Two-hole quasiparticles and pairing in the Hubbard model of high-T_c superconducting cuprates

1996 J. Phys.: Condens. Matter 8 L265

(http://iopscience.iop.org/0953-8984/8/17/003)

J. Phys.: Condens. Matter **8** (1996) L265–L269. Printed in the UK

LETTER TO THE EDITOR

Two-hole quasiparticles and pairing in the Hubbard model of high-T_c superconducting cuprates

Michele Cini and Adalberto Balzarotti

INFM, Dipartimento di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 1-00133 Roma, Italy

Received 8 March 1996

Abstract. We propose a configuration interaction mechanism that leads to hole pairs with zero repulsion energy which are exact eigenstates of the two-band Hubbard Hamiltonian. The two-hole pairs have $^1B_2(xy)$ symmetry and arise from degenerate states at the Fermi level; we show that they must exist independently of the band filling. To discuss the possible relevance of these states to the problem of pairing in high-T_c superconductors we solve five- and nine-site model clusters with four holes. The quasiparticles become dressed by the interaction with the background holes and get paired with a set of valence band parameters well established for high-T_c cuprates. We predict a number of important experimental facts such as binding energies of the correct order of magnitude, the $^1B_1(x^2 - y^2)$ symmetry of the order parameter and the singlet–triplet energy separation of the Cooper pairs.

The question of the physical mechanism underlying pairing in high-T_c superconductors is still unsettled, and there are several alternative models under investigation. A class of them [1] is based on single- or multiple-band Hubbard Hamiltonians containing large on-site Coulomb repulsive energies between holes with opposite spins which tend to reduce double occupancy of these sites. Attention has been focused on the physics of the Cu–O plane, which is commonly supposed to be the seat of superconducting pairs. On doping the plane, the added holes go mainly onto the oxygen states [2]. Much progress has been achieved using perturbative approaches such as the t–J model that leads to pairing and predicts the correct trend for a number of properties [3]. Such models force the holes to avoid on-site interactions by letting U be very large (or infinite) so that eventually pairing may be achieved through small residual attractive interactions. This approximation aims to mimic an effect that the holes actually achieve by correlation. In this sense the problem is circumvented, but not solved. In a forthcoming paper [4], we show that the holes avoid the on-site interaction via a correlation mechanism which is effective for any U/t. We demonstrate this correlation effect, showing that its basic ingredient is a configuration mixing driven by the symmetry of the system which entails the presence of degenerate hole states at the Fermi level. The orthogonal states Ψ and $R\Psi$ which interact are connected by a $\pi/2$ rotation R, and have the same total-symmetric (A_1) charge density; the combination $\Phi = (\Psi - R\Psi)/\sqrt{2}$ is the ground state. Moreover, we provide evidence that the *same* configuration mixing which produces the two-hole eigenstates can, when applied to the many-body problem, also produce pairing between the holes.

We adopt a Hubbard-like Hamiltonian in the hole representation:

$$H = h + H_c = \sum \varepsilon_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum U_i n_{i+} n_{i-} \tag{1}$$

0953-8984/96/170265+05$19.50

with $\varepsilon_{ii} = \varepsilon_p$ and $U_i = U_p$ if i is an oxygen site, $\varepsilon_{ii} = \varepsilon_d$ and $U_i = U_d$ for a Cu site, $\varepsilon_{ij} = t$ for a Cu–O bond and $\varepsilon_{ij} = t_{ox}$ for an O–O bond. Some authors use different prescriptions for the signs of t and t_{ox} which correspond to changing the phases of some orbitals without modifying the underlying physics. The parameter values derived from electron spectroscopy for superconducting cuprates are (in eV) $\varepsilon_d = 0$, $\varepsilon_p = 3.5$, $t = 1.3$, $t_{ox} = -0.65$, $U_p = 6.0$ and $U_d = 5.3$. We have checked the above parametrization by reproducing the results of van Veenendaal and Sawatzky [5] for the Cu core photoemission spectrum.

Symmetry dictates the existence of pair eigenstates of H such that they are also eigenstates of H_c with the eigenvalue $W = 0$. In the CuO_4 cluster, the one-body states [6] $|b\rangle = \frac{1}{2}(|3\rangle + |4\rangle - |2\rangle - |5\rangle)$ and $|\beta\rangle = \frac{1}{2}(-|3\rangle + |4\rangle - |2\rangle + |5\rangle)$ are orthogonal and $|\beta\rangle = R|b\rangle$. They have the same uniform density $n_b = n_\beta = 1/4$ on the oxygens. The singlets $|b_+b_-|$ and $|\beta_+\beta_-|$ feel the on-site interaction, but $(|b_+b_-|-|\beta_+\beta_-|)/\sqrt{2}$ is a $W = 0$ pair [4]. This state is $^1B_2$ which transforms like xy, irrespective of phase conventions.

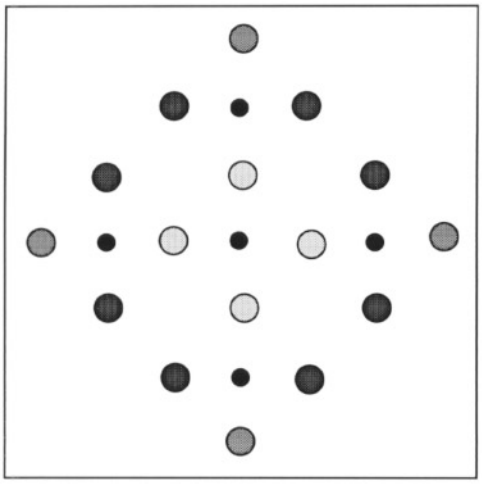

Figure 1. The charge distribution of a $W = 0$ pair eigenstate. Black discs represent Cu atoms which have zero hole densities. The hole densities on the nearest-neighbour, second-nearest-neighbour and third-nearest-neighbour oxygens of the central copper are 0.2842, 0.0191, 0.1776, respectively. They are invariant under $\pi/2$ rotations.

For any finite cluster having the full C_{4v} symmetry and a Cu atom at the centre, we can obtain $W = 0$ pair eigenstates. The simplest method consists in looking for degenerate states $|b\rangle$ and $|\beta\rangle$ such that $n_b = n_\beta$, and repeating the above procedure. The calculated density distribution of such a $W = 0$ pair of a 21-site symmetric cluster is shown in figure 1. In this example, the pair was derived from nonbonding states. It is important to realize, however, that bonding states also give rise to $W = 0$ pairs, despite the fact that Cu sites are visited by holes of both spins. We stress that the $W = 0$ pairs cannot possibly arise unless the clusters have the full symmetry which is required to form (b, β) pairs with $n_b = n_\beta$. The above argument brings out the essential role of symmetry. On the other hand, clusters of C_{4v} symmetry but not centred around Cu have no (b, β) pairs having $n_b = n_\beta$, and no $W = 0$ pairs are obtained in this way [4].

Next, we demonstrate that $W = 0$ pairs exist in the infinite solid at the Fermi level independently of its position, and are obtained from degenerate states belonging to the bonding as well as the nonbonding bands. To see that, let us consider the Bloch eigenstates

of the one-body Hamiltonian h of the solid. They can be taken in the real form

$$s(\boldsymbol{k}, \boldsymbol{r}, \sigma) = \sin[\boldsymbol{k} \cdot \boldsymbol{r}]u(\boldsymbol{k}, \boldsymbol{r})\xi \tag{2}$$

$$c(\boldsymbol{k}, \boldsymbol{r}, \sigma) = \cos[\boldsymbol{k} \cdot \boldsymbol{r}]u(\boldsymbol{k}, \boldsymbol{r})\xi \tag{3}$$

where $u(\boldsymbol{k}, \boldsymbol{r})$ is the periodic part and $\xi = \alpha$ or β is a spin function. Consider any band with dispersion $E(\boldsymbol{k})$ which is cut by the Fermi energy E_F and the wavevectors $\boldsymbol{k}_+ = (k_0, k_0)$ and $\boldsymbol{k}_- = (k_0, -k_0)$ at the Fermi surface. One-hole states with wavevectors $\boldsymbol{k}_+$ and $\boldsymbol{k}_-$ have the same charge density, and must give rise to $W = 0$ pairs, as noted above. Indeed, the one-determinant two-hole singlets like

$$|s(\boldsymbol{k}_-, \boldsymbol{r}_1, +)s(\boldsymbol{k}_-, \boldsymbol{r}_2, -)| \tag{4}$$

(where $\boldsymbol{r}_1 = (x_1, y_1)$ and $\boldsymbol{r}_2 = (x_2, y_2)$ denote the lattice sites where the holes 'sit') are eigenstates of h; when H_c is also included, they 'feel' the on-site interactions and fail to be eigenstates of the total Hamiltonian H. However, the symmetry of the system allows mixing of several degenerate singlets to form the pair state:

$$\begin{aligned}\Phi(k_0, \boldsymbol{r}_1, \boldsymbol{r}_2) = N\{&|s(\boldsymbol{k}_-, \boldsymbol{r}_1, +)s(\boldsymbol{k}_-, \boldsymbol{r}_2, -)| - |s(\boldsymbol{k}_+, \boldsymbol{r}_1, +)s(\boldsymbol{k}_+, \boldsymbol{r}_2, -)| \\ &+|c(\boldsymbol{k}_-, \boldsymbol{r}_1, +)c(\boldsymbol{k}_-, \boldsymbol{r}_2, -)| - |c(\boldsymbol{k}_+, \boldsymbol{r}_1, +)c(\boldsymbol{k}_+, \boldsymbol{r}_2, -)|\}\end{aligned} \tag{5}$$

where N is a normalization factor. It follows that

$$\begin{aligned}\Phi(k_0, \boldsymbol{r}_1, \boldsymbol{r}_2) = N\{&\cos[k_0(x_1 - x_2 - y_1 + y_2)] \\ &- \cos[k_0(x_1 - x_2 + y_1 - y_2)]\}u(\boldsymbol{k}_+, \boldsymbol{r}_1)u(\boldsymbol{k}_-, \boldsymbol{r}_2)\chi^{(s)}\end{aligned} \tag{6}$$

where $\chi^{(s)}$ is a spin-singlet function. Φ vanishes for $\boldsymbol{r}_1 = \boldsymbol{r}_2$ and is an eigenstate of H_c with eigenvalue 0; therefore it is a $W = 0$ two-hole eigenstate of H. By expanding the cosine functions it is easily verified that Φ has $B_2(xy)$ symmetry. We can obtain infinite $W = 0$ pairs by direct diagonalization of the two-hole Hamiltonian.

Let us now consider the CuO_4 planar cluster with four holes, in the non-interacting limit: the first two holes go into a bonding level of a_1 symmetry (b_1 if one adopts the alternating-signs convention), and the next two go into a nonbonding level of e symmetry, with orbitals transforming like x, y. Group theory predicts that the interactions resolve the sixfold-degenerate ground state into $^3A_2$, $^1A_1$, $^1B_1$ and $^1B_2$. The two-body calculations suggest that $^1B_2$ and the triplet are lowest, since $W = 0$ for both; this turns out to be true. The symmetry-adapted four-hole states for $^1B_2$ and $^3A_2$ symmetries are obtained as $^1v_i = P(^1B_2)c_i$, $^3v_i = P(^3A_2)c_i$, respectively, where $P(^1B_2)$ and $P(^3A_2)$ are the projection operators and c_i are hole configurations. With the notation $(ijkl)$, where the indices denote sites, and ij with $i > j$ are for spin up and kl with $k > l$ for spin down, the relevant configurations are $c_1 = (2131)$, $c_2 = (2152)$, $c_3 = (2143)$, $c_4 = (2153)$, $c_5 = (5242)$, $c_6 = (4253)$, $c_7 = (4343)$, $c_8 = (3254)$, and $c_9 = (3252)$.

Only $^1v_9$ vanishes, and the configuration mixing for $^1B_2$ involves an 8×8 matrix; on the other hand, only $^3v_7$ and $^3v_8$ vanish, leading to a 7×7 problem for the triplet with $M_s = 0$. It is clear that the configuration c_8, which contributes to the singlet but not to the triplet, has no on-site interactions; this explains why the singlet is lower than the triplet, and the singlet–triplet separation grows with U_p. The $\Phi = (\Psi - R\Psi)/\sqrt{2}$ mixing is implicit in the above argument, since a rotation by $\pi/2$ has -1 character for the B_2 symmetry. The degenerate components of the noninteracting ground state $|a_+a_-x_+y_-|$ and $|a_+a_-y_+x_-|$ are connected by a $\pi/2$ rotation R. There is no first-order matrix element of H_c connecting them. However, the system is able to oscillate between them and to open a singlet–triplet

gap because the states are connected by second-order interactions such that the 'anomalous' propagator

$$\langle a_+ a_- x_+ y_- | \frac{1}{\omega - H} | a_+ a_- y_+ x_- \rangle$$

does not vanish. In this way x pairs to y.

Given a finite system with m holes, the relevant quantity for pairing is $\Delta = E(m) + E(m-2) - 2E(m-1)$, where $E(n)$ is the ground-state energy of the system with n holes. Since the CI mechanism requires pairs in degenerate states and the lowest state is nondegenerate, the simplest case is $m = 4$. The number of configurations grows quickly with increasing m. A detailed study [4] of Δ as a function of the parameters shows that pairing prevails with the accepted values, except that t_{ox} should be 10% less negative: the binding energy has a maximum of about 36 meV for $t_{ox} = 0$. The inclusion in the Hamiltonian of the off-site interactions [7], U_{pd} between O and Cu and $U_{pp'}$ between O sites, was already considered in [4], and brings the best estimate of all parameters, including t_{ox}, well inside the region where $\Delta < 0$. Previously, $\Delta < 0$ seemed to be possible only with unphysical parameters. The main difference between those calculations [8] and the present ones is the symmetry of the cluster. Besides, our estimate of the singlet–triplet separation depends on the parameters, but is consistent with the 45 meV excitation observed in high-resolution electron energy-loss spectra [9] and the 41 meV resonance found in polarized neutron scattering experiments [10] on superconducting $YBa_2Cu_3O_7$.

The total hole concentration which corresponds experimentally to the superconducting state is $c \approx 0.4$ per atom. In the CuO_4 cluster we need four holes to operate the CI mechanism, because we need two holes in degenerate states; therefore c is too large by a factor of two. It is important to realize that this is a size effect, which has already disappeared in Cu_5O_4, the next larger cluster of the same symmetry. In fact, four holes are still sufficient to reach degenerate states, but $c \approx 0.44$ is much closer to the experimental value. The degenerate states are bonding, in contrast to the CuO_4 case, and the holes now spend a large fraction of their time on Cu sites. We have computed Δ for Cu_5O_4 with $t_{ox} = 0$, which yields the maximum binding energy in CuO_4. The size of the problem with four holes is 1296; it reduces to 81 on projecting to the $^1B_2$ symmetry of the ground state. We find that $\Delta = -15.7$ meV; thus the binding energy $|\Delta|$ is about half the CuO_4 value. A decrease of the binding energy with reducing c is expected, since for vanishing c no pairing should take place. However the decline of c with increasing number of atoms is slow enough to allow a significant contribution to the binding for cluster sizes that correspond to the actual size ($\xi_{a,b} = 10$–20 Å) of the superconducting pair.

Thus, the $W = 0$ pairs become dressed quasiparticles in the many-body system. The pair symmetry can give a clue on the crucial problem: can the dressed quasiparticles be related to the superconducting pairs? The symmetry of Φ for our quasiparticles is $B_2(xy)$ in all cases. There is accumulating experimental evidence [11] that the order parameter, which is proportional to the gap function $\Delta(\boldsymbol{r})$, has $B_1(x^2 - y^2)$ symmetry in high-T_c superconductors. We distinguish between the internal symmetry of the pair, which describes the relative positions of the two holes, and the symmetry of the order parameter, whose square modulus is proportional to the density of superconducting holes. The two symmetries coincide in conventional superconductors. The reason for this is that in the BCS theory using the hole representation,

$$\Delta(\boldsymbol{r})_{BCS} \propto \langle \Psi_\downarrow(\boldsymbol{r})^\dagger \Psi_\uparrow(\boldsymbol{r})^\dagger \rangle \tag{7}$$

where $\Psi_\downarrow(\boldsymbol{r})$ and $\Psi_\uparrow(\boldsymbol{r})$ are field operators for the opposite-spin holes and the angular brackets denote thermal averages in the grand canonical ensemble. Expanding in the relevant

hole states $\phi_x(\boldsymbol{r})$ and $\phi_y(\boldsymbol{r})$ transforming like (x, y),

$$\Psi_\downarrow(\boldsymbol{r}) = \phi_x(\boldsymbol{r})C_{x\downarrow} + \phi_y(\boldsymbol{r})C_{y\downarrow} \tag{8}$$

and the like, we find that $\Delta(\boldsymbol{r})_{BCS}$ vanishes identically for the $W = 0$ pairs. However, the BCS definition is appropriate when $\boldsymbol{k}\uparrow$ is coupled to $-\boldsymbol{k}\downarrow$; this is not the case here, since x pairs to y. Therefore we suggest

$$\Delta(\boldsymbol{r}) \propto \langle \Psi_\downarrow(\boldsymbol{r})^\dagger \Psi_\uparrow(R^{-1}\boldsymbol{r})^\dagger \rangle. \tag{9}$$

With this definition and (8), one readily finds that $\Delta(\boldsymbol{r})$ does not vanish and transforms like $x^2 - y^2$. This conclusion is in line with the pair charge density shown in figure 1: it is evident that the density does not vanish along the x, y axes, but has maxima there. Thus the symmetry that we predict is consistent with experiment [11]. On the other hand, all information concerning the internal state of the pair is excluded from $\Delta(\boldsymbol{r})$ and is contained in the $W = 0$ pair wave function.

The pairs are bound states only in part of the parameter space and their existence *does not suggest* that any two-dimensional system of the appropriate symmetry and on-site interactions is going to superconduct. We recall that there are regions of the parameter space where $\Delta > 0$ also in the CuO_4 cluster.

In summary, we have demonstrated a quantum mechanical effect which is specific to the symmetry of the CuO plane. Two holes in degenerate states at the Fermi level form pairs such that the direct on-site Coulomb interaction W vanishes identically. Indirect interactions produce bound states in small clusters in the accepted parameter range, with the appropriate symmetry, singlet–triplet separation and binding energies of a few tens of meV. All this suggests that the present simplified model still contains useful ingredients for a future theory of high-T_c superconductivity.

References

[1] Anderson P W 1987 *Science* **235** 1196
Emery V J 1987 *Phys. Rev. Lett.* **58** 2794
Hirsch J E 1987 *Phys. Rev. Lett.* **59** 228
Varma C M, Schmitt-Rink S and Abrahams E 1987 *Solid State Commun.* **62** 681
Zhang F C and Rice T M 1988 *Phys. Rev.* B **37** 3759
Laughlin R B 1988 *Science* **242** 525
Schrieffer J R, Wen X G and Zhang S C 1988 *Phys. Rev. Lett.* **60** 944
Monthoux P, Balatsky A V and Pines D 1991 *Phys. Rev. Lett.* **67** 3448

[2] Fink J *et al* 1991 *Physica* C **185–189** 45
and references therein. See also articles in
Ginsberg D M (ed) 1989, 1990 *Physical Properties of High-Temperature Superconductors* vols 1 and 2 (Singapore: World Scientific)

[3] For a review on the t–J model see, e.g.,
Dagotto E 1994 *Rev. Mod. Phys.* **66** 763

[4] Cini M and Balzarotti A 1996 *Nuovo Cimento* D **18** 89

[5] van Veenendaal M A and Sawatzky G A 1993 *Phys. Rev. Lett.* **70** 2459

[6] Site 1 is the central Cu atom and sites 2–5 are the O atoms. The axes are parallel to the Cu–O bonds.

[7] Schluter M 1990 *Superconductivity and Applications* ed H S Kwok *et al* (New York: Plenum) p 1

[8] Hirsch J E, Tang S, Loh E Jr and Scalapino D J 1988 *Phys. Rev. Lett.* **60** 1668; 1989 *Phys. Rev.* B **39** 243

[9] Demuth J E *et al* 1990 *Phys. Rev. Lett.* **64** 603

[10] Rossat-Mignod J *et al* 1991 *Physica* C **185–189** 86

[11] For a recent review on the subject, see, e.g.,
Van Harlingen D J 1995 *Rev. Mod. Phys.* **67** 515