The intercalated layer compound Na$_x$CoO$_2$ has been intensely studied during the recent years since as a function of Na doping it exhibits a variety of fascinating properties. The relevant valence bands near the Fermi level consist of Co $t_{2g}$ states with occupancy 3$d^{5+}\alpha$. For $x \approx 0.50 - 0.75$ an unusually large thermopower is observed [1]. For $x \approx 0.3$ hydration gives rise to a superconducting transition at 4.5 K [2]. In a narrow region near $x = 0.5$ the material undergoes a metal insulator transition [3, 4]. The end-member at $x = 0$ with a single hole per Co atom is believed to be a Mott insulator. At $x = 1$, since the filled $t_{2g}$ bands are separated by about 1.5 eV from the empty $e_g$ bands, one finds a band insulator.

Despite considerable experimental and theoretical effort, fundamental electronic properties of Na$_x$CoO$_2$ such as the qualitative topology of the Fermi surface remain controversial and are not well understood. In the metallic phase the hexagonal Fermi surface predicted by band theory within the local density approximation (LDA) consists of a large hole pocket centered at $\Gamma$ and six small hole pockets near $K$ [5] (see Fig. 1). Because of the layered structure the $t_{2g}$ levels split into an $a_{1g}$ level and doubly degenerate $e_g'$ levels. The large Fermi surface stems mainly from the $a_{1g}$ bands while the small hole pockets have predominantly $e_g'$ character. The existence of these hole pockets is thought to be crucial for the understanding of the superconducting phase [6]. On the other hand, angle resolved photoemission spectra (ARPES) for $x = 0.7$ [7] and $x = 0.6$ [8] provide evidence only for $a_{1g}$ bands crossing the Fermi level. These data suggest that the $e_g'$ bands are filled due to inter-orbital charge transfer not described within the LDA. New ARPES data for $x = 0.3 \cdots 0.7$ [9] and $x = 0.3$ [10] also do not show the small $e_g'$ hole pockets.

To address the question of possible modifications of the Fermi surface via Coulomb correlations not included in the LDA, several theoretical studies were carried out for the half-metallic, magnetic region near $x = 0.7$ [11], using the LDA+U approach [12]. For a relatively large local Coulomb energy ($U > 3$ eV), the $e_g'$ subbands are indeed filled. In the metallic phase, however, in particular, for Coulomb energies comparable to the single-electron band width, it is well known that correlations have an important dynamical component not captured within the LDA+U.

The aim of this work is to elucidate the possibility of modifying the Fermi surface of Na$_{0.3}$CoO$_2$ via dynamical Coulomb correlations. More specifically we focus on the charge transfer between the paramagnetic $t_{2g}$ subbands. Since only the total electron number is conserved when correlations are taken into account, the occupations of individual subbands may vary with the strength of the local intra- and inter-orbital Coulomb energies. In a single-band picture, the key effect of dynamical fluctuations is the spectral weight transfer from the quasi-particle peak near $E_F$ to the incoherent satellites associated with the lower and upper Hubbard bands. In a multi-band ma-
terial, this spectral weight transfer is orbital dependent, opening the possibility of redistributing electronic charge among the valence orbitals and modifying the shape of the Fermi surface.

To investigate these multi-band correlation effects we use the dynamical mean field theory (DMFT) combined with the Quantum Monte Carlo (QMC) method. The remarkable result of this work is that in the metallic domain of Na$_{0.3}$CoO$_2$ near $x = 0.3$ dynamical correlations shift charge from the $e_g$ states to the $a_{1g}$ bands, thereby stabilizing the $e_g$ hole pockets and slightly reducing the $a_{1g}$ Fermi surface. The overall topology of the Fermi surface remains the same as in the LDA.

Fig. 1 shows a tight-binding fit to the Na$_{0.3}$CoO$_2$ bands calculated within the LDA and using the linearized augmented plane wave (LAPW) method. We consider the paramagnetic phase observed experimentally at $x = 0.3$. Since we are interested in the qualitative issue of charge transfer between $t_{2g}$ subbands the weak dispersion along the $c$-axis is neglected. The full band structure involving Co 3$d$ and O 2$p$ states is down-folded to a $3 \times 3$ Co $t_{2g}$ tight-binding Hamiltonian in which on-site energies and hopping integrals represent effective energies accounting for direct Co-Co and indirect Co-O-Co interactions. Including three neighbor shells, with $ddr$, $dxy$ and $ddg$ matrix elements, an excellent fit to the LAPW band structure is achieved. The details of the tight binding model and down-folding procedure will be given elsewhere.

Because of the planar structure of the system, it is convenient to transform the $d_{xy,xz,yz}$ orbitals into $a_{1g}$ and $e_g'$ states, where $a_{1g} = (d_{xy} + d_{xz} + d_{yz})/\sqrt{3}$, $e_g' = (d_{xz} - d_{yz})/\sqrt{2}$, $e_g'' = (2d_{xy} - d_{xz} - d_{yz})/\sqrt{6}$. Quantities such as the local density of states and local quasi-particle self-energy are diagonal in this representation. For instance, the $a_{1g}$ and $e_g'$ density of states are $\rho_a = \rho_{ii} + 2\rho_{ij}$, $\rho_e = \rho_{ii} - \rho_{ij}$, where $\rho_{ii}$ ($\rho_{i1} = \rho_{22} = \rho_{33}$) and $\rho_{ij}$ ($\rho_{i2} = \rho_{i3} = \rho_{23}$) are the diagonal and off-diagonal elements of the $t_{2g}$ density of states matrix.

Fig. 2 shows the $a_{1g}$ and $e_g'$ quasi-particle spectra for Na$_{0.3}$CoO$_2$ as calculated within the DMFT. The local Coulomb interaction defining the quantum impurity problem is characterized by intra- and inter-orbital matrix elements $U = U_{ii}$ and $U' = U_{i\neq j} = U - 2J$, where $J$ is the Hund’s rule exchange integral. The value of $U$ for the entire $t_{2g}$, $e_g'$ manifold (total width about 4 eV) was estimated at 3.7 eV. For the narrower $t_{2g}$ bands a smaller value should be more appropriate to account for screening involving empty $e_g'$ states. Since accurate values of $U$ and $J$ are not available, DMFT calculations for several values were carried out to study their effect on the inter-orbital charge transfer. The temperatures were $T \approx 385$ and 770 K corresponding to about 30 and 60 meV thermal broadening. Up to $10^8$ sweeps were done in the QMC calculations. The quasi-particle spectra are obtained via maximum entropy reconstruction.

The quasi-particle spectra show the characteristic band narrowing near $E_F$ caused by dynamical correlations and the transfer of weight from the coherent to the incoherent spectral region. In the slightly narrower $e_g'$ band correlations are strong enough to give rise to a lower Hubbard band. Also noticeable is the substantial lifetime broadening of valence states due to creation of electron hole pairs. The occupations of these distributions are: $n_a = 0.853$, $n_e = 0.899$, which should be compared to the LDA values $n_a = 0.797$, $n_e = 0.927$.

To illustrate the variation of the $t_{2g}$ subband occupations with local Coulomb and exchange energies, we show in Fig. 3(a) the trend obtained within the DMFT for $U' = U/2$, $J = U/4$ and $U' = U$, $J = 0$. In both cases charge transfer proceeds from $e_g'$ to $a_{1g}$, i.e., orbital polarization is reduced. We have evaluated the DMFT quasi-particle spectra both in the non-diagonal $t_{2g}$ and diagonal $a_{1g}$, $e_g'$ representations. Both versions are in excellent agreement, indicating that in the present system the effect of non-diagonal coupling among $t_{2g}$ states is fully taken into account within the $a_{1g}$, $e_g'$ representation.

The variation of the $a_{1g}$, $e_g'$ subband occupations with $U$ derived within the DMFT differs from the one found in the LDA+U, as illustrated in Fig. 3(b). While dynamical correlations lead to reduced orbital polarization for $J = U/4$ and $J = 0$, the LDA+U treatment gives this trend only for $J = U/4$; $J = 0$ yields the opposite effect. This dependence of the orbital polarization on the ratio $J/U$ within the LDA+U follows...
from the Hartree Fock self-energy. For a paramagnetic $t_{2g}$ complex with one-fold $a_{1g}$ and two-fold $e_{g'}$ subbands, the orbital dependent potential is given by \[^{17}\]:

$$V^{\text{LDA}+U} = \Sigma_{ij}^{\text{HF}} = \delta(U - 5J),$$

with $\delta = (n_{e} - n_{a})/3$. The diagonal term $\Sigma_{ii}^{\text{HF}} = 5\delta(U - 2J)$ gives an overall energy shift, where $\bar{n} = (n_{a} + 2n_{e})/3$. Within the $a_{1g}$, $e_{g'}$ basis, the self-energies are $\Sigma_{ii}^{\text{HF}} = 2\Sigma_{ij}^{\text{HF}}$, $\Sigma_{ij}^{\text{HF}} = \Sigma_{ii}^{\text{HF}} - \Sigma_{ij}^{\text{HF}}$. Subtracting the diagonal term the shifted band energies are:

$$\epsilon_{i}(k) = \epsilon_{i}(k) + 2\delta(U - 5J)$$

and

$$\epsilon_{e}(k) = \epsilon_{e}(k) - \delta(U - 5J).$$

Thus, for $n_{e} > n_{a}$ the $a_{1g}$ ($e_{g'}$) energies are shifted up (down) as long as $J < U/5$. For $J > U/5$ this trend is reversed. For realistic $U = 3.0 \cdots 3.5$ eV, $J \approx 0.8$ eV, the latter condition is satisfied, implying reduced orbital polarization also in the static limit.

Comparing the static self-energy with the one obtained in second-order perturbation theory \[^{17}\] we find that, because of the small difference between $n_{a}$ and $n_{e}$, for increasing $U$ static correlations are rapidly dominated by dynamical correlations. Also, the more compact $e_{g'}$ density of states ensures that $\text{Re} \Sigma_{ij}^{(2)}(\omega = 0) > \text{Re} \Sigma_{ii}^{(2)}(\omega = 0)$ for $J = 0$ and $J = U/4$, implying diminishing orbital polarization \[^{18}\]. Thus, static and dynamical correlations exhibit qualitatively different dependencies on the ratio $J/U$. In addition, the reduced orbital polarizations found for $J = U/4$ in the static and dynamical cases arise for different physical reasons.

The results in Fig. 3 demonstrate that in the metallic phase it is crucial to include dynamical correlations. Evidently, the new degrees of freedom generated by quasiparticle interactions, such as spectral weight transfer between low and high frequencies, relaxation shifts (band narrowing) and decay processes, which are beyond the LDA and LDA+U treatments, contribute to the charge balance between non-equivalent orbitals. It is to be expected that these dynamical correlations also depend on the single-particle bands, i.e., on the available density of occupied and unoccupied states involved in excitation processes. To illustrate this point we show in Fig. 4 the subband occupations for an analogous 3-band model with elliptical density of states; band fillings as in Na$_{0.3}$CoO$_2$; DMFT. Solid dots: $J = U/4$, empty dots: $J = 0$. The lines are guides for the eye.

![FIG. 3: Occupations of $a_{1g}$ and $e_{g'}$ subbands of Na$_{0.3}$CoO$_2$ as a function of $U$. (a) DMFT; (b) LDA+U. Solid dots: $J = U/4$, empty dots: $J = 0$. The lines are guides for the eye.](image)

![FIG. 4: Occupations of 3-band model: elliptical density of states; band fillings as in Na$_{0.3}$CoO$_2$; DMFT. Solid dots: $J = U/4$, empty dots: $J = 0$. The lines are guides for the eye.](image)
It is interesting to compare the influence of dynamical correlations on the subband occupations of Na$_{0.3}$CoO$_2$ to those found in other multi-band materials. The $t_{2g}$ valence bands of the layer perovskite Sr$_2$RuO$_4$ also have $a_{1g}$, $e_g'$ symmetry, but are 2/3 filled. Because of the smaller width of the $e_g'$ bands DMFT predicts a charge transfer to the $a_{1g}$ band [17], shifting the $a_{1g}$ van Hove singularity closer to $E_F$ than in the LDA [21]. The basic shape of the Fermi surface is preserved. The transfer from $e_g'$ to $a_{1g}$ agrees with the one found here for Na$_{0.3}$CoO$_2$. A similar inter-orbital charge transfer was recently obtained in DMFT calculations for BaVS$_3$ [22].

In the orthorhombic phase this 3$d^1$ material exhibits a wide $a_{1g}$ band and weakly occupied, narrow $e_g'$ bands. Dynamical correlations were found to cause a transfer of electrons from $a_{1g}$ to $e_g'$ states, thereby reducing orbital polarization. As in the present system, the same trend was obtained for small and large Hund’s rule exchange terms ($J = U/7$, $U/4$). On the other hand, as recently shown by Pavarini et al. [23] for several 3$d^1$ perovskites, non-diagonal $t_{2g}$ coupling caused by octahedral distortions decreases orbital fluctuations and enhances insulating behavior. Also, Manini et al. [24] studied the Mott transition in a model consisting of two equal subbands with unit total occupancy. With increasing chemical filling of the $a_{1g}$ band [17], shifting the nearly full $e_g'$ subbands yielding characteristic hole pockets of the Fermi surface. Accounting for correlations within the DMFT we have shown that electronic charge is shifted from the $e_g'$ subbands to the $a_{1g}$ band, thus slightly enlarging the small $e_g'$ hole pockets and reducing the main $a_{1g}$ pocket centered at $\Gamma$. Further studies are needed to reconcile these theoretical findings with the photoemission data.

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