

Spin gap in low-dimensional Mott insulators with orbital degeneracy

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We consider the exchanged Hamiltonian $H_{ST} = -J \sum_{\langle rr' \rangle} (2\mathbf{S}_r \cdot \mathbf{S}_{r'} - \frac{1}{2})(2\mathbf{T}_r \cdot \mathbf{T}_{r'} - \frac{1}{2})$, describing two isotropic spin-1/2 Heisenberg antiferromagnets coupled by a quartic term on equivalent bonds. The model is relevant for systems with orbital degeneracy and strong electron-vibron coupling in the large Hubbard repulsion limit. To investigate the ground state properties we use a Green's Function Monte Carlo, calculating energy gaps and correlation functions, the latter through the forward walking technique. In one dimension we find that the ground state is a "crystal" of valence bond dimers. In two dimensions, the spin gap appears to remain finite in the thermodynamic limit, and, consistently, the staggered magnetization—signal of Néel long range order—seems to vanish. From the analysis of dimer-dimer correlation functions, however, we find no sign of a valence bond crystal. A spin liquid appears as a plausible scenario compatible with our findings. © 1999 American Institute of Physics. [S0021-8979(99)53908-X]

The object of this study is a particular spin-exchange Hamiltonian in which two spin-1/2 variables—a standard spin \mathbf{S} , and a pseudospin \mathbf{T} representing an orbital degree of freedom—are coupled together in the following way:

$$H_{ST} = -J \sum_{\langle rr' \rangle} (2\mathbf{S}_r \cdot \mathbf{S}_{r'} - \frac{1}{2})(2\mathbf{T}_r \cdot \mathbf{T}_{r'} - \frac{1}{2}), \quad (1)$$

the lattice summation running over the nearest neighbor sites of a lattice. The symmetry group displayed by Eq. (1) includes $SU(4)$.¹ This Hamiltonian was shown to describe the low-energy physics of an insulating crystal with one-electron per site in a twofold degenerate orbital, in the limit of large on-site repulsion (Mott insulator) and in presence of Jahn-Teller effect.¹ The derivation of Eq. (1), henceforth referred to as ST model, is standard.¹⁻³ The crucial physical condition to be verified is that, among the possible two-particle states obtained upon virtual hopping, the *interorbital singlet* should turn out to be the lowest in energy, which is indeed the case when a strong dynamical JT effect is at play. A different (perhaps more common) physical situation is that the lowest two-particle intermediate state is a triplet (as a result of a Hund's rule), in which case the exchange Hamiltonian has a different form and spin ferromagnetism is the natural outcome.^{4,2} In the general case, the exchange Hamiltonian contains pseudospin anisotropic terms, and its phase diagram has been addressed with different techniques in Refs. 2 and 5.

C_{60} charge transfer compounds, based on C_{60}^- ions,⁶ or molecular compounds with similar characteristics, are potential candidates to the realization of a scenario in which the Hamiltonian in Eq. (1) is possibly relevant. C_{60} has a triply degenerate t_{1u} molecular orbital, coupled to several intramolecular vibrations, resulting in an important dynamical JT effect.⁷ The electron-phonon coupling leads to a substantial pairing energy ≈ 0.1 eV which is, however, overwon by a substantially larger Hubbard $U \approx 1-1.5$ eV,⁸ resulting in a Mott insulating behavior. The lattices tend to have anisotropic lattice constants, with a pronounced quasi-one-dimensional character.⁶ As for the virtual intermediate states of C_{60}^{2-} , singlets and triplet are close in energy, at least in solutions.⁹ If the triplet prevails, as is possibly the case in $TDAE-C_{60}$,^{2,10} there can be spin ferromagnetism. We believe, however, there is room in some future system for the alternative possibility of a spin gap, and the formation of the spin-orbital valence bond (VB) state described here.

Simple variational arguments are quite instructive in elucidating, as a function of the dimensionality of the lattice, the physical role played by the quadratic and quartic terms in which the ST model can be rewritten, $H_{ST} = J \sum_{\langle rr' \rangle} [\mathbf{S}_r \cdot \mathbf{S}_{r'} + \mathbf{T}_r \cdot \mathbf{T}_{r'} - 4(\mathbf{S}_r \cdot \mathbf{S}_{r'})(\mathbf{T}_r \cdot \mathbf{T}_{r'})]$. The quadratic terms are standard antiferromagnetic couplings, which, alone, would drive the system to a Néel ordered state for both spin and orbital variables. The quartic term, on the contrary, gains from large values of $\langle \mathbf{S}_r \cdot \mathbf{S}_{r'} \rangle$ and $\langle \mathbf{T}_r \cdot \mathbf{T}_{r'} \rangle$: the optimal situation is a singlet VB state for both S and T variables, where $\langle \mathbf{S}_r \cdot \mathbf{S}_{r'} \rangle = \langle \mathbf{T}_r \cdot \mathbf{T}_{r'} \rangle = -3/4$. Let us compare the energy of the following two states: (i) The product of two independent Heisenberg ground states, $|\Psi_{2-H}\rangle = |\Psi_H^{(S)}\rangle \otimes |\Psi_H^{(T)}\rangle$, and (ii) the product of two VB states, $|\Psi_{2-VB}\rangle = |\Psi_{VB}^{(S)}\rangle \otimes |\Psi_{VB}^{(T)}\rangle$ where each VB state has the simple form of a product of dimers on adjacent sites. In $D=1$, we take $|\Psi_{VB}\rangle = (12) \times (34) \cdots (L-1L)$, where (ij) denotes a singlet between

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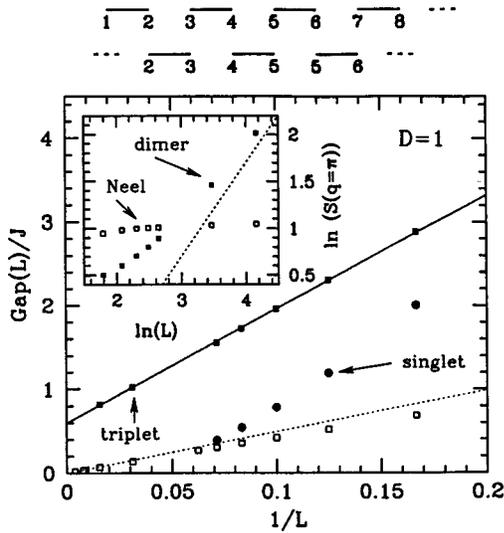


FIG. 1. Finite size gaps for the lowest excited states of H_{ST} in $D=1$ (solid symbols) compared to the Heisenberg chain case (open squares). The excited state for the Heisenberg case extrapolates to $\Delta E/J = \pi^2/(2L) + \dots$, shown by the dashed line. The solid straight line, extrapolating to ≈ 0.5969 for $L \rightarrow \infty$ is obtained by a quadratic fit. Inset: Log-log plot of $\sum_r (-1)^r \langle S_0^z S_r^z \rangle$ (open squares) and of $\sum_r (-1)^r \langle (S_0^z S_1^z) (S_r^z S_{r+1}^z) \rangle$ (solid squares). The dashed line has slope 1, for comparison. Top: Schematic illustration of the two crystal VB ground states of a linear chain.

sites i and j . In $D=2$, we consider any state with nearest-neighbor pairs coupled into singlets. The energy contribution of the quartic term is substantially lower for the VB state, $-4J(1/2)(-3/4)^2$, than for the Heisenberg state for $D \leq 2$, $-4JD(\epsilon_H/DJ)^2$, where $\epsilon_H/J = D \langle \Psi_H^{(S)} | \mathbf{S}_r \cdot \mathbf{S}_{r'} | \Psi_H^{(S)} \rangle \approx -0.4431$, in $D=1$, or ≈ -0.66 , in $D=2$. The energy per site of the two states including the quadratic terms are: $\epsilon_{2-H} = 2\epsilon_H - 4JD(\epsilon_H/DJ)^2$, and $\epsilon_{2-VB} = 2\epsilon_{VB} - 4J(1/2)(-3/4)^2$, where $\epsilon_{VB} = (-3/8)J$ is the energy per site of the VB state. In $D=1$, the VB state wins over the Heisenberg state. In $D=2$, the previous crude variational estimate would give the Heisenberg state as favored. The VB state considered here is, however, very poor: its energy per site, neglecting the quartic term, is only $-0.375J$, whereas it is well known that resonating VB states close in energy to the Heisenberg ground state can be constructed in $D=2$.¹¹

To show that the VB scenario is correct in 1D, we calculate gaps and correlation functions using exact Lanczos diagonalizations of chains up to 14 sites, and Green Function Monte Carlo (GFMC) for longer chains employing the bias-correction scheme of Calandra and Sorella.¹² The trial wave function we have used is a Jastrow-type function $\langle R | \psi_{\text{trial}} \rangle = \langle R | \exp\{-\sum_{\langle rr' \rangle} [v_{rr'} (S_r^z S_{r'}^z + T_r^z T_{r'}^z) - 4w_{rr'} (S_r^z S_{r'}^z)] \} | R \rangle$, where $|R\rangle$ is a configuration in the basis in which S_r^z and T_r^z are diagonal. We allow, in general, long range tails in $v_{rr'}$ and $w_{rr'}$, which are adjusted through a variational calculation. Figure 1 shows the finite-size value of the gap between the ground state and the first excited state both in the $S_{\text{tot}}^z = T_{\text{tot}}^z = 1$ (\square) and in the $S_{\text{tot}}^z = T_{\text{tot}}^z = 0$ (sectors) (\circ). The full symbols refer to H_{ST} , whereas the open symbols refer to two decoupled Heisenberg chains [no quartic term in Eq. (1)]. All these excited states have momentum π relative to the ground state. For the Heisenberg case, the

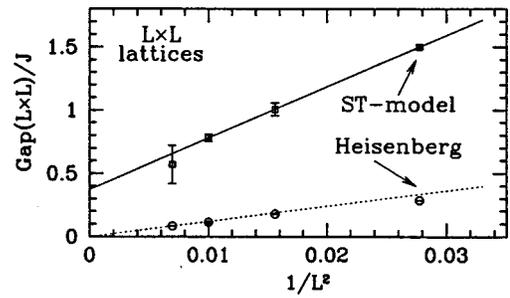


FIG. 2. Finite size gap between the ground state and the first excited triplet state for the ST model (squares) and for the Heisenberg model (circles) on the square lattice (see Ref. 12). The data for the ST model are compatible with the existence of a spin gap in the thermodynamic limit.

excited state is a triplet and the model has gapless excitations with gaps decreasing as $1/L$ for $L \rightarrow \infty$ (dashed line). For H_{ST} , the situation is different: The lowest excited state is a singlet, with a finite size gap $\Delta E(S=0)$ decreasing faster than $1/L$ for $L \rightarrow \infty$. The triplet, instead, lies above with a gap $\Delta E(S=1)$ extrapolating to a finite value as $L \rightarrow \infty$, $\Delta E(S=1) \approx 0.5969$. This is a clear signal of a *degenerate* infinite volume ground state with a *spontaneous breaking of translational symmetry* and a gap to all excitations, consistent with a VB phase. Further support to this interpretation can be gained by direct inspection of the spin-spin correlations, $\langle S_0^z S_i^z \rangle$, and the dimer-dimer correlations along the chain $\langle (S_0^z S_1^z) (S_r^z S_{r+1}^z) \rangle$. The inset of Fig. 1 shows a log-log size scaling of the peak of the two structure factors, located at momentum π . While the dimer-dimer structure factor peak, $\sum_r (-1)^r \langle (S_0^z S_1^z) (S_r^z S_{r+1}^z) \rangle$ tends to diverge linearly with the length L of the chain, the usual spin-spin structure factor tends to a finite value as $L \rightarrow \infty$.

The possibility that a valence bond state might be the ground state of the ST model even in 2D was put forward in Ref. 1. The argument was based on a $SU(n)$ -invariant model, due to Affleck,¹³ which is unitarily equivalent to the ST model in Eq. (1) for $n=4$. It turns out that in the $n \rightarrow \infty$ limit such a $SU(n)$ -invariant model should be characterized, in $D=2$, by a plaquette resonating VB state,¹ as discussed in Ref. 14. Such a phase has resonating VB plaquettes forming alternating disordered columns, but breaks translational invariance along the axis perpendicular to the disordered columns.

We are now going to discuss the results we obtain with the GFMC for the ST model on the square lattice. Figure 2 shows the finite size gap between the ground state and the lowest excited triplet state for the ST model on a $L \times L$ lattice as a function of the inverse volume. The data for the ST model, at variance with those of the Heisenberg model, suggest the presence of a spin gap in the thermodynamic limit, although some care should be exercised because of the large error bar on the largest sample data, and the possibility of a nontrivial size scaling. The solid line is simply a straight line going through the two data points for a 6×6 and 10×10 lattices. The extrapolated value of the spin gap is $\sim 0.373J$.

In principle, either a VB crystal with broken translational symmetry or a homogeneous spin liquid is compatible with the existence of a spin gap. In order to investigate more

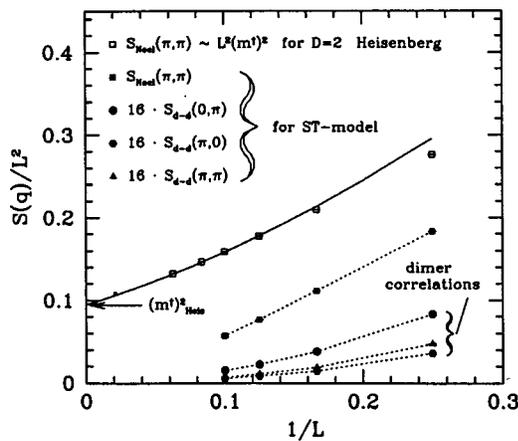


FIG. 3. Finite size structure factors obtained by GFMC with the forward walking technique. The important components of the Fourier transform of the dimer–dimer correlation functions look to grow slower than volume. Therefore we can exclude the presence of any kind of valence bond solid. For the Néel order parameter, we find no clear sign of long range order. The size scaling of the Néel order parameter for the Heisenberg model is shown for comparison (Ref. 12).

closely the possible kinds of long range order which might characterize the ground state of the ST model in $D=2$, we have calculated the expectation value of several spin–spin correlation functions by the forward walking technique.¹² Figure 3 shows the results for the structure factors related to both standard spin–spin correlations $\sum_r (-1)^r \langle S_0^z S_r^z \rangle$ (solid squares) and dimer–dimer correlations in \hat{x} direction $\sum_r e^{iqr} \langle (S_0^z S_{0+\hat{x}}^z) (S_r^z S_{r+\hat{x}}^z) \rangle$ for different momenta: $(0, \pi)$ (circles), $(\pi, 0)$ (hexagons) (π, π) (triangles). For comparison, we include the results for the (π, π) spin–spin structure factor of the $D=2$ Heisenberg model, $\sum_r (-1)^r \langle S_0^z S_r^z \rangle$ (open squares). We observe that all the dimer–dimer correlations considered show no sign whatsoever of diverging linearly with the volume, i.e., we find that $S_{\text{dim-dim}}(q)/L^2 \rightarrow 0$. This finding rules out the possibility of a crystalline VB state, even in the form of a plaquette resonating VB.¹⁴ On the other hand, the standard (π, π) spin–spin structure factor, signal of a Néel ordered state, does not seem either to diverge linearly with the volume, i.e., $S(\pi, \pi)/L^2$ also seems to go to zero. The latter finding is compatible with the presence of a gap suggested by the results in Fig. 2. Summarizing, although further work is necessary for a definite answer to the nature of the ST model ground state on the square lattice, it seems fair to conclude that our data suggest a disordered VB state as the most likely candidate.

In conclusion, we have studied a particular exchange

Hamiltonian, Eq. (1), which describes the low-energy physics of a Mott insulator with orbital degeneracy in the regime in which the interorbital singlet is the lowest-energy intermediate state available to virtual hopping. This regime tends to be further favored by a relatively strong electron-phonon coupling. The basic ingredients needed for a realistic system to be a candidate VB described in this work are: (i) orbital degeneracy not trivially removed by cooperative JT and/or crystal field effects; (ii) relatively large molecules with a strong electron-phonon coupling, so as to make the interorbital singlet favored as compared to the Hund’s rule triplet; (iii) narrow bands with relatively large on-site Hubbard U , so as to stabilize a Mott–Hubbard insulator at exactly one electron per site; (iv) reduced dimensionality. At variance with the standard Hund’s rule case (the high spin two-particle state has lowest energy), which would instead favor spin ferromagnetism, we find in our case a strong tendency to the formation of VB phases. In $D=1$, the presence of a statically ordered crystal of VBs is firmly established. Given the presence of a sizeable spin gap, weakly coupled chains should also have a crystal VB ground state. In $D=2$, on the square lattice, a spin gap is suggested by our data, but no sign of crystalline dimer order is found from the relevant correlation functions. A homogeneous liquid of resonating valence bonds appears as the natural candidate ground state for this model.

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- ¹G. Santoro, L. Guidoni, A. Parola, and E. Tosatti, *Phys. Rev. B* **55**, 16168 (1997).
- ²D. P. Arovas and A. Auerbach, *Phys. Rev. B* **52**, 10114 (1995).
- ³M. Fabrizio, M. Airoidi, and E. Tosatti, *Phys. Rev. B* **53**, 12086 (1996).
- ⁴For a review on early work, see, for instance, K. I. Kugel’ and D. I. Khomskii, *Sov. Phys. Usp.* **25**, 231 (1982).
- ⁵S. K. Pati, R. P. Singh, and D. Khomskii, preprint cond-mat/9807270.
- ⁶See, for instance, *Physics and Chemistry of Fullerenes and Derivatives*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1995).
- ⁷A. Auerbach, N. Manini, and E. Tosatti, *Phys. Rev. B* **49**, 12998 (1994); N. Manini, A. Auerbach, and E. Tosatti, *ibid.* **49**, 13008 (1994).
- ⁸O. Gunnarsson, *Rev. Mod. Phys.* **69**, 5754 (1997).
- ⁹Z. Gasyna, L. Andrews, and P. N. Schatz, *J. Phys. Chem.* **96**, 1525 (1991).
- ¹⁰D. Arcón, P. Cevc, A. Omerzu, and R. Blinc, *Phys. Rev. Lett.* **80**, 1529 (1998).
- ¹¹S. Liang, B. Douçot, and P. W. Anderson, *Phys. Rev. Lett.* **61**, 365 (1988).
- ¹²M. Calandra and S. Sorella, *Phys. Rev. B* **57**, 11446 (1998).
- ¹³I. Affleck, *Phys. Rev. Lett.* **54**, 966 (1985).
- ¹⁴P. W. Leung, K. C. Chiu, and K. J. Runge, *Phys. Rev. B* **54**, 12938 (1996).

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