Dynamical mean field theory of an effective three-band model for Na$_2$CoO$_2$

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We derive an effective Hamiltonian for highly correlated $t_{2g}$ states centered at the Co sites of Na$_2$CoO$_2$. The essential ingredients of the model are an O mediated hopping, a trigonal crystal-field splitting, and on-site effective interactions derived from the exact solution of a multi-orbital model in a CoO$_2$ cluster, with parameters determined previously. The effective model is solved by dynamical mean-field theory (DMFT). We obtain a Fermi surface (FS) and electronic dispersion that agrees well with angle-resolved photoemission spectra (ARPES). Our results also elucidate the origin of the "sinking-pockets" in different doping regimes.

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The construction of the appropriate low-energy Hamiltonian to describe a highly correlated system is a crucial task for an advance in its physical understanding. A clear example is the case of the superconducting cuprates. The starting point for the description of those materials is a three-band model containing the most relevant Cu and O orbitals. The parameters of that model were determined by constrained-density-functional theory [1]. On the basis of the exact solution of the multi-band model in a CuO$_2$ cluster (containing one Cu atom and its four nearest neighbors), Zhang and Rice suggested that the essential low-energy physics of the model is captured by a one-band model containing only effective Cu orbitals [2]. This has been confirmed by systematic derivations of the ensuing one-band Hubbard and $t$-$J$ models [3, 4]. These models have led to a considerable progress in the understanding of the high-$T_c$ cuprates. Similar low-energy effective models were derived and used successfully to explain the properties of nickelates [5, 6] and other transition metal oxides [7].

In the cobaltates Na$_2$CoO$_2$ a consensus has not yet been reached on the appropriate low-energy effective Hamiltonian, as different approaches have provided conflicting results. The cobaltates present a clear cut example of strong correlation effects. Not only by its rich phase diagram that includes a charge ordered insulator and a superconducting state at intermediate dopings, but also by the complete failure of the ab-initio band structure calculations to describe the shape and topology of the Fermi surface measured in ARPES experiments [8, 9]. Specifically, first-principles calculations done in the local-density approximation (LDA) [10] predicted a Fermi surface with six prominent hole pockets along the $\Gamma-K$ direction, which were never detected in photoemission. In addition, the ARPES experiments have revealed the presence of dispersive features at the momenta positions where those pockets were expected but they were observed at about 0.2 eV beneath the Fermi surface. Thus, they were termed "sinking pockets" and are still awaiting a clear physical interpretation.

Initial theoretical progress was seemingly achieved by Zhou et al. [11] who included correlation effects on top of a tight-binding model fit to the band-structure from first principles calculations in the local-density approximation LDA [10]. They showed that correlation effects may in fact wipe out the pockets by a reduction of the bandwidth of the bands crossing the Fermi energy. However, the approach of Zhou et al. relied on a simplified static Gutzwiller approximation (GA) where the rather unrealistic assumption of an infinite strength for the local effective $t_{2g}$ Coulomb repulsion $U$ is made. In a different approach to the problem, Ishida et al. [12] used the more elaborate DMFT methodology to treat the correlation effects, on top of a similar LDA-derived tight-binding Hamiltonian. Significantly, the DMFT method allowed for the assumption of finite effective Coulomb interactions. The main finding of that work was the prediction that the effect of $U$ is, in marked contrast to the GA, to actually increase the size of the LDA pockets, that get stabilized due to charge transfer between the $e'_g$ and $a_{1g}$ bands.

Marianetti et al. [13] using a DMFT calculation similar to Ishida et al. found that the pockets can be made to disappear for sufficiently large values of $U$ (above 6 eV), which explained their absence in the infinite $U$ calculation. Although for realistic values of $U$ the pockets still remained, those authors also pointed out that using the $e'_g-a_{1g}$ crystal field splitting as a free fitting parameter, they could eventually be made to disappear. More recently, Liebsch and Ishida [14] critically discussed the various previous approaches that were based on the LDA band-structure as the starting point for the calculation of correlation effects. They concluded that, at values $U \sim 3$ eV which they considered realistic, the presence of pockets in the Fermi surface is always predicted. They argued that this feature, which is in conflict with ARPES data,
is robust with respect to the details of the LDA-fits and to the form of the interaction term.

From a more general perspective, one may expect that a simple-minded identification of the LDA-derived conduction bands as the relevant manifold where correlations are to be included through Hubbard-like interactions in an LDA+DMFT treatment may not be fully justified when systems have a strong covalent character, as it is the case of the cobaltates. In particular it was shown that the above procedure fails in NiO, and agreement with experiments in LDA+DMFT calculations is only achieved once the O bands are explicitly included in the model [13]. Interestingly, the results of that approach also agree with results from effective models where the O atoms have been integrated out using low-energy reduction procedures that take into account correlations from the beginning [5, 15].

We propose to address the problem of the low-energy description of the band-structure of the cobaltates by taking a different approach and altogether leave the LDA as the starting point of our calculation. Thus, in this Letter we perform a low-energy reduction to derive an effective Hamiltonian $H_{\text{eff}}$, that includes the determination of the values of effective local repulsive interactions, and then study its physical behaviour using DMFT. The derivation of $H_{\text{eff}}$ follows the ideas of previous research in the cuprates which used the cell-perturbation method [3] and non-orthogonal Zhang-Rice singlets [2, 4] constructions. Basically, the procedure is to divide the system in different cells that are solved exactly, and retain their lowest energy states. Then, one includes the inter-cell terms along with the effect of the other states as perturbations to this low-energy subspace. The resulting effective Hamiltonian differs substantially from those previously adopted. In particular, our calculated value of $U$ is significantly smaller. Again raising questions on the justification of the assumption of an infinite value for the Coulomb interaction made in Gutzwiller-type of approaches. This observation also applies to a recent Gutzwiller Density-Functional calculation that reports good agreement with ARPES data, in which $U > 5$ eV was assumed [10]. A previously derived $H_{\text{eff}}$ also assumed infinite effective on-site $t_{2g}$ Coulomb repulsions instead of calculating them [17].

We start from the exact solution of a CoO$_6$ cluster model containing all 3d orbitals of a Co atom and all 2p orbitals of its six nearest-neighbor O atoms, assuming cubic (O$_h$) symmetry and neglecting spin-orbit coupling. All interactions inside the 3d shell are included [18]. The parameters were determined fitting XAS experiments and its polarization dependence [18]. The results, which agree with previous similar studies [19], show a large Co-O covalency and an intra-orbital repulsion $U_m = 4.5$ eV, larger than the Co-O charge-transfer energy. The subscript $m$ refers to the original multiband model, to distinguish $U_m$ from the corresponding repulsion $U$ of the effective model, which as shown below, is strongly reduced due to Co-O covalency. We recall that in the cuprates, $U_m \sim 10$ eV [1], while in their effective low-energy one-band Hubbard model $U \sim 3$ eV [3].

The effective model $H_{\text{eff}}$ is obtained mapping the ground state of the CoO$_6$ cluster with four holes onto the on-site vacuum of $H_{\text{eff}}$ (no $t_{2g}$ holes at a Co site, i.e. Co$^{+3}$), and the 6-fold degenerate (spin doublet and orbital triplet) ground state for five holes onto the corresponding states with one $t_{2g}$ hole of $H_{\text{eff}}$. Details of the mapping are given in Ref. [17]. We remark that Co$^{+3}$ and Co$^{+4}$ in $H_{\text{eff}}$ actually represent highly correlated states with a Co valence near 2.04 and 2.56 respectively [18]. $H_{\text{eff}}$ reads

$$H_{\text{eff}} = H_0 + H_I,$$

where the “non-interacting” part can be written as

$$H_0 = \sum_{i,j} \sum_{\alpha,\alpha',\sigma} \left( t^{ij}_{\alpha\alpha'} + t^{ij}_{\alpha'\alpha} \delta_{\alpha\alpha'} + D_{\alpha\alpha'} \delta_{ij} \right) d^\dagger_{i\alpha\sigma} d_{j\alpha'\sigma},$$

where $d^\dagger_{i\alpha\sigma}$ creates a hole in the $t_{2g}$ orbital $\alpha$ ($xy, yz$ or $zx$) with spin $\sigma$ at site $i$. However, physically this operator represents a non trivial excitation of the same symmetry, which involves also 3d $e_g$ orbitals of Co and 2p orbitals of nearest-neighbor O sites. $t'$ and $t$ correspond to the direct Co-Co hopping and to that mediated by O 2p$_\sigma$ orbitals [20] respectively. The latter is the most important one and has been calculated before using many-body eigenstates of the CoO$_6$ cluster [17]. Finally $D$ accounts for the trigonal crystal-field splitting $\Delta = 3D$ between $e'_g$ and $a_{1g}$ orbitals. We take it from quantum-chemistry configuration-interaction calculations [21]. These are the most reliable methods to determine crystal-field excitations. Incidentally, it is known that while the LDA may provide a good description of the ground state, it does not get the energy of excited states right. Therefore it is not expected to provide accurate values for $D$ in a highly correlated system. Note that although $H_0$ has the form of a non-interacting Hamiltonian, the derivation of its parameters already involve many-body calculations [17, 21]. In fact, similarly as in the studies of cuprates, most of the original Co on-site interaction is already included in the derivation of $H_{\text{eff}}$ through the diagonalization of the CoO$_6$ cluster.

The interacting part of $H_{\text{eff}}$ is

$$H_I = \sum_{\alpha} H_I^\alpha; \quad H_I^\alpha = U \sum_{i} n_{i\alpha\sigma} n_{i\alpha\downarrow} + \frac{1}{2} \sum_{\alpha \neq \beta, \sigma \sigma'} \left( U' n_{i\alpha\sigma} n_{i\beta\sigma'} + J d^\dagger_{i\alpha\sigma} d^\dagger_{i\beta\sigma'} d_{i\alpha\sigma} d_{i\beta\sigma} \right) + J' \sum_{\alpha \neq \beta} d^\dagger_{i\alpha\uparrow} d^\dagger_{i\beta\downarrow} d_{i\beta\uparrow} d_{i\alpha\downarrow}. \quad (3)$$
where the interaction parameters were calculated from the comparison between the energy of adding two holes in the same CoO$_6$ cluster with given symmetry and spin, or in different clusters. The eigenvalues of $H'_I$ with two holes should coincide with the corresponding lowest energy levels for 6 holes in the cluster. The resulting parameters of the model become $t = 0.10$ eV, $D = 0.105$ eV, $U = 1.86$ eV, $U' = 1.27$ eV, $J = 0.35$ eV and $J' = 0.17$ eV. To our knowledge, this the first time that a calculation of the interaction terms is reported in this system. Note that the values of the $U$ parameters are smaller than those used in previous calculations [11, 12, 13], but are still much larger than the bandwidth. We have also added a direct hopping between orbitals of the same symmetry $t' = 0.02$ eV that provide the best agreement with experiments, however our main results are not affected by the specific chosen value.

Here we solve $H_{\text{eff}}$ using the DMFT [22]. The associated quantum impurity problem is a three-orbital Anderson impurity that is solved using the Hirsch-Fye quantum Monte Carlo (QMC) algorithm [23]. Due to the symmetry of the band structure of $H_0$, the DMFT quantum impurity problem and its corresponding self-consistency constraint (Dyson Equation) are diagonal in orbital and spin indexes. Thus, the resulting local self-energies $\Sigma_{\text{DMFT}}^{\alpha,\sigma}$ are also diagonal. In order to obtain the momentum and energy resolved Green's functions, the local self-energies have to be analytically continued to the real frequency domain. Thus, we obtained high quality QMC data using over one million sweeps to reliably perform the continuation by means of a standard maximum entropy method [24]. In the calculations presented here, $J'$ and the spin flip terms in Eq. 3 were neglected. This simplification introduces tiny modifications in the results [14]. Thus, we adopt the interaction parameters $U_{\alpha,\sigma} = U = 1.86$ eV for the intra-orbital repulsion, and $U_{\alpha,\sigma,-\sigma}^{\sigma,-\sigma} = U' = 1.27$ eV and $U_{\alpha,\sigma,-\sigma}^{\sigma,\sigma} = U' - J = 0.92$ eV, for the inter-orbital repulsions with opposite or the same spin, respectively.

The predicted band structure is then obtained from the imaginary part of the lattice Green's functions given by (we study paramagnetic solutions so we drop the spin index) $G_0(k, \omega) = [\omega - \epsilon_{k,\sigma} - \Sigma_{\text{DMFT}}^{\alpha,\sigma}(\omega)]^{-1}$ and the Fermi surface is mapped out from the $\omega = 0$ crossings of the interacting bands.

We focus our study on the cases that are experimentally most relevant, i.e., for doping $x=0.3$, 0.5 and 0.7, which range from stronger to weaker correlations. For reasons of space, the data displayed in the figures are for $x=0.3$ and 0.7. Due to their high computational cost, the lowest temperature that we study is $T = 360$ K. Comparison with calculations at higher temperatures ($\sim 720$ K) indicates that we have indeed achieved the low $T$ limit. In addition, as will be shown latter, the width of the quasiparticle band at the Fermi energy, which is the smallest energy scale in the electronic structure, is much larger than the temperature of the calculation.

In Fig. 1 we show our results for the evolution of the Fermi surface as function of increasing doping along with the respective experimental ARPES data. We observe good agreement in the shape and size of the FS at all doping levels. Significantly, the hole pockets are absent in our results.

The experimental FS for $x = 0.3$ is somewhat more rounded than the theoretical one. This may partially be due to the relatively large thermal broadening in the calculation, but may also be due to lack of hopping terms at longer distances, beyond those included in $H_0$.

The details of the band structure are shown in Fig. 2. We observe that the data reveal several contributions that can be associated to either coherent (i.e. quasiparticle like) or incoherent (i.e. Hubbard) bands. The incoherent bands are characterized by dispersive structures similar to those of the “non-interacting” Hamiltonian $H_0$ (though usually less defined due to shorter lifetimes) that appear far from the Fermi energy. These large energy shifts are of course due to the local interactions of $H_{\text{eff}}$ [Eq. 4]. In the top left panel of Fig. 2 we show the full band-structure for the strongly correlated case $x = 0.3$. There, one can observe several incoherent bands that appear shifted down in energy, at $\sim -1$, -1.75 and -3 eV, with the first one carrying a large part of the spectral intensity. Their shapes reveal their dominant orbital content and their energy shifts can be understood from the values of the inter- and intra-orbital Coulomb repulsions. At higher dopings, the correlation effects decrease and these incoherent bands rapidly loose spectral intensity. On the other hand, the coherent bands are near the Fermi energy and their band structure is somewhat narrowed with respect to that of $H_0$ [Eq. 2] due to the effect of $H_I$ [Eq. 3], indicating the enhancement of the effective mass.

The top right panel of the figure shows details of the band structure at $x=0.3$ and, for comparison with the less correlated case, the lower right panel shows similar data.
for $x=0.7$. Interestingly, these results reveal a novel insight on the nature of the "sinking pockets", whose experimental data we reproduced in the lower left panel. We find that while the sinking pockets are present at both, low and high dopings (they are indicated by boxes in the respective panels), their physical origin is qualitatively different. At higher $x$, correlations are low and the band structure does not differ much from the non-interacting case. Thus, the sinking pocket in this case can be simply associated to the top of the band with mostly $e_g$ character [indicated by a box in panel (d)]. In contrast, at $x=0.3$, in the strong correlation case, as we discussed before, the band structure is dramatically modified and that interpretation is no longer possible. In fact, the strongest contribution to the $e_g$ band is shifted down in energy by about 1 eV. This shift is due to the inter-orbital Hubbard repulsion, and can be more easily understood by about 1 eV. This shift is due to the inter-orbital separation of the bands as discussed above. However, for respect to LDA calculations is how the effect of correlations also not present in our results. One difference with respect to the experimental data. Importantly, the LDA-predicted evolution of the Fermi surface is in good agreement with our results. Nevertheless, the experimental situation is less clear for the determination of the QMC code, and V. Brouet for discussions on ARPES data. This investigation was sponsored by PIP 5254 of CONICET and PICT 2006/483 of the ANPCyT, and by the ECOS-Sud program. AAA is partially supported by CONICET.

FIG. 2: (Color online) (a) Full band structure for $x=0.3$. The $x=0.3$ and $x=0.7$ cases are detailed in (b) and (d) respectively, where the structures in the dispersion corresponding to the sinking pockets are highlighted by a box. (c) sinking pockets for various dopings, with comparison to LDA.
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