

Magnetism course 2014, Supplementary problems

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1 Introduction

1.1 Spin operators

As you know from Blundell 1.3.3, the spin raising and lowering operators are defined as $s^\pm = s^x \pm is^y$. These operators have the following effect on a (total ionic) spin s in the state with a particular m -value $|s, m\rangle$:

$$s^\pm |s, m\rangle = \sqrt{(s \mp m)(s \pm m + 1)} |s, m \pm 1\rangle. \quad (1)$$

1. Calculate from this the commutators $[s^-, s^+]$ and $[s^z, s^\pm]$.
2. Show that the very common scalar product of two vector operators $\mathbf{s}_1 \cdot \mathbf{s}_2$ may be written as $s_1^z s_2^z + \frac{1}{2}(s_1^+ s_2^- + s_1^- s_2^+)$.

1.2 Magnetic interaction of two particles

We consider two interacting particles of spin $s = 1/2$. Using the basis where the spins point up/down along the z-axis, convince yourself that the Hilbert space is spanned by 4 basis states (write down what they are). Calculate the eigenstates and eigenenergies for the following Hamiltonians. Assume an antiferromagnetic coupling where $J < 0$. Hint: remember the solution to Problem 1.1.

1. The Ising Hamiltonian $H_I = -2Js_1^z s_2^z$.
2. The Heisenberg Hamiltonian $H = -2J\mathbf{s}_1 \cdot \mathbf{s}_2$.

3. The XY-Hamiltonian $H_{xy} = -2J(s_1^x s_2^x + s_1^y s_2^y)$
4. The more general anisotropic Hamiltonian $H_{xxz} = -2J_x(s_1^x s_2^x + s_1^y s_2^y) - 2J_z s_1^z s_2^z$.
5. Add a magnetic field, giving rise to a Zeeman term $H_Z = -g\mu_B B S^z \equiv -hJ(s_1^z + s_2^z)$ to the Ising, Heisenberg, and XY Hamiltonians. Draw the energies of the states as a function of field.

2 Isolated magnetic moments

2.1 Hund's rules

From Hund's rules, construct a table of the 11 configurations of the $3d$ shell (0-10 times occupied) for a free ion: List the values of S , L , and J . Place the most common transition metal ions in these groups. (You may want to consult a periodic table, Blundell p.33, and perhaps a textbook on inorganic chemistry.)

Which ions would you prefer to study if you were interested in quantum effects?

3 Environments

3.1 Kramers doublet

A crystal field can give rise to quenching of the orbital moment, as described in Blundell, 3.1. The crystal field can in addition give rise to a single-ion anisotropy, described by an effective spin Hamiltonian.

Consider an Mn^{4+} ion in an anisotropic crystal field, described by the general expression

$$H = DS_z^2 + E(S_x^2 - S_y^2). \quad (2)$$

Consider the case $D > 0, E > 0, D > E$. Calculate the energy eigenvalues and eigenstates of the ion and show explicitly that the ground state is doubly degenerate. You may want to study Problem 1.1 first, and use the spin raising and lowering operators defined there.

There is a general theorem in magnetism saying that a half-integer system is always at least doubly degenerate. The ground state of such a system is called a *Kramers doublet*.

3.2 Crystal field splitting of p orbitals

Although p -orbitals are not interesting from a magnetic point of view, we will here use these orbitals to illustrate the mechanism of crystal field splitting, discussed in Yosida 3.2. As a simplification, we consider only a single electron in the p orbitals.

1. **The p -orbitals.** Unless you are well off in atomic physics, use Yosida (1.12 - 1.16) to show that the p orbitals are given by

$$\phi_{n1m} = R_{n1}(r)Y_1^m(\theta, \phi), \quad (3)$$

where the spherical harmonics are given by

$$\begin{aligned} Y_1^1(\theta, \phi) &= -\sqrt{\frac{3}{8\pi}} \sin(\theta) e^{i\phi} \\ Y_1^0(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos(\theta) \\ Y_1^{-1}(\theta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{-i\phi} \end{aligned}$$

2. **Inversion symmetry.** Use Yosida (3.11) to show that in a crystal with inversion ($\mathbf{r} \rightarrow -\mathbf{r}$) symmetry, the coefficients K_{lm} vanish for odd l .
3. **Cubic symmetry.** Show (by general arguments), that in cubic symmetry the terms K_{20} , K_{22} , and K_{42} in Yosida (3.13- 3.14) vanish.
4. **Orthorhombic symmetry.** Assume now that the crystal has orthorhombic symmetry (x and y are still equivalent, but there is a distortion from cubic symmetry in the z direction). Argue that K_{22} and K_{42} still vanish.
5. **Matrix elements of the crystal field** Calculate explicitly the matrix elements, $\langle \phi_{n1m} | f(\mathbf{r}) | \phi_{n'1m'} \rangle$, between the three p orbitals of the functions $f(\mathbf{r}) =$

$$3z^2 - r^2 \quad (4)$$

$$35z^4 - 30z^2r^2 + 3r^4 \quad (5)$$

$$x^4 - 6x^2y^2 + y^4 \quad (6)$$

and calculate the equivalent operator expressions, similar to Yosida (3.17). Calculate also the coefficients corresponding to α and β .

6. **The crystal field splitting.** Assume $K_{20} > K_{40} > K_{44} > 0$. Calculate the crystal field splittings and create a diagram like one of the four in Yosida Figure 3.3.

4 Interactions

4.1 Exchange in the H_2 molecule

In this problem we shall study how the kinetic exchange (superexchange) appears in a small system that is exactly solvable. The problem is to a large extent borrowed from Ashcroft and Mermin (ch. 32, 5).

We describe a hydrogen molecule from the atomic point of view: An electron may be located on either of the two atoms, and there is a small probability of hopping from one atom to the next. This is often described by the Hubbard Hamiltonian, the formalism of which is out of the scope for this course.

We consider electrons in the ground state atomic orbital only. The energy of an electron in this orbital is $\epsilon < 0$. We can consider ϵ as being the eigenenergy of the (trivial) starting Hamiltonian, H_0 .

We now allow the electron to hop - with no spin flip - from one atom to another, with the amplitude t . This is described by the (hermitean) Hamiltonian term H_t , which has the matrix elements

$$\langle 1 \uparrow | H_t | 2 \uparrow \rangle = -t. \quad (7)$$

Here, $|i \uparrow\rangle$ is our notation for the electron being on site i with spin up. The similar matrix element for spin down also has the value $-t$.

1. Consider first the single electron in the hydrogen molecular ion, H_2^+ . Argue that the energy does not depend upon the spin of the electron and that there are in total 4 different states in the subspace.
2. Using the Hamiltonian $H = H_0 + H_t$, show that the energies are doubly degenerate and that the values are $\epsilon \pm t$.
3. Are the groundstates symmetric or antisymmetric with respect to exchange of the two atomic labels?
4. Consider now the H_2 molecule with two electrons. Note that the hopping term (7) in the Hamiltonian now works for either of the two electrons - but does not allow a simultaneous hop of both electrons.

In the independent electron approximation (ignoring the Pauli principle and the Coulomb repulsion), calculate the energy of the “naive ground state”.

5. In the ground state found above, argue that the probability for two electrons being on the same site equals $1/2$.
6. We now include an energy penalty U if the two electrons are on the same site (zero otherwise). The corresponding Hamiltonian, H_U is diagonal and is exemplified by its matrix element

$$\langle \uparrow_i; \downarrow_i | H_U | \uparrow_i; \downarrow_i \rangle = U. \quad (8)$$

Taking H_U as a first order perturbation term, argue that the improved estimate of the ground state energy becomes $E_{U1} = 2(\epsilon - t) + U/2$.

7. When you take electron correlations into account, things become more interesting – but also more difficult. When ignoring the Pauli principle, you have a subspace of in total 16 different configurations. Convince yourself about that, and find the 6 states allowed by the Pauli principle.
8. How many of these states are symmetric with respect to coordinate exchange in spin space (triplets) – and how many with respect to real space (singlets)?
9. Using the full Hamiltonian, $H = H_0 + H_t + H_U$, show that the energy of the triples state(s) is $E_{\text{trip}} = 2\epsilon$.
10. Show that the Hamiltonian of the singlet states may be written as

$$H_s = \begin{pmatrix} 2\epsilon & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 2\epsilon + U & 0 \\ -\sqrt{2}t & 0 & 2\epsilon + U \end{pmatrix}. \quad (9)$$

11. Find the energies of the singlet states and argue that the total ground state (energy E_0) is found in this subspace.
12. What is the behaviour of E_0 for small U/t and for large U/t ? For the latter case, comment on the similarity between this system and the two-atom antiferromagnet in problem 1.2.
13. Find the exact ground state and calculate the probability that two electrons are on the same site. Investigate the limits small U/t , and large U/t . Comment on the physical understanding of the latter case.

5 Order and magnetic structures

5.1 Geometrical frustration in antiferromagnetism

Let us consider a system of N $S = 1/2$ spins, interacting via the nearest neighbour antiferromagnetic Ising Hamiltonian ($J < 0$):

$$\mathcal{H} = -2J \sum_{\langle i,j \rangle} S_i^z S_j^z - g\mu_B B \sum_j S_j^z. \quad (10)$$

1. Consider a two-dimensional square lattice at zero field. How will the spin configuration of the ground state look and what is the energy?
2. How many different ground states can you find?
3. Which value of the field do you need to change the ground state configuration?
4. Consider a two-dimensional triangular lattice at zero field. Find one ground state configuration and calculate its energy.
5. Construct a ground state where (at least) one spin may be flipped without affecting the total energy.
6. How many different ground states can you find? (You will surely not find all, but try anyway).
7. Give an estimate of the $T = 0$ spin entropy in terms of the largest possible spin entropy: $S_{\max} = Nk_B \ln(2)$. Hint: Remember that the $T = 0$ entropy is $S_0 = k_B \ln(W_0)$ where W_0 is the number of ground states. Hint 2: What is the entropy of a triangle of spins?
8. Consider the triangular lattice at $B > 0$. How does the ground state look like at small fields?
9. Calculate the ground state energy and spin entropy.
10. How large a field is necessary to turn all spins in the same direction?

5.2 The spin-flop transition

This problem deals with a simplified calculation of the spin-flop transition.

Let us deal with only two classical spins and assume that they interact via an anisotropic antiferromagnetic interaction with a field applied along the z -axis

$$H = -2J^z s_1^z s_2^z - 2J^{xy}(s_1^y s_2^y + s_1^x s_2^x) - g\mu_B H(s_1^z + s_2^z), \quad (11)$$

where $J^z < J^{xy} < 0$. Temperature effects are neglected, $T = 0$.

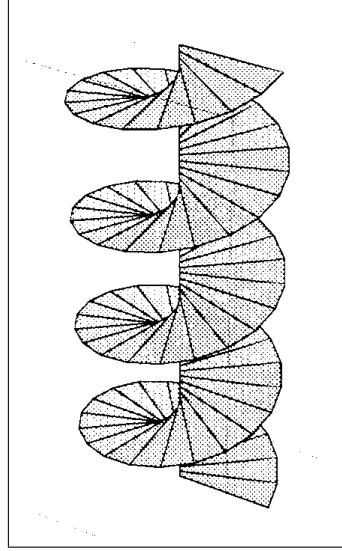
1. Argue that in zero field the two spins arrange themselves so that one spin points up and the other points down along the z -axis (scenario 1).
2. In applied fields the spins may rearrange to find the lowest energy. Consider the situation where the spin pointing down turn an angle θ in order to lower its Zeeman energy. Show that as a function of field, only the angles $\theta = 0$ and π are energy minima. Calculate the field, H_1 , where $\theta = \pi$ becomes the ground state.
3. Consider the state where the two spins both lie in the (x, y) -plane, pointing opposite ways. Calculate the energy of that state in zero field.
4. With increased field, the spins may turn towards the z -direction; assume they both tilt the same angle, ϕ , (scenario 2). Show that with increasing field, different values of ϕ are chosen and calculate $\phi(H)$.
5. Compare the energies of the two scenarios above by plotting $E(H)$ for the two scenarios, and for the state where both spins point along the field. Calculate the field value, H_{flop} where the *spin-flop transition* between scenario (1) and (2) takes place.
6. Calculate the susceptibility, χ , in the spin-flop phase.

5.3 The Heisenberg model — Helical structures, classical treatment

In spite of its simplicity, the Heisenberg model is a source of great complexity. It has proved ideal as a test case for many different many-body techniques. The one-dimensional large- S limit where quantum fluctuations are small is a good model for most of the rare earth elements.

In heavy rare earths a strong ferromagnetic coupling causes all the moments within a hexagonal basal plane to align parallel, while the direction of the moments vary from plane to plane. We are therefore left with an effectively one-dimensional model.

As described in Blundell 5.4, one of the encountered structures corresponds to a helical structure, where each hexagonal basal plane of ferromagnetically aligned magnetic moments is rotated a given angle with respect to the previous. This structure is observed in the rare earth elements Tb, Dy and Ho within certain temperature ranges.



Consider a linear chain of classical angular momenta separated by the distance a along the z -axis. The moments are coupled through the Heisenberg interaction, which for a classical system should be minimised to find the ground state:

$$E = -2 \sum_{\langle m,n \rangle} \mathcal{J}_{mn} \mathbf{S}_m \cdot \mathbf{S}_n \quad (12)$$

1. Which of the following rewritings of the lattice summation is correct for our linear chain of N atoms?

$$E = -2 \sum_n \sum_{\rho=1}^N \mathcal{J}_{\rho} \mathbf{S}_n \cdot \mathbf{S}_{n+\rho} \quad (13)$$

$$E = - \sum_n \sum_{\rho=1}^N \mathcal{J}_{\rho} \mathbf{S}_n \cdot \mathbf{S}_{n+\rho} \quad (14)$$

$$E = -\frac{1}{2} \sum_n \sum_{\rho=1}^N \mathcal{J}_{\rho} \mathbf{S}_n \cdot \mathbf{S}_{n+\rho} \quad (15)$$

2. Assume the moments to have form of figure 5.15 in Blundell. In fact there exist another structure for non-zero Q with exactly the same energy — which?
3. Show that if the only non-zero coupling is between nearest neighbours, the system will order ferro- or antiferromagnetically depending on the sign of the coupling.
4. Show by direct evaluation of (12) that when also next nearest neighbour interaction is included a ground state with nonzero Q can occur provided that $\mathcal{J}_2 < 0$ while $|\mathcal{J}_2| > |\mathcal{J}_1|/4$.
5. Let us define the Fourier transform of J as

$$\mathcal{J}(\mathbf{q}) = \sum \exp(i\mathbf{q} \cdot \rho) J_\rho, \quad (16)$$

where ρ denotes the vectors connecting one moment to its different neighbours. Plot the Fourier transform of the interaction $\mathcal{J}(q_z)$ for different interesting choices of $\mathcal{J}_2/\mathcal{J}_1$.

6 Order and broken symmetry

6.1 Spinwaves in an anisotropic ferromagnet

We will here slowly work our way through the quantum mechanical calculation of the spin waves in a one-dimensional spin S ferromagnet with localized atomic moments, like in Chapter 6.6.1. Notice that the problem is general, *i.e.*, one cannot assume $S = 1/2$.

This problem owes much to the problems 33.4 and 33.5 in Ashcroft and Mermin.

Let us first define the Fourier transform of J as

$$\mathcal{J}(\mathbf{q}) = \sum \exp(i\mathbf{q} \cdot \rho) J_\rho, \quad (17)$$

where ρ denotes the vectors connecting one moment to its different neighbours.

Next, consider a ferromagnetic Hamiltonian of the form

$$H = - \sum_{j,\rho} \left(J_\rho^z s_j^z s_{j+\rho}^z + J_\rho^{xy} (s_j^y s_{j+\rho}^y + s_j^x s_{j+\rho}^x) \right) - g\mu_B H \sum_j s_j^z, \quad (18)$$

where ρ can be thought of as a vector connecting nearest (and perhaps next-nearest) neighbours. The z -direction is "easy" (*i.e.* $J_\rho^z > J_\rho^{xy} > 0$) and the

field is applied along this direction. We assume translational symmetry and periodic boundary conditions, $\mathbf{s}_{N+1} \equiv \mathbf{s}_1$.

1. Prove that the state with all spins up is an eigenstate of the system. Argue that this state, $|0\rangle$, is the ground state and calculate its energy.
2. Denote the state with one lowered spin as $|j\rangle = (2S)^{-1/2} s_j^- |0\rangle$. Prove that $|j\rangle$ is only an eigenstate of H if $J_{xy} = 0$ (the Ising case) and calculate $H|j\rangle$.
3. Denote the Fourier transform of the spin lowering operator as $s_k^- = 1/\sqrt{N} \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) s_j^-$. Prove that the spin wave state

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{2S}} s_k^- |0\rangle \quad (19)$$

is an eigenstate of H .

4. Calculate the energy of the spin wave state, $|\mathbf{k}\rangle$. Show that for nearest-neighbour interactions only and in the Heisenberg limit, $J_\rho^z = J_\rho^{xy}$, you reach Blundell (6.25).

6.2 Long-range order of low-dimensional magnets

We shall in this problem go deeper into the Mermin-Wagner theorem: The absence of long-range magnetic order of isotropic magnets in one and two dimensions.

Let the Hamiltonian be given by

$$H = -2 \sum_{n,\rho} J_\rho \mathbf{s}_n \cdot \mathbf{s}_{n+\rho}, \quad (20)$$

J_ρ being either ferro- or antiferromagnetic.

1. Show (using results from the book) that in the limits of low wavenumber the ferromagnetic spinwave energy (with no anisotropy) may be approximated by

$$\hbar\omega_{\text{FM}}(\mathbf{k}) \approx C_{\text{FM}} k^2, \quad (21)$$

The corresponding equation for the antiferromagnet reads

$$\hbar\omega_{\text{FM}}(\mathbf{k}) \approx C_{\text{AFM}} k \quad (22)$$

2. Show that the mean number of spinwaves, $\langle n(\mathbf{k}) \rangle$, is given by the Bose occupation number, eqn. (8.21).
3. Argue that the total number of spinwaves may be approximated by an integral over \mathbf{k} -space, given for 3 dimensions by eqn. (8.22).
4. Investigate whether this integral is convergent for the ferro- and anti-ferromagnetic case in 1 and 2 dimensions.
5. How would you interpret the fact that one or more of the above integrals may diverge?

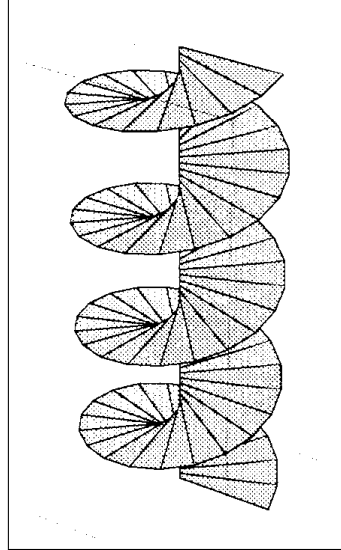
9 Advanced problems

9.1 The Heisenberg model — Helical structures, quantum mechanical treatment

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In heavy rare earths a strong ferromagnetic coupling causes all the moments within a hexagonal basal plane to align parallel, while the direction of the moments vary from plane to plane. We are therefore left with an effectively one-dimensional model.

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(This part of the problem cannot be solved from Blundell!) In the previous we investigated the classical Heisenberg system, where of course quantum fluctuations are neglected. The full quantum Heisenberg Model comprises a complicated many-body problem which cannot be solved in

general. The many-body nature of the problem is evident from the Hamiltonian $\mathcal{H} = -\sum_{n,m} \mathcal{J}_{nm} \mathbf{S}_n \cdot \mathbf{S}_m$, which acts on two spins at the same time. The mean field (also known as molecular field) approximation is a way of approximating this two-body operator by an effective one-body operator.

1. Write down the term that has been neglected in the approximation of equation (12) above.
2. Write down the mean field Hamiltonian in terms of the effective magnetic field, ignoring the constant terms.
3. Argue that equation (5.32) is the thermal expectation value $|\langle \mathbf{S}_n \rangle|/S = \text{Tr}\{(|\mathbf{S}_n|/S)e^{-\beta\mathcal{H}}\}/Z$ of the spin operator, especially what concerns the $J(Q)$ term.
4. Find the Néel temperature (5.35) below which spontaneous ordering can occur, and give it in terms of \mathcal{J}_1 and \mathcal{J}_2 .
5. Well above T_N we can regard the mean field approximation as a weak perturbation of the Zeeman term (5.38) from a sufficiently strong external field. Assume $|\langle S_n \rangle| = \sigma$ and write down H_{eff} .
6. Derive the result in Eq. (5.39) and give it in terms of \mathcal{J}_1 and \mathcal{J}_2 .
7. For a specific physical system, how would you measure \mathcal{J}_1 and \mathcal{J}_2 experimentally?

9.2 Exact diagonalization

To obtain knowledge about small quantum spin system, one can use a brute force solving of the Hamiltonian (also known as *exact diagonalization*). By extrapolating to larger system, one can often also obtain information on the system in the thermodynamic limit.

In this problem, we constrain ourselves to study $s = 1/2$ systems interacting with the nearest (antiferromagnetic) neighbour Heisenberg interaction

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j - hJM, \quad (23)$$

with $J > 0$ and $M = \sum_i s_i^z$

We shall obtain the eigenstates and their energies and magnetization values, and use that to calculate the system magnetization and susceptibility.

1. Argue that the eigenstates, i , can be chosen so that their energies, E_i can be written as a sum of their interaction energy, $E_{\text{Heis},i}$, and their Zeeman energy, $E_{Z,i}$.
2. Calculate a general expression for the system susceptibility, $\chi(T) = \partial M(T)/\partial h$, given that the magnetization can be written $M(T) = Z^{-1} \sum_i M_i \exp(-E_i \beta)$, where the sum runs over all energy eigenstates, i .
3. Consider the $N = 2$ system with 1 interaction. Calculate the 4 values of E_i and m_i . Calculate $M(T)$ and $\chi(T)$, where T is given in units of J . Hint: When setting up the Hamiltonian matrix, remember that \mathcal{H} commutes with the total magnetization operator M .
4. Consider the $N = 3$ system shaped as a triangle, where each of the 3 sides represents an interaction. Calculate the 8 values of E_i and m_i . Calculate $M(T)$ and $\chi(T)$, where T is given in units of J . Hint: To diagonalize the (3×3) matrix, you may simply guess the solutions - or use MATLAB.
5. Consider the $N = 4$ system shaped as a square, where each of the 4 sides represents an interaction. Calculate the 16 values of E_i and m_i . Calculate $M(T)$ and $\chi(T)$, where T is given in units of J . Hint: Utilize that \mathcal{H} commutes with the operator T that rotates the spin cluster by 90° to make linear combinations of Ising states that are immediate eigenvalues of T .
6. Consider the $N = 4$ system shaped as a tetrahedron, where each of the 6 sides represents an interaction. Calculate the 16 values of E_i and m_i . Calculate $M(T)$ and $\chi(T)$, where T is given in units of J . Hints: a) Rewrite \mathcal{H} in terms of $\mathbf{S} \cdot \mathbf{S}$, where S is the total spin of the eigenstate. b) Then consider the eigenstates of the $N = 4$ square problem.
7. Plot the susceptibilities for the 4 systems in the same graph. Discuss the results. Are the effects of frustration visible?

The geometries of the four spin systems to diagonalize is shown in Fig. 1.

9.3 High Temperature Expansion

For an interacting spin system the thermodynamical properties are much more difficult to calculate than for the non-interacting (paramagnetic) sys-

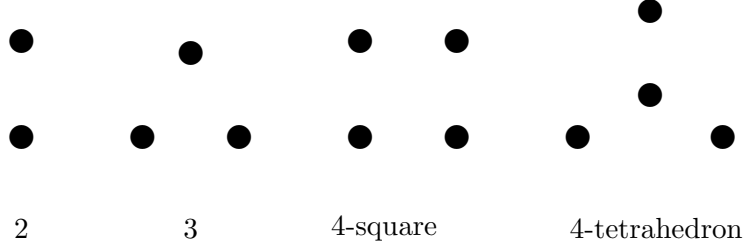


Figure 1: Illustration of the 4 spin geometries present in the exact diagonalization problem.

tem. One very commonly used approximation scheme is the *High Temperature Expansion*.

Assume that we have a pure Heisenberg system in a magnetic field and that $S = 1/2$ for simplicity. We have the following Hamiltonian for the $N \rightarrow \infty$ spins

$$H = H_Z + H_H \equiv -g\mu_B H \sum_j S_j^z - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (24)$$

As known from statistical mechanics, all thermodynamical properties may be extracted from (derivatives of) the partition function

$$Z = \text{tr}\{\exp(-\beta H)\}, \quad (25)$$

where $\beta = 1/k_B T$ and the matrix operator "tr" denotes the trace. The high temperature expansion begins with an expansion of the exponential function into powers of β :

$$Z \approx \text{tr}\{1 - \beta H + \beta^2 H^2/2 - \dots\}. \quad (26)$$

As known from linear algebra, the trace of a matrix is invariant to the choice of basis, so we choose the basis where each spin has a fixed value of S_j^z (the Ising basis). In other words: In this problem, each spin points either up or down.

1. Argue that the zero'th order expansion gives the result $Z^{(0)} = 2^N$.
2. Show that all first order HTE terms vanish: $Z^{(1)} = Z^{(0)}$. Hint: It can be seen that the trace of any n -spin operator O_n may be written as $\text{tr}\{O_n\} = 2^{N-n} \text{tr}_n\{O_n\}$, where the subscript n indicates that the trace is performed only over the 2^n dimensional subspace containing the relevant n spins.

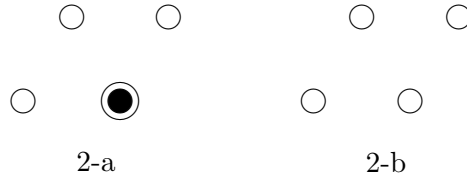


Figure 2: The two only contributing diagrams in second order HTE.

3. Calculate the magnetic heat capacity, C_B , to first order in β (1st order HTE). Calculate also M , χ , and S . Hint: From statistical mechanics, you know that

$$U = -\frac{\partial}{\partial \beta} \ln(Z). \quad (27)$$

4. In the second order HTE, the term $\text{tr}\{H^2\}$ occurs, and things grow complicated. It is now convenient to express the different terms diagrammatically. Let a line between two spins represent the spin-spin interaction, while a filled circle represent the Zeeman interaction of one spin with the field. Two concentric circles denotes the product of two Zeeman terms on the same spin.

Argue that the two diagrams on figure 2 represents the only terms contributing to second order.

5. Calculate U and C_V in second order HTE. Hint: a) Perform also a series expansion of $\ln(Z)$ around $Z = 2^N$, keeping terms up to the relevant power of β . b) When dealing with double sums, assume that all spin sites are equivalent.) Plots the results and compare with the exact solution for a pair of non-interacting spins.
6. When you perform adiabatic demagnetisation of a paramagnetic system, you can change the temperature of the system, according to

$$\frac{B^2 + B_{\text{loc}}^2}{T^2} = \text{const.} \quad (28)$$

Argue for this using $S = U/T + k_B \ln Z$ and derive an expression for B_{loc} to second order HTE.

7. The magnetization is given by

$$M = \frac{1}{\beta} \frac{\partial}{\partial H} \ln(Z). \quad (29)$$

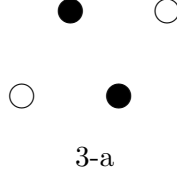


Figure 3: The diagram for the only contribution term to the susceptibility in the 3rd order HTE.

Calculate $\chi(T) = \partial M(T)/\partial H$ in the HTE up to 2nd order. Verify the result, the Curie Law:

$$\chi(T) = \frac{C}{T}, \quad (30)$$

where the Curie constant is given by

$$C = \frac{NS(S+1)\mu_B^2 g^2}{3k_B}. \quad (31)$$

8. Argue that in the HTE of 3rd order, the only non-zero contribution to $\chi(T)$ comes from the product of two Zeeman terms and an interaction term (illustrated in figure 3). (Note that Z has several contributions which do not contribute to the susceptibility.)
9. Calculate $\chi(T)$ by HTE to 3rd order. Compare the result with the Curie-Weiss law, found by mean field theory, e.g. in Blundell :

$$\chi(T) = \frac{C}{T - \Theta}, \quad (32)$$

where $\Theta = S(S+1)J(0)/(3k_B)$.

10. Assume you have a series of measurements of χ at different temperatures. How would you decide whether the interactions are predominantly ferromagnetic or antiferromagnetic?
11. Argue that the diagram in figures 4 are the only other 3rd order term for the triangular lattice. Argue that this appears only in nearest neighbour magnets that are frustrated. Calculate this term and plot the heat capacity of the system with and without this term in zero field and in a moderate applied field.

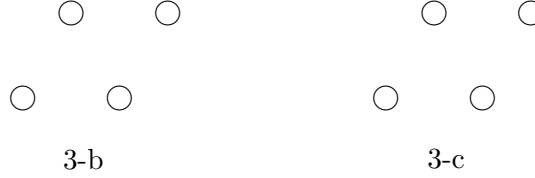


Figure 4: The two diagrams giving the zero-field terms to the heat capacity on a frustrated lattice in the 3rd order HTE.

12. Perform the HTE to 4th order for the non-interacting spin system and calculate U, S, C_B, M , and χ . Compare to the exact solution for non-interacting spins.

11 Neutron scattering

11.1 Magnetic diffraction from manganites

This problem deals with neutron diffraction from a spin valve system, described in Ref. [17]. Figures 5 and 6 from Ref. [17] will be used in the problem.

1. **Crystal structure.** The crystal structure of $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ is tetragonal, *i.e.* the unit vectors are perpendicular, and $a = b \neq c$. The Mn double layers lie in the $a-b$ plane, and there are two double layers in each unit cell, which has the parameters $a = 3.86 \text{ \AA}$, $c = 20.38 \text{ \AA}$ for $x = 0.3$. [18]

Calculate the shape of the reciprocal unit cell for the system. Calculate the length of the reciprocal lattice vectors, a^*, b^*, c^* .

2. **Braggs law.** Using neutrons of wavelength $\lambda = 4.41 \text{ \AA}$, what are the scattering angles 2θ for the (004) and (005) Bragg reflections? (I.e. for $q = 4$ (or 5) \mathbf{c}^* .)
3. **Ferromagnetism.** Argue that the magnetic intensity of the (00 j) reflections must vanish for j odd when the Mn moments are ordered ferromagnetically. Use Eq. (2.2.6) in the notes, and assume one Mn ion per magnetic layer, situated in $\mathbf{R}_1 = (0, 0, 0)$, $\mathbf{R}_2 = (a/2, b/2, c/2)$.
4. **Antiferromagnetism.** Argue that the (00 j) reflections are allowed for odd j when the substance is ordered antiferromagnetically. Use

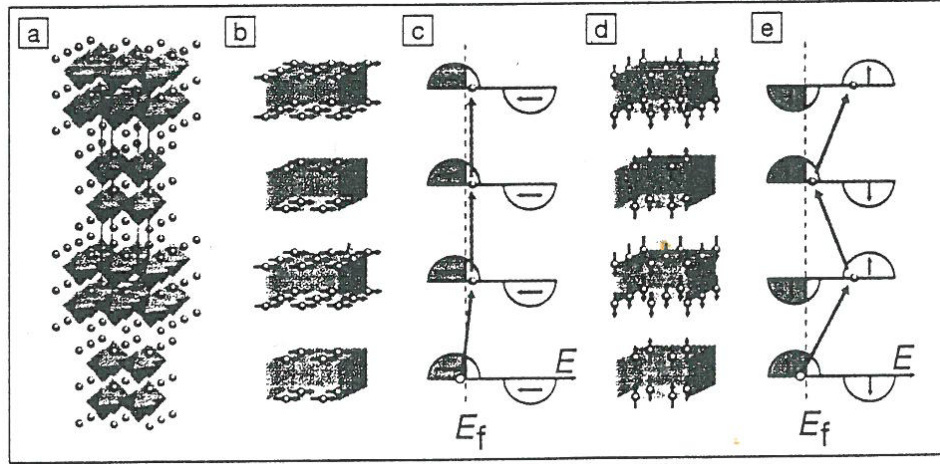


Figure 5: (a) Structure of $\text{La}_{2.2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. Circles represent La and Sr, while the Mn ions are at the centers of the MnO_6 octahedra. (b) Magnetic structure, deduced from neutron diffraction, for the Mn ions for $x = 0.3$ and $H = 1.5$ T. (c) Electronic structure for (b). (d) Magnetic structure for $x = 0.3$, low temperatures and $H = 0$. (e) Electronic structure for (d). Carriers propagate along the stacking direction by tunneling across not only $(\text{La}, \text{Sr})_2$ layers, as in (c), but also oppositely polarized intervening MnO_2 bilayers. The electrical resistivity for (d) and (e) is substantially higher than that for (b) and (c). From Ref. [17].

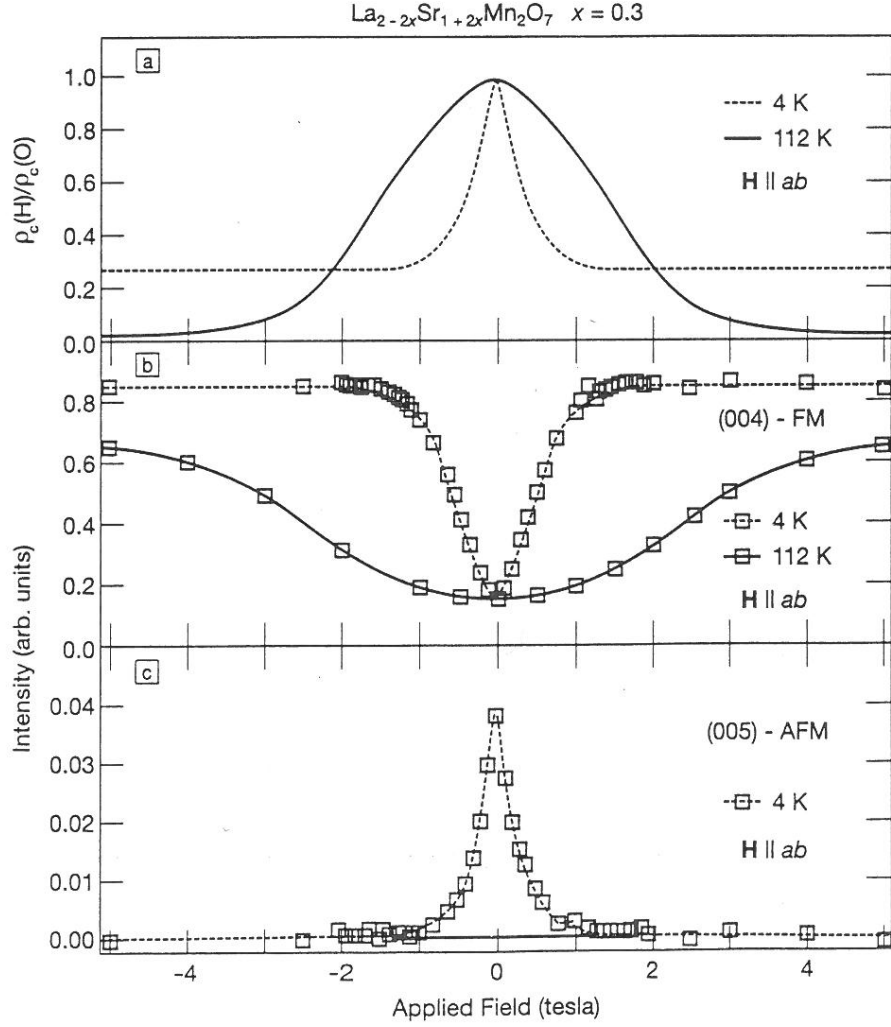


Figure 6: Field-dependent switching of (a) resistivity (ρ_c is the resistivity parallel to the c axis), (b) ferromagnetic (FM), and (c) antiferromagnetic (AFM) Bragg intensities measured using cold neutron diffraction at the iRiS time-of-flight spectrometer at the ISIS facility in the tunneling ($T = 44$ K) and colossal ($T = 112\text{K} > T_c$) magnetoresistance regimes. From Ref. [17].

Eq. (2.2.6) in the notes to calculate the relative intensity of the (005) AFM reflection to the (004) FM reflection. Assume that the magnetic form factor, $F(q)$, is constant, and that the magnetic moments are perpendicular to the scattering vector, κ .

5. **Magnetic intensities.** Consider the magnetic structure in Fig. 1 and the data in Fig. 2, Ref. [17], and Eq. (2.2.4) in the notes. Argue that the Mn moments must be tilted somewhat away from the c -axis. Calculate the approximate tilting angle.

11.2 Inelastic neutron scattering on nanoparticles

1. **Size broadening of Bragg scattering.** For small particles the nuclear Bragg peaks are observed to broaden. Explain this and give an estimate of the broadening (in units of wavevector) as a function of d . See the notes, Fig. (2.1.1). A typical value of the resolution of a neutron spectrometer is 0.01 \AA^{-1} . For roughly which particle sizes can the Bragg peaks be seen to broaden?
2. **Signature of superparamagnetic scattering.** A small ferromagnetic particle may experience thermally activated magnetization reversals between the two directions of the easy z -axis, also known as superparamagnetism. It is reasonable to assume that all spins move coherently and that the relaxation is completely random, *i.e.*

$$\langle S_0^z(0)S_j^z(t) \rangle = \langle S_0^z(0)S_0^z(t) \rangle = S^2 \exp(-|t|/\tau). \quad (33)$$

The inelastic magnetic scattering cross section can be written in a form, where it is proportional to the space and time Fourier transformed spin-spin correlation function.

$$\frac{d^2\sigma}{d\Omega dE} \propto \sum_l \exp(i\mathbf{q} \cdot \mathbf{r}_l) \int_{-\infty}^{\infty} \exp(-i\omega t) \langle s_0^\alpha(0)s_l^\alpha(t) \rangle dt \quad (34)$$

Argue that the largest contribution to the cross section is found for q being zero (plus any reciprocal lattice vector). Calculate the ω -dependence of the scattering.

3. **Relaxation time scales.** A typical cold-neutron spectrometer has an energy resolution of 0.1 meV. Estimate the relaxation time scales for which neutron scattering is sensitive.

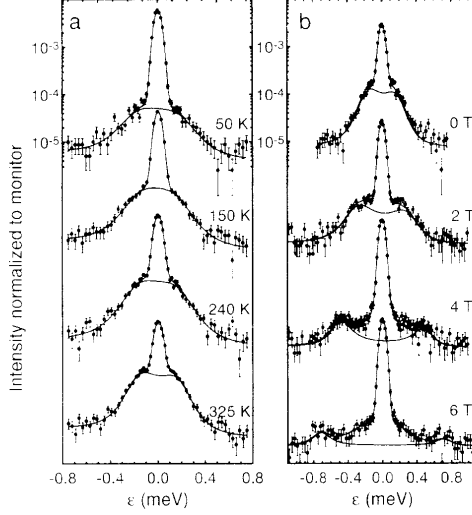


Figure 7: Neutron scattering data for $d = 15$ nm hematite particles, from [19]. Left column shows data in zero applied field; right column for a constant temperature of 200 K.

4. **Antiferromagnetic nanoparticles.** In small particles of hematite ($\alpha\text{-Fe}_2\text{O}_3$) (and in bulk hematite above $T_M \approx 260$ K) the spins are ordered in a canted antiferromagnetic two-sublattice structure, with a small canting giving a net magnetic moment.

Argue that the elastic magnetic cross section has both a small ferromagnetic ($q = 0$) and a large antiferromagnetic ($q = Q_{\text{AFM}}$) contribution.

5. **Fluctuations around the energy minimum.** At temperatures where the superparamagnetic magnetization reversal happens less often, the spin system of the nanoparticles will experience small, thermally activated, fluctuations around the energy minimum, also known as collective magnetic excitations.

Argue that the magnetic anisotropy Hamiltonian for small fluctuations may be approximated by an effective field in which the spins will precess. Calculate the effect of a precession with the frequency ω_0 on the energy dependence of the inelastic cross section. Compare qualitatively to the experimental results in figure 7.

11.3 BCC lattice and AFM 2d lattice

1. Consider a BCC (body centered cubic) lattice with lattice constant a . What are the coordinates of the atoms in the unit cell? Find the allowed reflections, i.e. the values of h, k and l that give a non-zero structure factor, $F(h, k, l) \neq 0$.
2. Consider now a two-dimensional square lattice in zero field in the ground state found in assignment 2. The lattice constant is a . What is the magnetic unit cell? Show that the magnetic reflections occur for half-integer values of h and k . Generalize to 3 dimensions.
3. Make a sketch of the reciprocal space and mark the positions of magnetic and nuclear peaks.

12 NMR

12.1 Spin echo

The technique of spin echoes is described in Blundell, p.59 and figure 3.13. Imagine that figure 3.13 is seen in the rotating frame. The rotating \mathbf{b}_1 field is applied along the positive x -axis exactly the length of time needed for a " $\pi/2$ " pulse. The result is a $\pi/2$ rotation of the \mathbf{M} -vector bringing it along the positive y -axis, figure 3.13(b).

1) Which sign does γ have?

2) Does panel (c) show the fastest or the slowest spins?

In the end, the echo appears along the negative y -axis.

3) Assume the opposite sign for γ and carry through the analogous derivation. Where does the echo appear?

12.2 Pulse sequences

Consider an experiment in which *initially* the magnetization is at its thermal equilibrium value, $\mathbf{k}M_0$, along a static field $\mathbf{k}B_0$. At $t = 0$ the magnetization is inverted by a π pulse. It then grows back towards its thermal equilibrium exponentially according to the equation

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{\tau_1}$$

At time t_1 , M_z is inspected by applying a $\pi/2$ pulse and observing the initial amplitude of the free induction signal generated in an rf coil oriented

transverse to \mathbf{B}_0 .

a) Show that M_x , the value of the transverse magnetization immediately after the $\pi/2$ pulse, is

$$M_x = M_0(1 - 2e^{-\frac{t_1}{T_2}})$$

b) Assume now that owing to natural line breadths, the transverse magnetization decays rapidly to zero. Suppose one now waits a time t_2 , long compared to the time for transverse magnetization to decay, then again applies a π pulse, and again applies a second $\pi/2$ pulse at time t_1 later.

Suppose one repeats this pulse sequence several times:

$$\dots \begin{array}{cccc} \leftarrow t_1 & \rightarrow & \leftarrow t_2 & \rightarrow \\ \pi & & \pi/2 & & \pi & & \pi/2 \end{array} \dots$$

Show that the initial value of the free induction decay following each $\pi/2$ pulse becomes

$$M_x = M_0[1 - 2e^{-\frac{t_1}{T_2}} + e^{-\frac{t_1+t_2}{T_2}}]$$

12.3 Dipolar couplings

A pair of identical spins of $I_1 = I_2 = \frac{1}{2}$ is coupled by their magnetic dipole moments. Assuming zero external static magnetic field, show that the proper eigenstates of the spins are the singlet and triplet states, and then find the energies of the different states.

12.4 Pake's doublet

Suppose in Problem 12.3 that a static magnetic field B_0 is applied parallel to the internuclear axis.

- Find the energy levels and eigenfunctions as a function of B_0
- An alternating magnetic field is applied perpendicular to the internuclear axis. Find the allowed transitions, their frequencies and relative intensities: (1) for B_0 much less than the dipolar coupling; (2) for B_0 much larger than the dipolar coupling.

12.5 The chemical shift

An atom has a single valence electron in an s-state and a nucleus of spin I . The electron spin-lattice relaxation time is so short that the nucleus experiences only the time-average magnetic field of the electron. Derive an expression for the resonance frequency of the nucleus when a static field is applied, giving your answer in terms of the electron susceptibility χ_e . Discuss the temperature and field dependence: (a) at high temperature (where $kT \leq \gamma_e \hbar B_0$) and (b) at low temperature (where $\gamma_e \hbar B_0 \sim kT$).

12.6 Dynamic polarization

Dynamic nuclear polarization is described in the notes, pp 8-10. Show that the nuclear polarization $\langle I_z \rangle$ produced by the scheme of Fig. 7.1, right, is the negative of that produced by the scheme of Fig. 7.1, left if $|A/2| \ll \gamma_e \hbar B_0$.

12.7 Pulse sequences (Slichter 2.9)

Consider an experiment in which *initially* the magnetization is at its thermal equilibrium value, $\mathbf{k}M_0$, along a static field $\mathbf{k}B_0$. At $t = 0$ the magnetization is inverted by a π pulse. It then grows back towards its thermal equilibrium exponentially according to the equation

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{\tau_1}$$

At time t_1 , M_z is inspected by applying a $\pi/2$ pulse and observing the initial amplitude of the free induction signal generated in an rf coil oriented transverse to \mathbf{B}_0 .

a) Show that M_x , the value of the transverse magnetization immediately after the $\pi/2$ pulse, is

$$M_x = M_0(1 - 2e^{-\frac{t_1}{\tau_1}})$$

b) Assume now that owing to natural line breadths, the transverse magnetization decays rapidly to zero. Suppose one now waits a time t_2 , long compared to the time for transverse magnetization to decay, then again applies a π pulse, and again applies a second $\pi/2$ pulse at time t_1 later.

Suppose one repeats this pulse sequence several times:

$$\begin{array}{ccccccc} \dots & \parallel \leftarrow t_1 \rightarrow \parallel & \leftarrow t_2 \rightarrow \parallel & \leftarrow t_1 \rightarrow \parallel & \dots \\ & \pi & \pi/2 & \pi & \pi/2 \end{array}$$

Show that the initial value of the free induction decay following each $\pi/2$ pulse becomes

$$M_x = M_0 \left[1 - 2e^{-\frac{t_1}{\tau_1}} + e^{-\frac{t_1+t_2}{\tau_1}} \right]$$

12.8 Dipolar couplings (Slichter 3.1)

A pair of identical spins of $I_1 = I_2 = \frac{1}{2}$ is coupled by their magnetic dipole moments. Assuming zero external static magnetic field, show that the proper eigenstates of the spins are the same as the singlet and triplet states of the Heisenberg exchange Hamiltonian, and then find the energies of the different states.

12.9 Pake's doublet (Slichter 3.2)

Suppose in Problem 3.1 that a static magnetic field B_0 is applied parallel to the internuclear axis.

- Find the energy levels and eigenfunctions as a function of B_0
- An alternating magnetic field is applied perpendicular to the internuclear axis. Find the allowed transitions, their frequencies and relative intensities: (1) for B_0 much less than the dipolar coupling; (2) for B_0 much larger than the dipolar coupling.

12.10 The chemical shift (Slichter 4.5)

An atom has a single valence electron in an s-state and a nucleus of spin I . The electron spin-lattice relaxation time is so short that the nucleus experiences only the time-average magnetic field of the electron. Derive an expression for the resonance frequency of the nucleus when a static field is applied, giving your answer in terms of the electron susceptibility χ_e . Discuss the temperature and field dependence: (a) at high temperature (where $kT \leq \gamma_e \hbar B_0$) and (b) at low temperature (where $\gamma_e \hbar B_0 \sim kT$).

Isotope	E_γ (keV)	τ (ns)
^{57}Fe	14.4	140
^{61}Ni	67.4	7.3
^{67}Zn	93.3	13260

Table 1: The γ energy, E_γ , and the life time, τ , for three Mössbauer isotopes.

12.11 Dynamic polarisation (Slichter 7.2)

Show that the nuclear polarization $\langle I_z \rangle$ produced by the scheme of Fig. 5.1, right, (Fig.7.8 in S) is the negative of that produced by the scheme of Fig.5.1, left (Fig.7.9 in S) if $|A/2| \ll \gamma_e \hbar B_0$.

13 Mössbauer spectroscopy

13.1 Mössbauer basics (S. Mørup)

Table 1 gives the γ energy, E_γ , and the life time, τ , for three Mössbauer isotopes. Calculate for each of the three isotopes the natural line width, Γ , the f -factor at $T = 0$ K, and the f -factor at $T = 300$ K, assuming that the atoms are situated in a material with a Debye temperature of $\Theta_D = 400$ K.

13.2 Temperature effects in Mössbauer spectroscopy (S. Mørup)

Figure 8 shows the temperature dependence of the isomer shift, $\Delta E/E$ and the logarithm of the f -factor for ^{57}Fe in W.

1. Calculate the Debye temperature
2. Calculate the r.m.s. value $\sqrt{\langle x^2 \rangle}$ of the amplitude of the thermal movement of the Fe nuclei at $T = 800$ K and at $T = 0$ K.
3. An extrapolation of the linear high-temperature dependence of $\Delta E/E$ to $T = 0$ K gives the isomer shift corresponding to an atom in rest. Determine the r.m.s. value $\sqrt{\langle v^2 \rangle}$ of the velocity of the iron nuclei at $T = 800$ K.

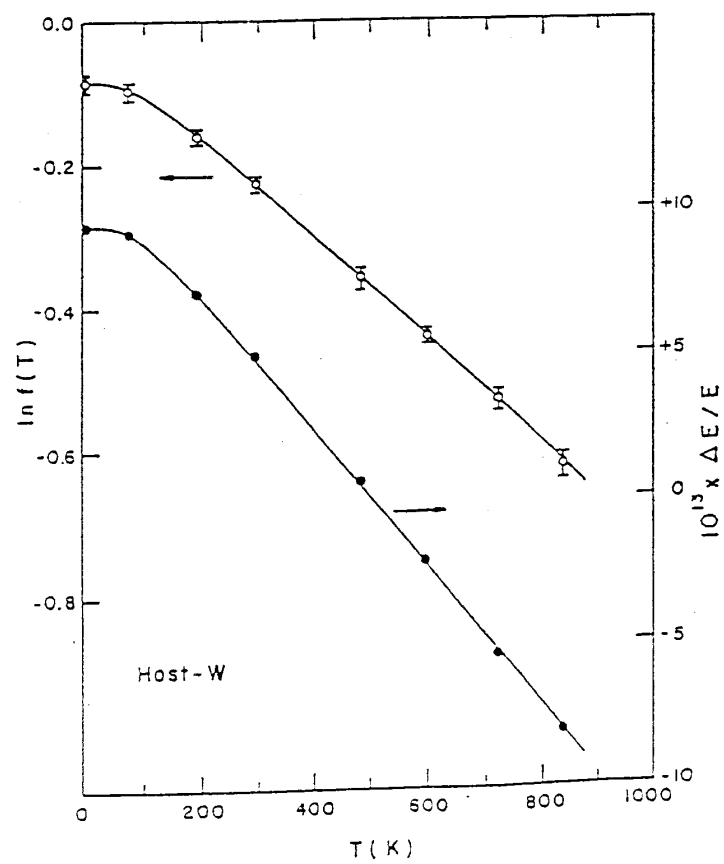


Figure 8: Figure to be used in Problem 13.2.

13.3 Magnetic splitting in Mössbauer spectroscopy (S. Mørup)

The effective magnetic field at the site of a ^{57}Fe nuclei in metallic Fe is $B = 33.02$ T. Both isomer shift and quadropole shift are zero. Determine the line postions (in mm/s) for the 6 lines in the Mössbauer spectrum.

13.4 Mössbauer spectroscopy on magnetic minerals (S. Mørup)

A strongly iron-containing reddish substance has often been observed at excavations of stone age graves at Vedbæk (Denmark). The substance has been studied by ^{57}Fe Mössbauer spectroscopy in order to identify the iron-containing minerals. The figure shows a typical spectrum, taken at $T = 298$ K.

1. The spectrum in Figure 9 contains components from Fe atoms in two different environments. One component is a doublet with line positions at -0.005 mm/s and at 0.785 mm/s. Determine the quadropole shift and the isomer shift.
2. Describe how you expect the isomer shift to change when the sample is cooled to $T = 80$ K. Argue for your expectations.
3. The second component in the spectrum is magnetically split with six line positions (in mm/s): $(-8.007, -4.328, -0.838, 1.785, 5.275, 8.573)$. Determine the effective magnetic field at the nuclear position, the isomer shift, and the quadropole shift.
4. Describe how you expect the Mössbauer spectrum to change when the sample is heated above room temperature. Argue for your expectations.

14 Problems for notes on unit systems

14.1 Magnetic units

What is the magnetic moment (along a certain direction) of an electron in cgs and SI units? Consider an electron in a magnetic field of 10^5 Gauss. In SI units, the corresponding Zeeman Hamiltonian is given by $H_Z = -g\mu_B B S_z$; assume $g = 2$. Calculate the energy difference between the maximum and minimum value of S_z . Present the energy difference in J, erg, electron Volts (eV), in Hz and equivalent temperature.

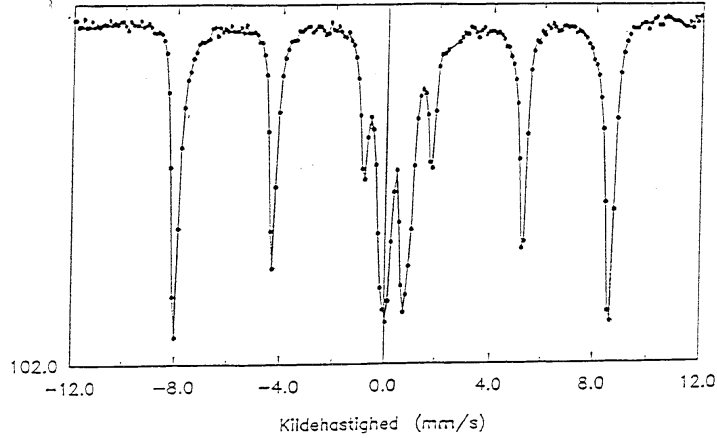


Figure 9: Figure for Problem 13.4

14.2 Dipole and exchange energies

The organic compound copper benzoate, $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$, has chains of interacting ($s = 1/2$) Cu^{2+} ions, which are separated by 3.15 \AA . The exchange interaction is antiferromagnetic and has the relatively small value $J = -1.57 \text{ meV}$, using the convention $H_{ij} = -J\mathbf{s}_i \cdot \mathbf{s}_j$ [20].

Estimate the magnitude of the magnetic dipolar energy

$$H_{\text{dip}} = \frac{\mu_0}{4\pi} \frac{g^2 \mu_B^2}{r_{12}^3} (\mathbf{s}_1 \cdot \mathbf{s}_2 - 3(\mathbf{s}_1 \cdot \hat{r}_{12})(\mathbf{s}_2 \cdot \hat{r}_{12})) \quad (35)$$

and compare that to the exchange energy.

15 Problems for notes on time reversal

15.1 Time reversal of quantum states

The following problem is an aid in comprehending the rather compact text material in the note.

1. Consider a spinless particle represented by a plane wave

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = c \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\}. \quad (36)$$

Construct the time reversed wave, $(\psi_{\mathbf{k}}(\mathbf{r}, t))_r$ and calculate its energy and momentum.

2. For the case of integer spin, consider an arbitrary state, $|a\rangle$. Construct a linear combination of $|a\rangle$ and its time reversed counterpart $\hat{K}|a\rangle$, which is “real” (unchanged under time reversal): $\hat{K}|a^r\rangle = |a^r\rangle$. Then show that from a state $|b\rangle$, orthogonal to $|a^r\rangle$, one may construct a “real” state, where $\langle b^r|a^r\rangle = 0$.
3. Prove that for half-integer S , the time reversed state is perpendicular to the original state eqn. (13.58). Hint: Use eqns. (13.48) and (13.55).

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