{(j_1)}, \tag{G4}$$

$$X^{(j_1j_2:0)} = \frac{1}{2}\left(\frac{\partial^2 X}{\partial\lambda_{j_1}\lambda_{j_2}}\right)_{|\lambda_{j_1}=\lambda_{j_2}=0}. \tag{G5}$$

The full generalization of all responses equations obtained in the present paper will appear in another work.

[1] See, e.g., R. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, Cambridge, 2004).

[2] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[3] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982); X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

[4] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[5] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[6] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1998).

[7] N. A. W. Holzwarth, G. E. Matthews, R. B. Dunning, A. R. Tackett, and Y. Zeng, Phys. Rev. B **55**, 2005 (1997).

[8] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[9] For a review, see S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001); For a recent

primer, see X. Gonze, G.-M. Rignanese, and R. Caracas, Z. Kristallogr. **220**, 458 (2005).

[10] X. Gonze, Phys. Rev. A **52**, 1096 (1995); **54**, 4591(E) (1996).

[11] X. Gonze, Phys. Rev. A **52**, 1086 (1995).

[12] X. Gonze, D. C. Allan, and M. P. Teter, Phys. Rev. Lett. **68**, 3603 (1992).

[13] X. Gonze and C. Lee, Phys. Rev. B **55**, 10355 (1997).

[14] X. Gonze and J.-P. Vigneron, Phys. Rev. B **39**, 13120 (1989); **44**, 3494(E) (1991).

[15] PWSCF/PHONON is part of the Quantum-ESPRESSO package, see S. Scandolo, P. Giannozzi, C. Cavazzoni, S. de Gironcoli, A. Pasquarello, and S. Baroni, Z. Kristallogr. **220**, 574 (2005); See also http://www.pwscf.org

[16] A. Dal Corso, A. Pasquarello, and A. Baldereschi, Phys. Rev. B **56**, R11369 (1997).

[17] A. Dal Corso, Phys. Rev. B **64**, 235118 (2001).

[18] S. Y. Savrasov, Phys. Rev. Lett. **69**, 2819 (1992); S. Y. Savrasov, Z. Kristallogr. **220**, 555 (2005); See also http://www.fkf.mpg.de/andersen/docs/interest.html

[19] R. Yu and H. Krakauer, Phys. Rev. B **49**, 4467 (1994).

[20] R. Heid and K.-P. Bohnen, Phys. Rev. B **60**, R3709 (1999).

[21] P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. B **69**, 235102 (2004).

[22] A. Debernardi and S. Baroni, Solid State Commun. **91**, 813 (1994); A. Debernardi, S. Baroni, and E. Molinari, Phys. Rev. Lett. **75**, 1819 (1995); A. Debernardi, Phys. Rev. B **57**, 12 847 (1998).

[23] A. Dal Corso, F. Mauri, and A. Rubio, Phys. Rev. B **53**, 15 638 (1996).

[24] G. Deinzer and D. Strauch, Phys. Rev. B **66**, 100301(R) (2002); G. Deinzer, G. Birner, and D. Strauch, *ibid.* **67**, 144304 (2003); G. Deinzer, M. Schmitt, A. P. Mayer, and D. Strauch, *ibid.* **69**, 014304 (2004); G. Deinzer and D. Strauch, *ibid.* **69**, 045205 (2004).

[25] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, and D. C. Allan, Comput. Mater. Sci. **25**, 478 (2002); X. Gonze, G.-M. Rignanese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, Ph. Ghosez, M. Veithen, J.-Y. Raty, V. Olevano, F. Bruneval, L. Reining, R. Godby, G. Onida, D. R. Hamann, and D. C. Allan, Z. Kristallogr. **220**, 558 (2005); see also http://www.abinit.org

[26] C. Audouze, internal report CEA-DAM (2005).

[27] S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995).

[28] D. R. Hamann, X. Wu, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **71**, 035117 (2005); D. R. Hamann, K. M. Rabe, and D. Vanderbilt, *ibid.* **72**, 033102 (2005).

[29] Although $\hat{\rho}$ is linked with $\hat{\rho}^k$ thanks to Eq. (10), we mention it explicitely in the list of arguments of $\widetilde{E}_{Hxc}$, because usually, $\hat{\rho}$ is evaluated on the real space grid, while $\hat{\rho}^k$ is evaluated on each atomic grid.

[30] Note the slightly peculiar case of no Y factor.

[31] The nonvariational expression given in a previous article [see the Eqs. (A7)–(A9) of Ref. 10] was not correct: Following the notations of Ref. 10, the term $\Sigma_\alpha \langle \psi_\alpha^{(0)} | v_{Hxc0}^{(1)} | \psi_\alpha^{(1)} \rangle$ was missing.

[32] E. Cancès and M. Barrault, personal communication (2003).

[33] X. Gonze, Phys. Rev. B **55**, 10337 (1997).

[34] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).