Rigorous Results on Valence-Bond Ground States in Antiferromagnets

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(Received 26 May 1987)

We present rigorous results on a phase in antiferromagnets in one dimension and *more*, which we call a valence-bond solid. The ground state is simply constructed out of valence bonds, is nondegenerate, and breaks no symmetries. There is an energy gap and an exponentially decaying correlation function. Physical applications are mentioned.

PACS numbers: 75.10.Jm

There is currently considerable interest in the ground-state properties of quantum antiferromagnets. In the one-dimensional case, it has been argued by Haldane[1] that Heisenberg antiferromagnets have an energy gap for integer, but not half-odd-integer, spin. Neutron-scattering data on $CsNiCl_3$, a highly one-dimensional spin-1 antiferromagnet, support this claim.[2] It has also been argued by Anderson[3] that two-dimensional antiferromagnets can have disordered ground states. The nature of these ground states may be important in the theory of high-T_c superconductors.[4]

A convenient basis for spin-singlet states of a spin $s=\frac{1}{2}$ antiferromagnet consists of all possible products of pairwise contractions of spins to form singlets (known as valence bonds): $(\uparrow\downarrow - \downarrow\uparrow)$. For an $s=\frac{1}{2}$ chain with a special ratio of first and second nearest-neighbor interactions it was shown by Majumdar and Ghosh[5] that the two exact ground states are given by the states with purely nearest-neighbor valence bonds. We represent these dimerized states in Fig. 1 by drawing lines between the pairs of spins which are contracted. These ground states have a translational symmetry broken from period 1 to period 2, ultrashort-range correlations, and, as we will prove in a companion paper,[6] an energy gap. The pure nearest-neighbor model, which was solved by the Bethe *Ansatz*, is believed to have a unique ground state with power-law correlations and no gap. This ground state can be thought of as a resonating–valence-bond state[3] in which quantum fluctuations restore the translational symmetry and mix in bonds of greater length. The absence of Néel order is believed to be a general feature of one-dimensional antiferromagnets. On the other hand, Néel order is generally expected to occur in two (or more) dimensions at zero temperature. However, it was suggested[3] that a disordered resonating–valence-bond ground state might occur in some two-dimensional $s=\frac{1}{2}$ cases: triangular lattice or square lattice with next-neighbor couplings. The latter is relevant to the copper-oxide planes in high-T_c superconductors.[4]

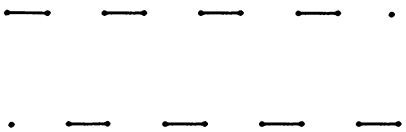

FIG. 1. The spin-$\frac{1}{2}$ dimerized valence-bond states.

In this Letter and the companion paper,[6] we will study exactly solvable Hamiltonians, in dimension one *and more*, with ground states constructed simply out of valence bonds, which have quite a different character than the Majumdar-Ghosh model. Unlike the dimerized ground states of Ref. 5, our models have unique ground states with no broken symmetries. As in the model of Ref. 5 there is a gap and short-range correlations. *This ground state, which we call a valence-bond solid (VBS)*, appears to be a good approximation to the ground state of the realistic spin-1 chain. We suspect that it may be a good approximation in other physically relevant cases as well. The existence of a short-range, nondegenerate phase in antiferromagnets was first suggested, for the one-dimensional case, by Haldane.[1] We present the first exact solution exemplifying this phase in one dimension, and extend the results to higher dimension.

We extend the notion of valence bonds in a natural way to higher spin. Spin s is obtained by symmetrization of $2s$ spin-$\frac{1}{2}$ variables. Thus, any spin-singlet state can be written with $2s$ valence bonds emanating from each site and terminating on different sites. (The symmetrization implies that we do not distinguish the $2s$ different bonds ending at a given site.)

Our simplest model, and the one with which we will be the most concerned, is an $s=1$ chain. We first present the ground state and then give the Hamiltonian. The VBS ground state is the (unique) state with a single valence bond connecting each nearest-neighbor pair of spins (see Fig. 2). This state was first introduced (as far as we know) in the discussion of the large-n limit of SU(n) chains.[7] Note that, unlike in the dimerized $s=\frac{1}{2}$ ground state,[5] the translational symmetry is unbroken. To find a Hamiltonian for which this is the ground state, note that the presence of a valence bond between each

FIG. 2. The spin-1 valence-bond-solid state.

neighboring pair implies that the total spin of each such pair cannot be 2. (After contracting two of the $s=\frac{1}{2}$ variables to form a singlet, the remaining $s=\frac{1}{2}$'s could form either a triplet or a singlet.) Thus, we choose our Hamiltonian to be a sum of projection operators onto spin 2 for each neighboring pair:

$$\begin{aligned} H &= \textstyle\sum_i P_2(\mathbf{S}_i+\mathbf{S}_{i+1}) \\ &= \textstyle\sum_i [\frac{1}{2}\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\frac{1}{6}(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^2+\frac{1}{3}]. \end{aligned} \tag{1}$$

Clearly, the ground-state energy is zero. We will calculate the exact ground-state correlation function below and prove the existence of a gap in Ref. 6. For a finite chain with open boundary conditions, there are several ground states, but we will prove in Ref. 6 that there is a unique ground state in the infinite-volume limit.

Various generalizations of this model immediately suggest themselves. The most interesting one is perhaps an $s=\frac{3}{2}$ anitferromagnet on a hexagonal (honeycomb) lattice. The VBS ground state has a single valence bond connecting each neighboring pair. The Hamiltonian is a projection operator onto spin 3 for each neighboring pair. The VBS state has no projection onto spin 3 for any pair because two of the six effective spin $\frac{1}{2}$'s on each pair of sites are contracted to form a singlet, allowing a maximum possible spin of 2. We will prove in Ref. 6 that the correlation function decays exponentially for this model. This implies that the ground state is not Néel ordered. We believe that there is a unique ground state in this model in the infinite-volume limit and that there is a gap, but we are unable to prove either of these conjectures. In general, there is a solvable model with a VBS ground state whenever $2s$ equals the coordination number of the lattice. The ground state has one valence bond on each lattice link and the Hamiltonian projects out spin $2s$ for each neighboring pair. More generally, there are solvable models with $2s$ equal to an integer multiple, n, of the coordination number, the ground state now containing n valence bonds on each lattice link. The Hamiltonian is a sum of projection operators for pairs of neighboring spins, onto spin $s'>2s-n$, with positive coefficients:

$$H=\sum_{\langle ij\rangle}\sum_{s'=2s-n+1}^{2s} a_{S'}P_{S'}(\mathbf{S}_i+\mathbf{S}_j), \tag{2}$$

with all $a_{S'}>0$. We refer to such a ground state as a valence-bond solid because the valence-bond structure mimics the lattice. This state can only exist if the lattice type and spin magnitude are commensurate in the way described above.

On the basis of the rigorous results mentioned above for $s=1$ in one dimension and $s=\frac{3}{2}$ on a hexagonal lattice, it is tempting to conclude that VBS states might generally have exponential decay, a gap, and no Néel order. However, this may not be the case in general. We will show[6] that the VBS state on a Cayley tree actually *has* Néel order for sufficiently large coordination number. Thus, we might expect Néel order for regular lattices of sufficiently high coordination number and dimension. We will relate this issue to the properties of certain random walks on the same lattice.[6] We generally refer to the VBS *phase* as the phase with a unique ground state, exponential decay, a gap, and no Néel order. We expect that it occurs for a range of Hamiltonians including the solvable ones and, in one dimension, the realistic ones. By the VBS *state*, we mean the state constructed simply out of valence bonds, as described above. With this terminology some Hamiltonians with a VBS *ground state* may not be in the VBS *phase.*

Other simple valence-bond ground states also exist which, unlike the VBS state, have only a period-2 translational symmetry. We will generally refer to these as dimerized ground states. The simplest example is the $s=\frac{1}{2}$ chain of Majumdar and Ghosh[5]:

$$\begin{aligned} H &= \textstyle\sum_i P_{3/2}(\mathbf{S}_i+\mathbf{S}_{i+1}+\mathbf{S}_{i+2}) \\ &= \textstyle\frac{4}{3}\sum_i [\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\frac{1}{2}\mathbf{S}_i\cdot\mathbf{S}_{i+2}+\frac{3}{8}], \end{aligned} \tag{3}$$

where $P_{3/2}$ projects onto spin $\frac{3}{2}$. The dimerized states of Fig. 1 have neighboring pairs of spins combined to form a singlet, and therefore each group of three neighboring spins is in an $s=\frac{1}{2}$ state.

This model has a direct generalization for arbitrary spin.[8] For an $s=1$ chain, a solvable Hamiltonian is a sum of projection operators onto spin 0, 2, and 3, with positive coefficients, for each group of three neighboring spins. The dimerized states with double valence bonds between pairs of neighboring spins (see Fig. 3) are ground states, since two of the spins in each group of three neighboring spins are contracted to form a singlet so that the total spin of the three spins is necessarily 1. The VBS state is *not* a ground state in this case, since in that state groups of three neighboring spins have a projection onto $s=0$. We expect that the two dimerized states are the only ground states. This construction generalizes to arbitrary spin s.[8] H is a sum of projections onto all spins but s, with positive coefficients, for each group of three neighboring spins. The ground state has $2s$ valence bonds on every second link.

There also exist Hamiltonians with partially dimerized ground states. Two such states for an $s=\frac{3}{2}$ chain are shown in Fig. 4. To construct a Hamiltonian for which these are the ground states, we begin with the sum of the projections onto $s=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$ for each group of three neighboring spins. The states in Fig. 4 are ground states, since each group of three neighboring spins contain three

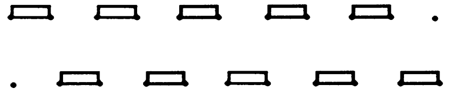

FIG. 3. The spin-1 dimerized states.

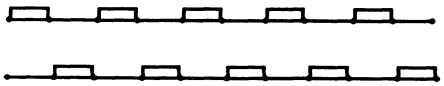

FIG. 4. The spin-$\frac{3}{2}$ partially dimerized states.

valence bonds and so have a maximum spin of $s=\frac{3}{2}$. The fully dimerized states which alternate between three and zero valence bonds between adjacent sites are also ground states. We expect that these fully dimerized ground states can be eliminated by adding to the Hamiltonian the projection onto $s=3$ for each pair of adjacent spins.

We now outline the calculation of the exact correlation function for the $s=1$ VBS model (more details will be given in Ref. 6). We label the two states of a spin-$\frac{1}{2}$ variable as ψ_α, where $\psi_1=(+)$ and $\psi_2=(-)$, and $\{(+),(-)\}$ is the standard S_z eigenstate basis. We will define a *raised* index by multiplication by ϵ: $\psi^\alpha \equiv \epsilon^{\alpha\beta}\psi_\beta$. Here $\epsilon^{\alpha\beta}$ is the antisymmetric tensor with $\epsilon^{12}=1$, and we use a summation convention for repeated indices. The Hermitian-conjugate state to ψ_α will be defined with a raised index $\psi^{\dagger\alpha}$. The normalization is given by $\psi^{\dagger\alpha}\psi_\beta=\delta^\alpha_\beta$, where δ^α_β is the Kronecker-δ tensor, the unit matrix. A valence bond between two spins corresponds to the state $\psi^\alpha \otimes \psi_\alpha$.

Our notation for higher spin is based on the representation of spin s as $2s$ symmetrized spin-$\frac{1}{2}$ variables. Thus, we write a spin-1 variable as $\psi_{\alpha\beta}=(\psi_\alpha\otimes\psi_\beta+\psi_\beta \otimes\psi_\alpha)/\sqrt{2}=\psi_{\beta\alpha}$. The VBS state for an open chain of N spins is

$$\chi_{\alpha_1}^{\alpha_{N+1}}=\psi_{\alpha_1\alpha_2}\otimes\psi^{\alpha_2\alpha_3}\otimes\psi_{\alpha_3\alpha_4}\otimes\psi^{\alpha_4\alpha_5}\otimes\cdots\otimes\psi^{\alpha_N\alpha_{N+1}},$$

where the pairs of symmetrized indices label the spin-1 variables along the chain. The basic result needed to obtain the correlation function is the ground-state normalization, $\chi^{\dagger\beta_1}_{\beta_{N+1}}\chi^{\alpha_{N+1}}_{\alpha_1}$. This is given by a product of N factors $(\delta^{\alpha_i}_{\beta_i}\delta^{\alpha_{i+1}}_{\beta_{i+1}}+\delta^{\alpha_i}_{\beta_{i+1}}\delta^{\alpha_{i+1}}_{\beta_i})$. Expanding the N factors and contracting all indices gives a geometrical sum which can be evaluated exactly, giving

$$\chi^{\dagger\beta_1}_{\beta_{N+1}}\chi^{\alpha_{N+1}}_{\alpha_1}=\frac{3^N-1}{2}\delta^{\beta_1}_{\alpha_1}\delta^{\alpha_{N+1}}_{\beta_{N+1}}+\delta^{\beta_1}_{\beta_{N+1}}\delta^{\alpha_{N+1}}_{\alpha_1}. \tag{4}$$

Acting on the VBS state with the spin operators, we find that $S^a_0 S^b_r$ breaks the string of valence bonds on one of the two links adjacent to site 0 and on one of the two links adjacent to site r, producing a product of two VBS states with the spin indices contracted with two Pauli matrices. Thus, the correlation function is determined by (4). We find, for an infinite chain,

$$\langle S^a_0 S^b_r\rangle=\delta^{ab}(-1)^r\tfrac{4}{3}3^{-r}\ (\text{for all } r>0).$$

Thus, the correlation function decays exponentially with correlation length $1/\ln 3 \approx 0.9$.

Our solvable Hamiltonian of (1) is a special case of the general bilinear-biquadratic Hamiltonian

$$H=\textstyle\sum_i[\mathbf{S}_i\cdot\mathbf{S}_{i+1}-\beta(\mathbf{S}_i\cdot\mathbf{S}_{i+1})^2],$$

with $\beta=-\frac{1}{3}$. The model with $\beta=1$ has been solved by the Bethe *Ansatz* method.[9] It has a unique ground state with *no* gap and appears to have *power-law* decay by standard field-theory arguments. We expect that $\beta=1$ is a critical point separating the VBS and dimerized phases (for $\beta<1$, and $\beta>1$, respectively). Translational symmetry is broken in one phase, but not the other. Exponential decay and a gap hold in both. A critical theory of this phase transition is given by Affleck[10] and Affleck and Haldane.[10] This picture is supported by finite-chain calculations.[11] For a *finite* even chain in the dimerized phase there is a unique ground state which is the symmetric combination of the two dimerized states. There is also an exponentially low-lying momentum-π singlet state which is the antisymmetric combination. For a finite odd chain, the ground state has spin 1 since there is one unpaired spin. We gave Hamiltonians above which had the simple dimerized ground states of Fig. 3. We can support this phase diagram by using the simple VBS and dimerized states as trial ground states for arbitrary β. The expectation of H (per link) in the VBS, dimerized, and Néel states is $(-\frac{4}{3}-2\beta)$, $(-1-8\beta/3)$, and $(-1-2\beta)$, respectively. Thus, the Néel state never has lowest energy while the VBS state is lowest for $\beta<\frac{1}{2}$, and the dimerized state for $\beta>\frac{1}{2}$. Of course, improving these variational VBS and dimerized states would change the estimated critical value of β.

For the realistic Hamiltonian with $\beta=0$, the energies are $-\frac{4}{3}$, -1, and -1. The exact value, obtained from finite-size extrapolation[12] is about -1.40. Since the VBS state is only higher in energy by about 0.07, it appears to be a good variational ground state. Perhaps more importantly, it provides a simple, intuitive picture of the nondegenerate massive phase.

A similar picture of the β dependence of the ground state is obtained from the large-n limit.[7] An SU(n) generalization of the bilinear spin-1 chain is obtained by letting the indices α run over $1,2,3,\ldots,n$. For the bilinear Hamiltonian, the VBS and dimerized states discussed above are both ground states in the large-n limit.[7] This is so because in that limit, H simply counts the number of nearest-neighbor valence bonds. The biquadratic term, in the large-n limit simply counts the number of nearest-neighbor *double* valence bonds.[6] Thus, the ground state is the VBS state for $\beta>0$, and the dimerized state for $\beta<0$. A first-order phase transition occurs at $\beta=0$. For the ordinary SU(2) case we expect the transition to be second order.[10]

A difference between integer and half-odd-integer spin chains, first predicted by Haldane,[1] emerges from the set of simple valence-bond states, as was observed earlier, in the context of the large-n limit.[7] While integer-spin chains can be in dimerized or VBS states, half-odd-integer spin chains are necessarily at least partially dimerized. Of course, if the Hamiltonian is modified, the valence bonds could "resonate"[3] and the broken translational symmetry could then be restored. If this happens, leading to a unique ground state, the rigorous results of Affleck and Lieb[13] prove that there is a vanishing gap for half-odd-integer s. On the other hand, integer-spin chains *can* have ground states of unbroken symmetry with a gap, as our example proves. Thus, we have rigorously established that there is a difference between integer and half-odd-integer spin chains.

The work of one of us (H.T.) is supported in part by National Science Foundation Grant No. PHY-85-15288-A01, and that of another (I.A.) is supported in part by National Science Foundation Grant No. PHY-80-19754. One of us (I.A.) is a Fellow of the A. P. Sloane Foundation and the Canadian Institute for Advanced Research, and another of us (T.K.) is a National Science Foundation Post-doctoral Fellow.

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