# Magnetic properties of the natural mineral Boleite

## **Bachelor Rapport**

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## Abstract

The magnetic properties of Boleite is the main target of investigation in this report. Especially how the spins of the copper ions in Boleite orders. This was investigated by making susceptibility measurements for the Boleite crystals and afterwards setting up a theoretical model to describe this data. By fitting the model to the data a guess for the spin exchange constants was found. These exchange constants will be used when further investigation of Boleite's magnetic properties is done via inelastic neutron scattering experiments.

## Chapter 1

# Introduction

In this report the magnetic properties of the natural mineral Boleite will be investigated. That Boleite is a natural mineral means that it is found in nature and not grown in the laboratory. The biggest concentrations of Boleite crystals are found in the desert in the western part of the border between the United States and Mexico. A picture of Boleite crystals found in nature can be seen in figure 1.1. The crystals used in the experiments for this rapport were found in a desert in Mexico in a region called Baja California.



Figure 1.1: This is how a stone containing Boleite would look like in nature. The Boleite crystals are the blue cubic shaped parts.[1]



Figure 1.2: Unit cell of Boleite. The colors represent different elements and the meaning of the color can be seen in the right side of the figure. A bond is drawn between the copper ions because it is the main structure for the magnetic properties.

Boleite has the chemical formula;  $KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$  and the unit cell [2] can be seen in figure 1.2.[3] [4] [5]

Boleite is thought to have interesting magnetic properties and a brief introduction to the origin of the magnetic properties and why it is interesting will be given in this introduction. The magnetic properties come from the 24 copper ions which can be seen in figure 1.2. Copper is the blue balls. Each copper ion has 9 3d-shell electrons. Together these electrons act as a free localized spin. Spins give rise to a magnetic moment and this is the origin of the magnetic properties of Boleite. The magnetic moment of the whole Boleite crystal is the sum of the magnetic moments from the spins. Spins can couple to each other through the so called *spin exchange* mechanism. This exchange can make the spins want to order in two ways, namely *ferromagnetic* or *antiferromagnetic*. Ferromagnetic means that coupling spins want to align their spins so they are in the same direction. Antiferromagnetic means that coupling spins want to anti-align meaning that they have opposing spins. For Boleite the exchange is antiferromagnetic and this makes the configuration of the triangular shape of the copper ions very interesting (There are 8 triangles in total; one at each corner of the almost cubic shape formed by the copper ions). Each copper ion in these triangles couples to the other two copper ions with an antiferromagnetic coupling. This has the effect that not all three spin-pairs in theses configurations can be antiferromagnetically aligned. If two of the spins order antiferromagnetically, then the last spin can not order antiferromagnetically for both neighbors. This is called *spin frustration* and it is the effect that gives Boleite the interesting magnetic properties.

The main purpose of this report is to get at good guess for the exchange constants. These constants tells about how strongly the spins interact. They have the unit of energy and the sign of the exchange constant is determined by the type of ordering. In other words, if the ordering is ferromagnetic or antiferromagnetic. Boleite is in this rapport expected to have two main exchange constants. They are in this rapport called  $J_1$  and  $J_2$ . Guesses for the exchange constants are found by making a theoretical model for the susceptibility in terms of the exchange constants. The exchange constants are adjusted to fit data for the susceptibility and from this a guess for the exchange constant can be given.

All words written in *italics* in the text above will be further explained in chapter 2.

## Chapter 2

# Theory and Magnetic Properties of Boleite

Before going head on with the experiments and the modeling the theory needed to understand this will be presented. It is presumed that the reader has a basic understanding of solid state physic [2], electro dynamics, quantum mechanics and statical mechanics[6]. All the theory about magnetism is found in [7] and [8].

## 2.1 Magnetism - in general

The basis for all magnetism is the quantity magnetic moment. It can be described by a current, I, looping in a circular wire which have an area, A, and the magnetic moment is given by  $\mu = I \cdot A$ . This magnetic moment has the same properties as a magnetic dipole. In an atom or ion the magnetic moment can originate from two effects. The first one is the electrons orbiting around the nucleus and from this having a net magnetic moment. The other one is the electron spin. This is a quantum mechanical effect but it may help to think of it as a classical object that is spinning around its own axes and here by having a magnetic moment. For all atoms it is only half filled shells that have a magnetic moment compensate each other. The main focus in this rapport would be on the magnetic moment coming from the spin.

The size of the magnetic moment for an electron is given by the *Bohr-magneton* having the value

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \cdot 10^{-24} \frac{J}{T} \tag{2.1}$$

Where e is the size of the electron charge,  $\hbar$  is the Plank constant and  $m_e$  is the electron mass.

The net magnetic moment of a crystal comes from the atoms or ions in the crystal that have a magnetic moment. The net magnetic moment is therefore the sum of the atoms' or ions magnetic moments.

In Boleite only copper ions have a magnetic moment. It is due to the  $3d^9$  configuration of  $Cu^{2+}$ . In Boleite these 3d electrons are localized at each ion, but the valence electrons prefers to do *spin exchange*.

### 2.2 Spin exchange

In order to understand spin exchange, it is necessary to understand the meaning of *singlet* and *triplet* states. This is easiest done by calculating an example. The example that will be used is two spin-1/2 particles that interact. The presumed Hamiltonian for this system is given by:

$$\mathcal{H} = J\mathbf{S}_{\mathbf{a}} \cdot \mathbf{S}_{\mathbf{b}} \tag{2.2}$$

Here  $\mathbf{S}_{\mathbf{a}}$  and  $\mathbf{S}_{\mathbf{b}}$  are the spin operators for spin *a* and *b*, respectively. For now *J* is just a constant, but physical meaning of it will be given later. The states for such a system have to fulfill the Pauli exclusion principle, which means that the states should be antisymmetric. This is done by either making the spatial or the spin part antisymmetric. With this knowledge 4 states can be made for this system:

$$1): \psi_{as} |\uparrow_a\uparrow_b\rangle \quad 2): \psi_{as} |\downarrow_a\downarrow_b\rangle \quad 3): \psi_{as} |\uparrow_a\downarrow_b + \downarrow_a\uparrow_b\rangle \quad 4): \psi_s |\uparrow_a\downarrow_b - \downarrow_a\uparrow_b\rangle$$
(2.3)

Where  $\psi_{as}$  is an antisymmetric spatial state and  $\psi_s$  is a symmetric spatial state.  $|\uparrow_a\downarrow_b \pm \downarrow_a\uparrow_b\rangle$  is short for the state  $2^{-1/2} (|\uparrow_a\downarrow_b\rangle \pm |\downarrow_a\uparrow_b\rangle)$ . These states can be divided into two groups, depending on the spin part. One group has a total spin of 0 and the other group has a total spin of 1. The division can be done by the use of the Clebsch Gordan coefficients. It turns out that the states with an antisymmetrical spatial part, have a total spin of 1 and the one state with a symmetrical spatial part has a total spin of 0.

Now the energies for this system will be found. This is done by rewriting the spin operators in terms of the operators  $S^z$ ,  $S^+$  and  $S^-$ , where  $S^{\pm} = S^x \pm iS^y$ . So the Hamiltonian can now be rewritten as:

$$\mathcal{H} = J\left(S_a^z S_b^z + \frac{1}{2}\left(S_a^+ S_b^- + S_a^- S_b^+\right)\right)$$
(2.4)

Here  $S^z$  gives the z projection of the spin and  $S^{\pm}$  raises or lowers the spin projection if it is possible, otherwise it gives zero.

Using the Hamiltonian on the states the following energies are found:

$$E = \begin{cases} \frac{J}{4} \text{ if } s = 1 \text{ (Triplet states)} \\ -\frac{3J}{4} \text{ if } s = 0 \text{ (Singlet state)} \end{cases}$$
(2.5)

It is seen that an energy splitting happens and this splitting happens in terms of the total spin. There are 3 states with E = J/4 and these states are therefore called the *triplet* states. The single state with s = 0 is called the *singlet* state. Splitting of the degenerate states when the spins are connected is the reason why this model is important for spin exchange.

Spin exchange has its origin in Coulomb repulsion between electrons. Whenever electrons come close they repel each other. The states  $\psi_s$  and  $\psi_{as}$  may have different repulsion energy. Then the energy splitting will indirectly depend on the the spin configuration. The Hamiltonian in equation 2.2 will be a good model for the spin exchange. A general Hamiltonian for the spin exchange is:

$$\mathcal{H} = \sum_{ij} J_{ij} \mathbf{S}_{\mathbf{i}} \cdot \mathbf{S}_{\mathbf{j}}$$
(2.6)

Here *i* and *j* are the sum over all interacting spins.  $J_{ij}$  is the *exchange constant*, which is a measure of the strength of the exchange between the spins. It has the unit of energy and it determines the energy scale for the spin configuration. The sign of *J* determines if the spin tends to order *ferromagnetic* or *antiferromagnetic*. Ferromagnetic means that the spins wants to order in the same direction. Antiferromagnetic means that they want to align in opposing directions. From equation 2.5 it is seen that a positive *J* makes the singlet state the ground state and this state has no net spin. The spins order antiferromagnetic which can be seen by state 4) in equation 2.3. If *J* is negative the triplet states are the ground states and the ordering is ferromagnetic.

The magnetic properties of Boleite is due to the s = 1/2,  $Cu^{2+}$  copper ions. The structure of the copper ions is seen in figure 2.1. There are 24 copper ions in the unit cell. The copper ions almost forms a cube where all corners are cut off. The triangles at each corner is what makes this system very interesting and this will be described in section 2.3. The copper ions have a high order of symmetry. This means that there are only two different neighbor lengths between the copper ions; the length between the ions in the triangles at each corner and the length between one corner of the triangle and the neighboring triangles. The distance between the copper ions in the triangles is 3.48 Å and the distance between the triangles is 2.89 Å (The numbers are found using VESTA [3]). The most intuitive interaction would be a so called direct exchange, where the atoms are so close, that the overlap of the electron shells favors  $\psi_{as}$  and ferromagnetism. But even though this might seem as the obvious cause of the exchange, this is rarely the case. The ionic radius of copper ions in a crystal is: 0.87 Å (this is for copper Cu<sup>+2</sup>). [9]. By comparing this with the distance between the copper ions, it is seen that this cannot be the explanation for the spin exchange for this system.

There is another mechanism called superexchange. Here the correlation is due to the connection between the oxygen and copper ions. This form of exchange is much stronger since the copper and oxygen ions share electrons. Here the d-shell valence electron of



Figure 2.1: The position of the copper ions within the unit cell. The copper ions almost forms a cube where all the corners are cut off. The interesting part of this structure is the triangle shape a each corner. This triangular shape is characteristic of a frustrated magnet.

copper is shared with the oxygen so that it has a full p-shell..

The possible spin configurations can be seen in 2.7. Now the spin configuration of a, b, c)



Figure 2.2: A sketch of superexchange mechanism. Here it is the d-shell of the copper ions interacting with the p-shell of the oxygen.

and d) is antiferromagnetic, while the spin configuration of e) is ferromagnetic. Looking at the antiferromagnetic configurations a, b, c) and d), the ground state for these configurations is a) because the spins can exchange position on all three sites and hereby

#### 2.3. SPIN FRUSTRATION

minimize the kinetic energy. On the other hand, the ferromagnetic configuration e) can also do this, but it does not have any higher excitations and this also raises the energy of this configuration. So configuration a) is the ground state for this system witch makes this kind of exchange antiferromagnetic.



Figure 2.3: The copper and oxygen ions with the bonds between them.



Figure 2.4: This is one corner of the copper and oxygen ion configuration. The effective exchange constants is also shown on the figure.

The structure of the copper and oxygen ions in Boleite can be seen in figure 2.3. Presuming that it is only the spins of the nearest neighbors that interact, there are two different exchange constants in play for this system. They are shown in figure 2.4. Here the exchange constants are called  $J_1$  and  $J_2$ . This notation shown will be kept throughout the report.

### 2.3 Spin frustration

One of the main reasons why Boleite was expected to have interesting magnetic properties is the triangular configuration at each corner. If the exchange is antiferromagnetic these triangles will make a so called *frustrated spin* configuration. When the exchange is antiferromagnetic the spins want to order, so that all the neighboring spins are in opposite direction, which is an impossible task for three quantum mechanical S = 1/2 spins. If two spins in this triangle make a singlet bond the last spin can not make singlet bonds with them. This explains why the system is called frustrated. There is no unique ground state for this system and the leftover spin acts as a free spin. This triangle system is calculated in detail in section 4.2.

### 2.4 Statical mechanics and magnetism

In order to get an estimate for the exchange constant a connection to data measured for Boleite is needed. The chosen data is found by *susceptibility* measurement.

Susceptibility is the connection between the magnetization and the applied field. This can mathematically be written as  $\mathbf{M} = \chi \mathbf{H}$  where  $\mathbf{M}$  is the sample magnetization,  $\mathbf{H}$  is the applied field and  $\chi$  is the susceptibility. It should be quite clear that if a function of the magnetization in terms of the applied field is known, then the susceptibility can be found by  $\chi = \partial M / \partial H$ .

The susceptibility measurements were done as a function of temperature, so this is the theoretical connection that is needed to be found. In order to find it, the magnetization is needed to be found as a function of temperature and applied field. To find the magnetization as a function of applied field the so called *Zeeman energy* is used. It is known from electrodynamics where it is written  $E = -\mu \cdot \mathbf{B}$ . Here  $\mu$  is the magnetic moment and  $\mathbf{B}$  is the magnetic field. The lowest energy is when the magnetic moment and field is aligned. With the Zeeman energy and the energy for the spin configuration, the thermal average can be found. The thermal average of a physical observable is known to have the form [6]:

$$\langle m \rangle = \frac{1}{Z} \sum_{states} m_i \exp\left(-\frac{E_i}{k_b T}\right) = \frac{1}{Z} \sum_{states} m_i \exp\left(-\frac{E_i^0}{k_b T} + \frac{m_i g \mu_B B}{k_b T}\right)$$
(2.8)

Where Z is the partition function given by:

$$Z = \sum_{states} \exp\left(-\frac{E_i^0}{k_b T} + \frac{m_i g \mu_B B}{k_b T}\right)$$
(2.9)

Here  $m_i$  is the magnetization of state i,  $E_i^0$  is the spin configuration energy of state i, g is the so called g-factor which depends the magnetic moment, whether it is the orbital motion or the spin,  $\mu_B$  is the Bohr magneton and B is the net magnetic field. For electrons not having an orbital moment, the g-factor is approximately g = 2. Since the energies for the spin configuration is not known in general, it is not possible to find an expression without the sums in equation 2.8. But the sums can be calculated using a computer.

The thermal average of the susceptibility is found by calculating  $\chi = \frac{\partial m}{\partial H}\Big|_{H=0}$ . This is the susceptibility at zero applied field. The relation between the applied field and the field the spins feel can be approximated by  $B \approx \mu_0 H$ , if the magnetization is negligible.

$$\chi = \left. \frac{\partial \langle m \rangle}{\partial H} \right|_{H=0} \tag{2.10}$$

$$= \frac{g\mu_0\mu_B}{k_bT} \left( \frac{1}{Z} \sum_{states} m_i^2 \exp\left(-\frac{E_i^0}{k_bT} + \frac{m_i g\mu_B \mu_0 H}{k_bT}\right) - \left(\frac{1}{Z} \sum_{states} m_i \exp\left(-\frac{E_i^0}{k_bT} + \frac{m_i g\mu_B \mu_0 H}{k_bT}\right)\right)^2 \right) \bigg|_{H=0}$$

$$(2.11)$$

$$=\frac{g\mu_0\mu_B}{k_bT}\left(\frac{1}{Z}\sum_{states}m_i^2\exp\left(-\frac{E_i^0}{k_bT}\right) - \left(\frac{1}{Z}\sum_{states}m_i\exp\left(-\frac{E_i^0}{k_bT}\right)\right)^2\right)$$
(2.12)  
$$\frac{g\mu_0\mu_B}{k_bT}\left(\frac{1}{Z}\sum_{states}m_i\exp\left(-\frac{E_i^0}{k_bT}\right)\right)^2$$
(2.12)

$$=\frac{g\mu_{0}\mu_{B}}{k_{b}T}\left(\left\langle m^{2}\right\rangle \left(0\right)-\left\langle m\right\rangle^{2}\left(0\right)\right)$$
(2.13)

For an antiferromagnet the average magnetization is zero. So from this the susceptibility is given by:

$$\chi = \frac{g\mu_B}{k_b T} \left\langle m^2 \right\rangle(0) \tag{2.14}$$

$$= \frac{g\mu_B}{k_b T Z} \sum_{states} m_i^2 \exp\left(-\frac{E_i^0}{k_b T}\right)$$
(2.15)

### 2.5 Curie-Weiss law

The *Curie-Weiss law* is a law that gives a connection between susceptibility and the temperature for an ideal ferro- or antiferromagnet [7]. The derivation is too cumbersome to do here and the law will just be presented. The law takes the form:

$$\chi = \frac{C}{T + \theta_C} \tag{2.16}$$

Here T is the temperature and C is the Curie constant. The exact form will be presented later.  $\theta_C$  is the Curie-temperature, a constant that depends on the strength and sign of the exchange constants. If the main exchange constants have the same sign then the sign of  $\theta_C$  tells which sort of exchange the magnetic system has. This means, that if the ordering is ferromagnetic, then  $\theta_C$  will be negative and for antiferromagnetic ordering  $\theta_C$ will be positive. The exact form of this constant will also be presented later. A special case for the Curie-Weiss law is where spins do not interact. Then  $\theta_C = 0$ . This type of behavior is called *paramagnetism*. If the inverse susceptibility is plotted, the law takes the form:

$$\frac{1}{\chi} = \frac{T}{C} + \frac{\theta_C}{C} \tag{2.17}$$

This is a linear form which most people find easy to recognize by eye. Many materials have temperature regions, where the inverse susceptibility is linear and by fitting this  $1/\chi$  in

this region some information about the magnetic ordering can be found. The information about the magnetic ordering can be found by knowing the exact form of the constants in the Curie-Weiss law. They are given by:

$$C = \frac{Ng^2\mu_B^2 S(S+1)}{3k_b}$$
(2.18)

$$\theta_C = \frac{2S(S+1)\sum_i J_i}{3k_b}$$
(2.19)

Here N is the number of spins participate in the susceptibility, g is the g-factor,  $\mu_B$  is the Bohr-magneton, S is the length of the spin,  $k_b$  is Boltzmann's constant and  $\sum_i J_i$  is the sum of the exchange constants for each spin. The interesting part is to find the number of spins participating and also to find the sum of the exchange constants. This will be done in section 3.2.3.

## Chapter 3

## Experiments

In this chapter the crystals that have been used for the experiments will be presented and then the experimental setup and data are presented.

## 3.1 Crystals

All the 14 crystals used for the experiments in this rapport were purchased from a crystallographer in the United States via eBay.com. Each crystal was given a letter in an alphabetic order, but letters that are easy to confuse by handwriting were avoided. A table with information about the crystals can be found in figure 3.1. A problem with crystals found in nature is that the purity of each crystal has to be analyzed. In the case of this experiment, it had to be analyzed whether the crystals were Boleite or not. Boleite has a unique blue color and cubic shape. But there is especially one other crystal that is easy to confuse with Boleite, namely Pseudoboleite. It almost looks the same on the outside and it is found in the same places as Boleite. But a key difference between the two crystals is their unit cell. The unit cell of Boleite is cubic [10] whereas the unit cell of Pseudoboleite is tetragonal [11]. This difference is easy to measure by X-ray diffraction.

Crystal	А	В	С	D	Е	F	G
Mass [mg]	361	424	1014	611	403	287	204
Molar [mmol]	33.0	38.8	92.7	55.9	36.8	26.2	18.7
Crystal	H	Κ	Μ	Ν	Р	Q	R
Crystal Mass [mg]	Н 221	K 263	M 179	N 245	P 236	Q 134	R 253

Figure 3.1: Table of the crystals. Each crystal was given a letter and here their mass are stated together with the number of molecules. The molar mass of Boleite is M = 10936 mg/mol.

Scattering from crystals makes diffraction patterns depending on the unit cell shape, unit cell size, and basis atoms as it is known from basic solid state physics. Due to lack of space in this rapport the more practical theory for such an experiment can not be given here, but all the crystals were tested and they all agreed with the Boleite crystal structure. The experiment is presented in appendix A.

### 3.2 Susceptibility measurements

In this section the measurement principle behind the two different instruments which have been used are shown along with the data. At last a plot of the inverse susceptibility is shown with the data from crystal P and the Curie-Weiss regions for Boleite are discussed.

#### 3.2.1 Instruments

The susceptibility measurements were performed with two different instruments at PSI (Paul Scherrer Institute) in Switzerland. Both instruments measure the magnetic moment by a measurement technique called VSM (Vibrating Sample Magnetometer). This principle will be sketched when the first instrument is presented. In order to do a VSM measurement a steady magnetic field needs to be applied. For both experiments the applied field was 0.1 T. The susceptibility that was measured was  $\chi = \partial M/\partial H \approx M/H$ , a linear approximation. This holds true if the typical energy of the spin configuration is much bigger than the Zeeman energy. This will be tested in chapter 4.

The first experiment was done in October 2012. During these experiments an instrument called PPMS (Physical Property Measurement System) from Quantum Design was used. The principle of VSM is to vibrate the sample, which is slightly magnetized due to the external field, and this oscillation induces an AC electromotive force in the pickup coil. This induction can be converted to at magnetic moment by the knowledge of the sample speed [12]. A sketch of the VSM principle can be seen in figure 3.2, where the VSM is the part within the dashed line. In the PPMS the induced electromotive force is measured directly with a voltmeter. There is also a compensation coil which is there to compensate for any changes in the applied field. Changes induces an electromotive force that is not wanted in the measurement. This is avoided by having the compensation-coil wounded opposite to the pickup coil and placed so far from the sample, that the sample practically does not induce any electromotive force in the compensation-coil.

The second experiment was done in November 2013. During this experiment an instrument called MPMS (Magnetic Property Measurement System) also from Quantum Design was used. The VSM measurement part is the same as described for the PPMS instrument. The main difference is how the MPMS detect the induced signal. Here the detection system exploits the high sensitivity of with the SQUID (Superconducting QUantum Interference Device) measuring technique [13].



Figure 3.2: Sketch of the VSM and SQUID measurement technique for the MPMS instrument. The VSM part is the same for the PPMS, but here the inductive electromotive force is measured directly instead of the SQUID.

A SQUID is based on a circuit of two so called Josephson junctions [14]. Josephson junction is two superconducting materials separated by a thin non-superconducting material. When a circuit with two Josephson junctions is made, something interesting happens. If a current runs through each of the junctions, but the current has different sizes (The direction of the current is not important) a voltage difference is produced over the junctions. This effect is exploited in the SQUID measurement technique. At first, a steady current is sent through the superconducting circuit, so that any prebias can be compensated. The VSM system is made so that it has a coil in the middle of the superconducting circuit (see figure 3.2). This means that if a current is running in the VSM system a magnetic field will be induced in the coil placed in the middle of the superconducting circuit. An effect of a superconducting ring is that the total magnetic flux through the ring will always stay the same as when the superconducting state was created. If the magnetic flux through the ring is changed, for example by the coil from the VSM system, a so called screening current is made in the superconducting ring and this compensates the change in the magnetic flux, so that the total flux stays the same. The screening current runs in opposing directions though the Josephson junction but the steady current runs in the same direction. So the net current through the junction has changed, and a voltage difference can be measured and converted to the magnetic moment of the sample. It is worth mentioning that this technique is very sensitive. The circuit of the Josephson junction can measure changes in the magnetic flux on the scale of the magnetic flux quanta.

#### 3.2.2 The data

In this section the data from PPMS and MPMS will be presented. For both instruments each data point is found by sampling the magnetic moment for a given period of time at a stable temperature. The average magnetic moment is passed on together with the standard deviation for the magnetic moment in the same period of time.

The data from the PPMS can be seen in figure 3.3. Only 6 crystals were tested: A, B D, E, F and R. Due to limited time. All the data has been normalized with respect to the number of Boleite molecules of each crystal (mol), see table 3.1. The standard deviation for each data point is not plotted, because it would dominate the plot and therefor be difficult to get any constructive information.



Figure 3.3: Graph of the data from the PPMS. Note the logarithmic scale for the susceptibility.

The data from the MPMS instrument can be seen in figure 3.4. Also this data is normalized with respect to the number of molecules. The following crystals were tested: H, K, N and P.

By comparing the curves in figure 3.3 and 3.4 it is seen that curves created with the MPMS instrument are much more smooth and that the SQUID measurement technique is much more stable. In figure 3.5 a comparison of the standard deviation given from the two instruments can be seen. Even though the noise of the PPMS is larger than of the MPMS, the error from the PPMS instrument is too big. This is the same for all the experiments done on the PPMS instrument so it is expected that there was something wrong with the machine or a mistake was done when setting it up.

Another thing that is seen in the measurements for both instruments, is that the susceptibility curves could be split into two types. There is one type where the curve keeps growing as the temperature goes to zero and another one where there is a kink at 3-4 K. It is not known what makes this difference, but in many cases single crystals can have paramagnetic contributions which will dominate at low temperatures. The expected susceptibility curve is the one with the kink at 3-4 K as will be discussed in chapter



Figure 3.4: Graph of the data from the MPMS. Notes the logarithmic scale for the susceptibility.



Figure 3.5: A compassion of the error given by the two instruments. The error from the PPMS instrument is too big even though there is more noise for the PPMS instrument.

4. It is expected that the system is antiferromagnetic and has a singlet ground state, which means that there is no free spin behavior. The susceptibility keeps growing as the temperature goes to zero. So for the rest of this rapport the "true" susceptibility behavior is presumed to be the one with the kink at 3 - 4 K.



#### 3.2.3 Inverse susceptibility and Curie-Weiss fit

Figure 3.6: A plot of the inverse susceptibility with Curie-Weiss fits for two linear temperature regions.

As described in chapter 2 it is common to look at the inverse susceptibility because many materials will act according to the Curie-Weiss law with linear behavior for the the inverse susceptibility at high temperature. The inverse susceptibility for crystal P and fits to the linear region can be seen in figure 3.6. The fits, of the form  $1/\chi = AT + B$ , can be translated into information about the magnetism of Boleite. In the low temperature Curie-Weiss region (the red line in figure 3.6), the fitted constants are given the subscript Low, and for the fitted constants at high temperature (the blue line) the subscript is High. By comparing the Curie-Weiss law and the linear form above it is seen that  $A_{High} = 1/C$ and by manipulating with the form of C an expression for the number of spins pr unit cell can found:

$$N_{High} = \frac{3k_b}{\mu_0 \mu_B S(S+1) N_A A_{High}} = 26.87 \pm 0.05 \tag{3.1}$$

The error has been adjusted so the reduced chi-square is 1. From this fit the error for the fitting parameters was found. There are 24 coppers ions and therefore it was expected that there were 24 spins participating. The difference between the expectations and result may come from a slight variation in the unit cell density or it could be that the calibration of the instruments is a little off. Both these types of error would make a systematic error for the number of spins. Another interesting thing to calculate is the sum of the exchange constants for each spin. This can be found by isolating it from the expression for  $\theta_C$  and

note that  $\theta_C = B/A$ .

$$\left(\sum_{i} J_{i}\right)_{High} = \frac{3kB_{High}}{2S(S+1)A_{High}} = 30.5 \pm 0.1 \text{ meV}$$
(3.2)

The sum of the exchange constants for each spin in this region is expected to be  $(\sum_i J_i)_{High} = 2J_1 + J_1$ . The same calculations can be done for the Curie-Weiss susceptibility at the low temperature region where it was found that:.

$$N_{Low} = 11.33 \pm 0.05 \tag{3.3}$$

$$\left(\sum_{i} J_{i}\right)_{Low} = 1.84 \pm 0.04 \text{ meV}$$
(3.4)

The number of participating spins in the low temperature region is a little under half of the total amount of spins. In this temperature region the triangular configuration only has access to the singlet bonds, which means that it is the  $J_2$  bonds that are the only ones present here. So an initial guess for the exchange constants of the  $J_2$  bonds would be  $J_2 = (\sum_i J_i)_{Low} = 1.84 \pm 0.04$  meV. By using this guess for  $J_2$ , a guess for  $J_1$  can be found:

$$J_1 = \frac{(\sum_i J_i)_{High} - J_2}{2} = 14.32 \pm 0.05 \text{ meV}$$
(3.5)

$$J_2 = 1.84 \pm 0.04 \text{ meV} \tag{3.6}$$

## Chapter 4

# Modeling the data

The main purpose of this section is to interpret the susceptibility curves from the experiments. This is done by setting up models which can be used to describe the data and from looking at these models, obtaining a guess for the size of the main exchange constants of Boleite.

### 4.1 Boleite - the full system (N=24 model)

As it was described in the theory chapter, the magnetic properties of Boleite come from the spins of the 24 copper ions. These interact through the oxygen ions. A general Hamiltonian for exchange systems was found, and by defining the main exchange constants of Boleite by  $J_1$  and  $J_2$ , as shown in figure 2.4, the Hamiltonian is given by:

$$H = \sum_{\langle i,j \rangle} J_1 \left( S_i^z S_j^z + \frac{1}{2} \left( S_i^- S_j^+ + S_i^+ S_j^- \right) \right) + \sum_{\langle k,l \rangle} J_2 \left( S_k^z S_l^z + \frac{1}{2} \left( S_k^- S_l^+ + S_k^+ S_l^- \right) \right)$$
(4.1)

 $\langle i, j \rangle$  is a short notation for nearest neighbors within each triangle and  $\langle l, k \rangle$  is a short notation for spins at the side bonds.

In principle it is just a matter of finding the magnetization and energy levels for this 24 spins system. If the energies were known in terms of the exchange constants for this model, it would just be a matter of adjusting the exchanges constants, and hopefully see that it fits the data very well. The problem in doing so, is that there are 24 spins, and since s = 1/2 there are  $2^{24} \approx 1.68 \cdot 10^7$  spin configurations. This means that in order to find the energies for this system a matrix of size  $2^{24} \times 2^{24}$  has to be diagonalized. Even though symmetries could be used to split the big matrix into smaller block-diagonal-matrices the matrices are still too big to diagonalize by hand. So simpler solvable models are set up.

### 4.2 Model N = 3

The first model that is tried is the N = 3 model. One state of the model can be seen in figure 4.1. This is the triangular spin configuration which earlier in this report was said to have the characteristic spin frustration. The calculation for this system will now be shown in detail. The Hamiltonian for this system is given by:



Figure 4.1: The N = 3 model. Here  $J_1$  means that this bond has an exchange constant with size of  $J_1$ .

Figure 4.2: Mirror symmetry for the N = 3 model

$$H = \sum_{i=\{1,3\}} J_1 \left( S_i^z S_{i+1}^z + \frac{1}{2} \left( S_i^- S_{i+1}^+ + S_i^+ S_{i+1}^- \right) \right) \quad (4 \to 1)$$
(4.2)

The operators are the same as was explained before, with  $S^z$  being the z projection of the spin and  $S^{\pm}$  being the raising and lowering operator. In order to make it easier to find the energies for this system, some nice general tricks for solving a system like this will be shown. The Ising basis is used for these calculations.

#### 4.2.1 Symmetries of the system

The trick is to exploit the symmetries of the systems to find subspaces that have the same energy levels or find states that can not couple with each other.

It can be seen that the Hamiltonian can not change the total amount of spins up or down, since the raising and lowering operators always come as pairs. From this it can be concluded that only states with the same amount of spins up or down can be connected by H. This leads to the fact that the state space can be split into subspaces with states that has the same magnetization m. For this system  $m = \{3/2, 1/2, -1/2, -3/2\}$ .

Another symmetry of this system is spin flip symmetry. This means that the Hamiltonian should be invariant for  $S^z \to S^{-z} = -S^z$  for all  $S^z$ . It is seen that also  $S^z$  always comes in pairs, so a double change of sign and the Hamiltonian is then invariant. From this symmetry it follows that  $E_{(m)} = E_{(-m)}$  meaning that states with the same size of magnetization, but opposing sign have the same energy. So it is only necessary to solve the system for  $m = \{3/2, 1/2\}$  since the energy is the same for  $m = \{-3/2, -1/2\}$ , respectively. There is one more symmetry for this system. There is spatial mirror symmetry along a vertical axis, as illustrated in figure 4.2. This symmetry is also found for H and it can be used to set up states that are symmetrical or antisymmetrical with respect to the mirror symmetry. This symmetry is seen used later. As mentioned earlier, these symmetries are general for a lot of spin systems and the real advantage of exploiting this can be seen, if the calculation for the next model (N = 6 model) is read in the appendix B. But first the energy and magnetization levels for the N = 3 model is found.

#### For subspace m = 3/2

The state in figure 4.1 has m = 3/2, and it is the only state in this subspace. The spin flip operators can not flip any spins simultaneously. So this state is an eigenstate with the energy:

$$E_{\left(m=\frac{3}{2}\right)} = E_{\left(m=-\frac{3}{2}\right)} = \frac{3}{4}J_1 \tag{4.3}$$

#### For subspace m = 1/2

In this subspace there are 3 states, witch are shown in figure 4.3. Now it can be seen that



Figure 4.3: States for with m = 1/2. The label above each state is referred to in the text.

state 2 and 3 are mirror images of each other along the vertical axis. The symmetrical and antisymmetrical states are:  $|2+3\rangle = 1/\sqrt{2}(|2\rangle + |3\rangle)$  and  $|2-3\rangle$ . It is possible to find out which states that couple to each other by calculating how the Hamiltonian work

#### 4.2. MODEL N = 3

on each state:

$$H|1\rangle = \frac{1-2}{4}J_1|1\rangle + \frac{1}{2}J_1(|2\rangle + |3\rangle)$$
(4.4)

$$= -\frac{1}{4}J_1 |1\rangle + \frac{1}{\sqrt{2}}J_1 |2+3\rangle$$
(4.5)

$$H|2+3\rangle = -\frac{1}{4}J_1|2+3\rangle + \frac{1}{2\sqrt{2}}J_1(|1\rangle + |3\rangle + |1\rangle + |2\rangle)$$
(4.6)

$$= \frac{1}{4}J_1 |2+3\rangle + \frac{1}{\sqrt{2}}J_1 |1\rangle$$
(4.7)

$$H|2-3\rangle = -\frac{1}{4}J_1|2+3\rangle + \frac{1}{2\sqrt{2}}J_1(|1\rangle + |3\rangle - |1\rangle - |2\rangle)$$
(4.8)

$$= -\frac{3}{4}J_1 |2 - 3\rangle \tag{4.9}$$

It is seen that state  $|1\rangle$  and  $|2+3\rangle$  couple and that  $|2-3\rangle$  is an eigenstate with energy  $E = -\frac{3}{4}J_1$ . To find the energies for the two remaining states the Hamiltonian matrix has to be diagonalized:

$$\begin{array}{c} |1\rangle & |2+3\rangle \\ \langle 1| & \left( -\frac{1}{4}J_1 & \frac{1}{\sqrt{2}}J_1 \\ \frac{1}{\sqrt{2}}J_1 & \frac{1}{4}J_1 \end{array} \right) \end{array}$$
(4.10)

,

This matrix can easily be diagonalized by solving the characteristic polynomial:

$$\left(-\frac{1}{4}J_1 - E\right)\left(\frac{1}{4}J_1 - E\right) - \frac{1}{2}J_1^2 = 0 \implies E = \begin{cases} \frac{3}{4}J_1 \\ -\frac{3}{4}J_1 \end{cases}$$
(4.11)

#### 4.2.2 Energies for the total N = 3 model

From this the following scheme for the energies of the 8 states can be found. Here the spin flip symmetry has been used for the energies in the subspaces with m = -1/2 and m = -3/2:

$$E = \frac{3J_1}{4}, \quad m_i = \begin{cases} 3/2 & 1 \text{ state} \\ 1/2 & 1 \text{ state} \\ -1/2 & 1 \text{ state} \\ -3/2 & 1 \text{ state} \end{cases} \quad E = -\frac{3J_1}{4}, \quad m_i = \begin{cases} 1/2 & 2 \text{ states} \\ -1/2 & 2 \text{ states} \end{cases}$$
(4.12)

As mentioned earlier, this model is the simplest model that captures spin frustration. This is also seen from the energy scheme in equation 4.12. It is here seen that the ground state

is 4 times degenerate with two different magnetization levels;  $m = \pm 1/2$ . This is the same degeneracy as a system with one free spin. A system like this is expected to have a paramagnetic susceptibility curve at temperatures  $k_bT \ll 3/2J_1$  since  $3/2J_1$  is the size of energy needed to break the singlet bond of the triangle. Only 1/3 of the spins will act as free spins because the two other spins form a singlet bond. This could be found by doing a Curie-Weiss fit for the susceptibility at low temperature.

#### 4.2.3 Comparing model N = 3 and data

In order to compare this model with the data, the inverse susceptibility was chosen. The inverse susceptibility for the N = 3 model is found as:

$$\frac{1}{\chi} = \frac{1}{\chi^0} \frac{\sum_{states} \exp\left(-\frac{E_i}{k_b T}\right)}{\sum_{states} m_i^2 \exp\left(-\frac{E_i}{k_b T}\right)}$$
(4.13)

Here  $E_i$  is the energy of state *i* which depends on the exchange constant found in equation 4.12 and  $m_i$  is the magnetization for state *i* also found in equation 4.12.  $1/\chi^0$  is a scaling constant to make the units right. So the independent parameters for the inverse susceptibility is the exchange constant  $J_1$  and the scaling  $1/\chi^0$ . The model N = 3 and the data from crystal P are plotted in figure 4.4. Here the independent parameters ( $J_1$ and  $1/\chi^0$ ) are adjusted so that the kink at high temperature in the data matches the kink for N = 3 model. To estimate the uncertainty for the fitted value of  $J_1$ , dashed lines are plotted where the uncertainty is added or subtracted. This also makes it possible to get a feeling of how sensitive the model depends on the exchange constant.

For the N = 3 model there is two Curie-Weiss regions. At low temperatures the susceptibility acts as a paramagnet, meaning that the inverse susceptibility tends to zero as the temperature goes to zero. Another Curie-Weiss region is seen at high temperature, where the thermal energy is high enough to break the singlet bond in the triangles and the system acts as a regular antiferromagnet.

The independent parameters for this model, were adjusted so that the curve fit the kink manually and not doing a chi square fit, the reason is that an initial guess for the kink at high temperatures was expected to be caused by a change in the ordering of the spins at the energy scale of the kink, and the ordering is determined by  $J_1$ . So by adjusting  $J_1$  to fit the kink, a good guess for the size of  $J_1$  is found. The model is too simple to capture an exact match for the Curie-Weiss regions, since it does not have the same amount of spins as the full N = 24 model. But it seems possible that the kink at high temperatures is due to a change of the ordering, at the energy scale of  $J_1$ . With this model the size of the  $J_1$  exchange constant is  $J_1 = 23.5 \pm 0.5$  meV.



Figure 4.4: The N = 3 model compared to the data, with the model parameters plotted. The dashed blue lines are the curves that come by adding or subtracting the uncertainty for the exchange constant.

### 4.3 The N = 6 model

The next move is to extend the model, so that it may describe the kink at low temperatures as well. This is done by letting two triangles interact via the exchange constant  $J_2$ . A state for this N = 6 model can be seen in figure 4.5. The calculation for this system is in



**Figure 4.5:** The N = 6 model. This system has 6 spins and two different exchange interactions written as  $J_1$  and  $J_2$  in the figure.

principle done the same way as for the N = 3 model although there are a lot more states and it is easy to make mistakes (and a lot of mistakes were made during the calculations, but they should be fixed by now  $\ddot{\smile}$ ). The full calculations will not be given here, but they can be found in appendix B. Here the first order approximation in terms of  $J_2/J_1$  of the energies will be given:

$$\begin{split} E_{(m=3)} &= E_{(m=-3)} &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State} \quad (4.14) \\ E_{(m=2)} &= E_{(m=-2)} \overset{\mathcal{O}\left(\frac{J_1^2}{J_1^2}\right)}{\approx} \begin{cases} &\frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}}{\frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^*}{\frac{1}{4}J_4 \quad 3 \text{ States}} \end{cases} 2 \times 6 \text{ States} \quad (4.15) \\ &\frac{1}{4}J_4 \quad 3 \text{ States}}{\frac{1}{2}J_2 \quad 1 \text{ State}^*} \end{cases} \\ E_{(m=1)} &= E_{(m=-1)} \overset{\mathcal{O}\left(\frac{J_1^2}{J_1^2}\right)}{\approx} \begin{cases} &\frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}^*}{\frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^*} \end{cases} \\ &= \frac{1}{5}J_2 \quad 2 \text{ States}^* \end{cases} 2 \times 15 \text{ States} \quad (4.16) \\ &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 + \frac{1}{36}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 2 \text{ States}^*} \end{cases} \\ &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*} \end{cases} \\ &= \frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*} \end{cases} \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 2 \text{ States}^*}{-\frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*}{-\frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^*} \end{cases} \\ &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 + \frac{1}{36}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 3 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* \\ &= \frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text$$

All states marked with a \* are first order approximations.

From these energies it can be seen that the system does not have a degenerate ground state. The singlet ground state is found in the subspace m = 0 and it is  $-\frac{3}{2}J_1 - \frac{3}{4}J_2$ . This means that the susceptibility would go to zero at low temperatures, since there is an energy gap (of  $\frac{7}{12}J_2$ ) to the first excited (triplet) state. From this, it would be expected to see an ordering on this energy scale of  $J_2$  and that this would be the energy scale for the kink at the low temperatures.



Figure 4.6: The N = 6 model compared to the data, with the model parameters plotted. The dashed blue lines are the curves that come by adding or subtracting the uncertainty for the exchange constant.

#### 4.3.1 Comparing model N = 6 and data

A plot of the data from crystal P and the N = 6 model can be seen in figure 4.6. The same numerical model as for the N = 3 model has been used. It can be seen in equation 4.13. With the energies for the N = 6 model there are now three independent parameters;  $J_1$ ,  $J_2$  and  $1/\chi^0$ . The model was fitted to the data from 100 K to 300 K, to make sure that the upper Curie-Weiss region was correct and that the kink at high temperatures was at the right place. Here the fitted parameters were  $J_1$  and  $1/\chi^0$ , since they are the dominant variables in this temperature range. This means that the  $J_2$  parameter was locked to a specified value. When the fit was satisfying for the fitted area the,  $J_2$  parameter was adjusted, so that the kink at 3 - 4 K happened at the same temperature, even though the magnetization was not the same. This was done manually. When the low temperature kinks were above each other, the procedure was started over again with fitting first and then manual adjusting until the fit did not change anymore.

It is seen that this model fits quite well all the way down to 50 K. But it is not an exact fit for the temperature range above 50 K. The Curie-Weiss behavior at high temperatures has a slope which is too small and the kink at high temperatures is overshot, meaning that the kink happens at a lower temperature in the model, than in the data. But the real difference comes at temperatures below 40 K. Here there is a big difference between the model and the data. One explanation for this could be that the model is too simple. The simplification can be split in to two types. One type is that the model is only a fraction of the whole system and hereby not capturing the exact behavior. Another type could be that this model only has the nearest neighbor interaction, even though the exchange might extent further than just the nearest neighbors. An argument for this explanation could be that the width of the ordering is wider than for the N = 6 model. If another exchange constant is on the scale of the  $J_2$  exchange constant the ordering could happen over a wider temperature range.

Although the model is not an exact description of the data, it might provide a good guess for the sizes of the exchange constants. The best guesses was found to be:  $J_1 = 18.87\pm0.3 \text{ meV}$  and  $J_2 = 0.85\pm0.15 \text{ meV}$ . Again the error was estimated by looking at how the model changes when changing the exchange constants. In section 3.2.3 a guess for the exchange constants was found with the values:  $J_1 = 14.32\pm0.05 \text{ meV}$  and  $J_2 = 1.84\pm0.04 \text{ meV}$ . The error for the values can not justify these values as being the same but the values are close and there is probably a significant systematic error for both values. But to have a guess for the size of the systematical error more work needs to be done.

With a guess for the exchange constants the linear approximation for the susceptibility  $(\chi = \partial M/\partial H \approx M/H)$  can be tested. The minimum energy scale of the spin configurations is on the order of  $J_2 \sim 10^{-3}$  eV and the the Zeeman energy is  $\mu_B 0.1 \text{ T} \sim 10^{-6}$  eV. So the approximation is valid.

## Chapter 5

# Conclusion

The crystal structure was measured and from this measurement it was found that all the crystals where Boleite.

The susceptibility for 10 single crystals was measured and it was found that the crystals could be separated in to two types. The type with an ordering at 3 - 4 K was chosen to be the basis for the studies in this rapport.

It was made possible to get a qualitatively understanding of the susceptibility curve from the frustrated spin triangles.

Models to simulate the susceptibility curves were set up and magnetization and energy levels for two models N = 3 and N = 6 were found.

It was possible to derive a guess for two exchange constants for the Boleite crystal. They where found to be;  $J_1 = 18.87 \pm 0.3$  meV and  $J_2 = 0.85 \pm 0.15$  meV in the modeling data and  $J_1 = 14.32 \pm 0.05$  meV and  $J_2 = 1.84 \pm 0.04$  meV in the Curie-Weiss fit. The model from which the size of the exchange constant was found did not make an exact fit with the data. Especially below 40 K the difference between the model and data was significant. The reason for this difference is not fully understood, but could be due to the simplified N = 6 model.

### 5.1 Outlook

The main reason that the size of the exchange constants are so interesting is that further analyses of the magnetic properties of Boleite include inelastic neutron scattering experiments. But without an initial guess for the main exchange constants it can be very difficult to know where to begin. Beamtime at the ILL in France in september-october 2014 for these studies is obtained. So the studies in this report serves as a foundation for further neutron experiments with Boleite and they also make it possible to find out which crystals had the same magnetic behavior at low temperatures.

The model might also be improved. This could be done by finding numerical solutions for the full N = 24 model. This process has already begun via the use of a program called RLexact[15], but the modeling has not yet reached a useful level. Another method that can be used to emulate the data is the so called Quantum Monte Carlo (QMC) [16] [17]. This is also a numerical model that will be applied in the future.

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## Appendix A

## Determining crystal structure

In order to check if the crystals where Boleite or not a diffraction experiment was done for each crystal. The reason to choose diffraction is that the main crystal often being confused with Boleite is the crystal Pseudoboleite and one of the differences between the two crystals is their unit cell. The unit cell of Boleite is cubic whereas the unit cell of Pseudoboleite is tetragonal. This difference is easy to measure with a scattering experiment. From solid state physics it is known that a lattice can make a diffraction pattern depending on Bragg's law. This is given by:

$$n\lambda = 2d\sin\theta \tag{A.1}$$

Where  $\lambda$  is the wave length of the incoming light, d is the distance between lattice plans and  $\theta$  is the angle between the incoming beam and the lattice plan. For this experiment a so called X-ray Laue was used. This type of machine is specially made to do diffraction of a single crystal. A single crystal is a crystal where the whole single crystal is translation invariant with respect to the unit cell for the whole crystal. This is opposed to a crystal powder where the translation invariance is only present for each little grain of crystal in the crystal powder. The main difference between these two types of scattering is that a single crystal will only fulfill the Bragg law in one direction as opposed to the scattering from a powder where each crystal grain might have different orientation and this would make a cone of diffracted light. The type of X-ray Laue used was backscattering. The principle of backscattering is illustrated in figure A.1. For this X-ray Laue the source of the X-rays is a heated wire of Tungsten where a voltage difference of 40 kV is made between the Tungsten wire and a metal plate. This type of X-ray source makes a spectrum of X-rays. So the Bragg law may be fulfilled for many different wave lengths at the same time. But since it is single crystal, scattering will only be fulfilled in certain directions, while the diffraction may be caused by X-rays with different wave lengths. By the use of a program called QLaue it is possible to make theoretical diffraction patterns. The program needs information about the unit cell, position of the basis atoms and the material of cathode with the voltage for the X-ray source. From the explanation of the difference between a single crystal and a crystal powder it should be clear that one of the main differences is that diffraction for the single crystal is directional dependent, meaning that the orientation of the crystal relative to the incoming beam is important. From experience it is known that the diffraction pattern differs quite much between a cubic unit cell and a tetragonal unit cell, if the incoming beam is radiated in the (1,1,1) direction with respect to the cubic unit cell. For the Boleite crystals this happens when the beam goes directly into one of the corners of the cubic crystals. The setup for this can be seen in figure A.2. The theoretical diffraction patterns made in QLaue can be seen in figure A.3 for Boleite and figure A.4 for Pseudoboleite. A difference that is easy to recognize, is the diagonal lines, which is not there for Pseudoboleite. The measured diffraction pattern for all the crystals can be seen in the figures A.5-A.18. From this is clearly seen that they are all Boleite.



the detector screen, (in this case

an X-ray sensitive CCD-array (Foto-

cell)), then hits the sample and

sends back a scattering signal which

is detected by the CCD-array.

Figure A.2: A picture of our setup. The crystal is mounted on a spherical goniometer at the angle  $\omega = 45^{\circ}$ and  $\chi = 35.5^{\circ}$ .



Figure A.3: The diffraction pattern for Boleite, made in QLaue.

Figure A.4: The diffraction pattern for Pseudoboleite, made in QLaue.



Figure A.5: X-ray diffraction pattern for Crystal A. The diagonal lines are clearly seen, which means that the crystal is Boleite.

Figure A.6: X-ray diffraction pattern for Crystal B. The diagonal lines are clearly seen, which means that the crystal is Boleite.



Figure A.7: Crystal C.

Figure A.8: Crystal D



Figure A.9: Crystal E.

Figure A.10: Crystal F



Figure A.11: Crystal G.

Figure A.12: Crystal H



Figure A.13: Crystal K.

Figure A.14: Crystal M



Figure A.15: Crystal N.

Figure A.16: Crystal P



Figure A.17: Crystal Q.

Figure A.18: Crystal R

## Appendix B

# Model N = 6 calculations

## B.1 Introduction to the model

In this section the calculations for the energies and magnetization levels for the N = 6 model are made.

One state of the system can be seen in figure B.1. The Hamiltonian for N = 6 model can



Figure B.1: One state for The N = 6 model. This is the only state in the subspace with m = 3.

be written as:

$$H = \sum_{i=\langle i,j\rangle} J_1 \left( S_i^z S_j^z + \frac{1}{2} \left( S_i^- S_j^+ + S_i^+ S_j^- \right) \right) + J_2 \left( S_3^z S_4^z + \frac{1}{2} \left( S_3^- S_4^+ + S_3^+ S_4^- \right) \right)$$
(B.1)

Here  $\langle i, j \rangle$  is a short for the nearest neighbors in the triangle structure. This system has 6 spins so there are  $2^6 = 64$  unique states. Before going head on with the calculations for

this system, the symmetries for this system will be mentioned.

As for the N = 3 model the Hamiltonian can only couple states with the same magnetization and there is also spin flip symmetry for this system, so that subspaces with the same magnetization have the same energy levels. From this the following subspaces are the onlyones that needs to be solved;  $m = \{3, 2, 1, 0\}$ . This system has two types of spatial symmetry from which independent orthogonal states can be made. The spatial symmetries can be seen in figure B.2. How this works will be shown later.



Figure B.2: The spatial symmetry for the N = 6 model

### **B.2** The calculations

#### B.2.1 m = 3 subspace

The first subspace to be solved is the subspace with m = 3. There is only one state in this subspace and it can be seen in figure B.1. The energy for this is found to be:

$$E_{(m=3)} = E_{(m=-3)} = \frac{3}{2}J_1 + \frac{1}{4}J_2$$
(B.2)

#### B.2.2 m = 2 subspace

The second subspace is the one with m = 2. The states for this system can be seen in figure B.3. Now the symmetries can be used to find states that do not couple. By using the horizontal symmetry the following states can be found to couple:  $|1\rangle$  and  $|2\rangle$ .  $|3\rangle$  and  $|4\rangle$ .  $|5\rangle$  and  $|6\rangle$ . With this, the following 6 states can be made:  $|1 \pm 2\rangle$ ,  $|3 \pm 4\rangle$  and  $|5 \pm 6\rangle$ . Here the plus and minus state is now independent. From the vertical symmetry it can be seen that the following states can couple:  $|1\rangle$  and  $|3\rangle$ .  $|2\rangle$  and  $|4\rangle$ . The 4 states that would seem obvious are:  $|1 \pm 2 + 1 \pm 4\rangle$ ,  $|1 \pm 2 - 1 \pm 4\rangle$ . But it turns out the actual independent states are:  $|1 \pm 2 + 1 \pm 4\rangle$ ,  $|1 - 3\rangle$  and  $|2 - 4\rangle$ . Now, by calculating the work of the Hamiltonian on each state it can be seen which states couple.



**Figure B.3:** States for m = 2. The states are labeled according to the derivation in the text

$$H\left|1\pm2+3\pm4\right\rangle = \left(\frac{1}{2}J_{1}+\frac{1}{4}J_{2}\right)\left|1\pm2+3\pm4\right\rangle + \frac{J_{1}}{4}\left(\overbrace{|3\rangle+|5\rangle}^{|1\rangle}\pm\overbrace{|4\rangle\pm|6\rangle}^{|2\rangle}+\overbrace{|1\rangle+|5\rangle}^{|3\rangle}\pm\overbrace{|2\rangle\pm|6\rangle}^{|4\rangle}\right)$$

$$(B.3)$$

$$= \left(J_1 + \frac{1}{4}J_2\right)|1 \pm 2 + 3 \pm 4\rangle + \frac{1}{\sqrt{2}}J_1|5 \pm 6\rangle$$
(B.4)

Here the notation  $|3\rangle + |5\rangle$  means that state  $|1\rangle$  can go into state  $|3\rangle$  or  $|5\rangle$  by flipping 2 allowed spins. This will not be written for all calculations but the logic will go through all the calculations with the state having the lowest number being the one written first and so on. Now for the state  $|5 \pm 6\rangle$ :

$$H|5\pm6\rangle = \left(\frac{1}{2}J_1 - \frac{1}{4}J_2\right)|5\pm6\rangle + \frac{1}{2\sqrt{2}}J_2\left(|6\rangle\pm|5\rangle\right) + \frac{1}{2\sqrt{2}}J_1\left(|1\rangle+|3\rangle\pm|2\rangle\pm|4\rangle\right)$$
(B.5)

$$= \left(\frac{1}{2}J_1 + \frac{1}{4}J_2(-1\pm 2)\right)|5\pm 6\rangle + \frac{1}{\sqrt{2}}J_1|1\pm 2 + 3\pm 4\rangle \tag{B.6}$$

Now for  $|1-3\rangle$ :

$$H|1-3\rangle = \left(\frac{1}{2}J_1 + \frac{1}{4}J_2\right)|1-3\rangle + \frac{1}{2\sqrt{2}}J_1(|3\rangle + |5\rangle - |1\rangle - |5\rangle)$$
(B.7)

$$=\frac{1}{4}J_2\left|1-3\right\rangle\tag{B.8}$$

And lastly for  $|2-4\rangle$ :

$$H|2-4\rangle = \left(\frac{1}{2}J_1 + \frac{1}{4}J_2\right)|2-4\rangle + \frac{1}{2\sqrt{2}}J_1(|4\rangle + |6\rangle - |2\rangle - |6\rangle)$$
(B.9)

$$=\frac{1}{4}J_2\left|2-4\right\rangle\tag{B.10}$$

From this it can be concluded that the following subspaces have to be diagonalized:

1) 
$$|1+2+3+4\rangle, |5+6\rangle$$
 (B.11)

2)  $|1-2+3-4\rangle, |5-6\rangle$  (B.12)

$$3) \left| 1 - 3 \right\rangle \tag{B.13}$$

$$4) \left| 2 - 4 \right\rangle \tag{B.14}$$

The last two is seen to be eigenstates.

The Hamiltonian matrix can be setup from the calculation above. The matrix for the subspace denoted by 1) is given by:

$$|1+2+3+4\rangle \quad |5+6\rangle \langle 1+2+3+4| \begin{pmatrix} J_1 + \frac{1}{4}J_2 & \frac{1}{\sqrt{2}}J_1 \\ \frac{1}{\sqrt{2}}J_1 & \frac{1}{2}J_1 + \frac{1}{4}J_2 \end{pmatrix}$$
(B.15)

And for 2):

$$|1 - 2 + 3 - 4\rangle \quad |5 - 6\rangle$$

$$\langle 1 - 2 + 3 - 4| \begin{pmatrix} J_1 + \frac{1}{4}J_2 & \frac{1}{\sqrt{2}}J_1 \\ \frac{1}{\sqrt{2}}J_1 & \frac{1}{2}J_1 - \frac{3}{4}J_2 \end{pmatrix}$$
(B.16)

By diagonalizing these matrices the remaining energies can be found. The characteristic polynomials and solutions are:

1) 
$$E^2 - \left(\frac{3}{2}J_1 + \frac{1}{2}J_2\right)E + \frac{3}{8}J_1J_2 + \frac{1}{16}J_2^2 = 0 \implies$$
 (B.17)

$$E = \begin{cases} \frac{3}{2}J_1 + \frac{1}{4}J_2 \\ \frac{1}{4}J_2 \end{cases}$$
(B.18)

2) 
$$E^{2} + \left(-\frac{3}{2}J_{1} + \frac{1}{2}J_{2}\right)E - \frac{5}{8}J_{1}J_{2} - \frac{3}{16}J_{2}^{2} = 0 \implies$$
 (B.19)

$$E = \frac{3}{4}J_1 - \frac{1}{4}J_2 \pm \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2}{J_1^2}\right)}{\approx} \begin{cases} \frac{3}{2}J_1 - \frac{1}{12}J_2\\ -\frac{5}{12}J_2 \end{cases}$$
(B.20)

#### B.2. THE CALCULATIONS

So the energies for the subspace m = 2 are:

$$E_{(m=2)} = \begin{cases} \frac{\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx \frac{J_1^2}{2}J_1 - \frac{1}{12}J_2 & 1 \text{ State} \\ \frac{1}{4}J_4 & 3 \text{ States} \end{cases}$$

$$\left( \frac{\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}}{\frac{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} - \frac{5}{12}J_2 \qquad 1 \text{ State} \right) \tag{B.21}$$

#### B.2.3 m = 1 subspace

The states for the m = 1 subspace can be seen in figure B.4. The exact way of using the symmetries will not be given, but it is the same as for the m = 2 subspace; looking for states that couple via the spatial symmetry. By the use of the symmetry and the knowledge of how the Hamiltonian works on the states, the following states can be found to couple:

$$5) |1+2+3+4\rangle, |5+6+7+8\rangle, |9\rangle, |10+11\rangle, |12+13\rangle, |14+15\rangle$$
(B.22)

6) 
$$|1+2-3-4\rangle, |5-6-7+8\rangle, |10-11\rangle$$
 (B.23)

$$7) |1 - 2 + 3 - 4\rangle, |5 - 6 + 7 - 8\rangle, |14 - 15\rangle$$
(B.24)

$$8) |1 - 2 - 3 + 4\rangle, |5 + 6 - 7 - 8\rangle, |12 - 13\rangle$$
(B.25)

The work of the Hamiltonian for these states are:

$$H |1+2\pm 3\pm 4\rangle = \left(-\frac{1}{2}J_1 - \frac{1}{4}J_2\right) |1+2\pm 3\pm 4\rangle + \frac{1}{4}J_2 (|6\rangle + |7\rangle \pm |8\rangle \pm |5\rangle) + \frac{1}{4}J_1 (|3\rangle + |9\rangle + |10\rangle + |12\rangle + |4\rangle + |9\rangle + |10\rangle + |13\rangle \pm (|1\rangle + |9\rangle + |11\rangle + |13\rangle + |2\rangle + |9\rangle + |11\rangle + |12\rangle))$$
(B.26)  
$$= \left(J_1 \left(-\frac{1}{2}\pm\frac{1}{2}\right) - \frac{1}{4}J_2\right) |1+2\pm 3\pm 4\rangle \pm \frac{1}{2}J_2 |5\pm 6\pm 7+8\rangle + J_1 \left(\frac{1}{2}\pm\frac{1}{2}\right) |9\rangle + \frac{1}{\sqrt{2}}J_1 |10\pm 11\rangle + \frac{1}{\sqrt{2}}J_1 |12+13\rangle$$
(B.27)



Figure B.4: States for m = 1. The states are labeled according to the derivation in the text

$$H |1 - 2 \pm 3 \mp 4\rangle = \left(-\frac{1}{2}J_1 - \frac{1}{4}J_2\right) |1 - 2 \pm 3 \mp 4\rangle + \frac{1}{4}J_2 (|6\rangle - |7\rangle \pm |8\rangle \mp |5\rangle) + \frac{1}{4}J_1 (|3\rangle + |9\rangle + |10\rangle + |12\rangle - |4\rangle - |9\rangle - |10\rangle - |13\rangle \pm (|1\rangle + |9\rangle + |11\rangle + |13\rangle) \mp (|2\rangle + |9\rangle + |11\rangle + |12\rangle))$$
(B.28)  
$$= \left(J_1 \left(-\frac{1}{2} \pm \frac{1}{2}\right) - \frac{1}{4}J_2\right) |1 - 2 \pm 3 \mp 4\rangle \mp \frac{1}{2}J_2 |5 \mp 6 \pm 7 - 8\rangle + \frac{1}{\sqrt{2}}J_1 \left(\frac{1}{2} \mp \frac{1}{2}\right) |12 - 13\rangle$$
(B.29)

$$H |5 \pm 6 \pm 7 + 8\rangle = \left(-\frac{1}{2}J_1 - \frac{1}{4}J_2\right) |5 \pm 6 \pm 7 + 8\rangle + \frac{1}{4}J_2 (|4\rangle \pm |1\rangle \pm |2\rangle + |3\rangle) + \frac{1}{4}J_1 (|7\rangle + |14\rangle \pm |8\rangle \pm |15\rangle \pm |5\rangle \pm |14\rangle + |6\rangle + |15\rangle)$$
(B.30)  
$$= \left(J_1 \left(\frac{1}{2} \pm \frac{1}{2}\right) - \frac{1}{4}J_2\right) |5 \pm 6 \pm 7 + 8\rangle \pm \frac{1}{2}J_2 |1 + 2 \pm 3 \pm 4\rangle + \frac{1}{\sqrt{2}}J_1 \left(\frac{1}{2} \pm \frac{1}{2}\right) |14 + 15\rangle$$
(B.31)

$$H |5 \mp 6 \pm 7 - 8\rangle = \left(-\frac{1}{2}J_1 - \frac{1}{4}J_2\right) |5 \mp 6 \pm 7 - 8\rangle + \frac{1}{4}J_2 (|4\rangle \mp |1\rangle \pm |2\rangle - |3\rangle) + \frac{1}{4}J_1 (|7\rangle + |14\rangle \mp |8\rangle \mp |15\rangle \pm |5\rangle \pm |14\rangle - |6\rangle - |15\rangle)$$
(B.32)  
$$= \left(J_1 \left(\frac{1}{2} \pm \frac{1}{2}\right) - \frac{1}{4}J_2\right) |5 \mp 6 \pm 7 - 8\rangle \pm \frac{1}{2}J_2 |1 - 2 \pm 3 \mp 4\rangle + \frac{1}{\sqrt{2}}J_1 \left(\frac{1}{2} \pm \frac{1}{2}\right) |14 - 15\rangle$$
(B.33)

$$H|9\rangle = \left(-\frac{1}{2}J_1 + \frac{1}{4}J_2\right)|9\rangle + \frac{1}{2}J_1\left(|1\rangle + |2\rangle + |3\rangle + |4\rangle\right)$$
(B.34)

$$= \left(-\frac{1}{2}J_1 + \frac{1}{4}J_2\right)|9\rangle + J_1|1 + 2 + 3 + 4\rangle \tag{B.35}$$

$$H |10 \pm 11\rangle = \left( -\frac{1}{2}J_1 + \frac{1}{4}J_2 \right) |10 \pm 11\rangle + \frac{1}{2\sqrt{2}}J_1 (|1\rangle + |2\rangle + |12\rangle + |13\rangle \pm (|3\rangle + |4\rangle + |12\rangle + |13\rangle))$$
(B.36)  
$$= \left( -\frac{1}{2}J_1 + \frac{1}{4}J_2 \right) |10 \pm 11\rangle + \frac{1}{\sqrt{2}}J_1 |1 + 2 \pm 3 \pm 4\rangle + J_1 \left( \frac{1}{2} \pm \frac{1}{2} \right) |12 + 13\rangle$$
(B.37)

$$H |12 \pm 13\rangle = \left( -\frac{1}{2}J_1 + \frac{1}{4}J_2 \right) |12 \pm 13\rangle + \frac{1}{2\sqrt{2}}J_1 (|1\rangle + |4\rangle + |10\rangle + |11\rangle \pm (|2\rangle + |3\rangle + |10\rangle + |11\rangle))$$
(B.38)  
$$= \left( -\frac{1}{2}J_1 + \frac{1}{4}J_2 \right) |12 \pm 13\rangle + \frac{1}{\sqrt{2}}J_1 |1 \pm 2 \pm 3 + 4\rangle + J_1 \left( \frac{1}{2} \pm \frac{1}{2} \right) |10 + 11\rangle$$
(B.39)

$$H |14 \pm 15\rangle = \left(\frac{1}{2}J_1 + \frac{1}{4}J_2\right) |14 \pm 15\rangle + \frac{1}{2\sqrt{2}}J_1 (|5\rangle + |7\rangle \pm (|6\rangle + |8\rangle))$$
(B.40)

$$= \left(-\frac{1}{2}J_1 + \frac{1}{4}J_2\right) |14 \pm 15\rangle + \frac{1}{\sqrt{2}}J_1 |5 \pm 6 + 7 \pm 8\rangle \tag{B.41}$$

#### B.2. THE CALCULATIONS

Now the Hamiltonian matrices can be set up; For subspace 5):

For subspace 6):

$$\begin{array}{c|c} |1+2-3-4\rangle & |5-6-7+8\rangle & |10-11\rangle \\ \langle 1+2-3-4| \begin{pmatrix} -J_1 - \frac{1}{4}J_2 & -\frac{1}{2}J_2 & \frac{1}{\sqrt{2}}J_1 \\ -\frac{1}{2}J_2 & -\frac{1}{4}J_2 & 0 \\ \langle 10-11| & \frac{1}{\sqrt{2}}J_1 & 0 & -\frac{1}{2}J_1 + \frac{1}{4}J_2 \end{pmatrix} \end{array}$$
(B.43)

For subspace 7):

$$\begin{array}{c|c} |1-2-3+4\rangle & |5+6-7-8\rangle & |12-13\rangle \\ \langle 1-2-3+4| \begin{pmatrix} -J_1 - \frac{1}{4}J_2 & \frac{1}{2}J_2 & \frac{1}{\sqrt{2}}J_1 \\ \frac{1}{2}J_2 & -\frac{1}{4}J_2 & 0 \\ \langle 12-13| & \frac{1}{\sqrt{2}}J_1 & 0 & -\frac{1}{2}J_1 + \frac{1}{4}J_2 \end{pmatrix} \end{array}$$
(B.44)

And at last subspace 8):

$$\begin{array}{c|c} |1-2+3-4\rangle & |5-6+7-8\rangle & |14-15\rangle \\ \langle 1+2-3-4| \begin{pmatrix} -\frac{1}{4}J_2 & -\frac{1}{2}J_2 & 0\\ -\frac{1}{2}J_2 & J_1 - \frac{1}{4}J_2 & \frac{1}{\sqrt{2}}J_1\\ & 0 & \frac{1}{\sqrt{2}}J_1 & \frac{1}{2}J_1 + \frac{1}{4}J_2 \end{pmatrix} \end{array}$$
(B.45)

The eigenvalues is not trivial to find by hand, but Maple can easily find them. It turns out that subspace 5) has three trivial eigenvalues and three nontrivial solutions so the characteristic polynomial can be factorized into a 3rd degree polynomial and three simple factors. Subspace 6) and 7) have the same eigenvalues. One of them is trivial so the characteristic polynomial can be made into a 2nd degree polynomial. The same goes for subspace 8). It also has one trivial eigenvalue. The solution for the 3rd degree polynomial can be found analytically, but it is not very informative to give here, so the characteristic polynomial is just presented. Below the energies can be seen:

5) 
$$E = \begin{cases} \frac{\frac{3}{2}J_1 + \frac{1}{4}J_2}{\frac{1}{4}J_2} \\ -\frac{3}{2}J_1 + \frac{1}{4}J_2 \\ E^3 + \frac{1}{4}E^2J_2 + \left(-\frac{5}{16}J_2^2 - \frac{9}{4}J_1^2 + \frac{1}{2}J_1J_2\right)E + \frac{1}{16}J_1^2J_2 - \frac{1}{8}J_1J_2^2 + \frac{3}{64}J_2^3 = 0 \end{cases}$$
(B.46)

6) 
$$E = \begin{cases} \frac{\frac{1}{4}J_2}{-\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{5}{12}J_2 \qquad (B.47) \\ -\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{3}{2}J_1 - \frac{1}{12}J_2 \end{cases}$$

7) 
$$E = \begin{cases} \frac{\frac{1}{4}J_2}{-\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} \approx -\frac{5}{12}J_2 \\ -\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} \approx -\frac{3}{2}J_1 - \frac{1}{12}J_2 \end{cases}$$
(B.48)

8) 
$$E = \begin{cases} \frac{\frac{1}{4}J_2}{\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} & \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \\ \frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}} & \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \\ \approx -\frac{5}{12}J_2 \end{cases}$$
(B.49) (B.50)

In Maple the solution for the 3rd degree polynomial can be taylor expanded to first order

in  $J_2/J_1$  to give:

$$E^{3} + \frac{1}{4}E^{2}J_{2} + \left(-\frac{5}{16}J_{2}^{2} - \frac{9}{4}J_{1}^{2} + \frac{1}{2}J_{1}J_{2}\right)E + \frac{1}{16}J_{1}^{2}J_{2} - \frac{1}{8}J_{1}J_{2}^{2} + \frac{3}{64}J_{2}^{3} = 0 \implies (B.51)$$

$$E \approx \left\{ \begin{array}{l} \mathcal{O}\left(\frac{J_2^*}{J_1^2}\right) \\ \approx \end{array} \right\} = \begin{cases} \frac{3}{2}J_1 - \frac{11}{36}J_2 \\ \frac{1}{36}J_2 \\ -\frac{3}{2}J_1 + \frac{1}{36}J_2 \end{cases}$$
(B.52)

With this the following scheme of energies can be found for the subspace m = 1:

$$\frac{\frac{3}{2}J_1 + \frac{1}{4}J_2}{\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1 \sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \frac{\frac{3}{2}J_1 - \frac{1}{12}J_2}{\frac{1}{2}J_2} \qquad 1 \text{ State}$$

$$\overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \frac{\frac{3}{2}J_1 - \frac{11}{26}J_2}{\frac{1}{2}J_2} \qquad 1 \text{ State}$$

$$\begin{array}{cccc} 2 & 30 & 2 \\ \hline \frac{1}{4}J_2 & & 4 \text{ State} \\ \hline \frac{1}{2}J_2 & & 1 \text{ State} \end{array}$$

$$2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \approx -\frac{5}{12}J_2 \qquad 2 \text{ States}$$

$$2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_2^2}\right)} \approx \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \approx -\frac{5}{12}J_2 \qquad 1 \text{ States}$$

$$\left( \begin{array}{ccc} -\frac{3}{J_1^2} \\ -\frac{3}{J_1^2} \end{array} 
ight) \approx -\frac{3}{12} J_2 & 1 \ \mathrm{States} \\ 1 \ \mathrm{State} & 1 \ \mathrm{State} \\ 1 \ \mathrm{State} & 1 \ \mathrm{State} \end{array}$$

$$-\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx -\frac{3}{2}J_1 - \frac{1}{12}J_2 \qquad 2 \text{ States}$$

#### B.2.4 m = 0 subspace

The states for the last subspace can be seen in figure B.5. For this subspace the spin flip symmetry can not be used to find subspaces with the same energy. But the spin flip symmetry can be used in the same way as the spatial symmetry, to make states that do not couple. The principle is the same - states that spin flip into each other are made in to two independent states. In figure B.5 the states that spin flip into each other is denoted by  $i^{\uparrow}$  and  $i^{\downarrow}$  (the logic behind this notation is that the states with  $\uparrow$  has 2 spins up in the upper triangle and just 1 spin down. It is of cause the opposite for the spin flipped states). The spin flip symmetry can be used to write all states as  $|i^{\uparrow} \pm i^{\downarrow}\rangle = |i^{\pm}\rangle$ . By using the symmetries and the work of the Hamiltonian on the states the following independent

(B.53)

subspaces can be found:

9) 
$$|1^+ + 2^+ + 3^+ + 4^+\rangle, |5^+ + 6^+\rangle, |7^+ + 8^+\rangle, |9^+\rangle, |0^+\rangle$$
 (B.54)

- $10) \quad \left|1^{-}+2^{-}+3^{-}+4^{-}\right\rangle, \left|5^{-}+6^{-}\right\rangle, \left|7^{-}+8^{-}\right\rangle, \left|9^{-}\right\rangle, \left|0^{-}\right\rangle$ (B.55)
- 11)  $|1^+ + 2^+ 3^+ 4^+\rangle, |5^+ 6^+\rangle$ (B.56)
- 12)  $\left|1^{-}+2^{-}-3^{-}-4^{-}\right\rangle, \left|5^{-}-6^{-}\right\rangle$ (B.57)
- 13)  $\left|1^{+}-2^{+}-3^{+}+4^{+}\right\rangle, \left|7^{+}-8^{+}\right\rangle$ (B.58)
- 14)  $|1^{-} 2^{-} 3^{-} + 4^{-}\rangle, |7^{-} 8^{-}\rangle$ 15)  $|1^{+} 2^{+} + 3^{+} 4^{+}\rangle$ (B.59)
- (B.60)
- 16)  $|1^- 2^- + 3^- 4^-\rangle$ (B.61)

The work of the Hamiltonian is found to be:

$$H \left| 1^{\pm} + 2^{\pm} + 3^{\pm} + 4^{\pm} \right\rangle = \left( -\frac{1}{2} J_{1} + \frac{1}{4} J_{2} \right) \left| 1^{\pm} + 2^{\pm} + 3^{\pm} + 4^{\pm} \right\rangle + \frac{1}{4} J_{1} \left( \left| 3^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle + \left| 4^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 8^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle + \left| 1^{\pm} \right\rangle + \left| 6^{\pm} \right\rangle + \left| 8^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle + \left| 2^{\pm} \right\rangle + \left| 6^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle \right)$$
(B.62)  
$$= \frac{1}{4} J_{2} \left| 1^{\pm} + 2^{\pm} + 3^{\pm} + 4^{\pm} \right\rangle + \frac{1}{\sqrt{2}} J_{1} \left| 5^{\pm} + 6^{\pm} \right\rangle + \frac{1}{\sqrt{2}} J_{1} \left| 7^{\pm} + 8^{\pm} \right\rangle + J_{1} \left| 9^{\pm} \right\rangle$$
(B.63)

$$H |7^{\pm} + 8^{\pm}\rangle = \left( -\frac{1}{2}J_{1} - \frac{1}{4}J_{2} \right) |7^{\pm} + 8^{\pm}\rangle$$

$$+ \frac{1}{2\sqrt{2}}J_{1} \left( |1^{\pm}\rangle + |4^{\pm}\rangle + |5^{\pm}\rangle + |6^{\pm}\rangle + |2^{\pm}\rangle + |3^{\pm}\rangle + |5^{\pm}\rangle + |6^{\pm}\rangle \right)$$

$$+ \frac{1}{4}J_{2} \left( |8^{\downarrow}\rangle \pm |8^{\uparrow}\rangle + |7^{\downarrow}\rangle \pm |7^{\uparrow}\rangle \right)$$

$$= \left( -\frac{1}{2}J_{1} + \frac{1}{4}J_{2} \left( -1 \pm 2 \right) \right) |7^{\pm} + 8^{\pm}\rangle + \frac{1}{\sqrt{2}}J_{1} |1^{\pm} + 2^{\pm} + 3^{\pm} + 4^{\pm}\rangle + J_{1} |5^{\pm} + 6^{\pm}\rangle$$

$$(B.67)$$

$$H\left|9^{\pm}\right\rangle = \left(-\frac{1}{2}J_{1} - \frac{1}{4}J_{2}\right)\left|9^{\pm}\right\rangle + \frac{1}{2}J_{1}\left(\left|1^{\pm}\right\rangle + \left|2^{\pm}\right\rangle + \left|3^{\pm}\right\rangle + \left|4^{\pm}\right\rangle\right) + \frac{1}{2}J_{2}\left|0^{\pm}\right\rangle \quad (B.68)$$

$$= \left(-\frac{1}{2}J_1 - \frac{1}{4}J_2\right)\left|9^{\pm}\right\rangle + \frac{1}{2}J_1\left|1^{\pm} + 2^{\pm} + 3^{\pm} + 4^{\pm}\right\rangle + \frac{1}{2}J_2\left|0^{\pm}\right\rangle \tag{B.69}$$

$$H \left| 0^{\pm} \right\rangle = \left( \frac{3}{2} J_1 - \frac{1}{4} J_2 \right) \left| 0^{\pm} \right\rangle + \frac{1}{2} J_2 \left| 9^{\pm} \right\rangle \tag{B.70}$$

$$H \left| 1^{\pm} + 2^{\pm} - 3^{\pm} - 4^{\pm} \right\rangle = \left( -\frac{1}{2}J_{1} + \frac{1}{4}J_{2} \right) \left| 1^{\pm} + 2^{\pm} - 3^{\pm} - 4^{\pm} \right\rangle$$

$$+ \frac{1}{4}J_{1} \left( \left| 3^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle + \left| 4^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 8^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle$$

$$- \left| 1^{\pm} \right\rangle - \left| 6^{\pm} \right\rangle - \left| 8^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle - \left| 2^{\pm} \right\rangle - \left| 6^{\pm} \right\rangle - \left| 7^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle \right)$$
(B.72)
$$= \left( -J_{1} + \frac{1}{4}J_{2} \right) \left| 1^{\pm} + 2^{\pm} - 3^{\pm} - 4^{\pm} \right\rangle + \frac{1}{\sqrt{2}}J_{1} \left| 5^{\pm} - 6^{\pm} \right\rangle$$
(B.73)

$$H \left| 5^{\pm} - 6^{\pm} \right\rangle = \left( -\frac{1}{2} J_1 - \frac{1}{4} J_2 \right) \left| 5^{\pm} - 6^{\pm} \right\rangle$$

$$+ \frac{1}{2\sqrt{2}} J_1 \left( \left| 1^{\pm} \right\rangle + \left| 2^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 8^{\pm} \right\rangle - \left| 3^{\pm} \right\rangle - \left| 4^{\pm} \right\rangle - \left| 7^{\pm} \right\rangle - \left| 8^{\pm} \right\rangle \right)$$

$$+ \frac{1}{4} J_2 \left( \left| 6^{\downarrow} \right\rangle \pm \left| 6^{\uparrow} \right\rangle - \left| 5^{\downarrow} \right\rangle \mp \left| 5^{\uparrow} \right\rangle \right)$$

$$= \left( -\frac{1}{2} J_1 + \frac{1}{4} J_2 \left( -1 \mp 2 \right) \right) \left| 5^{\pm} - 6^{\pm} \right\rangle + \frac{1}{\sqrt{2}} J_1 \left| 1^{\pm} + 2^{\pm} - 3^{\pm} - 4^{\pm} \right\rangle$$
(B.75)

$$= \left(-\frac{1}{2}J_1 + \frac{1}{4}J_2\left(-1\mp 2\right)\right) \left|5^{\pm} - 6^{\pm}\right\rangle + \frac{1}{\sqrt{2}}J_1\left|1^{\pm} + 2^{\pm} - 3^{\pm} - 4^{\pm}\right\rangle$$
(B.75)

$$H \left| 0^{\pm} \right\rangle = \left( \frac{3}{2} J_1 - \frac{1}{4} J_2 \right) \left| 0^{\pm} \right\rangle + \frac{1}{2} J_2 \left| 9^{\pm} \right\rangle \tag{B.76}$$

(B.77)

$$H \left| 1^{\pm} - 2^{\pm} - 3^{\pm} + 4^{\pm} \right\rangle = \left( -\frac{1}{2} J_1 + \frac{1}{4} J_2 \right) \left| 1^{\pm} - 2^{\pm} - 3^{\pm} + 4^{\pm} \right\rangle$$
$$+ \frac{1}{4} J_1 \left( \left| 3^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle - \left| 4^{\pm} \right\rangle - \left| 5^{\pm} \right\rangle - \left| 8^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle$$
$$- \left| 1^{\pm} \right\rangle - \left| 6^{\pm} \right\rangle - \left| 8^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle + \left| 2^{\pm} \right\rangle + \left| 6^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle \right)$$
(B.78)
$$= \left( -J_1 + \frac{1}{4} J_2 \right) \left| 1^{\pm} - 2^{\pm} - 3^{\pm} + 4^{\pm} \right\rangle + \frac{1}{\sqrt{2}} J_1 \left| 7^{\pm} - 8^{\pm} \right\rangle$$
(B.79)

$$H |7^{\pm} - 8^{\pm}\rangle = \left( -\frac{1}{2}J_1 - \frac{1}{4}J_2 \right) |7^{\pm} + 8^{\pm}\rangle$$

$$+ \frac{1}{2\sqrt{2}}J_1 \left( |1^{\pm}\rangle + |4^{\pm}\rangle + |5^{\pm}\rangle + |6^{\pm}\rangle - |2^{\pm}\rangle - |3^{\pm}\rangle - |5^{\pm}\rangle - |6^{\pm}\rangle \right)$$

$$+ \frac{1}{4}J_2 \left( |8^{\downarrow}\rangle \pm |8^{\uparrow}\rangle - |7^{\downarrow}\rangle \mp |7^{\uparrow}\rangle \right)$$

$$= \left( -\frac{1}{2}J_1 + \frac{1}{4}J_2 \left( -1 \mp 2 \right) \right) |7^{\pm} - 8^{\pm}\rangle + \frac{1}{\sqrt{2}}J_1 |1^{\pm} - 2^{\pm} - 3^{\pm} + 4^{\pm}\rangle$$

$$(B.81)$$

$$H \left| 1^{\pm} - 2^{\pm} + 3^{\pm} - 4^{\pm} \right\rangle = \left( -\frac{1}{2} J_1 + \frac{1}{4} J_2 \right) \left| 1^{\pm} - 2^{\pm} + 3^{\pm} - 4^{\pm} \right\rangle$$

$$+ \frac{1}{4} J_1 \left( \left| 3^{\pm} \right\rangle + \left| 5^{\pm} \right\rangle + \left| 7^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle - \left| 4^{\pm} \right\rangle - \left| 5^{\pm} \right\rangle - \left| 8^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle$$

$$+ \left| 1^{\pm} \right\rangle + \left| 6^{\pm} \right\rangle + \left| 8^{\pm} \right\rangle + \left| 9^{\pm} \right\rangle - \left| 2^{\pm} \right\rangle - \left| 6^{\pm} \right\rangle - \left| 7^{\pm} \right\rangle - \left| 9^{\pm} \right\rangle \right)$$
(B.82)
$$= \frac{1}{4} J_2 \left| 1^{\pm} - 2^{\pm} + 3^{\pm} - 4^{\pm} \right\rangle$$
(B.83)

With this the Hamiltonian matrices can be made. Starting with the one for the subspace 9):

$$\begin{aligned} |1^{+}+2^{+}+3^{+}+4^{+}\rangle & |5^{+}+6^{+}\rangle & |7^{+}+8^{+}\rangle & |9^{+}\rangle & |0^{+}\rangle \\ \langle 1^{+}+2^{+}+3^{+}+4^{+}| & \begin{pmatrix} \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} & \frac{1}{\sqrt{2}}J_{1} & J_{1} & 0 \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1}+\frac{1}{4}J_{2} & J_{1} & 0 & 0 \\ \frac{1}{\sqrt{2}}J_{1} & J_{1} & -\frac{1}{2}J_{1}+\frac{1}{4}J_{2} & 0 & 0 \\ \frac{1}{\sqrt{2}}J_{1} & J_{1} & 0 & 0 & -\frac{1}{2}J_{1}-\frac{1}{4}J_{2} & \frac{1}{2}J_{2} \\ \langle 0^{+}| & 0 & 0 & 0 & \frac{1}{2}J_{2} & \frac{3}{2}J_{1}-\frac{1}{4}J_{2} \end{pmatrix} \\ (B.84) \end{aligned}$$

Next is the subspace 10):

$$\begin{aligned} |1^{-}+2^{-}+3^{-}+4^{-}\rangle & |5^{-}+6^{-}\rangle & |7^{-}+8^{-}\rangle & |9^{-}\rangle & |0^{-}\rangle \\ \langle 1^{-}+2^{-}+3^{-}+4^{-}| & \begin{pmatrix} \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} & \frac{1}{\sqrt{2}}J_{1} & J_{1} & 0 \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1}-\frac{3}{4}J_{2} & J_{1} & 0 & 0 \\ \frac{1}{\sqrt{2}}J_{1} & J_{1} & -\frac{1}{2}J_{1}-\frac{3}{4}J_{2} & 0 & 0 \\ \frac{1}{\sqrt{2}}J_{1} & J_{1} & 0 & 0 & -\frac{1}{2}J_{1}-\frac{1}{4}J_{2} & \frac{1}{2}J_{2} \\ \langle 0^{-}| & 0 & 0 & 0 & \frac{1}{2}J_{2} & \frac{3}{2}J_{1}-\frac{1}{4}J_{2} \end{pmatrix} \\ \langle 0 & 0 & 0 & 0 & \frac{1}{2}J_{2} & \frac{3}{2}J_{1}-\frac{1}{4}J_{2} \end{pmatrix} \end{aligned}$$
(B.85)

For the subspace 11):

$$|1^{+} + 2^{+} - 3^{+} - 4^{+}\rangle \quad |5^{+} - 6^{+}\rangle$$

$$\langle 1^{+} + 2^{+} - 3^{+} - 4^{+}| \begin{pmatrix} -J_{1} + \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1} - \frac{3}{4}J_{2} \end{pmatrix}$$

$$(B.86)$$

For the subspace 12):

$$|1^{-} + 2^{-} - 3^{-} - 4^{-}\rangle \qquad |5^{-} - 6^{-}\rangle$$

$$\langle 4^{-} + 2^{-} - 3^{-} - 4^{-}| \begin{pmatrix} -J_{1} + \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1} + \frac{1}{4}J_{2} \end{pmatrix} \qquad (B.87)$$

For the subspace 13):

$$|1^{+} + 2^{+} - 3^{+} - 4^{+}\rangle \qquad |7^{+} - 8^{+}\rangle$$

$$\langle 1^{+} + 2^{+} - 3^{+} - 4^{+}| \begin{pmatrix} -J_{1} + \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1} - \frac{3}{4}J_{2} \end{pmatrix} \qquad (B.88)$$

For the subspace 14):

$$|1^{-} + 2^{-} - 3^{-} - 4^{-}\rangle \quad |7^{-} - 8^{-}\rangle$$

$$\langle 1^{-} + 2^{-} - 3^{-} - 4^{-}| \begin{pmatrix} -J_{1} + \frac{1}{4}J_{2} & \frac{1}{\sqrt{2}}J_{1} \\ \frac{1}{\sqrt{2}}J_{1} & -\frac{1}{2}J_{1} + \frac{1}{4}J_{2} \end{pmatrix}$$

$$(B.89)$$

And at last the subspace 15) and 16).

$$H\left|1^{\pm} - 2^{\pm} + 3^{\pm} - 4^{\pm}\right\rangle = \frac{1}{4}J_2\left|1^{\pm} - 2^{\pm} + 3^{\pm} - 4^{\pm}\right\rangle \tag{B.90}$$

The eigenvalues for subspace 9) is found in Maple. For this subspace there are three trivial solutions so the characteristic polynomial can be factorized to at 3rd degree polynomial.

This 3rd degree polynomial is in fact the same as for the subspace m = 1. It is also seen that many of the eigenvalues are found in the other subspaces. The following energies where found:

$$\begin{array}{l} 9) \quad E = \begin{cases} \frac{3}{2}J_1 + \frac{1}{4}J_2 \\ -\frac{3}{2}J_1 + \frac{1}{4}J_2 \\ E^3 + \frac{1}{4}J_2E^2 + \left(-\frac{9}{4}J_1^2 + \frac{1}{2}J_1J_2 - \frac{5}{16}J_2^2\right)E + \frac{1}{16}J_1^2J_2 - \frac{1}{8}J_1J_2^2 + \frac{3}{64}J_2^3 = 0 \\ \\ -\frac{3}{2}J_1 - \frac{3}{4}J_2 \\ \frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}}{2}\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) &\approx \frac{3}{2}J_1 - \frac{1}{12}J_2 \\ \\ \frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)}}{2}\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) &\approx -\frac{5}{12}J_2 \\ \\ -\frac{1}{4}J_2 + \frac{3}{2}J_1\sqrt{1 - \frac{2}{9}\frac{J_2}{J_1} + \frac{1}{9}\frac{J_2^2}{J_1^2}}} &\approx \left(\frac{3}{2}J_1 - \frac{5}{12}J_2 \\ -\frac{1}{4}J_2 - \frac{3}{2}J_1\sqrt{1 - \frac{2}{9}\frac{J_2}{J_1} + \frac{1}{9}\frac{J_2^2}{J_1^2}}} &\approx -\frac{3}{2}J_1 - \frac{1}{12}J_2 \\ \end{array} \right) \\ 1) \quad E = \begin{cases} \frac{1}{4}J_2 \\ -\frac{3}{2}J_1 + \frac{1}{4}J_2 \\ \end{array} \right) \\ (B.92) \\ 12) \quad E = \begin{cases} \frac{1}{4}J_2 \\ -\frac{3}{2}J_1 + \frac{1}{4}J_2 \\ \end{array} \right) \\ \end{array}$$

13) 
$$E = \begin{cases} -\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{5}{12}J_2 \\ -\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{3}{2}J_1 - \frac{1}{12}J_2 \end{cases}$$
(B.94)

14) 
$$E = \begin{cases} -\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx -\frac{5}{12}J_2 \\ -\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx -\frac{5}{12}J_2 \end{cases}$$
(B.95)

$$\left(-\frac{3}{4}J_{1} - \frac{1}{4}J_{2} - \frac{3}{4}J_{1}\sqrt{1 + \frac{4}{9}\left(-\frac{J_{2}}{J_{1}} + \frac{J_{2}}{J_{1}^{2}}\right)} \quad \approx^{-1}J_{1} - \frac{3}{2}J_{1} - \frac{1}{12}J_{2}$$

$$(B.06)$$

15) 
$$E = \frac{1}{4}J_2$$
 (B.96)

16) 
$$E = \frac{1}{4}J_2$$
 (B.97)

So to sum up, the following energies were found:

$$E_{(m=3)} = \frac{3}{2}J_1 + \frac{1}{4}J_2 \qquad 1 \text{ State} \qquad (B.98)$$

$$\frac{3}{2}J_1 + \frac{1}{4}J_2 \qquad \qquad 1 \text{ State}$$

$$E_{(m=2)} = \begin{cases} \frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx \frac{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \approx \frac{3}{2}J_1 - \frac{1}{12}J_2 & 1 \text{ State} \\ \frac{1}{4}J_4 & 3 \text{ States} \end{cases}$$
(B.99)

$$\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx \binom{\binom{J_2^2}{J_1^2}}{\approx} -\frac{5}{12}J_2 \qquad 1 \text{ State}$$
$$\frac{3}{2}J_1 + \frac{1}{4}J_2$$

1 State

$$\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \overset{\mathfrak{I}}{\approx} \frac{3}{2}J_1 - \frac{1}{12}J_2 \qquad 1 \text{ State}$$

$$\frac{1}{4}J_2 \qquad 4 \text{ State}$$

$$-\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{5}{12}J_2 \qquad 2 \text{ States}$$

$$\frac{\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx -\frac{5}{12}J_2 \qquad 1 \text{ States} \\ -\frac{3}{2}J_1 + \frac{1}{4}J_2 \qquad 1 \text{ State}$$

$$\frac{1}{\left(\frac{J_2^2}{J_1^2}\right)} \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \qquad 1 \text{ Source}$$

$$-\frac{3}{4}J_1 - \frac{1}{4}J_2 - \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx -\frac{3}{2}J_1 - \frac{1}{12}J_2 \qquad 2 \text{ States}$$

$$E^3 + \frac{1}{4}E^2J_2 + \left(-\frac{5}{16}J_2^2 - \frac{9}{4}J_1^2 + \frac{1}{2}J_1J_2\right)E + \frac{1}{16}J_1^2J_2 - \frac{1}{8}J_1J_2^2 + \frac{3}{64}J_2^3 = 0 \qquad 3 \text{ Stats}$$

(B.100)

$$\frac{3}{2}J_1 + \frac{1}{4}J_2 \qquad \qquad 1 \text{ State}$$

$$\frac{1}{4}J_2$$
 4 States

$$\begin{array}{c} -\frac{3}{2}J_{1} + \frac{1}{4}J_{2} & 3 \text{ State} \\ -\frac{3}{2}J_{1} - \frac{3}{4}J_{2} & 1 \text{ States} \end{array}$$

$$1 = \frac{3}{4}J_2$$
 1 States

$$\frac{1}{\frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \approx \frac{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \approx \frac{3}{2}J_1 - \frac{1}{12}J_2 \qquad 1 \text{ State}$$

 $\frac{\frac{3}{4}J_{1} - \frac{1}{4}J_{2} + \frac{3}{4}J_{1}\sqrt{1 + \frac{4}{9}\left(\frac{J_{2}}{J_{1}} + \frac{J_{2}}{J_{1}^{2}}\right)} \sim 2^{-2} - \frac{J_{2}}{J_{2}}$   $\frac{\frac{3}{4}J_{1} - \frac{1}{4}J_{2} - \frac{3}{4}J_{1}\sqrt{1 + \frac{4}{9}\left(\frac{J_{2}}{J_{1}} + \frac{J_{2}^{2}}{J_{1}^{2}}\right)} \approx -\frac{5}{12}J_{2}$   $\int \frac{J_{2}}{J_{2}} + \frac{J_{2}^{2}}{J_{2}} \mathcal{O}\left(\frac{J_{2}^{2}}{J_{1}^{2}}\right) \approx \frac{3}{2}J_{1} - \frac{5}{12}J_{2}$ 1 State

$$E_{(m=0)} =$$

 $E_{(m=1)} = \left\{ \right.$ 

$$-\frac{1}{4}J_2 + \frac{3}{2}J_1\sqrt{1 - \frac{2}{9}\frac{J_2}{J_1} + \frac{1}{9}\frac{J_2^2}{J_1^2}} \approx \frac{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} \approx \frac{3}{2}J_1 - \frac{5}{12}J_2 \qquad 1 \text{ State}$$

$$-\frac{1}{4}J_2 - \frac{3}{2}J_1\sqrt{1 - \frac{2}{9}\frac{J_2}{J_1} + \frac{1}{9}\frac{J_2^2}{J_1^2}} \overset{\mathcal{O}\left(\frac{J_2}{J_1^2}\right)}{\approx} -\frac{3}{2}J_1 - \frac{1}{12}J_2 \qquad 1 \text{ State}$$

$$-\frac{3}{4}J_1 - \frac{1}{4}J_2 + \frac{3}{4}J_1\sqrt{1 + \frac{4}{9}\left(-\frac{J_2}{J_1} + \frac{J_2^2}{J_1^2}\right)} \overset{\mathcal{O}\left(\frac{J_2^2}{J_1^2}\right)}{\approx} -\frac{5}{12}J_2 \qquad 2 \text{ States}$$

$$-\frac{3}{4}J_{1} - \frac{1}{4}J_{2} - \frac{3}{4}J_{1}\sqrt{1 + \frac{4}{9}\left(-\frac{J_{2}}{J_{1}} + \frac{J_{2}^{2}}{J_{1}^{2}}\right)} \approx -\frac{3}{2}J_{1} - \frac{1}{12}J_{2} \qquad 2 \text{ States}$$

$$+\frac{1}{4}J_{2}E^{2} + \left(-\frac{9}{2}J_{2}^{2} + \frac{1}{4}J_{1}J_{2} - \frac{5}{2}J_{2}^{2}\right)E + \frac{1}{4}J_{2}^{2}J_{2} - \frac{1}{4}J_{1}J_{2}^{2} + \frac{3}{4}J_{3}^{3} - 0 \qquad 3 \text{ States}$$

$$E^{3} + \frac{1}{4}J_{2}E^{2} + \left(-\frac{9}{4}J_{1}^{2} + \frac{1}{2}J_{1}J_{2} - \frac{5}{16}J_{2}^{2}\right)E + \frac{1}{16}J_{1}^{2}J_{2} - \frac{1}{8}J_{1}J_{2}^{2} + \frac{3}{64}J_{2}^{3} = 0 \qquad 3 \text{ State}$$
(B.101)

To give at better overview, a scheme of the first order approximations in  $J_2/J_1$  is given below.

$$\begin{split} E_{(m=3)} &= \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State} & (B.102) \\ E_{(m=2)} &\approx \begin{pmatrix} \mathcal{O}\left(\frac{J_1^2}{J_1^2}\right) \\ \approx \end{pmatrix} \begin{cases} \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State} \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^* & (B.103) \\ \frac{1}{4}J_4 \quad 3 \text{ States} \\ -\frac{5}{12}J_2 \quad 1 \text{ State}^* & (B.103) \\ \frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}^* & (B.103) \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^* & (B.104) \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^* & (B.104) \\ -\frac{5}{12}J_2 \quad 3 \text{ States}^* & (B.104) \\ -\frac{5}{12}J_2 \quad 3 \text{ States}^* & (B.104) \\ -\frac{5}{12}J_2 \quad 3 \text{ States}^* & (B.104) \\ -\frac{5}{12}J_1 + \frac{1}{4}J_2 \quad 1 \text{ State}^* & (B.104) \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 2 \text{ State}^* & (B.104) \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 2 \text{ State}^* & (B.105) \\ \frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 1 \text{ State}^* & \frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^* & (B.105) \\ E_{(m=0)} &\approx \begin{pmatrix} \mathcal{O}\left(\frac{J_2^2}{J_1^2}\right) \\ \frac{1}{36}J_2 \quad 1 \text{ State}^* & \frac{3}{2}J_1 - \frac{1}{12}J_2 & 3 \text{ State}^* & (B.105) \\ \frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^* & \frac{3}{2}J_1 - \frac{1}{36}J_2 \quad 1 \text{ State}^* & (B.105) \\ -\frac{5}{12}J_2 \quad 3 \text{ States}^* & -\frac{3}{2}J_1 + \frac{1}{4}J_2 \quad 3 \text{ State}^* & -\frac{3}{2}J_1 + \frac{1}{36}J_2 \quad 1 \text{ State}^* & (B.105) \\ -\frac{5}{12}J_1 + \frac{1}{36}J_2 \quad 1 \text{ State}^* & -\frac{3}{2}J_1 - \frac{1}{12}J_2 \quad 3 \text{ State}^* & -\frac{3}{2}J_1 - \frac{1}{3}J_2 \quad 1 \text{ State}^* & -\frac{3}{2}J_1 - \frac{3}{4}J_2 \quad 1 \text{ State}^* & -\frac{3}{2}J$$

 $\ast$  the energies that is a first order approximation.



Figure B.5: States for m = 0. The states are labeled according to the derivation in the text