A Quantum Chemistry Plus Dynamical Mean-Field Approach for Correlated Insulators: Application to $La_2CuO_4$.

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While the traditional local-density approximation (LDA) cannot describe Mott insulators, ab-initio determination of the Hubbard $U$, for example, limits LDA-plus dynamical mean field theory (DMFT) approaches. Here, we attempt to overcome these bottlenecks by achieving fusion of the quantum chemistry (QC) approach with DMFT. QC+DMFT supplants the LDA bandstructure by its QC counterpart as an input to DMFT. Using QC+DMFT, we show that undoped $La_2CuO_4$ is a $d$-Mott insulator, and qualitatively discuss the circulating current- and incoherent metal phase, at small but finite hole doping. Very good quantitative agreement with experimental photoemission- and optical spectra constitutes strong support for efficacy of QC+DMFT. Our work thus opens a new avenue for truly ab-initio correlation-based approaches to describe correlated electronic systems in general.

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High-$T_c$ superconductivity (HTSC) in quasi-two-dimensional (2D) cuprates is an outstanding, unsolved problem in modern condensed matter physics. These materials are stochiometric Mott insulators (MI). Upon hole doping ($x$), a highly unusual, $d$-wave pseudogapped “metal” with strongly non-Fermi liquid (nFL) properties smoothly evolves into the “strange metal” around optimal doping ($x_c$), where singular responses reminiscent of a 1D Luttinger liquid are observed. At lower $T$, $d$-wave superconductivity, peaking around $x_c$, is seen. Upon overdoping, $d$-SC rapidly disappears along with a rapid crossover to a low-$T$ FL metal. These unique observations defy understanding in any FL picture, forcing one to search for non-FL alternatives.

In reality, cuprates are charge-transfer (CT) “Mott” systems. (i) Strong particle-hole asymmetry is indeed necessary for a quantitative description. LDA based studies suggest that the maximum $T^{\text{max}}$ correlates with $t'/t$. Moreover, $t''/t'$ is controlled by axial orbitals. (ii) The role of these apical orbitals in cuprates is ill-understood; they may be relevant for the “hidden order” in the pseudo-gap (PG) phase, presumed to be of the circulating current (CC) type. If true, how does this constrain a minimal model for cuprates? (iii) A host of experiments clearly reveal the $k$-space differentiation of quasiparticle (QP) states in doped cuprates. The normal-state PG has the same $d$-wave symmetry as the SC at lower $T$. Quantum oscillation measurements show that small hole pockets for small $x$ evolve, possibly via multiple electron- and hole-like sheets, into a full, Luttinger Fermi surface (FS) around optimal doping ($x_{\text{opt}}$). (iv) Finally, near $x_{\text{opt}}$, singular low energy responses suggest a branch cut, rather than a pole-like analytic structure of the one-particle Green’s function, $G(k,\omega)$, near $E_F$. This goes hand-in-hand with FS reconstruction at $x_{\text{opt}}$. Are these findings linked to a possible quantum critical point (QCP) at $x \approx x_{\text{opt}}$, as in $f$-band compounds? If so, does the PG state have a “hidden” order? Developing an ab-initio formulation capable of reconciling (iii) – (iv) above; i.e, the quantum oscillation (dHvA) data and angle-resolved photoemission (ARPES) dispersion with one- and two particle dynamical responses is a challenge for theory, and has hitherto been studied within effective models. If, however, the $d$-PG phase indeed carries CC order, these issues must be studied using an extended Hubbard model involving both planar- and apical $p - d$ states.

In light of (i) – (iv), inclusion of strong electronic correlations in a multi-band Hubbard model (with planar and apical $p - d$ states) is mandatory. Here, we extend earlier work to compute the dynamical responses by marrying the quantum-chemical (QC) band structure with multi-orbital DMFT. We “derive” an effective model for cuprates that, by construction, is consistent with (i) – (iii) above. We show how both one- and two-particle spectra (PES and optics) in the CT-MI are quantitatively described by QC+DMFT. This is a novel theoretical route, hitherto unexplored, and avoids the “$U$” problem in LDA-based approaches, as detailed below.

Earlier QC work is essentially a variational calculation, using a multi-configurational wave-function similar to that used for the one-band Hubbard model, but including local and nearest neighbor (n.n) $p - d$ and $d - d$ excitations, and quantitatively captures the strong renormalization of a doped carrier in a MI. Short range electronic (AF spin) correlations anisotropically renormalize the bare band structure, leading to $k$-space differentiation, as derived before in the one-band context, and in good quantitative agreement with both the ARPES dispersion, and the Shubnikov-de Haas data. The nodal (N) QPs have predominantly planar character, while the anti-nodal (AN) QPs...
have significant mixing of apical $d_{z^2} - p_z$ states. However, the QC work cannot compute dynamical spectra. To address (ii) and (iv) above, the QC work needs to be “married” with DMFT/cluster-DMFT calculations. Cluster-DMFT successfully reproduces various anomalous responses in cuprates, but within an effective model framework. Here, we harmonize the successes of the QC method and DMFT-like approaches for the CT-MI phase in an ab-initio framework; the doped case will be treated separately.

Labelling the $d_{x^2-y^2} - p_x$ and $d_{z^2} - p_z$ bands found in the QC work by “1, 2” leads to an effective “two-band” Hubbard model, $H = H_0 + H_1 + H_{mix}$, where $H_0 = \sum_{k,a=1,2} \epsilon_{k,a} c_{k,a} ^\dagger c_{k,a} + \sum_{i,a=1,2} \Delta a_{n_{ia}}$.

$$H_1 = U \sum_{i,a=1,2} n_{ia} n_{ia} + U' \sum_{i,a\neq b} n_{ia} n_{ib} - J \sum_{i,a\neq b} S_{ia} S_{ib}$$ (1)

and

$$H_{mix} = \sum_{k,\sigma} t_m(k)(\epsilon_{k,\sigma}^0 c_{k,\sigma} ^\dagger + h.c)$$ (2)

where $t_m(k) = t_m(\cos k_x \cos k_y)$ is the d-wave form factor associated with interleave, inter-orbital $d_{x^2-y^2} - d_{z^2}$ one-particle hopping. ($\Delta_1 - \Delta_2$ is 1.15 eV and $U \simeq 5.0$ eV is chosen from the QC result ($\sum_{\alpha} + E_N - 12E_N \simeq 5.0$ eV), while $J = 0.6$ eV is taken from atomic tables, and $U' \simeq U - 2J = 3.8$ eV. As for the hoppings, $t = 0.45$ eV is chosen to be its “bare” value, while $(t', t'')$, $t_m = 0.01, 0.075, 0.2$ eV in $H$ are renormalized (by short-range static AF correlations) values taken from QC results [16]. This is because DMFT mainly renormalizes $t$, but the farther-neighbor hoppings are renormalized by non-local correlations beyond DMFT; we take the QC (static) renormalizations for these as an input into the DMFT machinery. Since QC already treats the effect of static correlations, [16], we do not include the static Hartree contribution in the DMFT treatment, thereby avoiding double counting of such terms. QC+DMFT now treats the effects of local dynamical correlations and non-local, static correlations on carrier dynamics in a single picture. The two dispersive bands are then given as $\epsilon_1(k) = -2t(c_x + c_y) - 2t'c_x c_y - 2t''(c_{x^2} + c_{y^2})$ and $\epsilon_2(k) = -2t(c_x + c_y)$ with $t_2 << t, t', t''$, $t_m$. Here, $c_\alpha = \cos(k_\alpha)$ with $\alpha = x, y, z$. While similar values for the bare hoppings are found in LDA approaches, an advantage of QC is an ab-initio estimate of the Hubbard $U$ within a correlated formulation, avoiding the problems associated with LDA in this context [17]. Also, in contrast to LDA-based approaches, the QC work [16] gives, remarkably, a d-wave form-factor, and strong, local, d-shell correlations. Our two-band model is thus an extended Anderson lattice model (EALM). Interestingly, Yin et al. [7] derive a similar two-band-like model from LDA$+$. In contrast to our QC results, however, without the d-wave hybridization. Within QC+DMFT, $t_m(k)$ gives a d-CT-Mott insulator, as we show below.

We solve $H$ within DMFT using the multi-orbital iterated perturbation theory (MO-IPT) as the impurity solver [24]. Though not numerically “exact”, it has many advantages: (i) it gives quantitatively accurate results for band-fillings up to half-filling [25] at arbitrary $T$, (ii) self-energies can be easily extracted, and (iii) it is numerically very efficient. More “exact” solvers either cannot reach low $T$ of interest (QMC) [24] or are prohibitively costly in real, multi-orbital cases (NRG,DMRG) [26]. The relevant DMFT formalism has been developed and used with very good success [26] for a variety of problems, and so we do not reproduce it here. The only input to the DMFT is the “free” density-of-states, given by $\rho_0(\epsilon) = \sum_k \delta(\epsilon - \epsilon_k(k))$. We restrict ourselves to the quantum paramagnetic phase, above the 3D Néel ordering temperature, $T_N$. With a non-local hybridization, the Green function (GF) is a $2 \times 2$ matrix, $G_{ab}(k, \omega)$, (with $a, b = 1, 2$) in orbital space, as are the local self-energies, $\Sigma_{ab}(k, \omega) = \Sigma_{ab}(\omega)$. These equations are similar to those appearing in the DMFT for the EALM [26]. The diagonal GFs (and self-energies) yield the total many body spectral function, $A(k, \omega) = \langle -1/\pi \rangle \text{Im}[1/ (\omega - \Sigma(k, \omega) - \epsilon_k(k) - t_m(k)G_{ab}(k, \omega))]$. The local DOS is just $\rho_0(\omega) = \sum_k G_{kk}(k, \omega)$. Using the spectral theorem, the off-diagonal spectral function, $\rho_{12}(k, \omega) = \langle -1/\pi \rangle \text{Im}G_{12}(k, \omega)$, is easily seen to describe d-wave particle-hole (exciton) order (cf. d-wave form of $t_m(k)$). The CT-MI (found below with QC+DMFT) thus has d-wave p-h order, shown by the fact that $\langle c_{i,\sigma}^\dagger c_{2,\sigma} \rangle = \langle c_{i,\sigma}^\dagger c_{i,\sigma} \rangle = 0$. As for the lower inset of Fig.1. Our two-band Hamiltonian will also yield circulating current (CC) order at finite doping concentration, $x$, as proposed by Varma [27]. Here, however, the apical p - d link is crucial for CC order with finite $\Delta_{12} = i\langle \epsilon_{1,\sigma} c_{2,i} c_{1,y} \rangle = \langle T^{(2)}_{i,j} \rangle \neq 0$ (see below). This can be readily seen in the large-$U$ limit of our model, where a second-order in $t/U$ expansion gives the “exchange” part as [27, 28].

$$H = \frac{2 \langle c_{i,j} \rangle}{U' - J} \sum_{i,j,>} P_{i,j} (T_{i,j}^{(1)} + T_{i,j}^{(2)})$$ (3)

with $P_{i,j} = (S_i S_j - 1/4)$, while $T_{i,j}^{(1)} = (t_{aa}^2 + t_{bb}^2 + 2t_{ab}^2)(T_{i,j}^z)^2 + 1/4)$ and $t_{aa} t_{bb}(T_{i,j}^+ T_{i,j}^- + h.c)$ and $T_{i,j}^{(2)} = (T_{i,j}^z + T_{i,j}^z) + (t_{ab} t_{ab})(T_{i,j}^z T_{i,j}^z + T_{i,j}^z T_{i,j}^z)$, where $T_{i,j}^z = (n_{i1} - n_{i2})/2$, $T_{i,j}^z = c_{i,\sigma}^\dagger c_{2,\sigma}$, $T_{i,j}^z = c_{i,\sigma}^\dagger c_{i,\sigma}$. At mean-field level [27], (notice the difference in our $T_{i,j}^z$s) this will yield a finite CC order, $\langle T_{i,j}^z \rangle \neq 0 \neq 27$. However, our CC pattern involves both planar and apical states, i.e., it is closer to that proposed by Weber et al. [8], involving three oxgens on faces of the octahedra. While this sup-
ports the view [27] that $p - d$ interactions are important in cuprates, our CC pattern is different in details.

We now present our results. In Fig. 1 we show the “unperturbed” DOS (using QC) for our two-orbital model as dash-line curves. Clearly, the planar states dominate at $E_F$, which lies very close to a van-Hove singularity (vHs); the apical states lie much ($\simeq 1.0 \text{ eV}$) lower. The many-body spectra within QC+DMFT, shown in bold lines, are dramatically different. Clear lower- and upper Hubbard bands are visible in the DOS for both orbitals. Dramatic and large-scale spectral weight transfer (SWT), driven by strong $U, U'$, is readily manifest. The CT-Mott gap equals $\Delta_{MH} = 1.1 \text{ eV}$. Our result can now be directly compared with the experimental photoemission (PES) [29] results for $La_2CuO_4$ above $T_N$.

In Fig. 2 we show this comparison. Quite remarkably, very good quantitative agreement with the PES spectrum up to $-2.5 \text{ eV}$ is clearly visible. The planar Zhang-Rice-like (ZR) states are the major contributor at low energy, but the apical states also contribute noticeably for energies $\omega \gtrsim 1.3 \text{ eV}$. Further, from the self-energy (not shown), we estimate an effective mass enhancement of $m^*/m_0 \simeq 4.0$, where $m_0$ is the LDA band mass. As a result, we get $(t, t', t'') \simeq (0.14, 0.01, 0.075) \text{ eV}$, and the resulting renormalized dispersion quantitatively fits the dispersion of the one-hole (“ZR-like”) states in ARPES [16] and the FS evolution with $x$, as $E_F$ shifts downward with hole doping. We show below that our QC+DMFT yields good quantitative agreement with the optical conductivity as well.

The theoretical optical conductivity is compared with the experimental data for $La_2CuO_4$ above $T_N$. In our two-band model, $\sigma(\omega)$ has two contributions: intraband transitions involving the planar- and apical states, and inter-band contributions involving transitions between the two bands. The usual DMFT equation for $\sigma(\omega)$ now reflects both these processes [30], and reads

$$\sigma(\omega) = \sigma_0 \int d\epsilon \rho_0(\epsilon) \int d\nu \frac{f(\omega + \nu) - f(\nu)}{\omega} \rho_\sigma(\omega + \nu) \rho_\sigma(\nu)$$

where $\rho_\sigma(\omega) = \sum_{\alpha=1}^{2} \rho_{\alpha}(\omega) = (-1/\pi) \sum_{\alpha=1}^{2} Im[1/(\omega + \mu_\alpha - \epsilon_\alpha - \Sigma_\alpha(\omega))]$.

Very good quantitative theory-experiment comparison is clearly seen in Fig. 2. Specifically, the relatively sharp peak-like structure at $\Omega = 2.0 \text{ eV}$, as well as the weaker shoulder (at $\Omega_s \simeq 1.2 \text{ eV}$) and the high-energy bump (at $\Omega_b \simeq 2.4 \text{ eV}$) are all in satisfying agreement with experiment [31]. Especially interesting is the shoulder-like feature at $\Omega_s$: given that $\Delta_{MH} = 1.1 \text{ eV}$, one would associate the $2.0 \text{ eV}$ structure with the onset of the corresponding optical absorption feature. The shoulder at $\Omega_s$ must then be interpreted in terms of a quasi-continuum “excitonic” feature pulled down below the Mott gap. In our two-band model, this arises directly from the inter-orbital transitions involving the planar- and apical bands. Thus, remarkably, QC+DMFT achieves very good quantitative agreement with both, one- and two-particle dynamical responses in the CT-MI phase, benchmarking its efficacy.

What do we expect at finite doping, $x$? For small $x$, we expect the lower-lying apical ($d_{z^2} - p_x$) band to remain Mott-localized, as is generic in MO-Hubbard mod-
els [20, 23], while the planar ZR band will selectively metallize. This would then be interpretable as an “orbital selective” Mott transition (OSMT). One should then expect nodal fermionic QPs to dominate the responses at small $x$ [20], also found in earlier QC work [16]. This OSMT would thus realize the famed N-AN dichotomy [3, 10] ubiquitous to cuprates. Eventually, around a critical doping, we expect the apical $p-d$ band to metallize as well, as $E_F$ shifts progressively downward with $x$. It is tempting to link the OSMT, where strong scattering between Mott localized (apical) and quasi- itinerant (planar) band carriers within DMFT would lead to low-energy infra-red singularities via the Anderson orthogonality catastrophe, to the doping driven avoided (pre-empted by $d$-SC) “quantum critical point” (QCP) around optimal doping, where low-energy singularities indeed dominate the “strange metal” [1, 2]. More work is needed to check this theoretically, and to see whether this coincides with a $T = 0$ melting of CC order [27]. These issues will be addressed in detail in forthcoming work.

In conclusion, we have proposed a new QC+DMFT method to compute the correlated electronic structure, along with the one- and two-particle spectra, for Mott (CT-Mott) insulators. Extending our earlier QC results, where very good agreement with the dispersion of one-hole “ZR-like” states and FS was found, we have shown how marrying QC with DMFT shows that, at “high” $T > T_N$, the CT-Mott insulator has $d$-wave order. The very good quantitative agreement with both PES and optical conductivity spectra in the insulating state of $La_2CuO_4$ constitutes strong support for this conclusion. Our QC+DMFT modelling thus reconciles the ARPES and dHvA results with one- and two-particle spectral responses for the CT-MI phase. In light of recent ideas [1, 9, 10, 27], these findings serve as an excellent starting point to study the physics of doped cuprates in detail within an ab-initio correlated approach. QC+DMFT should also serve as a new theoretical tool with wide application to other correlated systems of great current interest.

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