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Pairing in the Hubbard model: the Cu_5O_4 cluster versus the Cu–O plane

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Abstract. We study the Cu_5O_4 cluster by exact diagonalization of a three-band Hubbard model and show that bound electron or hole pairs are obtained at appropriate fillings, and produce superconducting flux quantization. The results extend earlier cluster studies and illustrate a canonical transformation approach to pairing that we have developed recently for the full plane. The quasiparticles that in the many-body problem behave like Cooper pairs are $W = 0$ pairs, that is, two-hole eigenstates of the Hubbard Hamiltonian with vanishing on-site repulsion. The cluster allows $W = 0$ pairs of d symmetry, due to a spin fluctuation, and s symmetry, due to a charge fluctuation. Flux quantization is shown to be a manifestation of symmetry properties that hold for clusters of arbitrary size.

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1 Introduction

In many high-T_c cuprates, one has superconductivity at concentrations about 1.2 holes/Cu atom, that is, somewhat above the antiferromagnetic region at half filling. In some cases, one finds superconductivity below half filling. Usually, one considers half filling as the vacuum and speaks of electron superconductivity in such cases. Electron pairing is actually realized [1], *e.g.*, in the T' structure of $(Nd,Ce)_2CuO_4$. The T' structure of this compound is different from the T structure of La_2CuO_4, but is still characterized by CuO_2 planes [2]. However, increasing experimental evidence obtained in several cuprate superconductors suggests that the pairs exist above the critical temperature either in the form of superconducting fluctuations or preformed pairs. The latter aspect is apparent in the underdoped (normal) region in which a clear pseudogap essentially of the same magnitude as the superconducting gap is measured [3]. The pairing state of these materials has $d-wave$ symmetry, probably mixed with $s-wave$ [4]. All these signatures put strict constraints to any microscopic model of the cuprates. Any theory of the paired state must predict d and s symmetries, and the pairing mechanism must be robust. It must survive well into the normal state, and operate in a wide range of concentrations far from optimum doping.

In BCS theory, the first-order repulsion between like charges is overcome by the second order interaction with phonons. In high-T_c superconductors the electron-phonon interaction is strong and phonons must be expected to contribute in an important way to the pairing interaction, although their task looks harder because the repulsion integral U is large (several eV). However, the straightforward idea that the high-T_c phenomena are just a rescaled version of BCS theory is not granted. The role of phonons may be important, but is different, and some other ingredient is essential.

Rather than proposing a new attractive interaction, we wish to point out that the popular repulsive Three-Band Hubbard model already leads to pairing. The model is:

$$H = H_0 + W \tag{1}$$

where the independent hole Hamiltonian reads, in the site representation

$$H_0 = \sum_{\mathrm{Cu}} \varepsilon_d n_d + \sum_{\mathrm{O}} \varepsilon_p n_p + t \sum_{\mathrm{n.n.}} \left[c_p^\dagger c_d + \mathrm{h.c.} \right] \tag{2}$$

where n.n. stands for nearest neighbors [5]. The on-site repulsion Hamiltonian will be denoted by

$$W = \sum_i U_i n_{i+} n_{i-}, \tag{3}$$

where $U_i = U_d$ for a Cu site, $U_i = U_p$ for an Oxygen. As in previous work [6], we use standard parameter values (in eV), *i.e.*, $U_d = 5.3$, $U_p = 6$, $t = 1.3$, $\varepsilon_d = 0$, $\varepsilon_p = 3.5$. The hole parameters $U_d = 5.3$ eV, $U_p = 6$ eV differ somewhat

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from other literature estimates [7], and must depend on the compound and doping. For La_2CuO_4, $U_p = 4$ eV and $U_d = 10.5$ eV have been recommended [8]. None of our results depends qualitatively on the precise value of the model parameters, since ours is basically a symmetry argument. The electronic properties of this model are under intense investigation by several approximations based on perturbation theory and the Bethe-Salpeter equation. The FLEX approximation is a generalized RPA [9] and leads to pairing and superconductivity in the three-band Hubbard model [10]. The excitation spectra of the 2D Hubbard model have also been studied by a related self-consistent and conserving T-matrix approximation by Dahm and Tewordt [11]; we mention incidentally that recently diagrammatic methods have been successfully applied to the photoelectron spectra of the cuprates in other contexts too, like the spin-fermion model [12]. A perturbative expansion around the strong coupling limit, in powers of the kinetic energy, requires a nonstandard cumulant expansion, but is feasible, as shown quite recently by Citro and Marinaro [13] for the $p - d$ model which is the present model with $U_p = 0$. In this way, they have shown that normal state properties like the specific heat as a function of doping can be well understood [14]; they also derived the effective pairing interaction in the same approximation [15] and studied the doping dependence of the superconducting transition temperature [16].

Our starting point is the observation that, due to the planar C_{4v} symmetry, there is actually no repulsion barrier to overcome. In a series of papers [6,17,18] we have introduced the two-hole singlet eigenstates of the Hamiltonian with zero Coulomb on-site repulsion (the so called $W = 0$ pairs). They arise in the full plane, and also in the clusters that possess the same full C_{4v} symmetry around a central Cu as the full plane. In the full plane, this situation is always realized, because $W = 0$ pairs can always be obtained from holes at the Fermi level; in clusters, on the other hand, the hole number (relative to the true hole vacuum) must be such that two holes partially fill a degenerate state. In the many-body problem, two holes at the Fermi level in a $W = 0$ pair state do not interact directly; however the pair is dressed by the interaction with the background particles. By exact diagonalization of cluster Hamiltonians with up to 21 atoms and 4 holes, we demonstrated [18] that the dressed $W = 0$ pair is a bound Cooper pair, and quantizes the magnetic flux like superconductors do. Any strong distortion of the cluster symmetry breaks the pairing and restores the normal repulsion [17]. We also considered first-neighbor O–O hopping and off-site interactions [17]. Remarkably, the off-site repulsive interactions, when included, tend to enhance the effect somewhat, so we devote the present study to the on-site interaction effects. The binding energy of the pairs in these clusters is of the order of tens of meV, which is not comparable to any of the U and t input parameters. The reason is that the interaction, which vanishes identically for the *bare* $W = 0$ pairs, remains *dynamically small* for the dressed quasiparticles. Indeed, by a diagrammatic analysis we demonstrated that low-order perturbation theory is a good approximation to the exact diagonalization results and allows to understand that the attraction in the d channel is due to virtual spin-flip excitations. This suggests that a *weak coupling* theory may be useful to study the pairing force, despite the fact that U is not small compared to t. It is an obvious limitation of the cluster approach that $W = 0$ pairs are possible at discrete values of the hole concentration. Our previous cluster calculations suggest that the mechanism operates in a much broader range of hole concentrations than is realized in actual cuprates, from very highly overdoped (as in CuO_4) to very low (as in Cu_5O_{16}). The diagrammatic analysis further demonstrates that the effective interaction is the result of a partial cancellation of positive and negative contributions, so it is not necessarily attractive in all cases; the general signature of $W = 0$ pairs is that the absolute value of the interaction is much smaller than in the other cases.

The mechanism we are considering is only a part of the story, but it seems to be a most peculiar part, being related to nothing but the C_{4v} symmetry. For similar reasons here we wish to make abstraction from phonon effects to see how far the idealized description can account for reality by itself. We believe that a mechanism which predictably gets attraction out of repulsion is by itself of theoretical interest.

Next, we have generalized the theory of pairing to the full plane [19]. In short, one finds $W = 0$ pairs at the Fermi level for any concentration and this leads to a Cooper-like instability of the Fermi liquid. Pairing prevails for a range of concentrations above half filling, in agreement with the results [20] of the Renormalization Group technique. We have shown that the full configuration interaction calculation can be performed recursively. At each step, one decouples a class of virtual excitations while renormalizing the matrix elements of H_0 and W. At the end, one obtains an exact, analytical canonical transformation producing an effective Hamiltonian for the dressed pair. In order to get actual numbers, however, we had to neglect the renormalizations in the final formula; this approximation is fully justified at weak coupling.

In the present paper we extend the analysis of reference [18] by diagonalizing the Cu_5O_4 cluster with increasing number n_h of holes. We wish to demonstrate that the power of the symmetry driven mechanism is such that attractive interactions arise even in small clusters with $n_h > 4$, despite the high hole concentration. One can proceed from the true hole vacuum and insert holes until the last two form a $W = 0$ pair; if the interactions produce a bound state we conventionally speak of *hole pairing*. Alternatively, one can proceed from the true electron vacuum and insert electrons until the last two form a $W = 0$ pair; if the interactions produce a bound state we conventionally speak of *electron pairing*. These two expressions simply mean that we get pairing by adding two holes (as in La_2CuO_4) or two electrons (as in $(Nd,Ce)_2CuO_4$), respectively [21]. The physical point here is that electron pairs and hole pairs are related by a charge conjugation symmetry and the very same basic mechanism or diagram

Table 1. One-hole levels of the Cu_5O_4 cluster, with their symmetry labels, degeneracies g, and energy eigenvalues ε with $t = 1.3$ eV, $\varepsilon_p = 3.5$ eV and $\varepsilon_d = 0$.

Symmetry	g	ε(eV)
a_1	1	-1.643
e, b_1	3	-0.43
a_1	1	0.0
e, b_1	3	3.93
a_1	1	5.143

is operating in both cases. We find new instances of electron and hole pairing, again with a binding energy of a few tenths of meV in the physical parameter space. We also find a case when a $W = 0$ pair leads to a weak repulsion. Further, we demonstrate how the two different symmetries (A_1 and B_2) of $W = 0$ singlet pairs allowed by the cluster are both necessary to produce the superconducting flux quantization phenomenon in this cluster.

One reason for considering clusters again, after much excellent work from several authors [22] and our own previous work on clusters and on the plane, is that in this way we can test our canonical transformation approach against the results of exact diagonalization. Another reason is that we wish to explore the relation of the flux quantization phenomenon to the symmetry group in the presence of the vector potential, which breaks the translational symmetry. Our main questions are: can pairing be reliably predicted by studying the behavior of the system at weak coupling? Is the superconducting flux quantization property exclusive of small clusters, or is it a general consequence of symmetry?

2 One-body energy levels of the symmetric 9-site cluster

In the hole picture, the one-body energy levels of Cu_5O_4 are those displayed in Table 1. Here, the hole vacuum is a state with no holes at all.

Two levels are triply degenerate, comprising twice degenerate states of $e(x, y)$ symmetry and states belonging to b_1; this *accidental* degeneracy is due to the fact that in this small cluster any permutation of the four Cu−O units bound to the central Cu is a symmetry; therefore, the full symmetry group of the cluster is S_4, which has C_{4v} as a subgroup, and admits degeneracy 3. Since this property does not extend to the plane, we continue using the irreducible representations (IRREPS) of C_{4v} anyhow.

In the electron picture, the levels are met in reverse order, but the sequence of symmetry labels remains the same. Thus, one notices that there is an approximate electron-hole symmetry, or charge conjugation symmetry, in this model.

3 W = 0 pairs

Both in the full plane and in clusters, the $W = 0$ pairs are due to the symmetry, but there are some differences between the two cases, that we wish to stress in this section. Let us first review the theory for the plane [19]. Omitting the band indices, we shall mean

$$|d[k]\rangle = \|k_+, -k_-\| = c^\dagger_{k,+} c^\dagger_{-k,-} |\mathrm{vac}\rangle \tag{4}$$

to be a two-hole determinantal state derived from the Bloch eigenfunctions ($|\mathrm{vac}\rangle$ is the true hole vacuum).

The point symmetry group of the Cu–O plane is C_{4v}. We introduce the determinants $Rd[k] = d[Rk], R \in C_{4v}$, and the projected states

$$\Phi_\eta [k] = \frac{1}{\sqrt{8}} \sum_{R \in C_{4v}} \chi^{(\eta)} (R) \, |Rd[k]\rangle \tag{5}$$

where $\chi^{(\eta)}(R)$ is the character of the operation R in the IRREP η. In the non-degenerate IRREPS, the operations that produce opposite Rk have the same character, and the corresponding projections lead to singlets. Let R_i, $i = 1$, ...8 denote the operations of C_{4v} and k, k' any two points in the Brillouin Zone (BZ). Consider any two-body operator $\hat{O}$, which is symmetric ($R_i^\dagger \hat{O} R_i = \hat{O}$), and the matrix with elements $O_{i,j} = \langle d[k]|R_i^\dagger \hat{O} R_j|d[k']\rangle$, where k and k' may be taken to be in the same or in different bands. This matrix is diagonal on the basis of symmetry projected states, with eigenvalues

$$O(\eta, k, k') = \sum_R \chi^{(\eta)} (R) \, O_R (k, k') \tag{6}$$

where

$$O_R (k, k') = \left\langle d[k]|\hat{O}|Rd[k'] \right\rangle . \tag{7}$$

Thus, omitting the k, k' arguments, we get in particular

$$\begin{aligned} O\left({}^1A_2\right) &= O_E + O_{C_2} + O_{C_4} + O_{C_4^3} \\ &\quad - O_{\sigma_x} - O_{\sigma_y} - O_{\sigma'_1} - O_{\sigma'_2} \end{aligned} \tag{8}$$

$$\begin{aligned} O\left({}^1B_2\right) &= O_E + O_{C_2} - O_{C_4} - O_{C_4^3} \\ &\quad - O_{\sigma_x} - O_{\sigma_y} + O_{\sigma'_1} + O_{\sigma'_2} . \end{aligned} \tag{9}$$

If $\hat{O}$ is identified with W, since $W_E = W_{C_2} = W_{\sigma_x} = W_{\sigma_y}$ and $W_{C_4} = W_{C_4{}^3} = W_{\sigma'_1} = W_{\sigma'_2}$, one finds $W\left({}^1A_2\right) = W\left({}^1B_2\right) = 0$. These are $W = 0$ pairs, like those studied previously [18] in clusters. In the full plane, however, $W = 0$ pairs are obtained from holes at the Fermi level for any filling.

Small clusters like Cu_5O_4 allow a nice illustration of the theory because they also allow $W = 0$ 2-body solutions. This property is a consequence of their full C_{4v} symmetry around the central Cu. However, there are no Bloch states in a finite cluster with open boundary conditions, and the $W = 0$ singlet pairs come out differently.

First, we may consider the orbitals of (x, y) symmetry in Table 1, and form 2-hole determinants

$$d[x,y] = \|x_+, y_-\| = c^\dagger_{x+} c^\dagger_{y-} |\text{vac}\rangle$$
$$d[y,x] = \|y_+, x_-\| = c^\dagger_{y+} c^\dagger_{x-} |\text{vac}\rangle; \quad (10)$$

they are eigenstates of H_0 and have the $W = 0$ property, since the amplitude of double occupation of any site is 0. Unlike the case of the full plane, no projection like that performed in equation (5) is necessary here to get the property. In Cu_5O_4, there are two sets of (x, y) states, so the x and y of the above equation may belong to the same or to different sets. If the x and y states are taken from the same set, the singlet

$$\psi_1(^1B_2) = \frac{d[x,y] + d[y,x]}{\sqrt{2}} \quad (11)$$

is an eigenstate of the kinetic energy and of W, belongs to the $W = 0$ eigenvalue and to $^1B_2$. $W = 0$ pairs of this symmetry and of $^1A_2$ exist in the full plane as well. If the x and y states are taken from the different sets, we denote one of the sets by a prime and consider two-hole determinants like $d[x, y']$; these are eigenstates of H_0 and are $W = 0$ pairs, however they do not belong to any of the IRREPS of C_{4v}. We can form singlet combinations with the $W = 0$ property both in the $^1B_2$ and $^1A_2$ symmetry, namely,

$$\psi_2(^1B_2) = \frac{d[x,y'] + d[y,x'] + d[x',y] + d[y',x]}{2}, \quad (12)$$

which belongs to $^1B_2$ and

$$\psi(^1A_2) = \frac{d[x,y'] - d[y,x'] + d[x',y] - d[y',x]}{2} \quad (13)$$

which belongs to $^1A_2$. In addition, there are also $^1A_1$ $W = 0$ pairs, using the degenerate x, y and $b \equiv b_1$ orbitals. The two-hole states

$$\frac{\|x_+x_-\| + \|y_+y_-\|}{\sqrt{2}} \equiv |x^2 + y^2\rangle \quad (14)$$

and

$$\|b_+b_-\| \equiv |bb\rangle \quad (15)$$

are a basis of degenerate eigenstates of H_0 having $^1A_1$ symmetry. Diagonalizing W in this basis we get two-hole eigenstates of H. The 2×2 matrix of W is:

$$\begin{vmatrix} \langle bb|W|bb\rangle & \langle bb|W|x^2+y^2\rangle \\ \langle bb|W|x^2+y^2\rangle & \langle x^2+y^2|W|x^2+y^2\rangle \end{vmatrix} = \begin{vmatrix} \frac{U_p}{4} & \frac{U_p}{2\sqrt{2}} \\ \frac{U_p}{2\sqrt{2}} & \frac{U_p}{2} \end{vmatrix}. \quad (16)$$

The lowest eigenvalue is 0 and the $W = 0$ pair is

$$\psi(^1A_1) = -\sqrt{\frac{2}{3}}|bb\rangle + \sqrt{\frac{1}{3}}|x^2+y^2\rangle. \quad (17)$$

This type of $W = 0$ pairs does not exist in the full plane. The upper eigenvalue is $\frac{3U_p}{4}$ and the eigenfunction $\sqrt{\frac{1}{3}}|bb\rangle + \sqrt{\frac{2}{3}}|x^2+y^2\rangle$ is strongly affected by the on-site repulsion.

Now consider the Cu_5O_4 cluster in the non-interacting limit with 2 holes, which sit the lowest level of a_1 symmetry that we denote a for short. Let this be the new vacuum state $|0\rangle$. Adding 2 holes, we partially fill the next degenerate levels, which can give rise to $W = 0$ pairs. Starting with the above defined two-hole d determinants, we can form 4-hole determinantal states, denoted by a capital D, like for example

$$D[x,y] = c^\dagger_{x,+} c^\dagger_{y,-} |0\rangle \equiv \|x_+a_+, y_-a_-\|; \quad (18)$$

in keeping with the notation of reference [19], below we shall denote such configurations with the background a orbital occupied for both spins as m states. We shall also need the other 4-hole determinantal states, namely, the α states, in which one of the background a spin-orbitals is not occupied by holes, and the β states in which both background a spin-orbitals are missing. For the Cu_5O_4 cluster in the non-interacting limit a similar situation is realised if the new vacuum state is taken with 10 holes, filling the lowest levels according to the *aufbau* principle. Adding 2 holes, again we partially fill the next degenerate levels, which can give rise to $W = 0$ pairs. A similar definition of m, α and β is possible, and more excited configurations also exist.

The matrix elements of W in this model have no exchange terms, since only holes of opposite spin can interact. The diagonal elements $W_{m,m}$ can be expressed in terms of orbitals p, q, r, s by the two-hole integrals

$$W(p,q,r,s) = \sum_i U_i p^*(i) q^*(i) r(i) s(i). \quad (19)$$

For example, the m state of equation (18) yields

$$W_{m,m} = W(x,a,x,a) + W(y,a,y,a) + W(a,a,a,a). \quad (20)$$

We note that this is the Hartree-Fock interaction. The last term of the expression refers to the interaction between the background particles in the a spin-orbitals and is the same for all the m states, and the rest brings out single-particle corrections to the energy of the orbitals and could be readsorbed in the definition of H_0. The important point is that no term contains both x and y; no direct interaction between the two added particles exists, because of the $W = 0$ property.

The matrix element of the two-body operator W between determinants which differ by two spin-orbitals are given by the well-known rule

$$\left\langle \|k_+, k_-, u_1 \dots u_n\| \, W \, \left\|k'_+, k'_-, u_1 \dots u_n\right\| \right\rangle = \left\langle \|k_+, k_-\| \, W \, \left\|k'_+, k'_-\right\| \right\rangle \quad (21)$$

where k is different from k' while $u_1 \dots u_n$ is a sequence of occupied spin-orbitals. Using equation (7), one finds that

in the full plane, the matrix elements between different m states $W_{m,m'}$ vanish for $W = 0$ pairs. In the cluster, this is not true. Let x denote the state of x symmetry taken from the lower e degenerate level, and y' denote the state of y symmetry taken from the upper e degenerate level. Then, the m states involving these orbitals are coupled by W to those involving x and y, and to those involving x' and y'. Such matrix elements are forbidden in the full plane by momentum conservation, but exist in finite systems with open boundary conditions, having no translational invariance. They couple m states belonging to different eigenvalues of H_0.

4 The effective interaction

We need a rigorous definition of the effective interaction between two holes in many-body systems, and this requires a careful analysis. Actually, we shall use two alternative definitions, one of which is suitable for numerical exact diagonalization work, while the other one is much more microscopic and analytical. Therefore, we have to show that these two definitions essentially agree and lead to the same physical conclusions. That will emerge from the analytical treatment of the present section and from the numerical results of Section 6.

4.1 First definition: Δ

When working by exact diagonalization, we consider a cluster with n_h holes; its interacting ground state energy $E_\mathrm{h}(n_\mathrm{h})$, obtained with the Hamiltonian of equations (1, 2, 3), is referenced to the hole vacuum for any n_h. In terms of these eigenvalues we define, following references [23,24]

$$\Delta_\mathrm{h}(n_\mathrm{h}) = E_\mathrm{h}(n_\mathrm{h}) + E_\mathrm{h}(n_\mathrm{h}-2) - 2E_\mathrm{h}(n_\mathrm{h}-1). \quad (22)$$

$\Delta_\mathrm{h}(n_\mathrm{h})$ is one definition of the pairing energy. This definition is simple, but requires computing the eigenvalues with great accuracy, and has several drawbacks. It says nothing about the dynamics which leads to pairing. Moreover, generally a negative Δ does not unambiguously imply pairing, and further problems arise [25] since the above definition depends on the comparison of systems with different n_h.

However, the application of equation (22) is safe in the specific case when the last two holes are in a $W = 0$ state; in reference [18], we have shown that in this case Δ really coincides with the ground state expectation value of the effective interaction, at least at weak coupling; if the interaction is attractive and produces a bound state, $\Delta_\mathrm{h}(n_\mathrm{h})$ is negative and $|\Delta_\mathrm{h}(n_\mathrm{h})|$ is the binding energy. These results were obtained by analyzing exact diagonalization results for clusters with $n_\mathrm{h} = 4$ by lowest-order perturbation theory. In the present paper, we wish to extend those results to larger n_h by exact diagonalization and a more powerful analytical method.

4.2 Second definition: W_{eff}

The alternative definition is intrinsic to the n_h holes system and much more transparent. We achieve it by a canonical transformation that determines the effective two-body Hamiltonian $\tilde{H}$ from the many-body H of equation (1). We set up the Schrödinger equation for the ground state of the cluster with n_h holes, namely

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle. \quad (23)$$

Here, $E_0 \equiv E_\mathrm{h}(n_\mathrm{h})$. We take the ground state configuration of the noninteracting $n_\mathrm{h} - 2$ system as our vacuum state (the non-interacting Fermi *sphere*). The exact $|\Psi_0\rangle$ can be expanded in terms of excitations over the vacuum:

$$|\Psi_0\rangle = \sum_m a_m|m\rangle + \sum_\alpha b_\alpha|\alpha\rangle + \sum_\beta c_\beta|\beta\rangle + ... \quad (24)$$

here m runs over pair states, α over 4-body states (2 holes and 1 e–h pair), β over 6-body ones (2 holes and 2 e–h pairs). In Cu_5O_4 with 4 holes, the vacuum is the a_1^2 configuration and the expansion terminates with the β states; it terminates anyhow in any finite system, after a finite number of terms, so there are no convergence problems. Next, we consider the effects of the operators on the terms of $|\Psi_0\rangle$. We write:

$$H_0|m\rangle = E_m|m\rangle,\ H_0|\alpha\rangle = E_\alpha|\alpha\rangle, ... \quad (25)$$

and since W can create or destroy up to 2 e–h pairs,

$$W|m\rangle = \sum_{m'} W_{m',m}|m'\rangle + \sum_\alpha |\alpha\rangle W_{\alpha,m} + \sum_\beta |\beta\rangle W_{\beta,m}. \quad (26)$$

For clarity let us first write the equations that include explicitly up to 6-body states; then we have

$$W|\alpha\rangle = \sum_m |m\rangle W_{m,\alpha} + \sum_{\alpha'} |\alpha'\rangle W_{\alpha',\alpha} + \sum_\beta |\beta\rangle W_{\beta,\alpha} \quad (27)$$

where scattering between 4-body states is allowed by the second term, and

$$W|\beta\rangle = \sum_{m'} |m'\rangle\, W_{m',\beta} + \sum_\alpha |\alpha\rangle\, W_{\alpha,\beta} + \sum_{\beta'} |\beta'\rangle\, W_{\beta',\beta}. \quad (28)$$

The Schrödinger equation (23) yields equations for the coefficients a, b and c

$$(E_m - E_0)\, a_m + \sum_{m'} a_{m'} W_{m,m'} + \sum_\alpha b_\alpha W_{m,\alpha} + \sum_\beta c_\beta W_{m,\beta} = 0 \quad (29)$$

$$(E_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} W_{\alpha,m'} + \sum_{\alpha'} b_{\alpha'} W_{\alpha,\alpha'} + \sum_\beta c_\beta W_{\alpha,\beta} = 0 \quad (30)$$

$$(E_\beta - E_0)\, c_\beta + \sum_{m'} a_{m'} W_{\beta,m'} + \sum_{\alpha'} b_{\alpha'} W_{\beta,\alpha'} + \sum_{\beta'} c_{\beta'} W_{\beta,\beta'} = 0 \quad (31)$$

where E_0 is the interacting ground state energy. In principle, the $W_{\beta',\beta}$ term can be eliminated by taking linear combinations of the complete set of β states. The complete set of β states can be chosen in such a way that

$$(H_0 + W)_{\beta,\beta'} = E'_\beta \delta(\beta, \beta') \quad (32)$$

with this choice, the $W_{\beta',\beta}$ terms are removed, while E'_β replaces the noninteracting eigenvalue E_β. In other terms, we get a self-energy correction to E_β and a mixing of the vertices, without altering the structure of the equations. Then, we may rewrite equation (31) in the simpler form

$$\left(E'_\beta - E_0\right) c_\beta + \sum_{m'} a_{m'} W_{\beta,m'} + \sum_{\alpha'} b_{\alpha'} W_{\beta,\alpha'} = 0. \quad (33)$$

Now, we exactly decouple the 6-body states by solving the equation (33) for c_β and substituting into (29, 30), getting:

$$(E_m - E_0)\, a_m + \sum_{m'} a_{m'} \left[W_{m,m'} + \sum_\beta \frac{W_{m,\beta} W_{\beta,m'}}{E_0 - E'_\beta} \right] + \sum_\alpha b_\alpha \left[W_{m,\alpha} + \sum_\beta \frac{W_{m,\beta} W_{\beta,\alpha}}{E_0 - E'_\beta} \right] = 0 \quad (34)$$

$$(E_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} \left[W_{\alpha,m'} + \sum_\beta \frac{W_{\alpha,\beta} W_{\beta,m'}}{E_0 - E'_\beta} \right] + \sum_{\alpha'} b_{\alpha'} \left[W_{\alpha,\alpha'} + \sum_\beta \frac{W_{\alpha,\beta} W_{\beta,\alpha'}}{E_0 - E'_\beta} \right] = 0. \quad (35)$$

Introducing renormalized interactions W', we may rewrite these equations in the form

$$(E_m - E_0)\, a_m + \sum_{m'} a_{m'} W'_{m,m'} + \sum_\alpha b_\alpha W'_{m,\alpha} = 0 \quad (36)$$

$$(E_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} W'_{\alpha,m'} + \sum_{\alpha'} b_{\alpha'} W'_{\alpha,\alpha'} = 0. \quad (37)$$

If in equations (29, 30) we drop the terms involving the β states, they reduce to the same form as equations (36, 37), except that in the latter equations some quantities are renormalized. In other terms, the rôle of 6-body states is just to renormalize the interaction in the equations for the 2-body and 4-body ones, and for the rest they may be forgotten about. If E_0 is outside the continuum of excitations, as we shall show below, the corrections are finite, and experience with clusters suggests that they are small. Had we included 8-body excitations, we could have eliminated them by solving the system for their coefficients and substituting, thus reducing to the above problem with further renormalizations. This is a recursion method to perform the full canonical transformation; it applies to all the higher order interactions, and we can recast our problem as if only 2− and 4-body states existed.

Again, the $W'_{\alpha',\alpha}$ term can be eliminated from equation (37) by taking linear combinations of the α states. This is achieved by choosing the complete set of α states in such a way that

$$(H_0 + W')_{\alpha,\alpha'} = E'_\alpha \delta(\alpha, \alpha'). \quad (38)$$

With this choice, the $W'_{\alpha,\alpha'}$ terms are removed, while E'_α replaces the noninteracting eigenvalue E_α. In other terms, we get a self-energy correction to E_α and a mixing of the vertices, without altering the structure of the equations. Now equation (37) becomes

$$(E'_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} W'_{\alpha,m'} = 0. \quad (39)$$

Solving equation (39) for b_α and substituting in equation (36) we exactly decouple the 4-body states as well. The eigenvalue problem is now

$$(E_0 - E_m)\, a_m = \sum_{m'} a_{m'} \langle m|S[E_0]|m'\rangle\,, \quad (40)$$

where

$$\langle m|S\left[E_0\right]|m'\rangle = W'_{m,m'} + \sum_\alpha \frac{\langle m|W'|\alpha\rangle\langle\alpha|W'|m'\rangle}{E_0 - E'_\alpha}\,. \quad (41)$$

We introduce the diagonal elements of the α summation:

$$F_{m,m} = \sum_\alpha \frac{\langle m|W'|\alpha\rangle\langle\alpha|W'|m\rangle}{E_0 - E'_\alpha}; \quad (42)$$

then, equation (40) becomes

$$E_0 a_m = (E_m + W'_{m,m} + F_{m,m}) a_m + \sum_{m' \neq m} a_{m'} \langle m|W_{\rm eff}|m'\rangle \quad (43)$$

where for $m \neq m'$

$$\langle m\,|W_{\rm eff}|\,m'\rangle = W'_{m,m'} + \sum_\alpha \frac{\langle m|W'|\alpha\rangle\langle\alpha|W'|m'\rangle}{E_0 - E'_\alpha}\,. \quad (44)$$

The $W'_{m,m'}$ term does not arise in reference [19] because in the full plane it vanishes by momentum conservation.

Equations (43, 44) determine the amplitudes a_m of the m states in the $n_{\rm h}$-hole state and the ground state eigenvalue E_0 relative to the hole vacuum. Their solution, inserted in equation (39) yields the coefficients b_α and we could proceed with the full calculation of Ψ_0; this appears to be hard for a large system. However, our task here is to find the effective two-body Hamiltonian; this is much less expensive.

Indeed, equation (43) is of the form of a Schrödinger equation with eigenvalue E_0 for pairs with effective interaction $W_{\rm eff}$. Then we may interpret a_m as the wave function of the *dressed pair*, which is acted upon by an effective Hamiltonian $\tilde{H}$. The change from the full many-body H to $\tilde{H}$ is a canonical transformation which holds to all orders. $W_{\rm eff}$ is the effective interaction between dressed holes, while F is a forward scattering operator for $W = 0$ pairs, which accounts for the self-energy corrections of the one-body propagators: it is evident from (43) that it just redefines E'_m. Also in Cooper theory [29] one meets electron-phonon self-energy terms, which do not contribute to the effective interaction. The basic spin-flip diagram responsible for $W_{\rm eff}$ had been identified before [18]. Any other pairing mechanism not considered here, like off-site interactions, inter-planar coupling and phonons, can be included as an extra contribution to $W'_{m',m}$ which just adds to $W_{\rm eff}$.

This way of looking at equation (43) is perfectly consistent, despite the presence of the many-body eigenvalue E_0, because we are not compelled to reference the energy eigenvalues to the hole vacuum. We note that if we shift H_0 by an arbitrary constant ΔE in equation (25), by setting

$$H'_0 = H_0 - \Delta E \tag{45}$$

the same shift applies to the eigenvalues E_m, E_α, E_β and so on, and also to the renormalized quantities like E'_α, E'_β. Therefore, the effective interaction $W_{\rm eff}$ of equation (44) and the F matrix elements are unaffected by the shift. Thus we can reference E_0 to a new energy origin by shifting the diagonal terms in equation (43) without changing the off-diagonal terms. Since we wish to regard equation (43) as a Cooper-like equation for the pair, it is natural to set ΔE equal to the interacting ground state energy eigenvalue for the $n_{\rm h} - 2$ hole system, relative to the hole vacuum,

$$\Delta E = E_{\rm h}(n_{\rm h} - 2). \tag{46}$$

This quantity is obtained by diagonalizing the cluster Hamiltonian with $n_{\rm h} - 2$ holes. In reference [19], dealing with the infinite plane, this was our choice. The energy of two independent holes, relative to the $n_{\rm h} - 2$ background, is $2E_{\rm F}$, where $E_{\rm F}$ is the Fermi energy; when the effective interaction is accounted for, the energy of the two bound holes is $2E_{\rm F} + \Delta$, where $|\Delta|$ is the binding energy.

Up to this point, the treatment is exact. However, we can make an easy use of equation (43) if we can neglect the renormalizations in equation (44), setting $W' \to W$ and $E'_\alpha \to E_\alpha$, which is fully justified in the weak coupling case. This is the approximation that we proposed in reference [19] and that we want to test in the present paper. In fact, if we are primarily interested in the symmetry of the ground state, and in the presence or absence of pairing, we can get these results without a large computational effort. We exemplify the procedure for Cu_5O_4 in the $n_{\rm h} = 4$ case. Two degenerate m states are lowest in the non-interacting limit, namely, the configuration $m = D[x, y]$ of equation (18) and $m' \equiv D[y, x]$, where the x, y orbitals belong to the lower e level; the $\psi(^1A_1)$ state also is degenerate with m, m', but by symmetry W cannot mix it to them. As already noted, m and m' do not interact through the $W_{m,m'}$ term. To calculate $W_{\rm eff}$, we rewrite W (Eq. (3)) in the orbital representation, with

$$c_i^\dagger = \sum_\nu^{\rm orb} \langle i|\nu\rangle c_\nu^\dagger \tag{47}$$

where ν runs over all the orbitals, obtaining

$$W = \sum_{\mu\nu\rho\sigma}^{\rm orb} W(\mu,\nu,\rho,\sigma) c_{\mu,+}^\dagger c_{\nu-}^\dagger c_{\sigma,-} c_{\rho,+}. \tag{48}$$

The pair (ρ_+, σ_-) which is annihilated may correspond to (y_+, x_-), (y_+, a_-), (a_+, x_-), (a_+, a_-). The first choice gives nothing since it corresponds to a $W = 0$ pair; the last choice yields a β state. To lowest order, only the α states contribute, involving the excitation of either the a_+ or the a_- hole. Many of the W matrix elements vanish by symmetry; we are going to neglect those connecting to excited x', y' orbitals, which occur at higher energies, because we are considering weak coupling.

Considering the contribution of (y_+, a_-), one finds that the only α states coupled to $D[y, x]$ by W are those of the form $|\mu a y x| \equiv |\mu_+ a_+ y_- x_-|$, in which the hole in a_- is promoted to y_- while y_+ is scattered into μ_+. Therefore,

$$E_\alpha = \varepsilon_a + \varepsilon_\mu + \varepsilon_x + \varepsilon_y, \tag{49}$$

where $\varepsilon_y = \varepsilon_x$. One finds

$$\langle|\mu a y x|\, W\, |y a x a|\rangle = -W(y, a, \mu, y) \tag{50}$$

and

$$\langle|x a y a|\, W\, |\mu a y x|\rangle = W(x, a, \mu, x). \tag{51}$$

Therefore, taking into account that each of the two background a holes can be promoted and this brings a factor of 2, using (43) we obtain

$$\langle m\,|W_{\rm eff}|\,m'\rangle = -2\sum_\mu \frac{W(y,a,\mu,y)W(x,a,\mu,x)}{E_0 - (\varepsilon_a + \varepsilon_\mu + 2\varepsilon_x)}\,. \tag{52}$$

Since $W(y, a, x, y) = W(x, a, y, x) = 0$, the empty (of holes) states μ belonging to the e representation yield 0. The empty orbitals that contribute are those of the a_1 symmetry, that will be denoted by a', and those of b_1 symmetry that we shall write b.

The a' orbitals contribute to the repulsion, and the b orbitals to the attraction. Indeed, $W(x, a, a', x) = W(y, a, a', y)$, and the contribution of the states of a_1 symmetry is $-2\sum_{a'} \frac{W(x,a,a',x)^2}{E_0 - (\varepsilon_a + \varepsilon_{a'} + 2\varepsilon_x)}$; since $E_\alpha > E_0$ this is positive. On the other hand, $W(x, a, b, x) = -W(y, a, b, y)$, since the orbitals of of b_1 symmetry change sign for a $\frac{\pi}{2}$ rotation. Therefore the contribution of the b states is attractive. This is an example of the interference

of opposite contributions to $W_{\rm eff}$, that we emphasised in reference [19].

Therefore, at this stage, a self-consistent treatment of equation (43) must be sought, because $W_{\rm eff}$ depends on the eigenvalue E_0. A straightforward recursion approach leads to a continued fraction solution, which has contributions from all orders of perturbation theory.

4.3 Equivalence of the two definitions at weak coupling

For weak coupling, however, a cruder but simpler approximation is justified: one calculates $W_{\rm eff}$ neglecting all self-energy corrections, in such a way that E_0 in (52) reduces to $2\varepsilon_x + 2\varepsilon_a$; this is the lowest (second-order) approximation $W_{\rm eff}^{(2)}$. In the same, lowest-order approximation, the shift in equation (46), which recasts equation (43) as a two-body problem, in the Cooper-like form, is $\Delta E = 2\varepsilon_a$; further, one considers only the mixing of the degenerate configurations $m = D[x, y]$ and $m' \equiv D[y, x]$. In the resulting 2×2 problem, the diagonal entries are identical, and the $W_{\rm eff}^{(2)}$ interaction produces the off-diagonal elements, with the result that the singlet is stabilized by $|W_{\rm eff}^{(2)}|$ and the triplet is destabilized by the same amount. Therefore [26], $\Delta(4)^{(2)} = W_{\rm eff}^{(2)}$. One obtains for $\Delta(4)^{(2)}$ the following second-order expression:

$$\Delta(4)^{(2)} = -2\left[\sum_b \frac{W(a,b,x,x)^2}{(\epsilon_b - \epsilon_a)} - \sum_{a'} \frac{W(a,a',x,x)^2}{(\epsilon_{a'} - \epsilon_a)}\right] \quad (53)$$

where the sums run only over the one-body states of a and b symmetry. This agrees with the result that we obtained earlier [18] from a diagrammatic analysis of equation (22). Thus, the two definitions of the effective interaction lead to the same result, at least in the weak coupling limit.

We stress again that the sign of $\Delta(4)^{(2)}$ is determined by the relative weights of the virtual excitations to the empty states of different point symmetry. In general, $W_{\rm eff}$ can produce attraction or repulsion, depending on the hole concentration. This crude approximation will turn out to be sufficient for qualitative purposes, *i.e.*, to predict when pairing occurs.

5 W = 0 pairs and charge conjugation

Consider the cluster with $n_{\rm h}$ holes. As shown above, the interesting situation arises when $n_{\rm h}$ is such that, filling the levels according to the *aufbau* principle,the last two holes go to a degenerate level. Accordingly, we expect that $\Delta_{\rm h}(n_{\rm h})$ measures the effective interaction between the holes of the $W = 0$ pair. In reference [18], we have shown that this is the case at weak coupling. If the interaction is attractive and produces a bound state, $|\Delta_{\rm h}(n_{\rm h})|$ is the binding energy. This situation can be realised with $n_{\rm h} = 4$ in highly symmetric Cu–O clusters containing up to 21 atoms [6]. The last 2 holes then go to the lowest level of e symmetry.

According to Table 1, the Cu_5O_4 cluster has an upper e level, which is reached with 12 holes, so we are interested in $\Delta_{\rm h}(4)$ and $\Delta_{\rm h}(12)$. Moreover, we can exploit the approximate electron-hole symmetry of the problem to obtain two more interesting cases. The approximate symmetry consists in the fact that the same sequence of symmetry labels is obtained by reading Table 1 from up to down and in reverse order. The reverse order corresponds to adopting the electron picture and starting from the electron vacuum. Going to the electron picture, the three-band Hubbard Hamiltonian becomes:

$$H = \sum_i (2\varepsilon_i + U_i) - \sum_{i\sigma} (\varepsilon_i + U_i) a^\dagger_{i\sigma} a_{i\sigma} - \sum_{<i,j>\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \sum_i U_i n_{i+} n_{i-}, \quad (54)$$

$W = 0$ *electron pairs* are obtained for $n_{\rm e} = 4$ and 12 electrons. Letting now $E_{\rm e}(n_{\rm e})$ denote the ground state energy of the cluster with $n_{\rm e}$ electrons, the effective interaction between the two electrons in the pair is measured by

$$\Delta_{\rm e}(n_{\rm e}) = E_{\rm e}(n_{\rm e}) + E_{\rm e}(n_{\rm e} - 2) - 2E_{\rm e}(n_{\rm e} - 1). \quad (55)$$

Since the dimensionality of the one-body basis is 18,

$$\begin{aligned}\Delta_{\rm e}(4) &= E_{\rm e}(4) + E_{\rm e}(2) - 2E_{\rm e}(3) \\ &= E_{\rm h}(14) + E_{\rm h}(16) - 2E_{\rm h}(15) = \Delta_{\rm h}(16)\end{aligned} \quad (56)$$

and, similarly, $\Delta_{\rm e}(12) = \Delta_{\rm h}(8)$.

We recall that we speak of *electron pairs* when two added electrons partially occupy a degenerate state and of *hole pairs* when the same situation is reached by adding two holes; however the final situation is exactly the same. For example, consider the $W = 0$ pair state of equation (11). One readily verifies that in a canonical transformation from holes to electrons, putting $a^\dagger_{i\sigma} = c_{i\sigma}$, the two-hole state becomes a two electron state of the same form. Therefore the two-body $W = 0$ state is invariant under charge conjugation, and if holes are paired, electrons are also paired. In order to avoid switching all the time between the two equivalent pictures, below we discuss everything in terms of holes. Summarizing the results of the present Section, we can test the effective interaction in Cu_5O_4 by calculating $\Delta_{\rm h}(n_{\rm h})$ with $n_{\rm h} = 4$, 8, 12 and 16.

6 Numerical results and discussion

By an enhanced Lanczos routine, we computed the ground state of the Cu_5O_4 cluster with even numbers $n_{\rm h}$ of holes and vanishing z component of the total spin; the parameter values are specified in the Introduction. The maximum size of the matrices (15,876) occurs for $n_{\rm h} = 8$;

Table 2. Exact diagonalization results for $\Delta_h(n_h)$ (meV), using $U_p = 6$ eV and $U_d = 5.3$ eV. For $n_h = 4$, 8 and 16 pairing takes place, and at $n_h = 12$ the repulsion is drastically reduced. For $n_h = 6$ and 14 the $W = 0$ pairs are *not* involved and the normal repulsion develops.

n_h	Δ_h (meV)
4	−15.7
6	1469.2
8	−10.85
12	43.72
14	1109.2
16	−25.47

the $n_h = 12$ and 16 cases are handled by transforming to the electron picture. The results for $\Delta_h(n_h)$ are summarized in Table 2. One sees that Δ_h for $n_h = 4$, 8, 12 and 16 is much smaller in absolute value than for other fillings, as expected. This confirms that W=0 pairs are involved. In particular, for $n_h = 4$, 8 and 16 $\Delta_h(n_h) < 0$ and pairing occurs, while for $n_h = 12$ a small repulsion prevails. When pairing is obtained, this means that the renormalization of the parameters inherent in the canonical transformation does not have important consequences. To see if the behavior at $n_h = 12$ is an exception, we have repeated the calculations with scaled U values. Using $U_p = 0.06$ eV and $U_d = 0.053$ eV, which are $\ll t$ and allow applying perturbation theory, we still get a positive result, namely $\Delta_h(12) = 0.0034$ meV. Thus, even second-order perturbation theory would suffice to predict $\Delta_h(12) > 0$ in this case.

For $n_h = 4$ we have an analytic second-order result (Eq. (53)) and we can check its degree of validity by comparing with the exact diagonalization values of Δ. Making use of the above standard values of the parameters we calculate the relative error $\delta = 2\left|\frac{\Delta-\Delta^{(2)}}{\Delta+\Delta^{(2)}}\right|$. It turns out that $\delta \leq 0.07$ up to U/t ≈ 1. Thus, already the second-order approximation is remarkably accurate in estimating the effective interaction. We conclude that our treatment based on the unrenormalized formula of equation (44) correctly predicts the presence or absence of pairing, depending of the hole concentration, and even a simple, second-order approximation to it has a semi-quantitative accuracy when compared with exact results.

The indications that we may draw from this section are: i) our mechanism is operating for a wide range of hole concentrations and produces a much reduced interaction $|\Delta|$, ii) this does not imply pairing at all concentrations, iii) we can predict if there is pairing or repulsion in a particular case by our theory. The cluster approach, however, has several limitations, the main size effect being that $W = 0$ pairs are possible at discrete values of the hole concentration. In Cu_5O_4 with 4 holes, we are doping with one electron, but in other cases we are far from the physical concentrations. However, we are not yet trying to make quantitative predictions, rather our point here is that of testing our approach against exact solutions, which is only feasible in small clusters.

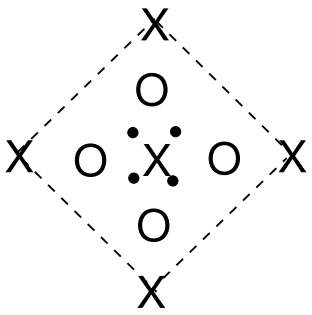

Fig. 1. The Cu_5O_4 cluster with 4 flux tubes (black dots) carrying flux ϕ. X stands for Cu. The dotted lines represent the t_d bonds providing a closed path around the center.

7 Flux quantization and pair symmetry

If a magnetic field is confined to a hole in any material (flux tube) the flux ϕ is quantized in integer multiples of the fundamental quantum $\phi_0 = \frac{hc}{e}$; a flux $\phi = \phi_0$ can be gauged away, and any physical property, for example the ground state energy, is a periodic functions of ϕ with period ϕ_0.

Bulk superconductors quantize the flux through a hole in integer and half-integer multiples of ϕ_0, because the quasiparticles that screen the vector potential carry charge $2e$. In finite systems the signature of superconductivity is a ground state energy minimum at $\phi = 0$ that is separated by a barrier from a second minimum at $\phi = \phi_0/2$. With increasing the size of the system, the energy (or free energy, at finite temperature) barrier separating the two minima becomes macroscopic, and bulk superconductors can swallow up only an integer or half integer number of flux quanta. As emphasized by Canright and Girvin [27], the flux dependence of the ground state energy is definitely a most compelling way of testing for superconductivity, and the existence of the two minima separated by a barrier is a strong indication of superconducting flux quantization.

In reference [27], superconducting pairing was obtained by assuming a negative U; a *ribbon* shaped cluster was closed on itself with periodic boundary conditions along its length, and the flux was inserted in the hole. In the present problem, with a repulsive Hubbard model, the mechanism of attraction is driven by the C_{4v} symmetry, and cannot operate with such an unsymmetric geometry. The flux must be inserted in such a way that the system is not distorted. On the other hand, we cannot make holes in our small cluster because it would fall apart in disconnected pieces. One should consider larger clusters like $Cu_{13}O_{36}$, which allow $W = 0$ solutions for $n_h \geq 10$, however the number of configurations $> 10^{12}$ is outside the scope of exact diagonalization methods.

So, we keep the Cu_5O_4 cluster geometry, but modify its topology by adding a small hopping t_d between the external Cu's, in order to introduce a closed path around the center, where screening currents can respond. Each t_d bond forms a closed triangular loop with the central Cu at the vertex (see Fig. 1).

This geometry is a compromise, because the magnetic field penetrates our small cluster; however, it lends itself to an extension to the full plane, such that only the 4 central plaquettes feel a magnetic field, and the rest of the plane only experiences a vector potential (see below). Finally, we observe that a flux of the order of a fluxon in a macroscopic system would be a small perturbation; in the small cluster, however, the perturbation is small only if the hopping integral t_d is taken small compared to t. Numerically, the computations were performed with $t_d = \pm 0.01$ eV.

We introduce a tube carrying flux ϕ inside each of the triangles formed in this way. Every bond collects the Peierls phase $\frac{2\pi \mathrm{i} \int \mathbf{A}\cdot \mathrm{d}\mathbf{r}}{\phi_0}$; by symmetry, t is unaffected by the flux, while

$$t_d \rightarrow t_d \mathrm{e}^{\frac{2\pi \mathrm{i}\phi}{\phi_0}} \tag{57}$$

for a clockwise path, and the complex conjugate expression a counterclockwise path.

7.1 Superconducting flux quantization: numerical results

According to Table 2, $\Delta_\mathrm{h}(n_\mathrm{h})$ is negative and pairing results at $\phi = 0$ for $n_\mathrm{h} = 4$, 8 and 16; in all three cases we found that the ground state energy $E_\mathrm{h}(n_\mathrm{h}, \phi)$ as a function of ϕ has clearly separated minima at zero and half a flux quantum. Moreover, our criterion for pairing ($\Delta < 0$) also leads us to a much more stringent criterion for superconducting flux quantization than is drawn from the literature, since we need that both minima in the ground state *versus* flux curves also correspond to negative Δ. This is a much clearer signature of superconducting flux quantization than the generally accepted presence of the two minima, because it implies that the superconductor remains a superconductor after swallowing up the half flux quantum. Therefore, we computed $\Delta_\mathrm{h}(n_\mathrm{h}, \phi)$ in order to determine the flux dependence of the effective interaction. *When* $\Delta_\mathrm{h}(n_\mathrm{h}, 0) < 0$, *then* $\Delta_\mathrm{h}(n_\mathrm{h}, \frac{\phi_0}{2})$ *is also negative.* For small enough t_d, the response function

$$R = \frac{\Delta_\mathrm{h}(n_\mathrm{h}, \phi) - \Delta_\mathrm{h}(n_\mathrm{h}, 0)}{|t_d|} \tag{58}$$

is an intrinsic property of the original cluster with $t_d = 0$. In Figure 2 we show R for several n_h values *versus* $\frac{\phi}{\phi_0}$. All the R curves have a local minimum at $\phi = 0$, where they vanish; $\phi = \phi_0/4$ is a maximum and a second minimum occurs at $\phi = \phi_0/2$; the $n_\mathrm{h} = 4$ curve is reduced by a factor of 3. The barrier gets lower with increasing n_h, but the same qualitative trend can be seen in all cases. The numerical data also show that changing the sign of t_d produces a rigid shift of the n_h curves by $\frac{\phi_0}{2}$ such that the two minima interchange their places.

In Figure 2 we also report the absolute value $|\langle \Psi_0(\phi) | \Psi_0(0) \rangle|$ of the overlap between the the ground state eigenvectors in the presence and in the absence of the flux, for $n_\mathrm{h} = 4$. It is clear that $|\left\langle \Psi_0(\frac{\phi_0}{2}) | \Psi_0(0) \right\rangle| = 0$, and therefore the pairing state at zero flux and half fluxon are orthogonal. There is a clear analogy with the BCS theory; in that case, the Cooper wavefunction has s symmetry and the total magnetic quantum number of the pair vanishes in the absence of flux, but not at half a flux quantum [28]. Similar results for the overlap are obtained for the other n_h values which correspond to partially filled shells.

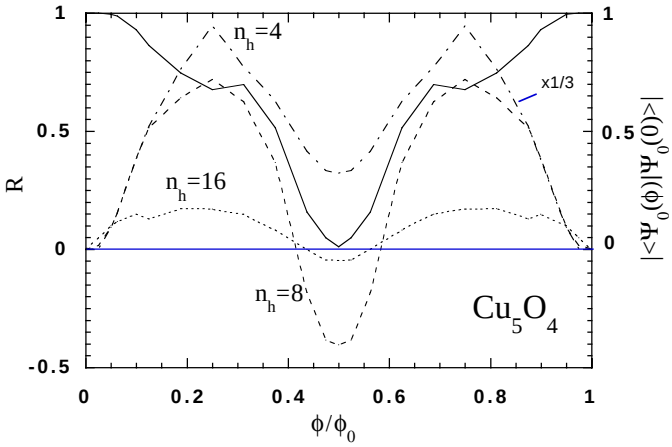

Fig. 2. Solid line (right scale):$|\langle \Psi_0(\phi) | \Psi_0(0) \rangle|$. The other lines (left scale) show the dimensionless response function R of equation (58) for $n_\mathrm{h} = 4$, 8 and 16. Note that for $n_\mathrm{h} = 4$, $\Delta_\mathrm{h}(4, \frac{\phi_0}{2}) - \Delta_\mathrm{h}(4, 0) \approx 0.3 t_d$, but $\Delta_\mathrm{h}(4, \frac{\phi_0}{2})$ is negative.

Our code automatically classifies the eigenvectors according to the IRREPS of C_{4v}. For positive t_d the point symmetry of the ground state wavefunction changes from ${}^1\mathrm{B}_2(x^2 - y^2)$ at ϕ=0 to ${}^1\mathrm{A}_1(x^2 + y^2)$ at $\phi = \frac{\phi_0}{2}$. For negative t_d the symmetry labels of the two minima are interchanged. For electron pairing, the symmetry of the states is the same as in the hole case.

Since the vector potential lowers the symmetry, the eigenvectors cannot generally be classified according to the IRREPS of C_{4v}; however numerical data show that at half fluxon, the symmetry is *dynamically* enhanced (see below).

7.2 Group theory aspects of superconducting flux quantization

These findings are required by general symmetry principles. In the absence of t_d, the full invariance group of the cluster is S_4 and the interacting ground state is degenerate, with ${}^1\mathrm{A}_1$ and ${}^1\mathrm{B}_2$ components. A nonzero t_d at $\phi = 0$ reduces the symmetry to the C_{4v} subgroup; it turns out that with a positive t_d the expectation value of the magnetic perturbation is negative on ${}^1B_2$ and positive on ${}^1A_1$; therefore the ground state is ${}^1\mathrm{B}_2$ at $t_d > 0$ but changes symmetry if the sign of t_d is reversed. Upon switching the vector potential $\mathbf{A}$, the Cu–Cu hopping is complex and chiral, so the symmetry is lowered again from

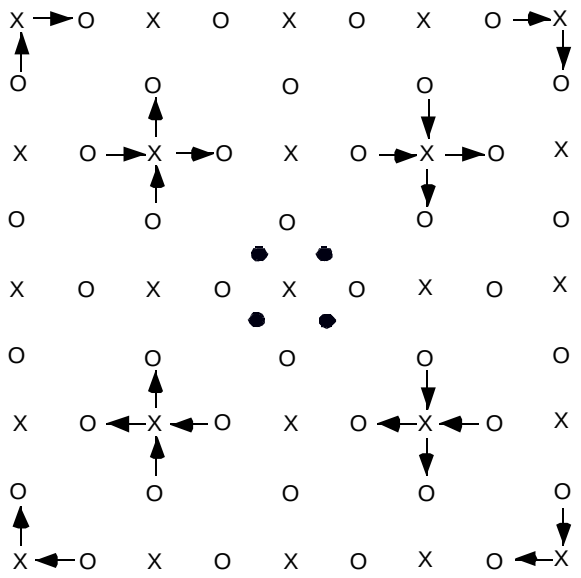

Fig. 3. Pattern of the vector potential A due to 4 flux tubes (black dots) carrying flux ϕ. X stands for Cu. The line integral of A along each bond parallel to the arrow is $\frac{\phi}{2}$.

C_{4v} to its subgroup Z_4, which contains only the rotations. Since Z_4 is abelian, there are no degeneracies for a generic ϕ, so there are no $W = 0$ pairs and repulsion prevails. With increasing the flux from 0, the ground state energy increases to a maximum. Then it decreases because, at $\phi = \frac{\phi_0}{2}$, the Cu–Cu hopping of equation (57) becomes $-t_d$, which is real; then the full C_{4v} symmetry is restored, resurrecting the $W = 0$ pairs. The recovery of C_{4v} at $\phi = \frac{\phi_0}{2}$ enables us to assign the eigenvectors to the IRREPs, as noted above. The change of symmetry of the pair is also readily understood: the perturbation caused by $t_d > 0$ at $\phi = 0$ becomes the opposite at half fluxon, so the $^1A_1$ state is lowest now. The signature of superconducting pairing is not only the existence of a well defined second minimum at half flux quantum, but also the fact that it corresponds to a $\Delta < 0$ situation, like at $\phi = 0$.

This symmetry argument extends to the full plane. To see that, consider the pattern of Figure 3. Here, the Cu sites are marked by X and the Oxygen sites by O; the black dots stand for tubes carrying flux ϕ each, symmetrically disposed around the central Cu. Varying ϕ by an integer multiple of ϕ_0 corresponds to a gauge transformation leaving all the physical properties invariant. The arrows help to visualize a convenient choice of the gauge at general ϕ. Namely, running along an oriented bond in the sense of the arrow,

$$\int_{\rightarrow} \mathbf{A} \cdot \mathrm{d}\mathbf{r} = \frac{\phi}{2}; \tag{59}$$

along the other Cu–O bonds, not marked in the figure, $\int \mathbf{A} \cdot \mathrm{d}\mathbf{r} = 0$. One sees that in this way the flux through any closed path corresponds to the number of tubes surrounded by the path. The reflection operations of C_{4v} are equivalent to $\phi \rightarrow -\phi$, reverse the directions of the arrows and for a generic ϕ the symmetry group reduces to Z_4. However, at $\phi = \frac{\phi_0}{2}$ the reversal of the magnetic field in the tubes corresponds to a jump by ϕ_0, and this is equivalent to a gauge transformation: this implies that the symmetry group gets larger, the new symmetry operations being reflections supplemented by a gauge transformation. Indeed, it follows from equation (59) that the hopping parameter becomes *it* along the arrows, while it remains equal to t along the unmarked bonds of Figure 3. Any reflection operation simply changes the signs of all the hoppings along the marked bonds. Now consider the unitary transformation S which changes the signs of all the Cu orbitals along both diagonal, except the central Cu. Since S also has the effect of reversing all the arrows, $\sigma \times S$ is a symmetry, for all reflections σ in C_{4v}. Moreover, since the product of two reflections is a rotation, the group $\tilde{C_{4v}}$ including the rotations and the reflections multiplied by S is isomorphic to C_{4v}. The $W = 0$ pairs appropriate for half a flux quantum must involve two holes belonging to the degenerate IRREP of $\tilde{C_{4v}}$. In this way, at $\phi = \frac{\phi_0}{2}$ the full symmetry is restored, allowing again for pairing and negative Δ. The $W = 0$ quasiparticles have just the correct symmetry properties in the presence of the vector potential to provide superconducting flux quantization in macroscopic systems.

8 Conclusions

We have examined the properties of the $W = 0$ pairs by performing numerical diagonalizations of the Cu_5O_4 cluster for various fillings. Some of these fillings are not representative of the concentrations that have been realised in the cuprates, but our theory depends on symmetry and the concentration range to which it applies is wider than that obtained experimentally. We have shown that the effective interaction between the two holes in the $W = 0$ pair can be obtained by computing Δ by exact diagonalization or, alternatively, by an analytical, recursive canonical transformation; we have detailed the latter approach, and derived a weak coupling approximation that agrees with the numerical results for Δ and with a previous diagrammatic analysis. Pairing occurs when $\Delta < 0$. An approximate symmetry under charge conjugation exists leading to *electron pairing* as well as *hole pairing* in the sense defined in the Introduction. The numerical data confirm that when the filling is such that $W = 0$ pairs are involved, Δ is small in absolute value, while the other fillings lead to strong repulsion. In one case, the $W = 0$ pair leads to a small repulsion, showing that the existence of pairing is not a general property independent on filling. In all cases, we found that pairing or its absence can be reliably predicted by studying the behavior of the system at weak coupling, which supports the approximations that we performed in a study of the full plane in reference [19] at least in some concentration ranges. We stress, however, that the instability of the Fermi liquid against a pairing interaction does not grant superconductivity, since there

is a competition with other order parameters. Further investigations are necessary to analyze this point very close to half filling, where the antiferromagnetic order prevails and the behavior could require a strong coupling analysis. Moreover, we expect that the renormalization of the dispersion relation cannot be neglected [20].

In the Cu_5O_4 cluster the exact diagonalization results show that $W = 0$ pairs quantize flux in the superconducting way. The ground states in presence of zero and half fluxon have different symmetries, like in BCS superconductors. The superconducting flux quantization property is due to the fact that the symmetry group appropriate at half flux quantum in isomorphic with C_{4v}, and this is not limited to small clusters, but general. Flux quantization and pairing fit well together, both being consequences of the same symmetry principle.

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