The role of non-spherical double counting in DFT+DMFT: total energy and structural optimization of pnictide superconductors

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A simple scheme for avoiding non-spherical double counting in the combination of density functional theory (DFT) with dynamical mean-field theory (DMFT) is developed. It is applied to total-energy calculations and structural optimization of the pnictide superconductor LaFeAsO. The results are compared to a recently proposed “exact” double-counting formulation. Both schemes bring the optimized Fe-As interatomic distance close to the experimental value. This resolves the long-standing controversy between DFT+DMFT and experiment for the structural optimization of LaFeAsO.

INTRODUCTION

Recent progress in realistic electronic structure calculations of correlated materials is based on a combination of the density functional theory (DFT) with the dynamical mean-field theory (DMFT). The DFT+DMFT approach opens unique possibilities to investigate electronic and structural properties of solids with partially-filled d- and f-electron shells. The main reason for this success is based on the optimal nature of the local self-energy scheme in the DMFT method, and on the development of efficient multi-orbital impurity solver within continuous-time quantum Monte-Carlo (CT-QMC) schemes.

The ability to treat the non-spherical part of local Coulomb interactions exactly in the CT-QMC scheme brings an additional aspect to the so-called double-counting correction in the DFT+DMFT approach, which is commonly used to account for Coulomb interactions already treated on the DFT level. In a standard DFT+DMFT scheme the double-counting corrections are spherical and are designed to repair only the average Coulomb interactions either in the DFT or the DMFT parts. Usually, as in the static mean-field like DFT+U scheme, the double-counting correction consists of a subtraction of an average Coulomb interaction, that is taken either in the limits of itinerant or localised electrons. With the full-potential DFT approach for different structural calculations, this will work only for a strictly spherical type of Hubbard U-corrections.

Already in the non-spherical rotationally-invariant DFT+U investigations of orbital ordering and structural instability in the KCuF₃ perovskite, care was taken to avoid full potential contributions of d-electrons in the DFT-part. Applications of the rotationally invariant DFT+U scheme to calculations of the complex crystal structure of cuprates and magnetic-anisotropy problems show importance of accurate treatments of the double-counting corrections.

Another way to solve the problem of the proper DFT+DMFT interface is related to transfer the double counting corrections to the DFT part, in order to subtract the part of exchange-correlations energy related with d- or f- electrons. Recently, a so-called “exact” double-counting correction to the DFT+DMFT scheme employs a similar idea to subtract the exchange-correlations term that correspond to local Yukawa-like short-range interaction. It is not clear which scheme is more appropriate for different classes of materials. For instance, a successful application of DFT+DMFT to the complicated problem of the anisotropic Fermi surface of Sr₂RuO₄ used a standard mean-field like double-counting correction for the itinerant limit.

In this communication, we introduce a proper double-counting scheme for the atomic limit and make comparison with the recent “exact” scheme. As a test case we choose the problem of structurally optimizing the Fe-As distance in the pnictide superconductor LaFeAsO.

METHODOLOGY

In a practical implementation, the total energy of the charge self-consistent DFT+DMFT reads,

\[ E^{\text{DFT+DMFT}} = E^{\text{DFT}}[\rho^{\text{DMFT}}(r)] + \sum_k \sum_\nu \epsilon_{k\nu} \Delta N_{\nu}^{(k)} + \langle \hat{H}_{\text{int}} \rangle - E_{dc} , \]

where \( E^{\text{DFT}} \) is a standard DFT functional acting on the DMFT charge density \( \rho^{\text{DMFT}} \), \( \epsilon_{k\nu} \) are the Kohn-Sham (KS) energy eigenvalues, \( \Delta N_{\nu}^{(k)} \) is the KS occupation matrix correction due to the DMFT self-energy, \( < \hat{H}_{\text{int}} > \) is an expectation value of the Coulomb vertex, and \( E_{dc} \) marks the double-counting correction. Eq. 1 assumes the use of the Bloch basis in which the kinetic energy operator is diagonal in a basis of the Kohn-Sham eigenstates.

The double-counting correction \( E_{dc} \) in eq. 1 accounts approximately for the mean-field value of the electron-electron interaction, already included in \( E^{\text{DFT}} \). Until recently, there was no precise solution of for the double counting when utilizing conventional DFT implemented in the local-density or generalized-gradient approximations (LDA or GGA). Most commonly used...
Double counting correction forms in the DFT+DMFT scheme are the so-called "fully localized (or atomic-like) limit" (FLL) \[1, 10\]
\[
E_{\text{dc}}^{(\text{FLL})} = \frac{U}{2} N(N - 1) - \frac{J}{2} \sum_{\sigma} N_\sigma (N_\sigma - 1), \tag{2}
\]
or, the "around mean field" (AMF) scheme \[17, 18\],
\[
E_{\text{dc}}^{(\text{AMF})} = U n_\uparrow n_\downarrow + \left( \frac{1}{2} n_\uparrow^2 + n_\downarrow^2 \right) \frac{2l}{2l + 1} (U - J), \tag{3}
\]
where \(n_\sigma = \text{Tr}[n_{m_\sigma, n_\sigma}], n = n_\uparrow + n_\downarrow\) is the total \(d\) (or \(f\)) on-site occupation, and \(U\) and \(J\) are the intratomic Coulomb repulsion and exchange parameter, respectively \[19\]. This \(E_{\text{dc}}\) stems from a spherically-symmetric treatment, while the DFT part of the Hartree and the exchange-correlation energies,
\[
E_{\text{H}} + E_{\text{XC}} = \frac{1}{2} \int d\rho d\rho^\prime \frac{\rho(\mathbf{r}) \rho(\mathbf{r}^\prime)}{|\mathbf{r} - \mathbf{r}^\prime|} + \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})), \tag{4}
\]
remain accounted together with the non-spherical contributions into the DFT+DMFT energy functional eq. \[1\] (for simplicity, we write everything in terms of a charge density only, while the inclusion of the spin is straightforward).

One way to exclude this "non-spherical" double counting is to keep only the spherically-symmetric contributions in the \((\hat{H}_{\text{int}})\) term of eq. \[7\]. But this is not what one truly aims for, the DFT+DMFT induced enhancement of the orbital polarization beyond DFT will be lost.

Alternatively, the non-spherical contributions entering the DFT part of the Hartree and the exchange-correlation energies from the \(d\) (or \(f\)) states can be excluded in a simple way, similar to what was proposed earlier in DFT+U \[20\], and DFT+HIA \[21, 22\], implementations of the full-potential linearized augmented plane wave (FLAPW) method \[23\].

In this work, we will use the mixed-basis pseudopotential method (MBPP) \[24, 27\], and expand the KS wave function for Bloch vector \(k\) and band \(\nu\) into plane waves (pw) and localized functions (lf),
\[
\psi_{k\nu}(\mathbf{r}) = \frac{1}{\sqrt{V_c}} \sum_{G} \psi_{G}^{k\nu} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} + \sum_{\gamma_{l\nu}} \beta_{\gamma_{l\nu}} \phi_{\gamma_{l\nu}}^{k}(\mathbf{r}) , \tag{5}
\]
where \(V_c\) is the unit-cell volume, \(G\) a reciprocal-lattice vector, \(\gamma\) labels an atom in the unit cell and \(l\nu\) are the usual angular-momentum quantum numbers. The localized functions are given by
\[
\phi_{\gamma_{l\nu}}(\mathbf{r}) = \delta_{\gamma_{l\nu}} \frac{1}{2} \sum_{\gamma_{l\nu}} g_{\gamma_{l\nu}}(\mathbf{r}) K_{\gamma_{l\nu}}(\mathbf{r}) , \quad \phi_{\gamma_{l\nu}}^{k}(\mathbf{r}) = \sum_{T} e^{i\mathbf{k}(T+R_\gamma)} \phi_{\gamma_{l\nu}}(\mathbf{r} - T - R_\gamma), \tag{6}
\]
whereby \(g\) is a radial function, and \(K\) is a cubic harmonic.

Accordingly, the MBPP electronic charge density \(\rho(\mathbf{r})\) consists of three terms, i.e.
\[
\rho(\mathbf{r}) = \sum_{k\nu} \left| \psi_{k\nu}(\mathbf{r}) \right|^2 = \rho_{\text{pw,pw}}^{\nu\nu}(\mathbf{r}) + \rho_{\text{pw,lf}}^{\nu\nu}(\mathbf{r}) + \rho_{\text{lf,lf}}^{\nu\nu}(\mathbf{r}) . \tag{7}
\]
For our concerns, the purely-local third term \(\rho_{\text{lf,lf}}^{\nu\nu}\) is of key interest. It is written as
\[
\rho_{\text{lf,lf}}^{l\nu l\nu}(\mathbf{r}) = \sum_{k\nu} \sum_{\gamma_{l\nu}} \beta_{\gamma_{l\nu}}^{k\nu} \phi_{\gamma_{l\nu}}^{k}(\mathbf{r}) \left| \phi_{\gamma_{l\nu}}(\mathbf{r}) \right|^2 = \sum_{T_{\gamma_{l\nu}}} \rho_{\gamma_{l\nu}}(\mathbf{r}) K_{\gamma_{l\nu}}(\mathbf{r}) , \tag{8}
\]
with \(r' = r - T - R_\gamma\), and hence can be understood as an expansion into the cubic harmonics on each site \(R_\gamma\).

We spherically average the purely local term \(\rho_{\text{lf,lf}}^{l\nu l\nu}\) in eq. \[8\] for those states which are corrected by DMFT (with \(l = 2\) for the \(d\) states, and \(l = 3\) for the \(f\) states). Thus, the local non-spherical parts in \(\rho_{\text{lf,lf}}^{l\nu l\nu}\) vanish on each site \(R_\gamma\), and do not contribute to the DFT part of the Hartree and the exchange-correlation energies eq. \[3\]. It removes the non-spherical double counting in the DFT+DMFT total energy charge self-consistent calculations.

Until recently, there was no exact solution of the double-counting problem. Density functional theory does not have a diagrammatic representation that would provide an explicit identification of corresponding many-body interaction terms. Also, it is not clear how to solve the Hubbard model by DFT. The FLL/AMF forms of \(E_{\text{dc}}\), which were discussed above, are derived in some static approximations to the Hubbard interaction term. The "physical" arguments prevailed in the choice of \(E_{\text{dc}}\).

In Ref. \[11\], K. Haule proposed a new "exact" form of the double-counting correction making use of the Luttinger-Ward functional representation for both DFT and DMFT. This \(E_{\text{dc}}\) was applied to a number of correlated solids, and good agreement between the theory and experiment was achieved. Importantly, the \(E_{\text{dc}}\) of Ref. \[11\] is free from the non-spherical double counting, and no additional correction is required. Therefore, we applied it to the structural optimisation of the pnictide superconductor LaFeAsO.

**RESULTS**

Electronic structure theory of the high-temperature superconductor LaFeAsO occupies a fundamental place in condensed matter physics and material science. The calculations are often performed either within the DFT or DFT+DMFT. Both approaches fall short in the correct description of the equilibrium crystal structure. When the paramagnetic high-temperature phase is modelled by a non-magnetic DFT calculation, a too short Fe-As distance, governed by the internal unit-cell parameter
z, is obtained. The latter has a drastic influence on the low-energy electronic structure \(^{28}\), and very precise electron-electron correlation effects need to be tackled. Charge self-consistency within DFT+DMFT becomes important and based thereon, previous studies \(^{29,30}\) indeed improved upon pure nonmagnetic DFT calculations. However still, those correlated electronic structure results remain ambiguous, and depend on the choice of the double counting correction (FLL or AMF).

We overtook the values of Hubbard-\(U = 2.7\) eV and Hund’s exchange of \(J = 0.8\) eV for the local Coulomb interactions from Ref. \(^{29}\), which were calculated within the constrained random-phase approximation (cRPA) \(^{31,32}\). The inverse temperature is set to \(\beta = 40\) eV\(^{-1}\), that corresponds to room temperature \(T = 290\) K. For the solution of the quantum impurity problem we apply the cthyb-QMC method \(^{33}\). The multiorbital Hubbard Hamiltonian of Slater-Kanamori form, parametrized by Hubbard-\(U\) and Hund’s exchange \(J\) is applied to the respective full five-orbital 3d manifold.

We performed the total-energy electronic structure DFT and DFT+DMFT calculations of LaFeAsO making use of the MBPP method \(^{34}\) and compared them with Wien2K calculations \(^{35}\). The FLL form of the double-counting correction was used, as well as the ”exact” double-counting from Ref. \(^{11}\). The total energy within the MBPP-based schemes are shown in Fig. 1\(A\), and are compared with Wien2K-based results shown in Fig. 1\(B\). The values of the As atom \(z\) parameter that correspond to the total-energy minima are given in Tab. 1.

Both MBPP and Wien2K DFT calculations yield for the As atom \(z\) parameter values substantially smaller (see Tab. 1) than the experimental value of \(z = 0.651\) \(^{28}\). Inclusion of correlation effects by DFT+DMFT(FLL) without the non-spherical double-counting correction has visible effect on the total energy, and improves the As atom \(z\) parameter over the DFT results. This is in agreement with the previous Wien2K-based DFT+DMFT calculations \(^{24}\). Still the difference \(\Delta z = 0.013\) between the experimental and theoretical values remains unresolved.

Note that within identical setting, DFT and DFT+DMFT calculations based on the pseudopotential (MBPP) method produce \(z\) parameter values by \(\approx 0.005\) smaller than corresponding all-electron (Wien2K) calculations. Nevertheless, the difference between DFT and DFT+DMFT results obtained with MBPP is the same as from the Wien2K calculations, and illustrates the important role of electron correlation effects.

It was proposed in Ref. \(^{30}\) that further improvement of the value of \(z = 0.643\) can be achieved by switching to the AMF form of \(E_{dc}\), suggesting partial delocalization of the 3d states in metallic LaFeAsO. However, no non-spherical double-counting corrections were used in these calculations. As it follows from our MBPP results shown in Fig. 1\(A\) and Tab. 1, avoiding non-sphericity in the FLL double counting leads to an increase of the \(z\) parameter to \(z = 0.638\) over the \(z = 0.633\) FLL result with no non-spherical double-counting correction. Taking into account that MBPP yields slightly smaller values for the \(z\) parameter, the proposed double counting correction brings the total energy minimum into close proximity of the experimental data.

### Table 1. Comparison of the As atom \(z\) position calculated with different methods and codes.

| Method          | \(z\) | Method          | \(z\) |
|-----------------|-------|-----------------|-------|
| DFT             | 0.628 | DFT             | 0.634 |
| DMFT(FLL)       | 0.633 | DFT(FLL)        | 0.638 |
| DMFT(FLL+NSPH)  | 0.638 | DFT(“exact”)    | 0.648 |

FIG. 1. (color online) The relative total energy of LaFeAsO as a function of the As height, expressed by the \(z\) parameter, in the unit cell, A: MBPP based, B: Wien2K based). Dashed line marks the experimental \(z\) position of the As atom.
Finally, we performed calculations with the "exact" double counting implementation \cite{11}, and obtained the total-energy minimum at $z = 0.648$ (see Fig. 1B and Tab. 1), now shifted close to the experimental value \cite{28}. This form is free from the non-spherical double counting. This supports our finding that the source of discrepancy between experiment and DFT+DMFT is not a form of the double-counting due to the metallic character of LaFeAsO, as suggested by Ref. \cite{30}, but because of the non-spherical double counting in DFT and DMFT parts of DFT+DMFT.

To conclude we developed a simple scheme for avoiding non-spherical double counting in DFT+DMFT and compared with the "exact" double counting scheme \cite{11}. As a proof of principles, the results show a similar shift of the Fe-As distance and bring results of DFT+DMFT closer to experiments. We think that the standard double-counting scheme in the atomic limit will be useful for strongly correlated \textit{d}- and \textit{f} systems with anisotropic Coulomb interaction close to insulating states.

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