Spin-Liquid Ground State in a Two-Dimensional Nonfrustrated Spin Model

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We consider an exchange model describing two isotropic spin-1/2 Heisenberg antiferromagnets coupled by a quartic term on the square lattice. The model is relevant for systems with orbital degeneracy and strong electron-vibron coupling in the large Hubbard repulsion limit, and is known to show a spin-Peierls-like dimerization in one dimension. In two dimensions we calculate energy gaps, susceptibilities, and correlation functions with a Green's function Monte Carlo method. We find a finite triplet and singlet gap, with no evidence of order of any kind. We conclude that the ground state is, most likely, a spin liquid of resonating valence bonds.

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The existence of a homogeneous resonating valence bond (RVB) ground state (GS) for two-dimensional (2D) spin systems is a long-standing problem in theoretical physics. The idea that the reduced dimensionality and a small spin value might enhance quantum fluctuations up to the point of destroying the classical Néel antiferromagnetic order was first put forward by Anderson in 1973 [1].

The subject became a hot topic after Anderson suggested that the parent compounds of the high-T_c copper-oxides—argued to be well described by a $S = 1/2$ Heisenberg model on a square lattice—might have a spin-liquid GS, and that superconductivity would result from doping such a spin liquid. Since then, many studies on the $S = 1/2$ 2D Heisenberg model have shown that reduced dimensionality and low spin are not sufficient to stabilize a RVB GS. It is now well established that the square lattice case is Néel ordered [2]. More surprisingly, three-sublattice Néel order is also likely to survive on the triangular lattice, where the model is frustrated [3,4]. A stronger lattice frustration—as in the kagomé lattice [5] or with multiple-spin exchange terms on the triangular lattice [6]—are likely more effective in stabilizing a spin-liquid GS [7]. The evidences for a triplet gap and the definite assessment about the liquid nature of the GS are, however, either limited to small lattice exact diagonalizations (36 sites) [5,6], or must cope, when Monte Carlo is used, with the sign problem [8]. Moreover, very strong frustration [5] is also likely associated to a large GS *degeneracy*, and a nonzero $T = 0$ entropy.

We propose here a clean example of a RVB ground state realized, in absence of any frustration, in a 2D exchange model where an extra spin-1/2 T, representing an orbital degree of freedom, is coupled to the usual spin **S** [9]. Specifically, the model we have considered is

$$H_{\mathrm{ST}} = \sum_{(ij)} \left[\mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{T}_i \cdot \mathbf{T}_j - 4(\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{T}_i \cdot \mathbf{T}_j) \right], \tag{1}$$

where the summation runs over the nearest-neighbor (nn) sites of a square lattice. Equivalently, we can write $H_{\mathrm{ST}} = -\sum_{(ij)} X^{(S)}_{i,j} X^{(T)}_{i,j}$, where $X^{(S)}_{i,j} = (2\mathbf{S}_i \cdot \mathbf{S}_j - 1/2)$, and $X^{(T)}_{i,j} = (2\mathbf{T}_i \cdot \mathbf{T}_j - 1/2)$. H_{ST} is an effective Hamiltonian describing, for instance, the low-energy physics of an insulating crystal with one electron per site in a twofold degenerate orbital, in the Mott insulator regime, and in presence of a strong dynamical Jahn-Teller (JT) effect, making the two-particle intrasite interorbital *singlet*—as opposed to the *Hund's triplet*—the lowest energy state available to virtual hopping [10–12]. Physical systems where these ingredients are at play, and the model is potentially relevant, are to be looked for in the large body of new molecular compounds based on C_{60} or larger fullerides [13], and some two-dimensional copolymers such as vinylidene fluoride-trifluoroethylene [14].

In the search for candidate non-Néel antiferromagnets, a whole class of SU(n)-invariant generalizations of the Heisenberg model [15,16] has been proposed, and studied in detail in the $n \to \infty$ limit. It turns out that H_{ST} is unitarily equivalent to a particular SU(4) model in that class, with $n_c = m = 1$ (notations of Ref. [16]). In the $n \to \infty$ limit, and for $n_c = m = 1$, a spin-Peierls GS has been found both in 2D [16–18], as well as in one dimension (1D) [15]. Whereas in 1D the spin-Peierls nature of the GS persists down to the H_{ST} point [10], $n = 4$, the situation in 2D is, we believe, richer and more subtle: We show in the present Letter that in 2D the GS is RVB for $n = 4$, in marked contrast with the $n \to \infty$ limit predictions [19]. This suggests that the most likely place for a possible RVB state is the region between the two ordered phases studied thus far, i.e., Néel and crystalline dimer phases.

The relationship between H_{ST} and the usual antiferromagnetic Heisenberg model—$H_{\mathrm{Heis}} = (1/2)\sum_{(ij)} X^{(S)}_{i,j}$—is transparent if we work with the overcomplete singlet basis set of valence bond (VB) configurations, i.e., products

of nonoverlapping singlet dimers (i,j) connecting pairs of sites on opposite sublattices and covering the lattice. More precisely, if $(i,j)_{S(T)} = (\uparrow_i \downarrow_j - \downarrow_i \uparrow_j)_{S(T)}$ denotes a singlet bond between sites i and j for the S (T) variables, we restrict the VB configurations considered to the invariant subspace—containing the GS, by positivity arguments—in which every singlet dimer (i,j) is a product of an S and a T singlet, $(i,j) = (i,j)_S(i,j)_T$. Since $(i,j)_{S(T)} = -(j,i)_{S(T)}$, we assume the sign convention that the leftmost index in the singlet pair always belongs to sublattice A. It is possible to show that the GS of both $H_{\rm ST}$ and $H_{\rm Heis}$ can be written as linear combinations with positive coefficients of VB configurations, with the previous restrictions and sign conventions. The construction of excellent variational wave functions based on combinations of VB configurations has been shown to be possible even for the Heisenberg case provided sufficiently long-ranged bonds are allowed [20]. On the other hand, whenever short-ranged bonds are the dominant ones, the GS will have a characteristic length ξ and there will be a finite gap, in the thermodynamic limit, to the lowest triplet excitations [20]. The bond operators $X^{(S)}_{i,j} = (2\mathbf{S}_i \cdot \mathbf{S}_j - 1/2)$, and similarly $X^{(T)}_{i,j}$, have simple properties when acting on VB configurations, because they affect at most two singlet pairs. Indeed, it is known that [1] $X^{(S)}_{i,j}(i,j)_S = -2(i,j)_S$, and $X^{(S)}_{j,k}(i,j)_S(k,l)_S = -(k,j)_S(i,l)_S$. From the rules for $X^{(S)}_{i,j}$ and $X^{(T)}_{i,j}$, it follows that the bond operators $X_{i,j} = -X^{(S)}_{i,j}X^{(T)}_{i,j}$ in $H_{\rm ST} = \sum_{(ij)} X_{i,j}$ obey

$$X_{i,j}(i,j) = -n(i,j)\,, \qquad X_{j,k}(i,j)\,(k,l) = -(k,j)\,(i,l)\,, \tag{2}$$

with $n = 4$, formally identical to those relevant to $H_{\rm Heis}$, except for a coefficient $n = 4$, in place of $n = 2$, when a nn Hamiltonian bond (ij) acts on a single dimer (i,j). This enhanced coefficient favors the formation of short-ranged bonds in the GS of $H_{\rm ST}$, making the suppression of Néel long-range order (LRO) more likely. In the limit $n \to \infty$ we recover, from Eq. (2), the known results both in 1D [15], and 2D [16]. Indeed, for $n \to \infty$ the only surviving VB configurations are those with nn dimers only. In 1D this leads to a doubly degenerate spin-Peierls GS [15]. In 2D the model maps [16] onto the purely kinetic limit of the quantum dimer model (QDM) [21], which is characterized by a fourfold degenerate [19] plaquette RVB GS [18], breaking translational invariance.

By working with the VB basis, the action of the Hamiltonian $H\psi_i$ on any basis element ψ_i defines a nonsymmetric matrix, $H\psi_i = \sum_j h_{j,i}\psi_j$, with all elements $h_{j,i}$ nonpositive, as implied by Eq. (2). The right eigenvector of $h_{j,i}$ with minimum eigenvalue, corresponding for $h_{j,i} \le 0$ to the GS of H, can be computed by applying the power method, as implemented stochastically by the Green's function Monte Carlo (GFMC) method. The GFMC is, in fact, not limited to symmetric matrices, and there is no sign problem when all $h_{j,i}$ are nonpositive [8]. Using the VB basis, the GFMC turns out to have extremely small statistical errors, compared to the more conventional algorithm [22] employing an Ising basis. In this formulation, the GFMC does not require the calculation of the overlaps $\langle\psi_i \,|\, \psi_j\rangle$ between VB configurations. Details will be given elsewhere [23]. Periodic boundary conditions are used in all simulations.

This new and simple GFMC allows us to obtain a very accurate determination of the triplet gap by performing two independent simulations of the singlet GS and the triplet lowest excited state. In the latter case, the basis employed is slightly modified, by allowing for the presence of a single triplet bond $(i,j)^t = (\uparrow_i \downarrow_j + \downarrow_i \uparrow_j)_S(i,j)_T$ in each element of the VB basis. The corresponding rules for the application of $X_{i,j}$ are $X_{i,j}(i,j)^t = 0$, and $X_{j,k}(i,j)^t(k,l) = -(k,j)\,(i,l)^t$. Notice that this implies the absence of a sign problem in the triplet subspace as well. Figure 1 shows the triplet gap Δ_L for $L \times L$ square lattices with $L \le 24$. For the Heisenberg model Δ_L [22], shown for comparison, scales to zero as $a/L^2 + b/L^3$. The dashed line (left inset of Fig. 1) shows our best two-parameter fit to the $H_{\rm ST}$ (ST) data obtained by imposing the same gap behavior as in the Heisenberg case: such a fit is clearly unsatisfactory. Instead, the solid line through the ST data is the result of a three parameter fit of the form $\Delta_L = \Delta + a/L^2 + b/L^4$ [24], giving a clear evidence of

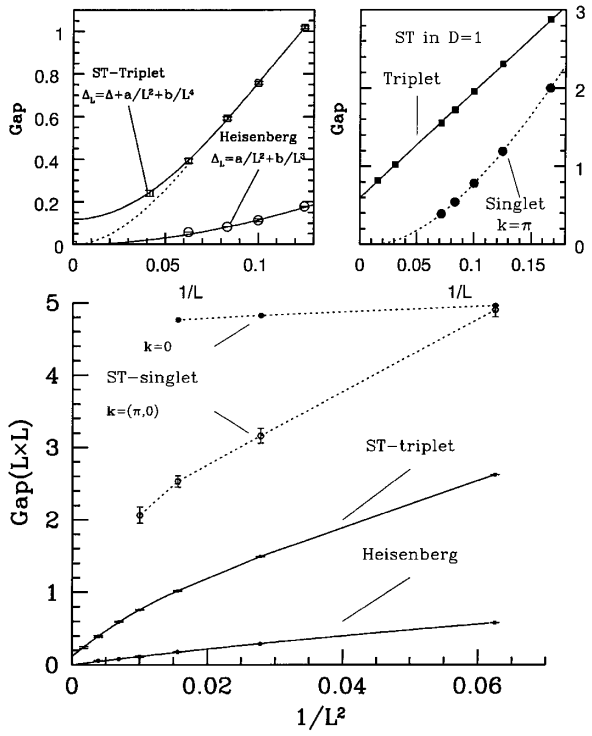

FIG. 1. Finite-size triplet gap for $H_{\rm ST}$ (ST) and for $H_{\rm Heis}$ [22] on the square lattice. The ST data are obtained with the new GFMC method employing the VB basis. The ST singlet gaps at $\mathbf{k} = (0,0), (\pi,0)$ are also shown. The ST data indicate the existence of a triplet gap $\Delta \approx 0.12$ for $L \to \infty$. The solid and dashed lines in the left inset are different fits described in the text. Right inset: The ST triplet and singlet gaps in 1D.

a finite triplet gap $\Delta \approx 0.12$ in the thermodynamic limit. By analyzing the imaginary-time dynamics intrinsic to our GFMC scheme, we were also able to extract the gaps of the lowest singlet excitations with different momenta, checked against exact 4×4 data. The smallest singlet gap, found at $\mathbf{k} = (\pi, 0)$, decreases with increasing L in a manner that closely resembles the size scaling of the triplet gap Δ_L, but remaining always larger than $\approx 2\Delta_L$. This is in marked contrast with what is found for H_{ST} in 1D (right inset), where a clear low-lying singlet associated to breaking of translation invariance is seen below the triplet gap for $L \geq 4$ [10]. Clearly, the detailed finite-size gap behavior of H_{ST} in 2D is nontrivial—requiring quite large lattices ($L = 24$) to pin down the presence of a gap—suggesting the presence of a length scale ξ of the order of $10 \div 15$ lattice spacings.

In principle, either a VB crystal with some broken spatial symmetry, as in 1D, or a homogeneous spin liquid is compatible with the existence of a triplet gap. The fact that we find no evidence for low-lying singlets for H_{ST} in 2D, as opposed to 1D, suggests that the GS is likely a homogeneous spin liquid in 2D. In order to investigate directly the possible kinds of LRO which might characterize the GS of H_{ST} in 2D, we can either (i) calculate the usual "square of the order parameter" by evaluating expectation values of correlation functions with a conventional GFMC algorithm and the forward walking technique [22,25], or (ii) calculate the susceptibility χ_O for several candidate symmetry-breaking operators $\hat{O}$. The approach in (i) is not particularly sensitive to LRO, especially if limited by the large statistical errors associated to the calculation of correlation functions, and to "small" system sizes ($L \leq 12$). Figure 2 shows the results obtained for the spin structure factor $S(\pi, \pi) = \sum_{\mathbf{r}} (-1)^{\mathbf{r}} \langle \mathbf{S}_0 \cdot \mathbf{S}_{\mathbf{r}} \rangle$. $S(\pi, \pi)/L^2$ converges to the square of the Néel staggered magnetization $m^{\dagger}$, as $L \to \infty$. The ST data for $S(\pi, \pi)$ suggest the absence of Néel order for H_{ST}, in agreement with the finding of a triplet gap. Results for the dimer-dimer structure factors with nn bonds in the $\hat{x}$-direction $S^{d-d}(\mathbf{q}) = \sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} \langle S^z_0 S^z_{0+\hat{x}} S^z_{\mathbf{r}} S^z_{\mathbf{r}+\hat{x}} \rangle$ are shown in the inset of Fig. 2. Mixed *SS*-*TT* dimer-dimer correlations (not shown) behave similarly, due to the fact that S and T dimers are perfectly coupled in the GS. The $\mathbf{q} = (\pi, \pi)$, $(0, \pi)$, and $(\pi, 0)$ dimer structure factors do not appear to diverge linearly with the volume, as LRO would require, but the present data are limited to too small sizes ($L \leq 12$) to be conclusive.

More convincing evidences of the absence of LRO are obtained with approach (ii), i.e., by calculating the susceptibility of the system to several perturbations breaking translation (T) and/or rotation (R) symmetry. This approach—which we implement in our new GFMC in the VB basis—provides a very sensitive tool for detecting LRO, whenever present, and requires the calculation of GS energies only. More precisely, we perturb H_{ST} by adding a term $\alpha \hat{O}$, with $\hat{O}$ an operator which breaks one of the spatial symmetries. We restrict our consideration to broken translation symmetry—$\hat{O} = \sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} X_{\mathbf{r},\mathbf{r}+\hat{x}}$—with momenta compatible with a real GS [$\mathbf{q} = (\pi, 0), (0, \pi), (\pi, \pi)$] as suggested by the lowest singlet excited states found, and/or broken $\pi/2$ rotation symmetry: $\hat{O} = \sum_{\mathbf{r}} (X_{\mathbf{r},\mathbf{r}+\hat{x}} - X_{\mathbf{r},\mathbf{r}+\hat{y}})$. This includes all types of crystalline dimer and plaquette order proposed thus far [16–18,21]. On finite size, the GS expectation value of $\hat{O}$ vanishes by symmetry, and the GS energy per site has corrections proportional to α^2,

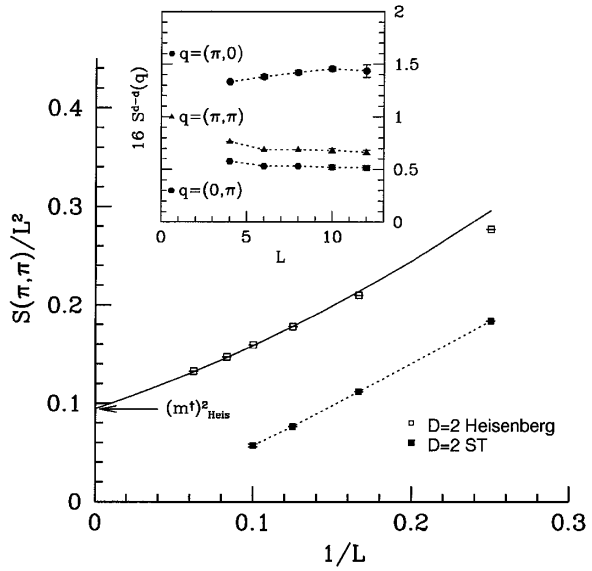

FIG. 2. Structure factors obtained with a standard GFMC [22] with the forward walking technique. $S(\pi, \pi)$ for H_{ST} (Heisenberg data [22] shown for comparison) suggests the absence of Néel LRO. Inset: The important components of the Fourier transform of the dimer-dimer correlation functions appear to be finite.

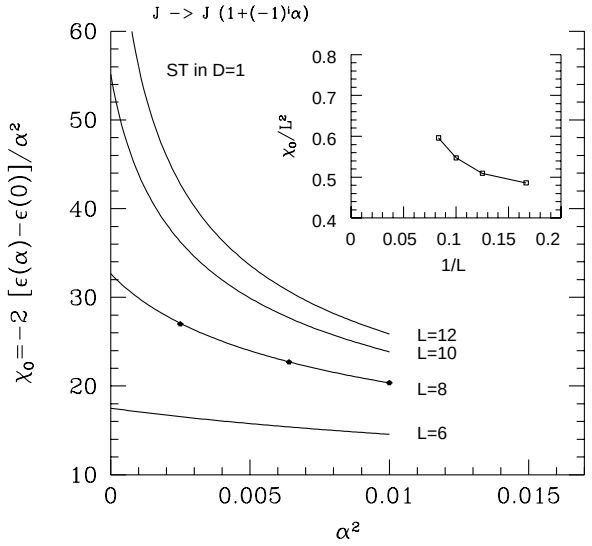

FIG. 3. The susceptibility to breaking translation symmetry for H_{ST} in 1D, where dimerization occurs [10]. Solid lines are obtained by exact diagonalizations, points for $L = 8$ by GFMC, as a check. Inset: $\alpha = 0$ values of χ_O divided by the system volume squared L^2.

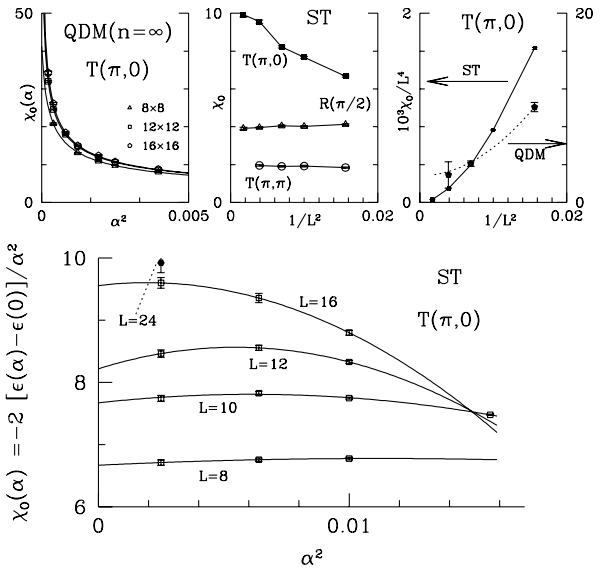

FIG. 4. Susceptibilities to breaking the most important crystal symmetries for H_{ST} in 2D. The finite-size, finite-α data for χ_O can be readily extrapolated, by quadratic fits, to $\alpha = 0$ values: notice the distinctly different behavior for the corresponding 1D results of Fig. 3, as well as from the QDM results (left inset). The right and central insets summarize the results obtained for the extrapolated χ_O.

$\epsilon_\alpha = \epsilon_0 - \chi_O \alpha^2/2$, χ_O being the generalized susceptibility associated to $\hat{O}$. On the other hand, if symmetry breaking occurs in the thermodynamic limit, it is possible to have $\lim_{\alpha\to 0}\lim_{L\to\infty}\langle \hat{O}/L^D\rangle = p \neq 0$. In the latter case, χ_O has to diverge as $L \to \infty$. More precisely, it is possible to show that χ_O is bounded from below by the order parameter times the system volume squared, $\chi_O > \mathrm{const} p^4 L^{2D}$. These susceptibilities are therefore a very sensitive tool—much more than the square of the order parameter—for detecting LRO. For instance, the presence of dimerization [10] for H_{ST} in 1D is readily inferred from the behavior of χ_O, with $\hat{O} = \sum_i (-1)^i X_{i,i+1}$, even for small chains ($L \leq 12$, Fig. 3). Figure 4 shows the results obtained for H_{ST} in 2D. For all the symmetry breaking operators considered, the associated susceptibilities are found to be finite. The largest susceptibility is found to be the one associated to breaking translations in the $\hat{x}$ direction by one lattice spacing [$T(\pi, 0)$ in Fig. 4], and is only weakly increasing with size, eventually saturating to a constant. This behavior is in marked contrast to the strong divergence seen for the same quantity both in 1D (see Fig. 3), and for the QDM case, corresponding to the limit $n \to \infty$ (left inset).

In conclusion, we have studied a 2D nonfrustrated exchange Hamiltonian with unbroken SU(4) symmetry, Eq. (1), which describes the low-energy physics of a Mott insulator with orbital degeneracy and a strong dynamical JT effect. We find a clear evidence for a nonzero triplet gap Δ without crystalline VB order, and with a gap to singlet excitations $\geq 2\Delta$. A homogeneous liquid of resonating valence bonds, with a gap to all excitations, appears as the natural candidate GS for this model.

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