A scenario for the electronic state in the manganate perovskites: the orbital correlated metal

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We argue that, at low temperatures and well into the ferromagnetic phase, the physics of the manganate perovskites may be characterized by a correlated metallic state near a metal insulator transition where the orbital degrees of freedom play a main role. This follows from the observation that a two-band degenerate Hubbard model under a strong magnetic field can be mapped onto a para-orbital single band model. We solve the model numerically using the quantum Monte Carlo technique within a dynamical mean field theory which is exact in the limit of large lattice connectivity. We argue that the proposed scenario may allow for the qualitative interpretation of a variety of experiments which were also observed in other (early) transition metal oxides.

There is a great current interest in transition metal compounds displaying colossal magnetoresistance (CMR). This effect is a strong dependence of resistivity with the applied magnetic field and is observed experimentally in compounds such as La$_{1-x}$A$_x$MnO$_3$, with A = Sr, Ca, Pr. From the point of view of the electronic structure, these systems have 3 electrons in a $t_{2g}$ band which due to a strong Hund’s rule coupling form a core 3/2--spin at each Mn site and 1 – x electrons that go into a quasi two-fold degenerate $e_g$ band. For x = 0 the Manganese atoms are (+4) and the compound has a nominal filling equal to 1. Since the bands are originated from partially filled d-orbitals, on general grounds one expects that correlation effects should play an important role in the low energy behavior, which is indeed the case in many other transition metal oxides (TMO) with the perovskite structure.

The most qualitative aspects of the CMR is explained by the double exchange mechanism (DEM) proposed by Zener almost 50 years ago. More recently, a detailed study of the ferromagnetic Kondo lattice sowed that while DEM is certainly a main ingredient, additional interactions must be added to obtain a more correct picture. Among those, the dynamical Jahn-Teller effect was studied in detail and there is experimental evidence of strong polaronic effects in many compounds. In spite of this recent progress, our understanding of the CMR compounds is still incomplete. In particular at low temperature and within the ferromagnetic (FM) phase where there are several experimental observations that remain unaccounted for: i) the enhancement of the density of states near the Fermi energy with decreasing T observed in photoemission, ii) the unusual redistribution of optical spectral weight as function of the temperature which occurs in the range of the eV, iii) the strong enhancement of the $A$ coefficient of the $T^2$ term in the resistivity as function of the composition in La$_{1-x}$Sr$_x$MnO$_3$, and iv) the suppression of the resistivity with applied pressure.

These features are not exclusive of the CMR manganese compounds, on the contrary, they had already been observed in other (early) transition metal oxides with perovskite structure. For instance, in V$_2$O$_3$, a redistribution of spectral weight in the optical response and a small enhancement of the density of states near the Fermi energy in the photoemission is observed as the temperature is lowered within the paramagnetic metallic phase. The La$_x$Sr$_{1-x}$TiO$_3$ system, on the other hand, displays a notable increase of the $T^2$ coefficient of the resistivity as a function of x. Both compounds also show suppression of the resistivity with applied pressure. These experiments on early TMO have recently received a qualitative interpretation within a dynamical mean field theory of the Hubbard model that becomes exact in the limit of large dimensions. The key feature is to realize that the mean field solution of the Hubbard model predicts a narrow quasiparticle resonance at the Fermi level when the system is close to a metal insulator transition (MIT). Thus, the proximity to a MIT provides with a dynamically generated small energy scale which allows for the qualitative interpretation of the unusual behavior observed in the experimental compounds.

In regard of these similarities between some early TMO and the manganese perovskites, one is motivated to consider the question whether a similar underlying mechanism may be responsible for the low energy behavior. However, an apparent reason that would mean to immediately discard this idea is that the observed phenomena in the CMR compounds occur as they evolve into a ferromagnetic (FM) state with a magnetic moment that saturates close to the classical value. Naively one may think that this is incompatible with the presence of coherent quasiparticles. Thus, the goal of this paper is to demonstrate that in the parameter regime relevant for the CMR manganates the system remains close to a MIT with a dynamically generated small energy scale as it goes in to the

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fully polarized FM state at low temperatures. The formal Hamiltonian for the CMR compounds has the following form [18]:

\[
H = \sum_{<ij>,a,b,\sigma} t_{ij}^{ab} c_{ia\sigma}^\dagger c_{jb\sigma} - J_H \sum_{i,a,\sigma} \hat{S}_{ci} \cdot \hat{S}_{di} + H_{J-T} + U \sum_{i,a,b,\sigma,\sigma'} n_{ia\sigma} n_{ib\sigma'} (1 - \delta_{ab}\delta_{\sigma\sigma'}) \tag{1}
\]

where \(a, b = 1, 2\) are the orbital indexes of the \(e_g\) bands and the local spins \(3/2\) are described by \(\hat{S}_{ci}\). The first two terms define the ferromagnetic Kondo lattice model and give a realization of the DEM while the third includes polaronic effects. The role of the local dynamical correlations due to the last term remains largely unaccounted and is a main concern in this work. Recent resonant photoemission experiments indicate that the manganese parent compound is in an intermediate state between a charge transfer and Mott-Hubbard insulator with \(U \sim 3.5\,\text{eV} \) [8]. Another important aspect which we shall consider explicitly here is the orbital degeneracy, and, as it turns out, we shall see that these degrees of freedom will play a crucial role within the proposed scenario.

In order to better focus on the role of local repulsion and orbital degeneracy we shall simplify the Hamiltonian [18]. Firstly, as we are concerned with the electronic state in the FM phase we neglect \(H_{J-T}\). This term is most relevant around and above \(T_c\), but moving deep into the FM metallic phase its strength rapidly decreases [20,21,5]. Also, well into the FM phase we can assume the local spins \(3/2\) to be uniform and static. Therefore, irrespective of the magnetization one expects that off-diagonal hopping is to contribute to the stability of the para-orbital state. Thus, irrespective of the magnetization one expects that off-diagonal hopping is to contribute to the stability of the para-orbital state. Finally, on general grounds one expects that off-diagonal hopping is to contribute to the stability of the para-orbital state that we shall encounter latter on. Nevertheless, a more important contribution, which renders our choice for \(t_{ij}^{ab}\) non crucial, is the fact that a rather large hopping \(t > 0.175\) is experimentally necessary for CMR. Thus, disorder is the main reason for the stability of the metallic state against orbital long range order, in analogy with the Néel state in a one band Hubbard model.

We shall consider the model within the dynamical mean field theory that becomes exact in the limit of large dimensions (or large lattice connectivity). We shall assume a semi-circular density of states \(\rho(\epsilon) = 1/(\pi D)\sqrt{1-(\epsilon/D)^2}\), with the half bandwidth \(D = 1\) and \(D = 2\sqrt{\Delta}\). This \(\rho(\epsilon)\) is realized in a Bethe lattice, and our choice is due to both simplicity and the realistic finite bandwidth that it provides. Band structure calculations give \(D \sim 1\,\text{eV} \) [8] which is similar to other TMO compounds.

The Hamiltonian can then be mapped onto its associated impurity problem (a degenerate Anderson impurity in a magnetic field), which is supplemented with a self-consistency condition that enforces the translational invariance [18]. The self-consistency condition reads,

\[
\left[G^0_{\sigma a}(z)\right]^{-1} = z + \mu - \sigma h_{\text{loc}} - t^2 [G_{\sigma a}(z) + G_{\sigma b}(z)] \tag{2}
\]

where \(G^0\) and \(G\) denote local Green functions, \(\mu = \pm \frac{3}{2}\) the spin, \(\mu\) the chemical potential and \(h_{\text{loc}}\) is the effective local magnetic field due to the \(J_H\) coupling of the conduction electrons with the localized spins \(3/2\). It is now clear from (2) the role of the off-diagonal hopping providing frustration in orbit space and favoring the stability of a para-orbital (orbital disordered) state.

We shall numerically solve this model using the quantum Monte Carlo technique [22,23]. To demonstrate that the model remains near a MIT as it goes into the FM phase we shall compute the mass renormalization \(m^*/m\). In the limit of large dimensions the self-energy \(\Sigma = G^0 - G^{-1}\) is local, thus, \(m^*/m = 1 - \partial \Sigma / \partial \omega\). Since our results are obtained at low but finite temperature we shall estimate this value using \(m^*/m \approx 1 - \Sigma(\omega_1)/\omega_1\), where \(\omega_1 = \pi T\) is the first Matsubara frequency. Another quantity that we shall obtain is \((n^0)\) vs \(\mu\) with \(n\) the particle number. The slope of this curve is proportional to the compressibility, therefore the (Mott) insulating states will be indicated by plateaux.

The physics of the two band degenerate Hubbard model has been recently considered within the dynamical mean field approach [22,23]. One of the main results is that, within the paramagnetic state, the phase diagram shows lines of Mott insulating states at integer fillings for values of the interaction \(U > U_c(n)\) at low enough temperatures. As these lines are approached as a function of filling, a divergency in the renormalized mass is observed which signals a correlated metallic state with an effective Fermi energy which vanishes as \((m^*/m)^{-1}\). These features are reminiscent of the solution of the single band Hubbard model which is known in quite detail [18]. The key observation that we shall demonstrate in this paper is that the two band model with \(n \leq 1\) and moderate \(U\) is near a MIT line even as it goes into a saturated FM state. Thus, irrespective of the magnetization the system always remains in a correlated metallic state with a small effective Fermi energy. The underlaying reason is simple, as the electrons become fully polarized one may map the two band model into a single band Hubbard model where the usual role of the spin indices is played by the orbital ones. In other words, under a strong magnetic field the operators carrying \(a\), say, \(\downarrow\) spin disappear from the Hamiltonian [18].

In figure 1 we show \(m^*/m\) as a function of the number of particles and different magnetic fields [27]. The most
striking feature is how, for any field, the mass renormalization maintains its divergent behavior when \( n \rightarrow 1 \) from below. As we argued above this occurs because the system crossover from two- to one-band behavior. In particular note that for the highest \( h_{\text{loc}} \) the \( m^*/m \) plot shows symmetry around \( n = 1 \), as is the case in a single band model. When the system becomes fully polarized, the model maps exactly to a one-band Hubbard model in orbital space. Its associated impurity model becomes a single Anderson impurity model with orbital indexes playing an analogous role as the usual spin. Thus, a small energy scale is dynamically generated as consequence of an “orbital Kondo” effect [29]. Our results also predict that the compounds with \( x \lesssim 0.175 \) should have an \( m^*/m \lesssim 3 \) which is consistent with the relative small enhancement observed in experiments on La\(_{1-x}\)Sr\(_x\)MnO\(_3\) [28].

In figure 2 we show the number of particles \( \langle n \rangle \) as a function of \( \mu \) for different local magnetic fields. We observe that plateaux are always present for fillings \( \langle n \rangle = 1 \) and 2 even in the case of a strong \( h_{\text{loc}} \). Since the slope of the curves is proportional to the compressibility, the system becomes an insulator at those fillings. In the case of \( \langle n \rangle = 1 \) we argued before that under a strong local magnetic field the Hamiltonian maps onto a half-filled para-orbital single band model, therefore, the insulating state corresponds to a Mott-Hubbard insulator for all \( h_{\text{loc}} \). However, the character of the insulating state at \( \langle n \rangle = 2 \) strongly depends on \( h_{\text{loc}} \). For \( h_{\text{loc}} = 0 \) the state is a Mott insulator since the bands are both half-filled. On the other hand, in the polarized state the insulator should be better thought of as a band insulator since the bands can accommodate only one electron each.

The previous discussion relayed heavily on the assumption that for \( h_{\text{loc}} = 1 \) the system is fully polarized. Thus, in figure 3 we plot the relative magnetic moment \( \langle n_\uparrow - n_\downarrow \rangle / \langle n_\uparrow + n_\downarrow \rangle \) vs \( \langle n \rangle \) at different magnetic fields in order to check the validity of the assumption. We observe that at zero field there is no magnetic moment as expected while for the largest field the magnetic moment is close to unity which indicates that all the electrons are almost fully polarized.

It is interesting to comment on the behavior of the magnetization in the intermediate case [31] which illuminates aspects of the competition between coherence and magnetization. At small fillings the correlation effects due to the on-site repulsion are not important and the magnetic moment relative to the particle number is rather small. As the particle occupation increases the correlation effects become more important (the effective mass increases) and the magnetic moment grows rapidly due to the enhanced susceptibility of the correlated metal. This almost saturated state persist up to filling one and is surprising to observe that this dramatic change in the magnetization has almost no noticeable effect on either \( m^*/m \) nor the compressibility (figures 1 and 2). The orbital degrees of freedom are now playing a crucial role in order to maintain the correlated metallic state. As we fill the system further, the associated impurity model goes into a mixed valence state and the enhanced charge fluctuations have the effect of lowering the magnetic susceptibility. Finally, approaching \( \langle n \rangle = 2 \) the repulsive interaction renders the electrons almost localized in a Mott state and the polarization grows again due to the large susceptibility of the almost free moments.

To conclude we have introduced a model that contains realistic features of the perovskite manganite oxides, namely, band degeneracy and strong electronic correlations. We demonstrated that for parameters which are appropriate for the CMR compounds the system remains in a correlated metallic state and close to a MIT as it goes into the saturated FM phase at low temperatures. The low energy physics can then be identified with that of a single band Hubbard model close to a MIT. We argued that, in analogy to other perovskite TMOs, this may allow for the qualitative interpretation of a variety of experiments which suggest the existence of a small energy scale. We identify this energy scale with the renormalized Fermi energy of the coherent quasiparticle peak that characterizes the proximity to the MIT in the dynamical mean field theory of the Hubbard model.

Finally, is interesting to observe that in our proposed scenario the orbital degrees of freedom are playing a crucial role. This seems to be emerging as a generic feature of correlated electron systems which contain quasi-degenerate bands as was recently demonstrated in the neutron scattering experiments on the classical transition metal oxide V\(_2\)O\(_3\) [31] and also in YTiO\(_3\) [32]. The application of similar techniques on the CMR compounds may serve as an experimental test for the validity of the scenario proposed in this work.

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FIG. 1. Renormalized mass as a function of the particle occupation for $U = 3, T = 1/8$ and $\mu_{\text{loc}} = 0, 0.5, 1$ (full, dashed, long dashed).

FIG. 2. Particle occupation as a function of the chemical potential for $U = 3, T = 1/8$ and $\mu_{\text{loc}} = 0, 0.5, 1$ (full, dashed, long dashed).
FIG. 3. Relative magnetic moment of the conduction electrons as a function of the particle number for $U = 3$, $T = 1/8$ and $h_{\text{loc}} = 0, 0.5, 1$ (full, dashed, long dashed).