Dynamical mean-field theory on the real-frequency axis: 
P-d hybridization and atomic physics in SrMnO₃

Daniel Bauernfeind,¹,∗ Robert Triábl,¹ Manuel Zingl,¹,² Markus Aichhorn,¹ and Hans Gerd Evertz¹,3
¹Institute of Theoretical and Computational Physics, Graz University of Technology, Graz 8010, Austria
²Center for Computational Quantum Physics, Flatiron Institute, New York, New York 10010, USA
³Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106, USA

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We investigate the electronic structure of SrMnO₃ with density functional theory plus dynamical mean-field theory (DMFT). Within this scheme the selection of the correlated subspace and the construction of the corresponding Wannier functions is a crucial step. Due to the crystal-field splitting of the Mn-3d orbitals and their separation from the O-2p bands, SrMnO₃ is a material where on first sight a three-band d-only model should be sufficient. However, in the present work we demonstrate that the resulting spectrum is considerably influenced by the number of correlated orbitals and the number of bands included in the Wannier function construction. For example, in a d-dp model we observe a splitting of the t₂g lower Hubbard band into a more complex spectral structure, not observable in d-only models. To illustrate these high-frequency differences we employ the recently developed fork tensor product state (FTPS) impurity solver, as it provides the necessary spectral resolution on the real-frequency axis. We find that the spectral structure of a five-band d-dp model is in good agreement with PES and XAS experiments. Our results demonstrate that the FTPS solver is capable of performing full five-band DMFT calculations directly on the real-frequency axis.

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I. INTRODUCTION

The combination of density functional theory (DFT) and dynamical mean-field theory (DMFT) has become the workhorse method for the modeling of strongly correlated materials [1–3]. For DMFT, a (multiorbital) Hubbard model is constructed in a selected correlated subspace, which usually describes the valence electrons of the transition-metal orbitals in a material. An adequate basis for these localized orbitals are projective Wannier functions [4,5]. In contrast to the Bloch wave functions, these functions are localized in real space, and therefore provide a natural basis to include local interactions as they resemble atomic orbitals and decay with increasing distance from the nuclei. However, the selection of the correlated subspace itself and the Wannier function construction are not uniquely defined.

In the present work, we use SrMnO₃ to analyze the differences of some common models. This perovskite is an insulator [6] with a nominal filling of three electrons in the Mn 3d shell. There are various works concerning its electronic structure, both on the experimental [7–12] as well as on the theoretical side [13–16]. For the construction of the correlated subspace, we explicitly identify the following meaningful cases: The first is a three orbital model for the t₂g states only. For the second choice, usually denoted as d-dp model, the transition metal 3d states and the oxygen 2p states are considered in the Wannier function construction, but the Hubbard interaction is only applied to the 3d states. The correlated subspace is then affected by the lower-lying oxygen bands due to hybridizations. In both cases, the full 3d manifold can be retained by including the eg orbitals in genuine five orbital models.

To assess the consequences of the different low-energy models, a good resolution of the spectral function on the real-frequency axis is beneficial. Due to its exactness up to statistical noise, continuous time quantum Monte Carlo (CTQMC) is often used as a DMFT impurity solver [17–19]. However, when using a CTQMC impurity solver, an analytic continuation is necessary, which results in spectral functions with a severely limited resolution at higher frequencies [20]. This can make it difficult to judge the influence of the choices made for the correlated subspace. In the present paper, we therefore employ the real-frequency fork tensor product state (FTPS) solver [20]. This recently developed zero-temperature impurity solver was previously applied to SrVO₃, making it possible to reveal an atomic multiplet structure in the upper Hubbard band [20]. This observation of a distinct multiplet structure in a real-material calculation is an important affirmation of the atom-centered view promoted by DMFT.

The present work also serves as a deeper investigation of the capabilities of the FTPS solver. We show that the FTPS solver can be applied to d-dp models, leading to insight into the interplay of the atomic physics of the transition metal impurity and hybridization effects with the oxygen atoms as a natural extension to the atom-centered view. Furthermore, the physics of SrMnO₃ is different from SrVO₃, since the manganate is an insulator, and thus it constitutes a challenge for the FTPS solver. While we presented a proof of concept for FTPS on a simple five-band model before [20], we now perform full five-band real-frequency DFT+DMFT calculations for both d-only and d-dp models.
We find that the choices made for the correlated subspace strongly affect the resulting spectral function and its physical interpretation. Additionally, we show that the interplay of atomic and hybridization physics can already be found in very simple toy models.

This paper is structured as follows. In Sec. II we discuss the methods employed, namely DFT, the different models obtained from different Wannier constructions, DMFT, and the impurity solvers used. Section III focuses on the results of the DMFT calculations and the underlying physics of these different models. This knowledge will then be used in Sec. IV to compare the spectral function to experiments by Kim et al. [12].

II. METHOD

A. DFT and Wannier basis

We start with the DFT density of states (DOS) from a non-spin-polarized DFT calculation for SrMnO$_3$ in the cubic phase (shown in Fig. 1). The calculation was performed with WIEN2K [21], using 969 $k$ points in the irreducible Brillouin zone and a lattice parameter of $a = 3.768$ Å. Around the Fermi energy $E_F$, SrMnO$_3$ has the characteristic steeplelike-shaped DOS, stemming from the Mn-$t_{2g}$ bands with a bit of O-$p_{xy}$ contribution. Below $-2.0$ eV, the DOS is mainly determined by oxygen bands which also exhibit manganese hybridizations. With the exception of some additional weight below $-5.0$ eV, the Mn-$e_g$ states lie mainly in the energy range from 0.0 eV to 5.0 eV.

In this work we use projective Wannier functions, where an energy interval has to be chosen as a projection window [4,5]. The bands around $E_F$ have mainly $t_{2g}$ character, suggesting a selection of only a narrow energy window for the Wannier function construction ($-2.0$–$0.82$ eV). We call this set of projective Wannier functions the three-band $d$-only model. However, the $t_{2g}$ orbitals also show a considerable hybridization with the O-$2p$ states below $-2$ eV, and hence, one might want to enlarge the projective energy window by setting its lower boundary to $-10$ eV. We refer to this model as the three-band $d$-$d$-$p$ model.

At the same time, we realize that also the $e_g$ orbitals are not entirely separated from the $t_{2g}$ orbitals in energy and that they have even some weight around $E_F$ (see middle graph of Fig. 1). These states lie directly above $E_F$ and therefore their influence on the resulting spectrum needs to be checked. One should then use a window capturing five bands, the $e_g$ and $t_{2g}$, as a correlated subspace (from $-2$ to 5 eV). This is a five-band $d$-only model. Note that empty orbitals do not pose a problem for the FTPS solver. Like before, we can again enlarge the energy window to include the oxygen hybridization ($-10$–$5$ eV). We denote this model as the five-band $d$-$d$-$p$ model.

In total, we end up with four different choices. The settings for these four models are summarized in Table I. All of them are justified, have different descriptive power, and have been employed in various DFT+DMFT calculations for SrMnO$_3$ [13,14,16].

B. DMFT

Once the correlated subspace is defined, we use DMFT [2,3,22,23] to solve the resulting multiband Hubbard model. As interaction term we choose the 5/3-band Kanamori Hamiltonian [24,25]. Within DMFT, the lattice problem is mapped self-consistently onto an Anderson impurity model (AIM) with

![Figure 1](image-url)

**FIG. 1.** Top: Total DFT-DOS for SrMnO$_3$. Middle: partial Mn-3$d$ DOS. Bottom: partial O-$2p$ DOS for SrMnO$_3$. Below approximately $-1.5$ eV, the band structure consists of oxygen bands that have mostly $p$ character but also have some $e_g$ and $t_{2g}$ weight due to hybridizations. The $t_{2g}$ bands are located around the Fermi energy from $-1.5$ eV to about 0.5 eV, which have small $p$ character. Directly above the Fermi energy and partly overlapping with the $t_{2g}$ bands we find the $e_g$ bands that have small $p$ contributions as well.

the Hamiltonian

$$H = H_{\text{loc}} + H_{\text{bath}},$$

$$H_{\text{loc}} = \sum_{m\sigma} \epsilon_m n_{m\sigma} + H_{\text{DD}} + H_{\text{SF-PH}},$$

$$H_{\text{DD}} = U \sum_m n_{m\uparrow} n_{m\downarrow} + (U - 2J) \sum_{m' > m, \sigma} n_{m\sigma} n_{m'\bar{\sigma}} + (U - 3J) \sum_{m' > m, \sigma} n_{m\uparrow} n_{m'\downarrow},$$

$$H_{\text{SF-PH}} = J \sum_{m' > m} (c_{m\uparrow}^\dagger c_{m'\downarrow}) (c_{m'\uparrow}^\dagger c_{m\downarrow} + \text{H.c.}) + J \sum_{m' > m} (c_{m\uparrow}^\dagger c_{m'\downarrow}^\dagger c_{m'\uparrow} c_{m\downarrow} + \text{H.c.}),$$
TABLE I. Summary of models with their projective energy windows and the parameters used in the FTPS solver: number of bath sites \(N_B\), Fourier transform broadening \(\eta_{FT}\), truncated weight \(t_w\), and maximal bond dimension allowed for the links between impurities as well as for the links between an impurity and the first bath tensor. We keep at most this number of states and increase \(t_w\) if needed. The number in brackets is the maximal bond dimension during ground state search, while the first number is used for the time evolution. The bath links were not restricted to any maximal bond dimension. The FTPS time evolution is performed up to \(t_{\text{max}}\), given in eV\(^{-1}\).

<table>
<thead>
<tr>
<th>Model</th>
<th>Window (eV)</th>
<th>Comments</th>
<th>(N_B)</th>
<th>(\eta_{FT})</th>
<th>(t_w)</th>
<th>Bond dim.</th>
<th>(t_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-band (d) only</td>
<td>−2.0−0.82</td>
<td>Only major (t_2) weight around (E_F)</td>
<td>79</td>
<td>0.08</td>
<td>(5 \times 10^{-9})</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>Five-band (d) only</td>
<td>−2.0−5.0</td>
<td>Include (\epsilon_f), neglect hybridizations</td>
<td>49</td>
<td>0.15</td>
<td>(1 \times 10^{-8})</td>
<td>200 (150)</td>
<td>12.0</td>
</tr>
<tr>
<td>Three-band (d-dp) model</td>
<td>−10.0−5.0</td>
<td>Include hybridized (t_2) weight on oxygen bands</td>
<td>59</td>
<td>0.1</td>
<td>(1 \times 10^{-8})</td>
<td>450 (150)</td>
<td>14.0</td>
</tr>
<tr>
<td>Five-band (d-dp) model</td>
<td>−10.0−5.0</td>
<td>(t_2) and (\epsilon_f) bands with hybridizations</td>
<td>49</td>
<td>0.2</td>
<td>(1 \times 10^{-8})</td>
<td>200 (150)</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\[
H_{\text{bath}} = \sum_{m\sigma} \epsilon_m n_{m\sigma} + V_{\text{ml}}(c_{m\sigma}^\dagger c_{m\sigma} + \text{h.c.}) + H_c. \tag{1}
\]

Here, \(c_{m\sigma}^\dagger\) (\(c_{m\sigma}\)) creates (annihilates) an electron in orbital \(m\), with spin \(\sigma\) at site \(l\) (site zero is the impurity), \(n_{m\sigma}\) are the corresponding particle number operators. \(\epsilon_m\) is the orbital dependent on-site energy of the impurity and \(\epsilon_m\) as well as \(V_{\text{ml}}\) are the bath on-site energies and the bath-impurity hybridizations, respectively.

The interaction part of Hamiltonian (1), \(H_{\text{DD}} + H_{\text{SF-PH}}\), is parametrized by a repulsive interaction \(U\) and the Hund’s coupling \(J\). For each of the models presented in Table I, we choose these parameters \textit{ad hoc} in order to obtain qualitatively reasonable results. In addition, for the full five-band \(d-dp\) model we also estimate them quantitatively via a comparison to an experiment.

Within DFT+DMFT, a so-called double counting (DC) correction is necessary, because part of the electronic correlations are already accounted for by DFT. For general cases, exact expressions for the DC are not known, although there exist several approximations [26–29]. In the present work we use the fully localized-limit (FLL) DC [Eq. (45) in Ref. [30]]. When needed, we adjust it to account for deviations from the true, unknown DC. Note that in the \(d\)-only models, the DC is a trivial energy shift that can be absorbed into the chemical potential [28], which is already adjusted to obtain the correct number of electrons in the Brillouin zone. This step, as well as all other interfacing between DFT and DMFT, is performed using the TRIQS/DFTTOOLS package (v1.4) [5,31–33].

C. CTQMC + MaxEnt

We compare some of our results to CTQMC data at an inverse temperature of \(\beta = 40\) eV\(^{-1}\) obtained with the TRIQS/CTHYB solver (v1.4) [17,34]. We calculate real-frequency spectra with an analytic continuation using the freely available \(\Omega\)-MaxEnt implementation of the maximum entropy (MaxEnt) method [35]. However, the analytic continuation fails to reproduce high-energy structure in the spectral function, as we have shown in Ref. [20] in the example of SrVO\(_3\). This is especially true when the imaginary-time Green’s function is subject to statistical noise, which is inherent in Monte Carlo methods.

There are in general two quantities for which one can perform the analytic continuation. First, one can directly calculate the real-frequency impurity Green’s function from its imaginary time counterpart (as done in Fig. 7). Second, one can perform the continuation on the level of the impurity self-energy [36] and then calculate the local Green’s function of the lattice model (as done in Fig. 8). In the latter case, the DFT band structure enters on the real-frequency axis, which increases the resolution of the spectral function.

D. FTPS

For all models studied we employ FTPS [20]. This recently developed impurity solver uses a tensor network geometry which is especially suited for AIMs. The first step of this temperature \(T = 0\) method is to find the absolute ground state including all particle number sectors with DMRG [37]. Then the interacting impurity Green’s function is calculated by real-time evolution. Since entanglement growth during time evolution prohibits access to arbitrary long times [38], we calculate the Green’s function up to some finite time (see Table I) and predict the time series using the linear prediction method [20,39] up to times \(O(100\) eV\(^{-1}\)). The linear prediction could potentially produce artifacts in the spectrum, and therefore we always make sure that every spectral feature discussed in this work is already present in the finite-time Green’s function without linear prediction.

The main approximations that influence the result of the FTPS solver are the broadening \(\eta_{FT}\) used in the Fourier transform [40], and the truncation of the tensor network [20]. The former corresponds to a convolution with a Lorentzian in frequency space making its influence predictable, while the truncation can be controlled by including more states. This control over the approximations allows us to analyze spectral functions in greater detail than what would be possible with CTQMC+MaxEnt. The parameter values for our FTPS calculations are listed in Table I.

Note that we choose \(\eta_{FT}\) larger than in our previous work [20]. The reason for doing this is twofold: First, some of the calculations we show in this work have a large bandwidht, which lowers the energy resolution if we keep the number of bath sites fixed. Second, FTPS uses a discretized bath to represent the continuous noninteracting lattice Green’s function \(G^0\). When calculating the self-energy \(\Sigma = G^0 - G^{-1}\), we can either use the discretized version of \(G^0\) or the continuous one, \(G^0\). In this work we choose \(G^0\), which is formally the correct choice. This then requires us to use a larger broadening to obtain causal self-energies that do not show finite discretization effects from inverting \(G^0\). However, when calculating the final impurity spectral function shown in all figures, we employ
a very small broadening of $\eta_{FT} = 0.01$ eV in order to obtain optimal resolution.

The real-frequency approach of FTPS allows us to resolve spectral features with higher precision than CTQMC+MaxEnt. This is especially true for high-energy multiplets. On the other hand, with FTPS and real-time evolution it is difficult to obtain perfect gaps, since the results are less precise at small $\omega$, encoded in the long-time properties of the Green’s function which we obtain only approximately using linear prediction [39].

With FTPS we calculate the greater and lesser Green’s functions separately [20]. Since the greater (lesser) Green’s function has no contribution at $\omega < 0 (\omega > 0)$ we restricted the contributions of the calculated Green’s functions in frequency space.

III. RESULTS

A. $d$-only models

First we focus on $d$-only calculations using a projective energy window with a lower energy boundary of $-2.0$ eV for the Wannier-function construction, neglecting the occupied Mn-3$d$ weight at lower energies (see Table I and the middle graph of Fig. 1). With this choice of the correlated subspace, the occupation of the $e_g$ orbitals is nearly zero and the three degenerate $t_{2g}$ orbitals are half filled.

Three-band calculation

Considering only the $t_{2g}$ subspace, the resulting impurity spectral function (Fig. 2) is gapped for the chosen interaction values. The peaks of the lower and upper Hubbard bands are separated by $5.0$ eV in energy, which is roughly $U + 2J = 5.2$ eV, as expected from atomic physics [41].

Contrary to SrVO$_3$, where a distinct three-peak multiplet structure in the upper Hubbard band is present [20], both SrMnO$_3$ Hubbard bands show only one dominant peak. The structure observed in SrVO$_3$ was well explained by the atomic multiplets of the interaction Hamiltonian $H_{\text{soc}}$ in Eq. (1) for a ground state with one electron occupying the $t_{2g}$ orbitals. The absence of such an atomic multiplet structure in this model for SrMnO$_3$ can be understood in a similar way: The large Coulomb repulsion in combination with Hund’s rules (due to the density-density interaction strengths $U$, $U - 2J$, and $U - 3J$) lead to a ground state $|\psi_0\rangle$ which consists mostly of the states $|\uparrow, \uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow, \downarrow\rangle$ on the impurity. Adding a particle, when calculating the Green’s function, produces a single double occupation, e.g., $c_{1 \downarrow}^\dagger |\psi_0\rangle = |\uparrow, \downarrow, \uparrow, \uparrow\rangle$. This state is an eigenstate of the atomic Hamiltonian, because it is trivially an eigenstate of $H_{\text{DD}}$, and both the spin-flip and pair-hopping terms annihilate this state. Hence, all $t_{2g}$ single-particle excitations from the ground state have the same energy, and as a consequence, only one atomic excitation energy is observed.

Although not included in the low-energy model, the uncorrelated states still need to be taken into account for the single-particle gap of SrMnO$_3$. On the unoccupied side, the onset of the $e_g$ orbitals leads to a reduction of the single-particle gap to about half the size of the $t_{2g}$ gap (see Fig. 2). On the occupied side, depending on $U$ and $J$, either the lower Hubbard band or the O bands (at about $-1.5$ eV) determine the gap size, and thus also the type of the insulating state (Mott or charge transfer insulator [42]). For SrMnO$_3$ to be clearly classified as Mott insulator, $U + 2J < 3.0$ eV would be required. However, it is questionable if the $d$-only picture is correct, as in this case the lower Hubbard band is not influenced by the $t_{2g}/O-2p$ hybridizations between $-6.0$ and $-2.0$ eV (see Fig. 1). We will discuss the effect of these hybridizations in detail in Secs. III B and III C.

Five-band calculation

Next, we add the $e_g$ orbitals to the correlated subspace, which now comprises the full Mn-3$d$ manifold. The resulting impurity spectral functions of the $e_g$ and $t_{2g}$ orbitals are shown in Fig. 3. The $t_{2g}$ spectral weight does not change much compared to the three-band calculation. This is to be expected, because the $e_g$ orbitals remain nearly empty during the calculation of the $t_{2g}$ Green’s function.

![Fig. 2. Three-band $d$-only calculation: $t_{2g}$ correlated spectral function for $U = 4.0$ eV and $J = 0.6$ eV, as well as $e_g$ DFT-DOS. The $t_{2g}$ spectrum shows a Mott insulator at half filling with pronounced lower and upper Hubbard bands.](image1.png)

![Fig. 3. Five-band $d$-only calculation: correlated spectral function of the $e_g$ and the $t_{2g}$ orbitals for $U = 4.0$ eV and $J = 0.6$ eV.](image2.png)
The $e_g$ spectral function, on the other hand, becomes much broader in comparison to the DFT-DOS, showing spectral weight above 4.5 eV. The unoccupied part of the spectrum is encoded in the greater Green’s function, i.e., adding a particle in an $e_g$ orbital to the ground state. If we again assume $|\psi_0\rangle \propto |\uparrow,\uparrow,\uparrow\rangle + |\downarrow,\downarrow,\downarrow\rangle$ as the $t_{2g}$ ground state, we can add a particle to the $e_g$ orbitals either in a high-spin or low-spin configuration:

$$
\epsilon_{\sigma}\psi^{\dagger}_{\sigma\uparrow}|\psi_0\rangle \propto |\uparrow,\uparrow,\uparrow\rangle \otimes |\uparrow,0\rangle + |\downarrow,\downarrow,\downarrow\rangle \otimes |\uparrow,0\rangle.
$$

Using the Kanamori Hamiltonian, the high-spin configuration [first term in Eq. (2)] generates a single atomic excitation energy, while the low-spin configuration [second term in Eq. (2)] leads to two energies (due to the spin-flip terms). According to this atomistic picture, the splitting of the $e_g$ peaks is proportional to Hund’s coupling $J$ (see Fig. 3). Their position relative to the upper $t_{2g}$ Hubbard band is influenced by the crystal-field splitting and $J$. From this clear atomic-like structure we see that even empty orbitals need to be included in the correlated subspace because of correlation effects with other occupied orbitals.

B. Three-band $d$-$dp$ model

In the energy region where the lower Hubbard band is located, we also find $t_{2g}$ weight stemming from the Mn-3d/O-2p hybridization (see the middle plot of Fig. 1). This suggests that those states should be included in the construction of the projective Wannier functions, i.e., a $d$-$dp$ model. In the following we will use the term high-energy spectral weight (HESW) to denote the Wannier function weight on the oxygen bands (located below $-1.5$ eV). The first and most obvious consequence of a larger projective energy window is an increased bandwidth of the Wannier DOS. To obtain a similar insulating behavior as in the $d$-only model we increase $U$ and $J$. Second, now also the DC correction has a nontrivial effect, since it shifts the correlated $t_{2g}$ states relative to the oxygen bands. The $t_{2g}$ weight on the oxygen bands is rather small, which means that the effect of the DC correction on the HESW is equally low. Third, in the three-band $d$-$dp$ model the impurity occupation grows (the exact value depending on $U$ and $J$), changing the character of the ground state to a mix of states with mainly three and four particles on the impurity, while in the three-band $d$-only calculation the occupation of the impurity was three electrons. Due to the increased complexity of the ground state, we expect a richer dependence of the spectrum on the interaction parameters $U$ and $J$.

In Fig. 4 we compare calculations for different values of $J$ (top) and different values of $U$ (bottom). Overall, the spectral functions consist of a (smaller) lower Hubbard band connected to states from the hybridized oxygen bands and an upper steeplelike Hubbard band of similar shape as in the $d$-only calculation. By comparing the two peaks at $-6.0$ and $-8.0$ eV, we observe that they behave differently when changing $U$ or $J$. While the former is only affected by $J$, the latter is not, but shifts with $U$. The resolution of the structure in the lower-Hubbard-band/HESW complex demonstrates the capabilities of the FTPS solver.

The $t_{2g}$ gap grows when increasing either $U$ or $J$, which is a typical sign of Mott physics at half filling [41]. Nevertheless, in the $d$-$dp$ model the gap size increases slowly: when increasing $U$ by 1.0 eV, the gap only grows by about half of that. Considering also the uncorrelated $e_g$ orbitals, we observe that the single-particle gap is not much affected by the interaction values studied. An artificial lowering of the DC correction by $-0.5$ eV, which corresponds to a relative shift in energy between the correlated subspace and the uncorrelated states, also increases the $t_{2g}$ gap (Fig. 5). This growth of the gap is mostly due to a shift of the $t_{2g}$ upper Hubbard band, since the chemical potential is pinned by the $e_g$ bands [43]. The first excitation below $E_F$ has a mix of $t_{2g}$ and O-$p$ character. This indicates that in this model, SrMnO$_3$ is not a pure Mott insulator, but a mixture between Mott and charge-transfer insulator. This classification is consistent with previous results [8,9,11,13].

Let us employ a simple toy model to qualitatively understand this intermediate regime. We use a correlated site coupled to only one noninteracting site:

$$
H = U(n_{0,\uparrow} - 0.5)(n_{0,\downarrow} - 0.5) + \sum_\sigma V_1(c_{0,\sigma}^\dagger c_{1,\sigma} + \text{H.c.}) + \epsilon_1 n_{1,\sigma}.
$$

FIG. 4. Three-band $d$-$dp$ model: spectral functions for different $J$ (top) and different $U$ (bottom). All interaction parameters are given in eV. Upon increasing both parameters the gap increases. Changing $J$ shifts the peak at around $-6.0$ eV, while changing $U$ only shifts the one at $-8.0$ eV.

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$$

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The occupation of the local Green’s function. The occupation of all other figures, in this plot we show the spectrum of the correlated 5.0 eV and that it does not cross the on-site energy to the lower Hubbard band for small values of 

The purpose of the noninteracting site is to mimic the effect of the HESW. We set the on-site energy to $U = 1.5$ eV (full lines). The atomic excitation spectra of this model 

(i) The peak highest in energy (above $e_1$) could be the first (last) peak of the split lower Hubbard band discussed above, and the other approaches $e_1$ from below, with diminishing weight.

(ii) The peak lowest in energy shows the opposite behavior. The uncorrelated site repels it towards lower energies and the atomic excitation spectra of this model 

(iii) The excitation at the on-site energy $e_1$ shifts to lower energy and splits under the influence of $U$. Upon increasing $U$, one part develops into the lower Hubbard band discussed above, and the other approaches $e_1$ from below, with diminishing weight.

The DMFT spectral functions (Fig. 4) also show roughly a three-peak structure, where the peaks at about $-1.5$ eV ($-8.0$ eV) could be the first (last) peak of the split lower Hubbard band of our toy model. The region in between then corresponds to the small, middle peak in the toy model stemming from the HESW.

The repulsion of the first peak explains why increasing $U$ (Fig. 4, lower graph) has only a relatively weak effect on the size of the gap. On the other hand, effectively shifting the oxygen bands with the DC correction to lower energies (Fig. 5) corresponds to shifting the bath energy $e_1$. This means that the repulsion gets weaker, which explains the growth of the gap. Furthermore, when increasing $U$ we find that the peak highest in energy gets smaller, while spectral weight is transferred to the lowest energy peak, which is also shifted to lower energies (Fig. 4). Additionally, a lowering of the DC correction leads to an opposite behavior, where the first peak below $E_F$ grows at two peaks together form what one could call a split lower Hubbard band.
the expense of the lowest one in energy. Note that the middle region of our DMFT spectrum shows a $J$ dependence (Fig. 4, top), which cannot be explained by a one-orbital toy model. Using a similar toy model with two orbitals and Kanamori interaction, we indeed observe a splitting proportional to $J$ in the spectra (not shown here). Since the effect is small we will refrain from discussing it in more depth.

We emphasize that the close relation between the toy model and the actual impurity Green’s function of SrMnO$_3$ in the $d$-$dp$ model suggests that the HESW has the effect of splitting the lower Hubbard band into two bands; their separation increases with the hybridization strength. Therefore, including the oxygen states in the model strongly influences the size of the gap.

C. Five-band $d$-$dp$ model

From the DFT-DOS in Fig. 1, we see that the $e_g$ orbitals are actually not empty. They possess additional spectral weight at around $-7.0$ eV, stemming from hybridizations with the oxygen bands. Similarly to the previous section where we included hybridizations of $t_{2g}$ and O-2$p$, we now also include the hybridizations of $e_g$ and O-2$p$.

As mentioned at the beginning, only approximations to the DC correction are known. For the present five-band calculation we find that using the FLL DC does not produce a pronounced gap. This can be traced back to the additional hybridizations of $e_g$ with O-2$p$ (see discussion below). Furthermore, the FLL formula is based on five degenerate orbitals. In the case at hand we find an approximately half filled $t_{2g}$ impurity ($\langle n_{t_{2g},0} \rangle \approx 0.5$) and about one electron in total on the $e_g$ part of the impurity ($\langle n_{e_g,0} \rangle \approx 0.2$). One therefore needs to adapt the DC correction to reproduce experimental results. In order to obtain a pronounced gap, we decrease the FLL DC energy by 2.0 eV. Note that it has been argued that very often the FLL-DC is too high [26]. A reduction of the DC can also be accomplished by adjusting $U$ in the FLL formula [13,27]. While we find that the $t_{2g}$ occupation is not much affected by the DC (similar to Fig. 5), its effect on the $e_g$ occupation is much stronger. Without a DC shift, we find $\langle n_{t_{2g},0} \rangle \approx 0.30$, while for a shift by $-2.0$ eV the occupation is $\langle n_{e_g,0} \rangle \approx 0.19$ compared to $\langle n_{e_g,0} \rangle \approx 0.28$ in the DFT calculation.

Figure 7 shows the spectral function of the full five-band $d$-$dp$ calculation with adjusted DC as well as the respective spectral function obtained by a DMFT calculation using CTQMC and performing the analytic continuation for the impurity Green’s function. Overall, the FTPS spectrum is in good agreement with the CTQMC+MaxEnt result. However, FTPS provides a much better energy resolution at high energies, which is especially apparent from the pronounced peak structure in the $e_g$ spectrum.

Instead of calculating the real-frequency spectrum of the impurity Green’s function as in Fig. 7, one can use the analytic continuation for the self-energy $\Sigma(\omega)$, and calculate the local Green’s function of the lattice model directly for real frequencies. This way, the dispersion of the DFT band structure enters on the real frequency axis directly, which increases the resolution of the CTQMC result, but is suboptimal for FTPS [45]. The resulting spectral function for the $e_g$ orbitals is shown in Fig. 8. As expected, we find that some features shown by the FTPS solver are now also present in CTQMC, but the $J$ multiplet in the unoccupied part of the spectrum still cannot be resolved. To calculate the FTPS self-energy, used to obtain the spectrum in Fig. 8, a broadening of $\eta_{FT} = 0.25$ was used, which explains the difference from Fig. 7.

From these comparisons we also see that the sharp, steplike shape of the $e_g$ spectrum at $\varepsilon_F$ is not an artifact of the FTPS solver. We note that for the five-band calculation presented in Fig. 7, FTPS (720 CPU-h) and CTQMC (600 CPU-h) need similar computational effort for one DMFT iteration [46].

The unoccupied part of the total spectrum (sum of the $e_g$ and $t_{2g}$ spectra shown in the bottom plot of Fig. 7) consists of a three peak structure with alternating $e_g$-$t_{2g}$-$e_g$ character, which is much more pronounced than in the five-band $d$-only calculation (Fig. 3). Compared to the three-band $d$-$dp$ model we find differences mainly in the occupied part of the $t_{2g}$ spectral function (Fig. 10). This is especially apparent in the lowest peak, which seems to be shifted from $-9.0$ to $-13.0$ eV. Although this high-energy excitation is small, the FTPS solver can reliably resolve it.
The differences in the position of this peak are again similar to the behavior of a toy model. Here we use a two-orbital AIM with a single bath site for each orbital:

\[
H = H_{\text{int}} + \sum_{m \in \{t_{2g}, e_g\}} E_m n_{0,m} + \sum_{\sigma} V_m (c_{0,m,\sigma} c_{1,m,\sigma} + \text{H.c.}) + \epsilon_m n_{1,m,\sigma}. \tag{4}
\]

For the interaction \( H_{\text{int}} \) we choose the Kanamori Hamiltonian. As before, we use a single bath site for each orbital to mimic the effect of the HESW. We are interested in the influence of the hybridizations of \( e_g \) and \( d-2p \) on the \( t_{2g} \) spectral function. In Fig. 9, we compare the spectrum without \( e_g \)-HESW states (\( V_{e_g} = 0 \)) with the one obtained from \( V_{e_g} = 2V_{1s} \) [47]. Although one would expect the \( e_g \) hybridization to only have a minor influence on the \( t_{2g} \) spectrum, we observe a rather surprising behavior. The additional hybridization leads to a stronger repulsion of the lowest energy peak from the bath energy, qualitatively explaining the shift from \(-9.0\) to \(-13.0\) eV in Fig. 10.

Additionally, this toy model provides an explanation for the necessary adjustment of the DC correction in the five-band calculation: The peak highest in energy in Fig. 9 is repelled more strongly with the additional \( e_g \) hybridizations, therefore the gap decreases. If we would want to obtain a similar \( t_{2g} \) gap as with \( V_{e_g} = 0 \), the interaction in the toy model would need to be increased to \( U \approx 20 \) eV (keeping \( J = U/10 \)). Since this is unphysical, the only other option is to shift the bath site energies of the toy model. In the DMFT calculation this corresponds to a shift in the DC correction, effectively shifting the HESW to lower energies. This behavior can be observed in Fig. 10, where we compare the spectra of the three- and five-band \( d-dp \) models. The onset of the lower-Hubbard-band/HESW complex is exactly at the same position in both spectra, although the DC shift differs by 2.0 eV.

![Image](1)

FIG. 8. Comparison of the \( e_g \) spectral functions of the local lattice Green’s function for the five-band \( d-dp \) model between FTPS and CTQMC+MaxEnt, when the analytic continuation is performed for the self-energy. To obtain the plot with FTPS we used \( \eta_{\text{FTPS}} = 0.25 \). Using the band structure on the real-frequency axis enhances the resolution of the CTQMC result at energies where the imaginary part of the self-energy is small, and increases its agreement with FTPS in the occupied part of the spectral function.

![Image](2)

FIG. 9. Effect of the \( e_g \) hybridizations on the \( t_{2g} \) spectrum of the toy model [Eq. (4)]. Parameters (in eV): \( U = 10.0, J = U/10, E_{t_{2g}} = -U/2, E_{e_g} = -U/2 + 1.0, \epsilon_{t_{2g}} = \epsilon_{e_g} = -5.0, \) and \( V_{1s} = 1.5 \). The grey dashed dotted line shows the bath energy levels. All spectra have been broadened by \( \eta_{\text{FTPS}} = 0.2 \) eV.

IV. COMPARISON TO EXPERIMENT

Equipped with a good understanding of the model-dependent effects on the spectral function, we are finally in a position to compare our results to experiments. Several studies concluded that the unoccupied part of the spectrum consists of three peaks with alternating \( e_g - t_{2g} - e_g \) character [10–12]. As we have shown, with DMFT+FTPS we are able to resolve such a structure when including the \( e_g \) states as correlated orbitals.

![Image](3)

FIG. 10. Comparison of the \( t_{2g} \) spectral functions of the three-band \( d-dp \) and five-band \( d-dp \) calculations at \( U = 6.0 \) eV and \( J = 0.8 \) eV, taken from Figs. 4 and 7. In the five-band calculation we shifted the double counting by \(-2.0 \) eV to increase the gap. The influence of the number of bands is most apparent in the high-energy features. The increased repulsion of the first peak of the lower-Hubbard-band/oxygen complex (Fig. 9) makes a shift in the DC necessary, if the single-particle gap should remain the same.
in a genuine five-band model. Additionally, we need to choose
the energy window, i.e., whether the HESW should be included
in the construction of the projective Wannier functions. The
nature of the insulating state (Mott or charge transfer) has been
debated in the literature [8,9,11,13], but it is likely that SrMnO3
falls in an intermediate regime where a clear distinction is diffi-
cult. In the present work we have come to the same conclusion.
This implies that the lower Hubbard band and the O-2p bands
are not separated in energy, which favors the use of a d-dp
model. We therefore conclude that a five-band d-dp model is
necessary to fully capture the low-energy physics of SrMnO3.

Having decided on the model for the correlated subspace,
we still need to determine the interaction parameters U and J
as well as the DC. To do so we use PES and XAS data for the
Mn-3d orbitals obtained by Kim et al. [12] and compare to
our total impurity spectrum [6Aeg(ω) + 4Aeg(ω) from Fig. 7].
According to Ref. [12], the XAS (PES) spectrum can be
considered to represent the unoccupied (occupied) Mn-3d
spectrum. In the measured spectrum the chemical potential
is in the middle of the gap. In all our calculations, the chemical
determination is potential by the onset of the unoccupied eg
spectrum. However, the absolute position in energy is not
exactly known in XAS [48]. Our calculation is in good
agreement with the experiment when we use a rigid shift of
0.8 eV to lower energies. Additionally, we deduce from the peak positions in the experiment that the
interaction parameters used for the calculations presented in
Fig. 7 are too high. The separation of the two eg peaks (~J)
and also the relative position of the t2g upper Hubbard band
are different than in the experiment. Therefore, we decrease
the interaction parameters to U = 5.0 eV and J = 0.6 eV but
keep the static shift of the FLL DC by ~2.0 eV. Note that these
parameters are similar to the ones used in other DFT+DMFT
studies on SrMnO3 [13,14].

The resulting spectral function for the new set of parameters
is compared to the experimental spectrum in Fig. 11. Notably,
the bandwidths of both the unoccupied and the occupied
spectrum agree very well with the experiment. The unoccupied
part of the experimental spectrum (XAS) shows that the first eg
peak is just a shoulder of the t2g upper Hubbard band, and
that the separation of the two eg peaks is about 3.2 eV, which is in
agreement with our result. Since this separation is proportional
to the Hund’s coupling, we conclude that J ≈ 0.6 eV for this
compound. The t2g upper Hubbard band at 2.0 eV is still
slightly too high in energy.

The experiment also shows a lower-Hubbard-band/oxygen
complex with two main peaks at about ~6.0 eV and ~2.0 eV.
As discussed in the previous sections (bottom plot of Fig. 7),
our results identify the first peak at ~2.0 eV to have mainly
t2g character and to correspond to the largest part of the split
lower Hubbard band, whereas the second peak at ~6.0 eV has both eg and t2g character and stems from the hybridiza-
tions with the oxygen bands. We note that the region be-
tween these two peaks has larger spectral weight in the
experiment than in our calculations. Importantly, no promi-

nent spectral features are observed in the experiment around
~8.0 eV, strengthening our conclusion that the three-band
d-dp model is not sufficient to describe the experiment (see
also Fig. 10).

V. CONCLUSIONS

We have studied the influence of the choice of the correlated
subspace, i.e., the number of bands and the energy window, on
the DFT+DMFT result for the strongly correlated compound
SrMnO3. For d-only models (neglecting p-d hybridizations),
we have shown that the empty eg orbitals should be included
in the correlated subspace because interactions with the half
filled t2g bands affect the spectrum, leading to a multiplet
structure and broadening of the eg DFT-DOS. Including
the Mn-3d/O-2p hybridizations in a three-band model for the
t2g bands only, i.e., the three-band d-dp model, we found
a situation similar to avoided crossing, which leads to an
interesting interplay of atomic physics (lower Hubbard band)
and Mn-d/O-2p hybridizations. In SrMnO3, the lower Hubbard
band hybridizes with the t2g Wannier weight on the oxygen
bands, giving rise to a spectrum that can be approximated
by three peaks. This result provides different perspectives on
an intermediate regime, where both Mott and charge transfer
physics are found. By performing a five-band calculation
including the p-d hybridization, we investigated the effect
of the eg hybridization on the t2g spectrum. The splitting
due to avoided crossing is heavily increased, which strongly
affects the three-peak structure and also decreases the gap.
Equipped with a good understanding of the different correlated
subspaces and the effects of the model parameters (U, J, DC)
we were able to obtain a spectral function in good agreement
with experimental data. We conclude that the choice of a
suitable model for the correlated subspace is important, since
the inclusion of both the O-2p hybridizations and the eg states

![Fig. 11. Photoemission spectroscopy (PES) and x-ray-
absorption spectroscopy (XAS) compared to the five-band
d-dp DMFT-FTPS results (U = 5.0 eV and J = 0.6 eV). The
experimental curves are reproduced from Ref. [12], Fig. 5. We
normalized the experimental curves to ∫ω Aexpdω = ∫ω AFTPSdω and
∫ω AXPsdω. FTPS as well as the experiments show a three-peak structure of alternating e.g - t2g - eg character in
the unoccupied part of the spectrum (indicated by arrows). For
the arrow labels we adopted the notation of Ref. [12], where e↓ is
an excitation into the eg spectrum with majority spin, while t2g and
e↑ are excitations into the t2g and eg spectrum with minority spin [see also Eq. (2)].](115156-9)
is essential for a correct description of the observed spectral function in SrMnO$_3$.

Finally, we would also like to stress that we have shown that FPTS is a viable real-time impurity solver for real material calculations with five bands.

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[6] Although most published works suggest that the compound is insulating, the experimental magnitude of the gap ranges from approximately 1.0 to 2.0 eV; see citations in the main text.
[25] Even for the five-band calculations we choose the Kanamori Hamiltonian over the Slater Hamiltonian [50], because the large number of interaction terms in the latter make a treatment with the FPTS solver more involved.
[40] We Fourier transform with a kernel $e^{i\omega t - \eta \tau}$ [3].
We found that the $e_g$ bands have a very small occupation already in the DFT calculation. This does not change during the DMFT calculations and therefore, the chemical potential is always pinned at the onset of the $e_g$ spectral function.

If we use a larger bath energy $\epsilon_1$, for example $\epsilon_1 = -5.0$ eV, the position of the first peak of the impurity spectrum is proportional to $U$ at small $U$, showing that it is indeed a lower Hubbard band.

To calculate the self-energy, we use the bath parameters to calculate the noninteracting Green’s function. To avoid finite-size effects, we need to use a larger broadening $\eta_{FT}$.

CTQMC used $128 \times 10^6$ measurements and the calculations were performed on the same processors: Intel Xeon E5-2650v2, 2.6 GHz with eight cores.

In the full five-band calculation, the $e_g$ bath spectral function is much larger than the one for the $t_{2g}$ orbitals in the energy region of the oxygen bands, which we mimic by a factor of 2 in $V_{e_g}$.

J. Kang (private communication).
