A theory about high-temperature superconductivity

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Abstract
We deal with a model for high-temperature superconductivity which maintains that in cuprates electrons running in the copper oxide layers, found in lattice of these materials, form spin-singlet bonds with electrons running in the neighbouring layers. This model reutilizes the BCS scheme, but with the essential difference that the electron pairs are characterized by equal, rather than opposite momenta as in Cooper pairs. In the present paper, we consider the electron pair formation and a peculiar canonical transformation analogous to the transformation once applied to the theory of pairing correlations in nuclear matter. It is shown that the quasi-particle energy spectrum remains that of the BCS theory, including the linear relationship between forbidden energy gap and critical temperature. The model is also applied to superconductivity of some copperless perovskites of mixed stoichiometry, whose features are of special worth in understanding the mechanism of the phenomenon. The possibility of enhancing critical temperature in cuprates by inserting monovalent ions into the lattice is considered.

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1. Introduction
Notwithstanding the great deal of work done till now, no theory about high temperature superconductivity has obtained a general consensus. It is common belief that even the basic nature of the phenomenon is not understood. In magazine notes appeared on ”Scientific American” in 2000 and 2004, the inadequacy of theoretical models in explaining superconduction in cuprates is stressed \(^1\). Owing to this state of affairs, we will now examine a mechanism, quite unlike those so far proposed, which has been conceived by keeping in mind, besides cuprates, the features of other kinds of unconventional superconductors different from cuprates \(^2\).

Cuprates are surely the most interesting superconductors as they allow for the highest critical temperatures so far recorded. But a variety of materials other than cuprates is known, showing a superconductivity not explained by the BCS theory. Actually, superconducting has been detected in perovskites of fractional stoichiometry, in mixed copper and alkaly-earth oxides, in organic

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\(^2\) In Ref. [2, 3, 4, 5]; some features of this mechanism have already been presented.
compounds and in fullerenes. This makes complex the study of superconductivity but, at the same time, provides a wide experimental basis with which theory must be compared. In our opinion, the simplest and most conservative hypothesis is that the essential superconduction mechanism is the same in all these materials in spite of their quite different natures. Accordingly, the very cause of superconductivity must be searched for in something which is shared by all materials. On that account, next Section is devoted to singling out the features which pertain to all above-mentioned superconductors.

2. Common features of unconventional superconductors

In reality, two remarkable peculiarities are shared by the superconductors cited before. The first is that all are characterized by complex layered lattices or uneven heterogeneous lattices showing discontinuous structures. The second is that all contain ions or atoms with unpaired electrons or electrons not included in closed shells. These points are emphasized hereinafter by considering a selection of various superconductors.

A) Perovskites with fractional stoichiometries. - Some of these perovskites are listed in the following Table.

| Material                  | $T_c$ (K) |
|---------------------------|-----------|
| SrTiO$_{3-\delta}$ [6]    | $\approx 0.3$ K |
| BaPb$_{0.7}$Bi$_{0.3}$O$_3$ [7] | $T_c = 13$ K |
| Ba$_{0.6}$K$_{0.4}$BiO$_3$ [8] | $T_c = 30$ K |
| Sr$_{0.5}$K$_{0.5}$BiO$_3$ [9] | $T_c = 12$ K |
| Sr$_{0.5}$Rb$_{0.5}$BiO$_3$ [9] | $T_c = 13$ K |

Their structure is characterized by lattice discontinuities found at the borders between cells with different ion compositions. The SrTiO$_{3-\delta}$ superconductor, which shows a partial lack of oxygen, is a reduced compound. But, also BaPb$_{0.7}$Bi$_{0.3}$O$_3$ and Ba$_{0.6}$K$_{0.4}$BiO$_3$ are indeed reduced compounds. In fact, owing to valence four of lead and five of the fully oxidized bismuth, their stoichiometries should be written as BaPb$_{0.7}$Bi$_{0.3}$O$_{3.15}$ and Ba$_{0.6}$K$_{0.4}$BiO$_{3.31}$, respectively. The same argument obviously is right for the strontium-substituted compounds. For these compounds, the lack of room in the stiff perovskitic cell prevents oxygen from entering the cell until metals are fully oxidized. Since oxygen is kept in the form of divalent O$^{-2}$ ions, when oxygen is removed as neutral atoms some electrons are left in the material and become bound to metal ions. It follows that unpaired electrons appear in excess to the noble gas shells of K$^{+1}$, Ba$^{+2}$, Sr$^{+2}$ ions or to 5d$^{10}$ shell of Pb$^{+4}$ and Bi$^{+5}$ ions.

B) Cuprates. - These materials show layered lattices formed by perovskitic or perovskitic-like cubes. As cuprates are the best known superconductors, we limit ourselves to few examples. The first discovered La$_{1.85}$Sr$_{0.15}$CuO$_4$ cuprate, which superconducts at 35 K, is characterized by the K$_2$NiF$_4$ structure, that is, an alternation of perovskitic and NaCl-like layers [10]. It shows a fractionary stoichiometry and is to be regarded as an oxidized superconductor because,
owing to substitution of trivalent lanthanum with divalent strontium, its stoichiometry should be written as La$_{1.85}$Sr$_{0.15}$CuO$_3$. The 92 K superconductor YBa$_2$Cu$_3$O$_7$, usually referred to as YBCO, is characterized by a stacking of yttrium and barium centred lacunar perovskitic cubes [11]. In the so-called TBCO superconductors, such as for instance the Tl$_2$Ba$_2$CaCu$_2$O$_8$ compound, different alternation of perovskitic-like layers of copper, calcium, barium and thallium oxide are found [12, 13]. As for the unpaired electrons, we point out that all cuprates contain divalent copper with the [Ar]3d$^9$ configuration showing just one unpaired 3d-electron.

C) Mixed copper and alkaly-earth oxides. These compounds deserve attention because they are cuprates lacking in perovskitic structure. The mixed oxide SrCuO$_2$ shows an orthorhombic lattice, it is not a superconductor but superconductivity appears at 40 K in the fractionary stoichiometry compound Sr$_{0.86}$Nd$_{0.14}$CuO$_2$ [14]. It is a reduced compounds because, owing to valence three of neodimium, its stoichiometry should be written as Sr$_{0.86}$Nd$_{0.14}$CuO$_2$.07. Apart from the different structure, it is like the superconductors of item A). Recently, using a field-effect technique, electrons were removed from (or injected into) the monoclinic CaCuO$_2$ compound. In this way, superconductivity was found at 89 K and 34 K depending on whether 0.15 electrons per molecule are removed or injected, respectively [15]. Even in this case, superconductivity is originated by introduction of unpaired electrons and of lattice discontinuities lying at the borders between cells of different degrees of oxidation (3).

D) Organic superconductors. We limit ourselves to the Bechgaard salt, that is, tetramethyl-tetraselena-fulvalene hexafluoro-phosphate (TMTSF)$_2$ PF$_6$ which superconducts at about 1 K [16]. This material is characterized by stackings of strongly bound molecules with a much weaker intermolecular bonding in direction transverse to the stackings. One electron is moved from one TMTSF molecule to one fluorine atom so that (TMTSF)$^{+1}$ cations and (PF$_6$)$^{-1}$ anions appear. Since in the neutral TMTSF molecules all electrons are coupled in $\sigma$— or $\pi$—bonds, one unpaired electron is present in the (TMTSF)$^{+1}$ cation.

E) Fullerenes. These materials are characterized by stacks of C$_{60}$ balls. Links between carbons in contiguous balls are weaker than those of carbons in the same ball. Superconductivity has been detected at 18 K in K$_3$C$_{60}$ and at 28 K in Rb$_3$C$_{60}$ [17]. The presence of potassium or rubidium atoms, showing the [Ar]4s and [Kr]5s configurations, respectively, inserts unpaired electrons in the C$_{60}$ stacks. With the field-effect technique, electrons were removed or injected into the C$_{60}$ balls, so leaving some unpaired electrons there. In this way, superconductivity was originated at peak temperatures of 52 K or 11 K when just three electrons were taken off or added to each ball, respectively [18].

The previous analysis confirms that uneven lattices and unpaired electrons are really features common to the superconductors considered above. However, different kinds of superconductors must be distinguished depending on the actual provenance of the unpaired electrons. Indeed, compounds of item

3) With the field-effect technique the average degree of oxidation of the material can be properly determined. On the contrary, lattice discontinuities related to the local degree of oxidation of the cells remain uncertain. Also incidental lattice defects might play a role.
The Sr0.86Nd0.14CuO2 compound are "reduced" superconductors. The La1.85Sr0.15CuO4 cuprate, on the contrary, is an "oxidized" superconductor. Cuprates as YBa2Cu3O7 or Tl2Ba2CaCu2O8 and the Bechgaard salt are to be regarded as "intrinsic" superconductors, since unpaired electrons are peculiar to their chemical composition. The alkaly-doped fullerene as well as fullerene and CaCuO2 oxide showing field-effect superconductivity are to be regarded as "doped" superconductors, because in these materials superconductivity is originated by an external agent.

In our opinion, the features examined above can be considered as a sort of "Rosetta stone" for disentangling the problem of high temperature superconductivity.

3. About properties of fermion systems

Let us recall some topics concerning properties of fermion systems which will be helpful in understanding the mechanism of superconduction in the materials cited above. In 1916, G.N. Lewis first discovered that covalent bonds consist of pairs of shared electrons [19]. This fact, inexplicable by the classical physics, was interpreted in 1927 by W. Heitler and F. London (HL) who applied quantum mechanics to the hydrogen molecule [20]. By considering two hydrogen atoms A and B in 1s states, they wrote a two-electron wave function of the form: \[ u_{1sA}(1) u_{1sB}(2) + u_{1sB}(1) u_{1sA}(2) \] in which each electron is found at the same time both on atom A and B. This function, symmetric with respect to exchange of electrons, was associated to an antisymmetric spin function: \[ \alpha(1) \beta(2) - \beta(1) \alpha(2) \] representing a spin-singlet state, allowing for the Pauli principle. In this way, in evaluating the expectation value of energy, integrals involving products of electron states: \[ u_{1sA}(1) u_{1sB}(2) \] and \[ u_{1sB}(1) u_{1sA}(2) \] appear in calculations. These exchange integrals account for covalent bond energy. A year later, W. Heisenberg, utilizing the same arguments, explained the origin of the Weiss field in ferromagnetic solids [21].

In 1933, exchange forces came back into evidence in a quite different field of physics. In this year, indeed, E. Majorana, in dealing with nuclear interactions, introduced forces which exchange the coordinates of the interacting nucleons [22]. These forces are mediated by charged pions and act only for nucleons in neighbouring momentum states [23]. The Majorana forces are of paramount importance since they account for the saturation effects in binding energy of nuclei.

In 1957 the famous BCS theory finally explained superconduction in metals [24]. The essential device of this theory are the Cooper pairs, that is, pairs of electrons of opposite momenta bound by a phonon coupling. Utilizing a special canonical transformation devised by N.N. Bogolyubov, the system of interacting electrons is substituted by a set of non-interacting quasi-particles showing an energy gap at the top of the distribution [25].

The great success of the BCS theory drew attention on the possibility of its application to nuclear physics. In 1958, A. Bohr, B.R. Mottelson and D. Pines proposed that the energy gap found in the spectra of even-even nuclei is originated by a mechanism analogous to that of superconduction in metals [26].
Indeed, when the main part of the nucleon-nucleon interactions is averaged so allowing for a self-consistent field, there remains a residual weak interaction, due to Majorana forces, which couples nucleons of like momenta. A thorough treatment of this problem was performed by S.T. Belyaev which modified the Bogolyubov transformation substituting the Cooper pairs with Majorana pairs of nucleons with equal linear momenta, but opposite projections of angular momenta along the quantization axis [27]. This treatment, however, leaves out the dependence on temperature of the energy gap, owing to the fact that nuclei are always on the ground state. An equivalent treatment was performed by L.P. Gor'kov and A.I. Alekseev utilizing the Green function technique [28, 29].

Since our treatment on superconductivity utilizes a method similar to that applied by Belyaev, an extensive account on this matter is given in Appendix A.

4. The superconducting Lewis pairs

The superconductor features highlighted in Section 2 and the arguments presented in Section 3 induce us to argue that at low temperature unpaired electrons running in a superconductor region bordering on a lattice discontinuity originate singlet pairs with electrons running in the region bordering on the opposite side of the lattice discontinuity. This is due to instability of the unpaired electrons that tend to form covalent bonds. Obviously, in order to set out a quantitative treatment, it is necessary to know, besides the electron wave functions, the actual nature of the lattice discontinuities. This occurs with the intrinsic superconductors, such as the the YBa$_2$Cu$_3$O$_7$ and the Tl$_2$Ba$_2$CaCu$_2$O$_8$ cuprates, or the Bechgaard salt. On the contrary, with the reduced superconductors of items A) and C) it is necessary to resort to special conjectures, since their fractional stoichiometries make the structure uncertain. These superconductors are investigated in Section 7. Also the fullerene-based superconductors give rise to difficulties of this kind. In practice, the materials most right for our investigations are the intrinsic cuprates.

The previously cited cuprates, are characterized by planes of oxygen lacunae and yttrium or calcium ions sandwiched between couples of contiguous CuO$_2$ layers (see [30] Ch. 7). In the following, these layers will be marked with labels $a$ and $b$. Two unpaired electrons, one running on layer $a$ the other on layer $b$, can be represented by the tight-binding (TB) wave functions

$$
\phi_a(k_a, r_1) = \frac{1}{\sqrt{N}} \sum_{p=1}^{N} \exp (i k_a \cdot u_p) \ a(r_1 - u_p),
$$

$$
\phi_b(k_b, r_2) = \frac{1}{\sqrt{N}} \sum_{q=1}^{N} \exp (i k_b \cdot v_q) \ b(r_2 - v_q),
$$

in which $k_a$ and $k_b$ mean the electron wave vectors, $a(r_1 - u_p)$ and $b(r_2 - v_q)$ the 3d-orbitals of the copper ions on layers $a$ and $b$ and $u_p$ and $v_q$ their lattice vectors, respectively. Each copper ion on layer $a$ is separated from a
corresponding ion on layer $b$ by the spacing $\lambda$ between the layers, that is,
\[ v_p - u_p = \lambda. \tag{2} \]

The energies of the unpaired electrons spoken of are
\[ W_a (k_a) = \langle \phi_a (k_a, r_1) | H_a (p_1, r_1) | \phi_a (k_a, r_1) \rangle, \]
\[ W_b (k_b) = \langle \phi_b (k_b, r_2) | H_b (p_2, r_2) | \phi_b (k_b, r_2) \rangle, \tag{3} \]
where the Hamiltonians $H_a$ and $H_b$ account for the electron kinetic energies $p_1^2/2m$ and $p_2^2/2m$ and for the Coulomb interactions of electrons 1 and 2 with the copper ions in positions $u_p$ and $v_p$, respectively. For $k_a = k_b$, energies $W_a (k_a)$ and $W_b (k_b)$ are equal, owing to equality of the CuO$_2$ layers. In Appendix B, utilizing a special model for the actual nature of the copper ion orbitals, energies $W_a (k_a)$ and $W_b (k_b)$ are evaluated on the ground of Eqs. (3).

Owing to the peculiar structure of the before cited cuprates, that is, the presence of oxygen lacunae on the yttrium or calcium planes placed between the copper ions, an unpaired electron of layer $a$ is allowed to form a covalent bond with an unpaired electron of layer $b$, like the 1s electron of a hydrogen atom $A$ forms a covalent bond with the 1s electron of another hydrogen atom $B$. On this ground, in analogy to the HL treatment of the hydrogen molecule [31], the wave function for a pair of electrons of layers $a$ and $b$ in a spin-singlet state is
\[ \Psi (r_1, r_2) = \frac{1}{\sqrt{2} (1 + \langle \phi_a | \phi_b \rangle^2)} [\phi_a (k_a, r_1) \phi_b (k_b, r_2) + \phi_a (k_a, r_2) \phi_b (k_b, r_1)] \times \]
\[ \times \frac{1}{\sqrt{2}} [\alpha (1) \beta (2) - \alpha (2) \beta (1)], \tag{4} \]
\[ \alpha (1) \text{ and } \beta (2) \text{ standing for the spin functions. In the following, these pairs are referred to as "Lewis pairs" since this author, already cited in Section 3, pioneered investigations on covalent bonds. The possibility of applying the HL treatment is due to the fact that it is implemented aside from the actual nature of the electron states, so that 1s$_A$ and 1s$_B$ or $\phi_a$ and $\phi_b$ states can be indifferently considered. This notwithstanding the fact that 1s states account for a single Coulomb potential centre, while $\phi$ states account for $N$ centres. Like in the HL treatment, energy $-W_P$ of the electron pair holds a "classic" contribution, that is, without exchange of electrons between $\phi_a$ and $\phi_b$ states and an exchange contribution in which both electrons are shared between $\phi_a$ and $\phi_b$ states (4), that is,
\[ -W_P = \langle \Psi (r_1, r_2) | H_{int} (r_1, r_2) | \Psi (r_1, r_2) \rangle = \]
\[ \text{Apart from substitution of 1s$_A$ and 1s$_B$ hydrogen-like states with $\phi_a$ and $\phi_b$ states and the presence of summations over the $N$ copper ions, the terms appearing in Eq. (5) are like the terms in Eq. (43-7) and (43-9) of reference [31] p. 342. We omit considerig terms for the spin-triplet state which, in HL treatment, originate repulsion between the hydrogen atoms.}
to unity. Only integrals \( K \) must be retained.

Consider the exchange integral of electrons with copper ions of effective charge \( Z \), given by

\[
\langle m \text{olecule} \rangle = \text{the squared overlap integral pair. These contributions are negligible as occurs in the case of the hydrogen terms.}
\]

We proceed now to evaluate the integrals appearing in Eq. (6). Let us first consider the exchange integral \( K' \). Taking into account Eqs. (1), we have

\[
K' = \langle \phi_a (k_a, r_1) \phi_b (k_b, r_2) | e^2 r_{1,2} | \phi_b (k_b, r_1) \phi_a (k_a, r_2) \rangle = \]

\[
= \frac{e^2}{N^2} \sum_{q, p=1}^{N} \exp \left( -i k_b \cdot v_q + i k_a \cdot u_p \right) b(r_2 - v_q) a(r_2 - u_p) \times \]

\[
\times \left[ \int \sum_{p, q=1}^{N} \exp \left( -i k_a \cdot u_p + i k_b \cdot v_q \right) \frac{a(r_1 - u_p) b(r_1 - v_q) d^3 r_1}{r_{1,2}} d^3 r_2. \right]
\]

This equation involves sums over \( N^4 \) terms. But, taking into account that the electron distributions in orbitals \( a(r_1 - u_p) \) or \( a(r_2 - u_p) \) and \( b(r_1 - v_q) \) or \( b(r_2 - v_q) \) are closely localized at the lattice positions \( u_p \) and \( v_q \), respectively, terms \( b(r_2 - v_q) a(r_2 - u_p) \) and \( a(r_1 - u_p) b(r_1 - v_q) \) are non-negligible only
when \( r_2 \simeq v_q \) and \( r_2 \simeq u_p \) and \( r_1 \simeq u_p \) and \( r_1 \simeq v_q \), which entails that \( v_q \simeq u_p \), that is, remembering Eq. 2, \( p = q \). It follows that the sums in Eq. (7) contain only \( N^2 \) non-negligible terms. This leads to

\[
K' = \frac{e^2}{N^2} \int \sum_{p=1}^{N} \exp \left[ i (k_a - k_b) (v_q - u_p - \lambda) \right] \times \\
\times \frac{b (r_2 - v_q) a (r_2 - u_q) a (r_1 - u_p) b (r_1 - v_q)}{r_{1,2}^3} d^3 r_1 d^3 r_2. \tag{8}
\]

In this sum, significant contributions appear only when \( r_{1,2} \) is small, that is, when \( r_2 \simeq r_1 \). This, as before, entails that only terms with \( v_q \simeq u_p \), that is, \( p = q \) are non-negligible. So we obtain

\[
K' = \frac{e^2}{N^2} \int \sum_{q=1}^{N} \frac{b (r_2 - v_q) a (r_2 - u_q) a (r_1 - u_p) b (r_1 - v_q)}{r_{1,2}^3} d^3 r_1 d^3 r_2 = \\
= O \left( \frac{1}{N} \right), \tag{9}
\]

which means that this integral, which accounts for Coulomb repulsion between electrons, can be neglected. We consider now the overlap integral

\[
\langle \phi_a (k_a, r_1) | \phi_b (k_b, r_1) \rangle = \\
= \frac{1}{N} \int \sum_{p=1}^{N} \exp \left[ -i k_a \cdot u_p + i k_b \cdot v_q \right] a (r_1 - u_p) b (r_1 - v_q) d^3 r_1. \tag{10}
\]

In this case, significant contributions are obtained only for orbitals with \( u_p \simeq r_1 \) and \( v_q \simeq r_1 \) which entails that \( u_p \simeq v_q \) and, as before, \( p = q \). We have thus

\[
\langle \phi_a (k_a, r_1) | \phi_b (k_b, r_1) \rangle = \\
= \int \exp \left[ -i (k_a - k_b) \cdot r_{1,1} \right] \frac{1}{N} \sum_{p=1}^{N} a (r_1 - u_p) b (r_1 - u_p - \lambda) d^3 r_1, \tag{11}
\]

in which only the parallel component \( r_{1,1} \) has been accounted for in the exponential factor since \( k_a \) and \( k_b \) are parallel to \( a \) and \( b \) layers. By putting

\[
F (r_{1,1}) = \frac{1}{N} \sum_{p=1}^{N} a (r_1 - u_p) b (r_1 - u_p - \lambda) d r_{1,1}, \tag{12}
\]

5) It is to be pointed out that Coulomb repulsion between electrons is screened by the presence of the positive ions which assure the electric neutrality of the material. Consequently, Coulomb repulsion decreases more quickly than \( e^2/r_{1,2} \). This is like what occurs with Cooper pairs in BCS theory.
Eq. (11) can be rewritten as a Fourier transform, that is,
\[ \langle \phi_a (k_a, r_1) \mid \phi_b (k_b, r_1) \rangle = \int \exp \left[ -i \left( k_a - k_b \right) \cdot r_1 \right] F(r_{11}) \, d^2 r_{11}. \quad (13) \]
Function \( F(r_{11}) \) shows a slight periodic dependence on \( r_{11} \) since, when \( r_{11} \) varies, about equivalent terms are always included in the sum over \( p \). In particular, if dependence on \( r_{11} \) of function \( F(r_{11}) \) is omitted we have
\[ \langle \phi_a (k_a, r_1) \mid \phi_b (k_b, r_1) \rangle = (2\pi)^2 F \delta (k_a - k_b). \quad (14) \]
Eqs. (13) and (14) entail that electrons of equal wave vectors, that is, of equal momenta, allow for the maximum value of overlap integral and, therefore, the maximum pairing energy. It is worth to point out that this result mimics that concerning the Majorana exchange forces, which likewise originate fermion pairs of equal momenta. But, with the Lewis pairs this is a consequence of antisymmetry of the wave function (4) which accounts for the Pauli’s principle, while with the Majorana pairs equality of momenta directly follows from the exchange nature of the forces, which are mediated by charged pions. On this ground, we consider in the following only electron pairs with \( k_a = k_b \). We find in this way
\[ \langle \phi_a (k_a, r_1) \mid \phi_b (k_b, r_1) \rangle = \frac{1}{N} \sum_{p=1}^{N} a(r_1 - u_p) b(r_1 - u_p - \lambda) d^3 r_1 = S_{a,b}, \quad (15) \]
where
\[ S_{a,b} = \int a(\rho) b(\rho - \lambda) \, d^3 \rho. \quad (16) \]
By applying the same procedure to exchange integral
\[ K = -\langle \phi_b (k_b, r_2) \mid \sum_{p=1}^{N} Z e^2 |r_2 - u_p| \mid \phi_a (k_a, r_2) \rangle, \quad (17) \]
we obtain
\[ K = -\frac{1}{N} \sum_{l=1}^{N} \int a(r_2 - u_l) Z e^2 |r_2 - u_l| b(r_2 - u_l - \lambda) d^3 r_2 = E_{b,a}, \quad (18) \]
where
\[ E_{b,a} = -\int a(\rho) Z e^2 |\rho - \lambda| b(\rho - \lambda) d^3 \rho. \quad (19) \]
Consequently, utilizing Eqs. (6), (9), (15) and (18), pairing energy for \( k_a = k_b \) turns out to be
\[ -W_P = 2 S_{a,b} E_{b,a}. \quad (20) \]
Energy $W_P$, of course, is expected to be very small in comparison with those of most covalent bonds, owing to the considerable separation of the interacting copper oxide layers which is larger than normal covalent bond lengths.

5. The canonical transformation

According to the above picture, electrons running on the contiguous copper oxide layers $a$ and $b$ constitute one set of $2N$ Fermi’s particles. An electron in this set with a given wave-vector $\mathbf{k}$ shows degeneration due to its spin components $\alpha$ and $\beta$ and degeneration due to options $\mathbf{k} = \mathbf{k}_a$ or $\mathbf{k} = \mathbf{k}_b$, that is, to its placing on layer $a$ or $b$. Owing to $\mathbf{k}$ degeneration, the electron set is split into two conjugated subsets $a$ and $b$. Each electron of subset $a$ is paired with an electron of subset $b$ of equal wave vector, that is, of equal momentum, with an energy $-W_P$ independent of the actual momentum. As follows from spin-singlet wave function (4), these pairs show spin zero so that can be regarded as weakly bound bosons.

On this ground, the second quantization Hamiltonian for Lewis pairs can be identified with the Belyaev’s Hamiltonian (45) considered in Appendix A in connection with systems of interacting particles characterized by symmetry of reflection in a plane. This, of course, barring substitution of indexes $R$ and $L$ with indexes $a$ and $b$. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_7$ cuprate, the plane of symmetry is to be identified with the plane of yttrium ions. In this way, by taking single particle energies into account, writing briefly $\epsilon_k$ for $W_a(\mathbf{k}_a)$ and $W_b(\mathbf{k}_b)$ and substituting $V_{k,k'}$ with $W_P$, the Hamiltonian for a system of electrons forming Lewis pairs can be written in the quick form

$$\hat{H} = \sum_k (\epsilon_k - \mu) \left( \hat{\alpha}_{ka}^+ \hat{\alpha}_{ka} + \hat{\alpha}_{kb}^+ \hat{\alpha}_{kb} \right) - W_P \sum_{k,k'} \hat{\beta}_{ka}^+ \hat{\beta}_{ka} \hat{\beta}_{kb}^+ \hat{\beta}_{kb}$$

(21)

$\mu$ standing for the chemical potential of the $2N$ electron set. In Appendix C, simple arguments are posed showing that this Hamiltonian conserves the momentum of the system.

Assuming coefficients which satisfy condition

$$U_k^2 + V_k^2 = 1,$$

(22)

the canonical transformation is

$$\hat{\alpha}_{ka} = U_k \hat{\beta}_{ka} + V_k \hat{\beta}_{kb}^+, \quad \hat{\alpha}_{kb} = U_k \hat{\beta}_{kb} - V_k \hat{\beta}_{ka}^+,$$

(23)

$\hat{\beta}_{ka}$ and $\hat{\beta}_{kb}$ standing for the quasi-particle destruction operators. Substitution of Eq. (23) into Eq. (21) leads to

$$\hat{H} = \sum_k \xi_k \left[ 2V_k^2 + (U_k^2 - V_k^2) (\hat{n}_{ka} + \hat{n}_{kb}) + 2U_kV_k \left( \hat{\beta}_{ka}^+ \hat{\beta}_{kb}^+ + \hat{\beta}_{kb} \hat{\beta}_{ka} \right) \right] -$$

$$- W_P \sum_{k,k'} \hat{B}_{k'}^+ \hat{B}_k,$$

(24)
where $\xi_k = \varepsilon_k - \mu$ and

$$\hat{B}_k = U_k^2 \hat{\beta}_{kb} \hat{\beta}_{ka} - V_k^2 \hat{\beta}_{ka}^* \hat{\beta}_{kb}^* + U_k V_k (1 - \hat{n}_{ka} - \hat{n}_{kb}),$$

(25)

$\hat{n}_{ka} = \hat{\beta}_{ka}^* \hat{\beta}_{ka}$ and $\hat{n}_{kb} = \hat{\beta}_{kb}^* \hat{\beta}_{kb}$ standing for the operators of quasi-particle numbers. These equations, apart from some obvious differences in symbols, are like those for the BCS theory given, for instance, in the Landau and Lifshitz treatise [32]. For this reason, reutilizing the same routine procedure, we limit ourselves to reporting the most significant issues. By taking condition (22) into account, considering the diagonal terms in the Hamiltonian and minimizing energy with respect to coefficient $U_k$ for given entropy, we find

$$2\xi_k U_k V_k = \Delta (U_k^2 - V_k^2),$$

(26)

with

$$\Delta = W_P \sum_{k'} U_{k'} V_{k'} (1 - n_{k'a} - n_{k'b}),$$

(27)

in which $n_{k'a}$ and $n_{k'b}$ now mean the actual numbers of quasi-particles. When Eq. (26) is verified, the non-diagonal second-order terms $\hat{\beta}_{kb} \hat{\beta}_{ka}$ and $\hat{\beta}_{ka}^* \hat{\beta}_{kb}^*$ are removed from Hamiltonian (24). From Eqs. (22) and (26), the usual relations for coefficients $U_k$ and $V_k$ are obtained,

$$U_k^2 = \frac{1}{2} \left( 1 + \frac{\xi_k}{\sqrt{\Delta^2 + \xi_k^2}} \right), \quad V_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{\sqrt{\Delta^2 + \xi_k^2}} \right),$$

(28)

which, when substituted into Eq. (27), lead to the equation which determines $\Delta$

$$W_P \sum_{k'} \frac{(1 - n_{k'a} - n_{k'b})}{\sqrt{\Delta^2 + \xi_{k'}^2}} = 1.$$  

(29)

The next step is to change summation on $k'$ to integration on energy. Taking into account that for $\varepsilon_k = 0$ and $\varepsilon_k = \mu$ we have $\xi_k = -\mu$ and $\xi_k = 0$, respectively, Eq. (29) becomes

$$W_P \int_{-\mu}^{0} \frac{(1 - n_{\xi a} - n_{\xi b})}{\sqrt{\Delta^2 + \xi^2}} \Omega (\xi) d\xi = 1,$$

(30)

$\Omega (\xi)$ standing for the density of states per unit cell. Owing to the expected smallness of $\Delta$ with respect to $\mu$, the main contribution to the integrand arises for $\xi \simeq 0$ so that we can put $\Omega (\xi) \simeq \Omega_F$. For $\xi = 0$, we have indeed $\kappa = \mu = \varepsilon_F$ since the chemical potential, apart from a small correction due to temperature,
coincides with the electron kinetic energy at the Fermi level \( \xi \). Consequently, at \( T = 0 \) K where \( n_{\xi a} = n_{\xi b} = 0 \), Eq. (30) yields

\[
W_P \Omega_F \int_{-\mu}^{0} \frac{d\xi}{\sqrt{\Delta^2_0 + \xi^2}} = W_P \log \frac{\Delta_0}{\sqrt{\Delta^2_0 + \mu^2} - \mu} \simeq W_P \log \frac{2\mu}{\Delta_0} = 1 \quad (31)
\]

which leads to

\[
\Delta_0 = 2\mu \exp\left(-1/W_P \Omega_F\right). \quad (32)
\]

This equation differs from the corresponding one of the BCS theory only in the substitution of the Debye energy \( \hbar \omega_D \) with twice the chemical potential \( \mu \). It follows from Eq. (32) that superconduction is ruled by three parameters, that is, pair energy \( W_P \), density of states \( \Omega_F \) at the Fermi level and chemical potential \( \mu \). Taking into account that \( \mu = \varepsilon_F \), a connexion between \( \mu \) and \( \Omega_F \) is expected, depending on the actual electron energy spectrum \( \xi \). In Appendix B, utilizing special assumptions for the copper ions orbitals, this connexion is found to be:

\[
\mu \Omega_F = 1 \quad (32)
\]

which allows Eq. (32) to be rewritten as

\[
\Delta_0 = 2\mu \exp\left(-0.78 \frac{\mu}{W_P}\right). \quad (33)
\]

For \( T > 0 \), substituting

\[
n_{\xi a} = n_{\xi b} = 1/\left[ \exp\left(\sqrt{\Delta^2 + \xi^2/kT}\right) + 1 \right] \quad (34)
\]

into Eq. (30), we obtain as in the BCS theory

\[
\log \frac{\gamma \Delta_0}{\pi k_B T} = \frac{7\zeta(3)}{8\pi^2} \left( \frac{\Delta}{k_B T} \right)^2, \quad (35)
\]

where \( k_B \) is the Boltzmann constant, \( \log \gamma = 0.577 \) the Euler constant and \( \zeta(3) = 1.202 \) the Riemann Zeta-function. By putting \( \Delta = 0 \) in this equation, the usual relationship between energy gap and critical temperature is found

\[
2\Delta_0 = \frac{2\pi}{\gamma} k_B T_c = 3.52 k_B T_c. \quad (36)
\]

\( ^6 \) See for instance [33] Ch. III.

\( ^7 \) In this equation \( \Delta_0 \) is a constant quantity. But, if in normalizing the TB functions \( \langle \theta \rangle \), overlap integrals of copper ion orbitals are not disregarded, \( \Delta_0 \) is substituted by a quantity \( \Delta(\theta) \) depending on the angle between the electron wave vector \( \mathbf{k} \) and the cell \( a \)-axis. This accounts for the \( d \)-symmetry of the order parameter. In Ref. [3] this matter has been thoroughly discussed.

\( ^8 \) For a tridimensional Fermi gas of \( N \) electrons in a volume \( V \), we have:

\[
N \Omega_F = \left( \frac{V}{2\pi^2} \right) \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F}, \quad \text{where:} \quad \varepsilon_F = \left( \frac{\hbar^2}{2m} \right) \left( 3\pi^2 N/V \right)^{2/3}. \quad \text{This, by letting} \quad \mu = \varepsilon_F, \quad \text{leads to:} \quad \mu \Omega_F = 1.5 \quad (33) \quad \text{(see for instance [33] Ch. III)}. \]
Likewise, by utilizing the Hamiltonian (24) and Eqs. (27) and (28), the quasi-particle energy spectrum is found to be the same as that of the BCS theory, that is,

$$w_k = \sqrt{\Delta^2 + (\varepsilon_k - \varepsilon_F)^2}.$$  \hspace{1cm} (37)

The actual magnitude of the energy gap is $2\Delta_0$ since quasi-particles appear in pairs as occurs in BCS theory. It is to pointed out that Eq. (36) has been successfully tested for various unconventional superconductors. An extensive tabulation of data concerned is given in [30] Ch. 6.

6. Experimental evidence in favour of the interacting-layer mechanism

We will now briefly examine some experimental results which substantiate the interacting-layer mechanism. They are reported here in order of increasing significance.

1) Coherence length - A first clue about the interaction between the superconducting layers is offered by measurements of the Hall effect on YBa$_2$Cu$_3$O$_7$ single crystals. It was found that the Ginzburg-Landau coherence length along the c-axis is 1.5 Å. Since the spacing of superconducting layers is near to c-axis lattice parameter 11.68 Å, the conclusion was drawn that "the two copper oxide planes which are spaced 3.2 Å, are tightly coupled and act as a single superconducting layer" [34].

2) The effect of internal pressure. - More direct evidence comes out from the effect of pressure on critical temperature. It is common knowledge that in cuprates $T_c$ considerably increases when samples are submitted to hydrostatic pressures on the order of few GPa. Eqs. (16) and (19), which relate pairing energy to the layer separation $\lambda$, explain this effect. Indeed, hydrostatic pressure lessens separation $\lambda$ thus increasing $W_p$ and, consequently, critical temperature. But hydrostatic pressure lessens the distances between copper ions in direction both parallel and orthogonal to CuO$_2$ layers. The effect of hydrostatic pressure, therefore, is unsuitable in distinguishing interactions inside each layer from those between contiguous layers so that no evidence in favour of the interacting-layer mechanism is obtained. The conclusion, however, is different if the so-called "internal" or "chemical" pressure is considered. Indeed, substitution of some ions with others of smaller radius originates a decrease in the cell size which is commonly regarded as the effect of an internal pressure. In this connection, let us quote, the following sentence by P. Chu highlighted in a note by K.A. Muller [35]: "Therefore, Paul Chu thought, O.K., instead of applying pressure, I rather use a rare-earth ion, namely the yttrium which is smaller than lanthanum, and thus get a higher $T_c$ owing to the induced internal pressure". Actually, the La$^{+3}$ ionic radius is 1.15 Å while that of Y$^{+3}$ is 0.93 Å. This is tantamount to saying that in YBCO $T_c$ increases just when the contiguous CuO$_2$ layers approach each other leaving unchanged copper ion distances parallel to the layers (9).

9) A clear evidence of the effect of internal pressure is offered by some thallium-based
3) The effects of yttrium-praseodymium substitution and of reduction in YBa$_2$Cu$_3$O$_7$. - Concerning the effect of ion substitutions in YBa$_2$Cu$_3$O$_7$, a surprising feature is the lack of superconductivity of the PrBa$_2$Cu$_3$O$_7$ compound [37, 38]. This fact cannot be ascribed to the praseodymium ionic radius which is not significantly different from the yttrium radius. To explain this peculiar result it should be taken into account that praseodymium originates both trivalent and tetravalent ions. Actually, magnetic susceptibility measurements have indicated that, in the compound dealt with, praseodymium is tetravalent [39, 40]. This means that one electron is released from praseodymium and transferred to the neighbouring copper ions on the CuO$_2$ layers so that each cell contains one divalent and one monovalent copper rather than two divalent coppers as in the yttrium compound. In the PrBa$_2$Cu$_3$O$_7$ compound praseodymium acts as an electron donor. Since monovalent copper shows the [Ar]3d$^{10}$ configuration lacking unpaired electrons, the superconducting pairs can no longer be originated. Consequently, superconductivity is shut out by the interacting-layer mechanism, just as expected.

A very interesting result concerns the effect of reduction on YBa$_2$Cu$_3$O$_7$ critical temperature. Samples of stoichiometry YBa$_2$Cu$_3$O$_7$–$x$ show a decreasing $T_c$ for increasing $x$. Actually, the $T_c$ versus $x$ plot is characterized by two plateaux, the first at 92 K, for $x$ less than 0.2, followed by a step decrease and by a second plateau at about 60 K, for $x$ near to 0.4. Measurements of distances of copper from nearby ions have shown that the effective valence (10) of copper on CuO$_2$ layers is characterized by a parallel behaviour. Indeed, the plot of copper effective valence versus $x$ shows just two plateaux for the same values of $x$ separated by a step decrease of 0.03 e/Cu effective charges [44]. This behaviour, like that originated by the yttrium-praseodimium substitution, depends on reduction of divalent copper on the CuO$_2$ layers. When oxygen is removed, a number of electrons is left into the lattice. Along the plateaux, only trivalent copper on the cell basal planes is reduced thus leaving $T_c$ unaffected. The $T_c$ decrease for 0.2 < $x$ < 0.4 corresponds to the decrease of effective valence of CuO$_2$ layer copper. In Reference [5] a thorough thermodinamic description of this effect is given.

4) The monolayered Tl$_2$Ba$_2$CuO$_6$ compound. - Several multilayered thallium-based superconductors are known. The compound mentioned here represents a special case since it is characterized by a single CuO$_2$ layer interposed between two BaO and two TlO layers on the outside of the BaO layers (see [30] Ch. 7). With this structure, the CuO$_2$ layers are well separated so that the interacting-layer mechanism cannot be active. In spite of this, this compound superconducts at 85 K [13]. This fact may seem to represent strong evidence against the mechanism we consider. In reality, the situation is quite opposite. In fact, only reduced samples of stoichiometry Tl$_2$Ba$_2$CuO$_6$–$δ$ superconduct. Experiments cuprates in which barium-strontium substitution slightly lessens the cell size along c-axis so originating $T_c$ enhancements as large as tens of K [36].

10) For the meaning of the "effective valence" parameter, otherwise referred to as the "bond valence sum", see [41, 42, 43]. It can be identified, in practice, with the copper average valence.
have shown that in fully oxidized samples superconductivity is destroyed just as expected on the ground of the mechanism dealt with [45]. Reduction introduces in the lattice unpaired electrons, as occurs in the perovskites with fractional stoichiometry listed in item A) of Section 2. As it will be shown in the next Section, these electrons originate additional layers of unpaired electrons with which electrons in the CuO$_2$ layers interact so allowing for superconductivity. On this ground, the sudden onset of superconductivity observed as soon as the oxygen content is reduced is not surprising. Indeed, even a minimum quantity of superconducting material embedded in an inert matrix is sufficient to set the sample resistance to zero.

By keeping the previous arguments in mind, the queer result that reduction sometimes causes and other times hinders superconductivity is explained. In Ref. [4], other evidences in favour of the interacting-layer mechanism are discussed.

7. Superconductivity of mixed stoichiometry perovskites

We extend our analysis to superconductivity of some mixed stoichiometry perovskites. As pointed out in Section 2, these materials are to be regarded as reduced compounds. Reduction decreases the actual cation valence, thus introducing unpaired electrons into the lattice. In the mechanism we consider, unpaired electrons are indeed the basic ingredient for superconductivity. However, the question is to be settled of the lattice structure which allows the interacting layer mechanism to operate. While cuprates show a quite tidy layered structure, in the mixed stoichiometry compounds oxygen lacunae or substitutional ions are placed at random. Despite this, for mere statistical reasons it can be expected that the lattice contains some domains in which ions are layered in the right order to allow superconductivity. We point out, in this connection, that the formation of Lewis pairs is allowed even when lattice vectors $v_q$ and $u_p$ are not ordered on plane surfaces, as occurs in cuprates. Even irregularly bent surfaces, such as those that are likely found in mixed stoichiometry compounds, are suitable, provided that a number of orbitals with unpaired electrons exist such that Eq. (2) can be applied. Therefore, remembering that even a minimum quantity of superconducting phase sets sample resistance to zero, the superconductivity of mixed stoichiometry perovskites can reasonably be explained.

To understand how this can occur, let us focus attention on the previously cited 30 K superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$. The most conservative assumption is that the unpaired electrons introduced by the potassium-barium substitution lie right on the barium, so that monovalent Ba$^{+1}$ ions substitute K$^{+1}$ ions. In this way, in fact, the lattice Madelung energy is kept unchanged at its former value. Evidence in favour of this assumption is offered by the fact that superconductivity was detected in the Sr$_{0.5}$K$_{0.5}$BiO$_3$ and Sr$_{0.5}$Rb$_{0.5}$BiO$_3$ compounds at 12 K and 13 K, respectively (see Table 1). This large $T_c$ decrease is to be ascribed to the strontium ionic radius which is smaller than the barium radius. Since the alkaline-earth ions are placed at the centre of the perovskitic cells, the smaller Sr$^{+1}$ ion radius reduces the orbital overlap and thus pairing
energy $W_P$. In Table 2, using the edge, face, centre [E F C] notation [30, 46], the probable layering scheme of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is shown together with those of the previously mentioned $\text{BaPb}_{0.7}\text{Bi}_{0.3}\text{O}_3$ and $\text{SrTiO}_{3−\delta}$ compounds. The ion arrangement which originates superconductivity is the same in all compounds. In particular, in all compounds an empty C-position separates the alkaline-earth ions, thus allowing formation of bonds as occurs in bilayered cuprates.

In Table 2, the probable layering scheme of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ is shown together with those of the previously mentioned $\text{BaPb}_{0.7}\text{Bi}_{0.3}\text{O}_3$ and $\text{SrTiO}_{3−\delta}$ compounds. The ion arrangement which originates superconductivity is the same in all compounds. In particular, in all compounds an empty C-position separates the alkaline-earth ions, thus allowing formation of bonds as occurs in bilayered cuprates.

Table 2: Probable layering schemes in mixed stoichiometry perovskites. Braces enclose the layers which activate superconductivity. Ions with unpaired electrons are represented by bold type.

Probable layering schemes of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6−\delta}$ compounds are also shown in Table 2. These cuprates are of special interest since both are characterized by isolated CuO$_2$ layers. In the oxidized $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ compound, trivalent $\text{Sr}^{+3}$ ions are included showing unpaired electrons in the krypton shell and forming bonds with copper. The situation, however, is quite different from that of bilayered cuprates. In fact, while copper is placed in E-position, strontium lies in the C-position of the overhanging layer. Consequently, each copper is allowed to form bonds with four strontium ions so that
the symmetry between the interacting layers peculiar to bilayered cuprates no longer exists. A possible equivalent interpretation assumes that divalent strontium causes an equal number of lanthanum ions to be oxidized to valence four, thus showing unpaired electrons in the xenon shell. The monolayered reduced compound Tl₂Ba₂CuO₆₋δ shows a similar situation. In this compound, monovalent Ba⁺⁺ ions with unpaired 6s electrons are present forming bonds with 3d-electrons of divalent copper. Both the compounds dealt with are indeed characterized by staggered overlaps of the interacting layers (11). This would require some modifications to calculations of Section 4, leaving however the essential results unchanged. In reality, the matters presented in this Section are based in part on conjectures owing to the lack of data on the actual placing of the unpaired electrons. Notwithstanding this, in our opinion, the reliability of the interacting layer mechanism is reasonably proved.

8. Discussion and conclusions

According to the electron pairing mechanism we propose, superconductivity in cuprates requires the presence of two neighbouring CuO₂ layers. In compounds like YBa₂Cu₃O₇, each couple of layers constitutes an independent superconductor. Contrary to this point of view, evidence has been claimed for nonexistence of superconductivity in an isolated CuO₂ bilayer. Organic chains (Py-CₙH₂ₙ₊₁)₂HgI₄ (2<n<12) were intercalated in the bilayered Bi₂Sr₂CaCu₂O₈ compound thus drastically increasing the distance between consecutive bilayers [47]. In this way, a complete disappearance of superconductivity was observed. This result was considered as a proof that superconductivity depends on a three-dimensional linkage between the couples of neighbouring CuO₂ layers. In opposition to this conclusion, we point out that pyridine is an efficient electron donor (see for instance [48]). Consequently, the observed disappearance of superconductivity is an expected donor-effect similar to that of yttrium-praseodimium substitution in YBa₂Cu₃O₇ discussed in item 3) of Section 6.

The question of the actual number of layers required for originating superconductivity in cuprates is certainly of primary importance. The idea that interlayer coupling plays a role in superconductivity dates from 1987 when Z. Tešanović proposed a mechanism that involves Coulomb interaction from the band at the Fermi surface to some of the fully occupied or empty bands away from the Fermi level [49]. Another momentous question is the basic interaction which allows the formation of electron pairs. In alternative to the phonon coupling peculiar to the BCS theory, in 1997 we proposed the inter-layer HL-type two-electron exchange [2], while T.M. Mishonov et al. proposed an inter-atomic two-electron exchange [50]. In contrast with this previous proposals, these authors recently have advanced the intra-atomic exchange of two electrons between 4s and 3dₓ²−ᵧ² states as the origin of high Tₙ superconduction in cuprates [51]. In our opinion, identification of exchange interactions as the very cause of superconductivity represents a major progress in this field of studies. But, for a full understanding of the phenomenon, the question remains to be settled if an unique mechanism or different mechanisms are active in the different kinds of

11) A state of affairs of this kind has been already considered in Ref. [3].
unconventional superconductors.

Leaving aside the theoretical issues, the most pressing thing appears to be the discovery of new superconductors of higher $T_c$ and, hopefully, of a 300 K superconductor. In reality, even a minor increase of pairing energy $W_p$ may originate a large increase of $T_c$, owing to the exponential dependence of $\Delta_0$ on $W_p$ given in Eq. (33). A sound argument in favour of this expectation is offered by the detection of a sharp superconductive transition at 235 K due to traces of an unidentified phase fortuitously mixed to a HgBa$_2$Ca$_2$Cu$_3$O$_8$ sample [52]. The approach we advise for improving critical temperature is based on the fact that all cuprates with divalent calcium sandwiched between the neighbouring CuO$_2$ layers show values of $T_c$ higher than 92 K, the YBa$_2$Cu$_3$O$_7$ critical temperature, in which trivalent yttrium is sandwiched between the layers. This fact can be explained by considering that the charge of unpaired electrons on copper ions is a little shifted towards the sandwiched positive ions, thus reducing overlap of unpaired electrons and, consequently, $W_p$. Obviously, this effect is expected to be less harmful with divalent calcium than with trivalent yttrium. This induces us to consider compounds of stoichiometry $M^{+1}M^{+3}_2Cu_3O_7$ derived from YBa$_2$Cu$_3$O$_7$ by substituting $Y^{+3}$ with monovalent $M^{+1}$ ions and $Ba^{+2}$ with trivalent $M^{+3}$ ions ($M^{+1} = Li, Na, K; M^{+3} = Y, La$). This substitution leaves the cell neutrality unchanged. Using the $[E, F, C]$ notation [8, 9], the substitution spoken of is shown in Table 3. Along the same line of reasoning, in the HgBa$_2$Ca$_2$Cu$_3$O$_8$ compound we can consider the substitution of $Ca^{+2}$ ions with $M^{+1}$ ions and $Ba^{+2}$ ions with $M^{+3}$ ions yielding the Hg$M^{+3}_2M^{+1}_2Cu_3O_8$ compound. Also the thallium based compounds Tl$_2$Ba$_2$CaCu$_2$O$_8$ and Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ are in principle suitable for substitution of calcium with monovalent ions. Of course, the possibility of obtaining these substituted compounds is a mere conjecture which should be confirmed by experiments.

\[
\begin{align*}
\text{[CuO}^{-}\text{]} & \quad \text{[CuO}^{-}\text{]} \\
\text{[O}^{-}\text{Ba}^{+2}] & \quad \text{[O}^{-}\text{M}^{+3}] \\
\{\text{[CuO}_2^{-}\text{]} \quad \{\text{[CuO}_2^{-}\text{]} \\
\text{[\text{\[Y\]}}^{-}\text{]} & \quad \text{[\text{\[M}^{+1}\text{\]}}^{-}\text{]} \\
\text{[CuO}_2^{-}\text{]} & \quad \text{[CuO}_2^{-}\text{]} \\
\text{[O}^{-}\text{Ba}^{+2}] & \quad \text{[O}^{-}\text{M}^{+3}] \\
\text{[CuO}^{-}\text{]} & \quad \text{[CuO}^{-}\text{]}
\end{align*}
\]

YBa$_2$Cu$_3$O$_7$

$T_c = 92$ K

$M^{+1}M^{+3}_2Cu_3O_7$

$T_c = ?$ K
$$\begin{align*}
&\text{[Hg} - - \text{][O} - \text{Ba]} \\
&\text{CuO}_2 - \text{[Ca]} \\
&\text{CuO}_2 - \text{[Ca]} \\
&\text{CuO}_2 - \text{[O} - \text{Ba]} \\
&\text{Hg} - -
\end{align*}$$

$$\begin{align*}
&\text{[Hg} - - \text{][O} - \text{M}^{+3}] \\
&\text{[CuO}_2 - \text{[M}^{+1}] \\
&\text{[CuO}_2 - \text{[M}^{+1}] \\
&\text{[CuO}_2 - \text{[O} - \text{M}^{+3}] \\
&\text{[Hg} - -
\end{align*}$$

| Layering Scheme | Temperature |
|-----------------|-------------|
| HgBa$_2$Ca$_2$Cu$_3$O$_8$ | $T_c = 133$ K |
| HgM$_2^{+3}$M$_2^{+1}$Cu$_3$O$_8$ | $T_c = ?$ K |

Table 3: Layering schemes of YBa$_2$Cu$_3$O$_7$ and HgBa$_2$Ca$_2$Cu$_3$O$_8$ cuprates and their respective modified counterparts $M^{+1}M^{+3}_2$Cu$_3$O$_7$ and HgM$_2^{+3}$M$_2^{+1}$Cu$_3$O$_8$. Braces enclose the layers which activate superconductivity.

Appendix A - Some remarks about the Belyaev Hamiltonian for pairing correlations in fermion systems

S.T. Belyaev during a stay at the Institute for Theoretical Physics of the University of Copenhagen wrote a paper entitled "Effect of pairing correlations on nuclear properties". We report hereinafter Subsection 1 (pag. 7) of this paper (12) in which the Hamiltonian for the system of interacting particles is given.

1. Hamiltonian

We consider a system of nucleons which are moving in a certain axially symmetric self-consistent well. (For simplicity, we do not distinguish between neutrons and protons). As basic functions of the second quantization representation we choose the wave functions of a nucleon in this well. States which differ only in the sign of the projections of angular momentum along the symmetry axis are degenerate. We call such states "conjugate" states and mark them with the index $k\sigma = (k+, k-)$. The wave functions of the conjugate states are assumed to transform into each other by complex conjugation and exchange of the spinor components**.

12) Published in Matematisk-fysiske Meddelelser (31, no. 11, 1959) a journal issued by the Royal Danish Academy of Sciences and Letters.
Let us introduce the Fermi operators $a_{k\sigma}^+; a_{k\sigma}$ which create and destroy a particle in the state $k\sigma$. The Hamiltonian for the system of interacting particles is then

$$H' = \sum_k \varepsilon_k \left( a_{k+}^+ a_{k+} + a_{k-}^+ a_{k-} \right)$$

$$-\frac{1}{2} \sum_{(k, \sigma)} \langle k_1 \sigma_1 k_2 \sigma_2 | G | k'_2 \sigma'_2 k'_1 \sigma'_1 \rangle a_{k_1 \sigma_1}^+ a_{k_2 \sigma_2}^+ a_{k'_2 \sigma'_2} a_{k'_1 \sigma'_1}, \quad (1)$$

where $\varepsilon_k$ is the single-particle energy in $k$-th state. (The sign of $G$ is chosen to be positive for an attractive interaction). The Hamiltonian (1) describes a system with a fixed number of particles $N$. Therefore, in a perturbation treatment in which $H'$ is split into two parts, each of these parts must commute with $N$. The problem is essentially simplified if we make a transition from the system with fixed $N$ ("$N$-system") to one with a fixed value of the chemical potential $\lambda$ ("$\lambda$-system"), which is described by the Hamiltonian

$$H = H' - \lambda N. \quad (2)$$

The choice of $\lambda$ determines only the average value of $N$ in the $\lambda$-system. Therefore, the solution which corresponds to the Hamiltonian, (2), will describe only average properties of nuclei and does not pretend to describe the individual nuclear properties for which one needs a fixed value of $N$. As will be shown later, the uncertainty in the value of $N$ is small. In practice, the averaging is done only over a few neighbouring nuclei, either all even or all odd.

Footnotes

*) In fact, even symmetry of reflection in a plane is enough for the definition of the conjugated states. We speak of axial symmetry only for definiteness.

**) If $\psi_+ = (\psi_1^+ \psi_2^+)$, then $\psi_- = (\psi_1^- \psi_2^-)$. The transformation $\psi_+ \rightarrow \psi_-$ is equivalent to the time reversal $T$.

Let the Hamiltonian for pair formation, given in Eq.(1) of the previous Belyaev’s paper, be written in the form

$$\hat{H}_{pair} = -\frac{1}{2} \sum_{(k, \sigma)} \langle k_1 \sigma_1 k_2 \sigma_2 | G | k'_2 \sigma'_2 k'_1 \sigma'_1 \rangle \hat{a}_{k_1 \sigma_1}^+ \hat{a}_{k_2 \sigma_2}^+ \hat{a}_{k'_2 \sigma'_2} \hat{a}_{k'_1 \sigma'_1}. \quad (38)$$

By appropriately defining indexes $k$ and $\sigma$, it assumes different meanings. Indeed, by putting

$$k_1 = k, \quad k_2 = -k, \quad k'_1 = k', \quad k'_2 = -k', \quad \sigma_1 = \sigma'_1 = \uparrow, \quad \sigma_2 = \sigma'_2 = \downarrow, \quad (39)$$
\frac{1}{2} \braket{k_1 \sigma_1 k_2 \sigma_2 | G | k'_2 \sigma'_2 k'_1 \sigma'_1} = \frac{1}{2} \braket{k \uparrow - k \downarrow | G | - k' \downarrow k' \uparrow} = V_{k', k} \quad (40)

and moving toward left the apex (t), \( \hat{H}_{\text{pair}} \) can be rewritten in the quick form

\begin{equation}
\hat{H}_{\text{pair}} = - \sum_{k, k'} V_{k, k'} \hat{\alpha}^+_k \hat{\alpha}^+_k \hat{\alpha}^-_{k'} \hat{\alpha}^-_{k'}, \quad (41)
\end{equation}

where arrows stand for spin components. This is the Hamiltonian for the Cooper pairs in the BCS theory. These pairs are characterized by opposite electron momenta, that is, by reflection symmetry around a center. In a different way, by allowing for the conjugated states considered in the Belyaev’s paper, we have

\begin{equation}
k_1 = k_2 = k, \quad k_1' = k_2' = k' \quad \sigma_1 = \sigma_1' = +, \quad \sigma_2 = \sigma_2' = -, \quad (42)
\end{equation}

\begin{equation}
\frac{1}{2} \braket{k_1 \sigma_1 k_2 \sigma_2 | G | k'_2 \sigma'_2 k'_1 \sigma'_1} = \frac{1}{2} \braket{k^+ + k^- | G | k'^- + k'^+} = V_{k^+, k^-} \quad (43)
\end{equation}

and

\begin{equation}
\hat{H}_{\text{pair}} = - \sum_{k, k'} V_{k, k'} \hat{\alpha}^+_k \hat{\alpha}^+_k \hat{\alpha}^-_{k'} \hat{\alpha}^-_{k'} \hat{\alpha}^+_{k'} \hat{\alpha}^+_k \hat{\alpha}^-_{k} \hat{\alpha}^-_{k}, \quad (44)
\end{equation}

which is the Hamiltonian for the Majorana pairs, characterized by opposite signs of the projections of angular momenta along the symmetry axis. We emphasize, finally, that as pointed out in footnote (*) of the Belyaev’s paper, even fermions of equal momenta which exhibit symmetry of reflection in a plane can be paired in conjugated states. The corresponding Hamiltonian can be written as

\begin{equation}
\hat{H}_{\text{pair}} = - \sum_{k, k'} V_{k, k'} \hat{\alpha}^+_k \hat{\alpha}^+_{k'} \hat{\alpha}^-_{k'} \hat{\alpha}^-_k \hat{\alpha}^+_k \hat{\alpha}^+_{k'}, \quad (45)
\end{equation}

where indexes \( L \) and \( R \) mean left and right with respect to the reflection plane. Symmetries of interacting fermion pairs are summarized in Table 4. Pairs showing planar symmetry have been named ”Lewis pairs”. This because, as explained in Sections 4 and 5, superconductivity in cuprates can be ascribed to pairs of electrons forming covalent bonds characterized just by this kind of symmetry.

| Pairs     | Conjugated states | Symmetry |
|-----------|-------------------|----------|
| Cooper    | \(-k, \downarrow\) | \(+, \uparrow\) | Central |
| Majorana  | \(k, \downarrow\) | \(+, \uparrow\) | Axial   |
| Lewis     | \(k, L\)          | \(+, R\)  | Planar  |
Appendix B - The electron energy spectrum

As shown in Eq. (3) and by writing briefly $W_k$ for $W_a(k_a)$ and $W_b(k_b)$, the energy of electrons running on the CuO$_2$ layers is given by the expectation value

$$W_k = \frac{1}{N} \left\langle \sum_{m=1}^{N} \exp \left(i \mathbf{k} \cdot \mathbf{u}_m \right) a(\mathbf{r} - \mathbf{u}_m) \right| H(\mathbf{p}, \mathbf{r}) \left| \sum_{n=1}^{N} \exp \left(i \mathbf{k} \cdot \mathbf{u}_n \right) a(\mathbf{r} - \mathbf{u}_n) \right\rangle$$

of Hamiltonian

$$H(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}^2}{2m} - \sum_{p=1}^{N} \frac{Ze^2}{|\mathbf{r} - \mathbf{u}_p|} + V_{lat}(\mathbf{r}).$$

This energy is of course the same for $a$ or $b$ layers. For completeness sake, in Eq. (47) the lattice potential $V_{lat}(\mathbf{r})$ has been included due to ions in positions other than $u_p$, that is, to oxygen, yttrium and barium ions neighbouring the copper ions. Orbitals of copper ions are solutions of equation

$$\left[ \frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{|\mathbf{r} - \mathbf{u}|} + V_{lat}(\mathbf{r}) \right] a(\mathbf{r} - \mathbf{u}) = E_{3d} a(\mathbf{r} - \mathbf{u})$$

$E_{3d}$ standing for the orbital energy. On the CuO$_2$ layers, copper ions form a square grid with Cu$^{+2}$ ions at the square vertices and O$^{-2}$ ions at the middle of the square sides. The Coulomb field of O$^{-2}$ ions cuts down the electron charge density of Cu$^{+2}$ ions along the square sides, thus increasing density along the square diagonals. So the electron charge distribution is expected to show the four-lobe shape peculiar to d-orbitals (13).

Cu$^{+2}$ ions placed at opposite ends of the square sides cannot interact directly owing to the interposite oxygens. On the contrary, Cu$^{+2}$ ions placed at opposite ends of the square diagonals are able to originate overlap and exchange integrals of significant values. This entails that Cu$^{+2}$ ions placed alternatively along the square sides form two independent but equivalent ion sets, each holding $N/2$ ions. It is therefore sufficient to consider one of these sets. So Eq. (46) can be rewritten as

$$W_k = \frac{2}{N} \sum_{m, n=1}^{N/2} \exp \left[i \mathbf{k} \cdot (\mathbf{u}_n - \mathbf{u}_m) \right] \int a(\mathbf{r} - \mathbf{u}_m) H(\mathbf{p}, \mathbf{r}) a(\mathbf{r} - \mathbf{u}_n) d^3\mathbf{r}.$$  

(49)

By taking into account that for $n \neq m$ only ions in the four neighbouring lattice positions $\mathbf{u}_l$ around $\mathbf{u}_m$ make a significant contribution, we have

(13) As for the real form of copper orbitals in CuO$_2$ layers, the most likely assumption is that they consist of a superposition of $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals. The $3d_{x^2-y^2}$ orbitals are lined up along the Cu-O-Cu chains, thus allowing for super-exchange interactions between coppers mediated by oxygen ions. Consequently, only the $3d_{xy}$ contributions should be considered when dealing with pairing energy of electrons on neighbouring CuO$_2$ layers (see Ref. [4]).
\[ W_k = \frac{2}{N} \sum_{m=1}^{N/2} \left[ \int a(r_m) H(p, r_m) a(r_m) d^3r_m + \right. \]
\[ \left. \sum_{i=1}^{4} \exp (i k \cdot \sigma_i) \int a(r_i + \sigma_i) H(p, r_i) a(r_i) d^3r_i \right], \tag{50} \]

where \( r_m = r - u_m, \ r_i = r - u_i \) and \( \sigma_i = u_i - u_m \). For an unlimited CuO\(_2\) layer, the sum over \( m \) is independent of position \( u_m \) so that all terms in the sum are equal. This allows us to write

\[ W_k = \int a(r) H(p, r) a(r) d^3r + \]
\[ + \sum_{i=1}^{4} \exp (i k \cdot \sigma_i) \int a(r_i + \sigma_i) H(p, r_i) a(r_i) d^3r_i. \tag{51} \]

On the other hand, we have from Eqs. (48) and (47)

\[ H(p, r_m) a(r_m) = \left( E_{3d} - \sum_{i=1}^{4} \frac{Z e^2}{|r_i|} \right) a(r_m), \tag{52} \]

in which, as for Eq. (50), only terms for ions in the four positions \( u_i \) around \( u_m \) have been included. Owing to square symmetry of these positions around \( u_m \), we obtain

\[ \int a(r) H(p, r) a(r) d^3r = E_{3d} - 4E_C, \tag{53} \]

where

\[ E_C = \int a(r) \frac{Z e^2}{|r - \sigma|} a(r) d^3r \tag{54} \]

means Coulomb energy of the ion in position \( u \) originated by the electric field of the ion in position \( u + \sigma \). By putting \( r_p = r - u_p \), we have analogously

\[ \int a(r_i + \sigma_i) H(p, r_i) a(r_i) d^3r_i = \]
\[ = E_{3d} \int a(r_i + \sigma_i) a(r_i) d^3r_i - \sum_{p(\neq i)=1}^{4} \int a(r_i + \sigma_i) \frac{Z e^2}{|r_p|} a(r_i) d^3r_i. \tag{55} \]

Since the product \( a(r_i + \sigma_i) a(r_i) \) shows a significant value only midway between the \( u_m \) and \( u_i \) positions, only the integral for \( p = m \) is to be accounted for. By omitting label \( i \) and introducing the overlap

\[ O = \int a(r + \sigma) a(r) d^3r \tag{56} \]
and exchange

\[ E_{ex} = \int a(\mathbf{r} + \sigma) \frac{Z e^2}{|\mathbf{r} + \sigma|} a(\mathbf{r}) \, d^3 r \]  

(57)

integrals, we obtain

\[ \int a(\mathbf{r_i} + \sigma_i) H(\mathbf{p}, \mathbf{r_i}) a(\mathbf{r_i}) \, d^3 r_i = OE_{3d} - E_{ex}. \]  

(58)

In this way, substitution of Eqs. (53) and (58) into Eq. (51) leads to

\[ W_k = E_{3d} - 4E_C + (OE_{3d} - E_{ex}) \sum_{i=1}^{4} \exp (i \mathbf{k} \cdot \sigma_i). \]  

(59)

This result mimics the one obtained in the case of tridimensional lattices in which six vectors \( \sigma_i \) have to be considered.

By assuming \( x \) and \( y \) axes parallel to vectors \( \sigma_i \), by letting \( W_0 = E_{3d} - 4E_C + 4(OE_{3d} - E_{ex}) \) and \( B = 4(OE_{3d} - E_{ex}) \) for ground state and band energies, respectively, the electron kinetic energy turns out to be

\[ \varepsilon_k = W_k - W_0 = \frac{B}{2} [2 - \cos (k_x \sigma) - \cos (k_y \sigma)], \]  

(60)

where \( \sigma = |\sigma_i| \). It follows that for \( k_x \sigma, k_y \sigma = \pm \pi \), kinetic energy attains its maximum value \( 2B \). By assuming the CuO\(_2\) plane to be a square of area \( a \times a \) with sides parallel to \( x \) and \( y \) axes and taking into account that \( k_x = n_x (\pi/a) \), \( k_y = n_y (\pi/a) \), \( n_x, n_y = 0, \pm 1, \pm 2 \ldots \), Eq. (60) can be rewritten as

\[ \varepsilon \left( \frac{n_x}{n_0}, \frac{n_y}{n_0} \right) = \frac{B}{2} \left[ 2 - \cos \left( \frac{n_x}{n_0} \right) - \cos \left( \frac{n_y}{n_0} \right) \right], \]  

(61)

where \( n_0 = a/\sigma \). To find the isoenergetic contours on the \( n_x, n_y \) plane, the initial values \( n_x/n_0 = \theta \) and \( n_y/n_0 = 0 \) are chosen corresponding to energy

\[ \varepsilon (\theta) = \frac{B}{2} [1 - \cos (\pi \theta)]. \]  

(62)

For \( \theta = 1 \), we have \( \varepsilon (1) = B \) which is the maximum value of kinetic energy on the isoenergetic contours. This means that \( B \) represents the actual band-width. Then, by keeping \( \varepsilon (n_x/n_0, n_y/n_0) = \varepsilon (\theta) \), \( n_y/n_0 \) is evaluated as a function of \( n_x/n_0 \) for various values of \( \theta \) by means of a numerical procedure which also finds the area enclosed in the contours. Owing to electron spin, twice this area represents the number \( N_s \) of states of energy less than \( \varepsilon (\theta) \). For \( \theta = 1 \), the contour is a square of half-diagonal \( n_0 \) and area \( 2n_0^2 \) (see Figure 1). Thus, for \( \theta = 1 \), \( N_s \) assumes its maximum value \( N_{s0} = 4n_0^2 \). On the other hand on the CuO\(_2\) planes each mesh of area \( \sigma^2/2 \) holds one electron, so that the overall number of electrons is \( 2n_0^2 \). This means that the band is half-filled. For \( N_s/N_{s0} = 0.5 \), we find \( \theta = 0.59 \). It follows, from Eq. (62), \( \varepsilon_F = 0.64B \) or, by identifying the Fermi energy with the chemical potential, \( \mu = 0.64B \). Utilizing
the previously mentioned numerical data, the density of states per unit cell at
the Fermi level is found to be

\[ \Omega_F = \frac{1}{N} \frac{dN_s}{d\varepsilon_F} = \frac{1}{N} \frac{N_s N_0}{B}, \quad (63) \]

which, taking into account that \( 2n_0^2 = N \), leads to the simple relationship

\[ \mu \Omega_F = 1.28. \quad (64) \]

It is to be pointed out that this result holds in general independently of band-
width \( B \), that is, of the actual values of overlap and exchange integrals.

Figure 1: Isoenergetic contours for electrons running on CuO\(_2\) planes. The
square contour for \( n_x/n_0 = 1 \) corresponds to band-width energy \( B \), the one for
\( n_x/n_0 = 0.59 \) to the Fermi energy \( \varepsilon_F \).

Appendix C - Conservation of momentum in fermion systems
Hamiltonian (21) conserves momenta of the interacting electrons. To realize how this occurs, we recall that in degenerate fermion systems, by letting \( n_r \) be the number of particles on the \( r \)-th level and \( \omega_r \) the level degeneracy, we have, at zero temperature, \( n_r = \omega_r \) below Fermi level and \( n_r = 0 \) above it. Consequently, taking into account that fluctuation of \( n_r \) is
\[ \delta n_r = \sqrt{n_r \left(1 - n_r/\omega_r\right)} , \] (65)
no fluctuation is allowed [53]. For the same reason, no scattering is possible either (14). This is a direct consequence of the Pauli principle. A clear evidence about this property of degenerate fermion systems is provided by the nuclear matter. In fact, nuclei can be described both by the liquid drop model, in which nucleons strongly interact among themselves, and by the shell model, in which nucleons behave as particles moving freely in a potential well. This confirms that in degenerate fermion systems interacting particles maintain unchanged their momenta.

We must therefore verify that Hamiltonian (21) really does not allow for scattering processes. We have
\[ \hat{H}_{\text{pair}} = -W_P \sum_{k, k'} \hat{\alpha}_{k'}^+ \hat{\alpha}_{k'} \hat{\alpha}_k \hat{\alpha}_k. \] (66)
Terms with \( k \neq k' \) change pairs with momenta \( k, a \) and \( k, b \) in pairs with momenta \( k', a \) and \( k', b \). But each term with \( k = p \) and \( k' = q \) is associated with a term with \( k = q \) and \( k' = p \). These terms represent opposite scattering processes. Omitting factor \( -W_P \), their contribution in \( \hat{H}_{\text{pair}} \) is
\[ \hat{S}_{pq} = \hat{\alpha}_q^+ \hat{\alpha}_p \hat{\alpha}_q \hat{\alpha}_p + \hat{\alpha}_p^+ \hat{\alpha}_p \hat{\alpha}_q \hat{\alpha}_q. \] (67)
Taking into account the Jordan and Wigner anticommutation rules, operator \( \hat{S}_{pq} \) can be rewritten in the ordered form
\[ \hat{S}_{pq} = \hat{\alpha}_q^+ \hat{\alpha}_p \hat{\alpha}_q \hat{\alpha}_p + \hat{\alpha}_q \hat{\alpha}_p \hat{\alpha}_q \hat{\alpha}_p^+. \] (68)
Operators \( \hat{\alpha} \) and \( \hat{\alpha}^+ \) and fermion states \(|0\rangle\) and \(|1\rangle\) can be represented by the matrices
\[ \hat{\alpha} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \hat{\alpha}^+ = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \] (69)
We have, indeed,
\[ \hat{\alpha} |1\rangle = |0\rangle, \quad \hat{\alpha}^+ |0\rangle = |1\rangle, \quad \hat{\alpha} |0\rangle = 0, \quad \hat{\alpha}^+ |1\rangle = 0. \] (70)

\(^{14}\) For \( T > 0 \) K, states in the Fermi level region are only partially occupied. Thus, in this region scattering processes can take place. But it is wrong to ascribe superconductivity to these scatterings because when \( T \) goes to zero scatterings are shut off while the superconducting energy gap \( \Delta_0 \) attains its maximum amplitude. Fermi level appears in Eq. (32) since \( \Delta \) is small with respect to chemical potential \( \mu \), as explained in Eq. (50).
We consider, moreover, the hermitian operator

$$\hat{\chi} = \hat{\alpha} + \hat{\alpha}^+ = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

(71)

which interchanges the fermion states, that is,

$$\hat{\chi} |0\rangle = |1\rangle, \quad \hat{\chi} |1\rangle = |0\rangle .$$

(72)

In this way, operator $\tilde{S}_{pq}$ can be written as the sum of two $8 \times 8$ matrices, each showing on the diagonal four $2 \times 2$ matrices for the $\hat{\alpha}$ and $\hat{\alpha}^+$ operators corresponding to $qa, pa, qb, pb$ states. So, by taking into account Eq. (71), we have

$$\tilde{S}_{pq} = \hat{\chi}_{qa} \hat{\chi}_{pa} \hat{\chi}_{qb} \hat{\chi}_{pb} .$$

(73)

By considering the four fermion state $|1, 1, 1, 1\rangle = |1\rangle_{qa} |1\rangle_{pa} |1\rangle_{qb} |1\rangle_{pb}$, we obtain

$$(1, 1, 1, 1)|\tilde{S}_{pq} |1, 1, 1, 1\rangle = \langle 1, 1, 1, 1 | 0, 0, 0, 0 \rangle = 0,$$

(74)

that is, the expectation value of $\tilde{S}_{pq}$ vanishes. The same result is found in general for all fermion states. Consequently, no scattering process is really accounted for in $\hat{H}_{pair}$ Hamiltonian. Only non-scattering terms with $k = k'$ give a contribution. This means that electron momenta are conserved in Lewis pairs. This argument applies unchanged to Cooper and Majorana Hamiltonians in which scattering terms can be eliminated in the same way. The lack of effective scattering processes entails that momentum of fermions is conserved for all the pairing mechanisms considered in Table 4.

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