



Single-Ion Magnetic Anisotropy

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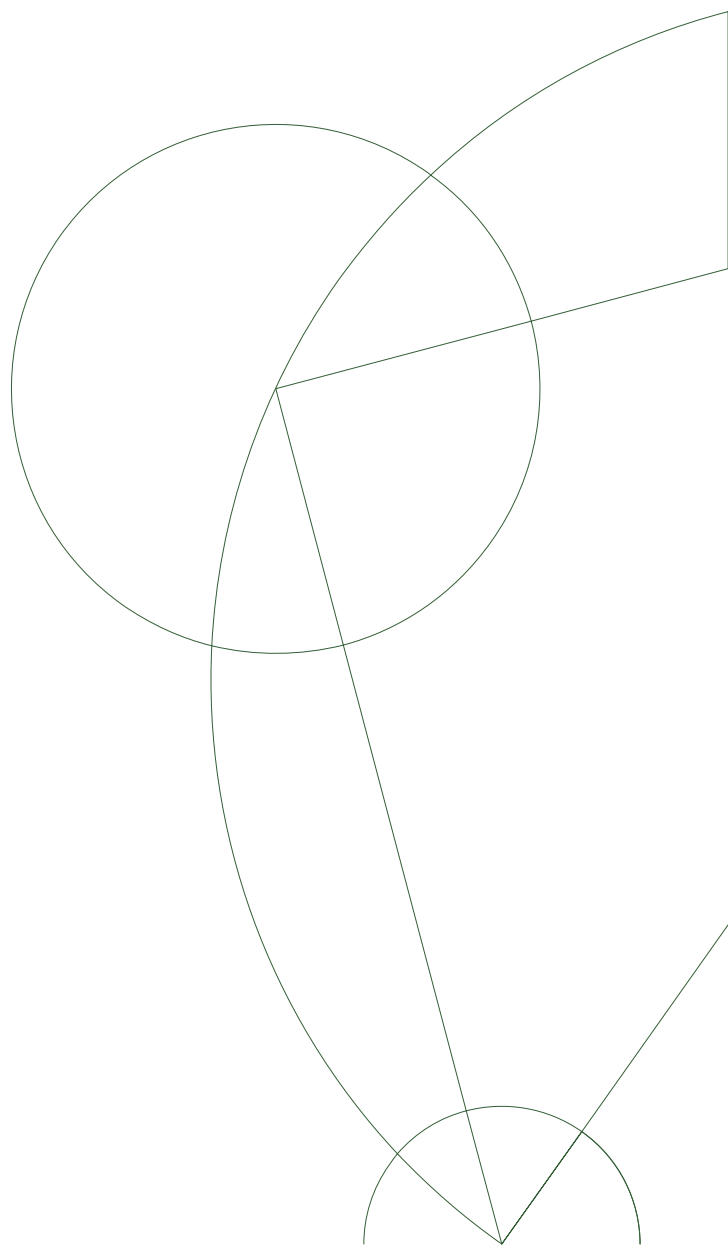
Bachelor's thesis in Physics

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Abstract

The purpose of the project is to use crystal field theory to find the form of the potential. The potential experienced by the valence electrons of an ion that is surrounded by a symmetric background a point charges, also known as a crystal field. Different methods such as the multipole expansion, the Wigner-Eckart theorem and group theory where used to determine the effect of the crystal field on the orbital energies. We also considered the magnetization of an atom in the crystal field which has an anisotropy spin Hamiltonian and the effect of crystal field structure on the stability of the magnetization. As we will see the three- and four-fold symmetric crystal field will have a long-lived spin and thus we can store information for longer time.

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1 Introduction

Magnetic storage devices are widespread today. Much of the ongoing research in this field is on various methods to reduce the data storage size to single atoms. Each magnetic moment represents a bit which, when magnetized in one direction, corresponds to "0" and when magnetized in the opposite direction stores "1". This is represented by the electron spin direction. The problem here is the challenge to keep the magnetization fixed. In other words, electrons unable to hold the information in one of the bit states for a meaningful amount of time due to fluctuations in the environment which flip the spin. To counter this problem, an atom of the rare-earth element Holmium has been used, since its electronic structure protects the magnetic moment from being flipped [1]. The stability of the magnetic moment of the Holmium atom depends on the symmetry of the crystal field. Crystal field theory is based on symmetry considerations of the negative point charges around a central metal ion. Crystal field theory is a broad subject, which is used to explain various phenomena in crystal structures. For this we will highlight another concept called magnetic anisotropy, which is one of the most important properties of magnetic materials. Magnetic anisotropy is the case where it requires different amounts of energy to magnetize a crystal in different directions, depending on the direction of the applied field relative to the crystal axes. The Holmium atom is explained via anisotropy spin Hamiltonian. Holmium atom was only a motivation, since we did not look specifically at the rare-earth group. In Figure 1, we can see different ways Holmium atom combined to the surface.

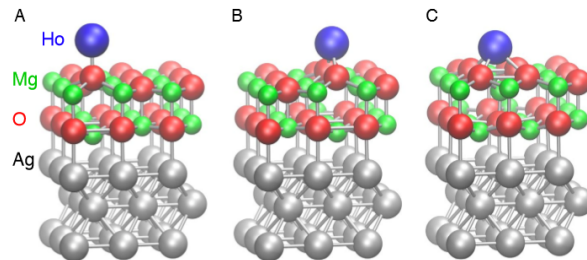


Figure 1: Holmium atom on 2 ML MgO/Ag(100). Ball-and-stick representation for the Ho adsorption on top of O (A), on the O-bridge site (B), and on top of Mg (C) [2].

2 Crystal field

Crystal field theory describes the change in energy levels of the valence orbitals of an ion due to the displacement of a set of symmetric ligands which are regarded as point charges around the ion. The presence of the point charges leads to an interaction between them and the electrons of the ion. The general Hamiltonian for a many electron system, neglecting all spin dependent interactions, takes the form [3]:

$$\hat{H} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} + \sum_i U(x_i, y_i, z_i) \quad (2.1)$$

The first term is the kinetic energy of electrons with momenta p_i , where the electrons interact via Coulomb interactions, whose energy is inversely proportional to distance r_{ij} between electron i and j . The Hamiltonian of the d -electrons is given by the first

two terms while the last term is the Coulomb potential due to the nuclear attraction. The reason that all spin-dependent interactions are neglected is that the crystal field effect is large compared to the LS coupling in iron-group (d -orbital), which make L and S remain approximately good quantum numbers. As the crystal field influence is only on the orbital position of the electrons, it will split the $2L+1$ degenerate energy levels into several groups, but will affect the spin degeneracy only via a weak spin orbit coupling. We therefore ignore spin completely and work with the orbital splittings [4]. The reverse is true in rare-earth elements (f -orbitals), which means that the LS coupling is the larger than the crystal field effect, since the f -orbitals are located closer around nucleus and thus the crystal field will be weaker due to f -orbitals are not affected by the surroundings of the crystal. We will now start to consider a $3d^1$ positive ion which is surrounded by six O^{-2} ions to form a model for an octahedral complex as shown in the diagram 2.

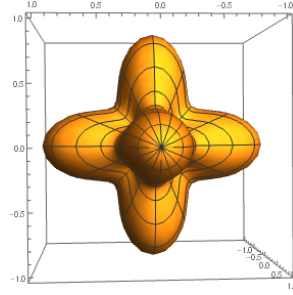


Figure 2: Spherical plot of the octahedral crystal field, where our $3d^1$ positive ion is surrounded by six O^{-2} with a distance of $\pm a$

By taking our origin at the center of the magnetic ion, the potential energy of an ion of charge $-q$ at $(0,0,a)$ is

$$U(x, y, z) = \frac{eq}{[x^2 + y^2 + (z - a)^2]^{\frac{1}{2}}} \quad (2.2)$$

Where e is the elementary positive charge. We can then make a Taylor expansion of this potential, by using the Legendre polynomials, which is valid when $|t| < 1$, $|u| \leq 1$ and $|t| < |u|$

$$\frac{1}{[1 - 2tu + t^2]^{\frac{1}{2}}} = \sum_{n=0}^{\infty} t^n P_n(u) \quad (2.3)$$

$$P_n(u) = \frac{1}{2^n n!} \left(\frac{d}{du} \right)^n (u^2 - 1)^n \quad (2.4)$$

Where $t = \frac{r}{a}$ and $u = \frac{z}{r}$.

$$\begin{aligned} P_0(u) &= 1, & P_1(u) &= u, & P_2(u) &= \frac{1}{2}(3u^2 - 1), \\ P_3(u) &= \frac{1}{2}(5u^3 - 3u), & P_4(u) &= \frac{1}{8}(35u^4 - 30u^2 + 3) \end{aligned} \quad (2.5)$$

In order for equation 2.3 to be the same as equation 2.2 we multiply it by $\frac{eq}{a}$.

$$U(x, y, z) = \frac{eq}{a} \sum_{n=0}^4 t^n P_n(u) = \frac{eq}{a} \left[1 + \frac{z}{a} + \frac{1}{2a^2} (3z^2 - r^2) + \frac{1}{2a^3} (5z^3 - 3zr^2) + \frac{1}{8a^4} (35z^4 - 30z^2r^2 + 3r^4) \right] \quad (2.6)$$

If another charge is located at $(0,0,-a)$ there is inversion symmetry, which makes all the odd powers of z drop out. If we then add the four charges at $(0,\pm a,0)$ and $(\pm a,0,0)$, where $t = \frac{r}{\pm a}$ and $u = \frac{i}{r}$ where i can be $\{x, y, z\}$ we get

$$U(x, y, z) = \frac{2eq}{a} \left[\left(1 + \frac{1}{2a^2}3z^2 - \frac{1}{2a^2}r^2 + \frac{1}{8a^4}35z^4 - \frac{1}{8a^4}30z^2r^2 + \frac{1}{8a^4}3r^4 \right) \right. \\ + \left(1 + \frac{1}{2a^2}3y^2 - \frac{1}{2a^2}r^2 + \frac{1}{8a^4}35y^4 - \frac{1}{8a^4}30y^2r^2 + \frac{1}{8a^4}3r^4 \right) \\ \left. + \left(1 + \frac{1}{2a^2}3x^2 - \frac{1}{2a^2}r^2 + \frac{1}{8a^4}35x^4 - \frac{1}{8a^4}30x^2r^2 + \frac{1}{8a^4}3r^4 \right) \right] \quad (2.7)$$

Since $r^2 = x^2 + y^2 + z^2$ the second and third terms cancel each other, and we do not look at a potential higher than fourth order for d -electrons since it will give zero. Our potential is then

$$U(x, y, z) = \frac{6eq}{a} \left[1 + \left(\frac{35}{24a^4} \right) (x^4 + y^4 + z^4 - \frac{3}{5}r^4) \right] \approx \frac{35eq}{4a^5} (x^4 + y^4 + z^4 - \frac{3}{5}r^4) \quad (2.8)$$

The first term is of little interest, since it is independent of x, y and z , and just gives an energy shift. The free-ion energy states will split, because of crystal field effect. In order to calculate the correction eigenenergy we use perturbation methods.

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots \\ = \epsilon_n + \langle \psi_n^0 | U | \psi_n^0 \rangle + \sum_{m \neq n} \frac{|\langle \psi_m^0 | U | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \quad (2.9)$$

The first term is the unperturbed energy, which can only be calculated exactly for the hydrogen atom and not for a many electron system. The second term is the first order correction to the energy, which mixes states with the same n together. It can either be calculated using the multipole expansion or the Wigner Eckart theorem. The third term is the second order correction to the energy, which mixes states with different n together. In our case, we only look at the d -multiplet, yet there may be some excited state, which gives a great energy difference but this part will be very small so we can ignore it

2.1 Multipole expansion

In order to do multipole expansion of our potential

$$U(x, y, z) = x^4 + y^4 + z^4 - \frac{3}{5}r^4 \quad (2.10)$$

we start by writing the function in spherical coordinates

$$U(r, \theta, \phi) = r^4 [\sin^4(\theta) \cos^4(\phi) + \sin^4(\theta) \sin^4(\phi) + \cos^4(\theta) - \frac{3}{5}] \quad (2.11)$$

which we then expand in angular momentum eigenstates

$$U(r, \theta, \phi) = \sum_l \sum_{m=-l}^l u_{lm}(r) Y_l^m(\theta, \phi) \quad (2.12)$$

where l is the Taylor expansion angular momentum, m is the magnetic quantum number, $Y_l^m(\theta, \phi)$ are the spherical harmonics and u_{lm} are the expansion coefficients, which is

$$u_{lm} = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) Y_l^{m*}(\theta, \phi) U(r, \theta, \phi) \quad (2.13)$$

After we have made multipole expansion, our potential will be

$$U(r, \theta, \phi) = r^4 U(\theta, \phi) = r^4 \left[\frac{2}{3} \sqrt{\frac{2\pi}{35}} Y_4^{-4}(\theta, \phi) + \frac{4\sqrt{\pi}}{15} Y_4^0(\theta, \phi) + \frac{2}{3} \sqrt{\frac{2\pi}{35}} Y_4^4(\theta, \phi) \right] \quad (2.14)$$

Our wave-function is factored into two parts, the radial part which is only a function of distance from the nucleus and an angular part. We can now calculate the first-order correction to the energy, which is equal to

$$\begin{aligned} E_{32mm'}^1 &= \frac{35eq}{4a^5} \left\langle R_{32}(r) Y_2^{m'}(\theta, \phi) | U(r, \theta, \phi) | R_{32}(r) Y_2^m(\theta, \phi) \right\rangle \\ &= \frac{35eq}{4a^5} \int_0^\infty r^2 |R_{32}(r)|^2 dr \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) Y_2^{m'*}(\theta, \phi) r^4 U(\theta, \phi) Y_2^m(\theta, \phi) \end{aligned} \quad (2.15)$$

where $n = 3$, $l = 2$ and $m = -l \dots l$. The integral can be factorized into a radial and an angular part. The radial factor is

$$\int_0^\infty r^4 r^2 |R_{32}(r)|^2 dr = \int_0^\infty r^6 \left| \frac{4}{81\sqrt{30}a_0^3} \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \right|^2 dr \quad (2.16)$$

as can be seen, the larger a_0 is the greater this term becomes. For the angular part since our ion is now in a crystal field will the d -orbitals no longer be degenerate, this means that we have five different m

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) Y_2^{m'*}(\theta, \phi) U(\theta, \phi) Y_2^m(\theta, \phi) = \begin{pmatrix} \frac{2}{105} & 0 & 0 & 0 & \frac{2}{21} \\ 0 & -\frac{8}{105} & 0 & 0 & 0 \\ 0 & 0 & \frac{4}{35} & 0 & 0 \\ 0 & 0 & 0 & -\frac{8}{105} & 0 \\ \frac{2}{21} & 0 & 0 & 0 & \frac{2}{105} \end{pmatrix}_{mm'} \quad (2.17)$$

The matrix is diagonalised so that the eigenvalues can be found. With the matrix rewritten in the diagonal basis, it can be seen that the energy has been split into two levels, where one is twice degenerate, while the other is thrice degenerate.

$$\begin{pmatrix} \frac{4}{35} & 0 & 0 & 0 & 0 \\ 0 & \frac{4}{35} & 0 & 0 & 0 \\ 0 & 0 & -\frac{8}{105} & 0 & 0 \\ 0 & 0 & 0 & -\frac{8}{105} & 0 \\ 0 & 0 & 0 & 0 & -\frac{8}{105} \end{pmatrix} \quad (2.18)$$

To explain that, we look at the five d -orbitals, which fall into two classes: the e_g orbitals which point along the x , y and z axes (which are d_{z^2} and $d_{x^2-y^2}$) and the t_{2g} orbitals which point between these axes, (which are d_{xy} , d_{xz} and d_{yz}). Here we make

use of crystal field theory, which is based on an ionic description of the metal-ligands bond. The three t_{2g} orbitals have a lower overlap with the O^{-2} neighboring p -orbitals than the two e_g orbitals and hence will have a lower electrostatic energy. The three t_{2g} orbitals will then be lowered in energy while the two e_g orbitals will be raised in energy, as shown in the Figure (3). One of the three t_{2g} orbitals has a linear combination which is $Y_2^2(\theta, \phi) - Y_2^{-2}(\theta, \phi)$ while the two others are $Y_2^{-1}(\theta, \phi)$ and $Y_2^1(\theta, \phi)$. Also one of the two e_g orbitals has a linear combination which is $Y_2^{-2}(\theta, \phi) + Y_2^2(\theta, \phi)$ and the other one is $Y_2^0(\theta, \phi)$.

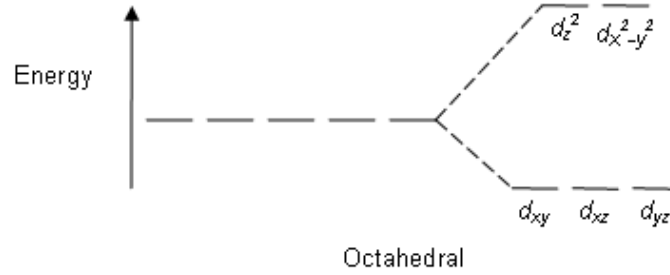


Figure 3: The energy levels of the $3d$ -orbitals in a Octahedral crystal field

2.2 Wigner-Eckart theory

Wigner-Eckart theory has the same principle as a multipole expansion. We will introduce something called an irreducible tensor operator (T_q^k) which is the same as Y_l^m in our case, where $q = m$ and $k = l$. The matrix elements of irreducible tensor operators can be expressed as the product of two factors. The first factor is the Clebsch-Gordan coefficient, and the second factor is the reduced matrix element, which is independent of the magnetic quantum numbers.

$$\langle \gamma' j' m' | T_q^{(k)} | \gamma j m \rangle = \langle j' m' | j k m q \rangle \langle \gamma' j' || T^{(k)} || \gamma j \rangle \quad (2.19)$$

j, j' are the angular momenta and γ stands for all other quantum numbers. In our case we consider an atom in a crystal field, so that $\gamma = n$ and $j = l$. The Wigner-Eckart theorem is useful to use since Clebsch-Gordan coefficients involving the coupling of angular momenta l and l' to obtain total angular momentum L . We are interested in that because tensor operators transform into themselves under rotations, and these rotations are generated by angular momentum. We will now calculate the Clebsch-Gordan coefficients $\langle l' m' | l k m q \rangle$ Where $l' = l = 2$, $m' = m = -l \dots l$, $k = 4$ and $q = -4, 0, 4$. For that we will get the same as equation 2.17 but multiplied by $\frac{2}{3} \sqrt{\frac{2\pi}{7\pi^2}}$, which we then diagonalize and get equation 2.18, and the reduced matrix element will give the same as the radial part of the multipole expansion.

2.3 Tetragonal symmetry

Assuming that the octahedral structure with ions at its apices producing the crystal field is distorted along one of the principal axes, here taken to be z-axis, by multiplying $\pm a$ with α . The potential becomes

$$\begin{aligned}
U(x, y, z) = \frac{2eq}{\alpha a} & \left[\frac{3}{2a^2} \left(\frac{z^2}{\alpha^2} + \alpha y^2 + \alpha z^2 \right) - \frac{30r^2}{8a^4} \left(\frac{z^2}{\alpha^4} + \alpha y^2 + \alpha z^2 \right) \right. \\
& \left. + \frac{35}{8a^4} \left(\frac{z^4}{\alpha^4} + \alpha y^4 + \alpha z^4 \right) - \frac{r^2}{2\alpha^2 a^2} (1 + 2\alpha^3) + \frac{3r^4}{8a^4} \left(\frac{1}{\alpha^4} + 2\alpha \right) \right]
\end{aligned} \tag{2.20}$$

We do the same as before, rewriting our potential in spherical coordinates and then calculating the first order correction to the energy, where we get five energies, three of them are different and two of them are the same. If we now assume that the octahedron of our ion producing the crystal field is distorted along two of the three principal axes, it means that all symmetries are broken and we therefore get five different energies. The energy levels corresponding to the three different symmetries of the $3d$ -orbital are shown in Figure 4. The differences in energies in the diagram depend on a and α , and as can be seen, the larger a is the smaller is the splitting between e_g and t_{2g} , and the larger α is the greater is the splitting of e_g and t_{2g} .

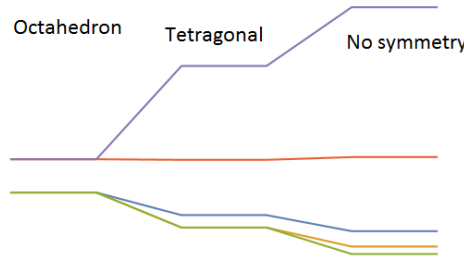


Figure 4: The energy levels of the $3d$ orbitals.

2.4 Group theory

We can also obtain the degeneracy of an atom in a field of a given symmetry directly by use of group theory, instead of rewriting our potential in spherical coordinates and then considering perturbation theory or instead of using the Wigner-Eckart theorem. The point group for an octahedral symmetry is O_h . This group contains the elements of $O = \{\hat{E}, 8\hat{C}_3, 3\hat{C}_2, 6\hat{C}_2, 6\hat{C}_4\}$ and other elements that have to do with the mirror plane. O_h has twice as many elements as O , we can then express (O_h) group as a direct product of the simpler group (O) with the group of the inversion $O_h = O \otimes i$. Where we only need to look at rotation groups. To explain that, we start by looking at the three rotations around the principal axes of the orthogonal coordinate system (x, y, z) given by

$$\begin{aligned}
\Gamma^{\hat{x}}(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin \alpha \\ 0 & \sin \alpha & \cos \alpha \end{pmatrix}, \quad \Gamma^{\hat{y}}(\alpha) = \begin{pmatrix} \cos \alpha & 0 & \sin \alpha \\ 0 & 1 & 0 \\ -\sin \alpha & 0 & \cos \alpha \end{pmatrix}, \\
\Gamma^{\hat{z}}(\alpha) = \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{aligned} \tag{2.21}$$

$\Gamma^{\hat{i}}$ is a given representation of a group \mathcal{G} in our case O_h containing the rotation elements. $\Gamma^{\hat{i}}$ are the rotation matrices for the three principal axes and the associated

characters are

$$\chi^i(\alpha) = \text{Tr } \Gamma^i(\alpha) = 1 + 2\cos\alpha \quad \text{for } i \in \{\hat{x}, \hat{y}, \hat{z}\} \quad (2.22)$$

If we then combine an inversion with the rotation by α , the matrix will change sign and the character will then be

$$\chi^i(\alpha, \hat{i}) = -1 - 2\cos\alpha \quad \text{for } i \in \{\hat{x}, \hat{y}, \hat{z}\} \quad (2.23)$$

Since eq 2.22 and 2.23 are identical up to a sign change, by using both equations we merely repeat each term. Hence we only have to look at rotations elements to find all the possible splittings. If we now look at the character table for the O group.

χ_i	\hat{E}	$8 \hat{C}_3$	$3\hat{C}_2$	$6 \hat{C}_2$	$6\hat{C}_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1

Table 1: The character table for point group O

The labels of the irreducible representations are A and B for one dimensional representations, E for two dimensional representation and T for three dimensional representations. The 24 elements are the identity operator, \hat{E} , which leaves everything unchanged and 23 \hat{C}_n operators which are generators of cyclic groups of order n . The rotational axes of the \hat{C}_n operators are oriented as follows. There are four three-fold rotation axes (belonging to \hat{C}_3) which pass through the center of the triangular sides and the center of the octahedron. The rotations can be either in the positive direction (\hat{C}_3^+) or in the negative direction (\hat{C}_3^-). Thus there are eight \hat{C}_3 operations. There are nine twofold rotation axes, (belonging to \hat{C}_2) divided into two classes which are not physically equivalent. The first class contains three of the \hat{C}_2 operators, with rotations about the x, y and z axes, while the second class contains six \hat{C}_2 operators with axes through the midpoints of opposite edges of the octahedron. There are six \hat{C}_4 operations with the same three axes as the three \hat{C}_2 , about the x, y and z axes, where again there are 3 \hat{C}_4^+ and 3 \hat{C}_4^- . In order to compute the characters of the group elements we use[5].

$$\chi^L(\alpha) = \frac{\sin(L+1)\alpha}{\sin(\frac{\alpha}{2})} \quad (2.24)$$

Where L is the angular momentum. In the case of d -orbitals $L = 2$ and we get

$$\begin{aligned} \chi^2(C_2) = \chi^2(\pi) = 1, \quad \chi^2(C_3) = \chi^2(\frac{2\pi}{3}) = \frac{\sin(\frac{5\pi}{3})}{\sin(\frac{\pi}{3})} = -1, \\ \chi^2(C_4) = \chi^2(\frac{\pi}{2}) = \frac{\sin(\frac{5\pi}{4})}{\sin(\frac{\pi}{4})} = -1 \end{aligned} \quad (2.25)$$

So the character table for the reducible representation D_2 is

χ_L	$\hat{E} = (2L+1)$	$8 \hat{C}_3$	$3\hat{C}_2$	$6 \hat{C}_2$	$6\hat{C}_4$
D_2	5	-1	1	1	-1

Table 2: The character table for the reducible representation D_2

D_L are the representations of the rotation group, which can be transformed into block diagonal form, where the diagonal blocks are the irreducible representations of the group O . To find out which irreducible representations spanning the basis set we use the frequency formula given by (3-20) [5]. The characters of representation matrices for operations acting on the basis sets are found by looking at how many of the features go into themselves during the operation.

$$a_i = \frac{1}{g} \sum_k N_k \chi_L(C_k) \chi_i(C_k) \quad (2.26)$$

Where $\chi_L(C_k)$ and $\chi_i(C_k)$ are characters of D_L and the O group respectively, N_k is the number of elements in each class and g is the number of elements in the whole O group.

$$a_{A_1} = \frac{1}{24}(1 \times 5 + 8 \times 1 \times (-1) + 3 \times 1 \times 1 + 6 \times 1 \times 1 + 6 \times 1 \times (-1)) = 0 \quad (2.27)$$

By doing it for all the other irreducible representations, the calculations give $a_\mu = 1$ for $\mu = E, T_2$ where $\nu = D_2$ while $a_\mu = 0$ for $\mu = A_1, A_2$ and T_1 where $\nu = D_2$. We can then decompose the representation D_L into irreducible representations and express it as

$$D_L = \sum_i a_i \Gamma_i \rightarrow D_2 = E \oplus T_2 \quad (2.28)$$

where a_i denotes the number of times a given irreducible representation Γ_i occurs in the block diagonal matrix D_L . From this result we see that a d -state splits into a twofold and a threefold degenerate energy level in an octahedral symmetric field. Which indicates that the degeneracy can be worked out by using group theory.

Consider now the case of tetragonal symmetry, where the crystal field is distorted along any of the three principal axes. The symmetry point group of the system is now the dihedral group D_4 . Below is the character table for D_4 .

χ_i	\hat{E}	$2 \hat{C}_4$	\hat{C}_2	$2\hat{C}'_2$	$2\hat{C}''_2$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

Table 3: The character table for point group D_4

To facilitate the explanation of the group elements, consider a system distorted along the z -axis. The two \hat{C}_4 operations have the same rotational axis as the \hat{C}_2 operations. The axis passes through the center of the xy plane and is perpendicular to it. As usual we have \hat{C}_4^+ and \hat{C}_4^- . Furthermore, there are two \hat{C}'_2 about the x - and y -axis, respectively. The two \hat{C}''_2 -axes lie in the xy -plane, and bisect the angles made up by the \hat{C}'_2 -axes. By use of equation 4.24 the character table for the reducible representation D_2 is found to be

χ_L	\hat{E}	$2\hat{C}_4$	\hat{C}_2	$2\hat{C}'_2$	$2\hat{C}''_2$
D_2	5	-1	1	1	1

Table 4: The character table for the reducible representation D_2 for the D_4 point group

Equation 2.28 is used to get $D_2 = A_1 + B_1 + B_2 + E$. It is seen that the d -state splits into three non-degenerate levels and a twofold degenerate level under tetragonal symmetry, when the crystal field is distorted along one of the principal axes, which means that both the E and T_2 irreducible representations from the octahedral must split, where

$$T_2 \rightarrow E + A_1 \quad \text{and} \quad E \rightarrow B_1 + B_2 \quad (2.29)$$

Thus the triply degenerate level in an octahedral structure splits into a doubly degenerate and a non-degenerate level, while the doubly degenerate one splits into two non-degenerate levels. The reason we do not just use group theory is that group theory gives no information about the arrangement or magnitudes of the energy levels splittings.

2.5 The Hamiltonian in terms of the angular momentum operator

The importance of writing the potential in terms of the angular momentum operator appear when we are in the same multiplet. This will allow us to evaluate its eigenvalue relatively easily, since the angular momentum has some properties as the commutation relation. Our potential is

$$U(x, y, z) = (x^4 + y^4 + z^4 - \frac{3}{5}r^4) \quad (2.30)$$

Where we want to make an equivalent operator which depends on the angular momentum and with the same matrix element, since the angular momentum is eigenstate for this matrix element. Both the position vector and the angular momentum transform as vectors, but the problem is that the angular momentum do not commute, therefore we must symmetries. We start by substituting x , y and z with the angular momentum L_x , L_y and L_z respectively

$$(x^4 + y^4 + z^4 - \frac{3}{5}r^4) \rightarrow (L_x^4 + L_y^4 + L_z^4 - \frac{3}{5}r^4) \quad (2.31)$$

where the last part

$$r^4 = r^2 r^2 = (x^2 + y^2 + z^2)(x^2 + y^2 + z^2) \rightarrow (L_x^2 + L_y^2 + L_z^2)(L_x^2 + L_y^2 + L_z^2) \quad (2.32)$$

may be rewritten as all the possible combinations relations between the angular momentum:

$$\frac{1}{3} \left[3L_x^4 + 3L_y^4 + 3L_z^4 + L_y^2 L_x^2 + L_y L_x L_y L_x + L_y L_x^2 L_y + L_x L_y^2 L_x + L_x L_y L_x L_y \right. \\ \left. + L_x^2 L_y^2 + L_z^2 L_x^2 + L_z L_x L_z L_x + L_z L_x^2 L_z + L_x L_z^2 L_x + L_x L_z L_x L_z + L_x^2 L_z^2 \right. \\ \left. + L_z^2 L_y^2 + L_z L_y L_z L_y + L_z L_y^2 L_z + L_y L_z^2 L_y + L_y L_z L_y L_z + L_y^2 L_z^2 \right] \quad (2.33)$$

This expression can be simplified by the use of a commutator relation. For example

$$L_z L_x L_z L_x = L_z^2 L_x^2 + L_z [L_x, L_z] L_x = L_z^2 L_x^2 - i L_z L_y L_x \quad (2.34)$$

the same thing will be done for

$$\begin{aligned} L_x L_z L_x L_z, \quad L_z L_y L_z L_y, \quad L_y L_z L_y L_z, \\ L_x L_y L_x L_y, \quad L_y L_x L_y L_x \end{aligned} \quad (2.35)$$

and we also use that

$$L_z L_x^2 L_z = i L_y L_x L_z + L_x L_z L_x L_z = i L_y L_x L_z + L_x^2 L_z^2 + i L_x L_y L_z \quad (2.36)$$

which is also applied to the similar, other parts. We then find that

$$\begin{aligned} -\frac{3}{5} r^4 &= -\frac{1}{5} \left[3L_x^4 + 3L_x^2 L_y^2 + 3L_x^2 L_z^2 + 3L_y^4 + 3L_y^2 L_x^2 + 3L_y^2 L_z^2 + 3L_z^4 + 3L_z^2 L_y^2 + 3L_z^2 L_x^2 - L^2 \right] \\ &= -\frac{3}{5} \left[L^4 - \frac{1}{3} L^2 \right] = -\frac{3}{5} \left[\left[L(L+1) \right]^2 - \frac{L(L+1)}{3} \right] = -\frac{1}{5} L(L+1)(3L^2 + 3L - 1) \end{aligned} \quad (2.37)$$

Our potential is thus

$$x^4 + y^4 + z^4 - \frac{3}{5} r^2 \rightarrow L_x^4 + L_y^4 + L_z^4 - \frac{1}{5} L(L+1) \left(3L^2 + 3L - 1 \right) \quad (2.38)$$

Which has the same matrix element as $U(r, \theta, \phi)$. Stevens operators make up a large topic which will not be considered in this thesis [6].

3 Anisotropy spin Hamiltonian

In order to describe one ion anisotropy we consider the effective Hamiltonian. Where we start by introducing the perturbative term due to the spin orbit coupling (LS-coupling) and the Zeeman-effect (BS-coupling), which is:

$$V = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B \mathbf{B} \cdot (2\mathbf{S} + \mathbf{L}) \quad (3.1)$$

λ is the spin orbit coupling constant, \mathbf{L} is the orbital angular momentum of the electron, \mathbf{S} is the spin angular momentum of the electron, where the spin couples to the crystal field only when we take into account the LS coupling, μ_B is the Bohr magneton and

B is the magnetic field. The second term, also known as the Zeeman energy, where the presence of a magnetic field leads to a splitting of a spectral line into two lines. We will now calculate the first and second order correction to the energies, in order to find the effective Hamiltonian.

$$E_n^1 = \langle \psi_n^0 | V | \psi_n^0 \rangle = \lambda \mathbf{S} \cdot \langle \psi_n^0 | \mathbf{L} | \psi_n^0 \rangle + \mu_B \mathbf{B} \cdot (2\mathbf{S} \langle \psi_n^0 | \psi_n^0 \rangle + \langle \psi_n^0 | \mathbf{L} | \psi_n^0 \rangle) = 2\mu_B \mathbf{B} \cdot \mathbf{S} = 2\mu_B \sum_{ij} B_i \delta_{ij} S_j \quad (3.2)$$

i and j represent position vectors. If we have a free ion, the ground state is degenerate, but when we now have an electric field due to the crystal structure of the material, the ground state will be non-degenerate (orbital state). The non-degenerate state is represented by real wave functions, while the angular momentum is imaginary. The angular momentum is a vector operator and can be written as $\mathbf{L} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$, where the quantum mechanical operators for the components of the angular momentum are

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \quad (3.3)$$

both the position and the momentum operator $p_i = i\hbar \frac{\partial}{\partial i}$ are Hermitian operators and thus \hat{L}_i is also Hermitian. The expectation value of the angular momentum over a non-degenerate ground state will be imaginary, but since our angular momentum is Hermitian, and has real eigenvalues, the expectation value must be zero, $\langle \psi_n^0 | \mathbf{L} | \psi_n^0 \rangle = 0$, which means that the orbital angular momentum is quenched. With the quenching of \mathbf{L} , we eliminate \mathbf{L} and then the magnetic moment of the ion is just given by the spin. The reason for the spin is left as an operator in this perturbation calculation, is that the spin wave function is independent of the orbital part. For the second order energy we get

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_n^0 | V | \psi_m^0 \rangle|^2}{E_n^0 - E_m^0} = - \sum_{ij} [\lambda^2 \Lambda_{ij} S_i S_j + 2\lambda \mu_B \Lambda_{ij} B_i S_j + \mu_B^2 \Lambda_{ij} B_i B_j] \quad (3.4)$$

because it is a change in the ground state energy so it is always negative since $E_0 - E_m < 0$, and Λ_{ij} is

$$\Lambda_{ij} = \sum_n \frac{\langle \psi_n^0 | L_i | \psi_m^0 \rangle \langle \psi_m^0 | L_j | \psi_n^0 \rangle}{E_m - E_n} \quad (3.5)$$

By adding the first and the second order energies we get the effective Hamiltonian for a non-degenerate ground state

$$H_S = E_n^1 + E_n^2 = \sum_{ij} [-\lambda^2 \Lambda_{ij} S_i S_j + 2\mu_B B_i (\delta_{ij} - \lambda \Lambda_{ij}) S_j - \mu_B^2 \Lambda_{ij} B_i B_j] \quad (3.6)$$

The first term is the anisotropy spin Hamiltonian, the second term is the effective Zeeman term where we use the g matrix ($g = \delta_{ij} - \lambda \Lambda_{ij}$) and the third term comes from the second order perturbation of the Zeeman energy. The anisotropy spin Hamiltonian may be expressed as in Appendix B

$$H = DS_z^2 + E(S_x^2 - S_y^2) = DS_z^2 + \frac{E}{2}(S_+^2 + S_-^2) \quad (3.7)$$

D and E are called longitudinal (uniaxial) and transversal (biaxial) anisotropy, respectively. While S_x , S_y , and S_z are the three components of the spin operator. Finally S_+ and S_- are raising and lowering spin operator. The value of D and E depends on the material for example in this article D and E is around the order 0.292 K and 0.046 K respectively [7], but the magnetic anisotropy of interfaces is in the range of 10^{-4} to 10^{-3} eV.atom $^{-1}$ [8]. After we have found our anisotropy spin Hamiltonian, we want to see how it depends on the spin. We look at both integer spin and half integer spin. To know how the anisotropy spin Hamiltonian depends on the spin, we must first know how S_z and S_{\pm} work. The eigenvector equation for the spin component along the z -axis is

$$S_z |sm_s\rangle = \hbar m_s |sm_s\rangle \quad (3.8)$$

Which is eigenstate for S_z so it produces only diagonal elements in our Hamiltonian. In the following, we set \hbar to be one for simplicity. For integer spin the first term of the equation 3.7 will split the energy levels into doubly degenerate states $S_z = \pm s, \pm(s-1), \dots, \pm 1$ and a non-degenerate one $S_z = 0$, whereas half integer spin gives only doubly degenerate states, which means the energy of states with same absolute value of m_s . If we then look at the Hamiltonian of (3.7) with $E = 0$ meV, the energy of the eigenstates of the \hat{H} is

$$\varepsilon_{m_s} = Dm_s^2 \quad (3.9)$$

and will lie on a parabola, as shown in Figure 5. Depending on the sign of the longitudinal anisotropy, our parabola will either have its legs pointing up or down. If we then set $E \neq 0$ the second term in the anisotropy spin Hamiltonian in (3.7) will not vanish, and has finite matrix elements between states with $\Delta S_z = \pm 2$. Thus, the raising and lowering spin operators will contribute

$$S_{\pm} |sm_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s(m_s \pm 1)\rangle \quad (3.10)$$

The spin raising and lowering operators acting on these eigenstates give another function with the same value of the spin quantum number, but another spin projection quantum number (m_s), which is greater for step up or lower for step down. For integer spin, the doubly degenerate energy states $S_z = \pm M$, which are produced by the first term in the Hamiltonian 3.7, are split by the second term, that they are no longer symmetrical. But for half-integer spin the difference between the doubly degenerate states $S_z = \pm M$ is an odd numbers, and then there will not be a matrix element between

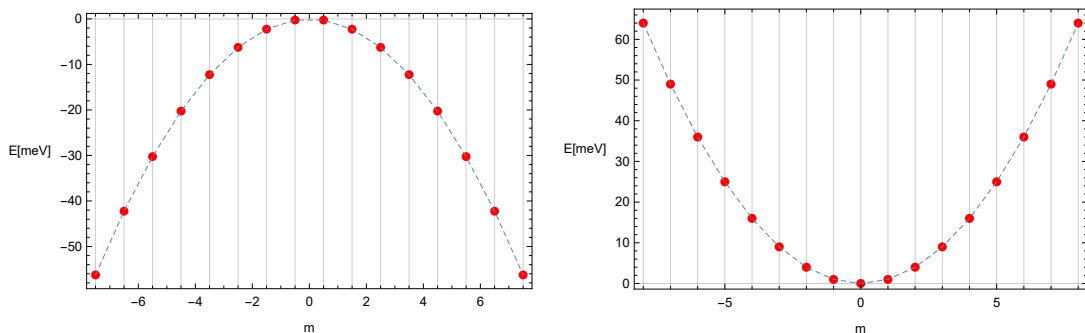


Figure 5: Energy levels of the Hamiltonian as a function of spin projection quantum number, when $E = 0$ for $D < 0$ and $D > 0$ respectively

these states. In other words there will not be a linear combination between the doubly degenerate energy states. This is called the Kramers theorem. Kramers theorem says that half-integer spin has a double degenerate ground state, when there is no magnetic field as it would break it, while Kramers doublet is a double degeneracy of the ground state if there is half-integer spin, that is, the ground state and its time reversal state with the same energy for $B = 0\text{T}$. When we apply a magnetic field the Hamiltonian will be

$$H = DS_z^2 + \frac{E}{2}(S_+^2 + S_-^2) + \tilde{\mathbf{B}} \cdot \mathbf{S}_i \quad (3.11)$$

Where the last term describes the Zeeman energy associated with an applied field, where $\tilde{B} = g\mu_B B$. The time reversal symmetry will be broken when there is a magnetic field, as we said before.

3.1 Magnetization

We have so far considered the magnetic anisotropy Hamiltonian. For a crystal exhibiting magnetic anisotropy, it requires different amounts of energy to magnetize the crystal in certain directions than in others, depending on the direction of the applied field relative to the crystal axes. We will calculate the magnetization, which is the same as the thermal average of the spin operator \hat{S}_i . Where the magnetization may be expressed as in Appendix A

$$M = g\mu_B \langle \hat{S}_i \rangle \quad (3.12)$$

The temperature is normally in the range 10 to 100 mK and $\tilde{B} = 0.1 \text{ meV}$ for $B = 1 \text{ T}$. For the plots in this subsection, we have used values for the parameters that are not necessarily physically realistic in order to illustrate the nature of the physical phenomena. If $E = 0 \text{ meV}$ the Zeeman term will be defined in the z -direction, and the two parameters that we can change are the longitudinal anisotropy (D) and the temperature.

$$H = DS_z^2 + g\mu_B B S_z \quad (3.13)$$

Depending on the sign of the longitudinal anisotropy, we can either have an easy or a hard axis. Easy axis ($D < 0$) means that it is easy to have the spin in the z -direction. Easy axis is the same as hard plane, which means that it is difficult to put the spin in the xy -plane. We will get the opposite for hard axis ($D > 0$), which means that it will be difficult to have the spin in the z -direction but easy to have it in the xy -plane. The two opposite directions along an easy axis are equivalent, and the actual direction of magnetization can be along either of them.

The magnetization is considered as a function of the external magnetic field in the z -direction. If $D = 0$ only the Zeeman term is present. The interval where magnetization is not approximately S or $-S$ depends on the temperature, and the greater the temperature is the greater is the interval. In an experimental available temperature such as 10^{-2} K , there will be a spin polarization already at zero external field. For $S = \frac{1}{2}$ the magnetization will behave as a hyperbolic tangent, as shown

$$M = -\frac{g\mu_B}{2} \tanh\left(\frac{g\mu_B B_z}{2k_B T}\right) \quad (3.14)$$

Where $\frac{g\mu_B}{k_B} \approx 1 \frac{K}{T}$. If $T \gg B_z$ the magnetization will approximately be

$$M(T \rightarrow \infty) = -\frac{g\mu_B B_z}{4T} \sim \chi \tilde{B}_z \quad (3.15)$$

In this case, if \tilde{B} is small our magnetization will go to zero. What happens is that the energy levels of spins are split up into different levels by the external magnetic field, and if $T \gg \tilde{B}$, these levels will be occupied with the same probability and thus the magnetization will be zero. Which also means that small change in the external field leads to a great change in the magnetization. However when $\tilde{B} \gg T$, only the lowest energy levels are occupied, since there is not enough thermal energy in the system to excite electrons into states of higher energy. The same applies for both integer and half-integer spin. In relation to our spectra there will not be any changes with temperature changing as shown in figure (6.a and 6.b). When we have an easy plane, will the spin be in the xy -direction, while we have the field in the z -direction, thus if $|D| = T$ it will require more external field to get spin polarization since the spin is not in the same direction as the external field. However if we have an easy axis there will be an internal polarization, as shown in figure (7.a), where mu in the figures stands for μ_B . If $|D| < T$, will we get the same behavior as for $|D| = T$ for both easy axis and easy plane but with the need of more field to get spin polarization as seen in figure 7.b.

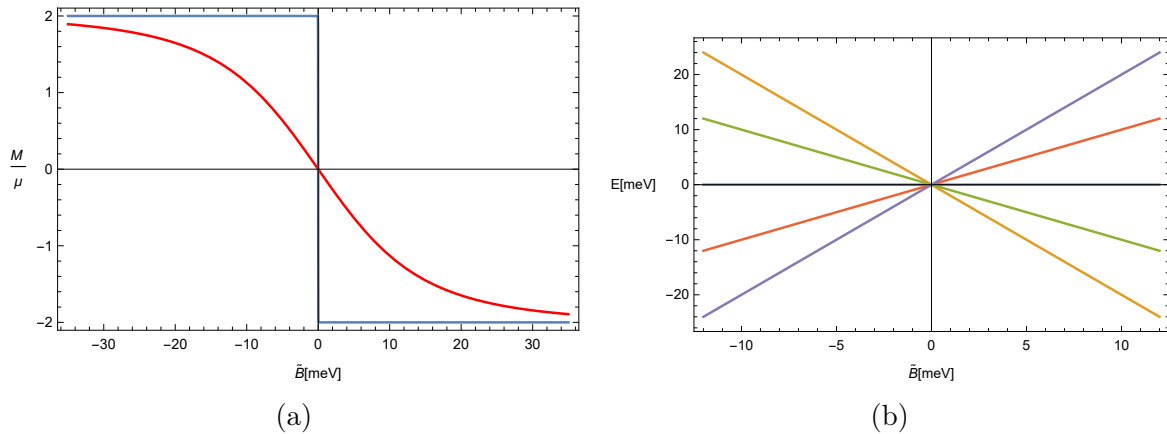


Figure 6: $\frac{M}{\mu_B}$ as function of \tilde{B} for $S = 2$. The blue and red plots indicate $T=10^{-2}K$ and $T = 15K$. Figure b is the energy as a function of \tilde{B} for $S = 2$, $D = E = 0$ meV

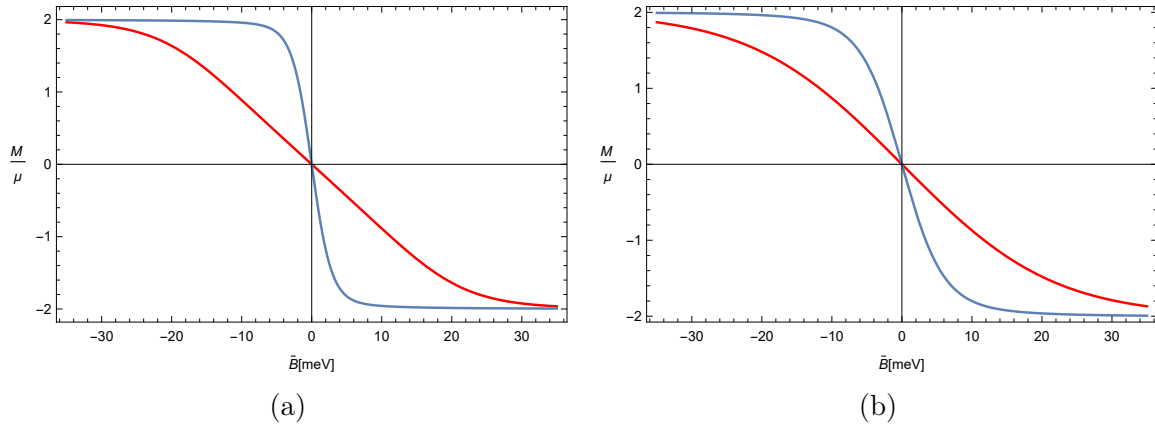


Figure 7: $\frac{M}{\mu_B}$ as function of \tilde{B} for $S = 2$ and $|D| = 5\text{meV}$, where the blue and red plots indicate easy axis and easy plane. For figure a $T = 5\text{K}$, while in b $T = 10\text{K}$.

When $|D| > T$ we will get a staircase. The difference between the half-integer and integer spin in this cases is illustrated in the figure 8. This difference occurs since the integer spin have an odd number of energy levels, where all the sates are degenerate at $\tilde{B}_z = 0\text{meV}$. When $|D| > 0$ will just each two of the levels be degenerate at $\tilde{B}_z = 0\text{meV}$ and the last level will stay along the \tilde{B}_z axis. There will also be other degeneration at $B_z > 0$, which increases with increasing the number of the spin operator. We will see the same for the half-integer spin, except for the level which was along the \tilde{B}_z axis, which is illustrated in figure 9. In cases where we have easy axis, we will not get any staircase, since the spin is in the same direction as the external field and we will get the same behavior as in $|D| > T$.

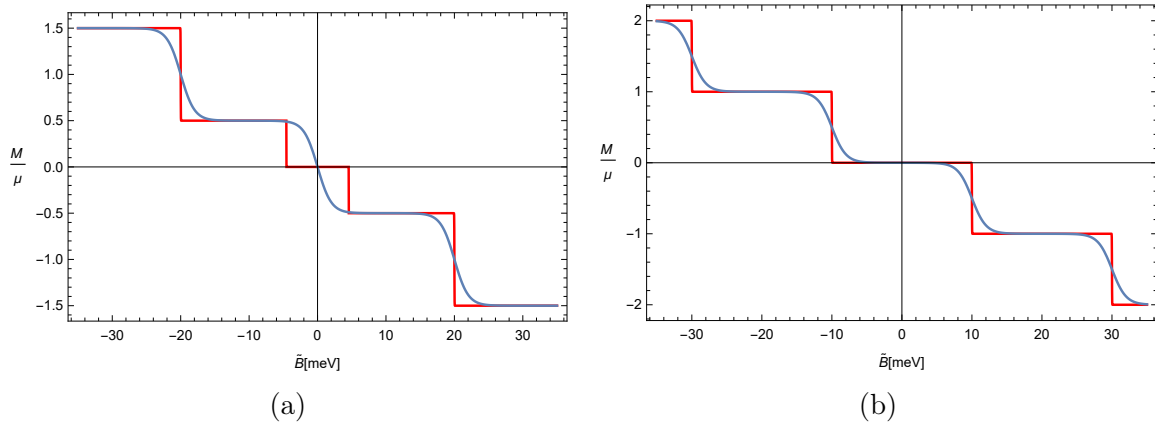


Figure 8: $\frac{M}{\mu_B}$ as function of \tilde{B} . In figure a $S = \frac{3}{2}$ and $D = 10\text{meV}$, where the red and blue plots indicate $T = 10^{-2}\text{K}$ and $T = 1\text{K}$, while in figure b the red and blue plots indicate $T = 10^{-2}\text{K}$ and $T = 1\text{K}$ for $S = 2$ and $D = 10\text{meV}$.

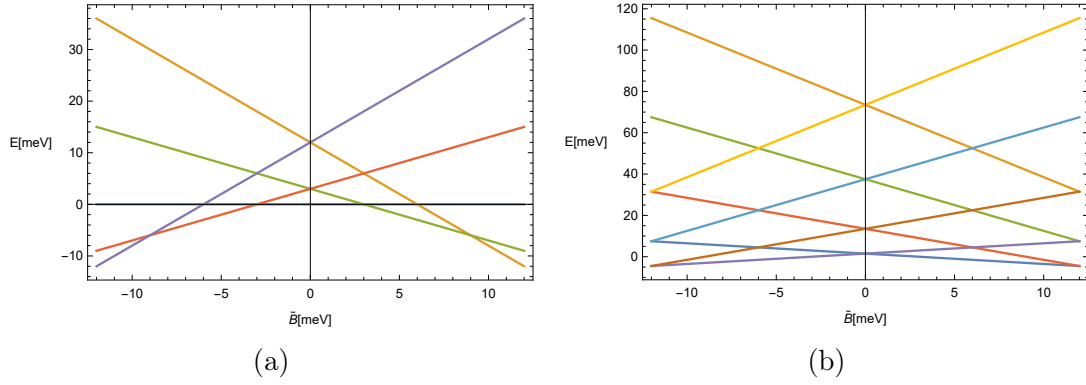


Figure 9: The energy as a function of \tilde{B} . In Figure a $S = 2$ and $D = 3$ meV, while figure b has $S = \frac{7}{2}$ and $D = 6$ meV.

In the case where both $D \neq 0$ and $E \neq 0$, we have eq. 3.11, where the Zeeman term is now $\tilde{\mathbf{B}} \cdot \mathbf{S}_i = \tilde{B}_x S_x + \tilde{B}_y S_y + \tilde{B}_z S_z$. For both the case where we have easy plane or easy axis and $|D| = T$ or $|D| < T$, will the change in E hardly be seen, the same will happen when there is an external field in both the x and y direction, as shown in Figure 10. Compared to the energy spectrum, once the transversal anisotropy $E \geq 0.01$ meV is raised, we will start to have an avoided crossing point, and the higher E is the higher is the distance between the avoided crossing point. An avoided crossing point is defined as the case when two or more eigenvalues cannot become equal in value. We will see the same for half-integer spin but with higher number of these avoided crossing points, as shown in Figure 11. From that we can conclude that if the spin is along the magnetic field, the magnetic will not have a large impact on the spin, since they are in the same direction, which means that it is an energetically favorable direction, and it goes toward a state of minimum energy, in contrast to if the spin is in a different direction than the magnetic field, thus we need more external magnetic field to get spin polarization, which means that it goes toward a state of maximum energy.

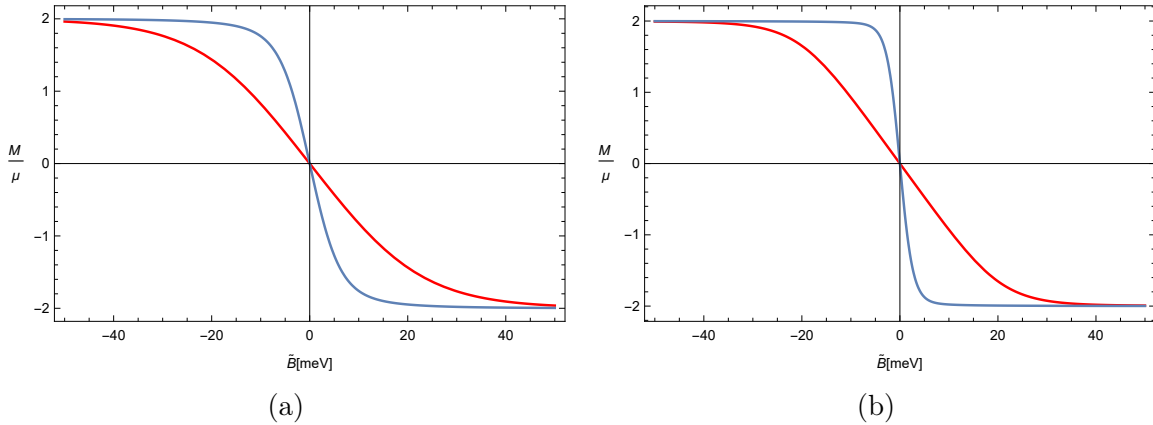


Figure 10: $\frac{M}{\mu_B}$ as function of \tilde{B} for $S = 2$, $|D| = 5$ meV and $T = 5$ K, where the blue and red plots indicate easy axis and easy plane. In figure a $E = 2$ meV and in figure b $\tilde{B}_x = \tilde{B}_y = 2$ meV

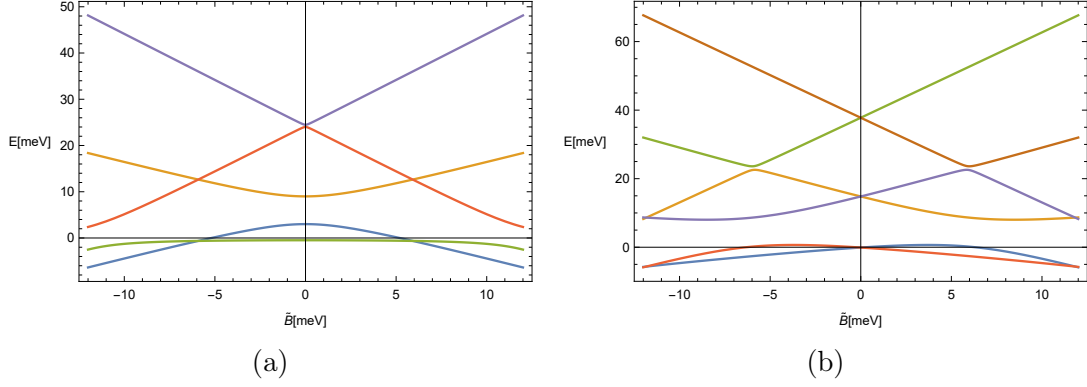


Figure 11: The energy as a function of \tilde{B} , where $D = 6$ meV and $E = 1$ meV. Figure a is for $S = 2$ and b for $S = \frac{5}{2}$

3.2 Stabilizing the magnetic moment of single Holmium atoms by symmetry

We are interested to know the probability of transition per unit time for a spin reversal between the ground states, affected by a perturbation, where we have three different symmetry-fold we will look at. The n -fold symmetry means a rotation by an angle of $\frac{360^\circ}{n}$ between atoms. We start by looking at the twofold symmetry which can be written as

$$H = DS_z^2 + \frac{E}{2}(S_+^2 + S_-^2) + \tilde{B}S_z \quad (3.16)$$

Where we put $\tilde{B} = 0$ meV in all cases. For half integer spin the raising and lowering spin operators will contribute to get a linear combination of the various S_z eigenstates as seen here

$$|\psi_2^+\rangle = \sum_{n=0}^{\hat{S}} c_n^+ |S - 2n\rangle \quad \text{and} \quad |\psi_2^-\rangle = \sum_{n=0}^S c_n^- |-S + 2n\rangle \quad (3.17)$$

We will look at the energy of the eigenstates of the H , when $D < 0$ with respect to the expectation values of $\langle \hat{S}_z \rangle$, which will lie on an inverted parabola, with two degenerate ground states as shown in Figure 12. Where a complete magnetization reversal over the full barrier is oppressed when $E = 0$ meV because it requires at least $2S$. Besides that the direct tunnel coupling between the ground states is not allowed when $E \neq 0$ meV, which means that $\langle \psi_2^\pm | S_z | \psi_2^\mp \rangle = 0$, since the ground states belonging to different combination of eigenstates. Thus the main mechanism for reversal are spin-flip by the exchange interaction with substrate electrons, wherein the perturbed Hamiltonian is

$$\hat{H}' = J\mathbf{S} \cdot \boldsymbol{\tau} = J\left[\frac{1}{2}(S_+\tau_- + S_-\tau_+) + S_z\tau_z\right] \quad (3.18)$$

$\boldsymbol{\tau}$ is the spin of the scattering electron (substrate spin) and J is the exchange interaction between these two spins. This exchange interaction with a single metal electron leads to spin flip which are described by the matrix elements of S_\pm . To figure out this probability, we use Fermi's golden rule

$$\Gamma_{f \leftarrow i} = \sum_{kk'} \frac{2\pi}{\hbar} \left| \langle f | \hat{H}' | i \rangle \right|^2 \delta(E_{fk'} - E_{ik}) n_F(\epsilon_k) (1 - n_F(\epsilon_{k'})) \quad (3.19)$$

The first part is the matrix element of the perturbation \hat{H}' , which is the matrix between the final and initial states which is needed to get spin reversal. That means that a single electron could flip the magnetic moment of the atom, if the matrix element calculated between the two ground states is non-zero.

$$\left| \langle f | \hat{H}' | i \rangle \right|^2 = \left| \langle f | J\mathbf{S} \cdot \boldsymbol{\tau} | i \rangle \right|^2 = \left| \langle f | J \left[\frac{1}{2} (S_+ \tau_- + S_- \tau_+) + S_z \tau_z \right] | i \rangle \right|^2 \quad (3.20)$$

This matrix element gives only something for half-integer spin, when we have a twofold symmetry, since the integer spin is protected from the direct tunneling coupling between to ground states with a single electron, it need two or more electrons for that. For half-integer spin and $E = 0.1D$, the higher the spin is the lower is the matrix element. We will get the same when $E = 0.01D$ multiplied by 10^{-2x-1} where 10^{-x} is what we got from $E = 0.1D$ and for $E = 0.001D$ will we get 10^{-3x-2} .

The crystal field symmetry has a large effect on the magnetization reversal. By placing an Holmium atom on the surface of a metal, it will give rise to a threefold symmetry [9], which have the point groups C_{3v} . Holmium atom is a part of the rare-earth group with electron configuration Ho = $[Xe]4f^{11}6s^2$. Thus the quenching is not important in Ho atom, since the effect of LS coupling is larger than the crystal field and the electronic states specified by the total angular momentum. For Holmium atom $J = 8$ but for simplicity we set $S = 8$ as we do not see especially on the rare-earth group. If we start looking at the Hamiltonian for the threefold symmetry

$$H_3 = D_3 S_z^2 + \tilde{B} S_z + E_3 [S_z (S_+^3 + S_-^3) + (S_+^3 + S_-^3) S_z] \quad (3.21)$$

We just include the lowest non-vanishing order of multi-axial anisotropy, which we refer to as the hexaxial anisotropy quantified by its E_3 [10]. For integer spin there we will be three distinctive groups of linear combination of eigenstates, which are

$$|\psi_3^+\rangle = \sum_{n=0}^{\lfloor \frac{2S}{3} \rfloor} c_n^+ |S - 3n\rangle, \quad |\psi_3^-\rangle = \sum_{n=0}^{\lfloor \frac{2S}{3} \rfloor} c_n^- |-S + 3n\rangle \quad \text{and} \quad |\psi_3^0\rangle = \sum_{-\frac{S}{3}}^{\lfloor \frac{S}{3} \rfloor} c_n^0 |3n\rangle \quad (3.22)$$

$\text{floor}(S) = \lfloor S \rfloor$ is the largest integer less than or equal to S . Each coupling $|S_z\rangle$ states with $\Delta S_z = 3$, which leads to a direct tunneling between the ground states for integer multiple of three, while it is avoided for other integer spin. The difference in threefold from the twofold symmetry is that the eigenstates of $|\psi_3^0\rangle$ are located in the barrier, which means that $\langle \psi_3^0 | S_z | \psi_3^0 \rangle = 0$, as illustrated in the figure 12. In threefold symmetry the single electron can not have a spin switching between the ground states, since two or more electrons are needed, which means that $\langle \psi_3^\pm | S_+ | \psi_3^\mp \rangle = \langle \psi_3^\pm | S_- | \psi_3^\mp \rangle = 0$, only if there is a magnetic field will this two terms not be zero, since it will break the time reversal symmetry. Thus the special in the threefold compared to the twofold symmetric system is that its symmetry protect it from a spin switching by a single electron, since it need two or more electron for doing that which is impossible to get

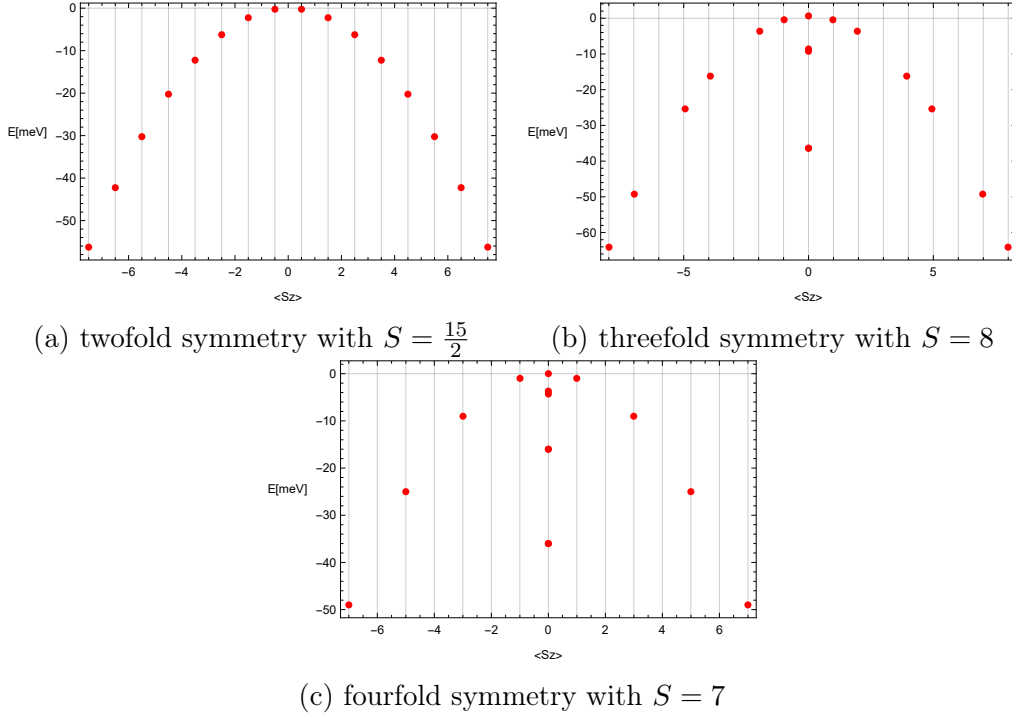


Figure 12: The energy levels of the three different fold symmetry as a function of the expectation value of S_z , where $D = -1 \text{ meV}$ and $E = 10^{-4} \text{ meV}$

two or more electron at the same time. Therefor the probability of keeping the spin magnetized higher. When we have two electrons will the probability to get spin switching being lower the lower E is.

Compared to the fourfold symmetry which have the point group C_4 , the Hamiltonian is

$$\hat{H}_4 = D_4 S_z^2 + \tilde{B} S_z + E_4 (S_+^4 + S_-^4) \quad (3.23)$$

E_4 is the coefficient of the multiaxial anisotropy. For odd integer spin there we will be four distinctive groups of linear combination of eigenstates, which are

$$\begin{aligned} |\psi_4^+\rangle &= \sum_{n=0}^{\lfloor \frac{S}{4} \rfloor} c_n^+ |S - 4n\rangle, & |\psi_4^-\rangle &= \sum_{n=0}^{\lfloor \frac{S}{4} \rfloor} c_n^- |S - 4n\rangle \\ |\psi_4^0\rangle &= \sum_{n=0}^{\lfloor \frac{2S-1}{4} \rfloor} c_n^0 |S - 1 - 4n\rangle, & |\psi_4^1\rangle &= \sum_{n=0}^{\lfloor \frac{2S-3}{4} \rfloor} c_n^1 |S - 3 - 4n\rangle, \end{aligned} \quad (3.24)$$

The reason for choosing odd integer spin, is in order to have the ground states belonging to different combination of eigenstates. Similar to the threefold the fourfold symmetric system is protected from direct tunneling between the two ground states with a single electron when $\tilde{B} = 0$. We will again see that there will be some states located in the barrier, which are the eigenstates for both $|\psi_4^0\rangle$ and $|\psi_4^1\rangle$.

In order to find the density of the final states, we must calculate the Fermi–Dirac distribution as shown in Appendix C, where we get

$$\Gamma_{f \leftarrow i} \propto \rho_F^2 \frac{\Delta}{\exp(\frac{\Delta}{k_B T}) - 1} \approx \begin{cases} \rho_F^2 \Delta \exp(-\frac{\Delta}{k_B T}) & T \ll \Delta \\ \rho_F^2 T & T \gg \Delta \end{cases} \quad (3.25)$$

where $J^2 \rho_F^2 = 0.1$. The density of the final states is a constant, while the the Bose-Einstein distribution $[\Delta n_B(\Delta)]$ will only give something if the matrix element is not

zero. If the matrix element is not zero, will Bose distribution depends on the temperature. The larger the temperature is the larger is the overlap between the final and initial states which can be seen in the Fermi-Dirac distribution (13.a), while figure (13.b) shows the Bose distribution which starts having an exponential decay and then grows linearly with the temperature.

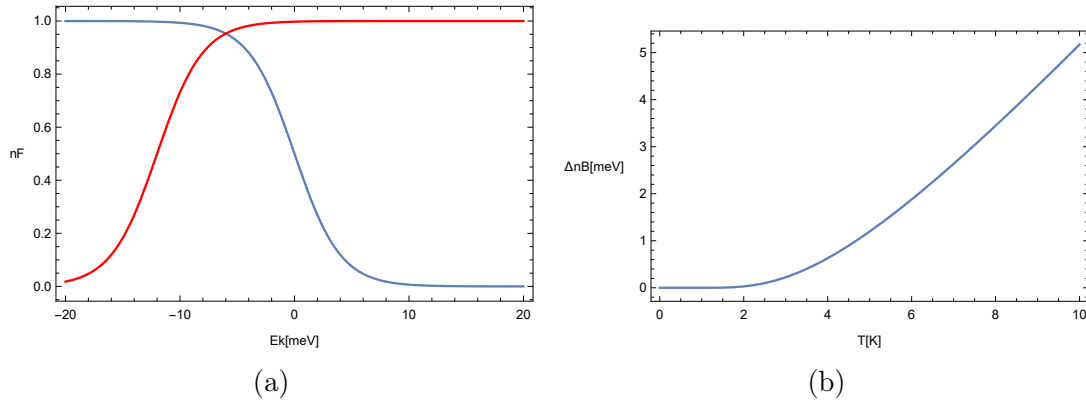


Figure 13: Figure a is the Fermi-Dirac distribution as a function of the Fermi energy, with $\Delta = 12$ meV and $T = 2$ K. The second figure is the Bose distribution with $\Delta = 12$ meV.

4 Conclusion

As we have shown the crystal field has a large influence on the free atom. Depending on the crystal field structure we will get different energy states splitting. The symmetry of the crystal field has also a great influence on keeping the magnetic moment magnetized, it determines if the spin is long-lived or not. The probability of transition per unit time is proportional to the matrix element, which is zero when we have a single electron for both three- and fourfold symmetry, and thus they have a long-lived spin. While for twofold symmetry the matrix element will not give zero with a single substrate electron, thus it does not have a long-lived spin.

5 References

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Appendix

A Magnetization

The magnetization may be expressed as

$$M = g\mu_B \sum_i \langle \hat{S}_i \rangle = g\mu_B \frac{\text{Tr}[\hat{S}_i \exp(-\beta \hat{H})]}{Z} = \frac{g\mu_B}{Z} \sum_{m,n=-S}^S \langle m | \hat{S}_i | n \rangle \langle n | \exp(-\beta \hat{H}) | m \rangle \quad (\text{A.1})$$

$$\begin{aligned} &= \frac{g\mu_B}{Z} \sum_{n=-S}^S \langle n | \hat{S}_i | n \rangle \delta_{mn} \exp(-\beta E_n) \\ &= \frac{g\mu_B}{Z} \sum_{n,\tilde{m},\tilde{m}'=-S}^S \langle n | \tilde{m} \rangle \langle \tilde{m} | \hat{S}_i | \tilde{m}' \rangle \langle \tilde{m}' | n \rangle \exp(-\beta E_n) \\ &= \frac{g\mu_B}{Z} \sum_{n,\tilde{m},\tilde{m}'=-S}^S U_{n\tilde{m}}^\dagger \hat{S}_{\tilde{m}\tilde{m}'}^i U_{\tilde{m}n} \exp(-\beta E_n) \end{aligned} \quad (\text{A.2})$$

$U_{\tilde{m}n}$ is the eigenvectors of our Hamiltonian transpose, and when we complex conjugate and transpose our $U_{\tilde{m}n}$ we gets $U_{n\tilde{m}}^\dagger$. Z is called the partition function.

$$Z = \sum_{i=1}^{N+1} \exp(-\beta E_i) \quad (\text{A.3})$$

E_i is the energy of the i th configuration of the system, $\beta = \frac{1}{k_B T}$ where $k_B \sim 10^{-23} \frac{J}{K}$. The energy of the system is given by the Hamiltonian. The partition function of our Hamiltonian is thus

$$Z = \sum_{n=-s}^s \exp(-\beta E_n) = \sum_{n=-s}^s \langle n | \exp(-\beta \hat{H}) | n \rangle = \text{Tr}[\exp(-\beta \hat{H})] \quad (\text{A.4})$$

The trace is the sum of the diagonal values (the eigenvalues) of \hat{H} .

B Anisotropy spin Hamiltonian

The anisotropy spin Hamiltonian represent the anisotropy energy for the spin direction. If take the principal axes of the crystal as our x -, y - and z -axis and by splitting Λ into x - y - and z -components our anisotropy spin Hamiltonian can be rewritten as

$$H = \Lambda_x S_x^2 + \Lambda_y S_y^2 + \Lambda_z S_z^2 \quad (\text{B.1})$$

since it only produce diagonal elements. This is the same as

$$\begin{aligned} \hat{H} = -\lambda^2 & \left[\frac{1}{3} \left(\Lambda_x + \Lambda_y + \Lambda_z \right) S \left(S + 1 \right) \right. \\ & + \frac{1}{3} \left[\Lambda_z - \frac{1}{2} \left(\Lambda_x + \Lambda_y \right) \right] \left[3S_z^2 - S(S + 1) \right] \\ & \left. + \frac{1}{2} \left(\Lambda_x - \Lambda_y \right) \left(S_x^2 - S_y^2 \right) \right] \end{aligned} \quad (\text{B.2})$$

The anisotropy Hamiltonian lifts the $(2S + 1)$ -fold degeneracy of the spin. Omitting the constant term, we obtain from (B.2) [4].

$$\hat{H} = D \hat{S}_z^2 + E(S_x^2 - S_y^2) \quad (\text{B.3})$$

C Fermi–Dirac distribution

In order to calculate the density of the final states, we start to find the Fermi–Dirac distribution which will only give something when we have

$$\begin{aligned} & \sum_{kk'} \delta(E_{fk'} - E_{ik}) n_F(\epsilon_k) (1 - n_F(\epsilon_{k'})) \\ = V \int \frac{d^3k}{(2\pi)^3} \delta(E_{fk'} - E_{ik}) & V \int \frac{d^3k'}{(2\pi)^3} \delta(E_{fk'} - E_{ik}) \left(\frac{1}{\exp(\frac{\epsilon_k - \mu}{k_b T}) + 1} \right) \left(1 - \frac{1}{\exp(\frac{\epsilon_k - \Delta - \mu}{k_b T}) + 1} \right) \end{aligned} \quad (\text{C.1})$$

Which only will give something when

$$E_{fk'} = E_{ik} \rightarrow E_f + \epsilon_{k'} = E_i + \epsilon_k \rightarrow \epsilon_{k'} = \epsilon_k + E_i - E_f = \epsilon_k - \Delta \quad (\text{C.2})$$

E_i and E_f is the energy of the states initial and final states respectively while ϵ_k and $\epsilon_{k'}$ are the fermi energy. The Fermi–Dirac distribution when we replace $\epsilon_{k'}$ with ϵ_k is then

$$\begin{aligned} n_F(\epsilon_k) (1 - n_F(\epsilon_{k'})) & = \left(\frac{1}{\exp(\frac{\epsilon_k - \mu}{k_b T}) + 1} \right) \left(1 - \frac{1}{\exp(\frac{\epsilon_k - \Delta - \mu}{k_b T}) + 1} \right) \\ & = \left(\frac{1}{\exp(\frac{\epsilon_k}{k_b T}) + 1} \right) \left(\frac{1}{\exp(\frac{-\epsilon_k + \Delta + \mu}{k_b T}) + 1} \right) \\ & = \frac{1}{\exp(\frac{\epsilon_k - \mu}{k_b T}) + \exp(\frac{\Delta}{k_b T}) + \exp(\frac{\Delta - \epsilon_k + \mu}{k_b T}) + 1} \end{aligned} \quad (\text{C.3})$$

If we then replace C.3 in C.1 we get

$$\begin{aligned}
V \int \frac{d^3k}{(2\pi)^3} \delta(E_{fk'} - E_{ik}) V \int \frac{d^3k'}{(2\pi)^3} \delta(E_{fk'} - E_{ik}) \int d\epsilon \frac{1}{\exp(\frac{\epsilon_k - \mu}{k_b T}) + \exp(\frac{\Delta}{k_b T}) + \exp(\frac{\Delta - \epsilon_k + \mu}{k_b T}) + 1} = \\
\rho_f^2 \int d\epsilon \frac{1}{\exp(\frac{\epsilon_k - \mu}{k_b T}) + \exp(\frac{\Delta}{k_b T}) + \exp(\frac{\Delta - \epsilon_k + \mu}{k_b T}) + 1}
\end{aligned} \tag{C.4}$$

We put

$$x = \frac{\epsilon_k - \mu}{k_B T} \quad \text{and} \quad \tilde{\Delta} = \frac{\Delta}{k_B T} \tag{C.5}$$

Then we get

$$\begin{aligned}
\int_{-\infty}^{-\infty} dx \frac{k_B T}{\exp(x) + \exp(\tilde{\Delta}) + \exp(\tilde{\Delta} - x) + 1} &= \frac{\ln(1 + \exp(x)) - \ln(\exp(\tilde{\Delta}) + \exp(x))}{\exp(\tilde{\Delta}) - 1} \\
&= \frac{\Delta}{\exp(\frac{\Delta}{k_B T}) - 1} \approx \begin{cases} \Delta \exp(-\frac{\Delta}{k_B T}) & T \ll \Delta \\ T & T \gg \Delta \end{cases}
\end{aligned} \tag{C.6}$$