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First-principles calculation of atomic force in the LSDA+U formalism

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We derive a formula for the atomic force within the LSDA+U formalism by differentiating analytically the LSDA+U total-energy functional with respect to atomic positions. The rotationally invariant form of the LSDA+U functional and the fully localized limit for the double-counting term are considered. The electronic wave functions are expanded with either plane waves or pseudoatomic orbitals (PAOs). In the PAO-basis case, the Pulay correction is also considered and included. Our formula for the atomic force is numerically tested with antiferromagnetic bulk NiO and reproduces successfully the forces obtained from numerical derivative of the total-energy values with respect to atomic displacements. As an application, we study atomic vibrations in NiO and MnO, and obtain transverse-optic phonon frequencies which are consistent with previous theoretical results. Our force formula will make it very efficient to perform large-scale calculations of atomic and phononic structures of strongly correlated materials using the LSDA+U method.

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I. INTRODUCTION

The density-functional theory (DFT) (Refs. 1 and 2) with the local spin-density approximation (LSDA) has been successful in describing electronic structures in various metals and semiconductors. However, in materials such as transition-metal oxides and rare-earth compounds which are insulating in spite of partially filled d (or f) shells, the DFT-LSDA method has poor accuracy since it underestimates the effect of the strong on-site Coulomb repulsion between d (or f) electrons. For example, the LSDA calculations of transition-metal compounds such as NiO and MnO predict much smaller values, than experiments, for the antiferromagnetic spin moments and the energy splittings between completely filled lower Hubbard bands and completely empty upper Hubbard bands.[3] To improve the accuracy of the LSDA method, the LSDA+U scheme[4] has been developed by adding to the LSDA total-energy functional a correction term arising from Coulomb interaction between localized d (or f) orbitals. The corrected LSDA+U functional produces much better estimates of the antiferromagnetic spin moments and the band gaps between upper and lower Hubbard bands in materials such as late-3d-transition-metal monoxides,[4] so the LSDA+U scheme is widely used in the magnetic- and electronic-structure calculations of transition-metal oxides.

Calculation of the atomic force plays a crucial role in predicting stable atomic structures of materials and it can be performed very efficiently if a relevant atomic-force formula is available. In plane-wave-basis LSDA methods, by using Hellmann-Feynman theorem,[5,6] the force formula can be derived analytically by partial differentiations of the total-energy functional with respect to atomic positions with no need to consider any change in the ground-state electron density. On the other hand, when the electronic wave functions are expanded with localized orbitals at atomic positions, the Pulay correction[7] should be taken into account in the atomic-force formula because the density variations due to the orbital-position changes are not considered when the total-energy functional is minimized for the ground-state electron density. While atomic-force formula in LSDA methods is well developed and published for both plane-wave and localized-orbital expansions of the wave functions,[8,9] derivation of the atomic-force formula within the LSDA+U scheme has been reported very rarely, and the published LSDA+U force formula[10] is only for the spherically averaged form[4] of the LSDA+U total-energy functional.

In this paper, we report on the derivation of the atomic-force formula from the LSDA+U total-energy functional with pseudoatomic orbital (PAO) and plane-wave bases for the wave functions. We consider the rotationally invariant form of the functional, which is not biased by specific choice of the z axis.[11] In the case of using a PAO basis set, the Pulay correction for the atomic force is considered and included. We implement the LSDA+U energy functional and our LSDA+U atomic-force formula into the SIESTA (Ref. 12) code and study atomic, electronic, and phononic structures of antiferromagnetic bulk NiO and MnO, as examples. The obtained band structures, band gaps, magnetic moments, and lattice constants agree well with previous LSDA+U calculations. As a test of our atomic-force formula, we compare the results of our force formula with the results from numerical derivative of the total-energy values with respect to atomic displacements, and find that they agree well with each other, confirming the validity of our atomic-force formula in the LSDA+U method. Using our atomic-force formula we investigate the optical phonon frequencies of NiO and MnO and analyze the results by comparing them with phonon frequencies calculated by LSDA force formula. Our atomic-force formula derived in our present work will be very useful in the optimization of atomic structures, in the investigation of vibrational structures, and even in molecular dynamic simulations of strongly correlated materials using the LSDA+U method.

This paper is organized as follows. In Sec. II, we briefly review the rotationally invariant form of the LSDA+U total-energy functional and present basic steps for the derivation of the force formula. In Sec. III, the LSDA+U force formula in PAO-basis methods is derived along with the Pulay correction. Section IV is the derivation of force formula in the plane-wave-basis method. In Sec. V, we present numerical tests of the LSDA+U atomic-force formula in the PAO-basis method. Frozen-phonon calculations of transverse optical modes in NiO and MnO using our method are presented in Sec. VI, followed by summary in Sec. VII.

II. DERIVATION OF ATOMIC-FORCE FORMULA IN THE LSDA+U SCHEME

In this section, we briefly review the rotationally invariant form of the LSDA+U energy functional and derive a general form of the atomic-force formula in LSDA+U scheme. The general form of the force formula will be used in the following two sections to derive specific forms of the force formula in the PAO-basis method and in the plane-wave-basis method, respectively.

This section consists of three subsections. In Sec. II A, the LSDA+U total-energy functional is introduced. In Sec. II B, the variation in the LSDA+U total-energy functional due to arbitrary variation in the Kohn-Sham wave functions is derived. In Sec. II C, a general form of the LSDA+U force formula is derived from the implicit and explicit dependences of the total-energy functional on the atomic positions.

A. LSDA+U energy functional

In Sec. II A, we will present briefly the LSDA+U total-energy functional to be used in deriving the LSDA+U force formula in the following subsections. Among various forms of the LSDA+U total-energy functional, we will consider in the present work the rotationally invariant form for the on-site Coulomb-energy term and the fully localized limit for the double-counting term. This LSDA+U total-energy functional will become the start point in deriving the force formula in the following subsections.

In the LSDA+U formalism, the total-energy functional is the sum of the LSDA energy functional E^{LSDA} and a correction term E^U which originates from the on-site Coulomb interaction among d (or f) electrons. Thus, the total-energy functional per unit cell in the LSDA+U scheme is given by

$$E^{\mathrm{LSDA}+U}[n(\mathbf{r}),\{\boldsymbol{\tau}\}] = E^{\mathrm{LSDA}}[n(\mathbf{r}),\{\boldsymbol{\tau}\}] + E^{U}[n(\mathbf{r}),\{\boldsymbol{\tau}\}], \tag{1}$$

where $n(\mathbf{r})$ is the ground-state electron density at position $\mathbf{r}$ and $\{\boldsymbol{\tau}\}$ are the positions of atoms. The LSDA energy functional E^{LSDA} per unit cell is defined as[1,2]

$$\begin{aligned}E^{\mathrm{LSDA}} = {} & \sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}} \int_{\Omega} d^3r \psi^{\sigma}_{n\mathbf{k}}(\mathbf{r})^{*}\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}) \\ & + \frac{e^2}{2}\int_{\Omega} d^3r \int_{V} d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n^{\uparrow}(\mathbf{r}),n^{\downarrow}(\mathbf{r})] \\ & + \sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}} \int_{\Omega} d^3r \int_{V} d^3r'\, \psi^{\sigma}_{n\mathbf{k}}(\mathbf{r})^{*} V_{ext}(\mathbf{r},\mathbf{r}')\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}') + E^{ii},\end{aligned} \tag{2}$$

where Ω and V are the unit-cell volume and the sample volume, respectively, $\psi^{\sigma}_{n\mathbf{k}}$ is the Kohn-Sham eigenfunction of the nth band of wavevector $\mathbf{k}$ in the first Brillouin zone and spin σ, $n^{\uparrow(\downarrow)}(\mathbf{r})$ is the density of spin-up (spin-down) electrons, E_{xc} is the LSDA exchange-correlation energy per unit cell, $V_{ext}(\mathbf{r},\mathbf{r}')$ is the electron-ion interaction potential, which is generally nonlocal in pseudopotential methods, and E^{ii} is the Coulomb repulsion energy between ions per unit cell. Asterisks represent complex conjugate. The integral over the sample volume V represents an integral over a real space which is N times as large as the unit-cell volume Ω, where N is the number of $\mathbf{k}$ vectors in the first Brillouin zone. The factor $f^{\sigma}_{n\mathbf{k}}$ is the Fermi-Dirac distribution function divided by N, which is

$$f^{\sigma}_{n\mathbf{k}} = \frac{1}{N}\frac{1}{e^{(\epsilon^{\sigma}_{n\mathbf{k}}-\mu)/k_BT}+1}, \tag{3}$$

where $\epsilon^{\sigma}_{n\mathbf{k}}$ is the Kohn-Sham eigenvalue defined below, μ is the chemical potential, and T is the temperature. In Eq. (2), the Kohn-Sham eigenfunction is normalized as

$$\int_{\Omega} d^3r |\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r})|^2 = 1 \tag{4}$$

and the explicit dependences of $V_{ext}(\mathbf{r},\mathbf{r}')$ and E^{ii} on the atomic positions $\{\boldsymbol{\tau}\}$ are omitted for simplicity. In the LSDA scheme, the electron density is defined as

$$n^{\sigma}(\mathbf{r}) = \sum_{n\mathbf{k}} f^{\sigma}_{n\mathbf{k}}\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r})^{*}\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}) \tag{5}$$

for each spin, and

$$n(\mathbf{r}) = \sum_{\sigma} n^{\sigma}(\mathbf{r}) \tag{6}$$

for both spins.

In this work, we employ the rotationally invariant form for the on-site Coulomb interaction among d (or f) electrons and take the fully localized limit[13] for the double-counting term. Then, the correction term E^U is

$$\begin{aligned}E^{U} = {} & \frac{1}{2}\sum_{\{m\}\sigma}[\langle m,m''|V_{ee}|m',m'''\rangle n^{\sigma}_{mm'}n^{-\sigma}_{m''m'''} \\ & + (\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle)n^{\sigma}_{mm'}n^{\sigma}_{m''m'''}] \\ & - \sum_{\lambda}\frac{1}{2}U_{\lambda}n_{\lambda}(n_{\lambda}-1) + \sum_{\lambda\sigma}\frac{1}{2}J_{\lambda}n^{\sigma}_{\lambda}(n^{\sigma}_{\lambda}-1),\end{aligned} \tag{7}$$

where m denotes the projector ϕ_m for the density matrix $n^{\sigma}_{mm'}$, covering all z components of the angular momenta of d (or f) orbitals of transition-metal atoms in the unit cell. The parameters U_{λ} and J_{λ} represent the Coulomb interaction among d (or f) electrons in the λth atom in the unit cell. The matrix elements $\langle m,m''|V_{ee}|m',m'''\rangle$ are zero if all the projectors ϕ_m, $\phi_{m'}$, $\phi_{m''}$, and $\phi_{m'''}$ are not associated with a same atom. The density matrix $n^{\sigma}_{mm'}$ and its reduced forms, n^{σ}_{λ} and n_{λ}, for the λth atom are given by

$$n^{\sigma}_{mm'} = \sum_{n\mathbf{k}} f^{\sigma}_{n\mathbf{k}}\langle\psi^{\sigma}_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^m+\mathbf{R}}\rangle\langle\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\psi^{\sigma}_{n\mathbf{k}}\rangle\delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^{m'}}, \tag{8a}$$

$$n^{\sigma}_{\lambda} = \sum_{m} n^{\sigma}_{mm}\delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^{\lambda}}, \tag{8b}$$

$$n_\lambda = \sum_\sigma n_\lambda^\sigma, \tag{8c}$$

where $|\phi_{m,\boldsymbol{\tau}^m+\mathbf{R}}\rangle$ represents the projector ϕ_m located at $\boldsymbol{\tau}^m+\mathbf{R}$ in the unit cell at $\mathbf{R}$, $\boldsymbol{\tau}^\lambda$ is the position of the λth atom in the unit cell at $\mathbf{R}=0$, and the bracket $\langle f|g\rangle$ of two functions $f(\mathbf{r})$ and $g(\mathbf{r})$ is defined as

$$\langle f|g\rangle = \int_V d^3r f(\mathbf{r})^* g(\mathbf{r}). \tag{9}$$

With this definition of the bracket, the normalization condition of Eq. (4) becomes $\langle\psi^\sigma_{n\mathbf{k}}|\psi^\sigma_{n\mathbf{k}}\rangle=N$. The projectors ϕ_m are short ranged so that projectors associated with different atoms do not overlap with each other, making the density matrix $n^\sigma_{mm'}$ nonzero only when the two projectors ϕ_m and $\phi_{m'}$ are at the same atom (i.e., $\tau^m=\tau^{m'}$), and satisfying the sum rule.[10] The density matrix $n^\sigma_{mm'}$ is independent of $\mathbf{R}$ because the Kohn-Sham wave functions satisfy the Bloch theorem. In Eq. (7), the matrix elements of the Coulomb interaction are defined conceptually and parameterized as

$$\begin{aligned}\langle m,m''|V_{ee}|m',m'''\rangle &= \int\int d^3r d^3r' \frac{\phi_m(\mathbf{r})^*\phi_{m''}(\mathbf{r}')^*\phi_{m'}(\mathbf{r})\phi_{m'''}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\ &= \sum_k a_k(m,m',m'',m''')F^k,\end{aligned} \tag{10}$$

where the integer k is in the range $0\le k\le 2l$. The coefficients $a_k(m,m',m'',m''')$ have the angular-momentum dependence of the projectors and are given by

$$a_k(m,m',m'',m''') = \frac{4\pi}{2k+1}\sum_{q=-k}^{k}\langle lm|Y_{kq}|lm'\rangle\langle lm''|Y^*_{kq}|lm'''\rangle. \tag{11}$$

Here, the basis $|lm\rangle$ is the complex spherical harmonics, and the coefficient, a_k, can be expressed using the Wigner $3-j$ symbols as follows:

$$\begin{aligned}a_k(m,m',m'',m''') = \sum_{q=-k}^{k}&(2l+1)^2(-1)^{m+q+m''}\\ &\times\begin{pmatrix} l & k & l\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix} l & k & l\\ -m & q & m'\end{pmatrix}\\ &\times\begin{pmatrix} l & k & l\\ -m'' & -q & m'''\end{pmatrix}.\end{aligned} \tag{12}$$

The coefficients F^k are radial integrals of the Coulomb interaction. In the case of d electrons ($l=2$), we need only three coefficients F^0, F^2, and F^4 in Eq. (10) since the others become zero by symmetry. If one takes unscreened Coulomb interaction, or a specific dielectric constant, one may evaluate F^ks by integrating the Coulomb interaction radially. However, instead of evaluating the integration, F^ks are regarded as parameters in our work, as in previous LSDA+U studies. In the case of d orbitals, the coefficients F^ks are related with the commonly used parameters U and J as $U=F^0$, $J=(F^2+F^4)/14$, and $F^4/F^2\sim 0.625$.[11] In Eq. (7), the parameters for the λth atom are denoted by U_λ and J_λ. The last line in Eq. (7) is the double-counting term which is the mean-field approximation of the orbital-dependent Coulomb interaction. An explicit derivation of the double-counting term is presented in Appendix A.

In summary, we presented in Sec. II A the LSDA+U total-energy functional [Eqs. (1), (2), and (7)] based on the rotationally invariant form of the on-site Coulomb interaction and the fully localized limit of the double-counting term. This energy functional will be the starting point in deriving the LSDA+U atomic-force formula in the following subsections .

B. Variation in the LSDA+*U* functional due to density variation

We will consider in Sec. II B the variation in the LSDA+U total-energy functional arising from arbitrary variation in the Kohn-Sham wave functions and introduce the Kohn-Sham Hamiltonian and equation. The variation in the total-energy functional in the LSDA scheme is derived in literatures[2,14] and the effective potential for rotationally invariant E^U energy functional is presented in Lichtenstein *et al.*[11] The variation in LSDA+U energy functional and the Kohn-Sham Hamiltonian presented in Sec. II B will be used in Sec. II C and the following sections.

In the LSDA method, the ground-state electron density and the total energy are obtainable by minimizing the total-energy functional with respect to the electron-density variation which is associated with the variation in the Kohn-Sham wave functions as

$$\delta n^\sigma(\mathbf{r}) = \sum_{n\mathbf{k}} f^\sigma_{n\mathbf{k}}\delta\psi^\sigma_{n\mathbf{k}}(\mathbf{r})^*\psi^\sigma_{n\mathbf{k}}(\mathbf{r}) + \sum_{n\mathbf{k}} f^\sigma_{n\mathbf{k}}\psi^\sigma_{n\mathbf{k}}(\mathbf{r})^*\delta\psi^\sigma_{n\mathbf{k}}(\mathbf{r}), \tag{13a}$$

$$\delta n(\mathbf{r}) = \sum_\sigma \delta n^\sigma(\mathbf{r}). \tag{13b}$$

In the LSDA+U method, for the E^U term the variation in the density matrix is also needed and it is related to the variation in the Kohn-Sham wave functions as follows:

$$\begin{aligned}\delta n^\sigma_{mm'} = \sum_{n\mathbf{k}} f^\sigma_{n\mathbf{k}}\{&\langle\delta\psi^\sigma_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^m+\mathbf{R}}\rangle\langle\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\psi^\sigma_{n\mathbf{k}}\rangle\\ &+\langle\psi^\sigma_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^m+\mathbf{R}}\rangle\langle\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\delta\psi^\sigma_{n\mathbf{k}}\rangle\}\delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^{m'}},\end{aligned} \tag{14a}$$

$$\delta n^\sigma_\lambda = \sum_m \delta n^\sigma_{mm}\delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^\lambda}, \tag{14b}$$

$$\delta n_\lambda = \sum_\sigma \delta n^\sigma_\lambda. \tag{14c}$$

Then, the variation in the LSDA+U total-energy functional with respect to the variation in the Kohn-Sham wave functions can be written as

$$\delta E^{\mathrm{LSDA}+U} = \frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}\{\langle \delta\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle \psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle\}, \tag{15}$$

where $\delta\psi^{\sigma}_{n\mathbf{k}}$ is an arbitrary variation in the Kohn-Sham wave function $\psi^{\sigma}_{n\mathbf{k}}$, the factor $1/N$ is introduced because the bracket notation is defined as an integral over the sample which is N times larger than the unit cell, and the Kohn-Sham Hamiltonian $\hat{H}^{\sigma}$ is defined as

$$\hat{H}^{\sigma} = \hat{H}^{\sigma}_{\mathrm{LSDA}} + \sum_{\mathbf{R}mm'} |\phi_{m,\boldsymbol{\tau}^{m}+\mathbf{R}}\rangle V^{\sigma}_{mm'}\langle \phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|. \tag{16}$$

In Eq. (16), the $\hat{H}^{\sigma}_{\mathrm{LSDA}}$ is the Kohn-Sham Hamiltonian in LSDA scheme which is defined as

$$\hat{H}^{\sigma}_{\mathrm{LSDA}}(\mathbf{r})\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}) = \left[-\frac{\hbar^{2}}{2m}\nabla^{2} + V_{H}(\mathbf{r}) + V^{\sigma}_{xc}(\mathbf{r})\right]\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}) + \int_{V} d^{3}r' V_{ext}(\mathbf{r},\mathbf{r}')\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}'), \tag{17}$$

where we used the Hartree potential

$$V_{H}(\mathbf{r}) \equiv e^{2}\int_{V} d^{3}r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{18}$$

and the exchange-correlation potential

$$V^{\sigma}_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta n^{\sigma}(\mathbf{r})}. \tag{19}$$

The term $V^{\sigma}_{mm'}$ comes from the variation in the E^{U} energy functional

$$\delta E^{U} = \sum_{mm'\sigma} V^{\sigma}_{mm'}\delta n^{\sigma}_{mm'}, \tag{20}$$

leading to a form

$$\begin{aligned} V^{\sigma}_{mm'} = &\sum_{m''m'''} \langle m,m''|V_{ee}|m',m'''\rangle n^{-\sigma}_{m''m'''} \\ &+ \sum_{m''m'''} (\langle m,m''|V_{ee}|m',m'''\rangle \\ &- \langle m,m''|V_{ee}|m''',m'\rangle) n^{\sigma}_{m''m'''} - \sum_{\lambda}\left\{U_{\lambda}\left(n_{\lambda}-\frac{1}{2}\right)\right. \\ &\left. - J_{\lambda}\left(n^{\sigma}_{\lambda}-\frac{1}{2}\right)\right\}\delta_{mm'}\delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{\lambda}}. \end{aligned} \tag{21}$$

The term $V^{\sigma}_{mm'}$ is zero if m and m' are associated with different atoms. By minimizing $E^{\mathrm{LSDA}+U}$ with the constraint that $\langle \psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle = N$, one can obtain the ground-state electron density and the total energy. The constrained minimization condition corresponds to

$$\delta E^{\mathrm{LSDA}+U} - \frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}\epsilon^{\sigma}_{n\mathbf{k}}\{\langle \delta\psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle \psi^{\sigma}_{n\mathbf{k}}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle\} = 0, \tag{22}$$

where we have introduced $\epsilon^{\sigma}_{n\mathbf{k}}$ as Lagrange multipliers and the condition reduces straightforwardly to the Kohn-Sham equation

$$\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle = \epsilon^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle. \tag{23}$$

In the expression of the Kohn-Sham equation, we can see that the only change in the LSDA+U method is the orbital-dependent interaction potential $V^{\sigma}_{mm'}$ occurring in the Kohn-Sham Hamiltonian.

To summarize, we introduced in Sec. II B the Kohn-Sham Hamiltonian in the LSDA+U method and expressed the variation in the LSDA+U total-energy functional with respect to arbitrary variation in the Kohn-Sham wave functions [Eq. (15)]. In Sec. II C, we will consider the change in the LSDA+U total energy due to atomic displacements which includes contributions from both the variation in the total-energy functional [Eq. (15)] from the variation in the wave functions and the explicit dependence of the total-energy functional on the atomic positions.

C. Atomic-force formula in the LSDA+U method

We will derive in Sec. II C a general form of the LSDA+U total-energy functional, considering both the explicit dependence of the functional on atomic positions and the implicit dependence of the functional on the change in the self-consistent Kohn-Sham wave functions induced by atomic displacements. The obtained general form will be used as the start point for the atomic-force formula in the PAO-basis and plane-wave-basis methods in Secs. III and IV, respectively.

In the DFT method, the atomic force can be obtained by differentiating the total-energy functional with respect to atomic positions $\boldsymbol{\tau}$, which can be written as

$$\mathbf{F}^{\mathrm{LSDA}+U} = -\frac{d}{d\boldsymbol{\tau}}E^{\mathrm{LSDA}+U}[n(\mathbf{r}),\{\boldsymbol{\tau}\}], \tag{24}$$

where the differentiation includes, in general, both explicit and implicit dependences of the total-energy functional on atomic positions $\boldsymbol{\tau}$. The explicit $\{\boldsymbol{\tau}\}$ dependence in the total-energy functional is due to the external potential V_{ext}, ion-ion interaction energy E^{ii}, and atomic projectors in E^{U} energy functional. The implicit $\{\boldsymbol{\tau}\}$ dependence is due to the self-consistent change $\delta\psi^{\sigma}_{n\mathbf{k}}$ of the Kohn-Sham wave functions caused by atomic displacements and can be described by Eq. (15). Thus, the variation in the total energy per unit cell by the displacement of atomic positions is

$$\begin{aligned} \delta E^{\mathrm{LSDA}+U} = &\frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}[\langle \delta\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle \psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle] \\ &+ \frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}\langle \psi^{\sigma}_{n\mathbf{k}}|\delta V_{ext}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \delta E^{ii} \\ &+ \sum_{mm'\sigma} V^{\sigma}_{mm'}\delta n^{\sigma}_{mm'}, \end{aligned} \tag{25}$$

where $\delta\psi^{\sigma}_{n\mathbf{k}}$ is the self-consistent change in the Kohn-Sham wave function caused by atomic displacements as mentioned above and δE^{ii} represents the change in ion-ion interaction energy due to atomic displacements. The variation in the density matrix, $\delta n^{\sigma}_{mm'}$, in Eq. (25) is not due to $\delta\psi^{\sigma}_{n\mathbf{k}}$ but due to the translation of projectors associated with the atom at $\boldsymbol{\tau}$

$$\delta n^{\sigma}_{mm'} = \sum_{n\mathbf{k}} f^{\sigma}_{n\mathbf{k}} [\langle \psi^{\sigma}_{n\mathbf{k}} | \delta\phi_{m,\boldsymbol{\tau}^{m}+\mathbf{R}}\rangle\langle\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle\psi^{\sigma}_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^{m}+\mathbf{R}}\rangle\langle\delta\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\psi^{\sigma}_{n\mathbf{k}}\rangle]\delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{m'}}, \quad (26)$$

which is different from $\delta n^{\sigma}_{mm'}$ of Eq. (14). Then, the atomic force exerted on the atom at $\boldsymbol{\tau}$ in the LSDA+U formalism is

$$\mathbf{F} = -\frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}\left[\langle\frac{d\psi^{\sigma}_{n\mathbf{k}}}{d\boldsymbol{\tau}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\frac{d\psi^{\sigma}_{n\mathbf{k}}}{d\boldsymbol{\tau}}\rangle\right] - \frac{1}{N}\sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}}\langle\psi^{\sigma}_{n\mathbf{k}}|\frac{\partial V_{ext}}{\partial\boldsymbol{\tau}}|\psi^{\sigma}_{n\mathbf{k}}\rangle - \frac{\partial E^{ii}}{\partial\boldsymbol{\tau}} - \sum_{mm'\sigma} V^{\sigma}_{mm'}\frac{\partial n^{\sigma}_{mm'}}{\partial\boldsymbol{\tau}}, \quad (27)$$

where the derivative of the density matrix in the last term is given by

$$\frac{\partial n^{\sigma}_{mm'}}{\partial\boldsymbol{\tau}} = \sum_{n\mathbf{k}} f^{\sigma}_{n\mathbf{k}}\left[\langle\psi^{\sigma}_{n\mathbf{k}}|\frac{\partial\phi_{m,\boldsymbol{\tau}^{m}+\mathbf{R}}}{\partial\boldsymbol{\tau}^{m}}\rangle\langle\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}|\psi^{\sigma}_{n\mathbf{k}}\rangle\delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}} + \langle\psi^{\sigma}_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^{m}+\mathbf{R}}\rangle\langle\frac{\partial\phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}}}{\partial\boldsymbol{\tau}^{m'}}|\psi^{\sigma}_{n\mathbf{k}}\rangle\delta_{\boldsymbol{\tau}^{m'},\boldsymbol{\tau}}\right]\delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{m'}}, \quad (28)$$

and the derivative $d\psi^{\sigma}_{n\mathbf{k}}/d\boldsymbol{\tau}$ is the solution of

$$(\hat{H}^{\sigma} - \epsilon^{\sigma}_{n\mathbf{k}})|\frac{d\psi^{\sigma}_{n\mathbf{k}}}{d\boldsymbol{\tau}}\rangle = -\left(\frac{d\hat{H}^{\sigma}}{d\boldsymbol{\tau}} - \frac{d\epsilon^{\sigma}_{n\mathbf{k}}}{d\boldsymbol{\tau}}\right)|\psi^{\sigma}_{n\mathbf{k}}\rangle. \quad (29)$$

Since the derivative of the Hamiltonian, $d\hat{H}^{\sigma}/d\boldsymbol{\tau}$, depends on the derivative of the electron density, $dn^{\sigma}(\mathbf{r})/d\boldsymbol{\tau}$, and $dn^{\sigma}(\mathbf{r})/d\boldsymbol{\tau}$ depends on $d\psi^{\sigma}_{n\mathbf{k}}/d\boldsymbol{\tau}$, Eq. (29) is a complicated self-consistent equation for $d\psi^{\sigma}_{n\mathbf{k}}/d\boldsymbol{\tau}$, requiring substantial computing time and resource. Thus, in order to find a useful atomic-force formula, it is essential to avoid calculating $d\psi^{\sigma}_{n\mathbf{k}}/d\boldsymbol{\tau}$, as shown in the following sections. In the LSDA+U formalism, the U term may contribute to the atomic force via $\hat{H}^{\sigma}$ and $V^{\sigma}_{mm'}$, which we elaborate in the following sections with PAO-basis and plane-wave basis for the electronic wave functions.

We derived in Sec. II C a general form of the LSDA+U atomic-force formula [Eqs. (27) and (28)], which will be used in the following sections to derive atomic-force formula in the PAO-basis and plane-wave-basis methods. The self-consistent derivative of the Kohn-Sham wave functions with respect to atomic positions will not appear in the atomic-force formula derived in the following sections.

III. LSDA+U ATOMIC-FORCE FORMULA IN PAO-BASIS METHODS

We consider in this section a representation of the atomic-force formula in the case that the wave functions are expanded with localized orbitals attached to atoms such as PAOs. First, in Sec. III A, we will expand the Kohn-Sham wave functions with PAOs and express the Kohn-Sham equation using a PAO-basis set. Then, in Sec. III B, we will derive PAO-basis representation of atomic-force formula in the LSDA+U scheme.

A. The density matrix and Kohn-Sham equation in a PAO-basis set

In Sec. III A, we express the Kohn-Sham wave functions and equation using a PAO-basis set. These will be used in Sec. III B for the atomic-force formula in PAO-basis methods.

The Kohn-Sham wave function is represented in a PAO-basis set as

$$\psi^{\sigma}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\mu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}+\mathbf{R})}\phi_{\mu}(\mathbf{r} - \boldsymbol{\tau}^{\mu} - \mathbf{R}), \quad (30)$$

where n is the band index, $\mathbf{k}$ is the wave vector in the first Brillouin zone, and $\boldsymbol{\tau}^{\mu}+\mathbf{R}$ is the position of the μth orbital ϕ_{μ} in the unit cell at $\mathbf{R}$. With ket symbols, we represent the wave function as

$$|\psi^{\sigma}_{n\mathbf{k}}\rangle = \sum_{\mu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\mu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}+\mathbf{R})}|\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}\rangle \quad (31)$$

and the norm of the wave function is

$$\langle\psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle = \sum_{\mu\nu\mathbf{R}\mathbf{R}'} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} \times \langle\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}'}\rangle. \quad (32)$$

By translating the orbitals by $-\mathbf{R}$, we obtain

$$\langle\psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle = \sum_{\mu\nu\mathbf{R}\mathbf{R}'} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} \times \langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}'-\mathbf{R}}\rangle \quad (33)$$

and after denoting $\mathbf{R}'-\mathbf{R}$ as $\mathbf{R}''$ and relabeling $\mathbf{R}''$ as $\mathbf{R}$, we have

$$\langle\psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle = N\sum_{\mu\nu\mathbf{R}} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})}S_{\mu\nu}(\mathbf{R}) = N\sum_{\mu\nu} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}S_{\mu\nu}(\mathbf{k}), \quad (34)$$

where N is the number of lattice vectors or equivalently the number of unit cells in the sample. The overlap matrices $S_{\mu\nu}(\mathbf{R})$ and $S_{\mu\nu}(\mathbf{k})$ in Eq. (34) are defined as

$$S_{\mu\nu}(\mathbf{R}) \equiv \langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle = \int_{V} d^{3}r\,\phi_{\mu}(\mathbf{r}-\boldsymbol{\tau}^{\mu})^{*}\phi_{\nu}(\mathbf{r}-\boldsymbol{\tau}^{\nu}-\mathbf{R}), \quad (35a)$$

$$S_{\mu\nu}(\mathbf{k}) \equiv \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R})} S_{\mu\nu}(\mathbf{R}), \tag{35b}$$

where $\mathbf{R}$ are lattice vectors. Since the basis functions $\phi_{\mu}(\mathbf{r})$ are short ranged, the integration over the sample is effectively equivalent to integration over infinite volume, and $S_{\mu\nu}(\mathbf{R})$ is zero if $|\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R}|$ is greater than the sum of the spatial extents of the two basis functions. Thus, the summation over $\mathbf{R}$ in the definition of $S_{\mu\nu}(\mathbf{k})$ includes only a finite number of $\mathbf{R}$ for nonzero $S_{\mu\nu}(\mathbf{R})$. Since $\langle\psi^{\sigma}_{n\mathbf{k}}|\psi^{\sigma}_{n\mathbf{k}}\rangle=N$, the normalization condition becomes

$$\sum_{\mu\nu} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} S_{\mu\nu}(\mathbf{k}) = 1. \tag{36}$$

Now, we consider PAO-basis representation of the density matrix of Eq. (8a). The projection of Kohn-Sham wave function to a projector $\phi_{m'}$ becomes

$$\begin{aligned}\langle\phi_{m',\boldsymbol{\tau}^{m'}}|\psi^{\sigma}_{n\mathbf{k}}\rangle &= \sum_{\nu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}+\mathbf{R})}\langle\phi_{m',\boldsymbol{\tau}^{m'}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle \\ &= \sum_{\nu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau}^{\nu})} S_{m'\nu}(\mathbf{R}) \\ &= \sum_{\nu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{m'}} S_{m'\nu}(\mathbf{k}) \end{aligned} \tag{37}$$

and its complex conjugate is

$$\begin{aligned}\langle\psi^{\sigma}_{n\mathbf{k}}|\phi_{m,\boldsymbol{\tau}^{m}}\rangle &= \sum_{\mu\mathbf{R}} C^{\sigma *}_{n\mathbf{k}\mu} e^{-i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\tau}^{\mu})} S_{\mu m}(-\mathbf{R}) \\ &= \sum_{\mu} C^{\sigma *}_{n\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{m}} S_{\mu m}(\mathbf{k}), \end{aligned} \tag{38}$$

where we have used $S_{\mu\nu}(\mathbf{R})^{*}=S_{\nu\mu}(-\mathbf{R})$. Then, the density matrix $n^{\sigma}_{mm'}$ can be expressed as

$$\begin{aligned} n^{\sigma}_{mm'} = & \sum_{\mathbf{k}n\mathbf{R}\mathbf{R}'\mu\nu} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \\ & \times S_{\mu m}(-\mathbf{R}) S_{m'\nu}(\mathbf{R}')\, \delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{m'}} \\ = & \sum_{\mathbf{k}n\mu\nu} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} S_{\mu m}(\mathbf{k}) S_{m'\nu}(\mathbf{k})\, \delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{m'}}. \end{aligned} \tag{39}$$

Here, we have used $e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{m'}-\boldsymbol{\tau}^{m})}=1$ for $\boldsymbol{\tau}^{m}=\boldsymbol{\tau}^{m'}$. As shown in Eq. (39), in the PAO-basis method, the density matrix $n^{\sigma}_{mm'}$ is a product of the two overlap matrices and the coefficients $C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu}$.

Starting from Eq. (23), the Kohn-Sham equation using a PAO-basis set is expressed as

$$\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle = \epsilon^{\sigma}_{n\mathbf{k}}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\psi^{\sigma}_{n\mathbf{k}}\rangle. \tag{40}$$

With the wave function expanded with the PAO basis, the left-hand side of Eq. (40) becomes

$$\begin{aligned}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle &= \sum_{\nu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}+\mathbf{R})}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle \\ &= \sum_{\nu\mathbf{R}} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}+\mathbf{R})} H^{\sigma}_{\mu\nu}(\mathbf{R}) \\ &= \sum_{\nu} e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}} H^{\sigma}_{\mu\nu}(\mathbf{k}) C^{\sigma}_{n\mathbf{k}\nu}, \end{aligned} \tag{41}$$

where we used the following definitions which are consistent with Eqs. (35a) and (35b):

$$\begin{aligned} H^{\sigma}_{\mu\nu}(\mathbf{R}) &\equiv \langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle \\ &= \int_{V} d^{3}r\,\phi_{\mu}(\mathbf{r}-\boldsymbol{\tau}^{\mu})^{*}\hat{H}^{\sigma}\phi_{\nu}(\mathbf{r}-\boldsymbol{\tau}^{\nu}-\mathbf{R}), \end{aligned} \tag{42a}$$

$$H^{\sigma}_{\mu\nu}(\mathbf{k}) \equiv \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R})} H^{\sigma}_{\mu\nu}(\mathbf{R}). \tag{42b}$$

By using Eq. (37), the right-hand side of Eq. (40) can be expressed as

$$\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\psi^{\sigma}_{n\mathbf{k}}\rangle = \sum_{\nu} e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}} S_{\mu\nu}(\mathbf{k}) C^{\sigma}_{n\mathbf{k}\nu}. \tag{43}$$

Therefore, the Kohn-Sham equation in PAO-basis methods becomes

$$\sum_{\nu} H^{\sigma}_{\mu\nu}(\mathbf{k}) C^{\sigma}_{n\mathbf{k}\nu} = \epsilon^{\sigma}_{n\mathbf{k}} \sum_{\nu} S_{\mu\nu}(\mathbf{k}) C^{\sigma}_{n\mathbf{k}\nu}. \tag{44}$$

This is a generalized eigenvalue problem in which eigenvectors correspond to the coefficients of the wave functions expanded with pseudoatomic orbitals.

We expressed in Sec. III A the Kohn-Sham wave functions [Eq. (31)] and the Kohn-Sham equation [Eq. (44)] using a PAO-basis set. These expressions will be used in Sec. III B for the atomic-force formula in PAO-basis methods.

B. LSDA + U atomic-force formula in PAO-basis methods

Considering the Pulay correction, we will derive in Sec. III B atomic-force formula in PAO-basis methods where wave functions are expanded with PAOs located at atomic positions.

In PAO-basis methods, the Kohn-Sham wave functions which are obtained self-consistently from the Kohn-Sham equation minimize the total-energy functional for arbitrary variations in the wave functions as long as they can be expanded with given basis orbitals. Thus, if the Kohn-Sham wave functions are varied with no change in the basis orbitals, there is no first-order change in the total energy. However, if the wave functions are changed with some changes in the basis orbitals, there exists first-order change in the total energy, since the changes in the basis orbitals are not considered in the minimization of the total-energy functional.

In order to calculate atomic forces, one needs to know the variation in the total-energy functional caused by atomic displacements. When an atom is shifted from its original position in a PAO-basis method, the shift makes some basis-function changes as well as changes in the Kohn-Sham equation. We first consider the change in the Kohn-Sham wave function induced by atomic displacements. Since both coefficients and pseudoatomic orbitals may change, in general, by using Eq. (31), we can express the variation in the Kohn-Sham wave function as follows:

$$\begin{aligned}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle = \sum_{\mu\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}[&\delta(e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma}_{n\mathbf{k}\mu})|\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}\rangle \\ &+ e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma}_{n\mathbf{k}\mu}|\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}\rangle]. \qquad (45)\end{aligned}$$

There is no change in the exponential term since the change in an atom position does not have any effect on either the lattice vector **R** or the crystal momentum vector **k**. In Eq. (45), the variation in the basis orbital, $\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}$, can be calculated easily but the variation in the coefficients, $\delta C^{\sigma}_{n\mathbf{k}\mu}$, requires self-consistent calculations. Thus, it is very important to modify the expression of the total-energy variation [Eq. (25)] to a form which does not have $\delta C^{\sigma}_{n\mathbf{k}\mu}$ explicitly, as follows. When Eq. (25) is expressed using pseudoatomic orbitals, the first term in the square bracket becomes

$$\begin{aligned}\langle\delta\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle &= \sum_{\mu\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}[\delta(e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma*}_{n\mathbf{k}\mu})\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle \\ &\quad + e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma*}_{n\mathbf{k}\mu}\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle] \\ &= N\epsilon^{\sigma}_{n\mathbf{k}}\sum_{\mu\nu}\delta(e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma*}_{n\mathbf{k}\mu})e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}S_{\mu\nu}(\mathbf{k})C^{\sigma}_{n\mathbf{k}\nu} \\ &\quad + N\sum_{\mu\nu\mathbf{R}'} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R}')}C^{\sigma*}_{n\mathbf{k}\mu} \\ &\quad \times C^{\sigma}_{n\mathbf{k}\nu}\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}'}\rangle, \qquad (46)\end{aligned}$$

where we have used the Kohn-Sham equation in the PAO method

$$\begin{aligned}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle &= e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle \\ &= e^{i\mathbf{k}\cdot\mathbf{R}}\epsilon^{\sigma}_{n\mathbf{k}}\sum_{\nu} e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}S_{\mu\nu}(\mathbf{k})C^{\sigma}_{n\mathbf{k}\nu} \qquad (47)\end{aligned}$$

and the expansion of the wave functions

$$\begin{aligned}\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle &= e^{i\mathbf{k}\cdot\mathbf{R}}\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle \\ &= e^{i\mathbf{k}\cdot\mathbf{R}}\sum_{\nu\mathbf{R}'} C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}+\mathbf{R}')} \\ &\quad \times\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}'}\rangle. \qquad (48)\end{aligned}$$

Similarly, we can express the second term in the square bracket as follows:

$$\begin{aligned}\langle\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle &= N\epsilon^{\sigma}_{n\mathbf{k}}\sum_{\mu\nu} e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\nu}}C^{\sigma*}_{n\mathbf{k}\mu}\delta(e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\nu}}C^{\sigma}_{n\mathbf{k}\nu})S_{\mu\nu}(\mathbf{k}) \\ &\quad + N\sum_{\mu\nu\mathbf{R}'} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R}')}C^{\sigma*}_{n\mathbf{k}\mu} \\ &\quad \times C^{\sigma}_{n\mathbf{k}\nu}\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\delta\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}'}\rangle. \qquad (49)\end{aligned}$$

We rewrite the normalization condition as

$$\sum_{\mu\nu}(e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma*}_{n\mathbf{k}\mu})(e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\nu}}C^{\sigma}_{n\mathbf{k}\nu})e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}-\boldsymbol{\tau}^{\nu})}S_{\mu\nu}(\mathbf{k}) = 1 \qquad (50)$$

and consider its variation under atomic displacements. Since the normalization condition is invariant under atomic displacements, we obtain a relation

$$\begin{aligned}&\sum_{\mu\nu} e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}\delta(e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\mu}}C^{\sigma*}_{n\mathbf{k}\mu})C^{\sigma}_{n\mathbf{k}\nu}S_{\mu\nu}(\mathbf{k}) \\ &\quad + \sum_{\mu\nu} C^{\sigma*}_{n\mathbf{k}\mu}e^{-i\mathbf{k}\cdot\boldsymbol{\tau}^{\nu}}\delta(e^{i\mathbf{k}\cdot\boldsymbol{\tau}^{\nu}}C^{\sigma}_{n\mathbf{k}\nu})S_{\mu\nu}(\mathbf{k}) \\ &= -\sum_{\mu\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})}C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}\delta(e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}-\boldsymbol{\tau}^{\nu})}S_{\mu\nu}(\mathbf{k})). \qquad (51)\end{aligned}$$

By exploiting this relation in order to convert the variation in the expansion coefficients, $C^{\sigma*}_{n\mathbf{k}\mu}$ and $C^{\sigma}_{n\mathbf{k}\nu}$, to that in the overlap matrix $S_{\mu\nu}(\mathbf{k})$, we have

$$\begin{aligned}\langle\delta\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\psi^{\sigma}_{n\mathbf{k}}\rangle + \langle\psi^{\sigma}_{n\mathbf{k}}|\hat{H}^{\sigma}|\delta\psi^{\sigma}_{n\mathbf{k}}\rangle &= -N\sum_{\mu\nu} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})}\epsilon^{\sigma}_{n\mathbf{k}}\delta(e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}-\boldsymbol{\tau}^{\nu})}S_{\mu\nu}(\mathbf{k})) \\ &\quad + N\sum_{\mu\nu\mathbf{R}} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R})}[\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\delta\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle + \langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle] \\ &= N\sum_{\mu\nu\mathbf{R}} C^{\sigma*}_{n\mathbf{k}\mu}C^{\sigma}_{n\mathbf{k}\nu}e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu}+\mathbf{R})}[\langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}-\epsilon^{\sigma}_{n\mathbf{k}}|\delta\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle + \langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\hat{H}^{\sigma}-\epsilon^{\sigma}_{n\mathbf{k}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle]. \qquad (52)\end{aligned}$$

Here, we have used

$$\delta[e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\mu}-\boldsymbol{\tau}^{\nu})}S_{\mu\nu}(\mathbf{k})] = \sum_{\mathbf{R}}\delta[e^{i\mathbf{k}\cdot\mathbf{R}}S_{\mu\nu}(\mathbf{R})] = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}(\langle\delta\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle + \langle\phi_{\mu,\boldsymbol{\tau}^{\mu}}|\delta\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}\rangle). \qquad (53)$$

Thus, the change in the total energy per unit cell due to the atomic displacements is

$$\delta E^{\mathrm{LSDA}+U} = \sum_{n\mathbf{k}\sigma\mu\nu\mathbf{R}} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} e^{i\mathbf{k}\cdot\mathbf{R}} \times [\langle \phi_{\mu,\boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma} - \epsilon^{\sigma}_{n\mathbf{k}} | \delta\phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle + \langle \delta\phi_{\mu,\boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma} - \epsilon^{\sigma}_{n\mathbf{k}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle] + \frac{1}{N} \sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}} \langle \psi^{\sigma}_{n\mathbf{k}} | \delta V_{ext} | \psi^{\sigma}_{n\mathbf{k}} \rangle + \sum_{mm'\sigma} V^{\sigma}_{mm'} \delta n^{\sigma}_{mm'} + \delta E^{ii}. \tag{54}$$

Evaluation of this expression requires the self-consistent Kohn-Sham wave functions *without* atomic displacements and change in basis orbitals due to atomic displacements but it does not require any self-consistent change in the wave-function coefficients. The first term in Eq. (54) is called Pulay correction which comes from the incompleteness of the PAO basis.

In order to obtain the atomic force exerted on the λth atom in the unit cell, we suppose that an atom located at $\boldsymbol{\tau}^{\lambda}$ experiences an infinitesimal position change

$$\boldsymbol{\tau}^{\lambda} \to \boldsymbol{\tau}^{\lambda} + \delta\boldsymbol{\tau}^{\lambda}. \tag{55}$$

By using Eq. (54), a force exerted on the λth atom in PAO-basis methods, $\mathbf{F}^{\mathrm{LSDA}+U}_{\lambda}$, becomes

$$\mathbf{F}^{\mathrm{LSDA}+U}_{\lambda} = - \sum_{n\mathbf{k}\sigma\mu\nu\mathbf{R}} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} e^{i\mathbf{k}\cdot\mathbf{R}} \left[\langle \phi_{\mu,\boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma} - \epsilon^{\sigma}_{n\mathbf{k}} | \frac{\partial \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}}{\partial \boldsymbol{\tau}^{\nu}} \rangle \delta_{\boldsymbol{\tau}^{\nu},\boldsymbol{\tau}^{\lambda}} + \langle \frac{\partial \phi_{\mu,\boldsymbol{\tau}^{\mu}}}{\partial \boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma} - \epsilon^{\sigma}_{n\mathbf{k}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle \delta_{\boldsymbol{\tau}^{\mu},\boldsymbol{\tau}^{\lambda}} \right] - \frac{1}{N} \sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}} \langle \psi^{\sigma}_{n\mathbf{k}} | \frac{\partial V_{ext}}{\partial \boldsymbol{\tau}^{\lambda}} | \psi^{\sigma}_{n\mathbf{k}} \rangle - \frac{\partial E^{ii}}{\partial \boldsymbol{\tau}^{\lambda}} - \sum_{n\mathbf{k}mm'\sigma} f^{\sigma}_{n\mathbf{k}} V^{\sigma}_{mm'} \left[\langle \psi^{\sigma}_{n\mathbf{k}} | \frac{\partial \phi_{m,\boldsymbol{\tau}^{m}}}{\partial \boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \psi^{\sigma}_{n\mathbf{k}} \rangle \delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{\lambda}} + \langle \psi^{\sigma}_{n\mathbf{k}} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \frac{\partial \phi_{m',\boldsymbol{\tau}^{m'}}}{\partial \boldsymbol{\tau}^{m'}} | \psi^{\sigma}_{n\mathbf{k}} \rangle \delta_{\boldsymbol{\tau}^{m'},\boldsymbol{\tau}^{\lambda}} \right] \tag{56}$$

since the variation in ϕ_{μ} with respect to the atomic displacement $\delta\boldsymbol{\tau}^{\lambda}$ is given by

$$\delta\phi_{\mu}(\mathbf{r} - \boldsymbol{\tau}^{\mu} - \mathbf{R}) = \delta_{\boldsymbol{\tau}^{\mu},\boldsymbol{\tau}^{\lambda}} \frac{\partial \phi_{\mu}(\mathbf{r} - \boldsymbol{\tau}^{\mu} - \mathbf{R})}{\partial \boldsymbol{\tau}^{\mu}} \delta\boldsymbol{\tau}^{\lambda}. \tag{57}$$

By using $\hat{H}^{\sigma}_{\mathrm{LSDA}}$ defined in Eq. (17), the force formula in Eq. (56) can be expressed as

$$\mathbf{F}^{\mathrm{LSDA}+U}_{\lambda} = - \sum_{n\mathbf{k}\sigma\mu\nu\mathbf{R}} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} e^{i\mathbf{k}\cdot\mathbf{R}} \left[\langle \phi_{\mu,\boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma}_{\mathrm{LSDA}} - \epsilon^{\sigma}_{n\mathbf{k}} | \frac{\partial \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}}{\partial \boldsymbol{\tau}^{\nu}} \rangle \delta_{\boldsymbol{\tau}^{\nu},\boldsymbol{\tau}^{\lambda}} + \langle \frac{\partial \phi_{\mu,\boldsymbol{\tau}^{\mu}}}{\partial \boldsymbol{\tau}^{\mu}} | \hat{H}^{\sigma}_{\mathrm{LSDA}} - \epsilon^{\sigma}_{n\mathbf{k}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle \delta_{\boldsymbol{\tau}^{\mu},\boldsymbol{\tau}^{\lambda}} \right] - \frac{1}{N} \sum_{n\mathbf{k}\sigma} f^{\sigma}_{n\mathbf{k}} \langle \psi^{\sigma}_{n\mathbf{k}} | \frac{\partial V_{ext}}{\partial \boldsymbol{\tau}^{\lambda}} | \psi^{\sigma}_{n\mathbf{k}} \rangle - \frac{\partial E^{ii}}{\partial \boldsymbol{\tau}^{\lambda}} - \sum_{n\mathbf{k}\mu\nu mm'\sigma\mathbf{R}\mathbf{R}'} f^{\sigma}_{n\mathbf{k}} V^{\sigma}_{mm'} C^{\sigma *}_{n\mathbf{k}\mu} C^{\sigma}_{n\mathbf{k}\nu} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^{\nu}-\boldsymbol{\tau}^{\mu})} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \times \frac{\partial}{\partial \boldsymbol{\tau}^{\lambda}} [\langle \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle]. \tag{58}$$

Here we have also used an expression

$$\frac{\partial}{\partial \boldsymbol{\tau}^{\lambda}} [\langle \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle] = \langle \frac{\partial \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'}}{\partial \boldsymbol{\tau}^{\mu}} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle \delta_{\boldsymbol{\tau}^{\mu},\boldsymbol{\tau}^{\lambda}} + \langle \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'} | \frac{\partial \phi_{m,\boldsymbol{\tau}^{m}}}{\partial \boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle \delta_{\boldsymbol{\tau}^{m},\boldsymbol{\tau}^{\lambda}} + \langle \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \frac{\partial \phi_{m',\boldsymbol{\tau}^{m'}}}{\partial \boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}} \rangle \delta_{\boldsymbol{\tau}^{m'},\boldsymbol{\tau}^{\lambda}} + \langle \phi_{\mu,\boldsymbol{\tau}^{\mu}+\mathbf{R}'} | \phi_{m,\boldsymbol{\tau}^{m}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \frac{\partial \phi_{\nu,\boldsymbol{\tau}^{\nu}+\mathbf{R}}}{\partial \boldsymbol{\tau}^{\nu}} \rangle \delta_{\boldsymbol{\tau}^{\nu},\boldsymbol{\tau}^{\lambda}}. \tag{59}$$

In Eq. (58), the first three terms correspond to the atomic force in the LSDA formalism and the last term is the additional term arising from the on-site Coulomb interaction. Thus, one can implement our LSDA+U force formula easily by adding the last term to an available computer code for LSDA force formula. However, one should note that, although the first three terms in the LSDA+U force formula are the same as the LSDA force formula, their actual values are usually different due to the difference in the Kohn-Sham wave functions obtained self-consistently in each method. We define the last term of $\mathbf{F}_\lambda^{\text{LSDA+}U}$ in Eq. (58) as $\mathbf{F}_\lambda^U$

$$\mathbf{F}_\lambda^U = - \sum_{n\mathbf{k}\mu\nu\mathbf{R}\mathbf{R}'mm'\sigma} f_{n\mathbf{k}}^\sigma e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^\nu - \boldsymbol{\tau}^\mu)} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} V_{mm'}^\sigma C_{n\mathbf{k}\mu}^{\sigma *} C_{n\mathbf{k}\nu}^\sigma \times \frac{\partial}{\partial \boldsymbol{\tau}^\lambda} [\langle \phi_{\mu,\boldsymbol{\tau}^\mu+\mathbf{R}'} | \phi_{m,\boldsymbol{\tau}^m} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \phi_{\nu,\boldsymbol{\tau}^\nu+\mathbf{R}} \rangle]. \quad (60)$$

We note that the expression of $\mathbf{F}_\lambda^U$ is simplified by adding Pulay contribution and that $\mathbf{F}_\lambda^U$ is proportional to the derivative of the products of two overlap matrices with respect to atomic positions.

We derived in this section the LSDA+U force formula [Eq. (58)] in the PAO method. The obtained formula can be regarded as the sum of the LSDA force formula and an additional term given by Eq. (60). Thus, our LSDA+U force formula can be easily implemented if a proper LSDA code is available.

IV. LSDA+U ATOMIC-FORCE FORMULA IN PLANE-WAVE-BASIS METHODS

We will derive in this section an atomic-force formula using the plane-wave-basis method. Since plane waves are independent of atomic displacements, there is no Pulay correction term. We will first express the density matrix with the plane-wave-basis set and then derive LSDA+U atomic-force formula.

In plane-wave-basis methods, the Kohn-Sham wave function is given in the Bloch form

$$\psi_{n\mathbf{k}}^\sigma(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}}^\sigma e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (61)$$

where Ω is the unit-cell volume and $\mathbf{G}$ is a reciprocal-lattice vector. We represent the Kohn-Sham wave function with ket symbols as

$$|\psi_{n\mathbf{k}}^\sigma\rangle = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}}^\sigma |\mathbf{k}+\mathbf{G}\rangle, \quad (62)$$

where $|\mathbf{k}+\mathbf{G}\rangle$ represents $\frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$. Using the plane-wave basis, we express the density matrix of Eq. (8a) as

$$\begin{aligned} n_{mm'}^\sigma &= \sum_{n\mathbf{k}} f_{n\mathbf{k}}^\sigma \langle \psi_{n\mathbf{k}}^\sigma | \phi_{m,\boldsymbol{\tau}^m+\mathbf{R}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}} | \psi_{n\mathbf{k}}^\sigma \rangle \delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^{m'}} \\ &= \sum_{n\mathbf{k}\mathbf{G}\mathbf{G}'} f_{n\mathbf{k}}^\sigma C_{n,\mathbf{k}+\mathbf{G}'}^{\sigma *} C_{n,\mathbf{k}+\mathbf{G}}^\sigma \\ &\quad \times \langle \mathbf{k}+\mathbf{G}' | \phi_{m,\boldsymbol{\tau}^m+\mathbf{R}} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}+\mathbf{R}} | \mathbf{k}+\mathbf{G} \rangle \delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^{m'}}. \end{aligned} \quad (63)$$

The change in the Kohn-Sham wave function due to atomic displacements can be written as

$$|\delta\psi_{n\mathbf{k}}^\sigma\rangle = \sum_{\mathbf{G}} \delta C_{n,\mathbf{k}+\mathbf{G}}^\sigma |\mathbf{k}+\mathbf{G}\rangle, \quad (64)$$

where $|\mathbf{k}+\mathbf{G}\rangle$ is not affected by atomic displacements. This change in the Kohn-Sham wave function does not contribute to the change in the total energy in the first order because the total energy is the value of the energy functional when it is minimized with respect to all possible variations in the wave functions. Thus the variation in the total energy is expressed as

$$\delta E^{\text{LSDA+}U} = \frac{1}{N} \sum_{n\mathbf{k}\sigma} f_{n\mathbf{k}}^\sigma \langle \psi_{n\mathbf{k}} | \delta V_{ext} | \psi_{n\mathbf{k}}^\sigma \rangle + \delta E^{ii} + \sum_{mm'\sigma} V_{mm'}^\sigma \delta n_{mm'}^\sigma, \quad (65)$$

where the variation in density matrix $\delta n_{mm'}^\sigma$ is due to the translation of projectors and it is given by Eq. (26).

Now, we suppose that the position of an atom located at $\boldsymbol{\tau}^\lambda$ is changed such that

$$\boldsymbol{\tau}^\lambda \to \boldsymbol{\tau}^\lambda + \delta\boldsymbol{\tau}^\lambda. \quad (66)$$

Then, the atomic force exerted on the λth atom in the plane-wave-basis method is

$$\begin{aligned} \mathbf{F}_\lambda^{\text{LSDA+}U} &= -\frac{1}{N} \sum_{n\mathbf{k}\sigma} f_{n\mathbf{k}}^\sigma \langle \psi_{n\mathbf{k}}^\sigma | \frac{\partial V_{ext}}{\partial \boldsymbol{\tau}^\lambda} | \psi_{n\mathbf{k}}^\sigma \rangle - \frac{\partial E^{ii}}{\partial \boldsymbol{\tau}^\lambda} - \sum_{n\mathbf{k}mm'\mathbf{G}\mathbf{G}'\sigma} f_{n\mathbf{k}}^\sigma C_{n,\mathbf{k}+\mathbf{G}'}^{\sigma *} C_{n,\mathbf{k}+\mathbf{G}}^\sigma \\ &\quad \times V_{mm'}^\sigma \left[\langle \mathbf{k}+\mathbf{G}' | \frac{\partial \phi_{m,\boldsymbol{\tau}^m}}{\partial \boldsymbol{\tau}^m} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \mathbf{k}+\mathbf{G} \rangle \delta_{\boldsymbol{\tau}^m,\boldsymbol{\tau}^\lambda} + \langle \mathbf{k}+\mathbf{G}' | \phi_{m,\boldsymbol{\tau}^m} \rangle \langle \frac{\partial \phi_{m',\boldsymbol{\tau}^{m'}}}{\partial \boldsymbol{\tau}^{m'}} | \mathbf{k}+\mathbf{G} \rangle \delta_{\boldsymbol{\tau}^{m'},\boldsymbol{\tau}^\lambda} \right] \\ &= -\frac{1}{N} \sum_{n\mathbf{k}\sigma} f_{n\mathbf{k}}^\sigma \langle \psi_{n\mathbf{k}}^\sigma | \frac{\partial V_{ext}}{\partial \boldsymbol{\tau}^\lambda} | \psi_{n\mathbf{k}}^\sigma \rangle - \frac{\partial E^{ii}}{\partial \boldsymbol{\tau}^\lambda} - \sum_{n\mathbf{k}mm'\mathbf{G}\mathbf{G}'\sigma} f_{n\mathbf{k}}^\sigma C_{n,\mathbf{k}+\mathbf{G}'}^{\sigma *} C_{n,\mathbf{k}+\mathbf{G}}^\sigma V_{mm'}^\sigma \frac{\partial}{\partial \boldsymbol{\tau}^\lambda} [\langle \mathbf{k}+\mathbf{G}' | \phi_{m,\boldsymbol{\tau}^m} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \mathbf{k}+\mathbf{G} \rangle], \end{aligned} \quad (67)$$

where we exploit the fact that plane-wave basis is invariant under any atomic displacement. Here, the atomic force F^U contributed by $V^{\sigma}_{mm'}$ is

$$\mathbf{F}^U_{\lambda} = - \sum_{n\mathbf{k}mm'\mathbf{G}\mathbf{G}'\sigma} f^{\sigma}_{n\mathbf{k}} C^{\sigma *}_{n,\mathbf{k}+\mathbf{G}'} C^{\sigma}_{n,\mathbf{k}+\mathbf{G}} V^{\sigma}_{mm'} \times \frac{\partial}{\partial \boldsymbol{\tau}^{\lambda}} [\langle \mathbf{k}+\mathbf{G}' | \phi_{m,\boldsymbol{\tau}^m} \rangle \langle \phi_{m',\boldsymbol{\tau}^{m'}} | \mathbf{k}+\mathbf{G} \rangle]. \qquad (68)$$

This is similar to $\mathbf{F}^U_{\lambda}$ in PAO-basis method [Eq. (60)] but $\mathbf{F}^U_{\lambda}$ in Eq. (60) includes contribution from displacements of basis functions.

Our derived LSDA+U atomic-force formula in the PAO and plane-wave methods does not require any information on the self-consistent change in the wave functions resulting from atomic displacements. In both of the two methods, the normalization condition of the Kohn-Sham wave function is useful to avoid any occurrence of the self-consistent variation of the wave functions in the force formula. This is related, in literatures, to the Pulay correction in the PAO method and the Hellmann-Feynman theorem in the plane-wave method, respectively.

V. TEST OF THE ATOMIC-FORCE FORMULA

We test our LSDA+U implementation to the SIESTA (Ref. 12) code and our LSDA+U force formula. In Sec. V A, we perform LSDA+U calculations for NiO and MnO to obtain lattice structures, magnetic moments, and band gaps in the antiferromagnetic phase and we compare our result with previous calculations as well as experimental measurements. In Sec. V B, we test out atomic-force formula by comparing results of our force formula with the numerical derivatives of the total-energy values.

A. Atomic and electronic structures of NiO and MnO

In our present work, we implemented to the SIESTA package the PAO-based LSDA+U method described in previous sections, and applied it to atomic and electronic structures in NiO and MnO, which will be presented in Sec. V A. We also implemented our LSDA+U force formula to the SIESTA package and its results will be presented in Sec. V B.

NiO and MnO are insulators in which magnetic moments are ordered antiferromagnetically at low temperatures below Néel temperatures [525K for NiO and 116 K for MnO (Ref. 15)], as shown in Fig. 1. The magnetic moments are in parallel within each (111) plane while they are in antiparallel between adjacent planes. It is known that this antiferromagnetic spin ordering distorts the original cubic structure of NiO and MnO slightly to a lower-symmetric rhombohedral structure. The known spin ordering and the rhombohedral unit cell are shown in Fig. 1.

Atomic, magnetic, and electronic structures of NiO and MnO are studied by our implementation of the LSDA+U method. Calculations are done with $8 \times 8 \times 8$ k points in the full Brillouin zone and with cut-off energy of 1500 Ry for real-space grid. Troullier-Martins norm conserving pseudopotentials[16] are used. For both Ni and Mn atoms, semicore pseudopotentials are generated with $3s$ and $3p$ electrons as valence electrons as well. With the semicore states, the large cut-off energy is used in order to suppress the error which could occur in the real-space integration. In the SIESTA code, the large cut-off energy does not increase computation time substantially, since increased real-space grid is used only for calculating the Kohn-Sham effective potential. Electronic wave functions are expanded with localized pseudoatomic orbitals (double-zeta polarization-basis set). For the LSDA+U energy functional, the values of U and J parameters are assigned as 8.0 eV and 0.95 eV for NiO, and 6.9 eV and 0.86 eV for MnO, respectively.[4]

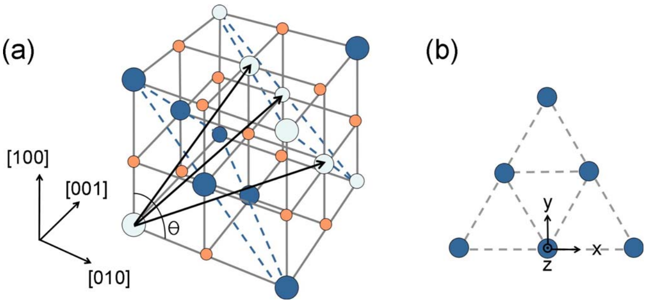

FIG. 1. (Color online) The atomic and magnetic structure of NiO and MnO. (a) Cubic rock-salt structure of NiO and MnO above the Néel temperature (T_N). Large dots [both dark and light blue (gray)] represent metal atoms and small [orange (gray)] dots are O atoms. Below T_N, magnetic moments of metal atoms are aligned ferromagnetically within each (111) plane and antiferromagnetically along the [111] direction. Together with the magnetic ordering, the lattice structure is contracted along the [111] direction, transforming to a lower-symmetric rhombohedral structure. The dark and light blue colors (grays) of the large dots represent up spin and down spin, respectively, and the three arrows are lattice vectors of the rhombohedral unit cell with two metal atoms and two O atoms. The angle θ represents rhombohedral distortion angle. (b) A ferromagnetic (111) plane of metal atoms and a Cartesian coordinate system. The x and y axes are the first and second nearest-neighbor directions within the plane, respectively, and the z axis is the out-of-plane direction.

Table I shows obtained lattice structures by minimizing the LSDA+U total-energy functional with respect to lattice vectors. Starting from the experimental structure, we calculate the total energy for each set of lattice vectors whose magnitudes are varied by 1% of their initial values. While the lattice vectors are varied, atomic positions are kept in symmetric positions since all the Ni, Mn, or O atoms are equivalent within each kind. Using a least-square fit, we obtain lattice vectors for the lowest total energy, which are very close to the experimental data. It is worth noting that in the structure of minimal LSDA+U total energy, the LSDA stress formula produces significant residual pressure which is about −6 kBar for NiO and −7 kBar for MnO. If the stress formula of the LSDA method were valid in LSDA+U scheme, there would be almost no pressure left in the structure of the minimum total energy. This indicates that the stress formulation needs to be developed in LSDA+U scheme.

In Table I, we also present band gaps and magnetic moments calculated by the LSDA+U method and the LSDA method, and compare our results with the experimental data.

TABLE I. Calculated and experimental lattice constants a (Å), rhombohedral distortion angles θ (°), spin magnetic moments M (μ_B), and band gaps E_g (eV) of NiO and MnO.

	NiO				MnO			
	a	θ	M	E_g	a	θ	M	E_g
Calc.(LSDA)	4.15	91.5	1.31	0.83	4.37	92.0	4.49	0.87
Calc. (LSDA+U)	4.19	90.1	1.73	2.7	4.42	91.0	4.74	1.44
Expt.	4.17[a]	90.075[a]	1.64[b],1.77[c], 1.90[d]	4.0[e],4.3[f]	4.445[g]	90.62[h]	4.58[d]–4.79[c]	3.9[i]

[a] Reference 17.
[b] Reference 18.
[c] Reference 19.
[d] Reference 20.
[e] Reference 21.
[f] Reference 22.
[g] Reference 23.
[h] Reference 24.
[i] Reference 25.

We find that for both NiO and MnO, our calculated lattice constants, magnetic moments, and band-gap values in the LSDA+U scheme are closer to the experimental data than results from the LSDA scheme. Especially the band-gap values by LSDA+U calculations are substantially enhanced compared with LSDA results. Even though the band gap is underestimated, our LSDA+U calculations predict insulating ground states whereas the LSDA calculations predict small-gap semiconducting ground states. The underestimation of the band gaps even in the LSDA+U method is understandable in the sense that calculational results based on DFT describe ground-state properties accurately but not the excited-state properties of materials such as the band gap. For antiferromagnetic spin moments, values obtained by our LSDA+U implementation are within the experimental range.

In the structure of minimum total energy, band structures of NiO and MnO are obtained along the high-symmetry lines of the rhombohedral structure, as shown in Fig. 2. Our calculated band structures are similar to other calculational results.[26,27] This also implies that the LSDA+U method is successfully implemented in our present work.

B. Test of the atomic-force formula

We test our atomic-force formula by comparing the force values and the total-energy values. From the density-functional methods, the atomic force exerted on an atom should be equal to the derivative of the total-energy functional with respect to the displacement of the atom. With antiferromagnetic NiO, we calculate the atomic force and the total energy in the LSDA+U method with either Ni or O atom displaced by −0.2 Å to 0.2 Å along x, y, or z direction. As plotted in Fig. 3, the obtained total-energy values are well fit to quadratic curves and the force values are fit to almost linear curves with respect to the displacement of Ni or O atom. When the values from our force formula and numerical derivatives of the total-energy curves are compared quantitatively, as shown in Fig. 3, they agree well with each other, confirming the validity of our force formula. We also compare second derivatives of total-energy curves and first derivatives of atomic forces, and find, as shown in Table II, that they agree with each other, within 2% difference, supporting strongly the validity of our implementation.

VI. FROZEN-PHONON CALCULATION OF NiO AND MnO

As an application, we apply our LSDA+U force formula to calculate the zone-center transverse-optic (TO) phonon frequencies in NiO and MnO. By the frozen-phonon method, TO phonon energies are calculated for the [111] mode and the in-plane mode which are illustrated in Fig. 4. In addition, phonon frequencies are calculated by LSDA+U and LSDA methods in the same structure to see how the presence of the E^U term in the energy functional affects phonon frequencies. The calculational results are presented in Table III including results from plane-wave LSDA+U method and those from experiments.

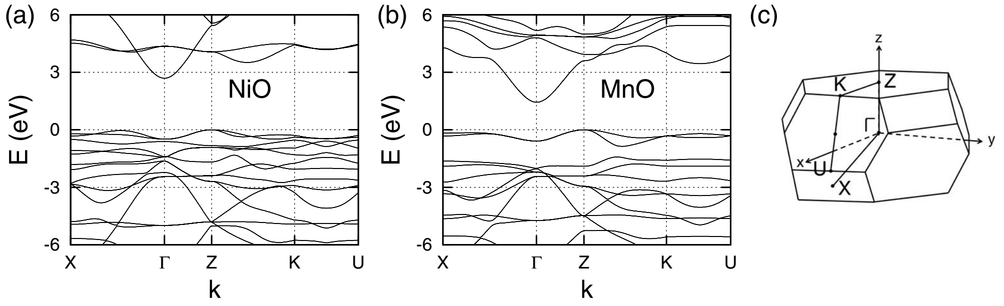

FIG. 2. LSDA+U band structures of (a) NiO and (b) MnO along high-symmetry lines. (c) The first Brillouin zone of the rhombohedral structure.

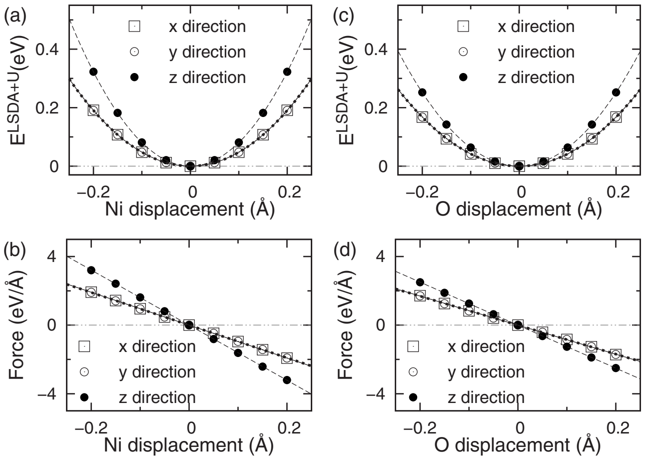

FIG. 3. LSDA+U total energies and forces vs atomic displacements in NiO. (a) Increase in $E^{\mathrm{LSDA}+U}$ per rhombohedral unit cell when one Ni atom in the rhombohedral unit cell is displaced in the x, y, or z direction, and (b) the LSDA+U force exerted on the displaced Ni atom. (c) Increase in $E^{\mathrm{LSDA}+U}$ per rhombohedral unit cell when an O atom is displaced instead of Ni, and (d) the LSDA+U force exerted on the displaced O atom. In (a) and (c), points are values of $E^{\mathrm{LSDA}+U}$ and curves are least-square fit to the points. In (b) and (d), points are atomic forces obtained from our LSDA+U force formula, while curves are the derivatives of the total-energy curves in (a) and (c), respectively. The x, y, and z directions are the same as those shown in Fig. 1(b).

Table III shows that our results agree with plane-wave-based LSDA+U results with differences less than 6% and also are in good agreement with experimental results except for the in-plane phonon frequencies of NiO. In experimental results, the phonon frequency of the in-plane mode in NiO is lower than the frequencies of the [111] mode whereas our calculation predicts that the in-plane mode is higher in frequency than the [111] mode. This discrepancy is also discussed by Luo *et al.*[28] and needs further investigation.

We also study the effect of E^U term in the energy functional on phonon frequencies by comparing the results of LSDA+U calculations with those of LSDA calculations. As shown in Table III, we obtain that introduction of the E^U term substantially increases phonon frequencies of both the [111] and the in-plane modes, decreasing their splitting. As shown in Table III, the $\mathbf{F}^U$ term is found to contribute only about 0.5% and 1% to the phonon frequencies of NiO and MnO, respectively, implying that the difference in the atomic forces in the LSDA+U method and the LSDA method is not mainly due to the presence of the $\mathbf{F}^U$ term in the force formula but due to the difference in the self-consistent electron densities in the two methods. Since the E^U term in the LSDA+U energy functional corrects the exchange-correlation energy, the small contributions of $\mathbf{F}^U$ to the atomic forces in NiO and MnO are consistent with the fact that the exchange-correlation energy has no contribution to the atomic force in the exact DFT. A detailed discussion on this is presented in Appendix B. Although it turns out that the $\mathbf{F}^U$ term has small contribution in NiO and MnO, we do not know yet whether the term would also be small in other materials in general.

TABLE II. Calculated second derivatives of the total energy and first derivatives of atomic forces (in eV/Å^2) in NiO.

	Ni atoms		O atoms	
Direction	$-\frac{\partial^2}{\partial R_i^2}E^{\mathrm{LSDA}+U}$	$\frac{\partial F_i}{\partial R_i}$	$-\frac{\partial^2}{\partial R_i^2}E^{\mathrm{LSDA}+U}$	$\frac{\partial F_i}{\partial R_i}$
x	−9.550	−9.597	−8.399	−8.487
y	−9.528	−9.532	−8.393	−8.463
z	−16.134	−16.076	−12.598	−12.553

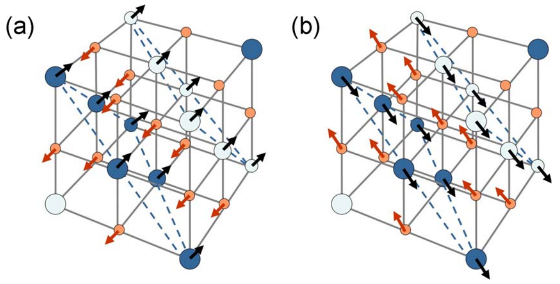

FIG. 4. (Color online) (a) [111] phonon mode for NiO and MnO. (b) In-plane phonon mode for NiO and MnO. Arrows represent atomic displacements in each phonon mode.

VII. SUMMARY

We have presented the derivation of atomic-force formula in the LSDA+U method, considering the rotationally invariant form of E^U energy functional, the fully localized limit of the double-counting term, and either PAOs or plane waves for the basis of the wave functions. In the case of PAO-basis methods, Pulay correction is considered and included to the atomic-force formula. As a test of our force formula, we compared the atomic forces from our force formula with the numerical derivatives of the curves fit to the total-energy values and they agree well with each other, supporting the validity of our implementation. As an application, we calculate TO phonon frequencies of NiO and MnO and they are consistent with the results from plane-wave-basis LSDA+U method as well as those from experiments. It turns out that, in NiO and MnO, the difference in forces in the LSDA and the LSDA+U methods originates mainly from the difference in the self-consistent electron densities in the two methods and that the additional term appearing in our LSDA+U atomic-force formula produces small contribution. It seems reasonable since it is only the exchange-correlation energy functional that is different in the LSDA and the LSDA+U methods but more extensive study is required on this issue. Although we derived the atomic-force formula for a specific form of the LSDA+U energy functional, our derivation procedure of the force formula can easily be generalized to different forms of the LSDA+U method. Our LSDA+U atomic-force formula requires almost negligible computational resources in calculating forces in the LSDA+U method so it will be very useful in optimizing atomic structure and investigating the vibrational structures of strongly correlated materials using the LSDA+U method.

TABLE III. Calculated and experimental values for the zone-center TO phonon energies (in meV) for MnO and NiO.

		This work				
	TO modes	LSDA+U	LSDA+U w/o $\mathbf{F}^U$	LSDA	LSDA+U [a]	Expt.[b]
NiO	[111]	51.6	51.3	38.5	50.4	~50
	In plane	53.4	53.1	46.2	52.2	~45
MnO	[111]	37.9	37.5	33.7	37.3	36.4
	In plane	35.3	34.7	12.6	33.5	33.3

[a] Reference 28; Calculated by plane-wave method.
[b] Reference 29.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE DOUBLE COUNTING TERM IN E^U

The E^U energy functional deals with the on-site Coulomb interaction between d (or f) orbitals. Since the interaction is also considered in the E_{xc} in the LSDA total-energy functional, we should subtract the contribution of the interaction considered in E_{xc} from E^U. Alternatively, we can subtract E^{dc}, which is mean-field evaluation of E^U, from E^U energy functional. Two methods are often used to calculate double-counting term. One is fully localized limit (FLL) and the other is around mean field.[3,30] We consider FLL, in the present work. In the FLL method, it is assumed that the density matrix is diagonal and can be written as

$$n^{\sigma}_{mm'} = \delta_{mm'} n^{\sigma}_{mm}. \tag{A1}$$

This is valid in the sense that one can always diagonalize the density matrix. Thus, we can write the E^{dc} as

$$\begin{aligned} E^{dc} = \frac{1}{2}\sum_{\{m\}\sigma} [& \langle m,m''|V_{ee}|m',m'''\rangle \delta_{mm'} \langle n^{\sigma}_{mm}\rangle \delta_{m''m'''} \langle n^{-\sigma}_{m''m''}\rangle \\ & + (\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle) \\ & \times \delta_{mm'}\delta_{m''m'''}\langle n^{\sigma}_{mm} n^{\sigma}_{m''m''}\rangle], \end{aligned} \tag{A2}$$

where the bracket on the density matrix denotes the averaged value. For the first term, we have separately taken the average of each of the two density matrices because the spin components are different. Since each orbital can be occupied with the same probability in the mean-field approximation, $\langle n^{\sigma}_{mm}\rangle$ is given by

$$\langle n^{\sigma}_{mm}\rangle = \frac{{}_{2l}C_{n^{\sigma}-1}}{{}_{2l+1}C_{n^{\sigma}}} = \frac{n^{\sigma}}{2l+1}. \tag{A3}$$

For the last term in Eq. (A2), we cannot separately calculate each density matrix because the two density matrices have the same spin. In this case, we have

$$\langle n^{\sigma}_{mm} n^{\sigma}_{m''m''}\rangle = \delta_{mm''}\frac{n^{\sigma}}{2l+1} + (1-\delta_{mm''})\frac{n^{\sigma}}{2l+1}\frac{n^{\sigma}-1}{2l}. \tag{A4}$$

In the case of $m=m''$, the product of two identical density matrices is just equal to one of them since each orbital is occupied by either zero or one electron of the given spin. The second term corresponds to the case of $m \neq m''$. Since the two orbitals are different, the probability of finding the two orbitals occupied simultaneously is given by

$$\frac{{}_{2l-1}C_{n^{\sigma}-2}}{{}_{2l+1}C_{n^{\sigma}}} = \frac{n^{\sigma}}{2l+1}\frac{n^{\sigma}-1}{2l}. \tag{A5}$$

Substituting Eqs. (A3) and (A4) into Eq. (A2), the double-counting term E^{dc} is

$$\begin{aligned} E^{dc} = \frac{1}{2}\sum_{\sigma mm'} \Bigg[& \langle m,m'|V_{ee}|m,m'\rangle \frac{n^{\sigma}}{2l+1}\frac{n^{-\sigma}}{2l+1} \\ & + \{\langle m,m'|V_{ee}|m,m'\rangle - \langle m,m'|V_{ee}|m',m\rangle\} \\ & \times \left\{\delta_{mm'}\frac{n^{\sigma}}{2l+1} + (1-\delta_{mm'})\frac{n^{\sigma}}{2l+1}\frac{n^{\sigma}-1}{2l}\right\}\Bigg], \end{aligned} \tag{A6}$$

where the terms with $\delta_{mm'}$ become zero by the minus sign of the matrix elements in the second line. By Eq. (10) and the definitions of U and J, we can further simplify E^{dc} as

$$\begin{aligned} E^{dc} &= \frac{1}{2}\sum_{\sigma}\Bigg[(2l+1)^2 U \frac{n^{\sigma}}{2l+1}\frac{n^{-\sigma}}{2l+1} \\ &\quad + \{(2l+1)^2U - (2l+1)U - 2l(2l+1)J\}\frac{n^{\sigma}}{2l+1}\frac{n^{\sigma}-1}{2l}\Bigg] \\ &= \frac{1}{2}\sum_{\sigma}[Un^{\sigma}(n^{\sigma}+n^{-\sigma}-1) - Jn^{\sigma}(n^{\sigma}-1)] \\ &= \frac{U}{2}n(n-1) - \frac{J}{2}\sum_{\sigma} n^{\sigma}(n^{\sigma}-1), \end{aligned} \tag{A7}$$

which is the double-counting term used in Eq. (7).

APPENDIX B: DISCUSSION ON THE EXACT DFT AND THE SIZE OF $\mathbf{F}^U$

Suppose that the exact density-functional theory is available. Then we can write the total-energy functional as

$$E^{exact}[n] = E_K[n] + E_H[n] + E_{ext}[n,\{\boldsymbol{\tau}\}] + E_{xc}[n] + E_{ii}[\{\boldsymbol{\tau}\}], \tag{B1}$$

where E_K is the kinetic energy, E_H represents the Hartree energy, E_{ext} is the electron-ion interaction energy, E_{xc} is the exact exchange-correlation energy, and E_{ii} represents the ion-ion interaction energy. In the exact density-functional theory, the exact E_{xc} is a functional of the electron density only, and it does not depend explicitly on positions of atoms.

In the density-functional theory, the force on an atom corresponds to the rate of the first-order change in the ground-state energy when the atom is moved. Since the ground-state energy is the value of the total-energy functional when it is minimized with respect to all possible variations in the electron density, a change in the ground-state energy due to a variation in the electron density caused by a change in atomic positions is always of the second order, making no contribution to the force.[5,6,8] In the exact total-energy functional, only V_{ext} and E_{ii} have explicit dependences on atomic positions so that only these terms can contribute to the force.

If the E^U term in the LSDA+U method, including the double-counting term, could correct the LSDA exchange-correlation energy E_{xc}^{LSDA} in the sense that $E_{xc}^{\mathrm{LSDA}}+E^U$ be equal to the exact E_{xc}, the E^U term would have no contribution to the atomic force because neither E_{xc}^{LSDA} nor the exact E_{xc} contributes to the force. Thus our result that the calculated $\mathbf{F}^U$ is relatively small in NiO and MnO may imply that the E^U term in the LSDA+U method is a good correction of the exchange-correlation energy in NiO and MnO.

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