Chapter 2

First-Principles Calculation of Exchange Interactions

Before introducing the first-principles methods for the calculation of exchange interactions in magnetic systems we will briefly review two different aspects of magnetism in solids and the main exchange mechanisms in local moment systems.

2.1 Models of magnetism

Magnetism has been a subject of great interest and intensive research in field of condensed matter physics over the last century. Two different physical models have been proposed to describe the magnetism in materials: one is localized and the other is the itinerant electron model. The former has been used successfully in magnetic insulators and rare earth (RE) elements and the latter for 3d transition metals and their alloys. These two models are opposed but complementary to each other and illustrate the intrinsic properties of magnetism of materials. However, they are still in the stage of development and in many cases they can not be separated from each other. For a deep understanding of magnetism in condensed matter there has been a trend to combine both models to develop a unified theory [16]. In this section we will briefly present these two models and introduce classical Heisenberg model for the treatment of the finite temperature magnetism in itinerant electron systems.

- Localized electron model

The modern theory of magnetism has started with the concept of a local magnetic moment of a fixed size. Within this concept Langevin gave an explanation for the Curie law of magnetic susceptibility [17]. Subsequently Weiss introduced the notion of an interaction (molecular field) between the atomic magnetic moments to explain the spontaneous magnetic order in solids. Combining this new concept with the studies of Langevin, Weiss was able to explain the finite temperature properties of ferromagnetic 3d transition metals [18].
Although Langevin-Weiss theory has explained quite successfully the essential properties of ferromagnets both below and above the Curie temperature, the magnitude of the molecular field which is responsible for magnetic order, could not be explained within the classical physics. Since the magnetic dipole-dipole interactions were known to give a value for the molecular field which is two or three orders of magnitude smaller than estimated from the observed value of $T_C$. This problem was resolved with the advent of quantum mechanics.

In 1928 Heisenberg attributed the origin of Weiss molecular field to the quantum mechanical exchange interaction between the magnetic moments and proposed a more general model [19]. If $S_i$ is the atomic magnetic moment for a given site then the Heisenberg model is given by

$$H = -\sum_{i,j} J_{ij} S_i S_j \quad (2.1)$$

where $J_{ij}$ is the interatomic exchange interaction constant which is introduced phenomenologically and its physical origin will be discussed in the next section. $J_{ij} > 0$ for ferromagnets while it is negative for antiferromagnets. In principle, various magnetic orderings such as ferrimagnetism, helimagnetism can be derived from Heisenberg model by generalizing the sign and range of the exchange interactions. Moreover, Heisenberg model has led to discovery of spin waves as elementary excitations.

- **Itinerant electron model**

Magnetism in metals is usually explained on the basis of itinerant electron picture. One of the main reasons for this is that the saturation magnetization in 3$d$ transition metals and their alloys is not integer.

Bloch first discussed the possibility of ferromagnetism in an electron gas on the basis of Hartree-Fock approximation [20]. Later Wigner pointed out the importance of electron-electron interactions on the suppression of the occurrence of ferromagnetism in electron gas [21]. Thus the occurrence of ferromagnetism in transition metals is considered to be connected with the atomic character of 3$d$ electrons and mainly intra-atomic exchange interactions. Stoner developed an itinerant electron model to explain ferromagnetism in 3$d$ transition metals [22]. In the Stoner model, magnetism in metals arises from a splitting between the up- and down-spin bands and it is favored when the density of states is high at the Fermi level. The instability of non-magnetic state with respect to formation of ferromagnetic order is given by the Stoner criterion which is define by

$$IN(E_F) > 1 \quad (2.2)$$

where $I$ is the intra-atomic exchange integral and $N(E_F)$ is the density of states at Fermi level. It can be seen from the Stoner criterion that whether there is ferromagnetism from itinerant electrons depends on the product of exchange integral and the DOS at the Fermi level. Stoner model explains very well why Fe, Co and Ni are ferromagnetic and several others are not. The calculated values of the $I$ and $N(E_F)$ for transition metals can be found
in [23]. It should be noted that the band structure calculations played a vitally important role in understanding itinerant electron magnetism [8]. The application of local spin density approximation (LSDA) in band theory has been remarkably successful in explaining ground state properties of transition metals and their alloys.

However, the Stoner model fails to reproduce the measured $T_C$ and the observed Curie-Weiss law above it. Calculated temperatures for 3$d$ metals appeared to be too high compared with observations. Improvements to the Stoner model have been made that take into account the effect of spin fluctuations in a self consistent renormalized (SCR) way [16]. These studies built a bridge between two extreme limits of models (localized and itinerant) and unified them into one picture. In particular, these new theories have been very successful in describing several properties of weak itinerant ferromagnets.

2.1.1 Classical Heisenberg model for itinerant electrons

Although magnetic properties of 3$d$ transition metals and their alloys are essentially defined by itinerant electrons, thermodynamic properties of such magnetic systems can quite often be quantitatively described by the Heisenberg model. This is because of the fact that in these systems the obtained Curie-Weiss susceptibility and observed temperature dependence of the magnetization show the main characteristics of local moment systems. Spin fluctuation theories show that only an effective classical Heisenberg model can be introduced for metals which provides a simple and accurate description of magnetism in these systems [16]. The procedure consists of mapping the complicated itinerant electron system onto an effective Heisenberg Hamiltonian with classical spins:

$$H_{\text{eff}} = -\sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j$$

(2.3)

where $J_{ij}$ is the effective exchange parameter and $\mathbf{e}_i$ is the unit vector pointing in the direction of the magnetic moment at site $i$. The values of magnetic moments are absorbed by the exchange parameter $J_{ij}$. The effective exchange interactions $J_{ij}$ between magnetic moments are determined from first-principles calculations.

Once the exchange parameters $J_{ij}$ are obtained, the spin dynamics and thermodynamic properties such as spin wave stiffness and Curie temperature can be determined from the effective Hamiltonian (2.3).

2.2 Origin of magnetism: Exchange interactions

In matter, magnetic moments are not usually free but interact with each other. These interactions result in a collective behavior of magnetic moments which manifest itself, below a critical temperature, by the onset of magnetic orders such as ferromagnetism or antiferromagnetism. Among the different interactions in magnetic systems only exchange interactions are
dominating and they are responsible for the microscopic magnetic behavior. It is thus of primary importance for determining the magnetic excitations and, hence, the Curie temperature of ferromagnetic systems.

The description of the fundamental features of the exchange interactions invokes a quantum mechanical approach, but their quantitative treatment is beyond the scope of this chapter. Loosely speaking, exchange is a combined effect of Pauli exclusion principle, electrostatic Coulomb repulsion and kinetic energy. Pauli exclusion principle keeps electrons with parallel spins apart, so reduces their Coulomb repulsion. The difference in energy between the parallel spin configuration and the antiparallel one is defined as the exchange energy. The magnetically ordered structures are the results of direct or indirect interactions between the local moments in sites or delocalized electronic moments in crystal. In the following we will briefly describe the three main exchange mechanisms which are most frequently observed in local moment systems.

- **Direct exchange**

This interaction is the direct consequence of the Pauli exclusion principle and depends strongly on the overlap of the participating wave functions (see Fig.). For small interatomic distances, antiferromagnetic coupling occurs (Cr and Mn). With increasing distance, ferromagnetic state becomes favorable (Fe, Co, Ni). For very large distances the coupling vanishes and paramagnetism is present [24].

- **RKKY exchange**

RKKY indirect exchange interaction (after Rudermann, Kittel, Kasuya and Yosida) takes over at distances beyond a few atomic spacings. It is mediated by the conduction electrons (s, p). A magnetic moment at site $i$ polarizes the s, p-electron gas and a second moment at site $j$ feels the induced polarization. This interaction starts out ferromagnetic at small distances and oscillates between negative and positive values with a period of $\lambda_F/2$, where $\lambda_F = 2\pi/k_F$ is the Fermi wavelength and $k_F$ is the Fermi wave-vector. In general the RKKY interaction gives rise to ferromagnetism if $k_F$ is small (nearly empty bands) and to antiferromagnetism when $k_F \sim \pi/a$ (half-filled band). This interaction can lead to long period magnetic structures (helimagnets, etc), that can be incommensurate with the lattice spacing.

This same mechanism is also responsible for the oscillatory interlayer exchange coupling in GMR structures [25, 26] and coupling of $4f$ electrons in rare earth elements. Furthermore the physics of spin glasses is discussed within the same context.

- **Superexchange**

In most of the magnetic insulators such as MnO, the magnetic atoms separated by diamagnetic atoms. Thus the magnetic ions are situated at distances too far for their $3d$ wave
2.2. Origin of magnetism: Exchange interactions

Functions to overlap and exchange interactions are mediated by the diamagnetic atoms, i.e., through the overlap of 3$d$ and $p$ wave functions. The value and sign of this exchange (or so-called superexchange) interaction depend strongly on the types of 3$d$ orbitals ($e_g$ or $t_{2g}$) involved, the number of electrons, and also the angle Mn-O-Mn. This complex mechanism can initiate ferro- and antiferromagnetic coupling character. Finally, this interaction is effective only over short distances.

In left part of Fig. 2.1 we present the schematic representation of the these three main exchange mechanisms between localized moments. In addition to them there are also other mechanisms which appear depending on whether the materials are insulators or metals and on which magnetic atoms (rare earths or transition metals) are involved such as double exchange and the exchange between the itinerant electrons. The most complicated situation is seen in 3$d$ transition metals. In these systems the 3$d$ electrons are partly delocalized into the Fermi sea and partly localized around atomic sites. Furthermore, these two aspects can not be distinguished completely, and this is related to correlated features of the 3$d$ electrons in these systems.

All these exchange interactions contribute to formation of diverse magnetically ordered structures through cooperative phenomena for macroscopic magnetism. Although these five kinds of exchange mechanisms were proposed for different cases and have been applied to various circumstances appropriately, there are no clear borderlines between them [28]. They are related to each other, and there are overlaps of their regions of applications. In right part of Fig. 2.1 we present the relationship between these five exchange interactions. The solid
circles represent the main region of application for each type of interaction, while the dashed circles indicates enlarged regions of applications. In fact in real systems it is possible that there are several exchange interactions which coexist and are mixed together.

Empirical values of the exchange interactions for various ferromagnetic metals have been calculated from specific heat measurements and from spin-wave spectra, whereas theoretical estimation of them have been one of the long standing and challenging problems in magnetism. Early attempts to calculate exchange integrals based on model Hamiltonian approaches resulted in unsatisfactory and even wrong results in some 3d systems [24]. For a quantitative study of magnetism and exchange interactions in solids the detailed consideration of electronic structure is necessary and should be introduced into the magnetic theory. This becomes possible with the recent developments of novel methods based on the results of numerical calculations of the electronic structure of solids [29]. Pioneering work in this field has been done mainly by two groups: the Russian group of Gubanov, Lichtenstein and others and Kübler and coworkers (Darmstadt) [8].

2.3 First-principles calculation of the exchange interactions

As mentioned in preceding section first-principles methods are the only way of obtaining exchange interactions in realistic systems. There are basically two different approaches, both rely on the adiabatic approximation in which the precession of the magnetization due to a spin-wave is neglected when calculating associated change of electronic energy. This approximation is valid under the conditions that the precession time of the magnetization should be large as compared to characteristic times of electronic motion, i.e., hopping time of an electron from a given site to a neighboring one and the precession time of the spin of an electron subject to the external field. Put differently, the spin-wave energies should be small as compared to the band with and exchange splitting. This is well justified for 3d systems (except Ni) and 4f rare earth elements. In principle, this approximation becomes exact in the limit of long wavelength magnons.

- **Real-space method**

Real-space approach was introduced by Liechtenstein et al., in 1987 for the calculation of interatomic exchange interactions from first-principles [30]. It is based on multiple-scattering theory and employs the magnetic force theorem to calculate the energy change associated with a constrained rotation of the magnetic moments at sites $i$ and site $j$ (see Eq. (2.3)). The energy change can then be related to the exchange interactions as

$$J_{ij} = \frac{1}{4\pi} \int_{E_F}^\infty dE \text{Im} \text{Tr}_L(\Delta_i \hat{T}^{ij}_\uparrow \Delta_j \hat{T}^{ji}_\downarrow)$$

(2.4)

This formula gives the expression for the pair exchange interaction parameter in the classical Heisenberg model (2.3). However, this approach has not been used in our calculations.
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- Frozen-magnon method

In contrast to real space approach frozen-magnon approach is a reciprocal space method [31]. It is based on the total energy calculation for spiral magnetic configurations. With the help of the generalized Bloch theorem discussed in preceding chapter such calculations can be performed very efficiently without resorting to large super-cells. Additional help is provided by the force theorem that allows to use band energy of non-self-consistent frozen magnon states for the estimation of the total-energy differences. The following subsection is devoted to the discussion of frozen-magnon method for the case of multi-sublattice Heisenberg Hamiltonian.

The real-space and frozen-magnon methods are formally equivalent and complementary to each other. The quantities that are directly calculated are the $J_{ij}$ and $E(q)$ in the former case and in the latter case, respectively. They are also related to each other by a Fourier transformation. A detailed discussion on the comparison of both methods can be found in Ref.[32].

2.3.1 Frozen-magnon method for multi-sublattice systems

Let us consider the following classical multi-sublattice Heisenberg Hamiltonian

$$H_{\text{eff}} = -\sum_{\mu,\nu} \sum_{R,R'} J_{\mu\nu R R'}^{\mu\nu} s_{\mu R}^\nu s_{\nu R'}$$ (2.5)

In Eq.(2.5), the indices $\mu$ and $\nu$ number different sublattices and $R$ and $R'$ are the lattice vectors specifying the atoms within sublattices, $s_{\mu R}^\nu$ is the unit vector pointing in the direction of the magnetic moment at site $(\mu, R)$.

Calculate interatomic Heisenberg exchange parameters involve few steps within frozen-magnon technique. In the first step, the exchange parameters between the atoms of a given sublattice $\mu$ are computed. The calculation is based on the evaluation of the energy of the frozen–magnon configurations defined by the following atomic polar and azimuthal angles

$$\theta_{\mu R} = \theta, \quad \phi_{\mu R} = q \cdot R + \phi_{\mu}. \quad (2.6)$$

In the calculation discussed in this paper the constant phase $\phi_{\mu}$ is always chosen equal to zero. The magnetic moments of all other sublattices are kept parallel to the z axis. Within the Heisenberg model (??) the energy of such configuration takes the form

$$E^{\mu\mu}(\theta, q) = E_{0}^{\mu\mu}(\theta) + \sin^2 \theta J^{\mu\mu}(q)$$ (2.7)

where $E_{0}^{\mu\mu}$ does not depend on $q$ and the Fourier transform $J^{\mu\mu}(q)$ is defined by

$$J^{\mu\mu}(q) = \sum_{R} J_{0 R}^{\mu\mu} \exp(iq \cdot R). \quad (2.8)$$
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\[ \phi_\mu = qR + \phi_\mu \]

Figure 2.2: (a) Spin spiral to calculate intra-sublattice exchange interactions. (b) The same for inter-sublattice exchange interactions.

In the case of \( \nu = \mu \) the sum in Eq. (2.8) does not include \( R = 0 \). Calculating \( E^{\mu\mu}(\theta, q) \) for a regular \( q \)-mesh in the Brillouin zone of the crystal and performing back Fourier transformation one gets exchange parameters \( J_{0R}^{\mu\mu} \) for sublattice \( \mu \).

To determine the exchange interactions between the atoms of two different sublattices \( \mu \) and \( \nu \) the frozen-magnon configurations (Eq. 2.6) are formed for both sublattices. The Heisenberg energy of such configurations takes the form

\[
E^{\mu\nu}(\theta, q) = E_0^{\mu\nu}(\theta) + \sin^2 \theta [J_0^{\mu\nu}(q) + J_0^{\nu\mu}(q)] + 2 \sin^2 \theta \Re J^{\mu\nu}(q)
\] (2.9)

where \( E_0^{\mu\nu}(\theta) \) is a \( q \)-independent part. Performing calculation of \( [E^{\mu\nu}(\theta, q) - E^{\mu\nu}(\theta, 0)] \) and subtracting single-sublattice contributions known from the previous step one finds \( \Re J^{\mu\nu}(q) - \Re J^{\mu\nu}(0) \). The back Fourier transformation of this expression gives for \( R \neq 0 \) the following combinations of the interatomic exchange parameters:

\[
J_R^{\mu\nu} = \frac{1}{2}(J_0^{\mu\nu} + J_0^{\nu\mu})
\] (2.10)

\( J_R^{\mu\nu} \) does not contain information about the interaction of the atoms within the first unit cell corresponding to \( R = 0 \). These exchange parameters can be found in a different way. For simplicity let assume that we have two magnetic atoms per unit cell. In this case we need at least two different magnetic configurations to calculate exchange interactions between these atoms. (see figure 2). The energies of such configurations is expressed as follows.

\[
E^I(0, 0) = E_0 - 2J_0^{\mu\nu}
\] (2.11)

\[
E^{II}(\theta, 0) = E_0 - 2\cos \theta J_0^{\mu\nu}
\] (2.12)
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where \( J_{0}^{\mu \nu} = \sum_{\mathbf{R}} J_{0R}^{\mu \nu} \). From Eqs. (2.11) and (2.12) one gets for \( J_{0}^{\mu \nu} \)

\[
J_{0}^{\mu \nu} = \frac{E_{I}(0,0) - E_{II}(\theta,0)}{2(1 - \cos \theta)} \quad (2.13)
\]

Combining Eq. (2.13 with the sum \( \sum_{\mathbf{R} \neq 0} J_{0}^{\mu \nu} \) which is known from the preceding step one can access the parameters with \( \mathbf{R} = 0 \).

If one interested in estimation of the Curie temperature in mean field approximation the above procedure of obtaining inter-sublattice exchange interactions greatly simplifies the calculations. If there are \( n \) magnetic atoms per unit cell then the number of different magnetic configurations required for estimation of intersublattice exchange parameters becomes

\[
\frac{n(n-1)}{2} + 1 = \begin{cases} 
2, & n = 2 \\
4, & n = 3 \\
7, & n = 4
\end{cases} \quad (2.14)
\]

As it seen from the Eq. (2.14) the number of different configurations scale as \( \sim \frac{n^2}{2} \) with number of magnetic atoms per unit cell. This requires few configurations for Heusler alloys with two or three magnetic atoms per unit cell studied in this thesis. However, the intra-sublattice exchange interactions should be obtained from the usual procedure.