Numerical simulation of the resonant valence-bond state

Joseph Callaway
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803-4001
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The resonant valence-bond state, proposed by Anderson as a possible ground state in certain antiferromagnetic systems, and relevant to the problem of high-temperature superconductivity, is studied by numerical simulation on a finite cluster. It is found to be the ground state of a simple Hubbard model with a half-filled band on a centered hexagon for a range of intermediate values of the electron interaction parameter. A singlet ground state is obtained away from the half-filled limit for the same parameters.

Some years ago, Anderson proposed that an unusual type of antiferromagnetic state [the resonating valence-bond (RVB) state] might be the ground state in spin-$\frac{1}{2}$ systems with localized (e.g., anisotropic Heisenberg) interactions and certain lattice structures, such as the triangular lattice.[1,2] More recently, he has suggested that the ground state in some high-temperature superconductors is closely related to the RVB state.[3]

In this Brief Report, it will be shown that the RVB state can be the ground state of the simple Hubbard Hamiltonian in the half-filled band case under certain circumstances. Its properties will be examined. Then we will study the properties of the system away from the half-filled limit, and find a singlet ground state for the same band parameters. In some situations, increasing electron interactions suppress a magnetic ground state, producing a singlet ground state. These results support the ideas of Anderson. Although the spin-$\frac{1}{2}$ triangular lattice considered by Anderson has been studied using Ising and Heisenberg Hamiltonians, I am not aware of previous work using the Hubbard model.

The calculation is carried out by numerical simulation on a small cluster. Specifically I consider a system of seven sites, the centered regular hexagon shown in Fig. 1. Arrows have been placed adjacent to the sites to illustrate that if "up" and "down" spins are alternately assigned around the ring the central spin must be frustrated in the sense that it will have both an up and down nearest neighbor. The seven-site system has been chosen because it is the largest that could readily be investigated with current computer facilities, and because the geometry suggested that the results might be particularly interesting (there is an "inside" site). The Hamiltonian is

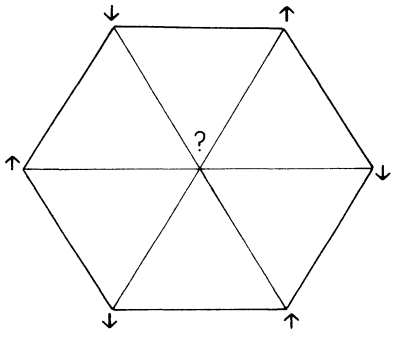

FIG. 1. Centered hexagon. If alternating spins are assigned around the ring, as illustrated by the arrows, the central site is frustrated (indicated by the question mark).

$$H = t \sum_{i,j,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} , \tag{1}$$

where $c_{i\sigma}$ are the usual fermion operators and $n_{i\uparrow(\downarrow)}$ is the number operator for up or down spins. Only positive values of U (repulsive interactions) will be considered. I will be primarily concerned here with the ground state of the system, although I have made calculations of thermodynamic properties using a canonical ensemble.

The computational technique employed is the explicit diagonalization of the Hamiltonian for the finite cluster of Fig. 1, using a basis of localized states.[4,5] All the eigenvalues and eigenvectors are determined. More details of this procedure can be found in Ref. 4, which may also be consulted for references to previous related work.

I begin by considering the so-called half-filled band case, in which the system contains seven electrons. The centered hexagon considered in this work differs in one important respect from most of those discussed in Refs. 4 and 5. Because the central site is not equivalent to those on the periphery, there are two kinds of first-neighbor correlation functions. Likewise, the local moment is different on the center and the outer sites. The correlation function of greatest interest in this work is that involving spins on the center and any one of the outside atoms. I call this L_1. In the ground state, it is given by

$$L_1 = \tfrac{1}{4} \langle 0 | (n_{0\uparrow} - n_{0\downarrow})(n_{1\uparrow} - n_{1\downarrow}) | 0 \rangle , \tag{2}$$

in which the subscript 0 refers the central atom and 1 to the one on the periphery. This particular function is suggested because it involves a frustrated inside site, and as such is most likely to give some indication of correlations in bulk material. In Ref. 2, the RVB state is described as one in which there is no definite spin direction for a given site. Therefore we expect the RVB state to be characterized by a small value of L_1 and this property is used to

identify the RVB state.

The calculated L_1 is shown in Fig. 2. For comparison, I show the corresponding nearest-neighbor correlation functions for any two atoms on the periphery. There are two transitions involving a change of ground state. Let us start in the large-U/t limit and follow the behavior of L_1 as U/t decreases. At large U/t, L_1 has a value of about -0.056. In a conventional two-sublattice state with alternating spin, the value of L_1 would be -0.25. The calculated value is about $\frac{1}{2}$ of the value of the correlation function for two first-neighbor atoms on the periphery. When U/t decreases to about 10.44, the ground state switches to a state I interpret as the RVB state. L_1 rises to a value very close to zero(-0.003). L_1 remains quite close to zero until U/t decreases to 4.27, at which point a doubly degenerate state becomes the ground state. The small value of L_1 results from a cancellation between separately large parallel-spin and antiparallel-spin correlation functions on the two atoms. The center atom has spin "up," but there is no preferred spin direction for the atoms around the ring. The RVB state can be identified for all values of U/t but it is the ground state only in the range $4.27 < U/t < 10.44$. At $U/t = 4.27$, the magnitude of L_1 increases (but it remains negative) with a value intermediate between the large U/t value and that of the RVB state. The correlation functions around the periphery are small compared to those in either of the preceding states. The small, though nonzero, correlations in this degenerate state lead me to refer to it as an itinerant state.

Calculations for another frustrated small system (a four-site rhombus) also show some unusually small correlation functions. The centered hexagon gives exceptionally clean results.

Next, I consider the system with one electron less or greater than the half-filled case (six or eight electrons). This is relevant to Anderson's arguments concerning pairing when a physical system with an RVB ground state is doped away from the half-filled band case. In these situations (unlike the half-filled case), the algebraic sign of t matters. Let there be n electrons distributed on N sites, and put $n' = 2N - n$. The energy of a state with n' electrons and one sign of t is related to that with n electrons and the other sign of t by

$$E_{n'}(t) = E_n(-t) + (N-n)U \ . \tag{3}$$

Hence it suffices to calculate E_n for positive t; the results for negative t can be found from (3).

In the case $n = 8$, the ground state is a singlet state for all values of U/t. No changes of symmetry occur. The separation between the ground state and the first excited state is fairly large and approaches $2t$ in the limit $U \to 0$. This is a consequence of the spectrum of single-particle states. The case $n = 6$ (but this applies to $n = 8$ if $t < 0$) is more complicated, and may be relevant to Anderson's proposals concerning superconductivity. Figure 3 shows the results graphically.

I begin by considering small values of $U/|t|$. In this case, the ground state has spin $S = 1$, corresponding to an unsaturated ferromagnet. The occurrence of a ground state with nonzero spin in the small-U limit can be under-

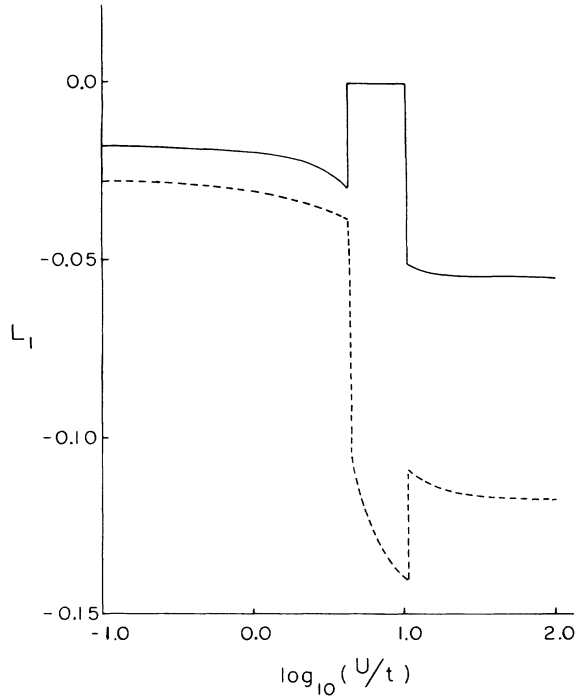

FIG. 2. First-neighbor spin-correlation functions for the centered hexagon in the half-filled case ($n = 7$) as functions of $\log_{10}(U/t)$. Solid line, center-outside function; dashed line, similar function defined for two atoms, both on the periphery.

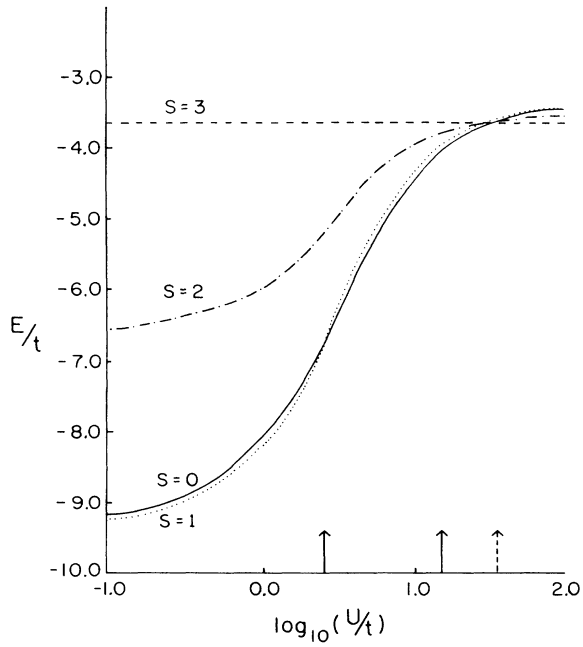

FIG. 3. Energies of the lowest state of given spin for $n = 6$, $t > 0$. Solid line, $S = 0$; dotted line, $S = 1$; dashed-dotted line, $S = 2$; dashed line, $S = 3$. Solid arrows mark the values of U/t where the transition between $S = 1$ and $S = 0$ and between the two different $S = 0$ states occur; the dashed arrow marks the transition to an $S = 3$ state.

TABLE I. Single particle energies (divided by t) for a centered hexagon. The number in parenthesis is the degeneracy.

−2.0 (1)
−1.646 (1)
−1.0 (2)
1.0 (2)
3.646 (1)

stood in terms of the occupancy of single-particle states whose energies and degeneracies are listed in Table I. The lowest two nondegenerate states are doubly occupied for small U; the two remaining electrons go into a doubly degenerate state.

If four electrons are assigned to the two lowest single-particle states, the two remaining electrons can form six states (three singlets and one triplet). Two of the singlets, which correspond to double occupancies of one of the single-particle states will be degenerate with each other. The third singlet has mixed occupancy and is not degenerate. Hund's rule, as discussed in Ref. 4, suggests that the triplet state will have the lowest energy in the presence of a weak, repulsive electron interaction.

Surprisingly, when U/t increases to 2.59, the doubly degenerate singlet state becomes the ground state. Since U is not large at this point compared to the bandwidth ($5.646t$) it should be a reasonable approximation to consider this state as a collection of singlet pairs, which is certainly the situation for small U/t. The pairing in this case results from the discrete nature of the single-particle spectrum which shows significant gaps between levels. The state is characterized by rather small values of the site-spin-correlation functions around the periphery (L_2 of order -0.04, $L_3 \sim 0.01$) as well as between the central and an outside site ($L_1 \sim -0.03$).

It is very unusual to find a case in which increasing $U/|t|$ leads from a magnetic ground state to a nonmagnetic ground state. I have yet not found any other example of this in the study of many small clusters of varying geometries. It occurs here in a region of values of U/t which overlaps those for which the RVB state was the ground state in the half-filled case, in accord with Anderson's proposal.

The doubly degenerate singlet state remains the ground state until U/t increases to 14.69. At this point, the ground state becomes a nondegenerate singlet, characterized by a rather large, negative value of the third-neighbor spin-correlation function for sites around the periphery ($L_3 \sim -0.15$).

When U/t increases to 34.7, the ground state changes again to a nondegenerate "ferromagnetic" state with $S=3$. This remains the ground state as U/t increases indefinitely beyond this point. It should be noted that the transition between $S=0$ and $S=3$ ground states is abrupt; i.e., intermediate-spin ground states do not intervene. Moreover, a quintet state ($S=2$) is not the ground state for any value of U/t. The occurrence of a ferromagnetic ground state for sufficiently large U/t is consistent with the arguments of Nagaoka[6] for infinite systems (but Nagaoka did not consider the specific lattice structure related to the cluster I have investigated).

In conclusion, on the basis of numerical calculations for a small cluster I find that (1) Anderson's proposed RVB state is the ground state of the Hubbard model in the half-filled case for a range of values of U/t for a particular geometry. (2) For a range of values U/t which includes the range in which the RVB ground state is obtained, a singlet ground state is found in a system with fewer electrons per site (more if $t<0$). This state can be regarded, at least approximately, as a collection of singlet pairs. In this case, correlations induce a gap between the ground singlet state and the first excited triplet state, in which a singlet pair is broken. This gap is not present in the $U \to 0$ limit for this structure, since the triplet state is then the ground state. (3) For values of U/t outside a bounded (but fairly large) range, the ground state in (2) is magnetic.

This does not demonstrate that the model considered would exhibit superconductivity if applied to a bulk system of suitable geometry. I cannot draw any conclusions concerning many essential properties of superconductors, such as pairing in bulk, or coherence, from calculations on a small system. However items (1) and (2) above are certainly consistent with Anderson's proposal. In particular, one characteristic property of a superconductor is established here: preference for a singlet ground state in a situation where magnetism would ordinarily be expected. Calculations for other geometries showing frustration are in progress, and larger models will be attempted.

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