

# Effective magnetic Hamiltonians from first principles

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**Abstract.** We construct effective magnetic Hamiltonians by using the first-principles electronic-structure calculations. These Hamiltonians are used to determine the ground state of solids and nanostructures, and, at  $T > 0$ , using the methods of statistical mechanics, also their magnetic properties as a function of temperature. The present approach is highly flexible and it makes possible to find magnetic structure of complex systems with the accuracy of ab initio methods. As illustrations we show (i) how the magnetic structure at  $T = 0$  and at  $T > 0$  can be determined for systems with anisotropic exchange and for systems with several sublattices, (ii) why the magnetic moment in fcc-nickel is unstable upon reversal, and (iii) how to calculate the size of magnetic moment in fcc-Ni at the Curie temperature, which is important for explanation of the spin-disorder resistivity in Ni.

## 1 Introduction

Theoretical search for the ground state of a magnetic system using an ab initio theory might be extremely difficult problem because only a small set of magnetic structures can be calculated and compared. Even more difficult is to find the magnetic structure at finite temperature or the Curie (or Néel) temperature, because the knowledge of total energy is not sufficient, as the entropy has to be calculated and this is not possible within the ab initio theory. The effective magnetic Hamiltonians with parameters determined from ab initio calculations can solve the problem. They make possible to scan all configurations of the system for the energy (or free energy) minimum and, using the methods of statistical mechanics, to study the magnetic properties (the magnetic structure as a function of temperature, magnon spectra, the Curie/Néel temperature, etc.) of complex magnetic systems.

The classical Heisenberg Hamiltonian

$$H^{\text{Heis}} = - \sum_{ij} J_{ij} \mathbf{M}_i \cdot \mathbf{M}_j \quad (1)$$

is well known and widely used. Here,  $J_{ij}$  are exchange interactions and  $\mathbf{M}_i$  is the moment on the  $i$ -th atom. For details see, e.g., [1, 2]. The Hamiltonian (1) describes many important situations quite well. There are, however, some cases in which it may fail, particularly, if moments are not rigid or the system contains non-magnetic atoms on which appear induced moments. Moreover, the Hamiltonian (1) contains only isotropic interactions while the anisotropic contributions are neglected.

Here we wish to investigate more general Hamiltonians than (1) and to show that they can be used to derive magnetic properties of solids and nanostructures. Such Hamiltonians will consist of three parts: (i) the local exchange part describing formation of local moments on individual atoms, (ii) the isotropic exchange part describing interactions between spin moments on different atoms and which

has the form of a classical Heisenberg Hamiltonian (1), and (iii) the anisotropic part which includes dipole-dipole interactions and relativistic effects.

The article is organized as follows: in Sec. 2 we discuss the local exchange, the isotropic interatomic exchange, and the anisotropic and higher order terms. In Sec. 3 we present the determination of the ground state ( $T = 0$ ) and the equilibrium state at  $T > 0$  for various types of interaction and different number of sublattices, and in Sec. 4 we show in some detail the behavior of moment in nickel upon reversal and at elevated temperatures. The conclusions are summarized in Sec. 5.

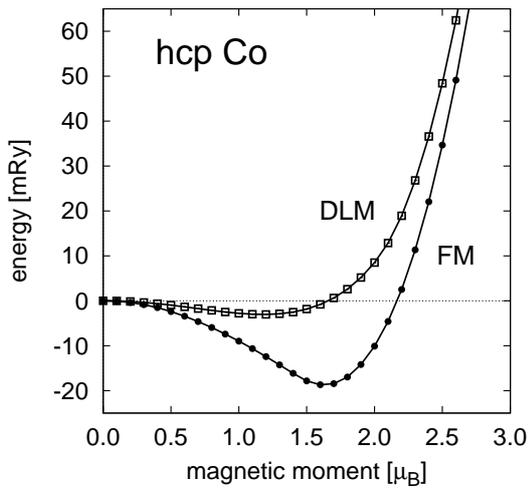
## 2 Exchange interactions

### 2.1 Intraatomic exchange

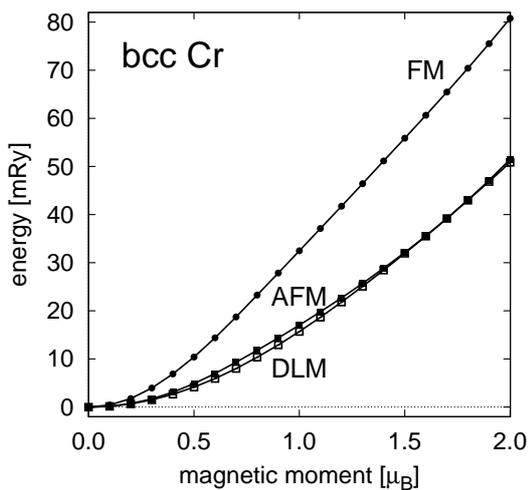
The intraatomic (local) exchange and the exchange field from other atoms lead to the formation of magnetic moments. The strength of the local exchange can be obtained using the fixed spin moment (FSM) method [3, 4]. In a ferromagnet, the intraatomic and the interatomic exchange act together. On the other hand, in the state with completely disordered moments the average value of the interatomic exchange field is zero. In order to calculate the intraatomic exchange, we have extended the fixed spin moment method to the state with disordered local moments (DLM). The dependence of total energy per atom on the moment,  $E(M)$ , for hcp-Co, bcc-Cr, and hcp-Ti is shown in Figs. 1, 2, and 3. The minima of  $E(M)$  for cobalt are found at  $M = 1.18 \mu_B$  in the DLM state and at  $M = 1.63 \mu_B$  in the ferromagnetic (FM) state. The latter value agrees well with the experiment.

Two approaches are used to implement the FSM method. In the first approach an external magnetic field  $H$  is introduced to provide the energy difference between the up- and down-spin electrons. A correction term of the type  $-HM$  has to be added to the total energy expression. The external field  $H$  is varied during the self-consistent iteration process

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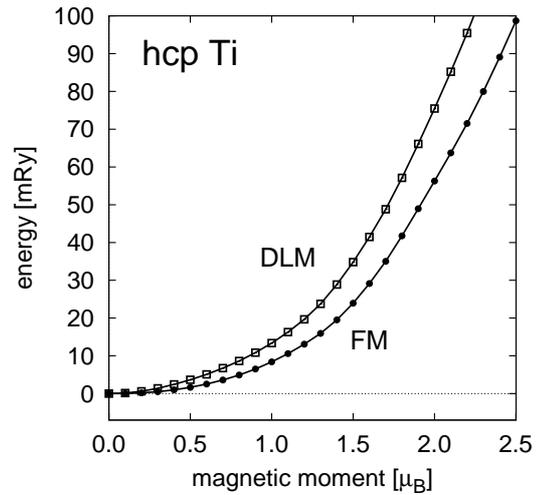
**Fig. 1.** The total energy per atom,  $E(M)$ , as a function of magnetic moment for hcp cobalt. The results for ferromagnetic (FM) and for disordered local moment (DLM) state are shown.



**Fig. 2.** The total energy per atom,  $E(M)$ , as a function of magnetic moment for bcc chromium. The results for ferromagnetic (FM), antiferromagnetic (AFM), and for disordered local moment (DLM) state are shown.

until the prescribed value of the magnetic moment  $M$  is achieved. The main drawback of this approach is that the function  $M(H)$  is a multivalued function of  $H$  in some systems. A different approach was therefore devised which makes use of two (generally several) Fermi energies  $E_F^\uparrow$  and  $E_F^\downarrow$  [3,4]. These Fermi energies are varied in the self-consistent calculation so as to get prescribed value of magnetization. This approach is now widely used and our calculations are also based on it. It has, however, some disadvantages, particularly the existence of two or more Fermi energies can make problems when calculating effective exchange interactions  $J_{ij}$  and also in calculations of transport properties because all pertinent expressions are formulated with one Fermi energy.

The FSM for ferromagnets is well known, but the adaptation for the DLM state deserves a short comment. It can be best explained on an example, say iron. It is described as



**Fig. 3.** The total energy per atom,  $E(M)$ , as a function of magnetic moment for hcp titanium. The results for ferromagnetic (FM) and for disordered local moment (DLM) state are shown.

a random alloy,  $\text{Fe}_{0.5}^\uparrow\text{Fe}_{0.5}^\downarrow$ , of two kinds of iron atoms,  $\text{Fe}^\uparrow$  and  $\text{Fe}^\downarrow$ . There are now 4 Fermi energies, namely,  $E_F^\uparrow(\text{Fe}^\uparrow)$ ,  $E_F^\uparrow(\text{Fe}^\downarrow)$ ,  $E_F^\downarrow(\text{Fe}^\uparrow)$ , and  $E_F^\downarrow(\text{Fe}^\downarrow)$ . Of course, only two of them are independent, because  $E_F^\uparrow(\text{Fe}^\uparrow) = E_F^\downarrow(\text{Fe}^\downarrow)$ ,  $E_F^\uparrow(\text{Fe}^\downarrow) = E_F^\downarrow(\text{Fe}^\uparrow)$ .

## 2.2 Interatomic exchange

A basic information on the interatomic exchange is provided by comparison of the total energies of the ferromagnetic (FM) and disordered local moment (DLM) states, because

$$E_{\text{tot}}^{\text{DLM}} \approx E_{\text{intra}}^{\text{exch}}, \quad E_{\text{tot}}^{\text{FM}} \approx E_{\text{inter}}^{\text{exch}} + E_{\text{intra}}^{\text{exch}}, \quad (2)$$

where  $E_{\text{intra}}^{\text{exch}}$  is the intraatomic exchange energy, and  $E_{\text{inter}}^{\text{exch}}$  is the interatomic exchange energy. Consequently

$$E_{\text{inter}}^{\text{exch}} = E_{\text{tot}}^{\text{FM}} - E_{\text{tot}}^{\text{DLM}}. \quad (3)$$

It is not surprising that the energies of chromium in the antiferromagnetic and in the DLM state are almost identical. It is interesting to compare the behavior of chromium and titanium: in Cr the energy of the DLM state is lower than the energy of the ferromagnetic state while in titanium the situation is just opposite. In other words, the interatomic exchange energy  $E_{\text{inter}}^{\text{exch}}$  in Cr is positive while in Ti it is negative. It is in agreement with the behavior of these materials: Ti is a paramagnetic metal while Cr has a tendency to formation of spin-density waves. The function  $E(M)$  for ferromagnetic materials can often be approximated by a polynomial of 4th order. In most cases,  $E(M)$  of non-magnetic materials for small  $M$  can be expressed in terms of 2nd order polynomial. However, for larger values of  $M$  this is not true, as can be seen in Figs.2, and 3.

A much detailed picture of the interatomic exchange is given by the Heisenberg Hamiltonian (1). The exchange parameters  $J_{ij}$  are calculated from Liechtenstein formula [1], for details see [2].

The isotropic interatomic exchange interactions are responsible for mutual orientation of the moments, but the orientation of moments with respect to crystallographic axes is indetermined.

We note that higher order interactions such as

$$\sum_{ijkl} J_{ijkl} (\mathbf{M}_i \cdot \mathbf{M}_j) (\mathbf{M}_k \cdot \mathbf{M}_l) \quad (4)$$

might be important in some cases.

### 2.3 Anisotropic exchange

Anisotropic exchange interactions originate from dipole-dipole interactions and from relativistic terms (spin-orbit coupling) and they are responsible for orientation of moments with respect to crystallographic axes. The corresponding Hamiltonian reads

$$H^{\text{anis}} = \sum_i K(\mathbf{M}_i) - \sum_{i,j} \mathbf{M}_i^T \cdot \mathbf{J}_{ij} \cdot \mathbf{M}_j. \quad (5)$$

Here,  $K(\mathbf{M}_i)$  is the on-site anisotropy energy and  $\mathbf{J}_{ij}$  is the tensor of interatomic exchange. It contains isotropic part (i.e.,  $J_{ij}$ ), the anisotropic symmetric part which includes crystal field effects and dipole-dipole interaction, and asymmetric part which contains spin-orbit coupling. The antisymmetric part can be expressed in terms of Dzyaloshinskii-Moriya vector  $\mathbf{D}_{ij}$  as  $\sum_{ij} \mathbf{D}_{ij} \cdot [\mathbf{M}_i \times \mathbf{M}_j]$ . For details see [5].

## 3 Determination of magnetic structure

### 3.1 Ground state

In systems with one sublattice in the isotropic case, the ground state is very often given by a single  $\mathbf{q}$ -vector spiral spin density wave

$$\mathbf{M}_i(\mathbf{q}) = M (\cos(\mathbf{q} \cdot \mathbf{R}_i), \sin(\mathbf{q} \cdot \mathbf{R}_i), 0) \quad (6)$$

which corresponds to the maximum of the Fourier transform of exchange interactions:

$$E(\mathbf{q}) = -M^2 J(\mathbf{q}) = -M^2 \sum_j e^{i\mathbf{q} \cdot \mathbf{R}_j} J_{0j}. \quad (7)$$

Here  $M$  is the size of magnetic moment. In the state (6) the moments lie in one plane. We denote the position of the minimum of  $E(\mathbf{q})$  as  $\mathbf{q}_0$ . If  $\mathbf{q}_0 = \mathbf{G}/2$ , where  $\mathbf{G}$  is a vector of the reciprocal lattice, the ground state may be a multi- $\mathbf{q}$  state in which the moments need not lie in one plane. In the anisotropic case, the energy of the ground state is given by the largest eigenvalue of the  $3 \times 3$  matrix  $\mathbf{J}(\mathbf{q})$  (i.e., the Fourier transform of the tensor  $\mathbf{J}$ ) and the orientation of moments follows from the corresponding eigenvector. In systems with two or more sublattices the theory becomes rather complicated [6].

The higher order terms in Hamiltonian, such as quartic ones, (4), are usually small. If one adopts the approximation of the spiral spin density wave (6) for the Hamiltonian with higher order terms, all higher order terms can be mapped onto  $J_{ij}$ 's as observed in [7]. The net effect

of higher order terms is then reduced to a renormalization of  $J_{ij}$ 's. This is, however, an approximation and to our knowledge, nothing is known about its validity, because an arrangement of moments different from (6) could yield lower energy. The point is that in contrast to Hamiltonians quadratic in moments such as (1) or (5) the search for the ground state is now a non-linear problem.

### 3.2 Finite temperature

At finite temperatures, various methods of statistical mechanics, such as the mean field approximation (MFA), the random-phase approximation (RPA), and the Monte Carlo simulations (MC) are used to find the magnetic structure stable at a given temperature. The MFA is numerically easy, but it is known for its low accuracy and it usually overestimates ordering temperature. On the other end are the MC simulations which are numerically highly demanding, but can be made highly accurate.

If ferromagnetic materials are treated with variable moments the statistical mechanics may become very difficult. This is clear already in the case of one site when the partition function for a moment  $\mathbf{M}$  in an external field  $\mathbf{H}$  reads

$$\begin{aligned} Z_0(\beta, H) &= \int d^3 M e^{\beta \mathbf{M} \cdot \mathbf{H} - \beta E(M)} \\ &= \frac{4\pi}{\beta H} \int_0^\infty dM M \sinh(\beta H M) e^{-\beta E(M)}. \end{aligned} \quad (8)$$

If the local energy is approximated by a 4th degree polynomial  $E(M) = A + BM^2 + CM^4$ , the problem is equivalent to a Mexican hat model in an external field, which is analytically intractable. This has to be contrasted with a rigid moment in the external field which is described by the Langevin function. One has to resort to some approximation, perhaps the simplest one consists in the replacement  $E(M) \approx \frac{1}{2} D(M - M_0)^2$  which leads to tractable expressions and is valid provided that the deviations of  $M$  from the equilibrium value  $M_0$  are not large.

The stable magnetic structure at finite temperature is given within the MFA by the largest eigenvalue of the tensor  $\mathbf{J}$  even for systems with several sublattices [8].

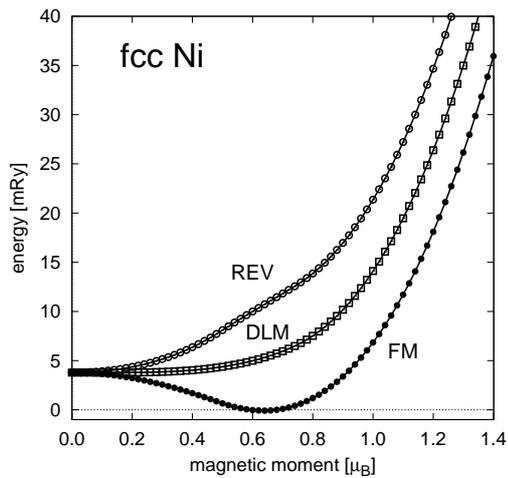
## 4 Case study: magnetic moment in Ni

### 4.1 Reversed moment

As an illustration we show the energy of a single Ni atom with a reversed moment in fcc-Ni. It is well known that this moment is unstable and the calculations based on the local density approximation (LDA) yield zero value. The reversed moment (REV) has the energy

$$E_{\text{tot}}^{\text{REV}} \approx E_{\text{intra}}^{\text{exch}} - E_{\text{inter}}^{\text{exch}}, \quad (9)$$

which has minimum for  $M = 0$  (see Fig. 4). On the other hand,  $E_{\text{tot}}^{\text{DLM}}(\text{Ni})$  has a shallow minimum for  $M = 0.118 \mu_B$ . This has to be contrasted with other ferromagnetic metals in which the reversed moments can exist. For example, for Fe the reversed moment is  $M = 1.6 \mu_B$ .



**Fig. 4.** The total energy per atom,  $E(M)$ , as a function of magnetic moment for fcc nickel. The results for ferromagnetic (FM) and for disordered local moment (DLM) state are shown together with the energy of a reversed moment (REV) calculated according to the Eq. (9).

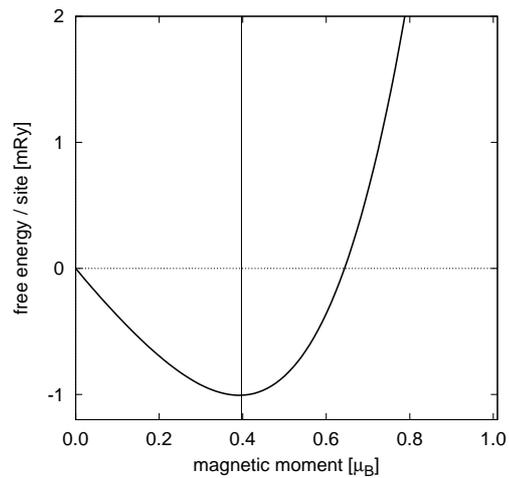
#### 4.2 Moment at Curie temperature

The magnitudes of magnetic moments have direct influence also on finite-temperature transport properties. The resistivity of magnetic metals and alloys is connected with three main scattering mechanisms, namely, (i) scattering of electrons on a static disorder (impurities, dislocations, etc.) which leads to the residual resistivity ( $\rho_0$ ), (ii) scattering on the disorder caused by atomic vibrations ( $\rho_{\text{vib}}$ ), and (iii) scattering on disordered magnetic moments giving rise to the spin disorder resistivity ( $\rho_{\text{mag}}$ ). These three contributions have different temperature dependence ( $\rho_0 = \text{const.}$ ,  $\rho_{\text{vib}}$  and  $\rho_{\text{mag}}$  are complicated functions of  $T$ ) and can be thus separated (see e.g. [9]). It turns out that theoretical and experimental values of  $\rho_{\text{mag}}$  agree quite well for Fe, but for Ni there is a discrepancy which could be removed, if one assumes that the value of the magnetic moment on Ni atom at the Curie temperature is reduced to  $0.3 - 0.4 \mu_B$  [10]. This is a plausible assumption as it is known that the magnetic moment of Fe atom is quite robust while the moment at Ni atom is rather soft.

A simple estimate of the moments on Ni atoms at Curie temperature can be based on the following assumptions: (i) the magnetic state of Ni at the Curie temperature can be represented by the DLM state, (ii) the average interatomic exchange field is zero in the DLM state, (iii) the energy per Ni atom in the DLM state is given by the 4th order polynomial  $A + BM^2 + CM^4$ , and (iv) the entropy per atom is  $\ln(2J + 1)$ , where  $J$  is the spin moment of Ni atom and  $M = g\mu_B J$  and  $g$  is the Landé factor [11]. We can minimize the free energy

$$F(M, T) = A + BM^2 + CM^4 - k_B T \ln(2J + 1) \quad (10)$$

at  $T = T_C$  with respect to  $M$ . The coefficient  $A$  is unimportant,  $B = 0.4575 \text{ mRy}/\mu_B^2$ ,  $C = 10.4771 \text{ mRy}/\mu_B^4$ , and  $T_C = 632 \text{ K}$ . We find  $M(T_C) = 0.397\mu_B$  (see Fig. 5). This value agrees well with a more quantitative theory ( $0.42 \mu_B$ ) of Ruban et al. [12].



**Fig. 5.** The free energy per atom,  $F(M)$ , as a function of magnetic moment for fcc nickel at  $T_C = 632 \text{ K}$ .

## 5 Conclusions

We have shown that effective magnetic Hamiltonians can be constructed from first principles and used as a versatile tool for determination of magnetic structures of solids, multilayers, and nanostructures with the accuracy of ab initio methods. They yield a deeper understanding of the formation and ordering of magnetic moments.

There are still open problems which we wish to solve in future as for example the statistical mechanics of variable-size moments, the dependence of exchange interactions on the size of moments, and a reliable determination of anisotropic interactions from first principles.

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