Multiplet effects in orbital and spin ordering phenomena: A hybridization-expansion quantum impurity solver study

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Orbital and spin ordering phenomena in strongly correlated systems are studied using the local-density approximation + dynamical mean-field theory approach. Typically, however, such simulations are restricted to simplified models (density-density Coulomb interactions, high symmetry couplings and few-band models). In this work we implement an efficient general hybridization-expansion continuous-time quantum Monte Carlo impurity solver (Krylov approach) which allows us to investigate orbital and spin ordering in a more realistic setting, including interactions that are often neglected (e.g., spin-flip and pair-hopping terms), enlarged basis sets (full d versus eg), low-symmetry distortions, and reaching the very low-temperature (experimental) regime. We use this solver to study ordering phenomena in a selection of exemplary low-symmetry transition-metal oxides: LaMnO3 and rare-earth manganites as well as the perovskites CaVO3 and YTiO3. We find that, in all considered cases, the minus sign problem mostly appears when off-diagonal crystal-field terms are present (and is strongly suppressed in the basis of crystal-field states), while off-diagonal terms of the hybridization function matrix are not as critical. We show that spin-flip and pair hopping terms do not affect the Kugel-Khomskii orbital-order melting transition in rare-earth manganites, or the suppression of orbital fluctuations driven by crystal field and Coulomb repulsion. For the Mott insulator YTiO3 we find a ferromagnetic transition temperature TC ∼ 50 K, in remarkably good agreement with experiments. For LaMnO3 we show that the classical t2g-spin approximation, commonly adopted for studying manganites, yields indeed an occupied eg orbital in very good agreement with that obtained for the full d 5-orbital Hubbard model, while the spin-spin eg−t2g correlation function calculated from the full d model is ∼ 0.74, very close to the value expected for aligned eg and t2g spins; the eg spectral function matrix is also well reproduced. Finally, we show that the t2g screening reduces the eg−eg Coulomb repulsion by about 10%.

PACS numbers: 71.10.Fd, 71.10.+w, 71.27.+a, 71.28.+d, 71.30.+h

I. INTRODUCTION

Orbital and magnetic ordering phenomena play a crucial role in the physics of strongly correlated transition-metal oxides. Their onset depends on symmetry, lattice distortions, super-exchange interaction and the form of the Coulomb tensor. The realistic description of ordering phenomena requires the ability of disentangling the effects of all these interactions. In recent years, the local-density approximation + dynamical mean-field theory approach (LDA+DMFT), which combines ab-initio techniques based on density functional theory in the local-density approximation (LDA), and the dynamical mean-field theory (DMFT), has lead to important progress in understanding such ordering phenomena. It has been shown that many-body super-exchange only weakly affects the onset of the orbital-order to disorder transition in rare-earth manganites while, in the presence of strong Coulomb repulsion, a small crystal-field is sufficient to strongly suppress orbital fluctuations and stabilize orbital order. However, the effects of subtle Coulomb interactions, such as spin-flip and pair-hopping terms or of quantum fluctuations, e.g., charge fluctuations between half-filled t2g and eg states in manganites or spin fluctuations, are not yet fully understood, while the origin of very low-temperature magnetism in multi-orbital materials remains little investigated in a realistic context. The hybridization-expansion continuous-time quantum Monte Carlo (CT-HYB) technique appears to date the most promising DMFT quantum impurity solver to study real materials at experimental temperatures, although most calculations so far have been limited to high-symmetry cases or systems for which the hybridization function is diagonal (or almost diagonal) in orbital space.

In the present work we study the effects of commonly adopted approximations on the origin of orbital and magnetic order in some exemplary low-symmetry transition-metal oxides. To do this, we use an efficient general implementation of the CT-HYB quantum Monte Carlo (QMC) LDA+DMFT solver for systems of arbi-
transition-metal oxides is given by

\[ H = - \sum_{i,\alpha,\sigma} \varepsilon_{i\alpha} c_{i\sigma}^\dagger c_{i\sigma} + \frac{1}{2} \sum_{i,\alpha,\alpha',m,m'} U_{m\alpha\sigma}^{m',\alpha'} c_{i\alpha\sigma}^\dagger c_{i\alpha'}^\dagger c_{i\alpha'} c_{i\alpha\sigma} \]  \( (1) \)

Here \( c_{i\sigma}^\dagger \) (\( c_{i\sigma} \)) creates (annihilates) an electron with spin \( \sigma \) in orbital \( m \) on lattice site \( i \); \( t_{i\alpha\sigma}^{m,m'} \) are the hopping integrals and \( \varepsilon_{i\alpha\sigma} \) the elements of the crystal-field matrix, obtained from LDA calculations.

We calculate the ferromagnetic transition temperature \( T_c \) by constructing a localized Wannier-function basis. Finally, in the Appendix we describe the details often adopted to describe \( \text{LaMnO}_3 \) and more general manganites.

The paper is organized as follows. In Section II we briefly discuss the approach in the context of the LDA+DMFT method. In Section III we present applications to rare-earth manganites, vanadates, and titanates. We show that spin-flip and pair-hopping terms do not affect the Kugel-Khomskii orbital-order transition and weakly affect orbital fluctuations in \( 3d^1 \) perovskites. We calculate the ferromagnetic transition temperature for the Mott insulator \( \text{YTiO}_3 \) and find excellent agreement with experiments, showing that orbital order is indeed compatible with ferromagnetism in this material, contrarily to early hypothesis. For \( \text{LaMnO}_3 \) we show that the \( e_g \) two-band Hubbard model commonly used to study the system, in which the \( t_{2g} \) electrons are treated as disordered classical spins interacting with the \( e_g \) spins via the Coulomb interaction, yields results in very good agreement with the full five-orbital \( 3d \) Hubbard model. Remarkably, the agreement is not only excellent for the occupied state in the orbitally ordered phase, but also very good for the orbital resolved \( e_g \) spectral function matrix. Finally, in the Appendix we describe the details of our implementation of the general CT-HYB solver.

II. MODEL AND METHOD

The most general multi-band Hubbard model for transition-metal oxides is given by

\[ H = - \sum_{i,\alpha,\sigma} \varepsilon_{i\alpha} c_{i\sigma}^\dagger c_{i\sigma} + \frac{1}{2} \sum_{i,\alpha,\alpha',m,m'} U_{m\alpha\sigma}^{m',\alpha'} c_{i\alpha\sigma}^\dagger c_{i\alpha'}^\dagger c_{i\alpha'} c_{i\alpha\sigma} \]

III. RESULTS

A. Orbital-order melting in rare-earth manganites

The origin of the orbital-order melting transition in the rare-earth manganites \( \text{RMnO}_3 \) with the \( t_{2g}^{2} e_g^{1} \) nominal electronic configuration has been debated since long. Recently, \( t_{2g}^{2} e_g^{1} \) we have shown that the many-body superexchange interaction plays a small role in determining the orbital-order melting temperature \( T_{OO} \) as well as its trends with decreasing radius of the rare-earth ions. However, spin-flip and pair-hopping terms, neglected in previous calculations, restore the full degeneracy of the \( S = 1 \) multiplet, and could enhance the strength of the super-exchange, or even modify the occupied orbital.
spins approximation for $t_{2g}$ orbitals. In such approximation the effects of the $t_{2g}$ spins ($S_{t_{2g}} = 3/2$) on the $e_g$ states is described through a local magnetic field due to the $e_g$-$t_{2g}$ Coulomb exchange interaction and a bandwidth renormalization factor arising from the spatial disorder in the orientation of the $t_{2g}$ spins. However, charge fluctuations between $t_{2g}$ and $e_g$ states or $t_{2g}$ multiplet fluctuations, not accounted for in such a model, could affect the orbital-order and the occupied orbital. In this section we use our implementation of the CT-HYB QMC solver to analyze these effects.

1. Role of spin-flip and pair-hopping interactions

First we analyze the role of spin-flip and pair hopping interactions on the orbital melting transition. The minimal Hubbard Hamiltonian which is believed to retain the essential physics to study this issue is a two-band Hubbard model for $e_g$ states coupled to disordered $t_{2g}$ spins via the Coulomb interaction, which acts as a local magnetic field $h = J_{t_{2g}} S_{t_{2g}}$. Thus in Hamiltonian (1) the one-electron term becomes

$$
\begin{align*}
\epsilon_{m,m'}^{\sigma} &= (\varepsilon_T \tau_z^{m'} + \varepsilon_T \tau_z^{m}) \delta_{\sigma,\sigma'} - h \sigma_z^m \\
t_{m,m'}^{\sigma\sigma'} &= u_{\sigma,\sigma'} t_{m,m'}^{\sigma\sigma'}.
\end{align*}
$$

The index $m$ runs over the $e_g$ Wannier orbitals $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$, $\tau_z$ is the Pauli $z$ matrix, while $\tau_x$ and $\tau_y$ are pseudospin operators acting on orbital degrees of freedom $(\tau_x |3z^2 - r^2\rangle = 1/2 |3z^2 - r^2\rangle, \tau_x |x^2 - y^2\rangle = -1/2 |x^2 - y^2\rangle, \tau_y |3z^2 - r^2\rangle = |x^2 - y^2\rangle)$. The energies $\varepsilon_T$ and $\varepsilon_T$ yield, respectively, the Jahn-Teller and tetragonal crystal-field splitting. Finally $u_{\sigma,\sigma'} = 2/3$ is a band renormalization factor which accounts for the disorder in the orientations of the $t_{2g}$ spins. For the effective magnetic field $h$, we present calculations for the theoretical estimate $h \sim 1.35$ eV; our results for the orbital-melting transition and the orbital polarization are however weakly dependent on $h$ in the relevant regime, in which $e_g$ and $t_{2g}$ spins are locally aligned. For the $e_g$ basis, the Coulomb interaction is composed of density-density interactions, spin-flip and pair hopping terms. We use the theoretical estimates $U_0 = 5$ eV and $J_{e_g} \sim J \sim 0.76$ eV for the $e_g$ screened direct and exchange on-site Coulomb interaction. In order to calculate the critical temperature due to superexchange only, we set the crystal-field parameters to zero: $\varepsilon_T = \varepsilon_T = 0$. This disentanglement procedure has been proposed in Ref. [7] and was successfully used to study orbital order in cuprates and manganese.

We show in Fig. 1 the results of our calculations based on our CT-HYB QMC solver; we use the Krylov approach for the model with spin-flip and pair hopping terms and the segment method for the model with density-density Coulomb terms only. The figure shows the orbital-order transition temperature due to superexchange only, $T_{KK}$, for relevant elements of the series of rare-earth manganites. This figure demonstrates that the spin-flip and pair hopping terms affect very little the overall trends and even the absolute value of $T_{KK}$. These results all reinforce previous conclusions that superexchange has a small influence in determining the orbital order to disorder transition observed in rare-earth manganites.

2. Classical $t_{2g}$ spins versus full 5-band model for LaMnO$_3$

Next we test the validity of the classical $t_{2g}$ spin approximation for the orbital-order melting transition. To do this, we compare the results of the previous section with those obtained for the full 5-band Hubbard model described by Hamiltonian (1). To study the orbital order due to superexchange only, we again set zero the crystal-field splitting within the $e_g$ doublet and $t_{2g}$ triplet; we retain however the cubic crystal field which splits $t_{2g}$ and $e_g$; finally, we perform the LDA+DMFT calculations at $T \sim 290$ K, i.e., well below $T_{KK}$. Since we have already shown that spin-flip and pair-hopping do not affect the transition temperature, we neglect them here to speed up the calculations. Furthermore, to compare directly the results of the two- and five-band model, we assume $J_{e_g-t_{2g}} \sim h/S_{t_{2g}}$ for the $e_g-t_{2g}$ exchange coupling and neglect other small Coulomb anisotropies. The LDA+DMFT calculation for the five-band model yields half-filled $t_{2g}$ states and almost fully polarized $e_g$ states. The occupied $e_g$ state $|\theta\rangle = \cos \theta |3z^2 - r^2\rangle - \sin \theta |x^2 - y^2\rangle$ is the orbital with $\theta \sim 90^\circ$, in excellent agreement with the results from the classical $t_{2g}$ spins approximation, which gives basically the same state. The spectral func-
We show the occupations $n_i$ of the natural orbitals (with $n_i > n_{i+1}$) at $T = 190$ K in CaVO$_3$ and YTiO$_3$ obtained by diagonalizing the occupation matrix.

### B. Orbital fluctuations and magnetism in CaVO$_3$ and YTiO$_3$

The importance of orbital fluctuations in the physics of 3d$^1$ perovskites has been debated since long. Single-site DMFT calculations have shown that in the presence of crystal-field splitting Coulomb repulsion strongly suppresses orbital fluctuations. However, these conclusions were based on a Hubbard model with density-density Coulomb interactions only. In this section we analyze the effect of the neglected spin-flip and pair-hopping Coulomb interactions. Furthermore, exploiting our efficient CT-HYB solver, we address the issue of the nature of the low temperature (30 K) ferromagnetic transition in YTiO$_3$.

#### 1. Orbital fluctuations

The minimal model to consider for 3d$^1$ transition-metal oxides is a three-band Hubbard model for the $t_{2g}$ bands including spin-flip and pair hopping terms, and with

$$
\begin{align*}
\varepsilon_{m\sigma m'\sigma'} &= \varepsilon_{mm'} \delta_{\sigma,\sigma'} \\
\tilde{t}_{m\sigma m'\sigma'} &= \tilde{t}_{mm'} \delta_{\sigma,\sigma'}
\end{align*}
$$

where $m, m' = xy, xz, yz$. For the Coulomb parameters we use $U_0 = 5$ eV and $J_{t_{2g}} \sim 0.68$ eV (CaVO$_3$) or $J_{t_{2g}} = 0.64$ eV (YTiO$_3$) from theoretical estimates and previous works. Because the local Hamiltonian mixes flavors even in the crystal-field basis, we perform the LDA+DMFT calculations using the Krylov version of our general CT-HYB QMC solver.

In Table I we show the occupations $n_i$ of the natural orbitals at ~190 K in CaVO$_3$ and YTiO$_3$. We find that CaVO$_3$ is a paramagnetic metal with a small orbital polarization. Instead, YTiO$_3$ is a paramagnetic insulator with orbital polarization $p = n_1 - (n_2 + n_3)/2 \sim 1$, i.e. basically full (orbitally ordered state). For this system, the double occupancies at 290 K are small, i.e., we find $\frac{1}{2} \sum_{\sigma \sigma'} \bar{n}_{m\sigma m'\sigma'} \sim 0.015$ for YTiO$_3$. The occupied orbital is $0.611|xy\rangle - 0.056|xz\rangle + 0.789|yz\rangle$. We find occupied state and orbital polarization are basically the same with full Coulomb and density-density approximation. Previous calculations in which spin-flip and pair-hopping terms have been neglected and $T \sim 770$ K are in line with these results. This shows that spin-flip and
pair-hopping terms do not change the conclusion that orbital fluctuations are strongly suppressed in the Mott insulator YTiO$_3$. In the CT-HYB QMC simulations the average sign is $\sim 0.9$ for YTiO$_3$ and $\sim 0.95$ for CaVO$_3$.

2. Ferromagnetism in YTiO$_3$

YTiO$_3$ is one of the few ferromagnetic Mott insulators. Neutron scattering experiments pointed out early on the difficulties in reconciling ferromagnetism and the expected orbital order and there have been suggestions that the ferromagnetic state could rather be associated with a quadrupolar order and large scale orbital fluctuations. However, second-order perturbation theory calculations indicate that ferromagnetism and orbital order could be reconciled, provided that the real crystal-structure of YTiO$_3$, including the GdFeO$_3$-type distortion (tilting and rotation of the octahedra, and deformation of the cation cage) is taken into account. To clarify this point, we check the instability towards ferromagnetism of the three-band $t_{2g}$ Hubbard model obtained for the experimental structure of YTiO$_3$. With this approach we calculate the ferromagnetic transition temperature $T_C$ due to super-exchange alone in the orbitally ordered phase. Since experimentally $T_C \sim 30$ K, we have to perform LDA+DMFT calculations down to very low temperatures, which becomes possible with the CT-HYB QMC solver. On lowering the temperature, we find that the sign problem becomes sizable (average sign $\sim 0.7$ at 40 K). However, we can basically eliminate it (average sign $\sim 0.97$) by performing the LDA+DMFT calculations in the basis which diagonalize the crystal-field matrix, even though the hybridization function has off-diagonal terms of comparable size in the two bases. In Fig. 3 we show the LDA+DMFT magnetization $m(T)$ of the $t_{2g}$ states as a function of the temperature. Remarkably, we find a transition at about 50 K, in excellent agreement with experiments which yield $T_C \sim 30$ K; the overestimation can be ascribed to the mean-field approximation, and to the fact that, since the critical temperature is very small, it is sensitive to tiny details. The occupied orbital does not change significantly in the magnetic phase, indicating that the occupied orbital remains the one that diagonalizes the crystal-field matrix, i.e., in the magnetic phase there is no sizable change of orbital fluctuations due to super-exchange.

IV. CONCLUSIONS

We implement an efficient general version of the continuous-time hybridization expansion (CT-HYB) quantum Monte Carlo solver, which allows us to investigate ordering phenomena in strongly correlated transition-metal oxides in a more realistic setting. Our implementation of CT-HYB QMC works for systems of arbitrary symmetry. In cases where symmetry allows it (i.e., if the local Hamiltonian does not mix flavors) we use the fast segment solver. In more realistic situations we use the Krylov approach and, away from phase transition, trace truncation. We find that in all considered cases the minus sign problem mostly appears when off-diagonal crystal-field terms are present (and is strongly suppressed in the basis of crystal-field states), while off-diagonal terms of the hybridization function matrix are not as critical. We show that spin-flip and pair-hopping terms hardly affect the strength of the super-exchange orbital-order transition temperature in rare-earth manganites. We show that the classical $t_{2g}$ spin approximation for LaMnO$_3$ works excellently, not only for what concerns orbital order, but, surprisingly, also for the overall shape of the spectral function matrix. We show that spin-flip and pair-hopping terms also do not change the conclusion that orbital-fluctuations are strongly suppressed in YTiO$_3$. Furthermore, we calculate the critical temperature for ferromagnetism in the orbitally ordered phase, and find excellent agreement with experiments. This shows that that the predicted orbital order is fully compatible with ferromagnetism.

ACKNOWLEDGMENTS

Calculations were done on the Jülich Blue Gene/Q and Juropa. We acknowledge financial support from the Deutsche Forschungsgemeinschaft through research unit FOR 1346.
Appendix A: General CT-HYB solver

In this appendix we fix the notation and explain the details of our implementation of the general CT-HYB quantum-impurity solver. The DMFT quantum-impurity Hamiltonian is \( H = H_{\text{loc}} + H_{\text{bath}} + H_{\text{hyb}} \), where

\[
H_{\text{loc}} = \sum_{\alpha} \xi_{\alpha\alpha} c_{\alpha}^\dagger c_{\alpha} + \frac{1}{2} \sum_{\alpha \alpha'} \sum_{\alpha} U_{\alpha\alpha'\alpha\alpha'} c_{\alpha}^\dagger c_{\alpha'}^\dagger c_{\alpha'} c_{\alpha},
\]

\[
H_{\text{bath}} = \sum_{\gamma} \epsilon_{\gamma} b_{\gamma}^\dagger b_{\gamma},
\]

\[
H_{\text{hyb}} = \sum_{\gamma} \sum_{\alpha} \left[ V_{\gamma,\alpha} c_{\alpha}^\dagger b_{\gamma} + \text{h.c.} \right].
\]

The combined index \( \alpha = m \sigma \) labels spin and orbital degrees of freedom (flavors). For the bath we use, without loss of generality, the basis which diagonalizes \( H_{\text{bath}} \), with quantum numbers \( \gamma \). Finally, we define \( \xi_{\alpha\alpha} = \xi_{\alpha\alpha} - \Delta \xi_{\alpha\alpha}^{\text{DC}} \), where \( \xi_{\alpha\alpha} \) is the crystal-field matrix and \( \Delta \xi_{\alpha\alpha}^{\text{DC}} \) is the double counting correction; in the cases considered in the present paper the latter is a shift of the chemical potential \( \mu \).

1. Hybridization-function expansion

By expanding the partition function in powers of \( H_{\text{hyb}} \) and going to the interaction picture \( H_{\text{hyb}}(\tau) = e^{\beta (H_{\text{bath}} + H_{\text{loc}})} H_{\text{bath}} e^{-\beta (H_{\text{bath}} + H_{\text{loc}})} \) with \( \beta = 1/k_B T \) we obtain the series

\[
Z = \text{Tr} \left[ e^{-\beta (H_{\text{bath}} + H_{\text{loc}})} \prod_{i=m}^{(m)} \text{Tr} \left[ e^{-\beta (H_{\text{bath}} + H_{\text{loc}})} I_{\text{hyb}}(\tau_i) \right] \right]
\]

where \( I \) is the time order operator, \( \tau = (\tau_1, \tau_2, \ldots, \tau_m) \) with \( \tau_{i+1} \geq \tau_i \) and

\[
\int_{(m)} d\tau = \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_m.
\]

In the trace only terms containing an equal number of creation and annihilation operators in both the bath and impurity sector, i.e., only even expansion orders \( m = 2n \) contribute. Introducing the bath partition function \( Z_{\text{bath}} = \text{Tr} e^{-\beta H_{\text{bath}}} \), the partition function can be factorized

\[
\frac{Z}{Z_{\text{bath}}} = \sum_{n=0}^\infty \int d\tau \int d\tilde{\tau} \sum_{\alpha \tilde{\alpha}} \sum_{\alpha \tilde{\alpha}} z_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}),
\]

with

\[
z_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) = \int_{\alpha \tilde{\alpha}} t_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) d_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}).
\]

The first factor is the trace over the impurity states

\[
t_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) = \text{Tr} \left[ e^{-\beta (H_{\text{loc}} - i\mu N)} \prod_{i=n}^1 c_{\alpha_i}^\dagger (\tau_i) c_{\alpha_i} (\tilde{\tau}_i) \right],
\]

where \( c_{\alpha_i}^{(i)}(\tau) = e^{\tau (H_{\text{loc}} - \mu N)} c_{\alpha_i}^{(i)} e^{-\tau (H_{\text{loc}} - \mu N)} \) and \( N \) is the total number of electrons on the impurity. For expansion order \( m = 2n \), the vector \( \alpha = (\alpha_1, \alpha_2 \ldots \alpha_n) \) gives the flavors \( \alpha_i \) associated with the \( n \) annihilation operators on the impurity at imaginary times \( \tau_i \), while the \( \tilde{\alpha} = (\tilde{\alpha}_1, \tilde{\alpha}_2 \ldots \tilde{\alpha}_n) \) are associated with the \( n \) creation operators at \( \tilde{\tau}_i \). The second factor is the trace over the non-interacting bath, which is given by the determinant

\[
d_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) = \det \left[ F_{\alpha,\tilde{\alpha}}(\tau, \tilde{\tau}) \right]
\]

of the \( n \times n \) square hybridization-function-matrix with matrix elements \( [F_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau})]_{\nu,\nu'} = F_{\alpha,\tilde{\alpha}}(\tau_i, \tilde{\tau}_i - \tau) \) given by

\[
F_{\alpha,\tilde{\alpha}}(\tau) = \sum_{\gamma} \int \frac{d\epsilon}{2\pi} \frac{1}{1 + e^{-\epsilon/\beta}} \frac{e^{-\epsilon/\beta}}{\epsilon - \epsilon_{\gamma}} \left\{ \begin{array}{cc} e^{-\epsilon/\beta} & \tau > 0 \\ e^{-\epsilon/\beta} & \tau < 0. \end{array} \right.
\]

On the Fermionic Matsubara frequencies, \( \omega_n \), its Fourier transform

\[
F_{\alpha,\tilde{\alpha}}(\omega_n) = \sum_{\gamma} \frac{V_{\gamma,\alpha} V_{\gamma,\tilde{\alpha}}}{i\omega_n - \epsilon_{\gamma}}
\]

is related to the bath Green-function-matrix \( G \) by

\[
F_{\alpha,\tilde{\alpha}}(\omega_n) = i\omega_n \delta_{\alpha,\tilde{\alpha}} - \xi_{\alpha,\tilde{\alpha}} - (G)^{-1}_{\alpha,\tilde{\alpha}}(\omega_n),
\]

as can be shown by downfolding. To speed up the calculations, we exploit symmetries. If \( \tilde{\nu} \) blocks of flavors are decoupled by symmetries, the hybridization function matrix is block-diagonal in those flavors. We then write the partition function in terms of the expansion orders \( n_b \) in each block, with \( n = \sum_{b=1}^{N_b} n_b \), and \( \alpha = \sum_{b=1}^{N_b} \alpha_b \). Thus

\[
Z = \left[ \prod_{b=1}^{N_b} \int_{n_b=0}^{\infty} d\tau_b \int_{n_b=0}^{\infty} d\tilde{\tau}_b \right] \sum_{\alpha,\tilde{\alpha}} \left[ z_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) \right]
\]

with

\[
d_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) = \prod_{b=1}^{N_b} d_{\alpha_b,\tilde{\alpha}_b}^{(n_b)}(\tau_b, \tilde{\tau}_b)
\]

and

\[
t_{\alpha,\tilde{\alpha}}^{(n)}(\tau, \tilde{\tau}) = \text{Tr} \left[ e^{-\beta (H_{\text{loc}} - \mu N)} \prod_{b=1}^{N_b} \prod_{i=n_b}^{1} c_{\alpha_{b_i}}^\dagger (\tau_{b_i}) c_{\alpha_{b_i}} (\tilde{\tau}_{b_i}) \right].
\]
2. Segment solver and Krylov approach

Calculating the trace over the impurity states involves propagating states in the impurity Hilbert space. For models with many orbitals this can become very demanding. We therefore use a multi-approach scheme. When the on-site Hamiltonian conserves the flavors we use the so-called segment approach\(\delta\) which is extremely fast. In such cases only terms with an equal number of creation and annihilation operators per flavor contribute to the local trace, and it is convenient to express the partition function in expansion orders \(n_a\) for flavors \(a\). The partition function then can be rewritten as

\[
\frac{Z}{Z_{\text{bth}}} = \left[ \prod_{a=1}^{N_a} \sum_{n_a=0}^{\infty} \int (n_a) \int (n_a) \right] \tilde{Z}^{(n)}(\tau, \bar{\tau}).
\]

Here \(\tau = \sum_{a=1}^{N_a} \tau_a\) and \(\bar{\tau} = \sum_{a=1}^{N_a} \bar{\tau}_a\), while the vectors \(\alpha = \sum_{a=1}^{N_a} \alpha_a\) and \(\bar{\alpha} = \sum_{a=1}^{N_a} \bar{\alpha}_a\) have the \(n_a\) components \(\alpha_{ai} = \bar{\alpha}_{ai} = a\). The local trace factors into

\[
\tilde{Z}^{(n)}(\tau, \bar{\tau}) = \text{Tr} \mathcal{T} e^{-\beta (H_{\text{loc}} - \mu N)} \prod_{a=1}^{N_a} c_a(\tau_{ai}) c_a^{\dagger}(\bar{\tau}_{ai})
\]

\[
= \prod_{a=1}^{N_a} s_a^{n_a} e^{-\sum_{a'=1}^{N_a} \left[ (\epsilon_{a} - \mu) \delta_{a, a'} + \frac{1}{2} g_{a a'} \right] |l_{a a'}|},
\]

where \(l_{a a'}\) is the length of the overlap of the \(\tau\) segments \(a\) and \(a'\), \(s_a = \text{sgn}(\tau_{ai} - \bar{\tau}_{ai})\) is the Fermionic sign, and \(g_{a a'} = U_{a a'} + U_{a a'}\) is the interaction.

In all the cases in which the local Hamiltonian mixes flavors, we adopt the Krylov method. At the beginning of the DMFT loop we calculate all the eigenstates of \(H_{\text{loc}}\), \(\{ |\Psi_n\rangle \}\), and their energies \(\{ E_n \}\); a given state \(|\Psi_n\rangle\) is then propagated with \(e^{-\gamma \tau_{E_n}}\); the first creation or annihilation operator met generates a new state \(|\Psi\rangle\), which we propagate with \(e^{-(\gamma_2 - \gamma_1)H_{\text{loc}}\tau}\) obtaining \(|\Psi(\gamma_2 - \gamma_1)\rangle\); we repeat the procedure till the last creation or annihilation operator is met. At the core of the procedure are the matrix-vector multiplications and the propagation of vectors. For the first aspect, we work in the occupation number basis, in which \(H_{\text{loc}}\), and the creation and annihilation operators are sparse matrices. Additionally, we arrange the states according to the symmetries\(\delta, 12\) of \(H_{\text{loc}}\), so that we have sparse block-diagonal matrices and can exploit to the maximum efficient sparse-matrix multiplication algorithms. We find that this typically reduces the CPU time by, e.g., about 15% for a three-band model. We use the Krylov approach to calculate \(|\Psi(\tau)\rangle = e^{-H_{\text{loc}}\tau} |\Psi\rangle\). First we construct the Krylov space of order \(r\), \(K_\tau(\{|\Psi\rangle\})\), i.e., the space spanned by \(|\Psi\rangle, H_{\text{loc}} |\Psi\rangle, H_{\text{loc}}^2 |\Psi\rangle \ldots H_{\text{loc}}^r |\Psi\rangle\). By means of the Lanczos\(\delta, 23\) technique we construct an orthonormal basis for \(K_\tau(\{|\Psi\rangle\})\), \(\{|\Psi\rangle\}\); in this basis \(H_{\text{loc}}\) is tridiagonal with eigenstates \(\{|\ell\rangle\}\) and energies \(\{\epsilon_l\}\). The matrix exponential \(e^{-H_{\text{loc}}\tau}\) is approximated by its projection onto the Krylov space, \(e^{-H_{\text{loc}}\tau} |\Psi\rangle \sim \sum_{l=0}^{r} e^{-\epsilon_l \tau} |l\rangle \langle l| |\Psi\rangle\). This procedure converges very rapidly with \(r\), typically for \(r\) much smaller than the dimension of the Hilbert space\(\delta, 24\) as illustrated in Fig.\(\delta\). We find that the convergence slightly deteriorates with increasing \(\tau\) and the complexity of the Hamiltonian (realistic Coulomb vertex, crystal-field matrix), but typically 2-3 steps are sufficient to obtain accurate results. To best exploit the power of the method, we keep \(r\) flexible. Furthermore, to avoid that the norm of the state becomes very large during the propagation, we set \(E_0\) to zero, i.e., substitute \(e^{-r_{H_{\text{loc}}}}\) with \(e^{-r_{H_{\text{loc}}}}\). In addition, the procedure (propagation and creation/annihilation) is carried out from both the left and the right side of the trace, to minimize the work needed to measure, e.g., the Green function matrix. Finally, at low temperatures or far from phase transitions we use the eigenvalues of \(H_{\text{loc}}\) to determine the relevant energy window and truncate adaptively the outer bracket of the trace. This further reduces the CPU time.

The performance of our CT-HYB QMC solver (Krylov and segment version) on the Jülich BlueGene/Q, and comparison with Hirsch-Fye QMC, is shown in Fig. 5.

3. Green-function and occupation matrix

The partition function \(\langle A \rangle\) can be seen as the sum over all configurations \(c = \{c_1, c_2, \ldots, c_N\}\) in imaginary time and flavors. In a compact form

\[
Z = \sum_c \langle Z \rangle_c = \sum_c w_c \sim \sum \text{sign}(w_c),
\]

where in the last term the sum is over a sequence of configurations \(c\) sampled by Monte Carlo using \(w_c\) as the probability of configuration \(c\). In the segment solver approach, we parametrize the configurations by intervals
FIG. 5. (Color on-line) Scaling of our CT-HYB QMC LDA+DMFT code on BlueGene/Q. Black line: Hirsch-Fye Quantum Monte Carlo solver, 2 orbitals. Other lines: CT-HYB Krylov (dark) and CT-HYB segment (light). Symbols: Two- (circles), three- (triangles) and five- (pentagons) band model. Open symbols: Truncated local trace. All points correspond to calculations of high quality (and with comparable error bars) for the systems considered in this work.

[0, β] (time-line), occupied by a sequence of creators and annihilators, which define segments on the time-line. The basic Monte Carlo updates are addition and removal of segments, antisegments or full lines. In the Krylov solver approach we use the insertion and removal of pairs of creation and annihilation operators as basic updates. In addition, we shift operators in time and exchange the configurations of blocks or flavors as global moves. Finally, a generic observable $O$ can then be obtained as Monte Carlo average

$$O \sim \sum_{\{c\}} \langle O \rangle_c \text{sign}(w_c) \sum_{\{c\}} \text{sign}(w_c)$$

where $\langle O \rangle_c$ is the value of the observable for configuration $c$, and $w_c$ runs over the configurations visited with probability $|w_c|$ during the sampling. The average expansion order increases linearly with the inverse temperature. For the case of YTiO$_3$, at $\sim 40$ K, the average expansion order is $n \sim 40$.

We calculate the Green function matrix in two ways, directly and via Legendre polynomials. In the first approach, the Green function matrix is obtained as Monte Carlo average with $\langle O \rangle_c = \langle G_{\alpha\bar{\alpha}} \rangle_c$, and

$$\langle G_{\alpha\bar{\alpha}} \rangle_c = \sum_{b=1}^{N_b} \sum_{i,j=1}^{n_h} \Delta(\tau, \tau_{bji} - \bar{\tau}_{bji}) |M^{(n)}|_{bji} \delta_{\alpha_{bji}} \delta_{\bar{\alpha}_{bji}}.$$

Here $M^{(n)} = [F^{(n)}]^{-1}$ is the inverse of the hybridization-function matrix, which we update at each accepted move, while $\Delta$ is given by

$$\Delta(\tau, \tau') = -\frac{1}{\beta} \begin{cases} \delta(\tau - \tau') & \tau' > 0 \\ -\delta(\tau - (\tau' + \beta)) & \tau' < 0 \end{cases}$$

and the $\delta$-function is discretized. In the second approach, we calculate the Legendre coefficients $\langle O \rangle_c = \langle G^{(l)}_{\alpha\bar{\alpha}} \rangle_c$, with

$$\langle G^{(l)}_{\alpha\bar{\alpha}} \rangle_c = \sum_{b=1}^{N_b} \sum_{i,j=1}^{n_h} P_l(\tau_{bji} - \bar{\tau}_{bji}) |M^{(n)}|_{bji} \delta_{\alpha_{bji}} \delta_{\bar{\alpha}_{bji}}.$$

$P_l(\tau)$ is a Legendre polynomial of rank $l$, with $x(\tau) = 2\tau/\beta - 1$, and we reconstruct the Green function matrix from

$$G_{\alpha\bar{\alpha}}(\tau) = \sum_{l=0}^{\infty} \frac{\sqrt{2l+1}}{\beta} p_l(x(\tau)) G^{(l)}_{\alpha\bar{\alpha}}.$$

For what concerns occupations, in the segment solver we calculate them from the total length of the segments of the different flavors in the Krylov solver we obtain them in two ways, directly from the Green’s function and by explicitly inserting the occupation number operator at the center of the operator sequence $(\tau = \beta/2$) and calculating the corresponding trace. The off-diagonal elements of the local occupation matrix $\langle c_{\alpha}^\dagger c_{\bar{\alpha}} \rangle$, which cannot be obtained by inserting the corresponding operators at $\tau = \beta/2$, are extracted from the Green function matrix only.

1. V.I. Anisimov, A.I. Poteryaev, M.A. Korotin, A.O. Anokhin, and G. Kotliar, J. Phys.: Condens. Matter 9, 7359 (1997); A.I. Lichtenstein and M.I. Katsnelson, Phys. Rev. B 57, 6884 (1998).
2. E. Pavarini, E. Koch, D. Vollhardt, and A. Lichtenstein (eds.), The LDA+DMFT approach to strongly correlated materials, Modeling and Simulation, Vol. 1 (Verlag der Forschungszentrum Jülich, 2011), http://www.cond-mat.de/events/correl11
3. See, e.g., E. Pavarini, The LDA+DMFT Approach, in Ref. 2.
4. A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
5. E. Pavarini and E. Koch, Phys. Rev. Lett. 104, 086402 (2010).
6. E. Pavarini, S. Biermann, A. Poteryaev, A.I. Lichtenstein, A. Georges, and O. K. Andersen, Phys. Rev. Lett. 92, 176403 (2004).
7. E. Pavarini, E. Koch, A.I. Lichtenstein, Phys. Rev. Lett. 101, 266405 (2008).
8. P. Werner, A. Comanac, L. de Medici, M. Troyer, and A.J. Millis, Phys. Rev. Lett. 97, 076405 (2006).
For a pedagogical introduction, see P. Werner, A.M. Läuchli and P. Werner, Phys. Rev. B 84, 085114 (2012).

For a one-dimensional chain, as done in Ref. 34 for the Anderson model and the Hirsch-Fye algorithm.

For observables that cannot be expressed as expectation values of density operators, measuring by insertion at \( \beta/2 \) is not necessarily ergodic. This is in particular apparent for, e.g., \( \langle c_\alpha^{\dagger} (\tau) c_\beta (\tau) \rangle \) with \( \alpha \neq \beta \); if the off-diagonal crystal-field matrix elements are zero, by inserting \( c_\alpha^{\dagger} (\beta/2) c_\beta (\beta/2) \) in the local trace we obtain \( \langle c_\alpha^{\dagger} (\tau) c_\beta (\tau) \rangle = 0 \), even if the hybridization-function matrix is not diagonal.