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The spin-partitioned total position-spread tensor: An application to Heisenberg spin chains

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The spin partition of the Total Position-Spread (TPS) tensor has been performed for one-dimensional Heisenberg chains with open boundary conditions. Both the cases of a ferromagnetic (high-spin) and an anti-ferromagnetic (low-spin) ground-state have been considered. In the case of a low-spin ground-state, the use of alternating magnetic couplings allowed to investigate the effect of spin-pairing. The behavior of the spin-partitioned TPS (SP-TPS) tensor as a function of the number of sites turned to be closely related to the presence of an energy gap between the ground-state and the first excited-state at the thermodynamic limit. Indeed, a gapped energy spectrum is associated to a linear growth of the SP-TPS tensor with the number of sites. On the other hand, in gapless situations, the spread presents a faster-than-linear growth, resulting in the divergence of its per-site value. Finally, for the case of a high-spin wave function, an analytical expression of the dependence of the SP-TPS on the number of sites n and the total spin-projection S_z has been derived. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4936585]

I. INTRODUCTION

The concept of localization tensor was introduced in the context of the theory of Kohn[1] to characterize the electrical conductivity properties. Indeed, in his seminal work, Kohn suggested that the most fundamental picture of electrical conductivity is more related to the delocalization of the ground-state wave function than to the simple gap closure. Subsequently, Resta and co-workers, with the introduction of the Localization Tensor (LT), provided an important tool to give a quantitative formulation of this localization.[2–6] According to their results, one of the key properties of this quantity is the following: it diverges in the thermodynamic limit for a conductor, while remaining finite for an insulator. A remarkable sum rule connecting explicitly electrical resistivity and localization tensor was later given by Souza, Wilkens, and Martin.[7]

The LT is an intensive quantity which makes it highly suitable to study systems in solid state physics. On the other hand, in a molecular context we prefer to consider the total position-spread (TPS) tensor,[8–10] which is nothing but the LT by a multiplication factor, i.e., the number of electrons. The TPS presents important properties for molecules such as size-consistency[11,12] which is crucial to describe bond breaking and chemical processes.[8,13–16] Hence, given that it encloses information about the overall wave function, the TPS is particularly appropriate to study finite-size systems.

Despite the fact that the TPS tensor has been subject of a variety of works in the last years,[13–15,17–24] the spin-partitioned TPS (SP-TPS) formalism is a new tool which has been introduced in our recent works on H_2 molecule[16] and hydrogen chains (H_n),[25] where we showed in detail how it allows to investigate separately the fluctuations of the same-spin and different-spin electrons in a system. In the present work, we focus our attention on the spin part of the wave function of linear systems, through the use of the Heisenberg model Hamiltonian. The importance of the Heisenberg model lies in its capability to describe and predict magnetic phenomena in real systems such as "superexchange" in copper-oxide ferromagnets,[26] phase transitions, and critical points. This model has also been used to derive the spin wave theory, and the study of experimental and theoretical spin currents.[27] We studied and compared different spin states with different multiplicity and values of the z-projection of the total spin S_z. These distinctions are indeed harder to achieve with quantum chemical calculations on the previously mentioned hydrogen chains, which show a low-spin ground-state as the result of an anti-ferromagnetic coupling between isolated atoms in the dissociation limit. Moreover, acting on the magnetic coupling between neighbor sites, we will analyze the effect of spin-pairing, depicting the spin part of the wave function of dimerized chains.

This paper is structured as follows: in Section II, a brief description of the Heisenberg model for linear spin chains is provided; in Section III, we recall the main aspects of the SP-TPS formalism and describe its application to this model Hamiltonian; after supplying a description of the computational details in Section IV, we present and discuss the numerical results in Section V; finally, our conclusions are drawn in Section VI; further details are given in Appendix B,

where we report the analytical derivation of the SP-TPS tensor dependence of the number of sites n and S_z for the ferromagnetic coupling.

II. THE HEISENBERG HAMILTONIAN AND ITS APPLICATION TO LINEAR CHAINS

Let us consider the Heisenberg Hamiltonian, which allows us to describe the magnetic interaction of a linear system consisting of n spins ν, having components $\{\hat{S}_\nu^x, \hat{S}_\nu^y, \hat{S}_\nu^z\}$ and nearest-neighbor spin coupling $\mathbf{J}_\nu = \{J_\nu^x, J_\nu^y, J_\nu^z\}$,

$$\hat{\mathcal{H}} = \sum_{\nu=1}^{n-1} J_\nu^x \hat{S}_\nu^x \hat{S}_{\nu+1}^x + J_\nu^y \hat{S}_\nu^y \hat{S}_{\nu+1}^y + J_\nu^z \hat{S}_\nu^z \hat{S}_{\nu+1}^z. \quad (1)$$

Notice that in the previous equation the sum over ν can also be seen as a sum over the nearest-neighbor spin pairs (or "bonds" in the chemists' language). The model Hamiltonian describing the case under study can be obtained as the strong Coulomb limit of a half-filled Hubbard Hamiltonian[28] that involves one electron per site. In its simplest form, the Hubbard Hamiltonian[29] for a linear chain is given by

$$\hat{\mathcal{H}}_U = -t \sum_{\nu=1}^{n} \sum_{\delta=-1,1} \sum_{\sigma=\alpha,\beta} \hat{c}_{\nu,\sigma}^+ \hat{c}_{\nu+\delta,\sigma} + U \sum_{\nu=1}^{n} \hat{n}_{\nu,\alpha} \hat{n}_{\nu,\beta}, \quad (2)$$

where $\hat{c}_{\nu,\sigma}$ ($\hat{c}_{\nu,\sigma}^+$) are annihilation (creation) operators of an electron with spin projection σ, and $\hat{n}_{\nu,\sigma}$ is the number operator, defined as $\hat{n}_{\nu,\sigma} = \hat{c}_{\nu,\sigma}^+ \hat{c}_{\nu,\sigma}$. In this equation, the sum over ν runs over all the sites of the system. On the other hand, the sum over δ ($\delta = -1$ or $\delta = +1$) restricts the range of the inter-center interaction to topologically connected pairs only. In a linear chain, the parameter t is the hopping integral between the connected sites ν and $\nu + 1$, while U is the one-center Coulomb repulsion. Since in the strong Coulomb limit $U \gg -t$, it is possible to treat the system by employing Rayleigh-Schödinger perturbation theory[30] for which the term $U \sum_\nu \hat{n}_{\nu,\alpha} \hat{n}_{\nu,\beta}$ in Eq. (2) is taken as the unperturbed part of the Hamiltonian $\hat{\mathcal{H}}_U$, whereas the $-t \sum_{\nu=1}^{n} \sum_{\delta=-1,1} \sum_{\sigma=\alpha,\beta} \hat{c}_{\nu,\sigma}^+ \hat{c}_{\nu+\delta,\sigma}$ part is treated as a perturbation. As described in Ref. 30, when considering the second-order equation, if the topologically connected site of an electron with spin projection σ is occupied by one electron of opposite spin then the former can hop to the neighboring site, and get back to its original position. Thus, this mechanism gives rise to an effective interaction that will favor neighboring electrons to have opposite spins (anti-ferromagnetic exchange) that in turn makes the kinetic energy to decrease. It can be shown[26] that the resulting effective model (that holds at temperatures and energies $\ll U$) corresponds to the Heisenberg anti-ferromagnetic model for the $S = 1/2$ electron spins, with $J = 4t^2/U$.

In the particular case where the coupling constant has the same value for each direction, the Heisenberg Hamiltonian reduces to

$$\hat{\mathcal{H}} = \sum_{\nu=1}^{n-1} J_\nu \left[\frac{1}{2} \left(\hat{S}_\nu^+ \hat{S}_{\nu+1}^- + \hat{S}_\nu^- \hat{S}_{\nu+1}^+ \right) + \hat{S}_\nu^z \hat{S}_{\nu+1}^z \right], \quad (3)$$

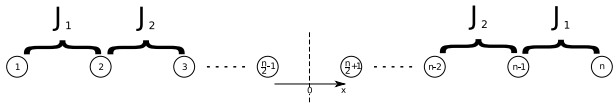

FIG. 1. Pictorial representation of the Heisenberg spin chain with different magnetic couplings and an even number of sites.

with $\hat{S}_\nu^+ = \hat{S}_\nu^x + i\hat{S}_\nu^y$ and $\hat{S}_\nu^- = \hat{S}_\nu^x - i\hat{S}_\nu^y$. In a Heisenberg chain, both the square of total spin $\hat{S}^2$ and the total spin z-component $S_z = \sum S_\nu^z$ commute with the Hamiltonian. This means that the eigenvectors $|\Psi\rangle$ of $\hat{\mathcal{H}}$ can be chosen in such a way that $\hat{S}^2|\Psi\rangle = s(s+1)|\Psi\rangle$ and $\hat{S}^z|\Psi\rangle = m|\Psi\rangle$. For this reason, it is convenient to label the ground-state wave function as $|^{s,m}\Psi_0\rangle$. It can be expressed in the basis consisting of the 2^n spin permutations $\{^m\phi_i\}$,

$$|^{s,m}\Psi_0\rangle = \sum_i C_i^{s,m} \, |^m\phi_i\rangle. \quad (4)$$

We stress the fact that our magnetic interaction J couples *nearest-neighbor centers only*. We will assume an even number of sites n and focus our attention on two different situations (see Figure 1 for a graphical illustration). In the first case (the "uniform" or "equal-J chain"), all J_ν have a common value of J. In this situation, J does not affect the eigenvectors of the Hamiltonian, but it does change their eigenvalues: for $J < 0$ the ferromagnetic case ($s = n/2$) is the ground-state of the system, while for $J > 0$ the ground-state is an anti-ferromagnetic singlet. In the second case (the "alternating" or "dimerized" chain), the coupling constants have two alternating values, J_1 and J_2, for ν odd (J_1) and even (J_2), respectively. By simply varying the $\eta = J_2/J_1$ ratio from 1 to 0, we studied the evolution of the system, that goes from a highly delocalized magnetic chain to a collection of non-interacting spin-pairs. This allows us to depict the evolution of the magnetic behavior of a chain of atoms if dimerization occurs. Notice that in the present work we limit our investigation to the case where J_1 and J_2 have the same sign. It has also to be underlined that, in order to minimize boundary effects, we will use the largest (in modulus) coupling constant J for the external bonds. In other words, we assume $|J_1| \geq |J_2|$. The calculation of the spread tensors is fully described in Secs. III and IV. Here, we want to stress the fact that the position of the centers is fixed, and independent on presence of dimerization that affects the value of J. In particular, the nearest-neighbor inter-center distance is assumed to be one bohr.

III. THE SPIN PARTITION OF TPS TENSOR FOR THE HEISENBERG WAVE FUNCTION

The general formalism of the spin-partitioned TPS tensor is fully unfolded in our previous works on the H_2 molecule[16] and hydrogen chains.[25] In the present paper, we summarize its main aspects and describe its application to the special case of Heisenberg chains. Indicating by $\hat{\mathbf{r}}(i)$, the vector operator associated to the position of electron i, it is possible to define the *total* position operator as the many-body operator given

by the sum of all the individual electron-position operators,

$$\hat{\mathbf{R}} = \sum_{i=1}^{n} \hat{\mathbf{r}}(i), \tag{5}$$

where the sum runs over all the n electrons of the system. The spin-summed TPS (SS-TPS) tensor is then defined as the second moment cumulant[12] of the total-position operator $\hat{\mathbf{R}}$,

$$\mathbf{\Lambda} = \langle\Psi|\hat{\mathbf{R}}^2|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}|\Psi\rangle^2. \tag{6}$$

The position operator of a single electron can be expressed as the sum of two terms arising from the α-spin and β-spin electrons (or *spin up* and *spin down* electrons in physicists' notation),[16]

$$\hat{\mathbf{r}} = \hat{\mathbf{r}}_\alpha + \hat{\mathbf{r}}_\beta. \tag{7}$$

Therefore, the total-position $\hat{\mathbf{R}}$ will be described by a similar sum,

$$\hat{\mathbf{R}} = \hat{\mathbf{R}}_\alpha + \hat{\mathbf{R}}_\beta. \tag{8}$$

By taking the square of Eq. (8), one trivially obtains

$$\hat{\mathbf{R}}^2 = \hat{\mathbf{R}}_\alpha^2 + \hat{\mathbf{R}}_\beta^2 + \hat{\mathbf{R}}_\alpha\hat{\mathbf{R}}_\beta + \hat{\mathbf{R}}_\beta\hat{\mathbf{R}}_\alpha. \tag{9}$$

Thus, each term in Eq. (6) splits in four joint cumulants[31] $\alpha\alpha$, $\beta\beta$, $\alpha\beta$ and $\beta\alpha$, so that

$$\mathbf{\Lambda} = \mathbf{\Lambda}_{\alpha\alpha} + \mathbf{\Lambda}_{\beta\beta} + \mathbf{\Lambda}_{\alpha\beta} + \mathbf{\Lambda}_{\beta\alpha}, \tag{10}$$

where the different components of the TPS tensor are

$$\mathbf{\Lambda}_{\alpha\alpha} = \langle\Psi|\hat{\mathbf{R}}_\alpha^2|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}_\alpha|\Psi\rangle^2, \tag{11}$$

$$\mathbf{\Lambda}_{\beta\beta} = \langle\Psi|\hat{\mathbf{R}}_\beta^2|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}_\beta|\Psi\rangle^2, \tag{12}$$

$$\mathbf{\Lambda}_{\alpha\beta} = \langle\Psi|\hat{\mathbf{R}}_\alpha\hat{\mathbf{R}}_\beta|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}_\alpha|\Psi\rangle\langle\Psi|\hat{\mathbf{R}}_\beta|\Psi\rangle, \tag{13}$$

$$\mathbf{\Lambda}_{\beta\alpha} = \langle\Psi|\hat{\mathbf{R}}_\beta\hat{\mathbf{R}}_\alpha|\Psi\rangle - \langle\Psi|\hat{\mathbf{R}}_\beta|\Psi\rangle\langle\Psi|\hat{\mathbf{R}}_\alpha|\Psi\rangle. \tag{14}$$

Different symmetry relations occur among the spin-partitioned components of $\mathbf{\Lambda}$. Because $\hat{\mathbf{R}}_\alpha$ and $\hat{\mathbf{R}}_\beta$ commute, $\mathbf{\Lambda}_{\alpha\beta}$ and $\mathbf{\Lambda}_{\beta\alpha}$ components are equal. In the Heisenberg model (unlike the $t-J$ model, for instance), there is always exactly one electron per site, and there is no charge fluctuation among the sites. Therefore, since the spin-summed TPS tensor measures the many-body variance of the total-position operator, its value is identically zero. On the other hand, the spin-partitioned TPS does not vanish, in general, because the α- and β-spins can fluctuate. As a consequence, for any Heisenberg wave function $\mathbf{\Lambda}_{\alpha\alpha} + \mathbf{\Lambda}_{\beta\beta} = -2\mathbf{\Lambda}_{\alpha\beta}$. Finally, in this special case it also occurs that $\mathbf{\Lambda}_{\alpha\alpha}$ and $\mathbf{\Lambda}_{\beta\beta}$ are identical. This can be shown considering that

$$\hat{\mathbf{R}}|^m\Psi(S)\rangle = \sum_i C_i^m(S)\,\hat{\mathbf{R}}|^m\phi_i\rangle = 0, \tag{15}$$

because $\hat{\mathbf{R}}|^m\phi_i\rangle = 0$ for any $|^m\phi_i\rangle$. It follows that

$$\hat{\mathbf{R}}_\alpha|^m\Psi(S)\rangle = -\hat{\mathbf{R}}_\beta|^m\Psi(S)\rangle, \tag{16}$$

from which

$$\begin{aligned}\hat{\mathbf{R}}_\alpha^2|^m\Psi(S)\rangle &= -\hat{\mathbf{R}}_\alpha\hat{\mathbf{R}}_\beta|^m\Psi(S)\rangle = -\hat{\mathbf{R}}_\beta\hat{\mathbf{R}}_\alpha|^m\Psi(S)\rangle \\ &= \hat{\mathbf{R}}_\beta^2|^m\Psi(S)\rangle.\end{aligned} \tag{17}$$

The equivalence $\mathbf{\Lambda}_{\alpha\alpha} = \mathbf{\Lambda}_{\beta\beta}$ is then easily proven. As a result of these equivalences, the evaluation of only one of the spin-partitioned terms will be sufficient. We will focus on $\mathbf{\Lambda}_{\alpha\alpha}$.

A further simplification can be achieved exploiting the independence from the origin of the TPS tensor. Indeed, one can assume a coordinate system with $\langle\Psi|\hat{\mathbf{R}}_\alpha|\Psi\rangle = 0$, so that the SP-TPS tensor can be written as

$$\mathbf{\Lambda}_{\alpha\alpha} = \langle\Psi|\hat{\mathbf{R}}_\alpha^2|\Psi\rangle. \tag{18}$$

Finally, it has to be underlined that, for a one-dimensional system like the one under study, only the longitudinal components of each spin-partitioned term of the TPS tensor are different from zero. Therefore, the considerations described in this work will only concern these scalar terms, which we will label as $\Lambda_{\alpha\alpha}^{s,m}$ for the ground-state wave function $|^{s,m}\Psi_0\rangle$.

IV. COMPUTATIONAL DETAILS

The computation of $\Lambda_{\alpha\alpha}^{s,m}$ can be achieved as

$$\begin{aligned}\Lambda_{\alpha\alpha}^{s,m} &= \langle^{s,m}\Psi_0|\hat{\mathbf{R}}_\alpha^2|^{s,m}\Psi_0\rangle \\ &= \sum_i (C_i^{s,m})^2\langle^m\phi_i|\hat{\mathbf{R}}_\alpha^2|^m\phi_i\rangle \\ &= \sum_i (C_i^{s,m})^2\langle^m\phi_i|\hat{\mathbf{R}}_\alpha|^m\phi_i\rangle\langle^m\phi_i|\hat{\mathbf{R}}_\alpha|^m\phi_i\rangle,\end{aligned} \tag{19}$$

since the orthonormal functions $|^m\phi_i\rangle = |\ldots\sigma_n\ldots\rangle$ are eigenfunctions of $\hat{\mathbf{R}}_\alpha$,

$$\begin{aligned}\hat{\mathbf{R}}_\alpha\,|\ldots\sigma_\nu\ldots\rangle &= \sum_{\nu=1}^{n}\hat{\mathbf{r}}_\nu^\alpha\,|\ldots\sigma_\nu\ldots\rangle \\ &= \sum_{\nu=1}^{n}\rho_\nu\,\delta_{\alpha,\sigma_\nu}\,|\ldots\sigma_\nu\ldots\rangle,\end{aligned} \tag{20}$$

$$\rho_\nu = \nu - \tfrac{n+1}{2}. \tag{21}$$

Using Eqs. (20) and (21), the matrix elements $\langle^m\phi_i|\hat{\mathbf{R}}_\alpha|^m\phi_i\rangle$ can be easily calculated and used to evaluate $\Lambda_{\alpha\alpha}^{s,m}$ if the coefficients $C_i^{s,m}$ are known. In order to evaluate them, we employed a numerical approach to solve the corresponding secular equations, diagonalizing the Heisenberg Hamiltonian matrix built up in the basis of the 2^n possible spin permutations $\{^m\phi_i\}$. This task was achieved through our licensed Python code HEISENBERG.[32] This way the values of $\Lambda_{\alpha\alpha}^{s,m}$ were computed for chains with increasing n and we could explore the effect of the total spin $\hat{S}^2$ and z-projection $\hat{S}_z$. We have introduced the notation $\lambda_{\alpha\alpha}^{\frac{n}{2},m} = \Lambda_{\alpha\alpha}^{\frac{n}{2},m}/n$ to represent the normalized values of the SP-TPS. Notice that, while the spin-summed TPS Λ is appropriate to describe non-homogeneous systems like atoms or molecules, the same quantity divided by the number of sites or electrons is more convenient when systems having different sizes are to be compared. As already stated, we focused on chains with an even number of sites only, which gave us the advantage of dealing with anti-ferromagnetic (singlet) and ferromagnetic ($s = n/2$) ground states. In Appendix A, the case $n = 4$ is reported as an explanatory example.

Because of the exponential growth of the configuration space as a function of n, full diagonalization can be easily achieved only for relatively small chain lengths. For larger

systems, an analytical approach, e.g., through the use of the Bethe Ansatz[33–36] can be a suitable option for the calculation of the total energy and wave function of the system. The Bethe Ansatz is an exact method to the calculation of the eigenvalues and eigenstates of some limited quantum many-body problems. This method has the following advantages: (i) eigenvalues and physical properties obtained using this method can be evaluated in the thermodynamic limit, (ii) avoid the need of exact diagonalizations which are time consuming, (iii) eigenstates can be labeled using quantum numbers to relate them to specific physical properties.[36] However, the calculation of the SP-TPS is far from being trivial with such an approach. In fact, a double sum over all the sites and configurations is involved, for which an analytical result could not be obtained. For this reason, we limited our investigation to a purely numerical study of chains, by taking $n \leq 18$, and extrapolated our results to $U \to \infty$ in order to obtain information about the thermodynamic limit. In the case of a ferromagnetic wave function, nevertheless, we were able to obtain an analytical expression for the SP-TPS.

In our numerical calculations, open boundary conditions were always employed. The use of periodic boundary conditions yields in general much faster convergence because of the absence of border effect and the high symmetry of the system due to translational invariance. However, even if they can be easily used within model Hamiltonians such as the Heisenberg Hamiltonian, it was not possible to exploit them for our investigation. This is because of the nature of the position operator used to compute the TPS tensor, which cannot be uniquely defined within periodic boundary conditions. Work in this direction is in progress in our group to achieve a TPS formalism for periodic boundary conditions.

V. RESULTS AND DISCUSSION

In this section, we discuss and compare the different behavior of equal-J and spin-paired Heisenberg chains. In the limit of an infinite number of sites, the spectra are known to be very different: in the equal-J case, a gapless low-lying energy spectrum is obtained for any value of J; in presence of spin-pair dimerization, on the other hand, a gap opens between the ground-state and the first-excited state. As underlined later, the differences in the energy gaps are reflected in different behaviors of the TPS.

A. Equal-*J* chains

Let us start analyzing the equal-J chains. As already stated, in this case the energy gap between the ground- and first excited-state goes to zero as n goes to infinity, both for a ferromagnetic and anti-ferromagnetic couplings. However, the behavior of this gap closure as a function of n depends on the sign of J and thus on the spin nature of the ground-state. In particular, for $J < 0$, the gap between a maximum-spin state, $s = n/2$, and a state with spin $s = n/2 - 1$, closes faster as n grows. Indeed, as it can be derived using the Bethe Ansatz[36,37] approach, this gap has the form

$$\Delta E = J\left(1 - cos\left(\tfrac{\pi}{n}\right)\right) = 2J\sin^2\left(\tfrac{\pi}{2n}\right), \tag{22}$$

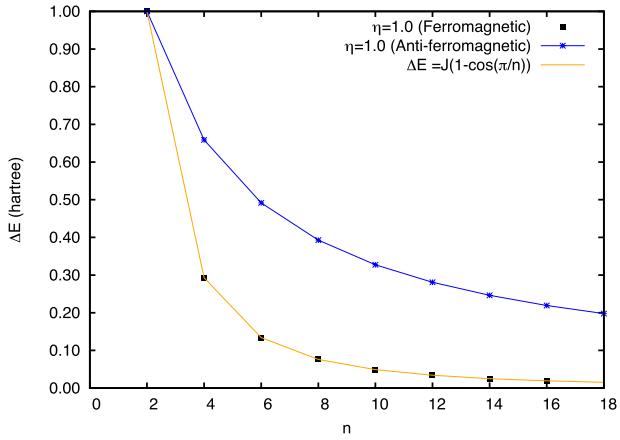

FIG. 2. Energy gaps between the ground-state and the first-excited state for the ferromagnetic and anti-ferromagnetic spin chains as a function of n.

which has the leading term $1/n^2$ (see Ref. 34). On the other hand, in the case $J > 0$, the gap[35] between the ground-state singlet and the first-excited state vanishes as $1/n$ for large n.

In Figure 2, the calculated energy gaps are reported for both cases as a function of the number of sites. These same gaps, multiplied by n^2 and n, for the ferromagnetic and anti-ferromagnetic cases, respectively, are reported in Tables I and II and Figures 1 and 2 of the supplementary material,[38] in order to emphasize their asymptotic behavior.

We analyze now the SP-TPS for the two different cases and observe how the different nature of gap closure is reflected in a different behavior of the TPS, corresponding to a different delocalization of the wave function, so that a faster gap closure corresponds to a quicker divergence of the SP-TPS.

1. Ferromagnetic case

Let us compare the behavior of the spin-partitioned TPS in the case of equal-J chains for the ferromagnetic state. This consists of a manifold of $n+1$ degenerate spin states having $m = s, s-1, \ldots, 0, \ldots, 1-s, -s$. These wave functions present very different SP-TPS values which, for a fixed value of n, show a quadratic dependence on the quantum number m, having a maximum for $m = 0$ and being zero for $m = \pm s$. In order to ease the comparison between the different chains, it is a common practice to normalize the TPS to the number of sites[16,25] as done in Figure 3, where the values of the $\lambda_{\alpha\alpha}^{\frac{n}{2},m} = \Lambda_{\alpha\alpha}^{\frac{n}{2},m}/n$ are reported as a function of m for different number of sites (the values can be found in Table III of the supplementary material[38]). As explained in detail in Appendix B, the $\alpha\alpha$ spin partitioned component obeys to the following law:

$$\lambda_{\alpha\alpha}^{\frac{n}{2},m}(n) = \frac{n+1}{12\,n}\left(\frac{n^2}{4} - m^2\right). \tag{23}$$

It should be noticed that the value of $\Lambda_{\alpha\alpha}^{\frac{n}{2},m}$ does not depend on the sign of m, which implies the equivalence $\Lambda_{\alpha\alpha} = \Lambda_{\beta\beta}$, as already discussed.

Finally, from Eq. (23) it can also be shown that the value of the maxima has a quadratic leading dependence on the number of sites. In fact, for the special case $m = 0$, it holds that

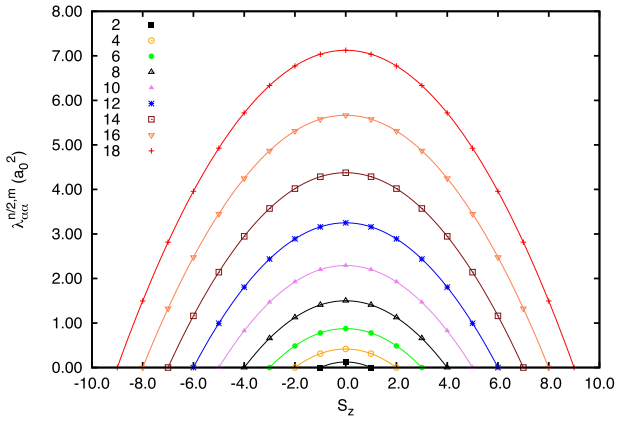

FIG. 3. Normalized $\alpha\alpha$ component of the spin partitioned total position-spread tensor calculated for the ferromagnetic states with different z-projection of the total spin. The dependence on the number of sites is also highlighted reporting data for $2 \leq n \leq 18$. The quadratic trends are expressed by Eq. (23).

$$\lambda^{\frac{n}{2},0}_{\alpha\alpha}(n) = \frac{n^2+n}{48}. \tag{24}$$

2. Anti-ferromagnetic case

The quadratic trend of Eq. (24) has to be compared with the one obtained for the anti-ferromagnetic state as shown in Figure 4 (unnormalized values are given in Table IV of the supplementary material[38]). As it can be seen, in the latter case the spin part of the wave function results to be less delocalized than in the ferromagnetic case and the normalized SP-TPS grows linearly with n. We observe that, in the range under study ($2 \leq n \leq 18$), $\lambda^{0,0}_{\alpha\alpha}$ can be very well fitted with a linear function.

It can be noticed that the behavior of the SP-TPS of the anti-ferromagnetic Heisenberg magnetic chain corresponds to that of the Hubbard Hamiltonian ground-state for small values of the ratio $-t/U$ discussed in our previous work.[16] The equivalence of the two results, which is shown in Figure 5, has

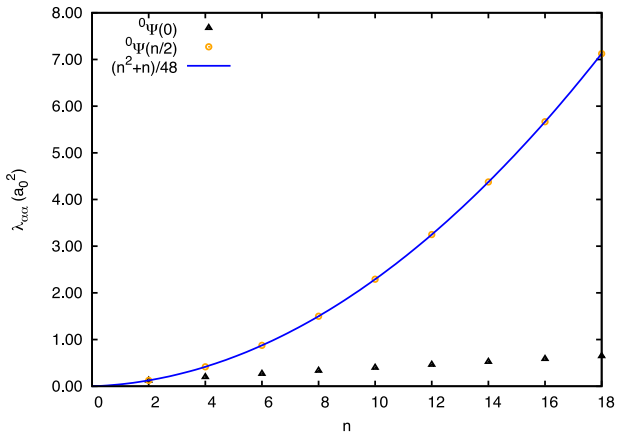

FIG. 4. Normalized $\alpha\alpha$ component of the spin partitioned total position-spread tensor calculated for the anti-ferromagnetic $^0\Psi(0)$ and the ferromagnetic $^0\Psi\left(\frac{n}{2}\right)$ eigenfunctions of the Heisenberg Hamiltonian with spin z-component $m = 0$. The analytical quadratic curve for the ferromagnetic case is also shown in comparison to the linear trend of $\lambda^{0,0}_{\alpha\alpha}$ for the anti-ferromagnetic state.

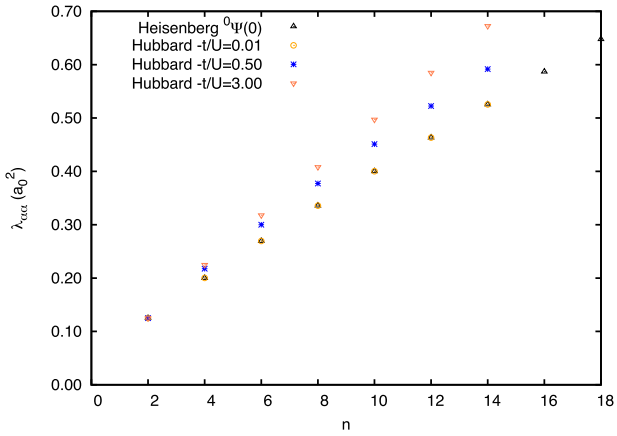

FIG. 5. Comparison between the normalized $\alpha\alpha$ component of the spin partitioned total position-spread tensor calculated for the anti-ferromagnetic state of Heisenberg chains and Hubbard chains with different $-t/U$ ratios. At $-t/U = 3.00$, the SP-TPS has converged to the limit $-t/U \to \infty$. The reported data were discussed in our previous work on the spin partitioned TPS.[16]

to be expected since the Heisenberg Hamiltonian corresponds to the limit of the Hubbard model for $-t/U \to 0$. Moreover, a comparison with the results obtained for large values of $-t/U$, whose upper limit brings to the Hückel (or tight-binding) chain,[20] shows that a similar linear dependence is obtained, although the physics of the two situations is very different. One can conclude that the larger effect on the delocalization of individual spins has to be attributed more to the magnetic interaction described by the Heisenberg Hamiltonian. Finally it has to be underlined that the linear growth of the normalized SS-TPS and SP-TPS of the Hückel tight-binding chains, whose behavior is very reminiscent of those of the Heisenberg SP-TPS, corresponds to a metallic behavior.

3. Other states with m = 0

Till this point, we have focused our attention only to the two situations of the anti-ferromagnetic and ferromagnetic states. Among the $n!/[(n/2)!]^2$ states with $m = 0$ these two represent indeed the possible ground states, depending on the value of J, as previously stated. It is maybe of interest also to depict the behavior of $\lambda^{s,0}_{\alpha\alpha}$ for the whole spectrum. In Figure 6, we report the SP-TPS calculated for $n = 8$, 10, and 12 as a function of the eigenvalues for all possible states with $m = 0$ (raw data available in Table V of the supplementary material[38]). As it can be seen, the anti-ferromagnetic and ferromagnetic states do not yield boundaries in the values that $\lambda^{s,0}_{\alpha\alpha}$ can adopt.

B. Spin-paired chains

As already stated, the Heisenberg wave function for the spin-paired chains can be used as a model to describe the behavior of the coupled spins in a dimerized hydrogen chain where we observe a Peierls transition.[25] The dimensionless real parameter $\eta = J_2/J_1$ was used to define the degree of spin-pairing: we have $\eta = 1$ for the equal-J chains, and $\eta < 1$ in presence of dimerization. In the limit case of $\eta = 0$ the

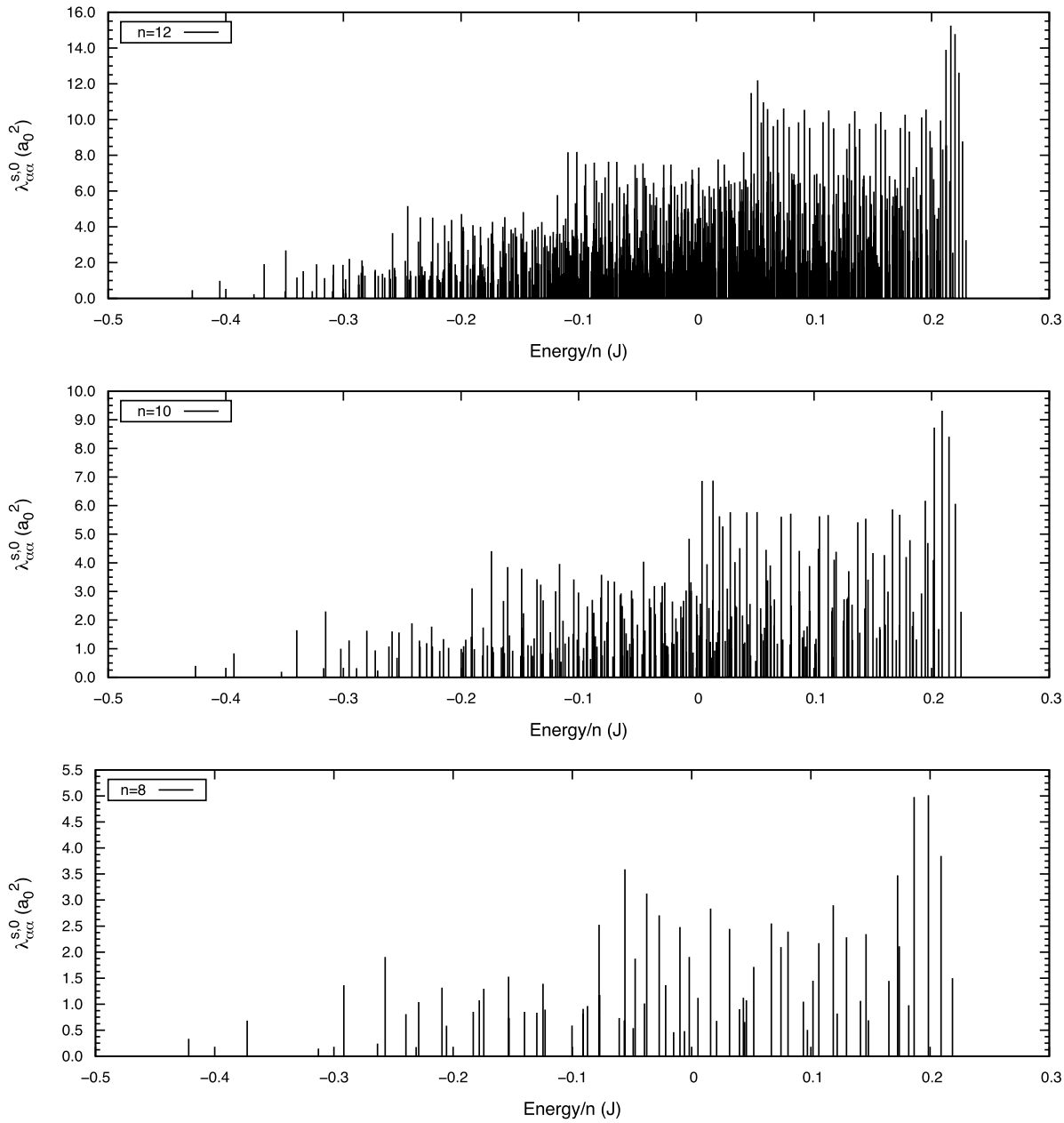

FIG. 6. Spin partitioned $\alpha\alpha$ component of the total position-spread tensor calculated for all the states with $m = 0$ as a function of the eigenvalues. Both $\lambda^{s,0}_{\alpha\alpha}$ and the energies are divided for the number of electrons, in order to achieve a better comparison. The anti-ferromagnetic and the ferromagnetic states are the lowest and highest in energy, respectively.

system is composed of $n/2$ non-interacting spin pairs. It has to be noticed that, for the ferromagnetic case, the SP-TPS results are totally independent from η. This is because the coefficients of the various components of the wave function are uniquely determined by the spin symmetry of the problem (they are all equal) and therefore do not depend on the relative values of J_1 and J_2. This means that the value $\lambda^{\frac{n}{2},m}_{\alpha\alpha}$ that was obtained for the equal-J case, Equation (23), is still valid for the dimerized chains. In this context, we stress the fact that, in our simple model, dimerization holds *on the coupling coefficients of the Hamiltonian*, not on the center positions, *that are kept fixed*. For this reason, our discussion here will be limited to the case of an anti-ferromagnetic coupling only. Moreover, it has to be underlined that we will restrict to the case $\eta \geq 0$.

In Figure 7, the values of $\lambda^{0,0}_{\alpha\alpha}$ for the different values of η are reported (see Table VI of supplementary material for numerical values[38]). The behavior of the tensor is qualitatively different in the equal-J and dimerized cases. In fact for the large values of n, as already anticipated in Subsection V A 2, the growth of $\lambda^{0,0}_{\alpha\alpha}$ appears to be linear if $\eta = 1$. On the other hand, as soon as η is decreased, the behavior evolves into a trend that saturates toward a constant value. Once again it turns out that this trend is very much similar to the one of SS-TPS of the dimerized Hückel chains that were discussed in Ref. 20.

We notice that also in this case the different divergences of the SP-TPS can be related to the different trends of the gap closure. In Figure 8, the gaps for several values of η are reported and, as it can be seen, as for the equal-J chains, a faster gap closure corresponds to a faster divergence while

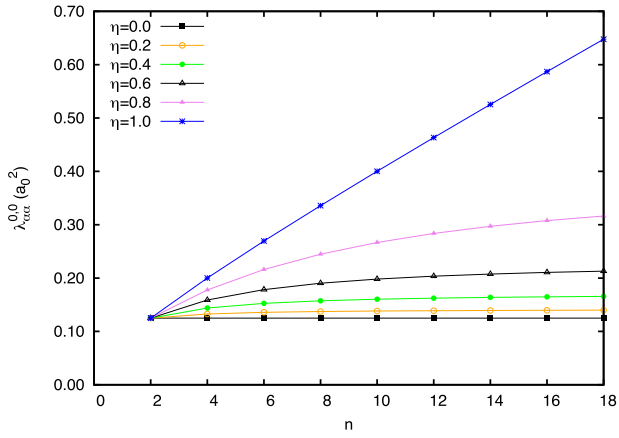

FIG. 7. Normalized $\alpha\alpha$ component of the spin partitioned total position-spread tensor, computed for the anti-ferromagnetic state and different values of $\eta = J_2/J_1$.

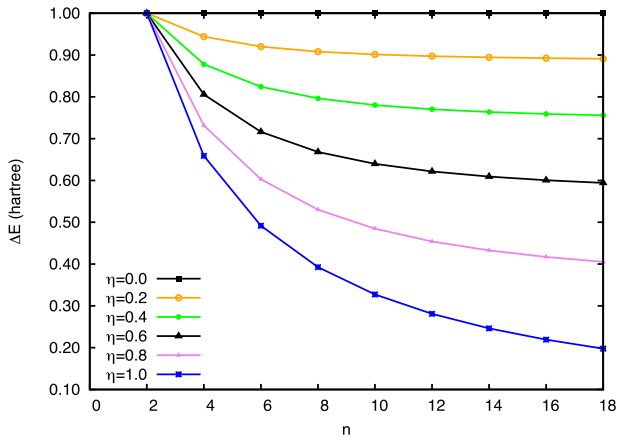

FIG. 8. Low-spin energy gap between the anti-ferromagnetic state and the first-excited state, for different $\eta = J_2/J_1$ values, as a function of n.

a size independence of $\lambda^{0,0}_{\alpha\alpha}$ is associated to the constant gap which characterizes the spin-paired chains. In Subsection V C, the large-n behavior of the gap and the TPS tensor will be addressed.

C. Energy gap and total-spread extrapolation

The fit of energy gaps and SP-TPS tensors will be now discussed, with a particular interest into the large-n behavior of these quantities. Although several possibilities have been tested in the past for the gap,[39] the limited number of n values available in the present work makes the fit a rather difficult task. Indeed, for the energy gap, we employed Heisenberg chains of $n = 4, 6, 8, 10, 12, 14, 16, 18$ sites whereas the SP-TPS was fitted using values computed for $n = 2, 4, 6, 8, 10, 12, 14, 16, 18$ sites. Note that, for the former case, the value of $n = 2$ was not considered because its addition causes an important increase of the Sum of Squared Residuals (SSR). For the sake of simplicity, we decided to use linear combinations of functions of the form n^k, where k is an integer number (either positive, negative, or zero). For the same reason, we limited the number of terms into the sum to a maximum of three: the use of large sets of functions, in our experience, certainly decreases the mean-square error, but produces large, unstable coefficients. Finally, we emphasize that in all cases the fits were accurate, with a maximum value of the SSR of 1.0858×10^{-05} (for the energy gap) and $2.913\,98 \times 10^{-04}$ (for $\lambda^{0,0}_{\alpha\alpha}$).

The low spin (LS) gaps (both for the equal-J and spin-paired chains) have been fitted with functions of the form

$$\Delta E(n) = a_0 + a_{-1}n^{-1} + a_{-2}n^{-2}, \tag{25}$$

while for the high spin (HS) gap the following expression has been used:

$$\Delta E(n) = a_0 + a_{-2}n^{-2} + a_{-3}n^{-3}. \tag{26}$$

The results of the fit operation for the gap are reported in Table I. Although the precision of this fit cannot be overestimated, it appears that the leading term of the ferromagnetic gap is in n^{-2}, and the reported coefficients are consistent with a zero gap in the large-n limit. In the same way, the non-dimerized LS gap has a very small a_0 parameter, again consistent with a zero gap in the large-n limit (although one order of magnitude larger than the HS corresponding value). In the case of spin-paired chains, on the other hand, the leading term is the constant a_0, which means that the gap does not close in the limit $n \to \infty$.

In Table II, the corresponding fit for the SP-TPS divided by n is reported. The HS value has been fitted via the formula

$$\lambda^{n/2,0}_{\alpha\alpha} = b_0 + b_1 n + b_2 n^2, \tag{27}$$

which is able to recover the exact parameters of the analytical solution (see Appendix B), with $b_0 = 0$. The LS results, on the other hand, have been fitted via the more flexible expression:

$$\lambda^{0,0}_{\alpha\alpha} = b_{-1}n^{-1} + b_0 + b_1 n. \tag{28}$$

In all spin-paired results, the linear term b_1 is very small, and this is coherent with a constant large-n behavior of $\lambda^{0,0}_{\alpha\alpha}$. Although the b_1 value is also relatively small for the spin-unpaired chains (but at least one order of magnitude larger than the largest spin-paired value), the linear term is essential in order to reproduce the fitted data in an acceptable way. This implies a linear growth of $\lambda^{0,0}_{\alpha\alpha}$ in spin-unpaired chains, in agreement with the general scenario discussed in this section.

TABLE I. Optimized coefficients for the energy gaps, obtained by fitting the functions in Eqs. (25) and (26) as a function of the number of sites. SSR: Sum of Squared Residuals.

Anti-ferromagnetic chains (LS)				
η	a_0	a_{-1}	a_{-2}	SSR
1	0.0202	3.4024	−3.3954	4.6653×10^{-6}
0.8	0.2950	2.0159	−1.0722	9.8311×10^{-6}
0.6	0.5321	1.0858	0.0435	1.0858×10^{-5}
0.4	0.7234	0.5490	0.2821	4.1237×10^{-6}
0.2	0.8777	0.2159	0.2022	8.9715×10^{-6}
0.0	1.0000	0.0000	0.0000	...
Ferromagnetic chains (HS)				
η	a_0	a_{-2}	a_{-3}	SSR
1	−0.0020	5.3994	−2.7825	3.7878×10^{-6}

TABLE II. Optimized coefficients for the SP-TPS obtained by fitting the functions in Eqs. (27) and (28) as a function of the number of sites. SSR: Sum of Squared Residuals.

Anti-ferromagnetic chains (LS)				
η	b_{-1}	b_0	b_1	SSR
1	−0.0667	0.0954	0.0310	1.7265×10^{-5}
0.8	−0.2151	0.2153	0.0067	2.9140×10^{-4}
0.6	−0.1479	0.1940	0.0017	4.7774×10^{-5}
0.4	−0.0804	0.1640	0.0004	4.0550×10^{-6}
0.2	−0.0319	0.1408	0.0001	1.1182×10^{-7}
0.0	0.0000	0.1250	0.0000	3.6378×10^{-29}
Ferromagnetic chains (HS)				
η	b_0	b_1	b_2	SSR
1	0.0000	0.0208	0.0208	5.8015×10^{-15}

VI. CONCLUSIONS

In the present investigation, the total position-spread tensor partitioned accordingly to its spin components (SP-TPS) has been computed and discussed for one-dimensional Heisenberg chains with open boundary conditions. The two qualitatively different cases of equal-J and dimerized nearest-neighbor couplings were considered, both for ferromagnetic and anti-ferromagnetic ground states. The equal-J finite chains present a band gap that tends to zero as the chain length is increased. In particular, the gaps are known to close as $1/n^2$ and $1/n$ for ferromagnetic and anti-ferromagnetic couplings, respectively. This difference is reflected by the behavior of the SP-TPS tensors that grow as n^3 and n^2 in these two different cases, respectively. This fact suggests that anti-ferromagnetic chains are less delocalized than ferromagnetic ones at the thermodynamic limit.

As a general property, the SP-TPS strongly depends on the z-projection of the total spin. In particular, the ferromagnetic Heisenberg eigenfunctions present a maximum value of the SP-TPS for $m = 0$ if n is kept fixed. Then, if m is increased, the number of spin configurations is reduced, and consequently the spin delocalization decreases. In the case of high-spin wave functions, all the different configurations have the same weight. Because of this particular structure of the eigenvector, we were able in this case to obtain an analytical expression of the SP-TPS tensor as a function of both m and n.

The effect of dimerization in Heisenberg chains was investigated for the anti-ferromagnetic ground-state, by varying the dimensionless parameter η (given by the ratio between the two coupling constants) from 1 to 0. These two limit cases correspond to an equal-J chain and a collection of non-interacting spin pairs, respectively. The SP-TPS was found to be very sensitive to the degree of dimerization present in the chain. In particular, as expected, the spin pairing reduces the delocalization of spins between the dimers in the strongly intra-pair correlated regime. In the limit case of a collection of non-interacting dimers ($\eta \to 0$), the value of the per-site SP-TPS tensor is damped to the value corresponding to an isolated dimer, as predicted by the size-extensivity property of the tensor.

These results confirm the fact that the SP-TPS is a powerful tool to analyze spin-fluctuations in magnetic systems, as we found in our previous investigations on Hydrogen chains.[16,25] At the moment, the application of this formalism to more realistic magnetic systems is under way.

Note added in proof: During the review process, one of the referees pointed out that Kohn's 1964 paper[1] can be fruitfully considered as a precursor of the so-called "modern theory of polarisation," as it employs similar mathematical tools. This view is in part based on Ref. 40 (see, e.g., page 901 therein). In fact, the modern theory of polarisation has been devised to bypass the use of the position operator with periodic boundary conditions.

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APPENDIX A: CALCULATION OF $\Lambda_{\alpha\alpha}^{S,m}$ FOR A HEISENBERG CHAIN WITH $n = 4$

As an explanatory example, we report the case of a Heisenberg chain with four sites in order to show how the terms $\Lambda_{\alpha\alpha}^{S,m}$ were calculated. Let us start by considering the N possible spin permutation ${}^m\phi_i$,

$$
\begin{aligned}
&{}^{+2}\phi_1 = |\uparrow\uparrow\uparrow\uparrow\rangle \\
&{}^{+1}\phi_1 = |\uparrow\uparrow\uparrow\downarrow\rangle \quad {}^{+1}\phi_2 = |\uparrow\uparrow\downarrow\uparrow\rangle \quad {}^{+1}\phi_3 = |\uparrow\downarrow\uparrow\uparrow\rangle \quad {}^{+1}\phi_4 = |\downarrow\uparrow\uparrow\uparrow\rangle \\
&{}^{0}\phi_1 = |\uparrow\uparrow\downarrow\downarrow\rangle \quad {}^{0}\phi_2 = |\uparrow\downarrow\uparrow\downarrow\rangle \quad {}^{0}\phi_3 = |\downarrow\uparrow\uparrow\downarrow\rangle \quad {}^{0}\phi_4 = |\uparrow\downarrow\downarrow\uparrow\rangle \quad {}^{0}\phi_5 = |\downarrow\uparrow\downarrow\uparrow\rangle \quad {}^{0}\phi_6 = |\downarrow\downarrow\uparrow\uparrow\rangle \\
&{}^{-1}\phi_1 = |\downarrow\downarrow\downarrow\uparrow\rangle \quad {}^{-1}\phi_2 = |\downarrow\downarrow\uparrow\downarrow\rangle \quad {}^{-1}\phi_3 = |\downarrow\uparrow\downarrow\downarrow\rangle \quad {}^{-1}\phi_4 = |\uparrow\downarrow\downarrow\downarrow\rangle \\
&{}^{-2}\phi_1 = |\downarrow\downarrow\downarrow\downarrow\rangle.
\end{aligned}
$$

By using Eq. (20) and (21) we can evaluate the eigenvalue of $\hat{\mathbf{R}}_\alpha$ for the basis ${}^m\phi_i$,

m	${}^m\phi_1$	${}^m\phi_2$	${}^m\phi_3$	${}^m\phi_4$	${}^m\phi_5$	${}^m\phi_6$
+2	0					
+1	−3/2	−1/2	1/2	3/2		
0	−2	−1	0	0	1	2
−2	3/2	1/2	−1/2	−3/2		
−2	0					

.

The expectation values $\langle {}^0\phi_i|\hat{\mathbf{R}}_\alpha^2|{}^0\phi_i\rangle$ are then simply calculated as the squares of these terms. Let us now consider the singlet ground-state wave function,

$$|{}^0\Psi(0)\rangle = \sum_{i=1}^{6} C_i^0(0)|{}^0\phi_i\rangle. \tag{A1}$$

From Eq. (19), the $\alpha\alpha$ component of the spin partitioned TPS results

$$\begin{aligned}\Lambda_{\alpha\alpha}^{0,0} &= \langle {}^0\Psi(0)|\hat{\mathbf{R}}_\alpha^2|{}^0\Psi(0)\rangle \\ &= \sum_{i=1}^{6} C_i^0(0)^2\langle {}^0\phi_i|\hat{\mathbf{R}}_\alpha^2|{}^0\phi_i\rangle \\ &= \sum_{i=1}^{6} C_i^0(0)^2\langle {}^0\phi_i|\hat{\mathbf{R}}_\alpha|{}^0\phi_i\rangle\langle {}^0\phi_i|\hat{\mathbf{R}}_\alpha|{}^0\phi_i\rangle \\ &= 4\cdot C_1^0(0)^2 + C_2^0(0)^2 + C_5^0(0)^2 + 4\cdot C_6^0(0)^2. \end{aligned} \tag{A2}$$

In a similar case, we can calculate $\Lambda_{\alpha\alpha}^{2,m}$ for each of the five ferromagnetic states with different values of m,

$$\Lambda_{\alpha\alpha}^{2,2} = 0, \tag{A3}$$

$$\Lambda_{\alpha\alpha}^{2,1} = \tfrac{9}{4}\cdot C_1^1(2)^2 + \tfrac{1}{4}\cdot C_2^1(2)^2 + \tfrac{1}{4}\cdot C_3^1(2)^2 + \tfrac{9}{4}\cdot C_4^1(2)^2, \tag{A4}$$

$$\Lambda_{\alpha\alpha}^{2,0} = 4\cdot C_1^0(2)^2 + C_2^0(2)^2 + C_5^0(2)^2 + 4\cdot C_6^0(2)^2, \tag{A5}$$

$$\Lambda_{\alpha\alpha}^{2,-1} = \tfrac{9}{4}\cdot C_1^{-1}(2)^2 + \tfrac{1}{4}\cdot C_2^{-1}(2)^2 + \tfrac{1}{4}\cdot C_3^{-1}(2)^2 + \tfrac{9}{4}\cdot C_4^{-1}(2)^2, \tag{A6}$$

$$\Lambda_{\alpha\alpha}^{2,-2} = 0. \tag{A7}$$

APPENDIX B: ANALYTICAL EXPRESSION FOR $\Lambda_{\alpha\alpha}^{S,m}$ IN THE FERROMAGNETIC STATE

In this appendix, we will prove the analytical expression for $\lambda_{\alpha\alpha}^{\frac{n}{2},m}$ shown in Eq. (24). Let us start considering N possible permutations of p identical spins (either α or β) distributed into n sites,

$$N = \frac{n!}{p!(n-p)!}, \tag{B1}$$

which can be rewritten as a function of the spin z-projection quantum number m considering the equivalence $p = n/2 \pm m$,

$$N(n,m) = \frac{n!}{\left(\frac{n}{2}+m\right)!\left(\frac{n}{2}-m\right)!}. \tag{B2}$$

As expressed in Eq. (4), an eigenfunction of the Heisenberg Hamiltonian with spin quantum numbers S and m is a linear combination of $N(n,m)$ basis $|{}^m\phi_i\rangle$. The crucial thing to consider is that for all ferromagnetic states the coefficients $C_i^m(S)$ have the same value that is $1/\sqrt{N(n,m)}$. Therefore, for a chain with an even number of sites and with the origin its middle, using the results of Eqs. (19) and (20) we can write

$$\Lambda_{\alpha\alpha}^{\frac{n}{2},m} = \sum_i^N C_i^m(S)^2\langle {}^m\phi_i|\hat{\mathbf{R}}_\alpha|{}^m\phi_i\rangle\langle {}^m\phi_i|\hat{\mathbf{R}}_\alpha|{}^m\phi_i\rangle \tag{B3}$$

$$= \frac{1}{N(n,m)}\sum_i^N \langle {}^m\phi_i|\hat{\mathbf{R}}_\alpha|{}^m\phi_i\rangle\langle {}^m\phi_i|\hat{\mathbf{R}}_\alpha|{}^m\phi_i\rangle \tag{B4}$$

$$= \frac{1}{N(n,m)}\sum_i^N\sum_{\nu,\mu} \langle {}^m\phi_i|\hat{\mathbf{r}}_\nu^\alpha|{}^m\phi_i\rangle\langle {}^m\phi_i|\hat{\mathbf{r}}_\mu^\alpha|{}^m\phi_i\rangle. \tag{B5}$$

In the case $|\nu| \neq |\mu|$, the corresponding contribution is given by four terms, having identical modulus, but opposite signs: (ν,μ), $(-\nu,\mu)$, $(\nu,-\mu)$, and $(-\nu,-\mu)$. This implies that the total sum will vanish. Therefore, the only terms that do not cancel out exactly are those of the type (ν,ν) and $(\nu,-\nu)$. The first one is a one-electron term, while the second one has a two-electron nature. (Notice that, since n is even, the case $\langle\hat{\mathbf{r}}_\nu^\alpha\rangle = 0$ is not possible.)

Let us consider first the one-electron term, the one with $\nu = \mu$. There are $N(n-1,m-1/2)$ identical such contributions, since the position μ is fixed, and one electron is sitting there. Using the results of Eq. (21), each contribution is given by $(\nu-(n+1)/2)^2$. The two electron term, $\nu = -\mu$, on the other hand, gives $N(n-2,m-1)$ identical contributions, since two different positions are fixed, and two electrons are sitting there. In this case, each contribution is now equal to the opposite of the previous one, $-(\nu-(n+1)/2)^2$. Therefore, the total result is given by

$$\begin{aligned}\Lambda_{\alpha\alpha}^{\frac{n}{2},m} &= \frac{N(n-1,m-\frac{1}{2}) - N(n-2,m-1)}{N(n,m)}\sum_{\nu=1}^{n}\left(\nu-\frac{n+1}{2}\right)^2 \\ &= \frac{\left(\frac{n}{2}+m\right)\left(\frac{n}{2}-m\right)}{n(n-1)}\sum_{\nu=1}^{n}\left(\nu-\frac{n+1}{2}\right)^2. \end{aligned} \tag{B6}$$

To solve the sum in Eq. (B6), we invoke the identity

$$\sum_{k=0}^{l}(2k+1)^2 = \frac{(2l+1)(2l+2)(2l+3)}{6}, \tag{B7}$$

from which we obtain

$$\begin{aligned}\Lambda_{\alpha\alpha}^{\frac{n}{2},m} &= \frac{\left(\frac{n}{2}+m\right)\left(\frac{n}{2}-m\right)}{n(n-1)}\frac{(n-1)n(n+1)}{12} \\ &= \frac{n+1}{12}\left(\frac{n^2}{4}-m^2\right). \end{aligned} \tag{B8}$$

Finally, Equation (24) is simply obtained by dividing Eq. (B8) by the number of sites.

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