Renormalization from density-functional theory to strong-coupling models for electronic states in Cu-O materials

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Strong-coupling models for the electronic structure of La_2CuO_4 are derived from the local-density-functional results in two successive stages of renormalization. First, a three-band Hubbard model is derived with parameters explicitly calculated from first principles using a constrained density-functional approach and a mean-field fit to the Cu-O $pd\sigma$ bands. Second, exact diagonalization studies of finite clusters within the three-band Hubbard model are used to select and map the low-energy spectra onto effective one-band Hamiltonians, e.g., the Heisenberg, one-band Hubbard, or "t-t'-J" model. At each stage, calculated observables are in quantitative agreement with experiment.

Proper treatment of the many-body correlations in the new Cu-O based superconductors is crucial to understanding their properties in the normal state as well as the mechanism for superconductivity.[1] Several simplified models for the electronic structure of the Cu-O planes have been proposed which include strong interaction effects in a nontrivial fashion.[2-8] The trend[2-5,7,8] has been to explore the phenomenology of a particular model as the parameters are varied with less emphasis on material-specific properties. Here we adopt the opposite approach. We start with an accurate quantum-chemical description of a Cu-O material (i.e., La_2CuO_4) and proceed to renormalize down in energy to simplified few-band models. We thus derive, from first principles, model parameters that explicitly reflect the properties of the materials. In the first step, a three-band Hubbard model is realized. It exhibits strong Coulomb interactions, important covalency, considerable chemical asymmetry between electron and hole doping, and shows the parent Cu-O materials to be charge-transfer insulators. In the second step, the low-energy spectrum of the three-band Hubbard model is found to accurately map onto an effective one-band model. The low-energy wave functions show a $\gtrsim 93\%$ projection onto the Hilbert space of the "t-t'-J" Hamiltonian, constructed from local singlets.[5] The Heisenberg superexchange (J) is in good agreement with experiment. The hopping integrals (t,t') governing motion of excess carriers show remarkable symmetry between electron and hole doping and include an important intrasublattice (t') contribution. These findings, the consequences of a quantum-chemical description of the cuprates, provide important support for, and limitations on, models presently being examined to explain the high-temperature superconductivity in this class of materials. Preliminary results have been presented previously.[9]

The local-density-functional approach (LDA) has been shown to accurately predict the cohesive properties (chemical bonding) of the Cu-O based materials including the delicate problem of the lattice vibrations.[10] Furthermore, the LDA energy bands, although not explicitly representing quasiparticle energies, clearly highlight the central role of the Cu-O $pd\sigma$ derived bands suggesting that carriers are largely confined to the antibonding band.[11] Quantitative analysis of these findings strongly motivates the use of a three-band Hubbard model to describe the important low-energy excitations in these materials (other degrees of freedom have only small admixture near the Fermi level):

$$H=\sum_{ij\sigma}\varepsilon_{ij}C^{\dagger}_{i\sigma}C_{j\sigma}+\tfrac{1}{2}\sum_{ij\sigma\sigma'}(U_{ij}C^{\dagger}_{i\sigma}C_{i\sigma}C^{\dagger}_{j\sigma'}C_{j\sigma'} +K_{ij}C^{\dagger}_{i\sigma}C_{i\sigma'}C^{\dagger}_{j\sigma'}C_{j\sigma}), \quad (1)$$

where the ij indices label the planar Cu and O sites, and $C^{\dagger}_{i\sigma}$ creates holes with spin σ in Cu $d_{x^2-y^2}$ or O $p\sigma_{x,y}$ orbitals relative to a Cu d^{10}, O p^6 vacuum state. The undoped ground state corresponds to one hole per CuO_2 unit. The one-electron parameters (including on-site energy difference $\varepsilon=\varepsilon_p-\varepsilon_d$ and near-neighbor hopping t) and the Coulomb integrals (including on-site and near-neighbor U and near-neighbor exchange K)[12] are illustrated in Fig. 1(a). These parameters are effectively

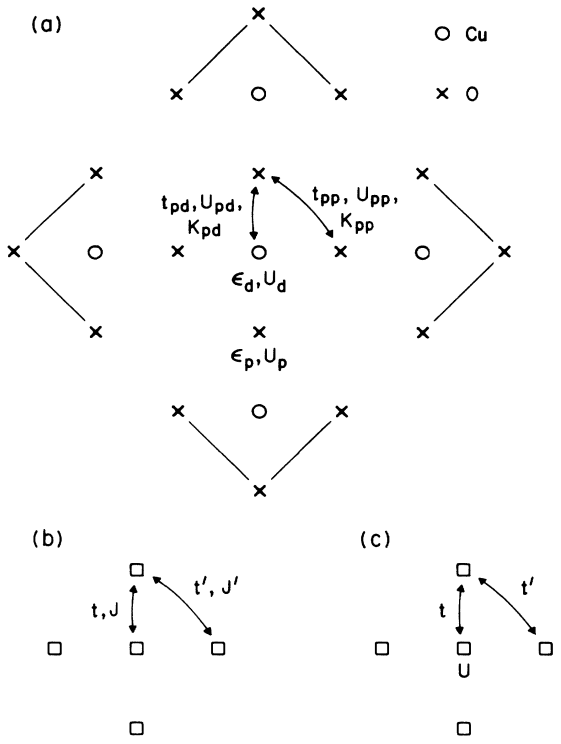

FIG. 1. (a) The largest cluster considered together with the parameters for the three-band Hubbard model. The corresponding effective one-band models: (b) "*t-t'-J*" and (c) one-band Hubbard.

screened by all those (higher-energy) degrees of freedom which have been explicitly discarded, e.g., the crystal field split Cu states or the oxygen π bands. Quantitative tests[13] show this approximation to be realistic for the low-energy motion of carriers.

The approach[14,15] for calculating the parameters in Eq. (1) is summarized here. The complexity of the problem derives from the effective screening of the Coulomb interaction parameters and the strong hybridization between the Cu $d_{x^2-y^2}$ and the O $p\sigma_{x,y}$ orbitals. In the constrained density-functional approach (CDFT), the variational energy surface is calculated as a function of imposed local charge fluctuations, e.g., Cu *d* charge. The kinetic-energy component to this energy surface is systematically handled by calculating the analogous energy surface within the three-band Hubbard model solved in mean field. The screened Coulomb parameters are those which give an accurate match to the CDFT energy surface for a given set of one-electron parameters. The ε_{ij} are derived by assuming that the energy bands of Eq. (1) solved in mean field correspond to the $pd\sigma$ bands in the LDA band structure. Thus the final parameters self-consistently match the CDFT energy surface and the $pd\sigma$ energy bands. Table I gives the resulting parameter set[14] together with small near-neighbor exchange integrals (estimated[6] from ionic wave functions). Notable in Table I are large on-site Coulomb energies, a large intersite difference in one-electron energies and strong hybridization.

TABLE I. Parameter values calculated for the three-band Hubbard model and used in the present exact diagonalization studies for the case of holes (in eV).

ϵ	3.6	U_d	10.5	K^{pd}	−0.18
t_{pd}	1.3	U_p	4	K_{pp}	−0.04
t_{pp}	0.65	U_{pd}	1.2		
		U_{pp}	0		

Direct diagonalization studies of the Hamiltonian Eq. (1) have been carried out for a sequence of clusters: CuO_4, Cu_2O_7, Cu_3O_{10}, Cu_4O_{12}, and Cu_5O_{16}. The clusters are embedded in an array of Cu d^9 sites which shift the effective on-site energy of the outer O orbitals due to the intersite Coulomb energy. The results are insensitive to details of this procedure. For some calculations, the outer O orbitals have been "phase-locked" in groups as single antibonding orbitals [see Fig. 1(a)], in order to reduce the number of degrees of freedom. This approximation has been explicitly tested. The resulting sparse Hamiltonian matrix is diagonalized using a block Lanczos technique. For each cluster, three cases are considered: $N-1$, N, and $N+1$ holes where N is the number of Cu sites. As expected from the values in Table I, the chemical character of the holes in the insulating ground state is Cu (80%) and O (20%) while added holes are of Cu (20%), O (80%) character and added electrons of Cu (80%), O (20%) character, in general agreement with experiment.[16] This shows that La_2CuO_4 is in the regime of a charge-transfer insulator[17] and confirms the pronounced chemical asymmetry between electrons and holes.

Several properties may be calculated for direct comparison to experiment. First, the charge transfer gap, $\Delta = E_{N+1} + E_{N-1} - 2E_N$, corresponds to the energy required to remove a *hole* from one region of the crystal and add it to another region beyond the range of excitonic correlations. The present calculations are summarized in Fig. 2 as a function of cluster size. The scaling is taken

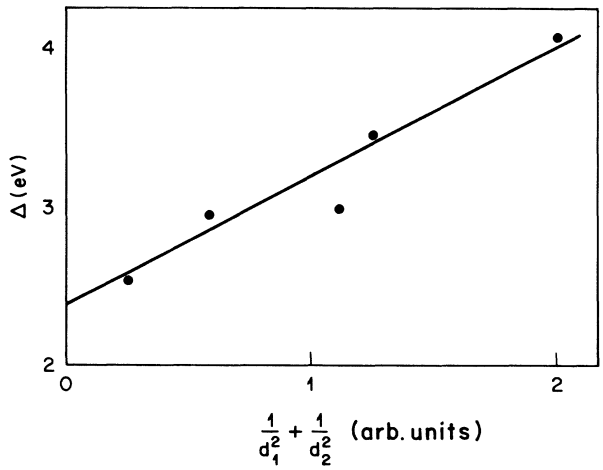

FIG. 2. Scaling of the calculated charge-transfer gap (Δ) as a function of cluster size.

from simple two-dimensional particle-in-a-box confinement energies with the distance scale set by a single Cu site, e.g., for the Cu_3O_{10} cluster, $d_1=3$ and $d_2=1$. The extrapolated value is $\Delta=2.4\pm0.3$ eV. Excited-state energies of the N-hole spectrum suggest that the excitonic transitions will be lower by about 0.5 eV. This is in good agreement with the available spectroscopic measurements where estimates of Δ vary from 1 to 3 eV.[18] In particular, optical reflectivity data[19] indicate an excitonic transition at 1.8 eV followed by an absorption edge (Δ) at 2.6 eV. Second, the spectral functions for (removal) addition of a hole, directly related to the spectra observed in (inverse) photoemission, can be evaluated. Detailed high-energy spectroscopy studies, however, necessitate the inclusion of degrees of freedom beyond the three-band model[20] and will be given later.[21] We only note here that the parameters in Table I are consistent with the measured high-energy excitations (satellite structure) in La_2CuO_4.

Several workers have stressed that the low-energy electronic structure of the Cu-O planes can be described by an effective one-band model, renormalizing away the higher-energy charge-transfer degrees of freedom contained in the three-band model.[2,5,7,8] Here we explicitly examine the validity of that controversial hypothesis starting from the three-band Hubbard model Eq. (1) with parameters that we have just shown to well represent the electronic structure of the Cu-O planes. The "t-t'-J" and one-band Hubbard models are considered explicitly.

The "t-t'-J" model Hamiltonian is

$$H=\sum_{ij\sigma} t_{ij}C^{\dagger}_{i\sigma}C_{j\sigma}+\sum_{\langle ij\rangle} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\ , \tag{2}$$

where i,j label a single effective site about each Cu in the plane [see Fig. 1(b)]. It is assumed that no configurations with double occupancy on a site are admitted, which dramatically reduces the number of configurations in comparison to the one-band Hubbard model. The mapping consists of three steps: (i) mapping of the spectrum, (ii) identification of the reduced subspace, and (iii) test of the accuracy of the "t-t'-J" wave functions.

For the insulating phase, the calculated low-energy spectra with N holes show the correct number of lines for a spin-$\frac{1}{2}$ Heisenberg model separated by a large ($\gtrsim 2.15$ eV) gap from the charge-transfer excitations, as already found in Ref. 6. The result of the mapping to Eq. (2) for all the clusters is $J=128\pm5$ meV and $J'=3\pm1$ meV, error bars indicating the variation with cluster size. The mapping is illustrated in Fig. 3(a) where the rms error is 1 meV. Note that $J'\ll J$, and is smaller than other estimates.[22] The calculated J is in excellent agreement with the value derived from two-magnon scattering experiments interpreted including quantum fluctuations [$J_{\rm expt}=128\pm6$ meV (Ref. 23)]. However the parameters in Table I have a precision of only about 10% which, due to the sensitivity of J, corresponds to a $\approx 50\%$ uncertainty in the calculated value of J. The experimentally derived values for J differ little ($\sim 10\%$) for the various Cu-O insulators[24] (La_2CuO_4, YBa_2CuO_6, Nd_2CuO_4, ...) and we expect our calculated electronic structure to be a generally good representation for all Cu-O materials in this class.

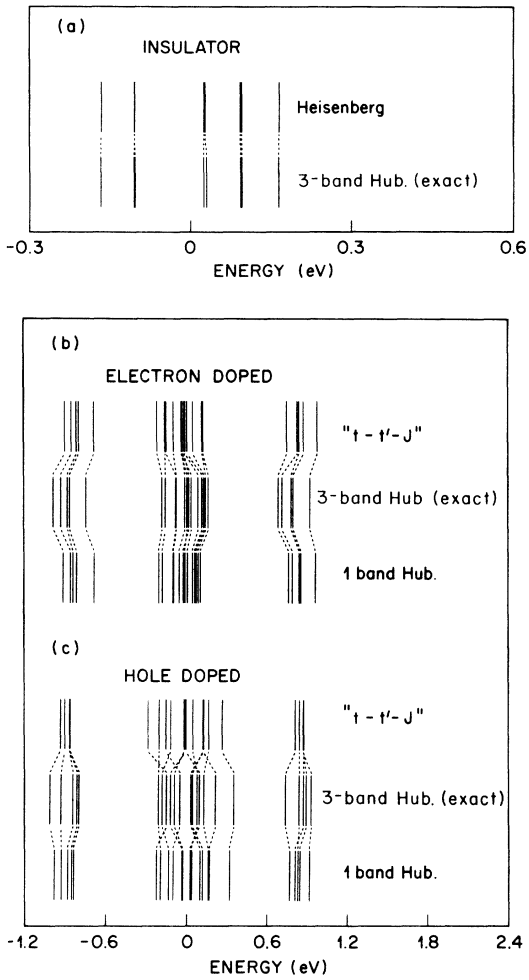

FIG. 3. The low-energy spectrum for the Cu_5 cluster calculated in the three-band Hubbard model in comparison to mappings onto effective one-band models: (a) five-hole case compared to the Heisenberg Hamiltonian, (b) four-hole case (electron doped), and (c) six-hole case (hole doped) compared to the "t-t'-J" and the one-band Hubbard models.

For the doped phases, the calculated low-energy spectra for $N-1$ (electron-doped) and $N+1$ (hole-doped) holes are considered. The number of lines is correct for the "t-t'-J" model and this spectrum is separated by a gap of about 2 eV from the higher-energy excitations. The spectral mapping has been done constraining J,J' to have the values found above. The mappings are illustrated in Figs. 3(b) and 3(c) where the rms error is 0.06 eV (about 3% of the bandwidth). The resulting values for t,t' (in meV) are

$$\begin{aligned} &t=410\pm5,\quad t'=-70\pm10\ \text{(electron doping)}\ ,\\ &t=440\pm5,\quad t'=-60\pm20\ \text{(hole doping)}\ , \end{aligned} \tag{3}$$

where the error bars reflect the cluster-to-cluster consistency. The signs of t,t' refer to hole notation.[25] The resulting effective low-energy carrier dynamics exhibits

remarkable symmetry between electrons and holes, despite the underlying chemical differences highlighted above. In the limit of many sites, the large values of t suggests that the top of the band will merge with the higher-energy (charge-transfer) continuum. Therefore, the "t-t'-J" model strictly applies only to the region near the bottom of the band. The mappings to the lowest manifolds may be further improved by weighting the low-energy portion of the spectra changing t' to ≈ -100 meV.

The subspace for the "t-t'-J" model has been identified using products of one-hole and two-hole wave functions derived from CuO_4 cluster calculations. The two-hole case corresponds to the singlet proposed by Zhang and Rice[5] but including full local correlations. The projection onto the space spanned by the low-energy wave functions in the three-band Hubbard model is at least 93% across the entire manifold of 30 states (Cu_5, six holes). Using this subspace, the individual "t-t'-J" wave functions from our mapping have a projection of greater than 90% onto the corresponding three-band Hubbard wave functions (except for two doublets near the center with greater than 80% projection). This is a strong test of the validity of a one-band model for the low-energy electronic structure because the block diagonal (by symmetry) "t-t'-J" model on five sites contains nontrivial couplings that accurately reproduce the effective interactions in the three-band Hubbard model.

Second, we consider the one-band Hubbard model, where the i,j in Eq. (1) run over a single effective site per Cu. The parameters defined in Fig. 1(c) are retained. Unconstrained mappings yield an effective U in the range $4.8 \lesssim U \lesssim 5.8$ eV, similar to the charge-transfer energy calculated for the CuO_4 cluster (4.1 eV). Fixing $U=5.4$ eV, the results for t,t' are nearly identical to Eq. (3) with an rms error of 0.05 eV. Further, all three spectra in Fig. 3 can be accurately reproduced with the single parameter set $U=5.4$ eV, $t=430$ meV, and $t'=-70$ meV. The one-band Hubbard model gives a somewhat better mapping for the lowest manifold in the $N+1$ hole case, reflecting the fact that some second order (in t) terms are dropped in the reduction to the "t-t'-J" model.

The present results have several important implications:

(i) For the case of hole doping, we stress that the diagonal hopping of the singlet (t') results from two *interfering* channels: direct hopping via t_{pp} and a second-order process involving a third Cu site. The first term dominates giving final signs of t,t' in agreement with other estimates.[26]

(ii) The singlet construction, proposed by Zhang and Rice,[5] is an excellent basis for the wave functions of the low-energy states of the doped Cu-O planes giving strong support to the viability of the one-band description for modest doping levels.

(iii) The second-neighbor hopping t' is non-negligible suggesting that the "t-t'-J" model is an irreducible description of the dynamics of low-energy carriers in the Cu-O materials. Furthermore, the t' will make a substantial contribution to carrier motion since the intrasublattice hopping involved does not, in contrast to t, flip spins. The importance of t' has been stressed[8] and may have implications for the superconducting state.

(iv) The mapping to the "t-t'-J" model is not exact. Interactions deriving from higher-energy excitation channels that do not trivially renormalize the parameters may be important. The form of such corrections is the subject of ongoing research. We stress that such corrections should be considered together with interactions deriving from channels outside the scope of the three-band Hubbard model that are in a similar energy range, e.g., oxygen p-π excitations[27] or Cu d excitations.[28]

(v) The values of t,t' can be tested experimentally by evaluating low-energy response functions (Raman, reflectivity, etc.) for the doped materials, also a subject of current work.

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