Some New Variational Resonating-Valence-Bond-Type Wave Functions for the Spin-$\frac{1}{2}$ Antiferromagnetic Heisenberg Model on a Square Lattice

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We consider a class of singlet resonanting-valence-bond wave functions on a square lattice, with the bond-length distribution as a variational parameter. This class contains the two limiting cases of the dimer wave function and of the Néel state. We present numerical calculations of the energy and the spin-spin correlation functions up to very large lattice sizes (180×180) both for disordered states with exponentially decaying correlation functions and for ordered states. The energy of a disordered state can be within 0.1% of our best ordered state ($-0.3344J$/bond).

The resonating-valence-bond (RVB) theory of high-T_c superconductivity recently developed by Anderson and co-workers[1] has been shown to be consistent with many striking experimental data. Its starting point is simply a two-dimensional large-U Hubbard model on a square lattice, which at half filling becomes a spin-$\frac{1}{2}$ Heisenberg antiferromagnetic model. This model has been extensively studied by many different techniques: spin-wave theory,[2] variational calculations,[3-5] exact diagonalization of small systems,[6] and Monte Carlo simulations.[7-9] For the spin-$\frac{1}{2}$ model on the square lattice, all these investigations seem to conclude that the ground state has long-range order, with a nonzero staggered magnetization. But in 1D, it is known that quantum fluctuations drive the system into a liquid singlet ground state. The key assumption of the RVB theory is that such a featureless singlet state may exist also in two dimensions, with an energy very close to the ground-state energy. Experimentally, it has indeed been shown that even a very small amount of doping can destroy Néel order. In this Letter, we construct explicitly a series of singlet wave functions with different kinds of long-range order (algebraic and exponential correlations). After optimization, we find that most of them have a very low energy, comparable to the best estimate previously found ($E = -0.334J$/bond).[10]

Let us consider then a spin-$\frac{1}{2}$ antiferromagnetic Heisenberg Hamiltonian on a square lattice. For any bipartite lattice, it is known that the ground state of such a Hamiltonian is a singlet.[3] Furthermore, Marshall has shown that the ground-state wave function written in the s^z representation is real, with a sign given by

$$\text{sgn}[\Psi(\sigma_1, \ldots, \sigma_n)] = (-1)^{P(\sigma_1, \ldots, \sigma_N)}, \qquad (1)$$

where

$$|\Psi\rangle = \sum_{\{\sigma_i\} = \pm 1} \Psi(\sigma_1, \ldots, \sigma_N) |\sigma_1, \ldots, \sigma_N\rangle$$

and $P(\sigma_1, \ldots, \sigma_N)$ denotes the number of down spins on sublattice A, for the spin configuration $(\sigma_1, \ldots, \sigma_N)$.

Moreover, it is possible to write any singlet state as a linear superposition of valence-bond states, corresponding to all possible pairings of sites into singlets. In order to enforce Marshall's sign rule, it is sufficient (but not necessary) to consider only bonds from one sublattice (A) to the other (B). We shall then introduce the following class of wave functions:

$$|\psi\rangle = \sum_{\substack{i_a \in A \\ j_\beta \in B}} h(i_1 - j_1) \cdots h(i_n - j_n)(i_1 j_1) \cdots (i_n j_n).$$

$$(2)$$

In Eq. (2), h stands for any positive function and can be interpreted as a weight factor for a bond as a function of its length. Also, for any two lattice sites i and j, (ij) represents a singlet bond connecting them. Indeed, for any configuration, with bonds from sublattice A to B only, Marshall's sign rule [Eq. (1)] is clearly satisfied. Any superposition of such valence-bond states with a positive amplitude will preserve this property. However, in Eq. (2), we have made the strong assumption that the amplitude in the wave function can be factorized into a product over bond amplitudes. Actually, calculations for small systems[11] have shown that our taking into account the inequivalence between dimer configurations has a much smaller effect on the ground-state energy than allowing longer bonds.[12]

Among all the states which can be described by Eq. (2), one limit is provided by the dimer wave function investigated by Sutherland,[13] as a model for an RVB state with short-range correlations. In the other limit, when the weight factor h is taken to be independent of the bond length, we get the projection of the Néel state on the singlet subspace. If h decreases with distance, by tuning its decay rate, we get a smooth way to transform a Néel state into a disordered state. In the intermediate stages of this process, we expect to find a featureless, liquidlike singlet, similar to the RVB state proposed by Anderson.

Another interesting feature of these wave functions is that the calculation of expectation values for the energy and the spin-spin correlation functions can be implemented with only a few simple rules. In order to calculate overlaps between two valence-bond configurations $|c_1\rangle$ and $|c_2\rangle$, and matrix elements of $S_i \cdot S_j$ between those states, we need first to consider the loop covering[13] of the plane associated to the configurations $|c_1\rangle$ and $|c_2\rangle$ (see Fig. 1). We have then the following rules: (i) $\langle c_1 | c_2 \rangle = 2^{N(c_1,c_2)}$, where $N(c_1,c_2)$ is the number of loops in the loop covering $\langle c_1 | c_2 \rangle$. (ii) $\langle c_1 | S_i \cdot S_j | c_2 \rangle = 0$ if i and j belong to two different loops. (iii) $\langle c_1 | S_i \cdot S_j | c_2 \rangle = \mp \frac{3}{4} \langle c_1 | c_2 \rangle$ if i and j belong to the same loop, with a minus sign when i and j belong to two different sublattices, and a plus sign otherwise.

It is important to note that this construction can be made only for a bipartite, and then unfrustrated, lattice.

Before discussing our numerical calculations, we would like to emphasize the fact that a wave function as shown in Eq. (2) is not in general equivalent to a Gutzwiller projection of a free Fermi sea. The difference comes from the fact that in order to go from the fermion representation to the spin representation, one has to take always the same ordering of the lattice sites. This induces an extra sign which cannot, in general, be expressed as a product over bond amplitudes.

We use a Monte Carlo method to evaluate the spin-spin correlation $C_{ij} = \langle \psi | S_i \cdot S_j | \psi \rangle$. Upon substitution of the wave function Eq. (2), it becomes a weighted sum over the ratio $c_{ij} = \langle c_1 | S_i \cdot S_j | c_2 \rangle / \langle c_1 | c_2 \rangle$:

$$C_{ij} = \sum_{c_1,c_2} P(c_1,c_2) \frac{\langle c_1 | S_i \cdot S_j | c_2 \rangle}{\langle c_1 | c_2 \rangle}, \tag{3}$$

where

$$w(c) = \prod_{a=1}^{n} h(i_a - j_a), \quad |c\rangle = \prod_{a=1}^{n} (i_a j_a),$$

$$P(c_1,c_2) = w(c_1) w(c_2) \langle c_1 | c_2 \rangle / \langle \psi | \psi \rangle.$$

Since the number of terms in the sum grows exponentially with the size of the system, the phase space to be summed over can be considered as an ensemble of pairs
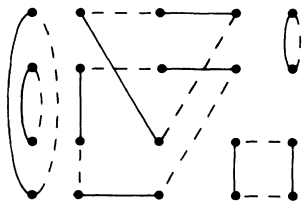

FIG. 1. The loop covering $\langle c_1 | c_2 \rangle$ is obtained by the overlapping of two sets of bonds $|c_1\rangle$ (solid lines) and $|c_2\rangle$ (dashed lines) on a square lattice. Each lattice site is connected by two bonds to form loops. A loop has half of its bonds from $|c_1\rangle$ and half from $|c_2\rangle$. In this example, there are six loops.

(c_1,c_2) with probability distribution $P(c_1,c_2)$. This interpretation is allowed because $P(c_1,c_2)$ is always positive. We define a fictitious energy for the pair (c_1,c_2), $E = \log P(c_1,c_2)$, and use the standard Metropolis algorithm as usual.[14]

The basic Monte Carlo step is to choose a site i and one of its next-nearest neighbors j at random; exchange the bonds connecting to the sites i and j with the transition probability that satisfies detailed balance. The matrix elements are simply evaluated according to rules (ii) and (iii) once the loop covering associated to the two configurations is known.

For the wave functions dominated by short bonds, we have a more efficient procedure: Find a loop that links only the nearest-neighbor sites with half of its links covered alternatively by dimers; shift all the dimers by one lattice unit along the loop; this gives us a new state. In practice, the loops are chosen by self-avoiding random walks that are biased to make them easy to close. The size of the loop (controlled by the bias) is made sufficiently large to ensure erogdicity. We define the transition amplitude similar to above. Since both Monte Carlo processes leave the weight invariant, any combination of them may be used. In our calculations, boundary conditions are periodic.

We have checked that the equilibrium does not depend on the initial states, which can be taken as short- and long-bond states. The computer program has been checked with the Néel state, where the expected results for correlations and finite-size corrections are recovered, and with diagonalization of a small system.[12]

In our investigation, our strategy has been to start from either the dimer state (the most disordered) or the Néel state and to let h vary around those reference states in order to lower the energy.

(a) Short-bond wave functions.—First, our results confirm that when the maximum bond length is finite, the associated wave function has short-range spin-spin correlations, with an exponential decay at large distances. This result has been obtained in the case of the dimer wave function from an approximate mapping[15] of the loop soup onto an $O(n)$ model with $n = 4$. Our numerical results may provide some indication that this mapping is also valid when longer bonds are included. We notice that after optimization, the correlation length increases quickly as a function of the maximal length of the bonds (see Table I and Fig. 2). The best estimate for the ground-state energy has been obtained by addition of an exponential tail to the weight function h (see Table I). We find $E_0 = 0.3341 J$/bond which is very close to the result of series expansion.[10] In this state the spin-spin correlation function goes to zero at large distance, and so there is no long-range order. At short distance, the correlation function seems to decay algebraically with an exponent around 1. But at large distance, this decay is faster. These results lead us to conclude that there exist some disordered states with a very low energy. This fact

TABLE I. A summary of the short-bond states. The states are defined by their variational parameters $a_l = h(2l+1)/h(2l-1)$ (with use of the Manhattan distance between i and j: $|x_i - x_j| + |y_i - y_j|$), which have uncertainties of about a few percent as estimated from the independent calculations of derivatives of energy. All energies E_0 (in the unit of J/bond) are obtained on a 32x32 lattice with statistical fluctuations 0.0002 from Monte Carlo simulation. The finite-size effect on such a lattice is smaller than the statistical error. For those states, spin-spin correlation functions fall off exponentially. The correlation lengths (ξ) for the first three states are obtained on lattice of sizes 32x32, 90x90, and 180x180. The large lattices are used to avoid finite-size effects. The unit of ξ is the lattice spacing.

State	E_0	ξ	Variational parameters
Dimer	−0.302	1.3	$h(1) = 1$
			$a_l = 0$ for $l > 1$
(1,3)	−0.330	7.1	$a_1 = 0.17$
			$a_l = 0$ for $l > 1$
(1,3,5)	−0.3325	15	$(a_1, a_2) = (0.14, 0.24)$
			$a_l = 0$ for $l > 2$
Exponential	−0.3341	⋯	$(a_1, a_2) = (0.125, 0.25)$
			$a_l = 0.33$ for $l > 2$

shows that an RVB state would be quite competitive compared with an ordered state. In order to make this comparison more accurate, we studied some wave functions with very long bonds.

    (b) *Wave functions with $h(l) = l^{-p}$ for large l.*— We have found that it is possible to generate wave functions with a nonzero staggered magnetization, if h is smooth and falls off asymptotically as $h(l) = l^{-p}$. However, the short-length behavior of h is the most important for the energy, and so we choose the following parametrization for h: $h(1) = 1$, $h(3)$ and $h(5)$ are free parameters, and $h(l) = h(5)(l/5)^{-p}$ for $l > 5$. We have performed the optimizations for the states with $p = 2$, 3, 4, and 5; we found that they all have very low energies, −0.3341, −0.3341, −0.3344, and −0.3337, with staggered magnetization 75%, 65%, 45%, and 30% of the Néel, respectively. The staggered magnetizations are obtained from the correlation function (see Fig. 1) on a 128×128 lattice. It decreases when p increases and seems to disappear when $p > 5$. (For $p = 5$, the correlation can be fitted with an algebraic decay with an exponent 0.6). This behavior is also consistent with what a mapping of the loop soup onto an $O(n)$ model with long-range couplings would give. The optimal energy within this class of states is $-(0.3344 \pm 0.0002)J$/bond, which is lower than what has been shown for the short-bond states (the error bar is derived from the statistical fluctuation in Monte Carlo sampling). This is consistent with an ordered ground state. However, the energy depends only weakly on the staggered magnetization. This behavior may have some analogy with the 1D spin-$\frac{1}{2}$ chain,
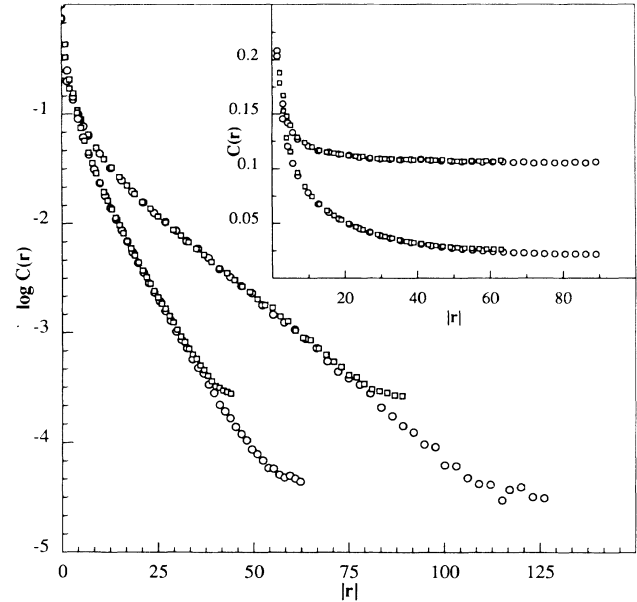

FIG. 2. The spin-spin correlation $C(\mathbf{r}) = (-1)^{x+y} \sum_i \langle \mathbf{S}_i \cdot \mathbf{S}_{i+r} \rangle / N$ as a function of distance. For a ordered state, $C(\mathbf{r})$ is not zero at large distance. This is shown in the upper curve of the inset for the state with bond amplitude $h(l)$ decaying algebraically at large distance, as discussed in the text with $p = 3$. The lower curve of the inset is for the state labeled "Exponential" in Table I. In this case, $C(\mathbf{r})$ goes to zero slowly. The small, but nonzero, value of $C(\mathbf{r})$ at large distance is due to finite lattice size (128×128), since, on a 256×256 lattice, this asymptotic value at large distance is reduced by roughly a factor of 2. For the short-range states with a sharp cutoff for the bond length, $C(\mathbf{r})$ decays exponentially with the distance. The upper and the lower curves in the main plot are states labeled (1,3,5) and (1,3) in Table I. The base of the logarithm is 10. Squares and circles denote $C(\mathbf{r})$ when $\mathbf{r}$ is along the axes and diagonals of the lattice.

where the staggered susceptibility diverges logarithmically with the system size. This implies that the energy does not change much when a staggered magnetization builds in. One might speculate from this that the 2D system could also be close to criticality. This question deserves further studies.

    One consistency check that we have approached the ground state from both the disordered and ordered sides is provided by the fact that after optimization the ratios $h(3)/h(1)$ and $h(5)/h(3)$ are very similar in the states with algebraic and exponential tails.

    It is worthwhile to stress that the spin-spin correlation functions are isotropic, and decay much more slowly with distance than the function h. This behavior is very different from the case of the Gutzwiller-projected free-fermion wave function, where the bond amplitude and the correlation function as well decay like power laws. This difference comes from the fact that we add coherently wave functions which all satisfy Marshall's criterion.

To conclude, we have shown how to generate singlet states which are very close in energy (the relative dispersion lies within 0.5%) and seem to be also close to the best known estimates for the ground-state energy. For the square lattice, those results confirm the claim that RVB is at least not far energetically from the ground state.[1] However, our method has certainly a wide range of application, since it provides a natural description of systems with large quantum fluctuations. For instance, it would be interesting to investigate systems where these fluctuations are strongly enhanced, by the reduction of the coordination number (honeycomb lattice), or by the introduction of frustration[16] (via second-neighbor interaction).

[1]P. W. Anderson, Science **235**, 1196 (1987); P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987); S. Kivelson, D. Rokhsar, and J. Sethna, Phys. Rev. B **35**, 8865 (1987).

[2]P. W. Anderson, Phys. Rev. **86**, 694 (1952); T. Oguchi, Phys. Rev. **117**, 119 (1960).

[3]W. Marshall, Proc. Roy. Soc. (London) **A232**, 48 (1955).

[4]H. Yokoyama and H. Shiba, J. Phys. Soc. Jpn. **56**, 1490 (1987).

[5]D. A. Huse and V. Elser, Phys. Rev. Lett. **60**, 2531 (1988).

[6]J. Oitmaa and D. D. Betts, Can. J. Phys. **56**, 897 (1978).

[7]J. D. Reger and A. P. Young, Phys. Rev. B **37**, 5978 (1988).

[8]T. Barnes and E. Swanson, Phys. Rev. B **37**, 9405 (1988).

[9]E. Manousakis and R. Salvador, Phys. Rev. Lett. **60**, 840 (1988).

[10]D. A. Huse, Phys. Rev. B **37**, 2380 (1988).

[11]P. L. Iske and W. J. Caspers, Physica (Amsterdam) **142A**, 360 (1987).

[12]On 4x4 lattice, after optimization of the only variational parameter $[h(3)/h(1)=0.278]$, the energy and all spin-spin correlations agree completely with the three-digit values quoted in Ref. 6. This result indicates that the factorization of the weight is not a bad assumption. We are grateful to D. Huse for suggesting this test.

[13]B. Sutherland, Phys. Rev. B (to be published).

[14]See, for example, *Applications of the Monte Carlo Method in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1984); details of our method will be explained in future publications.

[15]M. Kohmoto and Y. Shapir, Phys. Rev. B **37**, 9439 (1988).

[16]P. Chandra and B. Doucot, to be published.