Ground state and thermodynamic properties of spin-1/2 isosceles Heisenberg triangles for \( V_6 \)-like magnetic molecules

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The spin-1/2 Hamiltonian for two coupled isosceles Heisenberg triangles, which is well suited for describing the \( V_6 \)-type magnetic molecules, is studied by exact diagonalization. The quantum phase transition diagram, at zero temperature, is obtained as a function of the theoretical parameters. The zero temperature magnetization is also obtained as a function of the external magnetic field. The thermodynamic behavior of the magnetization, entropy, susceptibility, and specific heat, as a function of temperature, are also computed and the corresponding magnetocaloric effect analyzed for various values of the Hamiltonian parameters.

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I. INTRODUCTION

The study of molecular magnets has attracted the attention of the scientific community for almost four decades now. In these systems, where the physical realizations occur either as crystals or powders, the intramolecular interaction is much stronger than the intermolecular interaction, making them behave mainly as an ensemble of single independent molecules \(^1\) \(^2\). In addition, their magnetic features promise a variety of applications in physics, magnetotechnology, biology, biomedicine, and material sciences \(^3\) \(^4\), as well as in quantum computing \(^5\) \(^6\) and spintronics (see Ref. \(^1\) and references therein).

It is well known that low dimensional magnetic systems have been broadly studied in the literature, both experimentally and theoretically, due to the interesting magnetic and thermodynamic properties they present at zero and finite temperatures as well. Some of these systems have also frustrated spins due to their geometric structure (see, for instance, \(^7\) \(^8\)). This fact makes the study of molecular magnets more attractive still, because it turns out to be a vast field of quantum phenomena in nanosystems, in particular zero-dimensional magnetic clusters with potential applicability in high-capacity data storage.

An interesting property that various types of these systems exhibit is the so-called magnetocaloric effect, which consists of an isothermal change in entropy or an adiabatic change in temperature when an external magnetic field is varied. This effect has in fact an immense potential application \(^9\). There are indeed several studies in the magnetocaloric effect on quasi-one-dimensional spin models, such as the diamond spin chain \(^10\) \(^11\) \(^12\), the antiferromagnetic triangular lattice \(^13\) \(^14\), and the octahedral chain \(^15\), among others.

It is thus clear from the above discussion that compounds of weakly coupled magnetic molecules allow us to study magnetic systems at the level of nanoscale. Among the family of molecular magnets are the various polyoxovanadates, which contain several spin-1/2 sites originating from the vanadium ions, denoted as \( V_3 \), \( V_6 \), \( V_{12} \), and \( V_{15} \) clusters, the numbers designating the corresponding quantity of vanadium ions always occurring in triangle geometries (for more details on references about theoretical and experimental realizations on these compounds see \(^20\)). In particular, the \( V_6 \) magnetic molecule is one of these systems consisting of a pair of triangles that are weakly antiferromagnetically coupled with a strong antiferromagnetic intratriangle coupling. This type of structure presents thus frustration in its fundamental state, being an interesting system to study its magnetic and thermodynamic properties \(^21\) \(^22\). There are in fact two species of \( V_6 \) magnetic molecule based on polyoxovanadates, which are given by the formulae \( \text{Na}_8\text{H}_8\text{V}_6\text{O}_8(\text{PO}_4)_4[(\text{OCH}_2)_3\text{CCH}_2\text{OH}]_2\cdot18\text{H}_2\text{O} \) and \( \text{Na}_4\text{H}_4\text{Na}_2\text{H}_4\text{V}_6\text{O}_8(\text{PO}_4)_4[(\text{OCH}_2)_3\text{CCH}_2\text{OH}]_2\cdot14\text{H}_2\text{O} \).

Earlier experimental and theoretical studies of both \( V_6 \) magnetic molecules presented above have shown that they can be described by a spin-1/2 Heisenberg model defined on identical uncoupled triangles (or trimers) of spins, where in each triangle the spins interact via isotropic antiferromagnetic exchange couplings \(^22\). However, two of the three V-V interactions have exchange constants that are equal and an order of magnitude larger than the third one, making thus a kind of an isosceles triangle in the energy configuration. In this case, for small external magnetic field the ground state of the molecule has a total \( S = 1 \) spin, while for higher magnetic field the molecular spin is \( S = 3 \).

On the other hand, additional experiments on \( V_6 \) compounds have further suggested that the triangles can in fact be weakly connected through an extra superexchange interaction which is still about 20 times smaller than the smallest triangle interaction \(^21\) \(^22\), making the molecule to behave as a hexamer. More recently, the coupled trian-
gles (hexamer) model with the experimental data of the exchange interactions obtained in Ref. [24] have been studied through exact diagonalization and it has been shown that the molecule presents a magnetocaloric behavior and an additional magnetic phase as a function of an external magnetic field [20]. To be more specific, besides the \( S = 1 \) and \( S = 3 \) spin phases for low and high magnetic fields, respectively, the authors detected an extra \( S = 2 \) spin phase. However, this new phase occurs only for a quite narrow intermediate range of the external magnetic field.

Motivated by these previous theoretical and experimental results, we have extended the analytical and numerical analysis of the two coupled isosceles triangles Hamiltonian to the whole range of the exchange parameters. We will see that this rather simple magnetic molecule actually exhibits a richness in its thermodynamic behavior which could not be forecast in the earlier studies due to fact that just weak intertriangle interactions have been considered.

By exactly diagonalizing the Hamiltonian matrix the entire energy spectrum and the corresponding eigenstates are obtained and the quantum phase transitions are determined. The extra spin \( S = 2 \) phase occurs indeed only with the presence of the antiferromagnetic intertriangle interaction and the range of this phase depends on the strength of this interaction. It will also be seen in the next sections that a new phase, with zero total spin \( S = 0 \), quite similar to an antiferromagnetic phase, is always present for low magnetic fields. In addition, due to the degeneracy of the ground states, these magnetic molecules present residual entropy for some range of the parameters as well as an enhanced magnetocaloric behavior.

We would like to stress that although the experimental realizations of \( V_6 \) magnetic molecules have specific interaction strengths, as reported in Refs. [24, 25], which are quite small and out of the range of the values considered in this work, the study of the proposed isosceles triangle spin Hamiltonian for general exchange interaction parameters are in fact quite interesting. The main reason lays on the fact that either other new related compounds could indeed present different stronger couplings, or even because the corresponding exchange couplings of the known polyoxovanadates can be altered, for instance, by applying an external hydrostatic pressure on the samples [26, 27].

The outline of this paper is as follows. In the next section, we describe the Hamiltonian model, present the exact analytical solution for the energy spectrum and corresponding eigenstates, followed by the ground state phase diagram. In section III we investigate the magnetic and thermodynamic properties of the system through the study of the magnetization, susceptibility, entropy, magnetocaloric effect and specific heat. Finally, some concluding remarks are drawn in the last section.

II. HAMILTONIAN MODEL, EIGENENERGIES, EIGENSTATES AND GROUND STATE PHASE DIAGRAM

A. Hamiltonian model

The \( V_6 \) magnetic molecule contains six vanadium ions disposed as two independent triangles, whose sites can be denoted by 1A, 2A, 3A and 1B, 2B, 3B, respectively, as sketched in figure 1. Each vanadium has spin-1/2 and their couplings are not symmetric but quite distorted. Spin in site 1A (1B) couples to spins in sites 2A and 3A (2B and 3B) with the predominant exchange interaction \( J_1 \). The coupling \( J_2 \) between sites 2A and 3A (2B and 3B) is one order of magnitude smaller than \( J_1 \). This gives the molecule an isosceles triangle character under the energy configuration point of view. Note that the superexchange couplings \( J_3 \) between the two triangles are also distorted, where site 1A couples only with 2B and 3B, site 2A couples with 1B and 3B, and site 3A couples with 1B and 2B [24, 25]. \( J_3 \) is still one order of magnitude smaller than \( J_2 \) for the vanadium \( V_6 \) magnetic compounds.

The corresponding Hamiltonian for these molecules can be written as

\[
\mathcal{H} = J_1(\vec{S}_{1A} \cdot \vec{S}_{2A} + \vec{S}_{1A} \cdot \vec{S}_{3A} + \vec{S}_{1B} \cdot \vec{S}_{2B} + \vec{S}_{1B} \cdot \vec{S}_{3B}) \\
+ J_2(\vec{S}_{2A} \cdot \vec{S}_{3A} + \vec{S}_{2B} \cdot \vec{S}_{3B}) \\
+ J_3(\vec{S}_{1A} \cdot \vec{S}_{2B} + \vec{S}_{1A} \cdot \vec{S}_{3B} + \vec{S}_{2A} \cdot \vec{S}_{1B} + \vec{S}_{2A} \cdot \vec{S}_{3B}) \\
+ \vec{S}_{2A} \cdot \vec{S}_{3B} + \vec{S}_{3A} \cdot \vec{S}_{1B} + \vec{S}_{3A} \cdot \vec{S}_{2B} \\
- B(S_{1A}^z + S_{2A}^z + S_{3A}^z + S_{1B}^z + S_{2B}^z + S_{3B}^z),
\]

where \( \vec{S}_i = (S_i^x, S_i^y, S_i^z) \) is the Heisenberg spin-1/2 operator with the components \( S_i^\alpha \) \((\alpha = x, y, z)\) given by the Pauli spin matrices and \( B \) is the external magnetic field applied in the \( z \)-axis direction. All the exchange interactions \( J_1, J_2, \) and \( J_3 \) are positive, making each triangle a prototype example of magnetically frustrated system. In this way, the first and second terms account for the intratriangle antiferromagnetic coupling, and the third term accounts for the intertriangle antiferromagnetic coupling. Note that for negative value of \( J_2 \) the frustration is partially removed from the molecule since each triangle would not be frustrated.

B. Eigenenergies and eigenstates

Taking the eigenstates of the \( z \)-component \( S_i^z \) spin operator to spam the vectorial space of \( \mathcal{H} \), the above Hamiltonian can be represented by a \( 64 \times 64 \) matrix that can be exactly diagonalized by resorting to some modern technical computing system like Maplesoft [30]. The 64 eigenvalues so obtained are explicitly given in the Appendix. The corresponding eigenstates are too lengthy to be reproduced in the Appendix and only those relevant for the quantum phase diagram will be discussed below.
gives the main magnetic behavior of the molecule.

the ground state picture can be slightly modified.

for different sets of exchange interactions

analyzing the corresponding eigenvalues and eigenvectors

there is one ferromagnetic phase with total spin

This phase is more commonly called paramagnetic phase

There are five most representative ferrimagnetic phases

2. Ferrimagnetic states with $S = 2$

There is one state where all spins are aligned with the field with $S_A^z = S_B^z = 3/2$, resulting in a molecular total spin $S = 3$. We shall call this a ferromagnetic (FM) state with energy $E_{FM}$ and eigenstate $|FM\rangle$ given by

$$E_{FM} = -3B + J_1 + \frac{1}{2}J_2 + \frac{3}{2}J_3,$$

$$|FM\rangle = |+,+,+,+,+,+,+.+\rangle.$$  

This phase is more commonly called paramagnetic in the literature, since all spin components are aligned with the field.

We present below the corresponding eigenstates of these more relevant eigenenergies grouping them according their total spin values, since it is this quantity that gives the main magnetic behavior of the molecule.

Figure 1: (color online) A schematic illustration of a V$_6$ molecule described by two triangles: one triangle with sites 1A, 2A, 3A, and a second triangle with sites 1B, 2B, 3B. The vanadium atoms, with spin-1/2, are represented by circles. The thicker lines represent the exchange interaction $J_1$, the thinner lines the exchange interaction $J_2$, and the dashed lines the intratriangle interaction $J_3$.

Note that the eigenenergies can be obtained for general values of the exchange interactions $J_1$, $J_2$, and $J_3$, as well as the external magnetic field $B$. It is then quite interesting to analyze their influence on the properties of the system in a wider Hamiltonian parameter region than that studied for only very small values of the intratriangle $J_2$ and intertriangle interaction $J_3$ [27]. A richer phase diagram is thus obtained where new phases, coming up from different spin orientations, are then allowed.

After diagonalizing the Hamiltonian matrix and analyzing the corresponding eigenvalues and eigenvectors one arrives at the following result for the most representative lower energy spectrum of the Hamiltonian [1]: 1 - there is one ferromagnetic phase with total spin $S = 3$; 2 - five ferrimagnetic phases with the total spin $S = 2$; 3 - four ferrimagnetic phases with the total spin $S = 1$; 4 - and finally three antiferromagnetic phases with the total spin $S = 0$. Individual phases distinguish from each other by spin arrangement as well as by the zero-temperature energies. It worthwhile to mention that the above general trend of the lower energies has been found for the Hamiltonian parameters considered in the following sections. For different sets of exchange interactions the ground state picture can be slightly modified.

We present below the corresponding eigenstates of these more relevant eigenenergies grouping them according their total spin values, since it is this quantity that gives the main magnetic behavior of the molecule.

1. Ferromagnetic state with $S = 3$

$$E_{FI2_1} = -2B + \frac{1}{2}J_1 - \frac{1}{2}J_2,$$

$$|FI2_1\rangle = \frac{1}{2}(|+,+,+;+,+,+,+,+,+,+,+\rangle + |-,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+,+).
It is interesting to notice that, in this case, both triangles are not in the eigenstates of the squared total spin operator. In fact, the quantum state of each molecule is a mixed state of equal statistical mixture of states with $S_3^i = 1/2$ and $S_2^i = 3/2$ or $S_3^i = 3/2$ and $S_2^i = 1/2$, as in FI2, FI3, and FI4, and different statistical weights as in FI2 and FI4.

3. Ferrimagnetic states with $S = 1$

There are four other ferrimagnetic phases with total $S = 1$ spin and denoted as FI1, $i = 1, 2, \ldots, 4$. The corresponding energies and eigenstates are

$$E_{FI1_i} = -B - J_1 - \frac{1}{2} J_2 + \frac{1}{2} J_3,$$

$$|FI1_i\rangle = \frac{1}{\sqrt{6}} \left[ |+, +, +, +, +, + \rangle + |+, +, +, +, +, - \rangle + |+, +, +, +, - , + \rangle + |+, +, +, +, - , - \rangle + |+, +, +, +, - , - \rangle \right],$$

$$E_{FI1_2} = -B - J_1 - \frac{1}{2} J_2 - \frac{1}{2} J_3$$

$$+ \frac{1}{4} \sqrt{9 J_1^2 - 10 J_1 J_3 + 17 J_3^2},$$

$$|FI1_2\rangle = \frac{1}{\sqrt{2 \sqrt{a^2 + 4b^2 + 4} + 4}} \left[ |+, +, +, +, +, - \rangle + a |+, +, +, +, +, + \rangle + b |+, +, +, +, +, + \rangle + a |+, +, +, +, - , + \rangle + a |+, +, +, +, - , - \rangle \right],$$

where

$$a = -J_1 - 2J_2 - J_3 - \sqrt{9 J_1^2 - 10 J_1 J_3 + 17 J_3^2},$$

$$b = -\frac{5J_1 + 2J_2 + 3J_3 - \sqrt{9 J_1^2 - 10 J_1 J_3 + 17 J_3^2}}{4J_3},$$

$$E_{FI1_3} = -B - J_1 - \frac{3}{4} J_2 - \frac{3}{4} J_3$$

$$+ \frac{1}{4} \sqrt{9 J_1^2 - 10 J_1 J_3 + 17 J_3^2},$$

$$|FI1_3\rangle = \frac{1}{\sqrt{2 \sqrt{a^2 + 4b^2 + 4} + 4}} \left[ |+, +, +, +, +, - \rangle + a |+, +, +, +, +, + \rangle + b |+, +, +, +, +, + \rangle + a |+, +, +, +, - , + \rangle + a |+, +, +, +, - , - \rangle \right],$$

where

$$c = \frac{4J_1 - 3J_3 + \sqrt{9 J_1^2 + 10 J_1 J_3 + 17 J_3^2}}{2J_3},$$

$$d = -\frac{2J_1 - J_2 + 3J_3 - \sqrt{9 J_1^2 + 10 J_1 J_3 + 17 J_3^2}}{J_3}.$$

In this ferrimagnetic phase there is statistical mixture of states with $S_3^i = S_2^i = 1/2$, with $S_3^i = 3/2$ and $S_2^i = -1/2$, and also $S_3^i = -1/2$ and $S_2^i = 3/2$. The only one with equal weights is FI1.

4. Antiferromagnetic states with $S = 0$

Finally, there are three antiferromagnetic phases $AF_i$ ($i = 1, 2, 3$) with zero total spin $S = 0$. The (field independent) energies and eigenstates are

$$E_{AF_1} = -J_1 - \frac{3}{2} J_2 - \frac{3}{2} J_3,$$

$$|AF_1\rangle = \frac{1}{2 \sqrt{3}} \left[ |+, +, +, +, +, - \rangle + |+, +, +, - , +, - \rangle \right],$$

$$E_{AF_2} = -\frac{3}{2} J_2 - \frac{3}{2} J_3,$$

$$|AF_2\rangle = \frac{1}{2 \sqrt{3}} \left[ |+, +, +, +, +, - \rangle + |+, +, +, - , - , - \rangle \right],$$

$$E_{AF_3} = -\frac{3}{2} J_2 - \frac{3}{2} J_3,$$

$$|AF_3\rangle = \frac{1}{2 \sqrt{3}} \left[ |+, +, +, +, +, - \rangle + |+, +, +, - , +, - \rangle \right].$$
where

\[
x = \frac{2J_1 + J_2 + J_3 - \sqrt{9J_1^2 - 18J_1J_3 + 13J_3^2}}{2(J_1 - J_3)},
\]

\[
y = \frac{2J_1 - J_2 - 3J_3 + \sqrt{9J_1^2 - 18J_1J_3 + 13J_3^2}}{2(2J_1 + J_3)}.
\]

AF$_1$ and AF$_2$ are equal statistical mixtures of states $S^z_A = 1/2$ and $S^z_B = -1/2$ and the inverse $S^z_A = -1/2$ and $S^z_B = 1/2$. State AF$_3$ has different weights with the additional states $S^z_A = 3/2$ and $S^z_B = -3/2$, and $S^z_A = -3/2$ and $S^z_B = 3/2$.

5. Brief overview of the entire energy spectrum

In Fig. 2 it is shown the complete spectrum of the energies as a function of the external magnetic field for some values of the exchange interactions. All quantities are parametrized by $J_1$. The different number of lines in each graph reflects the fact the for some particular values of the exchange interactions the degree of the degeneracy is different. For instance, in Fig. 2(a) we have $J_3 = 0$, meaning that both triangles are decoupled and the spectrum is dramatically reduced, even for zero external field. In this case, for $J_2/J_1 = 1$ and $B/J_1 < 1.5$ the stable phase is the ferrimagnetic FI$_1$ phase with total spin $S = 1$, while for $B/J_1 > 1.5$ the stable phase is the ferromagnetic FM with $S = 3$. This result is completely equivalent to that obtained in Ref. 20 when one has two independent triangles Hamiltonian for the V$_6$ magnetic molecules.

In Fig. 2(b) we have $J_2/J_1 = 0.5$ and we consider an even weaker coupling between the triangles $J_3/J_1 = 0.3$. We can see that the intertriangle interaction induces a new ferrimagnetic phase with molecular spin $S = 1$ in a small region between the external fields $1.57 < B_0/J_1 < 1.95$, where the ferrimagnetic state FI$_2$ becomes the ground state with energy given by Eq. 20. The weaker the interaction $J_3$ the smaller the field region of the stability of the FI$_2$ phase, which eventually disappears for $J_3 = 0$ [in fact, this phase becomes identical to the ones with $S = 3$ and $S = 1$ at this point in a multiphase point, as can be seen in Fig. 2(a)]. This is the reason in Ref. 20 a very small range of the external field for this phase has been obtained, since the intertriangle interaction was taken very small. However, by increasing the intertriangle interaction, not only the range of the FI$_2$ phase increases, but also one of the antiferromagnetic phases (AF$_1$), with total spin $S = 0$, becomes stable for smaller external fields, as shown in Fig. 2(c) for $J_2/J_1 = 1$ and $J_3/J_1 = 1$. This zero spin phase persists by still increasing the $J_3$ interaction, but the antiferromagnetic AF$_2$ phase becomes stable instead, as depicted in Fig. 2(d) for $J_2/J_1 = 0.5$ and $J_3/J_1 = 2$.

C. Ground state phase diagram

By expanding the analysis done above to other values of the exchange interactions, it is possible to draw the ground state phase diagram by seeking the lowest energy as a function of the Hamiltonian parameters. Fig. 3 shows the corresponding phase diagrams in the $B/J_1$
versus $J_2/J_1$ plane for different values of the intertriangle interaction $J_3/J_1$. In Fig. 3(a), for $J_3 = 0$ (degenerate coupled triangles), we have only three different ground states, two ferrimagnetic phases, namely FI1$_3$ and FI1$_4$, and one ferromagnetic phase FM. From the equations of the previous subsection it is easy to see that the transition line between phases FI1$_3$ and FI1$_4$ at $J_2 = J_1$ is indeed a quadruple line, since the energy of all four ferrimagnetic phases with total spin $S = 1$ become equal in this case (the degeneracy is broken when $J_2/J_1$ is different from 1). Similarly, quadruple lines are obtained for $J_2/J_1 < 1$, with the coexisting FM, FI1$_4$, FI2$_2$, and FI2$_4$ phases, and for $J_2/J_1 > 1$ phases FM, FI1$_3$, FI2$_1$, and FI2$_3$ coexist. The meeting point of these three lines turns out to be a nonuple point, where nine phases have the same energy. As both triangles of the magnetic molecule are decoupled, a simpler phase diagram for each one of them could be obtained. However, it is worthwhile to have this highly degenerated phase diagram in order to better understand the limiting case of the molecule when $J_3 \to 0$. It is also interesting to see that this magnetic molecule should present a residual entropy, given by the natural logarithm of the degeneracy of the ground state. This feature will be more clearly seen in the next section.

The degeneracy present in the phase diagram is partly broken when the intertriangle interaction $J_3$ is switched on. Fig. 3(b) shows the corresponding phase diagram for $J_3/J_1 = 0.3$. Only two-phase coexistence lines and triple points are obtained. For $J_3/J_1 = 1$ an additional triple line with coexisting FI1$_2$, FI1$_3$, and FI1$_4$ phases appears, with a quadruple and a quintuple point at its ends, as shown in Fig. 3(c). For still greater values of the intertriangle interaction, $J_3/J_1 = 2$ in Fig. 3(d), again only two-phase coexistence lines and triple points are obtained.

It should be noticed that the intertriangle interaction, in all diagrams depicted in Fig. 3, induces an antiferromagnetic phase with zero total spin for small values of the external field. In fact, in Fig. 3(a), only for $B = 0$ the antiferromagnetic phase AF$_3$ has the same energy as phase FI1$_4$ for $J_2/J_1 < 1$, while for $J_2/J_1 > 1$ AF$_2$ and FI1$_3$ have the same energy.

The vertical lines, in the bottom region of the phase diagrams of Fig. 3, extend to smaller and eventually any negative values of $J_2$. Note that negative values of the exchange coupling $J_2$ allow ferromagnetic exchange interactions between sites 2 and 3 (see Fig. 1). As a result, there is a break in the frustration present in each triangle, although the frustration still persists in the whole molecule due to the intertriangle antiferromagnetic interaction. One should say that with negative values of $J_2$ the molecule becomes less frustrated. These vertical lines can be located at particular values of critical external magnetic field $B_c$ (although improperly termed critical field in earlier works of $V_6$ magnetic molecules, we will use this same nomenclature for this field). The corresponding values of $B_c$ are given in Table I for the different transition lines shown in Fig. 3.

![Figure 3: (color online) Ground-state phase diagram in the $B/J_1$ versus $J_2/J_1$ plane. The full lines represent transitions where two phases coexist, the dashed-dotted line where three phases coexist (triple line), and along the dashed lines one has four phases coexisting (quadruple line). Accordingly, the triangles are triple points, the square is a quadruple point, and the asterisk represents a nonuple point (nine phases coexisting). The labels describe the corresponding ordering according to the text. We have, in increasing value of $J_3$: (a) $J_3/J_1 = 0$; (b) $J_3/J_1 = 0.3$; (c) $J_3/J_1 = 1$; and (d) $J_3/J_1 = 2$.](image)

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Table I: Critical external magnetic field $B_c$ for the vertical transition lines in the bottom region of the phase diagrams shown in Fig. 3

| Transition | External field $B_c$ |
|------------|----------------------|
| FM$\leftrightarrow$FI1$_4$ | $\frac{3}{4}J_1 + \frac{5}{4}J_3 + \frac{1}{4}\sqrt{9J_2^2 - 10J_1J_3 + 5J_3^2}$ |
| AF$_1$$\leftrightarrow$FI1$_3$ | $\frac{1}{2}J_1 + J_2 + \frac{1}{2}J_3 - \frac{1}{2}\sqrt{9J_2^2 - 10J_1J_3 + 5J_3^2}$ |
| FI2$_2$$\leftrightarrow$FI1$_4$ | $J_3 + \frac{1}{2}\sqrt{9J_2^2 - 10J_1J_3 + 5J_3^2}$ |
| FI2$_2$$\leftrightarrow$FM$\leftrightarrow$AF$_3$$\leftrightarrow$FI1$_4$ | $\frac{3}{2}J_1 + \frac{3}{2}J_3$ |

Figs. 4(a)-(d) show the phase diagrams in the $B/J_1$ versus $J_3/J_1$ plane for different values of the intratriangle
interaction $J_2$. It is instructive to see that now, instead of straight transition lines, we have some curves due to the square root dependence of some energies on $J_3$. For fixed values of $J_3$, the square roots appearing in all energies become constant, since they strictly depend on the ratio $J_3/J_1$. Accordingly, only linear behavior for the transition lines are obtained in Figs. 3 There are, however, some new features in the phases topology in this field versus intratriangle interaction that has not been seen in the phase diagrams of Figs. 3 namely an additional sextuple point, where the six phases FM, FI1, FI12, FI13, FI2, and FI24 coexist, and an extended region of two phases coexistence (not a line or point), as is depicted in Fig. (c). In the ruled area FI13, this phase coexists with FI12, whereas in the ruled area FI22, this phase coexists with FI21 phase.

![Figure 4](image)

Figure 4: (color online) Ground-state phase diagram in the $J_3/J_1$ versus $B/J_1$ plane, for different values of $J_2$. The lines, symbols and geometric shapes have the same meaning as in Fig. 3 with the additional sextuple point represented by the full circle and a delimited region of two phases coexistence, given by the ruled areas. In increasing values we have: in (a) $J_2/J_1 = 0.5$; (b) $J_2/J_1 = 0.8$; (c) $J_2/J_1 = 1$; and (d) $J_2/J_1 = 1.5$. In (d) one has a very narrow region, represented in this case by just a thicker line, where the phase FI23 is stable.

### III. MAGNETIC AND THERMODYNAMIC PROPERTIES

Let us now turn our attention to the thermodynamic properties of these $V_6$-like molecules in the extended region of the Hamiltonian parameters. As the intermolecular interactions are quite weak, one can think of this system as composed of an assembly of $N$ independent single molecules. As a result, the total Hamiltonian is given by a sum of $N$ Hamiltonians as defined in Eq. 1, and the corresponding partition function is a product of $N$ partition functions for each molecule. In the thermodynamic limit, all the thermal properties (per molecule) of the whole system is thus obtained from the partition function of one single molecule, which can be explicitly written as

$$Z = \sum_{i=1}^{64} e^{-\beta \varepsilon_i},$$

where $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\varepsilon_i$ are all the Hamiltonian eigenvalues, which are described in the Appendix. The corresponding free energy per molecule is

$$F = -k_B T \ln(Z).$$

The magnetothermodynamic quantities per molecule, such as magnetization $M$ and susceptibility $\chi$, entropy $S$ and specific heat $C$, can thus be calculated from the well known thermodynamic relations

$$M = -\left(\frac{\partial F}{\partial B}\right)_T, \quad \chi = \left(\frac{\partial M}{\partial B}\right)_T,$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_B, \quad C = T \left(\frac{\partial S}{\partial T}\right)_B.$$

Another interesting quantity that can be studied in this system is the so called magnetocaloric effect, which is defined by the adiabatic temperature change, or the isothermal entropy change, as the external magnetic field is varied. This effect is can be quantified by the following relation

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{(\partial S/\partial B)_T}{(\partial S/\partial T)_B}.$$  

In the next subsections a detailed study of these properties is presented for several values of the Hamiltonian parameters. The partition function, given by Eq. 28, is thus numerically obtained from the corresponding energy spectrum transcribed in the Appendix. In all figures below we have, for simplicity, taken $k_B = 1$ and the corresponding temperature has been parametrized by $T/J_1$ (reduced temperature).

#### A. Magnetization

Fig. 5 illustrates the total magnetization $M$, as a function of the magnetic field $B/J_1$, for different reduced temperatures $T/J_1$ and various values of the exchange interactions. The exchange interactions have been chosen in such a way that one has all possible transitions from the different total molecular spin $S$, ranging from zero to three. For clarity, the label of the phases has been
omitted in Fig. 5. Note that when the molecules have a nonzero magnetization at $T = 0$, as in Figs. 5(a) and (b), the temperature totally breaks the order of the molecular spins. This reflects the fact that each molecule, being a zeroth dimensional quantum system, is indeed equivalent to a one-dimensional classical spin model, which in turn has no phase transition at finite temperatures.

For other values of the external field, the excited states are the same as those in Fig. 5 and the fields are chosen so as a function of temperature for some external magnetic fields. The exchange interactions in each graphic are formed by those having smaller values of the total molecular spin. Thus, increasing the temperature from zero those excited states decreases the magnetization. Eventually, in either case, the magnetization goes to zero at high temperatures, as expected.

The behavior of the molecular magnetization at low temperatures can be understood by looking at the spectrum of the molecule as shown in Fig. 6. For some given values of the external field, the excited states are those having higher values of the total molecular spin. Thus, increasing the temperature from zero those excited states are populated, which in turn increases the magnetization. For other values of the external field the excited states are formed by those having smaller values of the total molecular spin so the increase in temperature actually decreases the magnetization. Eventually, in either case, the magnetization goes to zero at high temperatures. It should be stressed that this behavior has also been experimentally observed in the polyoxovanadate-based mag-

Figure 5: (color online) Total molecular magnetization $M$ as a function of the magnetic field $B/J_1$ and different values of temperature. In (a) $J_2/J_1 = 1$ and $J_3/J_1 = 0$; in (b) $J_2/J_1 = 0.5$ and $J_3/J_1 = 0.3$; in (c) $J_2/J_1 = 1$ and $J_3/J_1 = 1$; in (d) $J_2/J_1 = 0.5$ and $J_3/J_1 = 2$.

Figure 6: (color online) Total molecular magnetization $M$ as a function of temperature $T/J_1$ for different values of the external fields. The exchange interactions in each graphic are the same as those in Fig. 5 and the fields are chosen so the behavior of the magnetizations are different in the low temperature region.
magnetic molecules [23].

B. Susceptibility

The susceptibility times temperature \( \chi T/J_1 \), as a function of temperature \( T/J_1 \) (in logarithmic scale to a better view of the whole range of \( T \)), for different magnetic fields \( B/J_1 \) and exchange interactions \( J_2/J_1 \) and \( J_3/J_1 \), is illustrated in Fig. 7. At high temperatures, the susceptibility turns out to be the same, independent of the external magnetic field, as expected. Also expected is the behavior at zero temperature, where the plateaux in Fig. 5 for the total magnetic spin results in a zero magnetic susceptibility. On the other hand, at the critical fields, \( \chi \) goes to infinity as the inverse of temperature. However, this is not a kind of quantum phase transition, rather a paramagnetic behavior following the Curie law. As a matter of comparison, in the one-dimensional Ising model \( \chi T \to \infty \), meaning that at zero temperature the system is indeed critical [28].

![Figure 7: (color online) Susceptibility times temperature, in units of \( J_1 \), \( \chi T/J_1 \), as a function of temperature \( T/J_1 \) (logarithmic scale), for different values of the magnetic field \( B/J_1 \). The exchange interactions in (a)-(b) are the same as in Fig. 5.](image)

We can see in Figs. 7 that for magnetic fields just above the smaller critical ones, \( \chi T \) increases from zero, reaches a maximum and then a round minimum is formed before saturating to its high temperature behavior. However, for higher values of the critical field, just a shoulder is present. The round minimum is also kind of suppressed by increasing the \( J_3 \) interaction even for smaller values of critical fields. It is interesting to stress that the qualitative behavior of the minimum shown in Fig. 7(a) has indeed been experimentally observed for the \( V_6 \) compounds in ref. [29]. The appearance of such round minimum in the temperature dependence of \( \chi T \) is a typical feature of quantum ferrimagnets, as has been discussed in Refs. 29, 30. In the present case it is enhanced close to the critical fields occurring at zero temperature.

C. Entropy

First, let us analyze the behavior of the entropy \( S \), as a function of temperature \( T/J_1 \), as shown in Fig. 8 for several values of the external magnetic field and exchange interactions. As \( k_B \) has been set to unity, in some special limits the entropy will be just given by \( S = \ln(\omega) \), with \( \omega \) being the number of states at that limit. For instance, we can easily see that at high temperatures, where all states are equally probable to occur, all curves go to the limit \( S = 4.1589 \), where \( \omega = 64 \). On the other hand, at low temperatures, depending on the value of the Hamiltonian parameters, different residual entropies are present in the molecule. The degree of degeneracy, here given by \( \omega \), is specified by the number of coexisting phases present at \( T = 0 \), and are explicitly written in Fig. 8. Several examples, for some particular values of the field and exchange interactions, are depicted in Figs. 8 and 9. Apart from infinite temperature, the highest degenerated state occurs at zero field for non-interacting isotropic triangles \( (J_3 = 0 \) and \( J_2 = J_1) \) with \( \omega = 16 \) (as this happens along the \( J_2/J_1 \) axis, it has not been shown in Fig. 8(a) for questions of clarity).

![Figure 8: (color online) Entropy \( S \) as a function of temperature \( T/J_1 \) (logarithmic scale) and different values of the magnetic field \( B/J_1 \). At low temperatures, \( \omega \) gives the degeneracy of the ground state. The exchange interactions in (a)-(b) are the same as those in Fig. 8.](image)
It is interesting to note in Fig. 8(a) that for $B/J_1 = 0.005$ and 0.02, before reaching the high temperature behavior, the entropy starts at $S = 2\ln(2)$ and quickly jumps to $S = 4\ln(2)$ at low temperature. Conversely, for $B/J_1 = 1.51$ and 1.54, the system has zero entropy at its ground state but at low enough temperatures it quickly jumps to the entropy value of $S = 2\ln(3)$ before reaching the high temperature behavior. The increase of the intertriangle interactions suppresses this intermediate jump behavior of the entropy, where only a small shoulder is still present in Fig. 8(b). However, as we will see right below, these entropy plateaux are indeed an important ingredient for the presence of magnetocaloric effects in these magnetic molecules.

![Figure 9](image_url)  
**Figure 9:** (color online) Density plot of the entropy, in a color gradient scale shown to the right, as a function the magnetic field $B/J_1$ and the temperature $T/J_1$ (in logarithmic scale). Some lines of constant entropy are also plotted. In (a) to (d) the exchange interactions are the same as in Fig. 8.

Another way to analyze the global entropic behavior of this system is to look at the entropy as a function of the external magnetic field and the temperature, as is illustrated in a gradient color scale in Fig. 10 for various values of the exchange interactions. To better visualize the topology of the surface, some lines of constant entropy have been added to the figure. These lines illustrate, basically, the isentropic variation of temperature with the external magnetic field. The spikes of the constant entropy lines at low temperatures are in fact related to the transitions at $T = 0$ and are located at the corresponding critical external magnetic fields. It can also be clearly seen that as the intertriangle interaction increases the degeneracy is systematically broken, specially at zero magnetic field. The magnetocaloric effect, enhanced during the adiabatic (de) magnetization, can be found at zero magnetic field in Figs. 10(a) and (b). This effect will be discussed in more details in the next subsection.

![Figure 10](image_url)  
**Figure 10:** (color online) Isothermal change of the entropy $-\Delta S$, as a function of the temperature $T/J_1$ (in logarithmic scale), for several values of the final magnetic field $B/J_1$. (a) and (b) for $J_2/J_1 = 1$ and $J_3/J_1 = 0$; (c) and (d) for $J_2/J_1 = 0.5$ and $J_3/J_1 = 0.3$; (e) and (f) for $J_2/J_1 = 1$ and $J_3/J_1 = 1$; (g) and (h) for $J_2/J_1 = 0.5$ and $J_3/J_1 = 2$.

D. Magnetocaloric effect

Relevant to the study of the magnetocaloric effect, which is in some way implicit in the results shown in Figs. 8 and 9 is the isothermal change of the entropy with the variation of the external magnetic field. Such a quantity, basically related to the numerator of Eq. (32), can be given by

$$\Delta S(B, T) = S(B_f, T) - S(B_i, T),$$

(33)

where $B_i$ and $B_f$ are, respectively, the initial and final magnetic field. Although it is not necessarily the ini-
all the following results. Fig. 10 shows $-\Delta S$ as a function of temperature $T/J_1$ for various final magnetic field values. We are plotting the negative of the isothermal entropy change because most experimental data have been reported in this way. For all values of the exchange parameters, $\Delta S = 0$ at high temperatures for any magnetic field, since in this case all entropies have the same value, as can be seen in Fig. 8. In Figs. 10(a) and (b) we have the results for uncoupled triangles ($J_3 = 0$). We can see that in this case $-\Delta S$ is always positive, reflecting the fact that at $B = 0$ the entropy has the greatest value, as can be clearly seen in Fig. 8(a). For values of the final magnetic field close to the critical field the curves show two plateaux with increasing the temperature. Above the critical field, the plateaux start developing a shoulder, that eventually transform in peaks that become higher and broader. This double peak structure, and in Figs. 10 (e)-(f) for $J_3 = 1$ and in Figs. 10 (g)-(f) for $J_3 = 2$. In these cases negative values for entropy change is obtained, including negative valleys and positive peaks.

Generally speaking, the peaks in Fig. 10 correspond to the called direct magnetocaloric effect, while the valleys correspond to the inverse magnetocaloric effect (see ref. [31] and references therein). We have also considered negative values of the exchange interactions and the behavior of the magnetocaloric effect has no qualitative changes compared to the results presented above.

E. Specific heat

For completeness, it is also instructive to discuss the specific heat behavior of these molecular magnets. Since the energy spectrum of the molecules are finite, the specific heat should present a kind of Schottky behavior in the sense that it should be zero as the temperature goes either to zero or infinity. This is indeed the fact, as is depicted in Fig. 11 where the specific heat $C$ has been plotted as a function of temperature $T/J_1$ (in logarithmic scale) for various values of the magnetic field and exchange interactions. The usual Schottky specific heat behavior has only one peak, due to the fact that the entropy is a monotonic increasing function of the temperature. At low temperatures, the entropy is close to zero (or to its residual value) with zero derivative, while at high temperatures all states are equally probable and the entropy reaches its temperature saturation value also with zero derivative. However, looking at the entropy behavior shown in Fig. 8 we can see that in some instances $S$ increases in two steps, with a plateau in between. Each side of the plateau will then contribute to a peak in the specific heat.

![Figure 11](image_url)

Figure 11: (color online) Specific heat $C$ as a function of temperature $T/J_1$ (in logarithmic scale) for various values of the magnetic field $B/J_1$. The exchange interactions in (a)-(d) are the same as those given in Fig. 8.

In Fig 12 we have the global specific heat $C$, in a color gradient scale, as a function of temperature $T/J_1$ (in logarithmic scale) and magnetic field. The lines are constant values of $C$ to better visualize the topology of the function. Here we can observe that for intermediate temperatures there is a maximum of specific heat (light color), and we also see that there are peaks of the specific heat near the critical magnetic field at low temperatures.

IV. CONCLUDING REMARKS

A quantum spin-1/2 Heisenberg model, composed of two coupled isosceles triangles with an external magnetic field applied along the z-axis, has been theoretically analyzed through the exact diagonalization of the Hamiltonian matrix. This model is suitable to describe $V_6$ magnetic molecules and has been previously studied only for small values of some exchange interactions that come
Figure 12: Specific heat $C$, in a color gradient scale shown to the right, as a function of temperature $T/J_1$ (in logarithmic scale). Some lines of constant $C$ are also plotted. In (a) to (d) the exchange interactions are the same as in Fig. 5.

from fits to the experimental realizations of polyoxovanadates compounds. We have here considered a wider range of the Hamiltonian parameters for different values of the external magnetic field.

We have studied the behavior of the system at zero temperature through its energy spectrum, making a detailed analysis of the corresponding phase diagrams for different coupling values. In addition, we have shown that the system presents not only a rich phase diagram, but also residual entropies at zero temperature. We have as well made a detailed study of the magnetic and thermodynamic properties of the system as a function of temperature. Magnetization, susceptibility, entropy, magnetocaloric effect and specific heat have been computed. In some limiting cases, the model makes indeed an excellent qualitative description of the $V_6$ magnetic molecules in comparison with the experimental results obtained in references [23, 25].

It is interesting that the model [11], being a quite simple example of a zero-dimensional quantum system, exhibits a very rich thermodynamic behavior and can be applied not only to generalizations of the $V_6$ molecules but also to low dimensional quantum models such as triangular chains.

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Appendix

Hamiltonian [11] is represented by a $64 \times 64$ matrix and can be exactly diagonalized using, for example, Maple-soft™ software. The eigenvalues $\epsilon_i$, with $1 \leq i \leq 64$, can be written as

$$\begin{align*}
\epsilon_1 &= 3B + J_1 + \frac{1}{2}J_2 + \frac{3}{2}J_3, \\
\epsilon_2 &= -3B + J_1 + \frac{1}{2}J_2 + \frac{3}{2}J_3, \\
\epsilon_3 &= 2B + \frac{1}{2}J_1 - \frac{1}{2}J_2, \\
\epsilon_4 &= -2B + \frac{1}{2}J_1 - \frac{1}{2}J_2, \\
\epsilon_5 &= 2B - \frac{1}{2}J_1 + \frac{1}{2}J_2, \\
\epsilon_6 &= -2B - \frac{1}{2}J_1 + \frac{1}{2}J_2, \\
\epsilon_7 &= 2B + \frac{1}{2}J_1 - \frac{1}{2}J_2 + J_3, \\
\epsilon_8 &= -2B + \frac{1}{2}J_1 - \frac{1}{2}J_2 + J_3, \\
\epsilon_9 &= 2B - \frac{1}{2}J_1 + \frac{1}{2}J_2 + J_3, \\
\epsilon_{10} &= -2B - \frac{1}{2}J_1 + \frac{1}{2}J_2 + J_3, \\
\epsilon_{11} &= 2B + J_1 + \frac{1}{2}J_2 + \frac{3}{2}J_3, \\
\epsilon_{12} &= -2B + J_1 + \frac{1}{2}J_2 + \frac{3}{2}J_3, \\
\epsilon_{13} &= 2B + J_1 + \frac{1}{2}J_2 - \frac{1}{2}J_3, \\
\epsilon_{14} &= -2B + J_1 + \frac{1}{2}J_2 - \frac{1}{2}J_3, \\
\epsilon_{15} &= B + \frac{1}{2}J_1 - \frac{1}{2}J_2, \\
\epsilon_{16} &= -B + \frac{1}{2}J_1 - \frac{1}{2}J_2, \\
\epsilon_{17} &= B - \frac{1}{2}J_1 + \frac{1}{2}J_2, \\
\epsilon_{18} &= -B - \frac{1}{2}J_1 + \frac{1}{2}J_2, \\
\epsilon_{19} &= B + \frac{1}{2}J_1 - \frac{1}{2}J_2 + J_3, \\
\epsilon_{20} &= -B + \frac{1}{2}J_1 - \frac{1}{2}J_2 + J_3, \\
\epsilon_{21} &= B - \frac{1}{2}J_1 + \frac{1}{2}J_2 + J_3, \\
\epsilon_{22} &= -B - \frac{1}{2}J_1 + \frac{1}{2}J_2 + J_3, \\
\epsilon_{23} &= B + \frac{1}{2}J_1 - \frac{1}{2}J_2 - J_3, \\
\epsilon_{24} &= -B + \frac{1}{2}J_1 - \frac{1}{2}J_2 - J_3, \\
\epsilon_{25} &= B - \frac{1}{2}J_1 + \frac{1}{2}J_2 - J_3.
\end{align*}$$
\[ \varepsilon_{26} = -B - \frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3, \]
\[ \varepsilon_{27} = B + J_1 + \frac{1}{2} J_2 + \frac{3}{2} J_3, \]
\[ \varepsilon_{28} = -B + J_1 + \frac{1}{2} J_2 + \frac{3}{2} J_3, \]
\[ \varepsilon_{29} = B + J_1 + \frac{1}{2} J_2 - \frac{1}{2} J_3, \]
\[ \varepsilon_{30} = -B + J_1 + \frac{1}{2} J_2 - \frac{1}{2} J_3, \]
\[ \varepsilon_{31} = B - J_1 - \frac{1}{2} J_2 + \frac{1}{2} J_3, \]
\[ \varepsilon_{32} = -B - J_1 - \frac{1}{2} J_2 + \frac{1}{2} J_3, \]
\[ \varepsilon_{33} = B - \frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{34} = -B - \frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{35} = B - \frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{36} = -B - \frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{37} = B - \frac{5}{4} J_1 + \frac{1}{2} J_2 - \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{38} = -B - \frac{5}{4} J_1 + \frac{1}{2} J_2 - \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{39} = B + \frac{3}{4} J_1 - \frac{3}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{40} = -B + \frac{3}{4} J_1 - \frac{3}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{41} = B - \frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 + \frac{1}{2} q, \]
\[ \varepsilon_{42} = -B - \frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 + \frac{1}{2} q, \]
\[ \varepsilon_{43} = B - \frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 - \frac{1}{2} q, \]
\[ \varepsilon_{44} = -B - \frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 - \frac{1}{2} q, \]
\[ \varepsilon_{45} = \frac{1}{2} J_1 - \frac{1}{2} J_2, \]
\[ \varepsilon_{46} = -\frac{1}{2} J_1 + \frac{1}{2} J_2, \]
\[ \varepsilon_{47} = \frac{1}{2} J_1 - \frac{1}{2} J_2 + J_3, \]
\[ \varepsilon_{48} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 + J_3, \]
\[ \varepsilon_{49} = \frac{1}{2} J_1 - \frac{1}{2} J_2 - J_3, \]
\[ \varepsilon_{50} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3, \]
\[ \varepsilon_{51} = J_1 + \frac{1}{2} J_2 - \frac{1}{2} J_3, \]
\[ \varepsilon_{52} = -J_1 - \frac{1}{2} J_2 - \frac{1}{2} J_3, \]
\[ \varepsilon_{53} = J_1 - \frac{1}{2} J_2 + \frac{1}{2} J_3, \]
\[ \varepsilon_{54} = J_1 + \frac{1}{2} J_2 + \frac{3}{2} J_3, \]
\[ \varepsilon_{55} = -J_1 - \frac{1}{2} J_2 - \frac{3}{2} J_3, \]
\[ \varepsilon_{56} = -\frac{3}{2} J_2 - \frac{1}{2} J_3, \]
\[ \varepsilon_{57} = -\frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{58} = -\frac{1}{4} J_1 - \frac{1}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{59} = -\frac{5}{4} J_1 + \frac{1}{2} J_2 + \frac{1}{4} J_3 + \frac{1}{4} p, \]
\[ \varepsilon_{60} = \frac{3}{4} J_1 - \frac{3}{2} J_2 - \frac{1}{4} J_3 - \frac{1}{4} p, \]
\[ \varepsilon_{61} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 + J_3 + \frac{1}{2} q, \]
\[ \varepsilon_{62} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 - \frac{1}{2} q, \]
\[ \varepsilon_{63} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 + \frac{1}{2} r, \]
\[ \varepsilon_{64} = -\frac{1}{2} J_1 + \frac{1}{2} J_2 - J_3 + \frac{1}{2} r, \]

where

\[ p = \sqrt{9J_1^2 - 10J_1J_3 + 17J_3^2}, \]
\[ q = \sqrt{9J_1^2 - 10J_1J_3 + 5J_3^2}, \]
\[ r = \sqrt{9J_1^2 - 18J_1J_3 + 13J_3^2}. \]

The corresponding eigenstates can also be obtained, but as they are rather lengthy they are not reproduced here. Only the most relevant ones for the quantum phase diagrams are given in the text.

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