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DIPLOMOVÁ PRÁCE



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Substituční neuspořádanost v systémech s korelovanými f-elektrony

Katedra fyziky elektronových struktur

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Souhlasím se zapůjčováním práce.

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Abstrakt: Pomocí teorie funkcionálu hustoty a lokální aproximace hustoty byla spočtena elektronová struktura, mřížkové konstanty a hustoty stavů pro europium, vanad a gadolinium při nulové teplotě. Dále je v práci popsána aproximace středního pole a aproximace náhodných fází (RPA) pro Heisenbergův Hamiltonián, které byly použity k numerickému výpočtu magnetizace a Curieovy teploty feromagnetů Gd, Co a slitiny Gd-Y, které mají hexagonální hcp mřížku. V poslední části je zmíněna technika CPA, která by mohla vést k realistickým aproximacím magnetických slitin při nenulové teplotě.

Klíčová slova: DFT, LDA, ASA, Heisenbergův Hamiltonián, MFA, RPA, CPA, Greenovy funkce, slitina

Title: Substitutional disorder in systems with correlated f-electrons Author: Peter Franek Department: Department of Electronic Structures Supervisor: RNDr. Ilja Turek, DrSc. Supervisor's e-mail address: turek@ipm.cz

Abstract: Using the Density Functional Theory and Local Density Approximation, the electronic structure, lattice constants and density of states has been computed for europium, vanadium and gadolinium at zero temperature. The Mean Field Approximation and Random Phase Approximation for the Heisenberg Hamiltonian is described here, that was used for numerical calculations of the magnetization and Curie temperature of the ferromagnets Gd, Co and the Gd-Y alloy with hcp lattice. In the last part the CPA technique is mentioned that could lead to a realistic approximation of the magnetic alloys at nonzero temperatures.

Keywords: DFT, LDA, ASA, Heisenberg Hamiltonian, CPA, MFA, RPA, Green functions, alloy

1. Density Functional Theory

1. 1. Theoretical Basis

The state of a quantum mechanical system is determined by it's Hamiltonian \mathcal{H} that gives us all the possible information about the system. The eigenstates of \mathcal{H} are the stationary states. We suppose that at zero temperature the system is in the *ground state*, the eigenstate of \mathcal{H} with the lowest energy.

The physical systems we study are bodies with an infinite periodic lattice with three basis vectors (in a 3D space) and translation symmetry. The sites are occupied by a finite number of atomic species.

The task of finding the eigenstates of the Hamiltonian is too complicated in systems with several particles (including nuclei, electrons and their spins) to be solved exactly. The first approximation to be mentioned is the *Born-Oppenheimer* approximation. It separates the wave function $\psi(\mathbf{R}_{\alpha}, \mathbf{r}_{i})$ in a product of a nuclei wave function $u(\mathbf{R}_{\alpha})$ and an electron wave function $v_{\{\mathbf{R}_{\alpha}\}}(\mathbf{r}_{i})$, which depends parametrically on the nuclei positions \mathbf{R}_{α} . In this work we treat the nuclei as classical particles with well-defined trajectory and assume that there exist an electron Hamiltonian $\mathcal{H}_{\{\mathbf{R}_{\alpha}\}}$, where $\{\mathbf{R}_{\alpha}\}$ are the positions of the nuclei. We also assume that the nuclei are not moving in the ground state and their kinetic energy is zero.

The variational principle can be used to find the positions $\{\mathbf{R}_{\alpha}\}$ which minimize the appropriate ground state energy of the system. This energy is the sum of the potential energy of the nuclei (created mostly by the coulomb interactions) and the lowest eigenvalue of the appropriate electron Hamiltonian $\mathcal{H}_{\{\mathcal{R}_{\alpha}\}}$. This state is (in our approximation) the ground state of the system at zero temperature.

We assume in all the further text that the positions of the nuclei are fixed and we denote the electron Hamiltonian \mathcal{H} instead of $\mathcal{H}_{\{\boldsymbol{R}_{\alpha}\}}$.

We usually know the positions of the nuclei from observations. The vari-

ational principle is practically used only to find a small number of parameters (as the lattice constants, assuming we know the type of the lattice).

The task of many programs is to calculate the ground state of \mathcal{H} . The quantum state of the electrons in the system we usually call *The Electronic Structure* (ES). The most common way to calculate it is based on the one-electron approximation using the *Density Functional Theorem*, proved by Hohenberg and Kohn in 1964 [1,2]:

Theorem (DFT). The ES of a non-degenerate ground state of an electron system and it's external potential are both determined by it's single-particle density $\rho(\mathbf{r})$, defined by

$$ho(m{r}) = N \int \psi^*(m{r},m{r}_2,\ldots,m{r}_N) \psi(m{r},m{r}_2\ldots,m{r}_N) dm{r}_2\ldots dm{r}_n$$

where ψ is the normalized wave function of the ES and N the number of electrons.

This justifies the definition of the total energy as a functional $\mathcal{E}[\rho]$ of the single-particle density. We use the variational principle for minimizing \mathcal{E} with respect to ρ under the condition $\int \rho(\mathbf{r}) d\mathbf{r} = N$ and $\rho \geq 0$.

It can be shown that the variational principle leads to equations that are equivalent to solving the problem of N non-interacting particles with the Hamiltonian $H_{eff} = -\Delta + V_{eff}$, the effective potential [1]

$$V_{eff}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + \int \frac{2\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}^{3}\boldsymbol{r} + \frac{\delta E_{XC}[\rho]}{\delta\rho(\boldsymbol{r})}$$
(1.1)

Here V_{ext} is the external potential of our electron system (it includes the coulomb electrostatic field of the nuclei) and E_{XC} is called the exchange-correlation energy and is caused by non-classical energy components. The last equation is to be understood as a functional equation: we identify $f(\mathbf{r})$ with a functional $g(\mathbf{r}) \to \int f(\mathbf{r})g(\mathbf{r})d\mathbf{r}$. The expression $\frac{\delta E_{XC}}{\delta\rho}$ is the differential of the E_{XC} in the point ρ (which is a functional). The density

 ρ is given by

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2$$
(1.2)

where ψ_i are the N lowest eigenfunction of this effective Hamiltonian.

If we know the functional E_{XC} we can find the density $\rho(\mathbf{r})$ of our system so that the eigenfunction of the effective Hamiltonian satisfy (1.1) and (1.2). The knowledge of ρ determines the total energy of ES and can be calculated by a simple formula.

This is solved by iterations in the numerical implementations. We choose some starting effective potential $V_{eff}^{(1)}$, compute the orbitals $\psi_i^{(1)}$ and the density $\rho^{(1)}$. Using $\rho^{(1)}$ and (1.1) we obtain a new potential $\tilde{V}_{eff}^{(2)}$. Now we let $V_{eff}^{(2)} = \epsilon \tilde{V}_e f f^{(2)} + (1 - \epsilon) V_{eff}^{(1)}$. We call ϵ the mixing parameter. It can be proved that for ϵ small enough this iterations will converge to a self-consistent effective potential V_{eff} .

There are several methods to determine E_{XC} . The simplest one is called *Local Density Approximation*: it approximates

$$E_{XC}[
ho] pprox \int
ho(oldsymbol{r}) \epsilon_{XC}(
ho(oldsymbol{r})) \mathrm{d}oldsymbol{r}$$

where ϵ_{XC} is a function. In this approximation the exchange-correlation energy depends on the density *locally*. For ϵ_{XC} we usually take the exchange-correlation energy of the homogeneous electron gas. We are able to compute this function to a high degree of accuracy. This approximation is suitable for systems where the electron density doesn't varies much. A better approximation called GGA (*General Gradient Approximation*) improves this by including the density gradient into the function $\epsilon_{XC} = \epsilon_{XC}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})).$

If we include the electron spin to our observation we get two electron densities: ρ_{\uparrow} and ρ_{\downarrow} for spin +1/2 and -1/2. The approximation

$$E_{XC}[
ho_{\uparrow},
ho_{\downarrow}] = \int
ho(oldsymbol{r}) \epsilon_{XC}(
ho_{\uparrow},
ho_{\downarrow}) \mathrm{d}oldsymbol{r}$$

is called *Local Spin Density Approximation* (LSDA). The models within LDA and LSDA are based on the homogeneous electron gas model.

1. 2. Other Approximations and Techniques Used by Calculating the Ground State ES

Many difficulties arise by solving the self-consistent Schrödinger equations with the potential (1.1) and density (1.2). One technique often used is to distinguish between the core electrons and valence electrons. We assume that the core electrons are localized inside their atomic spheres and that they don't interact with other atoms. Therefore we treat them independently and their total energy is the sum of the core electron energies over all the atoms. We use a technique of the Hamiltonian resolvents defined by $C(r) = (r - 2t)^{-1}$

$$G(z) = (z - \mathcal{H})^{-}$$

to calculate the energy of valence electrons. This operator in the space representation is called *Green function* (GF):

$$G(\boldsymbol{r}, \boldsymbol{r}', z) := \langle \boldsymbol{r}' | G(z) | \boldsymbol{r} \rangle = \sum_{i} \frac{\psi_i(\boldsymbol{r}) \psi_i^*(\boldsymbol{r}')}{z - \epsilon_i}$$
(1.3)

where $\psi_i(\mathbf{r})$ are the eigenfunctions of \mathcal{H} and ϵ_i it's eigenvalues. We assume that $\mathcal{H} = -\Delta + V_{eff}(\mathbf{r})$, V_{eff} is the effective potential from (1.1).

We use now the distributional identity

$$\frac{1}{x+i0} = \mathcal{P}\frac{1}{x} - i\pi\delta(x) \tag{1.4}$$

where δ is the dirac distribution, $\int \varphi(x)\delta(x)dx = \varphi(0)$ and (\mathcal{P}) means the principal value. From (1.3) and (1.4) we have

$$w(r, E) := -\frac{1}{\pi} \operatorname{Im} G(\boldsymbol{r}, \boldsymbol{r}, E + i0) = \sum_{i} |\psi_i(\boldsymbol{r})|^2 \delta(E - \epsilon_i)$$
(1.5)

From the knowledge of the GF for an electron system the quantity w can be calculated and from (1.5) we easily derive the energy resolved density of state (DOS) and the electron density:

$$\rho(\mathbf{r}) = \int w(\mathbf{r}, E) dE \qquad (1.6)$$

$$n(E) = \int w(\mathbf{r}, E) \mathrm{d}\mathbf{r}$$
(1.7)

The point is that we can calculate the density ρ without the knowledge of the orbitals $\psi_i(\mathbf{r})$. If we integrate in (1.6) from $-\infty$ to the Fermi energy E_F , we obtain the total density of electrons. If we need the density of valence electrons only, we integrate in (1.6) over the energies of the valence electrons.

One important quality of the GF is that it is analytic in the upper complex half-plane. Therefore we can compute the integral (1.6) by integrating over a circle in the upper complex half-plane what is more convenient from the numerical point of view.

The density $\rho(\mathbf{r})$ can be determined from the GF for the effective Hamiltonian with the potential (1.1) using (1.6) and this density determines a new potential V_{eff} and a new effective Hamiltonian.

The problem we still have is to find the Green function G for some potential V_{eff} .

Here other approximation are used. The first one to mention is the Atomic Sphere Approximation (ASA) where we approximate the potential $V_{eff}(\mathbf{r})$ by a potential V that is spherically symmetric inside nonoverlapping spheres and constant in the *interstitial region* outside the spheres. We assume that the atomic spheres have all the same radius, the nuclei are in their centers and the potential inside the \mathbf{R} th sphere depends only on the distance from the center. We assume that the wave functions solve the Laplace equation (not Schrödinger) in the interstitial region what corresponds to the demand for zero kinetic energy. The energy contribution from the interstitial region is zero in this approximation and we solve the Schrödinger equation with the potential (1.1) only in the region of the atomic spheres.

If starting with a spherically symmetric potential, we obtain an electron density that is no more spherically symmetric but we symmetrize it taking $\rho(\mathbf{r}_{\mathbf{R}})$ to be the average of $\rho(\mathbf{r}_{\mathbf{R}})$ on the sphere $\{\mathbf{r}_{\mathbf{R}} = \mathbf{r}_{\mathbf{R}}\}$. We also approximate the external potential V_{ext} in (1.1) by it's spherically symmetric part and obtain a new potential that is spherically symmetric inside the atomic spheres.

It can be derived that the GF for the points $\mathbf{r} + \mathbf{R}$, $\mathbf{r}' + \mathbf{R}'$, where $\mathbf{r} + \mathbf{R}$ lies in the \mathbf{R} th sphere and $\mathbf{r}' + \mathbf{R}'$ lies in the \mathbf{R}' th sphere, can be expressed as [1]

$$G(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}', z) = \delta_{\mathbf{R}\mathbf{R}'} \sum_{L} \frac{\varphi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}^{<}, z) \tilde{\varphi}_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}^{>}, z)}{\{\varphi_{\mathbf{R}l}(\mathbf{r}_{\mathbf{R}}, z), \tilde{\varphi}_{\mathbf{R}l}(\mathbf{r}_{\mathbf{R}}, z)\}} + \sum_{LL'} \varphi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}, z) G_{\mathbf{R}L\mathbf{R}'L'}(z) \varphi_{\mathbf{R}'L'}(\mathbf{r}'_{\mathbf{R}'}, z)$$
(1.8)

where $\mathbf{r}_{\mathbf{R}} = \mathbf{r} - \mathbf{R}$ for all \mathbf{r} and \mathbf{R} , $\mathbf{r}_{\mathbf{R}}^{\geq}$ resp. $\mathbf{r}_{\mathbf{R}}^{\leq}$ is that one from $\mathbf{r}_{\mathbf{R}}, \mathbf{r}'_{\mathbf{R}'}$ with the larger resp. smaller absolute value, $\varphi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}, z)$ resp. $\tilde{\varphi}_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}, z)$ is the regular resp. irregular solution of the Schrödinger equation $(-\Delta + V_{eff} - z) = 0$ in the \mathbf{R} th sphere with the angular momentum L = (l, m), $\varphi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}l}, z)$ is the radial part of $\varphi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}L}, z)$, {} is the Wronskian of the radial functions defined by $\{f(r), g(r)\} := r^2(f(r)g'(r) - f'(r)g(r))$ and the constants $G_{\mathbf{R}L\mathbf{R}'L'}(z)$ defined by (1.8) can be computed from the equation

$$G(z) = -\frac{1}{2}\frac{\ddot{P}(z)}{\dot{P}(z)} + \sqrt{\dot{P}(z)}[P(z) - S]^{-1}\sqrt{\dot{P}(z)}$$
(1.9)

where

$$P_{\mathbf{R}L,\mathbf{R}'L'}(z) = \delta_{\mathbf{R}l\mathbf{R}'l'} \frac{\{K_{\mathbf{R}l}(r),\varphi_{\mathbf{R}l}(r,z)\}}{\{J_{\mathbf{R}l}(r),\varphi_{\mathbf{R}l}(r,z)\}}|_{r=s_r}$$
(1.10)

 K_{Rl} and $J_{Rl}(r)$ are the irregular and regular solutions of the Laplace equation, s_r is the radius of the atomic spheres in ASA, the dot over P is the energy derivation and the matrix S is defined by

$$K_L(m{r_R}) = -\sum_{L'} S_{m{R}l,m{R}'L'} J_{L'}(m{r_{R'}})$$

The matrix S is called canonical structure constants matrix and it depends only on the atomic positions $\{\mathbf{R}_{\alpha}\}$. For an ideal crystal it is a non random matrix.

This way the Green function can be determined and from the GF all the one-electron properties of the system can be calculated using (1.1) and LDA or LSDA.

1. 3. Numerical Results

Most of the existing programs for calculating the ground state energies are based on the LSDA and Greens function technique described shortly in the previous paragraph. Other approximation are used by solving the one-electron Schrödinger equation with $\mathcal{H} = -\Delta + V_{eff}(\mathbf{r})$ even within ASA. One common way is the using of the variational principle and finding the approximate solution in a subspace generated by some set of special functions. The Schrödinger equation then leads to a system of linear equations. The quality of the method depends on the choice of the generating functions. One common method is the technique of linear muffin-tin orbitals (LMTO) described in [1].

One interesting fact is that in order to obtain reasonable results we have to treat the f-electrons in lanthanides as core electrons, although their energy is high. Several calculations have been performed showing that the f-electrons are more localized then the valence d-electrons and that f-electron interactions between various lattice sites are negligible.

I used existing programs of RNDr. Ilja Turek to calculate the energies of europium and vanadium as a function of the Wigner-Seitz radius *s* defined by $(4/3)\pi s^3 = \Omega$, Ω is the volume per atom. Both europium and vanadium have the bcc structure with 2 atoms in each lattice cell. There are no *f*-electrons present in vanadium and it's Wigner-Seitz radius is 2.81 a.u. (1 a.u. ≈ 0.0529177 nm). I obtained FIG. 1.1 for the total atomic energy (using LDA).

The numerical result is about 2.75 a.u. as we see from the picture, what is, compared with the experimental value 2.81 a.u. an error of about 2%. A good illustration of an f-electron system is europium (bcc structure). FIG. 1.2 shows the dependence of it's atomic energy on the Wigner-Seitz radius. The magnetic properties are not negligible in europium and we have to use the spin polarized LSDA approximation. FM means the ferromagnetic europium with all atoms having the same magnetic moment (we denote it's projection onto the magnetization axis J). AFM is the anti-ferromagnetic europium. It is a solid with 2 different europium atoms in each primitive cell: one atom having the projection of the magnetic moment onto the magnetization axis +J and one atom having this pro-



FIG. 1.1 The total ground state energy of vanadium within LDA and ASA for various Wigner-Seitz radii. The zero energy is set to be the ground state energy.



FIG. 1.2 The total ground state energy of FM, AFM and DLM europium within LSDA and ASA for various Wigner-Seitz radii. The minimum energy is here about 4.2 a.u.

jection -J (where J is the total magnetic moment of an atom). Finally, DLM means disordered local moments and it is an europium with random magnetic moments (in this case the CPA approximation have to be used, see chapter 5). We see that in all this cases the radius s corresponding to the minimal energy is approximately the same, about 4.2 a.u.

We can conclude from this example that the atomic radius is almost independent of the configuration of the magnetic moments. The real configuration of europium ground state is a *spin spiral*. The experimental value is s = 4.238 a.u. In this calculations the *f*-electrons are core electrons and the results are good. If we treat them as valence electrons, we obtain a larger error, as can be seen from FIG. 1.3.



FIG. 1.3 The total ground state energy of europium depending on the Wigner-Seitz radius s. The black circles and squares denote two various calculations within LSDA and the empty squares are GGA calculations (see 1.1). Here the f-electrons are treated as valence electrons.

Another interesting result is the energy resolved density of states that we obtain from (1.7). Some results for Eu are shown in FIG. 1.4 and FIG. 1.5. We see in FIG. 1.4 a sharp peak in the DOS of *f*-electrons.



FIG. 1.4 Spin polarized density of states for FM europium (s = 4.19 a.u.) total (full lines), *spd*-projected (dashed) and *f*-projected (dotted).



FIG. 1.5 Spin polarized density of states for FM europium, f-electrons in the core. The dashed line marks the position of the occupied 4f-level.

2. Ferromagnets and Curie Temperature

2. 1. The Heisenberg Hamiltonian

The magnetism we observe in real solids is due to the spin and orbital momentum of the valence electrons. Each atom has a total magnetic moment depending on it's electronic configuration. This configuration in the ground state is determined by the *Hund rules*. In a crystal the spin magnetization density within LSDA is

$$m(\mathbf{r}) =
ho_{\uparrow}(\mathbf{r}) -
ho_{\downarrow}(\mathbf{r})$$

and the total spin per atom within ASA we obtain by integrating m over one atomic sphere.

Let as assume that there is one atom in each primitive cell *i* creating a non-zero magnetic moment $J_i = (J_i^x, J_i^y, J_i^z)$. In the following text we denote the lattice cells by *i*, *j* instead of \mathbf{R}, \mathbf{R}' etc.

The magnetic energy of a non-interacting system of magnetic moments is $W = -\gamma B \sum_j J_j^z$, where $\gamma > 0$ and z is the axis of the external field **B** (the Zeeman energy term). We get a more realistic Hamiltonian after considering the dipole-dipole interactions between various lattice sites. The *Heisenberg Hamiltonian* is defined [3,4,5,6]

$$\mathcal{H} = -\sum_{i,j} J_{ij} \boldsymbol{J}_i \boldsymbol{J}_j - \gamma B \sum_j J_j^z$$
(2.1)

This model Hamiltonian operates only on the momentum space and we consider now all the other energy components as constants.

The constants J_{ij} are called Heisenberg exchange parameters. In the further text we assume that we have an ideal infinite lattice with translation symmetry, $J_{ji} = J_{ij} = J_{0j-i}$ and $J_{ii} = 0$. In the quantum mechanical description \boldsymbol{J} are the spin operators, $\boldsymbol{J}_i \boldsymbol{J}_j = J_i^x J_j^x + J_i^y J_j^y + J_i^z J_j^z$. If there are many valence electrons present and the spin is high, we treat the momentum as a classical vector and the product $\boldsymbol{J}_i \boldsymbol{J}_j$ as a scalar vector product. In this classical description we normalize this vector $J^2 = J^2$, where J is the total magnetic moment per atom.

The system is in it's ground state at zero temperature, which can be in particular cases (depending on the J_{ij} constants) a ferromagnetic state (i.e. all the moments have the same direction).

At nonzero temperatures the system is in a statistical mixture of different states with the density operator $\rho = e^{-\beta \mathcal{H}}$, $\beta = 1/(k_B T)$, T is the temperature and k_B the Boltzmann constant. The statistical mean value of an observable A is defined by

$$\langle A \rangle := \frac{\operatorname{Tr}(\rho A)}{\operatorname{Tr}(\rho)}$$

The constants J_{ij} can be obtained from the knowledge of the spin resolved GF and the (spin resolved) potential functions (1.10) within LSDA, ASA, and TB-LMTO (see eq. (3) in [4] and [9]).

It can be shown that the amplitude of J_{ij} for distant lattice sites i, j decreases to zero like d^{-3} where d = |i - j| is the distance between the lattice sites. A finer approximation is $J_{ij} \approx A \sin(\kappa d + \phi)/d^3$. FIG. 2.1 shows the dependence of the exchange coefficients on the distance.

2. 2. Langevin Paramagnetism

Let us derive an equation for the average magnetization $\overline{\mu} := \langle J_i^z \rangle = \langle J_z \rangle$ (independent of *i*) if the Hamiltonian is just $\mathcal{H} = -\gamma B \sum_i J_i^z$ (the Zeeman term) and assume that the spins $J_i^Z \in \langle -J, J \rangle$ as in the classical description. The partition function can be computed [4]

$$Z = \int \mathrm{d}\Omega_1 \dots \mathrm{d}\Omega_N e^{\beta \gamma B J \sum_i \cos \phi_i} = \left(\int \mathrm{d}\Omega e^{\beta \gamma B J \cos \phi}\right)^N = (z(a))^N$$

where ϕ_i is the angle between the z-axis and the direction of J_i ,

$$z(a) = \frac{\pi}{a}\sinh(a), \qquad (2.2)$$



FIG. 2.1 The J_{ij} constant from the Heisenberg Hamiltonian for bcc europium and their dependence on the distance d = |i - j| without and with a prefactor d^3 . Here a is the lattice constant.

N is the number of atoms and $a = \beta B J \gamma$. The magnetization is

$$\langle J^z \rangle = -\frac{1}{\gamma} \frac{\partial f}{\partial B} \tag{2.3}$$

where f is the Gibbs free energy per particle. From the statistical physics we know $f = -(1/\beta) \log z(a)$. From (2.3) and (2.2) can be easily derived that the

$$\overline{\mu}/J = L(a) \tag{2.4}$$

where we define the Langevin function

$$L(a) := \coth(a) - 1/a \tag{2.5}$$

(2.4) is an equation for the magnetization. It describes a phenomenon called *Langevin paramagnetism*. This equation is exact for noninteracting

classical magnetic moments (the approximation was used only in the choice of the Hamiltonian and the classical treatment of the magnetic moment as a vector).

2. 3. Mean Field Approximation

Each of the moments J_i creates it's own magnetic field that interact with all other magnetic moments. In the *Mean Field Approximation* we assume that each magnetic moment is affected only by an average field from all other moments. A natural assumption is that the created field is proportional to the magnetization $\overline{\mu} = \langle J^z \rangle$:

$$B_{loc} = \lambda \overline{\mu} \tag{2.6}$$

We assume that the average magnetization doesn't depend on the lattice cell i.

Let us consider a system of magnetic moments with the Heisenberg Hamiltonian (2.1). If we choose an "unperturbed" Hamiltonian \mathcal{H}_0 close to \mathcal{H} , then the appropriate free energy per particle can be approximated by

$$f \approx f_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

We denote $\langle A \rangle_0$ the mean value of A with respect to the density operator $\rho_0 = e^{-\beta \mathcal{H}_0}$.

This equation can be derived from the perturbation theory and the error is of order $\langle \mathcal{H} - \mathcal{H}_0 \rangle_0^2$.

The following theorem has been proved:

Theorem. [3,4] If F_0 is the free energy of the system, corresponding to some Hamiltonian \mathcal{H}_0 then for the free energy F corresponding to \mathcal{H} the following inequality holds:

$$F \le F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \tag{2.7}$$

In the Mean Field Approximation approximate the Hamiltonian by

$$\mathcal{H}_0 = -\gamma B_{eff} \sum_i J_i^z$$

where $B_{eff} = B + B_{loc}$, B_{eff} is the projection of B_{eff} onto the z-axis, B is the external field and B_{eff} is chosen so that the expression $F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ is minimal. The approximate Hamiltonian \mathcal{H}_0 is a function of B_{eff} . We denote the right hand side of (2.7) by ϕ . We obtain from (2.7) that in order to obtain the best approximation for the free energy of the system ϕ must be minimal and the derivations of ϕ with respect to it's free parameters must be zero.

This is the way how to obtain the B_{eff} in the MFA.

It is easy to verify

$$\langle H_0 \rangle_0 = -\gamma (B_{loc} + B)\overline{\mu}N \langle H \rangle_0 = -(J_0\overline{\mu}^2 - \gamma B\overline{\mu})N$$
 (2.8)

where $J_0 = \sum_i J_{0i}$, $\overline{\mu} = \langle J^z \rangle_0$ and N is the number of magnetic moments in the system. We don't know the relation between B_{loc} and $\overline{\mu}$ so far but we treat them as independent parameters of $\phi = \phi(B_{loc}, \overline{\mu})$. The dependence $B_{loc}(\overline{\mu})$ will be determined from the condition of minimizing ϕ .

The free energy is $F_0 = -1/\beta \log Z_0$. We have computed Z_0 in the previous paragraph (see (2.2)). We see that Z_0 doesn't depend explicitly on the magnetization, $Z_0 = Z_0(\beta, B_{eff})$. If we want to find the minimum of ϕ with respect to $\overline{\mu}$ and use (2.8) we obtain the condition

$$\frac{\partial \phi}{\partial \overline{\mu}} = \frac{\partial \langle \mathcal{H} - \mathcal{H}_0 \rangle_0}{\partial \overline{\mu}} = \frac{\partial}{\partial \overline{\mu}} (-J_0 \overline{\mu}^2 + \gamma B_{loc} \overline{\mu}) = 0$$

Therefore $B_{loc} = (2J_0/\gamma)\overline{\mu}$ and $\lambda = 2J_0/\gamma$ (see (2.6)).

We have estimated the mean field Hamiltonian $\mathcal{H}_0 = -\gamma (B + \lambda \overline{\mu}) \sum_i J_i^z$.

This is the same Hamiltonian as that described in the previous paragraph 2.2 and we derive the same way that $\overline{\mu}/J = L(a), a = \beta \gamma (B + \lambda \overline{\mu}) J$.

Assume now that the external field **B** is zero. Then $B_{eff} = B_{loc} = \lambda \overline{\mu}$ and we get

$$\overline{\mu}/J = L(2J_0\beta J\overline{\mu}) \tag{2.9}$$

This is a self-consistent equation for the magnetization $\overline{\mu}$. It has a nonzero solution if $J_0 > 0$ for some $\beta > \beta_C^{MFA}$. The magnetization $\overline{\mu}$ and the argument of the Langevin function in (2.9) goes to zero as $\beta \searrow \beta_C^{MFA}$. The Langevin function can be approximated

$$L(a) \approx a/3 + O(a^2) \tag{2.10}$$

Substituting (2.10) into (2.9) the Mean Field Curie temperature can be determined

$$\frac{1}{\beta_C^{MFA}} = \frac{2}{3} J_0 J^2 \tag{2.11}$$

So far we have considered only one atom in each primitive cell. Let us have a system with translation symmetry and n atoms in each cell. We denote them by the index $B \in \{0, ..., n-1\}$. The Heisenberg Hamiltonian is

$$\mathcal{H} = -\sum_{iB,jB'} J_{iB,jB'} J_{iB} J_{jB'} - \gamma B \sum_{iB} J_{iB}^z$$

The derivation of T_C^{MFA} is unchanged and the condition (2.11) holds with

$$J_0 = \sum_{j,B'} J_{00,jB'}$$

The T_C^{MFA} is usually higher than the experimental Curie temperature. A better approximation called *Random Phase Approximation* is described in the next chapter.

3. Green Functions

3. 1. Mathematical Formalism.

Let \mathcal{H} be the Hamiltonian of a system and A(t), B(t) some observables in the Heisenberg picture (defined by $A(t) = e^{i\mathcal{H}t/\hbar}A e^{-i\mathcal{H}t/\hbar}$). Suppose that there is a nonzero temperature T and the system is in a statistical mixture of quantum states with the Boltzmann statistics. The statistical average of an observable A we mark $\langle A \rangle = Tr(e^{-\beta\mathcal{H}}A)/Tr(e^{-\beta\mathcal{H}})$, where $\beta = 1/k_BT$, k_B is the Boltzmann constant and $e^{-\beta\mathcal{H}}$ is the density operator. We consider a time-independent Hamiltonian.

We define the retarded Green function $G_{AB}^{(r)}(t,t')$ and the advanced Green function $G_{AB}^{(a)}(t,t')$

$$G_{AB}^{(r)}(t,t') := \langle \langle A(t), B(t') \rangle \rangle^{(r)} := \Theta(t-t') \langle [A(t), B(t')] \rangle$$

$$G_{AB}^{(a)}(t,t') := \langle \langle A(t), B(t') \rangle \rangle^{(a)} := -\Theta(t'-t) \langle [A(t), B(t')] \rangle$$
(3.1)

 Θ is the Heaviside step-function, $\Theta(t) = 1$ for t > 0 and 0 for t < 0. It can be shown that for a time-independent Hamiltonian the Green function depends only on the difference t - t' and we can write $G_{AB}^{(j)}(t, t') = G_{AB}^{(j)}(t - t', 0) = \langle \langle A(t - t'), B \rangle \rangle^{(j)}$ meaning $B = B(0), (j) \in \{(r), (a)\}$. Therefore we can make the time-fourier transformation and get

$$G_{AB}^{(j)}(\omega) := \langle \langle A, B \rangle \rangle^{(j)}(\omega) := \frac{1}{2\pi} \int \langle \langle A(t), B \rangle \rangle^{(j)} e^{i\omega t} dt$$

(j) = (r) or (j) = (a). All the operators must fulfill the equation of motion in the Heisenberg picture

$$i\hbar \frac{\mathrm{d}A(t)}{\mathrm{d}t} = [A(t), \mathcal{H}]$$

The time derivation of the GF is

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \langle \langle A(t), B \rangle \rangle^{(j)} = i\hbar \delta(t) \langle [A, B] \rangle + \langle \langle [A(t), \mathcal{H}], B \rangle \rangle^{(j)}$$
(3.2)

The equation holds both for (j) = (r) and (j) = (a). In the Fourier transform we obtain the equation of motion

$$\hbar\omega\langle\langle A,B\rangle\rangle^{(j)}(\omega) = \frac{i\hbar}{2\pi}\langle[A,B]\rangle + \langle\langle[A,\mathcal{H}],B\rangle\rangle^{(j)}(\omega)$$
(3.3)

It is useful to note that the GF is not fully determined by the last equation because it is valid for both advanced and retarded GF. We mention now the useful identities

$$\langle \langle A, B \rangle \rangle^{(r)}(\omega) = \langle \langle A, B \rangle \rangle^{(r)}(\omega + i0) \langle \langle A, B \rangle \rangle^{(a)}(\omega) = \langle \langle A, B \rangle \rangle^{(r)}(\omega - i0)$$

$$(3.4)$$

To prove this, we can write the definition of the Fourier transform of the time dependent GF for $\omega + i\epsilon$ and get an additional term of $e^{-\epsilon t}$ under the integral in the retarded GF which converges to unity for t > 0, $\epsilon \searrow 0$. Because of the Θ function we integrate over the positive times only. The same way we obtain that a small negative ϵ does not spoil the convergence of the advanced GF.

We can therefore consider (3.3) as 2 equation for $\omega = \omega \pm i0$ which corresponds to the equation for the retarded and advanced GF.

If we are able to approximate the last term in (3.3)

$$\langle \langle [A, \mathcal{H}], B \rangle \rangle(\omega) \approx F \langle \langle A, B \rangle \rangle(\omega)$$

we can express the GF explicitly in terms of $\langle [A, B] \rangle$ and F. This approximation is called *decoupling*.

If we know the GF, we can compute the averaged product $\langle A(t)B \rangle$. Define $I_{AB}(\omega)$ as the Fourier transform of $\langle BA(t) \rangle$ so that

$$\langle BA(t)\rangle = \int I_{AB}(\omega)e^{-i\omega t}\mathrm{d}\omega$$

It can be shown that then $\langle A(t)B\rangle = \int I_{AB}(\omega)e^{\beta\omega\hbar}e^{-i\omega t}d\omega$ and consequently

$$\langle [A(t), B] \rangle = \int I_{AB}(\omega) (e^{\beta \omega \hbar} - 1) e^{-i\omega t} d\omega$$

Now we can express the retarded and advanced GF from the definition as

$$\langle \langle A,B \rangle \rangle^{(r)}(E) = \langle \langle A,B \rangle \rangle^{(r)}(E+i0)$$

= $\frac{1}{2\pi} \int dt e^{i(E+i0)t} \Theta(t) \int d\omega I_{AB}(\omega) (e^{\beta\omega\hbar} - 1) e^{-i\omega t}$
= $\frac{1}{2\pi} \int d\omega I_{AB}(\omega) (e^{\beta\omega\hbar} - 1) \int dt e^{i(E+i0-\omega)t} \Theta(t)$ (3.5)

The last integral can be computed:

$$\int \mathrm{d}t e^{i(E+i0-\omega)t} \Theta(t) = \int_0^\infty e^{i(E+i0-\omega)t} \mathrm{d}t = \left[\frac{e^{i(E+i0-\omega)t}}{i(E+i0-\omega)}\right]_{t=0}^\infty =$$

$$= \frac{i}{E+i0-\omega}$$
(3.6)

The small imaginary part *i*0 is necessary due to the convergence of $\int_0^\infty e^{i(E+i0-\omega)} dt$.

Substituting (3.6) into (3.5) we obtain

$$\langle\langle A,B\rangle\rangle^{(r)}(E) = \frac{i}{2\pi} \int d\omega \ I_{AB}(\omega) \frac{e^{\beta\omega\hbar} - 1}{E + i0 - \omega}$$
 (3.7)

For the advanced GF we obtain a similar formula, which differs from (3.7) by having $E - \omega - i0$ in the denominator only. This justifies us to define a *complex* Green function by

$$G_{AB}(z) = \langle \langle A, B \rangle \rangle(z) = \frac{i}{2\pi} \int d\omega \ I_{AB}(\omega) \frac{e^{\beta \omega \hbar} - 1}{z - \omega}$$

This function is analytic in the upper half-plane and in the lower halfplane. The retarded resp. advanced GF are limits of this complex Green function from the upper resp. lower half-plane at the real axis. Let us now recall the identity

$$\frac{1}{x\pm i0} = (P)\frac{1}{x} \mp \pi\delta(x) \tag{3.8}$$

Using (3.8), (3.7) we obtain

$$G_{AB}(E+i0) - G_{AB}(E-i0) = I_{AB}(E)(e^{\beta E\hbar} - 1)$$
(3.9)

We see that the knowledge of the retarded and advanced GF can be used for computing $I_{AB}(E)$ which is the Fourier transformation of $\langle BA(t) \rangle$. In the next chapter we will approximate some Green function G_{AB} and use the relation

$$\langle B(0)A(0)\rangle = \int I_{AB}(\omega)d\omega = \int \frac{G_{AB}^{(r)}(\omega) - G_{AB}^{(a)}(\omega)}{e^{\beta\omega\hbar} - 1}d\omega \qquad (3.10)$$

The analyticity of G_{AB} in the half-planes is an important fact from the numerical point of view. We can compute the limit of G_{AB} from the upper and lower half-plane using the analytic deconvolution.

3. 2. Random Phase Approximation for Spin 1/2

We use the formalism of the Green functions for improving the Mean Field Approximation of the Curie temperature. Let us consider the Heisenberg Hamiltonian

$$\mathcal{H} = -\sum_{i,j} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j \tag{3.11}$$

with zero external field. S_i is the spin operator, $S_i = (S_i^x, S_i^y, S_i^z)$. The spins are localized at the sites of a perfect crystal lattice. We assume in this simple model that the magnetic moments in the Heisenberg Hamiltonian (2.1) are created by spins only, the system has translation symmetry, all sites are equivalent, there is only one atom in each primitive cell and $J_{ij} = J_{ji} = J_{0(j-i)}$. Suppose further that there is a nonzero magnetization at low temperatures (without external field) and we denote the magnetization axis by z. Such a system is called *isotropic Heisenberg* ferromagnet.

In the simplest case the spin operators S_i are spin 1/2 operator and the spin at the site *i* is a spin 1/2 quantum state (a two dimensional vector in the spin space). By a finite non-zero temperature the system is in a statistical mixture of quantum states. We want to express the averaged magnetic moment $\langle S_i^z \rangle$ and find a condition for the temperature so that $\langle S_i^z \rangle \searrow 0$ for $T \nearrow T_C$. In the case of spin 1/2 we have $S_i^z = 1/2 - S_i^- S_i^+$,

where $S^{\pm} = S^x \pm iS^-$ are the creation and annihilation spin operators. If averaged, $\langle S_i^z \rangle = 1/2 - \langle S_i^- S_i^+ \rangle$. Let us mark for simplicity $\overline{S^z} = \langle S_i^z \rangle$ (independent of *i* in a system with translation symmetry).

We will define the Green functions $\langle \langle S_0^+(t), S_j^- \rangle \rangle^{(j)}$, (j) = (r) and (a) and after approximating it by an explicit formula use (3.10) to express $\langle S_0^- S_0^+ \rangle$. The equation of motion (3.3) reads

$$\hbar\omega\langle\langle S_0^+, S_j^-\rangle\rangle(\omega) = \frac{i\hbar}{\pi}\delta_{0j}\overline{S^z} + 2\sum_m\langle\langle J_{0m}(-S_0^z S_m^+ + S_m^z S_0^+), S_j^-\rangle\rangle(\omega)$$
(3.12)

what is easy to check out considering the commutators $[S_0^+, S_j^-], [S_0^+, \mathcal{H}],$ Hamiltonian (3.11) and the relationship $S_i S_j = 1/2(S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z$.

The *Random Phase Approximation* consists in the "decoupling" of the last terms in (3.12):

$$\frac{\langle \langle S_0^z S_m^+, S_j^- \rangle \rangle \approx \langle S^z \rangle \langle \langle S_m^+, S_j^- \rangle \rangle}{\langle \langle S_m^z S_0^+, S_j^- \rangle \rangle \approx \langle S^z \rangle \langle \langle S_0^+, S_j^- \rangle \rangle}$$
(3.13)

for $j \neq 0$ (the case j = 0 is not interesting as $J_{00}=0$). The equation of motion holds both for retarded and advanced GF. The only unknown in the equation (3.12) after "decoupling" (3.13) are $\overline{S^z}$ and the functions $G_{0j}(\omega) = \langle \langle S_0^+, S_j^- \rangle \rangle$. The equation of motion after decoupling is

$$\hbar\omega G_{0j}(\omega) = \frac{i\hbar}{\pi} \delta_{0j} \overline{S_z} + 2\overline{S_z} \sum_m \left(-J_{0m} G_{mj}(\omega) + J_{0m} G_{0j}(\omega) \right) \quad (3.14)$$

In a system with translation symmetry we can make the lattice Fourier transformation (LFT) of J_{ij} and $G_{ij}(\omega)$. We obtain functions defined in the first Brillouin zone J(q) and $G(q,\omega)$ defined by $J(q) = \sum_{j} J_{0j} e^{ijq}$ and $G(q,\omega) = \sum_{j} G_{0j}(\omega) e^{ijq}$.

If we multiply (3.14) by e^{ijq} and sum over j, we get

$$\hbar\omega G(q,\omega) = \frac{i\hbar}{\pi}\overline{S^z} + 2\overline{S^z}(J(0) - J(q))G(q,\omega)$$
(3.15)

$$G(q,\omega) = \frac{i\hbar}{\pi} \frac{\overline{S^z}}{\hbar\omega - \lambda(q)}$$
(3.16)

where

$$\lambda(q) = 2\overline{S_z}(J(0) - J(q)) \tag{3.17}$$

is the energy of the "spin wave" with the wave vector $q \in BZ$.

Let us recall that for determining the retarded resp. advanced GF we can take $\omega + i0$ resp. $\omega - i0$ instead of ω .

We use now the equation (3.10):

$$\langle S_0^-, S_0^+ \rangle = \int d\omega \frac{G_{00}^{(r)}(\omega) - G_{00}^{(a)}(\omega)}{e^{\beta\omega\hbar} - 1} = \frac{1}{\Omega_{BZ}} \int d\omega \int dq \frac{G(q, \omega + i0) - G(q, \omega - i0)}{e^{\beta\omega\hbar} - 1}$$
(3.18)

After changing the order of integration, substituting (3.16) for G and using the identity (3.8) we obtain

$$1/2 - \overline{S^z} = \langle S_0^-, S_0^+ \rangle = \frac{2\overline{S^z}}{\Omega_{BZ}} \int \mathrm{d}q \frac{1}{e^{\beta\lambda(q)} - 1}$$

This is a self-consistent equation for the magnetization $\overline{S^z}$. We are interested in finding the temperature β_C so that $\overline{S^z} \searrow 0$ for $\beta \searrow \beta_C$.

We simplify the last equation by writing

$$\frac{1}{2\overline{S^z}} = \frac{1}{\Omega_{BZ}} \int \mathrm{d}q \left(1 + \frac{2}{e^{\beta\lambda(q)} - 1}\right) = \frac{1}{\Omega_{BZ}} \int \coth(\frac{1}{2}\beta\lambda(q)) \mathrm{d}q \quad (3.19)$$

The argument of the coth goes to zero as $\overline{S^z} \searrow 0$ and we approximate $\operatorname{coth} x \approx x^{-1}$. Multiplying both sides of (3.19) by $\overline{S^z}$ we obtain an equation for β_C which does not depend on $\overline{S^z}$:

$$\beta_C = \frac{1}{\Omega_{BZ}} \int \frac{2}{J(0) - J(q)} \mathrm{d}q \qquad (3.20)$$

The denominator approaches to zero as $q \to 0$. We assume J(0) - J(q) to be positive in the ferromagnets because J(0) - J(q) is proportional to the

energy of the spin waves and in the ground state of a ferromagnet all spins have the same directions and no spin waves are present. If we assume that J(q) has a continuous first derivation in q = 0 (this is obvious, if we take only a finite number of nonzero J_{0j}), we can write $J(0) - J(q) \approx Dq^2$ for some D > 0 and small q-vectors. The convergence of (3.20) is given by the convergence of $\int q^{-2}$. This integral converges only in a space of dimension greater then 2. Therefore in the RPA approximation the ferromagnetic materials can exist only in a space of dimension 3 or more. This is a difference from the MFA where the the only condition for a nonzero Curie temperature is $J_0 > 0$ and the ferromagnetism exists on 2 dimensional surfaces as well.

3. 3. RPA for More Atoms in a Primitive Cell

If we have two or more atoms in each primitive cell, all the functions used in the previous section become matrices. Let us mark the different atoms in a cell by $B \in \{0, ..., n-1\}$. The Hamiltonian is

$$\mathcal{H} = -\sum_{iB,jB'} J_{iB,jB'} \boldsymbol{S}_{iB} \boldsymbol{S}_{jB'}$$
(3.21)

In the case of spin 1/2 we get $1/2 - \langle S_{0B}^z \rangle = \langle S_{0B}^-, S_{0B}^+ \rangle = \langle S_0^-, S_0^+ \rangle_{BB}$. We consider the matrix $\langle S_0^-, S_0^+ \rangle_{BB'}$ of dimension $n \times n$ and are interested in it's diagonal elements. We define the GF matrices $[G_{ij}^{(j)}(\omega)]_{BB'}$, $(j) \in \{(r), (a)\}$. The equation of motion (3.3) is

$$\begin{split} \hbar\omega \Big[G_{0j}(\omega)\Big]_{BB'} &= \frac{i\hbar}{\pi} \delta_{0j} \delta_{BB'} \overline{S_z} \mathbb{1} + \\ &+ \sum_{nB''} \Big(\langle \langle S_{0B}^+, S_{jB'}^- \rangle \rangle(\omega) J_{0B,nB''} - \langle \langle S_{0B}^z S_{nB''}^+, S_{jB'}^- \rangle \rangle(\omega) J_{0B,nB''} \Big) \end{split}$$

We make the decoupling of the r.h.s. analogous to (3.13) and after LFT we obtain the expression

$$\hbar\omega[G(q,\omega)]_{BB'} = \frac{i\hbar}{\pi}\overline{S^z}\mathbb{1} + [\overline{S^z}(J_{0B} - J(q))G(q,\omega)]_{BB}$$

This is similar to (3.15) but it is a matrix equation now, the product on the r.h.s. is a matrix product and $J_{0B} = \sum_{B'} J(0)_{BB'}$. We will assume that for all $B \ J_{0B} = J_0 = \sum_{jB'} J_{00,jB'}$.

We obtain

$$G(q,\omega) = \frac{i\hbar}{\pi} \overline{S_z} \Big(\hbar\omega - \overline{S_z}(J_0 - J(q))\Big)^{-1}$$

As before, the retarded GF corresponds to $\omega = \omega + i0$ and the advanced GF to $\omega = \omega - i0$. The equation (3.18) still holds as a matrix equation. We need now a generalization of the identity (3.8):

Lemma. If A is a hermitian operator, λ_i it's eigenvalues and P_i are the projection operators onto the appropriate eigenspaces, then (in the sense of distributions)

$$\operatorname{Im}((\omega+i0)\mathbb{1}-A)^{-1} = -\pi \sum_{i} \delta(\lambda_i) P_i$$
(3.22)

Especially, if λ_i are non-degenerate with the normalized eigenvectors $|\lambda_i\rangle$, then $\operatorname{Im}((\omega + i0)\mathbb{1} - A)^{-1} = -\pi \sum_i \delta(\lambda_i) |\lambda_i\rangle \langle \lambda_i|$

The proof consists in the generalization of the residual theorem to matrix functions. The matrix function we call analytic, if it can be locally expressed as $f(z + \epsilon) = \sum_{j>j_0} A_j \epsilon^j$, $j_0 \in \mathbb{Z}$. The matrix A_{-1} is called residuum and a complete analogy of the residuum theorem holds.

As a consequence we get the equation (3.19) with $\lambda(q) = 2\overline{S^z}(J_0 - J(q))$ a matrix. The equation (3.20) holds too. The diagonal elements of $\langle S_0^-, S_0^+ \rangle$ are then the diagonal elements of the right hand side of the equation (3.20) and therefore the formula for expressing the RPA Curie temperature is the same as (3.20), where we just substitute $J_0 = \sum_{jB'} J_{00,jB'}$ and take the diagonal elements of the r.h.s. matrix. This diagonal elements could be in general various and would correspond to the magnetizations $\langle J_{0B}^z \rangle$, $B \in \{0, \ldots, n-1\}$ but in the cases we study (hcp and bcc structure) all the atoms are equivalent and all the magnetizations are the same.

3. 4. RPA for Classical Spin

The RPA technique used for the derivation of (3.20) can be generalized for an arbitrary spin (or magnetic momentum) but it becomes very complicated. It's more convenient to use the classical spin description what corresponds to the quantum mechanical $\hbar \to 0$ limit. Instead of the commutators we use the classical Poisson brackets {} and the GF defined by

$$\langle \langle A(t), B(t') \rangle \rangle^{(r)} = \Theta(t - t') \langle \{A(t), B(t')\} \rangle \langle \langle A(t), B(t') \rangle \rangle^{(a)} = -\Theta(t' - t) \langle \{A(t), B(t')\} \rangle$$

If we denote the components of the classical magnetic moment $\mathbf{r} \times \mathbf{p}$ by x, y, z, we obtain the relations $\{x, y\} = z$ etc. The equation of motion for a quantity A is $dA/dt = \{A, \mathcal{H}\}, \mathcal{H}$ is the classical Hamiltonian.

We normalized the spin to unity,

$$x^2 + y^2 + z^2 = 1$$

This can always be achieved by normalizing the constant J_{ij} in the Hamiltonian.

We define the GF $G_{jn}(t,t') = \Theta(t-t')\langle \{x_j + ix_j, w_n\}\rangle$, where w_n is a function depending on x_n, y_n, z_n only. If we find the Poisson bracket $\{x_j + iy_j, \mathcal{H}\}$, write the equation of motion, use the classical decoupling analogous to (3.13):

$$\langle \langle z_j(x_m + iy_m), w_n \rangle \rangle \approx \langle z_j \rangle \langle \langle x_m + iy_m, w_n \rangle \rangle$$

and make the time Fourier transformation, we obtain a system of equation analogous to (3.14)

$$\omega G_{0j}(\omega) = \frac{i}{2\pi} \delta_{0j} \langle \{x_0 + iy_0, w_0\} \rangle + 2\overline{z} \sum_m (J_{0m} G_{0j}(\omega) - J_{0m} G_{mj}(\omega))$$

where $\overline{z} = \langle z_j \rangle$ is assumed to be independent of j. Making the LFT we obtain, similar to (3.16)

$$G(q,\omega) = \frac{i}{2\pi} \frac{\langle \{x_0 + iy_0, w_0\} \rangle}{\omega - \lambda(q)}$$
(3.23)

where $\lambda(q)$ is defined by (3.17). We need a classical analogy of (3.10) here. It can be shown that it is

$$\langle B(0)A(0)\rangle = \int \frac{i\left(G_{AB}^{(r)}(\omega) - G_{AB}^{(a)}(\omega)\right)}{\beta\omega} d\omega \qquad (3.24)$$

what corresponds to the $\hbar \to 0$ limit (compare to (3.10)). Substituting (3.24) into (3.23) for $A = x_0 + iy_0$ and $B = w_0(x_0, y_0, z_0)$ we obtain

$$\langle (x_0 + iy_0)w_0 \rangle = \frac{i\langle \{x_0 + iy_0, w_0\}\rangle}{\Omega_{BZ}} \int \frac{1}{\beta\lambda(q)} dq =$$

= $ik\langle \{x + iy, w\}\rangle$ (3.25)

 $k \in \mathbb{R}$ is defined by this equation.

We choose $w_n := e^{az_n}(x_n + iy_n)$, where *a* is a real parameter and denote $\Phi(a) := \langle e^{az_0} \rangle = \langle e^{az} \rangle$ (it is independent from the site) then $\Phi'(a) = \langle ze^{az} \rangle$ and $\Phi''(a) = \langle z^2 e^{az} \rangle$.

The function $\Phi(a)$ determines the magnetization, $\langle z \rangle = \Phi'(0)$. If we use (3.25) and compute the Poisson bracket on the r.h.s. $\{x + iy, (x - iy)e^{az}\}$ from the definition of the Poisson bracket, we obtain

$$\langle (x+iy)(x-iy)e^{az} \rangle = ik \langle \{x+iy, e^{az}(x-iy)\} \rangle =$$

= $-k \langle (a-2z-az^2)e^{az} \rangle =$ (3.26)
= $-k (\Phi(a) - 2\Phi'(a) - a\Phi''(a))$

From another point of view (the spin vector is normalized to unity, $x^2 + y^2 + z^2 = 1$)

$$\langle (x+iy)(x-iy)e^{az} \rangle = \langle (1-z^2)e^{az} \rangle = \Phi(a) - \Phi''(a)$$
(3.27)

Comparison of (3.26) and (3.27) leads to a differential equation for $\Phi(a)$ with an initial condition $\Phi(0) = 1$. It's solution is

$$\Phi(a) = \frac{\sinh(a + \frac{1}{k})}{(ka+1)\sinh(\frac{1}{k})}$$

and the magnetization

$$\overline{z} = \Phi'(0) = L(\frac{1}{k}) \tag{3.28}$$

where L is the Langevin function defined by (2.5).

We substitute k from (3.25) into (3.28) and obtain an equation for the classical RPA magnetization

$$\overline{z} = L \left[\left(\frac{1}{\Omega_{BZ}} \int \frac{1}{\beta \lambda(q)} \mathrm{d}q \right)^{-1} \right]$$
(3.29)

with $\lambda(q) = 2\overline{z}(J_0 - J(q))$. This equation can be solved numerically. If we are interested in the Curie temperature, we limit $\overline{z} \searrow 0$, use the identity $L(x) \approx x/3$ for small x and get the Curie temperature

$$\beta_C^{RPA} = \frac{3}{2} \frac{1}{\Omega_{BZ}} \int \frac{1}{J_0 - J(q)} dq$$
(3.30)

If we have more then one atom in each cell, (3.25) will be a matrix equation, k will be the diagonal element of the matrix

$$\frac{1}{\Omega_{BZ}} \int \frac{1}{\beta \lambda(q)} \mathrm{d}q \tag{3.31}$$

and (3.28) stays unchanged. Similarly, the equation (3.30) holds as an equation for diagonal matrix elements with $\beta_C^{RPA} \equiv \beta_C^{RPA} \mathbb{1}$.

3. 5. Comparison of RPA and MFA

Let us now compare the Mean Field Curie temperature (2.11) with the RPA Curie temperature (3.30). If the spin (or, generally, magnetic moment) is normalized to unity, then the MFA formula is

$$(\beta_C^{MFA})^{-1} = \frac{2}{3}J_0 \tag{3.32}$$

Because of $J_{00} = 0$ and

$$J_{00} = \frac{1}{\Omega_{BZ}} \int J(q) \mathrm{d}q$$

we see that $\int J(q) dq = 0$ and (3.32) can be written

$$(\beta_C^{MFA})^{-1} = \frac{2}{3} \frac{1}{\Omega_{BZ}} \int_{BZ} (J_0 - J(q)) \mathrm{d}q$$
(3.33)

Comparing (3.30) and (3.33) we see that $[(2/3)\beta_C^{MFA}]^{-1}$ is the arithmetic mean value of $J_0 - J(q)$ in the first BZ and $[(2/3)\beta_C^{RPA}]^{-1}$ is it's harmonic mean value. From the convexity of the function 1/x can be easily derived that the harmonic mean value of some numbers is always smaller then the arithmetic mean value. Therefore

$$T_C^{RPA} < T_C^{MFA} \tag{3.34}$$

The same result can be proved if (3.33) and (3.30) are equation of matrix diagonal elements. Assume that the diagonal elements are identical and therefore proportional to the trace. Let as denote $x(q) := (J_0 - J(q))$ and $\overline{x(q)}$ it's arithmetical mean value. We want to prove

$$\operatorname{Tr} \overline{x(q)} > (\operatorname{Tr} \overline{x^{-1}(q)})^{-1}$$
(3.35)

Denote the eigenvalues of x(q) by $\lambda_i(q), i = 1, ..., n$. The equation (3.35) is then

$$\sum_{i} \overline{\lambda_i(q)} > \left(\sum_{i} \overline{\lambda_i^{-1}(q)}\right)^{-1}$$
(3.36)

We know already that for each $i \overline{\lambda_i(q)} > (\overline{\lambda_i^{-1}(q)})^{-1}$. From this we easily prove (3.36) and therefore (3.35) and (3.34) are fulfilled.

4. Numerical implementation

4. 1. Curie Temperature of gadolinium and cobalt

Using the RPA model described in the previous chapter I computed the Curie temperature of the ferromagnets cobalt and gadolinium. They have both a hexagonal close packed lattice.

For computing the Curie temperature I treat the spin of the valence electrons as a classical vector. Gd has 7 valence f-electrons and 1 d-electron. This system are large enough to be treated classically. The Curie temperature of a ferromagnet can be estimated from the equation (3.30).

The main task is to compute the integral in the equation (3.30). The hcp lattice has 2 atoms in each cell and (3.30) must be used as a matrix equation.

The exchange coefficients J_{ij} I obtained as an output of existing programs written by my diploma teacher RNDr. Ilja Turek. In this programs the J_{ij} coefficients are calculated using the LSDA approximation, Green function method, ASA and tight-binding LMTO, see [5]. A file with these constants (containing about 400 exchange parameters, where all the others, describing the interactions between very distant lattice sites, are neglected) is an input file for my program.

To calculate the right hand side of (3.30) I had to make the LFT of the exchange constants for a set of q-vectors from the first BZ.

The average value of $[J_0 - J(q)]^{-1}$ in the first BZ I approximated with a finite sum

$$\frac{1}{\Omega_{BZ}} \int_{BZ} [J_0 - J(q)]^{-1} \approx \frac{1}{N} \sum_{i=1}^N [J_0 - J(q_i)]^{-1}$$
(4.1)

where q_i are some points from the BZ. I chose the points q_i to form an equidistant mesh and magnified N until the convergence of (4.1) became clear.

It is not necessary to integrate over the whole BZ because some q-points are equivalent. This is because of the symmetries of the hcp lattice. Each symmetry in the real lattice corresponds to a degeneracy of each q-vector in the BZ. I give an example here: the hcp lattice doesn't change if we mirror it around the xy plane. Denote $q' = (q_x, q_y, -q_z)$ and $R' = (R_x, R_y, -R_z)$. Then $e^{iq'R} = e^{iqR'}$. Because of the lattice symmetry $J_{0R} = J_{0R'}$ (the sites R and R' are equivalent) we obtain J(q) = J(q'). We see that the symmetry in the real lattice reduces the part of the BZ which we have to treat independently. In fact, there are more symmetries in the hcp lattice (rotation around the z-axis about 60° or 120°) and we need to integrate only over one 24th of the BZ, called *irreducible Brillouin zone* (IBZ). The IBZ for the hcp lattice it is shown in the FIG. 4.1.



FIG. 4.1 The first Brillouin zone for the hcp lattice and it's irreducible part.

If integrating $[J_0 - J(q)]^{-1}$ a difficulty is that this matrix is not defined for q = 0 and becomes very large for $q \approx 0$. The convergence of the integral

 $\int [J(0) - J(q) + z\mathbb{1}]^{-1}$ is much faster for z a small complex number. The function $\int [J(0) - J(q) + z\mathbb{1}]^{-1}$ is analytic in z. For $z \neq 0$ and z not a positive real number there are no singularities when integrating. We can compute it for a few z points near to zero and use the analytical deconvolution for determining it's value in z = 0.

Let f(z) be the function we want to compute in z = 0. I used the following formula for the deconvolution:

$$f(0) \approx 4f(i\epsilon) - f(2i\epsilon) - f(\epsilon + i\epsilon) - f(-\epsilon + i\epsilon)$$
(4.2)

for some $\epsilon > 0$.

It is easy to show that this formula gives an error in order of only ϵ^4 for an analytic function f. We don't use any z on the real axis to avoid possible singularities in $[J_0 - J(q) + z\mathbb{1}]^{-1}$. The parameter ϵ is supposed to be small compared with the eigenvalues of $J_0 - J(q)$. For gadolinium $J_0 \approx 3.3$ mRy.

I used several ϵ and I increased the number of points N along one line in the irreducible BZ for each of them until i got convergence with respect to both N and ϵ .

The FIG. 4.2 shows some results for gadolinium (the total number of q-points used for numerical integration over the IBZ is proportional to the third power of N).

As we see from the figure, the RPA Curie temperature is 305K for gadolinium. The same way I obtained the cobalt RPA Curie temperature 1369K. The experimental results are 1388K for cobalt (in the fcc structure) and 295K for gadolinium. The T_C^{RPA} error for gadolinium is about 3.3%. The MFA approach gives 1683K for cobalt and 343K for gadolinium. We see that the RPA is a better approximation of the Curie temperature then MFA and that indeed $T_C^{RPA} < T_C^{MFA}$.

All this results are based on the J_{ij} constants computed for fixed lattice constants a and c. I denote a the distance between the nearest neighbours in the xy plane and c the distance between the vertical nearest neighbours. The experimental value of c/a is 1.597.



FIG. 4.2 Numerical calculation of the Curie temperature for gadolinium. ϵ is the constant from (4.2).

We can observe how the RPA and MFA Curie Temperatures change if we change the lattice constants by a fixed proportion c/a. This corresponds to a homogeneous compression of the crystal and can be compared with experimental data.

Some of the results are on FIG. 4.3. The letter s denotes here $3/(4\pi)\Omega^{1/3}$, Ω is the volume per atom.

The experimental lattice constant s is about 3.762 a.u. By pressing it and decreasing the volume the Curie temperature becomes smaller in the experiment, which is in conflict with the calculations. The reason for this discrepancy is not known at present.



FIG. 4.3 The dependence of the MFA and RPA Curie temperature for gadolinium on the Wigner-Seitz radius s.

4.2. Magnon Spectrum

Let us consider a Heisenberg ferromagnet with the Hamiltonian (3.11)and spin S at each lattice site. The eigenstates of this Hamiltonian are called *magnons*, or *spin waves*. It can be shown that the spectrum of this Hamiltonian is connected to the poles of the Green function (3.16) resp. (3.23). Each magnon can be characterized by a vector from the first BZ. Be zero temperature the magnon energies are

$$\lambda(q) = 2S(J_0 - J(q)) + E_0 \tag{4.3}$$

where E_0 is the energy of the ground state. We can choose the energy scale so that $E_0 = 0$.

For nonzero temperature the magnon energy is decreasing proportionally to the magnetization $\overline{S^z}$, as can be seen from (3.17).

If there are more atoms in each lattice cell, the magnon energies are the eigenvalues of the matrix (4.3).

To compute this energies I made the LFT of the exchange constants J_{ij} for various q-vectors from the first BZ.

I computed the magnon energies for the ferromagnets gadolinium and cobalt. FIG. 4.4 shows the results for some special points in the first BZ for gadolinium at zero temperature. The positions of the points Γ , M, K and A in the first BZ can be seen on FIG. 4.1.



FIG. 4.4 Gadolinium magnon energies at zero temperature for special points on the border of the first BZ.

In both Gd and Co the energy has a maximum in the point M. Two lines in the picture corresponds to the two eigenvalues of the 2×2 matrix (the hcp lattice has 2 atoms in each cell). We see that the energies are always nonzero and positive: this is a consequence of the fact that gadolinium and cobalt are ferromagnets (the ground state is not a spin wave). The cobalt magnon spectrum is similar. To compute the magnetization and magnon energies at nonzero temperature we use the RPA model and formula (3.29). The integral in (3.29)is not needed to be computed so far we already have computed the RPA Curie temperature given by (3.30). Comparing (3.30), (3.29), the constant k as the diagonal term of (3.31) and the definition of the magnon energies (3.17) we see that k depends on the temperature like

$$k = \frac{1}{3\overline{z}} \frac{T}{T_C^{RPA}}$$

Substituting this into (3.29) and solving (3.29) I obtained the following magnetization for gadolinium at $T < T_C^{RPA}$:



FIG. 4.5 The dependence of the gadolinium magnetization on the temperature. The spin per atom at zero temperature is normalized to unity.

The magnon energies at nonzero temperature $T < T_C^{RPA}$ are exactly $\overline{S^z}/S$ times smaller then at zero temperature. FIG. 4.6 compares some experimental data for magnon energies along the border of the first BZ at the temperature 78K with the RPA result.



FIG. 4.6 The experimental gadolinium magnon energies at the temperature 78 K (points) and the RPA result calculated for 78 K (smooth lines). The experimental data are from [7].

5. Alloys with Substitutional Disorder

5. 1. Coherent Potential Approximation

Systems with substitutional disorder are systems with an ideal lattice where the lattice sites are randomly occupied by various atoms. In the simplest case there are two atoms A and B and their concentrations c^A and c^B so that $c^A + c^B = 1$. We assume that each lattice site is occupied fully randomly either by atom A (with the probability c^A) or by atom B(probability c^B) with no correlations between various lattice sites.

We want to compute the electronic structure of such a system. The LDA or LSDA and ASA approximations (see chapter 1) and the GF technique can be used again. The effective potential (1.1) or it's spherically symmetric approximation in one atomic sphere depends now on the occupation of the sphere. We obtain two potentials V_{eff}^Q , $Q \in \{A, B\}$. This indicates two different regular and irregular solutions $\varphi_{\mathbf{R}L}^Q(\mathbf{r}_{\mathbf{R}}, z)$ and $\tilde{\varphi}_{\mathbf{R}L}^Q(\mathbf{r}_{\mathbf{R}}, z)$ and two potential functions $P_{\mathbf{R}L}^Q(z)$ (see (1.10)). The physical properties of the system can be computed from the knowledge of the imaginary part of the Green function $G(\mathbf{r}, \mathbf{r}, z)$. The GF can be computed from (1.8). It can be shown that the first term on the right hand side of (1.8) is real for a real potential V_{eff} and we need to calculate the "physical GF matrix" $G_{\mathbf{R}L\mathbf{R}L'}(z)$ only.

To obtain reasonable result we have to average this matrix over all the possible configurations. If we denote $\overline{G}_{RLRL'}(z) := \langle G \rangle$ the configurational average of this matrix and

$$\overline{G}^Q_{\mathbf{R}L\mathbf{R}L'}(z) := (c^Q)^{-1} \langle \eta^Q_{\mathbf{R}} \overline{G}_{\mathbf{R}L\mathbf{R}L'}(z) \rangle$$

the average over all configurations having the atom Q at the site \mathbf{R} ($\eta_{\mathbf{R}}^{Q}$ is the "indicator" of the atom Q at the site \mathbf{R} , $\eta_{\mathbf{R}}^{Q} = 1$ if the site Q is occupied by the atom Q and 0 otherwise), then the randomness of the disorder gives the relation

$$\overline{G}_{\boldsymbol{R}L\boldsymbol{R}L'} = \sum_{Q} c^{Q} \overline{G}_{\boldsymbol{R}L\boldsymbol{R}L'}^{Q}$$

Let us define the "auxiliary GF" $g_{RLR'L'}(z)$ by the relation

$$G(z) = -\frac{1}{2}\frac{\dot{P}(z)}{\dot{P}(z)} + \sqrt{\dot{P}(z)}g(z)\sqrt{\dot{P}(z)}$$

We see from (1.10) that for a homogeneous solid $g = (P - S)^{-1}$, where P is the diagonal potential function matrix and S the matrix of the structure constants. We define a matrix \mathcal{P} by

$$\overline{g} = (\mathcal{P} - S)^{-1}$$

This matrix is generally nondiagonal. The Coherent Potential Approximation an approximating \mathcal{P} by a site-diagonal matrix. This means physically that we substitute the real alloy by a homogeneous solid with some "effective atoms". The condition on \mathcal{P} is that the average scattering from putting a single impurity A or B with the probability c^A or c^B into the effective medium is zero. The detailed CPA condition and additional theory can be found in [1].

CPA can be used not only for calculating the electronic structure of an alloy ground state but for a substance with randomly oriented spins as well. An example is the DLM europium that can be described as an "alloy" of two components: europium atoms with spin up and europium atoms with spin down. The energy dependence on the lattice parameter is shown in FIG. 1.2.

The figure FIG. 5.1 shows the density of states of the gadolinium-yttrium alloy at zero temperature and yttrium concentration 20%.

5. 2. Mean Field Magnetization and Curie Temperature

The Heisenberg Hamiltonian for an alloy is

$$\mathcal{H} = -\sum_{i,j,Q,Q'} J_{ij}^{QQ'} \boldsymbol{J}_i^Q \boldsymbol{J}_j^{Q'} \eta_i^Q \eta_j^{Q'} - \gamma B \sum_{j,Q} J_j^{Q,z} \eta_j^Q$$

where η_i^Q is the indicator of an atom Q at the site *i*. Assume that we have a ferromagnet and zero external field. We consider two "magnetizations"



FIG. 5.1 The gadolinium (full line) and yttrium (dashed line) projected DOS of the $Gd_{0.8}Y_{0.2}$ alloy (*f*-electrons in the core).

 $m^Q := \langle J^{Q,z} \rangle$. Let J_Q be the total magnetic moment of the atom of type Q. The Mean Field magnetization is, analogous to (2.9)

$$\frac{m^Q}{J_Q} = L(2\beta \sum_{Q'} J_0^{QQ'} m^{Q'} J_{Q'})$$
(5.1)

L is the Langevin function (2.3) and $J_0^{QQ'} := \sum_j J_{0j}^{QQ'}$.

The condition for the MFA Curie temperature is that all the magnetizations go to zero. We use the quality of the Langevin function $L(a) \approx a/3$ for a small argument a and obtain a system of equations

$$\frac{1}{\beta_C} \frac{m^Q}{J_Q} = \frac{2}{3} \sum_{Q'} J_0^{QQ'} J_Q J_{Q'} \frac{m^{Q'}}{J_{Q'}}$$

We see that the MFA Curie temperature $k_B T_C^{MFA}$ is an eigenvalue of the matrix $(2/3)J_0^{QQ'}J_QJ_{Q'}$. It is the maximal eigenvalue of this matrix



FIG. 5.2 The mean field and experimental Curie temperature of the gadoliniumyttrium alloy as a function of the yttrium concentration. The experimental data are from [10].

because for $k_B T$ smaller then the maximal eigenvalue there still exist a nonzero solution of the equations (5.1)

FIG. 5.2 shows the T_C^{MFA} for the Gd-Y alloy as a function of the Y concentration. The Curie temperature decreases with increasing Y concentration in qualitative agreement with experiments.

A more realistic approximation like RPA for alloys would be suitable but is not known yet. Some attempts to describe the finite temperature magnetization in alloys with CPA and RPA are in [8].

Conclusions

The density functional theory has enabled realistic computer calculations of the ground state properties of large electron systems with a translationally symmetric lattice. In the numerical implementations several approximations are used, e.g. LSDA, GGA, ASA. In this work I computed the magnetization and Curie temperature of gadolinium and cobalt within the Random Phase Approximation and Mean Field Approximation using the model of the Heisenberg Hamiltonian with exchange interactions constants calculated within the LSDA theory. I described the theoretical Green function formalism that leads to the RPA theory.

The Curie temperature within the RPA model is more realistic as the Mean Field Curie temperature and gives an error of about 3% from experiment. The calculations has been performed using the compter language C. The code includes integrating of a matrix function over the irreducible part of the first Brillouin zone for hexagonal closed packed lattice.

Making the lattice Fourier transformation of the exchage interaction constants I obtained the spin wave spectrum of gadolinium at finite temperatures. It is in good agreement with experimental results.

In order to describe the electronic structure of substitutionally disordered alloys at zero temperature the Coherent Potential Approximation can be used. I calculated the mean field Curie temperature for the Gd-Y alloy as a function of the yttrium concentration and found good qualitative agreement with experiment.

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