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"W = 0" pairing in Cu-O clusters and in the plane

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Abstract. The Cu-O plane and the clusters that possess the same C_{4v} symmetry around a Cu ion have 2-hole eigenstates of the kinetic energy with vanishing on-site repulsion ($W = 0$ pairs). Cluster calculations by exact diagonalisation show that these are the quasiparticles that lead to a paired ground state, and have superconducting flux-quantisation properties. Here, we extend the theory to the full plane, and show that the $W = 0$ quasiparticles are again the natural explanation of superconducting flux-quantisation. Moreover, by a new approach which is exact in principle, we calculate the effective interaction $W_{\rm eff}$ between two holes added to the ground state of the repulsive three-band Hubbard model. To explain how a noninteracting electron gas becomes a superconductor when switching the local Coulomb interaction, we obtain a closed-form analytic expression including the effects of all virtual transitions to 4-body intermediate states (exchange of an electron-hole pair). Our scheme is ready to include other interactions which are not considered in the Hubbard model but may be important. In the plane, the $W = 0$ pairs have $^1B_2$ and $^1A_2$ symmetry. The effective interaction in these channels is attractive and leads to a Cooper-like instability of the Fermi liquid, while it is repulsive for triplet pairs. From $W_{\rm eff}$, we derive an integral equation for the pair eigenfunction; the binding energy $|\Delta|$ of the pairs is in the range of tens of meV. However, our symmetry-based method is far more general than the model.

PACS. 74.20.Mn Nonconventional mechanisms (spin fluctuations, polarons and bipolarons, resonating valence bond model, anyon mechanism, marginal Fermi liquid, Luttinger liquid, etc.) – 71.10.Li Excited states and pairing interactions in model systems

1 Introduction

The controversy about the physical origin of high-$T_{\rm C}$ superconductivity [1] continues with undiminished intensity, and papers in the field starting from different model Hamiltonians are currently regarded as belonging to alternative and non-communicating schools of thought. For instance, is the mechanism electronic or phononic? However, it is evident *a priori* that all the degrees of freedom must be important in the final theory, and so this is not an entirely well-posed problem. The idea that the mechanism is exclusively electronic or exclusively phononic is evidently too extreme; a theoretical framework is needed where the different degrees of freedom can coexist and can be compared on equal footing. The most fundamental question is rather: what is the quasi-particle, which, when dressed by all the relevant interactions, becomes the Coope-liker pair? Here we show that it is a novel type of singlet, that we called the $W = 0$ pair.

In order to present such a scheme, however, any approach must start with a model Hamiltonian that takes into account the large on-site interactions, like the Hubbard [2,3] or t-J models [4]. Should it turn out eventually that the phonons play a major rôle *via* an enhanced electron-phonon vertex [5], with or without a polaron or bipolaron behavior [6], that would mean that the large repulsive interactions have been avoided in some way. The reason is that Cooper pairs in high-$T_{\rm C}$ superconductors are more tightly bound and spatially localized than in ordinary BCS ones; if phonons prevail, the wave function of the hole system must be such that the repulsion barrier is minimized and can be overcome by phonon exchange. Only a suitable quasiparticle can achieve that.

Several authors have pushed the argument further, proposing that correlation effects alone could be so strong to turn the repulsion into attraction by some sort of overscreening and lead to pairing. There is a fascinating *paradox* in this proposal, since attraction must eventually result from repulsion, and this possibility has been proposed by several authors before us. Indeed, this result is borne out, in a new perspective, by the present approach.

So, although our method can be applied to any model and in principle to the microscopic Hamiltonian, we start with the three-band Hubbard model. The Hamiltonian is

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

and the independent hole term reads, in the site representation

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

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where n.n. stands for nearest neighbors. The on-site repulsion term 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 O site.

The electronic properties of this model are under intense investigation by several groups. There are interesting approaches based on perturbation theory and the Bethe-Salpeter equation. One of the most promising is the FLEX approximation, which is a generalized RPA [7] and leads to pairing and superconductivity in the three-band Hubbard model [8]. 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 [9]; 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 [10]. 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 [11] 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 [12]; they also derived the effective pairing interaction in the same approximation [13] and studied the doping dependence of the superconducting transition temperature.

Our new method, the canonical transformation approach, is a particularly efficient way to perform the configuration interaction calculation. It is based on the symmetry, and dramatically displays the mechanism of pairing in the CuO plane. Usually, Group theory arguments are just a method to optimise the computer code; here, instead, the symmetry determines the dynamics, rather than improving its description. The basic idea [14] was prompted to us initially by the properties of clusters having degenerate ground states in the noninteracting limit. In the next Section, we review the essentials of the cluster approach, and show that the $W = 0$ pairs are the quasiparticles that lead to pairing. Then, we present the general theory for the full plane; a short account of our approach, following the hint provided by diagrams derived from the cluster studies, is forthcoming [15]. In Section 3 we show how $W = 0$ pairs in the full plane arise at the Fermi level for any filling, and that their symmetry properties naturally lead to superconducting flux-quantisation. Section 4 is devoted to the general canonical transformation leading to the effective Hamiltonian for pairs [16]. Our new method is free from the limitations of perturbation theory; the relation of the present formalism to Cooper theory from one side and to the cluster results from the other is discussed. Also, we show that the present method is ready to accommodate further effects such as phonons, off-site interactions [14], and interplanar coupling [17]. The final result of the analysis is an integral equation for pairs in the full plane, which is suitable for a numerical study. Section 5 is devoted to the method we used to solve the hard integral equation. We first solve it in finite supercells and then take the asymptotic limit in Section 6. Two kinds of bound states of different symmetries result, and we explore the dependence of Δ on the filling and other parameters. The main conclusions of this work are discussed in Section 7.

2 "W = 0" pairing and flux quantisation in small clusters

The theory that we present below holds for the full plane and for any finite cluster which has the same C_{4v} symmetry as the full plane around a Cu site.We insist on clusters here primarily because the evidence about them rests on exact diagonalisation, and is an independent confirmation of the analytical results that we present below. In the early cluster studies, which are ten years old, however, symmetry was not supposed to be relevant. Several groups [18–20] using exact diagonalisation methods in cluster calculations had explored the possibility that pairing could result from repulsive interactions. They proposed the following definition of the energy of the pair relative to independent holes:

$$\Delta = E(N+2) + E(N) - 2E(N+1), \tag{4}$$

where $E(N)$ is the ground state energy of the cluster with N holes. A negative Δ means that the ionisation potential decreases with increasing the number of holes, and this may be taken as an indication of pairing. Several clusters were studied for $N = 2$. It turned out that $\Delta < 0$ is possible only outside the physical range of parameters (the off-site U between Cu and O should be too large (about 5 eV) and $|\varepsilon_p - \varepsilon_d|$ too small). Ogata and Shiba [21,22] studied the Cu_4O_4 cluster and found that $\Delta < 0$ is possible for $U_p = 0$ but the effect disappears if the repulsion on O is allowed. Moreover, even when $\Delta < 0$, the physical interpretation was far from obvious; it *could* be pairing, but there was no clear-cut reason for excluding the formation of hole bags, or phase separation. Also, interestingly, Mazumdar *et al.* [23] argued that $\Delta < 0$ could be an artifact due to the neglect of the degrees of freedom of the nuclei: when they are free to move, the state with $N + 1$ holes could gain enough energy from Jahn-Teller distortion that Δ could turn out to be positive, after all. Thus, the relevance of the cluster calculation to the problem of pairing was very unclear.

Later, we pointed out [14] that a couple of key ingredients were missing, namely, symmetry and $W = 0$ pairs. $W = 0$ pairs are two-hole eigenstates of the kinetic energy H_0 that are also eigenstates of the on-site repulsion term W with eigenvalue 0. There is no on-site repulsion barrier to overcome in $W = 0$ pairs. In the full plane, each Cu site is the center of the symmetry operations of the C_{4v} group. Only the fully symmetric clusters centered on a Cu ion have the same point symmetry as the plane and allow $W = 0$ pairs. The planar lattice structure is also essential, because no $W = 0$ pairs occur in 3D or in

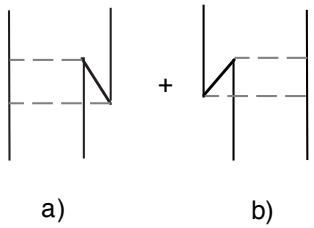

Fig. 1. The second-order diagrams for the two-hole amplitude.

a continuous model, where the interaction term (3) becomes a contact term. We started [14] by the above definition of Δ, and studied the fully symmetric clusters with up to 21 atoms by exact diagonalisation; Δ was found to be negative when (and only when) the two least bound holes formed a $W = 0$ pair. The Hamiltonian had been parametrised by electron spectroscopy studies [24] and *ab initio* calculations [25], and we used literature values. We also considered first-neighbor off-site interactions [14]. The O-O hopping can change the order of single-hole levels, thereby changing the occupation number necessary to get a partially occupied degenerate state; however, when the conditions are satisfied, the $\Delta < 0$ behavior results without important modifications. The first neighbor off-site Cu-O interactions were found to enhance the effect; the first neighbor off-site O-O interactions unpair it, but their effect is small if the recommended values of the parameters are used. In the present paper, such terms are dropped for the sake of simplicity, since they are not essential for our present scope. Recent calculations by Schüttler *et al.* [26], based on a combination of diagrammatic and Quantum Monte Carlo methods on an Extended Hubbard Model, support the present view that the screened interaction is attractive and the attraction is robust against the long-range part of the Coulomb repulsion.

In the fully symmetric Cu-O clusters a genuine pairing takes place, due to an effective interaction which is attractive for singlets and repulsive for triplets. Let us summarize why this conclusion is free from the ambiguity pointed out in reference [23]. First, we computed Δ for our clusters by second-order ground state energy diagrams (modified for degenerate ground states, when appropriate) [27]. It is convenient to denote the hole orbitals by their symmetry labels, with b for b_1 and a, (a') for the occupied (empty) orbitals of a_1 symmetry: we obtained

$$\Delta^{(2)} = -2\left[\sum_b \frac{W(a,b,x,x)^2}{(\varepsilon_b - \varepsilon_a)} - \sum_{a'} \frac{W(a,a',x,x)^2}{(\varepsilon_{a'} - \varepsilon_a)}\right], \tag{5}$$

where ε_a is the one-hole energy of the a orbital and so on; the sums run over all empty states of the appropriate symmetries and involve the matrix elements of the on-site interaction W. No contributions arise to second-order from the empty states of e symmetry since the relevant matrix elements vanish.

Second, we computed to second-order the two-hole amplitude for holes of opposite spins in the degenerate (x, y) orbitals. The only contributions are the second-order diagrams of Figure 1.

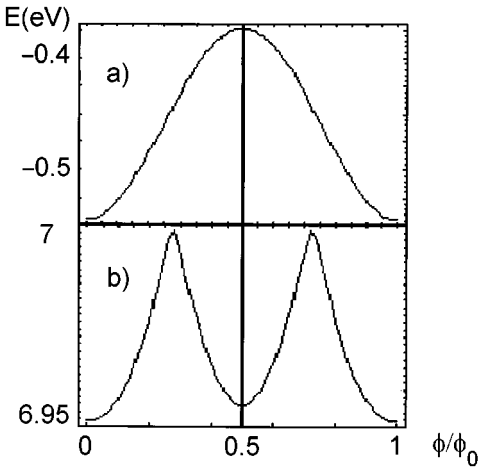

Fig. 2. Flux dependence of the ground state energy, with (in eV) $t = 1.2$, $\varepsilon_p - \varepsilon_d = 3.5$, $U_p = 6$, $U_d = 5.3$; a small O-O hopping ($t_{ox} = -0.05$) ensures a closed path for the screening current. a) CuO_4 with 2 holes (Zhang-Rice singlet) b) CuO_4 with 4 holes. ϕ is the flux within each CuO_2 plaquettes.

The system makes virtual transitions to 4-body (3 holes and 1 electron) states. We demonstrated that this produced an effective interaction, which pushes down the singlet and up the triplet by $|\Delta^{(2)}|$. In this way, Δ can be redefined without any reference to the ground state of clusters with a different number of holes, and we are free from the objections based on the Jahn-Teller distortion of odd-N clusters. Good agreement between the second-order calculation and the numerical exact diagonalisation results supported the interpretation. Thus, the cluster calculations [28–30] showed that $W = 0$ pairs are the "bare" quasiparticles that, when "dressed", become a bound state.

Inserting 4 flux tubes ϕ at the centre of the allowed clusters, the rotations of C_{4v} continue to be symmetry operations but every reflection σ of C_{4v} must be replaced by $K\sigma$, where K is the complex-conjugate operation reversing the field. We have computed the ground state energy of the clusters (up to 21 atoms) as a function of the magnetic flux ϕ by exact diagonalisation [27,31]. Due to the smallness of the system under study, the hopping parameters that contribute a closed path around the central Cu must be kept very small to prevent the magnetic perturbation from growing large and destroying the structure of the ground state multiplet. The energy $E(\phi)$ is trivially a periodic function of ϕ with period the flux quantum ϕ_0, since such a change of the flux involves a Gauge transformation. If E has two deep minima at zero flux and at $\phi_0/2$, separated by large barriers, that is the signature of superconducting flux-quantisation. We found that this happens when (and only when) the filling is such to ensure $W = 0$ pairing. Remarkably, this phenomenon, like the negative-Δ, is already displayed by CuO_4, which is the smallest allowed cluster. The lowest one-hole level in that cluster is nondegenerate. Placing two holes there one forms the so-called Zhang-Rice singlet [32], which does not have the $W = 0$ property. The next one-hole level is degenerate,

and allows a $W = 0$ pair [14]; the 4-hole ground state yields the negative Δ. In Figure 2, we present the contrasting behaviour of $E(\phi)$ in both cases. While in case b) the $W = 0$ pair causes pairing and superconducting flux-quantisation, in case a) there is no pairing and flux is quantized trivially.

In the above example and in the bigger allowed clusters discussed in references [27,31], the two minima in $E(\phi)$ are of comparable depth. This suggests an interpretation of the flux quantization property which is based again on symmetry arguments. Indeed, an arbitrary magnetic flux causes a reduction of the symmetry of the Hamiltonian and a splitting of the degenerate levels. In such conditions, the $W = 0$ pairs do not exist any more and the first-order hole-hole repulsion causes an increase of the ground-state energy. This is seen as the barrier separating the two minima. The $W = 0$ pairs are again allowed at $\phi = \phi_0/2$. This is clearly related to an enhanced symmetry; in fact, the K operation, which reverses the magnetic field, is then equivalent to the Gauge transformation taking from $-\phi_0/2$ to $\phi_0/2$. These problems will be discussed in more detail in a future publication.

3 "W = 0" pairs and flux quantisation in the plane

The eigenstates of

$$H_0\psi^{(\nu)}(k,r) = \varepsilon^{(\nu)}(k)\,\psi^{(\nu)}(k,r) \tag{6}$$

where ν is a band index, are written according to Bloch's theorem

$$\psi^{(\nu)}(k,r) = \mathrm{e}^{\mathrm{i}kr}\phi^{(\nu)}(k,r), \tag{7}$$

where ϕ is periodic. If $r = 0$, $r = a$ and $r = b$ are the positions of Cu and of the two oxygens, respectively, the non-bonding band is characterized by $\phi^{(\mathrm{nb})}(k,0) = 0$; one then finds

$$\phi^{(\mathrm{nb})}(k,a) = \frac{\cos\left[\frac{k_x d}{2}\right]}{\sqrt{N_\mathrm{C}\left(\cos^2\left[\frac{k_x d}{2}\right] + \cos^2\left[\frac{k_y d}{2}\right]\right)}}, \tag{8}$$

$$\phi^{(\mathrm{nb})}(k,b) = \frac{\cos\left[\frac{k_y d}{2}\right]}{\sqrt{N_\mathrm{C}\left(\cos^2\left[\frac{k_x d}{2}\right] + \cos^2\left[\frac{k_y d}{2}\right]\right)}}, \tag{9}$$

where N_C is the number of cells in the crystal and d the lattice parameter. For the other bands, one obtains the eigenvalue equation

$$\varepsilon^{(\pm)}(k) = \frac{\varepsilon_p \pm r}{2} \tag{10}$$

(+ for the antibonding and - for the bonding band), with

$$r = \sqrt{\varepsilon_p^2 + 16t^2\left[\cos^2\left[\frac{k_x d}{2}\right] + \cos^2\left[\frac{k_y d}{2}\right]\right]} \tag{11}$$

Table 1. The character table of the C_{4v} Group.

C_{4v}	E	C_2	$2C_4$	2σ	$2\sigma'$	
A_1	1	1	1	1	1	x^2+y^2
A_2	1	1	1	−1	−1	R_z
B_1	1	1	−1	1	−1	x^2-y^2
B_2	1	1	−1	−1	1	xy
E	2	−2	0	0	0	(x,y)

from which it is possible to compute the Cu and O amplitudes.

The number of holes per spin per unit cell below E_F in the bonding band above half filling is

$$N(E_\mathrm{F}) = \left(\frac{d}{2\pi}\right)^2 \iint \mathrm{d}^2k\,\theta\left(E_\mathrm{F} - \varepsilon(k)\right) \tag{12}$$

differentiating, one finds the density of states

$$\rho(\varepsilon) = \frac{\varepsilon_p - 2\varepsilon}{2\pi^2 t^2}\int_{\arccos[q+1]}^{\pi} \frac{\mathrm{d}x}{\sqrt{1-(q-\cos(x))^2}}, \tag{13}$$

where

$$q = q(\varepsilon) = \frac{\varepsilon(\varepsilon-\varepsilon_p)}{2t^2} - 2. \tag{14}$$

Taking care of the singularity of the integrand at the lower limit, this expression is convenient for the numerical evaluation, and shows a logarithmic singularity at half filling (Van Hove singularity). Fourier transforming the fermion fields by means of the Bloch function previously introduced we can write

$$c_\sigma^\dagger(r_i) = \sum_{k,\nu} c_{k,\nu,\sigma}^\dagger \psi_\sigma^{(\nu)*}(k,r_i), \tag{15}$$

where k runs over the BZ and ν over bands.

Omitting the band indices, we shall denote by

$$d[k] = \|k_+, -k_-\| = c_{k,+}^\dagger c_{-k,-}^\dagger|\mathrm{vac}\rangle \tag{16}$$

a two-hole determinantal state derived from the k eigenfunctions. Since $\phi(-k,r) = \phi(k,r)$, as is required by time-reversal symmetry, $d[k]+d[-k]$ is singlet while $d[k]-d[-k]$ is triplet.

The point symmetry Group of the Cu-O plane is C_{4v}, whose character Table is shown in Table 1.

We introduce the determinants $Rd[k] = d[Rk] = d[k_R]$, $R \in C_{4v}$, and the projected states

$$\Phi_\eta[k] = \frac{1}{\sqrt{8}}\sum_{R\in C_{4v}} \chi^{(\eta)}(R)\,Rd[k] \tag{17}$$

where $\chi^{(\eta)}(R)$ is the character of the operation R in the Irreducible Representation (Irrep) η. In non-degenerate Irreps, the operations that produce opposite k_R have

the same character, and the corresponding projections lead to singlets. The explicit form for $\eta = {}^1B_2$, ${}^1A_2$ is

$$\begin{aligned}\Phi_{^1B_2}[k,r_1,r_2] = \frac{\chi_0}{\sqrt{2}}\{&\cos[k(r_1-r_2)]\,\phi(k,r_1)\,\phi(k,r_2)\\ &-\cos[k_{C_4}(r_1-r_2)]\,\phi(k_{C_4},r_1)\,\phi(k_{C_4},r_2)\\ &-\cos[k_\sigma(r_1-r_2)]\,\phi(k_\sigma,r_1)\,\phi(k_\sigma,r_2)\\ &+\cos[k_{\sigma'}(r_1-r_2)]\,\phi(k_{\sigma'},r_1)\,\phi(k_{\sigma'},r_2)\}\end{aligned} \quad (18)$$

and

$$\begin{aligned}\Phi_{^1A_2}[k,r_1,r_2] = \frac{\chi_0}{\sqrt{2}}\{&\cos[k(r_1-r_2)]\,\phi(k,r_1)\,\phi(k,r_2)\\ &+\cos[k_{C_4}(r_1-r_2)]\,\phi(k_{C_4},r_1)\,\phi(k_{C_4},r_2)\\ &-\cos[k_\sigma(r_1-r_2)]\,\phi(k_\sigma,r_1)\,\phi(k_\sigma,r_2)\\ &-\cos[k_{\sigma'}(r_1-r_2)]\,\phi(k_{\sigma'},r_1)\,\phi(k_{\sigma'},r_2)\},\end{aligned} \quad (19)$$

where χ_0 is a singlet spin function. Using the Bloch states one can verify that both vanish for $r_1 = r_2$. This means that the two-holes singlet states (18, 19) are simultaneously eigenfunctions of H_0, with eigenvalue $2\varepsilon_-(k)$, and of W, with eigenvalue 0. These are the $W = 0$ pairs, like those studied previously [27], but with an important change, since in the cluster calculations the symmetry of the $W = 0$ pairs were found [31] to be ${}^1B_2$ and ${}^1A_1$. The reason for this change is a two fold size effect. On one hand, ${}^1A_1$ pairs have the $W = 0$ property only in the small clusters, having the topology of a cross, where the symmetry Group is S_4, but do not generalize as such to the full plane, where the symmetry is lowered to C_{4v}; on the other hand, small clusters admit no solutions of ${}^1A_2$ at all.

One necessary condition for pairing in clusters is that the least bound holes form such a pair, and this dictates conditions on the occupation number. In the full plane, as we have seen, $W = 0$ pairs exist for any filling. All the distinct $W = 0$ pairs of each symmetry may be labeled from the k points in 1/8 of the empty part of the BZ: for instance, those with $k_x > k_y > 0$. We shall denote such a region by $e/8$.

As already noted $W = 0$ pairs exist only in planar lattice structure with a certain point symmetry Group. So we expect that the CuO_2 geometry is not the only one where $W = 0$ property is present. In the following we want to show that in the simple Hubbard model also, where the point symmetry Group is still C_{4v}, we can build $W = 0$ pairs and that they continue to exist even in the presence of magnetic field if and only if the magnetic flux is quantized in units of $\phi_0/2$. Let us start with the one-body Hamiltonian

$$H_0 = \frac{t}{2}\sum_{(i,j)}(c_i^\dagger c_j + \text{h.c.}) + M\sum_i c_i^\dagger c_i \quad (20)$$

where (i,j) stands for nearest neighbors. We take the x, y axes parallel to the bonds and fold the plane on itself after N lattice spacings in both directions, forming the torus shown in Figure 3. Since we are dealing with complex fermion fields, the most general boundary conditions are

$$c_{i+\tau_a} = \mathrm{e}^{\mathrm{i}\alpha}c_i \qquad c_{i+\tau_b} = \mathrm{e}^{\mathrm{i}\beta}c_i \quad (21)$$

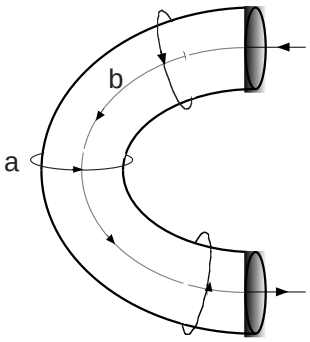

Fig. 3. The geometry of the Torus and of the magnetic field used to discuss the flux quantisation properties of the $W = 0$ pairs.

where τ_a and τ_b are the torus periods. The fermions fields can then be expanded as

$$c_j = \frac{1}{N}\sum_k \mathrm{e}^{\frac{2\pi\mathrm{i}}{N}(k+\tau)j}c_k \quad (22)$$

with $\tau = (\alpha/2\pi, \beta/2\pi)$. Turning on a constant magnetic field $B = (B_a, B_b)$, the flux through a circular surface $S_{a,b}$ of radius $r = Nd/2\pi$, with d lattice spacing, perpendicular to the (b,a) direction will be

$$\phi_{a,b} = \int_{S_{a,b}} B\,n\,\mathrm{d}\sigma = \oint_{\partial S_{a,b}} A\,\mathrm{d}l = 2\pi r A_{a,b} \quad (23)$$

with n the surface versor. The above equation enables us to compute, using the Peierls prescription, how the presence of this particular constant magnetic field changes the original Hamiltonian H_0. The final result is

$$\begin{aligned}H_0 \to H = \frac{t}{2}&\sum_{(i,j)_a}(\mathrm{e}^{\frac{2\pi\mathrm{i}}{N}(\phi_a/\phi_0)}c_i^\dagger c_j + \text{h.c.})\\ &+\sum_{(i,j)_b}(\mathrm{e}^{\frac{2\pi\mathrm{i}}{N}(\phi_b/\phi_0)}c_i^\dagger c_j + \text{h.c.}) + M\sum_i c_i^\dagger c_i\end{aligned} \quad (24)$$

where $(i,j)_{a,b}$ are two nearest neighbor sites along the (a,b) direction. The spectrum of the new Hamiltonian is the same of the original one if

$$\alpha \to \alpha + 2\pi\frac{\phi_a}{\phi_0} \qquad \beta \to \beta + 2\pi\frac{\phi_b}{\phi_0}\,. \quad (25)$$

In this sense we can say that a change in boundary conditions is the same of turning on gauge fields [33]. Off course the choice which physically corresponds to the unperturbed infinite plane is $\alpha = \beta = 0$ (Born-von Karman boundary conditions).

Denoting with

$$\begin{matrix}\mathrm{e}^{\mathrm{i}\alpha}\\ \mathrm{e}^{\mathrm{i}\beta}\ \square\ \phi_b\\ \phi_a\end{matrix} \quad (26)$$

the configuration for which the boundary conditions are $e^{i\alpha}$ and $e^{i\beta}$ and the flux is ϕ_a and ϕ_b along the the a and b direction respectively, explicit calculations show that for the Hamiltonian (24) $W = 0$ pairs of $^1A_2$, $^1B_2$ and $^1B_1$ symmetry exist if and only if one of the following configurations is realized

$$\begin{array}{ccc} & e^{i\alpha} & \\ e^{i\beta} & \square & \frac{\phi_0}{2}\left(n_\beta - \frac{\beta}{\pi}\right) \\ & \frac{\phi_0}{2}\left(n_\alpha - \frac{\alpha}{\pi}\right) & \end{array} \tag{27}$$

with $(-1)^{n_\alpha} = (-1)^{n_\beta}$.

From (27) we see that only two configurations allow for $W = 0$ pairs in absence of magnetic field; they correspond to choosing boundary conditions both periodic or antiperiodic along two orthogonal directions. With such boundary conditions $W = 0$ pairs exist even in a magnetic field if and only if the flux is quantised in multiples of half the fundamental fluxon. For any other choice of boundary conditions, flux is still quantised in a similar manner, but we need a zero point flux in order to have $W = 0$ pairs, so that they do not exist at zero magnetic field. If we assume dressed $W = 0$ pairs to be quasiparticles of the superconducting phase, then flux is quantized in a superconducting way. In the following we will prove rigorously that this is the case, by studying the role of $W = 0$ pairs in the many-body problem and showing how they become a genuine bound state by means of the electronic correlation.

4 Canonical transformation

In the Cooper theory [34], an effective interaction involving phonons is introduced *via* an approximate canonical transformation. In the Three-Band Hubbard Model, the holes can exchange particle-hole pairs, and more complex electronic excitations, rather than phonons, but one can approach the problem in a similar way. Suppose we add two holes to a background Fermi *sphere*. We use Roman indices for the zeroth-order pair states, which satisfy

$$H_0 |m\rangle = E_m |m\rangle \tag{28}$$

with $E_m = 2\varepsilon(m)$. The basic idea here is that of obtaining an effective interaction for two holes using the process of the diagrams in Figure 1. Accordingly, the pair states are coupled to the set of 3 hole-1 electron intermediate states, which satisfies

$$H_0 |\alpha\rangle = E_\alpha |\alpha\rangle . \tag{29}$$

Thus, the effect of the perturbation is of the form

$$W |m\rangle = \sum_{m'} |m'\rangle W_{m',m} + \sum_{\alpha} |\alpha\rangle W_{\alpha,m} \tag{30}$$

where $W_{m',m}$ stands for the interaction between pairs, while α is the set of 3 hole-1 electron intermediate states which are coupled to the pairs by the diagram; in addition,

$$W |\alpha\rangle = \sum_{m} |m\rangle W_{m,\alpha}. \tag{31}$$

The off-diagonal $W_{m',m}$ elements vanish for $W = 0$ pairs; on the other hand, in the many-body problem, the diagonal elements $W_{m,m}$ do not vanish, because of the tadpole-diagram contributions to the self-energy of the holes. However, the diagonal terms do not contribute to the effective interaction, but simply renormalize the ε parameters in H_0. We had already met these tadpole diagrams in the calculation of $\Delta^{(2)}$ for clusters [27] where they were seen to cancel in the calculation of (4). Anyway, we keep $W_{m',m}$ in (30) which allows to introduce the effects of other interactions which are not included in the Hubbard model. If W is a "small" operator, we can keep a strict analogy with the Cooper theory, and look for an approximate canonical transformation such that the new Hamiltonian $\tilde{H}$ decouples the α states to first order; then, $\tilde{H}$ operates on the space of pairs. In other terms, we seek a first-order anti-Hermitean operator Λ such that

$$\tilde{H} = e^{-\Lambda} H e^{\Lambda} \tag{32}$$

has no linear term connecting the $|\alpha\rangle$ states with the $|m\rangle$ states. The α states are 3 hole-1 electron determinants which carry no quasi-momentum. We write

$$|\alpha\rangle = |\,\|(k' + q + k_2)_+, \bar{k}_{2-}, -q_-, -k'_-\|\rangle \tag{33}$$

where $\bar{k}_{2+}$ is the electron state and subscripts refer to the spin direction; α states with opposite spin indices arise from the specular diagram, contribute similarly and yield a factor of 2 at the end. The unperturbed eigenvalues are:

$$E_\alpha = \varepsilon(k' + q + k_2) - \varepsilon(k_2) + \varepsilon(q) + \varepsilon(k') . \tag{34}$$

This approach is developed in reference [15]. One calculates the interaction matrix element:

$$\begin{aligned} \langle \|(k' + q + k_2)_+, \bar{k}_{2-}, -q_-, -k'_-\| \, |W| d[s]\rangle = \\ \delta(q - s)\, U(q + k' + k_2, -k', s, k_2) \\ - \delta(k' - s)\, U(q + k' + k_2, -q, s, k_2) \end{aligned} \tag{35}$$

and ends up with

$$\tilde{H} = H_0 + F + \tilde{W}_{\text{eff}}, \tag{36}$$

where F is diagonal in the pair space, like H_0, and corresponds to the unlinked self-energy diagrams, while the effective interaction operator is $\tilde{W}_{\text{eff}}$. The interaction between determinantal states (with s and p empty) turns out to be

$$\begin{aligned} \langle d[p]| \tilde{W}_{\text{eff}} |d[s]\rangle = 2 \sum_{k}^{\text{occ}} \theta(\varepsilon(s + p + k) - E_{\text{F}}) \\ \times U(s + p + k, -p, s, k)\, U(p, k, s + p + k, -s) \\ \times \left\{ \frac{1}{\varepsilon(s + p + k) - \varepsilon(k) - \varepsilon(s) + \varepsilon(p)} \right. \\ \left. + \frac{1}{\varepsilon(s + p + k) - \varepsilon(k) - \varepsilon(p) + \varepsilon(s)} \right\}. \end{aligned} \tag{37}$$

The interaction between symmetry projected states is then obtained using (17, 37) and is given by

$$\langle \Phi_\alpha [p]| \tilde{W}_{\rm eff} |\Phi_\alpha [s]\rangle = \sum_R \chi^{(\alpha)}(R) \Big\langle d[p] \Big| \tilde{W}_{\rm eff} \Big| Rd[s] \Big\rangle . \tag{38}$$

The above approximate canonical transformation assumes that W be "weak". When the levels form a continuum, its applicability is far from obvious. Perturbation theory may be safe if carried out to all orders. The expansion of Λ can be continued systematically to produce the perturbation series. Including all the diagrams of a generalized RPA would lead to something like the well-known FLEX approximation [7] whose implications for the superconductivity in the three-band Hubbard model have been explored recently in a series of papers [8]. The fact that both expansions about the weak and strong coupling [13] limits lead to pairing and superconductivity is certainly suggestive, but the mechanism of pairing is best understood by realizing the key rôle of $W = 0$ pairs in this problem. They strongly help intuition. Moreover, the properties of $W = 0$ pairs rest on symmetry and are largely model-independent. Here, we wish to take advantage of that to propose a non-perturbative approach to pairing based on a different way of performing the canonical transformation. This puts the theory on a clearer and firmer basis.

Suppose the Cu-O plane is in its ground state with Fermi energy $E_{\rm F}$ and a couple of extra holes are added. We wish to show that by a canonical transformation [16] one obtains an effective Hamiltonian which describes the propagation of a pair of *dressed* holes, and includes *all* many-body effects.

The exact many-body ground state with two added holes may be expanded in terms of excitations over the vacuum (the non-interacting Fermi *sphere*) by a configuration interaction:

$$|\Psi_0\rangle = \sum_m a_m |m\rangle + \sum_\alpha b_\alpha |\alpha\rangle + \sum_\beta c_\beta |\beta\rangle + ... \tag{39}$$

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), and so on. To set up the Schrödinger equation, we consider the effects of the operators on the terms of $|\Psi_0\rangle$. We write:

$$H_0|m\rangle = E_m|m\rangle,\ H_0|\alpha\rangle = E_\alpha|\alpha\rangle, ... \tag{40}$$

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

$$W|m\rangle = \sum_{m'} W_{m',m}|m'\rangle + \sum_\alpha |\alpha\rangle W_{\alpha,m} + \sum_\beta |\beta\rangle W_{\beta,m}. \tag{41}$$

As explained in the previous Section, $W_{m',m}$ does not contribute to the effective interaction for $W = 0$ pairs in our model; however we keep it for the sake of generality. It allows to introduce the effect of the exchange of phonons and other quasiparticles that we are not considering. For clarity let us first write the equations that include explicitly up to 6-body states; then we have

$$W|\alpha\rangle = \sum_m |m\rangle W_{m,\alpha} + \sum_{\alpha'} |\alpha'\rangle W_{\alpha',\alpha} + \sum_\beta |\beta\rangle W_{\beta,\alpha} \tag{42}$$

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

$$W|\beta\rangle = \sum_{m'} |m'\rangle\, W_{m',\beta} + \sum_\alpha |\alpha\rangle\, W_{\alpha,\beta} + \sum_{\beta'} |\beta'\rangle\, W_{\beta',\beta}. \tag{43}$$

In principle, the $W_{\beta',\beta}$ term can be eliminated by taking linear combinations of the complete set of β states: when this is done, we get a self-energy correction to E_β and a mixing of the vertices, without altering the structure of the equations. The Schrödinger equation yields equations for the coefficients a, b and c

$$(E_m - E_0)\, a_m + \sum_{m'} a_{m'} W_{m,m'} + \sum_\alpha b_\alpha W_{m,\alpha} + \sum_\beta c_\beta W_{m,\beta} = 0 \tag{44}$$

$$(E_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} W_{\alpha,m'} + \sum_{\alpha'} b_{\alpha'} W_{\alpha,\alpha'} + \sum_\beta c_\beta W_{\alpha,\beta} = 0 \tag{45}$$

$$(E_\beta - E_0)\, c_\beta + \sum_{m'} a_{m'} W_{\beta,m'} + \sum_{\alpha'} b_{\alpha'} W_{\beta,\alpha'} = 0 \tag{46}$$

where E_0 is the interacting ground state energy. Then, we exactly decouple the 6-body states by solving the equation for c_β and substituting into (44, 45), getting:

$$(E_m - E_0)\, a_m + \sum_{m'} a_{m'} \left[W_{m,m'} + \sum_\beta \frac{W_{m,\beta} W_{\beta,m'}}{E_0 - E_\beta} \right] + \sum_\alpha b_\alpha \left[W_{m,\alpha} + \sum_\beta \frac{W_{m,\beta} W_{\beta,\alpha}}{E_0 - E_\beta} \right] = 0 \tag{47}$$

$$(E_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} \left[W_{\alpha,m'} + \sum_\beta \frac{W_{\alpha,\beta} W_{\beta,m'}}{E_0 - E_\beta} \right] + \sum_{\alpha'} b_{\alpha'} \left[W_{\alpha,\alpha'} + \sum_\beta \frac{W_{\alpha,\beta} W_{\beta,\alpha'}}{E_0 - E_\beta} \right] = 0. \tag{48}$$

Thus we see that the rôle of 6-body states is just to renormalize the interaction between 2-body and 4-body ones, and for the rest they may be forgotten. 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. In principle, the method 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 by taking linear combinations of the α states: when this is done, we get a self-energy correction to E_α and a mixing of the $W_{m,\alpha}$ vertices. Denoting W' and E' the renormalised quantities, which can be determined by the procedure outlined above, the equations become

$$(E'_m - E_0)\, a_m + \sum_{m'} a_{m'} W'_{m,m'} + \sum_{\alpha} b_\alpha W'_{m,\alpha} = 0 \quad (49)$$

$$(E'_\alpha - E_0)\, b_\alpha + \sum_{m'} a_{m'} W'_{\alpha,m'} = 0. \quad (50)$$

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

$$(E_0 - E'_m)\, a_m = \sum_{m'} a_{m'} \left\{ W'_{m,m'} + \langle m|S[E_0]|m'\rangle \right\}, \quad (51)$$

where

$$\langle m|S\left[E_0\right]|m'\rangle = \sum_{\alpha} \frac{\langle m|W'|\alpha\rangle\langle\alpha|W'|m'\rangle}{E_0 - E'_\alpha}\,. \quad (52)$$

Equation (51) is of the form of a Schrödinger equation with eigenvalue E_0 for pairs with an effective interaction $W + S$. Then we 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 the canonical transformation which generalizes the second-order one to all orders. In the new picture, the holes interact through an effective vertex with infinitely many contributions, some of which are shown in Figure 4. The linked contributions represent repeated exchange of electron-hole pairs, and may contain self-energy insertions; all these contributions make up the effective interaction. The unlinked diagrams are pure self-energy. Thus, the scattering operator S is of the form $S = W_{\text{eff}} + F$, where W_{eff} is the effective interaction between dressed holes, while F is a forward scattering operator, diagonal in the pair indices m, m' which accounts for the self-energy corrections of the one-body propagators: it is evident from (51) that it just redefines the dispersion law E'_m. Therefore F must be dropped, as in Cooper theory [34]. So, letting $a = \sum_m a_m |m\rangle$, the effective Schrödinger equation for the pair reads

$$\left(H_0 + W' + W_{\text{eff}}\right)|a\rangle = E_0|a\rangle \quad (53)$$

and we are interested in the possibility that $E_0 = 2E_{\text{F}} - |\Delta|$, with a positive binding energy $|\Delta|$ of the pair. 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_{eff}.

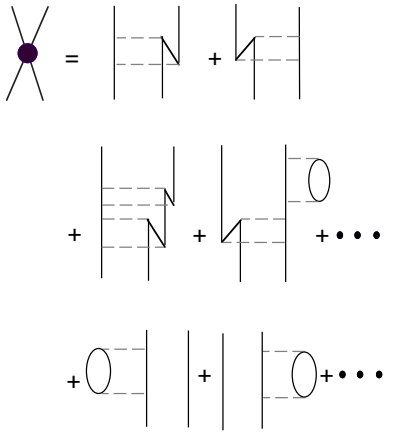

Fig. 4. Some terms of the infinite expansion of the effective hole-hole vertex (blob) defined by $\tilde{H}$. The dashed lines represent renormalised W' two-body interactions. Only 2-body and 4-body intermediate states appear. Linked diagrams belong to $\tilde{W}_{\text{eff}}$, and unlinked ones to F.

We emphasized the fact that in principle the canonical transformation is exact because in this way our framework does not require U/t to be small. In the numerical calculations, some approximation is needed. Below, we shall compute the bare quantities; that is, we shall neglect the 6-body and higher excitations in the calculation of W_{eff} and drop the W' term of equation (53) for $W = 0$ pairs. This is a reasonable approximation if we compute small corrections to a Fermi liquid background. However the structure of the solution is exact when expressed in terms of renormalized matrix elements, and the process can be systematically improved, as outlined above. The α states are those of equation (33) and the interaction matrix element is given in equation (35). Working out (52) we find that the product in the numerator yields 4 terms; two are proportional to $\delta(p-s)$ and belong to F, while the cross terms yield identical contributions to W_{eff}. Thus we obtain the following effective interaction between $W = 0$ pairs:

$$\langle \Phi_\eta\left[p\right]|\, W_{\text{eff}}\, |\Phi_\eta\left[s\right]\rangle = 4 \sum_{R\in C_{4v}} \chi^{(\eta)}\left(R\right) \sum_{k}^{\text{occ}} \theta\left(\varepsilon\left(Rs+p+k\right) - E_{\text{F}}\right) \times \frac{U\left(Rs+p+k, -p, Rs, k\right) U\left(p, k, Rs+p+k, -Rs\right)}{\varepsilon\left(Rs+p+k\right) - \epsilon\left(k\right) + \epsilon\left(s\right) + \epsilon\left(p\right) - E_0}\,. \quad (54)$$

The sum is over occupied k with empty $Rs + p + k$. Note that W_{eff} does not depend on the sign of U. We may see that perturbation theory yields the arithmetical mean of the two unperturbed limits $E_0 \to 2\varepsilon\left(p\right)$ and $E_0 \to 2\varepsilon\left(s\right)$. The diagonal elements of (54) are also clearly related to the $\Delta^{(2)}$ expression derived from perturbation theory for the fully symmetric clusters [27], which are special cases of the present theory. The expressions (5, 38, 54) are characterized by the symmetry-induced quantum mechanical interference of several terms. The sum can be positive or negative depending on the Irrep. This interference

produces a partial cancellation, and the absolute value of the result is typically much smaller than individual contributions. This explains why the interaction is dynamically small for $W = 0$ pairs: they have no direct interaction, and because of the interference the effective interaction is reduced compared to what one could expect by a rough order-of-magnitude estimate. However, the presence of the θ functions and the anisotropy of the integrands prevent a total cancellation.

In (5), the vanishing of the denominators is prevented by the discrete spectrum of the cluster; however, when applying (38) to the plane the integrand is singular. This complication disappears in the full expression (54) since we are interested in bound pairs; then, E_0 is below the continuum and the denominators never vanish.

The s and p indices run over 1/8 of the BZ. We denote such a set of empty states $e/8$, and cast the result in the form of a (Cooper-like) Schrödinger equation

$$2\varepsilon(k)\,a(k) + \sum_{k'}^{e/8} W_{\text{eff}}(k,k')\,a(k') = E_0 a(k) \qquad (55)$$

for a self-consistent calculation of E_0 (since W_{eff} depends on the solution). Let N_{C} be the number of cells in the crystal. The U matrix elements scale as N_{C}^{-1} and therefore W_{eff} scales in the same way. For an infinite system, $N_{\text{C}} \to \infty$, this is a well defined integral equation. The existence of a clear-cut continuum limit means that the problem is well posed, but this equation is very difficult to treat analytically. The interaction matrix is complicated by the Umklapp discontinuities, other discontinuities come from the limitations to occupied or empty states, and there are several independent variables since everything is anisotropic. Therefore, we must resort to a numerical treatment. For the sake of simplicity, we shall neglect the minor contributions from the higher bands and consider the dominant intra-band processes, in which empty states belong to the bonding band.

5 Numerical method

Using the analytical expression (Eq. (54)) for the effective interaction in the full plane, we have performed exploratory numerical estimates of Δ by working on supercells of $N_{\text{SC}} \times N_{\text{SC}} = N_{\text{C}}$ cells, with periodic boundary conditions (pbc). Here we solved the problem in a virtually exact way for N_{SC} up to 40. Several good supercell calculations devoted to the problem of pairing have been reported to date [36], but no conclusive evidence was reached, because of the difficulty of dealing with size effects. First, we searched for triplet solutions with negative energy without success, since, as in the clusters, W_{eff} is repulsive for triplets. On the contrary, $W = 0$ singlets did show pairing, in line with our previous findings in small clusters [14,27–30]. We took as input data the set of current parameters, already used for clusters, that is (in eV) $t = 1.3$, ε_p =3.5, $\varepsilon_d = 0$, $U_p = 6s$, $U_d = 5.3s$, where s is a scale factor induced by renormalization. Since screening excitations are explicitly accounted for in the Hamiltonian, it is likely that U is a bare (unscreened) quantity, which justifies $s > 1$. A stronger interaction causes smaller pairs and speeds up convergence within attainable supercell sizes. In Table 2, we report the results for $^1B_2$ pairs at $s = 3/\sqrt{2} = 2.121$ with $E_{\text{F}} = -1.3$ eV (half filling corresponds to $E_{\text{F}} = -1.384$ eV). We see that although $|\Delta|$ decreases monotonically with increasing supercell size, V_{eff} is *not* dropping to 0, but remains fairly stable around 6 to 7 eV. Calculations for $^1A_2$ have also been performed and the results are presented below.

Table 2. Binding energy of $^1B_2$ pairs in supercells.

N_{SC}	n_{tot}	$-\Delta$ (meV)	V_{eff} (eV)	$-\Delta_{\text{asympt}}$ (meV)
18	1.13	121.9	7.8	41.6
20	1.16	42.2	5.0	9.0
24	1.14	59.7	7.0	28.9
30	1.14	56.0	5.7	13.2
40	1.16	30.5	6.6	23.4

6 Uniform interaction model (UIM)

With supercell sizes $N_{\text{SC}} > 40$ calculations become hard. Since we are concerned with the asymptotic behavior for $N_{\text{C}} \to \infty$ and Δ depends on U's and N_{C} in a peculiar way, increasing with N_{C} for large U's and dropping for small U's, we need a simple solvable model in supercells and in the infinite plane to make reliable extrapolations of numerical results. To this end, we define the Uniform Interaction Model (UIM) in which a constant negative interaction $-V$, $V > 0$ prevails for k and k' in $e/8$. In the Cooper formula [34] for the binding energy of the pair,

$$|\Delta_{\text{C}}| = \frac{2\omega_{\text{D}}}{\mathrm{e}^{\frac{1}{V_{\text{C}}\rho_{\text{F}}}} - 1}, \qquad (56)$$

where ρ_{F} is the density of states at the Fermi level, $-V_{\text{C}}$ is a (constant) attractive interaction per cell in a shell of thickness $2\omega_{\text{D}}$ surrounding the Fermi surface; on the other hand, in the UIM no Debye frequency ω_{D} is involved, and all the empty states in $e/8$ contribute to Δ [35]. Both the Cooper and the UIM models can be solved in supercell calculations, and show the same qualitative behavior with increasing N_{C}.

For small N_{C}, Δ is of the same order as V, while in the thermodynamic limit ($N_{\text{C}} \to \infty$), the asymptotic value of Δ ,Δ_{asympt}, can easily be estimated. Setting $W_{\text{eff}} = -V/N_{\text{C}}$, we get from equation (55)

$$(2\varepsilon(k) - E_0)a(k) = \frac{V}{8N_{\text{C}}}\frac{\mathrm{d}^2 N_{\text{C}}}{(2\pi)^2}\int \mathrm{d}k'\, a(k') = C. \qquad (57)$$

Writing $a(k) = C/(2\varepsilon(k) - E_0)$ and $E_0 = 2E_{\text{F}} - |\Delta|$, we obtain

$$\frac{8}{V} = \int_{E_{\text{F}}}^{0} \frac{\mathrm{d}\epsilon\rho(\varepsilon)}{2(\varepsilon - E_{\text{F}}) + |\Delta_{\text{asympt}}|}\,. \qquad (58)$$

Table 3. Effective Cooper parameters for fitting the V dependence of Δ at several E_F values.

E_F(eV)	ω_D(eV)	ρ_F(eV^{-1}/Cell)
−1.35	0.4545	0.0486
−1.3	0.492	0.0415
−1.2	0.520	0.0338
−1.1	0.5237	0.02905

Table 4. Data for $^1B_2$ pairs at $E_F = -1.2$ eV; V_{eff} is in eV.

	$s=$	$\sqrt{2}$	$s=$	$\frac{3}{\sqrt{2}}$	$s=$	$2\sqrt{2}$
N_{SC}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}
12	126	6.75	251.	10.	469.	14.23
20	63.	6.9	135.	10.6	320.5	15.9
30	27.	6.3	198.	13.8	460.	20.8
∞	8.8	6.3	131.	13.8	333.	20.8

Table 5. Data for $^1B_2$ pairs at $E_F = -1.1$ eV; V_{eff} is in eV.

	$s=$	$\sqrt{2}$	$s=$	$\frac{3}{\sqrt{2}}$	$s=$	$2\sqrt{2}$
N_{SC}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}
12	163.	9.	409.	15.7	688.	22.1
20	151.	10.8	371.	17.6	635.5	24.3
30	80.	10.3	270.	17.66	520.	24.9
∞	35.6	10.3	170.8	17.66	362.	24.9

Here, ρ is not a constant, as in the Cooper formula, and its values in the integration range are sensitive to filling; however its order of magnitude does not differ much from the BCS case except at half filling. Good fits can be obtain using the Cooper formula with effective ω_D and ρ_F parameters, like those shown in Table 3.

In Table 4, we consider $^1B_2$ pairs at $E_F = -1.2$ eV and report values of Δ and V_{eff} for supercell calculations at $N_{SC} = 12$, 20 and 30 for 3 values of the scale factor s. The filling is $n_{tot} \sim 1.3$ at $N_{SC} = 30$. Fixing V_{eff} at the value of $N_{SC} = 30$ we calculate Δ_{asympt} for $N_{SC} \to \infty$.

We see that the relatively mild N_{SC} dependence of V_{eff} supports the use of the UIM to extrapolate the results to the thermodynamic limit, and there is a clear indication of pairing with sizable binding energies. The s dependence of V_{eff} is roughly linear, while Δ depends exponentially on s. Table 5 presents the results for $^1B_2$ pairs at $E_F = -1.1$ eV ($n_{tot} \approx 1.4$ at $N_{SC} = 30$). The trend is similar, but V_{eff} is seen to increase with doping. Tables 6 and 7 show the results for the $^1A_2$ pairs. These are seen to lead to bound states as well, with comparable Δ values; the trend with doping is opposite, however, and the gap is nearly closing at $E_F = -1.1$ eV. A necessary condition for superconducting flux quantization is that two kinds of pairs of similar binding energy and different symmetries exist [31]. A similar conclusion was reached independently by other authors [26]. Moreover, evidence of mixed $(s+id)$ symmetry for the pairing state has been amply reported in angle-resolved photoemission studies [37]. This remark leads to the prediction that in this model superconductive pairing disappears with increasing n_{tot}, while a different sort of pairing prevails; in reality the Cu-O plane prefers to distort at excessive doping, and in a distorted plane the present mechanism, based on symmetry, could be destroyed.

Table 6. Data for $^1A_2$ pairs at $E_F = -1.2$ eV; V_{eff} is in eV.

	$s=$	$\sqrt{2}$	$s=$	$\frac{3}{\sqrt{2}}$	$s=$	$2\sqrt{2}$
N_{SC}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}
12	141.	7.2	274.	10.43	423.	13.4
20	46.2	6.5	96.	9.1	158.2	11.4
30	25.9	6.23	64.8	8.8	131.	11.6
∞	8.35	6.23	34.	8.8	81.7	11.6

Table 7. Data for $^1A_2$ pairs at $E_F = -1.1$ eV; V_{eff} is in eV.

	$s=$	$\sqrt{2}$	$s=$	$\frac{3}{\sqrt{2}}$	$s=$	$2\sqrt{2}$
N_{SC}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}	$-\Delta$ (meV)	V_{eff}
12	72.	5.5	144.	8.4	228.	11.
20	10.	2.4	26.5	4.38	61.	6.78
30	5.48	2.5	19.	5.8	45.	8.16
∞	1.5	2.5	2.6	5.8	14.4	8.16

7 Conclusions

We have presented the following evidence that the $W = 0$ pairs are the quasi-particles that, once dressed, play the rôle of Cooper pairs: 1) as two-body states they do not feel the large on-site repulsion, that would come in first-order perturbation in any theory of pairing with any other kind of pairs. 2) The indirect interaction with the background particles gives attraction, and bound states with physically appealing binding energies. 3) The same results are also borne out by exact diagonalisation in finite clusters, if and only if they have the correct symmetry and filling to give raise to $W = 0$ pairs. 4) Both in clusters and in the plane, superconducting flux quantisation results from the symmetry properties of $W = 0$ pairs.

Our framework for the effective interaction between two holes, although it is based on the three-band Hubbard model, is quite general, and is ready to include extra interactions as well, like those due to phonons. An effective Hamiltonian can in principle be obtained by a systematic canonical transformation including any kind of virtual intermediate states. We obtained the closed-form analytic expression of the effective interaction including 4-body virtual states. This describes repeated exchange of an electron-hole pair. The argument does not depend in any way on perturbation theory, and the equations retain their form, with renormalized parameters, at all orders. The previous exact-diagonalisation results of cluster

calculations are special cases. The resulting integral equation (55), with the effective interaction (54), is *valid for the full plane*. Since an analytic treatment is prohibitive, we resort to a numerical treatment. We do so by supercell calculations, but even so, the solution is hard. Depending on the parameters, extremely large supercells are needed to obtain the convergence of the pair energy Δ to the bulk limit; however, we find that precisely the same effect occurs in the UIM where a constant effective interaction V is assumed. We define $V_{\rm eff}$ as the value of V that inserted in the UIM yields the same Δ in supercell calculations as our integral equation. Since $V_{\rm eff}$ converges to the bulk value much more readily, we are able to go to the asymptotic limit, and to show the instability of the Fermi liquid in the model at hand. $\Delta_{\rm asympt}$ values in the range of several tens to a few hundreds of meV are obtained if we multiply the U parameters by a scale factor s which is somewhat larger than 1. The values $U_d = 5.3$ eV, $U_p = 6$ eV differ appreciably from other literature estimates [38], and must depend on the compound and doping. For example, in La_2CuO_4, $U_p = 4$ eV and $U_d = 10.5$ eV have been recommended [39]. However, since the screening excitations are explicitly accounted for in the Hamiltonian, it is reasonable that the input U's must be somewhat larger than the fully screened interaction. Moreover, contributions from phonons and other mechanisms can be included as additive terms of W, and must be relevant for a comparison with experiment. We find that ${}^1A_2$ pairs are more tightly bound close to half filling, but ${}^1B_2$ pairs are favored when the filling increases. We remind the reader here that these symmetry labels are not absolute, but depend on the choice of a gauge convention [40]. We get attraction and pairing at all fillings we have considered (above half filling), but the binding energy of the ${}^1A_2$ pairs drops by orders of magnitude as the filling increases; thus, there is no chance of superconducting flux quantization too far from half filling. So, we do not predict that superconductivity occurs outside some range of hole concentration. However, pairing is still there, even for large doping: since the present mechanism is driven by symmetry it works unless the system distorts. In fact, at excessive dopings the real superconductors develop stripes, and become normal metals. The three-band Hubbard model might be too idealized to allow a detailed comparison with experiments; however we stress that the approach presented is far more general than the model we are using, and can be applied to more realistic Hamiltonians. This is the main result of the present paper.

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40. In comparing these results with those of various calculations from other authors, one should bear in mind that in the three-band Hubbard model for the Cu-O plane different conventions have been widely used in the literature for the phase of orbitals, which are equally possible because of the gauge invariance of the theory. We are using a model Hamiltonian (2), which is simplest because a Cu ion is bonded to the nearest neighbor O by identical hopping integrals t; however, various authors prefer an alternating bond convention, with hopping integrals changing sign for a 90^0 rotation. With to the choice of the gauge, the symmetry labels vary, according to the multiplication table of Irreps of the C_{4v} Group.