https://doi.org/10.26565/2220-637X-2024-42-06 ISSN 2220-637X
УДК: 544.163.3-386:539.192:537.611.2

ON STRUCTURAL INVARIANTS OF ENERGY SPECTRUM OF S=1 HEISENBERG ANTIFERROMAGNETS WITH SINGLE-ION ANISOTROPY

V. V. Tokariev[*,†,a], M. A. Fedorenko[*,b]

[*]*V. N. Karazin Kharkiv National University, School of Chemistry, 4 Svobody sqr., Kharkiv, 61022 Ukraine*

[†]*SSI "Institute for Single Crystals" of NAS of Ukraine, 60 Nauky ave., Kharkiv, 61070, Ukraine*

a) victor.tokarev@karazin.ua https://orcid.org/0000-0002-8874-0032
b) f3d0r3nk0000@gmail.com https://orcid.org/0009-0001-4077-4444

We study the relationship of the energy spectrum of finite S=1 Heisenberg antiferromagnets with their structure in the presence of single-ion anisotropy. We show that in the limit of strong easy-plane anisotropy magnets with the structure of adjacency cospectral graphs have equal ground state energies with magnetization M=0. We derive additional necessary condition for equality of lowest energy levels with M=±1. For strong easy-axis anisotropy we found that bipartite S=1 magnets with structures, for which S=1/2 Ising models have equal spectra for arbitrary longitudinal magnetic field, have close energy spectra of S=1 antiferromagnets for arbitrary parameter of single-ion anisotropy. For moderate easy-axis anisotropy bipartite S=1 antiferromagnets with equal energies of spin waves in linear approximation are also approximately isoenergetic. Overall, this explains the remarkable similarity of energy spectra in M=0 subspace for S=1 antiferromagnetic Heisenberg model on bipartite cospectral regular graphs.

Keywords: *molecular nanomagnet, Heisenberg model, Ising model, single-ion anisotropy, spin wave theory.*

1. Introduction

Quasi-zero-dimensional magnetic complex compounds (also termed molecular nanomagnets (MNMs) have perspective applications in quantum computing as qubits and qudits [1,2], and in molecular spintronics [3]. MNMs with high barriers for magnetization reversal (resulting in slow relaxation of magnetization at low temperatures) are considered promising materials for magnetic cooling [4,5] and are also known as single-molecule magnets (SMMs).

For polynuclear SMMs based on abundant transition metal compounds the interplay of exchange interactions and magnetic anisotropy complicates the structural dependence of the magnetization reversal barrier. This factor, together with quantum tunneling of magnetization and spin-phonon relaxation [6], made a systematic increase of barrier U and blocking temperature T_b problematic, and eventually major synthetic efforts shifted towards lanthanide-based single-ion magnets [7].

Structure optimization of MNMs for magnetic cooling was discussed, for example, in the work of Garlatti *et al.* [8] for the particular case of S=3/2 SMMs. While later it was noted [9] that such optimization should depend on the specific type of magnetic cooling cycle, we would like to stress that in [8] only a single type of SMMs was studied. The structure of these SMMs allows to calculate exactly the energy spectrum for the isotropic Heisenberg model with only a straightforward application of angular momentum addition rules. The more general method to construct Hamiltonians maximizing a specific observable using automatic differentiation and exact diagonalization was presented in [10]. Unfortunately, for a large enough system size such direct structural optimization of magnetic properties is unfeasible even in the approximation of Heisenberg model, because Hilbert space dimension and computational resources necessary to calculate the energy spectrum of this model for a single MNM grow exponentially with increase of the number n of magnetic atoms in it.

For spin models, few exact results on structure-property correspondence are known. For example, in [11] it was proved that correlation functions of Heisenberg magnet with anisotropic exchange completely determine its structure. Authors of [12] showed that quantum dynamics of magnetization always allows to distinguish non-isomorphic magnets with S=1/2 in case of precise initial state preparation. In contrast, the energy spectrum (determining magnetocaloric efficiency and magnetization reversal barrier U) is not uniquely determined by the structure of a magnet. In [13] for

© Tokariev V. V., Fedorenko M. A., 2024
This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0.

S=1/2 XY model the existence of an infinite number of pairs of non-isomorphic systems with equal energy spectra for some fixed magnetization M was proved. In [14] for the case of magnetization $M=M_{max}-2$ it was shown that non-isomorphic strongly regular graphs with equal parameters possess equal energy spectra of S=1/2 XY model. Importantly, in [15] the family of S=1/2 isotropic Heisenberg triangles with completely equal energy spectra was constructed. Earlier one of the authors also reported examples of antiferro- and ferrimagnets with equal energies of ground and lower excited states of spin-S Heisenberg model in spin wave approximation [16,17].

This motivates further development of approximate structure-property relationships that allow to group together MNMs with similar properties. In this work, we study the relation of a magnet structure with its low-energy spectrum in the presence of single-ion anisotropy. While in the general metal complex the local anisotropy axes can be aligned in arbitrary directions, here we adopt a simplified picture of homogeneous single-ion anisotropy with equal strength and axis direction, which results in a single parameter D that controls magnetic anisotropy strength. The spin quantum number of magnetic ions is taken to be S=1 as the lowest one, which accounts for spin anisotropic effects and still allows for the exact computation of the lower part of the energy spectrum of medium-sized MNMs.

We analyzed two limiting cases of strong easy-plane ($D>0$) and easy-axis ($D<0$) anisotropy using perturbation theory. In the first case (Section 3) the ground state energy with M=0 depends only on the spectrum of $\boldsymbol{J}$ matrix, the energies of M=1 excited states depend only on the matrices $\boldsymbol{J}$ and $\boldsymbol{W}=2\boldsymbol{d}-\boldsymbol{J}^2$. We have found finite S=1 antiferromagnets possessing equal moments of these matrices and confirmed that indeed for $D>0$ they have numerically close lowest parts of energy spectra.

For the case of strong easy-axis anisotropy low-energy spectrum in the first order of perturbation theory is determined by S=1/2 Ising model. In Section 4 we demonstrate numerically that a known pair of bipartite S=1 antiferromagnets with equal spectra of S=1/2 Ising model (in every subspace with fixed M) have remarkably numerically close energy spectra for arbitrary anisotropy parameter D.

Additionally, we used linear spin wave theory to find bipartite isomers of MNMs that have equal magnon energies for arbitrary spin quantum number S. Examples of S=1 antiferromagnets with such structures are approximately isoenergetic for moderate easy-axis anisotropy ($D \gtrsim -|J|$).

2. Model, Definitions and Methods

Here we study S=1 antiferromagnetic Heisenberg model with homogeneous single-ion anisotropy with Hamiltonian

$$H = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j + D\sum_{i=1}^{n}(S_i^z)^2 = H_{ex} + D\,H_{an}, \quad (1)$$

Where $J_{ij} \geq 0$ – parameter of magnetic exchange interaction between ions i and j, D – parameter of single-ion anisotropy, $\boldsymbol{S}_i \cdot \boldsymbol{S}_j = \sum_{\alpha=x,y,z} S_i^\alpha S_j^\alpha$ – operator of isotropic exchange between magnetic ions i and j. Both operators commute with $\sum_i S_i^z$ and thus conserve total magnetization M.

Eigenstates of H_{an} are product states $|m_1, m_2, \ldots m_n\rangle$ with local z-projection of spin $m_i = 0, \pm 1$. We will also use short notation $|i\rangle$ for product states with $m_j = 0$ for all j except i, where $m_i = 1$.

If not stated otherwise, we will identify matrix $\boldsymbol{J}$ of exchange parameters that has elements $(\boldsymbol{J})_{ij} = J_{ij}$, $J_{ii} = 0$ with adjacency matrix $\boldsymbol{A}$ of undirected unlabeled graph G. We will also refer to matrix $\boldsymbol{L} = \boldsymbol{d} - \boldsymbol{J}$ as a Laplacian of graph, where diagonal matrix $(\boldsymbol{d})_{ij} = \delta_{ij} d_i$ contains vertex valences $d_i = \sum_{j=1}^{n} J_{ij}$. Adjacency cospectral graphs share eigenvalues of adjacency matrices. Graphs with equal eigenvalues of Laplacians are also called $\boldsymbol{L}$-cospectral [18]. In the following we will denote as ($\boldsymbol{A}$, $\boldsymbol{B}$)-cospectral pairs of graphs which have equal spectra (sets of eigenvalues λ) of two matrices, i.e. for i=1, 2, … n $\lambda_i(\boldsymbol{A}(G_1)) = \lambda_i(\boldsymbol{A}(G_2))$ and $\lambda_i(\boldsymbol{B}(G_1)) = \lambda_i(\boldsymbol{B}(G_2))$.

Expressions for effective Hamiltonians and energy values in the main text are presented for case of unweighted graphs (where elements of $\boldsymbol{J}$ matrix equal 0 or 1), expressions for weighted graphs are listed in the Appendix.

In this work we use Lanszos exact diagonalization (ED) as implemented in ALPS 2.0 package [19] to calculate the energy spectrum of anisotropic Heisenberg model (1). For the generation of non-isomorphic graphs we used package nauty [20]. Analysis of structural dependence of MNM low-energy spectra was done using Brillouin-Wigner (BW) perturbation theory and second-order

degenerate perturbation theory (PT) with exchange operator H_{ex} as a perturbation and *1/D* as a small parameter. Linear spin wave theory (LSWT) is used in its matrix formulation for bipartite antiferromagnets [21,22].

3. Analysis of strong easy-plane anisotropy limit (*D* > *0*)

Large easy-plane anisotropy is typically associated with ferromagnetic Ni complexes (for example [23]), but antiferromagnets with $D \simeq J$ (e.g. one-dimensional chains in $[Ni(HF_2)(pyz)_2]SbF_6$ [24]) and $D \gg J$ (zero-dimensional Ni_6Cr nanowheels [25]) are also known.

For $D > 0$ the unperturbed ground state of H_{an} $|m_i = 0\rangle$ is non-degenerate and has $M=0$, first excited states $|\pm 1_i\rangle$ are n times degenerate and have M = ±1. So, in this limit MNMs are not suited for magnetic cooling, as zero-field low-temperature magnetic entropy is negligible.

In the third order of BWPT the expression for ground state energy depends only on $Tr\boldsymbol{J}^m, m = 2, 3$:

$$E_0 = (E_0 - 2D)^{-1} Tr\boldsymbol{J}^2 + (E_0 - 2D)^{-2}(Tr\boldsymbol{J}^3 - Tr\boldsymbol{J}^2) \quad (2)$$

Expression (2) depends only on the number of edges and triangles in a graph. Fourth-order expression for E_0 also depends only on the spectrum of $\boldsymbol{J}$ matrix (see Appendix).

For excited states with M=1 the second order of degenerate perturbation theory gives the following effective Hamiltonian in the basis of states $|\pm 1_i\rangle$:

$$H_{eff} = \boldsymbol{J} + (2D)^{-1} Tr\boldsymbol{J}^2 - (2D)^{-1}\boldsymbol{W} \quad (3)$$

Matrix elements of effective Hamiltonian (3) depend only on the matrices $\boldsymbol{J}$ and $\boldsymbol{W}=2\boldsymbol{d}-\boldsymbol{J}^2$. Equality of spectra of effective Hamiltonians for pair of graphs (G_1, G_2) is achieved if $Tr\left(H_{eff}(G_1)\right)^m = Tr\left(H_{eff}(G_2)\right)^m$ for m=0, 1, … n [26]. Each moment $Tr\left(H_{eff}(G_1)\right)^m$ is a polynomial in powers of 1/*D*, and equality of spectra for arbitrary D is achieved only if all coefficients of these polynomials are equal. As every such moment contains terms $Tr(\boldsymbol{J}(G_i))^m$ and $Tr(\boldsymbol{W}(G_i))^m/(2D)^m$, ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectrality is the necessary condition for equality of lowest energy levels with M = ±1.

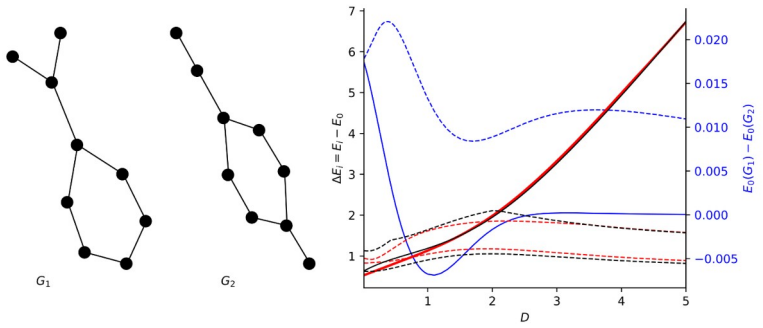

Figure 1. Left panel: example of ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectral graphs G_1 and G_2. Right panel: dependence of excitation energies $\Delta E_i = E_i - E_0$ of G_1 (black) and G_2 (red) on anisotropy parameter D, and difference $\Delta E_i = E_0(G_1) - E_0(G_2)$ of ground state energies of G_1 and G_2 (blue). Solid lines correspond to M=0 states, dashed to M=1 states.

Using nauty, we generated all non-isomorphic graphs with $n < 11$ vertices and found all ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectral graph groups (pairs, triples etc). We computed moments of these matrices instead of direct calculation of matrix spectra in order to avoid floating-point errors.

Number of found ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectral groups quickly grows with increase of n: for n<9 there are no ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectral graphs, for n=9 there are 30 pairs, while for n=10 there are 5172 pairs, 5 triples and 4 quadruples.

For graphs in these groups we computed energies of the lowest 10 eigenstates for values of anisotropy parameter $D \in [0, 5]$. Typical example of such pair is shown on Figure 1 (left). Note that

energies are visually indistinguishable, so only ground state energy differences $\Delta E_0 = E_0(G_1) - E_0(G_2)$ between two MNMs and excitation energies $\Delta E_i = E_i - E_0$ for individual MNMs are shown. Ground state energies of S=1 AFM Heisenberg model on G_1 and G_2 are numerically close down to $D \sim 2.5\ J$ in M=0 subspace. For M=1 the numerical equality of ground and excited state energies is achieved for much larger $D \sim 5$, where second order of PT is valid.

4. Analysis of strong easy-axis anisotropy limit ($D < 0$)

Strong easy-axis anisotropy limit is relevant to multiple Ni-based SMMs [27, 28]. In this limit the ground state of H_{an} with M=0 is 2^n-times degenerate. In the second order of degenerate perturbation theory the effective Hamiltonian acting on this 2^n-dimensional subspace is

$$H_{eff} = -nD + \sum_{i<j} J_{i,j} S_i^z S_j^z + (2D)^{-1} \sum_{i<j} J_{ij}\left(-5I + P_{i,j} - \pi_{i,j}\right) \quad (4)$$

where operator $P_{i,j}$ permutes S^z projections for atoms i and j ($P_{i,j}|m_i, m_j\rangle = |m_j, m_i\rangle$), $\pi_{i,j}$ projects onto subspace with $m_i \neq 0, m_j \neq 0$.

This expression can be rewritten using the Dirac identity $|m_i, m_j\rangle\langle m_j, m_i| = \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + 1/2$ as a Hamiltonian of highly anisotropic S=1/2 XXZ model:

$$H_{eff} = const + \sum_{i<j}(4J_{i,j} - 5\,{J_{i,j}}^2/D)\,\sigma_i^z\sigma_j^z + (2D)^{-1}\sum_{i<j} J_{ij}\left(\sigma_i^+\sigma_j^- + \sigma_i^-\sigma_j^+\right) \quad (5)$$

4.1. Magnets with equal spectra of S=1/2 Ising model

In the first order of perturbation theory effective Hamiltonian (4) is simply proportional to Hamiltonian of S=1/2 Ising model:

$$H_{eff} = -nD + \sum_{i<j}(4J_{i,j} - 5\,{J_{i,j}}^2/D)\,S_i^z S_j^z \quad (6)$$

Examples of MNMs with equal spectra of S=1/2 Ising model are known from studies of graph polynomials. In [30] it was demonstrated that Tutte polynomial T of underlying graph G is related to zero-field partition function Z(β) of S=1/2 Ising model:

$$Z(\beta) = 2^k \nu^{n-k} T\left(\frac{2+\nu}{\nu}, \nu + 1\right) \quad (7)$$

where $\beta = 1/k_B T$ is the inverse temperature, k_B – Boltzmann constant, $\nu = e^{\beta} - 1$, k is the number of connected components of graph G. Combinatorial properties of Tutte polynomial are well-known. It represents a generalization of chromatic polynomial and can be generated using a recursive deletion-contraction procedure [29].

From (6) we can conclude that finite graphs with equal Tutte polynomials must have equal partition functions of S=1/2 Ising model for arbitrary inverse temperatures β and zero external magnetic field, and so equal energy spectra. This is not sufficient for equality of spectra of effective Hamiltonian (5), because it's restricted to M=0 subspace, as co-Tutte graphs may have equal energies from subspaces with different M. However, such M-restricted polynomials are unknown to authors. To achieve spectrum equality of S=1/2 Ising model for the arbitrary homogeneous magnetic field along z-direction graphs must share U-polynomials [30, theorem 5.2].

We have conducted ED study of known graph pairs with S=1/2 Ising models being isoenergetic for arbitrary external z-field. The first example is pair (G_{13}, G'_{13}) from [31] (see Fig. 2), for which ground state energy differences are not monotonic, but small ($< 10^{-2}\ J$) in the whole investigated interval of D parameter values (Fig. 2, right pane, blue line). It is expected from the 1st order of perturbation theory that equality of excited state energies (for example, E_2 and E_5) is achieved only for $D \ll J$ (in this case $D < -2J$), and for larger D the level crossings induce significant energy differences. But the remarkable numerical equality of energy spectra for $D > 0$ is unexpected, as these graphs are not ***J***-cospectral. This suggests the existence of additional invariants of low-energy theory, which are preserved by the transfer of a single pendant atom (Fig. 2, left, red ellipse). It should be noted that graphs G_{13} and G'_{13} are bipartite. On the contrary, non-bipartite pair of graphs with equal U-

polynomials from [32], while being (***J***, ***L***, $\boldsymbol{H}_+$)-cospectral, have multiple energy crossings and so large energy differences for intermediate $D \in [-2,2]$

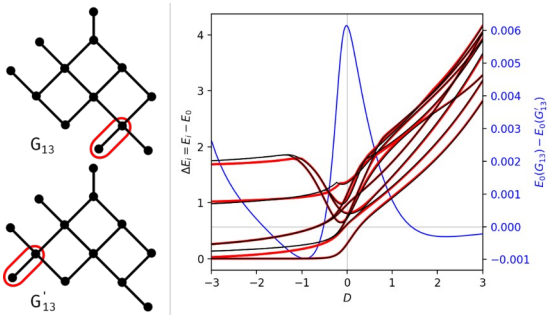

Figure 2. Left panel: pair of graphs from [32] that have S=1/2 Ising model with equal energies in the presence of arbitrary magnetic field, oriented along z-axis. Red ellipse indicates location of differing edge. Right panel: dependence on anisotropy parameter *D* of excitation energies $\Delta E_0 = E_i - E_0$ for G_{13} (black) and G'_{13} (red), and difference of ground state energies $E_0(G_{13}) - E_0(G'_{13})$ (blue) calculated for S=1 AFM Heisenberg model on these graphs.

4.2. Application of linear spin wave approximation to bipartite magnets

For bipartite antiferro- and ferrimagnets spin wave theory is a good approximation for the energy of ground and lowest excited states. The accuracy of this approach grows with the increase of atomic spin quantum number S and system dimensionality. In linear spin wave (LSW) approximation the spin Hamiltonian is mapped to the quadratic boson Hamiltonian. Energies ω_k of spin waves can be found by solving its equations of motion, which results in a non-symmetric eigenproblem for so-called grand canonical matrix [21].

Earlier [16] we calculated ω_k^2 for the isotropic Heisenberg model as eigenvalues of non-symmetric matrices $\boldsymbol{H}_\pm = S^2(\boldsymbol{d}^2 - \boldsymbol{J}^2 \pm [\boldsymbol{d}, \boldsymbol{J}])$. Traces $\tau_m = Tr\boldsymbol{H}_+^m$ are polynomials of J_{ij}, S_i, and can be used as structural invariants of LSW spectrum.

For regular graphs $[\boldsymbol{d}, \boldsymbol{J}] = 0$, magnon energies are simplified to $\omega_k^2 = d^2 - \lambda_k^2$, so the spectrum of $\boldsymbol{H}_+$ is determined by eigenvalues λ_k of ***J***, and adjacency cospectral graphs have equal LSW spectra. For $D < 0$ direct account for H_{an} results only in the addition of the constant term $-2D$ to diagonal matrix ***d***. Moreover, LSW approximation can be written for effective Hamiltonian (4) in M=0 subspace. In this case for unweighted graphs matrix ***d*** becomes $(2 - 5/2D)\boldsymbol{d}$, and matrix ***J*** becomes ***J***/*D*. In result, for both cases the spectrum of $\boldsymbol{H}_+$ of cospectral regular graph is determined by eigenvalues of ***J***. This, together with results of Section 3, explains the remarkable similarity of energy spectra of cospectral regular graphs in the whole investigated range of parameter *D* (see Figure 3).

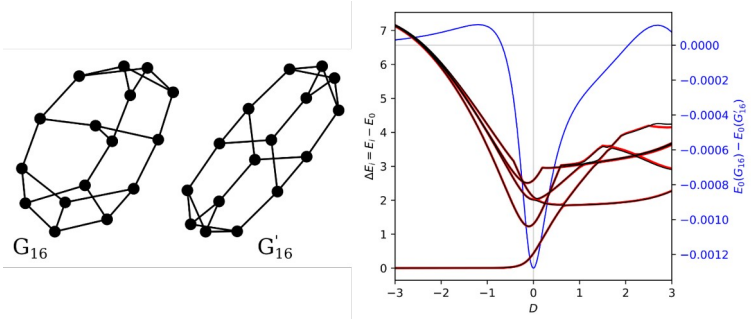

Figure 3. Left panel: pair of ***J***-cospectral cubic graphs (G_{16}, G'_{16}) – a pair of S=1 AFMs with equal energies of LSW and $D \gg J$ approximations. Right panel: dependence of excitation energies and difference of ground state energies in M=0 subspace.

Discussion

Here we presented a simple method to derive relationships of structure with energy spectrum for correlated lattice models:

1. with the help of PT, LSWT or other theories derive matrix functions $\boldsymbol{F}_i$ from which approximate energies of ground state and/or lowest excitations can be calculated,
2. generate non-isomorphic finite graphs G and group them according to moments $Tr\left(\boldsymbol{F}_i(G)\right)^m$ (m=0, 1, … $dim(\boldsymbol{F}_i(G))$) of matrix functions.

Importantly, to make computations of all moments practical, the dimensions of matrices $\boldsymbol{F}_i(G)$ should scale linearly with system size.

Using this approach we have found novel approximately isoenergetic isomers of S=1 Heisenberg model. While approximately isoenergetic isomers can be also constructed using energy gradient $\partial E_0 / \partial J_{i,j} = \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle$ (such that $\sum_{i<j} \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle \Delta J_{i,j} = 0$), this method requires computation of exact correlation functions $\langle \boldsymbol{S}_i \cdot \boldsymbol{S}_j \rangle$ and should be valid only for small changes in structure.

Our considerations give additional arguments for remarkable closeness of energy spectra of S=1 Heisenberg model on ***J***-cospectral regular graphs for arbitrary D.

Despite that we have demonstrated smallness of energy differences for a few pairs of (***J***, ***W***)- and $\boldsymbol{H}_+$-cospectral MNMs, the results must be compared with ΔE_0 for magnets that do not share spectra of these matrices. We have calculated $|\Delta E_0(D = 4)|$ for all pairs of ***J***-cospectral graphs with n=9. Also, it can be noted that $\boldsymbol{H}_+ = \boldsymbol{(d-J)(d+J)}$ is a product of Laplacian ***L*** and signless Laplacian $\boldsymbol{d} + \boldsymbol{J}$. So, to test whether Laplacian cospectrality can be used a proxy for $\boldsymbol{H}_+$-cospectrality, we calculated $|\Delta E_0(D = -1)|$ in subspace with magnetization M=0 for all pairs of ***L***-cospectral bipartite graphs with n=12. Note that the number of graphs in larger cospectral groups (triples, quadruples etc) is negligible. The total number of pairs of (***J***, ***W***)- and $\boldsymbol{H}_+$--cospectral graphs is small (17 and 139), but the number of ***J***- and ***L***-cospectral graphs grows very quickly with n, so we could not compute E_0 for all graphs with $n \geq 9$.

The distributions of energy differences per bond $|\Delta E_0|/N_e$ (Figure 4) show that accounting for structural invariants arising from PT and LSWT allows to filter out pairs with significantly different ground state energies, but many pairs with small $|\Delta E_0|/N_e$ are filtered too. Per-pair inspection shows that larger $|\Delta E_0|/N_e$ for (***J***, ***W***)-and ***L***-cospectral pairs is due to energy level crossings and intruder states.

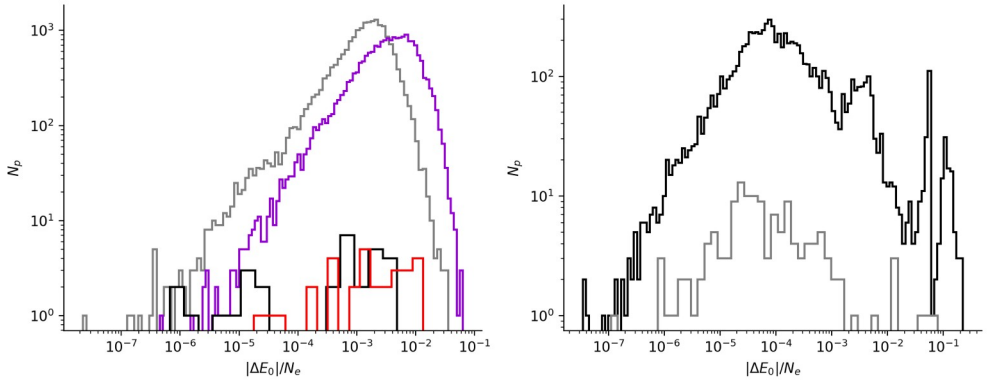

Figure 4. Distributions of ground state energy differences of S=1 MNMs sharing graph spectra. Left panel: histogram of $|\Delta E_0(D = 4)|$ for all pairs of magnets with n=9, which are ***J***-cospectral (gray for M=0, violet for M=1) or (***J***, ***W***)-cospectral (black for M=0, red for M=1). Right panel: histogram of $|\Delta E_0(D = -1, M = 0)|$ for all pairs of ***L***-cospectral magnets (black) and for all pairs of $\boldsymbol{H}_+$-cospectral magnets (gray) with n=12 atoms.

Unfortunately, the presented approach does not allow to find magnets with extremal properties (for example, energy gap $\Delta E = E_1 - E_0$ or magnetic cooling efficiency). Moreover, equality of energy spectra is not necessary for equal low-temperature magnetization, entropy and specific heat, as these require only equality of excitation energies. This approach is also not total, as there are more magnets

with small of $|\Delta E_0|$ for a given D value, but we're unable to find them due to the limits of used approximate methods. It's also well known that perturbation theory is prone to intruder state problem. Level crossings are typical for non-bipartite graphs, which exhibit larger ground state energy differences.

The set of generated graphs with numerically close energy spectra contains a variety of high- and low-valence graphs, including ones that can correspond to real quasi-zero-dimensional transition metal complexes. Here we used the simplest method of exhaustive graph enumeration to find $\mathbf{H}_{\pm}$ and ($\boldsymbol{J}$, $\boldsymbol{W}$)-cospectral graphs. However, graph-theoretic methods similar to Godsil-McKay switching to construct adjacency cospectral graphs [33] should be possible.

Conclusions

We analyzed the structural dependence of the lowest energy levels of finite S=1 Heisenberg antiferromagnets with single-ion magnetic anisotropy using perturbation theory and linear spin wave approximation. Obtained invariants of approximate low-energy theories allow us to find multiple S=1 MNMs with numerically close low-energy spectra. This approach can be straightforwardly generalized to higher-spin and mixed-spin systems, non-equal values of exchange coupling parameters and other types of magnetic anisotropy. Our method can be used to guide the synthesis of perspective magnets with diverse structures and sufficiently similar low-temperature properties (magnetic entropy, specific heat, magnetization etc) that depend on excitation energies.

Acknowledgement

Authors acknowledge support by the program "Magnetism in Ukraine Initiative" (IEEE Magnetics Society and the Science and Technology Center of Ukraine, Project No. 9918).

References

1. Chilton, N. F. Molecular Magnetism. *Annu. Rev. Mater. Res.* **2022**, *52*, 79-101. https://doi.org/10.1146/annurev-matsci-081420-042553.
2. Chiesa, A., Santini, P., Garlatti, E., Luis, F. and Carretta, S. *Rep. Prog. Phys.* **2024**, 87, 034501. https://doi.org/10.1088/1361-6633/ad1f81.
3. Forment-Aliaga, A., Gaita-Ariño, A. Chiral, magnetic, molecule-based materials: A chemical path toward spintronics and quantum nanodevices. *J. Appl. Phys.*, **2022**, 132(18). https://doi.org/10.1063/5.0118582.
4. Hu, J. J., Peng, Y., Liu, S. J., and Wen, H. R. Recent advances in lanthanide coordination polymers and clusters with magnetocaloric effect or single-molecule magnet behavior. *Dalton Trans.*, **2021**, *50*(43), 15473-15487. https://doi.org/10.1039/D1DT02797B.
5. Wang, J. H., Li, Z. Y., Yamashita, M., and Bu, X. H. Recent progress on cyano-bridged transition-metal-based single-molecule magnets and single-chain magnets. *Coord. Chem. Rev.*, **2021**, *428*, 213617. https://doi.org/10.1016/j.ccr.2020.213617.
6. Gu, L., Li, J., and Wu, R. Reconsidering spin-phonon relaxation in magnetic molecules. *J. Magn. Magn. Mater.*, 2022, 170138. https://doi.org/10.1016/j.jmmm.2022.170138.
7. Neese, F., Pantazis, D. A. What is not required to make a single molecule magnet. *Farad. Disc.*, **2011**, *148*, 229-238. https://doi.org/10.1039/C005256F.
8. Garlatti, E., Carretta, S., Schnack, J., Amoretti, G., and Santini, P. Theoretical design of molecular nanomagnets for magnetic refrigeration. *Appl. Phys. Lett.*, **2013**, *103*(20). https://doi.org/10.1063/1.4830002.
9. Evangelisti, M., Lorusso, G., and Palacios, E. Comment on "Theoretical design of molecular nanomagnets for magnetic refrigeration" [Appl. Phys. Lett., 2013, 103, 202410]. *Appl. Phys. Lett.*, **2014**, 105(4). https://doi.org/10.1063/1.4891336.
10. Inui, K., Motome, Y. Inverse Hamiltonian design by automatic differentiation. *Commun. Phys.* **2023**, 6, 37. https://doi.org/10.1038/s42005-023-01132-0.
11. Quintanilla, J. Relationship between the wave function of a magnet and its static structure factor. *Phys. Rev. B*, **2022**, *106*(10), 104435. https://doi.org/10.1103/PhysRevB.106.104435.

12. Albertini, F., D'Alessandro, D. Model identification for spin networks. *Linear Algebra Appl.*, **2005**, 394, 237-256. https://doi.org/10.1016/j.laa.2004.07.007.
13. Barghi, A. R., Ponomarenko, I. Non-isomorphic graphs with cospectral symmetric powers. *Electron. J. Comb.*, **2009**, R120-R120. https://doi.org/10.37236/209.
14. Audenaert, K., Godsil, C., Royle, G., and Rudolph, T. Symmetric squares of graphs. *J. Combin. Theory, Ser. B*, **2007**, 97(1), 74-90. https://doi.org/10.1016/j.jctb.2006.04.002.
15. Schmidt, H. J., Luban, M. Continuous families of isospectral Heisenberg spin systems and the limits of inference from measurements. *J. Phys. A*, **2001**, *34*(13), 2839. https://doi.org/10.1088/0305-4470/34/13/313.
16. Tokarev, V. V. Quantum magnets with equal spin-wave ground state energies, VIII International Conference for Professionals & Young Scientists "Low Temperature Physics", Kharkiv, **2017**, p 88.
17. Tokarev, V. V. Invariant transformations for spin wave models of ferrimagnets, 6th International Conference on Superconductivity and Magnetism, Antalya, Turkey, **2018**, p 552.
18. Brouwer, A. E., Haemers, W. H. Spectra of graphs. Springer New York; New York, 2011. ISBN: 978-1-4614-1938-9.
19. Bauer, B. *et al*. The ALPS project release 2.0: open source software for strongly correlated systems. *J. Stat. Mech.: Theory Exp.*, **2011**, 05, P05001. https://doi.org/10.1088/1742-5468/2011/05/P05001.
20. McKay, B. D., Piperno, A. Practical graph isomorphism, II. *J. Symb. Comput.*, **2014**, 60, 94-112. https://doi.org/10.1016/j.jsc.2013.09.003.
21. Colpa, J. H. P. Diagonalization of the quadratic boson Hamiltonian. *Phys. A: Stat. Mech. Appl.*, **1978**, 93(3-4), 327-353. https://doi.org/10.1016/0378-4371(78)90160-7.
22. Toth, S., Lake, B. Linear spin wave theory for single-Q incommensurate magnetic structures. *J. Condens. Matter Phys.*, **2015**, 27(16), 166002. https://doi.org/10.1088/0953-8984/27/16/166002.
23. Maurice, R. Magnetic anisotropy in a cubane-like Ni_4 complex: an ab initio perspective. *Inorg. Chem.*, **2021**, 60(9), 6306-6318. https://doi.org/10.1021/acs.inorgchem.1c00047.
24. Jamie L. Manson, Paul A. Goddard, John Singleton et al., Enhancing easy-plane anisotropy in bespoke Ni(II) quantum magnets, *Polyhedron*, 180, **2020**, 114379, https://doi.org/10.1016/j.poly.2020.114379.
25. Antkowiak, M., Brzostowski, B., Florek, W., Kamieniarz, G. Metallic core $[Ni_6^{II}Cr^{III}]$ as an example of centered heterometallic rings displaying quantum effects, *J. Magn. Magn. Mater.*, **2022**, 544, 168701, https://doi.org/10.1016/j.jmmm.2021.168701.
26. Lewin, M. On the coefficients of the characteristic polynomial of a matrix, *Discrete Math.*, **1994**, 125(1–3), 255-262. https://doi.org/10.1016/0012-365X(94)90166-X.
27. Chiesa, A., Whitehead, G., Carretta, S. et al. Molecular nanomagnets with switchable coupling for quantum simulation. *Sci. Rep.*, **2014**, 4, 7423. https://doi.org/10.1038/srep07423
28. Smolko, R., Dušek, M., Kuchár, J., Čižmár, E., Černák, J., Syntheses, characterizations and crystal structures of two Ni(II) complexes $[Ni_2(neoc)_4(H_2O)(CO_3)](NO_3)_2{\cdot}3H_2O$ and $[Ni(bapa)_2](NO_3)_2{\cdot}H_2O$ and magnetic properties of the carbonato complex, *Polyhedron*, **2024**, 255, 116953. https://doi.org/10.1016/j.poly.2024.116953.
29. Beaudin, L., Ellis-Monaghan, J., Pangborn, G., and Shrock, R. A little statistical mechanics for the graph theorist. *Discrete Math.*, **2010**, 310(13-14), 2037-2053. https://doi.org/10.1016/j.disc.2010.03.011.
30. Ellis-Monaghan, J. A., Moffatt, I. The Tutte–Potts connection in the presence of an external magnetic field, *Adv. Appl. Math.*, **2011**, 47(4), 772-782. https://doi.org/10.1016/j.aam.2011.02.004.
31. Vinci, W., Markström, K., Boixo, S., Roy, A., Spedalieri, F. M., Warburton, P. A., and Severini, S. Hearing the shape of the Ising model with a programmable superconducting-flux annealer. *Sci. Rep.*, **2014**, 4(1), 5703. https://doi.org/10.1038/srep05703.
32. Brylawski, T. Intersection theory for graphs, *J. Combin. Theory, Ser. B*, **1981**, 30(2), 233-246, https://doi.org/10.1016/0095-8956(81)90068-X.
33. Godsil, C. D., McKay, B. D., Constructing cospectral graphs, *Aequ. Math., **1982**, 25(1), 257-268. https://doi.org/10.1007/BF02189621*.

Appendix. Results of perturbation theory for molecular nanomagnets with general exchange parameters J_{ij}

For $D \gg J$ limit equation (2) for ground state energy with M=0 has the form:

$$E_0 = (E_0 - 2D)^{-1} \sum_{k \neq l} J_{k,l}^2 + (E_0 - 2D)^{-2} \left(TrJ^3 - 2TrJ^2 diag(J) - \sum_{i,j} J_{i,j}^3 \right) \quad \text{(A1)}$$

The 4th order BWPT correction to E_0 is:

$$E_0^{(4)} = \left((E_0 - 2D)(E_0 - 4D) \right)^{-1} \sum_{(i,j,k,l)} J_{i,j} J_{k,l} \left[2J_{i,j} J_{k,l} + J_{j,k} J_{i,l} \right] + (E_0 - 2D)^{-3} \left(\sum_{(i,j)} J_{i,j}^4 - \right.$$
$$\left. - 4 \sum_{(i,j,k)} J_{i,j} J_{i,k} J_{k,j}^2 \right) + 4(E_0 - 2D)^{-3} \sum_{(i,j,k,l)} J_{i,j} J_{i,k} J_{k,l} J_{l,j} \quad \text{(A2)}$$

where summations are carried over subsets of distinct atom indices.
Matrix elements of effective Hamiltonian (3) in M=1 subspace are

$$\langle +1_i | H_{eff} | +1_j \rangle = J_{i,j} + (2D)^{-1} \left(\delta_{i,j} \sum_{l \neq i} \sum_{p \neq l,i} J_{l,p}^2 + \left(1 - \delta_{i,j} \right) \sum_{p \neq i,j} J_{i,p} J_{p,j} \right) \quad \text{(A3)}$$

Received 05.04.2024 *Accepted 07.06.2024*

В. В. Токарєв[*†], М. А. Федоренко[*]. Щодо структурних інваріантів енергетичного спектру S=1 антиферомагнетиків Гейзенберга з одноіонною анізотропією.

[*]*Харківський національний університет імені В.Н. Каразіна, хімічний факультет, майдан Свободи, 4, Харків, 61022, Україна*
[†]*ДНУ «Інститут монокристалів» НАН України, пр. Науки, 60, Харків, 61070, Україна.*

Ми дослідили зв'язок енергетичного спектру скінченних антиферомагнетиків Гейзенберга з S=1 та їхньою будовою в присутності одноіонної анізотропії. Було показано, що ліміті сильної анізотропії типу «легка площина» магнетики з будовою, що відповідають графам з однаковим спектром матриці суміжності, мають однакові енергії основного стану з намагніченістю M=0. Ми отримали додаткову умову, необхідну для рівності нижніх рівнів з $M = \pm 1$. Для сильної анізотропії типу «легка вісь» дводольні магнетики з S=1 та будовою, для якої досягається рівність енергетичних спектрів S=1/2 моделей Ізінга при довільному значенні продольного магнітного поля, також мають близькі енергетичні спектри для довільного значення параметра анізотропії. Для проміжних значень анізотропії типу «легка вісь» дводольні S=1 антиферомагнетики з однаковими енергіями спінових в лінійному наближенні також є наближено ізоенергетичними. В цілому, це пояснює значну близькість енергетичних спектрів в підпросторі з M=0 для S=1 антиферомагнетиків з будовою дводольних ізоспектральних регулярних графів.

Ключові слова: *молекулярний наномагнетик, модель Гейзенберга, модель Ізінга, теорія спінових хвиль.*

Надіслано до редакції 05.04.2024 *Прийнято до друку 07.06.2024*