Dynamical Mean Field Theory of Nickelate Superlattices

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The electronic properties of transition metal oxides are of central importance to condensed matter physics and materials science, both for their fundamental scientific interest and for their potential for novel applications. Of particular current interest are the new possibilities enabled by advances in atomic-scale layer-by-layer growth of combinations of complex oxide materials. Experiments report remarkable and unexpected properties including interface superconductivity, growth of combinations of complex oxide materials is now routine.

However, band theory provides an incomplete description of the relevant electronic states in materials with strong electronic correlations. In this paper we show that strong correlations in superlattices such as the rare earth nickelates motivates an examination of the effects of correlations. In this paper we show that strong correlation effects actually decrease the polarization. The key feature aspect of our calculation is the use of a realistic Hamiltonian which is derived from the density functional band calculations of Ref. and in particular takes oxygen states into account explicitly. The possibility of charge transfer to the oxygen affects the results in an important way. The model is of the general form

\[ H = H_d + H_{hyb} + H_{ligand} \]  

The Hamiltonian for the correlated \("d"\) subspace is

\[ H_d = \sum_{j,a,\sigma} \varepsilon_d d_{j,a\sigma}^{\dagger} d_{j,a\sigma} + \frac{U}{2} \tilde{N}_d \left( \tilde{N}_d - 1 \right) + H_J \]  

with \(a = 1, 2\) labelling the \(x^2 - y^2\) and \(3z^2 - r^2\) d states.
The charge transfer energy $\Delta = \varepsilon_p - \varepsilon_d$ is renormalized from the band theory value $\Delta$ to reveal the quasiparticle behavior in all orbital sectors. Panel

To treat the many-body physics we use the single-site dynamical mean field approximation (DMFT) which marks the limit of stability of the metallic phase and a lower critical interaction strength $U_{c1}$ which marks the limit of stability of the insulating phase. Fig. 1 presents $U_{c1}$ of $\Delta$. The location of the rare earth nickelates on the phase diagram is not known. $LaNiO_3$ is metallic in bulk and (except for one and perhaps 2 monolayer samples) in thin film form. Other members of the family such as $NdNiO_3$ have insulating ground states, suggesting that the materials are close to a metal/charge-transfer insulator phase boundary, but the origin of the insulating phase is controversial. We therefore study a range of parameters in the metallic state. In DMFT the insulating state typically exhibits some form of orbital order, making the interpretation less clear.

The many-body electronic structure is represented by the local spectral function (many-body density of states) $A_{\nu}(\omega) = \text{Im} (-i \int d\tau e^{-i\omega \tau} \langle \psi_{\nu}^{\dagger}(j,\tau) \psi_{\nu}(j,\tau) \rangle$ (here $\nu$ labels an orbital and $j$ a unit cell in the lattice). Panel

FIG. 2: (Color online) Analytically continued spectral function $A(\omega)$, for Ni $d_{x^2-y^2}$ (dotted, blue on line), $d_{d_{xz-yz}}$ (solid, red on line) orbitals and sum of all O orbitals (dashed, magenta on line). Parameters (Nd computed from integral of the many-body DOS over the entire manifold of occupied states) $N_d = 1.99$, $\varepsilon_d = -1.22$ eV, $\varepsilon_p = -5.2$ eV. (b) $U = 4$ eV, $N_d = 1.60$, $\varepsilon_d = -3.91$ eV, $\varepsilon_p = -7.89$ eV. (c) $U = 6$ eV, $N_d = 2.12$, $\varepsilon_d = -8.95$ eV, $\varepsilon_p = -4.93$ eV. (d) $U = 6$ eV, $N_d = 1.52$, $\varepsilon_d = -5.75$ eV, $\varepsilon_p = -7.73$ eV. Fermi level is zero. $J = 0.5$ eV and $T = 0.1$ eV. Computed polarization $P$ from Eq. 4 with $E_{\text{corr}} = -3$eV shown on each panel. The $P$ values corresponding to integration over the energy range of the entire $p - d$ manifold are $P = (0.16, 0.14, 0.11, 0.11)$ for panels a-d respectively.
The occupancy $n_a$ for a given orbital $a$ is defined as

$$n_a = \int_{E_{low}}^{\mu} \frac{d\omega}{\pi} A_a(\omega)$$

and the orbital polarization is

$$P = \frac{n_{x^2-y^2} - n_{3z^2-r^2}}{n_{x^2-y^2} + n_{3z^2-r^2}}$$

We have chosen the zero of energy such that $\mu = 0$. We believe it is most physically reasonable to focus on the difference in occupancy of near Fermi-surface states, corresponding to taking $E_{low} = -3eV$ to capture the antibonding but not the bonding bands. Alternatively, one may integrate over the whole (many-body) bandwidth. We have provided the $P$ corresponding to both definitions; the results are very similar and the conclusions are not changed. The computed $d$ occupancies and polarizations are given in the caption and panels of Fig. 2.

Interactions decrease the polarizations.

An alternative, low-energy definition of orbital polarization may be obtained from the Fermi surface. In pseudocubic LaNiO$_3$ the calculated Fermi surface has two sheets, corresponding to the two relevant $d$ orbitals.

In single-layer high-$T_c$ cuprates the Fermi surface has only one sheet, corresponding to a single relevant $d$ band, so one may identify a single-sheeted Fermi surface with an orbitally polarized low energy theory. Fig. 3 shows the evolution of the Fermi surface of the nickelate superlattice as the interaction strength is increased at fixed $\Delta \approx -2$. The non-interacting model has a substantial degree of orbital polarization, as seen from the very small size of the central Fermi surface region, but as soon as the interaction is turned on the size of the central patch increases and then does not change over the entire metallic region, consistent with the values of $P$ given in the caption of Fig. 2. (The Fermi surface in panel (d) is slightly smaller because at the lowest accessible temperature the fully coherent Fermi liquid state was not achieved.)

The small value of $P$ we find is in agreement with recent resonant X-ray absorption experiment but does not agree with results of previous dynamical mean field studies of Hansmann and collaborators. While there are minor technical differences (including the use, by Hansmann et. al. of an Ising approximation to the Hund's interaction) we believe that the most important issue is the model. Refs. [34,35] downfolded the band theory results to a two-band model representing only the antibonding band, whereas in our work the $Ni-O$ charge transfer plays an important dynamical role, enabling the high spin $d^8\bar{L}$ configuration which is not susceptible to orbital polarization.

Our results suggest that in realistic models of nickelate superlattices, a significant orbital polarization will be very difficult to achieve. However, the two orbitals will not have identical properties. We present in Fig. 4 the difference $\Delta A(\omega) = A_{x^2-y^2}(\omega) - A_{3z^2-r^2}(\omega)$ calculated for parameters corresponding to Fig. 2(a)-(d). The (a) of Fig. 3 presents the noninteracting ($U = 0$) case, for which $\Delta \approx -4eV$. These spectra are consistent with previously published GGA result (the small differences arise from the difference between the two dimensional model used here and the fully three dimensional model of Ref. [17]. Two energy regions are evident: a near Fermi surface region representing the $d - p$ antibonding band and a lower energy region representing the bonding combination of $d$ and $p$. The $p$ level energy is visible as a sharp peak in this energy region. Panel (b) shows the result of increasing the interaction strength to $U = 4eV$ while keeping both the total electron count and $\Delta$ fixed. Comparison to Fig. 4 shows that this change moves the system close to the metal-insulator phase boundary. We see that the splitting between the bonding and antibonding regions of the spectrum increases, essentially because the interaction increases the effective $d$-level energy. We also see that the differences between the spectra of the two $d$ orbitals are smaller than in panel (a). Panels (c) and (d) of Fig. 3 shows spectra obtained for a stronger interaction $U = 6eV$. Panel (c) shows a double-counting correction corresponding to $\Delta = 4eV$ and chosen to undo the shift in the $d-p$ splitting. The parameters are far from the metal-insulator phase boundary and the spectra are seen to be very similar to those computed for the noninteracting model. In panel (d) we have chosen the double counting correction to keep the energy separation between the $O$ states and antibonding $p-d$ states approximately the same as in panel (b). The features near the Fermi level are narrower than in panel (b) because the system is closer to the metal-insulator phase boundary, but the spectra are otherwise similar.

FIG. 3: Calculated Fermi surfaces at $J = 0.5$ eV and $\Delta = -1.88$ eV. (a) $U = 0$, $N_d = 2.44$, $\varepsilon_d = -1.81$ eV. (b) $U = 4$ eV, $N_d = 1.65$, $\varepsilon_d = -4.65$ eV. (c) $U = 6$ eV, $N_d = 1.45$, $\varepsilon_d = -5.78$ eV. (d) $U = 7$ eV, $N_d = 1.34$, $\varepsilon_d = -6.02$ eV. For panels (a)-(c) $T = 0.05$ eV; for panel (d) $T = 0.025$ eV.
d-spectral function may be measured in resonant x-ray scattering experiments, and difference spectra are relatively insensitive to experimental complications such as core-exciton and final-state corrections. We see that the different electronic structures lead to observable effects in the N\textsubscript{d} \sim 2.0 case (corresponding to panels (a) and (c) in Fig. 2) the difference spectra reveal prominent peaks just below the Fermi level (\sim −0.5 eV) and around \sim ±2.0 eV. These features do not appear in the N\textsubscript{d} \sim 1.45 cases, (panels (b) and (d) in Fig 2). Also the two feature provide a measure of the physical \varepsilon_{p} − \varepsilon_{d}. Comparison of these calculations to new generations of X-ray absorption experiment\textsuperscript{[12]} may help evaluate the orbital polarization and pin other material parameters.

In summary, we have shown that in a realistic many-body model of nickelate heterostructures, it is essentially not possible to achieve a significant degree of orbital polarization, so that the idea\textsuperscript{[13]} of obtaining a single-band electronic structure must be discarded. Further, we showed that a reduction of the full Hamiltonian to a Hubbard-like model\textsuperscript{[16,12]} which includes only the correlated orbitals yields a fundamentally misleading picture of the electronic structure. We presented spectra which should help in establishing the actual value of the double-counting correction for these materials, which is crucial to the metal-insulator transition behavior.

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