A self-consistent DFT + DMFT scheme in the projector augmented wave method: applications to cerium, Ce$_2$O$_3$ and Pu$_2$O$_3$ with the Hubbard I solver and comparison to DFT + $U$

B Amadon

CEA, DAM, DIF, F 91297 Arpajon, France

E-mail: bernard.amadon@cea.fr

Received 12 December 2011, in final form 10 January 2012
Published 2 February 2012
Online at stacks.iop.org/JPhysCM/24/075604

Abstract
An implementation of full self-consistency over the electronic density in the DFT + DMFT framework on the basis of a plane wave–projector augmented wave (PAW) DFT code is presented. It allows for an accurate calculation of the total energy in DFT + DMFT within a plane wave approach. In contrast to frameworks based on the maximally localized Wannier function, the method is easily applied to f electron systems, such as cerium, cerium oxide (Ce$_2$O$_3$) and plutonium oxide (Pu$_2$O$_3$). In order to have a correct and physical calculation of the energy terms, we find that the calculation of the self-consistent density is mandatory. The formalism is general and does not depend on the method used to solve the impurity model. Calculations are carried out within the Hubbard I approximation, which is fast to solve, and gives a good description of strongly correlated insulators. We compare the DFT + DMFT and DFT + $U$ solutions, and underline the qualitative differences of their converged densities. We emphasize that in contrast to DFT + $U$, DFT + DMFT does not break the spin and orbital symmetry. As a consequence, DFT + DMFT implies, on top of a better physical description of correlated metals and insulators, a reduced occurrence of unphysical metastable solutions in correlated insulators in comparison to DFT + $U$.

(Some figures may appear in colour only in the online journal)

1. Introduction
Electrons in localized orbitals exhibit strong interaction effects. Their ab initio description, in condensed matter physics, has made progress thanks to the development of the DFT + $U$ [1, 2] and DFT + DMFT methods [3, 2, 4–7]. This last method has, in particular, been very successful for describing both the itinerant and localized behaviour of strongly interacting electrons.

Whereas DFT + $U$ is implemented routinely in DFT electronic structure codes to compute all kinds of properties, frameworks to implement DFT + DMFT for an arbitrary basis (e.g. plane waves) have emerged only recently. Two different schemes both using Wannier functions were used: the construction [8] of the maximally localized Wannier function (MLWF) [9] or Nth-order muffin tin orbitals (NMTO) [10] and the calculation of projected local orbitals (PLO) [11–15]. The PLO framework is simple and does not require the calculation of the MLWF: in particular, the MLWF for f electron systems might be technically difficult to compute.

Besides, the need for a precise method to compute the total energy requires self-consistency over the electronic density to be achieved [16–19, 15, 20, 21]. Calculations of the total energy using self-consistency over the density are scarce...
In DFT + DMFT [16, 18, 19, 21, 15]. Simplified schemes designed for the Hubbard I approximation have also included the self-consistency and have been successful in describing actinide compounds [21].

In this paper, we present an implementation of DFT + DMFT with the total energy in the PLO scheme, using the self-consistency over density in a plane wave (PW) based PAW code. This implementation is carried out in the code ABINIT [22] and is an extension of a previously published non-self-consistent (NSCF) projected local orbital scheme in PAW [12]. Since then, a similar NSCF implementation from the output of the PAW code VASP [23] has been described [24]. The projector augmented wave [25] framework in combination with, e.g., a plane wave basis is a widely used tool [26–28] to carry out accurate electronic structure calculations. The framework of our implementation is general and could also be used in, e.g., the real-space-based PAW code [29, 30]. Moreover, our implementation puts the computation of energy in DFT + DMFT on the same footing as the LDA: a wide range of systems are available for the description.

The plan of the paper is the following. In section 2, the PLO framework for DMFT is briefly described, expressions for the total energy are given and the way the self-consistency is achieved is detailed. We emphasize in particular that having two expressions for the total energy is a check to avoid any errors in the implementation. Technicalities related to the PAW formalism are given in appendices A and D for self-consistency and appendix B for the PLO scheme.

In section 3, we study three correlated systems with f orbitals. Actinides and lanthanides have recently attracted a lot of theoretical interest [31, 18, 32–37]. For these systems, our PLO scheme for DFT + DMFT is particularly suitable: the use of the MLWF would be possible, but the determination of the MLWF is presently not a straightforward task for f electron systems. We first investigate cerium and cerium oxide (Ce2O3). A previous implementation of self-consistency in DFT + DMFT using an ASA basis was applied to these compounds [18]. This is thus the opportunity to put forward the improvement brought by our approach for these systems: because of the PW–PAW basis, the physical accuracy is better, and the method is more flexible. Besides, we illustrate, for the sake of clarity, the difference between the self-consistent densities obtained in DFT + U and DFT + DMFT for Ce2O3. We then present a study of Pu2O3. We compare this compound to cerium oxide and our results to previous DFT + U calculations. For these systems, we emphasize that DFT + DMFT should decrease the number of spurious metastable states from that found in DFT + U [38, 31, 39, 40, 33, 41, 42]. Especially for cerium, on the basis of our calculations on γ cerium, the calculation of complex phases of cerium, such as β cerium, should be easier in comparison to DFT + U [39]. In view of this, the simple Hubbard I approximation would be useful for large scale calculations on defects and surfaces.

In appendix B, we show that our implementation can be precisely compared with a DFT + U implementation, when the self-energy in DMFT is chosen to be the static mean field self-energy. We illustrate this for the case of cerium. The agreement between the two calculations shows the consistency of the two implementations. In appendix C, we discuss the impact of the windows of energy used to compute the Wannier orbitals on the spectral function of cerium: it underlines the need for a consistent determination of U with the choice of the energy window.

2. Theoretical framework

2.1. DFT + DMFT formalism: projected local orbitals

In DFT + U or in the combination of density functional theory and dynamical mean field theory, a peculiar treatment is reserved for correlated electrons. As a consequence, correlated orbitals need to be defined; this is the focus of this section.

We first summarize the main equations from the projected local orbital framework [11, 9, 12, 13]. In this framework, a subspace $W$ of the total Hilbert space is used as a basis for the DMFT calculation. This subspace is spanned by a given number of DFT Kohn–Sham (KS) Bloch wavefunctions. The local orbitals on which the Coulomb interaction applies are defined in the following way: the KS Bloch wavefunctions $\Psi_k$ are projected on local orbitals $|\chi_{km}\rangle$ (e.g. atomic orbitals). Let us define $p^{R}_{m}(k)$ as

$$p^{R}_{m}(k) = \langle \chi_{km} | R \Psi_{k} \rangle,$$  

(2.1)

where $m = 1, \ldots, M$ is an orbital index within the correlated subset, $R$ denotes the correlated atom within the primitive unit cell, $k$ is a $k$-point in the Brillouin zone, and $v$ is the band index. In appendix B.2, we discuss the technical calculation of the projection in PAW. This projection defines the Wannier functions. These Wannier functions are built upon the local orbitals and are an orthonormalized linear combination of a limited number of KS wavefunctions. Let us define

$$|\bar{x}_{km}^{R}\rangle = \sum_{v \in W} \langle \Psi_{kv} | \chi_{km}^{R} \rangle |\Psi_{kv}\rangle.$$  

(2.2)

The orthonormalization of $|\bar{x}_{km}^{R}\rangle$ gives the Wannier functions $|\psi_{km}^{R}\rangle$. We call $p^{R}_{m}(k)$ the accordingly orthonormalized projections.

The flexibility in the choice of $W$, and thus in the choice of Wannier functions enables us an easy comparison to calculations using maximally localized Wannier functions [9, 12] or atomic orbitals (which are used in the PAW DFT + U implementations [43, 39]).

From the orthonormalized projections, the local quantities can be linked to the quantity defined on the lattice. For the Green’s function and the self-energy, we thus have

$$G_{mm'}^{\text{imp}}(i\omega_n) = \sum_{k, \nu, \nu'} \tilde{p}^{R}_{m}(k) c_{\nu}(k, i\omega_n)^\dagger \tilde{p}^{R*}_{m'}(k).$$  

(2.3)
The DFT Hamiltonian is built and diagonalized. The new KS Bloch wavefunctions and the eigenvalues are then used to compute the Green’s function \( G \) and the self-energy \( \Sigma \). Secondly, the lattice Green’s function \( G_{\text{latt}} \) is computed from the impurity self-energy, and the self-consistency condition states that the local Green’s function is also the impurity Green’s function. When this DMFT loop is converged, the DFT Hamiltonian is built and diagonalized: the new KS bands with a good accuracy are extracted. Special care is taken to obtain the new KS bands with a good accuracy for each new electronic density, especially for unoccupied KS states. Then, the projections (2.1) are recomputed to build Wannier functions for the next DMFT loop. KS eigenvalues are also used to compute the Green’s function using equation (2.5).

The peculiarities of the PAW formalism for the computation of the electronic density are described in appendix A.

2.3. Calculation of the internal energy in DFT + DMFT

The DFT + DMFT formalism can be derived from a functional \([44]\) of both the local density \( n(r) \) and the local Green’s function \( G_{\text{loc}} \). The internal energy can be derived and one obtain the general formula of equation (3) of \([45]\). We first write two terms which appear in this equation:

\[
\Delta \Sigma_{\nu,\nu'}(k, i\omega_n) = \sum_{R,m} \frac{R_{\nu,m}^R(k)}{\Delta \Sigma_{\nu,m}(i\omega_n)} G_{\nu,m'}^{\nu}(k),
\]

where

\[
G_{\nu}^{\nu}(k, i\omega_n) = [(i\omega_n + \mu - \epsilon_{\nu,k})\delta_{v_1,v_1'} - \Delta \Sigma_{\nu,\nu'}(k, i\omega_n)]^{-1}_{v_1,v_1'},
\]

\[
\Delta \Sigma_{\nu,m}(i\omega_n) = \Sigma_{\nu,m}(i\omega_n) - \Sigma_{\nu,m}^{\text{dc}}.
\]

Equation (2.5) contains an inversion of a band matrix (of dimension the size of \( \mathcal{W} \)) for each frequency and \( k \)-point. \( \epsilon_{\nu,k} \) is the DFT Kohn–Sham eigenvalue for band index \( \nu \) and \( k \)-point \( k \). \( \Sigma_{\nu,m} \) and \( \Delta \Sigma_{\nu,m} \) are respectively the self-energy of the impurity problem, and the double counting term. The self-energy of the impurity problem is computed with the Dyson equation and is used to compute the lattice Green’s function as expressed by equations (2.5) and (2.4).

The DFT + DMFT scheme is summarized in figure 1.

2.2. DFT + DMFT formalism: self-consistency over density

The scheme of the self-consistency over electronic density within DFT + DMFT is shown in figure 1 and briefly described in the caption. In more detail, from the DMFT loop, the non-diagonal occupation in the Bloch band index can be extracted from (2.5) and used to compute the density using

\[
n(r) = \langle \hat{n} | \hat{n} | r \rangle = \sum_{k,v,v'} \langle \hat{n} | \Psi_{k,v'} \rangle \langle \Psi_{k,v'} | \hat{n} | \Psi_{k,v} \rangle \langle \Psi_{k,v} | r \rangle
\]

\[
= \sum_{k,v,v'} \langle \hat{n} | \Psi_{k,v'} \rangle f_{v,v'}(k) \langle \Psi_{k,v} | \Psi_{k,v'} \rangle \langle \Psi_{k,v'} | r \rangle;
\]

\( \hat{n} \) is the density operator in these equations.

Then, the DFT Hamiltonian is built and diagonalized: new KS eigenvalues and eigenfunctions are extracted. Special care is taken to obtain the new KS bands with a good accuracy for each new electronic density, especially for unoccupied KS states. Then, the projections (2.1) are recomputed to build Wannier functions for the next DMFT loop. KS eigenvalues are also used to compute the Green’s function using equation (2.5).

The peculiarities of the PAW formalism for the computation of the electronic density are described in appendix A.

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\[
\text{Tr}(G_{\text{DFT}} H_{\text{KS}} - \text{DFT}) = \sum_{v,k} G_{v,k}^{\text{DFT}}[n(r)] e_{v,k}^{\text{KS}-\text{DFT}}[n(r)],
\]

\[
\text{Tr}(G_{\text{DFT+DMFT}} H_{\text{KS}} - \text{DFT}) = \sum_{v,k} G_{v,k}^{\text{DFT+DMFT}}[n(r)] G_{\text{loc}}[n(r)]
\]

\[
\times e_{v,k}^{\text{KS}-\text{DFT}}[n(r)].
\]

In the above equations and below \( n(r) \) and \( G_{\text{loc}} \) are the converged density and local Green’s function of the full self-consistent DFT + DMFT cycle. For a given electronic density \( n(r) \), and thus a given Kohn–Sham DFT Hamiltonian \( H_{\text{KS}} - \text{DFT}[n(r)] \), \( e_{v,k}^{\text{KS}-\text{DFT}}[n(r)] \) are the Kohn–Sham eigenvalues of this Hamiltonian. \( G_{\text{DFT}} \) is the Kohn–Sham DFT Green’s function and \( G_{\text{DFT+DMFT}} \) is the DFT + DMFT Green’s function. We stress that \( G_{\text{DFT}} \) and \( G_{\text{DFT+DMFT}} \) can both be computed on the basis of Kohn–Sham wavefunctions. But this basis is just a practical way to express these quantities. Physically, \( G_{\text{loc}} \) stands for \( G_{LL'}^{\text{loc}}(i\omega_n) \), where \( L \) and \( L' \) are indices for spin and orbital momenta.
$G_{\text{DFT+DMFT}}$ is computed with equation (2.5) which contains the current Kohn–Sham Hamiltonian and the self-energy, whereas $G_{\text{DFT}}$ is computed with the same expression but without the self-energy. $f_{\text{DFT+DMFT}}^{\nu,k}[n(r), G_{\text{loc}}]$ is the DFT + DMFT occupation computed directly by integration over the frequency of the DFT + DMFT Green’s function $G_{\text{DFT+DMFT}}^{\nu,k}(k, i\omega_n)$ expressed in the Bloch Kohn–Sham basis. $f_{\nu,k}^{\text{DFT}}[n(r)]$ is the Fermi Dirac occupation and can also be computed directly by integration over the frequency of the Kohn–Sham DFT Green’s function expressed in the Bloch Kohn–Sham basis $G_{\nu}^{\text{DFT}}(k, i\omega_n)$.

With the notation from equation (3) of [45], we have $\text{Tr}[G_{\text{DFT}}H_{\text{KS–DFT}}] = \sum_{\nu} n_{\nu}^{\text{KS}}$ and $\text{Tr}[G_{\text{DFT+DMFT}}H_{\text{KS–DFT}}] = \langle H_{\text{KS}} \rangle$.

We can thus rewrite equation (3) of [45]:

$$E_{\text{DFT+DMFT}} = \frac{-E_{\text{H}[n(r)]} + E_{\text{xc}[n(r)]} - \int v_{\nu,n}(r)dr}{\text{Tr}[G_{\text{DFT}}H_{\text{KS–DFT}}]} + \text{Tr}[H_{\text{KS–DFT}}G_{\text{DFT+DMFT}}] + \langle H_{U} \rangle - E_{\text{Dc}}. \quad (2.10)$$

In this equation, $E_{\text{H}[n(r)]}$ and $E_{\text{xc}[n(r)]}$ are the Hartree and exchange correlation energies, and $v_{\nu,n}$ is the exchange and correlation potential. $(H_{U})$ and $E_{\text{Dc}}$ depend only on $G_{\text{loc}}$ and are computed from the resolution of the impurity problem. The H-I solver, $(H_{U})$ is computed with the Migdal formula with a scheme similar to the one detailed in [18]. $E_{\text{DFT}}[n(r)]$ is computed from the knowledge of the density computed in equation (2.7) (see also appendix D). The full localized limit (FLL) version of the double counting is used here as in [18]. The application of this double counting with the Hubbard I approximation is described in appendix E.

Thus we have the following expression for the total energy in DFT + DMFT:

$$E_{\text{DFT+DMFT}}^{1} = \sum_{\nu,k}^{\text{DFT+DMFT, KS–DFT}} \frac{E_{\text{DFT}}^{\nu,k}}{\epsilon_{\nu,k}} + \frac{E_{\text{DFT DC}}^{\nu,k}[n(r)]}{\epsilon_{\nu,k}^{\text{DFT DC}}} + \langle H_{U} \rangle - E_{\text{Dc}}. \quad (2.11)$$

Alternatively, one can write

$$E_{\text{DFT+DMFT}}^{2} = T_{0}^{\text{DFT+DMFT}} + E_{\text{xc+H}[n(r)]}$$

with $T_{0}^{\text{DFT+DMFT}}$ the analogue of the DFT kinetic energy in the DFT + DMFT scheme. The comparison of (2.11) and (2.10) yields

$$T_{0}^{\text{DFT+DMFT}} = \text{Tr}[H_{\text{KS–DFT}}G_{\text{DFT+DMFT}}] - 2E_{\text{H}[n(r)]} - \int v_{\nu,n}(r)dr - \int v_{\nu,n}(r)
\int \Psi_{\nu,k}(r)\frac{V_{\nu,k}^{2}}{2}\Psi_{\nu,k}(r)$$

$$= - \int dr \sum_{\nu,'} f_{\nu,'}^{\text{DFT+DMFT}} \Psi_{\nu,k}(r) = \sum_{\nu,'} \int f_{\nu,'}^{\text{DFT+DMFT}} \Psi_{\nu,k}(r)$$

Equation (2.11) is the so-called double counting expression of the total energy and equation (2.12) is the direct one. We emphasize the importance of non-diagonal terms in the calculation of the true kinetic energy in expression (2.12). This is essential for the correct calculation of energy. The exact numerical equality of these two expressions is used in our calculations, as a test of both the correctness of the numerical scheme and of the convergence [28]. This is an important test of the implementation.

This implementation has been carried out in the code ABINIT [22] using the PW–PAW scheme [28].

### 3. Applications

We show here the application of the self-consistent DFT + DMFT implementation to cerium, Ce$_2$O$_3$ and Pu$_2$O$_3$. The first two systems have already been studied with a fully self-consistent LDA(ASA) + DMFT technique [18]. This implementation was based on an LMTO-ASA [46] framework. We will thus be able to check both whether physical effects due to self-consistency are recovered in our implementation and what the improvement brought by the use of the PW–PAW method is. Indeed, the PW–PAW implementation is more flexible and more precise: the inclusion of semicore states is easier and structural and the thermodynamical properties are expected to be more precisely computed.

We have performed both DFT + $U$ calculations and DFT + DMFT calculations. Moreover for DFT + DMFT, two solvers were used: the first one—the static Hartree Fock solver—was used in order to check that DFT + $U$ results were recovered with this approach (see appendix B.3) and thus to check a part of the implementation of self-consistency over the electronic density. The second solver we used was the Hubbard I solver, as in [18] (see appendix E).

For simplicity, we restrict our DFT + DMFT calculations to the paramagnetic phase of these compounds.

#### 3.1. Cerium

Cerium metal exhibits an isostructural phase transition between the large volume ($\gamma$) phase and a small volume ($\alpha$) phase. In the $\gamma$ phase, the electrons are localized, whereas upon pressure, the electrons are more and more delocalized [47]. Several studies using a variety of methods have been carried out to understand the electronic structure of the $\gamma$ phase or the mechanism of the transition [48, 49, 38, 50–56, 45, 39]. In this DFT + DMFT study, we are using a simplified solver for the impurity model. We thus study only the $\gamma$ phase in order to compare our results to the calculations of Pourovskii et al. [18]. We focus here on the spectral function and on the structural properties.

#### 3.1.1. Computational scheme and details

In the PAW datasets, 5s, 5p, 6s, 5d and 4f states are included in the set of valence states. Atomic data for PAW are taken from [39]. The cutoff energy for the plane wave expansion is 12 Ha. We
emphasize that, in our framework, the inclusion of semicore but the magnitude of the effect is larger in PW–PAW. We thus qualitatively similar to the study of Pourovskii et al. However, the main effect is the same in LDA + U and LDA + DMFT, in PAW and in ASA [18]. For an appropriate comparison, the PAW/LDA + U calculations are carried out with the expression of the density matrix shown in appendix B. 

Table 1. The lattice parameter \( a \) and bulk modulus \( B_0 \) of \( \gamma \)-cerium according to experimental data and calculations within LDA + U and LDA + DMFT, in PAW and in ASA [18]. For an appropriate comparison, the PAW/LDA + U calculations are carried out with the expression of the density matrix shown in appendix B.

|            | \( a \) (au) | \( B_0 \) (GPa) |
|------------|-------------|-----------------|
| Exp [57, 58] | 9.76        | 19/21           |
| PAW/LDA + U  | 9.58        | 32              |
| PAW/LDA + DMFT NSCF (H-I) | 9.41        | 38              |
| PAW/LDA + DMFT SCF (H-I) | 9.58        | 36              |
| ASA/LDA + U [18] | 9.44        | 49              |
| ASA/LDA + DMFT NSCF (H-I) [18] | 9.28        | 50              |
| ASA/LDA + DMFT SCF (H-I) [18] | 9.31        | 48              |

We then compare the ASA and PAW results with the experiment [59, 60] is slightly better compared to ASA calculations [18].

3.1.3. Origin of the variation of the energy versus volume. We discuss now the behaviour of the energy versus volume curve in DFT + DMFT. We can split the energy into two contributions: the first one includes the interaction \( U \), namely \( \langle H_U \rangle - E_{DC} \), and the second includes all the other terms and is \( E_{LDA}[n_{LDA+DMFT}] \). If we separate these two contributions as a function of volume, one thus sees that the first term is negligible for cerium in DFT + DMFT (Hubbard I). It comes from the fact that the number of \( f \) electrons found in the solver is approximately one in this approximation, for each volume. In other words, the variation of energy as a function of volume is completely described by \( E_{LDA}[n_{LDA+DMFT}] \). This means that, for each volume, DFT + DMFT converges to a new density, \( n_{LDA+DMFT} \), and that the LDA energy alone for this set of densities shows the behaviour plotted in figure 3. In LDA + U, the energy decomposition shows a slightly different behaviour: the term \( \langle H_U \rangle - E_{DC} \) is not completely negligible. In fact, computing the energy variation with only \( E_{LDA}[n_{LDA+U}] \) leads to a lattice parameter of 9.35 au (about 2% less than the LDA + U value). It comes directly from the fact that the number of correlated electrons in LDA + U changes as the volume changes and modifies \( \langle H_U \rangle - E_{DC} \). However, the main effect is the same in LDA + U and LDA + DMFT: the change of the electronic density induced by correlation shows a variation as a function of volume, which shifts the equilibrium volume mainly because of the variation of \( E_{LDA}[n_{LDA+DMFT}] \).

Let us now analyse the variation of the converged densities as a function of volume with respect to the energy. In fact, we observe that the variation of \( E_{LDA}[n] \) for a

![Figure 2](image-url) 

Figure 2. The spectral function of \( \gamma \)-cerium, computed in LDA + DMFT (H-I) with and without self-consistency on the charge density.

![Figure 3](image-url) 

Figure 3. The energy versus volume curve for \( \gamma \) cerium computed in the LDA + DMFT framework with the Hubbard I solver. As discussed in the text, this energy variation comes mainly from \( E_{LDA}[n_{LDA+DMFT}] \).
given density can be qualitatively linked to the number of f electrons: for an increase of volume of 12% around the equilibrium volume, the number of f electrons increases by 0.007 in the LDA, and decreases by 0.002 in LDA + U and 0.03 in LDA + DMFT. The Hartree interaction energy between f electrons should thus decrease as a function of volume in the case of LDA + U/LDA + DMFT because the number of f electrons decreases. In these three methods, however, the impact of these variations is not the same on the interaction energies: LDA + U and LDA + DMFT give the same equilibrium volume whereas the variations of the number of electrons are very different. This might come from the different density matrices which are the results of these three calculations. In LDA + DMFT, the electrons are more homogeneously distributed because of possible fluctuations between different localized atomic states. In contrast, in LDA + U, the electron is localized in a single orbital. A general principle is, however, that the Hartree interactions between electrons belonging to different orbitals are not the same and should be lower than the Hartree self-interaction of one electron in one orbital. So the Hartree interaction should be lower in LDA + DMFT with respect to LDA + U. It might appear logical that the large variation of the number of electrons in DFT + DMFT is in fact expected to recover the same variation of volume. As a consequence, the variation of the number of electrons as a function of volume is only a qualitative hint to understanding the variation of energy, but a complete understanding requires the knowledge of the density matrix, or of the total electronic density.

In the case of non-self-consistent LDA + DMFT calculations, the expression (2.11) is used for the total energy [45]. As a consequence, the main effect comes from the band energy. Moreover, one can see that the difference between the DMFT band energy and the LDA band energy decreases when the volume increases as previously observed [45]. However, the intensity of this variation is weaker than the correct variation at the self-consistent density. Moreover, in the SCF calculation, this large variation is partially compensated by LDA double counting terms. It shows that to have a physically correct behaviour of the different terms of the energy, the achievement of convergence to the LDA + DMFT density is mandatory. As emphasized before, this is the very change of the electronic density which makes the difference in \( E_{\text{LDA}} \). Such a change cannot be reproduced by a non-self-consistent calculation.

3.1.4. Search for the ground state of the system, metastable states. As underlined in the previous section, the orbital anisotropy obtained in the ground state with LDA + DMFT is very small and is thus different from the ground state obtained in LDA + U which has a large orbital anisotropy [38, 39]. We thus expect the convergence in the case of a complex system with a large unit cell (such as Ce) to be much easier with the LDA+DMFT method than with the LDA+U method [39].

CeO3 is a Mott antiferromagnetic insulator with an optical band gap of 2.4 eV [61] and a Néel temperature of 9 K. An ionic counting of electrons leads to one f electron in the valence band. The qualitative picture of an insulator has been obtained by first principles calculation using the LDA + U [62–65], hybrid functional [65], DFT + DMFT framework [18, 66], and GW + LDA + U [34]. In most of these calculations, one electron is localized and the ground state is an antiferromagnet. LDA + DMFT is able to describe a paramagnetic insulating solution [18]. In this section, the results of the application of the LDA + DMFT scheme to this compound using the PW–PAW framework are given.

3.2. CeO3

CeO3 is a Mott antiferromagnetic insulator with an optical band gap of 2.4 eV [61] and a Néel temperature of 9 K. An ionic counting of electrons leads to one f electron in the valence band. The qualitative picture of an insulator has been obtained by first principles calculation using the LDA + U [62–65], hybrid functional [65], DFT + DMFT framework [18, 66], and GW + LDA + U [34]. In most of these calculations, one electron is localized and the ground state is an antiferromagnet. LDA + DMFT is able to describe a paramagnetic insulating solution [18]. In this section, the results of the application of the LDA + DMFT scheme to this compound using the PW–PAW framework are given.

3.2.1. Computational scheme and details. The PAW atomic data for cerium are the same as in section 3.2. For oxygen, the 2s and 2p electrons are taken in the valence band. The PAW matching radius for oxygen is 1.52 au. The cutoff energy for the plane wave expansion is 30 Ha. We use 32 k-points in the irreducible Brillouin zone. The structural properties are converged to less than 0.01 au for the lattice parameter and less that 0.1 Mbar for the bulk modulus. For simplicity, we do not relax the internal parameters: the volume is the only variable of the system.

The calculations are carried out at a temperature of 273 K. 52 Kohn–Sham bands are used to define the correlated orbitals and thus as a basis for the DMFT calculations. This number of bands is appropriate for making a comparison with previous calculations with the ASA formalism using a basis containing the same number of bands. The value of \( U \) is taken to be 6.0 eV and \( J \) is 0 eV.

3.2.2. Results and discussion. The spectral functions are given in figure 4 and the structural properties are gathered in table 2.

Concerning the first LDA + U results for the structural parameters, our calculations for the ground state, with antiferromagnetism (AFM), are in good agreement with the calculations of [65]. The slight disagreement concerning the bulk modulus might come from the absence of relaxation of the internal parameters in our calculations.
Table 2. The lattice parameter $a$ and bulk modulus $B_0$ of Ce$_2$O$_3$ according to experimental data and calculations with various frameworks. In our calculation and in [18], the $c/a$ ratio is fixed to the experimental value (1.56). The PAW/LDA + $U$ calculations are carried out with the expression of the density matrix corresponding to equation (B.1) and with $U = 6$ eV. The calculations are carried out at a temperature of 273 K. Note that the entropy is neglected in these calculations. The calculations from Da Silva [65] and Pourovskii et al [18] use $U = 5.3$ eV and 5.4 eV respectively.

|            | $a$ (Å) | $B_0$ (Mbar) |
|------------|---------|--------------|
| Exp [67]   | 3.89    | 1.11         |
| PAW/LDA + $U$(AFM) [65] | 3.87    | 1.3          |
| PAW/LDA + $U$(AFM) | 3.85    | 1.5          |
| PAW/LDA + DMFT (H-I) NSCF | 3.76    | 1.7          |
| PAW/LDA + DMFT (H-I) SCF | 3.83    | 1.6          |
| ASA/LDA + $U$ [18] | 3.84    | 1.5          |
| ASA/LDA + DMFT(H-I) NSCF [18] | 3.79    | 1.6          |
| ASA/LDA + DMFT(H-I) SCF [18] | 3.81    | 1.6          |

The results from the LDA + DMFT calculations reveal that the effect of self-consistency over the spectra and structural properties is qualitatively similar to the study of Pourovskii et al: the volume increases and the gap slightly decreases in the self-consistent calculation with respect to the non-self-consistent one. The quantitative results are, however, different from [18]: the ASA approximation induces a slight error of 1% in the determination of the lattice parameter with respect to the full potential codes. We correct this error in the PW–PAW implementation of the LDA + DMFT calculations.

The spectral function computed with LDA + DMFT with the PW–PAW basis shows a good agreement with the optical gap of 2.4 eV [68], as encountered also in LDA + $U$ [65]. However, the oxygen p band is not in good agreement with respect to the photoemission spectrum [69]. GW or hybrid functionals in combination with DFT + $U$ or DMFT can improve the agreement [34, 66].

3.2.3. Comparison of the LDA, LDA + $U$ and LDA + DMFT densities. The analysis of the variation of different energy terms as a function of volume leads to the same conclusion as for cerium: the variation of energy is mainly due to $E_{\text{LDA}}$ and is correlated to the variation of the number of f electrons. As the volume increases, this number increases in the LDA, decreases in LDA + DMFT and is nearly constant in LDA + $U$. However, a more detailed view on the electronic densities is most useful to illustrate the impact of the different approximations. In particular, as observed in the case of cerium, the orbital anisotropies are different in the LDA + $U$ results and the DMFT calculations. In particular, one f orbital is filled with the LDA+$U$ method whereas in DMFT, electrons are allowed to fluctuate between different orbitals, hence the diagonal terms in the occupation matrix of the local orbital basis are similar and not far from 0.07.

To illustrate the differences between the LDA + DMFT and LDA + $U$ electronic densities, we have plotted [70] in figure 5 the isosurfaces of the differences between the LDA + $U$/LDA + DMFT and LDA electronic densities. LDA + $U$ shows a localization of one electron in only one f orbital which is coherent with the breaking of orbital and spin symmetry in DFT + $U$. In contrast, in LDA + DMFT, as a consequence of the fluctuations, the f electron is spread among the f orbitals. As a consequence, the difference between the LDA + DMFT and LDA densities is weaker.

3.2.4. Thermodynamical study. From the energies obtained for cerium and cerium oxide, one can compute the variation of internal energy $\Delta E$ of the following reaction:

$$2\text{Ce} + \frac{3}{2}\text{O}_2 \rightarrow \text{Ce}_2\text{O}_3.$$ (3.1)

We have thus minimized the structure of the molecule $\text{O}_2$. The distance is found to be 1.22 Å and the cohesive energy is 7.6 eV in agreement with previous results (see e.g. [40]). $\Delta E$ computed in LDA + DMFT with the Hubbard I solver gives thus a value of $-19$ eV $\pm 0.1$ eV, within 1 eV of the experimental results ($-18.63$ eV) [71] and in the range of existing values computed in the LDA, and LDA+$U$ [65, 63, 64]. Upon variation of $U$ between 5 and 7 eV, the computed energy shows a change of less than 0.15 eV. This result shows that LDA + DMFT may have the same precision as LDA + $U$ in the calculation of thermodynamical quantities. Moreover, LDA + DMFT enables us to compute this energy of reaction for the true paramagnetic phases of cerium and Ce$_2$O$_3$.

3.3. Pu$_2$O$_3$

Pu$_2$O$_3$ is a paramagnetic metal insulator above 10 K [72]. Its conductivity gap is 1.8 eV and in an ionic picture it should contain five f electrons. In this section, we describe this compound with GGA(PBE) + DMFT (Hubbard I) and compute the spectral properties of this system and we discuss the improvement with respect to GGA(PBE) + $U$ [73, 40].

3.3.1. Computational scheme and details. We use the same parameters as for cerium oxide. For the PAW basis, semicore states are included in the atomic dataset [40] and for the PW basis, the cutoff energy for the plane wave is 30 Ha. The value of $U$ is taken to be 4 eV. As for cerium oxide, 52 Kohn–Sham bands are used to compute the Wannier f orbitals.

3.3.2. Results and discussion. The GGA + DMFT spectral functions obtained from the SCF and NSCF calculations are shown in figure 6. The GGA + DMFT calculations describe Pu$_2$O$_3$ as a Mott Hubbard insulator with an f–f gap of 1.8 eV. This is similar to what is obtained with the GGA + $U$ method [40]. However, in GGA + DMFT, we are able here to describe the paramagnetic phase. Concerning the self-consistency effect, it shifts the f peak towards higher energy with respect to the O p band and to the conduction band. This is similar to the behaviour encountered for Ce$_2$O$_3$.

The agreement with experimental data is good. The gap is near the experimental conductivity gap of 1.8 eV [74], which contains, however, two particle excitations. The structural properties, shown in table 3, are also in rather good agreement with the experiment.

As observed in cerium oxide, the density matrix obtained in the paramagnetic solution highlights particularly the role of
fluctuations inside the atomic orbitals brought by the Hubbard I solver. However, in contrast to the case of Ce₂O₃, there is still an orbital anisotropy coming mainly from the crystal field: the crystal field splitting is indeed larger in plutonium oxide, in agreement with the fact that cerium f orbitals are more localized than Pu f orbitals. From the energy levels computed in Hubbard I (expression (E.1)), we can estimate the crystal field splitting to be 0.05 eV in Ce₂O₃ and 0.5 eV in Pu₂O₃. This explains why orbital anisotropy is observed in Pu₂O₃ but not in Ce₂O₃: it comes from the direct physical effect that lower levels have more statistical weight, and in Pu₂O₃ the difference in energy between levels is sufficient. Indeed, logically it is the same orbitals that are filled in LDA + U which have a nearly degenerate energy are treated on the same footing in the DMFT Green’s function.

4. Conclusion

In this paper we have presented a new implementation of self-consistent DFT + DMFT and application of this formalism to some f electron systems.

From the methodological side, a self-consistent implementation of DFT + DMFT using the projected local orbital formulation is shown. This implementation is carried out inside a plane wave–projector augmented wave (PAW) framework. It allows us to carry out DFT + DMFT calculations of spectra and total energy with the precision of an all-electron code and the flexibility of a plane wave code, which opens the way for relaxation and dynamics. The applications are carried out with the Hubbard I solver, but the scheme is completely general and could be used in combination with the Quantum Monte Carlo Solver. Moreover, we discuss the comparison of this scheme with schemes using the MLWF or ASA basis and explain how to compare these schemes for f electrons.
electron systems. We stress that for f electron systems, DFT + DMFT is particularly well adapted, but that such systems are notoriously difficult to treat using the MLWF in combination with DFT + DMFT. The current framework, which avoids the construction of the MLWF, is thus well adapted and we show its success for several f electron compounds.

We show the application of this framework to three strongly correlated systems with f orbitals. First, we study cerium and Ce$_2$O$_3$. We compare our calculations to a previous study using the ASA basis. This is the opportunity to highlight the improvement brought by a correct description of the potential and the density with respect to the ASA: the structural parameters are greatly improved and thermodynamical quantities, such as formation energies, can be computed. More generally, with this new implementation, the calculation of energy in DFT + DMFT is on the same footing as the same calculation in DFT: semicore states are easily included, and energies of different structures can be easily compared.

Finally, we show the first study of the structural and spectral properties of plutonium sesquioxide within DFT + DMFT. We compare this compound to cerium sesquioxide and underline the reduced occurrence of spurious metastable states in DFT + DMFT in comparison to DFT + U.

The existence of non-physical metastable states is an important drawback of DFT + U which prevents one from finding the ground states of large heterogeneous systems, especially for f elements [38, 31, 39, 40, 33, 41]. Therefore, DFT + DMFT, besides giving a better physical description of correlated systems, suppresses the problem at least partially. The computational cost of DFT + DMFT is, however, much larger than DFT + U, but could be much reduced by using a simplified solver, such as Hubbard I, provided the system studied is a Mott insulator.

The general DFT + DMFT framework with the accurate PW–PAW basis opens the way to calculations of other properties, such as forces and phonons [77]. Our implementation was carried out within the open source code ABINIT [22] (see footnote 1).

Acknowledgments

I thank M Torrent and F Jollet for fruitful discussions. I am also grateful to Yann Pouillon for helpful technical support (with the system build of ABINIT). This work was granted access to the HPC resources of CCRT under the allocations 2010096008 and 2011096681 made by GENCI (Grand Equipement National de Calcul Intensif). We thank the CCRT team for support. The work was supported by ANR under project CORRELMAT.

Appendix A. Self-consistency over charge density: peculiarities of the PAW formalism

In this appendix, we derive the expression for the density used in self-consistent DFT + DMFT within PAW.

The electronic density (we neglect spin in this section) is obtained from (2.7). We have

$$n(r) = \sum_{v,v',k} f_{v,v',k} \langle \Psi_{v,k}(r) | r | \Psi_{v',k} \rangle. \quad (A.1)$$

Then, using the fundamental relation (11) of [25] for the operator $|r\rangle\langle r|$, we have

$$n(r) = \sum_{v,v',k} f_{v,v',k} \tilde{\psi}_{v,k}^\dagger(r) \tilde{\psi}_{v',k}(r) + \sum_{\nu} \sum_{v,v',k} f_{v,v',k} \times \langle \tilde{\psi}_{v,k}(\tilde{p}_j) | (\psi_{\nu} | r | \psi_{\nu}) \rangle$$

$$- \langle \psi_{\nu} | r | \psi_{\nu} \rangle \langle \tilde{p}_j | \tilde{\psi}_{v',k} \rangle, \quad (A.2)$$

where $\tilde{p}_j$ is the $n$th projector, for the angular momentum $l_j$, and its projection $m_j$ on atom $R$. $\tilde{\psi}$ and $\psi$ are respectively the pseudo and all-electron atomic wavefunctions. The indices for atoms are neglected on $\tilde{p}_j$, $\psi$ and $\tilde{\psi}$. We can rewrite this equation as

$$n(r) = n'(r) + n^{I}(r) - \tilde{n}^{I}(r), \quad (A.3)$$

with

$$n'(r) = \sum_{v,v',k} f_{v,v',k} \tilde{\psi}_{v,k}^* \tilde{\psi}_{v',k}(r), \quad (A.4)$$

$$n^{I}(r) = \sum_{\nu} \sum_{j} \rho_{ij}^{\nu}(\psi_{\nu}(r) \psi_{\nu}(r)), \quad (A.5)$$

$$\tilde{n}^{I}(r) = \sum_{\nu} \sum_{j} \rho_{ij}^{\nu}(\tilde{\psi}_{\nu}(r) \tilde{\psi}_{\nu}(r)), \quad (A.6)$$

and

$$\rho_{ij}^{\nu} = \sum_{v,v',k} f_{v,v',k} \langle \tilde{\psi}_{v,k}(\tilde{p}_j) | \tilde{\psi}_{v',k} \rangle. \quad (A.7)$$

So, for the on site terms of the density, we just have to compute $\rho_{ij}^{\nu}$, and then use it instead of $\rho_{ij}$ everywhere in the formalism.

Appendix B. Definition of local orbitals and comparison of DFT + DMFT and DFT + U implementations

DFT + U and DFT + DMFT can be seen as two different approximations for the same functional. DFT + U is a static mean field solution, and DFT + DMFT contains dynamical fluctuations. However, their practical implementations are quite different. In DMFT, one needs a frequency dependent local Green’s function, whereas in DFT + U, only the integral of it is used. In this technical appendix, we first briefly compare the definitions of local orbitals in these two methods (appendix B.1), then we compare the implementations in the PAW method (appendix B.2), and we give a careful numerical comparison with our implementations (appendix B.3).

B.1. Definition of the local orbital, and the density matrix in the PLO scheme for a complete KS basis

We compare here the DFT + DMFT PLO formulation and the DFT + U treatment of local orbitals in a specific case. In
DFT + DMFT, projections in the PLO scheme are defined by equation (2.1). We assume here that \( \chi_R^m \) are a set of orthonormalized orbitals, such as MLWF or atomic orbitals. If we also use an infinite window for the construction of \( \chi_R^m \) (equation (2.2)), then we have \( \chi_R^m = | \chi_{K,m}^R \rangle \), because the basis of Kohn–Sham functions is complete. In this case, the construction of Wannier orbitals from \( \chi^m \) is just a renormalization with \( \langle \chi_m^R | \chi_R^m \rangle = | \chi_R^R \rangle \).

In this last case, the density matrix of correlated electrons can be written as

\[
\rho_{m,m'}^{R,\sigma} = \sum_{k \nu} \langle \chi_m^R | \psi_{R\nu}^k \rangle \langle \psi_{R\nu}^k | \chi_{m'}^R \rangle \langle \chi_{m'}^R | \chi_R^R \rangle. \tag{B.1}
\]

So, if a DFT + U calculation is carried out with this formulation of the density matrix, the results can be compared to a DFT + DMFT calculation with the PLO scheme at convergence of the KS basis.

**B.2. Application to the PAW formalism**

In our PAW implementation of the PLO scheme for DFT + DMFT, we follow the lines of [12]. Equation (2.1) is thus written as equation (A.2) of [12] in the PAW method:

\[
\rho_{m,m'}^{R}(k) = \sum_{n} \langle \chi_m^R | \psi_{n}^k \rangle \langle \psi_{n}^k | \chi_{m'}^R \rangle \langle \chi_{m'}^R | \chi_R^R \rangle. \tag{B.2}
\]

where \( \rho_{m}^{R} \) is the projector \( m \) for angular momenta \( l \), and its projection \( m \) on atom \( R \) and \( \chi_m^R \) is chosen to be the atomic eigenfunction for the given angular momentum.

The \( \chi_m^R \) are not completely orthonormalized because in our implementation they are used only inside the PAW sphere. However, 96% of their density is located inside the sphere, so in this discussion we neglect this slight non-orthonormalization. As we use only the part of the density matrix computed inside the sphere with the all-electron wavefunction (see [12, 39]), \( \langle \chi_R^R | \chi_R^R \rangle \) represents the integral of the atomic wavefunction inside the PAW sphere. Equation (B.1) is thus written, in the PAW framework, as (the \( m \) indices are removed for simplicity in the equation because the integrals are carried out here over the radial part of the wavefunction)

\[
\rho_{m,m'}^{R}(k) = \sum_{n} \langle \chi_{m}^{R} | \psi_{n}^{k} \rangle \langle \psi_{n}^{k} | \chi_{m'}^{R} \rangle \langle \chi_{m'}^{R} | \chi_{R}^{R} \rangle. \tag{B.2}
\]

It is thus the density matrix in the subset of correlated orbitals used in DFT + DMFT at convergence of the KS basis. We will compare in appendix B.3 the application of this expression in DFT + U to the PAW scheme in DFT + DMFT.

**Table B.1.** The lattice parameter \( a \) and bulk modulus \( B_0 \) of \( \gamma \)-cerium according to calculations using LDA + U with expression (B.3) for the density matrix and LDA + DMFT using 30 bands ranging from \(-32 \) to \(30 \) eV around the Fermi level.

|        | \( a \) (au) | \( B_0 \) (GPa) |
|--------|-------------|----------------|
| PAW/LDA + U | 9.58        | 32            |
| PAW/LDA + DMFT(HF) | 9.59        | 31            |

Another way of computing the projection (2.1) and occupation matrices exists, such as an integrated value in the PAW sphere of angular-momentum-decomposed charge densities [43, 24]. The slight drawback of such a scheme is that the starting atomic orbitals \( | \chi_R^R \rangle \) are not easily defined in this approach. The advantage is that the spectral weight is not lost [15] as long as the projection is carried out with all the terms of equation (A.1) of [12]. The differences between this scheme and the latter are, however, small [39, 24].

We underline that the atomic data that are used with this framework have to be transferable in a large energy range because unoccupied excited states are used in the framework. In particular, the closure relation over KS states does not hold if the atomic data are not transferable in the relevant energy range.

**B.3. Numerical comparison of the two schemes**

We have carried out this comparison for the volume and spectra of \( \gamma \)-cerium. The parameters for the calculation are similar to those of section 3.1. The calculations are carried out at a temperature of 273 K. Moreover, the calculations using DFT + U are carried out with expression (B.3) for the density matrix and DFT + DMFT uses 30 bands ranging from \(-32 \) to \(30 \) eV (the Fermi level is at zero energy). To assess the lack of completeness of the Kohn–Sham basis, one can compute the value of \( \langle \chi_{R}^{R} | \chi_{R}^{R} \rangle \) using the closure relation:

\[
\langle \chi_{R}^{R} | \sum_{k,\nu,\sigma} \langle \psi_{R,\nu}^{k} | \langle \psi_{R,\nu}^{k} | \chi_{R}^{R} \rangle \rangle. \tag{B.4}
\]

For our PAW atomic data, and the bands chosen (see the caption of table B.1), we find an average value of 0.95, whereas the numerical value of \( \langle \chi_{R}^{R} | \chi_{R}^{R} \rangle \) is 0.964. The Kohn–Sham basis thus describes the atomic wavefunction with an error of less than 2%.

The spectral functions for the two formulations of DFT + U, as shown in figure B.1, are nearly identical. The structural properties gathered in table B.1 show variations smaller than 0.1% in the lattice parameters and 1% in the bulk modulus. This is a confirmation of the coherence of the two implementations.
Appendix C. Impact of the energy windows used to define the Wannier functions on the physical properties

In this section, we study the dependence of the spectral function as a function of the number of KS states used to define the Wannier functions. The calculations are carried out for the case of γ cerium. This is an important issue because the choice of the KS basis implicitly defines the local orbital subset as an orthonormalized linear combination of these states.

The spectral functions for different choices of the KS basis are plotted in figure C.1. As more and more KS states are included, the lower (respectively upper) Hubbard band is shifted from −2.5 to −1 eV (respectively 3.5–5 eV). In the Hubbard I approximation used here, the positions of the Hubbard bands are governed by the level positions computed in equation (E.1). In this equation, the double counting correction is computed with the number of electrons used in the Hubbard I solver [18], which is nearly one, and does not depend on the window of energy. The shift of the Hubbard band thus comes from the definition of the LDA atomic levels (equation (E.1)): as more and more Kohn–Sham states are included in the sum, the mean energy of the levels increases tangentially, until the basis is complete. However, we stress that this effect is substantially increased by the self-consistent loop. The consequence of the higher energy level of the f orbitals is an increase of the number of f electrons (see table C.1) because of a larger hybridization with other orbitals. We stress that in this limit, we are moving away from the atomic limit and the Hubbard I solver is not adequate. Besides, a more extensive physical investigation would require the computation of a different value of $U$ for each window of energy (or number of KS states) used to define the correlated Wannier functions: as the windows of energy are increased, the orbitals are more and more localized and thus the value of $U$ should increase.

However, we emphasize that the results of this convergence only correspond to a given choice of correlated orbitals, namely, atomic orbitals. Other legitimate choices exist: we found that, in order to make an adequate comparison between the PLO scheme and a scheme using LMTO-ASA, it is especially important to use the same number of KS states as the number of muffin tin orbitals used in the LMTO-ASA calculation. This comes from the fact that the Wannier functions that are used as correlated orbitals in the two schemes are thus built with the same window of energy. For γ cerium, the ASA calculations of [18] are made with a basis set of 20 states (5s, 5p, 6s, 6p, 5d and 4f states). A calculation with the PLO scheme must use 20 bands in the KS basis in order to use roughly the same correlated orbitals.

Appendix D. Total energy in DFT + DMFT in the PAW formalism

In this section, we briefly show that the knowledge of $f_{\nu,\nu',k}$ is sufficient to compute all the energy terms in the PAW method. We use some notations of [28].

According to the calculation of $f_{\nu,\nu',k}$, one may compute $\rho_{ij}$ and the pseudo-density with equations (A.2) and (A.7). All the terms of the energy which depend on the local quantities ($E^1, E^1_{\text{xc}}, E^1_{\text{dc}}$) are computed with $\rho^1_{ij}, n^1$ and $\bar{n}^1$ (see [28]). In the plane wave basis, $E_{\text{xc}}$, $E_{\text{dc}}$ are computed directly from the computed DFT + DMFT density. The sum over eigenvalues and the kinetic energy are directly computed as above (equations (2.11) and (2.12)). We emphasize that there is no approximation to a tight binding model for the computation of the kinetic energy or the sum over KS eigenvalues.

Appendix E. Hubbard I solver and interaction

To solve the impurity model, we use in this paper the Hubbard I method. This method neglects the hybridization between the impurity and the bath in the resolution of the Anderson impurity model. We implement this method in the same spirit as in [18]: we impose that the impurity Green’s function and the local Green’s function have the same limit at high frequencies. The definition of the atomic level follows (see also [14]):

$$
e_{\sigma}^{R_{\nu,\nu'}} = \sum_{k} \bar{\rho}_{\nu,\nu'}^{k} (k) e_{\nu,\nu'}^{\sigma} R_{\nu,\nu'}^{\sigma} (k) - \sum_{\nu,\nu'}^{\text{DC}} \rho^{\nu,\nu'} - \mu. \quad (E.1)$$

As H-I solves an atomic problem without coupling to the bath, the number of electrons computed in the resolution of the impurity problem is nearly an integer (see [18]). For the sake of comparison with [18], this number is used to compute the FLL double counting. However, we stress that our implementation is completely general and that the value of the double counting used in Hubbard I is just a consequence of the approximate nature of the H-I solver.

Table C.1. The range of energy for the LDA eigenvalues for several sets of KS states. The lowest KS states, corresponding to 5s orbitals, are located −1.25 Ha under the Fermi level. The number of electrons is obtained in the corresponding LDA + DMFT calculations.

| Number of KS bands | 15 | 20 | 25 |
|--------------------|----|----|----|
| Energy range (Ha)  | 1.4| 1.8| 2.0|
| Number of f electrons | 1.03 | 1.16 | 1.14 |

Figure C.1. The spectral function of γ-cerium, computed in LDA + DMFT (H-I) for different choices of the KS basis.
We choose $J = 0$ in all calculations and we specify the value of the interaction $U$ chosen for each system. As the Hubbard $I$ approximation is a valid approximation for well localized systems, we expect, however, this approximation to be valid only for large values of $U$ and/or low hybridization (i.e. high volumes). In other cases, a more accurate solver should be used.

Note added. After the writing of this manuscript was completed, we became aware of a related work of Zhao et al [78] on an implementation of LDA + DMFT in a pseudopotential plane wave framework.

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