Correlation effects on the doped triangular lattice in view of the physics of sodium-rich Na$_x$CoO$_2$

Frank Lechermann

I. Institut für Theoretische Physik, Universität Hamburg, D-20355 Hamburg, Germany

The peculiar correlation effects on the triangular lattice are studied by means of the rotationally invariant slave boson method in a cellular cluster approach. Hence nonlocal correlations are included in a short-range regime. Their impact for the single-band Hubbard model is studied at half filling, i.e., on the Mott transition, and with doping. Using the realistic band structure of Na$_x$CoO$_2$, we may also shed light on the cobaltate physics for $x\geq 1/3$, with the in-plane transition from antiferromagnetic tendencies towards the onset of ferromagnetism for a finite Hubbard $U$.

PACS numbers: 71.27.+a, 71.30.+h, 71.10.Fd, 75.30.Cr

The transition-metal oxide Na$_x$CoO$_2$, consisting of CoO$_2$ layers and Na ions inbetween, is one of the most fascinating examples of a doped correlated electron system on the triangular lattice. Albeit evidently the bare CoO$_2$ ($x=0$) compound is metallic [1], surprisingly, the effect of strong correlation appears to be severe close to the band-insulating ($x=1$) limit. Several experimental studies have revealed a rather rich phase diagram with highlighted physical properties such as superconductivity close to $x=0.3$ (when intercalated with H$_2$O) [2], Pauli(Curie-Weiss)-like metallicity for $x<0.5(>0.5)$ [3], in-plane antiferromagnetic (AFM) order at $x=0.5$ [4], large thermopower around 0.71<$x<$0.84 [5], charge disproportionation for $x>0.5$ [6] and in-plane ferromagnetic (FM) order for 0.75<$x<$0.9 [7,8]. Due to the sizable $(t_{2g},e_g)$ crystal-field (CF) splitting, the Co ion is expected to be in a low-spin state, with $x$ controlling the residual occupation of the $t_{2g}$ manifold. Hence Co$^{4+}$ ($S=1/2$) for $x=0$ and Co$^{3+}$ ($S=0$) for $x=1$. Yet the respective $t_{2g}$ fillings and apparent Fermi surface (FS) for smaller $x$ are still a matter of debate [9]. Though calculations based on the local density approximation (LDA) yield an $t_{2g}$-internal $a_{1g}$-$e_g$ CF splitting of -0.1 eV [10, 11], only the $a_{1g}$-like bands are expected to be partially depleted for larger $x$. Those should form a single hexagonal FS sheet that is hole-like, i.e., the hopping $t$ within a nearest-neighbor (NN) tight-binding (TB) model is negative.

Concerning magnetism, LDA suggests FM order for already small $x$, although the AFM state is very close in energy [12, 13]. Dynamical mean-field theory (DMFT) studies for the NN-TB Hubbard model on a triangular lattice [14, 15] show an instability towards FM order only for $t>0$. Gao et al. [16] described the appearance of a renormalized Stoner instability in an infinite-$U$ Gutzwiller treatment of a third NN-TB model for Na$_x$CoO$_2$ (with the NN $t<$0) at $x\sim 0.67$. Recently, a finite-$U$ LDA+Gutzwiller approach obtained intralayer FM order at larger $x$ [17], but contrary to experiment [1] finds full FM order at low doping. There are cluster approaches to the Hubbard model on the triangular lattice (e.g. [18, 19]) but without incorporating the detailed electronic structure of Na$_x$CoO$_2$.

In the present work, realistic sodium cobaltate is investigated at larger Na doping, finite $U$ and by explicitly including NN correlation effects via the cellular cluster scheme. The puzzling change from AFM tendencies at small $x$ towards the onset of intralayer FM order may be described within a Hubbard-like model using LDA dispersions and moderate $U$. The recently generalized rotationally invariant slave boson mean-field theory [20] (RISB) is applied to the problem [20], thereby tiling the lattice into NN triangles (see Fig. 1). To benchmark this approach in the present setup, we first studied the NN-TB single-band Hubbard model, written in the cellular cluster scheme as $H=H(K)+H_{\alpha}$, i.e.,

$$H = \sum_{K \sigma} \epsilon_{ij\sigma}^K c_{ij\sigma}^\dagger c_{ij\sigma} - t \sum_{\alpha \alpha'} c_{\alpha\sigma}^\dagger c_{\alpha'\sigma} + U \sum_{\alpha} n_{\alpha\uparrow} n_{\alpha\downarrow},$$

(1)

where $\alpha$ marks the cluster, $ij$ are site indices on the cluster, $\sigma$ denotes the spin ($\uparrow, \downarrow$) and $K$ is the cluster wave vector. Note that for the cluster dispersion $\sum_{K \sigma} \epsilon_{ij\sigma}^K = 0$ holds and the intralayer hopping is taken care of by the second term in (1). Within RISB the electron operator $c_{\alpha\sigma}$ is represented as $c_{\alpha\sigma} = \hat{R}(\phi)_{ij\sigma}^\alpha f_{ij\sigma}^\dagger$, where $\hat{R}$ is a non-diagonal transformation operator that relates the physical operator to the quasiparticle (QP) operator $f_{ij\sigma}$. The transformation $\hat{R}$ is written in terms of slave bosons $\{ \phi_{An} \}$ with two indices, namely $A$ for the physical-electron state and $n$ for the QP Fock state. It follows that the kinetic part of (1) is expressed via the QP operators with renormalized dispersions and the operator character of the local part is carried solely by the slave bosons $\{ \phi_{An} \}$ [20]. Two constraints, namely $\sum_{K} \phi_{ij\sigma}^A \phi_{ij\sigma}^A = 1$ and $\sum_{A \nu} \phi_{ij\sigma}^A \phi_{ij\sigma}^A \langle n | f_{ij\sigma}^\dagger f_{ij\sigma}^\dagger | n' \rangle = f_{ij\sigma}^\dagger f_{ij\sigma}$, to select the physical states are imposed through a set of Lagrange multipliers $\{ \lambda \}$. A saddle-point solution is obtained by condensing the bosons and extremalizing the corresponding free energy $F(\{ \phi \}, \{ \lambda \})$ [31]. The nonlocal QP weight matrix at saddle point reads $Z = \text{RR}^\dagger$.

In the following, we study the paramagnetic (PM) phase where $x$ denotes the electron doping normalized
to a single orbital. The QP density of states (DOS) of the noninteracting model (bandwidth $W=9t$), along with comparative interacting cases, is shown in Fig. 1. As displayed in Fig. 2 the RISB treatment for $x=0$ reveals a first-order Mott transition at $U_c\sim12.2t=1.36W$, in agreement with values from exact diagonalization ($\sim12.1t$), cellular DMFT, and variational cluster approximation ($\sim10.5t$) and variational cluster approximation ($\sim12t$). Upon doping, the metallic state may be extended to larger $U$, although a breakdown of the conventional PM phase is found for small $x$ at $U>U_c$. The magnitude of the offdiagonal QP weights $Z_{ij}$ as well as of the NN spin correlation $\langle S_iS_j \rangle$ are enhanced close to the Mott transition. Note that $\langle S_iS_j \rangle$ is negative, i.e., of AFM character. Close to half filling, the $Z_{ij}$ depend strongly on $x$ and the on-site spin correlation is substantially enhanced for $U\neq0$. The AFM strength of the intersite $\langle S_iS_j \rangle$ is decreasing with $x$, but remains slightly above the $U=0$ case in the (meta)stability range of the PM phase. Note that the global FM instability was located around $x\sim0.35$. For a realistic description of Na$_x$CoO$_2$ we first performed LDA calculations at different stoichiometries. A supercell involving the NN Co triangle of a given CoO$_2$ layer served as the base structure. Decorating the latter with additional Na ions above the Co sites yields the dopings $x=0,1/3,2/3,3,1$. No sodium ions above/below oxygen positions are considered, which should be adequate for the overall behavior with doping. A minimal model for the band structure is derived by representing the low-energy states by three maximally-localized Wannier functions (WFs) of $a_{1g}$ type (see Fig. 3). Thus the full dispersions ($W\sim1.2$ eV) are approximated through a downfolding procedure via three $a_{1g}$-like bands. Allowing for the essential behavior with $x$, a doping dependent hamiltonian is obtained through a linear interpolation $H^{\text{LDA}}_{\text{Co}}(K,x)=xH^{\text{LDA}}_{\alpha}(K)+(1-x)H^{\text{LDA}}_{\alpha}(K)$, where $x_{\alpha},x_{\beta}$ are the neighboring LDA-treated dopings. Note that the K points are generally on a 3-dimensional (3D) mesh, describing the full band dispersions. In the full hamiltonian the kinetic term is now given by $H^{\text{LDA}}_{\alpha}(K,x)$ without its onsite (cluster) term $t_{ij}$. The latter replaces the model $t$ in the “onsite” quadratic term of $H$, incorporating both, the intersite hoppings on the Co cluster and the CF-terms on the individual ions. Be aware that the level of frustration is diminished via the symmetry-breaking Na occupations for intermediate $x$.

Contrary to the former model study, the realistic NN hoppings are now negative. Their absolute value is more or less linearly decreasing with $x$, in average from 0.21 eV ($x=0$) to 0.11 eV ($x=1$). Any further explicit exchange couplings $J$ are neglected. Integrating out the O states should render such couplings necessary (e.g., (A)FM exchange between the Co ions). Yet a rigorous computation for metals is hard and experiments revealed that the values for a pure spin hamiltonian are small. Calculations including Heisenberg-like terms in $H$ resulted in no qualitative change for reasonable values of $J$ (see footnote on the spin susceptibility). No long-range Coulomb potential is included, hence explicit charge-disproportionated states do not appear (though site occupations surely differ). We concentrate the discussion on the phases for $x>1/3$, since neglecting the remaining $e_g$ orbitals at small $x$ may not be improper. In fact, when performing the RISB calculation at $x=0$, the Mott transition sets in at $U_c\sim3.1$ eV. But this value is surely too small because of our orbital restrictions.

Figure 4 shows RISB results for $x=1/3,2/3$ and with varying Na content for reasonable ranges/values of the interaction strength $U$. The resulting moderate size of the diagonal QP weight is in good agreement with experiment. Note that for $x=1/3$ the offdiagonal $Z_{ij}$ between sites on the triangle is positive with a maximum at $U_c\sim3$ eV. For $x=2/3$ its value is negative and still increasing in magnitude in the studied $U$ range. The sign change implies that the hierarchy in the correlation strength within
becomes lower than in the latter case. Thus the AFM crossover at \( U \) seems reminiscent of the Nagaoka mechanism \([24]\) for the \( Z \) were used. There the intersite local spin correlations are strongly increased for finite \( U \) close to half filling \([18]\). The AFM character of the NN and has a minimum close to \( \frac{Na}{3} \). Large blue (dark) balls denote Na ions, small red (gray) ball mark O ions.

The bonding-antibonding cluster orbitals is reversed. The onsite spin correlations are saturating for large \( U \), while the intersite \( \langle S_i S_j \rangle \) are always negative but decrease in magnitude in the latter regime. For \( x=1/3 \) the NN (spin) correlations are enhanced in magnitude between Co sites without Na on top. Due to CF effects, the orbital filling on a Co site tends generally to increase when placing Na on top. For the doping study, \( U=3 \) eV and \( U=5 \) eV were used. There the intersite \( Z_{ij} \) changes sign at \( x<0.5 \) and has a minimum close to \( x=2/3 \). As expected, the local spin correlations are strongly increased for finite \( U \) close to half filling \([13]\). The AFM character of the NN spin correlations is strengthened for intermediate \( x \) compared to the \( U=0 \) case. However interestingly, there is a crossover at \( x \to 2/3 \) where the AFM magnitude for \( U \neq 0 \) becomes lower than in the latter case. Thus the AFM tendencies are surpressed by electronic correlations for large \( x \), where the superexchange is diminished. This seems reminiscent of the Nagaoka mechanism \([24]\) for the infinite-\( U \) Hubbard model on the square lattice, leading to FM order. But the Nagaoka state is not a ground state on the triangular lattice for a single hole \([23]\).

To elucidate the problem of magnetic instabilities, a residual magnetic field \( H_z=\delta h \) is applied in the PM phase. Therefrom the uniform magnetic susceptibility is determined as \( \chi=\partial M/\partial H_z=\delta M/\delta h \), where \( \delta M \) is the residual magnetization induced by \( \delta h \). Figure \( 3 \) shows the normalized response \( \chi/\chi_0 \), where \( \chi_0 \) is the susceptibility for \( U=0 \) \([32]\). It is seen that there is strong response for \( x \sim 2/3 \) and \( U=5 \) eV, similar to results in the infinite-\( U \) limit \([11]\). Additionally, there is already a precursive regime for \( x \geq 0.62 \) where FM ordering tendencies show up. This coincides with recent NMR measurements by Lang et al., who find a crossover from AFM to FM correlations at \( x=0.63-0.65 \) \([20]\). From the site- and component resolved intersite spin correlations in the applied field, the dominant response of \( \langle S_i z S_j z \rangle \) in the doping regime \( 0.62 \leq x \leq 0.7 \) is again obvious. Note that also \( U=3 \) eV exhibits minor FM ordering tendencies there. Interestingly, for \( x \sim 0.35 \) one may observe intralayer AFM response for both values of \( U \). An AFM ordering signal is identified through locally favorable spin antialignment between Co(1)-Co(2) and Co(1)-Co(3), whereas Co(2)-Co(3) favor spin alignment. Remember that for \( x=1/3 \) the Na ion is above Co(1), thus the Co differentiation via neighboring Na ions obviously triggers the AFM tendencies. The outer-field induced AFM response is in line with the observation that such a field can lift the effects of kinetic-energy frustration on a triangular cluster \([27]\).

The fact that no clear long-range order is visible for larger \( x \) (i.e., negative \( \chi/\chi_0 \)) may be explained by the present 3D model that cannot stabilize the A-type AFM phase (no proper interlayer resolution). Yet it is possible to stabilize FM order within a single layer by using only the 2D-projected LDA dispersion. Figure \( 4 \) shows the tie-line construction between the PM and FM phase in this case. A stable homogeneous FM order is revealed for \( x \geq 0.74 \), with magnetic moments close to experimental values. The onset of the heterogeneous phase at \( x \sim 0.6 \) matches the begin of FM tendencies in the full 3D model. In this context, hints for a spin-liquid ground state at \( 0.71 \leq x < 0.75 \) \([28]\) are rather interesting. Either 2D phase becomes hard to stabilize numerically for \( x \geq 0.87 \). Though at \( x=2/3 \) the Fermi level is located in the upper maximum peak of the QP DOS (see Fig. \( 4 \)), our study reveals that a Stoner instability can not be the sole origin for magnetic ordering. The nonmonotonic behavior of \( Z_{ij} \), the subtle change of the frustration level with \( x \), the presursive FM regime, the PM-FM phase competition as well as the breakdown of the 2D phases at very large doping are all pointing towards nonlocal correlations as an additional important ingredient. As a side effect, plotting \( \partial^2 F/\partial x^2 \) (Fig. \( 4k \)) shows that the present 3D-PM phase becomes unstable with respect to doping for \( x \geq 0.7 \), while \( U \) stabilizes the phase for \( x<0.5 \).
that correlated regime is already reached, without implying
 supported by the SFB 668. P. S. Cornaglia for helpful discussions. This work was
 relations are needed to clarify more details. Further studies, also
 at small doping, including long-range and interlayer cor-
 (e.g. [29] and references therein).

 FIG. 5: (color online) Ordering tendencies and phase stability in Na$_2$CoO$_2$. (a) normalized magnetic susceptibility, (b-d) component-resolved NN spin correlation in the small field $\delta h$. Solid black line: $\langle S_{i\nu} S_{j\nu}\rangle_{\delta h}$ for $U=0$. (e) QP DOS for $x=2/3$. (f) RISB free energies for PM and FM phase of the single layer for $U=5$ eV. Straight cyan (lightgray) line: common tangent. Inset: net magnetic moment per Co ion in the FM phase. (g) Second derivative of the full PM free energy.

 Phase separation is experimentally indeed observed at large $x$ (e.g. [29] and references therein).

 In conclusion, it was shown that the RISB formalism may describe the essential physics of the NN-TB Hubbard model on the triangular lattice, including the first-order Mott transition and the Fermi-liquid upon doping. The magnetic behavior with doping in Na$_2$CoO$_2$ can be understood with a cluster Hubbard model using LDA dispersions. In very good quantitative agreement with experimental data, the change from AFM to FM tendencies with a final first-order transition in $x$ into an in-plane FM phase was revealed. For the correlated physics with intralayer FM tendencies starting at $x\gtrsim 0.62$ and 2D-FM order for $0.74<x<0.87$, an interaction strength $U>3$ eV is sufficient. Since then $U/W\gtrsim 2.5$ and the strongly-correlated regime is already reached, without implying that $x=0$ is Mott insulating (due to the probably increased orbital fluctuations there). Further studies, also at small doping, including long-range and interlayer correlations are needed to clarify more details.

 The author is indebted to M. Potthoff, I. I. Mazin and P. S. Cornaglia for helpful discussions. This work was supported by the SFB 668.

 [1] C. de Vaulx, M.-H. Julien, C. Berthier, et al., Phys. Rev. Lett. 98, 246402 (2007).

 [2] K. Takada, H. Sakurai, E. Takayama-Muromachi, et al., Nature 422, 53 (2003).

 [3] M. L. Foo, Y. Wang, S. Watauchi, et al., Phys. Rev. Lett. 92, 247001 (2004).

 [4] P. Mendels, D. Bono, J. Bobroff, et al., Phys. Rev. Lett. 94, 136403 (2005).

 [5] Y. Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature 423, 425 (2003).

 [6] I. R. Mukhamedshin, H. Alloul, G. Collin, and N. Blanchard, Phys. Rev. Lett. 94, 247602 (2005).

 [7] A. T. Boothroyd, R. Coldea, D. A. Tennant, et al., Phys. Rev. Lett. 92, 197201 (2004).

 [8] S. P. Bayrakci, I. Mirebeau, P. Bourges, et al., Phys. Rev. Lett. 94, 157205 (2005).

 [9] C. A. Marianetti and G. Kotliar, Phys. Rev. Lett. 98, 176405 (2007).

 [10] F. Lechermann, S. Biermann, and A. Georges, Progress of Theoretical Physics Supplement 160, 233 (2005).

 [11] D. Pillay, M. D. Johannes, I. I. Mazin, and O. K. Andersen, Phys. Rev. B 78, 012501 (2008).

 [12] D. Singh, Phys. Rev. B 61, 13397 (2000).

 [13] M. D. Johannes, I. I. Mazin, and D. J. Singh, Phys. Rev. B 71, 214410 (2005).

 [14] J. Merino, B. J. Powell, and R. H. McKenzie, Phys. Rev. B 73, 235107 (2006).

 [15] K. Aryapour, W. E. Pickett, and R. T. Scalettar, Phys. Rev. B 74, 085117 (2006).

 [16] M. Gao, S. Zhou, and Z. Wang, Phys. Rev. B 76, 180402 (2007).

 [17] G.-T. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 101, 066403 (2008).

 [18] B. Kyung, Phys. Rev. B 75, 033102 (2007).

 [19] P. Sahelsra and D. Sénéchal, Phys. Rev. Lett. 100, 136402 (2008).

 [20] F. Lechermann, A. Georges, G. Kotliar, and O. Parcollet, Phys. Rev. B 76, 155102 (2007).

 [21] M. Capone, L. Capriotti, F. Becca, and S. Caprara, Phys. Rev. B 63, 085104 (2001).

 [22] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).

 [23] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).

 [24] Y. Nagaoka, Phys. Rev. 147, 392 (1966).

 [25] J. O. Haerter and B. S. Shastry, Phys. Rev. Lett. 95, 087202 (2005).

 [26] G. Lang, J. Bobroff, H. Alloul, G. Collin, and N. Blanchard, arXiv:0807.3116 (2008).

 [27] W. Barford and J. H. Kim, Phys. Rev. B 43, 559 (1991).

 [28] L. Balicas, Y. J. Jo, G. J. Shu, F. C. Chou, and P. A. Lee, Phys. Rev. Lett. 100, 126405 (2008).

 [29] M. Lee, L. Viciu, L. Li, et al., Nat. Mat. 5, 537 (2006).

 [30] A different slave spin cluster mean field theory was presented recently in a similar context by S. R. Hassan and L. de’ Medici, arXiv:0805.3550 (2008).

 [31] Gaussian smearing of $\sim 1$ meV is used for the K point integration, introducing a small effective temperature.

 [32] A magnetic response of the cobaltate model for $U=0$ may surely be achieved via an explicit exchange term.