Nearest-neighbor resonating-valence-bond state in two dimensions

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The ground state of the spin-$\frac{1}{2}$ Heisenberg model with antiferromagnetic coupling on a square lattice is analyzed in terms of nearest-neighbor resonating pair-bond states. Extrapolating from finite lattice calculations it is found that the pair-bond state provides a much closer variational estimate of the ground-state energy than the widely used Gutzwiller wave function. The effect of an orthorhombic distortion of the square lattice, such as that observed in the Cu-O planes in the high-T_c oxides, on the spin state is analyzed by exact calculation for finite lattices. From total-energy considerations it is found that the system has a slight tendency towards such a lattice distortion.

I. INTRODUCTION

It is well known[1] that in the large-U limit the half-filled Hubbard model can be transformed into the spin-$\frac{1}{2}$ Heisenberg model with antiferromagnetic coupling. The latter was solved exactly for a one-dimensional chain by Bethe,[2] and analyzed in terms of pair-bond states by Hulthén.[3] For two dimensions no exact solution is available; however, finite lattice[4] and quantum Monte Carlo calculations[5] have been carried out for the square lattice. The ground state has long-range order smaller than expected from the naive Néel state; the extrapolated ground-state energy is very close to spin-wave calculations.[6,7]

For the spin-$\frac{1}{2}$ antiferromagnet on a triangular lattice, Anderson[8] argued that a resonating pair-bond state [resonating valence bond (RVB)] such as that which arises in the one-dimensional (1D) case is a much closer description of the ground state than the Néel state. This description has taken new significance with Anderson's suggestion[9] that the RVB state is relevant to the high-T_c superconducting oxides. The expectation is that doping or lattice coupling would stabilize the RVB state in the square lattice representing the Cu–O planes in these materials. This has led to a resurgence of interest in the Hubbard model in the large-U limit, notably in terms of Gutzwiller variational calculations.[10,11] Although it is known[12] that in one dimension the Gutzwiller form gives an excellent description of the ground state for the large-U transformed Hamiltonian, the same cannot be said in higher dimensions. In fact, the Gutzwiller variational energy[11] for the half-filled case for a square lattice is 15% higher than the exact energy. When the filling is less than one-half a state without long-range order is likely stable, but whether the Gutzwiller form,[9–11] which can be viewed as an RVB state with a wide range of bond lengths, is a good variational state is uncertain. A somewhat different view, in which the RVB state is pictured in terms of short-range pair-bond states, has been adopted by other authors.[13]

In this note, we examine the spin-$\frac{1}{2}$ Heisenberg antiferromagnet on a square lattice directly in terms of the pair-bond states much in the spirit of Anderson's original suggestion.[8] Our motivation is to compare the widely used Gutzwiller correlated state to the pair-bond state. We also investigate the effect of a lattice distortion representing the orthorhombic deformation observed[14–17] in the new materials on the ground state of the system.

II. RVB ANALYSIS OF THE SQUARE ANTIFERROMAGNET

A. Background and definitions

Following Hulthén[3] we use the notation (ij) to represent a singlet state of two spin-$\frac{1}{2}$ objects,

$$(ij)=\frac{1}{\sqrt{2}}(\alpha_i\beta_j-\beta_i\alpha_j)\ , \tag{1}$$

where α and β are the usual S_z eigenstates. Define a pair-bond state of N spins to be a direct product of $N/2$ such terms:

$$|pb\rangle=(i_1i_2)(i_3i_4)\cdots(i_{N-1},i_N)\ . \tag{2}$$

The set of pair-bond states consists of all such states with every possible pairing of spins, a set consisting of $(N-1)!!$ states. The most general definition of an RVB state is as any superposition of such pair-bond states.[3,8] The more recently proposed forms for the RVB state[9–11] are particular choices within this general category. In what follows, we will use the term RVB in the more general sense.

There are two difficulties in dealing with pair-bond states: they are nonorthogonal, and the set of all such states is hugely overdetermined. The linear dependence is evident from the relation[3]

$$(ij)(kl)+(il)(jk)+(ik)(lj)=0\ , \tag{3}$$

which can be readily established from (1). This relation may be represented graphically as in Fig. 1(a). A way to extract a linearly independent set of pair-bond states was enunciated by Rumer:[18] write labels $1,2,\ldots,N$ (representing the spins) along the circumference of a circle, in

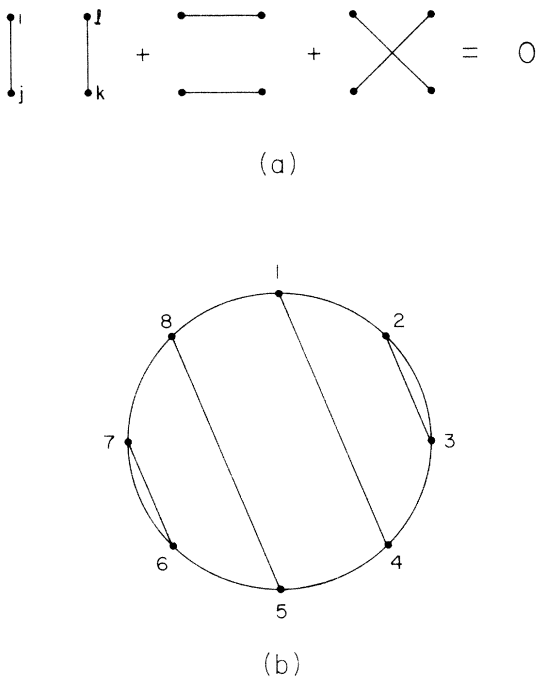

FIG. 1. (a) Graphical representation of the linear dependence of pair-bond states [Eq. (3)]; (b) Rumer's graph of the pair-bond state (14)(23)(58)(67).

any order; represent each singlet pair in a pair-bond state by drawing a line segment between the corresponding labels [see Fig. 1(b)]; then, the set of linearly independent pair-bond states corresponds to the set of graphs in which no two segments cross. A graph in which two segments cross can be expressed, as in Fig. 1(a), as a sum of two other graphs in which the segments are uncrossed. By uncrossing one pair at a time, every graph can be written as a sum of noncrossing graphs. In the following, we refer to these as the linearly independent pair-bond (LIPB) states.

It is evident that a pair-bond state is a spin-0 state, since it is a direct product of spin singlet-pair states. Bloch[19] showed that the number of independent ways in which spin-0 states can be formed from N spin-$\frac{1}{2}$ particles is

$$M_N = N!/[N/2!(N/2+1)!] . \tag{4}$$

The rule for enumerating LIPB states given above generates exactly M_N states; the LIPB states are, in fact, independent[20] and span the subspace described by Bloch. The LIPB states can be chosen in a very large number of ways: every rearrangement of the labels on the circle generates a different set; furthermore, different sets of LIPB, not expressible in terms of Rumer's noncrossing graphs, can also be chosen. In passing, we note a relation useful in generating the Hamiltonian matrix for the Heisenberg Hamiltonian:[3,7]

$$(\tfrac{1}{2} - 2\mathbf{S}_j \cdot \mathbf{S}_k)(ij)(kl) = (jk)(li) . \tag{5}$$

In the following, we will have occasion to consider two smaller sets of pair-bond states, the set of nearest-neighbor pair-bond (NNPB) states and its subset of linearly independent nearest-neighbor pair-bond (LINNPB) states.

The original work of Hulthén[3] applied the pair-bond concept to the Heisenberg antiferromagnetic chain. By a recursive approach he showed that the best variational energy for a ground state constructed out of a superposition of LIPB states reproduced the exact $N \to \infty$ Bethe result quite well. Anderson[8] proposed that such a state also described the ground state of the Heisenberg antiferromagnet on a two-dimensional triangular lattice, where the simple Néel state is frustrated. As already mentioned, he has more recently proposed[9] that such a state, or a spin liquid state similar to it, is responsible for the unusual properties of the high-T_c oxides.

B. Pair-bond analysis and discussion

We first note the almost trivial result that the ground state of the spin-$\frac{1}{2}$ Heisenberg antiferromagnetic Hamiltonian,

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j , \tag{6}$$

on a square lattice (where $J > 0$, and the sum is over nearest neighbors) can, in fact, be expressed exactly as an RVB state (with the RVB state defined in the original sense as a superposition of LIPB states). The proof follows. For any lattice consisting of two interpenetrating sublattices, Marshall, following a suggestion by Peierls, showed that the ground state of the Heisenberg antiferromagnet must be a total spin-zero state.[21] Since the LIPB states span the $S=0$ subspace, as discussed above, the ground state must be expressible as a superposition of LIPB, i.e., as an RVB state. (For the same reason, Hulthén's LIPB formulation of the ground state of the 1D chain should be exact.) This conclusion does not preclude the possibility of long-range order: since the set of LIPB states includes states in which greatly separated spins are paired in singlets, an RVB state defined in this manner could possess long-range order. The intuitive picture implied by Anderson[8,9] and adopted by others[13] emphasizes short-range singlet pairs. Accordingly, we restrict our attention to the smaller set formed by the linearly independent nearest-neighbor pair-bond (LINNPB) states.

The Rumer procedure for generating the LIPB set does not contain any geometric input. Nor, given a pair-bond state, is there any simple way to determine its projection on, say, nearest-neighbor pair-bond states. We have found it simpler to start from the opposite end, namely, to construct an LINNPB set by pairing each spin successively with all of its nearest neighbors and retaining only those that are linearly independent. These form the basis for a variational wave function. Obviously, the LINNPB set depends on the lattice under consideration, and for finite lattices, on the cell chosen. For the square lattice one can construct periodically extended square cells for which the interpenetrating two-sublattice feature is retained for cells of size $N = 2k = i^2 + j^2$, where i,j,k are integers. Cells for $N=4$ and $N=20$ are shown in Fig. 2. The number of LINNPB states for values of N up to 20 are given in Table I. We note that for $N=4$ and 8, the LINNPB states, in fact, span the $S=0$ subspace by themselves. In

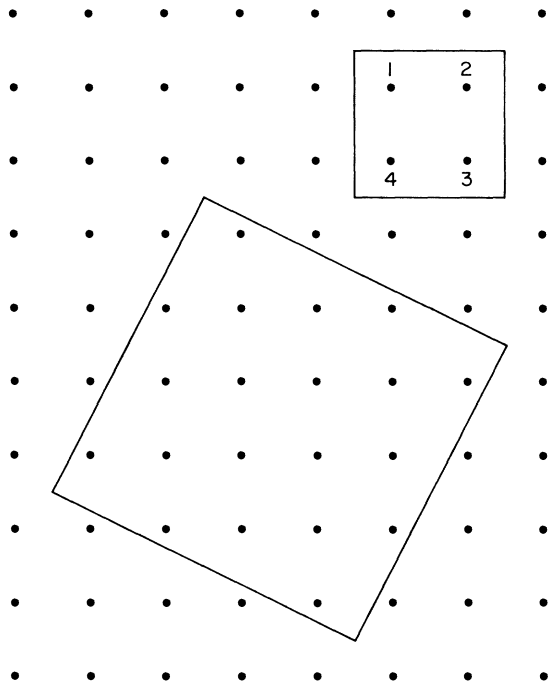

FIG. 2. Unit cells for $N=4$ and $N=20$.

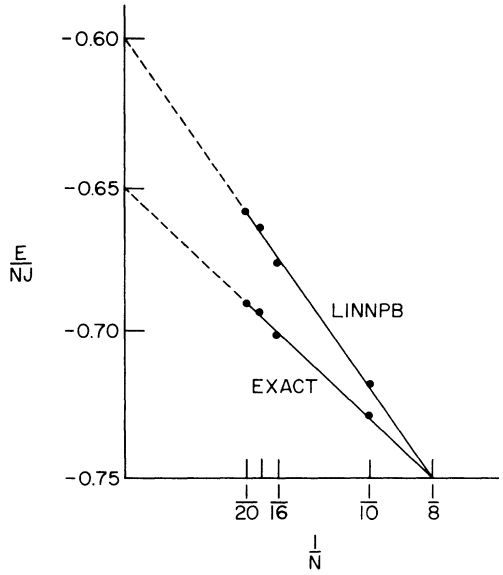

FIG. 3. Extrapolation of finite cell results to the infinite lattice; the LINNPB and exact ground-state energies are shown.

Table I, the number of LIPB states [which is independent of geometry, and is given by Eq. (4)] is also listed for each N. As N grows, the LINNPB set forms an ever smaller subset of the LIPB set. In a system well described as a quantum spin liquid, this small subset should contain the physically important states and provide a good description of the ground state.

We have calculated the variational ground-state energy of the Heisenberg antiferromagnet for the square lattice within the manifold of LINNPB states for periodically extended finite systems with $N=4$, 8, 10, 16, 18, and 20 spins. The ground-state energy estimates thus obtained can be compared with the exact finite cell ground-state energies calculated by Oitmaa and Betts[4] (extended by us here to include $N=20$). For both the variational calculation and the exact calculation, the computational effort grows rapidly with N, and becomes excessive beyond 20 spins. For instance, the exact calculation for $N=20$ required approximately 2 h CRAY time.

The results are listed in Table I and plotted in Fig. 3. The calculated energies are linear in $1/N$ for $N>8$, with a small oscillation. Fitting the results to a straight line, the extrapolated ground-state energy is $E/JN=-0.651 \pm 0.005$ for the exact calculation, and -0.600 ± 0.005 for the LINNPB state.

Using the Gutzwiller variational wave function on a square lattice, Gros, Joynt, and Rice[11] found $E/JN=-0.550$ (15% higher than the exact energy), to be compared with the LINNPB energy of -0.600 (8% higher than the exact value). Evidently, the LINNPB is a better variational form in this case. The various $N\rightarrow\infty$ energies are shown in Table II.

As mentioned earlier, the ground state of this system very probably possesses long-range order.[4-7] For example, spin-wave calculations yield a ground-state energy very close to the exact (numerical) value for a state with a Néel-type order (although greatly reduced from the naive Néel value).[6,7] Nevertheless, the LINNPB state gives a surprisingly good answer for the ground-state energy,

TABLE I. Exact and variational ground-state energies for periodically extended finite cells on the square lattice. The columns headed by LIPB, NNPB, and LINNPB contain, respectively, the number of linearly independent pair-bond states, nearest-neighbor pair-bond states, and linearly independent nearest-neighbor pair-bond states.

N	LIPB	NNPB	LINNPB	$-E/NJ$ (exact)	$-E/NJ$ (LINNPB)
4	2	2	2	1.00000	1.00000
8	14	24	14	0.75000	0.75000
10	42	44	37	0.73007	0.71865
16	1430	272	272	0.70178	0.67668
18	4862	448	447	0.69399	0.66569
20	16796	808	808	0.69081	0.65926
26	742900	4684	...	...	...

TABLE II. Ground-state energy of the infinite square lattice computed several ways.

Calculational approach	E/NJ
Néel state	-0.500
Gutzwiller state[a]	-0.550
LINNPB state	-0.600 ± 0.005
Spin wave[b]	-0.645
Exact numerical[c]	-0.651 ± 0.005

[a]Reference 11.
[b]Reference 6.
[c]Reference 4, extended to $N=20$.

better in this limit than the Gutzwiller form. Away from the half-filled limit of the large-U Hubbard model, where it is likely that the ground state lacks long-range order,[9,11,13] the LINNPB should fare better as a variational ground state by comparison. This question is currently under investigation.

III. ORTHORHOMBIC DISTORTION

Both the 30-K oxides and the 90-K oxides undergo a tetragonal-to-orthorhombic transition before they attain the superconducting state.[14-17] It is known that suppressing the tetragonal-orthorhombic transition (e.g., by regulating oxygen content) also suppresses superconductivity. Anderson, Baskaran, Zou, and Hsu[22] have found in a mean-field treatment of the RVB state a "twitch" transition which they identify with the observed crystal distortion. Further, Mattis and Mattis[23] have advanced a theory which uses the in-plane bond asymmetry to explain the high transition temperature. Thus, one might ask whether the 2D square Heisenberg model ground state shows any tendency for a lattice distortion. To investigate this, we write the spin Hamiltonian in the following form:

$$H = J_x \sum_{\langle ij \rangle} \mathbf{S}_{ij} \cdot \mathbf{S}_{i+1,j} + J_y \sum_{\langle ij \rangle} \mathbf{S}_{ij} \cdot \mathbf{S}_{i,j+1} , \tag{7}$$

where $\mathbf{S}_{ij}$ denotes the spin at lattice location (i,j) on the simple quadratic lattice. The difference between J_x and J_y arises from the difference in the hopping integral between neighbors along the x and y directions in the large-U Hubbard Hamiltonian caused by an orthorhombic distortion of the square lattice. For simplicity, and in close approximation to the experimental situation, we assume the distortion is area preserving to lowest order, i.e., $a \rightarrow a(1+\delta)$ along y, and $a \rightarrow a(1-\delta)$ along x. If we write the hopping integral as[13]

$$t = t_0 = au , \tag{8}$$

where $u = \pm a\delta$ is the change in hopping distance, then, to lowest order,

$$J_{x,y} = J_0(1 \pm \Delta/2) , \tag{9}$$

where $\Delta = 4a\alpha\delta/t_0$ and $J_0 = 4t_0^2/U$ is the coupling strength for the undistorted square lattice. Note that we are not considering here a spin-Peierls type of distortion[24] in which alternating pairs along a chain would have different couplings. This will be considered elsewhere.

We have carried out exact calculations of the ground state for the above model for periodically continued cells with $N=8$, 10, 16, and 18 for several small values of Δ. The procedure we use is identical to that described by Oitmaa and Betts[4] for the case $J_x = J_y$. Marshall's proof[21] that the ground state is a singlet can be readily generalized to the case where $\Delta \neq 0$. Here the basis set is larger due to the reduced symmetry. The difference in energy between the undistorted and distorted lattices is linear for small Δ:

$$(E' - E)/N = Jg|\Delta| . \tag{10}$$

In Table III, our results for g are shown. Note that g is nearly constant (≈ -0.009), independent of N. We see that the energy of the spin system is lowered by such a distortion, which can easily be understood. In the limit when $J_y/J_x \rightarrow 0$ (i.e., $\Delta \rightarrow 2$), the system is equivalent to a noninteracting set of antiferromagnetic one-dimensional chains, for which $E' - E$ is $-0.235NJ$ (using the exact numerical result[4] for the square lattice, and the analytical result[2] for the chains). The adiabatic theorem suggests that the system evolves continuously from 2D to 1D as the anisotropy in the coupling strength is increased.

We have also carried out a variational calculation of the ground-state energy for the distorted system within the LINNPB manifold. Our motivation was to determine whether the distortion might be related to a reduction in long-range order. We find, however, that the degree of agreement between the LINNPB ground-state energy and the exact energy is nearly independent of Δ for small Δ, extrapolating as above to 8% as $N \rightarrow \infty$.

Using our estimate (10) of the reduction in the electronic energy due the lattice distortion, we may now calculate the expected size of the distortion. The analysis below is simplified in that it ignores quantum fluctuations. The change in the total energy of the system, including elastic energy, due to the lattice distortion is

$$(E_t' - E_t)/N = J_0 g\Delta + \tfrac{1}{2} K(a\delta)^2 , \tag{11}$$

where K is an appropriate elastic force constant and all other quantities have been defined earlier. Minimizing with respect to δ gives

$$\delta^* = -4g\alpha J_0/(Kat_0) . \tag{12}$$

According to band-structure calculations, (Ref. 25) $t_0 \approx 0.5$ eV; from Weber's work[26] on the electron-phonon interaction we estimate $\alpha \approx 2.5$ eV/Å; from the Raman observation[27] of phonon modes we take $K \approx 4$ eV/Å^2; a is known from experiments to be 3.8 Å; following Anderson and Zou[28] we take $J_0 \approx 1000$ K. This gives $\delta^* \approx 10^{-3}$.

TABLE III. Energy change of the spin system due to lattice distortion for various cell sizes: $E_{\rm dis} - E_0 = g\Delta NJ$.

N	8	10	16	18
g	-0.0091	-0.0088	-0.0113	-0.0089

The observed $T=0$ distortion is of this order of magnitude in the La-Sr-Cu-O system,[16] and an order of magnitude larger in the Y-Ba-Cu-O material.[17] However, the energy gain we find is very small ($\approx 5\times 10^{-5}$ eV), while the observed structural transition occurs at several hundred K, which implies that the observed distortion cannot be explained solely in terms of the large-U Hubbard model. In the Y-Ba-Cu-O material it is believed that the tetragonal-orthorhombic distortion is driven by oxygen vacancies in the intervening Cu—O chains.[29]

IV. SUMMARY AND CONCLUSION

We have performed a variational calculation of the ground-state energy of the 2D square Heisenberg antiferromagnetic Hamiltonian within the manifold of resonating nearest-neighbor pair-bond states. Such states are an explicit representation of the intuitive picture used for the RVB. Compared with the (numerical) exact ground-state energy, we find that the pair-bond state gives a much closer estimate than the widely used Gutzwiller state. If this result extends to the partially filled case, as we suspect, then the short-range pair-bond state should be a better candidate for an RVB state lacking long-range order than the Gutzwiller form. By exact small-cell calculations we have found that the spin energy is lowered by an orthorhombic distortion. Our estimate of the energy gain indicates, however, that this effect is not significant in driving the observed crystal distortion.

Note added in proof. Kohmoto [Phys. Rev. B **37**, 3812 (1988)] has also performed a similar analysis of the 2D Heisenberg antiferromagnet.

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