Orbital Kondo Effect in CrO$_2$: A LSDA+DMFT Study

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Motivated by a collection of experimental results indicating the strongly correlated nature of the ferromagnetic metallic state of CrO$_2$, we present results based on a combination of the actual bandstructure with dynamical mean-field theory (DMFT) for the multi-orbital case. In striking contrast with LSDA+(U) and model many-body approaches, much better semiquantitative agreement with (i) recent photoemission results, (ii) domain of applicability of the half-metal concept, and (iii) thermodynamic and dc transport data, is obtained within a single picture. Our approach has broad applications for the detailed first principles investigation of other transition metal oxide-based half-metallic ferromagnets.

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A lot of attention has recently been focused on CrO$_2$, widely used in magnetic recording, and with potential applications for spintronics. In contrast to the CMR manganites, stoichiometric CrO$_2$ is already a ferromagnetic metal. Given the formal 4+ valence state of Cr, the two 3d electrons occupy $t_{2g}$ orbitals. One would intuitively expect to form $S = 1$ spin on each site, and an antiferromagnetic Mott insulator. Why CrO$_2$ is a ferromagnetic metal instead, has been answered by Korotin et al., who have carried out insightful (LDA + U) calculations for this material. Their main conclusions are: (i) The triple-degeneracy of the $t_{2g}$ d-orbitals is lifted by tilting and rotation of the Cr–O octahedra in the basic rutile structure, resulting in three bands with $xy$, $yz$ ± $zx$ character in the solid. The $O$ 2$p$ band(s) act, at least partially, as hole reservoirs resulting in Cr being mixed-valent (like $Mn$ in doped manganites), explaining metallic via self-doping in the negative charge-transfer situation realized in CrO$_2$. (ii) An almost dispersionless majority spin band of predominantly $d$ character at about 1 eV below $E_F$ over a large region of the Brillouin zone. This corresponds to strongly localized $xy$ orbitals completely occupied by one majority spin electron. But the $d$ states (shown in Fig. 1) of predominantly $yz$ ± $zx$ character hybridize with the $O$ 2$p$ band and disperse, crossing $E_F$. The Hund’s rule coupling between the localized $dz^2$ spin and the spin density of the band $d_{yz}+d_{zx}$ electrons polarizes the latter, giving a ferromagnetic state via the double-exchange (DE) mechanism. Thus, both the metallicity and ferromagnetism are correlated well with each other.

Closer examination reveals that CrO$_2$ is a strongly correlated metal, implying that many-body correlation effects beyond the LDA (or its variants) need to be considered. A number of experimental observations support such a view:

1. Polarization dependent XAS measurements reveal substantial ligand orbital polarization. An exchange splitting energy of $\Delta_{xx-spl} \simeq 3.2$ eV was deduced, implying substantial correlation effects, while LSDA calculations yield $\Delta_{xx-spl} \simeq 1.8eV$!

2. The resistivity has a characteristic correlated Fermi liquid (FL) form: $\rho(T) = \rho_0 + AT^2 + BT^{7/2}$, and, in fact, CrO$_2$ is a “bad metal” at high $T$, with $\rho_{dc}(T > T_{FM}^c = 390K)$ exceeding the Mott limit.

3. Optical conductivity studies reveal a Drude part at low energies, followed by a broad bump around 0.8 eV and high-energy features centered around 3 eV. LDA+U predicts only the small Drude part correctly. In addition, noticeable spectral weight transfer (SWT) from high to low energy is found as $T$ is reduced. This SWT scales with magnetization, $M(T)$, as in the CMR materials, showing clearly the correlated nature of the metallic state (the SWT is a dynamical many body correlation effect, and cannot be accessed by LSDA+U).

4. Recent measurements show that the integrated photoemission (PES) lineshape is characterized by a low-energy quasicoherent feature along with an incoherent broad feature at lower energies. This satellite feature observed in PES is a signal for the importance of dynamical, many-body correlation effects beyond LDA+U.

5. Finally, recent optical and tunneling measurements show half-metallic character only close to (about $\simeq 0.5$ eV around) $E_F$. Direct comparison with LSDA+U shows that these calculations would yield half-metallicity up to 1.5 eV. It is not easy to cure this within LSDA+U. One could, of course, refer to LSDA results, where the minority-spin band does have a threshold around 0.6 eV, but LSDA gives results directly in conflict with (1)-(4).

The emergence of a correlated FL scale required to understand the above features is out of reach of LSDA or pure DE models, because these are observed well below $T_{c}$, and are thus related to additional scattering mechanisms in a half-metallic situation. We argued previously that the above effects could be understood...
by invoking the important role of local, dynamical orbital correlations in the \(t_{2g}\) sector. However [14], a model (gaussian) density of states was used there, limiting direct comparison to experimental results. To do this, one has to extend a model-based approach to include real bandstructure features via the LDA+DMFT method. We choose LDA+DMFT because although approximations like LSDA+U do generate the correct ordered, insulating state(s), they fail to describe the correlated paramagnetic states, or the Mott transition accompanied by dynamical SWT. As discussed in detail [15], very good agreement with experiment is achievable within LDA+DMFT. In practice, this is a highly non-trivial task, and very computationally expensive. Here, we describe \(CrO_2\) within this “first-principles bandstructure” for correlated metals. The results are found to be in very good semiquantitative agreement with experiments probing both the occupied parts of the one-particle DOS \((\rho(\omega))\) as well as with thermodynamic and dc transport data cited above.

An understanding of features mentioned above should go hand-in-hand with the basic electronic structure. Our starting point is the LSDA+U work of Korotin et al. [3], which yields the partial bandstructure of \(CrO_2\) (notice that the Hartree-Fock shift is already incorporated in LSDA+U). In Fig. 1, we show the partial \(t_{2g}\) DOS for the half-metallic situation realized in \(CrO_2\). In the real material, only the \(t_{2g}\) states of \(Cr\) hybridized with \(O\)-2p states are important, and so we neglect the higher energy \(e_g\) bands. Following [3], we suppose the \(O\)-2p states to introduce a small number of holes into the \(d_{yz\pm xz}\) bands. In fact, \(\int_{-1.5}^{1.3} \rho_{t_{2g}}(\omega) d\omega = 1.82 < 2\). Given that the \(O\)-2p spectral density is small compared to \(\rho_{t_{2g}}(\omega)\), we keep only the \(t_{2g}\) bands in what follows. With the LSDA bandstructure, the one-particle part of the Hamiltonian is:

\[
H_0 = \sum_{\mathbf{k},\alpha,\beta} \epsilon_{\alpha\beta}(\mathbf{k}) \hat{c}^\dagger_{\mathbf{k}\alpha} \hat{c}_{\mathbf{k}\beta}\tag{1}
\]

with \(\rho_{t_{2g}}(\omega) = \sum_{\alpha\beta} \delta(\omega - \epsilon_{\alpha\beta}(\mathbf{k}))\) and \(\alpha, \beta = xy, yz \pm xz\). To avoid double counting of Coulomb interaction contributions already contained in \(H_{\text{LDA}}\), a term \(H_0^{\text{U}}\) is subtracted from \(H_0\). Following [13], the final result is,

\[
H_0 = \sum_{\mathbf{k},\alpha,\beta} \epsilon_{\alpha\beta}(\mathbf{k}) \hat{c}^\dagger_{\mathbf{k}\alpha} \hat{c}_{\mathbf{k}\beta} + \sum_{\mathbf{i},\sigma} \epsilon_{i\sigma\alpha} n_{i\sigma\alpha},\tag{2}
\]

where \(\epsilon_{i\sigma\alpha} = \epsilon_{i\sigma\alpha} - U(n_{i\sigma\alpha} - 1/2) + (1/2)J_H(n_{i\sigma\alpha} - 1)\), and \(U\) and \(J_H\) are defined below in \(H\).

The full many body Hamiltonian for \(CrO_2\) is:

\[
H = H_0 + \frac{1}{2} \sum_{i\sigma\sigma'} U_{\alpha\beta} n_{i\sigma\alpha} n_{i\sigma\beta'} - \frac{1}{2} \sum_{i\sigma\sigma'} J_H S_{i\sigma} S_{i\sigma'},\tag{3}
\]

To make progress, we notice that LSDA+U pushes the minority spin \(t_{2g}\) bands to high energy \(\omega > 2\text{eV}\). To begin with, we focus on the majority-spin \(t_{2g}\) sector. A valid choice of parameters to describe this situation is given by the intra-orbital \(U = 5\text{ eV}\), and the Hund’s rule coupling \(J_H = 1\text{ eV}\), close to the LSDA deduced values, along with the inter-orbital local interaction \(U' = U - 2J_H\), for \(t_{2g}\) orbitals. Notice that \(U', J_H\) couple the three \(xy, yz \pm xz\) bands, requiring an extension to treat multi-orbital effects.

![FIG. 1. \(t_{2g}\) LSDA+U density of states per formula unit for both spin channels obtained from [3], Figs. 3 (spin-down) and 4 (spin-up).](image)

We solve this multiband hamiltonian in \(d = \infty\) using the iterated perturbation theory (IPT), suitably generalized for the multi-orbital case. Notice that \(CrO_2\) falls into the class of TM oxides with well-separated \(t_{2g}\) and \(e_g\) bands [3]. Moreover, \(G_{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta} \delta_{\sigma\sigma'} G_{\alpha\sigma}(\omega)\) and \(\Sigma_{\alpha\beta\sigma\sigma'}(\omega) = \delta_{\alpha\beta} \delta_{\sigma\sigma'} \Sigma_{\alpha\sigma}(\omega)\).

In the \(t_{2g}\) sub-basis, a DMFT solution involves (i) replacing the lattice model by a self-consistently embedded multi-orbital, asymmetric Anderson impurity model, (ii) and a self-consistency condition which requires the local impurity Green function to be equal to the local GF for the lattice, given by

\[
G_{\alpha}(\omega) = \frac{1}{V_B} \int d\mathbf{k} \int d^{3}\mathbf{\delta} \left[ \frac{1}{(\omega + \mu) - H_{\text{LDA}}(\mathbf{k}) - \Sigma(\omega)} \right] .\tag{4}
\]

Using the locality of \(\Sigma_{\alpha\beta}\) in \(d = \infty\), we have \(G_{\alpha}(\omega) = G_{\alpha}(\omega - \Sigma_{\alpha}(\omega))\) using the Hilbert transform of the LSDA DOS. In contrast to [13], the inter-orbital coupling scatter electrons between the \(xy, yz \pm xz\) bands, so only the total number, \(n_{\text{d}_{yz\pm xz}}\), is conserved in a manner consistent with Luttinger’s theorem. Further, in \(CrO_2\), due to a highly asymmetric LDA DOS (Fig. 1), we expect the final spectral function to reflect the interplay of the complicated bandstructure and inter-orbital...
correlations.

The calculation follows the philosophy of the IPT for the one-band Hubbard model, but the self-energies and propagators are matrices in the orbital indices [16]. Leaving details for a longer paper, we present here the final equations. The local propagators are given by,

\[ G_\alpha(\omega) = \frac{1}{N} \sum_{k} \frac{1}{\omega - \Sigma_\alpha(\omega) - \epsilon_\alpha}, \]

where \( \alpha = xy, yz \pm zx \). The local self-energies are computed from a generalized IPT formalism that takes into account the Luttinger theorem constraint of half-filling, [15] (generalized Friedel sum rule). Explicitly,

\[ \Sigma_\alpha(\omega) = \frac{A_\alpha[\Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega) - \Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega)]}{1 - B_\alpha[\Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega) + \Sigma_\alpha^{(2)}(\omega)]} \]

where, for example, \((\alpha \neq \beta \neq \gamma)\)

\[ \Sigma_\alpha^{(2)}(i\omega) = \left( \frac{U_{\alpha\beta}}{\beta} \right)^2 \sum_{n,m} G_\alpha^0(i\omega_n) G_\beta^0(i\omega_m) G_\beta^0(i\omega_n + i\omega_m - i\omega) \]

and \( G_\alpha^0(\omega) = [\omega + \mu_\alpha - \Delta_\alpha(\omega)]^{-1} \) In Eqn. [6],

\[ A_\alpha = \frac{n_\alpha(1-2n_\alpha) + D_{\alpha\beta}[n]}{n_\alpha(1-n_\alpha)} \text{ and } B_\alpha = \frac{(1-2n_\alpha)\epsilon_\alpha + \mu_\alpha - \mu_{\alpha'}}{2U_{\alpha\beta}n_\alpha(1-n_\alpha)}. \]

Here, \( n_\alpha \) and \( n_\alpha^0 \) are particle numbers determined from \( G_\alpha \) and \( G_\alpha^0 \) respectively, and \( D_{\alpha\beta}[n] = \langle n_\alpha n_\beta \sigma' \rangle \) is calculated using \( \langle n_\alpha n_\beta \sigma' \rangle = \langle n_\alpha \sigma \rangle \langle n_\beta \sigma' \rangle - \frac{1}{U} \int_{-\infty}^{\infty} f(\omega)\Sigma_\alpha(\omega) G_\alpha(\omega) d\omega \). The last identity follows directly from the equations of motion for \( G_\alpha(\omega) \).

FIG. 2. LSDA+DMFT partial and total density of states for the \( Cr \) \( t_{2g} \) orbitals for \( U' = 3.0 \) eV.

We now present our results. In Fig. 3 we show the renormalized, total spectral function (sum of the partial \( t_{2g} \) DOS) of \( CrO_2 \) for \( T = 0 \). Notice the high-energy “Hubbard bands” appearing as manifestations of dynamical effects of strong orbital correlations in the \( t_{2g} \) sector. As is also clear, the Luttinger theorem is obeyed to a very good accuracy. Additionally, the self-energies show characteristic correlated Fermi liquid behavior. Based on these results, we interpret the low energy quasicoherent features as arising from collective orbital Kondo screening of \( t_{2g} \) orbital moments in the fully spin polarized half-metal.

We emphasize the quantitative differences between the results of this work with an earlier one [14], where an idealized (gaussian) unperturbed DOS was used; no low-energy (LSDA related) pseudogap-like feature was visible there. Further, the \( d_{xy} \) band was replaced there by a dispersionless, local level playing the role of polarizing the \( yz \pm zx \) bands via strong \( J_H \), making it impossible to access changes resulting from the interplay of the realistic bandstructure and strong orbital correlations. These differences are especially important when one attempts to describe spectroscopy results quantitatively (see below).

In Fig. 3 we show the integrated PES lineshape for low \( T \), obtained directly from \( I_{PE}(\omega) = f_F(\omega - E_F) \rho_{t_{2g}}(\omega) \). Quite satisfactorily, the quasicoherent spectral weight at \( \mu \) is larger than what was reported in earlier experimental work [17], and in quite good agreement with results obtained recently from thin films [12]. In particular, it is gratifying to see good quantitative agreement between theory and experiment in the region \( -1.2 < \omega < E_F \). Specifically, the small, but clear dip seen in the LSDA+U DOS is absent in LSDA+DMFT, in agreement with the thin film results. At higher binding energy, we do not expect quantitative agreement because both \( O-2p \) and \( e_g \)
bands of $Cr$ begin to contribute, and also because the minority spin $t_{2g}$ band leads to a breakdown of our approach, which neglected the minority-spin sector. Consequently, further work is needed to make comparison with the recent tunnelling and optical measurements of $\uparrow\downarrow$, since these measurements probe the minority spin band at higher energies. Optical measurements reveal that the almost complete spin polarization near $E_F$ is reduced at higher energy $\omega \geq 0.5 \, eV$.

To this end, we extend the above calculation to include the minority-spin $t_{2g}$ bands, which (see Fig. 1) are pushed to high energy $\omega > 2 \, eV$ by LSDA+U. Inter-orbital correlations between the $t_{2g} \uparrow, \downarrow$ bands are accounted for in a way similar to that described above for the majority-spin sector. However, a larger $U_{\uparrow\downarrow} = U' + 2J_H$ is now required for the calculation of the minority spin DOS, $\rho_{t_{2g}}^{\downarrow}(\omega)$, alongwith a Hartree shift of $-J_{HM}$ (where $m$ is the magnetization per site) for the $\downarrow$-spin sector. The interaction-corrected minority spin DOS (lower panel of Fig. 2) shows interesting features. First, $U_{\uparrow\downarrow}$ broadens out the sharp LSDA features, and more importantly, transfers dynamical spectral weight from high- to lower energy $\omega \simeq 0.7 \, eV$. As a result, above 0.7 $eV$, the spin polarization decreases continuously from saturation, in nice agreement with indications from optical and tunnelling measurements [13]. Notice that LSDA+U would predict complete half-metallicity up to a much higher energy $\omega \simeq 1.5 \, eV$. This represents strong evidence for the importance of treating dynamical SWT correctly, an effect missed by LSDA+U, but treated adequately by LSDA+DMFT. In fact, in our view, optical and tunnelling results provide a direct confirmation of the importance of dynamical correlation effects. Indeed, one could argue that the near similarity of the LSDA- and LSDA+DMFT spectral functions for $t_{2g}$ sector for $-0.7 \leq \omega \leq 0.2 \, eV$ is a sign of the adequacy of LSDA+U. As discussed above, however, consistency with optics and tunnelling results as well is only achieved within LSDA+DMFT.

The results obtained above are also consistent with the low-$T$ thermodynamic and dc resistivity of $CrO_2$. Indeed, from the computed self-energy, we estimate a moderate quasiparticle renormalization, $Z$. From the fact that $\text{Im} \Sigma_{yz\pm\pm}(\omega) \simeq -i\omega^2$, we infer that the low-$T$ dc resistivity should follow $\rho_0(T) = \rho_0 + A T^2$. In fact, using $A = (m^*/n^*)^2 (\partial^2 \Sigma(\omega)/\partial \omega^2)_{\omega=E_F}$ from $\text{Im} \Sigma_{yz\pm\pm}(\omega)$, we estimate the Woods-Saxon ratio, $\frac{A}{\gamma^2} \simeq 3.5 \times 10^{-5}$, close to the value found experimentally [6].

To conclude, we have extended the LSDA+U calculation [10] to explicitly include the dynamical correlation effects arising from local electronic correlations in the $t_{2g}$ sector in the multi-orbital system $CrO_2$. Puzzling signatures of strong correlations in the half-metallic state are understood as manifestations of collective orbital Kondo effect in the $t_{2g}$ sector, originating from a non-trivial interplay between the realistic hopping in the rutile structure and inter-orbital ($t_{2g}$) correlations. Much better quantitative agreement with PES is obtained with LSDA+DMFT than with LSDA or LSDA+U, showing clearly the importance of dynamical correlation effects. Further, our results are also in semiquantitative agreement with thermodynamic and $dc$ transport measurements. Essentially similar techniques can also be used fruitfully for other transition metal oxide-based ferromagnets currently of great interest [17].

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