Effect of pair hopping and magnitude of intra-atomic interaction on exchange-mediated superconductivity

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It is shown that the kinetic exchange Hamiltonian for a partially filled narrow band contains a term responsible for hopping of neighboring pairs of electrons in the singlet spin state. In this way we introduce explicitly the dynamics of the resonant valence bond into the formalism describing the exchange-mediated high-T_c superconductivity. The role of the magnitude of the intra-atomic Coulomb interaction on the onset of superconducting phase is also discussed.

The purpose of this paper is twofold: first, to extend the recent works[1-3] on real-space pairing of electrons by incorporating the processes of hopping of these pairs of electrons located on neighboring sites and in the singlet spin state into the formalism of exchange-mediated superconductivity. This extension follows naturally from our earlier work[4-6] on the generalization of the kinetic exchange Hamiltonian due to Anderson[7] to the case of a partially filled band; second, to discuss the effect of electron correlations combined with the kinetic exchange on the onset of a superconducting phase near the Mott transition to the insulating phase. In this way we can supplement the magnetic phase diagram for the correlated system proposed recently[8] with the stability conditions for the superconducting phase.

In the case of a half-filled band the kinetic exchange formalism leads to the effective Heisenberg Hamiltonian with antiferromagnetic[7] or frustrated[9,10] types of equilibrium states, depending on the type of lattice and the range of the interaction. In the case of a less- or more-filled band the situation is not so simple because the virtual hopping processes responsible for the antiferromagnetism compete with the real hopping processes which may mix the magnetic sublattices. Those hopping processes are of two types: the single-particle hopping and the hopping of pairs of electrons in the singlet spin state, each of them located on a different site. All these processes are depicted schematically in Figs. 1(a)–1(c).

To incorporate those processes in a systematic way we proceed in the same way as in Ref. 4. This means we divide the full Hilbert space of the electron states forming a strongly correlated narrow band into two subspaces: the lower with no doubly occupied site configurations and the upper containing the remaining states. This projection reflects the Hubbard subband structure[11] for strongly correlated systems and can be represented by the projected effective Hamiltonians $P_1\tilde{H}P_1$ and $P_2\tilde{H}P_2$, for the lower and upper subbands, respectively. Their explicit forms are as follows:

$$P_1\tilde{H}P_1=\sum_{ij\sigma}t_{ij}a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}(1-n_{j-\sigma})+\sum_{ij}(2t_{ij}^2/U)\left(\mathbf{S}_i\cdot\mathbf{S}_j-\tfrac{1}{4}\sum_{\sigma\sigma'}n_{i\sigma}(1-n_{i-\sigma})n_{j\sigma'}(1-n_{j-\sigma'})\right)$$
$$+\sum_{\substack{ijk\\\sigma\sigma'}}(t_{ij}t_{jk}/U)a_{j\sigma'}^{\dagger}(1-n_{j-\sigma'})a_{k\sigma}n_{k-\sigma'}a_{k\sigma}^{\dagger}n_{k-\sigma}a_{i\sigma}(1-n_{i-\sigma})\ , \tag{1}$$

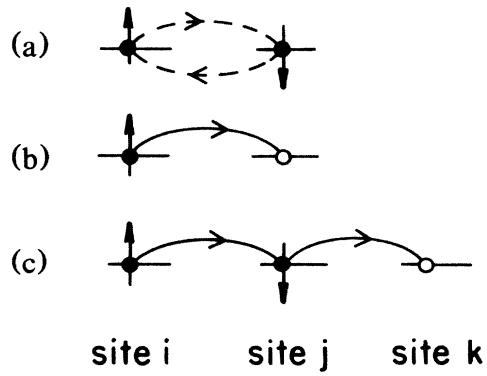

FIG. 1. Various hopping processes in narrow-band systems in partial band filling case.

and

$$P_2\tilde{H}P_2=\sum_{ij}t_{ij}a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}n_{j-\sigma}+U\sum_i n_{i\uparrow}n_{i\downarrow}+\cdots\ . \tag{2}$$

In these expressions t_{ij} is the hopping integral for the neighbors i and j, and U is the magnitude of intra-atomic interaction. We discuss first the part (1) representing the lowest Mott-Hubbard subband. It is the only relevant part in the limit of strong correlations $U\gg U_c\simeq 8|\bar{\varepsilon}|$ ($\bar{\varepsilon}$ is the bare band energy per particle) and for the band filling $n\leq 1$. The Hamiltonian (1) can be written in a different form if we introduce the single-particle and the two-particle operators

$$b_{i\sigma}^{\dagger}\equiv a_{i\sigma}^{\dagger}(1-n_{i-\sigma});$$
$$v_{i\sigma}\equiv b_{i\sigma}^{\dagger}b_{i\sigma}=n_{i\sigma}(1-n_{i-\sigma}), \tag{3}$$

and

$$b_{i\sigma}^{\dagger} \equiv \frac{1}{\sqrt{2}}(b_{i\uparrow}^{\dagger} b_{j\downarrow}^{\dagger} - b_{i\downarrow}^{\dagger} b_{j\uparrow}^{\dagger}); \qquad b_{ij} \equiv \frac{1}{\sqrt{2}}(b_{i\downarrow} b_{j\uparrow} - b_{i\uparrow} b_{j\downarrow}) \ . \tag{4}$$

The operator $b_{i\sigma}^{\dagger}$ creates the electron in a single-particle state on site i and with spin σ provided there is *no* electron with opposite spin on this site. The operator b_{ij} creates a pair of electrons: one on site i and one on site j, in the singlet spin state. The quantities $\{b_{i\sigma}^{\dagger}\}$ and $\{b_{i\sigma}\}$ replace the fermion creation $\{a_{i\sigma}^{\dagger}\}$ and annihilation $\{a_{i\sigma}\}$ operators in the limit of strong correlations.[4-6] Using (3) and (4) the Hamiltonian (1) can be rewritten as

$$P_1 \tilde{H} P_1 = \sum_{ij\sigma} t_{ij} b_{i\sigma}^{\dagger} b_{j\sigma} - \sum_{ijk} (2 t_{ij} t_{jk}/U) b_{ij}^{\dagger} b_{kj} \ . \tag{5}$$

To interpret it more explicitly we assume that $t_{ij} = t \neq 0$ only for nearest-neighboring (NN) pairs $\langle ij \rangle$. Then

$$P_1 \tilde{H} P_1 = t \sum_{\substack{\langle ij \rangle \\ \sigma}} b_{i\sigma}^{\dagger} b_{j\sigma} - \frac{2t^2}{U} \sum_{\langle ij \rangle} b_{ij}^{\dagger} b_{ij} - \frac{2t^2}{U} \sum_{\substack{i,k \\ j(i,k)}} b_{ij}^{\dagger} b_{jk} \ , \tag{6}$$

where $j(k,i)$ means the site j is NN of both k and i, $i \neq k$. The first term represents the hopping of electrons between singly occupied and empty sites, the second supplies the binding energy for the NN singlet pairs, and the third the hopping of those pairs, as illustrated in Fig. 1(c). Thus the last term provides a translational motion of the singlet pairs *(a "resonant" character of the pair bond).* This type of process takes place only if there is at least one unoccupied site as a NN of one of the sites on which the singlet pair is located. Hence, it takes place for strongly correlated electrons only for the non-half-filled case. The Hamiltonian (5) generalizes that of Baskaran, Zou, and Anderson[3] as well as puts their considerations on a more formal ground.

The operators $\{b_{i\sigma}\}$ and $\{b_{i\sigma}^{\dagger}\}$ possess *non*fermion anticommutation relations, while the operators $\{b_{ij}\}$ and $\{b_{ij}^{\dagger}\}$ posses *non*boson commutation relations. This is one of the reasons why an exact solution of the Hamiltonian (6) has not been achieved as yet. Therefore, to make the problem tractable at this point one replaces[2,3,8] the operators in (6) by the fermion operators $\{a_{i\sigma}\}$ and $\{a_{i\sigma}^{\dagger}\}$ and renormalizes the parameters t and t^2/U in such a way that they reflect the restriction on hoppings (single particle as well as that of pairs) imposed by the removal of the doubly occupied site configurations from the physical space. This type of treatment follows naturally from the Gutzwiller variational approach,[12] as well as from others.[13,14] In effect, the Hamiltonian (6) is approximated by

$$P_1 \tilde{H} P_1 = t\Phi \sum_{\langle ij \rangle \sigma} a_{i\sigma}^{\dagger} a_{j\sigma} - \frac{2t^2}{U}(1-\Phi) \sum_{\langle ij \rangle} b_{ij}^{\dagger} b_{ij} - \frac{2t^2}{U} \Phi(1-\Phi) \sum_{\substack{i,k \\ j(k,i)}} b_{ij}^{\dagger} b_{jk} \ , \tag{7}$$

where now[3,15]

$$b_{ij}^{\dagger} = \frac{1}{\sqrt{2}}(a_{i\uparrow}^{\dagger} a_{j\downarrow}^{\dagger} - a_{i\downarrow}^{\dagger} a_{j\uparrow}^{\dagger}) \ , \tag{8}$$

and Φ describes the degree of itineracy of electron on a macroscopic scale[12,13] [it reduces to $\Phi = (1-n)/(1-n/2)$ in the limit $U/W \gg 1$; W is the bare band width]. Analogously, one can say[8] that $(1-\Phi)$ describes the probability that a particle is localized on a macroscopic scale; hence the factor $(1-\Phi)$ before the exchange part.

We have argued[8] that one can generalize the effective Hamiltonian (7) to a more general situation, including the metallic phase near the metal-insulator (Mott) transition, by including the part $P_2 \tilde{H} P_2$ and neglecting irrelevant[16] terms in (2). Hence, one obtains the effective Hamiltonian

$$\tilde{H} = t\Phi \sum_{\langle ij \rangle \sigma} a_{i\sigma}^{\dagger} a_{j\sigma} + U\eta - \frac{2t^2}{U}(1-\Phi) \sum_{\langle ij \rangle} b_{ij}^{\dagger} b_{ij} - \frac{2t^2}{U} \Phi(1-\Phi) \sum_{\substack{i,k \\ j(i,k)}} b_{ij}^{\dagger} b_{jk} \ , \tag{9}$$

where the explicit expression for the band-narrowing factor Φ for arbitrary n and U/W has been given in Ref. 13. The factor Φ contains renormalization in single-site approximation. $\tilde{H}$ depends parametrically on the two-particle correlation function $\eta = \langle n_{i\uparrow} n_{i\downarrow} \rangle$ which is determined variationally within the approach equivalent to that of Brinkman and Rice[13] for $n = 1$ and in the paramagnetic phase. In the strong correlation limit $U > U_c$, i.e., for $\eta \to 0$, our effective Hamiltonian reduces with minor corrections[17] to that discussed earlier.[2,3] However, since (9) is valid also for $U \lesssim U_c$ one can study an evolution of the superconducting phase from the situation corresponding to nearly localized Fermi liquid to the limit of strongly correlated electrons $U \gg U_c$.

In treatment of Hamiltonians (7) (Refs. 2 and 3) or (9) (Ref. 8) one makes two further assumptions: First, one assumes that either the band energy part in (7) or the first two terms in (9) combined together are much larger than the remaining two. This is because the Hartree-Fock approximation we are going to make is valid only if either $\Phi|\bar{\varepsilon}|$ (for $U \geq U_c$) or $|\Phi\bar{\varepsilon} + U\eta|$ (for $U \leq U_c$) is substantially larger than the second-order contribution. Furthermore, one approximates the second-order terms by their Hartree-Fock expressions and takes the Hamiltonian $\tilde{H} - \mu N_e$ to preserve the total number N_e of electrons in the system.

On adopting the Hartree-Fock approximation to (9) one uses the expressions

$$b_{ij}^{\dagger} b_{ij} \simeq b_{ij}^{\dagger} \langle b_{ij} \rangle + \langle b_{ij}^{\dagger} \rangle b_{ij} - \langle b_{ij}^{\dagger} \rangle \langle b_{ij} \rangle - \left[\frac{n_i n}{4} + \frac{n_j n}{4} - S_i^z \langle S_j^z \rangle - \langle S_i^z \rangle S_j^z + \langle S_i^z \rangle \langle S_j^z \rangle \right] + \cdots \tag{10}$$

and

$$b_{jk}^{\dagger}b_{ik} \simeq b_{jk}^{\dagger}\langle b_{ik}\rangle + \langle b_{jk}^{\dagger}\rangle b_{ik} - \langle b_{jk}^{\dagger}\rangle\langle b_{ik}\rangle \ . \tag{11}$$

The nonzero averages of $\langle S_i^z\rangle$ and $\langle b_{ij}^{\dagger}\rangle$ point to the possibility of a coexistence of antiferromagnetism and superconductivity. Here, for the sake of simplicity of our argument we assume that $\langle S_i^z\rangle = 0$ if $\langle b_{ij}^{\dagger}\rangle \neq 0$. For the same reason we neglect also the renormalization of NN hopping.

Thus, after taking the space Fourier transform to the reciprocal ($\mathbf{k}$) space we have that

$$\tilde{H} = \sum_{\mathbf{k}\sigma}[\Phi(\eta)\varepsilon_{\mathbf{k}} - \mu]n_{\mathbf{k}\sigma} + U\eta$$
$$- J_0\sum_{\mathbf{k}}(\Delta_{\mathbf{k}}a_{\mathbf{k}\uparrow}^{\dagger}a_{-\mathbf{k}\downarrow}^{\dagger} + \Delta_{\mathbf{k}}^{*}a_{-\mathbf{k}\downarrow}a_{\mathbf{k}\uparrow} - |\langle b\rangle|^2) \ , \tag{12}$$

where $\Delta_{\mathbf{k}} \equiv \sqrt{2}\gamma_{\mathbf{k}}\langle b\rangle$, $\langle b\rangle = \langle b_{ij}\rangle$ for NN pairs,

$$\gamma_{\mathbf{k}} = (1/z)\sum_{j(i)}\exp[i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)] \ , \tag{13}$$

is the structure factor, $\varepsilon_{\mathbf{k}} \equiv zt\gamma_{\mathbf{k}}$, z is the number of nearest neighbors, and

$$J_0 \equiv \frac{2t^2}{U}z(1-\Phi)[1+(z-1)\Phi] \ . \tag{14}$$

The last factor in (14) is due to hopping of the pairs. We see that (12) reduces to the Hamiltonian of Cyrot[2] and Baskaran *et al.*[3] in the limit[17] $\eta = 0 (U > U_c)$.

The Hamiltonian (12) can be diagonalized by standard Bogolyubov transformation: One obtains quasiparticles with energies

$$E_{\mathbf{k}} = [(\Phi\varepsilon_{\mathbf{k}} - \mu)^2 + (J_0|\Delta_{\mathbf{k}}|)^2]^{1/2} \ ,$$

where μ is the Fermi energy. Hence, the self-consistent equation for the s-wave gap parameter $\Delta_{\mathbf{k}}$ is[3]

$$\frac{1}{J_0} = \frac{1}{N}\sum_{\mathbf{q}}\frac{\gamma_{\mathbf{q}}^2}{E_{\mathbf{q}}}\tanh\left(\frac{\beta E_{\mathbf{q}}}{2}\right) \ . \tag{15}$$

This equation must be supplemented with the equation for the chemical potential. To illustrate the results we consider with some the case $n = 1$ with a symmetric form of bare density of states, $\rho^0(\varepsilon) = \rho^0(-\varepsilon)$. Then, we have for all $\mu = 0$ temperatures as well as a gapless spectrum

$$E_{\mathbf{k}} = (J_0/W)|\varepsilon_{\mathbf{k}}| = (J_0/2)|\gamma_{\mathbf{k}}| \ ,$$

and Eq. (15) leads to the following condition for the transition temperature:

$$\frac{W^2\Phi}{8J_0} = \int_0^{W/2}\rho^0(\varepsilon)\,\varepsilon\tanh\left(\frac{\Phi\epsilon}{2k_BT_c}\right)d\varepsilon \ . \tag{16}$$

This equation has been solved numerically for the density of states $\rho^0(\varepsilon) = 1/W$ for $|\varepsilon| < W/2$, and the result is plotted in Fig. 2. The equilibrium value of η was determined minimizing the expression for the free-energy functional.[8] From Fig. 2 it follows that as $U \to U_c$, T_c evolves continuously to the limiting value $k_BT_c/W \simeq 0.01$, related to the mean-field value of the Néel temperature for the Mott insulator, $k_BT_N/W = t^2z/UW \simeq 0.03$ by the factor $\frac{1}{3}$. However, the energy of the correlated normal phase

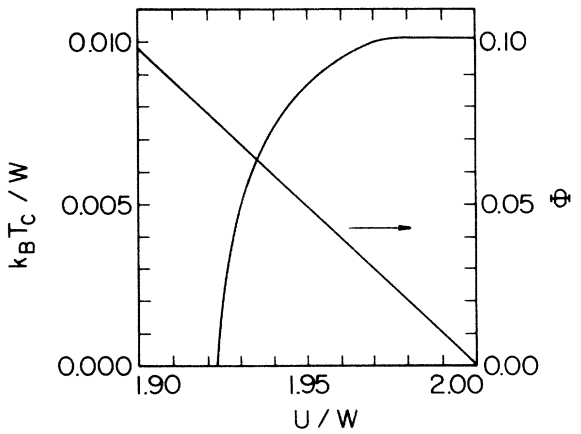

FIG. 2. The superconducting critical temperature as a function of electron-electron interaction U/W near the Mott transition. The band-narrowing factor at $T = 0$ has been drawn for comparison.

$[\Phi(\eta_0)\bar{\varepsilon} + U\eta_0]$ becomes very rapidly of the same magnitude as k_BT_c, so that the Hartree-Fock approximation may not be appropriate for either $U/W \geq 1.95$ or n close to unity. For $T = 0$ Eq. (16) has the solution

$$\Delta(0) \equiv J_0\sqrt{2}\langle b\rangle = 2|\bar{\varepsilon}|[(J_0/4\bar{\varepsilon})^2 - \Phi_0^2]^{1/2} \ . \tag{17}$$

where $\Phi_0 = (1-\mu/\mu_c)^2$. Hence, close to the Mott localization we have that $2\Delta(0)/k_BT_c = 6$.

The antiferromagnetic phase is the stable phase for $U/W \to 2$ and the density of states chosen.[8] This means that in order to get a stable superconducting phase one must indeed have the situation with $n < 1$, since then the magnetic phase disappears quite rapidly.[6]

The main physical conclusions coming from our work for $n < 1$ and $U > U_c$ are similar to those of Refs. 1–3. Furthermore, we can make the following prediction which may help in establishing the nature of electronic states in $(La,Sr)_2CuO_{4-\delta}$ systems. Namely, if they can be regarded as those on the insulating side of the Mott transition ($U > U_c$), then the value of T_c should increase with pressure. For the systems with $U < U_c$ the opposite should be true. This is because for $U > U_c$ we increase the overlap of atomic orbitals and enhance the virtual hopping processes (increase J_0). On the other hand, for $U < U_c$ (i.e., on the metallic side of the Mott transition) the net effect of two processes [cf. Eq. (14)] is a decrease of T_c (cf. Fig. 2).

An increase of T_c with pressure was observed in both La-Ba-Cu-O (Ref. 18) and Y-Ba-Cu-O (Ref. 19) compounds (it is much larger in the former case).

Summarizing, I have shown that the models of exchange-mediated superconductivity[1-3] should contain the term responsible for the hopping of NN pairs. There are two types of such processes: with and without spin-flip exchange. They favor superconducting states at the expense of an antiferromagnetic phase for $n < 1$. I have also suggested how to extend the theory to study the onset of superconductivity on the metallic side of the Mott transition.

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[1]P. W. Anderson, Science **235**, 1196 (1987).

[2]M. Cyrot, Solid State Commun. **62**, 821 (1987).

[3]G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[4]K. A. Chao, J. Spałek, and A. M. Oleś, J. Phys. C **10**, L271 (1977).

[5]J. Spałek and A. M. Oleś, Physica B **86–88**, 375 (1977).

[6]J. Spałek, K. A. Chao, and A. M. Oleś, Phys. Status Solidi (b) **108**, 329 (1981).

[7]P. W. Anderson, Phys. Rev. **115**, 2 (1959).

[8]J. Spałek, A. Datta, and J. M. Honig, Phys. Rev. Lett. **59**, 728 (1987). In our treatment we assume that the exchange interaction does not influence the correlation function η which is determined as resulting from the balance between the band and the Coulomb interaction energies calculated at $T=0$.

[9]P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[10]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[11]J. Hubbard, Proc. Roy. Soc. London Ser. A **281**, 401 (1964).

[12]W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).

[13]J. Spałek, A. M. Oleś, and J. M. Honig, Phys. Rev. B **28**, 6802 (1983).

[14]P. Richmond and G. L. Sewell, J. Math. Phys. **9**, 349 (1968).

[15]J. E. Hirsch, Phys. Rev. Lett. **54**, 1317 (1985).

[16]The additional terms in (2) do not change the physics of the problem as long as the effective value of U is large and positive.

[17]The authors in Refs. 2 and 3 assume that $\Phi=1-n$ whereas we have that $\Phi=(1-n)/(1-n/2)\simeq 2(1-n)$ as $n\rightarrow 1$.

[18]C. W. Chu *et al.*, Phys. Rev. Lett. **58**, 405 (1987).

[19]P. H. Hor *et al.*, Phys. Rev. Lett. **58**, 911 (1987); K. Murata *et al.*, Jpn. J. Appl. Phys. **26**, L471 (1987).