

Exact diagonalization dynamical mean-field theory for multiband materials: Effect of Coulomb correlations on the Fermi surface of $\text{Na}_{0.3}\text{CoO}_2$

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Dynamical mean-field theory combined with finite-temperature exact diagonalization is shown to be a suitable method to study local Coulomb correlations in realistic multiband materials. By making use of the sparseness of the impurity Hamiltonian, exact eigenstates can be evaluated for significantly larger clusters than in schemes based on full diagonalization. Since finite-size effects are greatly reduced this approach allows the study of three-band systems down to very low temperatures, for strong local Coulomb interactions and full Hund exchange. It is also shown that exact diagonalization yields smooth subband quasiparticle spectra and self-energies at real frequencies. As a first application the correlation induced charge transfer between t_{2g} bands in $\text{Na}_{0.3}\text{CoO}_2$ is investigated. For both Hund and Ising exchange the small e'_g Fermi surface hole pockets are found to be slightly enlarged compared to the noninteracting limit, in agreement with previous quantum Monte Carlo dynamical mean-field calculations for Ising exchange, but in conflict with photoemission data.

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I. INTRODUCTION

Dynamical mean-field theory^{1,2} (DMFT) has been used successfully during recent years to describe the electronic properties of a variety of strongly correlated materials.³ The hallmark of these systems are their complex lattice geometries, giving rise to intricate single-particle properties, accompanied by complex many-electron interactions in partially filled, nearly localized atomic orbitals. These characteristics lead to a wealth of physical phenomena such as metal insulator transitions, exotic magnetic structures, and unconventional superconducting phases.⁴ The virtue of DMFT is that it treats single-electron and many-electron features on the same footing. The key conceptual advance of this approach is the mapping of the lattice problem onto an effective impurity problem which is solved numerically exactly. The local self-energy is then determined via a self-consistency procedure.

The many-body impurity problem can be solved, in the case of single-band systems, by using techniques such as numerical renormalization group⁵ (NRG), exact diagonalization⁶ (ED), quantum Monte Carlo⁷ (QMC), or other schemes.¹ For computational reasons dynamical correlations in realistic multiband materials have so far been investigated mainly within QMC,³ iterated perturbation theory⁸ (IPT), and the fluctuation exchange method⁹ (FLEX). The versatility of the QMC approach is made feasible by allowing only for Ising-like exchange interactions to avoid serious sign problems at low temperatures.¹⁰ Extensions of QMC including full Hund's exchange are presently limited to $T=0$ ¹¹ and rather high temperatures ($T>1500$ K).¹² Spin-flip interactions at low finite temperatures can be taken into account in two recently developed schemes, namely, the continuous-time QMC method^{13,14} and the combination of the Hirsch-Fye algorithm with a perturbation series expansion.¹⁵

The aim of this work is to demonstrate that multiband ED/DMFT is a highly useful scheme for the investigation of

Coulomb correlations in realistic materials. In the past, applications of ED/DMFT were limited to one-band and two-band systems because of the extremely rapid increase of the Hilbert space when the size n_s of the cluster used to simulate the solid is enlarged.^{16–18} For instance, ED with two impurity orbitals, each coupled to three bath levels ($n_s=8$), requires diagonalization of matrices with dimension up to 4900 which roughly represents the time and storage limit of what is computationally meaningful.¹⁹ We show here that a considerable simplification of this task can be achieved by exploiting the extreme sparseness of the Hamiltonian matrices and focusing on the limited number of excited states relevant at low temperatures. As a result the cluster size $n_s=12$ can be treated at about the same computational cost as full diagonalization for $n_s=8$. This improvement allows the application of ED/DMFT to realistic three-band systems.

In this work we study the intercalated layer compound Na_xCoO_2 which exhibits an unusual range of electronic properties as a function of Na doping: unconventional superconductivity, magnetic and charge ordering, and metal insulator transition. Here we focus on one of the most puzzling and controversial aspects, namely, the topology of the Fermi surface at $x=0.3$, the Na concentration at which the system becomes superconducting when additionally doped with water.²⁰ As a result of the octahedral crystal field, the Co $3d$ bands are split into t_{2g} and e_g subbands separated by a finite energy gap. With Na doping the filling of the t_{2g} bands can be continuously tuned between $n=5$ and $n=6$. The rhombohedral symmetry at Co sites yields a further splitting of t_{2g} orbitals into an a_g and two doubly degenerate e'_g orbitals. According to density functional theory within the local density approximation (LDA) the Fermi surface consists of a large a_g hole surface centered at Γ and six small e'_g hole pockets along the ΓK directions.²¹ At $x=0.3$ the 0.7 holes in the t_{2g} band consist of about 0.4 a_g holes and 0.3 e'_g holes. Thus, both types of states should be important for a variety of electronic and magnetic properties.

In striking contrast to these LDA predictions, angle-resolved photoemission spectroscopy (ARPES) experiments

reveal only the large a_g Fermi surface, the e'_g bands being completely filled.^{22–24} To resolve this discrepancy several possible explanations have been discussed in the literature. Since the onsite Coulomb energy U among Co $3d$ electrons is about twice the width of the t_{2g} bands a correlation induced inter-orbital charge transfer among t_{2g} states could in principle modify the shape of the Fermi surface. Dynamical correlations evaluated within multiband QMC/DMFT for a realistic single-particle Hamiltonian predict slightly enlarged e'_g Fermi surface pockets.²⁵ The same trend was found in recent QMC/DMFT calculations.^{26,27} On the other hand, accounting approximately for band narrowing via the Gutzwiller approach, filled e'_g bands were obtained in the strong-coupling $U \rightarrow \infty$ limit,²⁸ but these calculations have not yet been extended to realistic values of U and finite exchange integrals J .

The role of the intercalated Na atoms has also been studied. Within LDA, disorder in the Na layer was shown to produce potential variations that can localize the e'_g Fermi surface pockets, at least for large doping.²⁹ A recent LDA+QMC/DMFT study of Na disorder also showed that the pockets are likely to disappear at large x , but to remain stable near $x=0.3$.²⁷

Although the QMC/DMFT results^{25–27} so far represent the most accurate analysis of correlation induced modifications of the Fermi surface of $\text{Na}_{0.3}\text{CoO}_2$, they are limited to Ising exchange because of the QMC sign problems alluded to above. Since the e'_g bands reach only about 100 meV above the Fermi level—an energy much smaller than typical exchange integrals—there arises the question to what extent the inclusion of full Hund's exchange might provide an explanation of the observed ARPES data.

To address this issue we have applied ED/DMFT to $\text{Na}_{0.3}\text{CoO}_2$. The important result of the present work is that dynamical on-site correlations within the Co t_{2g} manifold for realistic values of Coulomb and exchange energies give rise to a transfer of electronic charge from the e'_g bands to the a_g band. For Hund's exchange and $T=10$ meV the number of a_g holes is decreased to 0.351 compared to the LDA value 0.40, while the number of e'_g holes is increased to 0.349 from the LDA value 0.30. Nearly identical values are found for Ising exchange: 0.345 (a_g) and 0.355 (e'_g). These results are qualitatively consistent with previous QMC/DMFT calculations for Ising exchange at $T=30\text{--}60$ meV. Local Coulomb correlations can therefore be ruled out as a possible explanation of the absence of the e'_g hole pockets in the ARPES data.

It remains to be investigated experimentally and theoretically to what extent the photoemission data are influenced by surface effects which have played a crucial role also in other transition metal oxides, such as Sr_2RuO_4 and $\text{Sr}_x\text{Ca}_{1-x}\text{VO}_3$. Also, we note that the present ARPES results do not seem to be consistent with recent Shubnikov–de Haas measurements of the Fermi surface of $\text{Na}_{0.3}\text{CoO}_2$.³⁶

The present work establishes multiband ED/DMFT as a useful scheme for describing strongly correlated materials. In this sense ED/DMFT can now be regarded as complementary to multiband QMC/DMFT. In comparison to standard Hirsch-Fye QMC treatments, important advantages of ED/DMFT are that spin-flip and pair-exchange interactions are

fully taken into account, large Coulomb energies pose no computational problems, and temperatures as low as 5 to 10 meV are readily accessible.

The outline of this paper is as follows. In Sec. II we present the main ingredients of the multiband ED/DMFT approach. We also argue that it is possible within this scheme to evaluate continuous spectral functions and self-energies at real frequencies for the extended material. Section III presents the application to $\text{Na}_{0.3}\text{CoO}_2$ where we focus on the correlation induced charge transfer among the partially filled t_{2g} bands. Summary and outlook are given in Sec. IV.

II. THEORY

A. Multiband ED/DMFT

Let us consider a material whose single-particle properties are characterized by a Hamiltonian $H(\mathbf{k})$. In the case of partially occupied t_{2g} bands of a transition metal oxide such as Na_xCoO_2 , $H(\mathbf{k})$ is a 3×3 matrix whose elements account for direct interactions between t_{2g} orbitals as well as indirect interactions via neighboring oxygen ions. In addition we consider on-site Coulomb interactions which are comparable to or larger than the t_{2g} band width. The purpose of single-site DMFT is to derive a local self-energy $\Sigma(\omega)$ which describes the modification of the single-particle bands caused by Coulomb interactions. The local lattice Green's function is then given by the expression

$$G_{\alpha\beta}(i\omega_n) = \sum_{\mathbf{k}} [i\omega_n + \mu - H(\mathbf{k}) - \Sigma(i\omega_n)]_{\alpha\beta}^{-1}, \quad (1)$$

where $\omega_n = (2n+1)\pi k_B T$ are Matsubara frequencies, μ is the chemical potential, and $\alpha, \beta = d_{xy}, d_{xz}, d_{yz}$ denotes the t_{2g} orbital basis. We consider paramagnetic systems and omit the spin index of Green's functions and self-energies for convenience.

In the case of a two-dimensional hexagonal lattice, local quantities such as $G_{\alpha\beta}(i\omega_n)$ have only two independent elements given by $G_{11}=G_{22}=G_{33}$ and $G_{12}=G_{13}=G_{23}$. It is therefore convenient to go over to the a_g, e'_g basis, where $a_g = (d_{xy} + d_{xz} + d_{yz})/\sqrt{3}$, $e'_{g1} = (d_{xy} + d_{xz} - 2d_{yz})/\sqrt{6}$, and $e'_{g2} = (d_{xy} - d_{xz})/\sqrt{2}$. Within this basis G becomes diagonal, with elements

$$G_{m=1} \equiv G_{a_g} = G_{11} + 2G_{12}, \quad (2)$$

$$G_{m=2,3} \equiv G_{e'_g} = G_{11} - G_{12}. \quad (3)$$

The reverse transformation is $G_{ii} = (G_{a_g} + 2G_{e'_g})/3$ and $G_{ij} = (G_{a_g} - G_{e'_g})/3$. Except for the Brillouin zone integral in Eq. (1) we perform all subsequent calculations in the diagonal a_g, e'_g basis denoted by $m=1, \dots, 3$. Analogous transformations hold for other lattice structures, such as square two-dimensional or cubic three-dimensional systems.

For the purpose of the quantum impurity calculation it is necessary to first remove the self-energy from the central site. This step yields the impurity Green's function

$$G_{0,m}(i\omega_n) = [G_m(i\omega_n)^{-1} + \Sigma_m(i\omega_n)]^{-1}. \quad (4)$$

Note that, since G_m , $G_{0,m}$, and Σ_m characterize the extended solid, they have smooth, continuous spectra at real frequencies.

Within ED/DMFT⁶ the lattice impurity Green's function $G_{0,m}$ is approximated via an Anderson impurity model for a cluster consisting of impurity levels $\varepsilon_{m=1,\dots,3}$ and bath levels $\varepsilon_k=4, \dots, n_s$ coupled via hopping matrix elements V_{mk} . Thus,

$$G_{0,m}(i\omega_n) \approx G_{0,m}^{\text{cl}}(i\omega_n), \quad (5)$$

where

$$G_{0,m}^{\text{cl}}(i\omega_n) = \left(i\omega_n + \mu - \varepsilon_m - \sum_{k=4}^{n_s} \frac{|V_{mk}|^2}{i\omega_n - \varepsilon_k} \right)^{-1}. \quad (6)$$

Here, $n_s=12$ is the cluster size used in the calculations discussed below. Since $G_{0,m}^{\text{cl}}$ is diagonal in orbital indices, each impurity level couples to its own bath containing three levels. Thus, the hopping elements $V_{1,4,\dots,6}$, $V_{2,7,\dots,9}$, and $V_{3,10,\dots,12}$ are finite, all others vanish. Each function $G_{0,m}^{\text{cl}}(i\omega_n)$ therefore involves seven fitting parameters: one impurity level, three bath levels, and three hopping elements. These parameters are found by using a standard minimization procedure. (We employ the routine MINIMIZE provided in Ref. 1.) Evidently, in contrast to $\text{Im } G_{0,m}$, at real ω $\text{Im } G_{0,m}^{\text{cl}}$ is discrete, with the number of poles determined by the cluster size.

The impurity Hamiltonian for the cluster is defined as

$$\begin{aligned} H = & \sum_{m\sigma} (\varepsilon_m - \mu) n_{m\sigma} + \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{mk\sigma} V_{mk} [c_{m\sigma}^+ c_{k\sigma} + \text{H.c.}] \\ & + \sum_m U n_{m\uparrow} n_{m\downarrow} + \sum_{m < m' \sigma'} (U' - J \delta_{\sigma\sigma'}) n_{m\sigma} n_{m'\sigma'} \\ & - \sum_{m \neq m'} J' [c_{m\uparrow}^+ c_{m\downarrow} c_{m'\downarrow}^+ c_{m'\uparrow} + c_{m\uparrow}^+ c_{m\downarrow}^+ c_{m'\downarrow} c_{m'\uparrow}], \quad (7) \end{aligned}$$

where $c_{m\sigma}^{(\pm)}$ are annihilation (creation) operators for electrons in impurity level $m \leq 3$ with spin σ and $n_{m\sigma} = c_{m\sigma}^+ c_{m\sigma}$, with a similar notation for the bath levels $k=4, \dots, n_s$. H.c. denotes Hermitian conjugate terms. The atomic part of the Hamiltonian is identical with the atomic part of the Hamiltonian of the extended material. The intraorbital and interorbital impurity Coulomb energies are denoted by U and U' . The exchange integral is J . Because of rotational invariance it obeys the relation $U' = U - 2J$. Spin-flip and pair-exchange terms are denoted explicitly by J' . In the case of isotropic Hund exchange, one has $J' = J$. In the case of Ising-like exchange these terms are neglected, so that $J' = 0$. The Coulomb and exchange integrals have the same values in the t_{2g} and a_g, e'_g representations.

Within the diagonal a_g, e'_g basis, the cluster Green's function has the spectral representation^{1,30}

$$\begin{aligned} G_m^{\text{cl}}(i\omega_n) &= \frac{1}{Z} \sum_{\nu\mu} \frac{|\langle \mu | c_{m\sigma}^+ | \nu \rangle|^2}{E_\nu - E_\mu - i\omega_n} [e^{-\beta E_\nu} + e^{-\beta E_\mu}] \\ &= \frac{1}{Z} \sum_{\nu} e^{-\beta E_\nu} [G_{m\sigma}^{\nu+}(i\omega_n) + G_{m\sigma}^{\nu-}(i\omega_n)], \quad (8) \end{aligned}$$

where E_ν and $|\nu\rangle$ are eigenvalues and eigenvectors of the impurity Hamiltonian and $Z = \sum_{\nu} \exp(-\beta E_\nu)$ is the partition function. The excited state Green's functions are given by

$$G_{m\sigma}^{\nu+}(i\omega_n) = \sum_{\mu} \frac{|\langle \mu | c_{m\sigma}^+ | \nu \rangle|^2}{E_\nu - E_\mu - i\omega_n}, \quad (9)$$

$$G_{m\sigma}^{\nu-}(i\omega_n) = \sum_{\mu} \frac{|\langle \mu | c_{m\sigma} | \nu \rangle|^2}{E_\mu - E_\nu - i\omega_n}. \quad (10)$$

In analogy to Eq. (4) the cluster self-energy is given by the expression

$$\Sigma_m^{\text{cl}}(i\omega_n) = G_{0,m}^{\text{cl}}(i\omega_n)^{-1} - G_m^{\text{cl}}(i\omega_n)^{-1}. \quad (11)$$

As will be discussed in more detail in Sec. II C, it is useful to regard the self-energy as the central quantity determined via DMFT. The key physical assumption within the ED approach is then that the cluster self-energy is an adequate representation for the self-energy of the extended solid, i.e.,

$$\Sigma_m(i\omega_n) \approx \Sigma_m^{\text{cl}}(i\omega_n). \quad (12)$$

From Eq. (4) it now follows that

$$G_m(i\omega_n) \approx G_m^{\text{cl}}(i\omega_n). \quad (13)$$

The approximate equalities here are important since they ensure that, as in the case of $G_{0,m}$, at real ω two alternative representations exist: a continuous one for the lattice Green's function G_m and self-energy Σ_m , and a discrete one for the cluster Green's function G_m^{cl} and self-energy Σ_m^{cl} . (See Fig. 13 of Ref. 1 for a nice illustration of the fact that continuous and discrete real- ω spectra can yield similar distributions at Matsubara frequencies.)

Transforming from the a_g, e'_g basis to the t_{2g} basis via $\Sigma_{ii} = \Sigma_{a_g} + 2\Sigma_{e'_g}$, $\Sigma_{i \neq j} = \Sigma_{a_g} - \Sigma_{e'_g}$, we insert this self-energy into the solid Green's function (1). The iteration cycle then has the schematic form

$$\Sigma \rightarrow G \rightarrow G_0 \approx G_0^{\text{cl}} \rightarrow G^{\text{cl}} \rightarrow \Sigma^{\text{cl}} \approx \Sigma. \quad (14)$$

This procedure is repeated until a self-consistent solution is found for a given chemical potential. This potential is then varied until the calculated total occupancy of the t_{2g} bands agrees with the desired occupancy.

In practice, we start from the noninteracting case, where the cluster levels ε_m and ε_k and hopping matrix elements V_{mk} are found for $G_{0,m}(i\omega_n) = G_m(i\omega_n)$ with $\Sigma_m = 0$. These cluster parameters are then used to begin the iteration at finite Coulomb and exchange energies for a particular temperature. Finally, the spectral distributions are given by

$$A_m(\omega) = -\frac{1}{\pi} \text{Im } G_m(\omega). \quad (15)$$

The transformation of $G_m(i\omega_n)$ and $\Sigma_m(i\omega_n)$ to real frequencies will be discussed in the following subsection.

At low temperatures, the Boltzmann factors in Eq. (8) ensure that only a small number of excited states $|\nu\rangle$ are needed. Because of the sparseness of the impurity Hamiltonian matrix, these states can be evaluated exactly by using the Arnoldi algorithm.³¹ For a given excited state the Green's functions $G_{m\sigma}^{\nu\pm}(i\omega_n)$ can then be calculated very accurately using the Lanczos procedure, by starting from the vectors $c_{m\sigma}^+|\nu\rangle$ and $c_{m\sigma}|\nu\rangle$, respectively,

$$G_{m\sigma}^{\nu+}(i\omega_n) = \frac{\langle \nu | c_{m\sigma} c_{m\sigma}^+ | \nu \rangle}{a_{0+} - i\omega_n + \frac{b_{1+}^2}{a_{1+} - i\omega_n + b_{2+}^2 / \dots}}, \quad (16)$$

$$G_{m\sigma}^{\nu-}(i\omega_n) = \frac{\langle \nu | c_{m\sigma}^+ c_{m\sigma} | \nu \rangle}{a_{0-} - i\omega_n + \frac{b_{1-}^2}{a_{1-} - i\omega_n + b_{2-}^2 / \dots}}. \quad (17)$$

The reformulation of the cluster Green's function in Eqs. (8), (9), (10) is similar to the one used by Capone *et al.*³⁰ in the single-band case, except that these authors calculate the excited states $|\nu\rangle$ by applying the Lanczos method. This is faster than the exact solution if only few excited states are important. However, once extensive reorthogonalization is required to obtain sufficiently accurate excited states, the Lanczos method becomes increasingly time consuming so that the exact approach is preferable.

The Arnoldi algorithm is very useful since it enormously reduces both storage and time requirements to carry out ED/DMFT calculations. For $n_s=12$ the largest Hilbert space for $n_\uparrow=n_\downarrow=6$ has dimension $N=853\,776$. Nevertheless, at most $M=23$ elements are finite in any given row of the Hamiltonian matrix. The size of the effective $N \times M$ matrix is therefore less than for full diagonalization of the largest sector (4900) in the case $n_s=8$. Moreover, at temperatures of about $T=10$ meV fewer than 30 of the 169 possible $(n_\uparrow, n_\downarrow)$ configurations have lowest eigenvalues with Boltzmann factors larger than 10^{-5} . Most of these sectors contribute only few excited states. Only in some $(n_\uparrow, n_\downarrow)$ sectors 20 to 40 eigenstates are important. Thus for a total of about 300 excited states the Green's functions $G_{m\sigma}^{\nu\pm}(i\omega_n)$ are calculated via the Lanczos procedure. Of course, this number increases at higher temperatures, and if Boltzmann factors smaller than 10^{-5} are included for higher precision. Finally, the Arnoldi algorithm requires as main computational step the matrix times vector operation $Hu=v$ where H has effective dimension $N \times M$, the vectors u, v are of length N and the internal sum extends only over the finite elements of H . Thus, in contrast to full diagonalization, this method is ideally suited for parallelization. A typical iteration, requiring about 8 h on a single fast pc, takes less than 30 min if 16 processors are employed in parallel. For a given chemical potential, convergence is usually reached after 5 to 10 iterations. We have tested the above procedure on the two-band model consisting

of half-filled subbands of different widths and found excellent agreement with previous results for $n_s=8$ based on full diagonalization.¹⁹

B. Quasiparticle spectra at real frequencies

In the ED/DMFT equations given above we explicitly distinguish, via the superscript ‘‘cl,’’ the cluster Green's functions and self-energy from the corresponding quantities of the extended solid. This is done in order to emphasize that ED/DMFT is well suited for evaluating continuous solid quasiparticle spectra at real frequencies, as we now explain.

The key point is that the solid spectra are to be derived from $G_m(\omega)$, Eq. (1), rather than $G_m^{\text{cl}}(\omega)$, Eq. (8). Although in the self-consistent limit both functions agree at Matsubara frequencies within some uncertainty determined by the cluster size, they differ fundamentally at real frequencies, with $G_m(\omega)$ exhibiting a smooth spectrum and $G_m^{\text{cl}}(\omega)$ consisting of δ functions. Within the spirit of finite-temperature ED/DMFT each iteration step involves the evaluation of the solid Green's function G_m via Eq. (1) and the subsequent approximation of the associated impurity function $G_{0,m}$ in Eq. (4) via the discrete cluster spectrum of $G_{0,m}^{\text{cl}}$, Eq. (6). At a given temperature, the quality of this projection onto the set of Matsubara frequencies depends strongly on the cluster size, i.e., on the number of poles at real ω .

The task at the end of the iteration procedure, of transforming the lattice subband Green's functions $G_m(i\omega_n)$ from Matsubara frequencies to real ω , is therefore similar to the one faced in QMC/DMFT. The difference is that the ED/DMFT data exhibit finite-size effects rather than statistical uncertainties.

Since the ED/DMFT calculations are free of statistical effects, a convenient extrapolation of $G_m(i\omega_n)$ to real frequencies can be achieved by using, for example, the routine RATINT³² based on an approximation in terms of rational functions. The polynomial basis of this extrapolation ensures that at real ω the correct continuous lattice spectrum is found for $\text{Im } G_m(\omega)$, rather than a discrete spectrum for fixed n_s , as obtained by fitting $G_{0,m}$ via the cluster impurity Green's function $G_{0,m}^{\text{cl}}$. We use the extrapolation routine RATINT in the next section to evaluate the complex subband quasiparticle Green's functions $G_m(\omega)$ for $\text{Na}_{0.3}\text{CoO}_2$.

C. Central role of self-energy

We like to point out that, rather than back transforming the lattice Green's function from imaginary to real frequencies, it is more appropriate to perform this transformation on the self-energy. In fact, as mentioned above, the self-energy may be regarded as the central quantity determined by the DMFT self-consistent quantum-impurity treatment. Since ultimately one is interested in the solid quasiparticle Green's function given in Eq. (1), the single-particle features determined by the Hamiltonian $H(\mathbf{k})$ can evidently be evaluated at real ω . Thus, only the real- ω variation of the self-energy is needed. As a result, \mathbf{k} -resolved spectra can be calculated via

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im } \text{Tr}[\omega + \mu - H(\mathbf{k}) - \Sigma(\omega)]^{-1}. \quad (18)$$

The usefulness of transforming Σ from Matsubara to real frequencies can be seen at small U . The spectral details of G are then almost entirely of single-particle character, whereas the self-energy becomes very smooth. Since Σ is a highly convoluted function, with contributions stemming from the occupied and unoccupied regions of the density of states, back transforming it to real ω becomes progressively simpler at small U . In contrast, the back transformation of G gets more difficult. Obviously, since $H(\mathbf{k})$ is known the back transformation of the single-particle part of G can be avoided altogether.

It is well known also that different cluster properties exhibit different convergence with increasing cluster size. Single-particle features, such as the local density of states at the impurity in a given energy window, converge most slowly. Integrated properties, such as the total energy, converge more rapidly. Since the phase space for two-particle interactions increases extremely fast with cluster size, many-body properties such as the self-energy exhibit even more favorable convergence properties. On the other hand, the cluster Green's function involves both single-electron and many-electron features. Only the latter converge rapidly with cluster size. These different behaviors also suggest that it is useful to regard $\Sigma \approx \Sigma^{\text{cl}}$ as the key quantity derived within ED/DMFT.

To extrapolate $\Sigma_m(i\omega_n)$ to real frequencies it is first necessary to remove the Hartree-Fock limit given by $\Sigma_m^{\text{HF}}(i\omega_n) = \Sigma_m(i\omega_n \rightarrow \infty)$. The remainder can then be transformed to real ω by using the same extrapolation routine RATINT as for the derivation of $G_m(\omega)$.³³ As in the latter case, this routine ensures that the correct continuous lattice self-energy is found, rather than the discrete version appropriate for the cluster self-energy. Since back-transformation of single-particle features is avoided, and quasiparticle features are calculated from Eq. (1) at real ω , finer spectral details are retained than when $G_m(i\omega_n)$ is transformed to the real axis. Nevertheless, in the following section we show that both schemes yield consistent spectra.

Before closing this section we note that the back transformation of the self-energy from Matsubara to real frequencies should also be useful within QMC/DMFT. By viewing QMC as a tool for evaluating Σ , the same separation of many-body features from single-particle aspects can be achieved if quasiparticle spectra are evaluated from Eq. (1) at real ω . Of course, the statistical uncertainties associated with QMC make the transformation of $\Sigma(i\omega_n)$ more subtle than in the present ED case. Nevertheless, after subtraction of the Hartree-Fock limit from the real part of Σ , and after proper normalization (determined by the asymptotic behavior of the imaginary part), the use of the maximum entropy method³⁴ on $\Sigma(i\omega_n)$, $\Sigma(\tau)$ should be more accurate than on $G(i\omega_n)$, $G(\tau)$, since the back transformation of single-particle features is avoided.

III. APPLICATION TO $\text{Na}_{0.3}\text{CoO}_2$

We have applied the multiband ED/DMFT approach discussed in the previous section to investigate the correlation induced charge transfer between t_{2g} bands of $\text{Na}_{0.3}\text{CoO}_2$. The

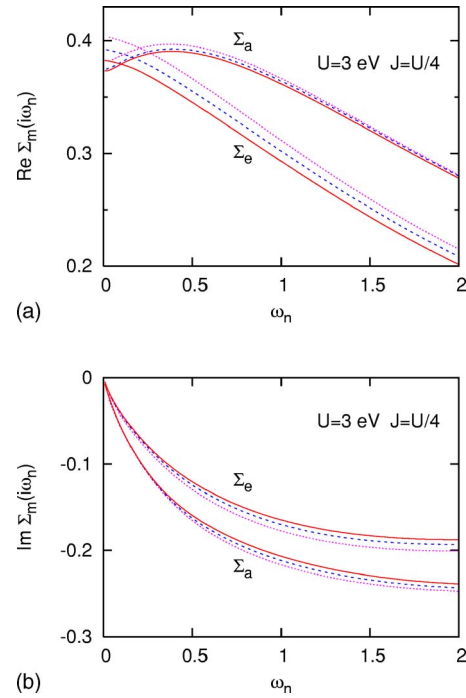


FIG. 1. (Color online) Subband self-energies $\Sigma_m(i\omega_n)$ of $\text{Na}_{0.3}\text{CoO}_2$ as calculated within ED/DMFT for $U=3.0$ eV, $J=0.75$ eV at several temperatures. Solid (red) curves: $T=2.5$ meV, dashed (blue) curves: $T=5$ meV, dotted (magenta) curves: $T=10$ meV. The Hartree-Fock limit is subtracted from $\text{Re } \Sigma_m(i\omega_n)$.

controversial small Fermi surface pockets arise from e'_g bands that extend less than 100 meV above E_F . Since onsite Coulomb energies are much larger than the t_{2g} band width, it is important to inquire whether correlations can lead to a filling of the e'_g bands.

The single-particle properties for this Na concentration were derived from a full-potential linear augmented plane wave (LAPW) calculation, which was then fitted to a 3×3 t_{2g} tight-binding Hamiltonian including three neighboring shells and $dd\sigma$, $dd\pi$, and $dd\delta$ matrix elements. Further details concerning the LDA band structure are given in Ref. 25.

For the combined t_{2g} and e_g bands of $\text{Na}_{0.3}\text{CoO}_2$ U was calculated to be about 3.7 eV.³⁵ For the t_{2g} subbands a smaller value might be appropriate to account for screening via e_g electrons. Since precise values of U and J are not known, ED/DMFT calculations up to $U=5$ eV were carried out, assuming $J=U/4$.

Figure 1 shows the Co a_g and e'_g subband self-energies $\Sigma_m(i\omega_n)$ for $U=3$ eV and $J=0.75$ eV at $T=10$ meV. Hund exchange is fully included, i.e., $J'=J$. As a result of the large cluster size the spacing between excited states of the impurity Hamiltonian is less than 0.001 eV. Although each impurity orbital hybridizes only with three bath levels, the Coulomb and exchange interactions at the impurity site induce coupling between all bath levels, so that the excited states of the total cluster are significantly more closely spaced than for $n_s=4$ in the single-band case. Thus, even at temperatures as low as $T=2.5$ meV finite-size effects are extremely small. The slight differences of the real part of the self-energy are related to the temperature dependence of the chemical potential.

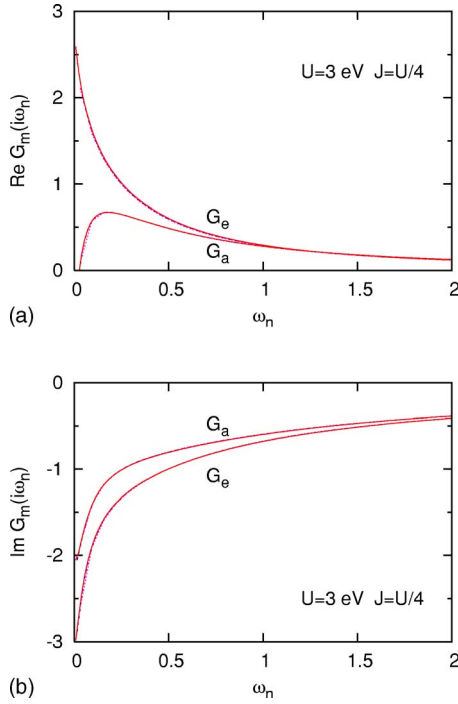


FIG. 2. (Color online) Subband Green's functions $G_m(i\omega_n)$ of $\text{Na}_{0.3}\text{CoO}_2$ for $U=3.0$ eV, $J=0.75$ eV, at several temperatures. Solid (red) curves: $T=2.5$ meV, dashed (blue) curves: $T=5$ meV, dotted (magenta) curves: $T=10$ meV.

In the case of the two-band model,¹⁹ finite-size effects for $n_s=6$ induce, even in the metallic phase, characteristic deviations from linear $\sim i\omega_n$ behavior of $\text{Im} \Sigma_m(i\omega_n)$ at low frequencies, indicating the presence of small pseudogaps caused by the finite level spacing. For $n_s=8$ the level spacing is sufficiently small so that deviations disappear, and good linear $\sim i\omega_n$ behavior is obtained down to very low temperatures. In the present three-band system with $n_s=12$, the level spacing is extremely small. As a result, the self-energies shown in Fig. 1 exhibit excellent linearity at low $i\omega_n$, demonstrating that finite-size effects are very small.

The a_g and e'_g quasiparticle weights $Z_m=1/[1-d\text{Re} \Sigma_m(\omega)/d\omega] \approx 1/[1-\text{Im} \Sigma_m(i\omega_0)/\omega_0]$ derived from these self-energies are $Z_{a_g} \approx 0.52$ and $Z_{e'_g} \approx 0.62$, giving effective masses $m_{a_g}^* \approx 1.9$ and $m_{e'_g}^* \approx 1.6$, respectively. The corresponding subband lattice Green's functions are plotted in Fig. 2 for the same parameters as in Fig. 1. As in the case of the self-energies, the distributions are very smooth and exhibit only very small deviations caused by finite-size effects.

Figure 3 shows the variation of the a_g and e'_g occupations with onsite Coulomb energy at $T=10$ meV. Both isotropic Hund exchange ($J'=J$) and Ising exchange ($J'=0$) are seen to give nearly identical charge transfer from e'_g to a_g bands. In the present ED/DMFT treatment this transfer is slightly less pronounced than the one found within QMC/DMFT for Ising exchange at higher T ,²⁵ but the trends in both DMFT treatments suggest that local Coulomb correlations stabilize the e'_g Fermi surface pockets. The overall topology of the Fermi surface therefore remains the same as predicted by the LDA,

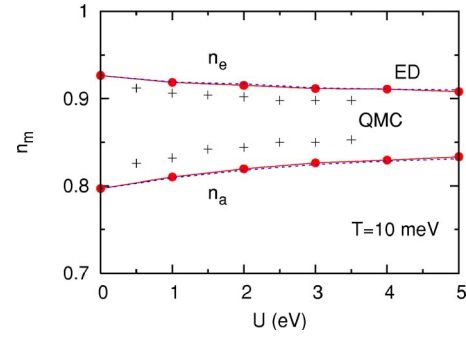


FIG. 3. (Color online) Subband occupations n_{a_g} and $n_{e'_g}$ (per spin band) of $\text{Na}_{0.3}\text{CoO}_2$ as a function of U , with $J=U/4$ at $T=10$ meV. Solid (red) curves: Hund exchange $J'=J$, dashed (blue) curves: Ising exchange $J'=0$. The corresponding QMC/DMFT results (Ref. 25) for $T=62.5$ meV are indicated by the symbols (+). The total occupation is $2n_{a_g} + 4n_{e'_g} = 5.3$.

i.e., correlation effects cannot explain the absence of the e'_g pockets from the ARPES data.

Note that up to $U=5$ eV the subband occupations show no sign of any reversal of charge transfer. The opposite result found using the Gutzwiller approach²⁸ in the $U=\infty$, $J=0$ limit might therefore be a consequence of the approximate treatment of dynamical correlations. In this scheme the true complex frequency dependent self-energy is replaced by two real coefficients representing the shift and narrowing of subbands.

Figure 4 shows the frequency variation of the subband self-energies, as obtained directly from $\Sigma_m(i\omega_n)$ via the ex-

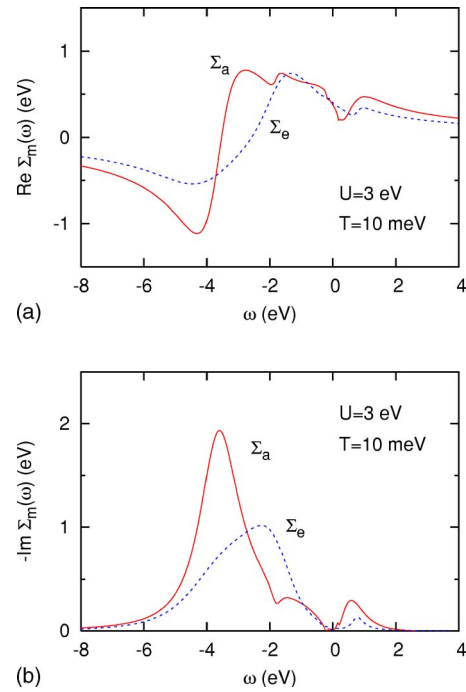


FIG. 4. (Color online) Subband self-energies $\Sigma_m(\omega)$ of $\text{Na}_{0.3}\text{CoO}_2$ at real frequencies, for the same parameters as in Fig. 1. Solid (red) curves: a_g bands, dashed (blue) curves: e'_g bands. (a) $\text{Re} \Sigma_m(\omega)$; (b) $-\text{Im} \Sigma_m(\omega)$. The Hartree-Fock limit is subtracted from the real part.

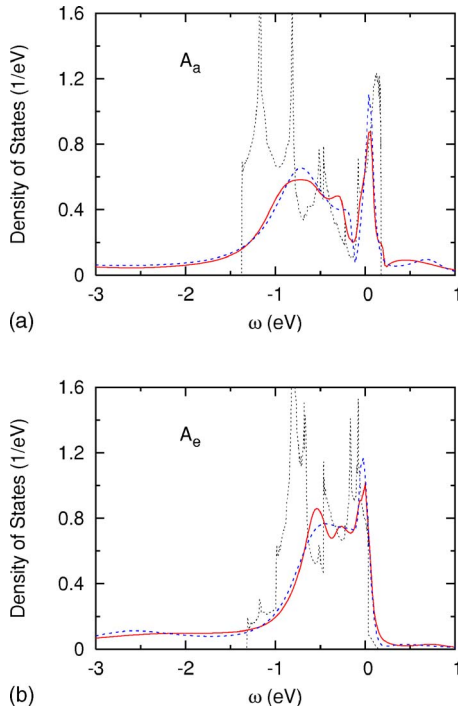


FIG. 5. (Color online) Quasiparticle spectra of (a) a_g and (b) e'_g subbands of $\text{Na}_{0.3}\text{CoO}_2$, calculated within ED/DMFT for the same parameters as in Fig. 1. Solid (red) curves: spectra derived from $G_m(\omega)$ via $\Sigma_m(\omega)$; dashed (blue) curves: spectra obtained by extrapolating $G_m(i\omega_n)$ to real ω ; dotted (black) curves: single-particle density of states.

trapolation routine RATINT. The Kramers-Kronig relations between the real and imaginary parts of $\Sigma_m(\omega)$ are very well satisfied. The striking asymmetry between the negative and positive frequency regions is a consequence of the near filling of the subbands.

As pointed out in the previous section, quasi-particle spectra at real frequencies can be derived by back transforming the solid Green's function $G_m(i\omega_n)$, or by first transforming $\Sigma_m(i\omega_n)$ and then applying Eq. (1) at real ω . The comparison shown in Fig. 5 proves that both methods are consistent, and that the latter scheme retains finer spectral details originating from the single-particle Hamiltonian. For instance, the e'_g spectrum obtained via Eq. (1) and $\Sigma_m(\omega)$ shows two peaks below E_F which evidently are the shifted and broadened density of states features near 0.4 and 0.8 eV below the Fermi level. Also, the peak close to E_F exhibits some of the fine structure of the single-particle density of states. These details are lost if the spectrum is instead derived via back transformation of $G_m(i\omega_n)$.

Interestingly, the a_g spectrum has a steep positive slope at E_F , while the e'_g spectrum has a strong negative slope. This holds true for both methods of evaluating the real frequency spectra. Also, the a_g quasiparticle spectrum exhibits a pronounced minimum at about 0.1 eV below E_F . This feature exists already in the single-particle density of states and is evidently not obliterated by correlation effects.

Both subbands exhibit the usual correlation induced band narrowing, quasiparticle damping, and incoherent spectral weight in the region below the bottom of the bands, associ-

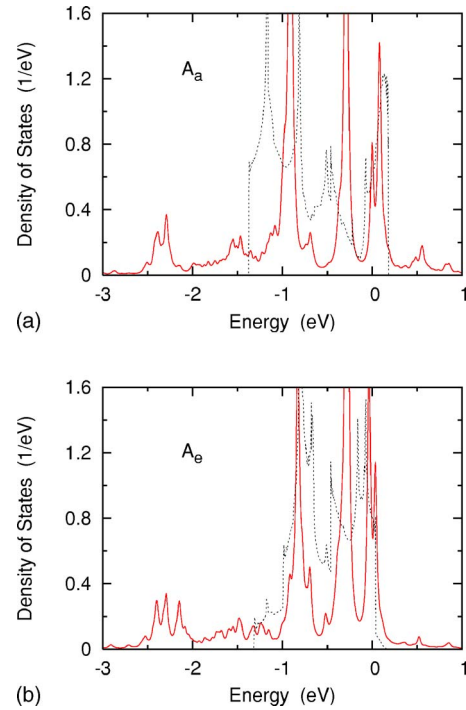


FIG. 6. (Color online) Cluster spectra of (a) a_g and (b) e'_g orbitals of $\text{Na}_{0.3}\text{CoO}_2$, as calculated from Eq. (8). Solid (red) curves: $-\frac{1}{\pi} \text{Im} G_m^{\text{cl}}(\omega+i\delta)$ with $\delta=25$ meV; dotted (black) curves: single-particle density of states.

ated with Hubbard peaks. Qualitatively, these spectra agree with the ones derived previously using the QMC/DMFT and the maximum entropy method.²⁵⁻²⁷

For comparison with the lattice spectra we show in Fig. 6 the cluster spectra obtained by evaluating Eq. (8) at $\omega+i\delta$ instead of $i\omega_n$. Because of the large cluster size, the level spacing between excited states in the metallic phase of $\text{Na}_{0.3}\text{CoO}_2$ is less than 10^{-3} eV. Thus, with only a minor broadening these cluster spectra look very smooth indeed. The spectral weight is located mainly in the t_{2g} band region, and there is clear evidence of incoherent weight associated with Hubbard bands. Both the a_g and e'_g spectral distributions exhibit three main features in the band region, as in the case of the bare density of states. Nevertheless, these features are much narrower than in the corresponding lattice spectra shown in Fig. 5. This is not surprising since, as pointed out in the previous section, the cluster Green's function depends on single-particle and many-body aspects. Only the latter, represented by the self-energy, converge rapidly with cluster size. Thus, increasing the artificial broadening of the cluster spectra does not yield the lattice spectra. Cluster spectra would resemble more closely those of the solid only if n_s is significantly increased. To analyze photoemission spectra of the solid material, Eq. (1) should therefore be used at real ω , rather than Eq. (8).

Transforming the subband self-energies $\Sigma_{a_g}(\omega)$ and $\Sigma_{e'_g}(\omega)$ to the t_{2g} basis, they can be used to evaluate the momentum dependence of the quasiparticle band structure, as indicated in Eq. (18). This is shown in Fig. 7 for the ΓK and ΓM symmetry directions of the hexagonal Brillouin

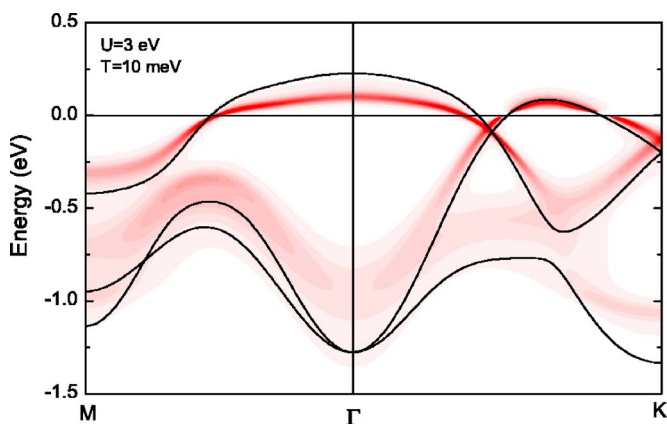


FIG. 7. (Color online) Broadened (red) distributions: dispersion of quasiparticle bands of $\text{Na}_{0.3}\text{CoO}_2$ along $\text{M}\Gamma$ and ΓK for $T = 10$ meV. Solid (black) curves: LDA bands derived from $H(\mathbf{k})$.

zone. The e'_g Fermi surface pockets are associated with the flat bands reaching just above E_F along ΓK . The maximum of this band is shifted down, but the crossing of E_F occurs slightly farther away from the maximum, leading to a weak enlargement of the hole pocket. Conversely, the diameter of the large a_g pocket centered at Γ is slightly reduced.

These results demonstrate that, although local correlation effects induce band narrowing and broadening, they do not alter the basic dispersion of the t_{2g} bands of $\text{Na}_{0.3}\text{CoO}_2$. In particular, it does not seem possible to interpret these bands in terms of a single-band model, with a flat a_g band limited to within a very narrow energy range near E_F .^{23,37,38}

Although the consistent description of correlation effects via ED and QMC/DMFT is encouraging, we point out that both schemes so far focus on single-site correlations and ignore spatial fluctuations. At present it is not known how important these effects might be in a hexagonal planar lattice geometry and whether they might modify the topology of the Fermi surface. In view of the small size of the e'_g hole pockets, related to the fact that these bands reach only about 100 meV above the Fermi level, this problem should be investigated, for instance, via a suitable cluster extension of the present single-site DMFT treatments. The momentum variation of the subband self-energies in $\text{Na}_{0.3}\text{CoO}_2$ is currently under investigation and will be discussed in a future publication.³⁹

IV. SUMMARY AND OUTLOOK

We have applied ED/DMFT to investigate the correlation induced charge transfer between the t_{2g} bands in $\text{Na}_{0.3}\text{CoO}_2$.

Since previous QMC/DMFT studies of this problem were limited to Ising exchange the role of full Hund's coupling had remained unresolved. The ED calculations show that the charge transfer follows the same trend for both Hund and Ising exchange: The e'_g bands donate some of their charge to the a_g bands, i.e., the e'_g Fermi surface hole pockets are slightly enlarged. These ED results fully confirm the trend obtained previously within single-site QMC/DMFT for Ising exchange. Thus, local Coulomb correlations cannot explain the absence of these pockets from the ARPES data.

The results presented in this paper suggest that ED/DMFT is a useful method for the study of strongly correlated three-band systems. By exploiting the sparseness of the impurity Hamiltonian the cluster size $n_s=12$ can now be investigated, without loss of accuracy, with about the same computational effort as $n_s=8$ using full diagonalization. The large cluster size ensures that the level spacing among excited states is very small, so that finite-size effects are greatly reduced.

With this improvement, ED/DMFT can now be regarded as complementary to QMC/DMFT. We point out, however, that in comparison to standard QMC/DMFT based on the Hirsch-Fye algorithm, the ED/DMFT approach is free of sign problems. Thus, complete Hund exchange and large on-site Coulomb interactions can be treated. In addition, very low temperatures can be reached. In principle, results for $T \rightarrow 0$ can also be generated within ED/DMFT. This limiting region, however, requires special care since certain system properties might be sensitive to remaining finite-size effects even for $n_s=12$.

We have also demonstrated that ED/DMFT provides continuous quasiparticle spectra and self-energies of the extended solid at real frequencies. Moreover, by considering the self-energy as the principal quantity derived within DMFT, a clear separation of single-electron and many-body aspects in spectral distributions can be achieved.

In the future it should be valuable to apply ED/DMFT to other multiband materials that have so far been studied only within Ising exchange and QMC/DMFT, but where full Hund's coupling is crucial. Also, by exploiting the fact that the present scheme can easily be parallelized, much larger cluster sizes are feasible. This opens the path for the study of various other material properties, including nonlocal effects.

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