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LETTERS TO THE EDITOR

The Resonating Hybrid Bonds and Superconducting Pairing in Metallic Oxides and Heavy-Fermion Systems

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We extend P. W. Anderson's idea of *real-space pairing* to correlated and hybridized systems. The pairing is provided by the antiferromagnetic exchange interaction between the electrons which form *resonating hybrid bonds*. In the solid state an ensemble of such pairs may condense into either *superconducting* or *Kondo-lattice states*.

The idea of *resonating valence bond* (RVB) has been used (*1*) to describe a bonding when bonds in a given system may be distributed in several equivalent configurations (e.g., the conjugated bonds in benzene). The total wave function is then a superposition (with the same weight) of all possible singlet–spin pair electron states (*2*). One may ask: What type of many-body state will be realized in a periodic solid starting from sets of paired electrons in the resonating valence bonds?

In principle, four states are possible: (i) the magnetic insulator with frustrated spins (*2*); (ii) the antiferromagnetic (Mott) insulator (*3*); (iii) the narrow-band metal with single–spin correlations which lead to either antiferromagnetism or superconductivity (*4*); and (iv) the dimerized (spin-Peierls) insulator (*5*). Anderson (*2, 4*) was the first to recognize the role of antiferromagnetic exchange interaction as the origin of both state (i) and of superconductivity. Both states can be formally treated in the occupation–number representation by introducing real-space pairing operators

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

and subsequently expressing the antiferromagnetic kinetic exchange interaction (*3*) between the electrons located on neighboring atomic sites $\langle ij \rangle$:

$$H_{\mathrm{ex}} = \sum_{\langle ij \rangle} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} N_i N_j) \qquad (2)$$

in the terms of these operators; i.e.,

$$H_{\mathrm{ex}} = \sum_{\langle ij \rangle} J_{ij} b_{ij}^{\dagger} b_{ij}^{\dagger}. \qquad (3)$$

In these equations $a_{i\sigma}^{\dagger}$ is the creation operator for an electron in the single-particle state $\Phi(\mathbf{r} - \mathbf{R}_i)$ centered on an atom positioned at $\mathbf{R}_i$ and with spin $\sigma = \pm 1$, $N_i = N_{i\uparrow} + N_{i\downarrow}$ is the particle-number operator for this state, $\mathbf{S}_i$ is the spin operator for the electron located on this site, and $J_{ij} \equiv 2t_{ij}^2/U$

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is the exchange integral (cf. Ref. (*3*) for details).

The representation (*3*) of Eq. (2) is convenient in the case of a partially filled-band case. Then the total Hamiltonian is composed of a band and an exchange part.[1] We have shown previously (*7*) that Eq. (3) also contains a pair-hopping term $\sim b_{ij}^{\dagger} b_{jk}$, responsible for pair motion (i.e., *resonant behavior of the bonds*). The occupation-number representation is particularly well suited for dealing with moving bonds.

In this note we generalize this formalism to the situation with *hybrid* bonds as in high-T_c superconductors, where $2p_x$ and $2p_y$ oxygen orbitals hybridize with $3d_{x^2-y^2}$ states of copper (*8*). We discuss only the main points of our approach which will be discussed in detail elsewhere (*9*).

The periodic Anderson Hamiltonian in the real-space (tight-binding) representation is

$$H = \sum_{mn\sigma} t_{mn} c_{m\sigma}^{\dagger} c_{n\sigma} + \varepsilon_f \sum_{i\sigma} N_{i\sigma} + U \sum_{i\sigma} N_{i\uparrow} N_{i\downarrow} + \sum_{im\sigma} V_{im} (a_{i\sigma}^{\dagger} c_{m\sigma} + c_{m\sigma}^{\dagger} a_{i\sigma}), \tag{4}$$

where indices (i, j) label atomic $(d_{x^2-y^2})$ states of Cu^{2+}, (m, n)-delocalized $(2p_\sigma)$ states of O^{2-}; $N_{i\sigma} \equiv a_{i\sigma}^{\dagger} a_{i\sigma}$ and $n_{m\sigma} \equiv c_{m\sigma}^{\dagger} c_{m\sigma}$ are the particle-number operators for these states with spin σ. The first two terms in Eq. (4) describe band and atomic energies for electrons in the $2p$ and $3d$ states, $\varepsilon_f \equiv \varepsilon_d - \varepsilon_p$ is the relative position of the d level with respect to O^{2-} atomic level. The third term represents an increase of the Coulomb energy either in the 2-particle Cu^{1+} configuration, or in the 2-hole Cu^{3+} configuration. The last term describes hybridization of the $3d$ and $2p$ states.

In most $3d$ magnetic oxides parameter U in Eq. (4) is far larger than any of the remaining energies. Hence, two physically distinct situations are possible: First, when $|\varepsilon_f| \lesssim |V_{\langle im \rangle}|$ ($\langle im \rangle$ labels pairs of nearest-neighbor sites); second, when $|\varepsilon_f| \gg |V_{\langle im \rangle}|$. Both cases are shown schematically in Fig. 1. For partially filled *Hubbard subbands*, both lower (Figs. 1a and 1c) and upper (Figs. 1b and 1d) are explicitly drawn in each case. One can show that the situations

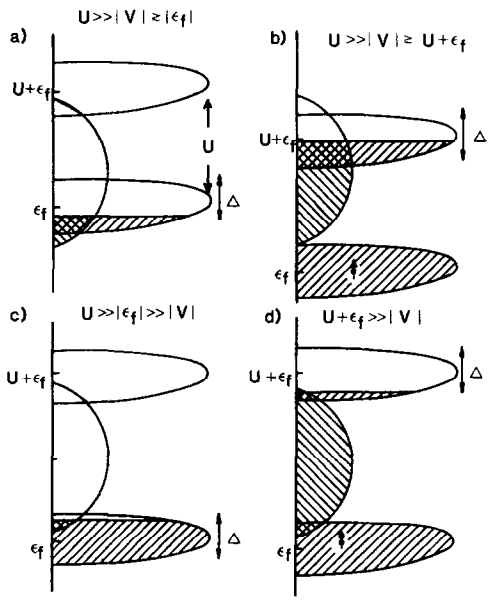

FIG. 1. Schematic representation of the electronic structure of hybridized systems composed of localized and itinerant electrons. The two narrow bands separated by energy U represent Hubbard subbands for bare atomic states, each accommodating up to N electrons. The wide band is the conduction band and can accommodate up to 2N electrons. (a and c) The situation with lower Hubbard subband filled; (b and d) those with the upper subband partially filled. The width Δ of the subbands is due to hybridization with the itinerant states.

[1] Such effective Hamiltonian is obtained beginning from the Hubbard model (cf. (*6*)).

shown in Figs. 1b and 1d are related to those of Figs. 1a and 1c by electron-hole transformation. Hence, it is sufficient to consider only the situations shown in Figs. 1a and 1c.

When $U \gg |V_{im}| \gtrsim |\varepsilon_f|$. We decompose the hybridization part according to

$$a_{i\sigma}^{\dagger}c_{m\sigma} + c_{m\sigma}^{\dagger}a_{i\sigma} \equiv (1 - N_{i-\sigma})(a_{i\sigma}^{\dagger}c_{m\sigma} + c_{m\sigma}^{\dagger}a_{i\sigma}) + N_{i-\sigma}(a_{i\sigma}^{\dagger}c_{m\sigma} + c_{m\sigma}^{\dagger}a_{i\sigma}). \quad (5)$$

The second part involves charge transfer processes with doubly occupied d level, i.e., the processes with energy $U + \varepsilon_f$ in highly excited states. Hence, we transform out canonically[2] this part and replace it by an effective interaction incorporating higher order virtual processes. The effective Hamiltonian in second order contains many terms discussed in detail elsewhere (*11*). Using the following pairing operators

$$\tilde{b}_{im}^{\dagger} = \frac{1}{\sqrt{2}}(a_{i\uparrow}^{\dagger}(1 - N_{i\uparrow})c_{m\downarrow}^{\dagger} - a_{i\downarrow}^{\dagger}(1 - N_{i\uparrow})c_{m\uparrow}^{\dagger}), \quad (6)$$

the effective Hamiltonian in the second order has the form

$$\tilde{H} = \sum_{mn\sigma} t_{mn}c_{m\sigma}^{\dagger}c_{n\sigma} + \varepsilon_f \sum_{i\sigma} N_{i\sigma}(1 - N_{i-\sigma}) + \sum_{im\sigma} V_{im}[(1 - n_{i-\sigma})a_{i\sigma}^{\dagger}c_{m\sigma} + \text{h.c.}] - \sum_{imn} \frac{2V_{mi}V_{in}}{U + \varepsilon_f} \tilde{b}_{im}^{\dagger}\tilde{b}_{in}. \quad (7)$$

The factor $(1 - N_{i-\sigma})$ in both Eqs. (6) and (7) eliminates the possibility of doubly occupied d states (the Cu^{1+} configurations in the situation depicted in Fig. 1a). The pairing part (i.e., the last term) involves both two-site (for $m = n$) and three-site (for $m \neq n$) terms. The former enumerate pairs $\langle im \rangle$ bound into hybrid bonds, whereas the latter represent the hybrid-pair hopping, i.e., *the resonant behavior* of these bonds. The itinerant character of d electrons is reflected in the third term in Eq. (7).

The effective Hamiltonian (7) contains both single-particle and singlet–pair dynamics, coupled each to other. In the limit $U + \varepsilon_f \to \infty$ the pairing part vanishes and $\tilde{H}$ represents a model discussed in the context of fluctuating-valence and heavy-fermion systems (*11*). In the complementary limit $\varepsilon_f \to -\infty$ the residual hybridization becomes ineffective in promoting electrons to the conduction band. Therefore, for $|\varepsilon_f| \to \infty$ Eq. (7) reduces to

$$\tilde{H} = \sum_{mn\sigma} t_{mn}c_{m\sigma}^{\dagger}c_{n\sigma} - \sum_{imn} \frac{2V_{im}V_{in}}{U + \varepsilon_f} \tilde{b}_{im}^{\dagger}\tilde{b}_{in}, \quad (8)$$

where now (for $m = n$)

$$\tilde{b}_{im}^{\dagger}\tilde{b}_{in} = -(\mathbf{S}_i \cdot \mathbf{s}_m - \tfrac{1}{4}N_i n_m), \quad (8a)$$

and for $n \neq m$

$$\tilde{b}_{im}^{\dagger}\tilde{b}_{in} = -\sum_{\sigma}[S_i^{\sigma}c_{m-\sigma}^{\dagger}c_{n\sigma} - N_{i-\sigma}c_{m\sigma}^{\dagger}c_{n\sigma}], \quad (8b)$$

where $\mathbf{S}_i$ and $\mathbf{s}_m$ are the spin operators for localized and itinerant electrons, respectively. Hence, in the localized-moment limit Eq. (7) contains both the Kondo type of coupling and the scattering of conduction electrons on the localized moments. One may claim that the Hamiltonian (8) represents the collective properties of a lattice with *resonating Kondo singlets*. The processes expressed by Eqs. (8a) and (8b) represent in essence the *Kondo-lattice behavior*. The effective Hamiltonian in the opposite limit when $|\varepsilon_f| \gg |V_{im}|$ reads

[2] The canonical transformation we utilize is a generalization of that proposed by us a decade ago for the magnetic impurity situation (cf. (*10*)).

$$\tilde{H} = \sum_{mn\sigma}{}' t_{mn} c^{\dagger}_{m\sigma} c_{n\sigma} + \varepsilon_f \sum_{i\sigma} \tilde{a}^{\dagger}_{i\sigma} \tilde{a}_{i\sigma} + \sum_{ijm\sigma} (V_{mi} V_{mj}/\varepsilon_f) \tilde{a}^{\dagger}_{i\sigma} \tilde{a}_{j\sigma} (1 - n_{m\sigma}) + \sum_{imn} \frac{2V_{mi} V_{in} U}{\varepsilon_f (U + \varepsilon_f)} \tilde{b}^{\dagger}_{im} \tilde{b}_{in}, \tag{9}$$

where $\tilde{a}^{\dagger}_{i\sigma} \equiv a^{\dagger}_{i\sigma}(1 - N_{i-\sigma})$, and $_{i\sigma} \equiv \tilde{a}_{i\sigma}(1 - N_{i-\sigma})$ are projected fermion operators onto the subspace with singly occupied atomic sites. The factor $(1 - n_{m\sigma})$ in the third term may be approximated by its expectation value $(1 - n_p/2)$, where n_p is the average number of p electrons per site. Equation (9) then represents a two-band system with an interband pairing. Equivalently, this Hamiltonian represents the dynamics of two sets of band electrons, one uncorrelated and one strongly correlated, with resonating bonds effecting their mutual coupling.

The principal advantage of using the operators $\tilde{b}^{\dagger}_{im}$ instead of limiting to the single-particle operators $\tilde{a}^{\dagger}_{i\sigma}$ and $c^{\dagger}_{m\sigma}$ only is the possibility of incorporating the bonding effects as the origin of superconducting pairing or magnetic ordering in both heavy-fermion systems and high-T_c superconductors. It is well known (*13*) that the nonzero average $\Delta_{\mathbf{k}} \equiv \langle c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} \rangle$ characterizes formally the superconducting state. For the effective Hamiltonians (7) and (9) (representing the situations depicted in Figs. 1a and 1c, respectively) this can be achieved by simply decoupling the pairing part in the Hartree–Fock approximation, as discussed in detail elsewhere (*9, 11*). This approximation leads to a BCS-type of Hamiltonian with $\Delta_k \equiv \langle c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} \rangle$ and an anisotropic pairing. The superconducting state represents a condensed super-fluid state of a collection of resonating hybrid bonds. In the localized-moment limit (i.e., when the d electrons are immobile) the condensed state is transformed into either normal metallic or insulating state with resonating Kondo singlets.

Summarizing, the *real-space pairing* concept of Anderson (*2*) has been extended to hybridized systems represented by the model Hamiltonian (*4*). The pairing is provided by the antiferromagnetic exchange interaction between the atomic (correlated) and conduction (uncorrelated) states that formally describes singlet hybrid bonding as well as the resonant behavior of these bonds. The infinite system of bonds may condense into either a superconducting or Kondo-lattice type of collective state. This approach connects the behavior on the molecular scale and the onset of collective behavior of the systems such as heavy-fermion and high-temperature superconductors (for a review on this subject, see Ref. (*12*)).

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