Resonating Valence Bond Wave Functions for Strongly Frustrated Spin Systems

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The resonating-valence-bond (RVB) theory for two-dimensional quantum antiferromagnets is shown to be the correct paradigm for large enough "quantum frustration." This scenario, proposed a long time ago but never confirmed by microscopic calculations, is strongly supported by a new type of variational wave function, which is extremely close to the exact ground state of the $J_1 - J_2$ Heisenberg model for $0.4 \lesssim J_2/J_1 \lesssim 0.5$. This wave function is proposed to represent the generic spin-half RVB ground state in spin liquids.

The question of whether a frustrated spin-half system is well described by a spin-liquid ground state (GS)—with no type of crystalline order—25 years after the first proposal [1] is still controversial, mainly because of the lack of reliable analytical or numerical solutions of model systems. For unfrustrated or weakly frustrated quantum antiferromagnets a deep understanding of the nature of the GS together with a quantitative description of the ordered phase is obtained by including Gaussian quantum fluctuations over a classical Néel state [2,3]. For sizable frustration, instead, this description is known to break down. However, the short-range resonating-valence-bond (RVB) state [4] does not prove a good starting point for the description of frustrated models; it rather turns out to be the exact GS of *ad hoc* Hamiltonians [4–6].

As a prototype of a realistic frustrated two-dimensional system, which has been recently realized experimentally in Li_2VOSiO_4 compounds [7], we investigate the spin-half Heisenberg model with nearest (J_1) and next-nearest neighbor (J_2) superexchange couplings:

$$\hat{\mathcal{H}} = J_1 \sum_{nn} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + J_2 \sum_{nnn} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j, \qquad (1)$$

on an N-site square lattice with periodic boundary conditions. In the ($J_2 = 0$) unfrustrated case, it is well established that the GS of the Heisenberg Hamiltonian has Néel long-range order, with a sizable value of the antiferromagnetic order parameter [8]. However, variational studies [9] have shown that disordered, long-range RVB states have energies very close to the exact one. It is therefore natural to imagine that by turning on the next-nearest neighbor interaction J_2, the combined effect of frustration and zero-point motion may eventually melt antiferromagnetism and stabilize a nonmagnetic GS of purely quantum-mechanical nature. Indeed, for $0.4 \lesssim J_2/J_1 \lesssim 0.6$ there is a general consensus on the disappearance of the Néel order towards a state whose nature is still much debated [10].

In a seminal paper [11], Anderson proposed that a physically transparent description of a RVB state can be obtained in fermionic representation by starting from a BCS-type pairing wave function (WF), of the form

$$|\psi_{BCS}\rangle = \exp\left(\sum_{i,j} f_{i,j} \hat{c}_{i,\uparrow}^\dagger \hat{c}_{j,\downarrow}^\dagger\right)|0\rangle. \qquad (2)$$

This WF is the GS of the well-known BCS Hamiltonian with a given (real) gap function $\Delta_k = \Delta_{-k}$ provided the Fourier transform f_k of the pairing function, $f_{i,j}$, satisfies: $f_k = \Delta_k/(\epsilon_k + \sqrt{\epsilon_k^2 + \Delta_k^2})$, where $\epsilon_k = -2[\cos k_x + \cos k_y]$ is the free-electron dispersion. The nontrivial character of this WF emerges when we restrict to the subspace of a fixed number of electrons (equal to the number of sites) and enforce Gutzwiller projection onto the subspace with no double occupancies: singlet pairs do not overlap in real space and this WF can be described by a superposition of valence bond (VB) states [11–13]. Though this WF has been already studied for the pure Heisenberg model by several authors [12,13] for $\Delta_k \propto (\cos k_x - \cos k_y)$, here we show that this type of RVB state represents an extremely accurate variational *ansatz* for *frustrated* systems.

A definite symmetry is guaranteed to the *projected* BCS (*p*-BCS) state provided the gap function Δ_k transforms according to a one-dimensional representation of the spatial symmetry group. A careful analysis [14], similar to the one carried out in [13], shows that the odd component of the gap function $\Delta_k = -\Delta_{k+(\pi,\pi)}$ may have spatial symmetries different from those of the even component $\Delta_k = \Delta_{k+(\pi,\pi)}$. We anticipate that the best variational energy is obtained when the former has $d_{x^2-y^2}$ symmetry, whereas the latter either vanishes or it has d_{xy} symmetry. In frustrated models, it is important to consider this generalization of the originally proposed WF [11,12], because only in this way is it possible to reproduce correctly the phases of the actual GS configurations. In the unfrustrated case it is well known that such phases are determined by the so-called Marshall-sign: on each real space configuration $|x\rangle$, the sign of the GS wave function is determined only by the number of spin down in one of the

two sublattices. This feature, rigorously valid for $J_2 = 0$, turns out to be a very robust property for weak frustration ($J_2/J_1 \lesssim 0.3$) [15]. However, it is clearly violated when frustration plays an important role.

In order to determine the best variational WF of this form we have used a recently developed quantum Monte Carlo (QMC) technique [16] that allows one to optimize a large number of variational parameters with modest computational effort. We first consider the largest square cluster $N = 6 \times 6$ where the exact GS can be numerically determined by exact diagonalization (ED). In order to show the quality of the present WF when frustration (J_2/J_1) is increased, we have computed the variational energy, the overlap of the p-BCS wave function with the exact GS, $|\psi_0\rangle$, and the average sign, defined for a generic variational state $|\psi_V\rangle$ as $\langle S \rangle = \sum_x |\langle x \,|\, \psi_V \rangle|^2 \times$ Sgn$[\langle x \,|\, \psi_V \rangle \langle x \,|\, \psi_0 \rangle]$. The Marshall sign (i.e., $\langle S \rangle = 1$ for $J_2 = 0$) is obtained using the p-BCS wave function, with only the $d_{x^2-y^2}$ component. However, for $J_2/J_1 \gtrsim 0.4$, the phases of the WF are considerably affected by the strong frustration and only when a sizable d_{xy} component is stabilized at the variational level, this property can be correctly reproduced, as clearly shown in Fig. 1. Remarkably, as shown in the same figure, this kind of WF is not only in qualitative agreement with the exact solution, but it is also impressively accurate in the region $J_2/J_1 \sim 0.45 \pm 0.05$ of large frustration, where the overlap of the variational WF is improved by more than an order of magnitude with respect to the $J_2 = 0$ case. This fact implies that the GS in the strongly frustrated regime is almost exactly reproduced by a RVB wave function, at least on clusters of this size.
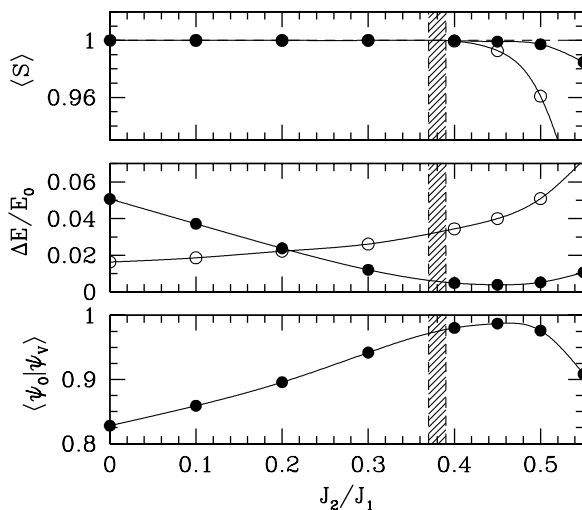

FIG. 1. Average sign, accuracy of the GS energy, and overlap between the GS and the p-BCS state (full dots) as a function of J_2/J_1, for $N = 6 \times 6$. Empty dots are the Marshall sign (top panel), and the energy accuracy of a Néel ordered spin-wave WF [3] (middle panel). Lines are guides for the eye and the shaded region indicates the location of the expected transition point to the nonmagnetic phase.

Further indications of the changes in the nature of the GS occurring by increasing the frustration ratio can be found in the ordering of states with different quantum numbers in the energy spectrum [17]. This information can be easily accessed by ED, which has been performed on the 6×6 cluster for three representative values of the frustration ratio: $J_2/J_1 = 0.2; 0.5; 0.8$. In the case of Néel order the two lowest states of the finite-size spectrum are a total-symmetric singlet and a triplet of momentum (π, π). This phase is clearly expected to occur for sufficiently small J_2/J_1. Analogously, in the large J_2/J_1 limit, the two sublattices decouple and a collinear state characterized by ferromagnetic stripes, staggered along the direction orthogonal to the stripe, is believed to prevail [18]. In this case, the symmetry breaking implies that four classes of states with different spatial symmetries become degenerate: the lowest representatives of these families are an s-wave and a d-wave singlet at zero momentum and two triplets at momenta $(0, \pi)$ and $(\pi, 0)$. Therefore the transition between these two ordered phases implies that, by increasing J_2/J_1, the (π, π) triplet should acquire a gap while the d-wave singlet and the $(0, \pi)$ and $(\pi, 0)$ triplets should collapse onto the GS. The low-energy spectrum is shown in Fig. 2, suggesting that the reshuffling of the lowest energy levels in the system occurs at least in two steps: first the triplet levels lift, leaving room for a nonmagnetic phase with a finite triplet gap, and then the d-wave singlet collapses.

In principle, either a homogeneous spin liquid or a VB crystal with some broken spatial symmetry is compatible with a triplet gap in the excitation spectrum. Indeed, there are several proposals that the GS for $J_2/J_1 \sim 0.5$ may be spontaneously dimerized [10,19,20] with broken translation-rotation symmetry (columnar VB state) as it is likely to happen in a generalization of the present model [6]. Alternatively, a plaquette VB state [21,22] with broken translational symmetry but preserving rotational
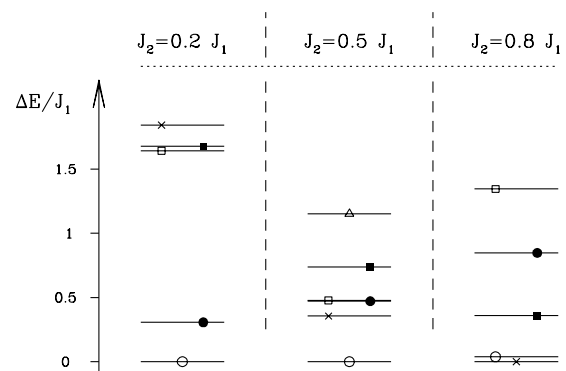

FIG. 2. Lowest energy states with given quantum numbers referenced to the GS energy: Singlet zero momentum s-wave (empty dot) and d-wave (cross), singlet at momentum $(0, \pi)$ (empty square), singlet at momentum (π, π) (empty triangle), triplets at momentum (π, π) s-wave (full dot), and at momentum $(0, \pi)$ (full square).

symmetry may be stabilized. Note that a plaquette VB state would imply the degeneracy of four singlet states at momenta $(0,0)$, $(\pi,0)$, $(0,\pi)$, and (π,π), while a columnar VB state [10,19,20] would result from the mixing of four singlets with different quantum numbers: two translationally invariant s-wave and d-wave states and the two singlets at momenta $(\pi,0)$ and $(0,\pi)$. The plaquette scenario recently proposed [21,22] turns out to be very unlikely in this model because the lowest singlet of momentum (π,π) lies very high in energy at all the couplings we have investigated. The presence of a d-wave singlet in the singlet-triplet gap, instead, has been also evidenced in the regime of strong frustration of the J_1-J_2 model on the 1/5-depleted square lattice, where the ground state is believed to be spin liquid [23]. On the other hand, on the basis of these ED data, it is clearly impossible to establish whether the GS is dimerized or disordered.

In order to clarify this issue we have extended the calculation to much larger system size, by also employing a few Lanczos iterations over the starting variational WF. The stochastically implemented Lanczos technique is a new QMC method with very good convergence properties when the initial WF well represents the actual GS [16]. This accuracy can be confirmed *a priori* even on large size, by studying the variance $\sigma^2 = (\langle \hat{\mathcal{H}}^2 \rangle - \langle \hat{\mathcal{H}} \rangle^2)/J_1^2 N$ of the energy, the variance being smaller (zero) for a better (exact) calculation. As shown in Fig. 3, also in the 10×10 cluster the variance as a function of J_2/J_1 behaves

similarly to the 6×6 case, strongly suggesting that the exceptional accuracy of the p-BCS wave function does not decrease for larger sizes. This is also confirmed by the extremely well-behaved approach to the zero-variance limit with few Lanczos iterations (shown in the same figure), leading to an almost exact estimate of the GS energy even for $J_2 = 0$, when the accuracy is the lowest.

Of course, the accuracy in the energy does not necessarily guarantee a corresponding accuracy in correlation functions. However, in the strongly frustrated regime, our approach is particularly reliable since the gap to the first excitation belonging to the same subspace of our best WF (with two Lanczos iterations) is bounded in all the most plausible cases (columnar, plaquette, nondegenerate singlet RVB) by the triplet gap ($\gtrsim 0.1 J_1$, [10,22]) and therefore is much larger than the estimated error in the total energy ($\sim 0.01 J_1$, see top panel of Fig. 3). Indeed, as shown in Fig. 4, the comparison of the magnetic structure factor $S(q) = \langle \hat{\mathbf{S}}_q \cdot \hat{\mathbf{S}}_{-q} \rangle$, with the exact result gives a clear indication that correlation functions obtained by the variational approach are essentially exact, indicating also the absence of long-range Néel order [12]. This fact is particularly evident because for all the lattice sizes considered, $S(\pi,\pi)$ is slightly depressed by few Lanczos iterations, meaning that the exact value of the magnetic structure factor is bounded by the one of the p-BCS wave function, with sizable antiferromagnetic correlations, but with no antiferromagnetic long-range order. Remarkably, correlation functions are smoothly depending on the energy variance, so that an estimate of the magnetic order parameter within $\sim 10\%$ can
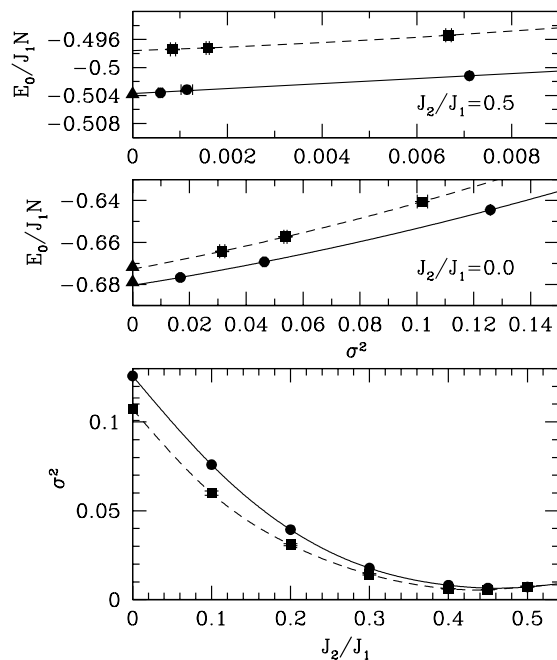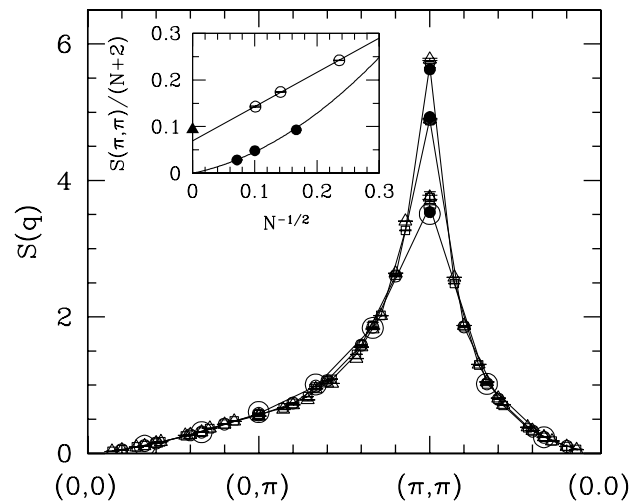

FIG. 3. Upper panels: energy vs decreasing variance for the p-BCS wave function with zero, one, and two Lanczos iterations. ED and QMC [8] (full triangles) are shown for comparison. Lower panel: variance vs J_2/J_1. In all the plots: $N = 6 \times 6$ (dots) and $N = 10 \times 10$ (squares).

FIG. 4. $S(q)$ for (from the lower to the upper curve) $N = 6 \times 6$, 10×10, and 14×14. Variational estimate (empty triangles), with one Lanczos iteration (empty squares), with two Lanczos iterations (empty dots). Full dots: variance-extrapolated values of $S(\pi,\pi)$; large empty circles: ED results. Inset: size scaling of the variance-extrapolated order parameter squared for $J_2/J_1 = 0.5$ (full dots) and $J_2 = 0$ (empty dots, Ref. [16]). The full triangle is the thermodynamic value for $J_2 = 0$ taken from Ref. [8].
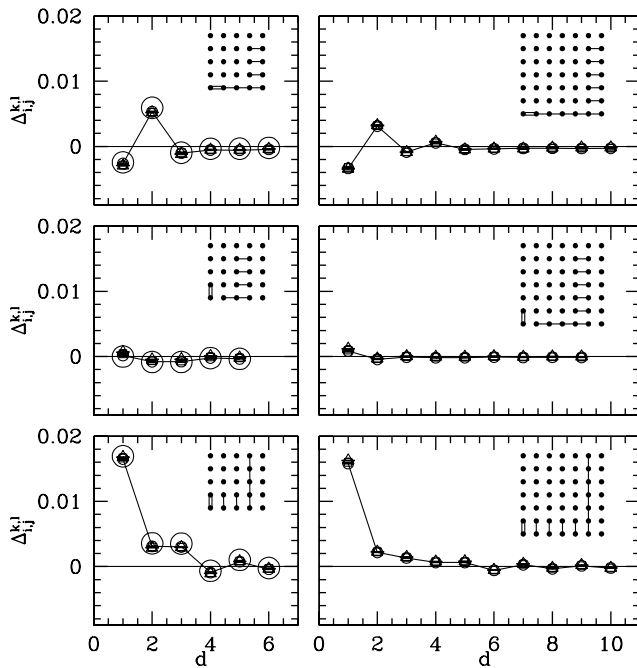
FIG. 5. Dimer-dimer correlation functions $\Delta_{i,j}^{k,l}$ obtained by keeping fixed the position of the leftmost bond (i, j) (double stick) and moving the bond (k, l) (single stick) along the indicated patterns. d is the Manhattan distance. 6×6 (left), 10×10 (right); symbols as in Fig. 4.

be achieved also for $J_2 = 0$, where our singlet WF is not particularly accurate and the spectrum is gapless (see the inset of Fig. 4).

In order to investigate the existence of long-range dimerlike correlations, as in the columnar or the plaquette VB state, we have calculated the dimer-dimer correlation functions, $\Delta_{i,j}^{k,l} = \langle \hat{S}_i^z \hat{S}_j^z \hat{S}_k^z \hat{S}_l^z \rangle - \langle \hat{S}_i^z \hat{S}_j^z \rangle \langle \hat{S}_k^z \hat{S}_l^z \rangle$. In the presence of a broken spatial symmetry, the latter should converge to a finite value for large distance. This is clearly ruled out by our results, shown in Fig. 5, with a very robust indication of the *liquid* character of the GS for $J_2/J_1 \simeq 0.5$, which is correctly described by our variational approach.

A totally symmetric spin-liquid solution proposed for this model in Ref. [4] was actually rather unexpected after the work of Read and Sachdev [20], providing arguments in favor of spontaneous dimerization. This conclusion was supported by series expansion [10,19] and QMC studies included the one done by two of us [22]. It is clear, however, that it is very hard to reproduce a fully symmetric spin liquid GS, with any technique, numerical or analytical, based on reference states explicitly breaking some lattice symmetry [24]. We do not know whether numerical methods and/or series expansions can ever solve this controversial issue. However, for the time being, we can safely state that in order to have something different from a spin-liquid GS, one has necessarily to improve the quality of our spin-liquid variational WF, e.g.,

with small symmetry breaking terms; a possibility that we have attempted (small dimerizations or plaquettelike perturbations) without success. Indeed, this seems a very difficult task due to the tiny energy range left ($\sim 10^{-3} J_1$ per site on the 6×6 lattice) by our variational WF.

In conclusion, the spin-liquid RVB ground state, originally proposed to explain high-Temperature superconductivity, is indeed very plausible for strongly frustrated spin systems. We expect that the p-BCS resonating valence bond wave function represents the *generic* variational state for a spin-half spin liquid, once the pairing function $f_{i,j}$ is exhaustively parametrized according to the symmetries of the Hamiltonian. In particular, the p-BCS wave function can be easily extended to the case of topologically frustrated lattices—such as the kagomé or the pyrochlore lattices—as well as to frustrated models on the $1/5$-depleted square lattice.

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