Pairing in the Hubbard model: the Cu$_5$O$_4$ Cluster versus the Cu-O plane

Michele Cini, Adalberto Balzarotti, and Gianluca Stefanucci

Istituto Nazionale di Fisica della Materia, Dipartimento di Fisica,
Università di Roma Tor Vergata, Via della Ricerca Scientifica, I-00133
Roma, Italy

We study the Cu$_5$O$_4$ 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 quantisation. 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 quantisation is shown to be a manifestation of symmetry properties that hold for clusters of arbitrary size.
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 \cite{1}, e.g., in the $T'$ structure of (Nd, Ce)$_2$CuO$_4$. The $T'$ structure of this compound is different from the $T$ structure of La$_2$CuO$_4$, but is still characterized by CuO$_2$ planes \cite{3}. 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 \cite{3}. The pairing state of these materials has $d$-wave symmetry, probably mixed with $s$-wave \cite{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 from optimum doping. The model is: $H = H_0 + W$ (1)

where the independent hole hamiltonian reads, in the site representation $H_0 = \sum_{Cu} \varepsilon_d n_d + \sum_{O} \varepsilon_p n_p + t \sum_{n.n.} [c_{i}^\dagger c_{j} + h.c.]$ (2)

where n.n. stands for nearest neighbors \cite{3}. The on-site repulsion Hamiltonian will be denoted by $W = \sum_{i} U_i n_{i+} n_{i-}$ (3)

where $U_i = U_d$ for a Cu site, $U_i = U_p$ for an Oxygen. As in previous work \cite{13}, we use standard parameter values, i.e., $U_d = 5.3$ eV, $U_p = 6$ eV, $t = 1.3$, $\varepsilon_d = 0$, $\varepsilon_p = 3.5$. The hole parameters $U_d = 5.3$ eV, $U_p = 6$ eV differ somewhat from other literature estimates \cite{15}, and must depend on the compound and doping. For La$_2$CuO$_4$, $U_p = 4$ eV and $U_d = 10.5$ eV have been recommended \cite{1}. 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 \cite{7} and leads to pairing and superconductivity in the three-band Hubbard model \cite{3}. 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 \cite{8}; 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 \cite{9}. 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 \cite{10} 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 \cite{12}; they also derived the effective pairing interaction in the same approximation \cite{13} and studied the doping dependence of the superconducting transition temperature \cite{14}.

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 \cite{13,15} 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 realised, 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 diagonalisation of cluster Hamiltonians with up to 21 atoms and 4 holes, we demonstrated \cite{13} 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 \cite{17}. We also considered first-neighbor O-O hopping and off-site interactions \cite{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 dy-
namically small for the dressed quasiparticles. Indeed, by a diagrammatic analysis we demonstrated that low-order perturbation theory is a good approximation to the exact diagonalisation 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 realised in actual Cuprates, from very highly overdoped (as in $CuO_4$) to very low (as in $Cu_2O_16$). 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 idealised 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 generalised the theory of pairing to the full plane [20]. 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 [19] 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 renormalising 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 renormalisations in the final formula; this approximation is fully justified at weak coupling.

In the present paper we extend the analysis of Ref. [18] by diagonalizing the $Cu_3O_4$ 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$_2$CuO$_4$) or two electrons (as in (Nd,Ce)$_2$CuO$_4$), respectively [24]. 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 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 quantisation phenomenon in this cluster.

One reason for considering clusters again, after much excellent work from several authors [23] 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 diagonalisation. Another reason is that we wish to explore the relation of the flux quantisation 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 quantisation property exclusive of small clusters, or is it a general consequence of symmetry?

II. ONE-BODY ENERGY LEVELS OF THE SYMMETRIC 9-SITE CLUSTER

In the hole picture, the one-body energy levels of $Cu_3O_4$ 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.

III. 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 [20]. Omitting the band indices, we shall mean

$$[d[k]] = \langle k_+, -k_- | c_{k,+}^\dagger c_{-k,-}^\dagger | \text{vac} >$$

(4)
to be a two-hole determinantal state derived from the Bloch eigenfunctions \((|\text{vac}>\) 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

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

(5)

where \(\chi^{(\eta)}(R)\) is the character of the operation \(R\) in the Irrep \(\eta\). 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 \((R_i^d \hat{O} R_i = \hat{O})\), and the matrix with elements \(O_{i,j} = <d[k]|R_i^d \hat{O} R_j|d[k']\rangle\), 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

\[
O(\eta, k, k') = \sum_R \chi^{(\eta)}(R) O_R (k, k')
\]

(6)

where

\[
O_R (k, k') = \left< d[k]|\hat{O}|d[k']\right>.
\]

(7)

Thus, omitting the \(k, k'\) arguments, we get in particular

\[
O(1, A_2) = O_E + O_{C_2} + O_{C_4} + O_C
\]

\[
- O_{\sigma_x} - O_{\sigma_y} - O_{\sigma'_x} - O_{\sigma'_y}
\]

(8)

\[
O(1, B_2) = O_E + O_{C_2} - O_{C_4} - O_C
\]

\[
- O_{\sigma_x} - O_{\sigma_y} + O_{\sigma'_x} + O_{\sigma'_y}
\]

(9)

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

Small clusters like \(Cu_{5}O_{4}\) 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

\[
d[x, y] = |x_+ y_-| |\text{vac}>
\]

\[
d[y, x] = |y_+ x_-| |\text{vac}>
\]

(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 (3) is necessary here to get the property. In \(Cu_{5}O_{4}\), 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

\[
\psi(1, B_2) = \frac{d[x, y] + d[y, x]}{\sqrt{2}}
\]

(11)

is an eigenstate of the kinetic energy and of \(W\), belongs to the \(W=0\) eigenvalue and to \(1, B_2\). \(W=0\) pairs of this symmetry and of \(1, A_2\) 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 \(W=0\) 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 \(1, B_2\) and \(1, A_2\) symmetry, namely,

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

(12)

which belongs to \(1, B_2\) and

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

(13)

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

\[
|\psi(1, A_1)\rangle = |bb\rangle
\]

(14)

and

\[
||b_+ b_-|| = |bb|
\]

(15)

are a basis of degenerate eigenstates of \(H_0\) having \(1, A_1\) symmetry. Diagonalising \(W\) in this basis we get two-hole eigenstates of \(H\). The \(2 \times 2\) matrix of \(W\) is:

\[
|W|bb\rangle = |bb\rangle |W|^2 + |bb\rangle |W|^2 + |x^2 + y^2\rangle |W|^2 + |x^2 + y^2\rangle
\]

(16)

The lowest eigenvalue is 0 and the \(W=0\) pair is

\[
|\psi(1, A_1)\rangle = -\sqrt{\frac{2}{3}} |bb\rangle + \sqrt{\frac{1}{3}} |x^2 + y^2\rangle
\]

(17)

This type of \(W=0\) pairs does not exist in the full plane. The upper eigenvalue is \(\frac{3\sqrt{6}}{4}\) and the eigenfunction \(\sqrt{\frac{2}{3}} |bb\rangle + \sqrt{\frac{1}{3}} |x^2 + y^2\rangle\) is strongly affected by the on-site repulsion.
Now consider the $Cu_2O_4$ 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 $|0>$. 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

$$D[x, y] = c_{x,+}^{e}c_{y,-}^{e} |0>$$

in keeping with the notation of Ref. [21], 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 $\alpha$ states, in which one of the background $a$ spin-orbitals is not occupied by holes, and the $\beta$ states in which both background $a$ spin-orbitals are missing. For the $Cu_2O_4$ 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 $m, \alpha$ and $\beta$ 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

$$W(p,q,r,s) = \sum_{i} U_{ip}^{*}(i)q^{*}(i)r(i)s(i).$$

For example, the $m$ state of Equation [13] yields

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

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 readabsorbed 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

$$\langle \|k_{+},k_{-},u_{1} \ldots u_{n}\|W\|k_{+}',k_{-}',u_{1} \ldots u_{n}\rangle = \langle \|k_{+},k_{-}\|W\|k_{+}',k_{-}'\rangle$$

where $k$ is different from $k'$ while $u_{1} \ldots u_{n}$ 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. 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 $H_0$.

### IV. 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 diagonalisation 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.

#### A. First definition: $\Delta$

When working by exact diagonalisation, we consider a cluster with $n_h$ holes; its interacting ground state energy $E_h(n_h)$, obtained with the Hamiltonian of Equations [11], is referenced to the hole vacuum for any $n_h$. In terms of these eigenvalues we define, following references [24, 25],

$$\Delta_h(n_h) = E_h(n_h) + E_h(n_h - 2) - 2E_h(n_h - 1).$$

$\Delta_h(n_h)$ 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 $\Delta$ does not unambiguously imply pairing, and further problems arise [21] 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 Ref. [18], we have shown that in this case $\Delta$ 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, $\Delta_h(n_h)$ is negative and $|\Delta_h(n_h)|$ is the binding energy. These results were obtained by analysing exact diagonalisation results for clusters with $n_h = 4$ by lowest-order perturbation theory. In the present paper, we wish to extend those results to larger $n_h$ by exact diagonalisation and a more powerful analytical method.
B. 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 trasformation that determines the effective two-body Hamiltonian $\tilde{H}$ from the many-body $H$ of Equation (6). We set up the Schrödinger equation for the ground state of the cluster with $n_h$ holes, namely

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle.$$  

(23)

Here, $E_0 \equiv E_h(n_h)$. We take the ground state configuration of the noninteracting $n_h - 2$ system as our vacuum state (the non-interacting Fermi sphere). The exact state of $\Psi_0$ can be expanded in terms of excitations over the vacuum:

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

(24)

where $m$ runs over pair states, $\alpha$ over 4-body states (2 holes and 1 e-h pair), $\beta$ over 6-body states (2 holes and 2 e-h pairs). In $C_{6s}O_4$ with 4 holes, the vacuum is the $a_1^2$ configuration and the expansion terminates with the $\beta$ 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:

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

(25)

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

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

(26)

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

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

(27)

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

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

(28)

The Schrödinger equation (24) yields equations for the coefficients $a, b$ and $c$
\[ (E_\alpha - E_0) b_\alpha + \sum_{m'} a_{m'} W'_{\alpha,m'} + \sum_{\alpha'} b_{\alpha'} W'_{\alpha,\alpha'} = 0 \]  

(37)

If in Equations (32-33) we drop the terms involving the \( \beta \) states, they reduce to the same form as Equations (26-27), except that in the latter equations some quantities are renormalised. 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 \( \alpha \) states. This is achieved by choosing the complete set of \( \alpha \) states in such a way that

\[ (H_0 + W')_{\alpha,\alpha'} = E'_\alpha \delta(\alpha,\alpha'). \]  

(38)

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

\[ (E'_\alpha - E_0) b_\alpha + \sum_{m'} a_{m'} W_{\alpha,m'} = 0 \]  

(39)

Solving Equation (39) for \( b_\alpha \) and substituting in Equation (38) we exactly decouple the 4-body states as well. The eigenvalue problem is now

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

(40)

where

\[ \langle m|S[E_0]|m'\rangle = W_{m,m'} + \sum_{\alpha} \frac{\langle \langle m|W'|\alpha > < \alpha|W'|m'\rangle}{E_0 - E'_\alpha}. \]  

(41)

We introduce the diagonal elements of the \( \alpha \) summation:

\[ F_{m,m} = \sum_{\alpha} \frac{\langle \langle m|W'|\alpha > < \alpha|W'|m\rangle}{E_0 - E'_\alpha}, \]  

(42)

then, Equation (40) becomes

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

(43)

where for \( m \neq m' \)

\[ \langle m|W_{eff}|m'\rangle = W'_{m,m'} + \sum_{\alpha} \frac{\langle \langle m|W'|\alpha > < \alpha|W'|m'\rangle}{E_0 - E'_\alpha}. \]  

(44)

The \( W'_{m,m'} \) term does not arise in Ref. [2] because in the full plane it vanishes by momentum conservation.

Equations (13-14) determine the amplitudes \( a_m \) of the \( m \) states in the \( n_h \)-hole state and the ground state eigenvalue \( E_0 \) relative to the hole vacuum. Their solution, inserted in Equation (39) yields the coefficients \( b_\alpha \) and we could proceed with the full calculation of \( \Psi_0 \); 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 (13) is of the form of a Schrödinger equation with eigenvalue \( E_0 \) for pairs with effective interaction \( W_{eff} \). Then we may interpret \( a_m \) as the wave function of the dressed pair, which is acted upon by an effective Hamiltonian \( \hat{H} \). The change from the full many-body \( H \) to \( \hat{H} \) is a canonical transformation which holds to all orders. \( W_{eff} \) is the effective interaction between dressed holes, while \( F \) is a forward scattering operator, which accounts for the self-energy corrections of the one-body propagators: it is evident from (13) that it just redefines \( E'_\alpha \). 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 \( W_{eff} \) 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 \( W_{eff} \).

This way of looking at Equation (13) 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 \( \Delta E \) in Equation (25), by setting

\[ H'_0 = H_0 - \Delta E \]  

(45)

the same shift applies to the eigenvalues \( E_m, E_\alpha, E_\beta \) and so on, and also to the renormalised quantities like \( E'_\alpha, E'_\beta \). Therefore, the effective interaction \( W_{eff} \) of Equation (14) 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 (14) without changing the off-diagonal terms. Since we wish to regard Equation (13) as a Cooper-like equation for the pair, it is natural to set \( \Delta E \) equal to the interacting ground state energy eigenvalue for the \( n_h - 2 \) hole system, relative to the hole vacuum,

\[ \Delta E = E_h(n_h - 2) \]  

(46)
This quantity is obtained by diagonalising the cluster Hamiltonian with \( n_b - 2 \) holes. In Ref. \[20\], dealing with the infinite plane, this was our choice. The energy of two independent holes, relative to the \( \infty \) plane, this was our choice. The energy of two bound holes is \( 2E_F + \Delta \), 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 renormalisations in Equation (44), setting \( W' \to W \) and \( E' \to E_\alpha \), which is fully justified in the weak coupling case. This is the approximation that we proposed in Ref. (20) and that we want to test in the present paper. In fact, 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 \( Cu_2O_4 \) in the \( n_b = 4 \) case. Two degenerate \( m \) states are lowest in the non-interacting limit, namely, the configuration \( m = D[x,y] \) of Equation (48) and \( m' = D[y,x] \), where the \( x,y \) orbitals belong to the lower \( \epsilon \) level; the \( \psi^{(1)}_A \) 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 \( W_{eff} \), we rewrite \( W \) (Equation (8)) in the orbital representation, with

\[
\psi_i^\dagger = \sum_\nu \langle \nu | \psi_i \rangle c_{\nu}^\dagger
\]

(47)

where \( \nu \) runs over all the orbitals, obtaining

\[
W = \sum_{\mu,\nu,\sigma \rho} W(\mu, \nu, \rho, \sigma) c_{\mu}^\dagger c_{\nu}^\dagger c_{\sigma} c_{\rho}.
\]

(48)

The pair \( (\rho_-, \sigma_-) \) 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 \( \beta \) state. To lowest order, only the \( \alpha \) 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 \( \alpha \) states coupled to \( D[y,x] \) by \( W \) are those of the form \( |\mu ayx\rangle \equiv |\mu a_y a_x a_- x_- \rangle \), in which the hole in \( a_- \) is promoted to \( y_- \) while \( y_+ \) is scattered into \( \mu_+ \). Therefore,

\[
E_\alpha = \epsilon_a + \epsilon_\mu + \epsilon_x + \epsilon_y,
\]

(49)

where \( \epsilon_y = \epsilon_x \). One finds

\[
\langle |\mu ayx| W |yaxa\rangle \rangle = -W(y, a, \mu, y)
\]

(50)

and

\[
\langle |xaya| W |\mu ayx\rangle \rangle = W(x, a, \mu, x)
\]

(51)

Therefore, taking into account that each of the two background \( a \) holes can be promoted and this brings a factor of \( 2 \), using (13) we obtain

\[
\langle m | W_{eff} | m' \rangle = -2 \sum_\mu W(y, a, \mu, y) W(x, a, \mu, x)
\]

\[
E_0 - (\epsilon_a + \epsilon_\mu + 2 \epsilon_x)
\]

(52)

Since \( W(y, a, x, y) = W(x, a, y, x) = 0 \), the empty (of holes) states \( \mu \) 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 \(-2 \sum a'_\mu \delta_{E_\mu} \). Since \( E_\mu > E_0 \) this is positive. On the other hand, \( W(x, a, b, x) = -W(y, a, b, y) \), since the orbitals 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 \( W_{eff} \), that we emphasised in Ref. (20).

Therefore, at this stage, a self-consistent treatment of Equation (13) must be sought, because \( W_{eff} \) 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.

C. Equivalence of the two definitions at weak coupling

For weak coupling, however, a cruder but simpler approximation is justified: one calculates \( W_{eff} \) neglecting all self-energy corrections, in such a way that \( E_0 \) in (22) reduces to \( 2 \epsilon_x + 2 \epsilon_a \); this is the lowest (second-order) approximation \( W_{eff}^{(2)} \). In the same, lowest-order approximation, the shift in Equation (46), which recasts Equation (13) as a two-body problem, in the Cooper-like form, is \( \Delta E = 2 \epsilon_a \); further, one considers only the mixing of the degenerate configurations \( m = D[x,y] \) and \( m' = D[y,x] \). In the resulting \( 2 \times 2 \) problem, the diagonal entries are identical, and the \( W_{eff}^{(2)} \) interaction produces the off-diagonal elements, with the result that the singlet is stabilised by \( W_{eff}^{(2)} \) and the triplet is destabilised by the same amount. Therefore [26], \( \Delta(4)^{(2)} = W_{eff}^{(2)} \). One obtains for \( \Delta(4)^{(2)} \) the following second-order expression:

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

(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 diagramatic analysis of Equa-
Since the dimensionality of the one-body basis is 18, electron pairs three-band Hubbard Hamiltonian becomes:

\[ H = \sum_{i} (2\varepsilon_i + U_i) - \sum_{\sigma} (\varepsilon_i + U_i) a_{i\sigma}^{\dagger} a_{i\sigma} \]

\[ - \sum_{i<j>\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + \sum_{i} U_i n_{i+} n_{i-}, \]  

\[ (54) \]

W=0 electron pairs are obtained for \( n_e = 4 \) and 12 electrons. Letting now \( E_e(n_e) \) denote the ground state energy of the cluster with \( n_e \) electrons, the effective interaction between the two electrons in the pair is measured by

\[ \Delta_e(n_e) = E_e(n_e) + E_e(n_e - 2) - 2E_e(n_e - 1). \]

\[ (55) \]

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

\[ \Delta_e(4) = E_e(4) + E_e(2) - 2E_e(3) = E_h(14) + E_h(16) - 2E_h(15) = \Delta_h(16) \]

\[ (56) \]

and, similarly, \( \Delta_e(12) = \Delta_h(8) \).

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 Eq. (1). One readily verifies that in a canonical transformation from holes to electrons, putting \( a_{i\sigma}^{\dagger} = c_{i\sigma} \), 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$_5$O$_4$ by calculating \( \Delta_h(n_h) \) with \( n_h = 4,8,12 \) and 16.

V. W=0 PAIRS AND CHARGE CONJUGATION

Consider the cluster with \( n_h \) holes. As shown above, the interesting situation arises when \( n_h \) is such that, filling the levels according to the aufbau principle, the last two holes go to a degenerate level. Accordingly, we expect that \( \Delta_h(n_h) \) measures the effective interaction between the holes of the W=0 pair. In Ref. [3], we have shown that this is the case at weak coupling. If the interaction is attractive and produces a bound state, \( |\Delta_h(n_h)| \) is the binding energy. This situation can be realised with \( n_h = 4 \) in highly symmetric Cu-O clusters containing up to 21 atoms [14]. The last 2 holes then go to the lowest level of e symmetry.

According to Table I, the Cu$_5$O$_4$ cluster has an upper e level, which is reached with 12 holes, so we are interested in \( \Delta_h(4) \) and \( \Delta_h(12) \). 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 I 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:

\[ H = \sum_{i} (2\varepsilon_i + U_i) - \sum_{\sigma} (\varepsilon_i + U_i) a_{i\sigma}^{\dagger} a_{i\sigma} \]

\[ - \sum_{i<j>\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + \sum_{i} U_i n_{i+} n_{i-}, \]

\[ (54) \]

W=0 electron pairs are obtained for \( n_e = 4 \) and 12 electrons. Letting now \( E_e(n_e) \) denote the ground state energy of the cluster with \( n_e \) electrons, the effective interaction between the two electrons in the pair is measured by

\[ \Delta_e(n_e) = E_e(n_e) + E_e(n_e - 2) - 2E_e(n_e - 1). \]

\[ (55) \]

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

\[ \Delta_e(4) = E_e(4) + E_e(2) - 2E_e(3) = E_h(14) + E_h(16) - 2E_h(15) = \Delta_h(16) \]

\[ (56) \]

and, similarly, \( \Delta_e(12) = \Delta_h(8) \).

VI. NUMERICAL RESULTS AND DISCUSSION

By an enhanced Lanczos routine, we computed the ground state of the Cu$_5$O$_4$ cluster with even numbers \( n_h \) 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 \( n_h = 8 \); the \( n_h = 12 \) and 16 cases are handled by transforming to the electron picture. The results for \( \Delta_h(n_h) \) are summarised in Table I. One sees that \( \Delta_h(n_h) = 4.8,12 \) 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 renormalisation of the parameters inherent in the canonical transformation does not have important consequences. To see if the behaviour at \( n_h = 12 \) is an exception, we have repeated the calculations with scaled \( U \) values. Using \( U_p = .06 \) eV and \( U_d = .053 \) eV, which are \( << t \) 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 (Equation [53]) and we can check its degree of validity by comparing with the exact diagonalisation values of \( \Delta \). Making use of the above standard values of the parameters we calculate the relative error \( \delta = 2 \left| \frac{\Delta - \Delta^{2}}{\Delta} \right| \). It turns out that \( \delta \leq .07 \) up to \( U/t \approx 1 \). Thus, already the second-order approximation is remarkably accurate in estimating the effective interaction. We conclude that our treatment based on the unrenormalised formula of Equation [43] 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 inter-
action $|\Delta|$, ii) this does not imply pairing at all con-
centrations, iii) we can predict if there is pairing or repul-
sion in a particular case by our theory. The cluster approach,
however, has several limitations, the main size effect be-
ing 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.

VII. FLUX QUANTIZATION AND PAIR
SYMMETRY

If a magnetic field is confined to a hole in any material
(flux tube) the flux $\phi$ is quantised 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 $\phi$ with
period $\phi_0$.

Bulk superconductors quantize the flux through a
hole in integer and half-integer multiples of $\phi_0$, because
the quasiparticles that screen the vector potential carry
charge $2e$. In finite systems the signature of supercon-
ductivity 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 separ-
ating the two minima becomes macroscopic, and bulk
superconductors can swallow up only an integer or half
integer number of flux quanta. As emphasized by Can-
right and Girvin [27], the flux dependence of the ground
state energy is definitely a most compelling way of test-
ing for superconductivity, and the existence of the two
minima separated by a barrier is a strong indication of
superconducting flux quantisation.

In Ref. [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 diagonalisation 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 centre, where screening currents can respond. Each
t_d bond forms a closed triangular loop with the central
Cu at the vertex (see Figure I). This geometry is a com-
promise, 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 experi-
ences a vector potential (see below). Finally, we observe
that a flux of the order of a fluxon in a macroscopic sys-
tem 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 $\phi$ inside each of the
triangles formed in this way. Every bond collects the
Peierls phase $2\pi i \int \mathbf{A} \cdot d\mathbf{r} / \phi_0$; by symmetry, $t$ is unaffected by
the flux, while

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

for a clockwise path, and the complex conjugate expres-
sion a counterclockwise path.

A. Superconducting flux quantisation: numerical
results

According to Table II, $\Delta_h(n_h)$ is negative and pairing
results at $\phi = 0$ for $n_h=4.8$ and 16; in all three cases
we found that the ground state energy $E_b(n_h,\phi)$ as a
function of $\phi$ 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 crite-
ron for superconducting flux quantisation than is drawn
from the literature, since we need that both minima in the
ground state versus flux curves also correspond to
negative $\Delta$. This is a much clearer signature of super-
conducting flux quantisation than the generally accepted
presence of the two minima, because it implies that the
superconductor remains a superconductor after swallow-
ning up the half flux quantum. Therefore, we computed
$\Delta_h(n_h,\phi)$ in order to determine the flux dependence of the
effective interaction. When $\Delta_h(n_h,0) < 0$, then
$\Delta_h(n_h,\phi)$ is also negative. For small enough $t_d$, the
response function

$$
R = \frac{\Delta_h(n_h,\phi) - \Delta_h(n_h,0)}{|t_d|}
$$

is an intrinsic property of the original cluster with $t_d = 0$.
In Figure II we show $R$ for several $n_h$ values versus
$\phi$. 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 $n_h = 4$ 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 II we also report the absolute value |⟨Ψ₀(φ)|Ψ₀(0)⟩| of the overlap between the the ground state eigenvectors in the presence and in the absence of the flux, for \( n_ħ = 4 \). It is clear that |⟨Ψ₀(φ)|Ψ₀(0)⟩| = 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 \( (\frac{1}{2}) \). Similar results for the overlap are obtained for the other \( n_ħ \) values which correspond to partially filled shells.

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 \( 1B_2(x^2 - y^2) \) at \( φ = 0 \) to \( 1A_1(x^2 + y^2) \) at \( φ = \frac{2π}{2} \). 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).

**B. Group theory aspects of superconducting flux quantisation**

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 \( 1A_1 \) and \( 1B_2 \) components. A nonzero \( t_d \) at \( φ = 0 \) 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 \( 1B_2 \) at \( t_d > 0 \) but changes symmetry if the sign of \( t_d \) is reversed. Upon switching the vector potential \( A \), the Cu-Cu hopping is complex and chiral, so the symmetry is lowered again from \( C_{4v} \) 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 \( φ = \frac{2π}{2} \), 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 \( φ = \frac{2π}{2} \) 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 \( φ = 0 \) 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 \( φ = 0 \).

This symmetry argument extends to the full plane. To see that, consider the pattern of Figure III. 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 visualise a convenient choice of the gauge at general \( ϕ \). Namely, running along an oriented bond in the sense of the arrow,

\[ \int A \cdot dr = \frac{ϕ}{2}; \]

along the other Cu-O bonds, not marked in the Figure, \( \int A \cdot dr = 0 \). 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 \( ϕ \rightarrow -ϕ \), reverse the directions of the arrows and for a generic \( ϕ \) the symmetry Group reduces to \( Z_4 \). However, at \( ϕ = \frac{2π}{2} \) 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 III. 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, \( σ × S \) is a symmetry, for all reflections \( σ \) in \( C_{4v} \). Moreover, since the product of two reflections is a rotation, the Group \( C_{4v} \) 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 \( C_{4v} \).

In this way, at \( ϕ = \frac{2π}{2} \) 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 quantisation in macroscopic systems.

**VIII. CONCLUSIONS**

We have examined the properties of the \( W = 0 \) pairs by performing numerical diagonalizations of the \( CuO_4 \) 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 diagonalisation 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 $\Delta$ 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, $\Delta$ 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 Ref(24) 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 analyse 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 renormalisation of the dispersion relation cannot be neglected [19].

In the $Cu_3O_4$ cluster the exact diagonalisation results show that $W=0$ pairs quantise 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 quantisation 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 quantisation and pairing fit well together, both being consequences of the same symmetry principle.

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In the full plane, the localised bound state is a superposition of many \( W=0 \) pair states, and \( W_{\text{eff}} \) cannot be identified with \( \Delta \); one has to solve a Cooper-like equation to obtain the binding energy. In the small clusters like \( Cu_5O_4 \), just two \( W=0 \) configurations contribute significantly at weak coupling, and thus effective interaction and binding energy are the same.

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**FIGURE CAPTIONS**

**FIGURE I** The \( Cu_5O_4 \) cluster with 4 flux tubes (black dots) carrying flux \( \phi \). \( X \) stands for Cu. The dotted lines represent the \( t_d \) bonds providing a closed path around the centre.

**FIGURE II** 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 \( n_h = 4, 8 \), and 16. Note that for \( n_h = 4 \), \( \Delta_h(4, \phi^2) - \Delta_h(4, 0) \approx 0.3t_d \), but \( \Delta_h(4, \phi^2) \) is negative.

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

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**TABLES**

| Symmetry | \( g \) | \( \varepsilon \)(eV) |
|----------|--------|-----------------|
| \( a_1 \) | 1      | -1.643          |
| \( e_b_1 \) | 3      | -0.43           |
| \( a_1 \) | 1      | 0.              |
| \( e_b_1 \) | 3      | 3.93            |
| \( a_1 \) | 1      | 5.143           |

TABLE I. One-hole levels of the \( Cu_5O_4 \) cluster, with their symmetry labels, degeneracies \( g \), and energy eigenvalues \( \varepsilon \) with \( t = 1.3 \) eV, \( \varepsilon_p = 3.5 \) eV and \( \varepsilon_d = 0 \).

| \( n_h \) | \( \Delta_h \)(meV) |
|-----------|-----------------|
| 4         | -15.7           |
| 6         | 1469.2          |
| 8         | -10.85          |
| 12        | 43.72           |
| 14        | 1109.2          |
| 16        | -25.47          |

TABLE II. Exact diagonalisation 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.
$R_{\phi/\phi_0}$

$|\langle 0^0 | h(\phi)^0 | 0^0 \rangle|$

$\text{Cu}_5\text{O}_4$

$n_h=4$

$n_h=16$

$n_h=8$
