Coulomb correlations do not fill the $e'_g$ hole pockets in Na$_{0.3}$CoO$_2$

A. Liebsch$^1$ and H. Ishida$^2$

$^1$Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany
$^2$College of Humanities and Sciences, Nihon University, and CREST JST, Tokyo 156, Japan

(Dated: February 1, 2008)

There exists presently considerable debate over the question whether local Coulomb interactions can explain the absence of the small $e'_g$ Fermi surface hole pockets in photoemission studies of Na$_{0.3}$CoO$_2$. By comparing dynamical mean field results for different single particle Hamiltonians and exact diagonalization as well as quantum Monte Carlo treatments, we show that, for realistic values of the Coulomb energy $U$ and Hund exchange $J$, the $e'_g$ pockets can be slightly enhanced or reduced compared to band structure predictions, but they do not disappear.

The Fermi surface of a material is one of its most fundamental properties. Usually, it can be understood, at least qualitatively, within density functional theory. It came as a surprise, therefore, when several angle-resolved photoemission (ARPES) studies on the intercalated layer compound Na$_{0.3}$CoO$_2$ [1] revealed a fundamentally different shape of the Fermi surface than predicted by local density approximation (LDA) band theory [2]. Recent bulk sensitive Shubnikov-de Haas data [3] also appear to be inconsistent with these calculations. On the other hand, the overall width of the Co $3d$ bands in the ARPES data was found to be only moderately reduced compared to the LDA value. Essentially, the partially filled Co $3d$ $t_{2g}$ bands should give rise to a large $a_g$ hole pocket centered around $\Gamma$, and six small hole pockets of $e'_g$ character along the $\Gamma K$ directions of the hexagonal Brillouin Zone. These $e'_g$ pockets have not yet been observed in experimental work. Their role for the superconducting hydrated phase of Na$_{0.3}$CoO$_2$ is also a subject of intense investigations [4]. In view of the narrow width of the Co $t_{2g}$ bands ($W \approx 1.5$ eV), one possible source of the discrepancy between ARPES and band theory might be the effect of intra-3$d$ Co Coulomb interactions which, in principle, could enhance orbital polarization by leading to a charge transfer from $a_g$ to $e'_g$ subbands, and, eventually, to a shift of the $e'_g$ bands below the Fermi level.

The role of Coulomb interactions in the topology of the Fermi surface of Na$_{0.3}$CoO$_2$ has been investigated by several groups, using various theoretical methods and levels of approximation. Ishida et al. [5] applied dynamical mean field theory (DMFT) [6] based on the multi-orbital quantum Monte Carlo (QMC) method, together with a single-particle Hamiltonian derived from an accurate tight-binding fit of the $t_{2g}$ bands to the linearized augmented plane wave (LAPW) band structure. The result of this work was that, for Coulomb energies $U \approx 3.0 \ldots 3.5$ eV and exchange $J = U/4$, the $e'_g$ hole pockets were slightly enlarged compared to the LDA Fermi surface, in contrast to the ARPES data. The width of the $t_{2g}$ bands, however, was found to be reduced to about 1 eV, in approximate agreement with ARPES. To avoid sign problems, only Ising-like exchange terms were included in the QMC calculation. It was also shown that an LDA+$U$ [7] treatment can lead to enlarged or reduced $e'_g$ hole pockets, depending on whether $U$ is smaller or larger than $5J$, respectively.

At the same time, Zhou et al. [8] investigated this problem within the Gutzwiller approach in the large $U$, $J = 0$ limit. Using a slightly different tight-binding fit to the LDA bands, these authors found that the $e'_g$ bands were shifted below $E_F$, and that the width of the $t_{2g}$ bands was strongly reduced from 1.5 eV to about 0.5 eV. Thus, while the Fermi surface appears to agree with the ARPES data, the band narrowing is much stronger than experimentally observed. Similar Gutzwiller calculations in the $U \rightarrow \infty$, $J = 0$ limit were recently carried out by Shorikov et al. [9], with results similar to those of Ref. [8]. Since the Gutzwiller method replaces the frequency dependent complex self-energy by parameters providing orbital depending energy shifts and band narrowing, it represents an approximation to DMFT. Moreover, for $U \rightarrow \infty$, complete orbital polarization is to be expected. Thus, for a meaningful comparison with ARPES data, it is important to extend the Gutzwiller approach to realistic Coulomb and exchange energies appropriate for Co.

The influence of correlations on the electronic properties of hydrated Na$_{0.35}$CoO$_2$ were also investigated by Landron and Lepetit [10] within quantum chemical methods for embedded Co$_6$ and Co$_2$O$_{10}$ clusters. The crystal field splitting between $a_g$ and $e'_g$ orbitals was found to be $\Delta = 315$ meV, and the Coulomb and exchange energies $U = 4.1$ eV and $J = 0.28$ eV. At present, it is not clear how these parameters, in particular, the large value of $\Delta$, would be modified for larger clusters that are required to describe the electronic properties of the extended system. Slave-boson mean field calculations by Bourgeois et al. [11] based on $\Delta = 315$ meV and $U \rightarrow \infty$ revealed a pure $a_g$ Fermi surface and a $t_{2g}$ band width of 0.5 eV, similar to the results of Ref. [8].

To examine the role of Hund exchange contributions not included in the QMC/DMFT calculations, Perroni et al. [12] applied a multi-band exact diagonalization DMFT scheme to Na$_{0.3}$CoO$_2$. This approach does not suffer from sign problems and includes density-density contributions as well as spin-flip and pair-exchange terms. Also, larger values of $U$ can be handled than via QMC. The result of this study was that in this material there is little difference between Hund and Ising exchange, and that, for $U = 3 \ldots 5$ eV and $J = U/4$, the $e'_g$ pockets were slightly enlarged, in agreement with
the QMC/DMFT results. Also, the band narrowing was found to be roughly 30\%, consistent with the QMC treatment and with the ARPES data.

Most recently, Marianetti et al. [13] studied the problem of the $e'_g$ hole pockets in Na$_{0.3}$CoO$_2$ by applying a new continuous-time QMC/DMFT version that allows to reach larger $U$ and lower temperatures. The single-particle Hamiltonian was the same as in Ref. [8], except for the crystal field splitting $\Delta = E_{a_g} - E_{e'_g}$ that shifts the $a_g$ bands up and the $e'_g$ bands down. For $U = 3 \ldots 5$ eV and $J = 0$, reduced $e'_g$ pockets are found for $\Delta = -10$ meV, and fully suppressed pockets if $\Delta$ is increased to 50\ldots100 meV. According to the authors, their results are “in agreement with Ref. [8] and in disagreement with Ref. [5]”. Since the DMFT calculations, however, were not done for the same input Hamiltonian and $U$, $J$ values as those in Refs. [3, 12], the origin of the conflicting trends is presently unknown.

The purpose of this work is to resolve this issue and to analyze the role of the single-particle Hamiltonian $H(k)$ and Coulomb and exchange energies for the charge transfer between $t_{2g}$ bands. In particular, we show that the ED and QMC many-body calculations are in perfect agreement if identical input parameters are employed. On the other hand, the two different versions of $H(k)$ used in Refs. [3, 12] and [8, 13] (below we refer to them as $H_1$ and $H_2$, respectively) give rise to a slight, but significant difference in the variation of $e'_g$ occupancy with $U$: Whereas $H_1$ yields decreasing $e'_g$ occupancy with increasing $U$, $H_2$ gives the opposite trend. We show that these differences are caused by the $t_{2g}$ crystal fields $\Delta$ contained $H_1$ and $H_2$. The key point, however, is that, for realistic Coulomb and exchange energies, i.e., $U \approx 3 \ldots 5$ eV and $J \approx 0.72$ eV [13], the differences caused by $H(k)$ are small and do not affect the controversy concerning the shape of the Fermi surface. Both versions of $H(k)$ yield the result that, without an additional $a_g/e'_g$ crystal field splitting, Coulomb interactions do not eliminate the $e'_g$ hole pockets. The overall topology of the Fermi surface remains the same as predicted by LDA band theory.

Fig. 1 shows the tight-binding fits to the partially occupied Co 3$d$ $t_{2g}$ bands used in Refs. [3, 12] and [8, 13]. The total occupancy is 5.3. The $a_g$ and $e'_g$ occupancies (per spin band) are $n_{a_g} \approx 0.80$ and $n_{e'_g} \approx 0.925$. Although both Hamiltonians give similar energy bands, they differ in a fundamental aspect: The predominant $a_g$ wave function character of the lowest LAPW band along $MK$ [2] is correctly reproduced via $H_1$, resulting in a van Hove singularity in the $a_g$ density of states near $-1.12$ eV. In contrast, the two lowest $H_2$ bands along $MK$ cross, so that this singularity is shifted to $-0.84$ eV, implying a significant effective narrowing of this subband. The lowest $H_2$ band at $M$ has $e'_g$ character and gives only a weak step at $-1.02$ eV in the density of states. Since the influence of Coulomb interactions is highly sensitive to the band width and the distribution of spectral weight within a band, these differences should affect also the correlation induced charge transfer between $t_{2g}$ bands.

The top of the $H_2$ $a_g$ band at $\Gamma$ is seen to exhibit a minimum which is absent for $H_1$ and leads to a pronounced peak in the density of states. This spectral weight is distributed over a slightly wider energy range in the case of $H_1$. The minimum is caused by interlayer interactions which are absent in $H_1$ as well as $H_2$. Moreover, the bulk $a_g$ density of states does not exhibit a sharp peak in this region. Thus, the $H_1$ $a_g$ density shown in Fig. 1 should be more appropriate than the one derived from $H_2$.

Despite these differences, near $E_F$ both Hamiltonians yield nearly identical bands. The $e'_g$ bands extend less than 100 meV above $E_F$, and both models exhibit the $a_g/e'_g$ crossing along $\Gamma K$ just below $E_F$. Note that these bands hybridize away from this symmetry direction, i.e., the crossing turns into an increasing hybridization gap as soon as the parallel momentum deviates from $\Gamma K$.

We now discuss the correlation induced changes of the $t_{2g}$ bands of Na$_{0.3}$CoO$_2$ as calculated within DMFT. We had previously demonstrated that, for the Hamiltonian $H_1$, the QMC and ED results of Refs. [3, 12] are in excellent agreement and that both schemes yield reduced orbital polarization with increasing $U$. Moreover, this trend was found to be insensitive to the choice of $J$. 
We have applied the ED approach of Ref. \[12\] to \(H_2\), in order to check its consistency with the QMC formalism used in Ref. \[13\]. For \(U = 3\) eV, \(J = 0\), the subband self-energies as a function of Matsubara frequency were found to be in almost quantitative agreement. In view of the inevitable slight numerical differences between these fundamentally different DMFT approaches, the excellent agreement between the ED and QMC results is indeed remarkable. We also point out that both DMFT schemes take proper account of static and dynamical correlations.

The unexpected result of this calculation is that, with \(H_2\) as input, both ED and QMC schemes yield enhanced orbital polarization: For \(U = 3\) eV, \(J = 0\), the subband occupancies are \(n_{a_g} = 0.735\), \(n_{e_g} = 0.957\), compared to the LDA values \(n_{a_g} = 0.8\), \(n_{e_g} = 0.925\). This charge transfer is opposite to the reduced orbital polarization obtained for \(H_1\): \(n_{a_g} = 0.825\), \(n_{e_g} = 0.91\).

Fig. 2 shows that similar systematic differences between \(H_1\) and \(H_2\) are found at other values of \(U, J\). To eliminate other sources of possible differences, all results are derived using the ED/DMFT approach of Ref. \[12\] at \(T = 20\) meV. Regardless of the choice of \(J, H_1\) leads to a reduction of \(n_{e_g}\) as a function of \(U\), whereas \(H_2\) yields increasing \(n_{e_g}\). Thus, although the single-particle band structure and density of states derived from \(H_1\) and \(H_2\) look qualitatively similar, these two Hamiltonians lead to a small, but significant difference in the variation of the subband occupancies with Coulomb energy.

To analyze the origin of this unusual behavior we simplify the evaluation of the quasi-particle Green’s function

\[
G(i\omega_n) = \sum_k [i\omega_n + \mu - H(k) - \Sigma(i\omega_n)]^{-1},
\]

where \(\omega_n = (2n+1)\pi/\beta\) are Matsubara frequencies, with \(\beta = 1/k_BT\) and temperature \(T\). \(G, H\) and \(\Sigma\) are matrices in the \(t_{2g}\) basis. Because of the planar hexagonal symmetry, the diagonal elements of \(G\) are identical, and so are the off-diagonal elements. The same applies to \(\Sigma\). In the \(a_g, e_g\) basis, these quantities become diagonal, with elements \(G_a = G_{11} + 2G_{12}\) and \(G_e = G_{11} - G_{12}\), and analogous expressions for \(\Sigma_{a,e}\). In this basis, the Green’s functions can be approximately written as

\[
G_t(i\omega_n) = \int d\omega \rho_t(\omega) [i\omega_n + \mu - \omega - \Sigma_t(i\omega_n)]^{-1},
\]

where \(\rho_t(\omega)\) are the \(a_g\) and \(e_g\) density of states components shown in Fig. 1. We have checked that Eq. (2) yields self-consistent DMFT solutions nearly identical to the ones derived from Eq. (1). Thus, the different solutions obtained for \(H_1\) and \(H_2\) are directly related to the different shapes of the respective density of states distributions. As is evident from Fig. 1, the \(e_g\) densities are quite similar for both Hamiltonians. Indeed, replacing one by the other does not alter the trends for the charge transfer shown in Fig. 2. It is clear, therefore, that the different shapes of the \(a_g\) density of states are the source of the opposite orbital polarization found for \(H_1\) and \(H_2\).

As pointed out above, the fact that the lowest \(H_2\) bands cross along \(MK\) leads to an upward shift of the lowest \(a_g\) van Hove singularity by about 0.3 eV. One can simulate this redistribution of spectral weight by reducing the \(a_g\) density of \(H_1\) in the range \(\omega < -0.7\) eV and amplifying it in the region \(-0.7 < \omega < 0\), such that the occupied weight remains 0.8. This deformation is sufficient to reverse the trend of \(n_\ell(U)\) and give rise to a weak enhancement of orbital polarization.

Evidently, the upward shift of spectral weight caused by the band crossing along \(MK\) implies a relative shift of 3d energy levels. In the case of \(H_1\), the centroids of the \(a_g\) and \(e_g\) density of states are \(E_{a_g} = -0.624\) eV and \(E_{e_g} = -0.491\) eV, whereas \(\Delta = E_{a_g} - E_{e_g} = -133\) meV is the \(t_{2g}\) crystal field splitting. In the tight-binding fit, \(\Delta\) was varied along with the hopping parameters, in order to achieve the optimum representation of the LAPW bands throughout the Brillouin Zone \([\mathbb{5}]\). Clearly, its value reflects the electronic structure of the extended system.

In the case of \(H_2\), the splitting was chosen as \(\Delta = -10\) meV, and only the hopping parameters were fitted \([\mathbb{5}]\). The \(a_g\) and \(e_g\) centroids therefore nearly coincide: \(E_{a_g} = -0.489\) eV and \(E_{e_g} = -0.479\) eV. Note that, in both cases, \(E_{a_g} < E_{e_g}\) despite \(n_{a_g} < n_{e_g}\).

As a result of these different level splittings, correlations lead to an intriguing reversal of interorbital charge transfer: For \(H_1\) with \(\Delta = -133\) meV, the large \(a_g/e_g\) splitting is enhanced and gives rise to a gradual filling of the \(a_g\) band with increasing \(U\). Since, at small \(U\), the \(a_g\) occupancy is lower than the \(e_g\) occupancy, this charge transfer amounts to an initial reduction of orbital polarization. (At larger \(U, n_{a_g}\) might become larger than \(n_{e_g}\), so that the same correlation induced \(e_g \to a_g\) charge transfer eventually could turn into enhanced orbital polarization.) In contrast, the small crystal field included.
in $H_2$, $\Delta = -10$ meV, is too weak to enforce a correlation induced downward shift of the $a_g$ band. Thus, the charge transfer is dominated by the larger $e'_g$ occupancy, giving enhanced orbital polarization even at small $U$. Since $H_1$ provides the more accurate fit to the LAPW bands, the correlation induced reduction of orbital polarization in the range of reasonable values of $U$ and $J$ should be more realistic than the opposite trend obtained for $H_2$. Thus, as argued in Refs. 5, 12, correlations slightly enhance the $e'_g$ hole pockets of Na$_{0.3}$CoO$_2$. We emphasize, however, that, according to Fig. 2, the opposite charge transfer obtained for $H_2$ is not large enough to push the $e'_g$ bands below $E_F$.

As pointed out in Ref. 13, a large positive crystal field can enhance orbital polarization, so that, in combination with local Coulomb interactions, the $e'_g$ hole pockets disappear 15. If we assume the ARPES data to be correct, the crucial question then concerns the physical origin of such a crystal field. Evidently, it is not related to on-site Coulomb interactions in the spirit of a single-site DMFT. Non-local effects stemming from the momentum dependence of the self-energy have not yet been explored and could be studied by using a cluster extension of the DMFT. Na disorder was shown to eliminate the pockets at large Na concentrations near $x = 0.7$ 10 17, but is believed to be too weak to have a significant effect on the Fermi surface near $x = 0.3$. Surface effects which have played an important role in ARPES data on other perovskites, such as Ca$_{2-x}$Sr$_x$RuO$_4$ and Ca$_{1-x}$Sr$_x$VO$_3$, should also be investigated, in particular, the effect of Na induced states on the first layer. Moreover, possible structural distortions, such as intra-planar buckling, and their connection to the opening of the $a_g/e'_g$ hybridization gap along $\Gamma K$ should be explored.

We finally mention that, as emphasized in Ref. 13, the $e'_g$ hole pockets are also important for the understanding of the heat capacity of Na$_{0.3}$CoO$_2$. At present, the experimental value, $\gamma \approx 12 - 16$ mJ/molCoK$^2$, is difficult to reconcile with the LDA result, $\sim 14$ mJ/molCoK$^2$, and an effective mass enhancement of about 2, as derived within the DMFT studies discussed above. For a more detailed analysis of this quantity it might be necessary to relax the pinning condition implied by the single-site approximation and allow for non-local effects.

In summary, we have resolved the puzzling discrepancies between DMFT results for the correlation induced $a_g/e'_g$ charge transfer in Na$_{0.3}$CoO$_2$. For identical input quantities, ED and QMC impurity treatments are in excellent agreement. Surprisingly, however, slight differences among the tight-binding Hamiltonians lead to increasing or decreasing orbital polarization. This reversal of subband occupancies as a function of $U$ underlines the importance of using a high-quality single-particle basis as input in the many-body calculation. In the present system, for realistic Coulomb and exchange energies, the differences resulting from these opposite trends are small, i.e., Coulomb interactions do not fill the $e'_g$ hole pockets. The topology of the Fermi surface of Na$_{0.3}$CoO$_2$ therefore remains the same as predicted by LDA band theory.

We hope that these results encourage further experimental work to study in more detail the geometrical and electronic structure of this fascinating material.

One of us (A.L.) likes to thank Chris Marianetti for extensive correspondence and for sending his QMC self-energy results, and Michelle Johannes and Igor Mazin for very useful discussions.

[1] M. Z. Hasan et al., Phys. Rev. Lett. 92, 246402 (2004); H.-B. Yang et al., ibid. 92, 246403 (2004); ibid. 95, 146401 (2005); D. Qian et al., ibid. 96, 046407 (2006); ibid. 97, 216405 (2006); T. Shimojima et al., ibid. 97, 267003 (2006).
[2] D. J. Singh, Phys. Rev. B 61, 13397 (2000).
[3] L. Balicas et al., Phys. Rev. Lett. 97, 126401 (2006).
[4] K. Kuroki, Y. Tanaka and R. Arita, Phys. Rev. Lett. 93, 077001 (2004); M. D. Johannes, I. I. Mazin, D. J. Singh and D. A. Papaconstantopoulos, Phys. Rev. Lett. 93, 097005 (2004); M. Mochizuki and M. Ogata, cond-mat/0609443; K. Kuroki et al., cond-mat/0610494.
[5] H. Ishida, M. D. Johannes, and A. Liebsch, Phys. Rev. Lett. 94, 196401 (2005).
[6] For a review, see: A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
[7] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991); A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).
[8] S. Zhou, M. Gao, H. Ding, P. A. Lee, and Z. Q. Wang, Phys. Rev. Lett. 94, 206401 (2005).
[9] A. O. Shorikov, V. I. Anisimov, and M. M. Korshunov, cond-mat/0705.1408.
[10] S. Landron and M. B. Lepetit, Phys. Rev. B 74, 18450785 (2006).
[11] A. Bourgeois, A. A. Aligia, T. Kroll, and M. D. Núñez-Regueiro, Phys. Rev. B 75, 174518 (2007).
[12] C. A. Perroni, H. Ishida, and A. Liebsch, Phys. Rev. B 75, 097704 (2007).
[13] C. A. Marianetti, K. Haule, and O. Parkollet, cond-mat/0612606.
[14] T. Kroll, A. A. Aligia, and G. A. Sawatzky, Phys. Rev. B 74, 115124 (2006).
[15] $\Delta \approx 50 - 100$ meV for $J = 0$. For $J = 0.7 - 0.9$ eV, $\Delta$ should be even larger. It might then be necessary to readjust the hopping parameters to describe the electronic properties of the system characterized by a large $\Delta$.
[16] D. J. Singh and D. Kasinathan, Phys. Rev. Lett. 97, 016404 (2006).
[17] C. A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. 92, 196405 (2002).