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Systems with resonating-valence-bond ground states: Correlations and excitations

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We consider a resonating-valence-bond state as a variational estimate for the ground state of a Heisenberg antiferromagnet. We derive an expression for the normalization of this wave function, which is a superposition of a very large number of singlet pair states, which we then use to show that the singularities, correlations, and low-lying excitations of this quantum system can be calculated from the partition function of a related dimerlike classical statistical mechanics problem. Possible calculational schemes are discussed.

The conventional understanding of spin systems interacting by the Heisenberg antiferromagnetic Hamiltonian $H=\sum J_{jk}\mathbf{S}_j\cdot\mathbf{S}_k$, is that the ground state is close to the Néel state with a staggered sublattice magnetization S evident in the two-spin correlation function $\langle \mathbf{S}_j\cdot\mathbf{S}_k\rangle \rightarrow (-1)^{j-k}S^2$. The excitations are built upon this state as spin waves.[1] This is expected to be valid for cubic lattices and large spin.

However, for spin-$\frac{1}{2}$ and low-dimensional lattices with significant frustration, this picture is incorrect.[2] For instance, the one-dimensional Heisenberg antiferromagnetic chain can be solved exactly, and the ground state is not of the Néel type.[3] For this reason, Anderson[4] proposed that in certain situations the ground state is actually closer to one in which pairs of spins are bound into singlet states. These pairs are visualized as valence bonds, and since in general there will be several alternative ways in which to pair the spins, the actual ground state will be a superposition over such products of singlet pairs—hence the resonating-valence-bond (RVB) state. Subsequent numerical work explored this possibility[5,6]

In fact, beginning with the work of Majumdar and coworkers,[7-9] and extended by Shastry and Sutherland,[10-12] many examples of spin systems have been found for which the ground state is exactly a product of singlet pairs (SP's). The resulting SP state is very similar to the spin Peierls state, although in this instance stabilization is provided by lattice topology instead of lattice distortion. Shastry and Sutherland[11] even found an exactly soluble one-dimensional example with a doubly degenerate SP ground state—hence an RVB ground state—which they could exploit to calculate approximately the excited states as solitons.

In this paper, we first introduce a method of calculation for RVB states, thus extending the results of Ref. 11 to cases of higher dimensionality and degeneracy. (Previously rules for calculation were presented in the early work of Rumer[13] and Pauling.[14]) We then proceed to use these results to relate the low-temperature properties of the quantum RVB system to the critical behavior of a classical thermodynamic system. This we feel is the most significant part of this paper. In particular, we demonstrate a relationship of the ground-state properties of the RVB problem to a classical statistical mechanics problem of the covering of a lattice by dimers first solved by Kasteleyn,[15,16] and Temperley and Fisher.[17,18] These papers in turn made use of powerful techniques of Kac and Ward.[19]

Recently, Anderson[20,21] has proposed that the RVB model may be important for the understanding of high-T_c superconductivity. These methods will apply as well to this model.

As our principal example, we consider a two-dimensional square lattice with $2N$ sites, and $4N$ bonds. A dimer is simply a line drawn from a site to one of its four nearest neighbors; we say the dimer sits on this pair of nearest-neighbor sites. A dimer covering is when every site is connected to exactly one of its nearest neighbors by a dimer. This obviously requires N dimers, and covers $\frac{1}{4}$ of the lattice bonds. We denote a particular dimer covering by an index a. The number of such coverings is[16] $Z_D=\sum_a 1=\exp(2NG/\pi)=(1.791\,622\ldots)^N$, where $G=1^{-2}-3^{-2}+5^{-2}-\cdots=0.915\,965\ldots$ is Catalan's constant.

Assume the dimers of a dimer covering sit on pairs of nearest-neighbor sites (j,k). Then we associate with this dimer covering a singlet-pair (SP) state ψ_a consisting of a product over dimers (j,k) of the dimer covering a, of singlet states $[j,k]=(\uparrow_j\downarrow_k-\downarrow_j\uparrow_k)/\sqrt{2}$. It only remains to specify the phase (sign) of the wave function. The singlet $[j,k]$ will be represented when necessary by an arrow on the dimer (j,k) pointing from k to j. Then the convention for ψ_a is that all arrows point right to left or down to up. In Fig. [1(a)] we show such a state ψ_a.

These basis states are not orthogonal, and we now need to calculate overlap matrix elements $\psi_b^\dagger\psi_a$ between two SP states ψ_a and ψ_b. We show ψ_b in Fig. 1(b), and in Fig. 1(c), we show the overlap $c=a+b$. We see that the transition or matrix element graph c of Fig. 1(c) is made up of closed loops u, each consisting of an even number $2L(u)$ of links. This we call a loop covering c, since each site sits on exactly one loop. A diagonal element $c=a+a$ is a loop covering with loops all of length 2, and each loop of c sits on a dimer of a.

We can evaluate the overlap of each loop u separately, by summing over the spins. Clearly a loop of length 2 gives unity upon summing over spins, since the singlet states are normalized. Consider a loop of length $2L(u)$. Upon summing over spins, the only nonzero elements are those corresponding to Néel states, where the spins alter-

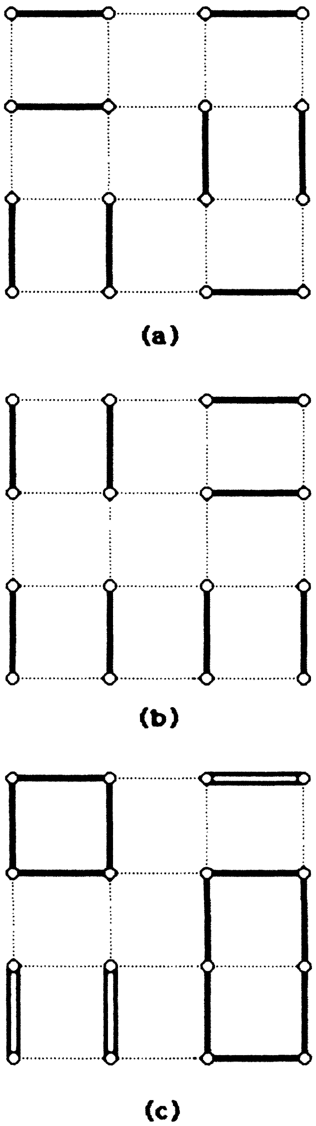

FIG. 1. (a) Shows the dimer covering a corresponding to the SP state a; (b) shows the dimer covering b corresponding to the SP state b; and (c) shows the loop covering $c = a+b$ corresponding to the matrix element $\psi_b^\dagger\psi_a$.

nate signs around the loop. There are two such states, and each has weight $2^{-L(u)}$ from the singlet normalization. The sign is positive, as can be seen from the following argument: Suppose we had picked the singlet phases to correspond to all arrows going clockwise around the loop. Then considering a Néel state the total phase would be $(-1)^{L(u)}$. However, our phase convention reverses exactly half the arrows, and so differs by a phase $(-1)^{L(u)}$. Thus, the sign is positive.

Therefore, the final result for the matrix element $c = a+b$ is $\psi_b^\dagger\psi_a = \prod_u 2\cdot 2^{-L(u)}$. The product is over all loops u in the loop covering c. This result can be simplified somewhat. Let $P_{2L}(c)$ be the number of loops of length $2L$ in the loop covering c, with $P(c)$ as the total number of loops. Then $2N = \sum_L 2LP_{2L}(c)$, so

$$\psi_b^\dagger\psi_a = \prod_u 2\cdot 2^{-L(u)} = 2^{P(c)-N} .$$

This is a particularly simple result.

It will be clear when we evaluate the energy matrix elements, that it is to our advantage to maximize the number of cross terms. Thus, we try as a variational wave function the RVB state $\psi = \sum_a \psi_a$, where the summation is over all dimer coverings a, or equivalently over all SP states ψ_a. Then the normalization is

$$\psi^\dagger\psi = \sum_b\sum_a \psi_b^\dagger\psi_a = \sum_c 2^{P(c)} w(c)/2^N .$$

The weight $w(c)$ is present because several different dimer coverings a,b can lead to the same loop covering $c = a+b$. In fact for a loop u of length $2L(u)$, with $L(u)$ greater than 2, i.e., nonzero area, alternate links could come from either a or b. Thus $w(c)$ has a factor of 2 for each loop of length greater than 2, or since $P_2(c)$ is the number of loops of length 2 in c,

$$w(c) = 2^{P(c)-P_2(c)} ,$$

and

$$\psi^\dagger\psi = \sum_c 2^{2P(c)-P_2(c)}/2^N .$$

The very important point we now want to make is that all terms in the summation are positive, the number of terms is exponential in N, so that we can interpret the logarithm of the weight as an entropy, and the summation as a partition function. In fact let us define a more general partition-generating function $Z(x)$ by

$$Z(x) = \sum_c 2^{P(c)-P_2(c)}(x/2)^{N-P(c)} .$$

Then we see that $Z(0) = Z_D$, $Z(1) = \psi^\dagger\psi$, $Z(2) = Z_D^2$. Other selector variables will be added to this basic partition function as needed.

A second point, important for numerical work, is that the weight for a loop covering c is a product of weights for the individual loops u of c. Each loop has a weight of 2 if it is of length 2, and 4 otherwise. (The overall factor 2^{-N} is not important.)

We wish to use this RVB wave function to make a variational estimate of the ground-state energy of the antiferromagnetic Heisenberg Hamiltonian $H = \sum_{\text{NN}} \sigma\cdot\sigma'$. We *do not* claim that the RVB state is necessarily the lowest-energy state for the square lattice. We only use this system to illustrate the technique, and assume that the RVB state will be stabilized by other means, such as next-nearest-neighbor interactions. The summation is over the $4N$ nearest-neighbor bonds. The variational estimate is understood as $E = \psi^\dagger H\psi/\psi^\dagger\psi = 4N\langle\sigma\cdot\sigma'\rangle$, where the average is an average over all the $4N$ bonds, and all the loop coverings c, with the appropriate weight.

We now examine particular matrix elements $\psi_b^\dagger\sigma\cdot\sigma'\psi_a$, for a loop covering $c = a+b$. We distinguish three cases, illustrated in Fig. 2, where a dashed line represents the operator $\sigma\cdot\sigma'$: (a) the dashed line is on a covered link of c; (b) the dashed line connects disjoint loops of c; (c) the dashed line connects two parts of a single loop of c.

It is clear that case (a) gives ε_s times the matrix element $\psi_b^\dagger\psi_a$, where $\varepsilon_s = -3$ is the singlet energy. Using simple identities, one can also establish that for case (c) we likewise have $\varepsilon_s\psi_b^\dagger\psi_a$, while for case (b) the phases on

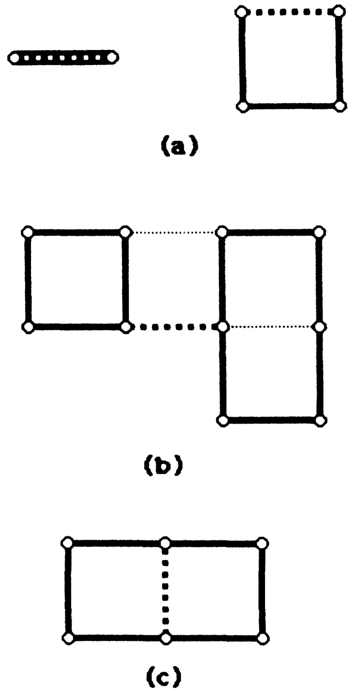

FIG. 2. (a) Demonstrates two examples of case (a), when the term in the Hamiltonian coincides with a link of the loop covering; (b) demonstrates an example of case (b), when the term in the Hamiltonian connects two disjoint loops of the loop covering; and (c) demonstrates an example of case (c), when the term in the Hamiltonian connects two sites of a single loop of the loop covering.

each disjoint piece cancel, so we have zero. [If we were to consider another lattice with cycles of bonds of odd length, such as the triangular lattice, then the matrix element for case (c) would be $\pm\varepsilon_s\psi_b^\dagger\psi_a$, depending on whether the dashed bond divides the loop into even or odd subloops.]

Thus, we have established that

$$\psi_b^\dagger H\psi_a=\sum_u E(u)\psi_b^\dagger\psi_a\ ,$$

where the summation is over all loops u in $c=a+b$. The quantity $E(u)/\varepsilon_s$ is the length of the loop u plus the number of bonds connecting two sites on the loop. It is very important for numerical work that the energy $E(c)$ of the loop covering c can be expressed as a sum of the energies of individual loops, by $E(c)=\sum_u E(u)$. Also, these results confirm the assertion we made earlier, that the presence of cross terms lowers the energy. Thus, our final result is

$$\psi^\dagger H\psi=\sum_c E(c)2^{2P(c)-P_2(c)}/2^N\ .$$

Let us now extend our definition of the partition function to

$$Z(x,y)=\sum_c 2^{P(c)-P_2(c)}(x/2)^{N-P(c)}y^{E(c)}\ .$$

Then we end with the tidy expression for the variational estimate of the energy $E=\partial\ln[Z(1,y)]/\partial y\,|_{y=1}$.

The analogy with statistical mechanics is clear. We may interpret $y^{E(c)}$ as the Boltzmann factor $e^{-E(c)/kT}$, and so we are to evaluate the energy in the limit of high temperature. The entropy as a function of energy E is simply the logarithm of the partial sum over all loop coverings c with $E(c)=E$. Free energy is related to the partition function in the usual way.

We will push the analogy with statistical mechanics further. Suppose the Hamiltonian had not been homogeneous and isotropic, but instead the interaction on different classes of bonds, such as horizontal and vertical, had different strengths J_s. Then it would be reasonable to weight the different classes of dimers in the trial wave function with different activities z_s. We then construct the partition function

$$Z(x,y,\{z_s\})=\sum_c 2^{P(c)-P_2(c)}(x/2)^{N-P(c)}\,y^{E(c,J)}\prod_s z_s{}^{G(s,c)}\ .$$

The quantity $G(s,c)$ is the number of times a link of type s occurs in the loop covering c. Then applying the variational principle, we determine

$$E(\{J_s\},\{z_s\})=\partial\ln[Z(1,y,\{z_s\})]/\partial y\,|_{y=1}\ .$$

Finally, we are to choose z_s so that $E(\{J_s\},\{z_s\})$ is a minimum. Thus, we have an energy minimum principle, rather than a free-energy minimum principle.

Now it is reasonable to suppose that singularities of the resulting $E(\{J_s\})$ occur when the corresponding z_s move across the singularities of $Z(1,1,\{z_s\})$, since the energy is just another thermodynamic function, and it is really the nature and singularities of the correlations themselves which are fundamental.

To go further, let us consider the partition function $Z(x,1,\{z_s\})$. We have agreed that it is the singularities of $Z(1,1,\{z_s\})$ which determine the phase diagram of the full problem. But $Z(x,1,\{z_s\})$ extrapolates between the exactly solvable dimer problem $Z_D(\{z_s\})$ and $Z_D^2(\{z_s\})$ as end points, when x varies between 0 and 2. In fact, the case of small x can usefully be viewed as a slight dilution of the pure dimer problem. It seems to us a reasonable conjecture that the physical problem for $x=1$ might then be in the same universality class as the dimer problem. Right or wrong, this is a very interesting conjecture, for the homogeneous dimer problem on a square lattice is equivalent to the Ising model at the critical point. However, a lattice system at the critical point has algebraic decay of correlations, while a lattice system off the critical point has exponential decay of correlations. As we shall soon see, exponential decay is associated with an energy gap for the low-lying excitations. It is not until we destroy the translational invariance of the dimer system by alternating the bond strengths that we move from the critical point. The dimer problem in general is soluble, and the nature of the correlations is sensitive to the exact form of the lattice.

We now wish to estimate the low-lying excitations, so as to determine the nature of the dispersion curves. Suppose that we break a singlet, and leave two up spins in its place. In order that we not have to break another singlet, the separation between the two spins must be odd. We now examine the overlap between two such states. The corresponding loop covering $c=a+b$ will now have loop segments connecting pairs of spins, one from each of the states a and b. Therefore, the distance between two such spins must always be even. Since there is no obvious energy advantage to pairing in the two-dimensional problem, a situation very different from the one-dimensional case, for now we assume this to be so, and consider each overturned spin individually. Thus, we try a trial wave function

$$\psi(k)=\sum_r\sum_a e^{ikr}\psi_a(r) \ ,$$

where $\psi_a(r)$ is the state with the overturned spin at r, and otherwise a dimer configuration a. (The second spin from the broken singlet we place at infinity.) Then our variational estimate is

$$E(k)=\partial\ln[Z(1,y\,|\,k)]/\partial y\,|_{y=1} \ ,$$

where

$$Z(1,y\,|\,k)=\sum_r\sum_{r'} e^{ik(r-r')}\sum_{c(r,r')}2^{2P(c)-P_2(c)}y^{E(c)}/2^N \ .$$

The notation $\sum_{c(r,r')}$ denotes a sum over loop coverings with a loop segment of even length between r and r'. Normalizing by subtracting off the ground-state energy, we arrive at the final result:

$$\begin{aligned}\omega(k)&=E(k)-E=\partial\ln[S(k\,|\,y)]/\partial y\,|_{y=1}\\&=S'(k\,|\,1)/S(k\,|\,1) \ ,\end{aligned}$$

where $S(k\,|\,y)$ is the structure factor, equal to the Fourier transform of the pair correlation function $g(r\,|\,y)$:

$$g(r-r'\,|\,y)=\frac{\sum_{c(r,r')}2^{2P(c)-P_2(c)}y^{E(c)}}{\sum_c 2^{2P(c)-P_2(c)}y^{E(c)}} \ .$$

This formula bears a striking resemblance to Feynman's theory for the excitations in superfluid liquid helium, where the peak in the structure factor is responsible for the roton minimum.

A general feature of our dispersion is that, since $g(r\,|\,y)$ is zero unless r is even, $\omega(k+\pi/a)=\omega(k)$ where a is the lattice constant. Thus the dispersion relation is characteristic of a sublattice of even sites and lattice constant $\sqrt{2}a$. Further, if the ground state were to have long-range order and thus a nonzero interfacial tension and exponential decay of correlations, a simple calculation for long wavelength or small k would verify an energy gap as in Ref. 11. However, arguments[22] indicate that instead the ground state is in the same universality class as the pure dimer problem, and thus at a critical point. Thus, we expect gapless excitations, as found by Baskaran, Zou, and Anderson[21] for a mean-field RVB state.

Similarly, by introducing vacancies into the magnetic system, and allowing them to hop from site to site, we may treat the strongly repulsive Hubbard model near a half-filled band by the same techniques.

Note added. After this manuscript was submitted for publication, it was pointed out to us that a similar approach has been taken by Iske and Caspers.[23] They, however, are more interested in numerical evaluation of general RVB states, and less in the partition function analogy we advocate. The following points in their paper support our simple RVB state: (1) our state gives a reasonable estimate of the energy; (2) this estimate is not significantly improved by longer-ranged spin pairs or changes of phase; (3) our state has the correct phase by a theorem of Marshall.

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