Hole pairing in high-T_c superconductors: symmetry-driven configuration interaction mechanism

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Summary. — A quantum-mechanical effect specific of the symmetry of the Cu-O plane in cuprate superconductors is presented. We show that pairs of holes in degenerate states are such that their mutual on-site Coulomb interaction W vanishes identically. A procedure for obtaining such $W = 0$ two-hole states in clusters of any size is outlined. Small clusters also display the effect provided they have the full C_{4v} symmetry and a Cu atom at the centre. In the many-body problem that arises when degenerate states are at the Fermi level, these holes interact indirectly through their screening clouds. This interaction is analysed by the exact diagonalization of an extended Hubbard Hamiltonian in doped CuO_4 clusters and is shown to be attractive with the literature values of all parameters. Bound states of $^1B_2$ symmetry and binding energies of the order of 10 meV are obtained. The hole-hole interaction readily returns strongly repulsive if impurity potentials lower the symmetry. Off-site interactions fit well into the scheme. If the current estimates of the parameters are correct, this correlation effect alone can explain pairing.

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1. – Introduction

Most superconducting oxides have large unit cells containing four or more elements and CuO_2 planes separated by intermediate layers which stabilize the lattice and act as a charge reservoir. A large amount of experimental and theoretical work has clarified that mobile holes on these planes are responsible for superconductivity. In the undoped solid the electrons are so strongly correlated that they cannot move freely as in a metal. When holes are introduced into the plane by doping, the system becomes conducting and even superconducting provided the hole density is within the appropriate range.

Ten years after the discovery of high-temperature superconductors it has not yet been firmly established if a modification of the Fermi liquid picture or an approach

based on a correlated ground state is the correct one. The class of theories based on correlation mechanisms start from single or multiple bands Hubbard Hamiltonians containing nearest-neighbours hopping matrix elements t between Cu and O and O-O and large on-site Coulomb repulsive energies U between holes with opposite spins which tend to reduce double occupancy of these sites. For $U \gg t$, such Hamiltonians map into Heisenberg-like Hamiltonians for holes propagating through an antiferromagnetic (AF) background with an exchange interaction J between neighbouring spins. Doping the plane the added holes go onto the oxygen states [1]. At optimum doping and temperature lower than T_c the long-range AF correlations vanish and eventually the attractive interactions overcome the repulsive bare interactions leading the holes to pair. Perturbative approaches such as the t-J model [2], force the holes to avoid on-site interactions by letting U to be very large (or infinite) so that eventually the pairing may be achieved through residual small attractive interactions [3]. In this way the problem is formally circumvented, but not solved. Such models *do not* identify from the outset the physical mechanism capable to nullify the huge repulsive Coulomb interactions among the holes. When U is given a physically plausible value, it is realized that, although $U \gg t$, we are far from the limit $U/t \to \infty$.

On the other hand, some authors achieved attractive interaction between holes using more realistic correlated models on clusters of different sizes and geometry, but these attempts are spoiled by the apparent need of unphysical parameter values. Therefore in recent years several proposals of pairing based on electronic mechanisms [4] have appeared, but many people argued that electronic mechanisms alone are unsufficient. More complicated interactions involving the lattice were deemed necessary, and an appropriate modification of the BCS theory was sought [5]. Several kinds of known boson quasi-particles and also exotic things like anyons were considered [6].

In this work, instead of seeking how to counteract the repulsive interactions between carriers in the strongly correlated CuO_2 plane, we propose a physical mechanism capable of cutting down the on-site interactions from the outset. Quantum mechanics naturally leads to such a seemingly paradoxical result in the presence of degenerate hole states at the Fermi level.

In sect. 2, we describe the Hamiltonian and discuss the parameters. In sect. 3, the relevant two-hole states and the configuration interaction mechanism are introduced. Section 4 is devoted to exact calculations on the CuO_4 cluster with on-site interactions only, showing that because of symmetry the effective interaction is attractive in many interesting cases. In the next section, off-site interactions are included. Section 6 contrasts the present result with previous cluster calculations, stressing the importance of symmetry and geometry. Finally, our conclusions are summarized in sect. 7 and perspectives for future developments are given.

2. – Hamiltonian

Our argument is based on symmetry and will turn out to be largely model-independent. For the sake of argument, however, we start by adopting a model hole Hamiltonian, which has been much used in electron spectroscopy studies. It is a generalized Hubbard model with first-neighbour hopping and Coulomb interactions

of the form

$$H = h + H_C \,, \tag{1}$$

where h is the one-hole part and H_C represents interactions;

$$h = \sum \varepsilon_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} \tag{2}$$

with $\varepsilon_{ii} = \varepsilon_p$ for an oxygen site, $\varepsilon_{ii} = \varepsilon_d$ for a Cu site, $\varepsilon_{ij} = t$ for a Cu-O bond and $\varepsilon_{ij} = t_{ox}$ for an O-O bond. We split the interactions as follows:

$$H_C = H_{site} + H_{off\text{-}site} \,, \tag{3}$$

where the on-site part is

$$H_{site} = \sum U_i n_{i+} n_{i-} \tag{4}$$

with $U_i = U_p$ for oxygen and U_d for Cu. The off-site interaction reads

$$H_{off\text{-}site} = H_{pd} + H_{pp'} \,, \tag{5}$$

where, restricting the sums to nearest-neighbour sites, and using obvious notation,

$$H_{pd} = U_{pd} \sum_{i\sigma}^{Cu} n_{i\sigma} \sum_{j\sigma'}^{Ox} n_{j\sigma'} \tag{6}$$

and

$$H_{pp'} = U_{pp'} \sum_{i\sigma}^{Ox} \sum_{j\sigma'}^{Ox} n_{i\sigma} n_{j\sigma'} \,. \tag{7}$$

This Hamiltonian has been parametrized by best fitting the results of up-to-date *ab initio* calculations [7]. The parameters have been further validated by comparing the calculated spectral line shape of the Cu $2p_{3/2}$ spectrum with the photoemission spectrum measured [8] in $YBa_2Cu_3O_{7-\delta}$. To allow for a mechanism of non-local screening of the holes beside the local screening due to the Zhang-Rice singlet [9], we have considered the Cu_3O_{10} cluster. Exact diagonalization of the Hamiltonian matrix with three valence holes has been performed to determine the ground and excited states. The ground state is a doublet of $^2B_2$ symmetry. By using the parameter values of table I without the off-site U_{pd} and $U_{pp'}$ interactions, the Cu $2p_{3/2}$ doublet main line and the satellite can be reproduced. Similar calculations have been previously done by van Veenendaal and Sawatzky [10] and the results indicate that the intersite screening of the Cu hole needs a delocalization space larger than that provided by the CuO_4 unit. The off-site interaction between oxygen and copper holes is estimated theoretically [10] to be $U_{pd} \approx 1.2$ eV, while the off-site $U_{pp'}$ interaction between

TABLE I. – *Hole parameters used in this work (in* eV*). Q is the Coulomb repulsion between core and valence holes; the other entries are defined in the text.*

ε_p	3.5	ε_d	0	t	1.3
t_{ox}	−0.65	U_p	6	U_d	5.3
U_{pd}	< 1.2	$U_{pp'}$	≪ 0.04	Q	7.7

oxygen sites is unknown experimentally, and the theoretical estimate [7] is consistent with 0. This means that it is negligibly small compared to the smallest non-zero energies reported in the same calculation, which are of the order of several tens of meV. Qualitatively, a small $U_{pp'}$ may be understood in terms of metallic screening and spread-out charge distributions. Our argument rests on general principles, and many of our conclusions do not depend on the detailed choice of these parameters.

3. – Pair states which are not affected by the on-site interaction

In this section, we limit the discussion to on-site interactions, the effect of the off-site terms is deferred to sect. 5. For the sake of simplicity, let us first consider the CuO_4 planar cluster with 4 holes, one intrinsic and three due to doping. Site 1 is Cu, and the others are oxygens. The single-hole energy level scheme *vs.* t_{ox} is shown in fig. 1. At $t_{ox} = -0.65$ eV, the first two holes go into a bonding level of a_1 symmetry, and the next two go into a non-bonding level of e symmetry, with orbitals transforming like the (x, y) pair. Denoting the bonding state by a, one could build the degenerate singlet configurations $|a_+ a_- x_+ x_-|$ and $|a_+ a_- y_+ y_-|$ and the triplet components $|a_+ a_- x_+ y_+|$ and $|a_+ a_- x_- y_-|$. In the Hartree-Fock (HF) approximation one would find spontaneous symmetry breaking of the singlet, and since parallel spin holes are not interacting in the model, the triplet would have lower energy.

Yet, the singlet energy can be much improved by configuration interaction (CI). First, let us replace the (x, y) pair by (b, β), where $b = (x + y)/\sqrt{2}$ and $\beta = (x - y)/\sqrt{2}$ are oriented in the O-O directions. The singlet configurations then read $\Psi_{bb} = |a_+ a_- b_+ b_-|$ and $\Psi_{\beta\beta} = |a_+ a_- \beta_+ \beta_-|$, both with HF energy

$$\langle \Psi_{bb} | H | \Psi_{bb} \rangle = \sum_{\sigma} (I_{a\sigma} + I_{b\sigma}) + \sum_{i} U(i)\, n_+(i)\, n_-(i), \tag{8}$$

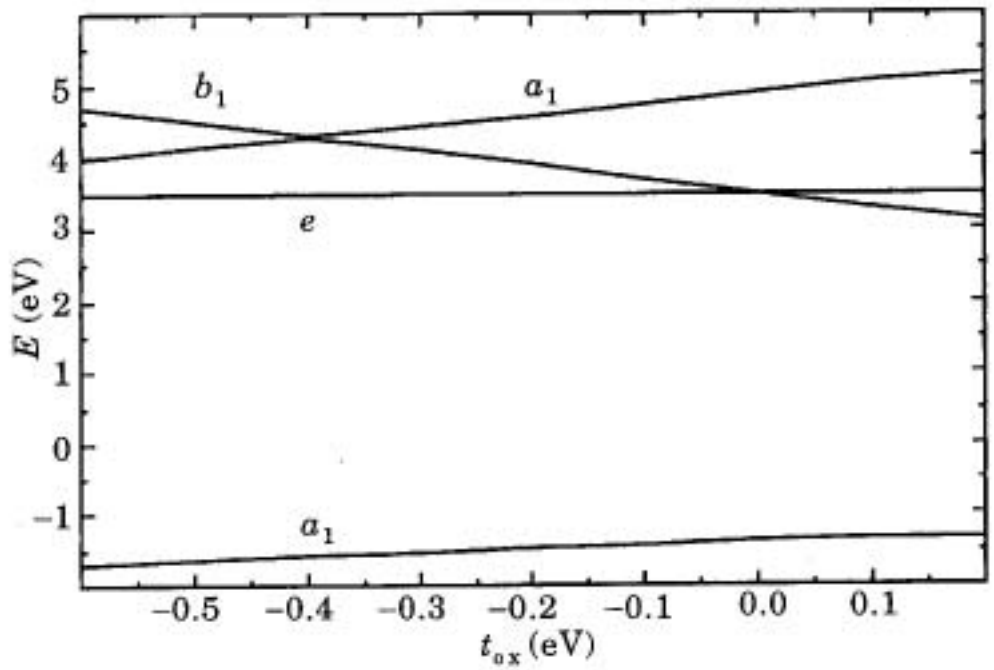

Fig. 1. – One-hole energy levels of the CuO_4 cluster *vs.* t_{ox}; the other parameters are specified in the text. The levels e and b_1 are non-bonding, the a_1 levels form a bonding-antibonding pair. The levels are labelled according to the representations of the C_{4v} group.

where the first term on the r.h.s. contains the one-body contributions

$$I_{k\sigma} = \sum_i \varepsilon_i |k_\sigma(i)|^2 + \sum_{ij} k^*_\sigma(i) t_{ij} k_\sigma(j) \qquad (k = a \text{ or } b) \tag{9}$$

the last sum runs over sites, and

$$n_\sigma(i) = |a_\sigma(i)|^2 + |b_\sigma(i)|^2 \equiv n_a(i) + n_b(i). \tag{10}$$

The configurations are mixed by

$$\langle \Psi_{bb} | H | \Psi_{\beta\beta} \rangle = \sum_i U(i) n_b(i) n_\beta(i). \tag{11}$$

The lowest eigenvalue corresponding to the choice

$$\Psi = \frac{\Psi_{bb} - \Psi_{\beta\beta}}{\sqrt{2}} \tag{12}$$

is

$$\varepsilon = \langle \psi_{bb} | H | \psi_{bb} \rangle - \langle \psi_{bb} | H | \psi_{\beta\beta} \rangle = \tag{13}$$

$$= \sum_\sigma (I_{a\sigma} + I_{b\sigma}) + \sum_i U(i)[n_a(i)^2 + 2n_a(i) n_b(i)] + W,$$

where

$$W = \sum_i U(i) n_b(i)[n_b(i) - n_\beta(i)] \tag{14}$$

represents the direct interaction between the non-bonding holes. At this point, the issue is decided by the peculiar property of the system that n_b and n_β *are identical, despite the fact that the quantum states are distinct and orthogonal*, and therefore the interaction between those holes is turned off exactly. We emphasize that the existence of degenerate states such that $n_b = n_\beta$ is the only condition.

The four-hole CI wave function (12) can be rewritten as

$$\Psi = \frac{1}{2}[S_{34} + S_{25} - S_{23} - S_{45}] c^\dagger_{a+} c^\dagger_{a-} |v\rangle, \tag{15}$$

where $|v\rangle$ is the hole vacuum and

$$S_{ij} = \frac{c^\dagger_{i+} c^\dagger_{j-} + c^\dagger_{j+} c^\dagger_{i-}}{\sqrt{2}} \tag{16}$$

creates a two-hole singlet on oxygen sites i and j. It is apparent that the non-bonding holes in this approximation are avoiding each other so that $W = 0$. Note, however, that the full expansion of the wave function in the site representation contains $\binom{5}{2}^2 = 100$ terms, and many of them like $|2_+ 2_- 5_+ 5_- |\rangle$ are affected by the interaction. This is what we mean for a non-interacting pair in the interacting system. The above argument brings out the essential role of symmetry, and can be extended to clusters of arbitrary size (see below). The lowest singlet is predicted to be $^1B_2$ which

transforms (*) like xy. There is no symmetry breaking, the lowest state belongs to a non-degenerate representation and has a totally symmetric charge distribution.

Since $W = 0$ for both $^1B_2$ and the triplet, two-body calculations cannot decide which is the ground state. One can use the two-determinant 4-hole CI of eq. (12) and minimize the energy with respect to the a, and b, β orbitals, or, better, resort to the exact diagonalization of the Hamiltonian. This is discussed in sect. 4, where we show that pairing is indeed achieved in part of the parameter space and a non-degenerate singlet ground state prevails.

To extend the above analysis of the two-body problem to clusters of any size let us first consider $t_{ox} = 0$. We may use the non-bonding states, which are eigenstates of the one-body part h of the Hamiltonian with eigenvalue ε_p. Those belonging to e occur in pairs, that we denote as (x_k, y_k). The combinations $b_k = (x_k + y_k)/\sqrt{2}$ and $\beta_k = (x_k - y_k)/\sqrt{2}$ are orbitals oriented in the O-O directions and we may build singlets Ψ_{bb} and $\Psi_{\beta\beta}$ as above. In general, for each k, one finds that $n_b \neq n_\beta$. However, diagonalizing H_{site} in the space of Ψ_{bb} and $\Psi_{\beta\beta}$ siglets, we obtain $W = 0$ pairs of $^1B_2$ symmetry and totally symmetric charge density. *These singlets are exact eigenstates of the two-hole problem with* $H = h + H_{site}$. Consider for example the Cu_9O_{24} cluster of

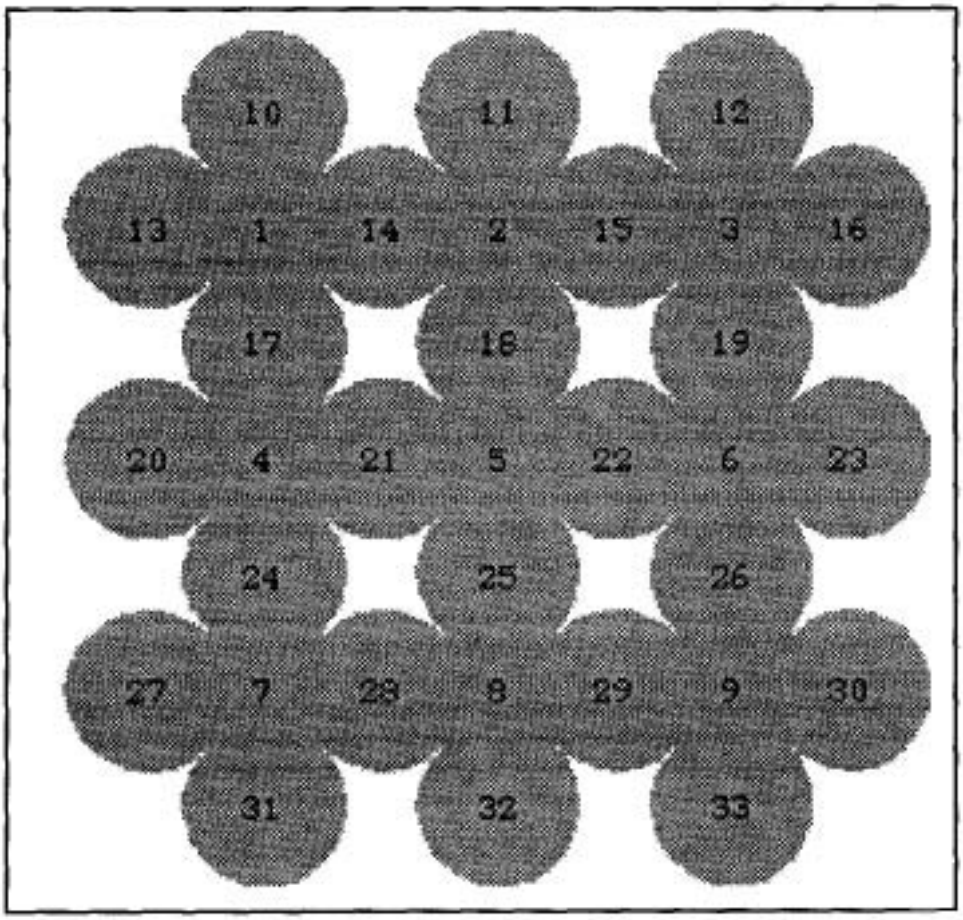

Fig. 2. – The symmetric Cu_9O_{24} cluster. Sites 1 to 9 are Cu.

(*) In octhahedral symmetry a xy state belongs to T_{2g} and would lead to a Jahn-Teller distortion. In the present two-dimensional problem we obtain the non-degenerate B_2 representation.

fig. 2. Some non-bonding states transforming like y may be written down by inspection:

$$(17)\qquad \begin{cases} y_1 = \dfrac{|10\rangle - |17\rangle + |24\rangle - |31\rangle}{2}, \\ y_2 = \dfrac{|11\rangle - |18\rangle + |25\rangle - |32\rangle}{2}, \\ y_3 = \dfrac{|12\rangle - |19\rangle + |26\rangle - |33\rangle}{2}. \end{cases}$$

Carrying out the above-described procedure with these states and their counterparts transforming like x we find two-particle eigenstates with $W = 0$. The calculated density distribution of such a pair is shown in fig. 3. The density distribution of a $W = 0$ pair arising from non-bonding states in the Cu_5O_{16} symmetric cluster is shown in fig. 4.

Degenerate bonding states can also produce pairs that do not feel the on-site repulsion. Consider for example, the Cu_5O_{16} cluster of fig. 4 with the input data of table I but $t_{ox} = 0$. The lowest hole level at -1.884 eV is non-degenerate; the next one at -1.384 eV is threefold degenerate. Thus 4 holes are enough to display the effect. (This cluster has 5 Cu atoms and 4 holes correspond to 1 electron doping.) From the space spanned by the three degenerate eigenvectors, one can extract the basis of the e

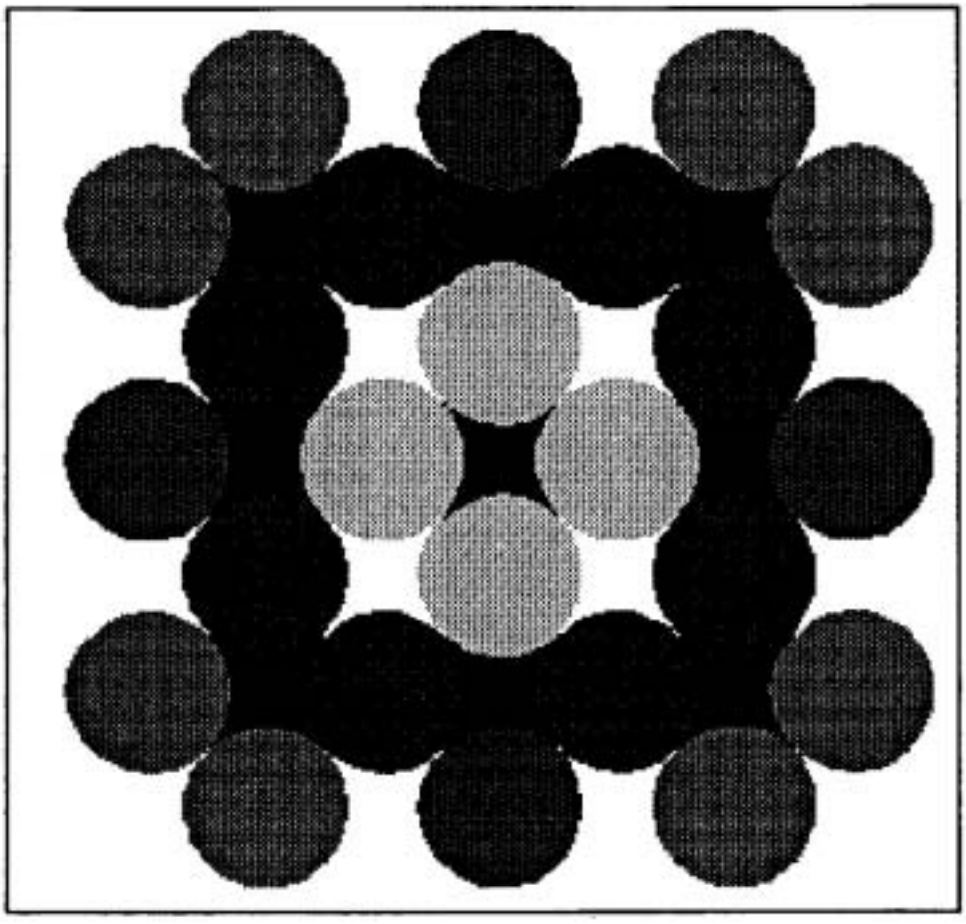

Fig. 3. – Charge distribution of a pair of e-symmetry holes in the Cu_9O_{24} cluster. The on-site interaction is removed exactly by the CI mechanism ($W = 0$). Several more such pairs exist. Lighter grey levels correspond to higher hole densities. Note that the density is invariant under 90° rotations.

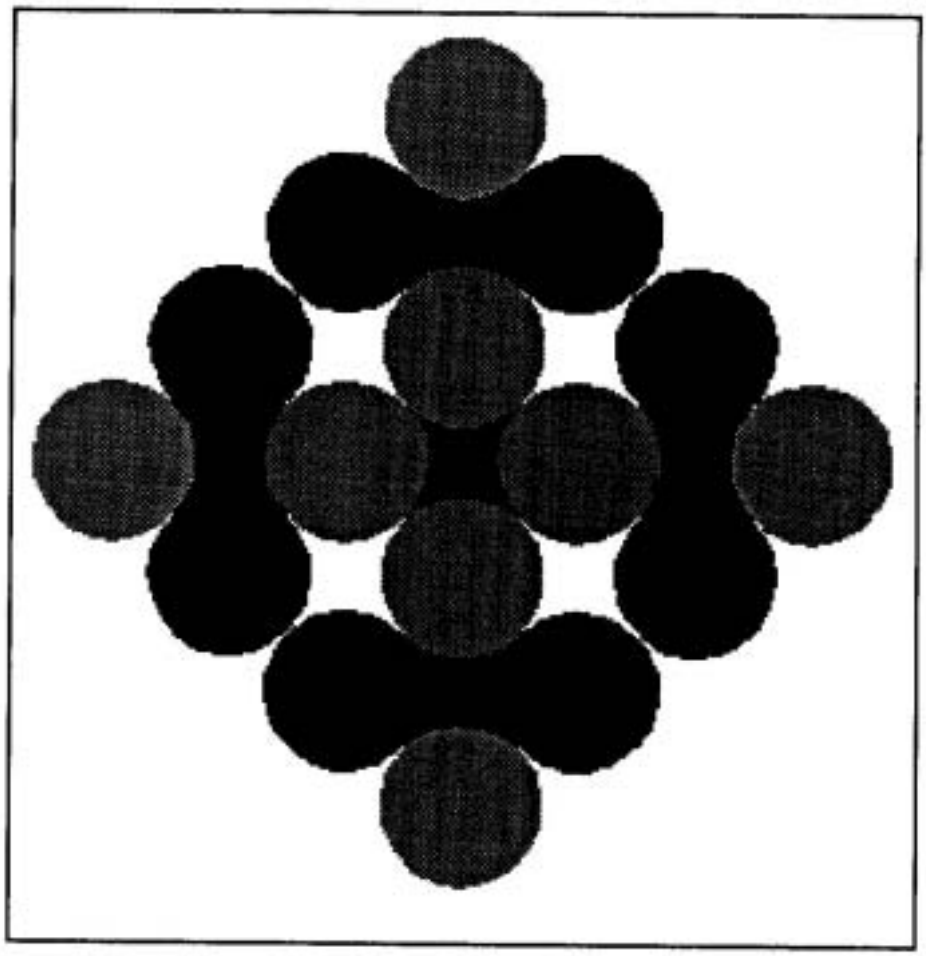

Fig. 4. – Charge distribution of one of the pairs having $W = 0$ in the Cu_5O_{16} cluster. Lighter grey levels correspond to higher hole densities. Note that the density is invariant under 90° rotations.

representation and form states which transform like b and β. These states are bonding, and their amplitude on Cu sites vanishes at the central Cu but is large at the other ones. We find that $n_b = n_\beta$, with densities equal to 0.194 on each non-central Cu atom and 0.0138 on each O. According to eq. (14), $W = 0$ and the on-site repulsion is turned off. Note that this result is achieved by mixing just two configurations.

At $t_{ox} = -0.65$, the lowest level of the same cluster occurs at -2.527 eV, and the next level at -1.736 eV is twice degenerate. Its basis may be used to form one-hole states which transform like b and β; one finds that $n_b \neq n_\beta$, and the on-site repulsion is not completely removed by this simple CI. However, the calculation yields $W = 2.24$ meV. This is small compared to the typical binding energies Δ estimated below and we believe that is not enough to prevent pairing by the present mechanism.

We conclude that the quantum effect leading to the suppression of W is not specific of the CuO_4 cluster but takes place in clusters of any size provided they have the appropriate symmetry and $t_{ox} = 0$. This is an indication in favour of pairing at $t_{ox} = 0$ and in some range of t_{ox} values.

4. – CI and exact solutions for the CuO_4 cluster: on site-interactions

In the present section, we wish to show that the peculiar properties of two-hole states discussed above are the signal of an anomalously low effective repulsion in the interacting system which readily goes negative and leads to pairing. For the moment,

TABLE II. – *Ground-state energy $E(n)$ of the CuO_4 cluster with $n = 1$ to 4 holes and effective repulsion $\Delta = E(4) + E(2) - 2E(3)$ between the holes of e symmetry.* HF: *Hartree-Fock approximation*; CI: *configuration interaction*; *exact*: *numerical diagonalization of the Hamiltonian.*

	HF	CI	Exact
$E(1)$	—	—	− 1.723 12
$E(2)$	− 1.305 23	—	− 1.656 03
$E(3)$	− 2.886 05	—	2.218 55
$E(4)$	8.52	7.012 87	6.100 6
Δ	1.46	− 0.064	0.007 47

we are still ignoring the off-site interactions. In table II we report the ground-state energies $E(n)$ of the CuO_4 cluster with n holes, $n = 1$ to 4, and the effective repulsion energy $\Delta = E(4) + E(2) - 2E(3)$. While W gives the direct interaction between the two holes in the CI calculation, Δ contains indirect interactions as well. The HF results (column 2) correspond to a spontaneously broken symmetry of the 4 hole singlet and fail to reproduce the quantum effect we are discussing. Accordingly, the effective on-site repulsion $\Delta = 1.46$ eV, which looks quite a large barrier to overcome before pairing can be attained. The $U/t \to \infty$ limit would correspond to neglecting this Δ. In the CI calculation (column 3) we assume the form (12) for the wave function and optimize the energy with respect to the orbitals. This leads to a small negative Δ and to a comparable lowering of the total energy. The exact diagonalization (column 4) yields a further large lowering of the total energy and confirms that Δ is essentially suppressed. Inspection of the wave function shows that the ground state is $^1B_2$ as predicted in sect. 3, the first excited state is a $^3A_2$ triplet lying $D = 18$ meV above it. Although the CI calculation gives a negative Δ value, the exact calculation yields a tiny positive one. However, if t_{ox} is increased, Δ does become negative, which shows that correlation effects may lead to pairing (see table III). The maximum binding occurs at $t_{ox} = 0$, when all the non-bonding orbitals are degenerate and the configuration mixing is thereby enhanced. On the other hand, at positive t_{ox}'s, Δ becomes large and positive, because the b_1 non-bonding level is pushed below the degenerate one, and the mechanism is hampered (at $t_{ox} = +0.65$, $\Delta = 0.53$ eV).

Next, we discuss the dependence of Δ on the other parameters. If we decrease ε_p, Δ decreases because this makes the system more polarizable. The ε_p dependence when all the other parameters are kept fixed according to table I is almost linear down to $\varepsilon_p = 0$. Pairing is obtained in most of the range (fig. 5). By contrast, the dependence of Δ on the Cu-O hopping parameter t is complex (see fig. 6). For small t,

TABLE III. – *Effective interaction Δ and energy D of the first excited triplet relative to the singlet ground state as a function of t_{ox} for the CuO_4 cluster.*

t_{ox}	−0.45	−0.25	−0.05	0
Δ	−0.0049	−0.0209	−0.0336	−0.0364
D	0.043	0.068	0.0915	0.097

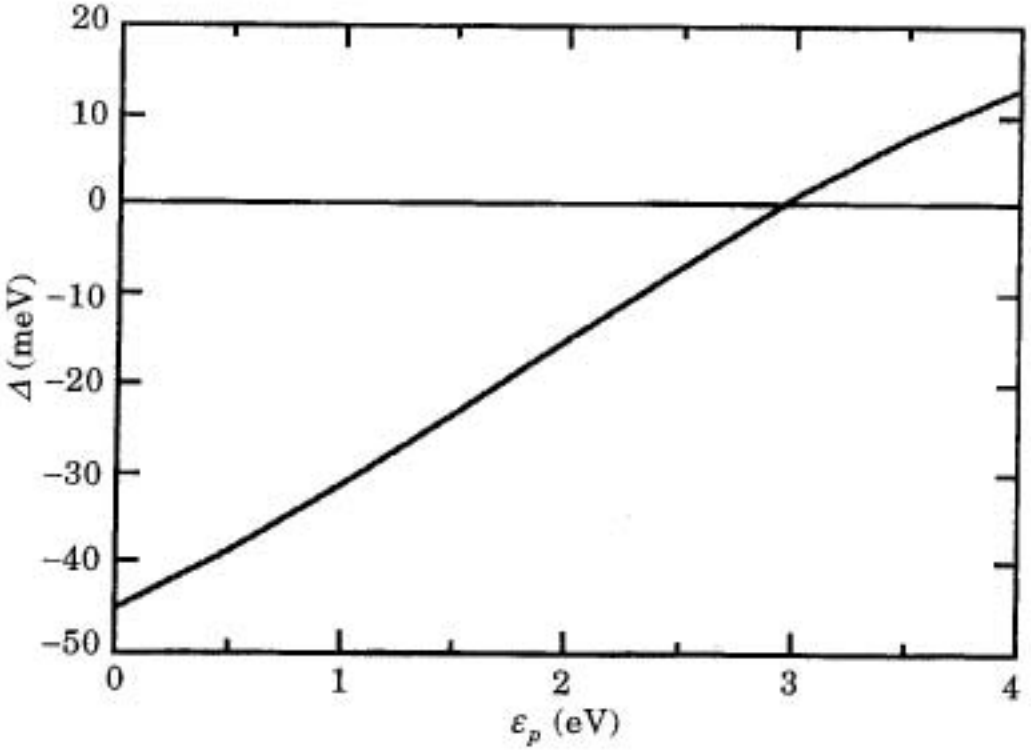

Fig. 5. – Dependence of Δ on ε_p. All the other parameters are fixed according to table I, except off-site interactions which are ignored.

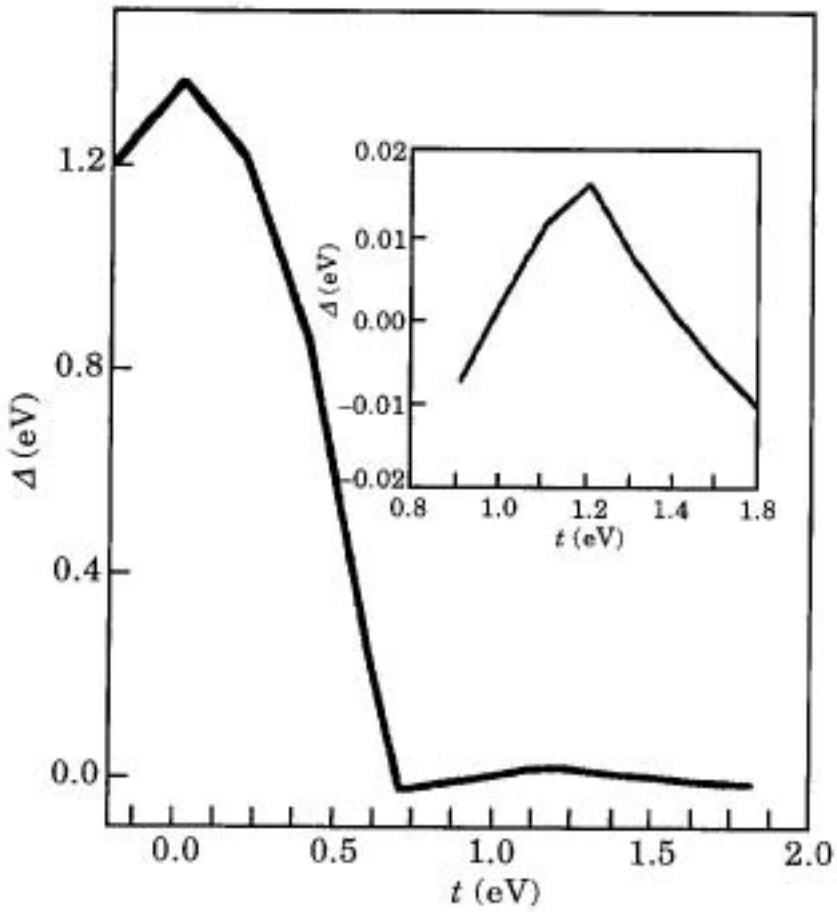

Fig. 6. – Dependence of Δ on the Cu-O hopping parameter t. The inset shows the details in a range of t values around $t = 1.2$ eV.

Δ is in the eV range, and falls to 0 at $t \approx 0.7$ and then goes negative up to $t \approx 1$. Negative values are again obtained for $t > 1.4$. To study the dependence of Δ on correlation and t_{ox} parameters, we choose to keep the U_p/U_d ratio fixed to the

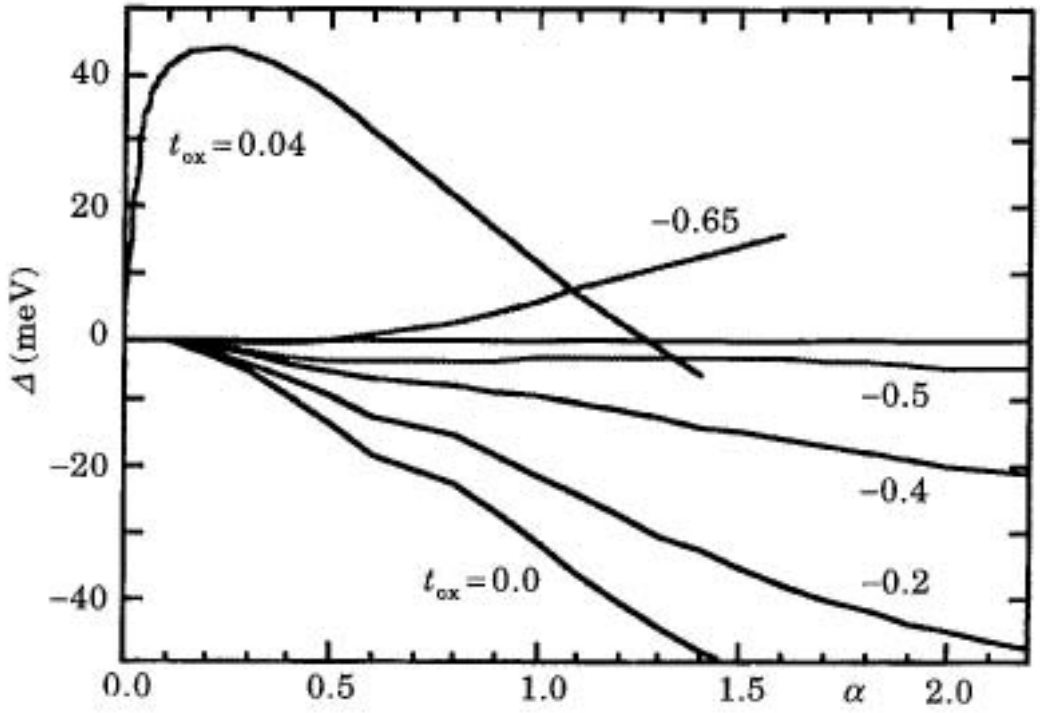

Fig. 7. – Dependence of the effective two-hole interaction Δ on α for several t_{ox} values.

recommended literature value [10] and multiply both U by a common factor α. The results are shown in fig. 7. For $-0.5 < t_{ox} < 0$, Δ becomes more and more negative with increasing correlation, which is not surprising, since it arises from the indirect interactions of the two holes in the degenerate level *via* their screening clouds. For more negative t_{ox}, a weak attraction results at small α, but as α increases the repulsion wins. Qualitatively, the weakening of the attraction may be understood, since at large $|t_{ox}|$ the spacing between the energy levels is large and the polarizability is small. On the other hand, for $t_{ox} > 0$, the holes go to a non-degenerate level of b_1 symmetry and $\Delta > 0$ for small α. With increasing α, however, eventually it becomes favourable for the holes to occupy the degenerate state, and the CI mechanism drives the system to binding [11].

Symmetry plays a key role in the analytical calculations of sect. 3; the numerical results on the CuO_4 cluster further demonstrate the fact that any lowering of the symmetry is reflected by a corresponding increase of Δ. Let us consider the substitutional replacement of one or two oxygens in the CuO_4 unit. Let $t_{ox} = -0.35$, which leads to pairing with $\Delta = -13.8$ meV. If one of the oxygen levels is raised from 3.5 to 4.5 eV, the Coulomb repulsion reappears and leads to $\Delta = 0.334$ eV. If one of the oxygen levels is lowered to 2.5 eV, the breakdown is even more dramatic ($\Delta = -0.53$ eV). Alternatively, we may distort the square, by replacing two opposite oxygens with atoms having $\varepsilon = 2.5$ eV; then x- and y-like states exist, but are no longer degenerate, and $n_b \neq n_\beta$. According to the above discussion, this destroys the ability of the CI to remove the interaction, and in fact one gets $\Delta = 0.83$ eV. This shows that the CI mechanism is working thanks to the C_{4v} symmetry, and it is cut off whenever the symmetry is lowered to C_{2v}.

5. – Exact solutions for the CuO_4 cluster: off-site interaction effects

Let us consider the effects of the H_{pd} and $H_{pp'}$ terms in eqs. (6) and (7), respectively. If the off-site U_{pd} interaction is allowed, its expectation value over the 4

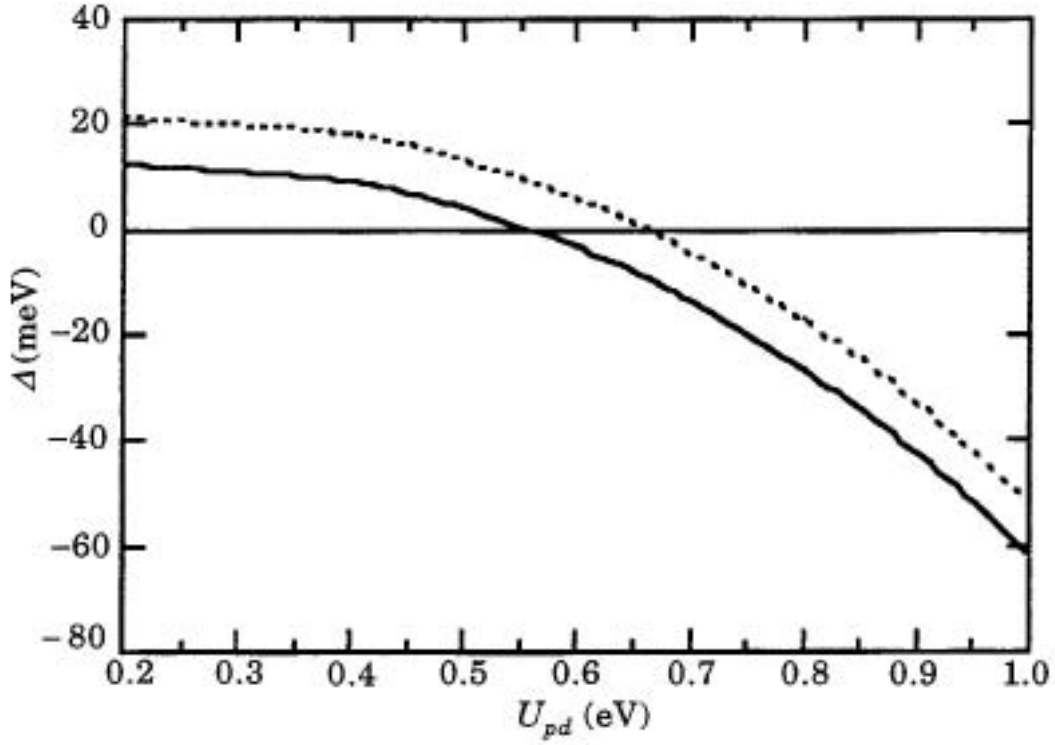

Fig. 8. – Dependence of the effective interaction Δ on the off-site U_{pd} interaction. Thick line: $U_{pp'} = 0$; thin line: $U_{pp'} = 10$ meV. The off-site interaction between oxygens produces a rigid shift of the curve to lower binding energies. Pairing by the CI mechanism might be attained also with larger $U_{pp'}$ values.

hole state, eq. (12), does not vanish. However, in a HF-like approximation replacing the $n_{i\sigma}$ operators by their average values, H_{pd} becomes a shift of the oxygen level with no first-order effect on the direct interaction W.

We report in fig. 8 the dependence of Δ on U_{pd} for the two values of $U_{pp'} = 0$ and 10 meV and the remaining parameters fixed as in table I. It is apparent that realistic values of $U_{pd} > 0.6$ do not spoil the mechanism, and tend to be synergic with it. A similar trend holds at other t_{ox} values. On the other hand, $U_{pp'}$ entails a direct contribution to W and may be expected to have a first-order bearing on Δ. Figure 8 shows that $U_{pp'}$ behaves very much as an additive constant to Δ, and the binding energy is rather sensitive to the magnitude of this parameter. Values of $U_{pp'}$ as large as 100 meV or more are still tolerable if $U_{pd} = 1.2$ eV suggesting that the parameter range comprises well the recommended experimental set.

6. – Additional remarks on symmetry

We have stressed above that the pairing mechanism depends on the full C_{4v} symmetry of the cluster and any large deviation from the full symmetry restores the normal on-site repulsion. This explains why our findings contrast with previous results. Indeed, Hirsch *et al.* [12] published cluster calculations leading to $\Delta < 0$ but, in order to achieve binding, they were forced to assume $\varepsilon_p \approx \varepsilon_d$ and the unphysically large off-site interaction $U_{pd} = 4$–6 eV. They used a nine-site and a sixteen-site cluster. Their nine-site cluster is not symmetric, and cannot give rise to the present mechanism. In fig. 9, we show the sixteen-site Cu_4O_{12} cluster used in ref. [12], where the sites 1 to 4 are Cu and the others are oxygens. It has the full C_{4v} point symmetry but, unlike the other clusters discussed here, it is not centred around a Cu site. This is a crucial difference, which prevents our mechanism from operating. Diagonalizing the

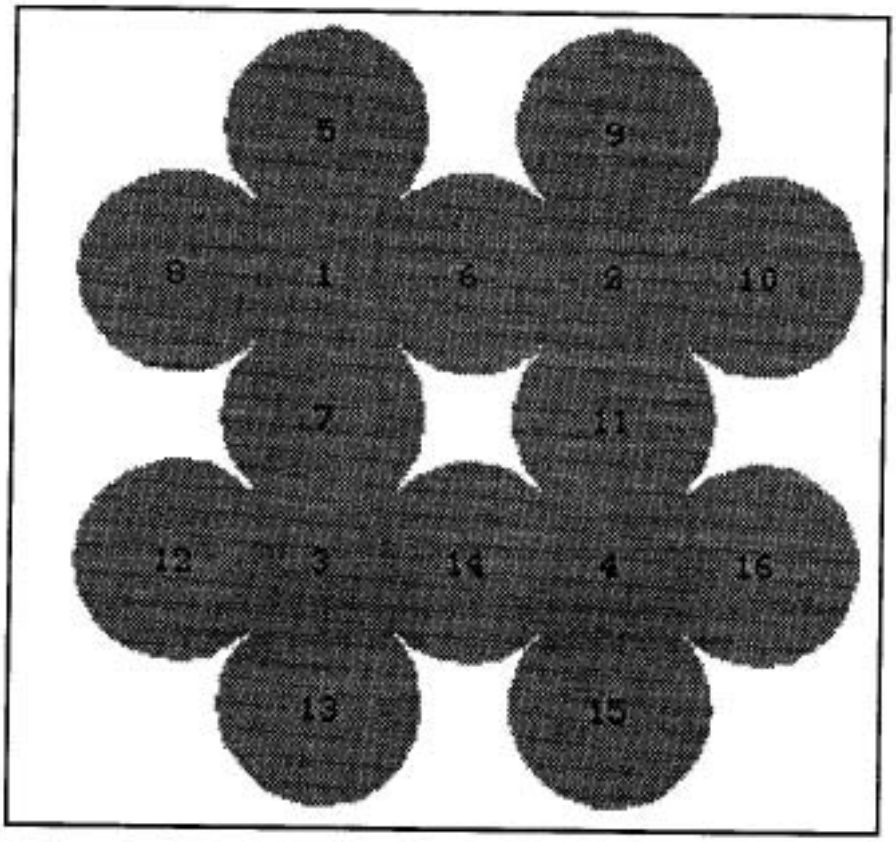

Fig. 9. – The Cu_4O_{12} cluster, where 1 to 4 are Cu sites, is not centred around Cu. With four holes it does not give rise to $W = 0$ pairs. Actually, the interaction between degenerate holes is quite large, and the CI mechanism is hampered.

one-particle Hamiltonian, with the parameters values of ref. [12] ($t = 1$ eV, $\varepsilon_p = 0$ and $t_{ox} = 0$), one finds that the lowest level is at -2.449 eV and the next one (at -2 eV) is twofold degenerate. This cluster with 4 holes is undoped. Treating the degenerate states at -2 eV according to the procedure described in sect. 3, one finds $n_\alpha \neq n_\beta$, and the on-site repulsion is not completely removed. While in the Cu_5O_{16} cluster $W \approx 2$ meV, in the Cu_4O_{12} cluster a similar calculation yields $W = 0.756$ eV. This W is so large that our mechanism cannot possibly operate, and in fact was not recognized in ref. [12]. Moreover, the presence of a normal on-site interaction between holes prevents pairing for physical parameter values, which appeared to be evidence against electronic mechanisms of pairing. Actually, pairing requires a vanishing or anomalously small W, and not all small clusters with C_{4v} point symmetry are suitable, but only those with a Cu at the centre. Similar remarks apply to the clusters considered in ref. [13].

7. – Conclusions

We have shown that a correlation effect (namely, the CI mechanism) leads to the exact removal of the direct Coulomb interaction W between pairs of degenerate holes in the CuO_2 plane. These $W = 0$ pairs are singlet eigenstates of the Hamiltonian without t_{ox} and off-site terms. The CI mechanism and the $W = 0$ two-hole singlets are consequences of the symmetry and electronic structure of the Cu-O plane, and do not depend on the size of the cluster. Moreover, similar considerations apply to two-dimensional systems of hexagons or triangles such that their point group includes the E irreducible representation.

We demonstrated pairing by the exact diagonalization of the Hamiltonian in small clusters. The striking fact is that (contrary to previous belief) one obtains binding energies of the correct order of magnitude (10 meV) for the set of parameters which corresponds to the best current estimates for actual systems. This opens up the possibility that the CI could be the essential reason for pairing, although more or less important contributions from the lattice are evidently to be expected on physical grounds.

Concerning this possibility, the above theory predicts a number of facts, including the relevant electronic states, the number of holes required for a given cluster and the binding energies of the pairs. It also suggests the internal structure of the pairs, which is consistent with the growing experimental evidence of *d*-wave symmetry [14]. A further consequence is that small clusters should show pairing if their symmetry conforms the criteria of sect. **6**, but not otherwise. This point should lend itself to experimental verification, *e.g.*, by the study of molecular ions.

We emphasize that our mechanism basically depends on symmetry arguments and is more general than the Hamiltonian that we have used for illustration. A fuller description of the system will involve band degeneracy and exchange interactions; however, the above theory does not need to be essentially modified, provided we form our pairs with particles of opposite spins, in analogy with Copper pairs.

On the other hand, much work is necessary before we can fully trust the capability of the correlation effect alone to produce binding in real superconductors. There is a clear need for numerical calculations in bigger clusters of the appropriate symmetry having enough holes to produce a partial occupancy of the degenerate states. In principle, our analysis can be implemented by *ab initio* density functional calculations, by mixing up Kohn-Sham [15] (instead of HF) configurations along the above lines.

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