Contraction of Atomic Orbitals in the Oxygen Anion Network and Superconductivity in Metal Oxide Compounds

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Abstract

Anion network in the CuO_2 plane of metal-oxide compound is considered as an intrinsic-hole metal with holes rather than electrons comprising a Fermi liquid immersed in the background of negative O^{2-} ions. Due to the contraction of p-orbital of oxygen as a result of occupation by a hole, hole hopping between nearest neighbor sites (i,j) is dependent upon hole occupation as $t_{ij,\sigma} = t_0 + V n_{i,-\sigma} n_{j,-\sigma} + W(n_{i,-\sigma} + n_{j,-\sigma})$. Coupling parameters W and V (additive and multiplicative "contraction interaction" terms) result in the binding of holes into singlet, on-site configuration, or into triplet, nearest-neighbor-site configuration, due to W and V respectively. In the weak coupling limit, W results in the BCS type of superconductive pairing (singlet, s-wave), whereas multiplicative contraction V provides for either singlet, d-wave, or triplet, p-wave-like pairing states. It is concluded that the latter state may result in a plausible mechanism for high-T_c superconductivity in metal oxide compounds. The superconducting p-phase is shown to be in accord with recently published symmetry tests of the order parameter in oxides.

1. Introduction

Since the discovery of high-temperature superconductivity in $La_{2-x}Ba_xCuO_4$[1] and $YBa_2Cu_3O_{6+x}$[2], great efforts have been devoted to the experimental study of physical properties of high-T_c superconductors and their extension to new materials, as well as to the theoretical investigation of the basic physical mechanisms of a new superconducting state. Concerning the latter, several radical changes in the state-of-art of condensed matter theory have been attempted. Non-fermi-liquid scenario of conductivity have been suggested and nontraditional quasiparticle statistics characteristic of two-dimensional systems have been proposed; momentum pairing as well as local pairing mechanisms of bosonization have been investigated; non-electron-phonon as well as

electron-phonon mechanisms of attraction between electrons has been discussed; strongly correlated electron models have been considered.

Experimental study of new superconductors does not give a clue to theory as it does not reveal the novel features of high-T_c superconducting state. All effects known for low-T_c superconductors (Meissner effect, the Abrikosov mixed state, flux quantization, Josephson effect, etc.) also exist in the oxide superconductors. The anomalous (almost vanishing) isotope effect in most-high-T_c materials [3] suggests that electron-phonon interaction may be not a unique mechanism of superconducting pairing.

Investigation of an issue as to which components of an intermetallic compound, e.g., $YBaCuO$ (the rare-earth elements ?   copper ions ?   oxygens ?) are most relevant to superconducting properties, indicates that oxygen is probably a key element since according to high-energy X-ray and electron scattering data [4,5], a Fermi-liquid unambiguously related to oxygen-derived electronic states develops in the same range of a dopant (barium, oxygen, etc.) concentration at which the metallic conductivity and superconductivity sets in.

The fact that oxygen has an almost filled p-shell configuration suggests that holes in a p^6 shell may play a similar role for the conduction in the oxides as do electrons originating from the almost empty atomic shells, in conventional metals. In the present paper, we shall follow this line of thought and will try to show that this "chemical" aspect of high-T_c materials may result in a new type of band conduction and quasiparticle interaction which seemingly show the possibility for high-T_c superconductivity.

Section 2 describes the idea of the intrinsic-hole metal, as opposed to the conventional "intrinsic-electron" metals and introduces a new type of hole interaction termed the "contraction interaction" [6,7]. Sections 3 and 4 show, in methodical manner, the physical origin of the contraction interaction effect on quasiparticle pairing. Sections 5 through 7 analyze a weak-coupling regime of contraction interaction. It is suggested that the triplet, odd orbital-symmetry (p-wave) gapless state is the most probable scenario for superconducting behavior in the new high-T_c materials. This state is shown to be in accord with recent symmetry tests of the order parameter in oxides.

2. The Intrinsic-Hole Metal

In the investigation of unusual electronic properties of metal-oxide compounds, it was proposed [6,7] that the new features in the electronic band conduction should be included. The first possibility is that intrinsic-hole rather than intrinsic-electron carriers may be dominant charge carriers. The second is that, assuming "intrinsic-holes" are at work, the one-particle picture of the electronic transport is not fully adequate, because the hopping of holes in itself is nonconstant and is strongly dependent upon site occupation.

In conventional metals like Na, the Fermi surface is formed by electrons removed from metallic atoms leaving behind the closed-shell cation network (Na^+). For the atoms

with almost filled atomic shells (O between those), anion configuration O^{2-} is expected to establish with holes, rather than electrons, condensing to a Fermi liquid in the space between anions. [Notice that this has nothing to do with the electron-like or hole-like carriers as evidenced by the Hall effect. The difference between "intrinsic-electron" and "intrinsic-hole" type metals is illustrated in Figure 1].
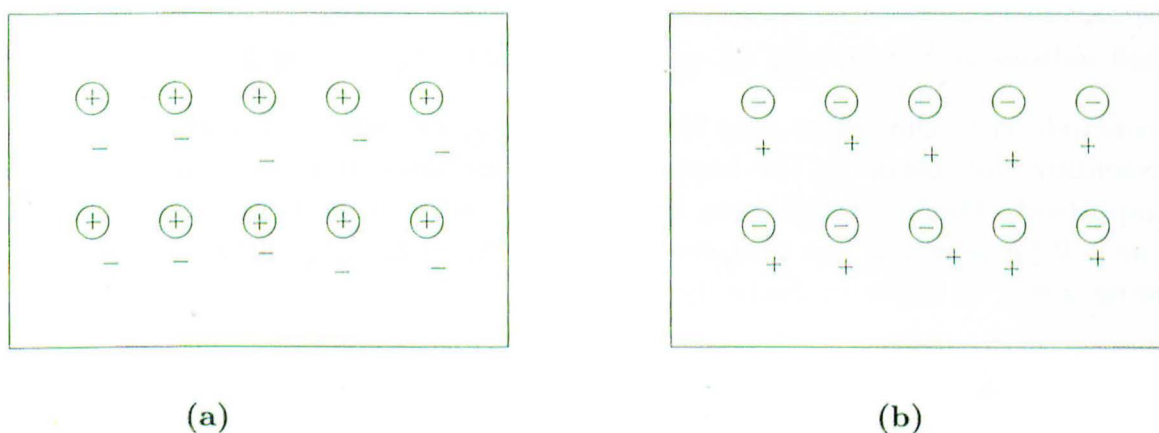

(a)

(b)

Figure 1. Cation network with the intrinsic electrons condensing to a Fermi liquid (a) and the anion network with intrinsic holes as a Fermi liquid of positive charge (b). Notice that this does not concern with the sign of the Hall coefficient which in principle can be both positive and negative in either case

Normally, for oxygen atoms this does not happen because two oxygens have a strong tendency to covalent bonding resulting in the formation of oxygen molecule, O_2. However, in a proper chemical surrounding this may not take place if the nearest neighbor atoms are not too close to each other. Then the other scenario will apply, reminiscent of metallic oxygen. We may suppose that this is just what happens in the metal-oxide superconductors. In the CuO_2 plane of the latter, due to large ionic radius of copper, oxygen orbitals are overlapping amongst themselves almost as strongly as the near-site oxygen and copper orbitals (see Fig.2 in which oxygen and copper radii are shown approximately in scale). Then, the O_2 molecules are not formed, and the holes derived from the p^6 shells are to be the itinerant carriers. Due to overlapping of hole wave functions at different ions, hole can propagate from the oxygen anion to the nearest one.

Intrinsic holes are not totally equivalent to the intrinsic electrons in the sense that they can not be fully removed from the parent atom. But the external atoms, like those in the ligand plane of copper-oxygen chains, can provide a proper surrounding in which the hole may reside. Charge transfer between holes at anions A_i, A_j in the CuO_2 plane,

$$(A_i + \text{hole}), \quad A_j \quad \Rightarrow \quad A_i, \quad (A_j + \text{hole}), \tag{1}$$

will be characterized by the occupation-dependent hopping amplitude t_{ij} exponentially

dependent upon distance between the ions (a is the effective anion radius)

$$| t_{ij} | \sim \exp(-R_{ij}/a) \tag{2}$$

If another hole (a hole with the antiparallel spin) is localized at the same anion, the anion radius will shrink as shown schematically by dotted line in Fig.2, thus changing the value of t_{ij}. From the known data concerning oxygen and oxygen ion radii [9],

$$O: \quad a = 0.7\mathring{A}, \qquad O^{2-}: \quad a = 1.36\mathring{A} \tag{3}$$

we conclude that this effect may be quite strong, i.e. the "contraction interaction" [7] representing the change in the hopping amplitude upon hole localization is expected to be important. This interaction can be labeled in terms of neither repulsion nor attraction but as will be shown in the next section, it results in binding of two holes in a pair thus showing a way to superconductivity [6,8].
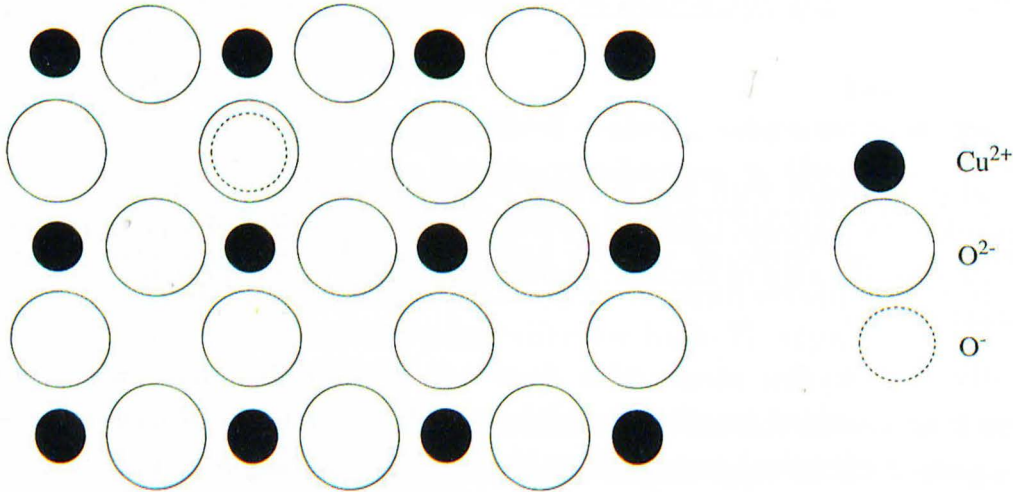

Figure 2. Atomic configuration in the CuO_2 plane of $YBCO$ and similar metal-oxide compounds. Full line, O^{2-} configuration; dotted line, O^- configuration corresponding to a hole nesting at the oxygen site. Contraction of the ion orbital due to extra positive charge of the ion core changes the hole hopping amplitude between this anion and the nearest neighbor anion

It was proposed that hopping amplitude is dependent upon site occupation according to [10]

$$t_{ij,\sigma} = t_0(1 - n_{i,-\sigma})(1 - n_{j,-\sigma}) + t_1[(1 - n_{i,-\sigma})n_{j,-\sigma} + n_{i,-\sigma}(1 - n_{j,-\sigma})] +$$
$$t_2 n_{i,-\sigma} n_{j,-\sigma}, \tag{4}$$

where $n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma}$ is particle number operator, and $a_{i\sigma}^+$ ($a_{i\sigma}$) is creation (annihilation) operator of hole with spin projection σ at site i.

In case of oxygen anions, quantities t_0, t_1, and t_2 are the amplitudes of the transitions:

$$
\begin{aligned}
t_0: & \quad O_i^- + O_j^{2-} & \Rightarrow & \quad O_i^{2-} + O_j^- \\
t_1: & \quad O_i + O_j^{2-} & \Rightarrow & \quad O_i^{2-} + O_j \\
t_2: & \quad O_i + O_j^- & \Rightarrow & \quad O_i^- + O_j.
\end{aligned} \tag{5}
$$

We expect that, due to the R-dependence of t_{ij} of the type represented by Eq.(2), t_1 will be smaller than t_0, and t_2 smaller than t_1 and can be estimated as

$$t_1 \sim t_0 e^{-S}, \quad t_2 \sim t_0 e^{-2S}, \tag{6}$$

where S is the ratio of the distance between the maximum of the lattice potential (presumably, at the Cu^{2+} location) and the anion position.

Occupation dependence of the hopping can also be represented in another form,

$$t_{ij,\sigma} = -t + V n_{i,-\sigma} n_{j,-\sigma} + W(n_{i,-\sigma} + n_{j,-\sigma}), \tag{7}$$

where, from (4),

$$t = -t_0, \quad V = t_0 - 2t_1 + t_2, \quad W = t_1 - t_0. \tag{8}$$

If we accept the estimate for the hopping amplitude (6), the contraction parameters V and W will become

$$V \sim -t(1 - e^{-S})^2, \quad W \sim t(1 - e^{-S}). \tag{9}$$

From this formula we conclude that the sign of V is expected to be opposite to the sign of the unperturbed hopping amplitude t, whereas W should have the same sign as that of t. This will have an important implication for the appearance of superconductivity in the corresponding regimes.

Including both type of contraction interaction, and also the Hubbard in-site repulsion, Hamiltonian of the system becomes

$$H = -t \sum_{<ij>,\sigma} a_{i\sigma}^+ a_{j\sigma} + H_U + H_V + H_W \tag{10}$$

with

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow}, \tag{11}$$

$$H_V = V \sum_{<ij>,\sigma} a_{i\sigma}^+ a_{j\sigma} n_{i,-\sigma} n_{j,-\sigma}, \tag{12}$$

$$H_W = W \sum_{<ij>,\sigma} a_{i\sigma}^+ a_{j\sigma} (n_{i,-\sigma} + n_{j,-\sigma}). \tag{13}$$

The effect of a coupling term W in (10) has been considered in much detail in the paper of Hirsch and Marsiglio [13], as well as in the author's papers [6,7,10]. Below, we consider the effect of both types of contraction pairing. In the weak coupling regime, the sign of W derived from (9) is unfavorable for superconductivity whereas the sign of V is. Moreover, pairing due to V is not subject to a suppression by the intersite Coulomb repulsion.

Models with different signs of t are in fact equivalent [11]. Change of the sign of t can be compensated by the momentum transformation $k_x \rightarrow k_x + \pi$, $k_y \rightarrow k_y + \pi$ corresponding to the shift of the elementary cell, and therefore of the Fermi surface, in the reciprocal lattice by a vector (π, π). If not stated otherwise, later we shall consider t in (7) as positive. Then, according to previous consideration, coupling parameter V is most likely expected to be negative whereas W a positive quantity.

3. Binding of Holes into Pairs via Contraction Mechanism (Singlet State)

To clarify the contraction mechanism of superconductivity, we consider in this section a simple problem of two holes in an empty one-dimensional host lattice interacting with one another via the occupation dependent hopping (13) and show that they bind into a singlet pair similar to a Cooper pair, at appropriate sign of the interaction term W. In the following section, we address the same problem of hole binding to a triplet state due to the contraction energy V. The reader who is already familiar with the pairing property of the interaction (7) may continue directly from Sect.5 which deals with superconductivity in a dense $2d$ Fermi liquid of holes.

The $1d$ version of interacting holes in an anion network is represented by the Hamiltonian including the contraction interaction (7) and the Hubbard term U accounting for the Coulomb interaction between holes at the same site

$$H = -t \sum_{i=1,\sigma}^{N} a_{i\sigma}^{+} a_{i+1,\sigma} + h.c. + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow} +$$

$$\sum_{i=1,\sigma}^{N} a_{i\sigma}^{+} a_{i+1,\sigma} [V n_{i,-\sigma} n_{i+1,-\sigma} + W(n_{i,-\sigma} + n_{i+1,-\sigma})] + h.c. \qquad (14)$$

Two holes in the noninteracting lattice ($U = V = W = 0$) have an energy

$$E^{(0)} = -t(\varepsilon_{k_1} + \varepsilon_{k_2}), \qquad \varepsilon_k = 2\cos k, \qquad (15)$$

where $k = \frac{2\pi}{N} n$ (n is an integer) is the momentum of a finite-size, cyclic-boundary-condition anion chain of length N. Consider solution to the Schrodinger equation $H\Psi = E\Psi$ in the form

$$\Psi = \sum_{x_1 x_2} f(x_1, x_2) a_{x_1\uparrow}^{+} a_{x_2\downarrow}^{+} \mid 0 >, \qquad (16)$$

where x_1, x_2 are integers. Changing from the coordinate representation $f(x_1, x_2)$ to the Fourier representation $f_{k_1 k_2}$ according to

$$f(x_1, x_2) = \sum_{k_1, k_2} f_{k_1 k_2} e^{i(k_1 x_1 + k_2 x_2)}, \qquad (17)$$

we obtain an equation for the wave function amplitude $f_{k_1 k_2}$

$$-[t(\varepsilon_{k_1} + \varepsilon_{k_2}) + E]f_{k_1 k_2} + \frac{U}{N}\sum_k f_{k_1-k,k_2+k} +$$

$$\frac{W}{N}\sum_k f_{k_1-k,k_2+k}(\varepsilon_{k_1} + \varepsilon_{k_2} + \varepsilon_{k_1-k} + \varepsilon_{k_2+k}) = 0. \qquad (18)$$

By introducing the functions

$$F_0(Q) = \frac{1}{N}\sum_k f_{k_1-k,k_2+k},$$

$$F_1(Q) = \frac{1}{N}\sum_k f_{k_1-k,k_2+k}(\varepsilon_{k_1-k} + \varepsilon_{k_2+k}), \qquad (19)$$

where $Q = k_1 + k_2$ is a total momentum of a pair, we obtain a solution

$$f_{k_1 k_2} = \frac{[U + W(\varepsilon_{k_1} + \varepsilon_{k_2})]F_0 + WF_1}{t(\varepsilon_{k_1} + \varepsilon_{k_2}) + E}, \qquad (20)$$

which, after substitution back to Eq.(18), results in the equation for E

$$\frac{(W - t)^2}{Ut^2 + W(W - 2t)E} = S(E), \qquad (21)$$

where $S(E)$ is the function

$$S(E) = \frac{1}{N}\sum_k \frac{1}{E + t(\varepsilon_k + \varepsilon_{Q-k})}. \qquad (22)$$

The function $S(E)$ is shown in Figure 3. By intersecting $S(E)$ with the left hand side of Eq.(21) we obtain the eigenvalues E related to the energies of the propagating states (11), and an additional energy below the edge of noninteracting holes $E < -4 \mid t \mid$ corresponding to the bound state of holes.
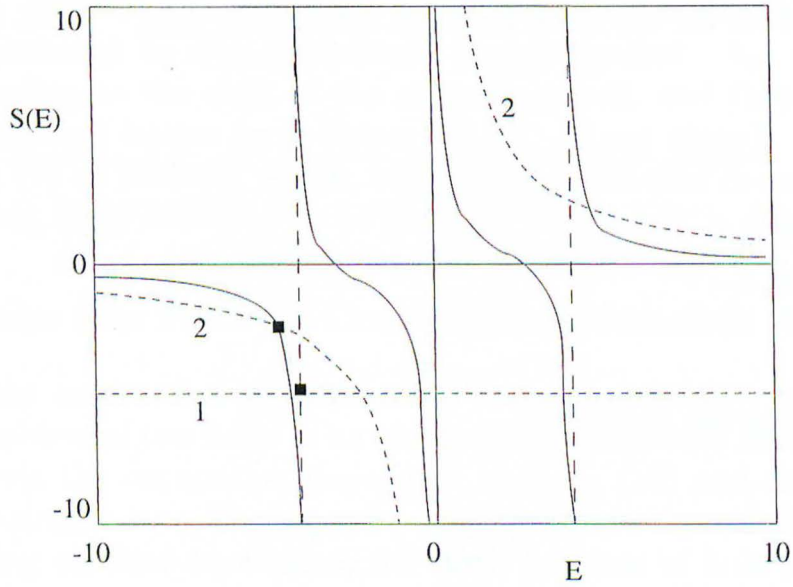
Figure 3. Function $S(E)$ for $N = 4, Q = 0$ (full line). Dotted lines - left-hand-side of Eq.(21) for $W = 0$, $U < 0$ (a), and for $U = 0$, $W < 0$ (b). Squares indicate bound states

In case of zero contraction and large negative Hubbard's U, the bound state energy is

$$E_b = - \mid U \mid - \frac{4t^2}{\mid U \mid}(1 + \cos Q), \quad U < 0, \quad \mid U \mid \gg \mid t \mid \qquad (23)$$

which corresponds to the binding energy $- \mid U \mid$ and an effective mass of a pair

$$m^* = \mid U \mid /4t^2 \qquad (24)$$

much greater than the single particle effective mass $m = 1/(2 \mid t \mid)$ (in the units $\hbar = a = 1$, where $\hbar$ is Planck constant and a is the intersite spacing).

In case of zero U and large W, Eq.(21) gives the energy of the bound hole-hole state

$$E_b = - \frac{\mid W \mid}{2(1 + \cos Q)} \qquad (25)$$

corresponding to the value of the binding energy at $Q = 0$ $E_b = - \mid W \mid /4$, and an effective mass

$$M^* = - \frac{8}{\mid W \mid} \qquad (26)$$

which is negative and much smaller in the magnitude than the free hole mass. Therefore we obtain in this limit highly mobile bosons coupled to an energy $- \mid W \mid /4$.

At small $\mid W \mid$, the symmetry between the positive and negative values of the contraction energy W is removed and pairing is produced in a restricted range of couplings W. The phase diagram in the (U, W) plane showing the effect of pairing is presented

in Fig.4. We consider here both cases of positive and negative t to show that the sign of W corresponding to pairing correlates with the sign of t in a manner opposite to the one expected for "normal" contraction, Eq.(9) (decrease of hopping amplitude with more localized holes, i.e. with extra positive charge on the anion).
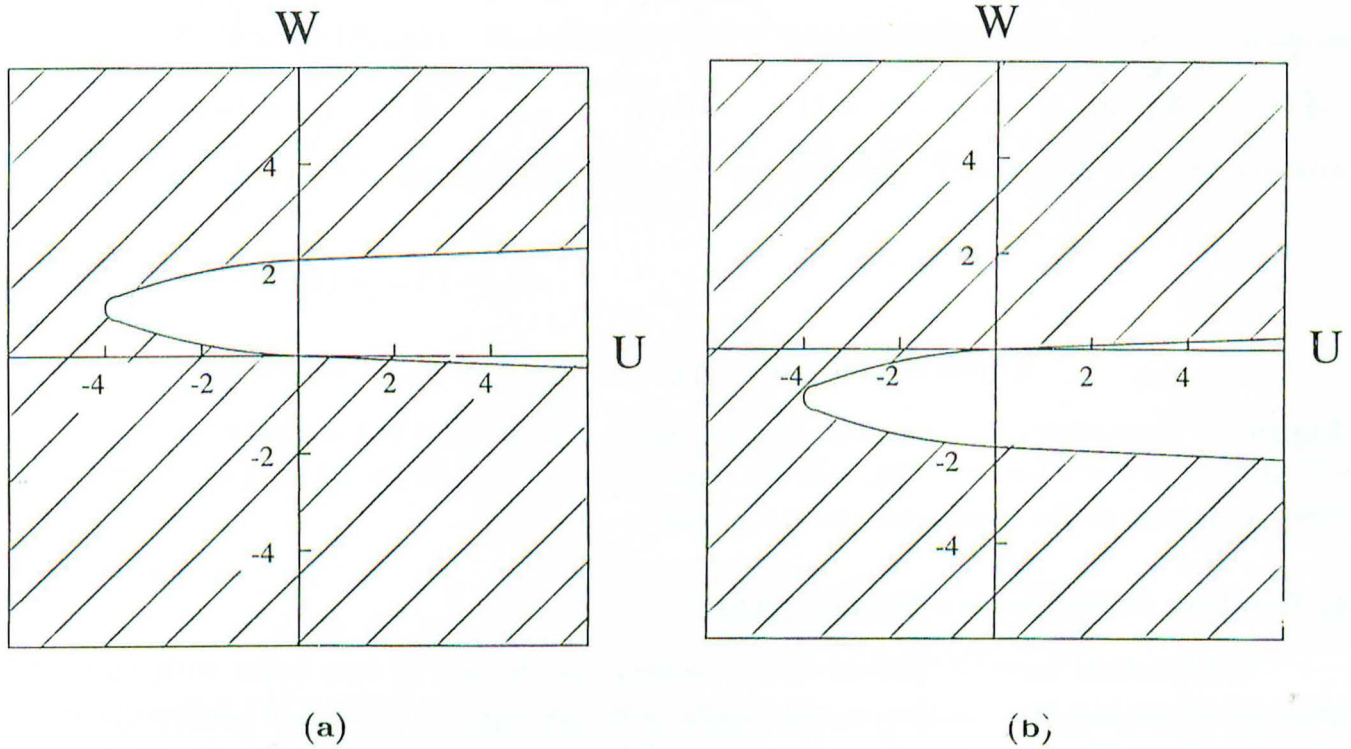

Figure 4. Phase diagram of hole binding into a singlet pair. Hatched region corresponds to binding, empty one to no binding. U is the Hubbard energy, W the contraction energy. (a) $t = 1$; (b) $t = -1$

However, it should be mentioned that this does not necessarily exclude the possibility of superconductivity due to contraction mechanism in the copper-oxide system, since, owing to the anisotropic nature of p-orbitals and to the possibility of reorientation of those from the direction $Cu - O$ to the direction $O - O$ at increasing filling, the "renormalized" W value can be of any sign and magnitude (in particular, $|W| > |t|$). The issue of the first-principle calculation of W has been addressed in the Hirsch's paper [14].

The origin of the pairing property within the contraction model can be explained as follows. Occupation dependence of hopping, Eq.(7), can be visualized as band narrowing (Fig.5,a) or widening (Fig.5,b), depending on the sign of W, near the location of spin-down hole. If signs of t and W are opposite to each other, an effective potential barrier is formed near the point at which the hole is located, thus repelling the other hole. In the opposite case when t and W are of the same sign, the potential well will be created near the hole attracting another hole. For large $|W|$, band inversion occurs (Fig.5,c) acting

as a trap for another hole irrespective of the sign of W. This explains the phase diagram for the occurence of hole binding shown in Fig.4.

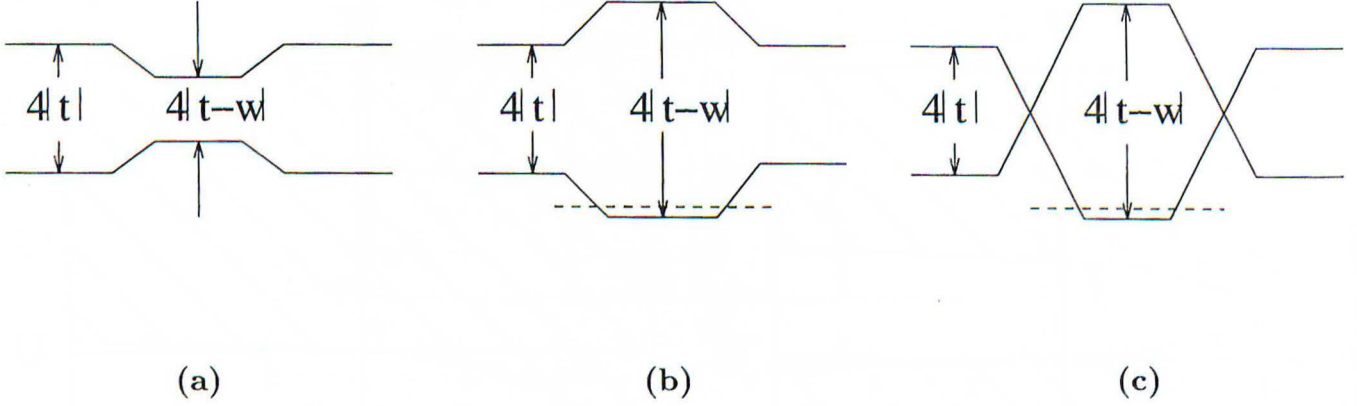(a)   (b)   (c)

Figure 5. Formation of the quantum barrier near a hole for $\text{sign}(W) = \text{sign}(t)$ (a), quantum well at $\text{sign}(W) = -\text{sign}(t)$ (b), and the band inversion at $|W| > 2|t|$ (c). Dotted line shows an energy of the bound state near the hole

4. Binding of Holes into Triplet State

Contraction term V proves to be inoperative in case of two holes with opposite spins in an empty host lattice as this term does not appear in Eq.(18) following from (14). However we may expect on the basis of Fig.5 that two holes with the same spin located at a nearest sites will create an effective potential well, if $\text{sign}(V) = \text{sign}(t)$, and therefore acting as a trap for the third hole having opposite spin. To verify whether this is the case we consider an eigenstate

$$\Psi = \sum_{x_1 x_2 x} f(x_1, x_2 \mid x) a_{x_1\uparrow}^{+} a_{x_2\uparrow}^{+} a_{x\downarrow}^{+} \mid 0 > \tag{27}$$

of the Hamiltonian with the interaction V alone,

$$H = \sum_{i=1,\sigma}^{N} a_{i\sigma}^{+} a_{i+1,\sigma} + V \sum_{i=1,\sigma}^{N} a_{i\sigma}^{+} a_{i+1,\sigma} n_{i,-\sigma} n_{i+1,-\sigma} + h.c. \tag{28}$$

The wavefunction amplitude $f(x_1, x_2 \mid x)$ is expected to be antisymmetric in x_1, x_2 and satisfies the equation

$$-t\sum_{\delta}[f(x_1 + \delta, x_2 \mid x) + f(x_1, x_2 + \delta \mid x) + f(x_1, x_2 \mid x + \delta)] +$$

$$V\sum_{\delta}(\delta_{x_1 x}\delta_{x_2,x_1+\delta} + \delta_{x_2 x}\delta_{x_1,x_2+\delta})f(x_1, x_2 \mid x + \delta) = Ef(x_1, x_2 \mid x), \tag{29}$$

where $\delta = \pm 1$ is the unit vector connecting nearest neighbor sites.

Consider solution to Eq.(29) with a fixed momentum Q

$$f(x_1, x_2 \mid x) = F(x_1 - x, x_2 - x)e^{iQ(x_1 + x_2 + x)}. \tag{30}$$

After expanding $F(x_1, x_2)$ in a Fourier series analogous to (17) we shall obtain an equation for the pairing amplitude $F_{k_1 k_2}$

$$-[t(\varepsilon_{k_1+Q} + \varepsilon_{k_2+Q} + \varepsilon_{-k_1-k_2+Q}) + E]F_{k_1 k_2} + \frac{V}{N^2}\sum_\delta F_\delta (e^{-ik_1\delta} - e^{-ik_2\delta})e^{iQ\delta} = 0, \tag{31}$$

with $F_\delta = F(0, -\delta) = -F(-\delta, 0)$.

Substitution of $F_{k_1 k_2}$ in to Eq.(29) gives an equation for F_δ

$$F_\delta = V\sum_{\delta'} S_{\delta\delta'} F_{\delta'} \tag{32}$$

where

$$S_{\delta\delta'} = \frac{1}{2N^2}\sum_{k_1 k_2} \frac{(e^{ik_1\delta} - e^{ik_2\delta})(e^{ik_1\delta'} - e^{ik_2\delta'})e^{iQ\delta'}}{t(\varepsilon_{k_1+Q} + \varepsilon_{k_2+Q} + \varepsilon_{k_1+k_2-Q}) + E}. \tag{33}$$

Choosing the total momentum of a bound state $Q = 0$, the eigenvalue equation will be

$$1 + VS_\pm(E) = 0, \tag{34}$$

where $S_\pm = S_1 \pm S_2$, $S_1 = S_{++} = S_{--}$, $S_2 = S_{+-} = S_{-+}$ and

$$S_+ = \frac{1}{N^2}\sum_{k_1 k_2} \frac{(\cos k_1 - \cos k_2)^2}{2t(\cos k_1 + \cos k_2 + \cos(k_1 + k_2)) + E},$$

$$S_- = -\frac{1}{N^2}\sum_{k_1 k_2} \frac{(\sin k_1 - \sin k_2)^2}{2t(\cos k_1 + \cos k_2 + \cos(k_1 + k_2)) + E}. \tag{35}$$

At large V, the energy of the bound state equals

$$E_b = -\mid V \mid, \quad \mid V \mid \gg \mid t \mid. \tag{36}$$

We will not consider the problem of binding in more detail since it serves only to provide some indication as to what may happen in a system composing of many holes. The strong coupling regime of the Hamiltonian (14) requires the numerical analysis [12]. The weak coupling regime will be analysed for a $2d$ network in the forthcoming sections.

5. The Cooper Instability

Contraction interactions in the anion network - terms (12), (13) in the Hamiltonian - result in the instability of the ground state of a fermi-liquid with respect to pairing of electrons in the zero-momentum state $(\mathbf{p}, -\mathbf{p})$. Spin structure of the paired state is however more complicated than in a standard BCS theory.

Consider first the weak coupling limit of an "additive contraction", Eq.(13). In the momentum representation, Hamiltonian H_W reads

$$H_W = \frac{W}{N} \sum_{\mathbf{p},\mathbf{p}',\sigma} \sum_{\mathbf{p}_1,\mathbf{p}_2} (\varepsilon_{\mathbf{p}} + \varepsilon_{\mathbf{p}'}) a^+_{\mathbf{p}\sigma} a_{\mathbf{p}'\sigma} a^+_{\mathbf{p}_1,-\sigma} a_{\mathbf{p}_2,-\sigma} \delta_{\mathbf{p}+\mathbf{p}_1,\mathbf{p}'+\mathbf{p}_2} \tag{37}$$

where

$$\varepsilon_{\mathbf{p}} = \sum_{\mathbf{s}} e^{i\mathbf{p}\mathbf{s}}. \tag{38}$$

$\mathbf{s}$ is a vector between a given site and its nearest neighbor.

Singular part of the interaction (37) corresponds to terms with $\mathbf{p}_1 = -\mathbf{p}$ and $\mathbf{p}_2 = -\mathbf{p}'$:

$$H'_W = \frac{W}{N} \sum_{\mathbf{p},\mathbf{p}',\sigma} (\varepsilon_{\mathbf{p}} + \varepsilon_{\mathbf{p}'}) a^+_{\mathbf{p}\sigma} a^+_{-\mathbf{p},-\sigma} a_{-\mathbf{p}',-\sigma} a_{\mathbf{p},\sigma}. \tag{39}$$

According to the Green-function formulation of the theory of superconductivity [15], it is needed to trace the behavior of the vertex part $\Gamma_{\mathbf{p}\mathbf{p}'}(\omega)$ in the apper half plane of complex frequency ω. The vertex part corresponding to Eq.(37) is represented as a sum of diagrams shown in Fig.6,a thus giving

$$\Gamma_{\mathbf{p}\mathbf{p}'}(\omega) = W(\varepsilon_{\mathbf{p}} + \varepsilon_{\mathbf{p}'}) + \frac{W^2}{N} \sum_{\mathbf{k}} \int \frac{d\varepsilon}{2\pi i} (\varepsilon_{\mathbf{p}} + \varepsilon_{\mathbf{k}})(\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{p}'}) G_{\mathbf{k}}(\varepsilon) G_{-\mathbf{k}}(\omega - \varepsilon) + \dots \tag{40}$$

where $G_{\mathbf{k}}$ is a one-electron Green function ($n_{\mathbf{k}}$ is the Fermi distribution at $T = 0$):

$$G_{\mathbf{k}} = \frac{n_{\mathbf{k}}}{\varepsilon - \xi_{\mathbf{k}} - i\delta} + \frac{1 - n_{\mathbf{k}}}{\varepsilon - \xi_{\mathbf{k}} + i\delta} \tag{41}$$

Subsequent terms of this series are powers of singular integral

$$\frac{1}{N} \sum_{\mathbf{k}} C(\mathbf{k}) \frac{1 - 2n_{\mathbf{k}}}{2\xi_{\mathbf{k}} - \omega} \tag{42}$$

with $\omega = i\Omega$ and $\xi_{\mathbf{k}} = -t\varepsilon_{\mathbf{k}} - \mu$. Therefore we shall have at $\xi_{\mathbf{p}} = \xi_{\mathbf{p}'} = 0$

$$\Gamma(i\Omega) \simeq \frac{2\mu W}{1 - 2\mu W \ln \frac{2\varepsilon_0}{\Omega}}. \tag{43}$$

ε_0 is the cutoff energy of the order of Fermi energy. Pole of (43) is a familiar Cooper instability. The instability occurs once μW is positive which means that W should be *negative* at hole concentration corresponding to less than half-filling of the electron energy band and *positive* in case of less than half-filling. This is in agreement with the result of the binding energy calculation in Sect.3.
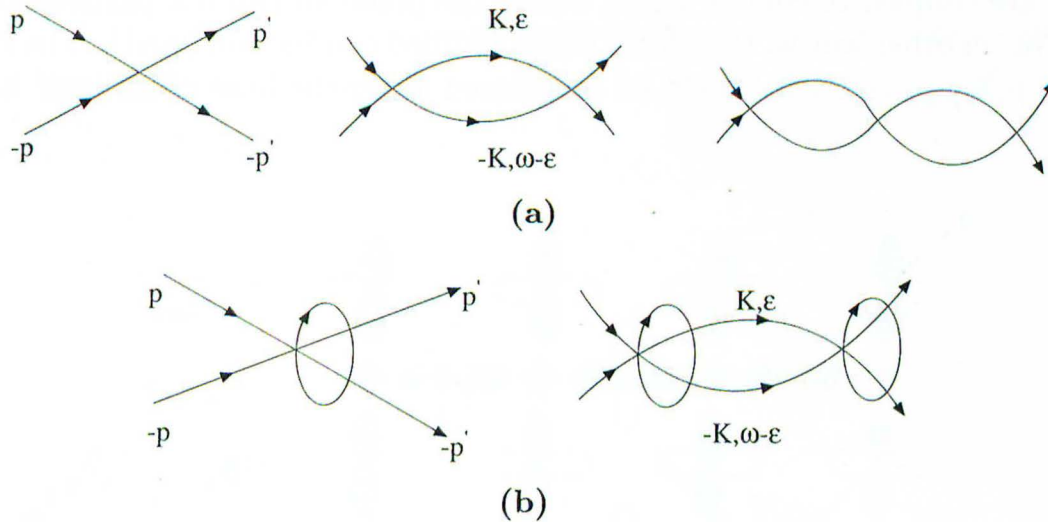

(a)

(b)

Figure 6.

The multiplicative part of the Hamiltonian function H_V takes form after transformation to momentum representation

$$H_V = \frac{V}{N^2} \sum_{\mathbf{pp'\sigma}} \sum_{\mathbf{p_1 p_2 k_1 k_2}} \varepsilon_{\mathbf{p+p_1-p_2}} a^+_{\mathbf{p}\sigma} a^+_{\mathbf{p'}\sigma} a^+_{\mathbf{p_1},-\sigma} a_{\mathbf{p_2},-\sigma} a^+_{\mathbf{k_1},-\sigma} a_{\mathbf{k_2},-\sigma} \times$$

$$\delta_{\mathbf{p-p_1+p_2},\mathbf{p'+k_1-k_2}} \tag{44}$$

Putting $\mathbf{p_1} = -\mathbf{k_1}$ and $\mathbf{p_2} = -\mathbf{k_2}$ gives the "singular" part of the Hamiltonian

$$H'_V = \frac{V}{N} \sum_{\mathbf{p}\sigma} \gamma_{\mathbf{p-p'},-\sigma} a^+_{\mathbf{p}\sigma} a^+_{-\mathbf{p}\sigma} a_{-\mathbf{p'}\sigma} a_{\mathbf{p'}\sigma} \tag{45}$$

with

$$\gamma_{\mathbf{q}\sigma} = \frac{1}{N} \sum_{\mathbf{k}} a^+_{\mathbf{k-q},\sigma} a_{\mathbf{k}\sigma}. \tag{46}$$

Cooper-type diagrams for the vertex part corresponding to the above Hamiltonian are showm in Fig.6,b. We will receive $\Gamma(\Omega)$ similar to (43) with a more complicated angular dependence. The singularity of the vertex part is a signature of superconducting transition. The calculation of the pairing state below the transition will be presented in the next section.

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6. Weak-Coupling Mean Field Theory of Superconductivity in an Anion Network

Oxygen orbitals in the CuO_2 plane of oxide compounds have states $p_{z\sigma}$ ($\sigma = \uparrow$ or $\downarrow$) directed perpendicular to the plane and coupled to electrons belonging to atoms outside the plane. Concerning two other states of the oxygen, $p_{x\sigma}, p_{y\sigma}$, a possible scenario may be that they are coupled to copper atoms within the plane and do not participate in band conduction (or, in other words, they form a totally filled conduction band). The remaining two orbitals, $p_{x\sigma}, p_{y\sigma}$ (see Fig.7) will be considered along the lines of intrinsic-hole metal approach.
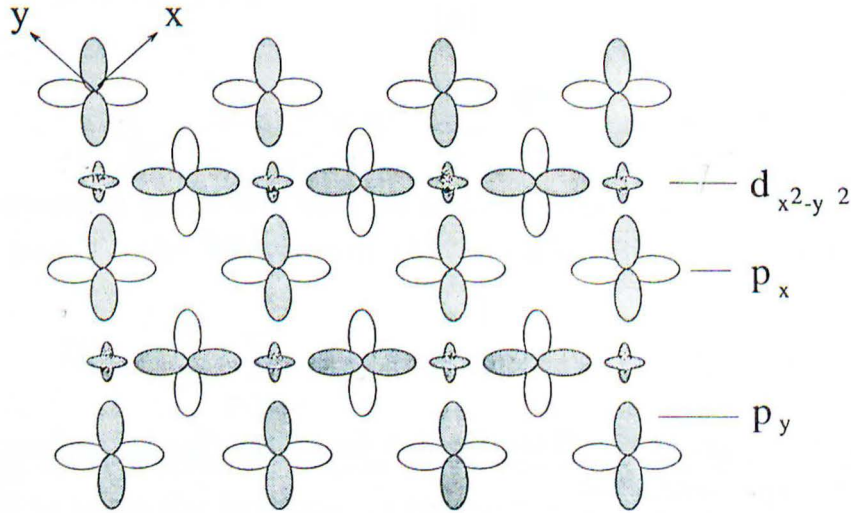
Figure 7. Anion network in the CuO_2 plane. p_z orbitals of oxygen are supposed to be included in the chemical bonding with the Cu cations whereas p_x, p_y oxygen states participate in the band conduction. p_x, p_y orbitals are rearranged pointing in the oxygen- oxygen direction to maximize the hybridization energy between the near oxygen sites

These states are filled in the $2p^6$ configuration (a vacuum state O^{2-}) and become progressively occupied by holes when the compound is doped with an acceptor. Such an acceptor can be Ba or Sr in case of the $La_{1-x}(Ba, Sr)_x CuO_4$ compound, or oxygen itself in the $YBa_2Cu_3O_{6+x}$ system. In latter case, dopant oxygen is supposed to occupy positions outside the CuO_2 plane whilst oxygen sites in the plane remain intact.

The hole system is described by the Hamiltonian

$$
H = -t\sum_{x\delta\sigma} a_{x\sigma}^+ a_{x+\delta,\sigma} + \sum_{x\delta\sigma} a_{x\sigma}^+ a_{x+\delta,\sigma}[V n_{x,-\sigma} n_{x+\delta,-\sigma} + W(n_{x,-\sigma} + n_{x+\delta,-\sigma})] +
$$
$$
U\sum_x n_{x\uparrow} n_{x\downarrow} + V_1\sum_{x\delta} n_{x\uparrow} n_{x+\delta,\downarrow} + W_1\sum_{x\delta\sigma} n_{x\sigma} n_{x+\delta,\sigma} \tag{47}
$$

including multiplicative (V) and additive (W) contraction energies as well as the Hubbard intra-site (U) and inter-site (V_1, W_1) terms.

Feynman diagrams corresponding to the interactions included in Eq.(47) are shown in Fig.8.

(a)   (b)

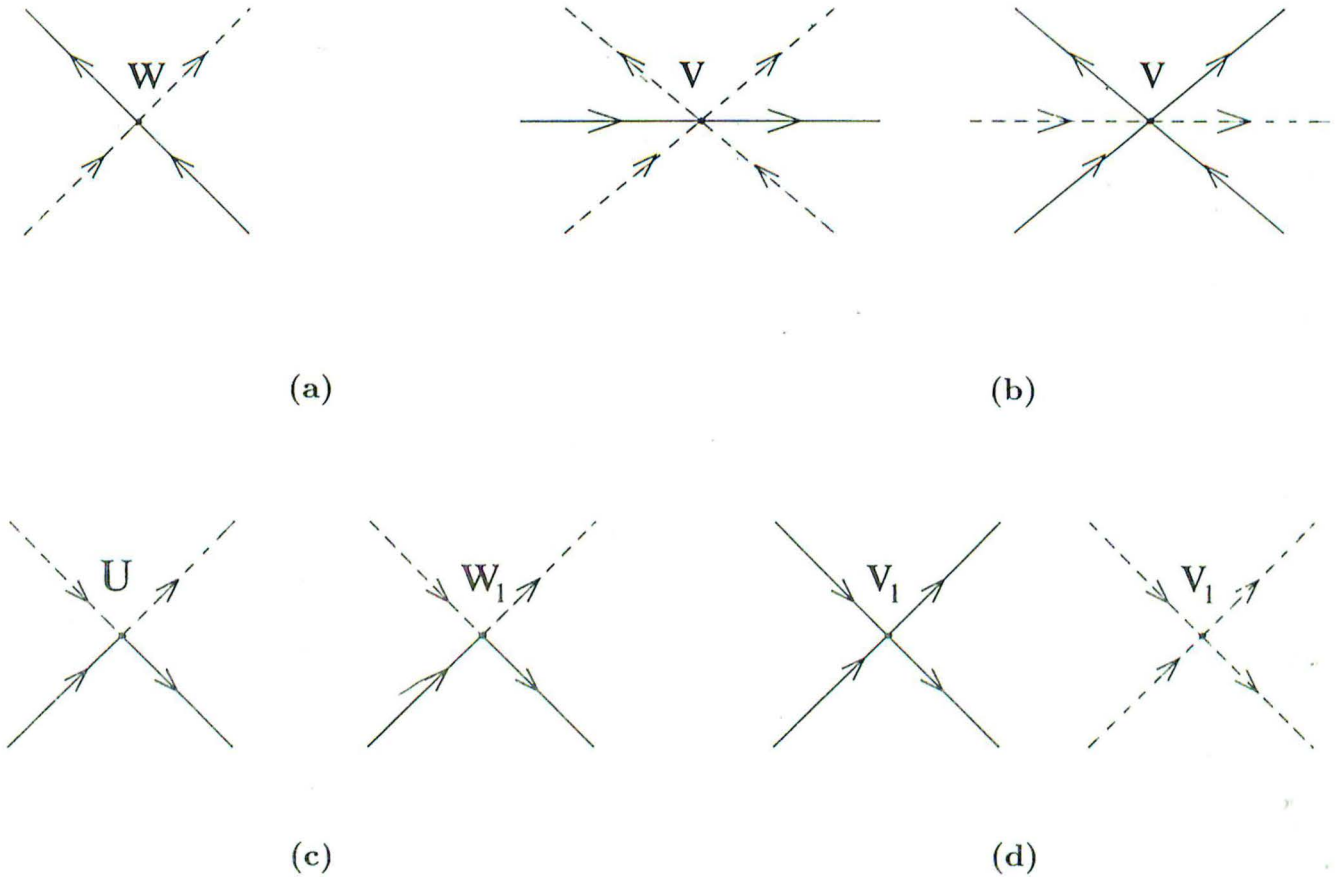(c)   (d)

Figure 8. Feynman diagrams for the electron- electron interaction representing the effect of contraction. (a)Additive contraction; (b)multiplicative contraction; (c)-(d)intra-site and inter-site Coulomb interactions U, V_1, W_1. Full and dotted lines distinguish between spin up and spin down states

Four-vertex diagrams correspond to W and to the Hubbard (Coulomb) interaction, whereas six-vertex diagrams refer to the V term. The Cooper effect in the interacting fermion system [15] manifests itself as a singularity in the two-particle scattering amplitude at zero momentum. Four-vertex interactions result in the singularity of the scattering amplitude at small momentum of the type shown in Fig.9,a whereas six-vertex interaction is represented by a block of diagrams of Fig.9,b-e. Of the latter, only diagrams (b) and (d) are singular as $\mathbf{k_1} + \mathbf{k_2} \to 0$, because in diagrams (c) and (e) the momentum conservation at the vertex does not require that the momenta of the Green functions are equal at $\mathbf{k} = 0$.

There is one-to-one correspondence between the diagrams of Figure 9 and the mean field Hamiltonian obtained from Eq.(47) by the Wick-decoupling of the product of the

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Fermi operators. We need to select only from those with the singular part and can neglect products which may be included in the renormalization of the chemical potential [15].
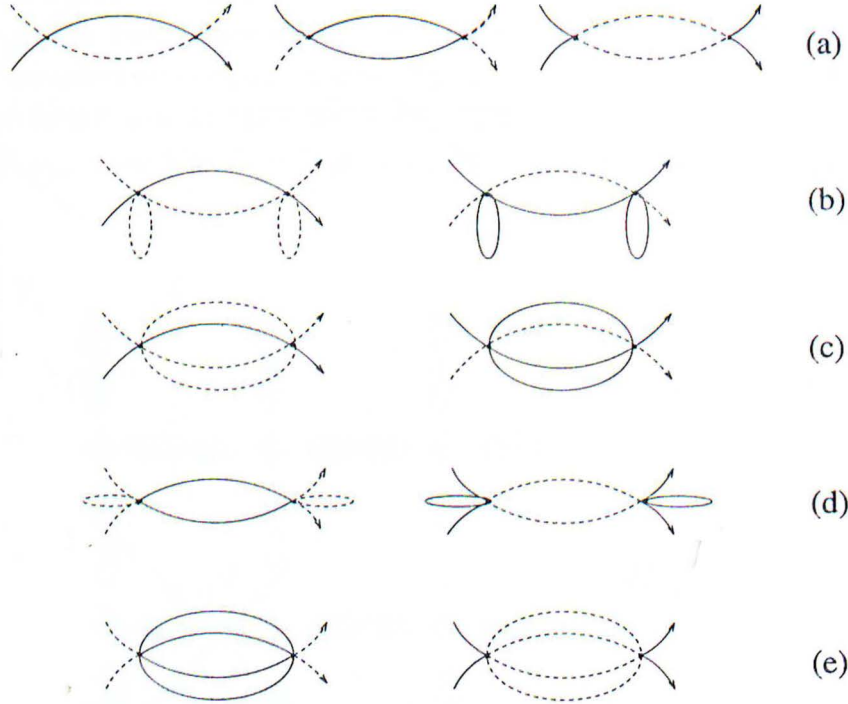

Figure 9. Cooper diagrams for four-vertex (a) and six-vertex (b)-(e) interactions. Of the latter, only diagrams (b) and (d) are singular at $\mathbf{k_1} + \mathbf{k_2} \to 0$

The singular part of the interaction (47) can be represented as a sum of three terms, according to their symmetry with respect to the transformation $\mathbf{k} \to -\mathbf{k}$:

$$H_{int} = H_{int}^{S=0} + H_{int}^{S_z=0,S=1} + H_{int}^{S_z=\pm 1}, \tag{48}$$

where superscript "$S = 0$" corresponds to pairing in a singlet state and the remaining two terms to pairing in the triplet states with the spin projection equal to 0 and to ± 1, respectively. These terms are selected according to their symmetry:

$$H_{int}^{S=0} = \frac{1}{N} \sum_{kk'} \{U + 2(V_1 - \frac{V}{N} \sum_q \varepsilon_q n_q)(\cos k_x \cos k'_x + \cos k_y \cos k'_y) +$$

$$2(\varepsilon_k + \varepsilon_{k'})(W + \frac{V}{N} \sum_q n_q) + V \sum_q \varepsilon_q (1 - n_q)\} a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ a_{-\mathbf{k}'\downarrow} a_{\mathbf{k}'\uparrow}, \tag{49}$$

$$H_{int}^{S_z=0,S=1} = \frac{1}{N} \sum_{kk'} (V_1 + \frac{2V}{N} \sum_q \varepsilon_q n_q)(\sin k_x \sin k'_x + \sin k_y \sin k'_y) a_{\mathbf{k}\uparrow}^+ a_{-\mathbf{k}\downarrow}^+ a_{-\mathbf{k}'\downarrow} a_{\mathbf{k}'\uparrow}$$

$$\tag{50}$$

$$H_{int}^{S_z=\pm 1} = \frac{1}{N}\sum_{kk'\sigma}(2W_1 + \frac{V}{N}\sum_q \varepsilon_q n_q)(\sin k_x \sin k'_x + \sin k_y \sin k'_y)a^+_{\mathbf{k}\sigma}a^+_{-\mathbf{k}\sigma}a_{-\mathbf{k}'\sigma}a_{\mathbf{k}'\sigma}.$$

(51)

The transformation to the momentum space have been carried according to

$$a_{\mathbf{x}\sigma} = \frac{1}{\sqrt{N}}\sum_k a_{\mathbf{k}\sigma}e^{i\mathbf{kx}}.$$

(52)

At the critical temperature T_c, there will appear the nonzero order parameters corresponding to the above states:

$$\Delta_k^{S_z=0} = \sum_{k'}\lambda_{kk'}^{S_z=0} < a_{-k'\downarrow}a_{k'\uparrow} >$$

(53)

or

$$\Delta_k^{S_z=2\sigma} = \sum_{k'}\lambda_{kk'}^{S_z=2\sigma} < a_{-k'\sigma}a_{k'\sigma} >$$

(54)

with the coupling amplitudes $\lambda_{kk'}$

$$\lambda_{kk'}^{S=0} = U + V[-\eta + 2\nu(\varepsilon_k + \varepsilon_{k'}) - \tfrac{1}{4}\eta(\varepsilon_k\varepsilon_{k'} + \tilde{\varepsilon}_k\tilde{\varepsilon}_{k'})] + \\ 2W(\varepsilon_k + \varepsilon_{k'}) + \tfrac{1}{4}V_1(\varepsilon_k\varepsilon_{k'} + \tilde{\varepsilon}_k\tilde{\varepsilon}_{k'})$$

(55)

and

$$\lambda_{kk'}^{S_z=0,S=1} = \frac{1}{4}(\frac{1}{2}V_1 + \eta V)(\sigma_k\sigma_{k'} + \tilde{\sigma}_k\tilde{\sigma}_{k'}),$$

(56)

$$\lambda_{kk'}^{S_z=\pm 1,S=1} = \frac{1}{4}(W_1 + \frac{1}{2}\eta V)(\sigma_k\sigma_{k'} + \tilde{\sigma}_k\tilde{\sigma}_{k'}).$$

(57)

In these formulas

$$\varepsilon_k = 2(\cos k_x + \cos k_y), \quad \tilde{\varepsilon}_k = 2(\cos k_x - \cos k_y),$$
$$\sigma_k = 2(\sin k_x + \sin k_y), \quad \tilde{\sigma}_k = 2(\sin k_x - \sin k_y),$$

(58)

and $\nu(\mu), \eta(\mu)$ are functions of the chemical potential (μ) determined through the identities

$$\nu = \frac{1}{N}\sum_k n_k, \quad \eta = \frac{1}{N}\sum_k n_k\varepsilon_k.$$

(59)

where $n_{\mathbf{k}} = 1/(\exp(t\varepsilon_{\mathbf{k}} - \mu)/T + 1)$ is the Fermi distribution at $\Delta = 0$. Notice that terms labeled with " $\sim$ " differ in their symmetry with respect to transformation $k_x \leftrightarrow k_y$ from those without " $\sim$ ".

Functions $\nu(\mu)$ and $\eta(\mu)$ can be calculated easily. For practical purpose, it is appropriate to specify ν and consider μ and η as functions of the filling factor ν. The dependences $\mu(\nu)$ and $\eta(\nu)$ for a $2d$ square lattice with nearest neighbor hopping are presented in Figure 10.
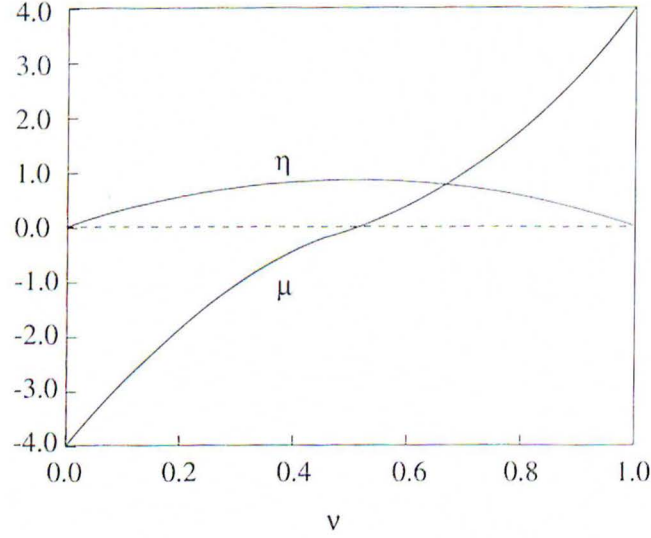
Figure 10. Functions $\mu(\nu)$ and $\eta(\nu)$ in a two-dimensional square lattice with the nearest-neighbor hopping. Exact value of η at $\nu = 0.5$ is $8/\pi^2$

After the introduction of the pairing amplitudes (53) and (54), the mean-field Hamiltonians corresponding to Eq. (47) becomes

$$H^{S_z=0} = t\sum_{k\sigma}\varepsilon_k a^+_{k\sigma}a_{k\sigma} + \sum_k \Delta^{S_z=0}_k a^+_{k\uparrow}a^+_{-k\downarrow} + h.c \tag{60}$$

for both $S = 0$ and $S = 1$ states (both having $S_z = 0$) differing only in the orbital symmetry of $\Delta_{\mathbf{k}}$ ($\Delta_{\mathbf{k}} = \Delta_{-\mathbf{k}}$ for $S = 0$ and $\Delta_{\mathbf{k}} = -\Delta_{-\mathbf{k}}$ for $S = 1, S_z = 0$), and

$$H^{S_z=\pm 1} = t\sum_{k\sigma}\varepsilon_k a^+_{k\sigma}a_{k\sigma} + \sum_k \Delta^{S=1}_k a^+_{k\sigma}a^+_{-k\sigma} + h.c \tag{61}$$

for the triplet states $S_z = 2\sigma = \pm 1$ corresponding to an odd symmetry $\Delta_{\mathbf{k}} = -\Delta_{-\mathbf{k}}$. Order parameter Δ vanishes at the critical temperature T_c. The actual transition will take place to one of the states (60)-(61) depending on the value and the sign of $\lambda_{\mathbf{kk'}}$, which provides for the maximal value of T_c. Below, we consider superconducting transitions to the singlet state (Sect.6), and to triplet states (Sect.7) separately.

7. Singlet Superconducting State

By standard procedure, Hamiltonian (60) results in the gap equation for $\Delta^{S=0}_{\mathbf{k}} = \Delta_{\mathbf{k}}$

$$\Delta_k = \int \frac{d^2k'}{(2\pi)^2}\lambda_{kk'}\Delta_{k'}\frac{\tanh(E_{k'}/2T)}{2E_{k'}} \tag{62}$$

with

$$E_k = \sqrt{\xi_k^2 + \Delta_k^2}, \quad \xi_k = t\varepsilon_k - \mu, \tag{63}$$

where μ is the chemical potential and

$$\lambda_{kk'} = \lambda_0 + \lambda_1(\varepsilon_k + \varepsilon_{k'}) + \lambda_2(\varepsilon_k \varepsilon_{k'} + \tilde{\varepsilon}_k \tilde{\varepsilon}_{k'}) \tag{64}$$

where

$$\lambda_0 = -U + \eta V, \quad \lambda_1 = -2(W + \nu V), \quad \lambda_2 = \frac{1}{4}(\eta V - V_1). \tag{65}$$

It follows from Eq.(48) that $\Delta_{\mathbf{k}}$ takes form

$$\Delta_{\mathbf{k}} = \Delta_s^1 \varepsilon_k + \Delta_s^2 + \Delta_d \tilde{\varepsilon}_k, \tag{66}$$

where Δ_s^1, Δ_s^2 and Δ_d are constants. The first two terms correspond to the dependence which does not change with the rotation by $\pi/2$ in the momentum space, whereas the last term changes its sign under such rotation. Therefore, $\Delta_s^{1,2}$ and Δ_d correspond to pairing into the s- and d-states, respectively.

After substitution of (66) into (62) we obtain a system of coupled equations for Δ_s^1, Δ_s^2 and Δ_d

$$\Delta_s^1 = \int \frac{d^2k}{(2\pi)^2}(\lambda_1 + \lambda_2 \varepsilon_k)(\Delta_s^1 \varepsilon_k + \Delta_s^2 + \Delta_d \tilde{\varepsilon}_k)T_{\mathbf{k}}$$

$$\Delta_s^2 = \int \frac{d^2k}{(2\pi)^2}(\lambda_0 + \lambda_1 \varepsilon_k)(\Delta_s^1 \varepsilon_k + \Delta_s^2 + \Delta_d \tilde{\varepsilon}_k)T_{\mathbf{k}}$$

$$\Delta_d = \int \frac{d^2k}{(2\pi)^2}\lambda_2 \tilde{\varepsilon}_k(\Delta_s^1 \varepsilon_k + \Delta_s^2 + \Delta_d \tilde{\varepsilon}_k)T_{\mathbf{k}}, \tag{67}$$

with $\quad T_{\mathbf{k}} = \tanh(E_k/2T)/2E_k$.

In the weak coupling limit $\lambda \to 0$ to which Eqs.(67) apply, the characteristic energy of a quasiparticle $\xi_{\mathbf{k}} = t\varepsilon_{\mathbf{k}} - \mu$ is small compared with the Fermi energy μ because the integrands of Eqs.(67) have singularity at the Fermi energy at $\Delta \to 0$. Therefore in the leading approximation $\xi_{\mathbf{k}}$ should be put equal to 0 and ε_k to μ, which means that the order parameter is energy independent. Moreover, in the limit $\lambda \to 0$ the third of the equations (67) decouples from the first two, because the leading (logarithmic) part of the corresponding integral is isotropic and $< \tilde{\varepsilon}_k >= 0$, where $< ... >$ denotes averaging over the Fermi surface.

Therefore, we shall have either isotropic and energy independent s-wave state found from the gap equation

$$1 = \lambda_s \int \frac{d^2k}{(2\pi)^2}T_{\mathbf{k}} \tag{68}$$

where

$$\lambda_s = \lambda_0 + \lambda_1 \mu/t + \lambda_2 \mu^2/t^2, \tag{69}$$

or an anisotropic d-wave state with the order parameter satisfying the equation

$$1 = \lambda_d \int \frac{d^2 k}{(2\pi)^2} T_{\mathbf{k}} (\cos k_x - \cos k_y)^2 \qquad (70)$$

with $\lambda_d = 4\lambda_2$. The latter state is gapless because the order parameter $\Delta_{\mathbf{k}} = \Delta_d \tilde{\varepsilon}_{\mathbf{k}}$ has nodes at the Fermi surface at $k_x = \pm k_y$.

Depending on the magnitude and on the sign of the coupling parameters V and W, we shall obtain either isotropic or anisotropic superconducting phase. At zero temperature, the corresponding order parameters will be

$$\Delta_s(0) = \varepsilon_0(\mu) \exp(-1/\lambda_s(\mu) N(\mu)) \qquad (71)$$

and

$$\Delta_d(0) = \varepsilon_0(\mu) \exp(-1/\lambda_d(\mu)\zeta(\mu)N(\mu)), \qquad (72)$$

where the cutoff energy ε_0 equals

$$\varepsilon_0(\mu) = 8\sqrt{t^2 - \mu^2/16}, \quad -4t < \mu < 4t. \qquad (73)$$

$N(\mu)$ is the density of states in a $2d$ network (Fig.11). Function $\zeta(\mu)$ is shown in Fig.12. As $N(\mu)$ has van-Hove singularity at $\mu = 0$, $\Delta(0)$ and critical temperature T_c are expected to have maxima near the half-filling $\nu = 1/2$. But since singularity is only logarithmic, any factor we neglected here like e.g. three-dimensional interaction will reduce and possibly eliminate this effect.

Notice that, apart from the Hubbard energies giving negative contributions to λ_s, λ_d, the "contractive" parts of both λ's expected from the "normal" contraction (9) are also negative. The question of the existence of such phases will be discussed after the next section in which we consider the triplet superconducting state.
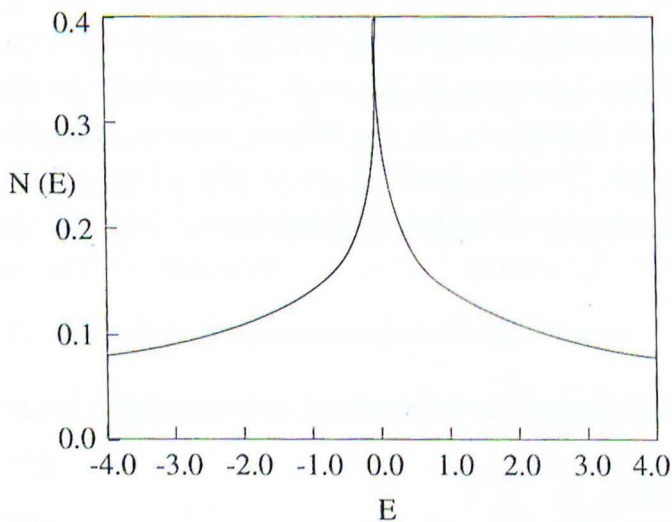

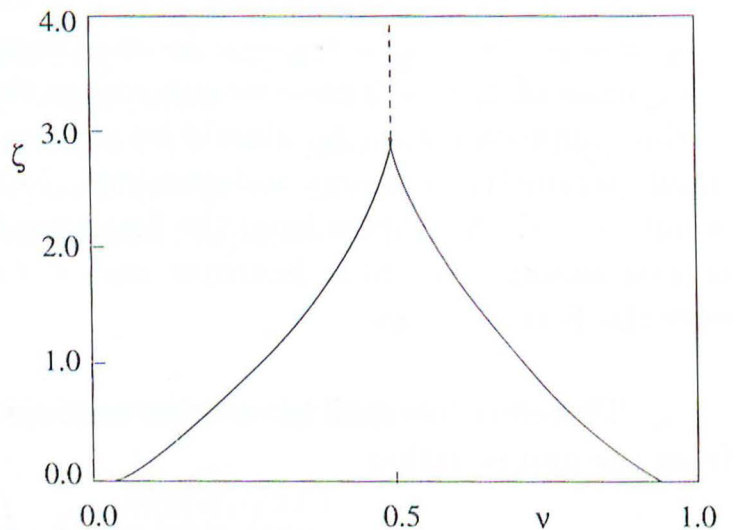**Figure 11.** Density of states in a $2d$ square lattice with the nearest-neighbor hopping

Figure 12. Function $\zeta(\nu)$. Exact value $\zeta(1/2) = 4$

8. Triplet Superconducting State

Both triplet phases ($S_z = 0$ and $| S_z | = 1$) have the same **k**-dependence of the order parameter Δ_k and the identical "gap equations" following from the Hamiltonians (60),(61)

$$\Delta_k = \lambda_p \int \frac{d^2 k'}{(2\pi)^2}(\sigma_k \sigma_{k'} + \tilde{\sigma}_k \tilde{\sigma}_{k'})\frac{\tanh(E_{k'}/2T)}{2E_{k'}}\Delta_{k'} \tag{74}$$

where $E_{\mathbf{k}} = \sqrt{(t\epsilon_{\mathbf{k}} - \mu)^2 + \Delta_{\mathbf{k}}^2}$ and differ only in the value of the coupling parameter λ_p:

$$\lambda_p = -\frac{1}{4}(\eta V + \frac{1}{2}V_1), \quad S_z = 0,$$

$$\lambda_p = -\frac{1}{4}(\frac{1}{2}\eta V + W_1), \quad S_z = \pm 1. \tag{75}$$

At small intra-site, opposite-spin and equal-spin, Coulomb repulsion terms V_1, W_1, coupling strength for a $S_z = 0$ phase proves to be twice larger than that for the $S_z = \pm 1$ phases, which means that the former state is expected to be the leading one. The sign of the product ηV is always negative at the "normal" contraction (9) because η is a positive quantity at any filling. The transition to the spin-triplet, zero-net-spin superconducting state, which we shall discuss below in some detail, is favored if the the magnitude of $2 | \eta V |$ is larger than the intra-site hole repulsion V_1.

Momentum dependence of the order parameter which follows from Eq.(74) is

$$\Delta_{\mathbf{k}}(T) = (\Delta_1(T)\sigma_k/4 + \Delta_2(T)\tilde{\sigma}_k/4, \tag{76}$$

where Δ_1, Δ_2 satisfy

$$(1 - \lambda_p T_{11})\Delta_1 - \lambda_p T_{12}\Delta_2 = 0,$$

$$-\lambda_p T_{12}\Delta_1 + (1 - \lambda_p T_{22})\Delta_2 = 0 \tag{77}$$

with

$$T_{11,22,12} = \int \frac{d^2 k}{(2\pi)^2}(\sigma_k^2, \tilde{\sigma}_k^2, \sigma_k \tilde{\sigma}_k)\tanh(E_k/2T)/2E_k. \tag{78}$$

It follows from (77) that, apart from the global phase factor $e^{i\varphi}$ (which we ignore), both Δ_1 and Δ_2 are real. This then means that $\Delta_{\mathbf{k}}$ has two nodes at the Fermi surface. From arguments similar to those of the previous section, we conclude that in the weak coupling limit $\lambda_p \to 0$, equations (77) will be decoupled. The singular part of T_{12} vanishes because of the identity $< \sigma_k \tilde{\sigma}_k > = 0$. From (77) we have

$$\frac{\Delta_1}{\Delta_2} = \frac{\lambda_p T_{12}}{1 - \lambda_p T_{11}(\Delta_1, \Delta_2)} \quad \text{and} \quad \frac{\Delta_2}{\Delta_1} = \frac{\lambda_p T_{12}}{1 - \lambda_p T_{22}(\Delta_1, \Delta_2)}, \tag{79}$$

which means that at $\lambda_p \to 0$ either $\Delta_1/\Delta_2 = 0$ at $\Delta_2 \neq 0$, or $\Delta_2/\Delta_1 = 0$ at $\Delta_1 \neq 0$. The two solutions

$$\Delta_\mathbf{k}^+ = \Delta_d(T)\sigma_k/4, \quad \Delta_\mathbf{k}^- = \Delta_d(T)\tilde{\sigma}_k/4 \tag{80}$$

are degenerate (and, in particular, they correspond to equal T_c's) and have nodes at $k_x = -k_y$ (at sign "+") or at $k_x = k_y$ (at sign "−"). This is the additional symmetry breaking supplementing the appearance of the conventional ("Josephson") phase φ. Later we shall restrict ourselves to the monodomain phase "+":

$$\Delta_\mathbf{k} = \Delta(T)\sigma_k/4 \tag{81}$$

with $\Delta(T)$ satisfying

$$1 = \lambda \int \frac{d^2k}{(2\pi)^2} \frac{\sigma_k^2 \tanh(\sqrt{\xi_k^2 + \Delta^2\sigma_k^2/4}/2T)}{2\sqrt{\xi_k^2 + \Delta^2\sigma_k^2/4}}. \tag{82}$$

Putting $\Delta = 0$ we obtain an equation for the critical temperature

$$1 = \lambda \int \frac{d^2k}{(2\pi)^2} \frac{\sigma_k^2 \tanh(\xi_k/2T_c)}{2\xi_k}. \tag{83}$$

The integral over the momentum space in Eqs.(82) and (83) can be reduced to

$$\int d^2k = \int d\xi_k \int \frac{dl}{v_\perp}, \quad \mathbf{v} = \partial\varepsilon_k/\partial\mathbf{k}, \tag{84}$$

where l is the length along the constant-energy line, Fig.13. By the introduction of the new variables

$$k_x = x + y, \quad k_y = x - y, \tag{85}$$

the second integral in Eq.(70) reduces to

$$\int \frac{dl}{v_\perp} = \int \frac{dx}{\partial\varepsilon/\partial y} = \int \frac{dx}{\cos x \sin y} = \int \frac{dx}{\sqrt{\sin^2 x_0 - \sin^2 x}}, \tag{86}$$

where x_0 is the maximal size of the Fermi surface in the momentum space

$$x_0 = \arccos(\mu/4). \tag{87}$$

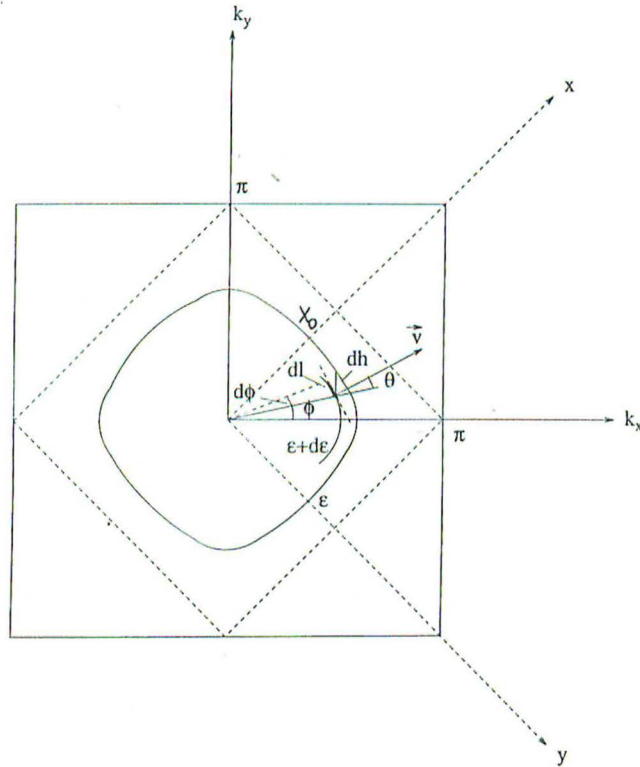With the new variables, angular dependence of the order parameter is represented as

Figure 13. Fermi surface geometry in a two dimensional lattice. Differential elements of the constant-energy line are $dk_\perp = dh \sin(\varphi + \theta)$, $dl = ds/\sin(\varphi + \theta)$, $ds = r d\varphi$. θ is the angle between the normal to the constant-energy line and the radius-vector

$$\Delta_k = \Delta \sin x \cos y \tag{88}$$

and the equation of the "Fermi surface" becomes

$$\cos x \cos y = \cos x_0. \tag{89}$$

It follows from (67) that Δ_k has two nodes at the Fermi surface (Fig.18) and therefore the superconducting state is gapless. However, the density of states $N(\epsilon)$ has a pronounced singularity at an energy $\epsilon = \Delta$ (Fig.15).

The dependence $N(\epsilon)$ follows from the equations Eqs.(72),(76):

$$\frac{N(\epsilon)}{N(0)} = \int_{x_1}^{x_0} \frac{dx}{\sqrt{\sin^2 x_0 - \sin^2 x}} \frac{\epsilon}{\sqrt{\epsilon^2 - \Delta^2 \tan^2 x \cos^2 x_0}} \Big/ \int_0^{x_0} \frac{dx}{\sqrt{\sin^2 x_0 - \sin^2 x}} \tag{90}$$

which, after some manipulations, reduces to

$$\frac{N(\epsilon)}{N(0)} = \begin{cases} \dfrac{t_1}{t_0} \dfrac{K(t_1/t_0)}{K(t_0)}, & \epsilon < \Delta \\ \dfrac{K(t_0/t_1)}{K(t_0)}, & \epsilon > \Delta \end{cases} \tag{91}$$

where $t_0 = \sin x_0$, $t_1 = \epsilon/\sqrt{\epsilon^2 + \Delta^2 \cot^2 x_0}$, and $K(k)$ is the full elliptic integral of the first kind.
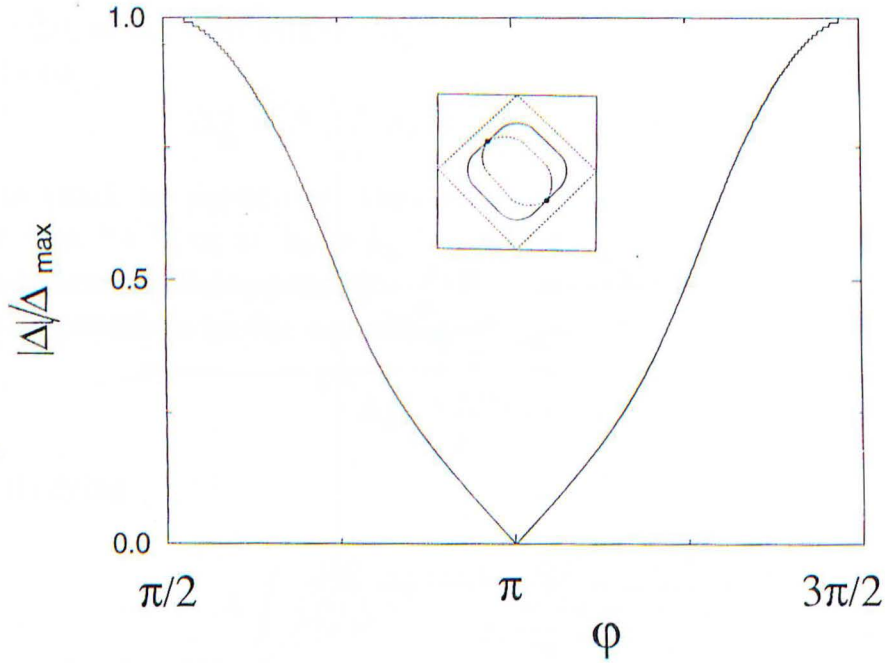
Figure 14. Angular dependence of Δ in a triplet p- state for $\nu = 0.25$. Inset shows nodes of Δ at the Fermi surface

Density-of-states singularity at $\epsilon = \Delta$ is logarithmic:

$$\frac{N(\epsilon)}{N(0)} \simeq \frac{\ln \frac{\pi^2 \sin x_0}{2 \cos^2 x_0 |\epsilon - \Delta|}}{2K(t_0)}, \quad |\epsilon - \Delta| \ll \Delta, \tag{92}$$

whereas $N(\epsilon)$ behaves linearly with energy in the gapless region:

$$\frac{N(\epsilon)}{N(0)} \simeq \frac{\pi}{2t_0 K(t_0)} \frac{\epsilon}{\Delta}, \quad \epsilon \ll \Delta. \tag{93}$$

At finite temperature, elimination of λ from Eq.(82) at the expense of Eq.(83) results in the identity

$$\int_0^\infty d\epsilon \int_0^{x_0} \frac{\tan^2 x \, dx}{\sqrt{\sin^2 x_0 - \sin^2 x}} \{ T \sum_\omega \frac{1}{\epsilon^2 + \omega^2 + \Delta_0^2 \tan^2 x / \tan^2 x_0} - \int_{-\infty}^\infty \frac{d\omega}{2\pi} \frac{1}{\epsilon^2 + \omega^2 + \Delta^2 \tan^2 x / \tan^2 x_0} \} = 0, \tag{94}$$

in which $\omega = (2n + 1)\pi T, n = 0, \pm 1, \ldots$ are the familiar discrete frequencies of the thermodynamic perturbation theory. [These appear in (94) through the identity

$$\frac{1}{2E} \tanh \frac{E}{2T} = T \sum_\omega \frac{1}{E^2 + \omega^2} \tag{95}$$

familiar from the Matsubara Green function technique [15].]

To find the temperature dependence of Δ, it is possible to further simplify Eq.(94):

$$\ln \frac{\Delta_0}{\Delta} = \tag{96}$$

$$\int_0^{\pi/2} F\left(\frac{\Delta}{2\pi T} \frac{\cos x_0 \sin \varphi}{\sqrt{1 - \sin^2 x_0 \sin^2 \varphi}}\right) \frac{\sin^2 \varphi d\varphi}{(1 - \sin^2 x_0 \sin^2 \varphi)^{3/2}} \Big/ \int_0^{\pi/2} \frac{\sin^2 \varphi d\varphi}{(1 - \sin^2 x_0 \sin^2 \varphi)^{3/2}},$$

where $F(x)$ is a function

$$F(x) = \lim_{N \to \infty} \left\{ \ln \frac{2N}{x} - \sum_{n=0}^{N} \frac{1}{\sqrt{(n + 1/2)^2 + x^2}} \right\}. \tag{97}$$

By using the Poisson summation formula (e.g., [17]), $F(x)$ can be reduced to an integral

$$F(x) = 2 \int_0^\infty \frac{dt}{e^{2\pi x \cosh t} + 1}. \tag{98}$$

Function $F(x)$ logarithmically increases as $x \to 0$ and vanishes exponentially as $x \to \infty$

$$F(x) \simeq \begin{cases} \ln \frac{a}{x}, & x \to 0 \\ \frac{1}{\sqrt{x}} e^{-2\pi x}, & x \to \infty \end{cases} \tag{99}$$

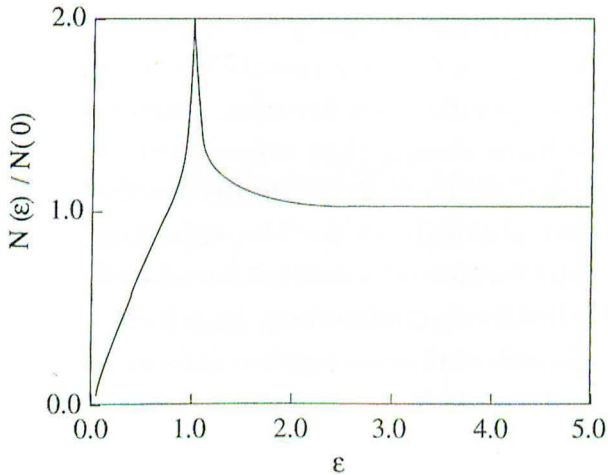where $a = \exp(-1 - C + \ln 2) = 0.2807$ (C is an Euler's constant $C = 0.577$).

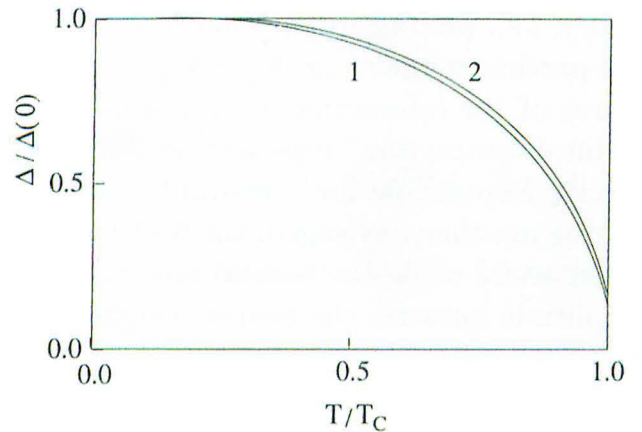**Figure 15.** Density of states in the triplet state for concentration $\nu = 0.25$

Figure 16. Angular dependence of Δ in a triplet p- state for $\nu = 0.25$. Inset shows nodes of Δ at the Fermi surface

The temperature dependence of Δ following from Eq.(96) is shown in Figure 16. It is very similar to $\Delta(T)$ in the BCS theory [16]; however, unlike the BCS theory, the

ratio $\Delta(0)/T_c$ is not a universal constant but depends upon hole concentration. The dependence found by the numerical solution of Eqs.(82) and (83) is presented in Figure 17.
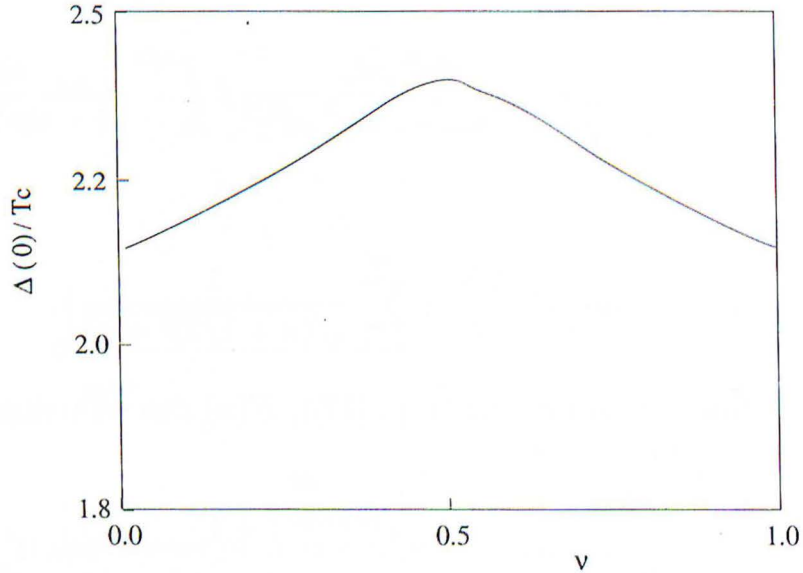

Figure 17. $\Delta(0)/T_c$ vs filling in a triplet state

9. Discussion

The analysis presented in this paper shows that the problem of superconductivity in the anion network of metal-oxide compounds can be formulated along the lines of the BCS theory, i.e., pairing mechanism in a Fermi liquid due to a Cooper instability at the total two-particle momentum $\mathbf{k_1} + \mathbf{k_2} \to 0$, but requires specific consideration concerning the source of the interaction resulting in pairing. We have shown that strong interaction of "orbital contraction" type is expected if intrinsic holes rather than electrons are the mobile species responsible for a metallic conduction. Two possibilities for the superconductive pairing are then envisaged, the first one being due to "additive" contraction of two nearest anion sites, while the second one due to "multiplicative" contraction in which hopping amplitude between the nearest neighbor sites depends nonlinearly upon site occupations. The first possibility results in the singlet pairing of two holes at the same anion site and therefore it should compete with the repulsive Hubbard interaction at this site. As the latter is never smaller than $U \sim 10 - 30eV$ and the contraction interaction, unlike in the electron-phonon case, scales not with U but with the hopping amplitude $t \sim 0.5 - 2eV$ (and therefore is smaller than U), it is not expected that the experimental situation may favor the singlet state.

The second possibility is the pairing of holes at different anion sites in a spin-triplet, orbital-odd symmetry configuration (a "p-state"). Such pairing should only compete with the intra-site Coulomb repulsion which, due to screening, is expected to be much smaller

than the inter-site (Hubbard) Coulomb repulsion. Reasonable estimate for the latter can be $1eV$, i.e., the same order of magnitude as the hopping energy t. In this case, the superconductivity due to orbital contraction will inevitably show up because the sign of the multiplicative contraction is favorable for hole pairing.

A specific feature of the p-state is that it is gapless, but the density of states near the Fermi energy preserves a singularity similar to the one in the BCS theory of superconductivity. As a result, tunneling between oxide superconductors will have a feature reminiscent of conventional superconductors and also that of the gapless superconductors [18,19]. It is interesting to note that measurements of the tunneling energy gap in the $YBa_2Cu_3O_{7-x}$ crystals as early as 1987 have given the value of $2\Delta/T_c \simeq 4.8$ [20] similar to what is expected for a p state according to Fig.17, and dI/dV versus V curve similar to one which can be derived on the basis of our $N(\epsilon)$ dependence (91) (Fig.15).

Many experimental observations for high-T_c superconductors are not in accord with the s-wave pairing theory (NMR spin-lattice relaxation [21], low-temperature penetration depth $\lambda(T)$ dependence [22], etc.) but conform with the models introducing gap nodes at the Fermi surface (e.g.[23]).

Unlike the d-wave state proposed for high-T_c superconductivity based on antiferromagnetic coupling [23] and having 4 nodes with a $\pi/2$ in-plane rotational symmetry, our p-state has 2 nodes, which is π-periodic in rotation. This corroborates with the observation of such periodicity in the transverse magnetic susceptibility of the perfect $LuBa_2Cu_3O_7$ crystals found recently by Buan et al.[24], and does not contradict (similar to the d-pairing model) with the angular dependence of Δ in the orientation-sensitive Josephson tunneling experiments [25].

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