# Force calculation for orbital-dependent potentials with FP-(L)APW + lo basis sets

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## ARTICLE INFO

## ABSTRACT

Within the linearized augmented plane-wave method for electronic structure calculations, a force expression was derived for such exchange–correlation energy functionals that lead to orbital-dependent potentials (e.g., LDA + $U$ or hybrid methods). The forces were implemented into the WIEN2k code and were tested on systems containing strongly correlated $d$ and $f$ electrons. The results show that the expression leads to accurate atomic forces.

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## 1. Introduction

The majority of present day electronic structure calculations on periodic solids are performed with the Kohn–Sham (KS) formulation [1] of density functional theory [2] using the local density (LDA) or generalized gradient approximations (GGA) for the exchange–correlation energy. Among the different methods to solve the KS equations, the full-potential (linearized) augmented-plane-wave and local-orbitals (FP-(L)APW + lo) methods [3,4] are among the most accurate schemes. For a given crystal structure one is very often interested in finding the atomic positions corresponding to the lowest energy. For solids with a complicated unit cell a direct minimization of the total energy is impractical, but the knowledge of atomic forces simplifies the structure optimization and allows one to move the atoms until the forces vanish. The formalism of the force calculation for the original LAPW basis set [5] was independently developed by Soler and Williams [6,7] and Yu et al. [8], leading to two formulations which later on were shown to be equivalent both from the formal as well as practical points of view [9–11]. The formulation of Yu et al. [8] was adopted for the WIEN2k code [12–15] (the details of the implementation can be found in Ref. [16]). Then, the formalism was adapted for the APW + lo basis set [4,17,18]. Other works on forces for the LAPW basis set can be found in Refs. [19,20].

There are important classes of solids for which the LDA and GGA functionals are known to yield even qualitatively incorrect ground states. Notorious examples are the so-called strongly correlated systems, e.g., the transition-metal oxides or rare-earth compounds. The ground state of such systems can often be described significantly better by using the LDA + $U$ [21,22] or hybrid functionals (see, e.g., Refs. [23,24]). The WIEN2k code, which is based on the FP-(L)APW + lo method, allows such calculations [24–26], but so far structural relaxation has not been possible due to the lack of an atomic force formalism for LDA + $U$ and hybrid functionals in the FP-(L)APW + lo basis set. Therefore, it is of great importance to develop such a formalism, which is presented here.

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The paper is organized as follows. The next section describes the theory, namely, the FP-(L)APW + lo basis set, the basic KS equations with orbital-dependent potentials, and the derivation of the atomic forces for such potentials. Then, numerical tests are presented in Section 3, and finally a summary is given in Section 4.

## 2. Theory

### 2.1. FP-L(A)PW + lo basis sets

In the FP-(L)APW + lo method, the unit cell volume is divided into two types of regions (see Ref. [3] for details): the interstitial I and the non-overlapping muffin-tin (MT) spheres $S_\alpha$ centered at the positions $\mathbf{R}_\alpha$ of the nuclei. The basis functions, which are used for the expansion of the crystal orbitals ($n$ is the band index, $\mathbf{k}$ is a vector in the first Brillouin zone, and $\sigma$ is the spin index)

$$\psi_{n\mathbf{k}}^\sigma(\mathbf{r}) = \sum_\mathbf{K} d_{n\mathbf{k}+\mathbf{K}}^\sigma \phi_{\mathbf{k}+\mathbf{K}}^\sigma(\mathbf{r}) + \sum_i d_{n\mathbf{k}+\mathbf{K}_i}^{\mathrm{LO}i\sigma} \phi_{\mathbf{k}+\mathbf{K}_i}^{\mathrm{LO}i\sigma}(\mathbf{r}), \tag{1}$$

are augmented plane waves (where $V$ is the unit cell volume and $\mathbf{r}_\alpha = \mathbf{r} - \mathbf{R}_\alpha$ is the position inside sphere $\alpha$):

$$\phi_{\mathbf{k}+\mathbf{K}}^\sigma(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} & \mathbf{r} \in \mathrm{I}, \\ \sum_{\ell,m}(a_{\mathbf{k}+\mathbf{K}}^{\alpha\ell m\sigma} u_{1,\ell}^{\alpha\sigma}(r_\alpha) + b_{\mathbf{k}+\mathbf{K}}^{\alpha\ell m\sigma} \dot{u}_{1,\ell}^{\alpha\sigma}(r_\alpha)) Y_{\ell m}(\hat{\mathbf{r}}_\alpha) & \mathbf{r} \in S_\alpha, \end{cases} \tag{2}$$

where $u_{1,\ell}^{\alpha\sigma}$ is a radial function evaluated at the energy $\epsilon_{1,\ell}^{\alpha\sigma}$ and $\dot{u}_{1,\ell}^{\alpha\sigma}$ is its energy derivative, and local orbital (LO) basis functions

$$\phi_{\mathbf{k}+\mathbf{K}_i}^{\mathrm{LO}i\sigma}(\mathbf{r}) = \begin{cases} (a_{\mathrm{LO}\mathbf{k}+\mathbf{K}_i}^{\alpha_i\ell_i m_i\sigma} u_{1,\ell_i}^{\alpha_i\sigma}(r_{\alpha_i}) + b_{\mathrm{LO}\mathbf{k}+\mathbf{K}_i}^{\alpha_i\ell_i m_i\sigma} \dot{u}_{1,\ell_i}^{\alpha_i\sigma}(r_{\alpha_i}) + c_{\mathrm{LO}\mathbf{k}+\mathbf{K}_i}^{\alpha_i\ell_i m_i\sigma} u_{2,\ell_i}^{\alpha_i\sigma}(r_{\alpha_i})) Y_{\ell_i m_i}(\hat{\mathbf{r}}_{\alpha_i}) & \mathbf{r} \in S_{\alpha_i}, \\ 0 & \mathbf{r} \notin S_{\alpha_i}. \end{cases} \tag{3}$$

Eqs. (2) and (3) are for the LAPW + LO basis set [3], while for the APW + lo basis set [4] the coefficients $b_{\mathbf{k}+\mathbf{K}}^{\alpha\ell m\sigma}$ in Eq. (2) and $c_{\mathrm{LO}\mathbf{k}+\mathbf{K}_i}^{\alpha_i\ell_i m_i\sigma}$ in Eq. (3) are zero.

### 2.2. DFT + U and hybrid functionals

In the WIEN2k code, the DFT + U and hybrid methods are implemented only inside the MT spheres [24–26], which is justified provided these methods are applied to electrons that are well localized inside the corresponding sphere, e.g., 3$d$ and 4$f$ electrons in transition-metal and rare-earth atoms, respectively. In essence, an orbital-dependent contribution to exchange and correlation is added within the MT spheres of the atoms which contain strongly correlated electrons and the corresponding LDA or GGA contribution is subtracted.

The DFT + U and hybrid total-energy functionals are given by (all equations are expressed in Hartree atomic units)

$$E = T_\mathrm{s} + E_\mathrm{Coul} + E_\mathrm{xc}^\mathrm{loc} + E_\mathrm{orb}, \tag{4}$$

where $T_\mathrm{s}$, $E_\mathrm{Coul}$, $E_\mathrm{xc}^\mathrm{loc}$, and $E_\mathrm{orb}$ are the KS kinetic, Coulomb (electron–electron, electron–nucleus, and nucleus–nucleus electrostatic interactions), (semi-)local (i.e., LDA or GGA) exchange–correlation, and orbital (Hubbard or hybrid) terms, respectively. The corresponding KS equations for the valence electrons are

$$\hat{H}^\sigma \psi_{n\mathbf{k}}^\sigma(\mathbf{r}) = \left(\hat{T} + v_{\mathrm{eff},\sigma}^\mathrm{KS}(\mathbf{r}) + \hat{U}^\sigma\right)\psi_{n\mathbf{k}}^\sigma(\mathbf{r}) = \epsilon_{n\mathbf{k}}^\sigma \psi_{n\mathbf{k}}^\sigma(\mathbf{r}), \tag{5}$$

where $\hat{T} = -\frac{1}{2}\nabla^2$ is the kinetic-energy operator,

$$v_{\mathrm{eff},\sigma}^\mathrm{KS}(\mathbf{r}) = v_\mathrm{Coul}(\mathbf{r}) + v_{\mathrm{xc},\sigma}^\mathrm{loc}(\mathbf{r}) \tag{6}$$

is the multiplicative effective KS potential [1], and $\hat{U}^\sigma$ is the non-multiplicative (i.e., orbital-dependent) operator associated with $E_\mathrm{orb}$ (see Refs. [27] and [26] for DFT + U and hybrid functionals, respectively):

$$\hat{U}^\sigma \psi_{n\mathbf{k}}^\sigma(\mathbf{r}) = \frac{\delta E_\mathrm{orb}}{\delta \psi_{n\mathbf{k}}^{\sigma*}(\mathbf{r})} = \sum_{\beta,m_1,m_2} \frac{\partial E_\mathrm{orb}}{\partial n_{m_1 m_2}^{\beta\ell\sigma}} \frac{\delta n_{m_1 m_2}^{\beta\ell\sigma}}{\delta \psi_{n\mathbf{k}}^{\sigma*}(\mathbf{r})} = \sum_{\beta,m_1,m_2} v_{m_1 m_2}^{\beta\ell\sigma} \hat{P}_{m_1 m_2}^{\beta\ell} \psi_{n\mathbf{k}}^\sigma(\mathbf{r}). \tag{7}$$

In Eq. (7), $m_i = -\ell, \ldots, \ell$, where $\ell$ is the angular momentum of the electrons of atom $\beta$, for which the Hubbard or hybrid correction is applied, $v_{m_1 m_2}^{\beta\ell\sigma} = \partial E_\mathrm{orb}/\partial n_{m_1 m_2}^{\beta\ell\sigma}$, $\hat{P}_{m_1 m_2}^{\beta\ell}$ is the projector which is defined such that

$$\langle f|\hat{P}_{m_1 m_2}^{\beta\ell}|g\rangle = \int_0^{R_\mathrm{MT}^\beta} \langle f|Y_{\ell m_1}\rangle_{\Omega,\beta} \langle Y_{\ell m_2}|g\rangle_{\Omega,\beta} r^2\,dr, \tag{8}$$

and $n_{m_1 m_2}^{\beta\ell\sigma}$ is the occupation matrix which is calculated in the following way (see Eq. (11) of Ref. [27]):

$$\begin{aligned} n_{m_1 m_2}^{\beta\ell\sigma} &= \sum_{n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \langle \psi_{n\mathbf{k}}^\sigma|\hat{P}_{m_1 m_2}^{\beta\ell}|\psi_{n\mathbf{k}}^\sigma\rangle = \sum_{n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \int_0^{R_\mathrm{MT}^\beta} \langle \psi_{n\mathbf{k}}^\sigma|Y_{\ell m_1}\rangle_{\Omega,\beta} \langle Y_{\ell m_2}|\psi_{n\mathbf{k}}^\sigma\rangle_{\Omega,\beta} r^2\,dr \\ &= \sum_{n,\mathbf{k},\mathbf{K},\mathbf{K}'} w_{n\mathbf{k}}^\sigma d_{n\mathbf{k}+\mathbf{K}}^{\sigma*} d_{n\mathbf{k}+\mathbf{K}'}^\sigma [a_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} a_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma} + b_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} b_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma} \langle \dot{u}_{1,\ell}^{\beta\sigma}|\dot{u}_{1,\ell}^{\beta\sigma}\rangle_{r,\beta} + c_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} c_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma} \\ &\quad + (a_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} c_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma} + c_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} a_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma}) \langle u_{1,\ell}^{\beta\sigma}|u_{2,\ell}^{\beta\sigma}\rangle_{r,\beta} + (b_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} c_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma} + c_{\mathbf{k}+\mathbf{K}}^{\beta\ell m_1\sigma*} b_{\mathbf{k}+\mathbf{K}'}^{\beta\ell m_2\sigma}) \langle \dot{u}_{1,\ell}^{\beta\sigma}|u_{2,\ell}^{\beta\sigma}\rangle_{r,\beta}], \end{aligned} \tag{9}$$

where $w_{n\mathbf{k}}^\sigma$ is the weight for the integration in the Brillouin zone. In Eqs. (8) and (9), $\langle f|g\rangle_{r,\beta}$ and $\langle f|g\rangle_{\Omega,\beta}$ denote radial and angular integrations in the sphere $S_\beta$, respectively. Using the sum of eigenenergies, the KS kinetic energy is given by

$$T_s = \sum_{\sigma,i} \epsilon_i^\sigma + \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \epsilon_{n\mathbf{k}}^\sigma - \sum_\sigma \int_{\text{cell}} v_{\text{eff},\sigma}^{\text{KS}}(\mathbf{r}) \rho^\sigma(\mathbf{r})\, d^3r - \sum_{\beta,\sigma,m_1,m_2} v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}, \tag{10}$$

where the first two sums are over the core and valence orbitals, respectively.

### 2.3. Forces for DFT + U and hybrid functionals

The force $\mathbf{F}_\alpha = -\nabla_{\mathbf{R}_\alpha} E$ which acts on the nucleus $\alpha$ is composed of two terms:

$$\mathbf{F}_\alpha = \mathbf{F}_\alpha^{\text{ES}} + \mathbf{F}_\alpha^{\text{IBS}}, \tag{11}$$

where $\mathbf{F}_\alpha^{\text{ES}}$ is the Hellmann–Feynman electrostatic (ES) force and $\mathbf{F}_\alpha^{\text{IBS}}$ is the so-called Pulay force [28] which arises due to the use of an atomic-position-dependent incomplete basis set (IBS). Details of the force formalism for LDA and GGA functionals (as implemented in the WIEN2k code) can be found in Refs. [8,16,18]. Therefore, only the term specific to the DFT + U or hybrid method, $\mathbf{F}_\alpha^{\text{orb}}$ (which is a part of $\mathbf{F}_\alpha^{\text{IBS}}$), will be shown below.

The first order variation of the energy $E_{\text{orb}}$ in Eq. (4) due to the displacement $\Delta\mathbf{R}_\alpha$ of the nucleus $\alpha$ is

$$\Delta E_{\text{orb}} = \sum_{\beta,\sigma,m_1,m_2} v_{m_1 m_2}^{\beta\ell\sigma} \Delta n_{m_1 m_2}^{\beta\ell\sigma}. \tag{12}$$

Similarly, the variation of the last term in Eq. (10) is

$$\Delta\left(- \sum_{\beta,\sigma,m_1,m_2} v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}\right) = -\sum_{\beta,\sigma,m_1,m_2} \left(\Delta v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma} + v_{m_1 m_2}^{\beta\ell\sigma} \Delta n_{m_1 m_2}^{\beta\ell\sigma}\right). \tag{13}$$

Adding Eqs. (12) and (13) yields

$$\Delta E_{\text{orb}} + \Delta\left(- \sum_{\beta,\sigma,m_1,m_2} v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}\right) = -\sum_{\beta,\sigma,m_1,m_2} \Delta v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}, \tag{14}$$

which is the term that has to be added to the force expression for LDA or GGA functionals (see Eq. (15) of Ref. [16]):

$$\mathbf{F}_\alpha = -\frac{\Delta E}{\Delta\mathbf{R}_\alpha} = \mathbf{F}_\alpha^{\text{ES}} - \frac{1}{\Delta\mathbf{R}_\alpha}\left(\sum_{\sigma,i} \Delta\epsilon_i^\sigma + \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \Delta\epsilon_{n\mathbf{k}}^\sigma - \sum_\sigma \int_{\text{cell}} \Delta v_{\text{eff},\sigma}^{\text{KS}}(\mathbf{r}) \rho^\sigma(\mathbf{r})\, d^3r - \sum_{\beta,\sigma,m_1,m_2} \Delta v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}\right). \tag{15}$$

Similar to Eq. (26) of Ref. [16], the first order variation of the eigenenergy of a valence electron in the state $\psi_{n\mathbf{k}}^\sigma$ is given as

$$\Delta\epsilon_{n\mathbf{k}}^\sigma = \sum_{\mathbf{K},\mathbf{K}'} d_{n\mathbf{k}+\mathbf{K}}^{\sigma*} d_{n\mathbf{k}+\mathbf{K}'}^\sigma \left(\langle\Delta\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\Delta\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\Delta\hat{H}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle\right)$$

$$= \sum_{\mathbf{K},\mathbf{K}'} d_{n\mathbf{k}+\mathbf{K}}^{\sigma*} d_{n\mathbf{k}+\mathbf{K}'}^\sigma \left(\langle\Delta\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\Delta\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\Delta\hat{T} + \Delta v_{\text{eff},\sigma}^{\text{KS}} + \Delta\hat{U}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle\right), \tag{16}$$

which leads to

$$\sum_{\sigma,i} \Delta\epsilon_i^\sigma + \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \Delta\epsilon_{n\mathbf{k}}^\sigma = \sum_{\sigma,i}\left(\langle\Delta\psi_i^\sigma|\hat{H}_{\text{core}}^\sigma - \epsilon_i^\sigma|\psi_i^\sigma\rangle + \langle\psi_i^\sigma|\hat{H}_{\text{core}}^\sigma - \epsilon_i^\sigma|\Delta\psi_i^\sigma\rangle\right)$$

$$+ \sum_{\sigma,n,\mathbf{k},\mathbf{K},\mathbf{K}'} w_{n\mathbf{k}}^\sigma d_{n\mathbf{k}+\mathbf{K}}^{\sigma*} d_{n\mathbf{k}+\mathbf{K}'}^\sigma \left(\langle\Delta\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\Delta\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle\right)$$

$$+ \sum_\sigma \int_{\text{cell}} \Delta v_{\text{eff},\sigma}^{\text{KS}}(\mathbf{r}) \rho^\sigma(\mathbf{r})\, d^3r + \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \langle\psi_{n\mathbf{k}}^\sigma|\Delta\hat{T} + \Delta\hat{U}^\sigma|\psi_{n\mathbf{k}}^\sigma\rangle. \tag{17}$$

Using Eq. (17) in Eq. (15) gives

$$\mathbf{F}_\alpha = \mathbf{F}_\alpha^{\text{ES}} - \frac{1}{\Delta\mathbf{R}_\alpha}\Bigg[\sum_{\sigma,i}\left(\langle\Delta\psi_i^\sigma|\hat{H}_{\text{core}}^\sigma - \epsilon_i^\sigma|\psi_i^\sigma\rangle + \langle\psi_i^\sigma|\hat{H}_{\text{core}}^\sigma - \epsilon_i^\sigma|\Delta\psi_i^\sigma\rangle\right)$$

$$+ \sum_{\sigma,n,\mathbf{k},\mathbf{K},\mathbf{K}'} w_{n\mathbf{k}}^\sigma d_{n\mathbf{k}+\mathbf{K}}^{\sigma*} d_{n\mathbf{k}+\mathbf{K}'}^\sigma \left(\langle\Delta\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle + \langle\phi_{\mathbf{k}+\mathbf{K}}^\sigma|\hat{H}^\sigma - \epsilon_{n\mathbf{k}}^\sigma|\Delta\phi_{\mathbf{k}+\mathbf{K}'}^\sigma\rangle\right)$$

$$+ \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \langle\psi_{n\mathbf{k}}^\sigma|\Delta\hat{T}|\psi_{n\mathbf{k}}^\sigma\rangle + \sum_{\sigma,n,\mathbf{k}} w_{n\mathbf{k}}^\sigma \langle\psi_{n\mathbf{k}}^\sigma|\Delta\hat{U}^\sigma|\psi_{n\mathbf{k}}^\sigma\rangle - \sum_{\beta,\sigma,m_1,m_2} \Delta v_{m_1 m_2}^{\beta\ell\sigma} n_{m_1 m_2}^{\beta\ell\sigma}\Bigg]. \tag{18}$$

With the help of Eq. (7), the term in Eq. (18) involving $\Delta\hat{U}^\sigma$ becomes

$$\sum_{\sigma,n,\mathbf{k}} w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\Delta\hat{U}^\sigma|\psi^\sigma_{n\mathbf{k}}\rangle = \sum_{\beta,\sigma,m_1,m_2}\Delta v^{\beta\ell\sigma}_{m_1 m_2}n^{\beta\ell\sigma}_{m_1 m_2} + \sum_{\beta,\sigma,m_1,m_2}v^{\beta\ell\sigma}_{m_1 m_2}\sum_{n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\Delta\hat{P}^{\beta\ell}_{m_1 m_2}|\psi^\sigma_{n\mathbf{k}}\rangle$$

$$= \sum_{\beta,\sigma,m_1,m_2}\Delta v^{\beta\ell\sigma}_{m_1 m_2}n^{\beta\ell\sigma}_{m_1 m_2} + \sum_{\sigma,m_1,m_2}v^{\alpha\ell\sigma}_{m_1 m_2}\sum_{n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\Delta\hat{P}^{\alpha\ell}_{m_1 m_2}|\psi^\sigma_{n\mathbf{k}}\rangle, \tag{19}$$

which leads to

$$\mathbf{F}_\alpha = \mathbf{F}^{\mathrm{ES}}_\alpha - \sum_{\sigma,i}\left(\left\langle\frac{d\psi^\sigma_i}{d\mathbf{R}_\alpha}\Big|\hat{H}^\sigma_{\mathrm{core}} - \epsilon^\sigma_i\Big|\psi^\sigma_i\right\rangle + \left\langle\psi^\sigma_i\Big|\hat{H}^\sigma_{\mathrm{core}} - \epsilon^\sigma_i\Big|\frac{d\psi^\sigma_i}{d\mathbf{R}_\alpha}\right\rangle\right)$$

$$- \sum_{\sigma,n,\mathbf{k},\mathbf{K},\mathbf{K}'}w^\sigma_{n\mathbf{k}}d^{\sigma*}_{n\mathbf{k}+\mathbf{K}}d^\sigma_{n\mathbf{k}+\mathbf{K}'}\left(\left\langle\frac{d\phi^\sigma_{\mathbf{k}+\mathbf{K}}}{d\mathbf{R}_\alpha}\Big|\hat{H}^\sigma - \epsilon^\sigma_{n\mathbf{k}}\Big|\phi^\sigma_{\mathbf{k}+\mathbf{K}'}\right\rangle + \left\langle\phi^\sigma_{\mathbf{k}+\mathbf{K}}\Big|\hat{H}^\sigma - \epsilon^\sigma_{n\mathbf{k}}\Big|\frac{d\phi^\sigma_{\mathbf{k}+\mathbf{K}'}}{d\mathbf{R}_\alpha}\right\rangle\right)$$

$$- \sum_{\sigma,n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\frac{d\hat{T}}{d\mathbf{R}_\alpha}|\psi^\sigma_{n\mathbf{k}}\rangle - \sum_{\sigma,m_1,m_2}v^{\alpha\ell\sigma}_{m_1 m_2}\sum_{n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\frac{d\hat{P}^{\alpha\ell}_{m_1 m_2}}{d\mathbf{R}_\alpha}|\psi^\sigma_{n\mathbf{k}}\rangle, \tag{20}$$

where (see Eq. (5.13.7) of Ref. [3])

$$\frac{d\phi^\sigma_{\mathbf{k}+\mathbf{K}}(\mathbf{r})}{d\mathbf{R}_\alpha} \simeq \begin{cases} \mathrm{i}(\mathbf{k}+\mathbf{K})\phi^\sigma_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) - \nabla\phi^\sigma_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) & \mathbf{r}\in S_\alpha, \\ 0 & \mathbf{r}\notin S_\alpha. \end{cases} \tag{21}$$

Note that the term involving $d\hat{T}/d\mathbf{R}_\alpha$ is non-zero since we use basis functions, whose second (LAPW basis set) or first two (APW + lo basis set) derivatives are discontinuous across the spheres boundaries [3,4,6,8,9,16–18,29]. Finally, combining the terms of the second line of Eq. (20) coming from the contribution of $\hat{U}^\sigma$ with the last term of Eq. (20) yields an additional term with respect to the expression for LDA or GGA functionals (see Eq. (27) of Ref. [16]) for the force expression due to the Hubbard or hybrid correction:

$$\mathbf{F}^{\mathrm{orb}}_\alpha = - \sum_{\sigma,n,\mathbf{k},\mathbf{K},\mathbf{K}'}w^\sigma_{n\mathbf{k}}d^{\sigma*}_{n\mathbf{k}+\mathbf{K}}d^\sigma_{n\mathbf{k}+\mathbf{K}'}\left(\left\langle\frac{d\phi^\sigma_{\mathbf{k}+\mathbf{K}}}{d\mathbf{R}_\alpha}\Big|\hat{U}^\sigma|\phi^\sigma_{\mathbf{k}+\mathbf{K}'}\rangle_\alpha + \langle\phi^\sigma_{\mathbf{k}+\mathbf{K}}|\hat{U}^\sigma\Big|\frac{d\phi^\sigma_{\mathbf{k}+\mathbf{K}'}}{d\mathbf{R}_\alpha}\right\rangle_\alpha\right) - \sum_{\sigma,m_1,m_2}v^{\alpha\ell\sigma}_{m_1 m_2}\sum_{n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\langle\psi^\sigma_{n\mathbf{k}}|\frac{d\hat{P}^{\alpha\ell}_{m_1 m_2}}{d\mathbf{R}_\alpha}|\psi^\sigma_{n\mathbf{k}}\rangle_\alpha$$

$$= - \sum_{\sigma,n,\mathbf{k},\mathbf{K},\mathbf{K}',m_1,m_2}w^\sigma_{n\mathbf{k}}d^{\sigma*}_{n\mathbf{k}+\mathbf{K}}d^\sigma_{n\mathbf{k}+\mathbf{K}'}v^{\alpha\ell\sigma}_{m_1 m_2}\frac{d}{d\mathbf{R}_\alpha}\langle\phi^\sigma_{\mathbf{k}+\mathbf{K}}|\hat{P}^{\alpha\ell}_{m_1 m_2}|\phi^\sigma_{\mathbf{k}+\mathbf{K}'}\rangle_\alpha$$

$$= 2\sum_{\sigma,n,\mathbf{k}}w^\sigma_{n\mathbf{k}}\mathrm{Im}\Bigg[\sum_{m_1,m_2}v^{\alpha\ell\sigma}_{m_1 m_2}\Big(A^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{A}^{\alpha n\mathbf{k}\sigma}_{\ell m_2} + B^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{B}^{\alpha n\mathbf{k}\sigma}_{\ell m_2}\langle\dot{u}^{\alpha\sigma}_{1,\ell}|\dot{u}^{\alpha\sigma}_{1,\ell}\rangle_{r,\alpha} + C^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{C}^{\alpha n\mathbf{k}\sigma}_{\ell m_2}$$

$$+ \big(A^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{C}^{\alpha n\mathbf{k}\sigma}_{\ell m_2} + C^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{A}^{\alpha n\mathbf{k}\sigma}_{\ell m_2}\big)\langle u^{\alpha\sigma}_{1,\ell}|u^{\alpha\sigma}_{2,\ell}\rangle_{r,\alpha} + \big(B^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{C}^{\alpha n\mathbf{k}\sigma}_{\ell m_2} + C^{\alpha n\mathbf{k}\sigma*}_{\ell m_1}\mathbf{B}^{\alpha n\mathbf{k}\sigma}_{\ell m_2}\big)\langle\dot{u}^{\alpha\sigma}_{1,\ell}|u^{\alpha\sigma}_{2,\ell}\rangle_{r,\alpha}\Bigg], \tag{22}$$

where

$$A^{\alpha n\mathbf{k}\sigma}_{\ell m} = \sum_\mathbf{K}d^\sigma_{n\mathbf{k}+\mathbf{K}}a^{\alpha\ell m\sigma}_{\mathbf{k}+\mathbf{K}}, \tag{23}$$

$$\mathbf{A}^{\alpha n\mathbf{k}\sigma}_{\ell m} = \sum_\mathbf{K}\mathbf{K}d^\sigma_{n\mathbf{k}+\mathbf{K}}a^{\alpha\ell m\sigma}_{\mathbf{k}+\mathbf{K}}, \tag{24}$$

and the same for $B^{\alpha n\mathbf{k}\sigma}_{\ell m}$, $\mathbf{B}^{\alpha n\mathbf{k}\sigma}_{\ell m}$, $C^{\alpha n\mathbf{k}\sigma}_{\ell m}$, and $\mathbf{C}^{\alpha n\mathbf{k}\sigma}_{\ell m}$. We note that Eq. (22) is a component of the total-force expression only for those atoms $\alpha$, for which the DFT + $U$ or a hybrid functional was applied. For the other atoms in the unit cell, the force expression for (semi-)local functionals remains correct.

## 3. Test cases: CoO and Ce$_2$O$_3$

We chose CoO and Ce$_2$O$_3$, which contain $3d$ and $4f$ electrons, respectively, as test cases to check the correctness of Eq. (22) and its implementation. At zero pressure and temperature, the most stable structure of CoO is a distorted rock-salt (see Ref. [30] and references therein), but for this test the wurtzite (space group $P6_3mc$) structure was used as it contains one free structural parameter. The wurtzite phase of CoO has been synthesized [31–33] and the experimental lattice constants of the unit cell (which contains two f.u.) are $a = 6.14$ and $c = 9.83$ bohr [32,33]. The atoms sit at the positions $(1/3, 2/3, u_z)$ and $(2/3, 1/3, u_z + 1/2)$ with $u^{\mathrm{Co}}_z = 0.416$ and $u^{\mathrm{O}}_z = 0$ for the Co and O atoms, respectively [32]. We mention that the structural parameters given in Ref. [31] differ somewhat from those given in Refs. [32,33]. While rock-salt CoO is an antiferromagnet, there are uncertainties concerning the magnetic phase of wurtzite CoO [32]. The most stable structure of the antiferromagnet Ce$_2$O$_3$ is hexagonal (space group $P\bar{3}m1$) whose experimental lattice constants are $a = 7.35$ and $c = 11.45$ bohr. The two Ce atoms sit at $\pm(1/3, 2/3, 0.2454)$ while the three O atoms sit at $\pm(1/3, 2/3, 0.6471)$ and $(0, 0, 0)$ [34]. It has been inferred that for both CoO [32] and Ce$_2$O$_3$ (see, e.g., Refs. [35–37]) LDA and GGA functionals are not accurate enough to properly describe the electronic and magnetic structures, but that the use of the LDA + $U$ or hybrid functionals improves the results.

The calculations were done using two functionals. The first functional is LDA + $U$, which consists of choosing (in Eq. (4)) $E^{\mathrm{loc}}_{\mathrm{xc}} = E^{\mathrm{LDA}}_{\mathrm{xc}}$ [38,39] and $E_{\mathrm{orb}} = E_{\mathrm{ee}} - E_{\mathrm{dc}}$, where $E_{\mathrm{ee}}$ is a rotationally invariant electron–electron (ee) interaction energy of Hartree–Fock-type [40] for the electrons of angular momentum $\ell$ and $E_{\mathrm{dc}}$ is the atomic limit version of the double-counting (dc) term [41]. The value of $U$ was chosen to be 6.9 and 4 eV for CoO [21] and Ce$_2$O$_3$ [35–37], respectively, while $J = 0$ was used in both cases. The second functional is the hybrid Fock-$\alpha_{\mathrm{x}}$ [23], i.e., $E^{\mathrm{loc}}_{\mathrm{xc}} = E^{\mathrm{LDA}}_{\mathrm{xc}}$ [38,39] and $E_{\mathrm{orb}} = \alpha_{\mathrm{x}}(E^{\mathrm{HF}}_{\mathrm{x}} - E^{\mathrm{LDA}}_{\mathrm{x}})$, where $E^{\mathrm{HF}}_{\mathrm{x}}$ and $E^{\mathrm{LDA}}_{\mathrm{x}}$ are the Hartree–Fock and LDA [38] exchange energies of the electrons of angular momentum $\ell$ and $\alpha_{\mathrm{x}} \in [0, 1]$. We chose the values $\alpha_{\mathrm{x}} = 0.35$ and $0.15$ for CoO and Ce$_2$O$_3$, respectively.
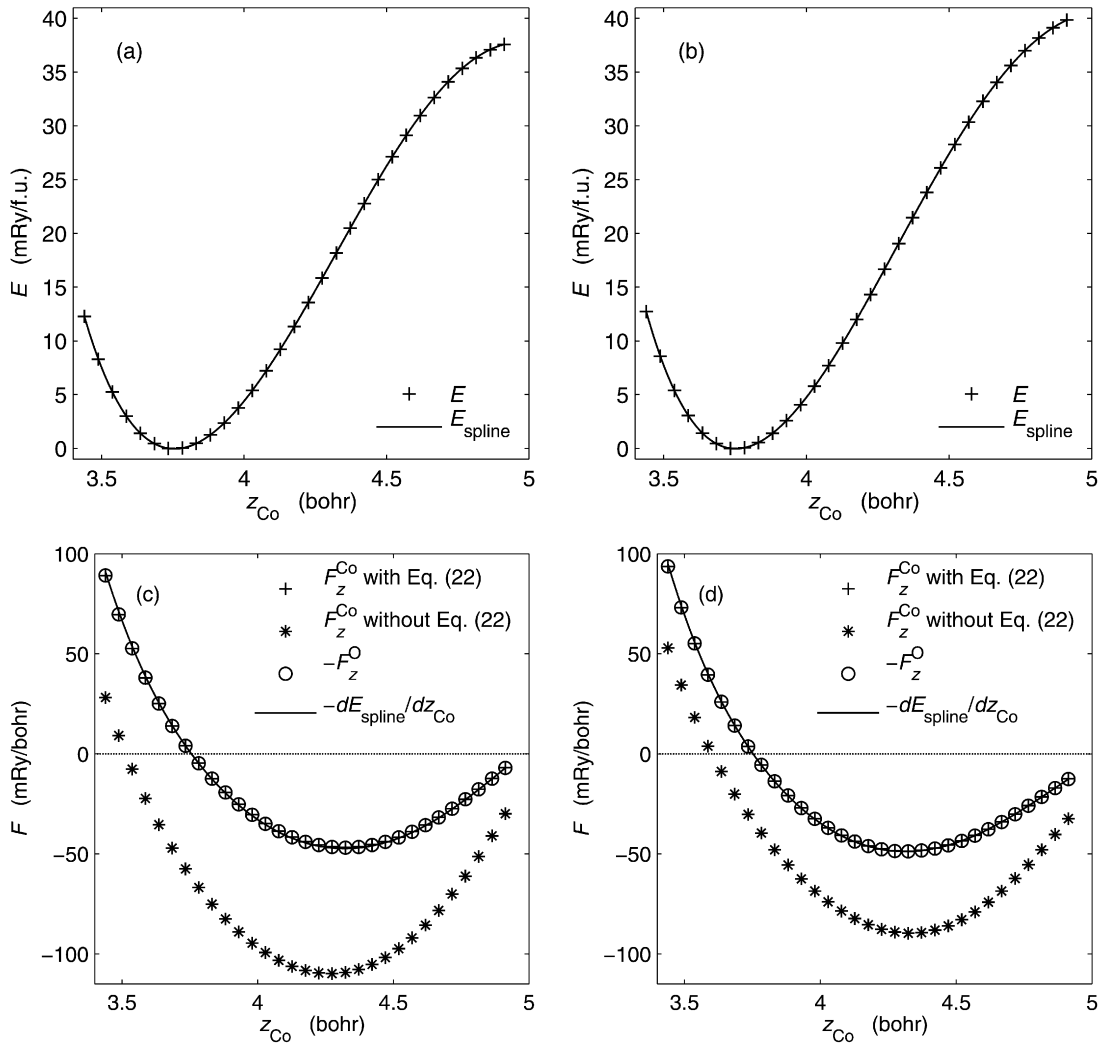
**Fig. 1.** The upper panels show the total energy $E$ ($E = 0$ is set at the minimum of the curve) of wurtzite CoO as a function of the $z$ coordinate of the Co atom in the unit cell, for (a) LDA + $U$ ($U = 6.9$ and $J = 0$ eV) and (b) Fock-0.35 functionals. The solid curve represents a cubic spline interpolation of the data. The lower panels show the $z$ component of the force acting on the Co and O atoms for (c) LDA + $U$ and (d) Fock-0.35 functionals.

We should mention that the Hartree–Fock energy and potential were implemented into the WIEN2k code using several approximations (see Refs. [24] and [26] for details). For instance, the implementation was done only inside the MT spheres, while outside them, the calculations are done with LDA or GGA exchange–correlation functional and potential. It is also worth to remind the reader that for any hybrid functional, the different terms ($E_{xc}^{loc}$ and $E_x^{HF}$) are evaluated with orbitals calculated with the corresponding hybrid potential, therefore the numerical value of $E_x^{HF}$ is not the same as the one calculated with the true Hartree–Fock orbitals.

The computational details are the following: The calculations on CoO and Ce$_2$O$_3$ were done for the ferromagnetic phase and the lattice constants $a$ and $c$ were kept fixed at the experimental values given above. The Brillouin zone integrations were performed on $9 \times 9 \times 5$ special point grids and $R_{MT}^{min} K_{max} = 6$ (the product of the smallest of the atomic sphere radii $R_{MT}$ and the plane wave cutoff parameter $K_{max}$) was used for the expansion of the basis set. The sphere radii were chosen as $(R_{MT}^{Co}, R_{MT}^O) = (1.8, 1.6)$ and $(R_{MT}^{Ce}, R_{MT}^O) = (2.1, 1.86)$ bohr for CoO and Ce$_2$O$_3$, respectively.

The upper panels of Fig. 1 ((a) for LDA + $U$ and (b) for Fock-0.35) show the total energy of wurtzite CoO plotted as a function of the position of the Co atom in the unit cell ($z_{Co}$). Also shown are solid curves which represent the cubic spline interpolations of the calculated points. From the spline interpolation, the minimum of the total energy is calculated to be at $z_{Co} = 3.756$ bohr ($u_z^{Co} = 0.382$) and 3.753 bohr ($u_z^{Co} = 0.382$) for LDA + $U$ and Fock-0.35 functionals, respectively. From the lower panels (c) and (d) of Fig. 1, which show the force acting on the Co and O atoms, we can observe that omission of $\mathbf{F}_\alpha^{orb}$ (Eq. (22)) violates the action–reaction principle, i.e., the $z$ component $F_z^{Co}$ of the force on Co is not equal to the force $F_z^O$ acting on O. The latter coincides with the numerical derivative of the total energy (solid lines in Fig. 1(c) and (d)). However, if we now include Eq. (22) in the calculation of $F_z^{Co}$, agreement is obtained, i.e., $F_z^{Co} = -F_z^O = -dE/dz_{Co}$, for both LDA + $U$ and Fock-0.35 functionals. The equilibrium positions of the Co atom given by the forces and the total energy agree within 0.0005 bohr, thus demonstrating the correctness of Eq. (22).

The results for the second test case, Ce$_2$O$_3$, are shown in Fig. 2. The coordinate $z_{Ce}$ of the Ce atom was varied while keeping the two O atoms fixed. Similarly as for CoO, the force calculation including Eq. (22) leads to very good agreement between $F_z^{Ce}$ and the numerical derivative of the total energy $-(1/2)dE/dz_{Ce}$, whereas without Eq. (22) the force on the Ce atom is clearly wrong. In Fig. 2(d) we note the somewhat erratic behavior of the force on the Ce atom calculated with the Fock-0.15 functional but without the correction (Eq. (22)).
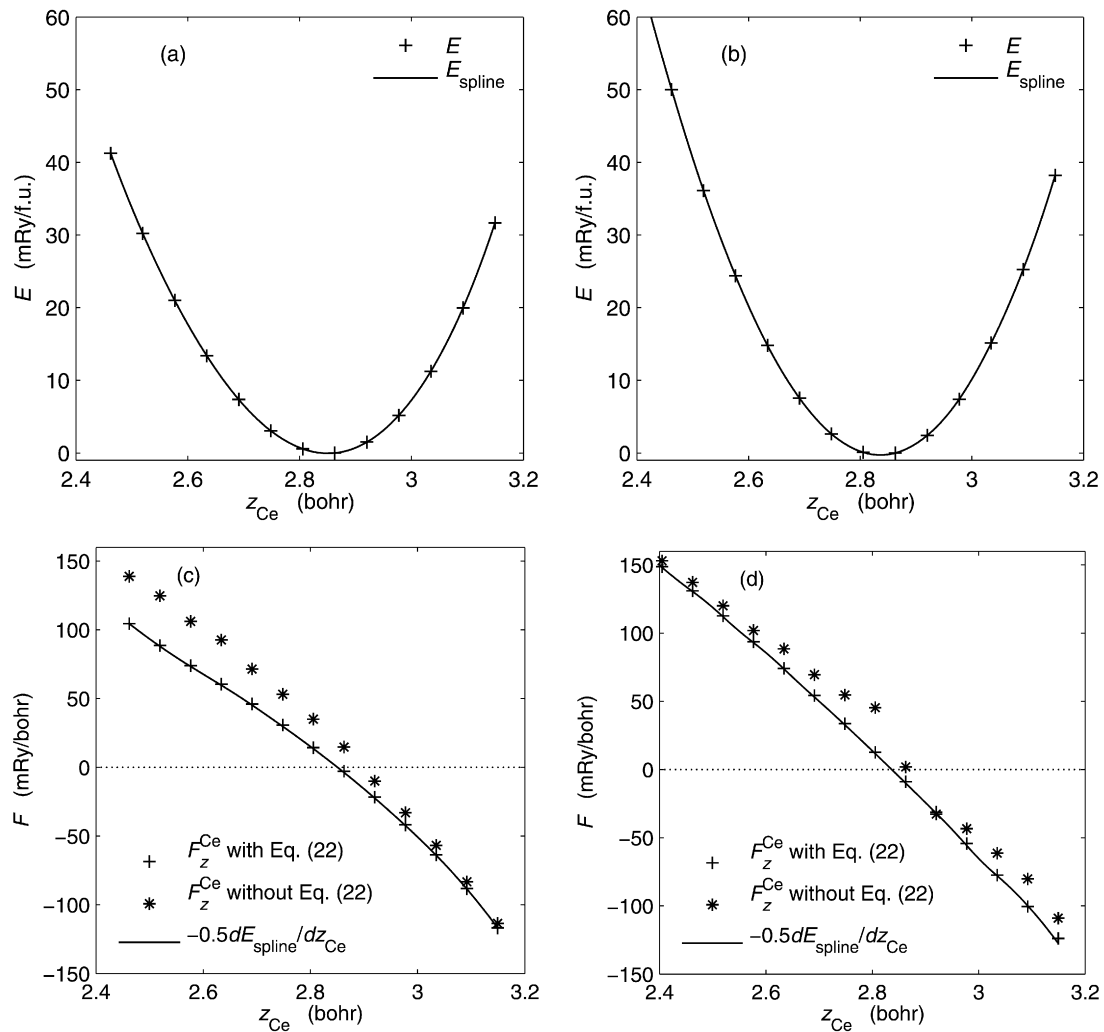
**Fig. 2.** The upper panels show the total energy $E$ ($E = 0$ is set at the minimum of the curve) of $Ce_2O_3$ as a function of the $z$ coordinate of the Ce atom in the unit cell, for (a) $LDA + U$ ($U = 4$ and $J = 0$ eV) and (b) Fock-0.15 functionals. The solid curve represents a cubic spline interpolation of the data. The lower panels show the $z$ component of the force acting on the Ce atom for (c) $LDA + U$ and (d) Fock-0.15 functionals.

## 4. Summary

The derivation of the force formalism for DFT $+ U$ and hybrid functionals (which lead to orbital-dependent potentials) within the FP-(L)APW $+$ lo basis sets has been presented. Test calculations on CoO and $Ce_2O_3$ using the WIEN2k code have demonstrated the reliability of this formalism and its implementation. We would like to mention that the forces have also been tested for complicated problems with more than 100 atoms per unit cell, and were found to work well. Nevertheless, we also observed (with any type of functional) that using very large MT spheres ($\sim$2.2 bohr) could eventually lead to a slight inconsistency between total energy and forces, which could arise from an incomplete convergence in the representation of, e.g., the electron density inside the spheres that becomes more crucial for large spheres. Therefore, we do not recommend using such large spheres for force calculations.

## Acknowledgements

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