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Calculating dynamical mean-field theory forces in *ab initio* ultrasoft pseudopotential formalism

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In this paper, we show how to calculate analytical atomic forces within the self-consistent density functional theory + dynamical mean-field theory (DFT + DMFT) approach in the case when ultrasoft or norm-conserving pseudopotentials are used. We show how to treat the nonlocal projection terms arising within the pseudopotential formalism and circumvent the problem of nonorthogonality of the Kohn-Sham eigenvectors. Our approach is, in principle, independent of the DMFT solver employed and was tested with the Hubbard I solver. We benchmark our formalism by comparing it against the forces calculated for Ce_2O_3 and PrO_2 by numerical differentiation of the total free energy as well as by comparing the energy profiles against the numerically integrated analytical forces.

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I. INTRODUCTION

The ability to calculate atomic forces in quantum systems allows for efficient exploration of the energy landscape. This, in turns, is the origin of several crucial approaches in condensed-matter physics: structural optimization, new material design, molecular dynamics, and so on. Within density functional theory (DFT), the calculation of forces is based on the variational properties of the DFT total energy functional, on the one hand, and on the Hellmann-Feynman theorem, on the other. As a result, the forces within the all-electron DFT can be calculated based on the explicit dependence of the ion-ion and ion-electron interaction terms on the atomic positions.

On the other hand, practical DFT calculations rely on approximate exchange-correlation functionals, which handicaps the ability of DFT to reproduce strongly correlated physics in many materials, notably those containing open d or f shell elements. Many strongly correlated materials exhibit properties useful for technological applications [1–3]. For example, copper oxides and iron pnictides are high-temperature superconductors [4–6], and cobaltates exhibit colossal thermoelectric power [7], which is useful for energy conversion. Several vanadates have peculiar room-temperature metal-insulator transitions, allowing the realization of a so-called intelligent window, which becomes insulating as the external temperature drops [8–11].

The failure of DFT's exchange-correlation functionals to capture strong correlation physics severely limits its use for nanoscale design of such important functional materials. In contrast to DFT, great progress has been made in describing strongly correlated materials with the dDynamical mean-field theory (DMFT) [12–20]. DMFT is a sophisticated method which offers a higher level of theoretical description than DFT and bridges the gap between DFT and Green's function approaches. Within DMFT, the treatment of local electronic correlation effects is formally exact, although the nonlocal electronic correlation effects are neglected. DMFT can be combined with DFT, giving rise to the DFT + DMFT method [14,16,17,21–24], in which the DMFT is applied to selected "correlated" d and/or f orbitals, while the rest of the system is treated at the DFT level. Moreover, within DFT + DMFT, a variational principle for the total free energy can be derived [16,25], and it can be shown that at self-consistency, the DFT + DMFT solution corresponds to a stationary point.

There have been several approaches to the calculation of forces within DFT + DMFT. In the work of Savrasov and Kotliar [26] the second derivatives of the DFT + DMFT functional were calculated at a finite $\mathbf{q}$ vector while neglecting some terms; the work of Leonov *et al.* [27] proposed the force calculation, which was not based on a stationary functional and required calculation of the two-particle vertex at all frequencies and implied building an effective Hubbard model to be solved by the DMFT method.

Recently, a method for analytical calculation of the atomic forces within the DFT + DMFT all-electron linearized augmented plane-wave (LAPW) formalism was proposed [28]. Compared to earlier approaches [26,27], it allowed the derivation of a general expression for the atomic forces which is independent of the DMFT solver used. It was shown [28] that the use of the total free energy functional at charge self-consistency greatly simplifies the final expression since several terms cancel out. The use of all-electron formalism allows us to consider only the standard terms in the Hamiltonian (ion-ion, ion-electron, electron-electron), which are local. On the other hand, the formalism employing the pseudopotentials, which would allow us to significantly extend the system size and would be capable of calculating the forces within the DFT + DMFT method, is still missing. In addition, the use of the nonorthogonal LAPW basis introduces additional terms into the formalism, and it would be desirable to extend the formalism to a simpler case of the plane-wave basis set.

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Motivated by the above considerations, in this paper, we show that the formalism developed in Ref. [28] can be efficiently extended to a case of both norm-conserving and ultrasoft pseudopotential DFT, derive all the necessary formulas and benchmark our formalism on real systems. The main difficulties outlined above will be addressed in detail in the subsequent sections.

This paper is organized as follows: in Secs. II and III we show how the theory of ultrasoft pseudopotentials can be combined with the DFT + DMFT formalism and how the atomic forces can be derived starting from the resulting free-energy functional; in Sec. IV we present the benchmark of our formalism for examples of Ce_2O_3 and PrO_2, and we give the conclusions in Sec. V.

II. GENERATING FUNCTIONAL

The DFT + DMFT total free energy functional was derived in Refs. [14,16,17,29] and is reported here for completeness. The starting point is the Baym-Kadanoff (or Luttinger-Ward) functional (for a review see Ref. [16]), which is a functional of the electronic density $\rho(\mathbf{r})$ and the lattice Green's function $G_{\nu,\nu'}(\mathbf{k}, i\omega_n) \equiv G$:

$$\begin{aligned}\Gamma[\rho, G] = {} & \mathrm{Tr}\ln G + U(\mathbf{R}) \\ & - \int d\mathbf{r}[V_{\mathrm{xc}}(\mathbf{r}) + V_H(\mathbf{r})]\rho(\mathbf{r}) - \mathrm{Tr}\big(G_0^{-1} - G^{-1}\big)G \\ & + E_H[\rho] + E_{\mathrm{xc}}[\rho] + \sum_I (\Phi^{\mathrm{DMFT}}[G] - \Phi^{\mathrm{DC}}[G]).\end{aligned} \tag{2.1}$$

Here, $E_H[\rho]$ is the Hartree density functional, $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation functional, $U(\mathbf{R})$ is the ion-ion Coulomb interaction energy, and G_0 is the DFT Green's function,

$$G_0^{-1} = i\omega_n + \boldsymbol{\mu} - \hat{T} - v_{\mathrm{KS}},$$

where $\boldsymbol{\mu}$ is the system's chemical potential, $\hat{T}$ is the kinetic energy operator, and v_{KS} is the Kohn-Sham (KS) potential,

$$v_{\mathrm{KS}} = V^{\mathrm{ion}} + V_{\mathrm{xc}} + V_H,$$

where V^{ion} is the periodic potential of the ions. $\Phi^{\mathrm{DMFT}}[G]$ is the DMFT interaction functional, and $\Phi^{\mathrm{DC}}[G]$ is the double-counting functional. For a detailed discussion of these functionals see Refs. [28,30]. Expression (2.1) for the Γ functional corresponds to the following expression for the free energy:

$$\begin{aligned}F = {} & \mathrm{Tr}\ln G + E_H - \mathrm{Tr}(V_H\rho) + E_{\mathrm{xc}} - \mathrm{Tr}(V_{\mathrm{xc}}\rho) \\ & + \sum_I (\Phi^{\mathrm{DMFT}}[G] - \Phi^{\mathrm{DC}}[G]) \\ & - \mathrm{Tr}G^{\mathrm{loc}}(\Sigma - V^{\mathrm{DC}}) + U(\mathbf{R}) + \boldsymbol{\mu}\mathcal{N}.\end{aligned} \tag{2.2}$$

Here, $\mathcal{N}$ is the number of electrons in the unit cell, and the reason why the term $\boldsymbol{\mu}\mathcal{N}$ was added to the free energy expression in the context of the force calculation will be explained in the subsequent sections. V_{xc} and V_H are the exchange and Hartree potentials, respectively, while Σ is the self-energy and V^{DC} is the double-counting potential:

$$V_{\mathrm{xc}} = \frac{\delta E_{\mathrm{xc}}}{\delta\rho}, \tag{2.3}$$

$$V_H = \frac{\delta E_H}{\delta\rho}, \tag{2.4}$$

$$\Sigma = \frac{\delta\Phi^{\mathrm{DMFT}}[G]}{\delta G}, \tag{2.5}$$

$$V^{\mathrm{DC}} = \frac{\delta\Phi^{\mathrm{DC}}[G]}{\delta G}. \tag{2.6}$$

Finally, G^{loc} is the local Green's function, which will be defined below.

The trace operator appearing in Eqs. (2.1) and (2.2) for a general matrix function (or operator) A is defined as

$$\mathrm{Tr}A = T\sum_{n,l} A_{ll}(i\omega_n)e^{i\omega_n 0^+}; \tag{2.7}$$

that is, it is traced over both orbital and imaginary-time indices at temperature T.

The lattice Green's function G and the electronic density ρ are obtained, respectively, as

$$\begin{aligned}G(\mathbf{k}, i\omega_n) &= [i\omega_n + \boldsymbol{\mu} - \hat{T} - v_{\mathrm{KS}} - \Sigma^B(\mathbf{k}, i\omega_n)]^{-1}, \\ \rho(\mathbf{r}) &= \mathrm{Tr}\langle\mathbf{r}|\hat{G}|\mathbf{r}\rangle.\end{aligned} \tag{2.8}$$

Here, Σ^B is the lattice self-energy obtained from Σ and V^{DC} using the so-called upfolding transformation:

$$\Sigma^B_{\nu,\nu'}(\mathbf{k}, i\omega_n) = \sum_{L,L'} P^{\star}_{\nu,L}(\mathbf{k})(\Sigma - V^{\mathrm{DC}})_{L,L'}P_{L',\nu'}(\mathbf{k}). \tag{2.9}$$

Within DFT + DMFT, Σ^B acquires $\mathbf{k}$ dependence, unlike the pure DMFT case, in which the self-energy is local. Here, we have implicitly introduced the projectors onto the localized states $\{\beta^I_m\}$:

$$P_{L,\nu}(\mathbf{k}) = \langle\beta^I_m|S|\phi_{\mathbf{k},\nu}\rangle = \langle\beta_L|S|\phi_{\mathbf{k},\nu}\rangle, \tag{2.10}$$

where the index L comprises the atom position I and the orbital index m: $L \equiv \{m, I\}$. The projectors are defined as the overlaps between localized states β_L and the KS orbitals $\phi_{\mathbf{k},\nu}$ with a metric S, which takes care of the nonorthogonality of the β states, as was pointed out in Ref. [21]. It will become evident in the following section that this matrix is the same S matrix introduced in the formalism of the ultrasoft pseudopotentials with the same scope. The opposite operation—downfolding—is required in order to obtain the local Green's function G^{loc} appearing in Eq. (2.2):

$$G^{\mathrm{loc}}_{L,L'}(\omega) = \sum_{\mathbf{k},\nu,\nu'} P_{L,\nu}(\mathbf{k})G_{\nu,\nu'}(\mathbf{k}, \omega)P^{\star}_{\nu',L'}(\mathbf{k}). \tag{2.11}$$

We would like to stress that the above formulas were derived for the all-electron case, as opposed to the pseudopotential case considered in the present work. As will be shown in the next section, in the latter case an additional nonlocal density dependent potential appears in the Hamiltonian, so that the above formalism cannot be applied in its present form. The scope of the present paper is to adapt the force formalism derived in Ref. [28] to the pseudopotential case.

III. VANDERBILT'S FORMALISM

Here, we extend the all-electron DFT + DMFT formalism to the case when the pseudopotentials are used. Ultrasoft pseudopotentials (USPPs) were first proposed in Refs. [31,32]. The advantage of USPPs over the norm-conserving pseudopotentials consists of lowering the cutoff energy for the plane waves thanks to relaxing the condition of norm conservation and allowing for nonorthogonality of the local projectors. The norm-conserving pseudopotentials can be viewed as a limiting case of USPPs if the norm conservation is imposed. With regard to the force calculation, several difficulties arise in the case when the pseudopotentials are employed within DFT + DMFT: (i) the DFT Hamiltonian contains a nonlocal projection term which implicitly depends on the density, (ii) the KS eigenvectors become nonorthogonal, (iii) the electronic density contains the augmentation part in addition to the usual plane-wave one, and (iv) the USPP method is formulated by using the total internal energy, while, for the force calculation, the total free energy is preferable. We show below how these points can be addressed and notice regarding point (ii) that Ref. [21] showed how the nonorthogonality of the local basis within DFT + DMFT can be efficiently taken into account using the projection overlap matrix S as a metric. We start by rewriting the USPP total energy; proceed by showing that the DFT forces, derived from this expression, are identical to the usual USPP formula; and, finally, extend the formalism to the case of DFT + DMFT.

1. Reformulating USPP free energy and forces

By using the KS eigenvalues

$$\sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\varepsilon_{\mathbf{k},\nu} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}| - \nabla^2 + V^{(0)}_{\mathrm{NL}}|\phi_{\mathbf{k},\nu}\rangle + \int d\mathbf{r}V_{\mathrm{eff}}(\mathbf{r})\rho(\mathbf{r}), \tag{3.1}$$

the USPP total energy can be rewritten (at self-consistency) as follows (in the notations of Ref. [32]):

$$E_{\mathrm{tot}} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\varepsilon_{\mathbf{k},\nu} + E_H[\rho] - \mathrm{Tr}(V_H\rho) + E_{\mathrm{xc}}[\rho] - \mathrm{Tr}(V_{\mathrm{xc}}\rho) + U(\mathbf{R}). \tag{3.2}$$

Here, $o_{\mathbf{k},\nu}$ is the νth KS level occupancy at momentum $\mathbf{k}$, $V^{(0)}_{\mathrm{NL}}$ is the "unscreened" nonlocal potential, and $V_{\mathrm{eff}}(\mathbf{r})$ is the effective potential,

$$V_{\mathrm{eff}}(\mathbf{r}) = V^{\mathrm{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}). \tag{3.3}$$

Finally, $U(\mathbf{R})$ is the interatomic Coulomb interaction energy, and ρ represents the full electronic charge density (plane wave plus augmentation).

Variating E_{tot} with respect to an atomic position $\mathbf{R}_\mu$, we obtain

$$\mathbf{F}_\mu = -\frac{\partial E_{\mathrm{tot}}}{\partial \mathbf{R}_\mu} = -\sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\frac{\delta\varepsilon_{\mathbf{k},\nu}}{\delta\mathbf{R}_\mu} + \mathrm{Tr}\left(\frac{\delta(V_H + V_{\mathrm{xc}})}{\delta\mathbf{R}_\mu}\rho\right) - \frac{\partial U}{\partial\mathbf{R}_\mu}. \tag{3.4}$$

$\frac{\delta\varepsilon_{\mathbf{k},\nu}}{\delta\mathbf{R}_\mu}$ can easily be obtained from the Schrodinger equation by using the Hellmann-Feynman theorem:

$$H|\phi_{\mathbf{k},\nu}\rangle = \varepsilon_{\mathbf{k},\nu}S|\phi_{\mathbf{k},\nu}\rangle$$

$$\frac{\delta\varepsilon_{\mathbf{k},\nu}}{\delta\mathbf{R}_\mu} = \langle\phi_{\mathbf{k},\nu}|\frac{\delta H}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle - \varepsilon_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\frac{\delta S}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle.$$

Here, H is the effective (nonphysical) Hamiltonian defined with the "screened" nonlocal part as

$$H = -\nabla^2 + V_{\mathrm{NL}} + V_{\mathrm{eff}}(\mathbf{r}), \tag{3.5}$$

$$S = 1 + \sum_{n,m,I} q_{nm}|\beta^I_n\rangle\langle\beta^I_m|, \tag{3.6}$$

with V_{NL} being the self-consistent nonlocal projection operator,

$$V_{\mathrm{NL}} = \sum_{n,m,I} D^I_{nm}|\beta^I_n\rangle\langle\beta^I_m|, \tag{3.7}$$

as opposed to the "bare" nonlocal projectors,

$$V^{(0)}_{\mathrm{NL}} = \sum_{n,m,I} D^{(0)}_{nm}|\beta^I_n\rangle\langle\beta^I_m|. \tag{3.8}$$

D^I_{nm} and $D^{(0)}_{nm}$ are connected through the charge augmentation:

$$D^I_{nm} = D^{(0)}_{nm} + \int d\mathbf{r}V_{\mathrm{eff}}(\mathbf{r})Q^I_{nm}(\mathbf{r}). \tag{3.9}$$

Here, the quantities $D^{(0)}_{nm}$ and $Q^I_{nm}(\mathbf{r})$ are the properties of the pseudopotential, as explained in Ref. [32], and $D^{(0)}_{nm}$ does not change when the atomic positions are varied. The local functions β^I_n are also part of the pseudopotential definition, although they are centered at the ions and do move rigidly with the atoms. The matrix S is the cause of the nonorthogonality of the KS eigenvectors.

In Eq. (3.4), we neglected the variation of $o_{\mathbf{k},\nu}$ because within the DFT USPP formalism the force calculations are carried out at zero temperature, and the occupancies are assumed to be step-function-like. Below, within DFT + DMFT formalism, the variation of DMFT occupancies will be shown to cancel out if the forces are derived from the total free energy.

Recording that

$$\frac{\delta H}{\delta\mathbf{R}_\mu} = \frac{\delta V_{\mathrm{eff}}(\mathbf{r})}{\delta\mathbf{R}_\mu} + \frac{\delta V_{\mathrm{NL}}}{\delta\mathbf{R}_\mu}$$

and after some simplifications, we get

$$\sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\frac{\delta H}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle = \mathrm{Tr}\left(\frac{\delta V_{\mathrm{eff}}}{\delta\mathbf{R}_\mu}\rho\right) + \sum_{n,m,I}\int d\mathbf{r}V_{\mathrm{eff}}(\mathbf{r})\frac{\partial Q^I_{nm}(\mathbf{r})}{\partial\mathbf{R}_\mu}\rho^I_{nm} + \sum_{n,m,I} D^I_{nm}\frac{\partial\rho^I_{nm}}{\partial\mathbf{R}_\mu}. \tag{3.10}$$

Here, we have used the following properties: (i) the definition of D^I_{nm} [Eq. (3.9)], (ii) the fact that $\delta D^{(0)}_{nm}/\delta\mathbf{R}_\mu = 0$, and (iii) the definitions of the full density $\rho(\mathbf{r})$, the quantity ρ^I_{nm}, and its derivative $\frac{\partial \rho^I_{nm}}{\partial \mathbf{R}_\mu}$ from the Ref. [32]:

$$\rho^I_{nm} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \langle \phi_{\mathbf{k},\nu} | \beta^I_n \rangle \langle \beta^I_m | \phi_{\mathbf{k},\nu} \rangle, \tag{3.11}$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} |\phi_{\mathbf{k},\nu}(\mathbf{r})|^2 + \sum_{n,m,I} Q^I_{nm}(\mathbf{r}) \rho^I_{nm}, \tag{3.12}$$

$$\frac{\partial \rho^I_{nm}}{\partial \mathbf{R}_\mu} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \left[\left\langle \phi_{\mathbf{k},\nu} \middle| \frac{\partial \beta^I_n}{\partial \mathbf{R}_\mu} \right\rangle \langle \beta^I_m | \phi_{\mathbf{k},\nu} \rangle \right.$$
$$\left. + \langle \phi_{\mathbf{k},\nu} | \beta^I_n \rangle \left\langle \frac{\partial \beta^I_m}{\partial \mathbf{R}_\mu} \middle| \phi_{\mathbf{k},\nu} \right\rangle \right]. \tag{3.13}$$

With these definitions, it is easy to derive Eq. (3.10).

On the other hand, the metrics part (containing the derivative of S) becomes

$$\sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \varepsilon_{\mathbf{k},\nu} \langle \phi_{\mathbf{k},\nu} | \frac{\delta S}{\delta \mathbf{R}_\mu} | \phi_{\mathbf{k},\nu} \rangle = \sum_{n,m,I} q_{nm} \frac{\partial \omega^I_{nm}}{\partial \mathbf{R}_\mu}.$$

Here, once again, we have used the definitions of ω^I_{nm} and $\frac{\partial \omega^I_{nm}}{\partial \mathbf{R}_\mu}$ from Ref. [32] with $\Lambda_{\mathbf{k},\nu;\mathbf{k}',\nu'} = \varepsilon_{\mathbf{k},\nu} \delta_{\mathbf{k},\nu;\mathbf{k}',\nu'}$, which corresponds to the equilibrium condition, as explained therein:

$$\omega^I_{nm} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \varepsilon_{\mathbf{k},\nu} \langle \phi_{\mathbf{k},\nu} | \beta^I_n \rangle \langle \beta^I_m | \phi_{\mathbf{k},\nu} \rangle, \tag{3.14}$$

$$\frac{\partial \omega^I_{nm}}{\partial \mathbf{R}_\mu} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \varepsilon_{\mathbf{k},\nu} \left[\left\langle \phi_{\mathbf{k},\nu} \middle| \frac{\partial \beta^I_n}{\partial \mathbf{R}_\mu} \right\rangle \langle \beta^I_m | \phi_{\mathbf{k},\nu} \rangle \right.$$
$$\left. + \langle \phi_{\mathbf{k},\nu} | \beta^I_n \rangle \left\langle \frac{\partial \beta^I_m}{\partial \mathbf{R}_\mu} \middle| \phi_{\mathbf{k},\nu} \right\rangle \right]. \tag{3.15}$$

Putting all the terms together, we, indeed, obtain the standard USPP force formula (see Ref. [32]):

$$\mathbf{F}_\mu = -\frac{\partial U}{\partial \mathbf{R}_\mu} - \mathrm{Tr}\left(\frac{\delta V^{\mathrm{ion}}}{\delta \mathbf{R}_\mu} \rho \right) - \sum_{n,m,I} \int d\mathbf{r} V_{\mathrm{eff}}(\mathbf{r}) \frac{\partial Q^I_{nm}(\mathbf{r})}{\partial \mathbf{R}_\mu} \rho^I_{nm} - \sum_{n,m,I} D^I_{nm} \frac{\partial \rho^I_{nm}}{\partial \mathbf{R}_\mu} + \sum_{n,m,I} q_{nm} \frac{\partial \omega^I_{nm}}{\partial \mathbf{R}_\mu}. \tag{3.16}$$

This expression is identical to Eq. (43) of Ref. [32].

2. *Formulating USPP* DFT + DMFT *free energy*

Now, we turn to Eq. (3.2). We can easily generalize it to the DFT + DMFT case and directly write the generating functional Γ and the free energy F:

$$\Gamma[G] = \mathrm{Tr} \ln \hat{G} - \mathrm{Tr}\big(\{ \hat{G}_0^{-1} - \hat{G}^{-1} \} \hat{G} \big) + E_H + E_{\mathrm{xc}}$$
$$+ \sum_I \Phi^{\mathrm{DMFT}}[G] - \sum_I \Phi^{\mathrm{DC}}[G] + U(\mathbf{R}), \tag{3.17}$$

$$F = \mathrm{Tr} \ln \hat{G} + E_H - \mathrm{Tr}(V_H \rho) + E_{\mathrm{xc}} - \mathrm{Tr}(V_{\mathrm{xc}} \rho)$$
$$+ \sum_I \Phi^{\mathrm{DMFT}}[G] - \sum_I \Phi^{\mathrm{DC}}[G] - \mathrm{Tr}[(\Sigma - V^{\mathrm{DC}}) G]$$
$$+ U(\mathbf{R}) + \boldsymbol{\mu} \mathcal{N}. \tag{3.18}$$

In passing from $\Gamma[G]$ to F the following expression for $\hat{G}$ was obtained:

$$\hat{G}(\mathbf{k}, i\omega_n) = [i\omega_n + \boldsymbol{\mu} - \varepsilon_{\mathbf{k},\nu} - \Sigma^B(\mathbf{k}, i\omega_n)]^{-1},$$

where, by definition, $\varepsilon_{\mathbf{k},\nu} = E_{\mathrm{kin}} + V^{\mathrm{ion}} + V_{\mathrm{NL}} + V_H + V_{\mathrm{xc}}$ in the KS basis and we cast G_0 (the Green's function in the absence of Σ and V_{DC}, the DFT Green's function) as

$$\hat{G}_0^{-1} = i\omega_n + \boldsymbol{\mu} - T - V^{\mathrm{ion}} - V_{\mathrm{NL}} - V_H - V_{\mathrm{xc}}$$
$$= i\omega_n + \boldsymbol{\mu} - \varepsilon_{\mathbf{k},\nu}.$$

Here, E_{kin} is the electron's kinetic energy, $\boldsymbol{\mu}$ is the system's chemical potential, and $\mathcal{N}$ is the number of electrons in the unit cell. The reason why the $+\boldsymbol{\mu}\mathcal{N}$ term is added is because the free energy is defined as $F = E - T\mathbf{S} - \boldsymbol{\mu}\mathcal{N}$, with $\mathbf{S}$ being the system's entropy, and we do not want the $-\boldsymbol{\mu}\mathcal{N}$ term to contribute to the forces. Comparing Eqs. (2.1) and (2.2) and Eqs. (3.17) and (3.18), we can see that the nonlocal projection term can be absorbed into the definitions of G and G_0, so that the final expressions for Γ and F are identical to those for the all-electron DFT + DMFT. In addition, we note that a Dyson equation holds in Bloch space:

$$\hat{G}^{-1}(\mathbf{k}, i\omega_n) = \hat{G}_0^{-1}(\mathbf{k}, i\omega_n) - \Sigma^B(\mathbf{k}, i\omega_n). \tag{3.19}$$

Now, we can check the limiting case of DFT forces by deriving them directly from F:

$$F^{\mathrm{DFT}} = \mathrm{Tr} \ln \hat{G} + E_H - \mathrm{Tr}(V_H \rho)$$
$$+ E_{\mathrm{xc}} - \mathrm{Tr}(V_{\mathrm{xc}} \rho) + U(\mathbf{R}) + \boldsymbol{\mu} \mathcal{N}.$$

In the DFT case, obviously, the KS Hamiltonian, expressed in the KS basis is a diagonal matrix with the corresponding eigenvalues $\varepsilon_{\mathbf{k},\nu}$ on the diagonal. Variating with respect to an ionic coordinate $\mathbf{R}_\mu$, we obtain

$$\mathbf{F}_\mu = -\mathrm{Tr}\left(G \frac{\delta \varepsilon_{\mathbf{k},\nu} - \delta \mu}{\delta \mathbf{R}_\mu} \right) + \mathrm{Tr}\left(\frac{\delta (V_H + V_{\mathrm{xc}})}{\delta \mathbf{R}_\mu} \rho \right)$$
$$- \frac{\partial U}{\partial \mathbf{R}_\mu} - \mathcal{N} \frac{\delta \boldsymbol{\mu}}{\delta \mathbf{R}_\mu}.$$

Once again, in the DFT case, $\varepsilon_{\mathbf{k},\nu}$ does not depend on ω, and hence, the sum on the ω part of the trace can be done, giving

$$\mathrm{Tr}\left(G \frac{\delta}{\delta \mathbf{R}_\mu} (\varepsilon_{\mathbf{k},\nu} - \boldsymbol{\mu}) \right) = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \frac{\delta}{\delta \mathbf{R}_\mu} (\varepsilon_{\mathbf{k},\nu} - \boldsymbol{\mu})$$
$$= \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \frac{\delta \varepsilon_{\mathbf{k},\nu}}{\delta \mathbf{R}_\mu} - \mathcal{N} \frac{\delta \boldsymbol{\mu}}{\delta \mathbf{R}_\mu}.$$

Putting everything together, we obtain

$$\mathbf{F}^{\mathrm{DFT}}_\mu = -\sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \frac{\delta \varepsilon_{\mathbf{k},\nu}}{\delta \mathbf{R}_\mu} + \mathrm{Tr}\left(\frac{\delta (V_H + V_{\mathrm{xc}})}{\delta \mathbf{R}_\mu} \rho \right) - \frac{\partial U}{\partial \mathbf{R}_\mu},$$

which is identical to Eq. (3.4). Here, the occupancies are defined according to definition (2.7) (except for the omitted summation on ν) as $o_{\mathbf{k},\nu} = \mathrm{Tr}G_{\nu,\nu}(\mathbf{k}, i\omega_n)$.

Let us see how the number of particles is calculated in Vanderbilt's pseudopotential formalism:

$$\begin{aligned}\mathcal{N} &= \int \rho(\mathbf{r})d\mathbf{r} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu} \int d\mathbf{r}\Big\{|\phi_{\mathbf{k},\nu}(\mathbf{r})|^2 + \sum_{n,m} Q_{n,m}(\mathbf{r})\langle\phi_{\mathbf{k},\nu}|\beta_n^I\rangle\langle\beta_m^I|\phi_{\mathbf{k},\nu}\rangle\Big\}\\ &= \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\Big\{\langle\phi_{\mathbf{k},\nu}|\phi_{\mathbf{k},\nu}\rangle + \sum_{n,m} q_{n,m}\langle\phi_{\mathbf{k},\nu}|\beta_n^I\rangle\langle\beta_m^I|\phi_{\mathbf{k},\nu}\rangle\Big\}\\ &= \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\{\langle\phi_{\mathbf{k},\nu}|\phi_{\mathbf{k},\nu}\rangle + \langle\phi_{\mathbf{k},\nu}|S-1|\phi_{\mathbf{k},\nu}\rangle\} = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|S|\phi_{\mathbf{k},\nu}\rangle = \sum_{\mathbf{k},\nu} o_{\mathbf{k},\nu}.\end{aligned}$$

Here, we used the fact that $q_{n,m} = \int Q_{n,m}(\mathbf{r})d\mathbf{r}$ and the definition of S from Ref. [32].

3. *USPP* DFT + DMFT *forces*

Variating with respect to $\mathbf{R}_\mu$ and using the above definitions, we obtain

$$\begin{aligned}\mathbf{F}_\mu^{\mathrm{DMFT}} =& -\mathrm{Tr}\sum_{\mathbf{k},\nu,\nu'} \frac{\delta\widetilde{\varepsilon}_{\nu\nu'}(\mathbf{k}, i\omega_n)}{\delta\mathbf{R}_\mu} G_{\nu'\nu}(\mathbf{k}, i\omega_n)\\ &+ \mathrm{Tr}\left(\rho\frac{\delta}{\delta\mathbf{R}_\mu}(V_H + V_{\mathrm{xc}})\right) - \frac{\partial U}{\partial\mathbf{R}_\mu}\\ &+ \mathrm{Tr}\left(G^{\mathrm{loc}}\frac{\delta}{\delta\mathbf{R}_\mu}(\Sigma - V^{\mathrm{DC}})\right),\end{aligned} \tag{3.20}$$

where $\widetilde{\varepsilon}_{\nu\nu'}(\mathbf{k}, i\omega_n) \equiv \varepsilon_{\mathbf{k},\nu}\delta_{\nu\nu'} + \Sigma^B_{\nu\nu'}(\mathbf{k}, i\omega_n)$ and the Green's function, density, and self-energy are expressed in the KS basis.

Therefore,

$$\begin{aligned}\frac{\delta\widetilde{\varepsilon}_{\nu\nu'}(k, i\omega_n)}{\delta\mathbf{R}_\mu} &= \delta_{\nu,\nu'}\frac{\delta\varepsilon_{k,\nu}}{\delta\mathbf{R}_\mu} + \frac{\delta\Sigma^B}{\delta\mathbf{R}_\mu}\\ &= \delta_{\nu,\nu'}\langle\phi_{\mathbf{k},\nu}|\frac{\delta H}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle\\ &\quad - \delta_{\nu,\nu'}\varepsilon_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\frac{\delta S}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle\\ &\quad + \frac{\delta P^\star_{\nu,L}(\mathbf{k})}{\delta\mathbf{R}_\mu}(\Sigma - V^{\mathrm{DC}})_{L,L'}P_{L',\nu'}(\mathbf{k})\\ &\quad + P^\star_{\nu,L}(\mathbf{k})(\Sigma - V^{\mathrm{DC}})_{L,L'}\frac{\delta P_{L',\nu'}(\mathbf{k})}{\delta\mathbf{R}_\mu}\\ &\quad + P^\star_{\nu,L}(\mathbf{k})\frac{\delta}{\delta\mathbf{R}_\mu}(\Sigma - V^{\mathrm{DC}})_{L,L'}P_{L',\nu'}(\mathbf{k}).\end{aligned}$$

The last term in this expression, when substituted into $\mathbf{F}_\mu^{\mathrm{DMFT}}$, cancels out the last term in Eq. (3.20), and we note that the first line, involving $\frac{\delta H}{\delta R_\mu}$ and $\frac{\delta S}{\delta R_\mu}$, is independent of frequency, so that the trace on ω can be evaluated, giving the DMFT occupancy:

$$o^{\mathrm{DMFT}}_{\mathbf{k},\nu} = \mathrm{Tr}G_{\nu,\nu}(\mathbf{k}, i\omega_n).$$

Moreover, the expression

$$\sum_{\mathbf{k},\nu} o^{\mathrm{DMFT}}_{\mathbf{k},\nu}\left\{\langle\phi_{\mathbf{k},\nu}|\frac{\delta H}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle - \varepsilon_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\frac{\delta S}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle\right\}$$

has the same functional form as in Vanderbilt's theory of USPPs and can be brought into the form of Eq. (3.16), where $o_{\mathbf{k},\nu}$ is substituted by $o^{\mathrm{DMFT}}_{\mathbf{k},\nu}$. In doing that, we have to remember that in Eq. (3.16) the terms $\mathrm{Tr}[\rho\frac{\delta}{\delta\mathbf{R}_\mu}(V_H + V_{\mathrm{xc}})] - \frac{\partial U}{\partial\mathbf{R}_\mu}$ are already taken into account and, in particular, the former is partially canceled out, leaving the $-\mathrm{Tr}(\frac{\delta V^{\mathrm{ion}}}{\delta\mathbf{R}_\mu}\rho)$ term.

The final formula for the DFT + DMFT forces can be expressed as follows, in analogy with Ref. [28]:

$$\mathbf{F}_\mu^{\mathrm{DMFT}} = \widetilde{\mathbf{F}}_\mu^{\mathrm{DFT}} + \mathbf{F}_\mu^{\mathrm{dyn}}, \tag{3.21}$$

where $\widetilde{\mathbf{F}}_\mu^{\mathrm{DFT}}$ is the force, calculated according to Eq. (3.16) with occupancy $o^{\mathrm{DMFT}}_{\mathbf{k}\nu}$ instead of $o^{\mathrm{DFT}}_{\mathbf{k}\nu}$ in the total density $\rho(\mathbf{r})$ (shown below) and in the following expressions (which is the reason for the tilde):

$$\begin{aligned}\widetilde{\rho}^I_{nm} &= \sum_{\mathbf{k},\nu} o^{\mathrm{DMFT}}_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\beta_n^I\rangle\langle\beta_m^I|\phi_{\mathbf{k},\nu}\rangle,\\ \widetilde{\omega}^I_{nm} &= \sum_{\mathbf{k},\nu} o^{\mathrm{DMFT}}_{\mathbf{k},\nu}\langle\phi_{\mathbf{k},\nu}|\beta_n^I\rangle\langle\beta_m^I|\phi_{\mathbf{k},\nu}\rangle\varepsilon_{\mathbf{k},\nu}.\end{aligned}$$

Now, the full charge self-consistency DFT + DMFT implies

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{\mathbf{k},\nu} o^{\mathrm{DMFT}}_{\mathbf{k},\nu}\Big\{|\phi_{\mathbf{k},\nu}(\mathbf{r})|^2 + \sum_{n.m} Q^I_{n,m}(\mathbf{r})\langle\phi_{\mathbf{k},\nu}|\beta_n^I\rangle\langle\beta_m^I|\phi_{\mathbf{k},\nu}\rangle\Big\}\\ &= \sum_{\mathbf{k},\nu} o^{\mathrm{DMFT}}_{\mathbf{k},\nu}|\phi_{\mathbf{k},\nu}(\mathbf{r})|^2 + \sum_{n,m} Q^I_{n,m}(\mathbf{r})\widetilde{\rho}^I_{nm}.\end{aligned}$$

On the other hand, V_{eff}, depending on the full electronic density $\rho(\mathbf{r})$ and entering into $\widetilde{\mathbf{F}}_\mu^{\mathrm{DFT}}$ explicitly and through $D^I_{n,m}$, has to be taken at the "self-consistency," as was pointed out in Ref. [28].

$\mathbf{F}_\mu^{\mathrm{dyn}}$ can be expressed as

$$\begin{aligned}\mathbf{F}_\mu^{\mathrm{dyn}} &= -\mathrm{Tr}\sum_{\substack{\mathbf{k},\nu,\nu'\\L,L'}}\left\{\frac{\delta P^\star_{\nu,L}(\mathbf{k})}{\delta\mathbf{R}_\mu}(\Sigma - V^{\mathrm{DC}})_{L,L'}P_{L',\nu'}(\mathbf{k}) + P^\star_{\nu,L}(\mathbf{k})(\Sigma - V^{\mathrm{DC}})_{L,L'}\frac{\delta P_{L',\nu'}(\mathbf{k})}{\delta\mathbf{R}_\mu}\right\}G_{\nu'\nu}(\mathbf{k}, i\omega_n)\\ &= -\mathrm{Tr}\sum_{L,L'}(\Sigma(i\omega_n) - V^{\mathrm{DC}})_{L,L'}\sum_{\mathbf{k},\nu,\nu'}\left\{P_{L',\nu'}(\mathbf{k})G_{\nu'\nu}(\mathbf{k}, i\omega_n)\frac{\delta P^\star_{\nu,L}(\mathbf{k})}{\delta\mathbf{R}_\mu} + \frac{\delta P_{L',\nu'}(\mathbf{k})}{\delta\mathbf{R}_\mu}G_{\nu'\nu}(\mathbf{k}, i\omega_n)P^\star_{\nu,L}(\mathbf{k})\right\}\\ &= -\mathrm{Tr}\sum_{L,L'}(\Sigma(i\omega_n) - V^{\mathrm{DC}})_{L,L'}\,\Xi_{L',L}(i\omega_n),\end{aligned}\tag{3.22}$$

where we have defined the function Ξ:

$$\Xi_{L',L}(i\omega_n) = \sum_{\mathbf{k},\nu,\nu'}\left\{P_{L',\nu'}(\mathbf{k})G_{\nu'\nu}(\mathbf{k}, i\omega_n)\frac{\delta P^\star_{\nu,L}(\mathbf{k})}{\delta\mathbf{R}_\mu} + \frac{\delta P_{L',\nu'}(\mathbf{k})}{\delta\mathbf{R}_\mu}G_{\nu'\nu}(\mathbf{k}, i\omega_n)P^\star_{\nu,L}(\mathbf{k})\right\}.\tag{3.23}$$

The use of the time reversal symmetry in the numerical evaluation of the Matsubara sums is exemplified in Appendix B.

4. Derivation of the projectors derivatives

In this section, we summarize the formulas necessary to calculate the derivatives of the projectors to the localized states $P_{L,\nu}(\mathbf{k})$. From definition (2.10) we have

$$\frac{\delta P_{L,\nu}(\mathbf{k})}{\delta\mathbf{R}_\mu} = \frac{\delta\langle\beta_L|S|\phi_{\mathbf{k},\nu}\rangle}{\delta\mathbf{R}_\mu}\tag{3.24}$$

$$= \left\langle\frac{\delta\beta_L}{\delta\mathbf{R}_\mu}\right|S|\phi_{\mathbf{k},\nu}\rangle + \langle\beta_L|\frac{\delta S}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle,\tag{3.25}$$

where

$$\frac{\delta}{\delta\mathbf{R}_\mu}|\phi_{\mathbf{k},\nu}\rangle = 0\tag{3.26}$$

since the KS orbitals do not depend explicitly on atomic coordinates [33–35]. The derivative of S can be readily calculated, starting from definition (3.6):

$$\frac{\delta S}{\delta\mathbf{R}_\mu} = \sum_{n,m,I}q_{nm}\left(\left|\frac{\delta\beta^I_n}{\delta\mathbf{R}_\mu}\right\rangle\langle\beta^I_m| + |\beta^I_n\rangle\left\langle\frac{\delta\beta^I_m}{\delta\mathbf{R}_\mu}\right|\right).\tag{3.27}$$

At this point, we would like to recall that the objects q_{nm} and $|\beta^I_n\rangle$ are determined at the pseudopotential generation stage and remain unchanged during DFT + DMFT density optimization. The only dependence on $\mathbf{R}_\mu$ in $|\beta^I_n\rangle$ comes from the fact that these localized orbitals move rigidly with their corresponding ions, so that the derivatives $|\frac{\delta\beta^I_n}{\delta\mathbf{R}_\mu}\rangle$ can be calculated by going into momentum representation, exactly as done in Refs. [31,32] and in Ref. [28].

IV. BENCHMARKS AND RESULTS

A. Forces in cerium sesquioxide

The results presented in this section are obtained by implementing the formulas presented above within the DFT + DMFT method implemented previously [21,22] in the widely used plane-wave DFT code CASTEP [36,37]. In order to benchmark our formalism, we apply it to cerium sesquioxide $\mathrm{Ce_2O_3}$, which has been studied for a long time [38–41]. It is known to be an antiferromagnetic insulator with a Néel temperature of $T_N = 9$ K and a gap of 2.4 eV. DFT + DMFT calculations in the literature normally address the high-temperature paramagnetic phase, so to benchmark our force calculations we also set the temperature to $T = 0.01$ eV. $\mathrm{Ce_2O_3}$ crystallizes in a hexagonal unit cell with space group $P\bar{3}m1$. The experimental parameters for the unit cell are $a = 3.89$ Å and $c/a = 1.557$, with the Wyckoff positions [42] Ce $2d$ $(\frac{1}{3}, \frac{2}{3}, \xi)$, O $2d$ $(\frac{1}{3}, \frac{2}{3}, \eta)$, and O $1a$ $(0, 0, 0)$, with $\xi = 0.24543$ and $\eta = 0.6471$. On the other hand DFT predicts $a = 3.81$ Å at the experimental ratio $c/a = 1.557$ and experimental ξ and η. We have performed calculations for both lattice constants $a = 3.81$ Å (minimum energy for the DFT + DMFT method) and $a = 3.89$ Å (the experimental value) while maintaining the ratio $c/a = 1.557$. We have used the norm-conserving Ce and O pseudopotential (NCP17 set), local density approximation (LDA) exchange-correlation potential, and a $31 \times 31 \times 17$ Monkhorst-Pack k-point mesh. We have also checked that similar results are obtained with the ultrasoft pseudopotentials too. The plane-wave basis cutoff was automatically determined to be 1012 eV. The values of Hubbard U and Hund J parameters were chosen to be $U = 6$ eV and $J = 0.7$ eV, respectively. The results for the $\mathrm{Ce_2O_3}$ density of states at the experimental geometry were given in our previous work [21] and exhibit excellent agreement with the reference calculations of Ref. [17]. As in our previous paper, the DMFT calculations were performed with the Hubbard I solver (extensions to the other types of solvers, e.g., Hubbard III [43,44] can be done) with a fixed occupancy of $n = 1$ per Ce atom (in the sense explained in Ref. [17]) within the fully localized limit (FLL) double-counting scheme.

For the benchmark to be fair, we compare the analytical forces calculated within our formalism against the numerical ones obtained from finite increment derivative of the free energy. On the other hand, we also compare the numerical free energy profiles against the curves obtained from the spline integration of the analytical forces. With regard to the evaluation of the numerical forces, we first note that most internal atomic coordinates are fixed by symmetry. We vary the remaining coordinates, which are the z coordinates of Ce $2d$ and O $2d$ atoms (the ones established from experiment). Obviously, the forces of the atoms related by symmetry are, in turn, related.

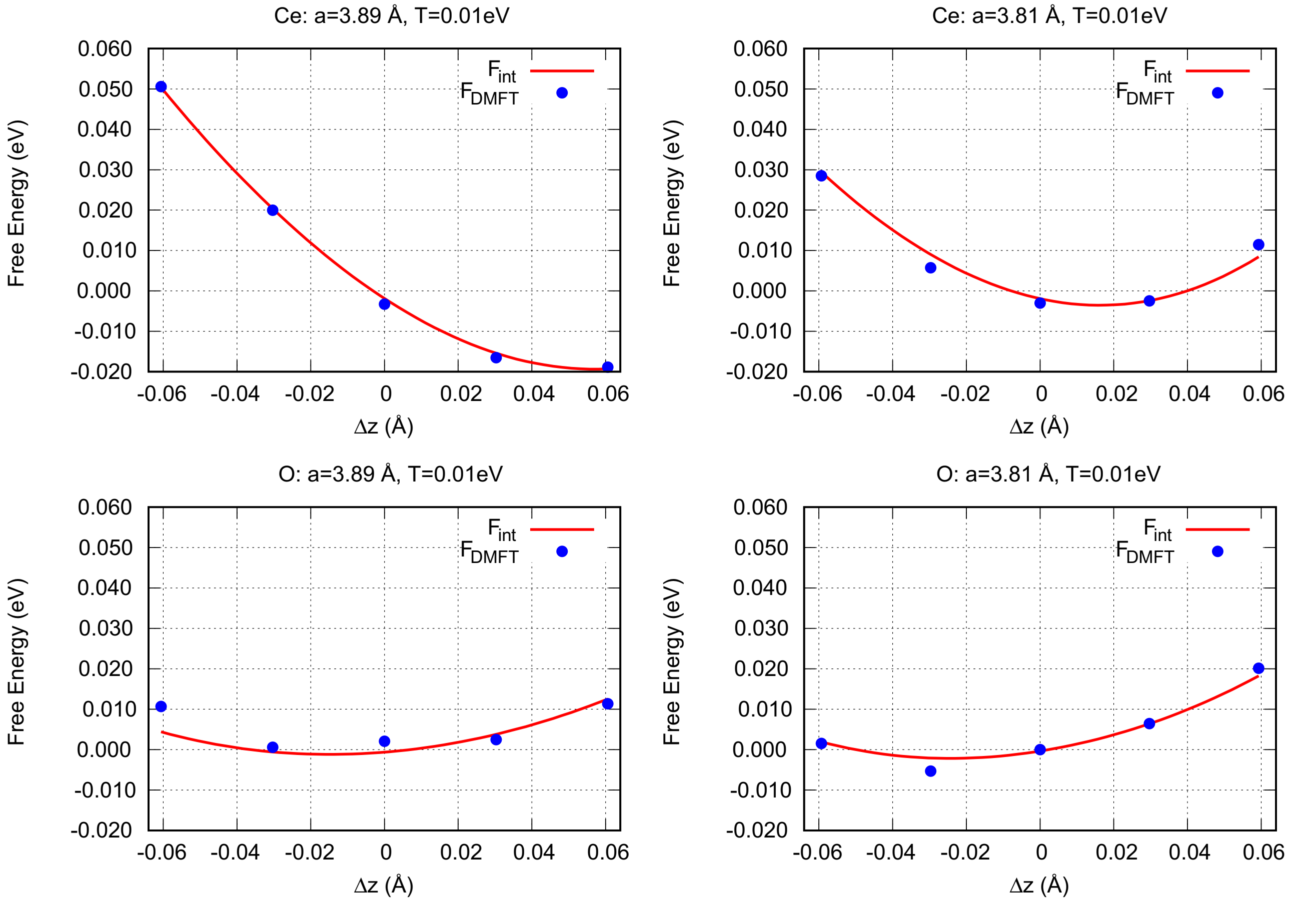

FIG. 1. Energy profiles (blue points) in Ce_2O_3 when displacing Ce (top row) and O (bottom row) along the z direction. The left column corresponds to $a = 3.89$ Å, while the right column corresponds to $a = 3.81$ Å. The red curves correspond to the free energy profiles derived from integrating the analytical DFT + DMFT forces.

During the finite increment of relevant atomic coordinates, we tested several Δz values in order to be sure that the free energy varies linearly over the length scale of Δz. The results of these tests are shown in Fig. 8 of Ref. [21], and in this work we fix $\Delta z = 1\%$ in units of the c dimension of the unit cell. The numerical forces were determined as follows:

$$\mathbf{F}_{z_i} = -\frac{\partial F_{\mathrm{tot}}}{\partial z_i}. \tag{4.1}$$

In addition, we emphasize that the total free energy as a function of Δz is a smooth differentiable function, thanks to the fact that both DFT (CASTEP) and DMFT subsystems in our calculations are well behaved, giving small responses to small perturbations. In order to be consistent with the formalism developed in the previous section, in the present work, the DFT + DMFT was self-consistently converged until the energy became stationary up to 10^{-6} eV.

A comparison between the analytical forces, calculated within the formalism presented in the previous section, and the numerical forces, derived from the total free energy according to Eq. (4.1), is shown in Figs. 1 and 2. The energy profiles are presented in Fig. 1, while the force comparison is illustrated in Fig. 2. The overall agreement appears to be very good, taking into account the inevitable numerical bias of the DFT + DMFT total free energy. The forces calculated within our formalism are correct for both Ce (correlated ion) and O ("uncorrelated ion"), on which the dynamical force is identically zero. We note that the local minimum (where the force is zero) with respect to the Ce displacement along the z axis is approximately +0.06 Å with respect to the experimental position for the $a = 3.89$ Å unit cell, while it is about +0.017 Å for the $a = 3.81$ Å unit cell. In the case of O displacement, the order of magnitude of forces is smaller, while the minimum positions are roughly −0.02 Å for both unit cells considered. Compared to the DFT forces (Table II of Ref. [21]), the Ce DFT + DMFT forces presented here are larger, while the O forces are smaller. Compared to the one-shot DFT + DMFT forces (Table II of Ref. [21]), the full charge self-consistency modifies significantly the resulting force: for Ce it is increasing, while for O it is decreasing. We conclude, therefore, that the one-shot DFT + DMFT somehow overshoots the forces with respect to the full self-consistent DFT + DMFT. It was shown in Ref. [17] that the full self-consistent DFT + DMFT gives somewhat better agreement with the experiment for the Ce_2O_3 equilibrium volume compared to the one-shot DFT + DMFT, thanks to the spectral weight redistribution. In addition, the difference between the DFT and the DMFT forces is larger on the correlated ions, although the uncorrelated ones are also modified due to the fact that the density is distributed differently in DFT + DMFT with respect to DFT. On the other hand, we have checked that the total vector sum of all the forces acting on all the atoms in the unit cell is

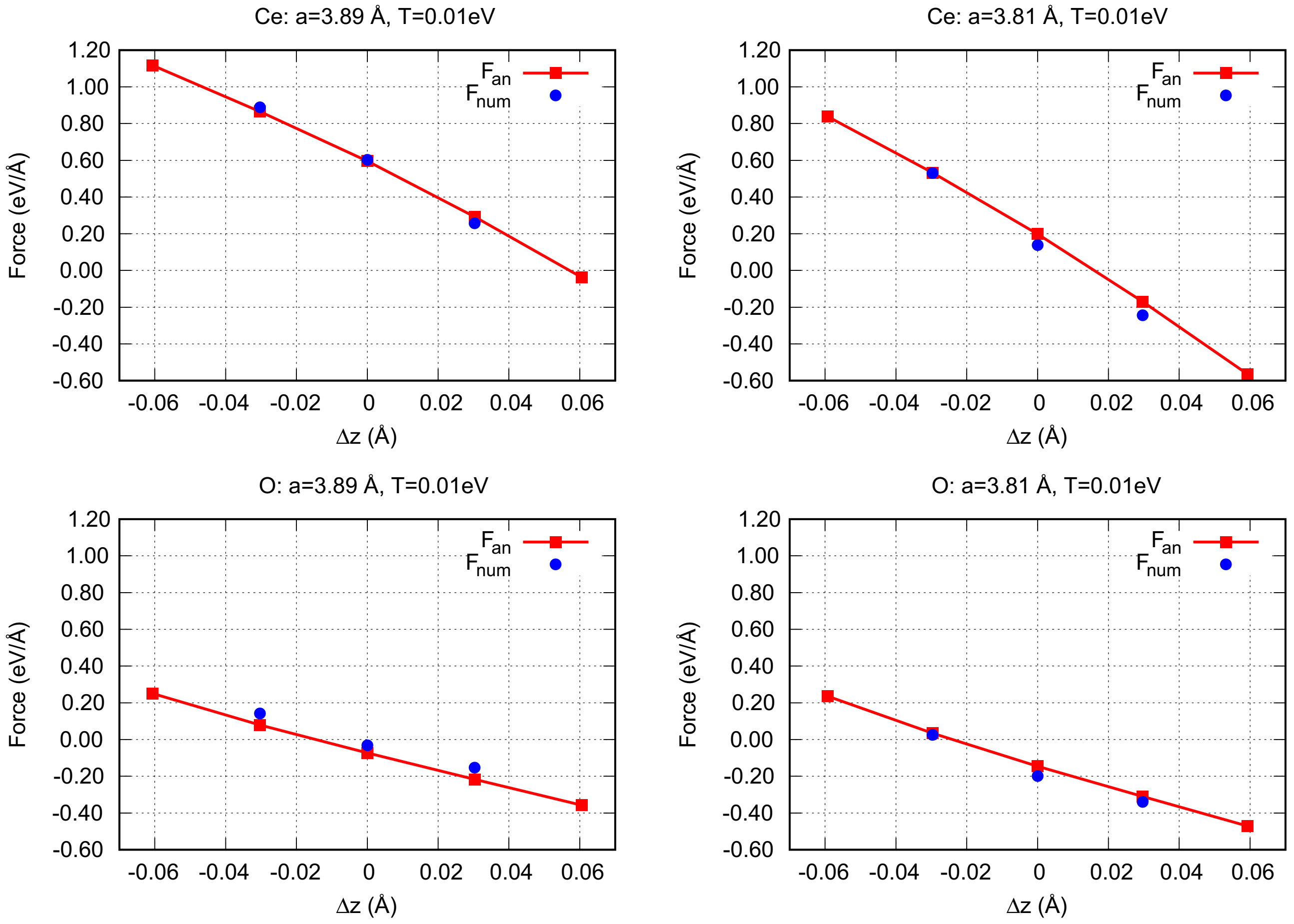

FIG. 2. Comparison of the DFT + DMFT forces. Red points: analytical forces; blue points: numerical derivative extracted from the numerical free energy profiles reported in Fig. 1. Forces acting on Ce (top row) and O (bottom row) along the z direction. The left column corresponds to $a = 3.89$ Å, while the right column corresponds to $a = 3.81$ Å.

zero within both DFT and DFT + DMFT, as it should be in equilibrium.

B. Forces in praseodymium dioxide

In order to enforce the validity of our approach, we have benchmarked the DMFT forces in yet another system: praseodymium dioxide (PrO_2). We consider PrO_2 in the rhombohedral unit cell (symmetry group $Fm\bar{3}m$) with $a = 4.0482$ Å and the following Wyckoff positions of the atoms: Pr at (0,0,0) and two oxygen atoms at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ [45,46]. Here, we have used ultrasoft pseudopotentials for both Pr and O (C17 set), the LDA exchange-correlation potential, and a $25 \times 25 \times 25$ Monkhorst-Pack k-point mesh. The plane-wave basis cutoff was automatically determined to be 653 eV. The values of the Hubbard U and Hund J parameters were chosen to be $U = 6$ eV and $J = 0.7$ eV, respectively. At the above Wyckoff positions, the net DFT + DMFT forces are zero due to symmetry, and the finite forces appear if the corresponding atoms are pushed away from their positions. Since both Pr and O atoms are placed on the cubic cell diagonal, in carrying out the finite displacements it is important to conserve the threefold axis along the diagonal. That is why in the present section, we perform the finite displacements of the Pr atom along the (111) direction. The free energy increment between two atomic positions $\mathbf{R}^1$ and $\mathbf{R}^2$ is then estimated by using the following

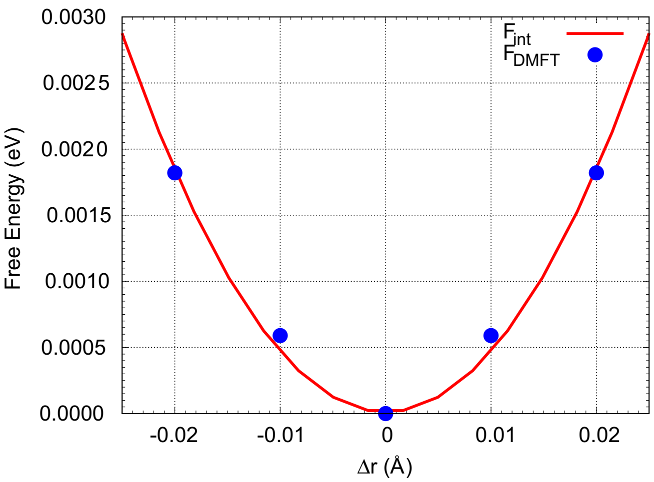

FIG. 3. Energy profiles (blue points) of PrO_2 when displacing the Pr atom along the (111) direction. F_{int} stands for the spline-integrated forces along the displacement path, while F_{DMFT} stands for the system's free energy calculated at given atomic positions using full charge self-consistency.

formula:

$$F_{\rm tot}(\mathbf{R}^2) - F_{\rm tot}(\mathbf{R}^1) = -\int_{\mathbf{R}^1}^{\mathbf{R}^2} \sum_{\mu} \mathbf{F}_{\mu}(\mathbf{R}) \mathrm{d}\mathbf{R}_{\mu}, \qquad (4.2)$$

where $\mathbf{F}_{\mu}(\mathbf{R})$ is the μ component of the force at the atomic position vector $\mathbf{R}$, while $\mathbf{R}_{\mu}$ is the μ Cartesian coordinate of the displaced Pr atom. The excellent agreement between $\delta F_{\rm tot}$ derived from the analytical forces and the free energy profiles calculated in the vicinity of the high-symmetry Wyckoff position of the Pr atom is shown in Fig. 3. The forces appear to be symmetric with respect to the displacements of the atoms along the diagonal in the positive and negative directions off the exact Wyckoff positions, and so does the free energy profile. We would like to point out that in the case of PrO_2 the order of magnitude of forces and energy increments associated with the atomic displacements are an order of magnitude smaller than those in the Ce_2O_3 case, which required additional accuracy in deriving a smooth free energy profile.

V. CONCLUSIONS

In conclusion, we have presented a formalism for analytic calculation of the atomic forces within the full charge self-consistent pseudopotential DFT + DMFT approach. Our approach extends that of Ref. [28] by taking into account the nonlocal projections terms in the KS Hamiltonian, which depend implicitly on charge distribution and arise from the pseudoization procedure. It inherits the useful properties of the DFT + embedded DMFT functional [28], in particular $\frac{\delta P}{\delta G} = 0$, and therefore, the terms most difficult to calculate cancel out in the final result. The plane-wave basis, employed within our implementation, greatly simplifies the formalism by avoiding the calculation of the augmentation charges. Our formalism is implemented within the DMFT framework inside the CASTEP *ab initio* code, which in the past already allowed for precise total free energy calculations within DFT + DMFT [21]. Our approach is general and suitable for both norm-conserving and ultrasoft pseudopotentials. The pseudopotential approach has the advantage of speeding up the calculations with respect to the all-electron methods by considering the core electrons to be frozen, while the ultrasoft pseudopotentials further speed up the calculations with respect to the norm-conserving pseudopotentials by relaxing the norm-conserving condition [31,32].

In addition, our approach does not use any specific DMFT solver property and hence would work equally well with all solvers. We have presented the benchmark of our approach using the example of Ce_2O_3, which showed excellent agreement between the forces analytically calculated within our approach and the forces obtained from numerical differentiation of the total free energy at very low temperature. In addition, we have compared the total free energy profiles against the integrated forces profiles, which also showed excellent agreement. We analyzed the differences of atomic forces within DFT, one-shot DFT + DMFT, and full charge self-consistent DFT + DMFT for the examples of Ce_2O_3 and PrO_2, with the applicability to the correlated metal close to the Mott transition being the subject of our future studies. Our approach allows for quick and reliable force calculations within the fully self-consistent pseudopotential DFT + DMFT and paves the way to the structural optimization and phonon and molecular dynamics calculations within DFT + DMFT.

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APPENDIX A: CALCULATION OF THE FREE ENERGY

We start from Eq. (3.18) for the total free energy. We also report for completeness the formula for the total internal energy, used, e.g., in our past work [21] (taking into account the ion-ion interaction energy):

$$\begin{aligned} E = \sum \varepsilon_{\mathbf{k},\nu} N_{\nu,\nu}(\mathbf{k}) + E_H - \mathrm{Tr}(V_H \rho) + E_{\rm xc} - \mathrm{Tr}(V_{\rm xc}\rho) \\ + \frac{1}{2}\mathrm{Tr}\Sigma G - \sum_I \Phi^{\rm DC}[G] + U(\mathbf{R}), \qquad (\mathrm{A1}) \end{aligned}$$

where $N_{\nu,\nu}(\mathbf{k}) = T\sum_n G(\mathbf{k}, i\omega_n)$ is the DMFT occupancy matrix and $\varepsilon_{\mathbf{k},\nu}$ are the DFT eigenvalues calculated at the DMFT density. With respect to the total internal energy calculation, the changes are the following:

(i) The term $\sum \varepsilon_{\mathbf{k},\nu} N_{\nu,\nu}(\mathbf{k})$ is substituted with the following expression:

$$\mathrm{Tr} \ln \hat{G} + \boldsymbol{\mu}\mathcal{N} - \mathrm{Tr}(\Sigma - V^{\rm DC})G. \qquad (\mathrm{A2})$$

(ii) The term $\frac{1}{2}\mathrm{Tr}\Sigma G$ is substituted with

$$\Phi^{\rm DMFT} = F_{\rm imp} - \mathrm{Tr} \ln G_{\rm imp} + \mathrm{Tr}\,\Sigma_{\rm imp} G_{\rm imp}. \qquad (\mathrm{A3})$$

The calculation of $\mathrm{Tr} \ln G$ with a general Green's function G is performed following the procedure outlined in Ref. [25], namely, the summation is split into two parts: the numerical sum up to a cutoff Matsubara frequency $i\omega_c$ with the most divergent part subtracted and an expression equal to the known analytical sum of the most divergent part. In this case, the most divergent part is

$$-T \sum_n \ln(-i\omega_n + \varepsilon) e^{i\eta\omega_n}\Big|_{\eta\to 0} = -T \ln\left(1 + e^{-\frac{\varepsilon}{T}}\right). \qquad (\mathrm{A4})$$

Therefore, the summation $\mathrm{Tr} \ln \hat{G}$ is evaluated as follows:

$$\mathrm{Tr}\ln\hat{G} = -T\sum_{\substack{|\omega_n|<\omega_c\\ \mathbf{k}}} \mathfrak{Tr}\big\{\ln\big[-i\omega_n + \varepsilon_{\mathbf{k},\nu} - \boldsymbol{\mu} + \Sigma^{B}_{\nu,\nu'}(\mathbf{k}, i\omega_n) - V^{\mathrm{DC}}_{\nu,\nu'}\big] - \ln[-i\omega_n + \varepsilon_{\nu,\nu'}(\mathbf{k},\infty)]\big\} \tag{A5}$$

$$-T\sum_{\mathbf{k}}\ln\left[1+\exp\left(-\frac{\varepsilon_{\nu,\nu'}(\mathbf{k},\infty)}{T}\right)\right], \tag{A6}$$

where $\varepsilon_{\nu,\nu'}(\mathbf{k},\infty) = \varepsilon_{\mathbf{k},\nu} - \boldsymbol{\mu} + \Sigma^{B}_{\nu,\nu'}(\mathbf{k},\infty) - V^{\mathrm{DC}}_{\nu,\nu'}$.

On the other hand, the summation $\mathrm{Tr}\ln G_{\mathrm{imp}}$ is evaluated as

$$\mathrm{Tr}\ln G_{\mathrm{imp}} = -T\sum_{|\omega_n|<\omega_c} \mathfrak{Tr}\big\{\ln\big[-i\omega_n + \varepsilon^{\mathrm{imp}}_{m,m'} + \Sigma^{\mathrm{imp}}_{m,m'}(i\omega_n)\big] - \ln\big[-i\omega_n + \varepsilon^{\mathrm{imp}}_{m,m'}(\infty)\big]\big\} \tag{A7}$$

$$-T\ln\left[1+\exp\left(-\frac{\varepsilon^{\mathrm{imp}}_{m,m'}(\infty)}{T}\right)\right], \tag{A8}$$

where this time $\varepsilon^{\mathrm{imp}}_{m,m'}(\infty) = \varepsilon^{\mathrm{imp}}_{m,m'} + \Sigma^{\mathrm{imp}}_{m,m'}(\infty)$. Here, the notation $\mathfrak{Tr}$ stands for the trace over the ν, ν' or m, m' indices (without the summation over Matsubara frequencies).

APPENDIX B: THE USE OF TIME REVERSAL SYMMETRY IN THE MATSUBARA SUMS

When doing sums like $-\mathrm{Tr}\Sigma(i\omega_n)G(i\omega_n)$, one usually makes use of the symmetry properties of Σ and G upon changing $i\omega_n \to -i\omega_n$:

$$G_{m,m'}(-i\omega_n) = G^{\star}_{m',m}(i\omega_n),$$
$$\Sigma_{m,m'}(-i\omega_n) = \Sigma^{\star}_{m',m}(i\omega_n),$$

so that

$$-T\sum_{n,m,m'}\Sigma_{m,m'}(-i\omega_n)G_{m',m}(-i\omega_n)$$
$$= -T\sum_{n,m,m'}G^{\star}_{m,m'}(i\omega_n)\Sigma^{\star}_{m',m}(i\omega_n)$$

and hence

$$-T\sum_{n,m,m'}G_{m,m'}(i\omega_n)\Sigma_{m',m}(i\omega_n)$$
$$= -2T\,\mathrm{Re}\sum_{m,m',\omega_n>0}G_{m,m'}(i\omega_n)\Sigma_{m',m}(i\omega_n).$$

Considering the definition of $\Xi(i\omega_n)$ given by Eq. (3.23), we see that indeed

$$\Xi_{m,m'}(-i\omega_n) = \Xi^{\star}_{m',m}(i\omega_n).$$

Therefore, we can still use the Green's function's symmetry properties and restrict the summation in Eq. (3.22) to the positive Matsubara frequencies, while the final formula for the DFT + DMFT forces is given by Eq. (3.21).

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