Resonating valence bonds and d-wave superconductivity

G. Kotliar
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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We show that the resonating-valence-bond mechanism for high-T_c superconductivity can lead to s-wave- and d-wave-like superconducting order parameters. The critical temperature for d-wave ordering is higher close to half-filling. At low temperatures, a mixture of d and s waves with a well-defined phase opens a full gap in the quasiparticle spectrum.

Following the discovery by Bednorz and Müller[1] of high-temperature superconductivity in rare-earth copper oxides a number of theoretical ideas have been proposed to explain the origin of this unexpected phenomenon. Theoretical arguments[2] suggest that the critical temperatures above liquid nitrogen observed in the $(Y_{1-x}B_x)_2CuO_{4-y}$ (Ref. 3) cannot be understood in terms of a phonon-mediated mechanism, and therefore the pairing mechanism responsible for the superconductivity is of electronic origin. Varma, Schmitt-Rink, and Abrahams[2] suggested a charge-transfer excitation (exciton) mediated pairing, while Hirsch[4] and Anderson[5] proposed a mechanism based on Bose condensation of tightly bound singlet pairs in a large-U Hubbard model. Anderson[5] describes the high-temperature superconductors in terms of a resonating-valence-bond (RVB) state which is a resonant mixture of singlet pairs with an approximate wave function

$$|\phi\rangle = P_G (b^\dagger)^N |0\rangle$$

with

$$b^\dagger = \sum_r \sum_n C^\dagger_{r\uparrow} C^\dagger_{r+n\downarrow} \ . \tag{1}$$

$C^\dagger_{r\uparrow}$ creates an electron at lattice site r with spin up, n runs over nearest-neighbor bonds, and P_G is a Gutzwiller projection operator which eliminates doubly occupied sites. At half-filling this wave function describes a singlet magnetic state lacking any obvious long-range order, a quantum liquid of singlet pairs.[6] Away from half-filling the pairs can Bose condense, giving rise to a rather large (of the order of the exchange energy) critical temperature. The Anderson mechanism for superconductivity was reinterpreted in terms of condensation of topological defects (solitons) by Kivelson, Rokshar, and Sethna.[7] Anderson's qualitative ideas were put on more quantitative grounds by the mean-field theory of Baskaran, Zou, and Anderson.[8] Their order parameter

$$\langle b^\dagger_{ij} \rangle = \langle C^\dagger_{i\uparrow} C^\dagger_{j\downarrow} - C^\dagger_{i\downarrow} C^\dagger_{j\uparrow} \rangle \tag{2}$$

is the pair amplitude of a singlet along a nearest-neighbor bond from site i to site j. Similar results were obtained independently by Ruckenstein, Hirschfeld, and Appell.[9] These authors considered, however, a link-independent pair amplitude $\langle b^\dagger_{ij} \rangle = b$ leading to an s-wave-like order parameter.

In this paper we show the following: (a) Anderson's order parameter has two complex degrees of freedom which correspond to an s-wave-like and d-wave-like self-consistent field. When both the s-wave- and d-wave-like order parameters are nonzero, their relative phase becomes a dynamical variable. (b) In a pure exchange model, within mean-field theory, the d-wave state has a higher transition temperature. This suggests that with the superconductivity obtained from doping, the resonating-valence-bond (RVB) state can be reached as a strong-coupling limit of the antiferromagnetic spin-fluctuation-induced singlet pairing which has been discussed by several authors.[10] (c) At low temperatures, close to half-filling, a mixture of s and d waves and a well-defined relative phase is energetically favored. The corresponding gap function vanishes only at four points on the Brillouin zone. This state opens a full gap in the quasiparticle spectrum. (d) In Anderson's theory the s-wave and d-wave order parameters (and their mixture) are rather close in energy. Microscopic details can favor the different types of order. Pair-hopping terms will raise the transition temperature of the s-wave state. The Coulomb repulsion will favor the d-wave state. This suggests the possibility of inducing transitions between the different superconducting states by applying pressure or a magnetic field.

The model under consideration is the pure exchange model treated by Baskaran, Zou, and Anderson,[8]

$$H = -t \sum_{i,j} C^\dagger_{i\sigma} C_{j\sigma} + J \sum_{i,j} C^\dagger_{i\sigma} \sigma^a_{\sigma\sigma'} C_{i\sigma'} C^\dagger_{j\sigma''} \sigma^a_{\sigma''\sigma'''} C_{j\sigma'''} - J \sum_{i,j} (C^\dagger_{i\sigma} C_{i\sigma}) (C^\dagger_{j\sigma'} C_{j\sigma'}) \tag{3}$$

in the space of empty and singly occupied states. J is an exchange energy, σ^a are the Pauli matrices, and i,j run over nearest-neighbor sites on a square lattice. Decoupling the order parameter $\langle b^\dagger_{ij} \rangle$, Baskaran *et al.*[8] obtained the mean-field equations:

$$\sum_{k'} \frac{V_{kk'} \Delta_{k'} \tanh(E_{k'}/2T)}{2E_{k'}} = \Delta_k \ , \tag{4}$$

$$\sum_k \left[1 - \frac{\varepsilon_k}{E_k} \frac{\tanh(\beta E_k/2)}{2} \right] = N(1-\delta) \ ,$$

$$V_{kk'} = J[\cos(k_x - k_{x'}) + \cos(k_y - k_{y'})] \ . \tag{5}$$

N is the number of sites, $1-\delta$ is the number of electrons per site. T the temperature, and one assumes a two-dimensional cubic lattice with dispersion $\varepsilon_k = -t(\cos k_x$

$+\cos k_y$) which is partially justified by band-structure calculations,[11] and we set the lattice spacing equal to 1. $E_k=[(\varepsilon_k-\mu)^2+|\Delta_k|^2]^{1/2}$ is the quasiparticle energy, t and μ are renormalized quasiparticle hopping matrix elements and chemical potentials. We use the crudest approximation for t, i.e., $t=t_0\delta$, with t_0 a bare matrix element, but a more-refined treatment along the lines of Ref. 12 is also possible. The only unusual features in this mean-field equation are the smallness of the effective hopping matrix element and the short-range nature of the pairing interaction in Eqs. (3) and (5) which is effective only among nearest neighbors [$(V_{k-k'})$ is just the Fourier transfer of K_{ij} defined by $K_{ij}=1$ for lattice sites of the nearest neighbors, and $K_{ij}=0$ otherwise]. Unlike weak-coupling theory the summations in Eq. (4) extend over the full Brillouin zone.

Baskaran and co-workers assumed an order parameter $\Delta_k=\Delta_s(\cos k_x+\cos k_y)$. Here we notice that the most general even-parity solution of Eq. (4) is of the form

$$\Delta_k=sC_0+C_2\ , \tag{6}$$

where $C_0=\cos k_x+\cos k_y$ and $C_2=\cos k_x-\cos k_y$ are s-wave-like and d-wave-like cubic harmonics, a fact which follows from the separability of the kernel in Eq. (5) and explore the consequences of a nonzero d. In particular, we show that the d-wave-like order parameter has a higher critical temperature and study the relative stability of the two superconducting phases.

The linearized equation for T_c

$$\Delta_k=\sum_{k'}V_{kk'}\Delta_{k'}\frac{\tanh[(\varepsilon_{k'}-\mu)/2T_c]}{2(\varepsilon_{k'}-\mu)} \tag{7}$$

has two even-parity gap eigenvectors $C_0(k')$ and $C_2(k')$ which belongs to the $+1$ and -1 representations of the cubic group, respectively. The transition temperature for condensation in each channel $T_c(i)$ is of the form

$$\frac{1}{J}=\sum_{k'}\frac{C_i(k')^2}{2(\varepsilon_{k'}-\mu)}\tanh\left(\frac{\varepsilon_{k'}-\mu}{2T_c(i)}\right)=I_i(T,\mu),\ i=0,2\ . \tag{8}$$

The subscripts $i=0$, $i=2$ denote s-wave and d-wave quantities, respectively. At half-filling the d and s eigenvectors have the same critical temperature since $I_0(T,\mu=0)=I_2(T,\mu=0)$. Notice that $C_0(k')$ vanishes when $\varepsilon_{k'}=0$ while $C_2(k')$ has two lines of zeros which intersect the Fermi surface $\varepsilon_k=\mu$ at two points. Close to half-filling the kernel $\tanh[(\varepsilon_{k'}-\mu)/2T]/(\varepsilon_{k'}-\mu)$ has its maximum very close to the line where the order parameter vanishes lowering the value of I_0 relative to I_2. This suggests that close to half-filling the d-wave solution has a higher transition temperature. This point is not completely obvious due to the strong-coupling nature of the problem which extends the integrals defining I_i over the full Brillouin zone.

We studied numerically Eqs. (4)–(8) and compared $T_c(0)$ and $T_c(2)$. J/t is a coupling measuring the relation strength of the pairing interaction and the kinetic energy. We find that in the mean-field approximation weak coupling favors d-wave superconductivity. A typical plot of the s-wave and the d-wave transition temperature as a function of filling is shown in Fig. 1. For very strong coupling, $J/t\sim 1$, the s- and d-wave states are almost degenerate but the d wave still has a slightly high T_c. For weaker couplings, $J/t\leq 0.2$, the d-wave state is much more favorable than the s wave whose transition temperature becomes negligible for $\delta\geq J/t$.

A more-realistic effective Hamiltonian should include pair hopping terms, ij and jl being nearest neighbors on a square lattice:

$$H_{\rm PH}=-t_{\rm PH}\sum_{i\neq j\neq l}(C^\dagger_{i\sigma}C^\dagger_{j-\sigma}C_{j-\sigma}C_{l\sigma}-C^\dagger_{i\sigma}C^\dagger_{j-\sigma}C_{j\sigma}C_{l-\sigma})\ . \tag{9}$$

Performing a canonical transformation, Hirsch[4] has shown that the Hubbard model in the limit of large on-site repulsion is equivalent to the sum of Hamiltonians (3) and (9) with $t_{\rm PH}$ of the order of $J\delta$. In this case $t_{\rm PH}$ is positive, reflecting the fact that allowing the pairs to hop reduces the kinetic energy. This effect favors the s-wave state. On the other hand, starting from a more-detailed model of the copper oxygen planes where the relevant single-particle states are admixtures of Cu and O orbitals, one can show that the s- and d-wave states have different Coulomb electrostatic energies. This effect can be modeled with the Hamiltonian of Eq. (9), but with a negative value of $t_{\rm PH}$ which favors the d-wave state. The net effect of Eq. (9) in mean-field theory is to replace J in Eq. (8) by $J_i=J+t_{\rm PH}(3-2i)$, $i=2$ and 0 for the d-wave and s-wave channels, respectively.

We investigate the low-temperature properties of the pure exchange model, substituting the order parameter Eq. (6) in the free energy:

$$\begin{aligned}F(d,s,\theta)&=\frac{1}{J}(|d|^2+|s|^2)\\&\quad-2T\sum_k\ln\left[\cosh\left(\frac{\beta E_K}{2}\right)\right]\ ,\\E_k&=[(\varepsilon_{k-\mu})^2+|d|^2C_2^2+|s|^2C_0^2\\&\quad+2sd\cos\theta C_0(k)C_2(k)]^{1/2}\ ,\end{aligned} \tag{10}$$

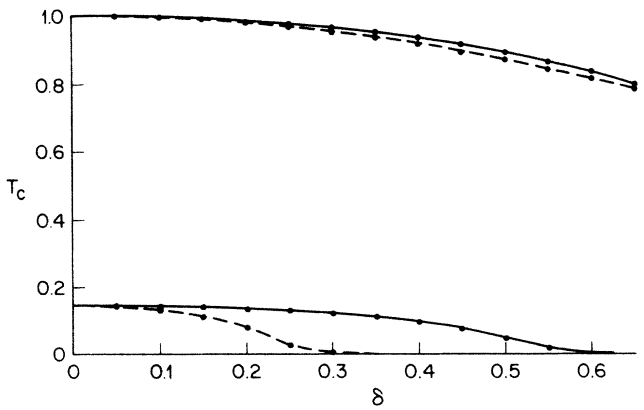

FIG. 1. D (solid line) and S (dotted line) critical temperatures in units of t versus proximity to half-filling δ in the pure exchange model for $J/t=0.145$ (lower curves) and $J/t=1.0$ (upper curves).

where s and d are the amplitude of the s- and d-wave order parameters and θ is their relative phase. Minimizing numerically Eq. (10), we find that at low temperatures a mixture of s and d waves with relative phase close to $\theta=\pi/2$ is energetically favored. At half-filling and zero temperatures, $s=d$, leading to a gap function of the form

$$\Delta_k=(\cos k_x+i\cos k_y)\ , \tag{11}$$

which only vanishes at four points in the Brillouin zone. This is to be compared with the pure s and the pure d states which vanish along lines in Brillouin zone. A realistic two-dimensional Fermi surface will generically intersect the zeros of the pure s and pure d gap functions, but will not generically intersect the four points where the mixed state of Eq. (11) vanishes.

The relative phase between the s and d order parameters can be understood in terms of a simple Landau-Ginzburg expansion:

$$F=\alpha_1|s|^2+\alpha_2|d|^2+\alpha_3|s|^4+\alpha_3|d|^4+\alpha_4|s|^2|d|^2 +\alpha_5(s^\dagger s^\dagger dd+d^\dagger d^\dagger ss)\ . \tag{12}$$

The only term involving the phase is the last one, and since α_5 is positive, this favors a relative phase of $\theta=\pi/2$. This mixed state is particularly interesting since in spite of its anisotropic character it opens a full gap in the quasiparticle spectrum in qualitative agreement with recent measurements of the temperature dependence of the penetration depth.[13]

In the Baskaran, Zou, and Anderson[8] (BZA) theory the mean-field transition temperature stays finite as one approaches half-filling. The true superconducting transition temperature is driven to zero by the phase fluctuations of the order parameter. Implementation of this idea requires a more-sophisticated treatment of the BZA auxiliary boson field, and it is outside the scope of the mean-field theory for the pairing of the Fermi operators. At half-filling the finite transition temperature is to be interpreted as the onset of strong singlet pairing. The spin excitations of the magnetic insulator can then be described as quasiparticle-quasihole excitations with dispersion E_k. This quasiparticle dispersion is calculable from the mean-field theory and is given by E_k. Since the mixed state persists up to half-filling, our analysis does not support the existence of a pseudo-Fermi surface in the insulating state. Our mean-field solution gives a quasiparticle dispersion relation $E_k=J(\cos^2 k+\cos^2 k_y)^{1/2}$, which vanishes at four points on the Fermi surface.

At half-filling $\alpha_1=\alpha_2$, and therefore close to half-filling α_1 and α_2 are fairly close in value, suggesting that one could induce transitions between the pure d-wave ($\alpha_2<0$, $\alpha_1>0$), pure s-wave ($\alpha_1<0$, $\alpha_2>0$), and the s-d mixture ($\alpha_2<0$, $\alpha_1<0$) as a function of pressure or of applied magnetic field.

In this note we suggested, on the basis of a mean-field analysis, that a very local pairing like the pairing interaction in Anderson's RVB theory, proximity to half-filling, and strong coupling favor a transition to a d-wave-like state. At low temperatures the superconducting order parameter is a mixture of s and d waves with a well-defined phase and a full gap. Two obvious limitations of the mean-field analysis is that it treats the double occupancy constraint in a very crude approximation and ignores fluctuations of the order parameter. These effects are probably very important very close to half-filling, and handling them properly will require a more-sophisticated theoretical treatment. Given these limitations, it is important to verify our suggestion by studying variationally more-general RVB wave functions[14]

$$|\phi\rangle=P_G\left(\sum_{n,r}C^\dagger_{\uparrow r+n}C^\dagger_{\downarrow r}d(n)\right)^N|0\rangle \tag{13}$$

with a *link-dependent pair-wave function d(n)*, and to look for evidence for pure and mixed anisotropic s- and d-wave pairings in quantum Monte Carlo simulations of the Hubbard model.

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