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Cu_4O_4 as a negative-U centre in high-T_c superconductors

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Abstract. Exact calculations of the ground-state energy of a Hubbard model for a planar Cu_4O_4 cluster show that, under certain conditions, two holes introduced into the $Cu^{2+}O^{2-}$ system may attract each other, even if both the copper and the oxygen atoms have on-site Coulomb repulsion $U > 0$. This result can be obtained without complicating the model by introducing terms such as nearest-neighbour repulsion. Clusters which contain only atoms with $U > 0$ but which behave as effective $U < 0$ centres may have relevance to high-T_c superconductivity. The calculations have been extended to larger Cu_4O_8 clusters in a few cases. The results suggest that the pairing is not merely an artefact of the extreme boundary conditions.

1. Introduction

It is generally agreed that the two-dimensional CuO_2 plane is the most important structural feature of most of the high-T_c superconductors. The Hubbard [1] Hamiltonian has been widely used to model the electron correlations in this system, although there are other approaches such as the resonating valence bond (RVB) [2]. Since exact solution of the 2D Hubbard problem is impossible, various approximations [3, 4] have been used for the infinite-lattice problem, and Monte Carlo [5] and exact diagonalisation [6, 7] methods have been used for finite clusters.

The problem of high-temperature superconductivity is characterised by a small condensation energy compared with the electronic energies, which means that great accuracy is required if the results are to be reliable, and also a short correlation length [8]. We take the view here that these characteristics suggest exact diagonalisation may be more relevant to the high-T_c problem than is the case in other electron correlation problems. We assume here that the mechanism is purely electronic; coupling to phonon modes is neglected.

The ground state of a simple Hubbard model for Cu_4O_4, in which only the $3d_{x^2-y^2}$ orbital on copper and the 2p orbital on oxygen are considered, has been examined in detail. The copper and oxygen atoms have been allowed to have different chemical potentials V and on-site Coulomb repulsions U. Thus

$$\mathcal{H} = -\sum_{\langle i,j \rangle} c_i^\dagger c_j + \sum_i V_i(n_{i\uparrow} + n_{i\downarrow}) + U_i n_{i\uparrow} n_{i\downarrow} \tag{1}$$

where $U_i = U_{Cu}$ and $V_i = V_{Cu}$ for $i = 1, 3, 5, 7$; $U_i = U_O$ and $V_i = V_O$ for $i = 2, 4, 6, 8$; we

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measure energies in terms of the copper–oxygen electron transfer matrix element $t = 1$. The present system is rather simpler than some others which have been examined.

Cu_4O_4 is the minimum unit to exhibit the symmetry of the CuO_2 lattice. Additional motivation for studying this particular cluster comes from the idea that, if two holes are added to the 12-electron system $4Cu^{2+}4O^{2-}$, they may be corrected on the opposite sides of the ring and hence in some sense divide the four-membered ring into two 'dimer-like' pairs each with some singlet character. The system produced would have electron density alternation similar to that associated with a Peierls instability. Dimerisation might also be expected on magnetic grounds since the magnetic energy of the ground state of a pair of antiferromagnetic coupled spins is anomalously low owing to the absence of zero-point energy. This is a purely quantum effect and is likely to be particularly important in low-dimensional $S = \frac{1}{2}$ systems. Hence there are reasons to expect a net interaction between the two holes which reduce their total energy, a negative effective U. Of course the real ground state will be some kind of 'resonance' between the two possible dimerisations and this resonance will give an additional lowering of the ground-state energy. In this sense the present idea has something in common with RVB theory.

This idea has been investigated by determining the ground-state energies of 12-, 11- and 10-electron systems under Hamiltonian (1) for a variety of U_{Cu}, U_O, V_{Cu} and V_O. Defining E_n as the (typically negative) ground-state energy of the n-electron system, if $(E_{12} - E_{11}) - (E_{11} - E_{10}) = U_{eff} < 0$, then the second hole is attracted to the first. Thus, if two holes are added to a system with many 12-electron Cu_4O_4 centres, the energy is minimised by having both holes on the same centre if U_{eff} is negative. In cases of interest, all systems with 8–15 electrons have been solved to check that no more complicated aggregation of electrons is possible. Only the ground state has been examined since the mattrices involved are rather large. For 12, 11 and 10 electrons there are 784, 1568 and 3136 basis states of minimum total S_z. Fortunately the calculations are made easier by the extreme sparseness of the matrices.

The value of U_{eff} is a function of the difference in chemical potentials, $V_{Cu} - V_O$, rather than their absolute values because the chemical potential for the system cancels from our definition of U_{eff}. Therefore V_O can be set to zero and the three-parameter space U_{Cu}, U_O, V_{Cu} examined.

2. Results

We have explored the three-parameter space U_{Cu}, U_O, V_{Cu} without, initially, any regard for their real values. It seems important first to establish whether $U_{eff} < 0$ can ever be obtained for $U_{Cu} > 0$, $U_O > 0$. Energy surfaces $U_{eff}(U_{Cu}, U_O)$ defined for fixed V_{Cu} have been examined for $U_{Cu} > 0$, $U_O > 0$ for various V_{Cu}. The detailed structures of these surfaces, and the effect of variation in the parameters on the correlation functions, are complicated and will be considered in more detail elsewhere. The most important result is that for a wide range of V_{Cu} there are two regions with $U_{eff} < 0$. One, 'region A', is characterised by large U_O and small U_{Cu}; the other, 'region B' has small U_O and less small U_{Cu}.

For $V_{Cu} = 0$ there is a symmetry between these regions as U_{Cu} and U_O can be interchanged without affecting U_{eff}. Some typical values of $U_{eff}(U_{Cu}, U_O)$ are listed in table 1. For $V_{Cu} > 0$, region A occurs for U_O slightly greater than V_{Cu}. The minimum in U_{eff} becomes deeper as V_{Cu} is increased. Although the magnitude of the most negative U_{eff} is small, about 1% of t, it should be remembered that t itself may be of the order of

Table 1. Values of U_{eff}, in units of $0.0001t$, for $V_{Cu} = 0$. The table shows a small region of $U_{eff} < 0$. Identical results are obtained if U_{Cu} and U_O are transposed.

	U_{eff}							
U_{Cu}	$U_O = 0.0$	$U_O = 0.5$	$U_O = 1.0$	$U_O = 1.5$	$U_O = 2.0$	$U_O = 2.5$	$U_O = 3.0$	$U_O = 3.5$
0.0	0.0	+13.8	−78.4	−141.0	−135.0	−21.8	+171.0	+390.0
0.1	0.6	+27.7	−0.5	−84.5	−102.0	−11.1	+168.0	+380.0
0.2	2.4	+34.4	+86.7	−20.0	−62.5	+4.7	+167.0	+372.0
0.3	5.5	+42.3	+138.0	+52.7	−15.9	+26.1	+170.0	+363.0
0.4	8.9	+51.8	+145.0	+134.0	+38.3	+53.3	+177.0	+362.0

an electron volt, and so U_{eff} may be about 100 K. Region B moves towards the origin as V_{Cu} is increased, i.e. it occurs for smaller U_{Cu}. Typical values for U_{eff} in region B are shown in table 2 for $V_{Cu} > 0$.

Correlation functions have been calculated for the ground-state wavefunctions. We define the spin–spin correlation function by $m_{ij} = \langle S_{zi} S_{zj} \rangle$, normalised to have a maximum possible value of unity, and an electron density correlation function $\rho_{ij} = \langle n_i n_j \rangle$, with a maximum value of four (two electrons at each site). The subscripts here refer to the labelling defined for equation (1). The spin–spin and electron density correlation functions for the ground state are quite different in the two regions defined above. For region A, $U_O > V_{Cu}$, $U_O > U_{Cu}$; therefore, as the first electrons are removed from the 16-electron system ($4Cu^{1+}4O^{2-}$), holes are formed on oxygen. The 12-electron system here contains four oxygen spins exchange coupled through copper. This is physically unrealistic.

Region B is more relevant to the real Cu_4O_4 system; now $U_{Cu} > U_O$, $U_{Cu} > V_O$ and hence the 12-electron system is well represented by a set of antiferromagnetically coupled Cu^{2+} ions. Values of these correlation functions for a 12-electron system typical of region B, with $V_{Cu} = 2$, $U_{Cu} = 1$, $U_O = 0.4$ and $U_{eff} = -0.0036$, are listed in table 3. It can be seen that the spin density is concentrated on copper. Since $m_{13} < 0$, $m_{15} > 0$, the coupling is strongly antiferromagnetic.

As further holes are introduced into the 12-electron system, they are mainly removed from the copper but, as long as V_{Cu} is not large, there is also some loss of electron density

Table 2. Values of U_{eff}, in units of $0.0001t$, for $V_{Cu} = 2$ showing the structure of region B.

	U_{eff}				
U_{Cu}	$U_O = 0.0$	$U_O = 0.2$	$U_O = 0.4$	$U_O = 0.6$	$U_O = 0.8$
0.0	0.0	+0.1	+0.2	+0.4	+0.8
0.2	−10.4	+31.5	+20.1	+22.9	+27.3
0.4	−45.7	−2.5	+69.6	+71.1	+73.9
0.6	−77.2	−39.0	+10.9	+74.9	115.1
0.8	−94.7	−63.9	−22.1	+32.8	103.7
1.0	−89.7	−68.2	−36.6	+7.3	+66.0
1.2	−59.6	−48.2	−27.8	+3.8	+49.0
1.4	−7.0	−5.0	+4.6	+24.0	+55.4
1.6	+63.0	+57.3	+57.7	+66.0	+84.6

Table 3. Ground-state correlation functions $m_{ij} = \langle S_{zi}S_{zj}\rangle$ and $\rho_{ij} = \langle n_i n_j\rangle$ of Cu_4O_4 with $U_{Cu} = 1.0$, $U_O = 0.4$, $V_{Cu} = 2.0$ (which has $U_{eff} = -0.0036t$), with 12 electrons.

	Spin correlation m_{ij}		
Cu–Cu	$m_{11} = +0.6962$	$m_{13} = -0.3401$	$m_{15} = +0.1444$
Cu–O	$m_{12} = -0.0660$	$m_{14} = -0.0142$	
O–O	$m_{22} = +0.1781$	$m_{24} = -0.0071$	$m_{26} = -0.0037$
	Charge-density correlation ρ_{ij}		
Cu–Cu	$\rho_{11} = 1.703$	$\rho_{13} = 1.394$	$\rho_{15} = 1.422$
Cu–O	$\rho_{12} = 2.086$	$\rho_{14} = 2.155$	
O–O	$\rho_{22} = 3.423$	$\rho_{24} = 3.228$	$\rho_{26} = 3.243$

at oxygen. This mixed electron loss, which means that states which contain both $Cu^{3+}O^{2-}$ and $Cu^{2+}O^{1-}$ are important, is essential for $U_{eff} < 0$ in region B. correlations for the 10-electron version of the system defined for table 3 are shown in table 4. It can be seen that the antiferromagnetic coupling between the copper ions is destroyed (m_{15} is negative) and there is a significant decrease in electron density, compared with that for the 12-electron system, on both copper and oxygen.

Two supplementary results have been obtained. The 'trimer' $(CuO)_3$ has been examined for $U_{eff} < 0$ in a similar way. No negative values of U_{eff} were obtained. This supports the idea that $U_{eff} < 0$ is a particular property of the four-membered ring. As a further test, the Cu–O–Cu system with four electrons (Cu^{2+}–O^{2-}–Cu^{2+}) and Hubbard parameters equal to those considered in table 3 has been solved for all eigenstates. The splitting between the lowest (singlet and triplet) states of this system gives a value of the exchange constant $-2J$ of about $0.35t$. Thus the antiferromagnetic exchange in the $Cu^{2+}O^{2-}$ system is very strong.

3. Conclusion

A simple Hubbard model of Cu_4O_4 gives $U_{eff} < 0$ for values of U_{Cu}, U_O and $V_{Cu} - V_O$ which seem reasonable from a chemical point of view since both atoms are expected to have small positive U-values because Cu^{2+} and O^{2-} are closed-shell ions. It does not seem appropriate at this stage to make a closer comparison with the U- and V-values obtained by spectroscopy since the act of removing the Cu_4O_4 subunit from the lattice will significantly modify the potentials, especially for the copper atom.

Table 4. Ground-state spin and electron density correlation functions for the 10-electron version of the system defined in table 3.

	Spin correlation m_{ij}		
Cu–Cu	$m_{11} = +0.5693$	$m_{13} = -0.0805$	$m_{15} = -0.1393$
Cu–O	$m_{12} = -0.1384$	$m_{14} = +0.0038$	
O–O	$m_{22} = +0.2864$	$m_{24} = -0.0073$	$m_{26} = -0.0025$
	Charge-density correlation ρ_{ij}		
Cu–Cu	$\rho_{11} = 1.101$	$\rho_{13} = 0.645$	$\rho_{15} = 0.644$
Cu–O	$\rho_{12} = 1.274$	$\rho_{14} = 1.384$	
O–O	$\rho_{22} = 3.043$	$\rho_{24} = 2.761$	$\rho_{26} = 2.770$

All calculations which model an infinite lattice by a finite cluster are inherently suspect since any interesting effects observed may be artefacts of the edge effects. This weakness is particularly relevant here because of the small magnitude of the observed effect (at least in terms of the electronic energies). In an attempt to remedy this defect, we have made a small number of calculations on larger Cu_4O_8 clusters. The largest calculations now involve 18 electrons, 12 sites and 48 400 basis states.

The Cu_4O_8 clusters are obtained by adding an oxygen atom to each corner of the Cu_4O_4 square. Even without periodic boundary conditions this cluster is more realistic since it has the same Cu : O ratio as the CuO_2 plane. When periodic boundary conditions are applied, both types of atom have the correct coordination number, and all oxygen atoms become once again equivalent.

The calculations referred to in tables 3 and 4 have been repeated with the same values of the U- and V-values for Cu_4O_8 with and without periodic boundary conditions. U_{eff} is now defined as $(E_{20} - E_{19}) - (E_{19} - E_{18})$. It is found that increasing the cluster size increases the magnitude of U_{eff}; thus, U_{eff} changes from $-0.0036t$ in Cu_4O_4 to $-0.0049t$ (non-periodic) and $-0.0052t$ (periodic) in Cu_4O_8. With non-periodic boundary conditions the correlation functions for the Cu_4O_4 square are only very slightly altered since a very small hole density is found on the terminal oxygen atoms. With periodic boundary conditions the modification of the correlation functions is such as to decrease slightly the hole density on the copper and to decrease significantly the hole density on the oxygen. Despite this change the correlation functions remain qualitatively similar to those found in Cu_4O_4. A detailed analysis of Cu_4O_8, similar to that given here for Cu_4O_4, is in progress.

Even with the limited data available the increase in U_{eff} with cluster size is very encouraging. It suggests that the hole pair is most energetically favourable when localised over an area somewhat larger than the Cu_4O_4 cluster but that the small cluster provides an approximation which is still useful because of its simplicity. Ideally the pair energy should be calculated for still larger clusters, but it appears to us that this would require techniques other than exact diagonalisation.

The present model is only a first step towards a description of superconductivity. In the spirit of the Hubbard model, we have ignored off-site Coulomb repulsion. The possibility of coupling to the lattice has not been investigated in detail, although it is noticeable that the intermediate 11-electron state has a ground state which consists of two degenerate doublets which may be split by lattice distortions. Hence Cu_4O_4 with this number of electrons might tend to act as a Jahn–Teller centre. We have not considered the way in which coherence is established between the hole pairs.

Nevertheless we hope that the calculations are useful in that they show quantitatively that, under certain rather special conditions, $U > 0$ centres can combine to create a $U_{\text{eff}} < 0$ centre, even within an unmodified Hubbard model. Systems such as this provide a test for more sophisticated models and methods, such as the Monte Carlo technique, which might be applied to much larger clusters—can they reproduce the $U_{\text{eff}} < 0$ found here? Finally we would like to comment that a pairing mechanism based on real-space correlation of electrons at opposite sides of a ring provides an appealing mechanism for superconductivity since the mechanism ensures that the attractive interaction occurs only between electrons of opposite momentum.

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