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Attractive interactions from repulsive forces in a multiband Hubbard model

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An extended multiband Hubbard model of the two-dimensional CuO_2 planes of high-T_c superconductors is examined by exact diagonalization of the Hamiltonian for small clusters with periodic boundary conditions. Holes are shown to bind in the limit of large Cu-site and nearest-neighbor Cu-O Coulomb repulsion. A simple explanation of the source of the binding energy is given in this strong-coupling limit. The more realistic case of relatively weak nearest-neighbor repulsion is also examined, and suggestive evidence is presented that the effective attraction will also exist in the thermodynamic limit for this case.

It is becoming increasingly clear that electronic correlation effects must be taken into account in understanding the properties of high-T_c materials.[1] The strongest single piece of evidence for strong correlation is the fact that the undoped reference materials such as La_2CuO_4 are antiferromagnetic insulators,[2] whereas standard band-structure calculations predict metallic behavior[3] with no tendency toward antiferromagnetism.[4] There has been considerable controversy over whether the essential physics is describable in terms of a single-band Hubbard model with large U, which is the basis for the resonating valence-bond (RVB) model,[5] or on the other hand by a multiband model where Cu and O degrees of freedom are explicitly allowed.[6,7] The answer to this question may depend to a large extent on the parameters assumed for the multiband model; at least in certain parameter regions it may be possible to reduce the problem to a single effective band.[8] These attempts to go from a multi- to a one-band model have been carried out in the limit where only the on-site Coulomb interaction is included, and may not easily generalize to models with longer-range interactions included.

It has been proposed[9,10] that the combination of large nearest-neighbor (NN) Coulomb repulsion V between holes on Cu and O sites together with a large on-site interaction U_{Cu} for Cu leads to binding of doped holes. In this Rapid Communication we present evidence from different finite-size diagonalization studies which support in part the observations of Hirsch, Tang, Loh, and Scalapino,[10] and discuss the physical mechanisms responsible for the negative binding energy. We conclude from our investigation of this extended multiband Hubbard model that there exist at least two distinct regions of parameter space with different binding mechanisms. In one region of parameter space with large V this effective attraction leads to the formation of hole droplets rather than pair formation. In the physically more realistic regime (small V), we find also indications that binding is likely to persist in the thermodynamic limit.

Our model Hamiltonian is the by now standard extended Hubbard model as discussed by Emery[7]

$$H=\sum_{(i,j),\sigma}\varepsilon_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\sum_{i}U_i n_{i\uparrow}n_{i\downarrow}+V\sum_{\langle i,j\rangle}n_i n_j\,. \tag{1}$$

Here the single-particle parameters ε_{ij} include site energies for hole occupancy ϵ_{Cu} and ϵ_O on Cu and O sites, respectively, as well as the NN hopping integral $t=-1$, taken as the unit of energy. The two-body interaction terms include on-site Coulomb terms U_{Cu} and U_O for the Cu and O sites, respectively, and a nearest-neighbor repulsion V.

The systems studied contain one Cu and two O sites per unit cell in the geometry of the CuO_2 planes of high-T_c materials. The low-lying eigenvalues and eigenvectors of this many-body problem are found for particular numbers of spin-up and -down holes by generating the complete set of atomic-limit basis states, finding all nonzero matrix elements of the Hamiltonian (1), and then employing the Lanczos[11] algorithm for diagonalization. The size of the matrices to be diagonalized is reduced slightly by use of translational symmetry to generate only states with a given total momentum. Special limits such as $U_{Cu}\rightarrow\infty$ are easily achieved by not generating basis states with any doubly occupied Cu sites, for example. We employ periodic boundary conditions (PBC), because these boundary conditions do not require any additional input and also seem to be more appropriate to the high-doping case pertinent to superconductivity. On the other hand, open boundary conditions (OBC) with a mean-field correction to the interaction term are used in Ref. 10. Both approaches have advantages and drawbacks, but it is useful to consider both in assessing the implications of small-system calculations for extended systems.

The binding energy is defined by $E_B=(E_2-E_0)-2(E_1-E_0)$, where E_0 is the ground-state energy of the undoped system (1 hole/unit cell) and $E_{1(2)}$ refer to the ground-state energies of systems with 1 (2) more holes. Figure 1 is an example of the dependence of binding energy on U_{Cu} for a system with 4 unit cells ($N_C=4$), $V=4$, $U_O=8$, and $\epsilon=\epsilon_O-\epsilon_{Cu}=0$. This figure should be compared to Fig. 4 of Ref. 10, where the same parameters are used. The trends visible here are observed in all cases examined; with PBC we do not find a positive maximum in E_B vs U_{Cu} at finite U_{Cu}, rather a monotonically decreasing function of U_{Cu}. The change of sign of binding energy with U_{Cu} always occurs at weaker interaction with PBC than with OBC, and the saturation value of the binding energy at large U_{Cu} is more negative with PBC. Furthermore, the first appearance of a negative binding energy

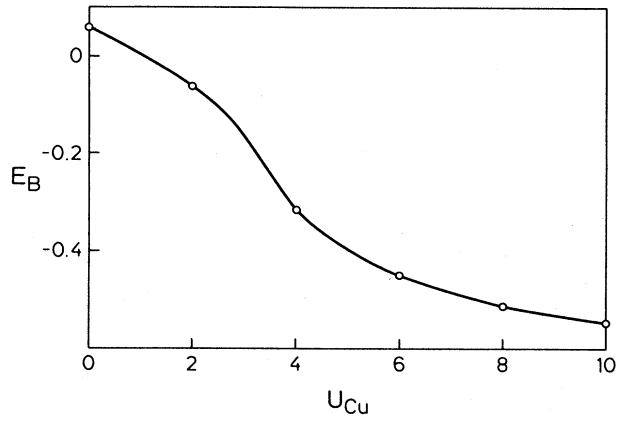

FIG. 1. The dependence of binding energy on U_{Cu} for a system with 4 unit cells and $\epsilon=0$, $U_O=8$, and $V=4$. Energies are in units of t ($t=1$).

occurs at a smaller value of V with PBC than with OBC.

All of these observations indicate the PBC are more conducive to binding than are OBC for these small systems. This is easily understood if the spatial extent of a pair is larger than the system size studied; as will be discussed more thoroughly later, the binding is associated with charge redistribution upon doping. The OBC of Ref. 10 however, fix the expectation value of hole density on the Cu sites outside the cluster at the value for the undoped system. This reduces the contribution of the O sites next to the boundary significantly, leading to weaker binding compared to PBC.

In an attempt to better understand the physical mechanism leading to the negative binding energy, it is helpful to consider some special limits. Noting that E_B saturates with large U_{Cu}, the limit $U_{Cu}\rightarrow\infty$ is instructive. Figure 2(a) shows the dependence of binding energy on V for systems with 4 unit cells, $\epsilon=2$ and (i) $U_{Cu}=\infty$, $U_O=0$; (ii) $U_{Cu}=\infty$,$U_O=\infty$; and (iii) a spin-polarized case. The similarity between these different cases shows clearly that the essence of this effect does not depend on the spin of the particles in this limit. The sudden increase in the strength of binding with increasing V suggests the existence of two different regimes for small and large V. The different character of states in these two regimes can be seen from Figs. 2(b) and 2(c), where the V dependence of Cu-hole occupancy and the NN density-density correlation function are depicted for the case $U_{Cu}=\infty$, $U_O=\infty$. For large V the NN occupancy is strongly suppressed also in the doped cases and in the undoped ground state there is one hole at each Cu.

In this strong coupling case the source of the negative binding energy is obvious. One additional hole would raise the energy by $2V$, however if holes rearrange from Cu to O sites, as there are more O than Cu sites available, this hole fits in while keeping $\langle n_{Cu}n_O\rangle\simeq 0$. The number of oxygens, N_O, within the droplet is essentially determined by the geometry of the lattice and its energy is to leading order $N_O\epsilon$ (Fig. 3). The attraction between two holes in this limit occurs because the number of unit cells where charge is redistributed is smaller when the two holes are nearby then when they are separated. From this simple picture a third added hole is also expected to bind to this cluster, which is what is found in our numerical calculations, and is contrary to the results reported in Ref. 10.

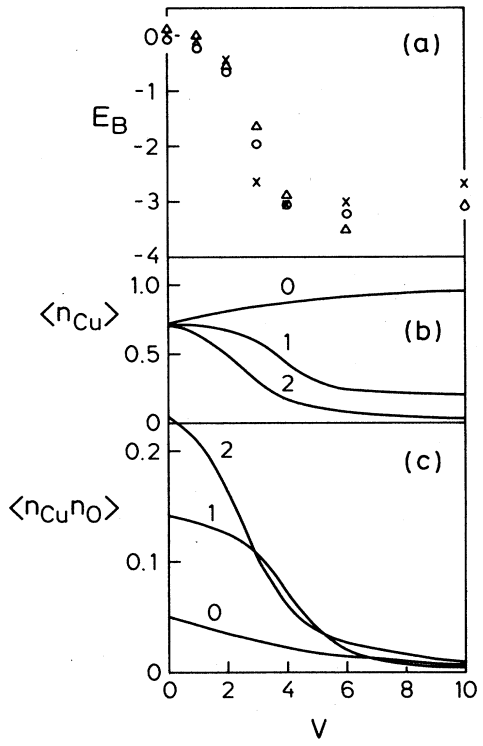

FIG. 2. (a) Binding energy vs nearest-neighbor Coulomb repulsion V for systems with 4 unit cells, $\epsilon=2$, for 3 different cases: (i) $U_{Cu}=\infty$, $U_O=0$ (⊙); (ii) $U_{Cu}=\infty$, $U_O=\infty$ (△); (iii) spin polarized (×). (b) Expectation value of copper hole occupancy for $\epsilon=2$, $U_{Cu}=\infty$, and $U_O=\infty$. The curves are labeled by the number of holes away from half filling. (c) The density-density correlation function between nearest-neighbor Cu and O sites for the same parameters as in (b).

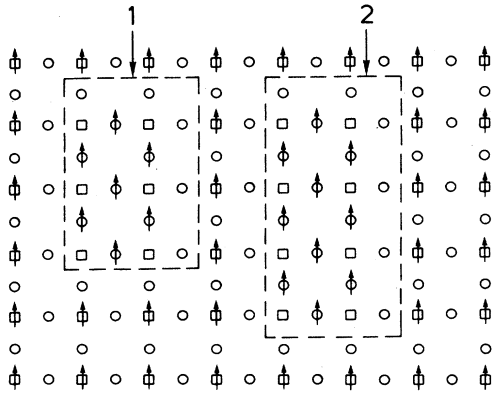

FIG. 3. Sketch of hole droplets with one and 2 additional holes for ϵ much greater than t, $U_{Cu}=U_O\rightarrow\infty$, and $V\rightarrow\infty$. The droplet labeled 1 contains 6 unit cells and 7 holes, with energy $\approx 7\epsilon-10t^2/\epsilon$ above the ground state of the half-filled case. The box labeled 2 contains 8 unit cells and 10 holes, and has energy $\approx 10\epsilon-12t^2/\epsilon$ above the undoped system. The estimated binding energy is $E_2-2E_1\approx -4\epsilon+8t^2/\epsilon$.

The size of the hole droplets would of course be limited by the long-range part of the Coulomb repulsion which is not included in our model Hamiltonian. At finite doping concentration charge-density-wave (CDW) solutions are more favorable.

For small values of ϵ, but V and U_{Cu} still large, even the half-filled ground state becomes unstable against the formation of droplets. For large ϵ the ground state corresponds to one hole localized on each copper site, while for small ϵ the Cu and O occupancies are comparable. This instability results from the hopping possibilities of electrons at the boundary of a droplet. This degree of freedom is not present in the state with one hole at each Cu, because of the constraint $\langle n_{Cu} n_O \rangle \simeq 0$. For $V=\infty$ this transition is discontinuous and at $\epsilon \simeq 1.1$ in the spin-polarized case. For intermediate values of V this transition as a function of ϵ becomes smeared, but a rather dramatic change in Cu occupancy can still be seen. One further speculation prompted by this observation concerns the behavior of the binding energy for $\epsilon=0$ and large V. The dominant contribution to the binding energy as displayed in Fig. 3 does not exist in this limit, because the site energies are equal, the charge redistribution costs no potential energy. The binding energy in this case arises purely from the frustration in the motion of holes introduced by doping. We find from diagonalization for $N_C \leq 10$ and $V \rightarrow \infty$ large finite-size fluctuations in the binding energy, with excursions to both positive and negative values. Our final conclusion is that binding is unlikely for large V and $\epsilon=0$, but for intermediate V the question remains open because the size dependence is not understood yet.

In the region ϵ greater than t, but with V small enough so that the suppression of nearest-neighbor occupancy is not complete, the simple picture presented above does not apply. Figure 4 indicates the source of the negative binding energy in this limit: the addition of a second hole causes a smaller additional change in the NN density-density correlation function than does the first one. Since the expectation value of the NN interaction term of the Hamiltonian is proportional to this correlation function, this leads directly to the negative binding energy. Of course the suppression of NN occupancy occurs at the cost of some kinetic energy. The relation between the correlations function $\langle n_{Cu} n_O \rangle$ and the binding energy reflects the formation of a charge-transfer (CT) "bipolaron." Contributions from spin degrees of freedom are not excluded in this regime, as can be seen by comparing the spin-polarized with non-spin-polarized results. From the further neighbor correlation functions we infer that the size of the "bipolaron" is at least of the size of the largest system studied. Figure 5 shows the size dependence of the binding energy and the ground-state energy per particle at half filling for the spin-polarized case with $V=1$ and 2. The similarity between the size dependence of the energy per particle and the binding energy is striking. The fact that by $N_C=6$ the fluctuations with changing system size of the ground-state energy per particle for $V=0$ are of order 2% or less compared to the infinite system limit suggests one possible extrapolation of the binding energy to a finite negative value.

Shiba and Ogata[12] reported negative binding energy even for $V=0$ and $U_O=0$. However, already small values of U_O result in the disappearance of the binding which they discuss. For reasonable values of U_O a finite value of V is essential for the existence of negative binding energies in these systems.

In these small systems the spin-correlation function be-

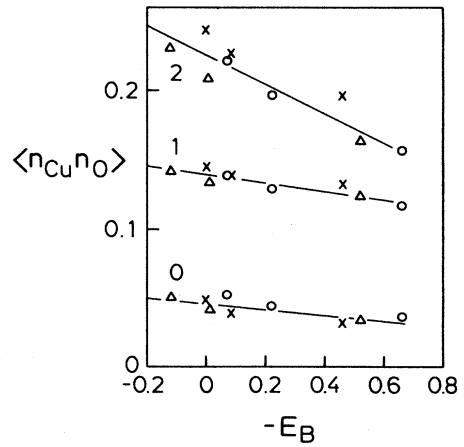

FIG. 4. Nearest-neighbor hole-correlation function vs binding energy for states with different number of holes away from half filling (0, 1, and 2). Parameters are chosen as in Fig. 2(a). The binding energies correspond to small values of V ($V \leq 2$). Lines are drawn as guide to the eye.

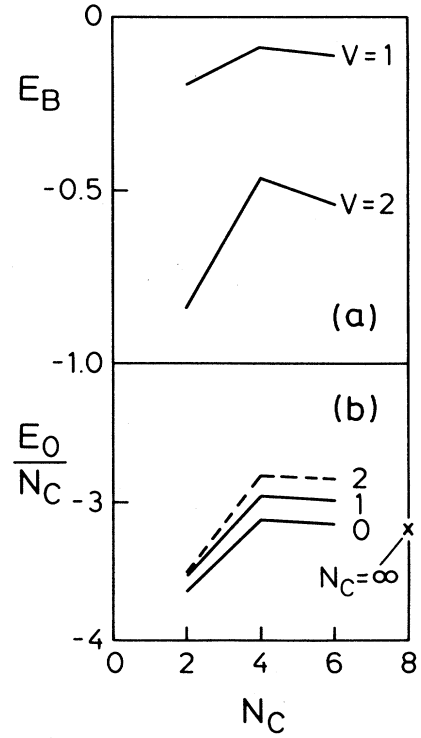

FIG. 5. (a) The size dependence of binding energy for the spin-polarized case with $\epsilon=2$ for $V=1$ and 2. (b) The ground-state energy per hole for the same parameters as in (a). Also included is a curve for $V=0$, with the infinite size limit indicated by ×.

tween NN Cu spins is strongly reduced when adding one hole, and is almost zero when a second hole is added. We note, however, a remarkable buildup of antiferromagnetic-correlations between near-neighbor oxygen sites when holes are added, also for realistic choices of parameters. This finding represents an enhancement of a tendency already observed in the noninteracting ground state, i.e., resulting from the exchange hole.

One further point which should be mentioned concerns the stability of these binding mechanisms with respect to extension of the model to include the Coulomb repulsion between holes on NN O sites V_{OO} and the corresponding hopping matrix element t_{OO}. As pointed out previously the effect of t_{OO} is minor for realistic values.[10] This is easily understood as the charge redistribution between Cu and O is not essentially influenced by this matrix element. However, in all cases studied binding is strongly suppressed by increasing V_{OO}, and the binding energy becomes positive near $V_{OO}/V \approx \frac{1}{3}$. This indicates that the question of hole binding in such an extended Hubbard model is quite subtle, and that care should be taken in interpreting the results of calculations with different truncations of the interactions. Finally, the lattice degrees of freedom not considered here are expected to contribute to binding. The importance of phonons in the case of the CT mechanism is well known, e.g., from the quasi-one-dimensional halogen-bridged metal compounds.[13] Further evidence for the phonon contribution to pairing oxide superconductors comes, e.g., from recent tunneling spectra[14] and from phonon self-energy effects.[15]

In conclusion, we have shown that attraction between holes exists in the extended multiband Hubbard model in the parameter regime V and U_{Cu} large, and ϵ of order t or larger, leading to the formation of hole droplets or CDW's. This part of parameter space is, of course, not likely to be relevant for high-T_c superconductors. In the physically more interesting region of intermediate V and large U_{Cu} our evidence is not quite as strong, but does indicate that binding is likely. In this regime the quasiparticles, i.e., holes on oxygen, are dressed by CT excitations from neighboring Cu sites to further-neighbor oxygen sites. Even in the case that no real-space pairs are formed, this electronic polarization mechanism might be relevant for superconductivity in oxide superconductors because it substantially contributes to the retarded interaction between quasiparticles.

Note added in proof. After we submitted this communication, we received unpublished work by J. E. Hirsch, E. Loh, D. J. Scalapino, and S. Tang in which they also come to the conclusion that large values of V favor nucleation rather than pairing.

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[1]See, for example, P. Fulde, Physica C **153-155**, 1769 (1988).
[2]D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Jr., Phys. Rev. Lett. **58**, 2802 (1987).
[3]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).
[4]J. Zaanen, O. Jepsen, O. Gunnarsson, A. T. Paxton, O. K. Andersen, and A. Svane, Physica C **153-155**, 1636 (1988).
[5]P. W. Anderson, Science **235**, 1196 (1987).
[6]C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987); E. Abrahams, Physica C **153-155**, 1622 (1988), and references therein.
[7]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987); V. J. Emery and G. Reiter, Phys. Rev. B **38**, 4547 (1988).
[8]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[9]E. R. Gagliano, A. G. Rojo, C. A. Balseiro, and B. Alascio, Solid State Commun. **64**, 901 (1987); C. A. Balseiro *et al.*, Phys. Rev. B **38**, 9315 (1988).
[10]J. E. Hirsch, S. Tang, E. Loh, Jr., and D. J. Scalapino, Phys. Rev. Lett. **60**, 1668 (1988).
[11]B. N. Parlett, *The Symmetric Eigenvalue Problem* (Prentice Hall, Englewood Cliffs, 1980).
[12]M. Ogata and H. Shiba, J. Phys. Soc. Jpn. **57**, 3074 (1988).
[13]D. Baeriswyl and A. R. Bishop, Phys. Scr. **T19**, 239 (1987).
[14]L. N. Bulaevskii *et al.* (unpublished).
[15]R. Zeyher and G. Zwicknagl, Physica C **153-155**, 1279 (1988).