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Copper-oxygen charge excitations and the effective-single-band theory of cuprate superconductors

H.-B. Schüttler
Center for Simulational Physics, University of Georgia, Athens, Georgia 30602

A. J. Fedro
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
and Department of Physics, Northern Illinois University, DeKalb, Illinois 60115
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We propose a formally controlled perturbative method for constructing an effective-single-band (SB) Hubbard theory from a multiband (MB) model for cuprate systems. Our SB theory explicitly incorporates the lowest MB Cu-O charge excitations, and thus possible charge-transfer instabilities, and remains valid, even for the extreme charge-fluctuation limit of the MB model, up to excitation energies of typically ~3–4 eV. This is contrasted with recent approximate slave-boson and diagrammatic studies of the MB model.

Whether the low-energy electronic excitations in the cuprate materials can be adequately described by the single-band (SB) Hubbard model[1] has been a controversial issue for several years. Zhang and Rice[2] (ZR) first pointed out how one might construct an effective-SB strong-coupling ("t-J model") theory in the spin-fluctuation limit[3] of the more complete three-band Hubbard model.[4] Numerical finite-lattice studies[5–7] have indeed confirmed the close, almost quantitative correspondence between the low-lying states of the three-band model and the "lower Hubbard band" states of the SB strong-coupling theory. On the other hand, certain approximate treatments[8,9] of the multiple-band (MB) model appear to suggest that effective SB behavior breaks down already at a very low "coherence" energy scale[8] and altogether in the charge fluctuation regime of the multiple-band system[3(b),8(a),8(b),9] where the bare Cu-to-O hole charge-transfer (CT) energy $\varepsilon \equiv \varepsilon_p - \varepsilon_d$ is comparable to the nearest neighbor (NN) Cu-O and O-O hybridization terms t_{dp} and t_{pp}, and to the NN Cu-O Coulomb repulsion V_{dp}. In the present paper, we outline an alternative approach to the MB-to-SB mapping problem which does not rely in any way on the strong-coupling assumptions implicit[3,5] in the original ZR mapping[2] and which thus remains valid in the charge fluctuation limit of the MB model, even when $|\varepsilon| \ll |t_{dp}|$, $|t_{pp}|$, and V_{dp}. The low-energy Cu-O charge excitations of the MB model are explicitly incorporated into the SB Hilbert space and are represented, quite naturally, by the states in the "upper Hubbard band."

While our approach is easily generalized to more complicated MB models for the cuprates, we will apply it here specifically to the three-band extended Hubbard model[4] for which detailed estimates of model parameters are available.[6,10] This model was originally formulated in terms of the atomiclike Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals of the two-dimensional (2D) CuO_2 square lattice,[11] and parametrized by ε, t_{dp}, t_{pp}, V_{dp}, and the d- and p-orbital on-site Coulomb repulsions, U_d and U_p, and ferromagnetic direct exchange couplings, K_{dp} and K_{pp}, respectively. However, this particular choice of a truncated orbital basis set is *in principle arbitrary* and rigorously justifiable only (if at all, c.f. Ref. 12) in the extreme tight-binding limit where the typical site-diagonal excitation energy scales dominate over the inter-site off-diagonal matrix elements, i.e., roughly speaking in the narrow-band limit.[13] Given the considerable hybridization strengths t_{dp} and t_{pp} in the cuprates,[6,10] there is thus no compelling reason to formulate the MB model in terms of such atomiclike orbitals and we propose here to represent the full MB model from the outset in terms of the Cu $3d_{x^2-y^2}$ and Cu-centered oxygen Wannier orbitals, ϕ_j and χ_j, chosen to transform like x^2-y^2 (B_{1g}) and x^2+y^2 (A_{1g}), respectively, under the point symmetry group of the Cu site j.[2,14] The most general three-band Hamiltonian, in d-ϕ-χ representation, can be decomposed into single-site ($1s$), two-site ($2s$), three-site ($3s$), and four-site ($4s$) contributions, $H = H_{1s} + H_{2s} + H_{3s} + H_{4s}$, where H_{vs} is defined to contain all possible terms which are quadratic or quartic in the Cu site-centered d-, ϕ-, χ-hole creation and annihilation operators with precisely v out of the (at most) four available Cu site indices differing from each other. The d-ϕ-χ matrix elements have not yet been calculated directly, but can be estimated from the d-p_σ matrix elements[6,10] via the $p_\sigma \rightarrow (\phi,\chi)$ orbital transformation. They are rapidly decreasing, both with increasing the number v of different sites involved and with increasing separation between the sites. For typical parameter values,[6,10] the characteristic excitation energy scale of H_{1s}, of order 5–6 eV, is about 1 order and, respectively, 2 orders of magnitude larger than the largest matrix elements of H_{2s} and of H_{vs}, $v=3$ and 4,[15] with the dominant $2s$ matrix elements being of order 0.3–0.5 eV and the dominant $3s$ and $4s$ matrix elements no larger than 0.05 eV. Thus, in contrast to the original d-p_σ representation, the d-ϕ-χ model conforms quite stringently to the narrow-band criterion, provided that Cu *and* O orbitals (d_j, ϕ_j, and χ_j) around the same site j and all respective on-site intra- and inter-orbital hybridizations and interactions are fully included in H_{1s}. Our basic approach is thus to start from H_{1s} as a zeroth-order approximation and to truncate the MB model Hilber space to a subspace $\mathcal{R}_{SB}$ of low-energy eigenstates of H_{1s}. For realistic (p- or n-type) dopant concentrations, <1 extra carrier per Cu site, $\mathcal{R}_{SB}$ can be re-

stricted to states containing only the $n_j=0$-, 1-, and 2-hole $1s$ ground-state configurations, with energies $E^{(0)}(n_j)$ and wave functions $|n_j\rangle^{(0)}$, respectively, given by $|0\rangle^{(0)}=|3d^{10}\rangle$ with spin $S=0$, $|1\rangle^{(0)}=0.86|3d^9\rangle+0.51|3d^{10}\underline{\phi}^1\rangle$ with spin $S=\frac{1}{2}$, and the ZR singlet state

$$|2\rangle^{(0)}=0.81|3d^9\underline{\phi}^1\rangle+0.51|3d^{10}\underline{\phi}^2\rangle+0.29|3d^8\rangle-0.03|3d^{10}\underline{\chi}^2\rangle$$

with spin $S=0$, where e.g., $|3d^9\underline{\phi}^1\rangle$ denotes the $1s$ basis configuration containing 1 hole in the Cu $3d_{x^2-y^2}$ and 1 hole in the surrounding O-ligand ϕ-orbital and prefactors indicate the mixing amplitudes for typical MB input parameters.[6]

These $1s$ ground-state configurations can now be straightforwardly identified with the corresponding four $n_j=0$-, 1-, and 2-hole $1s$ configurations of the SB Hubbard model. The effective SB Hamiltonian, to first order in $\Delta H\equiv H-H_{1s}$, is then obtained by projection of H onto $\mathcal{R}_{SB}$ which, in SB language, has the form

$$H^{(1B)}=\sum_j Un_{j\uparrow}n_{j\downarrow}+\sum_{j\neq m}\sum_{\kappa,\lambda,\sigma}t_{\kappa\lambda}(j-m)c^\dagger_{j\kappa\sigma}c_{m\lambda\sigma}+\sum_{j\neq m}\frac{1}{2}\left[\sum_{\kappa,\lambda}V_{\kappa\lambda}(j-m)n_{j\kappa}n_{m\lambda}\right]+\tfrac{1}{2}K(j-m)\mathbf{S}_j\cdot\mathbf{S}_m+\sum_{j\neq m}L(j-m)c^\dagger_{j\uparrow}c^\dagger_{j\downarrow}c_{m\downarrow}c_{m\uparrow}+H^{(1B)}_{3s}+H^{(1B)}_{4s}. \quad (1)$$

Here $c^\dagger_{j\sigma}$ creates a hole in the SB model at site j, with spin $\sigma=\uparrow,\downarrow$, $n_{j\sigma}=c^\dagger_{j\sigma}c_{j\sigma}$, and $n_j=\sum_\sigma n_{j\sigma}$. Correlated occupation and creation operators are respectively defined as $n_{j\kappa\sigma}=P_{j\kappa\sigma}n_{j\sigma}$, $n_{j\kappa}=\sum_\sigma n_{j\kappa\sigma}$, and $c^\dagger_{j\kappa\sigma}=P_{j\kappa\sigma}c^\dagger_{j\sigma}$ with projection operators $P_{j,1,\sigma}=1-n_{j,-\sigma}$ and $P_{j,2,\sigma}=n_{j,-\sigma}$ for $\kappa=1,2$. The terms $H^{(1B)}_{3s}$ and $H^{(1B)}_{4s}$ arise from the corresponding terms H_{3s} and H_{4s} in the MB model. Their matrix elements, as well as those of the second- and more distant neighbor $2s$ term, are typically at least 1 order of magnitude smaller than the NN $2s$ terms. The effective-SB on-site repulsion $U\equiv E^{(0)}(2)+E^{(0)}(0)-2E^{(0)}(1)$, of order 3-3.5 eV (c.f. Table I), is smaller than the Cu d-orbital on-site repulsion $U_d\sim 8$-12 eV, although comparable to its ionic ($t_{dp}\equiv 0\equiv t_{pp}$) value for a charge-transfer insulator[16] where $U\sim\varepsilon+V_{dp}<U_d$. Due to the local Coulomb correlations in H_{1s}, both the SB delocalization ($t_{\kappa\lambda}$) and the extended repulsion ($V_{\kappa\lambda}$) terms become occupancy dependent. Our estimates for $V_{\kappa\lambda}$ and U would probably increase by ~ 0.2-0.4 eV if O-O NN and second NN as well as Cu-Cu NN. Coulomb repulsion terms were taken into account in the corresponding MB model.

The higher-energy, "non-SB" $1s$ configurations discarded in our first-order truncation are separated from those retained by an energy $\Delta_{NSB}\sim 3.5$-4 eV, measured from the lower Hubbard band states, i.e., from the ground-state energy of H_{1s}, at half filling. Δ_{NSB} determines roughly the excitation energy scale above which the effective-SB description breaks down and MB effects have to be explicitly taken into account.[17] This should be contrasted with slave-boson $1/N$-expansion results[8] which appear to suggest that non-SB behavior asserts itself already at a much lower coherence energy scale, well below 0.1 eV. Since Δ_{NSB} is about 1 order of magnitude larger than the typical matrix elements of H_{vs}, $v\geq 2$, virtual transitions from $\mathcal{R}_{SB}$ into the non-SB states will give only small second-order corrections for the on-site and NN matrix elements in Eq. (3). We reemphasize[16,18] that this large stabilization energy of the low-lying SB states, Δ_{NSB}, relative to the non-SB excitations arises primarily from the Cu-O and O-O hybridization terms and not, as is sometimes incorrectly assumed, from the CT energy ε or the Coulomb repulsions U_d. Our approximate mapping scheme and hence the effective-SB theory (which are based on the smallness of $\Delta H\equiv H-H_{1s}$ relative to Δ_{NSB}, and not on the smallness of, say, $|t_{dp}|,|t_{pp}|$ relative to ε) therefore remain valid even in the extreme charge fluctuation limit, $|\varepsilon|\ll|t_{dp}|$, $|t_{pp}|$, and V_{dp}, of the d-p_σ MB model, as evidenced by the smallness of, e.g., $|t_{\kappa\lambda}|/\Delta_{NSB}$ even for $\varepsilon=0$ (c.f. Table I). This is in contrast to the conclusions of Refs. 3(b), 8(a), 8(b), and 9. The SB picture *may* break down, at much lower low-energy scales ($\ll|t_{pp}|$), in the Kondo limit where $|t_{dp}|\ll|t_{pp}|$ or for very large Cu-O repulsion $V_{dp}\gg U_d,t_{dp}$.

In the limit $U\gg|t_{12}|$, a strong-coupling expansion to order t_{12}^2 reduces $H^{(1B)}$ to a t-J model[1,2] with hopping ma-

TABLE I. MB Hubbard model input parameters from Ref. 6 (HSSJ) and Ref. 10(c) [McMahan, Annett, and Martin (MAM)], our resulting on-site and NN inter-site SB parameter estimates, and direct MB estimates [$J^{(MB)}$, $\Delta^{(MB)}_{MH}$, from Ref. 6], in units of eV. Results in parentheses are for the same two MB parameter sets, but with $\varepsilon=0$.

	HSSJ		MAM	
U_d	10.5		9.4	
U_p	4.0		4.7	
V_{dp}	1.2		0.8	
t_{dp}	−1.3		−1.5	
t_{pp}	0.65		0.60	
K_{dp}	−0.18		. . .	
K_{pp}	−0.04		. . .	
ε	3.6	(0)	3.5	(0)
Δ_{NSB}	5.6	(3.9)	6.2	(4.2)
U	3.5	(1.7)	3.0	(1.6)
t_{11}	0.42	(0.57)	0.48	(0.60
t_{22}	0.32	(0.35)	0.42	(0.41)
t_{12}	0.41	(0.47)	0.48	(0.52)
V_{11}	0.11	(0.17)	0.092	(0.14)
V_{22}	0.14	(0.14)	0.11	(0.13)
V_{12}	0.15	(0.16)	0.11	(0.14)
K	−0.035	(−0.11)	−0.023	(−0.092)
L	0.054	(0.11)	0.058	(0.11)
$J^{(PT)}$	0.152	(0.485)	0.27	(0.66)
$J^{(NPT)}$	0.143	(0.347)	0.25	(0.45)
$J^{(MB)}$	0.128	(· · ·)	· · ·	(· · ·)
Δ_{CTI}	1.5	(0.50)	1.3	(0.50)
Δ_{MII}	2.54	(0.84)	2.0	(0.95)
$\Delta^{(MB)}_{MII}$	2.4	(· · ·)	· · ·	(· · ·)

trix elements $t(j-m)=t_{11}(j-m)$ and $t(j-m)=t_{22}(j-m)$ in the electron- and hole-doped case, respectively, and antiferromagnetic (AF) NN spin-exchange coupling J. J is estimated perturbatively as $J^{(PT)}=-|K|+4t_{12}^2/(U+6V_{12}-7V_{11}-\frac{3}{4}|K|+L)$ and non-perturbatively ($J^{(NPT)}$) as the singlet-triplet splitting of a $2s$ NN cluster embedded in six surrounding sites where $n_j=1$ is frozen. Our SB estimate $J^{(NPT)}$ from the Hybertsen, Stechel, Schlüter, and Jennison (HSSJ, Ref. 6) MB input parameters agrees to within 12% with their[6] value $J^{(MB)}$ which is obtained directly from the MB model and thus takes into account higher-order renormalizations of the effective-SB parameters due to virtual excitations into non-SB states. $J^{(MB)}-J^{(NPT)}$ is a rough measure of the magnitude of these higher-order $[O(\Delta H^2)]$ corrections, neglected in our first-order truncation. Our HSSJ-based SB estimates for J are also in good agreement with available experimental values $J^{(expt)}=0.128(6)$ eV for the cuprates.[6] Our J estimates, based on various MB parameter sets of McMahan and coworkers,[10(b),10(c)] are about 2–4 times larger which, as pointed out earlier,[3(b)] is the combined result of their[10(b),10(c)] somewhat larger input values for t_{dp}, smaller values for ε, and neglect of direct exchange (K_{dp} and K_{pp}) terms.

The low-lying charge excitations of the MB system correspond in the SB picture to states in the upper Hubbard band, i.e., to the creation of a $1s$ ZR singlet ($n_{j'}=2$) and a $|3d^{10}\rangle$ configuration ($n_j=0$) by inter-site ($j\rightarrow j'$) hole transfer. For sufficiently large U_d, this excitation is accompanied by a net charge transfer from Cu to O orbitals, since the average oxygen site occupation per hole, $\langle n_{j\phi}+n_{j\chi}\rangle/n_j$, in the ZR singlet $1s$ state is substantially larger than in the single-hole $1s$ state. However, in contrast to d-p_σ-based descriptions of the Cu-O CT excitation,[3(b),8(a),9,19] the current approach takes both local Coulomb correlations *and* local hybridizations into account already in zeroth order. The Cu-O CT instability, first discussed within the context of the MB model,[3(b),8(a),9,19] can now also be described straightforwardly within the corresponding SB model, in contrast to assertions in Refs. 9. In the SB model, the instability would manifest itself in a transition from a ground state favoring singly occupied sites and hence, near half filling, maximally homogeneous charge distribution (HC), to a competing ground state, favoring doubly occupied and empty sites, i.e., near half filling a maximally inhomogeneous charge distribution (IC), that is, charge disproportionation, between the two Cu sublattices. From the exact solution of the model in the ionic limit ($t_{\kappa\lambda}=K=L=0$), we infer that, at half filling, the IC state exhibits charge-density-wave (CDW) order, while the HC state, for small $t_{12}\neq 0$, develops AF spin-density-wave (SDW) order. For $U>16(V_{12}-V_{22})$, either p- or n-type dopant-induced carriers are accommodated in the IC phase as singly occupied sites in the appropriate sublattice and the SB ionic-limit stabilization energy of the HC state relative to the IC state, that is, the IC-HC ground-state energy difference, per Cu site is

$$\Delta_{CTI}=(U-4V_{11})(\tfrac{1}{2}-|c|)\,, \qquad (2)$$

where $c\equiv(N_h-N)/N$ is the number of dopant-induced hole carriers per number of Cu sites N, i.e., $c>0$ and $c<0$ for p and n doping, respectively. Thus, in the SB picture, the CT instability arises essentially from the competition between the effective SB on-site and NN repulsions, U and V_{11}, and the HC-IC phase boundary [where $\Delta_{CTI}(U,V_{11},c)=0$] is independent of the dopant concentration, up to $|c|=50\%$.[20] As shown in Table I, we find the HC state to be well stabilized with $\Delta_{CTI}\cong+1.3-1.5$ eV >0 at half filling. Since increasing V_{dp} in the MB model enhances both V_{11} *and* U in the SB model, we would have to raise V_{dp} to about 22 eV or 6.5 eV, assuming HSSJ MB parameter values with $\varepsilon=3.6$ or 0 eV, respectively, in order to drive the HC state unstable. For $t_{\kappa\lambda}\neq 0$, Δ_{CTI} is likely to be enhanced by the SB delocalization energy.[20] We caution that for such large values of V_{dp} (~ 22 eV $\gg U_d,\varepsilon,t_{dp}$) our present single-site-based perturbative approach is likely to break down in a quantitative sense. Nevertheless, the foregoing results *do* suggest strongly, in contrast with Ref. 9, that the cuprate materials are very far from any purely electronically driven CT instability, if one assumes realistic parameter values[6,10] with, e.g., $V_{dp}\lesssim\varepsilon$. The possibility of a phonon-driven CT instability, due to coupling to the oxygen breathing modes, is currently under study.[20] The foregoing CT instability phenomenon should be clearly distinguished from a phase-separation (PS) instability which has been suggested to occur in the p-doped MB model for $V_{dp}\gtrsim 2\varepsilon$.[8(a),21] The PS instability is well reproduced by our corresponding SB model where it arises as a consequence[22] of the hole hopping matrix element t_{22} changing its sign, and hence $t_{22}\rightarrow 0$ (while $t_{12},J,t_{11}\neq 0$) at some sufficiently large V_{dp}. For the HSSJ parameters, this happens when $V_{dp}\cong 7.0$ and 4.7 eV, if $\varepsilon=3.6$ and 0 eV, respectively.

The Mott-Hubbard (MH) gap, that is, the charge excitation energy for creating a spatially well-separated SB electron-hole pair at half filling, can be estimated as

$$\Delta_{MH}\cong U+8(V_{12}-V_{11})+\Delta E(t_{11},J)+\Delta E(t_{22},J)\,. \qquad (3)$$

Here, $U+8(V_{12}-V_{11})$ is the MH gap in the ionic limit ($t_{\kappa\lambda}=K=L=0$), $J=J^{(NPT)}$, and $\Delta E(t,J)<0$ is the SB delocalization energy gain of a single carrier with hopping matrix element t injected into the half-filled AF ground state. $\Delta E(t,J)$ can be estimated from 0- and 1-hole t-J model ground-state energies.[23] Our SB result, $\Delta_{MH}=2.54$ eV, from the HSSJ MB parameters,[6] is again in good agreement with their value of $\Delta_{MH}^{(MB)}=2.4(3)$ eV,[6] obtained directly from the MB model. It also agrees well with the suggested[6] experimental value of 2.6 eV in La_2CuO_4. We caution that Δ_{MH} is larger than the experimentally observed onset energy for optical absorption $\Delta_{OA}\sim 1.8$ eV which probably corresponds to an excitonic (i.e., electron-hole *bound* state) transition.[6] Δ_{MH} can be unambiguously determined only by photoconductivity experiments.

To summarize, starting from a ZR d-ϕ-χ Wannier orbital representation of the full three-band Hubbard model, we have developed a systematic perturbation mapping onto an effective SB theory which explicitly incorporates

the lowest Cu-O charge excitations, as well as possible Cu-O charge instabilities, into an effective-SB model. The SB estimates for the AF exchange coupling J and for the Mott-Hubbard gap Δ_{MH} are found to be in good agreement with results obtained directly from the corresponding three-band Hamiltonian. We assert that the effective-SB description is valid up to excitations energies $\Delta_{NSB} \sim 3$–4 eV and does not break down in the charge fluctuation limit of the MB model. It is possible that certain slave-boson $1/N$-expansion[8] or diagrammatic[9] approaches to the MB model (which are principally uncontrolled approximations) do not capture the essential *local* physics arising from the strong Cu-O and O-O hybridization overlap and may lead therefore to conclusions which are different from ours.

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