



LOWER BOUND FOR THE ENERGY OF THE SPIN-S HEISENBERG ANTIFERROMAGNET ON THE PYROCHLORE LATTICE

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Abstract

The nature of the ground state of the antiferromagnetic Heisenberg model on the pyrochlore lattice is still an open question. Many numerical approaches have been used to tackle the problem in recent years, narrowing down the possible scenarios. Among others, variational methods provide an upper bound for the ground state energy. A way to see how close these are to the true ground state is to compare them with a lower bound for the ground state energy.

We calculated lower bounds in this work by extending Anderson's method [1]. We write the Hamiltonian as a sum of sub-Hamiltonians defined on finite clusters, which build the infinite lattice. We investigated a 7- and an 18-site open cluster formed by two and six tetrahedra, respectively. We allow all possible two-site exchanges within the sites of the clusters with weights respecting the D_{3d} point group so that the Hamiltonian on the full lattice is the sum of the translated and rotated Hamiltonian of the cluster. For this to happen, the exchanges in the clusters must obey certain constraints. We determine these constraints and the remaining free parameters in the Hamiltonian for the small clusters. To get lower bounds, we maximize the ground state energy of the clusters by varying the free parameters. For the 7-site cluster, the energies are exact, while we use the Lánczos algorithm to determine the ground state energy for the 18-site cluster.

The 7-site cluster provides us with

$$-S(S+1)\left(1-\frac{1}{4S+2}\right)J$$

for the lower bound of the ground state energy per site for an arbitrary spin S and J is the nearest neighbor exchange. For the S = 1/2 case, this gives -0.5625J, while from the 18-site cluster we get -0.5498(3)J. These results are comparable with -0.56J [2] and -0.572J [3] energies and raise the possibility of a lower ground state energy than the -0.4917(5)J determined by NLCE [4]. In the case of S = 1 the 7-site cluster gives $-\frac{5}{3}J = -1.6667J$ and the 18-site cluster grants -1.6329(8)J energy, which is also comparable with the -1.490(1)J variational wave function [4] and the -1.520(6)J DMRG [5] results.

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Chapter 1 Introduction [4],[5],[6],[7]

Nowadays, frustrated magnets are a popular topic in condensed matter physics because of their possible exotic ground states. One of the best-known three-dimensional examples is the Heisenberg antiferromagnet on the pyrochlore lattice, in particular, the spin-1/2 case. The pyrochlore lattice shown on Fig. 2.1 is a formation of corner-sharing tetrahedra realized by metal ions A and magnetic metal ions B in pyrochlores with the chemical formula $A_2B_2O_7$ or in spinels $A_2B_2O_4$. In the case of large spin-S for the classical Heisenberg model on the pyrochlore lattice, it turns out to have an extensively degenerate ground state manifold, leading to a classical spin liquid called *spin ice* [8].

In the extreme quantum limit of small *S*, the ground state properties of the pyrochlore Heisenberg antiferromagnet are still open to both theoretical and experimental investigation. Theoretical investigations are limited to state-of-the-art numerical methods such as exact diagonalization (ED), density-matrix renormalization group (DMRG), many variable variational Monte Carlo, Numerical linked-cluster expansion (NLCE), variational wave functions, pseudofermion functional renormalization group (PFFRG), where different approaches lead to different possible scenarios. For spin-1/2 there are some proposals for quantum spin liquid ([2],[9],[10]) or valence bond crystal ([11],[6],[12],[13],[4]) ground state. One of the most promising results was provided in a recent DMRG study [6], where the ground state of the spin-1/2 Heisenberg antiferromagnet discards lattice inversion symmetry in favor of a breathing pattern. The possibility of spontaneous lattice symmetry breaking was further investigated in [4], where a family of valence-bond crystals was proposed as a potential ground state for the spin-1/2 and spin-1 cases, where this ground state spontaneously breaks rotation, inversion, and translational symmetries.

The case of the spin-1 is even less clear due to the numerical limitations since methods such as ED with the Lánczos algorithm depend on the size of the Hilbert space. For example, the current ED limit for spin-1/2 is 48 sites [14]. For spin-1, this size is more hopeless. However, with DMRG, it is possible to study much larger clusters. For example, for spin-1/2, a 128-site cluster [6], or for spin-1, a 48-site cluster [5] was examined. A PFFRG study [7] of the $J_1 - J_2$ Heisenberg model showed that the spin-1 case is close to the classical limit when $J_2 \neq 0$ otherwise a non-magnetic phase is predicted, whose width is reduced compared to the spin-1/2 case. On another front, DMRG and PPFRG calculations [5] suggest that the tendency towards rotational or combined rotational and inversion symmetry breaking is stronger in the spin-1 case than the spin-1/2 case.

Chapter 2 Lower bound

In most cases, finding the ground state of a many-body Hamiltonian is challenging or nearly impossible. The best we can do is investigate numerically the problem, which evolves into methods like DMRG, PFFRG, etc. With these techniques, we can better understand the behavior of the ground state of our investigated system. Most of these numerical methods tend to approximate the true ground state in a variational way, which results in an upper bound for the ground state energy of the Hamiltonian.

Here, we explore a different path: we will provide a numerical and analytical estimate for the lower bound of the ground state energy. The following method was proposed by Anderson in 1951 [1], which is based on a simple idea that the Hamiltonian may be decomposed into sub-Hamiltonians,

$$H = \sum_{i=1}^{M} H_i,$$
 (2.1)

where M denotes the number of the sub-Hamiltonians. If we suppose that we know the ground state $|\Psi_{GS}\rangle$ of our Hamiltonian, we can write the eigenstate equation:

$$H |\Psi_{\rm GS}\rangle = E_{\rm GS} |\Psi_{\rm GS}\rangle, \qquad (2.2)$$

where the E_{GS} is the true ground state energy. Then the $|\Psi_{GS}\rangle$ can serve as a variational wave function for the H_i sub-Hamiltonian, so by the variational principle:

$$E_0^i \leqslant \left\langle \Psi_{\rm GS} | H_i | \Psi_{\rm GS} \right\rangle, \tag{2.3}$$

where E_0^i is the ground state energy of the Hamiltonian H_i . Therefore, if we perform the summation for the sub-Hamiltonians, we get the following estimate for the ground state energy of the investigated Hamiltonian H:

$$\sum_{i=1}^{M} E_{0}^{i} \leqslant \left\langle \Psi_{\rm GS} \left| \sum_{i=1}^{M} H_{i} \right| \Psi_{\rm GS} \right\rangle = \left\langle \Psi_{\rm GS} \right| H |\Psi_{\rm GS} \right\rangle = E_{\rm GS}, \tag{2.4}$$

so the lower bound for the ground state energy of the H Hamiltonian can be calculated from the ground state energy of the sub-Hamiltonians.

For a translationally invariant Hamiltonian, we can choose the sub-Hamiltonians H_i that are related by translations and whose ground state energies are identical, $E_0^i = E_0$. The ground state energy is then

$$E_{\rm GS} \ge M \times E_0. \tag{2.5}$$

In this case, the M would count the number of primitive unit cells of the lattice.

In the following sections, we aim to calculate the E_0 ground state energy for different sub-Hamiltonians in the case of the antiferromagnetic spin-S Heisenberg model on the pyrochlore lattice, where we are interested in the ground state energy per site:

$$\frac{E_{\rm GS}}{N} \ge \frac{M(N)}{N} E_0 \equiv E_{LB},\tag{2.6}$$

where the number of the M sub-Hamiltonians is a function of the N number of sites in the lattice.

2.1 Lower bound with a 7-site motif

In this section, we would like to give a lower bound for the energy of the nearest neighbor antiferromagnetic Heisenberg Hamiltonian on the pyrochlore lattice, which is just

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \mathbf{S}_j, \qquad (2.7)$$

where J is the nearest neighbor exchange and in the sum $\langle i, j \rangle$ runs for the nearest neighbor pairs just once for every i, j pair. A fragment of the lattice can be seen on Fig. 2.1.



Figure 2.1: A fragment of the pyrochlore lattice, which consists of corner sharing-tetrahedra

The smallest H_i we can consider is simply the $S_i S_j$ term of the Hamiltonian, which we can rewrite as

$$H_i = J\mathbf{S}_i\mathbf{S}_j = \frac{J}{2}\left(\mathbf{S}_i + \mathbf{S}_j\right)^2 - S(S+1)J.$$
(2.8)

This operator has the ground state energy for the singlet state, which results in $E_0 = -S(S+1)J$. This lower bound for the energy, e.g., for spin-1/2, is -3/4J = -0.75J, and for spin-1 is -2J. Since in the lattice, there are M = 3N such sub-Hamiltonians, the lower bound for the ground state energy per site is $E_{LB} = 3E_0$.

The next H_i we can consider is a triangle, formed by three nearest neighbor sites, i.e., $H_i = \mathbf{S}_i \mathbf{S}_j + \mathbf{S}_i \mathbf{S}_k + \mathbf{S}_j \mathbf{S}_k$. Again, it can be written as a full square:

$$H_{i} = \frac{J}{2} (\mathbf{S}_{i} + \mathbf{S}_{j} + \mathbf{S}_{k})^{2} - \frac{3}{2} S^{2} J.$$
(2.9)

If we consider three spins of length S, the possible smallest value for the total spin $(\mathbf{S}_i + \mathbf{S}_j + \mathbf{S}_k)^2 = S(S+1)$ from which we get the $E_0 = -S(S+1)J$ ground state energy. Since the number triangles is M = 2N, the lower bound for the ground state energy is $E_{LB} = 2E_0$.

A bigger H_i is a tetrahedron formed by four spin-S sites, which can be written as

$$H_{i} = J(\mathbf{S}_{i}\mathbf{S}_{j} + \mathbf{S}_{i}\mathbf{S}_{k} + \mathbf{S}_{i}\mathbf{S}_{l} + \mathbf{S}_{j}\mathbf{S}_{k} + \mathbf{S}_{j}\mathbf{S}_{l} + \mathbf{S}_{k}\mathbf{S}_{l})$$

$$= \frac{J}{2}(\mathbf{S}_{i} + \mathbf{S}_{j} + \mathbf{S}_{k} + \mathbf{S}_{l})^{2} - 2S(S+1)J. \qquad (2.10)$$

The smallest possible value for $(\mathbf{S}_i + \mathbf{S}_j + \mathbf{S}_k + \mathbf{S}_l)^2 = 0$. This results in $E_0 = -2S(S+1)J$. The number of tetrahedra in the lattice is M = N/2, so the lower bound for the ground state energy per site is $E_{LB} = E_0/2 = -S(S+1)J$. The general tendency is that increasing the number of spins in H_i increases the lower bound.

In the following, we will take a 7-site spin-S system as the sub-Hamiltonian and determine the lower bound for the ground state energy per site.

2.1.1 Constructing the Hamiltonian

To determine the H_i Hamiltonians in Eq. (2.1), we take a cluster from the pyrochlore lattice, which we will call motif in the following. This motif, seen on Fig. 2.2, consists of two tetrahedra sharing a common site and has an hourglass shape. We take the all possible $S_i S_j$ in the motif with weight $c_{i,j}$, so we can write the Hamiltonian for the motif as

$$H_{\text{motif}} = \sum_{i=1< j}^{7} c_{i,j} \mathbf{S}_i \mathbf{S}_j.$$
(2.11)



Figure 2.2: The 7-site cluster consisting of two tetrahedra.

To decrease the number of the $c_{i,j}$ parameters, we require the Hamiltonian to respect the geometrical symmetry of the motif so that [H, g] = 0, for all $g \in G$, where G is the point group of the motif. In the current case, the group is the D_{3d} . To fulfill this, we classify the $S_i S_j$ interactions, where $i \neq j \in \{1, 2, 3, ..., 7\}$, into orbits so

$$o_{i,j} = G \cdot \mathbf{S}_i \mathbf{S}_j = \{g \cdot \mathbf{S}_i \mathbf{S}_j : g \in G\}.$$
(2.12)

Let us denote this set of orbits, which can be seen in Tab. 2.1, with $O = \{o_1, o_2, o_3, o_4\}$, and their weights with c_1, c_2, c_3, c_4 , respectively.

Orbit	Weight	$\mathbf{S}_i \mathbf{S}_j$
o_1	c_1	(1, 2), (1, 3), (1, 4), (1, 5), (1, 6), (1, 7)
O_2	c_2	(2,3), (2,4), (3,4), (5,6), (5,7), (6,7)
O_3	c_3	(2,5), (2,6), (3,5), (3,7), (4,6), (4,7)
O_4	c_4	(2,7), (3,6), (4,5)

Table 2.1: The orbits of the $S_i S_j$ interactions in the 7-site cluster with their weights.

With these, the Hamiltonian of the motif can be written as

$$H_{\text{motif}} = \sum_{m=1}^{4} \sum_{\mathbf{S}_i \mathbf{S}_j \in o_m} c_m \mathbf{S}_i \mathbf{S}_j.$$
(2.13)

As a last step, we need to write our nearest neighbor Hamiltonian Eq. (2.7) as a sum of the all possible motif coverings:

$$H = \sum_{i} H^{i}_{\text{motif}}.$$
 (2.14)

As we can see, we have an equation that the c_i parameters need to satisfy. To solve this, we take a 128-site periodic cluster, with lattice vectors $\mathbf{v}_1 = (8, 0, 0)$, $\mathbf{v}_2 = (0, 8, 0)$, $\mathbf{v}_3 = (0, 0, 8)$ and construct the H_{128} nearest neighbor Hamiltonian for this cluster. Then we need to give the motif coverings of this 128-site cluster. First, we construct the group H of this cluster, which is $H = T_d \times i \times T$, where \times now means the Cartesian product, T denotes the translation group and i is the inversion. Having the H group, we need only the F group, which translates and rotates the motif, which we can get from $H = F \times G$ relation. In the end,

$$H_{128} = \sum_{f \in F} f H_{\text{motif}}, \qquad (2.15)$$

from which the constraints for the c_i parameters can be determined. In this case, these are $c_2 = \frac{J}{2} - c_1$, $c_3 = 0$, $c_4 = 0$, which results in the following Hamiltonian:

$$H_{\text{motif}} = \mathcal{J} \left(\mathbf{S}_{1} \mathbf{S}_{2} + \mathbf{S}_{1} \mathbf{S}_{3} + \mathbf{S}_{1} \mathbf{S}_{4} + \mathbf{S}_{1} \mathbf{S}_{5} + \mathbf{S}_{1} \mathbf{S}_{6} + \mathbf{S}_{1} \mathbf{S}_{7} \right) + \left(\frac{J}{2} - \mathcal{J} \right) \left(\mathbf{S}_{2} \mathbf{S}_{3} + \mathbf{S}_{2} \mathbf{S}_{4} + \mathbf{S}_{3} \mathbf{S}_{4} + \mathbf{S}_{5} \mathbf{S}_{6} + \mathbf{S}_{5} \mathbf{S}_{7} + \mathbf{S}_{6} \mathbf{S}_{7} \right),$$
(2.16)

where we denote c_1 by \mathcal{J} .

After all, we got a Hamiltonian with a free parameter that can take arbitrary values. By varying \mathcal{J} we can maximize the ground state energy, which gives us a lower bound for the ground state energy in the thermodynamic limit.

2.1.2 Spin-1/2 case

First of all, we would like to examine the S = 1/2 case for which we can write the Heisenberg exchange using a permutation operator:

$$P_{i,j} = 2\mathbf{S}_i \mathbf{S}_j + \frac{1}{2},\tag{2.17}$$

where $P_{i,j}$ exchanges the spins on the sites *i* and *j*. With permutation operators, the Eq. (2.16) Hamiltonian can be written as:

$$H_{\text{motif}} = -\frac{3J}{4} + \frac{\mathcal{J}}{2} \left(P_{1,2} + P_{1,3} + P_{1,4} + P_{1,5} + P_{1,6} + P_{1,7} \right) + \frac{1}{2} \left(\frac{J}{2} - \mathcal{J} \right) \left(P_{2,3} + P_{2,4} + P_{3,4} + P_{5,6} + P_{5,7} + P_{6,7} \right)$$
(2.18)

We take the matrix representation of the Hamiltonian in the 128-dimensional basis: $|\{S_i^z\}\rangle = |S_1^z, S_2^z, S_3^z, ..., S_N^z\rangle$, where $S_i^z \in \{-S, -S+1, ..., S-1, S\}$, in this case $S_i^z = \uparrow, \downarrow$ and N = 7 is the number of sites. Since it is computationally expensive or impossible to diagonalize a 128-dimensional matrix with parameters, we use a group theoretical approach to tackle the problem.

Decomposition of the Hamiltonian

If we have a G point group, for which [H, g] = 0, for all $g \in G$, one can decompose the Hamiltonian into block-diagonal form, according to the Γ_i irreducible representations of G. Now, we give a method that one can use to get the block-diagonal form of the Hamiltonian.

Taking our basis vectors $|\{S_i^z\}\rangle$ we can give the orbits of the basis elements $G |\{S_i^z\}\rangle = \{g |\{S_i^z\}\rangle | g \in G\}$. Let us denote the set of orbits by $O = \{o_k | k \in \{1, 2, 3, ..., p\}\}$, where p denotes the number of independent orbits. Then by taking an element from each orbit o_k^l as a basis, we can give the matrix representation of the action of the g_i group element, which we denote by $R(g_i, \{o_k^l\})$, where $R(g_i, \{o_k^l\})$ is a $|O| \times (2S + 1)^N$ dimensional matrix in which the components are

$$R(g_i, \{o_k^l\}) = \begin{cases} 1, & \text{for } g_i o_k^l, \forall l \\ 0, & \text{for the other basis elements} \end{cases}$$

Then taking the the elements of the $M_{\Gamma_n^i}$ matrix representation of Γ_n^i , which is the n^{th} irreducible representation of g_i , which is $M_{\Gamma_n^i}^{a,b}$, where a and b are the index of the row and column, we can take the sum of $\sum_i M_{\Gamma_n^i}^{a,b} R(g_i, \{o_k^l\})$, whose columns laves us with |O| number of vectors. It can be done for a given a for all b, which in the end results in $|O| \times \dim M_{\Gamma_n}$ vectors. For next step, we need to orthogonalize these vectors, which can be done by *Gram-Schmidt orthogonalization* and it results in $\{|\chi_i\rangle| \ i \in \{1, 2, 3, ..., \text{number of linearly independent vectors}\}$. We are interested in the different S subspaces too, so we take the S^2 operator and the $\langle \chi_i | S^2 | \chi_j \rangle$ matrix elements in this $|\chi_i\rangle$ basis and look for the eigenvectors of this matrix. The nullspace of $\langle \chi_i | S^2 | \chi_j \rangle - S(S+1) \langle \chi_i | \chi_j \rangle$ for a given S provides the eigenvectors, which we denote by $|S, \tilde{\chi}_m \rangle$, where m is the index of the m^{th} vector. In the end the searched decomposed matrix is just $[H_{S,\Gamma_i}]_{m,n} = \langle S, \tilde{\chi}_m | H | S, \tilde{\chi}_n \rangle$.

The energies of the sub-Hamiltonian

We would like to decompose our 128-dimensional Hamiltonian according to the irreducible representations of the D_{3d} . To get the irreducible representations, we use GAP, which returns the irreducible representations of the group generators. The generators with permutations are:

$$i = P_{2,7}P_{3,6}P_{4,5},$$

$$\sigma_d = P_{3,4}P_{5,6},$$

$$C_3 = P_{2,3,4}P_{5,7,6},$$
(2.19)

and the irreducible representations of the generators, computed with GAP, can be found in Tab. 2.2. With the irreducible representations, one can give the character table of the D_{3d} point group, which can be seen in Tab. 2.3.

D_{3d}	i	σ_d	C_3
A_{1g}	(1)	(1)	(1)
A_{2g}	(1)	(-1)	(1)
E_g	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} e^{i\frac{2\pi}{3}} & 0\\ 0 & e^{-i\frac{2\pi}{3}} \end{pmatrix}$
A_{1u}	(-1)	(-1)	(1)
A_{2u}	(-1)	(1)	(1)
E_u	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} e^{i\frac{2\pi}{3}} & 0\\ 0 & e^{-i\frac{2\pi}{3}} \end{pmatrix}$

Table 2.2: The irreducible representations of the generators of the D_{3d} point group.

D_{3d}	E	$2C_3$	$2C'_2$	i	$2S_6$	$3\sigma_d$
A_{1g}	1	1	1	1	1	1
A_{2g}	1	1	-1	1	1	-1
E_{g}	2	-1	0	2	-1	0
A_{1u}	1	1	1	-1	-1	-1
A_{2u}	1	1	-1	-1	-1	1
E_u	2	-1	0	-2	1	0

Table 2.3: The character table of the D_{3d} point group.

Having carried out the decomposition, we get the energies shown in Tab. 2.4 and plotted on Fig. 2.3, where we set J = 1 for simplicity.

$S_{\rm tot}$	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
1/2	$rac{rac{3}{4}-rac{5}{2}\mathcal{J}}{-rac{3}{4}-rac{1}{2}\mathcal{J}}$	$-\frac{3}{4}+\frac{3}{2}\mathcal{J}$	$-rac{3}{4}+rac{1}{2}\mathcal{J} \ -\mathcal{J}$	$-\frac{3}{4}+\frac{1}{2}\mathcal{J}$	$\frac{-\frac{3}{4}+\frac{3}{2}\mathcal{J}}{\frac{3}{4}-\frac{3}{2}\mathcal{J}}$	$-rac{3}{4}+rac{3}{2}\mathcal{J} \ -\mathcal{J}$
3/2	$\frac{-\frac{3}{4}+2\mathcal{J}}{\frac{3}{4}-\mathcal{J}}$	-	$-\frac{3}{4} + 2\mathcal{J} \\ -\frac{3}{2}\mathcal{J} \\ \frac{1}{2}\mathcal{J}$	$-\frac{3}{4}+2\mathcal{J}$	$\frac{3}{4} - 3\mathcal{J}$	$rac{-rac{3}{2}\mathcal{J}}{rac{1}{2}\mathcal{J}}$
5/2	$\frac{3}{4} - \frac{7}{2}\mathcal{J}$	-	$\mathcal{J}^{\mathcal{Z}}$	-	$\frac{3}{4} - \frac{1}{2}\mathcal{J}$	${\mathcal J}$
7/2	$\frac{3}{4}$	-	-	-	-	-

Table 2.4: The eigenvalues of the 7-site motif Hamiltonian with J = 1. The degeneration of the states can be computed by $S_{\text{tot}}(S_{\text{tot}} + 1) \times \dim \Gamma_i$, where Γ_i denotes the irreducible representation.



Figure 2.3: The energies (blue lines) of the motif Hamiltonian in the function of \mathcal{J} with J = 1. The energies in Tab. 2.5 from top to bottom are denoted by red, green and magenta colors respectively and their intersection is marked as a black dot.

To maximize the ground state energy, we take the lowest lying lines, whose intersection gives the maximal ground state energy. These lines are shown in Tab. 2.5.

E	$S_{\rm tot}$	Irreps
$\frac{3}{4} - \frac{7}{2}\mathcal{J}$	5/2	A_{1g}
$-\frac{3}{2}\mathcal{J}$	3/2	E_g, E_u
$-\frac{3}{4} + \frac{1}{2}\mathcal{J}$	1/2	A_{1g}, A_{1u}, E_g

Table 2.5: The lowest lying energies at the $\mathcal{J}_{LB} = 3/8$ point with J = 1. In the second column the total spin can be seen and in the last column, to which irreducible representation do the wave functions belong.

At the intersection of the lines $\mathcal{J}_{LB} = \mathcal{J} = 3/8$ and the energy at this point is $E_0 = -9/16 = -0.5625$. Since the number of this motif M in the Hamiltonian is equal to the number of sites N, the lower bound energy for the ground state energy per site is $E_{LB} = E_0$.

2.1.3 Spin-1 case

In the case of S = 1, the whole basis is $3^7 = 2187$ dimensional, but computing exact eigenvalues for this size of a matrix is computationally expensive or impossible. So, instead of the 2187 dimensional full basis, we take the $S_z = 0$ subspace, in which our Hamiltonian becomes 393 dimensional. To get the energies of the Hamiltonian, we numerically decompose the 393-dimensional matrix according to the irreducible representations. Having

decomposed the matrices, we set J = 1 and plot the energies as a function of \mathcal{J} . One of these can be seen on Fig. 2.4. Since the spectrum seems to be linear in \mathcal{J} , we take e.g. $\mathcal{J}_1 = 0$ and $\mathcal{J}_2 = 1/10$ points and calculate the energies in these points. Then we convert these inexact numbers to rational form and fit lines on them, which hopefully are exact. We repeat this procedure for all the decomposed matrix and then compare them with the energies calculated from the 393 dimensional matrix on the $\mathcal{J} \in [-1, 1]$ interval, divided uniformly into 1000 points. As a result, the energies are identical up to 12 digits.



Figure 2.4: The energies of the decomposed matrix according to the E_g irrep with $S_{tot} = 0$, in the function of the \mathcal{J} parameter. The red points denote the numerical eigenvalues, and the blue lines denote the fitted lines.

We select the lines whose intersection gives the greatest ground state energy to get the lower bound. These lines can be seen in Tab. 2.6. Their intersection take place at $\mathcal{J}_{LB} = \mathcal{J} = 1/3$, which gives $E_{LB} = -5/3 = -1.6$ energy as a lower bound.

Energy	$S_{\rm tot}$	Irrep multiplicity					
Lifergy		A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
$-5\mathcal{J}$	3	1	-	2	1	-	-
$-1-2\mathcal{J}$	3	1	1	4	1	1	4
$-2+\mathcal{J}$	1	2	-	4	1	-	2

Table 2.6: The energy lines in the $\mathcal{J}_{LB} = 1/3$ point with J = 1.



Figure 2.5: The energies (blue lines) of the motif Hamiltonian in the function of \mathcal{J} with J = 1. The energies in Tab. 2.6 from top to bottom are denoted by red, green and magenta colors respectively and their intersection is marked as a black dot.

2.1.4 Spin-3/2 case

In the case of S = 3/2, the whole basis is $4^7 = 16384$ dimensional, so again, instead of the 16384-dimensional full basis, we take the $S_z = 1/2$ subspace, in which our Hamiltonian becomes 2128 dimensional. To get the energies of the Hamiltonian, we numerically decompose this 2128-dimensional matrix according to the irreducible representations. Having the decomposed matrices, we set J = 1 and plot the energies as a function of \mathcal{J} . One of these can be seen in Fig. 2.6. Since the spectrum seems to be linear in \mathcal{J} , we take e.g. $\mathcal{J}_1 = 0$ and $\mathcal{J}_2 = 1/1000$ points and calculate the energies in these points. Then we convert these inexact numbers to rational form and fit a line on them, which hopefully is exact. We repeat this procedure for all the decomposed matrix and then compare them with the energies calculated from the 393 dimensional matrix on the $\mathcal{J} \in [-1, 1]$ interval, divided uniformly into 100 points. As a result, the energies are identical up to 12 digits.



Figure 2.6: The energies of the decomposed matrix according to the A_{1g} irrep with $S_{tot} = 1/2$, in the function of the \mathcal{J} parameter. The red points denote the numerical eigenvalues, and the blue lines denote the fitted lines.

To get the lower bound, we select the lines, whose intersection gives the greatest ground state energy. These lines can be seen in Tab. 2.7. Their intersection takes place at $\mathcal{J}_{LB} = \mathcal{J} = 5/16$, which gives $E_{LB} = -105/32 = -3.28125$ energy as a lower bound.



Figure 2.7: The energies (blue lines) of the motif Hamiltonian in the function of \mathcal{J} with J = 1. The energies in Tab. 2.7 from top to bottom are denoted by red, green and magenta colors respectively and their intersection is marked as a black dot.

Energy	S	Irrep multiplicity					
Lifergy	$\mathcal{O}_{\mathrm{tot}}$	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
$-\frac{4}{5}-\frac{13}{2}\mathcal{J}$	7/2	2	-	4	1	-	2
$-\frac{5}{2}-\frac{5}{2}J$	5/2	2	2	8	2	2	8
$-\frac{\overline{15}}{4} + \frac{\overline{3}}{2}\mathcal{J}$	3/2	3	1	6	2	-	4

Table 2.7: The energy lines at the $\mathcal{J}_{LB} = 5/16$ point with J = 1.

2.1.5 The case of arbitrary S

If we look at the determined energies and parameters in the different spin cases, we can give Tab. 2.8, where we also give the parameters and energies divided by the eigenvalue of the S^2 operator.

S	\mathcal{J}_{LB}	$\frac{\mathcal{J}_{LB}}{S(S+1)}$	E_{LB}	$\frac{E_{LB}}{S(S+1)}$
1/2	3/8	1/2	-9/16	-3/4
1	1/3	1/6	-5/3	-5/6
3/2	5/16	1/12	-105/32	-7/8

Table 2.8: The determined lower bound for the energy in the case of S = 1/2, 1 and 3/2 with J = 1.

If we look at the $\frac{E_{LB}}{S(S+1)}$ column, we can see some pattern, like for a given S, we can get the energy as

$$\frac{E_{LB}}{S(S+1)} = -\frac{\text{odd number}}{\text{odd number} + 1},$$
(2.20)

where the odd number is 3 for S = 1/2 and for the next S, which is now S = 1 is just the next odd number, now 5, and the same goes on for the higher spins. We can write this patterns as

$$\frac{E_{LB}}{S(S+1)} = -\frac{4S+1}{4S+2}.$$
(2.21)

Rewriting this equation, we can get the lower bound energy for an arbitrary S with the following expression:

$$E_{LB} = -S(S+1)\left(1 - \frac{1}{2(2S+1)}\right)$$
(2.22)

Examining the $\frac{\mathcal{J}_{LB}}{S(S+1)}$, we can give a similar pattern for \mathcal{J}_{LB} :

$$\mathcal{J}_{LB} = \frac{S+1}{2(2S+1)}.$$
(2.23)

This is a pretty result, but it comes from the fact, that we supposed, that the spectrum is linear in \mathcal{J} and this assumption is only confirmed up to 12 digits, in the S = 1, 3/2 case, but in the S = 1/2 case it is exact.

However, if we examine the Hamiltonian Eq. (2.18), we can rewrite that in the following way:

$$H_{\text{motif}} = J \left[\underbrace{\frac{1}{2} \left(\sum_{i=1}^{7} \mathbf{S}_{i} \right)^{2}}_{1 = 1} - \frac{7}{2} S(S+1) \right] - J \left[\underbrace{\frac{1}{2} \left(\sum_{i=2}^{7} \mathbf{S}_{i} \right)^{2}}_{1 = 2} - 3S(S+1) \right] \\ + \left(\frac{J}{2} - \mathcal{J} \right) \left[\underbrace{\frac{1}{2} \left(\mathbf{S}_{2} + \mathbf{S}_{3} + \mathbf{S}_{4} \right)^{2}}_{S_{234}^{2}} + \underbrace{\frac{1}{2} \left(\mathbf{S}_{5} + \mathbf{S}_{6} + \mathbf{S}_{7} \right)^{2}}_{S_{567}^{2}} - 3S(S+1) \right] \\ = \frac{J}{2} \left(S_{\text{tot}}^{2} - S_{234567}^{2} - S(S+1) \right) + \left(\frac{J}{4} - \frac{\mathcal{J}}{2} \right) \left(S_{234}^{2} + S_{567}^{2} - 6S(S+1) \right).$$
(2.24)



Figure 2.8: The visualization of Eq. (2.24), where the different colors denote the different weights.

For SU(2), we know that the direct product of S and S' Hilbert spaces can be decomposed into irreducible representations the following way:

$$S \otimes S' = (S + S') \oplus (S + S' - 1) \oplus \dots \oplus |S - S'|$$

$$(2.25)$$

Using this, for three arbitrary spins, we can write

$$S \otimes S' \otimes \tilde{S} = S \otimes \left[(S' + \tilde{S}) \oplus (S' + \tilde{S} - 1) \oplus \dots \oplus \left| S' - \tilde{S} \right| \right]$$

$$= (S + S' + \tilde{S}) \oplus (S + S' + \tilde{S} - 1) \oplus \dots \oplus \left| S - S' - \tilde{S} \right|$$

$$\oplus (S + S' + \tilde{S} - 1) \oplus (S + S' + \tilde{S} - 2) \oplus \dots \oplus \left| S - S' - \tilde{S} + 1 \right|$$

$$\oplus \dots \oplus \left(S + \left| S' - \tilde{S} \right| \right) \oplus \left(S + \left| S' - \tilde{S} \right| - 1 \right) \oplus \dots \oplus \left| S - \left| S' - \tilde{S} \right| \right|.$$

(2.26)

For example, for three S = 1/2, we get

$$\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} = \frac{1}{2} \otimes (1 \oplus 0) = \frac{3}{2} \oplus \frac{1}{2} \oplus \frac{1}{2}, \qquad (2.27)$$

so, since we need the eigenvalues of S_{234}^2 and S_{567}^2 operators in Eq. (2.24), we just need to consider, when $S_{234}, S_{567} \in \{1/2, 3/2\}$. For three S = 1, we get

$$1 \otimes 1 \otimes 1 = 1 \otimes (2 \oplus 1 \oplus 0) = 3 \oplus 2 \oplus 1 \oplus 2 \oplus 1 \oplus 0 \oplus 1, \qquad (2.28)$$

so again, $S_{234}, S_{567} \in \{3, 2, 1, 0\}$. Knowing the possible S_{234}, S_{567} values for three arbitrary equal S, we can also give S_{234567} , since

$$S_{234} \otimes S_{567} = (S_{234} + S_{567}) \oplus (S_{234} + S_{567} - 1) \oplus \dots \oplus |S_{234} - S_{567}|$$
(2.29)

thus $S_{234567} \in \{S_{234} + S_{567}, S_{234} + S_{567} - 1, ..., |S_{234} - S_{567}|\}$. Finally, knowing S_{234567} for a given S_{234} and S_{567} , S_{tot} is also can be given from

$$S_{234567} \otimes S = (S_{234567} + S) \oplus (S_{234567} + S - 1) \oplus \dots \oplus |S_{234567} - S|,$$
(2.30)

so $S_{\text{tot}} \in \{S_{234567} + S, S_{234567} + S - 1, ..., |S_{234567} - S|\}.$

As discussed above, we can give the all possible S_{tot} , S_{234567} , S_{234} , S_{567} configurations, and with Eq. (2.24), the spectrum of the Hamiltonian, which is linear in \mathcal{J} . Looking at these energies for S = 1/2, 1, 3/2, we get back the same analytic energies, which we determined in the previous sections. Using Eq. (2.23), we can check, which are the configurations, which provides us with the lower bound energy. These can be seen in Tab. 2.9.

S	\mathcal{J}_{LB}	E_{LB}	S_{234}	S_{567}	S_{234567}	$S_{\rm tot}$
			1/2	1/2	1	1/2
1/2	2/0	0/16	1/2	3/2	2	3/2
1/2	5/0	-9/10	3/2	1/2	2	3/2
			3/2	3/2	3	5/2
	1/3	-5/3	1	1	2	1
1			1	2	3	2
1			2	1	3	2
			2	2	4	3
			3/2	3/2	3	3/2
212	5/16	-105/32	3/2	5/2	4	5/2
512	5/16		5/2	3/2	4	5/2
			5/2	5/2	5	7/2

Table 2

From Tab. 2.9 we can see, that the configurations, which maximize the ground state energy for an arbitrary S results in Tab. 2.10. One of the configurations is when the triangles minimizes their S_{234} and S_{456} value, which is S. The other configurations are a mixture of the S, S + 1 values. The S_{234567} and S_{tot} can be interpreted as, that the two triangles have ferromagnetic coupling and the remaining spin couples antiferromagnetically to them as on Fig. 2.9.

S	\mathcal{J}_{LB}	E_{LB}	S_{234}	S_{567}	S_{234567}	$S_{ m tot}$	
			S	S			
C	S+1	$S(S+1)$ $\begin{pmatrix} 1 & 1 \end{pmatrix}$	S	S+1	$\mathbf{C} + \mathbf{C}$	$(\mathbf{C} + \mathbf{C}) = \mathbf{C}$	
5	$\overline{2(2S+1)}$	$-S(S+1)\left(1-\frac{1}{2(2S+1)}\right)$	S+1	S	$S_{234} + S_{567}$	$(S_{234} + S_{567}) - S$	
			S+1	S+1			



Figure 2.9: A visualization of the deterimend configurations. The different triangles, blue and orange, couples ferromagnetically and the middle spin couples antiferromagnetically to them.

2.1.6 First and second nearest neighbor spin-1/2 Hamiltonian

In this section, we would like to give a lower bound for the enrgy of the first and second nearest neighbor spin-1/2 antiferromagnetic Hamiltonian on the pyrochlore lattice, which now can be written as

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \mathbf{S}_j + J_2 \sum_{\langle \langle i,j \rangle \rangle} \mathbf{S}_i \mathbf{S}_j, \qquad (2.31)$$

where J is the nearest neighbor and J_2 is the second nearest neighbor exchange and in the sum $\langle i, j \rangle$ runs for the nearest neighbor and $\langle \langle i, j \rangle \rangle$ for the second nearest neighbor pairs just once for every i, j pair.

To construct the 7-site motif Hamiltonian, we do the same procedure as in Sec. 2.1.1, but now, we take into consideration the second nearest neighbor exchanges in the 128-site periodic cluster. In this case, the constraints becomes: $c_2 = \frac{J}{2} - c_1$, $c_3 = J_2$, $c_4 = 0$, which results in the following Hamiltonian:

$$H_{\text{motif}} = \mathcal{J} \left(\mathbf{S}_{1} \mathbf{S}_{2} + \mathbf{S}_{1} \mathbf{S}_{3} + \mathbf{S}_{1} \mathbf{S}_{4} + \mathbf{S}_{1} \mathbf{S}_{5} + \mathbf{S}_{1} \mathbf{S}_{6} + \mathbf{S}_{1} \mathbf{S}_{7} \right) + \left(\frac{J}{2} - \mathcal{J} \right) \left(\mathbf{S}_{2} \mathbf{S}_{3} + \mathbf{S}_{2} \mathbf{S}_{4} + \mathbf{S}_{3} \mathbf{S}_{4} + \mathbf{S}_{5} \mathbf{S}_{6} + \mathbf{S}_{5} \mathbf{S}_{7} + \mathbf{S}_{6} \mathbf{S}_{7} \right) + J_{2} \left(\mathbf{S}_{2} \mathbf{S}_{5} + \mathbf{S}_{2} \mathbf{S}_{6} + \mathbf{S}_{3} \mathbf{S}_{5} + \mathbf{S}_{3} \mathbf{S}_{7} + \mathbf{S}_{4} \mathbf{S}_{6} + \mathbf{S}_{4} \mathbf{S}_{7} \right), \qquad (2.32)$$

where we denote c_1 by \mathcal{J} . For now on, we set J = 1 and we will work with permutations, so we rewrite Eq. (2.32) with Eq. (2.17):

$$H_{\text{motif}} = -\frac{3}{4} \left(J + 2J_2 \right) + \tilde{\mathcal{J}} \left(P_{1,2} + P_{1,3} + P_{1,4} + P_{1,5} + P_{1,6} + P_{1,7} \right) + \left(\frac{J}{4} - \tilde{\mathcal{J}} \right) \left(P_{2,3} + P_{2,4} + P_{3,4} + P_{5,6} + P_{5,7} + P_{6,7} \right) + \frac{J_2}{2} \left(P_{2,5} + P_{2,6} + P_{3,5} + P_{3,7} + P_{4,6} + P_{4,7} \right),$$
(2.33)

where $\tilde{\mathcal{J}} = \frac{\mathcal{J}}{2}$. Having the Hamiltonian, now we determine the energies with the same method used in Sec. 2.1.2, which can be seen in Tab. 2.11, 2.12, 2.13.

$S_{\rm tot} = 1/2$	Index	Energy
A_{1g}	[1,-]	$-J_2 - 2\tilde{\mathcal{J}} \pm \frac{1}{4}\sqrt{20J_2^2 + 9(1-4\tilde{\mathcal{J}})^2 - 20J_2(1-4\tilde{\mathcal{J}})}$
A_{2g}	[2]	$-\frac{3}{4} + \frac{3J_2}{2} + 3\tilde{\mathcal{J}}$
E_g	[3,-]	$-\frac{3}{8} - \frac{J_2}{4} - \frac{\tilde{\mathcal{J}}}{2} \pm \frac{1}{8}\sqrt{68J_2^2 + 9(1 - 4\tilde{\mathcal{J}})^2 - 20J_2(1 - 4\tilde{\mathcal{J}})}$
A_{1u}	[4]	$-rac{3}{4}+rac{J_2}{2}+ ilde{\mathcal{J}}$
A_{2u}	[5,-]	$-J_2 \pm \frac{1}{4}\sqrt{52J_2^2 + 9(1-4\tilde{\mathcal{J}})^2 - 36(1-4\tilde{\mathcal{J}})}$
E		$-J_2 - 2 ilde{\mathcal{J}}$
D_u		$-rac{3}{4}-rac{J_2}{2}+3 ilde{\mathcal{J}}$

Table 2.11: The determined analytic energies for the $S_{\text{tot}} = 1/2$ subspace. The degeneration of the states can be computed by $S_{\text{tot}}(S_{\text{tot}} + 1) \times \dim \Gamma_i$, where Γ_i denotes the irreducible representation. The indices are for labeling the phase diagram, where e.g. [1,-] means that from the \pm the minus sign should be considered.

$S_{\rm tot} = 3/2$	Index	Energy
A_{1g}	[6,-]	$-J_2 + \tilde{\mathcal{J}} \pm \frac{1}{4}\sqrt{20J_2^2 + 9(1-4\tilde{\mathcal{J}})^2 - 20J_2(1-4\tilde{\mathcal{J}})}$
A_{2g}		-
E_{π}	[7]	$-3\tilde{\mathcal{J}}$
$\perp g$	[8,-]	$-\frac{3}{8} - \frac{J_2}{4} + \frac{5\tilde{\mathcal{J}}}{2} \pm \frac{1}{8}\sqrt{68J_2^2 + 9(1-4\tilde{\mathcal{J}})^2 - 20J_2(1-4\tilde{\mathcal{J}})}$
A_{1u}	[9]	$-\frac{3}{4}+\frac{J_2}{2}+4\tilde{\mathcal{J}}$
A_{2u}	[10]	$\frac{3}{4} - \frac{J_2}{2} - 6\tilde{\mathcal{J}}$
E		$-J_2 + \mathcal{J}_{\tilde{a}}$
L_u		$J_2 - 3\mathcal{J}$

Table 2.12

$S_{\rm tot} = 5/2$	Index	Energy
A_{1g}	[11]	$\frac{3}{4} + \frac{3J_2}{2} - 7\tilde{\mathcal{J}}$
A_{2g}		-
E_g		$2\tilde{\mathcal{J}}$
A_{1u}		-
A_{2u}		$\frac{3}{4} - \frac{J_2}{2} - \tilde{\mathcal{J}}$
E_u		$J_2 + 2\tilde{\mathcal{J}}$
$S_{\rm tot} = 7/2$		Energy
A_{1g}	[12]	$\frac{3}{4} + \frac{3J_2}{2}$

Tab	le	2.	13
Inc			10

From the (Tab. 2.11, 2.12, 2.13) energies, we would like to get the ground state energy for a given $\tilde{\mathcal{J}}$, which can achieved by giving the $J_2 - \tilde{\mathcal{J}}$ phase diagram. We select the lowest lying curves on a given region, by dividing the that into several points uniformly. Then by computing the energies in these points, we can select the curves, which have the minimal energy at a given point. For these curves, we can give their intersections, from which, we can get the phase boundaries. Having the $J_2(\tilde{\mathcal{J}})$ curves (black lines on Fig. 2.10), which provide the maxima of the ground state energy, we can give the E_{LB} in the function J_2 . The $E_{LB}(J_2)$ function can be seen on Fig. 2.11, where the black points denote the intersection of the lines. As we can see, the ground state energy is maximal at $J_2 = 0$ and the ferromagnetic state becomes ground state for $J_2 \leq -2$.



Figure 2.11: The E_{LB} lower bound energy in the function of J_2 for J = 1. The black points denote the intersection of the curves.



Figure 2.10: The $J_2 - \tilde{\mathcal{J}}$ phase diagram, with J = 1. The indices denote the energy in Tab. 2.11, 2.12, 2.13, where e.g. [1,-] means selecting the minus sign from \pm . The grey curves denotes the phase boundaries, and the grey and black points the intersection of the boundaries. At the black lines, we have the E_{LB} energy.

2.1.7 Nearest neighbor and four-site exchange spin-1/2 Hamiltonian

In this section, we would like to give a lower bound for the energy of the spin-1/2 Heisenberg antiferromagnetic Hamiltonian on the pyrochlore lattice with four site exchanges defined on the tetrahedral units in the lattice. This Hamiltonian takes the following form:

$$H = J \sum_{\langle i,j \rangle,\alpha} \mathbf{S}_{i}^{\alpha} \mathbf{S}_{j}^{\alpha} + J_{4} \sum_{\alpha} \left((\mathbf{S}_{i}^{\alpha} \mathbf{S}_{j}^{\alpha}) (\mathbf{S}_{k}^{\alpha} \mathbf{S}_{l}^{\alpha}) + (\mathbf{S}_{i}^{\alpha} \mathbf{S}_{k}^{\alpha}) (\mathbf{S}_{j}^{\alpha} \mathbf{S}_{l}^{\alpha}) + (\mathbf{S}_{i}^{\alpha} \mathbf{S}_{l}^{\alpha}) (\mathbf{S}_{j}^{\alpha} \mathbf{S}_{l}^{\alpha}) \right), \quad (2.34)$$

where J is the nearest neighbor exchange strength and J_4 is the four site exchange strength. The α denotes a tetrahedron in the lattice with i, j, k, l sites and in the sum $\langle i, j \rangle$ runs for the nearest neighbor pairs in the tetrahedron just once for every i, j pair. Rewriting this Hamiltonian with Eq. (2.17) we get

$$H = \sum_{\alpha} \left[\left(\frac{J}{2} - \frac{J_4}{8} \right) \left(\sum_{\langle i,j \rangle} P_{i,j}^{\alpha} \right) + \frac{J_4}{4} \left(P_{i,j}^{\alpha} P_{k,l}^{\alpha} + P_{i,k}^{\alpha} P_{j,l}^{\alpha} + P_{i,l}^{\alpha} P_{j,k}^{\alpha} \right) + \left(\frac{3J_4}{16} - \frac{3J}{2} \right) \right]$$
(2.35)

To construct the motif Hamiltonian, we do the same method provided in Sec. 2.1.1, but now, instead of the $S_i S_j$ operator, we use the $P_{i,j}$ permutation form. We take the all possible $P_{i,j}$ and $P_{i,j}P_{k,l}$ permutations in the motif with weight $c_{i,j}$ for the 2-site exchanges and $d_{i,j,k,l}$, where $i \neq j \neq k \neq l$, so we can write the Hamiltonian for the motif as

$$H_{\text{motif}} = c_0 + \sum_{i=1 < j}^{7} c_{i,j} P_{i,j} + \sum_{i < j < k < l} d_{i,j,k,l} P_{i,j} P_{k,l}, \qquad (2.36)$$

where we added a possible c_0 constant. The independent orbits for the 2-site exchanges can be seen in Tab. 2.14 and for the 4-site exchanges in Tab. 2.15.

Orbit	Weight	$P_{i,j}$
01	c_1	(1,2), (1,3), (1,4), (1,5), (1,6), (1,7)
O_2	c_2	(2,3), (2,4), (3,4), (5,6), (5,7), (6,7)
O_3	c_3	(2,5), (2,6), (3,5), (3,7), (4,6), (4,7)
o_4	c_4	(2,7), (3,6), (4,5)

Table 2.14: The orbits of the $P_{i,j}$ permutations.

Orbit	Weight	$P_{i,j}P_{k,l}$
u_1	d_1	((1,2),(3,4)), ((1,3),(2,4)), ((1,4),(2,3)), ((1,5),(6,7)), ((1,6),(5,7)), ((1,7),(5,6))
110	da	((1,2),(3,5)), ((1,2),(4,6)), ((1,3),(2,5)), ((1,3),(4,7)), ((1,4),(2,6)), ((1,4),(3,7)),
<i>u</i> .2	a_2	((1,5),(2,6)), ((1,5),(3,7)), ((1,6),(2,5)), ((1,6),(4,7)), ((1,7),(3,5)), ((1,7),(4,6))
110	da	((1,2),(3,6)), ((1,2),(4,5)), ((1,3),(2,7)), ((1,3),(4,5)), ((1,4),(2,7)), ((1,4),(3,6)),
uz	u_3	((1,5),(2,7)), ((1,5),(3,6)), ((1,6),(2,7)), ((1,6),(4,5)), ((1,7),(3,6)), ((1,7),(4,5))
21.	d.	((1,2),(3,7)), ((1,2),(4,7)), ((1,3),(2,6)), ((1,3),(4,6)), ((1,4),(2,5)), ((1,4),(3,5)),
u_4	u_4	((1,5),(4,6)), ((1,5),(4,7)), ((1,6),(3,5)), ((1,6),(3,7)), ((1,7),(2,5)), ((1,7),(2,6))
u_5	d_5	((1,2),(5,6)), ((1,3),(5,7)), ((1,4),(6,7)), ((1,5),(2,3)), ((1,6),(2,4)), ((1,7),(3,4))
11.0	d	((1,2),(5,7)), ((1,2),(6,7)), ((1,3),(5,6)), ((1,3),(6,7)), ((1,4),(5,6)), ((1,4),(5,7)),
u_6	a_6	((1,5),(2,4)), ((1,5),(3,4)), ((1,6),(2,3)), ((1,6),(3,4)), ((1,7),(2,3)), ((1,7),(2,4))
u_7	d_7	((2,3),(4,5)), ((2,4),(3,6)), ((2,7),(3,4)), ((2,7),(5,6)), ((3,6),(5,7)), ((4,5),(6,7))
210	da	((2,3),(4,6)), ((2,3),(4,7)), ((2,4),(3,5)), ((2,4),(3,7)), ((2,5),(3,4)), ((2,5),(6,7)),
u_8	u_8	((2,6),(3,4)), ((2,6),(5,7)), ((3,5),(6,7)), ((3,7),(5,6)), ((4,6),(5,7)), ((4,7),(5,6))
u_9	d_9	((2,3),(5,6)), ((2,3),(5,7)), ((2,4),(5,6)), ((2,4),(6,7)), ((3,4),(5,7)), ((3,4),(6,7))
u_{10}	d_{10}	((2,3),(6,7)), ((2,4),(5,7)), ((3,4),(5,6))
u_{11}	d_{11}	((2,5),(3,6)), ((2,6),(4,5)), ((2,7),(3,5)), ((2,7),(4,6)), ((3,6),(4,7)), ((3,7),(4,5))
u_{12}	d_{12}	((2,5),(3,7)), ((2,5),(4,6)), ((2,6),(3,5)), ((2,6),(4,7)), ((3,5),(4,7)), ((3,7),(4,6))
u_{13}	d_{13}	((2,5),(4,7)), ((2,6),(3,7)), ((3,5),(4,6))
u_{14}	d_{14}	((2,7),(3,6)), ((2,7),(4,5)), ((3,6),(4,5))

Table 2.15: The orbits of the $P_{i,j}P_{k,l}$ permutations.

Using the independent orbits, we can write the motif Hamiltonian as

$$H_{\text{motif}} = c_0 + \sum_{m=1}^{4} \sum_{P_{i,j} \in o_m} c_m P_{i,j} + \sum_{m=1}^{14} \sum_{P_{i,j} P_{k,l} \in u_m} d_m P_{i,j} P_{k,l}.$$
 (2.37)

After fulfilling the constraints, the remaining nonzero parameters are: $c_0 = -\frac{3J}{4} + \frac{3J_4}{32}$, $c_2 = \frac{J}{4} - \frac{J_4}{16} - c_1$, $d_1 = \frac{J_4}{16}$. With these parameters our Hamiltonian takes the following form:

$$\begin{split} H_{\text{motif}} &= -\frac{3J}{4} + \frac{3J_4}{32} + \tilde{\mathcal{J}} \left(P_{1,2} + P_{1,3} + P_{1,4} + P_{1,5} + P_{1,6} + P_{1,7} \right) \\ &+ \left(\frac{J}{4} - \frac{J_4}{16} - \tilde{\mathcal{J}} \right) \left(P_{2,3} + P_{2,4} + P_{3,4} + P_{5,6} + P_{5,7} + P_{6,7} \right) \\ &+ \frac{J_4}{16} \left(P_{1,2}P_{3,4} + P_{1,3}P_{2,4} + P_{1,4}P_{2,3} + P_{1,5}P_{6,7} + P_{1,6}P_{5,7} + P_{1,7}P_{5,6} \right), \end{split}$$
(2.38)

where we denote c_1 by $\tilde{\mathcal{J}}$. Doing the same decomposition as in Sec. 2.1.2, we get the energies shown in Tab. 2.16, where we set J = 1.

$S_{\rm tot}$	Index	Energy	Irreps
		$\frac{3}{4} - \frac{7J_4}{32} - 5\tilde{J}$	A_{1g}
	[1]	$-\frac{7J_4}{32} - 2\mathcal{J}$	E_g, E_u
1/2	[2]	$-rac{3}{4}+rac{11J_4}{32}+ ilde{\mathcal{J}}$	A_{1g}, A_{1u}, E_g
		$\frac{3}{4} - \frac{3J_4}{32} - 3\mathcal{J}_1$	A_{2u}
	[3]	$-\frac{3}{4} + \frac{3J_4}{32} + 3\tilde{\mathcal{J}}$	A_{2u}, A_{2g}, E_u
		$rac{3}{4}-rac{9J_4}{32}-6 ilde{\mathcal{J}}$	A_{2u}
3/2		$rac{3}{4}-rac{J_4}{32}-2 ilde{\mathcal{J}}$	A_{1g}
512	[4]	$-\frac{3}{4} - \frac{J_4}{32} + 4\tilde{\mathcal{J}}$	A_{1g}, A_{1u}, E_g
	[5,-]	$\frac{J_4}{32} - \tilde{\mathcal{J}} \pm \frac{1}{8\sqrt{2}}\sqrt{5J_4^2 + 40J_4\tilde{\mathcal{J}} + 512\tilde{\mathcal{J}}^2}$	E_g, E_u
		$rac{3}{4}+rac{J_4}{32}- ilde{\mathcal{J}}$	A_{2u}
5/2	[6]	$\frac{3}{4} - \frac{11\tilde{J}_4}{32} - 7\tilde{\mathcal{J}}$	A_{1g}
		$rac{J_4}{32}+2 ilde{\mathcal{J}}$	E_g, E_u
7/2		$\frac{3}{4} + \frac{3J_4}{32}$	A_{1g}

Table 2.16: The determined analytic energies. The degeneration of the states can be computed by $S_{\text{tot}}(S_{\text{tot}} + 1) \times \dim \Gamma_i$, where Γ_i denotes the irreducible representation. The indices are for labeling the phase diagram, where [5,-] means that from the \pm the minus sign should be considered.

Having the energies, we can give the $J_4 - \tilde{\mathcal{J}}$ phase diagram, using the same method as in Sec. 2.1.6, which results in Fig. 2.12. The lower bound energy E_{LB} can be given from the determined $J_4(\tilde{\mathcal{J}})$ function, which is plotted on Fig. 2.13. As we can see on this figure, the E_{LB} energy is not maximal at the $J_4 = 0$ point, but at $J_4 = 4/5$, when $\tilde{\mathcal{J}} = 1/10$ and the energy becomes $E_{LB} = -3/8 = -0.375$. To examine this $J_4 = 4/5$ point, let us look at the following Hamiltonian [15]

$$H_p = \frac{J_1}{2} \sum_{\boxtimes} \mathbf{S}_{\boxtimes}^2 + \frac{J_2}{4} \sum_{\boxtimes} \mathbf{S}_{\boxtimes}^4, \qquad (2.39)$$

where J_1 and J_2 are arbitrary weights, $\mathbf{S}_{\boxtimes} = \sum_{i \in \boxtimes} \mathbf{S}_i$ and \boxtimes means a tetrahedral unit. If we look at a single tetrahedron with S = 1/2 spins, the 16 dimensional Hilbert space can be decomposed as

$$\frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 0 \oplus 1 \oplus 1 \oplus 1 \oplus 1 \oplus 2$$
(2.40)

where $S_{\boxtimes} = 0$ is a singlet state, $S_{\boxtimes} = 1$ is a triplet state and $S_{\boxtimes} = 2$ is a quintet. Writing these cases into Eq. (2.39), for the energies we get $E(S_{\boxtimes} = 0) = 0$, $E(S_{\boxtimes} = 1) = J_1 + J_2$ and $E(S_{\boxtimes} = 2) = 3J_1 + 9J_2$. If we choose $J_1 = -J_2$ we get $E(S_{\boxtimes} = 0, 1) = 0$ and $E(S_{\boxtimes} = 2) = 6J_2$, which is basically a projector, since it annihilates the $S_{\boxtimes} = 0, 1$ states



Figure 2.12: The $J_4 - \tilde{\mathcal{J}}$ phase diagram, with J = 1. The indices denote the energy in Tab. 2.16, where [5,-] means selecting the minus sign from \pm . The grey curves denotes the phase boundaries, and the grey and black points the intersection of the boundaries. At the black lines, we have the E_{LB} energy.

and projects out the $S_{\boxtimes} = 2$ states. Using this observation, we can write the Eq. (2.39) Hamiltonian as sum of projection operators:

$$H_p = 6J_2 \sum_{\boxtimes} \mathcal{P}^{\boxtimes}, \tag{2.41}$$

where $\mathcal{P}^{\boxtimes} = -\frac{1}{12}\mathbf{S}_{\boxtimes}^2 + \frac{1}{24}\mathbf{S}_{\boxtimes}^4$. Since the Hamiltonian is sum of projection operators, the ground state energy will be the sum of the ground state energy of the projector, which is zero and it will be equal to Anderson's lower bound energy. To see, how it connects to Eq. (2.34,2.35), let us rewrite Eq. (2.39) with Eq. (2.17). The first term, which is \mathbf{S}_{\boxtimes}^2 can be written as:

$$\mathbf{S}_{\boxtimes}^{2} = \sum_{\langle i,j \rangle} \left(2(\mathbf{S}_{i}\mathbf{S}_{j}) - 4S^{2} \right) = \sum_{\langle i,j \rangle} P_{i,j}, \qquad (2.42)$$



Figure 2.13: The E_{LB} lower bound energy in the function of J_4 for J = 1. The black points denote the intersection of the curves.

where we used that the eigenvalue of the S^2 operator for spin-1/2 is 3/4 and the number of nearest neighbor bonds in a tetrahedral unit is 6. With this result the $S^4_{|x|}$ operator is

$$\mathbf{S}_{\boxtimes}^{4} = \left(\sum_{\langle i,j \rangle} P_{i,j}\right)^{2} = -6 + 6 \sum_{\langle i,j \rangle} P_{i,j} + 2 \sum_{i < j < k < l \in \boxtimes} P_{i,j} P_{k,l}, \qquad (2.43)$$

where we used Eq. (4.16) form appendix. Writing these together, we get the final permutational form of Eq. (2.39):

$$H_{p} = \sum_{\alpha} \left[\left(\frac{J_{1}}{2} + \frac{3J_{2}}{2} \right) \sum_{\langle i,j \rangle} P_{i,j}^{\alpha} + \frac{J_{2}}{2} \left(P_{i,j}^{\alpha} P_{k,l}^{\alpha} + P_{i,k}^{\alpha} P_{j,l}^{\alpha} + P_{i,l}^{\alpha} P_{j,k}^{\alpha} \right) - \frac{3}{2} J_{2} \right], \quad (2.44)$$

where α runs over the tetrahedral units. As we can see, Eq. (2.35) and Eq. (2.44) has the same form up to a constant deviation, which means, we can set the parameters such that, the Hamiltonian (2.35) becomes a sum of projection operators. To get these parameters, we solve $H = H_p + E_0$ equation with $J_1 = -J_2$ constraint, where E_0 is a constant. So for the parameters, we get the following equations:

$$\frac{J}{2} - \frac{J_4}{8} = J_2,
\frac{J_4}{4} = \frac{J_2}{2},$$
(2.45)

from which we get $J_4 = \frac{4}{5}J$ and $J_2 = \frac{2}{5}J$ and with these $E_0 = -\frac{3}{4}J$. So this $J_4 = \frac{4}{5}J$ point provides us with an exact $\frac{E_{GS}}{N} = \frac{E_0}{2} = -\frac{3}{8}J$ energy per site in the thermodynamic limit, where the number of tetrahedra is M = N/2.

This is an important result, since on the phase diagram Fig. 2.12, we have a point, where the lower bound energy and the ground state energy is identical.

2.2 Lower bound with a 16-site motif

In this section we take a larger cluster as a motif, which consist of 4 corner sharing tetrahedra and it can be seen on Fig. 2.14. To determine the lower bound for the spin-1/2 Heisenberg antiferromagnetic Hamiltonian, we construct the motif Hamiltonian with the same procedure as in Sec. 2.1.1. In this case, the cluster has T_d point group and we take the all possible two site exchanges, which need to respect this symmetry. The group generators of T_d with permutations are:

$$S_4 = P_{1,4,16,13} P_{2,8,15,9} P_{3,12,14,5} P_{6,7,11,10},$$

$$C_3 = P_{1,14,12} P_{2,9,16} P_{3,8,4} P_{5,13,15} P_{6,10,11}.$$
(2.46)



Figure 2.14: The 16-site cluster, which consist of 5 tetrahedra.

Orbit	Weight	$\mathbf{S}_i\mathbf{S}_j$
01	c_1	(1,2), (1,5), (2,5), (3,4), (3,8), (4,8), (9,13), (9,14), (12,15), (12,16), (13,14), (15,16)
O_2	c_2	(1,3), (1,9), (2,4), (2,12), (3,9), (4,12), (5,13), (5,15), (8,14), (8,16), (13,15), (14,16)
O_3	c_3	(1,4), (1,13), (2,3), (2,15), (3,14), (4,16), (5,9), (5,12), (8,9), (8,12), (13,16), (14,15)
O_4	c_4	(1,6), (2,6), (3,7), (4,7), (5,6), (7,8), (9,10), (10,13), (10,14), (11,12), (11,15), (11,16)
O_5	C_5	(1,7), (1,10), (2,7), (2,11), (3,6), (3,10), (4,6), (4,11), (5,10), (5,11), (6,9), (6,12), (6,13),
-0	-0	(6,15), (7,9), (7,12), (7,14), (7,16), (8,10), (8,11), (10,15), (10,16), (11,13), (11,14)
0c	Ce	(1,8), (1,12), (1,14), (1,15), (2,8), (2,9), (2,13), (2,16), (3,5), (3,12), (3,13), (3,16), (4,5),
00	\mathcal{C}_0	(4,9), (4,14), (4,15), (5,14), (5,16), (8,13), (8,15), (9,15), (9,16), (12,13), (12,14)
O_7	C_7	(1,11), (2,10), (3,11), (4,10), (5,7), (6,8), (6,14), (6,16), (7,13), (7,15), (9,11), (10,12)
O_8	c_8	(1,16), (2,14), (3,15), (4,13), (5,8), (9,12)
O_9	c_9	(6,7), (6,10), (6,11), (7,10), (7,11), (10,11)

Table 2.17: The orbits of the $S_i S_j$ interactions.

The obtained orbits can be seen in Tab. 2.17. Then the motif Hamiltonian can be written as:

$$H_{\text{motif}} = \sum_{m=1}^{9} \sum_{\mathbf{S}_i \mathbf{S}_j \in o_m} c_m \mathbf{S}_i \mathbf{S}_j.$$
(2.47)

The constraints for this motif are: $c_9 = J - 2c_1 - 2c_4$ and the other parameters are zero, which result in the following Hamiltonian:

$$\begin{split} H_{\text{motif}} = &\alpha (\mathbf{S}_{1}\mathbf{S}_{2} + \mathbf{S}_{1}\mathbf{S}_{5} + \mathbf{S}_{2}\mathbf{S}_{5} + \mathbf{S}_{3}\mathbf{S}_{4} + \mathbf{S}_{3}\mathbf{S}_{8} + \mathbf{S}_{4}\mathbf{S}_{8} \\ &+ \mathbf{S}_{9}\mathbf{S}_{13} + \mathbf{S}_{9}\mathbf{S}_{14} + \mathbf{S}_{12}\mathbf{S}_{15} + \mathbf{S}_{12}\mathbf{S}_{16} + \mathbf{S}_{13}\mathbf{S}_{14} + \mathbf{S}_{15}\mathbf{S}_{16}) \\ &+ \beta (\mathbf{S}_{1}\mathbf{S}_{6} + \mathbf{S}_{2}\mathbf{S}_{6} + \mathbf{S}_{3}\mathbf{S}_{7} + \mathbf{S}_{4}\mathbf{S}_{7} + \mathbf{S}_{5}\mathbf{S}_{6} + \mathbf{S}_{7}\mathbf{S}_{8} + \mathbf{S}_{9}\mathbf{S}_{10} \\ &+ \mathbf{S}_{10}\mathbf{S}_{13} + \mathbf{S}_{10}\mathbf{S}_{14} + \mathbf{S}_{11}\mathbf{S}_{12} + \mathbf{S}_{11}\mathbf{S}_{12} + \mathbf{S}_{11}\mathbf{S}_{15} + \mathbf{S}_{11}\mathbf{S}_{16}) \\ &+ (J - 2\alpha - 2\beta)(\mathbf{S}_{6}\mathbf{S}_{7} + \mathbf{S}_{6}\mathbf{S}_{10} + \mathbf{S}_{6}\mathbf{S}_{11} + \mathbf{S}_{7}\mathbf{S}_{10} + \mathbf{S}_{7}\mathbf{S}_{11} + \mathbf{S}_{10}\mathbf{S}_{11}), \quad (2.48) \end{split}$$

where we denoted c_1 by α and c_4 by β .

To get the lower bound, first we construct the matrix representation of the Hamiltonian in the $S_z = 0$ subspace, which is 12870 dimensional. Since it is impossible to analytically diagonalize such a huge parametric matrix even with decomposing the Hamiltonian according to the irreducible representations, we use the *Lánczos* algorithm to do exact diagonalization. The *Lánczos* algorithm is an iterative method, which depending on the input vector, can give the *m* smallest/largest eigenvalues and eigenvectors of an $n \times n$ Hermitian matrix. To maximize the ground state energy, we use the *Nelder-Mead* method, which is a numerical method to find the minimum/maximum of a function in a multidimensional space. So during the maximization, for a give, α , β point, we calculate the ground state energy with the *Lánczos* algorithm and this is returned to the *Nelder-Mead* maximization. As a result, the energy of the cluster is $E_0 = -1.120097(4)$ for $\alpha = 0.056972(5)$ and $\beta = 0.190341(9)$. Since there are M = N/2 such motif in an *N*-site lattice, the lower bound energy is $E_{LB} = E_0/2 = -0.560048(7)$. Since we will consider a greater matif in the next section, we do not investigate this formation further.

2.3 Lower bound with a 18-site motif

The larges open cluster, which we examine to get a lower bound for the ground state energy of the nearest-neighbor Heisenberg antiferromagnet on the pyrochlore lattice is a hexagonal structure, which consist of 6 corner sharing tetrahedra as it can be seen on Fig. 2.15. The procedure to construct the motif Hamiltonian is the same as in Sec. 2.1.1. We take the all possible two site exchanges in the motif and determine the orbits of the exchanges according to the the D_{3d} point group, whose generators with permutations are:

$$i = P_{1,18}P_{2,17}P_{3,16}P_{4,15}P_{5,14}P_{6,13}P_{7,12}P_{8,11}P_{9,10},$$

$$\sigma_d = P_{3,6}P_{4,5}P_{7,9}P_{8,11}P_{10,12}P_{13,16}P_{14,15},$$

$$C_3 = P_{1,9,7}P_{2,16,13}P_{3,6,17}P_{4,11,14}P_{5,15,8}P_{10,12,18}.$$
(2.49)

Orbit	Weight	$\mathbf{S}_i\mathbf{S}_j$
01	c_1	(1,2), (3,10), (6,12), (7,13), (9,16), (17,18)
O_2	c_2	(1,3), (1,6), (2,10), (2,12), (3,7), (6,9), (7,17), (9,17), (10,13), (12,16), (13,18), (16,18)
O_3	c_3	(1,4), (1,5), (4,10), (5,12), (7,8), (7,14), (8,10), (9,11), (9,15), (11,12), (14,18), (15,18)
O_4	c_4	(1,7), (1,9), (7,9), (10,12), (10,18), (12,18)
O_5	C_5	(1,8), (1,11), (4,7), (4,12), (5,9), (5,10), (7,15), (8,18), (9,14), (10,14), (11,18), (12,15)
o_6	c_6	(1,10), (1,12), (7,10), (7,18), (9,12), (9,18)
07	c_7	(1,13), (1,16), (2,7), (2,9), (3,12), (3,18), (6,10), (6,18), (7,16), (9,13), (10,17), (12,17)
O_8	c_8	(1,14), (1,15), (4,9), (4,18), (5,7), (5,18), (7,11), (8,9), (8,12), (10,11), (10,15), (12,14)
O_9	c_9	(1,17), (2,18), (3,9), (6,7), (10,16), (12,13)
o_{10}	c_{10}	(1,18), (7,12), (9,10)
o_{11}	c_{11}	(2,3), (2,6), (3,13), (6,16), (13,17), (16,17)
o_{12}	c_{12}	(2,4), (2,5), (3,4), (3,8), (5,6), (6,11), (8,13), (11,16), (13,14), (14,17), (15,16), (15,17)
o_{13}	c_{13}	(2,8), (2,11), (3,5), (3,14), (4,6), (4,13), (5,16), (6,15), (8,17), (11,17), (13,15), (14,16)
o_{14}	c_{14}	(2,13), (2,16), (3,6), (3,17), (6,17), (13,16)
O_{15}	c_{15}	(2,14), (2,15), (3,11), (3,15), (4,16), (4,17), (5,13), (5,17), (6,8), (6,14), (8,16), (11,13)
o_{16}	c_{16}	(2,17), (3,16), (6,13)
O_{17}	c_{17}	(4,5), (4,8), (5,11), (8,14), (11,15), (14,15)
o_{18}	c_{18}	(4,11), (4,14), (5,8), (5,15), (8,15), (11,14)
o_{19}	c_{19}	(4,15), (5,14), (8,11)

Table 2.18: The orbit of the $S_i S_j$ interactions.

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With the orbits, we can write the motif Hamiltonian as:

$$H_{\text{motif}} = \sum_{m=1}^{19} \sum_{\mathbf{S}_i \mathbf{S}_j \in o_m} c_m \mathbf{S}_i \mathbf{S}_j.$$
(2.50)

Then we use the constraint that $H_{128} = \sum_{f \in F} f H_{\text{motif}}$ from which for the nonzero parameters we get:

$$c_{13} = -\frac{c_6}{2}, \ c_{15} = -c_7, \ c_{17} = \frac{J}{2} - c_1 - 2c_3 - 2c_{12}, \ c_{18} = -2c_2 - 2c_5 - c_{11}, \ c_{20} = -2c_5.$$



Figure 2.15: The 18-site cluster, which consist of 6 tetrahedra.

Using these restrictions the motif Hamiltonian takes the form:

$$\begin{split} H_{\text{motif}} = &c_1 (\mathbf{S}_1 \mathbf{S}_2 + \mathbf{S}_3 \mathbf{S}_{10} + \mathbf{S}_6 \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_{13} + \mathbf{S}_9 \mathbf{S}_{16} + \mathbf{S}_{17} \mathbf{S}_{18}) \\ &+ c_2 (\mathbf{S}_1 \mathbf{S}_3 + \mathbf{S}_1 \mathbf{S}_6 + \mathbf{S}_2 \mathbf{S}_{10} + \mathbf{S}_2 \mathbf{S}_{12} + \mathbf{S}_3 \mathbf{S}_7 + \mathbf{S}_6 \mathbf{S}_9 \\ &+ \mathbf{S}_7 \mathbf{S}_{17} + \mathbf{S}_9 \mathbf{S}_{17} + \mathbf{S}_{10} \mathbf{S}_{13} + \mathbf{S}_{12} \mathbf{S}_{16} + \mathbf{S}_{13} \mathbf{S}_{18} + \mathbf{S}_{16} \mathbf{S}_{18}) \\ &+ c_3 (\mathbf{S}_1 \mathbf{S}_4 + \mathbf{S}_1 \mathbf{S}_5 + \mathbf{S}_4 \mathbf{S}_{10} + \mathbf{S}_5 \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_8 + \mathbf{S}_7 \mathbf{S}_{14} \\ &+ \mathbf{S}_8 \mathbf{S}_{10} + \mathbf{S}_9 \mathbf{S}_{11} + \mathbf{S}_9 \mathbf{S}_{15} + \mathbf{S}_{11} \mathbf{S}_{12} + \mathbf{S}_{16} \mathbf{S}_{18} + \mathbf{S}_{15} \mathbf{S}_{18}) \\ &+ c_4 (\mathbf{S}_1 \mathbf{S}_7 + \mathbf{S}_1 \mathbf{S}_9 + \mathbf{S}_7 \mathbf{S}_9 + \mathbf{S}_{10} \mathbf{S}_{12} + \mathbf{S}_{10} \mathbf{S}_{18} + \mathbf{S}_{12} \mathbf{S}_{18}) \\ &+ c_5 (\mathbf{S}_1 \mathbf{S}_8 + \mathbf{S}_{11} + \mathbf{S}_4 \mathbf{S}_7 + \mathbf{S}_4 \mathbf{S}_{12} + \mathbf{S}_5 \mathbf{S}_9 + \mathbf{S}_5 \mathbf{S}_{10} \\ &+ \mathbf{S}_7 \mathbf{S}_{15} + \mathbf{S}_8 \mathbf{S}_{18} + \mathbf{S}_9 \mathbf{S}_{14} + \mathbf{S}_{10} \mathbf{S}_{14} + \mathbf{S}_{11} \mathbf{S}_{18} + \mathbf{S}_{12} \mathbf{S}_{15}) \\ &+ c_6 (\mathbf{S}_1 \mathbf{S}_{10} + \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_{10} + \mathbf{S}_7 \mathbf{S}_{18} + \mathbf{S}_{9} \mathbf{S}_{12} + \mathbf{S}_3 \mathbf{S}_{18} \\ &+ \mathbf{S}_6 \mathbf{S}_{10} + \mathbf{S}_6 \mathbf{S}_{18} + \mathbf{S}_7 \mathbf{S}_{16} + \mathbf{S}_9 \mathbf{S}_{13} + \mathbf{S}_{10} \mathbf{S}_{17} + \mathbf{S}_{16} \mathbf{S}_{17}) \\ &+ c_{11} (\mathbf{S}_2 \mathbf{S}_3 + \mathbf{S}_2 \mathbf{S}_6 + \mathbf{S}_3 \mathbf{S}_{13} + \mathbf{S}_{6} \mathbf{S}_{16} + \mathbf{S}_{13} \mathbf{S}_{17} + \mathbf{S}_{16} \mathbf{S}_{17}) \\ &+ c_{12} (\mathbf{S}_2 \mathbf{S}_4 + \mathbf{S}_2 \mathbf{S}_5 + \mathbf{S}_3 \mathbf{S}_{14} + \mathbf{S}_{14} \mathbf{S}_{17} + \mathbf{S}_{15} \mathbf{S}_{16} + \mathbf{S}_{15} \mathbf{S}_{17}) \\ &- \frac{c_6}{2} (\mathbf{S}_2 \mathbf{S}_8 + \mathbf{S}_2 \mathbf{S}_{11} + \mathbf{S}_3 \mathbf{S}_5 + \mathbf{S}_3 \mathbf{S}_{14} + \mathbf{S}_4 \mathbf{S}_6 + \mathbf{S}_4 \mathbf{S}_{13} \\ &+ \mathbf{S}_5 \mathbf{S}_{16} + \mathbf{S}_6 \mathbf{S}_{15} + \mathbf{S}_8 \mathbf{S}_{17} + \mathbf{S}_{13} \mathbf{S}_{15} + \mathbf{S}_{14} \mathbf{S}_{16}) \\ &- c_7 (\mathbf{S}_2 \mathbf{S}_{14} + \mathbf{S}_2 \mathbf{S}_{15} + \mathbf{S}_3 \mathbf{S}_{11} + \mathbf{S}_3 \mathbf{S}_{15} + \mathbf{S}_4 \mathbf{S}_{16} + \mathbf{S}_{11} \mathbf{S}_{13}) \\ &+ (J/2 - c_1 - 2c_3 - 2c_{12}) (\mathbf{S}_4 \mathbf{S}_5 + \mathbf{S}_4 \mathbf{S}_8 + \mathbf{S}_5 \mathbf{S}_{11} + \mathbf{S}_8 \mathbf{S}_{14} \\ &+ \mathbf{S}_{11} \mathbf{S}_{15} + \mathbf{S}_{14} \mathbf{S}_{15}) - 2 (c_2 + c_5 + c_{11}) (\mathbf{S}_4 \mathbf{S}_{11} + \mathbf{S}_4 \mathbf{S}_{14} + \mathbf{S}_5 \mathbf$$

As we can see, it is a complicated Hamiltonian, which contains not just nearest neighbor exchanges but exchanges of greater distances too.

2.3.1 Spin-1/2 case

To determine the lower bound, we take the matrix representation of the Eq. (2.51) Hamiltonian in the $S_z = 0$ subspace, which is 48620 dimensional. Since, it is impossible to give analytical result, we use again the method provided in Sec. 2.2, but now, we have 9 independent parameters. It is a huge task to find the optimal value for the parameters, since for every calculation in the *Nelder-Mead* method, we need to do an exact diagonalization with the *Lánczos* algorithm, which results in a long calculation time. We run the this maximization several times and the best energy we could find is $E_{LB} = -0.549832(8)$ with the parameters listed below:

$$c_{1} = 0.037416(7)$$

$$c_{2} = 0.001151(3)$$

$$c_{3} = 0.083729(9)$$

$$c_{4} = 0.0000415(5)$$

$$c_{5} = -0.000546(9)$$

$$c_{6} = -0.000210(9)$$

$$c_{7} = -0.000539(3)$$

$$c_{11} = 0.001764(2)$$

$$c_{12} = 0.080243(4).$$
(2.52)

As we can see, the first nearest neighbor couplings c_1 , c_3 , c_{12} are at least one order greater, than the other exchanges.

Simplification of the Hamiltonian

The previous calculation provides us with a lower bound, which was found by numerical maximization. Since we can not know that the found energy is a local or global maximum, we would like to find a way, which gives us a global maximum ground state energy comparable with the found $E_{LB} = -0.549832(8)$ and provides us more information about the ground state wave functions.

In Sec. 2.1.5 we found that we can get the energies from the spin of the triangles "above" and "below". We can not give a simplification such like that in this case, but we can take the spin-pairs out of the hexagon for each tetrahedra as on Fig. 2.16 and require the S_{pair}^2 operators to commute with the Hamiltonian (2.51), since then the total spins of the pairs at the edges of the motif are conserved. In other other words:

$$[\mathbf{S}_i \mathbf{S}_j, H_{\text{motif}}] = 0, \qquad (2.53)$$

where the pairs $\{i, j\} \in \{\{1, 2\}, \{6, 12\}, \{9, 16\}, \{17, 18\}, \{7, 13\}, \{3, 10\}\}$. This constraint gives the following relations between the parameters: $c_2 = c_6 = c_{11} = -2c_5$, $c_4 = c_7 = 0$, $c_{12} = c_3$ and the motif Hamiltonian becomes:

$$\begin{split} H_{\text{motif}} = &c_1 \big(\mathbf{S}_1 \mathbf{S}_2 + \mathbf{S}_3 \mathbf{S}_{10} + \mathbf{S}_6 \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_{13} + \mathbf{S}_9 \mathbf{S}_{16} + \mathbf{S}_{17} \mathbf{S}_{18} \big) \\ &- 2 c_5 \big(\mathbf{S}_1 \mathbf{S}_3 + \mathbf{S}_1 \mathbf{S}_6 + \mathbf{S}_2 \mathbf{S}_{10} + \mathbf{S}_2 \mathbf{S}_{12} + \mathbf{S}_3 \mathbf{S}_7 + \mathbf{S}_6 \mathbf{S}_9 \\ &+ \mathbf{S}_7 \mathbf{S}_{17} + \mathbf{S}_9 \mathbf{S}_{17} + \mathbf{S}_{10} \mathbf{S}_{13} + \mathbf{S}_{12} \mathbf{S}_{16} + \mathbf{S}_{13} \mathbf{S}_{18} + \mathbf{S}_{16} \mathbf{S}_{18} \big) \\ &+ c_3 \big(\mathbf{S}_1 \mathbf{S}_4 + \mathbf{S}_1 \mathbf{S}_5 + \mathbf{S}_4 \mathbf{S}_{10} + \mathbf{S}_5 \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_8 + \mathbf{S}_7 \mathbf{S}_{14} \\ &+ \mathbf{S}_8 \mathbf{S}_{10} + \mathbf{S}_9 \mathbf{S}_{11} + \mathbf{S}_9 \mathbf{S}_{15} + \mathbf{S}_{11} \mathbf{S}_{12} + \mathbf{S}_{14} \mathbf{S}_{18} + \mathbf{S}_{15} \mathbf{S}_{18} \big) \\ &+ c_5 \big(\mathbf{S}_1 \mathbf{S}_8 + \mathbf{S}_1 \mathbf{S}_{11} + \mathbf{S}_4 \mathbf{S}_7 + \mathbf{S}_4 \mathbf{S}_{12} + \mathbf{S}_5 \mathbf{S}_9 + \mathbf{S}_5 \mathbf{S}_{10} \\ &+ \mathbf{S}_7 \mathbf{S}_{15} + \mathbf{S}_8 \mathbf{S}_{18} + \mathbf{S}_9 \mathbf{S}_{14} + \mathbf{S}_{10} \mathbf{S}_{14} + \mathbf{S}_{11} \mathbf{S}_{18} + \mathbf{S}_{12} \mathbf{S}_{15} \big) \\ &- 2 c_5 \big(\mathbf{S}_1 \mathbf{S}_{10} + \mathbf{S}_1 \mathbf{S}_{12} + \mathbf{S}_7 \mathbf{S}_{10} + \mathbf{S}_7 \mathbf{S}_{18} + \mathbf{S}_{9} \mathbf{S}_{12} + \mathbf{S}_9 \mathbf{S}_{18} \big) \\ &- 2 c_5 \big(\mathbf{S}_2 \mathbf{S}_3 + \mathbf{S}_2 \mathbf{S}_6 + \mathbf{S}_3 \mathbf{S}_{13} + \mathbf{S}_6 \mathbf{S}_{16} + \mathbf{S}_{13} \mathbf{S}_{17} + \mathbf{S}_{16} \mathbf{S}_{17} \big) \\ &+ c_3 \big(\mathbf{S}_2 \mathbf{S}_4 + \mathbf{S}_2 \mathbf{S}_5 + \mathbf{S}_3 \mathbf{S}_4 + \mathbf{S}_3 \mathbf{S}_8 + \mathbf{S}_5 \mathbf{6} + \mathbf{S}_6 \mathbf{S}_{11} \right) \\ &+ c_5 \big(\mathbf{S}_2 \mathbf{S}_8 + \mathbf{S}_2 \mathbf{S}_{11} + \mathbf{S}_3 \mathbf{S}_5 + \mathbf{S}_3 \mathbf{S}_{14} + \mathbf{S}_{13} \mathbf{S}_{16} + \mathbf{S}_{15} \mathbf{S}_{17} \big) \\ &+ c_5 \big(\mathbf{S}_2 \mathbf{S}_8 + \mathbf{S}_2 \mathbf{S}_{11} + \mathbf{S}_3 \mathbf{S}_5 + \mathbf{S}_3 \mathbf{S}_{14} + \mathbf{S}_4 \mathbf{S}_6 + \mathbf{S}_4 \mathbf{S}_{13} \right) \\ &+ \big(J/2 - c_1 - 4 c_3 \big) \big(\mathbf{S}_4 \mathbf{S}_5 + \mathbf{S}_4 \mathbf{S}_8 + \mathbf{S}_5 \mathbf{S}_{11} + \mathbf{S}_8 \mathbf{S}_{14} \\ &+ \mathbf{S}_{11} \mathbf{S}_{15} + \mathbf{S}_{14} \mathbf{S}_{15} \big) + 6 c_5 \big(\mathbf{S}_4 \mathbf{S}_{11} + \mathbf{S}_4 \mathbf{S}_{14} + \mathbf{S}_5 \mathbf{S}_{8} \\ &+ \mathbf{S}_5 \mathbf{S}_{15} + \mathbf{S}_8 \mathbf{S}_{15} + \mathbf{S}_{11} \mathbf{S}_{14} \big), \qquad (2.54) \end{split}$$

which has now just 3 independent parameters, from which 2 are nearest neighbor exchange weights. Searching for the lower bound energy in this case, we again do the numerical *Nelder-Mead* method, which provides us with $E_{LB} = -0.550014(7)$ and

$$c_1 = 0.038686(6)$$

$$c_3 = 0.081710(6)$$

$$c_5 = 0.000193(7).$$

(2.55)

If we set $c_5 = 0$, we get a $E_{LB} = -0.550158(2)$ lower bound energy with $c_1 = 0.038141(4)$ and $c_3 = 0.081795(7)$ parameters. As we can see, these results are very close to each other and to the determined energy with the all possible parameters.



Figure 2.16: The spin-pairs denoted by thick red line, whose total spin is conserved.

The Hilbert space of two $S=1/2\ {\rm spin}\ {\rm can}$ be decomposed into a singlet and triplet states:

$$\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1 \tag{2.56}$$

so rather than investigating the previous H_{motif} Hamiltonian, we can take an effective Hamiltonian, where instead of the $\mathbf{S}_i \mathbf{S}_j$ interaction for i, j sites out of the hexagon, we take an $\tilde{\mathbf{S}}_{i,j} = \mathbf{S}_i + \mathbf{S}_j$ operator, with $\tilde{S}_{i,j} = 0, 1$ property and introduce new interactions $\tilde{\mathbf{S}}_{i,j}\mathbf{S}_k$ and $\tilde{\mathbf{S}}_{i,j}\tilde{\mathbf{S}}_{k,l}$. This new system can be seen on Fig.2.17, where we re-indexed the sites. For simplicity, we strict ourself for the nearest neighbor interaction, so we set $c_5 = 0$, therefore we need to consider only the $\tilde{\mathbf{S}}_{i,j}\mathbf{S}_k$ operators and we denote $c_1 = \alpha$ and $c_3 = \beta$.



Figure 2.17: The visualization of the effective Hamiltonian, where we denoted the different weights with different colors.

The $\tilde{\mathbf{S}}_{i,j}\mathbf{S}_k$ operators can be given from the $\mathbf{S}_i, \mathbf{S}_j, \mathbf{S}_k$ operators, by examining three S spins in a triangle configuration, such as on Fig. 2.18(a), with different $\alpha/2$, β weights for the pairs:

$$H_{\Delta} = \frac{\alpha}{2} \mathbf{S}_{1} \mathbf{S}_{2} + \beta \left(\mathbf{S}_{1} \mathbf{S}_{3} + \mathbf{S}_{2} \mathbf{S}_{3} \right) = \frac{\alpha}{2} \left[\frac{1}{2} \left(\mathbf{S}_{1} + \mathbf{S}_{2} \right)^{2} - S^{2} \right] + \beta \left(\mathbf{S}_{1} + \mathbf{S}_{2} \right) \mathbf{S}_{3}$$
$$= \frac{\alpha}{2} \left(\frac{1}{2} \tilde{S}_{1,2}^{2} - S^{2} \right) + \beta \tilde{\mathbf{S}}_{1,2} \mathbf{S}_{3} = \frac{\alpha}{2} \left(\frac{1}{2} \tilde{S}_{1,2} (\tilde{S}_{1,2} + 1) - S(S + 1) \right) + \beta \tilde{\mathbf{S}}_{1,2} \mathbf{S}_{3}$$
$$= \frac{\alpha}{2} E_{1,2} (S, \tilde{S}_{1,2}) + \beta \tilde{\mathbf{S}}_{1,2} \mathbf{S}_{3}, \tag{2.57}$$

where $\tilde{\mathbf{S}}_{1,2} = \mathbf{S}_1 + \mathbf{S}_2$ and $E_{1,2}(S, \tilde{S}_{1,2}) = \frac{1}{2}\tilde{S}_{1,2}(\tilde{S}_{1,2} + 1) - S(S + 1)$, where $\tilde{S}_{1,2}$ can be given with $S \otimes S$ using Eq. (2.25). For S = 1/2 this energy is $E_{1,2}(\tilde{S}_{1,2} = 0) = -3/4$ or $E_{1,2}(\tilde{S}_{1,2} = 1) = 1/4$. If we examine the $\tilde{\mathbf{S}}_{1,2}\mathbf{S}_3$ operator, we can rewrite it in the following form:

$$\tilde{\mathbf{S}}_{1,2}\mathbf{S}_{3} = (\mathbf{S}_{1} + \mathbf{S}_{2})\mathbf{S}_{3} = (\mathbf{S}_{1}\mathbf{S}_{3} + \mathbf{S}_{2}\mathbf{S}_{3} + \mathbf{S}_{1}\mathbf{S}_{2}) - \mathbf{S}_{1}\mathbf{S}_{2}$$

$$= \frac{1}{2}(\mathbf{S}_{1} + \mathbf{S}_{2} + \mathbf{S}_{3})^{2} - \frac{3}{2}S^{2} - \left(\frac{1}{2}(\mathbf{S}_{1} + \mathbf{S}_{2})^{2} - S^{2}\right)$$

$$= \frac{1}{2}\left(S_{\triangle}^{2} - \tilde{S}_{1,2}^{2} - S^{2}\right), \qquad (2.58)$$

(2.59)

where $S_{\Delta}^2 = (\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3)^2$. If $\tilde{S}_{1,2} = 0$ then $S_{\Delta}^2 = S^2$ so $\tilde{\mathbf{S}}_{1,2}\mathbf{S}_3 = 0$, which is what we expected.



Figure 2.18: (a): The visualization of Eq. 2.58, where the spin-pair, whose total spin is conserved is denoted by thick red line. (b): The depiction of the new interaction.

With these triangles, we can cover our cluster like on Fig. 2.19, so the motif Hamiltonian Eq. (2.54) can be built up as:

 $H_{\text{motif}} = \sum_{i} H_{\triangle_i} + \beta \sum_{\langle i,j \rangle \in \mathcal{O}} \mathbf{S}_i \mathbf{S}_j.$



Figure 2.19: The triangle coverage of the motif. The different colors means different weights for the interactions.

Using the new indeces, we can write the motif Hamiltonian in its final form:

$$H_{\text{motif}} = \left(\frac{J}{2} - \alpha - 4\beta\right) \left(\mathbf{S}_{1}\mathbf{S}_{2} + \mathbf{S}_{2}\mathbf{S}_{3} + \mathbf{S}_{3}\mathbf{S}_{4} + \mathbf{S}_{4}\mathbf{S}_{5} + \mathbf{S}_{5}\mathbf{S}_{6} + \mathbf{S}_{1}\mathbf{S}_{6}\right) + \beta (\tilde{\mathbf{S}}_{7}\mathbf{S}_{1} + \tilde{\mathbf{S}}_{8}\mathbf{S}_{1} + \tilde{\mathbf{S}}_{8}\mathbf{S}_{2} + \tilde{\mathbf{S}}_{9}\mathbf{S}_{2} + \tilde{\mathbf{S}}_{9}\mathbf{S}_{3} + \tilde{\mathbf{S}}_{10}\mathbf{S}_{3} + \tilde{\mathbf{S}}_{10}\mathbf{S}_{4} + \tilde{\mathbf{S}}_{11}\mathbf{S}_{4} + \tilde{\mathbf{S}}_{11}\mathbf{S}_{5} + \tilde{\mathbf{S}}_{12}\mathbf{S}_{5} + \tilde{\mathbf{S}}_{12}\mathbf{S}_{6} + \tilde{\mathbf{S}}_{7}\mathbf{S}_{6}) + \alpha (E_{1,2} + E_{6,12} + E_{9,16} + E_{17,18} + E_{7,13} + E_{3,10})$$
(2.60)

which is depicted on Fig. 2.20.

In the case of spin-1/2 for the \tilde{S}_i we have two possibilities 0 and 1, so we can have $2^6 = 64$ different Hamiltonians. Instead of investigating these cases, we can do some symmetry classification. Taking the graph formed by the possible (i, j) pairs in the Hamiltonian, which is basically Fig. 2.20, we can determine the automorphism group of the graph, which is a form of symmetry, in which the graph is mapped onto itself, while preserving the edge-vertex connectivity. In this case, it can be interpreted as the D_6 point group, since the generators of the automorphism group are:

$$C'_{2} = P_{2,6}P_{3,5}P_{7,8}P_{9,12}P_{10,11},$$

$$C_{6} = P_{1,2,4,5,6}P_{7,8,9,10,11,12}$$
(2.61)



Figure 2.20: The final form of the simplified Hamiltonian with the new $\tilde{S}_i S_j$ interactions which are denoted by thick red lines. The $S_i S_j$ interactions are denoted by blue lines.

Orbits	\tilde{S}_7	\tilde{S}_8	\tilde{S}_9	\tilde{S}_{10}	\tilde{S}_{11}	\tilde{S}_{12}
h_1	0	0	0	0	0	0
h_2	0	0	0	0	0	1
h_3	0	0	0	0	1	1
h_4	0	0	0	1	0	1
h_5	0	0	1	0	0	1
h_6	0	0	0	1	1	1
h_7	0	0	1	0	1	1
h_8	0	1	0	1	0	1
h_9	0	0	1	1	1	1
h_{10}	0	1	0	1	1	1
h_{11}	0	1	1	0	1	1
h_{12}	0	1	1	1	1	1
h_{13}	1	1	1	1	1	1

With the D_6 point group, we can specify the independent orbits of the set of the possible $\{\tilde{S}_i\}$ sets, which can be seen in Tab. 2.19.

Table 2.19: The orbits of the $\{\tilde{S}_i\}$ configurations.

Taking each orbit we can give the related Hamiltonian, which we denote by H_{h_i} . We take the matrix representation of these Hamiltonians in the $S_z = 0$ subspace. The basis for a h_i orbit is $\left|S_1^z, S_2^z, ..., S_6^z, \tilde{S}_7^z, \tilde{S}_8^z, ..., \tilde{S}_{12}^z\right\rangle$, where if $\tilde{S}_i = 0$ we skip that index and if $\tilde{S}_i = 1$ the possible quantum numbers are $\tilde{S}_i^z = -1, 0, 1$. The dimensions of the different basises can be seen in Tab. 2.20.

Number of $\tilde{S} = 1$ in h_i :	0	1	2	3	4	5	6
dim H_{h_i} :	20	50	132	358	988	2760	7780

Tabl	e 2.	.20
raun	υ <i>Δ</i> .	-20

To determine the lower bound for the energy, we use again the numerical *Nelder-Mead* method for the maximization and in each step, we calculate the ground state energy of each H_{h_i} Hamiltonian and take the minimum of them, which result in the ground state energy of the original motif Hamiltonian Eq. (2.54) with $c_5 = 0$. As a result, we get $E_{LB} = -0.550158(2)$ lower bound for the ground state energy per site with $\alpha_{LB} = c_1 = 0.038140(2)$ and $\beta_{LB} = c_3 = 0.081795(5)$ parameters. This result is identical with the already determined lower bound for the original motif Hamiltonian.

If we examine the ground state energies of the H_{h_i} Hamiltonian at α_{LB} and β_{LB} , we get that the h_8 and h_{11} configurations will have the minimal energy at this point. To investigate these configurations further, we take the graph automorphism groups of the graphs shown

on Fig. 2.21(a,b), which is the D_3 subgroup of D_6 for the *a*-graph belonging to the h_8 orbit and the D_2 subgroup of D_6 for the *b*-graph belonging to the h_{11} orbit.



Figure 2.21: (a): The *a*-graph formed from the interactions of sites in the H_{h_8} Hamiltonian. Since the $\tilde{S} = 0$ sites do not interact, these are not included in the graph. (b): The *b*-graph formed from the interactions of sites in the $H_{h_{11}}$ Hamiltonian.

The generators of the D_3 group are:

$$C'_{2} = P_{1,2}P_{3,6}P_{4,5}P_{10,12},$$

$$C_{3} = P_{1,3,5}P_{2,4,6}P_{8,10,12}.$$
(2.62)

With the generators, using GAP, we can determine the irreducible representations of the generators, which can be seen in Tab. 2.21. From the irreducible representations, one can compute the character table of the D_3 group, which can be seen in Tab. 2.22.

D_3	C'_2	C_3		
A_1	(1)	(1)		
A_2	(-1)	(1)		
E	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} e^{i\frac{2\pi}{3}} & 0\\ 0 & e^{-i\frac{2\pi}{3}} \end{pmatrix}$		

Table 2.21: The irreducible representations of the D_3 point group.

D_3	E	$2C_3$	$3C'_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Table 2.22: The character table of the D_3 point group.

Decomposing the H_{h_8} with the irreducible representation, it turns out that the ground state wave function belongs to the A_1 irrep and to the S = 0 subspace.

The generators of the D_2 group are:

$$C_2^y = P_{1,3}P_{4,6}P_{8,9}P_{11,12},$$

$$C_2^z = P_{1,4}P_{2,5}P_{3,6}P_{8,11}P_{9,12}.$$
(2.63)

Again, with GAP we can determine the irreducible representations Tab. 2.23 and with them, the character table Tab. 2.24.

D_2	C_2^y	C_2^z
A	(1)	(1)
B_1	(-1)	(1)
B_2	(1)	(-1)
B_3	(-1)	(-1)

 $\begin{array}{ccc} E & C_2^x \\ 1 & 1 \end{array}$ C_2^y D_2 C_2^z A B_1 1 -1 -1 1 B_2 1 -1 1 -1 B_3 1 -1 -1

Table 2.23: The irreducible representations of the D_2 point group.

Table 2.24: The character table of the D_2 point group.

Decomposing the $H_{h_{11}}$ with the irreducible representation too, we get that the ground state wave function belongs to the B_2 irrep and to the S = 0 subspace.

2.3.2 Spin-1 case

In this section, we would like to give a lower bound for the energy for the spin-1 Heisenberg antiferromagnet on the pyrochlore lattice. To fulfill our wish, we again consider the 18-site motif Hamiltonian Eq. (2.51). If we try to take the matrix representation of this matrix in the $S_z = 0$ subspace, it turns out that the Hilbert space is 44152809 dimensional, which might still be manageable computationally, e.g. the diagonalization with the *Lánczos*-algorithm, but the numerical maximization with the *Nelder-Mead* method would take drawn-out calculation time.

Fortunately, in the previous section, we provided a method, with we can map our spin-1 system into a set of interacting spin-1/2-1-2 systems, which then becomes more manageable. We need to do the same procedure as in Sec. 2.3.1, but now the possible \tilde{S}_i spins are 0,1 or 2, so now, the whole number of possible configurations are $3^6 = 729$. Insted of dealing with these configurations, we again determine the orbits according to the D_6 group, which results in 92 h_i orbit, which we do not list here because of its large size. Taking the matrix representation of these H_{h_i} Hamiltonians, where in the basis the $\tilde{S}_i^z = -2, -1, 0, 1, 2$ elements also can appear, which results in a 1116220 dimensional matrix for the orbit, where all the $\tilde{S}_i = 2$. Since this is the larges possible matrix, which is relatively easy to handle and the others are necessarily smaller, we are in a position, where we can calculate the ground state energy for the original motif Hamiltonian in the case, where only the nearest neighbor interactions appear.

Again doing numerical diagonalization with the *Lánczos* algorithm for the different H_{h_i} Hamiltonians and numerical maximization with the *Nelder-Mead* method for the minimum of their ground state energies, we get a $E_{LB} = -1.632985(8)$ energy for the lower bound with $\alpha_{LB} = c_1 = 0.053466(8)$ and $\beta_{LB} = c_3 = 0.082726(1)$ parameters. The configurations, which has the minimal energy at this point can be seen on Fig. 2.22.



Figure 2.22: (a): The *a*-graph formed from the interactions of sites. (b): The *b*-graph formed from the interactions of sites.

Chapter 3

Summary

We investigated the lower bound for the energy of the spin-S pyrochlore Heisenberg antiferromagnet using clusters of different sizes.

The smallest, 7-site motif, provided us with an analytic expression Eq. (2.22), which in the case of spin-1/2 gives -0.5625J as a lower bound for the gound state energy. This is comparable with energies predicted from spin-wave calculations: -0.572 [3] and -0.56 [2]. Examining larger clusters – a 16-site and an 18-site motif – improved the lower bound to -0.56048J and -0.549832J, which is the best we could reach. We compare this energy with the known estimates for the ground state energy in Fig. 3.2. We may conclude that the early calculations underestimated the ground state energy. At the same time, there is a gap of about $\approx 0.06J$ between our estimate and state-of-the-art numerical results.

For the spin-1/2 case, we also considered the nearest and next-to-nearest neighbor Heisenberg model for which we could give an analytic lower bound for the ground state energy as a function of the J_2 next-to-nearest exchange. We plotted the diagram showing the lowest energy irreducible representations as a function of the nearest (J_1) and nextto-nearest neighbor (J_2) exchanges in Fig.3.1a. We also show the $J_1 - J_2$ phase diagram obtained by PFFRG [7] in Fig. 3.1b. As we can see, our lower bound approach shows some similarities with the PFFRG phase diagram, like the appearance of the ferromagnetic state (index 12 on Fig.3.1a). While we find it difficult to interpret the relationship between the "phases" of the two methods, it turns out that examining the transition points can provide information about the phase diagram. From the PFFRG method, the ferromagnetic order undergoes a phase transition at $J_2/J_1 = -1.252$ into the antiferromagnetic Kawamura state. Our phase transition from the ferromagnetic state occurs at $J_2/J_1 = J_2/1 = -2$, but another point appears at $J_2/J_1 = -1.3126(7)$. The paramagnet ranges from $-0.25(3) \leq$ $J_2/J_1 \leq 0.22(3)$. In this interval, our points take the following values: $J_2/J_1 = -1/6, 0,$ 1/10, and 1/4. In the middle of the $\mathbf{k} = 0$ phase $J_2/J_1 \approx 0.36$, marked by a black dot on Fig. 3.1b, the RG flow of the spin susceptibility diverges, indicating an onset of magnetic order. In our diagram, a phase transition also occurs at $J_2/J_1 = 0.3436(6)$. The k = 0 state undergoes a phase transition at $J_2/J_1 = 1/2$ into an incommensurate planar spiral magnetic order in Fig. 3.1b, which matches with our $J_2/J_1 = J_2/1 = 1/2$ point.

In the case of the nearest neighbor and four-site exchange Hamiltonian, we also determined an analytic phase diagram. We identified a point where the exact ground state energy and the lower bound energy are identical.



(a) The $J_1 - J_2$ phase diagram obtained with the lower bound calculation, where at least two phases meet at the boundaries. The inner and outer circles show the intersecting irreducible representations with degenerate energies that provide the lower bound estimate in Fig. 2.10.



(b) The classical and quantum phase diagram of the $J_1 - J_2$ Heisenberg model on the pyrochlore lattice. The inner rings correspond to the classical and the outer ring to the quantum phases. The picture is taken from [7].

Figure 3.1: The phase diagram obtained in this work and with PFFRG[7].

For the spin-1 pyrochlore antiferromagnet, we get -5J/3 = -1.66667J per site for the lower bound on the ground state energy with the 7-site motif. The 18-site cluster, with simplification, yields a $E_{LB} = -1.632985J$. This is a less studied case in the literature: a DMRG calculation [5] for a 32-site periodic cluster provided -1.5396(6)J and a 48-site -1.520(6)J and a variational wave function method [4] gives an upper bound -1.490(1)Jfor the ground state energy per site.

We can conclude that, even today, the simple method of Anderson, originally introduced 72 years ago, can provide valuable insights into the behavior of the Heisenberg model on the pyrochlore lattice.



Figure 3.2: Various estimates for the E_0 ground-state energy per site (indicated by horizontal lines) of the spin-1/2 antiferromagnetic Heisenberg model on the pyrochlore lattice in the thermodynamic limit with J = 1: Sobral and Lacroix -0.572 [3], Canals and Lacroix -0.56 [2], Drezhko *et al.* -0.52 [16], Schäfer *et al.* -0.4917 [4], Hagymási *et al.* -0.490 ± 0.006 [6]. An upper bound obtained by Schäfer *et al.* -0.489472 [4] and a lower bound obtained in this work -0.549832.

Chapter 4

Appendix

4.1 Three and four site exchanges

The well-known Pauli matrices takes the form with upper indexes

$$\sigma^{1} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \sigma^{2} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \sigma^{3} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
(4.1)

The commutation and anticommutation relation of these matrices is

$$\left[\sigma^{\alpha}, \sigma^{\beta}\right] = 2i\epsilon^{\alpha\beta\gamma}\sigma^{\gamma} \text{ and } \left\{\sigma^{\alpha}, \sigma^{\beta}\right\} = 2\delta^{\alpha\beta}I, \qquad (4.2)$$

where I is the 2×2 identity matrix, $\delta^{\alpha\beta}$ is the Kronecker delta, the $\epsilon^{\alpha\beta\gamma}$ is the Levi-Civita symbol and the indexes $\alpha, \beta, \gamma \in \{1, 2, 3\}$. Adding the commutator to the anticommutator we get the product of the Pauli matrices:

$$\frac{1}{2}\left(\left[\sigma^{\alpha},\sigma^{\beta}\right]+\left\{\sigma^{\alpha},\sigma^{\beta}\right\}\right)=\sigma^{\alpha}\sigma^{\beta}=\delta^{\alpha\beta}I+i\epsilon^{\alpha\beta\gamma}\sigma^{\gamma}.$$
(4.3)

For S = 1/2 with the notation used so far $S^{\alpha} = \frac{1}{2}\sigma^{\alpha}$, so the Eq. (4.3) can be rewritten:

$$S^{\alpha}S^{\beta} = \frac{1}{4} (\delta^{\alpha\beta}I + 2i\epsilon^{\alpha\beta\gamma}S^{\gamma}) .$$
(4.4)

4.1.1 Four site exchange

Writing up $P_{i,j,k,l}$ with $S_i S_j$ products using Eq. (2.17), we obtain the following relation:

$$P_{i,j,k,l} = P_{i,j}P_{i,k}P_{i,l} = (2\mathbf{S}_i\mathbf{S}_j + \frac{1}{2})(2\mathbf{S}_i\mathbf{S}_k + \frac{1}{2})(2\mathbf{S}_i\mathbf{S}_l + \frac{1}{2})$$

= $8((\mathbf{S}_i\mathbf{S}_j)(\mathbf{S}_i\mathbf{S}_k)(\mathbf{S}_i\mathbf{S}_l) + \frac{1}{4}((\mathbf{S}_i\mathbf{S}_k)(\mathbf{S}_i\mathbf{S}_l) + (\mathbf{S}_i\mathbf{S}_j)(\mathbf{S}_i\mathbf{S}_l) + (\mathbf{S}_i\mathbf{S}_j)(\mathbf{S}_i\mathbf{S}_l))$
+ $\frac{1}{16}((\mathbf{S}_i\mathbf{S}_l) + (\mathbf{S}_i\mathbf{S}_k) + (\mathbf{S}_i\mathbf{S}_j)) + \frac{1}{64}).$ (4.5)

Slightly modifying the double product we get:

$$(\mathbf{S}_{i}\mathbf{S}_{n})(\mathbf{S}_{i}\mathbf{S}_{m}) = S_{i}^{\alpha}S_{n}^{\alpha}S_{i}^{\beta}S_{m}^{\beta} = S_{n}^{\alpha}S_{m}^{\beta}\frac{1}{4}(\delta^{\alpha\beta}I + 2i\epsilon^{\alpha\beta\gamma}S_{i}^{\gamma}) = \frac{1}{4}(\mathbf{S}_{n}\mathbf{S}_{m}) + \frac{i}{2}\epsilon^{\alpha\beta\gamma}S_{n}^{\alpha}S_{m}^{\beta}S_{i}^{\gamma}.$$

$$(4.6)$$

Rewriting the triple product we obtain the following relation:

$$(\mathbf{S}_{i}\mathbf{S}_{j})(\mathbf{S}_{i}\mathbf{S}_{k})(\mathbf{S}_{i}\mathbf{S}_{l}) = S_{i}^{\alpha}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}S_{l}^{\gamma} = S_{i}^{\alpha}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}\frac{1}{4}(\delta^{\beta\gamma}I + 2i\epsilon^{\beta\gamma\rho}S_{l}^{\rho})$$

$$= \frac{1}{4}(\mathbf{S}_{i}\mathbf{S}_{j})(\mathbf{S}_{k}\mathbf{S}_{l}) + \frac{i}{8}\epsilon^{\beta\gamma\rho}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}(\delta^{\alpha\rho}I + 2i\epsilon^{\alpha\rho\lambda}S_{i}^{\lambda})$$

$$= \frac{1}{4}(\mathbf{S}_{i}\mathbf{S}_{j})(\mathbf{S}_{k}\mathbf{S}_{l}) + \frac{i}{8}\epsilon^{\alpha\beta\gamma}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma} - \frac{1}{4}\epsilon^{\rho\beta\gamma}\epsilon^{\rho\lambda\alpha}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}S_{i}^{\lambda}$$

$$= \frac{1}{4}(\mathbf{S}_{i}\mathbf{S}_{j})(\mathbf{S}_{k}\mathbf{S}_{l}) + \frac{i}{8}\epsilon^{\alpha\beta\gamma}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma} - \frac{1}{4}(\delta^{\beta\lambda}\delta^{\gamma\alpha} - \delta^{\beta\alpha}\delta^{\gamma\lambda})S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}S_{i}^{\lambda}$$

$$= \frac{1}{4}((\mathbf{S}_{i}\mathbf{S}_{j})(\mathbf{S}_{k}\mathbf{S}_{l}) - (\mathbf{S}_{k}\mathbf{S}_{i})(\mathbf{S}_{j}\mathbf{S}_{l}) + (\mathbf{S}_{j}\mathbf{S}_{k})(\mathbf{S}_{l}\mathbf{S}_{i})) + \frac{i}{8}\epsilon^{\alpha\beta\gamma}S_{j}^{\alpha}S_{k}^{\beta}S_{l}^{\gamma}$$

$$(4.7)$$

To get a hermitian operator, we add the inverse of $P_{i,j,k,l}$, which is the adjoint of $P_{i,j,k,l}$, to itself, and using the results of Eq. (4.6) and Eq. (4.7) we get:

$$P_{i,j,k,l} + P_{i,j,k,l}^{-1} = \sum_{n < m} \mathbf{S}_n \mathbf{S}_m + 4\left((\mathbf{S}_i \mathbf{S}_j)(\mathbf{S}_k \mathbf{S}_l) + (\mathbf{S}_j \mathbf{S}_k)(\mathbf{S}_l \mathbf{S}_i) - (\mathbf{S}_k \mathbf{S}_i)(\mathbf{S}_j \mathbf{S}_l)\right) + \frac{1}{4},$$
(4.8)

where the imaginary part cancels and $n, m \in \{i, j, k, l\}$ with the sorting i < j < k < l.

4.1.2 Three site exchange

Writing up $P_{i,j,k}$ with $S_i S_j$ products using Eq. (2.17), we obtain the following relation:

$$P_{i,j,k} = P_{i,j}P_{i,k} = (2\mathbf{S}_i\mathbf{S}_j + \frac{1}{2})(2\mathbf{S}_i\mathbf{S}_k + \frac{1}{2}) = 4(\mathbf{S}_i\mathbf{S}_j)(\mathbf{S}_i\mathbf{S}_k) + \mathbf{S}_i\mathbf{S}_k + \mathbf{S}_i\mathbf{S}_j + \frac{1}{4}$$
$$= \frac{1}{4} + \mathbf{S}_i\mathbf{S}_j + \mathbf{S}_i\mathbf{S}_k + \mathbf{S}_j\mathbf{S}_k + 2i\epsilon^{\alpha\beta\gamma}S_j^{\alpha}S_k^{\beta}S_i^{\gamma}$$
(4.9)

$$= \frac{1}{4} + \mathbf{S}_i \mathbf{S}_j + \mathbf{S}_i \mathbf{S}_k + \mathbf{S}_j \mathbf{S}_k + 2i \mathbf{S}_i (\mathbf{S}_j \times \mathbf{S}_k) .$$
(4.10)

$$P_{i,j,k} + P_{i,j,k}^{-1} = \frac{1}{2} + 2\sum_{n < m} \mathbf{S}_n \mathbf{S}_m , \qquad (4.11)$$

where the imaginary part cancels and $n, m \in \{i, j, k\}$ with the sorting i < j < k. The same equation can be written with permutations as:

$$P_{i,j,k} + P_{i,j,k}^{-1} = -1 + \sum_{n < m} P_{n,m}.$$
(4.12)

4.2 S^4 operator for a tetrahedral unit

$$\left(\sum_{\langle i,j\rangle} P_{i,j}\right)^2 = (P_{i,j} + P_{i,k} + P_{i,l} + P_{j,k} + P_{j,l} + P_{k,l})^2$$
(4.13)

The element of this square can be seen in Tab. 4.1, where in the diagonal we get a 6 contribution to the Hamiltonian and in the off-diagonal, we get the $2\sum_{i < j < k < l \in \mathbb{N}} P_{i,j}P_{k,l}$ contribution:

$$\left(\sum_{\langle i,j\rangle} P_{i,j}\right)^2 = 6 + 2 \sum_{i < j < k < l \in \mathbb{N}} P_{i,j} P_{k,l} + \text{remaining permutations.}$$
(4.14)

Permutation	$P_{i,j}$	$P_{i,k}$	$P_{i,l}$	$P_{j,k}$	$P_{j,l}$	$P_{k,l}$
$P_{i,j}$	1	$P_{i,j}P_{i,k}$	$P_{i,j}P_{i,l}$	$P_{i,j}P_{j,k}$	$P_{i,j}P_{j,l}$	$P_{i,j}P_{k,l}$
$P_{i,k}$	$P_{i,k}P_{i,j}$	1	$P_{i,k}P_{i,l}$	$P_{i,k}P_{j,k}$	$P_{i,k}P_{j,l}$	$P_{i,k}P_{k,l}$
$P_{i,l}$	$P_{i,l}P_{i,j}$	$P_{i,l}P_{i,k}$	1	$P_{i,l}P_{j,k}$	$P_{i,l}P_{j,l}$	$P_{i,l}P_{k,l}$
$P_{j,k}$	$P_{j,k}P_{i,j}$	$P_{j,k}P_{i,k}$	$P_{j,k}P_{i,l}$	1	$P_{j,k}P_{j,l}$	$P_{j,k}P_{k,l}$
$P_{j,l}$	$P_{j,l}P_{i,j}$	$P_{j,l}P_{i,k}$	$P_{j,l}P_{i,l}$	$P_{j,l}P_{j,k}$	1	$P_{j,l}P_{k,l}$
$P_{k,l}$	$P_{k,l}P_{i,j}$	$P_{k,l}P_{i,k}$	$P_{k,l}P_{i,l}$	$P_{k,l}P_{j,k}$	$P_{k,l}P_{j,l}$	1

Table 4.1

The remaining permutations consist of pairs like $P_{i,j}P_{i,k}$ and $P_{i,k}P_{i,j}$, which are just the $P_{i,j,k}$ and $P_{i,k,j}$ permutations, where the last is the inverse permutation of $P_{i,j,k}$. So in the Hamiltonian we get terms like $P_{i,j,k} + P_{i,j,k}^{-1}$, which is exactly Eq. (4.12). In Tab. 4.1 we have 12 pairs like that, so the sum of the remaining parts are:

$$-12 + 3\sum_{t_3 \in T_3} \sum_{n < m \in t_3} P_{n,m} = -12 + 6\sum_{\langle i,j \rangle} P_{i,j},$$
(4.15)

where the first sum runs over the remaining all possible 3-site combinations $T_3 = \{\{i, j, k\}, \{i, j, l\}, \{i, k, l\}, \{j, k, l\}\}$, since e.g. $P_{i,j,k} = P_{j,k,i} = P_{k,i,j}$ which brings the multiplication by 3 into the sum. Overall Eq. (4.13) takes the form:

$$\left(\sum_{\langle i,j\rangle} P_{i,j}\right)^2 = -6 + 6 \sum_{\langle i,j\rangle} P_{i,j} + 2 \sum_{i < j < k < l \in \boxtimes} P_{i,j} P_{k,l}.$$
(4.16)

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