Local Enhancement of Antiferromagnetic Correlations by Nonmagnetic Impurities

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The local enhancement of antiferromagnetic correlations near vacancies observed in a variety of spin systems is analyzed in a single framework. Variational calculations suggest that the resonating-valence-bond character of the spin correlations at short distances is responsible for the enhancement. Numerical results for uniform spin chains, with and without frustration, dimerized chains, ladders, and two dimensional clusters are in agreement with our conjecture. This short distance phenomenon occurs independently of the long distance behavior of the spin correlations in the undoped system. Experimental predictions for a variety of compounds are briefly discussed. [S0031-9007(97)03060-3]

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Studies of ladder compounds continue producing fascinating results. In addition to the discovery of a spin gap in undoped even-leg ladders [1], superconductivity at high pressure in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$, with two-leg ladders and chains in its structure, has been recently reported [2]. Both properties, predicted by theoretical arguments [3], indicate a close interplay between the spin and charge degrees of freedom leading to a rich phase diagram. More recently, the doping of ladders with nonmagnetic impurities (replacing spin-$\frac{1}{2}$ Cu^{2+} by spin-0 Zn^{2+}) has revealed another surprising property: The spin gap is rapidly suppressed as the Zn concentration increases, and an antiferromagnetic (AF) phase is stabilized [4]. A similar behavior has also been observed in spin-Peierls chains [5], which have a spin gap produced by dimerization. The phenomenon is interesting since a spin ordered state is generated by the random replacement of spins by vacancies, an apparently disordering procedure. These results have been recently addressed with one dimensional (1D) spin models using field theory [6] and numerical techniques. Computational studies found that the AF correlations near a vacancy in dimerized chains [7] and two-leg ladders [7,8] are enhanced with respect to the undoped case. It was conjectured that this local enhancement may trigger the 3D AF order in Zn-doped dimerized chains and ladders. In-gap weakly interacting $S = \frac{1}{2}$ localized states were found near Zn [9]. However, the microscopic origin of the local AF enhancement near a vacancy is still not intuitively understood.

Independently of these recent developments, related phenomena have been discussed in a variety of contexts: (1) A staggered moment appears near a vacancy for 1D $S = 1$ Heisenberg systems [10]; (2) the undimerized 1D $S = \frac{1}{2}$ Heisenberg model has an enhanced spin structure factor $S(\pi)$ near vacancies according to boundary conformal field theory and Monte Carlo (MC) simulations [11]; (3) near a vacancy injected into a 2D Néel ordered state, the staggered moment increases with respect to the undoped system [12].

In this paper it is proposed that all these examples of locally enhanced antiferromagnetism near a vacancy, which have been studied independently in the literature, may have a simple common explanation. The unifying picture relies on the resonating-valence-bond (RVB) character of the spin correlations at short distances for a variety of Heisenberg spin systems where the nearest-neighbor (NN) interaction, regulated by a coupling J_1, is the largest. Independently of the long distance properties of the model, the small distance behavior, at least for small spin S, is dominated by the formation of short spin singlets resonating in all their possible arrangements [13]. Actually, RVB variational states have large overlaps with exact ground states of finite clusters, even for 2D Néel ordered systems [14]. Corrections involve long singlets and triplets with a weight decaying as the spin-spin distance grows.

In the case of a 1D $S = \frac{1}{2}$ chain, Figs. 1(a) and 1(b) illustrate two arrangements of spin singlets that carry important weight in the undoped ground state. Consider now a vacancy introduced at site 0, effectively cutting the chain if a NN spin Hamiltonian is used. In this situation configuration Fig. 1(b) is replaced by Fig. 1(c) that contains

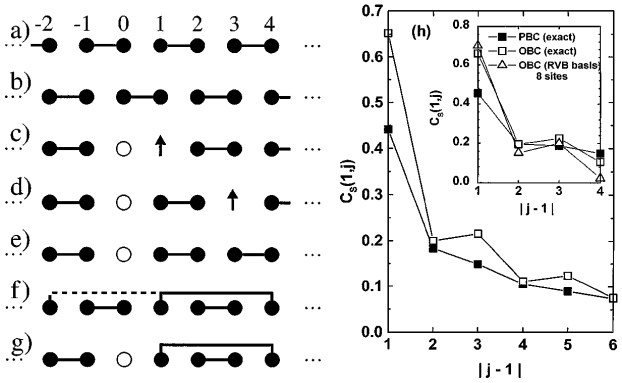

FIG. 1. (a)–(g) Examples of spin singlets relevant for our discussion (see text); (h) $C_S(1, j)$ for a $S = \frac{1}{2}$ Heisenberg model on a 128 sites chain calculated with DMRG. The open (full) squares are results with (without) a vacancy at site 0. The inset contains the RVB variational results (see text) for eight sites with OBC compared against exact results for the same chain with OBC and PBC. 1 is the first site of the chain.

a "free" spin. The NN exchange strongly favors the coupling of this free spin with the spin at site 2. Then, configuration Fig. 1(d) is equally probable, and the argument can be repeated moving the free spin over large distances (spin-charge separation). The final dominant configuration near a vacancy has the form shown in Fig. 1(e). The key detail to understanding the AF enhancement is that in the absence of the vacancy the spin at 1 spends roughly half the time coupled into a singlet with the spin at 2 and the other half with the spin at 0, while with a vacancy the spin at 1 forms a singlet most of the time with the spin at 2. Then, the 1-2 spin correlation is now enhanced. The vacancy has *pruned* the possible singlet configurations and the spins next to it no longer "resonate," but their singlet partners are fixed by geometry.

The same pruning of RVB states occurs when corrections to Figs. 1(a) and 1(b) are included. Consider a configuration with a singlet linking sites 1 and 4 [Fig. 1(f)]. Such a configuration produces the largest contribution to the spin correlation at distance 3. As in the previous case, the spin at 1 divides its tendency to form singlets equally between sites 4 and -2. But when a vacancy is introduced, only one possibility for the coupling of the spin at 1 with partners at distance 3 remains [Fig. 1(g)], enhancing the correlation at that distance. Again the nonmagnetic impurity has pruned the singlet configurations increasing the AF correlations in its vicinity. The same argument applies for longer singlets, although moving away from the vacancy the AF enhancement is reduced since eventually both Figs. 1(a) and 1(b) must dominate in the bulk. Results for the ground state staggered spin correlation $C_S(i,j) = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle (-1)^{i+j}$, in the standard notation, calculated with density matrix renormalization group (DMRG) techniques [15], are shown in Fig. 1(h) for the spin-$\frac{1}{2}$ Heisenberg chain. The AF enhancement is large (48% for the bond next to the vacancy). The effect can be rephrased as an increase in $S(\pi)$ as previously observed by Eggert and Affleck [11]. We here confirm their results and provide a simple explanation for the origin of the enhancement.

To provide further support to these ideas, a RVB variational calculation on a chain of eight sites with open boundary conditions (OBC) was performed. The state used is a linear combination of (a) the state with four NN singlets, (b) all states with three NN singlets and one singlet of length 3, and (c) all states with two triplets of length 2 and two NN singlets. The relative weights are fixed minimizing the energy. The spin correlations in this variational state are also shown in Fig. 1(h) (inset). Contrasting the results against exact calculations with OBC, it is clear that such a simple state contains the main features observed in the actual ground state of longer chains.

The discussion can be easily extended to NN $S = \frac{1}{2}$ Heisenberg models with a larger coordination number. Consider first a two-leg ladder. Snapshots of the spin arrangement in the vicinity of an arbitrary site, e.g., 1, would show that this spin spends most of its time singlet coupled with spins 2, 3, and 4 [Fig. 2(a)] [16]. When a vacancy is introduced at site 2, now the spin at 1 forms singlets only with two partners rather than three [Fig. 2(b)]. This pruning of the RVB basis enhances the spin correlation at distance 1 along the chain, as in 1D. Figure 2(d) contains $C_S(i,j)$ for a two-leg ladder. Shown are the DMRG spin correlations both along the leg where the vacancy is, and in the opposite leg. The results are in good agreement with previous calculations [8]. The enhancement is substantial only for same-leg correlations, and even in this case it is smaller than for the $S = \frac{1}{2}$ chain, in agreement with the picture discussed before (i.e., counting links the naive enhancement ratio would be $\frac{3}{2}$ for ladders vs $\frac{2}{1}$ for chains). At distance 1 and for same-leg correlations, the actual enhancement is $\sim 22\%$.

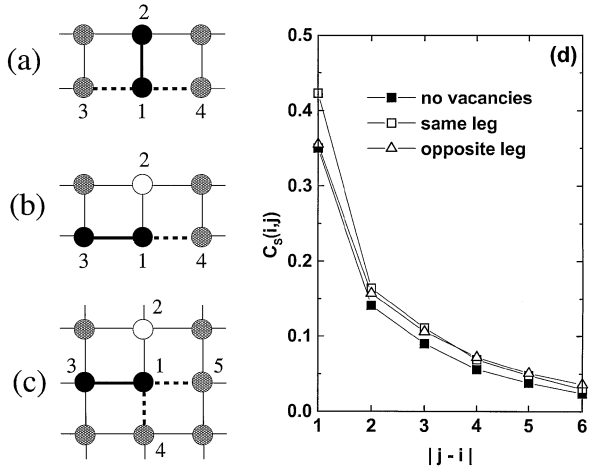

FIG. 2. (a)–(c) Spin singlets relevant for ladders and hypercubic systems (see text); (d) $C_S(i,j)$ for a two-leg ladder calculated with DMRG on a 2×32 cluster. The open squares (triangles) are spin correlations along the same (opposite) leg where the vacancy is located, with a starting site i next to the vacancy. The full squares are results without vacancies. The vacancy is located at the center of the cluster.

Numerically, the short distance spin correlations smoothly interpolate between the results of chains and two-leg ladders as the rung coupling $J_\perp$ is reduced with respect to the chain coupling J. As an example, in Fig. 3(a) exact diagonalization (ED) [17] results are shown for $J_\perp/J = 0.5$ using periodic boundary conditions (PBC) and OBC. They suggest that the short distance AF enhancement of chains and ladders have a common origin independent of the long distance behavior of their spin correlations (power law vs exponential decay). Only the range of the Zn-induced disturbance is affected by the presence of a spin gap. For example, due to spin-charge separation in 1D, the $S = \frac{1}{2}$ state obtained by removing one spin from an even site chain is uniformly distributed over the chain [9]. However, near the vacancy the AF correlations are, nevertheless, enhanced [Fig. 1(h)]. Thus, the short distance effect discussed here does not seem correlated with the presence of a $S = \frac{1}{2}$ localized state near the vacancy. To further confirm these ideas, correlations

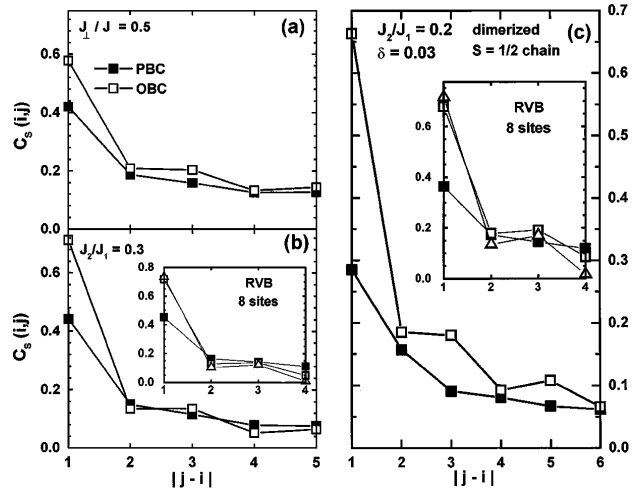

FIG. 3. $C_S(i,j)$ obtained with ED for (a) a two-leg ladder with $J_\perp/J = 0.5$ using PBC (full squares) and OBC (open squares). The correlations are measured from the edge of a 2×10 cluster; (b) a $S = \frac{1}{2}$ chain with $J_2/J_1 = 0.3$ and 14 sites. Open squares denote results from the end of an open chain, while full squares are results for a ring. The inset shows RVB variational results with the same state used in Fig. 1(h). Open (full) squares are exact results with open (periodic) boundary conditions. The triangles denote the variational predictions; (c) a dimerized $S = \frac{1}{2}$ chain with OBC, 14 sites, and $J_2/J_1 = 0.2$, $\delta = 0.03$. i is the first spin on the chain. The inset contains RVB results on an eight-site open chain. The symbols are as in Fig. 3(b). The first link in the chain near the edge is "weak."

for a $J_1 - J_2$ chain (J_2 being a next to NN coupling) were calculated varying J_2/J_1 from 0 (no gap in the ground state) to the exactly solvable point 0.5 (dimerized gapped state). A smooth interpolation between the two regimes was observed at short distances [see, e.g., Fig. 3(b), which includes a RVB variational calculation]. As the Zn impurity density grows, the short distance effects will eventually govern the behavior of the system, and the tail in the spin disturbance becomes irrelevant.

The analysis of models for $CuGeO_3$ requires a special discussion. Here a dimerization occurs at low temperatures [5] which will be represented by a modulation of the original NN exchange using $J(1 \pm \delta)\mathbf{S}_i \cdot \mathbf{S}_j$, with $\delta \sim 0.03$ [18]. Note that a more proper description of $CuGeO_3$ requires the inclusion of phonons to generate the dimerization dynamically. However, the model used here is sufficient for our qualitative studies. The $+(-)$ sign corresponds to "strong" ("weak") links. The addition of a next NN interaction $J_2/J_1 \sim 0.2$–0.3 is also needed in $CuGeO_3$ [18]. Based on the RVB picture discussed before it would not be surprising that AF enhancements of short distance spin correlations will also appear in Zn-doped spin-Peierls chains. In fact, we found the surprising effect that the enhancement in this case is the largest among the family of models studied here. As an example, consider the results of Fig. 3(c), obtained exactly on a finite chain with OBC. The pattern of strong vs weak links considered here is such that sites 1 and 2 next to the end are connected by a weak link. Figure 3(c) shows a large $\sim 84\%$ enhancement of $C_S(1,2)$ compared with results for a ring. The reason is that for a ring spins 1 and 2 are not much correlated since each can form a strong bond with a neighboring spin, while for an open chain the spin at 1 is free and strongly tries to form a singlet with its neighbor regardless of the smaller value of the coupling $J(1 - \delta)$ in this link. Thus, the relative enhancement is large. If the pattern of weak vs strong bonds is shifted in one lattice spacing, then the AF enhancement is smaller since the spins of the now strong bond 1-2 are strongly correlated for both a ring and a chain with OBC.

The local RVB picture presented here predicts that AF enhancement should also occur in dimensions higher than 1, but with a strength reduced from the results in 1D. In general, a given spin of an hypercubic lattice would tend to form singlets with $2 \times D$ partners in the absence of a vacancy and with $2 \times D - 1$ partners when a vacancy is introduced next to it [as exemplified in Fig. 2(c) for $D = 2$]. The ideal enhancement factor F would be $F \sim (2 \times D)/(2 \times D - 1)$, but it is certainly reduced by the inclusion of corrections beyond NN singlets. In Fig. 4(a), $C_S(i,j)$ for a (tilted) square cluster of 26 sites is shown with and without a Zn impurity. The relative enhancement at distance 1 along an axis away from the vacancy is $\sim 11\%$, i.e., smaller than in 1D, as predicted. Our picture does not depend on the presence of long-range order, as exemplified by calculations of $C_S(i,j)$ for the frustrated $J_1 - J_2$ 2D Heisenberg model with a vacancy.

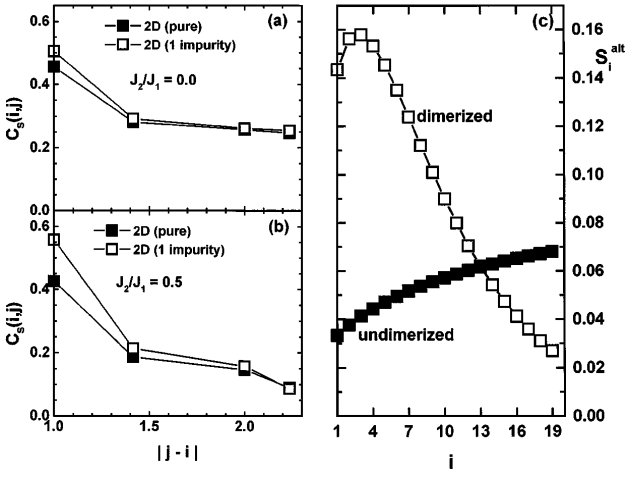

FIG. 4. $C_S(i,j)$ on a 26-sites tilted square cluster calculated with ED. Open (full) squares denote results with (without) a vacancy. i is the site next to the vacancy if present. Correlations at distances 1, $\sqrt{2}$, 2, and $\sqrt{5}$ away from the impurity are shown; (b) The same as (a) but introducing frustration $J_2/J_1 = 0.5$; (c) Alternating contribution to the *local* spin correlations S_i (see text and Ref. [11]) for a $J_1 - J_2 - \delta$ model with $J_2/J_1 = 0.2$ and $\delta = 0.03$ using DMRG on a chain of 160 sites with OBC (open squares). The full squares are results for $J_2 = \delta = 0.0$ on the same chain. In both cases 16 states are kept in the DMRG method, and the end of the chain is at site 0.

Figure 4(b) actually shows an AF enhancement near the vacancy *larger* at $J_2/J_1 = 0.5$ (where the long-range AF order is suppressed) than at $J_2/J_1 = 0.0$ ($\sim 31\%$ vs $\sim 11\%$ for the correlation at distance 1). A smooth connection between the two results was observed numerically, and thus once again the local AF enhancement seems caused by the RVB character of the short distance fluctuations independently of the long distance properties of the model.

It is also possible to predict the strength of the enhancement for models with spins $S > \frac{1}{2}$. Consider first a 1D chain. In the limit of $S \to \infty$, the zero temperature ground state is antiferromagnetically ordered and the picture based on RVB singlets is no longer useful. In this limit the presence of a nonmagnetic impurity is irrelevant for the spin correlations which remain of maximum strength. Assuming a monotonous crossover from $S = \frac{1}{2}$ to $S = \infty$, a Zn-induced enhancement of $C_S(i, j)$ for all S would be expected, but of decreasing magnitude as S grows. Indeed, for a $S = 1$ chain the spin correlation at distance one near an end is $\sim 16\%$ larger than in the bulk [10], an enhancement smaller than for $S = \frac{1}{2}$ [18]. Thus, the vacancy-induced antiferromagnetic enhancement seems to occur in any dimension D and spin S, but the effect is the largest for 1D $S = \frac{1}{2}$ systems where quantum fluctuations are crucial.

The results obtained in this paper allow us to make predictions for the NMR spectra of a variety of compounds similarly as done before for 1D $S = \frac{1}{2}$ chains [11,20]. In Fig. 4(c) the *alternating* part of the local spin correlations $S_i = \sum_j \langle S_i^z S_j^z \rangle$ (proportional to the local susceptibility χ_i) is shown. Here $\langle\,\rangle$ represents the expectation value in the lowest energy state of the subspace of spin one, which would contribute to χ_i as the temperature or an external magnetic field is increased from zero (S_i in the singlet ground state of a finite lattice would trivially vanish). The figure shows that both dimerized and undimerized chains have a nonzero local staggered magnetization near vacancies. In the former the enhancement is concentrated in the vicinity of the impurity, while in the latter it is spread over all the chain due to spin-charge separation in excellent agreement with Ref. [11]. NMR experiments should detect a broadening in their spectra associated with this effect in several compounds such as $CuGeO_3$. At a more speculative level, the AF enhancement discussed in this paper may be responsible for the transition to a 3D Néel order state in Zn-doped dimerized chains and ladders [7,8] . Note, however, that this effect may depend on the strength of the (small) coupling between the structures discussed here, and thus may vary appreciably from compound to compound.

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