Superconductivity in the CuO Hubbard model

with long-range Coulomb repulsion

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Abstract

A multiband CuO Hubbard model is studied which incorporates long-range (LR) repulsive Coulomb interactions. In the atomic limit, it is shown that a charge-transfer from copper to oxygen ions occurs as the strength of the LR interaction is increased. The regime of phase separation becomes unstable, and is replaced by a uniform state with doubly occupied oxygens. As the holes become mobile a superfluid condensate is formed, as suggested by a numerical
analysis of pairing correlation functions and flux quantization. Although most
of the calculations are carried out on one dimensional chains, it is argued that
the results are also applicable to two dimensions.

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The study of high-\(T_c\) superconductors\(^1\) continues attracting much attention. Recent progress has been made in the theoretical search for ground state superconductivity in one band electronic models. The two dimensional \(t-J\) model has shown indications of d-wave superconductivity\(^2\) when analyzed near the phase separation regime\(^3\) at intermediate densities. It would be desirable to extend these observations about superconductivity to more realistic three band versions of the Hubbard model, such as those introduced by Emery\(^4\) and Varma and collaborators.\(^5\) Not much is known for the superconducting properties of these models. Weak coupling and large \(N\) mean-field calculations applied to this extended model have indeed shown that a region of superconductivity exists near phase separation as in the one band case.\(^6\) However, these techniques are only approximate and should be supplemented by studies of the multiband Hubbard model with unbiased computational methods, like exact diagonalization and quantum Monte Carlo\(^7,8\).

Varma and collaborators\(^5\) have suggested that the inclusion of a short-range Coulomb repulsion induces a charge transfer process, leading to the formation of tightly bound hole pairs on the oxygen ions. If these pairs are mobile they naturally lead to a superfluid condensate. Unfortunately, the charge transfer mechanism seems systematically correlated with a phase separation process, as was recently discussed in the atomic limit.\(^9\) Phase separation occurs between a phase with a density of one hole per unit cell on the copper ions and a second phase which has a density of two holes per unit cell, with the charge located on double occupied oxygens. These pairs
are not mobile, and thus the system cannot become superfluid. In this sense, phase separation is an unwelcomed effect in this model. In spite of this problem, Sudbø et al.\textsuperscript{10} recently found indications that the one dimensional model exhibits superconducting correlations immediately before phase separation. This conclusion is based on a study of the conformal field theory parameter $K_\rho$; $K_\rho > 1$ indicates that superconducting power-law correlations are dominant in the ground state. (Unfortunately the actual pairing correlations in the ground state decay rapidly with distance\textsuperscript{11}.)

While this result is very encouraging, it is difficult to predict in advance whether a region of superconductivity would exist near phase separation in the more realistic two dimensional problem. Thus, it would be desirable to have a model which exhibits robust superconducting correlations in the ground state, and whose main features can be understood intuitively, allowing its extension to two dimensions where explicit numerical simulations are difficult.

In this paper, a simple modification of the standard three band model is presented that addresses these issues. Even in the atomic limit, a clear separation between the parameter values associated with charge transfer and phase separation is evident. Including a hopping term, robust numerical evidence of superconducting correlations is observed. This three band Hubbard model for the Cu-O cuprates is defined by,\textsuperscript{4,5}

\begin{equation}
H = -t_{pd} \sum_{<ij>\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U_d \sum_i n_i^\uparrow n_i^\downarrow + U_p \sum_j n_j^\uparrow n_j^\downarrow + \epsilon_d \sum_i n_i + \epsilon_p \sum_j n_j, \quad (1)
\end{equation}

where the operators are hole number and hole creation and annihilation operators,
$U_d$ and $U_p$ are the Coulomb on-site repulsion energies for the copper and oxygen sites respectively, and $\epsilon_d$ and $\epsilon_p$ are the ion energies. The label $i$ corresponds to Cu sites, and $j$ denotes O sites and they are connected by a hopping amplitude $t_{pd}$. The charge transfer energy is defined by $\Delta = \epsilon_p - \epsilon_d$. It is generally accepted that $U_d > \Delta, U_p$ in the cuprates, so we will work in this regime. The doping fraction is $x = n_h/N$, where $n_h = (N_h - N)$ is the number of doped holes, $N_h$ is the total number of holes and $N$ is the number of Cu-O cells. At half-filling, $N_h = N$, as in the insulating Cu-O compounds. Most of the results presented here correspond to low and intermediate doping ($x \leq 0.66$).

As explained before, Varma et al.\textsuperscript{5} argued that the Hamiltonian Eq.(1) needs to be supplemented by a nearest-neighbor Coulomb repulsion,

$$H_{nn} = V \sum_{<ij>} n_i n_j,$$

(2)

(where $V$ is a positive number, and $n_{i,j}$ are hole number operators) to induce the charge transfer mechanism, but this term also induces phase separation, at least in the atomic limit. To avoid this problem we have extended the range of the density-density correlations of Eq.(2). The relevance of the long range part of the Coulomb interaction between the holes, which prohibits phase separation was emphasized in a recent work by Emery and Kivelson.\textsuperscript{12} In this work, experimental evidence was provided in support of the “frustrated phase separation” scenario which results in the presence of long range Coulomb interaction.\textsuperscript{13} In particular, if the interactions
are of infinite range, then phase separation is certainly eliminated. This leads us to replace Eq.(2) by a more general interaction

\[
H_C = \frac{V}{2} \sum_{l \neq m} n_l n_m \frac{d_{lm}}{d_{lm}^\lambda},
\]

where \(d_{lm} = |r_l - r_m|\), and \(\lambda\) is the range of the screened Coulomb repulsion. If \(\lambda = \infty\), the interaction decays as the inverse of the distance, and it is of infinite range. Most of the results presented are for this limit. We also consider finite values of \(\lambda\) to show that our conclusions are qualitatively valid even for finite range forces, provided that they operate over distances larger than a few lattice spacings.

To motivate the introduction of a long-range term in the Hamiltonian it is convenient to first consider the atomic limit \(t_{pd} = 0\). Let us consider the one dimensional case first. In this case, it is not difficult to guess which are the possible states with lowest energy for different values of \(V\). We have then checked that some of these states are effectively the ground state in a certain region of \(V\) using a simulated annealing algorithm described below. In Fig.1a we show the ground state in the regime of small \(V\). This state (denoted by I), has a hole at every copper ion, and the remaining of the holes are on singly occupied oxygens, distributed in a regular pattern to minimize the newly introduced long-range potential energy. In this region, for the two dimensional (2D) model, and for not too high doping, some antiferromagnetic (AF) correlations are expected to develop. On increasing \(V\) a phase separated state (denoted by II and shown in Fig.1b) becomes energetically competitive with state I. It contains a
large region of doubly occupied oxygens and another separated region with one hole per copper ion. These two densities coexist and changing the number of holes just increases or reduces their relative size. However, there is a third possibility which becomes energetically favorable due to the long-range Coulomb interaction. In Fig.1c we show a state (III) where all the holes are on doubly occupied oxygens. The reason for considering this state is that charge tends to spread uniformly over the lattice in the presence of long-range forces, rather than separating into different densities, as in the phase separated state. State III is a configuration with “preformed” pairs on the oxygens, and if this state becomes stable in the atomic limit, a finite hopping amplitude may render it superfluid. In other words, once the pairs are preformed at zero hopping, it is reasonable to expect that they will behave as hard-core bosons when they are allowed to move, at least for a small hopping amplitude. Similar behavior is observed in the attractive Hubbard model at large $|U|/t$. Note that state III resembles a Wigner crystal of charge 2e pairs at the oxygens which is precisely expected to be stable due to long-range interactions. We have compared the energies of states I, II and III numerically in the atomic limit for 12, 24 and 48 CuO cells. We have considered $U_d = 7$, $U_p = 1$, $\Delta = 1.5$, in arbitrary units, and $x = 0.33$. For the 12 cell lattice there is a small interval of $V$, [3.1, 3.7], where state II has the lowest energy. For the 24 cell lattice this interval is smaller and finally, for the 48 cell lattice there is a direct crossing from state I to state III at $V_c \approx 3.38$. Similar arguments are obviously valid in the two dimensional case, so our results are not
restricted to chains only. For illustration we have carried out an explicit calculation for a $4 \times 4$ CuO$_2$ periodic cluster with four doped holes ($x = 0.25$). In this case the ground state is not obvious, and it is difficult to determine it by calculating the energy of each possible configurations because their number grow exponentially with the number of atoms. For this reason we developed a simulated annealing$^{15}$ program to find the ground state. This algorithm can be described as a sequence of Markov chains, each one generated at a fixed value of the temperature. The temperature is decreased between subsequent Markov chains. At each step of the Markov chain, the algorithm attempts to transform the current state into an state obtained by moving one hole to a nearest-neighbor site. The variation of the energy is computed, and the local change is accepted according to the Metropolis criterion. Using this technique we have determined the ground state of this cluster for the same set of parameters $U_d$, $U_p$ and $\Delta$ as before. For small $V$, the ground state has one hole per Cu atom and the doped holes are in O sites locates as far as possible from each other. As $V$ is increased, a charge transfer from Cu to O sites starts to develope. For $V \approx 3$, a state with doubly occupied O sites separated from a region of single-occupied Cu sites becomes stable. For larger values of $V$, the ground state has the form illustrated in Fig.1d. These results in two dimensions give further support to our intuitive conclusion that in the presence of strong long-range interactions, there is a phase with preformed pairs without phase separation.

In order to find the $\lambda$ dependence of our results, numerical calculations where
carried out using the simulated annealing technique on chains of 12 and 24 CuO cells \((x = 0.33)\). We have considered the same parameters as above. As an order parameter we used the number of doubly occupied oxygen sites. The results are shown in Fig.2a. We observed that our intuitive ideas about states I, II, and III are qualitatively correct, and they are dominant in a large region of parameter space. Only in narrow regions near the phase boundaries, especially for large values of \(\lambda\), did we observe other types of states become competitive. However, these states are simple variations of states I, II, and III (for example, including small fluctuations), so the essential features shown in Fig.2a are correct. Note that, for the 12 cell chain, there is a particular value of \(\lambda \sim 8\) where the phase separated regime becomes very narrow, and it may disappear when the hopping parameter is switched on. (State III will reduce its energy by providing mobility to the pairs, but state II is too rigid to take advantage of this possibility.) This value of \(\lambda\) reduces to \(\sim 4\) for the 24 cell chain. We conjecture therefore that the phase separated regime does not exist for \(\lambda > 4\) or perhaps for even smaller values of \(\lambda\), so it is not necessary to have a fully unscreened \(1/r\) interaction to obtain the effects described here. This value of \(\lambda\) corresponds to two Cu-Cu lattice spacings (about 7.6Å in the cuprates), and thus it is not physically unrealistic. The main features in Fig.2a are also present for the case of 8 doped holes \((x = 0.66)\). Similar calculations for the \(4 \times 4\) and \(6 \times 6\) CuO\(_2\) clusters, for \(x \approx 0.25\), give essentially the same phase diagram, as it can be seen in Fig.2b.
The results summarized in Figs.1 and 2a,b were obtained in the atomic limit. Although they are very suggestive, the ultimate test of these ideas requires a finite kinetic energy term to give mobility to the carriers. The actual boundaries in parameter space between different ground states will be determined by the competition between the Coulomb potential energy and the kinetic energy. To study this interplay, and to establish the assumed existence of a superconducting regime, Lanczos diagonalization techniques were used to obtain the ground state of the Hamiltonian Eq.(1,3) explicitly on a finite chain. Due to the large number of states per unit cell the lattices that can be studied numerically are limited to a small number of cells. In this paper we studied 6 cells (12 atoms) with various hole numbers. For the results shown below we chose $U_d = 7$, $U_p = 1$ and $\Delta = 1.5$ in units of $t_{pd}$. These are reasonably realistic values for the cuprates.\textsuperscript{16} We have also observed that our results are qualitatively similar over a broad range of parameters.

First, let us numerically consider the issue of charge-transfer versus phase separation numerically. A quantitative measure of charge transfer from Cu to O sites is given by the expected occupation of oxygen sites. However, a sharper indication of charge transfer is given by the susceptibility associated with that quantity, $\chi_{CT} =< n^2_O > - < n_O >^2$, ($n_O$ is the number of holes on the oxygens).\textsuperscript{8} The results for this susceptibility are shown in Fig.2c for $n_h = 2$ and $n_h = 4$ on the 12 atom chain and a long range interaction. In both cases a peak is observed at a particular value of $V \approx 4$. This peak presumably signals the onset of a charge transfer process.
in this model. (Note also that $\chi_{CT}$ in the region $V > U_d$ shows additional structure, although this is an unphysical region.) $\chi_{CT}$ however does not distinguish between the states II and III in Fig.1. To confirm that phase separation does not occur in the presence of long-range interactions, we have measured the short wavelength component of the susceptibility associated with the correlations of pairs of holes on O sites.$^{17}$ This quantity (denoted by X) is normalized to 1 for a fully phase separated state. In Fig.2d, X is shown for the case $n_h = 2$ on the 12 atom chain. With a short range interaction, X $\rightarrow$ 1 as V is increased. On the other hand, in the presence of long-range interactions, X goes through a maximum, and then converges to zero at large V, showing the absence of phase separation in this limit. The peak at intermediate V is due to the proximity of the phase separated state in the spectrum (as discussed previously in the atomic limit). At this point it is important to remark that the critical value of V ($V_c$) at which the charge transfer process occurs (namely $\sim 3t_{pd}$) is physically acceptable. Some calculations suggest that $t_{pd} \sim 1.3$eV in the cuprates,$^{16}$ and thus $V_c$ obtained here is approximately 4eV. This is not far from estimations$^{18}$ of V based on measurements of the dielectric constant that suggest $V \sim 2 - 3$eV.

Now let us investigate whether state III of Fig.1c becomes superfluid when the holes acquire mobility in the presence of LR interactions. For this purpose, we consider the pairing correlation,

$$C(m) = \frac{1}{N} \sum_j < \Delta_{j+m}^{\dagger} \Delta_j >,$$  \hspace{1cm} (4)
where the pairing operator is defined as $\Delta_j = c_{j\uparrow} c_{j\downarrow}$, and $j, j + m$ indicates O sites. In Fig.3a-b, the pairing correlations are plotted as a function of distance for two different densities, for $t_{pd} = 1$, $U_d = 7$, $U_p = 1$, and $\Delta = 1.5$, and several values of $V$. For $n_h = 2$ the correlations are robust at distance one which is the distance between two oxygen sites ($\sim 3.8\text{Å}$ in the cuprates). At larger distances the correlations decay rather rapidly, so our hypothesis is not clearly supported by these results (note however that these correlations are already stronger than those found in one band models near half-filling). On the other hand, with 16 holes on the chain ($n_h = 4$) the pairing correlation is very strong even at the largest distances available on our finite clusters. The signal monotonically increases with $V$, for $V < U_d$.\textsuperscript{19}

The results presented thus far support a scenario in which s-wave (local) superconductivity appears with increasing $V$ if LR interactions are included. To give further support to these claims, we have studied the dependence of the ground state energy on an external magnetic flux $\Phi$. To analyze this response, a phase factor $e^{i\Phi/N}$ is introduced in the hopping term in Eq.(1).\textsuperscript{2,10} This is equivalent to allowing a magnetic flux through the Cu-O ring (chain with periodic boundary conditions). In Fig.4, the ground state energy measured with respect to the energy at zero flux, $\Delta E = E(\Phi) - E(\Phi = 0)$, is shown as a function of $\Phi$ for $n_h = 4$ and a pure LR interaction ($\lambda = \infty$). For small $V$ the energy has a single minimum at $\Phi = 0 \ (mod 2\pi)$. For $V$ larger than a critical value the energy develops a second minimum at $\Phi = \pi$, indicating the presence of mobile carriers with charge $2e$ in the ground state.\textsuperscript{20} This
anomalous flux quantization is in agreement with results obtained from the pair corre-
relations.

In summary, we have considered an extension of the standard Cu-O electronic Hub-
bard-like model for the cuprates which incorporates long-range interactions. We
found that in the atomic limit a charge-transfer process exists without phase sepa-
ration. The new dominant state in this regime has preformed pairs on the oxygen sites.
With a hopping term that provides mobility to the holes, this state appears to become
superfluid. The effects observed here are intuitively evident, and are valid both in
one and two dimensions. These effects occur not only with a pure 1/r interaction but
also for a finite-range Coulomb repulsion ($\lambda \sim 4$) which might correspond to the real
cuprate compounds.

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References

1. J. Bednorz and K. Müller, Z. Phys. B 64, 188 (1986); Rev. Mod. Phys. 60, 585 (1988).

2. E. Dagotto and J. Riera, Phys. Rev. Lett. 60, 682, (1993).

3. V. J. Emery, S. A. Kivelson and H. Q. Lin, Phys. Rev. Lett. 64, 475 (1990).

4. V. J. Emery, Phys. Rev. Lett. 58, 2794 (1987).

5. C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Comm. 62, 681 (1987).

6. P. B. Littlewood, C. M. Varma, and E. Abrahams, Phys. Rev. Lett. 63, 2602 (1989); P. B. Littlewood et al., Phys. Rev. B 39, 12371 (1989); M. Grilli, R. Raimondi, C. Castellani, C. Di Castro, and G. Kotliar, Phys. Rev. Lett. 67, 259 (1991); C. Di Castro and M. Grilli, Physica Scripta Vol. T45, 81 (1992); R. Raimondi, et al., Phys. Rev. B 47, 3331 (1993).

7. For a recent review see E. Dagotto, “Correlated Electrons in High Temperature Superconductors”, NHMFL preprint (1993), to appear in Rev. Mod. Physics.

8. R. T. Scalettar, D. J. Scalapino, R. L. Sugar, and S. R. White, Phys. Rev. B 44, 770 (1991). See also M. Frick, P. Pattnaik, I. Morgenstern, D. Newns, and W. von der Linden, Phys. Rev. B 42, 2665 (1990); G. Dopf, A. Muramatsu, and W. Hanke, Phys. Rev. B 41, 9264 (1990).

9. A. Sudbø, S. Schmitt-Rink, and C. M. Varma, Phys. Rev. B 46, 5548 (1992).

10. A. Sudbø, C. M. Varma, T. Giamarchi, E. B. Stechel, and R. T. Scalettar, Phys. Rev. Lett. 70, 978 (1993). See also K. Sano and Y. Ono, Physica C 205, 170 (1993).

11. E. Dagotto, J. Riera, Y. C. Chen, A. Moreo, A. Nazarenko, F. Alcaraz, and F. Ortolani, FSU preprint, Sept. 1993.

12. V. J. Emery, and S. A. Kivelson, Physica C 209, 597 (1993).

13. Experimental results suggesting the presence of phase separation in $La_{2}CuO_{4+\delta}$ have been presented in P. C. Hammel, et al., Phys. Rev. B 42, 6781 (1990); Physica C 185, 1095 (1991).
14. Previous work in the three band Hubbard model and t-J models have also found that phase separation is destroyed by a long-range interaction. For example, see G. A. Medina and M. D. Núñez Regueiro, Phys. Rev. B\textbf{42}, 8073 (1990); A. Aligia, H. Bonadeo, and J. Garces, Phys. Rev. B\textbf{43}, 542 (1991); and M. Troyer, H. Tsunetsugu, T. M. Rice, J. Riera, and E. Dagotto, Phys. Rev. B\textbf{48}, 4002 (1993).

15. S. Kirkpatrick, J. of Stat. Phys. \textbf{34}, 975 (1984).

16. See for example, M. S. Hybertsen, E. B. Stechel, M. Schluter and D. R. Jennison, Phys. Rev. B\textbf{41}, 11068 (1990); E. B. Stechel and D. R. Jennison, Phys. Rev. B\textbf{38}, 4632 (1988).

17. C. M. Varma, private communication.

18. F. F. Assaad and D. Wurtz, Phys. Rev. B\textbf{44}, 2681 (1991).

19. In the atomic limit, for $V > U_d$, another state in which there are both Cu and O doubly occupied sites becomes energetically favourable. This state is more rigid than the state III, so the signal slowly decreases with increasing $V$.

20. Note that in 1D there is no Meissner effect, and thus the superfluid density cannot be obtained from the curvature of the energy versus flux, at zero flux. This quantity only measures the Drude weight contribution to the optical conductivity.
FIG. 1 a) Ground state of the Hamiltonian Eq.(1) with long-range interactions for small $V$, in the atomic limit. The copper ions are represented by large circles and the oxygens by small circles. In this and the following figures in the atomic limit the alignment of spins is arbitrary. This state is ground state in the large $U_d$ regime if $U_p$ is nonzero, otherwise it becomes energetically favorable to move the holes of singly occupied oxygens into doubly occupied oxygens. b) Ground state of the model in the region of small $\lambda$ (short-range interactions) and large $V$. This state has phase separation and corresponds to the state previously discussed in Ref.[9]; c) New state discussed in this paper. It becomes the ground state of the problem in the case of large $\lambda$ (i.e. with long-range interactions) and sufficiently large $V$. This state has preformed pairs, and is not phase separated. d) Generalization of the state shown in Fig.1c to a two dimensional lattice.

FIG. 2 a) Phase diagram of the Hamiltonian Eqs.(1,3) in the atomic limit, obtained from a chain with 12 CuO cells (solid lines) and from a chain with 24 CuO cells (dotted lines), $U_d = 7$, $U_p = 1$, and $\Delta = 1.5$ (in arbitrary units), as a function of $\lambda$ and $V$. The doping fraction is $x = 0.33$. The boundaries were obtained numerically using a simulated annealing algorithm. “PM” denotes a region dominated by the states like the one shown in Fig.1a; “Ph.Sep.” denotes the region where state Fig.1b dominates; and “Pairs” is the region with preformed pairs in the ground state, as exemplified by Fig.1c and 1d. b) Same as a) for the 4 x 4 (solid lines) and 6 x 6 (dotted lines) and $x = 0.25$. c) Susceptibility $\chi_{CT}$ (see text) as a function of $V$ for a 6 cell chain (12 atoms), $t_{pd} = 1$ and other parameters as in Fig.2a. The full squares denote $n_h = 2$ and the circles $n_h = 4$. d) Order parameter $X$ (see text) used to study phase separation versus $V$. The full squares denote $\lambda = \infty$, and the open circles are for the nearest-neighbor interaction. The number of holes is 8 ($n_h = 2$).

FIG. 3 a) Superconducting correlations $C(m)$ (as defined in the text) for the long-range model at several values of $V$, on a chain with 12 atoms (6 cells) and 8 holes ($n_h = 2$). Note that $m$ measures O-O distances. The full triangles denote results for $V = 2$, the open squares $V = 4$, and the full squares $V = 6$; b) As a) but with 10 holes ($n_h = 4$).

FIG. 4 The ground state energy $\Delta E(\Phi)$ (measured with respect to the energy at zero flux) versus flux $\Phi$ for a 6 cell-ring for various $V$ and a long-range interaction ($\lambda = \infty$).