



The Resonating Valence Bond State in La_2CuO_4 and Superconductivity

P. W. Anderson

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nating the kinetics of water release and mobility helping to reduce the energetic costs of correlated, local, side-chain movements (1). In effect, the proposed mechanisms of antigen-antibody union show striking similarities to the induced fit mechanisms often implied in enzyme-substrate (15, 20) and DNA-protein interactions (24).

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- Affinity measurements were performed by overnight incubation of serially diluted ^{125}I -MHR with antibodies to MHR (anti-MHR) purified over Sepharose-peptide columns. Purified MHR (100 μg) was labeled with ^{125}I by the chloramine T method and dialyzed overnight to remove unbound ^{125}I . The specific activity of the labeled MHR was calculated to be 14.2 Ci/mmol, on the basis of precipitation by 10 percent trichloroacetic acid. The MHR antisera were affinity-purified over peptides conjugated to Sepharose beads by cyanogen bromide. Purified antibodies were eluted by an abrupt change of pH (diethylamine, pH 11.0), neutralized immediately, and concentrated by dialysis against polyethylene glycol. After overnight incubation of serially diluted ^{125}I -labeled MHR with purified anti-MHR, the antigen-antibody complexes were precipitated with 40 μl of *Staphylococcus aureus*, washed once with phosphate-buffered saline (10 mM sodium phosphate, 0.15M NaCl, pH 7.2) and twice with 500 mM LiCl and 100 mM tris, pH 8.0, and the radioactivity was counted. Dilutions of MHR ranged from 3×10^{-7} to $3 \times 10^{-9}\text{M}$. Each concentration point was done in triplicate and the background values for the "preimmune" serum were subtracted for each point. Affinity constants were derived by Scatchard analysis, with the ratio of the bound to the unbound plotted as a function of the bound, and were expressed as dissociation constants [J. A. Berzofsky and I. J. Berkower, in *Fundamental Immunology*, W. E. Paul, Ed. (Raven, New York, 1984), p. 600].
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The Resonating Valence Bond State in La_2CuO_4 and Superconductivity

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The oxide superconductors, particularly those recently discovered that are based on La_2CuO_4 , have a set of peculiarities that suggest a common, unique mechanism: they tend in every case to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. This insulating phase is proposed to be the long-sought "resonating-valence-bond" state or "quantum spin liquid" hypothesized in 1973. This insulating magnetic phase is favored by low spin, low dimensionality, and magnetic frustration. The preexisting magnetic singlet pairs of the insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly. The mechanism for superconductivity is hence predominantly electronic and magnetic, although weak phonon interactions may favor the state. Many unusual properties are predicted, especially of the insulating state.

RECENTLY HIGH-TEMPERATURE superconductivity has been observed in a number of doped lanthanum copper oxides near a metal-insulator transition (1), a pattern exhibited previously by $(\text{Ba,Pb})\text{BiO}_3$ (2). The crystal structure suggests that the Cu^{2+} is in an $S = 1/2$, orbital nondegenerate state, strongly hybridized with the surrounding oxygen p -levels, and this is in agreement with high-temperature magnetic data (3) on the stoichiometric, insulating compound La_2CuO_4 .

The appropriate model seems to be the basic nearly half-filled Hubbard model (4) with moderately large repulsion energy U and antiferromagnetic exchange constant $J = t^2/U$ where t is the site-hopping matrix element. The K_2NiF_4 structure is a well-known case in which the magnetic layers are relatively weakly interacting, and in the temperature range 30 to 70 K we can assume magnetic two-dimensionality. This led me

to reexamine the idea of the "resonating valence-bond" (RVB) state (5).

Early doubts about the nature of the ground state of the antiferromagnetic Heisenberg Hamiltonian

$$H = J \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j \quad (1)$$

of Hulthén (6) and Marshall (7) (where \vec{s}_i is the spin at site i and $\langle ij \rangle$ indicates summation over nearest neighbors i and j) seemed to have been laid to rest by arguments from quantum fluctuations of spin waves in the Néel state (8) in >1 dimension, and by experimental observations of antiferromagnetism. In 1973, however, Anderson (5) proposed that, at least in the triangular two-dimensional antiferromagnet for $S = 1/2$, and perhaps in other cases, the ground state might be the analog of the precise singlet in the Bethe solution of the linear antiferromagnetic chain (6). In both cases, the zeroth order energy of a state consisting purely of nearest neighbor singlet pairs is more nearly realistic than that of the Néel state, and I

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proposed that higher order corrections, allowing the singlet pairs to move or “resonate” à la Pauling, might make this insulating singlet or RVB state more stable. This state is quite clearly distinct from two other locally stable possibilities, the Néel state and the “spin-Peierls” state of a self-trapped, localized array of singlet pairs. Each of these other states has a broken symmetry relative to the high-temperature paramagnetic state, and would exhibit a phase transition with temperature. Fazekas and Anderson (9) improved on my numerical stability estimates, and Hirakawa *et al.* (10) have proposed application of the RVB state to specific compounds.

The triangular lattice is not the only possible candidate: the two-dimensional square lattice, for instance, will undoubtedly exhibit an RVB state if either or both of two possibilities occurs: a next nearest neighbor antiferromagnetic interaction strong enough to frustrate the Néel state, or virtual phonon interactions short of being strong enough to allow a spin-Peierls instability. [Hirsch (11) has shown numerically that the simple square lattice probably retains a magnetization but that finite U may favor the RVB state.] It is our hypothesis that pure La_2CuO_4 is in an RVB state; this proposal is supported to some extent by the magnetic susceptibility data of Ganguly and Rao (3).

It is not easy to calculate with RVB states or to represent them. I want to give here a representation in terms of Gutzwiller-type projections of mobile-electron states, which is probably not particularly useful computationally but is suggestive. This representation was in turn suggested by Rice and Joynt’s remarks (12) on the Gutzwiller approximation to the Bethe solution.

A single pair of electrons in a mobile valence bond along a lattice vector τ may be written

$$b_{\tau}^{+} \Psi_0 = \frac{1}{\sqrt{N}} \left(\sum_j c_j^{\dagger \uparrow} c_{j+\tau \downarrow} \right) \Psi_0 = \frac{1}{\sqrt{N}} \left(\sum_k c_k^{\dagger \uparrow} c_{-k \downarrow} \exp i(k \cdot \tau) \right) \Psi_0 \quad (2)$$

where b_{τ}^{+} is the electron-pair creation operator, c_j^{\dagger} is the single-electron creation operator, and N is the total number of sites. A linear combination of all nearest neighbor bonds may be written

$$b_{nn}^{+} = \sum_{\tau=(nn)} b_{\tau}^{+}$$

where nn indicates summation over nearest neighbors, or in general, if we want a distribution of bond lengths, the linear combination may be written as

$$b^{+} = \sum_k a(k) c_{k \uparrow}^{\dagger} c_{-k \downarrow}^{\dagger} \quad (3)$$

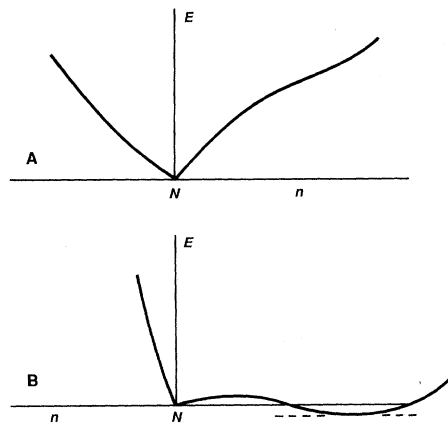


Fig. 1. Total energy E as a function of average occupation number n . (A) Insulating case. (B) Metallic case. N is the total number of lattice sites.

with the condition on the expansion coefficients

$$\sum_k a(k) = 0 \quad (4)$$

if we do not allow double occupancy.

Unfortunately, if we now try to make a Bose condensation of N electrons in mobile valence bond states by forming

$$\Psi = (b^{+})^{N/2} \Psi_0 \quad (5)$$

this state contains large numbers of empty and doubly occupied sites. To make up a genuine RVB state we may try one of two roughly equivalent projection techniques. The simplest is the straightforward Gutzwiller method: form the projection operator

$$P_d = \prod_i (1 - n_{i \uparrow} n_{i \downarrow}) \quad (6)$$

where n_i is the occupation number, and

$$\Psi_{\text{RVB}} = P_d (b^{+})^{N/2} \Psi_0 \quad (7)$$

is our trial wave function.

We may also use quasifermion operators with the double occupancy projected out (13), for example,

$$\xi_{i \uparrow} = c_{i \uparrow}^{\dagger} (1 - n_{i \downarrow})$$

and write

$$b^{+} = \sum_k a(k) \xi_{k \uparrow}^{\dagger} \xi_{-k \downarrow}^{\dagger} \quad (8)$$

in Eq. 5.

At this point we resort to the Dyson transformation between product states and Bardeen-Cooper-Schrieffer (BCS) states. As shown by Dyson (14), if we note that $(b_k^{+})^2 = 0$ (with $b_k^{+} = c_{k \uparrow}^{\dagger} c_{-k \downarrow}^{\dagger}$),

$$1 + a_k b_k^{+} = \exp(a_k b_k^{+})$$

hence

$$\begin{aligned} \Psi_{\text{BCS}} &= \prod_k (\sqrt{1 - b_k} + \sqrt{b_k} b_k^{+}) \Psi_0 \\ &\propto \exp \left[\sum_k \sqrt{\frac{b_k}{1 - b_k}} b_k^{+} \right] \Psi_0 \end{aligned} \quad (9)$$

where b_k is the variational parameter in the standard BCS treatment.

If we project Ψ_{BCS} on the state with just $N/2$ pairs, we obtain

$$P_{N/2} \Psi_{\text{BCS}} = \left[\sum_k \left[\frac{\sqrt{b_k}}{\sqrt{1 - b_k}} \right] b_k^{+} \right]^{N/2} \Psi_0 \quad (10)$$

or, in other words, Eq. 5 is just a projected BCS function. These transformations are not singular as they are for conventional BCS. Thus our approximate Ψ_{RVB} is also related to the appropriate projection of a BCS function:

$$\begin{aligned} \Psi_{\text{RVB}} &= P_{N/2} P_d \prod_k \left[\frac{1}{\sqrt{1 + a_k^2}} \right. \\ &\quad \left. + \frac{a_k}{\sqrt{1 + a_k^2}} c_{k \uparrow}^{\dagger} c_{-k \downarrow}^{\dagger} \right] \Psi_0 \end{aligned} \quad (11)$$

$$\begin{aligned} \text{or} \quad &= P_{N/2} \prod_k \left[\frac{1}{\sqrt{1 + a_k^2}} \right. \\ &\quad \left. + \frac{a_k}{\sqrt{1 + a_k^2}} \xi_{k \uparrow}^{\dagger} \xi_{-k \downarrow}^{\dagger} \right] \Psi_0 \end{aligned}$$

In the insulating state every site i is filled once so that $|a_k|$ might as well be constant, $a_k = \pm 1$, and the wave function contains a “pseudo-Fermi surface” at which a_k changes sign. There is no reason why this surface should coincide with the Fermi surface of any energy in the system, since the pseudo-Fermi surface is controlled by the condition that it divide k -space into equal halves and by the choice of τ values for the valence bonds. The existence of a pseudo-Fermi surface, I believe, is real and the spin excitations may resemble those of a real Fermi liquid. This would explain the experimental observation of a Fermi-like susceptibility.

On the other hand, considered as a solution to the Hubbard model, there is a gap for any charged excitation. By assumption, U is so large that adding the $(N + 1)$ th electron costs an extra $\sim U$ in energy, relative to adding the N th, and the Fermi energy lies in this gap for the stoichiometric compound. There is a cusp in total energy as a function of occupation number at $n = N$ (Fig. 1A). In this case the $P_{N/2}$ projection operator may not be omitted. One may represent $P_{N/2}$ explicitly by giving a_k a phase $e^{i\theta}$ and writing

$$\begin{aligned} \Psi_{\text{RVB}} &= P_d \int d\theta e^{-iN/2\theta} \\ &\quad \times \prod_k \left[\frac{1}{\sqrt{1 + a_k^2}} + \frac{e^{i\theta} a_k b_k^{+}}{\sqrt{1 + a_k^2}} \right] \Psi_0 \end{aligned}$$

Thus in this insulating state there is no meaning to the phase of a_k ; a wave function with fixed phase contains states of necessarily widely different energy.

Now let us consider the state obtained if we dope the system in order to remove the

"half-filled" criterion and make it into a metal. From a "mean field" point of view, as soon as the system is metallized it becomes a superconductor, since the pairing already exists in the RVB state, and an energy $\sim J$ is required to break a valence-bonded pair. As shown in Fig. 1B, as soon as the occupancy leaves N , there is no cusp in the energy, the compressibility becomes finite, and by the standard arguments the state can acquire a fixed θ rather than n .

As a practical matter, the effective mass of quasiparticles will be of order $m^* = m/\delta$, where δ is the fractional doping $n = N(1 - \delta)$. Correspondingly, the coherence length ξ_0 will be of order

$$k_F \xi_0 = \frac{E_F}{\Delta} \ll 1$$

where k_F and E_F are the Fermi wave vector and energy, respectively, Δ is the energy gap, and the kinetic energy is of order $t\delta$. Thus the transition temperature T_c will at first be dominated by phase fluctuations. (In actual physical fact, at first the dopant ions will be screened out by bound quasiparticles, and it will take a finite dopant concentration to metallize the sample.) The maximum T_c , of order or less than $t^2/U = J$, will occur when $t/U \sim \delta$ and kinetic and pair-binding energies match. Pressure will increase t and, within limits, increase T_c as well.

From a theoretical point of view, the most exotic feature of these experimental results (1) is that they confirm the existence of a new liquid, only conjectured previously (3, 5, 10). This liquid is insulating only by virtue of a "commensurability gap," and therefore resembles the Laughlin state in the fractional quantum Hall effect (15). Both of these states may be described as "Mott liquids" since the basic physics is that of the "Mott transition" (16), and their key feature is that there is no symmetry breaking vis-à-vis the high-temperature state.

There are several experimental consequences of the above. The key point is the observation of the RVB state in the stoichiometric La_2CuO_4 , which should be easy with neutrons, especially if there is a pseudo-Fermi surface. Second, the pseudo-Fermi surface may or may not cross the real Fermi surface, defining lines of zeroes of the gap function. The occurrence of lines of zeroes and of antiferromagnetic correlations in some heavy fermion superconductors suggests a family resemblance to the RVB state, although the parameter values are totally different.

Finally, I would call attention to the numerous unreproducible reports of high-temperature superconductivity in special samples of CuCl . In every case it is reason-

able to imagine a surface layer of Cu^{2+} with or without the appropriate degree of oxidation; such reports should sharpen the search for still more RVB superconductors. It is also noteworthy that the first oxide superconductor, Li_2TiO_4 (17), closely resembles NaTiO_2 , the only other likely RVB material.

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The Onshore Transport of an Oil Spill by Internal Waves

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Internal waves generated by tidal currents concentrated and transported an oil spill (liquid asphalt) onshore. Plankton net samples were collected in front of and behind a set of internal waves as well as in the convergence and divergence zones over the waves. Tar "balls" were most abundant (greater than 30-fold) in the samples from the convergence zone. Comparison of the abundance of tar balls in front of and behind the set of waves suggests that the internal waves "caught" about 68% of the asphalt encountered and concentrated and swept shoreward tar balls from almost 8 kilometers of ocean.

TIDAL CURRENTS FLOWING OFF THE continental shelf or across reefs or banks produce large internal waves (1, 2). Those waves formed at the shelf break propagate onshore (3). Surface currents over the waves produce alternating zones of convergence and divergence. Flotsam swept into the convergence, if buoyant enough, will be trapped there and carried onshore. Some types of larval invertebrates and fish migrate onshore by this mechanism (4, 5). Most oils float on water and potentially could be carried onshore by internal waves. This study shows that floating oil (spilled asphalt) was swept up by currents over a set of internal waves, concentrated in the convergence zones over the waves, and transported onshore. To my knowledge, this is the first time that onshore transport of an oil spill by internal waves has been observed

and recognized, although it might be expected from the known properties of internal waves (6).

On 21 June 1985 a large (about 1.5×10^6 liters) tank of liquid asphalt burst at the Morehead City port in North Carolina ($75^\circ 5'N$, $35^\circ 4'W$) (Fig. 1). Some of this asphalt spilled into the Beaufort Inlet and was carried out to sea by the tide.

Three days later surface plankton samples (from the top 26 cm of the water column) were collected with a Manta net (7) (26 by 96 cm, mouth opening; 0.333 mm, net mesh) from the waters around a set of internal waves (8). The set of internal waves was about 4 km offshore (Fig. 1). Replicate ($n = 3$) 5-minute tows ($>50 \text{ m}^3$ of water filtered) were made in front of and behind

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¹ **Superconductivity at 52.5 K in the Lanthanum-Barium-Copper-Oxide System**

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