Classical Magnetism of Short Odd-Numbered Chains

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The magnetism of short odd open chains with classical spins is investigated for bilinear and biquadratic exchange interactions. The zero field residual magnetization generates differences with the magnetic behavior of even chains, as the odd chain is like a small magnet for weak magnetic fields. The lowest energy configuration is calculated as function of the total spin $S$, even for $S$ less than the zero field residual magnetization. Analytic expressions and their proofs are provided for the threshold magnetic field needed to drive the system away from the antiferromagnetic configuration and the polar angles in its vicinity when the biquadratic interaction is relatively weak, the saturation magnetic field and the polar angles close to it, as well as the maximum magnetization in zero magnetic field for stronger biquadratic interaction, where the lowest energy configuration is highly degenerate.

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I. INTRODUCTION

In recent years important advances in synthetic chemistry have led to the production of molecules that have interesting magnetic properties and could potentially provide the building blocks for quantum computers and memory devices. This class of molecules has been coined molecular nanomagnets [1]. Another route for the production of small entities with interesting magnetic properties that has recently seen intense activity is the artificial engineering of molecular nanomagnets, magnetic clusters and arrays of magnetic adatoms, which are fabricated directly on surfaces with Scanning Tunneling Microscopy (STM) [2, 3]. STM is also used to measure their magnetic properties. These entities have brought forward the need to understand thoroughly magnetic interactions between a few magnetic centers and their collective magnetic behavior [2, 3], especially since their properties are expected to be different in comparison with systems that contain many magnetic centers and are relatively close to the thermodynamic limit [2, 8].

Perhaps the simplest non-trivial magnetic entity is an open linear chain with equivalent magnetic centers and bilinear antiferromagnetic (AFM) exchange interactions between them. Its quantum-mechanical behavior as function of the spin magnitude of the magnetic centers $s$ has been the subject of extensive investigation. For $s = 1/2$ and nearest neighbor interactions the model is integrable via the Bethe ansatz [9]. The Haldane conjecture differentiates the magnetic properties of the infinite chain according to the parity of $s$ [10, 11]. For finite chains the boundary conditions play an important role [12, 14]. An open odd-membered chain is not frustrated, in contrast to its closed counterpart where frustration forces the spins in a non-collinear configuration at the classical level. In contrast the open chain, even though it lacks frustration, is more susceptible towards the edges to an external magnetic field due to the lack of translational symmetry, and as a result it possesses interesting magnetic properties even at the classical level. Even and odd short open chains show pronounced differences in their magnetic behavior. The lowest energy as function of total spin $S$ depends on the parity of the chain [12]. At the classical level the lowest energy configuration of an even chain is always noncollinear in a field [15, 16], while an odd chain changes from a ferrimagnetic to a noncollinear configuration at a threshold value of the field [17, 18]. This is because in zero field nearest neighbor spins are antiparallel, however the net magnetization of an odd chain is not zero due to the single uncompensated spin. Thus in small fields the chain is behaving like a small magnet that gains magnetic energy without having to break the AFM configuration. It takes a finite magnetic field to destroy the zero field AFM configuration, whereas an even chain immediately responds to a field. Another consequence of the residual magnetization in classical odd chains is that unlike an even chain the lowest configuration is not accessible with a magnetic field for magnetizations less than the residual.

Consideration of magnetic models for classical spins provides a first estimate of the influence of connectivity and boundary conditions on magnetic properties, before quantum fluctuations are taken into account. For more complicated connectivities than the chain, or more generally for structures that are not bipartite or for bipartite structures with competing interactions frustration plays an important role. Magnetization discontinuities have been found in frustrated clusters, where specific ranges of $S$ never include the lowest energy configuration in a magnetic field. Such is the case for fullerene clusters with icoshedral $I_h$ spatial symmetry, where the dependence of the spin polar angles on the field can also be non-monotonic like an even or odd chain [19, 20], and the icoshedron which also has $I_h$ spatial symmetry [21]. The classical approach is also important as it describes the quantum problem for relatively high quantum numbers [3]. In the case of open chains this description is valid for relatively low $s \geq \frac{1}{2}$ [12]. This agreement has
Inclusion of biquadratic exchange interactions in the Hamiltonian further complicates the problem. In contrast to the AFM bilinear exchange interaction which favors antiparallel nearest neighbor spins, the biquadratic interaction with a positive prefactor is minimized for perpendicular nearest neighbors. The competition of the two terms determines the lowest energy configuration which can now be noncollinear even in the absence of a field when the biquadratic interaction is strong enough. This lack of collinearity introduces a continuous degeneracy of the ground state and its degenerate manifold corresponds to a range of values of the residual magnetization \[22\].

In this paper the bilinear-biquadratic Heisenberg model is considered for odd open chains with AFM bilinear exchange interaction and positive biquadratic interaction. The lowest energy configuration is determined for the whole range of \(S\), even in the case where \(S\) is less than the zero field residual magnetization. The latter is 1 when the biquadratic interaction is less than half of the bilinear interaction and corresponds to a range of values in the opposite case, whose maximum is analytically derived while the minimum is calculated numerically. The analytic expression and its derivation are provided for the threshold magnetic field above which the residual spin starts to respond when the biquadratic interaction is less than half the bilinear interaction, and the corresponding values of the spin polar angles are also analytically calculated. The same is done for the saturation magnetic field, with formulas here also valid for even chains.

The plan of the paper is as follows: in Sec. \(\text{II}\) the model is presented along with the methods of calculation of the lowest energy configuration as function of \(S\). Sec. \(\text{III}\) includes analytic expressions for the ground state configuration and its magnetization in the absence of a field, as well as the threshold and saturation field and the spin polar angles in their immediate vicinity. Sec. \(\text{IV}\) presents results for the lowest energy configuration as function of \(S\) for zero biquadratic interaction, while Sec. \(\text{V}\) presents results for non-zero biquadratic interaction. Sec. \(\text{VI}\) gives the conclusions. Various appendices provide derivations of analytic expressions presented in the main text.

II. MODEL

The Hamiltonian of the bilinear-biquadratic exchange Heisenberg model for an open chain is

\[ H = \sum_{i=1}^{N-1} \left[ J s_i \cdot s_{i+1} + J' (s_i \cdot s_{i+1})^2 \right] - h \sum_{i=1}^{N} s_i^z \]  (1)

\(N\) is the number of spins, taken to be odd. \(J\) is the strength of the bilinear and \(J'\) of the biquadratic exchange interaction. Both of them are taken positive, with \(J\) defining the unit of energy. The magnetic field \(h\) is taken along the \(\hat{x}\) direction. The spins \(s_i\) are classical unit vectors and each is defined by a polar and an azimuthal angle. Hamiltonian \(\text{(1)}\) is minimized with respect to these angles \[19, 20, 24\]. All the lowest energy configurations are coplanar, so it suffices to consider Hamiltonian \(\text{(1)}\) in polar coordinates where the angles \(\theta_i\) with \(i = 1, \ldots, N\) fully determine the spin configuration. The bilinear exchange interaction favors antiparallel nearest-neighbor spins, while the biquadratic perpendicular. The biquadratic interaction is the square of the bilinear, therefore its weaker in strength. Simultaneously the magnetic field tends to align the spins along its direction, therefore the physics is determined by the competition of the three terms. As the field varies it singles out the lowest energy configurations for \(S\) greater than the (maximum) value in the global (irrespective of \(S\)) ground state(s), and essentially one can think of the ground state for a given \(S\) as being effected by the field. In it spins symmetrically placed with respect to the center have the same polar angle. The lowest energy configuration for \(S\) less than the (minimum) value in the global ground state(s) is calculated by adding to Hamiltonian \(\text{(1)}\) instead of the magnetic field energy the term \(G S^2 = G(\sum_{i=1}^{N} s_i^2) = G(2 \sum_{i>j} s_i \cdot s_j + N)\), with \(G > 0\). With this addition the \(S = 0\) lowest state is generated when \(G \to \infty\). From a numerical point of view when \(G\) is very large and consequently \(S\) approaches zero loss of numerical precision precludes the very accurate calculation of the corresponding lowest energy configuration. In this case the accurate results for very small \(S\) are extrapolated down to \(S = 0\). Comparing with the \(N = 3\) analytic solution and judging by the consistency of the results as more points are included in the extrapolation for arbitrary \(N\) the extrapolated results are very accurate. In addition results for different \(N\) are absolutely consistent with each other. In the lowest energy configurations for \(S\) less than the (minimum) value in the global ground state(s) spins symmetrically placed with respect to the center have angles adding up to \(2\pi\). For the smallest chain \(N = 3\) analytic results can be generated for the whole range of \(S\), and these will be presented in Secs \(\text{IV}\) and \(\text{VI}\).

III. GENERAL ANALYTIC RESULTS

A. Zero Field Lowest Energy State

In the absence of magnetic field Hamiltonian \(\text{(1)}\) can be written as

\[ H_{h=0} = J' \sum_{i=1}^{N-1} (s_i \cdot s_j + \frac{J}{2J'})^2 - (N - 1) \frac{J^2}{4J'} \]  (2)

Minimization of Hamiltonian \(\text{(2)}\) gives the global lowest energy configuration, and requires minimization of the square. For \(J' \leq \frac{J}{2}\) Hamiltonian \(\text{(2)}\) is minimized by the AFM configuration, with \(E_g = -(N - 1)(J - J')\).
For $J' > \frac{J}{2}$ the nearest neighbor angle that minimizes Hamiltonian (2) is $\theta_g = \arccos(-\frac{J}{2J'})$, with $E_g = -(N-1)\frac{J^2}{2J'}$ and $\theta_g$ decreases with increasing $J'$ from $\pi$ to $\frac{\pi}{2}$. While the spin configuration is well-defined in the AFM state with a residual magnetization $S_{g,J'\leq\frac{J}{2}} = 1$, when $J' > \frac{J}{2}$ the only requirement is that the angle between any two neighboring spins is $\theta_g$. This is satisfied by a degenerate manifold of states that are in general non-coplanar (23).

### B. Maximum Residual Magnetization of the Global Ground State Manifold for $J' > \frac{J}{2}$

The configuration of the global ground state manifold with maximum spin $S^\text{max}_{g,J'\geq\frac{J}{2}}$ is selected by an infinitesimal magnetic field. To maximize the spin (and the magnetic energy) all spins are coplanar. In particular, $\frac{N+1}{2}$ spins are at an angle $\theta_0 = \arctan\sqrt{\frac{1-J^2}{J^2-2JJ'}}$ with the field, while the rest form an angle $\theta_g$ with their neighbors and $\theta_g - \theta_0$ with the field (see App. A). It is noted that $\theta_0$ does not change significantly for larger $N$. The maximum total spin is

$$S^\text{max}_{g,J'\geq\frac{J}{2}} = \frac{1}{2} \sqrt{1 + \frac{1+J^2}{\left(\frac{N+1}{2} \frac{J}{J'}\right)^2}} [N+1 + (N-1)(\frac{J}{2J'} + \frac{1}{\frac{N+1}{2} - \frac{J^2}{J'^2}})] \quad (3)$$

and is plotted in Fig. II. The limiting forms are $\frac{S^\text{max}_{g,J'\geq\frac{J}{2}}}{N} \rightarrow \frac{1-J^2}{2J'}$ and $\frac{S^\text{max}_{g,J'\geq\frac{J}{2}}}{N} \rightarrow \sqrt{\frac{N^2+1}{2N^2}}$.

When $J' > \frac{J}{2}$ the minimum spin configuration of the ground state manifold is also coplanar and has the spins spread out as much as possible. Its total spin $S^\text{min}_{g,J'\geq\frac{J}{2}}$ is determined numerically and is plotted in Fig. I.

### C. Threshold Magnetic Field for $J' \leq \frac{J}{2}$

When $J' \leq \frac{J}{2}$ the lowest energy configuration in the absence of a field is AFM, and remains so for small non-zero fields. Unlike an even chain which has no zero field residual magnetization, the odd chain gains immediately magnetic energy in a field while simultaneously allowing the exchange energy not to change. Thus it takes a finite magnetic field to destroy the AFM configuration in order to increase the magnetic energy even more at the expense of the exchange energy. This threshold value of the field (given in [18] for $J' = 0$) is

$$h_t = 2(J-2J')\sin\frac{\pi}{2N} \quad (4)$$

(see App. B). $h_t$ is proportional to $J$ but decreases with $J'$, and vanishes for an infinite chain where the parity of the chain makes no difference. The spin polar angles right above $h_t$ are

$$\theta_i = \{\sin[\frac{\pi}{2N}(i-1)] + \cos[\frac{\pi}{2N}i]\} \theta_0, \ i \text{ odd}$$

$$\theta_i = \pi + \{\sin[\frac{\pi}{2N}i] + \cos[\frac{\pi}{2N}(i-1)]\} \theta_0, \ i \text{ even} \quad (5)$$

with $i = 1, \ldots, N$ and $\theta_0$ a very small parameter that goes to $0$ at the AFM configuration (see App. B).

### D. Saturation Magnetic Field

The saturation magnetic field required to reach the ferromagnetic configuration is

$$h_s = 2(J + 2J')(1 + \cos\frac{\pi}{N}) \quad (6)$$

(see App. C). This formula is also valid for even chains. For an infinite chain $\lim_{N \rightarrow \infty} h_s = 4(J + 2J')$. The spin polar angles right below saturation are

$$\theta_i = \pi[1 + (-1)^i] - (-1)^i \sin[\frac{\pi}{2N}(2i-1)] \theta_0 \quad (7)$$

with $i = 1, \ldots, N$ and $\theta_0$ a very small parameter that goes to $0$ at the ferromagnetic configuration (see App. C).

### IV. $J' = 0$

For the smallest odd chain $N = 3$ and an analytic solution is possible. According to Eqs (4) and (6) it is $h_t = J$ and $h_s = 3J$, and for this range of fields $S' = \frac{J}{2} \leq S_{g,J'\leq\frac{J}{2}} = 1$. The polar angles and ground state energy are ($\theta_3 = \theta_1$ due to symmetry)

$$\cos\theta_1 = \frac{S^2 + 3}{4S}$$

$$\cos\theta_2 = \frac{S^2 - 3}{2S}$$

$$E(S) = -\frac{J}{2}(5 - S^2) \quad (8)$$

When $S < S_{g,J'\leq\frac{J}{2}}$ it is $S = \frac{J}{2G'}$ (refer to Sec. I) with $G' \geq \frac{J}{2}$, $\theta_3 = 2\pi - \theta_1$ and $\theta_2 = \pi$, and

$$\cos\theta_1 = \frac{S + 1}{2}$$

$$E(S) = -J(1 + S) \quad (9)$$

The dependence on $S$ is linear, in contrast to the quadratic dependence for $S \geq S_{g,J'\leq\frac{J}{2}}$. It is $\theta_1(S = 0) = \frac{\pi}{3}$ (Fig. III), and the angle between the edge spins and the central spin is $\frac{2\pi}{3}$, thus the $S = 0$ lowest energy configuration is the same with the ground state of the frustrated $N = 3$ closed chain.
For $N > 3$ the lowest energy configuration as function of $S$ was calculated numerically. Results for $N = 11$ are shown in Fig. [2]. For $S \geq S_{g,J'\leq \frac{1}{2}} = 1$ the polar angles deviate from the AFM configuration to gain magnetic energy and their dependence on $S$ is not necessarily monotonic, similarly to the even $N$ case [13]. The odd chain behaves like a small magnet for small fields due to its residual magnetization, while the even chain has no residual magnetization. The odd spins practically point along an infinitesimal field and move away from it with increasing field the more the closer to the center they are, but eventually move back towards it as the magnetic energy becomes much stronger than the exchange energy for higher fields. The even spins are antiparallel to an infinitesimal field and vary monotonically with increasing field until they align themselves with it at saturation. Like the odd spins, the closer to the center a spin is the more it deviates from being antiparallel to the field. Similarly to even chains there exists a value of $S$ where all spins have the same polar angle except from the edge spins, coined knot point in Ref. [13], where the relative deviation from the $x$ axis changes order for the even spins, but not for the odd spins. For even chains the relative deviation changes order at the knot point for both even and odd spins. When $S < S_{g,J'\leq \frac{1}{2}}$ the central spin is fixed along the $\pi$ direction. Spins that come in pairs sharing the polar angles for $S \geq S_{g,J'\leq \frac{1}{2}}$ now split up symmetrically with respect to the $x$ axis, while the deviation from the $x$ axis of the spins within the two groups which have values less and greater than $\pi$ reverses its order in comparison to the $S \geq S_{g,J'\leq \frac{1}{2}}$ case before the knot point. Thus spins closer to the center deviate the least from their directions in the AFM configuration.

The polar angles for the lowest energy configuration with $S = 0$ are plotted in Fig. 3 for varying $N$. The central spin lies along the $\pi$ direction. The angles tend to limiting values as functions of $N$, under the constraint that for two adjacent sizes the values of the polar angle of a spin at a fixed distance from the edge tend to become supplementary as $N \rightarrow \infty$. Convergence of the angles with $N$ is faster going towards the edges. Spins tend to be antiparallel with increasing $N$ the closer to the edge they are, when counting of pairs starts from the second and third spin from the edge.

V. $J' \neq 0$

When $N = 3$ according to Eqs (4) and (5) it is $h_4 = J - 2J'$ and $h_3 = 3(J + 2J')$. An analytic solution can now be found for $S_{g,J'\leq \frac{1}{2}}^{\min} = [1 - \frac{J}{J'}]$. For $S < S_{g,J'\leq \frac{1}{2}}$ the ground state has $S = \frac{2\pi}{\theta_0 - \theta_1}$ with $G \geq \frac{1}{2} - J'$ (refer to Sec. [11]), and like the $J' = 0$ case $\theta_3 = 2\pi - \theta_1$ and $\theta_2 = \pi$, with $\cos \theta_0 = \frac{S + 1}{2}$. The energy is $E(S) = -(J - \frac{1+S}{2}J')(1+S)$. For $N > 3$ numerical results are again presented for $N = 11$. Fig. [4] shows the lowest energy per bond as function of $S$ for different $J'/J$. The energy decreases in magnitude with increasing $J'/J$ due to the stronger competition between the biquadratic and the bilinear exchange. For $J' > \frac{1}{4}$ the lowest energy corresponds to the ground state manifold that has $S$ between $S_{g,J'\leq \frac{1}{2}}^{\min}$ and $S_{g,J'\leq \frac{1}{2}}^{\max}$ (Sec. [11]). For $\frac{J}{J'} \sim 0.75$ all the energy curves are close to zero, the reason being that nearest-neighbor spins are very close to normal.

Fig. 4 shows the lowest energy configuration for $N = 11$ as function of $\frac{J}{J'}$ for $J' = 0.49$. In comparison with $J' = 0$ (Fig. [2]) nearest-neighbor polar angles do not differ much for $S \geq S_{g,J'\leq \frac{1}{2}}$ even though now the biquadratic is strongly competing with the bilinear exchange interaction, bearing in mind the differences in the threshold and saturation field (Sec. [11] and [13]). Still it takes a larger $\frac{1}{2}$ to reach the knot point, where all angles but the external ones are equal. One can think of $S$ as generated by the external magnetic field that now has to compensate also for the biquadratic energy to drive the system towards saturation (refer to Eq. (6) for the saturation field where $J$ and $J'$ add up). For $S < S_{g,J'\leq \frac{1}{2}}$ the angles are more spread out within the three different groups in comparison with $J' = 0$.

In Fig. 6 the polar angles in the lowest energy configuration for $N = 11$ are plotted as function of $\frac{J}{J'}$ for $J' = 1$. The ground state is continuously degenerate and corresponds to $S$ values ranging from $S_{g,J'\leq \frac{1}{2}}^{\min} = 1$ to $S_{g,J'\leq \frac{1}{2}}^{\max} = \sqrt{31}$ (Eq. (3)), and the polar angles are plotted for $S$ outside this range. In comparison with Figs 2 and 4 and due to the reduced spin range the configuration is monotonic for $S \geq S_{g,J'\leq \frac{1}{2}}^{\max}$. For $S \leq S_{g,J'\leq \frac{1}{2}}^{\max}$ spins 4 and 8 have left the middle group where they belonged to for $J' \leq \frac{1}{2}$ and are now the spins closest to the $x$ axis among all spins.

VI. CONCLUSIONS

The lowest energy configuration of the classical AFM Heisenberg model with bilinear and biquadratic exchange interactions has been calculated for small odd chains. The odd chains differ from their even counterparts in that they have a residual magnetization for zero field, therefore they act like small magnets for small fields. The lowest energy and the corresponding spin configuration as functions of $S$ depend on the relative ratio of the biquadratic to the bilinear exchange interaction. They have been calculated for the whole range of $S$, even when $S$ is smaller than the (minimum) value of the global energy minimum. Analytic expressions were derived for the threshold and saturation field and the polar angles in their vicinity, as well as the maximum residual magnetization in the absence of a field for relatively stronger biquadratic interaction. The richer physics of the odd chain makes it more applicable for use in various magnetic devices in comparison with its even counterpart.
Appendix A: Maximum Residual Magnetization of
the Ground State Manifold for $J' > \frac{1}{2}$

An infinitesimally small magnetic field picks out from
the $J' > \frac{1}{2}$ degenerate zero field configurations (Sec. III A) the one with maximum residual spin $S^{max}_{g,J' > \frac{1}{2}}$. Nearest-neighbor spins are at a relative angle $\theta_g = \arccos(-\frac{J}{\sqrt{J^2 + \sigma^2}})$, and to maximize $S_{g,J' > \frac{1}{2}}$ (and the magnetic energy) all spins must lie in a plane that includes the infinitesimal magnetic field. If the first spin is at an angle $\theta_0 \leq \frac{\pi}{4}$ with respect to the field direction, the second will be at an angle $\theta_g - \theta_0$. It is $\frac{\pi}{4} \leq \theta_g < \pi$, therefore to maximize $S_{g,J' > \frac{1}{2}}$ and avoid any spins with positive magnetic energy all subsequent spins will successively be directed at these two angles. Thus there are $\frac{N-1}{2}$ spins at an angle $\theta_g$ with the field and $\frac{N-1}{2}$ spins at an angle $\theta_g - \theta_0$. The total maximum residual spin is

$$S^{max}_{g,J' > \frac{1}{2}} = \frac{N + 1}{2} \cos \theta_0 + \frac{N - 1}{2} \cos(\theta_g - \theta_0) \quad (A1)$$

Taking the derivative with respect to $\theta_0$ and setting it to zero (which also guarantees that the component of $S^{max}_{g,J' > \frac{1}{2}}$ perpendicular to the field is zero) it is after some algebra

$$\theta_0 = \arctan \frac{\sin \theta_g}{\frac{1}{N} + \cos \theta_g} \quad (A2)$$

Since $\frac{\pi}{4} \leq \theta_g < \pi$ it is $\sin \theta_g > 0$, thus $\sin \theta_g = \sqrt{1 - \cos^2 \theta_g} \Rightarrow \sin \theta_g = \sqrt{1 - \frac{J^2}{4 J^2}}$. Then

$$\theta_0 = \arctan \sqrt{1 - \frac{J^2}{4 J^2}} \quad (A3)$$

It is $\theta_0(J' >> J) = \arctan \frac{N - 1}{N + 1}$. For an infinite chain $\theta_0(J' >> J, N \to \infty) \to \frac{\pi}{4}$.

The numerator and denominator in Eq. (A3) are both positive, therefore $\theta_0 \leq \frac{\pi}{2}$ as it should be to maximize the magnetic energy. Then it is

$$\cos \theta_0 = \frac{1}{\sqrt{1 + \tan^2 \theta_0}} \Rightarrow \cos \theta_0 = \frac{1}{\sqrt{1 + \frac{1 - \frac{J^2}{4 J^2}}{\frac{J^2}{4 J^2}}}} \quad (A4)$$

Similarly

$$\sin \theta_0 = \frac{\tan \theta_0}{\sqrt{1 + \tan^2 \theta_0}} \Rightarrow \sin \theta_0 = \frac{\frac{\tan \theta_0}{\sqrt{1 + \frac{1 - \frac{J^2}{4 J^2}}{\frac{J^2}{4 J^2}}}}}{\sqrt{1 + \frac{1 - \frac{J^2}{4 J^2}}{\frac{J^2}{4 J^2}}}} \quad (A5)$$

After some algebra (A1) gives

$$S^{max}_{g,J' > \frac{1}{2}} = \frac{N + 1}{2} \cos \theta_0 + \frac{N - 1}{2} (\cos \theta_g \cos \theta_0 + \sin \theta_g \sin \theta_0) \Rightarrow$$

$$S^{max}_{g,J' > \frac{1}{2}} = \frac{1}{2 \sqrt{1 + \frac{1 - \frac{J^2}{4 J^2}}{\frac{J^2}{4 J^2}}}} \left( [N + 1 + (N - 1) \right.$$

$$\left. - \frac{J}{2 J'} + \frac{1 - \frac{J^2}{4 J^2}}{\frac{J^2}{4 J^2}}] \right)$$

(A6)

For an infinite chain $\frac{S^{max}_{g,J' > \frac{1}{2}} N \to \infty}{N} = \frac{1}{\sqrt{2}}$. When $J' \to \infty$ it is $S^{max}_{g,J' \to \infty} = \sqrt{\frac{N^2 + 1}{2}}$.

Appendix B: Threshold Magnetic Field for $J' \leq \frac{1}{2}$

An odd chain with length $N$ in a magnetic field maintains its AFM configuration up to a threshold field $h$. For $h \leq h_1$ odd spins have $\theta_i = 0, i = 1, 3, \ldots, N$, while even spins $\theta_i = \pi, i = 2, 4, \ldots, N - 1$. Hamiltonian (I) of the main paper is in polar coordinates

$$H = \sum_{i=1}^{N-1} \left[ J \cos(\theta_i - \theta_{i+1}) + J' \cos^2(\theta_i - \theta_{i+1}) \right] -$$

$$h \sum_{i=1}^{N} \cos \theta_i \quad (B1)$$

Rewriting the Hamiltonian according to even and odd sites

$$H = \sum_{i=1}^{N-1} \left[ J \cos(\theta_{2i-1} - \theta_{2i}) + \cos(\theta_{2i} - \theta_{2i+1}) \right] +$$

$$J' \cos^2(\theta_{2i-1} - \theta_{2i}) + \cos^2(\theta_{2i} - \theta_{2i+1}) \right] -$$

$$h \sum_{i=1}^{N-1} \left( \cos \theta_{2i-1} + \cos \theta_{2i} \right) - h \cos \theta_N \quad (B2)$$

For every even spin the transformation $\theta_{2i} \to \theta_{2i} - \pi$ is performed due to the low field AFM configuration, and (B2) becomes

$$H = - \sum_{i=1}^{N-1} \left[ J \cos(\theta_{2i-1} - \theta_{2i}) + \cos(\theta_{2i} - \theta_{2i+1}) \right] -$$

$$J' \cos^2(\theta_{2i-1} - \theta_{2i}) + \cos^2(\theta_{2i} - \theta_{2i+1}) \right] -$$

$$h \sum_{i=1}^{N-1} \left( \cos \theta_{2i-1} - \cos \theta_{2i} \right) - h \cos \theta_N \quad (B3)$$
If the spins start to slightly tilt away from their AFM configuration a small angle expansion of (B3) gives

\[ H = -(N - 1)(J - J') - h + \frac{1}{2}(J - 2J') \]

\[ \sum_{i=1}^{N-1} [\theta_{2i-1} - \theta_{2i}]^2 + (\theta_{2i} - \theta_{2i+1})^2 ] + \]

\[ \frac{h}{2} \sum_{i=1}^{N-1} (\theta_{2i-1}^2 - \theta_{2i}^2) + \frac{h}{2} \theta_N^2 \]

(B4)

The derivatives of Hamiltonian (B4) with respect to the \( \theta \) are:

\[ \frac{\partial H}{\partial \theta_1} = (J - 2J')(\theta_1 - \theta_2) + h\theta_1 \]

\[ \frac{\partial H}{\partial \theta_{2i}} = (J - 2J')(2\theta_{2i} - \theta_{2i+1} - \theta_{2i-1}) - h\theta_{2i}, \]

\[ i = 1, \ldots, \frac{N-1}{2} \]

\[ \frac{\partial H}{\partial \theta_{2i-1}} = (J - 2J')(\theta_{2i-1} - \theta_{2i-2}) + h\theta_{2i-1}, \]

\[ i = 2, \ldots, \frac{N-1}{2} \]

\[ \frac{\partial H}{\partial \theta_N} = (J - 2J')(\theta_N - \theta_{N-1}) + h\theta_N \]

(B5)

To get the minima derivatives (B5) are set equal to 0. To simplify the expressions \( \alpha \equiv J - 2J' \). Then Eqns (B5) define the following system:

\[
egin{pmatrix}
\theta_1 \\
\theta_2 \\
\vdots \\
\theta_{N-2} \\
\theta_{N-1} \\
\theta_N 
\end{pmatrix} = \begin{pmatrix}
\alpha + h & -\alpha & 0 & 0 & 0 & \ldots & 0 & 0 & 0 \\
-\alpha & 2\alpha + h & -\alpha & 0 & 0 & \ldots & 0 & 0 & 0 \\
0 & -\alpha & 2\alpha + h & -\alpha & 0 & \ldots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ldots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & \ldots & -\alpha & 2\alpha + h & -\alpha \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & -\alpha & 2\alpha + h \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & -\alpha \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & -\alpha
\end{pmatrix} \begin{pmatrix}
\theta_1 \\
\theta_2 \\
\vdots \\
\theta_{N-2} \\
\theta_{N-1} \\
\theta_N 
\end{pmatrix} 
\]

The system of equations is homogeneous and has a solution if the determinant of the matrix is zero. The characteristic polynomial of the matrix, which is in Toeplitz form, is [23, 25]

\[ \Delta_n = \frac{\alpha^{N-1} h}{\sin(2\theta)} \left\{ \sin[(N+1)\theta] - \frac{\sin[(N-1)\theta]}{(h + \lambda) \sin[(N-1)\theta]} \right\} \]

(B6)

where \( \lambda \) is an eigenvalue of the matrix and

\[ (2\alpha + h - \lambda)(2\alpha - h - \lambda) = 4\alpha^2 \cos^2 \theta \]

(B7)

To calculate the determinant \( \lambda = 0 \) must be taken, and (B6) gives

\[ \Delta_n(\lambda = 0) = \frac{\alpha^{N-1} h}{\sin(2\theta)} \left\{ \sin[(N+1)\theta] - \frac{\sin[(N-1)\theta]}{(h + \lambda) \sin[(N-1)\theta]} \right\} \]

and from (B7) it is \( h_t = 2\alpha \sin \theta \). Taking into account that \( \sin[(N+1)\theta] = 2\cos \theta \sin(N\theta) - \sin[(N-1)\theta] \) it is eventually

\[ \Delta_n(\lambda = 0) = \frac{\alpha^{N-1} h \cos[(N-1)\theta]}{\sin(2\theta)} \left\{ \sin(2\theta) - [1 - \cos(2\theta)] \right\} \]

\[ \tan[(N-1)\theta] \]

(B9)

After some algebra \( \Delta_n(\lambda = 0) = 0 \) implies that

\[ \tan[(N-1)\theta] = \cot \theta \Rightarrow (N-1)\theta + \theta = \frac{\pi}{2} \Rightarrow N\theta = \frac{3\pi}{4} \]
\[ \theta \Rightarrow \theta = \frac{\pi}{2N}. \] Then it is \( h_t = 2\alpha \sin \frac{\pi}{2N} \) or (given in [18] for \( J' = 0 \))

\[ h_t = 2(J - 2J')\sin \frac{\pi}{2N} \quad (B10) \]

\( h_t \) is a monotonic function of \( N \) with limit \( N \to \infty h_t = 0 \). The eigenvector that corresponds to \( \lambda = 0 \) and \( \theta = \frac{\pi}{2N} \) is given by [22]

\[ \theta_i = (-\alpha)^N \{ \sin \left( \frac{\pi}{2N} (N - i + 2) \right) - (\alpha - h_t) \sin \left( \frac{\pi}{2N} (N - i) \right) \}, \text{ i odd} \]

\[ \theta_i = (-\alpha)^N \{ (\alpha + h_t) \sin \left( \frac{\pi}{2N} (N - i + 1) \right) - \sin \left( \frac{\pi}{2N} (N - i - 1) \right) \}, \text{ i even} \quad (B11) \]

with \( i = 1, \ldots, N \). After some algebra and replacing \( h_t \) it is

\[ \theta_i = 2(-\alpha)^{N+1} \sin \frac{\pi}{2N} \{ \sin \left( \frac{\pi}{2N} (i - 1) \right) + \cos \left( \frac{\pi}{2N} i \right) \}, \text{ i odd} \]

\[ \theta_i = 2(-\alpha)^{N+1} \sin \frac{\pi}{2N} \{ \sin \left( \frac{\pi}{2N} i \right) + \cos \left( \frac{\pi}{2N} (i - 1) \right) \}, \text{ i even} \quad (B12) \]

with \( i = 1, \ldots, N \). To simplify the expressions the constant \( 2(-\alpha)^{N+1} \sin \frac{\pi}{2N} \equiv C_N \). Then

\[ \theta_i = C_N \{ \sin \left( \frac{\pi}{2N} (i - 1) \right) + \cos \left( \frac{\pi}{2N} i \right) \}, \text{ i odd} \]

\[ \theta_i = C_N \{ \sin \left( \frac{\pi}{2N} i \right) + \cos \left( \frac{\pi}{2N} (i - 1) \right) \}, \text{ i even} \quad (B13) \]

with \( i = 1, \ldots, N \). The even spins have undergone the transformation \( \theta_{2i} \to \theta_{2i} - \pi \), thus it finally is

\[ \theta_i = C_N \{ \sin \left( \frac{\pi}{2N} (i - 1) \right) + \cos \left( \frac{\pi}{2N} i \right) \}, \text{ i odd} \]

\[ \theta_i = \pi + C_N \{ \sin \left( \frac{\pi}{2N} i \right) + \cos \left( \frac{\pi}{2N} (i - 1) \right) \}, \text{ i even} \quad (B14) \]

By substituting \( N - i + 1 \) for \( i \) it is straightforward to show that these expressions are symmetric with respect to the center of the chain.

**Appendix C: Saturation Magnetic Field**

The following derivation does not depend on the parity of \( N \) and is thus also valid for even chains. Hamiltonian (11) of the main paper is in polar coordinates

\[ H = \sum_{i=1}^{N-1} \left[ J \cos(\theta_i - \theta_{i+1}) + J' \cos^2(\theta_i - \theta_{i+1}) \right] - \frac{\hbar}{2} \sum_{i=1}^{N} \cos \theta_i \]

(C1)

For spins very close to saturation the odd polar angles \( \theta_i, i = 1, 3, \ldots, N \) are very small. The even angles \( \theta_i, i = 2, 4, \ldots, N - 1 \) are very close to \( 2\pi \), therefore the transformation \( \theta_{2i} \to 2\pi - \theta_{2i} \) is performed and \( (C1) \) becomes, since every bond has one even spin

\[ H = \sum_{i=1}^{N-1} \left[ J \cos(\theta_i + \theta_{i+1}) + J' \cos^2(\theta_i + \theta_{i+1}) \right] - \frac{\hbar}{2} \sum_{i=1}^{N} \cos \theta_i \]

(C2)

If the spins start to slightly tilt away from their ferromagnetic configuration a small angle expansion of \( (C2) \) leads to

\[ H = (N - 1)(J + J') - N\hbar - \frac{1}{2}(J + 2J') \]

\[ \sum_{i=1}^{N-1} (\theta_i + \theta_{i+1})^2 + \frac{\hbar}{2} \sum_{i=1}^{N} \theta_i^2 \]

(C3)

The derivatives of Hamiltonian \( (C3) \) with respect to the \( \theta_i \) are

\[ \frac{\partial H}{\partial \theta_1} = -(J + 2J')(\theta_1 + \theta_2) + h\theta_1 \]

\[ \frac{\partial H}{\partial \theta_i} = -(J + 2J')(2\theta_i + \theta_{i+1} + \theta_{i-1}) + h\theta_i \quad i = 2, \ldots, N - 1 \]

\[ \frac{\partial H}{\partial \theta_N} = -(J + 2J')(\theta_N + \theta_{N-1}) + h\theta_N \]

(C4)

To get the minima derivatives \( (C4) \) are set equal to 0. To simplify the expressions \( \alpha \equiv J + 2J' \). Then Eqs \( (C4) \) define the following system:
The system of equations is homogeneous and has a solution if the determinant of the matrix is zero. One has to calculate the eigenvalues of the matrix, which is in Toeplitz form, and pick out the zero eigenvalue. The eigenvalues are

$$\lambda_s = 2a - h + 2a \cos \frac{\pi k}{N}, \quad k = 1, \ldots, N$$

and substituting $\alpha$

$$\lambda_s = 2(J + J') - h + 2(J + J') \cos \frac{k\pi}{N}, \quad k = 1, \ldots, N$$

Setting $\lambda_s = 0$ it is

$$h' = 2(J + J')(1 + \cos \frac{\pi k}{N}), \quad k = 1, \ldots, N$$

The maximum value for $h'$ is generated when the argument of the cosine is minimum, and this corresponds to $k = 1$, therefore

$$h_s = 2(J + J')(1 + \cos \frac{\pi}{N}) \quad (C5)$$

$h_s$ is a monotonic function of $N$ with $\lim_{N \to \infty} h_s = 4(J + 2J')$. The corresponding normalized eigenvector for $k = 1$ is [26]

$$\theta_i = \sqrt{\frac{2}{N}} \sin \frac{\pi}{2N}(2i - 1), \quad i = 1, \ldots, N$$

To simplify the expression the constant $\sqrt{\frac{2}{N}} \equiv C_N$. Then

$$\theta_i = C_N \sin \frac{\pi}{2N}(2i - 1), \quad i = 1, \ldots, N$$

The even spins have undergone the transformation $\theta_{2i} \to 2\pi - \theta_{2i}$, thus it finally is

$$\theta_i = \pi[1 + (-1)^i] - (-1)^i C_N \sin \frac{\pi}{2N}(2i - 1), \quad i = 1, \ldots, N$$

By substituting $N - i + 1$ for $i$ it is straightforward to show that the expression is symmetric with respect to the center of the chain.

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FIG. 1: Maximum reduced $S_{g,J'>J/2}^{\text{max}}/N$ (long dashed lines) and minimum $S_{g,J'>J/2}^{\text{min}}$ (continuous lines) global ground state magnetization for open chains of different length $N$ as function of $J'/J$. It is $S_{g,J'<J/2} = 1$. The maximum reduced magnetization does not change significantly for large $N$.

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FIG. 2: Polar angles $\theta_i$ in units of $\pi$ for the lowest energy configuration as function of the reduced total magnetization $S/N$ for $N = 11$ and $J' = 0$. The threshold field $h_t = 0.285J$ and the saturation field $h_s = 3.919J$ (Eqs (4) and (6)). The location of the residual magnetization $S_{g,J'\leq J/2} = 1$ is shown with the red arrow. The colors relate to the location of the spins with respect to the edge: $i = 1, 11$: black, $i = 2, 10$: red, $i = 3, 9$: green, $i = 4, 8$: blue, $i = 5, 7$: brown, $i = 6$: violet. For $S \geq S_{g,J'\leq J/2}$ the polar angles are symmetric with respect to the center of the chain. For $S < S_{g,J'\leq J/2}$ they add up to $2\pi$ for spins located symmetrically with respect to the center, and to show this the angles for the right half of the chain are indicated with long dashed lines.
FIG. 3: Polar angles $\theta_i$ in units of $\pi$ for the $S = 0$ lowest energy configuration as function of the number of sites $N$ for $J' = 0$. Different symbols denote different distance from the edge. Only spins from one side of the chain are shown as the symmetric ones have polar angles equal to $2\pi - \theta_i$. For $N = 3$ the black circle corresponds to the edge spin and the red box to the central spin. For every subsequent odd $N$ a single angle is added, which always starts out at the center of the chain directed along $\pi$ and has its own symbol and distance from the edge $\frac{N+1}{2}$. 
FIG. 4: Lowest energy per bond as function of the reduced magnetization $S/N$ for different $J'/J$. For $J'/J \leq 1/2$ it is $S_{g,J'} \leq J/2 = 1$ (shown with the red arrow) for the global lowest energy, while for $J'/J > 1/2$ the global lowest energy corresponds to spin values ranging from $S_{g,J'}^{\min} > J/2$ to $S_{g,J'}^{\max} > J/2$ (Fig. 1), highlighted with dashed lines. The inset focuses on spin values less than the minimum of the global lowest energy state, with the energies divided by the absolute value of the global energy minimum. For $J'/J = 0.52$ and 0.65 the spin range is much smaller and the corresponding reduced energies are very close to -1.
FIG. 5: Polar angles $\theta_i$ in units of $\pi$ for the lowest energy configuration as function of the reduced total magnetization $S/N$ for $N = 11$ and $J'/J = 0.49$. The threshold field $h_t = 5.693 \times 10^{-3}J$ and the saturation field $h_s = 7.760J$ (Eqs (4) and (6)). The location of the residual magnetization $S_{g,J'\leq J/2} = 1$ is shown with the red arrow. The colors relate to the location of the spins with respect to the edge: $i = 1, 11$: black, $i = 2, 10$: red, $i = 3, 9$: green, $i = 4, 8$: blue, $i = 5, 7$: brown, $i = 6$: violet. For $S \geq S_{g,J'\leq J/2}$ the polar angles are symmetric with respect to the center of the chain. For $S < S_{g,J'\leq J/2}$ they add up to $2\pi$ for spins located symmetrically with respect to the center, and to show this the angles for the right half of the chain are indicated with long dashed lines.
FIG. 6: Polar angles $\theta_i$ in units of $\pi$ for the lowest energy configuration as function of the reduced total magnetization $S/N$ for $N = 11$ and $J'/J = 1$. The saturation field $h_s = 11.757J$ (Eq. (6)). The minimum and maximum values of the residual magnetization are $S_{g,J/2}^{\min} = 1$ and $S_{g,J/2}^{\max} = \sqrt{3}$ (Eq. (3)) and are shown with red arrows. The plot is for spins outside this range. The colors relate to the location of the spins with respect to the edge: $i = 1, 11$: black, $i = 2, 10$: red, $i = 3, 9$: green, $i = 4, 8$: blue, $i = 5, 7$: brown, $i = 6$: violet. For $S \geq S_{g,J/2}^{\max}$ the polar angles are symmetric with respect to the center of the chain. For $S \leq S_{g,J/2}^{\min}$ they add up to $2\pi$ for spins located symmetrically with respect to the center, and to show this the angles for the right half of the chain are indicated with long dashed lines.