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Binding of holes in one-band models of oxide superconductors

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We have performed exact-diagonalization studies of the ground state of the one-band Hubbard model and the related strong-coupling Hamiltonian near half-filling. A tendency towards superconductivity, indicated by a negative "binding energy," is found to be greater for the strong-coupling Hamiltonian. We find that two holes are attracted to each other for parameter values where the binding energy is negative. The symmetry of the two-hole bound state of the strong-coupling Hamiltonian is predominantly $d_{x^2-y^2}$, in agreement with other calculations.

There is a considerable amount of experimental data pointing out the relevant role that the copper-oxide planes play in the high-T_c perovskite superconductors.[1] Observations such as the smallness of the isotope effect,[2] antiferromagnetism in related undoped materials,[3] and the strong electron-electron interaction in Cu sites,[4] suggest that a phonon mechanism alone cannot describe these superconducting materials, and that the pairing mechanism could be provided by spin fluctuations. These facts have motivated a great theoretical effort to study the properties of two-dimensional correlated electronic systems and the related nondoped insulating materials.

Following Anderson's initial suggestion,[5] these models are usually taken to be some variation of the Hubbard model. Most commonly, the single-band Hubbard model[6-10] on the square lattice or an effective Hamiltonian obtained from it in the limit of large Coulomb repulsion, has been studied. Even for this well-studied case, the possibility of superconductivity remains controversial. Monte Carlo variational studies on the strong-coupling Hamiltonian,[6,7] find a stable superconducting state below half-filling in the $d_{x^2-y^2}$ pairing mode. On the other hand, both quantum Monte Carlo simulations[8] and exact diagonalization results on the Hubbard model[9] showed that all pairing susceptibilities are suppressed by the Coulomb repulsion, which was interpreted as evidence that this model does not exhibit superconductivity. It is therefore of interest to understand whether this difference could arise from the different models that were being used; the Hubbard model in the case of the quantum Monte Carlo calculations, and the strong-coupling Hamiltonian, which is only equivalent to it in the limit of very large Coulomb energy, in the variational Monte Carlo work. Actually, in more recent Monte Carlo work,[10] which computed interaction vertices, evidence for pairing, and hence possible superconductivity, in the $d_{x^2-y^2}$ channel *was* obtained. Nonetheless, it is clearly desirable to compare the behavior of these models for realistic values of the parameters; to our knowledge, this has not been done before.

We have therefore investigated the ground-state properties of the one-band Hubbard model and the strong-coupling Hamiltonian near half-filling by exact diagonalization. The Hubbard Hamiltonian is defined by

$$H_{\mathrm{Hubb}} = -t \sum_{\langle i,j\rangle,\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} , \tag{1}$$

where $\langle i,j\rangle$ indicates nearest-neighbor pairs, each distinct pair being summed over once, $c_{i\sigma}^{\dagger}$, $c_{i\sigma}$ are creation and annihilation operators of an electron on site i with spin σ, and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$. In the limit of large U, one can use a canonical transformation to eliminate the states with doubly occupied sites, and thus the size of the Hilbert space is reduced from 4^N to 3^N states, where N is the number of sites. Following Ref. 11, the ensuing strong-coupling Hamiltonian H_{SC} can be written

$$H_{\mathrm{SC}} = H_{\mathrm{NN}} + H_{\mathrm{NNN}} , \tag{2}$$

where

$$H_{\mathrm{NN}} = -t \sum_{\langle i,j\rangle,\sigma} (\tilde{c}_{i\sigma}^{\dagger} \tilde{c}_{j\sigma} + \tilde{c}_{j\sigma}^{\dagger} \tilde{c}_{i\sigma}) + \frac{4t^2}{U} \sum_{\langle i,j\rangle} \left((\mathbf{S}_i \cdot \mathbf{S}_j) - \frac{n_i n_j}{4} \right) , \tag{3}$$

where $\tilde{c}_{i\sigma} = c_{i\sigma}(1 - n_{i,-\sigma})$, the factor of $(1 - n_{i,-\sigma})$ enforcing the constraint of no double occupancy, $\mathbf{S}_i$ is the spin on site i, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. H_{NNN} is given by

$$H_{\mathrm{NNN}} = -\frac{t^2}{U} \sum_{\langle i,j,k\rangle} [(\tilde{c}_{i\uparrow}^{\dagger} \tilde{c}_{j\uparrow}^{\dagger} \tilde{c}_{j\downarrow} \tilde{c}_{k\uparrow} + \tilde{c}_{j\uparrow}^{\dagger} \tilde{c}_{i\uparrow}^{\dagger} \tilde{c}_{k\downarrow} \tilde{c}_{j\uparrow}) + (\tilde{c}_{i\uparrow}^{\dagger} \tilde{c}_{j\downarrow}^{\dagger} \tilde{c}_{k\downarrow} \tilde{c}_{j\uparrow} + \tilde{c}_{j\uparrow}^{\dagger} \tilde{c}_{i\downarrow}^{\dagger} \tilde{c}_{j\downarrow} \tilde{c}_{k\uparrow})] + (k \leftrightarrow i) , \tag{4}$$

where $\langle i,j,k\rangle$ indicates a sum over sites such that (i,j) and (j,k) are nearest neighbors. H_{NNN} represents a particle making a second-neighbor hop from i to k passing through a virtual intermediate state with double occupancy on j. The first and second terms of Eq. (4) describe processes in which the spin on the intermediate site j remains fixed and is flipped, respectively.

Note that Eq. (2) includes only the first terms in an expansion of the Hamiltonian in powers of t/U. Neglected terms are of order t^3/U^2 or higher, so H_{SC} and the Hubbard Hamiltonian should agree for sufficiently small t/U. Since H_{NN} and H_{NNN} are the same order in t/U, they

should both be included for consistency. However, $H_{\rm NNN}$ is often neglected so we have also computed results for $H_{\rm NN}$ by itself. In the strong-coupling Hamiltonian, a "hole" is just an empty site, so the number of holes n_h is defined to be $n_h = N - n_e$, where N is the number of sites and n_e is the number of electrons. In the half-filled case, i.e., no holes present, the model becomes equivalent to the spin-$\frac{1}{2}$ Heisenberg antiferromagnet.

We took a square lattice with periodic boundary conditions, the largest sizes being 4×4 for $H_{\rm SC}$, and $\sqrt{8}\times\sqrt{8}$ for the Hubbard model. We only included configurations with the smallest z component of total spin, but this is not really a restriction because these span *all* possible values of the total spin itself. For the 4×4 lattice, we considered additional geometrical symmetries (translations by two lattice spacings in each of the two directions and two reflections) and spin reversal symmetry when applicable. As a result, the largest matrix that we had to diagonalize had dimension 60060. We used a conjugate gradient method[12] to compute the minimum eigenvalue of the Hamiltonian matrix and its eigenvector within each subspace of different symmetry. We checked to see if the ground state is degenerate and, if so, we averaged over all the ground states.

In order to determine the possibility of superconductivity in this model, we study the binding energy of two holes defined by

$$E_{B,2} = (E_2 - E_0) - 2(E_1 - E_0)\,, \tag{5a}$$

where E_m is the ground state of the system with m holes. A negative value of $E_{B,2}$ presumably indicates an attractive interaction between holes. We must, however, distinguish pairing, which could lead to superconductivity, from phase separation of holes. We have therefore also studied the binding energy of three holes with respect to splitting into a pair and a single hole, defined by

$$E_{B,3} = (E_3 - E_0) - (E_2 - E_0) - (E_1 - E_0)\,, \tag{5b}$$

and the binding energy of four holes with respect to forming two pairs, defined by

$$E_{B,4} = (E_4 - E_0) - 2(E_2 - E_0)\,. \tag{5c}$$

Both $E_{B,3}$ and $E_{B,4}$ would be negative if phase separation occurs. Superconductivity is therefore indicated by $E_{B,2}$ being negative and $E_{B,3}$ and $E_{B,4}$ being positive.

In Fig. 1 we show the results for $E_{B,2}$ on the tilted $\sqrt{8}\times\sqrt{8}$ lattice[9] for the Hubbard model, Eq. (1), the strong-coupling Hamiltonian, Eqs. (2)–(4), and the strong-coupling Hamiltonian with nearest-neighbor interactions only, Eq. (3). We see that while $E_{B,2}$ is only slightly negative for the Hubbard model, there is a larger binding in the strong-coupling Hamiltonian, and an even larger effect if only the nearest-neighbor hopping is included. Note that the strong-coupling regime corresponds to *small* t/U. In Fig. 2 we show the results of the binding energy of two holes added to half-filled band for various sizes as a function of t/U, obtained with the full strong-coupling Hamiltonian. For $t/U \gtrsim 0.1$ it is encouraging that our results are not very size dependent, except for the 2×2 lattice which is clearly too small to be very useful.

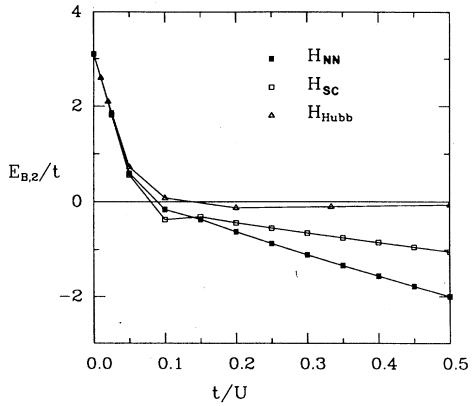

FIG. 1. Binding energy, $E_{B,2}$, of two holes added to the half-filled band for the tilted $\sqrt{8}\times\sqrt{8}$ lattice (Ref. 9). The results are for the ground state of the Hubbard model, $H_{\rm Hubb}$, the strong-coupling Hamiltonian, $H_{\rm SC}$, and the strong-coupling Hamiltonian with nearest-neighbor hopping only, $H_{\rm NN}$.

The value of t/U at which $E_{B,2}$ changes from positive to negative decreases with increasing size and it is interesting to speculate on whether this value tends to zero[13] $N\to\infty$. We find that the one-hole system is ferromagnetic, i.e., has maximum total spin, for very large U, in accord with Nagaoka's theorem.[14] For the 4×4 lattice we find that ferromagnetism disappears for $t/U \gtrsim 0.025$, in agreement with Dagotto *et al.*[15] For two holes we find that the ground state is *always* a singlet. Results for magnetic properties of the model will be published separately.

Our results for $E_{B,2}$, $E_{B,3}$, and $E_{B,4}$ are shown in Fig. 3 for $H_{\rm SC}$ on the 4×4 lattice. It is seen that both $E_{B,3}$ and $E_{B,4}$ change sign at about the same value of t/U consistent with the idea, discussed above, that they both become negative when phase separation of holes occurs. Notice that there is a window of values of t/U, roughly in the range $0.06 \lesssim t/U \lesssim 0.16$, where $E_{B,2}$ is negative while $E_{B,3}$ and $E_{B,4}$ are positive, indicating possible superconductivity.

Another indication of the attraction between two holes

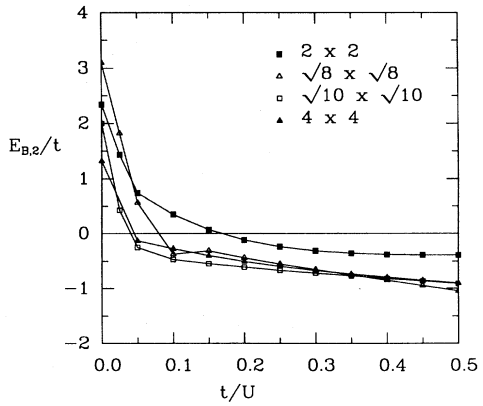

FIG. 2. Binding energy, $E_{B,2}$, in the ground state of the strong-coupling Hamiltonian, with two holes added to the half-filled band, for various sizes.

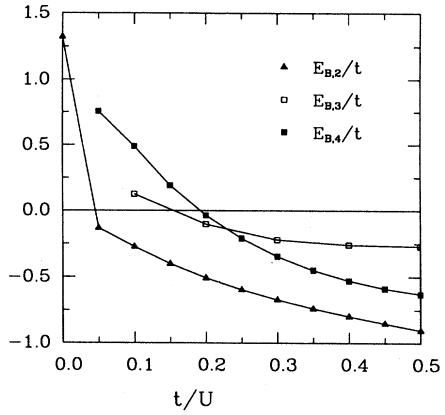

FIG. 3. $E_{B,2}$, $E_{B,3}$, and $E_{B,4}$ are the "binding energy" of two, three, and four holes, respectively, defined in Eq. (5) in the text, at zero temperature. The results are for different values of t/U for H_{SC} on the 4×4 lattice. For superconductivity one expects $E_{B,2}$ to be negative and $E_{B,3}$ and $E_{B,4}$ to be positive.

is given by the hole-hole correlation function, defined by

$$C(\mathbf{r}) = \frac{1}{n_h} \sum_i \langle (1-n_i)(1-n_{i+\mathbf{r}}) \rangle , \tag{6}$$

which gives the probability that there is a hole at r given there is one at the origin. On the 4×4 lattice there are only five different neighbor distances and two of these (second and third neighbors) are equivalent because of an extra symmetry on the 4×4 lattice with periodic boundary conditions.[16] The behavior of these correlation functions is shown, as a function of t/U, in Fig. 4 for two holes. We can see that at $t/U \lesssim 0.05$ the holes tend to be as far as possible on the lattice. As t/U increases into the region where the binding energy $E_{B,2}$ shown in Fig. 3, is negative, this situation is reversed and the holes tend to be as close as possible, as one would intuitively expect.

In order to study pairing, we compute the pairing correlation matrix defined by

$$P_{lm} = \tfrac{1}{2} \langle \Delta_l \Delta_m^\dagger + \Delta_m^\dagger \Delta_l \rangle , \tag{7}$$

where

$$\Delta_l = \frac{1}{\sqrt{N}} \sum_i \tilde{c}_{i\downarrow} \tilde{c}_{i+l\uparrow} , \tag{8}$$

are the usual pairing operators. This is just the correlation function corresponding to the response functions computed in Refs. 8–10. Both the correlation and response functions should provide evidence for long-range superconducting order, if it exists, for sufficiently large sizes. In particular, the correlation function, Eq. (7), should diverge proportional to N in this case. Substituting Eq. (8) into Eq. (7), one has averages of four fermion operators. Terms where the sites of two or more of these operators coincide correspond to spin or charge correlations rather than pairing correlations. We therefore feel that the most useful quantity to study is the restricted average where all four sites are different. Note also that, with this restriction (i) the two terms in Eq. (7) are the same; (ii) doubly occupied intermediate states can never appear so one can replace the $\tilde{c}$ by regular electron operators c; and (iii) one can also replace electron operators by hole operators h defined by $h_{i\sigma}^\dagger = c_{i,-\sigma}$.

By diagonalizing the $N \times N$ pairing correlation matrix we are able to study pairing modes of different symmetries. On the square lattice the only possible symmetries are s,p which is doubly degenerate, $d_{x^2-y^2}$ and d_{xy}. In Fig. 5 we show the largest eigenvalue, λ, of each symmetry for different values of t/U for H_{SC} on the 4×4 lattice. For $t/U \gtrsim 0.06$, which is roughly the point at which $E_{B,2}$ becomes negative, the eigenvalue of $d_{x^2-y^2}$ symmetry dominates. Furthermore, the eigenvector has largest weight on nearest-neighbor sites. We find very similar results for H_{NN}. If we allow the four sites in Eq. (7) to be the same, then there is a large contribution to P from the resulting spin and charge fluctuations, and the largest eigenvalue has s-wave symmetry, though the

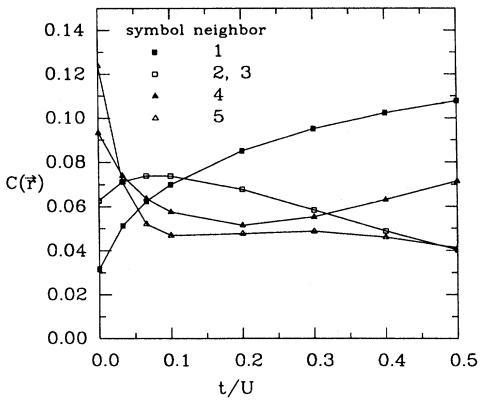

FIG. 4. A plot of hole-hole correlation functions, $C(\mathbf{r})$ defined by Eq. (6) of the text, for all inequivalent separations of the holes (first neighbor, second neighbor, etc.) for the ground state of the strong-coupling Hamiltonian on a 4×4 lattice, as a function of t/U.

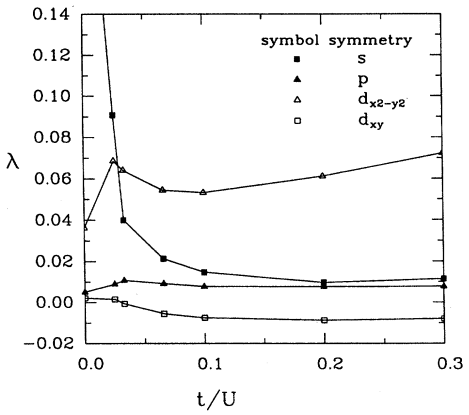

FIG. 5. A plot of the largest eigenvalue, λ, of each symmetry of the $N \times N$ matrix P_{lm}, defined in Eq. (7) of the text, with the restriction that the sites of all four fermion operators are different. The results are for the ground state of the strong-coupling Hamiltonian on a 4×4 lattice.

$d_{x^2-y^2}$ eigenvalue is the next largest. We feel, however, that information about pairing is better contained in the results with restriction to *different* sites because these are uncontaminated with charge and spin fluctuations. This argument is supported by the result that the $d_{x^2-y^2}$ mode begins to dominate very close to the value of t/U where $E_{B,2}$ becomes negative. For H_{NN}, however, we find that the $d_{x^2-y^2}$ fluctuations dominate even if one includes terms where sites are the same.

To conclude, we have provided evidence suggesting, but by no means proving, that the one-band strong-coupling Hamiltonian has a *d*-wave superconducting phase for small concentrations of holes below half-filling. This is in agreement with earlier studies using a Gutzwiller-type variational wave function[6,7] for the nearest-neighbor strong-coupling Hamiltonian and recent Monte Carlo simulations of the Hubbard model.[10] We feel that our work is complementary to these studies in that, although we work with smaller lattice sizes, we do not have to guess the form of the wave function, as in Refs. 6 and 7, and we can work at $T=0$ whereas the results in Ref. 10 are restricted to moderately high temperatures. We have also given a more detailed study of the behavior as a function of t/U. It is interesting to note that the spin-bag model[17] also predicts a pairing wave function with $d_{x^2-y^2}$ symmetry in real space. Although we have been unable to study the 4×4 Hubbard model we do find, for the tilted $\sqrt{8}\times\sqrt{8}$ lattice, that two holes are attracted to each other in real space for t/U values where $E_{B,2}$ is negative, just as occurred for H_{SC} on the larger lattice. It would be very interesting to compute the pairing functions of the 4×4 Hubbard model, to see if there is a dominant $d_{x^2-y^2}$ mode there too. Imada, Hatsugai, and Nagaosa[18] have studied a somewhat more general model than ours and also concluded that there are parameter values where two holes bind. They do not, however, report in detail how the results depend on the parameters of the model and do not look at the symmetry of the bound state.

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