PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Microscopic model of hybrid pairing: II. Exact solution for a single pair

K. Byczuk and J. Spałek
Institute of Theoretical Physics, Warsaw University, ul. Hoża 69, PL-00-681 Warszawa, Poland

W. Wójcik
Institute of Physics, Technical University, ul. Podchorążych 1, PL-30-084 Kraków, Poland

(Received 4 March 1992)

We determine the binding energy and the wave function of a single Cooper pair in a system composed of hybridized strongly and weakly correlated electrons, using an approach proposed previously [cf., Phys. Rev. B **38**, 208 (1988)]. The difference between the pairing and local Kondo singlet state and the Cooper pair is emphasized. The three-component characteristic of the appropriate wave function is explicitly introduced; each of the components decays on the scale of few interatomic distances.

I. INTRODUCTION

In current theoretical discussions of pairing concerning correlated electrons, exchange interactions play a prominent role. In the simplest approach one considers a one-band (t-J) model[1,2] in which the pairing involves[3] so-called kinetic exchange interaction among $3d$ electrons.[4] The applicability of a single-band approach to high-temperature superconductivity has been questioned;[5] hybridization between strongly and weakly correlated electron states is believed to be necessary to explain the Fermi liquid properties of the $4f$ electrons in heavy fermion systems.[6] We have developed[7,8] an approach to hybridized systems completely analogous to that used previously,[1] to derive kinetic exchange interactions among strongly correlated electrons in the metallic state. In this approach one decomposes hybridization processes into low-energy and high-energy parts (see Fig. 1), incorporates the former into the unperturbed part H_0 of the total Hamiltonian, and treats the latter within the canonical perturbation expansion scheme. In this manner, the effective Hamiltonian contains both a residual hybridization (with doubly occupied atomic configurations for correlated electrons projected out) and exchange interactions in powers of $V/(U+\epsilon_f)$, where V is the magnitude of hybridization, U is the intra-atomic Coulomb interaction energy for correlated electrons, and ϵ_f is the position of atomic level for correlated electrons measured with respect to the middle of the band of weakly correlated (conduction) electrons. To second order $[\sim V^2/(U+\epsilon_f)]$ one obtains among other terms the Kondo-type interaction, while to the fourth order $\sim V^4/(U+\epsilon_f)^3$ the superexchange interactions appear both for correlated and carrier states.[8] It must be stressed that our approach applies when $|V| \ll U+\epsilon_f$, $|V| \gtrsim |\epsilon_f|$, i.e., when the periodic version of the Schrieffer-Wolff transformation[9] fails. While it is not entirely obvious whether the condition $|V| \ll |\epsilon_f|$ holds for high-T_c systems, we believe it is valuable to explore the model which properly separates the mixing processes into real processes they hybridize, the single-particle states, and the virtual processes which are responsible for singlet pairing. The latter processes correlate to the motion of pairs and contain exchange interactions. The limit $|V| \sim |\epsilon_f|$ is certainly relevant to the physics of heavy-fermion and fluctuating-valence systems; in this respect we include finite-U processes in the second order.

A somewhat similar pairing mechanism has been proposed by Newns and co-workers[10] using the slave boson formulation. However, these authors utilize the mean-field approximation for the Bose field, $d_i^\dagger$ representing the doubly occupied atomic sites. Strictly speaking, such an approximation requires a nonzero number of doubly occupied sites, which is difficult to fulfill in the limit of $U \gg |V|, W$, where W is the bare bandwidth. A reformulation[11] of our canonical perturbation expansion approach within the slave boson approach of Zou and Anderson[12] leads to the same results as before[7] in the limit

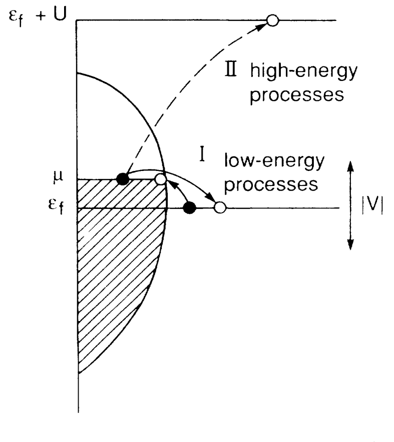

FIG. 1. Schematic representation of the mixing (hybridization) processes and their division into low- and high-energy parts. The former involves only empty and singly occupied atomic level configurations, while the latter takes place via double occupancies in either initial or final states.

$\langle d_i^\dagger d_i \rangle \to 0$. It must be stressed that, within the mean-field approach, the characters of the superconducting gap obtained by us and by Newns are of the same type.

In this paper we present a rigorous analysis of a single pair and analyze its binding under the condition that the band is empty. This problem does not reflect the actual situation of high-T_c or heavy-fermion systems, with one particle per pair of orbitals. However, the simplicity of the case studied here allows us to examine the detailed nature of hybrid pairing and its influence on the pairing induced within subsystems of correlated and uncorrelated electrons. In particular, we show how the three-component wave function emerges and what is the difference between a mobile bound pair and a local Kondo singlet. As a concrete application we calculate the binding energy in a two-dimensional system and show that the pair binding energy matches the temperature scale ($k_B T_c$) of critical temperatures encountered in high-temperature superconductors. We also compare our results with the corresponding analysis in a single narrow-band situation.

II. THE MODEL

We start from the effective Hamiltonian obtained earlier[7,8] to the first nontrivial order in V/U, which may be written as

$$\begin{aligned}\tilde{H} = & \sum_{mn\sigma} t_{mn} c_{m\sigma}^\dagger c_{n\sigma} + \epsilon_f \sum_{i\sigma} N_{i\sigma}(1-N_{i-\sigma}) \\ & + \sum_{im} [V_{im} a_{i\sigma}^\dagger (1-N_{i\sigma}) c_{m\sigma} + \text{H.c.}] \\ & - \sum_{imn} \frac{2V_{in}V_{mi}^*}{U+\epsilon_f} B_{im}^\dagger B_{in} \,, \qquad (2.1)\end{aligned}$$

where the real-space hybrid pairing operators $B_{im}^\dagger$ are defined as

$$B_{im}^\dagger \equiv \frac{1}{\sqrt{2}} (a_{i\uparrow}^\dagger (1-N_{i\downarrow}) c_{m\downarrow}^\dagger - a_{i\downarrow}^\dagger (1-N_{i\uparrow}) c_{m\uparrow}^\dagger) \,. \qquad (2.2)$$

The first three terms in (2.1) comprise the Anderson lattice Hamiltonian in the real-space representation in a standard manner[6–8] and in the limit $U \to \infty$. The last term represents the real-space singlet pairing part which contains for $m=n$ the negative energy shift due to virtual mixing processes $c \leftrightarrow a$ with the formation of a double occupancy on site i in the intermediate state. This term also contains the hopping of the singlet pair from the (i,n) pair of sites to the (i,m) pair site configuration.

By noting the identify

$$B_{im}^\dagger B_{im} \equiv - \left[\mathbf{S}_i \cdot \mathbf{s}_m - \frac{1}{4} \sum_{\sigma,\sigma'} N_{i\sigma}(1-N_{i-\sigma}) n_{m\sigma'} \right] \,, \qquad (2.3)$$

we see that pair binding is caused by the Kondo interaction, where the spin $\mathbf{S}_i$ and $\mathbf{s}_m$ represent the two subsystems. In the limit when the number of electrons on each site is conserved, i.e., when $n_i + N_i = 1$, the Hamiltonian (2.1) reduces to the Kondo model, with the exchange integral $J_{in}^{pd} = 2|V_{in}|^2/(U+\epsilon_f)$.

III. SOLUTION FOR A SINGLE PAIR

We solve (2.1) for a single pair by introducing a three-component wave function as follows:

$$|\phi\rangle = \frac{1}{N} \sum_{i,m} \alpha_{im} B_{im}^\dagger |0\rangle \,, \qquad (3.1a)$$

$$|\Psi\rangle = \frac{1}{N} \sum_{m,n} \beta_{mn} C_{mn}^\dagger |0\rangle \,, \qquad (3.1b)$$

$$|\chi\rangle = \frac{1}{N} \sum_{i,j} \gamma_{ij} D_{ij}^\dagger |0\rangle \,, \qquad (3.1c)$$

where N is the number of sites, α_{im}, β_{mn} and γ_{ij} are the coefficients to be determined, $|0\rangle$ is the empty lattice state, and

$$C_{mn}^\dagger \equiv \frac{1}{\sqrt{2}} \sum_\sigma \sigma c_{m\sigma}^\dagger c_{n-\sigma}^\dagger \,, \qquad (3.2a)$$

$$D_{ij}^\dagger \equiv \frac{1}{\sqrt{2}} \sum_\sigma \sigma a_{i\sigma}^\dagger (1-N_{i-\sigma}) a_{j-\sigma}^\dagger (1-N_{j\sigma}) \,. \qquad (3.2b)$$

The operators $B^\dagger$, $C^\dagger$, and $D^\dagger$ acting on the vacuum state create a pair of electrons in the spin singlet state, either in a hybrid or in the carrier or the atomic states, respectively. The three-component nature of the wave function arises because even if we start from an *a-c* (hybrid) configuration, the hybridization will mix this state with *a-a* and *c-c* configurations of the pair, and vice versa. Also, if we have not projected the double occupancies from the operator $D_{ij}^\dagger$ we would have to impose the conditions $\gamma_{ii} \equiv 0$. In order to prove explicitly that the triad (3.1a)–(3.1c) forms a complete set of states spanning the solution we calculate $\tilde{H}|\cdots\rangle$. Such calculation provides the following set of coupled equations:

$$\begin{aligned}\tilde{H}|\phi\rangle = \frac{1}{N} \sum_{in} \alpha_{in} \Bigg[& \sum_m t_{mn} B_{im}^\dagger + (\epsilon_f - J_{in}^{pd}) B_{in}^\dagger \\ & + \sum_m V_{im}^* C_{mn}^\dagger + \sum_j D_{ij}^\dagger \Bigg] |0\rangle \,, \qquad (3.3a)\end{aligned}$$

$$\tilde{H}|\Psi\rangle = \frac{2}{N} \sum_{mn} \beta_{mn} \left[\sum_l t_{ln} C_{pn}^\dagger + \sum_i V_{im} B_{in}^\dagger \right] |0\rangle \,, \qquad (3.3b)$$

$$\tilde{H}|\chi\rangle = \frac{2}{N} \sum_{ij} \gamma_{ij} \left[\epsilon_f D_{ij}^\dagger + \sum_m V_{im}^* B_{jm}^\dagger \right] |0\rangle \,. \qquad (3.3c)$$

So the system of the three Schrödinger equations is indeed closed. In the above equations we have assumed that $t_{mn} \neq 0$ only for $m \neq n$ (the $m=n$ term is absorbed in ϵ_f). This system of equations will be solved variationally by defining the total wave function of the pair $|F\rangle \equiv |\phi\rangle + |\psi\rangle + |\chi\rangle$, and then minimizing the total energy

$$E = \frac{\langle F|\tilde{H}|F\rangle}{\langle F|F\rangle} \qquad (3.4)$$

with respect to α_{ij}, β_{ij}, and γ_{ij}. The normalization condition leads to

$$\frac{1}{N} \left[\sum_{in} |\alpha_{in}|^2 + \sum_{m,n} |\beta_{mn}|^2 + \sum_{ij}{}' |\gamma_{ij}|^2 \right] = 1 \,. \qquad (3.5)$$

In order to calculate the total energy and utilize explicitly the translational invariance for the problem we carry out a Fourier transformation to reciprocal space. This means that each of the wave-function components is transformed in the same manner as, for example,

$$\alpha_{im}=\frac{1}{\sqrt{N}}\sum_{k}\alpha_{k}\exp[i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_m)]\ . \tag{3.6}$$

Also, the band energy and the interaction parameters are transformed via, e.g.,

$$\epsilon_{\mathbf{k}}=\sum_{m(n)}t_{mn}\exp[-i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)]\ . \tag{3.7}$$

In the $\mathbf{k}$ representation the expectation value $\langle F|\tilde{H}|F\rangle\equiv E\{\alpha_{\mathbf{k}},\beta_{\mathbf{k}},\gamma_{\mathbf{k}}\}$ now becomes

$$\begin{aligned}E\{\alpha_{\mathbf{k}1}\beta_{\mathbf{k}1}\gamma_{\mathbf{k}}\}&\\ =\sum_{\mathbf{k}}\{&2\epsilon_{\mathbf{k}}|\beta_{\mathbf{k}}|^2+(\epsilon_{\mathbf{k}}+\epsilon_f)|\alpha_{\mathbf{k}}|^2+2\epsilon_f|\gamma_{\mathbf{k}}|^2\\ &+\alpha_{\mathbf{k}}^*\beta_{\mathbf{k}}V_k+2\alpha_{\mathbf{k}}^*\gamma_{\mathbf{k}}V_{\mathbf{k}}^*+\alpha_{\mathbf{k}}\beta_{\mathbf{k}}^*V_{\mathbf{k}}^*+\alpha_{\mathbf{k}}\gamma_{\mathbf{k}}^*V_{\mathbf{k}}\\ &-\frac{1}{N}\sum_{\mathbf{k}'}\alpha_{\mathbf{k}}^*\alpha_{\mathbf{k}'}J_{\mathbf{k}-\mathbf{k}'}\}\ .\end{aligned} \tag{3.8}$$

The Schrödinger equation for the components is obtained by minimizing $E\{\cdots\}$ under the condition that the total wave function be normalized, i.e., that

$$\sum_{\mathbf{k}}(|\alpha_{\mathbf{k}}|^2+|\beta_{\mathbf{k}}|^2+|\gamma_{\mathbf{k}}|^2)=1\ . \tag{3.5a}$$

Thus by using the method of Lagrange multipliers one writes the wave equation in the form

$$\frac{\delta E}{\delta\alpha_{\mathbf{k}}^*}-\gamma\alpha_{\mathbf{k}}=0\ , \tag{3.9}$$

and similarly for $\beta_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$. Such procedures yield the following set of equations:

$$\alpha_{\mathbf{k}}(\epsilon_{\mathbf{k}}+\epsilon_f)-\frac{1}{N}\sum_{\mathbf{k}'}\alpha_{\mathbf{k}'}J_{\mathbf{k}-\mathbf{k}'}+2\beta_{\mathbf{k}}V_{\mathbf{k}}+2\gamma_{\mathbf{k}}V_{\mathbf{k}}^*=\lambda\alpha_{\mathbf{k}}\ , \tag{3.10a}$$

$$\alpha_{\mathbf{k}}V_{\mathbf{k}}^*+2\beta_{\mathbf{k}}\epsilon_{\mathbf{k}}=\lambda\beta_{\mathbf{k}}\ , \tag{3.10b}$$

$$\alpha_{\mathbf{k}}V_{\mathbf{k}}+2\epsilon_f\gamma_{\mathbf{k}}=\lambda\gamma_{\mathbf{k}}\ , \tag{3.10c}$$

where the eigenvalue λ is simply the Lagrange multiplier for the problem. Equations (3.10b) and (3.10c) provide the relations

$$\beta_{\mathbf{k}}=\alpha_{\mathbf{k}}\frac{V_k^*}{\lambda-2\epsilon_{\mathbf{k}}}\ , \tag{3.11a}$$

$$\gamma_{\mathbf{k}}=\alpha_{\mathbf{k}}\frac{V_{\mathbf{k}}}{\lambda-2\epsilon_f}\ . \tag{3.11b}$$

Substituting these expressions into (3.10a), we obtain the equation for $\alpha_{\mathbf{k}}$ in explicit form:

$$\begin{aligned}\alpha_{\mathbf{k}}&\left[\epsilon_{\mathbf{k}}+\epsilon_f-\lambda+\frac{2|V_{\mathbf{k}}|^2}{\lambda-2\epsilon_{\mathbf{k}}}+\frac{2|V_{\mathbf{k}}|^2}{\lambda-2\epsilon_f}\right]\\ &-\frac{1}{N}\sum_{\mathbf{k}'}\alpha_{\mathbf{k}'}J_{\mathbf{k}-\mathbf{k}'}=0\ .\end{aligned} \tag{3.12}$$

Now we examine in detail the case $J_{in}^{pd}=J\delta_{in}$, i.e., when only the intra-atomic part of the hybridization is taken into account ($V_{\mathbf{k}}=V$). Under these conditions the bound states are determined by the condition

$$\alpha_{\mathbf{k}}=\frac{J}{\lambda-\left[\epsilon_f+\epsilon_{\mathbf{k}}+\dfrac{2V^2}{\lambda-2\epsilon_{\mathbf{k}}}+\dfrac{2V^2}{\lambda-2\epsilon_f}\right]}\frac{1}{N}\sum_{\mathbf{k}'}\alpha_{\mathbf{k}'}\ . \tag{3.13}$$

Summing both sides over $1/N\sum_{\mathbf{k}}$ and dividing them by a common factor, we obtain the condition for the ground state in the form

$$\frac{1}{J}=\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{\lambda-\left[\epsilon_{\mathbf{k}}+\epsilon_f+\dfrac{2V^2}{\lambda-2\epsilon_{\mathbf{k}}}+\dfrac{2V^2}{\lambda-2\epsilon_f}\right]}\ . \tag{3.14}$$

This is our central result. Before going into detailed numerical analysis we discuss two interesting particular situations.

A. Case A: $J=0$ but $V\neq0$ (mixed-valence limit)

In this case the hybridized states of electron pairs are specified by the poles of Eq. (3.14), i.e.,

$$\lambda\equiv\lambda_{1,2\mathbf{k}}=\epsilon_{\mathbf{k}}+\epsilon_f\pm[(\epsilon_{\mathbf{k}}-\epsilon_f)^2+4V^2]^{1/2}\ . \tag{3.15}$$

It is easy to show that these eigenvalues are twice the values of the eigenenergies for independent particles in a hybridized band. Therefore, if there is no Kondo coupling, the pair dissociates into independent itinerant constituents. At first sight this result is unexpected; for even in the limit $J_{in}^{pd}=0$ [i.e., for $U=\infty$ in Eq. (2.1)] one is left with a projected hybridization part which hinders the motion of a second particle when the first is already present in the system. However, this effect is of the order $1/N$ for itinerant states and therefore entirely negligible in the thermodynamic limit.

B. Case B: $V=0$ (the Kondo limit)

In this case, Eq. (3.14) is easily solvable in a model case after transformation to the explicit integral form, i.e.,

$$\frac{1}{J}=\int_{-W/2}^{W/2}\rho(\epsilon)\frac{d\epsilon}{\lambda-\epsilon_f-\epsilon}\ , \tag{3.16}$$

where $\rho(\epsilon)$ is the density of states in the band (per site per spin). For a constant density of states $\rho(\epsilon)=1/W$, one obtains the eigenvalue

$$\lambda=\epsilon_f-W/2-W\exp(-W/J)\ . \tag{3.17}$$

This result has a simple interpretation: The first two terms represent the noninteracting pair of electrons, one of which is placed at the bottom of the conduction band (i.e., at $-W/2$), while the other is placed at the atomic level (at ϵ_f). The third term represents the energy of the Kondo coupling and may be rewritten in the form

$$E_B\sim-2E_F\exp\left[-\frac{1}{J\rho(E_F)}\right]\ , \tag{3.18}$$

where E_F is the Fermi energy. Note that $W/J=W(U+\epsilon_f)/2V^2$ is usually much smaller than unity, so the binding energy $|E_B|\ll E_F$. Equation (3.18) thus represents a binding energy into a local Kondo singlet in a diluted system of electrons.

C. Case C: $J\neq 0$, $V\neq 0$ (general case)

In the general case, the integral version of Eq. (3.14) reads

$$\frac{1}{J}=(\lambda-2\epsilon_f)\int_{-W/2}^{W/2}\rho(\epsilon)\frac{d\epsilon(\lambda-2\epsilon)}{a\epsilon^2+b\epsilon+c}\;, \tag{3.19}$$

with

$$a=2(\lambda-2\epsilon_f)\;,$$

$$b=2(\lambda-2\epsilon_f)(\epsilon_f-\lambda)+4V^2\;,$$

$$c=-2V^2\lambda+(\lambda-2\epsilon_f)[\lambda(\lambda-\epsilon_f)-2V^2]\;.$$

This equation has been solved in two cases: (i) for a model density of states $\rho(\epsilon)=1/W$, and (ii) in a two-dimensional case taking $\rho(\epsilon)$ for a square lattice (with a logarithmic singularity in the center of the band). Next, we have subtracted from λ the lowest value of energy (3.15) for noninteracting particles which is $\epsilon_f+\epsilon_{\min}-[(\epsilon_f-\epsilon_{\min})^2+4V^2]^{1/2}$ is the lowest energy in the bare band. The difference is then the binding energy, which is displayed in Figs. 2 and 3 for the two cases, respectively. We note several features of these results. First, the binding energy for the selected model density of states is about two orders of magnitude higher than that for the square-lattice case. This is partly due to the larger value of the density of states at the band bottom. This also indicates that the binding energy depends strongly on the detailed shape of the band. Second, if one sets of $2t=1$ eV (i.e., the quantity often taken as the value for $2t_{pp}$, where t_{pp} is the hopping integral between neighboring p_σ states in the CuO$_2$ plane of high-T_c systems), as well as $U\simeq 8$ eV and $|V|\sim 1.5$ eV and $\epsilon_f\sim -4$ eV, one obtains binding energies in the range 10–100 K, a strikingly realistic number in view of the fact that we consider a single pair only (not the complementary limit of two holes in the background of half-filled d states). Also, a large binding increase is observed in the regime $2V^2/(U+\epsilon_f\gtrsim 1$ eV), under which the effective Hamiltonian (2.1) cannot be applied. This is the reason for displaying in Fig. 3 only the binding energy for $V/2t\leq 2$. Note also that the binding energy becomes negligible in the fluctuating valence regime, where $|\epsilon_f|\leq|V|$.

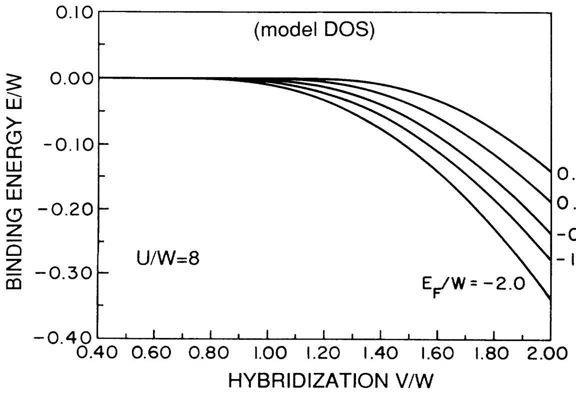

FIG. 2. Binding energy for a hybrid pair for the case with constant density of states (DOS) in the bare band.

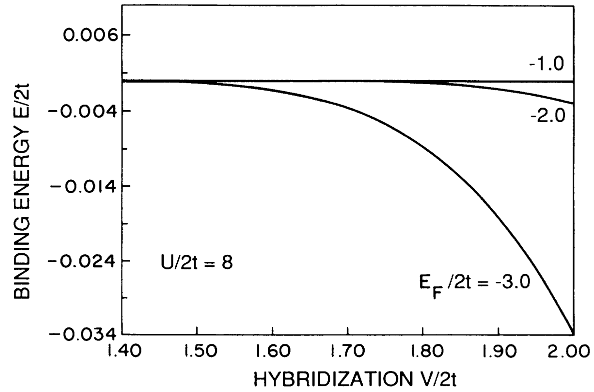

FIG. 3. Same as in Fig. 2 for the case of a two-dimensional square lattice.

D. Case D: molecular states

Strictly speaking, we should also consider the difference between the translationally invariant bound state, whose energy is displayed in Figs. 2 and 3, and a molecular hybrid state. For this purpose we quote our earlier results[13] for the case of two electrons. For two states, one with starting energy E_1, the other with E_2, one can write the complete Hamiltonian for this two-state hybridized system as

$$\begin{aligned}H=&E_1\sum_\sigma n_\sigma+E_2\sum_\sigma N_\sigma+V\sum_\sigma(a_\sigma^\dagger c_\sigma+c_\sigma^\dagger a_\sigma)\\&+U_1n_\sigma n_{-\sigma}\\&+U_2N_\sigma N_{-\sigma}+(K-\tfrac{1}{2}J)\sum_{\sigma\sigma'}N_\sigma n_{\sigma'}-2J\mathbf{S}\cdot\mathbf{s}\\&+\tilde{V}\sum_\sigma(n_\sigma+N_\sigma)(a_{-\sigma}^\dagger c_{-\sigma}+c_{-\sigma}^\dagger a_{-\sigma})\\&+\tilde{J}(a_\uparrow^\dagger a_\downarrow^\dagger c_\downarrow c_\uparrow+c_\uparrow^\dagger c_\downarrow^\dagger a_\downarrow a_\uparrow)\;.\end{aligned} \tag{3.20}$$

Here K is the magnitude of the interorbital Coulomb interaction energy, $\tilde{J}$ is the direct exchange integral, and $\tilde{V}$ is the hybridization energy induced by Coulomb interaction. This most general Hamiltonian for the two-state two-electron system can be easily diagonalized and the lowest hybrid singlet state $|-\rangle$ is of the form

$$\begin{aligned}|-\rangle=&[4D(D-U+K)]^{-1/2}\{4(V+\tilde{V})(a_\uparrow^\dagger c_\downarrow^\dagger-a_\downarrow^\dagger c_\uparrow^\dagger)\\&-(D-U+K)(a_\uparrow^\dagger a_\downarrow^\dagger+c_\uparrow^\dagger c_\downarrow^\dagger)\}|0\rangle\;,\end{aligned} \tag{3.21}$$

with the corresponding eigenenergy

$$E_0=E_1+E_2+\tilde{J}+K+\tfrac{1}{2}(U+K-D)\;, \tag{3.22}$$

where $U\equiv(U_1+U_2)/2$ and $D\equiv\{(U-K)^2$

$+16(V+\tilde{V})^2\}^{1/2}$. In the limit of large U the eigenenergy takes the form

$$E \approx E_1+E_2+\tilde{J}+K-\frac{4(V+\tilde{V})^2}{U-K} .$$

To compare this energy with our previous case we have to set $E_1=\epsilon_f$, $E_2=0$, $\tilde{J}=K=\tilde{V}=0$: we then obtain $E_- \approx \epsilon_f - 4V^2/U$, where $(-4V^2/U)$ is the binding energy. This energy exceeds by far the binding energy displayed in Fig. 3 and corresponds to the energy of a local hybrid singlet. It is this singlet binding energy which Zhang and Rice[2] regard as large; they therefore treat the whole pairing problem within the singlet subspace. Subsequently, they ascribe pairing to *d*-*d* coupling which is of fourth order in V/U. Our singlet is of a collective nature already at the level of one pair. Our pair state is also more stable because the reference energy for the itinerant state is much lower than that of molecular states because of the band energy $(-W/2)$ and hybridized nature of states. However, one must emphasize again that we consider here the motion of a single pair of electrons that is not hindered by the presence of other electrons.

IV. PAIR WAVE FUNCTION

Equations (3.11a), (3.11b), and (3.12) provide the coefficients (up to a normalizing factor) of the total wave function. We define the pair wave function in the position representation as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) \equiv \langle \mathbf{r}_1,\mathbf{r}_2|F\rangle = \Psi_{ac}(\mathbf{r}_1,\mathbf{r}_2)+\Psi_{cc}(\mathbf{r}_1,\mathbf{r}_2) + \Psi_{aa}(\mathbf{r}_1,\mathbf{r}_2) , \tag{4.1}$$

where for example

$$\begin{aligned}\Psi_{ac}(\mathbf{r}_1,\mathbf{r}_2) &\equiv \sum_{i,m} \alpha_{im} \langle \mathbf{r}_1|\langle \mathbf{r}_2| \frac{1}{\sqrt{2}}(a_{i\uparrow}^\dagger c_{m\downarrow}^\dagger - a_{i\downarrow}^\dagger c_{m\uparrow}^\dagger)0\rangle \\ &= \sum_{im} \alpha_{im} \frac{1}{\sqrt{2}}[\Phi_{a\uparrow}(\mathbf{r}_1-\mathbf{R}_i)\Phi_{c\downarrow}(\mathbf{r}_2-\mathbf{R}_m) \\ &\qquad - \Phi_{a\downarrow}(\mathbf{r}_2-\mathbf{R}_i)\Phi_{c\uparrow}(\mathbf{r}_1-\mathbf{R}_m)] ,\end{aligned} \tag{4.2}$$

and Φ_a and Φ_c are the single-particle (Wannier) functions representing the *a* and *c* states, respectively. In other words, the wave function for the bound pair has been expanded in the basis of noninteracting pair states; the interaction is contained in the coefficients α_{im}. For this reason one can separate the expression in $[\cdots]$ into space and spin parts. For the case of interest involving spin singlet bound state the space part is symmetric, i.e.,

$$\begin{aligned}[\cdots] = \frac{1}{\sqrt{2}}&[\Phi_a(\mathbf{r}_1-\mathbf{R}_i)\Phi_c(\mathbf{r}_2-\mathbf{R}_m) \\ &+\Phi_a(\mathbf{r}_2-\mathbf{R}_i)\Phi_c(\mathbf{r}_1-\mathbf{R}_m)] \\ &\times[\chi_\uparrow(1)\chi_\downarrow(2)-\chi_\downarrow(1)\chi_\uparrow(2)] .\end{aligned}$$

Therefore, the space part of the wave function can be determined by a Fourier transformation of $\alpha_\mathbf{k}$ back to real space, i.e.,

$$\Psi_{ac}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{N}} \sum_\mathbf{k} \alpha_\mathbf{k} \sum_{im} e^{-i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_m)}[\Phi_a(\mathbf{r}_1-\mathbf{R}_i)\Phi_c(\mathbf{r}_2-\mathbf{R}_m)+\Phi_a(\mathbf{r}_2-\mathbf{R}_i)\Phi_c(\mathbf{r}_1-\mathbf{R}_m)] . \tag{4.3}$$

Analogously, we obtain the *c*-*c* component as

$$\Psi_{cc}(\mathbf{r}_1,\mathbf{r}_2) = \left[\frac{2}{N}\right]^{1/2} \sum_\mathbf{k} \beta_\mathbf{k} \sum_{mn} e^{-i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_m)} \Phi_c(\mathbf{r}_1-\mathbf{R}_m)\Phi_c(\mathbf{r}_1-\mathbf{R}_n) . \tag{4.4}$$

The situation for the *a*-*a* component is different in that $\gamma_{ii} \equiv 0$. Hence, to avoid any inaccuracies we write

$$\Psi_{aa}(\mathbf{r}_1,\mathbf{r}_2) = \left[\frac{2}{N}\right]^{1/2} \sum_{ij} (\gamma_{ij}-\gamma_{ii}\delta_{ij})\Phi_a(\mathbf{r}_1-\mathbf{R}_i)\Phi_a(\mathbf{r}_2-\mathbf{R}_j) . \tag{4.5}$$

Next, we choose for $\Phi_a(\mathbf{r})$ the atomic 1*s*-like function

$$\Phi_a(\mathbf{r}) = \frac{1}{\sqrt{\pi a_B^3}} \exp\left[-\frac{|\mathbf{r}|}{a_B}\right] , \tag{4.6}$$

where a_B is the effective Bohr radius. Such a choice renders the wave functions $\{\Phi_a(\mathbf{r}-\mathbf{R}_i)\}$ nonorthogonal. However, since we assume that a_B is much smaller than the interatomic distance (taken as unit of length), the error introduced in this manner should not be substantial. Also, we choose $\phi_c(\mathbf{r})$ as a Wannier function for the plane-wave state. Hence, up to a normalizing constant

$$\Phi_c(\mathbf{r}-\mathbf{r}_i) = \delta(\mathbf{r}-\mathbf{R}_i) . \tag{4.7}$$

Substituting (4.6) and (4.7) for (4.3)–(5) we obtain the final expression for the components of the space wave function in the form

$$\Phi_{ac}(\mathbf{r}_1-\mathbf{r}_2)=\frac{1}{(\pi a_B^3)^{1/2}}\frac{1}{\sqrt{N}}\sum_i\left\{\exp\left[-\frac{|\mathbf{r}_1-\mathbf{R}_i|}{a_B}\right]\sum_{\mathbf{k}}\alpha_k\cos[\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{R}_i)]+\exp\left[-\frac{|\mathbf{r}_2-\mathbf{R}_i|}{a_B}\right]\sum_{\mathbf{k}}\alpha_k\cos[\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{R}_i)]\right\}, \tag{4.8a}$$

$$\Phi_{cc}(\mathbf{r}_1-\mathbf{r}_2)=\left[\frac{2}{N}\right]^{1/2}\sum_k\beta_{\mathbf{k}}\cos[\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)], \tag{4.8b}$$

and

$$\Phi_{aa}=\frac{1}{\pi a_B^3}\left[\frac{2}{N}\right]^{1/2}\sum_{ij}\exp\left[-\frac{|\mathbf{r}_1-\mathbf{R}_i|+|\mathbf{r}_2-\mathbf{R}_j|}{a_B}\right]\times\left\{\sum_{\mathbf{k}}(\gamma_{\mathbf{k}}\cos[\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)]-1)\right\}. \tag{4.8c}$$

To perform numerical analysis we have assumed that the system is two dimensional, with dispersion of energies in the bare band given by

$$\epsilon_{\mathbf{k}}=2|t|[\cos(k_xa)+\cos(k_ya)],$$

where $2t=1$ and $a=1$ has been assumed subsequently. In Figs. 3–6 we display the components of the wave function in the x direction, taking the coordinate $\mathbf{r}_1$ at origin. One sees clearly that all the components decay on the length scale of a few lattice constants. Additionally, the *a-a* component exhibits markedly different behavior. This occurs because the electrons repel strongly. Therefore the probability of finding the two electrons close to each other is small. In general, the value $\Phi_{aa}(0)$ is small but nonzero in our treatment, particularly when a_B is a sizable fraction of the lattice constant; this artifact arises in approximating the Wannier function Φ_{aa} by an atomic function. We did not attempt to include the overlap integrals to eliminate the unphysical feature that $\Phi_{aa}(0)$ is nonzero, since we believe that this would not change the main features of the spatial dependence of Φ_{aa}.

The rapid decay rate of the wave function is in sharp contrast with the large spatial extent $\sim 10^4$ Å of the wave function for the Cooper pair; in the latter case the extension is determined by the ratio of the Fermi energy to the binding energy. Here the Fermi energy is zero. However, the pair coherence length $\zeta\sim 3-5a$ obtained here in the dilute limit constitutes an upper bound for the corresponding quantity for the dense system of one hole per atom. This is so because in the limit of high concentration the pairs bind more strongly since the correlated electrons are heavy and mutually hinder their kinetic motion. In other words, the system is driven toward a liquid consisting of local singlets. The difference between the bound states considered here and the Cooper pair is also illustrated in Fig. 7, where we have plotted the pair binding energy as well as the best fit to the dependence $E\simeq a\exp(-bx)$, with $x=1/J$. One can see that even in this "best" case the binding energy can be represented only approximately by the standard expression for the Cooper pair binding. We therefore conclude that hybrid pairing containing the exchange interaction of the Kondo type leads (at least, in a dilute limit) to a new itinerant bound state which differs from the local Kondo singlet, or from the local singlet of Zhang and Rice[2] or from the standard Cooper pair. It remains to be seen whether the assembly of such pairs evolves into a condensed BCS type of state discussed earlier[7,8,10] within the mean-field-type approximation.

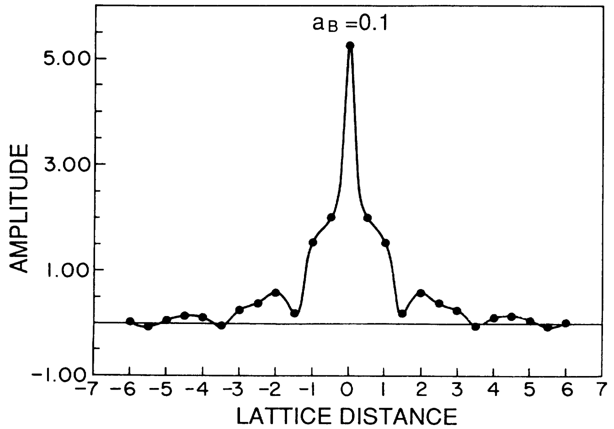

FIG. 4. The *a-c* component (Ψ_{ac}) component of the pair wave function as a function of relative distance along the x axis for the square lattice. The parameters are $U=8$, $\epsilon_f=-2$, and $V=-2$ (in units of $2t$).

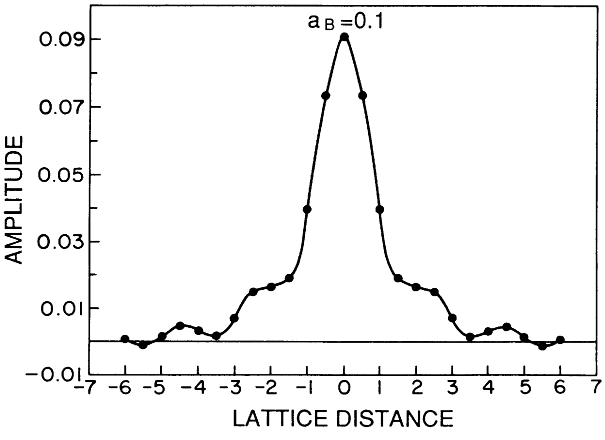

FIG. 5. Same as in Fig. 4 but for the *c-c* component (Ψ_{cc}).

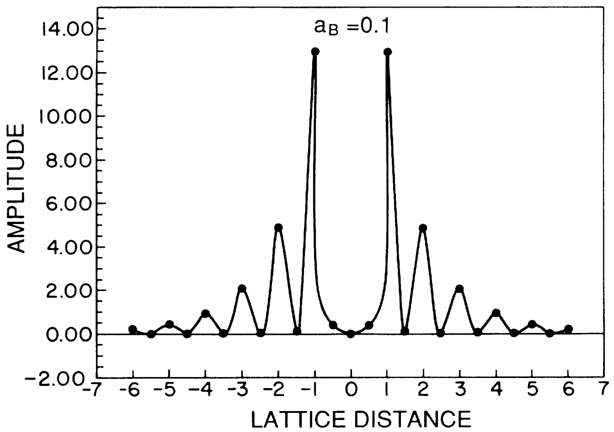

FIG. 6. Same as in Fig. 4 but for the *a*-*a* component (Ψ_{aa}).

V. A COMMENT: COMPARISON WITH A SINGLE-BAND CASE

Since the *t*-*J* model is often regarded as containing the principal physics of high-temperature superconductors,[2,3] it is interesting to compare our results with those for a single-band case. The starting Hamiltonian in that case is

$$H=\sum_{ij,\sigma} t_{ij} a^{\dagger}_{i\sigma}(1-N_{i-\sigma})a_{j\sigma}(1-N_{j-\sigma}) - \sum_{ijk} \frac{2t_{ij}t_{jk}}{U} D^{\dagger}_{ij} D_{kj} \ . \tag{5.1}$$

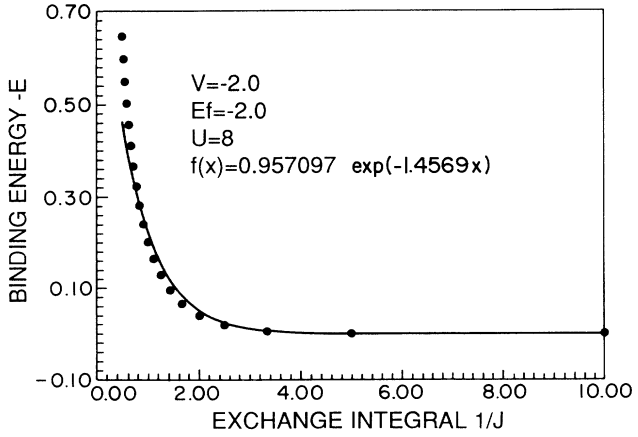

FIG. 7. Comparison of the results for the pair binding energy as a function of the Kondo coupling constant (points) with the analytic form [$f(x)$, solid line] for the Cooper pair (Ref. 14). Note that $x=1/J$.

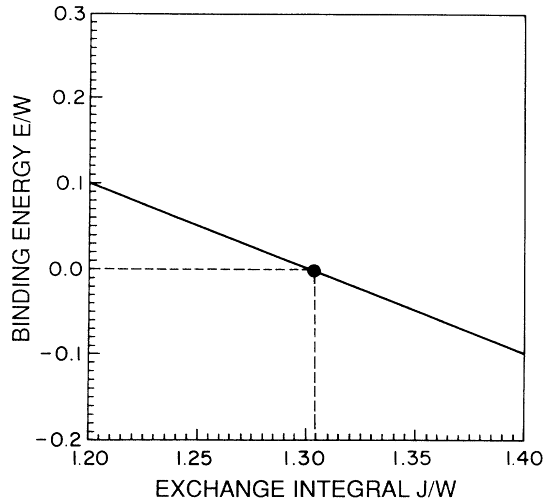

FIG. 8. The binding energy of a single spin singlet pair in the case of a two-dimensional narrow band.

For simplicity we consider only the $k=i$ terms. One can solve the single-pair problem by considering only the $|\chi\rangle$ component (3.3c). In the two-dimensional square-lattice case, this leads to the following implicit equation for the eigenvalues $\epsilon_{\mathbf{k}}$:

$$1/2J=\frac{1}{N}\sum_{\mathbf{k}} \frac{(\cos k_x \pm \cos k_y)^2}{2\epsilon_{\mathbf{k}}-\lambda} \ , \tag{5.2}$$

where $J=2t^2/U$ and t is the hopping integral involving nearest neighbors. The pair binding energy $\Delta=\lambda-2zt$, where z is the number of nearest neighbors, is plotted in Fig. 8. A bound state occurs if the negative sign is taken in Eq. (5.2). We see that the binding state appears only for $J \gtrsim 1.31W$, i.e., in the unphysical limit of the *t*-*J* model in which $J \ll |t|$. Additionally, there is no bound state for a single pair in three dimensions. Obviously, this does not preclude a stable bound state for an almost half-filled band case (e.g., with two holes), the limit which is studied extensively.[16] Also, in one dimension case the effective Hamiltonian (5.1) always lead to a bound state with energy $\lambda=-\sqrt{(2zt)^2+(4J)^2}$. Therefore, the existence of single-pair bound states in the *t*-*J* model is limited to low-dimensional lattices ($D=1$ and 2).

VI. CONCLUSIONS

We have studied bound states for a single electron pair that are induced by exchange interaction between the particles. While the practical importance of these results is limited, they may serve as a check on accuracy of approximate solutions adopted for studies of the many-particle case. The contact Kondo interaction induces an itinerant bound state in the mixed-valence situation, i.e., when part of the hybridization is retained in the effective Hamiltonian. It will be interesting to compare these results with corresponding ones for two holes on an otherwise singly occupied level situation.

Finally, the inclusion of superexchange interactions in our model (fourth-order effect in V/U) would be desirable to determine the relative importance of *d*-*d* vs *p*-*d* exchange interaction in high-T_c systems. Work along these lines is in progress.

Note added in proof. We recently calculated a relative contribution of different components to the total wave function $|F\rangle$. For that purpose we have determined the area under each of the components (cf., Figs. 4–6) squared. Next, we divided each of the areas by their sum $S \equiv S_{aa}+S_{ac}+S_{cc}$. The numbers that provide the relative probabilities are $S_{aa}/S=0.85$, $S_{ac}/S\simeq 0.15$, and $S_{cc}/S\simeq 0.007$. The pairing is mainly of the a-a character. This surprising result speaks in favor of an effective f-f pairing, even without inclusion of the superexchange [fourth-order processes in $V/(U+\epsilon_f)$ in the Hamiltonian (2.1)].

ACKNOWLEDGMENTS

The authors acknowledge the support of the Committee of Scientific Research (KBN) of Poland, Grant No. 2 0429 91 01. One of the authors (J.S.) acknowledges also support by MISCON Grant No. DE-FG02-90ER45427. We are also grateful to Dr. Tomasz Gawron for assistance in numerical calculations of the wave function. The authors are also grateful to J. M. Honig for a critical reading of the manuscript. Part of this work was done in the Department of Physics, Purdue University, West Lafayette, IN 47907.

---

[1] K. A. Chao, J. Spalek, and A. M. Oles, J. Phys. C **10**, L271 (1977); J. Spalek, Phys. Rev. B **37**, 533 (1988).

[2] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

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

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

[5] V. J. Emery and G. Reiter, Phys. Rev. B **38**, 11 938 (1988); **41**, 7247 (1990).

[6] For review, see P. A. Lee, T. M. Rice, J. W. Serene, and J. W. Wilkins, Comments Condens. Matter Phys. **12**, 99 (1986).

[7] J. Spalek, Phys. Rev. B **38**, 208 (1988).

[8] J. Spalek and P. Gopalan, J. Phys. (Paris) **50**, 3269 (1989).

[9] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

[10] D. M. Newns, M. Rasolt, and P. C. Pattnaik, Phys. Rev. B **38**, 6513 (1988).

[11] J. Karbowski and J. Spalek (unpublished).

[12] Z. Zou and P. W. Anderson, Phys. Rev. B **37**, 627 (1988).

[13] J. Spalek, A. M. Oles, and K. A. Chao, Phys. Status Solidi B **108**, 329 (1981).

[14] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

[15] J. Spalek and P. Gopalan, Physica B **163**, 151 (1990).

[16] Cf., e.g., R. Eder, Phys. Rev. B **45**, 319 (1992), and references therein.