

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

(Received December 5, 1972; Invited**)

ABSTRACT

The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for $S = 1/2$. An estimate of its energy is made in one case.

Many years ago Pauling gave a "resonating valence bond" theory of metals (1) which virtually ignored the electron gas nature of the metallic state and instead tried to relate the binding energies semiquantitatively to known valence bond concepts. Only recently has the conventional Fermi gas theory begun to address itself more analytically to the same problems. But Pauling's attempt leaves behind a very interesting problem of principle: is a state in which valence bonds move around freely between pairs of atoms a metal in fact? Does it conduct electricity in the characteristic metallic way? More

*Work at the Cavendish Laboratory supported in part by the Air Force Office of Scientific Research Office of Aerospace Research, U. S. Air Force, under grant No. 1052-69.

**This paper was originally intended for the Pauling Festschrift, Volume 7, Number 11 (November 1972).

fundamentally, does it exist?

Pauling, of course, gave the correct and rather obvious answer on the conductivity: it is not, so he supplemented his resonating valence bonds with a fraction of ionized states. The state which is described only as a superposition of valence bonds cannot conduct electricity at absolute zero because presumably there is an energy gap to any state which has any long range charge fluctuations, by the standard arguments which apply to the Mott insulator. If there were not, it would be better described as a more or less strongly correlated metal.

Our concern here is with the question of the insulating r-v-b state (resonating-valence-bond) and with whether or not there can be a physical representative of this state. We make the basic physical assumption of Pauling's early work on r-v-b states of aromatic molecules: that the effect of covalent bonding in connection with the repulsive interactions between electrons in the same orbital is best described by what is now known as a Heisenberg Hamiltonian and was then called the Heitler-London theory:

$$H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1)$$

This is the same as the Hamiltonian of the spin 1/2 antiferromagnet. We will give a very brief report here of some results on the ground state of a system of this kind, which summarizes results of a paper now in preparation.

The ground state of many magnetic materials with three-dimensional lattices and spins greater than 1/2 is known experimentally to be close to the "Néel" antiferromagnetic state, in which the spins are lined up in the arrangement which classical spins would assume, only deviating because of quantum zero-point motion. On the theoretical side (2), the success of estimates of energy and spin deviation (3), and the physical plausibility of the picture of the antiferromagnet as a clear case of "broken symmetry" and of the spin-waves as a "Goldstone mode", quelled most of the doubts (4) expressed earlier about the nature of this ground state.

The experimental situation for $S = 1/2$ is entirely another matter. Except for certain copper salts and Ir complexes where anisotropy is non-negligible relative to J , there are no experimental cases of antiferromagnet-

ism. Characteristically, materials like VO_2 and Ti_2O_3 undergo "pairing" transitions in which the lattice distorts in such a way as to form pairs of d^1 ions, which are joined more or less by a valence bond. But many compounds, such as some of the Magnéli phases and TaS_2 in the 1T form, as well as other lower d-band compounds (such as VO_x) show essentially mysterious behavior.

The main thrust of our argument will be to show that in at least one case where a Néel state is locally stable, the triangular layer lattice, there is another quite distinct ground state which is lower in energy. We visualize the relation between the two as being that of a quantum liquid vs. a quantum solid. The Néel state is like a solid: it has condensed into a spin lattice, whereas the real ground state is a fluid of mobile valence bonds, i. e. pairs of spins correlated together into singlets. Other authors (4), Marshall particularly, have suggested that the ground state is disordered; we are merely offering new evidence for this as well as a more modern point of view. The question of what is meant by two "ground states" for the system is, I think, a perfectly meaningful point: the clear example is either isotope or helium, where either a solid or a liquid ground state is available, depending on density. The two states are so far apart in phase space as to be unavailable quantum-mechanically to each other. This probably cannot be the case in one dimension, so that no really clear distinction between Néel state and r-v-b liquid is possible there; thus, in principle an insulating r-v-b state does exist in that case.

Let us, however, discuss the one-dimensional case for orientation. The energy of a pure Néel state

$$\Psi_{\text{Néel}} = \alpha(1)\beta(2)\alpha(3)\beta(4) \dots \quad (2)$$

in this case is

$$U = -NJ \frac{Z}{2} S^2 = -NJ \frac{1}{4} \quad (3)$$

whereas the correct energy is much lower (5),

$$U_0 = -NJ \frac{1}{4} \times 1.773 = -0.443 \text{ NJ}. \quad (4)$$

A much closer estimate than eqn. (3) can be obtained by using an alternating chain of paired atoms,

$$\Psi = \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{2}} (34)(56) \dots, \quad (5)$$

(in Hulthén's obvious notation), which gives

$$U = -\frac{NJ}{2} S(S+1) = -0.375 NJ. \quad (6)$$

Thus, the ground state must, in some sense, be closer to eqn. (5) than (2).

The best estimate from spin wave theory is Kubo's variational one:

$$(U_{s-w})_{\text{variational}} = -NJ \left(\frac{1.396}{4} \right) = -0.349 NJ, \quad (7)$$

worse than the wave function eqn. (5) which is obviously variational. On the other hand, it is easy to improve eqn. (5) either by perturbation theory or by the simple procedure of Hulthén (5). He solves for the energies of chains of 2, 4, 6, 8, and 10 atoms, using the identities

$$(1 - P_{\ell m})(k\ell)(mn) = (\ell m)(nk) \quad (8)$$

where

$$1 - P_{\ell m} = \frac{1}{2} - 2S_{\ell} \cdot S_m$$

and

$$(k\ell)(mn) + (kn)(\ell m) + (km)(n\ell) = 0. \quad (9)$$

These two identities allow one to calculate the effect of the Hamiltonian eqn. (1) on any wave function of a configuration expressed in the form $(k\ell)(mn) \dots$. Rumer (7) and Pauling (8) have given rules for determining which and how many of these configurations are independent: as we see from eqn. (9), in general one configuration (which may be expressed in terms of a "Lewis bonding diagram") is not orthogonal to, nor even independent of, another. This makes the algebra of valence bonds quite a bit more complicated than that of simple bosons or fermions. But, in general, as Pauling has shown, configurations without crossed bonds are at least independent. Having calculated $H\Psi$ in terms of bonding structures, the secular equation may be set up directly, as Hulthén points out, without recourse to an orthonormal function set. The results extrapolate well to the exact answer.

These chain solutions are obtained by writing the wave function as a linear combination of products of pair-bond wave functions of the type of eqn. (5). Thus, they are much more closely related to eqn. (5) than to eqn. (2).

It is, however, observed (9) that in the final ground state there is a branch of triplet excitations with very low energies, going linearly to zero with momentum k . This branch does not agree in multiplicity or energy with spin wave theory, yet is often cited as evidence for its essential correctness. We feel equally valid interpretations exist within the r-v-b context. This all may be relevant to actual physics in the case of some systems in which chains of relatively strongly coupled spin $1/2$ ions are weakly coupled to each other.

Now let us consider two dimensions, and specifically the triangular layer lattice. First, what is the Néel state? The best one is not a simple antiferromagnetic; it is obtained by dividing the lattice into three sublattices and setting the spins of the three lattices at 120° to each other. The energy of this state is

$$\begin{aligned}(E_{\text{Néel}}^{\Delta})_0 &= -NJ \left(3 \times \frac{1}{2} \times S^2\right) \\ &= -0.375 NJ.\end{aligned}\tag{10}$$

This is the energy which is comparable with eqn. (3) and corresponds to a wave function like eqn. (2), with each spin parallel to its local field. This energy may be improved as usual by estimating the decrease in spin-wave zero point energy due to dynamic coupling of the spins.

The energy, calculated by the technique of Stern (10), and corrected according to Kubo (6) is roughly

$$(\Delta E_{\text{Néel}}^{\Delta}) = (-0.463 \pm 0.007)NJ.\tag{11}$$

The spin waves have convergent zero-point motion. We estimate that its amplitude corresponds to $\bar{S}_z \simeq 0.32$. Thus at absolute zero the Néel state can be consistently postulated to be a locally stable minimum in the total energy. What we now set out to indicate is that it is not the absolute minimum. The only way at present available is to estimate the actual ground-state energy and show that it is appreciably lower than eqn. (11).

The two-dimensional case also permits a pair-bond trial wave function. In fact, there are an infinity of them of the same energy, so many as to have an appreciable entropy, since pair bonds may be laid down on the lattice in at least $2^{3N/8}$ ways. The energy of each is the same as eqn. (12):

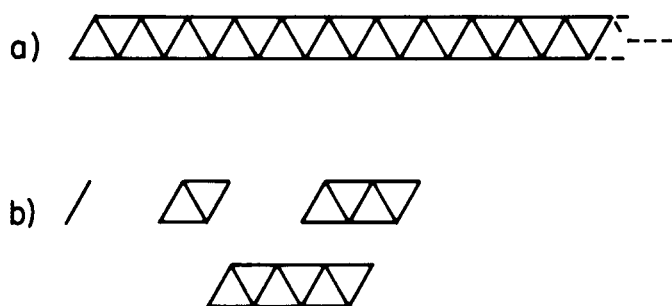


FIG. 1

- (a) The railroad-trestle lattice.
 (b) Successive approximations to it with
 $n = 2, 4, 6, 8, \dots$

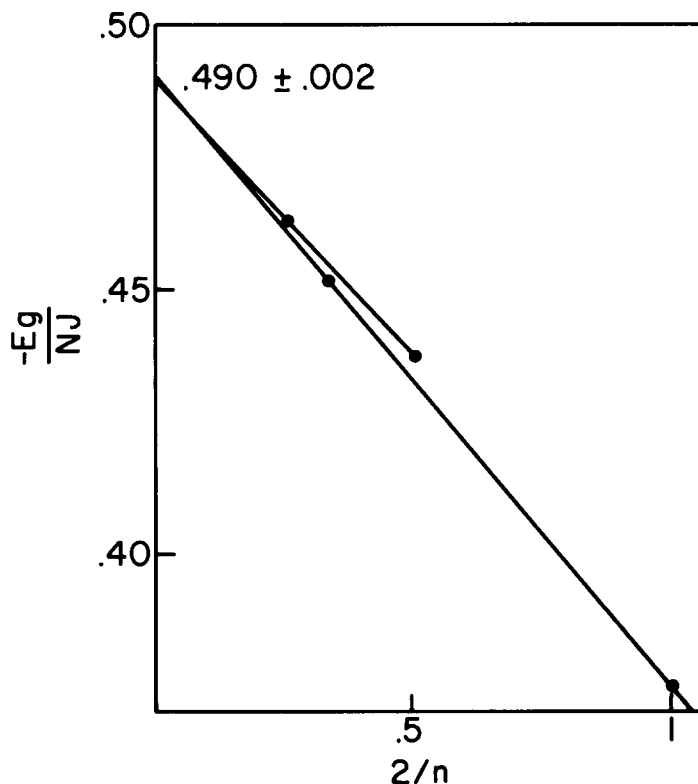


FIG. 2

Approximate energies for the railroad-trestle:
 successive $n = 2, 4, 6, 8$ estimates and
 extrapolation.

$$E_{\text{pair-bond}}^0 = -0.375 \text{ NJ. (12)}$$

It seems likely that at finite temperatures the entropy involved may often lead to a classical pair-bond liquid state; in a rather different case, McWhan and Rice have suggested this possibility (11). We, however, are looking for ground states in which these many different bond configurations are linearly combined in the same wavefunction to lower the energy.

The simplest system in which many degenerate pair-bond states exist is a one-dimensional system we may call the railroad trestle lattice (see Fig. 1a). It is a piece of the triangular layer and as such its energy is variational for that of the layer. Its Néel state energy is no better than the linear chain, its pair bond energy, as always, just (12). We have developed a sequence of variational approximations to

its energy, again simply by solving a sequence of small pieces of the lattice, containing 2, 4, 6, and 8 atoms (see Fig. 1b), using Hulthén's algebraic techniques. The results are shown in Fig. 2. The last of these energies is already as good as the spin wave result, and is, of course, variational. The

energies extrapolate rather smoothly to

$$E_{\text{railroad}} \simeq -0.490 \text{ NJ} \pm 0.005 \quad (13)$$

which should be quite accurate and is unmistakeably better than the spin-wave result.

A less accurate extrapolation may be made from the linear chain via the railroad trestle to the entire triangle lattice. One finds

$$E_{\Delta} \simeq -(0.54 \pm 0.01) \text{ NJ}. \quad (14)$$

This is nearly 20% lower than the spin-wave energy (11) of the Néel state. It seems almost certain that it represents the energy of a qualitatively different state.

Let us make some brief comments about the nature of this state. A disclaimer is in order: we really know very little about it. On the other hand, there are a few very basic things which can be said. We note that wherever two

bonds are parallel neighbors, such as (12) and (34) in Fig. 3a, either $(S_1 \cdot S_2)$ or $(S_3 \cdot S_4)$ provides a matrix element to the degenerate configuration (23)(41),

while only $(S_1 S_3)$ gives a matrix element of opposite sign. Thus we can always gain energy by linearly combining different configurations in which such bonds are interchanged. Since there are in any random configuration like Fig. 3b great numbers of sets of parallel bonds, one can arrive at any configuration from any other; and return to the original one by very many paths. What is not clear is that one will return to the same state in the same phase by traversing different paths. If one did, the state would be essentially a Bose condensed state of pair-bonds with a form of ODLRO. This would be closely re-

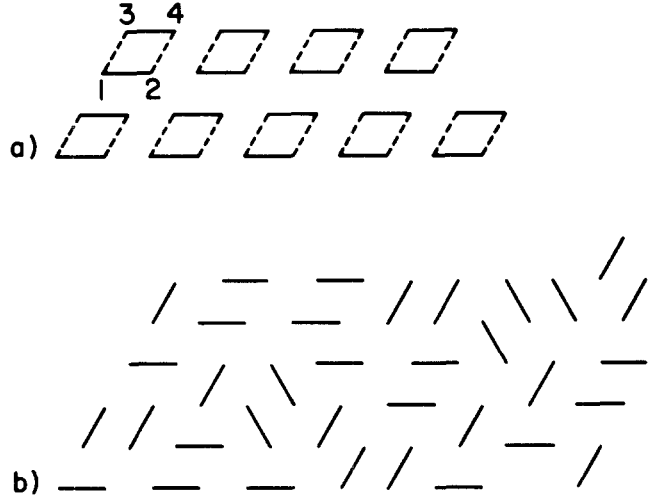


FIG. 3

Random arrangements of pair bonds on a triangle lattice. (a) Shows a regular arrangement with $2N/4$ alternative distinct pairings ('rhombus' approximation). (b) An arbitrary arrangement.

lated to a condensation of excitonic molecules. But this is not necessarily the case, and only local phase coherence may be present in the ground state, as in a Fermi rather than a Bose liquid. So in particular, it is not clear whether one must undergo a true phase transition from a "classical pair bond liquid" state to this state.

Next excitations: In two dimensions, it is not at all clear that the two spins in a singlet necessarily ever separate by any appreciable distance, in which case there may be an energy gap to the lowest triplet excitation, so that the state need be only weakly paramagnetic if at all. But especially if it is a Bose state, it will probably have low-energy excitations, which may in this case be purely singlet. Two puzzling results to which this is relevant on TaS_2 (1T) are the low paramagnetic susceptibility and the large, not quite linear, specific heat.

I would like to acknowledge stimulating conversations at various times with H. A. Kramers, W. Marshall, and T. M. Rice, and discussions of their data with D. McWhan and T. Geballe.

References

1. L. Pauling, Proc. N.A.S. 39, 551 (1953); Nature of the Chemical Bond, p. 394. Cornell University Press, Ithaca, New York (1960).
2. P. W. Anderson, Phys. Rev. 86, 694 (1952).
3. H. W. deWijn, R. E. Walstedt, L. R. Walker and H. J. Guggenheim, J. Appl. Phys. 42, 1595 (1971).
4. W. Marshall, Proc. Roy. Soc. 232, 49, 69 (1955); H. A. Kramers, Physica 18, 101 (1951).
5. L. Hulthén, Ark. Mat. Astro. Fys. 26A, #11 (1938).
6. R. Kubo, Revs. Mod. Phys. 25, 344 (1953).
7. G. Rumer, Nachr. d. Ges. d. Wiss. zu Gottingen, M. P. Klasse, 337 (1932).
8. L. Pauling, J. Chem. Phys. 1, 280 (1933).
9. J. des Cloiseaux and J. J. Pearson, Phys. Rev. 128, 2131 (1962).
10. F. Stern, Phys. Rev. 94, 1412 (1954); also unpublished manuscript.
11. D. B. McWhan, preprint; T. M. Rice, private communication.