Dynamical cluster approximation within an augmented plane wave framework: Spectral properties of SrVO$_3$

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We present a combination of local-density approximation (LDA) with the dynamical cluster approximation (LDA + DCA) in the framework of the full-potential linear augmented plane wave method, and compare our LDA + DCA results for SrVO$_3$ to LDA with the dynamical mean-field theory (LDA + DMFT) calculations as well as experimental observations on SrVO$_3$. We find a qualitative agreement of the momentum resolved spectral function with angle-resolved photoemission spectra (ARPES) and former LDA + DMFT results. As a correction to LDA + DMFT, we observe more pronounced coherent peaks below the Fermi level, as indicated by ARPES experiments. In addition, we resolve the spectral functions in the K$_0 = (0,0,0)$ and K$_1 = (\pi,\pi,\pi)$ sectors of DCA, where band insulating and metallic phases coexist. Our approach can be applied to correlated compounds where not only local quantum fluctuations but also spatial fluctuations are important.

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I. INTRODUCTION

The development of reliable numerical tools for the description of the electronic structure of correlated compounds is one of the most challenging tasks in the condensed-matter community. As an example, transition-metal perovskites with partially filled d$_{x^2}$ orbitals are predicted to be conventional metals in the framework of one-electron approaches like density-functional theory (DFT) in the local-density approximation (LDA). Nevertheless, a few perovskite families show a markedly different behavior; SrVO$_3$ and CaVO$_3$ are correlated metals with significant mass enhancement and LaTiO$_3$ displays features of a Mott insulator. In all compounds, this anomalous behavior may be caused by correlations resulting from Coulomb repulsion effects. Therefore progress on methods including correlation effects beyond DFT is very desirable.

Dynamical mean-field theory (DMFT) takes local quantum fluctuations fully into account but the momentum dependence of the self-energy is neglected. This method has been developed over the last twenty years and successfully describes the metal-to-Mott insulator transition in frustrated systems to the spin-Peierls system TiOCl—where pairing correlations are important—within an N/4th-order muffin-tin orbital (NMTO) approach combined with DCA as well as NMTO combined with a variational cluster approach (VCA). In this work, we present an alternative approach where we extend a newly developed implementation of the LDA + DMFT approach to the context of the full potential linearized augmented plane wave (FLAPW) method by including spatial fluctuations within DCA (LDA + DCA), and we investigate the spectral properties of SrVO$_3$ as a test case.

The paper is organized as follows: in Sec. II, we describe our LDA + DCA implementation with a weak-coupling continuous-time quantum Monte Carlo (CT-QMC) algorithm for multiorbital systems with multiple sites. In Sec. III, we present results for SrVO$_3$ within LDA + DCA with a cluster of two sites and compare them with single-site LDA + DMFT calculations as well as experimental observations and in Sec. IV we summarize our findings.

II. THEORETICAL FRAMEWORK

A. LDA + DCA in the APW framework

In this work, we extend a recent implementation of LDA + DMFT to LDA + DCA, which includes short-range spatial correlations. We first shortly review the projection operators within the WIEN2K code. The local atomiclike Wannier orbital functions inside an appropriate energy window $W$ can be expanded over the Bloch basis set as

$$|\chi^\nu_{\mathbf{k},m}\rangle = \sum_{\nu \in W} \langle \psi^\nu_{\mathbf{k},\nu}| \psi^\alpha_{m}\rangle |\psi^\nu_{\mathbf{k},\nu}\rangle,$$

where $\alpha$ indicates the correlated atom, $\nu$ is the band index, $\sigma$ is the spin index, and $m$ is the orbital index. Here, $|\psi^\nu_{\mathbf{k},\nu}\rangle$ is the Bloch eigenfunction in the augmented plane wave basis and

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the correlated orbital \(|\chi_i^{a,\sigma}\rangle\) is given as \(|\chi_i^{a,\sigma}\rangle = |u_i^{a,\sigma}(E_i)Y^l_m\rangle\) within the muffin-tin sphere, where \(E_i\) are chosen linearization energies, \(u_i^{a,\sigma}\) is the radial wave function, and \(Y^l_m\) is the spherical harmonic function. The orthonormalized projector operators for the DMFT and DCA self-consistent equations are calculated by

\[
P_{m',m}^{\sigma,\sigma'}(k) = \sum_{\alpha,\alpha'} \langle u_{l}^{\alpha,\alpha'}(E_i)Y^l_m | \psi_{k,v}^{\alpha} | O(k,\sigma) \rangle^{-1/2} \langle \tilde{\chi}_{m',m}^{\alpha,\sigma'} \rangle_{k,\alpha},
\]

where \(O(k,\sigma|\tilde{\chi}_{m',m}^{\alpha,\sigma'}\rangle\) is the overlap function, which is given as

\[
O(k,\sigma|\tilde{\chi}_{m',m}^{\alpha,\sigma'}\rangle = \sum_{\nu\in W} \langle \chi_{m',m}^{\alpha,\sigma}\rangle_{\nu,\nu} | \psi_{k,v}^{\alpha} | \chi_{m,m}^{\sigma,\sigma'}\rangle.
\]

For the LDA + DCA self-consistency procedure, the lattice Green’s function is given as

\[
G_{v,v'}^\sigma(k + \hat{k}, i\omega_n) = \frac{1}{i\omega_n - \mu - \Sigma_{v,v'}^\nu(k + \hat{k}, i\omega_n) - \Sigma_{v,v'}^\nu(k + \hat{k}, i\omega_n)},
\]

where we have defined \(k = K + \hat{k}\) with \(K\) being the cluster momenta and \(\hat{k}\) running over each Brillouin zone (BZ) sector. \(\omega_n\) is the Matsubara frequency, \(\mu\) is the chemical potential, \(\Sigma_{v,v'}^\nu(k + \hat{k}, i\omega_n)\) are the Kohn-Sham (KS) eigenvalues, and \(\Sigma_{v,v'}^\nu(k + \hat{k}, i\omega_n)\) is the lattice self-energy, which is calculated as an expansion of the cluster self-energy over the Bloch basis:

\[
\Sigma_{v,v'}^\nu(k + \hat{k}, i\omega_n) = \sum_{a,m,m'} P_{a,m}^{\sigma,\sigma'}(k + \hat{k}) \times \Delta \Sigma_{v,v'}^\nu(\hat{k}, i\omega_n) P_{a,m}^{\sigma,\sigma'}(k + \hat{k})\]

From the self-energy we need to subtract the contribution to correlations that is already included in the LDA calculation, commonly called double counting (DC) correction,

\[
\Delta \Sigma_{v,v'}^\nu(\hat{k}, i\omega_n) = \Sigma_{v,v'}^{imp}(\hat{k}, i\omega_n) - \Sigma_{v,v'}^{dc}(\hat{k}, i\omega_n),
\]

where \(\Sigma_{v,v'}^{imp}(\hat{k}, i\omega_n)\) is calculated by the continuous time quantum Monte Carlo (CT-QMC) cluster solver and the Dyson’s equation. Calculating the DC correction is not possible exactly, but some approximate expressions have been introduced. Here, we use as the double counting correction

\[
\Sigma_{v,v'}^{dc}(\hat{k}, i\omega_n) = \delta_{m,n} \left[ U' \left( N_c - \frac{1}{2} \right) - J \left( N^\uparrow - \frac{1}{2} \right) \right],
\]

where \(U' = U - 2J\), \(U\) is the on-site Coulomb interaction, \(J\) is the Hund’s coupling, and \(N_c\) and \(N^\uparrow\) denote the number of total occupied states and spin-resolved occupied states in the correlated orbitals, respectively.\(^{48}\) The local cluster Green’s functions are given as

\[
G_{m,m}^{\sigma,loc}(k, i\omega_n) = \sum_{k',v'} P_{m,m'}^{\sigma,\sigma'}(k + \hat{k}) \times \Delta \Sigma_{v,v'}^{imp}(\hat{k}, i\omega_n) P_{m,m'}^{\sigma,\sigma'}(k + \hat{k}),
\]

where the summation over \(\hat{k}\) is calculated in each Brillouin-zone sector. The LDA + DCA self-consistency condition states that these local cluster Green’s functions, Eq. (8), have to be equal to the impurity Green’s functions as calculated by CT-QMC. The DMFT update of the Weiss field is given by the Dyson’s equation as

\[
\left[ G_{m,m}^{\sigma,0}(k, i\omega_n) \right]^{-1} = \Sigma_{m,m'}^{imp}(k, i\omega_n) + \left[ G_{m,m}^{\sigma,loc}(k, i\omega_n) \right]^{-1}.
\]

B. Many-body interactions and CT-QMC algorithm

In order to describe the electronic behavior of SrVO\(_3\) one has to consider the multiorbital Hubbard Hamiltonian where the interaction term is given by

\[
H_I = U \sum_{m} n_{m}^{\uparrow} n_{m}^{\downarrow} + \sum_{m<n,\sigma} \left[ U' n_{m\sigma} n_{n\bar{\sigma}} + (U' - J) n_{m\sigma} n_{m\bar{\sigma}} \right] - J' \sum_{\sigma} \sum_{m<n,\sigma} \left[ c_{m\sigma}^\dagger c_{m\bar{\sigma}} c_{n\bar{\sigma}} c_{n\sigma} - J' \sum_{\sigma} c_{m\sigma}^\dagger c_{m\bar{\sigma}} c_{n\bar{\sigma}} c_{n\sigma} \right],
\]

and \(m,n\) denote the \(t_2g\) orbitals. In order to solve this model we employ a weak-coupling CT-QMC algorithm. While the weak-coupling CT-QMC algorithm can easily treat a multiple number of sites in the cluster, it is difficult to deal with the full rotationally invariant form of the interaction Hamiltonian due to the fermionic sign problem, in contrast to the strong-coupling CT-QMC algorithm.\(^{49,50}\) Therefore in what follows we shall consider a simplified Hubbard model where the spin-flip and pair-hopping terms in Eq. (10) are neglected (\(J' = 0\)).

The main idea of the weak-coupling CT-QMC method is to divide the total action \(S\) into an unperturbed term \(S_0\) and the interaction term \(I\) which is expanded in a Taylor series. The partition function is rewritten as

\[
\mathcal{Z} = \sum_\mathcal{Z} Z_0 \int d\tau_1 \cdots d\tau_k \int D[c, \tilde{c}] \times \langle n^{\uparrow}_{l_1} c^{\dagger}_{l_2} n^{\uparrow}_{l_3} c^{\dagger}_{l_4} \cdots n^{\uparrow}_{l_k} c^{\dagger}_{l_k} (\tau_k) \rangle,
\]

where \(\langle n^{\uparrow}_{l_1} c^{\dagger}_{l_2} n^{\uparrow}_{l_3} c^{\dagger}_{l_4} \cdots n^{\uparrow}_{l_k} c^{\dagger}_{l_k} (\tau_k) \rangle\) is determined by the noninteracting Green’s function and Wick’s theorem, \(k\) is the perturbation order, \(Z_0 = \text{Tr}(T e^{-S_0})\) corresponds to the unperturbed term, and \(l, l', \text{ and } t_k\) are randomly sampled. \(I\) is given as

\[
I = \bar{U} \beta N M (2M - 1),
\]

where \(\beta\) is the inverse temperature, \(N\) and \(M\) are the number of sites and the number of orbitals in the cluster, respectively, and \(\bar{U}\) is one of \(U, U',\) or \(U' - J\) depending on the operators considered in the random walk in the average \(\langle \cdot \cdot \cdot \rangle\) in Eq. (11). The impurity Green’s functions are calculated by numerically averaging Eq. (11).

III. RESULTS

SrVO\(_3\), which is thought to be a prototypical paramagnetic correlated metal with intermediate electron-electron interactions, has served in the past as a testing ground for numerous newly developed LDA + DMFT approaches.\(^{31-35,38}\) In SrVO\(_3\), the V 3d\textsuperscript{3} orbitals are split by the crystal field into triply degenerate \(t_{2g}\) and doubly degenerate \(e_{g}\) states. The LDA calculations show that the degenerate \(t_{2g}\) states of V form bands crossing the Fermi level which are well separated from the \(e_{g}\) bands.
the BZ sectors are constant. In real space, the on-site and nearest-neighbor-site Green’s functions are extended the LDA + DMFT solution to LDA + DCA approaches, with \( U = 4.0 \text{ eV}, J = 0.65 \text{ eV}, \) and \( T = 0.1 \text{ eV} \). The density of states \( \rho(\omega) \) for LDA + DCA is calculated by \( \rho(\omega) = \frac{1}{\pi} [A(K_0,\omega) + A(K_1,\omega)] \), with \( K_0 = (0,0,0) \) and \( K_1 = (\pi,\pi,\pi) \) sectors. Both on-site and nearest-neighbor-site Green’s functions are inserted into the CT-QMC impurity solver, and the LDA + DCA self-consistency is achieved by Eqs. (8) and (9).

For our calculations on SrVO\(_3\), we chose the energy window \( W \) from \(-1.35 \) to \( 2.0 \text{ eV} \) for the \( t_{2g} \) orbitals which can then be effectively described by the degenerate three-orbital Hubbard model in Eq. (10). We first reproduced the results of LDA + DMFT from Ref. 31, considering a temperature \( T = 0.1 \text{ eV} \) and the same Coulomb interaction \( U = 4.0 \text{ eV} \), and Hund’s rule coupling \( J = 0.65 \text{ eV} \). In the next step, we extend the LDA + DMFT solution to LDA + DCA with two sites in the cluster \( N = 2 \). Within the DCA method, \( N = 2 \) implies that we have two BZ sectors and the self-energies in the BZ sectors are constant.

The BZ of SrVO\(_3\) has cubic symmetry and the self-energies in the cluster momenta \( K_0 = (0,0,0) \) and \( K_1 = (\pi,\pi,\pi) \) are calculated in the BZ sectors shown in Figs. 1(a) and 1(b). In real space, the on-site and nearest-neighbor-site Green’s functions are \( G_{R=0}(i\omega_n) = \frac{1}{2}[G_{K_0}(i\omega_n) + G_{K_1}(i\omega_n)] \) and \( G_{R=1}(i\omega_n) = \frac{1}{2}[G_{K_0}(i\omega_n) - G_{K_1}(i\omega_n)] \), respectively. Here, the DCA formalism with \( N = 2 \) for cubic lattice has been clearly presented in Ref. 51. Both on-site and nearest-neighbor-site Green’s functions are inserted into the CT-QMC impurity solver, and the LDA + DCA self-consistency is achieved by Eqs. (8) and (9).

The spectral functions \( \rho(\omega) \) for the vanadium \( t_{2g} \) orbitals obtained within the LDA + DCA, \( \rho(\omega) = A(\omega) \) and LDA + DCA, \( \rho(\omega) = \frac{1}{\pi} [A(K_0,\omega) + A(K_1,\omega)] \), with \( K_0 = (0,0,0) \) and \( K_1 = (\pi,\pi,\pi) \) sectors. Both on-site and nearest-neighbor-site Green’s functions are inserted into the CT-QMC impurity solver, and the LDA + DCA self-consistency is achieved by Eqs. (8) and (9).

In Figs. 2(b) and 2(c) we present the spectral functions for the \( K_0 = (0,0,0) \) and \( K_1 = (\pi,\pi,\pi) \) sectors within LDA and LDA + DCA. The new features obtained in LDA + DCA are a broad peak around \( 1.5 \text{ eV} \) and a coherent peak around \( 0.2 \text{ eV} \) below \( E_F \). LDA results [see Fig. 2(b)] as well as the new features of the LDA + DMFT results [see also Fig. 2(a)] exhibit neither a broad peak nor a clear coherent peak below \( E_F \). Recent angle-resolved photoemission (ARPES) experiments,\(^{34,36}\) have observed, in fact, a broad peak around \( 1.5 \text{ eV} \) and a coherent peak around \( 0.4 \text{ eV} \) below \( E_F \).
that our LDA + DCA estimates give a slightly smaller mass enhancement than LDA + DMFT estimates with a larger error bar. Both sets of results are in accordance with ARPES estimates of $m^*/m \approx 1.8 \pm 0.2$.

IV. CONCLUSIONS

In conclusion, we have presented an implementation of the LDA + DCA method within the linear augmented plane wave framework. We have compared our benchmark results on SrVO$_3$, which is modeled in terms of a three-band Hubbard Hamiltonian, with earlier LDA + DMFT calculations as well as experimental data. Since the LDA + DCA approach considers both local quantum as well as short-range spatial fluctuations, it offers a more complete description of correlated materials compared to the LDA + DMFT approach, where only local quantum fluctuations are taken into account.

Unlike the LDA + DMFT, the LDA + DCA approach reproduces both coherent and broad peaks for SrVO$_3$ below the Fermi level, observed in angle integrated photoemission experiments. The analysis of the spectral functions at $K_0 = (0,0,0)$ and $K_1 = (\pi,\pi,\pi)$ reveals the source of these peaks. While the broad peak is due to the spectral function in the $K_0 = (0,0,0)$ sector, the coherent peak has its origin in the spectral function at the $K_1 = (\pi,\pi,\pi)$ sector. We also observe a metallic and a band insulating state at the $K_0 = (0,0,0)$ and $K_1 = (\pi,\pi,\pi)$ sectors, also present in the LDA results.

In summary, we believe that the presented LDA + DCA approach is very promising and can be applied to a large variety of multiorbital correlated compounds at different fillings.

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