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Ground-state functional for quantum spin chains with bond defects

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We have developed a nonlocal functional of the exchange interaction for the ground-state energy of quantum spin chains described by the Heisenberg Hamiltonian. An alternating chain is used to obtain the correlation energy and a local unit-cell approximation is defined in the context of the density-functional theory. The agreement with our exact numerical data, for small chains, is significantly better than a previous formulation, even for chains with several ferromagnetic or antiferromagnetic bond defects. The results can be particularly relevant in the study of finite spin-1/2 Heisenberg chains, with exchange couplings changing, magnitude, or even sign, from bond-to-bond.

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I. INTRODUCTION

Spin Hamiltonians are among the most relevant in condensed matter, since they describe magnetism with origin in localized moments,[1] which is very common in real materials. Sophisticated procedures have been developed in order to obtain the energy spectra of those Hamiltonians, or at least, the ground-state energy (GSE) in the cases of more complex spin models. The homogeneous, translational invariant, spins-1/2 Heisenberg model can be solved by Bethe ansatz. However, if translational symmetry is broken, like in most real systems, powerful numerical methods, such as Monte Carlo simulations, can be applied, but at high computational cost. More than challenges to our theoretical approaches, real-life complications, such as magnetic impurities, bond defects, finite-size effects, vacancies, etc, are important ingredients to be added to models today, due to the crescent interest in novel materials.

For realistic models, sometimes we just have good estimates for fundamental properties, such as correlation energies. The mean-field (MF) approximation, although can always be applied, is not, in general, accurate enough. In this Brief Report we describe one analytical procedure to estimate beyond-mean-field energies for finite spin-1/2 chains with bond defects. We apply density-functional theory (DFT) (Ref. 2) in the context of the Heisenberg model, as described in Refs. 3–6, where the GSE was computed for antiferromagnetic chains or lattices containing impurity spins. In all applications in those references, the exchange interactions have the same value and sign (all antiferromagnetic). We want to go beyond this limitation.

The DFT procedure to construct a spin functional starts with a homogeneous system for which we know the correlation energy as a function of the spin S. The simplest way to build the correlation-energy functional for a nonhomogeneous system is the use of local approximations. References 3–6 define the local-spin approximation (LSA), consisting in replacing the spin S by its value S_i at each site i. An analogous procedure was used in Ref. 8 to build an energy functional of the bond distribution J_b (index b labels the bond between two successive spins), defining a local-bond approximation (LBA) in the same way LSA is made, that is, substituting J by its local value J_b in the correlation energy of the homogeneous system. We follow the same lines but we obtain a functional of the ratio J_{b+1}/J_b of successive exchange interactions. In this context, this represents a step in the direction of defining nonlocal functionals. The main idea here is to start with a homogeneous system that has already some characteristics of the inhomogeneous systems of interest. We propose the use of an alternating chain,[9] a system of spins 1/2 with exchange interactions J and αJ alternating from bond-to-bond. In terms of unit cells consisting of two successive bonds each, this chain is homogeneous in the variable α. Thus, a local unit-cell approximation can be introduced, as described below. Our results are significantly more accurate than those of Ref. 8 but they are restrict to chains of spins 1/2. We assess the validity of our results by comparing them with exact numerical data obtained for small chains using the power method algorithm.

II. LOCAL UNIT-CELL APPROXIMATION

The basic assumption of DFT about spin systems is that the ground state $|\psi_0\rangle$ is a functional of the classical spin-vector distribution $\{\vec{S}_i\}$, for a given set of exchange interaction $\{J_i\}$. Hence, the expectation value $\langle\Psi_0[\vec{S}_i]|\hat{O}|\Psi_0[\vec{S}_i]\rangle$ of any spin operator $\hat{O}$ is also a functional of the spin distribution, and in particular, the GSE $E_0=E_0[\vec{S}_i]=\langle\Psi_0[\vec{S}_i]|\hat{H}|\Psi_0[\vec{S}_i]\rangle$. This makes possible the use of DFT in nonhomogeneous systems, but in general, an approximation is required to obtain $E_0[\vec{S}_i]$. Since the MF term $E_0^{\mathrm{MF}}[\vec{S}_i]=\Sigma_{\langle i,j\rangle}J_i\vec{S}_i\cdot\vec{S}_j$ is already a functional of the vector $\vec{S}_i$, we may write

$$E_0[\vec{S}_i]\equiv E_0^{\mathrm{MF}}[\vec{S}_i]+E_c[\vec{S}_i], \tag{1}$$

which defines the correlation energy functional $E_c[\vec{S}_i]$. To obtain an approximation for $E_c[\vec{S}_i]$, we take a related homogeneous system and calculate for it $E_c(S)=E_0(S)-E_0^{\mathrm{MF}}(S)$. Knowing any approximation for $E_0(S)$ better than MF, e.g., from spin-wave theory, we can obtain an approximation for $E_c(S)$. The simplest way to build the correlation functional for an inhomogeneous system is through a local-spin approximation

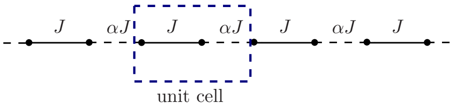

FIG. 1. (Color online) Spin chain with exchange interaction J and αJ alternating from bond-to-bond. Two successive bonds, J and αJ, defines one unit cell. The sequence of unit cells is a homogeneous chain in α.

$$E_c^{\mathrm{LSA}}[J,\vec{S}_i]=\sum_{i=1}^{N}\frac{E_c(J,S)}{N}\bigg|_{S\to|\vec{S}_i|},\tag{2}$$

where the sum runs over N spins. This approximation resembles the famous local-density approximation for electronic systems.[2,7] LSA has been applied to Heisenberg model with impurity spin, in one, two or three dimensions,[3–6] but in all cases to systems with antiferromagnetic uniform exchange interactions J.

To extend the local-approximation scheme to spin Hamiltonians with bond defects, Ref. 8 proposed the following *local-bond approximation*:

$$E_c^{\mathrm{LBA}}[J_b,S]=\sum_{b=1}^{N_b}\frac{E_c(J,S)}{N_b}\bigg|_{J\to J_b},\tag{3}$$

where the sum runs over N_b bonds.

Consider now a chain of spins 1/2 as a sequence of $N_u=N_b/2$ unit cells, each cell with one bond J and the successive bond αJ. This alternating chain, illustrated in Fig. 1, is defined by the Heisenberg-type Hamiltonian

$$\hat{H}=\sum_{i=1}^{N}[J\hat{S}_{2i-1}\cdot\hat{S}_{2i}+\alpha J\hat{S}_{2i}\cdot\hat{S}_{2i+1}]\tag{4}$$

with $\hat{S}_i$ a spin operator (not the classical vector $\vec{S}_i$).

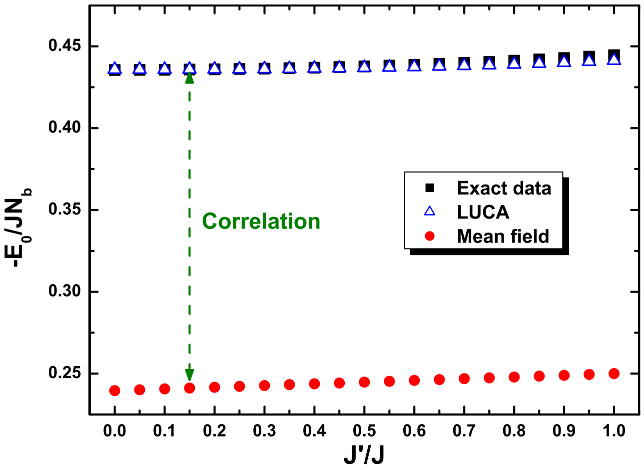

FIG. 2. (Color online) GSE, per unit of JN_b, of 24 spins 1/2 in a ring with one antiferromagnetic defect of strength J', as a function of the ratio J'/J. The agreement between the exact numerical data (squares) and those from LUCA (triangles) is very good. The difference between MF results (circles) and the exact data is the correlation energy, which value is about half of the exact energy.

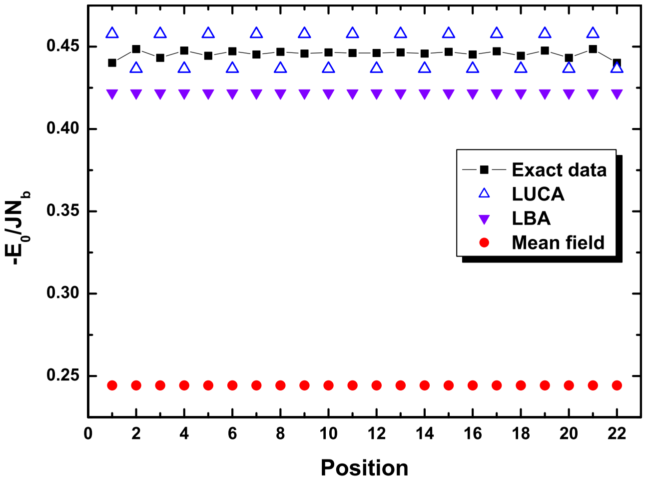

FIG. 3. (Color online) GSE, per unit of JN_b, of an open chain with 24 spins 1/2, as a function of the position of one defect of strength $J'=0.5J$. Exact data (squares) and LUCA results (open triangles) show oscillatory pattern, absent in the MF (circles) and in the LBA (full triangles) results.

The chain made of unit cells can be seen as being homogeneous in α, and thus a *local unit-cell approximation* (LUCA) can be defined as

$$E_c^{\mathrm{LUCA}}[\alpha_u]=\sum_{u=1}^{N_u}\frac{E_c^{alt}(\alpha)}{N_u}\bigg|_{\alpha\to\alpha_u},\tag{5}$$

where $E_c^{alt}(\alpha)$ is the correlation energy of the alternating chain. α_u is the local value of α in the u cell. Although local in α, $E_c^{\mathrm{LUCA}}[\alpha_u]$ is nonlocal in J_i since $\alpha_u=J_{i+1}/J_i$.

In the work of Barnes *et al.*,[9] the GSE, per site and in units of J, of an alternating chain is expressed as the following polynomial expansion valid for $0\leq\alpha<1$:

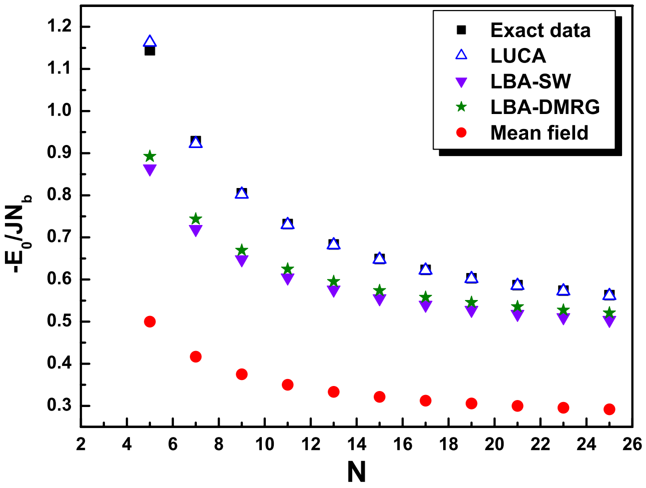

FIG. 4. (Color online) Size dependence of the GSE, per unit of JN_b, of rings with one defect of strength $J'=5\ J$. Results from LUCA (open triangles) agree much better with the exact data (square) than those from LBA-SW (full triangles) or from LBA-DMRG (stars).

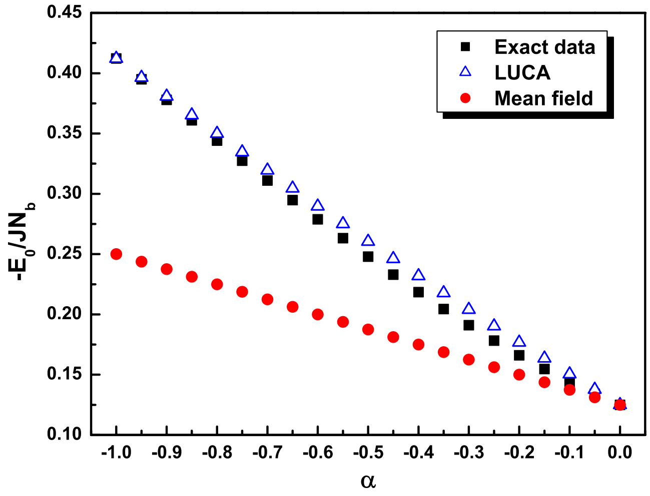

FIG. 5. (Color online) GSE, per unit of JN_b, of 24 spins 1/2 in a ring with ferromagnetic and antiferromagnetic exchange interaction alternating from bond-to-bond, as a function of the ratio α. Exact data (squares) are compared with LUCA results (triangles) and MF data (circles).

$$e_0(\alpha) = -\frac{3}{8} + f(\alpha) \tag{6}$$

with

$$f(\alpha) = -\frac{3}{2^6}\alpha^2 - \frac{3}{2^8}\alpha^3 - \frac{13}{2^{12}}\alpha^4 - \frac{89}{2^{14}\times 3}\alpha^5 - \frac{463}{2^{17}\times 3}\alpha^6 - \frac{7\times 61\times 191}{2^{22}\times 3^3}\alpha^7 - \frac{11\times 139\times 271}{2^{21}\times 3^4\times 5}\alpha^8 - \frac{107\times 22005559}{2^{30}\times 3^5\times 5^2}\alpha^9. \tag{7}$$

For $\alpha > 1$, we use $e_0(\alpha) = \alpha\, e_0(\alpha^{-1})$, a property that follows directly from the Hamiltonian. For $\alpha = 0$, the chain reduces to N_b free bonds and $e_0(0) = -3/8$ is exact. For $\alpha = 1$ the chain is uniform, and $e_0(1) \approx -0.441325$ is only 0.4% from the Bethe-ansatz value -0.443147, a good result for an expansion valid for $\alpha < 1$.

The MF approximation for the alternating chain of N spins 1/2 gives $e_0^{\rm MF}(\alpha) = -(1+\alpha)/8$ for the GSE per bond. Thus, the correlation energy $e_c(\alpha) = e_0(\alpha) - e_0^{\rm MF}(\alpha)$ is

$$e_c(\alpha) = -\frac{1}{4} + \frac{\alpha}{8} + f(\alpha) \tag{8}$$

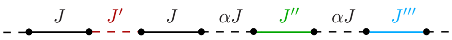

FIG. 6. (Color online) Alternating ring with three defects, $J' = 0.5J$ in an αJ-type bond, defects $J'' = 0.7J$ and $J''' = 0.9J$ in a J-type bond.

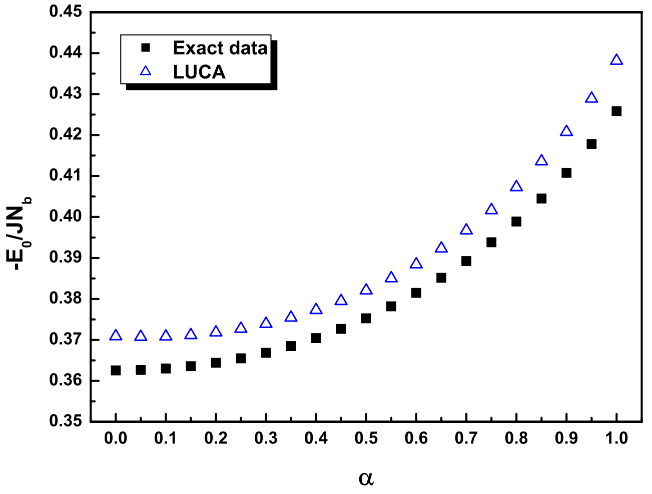

FIG. 7. (Color online) Dependence on α of the GSE, per unit of JN_b, of 24 spins 1/2 in a ring with three defects arranged as in Fig. 6. Exact data (squares) deviate about 2% from LUCA results (triangles).

resulting, after the use of Eq. (5)

$$E_c^{\rm LUCA}[\alpha_u] = J\sum_{u=1}^{N_u} 2[e_c(\alpha_u)\theta(1-\alpha_u) + \alpha_u e_c(\alpha_u^{-1})\theta(\alpha_u - 1)], \tag{9}$$

where $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$ is the Heaviside function, introduced to take into account defects with $\alpha_u < 1$ or $\alpha_u > 1$. Finally, the GSE is found minimizing the following functional respect to the spins variables $\vec{S}_i$ (obeying the constraint $|\vec{S}_i| = 1/2$):

$$E^{\rm LUCA}[\alpha_u, \vec{S}_i] = \sum_{i=1}^{N} J_i \vec{S}_i \cdot \vec{S}_{i+1} + E_c^{\rm LUCA}[\alpha_u]. \tag{10}$$

III. RESULTS

We show results using the above functional for finite chains containing bond defects and/or boundary effects. Better results are expected for chains similar to the alternating one and with $0 \leq \alpha_u \ll 1$ or $\alpha_u \gg 1$ since this is the base upon the functional was built. However, the functional is robust and gives good estimates even for α out of that range. We also observe that the deviations from the exact data are smaller when the defects are in the bond type αJ. Although the functional can be easily applied for chains with arbitrary size, we limit our examples to chains with 24 spins 1/2 in order to compare our estimates with exact results. These are obtained using the well-known power algorithm,[8] performing

$$E_0 = \lim_{k\to\infty} \frac{\langle\phi|(\hat{H}-\epsilon)^{k+1}|\psi_T\rangle}{\langle\phi|(\hat{H}-\epsilon)^{k}|\psi_T\rangle} + \epsilon. \tag{11}$$

This defines a sequence of k steps to reach convergence. For the trial vector $|\Psi_T\rangle$ we use the MF ground state. $|\phi\rangle \equiv (\hat{H}-\epsilon)^{k-1}|\psi_T\rangle$ used at step k is obtained in the step $k-1$. The constant ϵ is an upper limit of the energy spectrum;

without it the power method would return the highest eigenvalue of $\hat{H}$.

Let's first consider a finite spin ring with antiferromagnetic bonds of strength J, except one, the defect, with strength J'. This case has little resemblance to an alternating chain, because we have $\alpha_u=1$ in all unit cells, except in one of them, where $\alpha_u=J'/J$. Figure 2 shows our results (triangles) for the GSE per bond as a function of the ratio J'/J. The agreement with exact results (squares) is very good, even for J' close to J where the deviation is less than $\approx 0.7\%$. Note the large value of the correlation energy, about half of the GSE; one has really a strong correlated system and the energy E_c is not just a perturbation in the MF term. The DFT plus the local approximation go beyond the simple perturbation theory.

In Fig. 3 we fixed $J'/J=0.5$ and show the GSE per bond as a function of the position of this defect in an open chain. Contrary to MF (circles) and the LBA results (full triangles),[8] the functional (open triangles) captures the oscillations present in the exact data (squares), although not the phase (the up and downs are reversed). This is an example of the importance of the correlation energy. The errors are larger than those of the previous figure, probably due to finite-size effects introduced by the open-boundary condition.

Figure 4 compares our results from the LUCA with two local-bond approximations developed in Ref. 8, for chains with different sizes and with one strong defect with strength $J'=5J$. The LBA-SW uses the results from spin-wave theory (SW) to build the correlation energy, whereas LBA-DMRG uses results from density matrix renormalization group (DMRG) to do that. Both approximations define functionals of J_b. The advantage of LUCA comes from its dependence on the ratio J_{b+1}/J_b.

Several compounds exhibit ferromagnetic and antiferromagnetic alternating-bond-type ordering, some of them even with one-dimensional characteristics.[10,11] We consider here a simple system consisting of a ring of spins 1/2. The results in Fig. 5 show that our functional (triangles) reproduces in the range $-1\leq\alpha<0$ quite well (errors less than 3%) the exact data (squares), whereas MF (circles) is good only near $J'=0$; in this limit, the chain is broken in twelve independent ferromagnetic dimers and for this ordering MF solution for the ground state is exact, therefore, there is no correlation energy at this point. For the special limit $\alpha=-1$, the numerical exact result for our finite ring is $e_0=-0.41225829$, whereas our estimate is -0.41210.

To illustrate a situation with several defects, we consider an alternating ring with three defects, $J'=0.1J$, $J''=0.7J$, and $J'''=0.9J$, arranged as depicted in Fig. 6. The first defect is in a bond of type αJ and the other two in bonds of type J. Figure 7 shows that the data from the functional (triangles) deviate about 3% from the exact results (squares). This error is large because two defects, J'' and J''', are in J-type bonds and this tends to raise the errors. For example, with J' and J'' in αJ-type bonds, while J''' in a J-type bond, the error drops to 0.5% for $0\leq\alpha<1$.

IV. CONCLUSIONS

Local approximations are common in the context of DFT (Ref. 7) but when used in models with several inhomogeneities the results may be not so good. Our local unit-cell approximation uses an alternating chain[9] as a starting point to build correlation energies. Thus, our functional already has characteristics of nonuniform chains, what yields much better estimates for the GSE than the previous formulation using LBA.[8] At present we are exploring the idea of unit cells to construct nonlocal spin functionals, and perhaps circumventing the major limitation of our present functional, applicable only to chains of 1/2 spins. In spite of this, our analysis covers theoretical issues related to important materials showing special magnetic ordering, such as tetrameric compounds described by Heisenberg antiferromagnetic chains.[11]

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